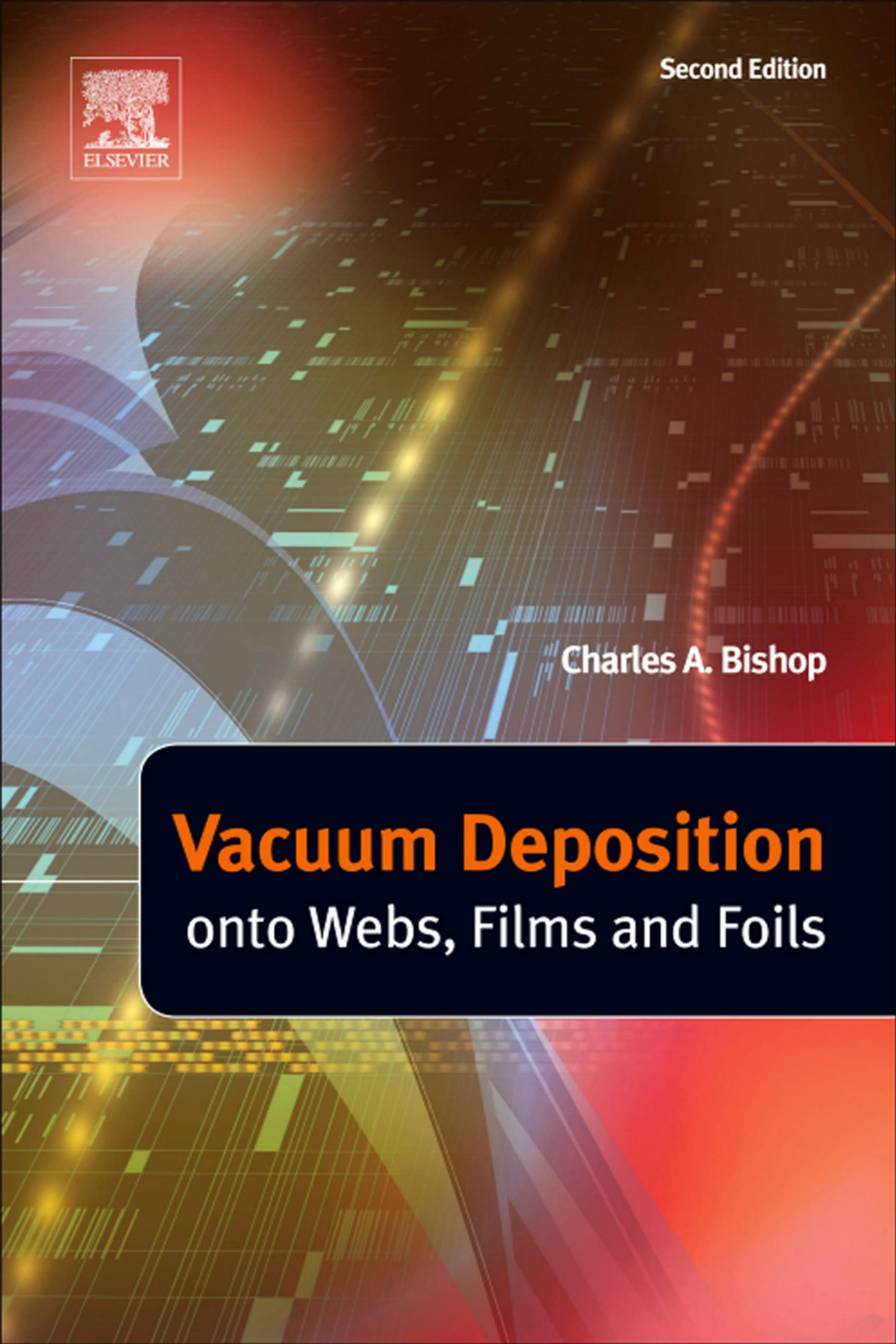


ELSEVIER

Second Edition

Charles A. Bishop

Vacuum Deposition onto Webs, Films and Foils

Vacuum Deposition onto Webs, Films, and Foils

Vacuum Deposition onto Webs, Films, and Foils

Second Edition

Charles A. Bishop

ELSEVIER

AMSTERDAM • BOSTON • HEIDELBERG • LONDON
NEW YORK • OXFORD • PARIS • SAN DIEGO
SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO
William Andrew is an imprint of Elsevier

William Andrew is an imprint of Elsevier
225 Wyman street, Waltham, MA 02451, USA
The Boulevard, Langford Lane, Oxford OX5 1GB, UK

First edition 2007
Second edition 2011

Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

ISBN: 978-1-4377-7867-0

For information on all William Andrew publications
visit our website at elsevierdirect.com

Typeset by MPS Limited, a Macmillan Company, Chennai, India
www.macmillansolutions.com

Printed in the United States of America

11 12 13 14 15 10 9 8 7 6 5 4 3 2 1

Contents

Preface

Roll-to-roll vacuum systems vary from very large systems that can coat 4.45 m wide rolls that can be 40 km long, or more, through to small laboratory systems with rolls that may only be a few centimeters wide and much less than 100 m long. The processes used can be as simple as the widely used resistance-heated boat thermal evaporation of aluminum at high winding speeds that can be in excess of 1250 m/min or can be more complex and include the lower speed magnetron sputtering process where the winding speed can be very much slower than 1 m/min. What all systems benefit from is that the web moves past the source and so, to some extent, this gives advantages of down web coating uniformity. Thus, whatever the uniformity is across the web will be reproduced all the way down the roll length.

With suitable attention to transverse uniformity and the stability of the source, to give longitudinal uniformity, roll coating has the potential to produce large quantities of highly uniform coated material. The process is still, more often than not, a batch process with a roll representing a batch, but because of the amount of material contained in each roll, it is still, for many products, a significant opportunity to lower the costs of the coating per unit area. As such, a number of products that are initially coated as discrete items migrate toward roll coating as a method of increasing manufacturing efficiency and reducing unit costs. Products that have benefited from this transition would include amorphous solar cells and solar absorbers. One current industry looking to gain the benefits from roll coating is the display industry where it is aimed at transferring the manufacturing process from coating individual sheets of material, usually glass, to a roll-to-roll process using polymers. This includes the organic light-emitting devices that are being developed for the fully flexible displays.

Other products, such as the transparent conducting coatings, have been copied from the glass industry and have been developed directly onto webs. Similarly, developed directly onto webs were the copper coatings for flexible circuits. Others have been developed as a progression from existing web coating processes such as the flake pigments where the coatings could be used in the continuous form, and then, by adding a release layer to the substrate, the same coating could be deposited but flake pigments produced. All of these diverse products benefit from the ability to produce high volumes of highly uniform coatings.

The aim of this book is to provide a broad appreciation of roll-to-roll vacuum deposition systems and processes.

Hopefully, it will encourage everyone to think about the vacuum deposition process more holistically. Not just looking at the vacuum system and process but also looking at the material supply, both substrate and deposition materials, through to the downstream processes that the vacuum coated product will encounter.

Over the years, there have been too many systems that have either been underspecified or the process underdeveloped or processes transferred to inappropriate systems. These have all given the system operators huge problems, often producing poor system efficiency leading to poor business performance.

Everybody will have suffered at sometime or the other from suppliers changing their process without considering what effects this might create for the subsequent users. The same thing also applies to vacuum depositing coatings. Changes to the vacuum deposition process also have the potential to change the coating properties. Hence, when developing a vacuum deposition process, checks should be done to make sure not only that there is the security of supply and consistency of incoming materials but also that the product remains compatible with subsequent downstream processing.

Thus, from the start it is essential to consider and include both upstream and downstream processes and materials when developing any new vacuum deposition process. Once the process has been defined in as much detail as possible, the system design and operation can then be worked on.

This book highlights some of the processes available and many of the choices that will have to be made in specifying a new machine. If nothing else, it will enable the reader to question machine manufacturers in more detail about their proposed designs and the reason behind some of the choices they have made.

It is not the aim of this book to cover in detail the basics of vacuum or vacuum pumping and gauging. There are already plenty of books that adequately cover this information and these have been referenced along with other relevant texts.

To make the book accessible to all, it has been an aim to minimize the mathematics included in the text. Those who wish to pursue the mathematics further should be able to find more detail in a number of the references supplied.

As with all books, it is almost impossible to know where to call a halt. There is always something else that could be added or covered in more detail. It is to be hoped that enough of the essentials have been covered and that it provides a useful source of information. Similarly, with a second edition it is difficult to know what to leave out and what else to add. It is my aim that nobody notices what has been left out but appreciates the additional information I have included.

Charles A. Bishop

Part I

Vacuum Basics

1 What Is a Vacuum?

1.1 What Is a Vacuum?

The word vacuum is derived from the Latin word "vacua" meaning empty. If we empty the chamber of gas, we produce a vacuum.

A vacuum could be described as where within an enclosed volume there is less gas per unit volume than is present in a similar volume in the atmosphere surrounding the enclosed volume. This is something that can be used to our advantage.

Those of us who drink tea have all heard tales of not being able to brew a good cup of tea when on the higher slopes of Mount Everest because of the lower pressure and the problem of boiling water at a lower temperature. This effect of reducing the boiling point of materials when under vacuum is one advantage that can be used to good effect.

Many materials, particularly when raised in temperature to the boiling point, are prone to oxidation. Thus, another advantage of operating in a vacuum is that materials that would normally be excessively affected by oxidation can have oxygen and water vapor kept away. This is achieved by being within a volume where there are few gas molecules, that is, a vacuum.

1.2 What Is a Gas?

If we look at materials in general, they can be in the form of a solid, liquid, or gas. The structure changes with each form. Solids have atoms closely spaced and in fixed positions. On heating the material, the form changes to a liquid where the atoms are disordered and the distance between atoms is greater. On further heating, the disorder is still greater and the spacing is also much greater. The speed of motion of the atoms also increases with temperature. So let us look at a few facts and figures about gases.

A gas is where atoms or molecules are free to move in any direction and are in constant motion. Typically, these particles are traveling at speeds of approximately 1650 kph (1000 mph).

In air, gas molecules occupy approximately 0.01% of the space as compared to a solid where the molecules occupy approximately 74% of the space. The particles

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00001-5

collide with each other or surfaces at a rate of 10,000,000,000 per second. These collisions mean that the gas particles have random motion and will rapidly expand to fill the whole volume. If the number of collisions seems to be large, bear in mind that there will be around 20,000,000,000,000,000,000 particles per cubic centimeter and the mean free path (the average distance a particle has to travel before it hits another particle) is only 100 nm.

1.3 Pressure

All atoms or molecules have mass, and when they hit and bounce off a surface they exert a force on that surface. This force per unit area is known as pressure.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

All atoms or molecules in the atmosphere with their mass are subjected to the gravitational pull of the earth and are attracted to the earth. Thus, at high altitudes the pressure is low because the density of gas is low.

At the top of Everest, the pressure is less than one third of that found at sea level. A simple rule of thumb is that the pressure is halved every 5 km away from the earth's surface (sea level).

Atmospheric pressure taken at sea level and 45°N latitude is 14.69 pounds per square inch (psi) or 1 kilogram force per square centimeter (kgf/cm^2). If the pressure is taken at a temperature of 0°C, the pressure is said to be 1 standard atmosphere (1 std atm).

Atmospheric pressure as a value is often rounded up for convenience:

$$14.69\ \text{psi} \cong 15\ \text{psi}$$

$$\begin{aligned} 15\ \text{psi} \cong 760\ \text{torr} \cong 1\ \text{std atm} \cong {} & 101,325\ \text{Pa}\ (\text{N/m}^2) \cong 1.01325\ \text{bar} \\ & 101.325\ \text{kPa} \qquad\quad \cong 1013.25\ \text{mbar} \end{aligned}$$

There is an issue regarding the units used to designate pressure that can be problematic. As long ago as 1978, pascal replaced torr as the acceptable measure of pressure. However, many vacuum systems that were built before this time are still in regular use, and also old habits die slowly, and so it is still common to find systems using torr as the measure of pressure.

The Italian, Torricelli, in 1644 made a measurement of pressure using a mercury manometer. His measurement of 760 mm Hg for atmospheric pressure is the basis of the torr scale used today:

1 mm Hg = 1 torr (an abbreviation of Torricelli in honor of his work)

$$1\ \mu\text{m Hg} = \frac{1}{1000}\ \text{mm Hg} = 0.001\ \text{mm Hg} = 0.001\ \text{torr} = 1\ \text{mtorr (mT)}$$

The European preferred unit of pressure is the pascal or the newton per square meter. As ever, the Europeans have adopted a unit of measurement of pressure that does not quite conform because of it not being related to the SI unit by a factor of 10^3. The unit is the bar where the base unit of 1 bar equals 100,000 Pa.

1 bar = 1000 mbar = 750 torr

Vacuums are often categorized as one of the four main types: low, medium, high, or ultrahigh vacuum. There are other descriptors that are used that may not always be recognized:

Low = soft = poor = rough vacuum = 1 − 1013 mbar
Medium = moderate vacuum = $10^{-3} - 1$ mbar
High = hard = good vacuum = $10^{-7} - 10^{-3}$ mbar
Ultrahigh = vacuum = below 10^{-7} mbar

It is worth noting that another confusion comes from the changing between describing a vacuum as a high vacuum and then changing to talking about a low-pressure system. Both are correct, as a system having a low pressure does have a high vacuum, but it helps to be consistent in the terminology used.

1.4 Partial Pressure

The total pressure of a system is the sum of all the individual gas pressures of the gases present in the system. Each of the gases exerts a pressure, and individually they are known as the partial pressures.

A common example is of a chamber open to atmosphere. The air around us is composed of a mixture of gases. Table 1.1 lists the gases present, their relative volumes,

Table 1.1 The Composition of Air

Gas Composition Air	Symbol	Percent by Volume	Partial Pressure Pa (N/m^2)	Partial Pressure torr
Nitrogen	N_2	78.08	79115	593.4
Oxygen	O_2	20.95	21227	159.2
Argon	Ar	0.93	942	7.07
Carbon dioxide	CO_2	0.03	30.4	0.23
Neon	Ne	0.0018	1.82	0.0137
Helium	He	0.0005	0.51	0.0038
Methane	CH_4	0.0002	0.2	0.00152
Krypton	Kr	0.0001	0.1	0.00076
Hydrogen	H_2	0.00005	0.051	0.00038
Xenon	Xe	0.0000087	0.0088	0.000066
Water	**H_2O**	**0.6−6.0**	**607−6079.5**	**4.56−45.6**

and the partial pressure of each gas. The partial pressure of each gas is relative to its percentage of the total volume; hence, the partial pressure is the volume times the percentage present. Thus, for oxygen, it is 20.95% × 101,325 Pa = 21,227 Pa.

The most common gas pumped to produce a vacuum is air, and Table 1.1 shows the most common constituents of air. It is important to note that there is one omission from the table that has a big impact on vacuum systems and that is water vapor. Depending on the local weather and temperature, the water vapor content of the atmosphere can be between 0.6 and 6.0 weight percent. Hence, in the table, the figures are for a basic dry air, and the water vapor, as it is a variable, is given as a range of values. If the water vapor present is at the upper end value, the other gases will have a slightly lower percentage volume, and hence a slightly lower partial pressure than shown.

1.5 Vapor Pressure

A vapor is a gas that has a tendency to turn back into liquid. In the same way that gases hitting a surface produce a pressure, a vapor bombards the surface and exerts a pressure. This is referred to as the vapor pressure.

If we think of a pool of liquid such as water, if we leave it for some time it can be seen to have lost some water by evaporation. If we raise the temperature of the water, this would be seen to happen more quickly. If we took the temperature up to the boiling point of the water, the water vapor would be seen as a cloud above the water and the water level would be seen to fall rapidly. So the vapor pressure gives an indication of the rate of evaporation of a material. Solids also have a vapor pressure, but, as you would expect, they are tiny by comparison with liquids.

The vapor pressure of all gases is the same at the boiling point in atmosphere, 760 torr, although the temperature at which they boil is different.

This becomes of practical interest when working with liquid precursors for chemical vapor deposition processes and also for physical vapor deposition processes using evaporation sources.

1.6 Saturated Vapor Pressure

If we go back to the pool of water, the water evaporates and once the molecules have left the surface they undergo collisions that give them a random motion and they diffuse away. This is an unsaturated vapor. If, however, we enclose our pool of water in a vessel, then the vapor will collide with the vessel walls and the chances of the vapor hitting the water pool and being recaptured are increased. The point where there is equilibrium between the rate of evaporation and the rate of recapture is known as the saturated vapor pressure. The rate of evaporation falls with reducing temperature and so the equilibrium point also falls and the saturated vapor pressure falls.

This property is utilized by cryopumps whereby a cold surface is placed in the vacuum vessel and vapors condense on the surface.

Under vacuum, the evaporation becomes faster because the evaporated molecules are less likely to collide with any gas particle and be bounced back to the liquid surface and recaptured. An everyday example of this is given by mountaineers who complain that the water boils at too low a temperature to make a good cup of tea on high mountains. This is because as the pressure reduces the boiling point reduces too. This is exactly the same in vacuum systems.

A key piece of information to note is that the pressure 2340 Pa (23.4 mbar, 17.55 torr) is the pressure at which water boils at room temperature (20°C). This pressure is significant in that if there is any water in the vacuum vessel, the system will not pump down beyond this figure until all the water has been evaporated.

It is also worth noting that a rapid evaporation of water requires heat and if there is insufficient heat, it will be extracted from the water and the water will freeze. The saturated vapor pressure for ice is 611 Pa (6.11 mbar, 4.48 torr). Thus, the pressure will fall. Typically, the water will be sat (situated) on a metallic surface and the rate of thermal diffusion is not high enough to sustain the evaporation of the water. Hence, the water freezes to ice initially, but as the heat diffuses through the ice it melts and evaporation starts again at high rate. This evaporation returns the pressure up to the water saturated vapor pressure of 2340 Pa. The same problem of supplying heat to maintain the evaporation can occur again, and the pressure will once again fall. If there is a water leak in the system, this will continue indefinitely; if it is just a large drop of water, this cycle may occur a few times and disappear (Fig. 1.1).

Water is always regarded as a problem to vacuum systems. Water vapor from the atmosphere is absorbed onto the surfaces in the vacuum system, and this has to be pumped out. To put it into perspective, we can look at a single drop of water as an example.

One drop of water of 1 g = 1 mL, but at a pressure of 0.133 Pa (0.0013 mbar, 1 mT), the same drop of water will occupy 1,000,000 L of volume. Typically, systems will pump to lower pressures and the volume will be higher still. If the system is pumped by a diffusion pump of a pumping speed 10,000 L/s, it will take 1.7 min just to pump out the single drop of water.

As water can slow the pumping of the system down so much, it is common for the system to include a pump designed to specifically pump water vapor very

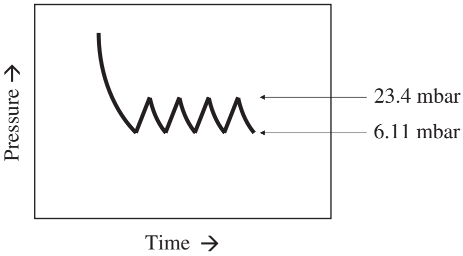


Figure 1.1 Schematic of a system with a characteristic water leak showing the cycling between the two saturated vapor pressures of ice and water.

quickly. These systems use a refrigerant gas pumped round to cool cold panels within the vacuum system where the water can be condensed efficiently. Typically, these panels will pump at over 100,000 L/s. These pumps are known as cryocoils or cryopanels.

1.7 Why Do We Need a Vacuum?

There are typically two reasons for requiring a vacuum. The first is as a way of controlling the reactivity of the deposition process and the second is to reduce the number of gas collisions, enabling higher energy particles to be used as part of the deposition process.

In the deposition process, oxidation can be regarded as a form of contamination of the deposited coating. The purity of the coating depends on the relative arrival rates of the desired material and the contaminant. Thus, if oxygen is a contaminant, then depositing in a vacuum is a method of reducing this source of contamination.

A vacuum is not a single pressure but can vary from just below atmospheric pressure through to ultrahigh vacuum. Vacuum that is near to atmospheric pressure will have similar properties and contamination rates will be similar. Thus, we need some form of measure that tells us what we can expect from different levels of vacuum. As contamination is something we are interested in, a measure that reflects this is of interest. Similarly, if we deposit material and want it to arrive at the substrate with all the energy it started with, it will have to arrive without any energy reducing collisions with the gas present. Hence, we need a measure that reflects the possibility of an atom undergoing a collision.

There are two measures that highlight the benefits of using vacuum: mean free path, which highlights the chances of undergoing a collision, and the time to form a monolayer, which allows us to estimate the contamination rate.

1.8 Mean Free Path

Gas particles move about randomly, colliding with others and bouncing off in a new direction. The average distance between collisions is termed the mean free path (mfp). The length of the mfp depends on the particle size, pressure, and temperature.

To calculate the mfp, it is necessary to know the molecular diameter of the gas particle, the density of molecules, and their average velocity. A more convenient method is to take one of the published values and to scale it according to pressure (Fig. 1.2). Thus:

$$\text{mfp} = \frac{6.4 \times 10^{-3}}{P}\ \text{cm} \quad \text{where } P = \text{pressure in mbar}$$

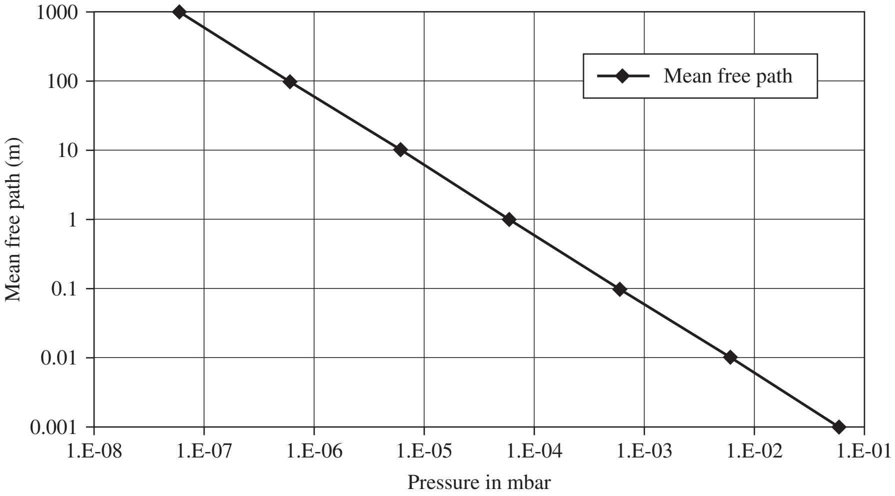


Figure 1.2 The mean free path (mfp).

Hence, at:

1.3×10^{-6}mbar (1×10^{-6} torr) mfp	= 49.23 m
0.0013 mbar (1 mT)	= 4.92 cm
1.3 mbar (1 torr)	= 0.049 mm = 49 μm
1013 mbar (760 torr)	= 63 nm

This information is important when depositing coatings because it will tell you if the coatings are to be deposited by a line-of-sight process or if there will be collisions and thus a different growth pattern. Typically, in evaporation processes, the base pressure is of the order of 10^{-5} mbar and the mfp would be a few meters. However, when deposition begins, the pressure rises to the 10^{-4} mbar range and so the mfp drops to the order of 0.5 m or less. In most system designs, this still means that there will be no gas scattering of the depositing material.

This is a useful rule of thumb, but it is worth bearing in mind that statistically some particles will be scattered. The bulk of the depositing material will hit surfaces that are in the line of sight, but there will be, over time, a small amount of material scattered which will reach other parts of the vessel.

The other piece of useful information that is related to pressure or molecular density is the time to form a monolayer of gas on a surface. This assumes that the sticking coefficient, the probability that a particle hitting a surface will stick to it, is 1.

At 1×10^{-3} mbar ($\sim$1 mT), a monolayer will form in 1 ms.
At 1×10^{-6} mbar, a monolayer will form in 1 s.

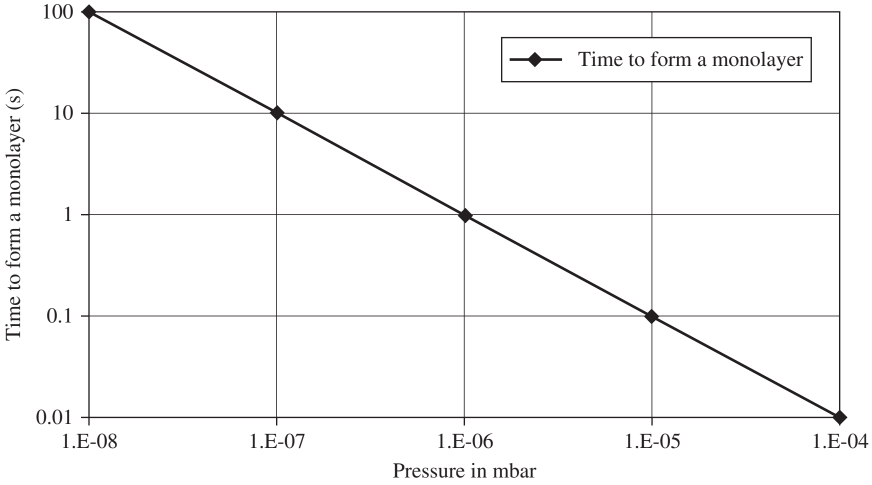


Figure 1.3 The time taken to form a monolayer in vacuum.

This also indicates the potential contamination rate of the growing coating due to residual gases within the system.

If we look at the graph of the time it takes to form a monolayer of atoms on a surface (Fig. 1.3), we can see that at a pressure of 1×10^{-6} mbar it takes 1 s to form a monolayer.

The aluminum metallization of polymer webs typically requires the system to be pumped out into the 10^{-6} mbar range, and when the deposition starts, the pressure typically rises into the 10^{-4} mbar region. If we take the pressure to be 1×10^{-4} mbar, the time to form a monolayer is only 0.01 s. Typically, assuming a winding speed of 600 m/min, the polymer passes through the aluminum deposition zone in 0.1 s (or less), and so there would be 10 monolayers of contaminants arriving at the same time as the aluminum arrives. At the typical metallizing thickness, this represents a contamination of approximately $1-2\%$.

For slower deposition processes and higher pressures, this contamination level can be higher.

Further Reading

[1] Harris NS. Modern vacuum practice. London, New York: McGraw-Hill; 1989. ISBN 0 07 707099 2.

[2] Basic vacuum practice. 3rd ed., Varian Associates, Lexington, MA 02173, 1992. Varian Part No. 900-0085.

[3] Hill RJ, editor. Physical vapor deposition. Glasgow: Temescal.; 1986 Part No. T-0186-6001-1.

[4] Roth A. Vacuum technology. Amsterdam: North Holland Publishing Co.; 1979 ISBN 0 444 10801 7.

[5] Maissel LI, Glang R. Handbook of thin film technology. New York: McGraw-Hill; 1983 (reissue) ISBN 0 07 039742 2.

[6] O'Hanlon JF. A user's guide to vacuum technology. Hoboken, NJ: Wiley Interscience; 1980.

[7] Guthrie A. Vacuum technology. New York: John Wiley and Sons; 1963.

[8] Weissler GL, Carlson RW, editors. Vacuum physics and technology, 14. New York: Academic Press; 1979.

[9] Zanker A. Accurate prediction of vapour pressures. Process Eng. 1977 November; p. 132−3.

[10] Tompkins HG. The fundamentals of vacuum technology. Monograph Series M:6 1997, American Vacuum Society, New York, NY.

[11] Tompkins HG. Vacuum technology: a beginning. Monograph Series HB-1 2002, American Vacuum Society, New York, NY 10017.

2 Products Using Vacuum Deposited Coatings

If we take as a measure the area in square meters of coated product, it has been estimated that around 98% of vacuum coated products are simple metallized coatings as used for packaging with 2% being for everything else. However, it has also been estimated that this 2% represents 25% of turnover. It is thought that metallized products represent around 550,000 tonnes of product, which is approximately 220,000 million square meters of coated film. As the number of other products increases and the volumes increase, this 2% is expected to grow. However, even with many millions of square meters of coatings for displays or photovoltaics, this is still a small fraction of the total quantity of coated films. Also, as many of these coatings are deposited at very slow winding speeds compared to aluminum metallizing, it makes it harder to achieve an increasing proportion of the volume, although if measuring the added value the changes are exaggerated and more easily seen. Within the area of metallized coatings, a substantial part of the business is for barrier coatings where the metal coatings are a barrier to water vapor, oxygen, other gases, and light to increase the shelf life of foods or other products. This market for barrier materials is about to increase with the advent of vacuum systems that are able to oxidize the aluminum metallized coating to produce low-cost transparent barrier coatings.

The market for other products is expected to be the fastest growing market; in particular in the area of transparent conducting coatings and ultrabarrier coatings. The reason for this is the rapid expansion of the flexible display and flexible solar cell markets. The ultrabarrier coatings differ from the food packaging barrier coatings as the ultrabarrier materials have a performance of around six orders of magnitude better than the food packaging barrier materials.

The following examples will start by describing in Sections 2.1–2.5 various products based on metallized films. Generally, when we talk of metallized coatings, we mean the coating is aluminum deposited using an aluminum wire-fed resistance-heated evaporation source. I have included holographic coatings in this group because the initial holograms were simple aluminum metallized coatings and only recently have they been developed with high refractive index coatings, patterning, semitransparent coatings, and combinations of these variations. Flake pigments are included for a similar reason. The bulk of the flake pigments is simple aluminum

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00002-7

metallized flakes. The basic process for flake manufacture can be used for almost any coating. There are lower volumes of other flakes produced although the value can be considerable.

Following this, there will be a section on barrier coatings as the bulk of the barrier coatings are based on aluminum metallized films. This will continue with a section that highlights the different requirements of ultrabarrier materials and the methods used to achieve the superior barrier performance.

Sections 2.6–2.14 will then generally give a snapshot of the types of products that are produced by methods other than aluminum metallization. Inevitably, there are other products, coatings, or applications that could have been mentioned, but hopefully those included will give a good indication of how diverse the uses of vacuum deposited coatings onto webs, foils, or films can be.

2.1 Metallized Packaging Film

Most of the vacuum coating that is done is thin metal coating for packaging applications. This covers many aspects of packaging. The metal coatings can be bright and highly reflective and hence provide more advertising impact than metallic inks which are duller.

The metallized polymer webs can be used directly by heat sealing, laminated to other webs, or have the metallic layer transferred onto other surfaces by a stamping process. These and other variations make the aluminized film very versatile as a packaging material.

Much of the wish to use the aluminized web is because of the high specular reflectance of the deposited metal. An extension of this drive for impact is to have bright metallic coatings plus an embossed hologram and then the visual impact is greater still as this creates a series of highly reflective color flashes.

Often the more important feature of the metal coating is that it provides a barrier performance against oxygen, water, and light. Foods that might, in earlier times, have been canned can be packaged in polymers provided there is sufficient barrier performance. The barrier performance of the metal thin film depends on the thickness of the coating and the cleanliness of the coating. Again, pinholes in the coating can be a problem.

This same metallized film can also be used to make metallized thread and yarn as shown in Fig. 2.2. If the film is microslit, it is called thread; if then twisted, it forms a yarn. This yarn or metallic thread is used in fabrics or more specialized versions used for security in currency. Lacquers can be used to color the aluminum-based silver metal to make golden thread or other metallic colors such as the blue lacquered thread as shown on the right-hand side of Fig. 2.2.

The use of lacquers or transparent colored inks also enables metallized papers to be overprinted and used to make more reflective printed products than can be achieved by metallic inks. Many of these applications of metallized paper are purely esthetic.

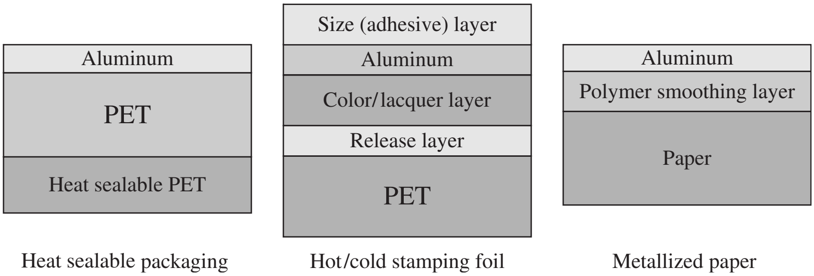


Figure 2.1 Schematics of some different aluminum metallized structures.

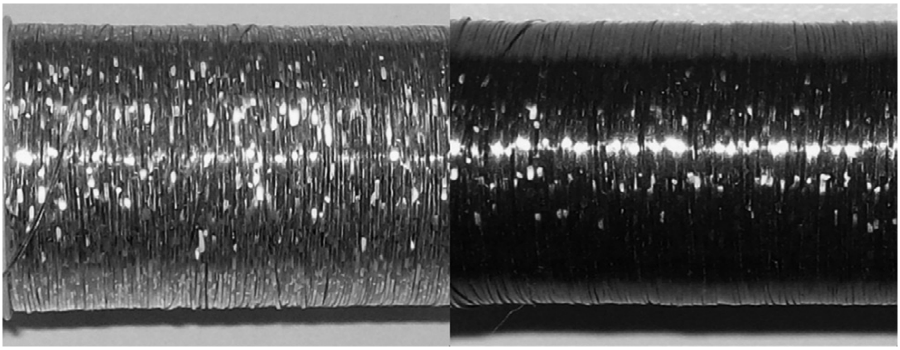


Figure 2.2 An example of metallized holographic thread; the left-hand thread is plain metallized and the right-hand one is blue lacquered.

2.1.1 Other Metallized Products

There are many other products that can be made using different combinations of substrate thickness, metal deposition, and other processes (Fig. 2.5) [1]. One such is mentioned at the end of Section 2.1 of microslitting a lacquered packaging film and making a metallic thread or yarn (Fig. 2.2).

Using the in-vacuum patterning process with a packaging film, it is possible to produce a microwave susceptor that can be used to heat food [2–5]. The pattern shape and spacing govern how the microwave power is converted, and weak points in the coating can be created that will limit the temperature the package reaches. As the film heats and expands, these weak points in the metallic coating break and the conductivity is lost, stopping the conversion of any more microwave power and thus limiting the heating (Fig. 2.3).

Simple electrical circuits such as antenna have also been made using this same combination of patterning and metallization [7] (Fig. 2.4). These have limitations on conductivity, which can limit the end use of the devices. Where the cost can be justified, other metals such as copper have been used, but this requires a different deposition source and is usually slower and so the cost per device can be much higher.

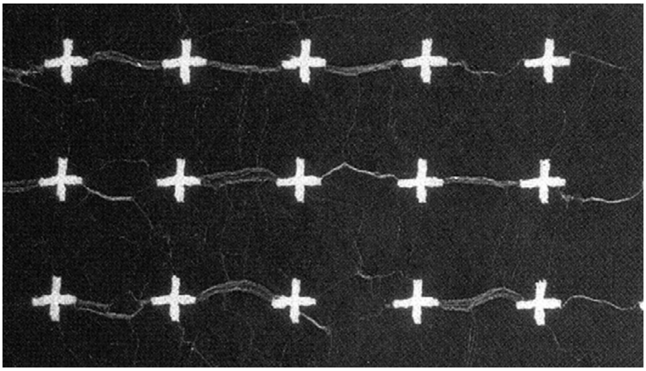


Figure 2.3 An example of a simple fused susceptor metallized film as produced by an in-vacuum pattern printing method [2, 3]. Photograph courtesy of Paper, Film & Foil Converter [6].

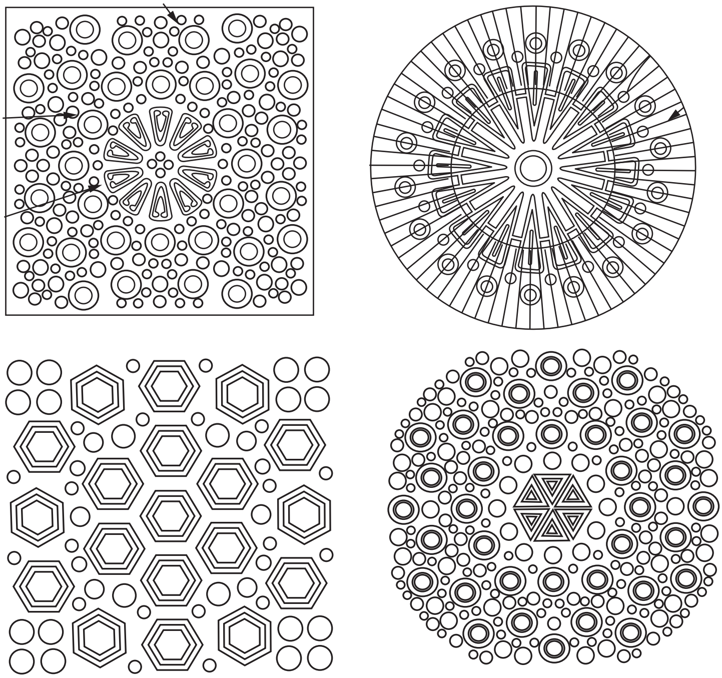


Figure 2.4 Some of the more complex patterns that are used for the antenna-type microwave susceptors [4]. The different shapes and sizes of antenna couple different proportions of the microwave energy and so heat different areas of the food at different rates and/or to different temperatures.

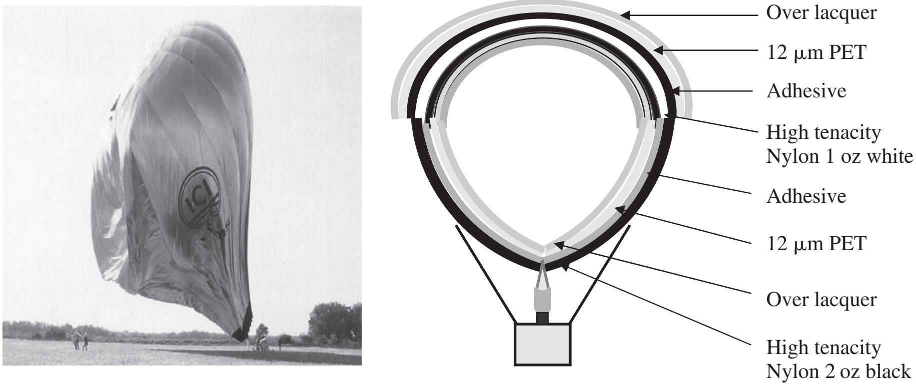


Figure 2.5 Metallized polyester laminated to make the envelope for balloons [8, 9]. Photograph courtesy of DuPont-Teijin Polyester Films (ex ICI Polyester Films).

2.2 Capacitor Films

These too are metal coatings usually deposited by evaporation onto thin polymer webs. The thinnest of the webs regularly coated is currently as low as 0.6 μm thick polyester film. The winding of such thin films is what makes this process special [10,11]. These thin webs are very sensitive to misalignment of rolls and poor control of speed and/or tension. The film can easily tear and so alignment and consistent tension are crucial. One of the tricks to keep the web well aligned is to have only very short free span lengths. This means that these machines may have more rolls included in the web path than is usual for a packaging metallizer.

The other common aspect of capacitor metallizers is the inclusion of a mechanism for making patterned coatings. This can be achieved by printing a pattern and after metallization washing off the pattern [12]. To save on process steps, two other methods have been developed. The first was to have a belt of the pattern rotating in a loop and being brought into contact with the web at the point of deposition [13−16]. The mask gets coated and leaves a blank on the web where it was in contact. The downside of this process is that the coating thickness builds up on the mask and can alter the width of the masked pattern with time. Also the coating on the mask can flake off and create much debris within the vessel, leading to additional pinholes in the coating. The second technique developed was to print on a pattern in the vacuum system [17]. This printing used diffusion pump oil to create the pattern that was printed on as a very thin layer. The metal deposition did not stick to the web because of the oil. The heat of condensation of the metal did, however, encourage the oil to be evaporated from the web such that, by the end of the deposition zone, the web was dry of oil and still without any metal coating in the printed areas. A more detailed description of the in-vacuum pattern metallization process is given in Chapter 13.

The reason for the masked stripes is to enable the web to be slit into narrower strips after deposition and to then roll up layers of material to make a capacitor of the desired capacitance. It is also common to have a slightly thicker deposition zone in the center of the metallized bands where they will be slit after deposition as shown schematically in Fig. 2.6. By alternating the uncoated edge and thicker coated edge, it is possible to then deposit metal contacts onto the opposing edges to create the finished capacitor.

The high edges can be achieved by shaping the masks that limit the deposition zone, allowing more deposition to obtain the thicker edge bands and restricting the deposition elsewhere. This reduces the material efficiency slightly but delivers the required product.

The range of products has increased over the years so that even with aluminized polyester there are many different variants available. Metallized capacitor film is probably one of the products that uses the thinnest polyester films that are regularly coated in a vacuum roll coating process. Films of thickness less than 1 μm (~0.6 μm) are used and thinner films still are desired.

Other developments were made using seeding layers and multilayer coatings with sharp or graded interfaces depending on whether the evaporation clouds overlapped. Some layers were also used for corrosion protection of higher performance

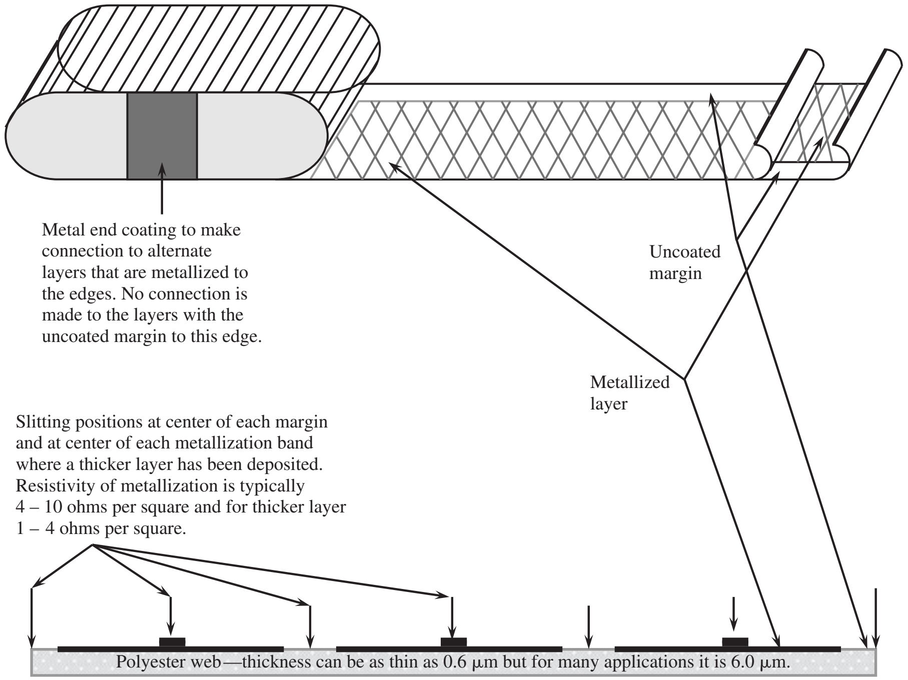


Figure 2.6 A schematic of the construction of a capacitor from thin metallized polyester.

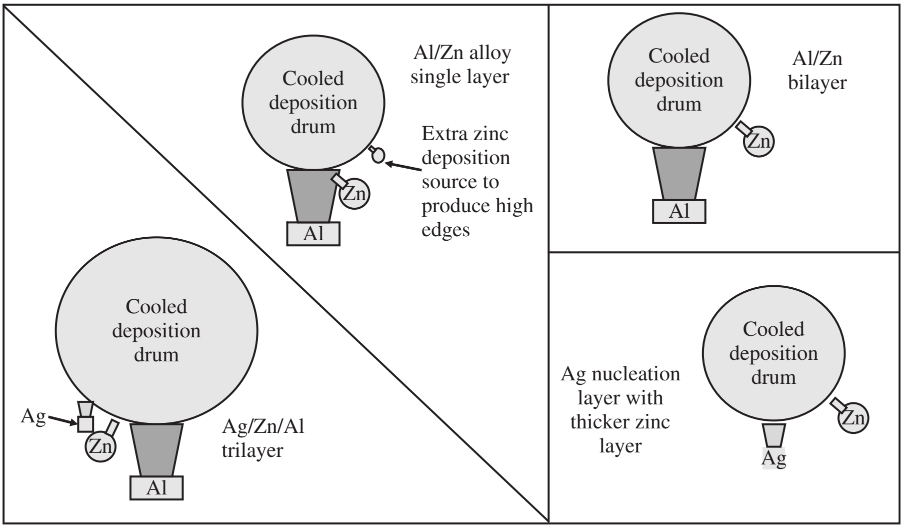


Figure 2.7 Schematics of the different system options for the manufacture of capacitors containing more than one layer.

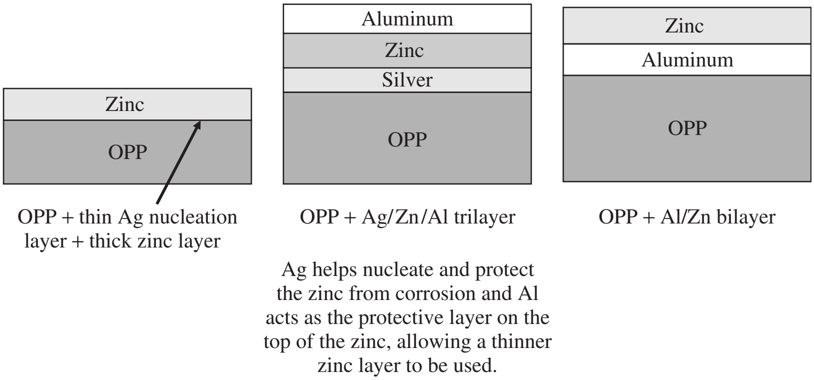


Figure 2.8 Schematics of the structure of various capacitors containing more than one layer.

materials. Figures 2.7 and 2.8 show some of the options for depositing additional layers, although generally all are from evaporation sources even if of different types. All sources were aimed at simple evaporation of metals from full-width sources that could all be run at high deposition speeds to allow for single-pass deposition.

In addition to all of this, there has now been added the deposition of polymer layers either as an initial smoothing layer or a final protective layer or both.

A list of the most common combinations would be as follows:

Aluminum
Zinc
Aluminum/zinc alloy
Aluminum + zinc
Aluminum + zinc + aluminum
Aluminum + zinc + silver
Zinc + aluminum
Silver + zinc
Silver + zinc + aluminum
Aluminum + silver + zinc + silver
Copper + zinc

2.2.1 Supercapacitors

There has recently been renewed interest in a new generation of vacuum deposited capacitors. These newer constructions are referred to as supercapacitors. They are being used as a method of energy storage and are being looked at for energy storage for a variety of different types of power generation. As the materials used are generally compounds, this usually means the capacitors cannot be deposited in the standard capacitor metallizers. The compounds are generally deposited in the more sophisticated systems containing sputtering sources, which also means the deposition rates are much slower and the cost of the capacitors is considerably higher. Examples of this would be amorphous ruthenium oxide (RuO_2) thin film electrode and an amorphous $Li_xPO_yN_z$ (Lipon) thin film electrolyte that are combined as RuO_2/LiPON/RuO_2/Pt as a thin film supercapacitor [18]. Alternatively, using the same electrolyte is the structure Co_3O_4/LiPON/Co_3O_4 [19]. Manganese oxide (MnO) onto graphite foils has been sputtered where the MnO is a possible cheaper option than RuO_2 that is very expensive. The market for supercapacitors is large, and there are a plethora of materials that can be used, many of which can be deposited by methods other than vacuum coating [20]. As with so many coatings, it will be the price/performance benefits that will determine which manufacturing process succeeds.

2.3 Optical Data Storage Tapes

Everybody will be familiar with compact discs that were a common form of optical data storage media. In the late 1980s, many different media types were being developed of which one was a tape form of optical data storage. This type of storage media was aimed at industries where very high capacity was essential, such as the continuous downloads from satellites or from geological survey ships. These tapes could store 1 TB of data [21—24]. Needless to say, technology has progressed and this type of storage media has been phased out.

The product works by using a high-power laser to write pits into an absorbing polymer layer and reading the difference in reflection between the pits and lands using a lower power read laser. The high reflectivity is required to keep the signal-to-noise level as high as possible. The aluminum coating thickness was around 30–40 nm, giving a reflectivity of in excess of 85% for the near IR.

This sounds to be quite an easy specification product, requiring only a good level of reflectivity that can be achieved by any/all of the different deposition techniques. The difficulty of producing this product is in the cleanliness requirements. This not only included the substrate but also the deposited metal. Oxidation of the metal reduced the reflectivity and so particular attention was paid to the removal of water and oxygen from the process.

Any debris on the web can result in a pinhole that can lead to a misreading of the information on the data storage tape. Hence, this product required cleaning of the substrate before deposition commenced. All the processing was done in a clean room. The deposition was done using magnetron sputtering as this was expected to be a cleaner process than evaporation. The energetic species bombarding the growing coating ensured that any loose material was removed during the deposition process.

2.4 Holographic Coatings

Holograms are bright, usually reflective, patterns or images that are used as decorative packaging and/or as security devices. In packaging, the brightness and changing colors are particularly eye-catching, and many products have benefited from increased sales after including holographic designs into their product packaging. The security holograms are very popular although for high-security applications are no longer regarded as very secure. This is because replication, copying, and manufacturing are now so easy and readily available.

Where holograms are used for packaging, they can be in the form of a small area integrated into the pack design or as a patterned background to the whole pack. As the technology has progressed and the availability has increased, the margins have fallen.

Hologram is a term that is often used to cover almost any reflective device that provides color. Hence, simple gratings through to kinograms and pixelgrams are all lumped together under the generic title holograms or optical variable devices (OVDs) even though technically they are not holograms.

The structure of holograms is quite simple in that a surface relief is embossed into the substrate surface and a reflective coating is added. The choice of method for embossing the surface relief and the choice of type and thickness of the coating give rise to a variety of performance options.

There are several types of holographic coatings that are now in common use. They are bright reflecting metallic coatings, semitransparent metallic coatings, demetallized coatings, and transparent high refractive index coatings [25,26].

2.4.1 Bright Metallic Holograms

This is a simple metal coating onto the embossed holographic structure in order to reflect the light. The metal acts as a mirror in reflecting the light; the colors derive from the embossed holographic structure.

2.4.2 Semitransparent Holograms

These holograms have only a very thin metal coating giving only a 5–10% reflectivity. This allows for the hologram to be laminated over some printing that can be read under the hologram. The semitransparent metal coating makes photocopying of the printing very difficult and thus the system is used for security applications. The low reflectivity makes these holograms more difficult to see compared to the bright metallic holograms, but at certain angles the colors will be bright and easily seen.

2.4.3 Demetallized Holograms

These holograms have had the full thickness bright metallic layer deposited, but then some of it is removed in a particular pattern [27]. This can be done in a way similar to the capacitor film by printing on a pattern in the vacuum system with diffusion pump oil. More commonly, the process adopted is to print the pattern onto the web either before metallization or postmetallization and to wash the web in a wet bath of appropriate solvent. This can give 50 μm line width patterns at 40 m/min speeds.

2.4.4 Transparent High Refractive Index Holograms

These holograms are completely transparent when viewed normal to the surface and the underlying printing is easily read [28–32]. At angle, the other colors and the holographic design then appear. These coatings are of either titanium dioxide or zinc sulfide, both of which have a high refractive index. The refractive index is a mismatch with the polymer such that the interface will give a reflection that can be seen. Titanium dioxide is the more robust coating but can affect the overall process. Some manufacturers buy web substrates already coated with the high index material, and then when they get an order for holograms, they take material from stock and emboss the hologram into it. This means that the high index coating is severely deformed in the embossing process. The titania coating is hard and brittle and will crack. This can affect the performance. If there is also poor adhesion, it is possible for this deformation to cause not only cracking but also an adhesion failure between the titania and the polymer, thus reducing the reflectivity. The other aspect of using the hard titania coating is that it will wear the embossing shim much more than a softer material. The zinc sulfide is a much softer and more compliant coating, and in general it survives the distortion from embossing more easily as well as being more gentle on the holographic shims. The refractive index is not as high as the titania and thus the reflectivity is not quite as high. Zinc sulfide can also be deposited at a much faster rate than the more difficult titania, and so it is a popular material for this application.

Figure 2.9 shows a schematic of the manufacture of a zero-order diffraction (ZOD) device showing two different structures made using directed deposition techniques [33–35].

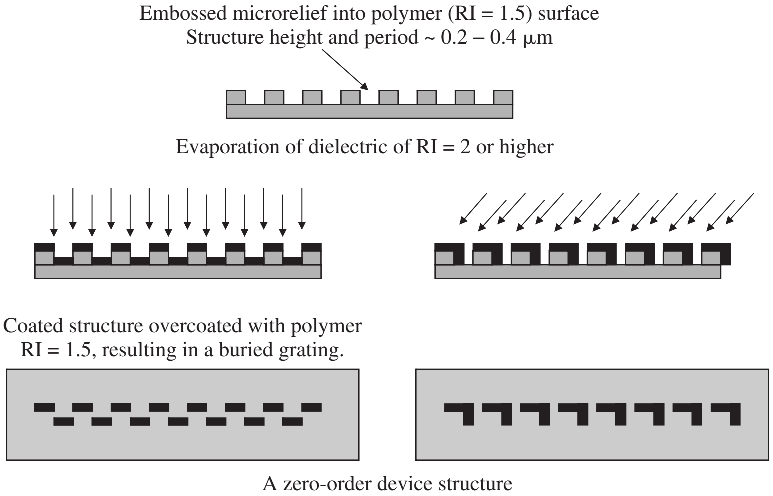


Figure 2.9 A schematic of a zero-order diffraction device.

2.5 Flake Pigments

One of the more curious products made by vacuum deposition onto webs has to be the manufacture of flake pigments. Traditionally, metallic flake pigments have been made by a variety of methods including pouring a liquid down a tower so that the liquid breaks up into droplets. These droplets then splat against an anvil, and a frozen splash of flat metal is the result. You can achieve the same effect by putting some solder onto the end of a soldering iron and then dropping or flicking the molten solder against a flat surface. The metal will flake off or can be peeled off the surface and looks like a “cornflake.” If the metal is aluminum, the flakes will look silver metallic but fairly dull (Fig. 2.10).

These “cornflakes” can also be produced by ball milling granular material. In this process, heavy balls of very hard materials are loaded into a barrel along with a quantity of aluminum powder and some oil [36,37]. As the barrel is rotated, the balls fall and smash against each other, and any powder that is between the balls gets crushed flat or flatter than the starting spherical material. After some time, many of these flakes will have undergone many of these collisions and a similar “cornflake” material is the result.

The customer requirement for brighter, more reflective metallic or silver pigments resulted in an improvement over the “cornflake” pigment. This was the lenticular pigment. This used “cornflake” pigment as the feedstock material into a polishing machine that used two large plates that used a planetary motion of one plate over the other with an oil slurry containing flakes and grinding material between the plates. The grinding and polishing action is used to smooth out the undulations of the “cornflake” surface, making the surface more reflective. The flakes cannot be held parallel to the platens and so they rock about resulting in the flakes being lenticular rather than parallel.

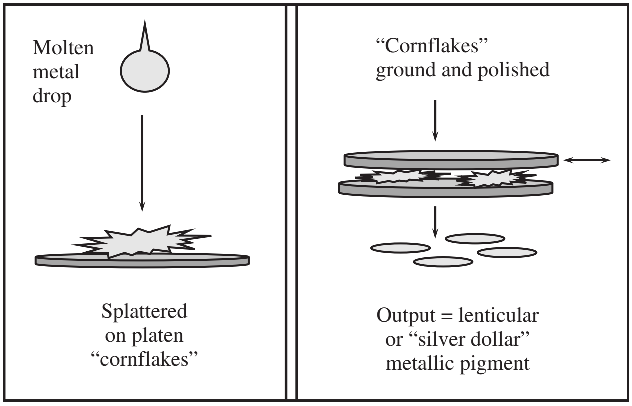


Figure 2.10 A schematic of the production of "cornflakes" (left) and lenticular flakes (right) that are commonly used in metallic inks and paints.

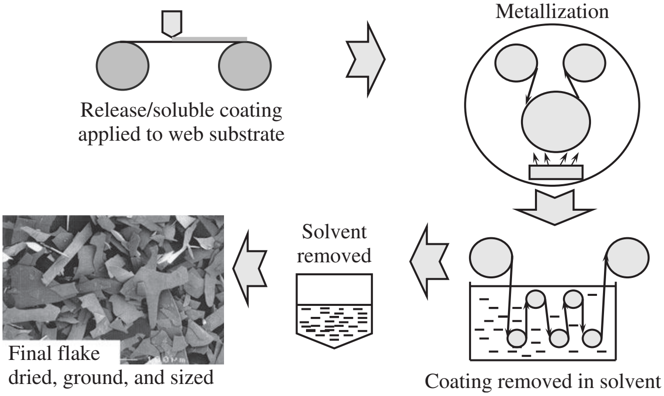


Figure 2.11 The production process of the vacuum deposited super flat bright aluminum flake pigment.

It was noticed that vacuum metallized polymer films could be used for mirrors. This indicated that the surface must be very flat, and it followed that a process was developed to produce even flatter, more reflective flake pigment. The metal was deposited onto a polymer web that already had a soluble release layer deposited on it. This soluble layer allowed the deposited metal layer to be removed by passing the web through a suitable solvent bath [38]. This slurry of pigment in solvent could be thickened by removing some solvent and then by adding other ingredients converted into paint or ink (Fig. 2.11).

This basic process is also used in the manufacture of colored and color shifting security pigments. Some of these multilayer structures are described in Section 2.12.

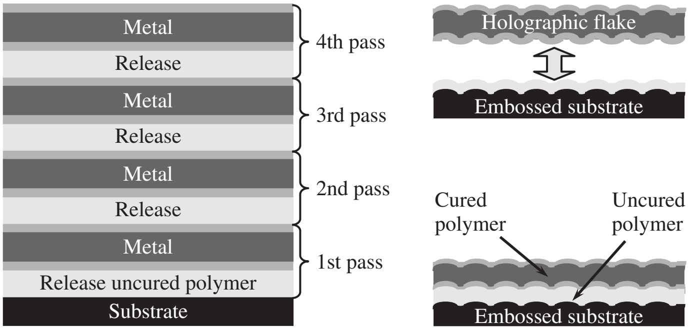


Figure 2.12 A schematic of a method of improving the production efficiency of metallic flakes and also using the same process producing embossed holographic pigment [39].

In an attempt to improve efficiency, a method of vacuum depositing a soluble layer was developed enabling multiple layers of flake materials to be produced in a series of passes but within a single vacuum pumpdown. As all the layers are very thin, they can each be deposited as a conformal layer and so any surface feature can be replicated. Thus, the polymer substrate surface can be embossed and the embossed structure can thus be replicated in the flakes produced. This method can be used for making holographic pigment.

One patent [39] describes the use of in-vacuum deposited polymer layers for the manufacture of pigment. The polymer when deposited but not cured acts as a soluble layer, but when deposited and cured acts as a protective layer on the aluminum, helping limit the rate of oxidation and making the metal more stable.

One of the newer uses of flake materials is as a method of improving the performance of barrier coatings (Fig. 2.13). In both metallized and transparent barrier coatings, the limitation in performance is primarily because of defects in the coatings, such as pinholes. These pinholes effectively have the same resistance to diffusion of oxygen or water vapor as air; however, this value can be changed significantly by adding a polymer coating. This changes the diffusion coefficient in the pinholes from air to that of the polymer, which can be a difference of a few orders of magnitude. This can be further improved if the polymer is filled using flake material that has a high aspect ratio but flake diameter well below 1 μm. These flake materials then make the diffusion path down the filled pinholes much more tortuous, or in some cases the flakes can plug the pinholes in which case the diffusion constant then becomes that of the flake material. This can improve the diffusion coefficient by further orders of magnitude.

2.6 Barrier Coatings

The barrier coatings are not just to prevent oxygen and water getting into the product from outside the package but may also be used to keep a modified gas atmosphere (MGA) from leaking out. The other one that many people forget is that light

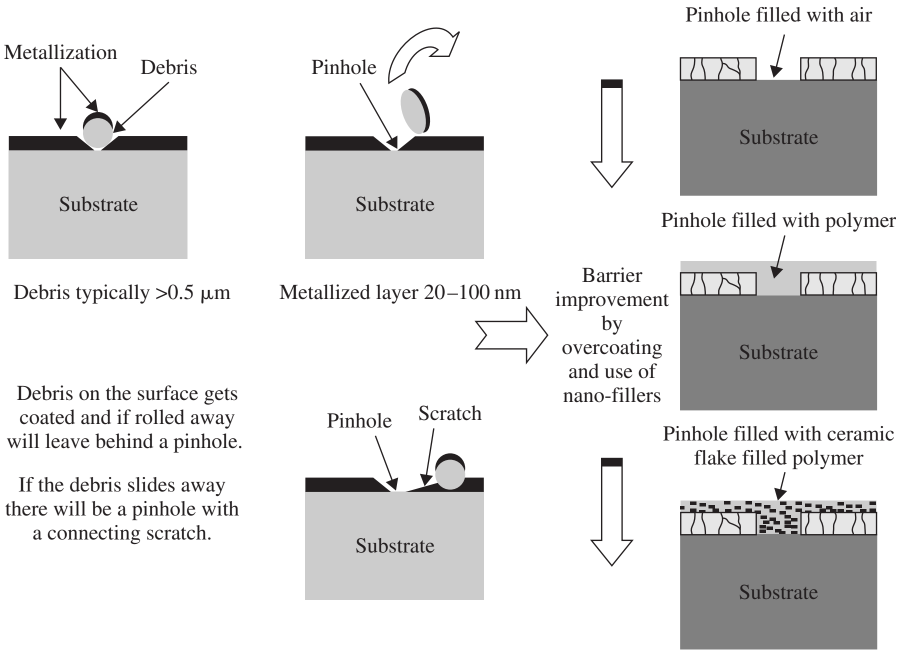


Figure 2.13 The cause of pinholes in vacuum deposited coatings and the way that an overcoating and use of nanoflake filler can improve the barrier performance [40].

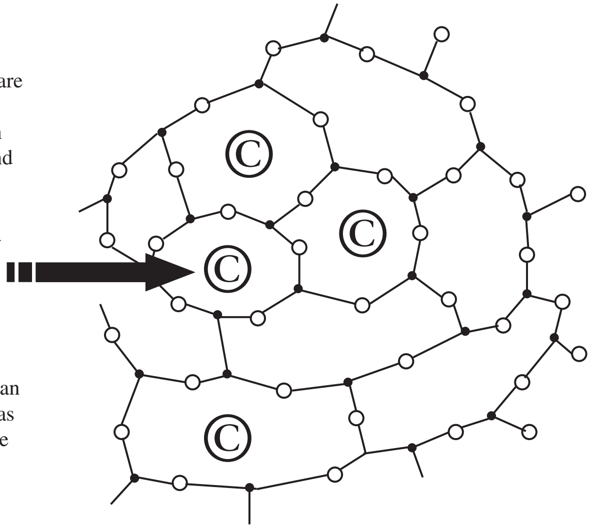
can turn fats rancid and so it is important to have the correct thickness of metal to limit the rate of this damaging process. This is referred to as the optical density of the coating, that is, OD 1.5 or OD 3.0.

2.6.1 Transparent Barrier Coatings

Not all products need to have a light barrier, and for some goods it is preferable to allow the consumer to see the goods. However, it may still be the case that oxygen and water vapor may degrade the product. Hence, there is a need for a transparent coating with the same barrier performance as the metallized coatings [41–45].

One of the most popular materials deposited for this application is silica. The structure is an amorphous network of silicon and oxygen atoms [46] (Fig. 2.14). It is believed that earlier coatings of this type were still quite porous because of this open network structure. Recent developments have included the use of carbon that sits in these open pores and substantially reduces the gas migration through the structure [47].

The difficulties of this process are to get the deposited coating to be color neutral, the barrier performance to be as good as possible, and the cost to be as near metallization as possible. The stoichiometry is critical to the color and to the barrier performance, and so there is a compromise on some of the performance. The cost has been lowered but is still anywhere from two to five times the cost of metallization.



Where the holes are large enough, carbon atoms can sit in the holes and block the oxygen diffusion path through the silica network.

PVD-deposited silica has little or no carbon. CVD-deposited silica can contain as much as 20% carbon in the coatings and has improved barrier performance.

Figure 2.14 A schematic of the silica network.

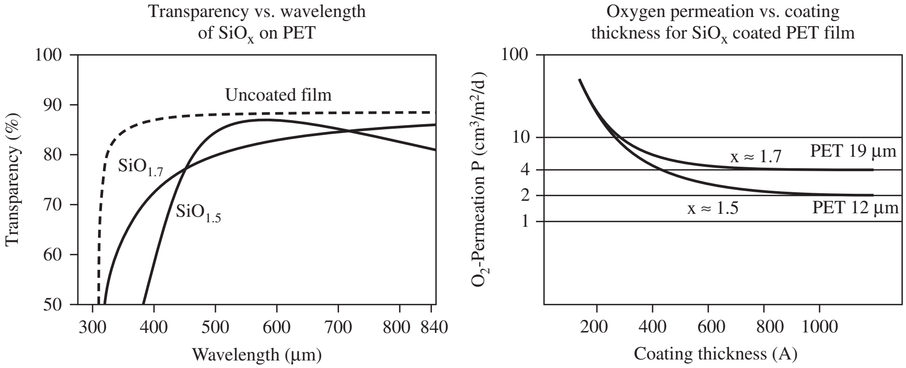


Figure 2.15 Graphs showing stoichiometry versus transparency and oxygen permeation versus coating thickness [48,50]. Courtesy of SVC [49].

The graph on the left of Fig. 2.15 shows how the silica is absorbing at the blue end of the spectrum, which creates a yellow tinge to the coating. In some applications, this is unacceptable and more “water white” coatings are required.

On the right-hand side graph of Fig. 2.15, it can be seen that changing the oxygen content in order to change the optical absorption can have an effect on the barrier performance too. In addition, when the composition is optimized for oxygen barrier performance, it may lose much of its water vapor barrier performance. Hence, very good compositional control is required for these coatings.

Silica has been evaporated from modified conventional metallizers as well as from e-beam metallizers. Alumina can be deposited by adding oxygen into the deposition zone or slightly after the deposition zone of a conventional metallizer. This makes those involved in making the capital investment more confident of a return on investment because if the barrier product were to struggle to make a profit, the machine could always revert to conventional opaque metallized coatings.

Other barrier materials being developed include carbon-based and melamine-based coatings. Carbon, melamine, and silica (which may contain up to 20% carbon) all can be deposited using chemical vapor deposition (CVD) [52–55]. In general, plasma CVD is the lower cost technology, but sweeping e-beam machines have been sold because if they fail to make barrier coatings cost-effective, they are versatile enough to make other saleable coatings. The plasma CVD machines tend to be only able to deposit the one coating type and so need a greater commitment by the customer when purchasing a machine.

Research has shown the biggest limitation to all barrier coatings to be the defects in the coating [56–58]. The largest of these is usually related to dust or debris on the surface being coated and then moved. Once these have been eliminated, the next level of defects becomes the limiting factor. These defects relate to the nucleation and subsequent growth process. Then, having eliminated debris-related defects and overcome the structural defects, the coating material can be optimized. This research has now found that silica and alumina are not necessarily the best materials to use, but until now this has been masked by the more gross problems created by the other defects that have masked this fine detail (Table 2.1).

High-quality barriers for use in organic light-emitting displays are required to be five or six orders of magnitude better than the transparent barriers used for food packaging as shown in Fig. 2.16.

This has been achieved by coating the web with a polymer in the vacuum system immediately before the silica deposition. This new polymer covers up all the dust or debris and provides a new, defect-free, and smooth surface on which to deposit a better quality barrier coating. This silica coating was still not as good as required and so more alternating layers of polymer and silica were deposited. Each combination of polymer and silica, as a pair, is known as a dyad. This multilayer material has achieved the stringent requirements for the display products. However, this product is of very high cost, and it is expected that in future different materials will be used that reduce the number of layers to achieve the same performance.

2.6.2 Structures

Many of these barrier materials are used in laminate structures. Although packaging materials of around 12 μm are required to be vacuum coated, the final packaging products may well be considerably thicker as they end up as a laminate. A couple of examples are shown in Fig. 2.17. Many of the transparent barrier coatings are not only very thin but also very fragile and have to be laminated to protect the

Table 2.1 Performance and Cost for Some of the Materials Used in Barrier Packaging

Barrier Material	Thickness	Oxygen Transmission [cm^3/m^2/day/atm]	Water Vapor Transmission [g/m^2/day/atm]	Deposition Process	Coating Type	Relative Cost
PET/Blank	12.00 μm	100	64.64			1×
PVdC	24.00 μm	8	0.3			
EVOH	24.00 μm	0.16–1.86[a]	N/A			3×
m-OPA	15.00 μm	30				
Aluminized PET (single)	~30 nm	0.31–1.55	0.31–1.55	Evaporation	Al	2×
Aluminized PET (double)	~30 nm each	0.03	N/A	Evaporation	Al	
Aluminum on PE	7 μm Al	0.001	N/A	Laminated	Al	
SiO_x on PET	10–80 nm	0.35–10[b]	0.46–1.24	Evaporation	SiOx	3×
SiO_x on PET or carbon-containing SiO_x	10–80 nm	0.08–1.55	0.5–5.0	PECVD	SiO_x or $Si(C)O_x$	3×
Al_2O_3 on PET	20 nm	1.5	5	Evaporation, or reactive evaporation	Al_2O_3	2.25–2.5×
Al_2O_3/SiO_x on PET	50 nm	2.0–3.0	1	Evaporation	Al_2O_3/SiO_x	2.5–3×
Diamond-like carbon on PET	20 nm	2	1.5	PECVD	Carbon (DLC)	2.5–3×
Melamine on PET	12.00 μm	<5		PVD	Melamine	2.5–3×
Melamine on OPP	20.00 μm/36 nm	30		PVD	Melamine	2.5–3×
OPP/Blank	20.00 μm	1600				

PET, polyethylene terephthalate; PVdC, polyvinylidene chloride; EVOH, ethylene vinyl alcohol; OPP, oriented polypropylene.

[a] Depending on relative humidity and ethylene content.

[b] Depending on process.

PVD = Physical Vapor Deposition.

PECVD = Plasma Enhanced Chemical Vapor Deposition.

DLC = Diamond Like Carbon.

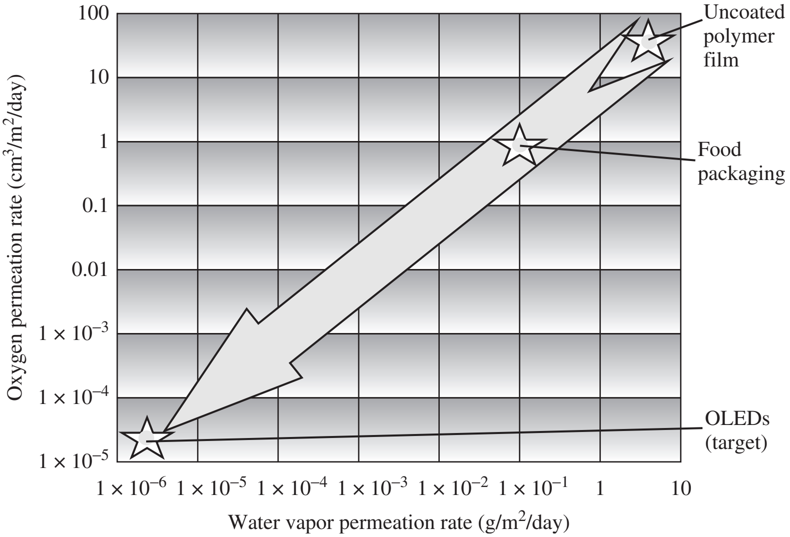
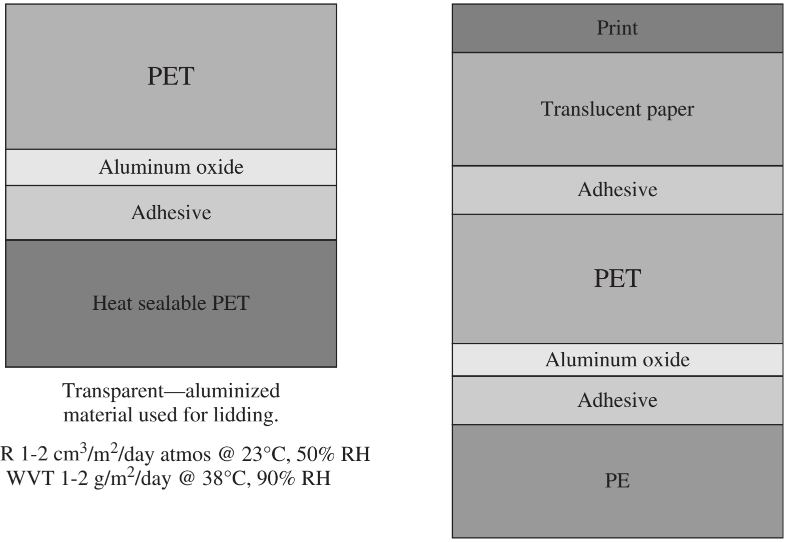


Figure 2.16 Barrier performance of uncoated polymers, coated polymers for food packaging, and the target for OLED ultrabarrier materials.



Transparent—aluminized material used for lidding.

OTR 1-2 cm^3/m^2/day atmos @ 23°C, 50% RH
WVT 1-2 g/m^2/day @ 38°C, 90% RH

Figure 2.17 Schematics of laminate barrier packaging materials.

coating from further damage. Others are expected to be more robust; however, as they are deposited onto a relatively soft substrate, they are still more prone to damage than if they were deposited onto more rigid substrates or were deposited as thicker coatings. Any damage, even damage that is invisible to the naked eye, is likely to be devastating to the barrier performance. Hence, to ensure ease of handling for downstream processes and thus maintain the best barrier performance, most vacuum coated transparent barrier films are laminated.

One particular method of manufacturing a transparent barrier is by the post or in-process oxidation of aluminum metallized film [59,60] (Fig. 2.18). This process has oxygen added to the process either during or just after the deposition zone. As the aluminum is very thin and highly reactive, it is oxidized and converts from being metallic and highly reflective to being transparent. This process originally was developed by one company [61−64] but more recently has been developed by system manufacturers [65−67]. The modification to the aluminum metallization process is relatively small and so the additional cost is much lower than for competing technologies. It is believed this will bring the vacuum coating costs down to close to that of metallizing and rapidly increase the use of transparent barrier coatings that has been predicted for many years but failed to materialize because the cost was always too high.

If this oxidation process is incomplete, the resultant film will be semitransparent or, in terms of microwaves, semiabsorbing. Thus, the coating can be used as a microwave susceptor (Fig. 2.19).

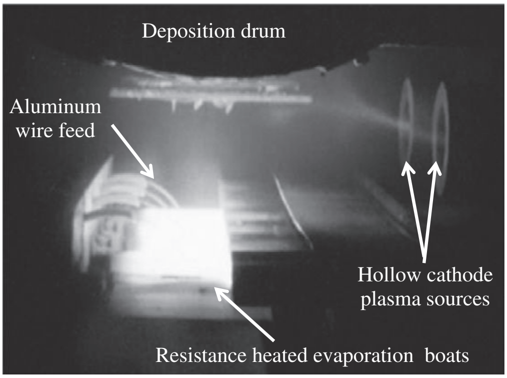
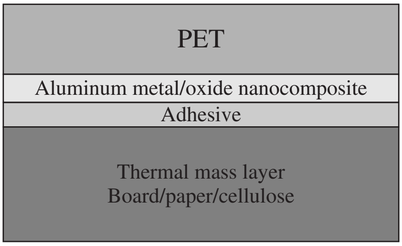


Figure 2.18 A picture courtesy of Fraunhofer FEP Dresden showing a hollow cathode secondary plasma source for the oxidation of evaporated aluminum to produce alumina.



Semitransparent—aluminized
material used as microwave susceptor

OTR <2 $\mathrm{cm}^3/\mathrm{m}^2$/day atmos @ 23°C, 50% RH
WVTR <1 $\mathrm{g/m}^2$/day @ 38°C, 90% RH

Figure 2.19 The laminate structure of a semitransparent partially oxidized aluminum microwave susceptor.

2.7 Transparent Conducting Oxides

There are many uses for transparent conducting oxide (TCO) coatings (see Figs. 2.20−2.25). There are many displays that use one or two layers of TCOs in their design. Currently, much of the vacuum coating is done onto glass. However, as more and more displays produced are for larger and larger applications, there is a wish to save on the manufacturing cost and also to save weight in the devices. Both of these factors are driving the technology toward vacuum coating onto polymer webs.

Another application of TCOs is in touch screens where two TCOs are held apart by spherical spacer beads, and when the film is pressed, the two surfaces come in contact and the circuit is made. The resistivity of the coating means that every point on the screen can be uniquely identified.

As the TCOs have some resistance, they have also been used as transparent low-level heaters. This was more to prevent heat loss than to heat up a volume. The TCOs have a plasma edge that rises just outside the visible and in the near IR. This gives the TCOs a heat mirror performance and so this can be used to enhance the greenhouse effect and again be used to reduce heat loss.

There are a range of TCOs that are technically possible [69−77], although some are rarely used because of the toxicity of the materials involved. An example of

Technical data

COATING CHARACTERISTICS							
PROPERTY	TYPICAL VALUE					UNITS	TEST METHOD
COATING	ITO			1-SERIES			
	ITO-400	ITO-200	ITO-100	I-20	I-5		
ELECTRICAL and OPTICAL:							
SHEET RESISTANCE	400	200	≤ 100	20	5	Ω/SQ.	ASTM D1044 (ILLUMINANT-C)
RESISTANCE UNIFORMITY	(+/−10)*	(+/−10)*	≤ 100	(+/−10)*	(+/−10)*	%	
TRANSMISSION (Tvis)**	≥ 85	≥ 85	≥ 85	≥ 80	≥ 60	%	

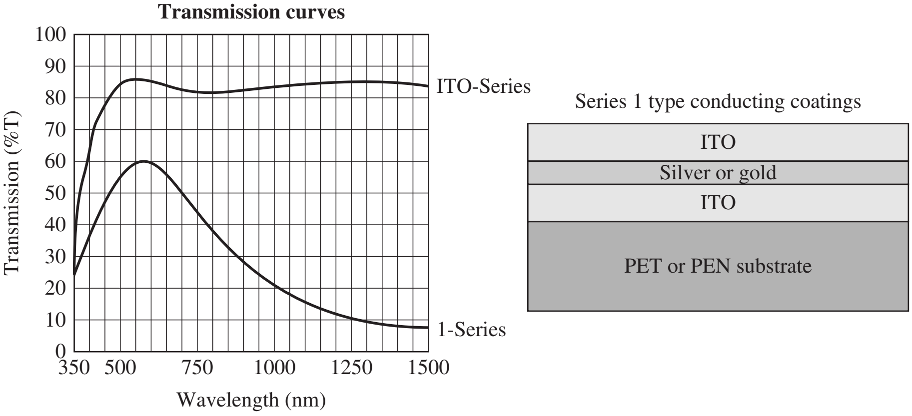


Figure 2.20 A graph comparing two ITO coatings and a table of some properties [68]. Graph and table courtesy of Flex Products Inc., a division of JDSU.

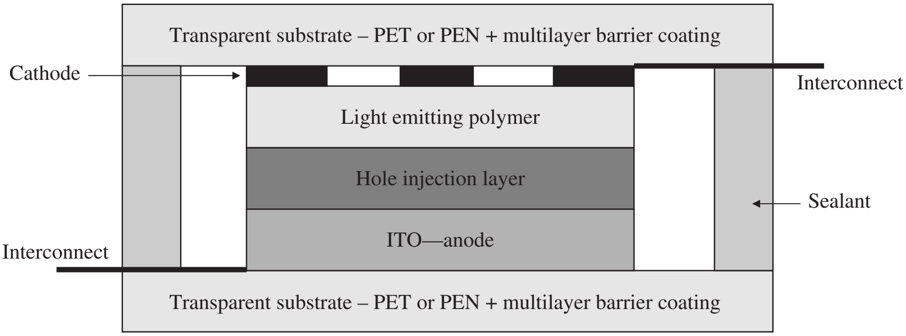


Figure 2.21 A schematic of an organic light emitting device (OLED).

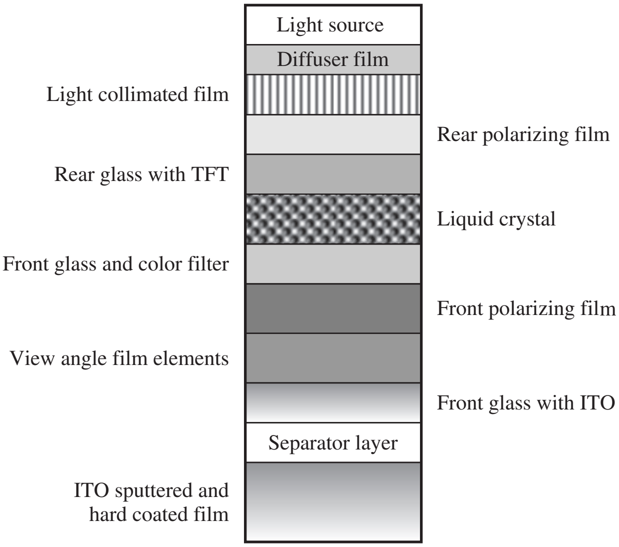


Figure 2.22 A schematic of an active matrix touch panel liquid crystal display.

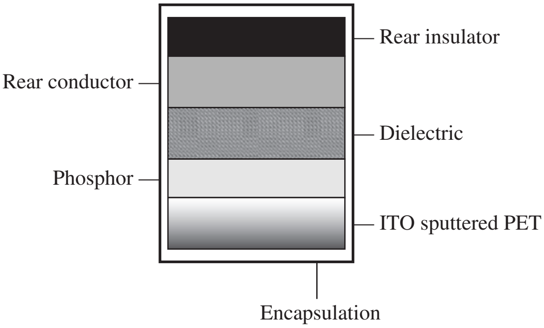


Figure 2.23 A schematic of an electroluminescent display.

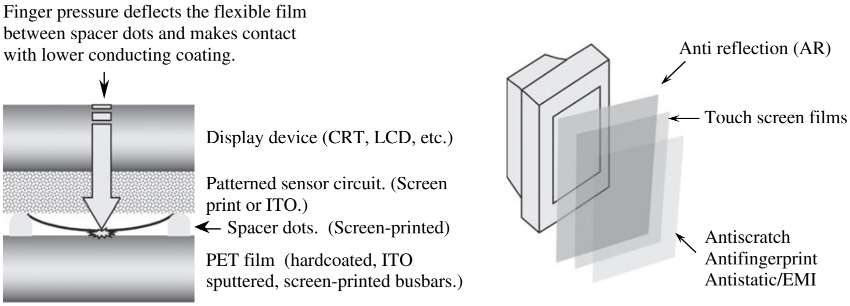


Figure 2.24 A schematic of a touch panel—as used with other layers for providing an active but also protective screen for the front of displays.

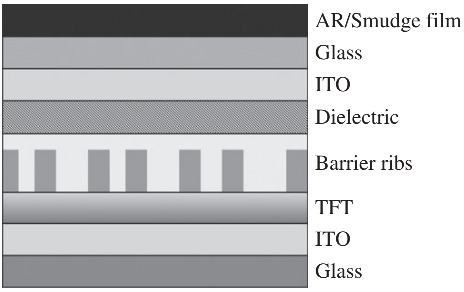


Figure 2.25 A schematic of the construction of a plasma display.

this would be cadmium, for the cadmium oxide or cadmium stannate coatings [78−80].

Of all the others, there is a preference to using indium tin oxide (ITO) as this can be produced with the highest conductivity. Indium oxide (IO) on its own is too soft and 20% tin content is too resistant to etching for making circuits, and hence the most popular composition is 90% indium + 10% tin.

Currently, there is a growing concern about the availability of indium as the use is exceeding the quantity extracted and stocks are reducing. Thus, the price has risen dramatically and is expected to rise further [81]. As the price rises, it becomes economic to process ore with a lower indium content. Indium suppliers have also worked on improving the efficiency of extraction and processing. Also, the users of sputtering targets are being more efficient about recycling the used targets and this has, at least temporarily, eased the demand for indium somewhat. However, with the massive increase in demand from the photovoltaic industry growing as quickly as the displays market, the problem of matching supply and demand will continue for some time. This is also made worse by some governments imposing tariffs on exports of indium. These tariffs are intended to either give an advantage to internal users or become a bargaining tool in trade negotiations.

The doped zinc oxides are looking like the materials most likely to replace the indium-based transparent conductors. These have been used on some flexible solar cell devices where an intrinsic zinc oxide is then coated with an aluminum-doped zinc oxide.

One of the problems with the TCOs is the thickness of the coatings, usually means that the ceramic nature of the materials does not allow much strain before the coating cracks and the conductivity is degraded. This has been addressed by one company by using two thinner TCO coatings separated by a polymer layer that is conducting enough to not affect the overall coating conductivity [82]. Others have looked elsewhere and have been developing conducting polymers to challenge the dominance of ITO [83]. These conducting polymers tend only to be a potential threat to the vacuum deposited TCOs where the requirement is a resistivity of 300 ohm/m^2 or greater. These conducting polymers are themselves under threat by the arrival of single-wall carbon nanotubes that can be coated to deliver the same resistivity of 300 ohm/m^2 or above but with a transmittance around 10% higher than the equivalent conducting polymer. The transparent carbon nanotubes have been used to coat flexible solar cells [84]. The development and use of carbon nanotubes are expected to advance and gradually challenge the use of TCOs for coatings with a resistivity lower than 300 ohm/m^2.

One of the methods for growing nanotubes is to coat a roll of polymer film, strip the coating off, and grind the coating into flakes that are then used to act as nucleation sites for individual nanotubes that then grow from the surface [85]. Another method directly deposits the carbon nanotubes as an array onto a moving substrate giving the potential for roll coating of carbon nanotubes [86].

2.7.1 Gas Sensors

It is possible to change the mobility by changing surface scattering and hence the conductivity of semiconductor coatings by the chemisorption of gas into the surface. This process of chemisorption is reversible and so too are the changes in conductivity. The change in conductivity is also proportional to pressure.

This makes TCOs suitable for use as gas sensors.

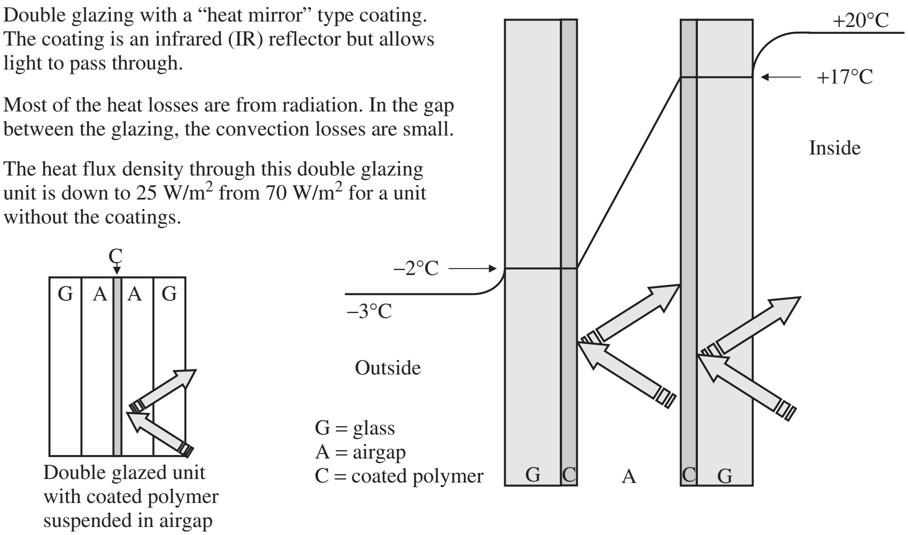
The most widely used TCO for this application is tin oxide, where it can be customized for use to detect methane or propane, carbon monoxide, hydrogen, ethanol, nitrogen oxide, and trimethylamine gas. Often to get the best out of these films, they are doped to be more selective and increase the sensitivity [87].

2.8 Energy Conservation Windows

There are two broad categories for energy conservation windows: solar gain or solar rejection windows [88,89].

2.8.1 Solar Gain

Solar gain windows are the likes of the “heat mirror” systems [90–96]. Here, the visible light is transmitted into a room where it is absorbed by the furniture and is



Double glazing with a “heat mirror” type coating. The coating is an infrared (IR) reflector but allows light to pass through.

Most of the heat losses are from radiation. In the gap between the glazing, the convection losses are small.

The heat flux density through this double glazing unit is down to 25 W/m^2 from 70 W/m^2 for a unit without the coatings.

Double glazed unit with coated polymer suspended in airgap

G = glass
A = airgap
C = coated polymer

Figure 2.26 A schematic of a low E-type coating [99].

re-emitted as infrared energy that is reflected by the window back into the room, thus building up the heat within the room and reducing the need to supply additional heat. A number of this type of coatings can be deposited onto polymers and laminated to windows. There are two types of coating that can work in this way. One is a fairly thick transparent conducting oxide coating and the other is a very thin metal coating that has antireflecting layers on either side. Both these coatings have their problems in manufacture. The transparent oxides need very precise control to get the stoichiometry right to make them conducting and the process is slow making the coating expensive. The thin metals are fragile and susceptible to corrosion and thus need to be protected, and thus at least a minimum of four layers are required and often seven layers or more. Again this makes the process expensive.

These coatings are for use in cold climates where reduction of heating costs is the predominant factor (Fig. 2.26).

2.8.2 Solar Rejection

Solar rejection is where the energy available from the sunlight is large and the heat buildup in the room can become intolerable and so air conditioning units are supplied to cool the rooms down [97,98]. The solar rejection coatings are visible reflectors and/or absorbers. Here, the coating restricts the light penetrating the room and thus limits the light that can be converted into infrared energy and heat up the room. These are typically thin metallic coatings that are semitransparent. The trade-off is just how little light to let into a building to make the occupants feel good and to not need lighting but to minimize the load on the air conditioning.

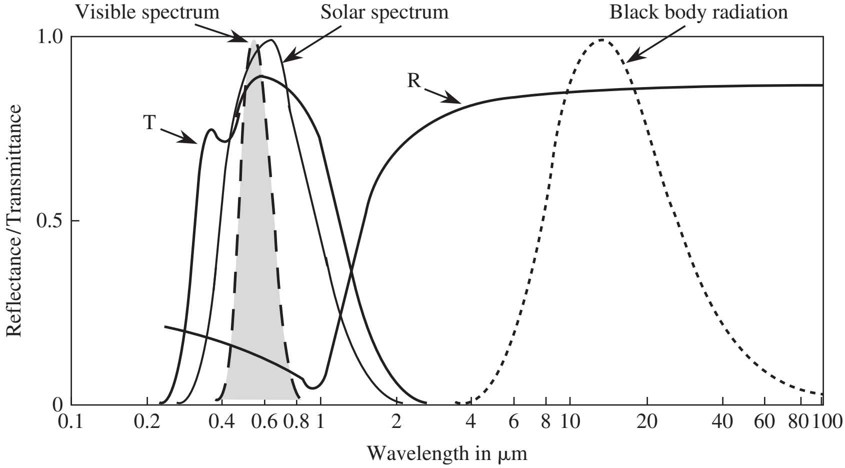


Figure 2.27 Reflection and transmission for an ITO coating overlaid on the solar spectrum, visible spectrum, and black body radiation.

This type of coating is only required in the warm climates within the world where air conditioning costs outweigh heating and lighting costs.

This type of coating is also being exploited in improving the comfort within automobiles. Cars have a large window area for the volume and this makes the inside act like a greenhouse taking a large amount of light and converting it to infrared energy within the body. This makes the cars hot even at moderate outside temperatures. Using solar rejection coatings can reduce this temperature and eliminate the need for adding air conditioning units to cars, which in turn improves the fuel economy.

Figure 2.27 shows the solar spectrum and where the solar gain comes from [100]. By moving the reflection curve to the left, more of the near-IR solar gain is rejected. In addition, by increasing the reflectivity across the IR, more of the black body radiation would be rejected. This would change the coating from solar gain to solar control or rejection.

2.9 Solar Cells

Solar cells, for the conversion of sunlight into electricity, are manufactured by depositing coatings onto a flexible stainless steel foil and have become a standard product for a number of years now. The production machines for these are generally based on CVD processes and in some respects are more akin to semiconductor processing than most of the other web coating processes [101,102] (Fig. 2.28).

The efficiency of solar cells is quite low, with amorphous silicon cells being around 10% efficient and polycrystalline cells around 15% efficient. Developments have produced tandem and triple- cell designs that are aimed at converting more

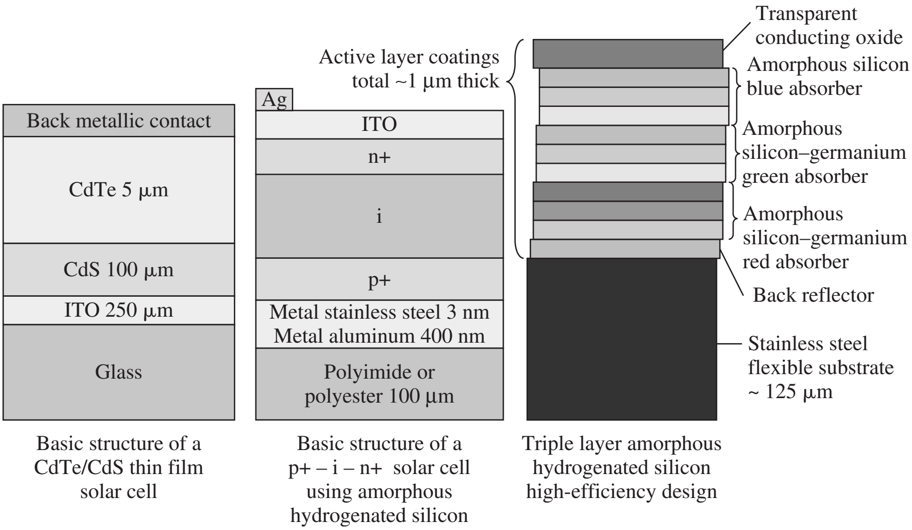


Figure 2.28 Two simple cell designs: the right-hand one aimed at vacuum deposition onto polymer substrates.

light into electricity. This is achieved by optimizing absorbers for different wavelength light and building one on top of another. This results in the incident light being absorbed sequentially as it passes through each of the different optimized layers. The problematic part of this design is that it requires almost three times as many coatings as in the single-cell design (Fig. 2.28). The deposition process control has to be very precise to achieve both the thickness and stoichiometry specification. This results in a large opportunity for producing out-of-specification coatings and as such the process efficiency suffers when moving up to the triple-cell design [103].

Any design has a hard standard to achieve. Current silicon wafer designs have been proven in the field and have guaranteed 80% of original performance after 15 years use. Thus, to get the highest efficiency and production yield, the deposited structure has little margin for error. The highest efficiency cells have the greatest number of layers, which provides a challenge to achieve high yields, as the greater the number of layers, the greater the opportunity for any one layer to be other than optimum.

The different layers may be deposited by different vacuum coating processes and may also require different substrate temperatures. The copper indium gallium diselenide (CIGS) layer (Figs. 2.29 and 2.30) is particularly challenging as not only is it preferable to have a graded stoichiometry through the thickness of the coating but also the grain size needs to be controlled. The buffer layer and transparent conducting coatings may also be deposited by a different process but still need to intimately contact the surface of the CIGS layer. An example of this complex multilayer structure is shown in Fig. 2.30.

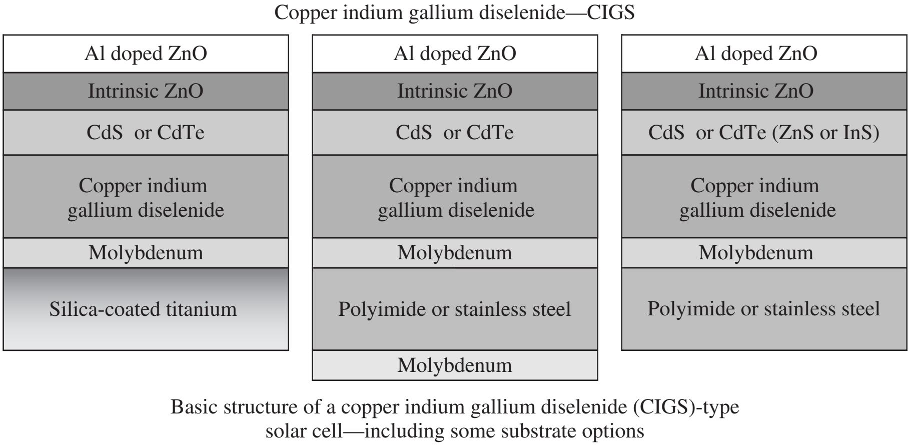


Figure 2.29 Some of the alternative structures possible on different flexible substrates.

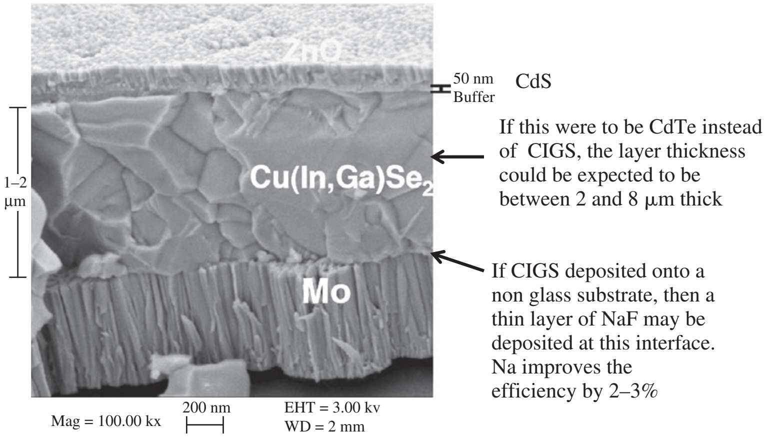


Figure 2.30 A micrograph of a CIGS solar cell structure. Courtesy of Ayodhya N. Tiwari, EMPA.

This market is growing and the rate of growth has occasional spurts as the cost of oil has sudden rises [104]. However, solar cells are not generally cost-effective for mass use. Solar cells win out financially in remote areas or where it is difficult to connect to a central supplier. Thus, satellites were an early use of the technology, so too was connecting remote populations to telephone services. The cost per watt of electricity is much higher than that available from power stations, and so to encourage more people to adopt this technology, governments often provide subsidies. Thus, the development has been speeded up and the market growth has been artificially increased. It is acknowledged that for this to continue, and for the technology to have a more major impact on fossil fuel power consumption, there has to be a step change in the technology to either massively increase the efficiency or to drastically reduce the cost. In this way, the continued growth of the market will no longer be dependent on subsidies.

There is a threat to the vacuum coated solar cells and that is the atmospheric pressure roll-to-roll coated solar cells. Currently, these are being produced at nearly 5% initial efficiency, although this degrades with time. If one looks at the history of the amorphous solar cells that are now a standard product at 10% efficiency, these were down at this same low level some 10−15 years ago. Thus, the expectation is that much cheaper, although low-efficiency, solar cells will displace some of the vacuum coated solar cell production within the next 5 years or so. The same option of producing tandem designs to increase the efficiency is already being taken by some companies before they have even perfected a single-cell design.

A critical problem for many for these designs is the need for a barrier coating. Often one or more layers can be sensitive to either oxygen or moisture or both, and in order to give the product a long lifetime, the cells have to be encapsulated using a barrier layer. Often this barrier layer needs to be of the ultrabarrier type and these materials are not yet widely available and the costs are high. A robust ultrabarrier material still represents an unmet need for both the display and photovoltaic markets.

2.10 Solar Absorbers

Solar absorbers are not the same as solar cells and do not convert energy from the sun into electricity. They do convert energy from the sun into heat. This heat is used to reduce the electricity used to produce the equivalent heat, and so they are still an energy-saving device and often come under the same category of energy conservation, and hence on occasions are confused with solar cells.

The method most commonly used for transferring the heat from the absorbers to where it is most needed is to use a liquid, commonly water. Central heating systems use copper pipes for transporting water around the heating circuit. Thus, if the copper pipes were to be exposed to the Sun, they would absorb some energy and heat the water within the pipe. This would not be particularly efficient and so work was done to improve the absorption efficiency of surfaces.

The ideal would be to have a single material that absorbs in the visible and converts the light to heat. Intrinsic solar selector single materials are wavelength selective such as hafnium carbide or tungsten. None are ideal materials with either the transition from low- to high-reflectance slope being too gradual or cutting off the solar spectrum too soon. The very low-tech approach is to coat the surface with a dull black paint, which would be a better absorber than the basic metal surface. However, the high-tech approach is to optimize the absorptance. There are several options such as the absorption/reflection combination where the substrate reflects the light back through the absorber for a second chance of absorbing the light. Another is a multilayer where there are alternating dielectric and semitransparent absorbing metallic layers. Alternatively, a heat mirror coating on a nonselective black substrate surface. Then, there are the composite structures where there can be an absorbing metal dispersed in a dielectric material, and this can take many forms with the size and density of the particles being greater close to the substrate surface and fewer and smaller toward the top surface. Many of these different coating options can also include an antireflection top coating to maximize the amount of light captured [105,106].

Table 2.2 gives some examples of vacuum deposited coatings that have been evaluated as solar absorbers. There are many more if other deposition processes such as sol-gel or spraying are included.

The result of research produced the structure as shown in Fig. 2.31. Light hitting the front surface meets an antireflecting coating and so almost all the light passes into the structure. The next layer is the most critical layer in that it is where the absorptance takes place. The material is absorbing to some extent, but not necessarily highly so. To improve the absorption efficiency, a second material is dispersed through the matrix material that creates scattering centers. The scattering

Table 2.2 Some Possible Vacuum Deposited Solar Absorber Materials

Absorber Materials	Foil	Deposition Method	Absorption
Ni-Nio$_x$/Cu-Ni	Al	Sputtering	95%
CrN-Cr$_x$Oy	Cu	Sputtering	93%
TiN$_x$Oy	Cu	Evaporation	95%
Cu-Cr-C	Cu	Sputtering	–
Ni/NiO$_x$	Al	Sputtering	–
Ag/Alumina	Al	Sputtering/Evaporation	95%
SS/Alumina	SS	Sputtering	94%
Cu/Alumina	Cu	Sputtering	–
Ti/Silica	Al	Sputtering	–

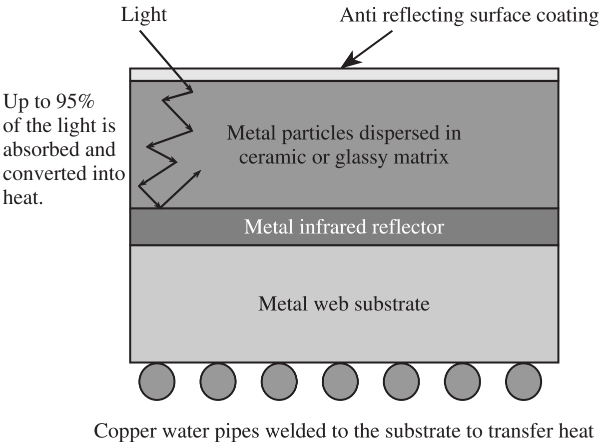


Figure 2.31 A schematic of the structure of a solar absorber.

increases the optical path length so that there is an increased chance of the light being absorbed. The final layer of the three is a reflecting layer that will send back any unabsorbed light back through the absorption layer with all the myriad of scattering centers. The net result of this is that around 95% of the incident light can be absorbed and converted into heat [107].

The choice of substrate is determined by several factors. The substrate has to efficiently conduct the heat from the absorber to the water. The copper pipes containing the water must be able to be attached to the substrate and also have good thermal conductivity. A simple copper foil web has been used, but it can be an expensive substrate. Others have used aluminum or stainless steel substrates that are also able to have the copper pipes brazed onto them as a downstream process to the vacuum deposition of the top surface coatings.

This combination of material types and wide range of layer thickness has given rise to some interesting machine designs in order to accommodate different deposition source types. This allows both sputtering and electron beam evaporation sources to be operated in a single-pass process.

2.11 Flexible Circuits

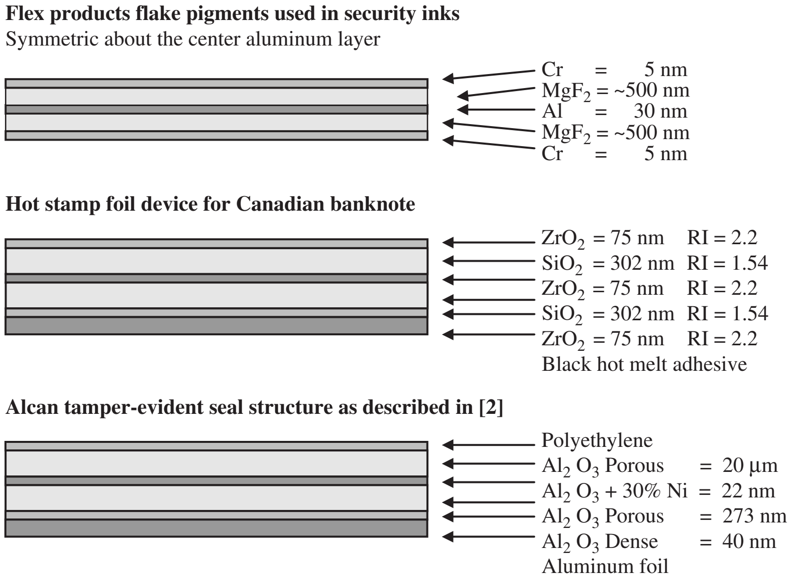
Many of us will have used equipment containing flex circuits such as mobile phones, laptop computers, or compact disc players. Electrical products that have a hinge included in the design and require the hinged parts to be connected electrically will have to have something included to connect the parts. Initially, this was achieved by cable, and as the sizes are reduced and the requirements are for reduced weight, it became advantageous to use ribbon cable. Ultimately, flexible circuits, where the copper "wires" are a vacuum deposited coating onto a flexible polymer web, were utilized as the lightest and thinnest solution.

The term "flexible circuits" covers a variety of different products from flexible interconnecting material to flexible circuit boards that have components soldered onto them. A subset would include tape-automated bonding, which is a carrier tape that has a set of interconnects to make it easier to connect to a microchip at different points in the manufacturing process [108–111].

The basic requirement for the material is that copper is deposited onto the polymer web with sufficient thickness to deliver the desired conductivity or sufficient thickness that will allow the copper to be plated up to the desired thickness [112–115].

2.12 Optical Variable Devices

"Optical variable device (OVD)" is one of those generic terms that covers many different types of coatings (Fig. 2.32). Holograms fall into this category as do a variety of interference coatings and ZOD devices. All of these exhibit the characteristic that as the viewing angle changes from the normal, the color or reflectivity changes dramatically.


Flex products flake pigments used in security inks
Symmetric about the center aluminum layer

Hot stamp foil device for Canadian banknote

Alcan tamper-evident seal structure as described in [2]

Figure 2.32 A schematic of three different optical variable devices.

The interference coatings are multilayer coatings that optimize the refractive index, absorption, and reflectivity to produce colors. This is like the iridescent colors that can be seen when there is a thin film of oil on water. The oil on water is an uncontrolled effect whereas we are able to control the thickness of each layer and so optimize the structure to give the maximum color effect.

It is also possible to control the adhesion of some of the layers so that the coating will fail at a particular interface or within a particular coating so that the color will change irreversibly, thus making the coating part of a tamper evident feature.

These OVDs can be stripped from the web and ground up into tiny flakes so that they can be incorporated into polymers, inks, or paints as a pigment, thus making color shifting polymers, inks, or paints [116–120]. Alternatively, they can have an adhesive added after metallization and can then be hot or cold stamped as a laminate onto some other surface.

As the color shifts with angle, it is impossible to copy the color of the inks by color photocopying, and hence they have been used as high security inks and appeared on banknotes of over 100 countries.

2.13 Magnetic Electronic Article Surveillance Tags

Theft of products from shops is a significant problem. One defense against this is to put an electronic tag onto the products that trigger an alarm if removed from the shop without being neutralized at the cash till. These tags are known as electronic article surveillance (EAS) tags (Fig. 2.33).

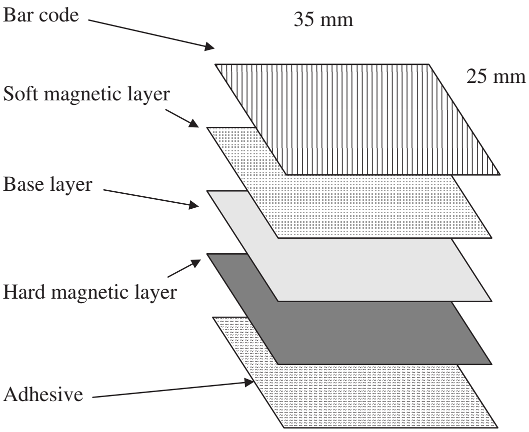


Figure 2.33 A schematic of the construction of a more conventional EAS magnetic security tag.

The previous generation of EAS tags falls into two categories: one that uses magnetic materials and the other that uses a resonant circuit for a radio frequency (RF) signal. One company manufactured the magnetic tags where only one of the magnetic layers could be deposited by magnetron sputtering, the other was too thick and was a cast material. The RF tags originally used a thin film circuit that was made by vacuum depositing a thin metal and printing and etching the circuit into the metal. This was very wasteful of the expensive metallization process and eventually conducting ink was developed so that the circuit could simply be printed directly onto the labels.

More recently, there has been a requirement for more information to be stored by the tags and ideally the possibility of producing an audit trail by having updatable tags. One extension of the RF tags has been to incorporate a chip into the circuit. These can still be printed using the conducting inks. The tags are expensive although the costs are expected to fall dramatically once volumes increase. As the conducting fillers improve in performance and the costs have fallen, this has become the preferred production process and vacuum deposited coatings are now only used for special applications.

Other types of magnetic tags have been developed such as one that uses a vacuum deposited thin film magnetic coating. The coated film is laminated as a series of layers at different orientations. Each orientation that has magnetic material contributes to the final signal. Thus, the signal can be read as a series of ones or zeros depending on whether at that orientation there is magnetic material or not. This binary code means that information can be stored. This is a relatively new technology, but it is hard to see how it would be competitive to the printed alternatives [121].

2.14 Pyrotechnics

A method of manufacture of pyrotechnics was developed using high-rate evaporation of magnesium onto a PTFE web [122,123]. The magnesium was the fuel and the fluorine in the PTFE was the oxidizer. Given ignition, the PTFE would melt releasing the fluorine, and this would react with the magnesium releasing heat that

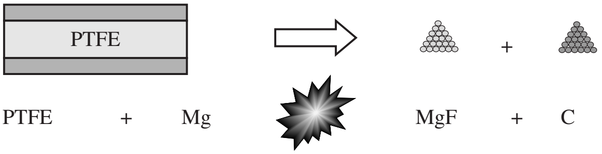
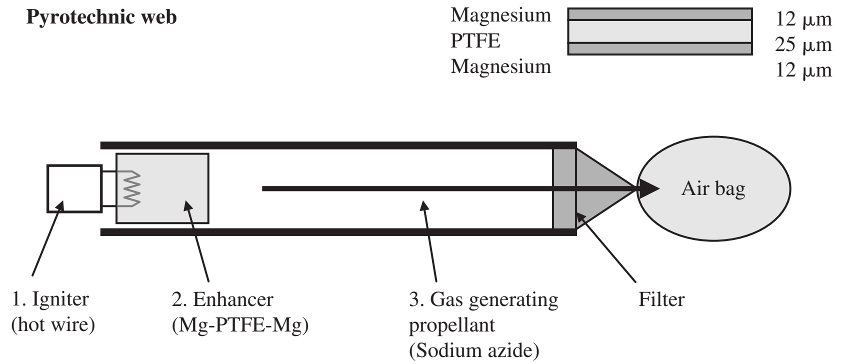


Figure 2.34 The reaction produces benign reaction products as powder.



1. Crash sensed—current dumped into hot wire igniter.
2. Hot wire ignites enhancer—changes ignition from point source to large surface area source.
3. Enhancer ignites large areas of gas propellant, generating a large volume of gas.
4. Gas is filtered to remove hot particles and inflates air bag within 50 ms of crash being sensed.

Figure 2.35 A schematic of the construction of an airbag showing the use of a vacuum deposited pyrotechnic product.

would help sustain the process [124,125]. The byproducts of the conflagration were magnesium fluoride and carbon, both of which are benign (Fig. 2.34).

The process was deemed a gasless and safe process, and the material was used to form the enhancer part of an airbag design for use in automobiles [126]. The enhancer takes the initial point source ignition and turns it into a large surface ignition for igniting a large surface area of the gas generating material that speeds up the inflation time for the airbag (Fig. 2.35).

This same technology has since been used to make foil sheet that can be used to attach materials together. If two materials are held tightly against each other with some foil between the mating surfaces and the foil ignited, it will melt and weld the surfaces together. As the reaction is very fast, the total energy is quite small and so the bulk temperature of materials can be kept quite low. This technique was used on welding semiconductor chips to heat sinks initially, but more recently it has been used to weld magnetron sputtering targets to backing plates [127].

2.15 Thin Film Batteries

There is an interest in producing very small, light, high-power batteries. These are used in modern electrical appliances such as mobile phones, personal organizers, laptop computers, miniature medical devices, and smart cards to name but a few. As time goes on, there is a continuing expectation for longer lifetimes and further miniaturization [128].

The development in the deposition of polymeric coatings in vacuum has enabled complete battery structures to be deposited without breaking the vacuum [129]. Other developments, enabling materials such as lithium [130−134] to be deposited quickly and safely, mean that when both techniques are used together, a device can be produced where the metal thin film can be encapsulated preventing later degradation.

References

[1] Cox JW. Industrial applications for metallized flexible substrates. In: Proc. polymers, laminations and coatings conference; 1987. p. 421−3.

[2] McCormick JA, Walters GJ. The fuse susceptor. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 47−51.

[3] McCormick JA, Walters GJ. Fused microwave conductive structure. US patent 5 412 187, 1995.

[4] Lai L, Zeng M. Microwavable container with heating element having energy collecting loops. US patent 5 698 127, 1997.

[5] Lai LMC. Abuse-tolerant metallic pattern arrays for microwave packaging materials. US patent 6 677 563, 2004.

[6] The safety susceptor features a patterned coating engineered to create 'fusible links.' Paper, Film & Foil Converter 1996 (June):90.

[7] Phillips RW, et al. Patterning techniques for roll coated films. In: Proc. 32nd annual technical conference of the Society of Vacuum Coaters; 1989. p. 175−86.

[8] ICI Films and Virgin Atlantic—the record breaking combination. ICI Films publicity literature ref. D.A.P./GJ/D.R.M.; 1987.

[9] Stratoquest—wherever your imagination takes you. ICI Films publicity literature ref. 907-20 10/88 5 M; 1988.

[10] Fusi A, et al. Ultra-thin film coating and coevaporation techniques for capacitors. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 135−44.

[11] Lackey Jr DV. A versatile capacitor web coater with multiple source capability. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 145−51.

[12] Aufderheide BE. Rapidly removable undercoating for vacuum deposition of patterned layers onto substrates. US patent 4 714 631; 1987.

[13] Tullo G. Display and decorative applications. In: Proc. 14th vacuum web coating conference; 2000. p. 141−51.

[14] Yamamori T. Margin generating mechanism in ULVAC's roll coater. In: Proc. 2nd international vacuum web coating conference; 1988. p. 58−76.

[15] Leybold AG. Vacuum web coating of capacitor films and papers with Al/Zn composite layers. Application note 13-230-02; 1989.

[16] Leybold AG. Vacuum web coaters for capacitor films. Application note 13-130-02; 1987.

[17] Walters GJ. Patterned metallized films used for higher energy density capacitor components. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 453−5.

[18] Lim JH, et al. Thin film supercapacitors using a sputtered RuO_2 electrode. J Electrochem Soc 2001;148(3):A275−8.

[19] Kim H-K, et al. Electrochemical and structural properties of radio frequency sputtered cobalt oxide electrodes for thin-film supercapacitors. J Power Sources 2001;102 (1−2):167−71.

[20] Jayalakshmi M, Balasubramanian K. Simple capacitors to supercapacitors—an overview. Int J Electrochem Sci 2008;3:1196−217.

[21] Abbott SJ. Flexible optical data storage. In: Proc. CompEuro '89. VLSI and computer peripherals. VLSI and microelectronic applications in intelligent peripherals and their interconnection networks; 1989. Section 1, p. 66−7.

[22] Abbott SJ. Digital paper: flexible optical data storage media. J Soc Motion Pict Telev Eng 1990;99(2):142−4.

[23] Spencer K. The optical tape recorder. Photonics Spectra 1990(February): 115−6.

[24] Fox B. Technologies compete for optical storage. New Scientist 1988(February):37.

[25] Collins D. Holograms and metallizing packaging. PIRA International Ltd. ISBN 1 85802930 9, 2003.

[26] Lancaster IM, editor. Holopack/holoprint guidebook. 2nd ed. PIRA International; 2000. ISBN 1 85802 254 1.

[27] Walters GJ. Patterned metallized print (PMP) hologram structures. In: Proc. 39th annual technical conference of the Society of Vacuum Coaters; 1996. p. 357−9.

[28] van Renesse RL, editor. Optical document security. Artech House Inc.; 1994. ISBN 0 89006 619 1; 2nd ed. Artech House Inc.; 1998. ISBN 0 89006 982 4.

[29] Souparis H. Application of see-through holograms. In: Proc. Holopack/Holoprint; 1993.

[30] Takeuchi S, et al. Transparent reflection type hologram. US patent 4 856 857; 1989.

[31] Cueli P. Semi-transparent reflection layer for phase hologram. US patent 5 351 142; 1994.

[32] Ahmed NAG, Whitnall M. Semi-transparent optical coatings for security holograms. In: Proc. 44th annual technical conference of the Society of Vacuum Coaters; 2001. p. 444−7.

[33] Knop K. Diffractive subtractive color filtering technique. US patent 3 957 354; 1976.

[34] Knop KH, Morf RH. Diffractive subtractive color filter responsive to angle of incidence of polychromatic illuminating light. US patent 4 484 797; 1984.

[35] Gale MT. Replication technology for holograms and diffractive optical elements. J Imaging Sci Tech 1997;41(3):211−20.

[36] Seubert J, Fetz A. PVD aluminium pigments: superior brilliance for coatings and graphic arts. Paint and Coatings Industry 2000; (June):40−8.

[37] Wheeler IR. Aluminium pigments—a history of development. European Coat J 1994; June:382−9.

[38] Todd DW, et al. Method for making patterned thin film. US patents 5 059 454 and 5 368 902; 1994.

[39] Josephy K et al. Process for making angstrom scale and high aspect functional platelets. US patent applications 20020041047A1 and US 20030178734A1; 2003.

[40] Ramadas S. Nanoparticulate barrier films and gas permeation measurement techniques for thin film solar and display application. In: Proc. AIMCAL technical fall conference and 23rd international vacuum web coating conference; 2009.

[41] Fayet P. Commercialisation of plasma deposited barrier coatings for liquid food packaging. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 15−6.

[42] Gavitt IF. Snack food packaging: how much is enough. In: Proc. 37th annual technical conference of the Society of Vacuum Coaters; 1994. p. 127–32.

[43] Bowler JF. Demand and supply for high barrier films. In: Proc. 5th vacuum web coating conference; 1991. p. 72–8.

[44] Chatham H. Oxygen diffusion barrier properties of transparent oxide coatings on polymeric substrates. Surf Coat Technol 1996;78:1–9.

[45] Leterrier Y. Durability of nanosized oxygen-barrier coatings on polymers. Prog Mater Sci 2003;48:1–55.

[46] Weston GF. Materials for ultrahigh vacuum. Vacuum 25(11/12): 469–84, 1975.

[47] Smith AW, et al. PECVD of SiOx barrier films. In: Proc. 45th annual technical conference of the Society of Vacuum Coaters; 2002. p. 525–9.

[48] Hartwig E, Krug, T. Food packaging films utilizing non-metallic and glass-like barriers. In: Proc. speciality plastics conference; Zurich, 1991.

[49] Krug TG. Transparent barriers for food packaging. In: Proc. 33rd annual technical conference of the Society of Vacuum Coaters; 1990. p. 163–9.

[50] Scateni G, et al. Transparent barrier coatings: test-runs on industrial equipment. In: Proc. 5th vacuum web coating conference; 1991. p. 104–13.

[51] Maddocks J, et al. Packaging barrier films deposited on PET by PECVD using new high density plasma source. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 672–3.

[52] Rochat G, et al. Cohesive strength and oxygen permeability of PECVD-based coatings on semicrystalline polymers. In: Proc. 46th annual technical conference of the Society of Vacuum Coaters; 2003. p. 50–5.

[53] Komada M, et al. Novel transparent gas barrier film prepared by PECVD method. In: Proc. 43rd annual technical conference of the Society of Vacuum Coaters; 2000. p. 352–6.

[54] Sacher E, et al. Moisture barrier properties of plasma-polymerized hexamethyldisiloxane. J Appl Polymer Sci: Appl Polymer Symp 1984;38:163–71.

[55] Affinito J, et al. A new hybrid deposition process, combining PML and PECVD, for high rate plasma polymerisation of low vapor pressure, and solid, monomer precursors. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 102–07.

[56] Jamison EHH, Windle AH. Structure and oxygen barrier properties of metallized polymer films. J Matls Sci 1983;18:64–80.

[57] Weiss J. Parameters that influence the barrier properties of metallized polyester and polypropylene films. Thin Solid Films 1991;204:203–16.

[58] Bishop CA. Roll-to-roll vacuum deposition of barrier coatings. Scrivener Publishing; 2010 [chapter 2]. ISBN 13: 978-0-470-60956-9.

[59] Schiller S, et al. How to produce Al_2O_3 coatings on plastic films. In: Proc. 7th international conference on vacuum web coating; 1993. p. 194–219.

[60] Schiller S, et al. Al_2O_3 layers on plastic films—ways to get high deposition rates. In: Proc. 8th international conference on vacuum web coating; 1994. p. 173–90.

[61] Kelly RSA. Development of clear barrier films in Europe. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 312–17.

[62] Kelly RS.A Development of aluminium oxide clear barrier films. In: Proc. 37th annual technical conference of the Society of Vacuum Coaters; 1994. p. 144–9.

[63] Kelly RSA. Transparent barrier coatings for films. In: Proc. AWA conference on metallized papers and films—Europe; February 2002. Paper IX.

[64] Web barrier packaging material. European patent application EP0437946; 1990.

[65] Schiller N, et al. Innovative clear barrier technology for the packaging industry. In: Proc. AIMCAL fall technical and 22nd international vacuum web coating conference; 2008.

[66] Schiller N, et al. Transparent barrier coatings on polymer films. In: Proc. AIMCAL fall technical and 23rd international vacuum web coating conference; 2009.

[67] Creating shelf impact. Coating and Converting (C2) Europe 2009; (November/December):7.

[68] Flex Products Inc. Electronic display materials—preliminary product information; 1991.

[69] Haake G. Transparent conducting coatings. Ann Rev Matl Sci 1977;7:73−93.

[70] Cormia RL, et al. Roll to roll coating of indium tin oxide, a status report. In: Proc. 41st annual technical conference of the Society of Vacuum Coaters; 1998. p. 452−7.

[71] Jin Z, Granqvist CG. Transparent and infrared-reflecting ZnO:Al films reactively sputtered onto polyester foil. Appl Opt 1987;26(16):3191−2.

[72] Bright C. How to specify and select transparent electrically conducting coatings. Optical Spectra 1983(June and July).

[73] Howson RP, Ridge MI. Deposition of transparent heat-reflecting coatings of metal oxides using reactive planar magnetron sputtering of a metal and/or alloy. Thin Solid Films 1981;77:119−25.

[74] Ridge MI, et al. Control of the optical properties of transparent conducting films prepared by reactive magnetron sputtering. SPIE 1983;401:301−6 Thin Film Technologies.

[75] Chopra KL, et al. Transparent conductors—a status review. Thin Solid Films 1983;102:1−46.

[76] Vossen JL. Transparent conducting films. Physics Thin Films 1977;9:1−71.

[77] Dawar AL, Joshi JC. Review: semiconducting transparent thin films: their properties and applications. J Matl Sci 1984;19:1−23.

[78] Haake G. Reactive sputtering from a Cd-Sn target. Thin Solid Films 1986;137:101−9.

[79] Pisarkiewicz T, et al. Preparation, electrical properties and optical characterisation of Cd_2SnO_4 and $CdIn_2O_4$ thin films as transparent and conductive coatings. Thin Solid Films 1987;153:479−86.

[80] Maniv S, et al. $CdSe_{1-x}O_y$ films prepared by reactive planar magnetron sputtering. J Vac Sci Tech 1982;20(1):1−6.

[81] Jansseune T. Indium price soars as demand for displays continues to grow. Compound Semiconductor 2005(May):34−5.

[82] McClure DJ, et al. Conducting film or electrode with improved optical and electrical performance. US patent application no. 20090316060; 2009.

[83] Wobser M. New PEDOT formulations enable highly-conductive PET. In: Proc. AIMCAL fall technical and 23rd international vacuum web coating conference; 2009.

[84] Trottier CM, et al. Properties and characterization of carbon nanotube based transparent conductive coatings. J Soc Info Display 2005;13(9):759−63.

[85] Pint CL, et al. Synthesis of high aspect-ratio carbon nanotube “flying carpets” from nanostructured flake substrates. Nano Lett 2008;8(7):1879−83.

[86] Guzmán de Villoria R, et al. High-yield growth of vertically aligned carbon nanotubes on a continuously moving substrate. Nanotechnology 2009;20(1−8):405611.

[87] Hartnagel HL, et al. Semiconducting transparent thin films. Institute of Physics; 1995. ISBN 0 7503 0322 0.

[88] Barth S, Memarian H. Solar control window films—a historical and technological perspective. In: Proc. 43rd annual technical conference of the Society of Vacuum Coaters; 2000. p. 329−34.

[89] Berning PH. Principles of design of architectural coatings. Appl Opt 1983;22(24):4127−41.

[90] Charton C, Fahland M. Tailoring of Ag thin films for solar control and transparent conducting coatings. In: Proc. 46th annual technical conference of the Society of Vacuum Coaters; 2003. p. 190−4.

[91] Fan JCC, et al. Transparent heat-mirror films of TiO_2/Ag/TiO_2 for solar energy collection and radiation insulation. Appl Phys Lett 1974;25(12):693−5.

[92] Fan JCC, Bachner FJ. Transparent heat mirrors for solar-energy applications. Appl Opt 1976;15(4):1012−7.

[93] Betts KH, et al. Heat mirror greenhouses. Appl Opt 1985;24(16):2651−4.

[94] Lampert CM. Solar optical materials for innovative window design. Energy Research 1983;7:359−74.

[95] Kostlin H, Frank G. Optimization of transparent heat mirrors based on thin silver film between antireflection films. Thin Solid Films 1982;89:287−93.

[96] Lampert CM. Heat-mirror coatings for energy-conserving windows. US Department of Energy. Contract W-7405-ENG-48 report; 1981.

[97] Melinex polyester film Industry note MX203. ICI Films, 6th ed. 1986.

[98] Martin M, Yang P. Optical device of low visible light transmission and reflection used for solar control films. In: Proc. 40th annual technical conference of the Society of Vacuum Coaters; 1997. p. 382−5.

[99] Kostlin H. Double-glazed windows with very good thermal insulation. Philips Tech Rev 1974;34(9):242−3.

[100] ASTM E490-73a. Solar constant and air mass zero solar spectral irradiance tables, 1999.

[101] Izu M, Ovshinsky SR. Roll-to-roll plasma deposition machine for the production of tandem amorphous silicon alloy solar cells. Thin Solid Films 1984;119:55.

[102] Izu M, et al. Roll-to-roll RF PECVD for a-Si solar cell manufacturing. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 120−3.

[103] Marti A, Luque A, editors. Next generation photovoltaics—high efficiency through full spectrum utilization. Institute of Physics; 2004. ISBN 0 7503 0905 9.

[104] Perlin J. From space to earth—the story of solar electricity. Harvard University Press; 2002. ISBN 0 674 01013 2.

[105] Gelin K. Preparation and characterization of sputter deposited spectrally selective solar absorbers. PhD thesis, Department of Engineering Sciences, University Uppsala; 2004.

[106] Kennedy CE. Review of mid- to high-temperature solar selective absorber materials. National Renewable Energy Laboratory (NREL) report no. NREL/TP-520-31267; July 2002.

[107] Kuster H, et al. Optical coatings on Al-strip. In: Proc. 2nd international symposium—coating of metallic strips and sheets; September 2002.

[108] Weale RD, et al. Metallized polymeric webs for flexible circuitry. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 70−4.

[109] Weale RD, et al. Evaluation of Kapton films for adhesiveless TAB/flex circuits. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 242−7.

[110] Coulman D, Edman J. Improved adhesion in two layer copper/polyimide clads. In: Proc. 37th annual technical conference of the Society of Vacuum Coaters; 1994. p. 212−6.

[111] Sallo JS. Copper-chromium-polyimide composite. US patent 4 863 808; 1989.

[112] Swisher RL. A decade of depositing copper onto polymer webs. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 448−52.

[113] Chen PC, et al. Plated copper line thickness effects on peel test values. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1990. p. 205−11.

[114] Chen PC, Oshida Y. Stresses of chromium, copper and Kapton on a two sided metallized web. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1990. p. 200−4.

[115] McClure DJ, et al. A low-cost flexible circuit on a polyester substrate. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 445−7.

[116] Phillips RW. Optical variable films, pigments and foils. SPIE vol. 1323, Optical thin films III: new developments 98; 1990.

[117] Argoitia A, Witzman M. Pigments exhibiting diffractive effects. In: Proc. 45th annual technical conference of the Society of Vacuum Coaters; 2002. p. 539−45.

[118] Walter H, et al. Cluster layers for surface enhanced absorption (SEA). In: Proc. 45th annual technical conference of the Society of Vacuum Coaters; 2002. p. 443−5.

[119] Counterfeit deterrent features for the next-generation currency design. Publication NMAB-472. National Academic Press; 1993. ISBN 0 309 05028 6.

[120] Phillips RW. Tamper evident devices based on interference thin films. In: Proc. 3rd vacuum web coating conference; 1989. p. 196−209.

[121] Shelley T. Parts coded by indestructible magnetism. Eureka 1999(December):22−3.

[122] Fonseca JJ, Gorton W. A novel roll coater for double sided heavy deposition of magnesium onto PTFE films. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 64−70.

[123] McCann MJ, Cox ER. Process modelling of a novel double-sided vacuum web coating system. In: Proc. 40th annual technical conference of the Society of Vacuum Coaters; 1997. p. 338−42.

[124] Allford FG. Pyrotechnic materials. WO 90/10611; 1990.

[125] Pyrotechnic sheet material. UK patent application no. 93305520.4; 1993.

[126] Sherman D. The rough road to air bags. Invention and Tech 1995(Summer):48−56.

[127] Weihs TP, et al. Effect of reactant and product melting on self-propagating reactions in multilayer foils. J Appl Phys 2002;92(9):5474−81.

[128] Malaspina SP. Lithium-ion rechargeable batteries and the portable communications user's expectations. In: Proc. 39th annual technical conference of the Society of Vacuum Coaters; 1996. p. 341−3.

[129] Affinito JD, et al. Vacuum deposition of polymer electrolytes on flexible substrates. In: Proc. 9th vacuum web coating conference; 1995. p. 20−36. Bakish Materials, Englewood Cliffs, NJ 07631.

[130] Vincent CA, et al. Modern batteries: an introduction to electrochemical power sources. Edward Arnold Ltd.; 1984. ISBN 0 7131 3469 0.

[131] Gross ME, et al. Li_3PO_4 : N/$LiCoO_2$ coatings for thin film batteries. In: Proc. 45th annual technical conference of the Society of Vacuum Coaters; 2002. p. 119−24.

[132] Swisher R, et al. Web coating with lithium—technical solution for metal anode structures in Li batteries. In: Proc. 45th annual technical conference of the Society of Vacuum Coaters; 2002. p. 535−8.

[133] Affinito J, et al. Thermal evaporation of Li: experiment and a novel thermodynamic model. In: Proc. 14th vacuum web coating conference; 2000. p. 77−94.

[134] Visco SJ, et al. Thin-film technology for solid-state lithium batteries employing solid redox polymerisation cathodes. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 89−92.

3 Pressure Measurement

As the range of vacuum used has widened, so too has the number of types of gauges that can be used to measure the vacuum achieved. Although there are many types of gauges available, some are more commonly used than others, and it is these that will be described.

The more complex the vacuum process and/or the more precise the coating produced, the more attention has to be paid to the gauging. It is important to choose the correct gauge for the process. The aim is to have a gauge with the optimal combination of sensitivity and stability that operates without drift over the pressure range used in the process. If the gauge is to be used as part of the process control system, it is important that the gauge is regularly maintained and calibrated. It is pointless to buy a high-quality gauge and then abuse it on the system or never check the calibration. It is also a waste of money to buy a gauge more sophisticated than the process requires, or to spend too much time cleaning, checking, and calibrating the gauge.

It is important to site the gauge in a suitable position within the vacuum system. Positioning the gauge directly in line with the gas input will give a false, high reading. Hiding the gauge away in the corner of the vessel will give a lower reading and will also give a slow response to any pressure changes. Placing the gauge close to the pumping orifice may also result in a reading lower than is representative of the process area that is of most interest.

If there are different zones within the system, it will be preferable to measure the pressure in each zone independently and not to rely on one gauge and infer the pressure in the other.

It is also worth being aware that the pressure reading can be different at different points, even within the same zone, depending on the components that fill the space.

Ideally, critical areas will have a back-up gauge available. It is invariably cheaper to have a second back-up gauge than to have to stop the process to replace a gauge because of a gauge failure. This is more critical with filament-type gauges that can burn out and have a shorter lifetime than some other gauges.

This duplication of gauges can have advantages when things go wrong. If a gauge tells you there is no vacuum, you then have the dilemma, is it the gauge that is correct, or is it the gauge that has stopped working? Having a second gauge aids troubleshooting and confirms either the loss of vacuum or the failure of the gauge.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00003-9

Table 3.1 Gauge types, measurement techniques, and range of measurement

Gauge type	Quantity measured	Approximate range	Comments
U-tube manometer	Height of a liquid column, usually mercury column	101–0.133 kPa 760–1 torr	Independent of gas species
Mechanical manometer, Bourdon, diaphragm, capsule	Mechanical deflection of diaphragm or thin wall	101–0.133 kPa 760–1 torr	Independent of gas species
Capacitance manometer	Capacitance change from diaphragm position	101 kPa–13 mPa 760–10^{-4} torr	Independent of gas species
Thermocouple gauge	Filament temperature change with pressure	1.33 kPa–133 mPa 10 torr–1 mT	Dependent on ambient temperature and gas species
Pirani gauge	Filament temperature change with pressure	133 Pa–133 mPa 1 torr–1 mT	Dependent on ambient temperature and gas species
Penning—cold cathode ionization gauge	Glow discharge current	1.3 Pa–1.3 mPa 10^{-2}–10^{-5} torr	Dependent on gas species
Bayard–Alpert hot ionization gauge	Ion current generated from constant electron emission current	133 mPa–1.3×10^{-9} mPa 10^{-3}–10^{-10} torr	Dependent on gas species
Spinning rotor	Spinning ball slows by molecular drag by gas	13–1.3×10^{-5} Pa 10^{-1}–10^{-7} torr	Dependent on gas species, pressure, temperature, and ball

If the duplication of gauges is regarded as too costly, then having isolation valves that allow the gauges to be exchanged, while the whole system is kept under vacuum, may be a suitable alternative solution.

Table 3.1 gives a quick summary of some of the most widely used gauges with the range they cover and some comments about their dependence on gas species.

3.1 Bourdon Gauge

On many large vacuum systems where a motor is used to close the vacuum vessel door, it is common to see a capsule gauge. This gauge uses a tube that is sealed at one end and open to the vacuum (Fig. 3.1). As the system is evacuated, the tube

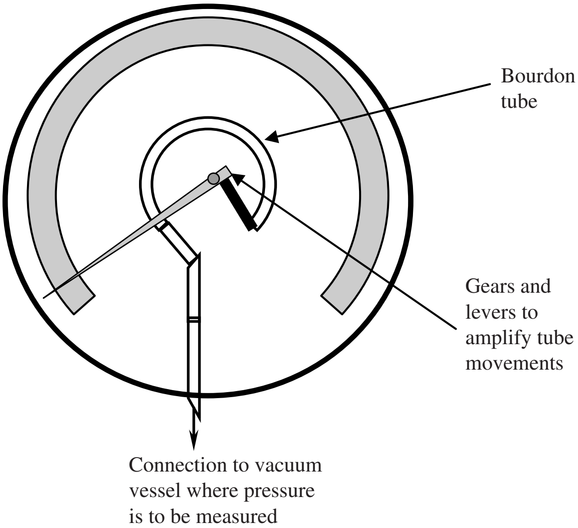


Figure 3.1 A schematic of a Bourdon gauge.

distorts. This movement is converted via levers and gears into a dial movement. Often the tube is in a spiral configuration.

The diaphragm version of this gauge has the lever mechanism welded to a diaphragm instead of the Bourdon tube. When the diaphragm distorts as the vacuum is applied, the lever is moved and the pressure indicated.

The main purpose of this gauge is to check that the door is sufficiently closed and the pumps are pulling vacuum. If the gauge does not show an immediate movement away from atmospheric pressure, it usually means that the door needs to be closed further. The accuracy of the gauge is poor but adequate for the purpose.

3.2 Pirani and Thermocouple Gauges

The backing lines and roughing gauges require something more accurate when reaching a lower pressure than the capsule gauges. The thermocouple and Pirani gauges fit this requirement (Fig. 3.2). These gauges use a current to heat a wire. The heated wire loses heat to the gas molecules that collide with the wire. Thus, the higher the pressure, the greater the number of molecules colliding with the wire, and hence the more the heat loss and the reduction in temperature of the wire. In the Pirani gauge, the wire is part of a bridge circuit and a change in the wire resistance can be measured. Similarly, if the pressure decreases, the temperature of the wire will increase and again the changed resistance can be measured. The resistance is converted into a reading of pressure. In the thermocouple gauge, a thermocouple is spot welded directly to the resistance wire and so a direct temperature measurement is taken and converted into a pressure measurement (Fig. 3.3).

The gauges are sensitive to the type of gas in the system. The different gases have different masses and hence will take different amounts of heat out of the wire.

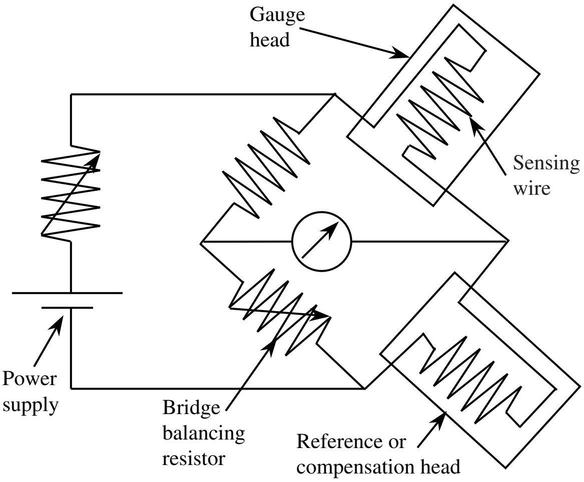


Figure 3.2 A schematic of a Pirani gauge.

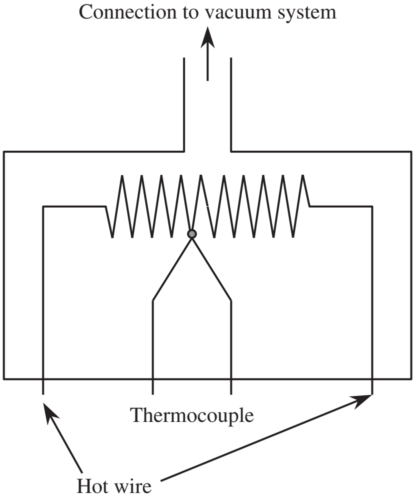


Figure 3.3 A schematic of a thermocouple gauge.

However, this does mean that if the gauge is calibrated using air and is then used to measure a process gas such as argon, there will be an error in the pressure measurement. The error is reproducible and so in most cases the pressure is accepted as being a relative, but reproducible, measure of pressure (Fig. 3.4).

3.3 Capacitance Manometer

A tube has a flexible diaphragm separating a vacuum at one end of the tube and the vacuum system at the other end of the tube. When the diaphragm deflects, the capacitance between the diaphragm and electrodes on one or both sides of the

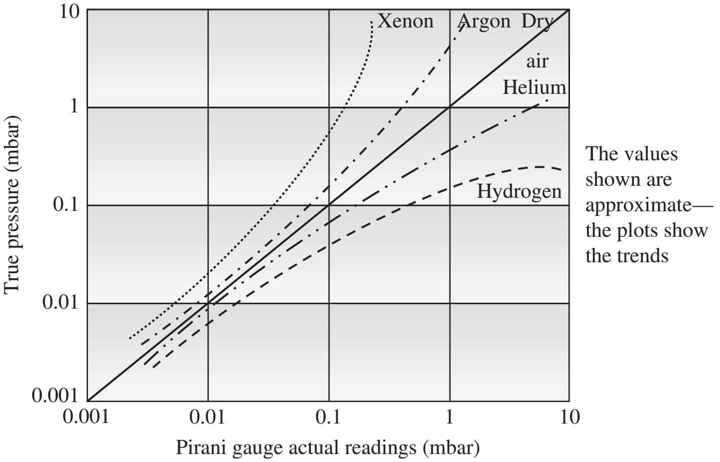


Figure 3.4 A graph showing the differences between the true and the actual readings for a gauge calibrated for dry air.

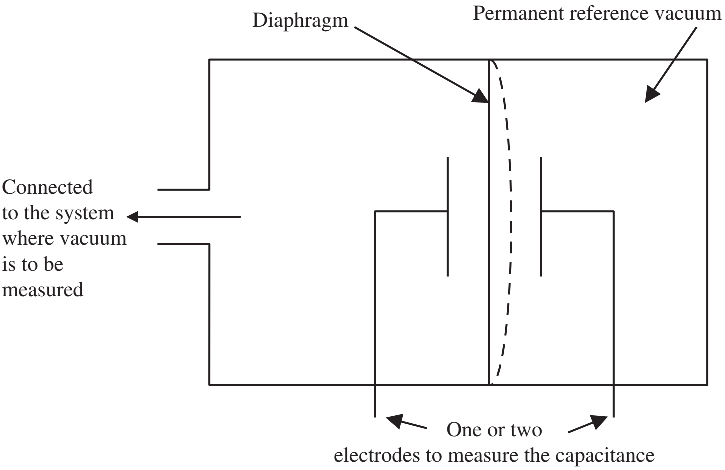


Figure 3.5 A schematic of a capacitance manometer.

diaphragm changes. These changes can be detected. The deflection is purely a measure of the pressure differential and does not depend on the gas species. This is an absolute measure of pressure (Fig. 3.5).

In early gauges, there was some drift with temperature, but more recent gauges have temperature compensation. One other area of drift or variation derives from some hysteresis in the gauge that can be caused from leaving the gauge at atmospheric pressure for a long time. The diaphragm can take some time to relax back to its optimum measurement state. As with many other items, the gauge works best if kept under vacuum.

The absolute pressure measurement makes this an increasingly popular type of gauge for active process control. These gauges are commonly referred to by the generic name Baratron; this is a trade name from the manufacturer that first made them widely available.

3.4 Penning or Cold Cathode Ionization Gauge

The Penning gauge is named after Penning who utilized the current produced by a glow discharge as a measure of the pressure. The basis of the gauge is to have an anode and cathode within a magnetic field (Fig. 3.6). A potential of around 2 kV is applied, and in its usable range, a self-sustaining glow discharge is produced. The electrons produced in the glow discharge spiral round in the magnetic field and increase the chance of undergoing further ionizing collisions. The positive ions that are less affected by the magnetic field reach the cathode and produce a current. The ion and electron emission currents are measured and used to indicate pressure.

The geometry of the gauges has varied, with early gauges having the cathodes as two flat plates and the anode as a loop of wire between the cathodes and the magnet surrounding both. The design was then changed to have a central anode and the cathode as a cylinder around the anode and the magnet concentric with both.

The gauge has its limitations. A glow discharge must be struck, and if the pressure is too high, it will not strike because too many collisions take place and the

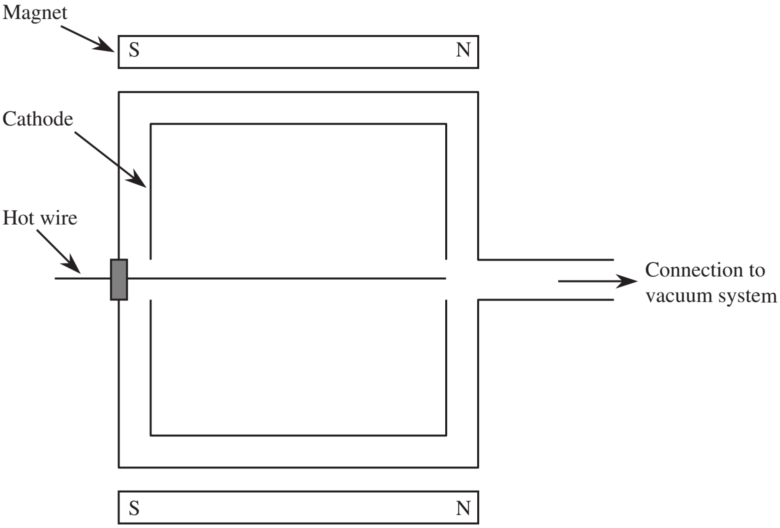


Figure 3.6 A schematic of a coaxial or inverted Penning gauge.

energy is lost and the glow will not self-sustain. If the pressure is too low, there are not enough collisions to sustain the glow discharge and again the gauge will not operate. Within the gauge operating range it is gas species dependent. Different gases have different ionization efficiencies, and, at worst, the gauge can be in error by as much as 50%.

In its favor, the gauge has no fragile filament, and this makes it very robust and easily cleaned. With care, it can be reliable and robust.

3.5 Ion or Hot Cathode Ionization Gauge

This gauge uses a hot wire to produce electrons by thermionic emission. The electrons are attracted to an anode grid. This grid is of an open structure such that many of the electrons overshoot the grid and oscillate past it a number of times before hitting it. The electrons in oscillating around the grid increase their chances of undergoing ionizing collisions. The ions that are produced are attracted to a third electrode producing a measurable current (Fig. 3.7).

The pressure is related to the ion current and the electron emission current. The ion gauge has the advantage that as the electrons are produced by thermionic emission the gauge can operate at lower pressures than the Penning-type gauge. The

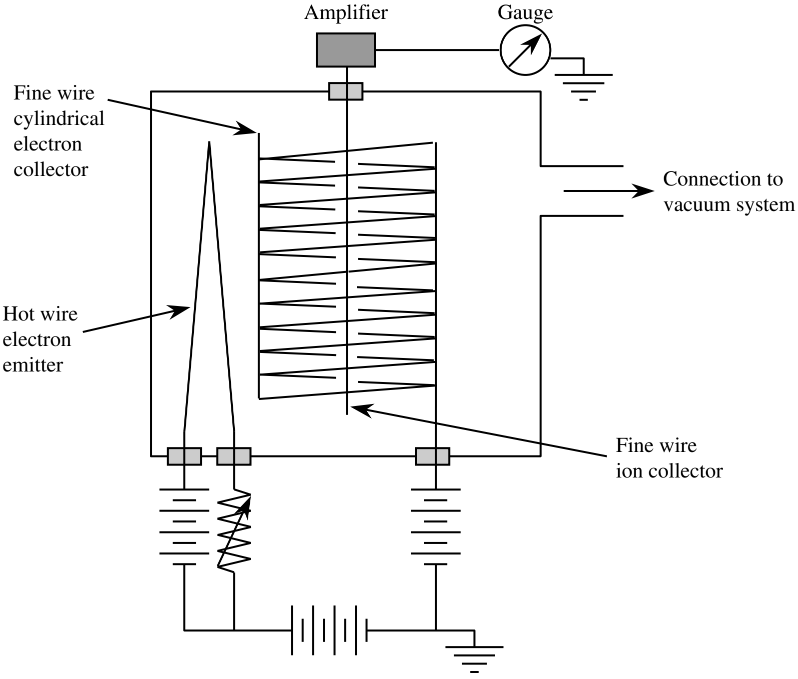


Figure 3.7 A schematic of a hot ionization gauge.

Table 3.2 Sensitivity of different gases normalized to nitrogen

Gas or vapor	Sensitivity normalized to nitrogen	Number of electrons
Acetone	4	–
Argon	1.19	18
Carbon dioxide	1.37	22
Carbon monoxide	1.07	14
Helium	0.15	2
Hydrogen	0.46	2
Krypton	1.86	36
Mercury	3.44	80
Neon	0.24	10
Nitrogen	1	14
Oxygen	0.84	16
Water	0.89	8
Xenon	2.73	54

accuracy of the gauge is also much better than that of the Penning gauge. The disadvantage is that the hot wire filament can be damaged by thermal shock, mechanical shock, and chemical attack. Thus, it is essential to take great care to switch off the gauge when bringing the system back up to atmospheric pressure. Also, if reactive gases are being used in the process, such as oxygen, it is better to switch off the gauge to preserve the filament.

The gauge still has the problem of being species dependent. Table 3.2 shows the sensitivity of ion gauges to different gases or vapors.

Further Reading

[1] Harris NS. Modern vacuum practice. McGraw-Hill; 1989 ISBN 0 07 707099 2.

[2] Basic vacuum practice. 3rd ed. Varian Associates; 1992. Varian part no. 900-0085.

[3] Hill RJ, editor. Physical vapor deposition. Temascal; A division of the BOC Group, Inc. 1986 Part no. T-0186-6001-1.

[4] Roth A. Vacuum technology. North Holland Publishing; 1979 ISBN 0 444 10801 7.

[5] Maissel LI, Glang R. Handbook of thin film technology. McGraw-Hill; 1983 [reissue] ISBN 0 07 039742 2.

[6] O'Hanlon JF. A user's guide to vacuum technology. Wiley Interscience; 1980.

[7] Guthrie A. Vacuum technology. John Wiley & Sons—Wiley Interscience; 1963.

[8] Weissler GL, Carlson RW, editors. Vacuum physics and technology, vol. 14. Academic Press; 1979.

[9] AVS recommended practices on vacuum measurements and techniques. Recommended practices and standards series S-2, vol. 1. American Vacuum Society, NY 10017; 1992.

[10] Utterback NG, Griffith Jr. T. Reliable submicron pressure readings with capacitance manometer. Rev Sci Inst 1966;37(7):866.

[11] Sullivan JS. Advances in capacitance manometer systems. Res Dev January 1976; 42−4.

[12] Sullivan JS. Modern capacitance manometers. Transducer Technol 1979;1(5):22−7.

[13] Mitchell AR. Pressure and vacuum standards review. Transducer Technol 1982;4(2):9 and continued in Transducer Technol 1982;4(4):8.

[14] Tompkins HG. Vacuum technology: a beginning. American Vacuum Society monograph series HB-1. 2002, NY 10017.

[15] Lewin G. An elementary introduction to vacuum technique. American Vacuum Society monograph series M:8. 1987, NY 10017.

[16] Tompkins HG. Vacuum gauging and control. American Vacuum Society monograph series M:12. 1994, NY 10017.

4 Pumping

The key to any vacuum system is pumping; after all, without the pumping there is no vacuum. There is no one pump that can be used to achieve all desired vacuum pressures. Thus, most systems have combinations of pumps that may operate sequentially or in series to progressively take the gas out of the enclosed volume.

There are many pump types available and many different combinations of pumps that can be used to pump a system for any particular process. The choice of pumps can have a large effect on the operational robustness of the process as well as on the product quality. There are two broad groups: those for roughing out the system and the high vacuum pumps. Below are the most commonly used pumps that are to be found on web coating systems.

4.1 Rotary or Roughing Pumps

Using Boyle's law that states $P_1V_1 = P_2V_2$, the rotary pumps use a rotational motion to reduce the volume, thus increasing the pressure of the trapped gas. This is shown schematically in Fig. 4.1.

The rotary pump can be made with two different chambers so that the exhaust of one chamber is further increased in pressure by going through a second stage of compression. These two-stage rotary pumps are probably the most widely used of the backing pumps.

4.1.1 Piston Pumps

This type of pump works on a similar principle of sequentially drawing in and compressing a trapped volume of gas, but instead of a rotational central shaft with expanding vanes to adapt to the eccentric cylinder, this uses an eccentric circular piston. This eccentric circular piston is moved around the cylinder via a reciprocating motion as shown schematically in Fig. 4.2. This also requires an oil seal between the metal surfaces of the piston and cylinder to separate out the incoming gas volume and exhausting volume.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00004-0

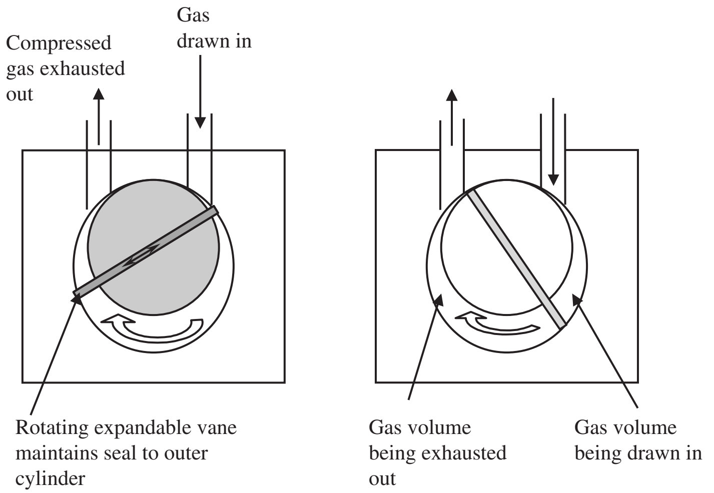


Figure 4.1 A schematic of a rotary vane pump.

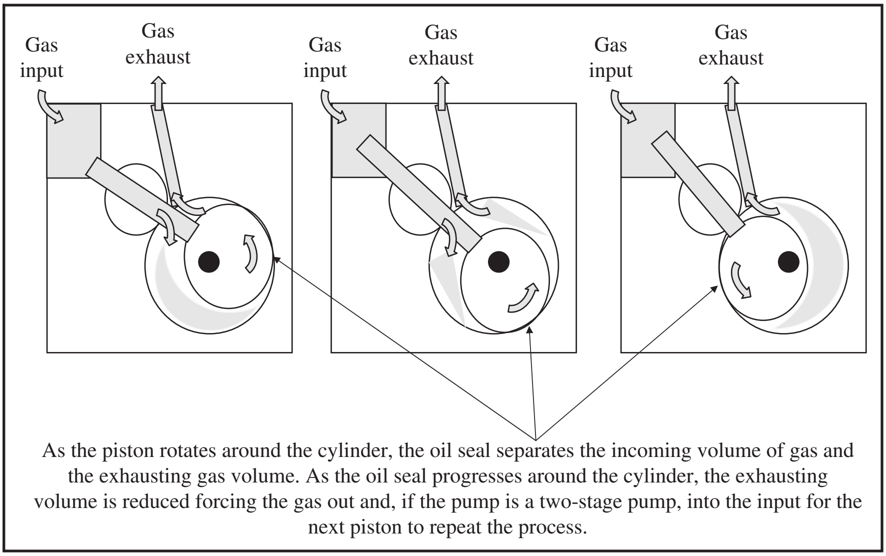
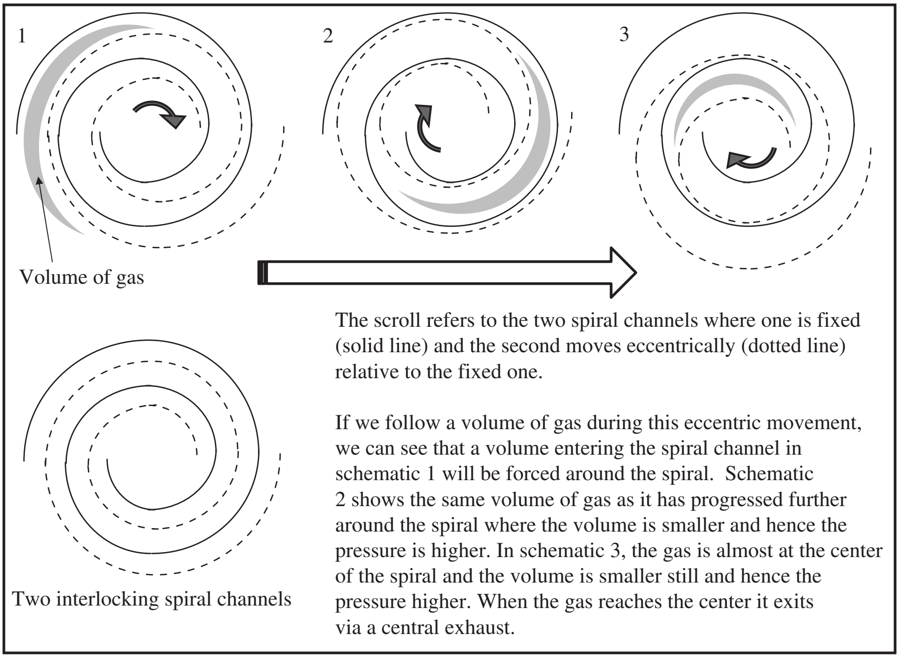


Figure 4.2 A schematic of a rotating piston pump.

4.1.2 Dry Pumps

Dry pumps were developed so that corrosive or flammable gases could be pumped. Rotary pumps that were lubricated with oil would have a thin film of oil on all the moving surfaces as well as produce a fine mist of oil. Inevitably, these pumps would heat up with the compression of the gas, and if oxygen were pumped in too high a concentration, the mixture of oxygen with the fine mist of hot oil could



The scroll refers to the two spiral channels where one is fixed (solid line) and the second moves eccentrically (dotted line) relative to the fixed one.

If we follow a volume of gas during this eccentric movement, we can see that a volume entering the spiral channel in schematic 1 will be forced around the spiral. Schematic 2 shows the same volume of gas as it has progressed further around the spiral where the volume is smaller and hence the pressure is higher. In schematic 3, the gas is almost at the center of the spiral and the volume is smaller still and hence the pressure higher. When the gas reaches the center it exits via a central exhaust.

Figure 4.3 A schematic of how a scroll pump operates.

become a potential explosion problem. Using ceramic components, it was possible to convert some of these pumps to run dry of oil.

As the requirement for these pumps increased, due to the expansion of the semiconductor industry, newer pump designs such as claw pumps or scroll pumps were developed. Recently, the prices of scroll pumps have fallen, which has encouraged a wider use of this type of pump (Fig. 4.3). In many cases, these have directly replaced rotary vane backing pumps even where oxygen is not considered a safety issue.

4.2 Roots Pumps or Blowers

This pump also works using Boyle’s law and has two counter-rotating shafts with lobed rotors that trap and reduce the volume, thus raising the gas pressure. This is shown schematically in Fig. 4.4.

These pumps are frequently used in series with roughing pumps. The way they do this is to allow the rotors to freewheel as the gas is initially drawn through from the chamber on the way to the roughing pumps. As the pressure in the system drops, the efficiency of the roughing pumps falls off. At this point, the Roots pump is then powered to increase the rotor speed, and this increases the output pressure, which becomes the supply pressure for the roughing pumps, bringing them back into their more efficient operating range.

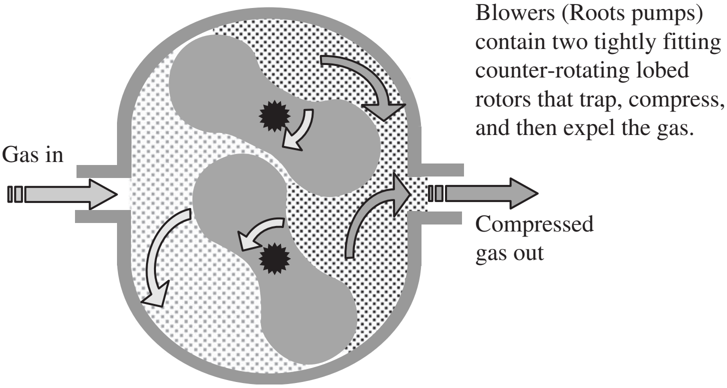


Figure 4.4 A schematic of a Roots pump.

4.3 Diffusion Pumps

This pump works on a different principle than the roughing pumps. Here, a liquid, usually oil, is heated and vaporized. The vapor is directed up the center of the pump and through jets that redirect the vapor downward toward the cooled body of the pump. As the vapor emerges from the jets, at speeds of up to 750 mph, it collides with the system gas knocking it toward the bottom of the pump. There is a series of these jets positioned down the pump. The combined effect is to compress the gas, raising the pressure at the base of the pump and reducing the pressure at the top of the pump. The vapor that hits the cooled sides of the pump drains down into the reservoir where it is heated to vaporize again to complete another cycle. This is shown schematically in Fig. 4.5. Also shown are the typical pressures at different points in the pump under normal operating conditions.

The right-hand half of Fig. 4.5 shows what happens when the pump is stalled. If the pressure is too high, the emerging jet of vapor undergoes too many collisions and the energy is diffused. The effect of this is that the vapor fails to reach the sides of the pump and it joins the system gas raising the pressure at the top of the pump. This condition is known as “backstreaming” and is where the oil vapor from the pump can contaminate the system.

It is common for the gas load to be reduced and baffles to be added to restrict the gas flow above the pump and thus limit the backstreaming. A better solution is to increase the pumping on the output of the diffusion pump (the backing pump) as this does not restrict the gas throughput and will increase the tolerance of the system.

Figures 4.6 and 4.7 are taken from a patent that is of the manufacture and use of rectangular and arrays of rectangular diffusion pumps. So far, these have not been adopted for use and only circular ones are in common use.

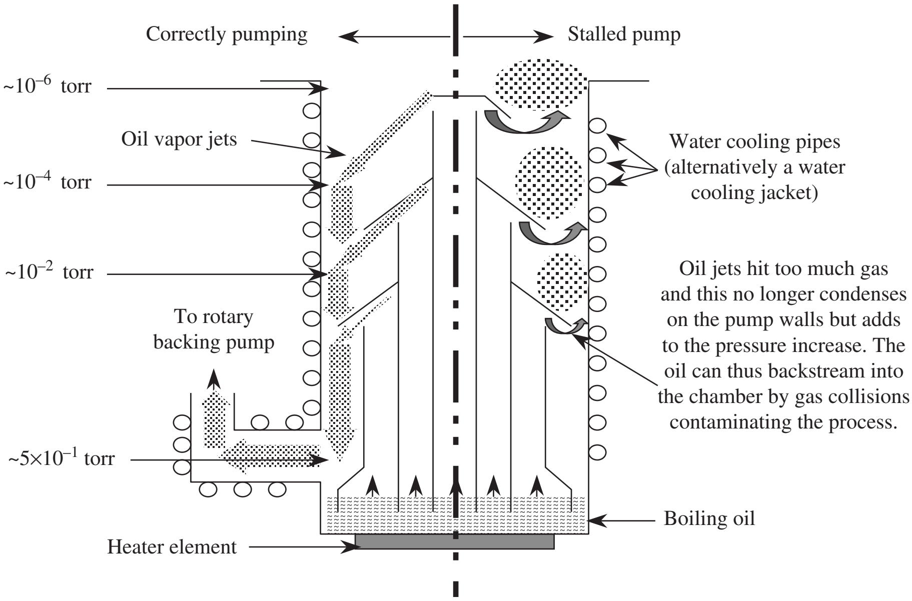


Figure 4.5 A schematic of an oil vapor diffusion pump.

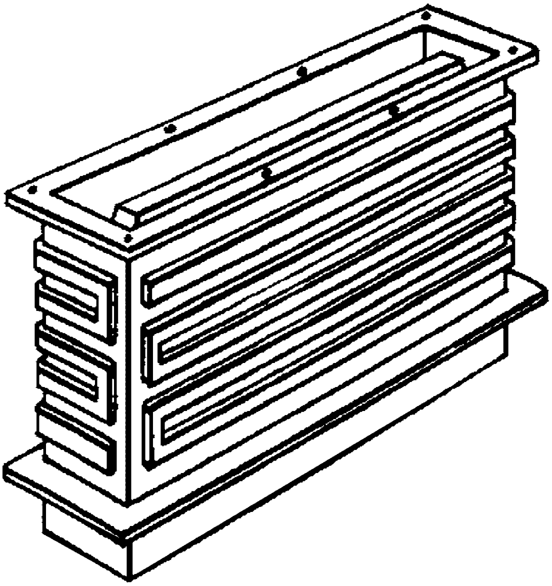


Figure 4.6 Rectangular diffusion pump [1].

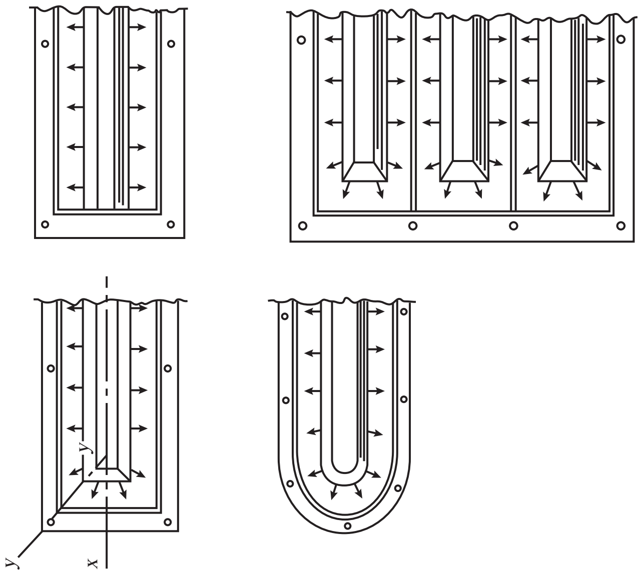


Figure 4.7 Different design options [1].

The advantage that these pumps would offer would be that they could be built to match the width of any roll coater. This would give uniformity of pumping across the whole width of the system without the need for manifolds that potentially decrease the overall pumping speed.

The perceived disadvantage of these pumps was in the ease of manufacture. In general, it was easier to fabricate the circular designs using spun metal processing to fabricate the central stack compared to the more laborious techniques that would be required for the rectangular shapes. Although this was true 25 years ago when the patents were new, this is no longer the case. Modern manufacturing techniques should make it no more difficult, or expensive, to manufacture rectangular pumps as circular ones. Conventional diffusion pumps are now produced at certain common sizes so that they are available "off the shelf." Anyone starting to make rectangular pumps may have difficulty in deciding upon some common sizes, and if they are always custom built, there may be some cost penalty.

4.4 Turbomolecular Pumps

This high vacuum pump uses a shaft rotating at high speed with a series of multibladed rotors on the shaft. The rotors alternate with multibladed stators (static rotors). The principle of operation is that as the shaft rotates, the gas molecules are hit by the angled blades of the rotor, knocking the gas molecules both forward and downward. The molecule then hits a stator also with an angled blade, which forces the molecule into the path of the next rotor. The net movement of the molecules is

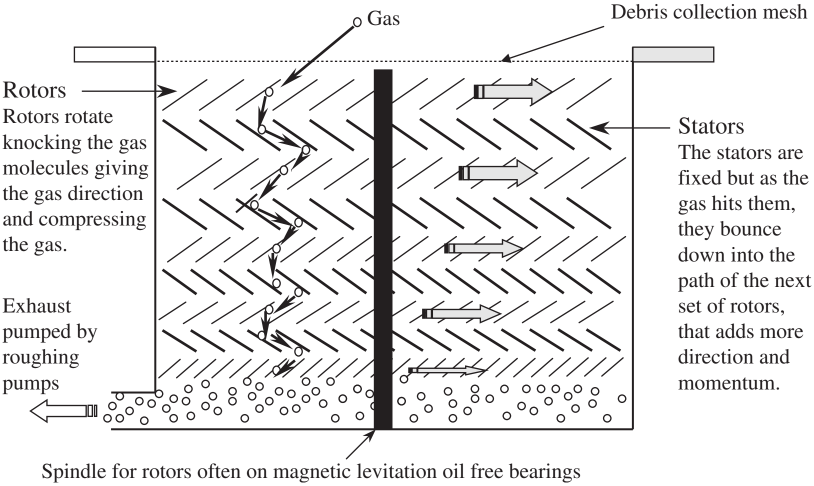


Figure 4.8 A schematic of a turbomolecular pump.

toward the base of the pump, thus compressing the gas. The speed of the rotors is often limited by keeping the blade tip speed to below the speed of sound. Thus, small diameter rotors can be rotating at speeds $>100{,}000$ rpm, while large turbomolecular pumps may only run at $<10{,}000$ rpm. A schematic is shown in Fig. 4.8.

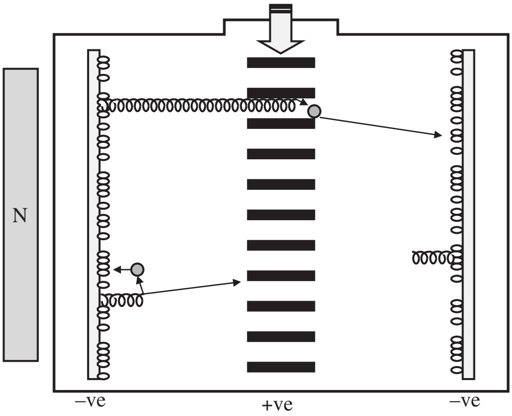
The turbomolecular pump is regarded as a clean pump compared to a diffusion pump.

Diffusion pumps depend on oil vapor to pump and so there is a lot of oil around. In theory, it is statistically possible to have some oil migrate against the general gas flow and contaminate the system chamber. The turbomolecular pump may have no oil at all in some designs or only a tiny amount sufficient enough to lubricate the bearings.

This pump can have magnetic bearings making the pump an oil-free pump. This can be important in some highly sensitive processes but also gives the pump another less common use. On occasions, in very large vacuum vessels, it is difficult to achieve the desired vacuum level in regions close to the center of the vessel. There are several reasons for this, of which one example might be having a number of isolation baffles that restrict the pumping. One solution used to combat this particular problem was to site some turbomolecular pumps inside the vacuum vessel. They happily operated in vacuum and as they were oil free did not contaminate the process. The exhausts from each could be piped out to a common roughing line. In standby, these pumps did not need to be operated but only powered up to start the process.

4.5 Getter or Sputter Ion Pump

These pumps are also regarded as clean pumps (Fig. 4.9). They tend not to be used on web coating systems because they are not designed for pumping large quantities



The ionized gas sputters the Ti metal, that getters the reactive gas.

The secondary electrons released by the sputtering undergo more ionizing collisions and keep sputtering fresh titanium.

These pumps are good for pumping reactive gases but can only trap inert gases making them less effective than other types of pumps.

Figure 4.9 A schematic of a sputter ion pump.

of gas. They are used for analytical type applications where reducing the risk of contamination may improve the confidence in the measurements. Thus, occasionally, they are used for mass spectrometers.

4.6 Cryopumps

Cryopumps work by compressing helium using a compressor that can be air or water cooled and then allowing the helium to expand to cool down a surface within the system that acts as a condensation pump. Most of the gases freeze or condense on the cold surface. The capacity of the pump is increased by using a porous material, such as activated charcoal, that will absorb the three gases—helium, hydrogen, and neon—that do not get condensed by the cryosurface (Fig. 4.10).

This is a capture pump with only limited capacity and so periodically it has to be heated to release all the condensed and absorbed gases that are then pumped away. This too is a clean pump with no oils to contaminate the system.

The capacity of the pump can be a problem for web coating systems. Webs often contain a small quantity of water, and if the process includes a plasma, it is possible to have the water cracked into its component gases. Once the water is cracked into oxygen and hydrogen, the oxygen is frozen out and the hydrogen is absorbed. The capacity for absorbing gases is very much less than for condensing or freezing out gases. Thus, the capacity of the pump can be reached very quickly due to the generation of large quantities of hydrogen.

4.7 Cryopanels

These differ from the cryopumps in that they are generally designed to pump water at very high speed but do not contribute in pumping down the chamber in any other

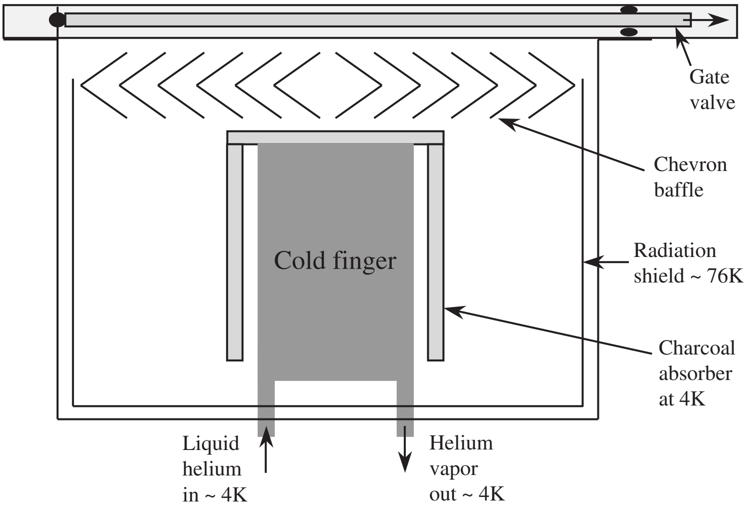


Figure 4.10 A schematic of a cryopump.

way. Usually these systems have a mixture of gases that will take the temperature of the copper coils down to a temperature around $-100°C$. At this temperature, if a water molecule hits the surface, it is most likely to stick and freeze and form a layer of ice. So long as the ice buildup is as a dense structure and not so rapid that the ice builds up as a very porous structure, the ice will remain cool enough at the surface to freeze the next layer of water that hits the surface. These pumps have a very high pumping speed for water, typically an order of magnitude faster than the pumping speed of a diffusion pump, but it is only for water vapor. As, once the system has been pumped of the volume of air, the main constituent of the system is water vapor as a result of outgassing from various surfaces, this becomes a crucial part of most vacuum systems.

Although these may be referred to as cryopanels, they are usually made from a long tube of copper that is bent in a serpentine fashion. This gives a large surface area but an open structure. Often these may appear to have been an afterthought with the serpentine pipe being fitted into a gap between the winding system and the chamber wall. This can be acceptable for a metal deposition process, but as we will see later for reactive deposition processes, it is important that all the pumps are situated to make sure there is pumping symmetry. This includes any cryopanels. It has also been shown that having cryopanels divided between the winding zone and the deposition zone is better than having the cryopanel sited in one zone only.

These panels are available as retrofit items so that if a substrate with a higher moisture content is going to be used, then additional pumping can be added so that the extra load does not adversely affect the pumpdown time. However, if additional cryopanels are to be added, it is important that they are sited where they can be most effective as well as across the full web width and so maintaining pumping symmetry.

4.8 Pumping Strategy

In recent times, there has been a trend to use oil-free pumps. This started with systems that were used for semiconductor production where very low base pressures were commonly used and the devices produced were particularly sensitive to oil contamination. This can be a suitable safety measure where high levels of oxygen are likely to be pumped. Also dry pumps can be useful where there is likely to be high levels of powders that might accumulate in the oil or chemicals that might convert to acids that also could accumulate in the oil.

Many technologies, developed by or for the semiconductor industry, are adopted by other industries almost without thought or any judgment of the merits. The technologies get used through the expectation that whatever is good for the production of semiconductor devices will be good for anything else. Unfortunately, this philosophy is flawed and this has been demonstrated by a number of systems that cost more to build but had worse productivity than the previous generation of system design.

An example of this would be where oil backstreaming from diffusion pumps was seen as a major source of contamination on semiconductor devices. So the semiconductor industry opted to eliminate oil from the pumping system by replacing the diffusion pumps by either turbomolecular pumps or cryopumps and directly exchanging dry roughing pumps for the oil-based rotary vane or piston pumps. Following this trend, set by the semiconductor industry, there were web coating systems that would normally have had two or three large diffusion pumps that had the system design changed so that the diffusion pumps could be replaced by turbomolecular pumps. As turbomolecular pumps tend to be limited in size in order to keep the rotating blade tip speed down, it was common to see the 2–3 diffusion pumps replaced by 25–30 turbomolecular pumps to be able to match the pumping capacity. It was stated by the operators that in the first 2 or 3 years, they never were able to run the process with all the turbomolecular pumps working at the same time. At any point in time, there would always be at least one of them not working for some reason or other. This made it difficult to maintain the product consistency. For many applications, the need for oil-free pumping was never proved, it was purely a preference. Many of the same products have been produced on systems using oil diffusion pumps without problems. This can make the capital and running cost expensive for only a preference rather than a proven need.

Similarly, other web coating systems were fitted with cryopumps, also regarded as a clean oil-free pumping alternative to diffusion pumps. Where these systems used sputtering sources, there could be a problem of very short times between regenerations for the cryosurfaces. What did happen is that the water given up by the polymer web was cracked into the component oxygen and hydrogen by the sputtering plasma. The oxygen was pumped by the cryopump but the hydrogen was a major problem. The cryosurfaces are not cold enough to condense and hence pump the hydrogen. The cryopumps remove hydrogen by using a cooled high surface area carbon absorbing material. The capacity of this material is low, and once the capacity was reached, the hydrogen could no longer be removed and the pressure in the system increased. This pressure increase would increase the gas bombardment of the cryopump and so raise the temperature, and with the rise in temperature a point would be reached where other gases would start to be released further raising the pressure. This would continue to the point where the cryopump stops operating altogether. This is known as "dumping the pump." I have known a vacuum roll coating system where the cryopump could be dumped after only 500 m of polyester web. Even after adding a large cryopanel to getter as much water as possible from the unwrapping roll, this only extended the length of the polymer to a little over 1000 m before the cryopump dumped. This highlighted how inappropriate the cryopumping system was for that particular process.

Thus, experience shows that the most reliable and robust pumping system for large vacuum web coating is still oil diffusion pumping. The roughing pumps are usually a combination of Roots pumps with either a two-stage rotary vane or a rotary piston pump. Where it is absolutely essential for the pumping to be oil free, turbomolecular pumping is then usually the pump of choice to replace the diffusion pump and then one of the oil-free dry pumps for the roughing pump.

There are a number of aspects to pumping of the system to achieve an adequate vacuum for the deposition process. Many systems are pumped to too low a pressure on both roughing the vessel and after crossover with the diffusion pump.

It is a common belief that pumping to the lowest possible base pressure is the best measure of a clean vacuum system. Pumping to a low pressure is often done to encourage moisture, which accumulates on the surfaces during the time the vessel is at atmospheric pressure, to be released and pumped away. Thus, the lower the pressure, the cleaner the system. Unfortunately, operating diffusion pumps at very low pressures leads to increased backstreaming so that lower pressures can mean lower water vapor but higher oil contamination. Thus, getting to the ultimate or even a very low base pressure does not ensure a clean process. Using the time it would take to get to the low base pressure to put clean dry gas into the system can be an equivalent method of producing the desired effect. This alternative method of releasing the moisture is to bombard the surface with gas [2]. Hence, partially pumping the vessel and introducing gas will bombard the surfaces with gas molecules that will speed up the release of moisture from the surface. Using heat or a UV lamp will provide energy and also speed up this release of gas. This means that the system need never be pumped to anywhere near its base pressure, hence minimizing any chance of backstreaming while also minimizing the water vapor levels.

The cleanliness of the deposited coatings does not depend on the base pressure, which the chamber reached prior to the deposition, but on the arrival rate of the contaminants on the depositing coating relative to the arrival rate of the depositing species. If the pumping is poor, the partial pressure of contaminants will rise with time, whereas if the pumping is good, it will be possible to add some inert gas to the system, which will provide a flow of gas helping to flush out the contaminants. This becomes more important in reactive deposition processes and in particular reactive CVD processes. In the CVD processes, the by-products from the precursor gas must be continuously pumped away to maintain a constant flow of fresh precursor gas to maintain the deposition rate. In the sputtering process, the plasma will not only sputter the target material but also bombard the vessel walls encouraging desorption of water, and so the potential for contamination rises. A higher throughput of inert gas will reduce the availability of this contaminant [3]. Thus, for sputtering processes, it is a good policy to sputter at the highest possible rate at the lowest possible sputtering pressure with the highest possible gas throughput.

In reactive sputtering, we have already seen that there may be a hysteresis loop if there is inadequate pumping. Many systems have large diffusion pumps but also have throttle valves because when there is a large gas load, the diffusion pump is operating near to the stall conditions. Rather than operate too near the stall conditions, the pump is throttled. The effect of this is to reduce the throughput of gas and allow the pressure above the diffusion pump to drop further away from the stall pressure. Unfortunately, the reduction in throughput of gas means that the contaminants are not being swept away as quickly and thus the purity of the coating is worsened. The reduction in the pumping speed of the reactive gas also means that the hysteresis loop gets larger and the reactive process increasingly unstable. Rather than throttle the diffusion pump, it is better to increase the capacity of the backing pump to recover some of the stability of the diffusion pump. It is unlikely that this alone will eliminate the hysteresis loop. It is likely that additional oil diffusion pumps would be required also needing high throughput backing pumps.

Many systems that were designed for depositing metals or some of the easier reactive coatings may have difficulties when trying to deposit the more reactive oxides such as titania and alumina. If a system is already built, then there will almost certainly be great difficulties in trying to add additional pumping. This problem has resulted in a number of alternative strategies being developed to allow such systems to deposit these materials. This is always at the expense of the deposition rate.

It is common to try to minimize the pumping of a system. This can be a false economy. To produce a titanium dioxide coating from a sputter target, it is possible to do it fully reactively or from an overoxidized target. The overoxidized target is the most commonly used method. This is invariably because the system is underpumped. The fastest process is from the metallic target that sputters of the order of 20 times faster than the oxide. If the pumping was increased to eliminate any hysteresis loop, the deposition rate would certainly be at least twice as fast as from the oxide and possibly many times faster. Even at double the speed, this effectively doubles the productivity of the system. It needs to have the full economics of each system analyzed in detail but the increased productivity ought to more than cover the cost of the additional pumping.

In choosing a pumping system, the aim should be to use the simplest and cheapest that will deliver a robust system capable of achieving the operating pressures required in an appropriate timescale. Where it can be proved that a particular type of pump is detrimental to the product, it can be eliminated from consideration. Pumps should not be eliminated just because of a prejudice or an assumption. If there is a concern that a type of pump could be detrimental to the process, then it ought to be possible to use experimentation to prove it one way or the other.

4.9 System Pumping

It is often believed that a vacuum vessel simply contains a volume of air and that this is what is pumped out to reduce the pressure. The reality is somewhat different. As is shown in Figs. 4.11 and 4.12, there are several different sources of gas besides

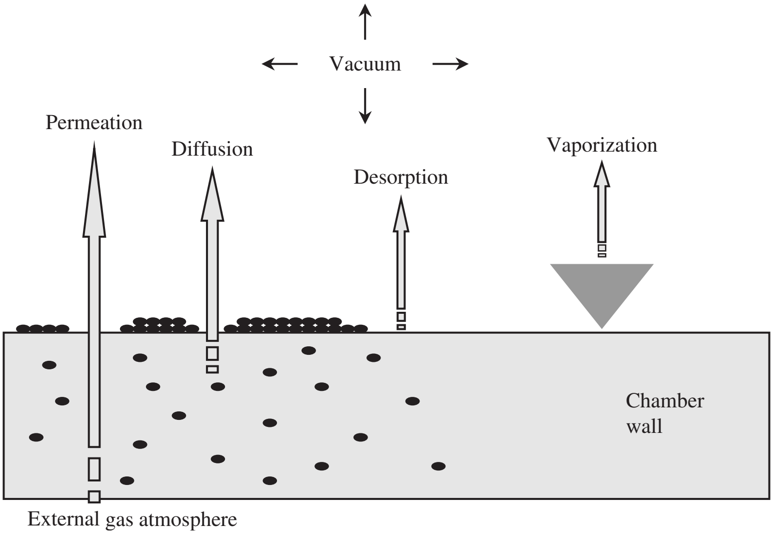


Figure 4.11 A schematic of the sources of gas during system pumpdown.

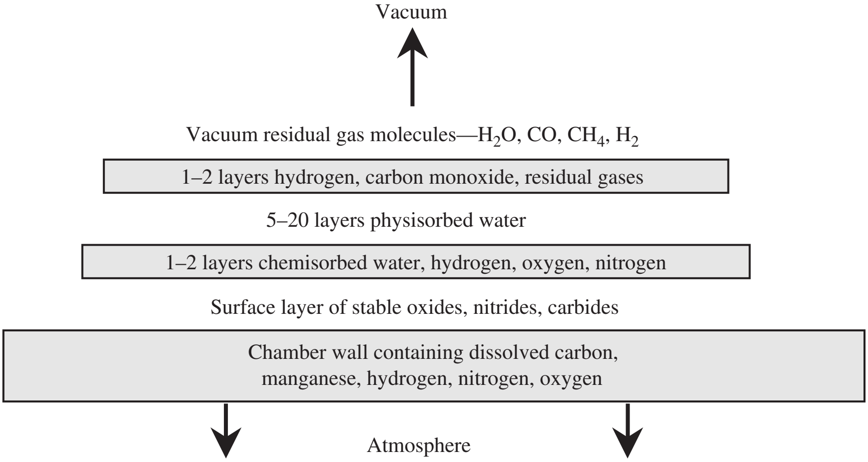


Figure 4.12 A schematic of the gases present at the chamber surface.

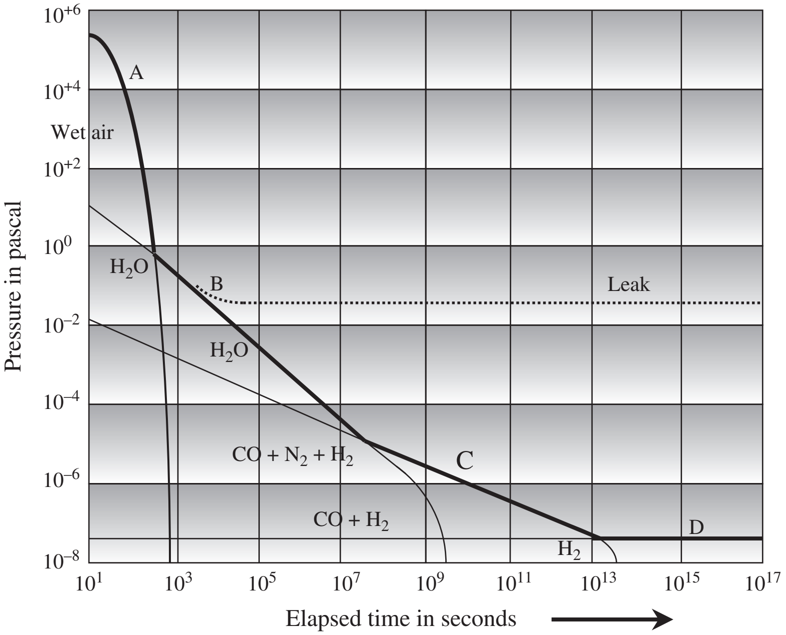


Figure 4.13 A curve of the gas sources that dominate the pumpdown curve for a vacuum vessel. A = volume gas, B = gas desorption from the surface, C = gas diffusion from bulk of materials and subsequent desorption, and D = gas permeation.

the enclosed volume of gas. The gas is given up at different rates and so will affect the vacuum in different proportions at different times.

If we look at how this affects a real system, we can plot the source of the gas as a vessel is pumped down. A curve of this is shown in Fig. 4.13.

If the vessel only contained the volume of contained gas, the curve would follow the line A all the way to the lowest pressure. However, as the volume gas is pumped away, the residual gas becomes dominated by gas being desorbed from the surfaces. This is a slower process than simply pumping the volume gas and so the slope of the curve changes as shown by line B. Similarly, once most of the gas has been desorbed from the surface, the gas load will become dominated by the gas diffusing out of the bulk of the materials, which, once it reaches the surface, will be desorbed. Again the slope will change as per line C. Once most of this gas load has been removed, there will be a small fixed gas load from the gas that can permeate from the atmosphere all the way through the vessel walls and provide a constant low gas load. This final line is the horizontal line shown as line D.

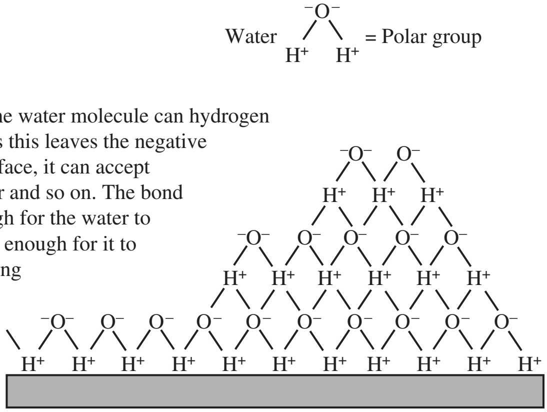
At any stage, there can always be a leak from the outside of the vessel and this would be seen as a horizontal line, an example of which is shown as the dotted line named “leak.”

These slopes can be changed by various means. Increasing the pumping can reduce the time and increase the slopes. In the case of desorption, the gas can be encouraged to leave the surface faster by increasing the surface bombardment or by adding some energy such as heat or ultraviolet radiation. This energy is absorbed by the loosely bound molecules and increases the volatility. The gases contained within the bulk of the materials also can be encouraged to move more quickly by heating the vessel. As the permeation is at such a low level, it usually is of no concern for roll-to-roll coating systems.

The rest are all of interest as the gas load can often become dominated by the water vapor absorbed by the massive surface area available that has been caused by stray coating material building up on the vessel walls and other surfaces. This material can be very porous and so contain a large amount of gas. The thicker the coating buildup, the greater the trapped gas and the longer to pump this gas away. The substrate can also be regarded as a gas reservoir, the precise amount of gas being determined by the type of polymer, the processing, and the storage conditions.

The water vapor does not just form a monolayer on the surface but can build up many layers, and each molecule will be desorbed individually (Fig. 4.14). Where the surface is not smooth and flat but has a porous coating deposited on the surface, it acts more like a sponge where water can be wicked into the pores.

As these slopes can be changed, they can be used as a measure of the system performance. The system pumpdown curve should be obtained for any new system where it is expected to be clean and dry and with a minimum surface area. Each time the system is pumped, the new curve can be compared to the original and any difference can be examined. The reduction in pumpdown performance can thus be used to trigger the timing of a major clean of the system to remove the coating buildup and reduce the surface area back to somewhere near the original.



The positive ends of the water molecule can hydrogen bond onto surfaces. As this leaves the negative oxygen as the new surface, it can accept a further layer of water and so on. The bond strength is weak enough for the water to be removed but strong enough for it to be a slow process, taking hours or days.

Figure 4.14 A schematic of the water that may be present on all surfaces.

4.10 Filtering

Many large roll-to-roll coating systems run without any filtering. The levels of dust or particles are kept low by vacuuming away any debris during the cleaning of the shields during the system downtime. However, there are a number of processes where a significant amount of particles can be generated during the deposition process, which means that the pumps need to be protected from large levels of particles that could abrade the close-fitting pumping surfaces or could clog up the oilways within oil-based pumps. Low melting point materials or compounds, which may have a high vapor pressure and low sticking coefficient, may get pumped as a vapor or, if the vapor is able to form particulates, the particles may be pumped directly. This type of problem is found in some of the copper indium gallium diselenide photovoltaic deposition processes, where selenium vapor gets everywhere, and in atomic layer deposition processes, where the process is designed to coat every surface uniformly.

In some cases, it is possible to use a cold trap to condense vapors before they reach the pumps where the liquid or solid can be collected for periodic removal. Alternatively, there are high surface area molecular filters that can do the same job. The particles can be trapped using filters similar to those used as air filters for automobiles, and these may be in series with progressively finer filters. For larger particulates, there are also cyclone filters that spiral the particulates to the outermost diameter of the cyclone and then pump from the central axis where only the lightest particles can remain.

4.11 Conclusions

Pumping should be kept as simple as possible and be robust. The simplest system for web coating applications is diffusion pumps backed by Roots blowers and rotary pumps. This pumping combination is often the cheapest option and so there ought to be a compelling reason why a different pumping combination needs to be used.

It is worth being skeptical of industry fads.

Skimping on pumping, to save money on the capital cost of a system, is likely to reduce the production performance and be paid for in the longer term in the loss of revenue. This is particularly true for systems operating reactive processes.

Positioning the pumps can be critical, depending on the process, but should aim to be symmetric about the centerline of the web winding path and uniformly distributed where possible. Reactive processes are much more sensitive to asymmetric pumping than simple metal deposition.

The problems of contamination by oil backstreaming can sometimes be overemphasized. In many cases, any backstreaming can be minimized by a mixture of good designs and by adopting the correct pumping strategy.

If there is a process hysteresis loop, then throttling diffusion pumps should be looked at as a last resort with increasing the total pumping and/or increasing the backing pumps looked at first.

Use the pumpdown performance as a warning system to tell of system health, that is, the onset of leaks or progressive dirtying of the surfaces by stray coating buildup.

References

[1] DE 26 19 411 [a German patent]. Optimisation of design of diffusion pump; Fr 2 310 482 [a French patent] 25 Nov 1976. Perfectionnements aux pompes a vide a diffusion. Fr 2, 310, 482 [a French patent] 4 May 1976.

[2] Shirn GA, Patterson WL. Vacuum systems for sputtering. J Vac Sci Technol 1970;7 (3):453−8.

[3] Falco CM. Figures of merit for sputtered superlattices. J Appl Phys 1984;54(4):1218−9.

Bibliography

[1] Harris NS. Modern vacuum practice. McGraw-Hill; 1989 ISBN 0 07 707099 2.

[2] Basic vacuum practice. 3rd ed. Varian Associates Inc. Lexington, MA 02173; 1992. Varian part no. 900-0085.

[3] Hill RJ, editor. Physical vapor deposition. Temescal, A Divison of the BOC Group, Inc, Berkeley, CA 94710; 1986 Part No. T-0186-6001-1.

[4] Roth A. Vacuum technology. North Holland Publishing Co.; 1979 ISBN 0 444 10801 7.

[5] Maissel LI, Glang R. Handbook of thin film technology. McGraw-Hill; 1983 [reissue] ISBN 0 07 039742 2.

[6] O'Hanlon JF. A user's guide to vacuum technology. John Wiley & Sons; 1980.

[7] Guthrie A. Vacuum technology. John Wiley & Sons—Wiley Interscience; 1963.

[8] Weissler GL, Carlson RW, editors. Vacuum physics and technology, Vol. 14. Academic Press; 1979.

[9] Gilbert R, editor. A primer on capture, sorb and cryopumping. Instructional materials series I−1. American Vacuum Society, New York, NY 10017; 1992.

[10] Haefer R.A. Cryopumping theory and practice. Clarendon Press, Oxford 1989, ISBN 978-0198548126.

[11] Hablanian MH. Diffusion pumps—performance and operation. American Vacuum Society monograph series M:5. American Vacuum Society, New York, NY 10017; 1983.

[12] Duval P. Vacuum problems in today's integrated circuit manufacturing systems. Solid State Technol 1982;25(9):124−30.

[13] Bentley PD. The modern cryopump. Vacuum 1980;30(4/5):145−8.

[14] Longsworth RC, Bonney GE. Cryopump regeneration studies. J Vac Sci Technol 1982;21(4):1022−7.

[15] Taylor KA, et al. Technical note: cryogenic vacuum pump characteristics in reactive D. C. magnetron sputtering processes. Surf Coat Technol 1897;33:379−91.

[16] Harris NS. Modern diffusion pump vs turbomolecular pump systems. Vacuum 1980;30 (4/5):175−81.

[17] Arbel A, Shapira Y. A decision framework for evaluating vacuum pumping technology. J Vac Sci Technol A 1986;4(2):230−6.

[18] Hablanian M, Bez E. Evacuate your chamber without messy oils. Res Dev 1987;120–2, October.

[19] Danielson PM. Rough pumping without oil contamination. Res Dev 1987;97–104, April.

[20] Knize RJ, Cecchi JL. Theory of bulk gettering. J Appl Phys 1983;54(6):3183–9.

[21] Casey F, et al. Design considerations of a high efficiency cryogenic pumping system for paper metallization. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 213–219.

[22] Schwarz W. Thermal limitations of the pumping speed of refrigerator cooled cryosurfaces. J Vac Sci Technol A 1987;5(4):2568–71.

[23] Paul PH, LaCourt DW. Optimized pumping of a web coating system. In: Proc. 12th vacuum web coating conference; 1998. p. 78–85.

[24] Paul PH, Missimer DJ. High speed water vapor cryopumping. In: Proc. 1st vacuum web coating conference; 1987. p. 40–49.

[25] Stenhouse J, Spencer AG. Coating improvements through better control of water vapour in vacuum deposition. In: Proc. 17th vacuum web coating conference; 2003. Session 2B, section 1, paper 3.

[26] Weston GF. Pumping systems. Vacuum 1985;35(10/11):493–7.

[27] Welch KM. Capture pumping technology: an introduction. Elsevier Science [Pergamon Press]. ISBN 0 804 0197 X.

[28] Penfold AS. The influence of pump size on D.C. reactive sputtering systems. In: Proc. 29th annual technical conference of the Society of Vacuum Coaters; 1986. p. 381–403.

[29] Tompkins HG. The fundamentals of vacuum technology. American Vacuum Society monograph series M:6. American Vacuum Society, New York, NY 10017; 1997.

[30] Tompkins HG. Vacuum technology: a beginning. American Vacuum Society monograph series HB-1. American Vacuum Society, New York, NY 10017; 2002.

[31] Lewin G. An elementary introduction to vacuum technique. American Vacuum Society monograph series M:8. American Vacuum Society, New York, NY 10017; 1987.

[32] Tompkins HG. Pumps used in vacuum technology. American Vacuum Society monograph series M:9. American Vacuum Society, New York, NY 10017; 1991.

5 Process Diagnostics and Coating Characteristics

The ideal would be to have enough knowledge of the process such that with precise control there would be no need to monitor the process. However, there is enough variation in the processes, because of which it is critical to controlling the deposition process to have some form of monitoring.

There are various measurement options and it depends on the deposition process and the coating deposited as to which technique is used.

For conducting coatings and using a calibration of the conductivity to the coating thickness, it is possible to monitor the coating and control the process. For nonconducting coatings other measurements need to be taken, such as transmittance and reflectance.

Some processes that have a plasma associated with the deposition process can utilize the light output from the plasma. The light will be characteristic of the excited atoms within the plasma. Once calibrated, it is possible to use ratios of selected emission lines to control the deposition of compounds and metals.

The use of this type of measurement is that it is potentially a "real-time" measurement and the response time to process fluctuations can be minimized. Whereas monitoring the coating properties tends to be done after the web has left the deposition drum and hence some time later.

For double drum deposition systems, double side deposition and multilayers deposited in a single pass process, there are additional complications of separating out the variations of each of the layers. For products with multilayers, there needs to be a greater understanding of how the individual layers affect the final product. Where monitoring takes place after multiple depositions and there is some time lag, the process needs to be, if anything, more stable than for more simple processes. This means that the process will not be going out of control faster than it can be monitored and corrective action can be implemented.

It is always a good policy to monitor the "health" of the process. Ideally the system will pump down in the same time and to the same base pressure. The starting point to the process will be the same and the process will require the same settings and produce the same quality coating every time. The reality is that the pumpdown time will vary, possibly every cycle and the base pressure will hence be different

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00005-2

after the same pumping time. If the base pressure is different, the process is likely to start from a different set of conditions. Some of the differences will be due to atmospheric differences such as a change in humidity, whereas others may be related to differences in the quality of cleaning the vessel undergoes by different operators. Some of these differences can take the form of a progressive worsening of performance and can be monitored by the likes of a residual gas analyzer.

For more complex processes, it is a good investment to have either a mass spectrometer or a lower cost residual gas analyzer permanently attached to the system to monitor the composition of the gases during pumpdown and during the process. This not only will help to monitor the "health" of the system and process but also it can be used for troubleshooting if the process is lost for any reason.

5.1 Reflectance (*R*), Transmittance (*T*), and Absorptance (*A*) Measurements

Thin film coatings, most commonly, can be characterized by measuring the reflectance and transmittance (Fig. 5.1) across the visible spectrum. For metallic coatings, this measurement is often converted into a measurement of optical density. This is a measurement of opacity and is important for packaging products that require a good light barrier. Examples of this would be for potato chips/crisps where light would help turn the fats rancid.

When taking measurements of *R* and/or *T* (and hence getting *A*), it is important to consider what is important to the product. It may not be necessary to take values across the whole of the visible spectrum if the requirement is for a specific performance only for near-infrared (IR) reflectance. It may also be equally good to use specific light-emitting diodes of wavelengths of specific interest rather than a scanning spectrometer. This may prove to be much more cost-effective and simple to achieve [1].

This system can be put to good effect for simple optical filters where there will be well-defined wavelengths of high and low transmittance values.

Once the relevant wavelengths are chosen, the type of illumination and detectors can also be chosen. For a scan across the whole of the visible spectrum, miniature scanning spectrometers are available. The use of fiber optics has enabled the costs to be brought down by using a common light source and detection system and then switching between multiple fibers to cover the whole web width. Care must be exercised to ensure that stray light does not skew the results. It is common to use computers to log the data and to use a stored reference spectrum taken at the time the process is started but no coating depositing to subtract from the output spectra during deposition to eliminate any stray light component and improve the sensitivity.

The use of miniature scanning spectrometers and cheap fiber optics and fast computing has also enabled the output to be converted into other units. Hence, it is possible to look at the color of a coating and to have the output as the standard CIE

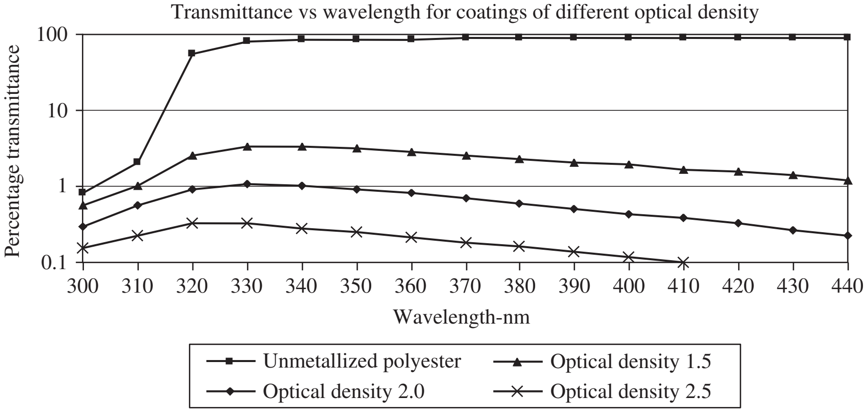


Figure 5.1 A comparison of coatings of different optical density showing transmittance versus wavelength.

(French International Commission on Illumination, Commission Internationale de L'Eclairage) color coordinates. This can be useful for coatings used for their color or where colored coatings are not acceptable. An example of this would be for the transparent barrier coatings where for some applications a yellow color to the coating is unacceptable but a more neutral gray is preferred.

Reflectance measurements tend to have the additional problem of needing to have the web kept flat. If the web is wrinkled for any reason, the reflected light will be scattered rather than reflected back to the photodetector; hence, the value will appear lower than it is in reality. It is common to have two rolls fairly close together and to take the measurements between the rolls where the web path is going to be well defined and with a short span is likely to be less troubled by wrinkling.

Using reflectance measurements after each of several different coatings, it is possible to extract the coating thickness of each layer's contribution to a final total coating optical performance [2].

5.2 Optical Density

The opacity of a coating is a measure of light that is incident on the coating divided by the amount of light that is transmitted. In metallizing, this is more usually expressed as the optical density (OD) of the coating where OD is opacity expressed as a logarithm to base 10. This measurement requires a white light source and a detector. The transmitted light value can be obtained before deposition starts each time to establish the 100% value (Box 5.1). Table 5.1 shows optical density, opacity, and transmittance. Figure 5.2 shows three transmittance optical monitors distributed across the web width.

Box 5.1 The relationship between opacity, transmittance, and optical density

$$\text{Opacity} = \frac{\text{Incident light}}{\text{Transmitted light}} \qquad \text{Transmittance} = \frac{\text{Transmitted light}}{\text{Incident light}}$$

$$\text{Opacity} = \frac{1}{T}$$

$$\text{Optical Density} = \log_{10}\text{Opacity} = \log_{10}\frac{1}{T}$$

Table 5.1 The relationship between optical density, opacity, and transmittance

Optical density	Opacity	Transmittance (%)
0	1	100
0.2	1.6	63
0.5	3.2	32
0.7	5	20
1	10	10
1.5	32	3.2
1.8	63	1.6
2	100	1
2.2	158	0.6
2.4	251	0.4
2.6	398	0.25
3	1,000	0.1
4	10,000	0.01

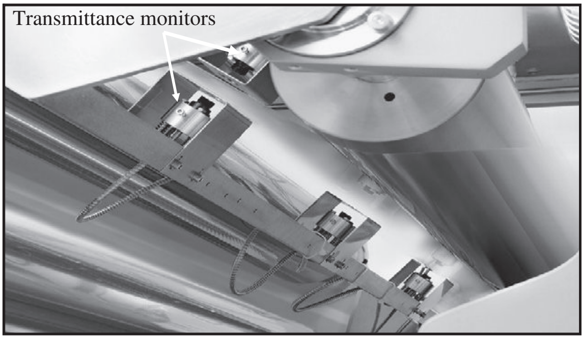


Figure 5.2 A photograph of three transmittance optical monitors distributed across the web width. Photograph courtesy of Applied Materials.

5.3 Conductivity/Resistivity

If you consider an electric current flowing across a surface, the surface resistivity (R_s), also known as sheet resistance, can be described as the ratio of the DC voltage drop per unit length to the surface current per width [3]. This can be thought of as the resistance between two opposite sides of a square and is independent of the size of the square or its dimensional units. This surface resistivity has units of ohms per square.

The bulk resistivity is still measured in ohms (Ω) and is the ratio of the applied voltage to the current passing through the material.

5.3.1 Sheet Resistance and Calculating Resistivity or Thickness

The most commonly used instrument for the measurement of sheet resistance is the four-point probe [4]. This instrument has a set of four contact probes arranged in a line and equally spaced. Four-point probe based instruments use a long established technique to measure the average resistance of a thin layer or sheet by passing current through the outside two points of the probe and measuring the voltage across the inside two points.

So long as the spacing between the probe points is constant, the conducting film thickness is less than 40% of the spacing, the edges of the film are more than four times the spacing distance from the measurement point, and the average resistance of the film or the sheet resistance is given by:

$$R_s = 4.53 \times \frac{V}{I}$$

The thickness of the film (in cm) and its resistivity (in ohm-cm) are related to R_s by:

$$R_s = \frac{\text{Resistivity}}{\text{Thickness}} = \frac{\rho}{d}$$

The resistance of a thin film resistor is directly proportional to the resistivity, ρ, and inversely proportional to the thickness, d.

Hence, it is possible to calculate the resistivity if the thickness of a film is known, or alternatively calculate the thickness if the resistivity is known.

The measurement is a quick off-line measurement. It can have some errors, such as where the measurement may be up to 20% too high if the area is surrounded by high conductivity material. Similarly, the measurement may be up to 10% too low if the measurement area is surrounded by insulating material.

The standard equipment for sheet resistance measurement is a four-point probe. This will give a measure of resistivity, but will not give the detailed measurements of mobility and carrier concentration; for this a large magnet is required to make Hall measurements [5–9].

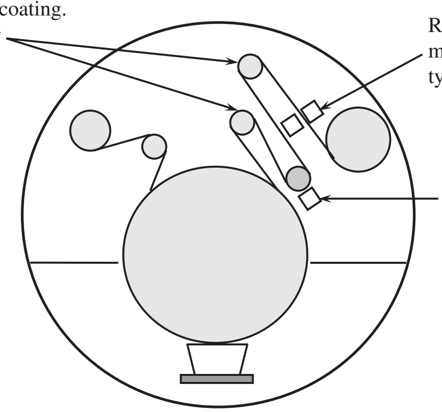
Several manufacturers make automated systems. These systems use probes in the van der Pauw configuration [10,11]. This extra complexity raises the cost of equipment up from a few hundred pounds to more than 20,000 pounds.

The four-point probe and the van der Pauw techniques both use sharp pointed contacts that can damage the conducting coating and in the case of the van der Pauw system the sample has to be cut out of the web. This makes the testing damaging or destructive. It is difficult to attempt to carry out these measurements on a continuously moving web.

An alternative technique has been developed that is nondestructive and can be used continuously on web coaters. The eddy current technique uses a coil that has a radio frequency (RF) field applied across it, and either on the same side or on the opposite side a detector measures the induced field. The conducting coating modifies the induced field that is detected. Although it is most commonly used to monitor the deposition thickness of metals in vacuum coating systems, any conducting coating is possible. If the thickness is known the conductivity can be obtained. This measurement technique averages the measurement from a large area. It is insensitive to small changes in conductivity from small areas. To map the resistivity in detail from a web would require one of the probe techniques and this would have to be done off-line.

5.4 Online Resistance Monitoring

It is possible to measure the resistance or conductivity of a thin film coating by using two front surface contacting rolls in the winding system and taking measurements through these rolls (Fig. 5.3). In this case there are problems, the rolls have to be isolated to ensure that the measurements are purely a measurement of the



Rolls in contact with coating. Measure conductivity between rolls to measure coating conductivity.

Reflectance & transmittance monitors or transmittance type eddy current monitor.

Coating on outside surface. If roll in nonconducting coating conductivity is measured by eddy current technique. In-contact probes may also be used but can damage the coating.

Figure 5.3 A schematic of online measurement options.

coating conductivity and not via some other leakage path. The second problem is to maintain a low-resistivity contact to the rollers that by their nature are rotating. This can be done using hard carbon or copper brushes, but these can give problems over time. The surfaces can age, harden, and/or the copper can become oxidized. Any of these can add some resistance to the contact, which may not even be consistent and so it adds a background noise to the measurement.

Similar to this was the system that used probes to either drag across the coating or use a rotating pinch roll with two embedded copper wires to make contact with the coating. A variant of this was to use four contacts and take the measurement as a four-point probe would and thus giving the result in ohms per square. A further variant of this was to have four contacts close together at several points across the web [12]. This then gave a four-point probe resistivity measurement at a number of points to check on the web uniformity. These contact methods could leave some evidence of the contact points having damaged the coating. This is particularly so with the conducting oxides, which are brittle, where microcracking could often be seen around the contact lines due to the localized pressure exerted. In taking a number of measurements across the web, the damage created could be seen as a stripe at each measurement head. This effectively ruined any wide web manufacturing process as the only undamaged material was between the stripes, which was very narrow. Thus, in-contact measurements rapidly lost popularity.

The more common and more elegant solution is to use a noncontact measurement technique. This has been developed over the last few years and is done using an eddy current monitor [13–16]. The construction of this type of monitor can vary but essentially there is a coil, which is used to generate a high frequency magnetic field from a RF supply, placed close to the web and if the thin film coating is conducting there is a change in frequency and a loss of signal intensity that can be detected. The change in frequency and intensity is dependent upon the material, the thickness, and the structure that define the conductivity.

There are two ways of arranging the source and detector. One is to have them placed directly opposite each other where the web is in free span as shown in Fig. 5.4. The other is to combine the source and detector within the same body and place this unit close to the metallized side of the web. In this design the transmitting and receiving coils are wound concentrically, making the unit quite compact.

The transmitted unit does not require the web to be any precise distance away from the source or sensor; it simply has to pass somewhere between them.

The single side sensor is sensitive to the distance between the web and the head. Because any change of distance will affect both the signal and detector, it is usual to site this unit at a position where the web is passing around a roller. In order to not affect the signal by the conductivity of the roller, these rolls are made of a nonconducting material such as fiberglass.

The coils are designed specifically to suit the particular coating and thickness range required. Changing the material and/or thickness of the coating can reduce the accuracy of the measurement significantly. Thus, the same monitor may not be used to measure the thickness of a metal and a transparent conducting oxide (TCO).

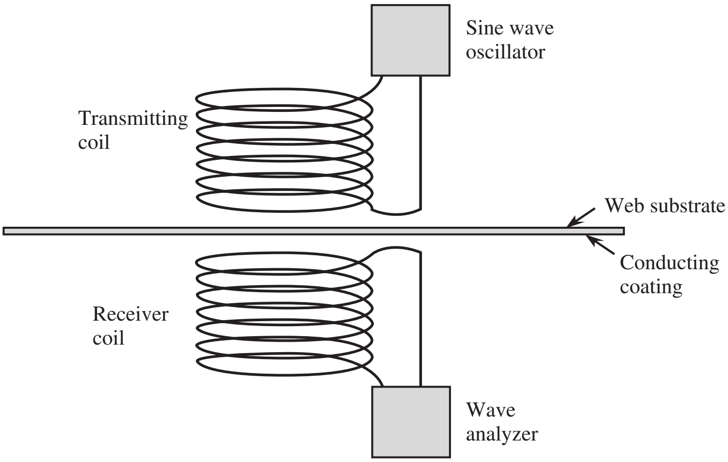


Figure 5.4 A schematic of an eddy current monitor.

The eddy current monitors can also be susceptible to changing thermal conditions and this can cause the signal to vary for material of the same conductivity. To eliminate this source of error, these monitors need to have some inbuilt temperature compensation system.

The significant parameters used for designing the coil are as follows:

δ, thickness of the layer
σ, conductivity of the layer
μ, magnetic permeability of the layer
ω, frequency of the oscillator
h, spacing between the head and the web

The changes that can be made to the coil are the number and diameter of turns.

The eddy current monitors average the conductivity from an area under the monitoring head (Fig. 5.5). The size of the head and the area it takes the signal from can be varied to some extent. It is common to use a series of heads to measure the conductivity of a web. As there can be boats of the order of 25 or more, the coating quality on the wider machines is required to be as good as that on smaller machines. It has resulted in the use of one head directly in line with each boat or in line with the midpoint between boats. This then allows for the output from each eddy current monitor to be the control signal for the boat that it is in line with.

For simple metals such as gold, silver, copper, or aluminum, it is common for calibration graphs to be drawn that relate the resistivity to the reflectance or transmittance. Once the calibration has been made for that particular machine and the deposition conditions, it is often accurate enough to reach a desired resistance coating simply by monitoring the optical characteristics [17]. This may save having to install another monitoring system such as an eddy current monitor.

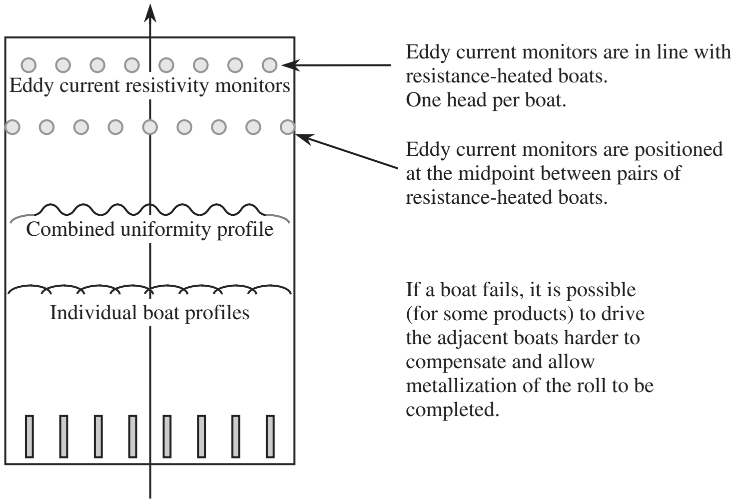


Figure 5.5 A schematic of the arrangement of eddy current monitors in a vacuum metallizer.

5.5 Transparent Conducting Coatings

The electrical performance is often defined as the sheet resistivity and is quoted as the number of ohms per square. Frequently, there will be a minimum light transmittance requirement linked to the sheet resistivity.

It is common for academic papers to define the TCOs more specifically using parameters such as the carrier concentration and mobility from Hall effect measurements [18]. The Hall effect is used as an off-line technique used to measure the fine detail of the coatings. The TCOs are regarded as semiconducting coatings and the carrier concentration and mobility give an indication of how many and how freely the electrons travel within the material. If the grains are large and contain few defects, the mobility will be high but with smaller grains and/or more growth defects or high stress, the mobility will be low.

A simple measurement of resistivity will not give this fine detail; however, once the process is defined, an online measurement of the resistivity may be all that is necessary for quality control.

The Hall effect is when a magnetic field is applied at right angles to the current flow in a thin film where an electric field is generated, which is mutually perpendicular to the current and the magnetic field and which is directly proportional to the product of the current density and the magnetic induction.

This measurement requires a well-defined sample shape, a very high powered reversible magnetic field, and some sensitive voltage and current supply and measurement equipment. This too requires a disposable sample and is not done as a continuous online measurement.

5.6 Residual Gas Analyzers

Another area where cost always tends to be an issue is that of diagnostics. In theory, the machine or process will work and never go wrong. In reality, the process will go wrong and until there is a substantial history of faults these will all need to be diagnosed from the information available. The greater the complexity of the process, the more diverse will be the ways the process can go wrong. A proportion of the problems will be obvious, some will be more difficult to find and others will be very obtuse and difficult to resolve.

One of the most useful diagnostic tools to have is a residual gas analyzer (RGA) (Fig. 5.6). An RGA is usually a more simplistic and cheaper design of mass spectrometer [19]. The mass range, discrimination, and sensitivity are all likely to be less than a mass spectrometer but are sufficient for the process diagnostics. The RGA system samples the gas from a process zone. The gas is charged and accelerated as a means of separating the different species from each other and a detector measures each of the component gases. If the RGA is plumbed into the system in a way that allows separate sampling of each of the zones, it is possible to analyze each zone and check the gas content during the dynamic deposition process. To do this requires that the RGA has a pumping system to enable a reasonable throughput of gas to get the best sensitivity from the detector and to allow for working at high system pressures. The separate pumping system also reduces the time delay especially when sampling from remote parts of the system. When a process goes out of tolerance it is frequently due to some form of gas contamination. This contamination can be from system leaks, higher than normal outgassing, higher than normal water content, or cross talk of a reactive gas from one of the other zones. The RGA enables the process to be actively monitored to check for this type of abnormality.

It is a good policy to use the RGA from day one as a way of routinely monitoring the state of the system. Once the system is built, and before it is used for deposition, if a trace is taken of the residual gas content, this will act as a reference baseline for

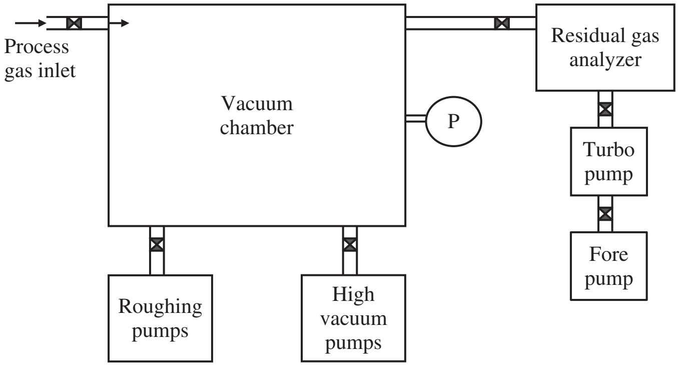


Figure 5.6 A schematic of an RGA.

the system. If a second reference trace is taken after several depositions just before the point of the system needing a clean, this can act as a threshold trace.

If the system cannot be pumped below this threshold within a certain time, it tells the operator that the system needs a clean. Other reference traces can be taken and used as comparators for the operators to use. The process traces can be stored and it then becomes possible to check back to see if a process has been degrading over a period of time or if it has failed in a more precipitate manner. All of this gives much more information than is available from the set points and readings of pressure gauges and voltage and current readouts from plasmas. This information makes it easier and quicker to find the cause of the more obscure problems that otherwise would cost a large amount of unproductive time.

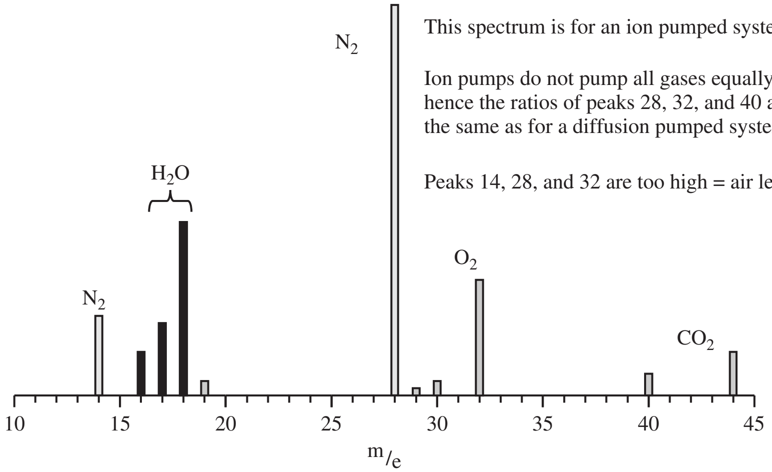
Figure 5.7 is typical of the output of an RGA where the characteristic peaks are identified as being from nitrogen and oxygen. Once the system has been pumped down, the residual gas left would be primarily from desorbed water and hence the presence of oxygen and nitrogen suggests the system has an air leak.

With more complex processes it is possible to use a single RGA head and sample each deposition zone sequentially and look for any cross-contamination.

Where an RGA is used to continuously monitor one single process, specific peaks can be monitored, which can be used to trigger alarms. The alarms can be triggered at an early sign of the process drifting out of specification or they can be used to trip an emergency shutdown procedure in the event of a more catastrophic change in the process.

It is this ability to react to the process as well as a way to shorten the diagnosis of problems that can be used to sell the RGA as a cost benefit rather than an expensive luxury.

If the RGA is already being used to monitor the process, it may also be used as part of the process control [20]. This is particularly useful if the process is a



This spectrum is for an ion pumped system

Ion pumps do not pump all gases equally and hence the ratios of peaks 28, 32, and 40 are not the same as for a diffusion pumped system

Peaks 14, 28, and 32 are too high = air leak

Figure 5.7 The output of an RGA that shows a vacuum system with an air leak.

reactive one. A reactive process may be controlled by stabilizing the reactive gas partial pressure relative to the background inert gas pressure. Large vacuum systems may prove to be a challenge as the RGA head may need to be quite far from the process zone. This might show up as a time lag between sensing a deviation and making the correction.

5.7 Plasma Emission Monitors

To some extent, it is possible to use a plasma emission monitor (PEM) for diagnostics. However, it tends to be not as sensitive and it requires that there is a plasma present to excite the gases, which means that zones where there is no plasma present cannot be examined unless some additional plasma is struck for the monitor. Hence, it is not as useful as the RGA for routine troubleshooting and so it has to be justified solely as a process control tool.

Figure 5.8 shows a typical light output from a plasma at three different power levels. The vertical arrows highlight where there are changes between the lowest and highest power level. This would be typical of where the lower power level is insufficient to break through the surface oxide of a sputtering target but where the higher powers do break through and so the metal line rises in intensity more than the oxygen line.

Where the PEM comes into its own is where there is a reactive sputtering process taking place. In this case, there is already a plasma present and it is possible to sample the process gases and the depositing species in real time. Hence, this can be a very sensitive controller. The emission monitor looks at the light output from the

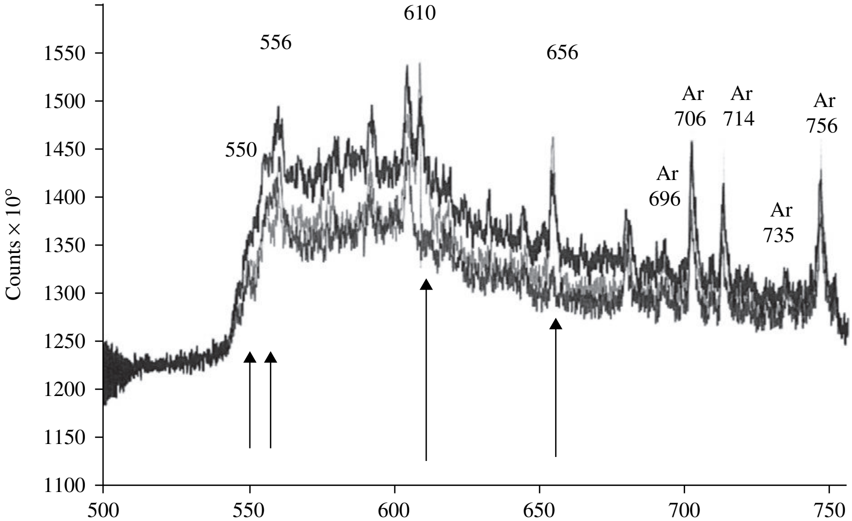


Figure 5.8 A typical spectrum from an early plasma emission monitor.

plasma; the primary peaks are from the excited species present. The ones used for control purposes are the emission wavelengths for the metal and the reactive gas. These two lines are kept at a constant ratio. There still needs to be a measurement of the deposited coating in order to set the correct ratio at which the desired coating is produced. Once this has been established, the deposition may then be controlled from the PEM. On very large cathodes, it has been known for several PEMs to be set along the length of the cathode where each is controlling the mass flow of the reactive gas for their own separate manifold (Fig. 5.9).

The control only works well if the time constant for the supply of the gas is equal or shorter than the speed with which the process can change. This gets to be more difficult on industrial size systems where the distances are greater and hence time constants longer.

The PEM increased in popularity when compact, low-cost scanning spectrometers became much more widely available [21].

The three traces in Fig. 5.10 also show typical outputs. The top trace has had the background illumination subtracted helping to make the background illumination fairly horizontal.

The middle trace is time-resolved. Between each trace is a time delay allowing the changes to be followed more easily. In this example, the oxygen gas was turned off and it can be seen that two of the peaks decay and then return much more rapidly as the gas was reintroduced.

The lower trace is of a metallic indium target at three different oxygen levels for the same applied power. Some peaks are unaffected but the main two show significant changes. It is these peaks that can be used as a ratio to the metal peaks and used as the signal to control the process.

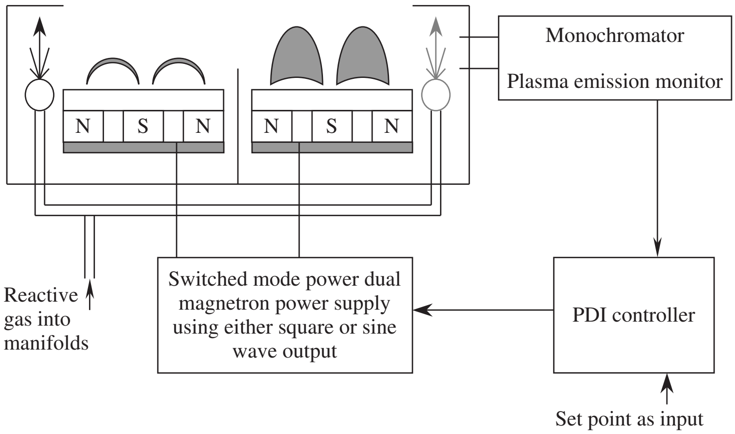
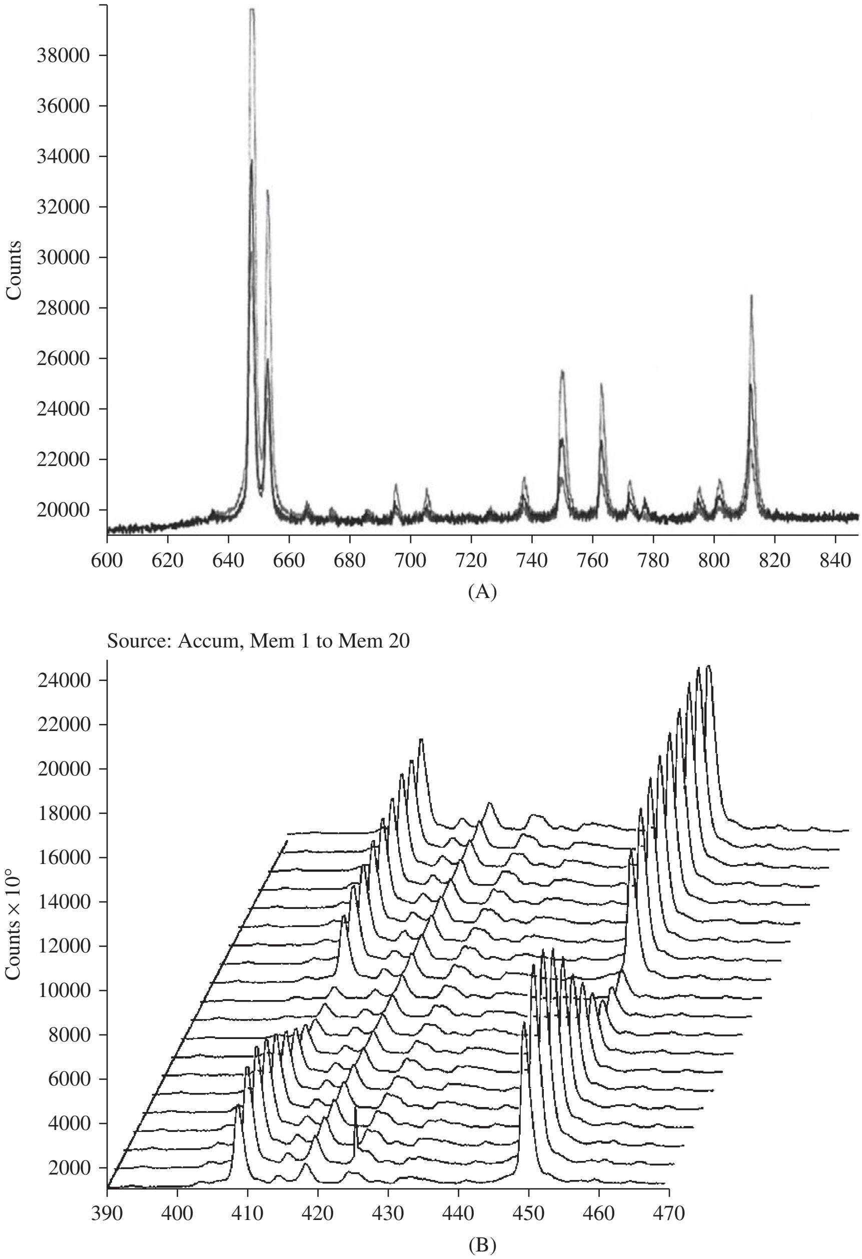


Figure 5.9 A schematic showing the application of a plasma emission monitoring system to control the reactive gas input to a switched mode dual magnetron sputtering source for the high-rate deposition of oxides [22−30].



Source: Accum, Mem 1 to Mem 20

Figure 5.10 (A, B, and C): Three further PEM spectra.

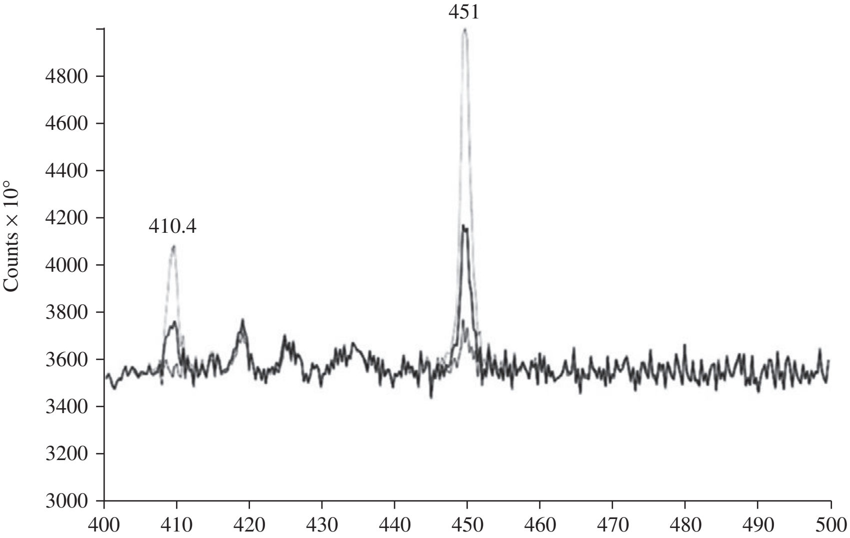


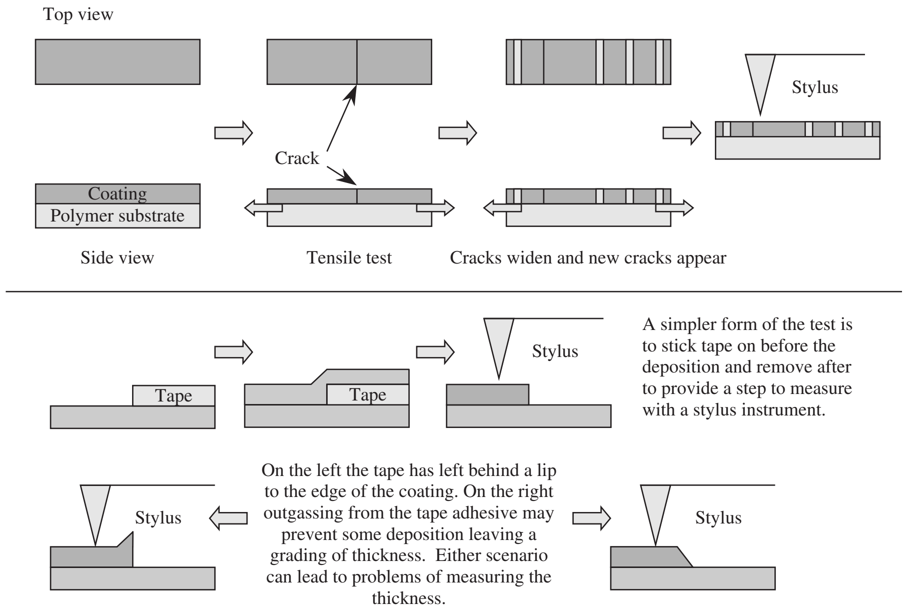
Figure 5.10 *Continued*

5.8 Thickness

It is common to refer to coatings by their thickness but often this is not measured directly. Often the transmittance or resistivity is measured and then by using a conversion chart the thickness is determined. This does depend on accurately knowing the correct conversion factor to use. In some instances, it is possible to take a measurement of the thickness directly but this tends to be limited in the range of materials that can be measured by the technique. Below are a number of different methods of measuring the coating thickness.

5.8.1 Stylus Techniques

Measuring the sheet resistivity requires knowledge of the thickness of the coating. The common way of obtaining this is to use a stylus instrument over a step in the coating. If a mask, such as sticky tape, were stuck onto the substrate before deposition and removed after deposition, a step will be created between the coated and uncoated material. The stylus is dragged across this step and a piezoelectric crystal sends out a signal that is proportional to the height of the step. So long as the stylus travel is sufficient to show parallel portions of the coating surface and substrate surface, there can be a high level of confidence in the thickness measurement. However, often the tape will either create a lip to the coating at the tape edge or outgassing of the adhesive may prevent some deposition toward the tape edge and so grading the coating down from the full thickness down to no coating. The same rule applies that so long as the stylus travel is sufficient to go beyond either of



A simpler form of the test is to stick tape on before the deposition and remove after to provide a step to measure with a stylus instrument.

On the left the tape has left behind a lip to the edge of the coating. On the right outgassing from the tape adhesive may prevent some deposition leaving a grading of thickness. Either scenario can lead to problems of measuring the thickness.

Figure 5.11 The use of a stylus instrument for thickness measurement. For very thin coatings this could be an AFM; for thicker coatings there are surface profilometers that are more appropriate and cheaper [31,32].

these variations and produce traces from the full thickness coating that will be parallel to the substrate surface, there can still be a high level of confidence in the thickness measurement. The possible variations are shown at the bottom of Fig. 5.11. However, if the stylus travel is short and the coating trace is angled to the substrate trace, the measurement is likely to be compromised.

Others have used an atomic force microscope (AFM) to do a similar thing. By using a tensile testing stage, cracks in the coating can be generated and the AFM can be scanned across the surface and the depth of the cracks measured.

5.8.2 Ellipsometry

Another alternative technique is to use ellipsometry. This uses an elliptically polarized laser reflected off the substrate to measure the substrate refractive index and then, once coated, the refractive index and thickness of the coating. This technique only works well for nonabsorbing coatings and is also easier for rigid samples.

It is possible to carry out ellipsometry as an online process [33–35]. Some systems need thick substrates so that the reflection from the back surface is sufficiently displaced and it does not confuse the front surface reflection signal. This can require substrates of several hundred microns. Other systems use deconvolution algorithms to be able to separate out individual layers. Using optical and thickness data of the substrate the first coating details can be determined, which can then be used to find the second coating characteristics, and this can be done for as many layers as are deposited. The other of the two main problems relates to the position of the substrate. To define the position of the substrate measurements are taken as the web travels round a roller, usually blackened to further reduce the back reflection problem. This makes the distance between the web and the laser and detector fixed. This obviously makes alignment critical as the laser beam is reflecting off a curved surface and the reflected beam will be expanding; therefore, the collector needs to be bigger or else the signal intensity will be reduced. The problem in measuring the web that is nominally flat between two sets of rollers is that when the web is being wound there is a tendency for the web to vibrate and on occasions flutter due to resonance. This vibration moves the position of the web so that the reflected beam moves around, and collecting a reproducible and meaningful signal is difficult. For all the problems of using a roller to fix the web position, it is the easier and more reliable arrangement and hence preferred. The light polarization is unaffected if the light passing through a thin layer is normal to the surface. This makes this monitoring system robust to use even where some of the optics might be close to the deposition zone and prone to contamination by some scattered deposition.

5.8.3 Weight Loss Measurement

Metallized aluminum coatings can also have the thickness calculated by using the weight loss method. The metallized sample is weighed and then the coating dissolved off and the uncoated sample measured; the measured weight loss represents the weight of the coating. Using this coating weight and assuming the coating density and also knowing the area of the sample, the coating thickness can be calculated. This does require making an informed estimate of the coating density.

5.8.4 Electron Microscopy

It is also possible to measure the thickness of the coating directly using scanning electron microscopy (SEM) or scanning transmission electron microscopy (STEM) [36]. Samples can be prepared for SEM by freeze-fracturing where the sample is cooled using liquid nitrogen and broken. The fractured surface is then examined using the SEM, and the thickness can be measured. It can be important to calibrate the system as moving the sample around to get the best image can sometimes lead to errors. The STEM requires samples that are thin enough to be transparent to the electrons. This usually requires the coated sample to be encased in a polymer and then thin slivers cut using a microtome. Again after suitable calibration a direct measurement of the coating thickness can be made. These direct measurement techniques have the advantage in that they measure the total coating thickness and are not affected by changes in stoichiometry. This is important for metallized coatings where the aluminum oxidizes both on the air surface and at the interface. When using eddy current or OD measurements, they measure only the conducting or opaque metal material and take no account of the insulating or transparent oxide component of the coating. Thus, any estimate of coating thickness using either the eddy current or OD techniques will not be accurate unless some conversion factor is included. This is covered in more detail in Chapter 16 (Section 16.5.3).

5.8.5 Quartz Crystal Monitor

This monitoring technique uses a resonating quartz crystal placed into the deposition flux and as the crystal becomes coated the resonant frequency changes. The change in resonant frequency is related to the change in mass of the crystal, as the coating thickness increases and the stiffness of the thin quartz crystal is affected. As this technique uses a change in mass of the quartz crystal, it is sometimes referred to as a quartz crystal microbalance. This measurement of changing mass per unit time will allow a calculation of the number of atoms of the depositing material that must have been deposited, and as the coating area is known the thickness or deposition rate can be determined. In reality, there is a problem in roll coating systems in that the amount of material that would be deposited during the complete length of a roll would deposit such a thick coating onto the quartz crystal that it would completely quench any resonance and no longer allow a measurement of the deposition rate.

There are strategies to overcome this problem, such as to place the quartz crystal in a position that only receives a fraction of the maximum deposition rate. The difference between the maximum deposition rate and the off-axis deposition rate is known as the tooling factor. Once a tooling factor has been determined, it can be used to multiply the measured off-axis deposition rate to give the maximum deposition rate for the substrate normal to the evaporation source. This can reduce the amount of coating substantially but still this is not enough for most roll-to-roll evaporation processes. The evaporation source can change the shape of the depositing vapor flux with a changing evaporation rate. If the power is increased, the shape of the deposition flux narrows and so the tooling factor can change with changing power. It is thus important that any changes in the process are accompanied by the correct change in tooling factor where appropriate.

Another method of further reducing the deposition to the crystal is to not allow a continuous deposition onto the crystal but to use a shutter to expose only the shutter to the deposition flux for a small fraction of time periodically. Thus, the crystal might be exposed for 1/10th or 1/100th of the total deposition time and with a tooling factor of 1:10; it is possible to significantly reduce the total coating thickness and so allow the quartz crystal monitor to be used in high rate deposition processes even in roll-to-roll coating systems.

This deposition rate measurement system can work well for evaporation systems where the source is a slot source across the full width of the web and where the uniformity of the depositing coating is well defined. It would be very difficult to arrange multiple quartz crystal monitors across the width of a web to monitor multiple sources across the width of the web. This complexity of multiple measuring heads is increased if you consider that for high deposition rates the measurement head needs to be water-cooled, and where the measurement is critical to the process it is common to have more than one crystal to allow for either sharing the deposition load or acting as a spare in case of failure of the original crystal.

Although this measurement technique is feasible for roll-to-roll systems, it is not often used.

5.9 Barrier

Barrier performance is the material's ability to prevent transmission of moisture or oxygen through the combined coating and substrate. These are quoted in $cm^3/m^2/$day for oxygen and $g/m^2/$day for moisture.

Barrier performance started with improving the basic barrier of the polymer webs for the packaging industry to help extend the shelf life of foods [37,38]. These barrier films fall into two categories, opaque and transparent. The opaque barrier films are mostly metallized with aluminum. This provides the food with not only a gas and moisture barrier but also a light barrier that is essential to help preserve some foods from degradation, such as preventing fatty foods from turning rancid. The transparent barrier coatings generally require an oxide ceramic coating that is more brittle than the more simple metal coating.

Recently, the world of barrier coatings changed with work being done to develop the necessary barrier coatings for the organic light-emitting devices. These are so sensitive to contamination, by oxygen and/or moisture, that the barrier coating

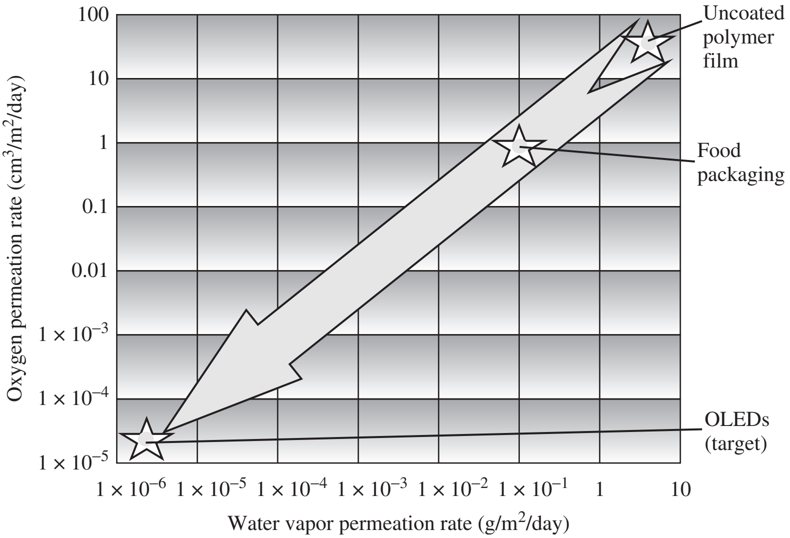


Figure 5.12 Barrier film requirements.

required has been calculated to be six orders of magnitude better than those required for food barrier packaging (Fig. 5.12).

Barriers of intermediate performance are required for many of the electronic applications because either or both oxygen and moisture can degrade the performance of the active layers such as the electroluminescent phosphors or polymers.

These display applications require at least one side to be transparent to let the light out and often it is convenient to use the same material for both sides. Glass substrates have an inherent advantage that they are a perfect barrier to oxygen and moisture. There is a driving force to convert from rigid substrates to flexible substrates, which will potentially enable faster and cheaper manufacturing. The lighter and thinner polymers are porous and hence need to have additional coatings to regain the barrier performance. The transparent ceramic oxide coatings ought to be as impervious as glass, but on an atomic scale they have many defects and hence are porous.

The worst problem is the dust or debris remaining on the surface of the polymer at the time of coating and then the debris is moved away leaving a pinhole. This type of defect will be easily seen in the metallized films simply by holding the film up to the light; the pinholes will show up as bright pinpricks of bright light. They will also be present in the transparent oxide coatings, but it will be impossible to see them easily.

To achieve the level of barrier for the display applications, it is essential to remove as much of the debris as possible and then cover the rest with a thin polymer coating to produce the cleanest, flattest, most perfect surface possible. The coating deposited on this will still not be a perfect barrier as there will be coating defects such as grain boundaries and even minute coating holes where the coating has not reached full continuity in such a thin film. To overcome these defects, the oxide coating is applied with another layer of polymer coating followed by another oxide layer. A polymer coating plus an oxide coating, as a pair, are referred to as a “dyad.” To achieve the six orders of magnitude better barrier than the food packaging, it is necessary to use several dyads on each side of the device to make the improvement.

A transparent oxide coating onto a polyester web will improve the barrier performance by two to three orders of magnitude. The systems for measuring the barrier performance were developed to easily measure these coatings. One of the current problems is that there is no system being sold that will measure these “super” barriers against a traceable standard. Most research groups, some of which sell some product, have built their own systems to test the barrier performance. None of these systems can be tested against any standard, and this has resulted in the declaration of performance figures that are impossible to verify.

Some of the problem in measuring the barrier performance was that as the barrier improved, the time taken to reach equilibrium, beyond which point the true barrier performance would become apparent, became longer. Until this was understood, the barrier performance after a fixed time was often quoted. This figure would then get much worse if the test were to be continued. Thus, extrapolating results to help predict display lifetimes could be wildly inaccurate.

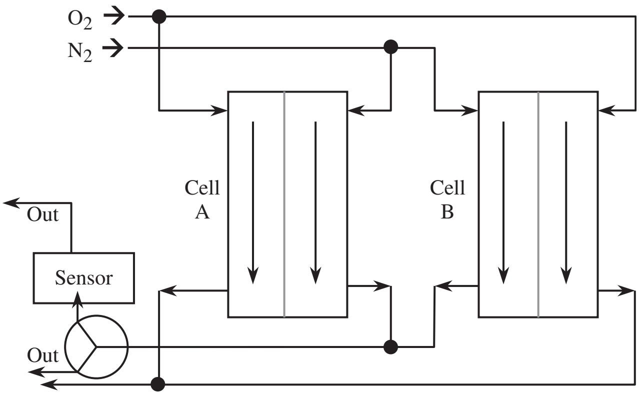


Figure 5.13 A schematic of the "Oxtran" [40] barrier measurement system.

Figure 5.13 shows a schematic of an oxygen barrier measurement system. The two cells have the test material clamped separating each cell into two chambers.

In one chamber oxygen is passed through and in the other chamber nitrogen. Nitrogen, containing some helium to flush out any residual oxygen in the carrier gas, passes through the chamber and goes to the sensor. The sensor works on the reverse fuel cell principle and allows the oxygen content to be converted into an electrical signal.

A similar version of this test, with different sensors, is available for measuring water vapor transmission.

This type of test has traditionally been conducted against a standard. However, this standard will only measure down to 5×10^{-4} g/m^2/day, which is two decades short of the required performance of the ultra barrier films. This is based on the premise that it is usual to have a test method that measures at least one decade better than the expected value of the item being tested. Thus, it will be some time before we can expect to have confidence in the measurement of these ultra barrier coatings.

Newer systems have tried to optimize existing systems by improving the joints and seals to minimize the leaks and so improve the minimum quantity of transmitted gas or vapor that can be reproducibly detected. Others have started from scratch and devised new systems entirely. Figure 5.14 shows a schematic of the calcium corrosion test. Here the calcium is coated on the glass and sealed using a sample of the barrier film separated from the glass using a gasket. A light is directed through the calcium, which is opaque, to a detector. As the calcium corrodes, it becomes transparent and so the changes, if any, are measured by the detector. This test is only applicable to moisture barrier performance. This test does appear to be very operator sensitive, requiring a high degree of expertise to obtain any degree of reproducibility. Thus, this is regarded very much as a research tool rather than a more widely applicable industry test.

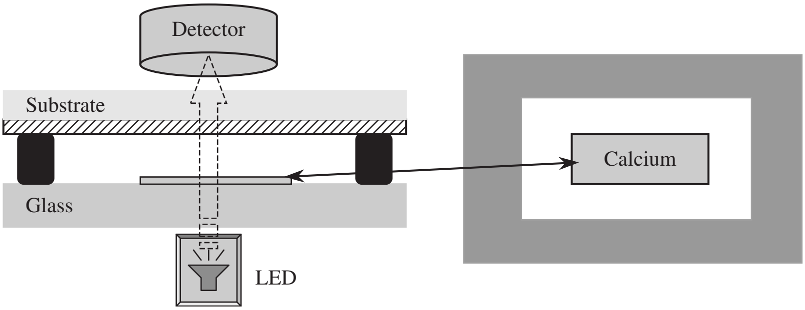


Figure 5.14 A schematic of the calcium corrosion test [39].

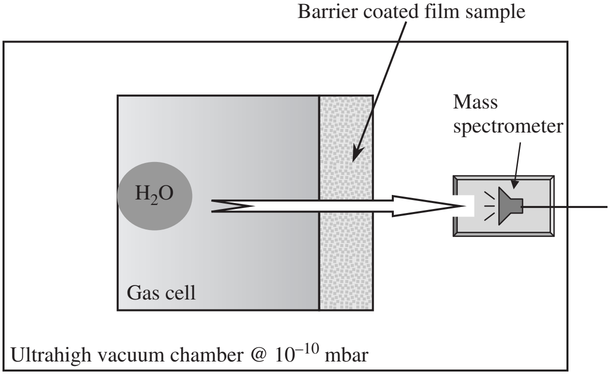


Figure 5.15 A schematic of one of the newer systems designed to measure the ultrabarrier coatings.

Figure 5.15 shows a cell within an ultrahigh vacuum system [41]. The sealed cell has a drop of water as the moisture source and anything leaking through the barrier coating is detected using a mass spectrometer. With a suitable source this can be used for other gases. This has the potential for delivering a reproducible answer and is capable of measuring down to the levels required by the display industry.

This is very much a subject that is changing rapidly and by the time this book is published no doubt there will be improvements in the measurement techniques and reliability.

5.10 Pinholes

Pinholes are almost a fact of life of vacuum-deposited coatings. Dust and debris accumulates on the polymer surface throughout the manufacturing and conversion processes. Any of this contamination present on the surface as the film passes through the deposition zone will be coated and will mask the substrate underneath. If the contamination is moved sometime after the deposition zone the area of uncoated substrate will be exposed; this is referred to as a pinhole [42]. It is these pinholes that are primarily responsible for the barrier coatings not achieving the barrier performance that they are expected to achieve. Theoretically, a thin metal, glass, or glass-like coating should be around six, or more, orders of magnitude better barrier than the polymer substrate, but the reality is that it is often only one to two orders of magnitude better due to pinholes and then, to a lesser extent, other structural defects.

In thin metal coatings measuring pinholes is relatively easy. The crudest method is to hold a sheet of metallized film up to the light and all the pinpricks of bright light correspond to pinholes. This can be improved upon by using a light box where a light is placed with diffuser screens so that the illumination is even over the whole top surface where a translucent plate is situated. The metallized film is placed on the plate and then an image is taken of a precise area of the metallized film. The image is then processed either by an operator counting the pinholes over a specific area or by using image analysis software where the number and size range of the pinholes can be tabulated. This enables any improvement to be evaluated with improvements showing fewer and smaller pinholes.

If you are in doubt about the cause of pinholes, a simple way to see the effect of touching the metallized surface is as follows. Take a metallized film that has not had the front surface touched and count the number of pinholes for a given area. Then using a soft camel-hair brush, as used by photographers to clean lenses, brush over the surface and see just how many more pinholes appear. An example of this type of quick test is shown in Fig. 5.16.

Transparent coatings such as barrier or conducting oxides also suffer from pinholes but it is impossible to see them in the same way. As both the film and the coating are transparent, there is no contrast between the coated and uncoated areas; therefore, finding and counting pinholes can only be done if the contrast can be

Figure 5.16 A photograph of pinholes in a 30 mm × 30 mm sample of metallized film simply held up in front of a table lamp. This is a severely damaged surface. A photograph of pinholes for a better quality film is shown in Chapter 8 (Fig. 8.13).

enhanced [43,44]. This is no longer a quick and easy test as the film has to be placed into a vacuum system and oxygen has to be etched. This etching process attacks the polymer in the uncoated regions much faster than the inorganic coating and so undermines the coating. This produces a void beneath the pinhole. Then, if a stain is painted across the coated surface it will accumulate in the voids and if the surface is then wiped clean of the stain the only place the stain will remain is in the voids. Thus, some contrast is obtained of the pinholes. The size of the pinholes will have been changed by the etching process. The original pinhole size can be estimated once the etching rate has been determined. Using the slope of changing diameter against time, the original diameter can be found once the final diameter has been determined.

5.11 Artificial Intelligence and Neural Network Control Systems

The use of artificial intelligence [45–48] and neural networks has started and will grow. It is a challenge to know when to move on from traditional well-developed control systems on a long established process and when to adopt a new control philosophy, which will need some time to be developed to match the existing system performance and more still to better it.

Figure 5.17 shows block diagrams of the system developed to control resistance-heated evaporation sources for the deposition of aluminum. The schematic that follows shows the whole system (Fig. 5.18). Additional sensors needed to be developed

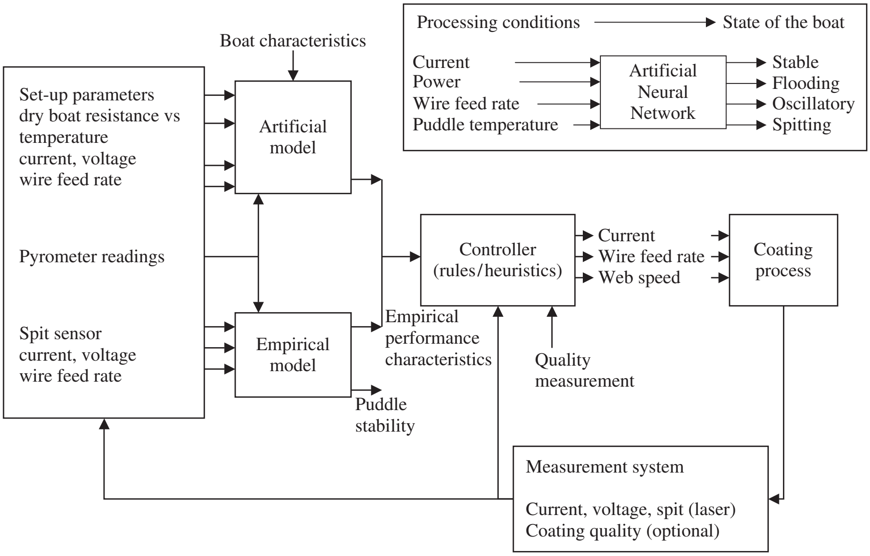


Figure 5.17 A line diagram of the neural network [49].

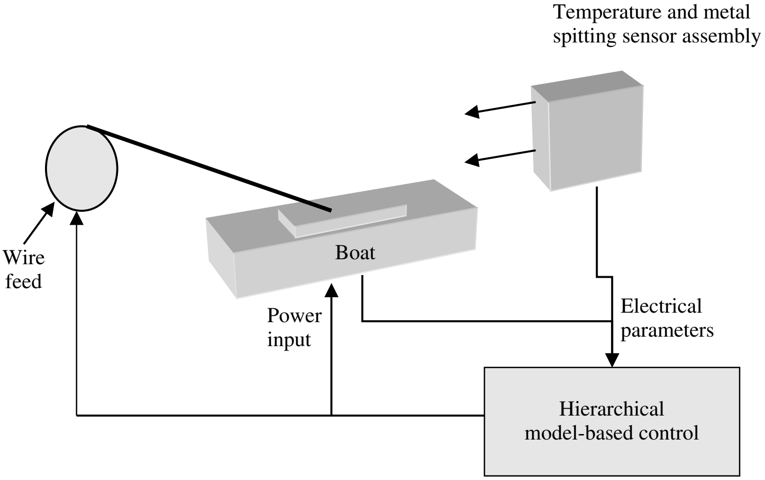


Figure 5.18 A schematic of a resistance-heated evaporation source and control.

to look at the boat temperature and to look for the source spitting. Spitting is where tiny lumps of material are thrown off the boat. Once the molten pool has been established, this spitting is associated with a change in the size of the molten pool. The aluminum wire is covered with a protective layer of the native aluminum oxide. This oxide forms a film over the surface of the molten pool and is known as slag. As more wire is fed into the pool, the quantity of slag increases and it tends to accumulate at the edge of the pool. As the slag is not molten but remains solid, it does not leave the surface as a vapor but as a particle that may or may not be incandescent. The spitting is an indication of too much slag being ejected and the boat possibly running too dry of aluminum. As aluminum is fed into the boat, the temperature of the boat will change as will the resistance.

The target was to produce a stable system where the evaporation rate was not oscillating between too fast or too slow and also that there was no spitting from the source with the deposition rate as fast as possible.

Traditionally, the boats were heated and the wire feed started and a skilled operator judged when the temperature was “about right” and the deposition started. Once deposition started, when the first of the coated web reached the coating sensors, a feedback signal could be produced to provide some more precise control of the power and wire feed. This needed to be done for every boat across the whole web, which could be as many as 25 boats. This system was aimed at removing the initial operator input and improving on the feedback control.

In setting up the neural network some algorithms had to be developed from the information gleaned over the years of running traditional systems.

This system is designed such that it is capable of having boats replaced with no changes required to the operation of the system. This is because the monitors will be looking at the surface temperature of the molten pool of aluminum and it does

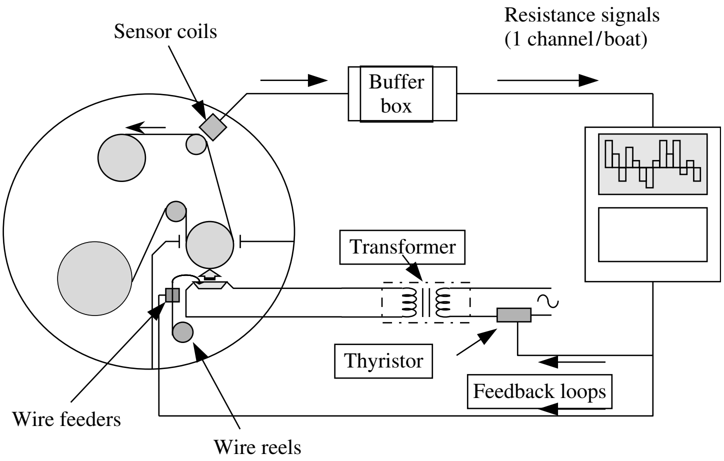


Figure 5.19 A schematic of the feedback system used in a metallizing system [50].

not matter about the age of the boat. The voltage and current used to provide the temperature will vary considerably between a new and an old boat, but as the deposition rate is related to temperature and area of the pool these will provide the primary control.

The feedback from the coating sensors can be included such that if a boat fails in service the adjacent boats will compensate automatically. This can be sensed faster and hence reacted to and optimized faster than in a more conventional system. This type of neural network control system is expected to replace the more traditional control system as shown in Fig. 5.19, although the industry is generally slow to adopt new technology, and as machines are often in service for more than 20 years with only minimal upgrades it will be a long time before it becomes the standard.

5.12 Chemometrics

It is common when troubleshooting to isolate the problem area and to look at that area in great depth. This is particularly true for complex processes. However, this can mean that interactions that are distanced from each other within the whole process are missed. In chemometrics, the data used can include information on parts of the process that might normally not be included. For example, if there is more than one supplier of raw materials, this information can be incorporated into the data, as too could be data from an earlier process such as an atmospheric wet coating or even the film-manufacturing process, if available. Thus, this technique can be regarded as truly holistic in nature.

The use of chemometrics or multivariate analysis enables the whole process to be analyzed at once [51,52]. Using tools such as hierarchical cluster analysis and principal component analysis enables interactions to be identified and, if necessary, tested. This technique is particularly powerful as it can be used on production processes, it is not exclusive to research, and it is not intrusive and hence not disruptive to production. Other methods of looking for interactions, for example design of experiments (DoE) type matrix experiments such as Taguchi, Fraction Factorial, Plackett–Burman, or Analysis of Variance (ANOVA), rely on forcing variables to high and low values to help produce information that, if used on a production line, would be disruptive to production. Chemometrics simply relies on the natural variations that occur within the process and all the settings can remain at whatever settings the operator deems to be optimum.

Finding out what ails a process can be difficult if the problems do not show any direct link to immediately observable and related circumstances. The usual assumption is that trouble is caused by something proximate [53]. Often it is hoped that statistical analysis will reveal the answers from current plant data.

There are problems with relying on statistical methods if you are not an expert.

There look to be two key issues:

(a) Analyzing data and not finding a cause/effect relationship when one exists.
(b) Analyzing data and finding a spurious cause/effect relationship and not knowing that it is spurious.

Typically, in statistical methods such as DoE, each data set needs to be processed several times, modifying the process each time to refine the output. With chemometrics it is good policy to log data from as many process parameters as can be thought of, even the ones that everybody is convinced are irrelevant. The reason for this is to make sure any interactions, no matter how remote and unlikely, are not missed. Once sufficient data has been collected and processed, decisions can be made as to which parameters are truly irrelevant and where data collection can be stopped. It is better to initially take extra measurements and be able to prove they are unnecessary than it is to not take the measurements and possibly miss something that affects the end product. There are also likely to be other parameters where it is indicated that there is insufficient control or measurement, and they need to have some process upgrade. Once this upgrade is done, the whole process starts again to further refine the process and the model. Once this point has been reached, the software can then be used to develop the process control algorithms so that it removes the requirement for any intervention by the operator. Intervention by operators on complex processes can often mean that there are options for choice of settings and different operators may make different choices and the resulting end product will reflect the different choices by different operators. Using automated feedback loops removes this variation and helps the product become more reproducible.

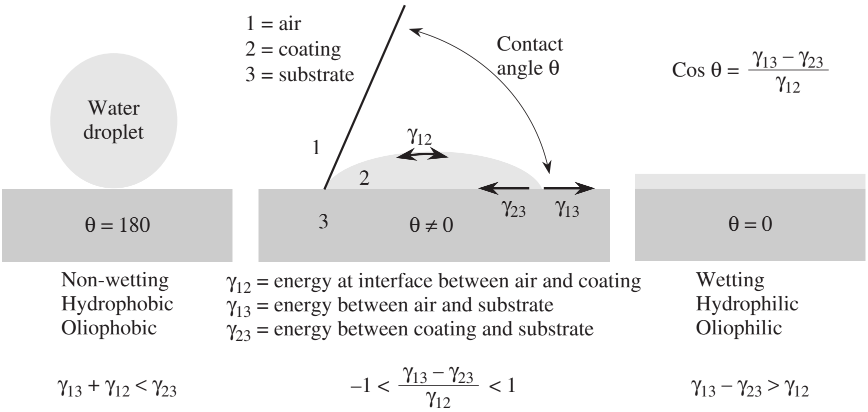
Often the substrate manufacturing takes place in a different location and on a different day to subsequent processing and the substrate may be wound or rewound at a different temperature and humidity each time. As the change in humidity and temperature can vary significantly over the different seasons in each year so too may the roll properties. Data on temperature and humidity are usually available and they can be added to the data set for each roll of film. If these variables are shown to affect the deposition process, action can be taken to better prepare the material supply such as by better control of the storage or room conditions. An example where this remote collection of data proved useful was where links were found to the season with high airborne pollen levels and an increase in the number of pinholes in metallized film.

This whole process of chemometrics is time-consuming and intellectually taxing, but the end result can be a full understanding of the whole of the manufacturing process. This then enables automatic feedback algorithms to be developed to improve the speed and sensitivity of the control. This should lead to reduced operator intervention, making improvements in product reproducibility. The tools are out there for us to be able to fully understand any manufacturing process from raw materials through end product no matter how complex it is.

Often the process is approached from simple datalogging and trend analysis [54]. This is much more limited but at least can show machine and process trends. If this is plotted for as many variables as possible, it then becomes a smaller step to move to chemometrics to look for relationships between variables.

5.13 Surface Energy Measurements

There are two main techniques for measuring the surface energy of a web surface (Fig. 5.20). The first uses a series of pens where each of the pens is filled with a specific liquid. Each liquid has a different but known surface energy. When the pens are wiped on a web surface, those that have a surface energy lower than the web will wet out the web surface and those with a surface energy higher than the web will ball up and not wet the surface.



Ideally γ_{13} wants to be as high as possible with γ_{23} as low as possible.
The system will want to form with the minimum total energy.

Figure 5.20 A schematic of the basics of surface wetting.

Table 5.2 The surface energy of some polymer surfaces and the surface tension values of some commonly used test liquids

Solids/ Polymers	Untreated surface free energy (dyne/ cm [N/mm])	Treated surface free energy (dyne/ cm [N/mm])	Liquids	Surface tension (dyne/ cm [N/mm])
Nylon	38−46	–	Water	72
Polyester	41−44	48−52	Glycerol	63
Cellulosics	42	–	Glycol	47
PVC, acrylic	39	–	Benzene, toluene, xylenes	29
PMMA	30−36	–	Cyclohexane	25
Polystyrene	38	–	Methyl, ethyl, isopropyl alcohols	–
Polystyrene (low ionomer)	33	–	*n*-Hexane	18
L/HDPE	30−31	38−40		
Polypropylene	29−31	39−41		
PTFE	19−20	–		

PVC, polyvinyl chloride; PMMA, Polymethylmethacrylate; L/HDPE, low/high-density polyethylene; PTFE, polytetrafluoroethylene.

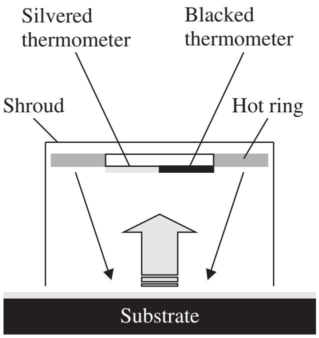
By checking the surface energy of the pen where there is a change from wetting to nonwetting behavior, it is possible to fix the surface energy of the web surface [55].

The second technique is slightly more time-consuming and requires some equipment, but is still fairly easy [56]. Using a syringe enables a drop of liquid, usually water, to be dropped from near the surface onto the web [57]. The water will either spread out and wet the surface or ball up depending on the surface energy of the web surface [58−60]. From one side of the web a light is directed through the edge of the web and the side of the water drop and the image is projected onto a protractor.

The angle that the water makes to the web can then be measured and used to calculate the surface energy of the web surface. The more the water spreads out, the higher the web surface energy; hence, the water spreads out to try to minimize the combined water, air, and web surface energies (Table 5.2). Where the surface energy of the web surface is low, the water will ball up; the more it approaches a sphere, the lower the web surface energy.

5.14 Emissivity

On occasions the coating emissivity can be used as a property that can be measured by a noncontact technique (Fig. 5.21). Although most often used as an off-line measurement, it has occasionally been used in vacuum and online.



The hot ring radiates IR heat down to the cold coated sample.

The silvered and blackened thermometers absorb and radiate different amounts of energy.

This allows the emissivity to be calculated from the differential temperature.

The accuracy of the measurement is down to about 0.01 where a typical low emissivity coating would measure ~0.1.

Figure 5.21 A schematic for the measurement of emissivity.

The measurement process is simple. A heated element radiates heat down onto the coated film and the coating reflects the heat toward a suitably placed detector. The amount of heat reflected is dependent upon the coated material and the structure of the coating. The arrangement of the heater and detector is commonly concentric where the heater is an annulus around a central detector. The detector comprises two thermometers, one blackened to maximize the heat absorption and one silvered to minimize the heat absorbed. This differential between the radiation and absorption of energy gives rise to two different temperatures being measured. This temperature differential along with the known energy from the heater element allows the coating emissivity to be calculated.

As the coated web moves under the detector, there will always be the same fresh material that has not had time to reach thermal equilibrium; therefore, there is the potential for some error in the measurement. As the technique heats an area, it measures the average value for the whole area. The proportion of material that is not at equilibrium is dependent upon the process speed. The highest error will be for high-speed processes. Thus, this measurement technique is more suited to the sputtering of transparent conducting coatings where the speeds are relatively slow rather than the higher speeds available for the evaporated coatings.

5.15 Lambda Probe/Sensor/Gauge

As many reactive coatings can be controlled quite successfully by monitoring the partial pressure of oxygen, it is useful to have a specific measure of the oxygen partial pressure in the vacuum system. The lambda sensor is based on an electrochemical ceramic sensor using solid electrolyte [61], where the oxygen content of the vacuum can be compared to atmospheric oxygen content. The absorption of oxygen onto the ceramic sensor surface gives a change in potential, and the vacuum sensor is compared to a reference sensor in air. The difference between the two gives a measure of the partial pressure of the oxygen in the vacuum. This measure of oxygen can then be used to control the oxygen gas flow to the reactive deposition process [62].

5.16 X-ray Fluorescence Sensor

This technique uses an X-ray source that is angled at the coated substrate and the solid state energy dispersion sensor is arranged at the complementary angle to collect the X-ray fluorescence (XRF). The X-rays cause electrons to be ejected followed by a movement of electrons into the electron vacancies, resulting in an electron relaxation that is accompanied by an emission of X-rays known as X-ray fluorescence. Because X-rays are material dependent, the composition of compounds can be determined. This makes this a measurement suitable for use in measuring coatings used for photovoltaics such as copper indium gallium diselenide (CIGS) [63,64]. As the deposition of these materials is often carried out at high temperature, the XRF measurement system needs to be protected and positioned somewhere where the temperature is lower, preferably below 200°C. The system can also be sensitive to contamination by selenium, which is one of the most difficult materials to control in the system with the vapor often migrating throughout the system.

5.17 Atomic Absorption Spectroscopy

In atomic absorption spectroscopy, the light from a hollow cathode lamp or laser is partially absorbed by the gas-phase atoms and the remaining light is passed through a monochromator and into a detector. Using the Beer–Lambert law, the energy absorbed by the vapor can be calculated and is proportional to the vapor flux. This technique can be used to measure the evaporation rate of various sources. Where lasers are used, a separate measurement system is required for each evaporation source. A xenon lamp and monochromator, if suitably arranged, can be directed through the vapor cloud from multiple sources and the separate elements can be monitored. The use of a single unit can reduce the monitoring costs where multiple evaporation sources are used in close proximity. This technique is used for CIGS deposition as part of the deposition control for each of the evaporation sources [65].

References

[1] Gale MT, et al. A simple optical thin film deposition monitor using LEDs and fibre optics. J Vac Sci Tech 1982;20(1):16–20.

[2] Lotz HG, et al. Production of color shift layers with electron beam technology for identification and decorative applications. In: Proc. 50th annual technical conference of the Society of Vacuum Coaters; 2007. p. 742–745.

[3] Maissel LI. Electrical properties of metallic thin films. In: Maissel LI, Glang R, editors. Handbook of thin film technology. McGraw- Hill; Reissue 1983. Chapt. 13, ISBN 0 07 039742 2.

[4] Valdes LB. Resistivity measurements on germanium for transistors. Proc IRE 1954;42:420–7.

[5] American Society for Testing and Materials. ASTM F76 standard method for measuring Hall mobility and Hall coefficient in extrinsic semiconductor single crystals.

[6] Frank V. On geometrical arrangements in Hall effect measurements. Appl Sci Res 1953;B3:129–40.

[7] Buehler MG. A Hall four-point probe on thin plates. Solid State Electron 1967;10:801–12.

[8] Green MA, Gunn MW. Four-point probe Hall effect and resistivity measurements upon semiconductors. Solid State Electron 1972;15:577–85.

[9] Lange J. Method for Hall mobility and resistivity measurements on thin layers. J Appl Phys 1964;35:2659–64.

[10] van der Pauw LJ. A method of measuring specific resistivity and Hall effect of discs of arbitrary shape. Philips Res Repts 1958;13:1–9.

[11] van der Pauw LJ. A method of measuring specific resistivity and Hall coefficient of lamellae of arbitrary shape. Philips Tech Rev 1959;20:220–4.

[12] European patent EU 0166477. Method and system for producing a reactively sputtered conducting transparent metal oxide film onto a continuous web; 1986.

[13] Zelisse JK. Accurate modelling of eddy current sensors for square resistance and thickness measurements. In: Proc. 5th international conference on vacuum web coating; 1991, p. 135–43.

[14] Duesbury P. A heuristic approach to temperature compensation in non-contact resistance meters for vacuum roll coaters. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993, p. 232–5.

[15] Brandenberg J, et al. Experiences of operating a closed-loop feedback system on a vacuum web coater. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992, p. 94–9.

[16] Scarr JM, Zelisse JK. A new topology for thickness monitoring eddy current sensors. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993, p. 228–31.

[17] Peters DW. Method for monitoring the surface resistivity of metallized film. US patent 3 935 458. 1976.

[18] McAlister S, Hurd C. A century of bent electrons. New Sci. 1979;4(1181):536–7.

[19] Mao FM, et al. Residual gas analysers and their use in high vacuum systems. Vacuum 1987;37(3/4):335–8.

[20] Patel H. Progress in monitoring and control of reactively sputtered ITO using optical emission and mass spectroscopy. In: Proc. 40th annual technical conference of the Society of Vacuum Coaters; 1997, p. 20–23.

[21] Angus B. A scanning spectrophotometer: design and applications. Opt Spectra 1980;49–51.

[22] Schiller S, et al. Fully automated control of reactive sputtering processes in web coaters by integrated PEM stabilisation. In: Proc. 1st international conference on vacuum web coating; 1987, p. 54–61.

[23] Greene JE. Optical spectroscopy for diagnostics and process control during glow discharge etching and sputter deposition. J Vac Sci Tech 1978;15(5):1718–29.

[24] Strumpfel J, et al. Production of optical multilayers on webs for Ar application by means of reactive dual magnetron sputtering. In: Proc. 11th international conference on vacuum web coating; 1997, p. 279−89.

[25] Fraval RH, Angus R. A novel optical spectrum analyser for plasma process monitoring. In: Proc. IPAT workshop "Semiconductor technology—thin film production and properties." CEP Consultants Ltd.; June 1986.

[26] Cilia M, et al. Optical emission spectroscopy study of the radio-frequency magnetron discharge used for the fabrication of X-ray multilayer mirror. Thin Solid Films 1998;312(1/2):320−6.

[27] Schiller S, et al. On the investigation of d.c. plasmatron discharges by optical emission spectrometry. Thin Solid Films 1982;96(3):235−40.

[28] Enjouji K, et al. The analysis and automatic control of a reactive d.c. magnetron sputtering process. Thin Solid Films 1983;108:1−7.

[29] Rossnagel SM, Saenger KL. Optical emission in magnetrons: nonlinear aspects. J Vac Sci Technol A 1989;7(3):968−71.

[30] Fukugami N, et al. Density measurement of thin glass layers for gas barrier films. J Vac Sci Technol A 1999;17(4):1840−2.

[31] Whitehouse DJ. Some ultimate limits on the measurement of surfaces using stylus techniques. Meas. Control 1975;8:147−51.

[32] Piegari A, Masetti E. Thin film thickness measurement: a comparison of various techniques. Thin Solid Films 1985;24:249−57.

[33] Strumpfel J, et al. In-situ optical measurements of transmittance and reflectance by ellipsometry on glass, strips and webs in large area coating plants. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999, p. 280−285.

[34] Aufderheide BE, et al. Methodology of multi-wavelength real-time ellipsometry control of ITO deposition on thin transparent polymer films. In: Proc. 10th international conference on vacuum web coating; 1996, p. 106−113.

[35] Amassian A, et al. In-situ ellipsometry and Monte-Carlo simulation studies of the role of ion bombardment in the growth of optical films. In: Proc. 49th annual technical conference of the Society of Vacuum Coaters; 2006, p. 280−87.

[36] McClure DJ, Copeland N. Evaporated aluminium on polyester: optical electrical and barrier properties as a function of thickness and time (part II). In: Proc. AIMCAL annual technical conference and 24th international conference on vacuum web coating; 2010.

[37] Brody AL. Glass-coated flexible films for packaging: an overview. Packag Technol Eng 1994;February:44−7.

[38] Chatham H. Oxygen diffusion barrier properties of transparent oxide coatings on polymeric substrates. Surf and Coat Technol 1996;78:1−9.

[39] Nisato G, et al. Evaluating high performance diffusion barriers: the calcium test. In: Proc. SID conference; November 2001.

[40] Oxtran Operating Manual. Modern Controls (Mocon) Inc. Minneapolis, MN 55428.

[41] American Society for Testing and Materials. ASTM D3985-95 standard test method for oxygen gas transmission rate through plastic film and sheeting using a Coulometric sensor. American Society for Testing and Material; 1995.

[42] Jamieson EHH, Windle AH. Structure and oxygen-barrier properties of metallized polymer films. J Mater Sci 1983;18:64−80.

[43] da Silva Sobrinho AS, et al. Detection and characterization of defects in transparent barrier coatings. In: Proc. 42nd annual technical conference of the Society of Vacuum Coatings; 1999, p. 316−9.

[44] Silva Sobrinho AS, et al. Defect-permeation correlation for ultrathin transparent barrier coatings on polymers. J Vac Sci Technol A 2000;18:149−57.

[45] Boswarva IM. The use of artificial intelligence techniques to provide real time process control and troubleshooting advice in vacuum roll coater operations. In: Proc. 7th international conference on vacuum web coating; 1993, pp. 80−84.

[46] Smith TH, Boning DS. Artificial neural network exponentially weighted moving average controller for semiconductor processes. J Vac Sci Technol A 1997;15(3):1377−84.

[47] Hopgood AA, et al. Fuzzy logic in a blackboard system for controlling plasma deposition processes. Artif Intell Eng 1998;12:253−60.

[48] Braithwaite NSJ, et al. On the control of low pressure plasmas for processing. In: Proc. 11th international conference on vacuum web coating; 1977, pp. 49−53.

[49] Parthasarathy S, et al. Modelling and identification of process parameters for thermal evaporation. In: Proc. 40th annual technical conference of the Society of Vacuum Coaters; 1997, pp. 344−9.

[50] Casey F. A non-contact resistance monitor and closed loop feedback system. In: Proc. 4th international conference on vacuum web coating; 1990, pp. 48−58.

[51] Hair F, et al. Multivariate data analysis. 4th ed. Prentice Hall; 1995.

[52] Morrison F. Multivariate statistical methods. 3rd ed. McGraw-Hill; 1990.

[53] McCann MJ, Bishop CA. Chemometrics—a holistic approach to troubleshooting. In: Proc. 40th annual technical conference of the Society of Vacuum Coaters; 1997, pp. 487−93.

[54] Dickson B, et al. Vacuum based process tool diagnostics. Vacuum and Thin Films, August 1999; pp. 30−33.

[55] American Society for Testing and Materials. ASTM 2578-99a standard test method for wetting tension of polyethylene and polypropylene films. (or ASTM 2578-84 (1984) same title). American Society for Testing and Materials; 1999.

[56] Hansen CM. Characterization of surfaces by spreading liquids. J Paint Technol 1970;42 (550):660−4.

[57] American Society for Testing and Materials. ASTM D5946-96 standard test method for corona-treated polymer films using water contact angle measurements. American Society for Testing and Materials; June 1996.

[58] Good RJ. Contact angle, wetting, and adhesion: a critical review. In: Mittal KL, editor. Contact angle, wetability and adhesion. VSP Utrecht; 1993. p. 3−36.

[59] Padday JF. Spreading, wetting and contact angles. In: Mittal KL, editor. Contact angle, wetability and adhesion. VSP Utrecht; 1993.

[60] Wetterman B. Contact angles measure component cleanliness. Precision Clean. 1997; Oct:21−4.

[61] Moos R, et al. Solid state gas sensor research in Germany—a status report. Sensors 2009;9:4323−65.

[62] Szczyrbowski J, et al. Apparatus for applying thin layers to a substrate. US patent 6 743 341. January 6, 2004.

[63] Britt J. Photovoltaic manufacturing cost and throughput improvements for thin film CIGS-based modules. Final technical report July 1998−September 2001. NREL/SR-520-32072. National Renewable Energy Laboratory, Golden, CO 80401-3393; April 2002, pp. 37−40.

[64] Eisgruber IL, et al. In situ X-ray fluorescence used for real-time control of $CuIn_xGa_{1-x}Se_2$ thin film composition. Thin Solid Films 2002;408(1−2):64−72.

[65] Fan B, Nagai T. In situ optical monitor system for CIGS solar cell applications. Chinese Opt Lett 2010;8(Suppl):186−8.

6 Leaks, Water Vapor, and Leak Testing

There are two types of leaks: real and imaginary.

6.1 Real Leaks

Take a vacuum system that has been pumped down and sealed off. If there is a real leak, the system pressure will rise and continue rising until it reaches the atmospheric pressure. Most systems will have some leaks, albeit small ones that can be tolerated because they are small enough not to deleteriously affect the process.

6.2 Imaginary Leaks

These leaks are characterized using the same method as before. The system is pumped down and then sealed off. Initially, the pressure will still rise, as before, but then the rate of rise will slow and the pressure will be seen to level off [1,2]. What is happening is that somewhere in the system there is a pocket of air with a poor conductance into the main chamber. When the chamber is evacuated, the air pocket will be pumped down very slowly, and there will be a pressure differential between the pocket and the main chamber. When the chamber is sealed off from the pumps, the pressure between the two volumes will gradually equilibrate. Generally, this is seen as a rise in pressure of the system and, if it could be measured, could also be seen as a corresponding drop in pressure in the trapped pocket of air (Fig. 6.1).

Figure 6.2 shows a screw thread that, if it did not have a pressure relief hole, would be a possible source of a virtual leak. The pressure relief hole can be through the block as shown in the figure or could be a hole down the center of the screw.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00006-4

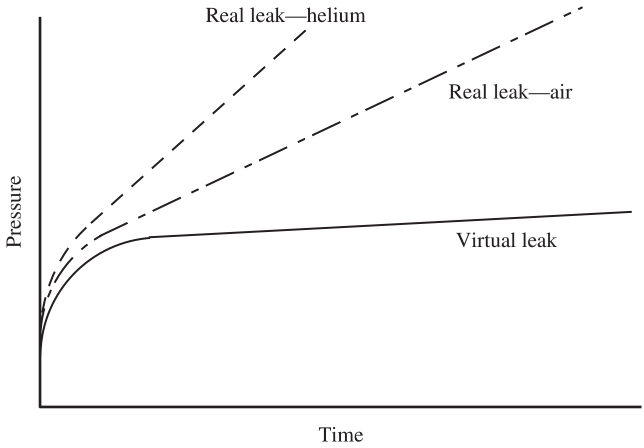


Figure 6.1 A chart showing the difference between a real and a virtual leak. Also showing the difference in sensitivity between air and helium.

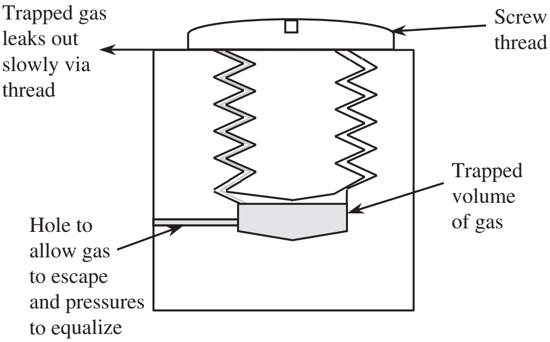


Figure 6.2 A schematic showing how something as simple as a locating screw could become a serious vacuum problem because of a trapped volume of air becoming a virtual leak.

6.3 Outgassing and Water Vapor

Air comprises 78% nitrogen and 21% oxygen, and all the other gases contribute to the final 1% (Table 6.1). There is an additional variable component that is more significant to vacuum processes and that is water vapor [2]. Once the pressure in the vacuum system reaches 10^{-3} mbar, the composition will be different, with up to 98% of the chamber content being water vapor. This is because the water vapor is absorbed onto the surfaces and is much harder and slower to remove from the system than the air.

$$\text{e.g., Nitrogen} = 78\% = 0.78 \times 760 = 593 \text{ torr}$$

Water is a highly polar molecule, which means that the positive charge on the hydrogen atoms will be attracted to any surface electrons, forming a bond with

Table 6.1 The Composition of Air

Composition of Air
Relative Volume and Corresponding Partial Pressure

Gas	**% volume**	**Partial Pressure**	
		Pascal (Pa)	**Torr**
Nitrogen	78	79,000	593
Oxygen	21	21,000	159
Argon	0.93	940	7.1
Carbon dioxide	0.03	33	0.25
Neon	0.0018	1.8	0.014
Helium	0.0005	0.53	0.004
Krypton	0.0001	0.11	0.00087
Hydrogen	0.00005	0.053	0.0004
Xenon	0.0000087	0.0088	0.000066
Water	Variable	Variable	Typically 5−50

With standard conditions (0°C and 760 torr), each gas will exert a pressure relative to its percentage of the total volume.

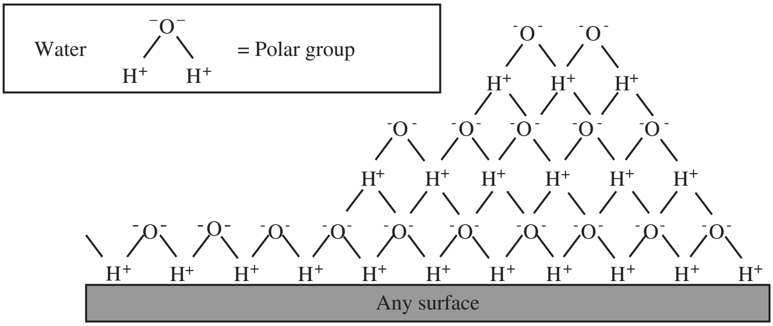


Figure 6.3 Water on surfaces.

the surface [3] (Fig. 6.3). The formation of this hydrogen bond means that the negatively charged oxygen atom is then sticking out and becomes the new surface that, as it is negatively charged, attracts more water molecules to bond to it. This can repeat several times and so several monolayers of water vapor can be attached to the exposed surfaces. The bond strength is weak enough that it is possible to remove the water from the surface simply by evacuating the system. The bond is also just strong enough that as a consequence the process to remove the water from the surface is slow. This process can take days and so where systems have to get to very low pressures, it is common to add energy, such as heat, to the whole system to speed up this process. Most vacuum coaters do not go to these levels of effort or detail although one glass coater did heat the system during any short downtime to limit the amount of water absorbed onto the vessel walls.

Pumping to a very low pressure does not necessarily speed up the outgassing of the absorbed water vapor. Most systems are too big and complex to be easily heated and baked, and there is usually insufficient time available without making the process uneconomic. Several other things can be done to add energy to speed up the process of water vapor removal. One method is to bleed gas in during the roughing pump stage of the pumpdown sequence. This gas introduction has the effect of the gas bouncing off the surfaces that assists in ejecting the water vapor molecules from the surfaces. Normally, the pumpdown will take the pressure down and so there will be fewer gas molecules hitting the surfaces to help eject the water vapor and so adding a dry gas, possibly with a heavier molecular weight, such as argon, will increase the bombardment. It will slow or stop the pumpdown at a high pressure, but once the gas supply is switched off, the resumed pumpdown will be quicker, as the contribution from the surface water vapor will have been reduced. This method of removing the water vapor also means that the system does not have to sit at a low base pressure where it could suffer from oil backstreaming. A second option is to use ultraviolet lamps that can also impart energy into the water vapor and thus speed up the desorption process [4].

In laboratories, it is common to use liquid nitrogen cold traps, Meisner traps, and cryocoils, whereas in industrial applications, a closed system is preferred where the consumable costs are lower. The most widely used cryocoil systems used in large metallizers are often referred to as Polycolds [5]. Polycold for many years was the only manufacturer of these systems, but more recently others have produced competing products. These are effectively large refrigerators that use a special gas mixture capable of taking the temperature down to −170°C. This gives a huge pumping speed for water vapor. It is not unknown for the cryocoils to have a pumping speed an order of magnitude faster than the main system pumps (Box 6.1), but, of course, this pumping speed is only for water vapor.

A key part of the design of cryocoil systems is the ability of the system to pump hot gas around the cryocoils. This happens so that at the end of the deposition process, just as the system pressure is brought back to atmospheric pressure, the coils are heated up and melt the ice in order that the water collected on the coils once melted can be drained off. This also prevents the cryocoil from acting as a water pump and condensing water vapor out from the ambient atmosphere. Were the coils to remain at a low temperature, they would be below the dew point and hence would condense out the water from the atmosphere, which would be particularly bad in countries where there are seasons with high humidity.

The other large surface area that contains moisture is that of the incoming roll of material. There are two possible components of this source of water vapor. One is the water vapor content of the air trapped between the layers of the film or the foil and the other is any water vapor that is part of the content of web material. The water content within the bulk of the web is material dependent. Foils will contain very little moisture, whereas some polymers can contain a few percent moisture and paper can contain as much as 20% moisture.

Box 6.1 Highlighting the effect of residual water on the pumping time for a vacuum system and the benefits of using a strategically placed cryopanel

1 drop of water = 1 g = 1 mL
1 drop of water @ 1 torr vapor would fill 1000 L
1 drop of water @ 1 mT vapor would fill 1,000,000 L
1 drop of water @ 0.1 mT vapor would fill 10,000,000 L

@ 0.1 mT & 1 drop of water, i.e., 10,000,000 L
For a diffusion pump speed of 10,000 L/s

$$\text{Pumping time} = \frac{10{,}000{,}000}{10{,}000} = 1000\ \text{s} = 17\ \text{min}$$

For a cryopanel with pumping speed of 100,000 L/s
Pumping time is 10 × faster = 1.7 min

6.3.1 Outgassing from Film

This section could be included in Chapter 8 on substrates or Chapter 24 on heat load. Outgassing from the substrate comprises two parts: the air trapped in the wound roll and the water vapor that may be contained in the bulk of the substrate that is material dependent. When the system is pumped down, much of the air remains trapped between the layers of material in the roll. The speed that the air can be pumped away from between the layers is dependent on the gap between the layers, which is related to surface roughness, roll tension, and quantity of gas trapped. As the gas is pumped away from the edges of the roll, the edges can collapse and make pumping the remaining air slower. It is common that once the winding is started, there is an accompanying rise in the system pressure, which is because this source of air is progressively exposed as the roll unwinds and the trapped air is released [6].

Once the substrate has moved away from the roll, the exposed surfaces will lose any surface moisture and this will be replaced by water that is contained within the bulk of the film. In the case of paper, it may be up to 20% by weight of the material but is negligible with foils and some polymers. If we take the case of a polymer film that does contain some moisture, this will typically be ~1% by weight (dependent on manufacturing conditions as well as the humidity during the previous winding process). The water can be removed from the surface as it appears, but the diffusion of the water to the surface takes time. The speed of diffusion to the surface can be increased by applying heat. Thus, when the film is bombarded during plasma cleaning, the film will be heated and the outgassing rate will increase [7].

Similarly, when the deposition starts, another heat load will be applied and there will be outgassing from the surfaces. The outgassing from the back surface can be useful and can increase the heat transfer coefficient as described in Chapter 24. The front surface will also outgas, but as the coating is deposited the surface will become sealed and the rate will fall. So the amount of gas that is desorbed from the substrate will depend on the length of time and temperature profile that the substrate is exposed to between the unwind and rewind rolls.

In the process of aluminum metallizing, the winding speed may be high, up to 1250 m/min (~ 200 m/s), and so for an exposed length of web of 10 m the web will only be exposed between rolls for 0.05 s and so there is little time for the moisture to diffuse to the web surface and outgas. In comparison for the same web path of 10 m but for a magnetron sputtering process that may be as slow as 10 m/min, the surface will be exposed for a minute. Some photovoltaic deposition machines have a much longer exposed web length and this is used to advantage by heating and plasma treating the substrate before the deposition zone to help minimize the outgassing of the substrate at the time of nucleation and growth of the initial coating layers.

Where the deposition process is sputtering or there is an additional plasma, the water vapor released from the web can be cracked into oxygen and hydrogen. Thus, if the water vapor level is being monitored, an increase will be seen as the winding is started and when any heat from the deposition source hits the substrate. There may also be a fall in the water vapor content when the plasma is struck as some of the water vapor is cracked into oxygen and hydrogen, the partial pressure of which should rise correspondingly. The oxygen and hydrogen should fall again as the plasma is stopped with the water vapor content rising slightly. The water vapor content should also fall as the deposition source cools and as the winding stops [6].

6.4 Leak Detection

There are many methods of detecting leaks. It depends on the pressure of the system as to how sensitive any particular technique is to any particular leak [1,8–20].

If the pressure of the vessel is near atmosphere and the leak is huge, then the best leak detection method may be as simple as walking around the system and listening carefully. Quite often, it is possible to hear the hissing/sucking sound of air rushing through the gap into the vessel. This type of leak is common where there is a large vessel opening and the door is shut using a drive motor. The door may pass an automatic stop for the drive motor, but any backlash in the mechanism may sometimes mean that the door is not quite closed. If the gap is small, then the pressure difference will cause the atmospheric pressure exerted on the door to close the door the remaining short distance. However, if the gap is too great, then there is sufficient area for enough air to leak in to prevent enough pressure difference from being created and the door will remain open by a small distance. In this instance,

@ A pressure of 23.4 mbar, water will boil at 20°C

@ 0°C the water vapor pressure is 6.11 mbar

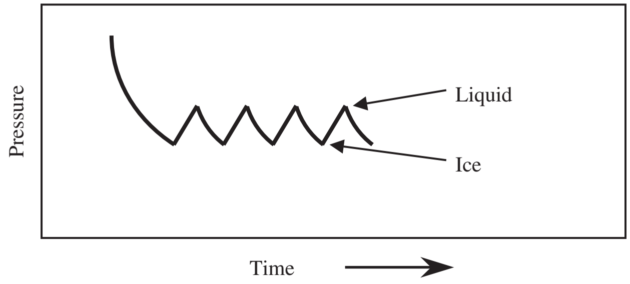


Figure 6.4 A graph showing the pressure oscillation characteristic of a water leak.

the air rushing in will usually make a significantly loud noise that the source of the leak can be readily identified.

Once the system is able to pump down to lower pressures, it is possible to use some of the vacuum gauges to test for leaks. The Pirani gauge can be used quite successfully because of the difference in performance of the gauge when measuring different gases. With the Pirani gauge reading being steady, any suspect joint can be squirted with a solvent, and if there is a leak it would be expected to see a marked pressure change. This occurs as a result of the change in conductivity arising from the alteration in the composition of the gas (as described in Section 3.2) as measured by the gauge. Obviously, the recommendation is not to be squirting solvents around and using a specialized helium leak detector is the preferred method of leak testing.

A common leak to identify with a Pirani gauge would be that of a small water leak. The schematic in Fig. 6.4 shows the characteristic trace that would be obtained if the Pirani gauge pressure were measured. Water enters the vacuum system through the leak and evaporates. The evaporation causes the water to freeze and the leak effectively stops lowering the pressure. The evaporation rate drops with the formation of the ice, and so the ice warms up and melts back into water. The water starts to evaporate again and the pressure rises again repeating the cycle.

6.4.1 Leak Testing Using Helium

If we look at Fig. 6.5, we can see three options for using helium. From top to bottom, there is an increase in the sensitivity of detection of helium. The top figure is where the normal pressure gauges are used and the difference in gas type is used to provide a gauge movement that can be detected and used as the sign of a leak. This is the same as using solvents with the Pirani gauge but using helium as the marker gas. After this, a residual gas analyzer or dedicated helium leak detector is used. These are based on the use of a mass spectrometer that has been optimized for the detection of helium gas.

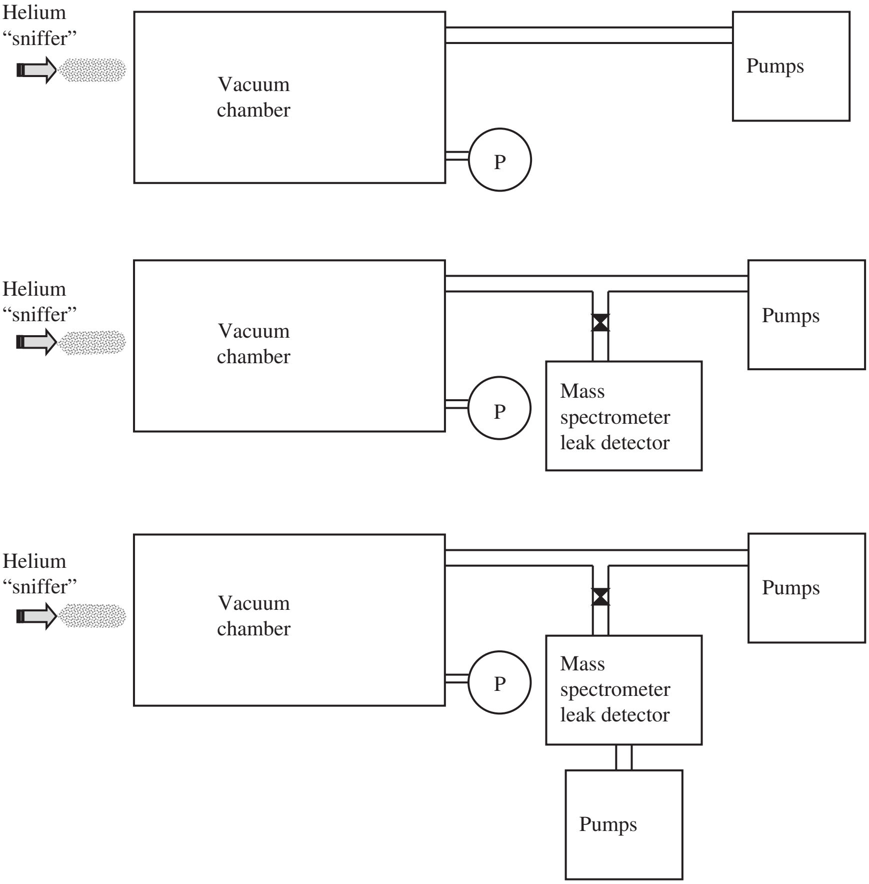


Figure 6.5 A schematic showing a mass spectrometer included in a basic system.

The principle of leak detection is similar to that used with the Pirani gauge. The difference is in the sensitivity of the dedicated leak detector. The leak detector is linked to the vacuum vessel and samples the gas content. The mass spectrometer ionizes the sampled gas and spirals the gas down a quadrupole spectrometer. The spectrometer separates different gases, with the lightest arriving at the detector first. Using a bottle of helium gas, small quantities of gas can be squirted around any suspect joints. The leak detector is then monitored to see whether any helium has been detected. This is usually connected to a sound generator so that it gives an audible signal of the quantity of helium detected.

The middle schematic in Fig. 6.5 shows the leak detector situated in the existing pumping line for the system. The pumps provide a continuous flow of gas and the leak tester samples from this gas flow. However, as there is no gas flow through the leak tester, the response may not be optimized. In the lowest schematic, the helium leak tester has its own pumping system and so has a higher throughput of gas and this improves the sensitivity of the sampling.

Care must be taken in squirting the gas because it is so light and mobile that if there are many joints close together, it can be confusing as to which of the joints is the one that is leaking. It is good policy to start with the higher joints first, as helium is lighter than air and so will rise and if the lower joints are tested first the escaping gas can rise and go past leaking joints higher on the vessel. If any of these higher joints are leaking, they will allow helium into the vessel and will show up as a leak, but as a lower joint was being tested it can result in the lower joint being diagnosed as the source of the leak rather than the real joint from higher up. Working from top to bottom helps to limit this type of false diagnosis.

Leak detecting can be time-consuming and in general it follows the law of diminishing returns. Once a target base pressure is achievable, the process should be stopped. Continuing, one is almost certain to identify further leaks, but they will be small, and unless they directly affect the product quality, they will not be worth the extra effort involved.

References

[1] Basic vacuum practice. 3rd ed. Pub. Varian Part No. 900-0085.

[2] Harris N. Modern vacuum practice. McGraw-Hill; 1989. ISBN 0-07-707099-2.

[3] Decker W, Henry B. Basic principles of thin film barrier coating. In: Proc. 45th annual technical conference of Society of Vacuum Coaters; 2002. p. 492−502.

[4] Lasky E. The UV/ozone process for ultra-cleaning before vacuum deposition. In: Proc. 34th annual technical conference of Society of Vacuum Coaters; 1991. p. 374−7.

[5] LaCourt D, Hall P. The PFC-330 in chamber water vapor cryopump. In: Proc. 41st annual technical conference of Society of Vacuum Coaters; 1998. p. 509−12.

[6] Rank R, et al. Adhesion promotion techniques for coating of polymer films. In: Proc. 47th annual technical conference of Society of Vacuum Coaters; 2004. p. 632−7.

[7] Song S, Placido F. Effect of gas release from polymer surfaces during microwave plasma pre-cleaning on the adhesion of metal films. In: Proc. 51st annual technical conference of Society of Vacuum Coaters; 2008. p. 574−8.

[8] Knarr OM. Leak testing and characterizing vacuum coaters. In: Proc. 41st annual technical conference of Society of Vacuum Coaters; 1998. p. 25−30.

[9] Hatton P. Process diagnostics, vacuum quality determination and leak detection in vacuum coating applications. In: Proc. 39th annual technical conference of Society of Vacuum Coaters; 1996. p. 104−7.

[10] Logan ML. Leak detection and trouble-shooting on large-scale vacuum systems. In: Proc. 39th annual technical conference of Society of Vacuum Coaters; 1996. p. 164−6.

[11] Worthington W. Practical aspects of leak detection. In: Proc. 27th annual technical conference of Society of Vacuum Coaters; 1984. p. 104−7.

[12] AVS std. (tentative). Calibration of leak detectors of the mass spectrometer type. J Vac Sci Technol 1973;10(4):568−77.

[13] AVS std. (tentative). Method for vacuum leak calibration. J Vac Sci Technol 1968;5 (6):219−22.

[14] AVS std. (tentative). Method for calibrating gas analysers of the mass spectrometer type. J Vac Sci Technol 1972;9(5):1260−74.

[15] Ehrlich CD, Basford JA. Critical review: recommended practices for the calibration and use of leaks. J Vac Sci Technol A 1992;10(1):1−17.

[16] Welch J.V. PPT series residual gas analyzers and sampling systems. In: Proc. 37th annual technical conference of Society of Vacuum Coaters; 1994. p. 451−6.

[17] Robinson T. Application of quadrupole residual gas analysers for the monitoring of, and troubleshooting in, vacuum process equipment. In: Proc. 29th annual technical conference of Society of Vacuum Coaters; 1986. p. 424−42.

[18] Allen BG. Residual gas analyzer applications. In: Proc. 13th annual technical conference of Society of Vacuum Coaters; 1970. p. 73−6.

[19] Tompkins HG. Vacuum gauging and control. America Vacuum Society Monograph Series M-12: 1994, New York, NY 10017.

[20] Schubert R. Partial pressure analyzers, analysis and applications. America Vacuum Society Monograph Series M-19: 2000, New York, NY 10017.

7 Mass Spectrometers, Helium Leak Detectors, and Residual Gas Analyzers

Mass spectrometers were once large, expensive analytical machines that precluded their use on production vacuum coating systems. However, there was a real need to determine the gas composition within commercial vacuum processes. This produced the development of cheaper, more compact mass spectrometers for industrial use. Initially, there were compromises made on the resolution and mass discrimination. These have steadily been improved with improved component designs along with more sophisticated electronics. These mass spectrometer systems are often sold as residual gas analyzers (RGAs) where they are used for partial pressure analysis [1].

The helium leak detector is a specialized mass spectrometer. The design and electronics are all devised to optimize the sensitivity of the system to helium. The leak detectors will not scan through a mass range and so can only be used for leak detection, whereas residual gas analyzers can not only scan over a given mass range but can also be used for leak detection, although it is harder work than using a dedicated leak detector.

Mass spectrometers have three distinct parts: the ionizer, the analyzer, and the detector. A sample of gas passes through the ionizer, where it is ionized, into the analyzer where the different mass ions are separated before they reach the detector. The detector detects the abundance of ions of each mass with increasing time.

The ionizer is a chamber through which an electron beam is passed. The electron beam produces electrons in the energy range 50−100 eV and these are sufficient to ionize any gas within the chamber. Using extraction grids, the ions can be directed to pass through the analyzer.

There are two types of analyzers that are commonly used. The first uses a magnet to deflect the ions. The mass and charge on the ions determine the extent of the deflection and thus allow the detector to scan through a mass range. The second type, which is the most popular one used for the residual gas analyzers, is the quadrupole [2,3]. In this design, there are four rods that are connected as pairs sequentially to a radio frequency (RF) supply. The result of this changing field is that as the ions pass down the center of the rods, they start to spiral around the centerline.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00007-6

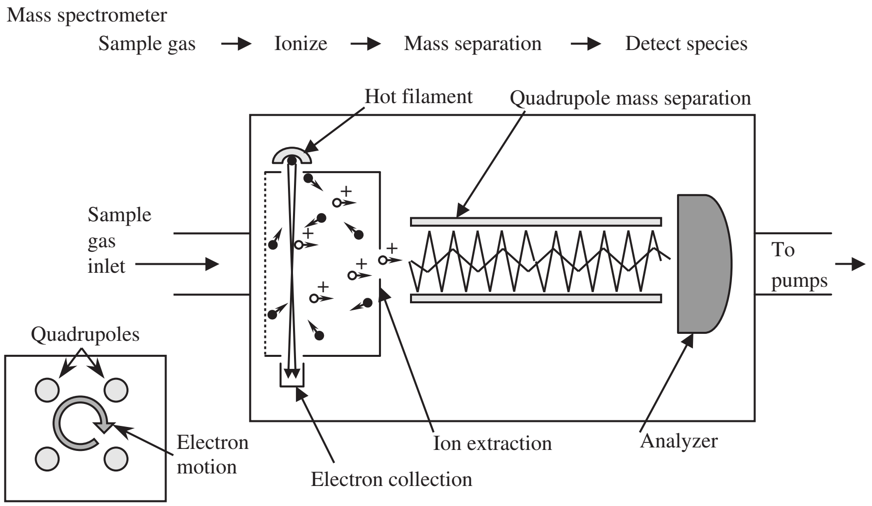


Figure 7.1 A schematic of a quadrupole mass spectrometer.

The mass and charge determine the radius of the spiral. The frequency of the RF supply can be varied, and for any given frequency, only a single mass will reach the detector, the rest of the ions will collide with the rods and be lost. Thus, by scanning through the frequencies, a mass range can be scanned. The ions colliding with the rods can cause some contamination with time and hence this type of detector needs to be maintained with regular cleaning.

The quadrupole (Fig. 7.1) is more compact and cheaper and hence its wider use. Provided the RGA has its own pumping system and the gas sample is a suitably small quantity, it is possible to sample processes at pressures as high as atmospheric pressure. This enables most processes to be monitored and makes the task of troubleshooting easier (Fig. 7.2).

There is also a choice of detectors with the two most commonly available being the Faraday cup detector and the electron multiplier. Each of these detectors must be capable of detecting the current from each ion impacting the detector surface.

An ion current of 1.6×10^{-19} A is equal to 1 ion/s.
Therefore, 1.6×10^{-13} A is 10^{6} ions/s. or, 1.6×10^{-6} A is 10^{13} ions/s.
A partial pressure of $\sim 10^{-11}$ torr gives an ion current of $\sim 10^{-15}$ A.

As can be seen, the currents that have to be detected can be very small, and careful design of the electronics is essential if large errors are to be eliminated.

The Faraday cup is pot shaped with a small entrance orifice. As the ion enters and hits the detector surface, the metal detector gives up an electron to neutralize the charge on the ion and this results in a current flow, which is measured. If the ion arrives with enough energy, it can eject a secondary electron. If this second electron is not recaptured by the surface, the current detected will be due to two lost electrons, not the one due to the neutralizing ion, and hence the reading will be

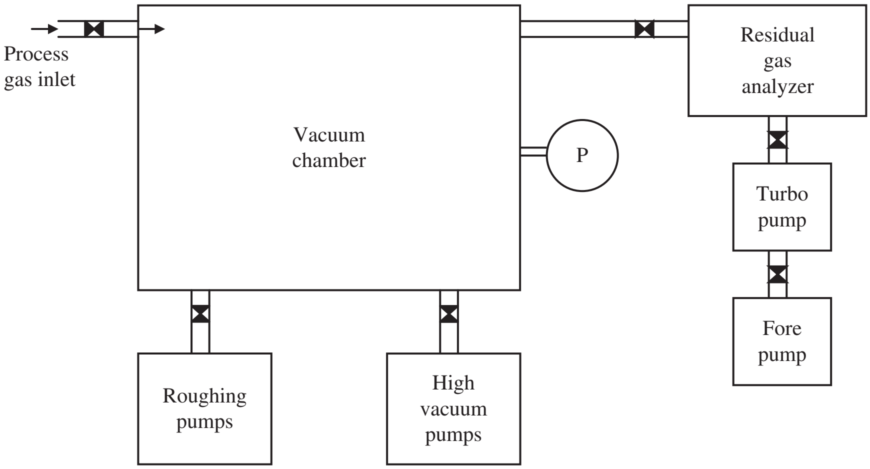


Figure 7.2 A schematic of a system with an RGA attached.

incorrect. Thus, the pot or cup shape to the detector is specifically designed to maximize the recapture of the ejected secondary electrons.

The electron multiplier utilizes the ejection of secondary electrons as a method of increasing the current and providing a larger signal for each ion impact. The detector plate is made of a material with a large secondary electron coefficient so that every ion impact will generate more than one secondary electron. These secondary electrons impact onto another plate and the process is repeated so that there is a cascade of electrons amplifying the detectable current from the first ion impact.

The final part of any system is how the results are presented to the user. Modern day RGAs have many options. The most common display is as a trace of the abundance of ions impacting the detector at each mass number in atomic mass units (amu). Although it is referred to a mass, it is *m*/*e*, where *e* indicates if the ion is singly, doubly, or triply ionized. It was agreed internationally that the major carbon isotope (6 protons and 6 neutrons) would be assigned a value of 12 amu. All other masses are referenced to this value for carbon.

When the sample gas is passed through the ionizer, it is impacted by the electrons and may be singly ionized or may be further impacted and lose further electrons and become doubly or triply ionized. The system is aimed at singly ionizing as much material as possible. The impact of the electron beam is also capable of fragmenting molecules. These fragments may also be ionized.

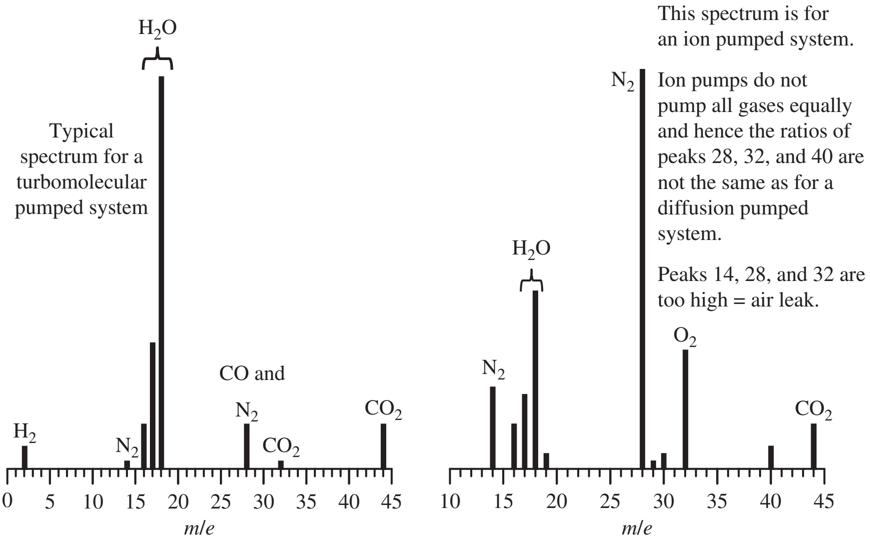
Thus, water in a vacuum system will produce a characteristic pattern made up of not only ionized H_2O^+ but also O^+ and OH^+. These three peaks will consistently be of predictable relative intensities and hence they have a characteristic position and pattern known as a “fingerprint.” Nitrogen (14 amu) exists as the molecule N_2 (2 atoms of 14 amu = 28 amu); however, the trace will also show a peak at 14 amu [4]. This is because the nitrogen molecule will have been separated into nitrogen atoms and singly charged, but there will also be a fraction of nitrogen molecules that are doubly charged (*m/e* = mass/level of charge = 28/2 amu).

The quality of the output is dependent on many things, including the quality and design of the analyzer and electronics as well as the geometry of where and how it is attached to the vacuum system. There are simple measurements of standard fingerprints where the peak to valley measurements give an indication of the system performance [5].

Residual gas analyzers can be used not only for monitoring the health of a process, troubleshooting a process, or leak testing but also, in some instances, as part of an active process control system [6–9]. The measure of partial pressure of a single gas can provide the feedback signal to control the mass flow controllers. In other cases, the triggers can be set to detect the end point of an etching process. The triggers can also be set as part of a safety system to detect a leak into a process to shut the process down before the leaking gas or liquid can react with the process materials.

An example of an RGA output being hard wired as an integral part of a safety system was for a system used to deposit magnesium where a water leak could have been catastrophic. The water would have provided the oxidizer to the magnesium fuel and the reaction would have been highly exothermic not to say explosive. In this case detecting a rise in the background water content, above a specific level, triggered an automatic shutdown of the process.

Gases such as CO and N_2 have equal masses, but by comparing the "fingerprints" of each it is possible to tell if solely CO or N_2 or both cause a peak at 28 amu. In Figs. 7.3–7.5 there are some "fingerprints" of gases commonly found



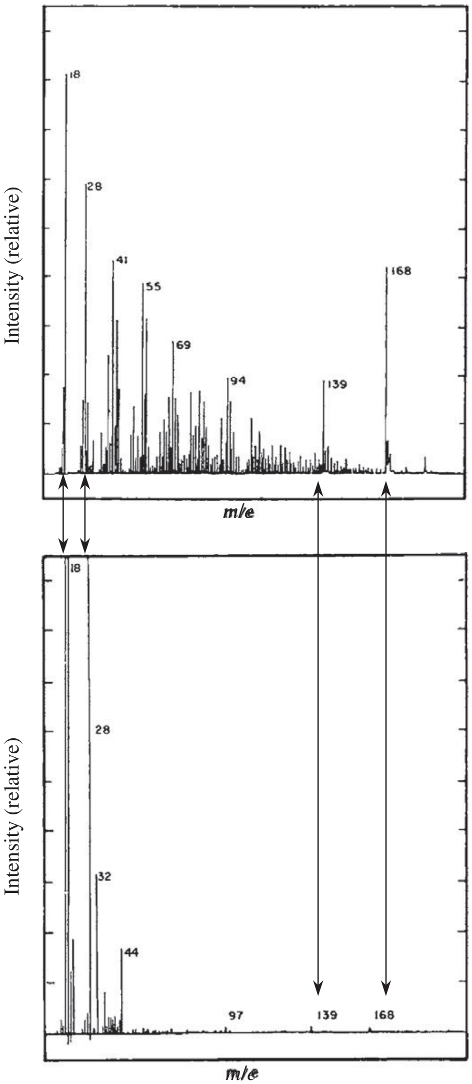
Typical spectrum for a turbomolecular pumped system

This spectrum is for an ion pumped system.

Ion pumps do not pump all gases equally and hence the ratios of peaks 28, 32, and 40 are not the same as for a diffusion pumped system.

Peaks 14, 28, and 32 are too high = air leak.

Figure 7.3 On the left is a spectrum typical for a turbomolecular pumped system. On the right is a spectrum for an ion pumped system where not all gases are pumped equally as well. The right-hand spectrum is also typical of there being an air leak.



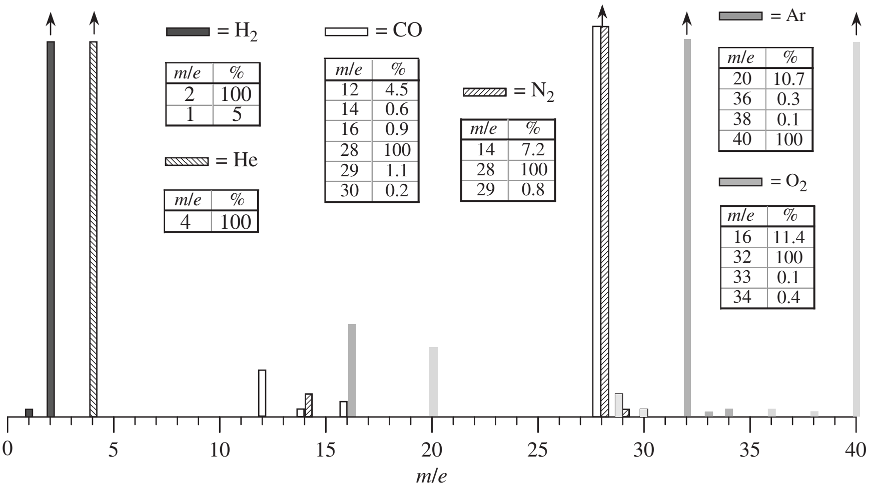
Restricted backing pumping to diffusion pumps

Santovac 5 pump oil

As the pumping is increased, the system shows reduced backstreaming for most of the higher-order hydrocarbon groups.

Increased backing pumping to diffusion pumps

Figure 7.4 The upper spectrum has been created by restricting the backing pump to the diffusion pump. This stalled the diffusion pump and caused backstreaming of the oil, which is seen in the spectrum. The lower spectrum has the backing pump speed increased and the level of backstreaming has been reduced, which is seen in the reduced amount of oil detected by the RGA [10].



m/e	%
2	100
1	5

m/e	%
4	100

m/e	%
12	4.5
14	0.6
16	0.9
28	100
29	1.1
30	0.2

m/e	%
14	7.2
28	100
29	0.8

m/e	%
20	10.7
36	0.3
38	0.1
40	100

m/e	%
16	11.4
32	100
33	0.1
34	0.4

Figure 7.5 A spectrum showing the contributions from some of the most common gases that will be found in vacuum processes.

in vacuum systems. The masses are plotted on the axis where mass is shown as *m*/*e*, where *e* indicates if the ion is singly, doubly, or triply ionized. The intensity of the peaks have been plotted on each graph and normalized to the highest peak. Thus, the highest peak can be taken to be 100% and the others then represent the relative percentage of each component peak.

Most of the time, the RGAs are not used for absolute measurements, instead they are used to compare spectra. Ideally, when a system is new and the base pressure is as good as it is going to be, a baseline spectrum can be recorded. Most modern RGAs can store many spectra and automatically subtract or compare spectra. Thus, the baseline spectrum can be subtracted from all subsequent spectra, and this will show the difference between the cleanest the system has been and the current state of the system. It is also possible to put limits on certain components so that once a limit has been reached it triggers a thorough clean up of the system, which should return the system back to something close to the cleanliness and the original baseline spectrum.

This recording of spectra when the process is working well can also be used as part of the troubleshooting process as described in Chapter 31. If you know what the spectra should look like when the product is good, then when the product is no longer acceptable you can look for differences. Once these differences have been eliminated, one would expect the product to return to becoming acceptable again.

References

[1] Vasile MJ, Dylla HF. Mass spectrometry of plasmas. In: Plasma diagnostics—vol. 1—discharge parameters and chemistry. Academic Press; 1989 [chapter 4]. ISBN 0 12 067635 4.

[2] Harris N. Modern vacuum practice. McGraw-Hill; 1989. ISBN 0 07 707099 2.

[3] Robinson T. Applications of quadrupole residual gas analysers for the monitoring of and troubleshooting in vacuum process equipment. In: Proc. 29th annual technical conference of the Society of Vacuum Coaters; 1986. p. 424−42.

[4] Craig RD, Harden EH. The interpretation of mass spectra in vacuum measurement. Vacuum 1966;16(2):67−73.

[5] Basford JA, et al. 'Recommended practice for the calibration of mass spectrometers'. J Vac Sc Technol 1993;11(3):A22 (19 pages).

[6] Mao FM, et al. Residual gas analysers and their use in high vacuum systems. Vacuum 1987;37(3/4):335−8.

[7] Wilson NG, Beavis LC. Handbook of vacuum leak detection. American Vacuum Society monograph series M-2. New York: American Vacuum Society New York, NY 10017; 1979.

[8] Schubert R. Partial pressure analyzers, analysis and applications. American Vacuum Society monograph series M-19. New York: American Vacuum Society; 2000.

[9] Tompkins HG. Vacuum gauging and control. American Vacuum Society monograph series M:12. New York: American Vacuum Society; 1994.

[10] Hablanian MH. Diffusion pumps—performance and operation. American Vacuum Society monograph series M:5. 2nd ed. New York: American Vacuum Society New York, NY 10017; 1995.

Part II

Substrates, Surface Modification, and Nucleation

8 Substrates and Surface Quality

8.1 Substrates

The bulk of roll coating processes utilize polymer webs and these are dealt with first.

8.1.1 Polymer Roll Quality

Polymer webs can be manufactured by a number of different processes. The most widely used are the bubble process and the stenter process for the biaxial orientation of an extruded polymer. A minority of polymers are made using the casting process where the monomer or solution is cast onto a moving belt. The cast material is heated and once it is self-supporting, it is peeled off the belt and the heating and drying process is completed. In the bubble process, a tube of polymer has a gas injected down the center of the tube and the polymer is inflated into a bubble. Eventually, the bubble is collapsed and the draw rolls take the flattened bubble to where it can be slit to produce two separate rolls of film. The diameter of the bubble and the draw speed govern the amount of biaxial orientation the polymer extrusion has given. The stenter process can be either a sequential or a simultaneous biaxial orientation process. In the sequential process, the extruded polymer is quenched as it falls onto the casting drum and then it enters the forward draw process. In the forward draw process, there are two sets of rolls: the first set of rolls is used to grip the film and heat it up; the second set of rolls winds at a faster speed than the first set of rolls and this causes the web to be drawn forward in the gap between the two sets of rolls. The final rolls in the second set are cooled and the elongation in the film is set. Following this forward draw, there is then the sideways or transverse draw process. The web is gripped by the stenter clips and then the web enters the stenter where it is reheated and the stenter clips are pulled sideways giving the web the second stretch. The final part of the stenter is where the web is heated or soaked allowing the molecules to stabilize in position. The web then exits the stenter and the edges where the stenter clips gripped the film are cut off (edge trim), leaving the rest of the film to be wound up as a mill roll. It is possible to combine these two orientation steps, which is done using the simultaneous stenters where the clips move both sideways as well as away from each other, thus

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00008-8

giving the biaxial stretch at the same time. This dual movement of the stenter clips can be done by spindle, pantograph, or linear motors.

The purpose of the biaxial orientation process is to change the properties of the polymer film. The polymer when extruded can be likened to a bowl of spaghetti where all the polymer chains are intermingled in a random manner and the polymer is regarded as amorphous. When the polymer is stretched, these individual polymer chains are pulled and begin to orient along the direction of stretch. Parts of different chains may become oriented parallel to each other and be pressed closer to each other such that they can form crystalline regions. The second orientation can increase this orientation and the crystallization process. The crystallites are denser and they help increase the tensile performance of the polymer film. This increase in crystallinity can also increase the transparency, reduce the haze, increase the tear resistance as well as increasing the polymer barrier performance as a result of the difference in diffusion coefficient between the amorphous and crystalline regions of the film.

The film produced by the stenter process or bubble process that is biaxially oriented can be 10 m or more wide [1,2]. Metallizers are frequently much less than this, anywhere from less than 1 m wide for some capacitor machines to as much as 4.45 m wide for some simple packaging metallizers. Most of them will be somewhere between 2 m and 2.5 m width. This means that the mill rolls produced have to be slit into narrower rolls. The more times the rolls are rewound and/or slit, the more chances there are of winding defects [3] occurring and the greater the quantity of debris attached to the surfaces. Some of the possible defects and causes are described below.

The stress within the web is not uniform, although it is often symmetric about the web centerline (Fig. 8.1). This can mean that there are differences between webs that are slit from the edges of the mill rolls and those that are from the center of the mill rolls.

The knock-on effect is that the rolls may handle differently in the vacuum web coater. Also because the rolls have slit edges, there is the quality of the slitting that too can cause winding problems depending on how sharp the blades were and how much of an edge lip has been raised during the slitting. Any extrusion of polymer through a die may have high spots and low spots and these may vary with time as debris builds up at the lips of the die and breaks away and new residues form (Fig. 8.2). Modern dies have many heaters to modify the extrusion profile and these too may drift or not be perfectly set; hence, there will be small thickness variations to the extruded film. When this film is stretched, these high spots are widened and become much less noticeable, but they will still be present. When a roll is wound, the air entrainment may well hide these high spots, but once the web is wound in vacuum, where there is no air entrainment, the roll will be very hard and the high spots will be highlighted.

When winding in vacuum, where there is no air entrainment, many of these defects become much more noticeable. The winding of hard rolls can press any protruding fillers hard into freshly coated surfaces. These filler particles can pick off the coating the next time the roll is unwound. Alternatively, with no air to act

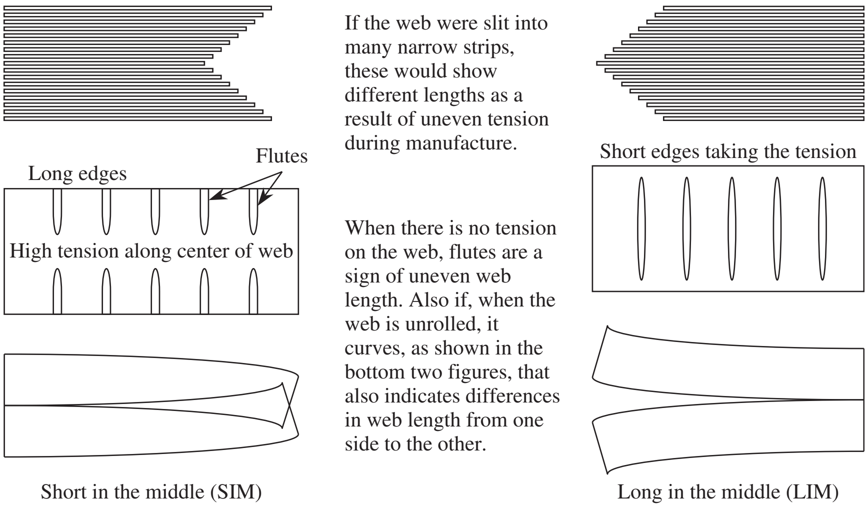


Figure 8.1 The figure shows some of the problems that occur with a web that is longer in the middle (LIM) or shorter in the middle (SIM) as a result of uneven tension during manufacture.

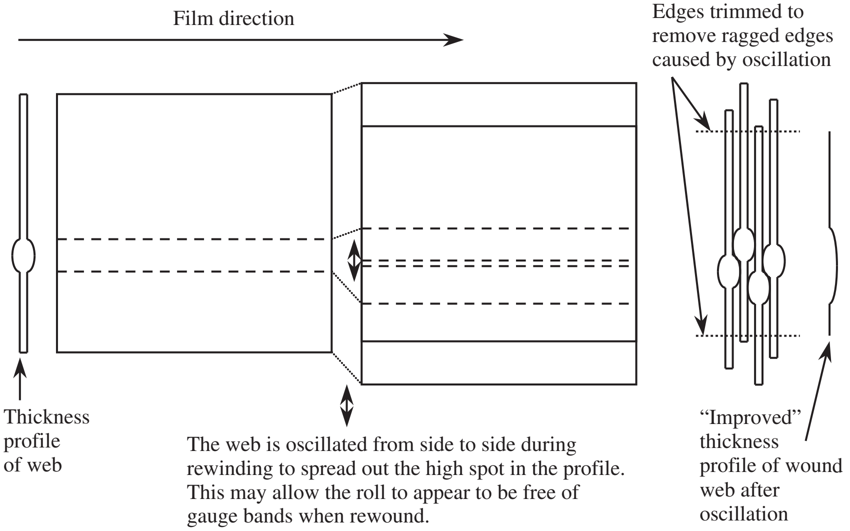


Figure 8.2 Where a high spot is known about by the film producer, they may well have oscillated the windup from side to side to spread the effects of the high spot, thus grading it in with the rest of the roll. This is shown schematically above where on the left is a schematic of a single thickness profile of the web. The middle schematic shows how the web can be oscillated so that the accumulated thickness profile of multiple layers of web has a broader but less pronounced "gauge band" or high spot.

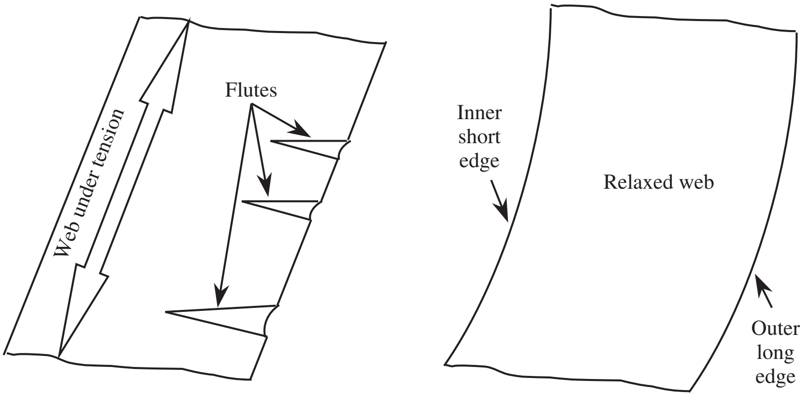
as a lubricant, the fillers can scratch the coating if there is any differential slip during the rewinding. The freshly deposited metal coatings are particularly susceptible to this. These coatings take time to oxidize a little and it is the oxidized surface that gives many of them their toughness. Typically, a day-old coating is much tougher than a coating only 1 hour old. As the oxidation of the surface is a logarithmic progression, it is little different once the initial oxidation has taken place.

High spots in the windup highlight thicker parts of the web. These thicker parts of the web will take most of the tension and another indication is whether the edges of the web appear to be wavy when viewed in free span between two rolls.

Similarly, if the biaxial orientation has not been done perfectly uniformly then it is possible that one edge of the roll is fractionally longer than the other edge. The roll can be wound perfectly straight because it is wound under some tension. This again becomes apparent at light tensions where one edge in free span is taut and the other is wavy (Fig. 8.3).

These types of variations, while manageable in most cases, may cause a problem if the vacuum coating process is pushed toward the limits. If there is different tension being pulled between one side of the web and the other then the pressure exerted by the web while taken around the deposition zone cooling drum will be different and thus the contact area could be expected to be different, which could result in the side that has the greater tension being better cooled than the side with less tension.

At the limits of the process if there is too little tension and thus insufficient cooling, the web will overheat and expand further, reducing the tension and thus taking the web out of contact with the cooling drum altogether. This can result in a



Taking the relaxed web roll and pulling some tension on the web, the inner shorter edge straightens first and takes all the tension. The web if held flat, then tries to make the longer edge straight with the excess length, forming the flutes.

Figure 8.3 A schematic showing web curvature and the flute produced when pulling tension on the curved web.

web break, loss of the process, tramlines from shadowing of the depositing flux, and loss of the product. This all indicates that it is well worthwhile paying close attention to the quality of the incoming web and treating it as a variable.

Checking for roll quality also applies to the more general quality of the rolls (Figs. 8.4, 8.5 and 8.6). If the web has been poorly wound and has been crushed, or if through temperature changes between night and day the tension on the web has been lost and the roll telescoped, it will all lead to winding problems of the rolls when in a vacuum system. The above are all faults that can be found on poorly wound rolls and are avoidable.

Another problem that is all too common is that of poorly slit edges [4,5] (Fig. 8.7). Slitting is achieved by use of metal blades that over time become blunt. Blunt blades can cause the blades to run hotter and the slit edge of the polymer can start to exhibit defects as shown in the schematic above such as a raised edge, polymer hairs, and even a ragged edge from tears.

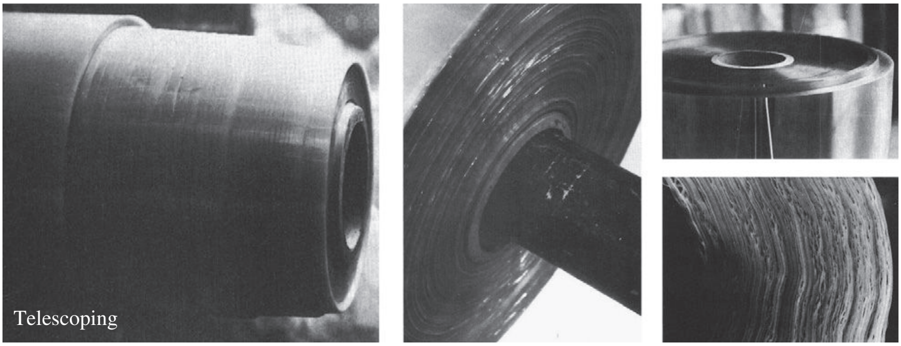


Figure 8.4 The roll on the left shows a bad case of telescoping, on the right the rolls are soft wound.

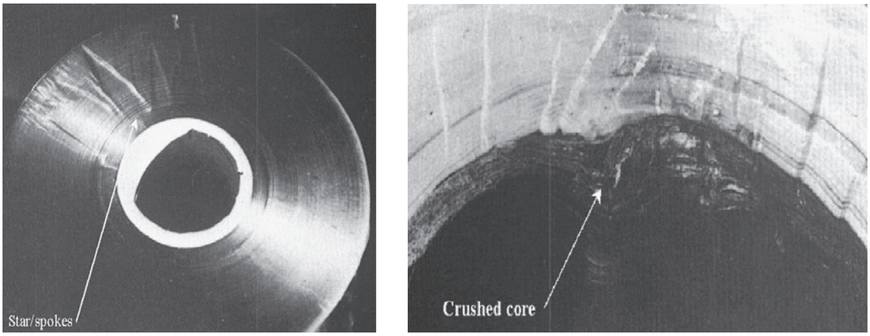


Figure 8.5 On the left the hard wound roll shows star spokes and on the right a crushed core.

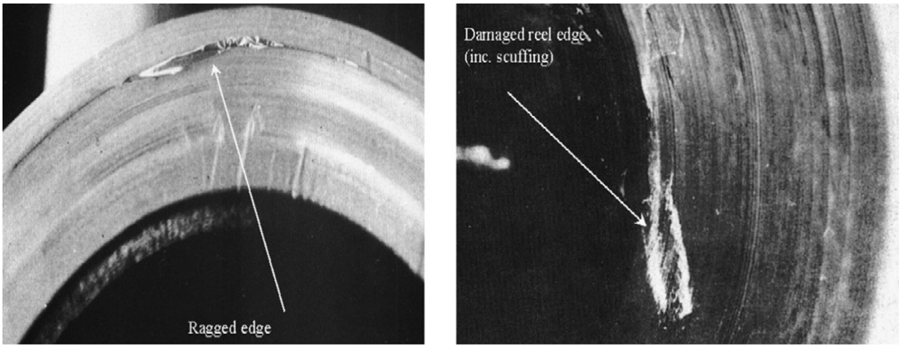


Figure 8.6 On the left is a roll with a ragged edge and on the right damage and scuffing can be seen.

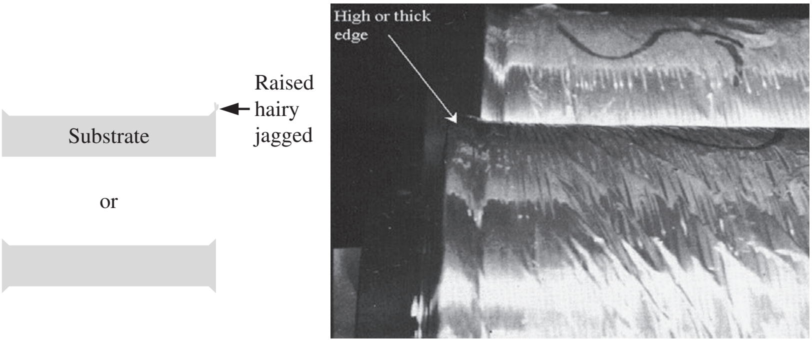


Figure 8.7 A schematic of the raised edges of a poorly slit web.

The raised edge is, in effect, a change in thickness profile and it can cause tensioning problems. Worse still is that, depending on how much the edge has been raised, the web as it is rewound in the vacuum no longer has the entrapped air to hide the profile difference and so the edges will grow much more rapidly than the rest of the roll. This raised edge can reach the point where the edge folds over. Obviously, the roll edge will then be growing at double the speed of the rest of the roll width. The resultant finished roll will have the appearance of a dog-bone with highly raised edges and normal parallel center section (Fig. 8.8).

8.2 Polymer Surface Quality

Substrates are an important variable in vacuum deposition processes. Not all polymer film is the same. This is true even for what the different suppliers manufacture

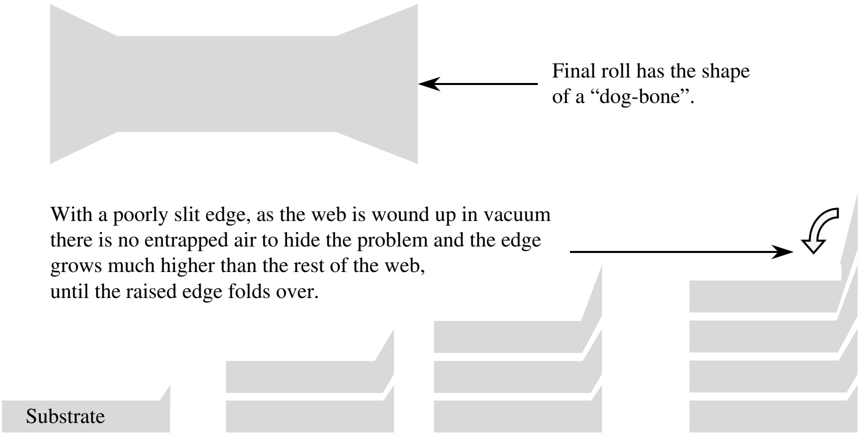


Figure 8.8 Schematic of the effect of winding film with a raised edge in a vacuum.

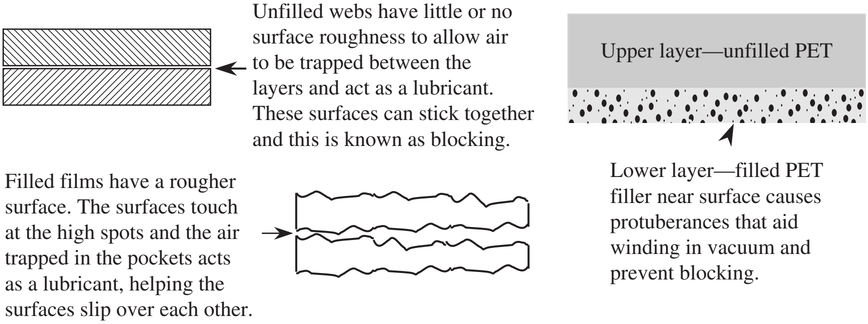


Figure 8.9 A schematic highlighting the difference between a perfectly smooth web and those with modifications or pretreatments to prevent blocking.

for the same market application. Polyethylene terephthalate (PET) can be manufactured by the bubble process or the stenter process and either sequentially biaxially stretched or simultaneously biaxially stretched. PET film without any treatment has very smooth surfaces and these, when wound up, would have many contact points with high friction between the surfaces. The high friction would prevent the surfaces slipping over each other, a problem known as blocking, thus producing poorly wound rolls (Fig. 8.9). Hence, all PET is pretreated in some way.

Every polymer manufacturer will have their proprietary method of producing a vacuum metallizable film with high optical clarity and good handling. This does, however, mean that changing the supplier of the polymer can result in a change in the performance of the deposited coating. Any surface treatment, which is developed for one particular grade of polymer and from one supplier, may or may not work as well on other grades of the same polymer or an equivalent grade from another supplier.

Another area of ongoing concern with all polymers relates to any potential adverse effect on human health, particularly where there is food contact. Thus, there is interest in the chemistry of the polymer surface and the rate of migration of any chemicals to the surface. In fact, there is plenty of information on the migration of oligomers available from work done in the testing of polymers for food contact approval [6,7]. Thus, we can see there is great interest in improved surfaces for most applications.

This pretreatment could take the form of fillers through the thickness of the polymer, coextrusion of a filled polymer and an unfilled polymer or by adding coatings on to one or both surfaces to change the surface properties. The fillers reduce the contact area of the surfaces and hence allow the film to slip more easily. The negative side of this is that the filler particles can protrude through the polymer surface [8] and cause other problems such as reduced barrier performance or coating pick off due to high compressive load at the filler peak (Fig. 8.10).

Cast polymers often have a different surface roughness naturally, as during manufacture one side of the film is in contact with the casting belt and the other side is in contact with the air. The side contacting the casting belt will be a mirror image of the surface roughness of the belt surface.

There is then contamination by dust or debris. The source of this contamination can be many and varied [9]:

- Human: skin debris, hair, clothing fibers, mascara, body powders, hand creams (give off vapors that can condense on polymer surface), human breath, etc.

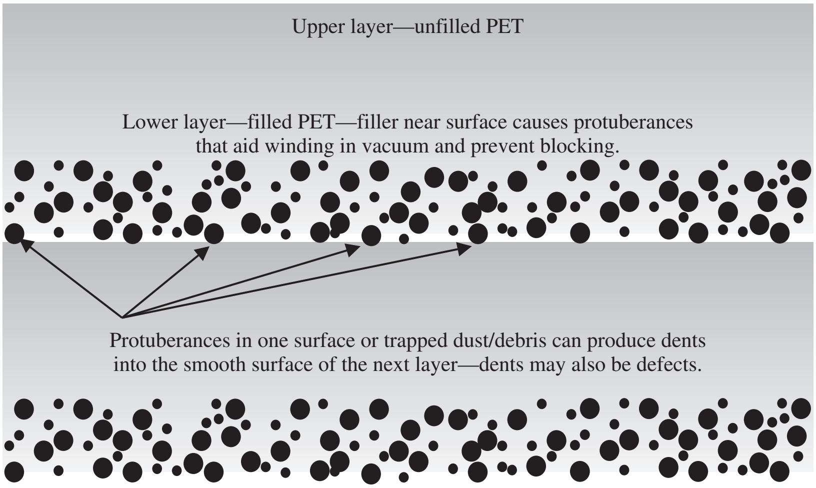


Figure 8.10 A schematic of a coextruded PET with one layer containing a filler that produces a roughened surface that helps prevent blocking of webs wound in vacuum but may cause front surface damage in some cases.

- Polymers: exudates—vaporized monomer condensing and falling back as white powder, slitting debris
- Others: machine debris, paint chippings, packaging debris (cardboard), airborne contaminants such as pollen or smoke stack particles, etc.

In the stenter process, in the manufacture of polymer films there can be a white powder that is deposited onto the web. The source of the white powder is unpolymerized monomer or volatiles that are given off from the surface while the polymer is at an elevated temperature. These volatiles will condense out on any cool surface and as the thickness of this material builds up it can fall or become airborne, in the circulating heated air, of which some will deposit back onto the polymer web passing through (Fig. 8.11). The cleanest that the film manufacturing process will be is when it is new and before the white powder has had time to accumulate. Also, as the plant ages there is also an accumulation of other debris. Some companies periodically clean the plant and so there may be periodic improvements, but the general trend is always for the film contamination to be increasing.

A second source of surface contamination derives from the edge trim and the pattern cutting of the web. Where the polymer film is gripped by the stenter clips, there is no biaxial orientation and the polymer is thicker than the stretched film and hence it is cut off. The slitting process is a dirty process. The metal blades generate slitting dust. This is less when the blades are sharp, but even then there is debris produced. The polymer surface will have a surface charge that is generated from the polymer web having traveled over some rollers. The mismatch in materials leads to an electrostatic charge being generated. The polymer film being nonconducting, this charge remains on the surface for some time. As the web has the edge trim cut away and the dust generated, there is a readymade electrophoretic pump in

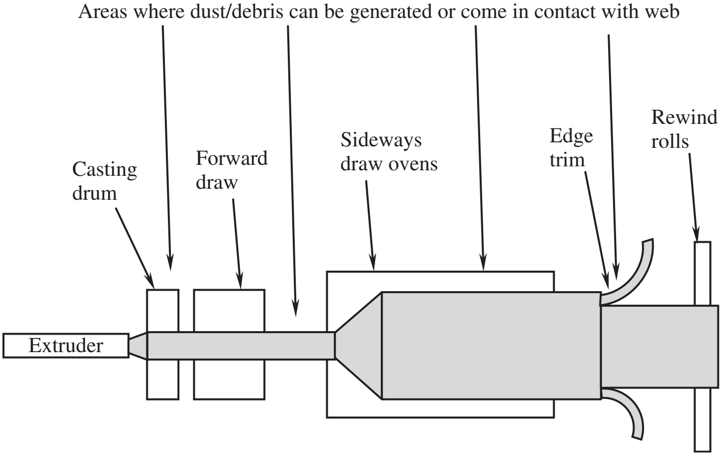


Figure 8.11 A schematic of a stenter process with the key areas where debris or dust can cause contamination of the web surface.

the polymer surfaces. Hence, the dust is attracted from the slitting area across the whole web.

The quality of the polymer film will vary from supplier to supplier, and the cleanliness is one of the factors that can vary enormously. This can be particularly noticeable when looking at the number of pinholes that are generated following metallization or when looking at the different transparent barrier coating performances (Figs. 8.12 and 8.13). These coatings are very thin and if there is debris left on the surface prior to metallization it will be covered with this thin coating. If, however, the debris is then moved by contact with a roll or during windup, there will be either a pinhole from where it was rolled away or a scratch where it was pushed across the surface [10]. Both of these defects will show up either as a pinhole in an otherwise opaque metal film or as a reduced barrier performance with the transparent coatings.

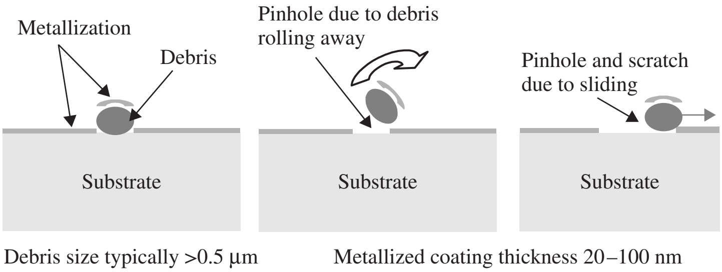


Figure 8.12 A schematic showing how residual debris on the web surface can result in a pinhole or a pinhole and scratch, in the vacuum deposited thin film coating.

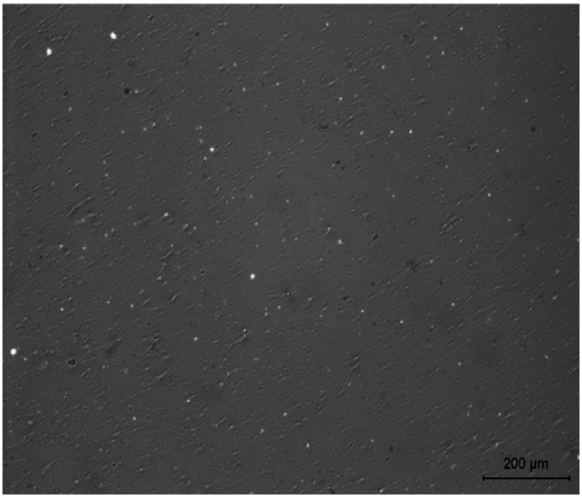


Figure 8.13 A photograph of a thin metallized polymer showing pinholes. Photograph courtesy of Applied Materials. A photograph of a poor quality film with many more pinholes is shown in Chapter 5.

A simple way of highlighting any pinholes in metallic coatings is to place the film on a photographic light box. The light box contains a light source and diffuse reflecting surfaces with a translucent polymer sheet on top of the box. The diffuse reflectors help produce a uniform light intensity over the whole surface of the translucent sheet. The placement of the metallized film on top of the translucent sheet enables a large area of film to be evaluated quickly. Each bright spot is a pinhole of an area of thin coating. This can be photographed and then image analysis can be used to count the number and size of pinholes over a particular area. This technique is of no use for transparent coatings.

Where a count of pinholes in transparent coatings is needed, the technique used is to place a sample of coated polymer in a vacuum chamber and to use an oxygen plasma to etch the coated surface. The oxygen plasma will etch the polymer at the bottom of the pinholes much faster than the transparent coating and so will undercut the coating. The etched film is then wiped with a colored dye and washed clean. Where there is a pinhole, the dye will penetrate under the coating into the pocket caused by the etched-away polymer. This makes the pinholes visible as shown in the schematic in Fig. 8.14. The diameter of the undercut can be measured, and after calibration it is possible to extrapolate back to find the original size of the pinholes. This is not as easy as for metal coatings but does make it possible to identify pinholes and check on substrate or process improvements.

Incident dark-field optical microscopy and differential interference contrast microscopy were the two techniques used to obtain the measurements shown in Fig. 8.16 and Table 8.1. Other techniques could be used [11]. The area used for the analysis was 170 μm × 170 μm with a magnification of 400×. As always there can be a temptation to look for "good" areas or "bad" areas rather than just random

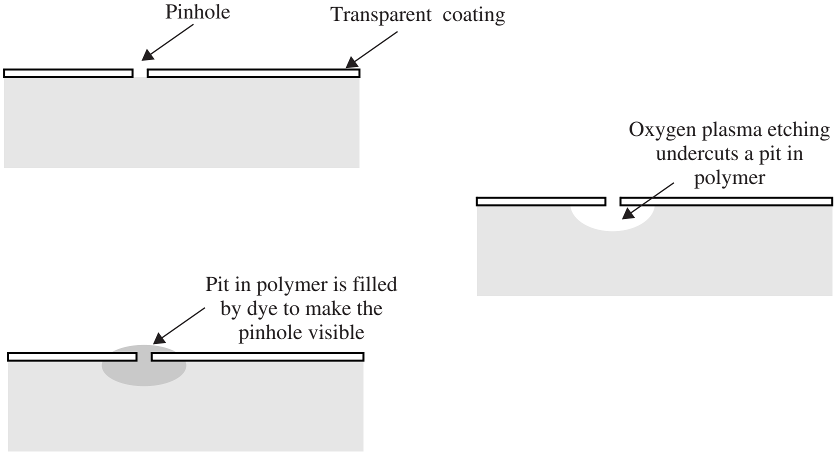


Figure 8.14 A schematic of how a pinhole in a transparent coating can be oxygen etched to produce a pit in the polymer that can be filled with dye to enhance the contrast, enabling the pinholes to be seen, measured, and counted.

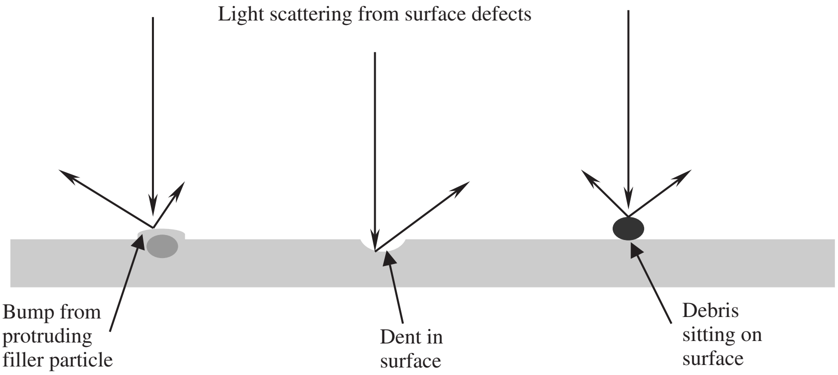


Figure 8.15 Light scattering from surface defects visible by dark-field or differential interference contrast microscopy.

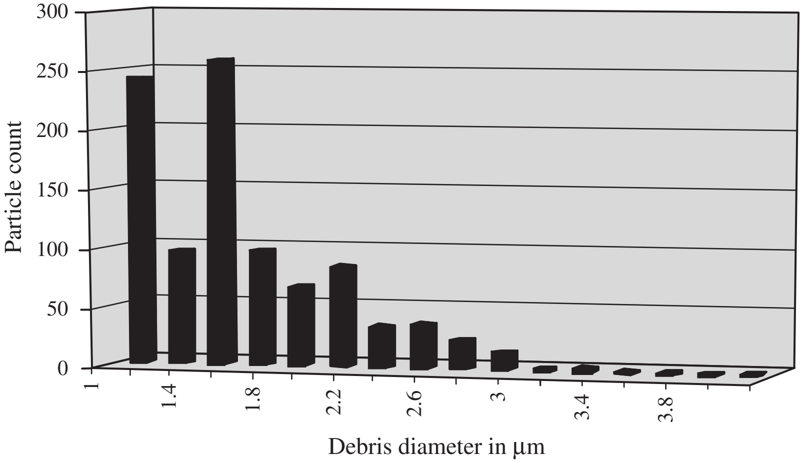


Figure 8.16 A histogram of debris.

areas. To try to take account of this, the average of six different fields of view was taken. Some computerized image analysis was used as a method of trying to reduce the amount of work in counting so many defects. As shown schematically in Fig. 8.15, bumps and dents will also contribute to the defects counted and not just particles on the surface. However, as shown in the schematic in Fig. 8.17, these bumps and dents will contribute to coating defects and certainly are a source of lower barrier performance and so are still relevant as surface defects. The number of defects below 1 μm is huge and is not shown. The smaller the size of the defects that are measured, the greater the number likely to be present in a given area. It is almost impossible to remove defects of 0.3 μm or less from the surface due to the

Table 8.1 A Selection of Films and the Defect Levels

Film Type	Thickness (μm)	Defect Count (Average of Six Fields)	Comments
Polycarbonate (cast)	100	82	
SKC—PET	75	650	
Mylar D—PET	23	400	
Mylar D—PET	75	550−650	
Upilex	75	35	Both sides same
Melinex "O" knurled—PET	75	45−300	
Melinex coex "A"—PET	23	125−150	Average 1−2 μm
Melinex coex "B"—PET	23	400−500	
ANO—PET	23	2500−3000	Not the worst tested

Most were polyester (PET) films from different suppliers with a couple of other materials used for comparison. It is worth noting that after slitting, the debris numbers doubled.

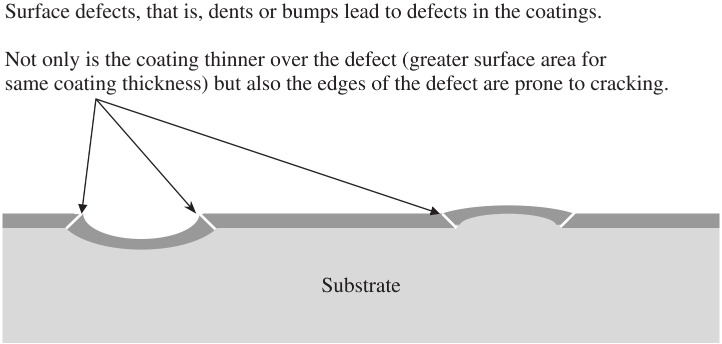


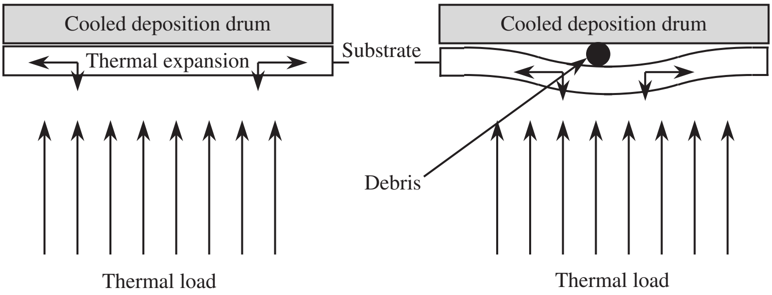
Figure 8.17 Coating defects as a result of indentations or bumps on the surface. The cracks will severely limit the barrier performance of any coating.

strong nature of the van der Waals force; hence, there will always be a high number of very small defects present if only cleaning is considered as a remedy.

Table 8.1 gives a snapshot of a selection of films that were sampled, looking for the cleanest film available. Many more were tested. Nothing we tested was clean enough to be used directly. Since this work was done the requirement for clean surface films has increased. It could be argued that the cleanest any film manufacturing plant is going to be is on day 1 when everything is new and clean. After day 1, there will be an accumulation of dust and debris on surfaces and it is likely that more of this will find its way onto the film substrate. This would appear to be an ever widening gap. It is not the manufacturers' fault and there are limited options

As the heat load is applied the substrate wants to expand but is constrained by the friction between the substrate and cooled deposition drum.

Now there is some debris preventing the web laying flat on the surface of the drum. There is then, locally, less cooling and the web wants to expand. As it is already off the surface this is easy to achieve and the wrinkle starts.



Advice—Keep the drum and substrate clean

Figure 8.18 A schematic showing how debris can be a source of wrinkles.

available to make improvements, most of which have a significant cost associated with them, such as clean air hoods, positive pressure rooms, nonrecirculated air, and direct web cleaning techniques.

One often-overlooked process problem that can have its origin in web contamination, or more specifically debris, is that of wrinkling. As the web passes round a cooled deposition drum, it initially tries to shrink when it is cooled and then it tries to expand as soon as it is hit with the heat load from the deposition process. In most cases, production machines are run very close to the limits of the process. It is often critical that the web has as much heat removed by the cooled deposition drum to keep the web from wrinkling. It has been found that debris on the back surface of the web can hold the web off the cooled deposition drum losing some of the cooling [12]. If the debris is large enough, so that the area of web not being cooled is above a critical amount, it is sufficient to initiate a wrinkle formation (Fig. 8.18). Thus, it is good practice to clean not just the side of the web to be coated but also the reverse side too.

Cleaning to remove the larger debris from the web surface can have benefits for other products such as capacitors. The capacitors can short out at the site of defects. One method to get over this problem is, following metallization, to use a high current to burn away these defects. A better method is to not have the defects in the first place.

In products that require fine-line patterning, the quality of the printing needs to have the maximum size of defects lower than the minimum line widths to minimize pattern problems and scrap levels.

For both of these applications, there would be advantages for using the same process as for obtaining the ultrabarriers, although it would probably only be necessary to use one dyad to achieve the necessary quality.

8.2.1 Oligomers

Polymer films often have unpolymerized monomer residues [13–17]. Not only can these be a source of volatiles that can condense and fall back onto the film surface as a surface dust contaminant but they can also be a cause of poor adhesion.

The level of residuals can be measured by soaking the polymer in a solvent and dissolving them off, a process known as extraction. For instance, PET using 1,1,1-trichloroethane will remove the surface oligomer, whereas chloroform will remove oligomer from the bulk polymer too. The polymer is then dried and the loss of weight gives an indication of the quantity present [18].

Also, evaporative rate analysis can be used to determine more about the polarity of the contamination [19,20]. Variations of this are to repeat the test after a period of time to give a measure of the rate of migration of the oligomers from the bulk to the surface. Other variations are to use different timescales and temperatures. Using mass spectrometry and chromatography also enables additional information to be gathered on the type of oligomer present in the extracts.

MHET: monohydroxyethyl terephthalate
BHET: bishydroxyethyl terephthalate
B-2: linear dimer
C-2: cyclic dimer
C-3: cyclic trimer
TA: terephthalic acid

The volatility of the main monomers and oligomers that are generated from PET resin in descending order is TA > BHET > MHET > C-3. On the other hand, the amount of each in PET resin in decreasing order is C-3 > C-2 > B-2 > BHET > TA > MHET. The MHET amount being much smaller than BHET.

BHET converts to MHET in air or when in contact with absorbed oxygen. BHET and TA are the main volatile substances in PET resins.

Taking PET, the unpolymerized monomer will be of low molecular weight and some can be linked as dimers, trimers, tetramers, etc (Figs. 8.20, 8.21 and 8.23). This oligomer will be present up to an equilibrium concentration of 1.5% by weight [21,22]. These short chains are poorly bound into the substrate bulk polymer and will migrate to the polymer surface over prolonged time or more quickly if heat is applied. This material can be present in different forms, initially amorphous when present in low concentrations but also as hexagonal crystals of up to 10 μm diameter at higher concentrations [23]. The most common form is cyclic tris(ethylene terephthalate) or "cyclic trimer" (Fig. 8.20). The cyclic trimer crystals may sublime at a temperature of 240°C, which is well below the melting point of 315–318°C. Anything deposited onto these oligomers can be easily pulled off as these will fail with either adhesive or cohesive failure of the oligomer. As such, the polymer surface is commonly treated to try to remove or bind-in the low molecular weight material.

The low molecular weight material not only appears on the surface where the vacuum deposited coating is due to arrive but also will be present on the reverse surface too. Any surface treatment ought to be carried out on both sides of the web.

Figure 8.19 PET (Melinex 442) after prolonged heating at 140°C. 2000 × magnification. Scanning electron micrograph showing growth of "mer" units into dimers, trimers, etc.

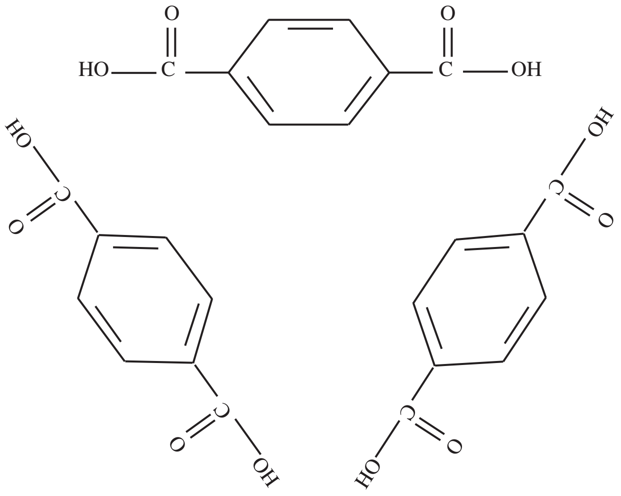
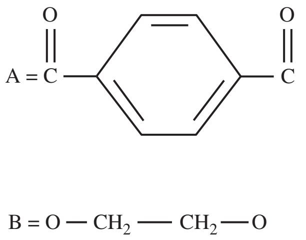


Figure 8.20 Cyclic tris(ethylene terephthalate) "cyclic trimer"—oligomer—two-dimensional representation.



Structure	Molecular weight	Melting point (°C)
H[AB]$_1$OH	210.2	178
H[AB]$_2$OH	402.4	200–205
H[AB]$_3$OH	594.6	219–223
H[AB]$_1$-B-H	254.2	109–110
H[AB]$_2$-B-H	446.4	173–174
H[AB]$_3$-B-H	638.6	200–205
H[AB]$_4$-B-H	830.8	213–216
H[AB]$_5$-B-H	1023.0	218–220
HO-A-[AB]$_1$OH	358.3	>360
HO-A-[AB]$_2$OH	550.5	280–281
HO-A-[AB]$_3$OH	742.7	268–270
HO-A-[AB]$_4$OH	934.9	252–255
HO-A-[AB]$_5$OH	1127.1	233–236

Figure 8.21 Representation of “acyclic” oligomer with the molecular weight and melting points of various structures.

	Melting Point (°C)
Cyclic dimer	175 224 229
Cyclic trimer (B type crystal)	319 317–320 321
Crystalline transition temperature (A type–B type)	199 195
Cyclic tetramer	326
Cyclic pentamer	256

Figure 8.22 Typical cyclic oligomers found in PET.

Material and/or contamination can be transferred from one surface to the other as the roll is wound up. Therefore, if only one surface is flame-, corona-, or atmospheric-plasma-treated, there can still be coating failures due to low molecular weight material that has been transferred. The level of failures could be expected to have been reduced compared to no treatment but not be as good as treating both sides. If the treatment is done in vacuum as a plasma treatment (Fig. 8.23), it too ought to be on both sides. In this case, the contamination can lead to failures in any downstream process such as printing or laminating.

Oligomers will be present in the bulk polymer at about $1 - 3\%$ depending on the process and conditions used (Fig. 8.22). As the manufacturing process is now better understood, the levels have reduced and can be expected to be toward the lower figure. Usually, there is a cost versus performance balance that has to be traded. PET film can be obtained with extractable oligomer levels $< 0.5\%$, but these are sold at a premium.

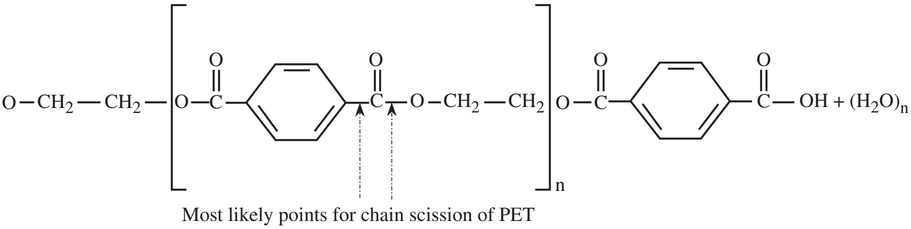


Figure 8.23 The PET polymer chain showing the likely scission points that get broken by plasma treatments.

Another point that may be relevant is that, even for a single type of polymer such as PET, each manufacturer will have a slightly different chemistry and process. Therefore, there will be tiny differences in the residuals left at the end of the processing. One of the differences can be the level of residual oligomers. It tends to take longer to process the polymer to minimize the level of oligomers adding to the process cost. Thus, for products that are intended for the packaging market, where minimizing cost is critical, it is likely that these substrates will have a higher level of oligomer present. Although a premium product is aimed at a market with a higher profit margin, there will be a stronger justification for the higher cost improved process that minimizes the problematic oligomers.

As the film will pass through a deposition zone, it will be subjected to a high temperature. Initially, this appears as a radiant heat load and is then followed by the additional heat of condensation as the coating is deposited. Diffusion pump oil is deposited onto the web to prevent deposition as a method of making patterned coatings, and the molecular weight and melting point of this oil are considerably higher than those shown above for the oligomer. Thus, it is entirely possible that some oligomer is removed by vaporization from the heat of both the radiant source and the depositing material. This may also lead to another set of coating defects similar to the pinholes caused by the debris.

Some high-performance substrates are offered with a planarization layer on the surface to be coated. This planarizing layer is aimed at producing a very smooth defect-free surface, but as a coating it also covers up exuded oligomer. The coating may act as a barrier layer to further oligomer exuding to the new surface. It may not be perfect and stop everything migrating through, but it does reduce the migration rate and so the amount of oligomer on the planarized surface is considerably lower than that on uncoated substrates.

8.2.2 Additives

There are other chemicals added to the polymer melt in order to assist producing the precise film performance that is expected of modern polymer webs. Polymer web suppliers are all trying to increase their market by making their polymer web closely match other existing materials. Thus, by increasing the performance of biaxially oriented polypropylene (OPP), it is hoped it can replace some of the polyester films with the attraction of being a lower cost material. Sometimes some of the desired properties can be enhanced by the use of modified chemistry or additives.

Thus, over the years the list of additives has grown and now can include the following:

Nucleation promoters
Antioxidation
Radical scavengers
UV absorbers
Cross-linking agents
Gloss improvers
Surface active agents
Antistatic
Anti-mist
Slip agents or lubricants
Antiblocking fillers
Colors (pigments or dyes) and/or whitening agents (optical brighteners)
Voiding agents
Viscosity modifiers
Dispersion stabilizers
Flame retardants
Foaming agents

In polypropylene (PP) the crystallization process, which controls stiffness and clarity, is helped by the addition of a nucleation additive such as benzoate salts (sodium, aluminum, potassium) or sorbitols, which are used at levels of up to 0.5%. PP is prone to oxidation and so phenolic or phosphite type antioxidants are added at levels between 0.01% and 0.5%.

Antistatic additives such as glycerol monoesters or ethoxylated secondary amines are used at concentrations between 0.1% and 1.0%. These additives are hydrophilic and also have limited solubility in the polymer; therefore, they too migrate to the surface where they are most effective.

The anti-mist agents are similarly hydrophilic and may be added as an additive or applied as a coating.

Colorants and whitening agents are too diverse to list and may or may not be stable in the polymer.

Slip Agents

Although slip agents are one of the most commonly used additives, for metallizers they can be one of the most problematic. These are the materials added to reduce the coefficient of friction (CoF). They are frequently added during the mixing and extrusion stage and operate by migrating through the polymer bulk to the surface. The slip agents have a designed incompatibility with the bulk polymer; hence, they are not bonded into the bulk but are free to migrate (Fig. 8.24). The size of the

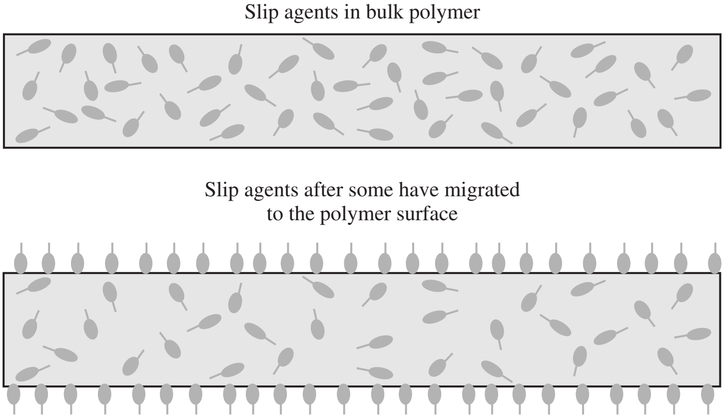
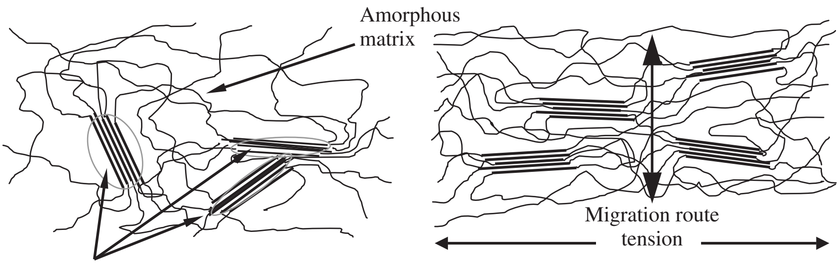


Figure 8.24 A schematic of the effect of slip agents. Initially, the slip agent is distributed throughout the bulk of the polymer. This is shown in the upper schematic. The lower schematic shows what happens after some time or with an increased temperature and lapse of some time. The slip agent has migrated through the polymer and a significant proportion resides on both the surfaces.

molecule determines the ease at which the slip agent will migrate through bulk polymer. The slip agents can be tuned by increasing the molecule chain length by adding or subtracting carbon atoms. Adding more atoms increases the chain length and slows down the speed of migration; it also increases the compatibility with the host polymer.

The speed of migration is also affected by the bulk polymer structure. Polypropylene (PP) is more crystalline than polyethylene (PE) and so the migration is slower in PP than that in PE. The slip agents are solubilized into the polymer when it is molten, but as the polymer cools it is precipitated out of the polymer where it crystallizes and acts as a lubricant. Figure 8.25 shows that if there is a proportion of amorphous polymer, there will be a migration route through the polymer.

Slip agents not only reduce the CoF but also reduce adhesion between the mould and injection-moulded polymer. The slip agents have exactly the same effect on metallization and reduce adhesion. It is worth noting that there is no control over which surface the slip agents appear on. They will migrate to both surfaces, thus if preparing a surface for vacuum coating, it is no use treating one side only before putting the roll into the vacuum system. After an atmospheric treatment, the side treated will be brought back into contact with the other surface as the roll is wound up and hence will become recontaminated. Vacuum treatment will allow the surface to be coated before it is recontaminated; however, the freshly deposited coating will become contaminated as the roll is wound up. Thus, there may not be an adhesion problem with the vacuum coating but there may be on the next coating applied to the vacuum deposited coating.



Where polymer chains run parallel, crystallites can form. The three crystallites shown here are in random orientation. A single polymer chain may be part of several crystallites with intermediate parts of the chain being in amorphous regions.

In pulling tension on the polymer, more of the polymer chains are brought in close proximity to each other and near to parallel. If heated, these will form crystallites that are oriented in the direction of the tension.

Figure 8.25 A schematic showing how polymer films change with orientation and how migration can be restricted with increasing crystallinity.

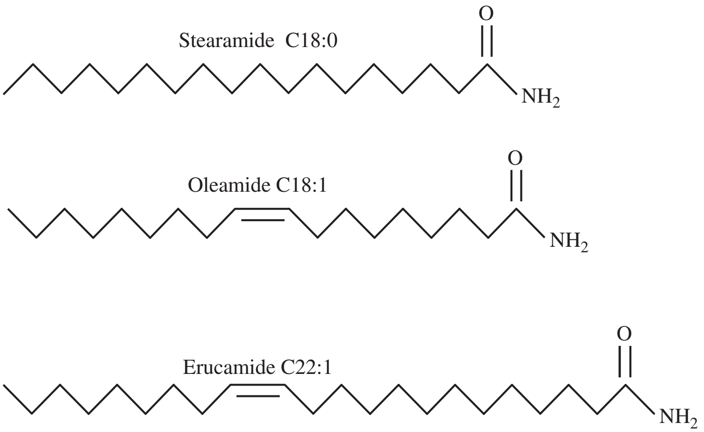


Figure 8.26 A schematic of the three basic slip agent structures.

Some slip agents are produced by the amidization of long-chain fatty acids. Examples of the most commonly used of these are stearamides, erucamides, and oleamides (Fig. 8.26).

Erucamides are longer chain, more heat stable, and more oxidation resistant than oleamides and with a lower vapor pressure create fewer volatiles during high-temperature processing. The oleamides migrate through to the surface more quickly and are sometimes referred to as “fast blooming.”

The aim is to provide sufficient slip additive so that with a suitable time for migration no more than a monolayer will have accumulated at the surface. More than a monolayer does not make any further improvements on the slip performance.

Stearamide is prepared by amidation of stearic acid (C18:0): melting point 98–104°C
Oleamide is prepared by amidation of oleic acid (C18:1): melting point 66–76°C
Erucamide is prepared by amidation of erucic acid (C22:1): Melting point 79–85°C

Waxes can also be used as slip agents. Waxes are similar to oils except they are solid at ambient temperature and generally have a melting point in excess of 40°C. A very interesting evaluation study with microcrystalline waxes clearly demonstrated that the harder the wax, the better the slip properties.

Antiblocking Additives

Slip Effect

This is the term applied to polymer films where there is the sliding of parallel polymer web surfaces over each other or of one polymer surface over some other surface.

Blocking

This is almost the opposite of slip. It is where the surfaces do not move over each other. An extreme case of blocking can also be where the web, once wound, cannot be peeled apart. This can occur during processing and/or during storage of the film. This can be made worse by processing at elevated temperatures and/or increased pressure. Thus, tightly wound warm films are much more likely to block than lower hardness ambient temperature rolls. Blocking can be controlled by the use of antiblocking additives and/or slip agents.

The tendency to block can be measured in accordance with ASTM 1893–67 and ASTM 3354. The first of these tests measures blocking and the second reblocking.

Blocking is worse for smoother film surfaces, for films with high electrostatic charge and for films with a high surface energy such as those corona treated.

Antiblocking Additives

These are fillers that are added to the polymer that will increase the surface roughness. The effect is that the two surfaces are kept apart by the fillers that protrude from the surface. This in turn reduces the contact surface area and when winding in air guarantees an amount of entrained air between the polymer surfaces. The effectiveness of the filler is dependent upon the number of fillers and the size and hence height that the fillers protrude from the surface. Antiblocking fillers do not migrate after the polymer has solidified; therefore, only a limited amount of the filler added will be present at the surface. As they increase the surface roughness, they increase the haze and reduce the specular reflectance. Typically, the haze increases by

0.4−1.0% per 1000 ppm of silica filler used. Thus, there is a balance between the ease of handling and the optical performance.

It is also common for a combination of antiblocking filler and slip agent to be used in order to minimize the impact on the optical performance. Also, it is common to find coextruded films with a thin outer layer including the filler to provide the handling performance, but because the bulk of the thickness does not contain filler the optical quality is kept high. Filler types can vary in shape, size, and hardness. Some examples are as follows:

Synthetic silica: high surface area, hydroxylated and microporous surface. A good match of refractive index for PE and PP and used to make highly transparent films.

Natural silica: a different mixture of shapes and sizes and often contains impurities that the synthetic silica does not. Cheaper than synthetic silica.

Talc: magnesium hydrosilicate, a lamella type of soft rock that has a refractive index that is also a good match to PE and PP.

Limestone: a low cost filler. Calcium carbonate and sometimes a mixture with magnesium carbonate. These are used in lower quality film applications.

HDPE, paraffin, and carnauba waxes are typically used in coatings to counteract blocking.

The use of antiblocking fillers can reduce the CoF down to 0.3−0.4, which may still be higher than required and so slip additives may be used in conjunction with the fillers.

Coefficient of Friction

The resistance to slip is measured as the coefficient of friction (Fig. 8.27). The measurement of this gives two measures, the static CoF, which is the force required to initiate slip and the kinetic CoF, which is the force required to keep the movement going at a predetermined speed. The measurement of CoF of polymer films is described in ASTM D1894−73.

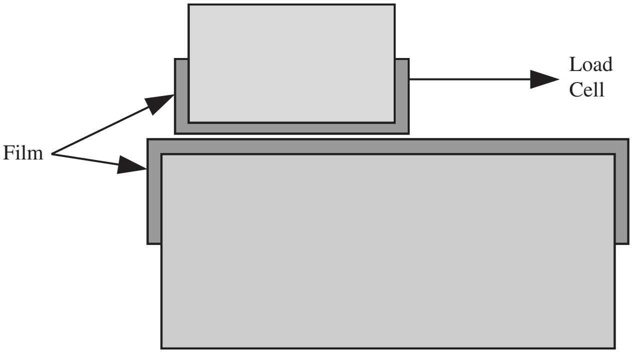


Figure 8.27 Method for measuring coefficient of friction. Two layers of film are in contact with each other with an applied load, and the force used to pull one film over the surface of the other is measured.

The CoF of LDPE can be as high as 0.7 but with 0.1% slip additive it can be reduced to below 0.2, where 0.16–0.2 CoF is regarded as acceptable for easy processing.

8.3 Polymer Substrate Cleaning

Ideally the polymer web manufacturers should be encouraged to take steps to improve the cleanliness of the polymer that is made available to customers. However, until that is done it remains up to those coating the polymer to try to recover the quality of the polymer surface.

There are several techniques that can be used; some are suitable only for use outside the vacuum system, whereas others have been developed further and can be used as an integral part of the deposition process.

One of the older methods of cleaning the surface is to use a sticky surface in contact with the surface to be cleaned and rely on the debris sticking to the sticky surface in preference to the substrate surface. This can be done using either a tack roll in direct contact with the surface to be cleaned or a tacky intermediate roll that transfers the debris between the substrate to be cleaned and a high adhesive roll [24,25]. A schematic of this is shown in Fig. 8.28.

This technique has been used just before the windup on mill rolls of up to 10 m width.

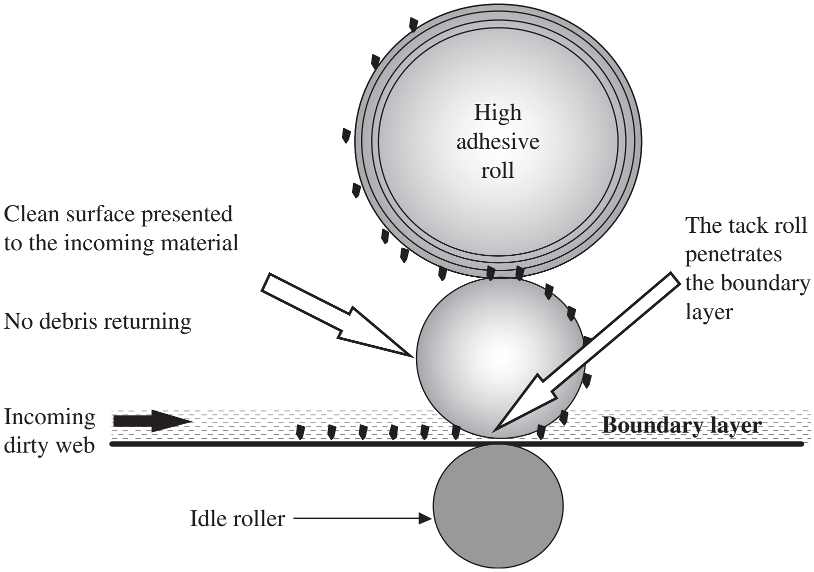


Figure 8.28 A schematic of the tack roll method of substrate cleaning.

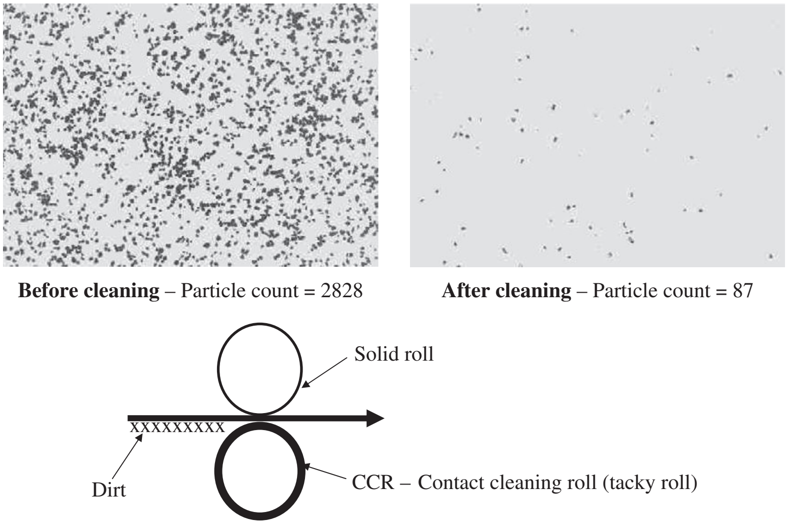
Although the schematic Fig. 8.28 shows one side of the web being cleaned, it is better if both sides are cleaned as the contamination is likely to be on both sides. Any dirt on one surface can be transferred to the other surface as the web is wound into a roll. Hence, cleaning one side is of limited benefit because the cleaned side will be recontaminated from the other surface during the next windup.

Figure 8.29 shows the benefit of using this type of cleaning process. The tacky rolls can be used in other configurations but this can reduce the effectiveness [25]. The effectiveness can also depend on speed with less debris removed at higher speeds. The tacky roll will be a material mismatch to the web and so will introduce a static charge; therefore, it is common to have an electrostatic neutralization unit placed immediately after the tacky roll nip.

There can be some problems with this type of cleaning method. Historically there have been cases where the tacky roll has left residues on the web surface and these residues have been a source of poor adhesion to the subsequent metal coating. Development on the elastomer composition means that modern tacky roll systems are no longer reported leaving behind residues. The other failing has been that there has been so much debris on the surface of the web that the adhesive roll has been covered in debris such that it has lost its adhesive performance and no longer collected any additional debris. This led to the development of ways to replenish the

Nip efficiency test – Cleaning efficiency = 96.9%

(10 μm particles on film) Photographed at 125X magnification



Before cleaning – Particle count = 2828

After cleaning – Particle count = 87

Figure 8.29 Images showing the benefits possible from cleaning webs prior to vacuum coating (25). Images courtesy of Polymag Tek, Inc.

adhesive surface with tear-off layers, or higher surface areas using belts rather than rolls. These solutions have been based on the removal of the debris at atmospheric pressure where operator intervention is available. The other problem is that if the web is rewound with a cleaning roll it will still generate a charge on the polymer surface while being wound through the process. If the system is not enclosed in a clean area, such as a class 1000 cleanroom or better, the surface can become recontaminated from attracting the airborne dust that is naturally present in most factories.

This technique has been tried inside a vacuum system. Under vacuum there are different problems. The adhesive can become dried out because of the vacuum removing any volatiles from the surfaces. Thus, in a relatively short time the adhesive loses its effectiveness and no longer collects the debris. The adhesive roll is also not easily accessible to the operator because of being under vacuum. Hence, the adhesive surface, when it becomes saturated with debris, cannot as easily be refreshed by an operator stripping off the old adhesive layer and exposing a new adhesive surface. The advantage of using this technique under vacuum is that there is no air and hence no airborne debris to recontaminate the surface once the loose debris has been removed.

A recent development has been to texture the tacky roll using a nanometer scale surface roughness as a method of trying to make the surface when pressed onto a dirty surface conform better to the surface and in doing so pick up more of the debris. The claims are that this modification enables smaller size debris to be picked off [26]. The second development has been to make the tacky roll slightly conducting in order to reduce or eliminate the generation of any static charge so that following the use of the cleaning roll the web does not immediately start to attract more debris onto the surface.

Another method of cleaning the substrate outside the vacuum system is by using a combination of electrostatic discharge, ultrasonic gas pulsing, and vacuum extraction. The electrostatic discharge is used to try to neutralize the web surface. A source of clean dry air is pulsed at an ultrasonic frequency and directed at the polymer web surface. This neutralized and pulsed gas jet shakes the surface of the polymer and dislodges debris from the surface. The vacuum extract is used to suck away any of the debris generated by this shaking. This technique is capable of removing debris down to a size of approximately 0.3 μm provided the debris is not embedded in the surface and is only held on the surface by the electrostatic charge.

The techniques shown in Fig. 8.30 are less effective than the adhesive roll in contact with the surface. There can be a tendency for the web to be cleaned at a high winding speed and this can limit the cleaning performance of the technique. As the polymer web is wound faster, there is a thicker boundary air layer that is dragged along with the polymer surface. This boundary layer can be greater than 50 μm and this air layer needs to be disrupted all the way to the polymer surface if as much of the debris is to be removed as possible. The faster the web is wound, the thicker this boundary layer becomes. Hence, the combination of the thicker boundary layer plus the shorter residence time in the active area means that the cleaning becomes less effective.

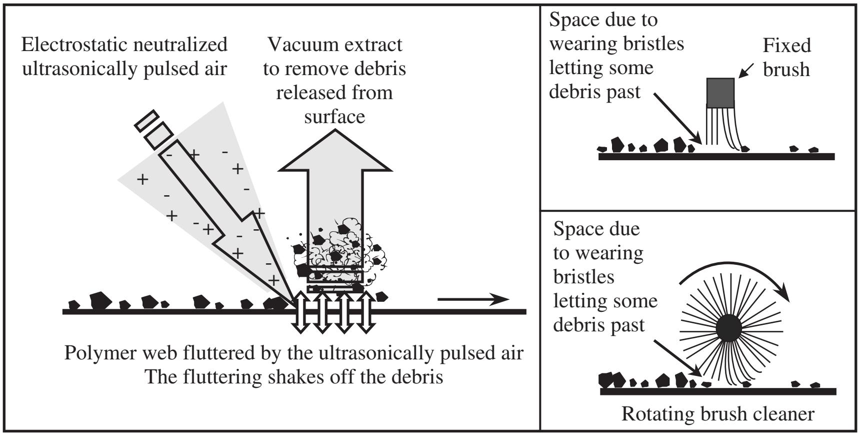


Figure 8.30 The schematics are of an ultrasonic cleaning system on the left and brushes on the right.

Cleaning in vacuum tends to be limited to removing organic contamination by plasma treatments. Many hydrocarbon residues can be removed by use of a glow discharge and a reactive gas such as oxygen. The physical bombardment of the surface ejects atoms into the plasma and also there may be some chemical sputtering by the bombardment of the reactive gas. The flow of gas through the zone cleans away the by-products keeping the recontamination rate low. The additional bonus of this type of cleaning is that the plasma effectively removes any electrostatic charge and any loosely bound debris can fall off, assuming the web to be in an orientation that allows for this.

Ultraviolet (UV) lamps can also be used to remove some hydrocarbons and also water from surfaces. The UV can also generate ozone that is an aggressive etchant and will also assist in cleaning the surface. The UV will not discharge the surface and so some debris may be carried forward, still held by the electrostatic surface charge.

8.4 Polymer Surface Etching

Plasma bombarding the polymer web surface can do several things to modify the surface that will have an effect on the adhesion of any subsequent coating. The bombarding atoms can break bonds, break chains, cross-link chains, or attach to reactive sites [27]. It becomes very difficult to predict what will happen to a surface and which gas will be the best for modifying the surface. In many cases, the development is done by the "suck it and see" method. One of the reasons for this may well be that the polymer surfaces are frequently modified by proprietary treatments or coatings. This means that there is no certainty that for a PET film there

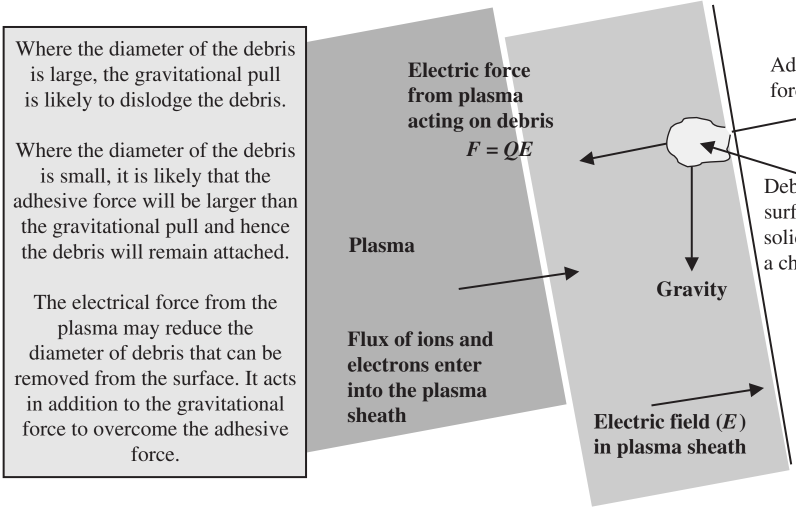


Figure 8.31 A schematic showing the forces holding debris to a web surface [28].

will be a PET surface or similarly for an OPP film there will be an OPP surface. So, it is probably not too surprising that what works on one film may not be as effective on a different grade of the same type of film.

Surface cleaning is regarded as beneficial; it removes loosely bound material and so any deposit will immediately have improved bonding to the true surface. This not only includes dust and debris that fall off once the electrostatic charge is removed but also includes removal of low molecular weight monomer or polymer fragments (Fig. 8.31).

Beyond the removal of loosely bound material, there are four other possibilities that can increase the bonding strength. These are to either raise or lower the surface energy of the surface and to inflict more physical damage to provide an increase in surface area and a more physical key. In general, increasing the surface energy will increase the wetting and adhesion of any subsequent coating. The fourth option is to functionalize the surface by chemically altering the bonding sites.

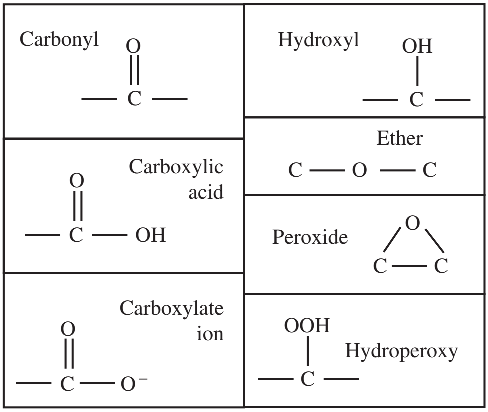
It is worth noting that the removal of any electrostatic charge with the expectation that clouds of debris will suddenly fall from the surface is sadly misguided.

As can be seen in Table 8.2, the very big debris may well be removed by passing the web over a roll that allows gravity to work and let the debris fall off the surface. As for the debris that is 1 μm or less, the van der Waals forces dominate and some positive action is required to force the debris off the surface [29].

If the web has been exposed to moisture at any time, such as winding through a slitter in a high humidity atmosphere, it is possible that, if the debris is hygroscopic, there will be water also helping bond the debris on the surface. Even if the moisture has subsequently evaporated, there may be a residue that can also act to glue the debris to the surface. Thus, with larger particles gravity is not enough to

Table 8.2 A Table of the Forces Holding Debris to a Surface

Force type	**Debris average diameter**					
	1 μm		**10 μm**		**100 μm**	
	Force (millidynes)	**%**	**Force (millidynes)**	**%**	**Force (millidynes)**	**%**
Van der Waals	0.4	99	4	97	40	29
Electrostatic	0.005	1	0.05	1	0.5	
Gravity	0.0001		0.1	2	100	71
Total	**0.4**		**4.1**		**140**	



All PET is pre-treated on at least one side, many grades do not have the expected PET surface.

Surfaces can be:-
Amorphous PET
Crystalline PET
Melamine formaldehyde
Latex AC201
Elfulgin
Styrene/maleic anhydride

Optimal treatment for one grade may not be as good for other grades.

Figure 8.32 On the left are some of the functional groups that can be formed by plasma treatment. On the right is an indication of what might be on the surface of some PET webs other than the expected PET.

loosen them from the surface. Again, some physical action is required (see Section 8.3).

So, using a plasma that is conducting while neutralizing most of the surface charge does not do a lot for cleaning the surface of debris. The main function of the plasma is to work on the surface at the more atomic scale by removing material atom by atom or using energetic particles to break bonds that increase surface reactivity.

Figure 8.32 shows some of the functional groups that may be produced. In theory once you have established a surface treatment for the polymer web, it should work for that material every time. However, it is also common that changing the supplier will result in the treatment not delivering the same results and thus needing to be reoptimized.

On the right of Fig. 8.32 is a list of some of the common surface treatments for PET web. Suppliers do not always let the customers know what the true surface of

Table 8.3 A Summary of Typical Treatment Gases and the Effects

Treatment	Effects of Treatment	Other Comments
Argon plasma	Creation of active sites Activation of existing functional groups Increased surface energy and wetability	Argon does not form volatile compounds, cannot remove hydrocarbon contaminants
Oxygen plasma	Chain scission and cross-linking	Modification depth typically about 10 nm
	Generation of oxygen-containing functional groups: C−O, C=O, O−C=O	Concentration of functional groups almost independent of the type of polymer
	Increased surface energy and wetability	Will remove hydrocarbon contaminants
Fluorine-containing plasma	Generation of fluorine-containing functional groups: CF, CF_2, CF_3 Decreased surface energy and wetability	As for oxygen
Nitrogen plasma	Generation of nitrogen-containing functional groups: C−N, C=N	As for oxygen
Low-dose plasma	Smoothing due to structural relaxation	
Ion beam up to 2 keV	Increased density of C−C bonds, cross-linking, carbonization, sputtering, and roughening Improved barrier properties	Modification depth may be as deep as 200 nm

the PET is; at best they will disclose if it is pretreated. Thus, it may be hard to predict which plasma treatment will be best and hence there is often a "suck it and see" approach to choosing the process.

The use of different gases, pressures, and powers gives the control of the process. Table 8.3 gives a list of the most commonly used gases and the treatments they provide.

The most commonly used gas is argon because it is inert. Typically, the target is to improve the adhesion sufficiently to pass the "sellotape" test. If a greater amount of adhesion is required then it is common to move to oxygen, air, or an argon/oxygen mixture.

8.5 Higher Specification Polymer Substrates

The typical evolution of polymer substrates is that the customer describes to the supplier what they intend to use the film for and the supplier suggests what they think is the best material. The customer then makes some product and tests it out and if there is a problem they may take the information back to the film supplier who may suggest an alternative grade of material with a slightly different balance of performance or if the best option material is already being used may suggest some substrate development. This could involve a small change in the film processing, such as a different level of fillers or a different coating. In some instances, a larger change is needed such as a coextrusion where a thin surface polymer is different to the bulk of the polymer. In this way, substrates are varied and improved. It does usually require a substantial volume of business before there is a cost justification for a new grade of film with all the work that goes into the development. The electronics and display industry has demonstrated a sufficiently large market opportunity that many film suppliers are vying to meet the exacting needs of this industry and supply them with a better film.

The improvements required have been in material stability, cleanliness, smoothness, low oligomer levels, and low moisture content while retaining the original properties that made the film a promising possibility. Leading the way in this rush to satisfy the electronics industry is PET and polyethylene naphthalate (PEN). These materials can be supplied with low extractables, moisture, and oligomer, as well as heat stabilized and also cleaned and coated with a planarizing layer that smoothes and seals the surface. This enables the substrate to be heated during processing up to much higher temperatures than the standard materials with minimal shrinkage and without an increased level of oligomer appearing at the surface. The cleaning and smoothing enables more perfect coatings to be deposited with fewer defects being generated from the substrate roughness or from contamination particles.

Most standard film is biaxially oriented and then cooled with an amount of residual stress still in the film so that when the film is heated this stress will act on the film and shrink the film. The higher this processing temperature, the more and quicker this shrinkage will be. In the electronics industry, where many layers are used in conjunction with each other to make a final product, it is preferable to be able to keep different layers in register with other layers. This is easier to do if the film is stable. To reduce this shrinkage problem, the film can be heated under a low level of tension and given time for the polymer chains to move and reach an equilibrium position, and in doing so the stresses are reduced. The higher this heat stabilization temperature, the higher the temperature at which the film can be used in processing. Even so, a film that has been heat stabilized to a quite high temperature, where it can be used for tens of minutes, may still be used at a higher temperature than this for a very short time and still the shrinkage will have been reduced. Although for vacuum deposition PET and PEN are most widely used, other materials such as polypropylene and nylon can also be heat stabilized, where not only does this help improve the thermal stability but it also reduces the water content.

The planarizing coating that is used to smooth the surface also acts as a block to the migration of oligomer and it takes much longer for the surface to become recontaminated. However, it is not perfect, and the longer and higher the storage temperature, the higher the level of oligomer that will be present compared to if the film were used quickly after planarizing.

Each of these improvements takes time and increases the cost of the substrate; therefore, it is important to be certain that the improved characteristics are definitely important to the product before specifying such a specialized film.

8.6 Metal Web and Surface Quality

In general, the same problems that cause winding difficulties with polymer webs will do exactly the same with metal webs too. The thickness profile is just as critical as is the quality of the web edges. One difference between the metal webs and polymer webs is the difference in the material elasticity; the metal webs can be less tolerant when winding with imperfect rolls. With thin metal foils, the first indication of a roll problem can be that the web has snapped or more accurately torn across.

Metal foils have the advantage that measuring the profile accurately is more easily achieved than with polymer films.

The method of producing the metal foils is different than the method of producing polymer webs. The metal starts out as an ingot or continuously cast as a thick foil. This starting material is passed between rolls with a gap set slightly less than the metal thickness, and as the billet is passed between the rolls it is squeezed thinner. In doing so the billet is elongated. This process is repeated many times until the desired metal thickness is achieved. Metal work hardens and so it may have to be annealed periodically to enable further working without any failures occurring due to embrittlement and stress cracking. The crystal structure of the metal can change many times during this whole process, with grain refinement, recrystallization, and grain growth all being possibilities.

Some rolling mills use double rolling where two foils are rolled at the same time with the inner surfaces ending up matt compared to the exterior air surface. These foils are rolled together but peeled apart as a final process.

The foils can be rolled at speeds of up to 2500 m/min and over 2 m wide, producing foils of down to 6 μm thick.

The surface quality can both be a reflection of some of these internal effects on the crystal structure as well as of the surface quality of the rolls used in the rolling mill. The profile of the foil can also be affected by the quality of the rolling mill. The work necessary to squeeze metal sheet thinner is large and it is common for the rolls to suffer from deflection and bending, which means the foil may well be thicker in the center unless something is done to counteract this problem.

Aluminum metal foils have always been held up as perfect barrier materials that aluminum metallized polymer films have difficulty in matching in quality. However, this is not strictly accurate as most foils have cracks or pinholes. Table 8.4 shows some typical values for pinholes that can be expected [30]. These are not guaranteed minimum values but only guidelines and I have seen maximum measured figures five times or more of these numbers. The source of the pinholes can be from rolling debris, aluminum fines, constituent silicates, or depressions

Table 8.4 Details of What One Foil Supplier Publishes as a Number of Pinholes that Can be Expected for Foils of Different Thickness

Foil Thickness (in.)	(μm)	Typical Pinhole Count/ft^2
0.00025	~6	41
0.00030	~7.5	20
0.00035	~9	12
0.00050	~12.5	6
0.00070	~18	1
0.00100 and above		0

Metal foils are not perfect—they contain cracks and pinholes.
Pinholes in aluminum foil—typically 10–50 μm, but may be oval and as large as 75 × 200 μm.

from the thicker foils that become pinholes as the foils are thinned down. Grain boundaries, as the foil is thinned down, can become cracks in some instances.

Metal foils used for applications such as photovoltaics may also need a primer layer similar to the planarizing layer on polymer films. This primer layer may serve one or two purposes. It may be required that the substrate is nonconducting to prevent shorting between cells and so an insulating primer layer may be required. The other possible need for a primer layer is to act as a barrier to prevent something in the foil from migrating into the photovoltaic device and degrading the performance. Metal foils are generally rougher than polymer films [31] and so a primer or planarization layer may also help to smooth the surface too.

8.7 Metal Surface Contamination and Cleaning

It is common when processing metals to use coolant and lubricant to make the process easier. It is equally as common for the metal foil to be cleaned to remove all traces of any lubricant that could act to lower the adhesion of any coating applied to the finished foil. These cleaning treatments can include acid or alkaline etches as well as a variety of different wash solutions.

While these cleaning processes may be adequate for plating, galvanizing, or similar such coating processes, they are often not sufficient for vacuum coating processes.

In vacuum the foil is like any other metal surface and will outgas not only the water that is present on all surfaces but will also bring to the surface some of the other processing liquid residues that have been absorbed deep into the grain boundaries. These will exude to the surface where they will inhibit the adhesion of any coating that is deposited in the vacuum. The deposition source usually adds a heat load to the substrate, which will increase the rate at which the contaminants are exuded.

Simple washing even including ultrasonic activation tends not to displace these contaminants. One of the best methods successfully utilized has been heating the substrate using a sweeping beam electron gun. This takes the temperature high enough to drive out most, if not all, of the residues. It may even carbonize and/or vaporize any hydrocarbons. This in itself does not necessarily make the surface clean enough to coat and it may still be necessary to use an oxygen-containing plasma to complete the cleaning process [32−37].

8.8 Paper

It does not matter if the paper is to be metallized or just vacuum plasma treated, it will have to be pumped down in a vacuum chamber. Compared to polymer webs, paper adds another variable to the coating equation or, more accurately, amplifies one of the existing variables. Moisture is the variable. There are two reasons for the increased interest based around the moisture content of the paper. Paper is hygroscopic. The moisture content can change to match the surrounding atmosphere by several percent. Indeed, if the relative humidity is 95% or greater, there may be a water content of near 20% in the paper [38]. Obviously, this will make the pumpdown time extremely slow, which, as it can significantly affect productivity, is undesirable.

This means that it is well worth considering storing the paper in a low-humidity air-conditioned environment prior to metallizing. At room temperature and with a relative humidity of around 50%, the moisture level in the paper will be around 7%. Obviously, with large rolls it will take some time for the moisture to be reduced and so the rolls may have to be stored for a few days to minimize the moisture content.

That brings us to the vacuum deposition process. To assist pumpdown, it becomes critical that the standard pumping system is augmented using cryopanels. These panels are specifically designed to pump water well and will often have pumping speeds over 100,000 L/s. These cryopanels work by condensing and freezing the water onto the cold surface [39−43]. This builds up an ice layer. Unfortunately, the thermal conductivity of ice is not as good as that of the copper pipe and so the performance of the cryopanels pump can decline. The capacity for water and the pumping speed can depend upon the loading too; if there is a very high water load initially, the ice that grows may be porous and this too will reduce the thermal conductivity. As the ice thickness increases, the surface temperature of the ice layer will rise to the point where the sticking coefficient starts to reduce, which results in losing some of the pumping performance. These cryopanels are usually on an automatic sequence so that as soon as the deposition process is stopped the panels start to heat and the ice begins to melt. The aim is to get the panels warmer than ambient temperature just as the vacuum chamber door is opened. This makes the surface warm enough so that water will not condense on the surface. This requires that there is a bucket located to catch all the water as it melts from the ice that had accumulated onto the cryopanels during the process. For a large roll that weighs several tonnes this can be several kilograms of water.

The paper will become stiffer and more brittle as it loses some of the moisture and so it is often preferable to remoisturize the roll following metallization. This may be done by winding the roll through a simple winder while in a high humidity atmosphere so that the entrained air is moistened, and this will be absorbed bringing the moisture content in the paper up quite quickly.

It is important to manage the moisture content as the metallization process will be significantly different for a roll with 10% moisture content and one with 5% moisture content. Water will want to react with the aluminum to make aluminum oxide and so there is a danger the reflectivity will be compromised and there may also be yellowing if the water is not pumped away as much as possible.

Papers also have a surface that may have a low-wetting performance. Typically, pure cellulose is hydrophilic with a water contact angle around 20–30°. An oxygen plasma treatment can improve this [44]. Similar to polymers, paper can have many surface treatments to whiten, smooth, and generally change the surface characteristics. Thus, changing paper suppliers may result in treating a different surface composition with different results. Metallized paper commonly has a filled coating added onto the surface to be coated. This filled coating smoothes the surface and so helps to increase the brightness and reflectivity of the metal surface.

8.9 Foams, Nonwovens, and Textiles

In many respects, foams, nonwovens, and textiles can have some of the same problems as paper in that they have a very high surface area to the material and so can hold more water than standard polymer webs. For some of the woven papers they can also be hygroscopic and so have the worst of both worlds, hygroscopic and very high surface area.

Many of these materials are also either very stretchy in nature as in foams or very fragile as in some of the nonwoven materials [45]. This means that the tension available to hold the materials onto the cold deposition drum may not be very high and so the cooling of the web may be poor and this will limit the deposition rate and winding speed.

There are an increasing number of processes available for both the plasma treatment of foams and textiles to change the wetting, dye uptake, and functionality of the material [46,47]. Most of these will require either a plasma treatment zone or deposition zone.

Many of the webs are not just porous but also optically translucent. In some cases, this includes the problem that if the deposition is done around the standard deposition drum, the drum will become coated. There are two ways around this. If a machine is being designed specifically for deposition onto these materials, then it becomes worth considering free-span deposition [48–50]. Here the web can be predeposition and postdeposition cooled using chilled rollers but passed in free span over the deposition source. This allows material passing through to be collected on a shield behind the web and also coating across the full width reducing the need for downstream slitting.

If there is not the option of a specifically designed machine, there is the option of putting a sleeve on the deposition drum that is disposable. Simple solutions would be a thick polymer stuck to the surface or aluminum foil similarly wrapped around and stuck down. Neither is ideal but both would work.

In the case of plasma treatment the open nature of the structure can be a bonus, allowing the plasma to penetrate deeper into the weave and producing a more uniform surface treatment [51,52]. In this case, free span offers the option of fully immersing both sides of the material in plasma.

8.10 Cores

Cores can often be an overlooked component in the roll- to- roll vacuum deposition process but can often have a significant effect on the final product although only because of problems with the cores. The cores should be straight and concentric and ideally clean and free of damage. If the cores are not straight or are not concentric, the unwind roll will wobble during unwinding and this will make controlling the tension difficult or impossible depending on how bad the wobble is. Damaged cores can lead to damage to some of the webs or can lead to higher debris levels and pinholes.

There are many different types of cores that can be used in vacuum systems. The most common are listed below:

Spiral wound paper
Polymer impregnated paper
Polymer: extruded pipe
Metal

Cores are often cut to length from a longer stock tube.

The common perception of the core is that it is a commodity item and needs to be as cheap as possible [53,54]. This may be true for a low-cost web product with a tight profit margin but may easily be a false economy for some of the higher added value products.

The cheapest of the core materials is the spiral wound cardboard core. The disadvantage of cardboard is the amount of dust that is associated with the material. This is particularly true if they are cut from a longer tube, as most are. In small production sites, it is common for all activities to be in the same work area and so the airborne debris from the core cutting operation will increase the particle count in any adjacent vacuum system area. It is likely that in this environment the pinhole count on thin metal coatings (or any other vacuum deposited coating) will be high.

One solution adopted for reducing the shedding of debris from the ends of cardboard cores is to have the ends sealed using a lacquer or even the whole core lacquered.

Moving the core cutting activity out of the vacuum system area and using sealed cores can be a significant improvement. A common method of mounting the cardboard cores is with tapered chucks. It is usual for these to be firmly pressed into the cardboard and this action can break the sealed surface. Thus, if cardboard cores are reused, the quality can decline as the sealed surface is broken and debris is shed from the chuck location surfaces.

The next step up is to use a laminated polymer or paper composite core. This is a much harder material and more resistant to damage. The surface quality is both smoother and more concentric than the plain cardboard cores.

Polymer extruded cores have been used. These are regarded as a compromise option. There is a larger industry producing polymer pipe for other industries. As the volumes are high, the cost of the pipe is low and so it is regarded as a cheap source of a low dust material. Care needs to be taken in sourcing the pipe as not all suppliers produce pipe that is straight. It is no use having a high tolerance on the winding system only to have a poor core to wind on to.

The higher cost option is to take the extruded pipe and machine it to get the location and winding areas straight and concentric but this puts the cost up.

The highest cost cores tend to be the metal cores. These are often custom made and they get used where the cores stay within a loop that ensures they are recycled.

Metal cores are the hardest surface but they too, if damaged, will cause problems. Cutting film off against the core will leave a burr that will need to be polished off if the surface of the core is not to become roughened. Dropping the core can put a permanent set into it so that is lobed.

All the cores have three key parameters that need to be looked at. These are waviness, roughness, and straightness.

Waviness is the variation in concentricity. This is not a problem at low speeds, but as the coating speed increases it gains in importance because the variations in concentricity will cause variations in tension and in extreme cases will cause vibration in the winding system that may worsen the tension variations.

Roughness of the core falls into two parts: the permanent defects in the surface that might be removed by polishing and the other is the transient roughness because of debris. Metal cores are easier to keep smooth and clean than cardboard ones.

As the width of webs increases it can be more difficult to maintain the straightness of the cylindrical cores which can result in winding problems. Over recent years, the trend has been to increase the core diameter from 3 to 6 in. and more recently to 10 in. There were two reasons for this: one was because the rolls were increased in length from 10 to 40 km and this required a stronger less compressible core. The second reason was that as the widths increased from 1 to >3 m, the straightness of the cores became much more critical and it was harder to produce straight cores at the smaller diameter. Warped or bowed rolls can cause uneven tensioning of the web, vibration at high speed, or even machine direction (MD) wrinkles.

8.10.1 Source of Problems

The most common problems are the damage put into the polymer web from the core by debris or attaching the web to the core.

Attaching the web can be done using an adhesive tape or adhesive strip applied to the core. The aim is to attach the web to the core in perfect alignment. The web is pulled through the system and over the core by hand. Once the alignment is considered acceptable, the core is rotated round and this brings into contact an area of the core that has an adhesive applied. The adhesive contacts the web and then the excess web can be cut away and then the core is rotated to make sure the adhesive has gripped the web sufficiently to hold tension. The quality of this attachment depends upon the adhesive being thin and it being applied across the full width. The adhesive is supplied on a release paper and once applied to the core the backing paper can be removed leaving only the adhesive behind. This is the thinnest adhesive that is used. The same can be done using double-sided tape, but in this case the tape comprises two layers of adhesive sandwiching a layer of paper and so this is considerably thicker than the single adhesive layer.

It is worth noting that the adhesive is best used in the transverse direction (TD). If the adhesive were applied in the MD, there would be a slightly thicker diameter at that point and this has the same effect as a gauge band in the polymer web. The tension would be slightly higher around that band.

Debris needs to be removed from the surface prior to attaching the web. Also, any defects in the core surface need to be removed. Burrs from knife cuts or other scrapes or dents need to be smoothed out. Anything left will be in intimate contact with the polymer web and will leave an impression in the surface.

It is worth noting that defects can be still seen 25–100 wraps later in the roll. In some materials, all of this product would have to be scrapped. Optical grade PET is particularly sensitive to this type of problem. Also, thinner films are more easily damaged and require higher quality cores.

8.11 Packaging

This is often unspecified and can be the source of problems either receiving damaged rolls or having your customer receiving damaged rolls.

Rolls can see extremes of heat and cold during transit. As the temperature varies, so too does the roll change in dimensions. The point when the roll is most vulnerable to damage is during the transition. If the roll is moved during this time, it can telescope unless it is constrained. If the movement is limited, the roll may not have telescoped but there may be many microscratches that have been put into the web or coating. On coated web these will be seen as an increase in pinholes or scratches in the coating, or for transparent barrier coatings the barrier performance would decline.

Again, it needs a cost-benefit analysis to be done on the packaging to determine the value that can be put into protecting the product. There also needs to be an agreed specification with the film supplier so that they too provide you with the best possible material to start with.

8.12 Cost Benefit

As with most items, a cost-benefit analysis needs to be performed on the cores and packaging. If the product is a high value added one, the potential loss of product because of poor quality cores may justify the investment in higher quality cores. Similarly, higher quality packaging to prevent in-transit or handling damage can also be justified for higher margin products.

As with any decision, it is ideally made before the machine is purchased. Deciding what diameter of core along with the maximum roll diameter will determine the maximum quantity of web that can be coated. The choice of core material will, to some extent, determine the chuck type that is used.

References

[1] Kanai T, Campbell GA, editors. Film processing. Hanser Gardner Publications, Munich; 1999 ISBN 1 56990 252 6 Carl Hanser Verlag ISBN 1 446 17882 1.

[2] Newton J. Polyester films uniqueness and economics, their coex, pretreats, microvoiding and down-gauging. In: Proc. 11th international conference on vacuum web coating; 1997. p. 64−81.

[3] Smith D. Slitter savvy: the art of winding good rolls. Paper, Film & Foil Converter 2001;August:46−54.

[4] Hawkins WE. Web handling: making a slitter/winder upgrade work for you. Paper, Film & Foil Converter 2000;May(Suppl.):3−14.

[5] Schable R. Spotlight on slitting – A troubleshooting guide to solving common slitting problems. Paper, Film & Foil Converter 1992;(Suppl.):1−24.

[6] Begley TH, Hollifield HC. Evaluation of polyethylene terephthalate cyclic trimer migration from microwave food packaging using temperature-time profiles. Food Addit Contam 1990;7:339−46.

[7] Castle L, et al. Migration of poly(ethyleneterephthalate) (PET) oligomers from PET plastics into foods during microwave and conventional cooking and into bottled beverages. J Food Prot 1989;52:337−42.

[8] Gerlach CFG. Modelling the influence of filler particles on surface geometry in drawn PET film. J Strain Anal Eng Des, 1996;13(1):65 −73.

[9] Wetzel LE. The invisible enemy—identification and control of airborne contaminants in the manufacturing environment. In: Proc. 33rd annual technical conference of the Society of Vacuum Coaters; 1990. p. 262−8.

[10] Jamieson EHH, Windle AH. Structure and oxygen-barrier properties of metallized polymer films. J Mater Sci 1983;18:64−80.

[11] Barnes SE. Identifying scatter-point defects in thin film coatings. Photonics Spectra 1992;July:127−30.

[12] McCann MJ, et al. Buckling or wrinkling of thin webs off a drum. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 638−43.

[13] De A, Freire MT, et al. Thermal stability of polyethylene terephthalate (PET): oligomer distribution and formation of volatiles. Packaging Tech Sci 1999;12 (1):29−36 (8).

[14] Peebles LH, et al. Isolation and identification of the linear and cyclic oligomers of poly (ethylene terephthalate) and the mechanism of cyclic oligomer formation. J Polym Sci A-1 1969;7(2):479–96.

[15] Goodman I, Nesbitt BF. The structures and reversible polymerization of cyclic oligomers from poly(ethylene terephthalate). Polymer 1960;1:384–96.

[16] Giuffria R. Microscopic studies of mylar film and its low molecular weight extracts. J Polym Sci 1961;49(152):427–36.

[17] Shukla SR, Kulkarni KS. Estimation and characterization of polyester oligomers. J Appl Polym Sci 1999;74:1987–91.

[18] Jackson LC. How to select a substrate cleaning solvent. Adhesives Age 1974; December:23–31.

[19] Anderson JL, et al. Measurement and evaluation of surfaces and surface phenomena by evaporative rate analysis. J Paint Tech 1968;40(523):320–7.

[20] Jackson LC. Surface characterisation based on solubility parameters. Adhes Age 1976; October:17–9.

[21] Ross SD, et al. Isolation of a cycle trimer from polyethylene terephthalate film. J Poly Sci 1954;13(70):406–7.

[22] Goodman I, Nesbitt BF, et al. The structures and reversible polymerization of cyclic oligomers from poly (ethylene terephthalate). J Poly Sci 1960;48(150):423–33.

[23] Perovic A, Sundararajan PR. Crystallization of cyclic oligomers in commercial poly (ethyleneterephthalate) films. Poly Bull 1982;6:277–83.

[24] Hamilton S. Yield improvement in metallizing lines by using contact cleaning technology. In: Proc. 51st annual technical conference of the Society of Vacuum Coaters; 2008. p. 778–80.

[25] Web cleaning efficiency using contact cleaning roll (CCRs). Downloaded from < http://www.polymagtek.com/pdf/dirt_rpt.pdf > ; 2011 [accessed 28.02.2011].

[26] Hamilton S. Advances in contact cleaning for yield improvement. In: Proc. AIMCAL fall technical and 22nd international conference on vacuum web coating; 2008.

[27] Liston EM. Plasma treatment for improving bonding: a review. J Adhesion 1989;30:199–218.

[28] Goree J, Sheridan TE. Particulate release from surfaces exposed to a plasma. J Vac Sci Technol A 1992;10(6):3540–4.

[29] Weiss H. Web cleaners can eliminate dust-adhesion problems. Paper, Film & Foil Converter 1991;November:91–4.

[30] Murray L. The impact of foil pinholes and flex cracks on the moisture and oxygen barrier of flexible packaging. In: Proc. polymers, laminates, adhesives, coatings, extrusions (PLACE); 2005.

[31] Sheehan C, Matias V. Solution deposition planarisation of long-length flexible substrates. In: Proc. AIMCAL annual technical and 24th international vacuum web coating conference; 2010.

[32] Clow H, Belkind A. Cleaning oil from metal substrates using a hollow cathode discharge. In: Proc. 8th vacuum web coating conference; 1994. p. 191–8.

[33] Baker MA. Plasma cleaning and the removal of carbon from metal surfaces. Thin Solid Films 1980;69(3):359–68.

[34] Holland L. Some characteristics and uses of low-pressure plasmas in materials science. J Vac Sci Technol 1977;14(1):5–15.

[35] Vossen JL. Contemporary preparation techniques. Academic Press; 1989. p. 202.

[36] Belkind A, et al. Linear plasma source for reactive etching and surface modification. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 432−6.

[37] Barankova H, Bardos L. Hollow cathode plasma cleaning and surface activation. In: Proc. 45th annual technical conference of the Society of Vacuum Coaters; 2002. p. 109−12.

[38] Niskanen K, editor. Paper physics. ISBN 952 5216 16 0. Fapet Oy. Helsinki, Finland; 1998. Book 16 in 'Papermaking Science and Technology' series of 19 books.

[39] Casey F, et al. Design considerations of a high efficiency cryogenic pumping system for paper metallization. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 213−19.

[40] Schwarz W. Thermal limitations of the pumping speed of refrigerator cooled cryosurfaces $\geq -90°C$. J Vac Sci Technol A 1987;5(4):2568−71.

[41] Sack N, et al. Properties of vacuum deposited water/ice films. In: Proc. National Institute of Standards and Technology/AVS workshop "Water: its measurement and control in vacuum"; 1994.

[42] Mahoney P. Design and placement of cryogenically cooled surfaces in web coating chambers: theory and practice. In: Proc. 9th vacuum web coating conference; 1995. p. 62−74.

[43] Stenhouse J, Spencer AG. Coating improvements through better control of water vapour in vacuum deposition AIMCAL. In: Proc. 17th vacuum web coating conference session 2B, section 1, paper 3; 2003.

[44] Strom G, Carlsson G. Wetability of kraft pulps—effect on surface composition and oxygen plasma treatment. In: Mittal KL,, editor. Contact angle, wetability and adhesion. Utrecht: VSP; 1993. p. 475−91.

[45] Cohen B, Metallization in elastic non-woven webs. In: Proc. 37th annual technical conference of the Society of Vacuum Coaters; 1994. p. 227−9.

[46] Yasuda T, et al. Effects of glow discharges on fibres and fabrics. J Appl Poly Sci —Appl Poly Symp 1984;29(38):201−14 in 'Plasma polymerisation and plasma treatment.' John Wiley & Sons Inc.

[47] Yializis A, Mikhael MG. Vacuum surface functionalisation of paper and woven or non-woven materials. In: Proc. 46th annual technical conference of the Society of Vacuum Coaters; 2003. p. 553−8.

[48] Casey F, et al. Properties of metallized film in a free span web metallizer. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 480−83.

[49] Yadin E, et al. Vacuum coating of materials having an open structure. In: Proc. 10th vacuum web coating conference; 1996. p. 245−51.

[50] Lipin Y, Yadin E. Specialities of non-woven materials coating technology and equipment. In: Proc. 13th vacuum web coating conference; 1999. p. 188−93.

[51] Palmers J, Ruys L. Roll-to-roll treatment of textiles in industrial plasma batch machines. In: Proc. techtextil. symposium, session 5.1; 1997. Plasma Finishing.

[52] Hollander A, Behnisch J. Semi-continuous plasma treatment of textiles. In: Proc. techtextil symposium session 5.1; 1997. Plasma Finishing.

[53] The need for quality cut cores when winding. Converter; June 1998, p. 38.

[54] Kearns RW, Munroe JH. Consider film cores when analysing costs. Paper, Film & Foil Converter 1995;August:54−5.

9 Adhesion and Adhesion Tests

Adhesion is one of the core requirements for most vacuum deposited coatings but is one of the more difficult properties to test. As we will see, there are many possible tests but few are easy to carry out and may be testing an applied adhesive or the operator carrying out the test. The best test is the fragmentation test, but this requires a microtensile testing stage and a microscope plus skill and time, so it is hardly a production test and more of a research and development test. It is this difficulty in finding a suitable quick and easy-to-use test that leads so many to use the "sellotape" test despite its shortcomings.

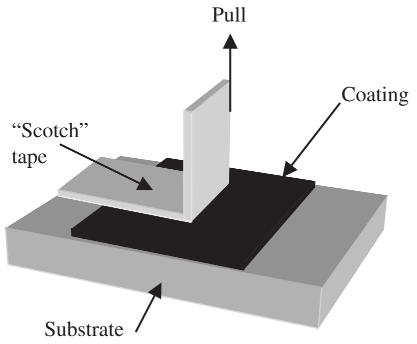
9.1 The "Sellotape" Test

This is the most widely used test for vacuum metallizers. It is referred to as the "sellotape" test because of that particular brand of tape being used. However, many people use the same procedure but a different brand of tape and still refer to it as the "sellotape" test. ASTM D3359−87 "Standard test methods for measuring adhesion by tape test" sets out the standard method (Fig. 9.1). In my opinion this is not a very good test. There are many variables that can affect the test such as manufacturer of the tape used, quality of the tape when it was manufactured, age of the tape, pressure with which it was applied, and rate of pull off and angle of pull off, to name but a few. If any of the coating is removed at all it does give an indication of very poor adhesion but if all the coating stays in place then there is no measure of how good the adhesion is. If a value for adhesion cannot be obtained then it becomes difficult to know when you have made a process improvement or if process change has damaged the process.

Different tape manufacturers may use different adhesives, and even with one manufacturer, the consistency of strength of the adhesive is variable and can depend on the temperature and humidity of the day it was manufactured. All these factors mean that a film that showed adhesive failure one day may pass it on another day and that the same film may be a total failure to one operator but acceptable to another.

Some users of the test scribe in regular scratches to form a crosshatch in the coating to give a matrix of squares. Then, after making the tape test over this whole

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00009-X



Advantages	Disadvantages
Cheap	Variable
Convenient	Qualitative
Quick	Operator sensitive
	Tape sensitive
	Rate sensitive
	Pressure sensitive

Figure 9.1 A schematic of the "sellotape" test [1].

area, there is a count of the number of squares that fail, and this gives a number for the quality of the coating. In some ways this is even worse because there is a number assigned to the coating and it is trusted even more than a qualitative "good" or "bad" judgment.

It can be understood how the test gets to be used. There is a lack of any other good, simple, accurate, quick, and cheap test and it is thought to be better than nothing. What is of most concern is the number of operators who are not aware of the shortcomings of the test and believe it as giving an absolute and meaningful result.

Trying to develop a plasma treatment process to get the best adhesion based solely on a tape test is poor practice. The test is so variable that it is, at best, unable to discriminate between the processes, except when gross differences occur, and at worst may be misleading in that the researcher may be sent in the wrong direction because of a couple of measurements that are at the extremes of the natural variability in the adhesive.

Where there is no alternative adhesion test it will still be used and attempts have been made to extend the test by using tapes of different levels of adhesion. Using tapes with adhesives having different track performance, generally higher than the tape specified on the ASTM D3359−87 test procedure, it is aimed at being able to discriminate between levels of pretreatment to make sure the surface treatment is optimized as much as possible.

9.2 Adhesion Tests

There are a variety of adhesion tests, many of which require items to be stuck to the coating and substrate and then a tensile testing machine used to pull the material apart [2]. Assuming there is no failure of these additional items, the test will be of the adhesion between the coating and substrate. These are much slower to perform and require more care and very expensive equipment and hence are often

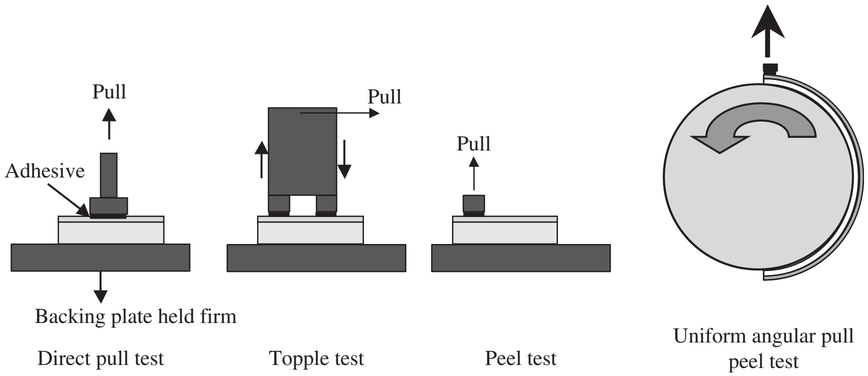


Figure 9.2 A schematic of several different adhesion test methods.

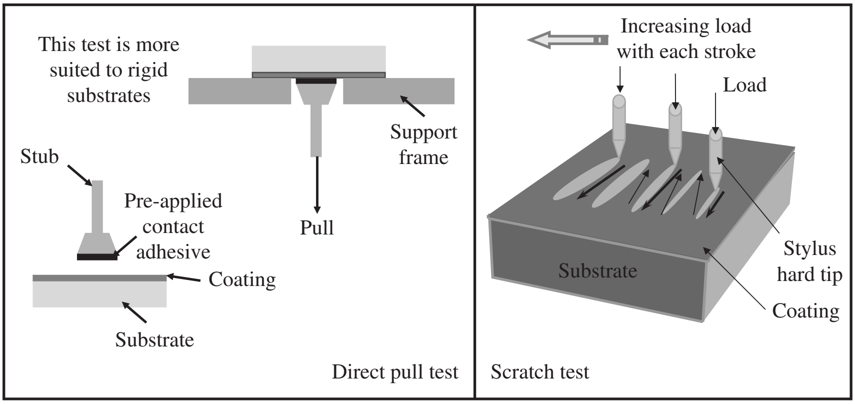


Figure 9.3 A schematic of two more adhesion test methods.

only used at the time of process development, if at all. They include lap shear, topple, pull, and peel as well as tensile tests [3], some of which are shown in Figs. 9.2 and 9.3.

Many are specific to an instrument from a single manufacturer and cannot easily be compared to any other tests. One that has been useful to coatings onto rigid substrates has been the scratch test, as shown schematically on the right-hand side of Fig. 9.3. This is where a diamond stylus is dragged across the surface with a steadily increasing force and using acoustic emission a detector listens for the cracking sound that precedes the adhesive failure. The limitation of this technique is the soft nature of the polymer substrates that may deform before the interface is affected. In a similar way, nano-indentation has also been used on thin coatings on a deformable substrate.

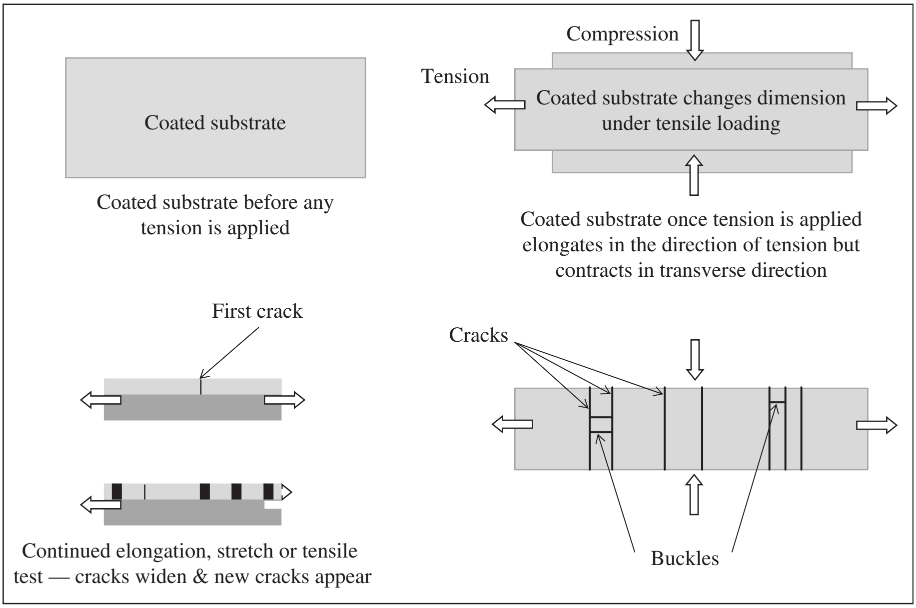


Figure 9.4 The use of tensile testing and crack formation for measuring adhesion.

One of the more useful adhesion tests to become more widely used is based on a tensile test but where the coating is monitored for cracks. Once the tensile test specimen has been pulled enough to produce a couple of cracks across the test specimen then the coating between the two cracks can only have any further load applied through the substrate and through the interface between the coating and substrate. A schematic of the use of tensile testing and crack formation to measure adhesion is shown in Fig. 9.4. As cracking is a stress-relieving mechanism, any further cracking between these two first cracks becomes a measure of the adhesion between the coating and substrate. The worse the adhesion between the coating and substrate the more the cracks will occur with any given increase in tensile load. This type of test is not necessarily easy to carry out. It requires a microtensile test stage that can be used with the surface being imaged at the same time. This is often done using a scanning electron microscope. Again, this makes the testing a specialist operation and not one that would be routinely done by a vacuum coating system operator.

This process has been developed and made more easy to use by no longer looking for the first two cracks and then the rate of additional cracks against tensile load but instead continuing the tensile loading until a point is reached at which the number of cracks appears to be saturated. This saturation of cracking is referred to as fragmentation and the test is often referred to as the fragmentation test [4−14]. Typically, the plot of crack density versus tensile load looks like the schematic in Fig. 9.5. Figure 9.6 shows a couple of micrographs taken of a sample with the load

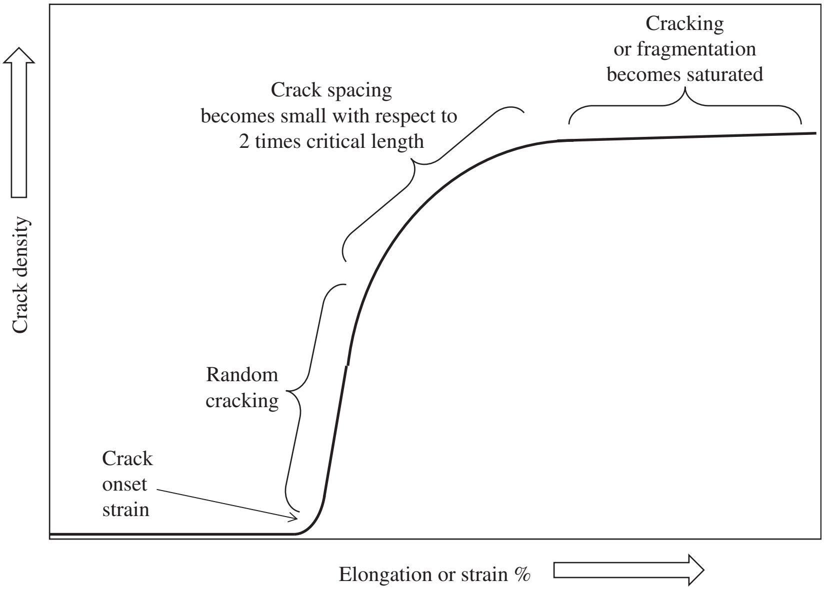


Figure 9.5 A schematic of a typical graph shape obtained by fragmentation test.

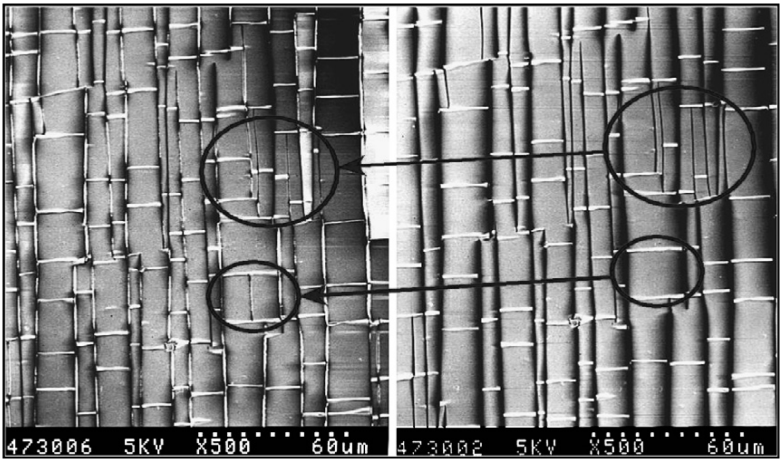


Figure 9.6 Cracking and buckling in a coating on a polymer substrate approaching the level of crack saturation.

increased between the micrograph on the right and that on the left. The highlighted rings show how additional cracks and buckles are present in the micrograph on the left where the sample is under an increased load compared to that on the right.

The graph in Fig. 9.5 is useful for two reasons. One is that the saturation of crack density allows for the adhesion to be calculated. The other is the onset of cracking. This too is an indication of the adhesion between the coating and substrate [15−18] as well as the coating cohesive strength. The higher the adhesion, the greater the strain before cracking starts.

The onset of cracking is sometimes used as the basis of a simple test that can be done by the machine operators. The coated samples are bent around a series of mandrels of decreasing size and examined for cracking. The samples are bent around the mandrel with the coating side outward, and the smaller the mandrel, the greater the tensile load in the coating. Thus the smaller the mandrel size before cracking occurs, the greater the adhesion.

In many cases this information is of practical use as the onset of cracking also marks a decrease in the barrier performance, as shown in Fig. 9.7, or an increase in the resistivity of transparent conducting coatings. Hence, for materials that are to be used for packaging applications and where the material has to be deformed to make the package, it becomes an indication of whether the material will be able to withstand the packaging process and maintain the barrier performance or if the barrier performance is likely to degrade. For transparent conducting coatings, the mandrel bending test can be used in conjunction with measuring the coating resistivity to determine the minimum radius where the resistivity can be maintained. This is useful for applications such as flexible displays or touch screens.

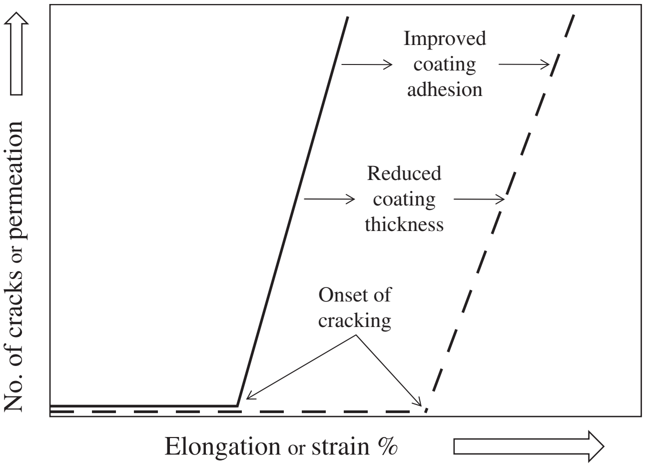


Figure 9.7 Using the onset of cracking for the same material, a change in coating thickness or coating adhesion can be seen as a change in number of cracks or change in barrier performance.

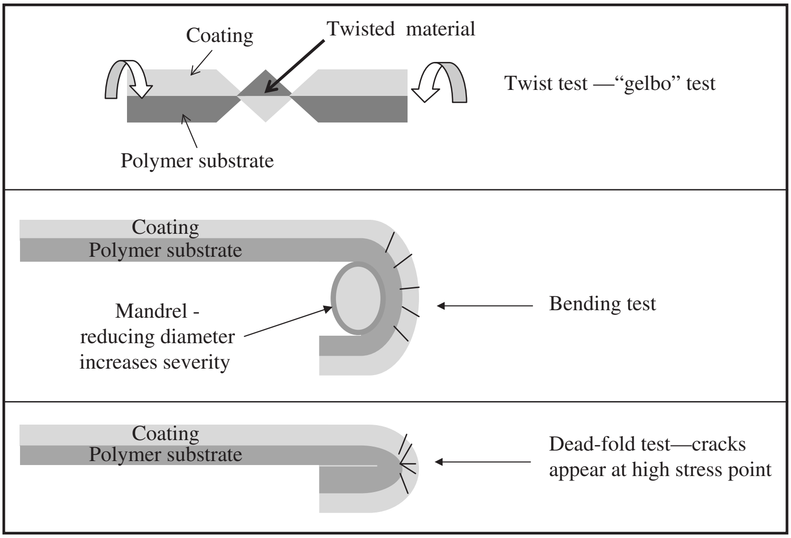


Figure 9.8 A schematic of some practical handling tests.

Figure 9.8 not only shows the mandrel bending test but also the dead-fold test and the “gelbo” twisting test. These other two tests also mimic some of the other handling procedures that the coated film is likely to undergo as part of a packaging process. Again the samples are examined after testing for signs of coating cracking. Some of these simple tests are also suitable for materials to be used in electronic devices [19] as they too need good barrier performance or in the case of inorganic conducting coatings, such as indium tin oxide, where they do not want to be cracked during flexing and lose some of their electrical performance.

9.3 Adhesion and Surface Analysis

One word of caution is around assuming that the failure is always at the interface. Simply because there has been a coating deposited does not mean that the failure has to be an adhesion failure between the substrate and the coating. Many polymers have what is referred to as a weak boundary layer at the surface. It is possible that the coating has adhered to the polymer but the failure is situated within the polymer and in particular at the surface of the thin polymeric weak boundary layer. It is worth considering using one of the surface analytical techniques (X-ray photoelectron spectroscopy, Auger electron spectroscopy, secondary ion mass spectrometry, etc.) to check on the failed surface [20−22]. It is possible that the metallic coating which appears to have not been adhered is in fact covered by a very thin polymer that is from a cohesive failure in the weak boundary layer. This thin polymer layer may only be a few nanometers thick and may not be easily visible to the eye.

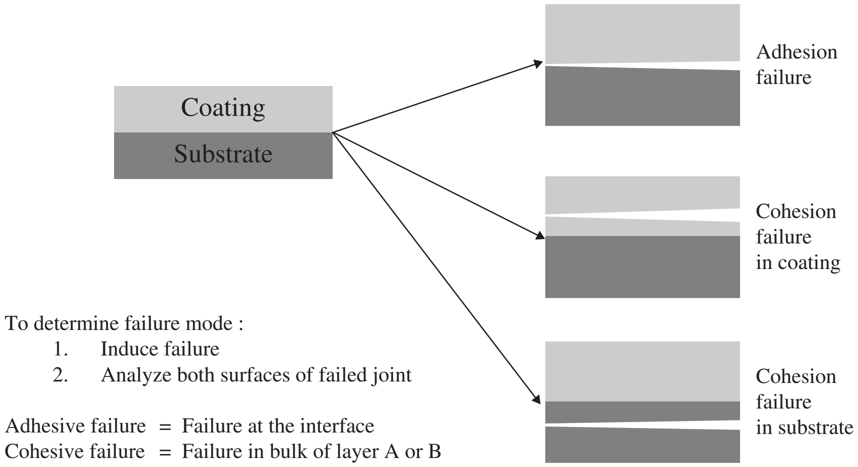


Figure 9.9 A schematic highlighting the difference between adhesive or true interfacial failure and cohesive failure.

The process to remove or cross-link better the weak boundary layer may well be different from improving the metal to polymer bond.

Figure 9.9 shows the three options that are possible when there is a failure. The coating or the substrate could suffer a cohesion failure in which case both surfaces produced at the failure should be the same. It is only when the coating separates from the substrate that the two surfaces should be different. In theory this should be easy to measure but the reality is so often very different. The separation is often not complete over the whole surface but there will be areas of adhesion failure next to an area where the failure might be cohesive. If this is the case, both failed surfaces will contain a variety of different chemical components that can make identifying the true failure mode ambiguous.

When troubleshooting an "adhesion" failure, the first step should always be to question if the failure is truly an adhesion failure or if it might be a cohesion failure.

References

[1] ASTM D3359−87. Standard test method for measuring adhesion by tape test. American Society for Testing and Materials; 1987.
[2] Hull TR, et al. Measurement of thin film adhesion. Vacuum 1987;37(3/4):327−30.
[3] Weaver C. Adhesion of metals to polymers. Faraday Spec Discuss Chem Soc 1972;2:18−25.
[4] Chow TS, et al. Direct determination of interfacial energy between brittle and polymeric films. J Polym Sci Polym Phys Edn 1976;14(7):1305−10.

[5] Rochat G, et al. Mechanical analysis of ultrathin oxide coatings on polymer substrates in situ in a scanning electron microscope. Thin Solid Films 2003;437:204−10.

[6] Leterrier Y, Månson J-AE. Mechanical integrity of thin films on polymer substrates. In: Proc. AIMCAL Fall technical conference and 18th international conference on vacuum web coating; 2004.

[7] Marras L, Sbaizero O. The fragmentation test applied to adhesion measurements and microstructural characterisation in plasma pretreated metallized plastic webs. Packaging Tech Sci 2009;22(5):293−302.

[8] Wheeler DR, Osaki H. Intrinsic bond strength of metal films on polymer substrates—A new method of measurement. ACS Symposium Series, vol. 440, 'Metallization of Polymers' [Chapter 36], Washington: American Chemical Society; 1990, p. 500−512.

[9] Leterrier Y, et al. Layer mechanics—Experimental methods and models; 2002. D4PU FLEXled-epfl-0209-002/Leterrier Sept. 2002, IST-2001-34215.

[10] Rochat G, et al. Mechanical properties of SiOx coated PET films characterised by AFM equipped with micro-tensile stage. In: Proc. AIMCAL Fall technical conference and 21st international conference on vacuum web coating; 2007.

[11] Marras L, Sbaizero O. The fragmentation test applied to adhesion measurements and microstructural characterization in plasma pre-treated metallized plastic webs. Packaging Tech Sci 2009;22(5):293−302.

[12] Teixeira V, et al. Stability of the electrical and optical response of mechanically deformed flexible ITO coated polymers. In: Proc. 50th annual technical conference of the Society of Vacuum Coaters; 2007, p. 584−7.

[13] Cairns DR. The mechanical reliability of sputter-coated indium tin oxide polyester substrates for flexible display and touchscreen applications. In: Proc. 44th annual technical conference of the Society of Vacuum Coaters; 2001, p. 160−5.

[14] Cairns DR. Strain-dependent electrical resistance of Tin-doped Indium Oxide on polymer substrates. Appl Phys Lett 2000;76:1425−7.

[15] Leterrier Y. Durability of nanosized oxygen-barrier coatings on polymers. Prog Mater Sci 2003;48:1−55.

[16] Felts JT. Transparent barrier coatings update: flexible substrates. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993, p. 324−31.

[17] Howells D, et al. The influence of the polyester substrate on the structure and performance of vacuum-deposited coatings. In: Proc. 48th annual technical conference of the Society of Vacuum Coaters; 2005, p. 638−43.

[18] Fayet P, et al. Effect of anti-blocking particles on oxygen transmission rate of SiOx barrier coatings deposited by PECVD on PET films. In: Proc. 48th annual technical conference of the Society of Vacuum Coaters; 2005, p. 237−40.

[19] Lewis J. Material challenge for flexible organic devices. Materials Today 2006;9 (4):38−45.

[20] DiNardo NJ. The application of surface analysis techniques to adhesion at metal-polymer interfaces. In: Proc. 5th international conference on vacuum web coating; 1991, p. 35−58.

[21] Mount III EM. Chemical analysis of the polyester/metal surface of a delamination failure. In: Proc. annual technical conference of the Society of Plastics Engineers; ANTEC 2006, p. 1022−6.

[22] Burger RW, Gerenser LJ. Understanding the formation and properties of metal/polymer interfaces via spectroscopic studies of chemical bonding. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991, p. 162−8.

10 Surface Treatment of Webs and Foils

There are several things that can be achieved by the treatment of webs and foils such as cleaning, sealing, physical etching, or functionalization.

The choice of treatment method will depend on the web/foil to be treated and the effect that is required as well as cost and availability of pretreatment winding machines [1]. More importantly, the choice may depend on the type and level of contamination of the web/foil.

The quality of the incoming materials is critical and can affect the process choices. I have seen a process where flame treatment on a polymer surface was shown to work at the concept stage but in production was failing to adequately clean the surface and bond failures were occurring too frequently to be acceptable. The problem was found to be that earlier in the manufacturing process an oil mist lubrication system had been added to some adjacent equipment. The operators were aware that it could contaminate the polymer but had been told that the flame treatment was there to clean up the surface from contamination. The contamination level from the oil mist was too great even for the flame treater. Protecting the polymer from the oil solved the problem, and the flame was the cheapest, most effective surface treatment for that particular product.

Hence where there is a problem with surface quality, it is always worth checking if there is an easier and cheaper method of getting a better quality of surface supplied rather than having to clean up the surface. This more particularly applies to the likes of dust, debris, and oil-type contamination.

If the need is to improve bond strength then it is more likely that the choice is how much of the surface needs to be modified and to what depth, which will determine the process type.

It is possible using most treatments to overtreat the surface [2,3]. This can result in a less than optimal adhesion. Indeed it can, in some instances, be worse than applying no treatment at all. This is shown schematically in Fig. 10.1. In metal foils, the overtreatment may be less significant unless the temperature rise causes a problem with the foil.

Polymers are much more sensitive and can be overtreated in several ways. Most often seen will be the overheating of the polymer that can lead to polymer

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00010-6

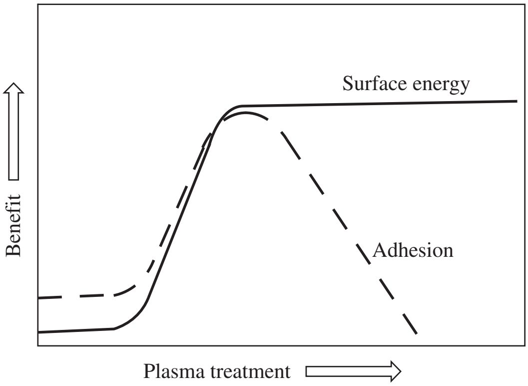


Figure 10.1 A schematic of surface over treatment where the surface energy remains high but the adhesion falls.

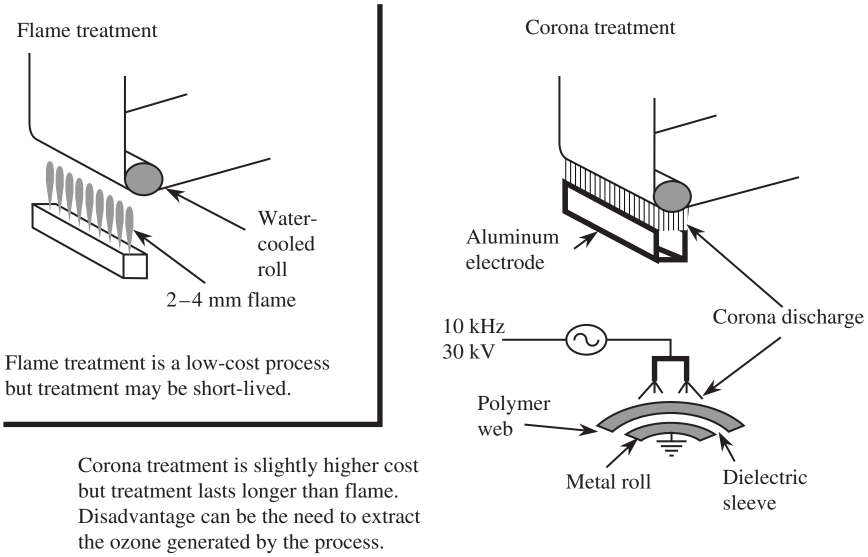
shrinkage, winding problems such as wrinkles or, with gross overheating, web-breaks. The other problems will be on the microscopic scale and will relate to the amount of functionalization and cross-linking on the surface. Overtreatment can lead to carbonization of the surface that could act as a weak interfacial layer [4]. This will be progressive and be seen as a progressive loss of adhesion away from the optimal treatment level.

In treating the surface, which includes bombarding the surface and breaking bonds, it is possible to change the surface roughness. In some instances, the plasma treatment can smooth the surface because some of the peaks are sputtered and reduced in height. In other cases the bombardment is great enough that the surface is roughened. It is hard to predict which way the plasma treatment will affect the surface until it has been used and the roughness measured. Plasma treatment units can include magnets to densify the plasma and so the substrate type, power, pressure, gas type, residence time, and magnetic configuration can all affect the surface treatment and hence the resultant chemistry and surface roughness.

The plasma treatment can functionalize the polymer surface, but to have the most benefit from this modification of the surface chemistry, the functionalization needs to be optimized to the specific coating that is to be deposited onto the surface. Polypropylene is basically a chain of carbon atoms and the adhesion to aluminum can be increased if the polypropylene surface can be modified to contain oxygen. By chain scission it is possible to bond oxygen onto the carbon ends where the chains have been broken. This will be a C=O double bond and then, when the aluminum is deposited, this can be modified to become C-O-Al covalent bonding that in effect bonds the aluminum into the polymer chain [5,6].

10.1 Atmospheric Treatments

Plasma treatment is a term generally applied to vacuum plasma treatment, although technically flame, corona, and atmospheric plasma [7—18] are also plasma treatments. Each of these plasma types has different characteristics and may have



Flame treatment is a low-cost process but treatment may be short-lived.

Corona treatment is slightly higher cost but treatment lasts longer than flame. Disadvantage can be the need to extract the ozone generated by the process.

Figure 10.2 A schematic of flame and corona treatment treaters.

different treatment depths as well as result in a different final surface chemistry. Additionally, there are various debris removal processes such as tacky roll and ultrasonic gas pulsing coupled to electrostatic neutralization and vacuum extract. The vacuum processes can include the debris removal by tacky rolls, UV, and a variety of plasma treatments as well as some precoating techniques such as printing or polymer deposition processes, which will be described in Chapter 11.

Figure 10.2 shows schematically the flame treatment on the left and corona treatment on the right.

Corona treatment has been a common general purpose treatment for web substrates prior to metallization and also postmetallization to help improve the adhesion to the metal coating. The metal coating will have a very high surface energy (>800 dynes/cm), but this will decline very quickly as the coating oxidizes and becomes contaminated by oligomer or additives such as slip agents. Corona helps restore a higher surface energy to improve the adhesion of any laminated, printed, or other coatings. Corona treatment systems can have a problem with arcing, which can damage polymer webs including piercing the polymer web making holes in it. To improve the plasma stability, the atmospheric plasma treatment systems were developed where the source frequency was increased and the mobility of gas atoms within the plasma increased by using helium. The higher frequency and lower mass of the helium gas enable any arc that starts to form to be quenched before it can damage the substrate. This has meant that the use of atmospheric plasma treatment sources is increasing. The uptake of the atmospheric plasma treatment tends to be a higher cost process as the power supply is more expensive and the consumption of helium also presents a higher running cost. More details of atmospheric plasma systems for deposition will be given in Chapter 18.

This section will concentrate on the vacuum processes, in particular the plasma processes.

10.2 Cleaning and Sealing

10.2.1 Debris Removal

Dust and debris on the surface that are held by electrostatic charge may be neutralized by the plasma and may fall off under the effect of gravity. Not all debris will be removed because the smaller sized debris will be held in place by van der Waals force. Other debris may be retained due to being embedded in the surface during the time it was wound as a roll. Residues from the evaporation of moisture that was attracted to the debris by capillary action may also act as a glue and hold the debris in place.

A tacky roll may also be used in vacuum for the removal of debris.

Both these simple cleaning techniques are common to both polymer webs and metallic foils.

10.2.2 Polymer Webs

Other contaminants on polymer surfaces can be exudates of unpolymerized monomers called oligomers, sometimes seen under a microscope as specific shapes such as dimers or trimers, as discussed in the last chapter. These oligomers tend to be weakly bonded to the surface and may cause poor adhesion. The weak bonding allows for easy removal of these oligomers. However, it is possible that following treatment more oligomers will exude back out of the surface. This may be seen as a fall in adhesion some time after metallization.

If the plasma treatment is extended it is possible to seal the surface such that no further exudation takes place. This is done by cross-linking more of the surface making it increasingly difficult for the oligomers to break through to the surface.

10.2.3 Metal Foils

Metal foils do not have the oligomer problem but commonly suffer from oil contamination from the foil manufacturing process. Metal foils can have been washed or pickled to clean the surface, but following metallization, spots of discoloration of the coating may become visible. These spots are often linked to oil contamination. The oil derives from the grain boundaries of the metal crystal structure. These grain boundaries are where the atoms are packed less densely than within the crystals and hence are porous. These grain boundaries act as a reservoir and it can take time to eliminate the oil completely.

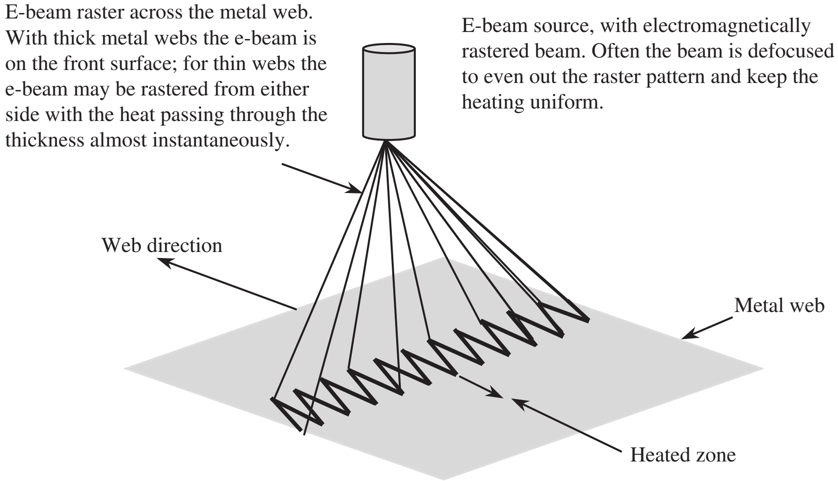


Figure 10.3 A schematic of a rastered electron beam used for preheating metallic foil webs.

Metal foils may have an advantage over polymer webs in terms of cleaning the surface in that not only can the foil be bombarded by the plasma but also heat can be applied to the foil [19−25] (Fig. 10.3). The heat can be applied in many ways, but often the plasma is used to heavily bombard the foil to provide the heat as well as the physical and/or chemical bombardment. The heat increases the oil mobility by reducing the viscosity and the plasma bombardment can be used to either volatilize the oil, which is then pumped away, or to polymerize or carbonize the oil, which then remains inert on the surface.

It is worth noting that there is a limit to what can easily be removed from a surface to clean it. I have seen a process where the foil required at least two high-power plasma treatments to neutralize the oil contamination, and this was after the foil had been through a wet "cleaning" process prior to the vacuum process.

Even though heat can be used to advantage, care still needs to be exercised in using heat and high-power plasmas as it is possible to raise the temperature quickly and also modify the crystal structure or any heat treatment of the foil by overheating. As with the deposition process, it is essential that provision for controlling the foil temperature during plasma treatment be considered, it can be an equally critical part of the process.

Some materials may benefit from a mechanical treatment at the surface. It has been found that a heavy duty brushing can put some lattice defects in the form of increased dislocation density at the surface [26−28]. The dislocations plus the arrival of material and heat can make the interface recrystallize and hence the bonding becomes much more intimate.

Another option that is available to metal strips is that of postannealing of the coating. In the same way that the strip can be scanned using an electron beam before the deposition, it can also be rastered across the surface after the deposition.

The postdeposition heating can encourage recrystallization or even melting of the coating and, if necessary, the substrate surface [29].

10.3 Cleaning

The mechanism for cleaning when using a plasma is that ion and electrons physically bombard the surface. Under this bombardment, the weakly bonded atoms can be sputtered from the surface or converted into easily volatilized species that do not polymerize or redeposit onto the web/foil [30–43]. Along with cleaning, the plasma will chemically change the surface allowing the depositing material to be better bonded to the surface.

10.3.1 Oxidizing Gases

Oxygen, air, water, or N_2O can all be used to remove organics by oxidation. These gases can also leave oxygen bonded into polymer surfaces that can act as a tie layer.

10.3.2 Reducing Gases

Hydrogen by itself or in mixtures may be used in some cases where the contaminant is sensitive to oxidation. The contaminants are converted to low molecular weight volatile species that do not polymerize and hence are more easily evaporated or sputtered from the surface into the plasma and thence pumped away.

10.3.3 Noble Gases

Noble gases usually mean that argon gas is used to give a more physical etch. The problem with noble gases is that there is no mechanism to convert the fragments into permanently volatile compounds and hence they tend to redeposit on the surface or be polymerized. The physical bombardment by heavier noble gases either causes more bond breaking to leave active sites or increases the amount of cross-linking, both of which can lead to a more stable and higher adhesion interface.

Noble gases are also used as carrier or diluent gases. The noble gases increase the vacuum ultraviolet (VUV) output of the plasma significantly. This can aid the dissociation of the other gas increasing reactivity and thus speeding up the process.

10.3.4 VUV and Ozone Cleaning

This cleaning process is not often used with web/foil processing. The process uses a high-powered quartz lamp as the source of UV energy. The UV energy is sufficient to speed up the desorption of water and carbon dioxide from surfaces. The lamp is usually positioned where it can illuminate a large area and hence assists in the desorption of these gases from the walls and vessel furniture during pumpdown.

Adding oxygen to the process can increase the effectiveness by increasing the production of ozone and atomic oxygen. This process can be particularly good at removing hydrocarbons.

10.4 System Design Considerations

As plasma treatment is a reactive process, it ought to be designed to have inherent symmetry. It is usually regarded as a robust, insensitive process but as the product is rarely tested in detail for adhesion limits the true sensitivity is unknown.

It is a good policy to design in the symmetry about the web/foil centerline rather than to have to try to correct for any asymmetry later.

To get symmetry about the web/foil centerline attention needs to be paid to the gas feed, plasma source, and pumping. The gas flows ought to be uniform at any point on the web within the plasma treatment zone. This requires uniformity of pumping across the web width as well as uniformity of gas feed.

Again as this is a reactive process, ample provision needs to be made to sweep out the by-products by having a good to high throughput of gas. If this is not done, there will be an accumulation of the contaminants generated from the surface treatment. This means that, over time, the efficiency of the treatment will decline and the levels of redeposited material will increase creating a variable product performance.

10.4.1 Plasma Types

This follows the same trend as for the sputter deposition sources. Early treaters were of relatively low energy and high voltage but more recently magnetic confinement similar to that used in magnetron sputtering sources has enabled high-density, high-power sources to be used. There are also the same options of using radio frequency (RF) or direct current (DC) power supplies. The modern DC supplies also allow for the use of switched mode where the polarity of the supply is changed to prevent undue charging of a nonconducting surface. This enables a DC magnetron plasma source to be used to sputter clean a polymer web surface. The high plasma density enables this to be done at high speeds that are now available on metallizing systems.

The RF systems for surface treatment tend to be of lower power than the DC systems, and, with the advent of the switched mode, DC supplies, are likely to be used less in future. There has been some work on using microwave plasmas for surface treatment but these are more complicated to install and operate and often offer no significant advantage over other plasma sources and so are likely to remain rarely used.

10.4.2 Back Surface Plasma Treatment

Many polymer webs and metal foils that have front surface contamination such as low molecular weight material or, in the case of metals, oil will have the same contamination on the back surface too.

This contamination can be present because it exudes from the substrate, but it may also be present because of transfer from the front surface when rolled up.

This contamination, if exuded from the surface, will probably be greater following the web traveling through the deposition zone where the elevated temperature will most likely speed up the exudation process.

This back surface contamination is rarely thought about and for many products may not be a problem. However, for a number of products where the coated front surface is coated, printed, laminated, or adhered there can be problems with adhesion or delamination that can be attributed to the contamination.

The contaminant can be transferred from the back surface to the front surface as the roll of material is wound up in the vacuum system. Usually where this contaminant is present on the surface, the surface energy will be reduced compared to the clean freshly deposited coating. This lower energy area will have a lower adhesion level to the rest of the higher energy coating. Nature tries to bring things to equilibrium. A freshly metallized surface may have a high surface energy of around 840 dynes/cm. When this surface is brought into contact with the back surface of the substrate as it is rewound, any low molecular weight, low surface energy, and highly mobile material present on the back surface will transfer to the higher energy front surface. The high difference in surface energy will be a high driving force encouraging material to transfer from the back surface to the front and in so doing reducing the surface energy of the freshly metallized surface. As the front surface energy declines, the difference in surface energy between the two surfaces declines and so the driving force for material transfer is reduced.

In the same way, the front surface can be stabilized by the use of a plasma treatment and so too can the back surface. The same type of plasma can be used to remove, volatilize, or cross-link the low molecular weight material or oil. Ideally, the plasma treatment would be carried out after the deposition zone to ensure that as much of the contamination is removed or sealed to the surface.

Where plasma treatment does not work well enough, some products may need to be wound up with paper interleaving.

One word of warning is that in cleaning the back surface it is possible that the ease of handling of the film may be compromised. Some films will have a slip agent added to aid handling, but this same slip agent makes adhesion difficult and so it needs to be removed to improve adhesion. As the slip agent will be on both sides, it will contaminate the freshly deposited coating, but if removed, will make handling more difficult. Hence, a compromise may be necessary.

References

[1] Mittal KL. Surface cleaning: recent developments and needs. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 13−17.

[2] Struller C. Effects of oxygen plasma surface treatment on biaxially oriented polypropylene film. Thesis. Technical University Munich; 2010. p. 90−95.

[3] Madocks J. Practical aspects of plasma treatment for thin film adhesion on polymers substrates. Society of Vacuum Coaters Bulletin, 2010;Fall:34−6.

[4] Morgner H, et al. High speed in-line treatment of plastic webs for vacuum coating. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 460−4.

[5] Rank R, et al. Adhesion promotion techniques for coating of polymer films. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 632−7.

[6] Burger RW, Gerenser LJ. Understanding the formation and properties of metal/polymer interfaces via spectroscopic studies of chemical bonding. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 122−168.

[7] Podhajny RM. Corona treatment of polymeric films. J. of Plastic film and sheeting 1987;4:177−88.

[8] DiGiacomo JD. Advanced technology flame plasma surface treating system. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 356−61.

[9] Briggs D. Surface treatments for polyolefins. In: Brewis DM, editor. Surface analysis and pretreatment of plastics and metals, Applied Science; 1982 [Chapter 9].

[10] Barankova H, Bardos L. Cold atmospheric plasma sources for surface treatment. In: Proc. 46th annual technical conference of the Society of Vacuum Coaters; 2003. p. 427−30.

[11] Mount III EM, editor. Metallizing technical reference. 3rd ed. The Association of Industrial Metallizers, Coaters and Laminators, Fort Mill, SC 29715 2001.

[12] Korzec D, et al. Atmospheric pressure plasma source for wire cleaning. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 455−550.

[13] Goodwin A, et al. Atmospheric pressure plasma technologies for surface modification of polymers.. In: Proc. AIMCAL 17th vacuum web coating conference. Session 2B, Section 2, Paper 1.

[14] Strobel M, et al. Analysis of air-corona-treated polypropylene and poly(ethylene terephthalate) films by contact-angle measurements and x-ray photoelectron spectroscopy. In: Mittal KL, editor. Contact angle, wetability and adhesion. Utrecht: VSP; 1993. p. 493−508.

[15] Briggs D, et al. X-ray photoelectron spectroscopy studies of polymer surfaces: Part 3, flame treatment of polyethylene. J Mater Sci 1979;14:1344−8.

[16] Briggs D, et al. Electrical discharge treatment of polypropylene film. Polymer. 1983;24:47.

[17] Briggs D, et al. Surface modification of polyethylene terephthalate by electrical discharge treatment. Polymer 1980;21:895.

[18] Owens DK. The mechanism of corona and ultraviolet light induced self adhesion of poly(ethylene terephthalate) film. J Appl Polym Sci 1975;19:3315−26.

[19] Clow H. and Belkind A. Cleaning oil from metal substrates using a hollow cathode discharge. In: Proc. 8th vacuum web coating conference; 1994. p. 191−8.

[20] Strohmeier BR. Improving the wetability of aluminium foil with oxygen plasma treatment. In: Mittal KL, editor. Contact angle, wetability and adhesion. Utrecht: VSP; 1993. p. 453−68.

[21] Baker MA. Plasma cleaning and the removal of carbon from metal surfaces. Thin Solid Films 1980;69(3):359−68.

[22] Holland. L. Some characteristics and uses of low-pressure plasmas in materials science. J Vac Sci Technol 1977;14(1):5−15.

[23] Vossen JL. Contemporary preparation techniques. Academic Press; 1989. p. 202.

[24] Belkind A, et al. Linear plasma source for reactive etching and surface modification. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 432−436.

[25] Schiller S, et al. A new sputter cleaning system for metallic substrates. Thin Solid Films 1976;33(3):331−9.

[26] Schiller S, et al. Pretreatment of metallic substrates by mechanical activation. Thin Solid Films 1980;72(2):351−9.

[27] Schiller S, et al. Advances in mechanical activation as a pretreatment process for vacuum deposition. Thin Solid Films 1981;83(1):7−16.

[28] Schiller S, et al. Pretreatment and surface alloying by mechanical activation combined with activation. In: Proc. 7th international conference on vacuum metallurgy; 1982. p. 125.

[29] Schiller S. and Panzer S. Electron beams for thermal surface modification. In: Proc. international conference on electron beam melting and refining; 1983. p. 273−94.

[30] Liston EM. Plasma treatment for improving bonding: a review. J. Adhesion 1989;30:199−218.

[31] Hall JR, et al. Activated gas plasma surface treatment of polymers for adhesive bonding. J Appl Polym Sci 1969;13:2085−96.

[32] Devine AT, Bodnar MJ. Effects of various surface treatments on adhesive bonding of polyethylene. Adhesives Age 1969;12(5):35.

[33] Kaplan SL. Cold gas plasma treatment of films, webs and fabrics. In: Proc. 41st annual technical conference of the Society of Vacuum Coaters; 1998. p. 345−8.

[34] Holland L. Substrate treatment and film deposition in ionized and activated gases. Thin Solid Films 1975;27:185−203.

[35] Schut JH. Plasma treatment: the better bond. Plastics Technol 1992;October:64−8.

[36] Kaplan SL. Cold gas plasma treatment for re-engineering films. Paper, Film & Foil Converter 1997;June:70−4.

[37] Holland L. Glow discharge excitation and surface treatment in low-pressure plasmas. In: Institute of Physics Conference. Ser. No. 54; 1980. p. 220−8 [Chapter 6].

[38] Smithson RLW. Nucleation and growth of gold films on bare and modified polymer surfaces. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 72−9.

[39] Schonhorn H, et al. Surface modification of polymers and practical adhesion. Polym Eng Sci 1977;17(7):440−9.

[40] Nickerson R. Plasma surface modification for cleaning and adhesion. Vac. Technol. and Coat 2000;June:56−60.

[41] Liston EM, et al. Plasma surface modification of polymers for improved adhesion: a critical review. J Adhesion Sci Technol 1993;7:1091−127.

[42] d'Agosino R, et al. Plasma processing of polymers. NATO ASI series, vol. 36, Netherlands: Kluwer; 1997.

[43] Mattox DM. Surface preparation: plasma cleaning. Vacuum Technol Coating 2000;1 (6):14.

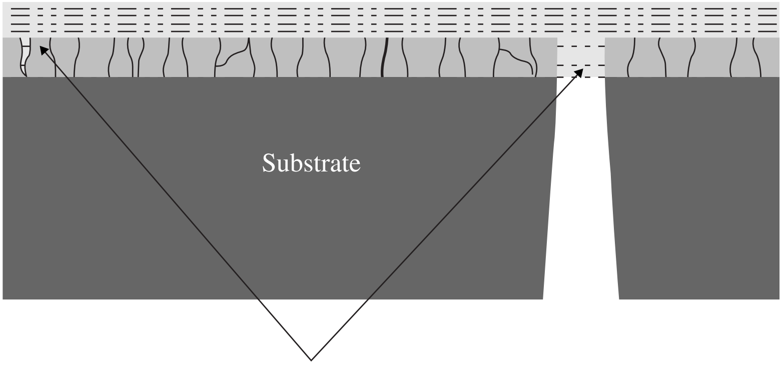
11 Polymer Coating Basic Information

There is currently an interest in the deposition of polymer coatings throughout the vacuum deposition industry. There are two market areas that have raised the interest in these coatings, one is displays and the other is photovoltaics. Both these markets have a need for ultrahigh barrier coatings, and one of the key issues in producing high performance barrier coatings is being able to deposit coatings onto smooth, defect-free substrate surfaces. To achieve this, one of the key steps is to clean up the substrate and deposit a planarizing layer onto the flexible web in vacuum immediately prior to the first vacuum deposition process. This planarization layer covers up all the existing defects, such as microscratches and debris, and allows a pinhole-free layer to be deposited. In addition, the planarizing or subbing layer can reduce further exudation of low molecular weight material to the coated surface. This will reduce the amount of oligomers or slip agents that could reappear on the surface. This planarizing or subbing layer improves the barrier performance by a few orders of magnitude. There are two routes being taken to reach the desired barrier performance; one is to aim for perfection in both the planarization layer and the subsequent inorganic coating and the other uses alternating polymer and inorganic layers to make sequential improvements. The pair of polymer and inorganic layers is referred to as a dyad.

Where there are still defects in the inorganic barrier coatings, such as pinholes, it is possible to improve the barrier performance by using an over coating (Fig. 11.1). This polymer coating fills the pinholes and as the diffusion rate through the polymer is orders of magnitude lower than through air, which would have been present in the unfilled pinhole, the barrier performance improves. This idea can be taken further, and if the polymer over coating has a lamellar inorganic filler of a suitably small size, the nanoflake filler can sink into the pores and pinholes and the diffusion coefficient then improves still further [1,2].

Either the gas or moisture diffusing through has to pass through by a very tortuous path and so the effective distance through the polymer increases significantly; this follows earlier lamellar barrier coatings that used clays, vermiculite, laponite, or similar flake fillers [3–6]. Where the nanoflakes differ is that they are small enough to plug up holes or pores and the gas has to pass through the inorganic

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00011-8



Lamellar or flake nanoparticle fillers settle parallel to the web surface and can overlap to give a tortuous path for gas or vapor to diffuse through the coating

In pinholes or pores, the nanoparticles may be small enough to plug any pores or pinholes and the diffusion coefficient of the filler is of the orders or magnitude lower than the polymer that is of the orders of magnitude lower than for air and so the total permeability is lowered more than for an unfilled coating

Figure 11.1 A schematic of how a flake filler can block up pinholes and pores and so further improve the barrier performance over an unfilled polymer coating.

material which will have a diffusion coefficient of the order of six orders of magnitude better than the polymer. Hence, this type of coating can change the barrier coating performance significantly.

An additional benefit is that the polymer over coating also protects the inorganic coating from further damage, which could have resulted in an increase in pinholes and a further degradation of the barrier performance. Many inorganic barrier coatings degrade with handling during downstream processing, as the web is bent, folded, or twisted as part of the packaging process. Over coating with a polymer can help to reduce this type of performance fallback.

In addition, the display industry has a need for robust transparent conducting coatings. These transparent conducting coatings can have the conductivity affected by cracking, which can be initiated more easily at substrate defects, and hence these products too can be improved by the use of planarizing layers.

The planarizing layer can be applied to the substrates at the manufacturing stage, during converting or in the vacuum system immediately before the inorganic coating is deposited. Polymer film manufacturers are trying to customize some grades for the display and photovoltaic markets, and they are aiming for these films to be the cleanest, most thermally stable, and smoothest possible. This idea of planarizing layers is not new, as the paper industry has used them for years in preparing the top surface for metallization by adding a smoothing layer to the paper to help increase the metal reflectivity. The polymer coatings added to the film before the film is put into the vacuum system can use any of the standard coating processes. Within the vacuum system, the most common method over the last few years has been a patented flash evaporation process followed by an electron beam cure. More recently, work has been done to try other in-vacuum methods such as direct evaporation and printing.

11.1 Polymer Coating Processes

Coating processes are aimed at transferring a liquid onto a web. The simplest forms of coating process rely on the viscosity of the liquid to control the thickness and uniformity. Coatings applied at atmospheric pressure have solvents added to reduce the viscosity and so assisting flow and leveling. Typically, they have a nonvolatile or solids content of between 10% and 50%.

The solvents fall into two basic groups: aqueous and nonaqueous. These typically require heated ovens to drive off the solvents and cure the remaining material. These ovens can be several tens of meters long.

The coating of polymers in vacuum requires the use of solventless coating materials. The viscosity of the liquid polymer can be adjusted by controlling the proportions of low to high molecular weight monomers and/or by heating the liquid during the coating process.

Relying on viscosity measurements alone may lead to problems. Many solventless coatings are thixotropic with viscosity increasing with working. The work put into the coating by transferring between rolls is sufficient to change the viscosity and hence produce a different coating thickness to what was expected.

The coatings after being transferred to the web need some time to level before being cured. Sometimes, heat is applied between the coating application and curing to aid this leveling process using the heat to reduce the viscosity.

Although these coatings are solventless or 100% solids, it does not mean that they do not shrink during curing. In fact, the polymerization can lead to a reduction in volume of up to 30%. This can lead to some interesting problems in measuring coating thickness, of where to take the thickness measurement and how it relates to the coating process.

11.1.1 Leveling

A coating will initially have thickness irregularities, possibly because of being coated using a gravure cylinder where the cell shape is replicated, or it may be from an inherent roughness of the surface the coating is deposited on. Liquid coatings will flow and these thickness irregularities will decay with time. This process is called leveling [7–10].

Leveling is primarily as a result of surface tension of the liquid and, in the cases where the surface is horizontal, gravity. The surface tension acts to minimize the surface energy of the coating by minimizing the surface area. Where gravity plays a role it is to minimize the potential energy by transferring material from areas where the coating is thicker than average to those where it is thinner than average.

Thin coatings are slower to level than thicker coatings, and lower viscosity coatings are quicker to level than high viscosity coatings. Also reducing imposed irregularities, such as by using smaller and less deep cells etched into the gravure roll that help determine the volume of oil transferred, can speed up leveling.

11.2 Coating Options

There are many coating options; however, some can be discarded because of being poorly controlled in both thickness and uniformity or because the process is not suitable for ease of use in a vacuum system [11−13].

- Direct gravure
- Reverse direct gravure
- Reverse angle doctor blade direct/reverse direct gravure
- Offset gravure
- Reverse offset gravure
- Simple coating (dip)
- Puddle or nip-fed coating
- Multiroll coating
- Fountain coating
- Slot die, melt, or extrusion coating
- Cascade coating
- Spray coating
- PML process
- Vacuum thermal, e-beam, or induction-heated evaporation and sputtering
- Vacuum printing by one of above printing techniques

Gravure would deposit thick coatings and the addition of offset rolls would improve the uniformity and allow thinner coatings to be applied.

Multiroll coating is to be preferred for thinner coatings with the thickness decreasing as the number of rolls increases.

Both of these techniques can have coating defects or thickness variations transferred from the coating process onto the substrate. Time then has to be available to allow the coating to level out before it is either cured or a further coating is added. The use of multiple rolls in vacuum, all with a thin film of polymer on the surface, could provide a low rate but large area source of material that could give off some volatiles. All these rolls would have to be shielded from stray UV light from other vacuum processes. Stray UV light might cause some of the polymer to be cured on these rolls rather than transferring the entire polymer to the web. This would, over time, change the roll contact pressures and the thickness of the coating being applied.

11.2.1 Evaporation

The evaporation of polymers can have several advantages. One is of not transferring any localized variations to the substrate. So long as the evaporation source has a uniform vapor pressure down the length of the slot source and the vapor pressure is maintained within the source, the uniformity of the exiting vapor will be good and hence the coating uniformity will be good (Fig. 11.2).

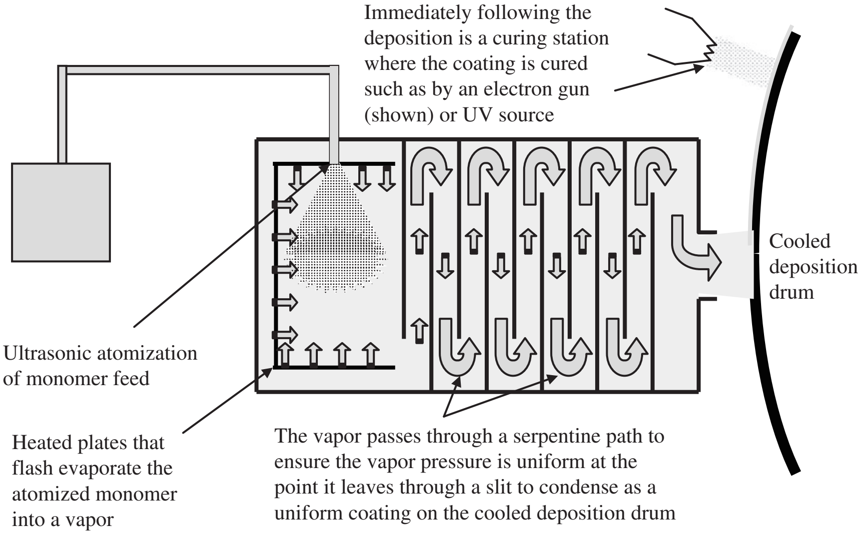


Figure 11.2 A schematic of the flash evaporation process for polymer deposition [14,15].

All of the processes need to have the T_g carefully chosen. The thermal evaporation source is less affected by the polymer viscosity than are the printing techniques. In fact, some polymers can be e-beam evaporated from the solid and do not require the source material to be liquid.

The source of thickness variation in evaporation sources is largely due to the quality of the control of temperature of the source. Many have end losses that are not well enough compensated for. The temperature needs to be maintained stable and uniform over the whole of the source to within a fraction of a degree. This is a hard target, but, even allowing for this, the complexity of an evaporation source would look to be much lower than for a multiroll or offset gravure printing process.

The current product offerings are based on a system where a monomer is pumped through an ultrasonic atomizer onto a hot plate where the mist of monomer is flash evaporated into a vapor. The vapor passes round various baffles before exiting from a slot onto the cooled deposition drum where the vapor condenses on the film. Soon afterward, the thin film is cured using an electron gun.

11.2.2 In-Vacuum Printing

One of the options is to print a monomer directly onto the web, but to do this successfully, the monomer must stay as a liquid long enough to be able to level and so produce a suitably smooth coating. The monomer also needs to be stable enough to enable the printing process to be carried out without the monomer being cured. Some monomers that are suitable for evaporation are too reactive for printing. The absorbed oxygen can act as an inhibitor, and this when removed by the vacuum makes the monomer more reactive than when used at atmospheric pressure. Coupled to this increased reactivity, the shearing action can trigger the polymerization of the monomer, thus coating the print rolls and degrading the printing process. By choosing monomers with low reactivity, such as some methacrylate types, this problem of shearing initiating the cure can be delayed long enough that the monomer can be printed and then cured once it is on the web [16,17]. The coating can then be cured by a low-voltage electron beam gun operating as low as 10−12 kV. The speed that this has been done at has reached 240 m/min that is compatible with a fairly slow metallization process.

Comment

Where printing is essential, such as for patterned coating, the simplest technique giving reasonable uniformity is offset gravure coating. Where thinner coatings are required, or more precision in coating thickness uniformity, multiroll printing is to be preferred.

Where no patterning is required, the use of a simple, but highly uniform and well-controlled temperature, evaporation source could be a simpler and cheaper option. The aim when using chemical mixtures is not to have problems of fractionation that could change the coating chemistry.

11.3 Radiation Cured Polymers—Acrylates

Monomers, however deposited, need some mechanism to cure them into a polymerized coating. There are several technologies used, of which the main five are listed below along with the primary cure mechanism.

1. Electron beam (e-beam) radiation:	Electronic excitation and ionization
2. Ultraviolet (UV) radiation:	Electronic excitation
3. Infrared (IR) radiation:	Thermal
4. Microwave:	Thermal
5. Radio frequency (RF):	Thermal

Of these five, the last three are aimed mainly at driving off water or organic solvents, allowing the chemistry to then take place. Only the first two are aimed at curing solventless coatings where the web has been coated with 100% solids [18].

11.3.1 Electron Beam Curing

The advantages of e-beam over thermal curing are in the speed, cost, and size of the equipment needed. The electrons penetrate the full depth of the coatings including through the web for laminates [19,20]. The penetration is less affected by fillers and so more opaque coatings can be cured. The low temperature of the process allows heat-sensitive substrates to be coated more easily, including very thick coatings.

The electrons are generated in a vacuum by any of a variety of means, of which filaments are the most common, although for production robustness filamentless sources are becoming more popular. The electrons are extracted and accelerated toward the coated web. The primary electrons and the backscattered electrons are more than 50 eV, and these electrons do not produce any chemical reaction. The secondary electrons that are formed are in the range of 3–50 eV, and these are then slow enough to ionize molecules and to form free radicals. Any electrons of energy less than 3 eV only induce excitation (heat).

The electron guns that are used in atmosphere have to penetrate a thin metal window that contains the vacuum preventing the filament from oxidizing. This results in the electrons having to be accelerated at several hundred kV. This high operating voltage has the effect that the electrons generate X-rays and so the guns have to be well shielded. The electrons lose energy as they penetrate the metal foil, and the residual energy on the electrons that successfully get through the foil is lower than the starting energy. The air in the gap between the foil and the polymer coating causes many collisions that can further attenuate the energy. The aim is that the electrons that reach the polymer have enough residual energy to activate the cure by generating free radicals. With too much energy, the electrons can penetrate the carrier substrate and damage the polymer, whereas with too little energy, there will be insufficient activation and the cure will be incomplete.

Electron guns used to cure coatings in vacuum do not have to penetrate the metal window or the air, and therefore they can be operated at a few tens of kV and do not have the same problems regarding X-ray generation.

In general, electron beam cured coatings are also sensitive to oxygen. The oxygen combines with the primary radicals that are formed and converts them to peroxy radicals. These tend to terminate chains rather than propagate the reaction, thus limiting the cure. The monomer does not contain photoinitiators or amines that can be used to offset the oxygen inhibition.

The problem of oxygen inhibition is only a problem if oxygen is available in large quantities as at atmospheric pressure. Here using a nitrogen blanket, to keep the oxygen away from the surface, is a commonly used option. However, under vacuum the quantity of oxygen is considerably lower and so too is the problem of oxygen inhibition.

Different polymers can have a different sensitivity to oxygen and thus protection levels may vary.

One downside of e-beam cured coatings is that they have a higher shrinkage than UV cured coatings. This is because the cure happens at all depths at once and the diffusion time is minimal. This can lead to a high gloss surface but a curled, highly stressed coating.

11.3.2 UV Radiation Curing

There are the following two basic types of chemistry that have been developed for curing by UV:

1. Free radical reaction
2. Cationic reaction

Of the two types of chemistry, the cationic curing is based on epoxies [21]. These coatings were developed for the hard coating of woods where it would be difficult to have all the coating exposed uniformly to the UV light. Hence, this chemistry uses the UV light to trigger the reaction, but once the reaction has started, it will continue without the lamp remaining on. Thus, the curing can propagate around corners. Cationic chemistry is critically affected by moisture, and the monomer and the coating surface need to be kept free of moisture until curing can take place [22].

Free radical chemistry is not sensitive to moisture but is sensitive to oxygen. Oxygen competes for the chain ends and can thus limit the extent of the cure. This has been regarded as a surface effect, but the definition of the surface in this industry is up to a thickness of 5 μm. Methods of offsetting the effects of oxygen are to increase the quantity of photoinitiator that will create many more free radicals and more chain ends. So long as the chain end generation is faster than the oxidation rate, curing can take place. This can be an expensive solution to the problem because the highest cost of the formulation is often the photoinitiator. The other method of eliminating oxygen is, as with electron beam curing, to use a nitrogen blanket.

The level of photoinitiator has other effects. Too much and the photoinitiator will remain active and can lead to coating embrittlement or other UV degradation such as yellowing. Too little and the cure time will be too long and may be incomplete leaving the coating softer than desired.

The photoinitiator absorbs the UV light and so high levels of photoinitiator will limit the depth of the cure that is possible. The photoinitiator near the surface absorbs a lot of the UV and effectively blocks much of the UV from reaching the polymer at deeper levels. At such high levels, there will also be a tendency for the surface to be over cured. This can result in a cured but powdery surface.

Again, as this is a process occurring in vacuum, the need for extra photoinitiator is eliminated.

The choice of UV source can also affect the process. Not all lamps produce the same heat load. The lamp diameter and the reflector type and design all have an influence on the heat load.

There are four types of UV sources that have been used to cure polymer coatings. Three are lamps that generally are classed as an encapsulated plasma and the fourth is an unencapsulated plasma. The list is as follows:

1. Medium pressure mercury arc, electrode
2. Medium pressure mercury, electrodeless
3. Excimer
4. Plasma

The medium pressure arc electrode arc lamps have a cathode at one end; an anode at the other end and the lamp envelope is evacuated and filled with appropriate chemicals to customize the wavelength of the light output. When current is passed through the lamp, the mercury vapor allows a plasma to be struck. As the lamp warms up, the rest of the dopants are vaporized and the output stabilizes. These lamps can run very hot, causing a significant heat load to hit the web substrate.

These lamps age with the dopants tending to crystallize out behind the electrodes, causing the glass-to-metal seal to fail. The light output from these lamps can start to fall very quickly, and although the plasma will still strike, they may become totally ineffective. The operator will still see the lamp as on, but the UV output will have been lost. There is an activated paper that can be used as a quick test of the ability to cure, but the error in this is large. There are also some measurement techniques using irradiance meters, but these are seldom used because they have to be passed through the cure zone, and for a web system, this is not always easy. In fact, either of these techniques is even more difficult to carry out accurately in a vacuum system. It is more common for the lamps to be overrated initially to allow for the lamp degradation. This puts a lot of extra heat load onto the web than is necessary.

The electrodeless lamps have the same chemicals enclosed in a quartz envelope, but because there are no electrodes, there are consequentially no glass-to-metal seals and hence there is no degradation of the performance of this type of lamp. These lamps are activated by a microwave power source. This tends to make the capital cost higher, but this is more than offset by the process reliability and reproducibility being much better. The quartz envelope of these lamps can be of a smaller diameter than those that need to have electrodes. This smaller profile means that there is a smaller cross-sectional area radiating heat to the web substrate. Hence, the heat load from this source can be as much as 50% less than the electrode-based lamps.

Another way the lamp performance can be degraded is by volatiles coming off the monomer coating. These volatiles can condense on the lamp and reflectors, blocking some of the output from the lamp and reducing the reflection efficiency.

Reflectors are used with the lamps to either focus the light to a narrow line with a high intensity for a short time or to diffuse the light into a large area cure zone of lower intensity.

The excimer lamps are the newest source, and these too are water-cooled.

For all of these systems, the reflectors and lamp body are cooled either by forced air-cooling or water-cooling. This would present some design difficulties to adapt these standard design of lamps for vacuum use.

A standard plasma in a vacuum system has been used with some success using the same acrylates as were used as part of the PML process. This work included a comparison of the cross-linking efficiency of e-beam, UV lamp, and plasma-cured coatings of the same thickness [14,23]. It was found that all could cross-link the monomer by the same amount. There were no details of the gases used in creating the plasma, but as no reference was made to the safety aspects of using mercury vapor, I assume that more standard gases such as argon were used.

This reference is encouraging because if it works well, it removes a number of the lifetime, reflector, and cooling problems that may become critical with the other lamp sources.

11.3.3 UV Sources

The ultraviolet (UV) part of the electromagnetic spectrum has been divided into different regions: UVA, UVB, and UVC.

UVA = 315–420 nm	Long wave radiation gives cure at depth and with fillers
UVB = 280–315 nm	Medium wave radiation takes the cure on from UVC
UVC = 180–280 nm	Quick start of reaction cures the surface

Doped mercury vapor lamps are available to maximize particular regions of the UV. It is possible to obtain other lamps with other dopants to give different spectral outputs. In choosing the dopant, it is important to match the peak output with the chemistry of the coating. Where photoinitiators are used, it is possible to get doped lamps that have been optimized for particular photoinitiators.

The aim of the lamp is to provide a fast surface cure to stabilize the surface and reduce oxidation problems and then to ensure the output is sufficient to cure the coating to the full depth. If the coatings are very thin, then the UVA content is less important than if the coatings are very thick.

The output of the UV lamps gives light across a broad spectrum in the ultraviolet and the output also contains both visible light and infrared heat. The precise spectrum is dependent on the mixture of gases that are enclosed in the tube.

A typical output from a mercury vapor lamp would include 60% IR, 10–20% visible light, and only 20–30% UV light. Thus, it is worth noting that the removal of heat becomes a significant part of UV curing. As an example, if we take the highest power density of lamp available, then we have powers available up to 240 W/cm length of lamp; this would require 12 kW for a 0.5 m cure width using a series of lamps. Thus, out of the 12 kW for a 0.5 m wide lamp, it would require 7.2 kW of heat to be removed per lamp whereas only 2.4–3.6 kW UV would be available.

This all shows UV curing to be complex and energy inefficient. Thus, it becomes clear why electron beam curing is preferred for the simplicity and compact nature of the electron source and its directionality. UV plasma may work equally as well and become more widely used once more development work is done to understand the parameters and optimize the process.

11.3.4 Chemistry

For UV curable coatings free radical chemistry is by far the largest sector. Within the free radical chemistry, the acrylates have over 80% of the sector. The primary four groups of acrylates are as follows:

1. Acrylic acrylates
2. Epoxy acrylates

3. Urethane acrylates
4. Polyester acrylates

There are the following four basic components to UV curable polymers:

1. Prepolymer
2. Reactive diluent
3. Additives
4. Photoinitiator

With the exception of the photoinitiator, the formulation can be the same for e-beam curable as for UV coatings.

The curing process has three distinct stages of cure, induction, and polymerization leading to full cure. The induction stage is the time it takes for the process to get started. The formation of end chains is not instantaneous and can be slowed by oxygen inhibition. The polymerization stage builds to a maximum rate and then, as an increasing amount of polymer is cross-linked, the mobility of the chains, with available bonding sites, to find other chains that also have bonding sites, which can bond to each other, becomes restricted and the rate slows. This ends at the point where the given radiation intensity cannot induce any further cross-linking. If irradiation continues beyond this point, it can start to induce damage by chain scission, degradation, and discoloration.

The coating will never achieve 100% cure, and it has been reported that some are cured up to a level of only 70%. One of the reasons for using reactive diluents is to change the mobility of the polymer chains during the cure in order to affect the level of cure achieved. The level can also be affected by the cure rate. If the rate of cure is very fast, it does not give the chains the time to move to find other chains to cross-link with. Hence, if a maximum cure is required, it may be preferable to slow down the cure rate.

The radiation cure industry has a “test” similarly as subjective as the “sellotape” test is for the metallized coatings: this is the “thumb” test [13].

The state of cure as measured online is done by initially touching the coating surface. The first test is to check whether it is tacky or not. If it is tacky, it is under cured. If it is not tacky, then the second test is to press with the ball of the thumb and twist the thumb by 90°. If the coating moves, it is under cured, and if it shows no damage to the thumb twist, then the third test is applied. The third test is to use the thumbnail to try to scratch the surface of the coating. If damage occurs, then the coating is under cured (assuming full cure would produce a coating that could not be damaged). These tests are of the “cheap and cheerful” type. It is hard to do curing checks online. Techniques such as differential scanning calorimetry are done in a laboratory and off-line.

Other coating performance tests that are common are ones such as the pencil hardness test as defined by ASTM D 3363 and the Taber abrasion test as defined by ASTM D4060. There are many other tests available such as ASTM D523 gloss evaluation, ASTM D1006 exposure testing, ASTM 2134 hardness, ASTM D3359 adhesion, ASTM D1653 water vapor permeability, ASTM D522 flexibility, etc.

Prepolymers

Prepolymers are often referred to as resins or oligomers. The reactive diluents are commonly called monomers. The boundaries between oligomers and monomers are blurred and what, for some manufacturers, is a monomer is, for others, an oligomer or prepolymer. Oligomers are, in general, high molecular weight, high viscosity liquids that may be too viscous to be directly coated. In many cases, the lower molecular weight monomers are used as a method of reducing the viscosity to enable the oligomer/monomer mixture to be directly coated. The use of low molecular weight monomers enables the coating to be maintained as a solvent-free, 100% solids coating. Also temperature may also be used to reduce the viscosity.

Some suppliers are claiming they have developed high molecular weight but low viscosity oligomers; however, they still need diluting to be manageable.

The prepolymers and reactive diluents form the cross-linked network that gives the cured coating its primary characteristics.

The acrylates are faster to cure than the methacrylates but are softer, the toxicity of methacrylates tends to be lower, and the T_g of the methacrylates tends to be higher as is the elongation, but this results in a lower tensile performance. The slower curing rate of the methacrylates also leads to lower shrinkage.

Reactive Diluents

Reactive diluents are low molecular weight monomers, and they have been classified by their acrylate functionality. Molecules containing one acrylate group are classified as monofunctional. Molecules with two or more acrylate groups are classified as difunctional, trifunctional, or multifunctional. The difference in functionality is critical because it affects the mobility of the chains as the cure takes place. Monofunctional monomers are primarily used to reduce viscosity.

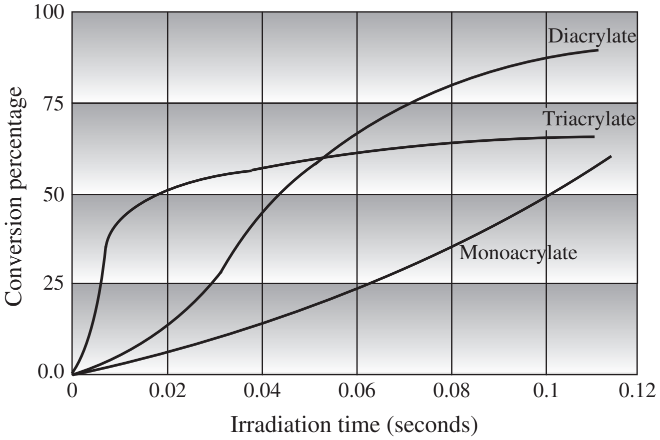
Increasing functionality can increase the initial speed of curing, but the pinning of the cross-linked chains would then limit the maximum cure and the cross-linking density could well be less than that obtained with a formulation with a lower average level of functionality.

The lower the functionality, the better it will act as a diluent. Similarly, a monofunctional monomer will produce a coating of better flexibility than those made with a multifunctional monomer. These will also tend to have a low amount of shrinkage.

The lower the functionality, the lower the hardness and solvent resistance (Fig. 11.3).

The functionality gives an indication of the number of cross-linking sites available, and this can affect the cross-linking density that might be achieved.

The lower molecular weight of the monomers giving them a low viscosity also results in a larger change in volume on curing and the shrinkage can be very high, as great as 30% in the worst cases.



The monoacrylate may cure to a greater extent than the triacrylate or the diacrylate but will take a much longer time to cure

This may have an additional advantage in that the shrinkage may also be less than for the faster curing material

Figure 11.3 The dynamics of curing of different functionality monomers.

Cure Rules of Thumb

Monofunctional cures slower than Difunctional cures slower than Trifunctional
Monofunctional cures more than Difunctional cures more than Trifunctional

Increasing the temperature can further increase the completeness of the cure.

Additives

Amine synergists can be used to reduce the level of stable peroxide formation during free radical polymerization in the presence of air. This reduces the effect of oxygen inhibition and can reduce the need to increase the photoinitiator levels.

The amine is a noncurable component of the formulation and it can migrate to the surface over time causing blooming.

Amine acrylates can be used in some cases to act not only as a synergist but also as a diluent as they are usually low molecular weight. This reduces the amount of noncurables in the formulation and hence can prevent blooming, although it is usually more expensive than using separate amine and diluent components.

The amine synergists cannot be used in formulations where there are acid-containing polymers. The acid-containing polymers are used where the coatings are deposited onto a metal and the acid helps to provide a good adhesion level to the metal. It might be expected to use this type of chemistry for the polymer overcoating of a metallized film to act as a protective surface to prevent the soft aluminum coating getting scratched.

Additives can be insoluble, and sometimes they are dissolved in a suitable solvent but without any indication that this has been done. Hence, when formulating a 100% composition and using additives, it can be later found that there are some volatile organic carbons (VOCs) being given off. Commonly, this has been found to be down to the additives that may only require 0.5% solvent to make it more soluble in the formulation.

Photoinitiators

Photoinitiators tend to make up around 5–10% of the formulation, but the cost represents a much higher proportion of the formulation. The photoinitiator type is chosen for the absorption to be maximized to match the output of the UV source being used.

Using formulations in vacuum has the advantage that there is no air to act as reaction inhibitor and hence the need for photoinitiator can be minimized. This reduces the level to the order of 1–5%, making the power required to cure the coating less and thus the heat load will also be less.

As the photoinitiator continues to work even after the coating has been completed, it can be a cause of yellowing and degradation. Thus, there can be benefits to the lifetime of the coating when the photoinitiator has been minimized and the coating cured in vacuum.

Some of the photoinitiators are yellow although when diluted into the formulation this color is diluted too and if the coating is thin this may not be noticeable at all.

The most commonly used photoinitiators are as follows:

- Diethoxyacetophenone (DEAP): Union Carbide
- Dimethoxyphenylacetophenone: Irgacure 651, Ciba-Geigy
- Benzoylcyclohexanol: Irgacure 184, Ciba-Geigy
- Hydroxydimethylacetophenone: Darocure 1173, Merck (now Ciba)

Health and Safety Issues

The chemicals used in radiation-cured polymers can have a number of problems associated with them. The primary ones are toxicity and irritancy. The toxicity issues are as for other chemicals. The irritancy issue is one that needs highlighting. With most coatings left in air, they dry and solidify, but with the curable formulations, they do not dry unless they are exposed to radiation. This can present operators with a problem in that if they get splashed or wipe off a surface and come in contact with the chemicals, they remain active on the skin until washed off. In general and when compared to other similar substances such as inks, they end up with a greater exposure because of the prolonged active contact. If operators become sensitized to the chemical, the reaction can be severe with amounts as low as a few parts per million being enough to trigger a reaction.

Cleaning cloths and papers and any excess of the formulation are often exposed to a UV source, which may be prolonged exposure to sunlight, as a method to cure and dry the chemicals. This effectively removes them as a source of irritation.

There are two types of irritant: those that irritate the skin and those that irritate the eyes. The test is that the chemical is wiped onto the skin and the level of erythema (reddening) and edema (swelling) is measured after 1 and 3 days. These numbers are added together and they make up the Draize Index (DI). The DI rating is on a scale $0-8$, with 8 being unacceptable and 0 being inert. Generally, the chemicals fall into the ranges slight irritation (DI <3), moderate (DI 3–6), and severe (DI 7 or above) [13,24].

For eye irritation, the tests are more segmented and the index is on a scale 0–110, with 110 being unacceptable and 0 being inert.

Over the years since this technology was first used, the quality of the chemicals used has improved and the DI value for some of the chemicals has fallen. In many industries, there are voluntary limits to the DI level that is deemed acceptable. This not only has reduced the problem but also has limited the chemistry available.

The UK Society of British Printing Ink Manufacturers did issue a list of monomers that are voluntarily excluded from radiation-cured coating for the British printing industry. This list excluded all monomers with a Draize value >3.5 and was expected to be revised to a lower Draize value as soon as suitable alternative materials were available. This has now been changed to a list of preferred chemicals because it was found that not being able to use some chemicals was potentially damaging to the industry. Now if the formulation has only components from the preferred list, it can be labeled as a totally benign coating. If any component in the formulation is not on the preferred list, it has to be highlighted as containing a potentially hazardous component. Therefore, the incentive is there to use chemicals from the preferred list, but there is no ban on using nonpreferred chemicals.

This listing only applied to the printing industry and within other industries, such as wood coating, monomers on the list can still be used. The difference tends to depend on the difference in the ways the monomers are handled and used. Printers tend to touch the inks, whereas the wood coating is often a hands-off automated process.

One of the other areas that may need consideration is the odor emanating from the chemicals. Some of these chemicals, although not toxic, can make the working environment a very unpleasant place to work in.

Formulation

The basic performance of the coating will depend on the oligomer used. This performance is modified by the diluent monomer. Some of this can be offset by choosing the functionality of the diluent or by mixing more than one diluent to provide a more balanced combination of properties.

The coating will not cure without a photoinitiator, but the aim is always not only to minimize the quantity of photoinitiator used to reduce the coating cost but also to limit the possible longer-term degradation of the coating. Other additives that can be used are synergists as a way of reducing the quantity of photoinitiator used and hence reducing cost or acrylic acid as a method of increasing the coating adhesion to metallic surfaces. Stabilizers are used to increase the shelf life of the formulation. Once the formulation is mixed it can start to react and hence it needs to be protected from sunlight and possibly from moisture. If this is not done the liquid can start to form gels within the mixture, and these will either block any filters or if unfiltered will cause coating defects. If the formulation is mixed in small batches and is used immediately, it may be possible to dispense with all stabilizers. However, if purchasing an off-the-shelf formulation, it may already have these added.

As some of the ingredients may be solids, the mixing of the formulation may take many hours or even days and may require elevated temperatures during the mixing. Hence, many coaters choose to buy complete formulations.

The dispersants are only used where fillers and/or pigments are included and so for an unfilled polymer the use of a dispersant should be unnecessary. The emulsifiers are only used to disperse the polymers in an aqueous carrier, and therefore in vacuum where no solvent is required, the emulsifiers can be eliminated.

If we look at the acrylates as used by those depositing using the polymer multilayer (PML) technology, they used tripropylene glycol diacrylate (TPGDA) and 1,6-hexanediol diacrylate (HDDA). These materials have a low viscosity of 15 and 10 mPa s, respectively, and both have a functionality of 2 (diacrylate).

Where good slip properties were required, Ebecryl 350 was used. This is a silicone diacrylate added to the TPGDA.

These systems were cured using e-beam and so did not need a photoinitiator but typically Darocur 1173, Irgacure 184, or Irgacure 651 (or mixtures) is used where UV curing is preferred.

One such UV formulation used was polyethylene glycol diacrylate (PEGDA) sold as Ebecryl 11 and a photoinitiator Darocur 4265.

11.4 Comments

This polymer deposition and curing was initially developed and patented for the production of capacitors and from this work many patents were filed [25].

In a recent paper, it was shown that it is possible to use and control a highly uniform thermal evaporation source for depositing polymers [26]. Companies are offering, off-the-shelf, slot source evaporators for polymers for depositing OLED polymers and other companies are developing in-house alternatives [27–29].

There has also been work done to show it is possible to use a simple plasma as a UV source for curing polymers without having to use special lamps or e-beam sources [14,23,30].

The above section on polymer acrylates, I think, shows that it is not a simple topic but very complex with a huge number of options. The formulation requires not only the knowledge to buy the right ingredients but also the knowledge of how to mix them to get all the components properly dispersed and to the right viscosity.

Having said all that about the complexity, there are training courses on the subject and many of the suppliers have information about standard coating formulations [31].

Hence, many companies are paying at least an order of magnitude more for a basic off-the-shelf formulation that they could make for themselves if only they had bothered to do some basic research to learn more about the chemistry.

References

[1] Ramadas S, et al. Nanoparticulate barrier films and encapsulation method for solar and display applications. In: Proc. Pro-flex conference “vacuum roll-to-roll processing of flexible substrates” Fraunhofer FEP, Dresden; September 21/22, 2010.

[2] Ramadas S, et al. Nanoparticulate barrier films and gas permeation measurement techniques for thin film solar and display applications. In: Proc. AIMCAL technical conference and 22nd international conference on vacuum web coating; 2008.

[3] Sankey SW, et al. Composite sheet. WIPO patent application WO/2000/066653. April 30, 1999.

[4] Sinha Ray S, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog Polym Sci 2003;28:1539−641.

[5] Osman MA, et al. The aspect ratio and gas permeation in polymer-layered silicate nanocomposites. Macromol Rapid Commun 2004;25:1145−9.

[6] Sakaya T, Osaki N. The potential of nanocomposite barrier technology. J Photopolym Sci Tech 2006;19(2):197−202.

[7] Satas D. Coatings technology handbook. Marcel Dekker, Inc.; 1991. ISBN 0-8247-8410-3.

[8] Orchard SE. On surface levelling in viscous liquids and gels. Appl Sci Res Ser A 1962;11:51.

[9] Anshus BE. The levelling process in polymer powder painting—a three dimensional approach. Am Chem Soc Div Org Coat Plast Chem Pap 1973;33:493.

[10] Kistler SF, Schweizer PM, editors. Liquid film coating—scientific principles and their technological implications. London, New York: Chapman and Hall; 1997. ISBN 0-412-064-81-2.

[11] Shepherd F. Modern coating technology systems. Croydon, UK: Emap Maclaren; 1995. ISBN 0-902098-18-7.

[12] Brinston JH. Coating and laminating. Part I. Converter 1992; October:8−12; Part II. Converter 1992; November:13−18.

[13] Oldring PKT, editor. Chemistry and technology of UV and EB formulation for coatings, inks and paints. London: SITA Technology; Vol.1, Markets and curing equipment. 1991. ISBN 0-947798-11-0; Vol. 2, Prepolymers and reactive diluents for UV and EB curable formulations, 1991. ISBN 0-947798-10-2; Vol.3, Photoinitiators for free radical and cationic polymerisation, 1991. ISBN 0-947798-16-1; Vol.4, Formulation, 1991. ISBN 0-947798-21-8; Vol.5, Speciality finishes, 1994; ISBN 0-947798-37-0; Vol. 6, Test methods for UV and EB curable systems, 1994. ISBN 0-947798-07-2.

[14] Affinito JD, et al. A new hybrid deposition process, combining PML and PECVD, for high rate plasma polymerisation of low vapor pressure, and solid, monomer precursors. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999, p. 102−6.

[15] Shaw DM, Langlois MG. A new high speed process for vapor deposition of arcylate thin films: an update. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993, p. 348−52.

[16] Decker W. Advanced coating technologies for roll to roll metallizers. In: Proc. AIMCAL annual technical conference and 24th international conference on vacuum web coating; 2010.

[17] Ferrari D. Properties of EB top-coated metallized films prepared in vacuum. In: Proc. AIMCAL annual technical conference and 24th international conference on vacuum web coating; 2010.

[18] Rechel CJ, editor. UV/EB curing primer: inks, coatings and adhesives. 4th ed North America: RadTech International North America; 1995. ISBN 1-878664-13-1.

[19] Menezes T. Control systems for today's EB equipment. RadTech Report 1995; May/June:19–21.

[20] Wild L. Electron beam—a window to the future. Converter 1997;October:21–5.

[21] Cunningham W. UV curing of acrylate resins versus cationic epoxies. Adhesives age Apl 1996:24–8.

[22] Price LN. Free radical and cationic photinitiators in ultraviolet light curable coatings. J Coat Technol 1995;67(849):27–34.

[23] Yalizis A. and Mikhael M. UV versus electron beam radiation curing of vacuum deposited polymer levelling coatings for high barrier applications. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004, p. 600–5.

[24] Zwanenburg R. How raw materials face the challenges of UV and EB curing. Polym Paint Col J 1995;October:15–6.

[25] Behn R, et al. Method and a device for the production of electrical components, in particular laminated capacitors. US 4,508,049, 1985; Behn R. Method and apparatus for producing laminated capacitors. US 4,378,382, 1983; Olson D. Capacitors containing polyfunctional acrylate polymers. US 4,490,774, 1984; Cichanowski S. Capacitor with dielectric comprising poly-functional acrylate polymer and method of making. US 4,499,520, 1985; Olson D. Acrylate-containing mixed ester monomers and polymers thereof useful as capacitor dielectrics. US 4,513,349, 1985; Olson D. Polyfunctional acrylate monomers and polymers thereof useful as capacitor dielectrics. US 4,515,931, 1985; Olson D. 1,2-Alkanediol diacrylate monomers and polymers thereof useful as capacitor dielectrics. US 4,533,710, 1985; Cichanowski S. Capacitor with dielectric comprising a polymer of polyacrylate polyether pre-polymer. US 4,586,111, 1986; Yalizis A and Shaw D. High speed process for coating substrates. US 4,842,893, 1989; Ham M. Nonthermionic hollow anode gas discharge electron beam source. US 4,647,818, 1987.

[26] Affinito J. Polymer film deposition by a new vacuum process. In: Proc. 45th annual technical conference of the Society of Vacuum Coaters; 2002, p. 425–39.

[27] Van Slyke S, et al. Linear source deposition of organic layers for full-color OLED. SID 02 Digest: SID International Symposium Digest of Technical Papers; 2002;886–9.

[28] Spahn RG. Source for thermal physical vapor deposition of organic electroluminescent layers. US 6,237,529 patent; 2001.

[29] Hoffmann U, et al. New in-line machine concept for OLED manufacturing. SID 02 Digest: SID International Symposium Digest of Technical Papers; 2002;691–3.

[30] Simonsis Y. The dawn of a new age in coating technology. Paper, Film & Foil Converter; February 1998;51–4.

[31] Formulary—starting formulations, coatings and overcoats. Sartomer Co; Formulary—starting formulations, coatings and overcoats. Henkel Corp; Formulary—starting formulations, coatings and overcoats. UCB Chem Corp; Examples—supplied for RadTech 1996 Advanced Chemistry Tutorial.

12 Nucleation, Coalescence, and Film Growth

There are several characteristic steps to the initial growth of coatings. These are nucleation, coalescence, network, percolation threshold, holes, continuous, and film growth.

12.1 Thin Film—Thick Film

There is always some ambiguity about what is a thin or a thick film. In the aerospace industry, coatings vacuum deposited for thermal barrier performance are many tens of microns thick, and any coating less than 10 μm is thought of as being a thin film. Similarly, abrasion- and corrosion-resistant engineering coatings are also often microns to tens of microns thick. In the metallizing for packaging industry, a coating of 1 μm would be regarded as a very thick coating. More typically, these coatings start at the point where they have just become continuous at <10 nm and most will be <50 nm thick.

To avoid ambiguity, I will define thick and thin coatings as follows:

- Thin film is a coating of less than 1 μm in thickness.
- Thick film is a coating of greater than 1 μm in thickness.

12.2 Nucleation

There is a large body of work on the nucleation and growth of coatings [1—12]. At times, it can be difficult to see where very low deposition rates in ultrahigh vacuum systems onto freshly cleaved single crystal materials have any relevance to the high deposition rates onto polymer substrates at only moderate vacuum. However, it is from the former that unraveling the structures deposited by the latter has been done.

The nucleation and film growth that produce the final thin film structure are influenced by the vapor source and the substrate, in particular the substrate

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00012-X

temperature. The vapor can arrive with or without any additional energy. The rate of arrival of the vapor can vary by several orders of magnitude. The substrate will have roughness and surface energy that can influence the nucleation and growth, but these can be modified by the use of surface treatments. How these can influence the growth is discussed below.

Whatever the source of vapor or the substrate, the basic sequence of nucleation is the same. The atoms arrive at the surface where they can stay or leave. The atoms that stay are absorbed on the surface and those that leave are desorbed or re-evaporated from the surface. Any atom arriving at the surface can be defined as having a probability of sticking to the surface. If all atoms stick to the surface, they have a sticking coefficient of 1. The value of the sticking coefficient depends on many factors such as the substrate temperature, the energy of the arriving atoms, the angle of arrival of the atoms, the type of substrate, and depositing material, to name but a few.

An atom that arrives on a surface and stays will either stay where it is or move around on the surface. The process of an atom moving around on the surface is known as surface diffusion. The higher the energy the atoms arrive with on the surface, the more and faster they move around on the surface. The atoms continue to move until they reach a position that minimizes the total energy. As more atoms arrive, they undergo the same process, but as there are already atoms sticking to the surface, some of these new atoms will contact the original atoms and the size of the nucleated particles will grow. Initially, these are metastable clusters, but once the nuclei reach a critical size, they will become stable and fixed.

There are various mechanisms for the further growth of the nuclei [13,14] (Fig. 12.1). Van der Merwe mechanism describes the method where the atoms cover the whole surface before a second layer is grown. If the nuclei grow as hemispheres and a thin film is formed once the hemispheres have grown large enough to touch each other, then it is referred to as the Volmer—Weber mechanism. If the growth process is a combination of the two by first covering the surface and then growing by hemispheres, it is referred to as the Stranski—Krastanov mechanism.

In roll coating onto polymer surfaces, the growth will be by the Volmer—Weber mechanism. The other mechanisms depend on there being a good match between the substrate crystal structure and the thin film crystal structure. This is impossible between the polymer substrate and metals or metallic compounds thin film. The mismatch is too great and also the surface roughness is too great compared to the cleaved or single crystal that would be required for van der Merwe growth.

In general, the nucleation will be in a random pattern. This too can be modified by the substrate (Fig. 12.2). If the substrate has any surface structure, either formed

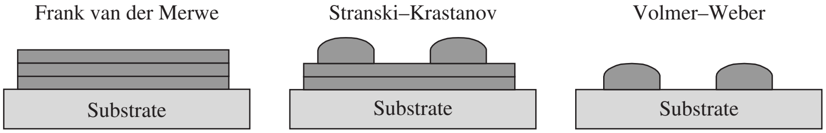
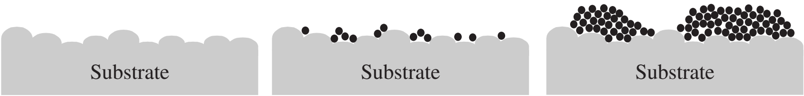


Figure 12.1 A schematic of the different growth techniques.



Substrate roughness will lead to preferential nucleation. Nucleation will start in the valleys between peaks. The coating will not be conformal and so the coating will have a similar or greater roughness to that of the substrate. The rougher the substrate the more pronounced this effect will be and thicker coatings will be required to obtain a continuous coating.

Figure 12.2 A schematic of the effect of surface roughness on nucleation.

during manufacture or imposed such as by selective etching or embossing, this can be transferred to the growing coating.

Hence, defects in the surface can generate defects in the subsequent coating. Any step on the surface will allow an atom to touch the surface at both the bottom and side of the atom, and that will always be more energetically favorable than only contacting at the bottom of the atom. As defects will always have steps, there will be a tendency for there to be a higher number of nucleation sites at defects than elsewhere. If the polymer surface has microscratches or protruding fillers on the surface, these may, in certain circumstances, still be seen after deposition because of differences in the coating quality or texture between damaged and undamaged areas. As most deposited coatings are not conformal, there will be a tendency for nucleation to take place in the valleys and growth to take place from these nuclei as shown schematically in Fig. 12.2. It will take a greater thickness to coat the peaks of a rougher surface than to coat the peaks on a smooth surface. This can be imagined if you think of the coating being a liquid where the liquid fills the valleys until it is deep enough to cover the peaks. This is not quite how it is in practice as the coating can be seen to follow the surface contours and evidence of scratches may still be seen in the surface of the coating.

Thus, substrate surface roughness can affect the coating quality and coating defects, which, in turn, will affect the barrier performance. An exception to this would be atomic layer deposition where the coating is conformal and peaks and valleys are coated equally as described further in Chapter 19.

With polymers, the surface is a mixture of amorphous and crystalline areas that encourages random growth. Efforts have been made to add structure by embossing a fine pattern into the polymer. The pattern controls the organization of steps and hence can produce a particular nucleation pattern.

12.3 Coalescence

As the randomly positioned nuclei increase in size into islands, there will be some that come into close proximity. Once the spacing between any two nuclei or islands gets to within a critical distance, they will move toward each other and coalesce

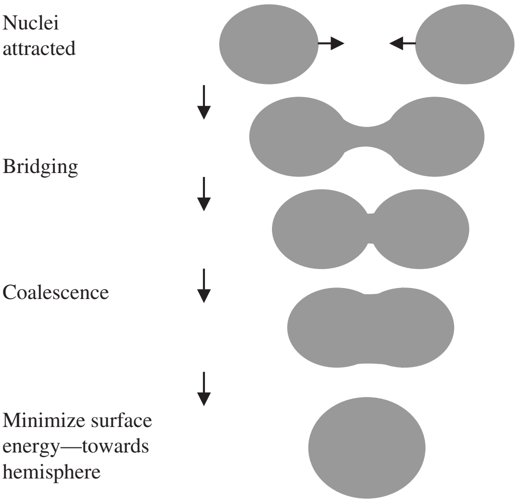


Figure 12.3 A schematic of the coalescence of a couple of nuclei.

into a single entity (Fig. 12.3). With the arrival of more atoms, the nuclei and islands continue to grow and coalescence continues. When larger islands coalesce, the area they move from is denuded of material and so new nuclei will form and grow [15].

Watching this process happen in real time, one might believe that the nuclei were liquid because they were so mobile. The melting point of metals falls as the diameter of the nuclei gets smaller. The melting point can be reduced by several hundred degrees as the diameter falls below 15 nm [16,17].

12.4 Network and Percolation Threshold

With the continued growth, there will be coalescence of several nuclei and islands into more complex shapes. Eventually, this will result in a network of interconnected islands. If the resistance of the thin film is measured from one edge of the surface to the other edge, the point at which there is evidence of conduction is referred to as the percolation threshold [18,19]. This indicates that there is at least one, albeit possibly convoluted, conduction path across the surface. This by no means indicates that the surface is completely covered.

12.5 Holes

The network will expand and undergo further coalescence, increasing the conduction paths for more efficient conduction and thus reducing the resistance. The surface will become more completely covered apart from some isolated holes. With

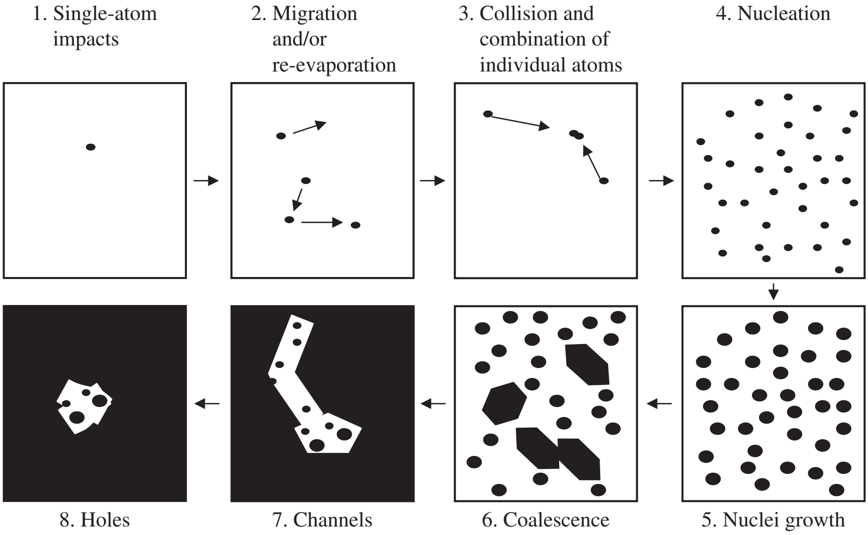


Figure 12.4 A schematic showing the stages of nucleation and initial growth [1].

continued deposition, the holes will continue to shrink until the coating becomes complete and is continuous.

Depending on the conditions, the coating might be quite thick before the last of the holes is filled in. Any material deposited at the bottom of one of these holes will still be quite mobile, and as the nuclei grow, they will be attracted to the crystals that surround them and will move toward them and coalesce and be absorbed into the larger crystal. Thus, the hole gradually shrinks in size. In real time, it is possible to see the formation of new nuclei that then move and disappear to be replaced by fresh nuclei (Fig. 12.4).

12.6 Film Growth

Once the surface is completely covered, the film thickness will then grow as dictated by the initial deposited layer. Crystals can grow with a variety of different orientations (Fig. 12.5). The different orientations can have different atomic spacing, and hence for the same arrival rate of atoms, some areas will grow faster than others.

The areas that grow faster will eventually shadow the slower growing areas and hence will expand and further starve the slower growing areas of additional atoms. This will result in columnar growth, and if nothing is done to disrupt the crystal growth, the surface will become very textured and rough, producing a matt surface rather than a specular reflecting mirror surface. Some of the larger nodules that

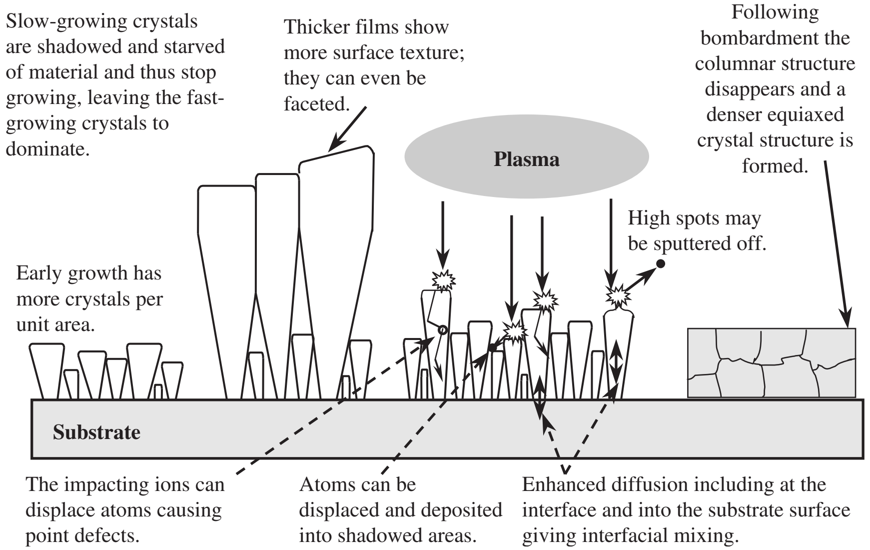


Figure 12.5 A schematic showing several different aspects of film growth.

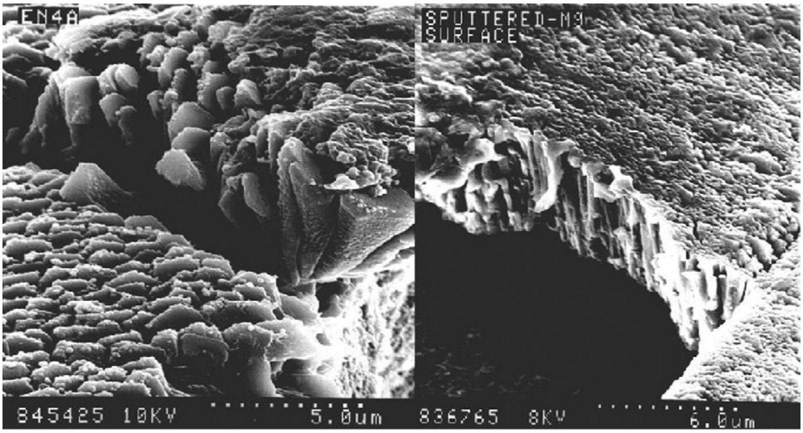


Figure 12.6 Micrographs of thick films showing columnar growth and the texture of surfaces.

may appear on the surface are often associated with defects in the substrate that have attracted early nucleation and faster growth [20−24] (Fig. 12.6).

Columnar growth is only associated with thicker films. With films below 1 μm, the process of growth in many of its aspects has only just started, and hence many features seen in thick films are not yet fully formed or easily seen. This can have some advantages such as the reflectivity is likely to be higher because of a smoother surface if a columnar structure or faceted crystal growth has yet to influence the surface roughness, but is likely to have disadvantages such as the presence of pinholes or pores from incomplete growth (this is in addition to any pinholes that will be produced from surface defects).

12.7 Energy

The use of energy can affect the nucleation and growth of the thin film [25–28]. The energy available during deposition will depend on the deposition source, the deposition rate, the substrate sensitivity, and the winding speed. The evaporation deposition source is very hot and will provide the front surface of the web with a radiant heat load as well as the energy transferred, called the latent heat of condensation, which is from the condensation of the atom in the vapor to a solid on the surface. The magnetron sputtering sources have a relatively cool surface and so the radiant heat is much lower. However, the atoms can arrive with all the energy transferred from the bombarding ion to the ejected atom out of the target surface. There will also be some energy from electron bombardment. The amount of this energy is dependent on the design of the magnetron source (balanced or unbalanced). There will also be the latent heat of condensation. The electron beam deposited atoms have some radiant heat from the source. They will also have some energy added to the deposition flux of atoms, which is added as the atoms pass through the electron beam on their way to the substrate.

We want to be able to control the growing structure so that we can optimize the coating performance in some way. Figure 12.7 shows the progression of improving the coating density and how that can correlate to the improvement in barrier, reflectivity, or surface smoothness. As the nucleation and growth can affect the coating attributes, if we can modify the way the coating nucleates and grows, we can to some extent control the final coating performance.

Throughout the deposition process, as the atoms land, they transfer the energy into the substrate, causing it to rise in temperature. Increasing the substrate temperature will allow the arriving vapor atoms to travel further and faster in search for the lowest energy nucleation site. Thus, increasing the substrate temperature will lead to fewer nucleation sites and to larger crystals in the final thin film.

Polymer webs have the problem that they are often temperature sensitive even at relatively low temperatures (Fig. 12.8). The webs that have been stretched can shrink back if the temperature is raised too much. Hence, most polymers have to be cooled during the deposition, but because of the poor rate of heat transfer between the polymer and the cooling drum, the web temperature will not be controlled but will continuously increase. Generally, the winding speed and/or deposition rate is limited to keep the maximum temperature the web reaches below a particular set point.

Double side coating of polymers will produce different thin film structures on each side as a result of the difference in the heat transfer coefficient between the

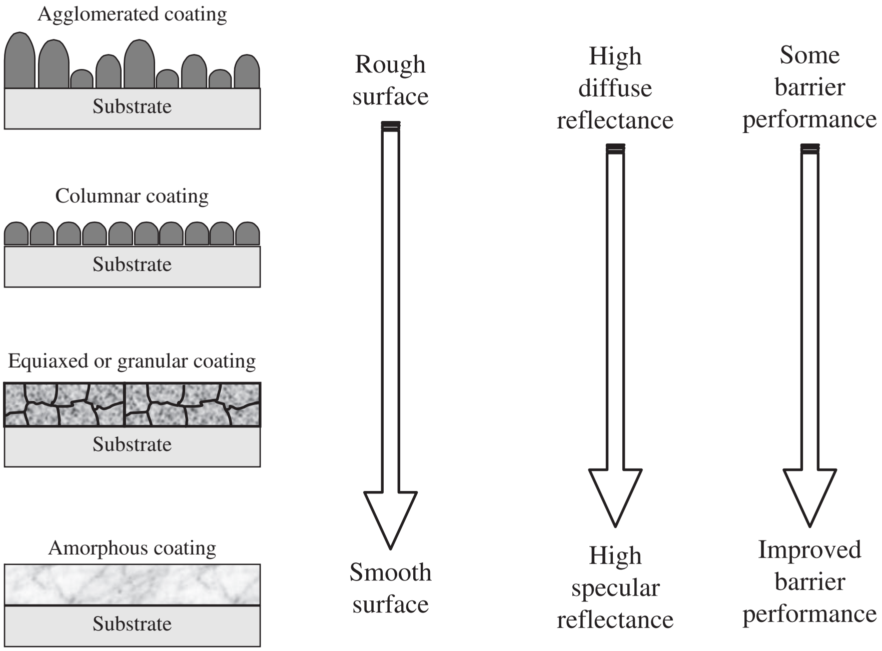
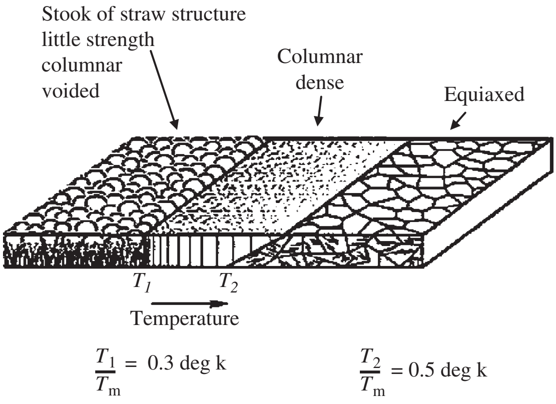


Figure 12.7 A schematic of how the coating density and structure can affect some of the coating attributes.



$\frac{T_1}{T_m}$ = 0.3 deg k

$\frac{T_2}{T_m}$ = 0.5 deg k

The addition of oxygen can alter the temperatures by 100°C. The zones grade into each other, there is not a sharp interface between zones.

T_m = melting point of material

Note: This is a trend only.
Movchan & Demchishin Phys. Met. Metallography 28, 83 (1969)
This work was for metal films deposited by evaporation to a thickness of several millimeters.

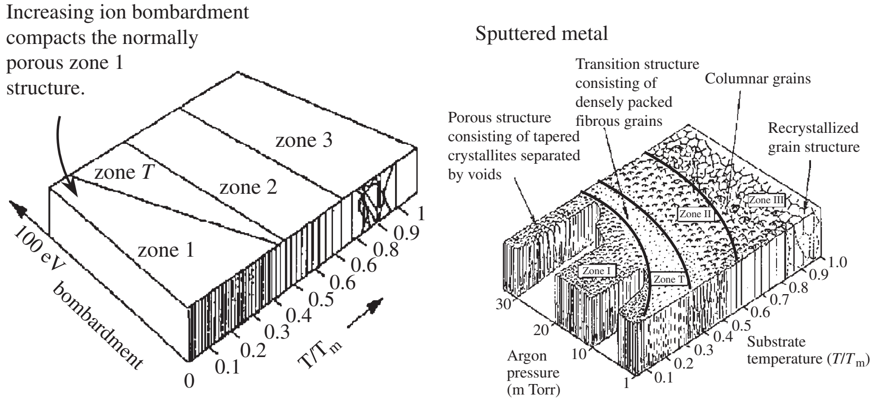
Figure 12.8 A schematic showing the effect of temperature on the growth structure [29].

polymer and cooled drum on one side and the metallized polymer and cooled drum on the second side.

Another method of changing the energy of the arriving atoms is to use an additional plasma, which will increase the percentage ionization of the vapor. Alternatively, the plasma can be sited over the deposition zone to increase the direct bombardment of the growing thin film. This bombardment assists in ejecting poorly adhered atoms and densifying the structure by collapsing many of the residual gas pockets. This does not mean the films will be 100% dense, but they will approach this level depending on the rate of growth and bombardment. The impact of the higher energy atoms can knock off poorly adhered atoms or can disrupt the surface causing mixing of the surface atoms. The net result of this is that the adhesion is improved both by removing poorly adhered atoms and by improving the thickness of the interface.

Figure 12.9 is an indication of the structures that can be formed by sputtering [30]. This diagram only uses pressure and temperature as the variables. This can be modified further using bombardment energy on the third axis.

There are many different ways to generate plasma: rod cathode activated deposition (RAD) [32], spotless arc activated deposition (SAD) [32], hollow cathode activated deposition (HAD) [32]—described in more detail in Chapter 16 (Section 16.9)—as well as microwaves [33]—shown in Fig. 12.10. This coating densification can also be achieved by using an ion gun pointing directly at the substrate deposition zone [34] to give the same sputter removal of less well adhered



A refinement of the growth model as put forward by Messier.

Thornton extension of Movchan and Demchishin zones

T = Temperature T_m = Melting point of material

Figure 12.9 A schematic showing how the growth structure can be extended to show the effects of deposition pressure [30, 31]. The numbers 1, 2, 3, and T refer to the Movchan−Demchishin zones.

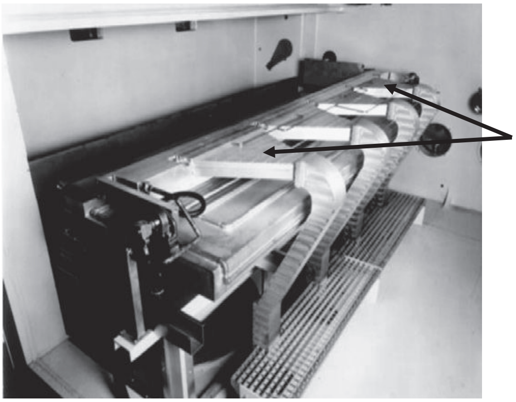


Figure 12.10 A photograph of a microwave-powered intermediate plasma used to increase any reactive process and to help densify the deposited coating. Photograph courtesy of Applied Materials [32].

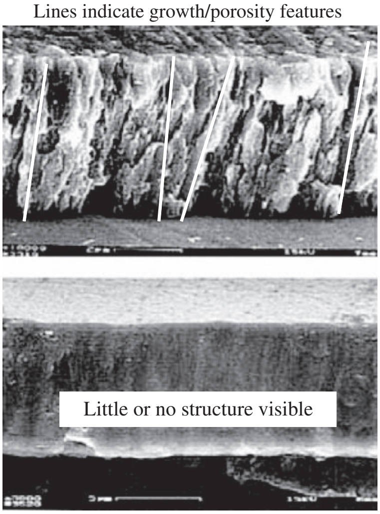
atoms during the deposition. It is to be noted that all of these techniques that remove poorly adhered atoms effectively reduce the deposition rate of the growing coating and increase the substrate heat load.

One of the problems that can often be seen with denser coatings is stress [35−45]. This is much more obvious for coatings onto polymer webs, particularly thin polymer webs, but will also be present on other substrates. Often part of the problem is related to the differential between the different coefficients of thermal expansion between the coating and the substrate. In porous films, there is room for the coating to distort and take up any of the changes in dimension. Dense coatings do not have this property and so any differential change in dimensions shows up as curl of the substrate, or if the adhesion is exceeded, buckling of the coating off the surface can be observed [46]. Increased pressure can lead to increased gas inclusion, reducing the density and the stress.

There are many parameters that can affect the amount of stress and even the sign of the stress. The most widely available parameter to change is pressure. This can be used even for simple evaporated coatings. Where there is a more energetic source and/or an additional plasma, there are more options (Figs. 12.11−12.13).

12.7.1 Angular Deposition

It has been assumed that the arrival of the atoms takes place normal to the surface. In reality, this is not the case. Evaporation sources act as point sources and the pressure is usually low enough that there are few, if any, gas collisions. Thus, the arrival of atoms onto the web will be from where the web first comes into line of sight with the source and through the position where the deposition is normal to the surface through to a point where the source disappears from line of sight from the web.



The micrographs on the left are for titanium onto steel strip. The upper micrograph is for an electron beam deposited coating at a deposition rate of 150 nm/s and the columnar structure is clearly visible.

The lower micrograph is for the same material but there has been an additional plasma used to densify the coating. The resulting coating has lost all evidence of columnar structure and the surface is smoother. The plasma bombardment sputters off loosely bound material and this material removal results in a lower deposition rate of 100 nm/s.

Figure 12.11 Micrographs showing the benefit of using an additional plasma during the deposition process. Courtesy of FEP Dresden [33].

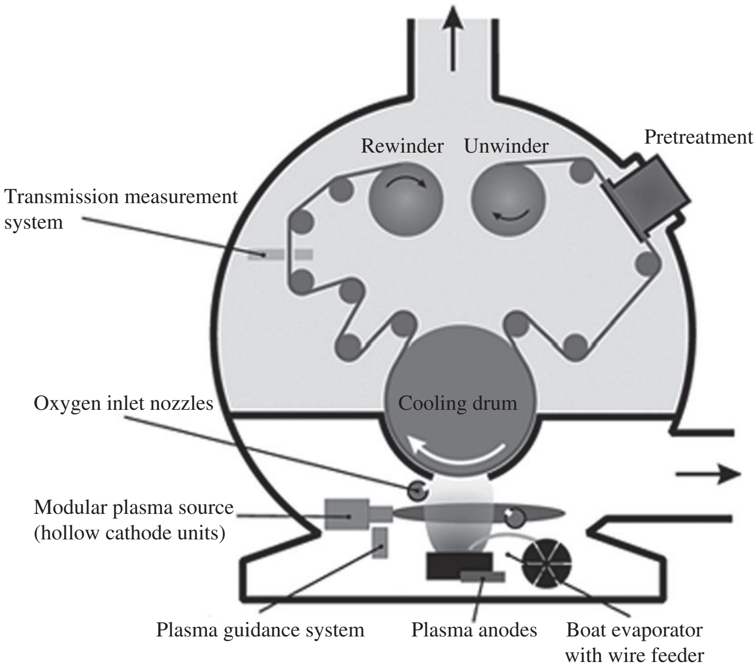
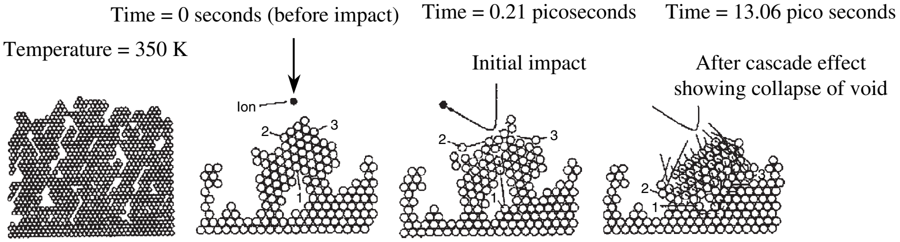


Figure 12.12 A schematic of a hollow cathode plasma activated (HAD) process used to assist the conversion and densification of aluminum oxide deposited from an aluminum evaporation source. Published with kind permission of the Society of Vacuum Coaters [47].



The left-hand diagram is of a loosely packed structure using an evaporation process. It was produced using a Monte-Carlo computer simulation program.

The three diagrams progressing from left to right show the effect of ion bombardment on such an evaporated coating. The ion impact has a cascade effect on the adjacent atoms and can cause collapsing of any voids making the resultant structure much more dense.

The bombardment and increased density coating can lead to more pronounced stress effects such as bending the substrate or even adhesion failure.

Figure 12.13 The figures show a Monte Carlo simulation for film growth without ion bombardment and then with some bombardment [48]. The porosity with bombardment is reduced but there will be entrapped gas.

In evaporation systems, there is a wish to increase the deposition efficiency. By using a larger deposition drum at the same distance away from the deposition sources, more evaporant will be collected (Fig. 12.14). However, at the wider deposition angles, there is an increase in shadowing, leading to greater porosity, lower density, and increased surface roughness, which can lead to lower reflectivity. Thus, there is a trade-off between material efficiency and coating performance [49]. Thus, there tends to be a preference toward deposition of the vapor normal to the substrate surface.

There are systems that have deliberately used a "grazing incidence" deposition to improve the coating performance. This was seen on some of the magnetic tape deposition systems where the thin film grown was a columnar structure and the mechanical performance was initially poor. The deposition source was moved from directly beneath the cooled deposition drum to be offset such that the deposition was underneath one half of the drum. The effect was that the columns were curved because of the changing angle of deposition and this gave the coating an increase in the mechanical performance. The downside of this was that, in effect, almost half of the depositing vapors was wasted because it coated the shields rather than the web (Fig. 12.15).

12.8 Electrical and Optical Performance

The optical performance of thin films can vary with structure (Fig. 12.16). This may not necessarily be obvious and seen in the visible but can become very

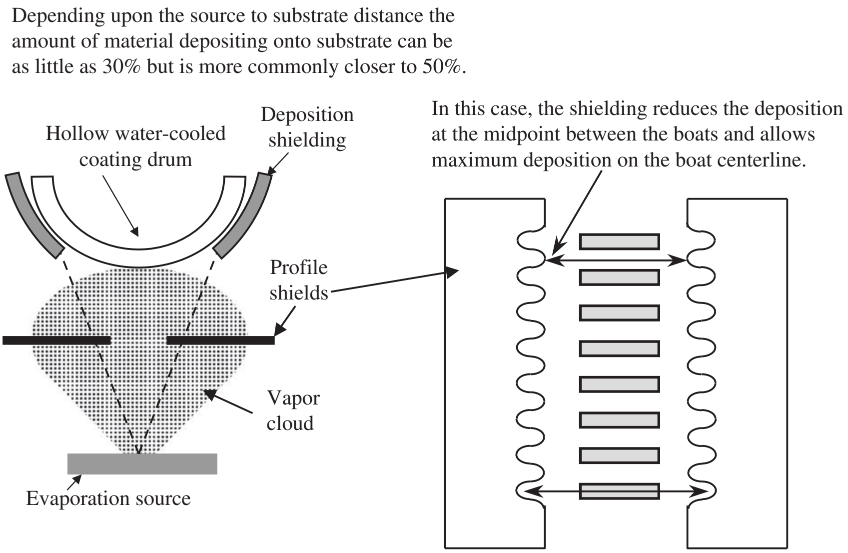


Figure 12.14 A schematic showing shielding or masking of the web from a point deposition source [50].

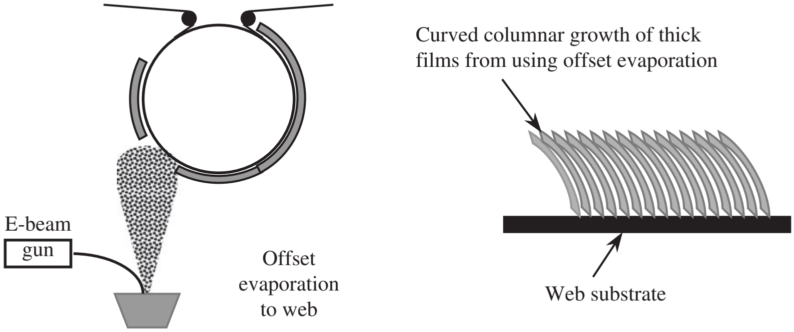
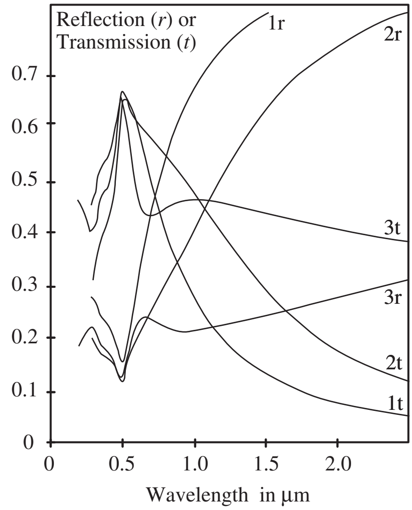


Figure 12.15 A schematic showing the effect of using an offset deposition source on the resultant structure of the coating [51].

noticeable in the near infrared. This is related to the crystal size and the scattering that this generates.

The transmittance trace in Fig. 12.17 shows the initial film growth where, as the metal nucleates, the transmittance decreases to a minimum. This minimum represents the maximum combination of absorption of light by the metal and scattering by the number and shape of the nuclei. As deposition continues, some of the nuclei coalesce and the light scattering reduces, and hence the transmittance increases to a maximum. This maximum is where the scattering is still being reduced, but the



Reflectance (r) and Transmittance (*t*) for three different microstructure films but each of approximately the same thickness of 12 nm.

1 = highest density
2 = medium density
3 = low density

With high-density coating the reflectivity rises more quickly in the near-infrared and reaches the maximum more rapidly.

The low-density coating has a worse performance with reflectivity having a very slow rise in the infrared. This would have poor performance for energy saving window type applications.

Figure 12.16 A graph showing the changing optical performance due to differences in the film structure [52−54]. Reprinted with permission from Elsevier [53].

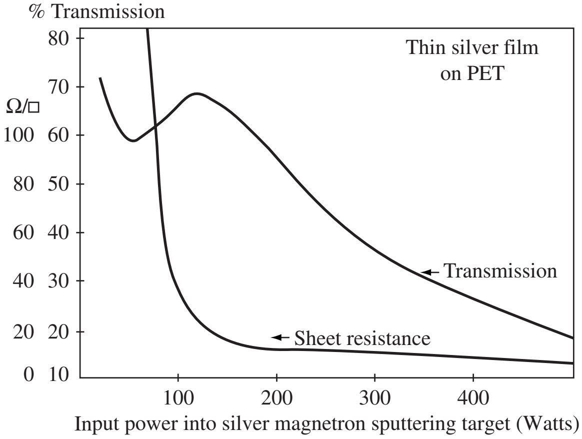


Figure 12.17 A graph showing the changing properties with increasing coating thickness [55].

turning point is reached where the surface area covered by the absorbing metal starts to dominate. From this point, the continued deposition fills in the remaining holes and builds up the coating thickness.

It is worth noting that soon after the early minimum in transmittance, the coating had reached the percolation threshold as can be seen by the appearance of the sheet resistance measurement. The traces of mobility and resistance would suggest that a continuous film is only achieved at around 15 nm (150 Å).

This performance is typical of a magnetron sputtered metal film deposited at room temperature. The same curves can be produced but shifted to the left or right on the thickness scale by changing the substrate temperature or by increasing or reducing the energy of the deposition source.

Barrier coatings can be produced at half of this thickness, at around 7 nm, which suggests that these materials can be produced as continuous coatings if attention is paid to the surface quality and energy. Atomic layer deposition of material produces coatings that are much more conformal, which would further reduce this minimum thickness at which continuous coatings can be formed.

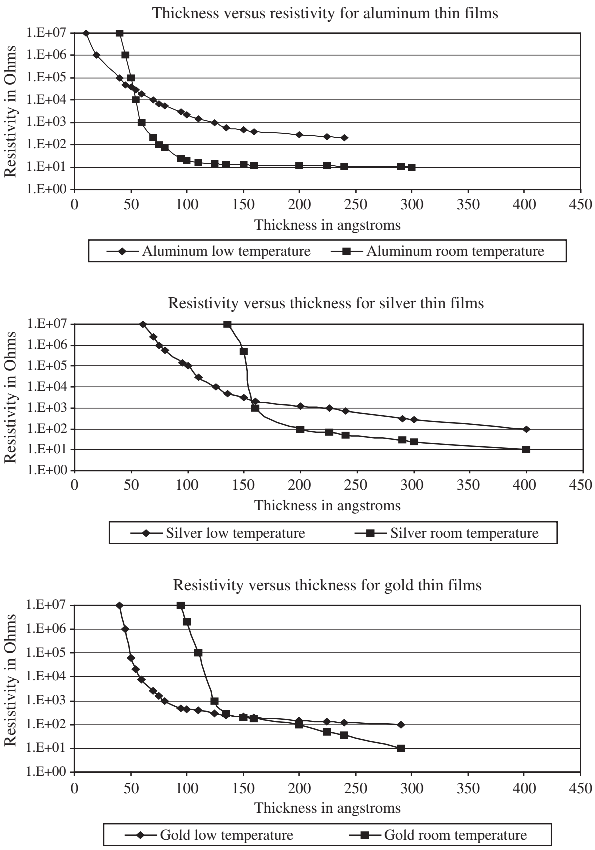
Optical coatings have another sensitivity relating to the grain structure, that of water vapor. When coatings are deposited in vacuum, they will have a particular measured performance. When the coatings are measured again once they have been brought out of vacuum, the performance may have changed. This can be due to the absorption of water into the pores at the grain boundaries. The more porous the coating, the greater the quantity of water absorbed and the greater the change in performance. Additional plasmas used during deposition will help densify the growing film minimizing the porosity.

The electrical performance is also affected by crystal size where the resistance is to some extent dependent on the number of grain boundaries.

Figure. 12.18 shows that low temperature produces a smaller crystal size. This is indicated by the fact that there are more nuclei and hence the coatings become conducting at a thinner thickness. However, the larger crystal films deposited at room temperature have fewer grain boundaries of higher electrical resistance, and hence with increased thickness it is possible to achieve a lower resistance than the films deposited at low temperature with the small crystal size and more grain boundaries.

12.9 Nodule Formation

It has been mentioned that the coating is not conformal and that debris on the surface can be a source of pinholes. This is true for large-scale surface contamination and low-energy evaporation sources. Where the coating is deposited with higher energy such as by sputtering or where there is plasma activation of depositing material, the coating may become more conformal. The large-scale surface debris can be removed from the surface as described in Chapter 8, but with the limitation that debris of less than approximately 300 nm in size cannot be removed because of the strong van der Waals force holding them onto the surface. Debris of this size can still lead to pinholes by being coated and moved. However, if we go down in scale and look at debris on the surface that is of a size comparable with the thickness of the coating or smaller, then there are other coating defects that can sometimes be seen, which are called nodules (Fig. 12.19). These become particularly noticeable on optical coatings where there may be multilayer coatings and the total coating thickness may exceed a micron taking it into the area I defined as thick coatings. This does not preclude these nodules being present on thin coatings, including very thin coatings of only a few tens of nanometers in thickness, which



The lower temperature gives a smaller crystal size and hence starts to show some conductivity at an earlier stage with a thinner average thickness than the films grown at room temperature.

However, thicker films show the films grown at room temperature,with the larger grain size, show a higher conductivity than those grown at low temperature. This is because larger grains mean that between any two contacts there are fewer high-resistance grain boundaries.

Figure 12.18 These graphs show the performance for gold, silver, and aluminum deposited at room temperature (RT) and low temperature (LT) [56].

means that they are more difficult to view and identify. Where the coating thickness is known and the nodule size is measured, it is possible to calculate the particle size that was the source of the nodule [57−59].

Where the coatings have been grown to a thickness of a few hundred nanometers, the nodule size is larger and easier to view and image [60,61], and this includes imaging a fracture surface where the shape of the nodule can be seen through the thickness of the coating. This is shown in Fig. 12.20 of a sputtered multilayer optical coating. It is not surprising that this surface roughness to the coating causes transmission and reflection losses because of light scattering. Also, with thick coatings it was possible to measure the proportion of the surface that was taken up by nodule growth and so to calculate the number of particle defects per unit area on the substrate that originated the nodules. This work showed many of the nodules were grown from particles of only a few nanometers in size. Even for smooth polymer films, there will still be oligomers present on the surface of the

Relationship between contaminant particle size and visible nodule size

$$h = d$$

$$D = (8\,d\,T)^{1/2}$$

For example for a 1micron thick coating and a nodule diameter of 200 nm

$$200 = (8 \text{ x } d \text{ x } 1000)^{1/2} = (8000d)^{1/2}$$

$$d \cong 5 \text{ nm}$$

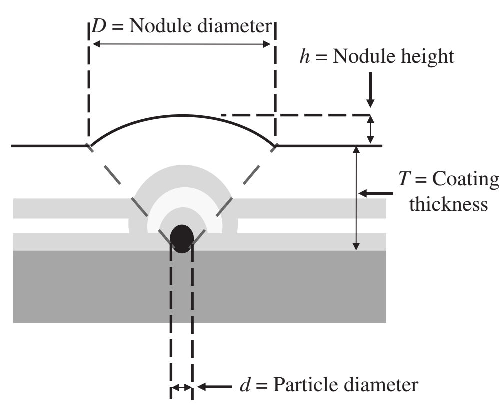
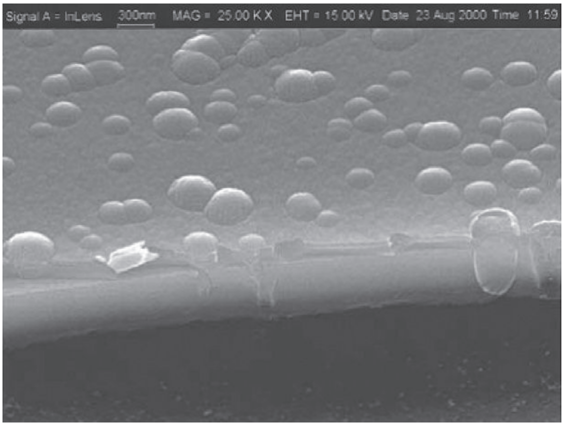


Figure 12.19 A schematic of a nodule that has grown from a surface particle and the relationship between the particle size, nodule diameter, and coating thickness [57–60].



SEM micrograph of the five-layer optical coating of Nb_2O_5 and SiO_2 on PET film.

Figure 12.20 A micrograph of an optical coating showing the nodules on the surface and from the fracture edge that the nodules originate from the polymer surface. Published with kind permission of the Society of Vacuum Coaters [60].

right size such that there will not be a shortage of suitable particles or defects that could lead to nodular growth (see Chapter 8, Section 8.2). In terms of thin coatings used for barrier applications, the edge of the nodule where it meets the coating on the polymer surface will be an area of weakness that, even if not already a region of higher diffusion, will crack easily and so will become an area of higher diffusion once the material has been flexed.

Even with thinner coating defects on the substrate surface, it is possible to see the effects. Figure 12.21 shows a number of bumps on the coated surface; this is

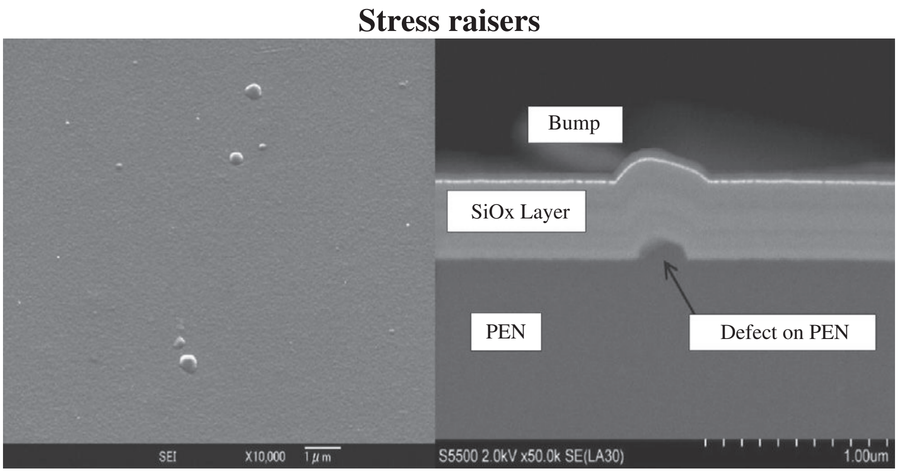


Figure 12.21 SEM image of the surface of SiOx coating on PEN (left) and low-angle SEM image of the cross section of a defect (right). Micrograph published with kind permission of the Society of Vacuum Coaters [62].

shown on the left-hand side micrograph. On the right-hand side micrograph, it can be seen that a 300 nm diameter size bump on the surface of the 300 nm thick coating and that it originated from a 100 nm surface bump on the substrate.

12.10 Crystal Structure

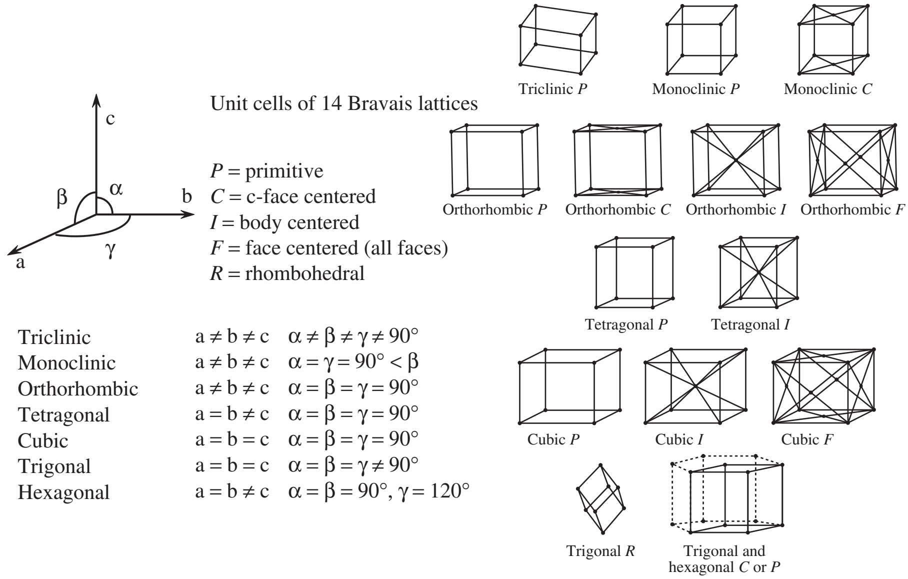
Not all elements and compounds have the same crystal structure. In some circumstances, it is possible to control the crystal growth to optimize the coating properties. Most of the time, with web coating, the most that can be controlled is the crystal size.

There are 14 different unit cells that are formed by different materials [63–65]. Any one material will usually only be able to deposit as one or another of these 14 types of lattice structure (Fig. 12.22).

The atoms when they first nucleate have no position in a lattice. It is only when a number of atoms coalesce that any structure will start to form. If you can imagine that as the atoms come into close proximity in a random fashion, the spacing will be different. If we use lines to connect up different atoms in the lattice models, we can see that there are many different options. Where the lines are connected, they are referred to as planes as shown in Fig. 12.23.

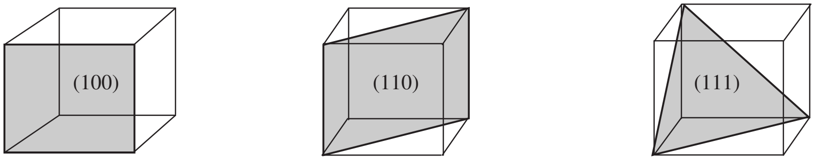
The dots at each corner represent the position of the atoms, and sometimes the lattice structures are drawn with solid spheres as shown in Fig. 12.24.

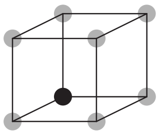
If we start stacking lattices on top of each other, we can see that different planes will have different spacing from each other. This is the basis of different growth



Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° < \beta$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$

Figure 12.22 A schematic showing the basic lattice types.
Reprinted with permission from Elsevier [65].





The above schematics are of the common planes found in cubic lattice systems. The notation used is as shown on the left. Starting with the atom shown in black in the lower left-hand corner, this atom is designated “0” is each direction. The next atom in any of the “*x*,” “*y*,” or “*z*” directions is then “1”.

Thus, each plane can be defined by where it cuts each axis. The left hand one only cuts the “*x*” axis and so is designated (100). The middle one cuts both the “*x*” and “*y*” axes and so is designated (110) and the right-hand schematic drawing shows the plane where it cuts all three axes and is designated (111).

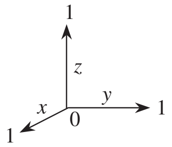
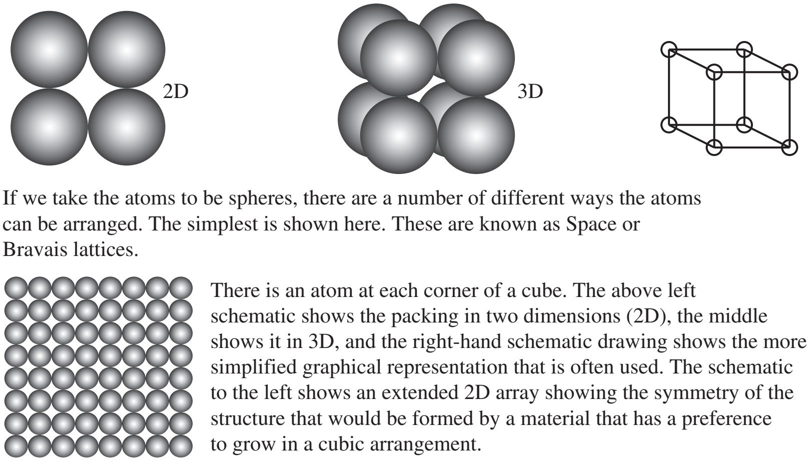


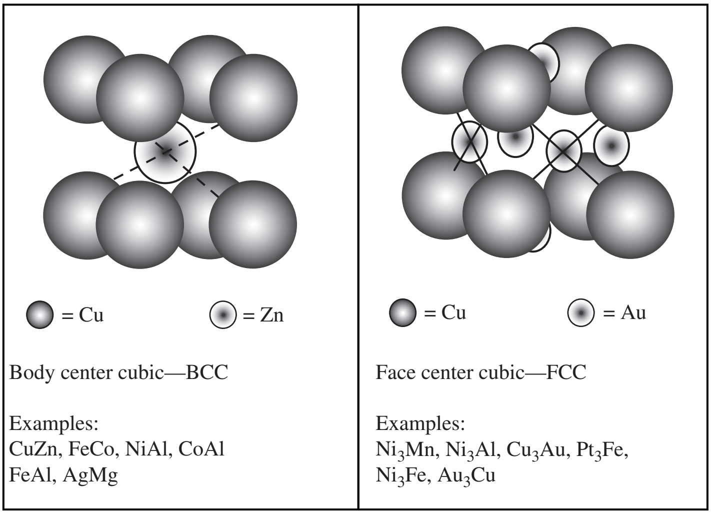
Figure 12.23 A schematic showing the relationship between the planes and the basic lattice structure.



If we take the atoms to be spheres, there are a number of different ways the atoms can be arranged. The simplest is shown here. These are known as Space or Bravais lattices.

There is an atom at each corner of a cube. The above left schematic shows the packing in two dimensions (2D), the middle shows it in 3D, and the right-hand schematic drawing shows the more simplified graphical representation that is often used. The schematic to the left shows an extended 2D array showing the symmetry of the structure that would be formed by a material that has a preference to grow in a cubic arrangement.

Figure 12.24 A schematic showing some basic principles used in describing lattice types and structures.



Body center cubic—BCC

Examples:
CuZn, FeCo, NiAl, CoAl
FeAl, AgMg

Face center cubic—FCC

Examples:
Ni_3Mn, Ni_3Al, Cu_3Au, Pt_3Fe,
Ni_3Fe, Au_3Cu

Figure 12.25 A schematic showing the lattice types of some common alloys.

speeds of some crystals from others. The ones with a larger spacing will appear to grow faster and hence will shadow the slower growing forms and starve them of atoms, thus causing columnar growth.

Alloys are where different atoms sit on particular positions in the crystal lattices with a specific chemical ratio, some examples of which are shown in Fig. 12.25.

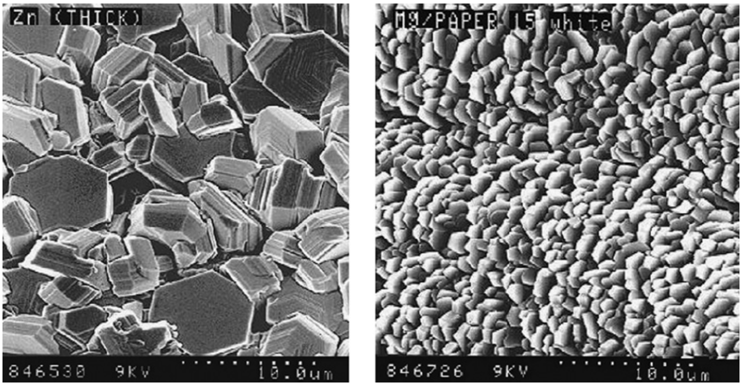


Figure 12.26 Micrographs of zinc and magnesium showing very different structures that are as a result of different preferential growth patterns that are dependent on the different lattice types.

Figure 12.26 shows two different metals seen at the same magnification showing very different growth patterns and crystal sizes. The semiconductor industry uses single crystal substrates to be able to continue with specific growth patterns during the epitaxial growth. On polymer webs, there is no atomic template for the atoms, and so the nucleation and growth are much more likely to be random. Once started, the differential growth rates will have an effect unless they are disrupted by some energetic bombardment. This could result in surface texture that may be of concern for optical coating such as mirrors.

12.11 Deposition Rules of Thumb

- Increasing temperature leads to increasing crystal size.
- Increasing energy leads to increasing temperature.
- Increasing temperature leads to increasing crystal size.
- Increasing deposition rate leads to decreasing crystal size.
- Increasing energy of deposition leads to increasing adhesion.

References

[1] Pashley DW, et al. The growth and structure of gold and silver deposits formed by evaporation inside an electron microscope. Phil Mag 1964;10:127−58.

[2] Chopra KL. Influence of electric field on the growth of thin metal films. J Appl Phys 1966;37(36):2249 −2254.

[3] Hirth JP, Moazed KL. Nucleation processes in deposition onto substrates. Fundam Phenom Mater Sci 1966;3:63−84; Surface phenomena.

[4] Campbell DS, Stirland DJ. The epitaxial growth of silver and gold films by sputtering. Phil Mag 1964;9:703–7.

[5] Stirland DJ. Electron bombardment induced changes in the growth and epitaxy of evaporated gold films. Appl Phys Lett 1966;8(12):326–8.

[6] Moazed KL, Hirth JP. On the contact angle in heterogeneous nucleation upon a substrate. Surf Sci 1964;3:49 –61.

[7] Venables JA. Kinetic studies of nucleation and growth at surfaces. Thin Solid Films 1978;50:357–9.

[8] Morris JE. Effects of charge on the structure of discontinuous thin gold films. Metallography 1972;5:41–58.

[9] Hill RM. Electrical conduction in discontinuous metal films. Contemp Phys 1969;10 (3):221–40.

[10] Behrndt KH. Influence of the deposition conditions on growth and structure of evaporated films. Vacuum 1963;13:337–47.

[11] Smith R, Richter A. Modelling thin film growth: Monte-Carlo models of fullerite films. Thin Solid Films 1999;343–344:1–4.

[12] Chopra KL. Thin film phenomena. New York: McGraw-Hill; 1969.

[13] Vook RW. Nucleation and growth of thin films. Opt Eng 1984;23(3):343–8.

[14] Freund LB, Suresh S. Thin film materials—stress, defect formation and surface evolution. Cambridge. UK: Cambridge University Press; 2004 ISBN 0 521 82281 5.

[15] Petrov I, et al. Microstructural evolution during film growth. J Vac Sci Technol A 2003;21(5):S117–128; Fig. 2.

[16] Siegel RW. Exploring mesoscopia: the bold new world of nanostructures. Phys Today 1993;Vol. 46 October:64–8.

[17] Heavens OS. Optical properties of thin solid films. New York: Courier Dover Publications; 1991. ISBN 0486669246.

[18] Stauffer D. Scaling theory of percolation clusters. Phys Rep 1979;54(1):1–74.

[19] Laibowitz RB, et al. Summary abstract: cluster formation and the percolation threshold in thin au films. J Vac Sci Technol A 1983;1(2):438–9.

[20] Spalvins T, Brainard WA. Nodular growth in thick sputtered metallic coatings. J Vac Sci Technol 1974;11(6):1186–92.

[21] Czigany Z, Radnoczi G. Columnar growth structure and evolution of wavy interface morphology in amorphous multilayered thin films. Thin Solid Films 1999;343–344:5–8.

[22] Bochkarev AA, et al. Evolution of crystals during vacuum deposition. Thin Solid Films 1999;343–344:9–12.

[23] Guenther KH. Microstructure of vapor-deposited optical coatings. Appl Opt 1984;23 (21):3806 –3816.

[24] Spalvins T, Brainard WA. Nodular growth in thick-sputtered metallic coatings. J Vac Sci Technol 1974;11(6):1186–92.

[25] Robinson CJ. The effects of glow discharge treatment on the nucleation of gold on organic substrates. Thin Solid Films 1978;51:L38–40.

[26] Robinson CJ. The effects of a glow discharge on the nucleation characteristics of gold on polymer substrates. Thin Solid Films 1979;57(2):285–9.

[27] Siewenie JE, He L. Characterization of thin metal films processed at different temperatures. J Vac Sci Technol 1999;A(4):1799–804.

[28] Schlemminger W, Stark D. The influence of deposition temperature on the crystalline and electrical properties of thin silver films. Thin Solid Films 1986;137:49 –57.

[29] Movchan BA, Demchishin AV. Study of the structure and properties of thick vacuum condensates of nickel, titanium, tungsten, aluminium oxide and zirconium dioxide. Fiz Metal Metalloved 1969;28(4):653−60.

[30] Thornton JA. High rate thick film growth. Ann Rev Mater Sci 1977;7:239−60.

[31] Messier R, et al. Revised structure zone model for thin film structure. J Vac Sci Technol A 1984;2(2):500−3.

[32] Metzner C, et al. Emergent technologies for large area PVD coating of metal strips. In: Proc. 46th annual technical conference of the Society of Vacuum Coaters; 2003. p. 222−6.

[33] Grimm H, et al. Vacuum-coating apparatus. EP 0 555 519 B1; 1992.[08:02:1992].

[34] Ahmed NAG, et al. Ion assisted deposition of TiO_2 on moving web using oxygen ions. In: Proc. 39th annual technical conference of the Society of Vacuum Coaters; 1996. p. 451−7.

[35] Thornton JA, Hoffman DW. Internal stresses in amorphous silicon films deposited by cylindrical magnetron sputtering using Ne, Ar, Kr, Xe and Ar + H_2. J Vac Sci Technol 1981;18(2):203−7.

[36] Maniv S, et al. Pressure and angle of incidence effects in reactive planar magnetron sputtered ZnO layers. J Vac Sci Technol 1982;20(2):162−70.

[37] Fuchs H, Gleiter H. Is the impact velocity of vacuum-deposited atoms of significance for the films structure. Thin Solid Films 1983;101:55−9.

[38] Thornton JA. The microstructure of sputter-deposited coatings. J Vac Sci Technol A 1986;4(6):3059−65.

[39] Schiller S, et al. Processing and instrumentation in PVD techniques. Vakuum-Technik 1986;35(4):35−54.

[40] Thornton JA, Hoffman DW. Stress-related effects in thin films. Thin Solid Films 1989;171:5−31.

[41] Neidhardt A, et al. Position dependences in planar magnetron sputtering. Thin Solid Films 1989;173:109−27.

[42] Windischmann H. Intrinsic stress in sputtered thin films. J Vac Sci Trechnol A 1991;9 (4):2431−6.

[43] Window B, Muller K-H. Strain, ion bombardment and energetic neutrals in magnetron sputtering. Thin Solid Films 1989;171:183−96.

[44] Blackwell KJ, et al. Investigation of curl and residual stress in metallized polyimide. In: Proc. 5th annual technical conference of the Society of Vacuum Coaters; 1992. p. 64−9.

[45] Teixeira V. Mechanical integrity in PVD coatings due to the presence of residual stresses. In: Proc. 3rd international conference on coatings on glass; 2000. p. 479−89.

[46] Weissmantle C, et al. Recent developments in ion-activated film preparation. Ion plating and allied techniques (IPAT) CEP Consultants Ltd, Edinburgh; 1979. p. 272−83

[47] Günther S, et al. Innovative transparent barrier for packaging. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 727−9.

[48] Rossnagel SM, Cuomo JJ. Ion beam deposition, film modification and synthesis. MRS Bull 1988;December:40−5.

[49] Kivaisi RT. Optical properties of obliquely evaporated aluminium films. Thin Solid Films 1982;97:153−63.

[50] Casey F, Ellis GH. Deposition uniformity and visual appearance in high speed web coaters. In: Proc. 10th vacuum web coaters; 1996. p. 123−32.

[51] Feuerstein A, et al. Production of metal evaporated video tape by electron beam evaporation. In: Proc. 28th annual technical conference of the Society of Vacuum Coaters; 1885. p. 42−52.

[52] Valkonen E, Ribbing CG. Optical selectivity of thin silver films prepared by RF-assisted DC magnetron sputtering. Mater Lett 1984;3(1,2):29−32.

[53] Abeles F. Optical properties of metallic films. Phys Thin Films 1969;6:151−204.

[54] Smith GB, et al. Nobel metal based transparent infrared reflectors: preparation and analysis of thin gold films. In: Proc. SPIE.562 paper 17; 1985.

[55] Bishop CA, Howson RP. Large area optical filters. Sol Energy Mater 1986;13:175−84.

[56] Siewenie JE, He L. Characterization of thin metal films processed at different temperatures. J Vac Sci Technol A 1999;17(4):1799−804.

[57] Tench RJ, et al. What those defects in optical coatings really look like. In: Proc. 37th annual technical conference of the Society of Vacuum Coaters; 1994. p. 63−8.

[58] Tench RJ, et al. Characterization of defect geometries in multilayer optical coatings. J Vac Sci Technol 1994;12(5):2808−13.

[59] Stolz C, et al. A comparison of nodular defect seed geometeries from different deposition techniques. California: Lawrence Livermore National Laboratory, University of California; 1995 UCRL-JC-121628.

[60] Lotz HG, et al. Thick optical multilayer systems on PET-film. In: Proc. 44th annual technical conference of the Society of Vacuum Coaters; 2001. p. 172−7.

[61] Tait RN, et al. Nodular defect growth and structure in vapor deposited films. J Electron Mater 1995;24(8):935−40.

[62] Tamagaki H, et al. Transparent high barrier coating on polymer web by PE-CVD roll coater. In: Proc. 53rd annual technical conference of the Society of Vacuum Coaters; 2010. p. 553−7.

[63] Reed-Hill RE. Physical metallurgical principles. Van Nostrand Reinhold; 1964.

[64] Cottrell AH. An introduction to metallurgy. London: Edward Arnold; 1967. ISBN 0 7131 2044 4.

[65] Chadwick GA. Metallography of phase transformations. London: Butterworths & Co Ltd.; 1972. ISBN 0 408 70325 3.

13 Pattern Metallization

There are a number of products where it is preferred to have selective areas without any coating. These may be of a simple stripe down the length of the substrate such as for the capacitors as described in Chapter 2 (Section 2.2) or of a more complex nature such as for antenna or electronic circuits. There are various methods for patterning that include both atmospheric processing and in-vacuum patterning techniques.

13.1 Atmospheric Patterning

If we start with the atmospheric patterning process, there are a couple of different options. One of which produces a positive pattern and the other a negative of the same pattern, as shown schematically in Fig. 13.1. The left-hand process requires three steps with the roll of film needing coating with a release material in the areas where the metal coating is to be removed [1]. The film then gets metallized, and following metallization the web needs another atmospheric process. This is where the film passes through a liquid bath that reacts with the release agent and floats off the metal coating on the release agent, as the release agent either dissolves or swells, dislodging the metal coating. This three-step process does just leave the metal coating on the substrate. The process shown on the right-hand side of Fig. 13.1 starts by metallizing the film and then it is possible to complete the rest of the process in a single pass. The atmospheric process is to print on a pattern that forms a protective coating over the areas of metal that are required to be preserved and then to etch away the metal that has not been protected [2]. This etching process for aluminum metallized coatings may be a simple solution of sodium or potassium hydroxide that etches away the aluminum very quickly. The metallized surface if oriented face downward can be brought into contact with the top surface of a liquid bath without fully immersing the film in the liquid. There is enough contact that the etching can take place with the minimum wetting of the film and the back surface remaining dry. The front surface needs to be washed to remove any residue of the etching solution and then dried with an air knife and oven. This process then leaves the metal coating but with a protective lacquer on the metal.

One limitation of the masking process is that it makes any transverse line problematic and so this process is usually limited to down-the-web stripes only.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00013-1

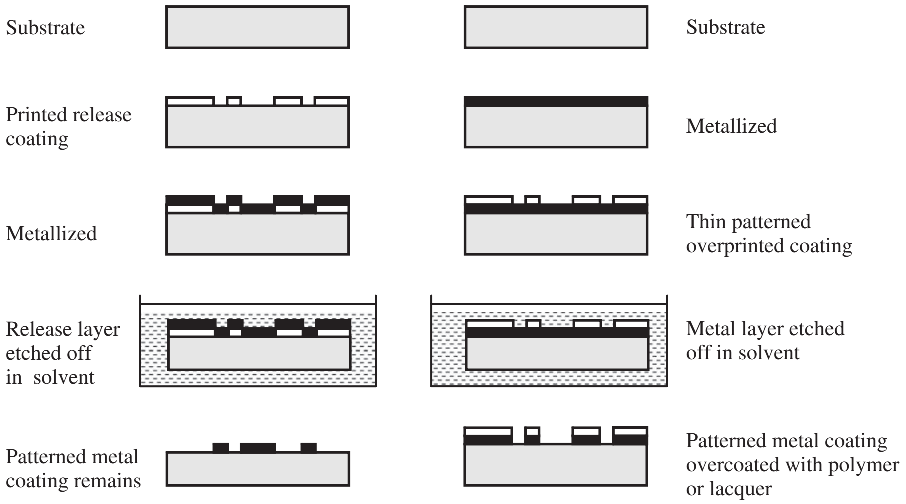


Figure 13.1 A schematic of the methods to make patterned coatings with either a positive or negative pattern.

13.2 In-Vacuum Patterning

To reduce costs it is preferable to reduce the number of process steps and this may be done using in-vacuum pattern metallization. The first process developed was to produce uncoated stripes down the length of the web as required for capacitors [2–4]. This could be done using fixed masks across the deposition zone; however, any permanent mask would have a clearance distance between the mask and the web and this would cause a shadow area where the metal thickness was graded down from full to zero. The customers wanted this transition to be sharp and so this process was not preferred. Also, the permanent shields would accumulate coating and over the full roll length would change size, so the masked area would progressively increase as the coating built up with time. An improvement to this process was to use a continuous belt that could be brought into contact with the film around the deposition drum. The belt, made of stainless steel or polyimide, would then pass round behind the deposition sources and be brought back into contact with the web. In this manner, a single short continuous belt of material could be used as a mask. As the mask is in direct contact with the web, there is no shadowing and the edge between metallized and unmetallized regions is sharp. The masking belt was passed over a series of serpentine (ripple) rolls designed to crack and encourage the coating to break off the masking belt. This may not remove the coating on every pass, but once the coating is thick enough the stress is usually sufficient to overcome the adhesion and break off the coating. The mask then does not grow in size and so the correct masking thickness can be maintained throughout

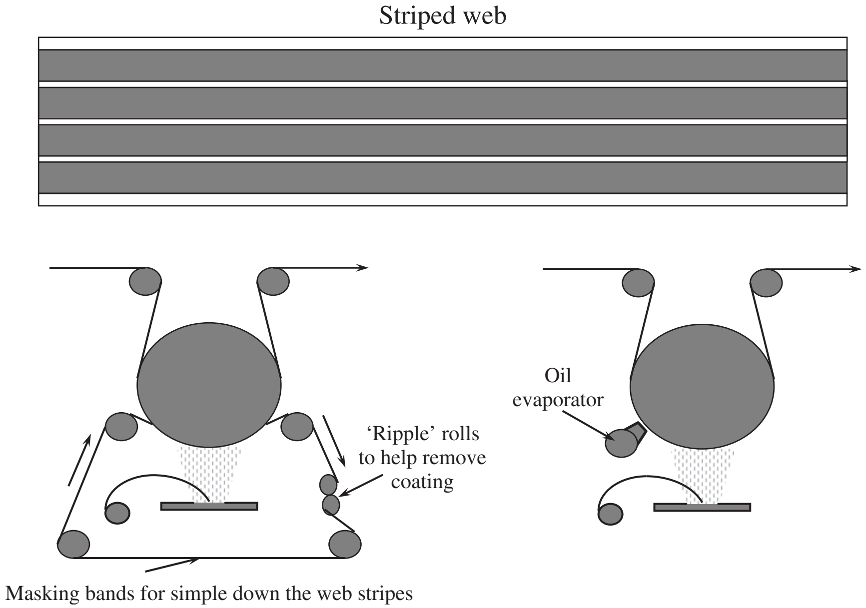


Figure 13.2 A schematic of the two basic processes to produce simple down-the-web stripes.

the deposition run. This deliberate generation of debris does make this process particularly dirty and there is an increased opportunity for coating pinholes.

The second process shown in Fig. 13.2 on the right-hand side represented an improvement in the masking process. It had been observed that the adhesion of vacuum deposited coatings was poor where there was oil backstreaming and so somebody had the idea that by deliberately using oil metallization could be prevented. This was done by using a tube filled with diffusion pump oil and a series of holes pointing at the web with one hole for each stripe. As the oil is heated, it evaporates out of each hole and deposits onto the web. This single tube of oil does require to be kept at a constant temperature and have good temperature uniformity across the whole web width. Alternatively, individual sources could be used although this increases the number of controls and is not necessarily of any cost benefit. Where the oil is present, the evaporating metal will have a low sticking coefficient and so the metal will not remain on the surface. It has been proposed that the metal as it leaves the surface may also remove some of the oil. The radiant heat from the evaporation sources is enough to evaporate the oil, so any depositing metal atoms will have to avoid collisions with this evaporating oil if the atoms are to reach the surface. This is shown schematically in Fig. 13.3. This process has to be in balance so that just enough oil is used to prevent any metal coating but no excess oil is used that could leave the surface of the film wet and cause problems

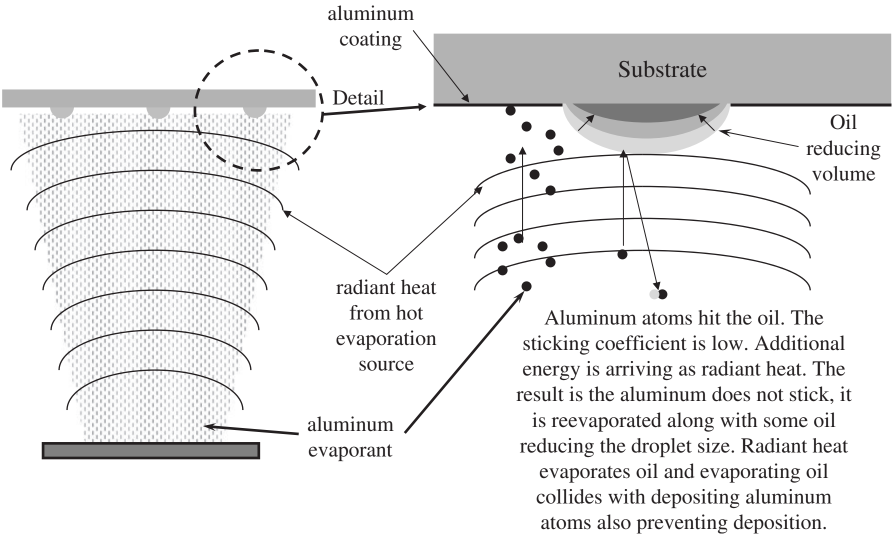


Figure 13.3 A schematic of how oil is thought to prevent coating deposition.

further downstream of the production process. The edge of the uncoated stripe does depend on the way the oil droplet shrinks as the oil evaporates. If it remains as a half cylindrical shape with the edges closing in as the volume reduces, the edges will have a graded coating. If the volume is reduced whereby the height of the droplet is reduced but the edges do not shrink inward, the edges will be sharper. The width of the oil track on the surface can be affected by any plasma treatment that is done to the surface. Raising the surface energy to help increase the adhesion will also encourage the oil to wet the surface and spread out. Thus, the production of narrower tracks can be made harder by any plasma treatment.

As the oil is a liquid, this can be transferred to the web by other techniques such as by printing processes and this then opens up the opportunity for patterns to be printed of the areas where no deposition is required [5] (Fig. 13.4). If one uses a printing process, there are then many more opportunities to deliberately produce graded coatings as well as simple 100% to 0% step changes, and gray scale pictures have been produced to demonstrate the range available [6]. This type of in-vacuum metallization has been used for microwave packaging and various types of holograms [7−10].

The simplest process is to evaporate the oil directly onto the gravure roll and the oil pattern transferred onto the web. Alternatively, indirect offset (gravure) printing using a flexographic or cliché plate for pattern metallization can be used [11,12]. This process can include a cooled anilox roll to condense the oil into the etched cells along with a wipe roll or doctor blade to limit the quantity of oil transferred. This adds to the precision of the oil thickness and helps enable narrower line widths to be achieved.

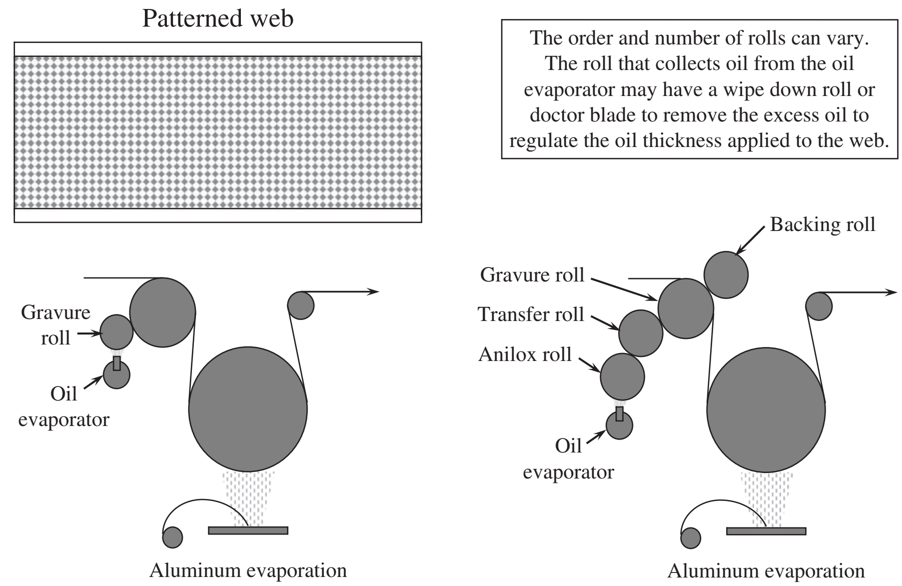


Figure 13.4 A schematic of a couple of pattern printing techniques to enable complex patterns to be produced.

Although this process sounds easy, the following is a list of the main factors that can affect the quality of the pattern:

- Oil characteristics (viscosity/vapor pressure)
- Boiler temperature
- Oil metering
- Anilox roll characteristics
  - Roll material
  - Cell etch quality
  - Cell size and depth
- Cliché plate characteristics
  - Material
  - Etch quality
- Contact pressure
- Process drum temperature
- Heat transfer coefficient (depends on materials, roughness, tension, gas injection)
- Heat load
  - Deposition rate
  - Evaporator temperature (radiant heat load)
- Line speed
- Substrate surface
  - Roughness
  - Surface energy (plasma treatment, chemistry giving wetting characteristics)

A number of these factors are possible variables, although as they affect the main deposition process they may well be already fixed. This could include the deposition process variables and deposition drum temperature and may also include the substrate. This only leaves the printing process variables that can be used to modify the process. Thus, the choice of oil type, deposition temperature, and contact pressure are the few online control options. The anilox and print (gravure or cliché plate) roll quality can be changed from run to run but as changing rolls can be slow and getting the transverse uniformity can be time-consuming, it tends to be done as few times as possible. Another variable that might be adjusted could be the plasma treatment, although this may be limited as it could affect the metallization adhesion.

The next progression in the in-vacuum pattern metallization has been to also include the option for in-register in-vacuum pattern metallization. There is a desire for this option because sometimes the incoming roll of film has already been printed or embossed with a holographic device and the metallization is required to coat certain areas but not others. In the past the material would have been fully metallized and then selective areas removed, but if the metal can be stopped from depositing to match the existing pattern, this would eliminate an additional process and so reduce costs. There are two dimensions that need to be controlled: one is the transverse direction position and the other is the down-the-web positioning. The transverse direction movement can be achieved by moving either the web winding system sideways relative to the printing rolls or vice versa. The more difficult control system is to enable the system to adjust the web position to get the down-the-web registration marks into the correct position. This is currently done by stretching the web slightly [12]. While this is acceptable for the current requirements of decorative packaging materials, it is not an acceptable method for other applications such as for electronic devices where stretching the substrate can cause premature cracking or buckling of the coatings that can reduce the conductivity of the coated tracks.

The in-register control system includes using small marks printed onto the substrate that are used in conjunction with an optical monitor. Changes in the intensity and position can be used to determine the position of the registration marks relative to the oil printing pattern and any corrections that are required. The oil pattern print widths are typically 30–50 μm wide and the in-register can be done to within 500 μm both in the transverse and machine directions. This is acceptable for packaging but needs to be improved upon if this is going to be useful to the electronics industry in the future. This is not a trivial problem as the substrate is not necessarily stable and the deposition process may take the substrate temperature up and down a hundred degrees, while under tension, in a short space of time. Thus, any process for registering the substrate needs to aim at not adding any additional stress to the process.

The other limitation of the oil-based masking process relates to changing deposition materials and increasing the coating maximum thickness. It would be desirable to be able to deposit flexible copper circuits directly without having to etch and plate the thin copper coatings. Others would like to deposit patterned indium tin oxide transparent conducting coatings. However, there is a limit to how much oil can be printed and how long this volume can be exposed to the deposition source before all the oil is evaporated and coating takes place. Alternative liquids with different viscosity and vapor pressure can be used but as yet there does not appear to be a table of alternative liquids and the maximum thickness of coatings that can be deposited by these new masking liquids. Care needs to be taken in the choice of masking liquids as some that look to be possible may be cross-linked by the ultraviolet component of any plasma and so instead of evaporating off may be converted into a new surface that can accept a coating.

It is worth noting that as any residual oil can represent a potential adhesion problem to other downstream processes the control of the oil deposition becomes an important issue. As this accuracy cannot be guaranteed, an alternative option may be to use a plasma treatment following the deposition zone so that any residual oil is either volatilized or cross-linked into a carbonized stable layer that does not compromise the adhesion.

If one looks forward to roll-to-roll deposition of displays and photovoltaics, there is a tendency to look at all vacuum deposited coatings or all printed coatings, but it is more likely that there will be a mixture of both vacuum and wet atmospheric coatings by a variety of techniques. For some devices, it may be possible to deposit coatings with little or no registration between layers but for others it will be essential for each layer to be deposited in register with one or more other layers. To achieve this, a significant change is required in how we manage our winding systems and substrates in order to obtain the precision required. This will lead to improved stability substrates including an increase in the availability of heat-stabilized films and also better control of other polymer properties such as profile and slitting that can affect the tension balance during winding.

Still looking forward, there is another possible development that could add an advantage to the vacuum deposition patterning process [13]. Ink-jet printing heads have been developed for the printing of fine lines (Fig. 13.5). The ink-jet head filled with a liquid and a piezoelectric crystal can be deformed so that it forces out

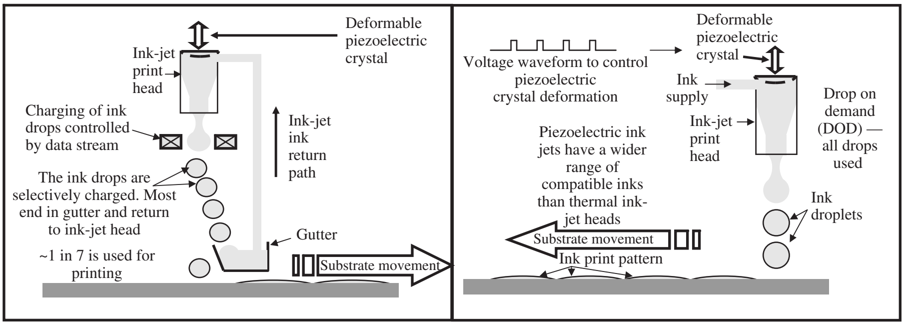


Figure 13.5 A schematic of the principle of ink-jet printing with the newer drop on demand (DOD) version on the right.

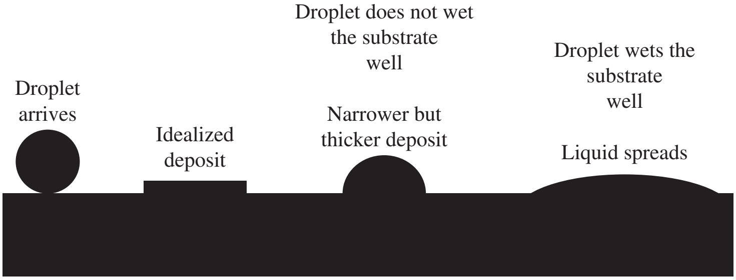


Figure 13.6 A schematic of the spreading options of a drop arriving at a substrate surface.

a drop of liquid out of a hole in the head. This drop can be down at the picoliter size range and there is continuing development work to further reduce the drop volume. At this 1 picoliter size, a droplet is of the order of 10 μm in diameter and this will produce a circular printed spot of 20 μm. These lines can be separated by a 10 μm gap. The ink-jet process offers two different process possibilities. One is the printing of oil with the ability of using programming to change the printed patterns quickly without the need to change rolls. The other is to directly print metals using a liquid metal ink-jet source [14]. It has been established that drops from an ink-jet head stay as drops in a vacuum and that when they hit a surface they spread to form a circular spot without any splatter. Other work proved that molten metal could be ink-jet printed and so it was only a matter of time before all this was brought together and tried as a vacuum deposition process for the deposition of copper circuits. This work was abandoned because of financial problems with the company running the research, but the principle has been proved. Although proved as a possibility, there are still questions to be answered regarding the economics, winding speed, and minimum line widths.

Where simple stripes are to be deposited and the deposition temperatures are relatively low, it is possible to consider using enclosed deposition sources that can have a deposition nozzle that is small and positioned close to the substrate web so that the deposit is defined by the nozzle size and shape and this no longer requires any technique to prevent deposition [15]. Thus, this process is inherently cleaner than the oil-masking process, with no risk of contamination from residual oil.

As with the oil pattern printing methods, there is still the question of what is the preferred substrate surface energy. For the best coating adhesion, the surface energy should be as high as possible as this improves the coating wetting. However, this same improved wetting will also spread out the ink-jet printed droplet as shown at the right-hand side of Fig. 13.6. To produce narrower lines, it would be better if the ink-jet printed droplet did not wet the substrate as also shown to the right of center in Fig. 13.6. It may be that the substrate surface energy is made as high as possible by the plasma treatment, but an ink-jet liquid type is chosen such that it still does not wet the substrate surface. As yet this process has not been optimized and there is plenty of detailed work still to be done.

References

[1] Aufderheide, BE. Rapidly removable undercoating for vacuum deposition of patterned layers onto substrates. US patent 4 714 631. 1987.

[2] Tullo G. Display and decorative applications. In: Proc. 14th international conference on vacuum web coating; 2000. p. 141–51.

[3] Chifen AN, et al. Free margin masking of capacitor films by flash evaporation. In: Proc. AIMCAL fall technical conference and 22nd international conference on vacuum webcoating; 2008.

[4] Yamamori T. Margin generating mechanism in ULVAC's roll coater. In: Proc. 2nd international conference on vacuum web coating; 1988. p. 58–76.

[5] Nagatomi K, et al. Process for producing metallized plastic film. US patent 4 832 983; 1989.

[6] Pagani A. et al. Patterned metallized films: state-of-the-art and growth opportunities. In: Proc. 50th annual technical conference of the Society of Vacuum Coaters; 2007. p. 757–61.

[7] Walters GJ. Patterned metallized print (PMP) hologram structures. In: Proc. 39th annual technical conference of the Society of Vacuum Coaters; 1996. p. 357–9.

[8] Walters GJ. Patterned metallized films used for higher energy density capacitor components. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 453–5.

[9] Collins D. Holograms and metallizing packaging. PIRA International Ltd. ISBN 1 85802 930 9.

[10] Lancaster IM, editors. Holopack/holoprint guidebook. 2nd ed. Surrey, UK: PIRA International; 2000. ISBN 1 85802 254 1.

[11] Fujimoto S. Patterning and high rate vacuum deposition on super thin film. In: Proc. AIMCAL fall technical conference and 21st international conference on vacuum web coating; 2007.

[12] Copeland N, et al. In-register in-vacuum pattern printing: from wish to reality. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 712–5.

[13] Bishop CA. Ink jet for in-vacuum patterning: a look at the feasibility. In: Proc. 20th international conference on vacuum web coating and AIMCAL fall technical conference; 2006.

[14] Swisher R. A review of processes for evaporatively deposited miscellaneous metals. In: Proc. 50th annual technical conference of the Society of Vacuum Coaters; 2007. p. 733–41.

[15] Marcus MA, et al. Device for depositing patterned layers in OLED displays. US patent 6 911 671; 2005.

Part III

Process

14 The DC Glow Discharge or Plasma

If a tube containing a cathode and an anode, which are positioned some distance apart, is evacuated and an inert gas is introduced, it is possible, when a potential is applied to the electrodes, to stimulate the system and for it then to become luminous. This emission of light is referred to as a glow discharge or plasma. The basic process that occurs is that when enough potential is applied across the gas, electrons collide with atoms to produce ions and more electrons. This process is initially a cascade process that subsequently becomes a steady state process. The electrons that are generated are called secondary electrons and may be further accelerated by the applied voltage. This acceleration means that they too are able to undergo ionizing collisions. The ions, being substantially larger in mass, are unable to be accelerated at the same rate as the electrons. This differing mobility is seen in the plasma as areas of differing light intensity.

The process of ionization is where an electron collides with an atom (or molecule) and removes an electron from the atom. For this to occur, the kinetic energy of the impinging electron must be at least equal to, and probably greater than, the work done to remove electrons from the outer shell of the atom against the force of attraction of the nucleus; the collisions involved in this process are known as inelastic collisions. The remaining kinetic energy is divided between the primary or incident electron and the secondary or liberated electron. Because of the large discrepancy of masses between the electron and the ion, virtually no energy is transferred to the ion. If the kinetic energy of the electron is too low for an inelastic collision to occur, the electron is usually reflected with negligible loss of energy; collision in this case is known as elastic collision.

The form that the ionization collision would take is:

$$e + Ar \rightarrow 2e + Ar^+$$

If the generation of electrons by collisions plus the generation of electrons by the bombardment of the cathode is greater than the loss of electrons from the plasma, then the discharge will be self-sustained. If the losses become greater, then the discharge will decay and extinguish. It is apparent from the emission that there is a high degree of activity in the discharge. Even when the luminous intensity appears greatest, the bulk of the gas is neutral and in the electronic ground state. It is typical in a magnetron sputtering plasma that less than 1% of the gas is ionized.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00014-3

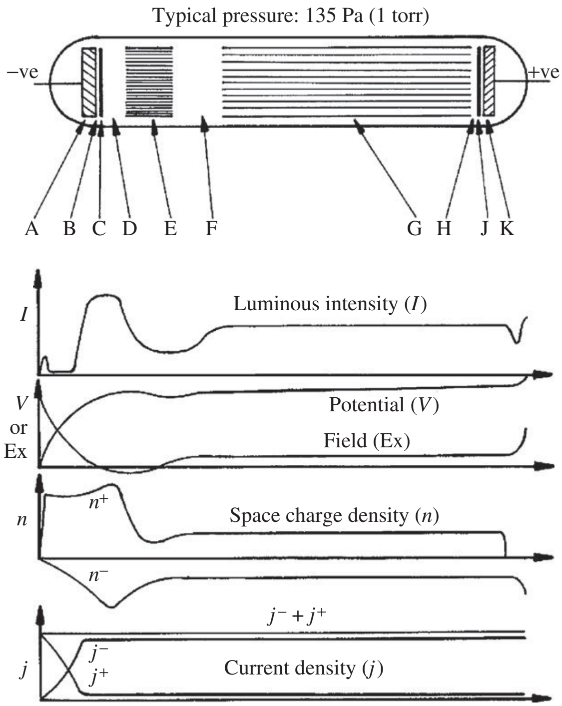


Figure 14.1 The figure shows a typical plasma obtained from an inert gas in a discharge tube at a pressure of 135 Pa (1 torr). The top figure shows a schematic of the tube and the different parts of the plasma [19,20]. The lower figures show schematics of the characteristics of the plasma.

A = Cathode
B = Aston dark space
C = Cathode layer
D = Crookes dark space
E = Negative glow
F = Faraday dark space
G = Positive column
H = Anode dark space
J = Anode glow
K = Anode

If we look at the process in more detail, we can separate the discharge into different parts that are as a result of differing processes within the plasma [1−18] (Fig. 14.1).

To describe the plasma in detail, it is necessary to use the current (or current density) versus voltage characteristic [20,21]. This is shown in Fig. 14.2 and is divided into six different regions: the Townsend discharge, the breakdown region, the transition region, the normal glow discharge, the abnormal glow discharge, and the arc.

14.1 The Townsend Discharge

If a potential is applied across a discharge tube between the cathode and anode, initially a very small current will pass, of the order 10^{-16} A. This is as a result of

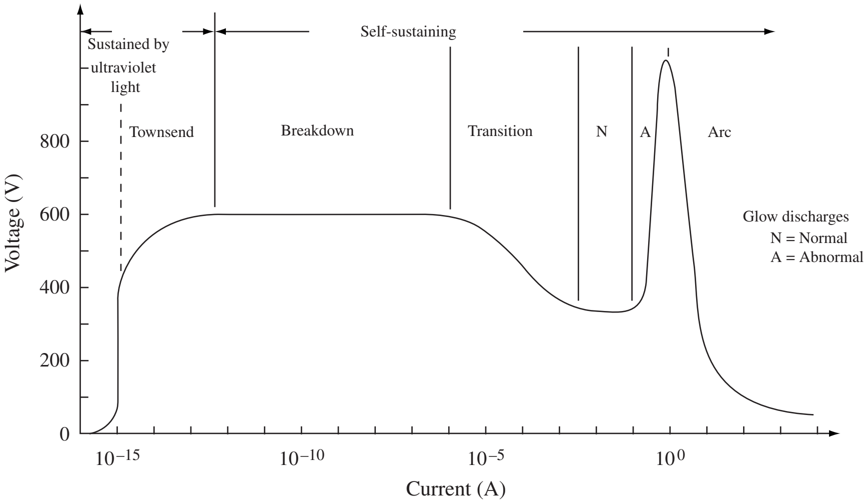


Figure 14.2 The voltage—current characteristic for a plasma discharge.

the generation of a few ions and electrons by some external source, that is, ultraviolet radiation, X-rays, cosmic rays, etc. This current will disappear if the external source of stimulation is removed.

In Fig. 14.3, the top right-hand figure is a repeat of the current versus voltage characteristic of the plasma shown schematically on the top left-hand side. The letters denoting key points on the voltage versus current characteristic are used on the left-hand lower three figures that show how the voltage profile varies between the cathode and anode. The lower two figures on the right-hand side show how, once the plasma is struck, the plasma position and shape vary.

Point A denotes the point where the current saturates in the Townsend discharge region. If the applied potential is increased, points B and C are reached. The potential distribution stays linear in the Townsend discharge region as can be seen on the voltage plot of A, B, and C on the left-hand figure. Point C also denotes the limit of the Townsend discharge region. The applied voltage is still not quite enough to accelerate a secondary electron ejected from the cathode to a fast enough velocity whereby it can undergo an ionizing collision before it reaches the anode. Beyond point C, at a constant voltage, the current rises by several orders of magnitude.

14.2 The Breakdown Voltage

The voltage at which breakdown occurs is dependent on the mean free path of the secondary electrons and the distance between the anode and cathode. Somewhere of the order of 10—20 ions must be produced by each secondary electron for the avalanche to occur. The onset of the rise in current is that the potential reaches

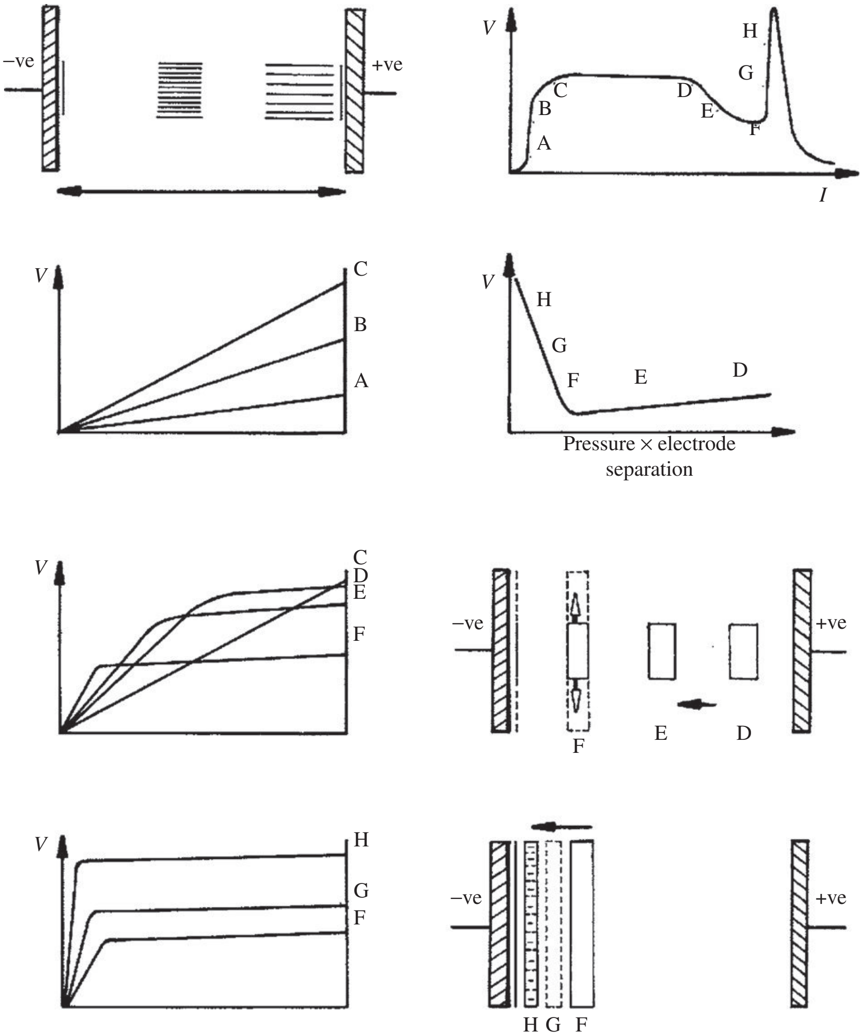


Figure 14.3 A schematic showing the changing voltage distribution across the plasma and also the changing position and shape of the plasma.

a voltage such that an electron can be accelerated to a high enough velocity to be able to take part in an ionizing collision. Initially, when the applied potential equals the ionizing potential, the current will be small. As the applied voltage increases, the position in the discharge tube where ionizing collisions can take place moves closer to the cathode, and so the distance left, where another ionizing collision is possible, increases. When the applied voltage is twice the ionizing collision voltage, it is possible for two electrons to be generated from the first electron. Similarly, from the two electrons generated, they could produce four electrons, and hence there is the start of a cascade process. Thus, when the applied voltage is very much greater than the ionizing voltage, breakdown occurs. In the same way as the electrons are accelerated to the anode, the ions too are accelerated to the cathode. When the ions bombard the cathode surface, they are able to liberate secondary electrons. This adds to the quantity of electrons, making further ionizing collisions and thus adding to the fast increasing ability of the plasma to pass current. At the point of breakdown, each electron liberated from the cathode is able to undergo enough ionizing collisions such that the subsequent bombardment of the cathode will result in the generation of another electron. This point of breakdown is denoted by point D on the voltage current characteristic plot.

Inelastic collisions can also modify the electron state without necessarily ionizing the atoms. The decay of the excited electron of the atom back to its ground state results in the characteristic light emission. Thus, at the breakdown voltage and beyond, the plasma has a characteristic light or glow and is known as a self-sustaining glow discharge.

The external circuit resistance governs the value to which the current rises at this breakdown voltage. If either the pressure or the electron spacing is too low, then the electrons cannot undergo enough ionizing collisions during their flight from cathode to anode. At the other extreme, if the pressure is too high and the electron separation too large, the ions produced by the collisions will undergo inelastic collisions that slow them down such that, in striking the cathode, the ions do not produce any secondary electrons. These two features are the basis of Paschen's law that relates the voltage to the product of pressure and electrode separation. This is shown graphically in the figure next to the top on the right-hand side of Fig. 14.3.

The gas used and the cathode materials also affect the precise values for the breakdown voltage and spacing. Different materials have different secondary electron coefficients and different electron-binding energies that result in different curves.

The product of pressure and electrode separation for a magnetron sputtering system is usually to the left of the minimum and so the striking voltage to start the plasma can be quite high. Power supplies are often made such that the striking voltage can be double the constant operating voltage.

A procedure to reduce the striking voltage is to introduce a pulse of gas into the system. The effect of this would be to push the required striking voltage to the right toward the minimum. This would make striking the plasma easier, and because it was only a pulse of gas, the pressure would soon fall back to the steady state value.

A change in potential also occurs at the breakdown voltage; this is depicted in plot D. The knee in the plot is because the space charge is positive due to there being more ions than electrons in the cathode dark space of the discharge because of the electrons having a greater mobility than the ions.

As the discharge is struck, a light appears on the anode from the negative glow region of the discharge and a similar glow on the cathode called the cathode glow, formed by the neutralization of incident ions. The region between the negative glow and the cathode is known as the cathode or Crookes dark space. The precise distance of the cathode dark space is hard to measure due to the diffuse nature of the negative glow.

The cathode dark space is an important region of the plasma. It is inversely proportional to the pressure, and the product of pressure and distance is slightly less than the minimum breakdown voltage. It is within the cathode dark space that most of the ions and electrons that carry the current are produced [1]. The negative glow is highly conducting and so has only a slight potential fall (a few tens of volts) that indicates that the number of ions and electrons is almost equal. The ions start accelerating from the edge of the negative glow across the dark space to the cathode and the secondary electrons ejected from the cathode accelerate across the dark space to the negative glow. These two opposing events result in a region with the most ionizing collisions [2].

14.3 The Transition Region

After the breakdown has occurred, the potential difference across the gas falls with increasing current. This region of negative resistance is known as the transition region. This region corresponds with a reduction in the cathode dark space. The potential falls to a value slightly higher than that of the ionizing potential. There is little drop in the potential in the negative glow and so the edge of the negative glow can be thought of as a virtual anode with the bulk of the voltage drop occurring between it and the cathode.

When the discharge is first established, the cathode dark space is virtually the whole distance between the cathode and anode. As the current is increased, the potential distribution is changed and the virtual anode of the edge of the negative glow is moved closer to the cathode. The glow beyond the dark space is highly conducting, and so for a small potential difference, a current flow can be sustained. The plots D, E, and F, with F being the extreme state, depict this.

14.4 The Normal Glow Discharge

In the normal glow discharge, the current density is constant. The current rise is due to the area of the cathode layer increasing to the point where the whole of the cathode is covered by the visible glow or luminous layer. Once the whole of the cathode is covered by the luminous cathode layer, any further increase in current has to be accompanied by a corresponding increase in voltage. This point is point F on the plots above.

14.5 The Abnormal Glow Discharge

Following the normal glow discharge, there is a region of increasing current for increasing voltage called the abnormal glow discharge. The reason for the increasing voltage is due to the virtual anode position becoming less than the cathode dark space. Thus, for the necessary number of electrons to perform enough ionizing collisions to give an increase in current, the acceleration of these electrons has to be increased by raising the potential. Two points are used to denote the abnormal discharge characteristics, G and H.

It is in this abnormal discharge region that most sputtering systems operate.

14.6 The Arc

As the current of the abnormal discharge is increased, it reaches a point where it changes character. The current increases rapidly and the voltage decreases, and the plasma shrinks from covering the whole cathode down to a small spot but with very high intensity. The current density at this spot can be of the order of 1000 A/cm^2 with the current being proportional to the cross-sectional area of the spot. The voltage falls to only a few volts (10–20 V would be typical).

The cathode and anode are both heated by the increased electron and ion bombardment as the current being passed through the plasma is increased. This can result in evaporation of the anode with the plasma becoming sustained in the anode material rather than the surrounding gas. Other features of the arc are the thermal ionization (which is the process of molecules being ionized by other molecules), the emission of positive ions directly from the anode, high-field emission due to the steep potential gradient at the cathode that is related to the very short cathode dark space ($<$1 mm), and thermionic emission. Any of these features will tend to increase the current and hence intensify the problem and thus the change from abnormal glow discharge to an arc can be extremely rapid and uncontrollable.

Magnetron sputtering sources frequently have high currents applied that make them operate well into the abnormal discharge region in order to obtain the maximum deposition rate. If there is any distortion of the electric field, or increased electron emission due to surface defects, then there is a strong probability that this will locally take the current density over into the avalanche region resulting in an arc occurring. From the graph of voltage/current, it can be seen that the slope from arc back to abnormal glow discharge is very steep and energetically very difficult to achieve. This is the reason why it is essential that any power supply positively quench an arc before trying to re-establish the plasma. In this way, the operating conditions are more easily approached from the normal glow discharge conditions, and the plasma has the least disruption.

14.7 Triodes and Magnetically Enhanced Plasmas

The sputtering of materials is one of the major uses of plasmas. There have been developments aimed at increasing the cathode bombardment to increase the

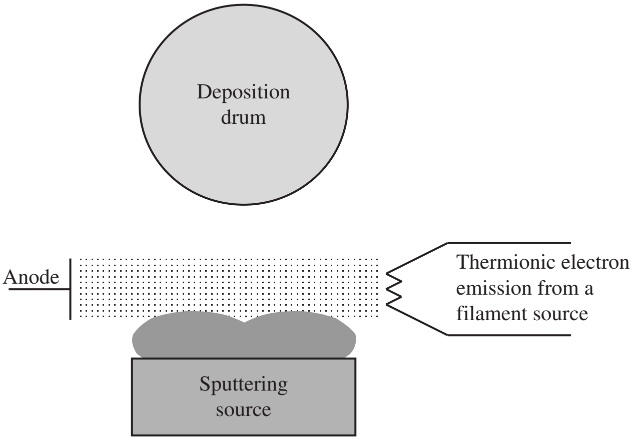


Figure 14.4 A schematic of a triode-type system.

sputtering and hence deposition rate. A plasma, at any given pressure, will find an equilibrium of electron generation and electron loss that defines the voltage versus current characteristic. One way to change the performance is to compensate for the electron loss by adding electrons to the plasma that allows the plasma to increase the current carrying capacity for any given voltage. Alternatively, it would allow the plasma to be sustained at a lower voltage for the same current [22,23].

Figure 14.4 shows the arrangement for this type of sputtering source. In this case, the shape of the plasma would suggest a magnetron sputtering source. The triode arrangement will work with magnetron sources equally as well as diode sputtering sources, both suffer from the loss of electrons, and so an additional source would have the same effect on each.

The magnetic confinement of electrons is another way of reducing the loss of electrons from the plasma. By reducing the loss, the operating voltage for any given current will be lower than without the magnetic confinement.

The main use of magnetic confinement is in the design of planar magnetron sputtering sources. The electrons are not only confined by the magnetic flux but also the motion of the electrons is affected. The electrons instead of moving in straight lines between the cathode and anode will spiral around the field lines from the magnets [24]. This spiraling effectively extends the distance between the cathode and anode by many orders of magnitude, and hence the chances of an electron making ionizing collisions also increase. So, fewer electrons are needed to sustain the plasma, or again for any given voltage more current can be carried. Not only do the electrons spiral along the field lines but they also precess around a racetrack over the cathode. Electrons making collisions can be knocked out of their orbit and hence can move further away from the magnetic influence or even be lost to the process altogether. Thus, there will still be some electrons lost to the process but much fewer than without the magnetic confinement.

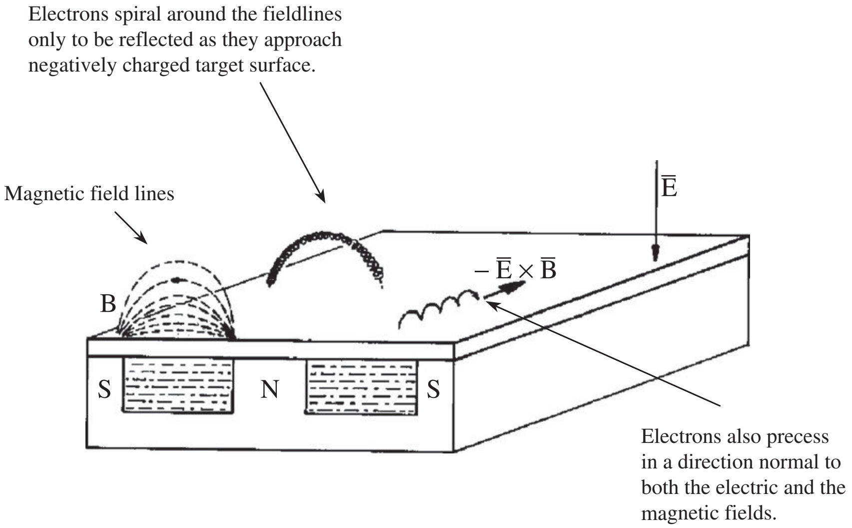


Figure 14.5 A schematic showing the basics of magnetic field lines and the resultant electron motion.

Figure 14.5 shows the magnetic arrangement of a planar magnetron sputtering source. Highlighted are the electron motion due to the crossed magnetic and electric field as well as the spiraling motion along the magnetic flux lines.

References

[1] Parker P. Electronics. London: Edward Arnold; 1950.

[2] Chapman BN. Glow discharge processes. New York: Wiley Interscience; 1978.

[3] Davis WD, Vanderslice TA. Ion energies at the cathode of a glow discharge. Phys Rev 1963;131:219.

[4] Penning FM, Druyvesteyn MJ. The mechanism of electrical discharges in gases of low pressure. Rev Mod Phys 1940;12(2):87−174.

[5] Bishop CA. The deposition of coatings onto polymer substrates by planar magnetron sputtering. PhD thesis. Loughborough University; 1986.

[6] Pfender E. Plasma generation. In: Szekely J, Apelian D, editors. Plasma processing and synthesis of materials, vol. 30. North-Holland, New York: Materials Research Society; 1984.

[7] Cobine JD. Gaseous conductors. NY: Dover 1958.

[8] von Engle A. Ionized gases. Oxford, UK: Clarendon Press; 1965.

[9] Kay E. Thin film sputtering techniques. Tech Met Res 1968;1(part 3):1296.

[10] Brown SC. Introduction to electrical discharges in gases. New York: Wiley; 1996.

[11] Penning FM. Electrical discharge in gases. New York: Macmillan; 1957.

[12] Aston FW. Experiments on the length of the cathode dark space with varying current densities and pressures in different gases. Proc Roy Soc A 1907;A79:80−95.

[13] Kay E. Impact evaporation and thin film growth in a glow discharge. Adv Electron 1962;17:245.

[14] Loeb LB. Basic processes of gaseous electronics. 2nd ed. Berkeley: University of California Press; 1961 LCCCN 55-5196.

[15] Loeb LB. Electrical coronas—their basic physical mechanisms. Berkeley: University of California Press; 1965 LCCCN 64-18642.

[16] Wehner GK, Anderson GS. The nature of physical sputtering. In: Maissel LI, Glang R, editors. Handbook of thin film technology. New York: McGraw-Hill; 1983 (reissue) ISBN 0070397422 [chapter 3].

[17] Roth JR. Industrial plasma engineering. vol. 1 Principles. Bristol and Philadelphia: Institute of Physics; 2000 ISBN 0 7503 0318 2.

[18] Holland L. Substrate treatment and film deposition in ionized and activated gases. Thin Solid Films 1975;27:185−203.

[19] Nasser E. Fundamentals of gaseous ionisation and plasma electronics. New York: Wiley Interscience; 1971.

[20] Lister GG. Review article: low-pressure gas discharge modelling. J Phys D Appl Phys 1992;25:1649−80.

[21] Vossen JL, Cuomo JJ. Glow discharge sputter deposition. In: Vossen JL, Kern W, editors. Thin film processes. New York: Academic Press Inc.; 1978 ISBN 0 12 728250 5 [chapter II − 1].

[22] Ectertova L. Physics of thin films. 2nd ed. New York: Plenum Press; 1986 ISBN 0 306 41798 7.

[23] Adachi R, Takeshita K. Magnetron sputtering with additional ionization effect by electron beam. J Vac Sci Tech 1982;20(1):98−9.

[24] Thornton JA, Penfold AS. Cylindrical magnetron sputtering. In: Vossen JL, Kern W, editors. Thin film processes. New York: Academic Press Inc.; 1978 ISBN 0 12 728250 5 [chapter II − 2].

15 Electron Beam (E-beam) Evaporation

It is always difficult to decide which material can be used for a resistance or thermally heated boat when wishing to evaporate high melting point materials. Ceramics may be either nonconducting or poor thermal conductors, both of which would make very inefficient sources. The electron beam technique gets round this problem by heating the source material from the same direction as the evaporant leaves from. A high current is passed through a wire filament that heats the filament up to a high temperature. At this high temperature, a stream of electrons is emitted from the surface. These electrons are accelerated, directed, and focused to hit the source material. This high-energy bombardment heats up the source to the point where it melts and evaporates (or sublimes). The source material can be held in a crucible that can or cannot be cooled. Some materials operate best using a water-cooled metallic crucible and rely on the thermal gradient between the crucible and the surface to enable a molten pool to form at the surface for evaporation but for some of the material, in contact with the crucible, to remain solid. In this way, the material stays pure and is much less likely to react with the crucible than if it were molten and in contact with the crucible where it might be possible for it to form an alloy or to have some crucible material diffuse into the molten pool (Figs. 15.1 and 15.2).

E-beam guns as large as 1.2 MW have been built for the coating of strip steel [1]. For sweeping e-beam systems to produce barrier coatings on to polymer web, the power would be approximately 250 kW/m width.

15.1 Filaments and Electron Emission

Using a low-voltage and high-current power supply, a filament can be raised in temperature to become white-hot. This filament will emit electrons in random directions from the surface (Fig. 15.3). By surrounding the filament with a negatively charged cathode surface except for a gap through which there is an anode, the charged electrons can be directed into a beam with movement in a specific direction [4]. It is preferable to do this at low pressures to prevent too many losses

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00015-5

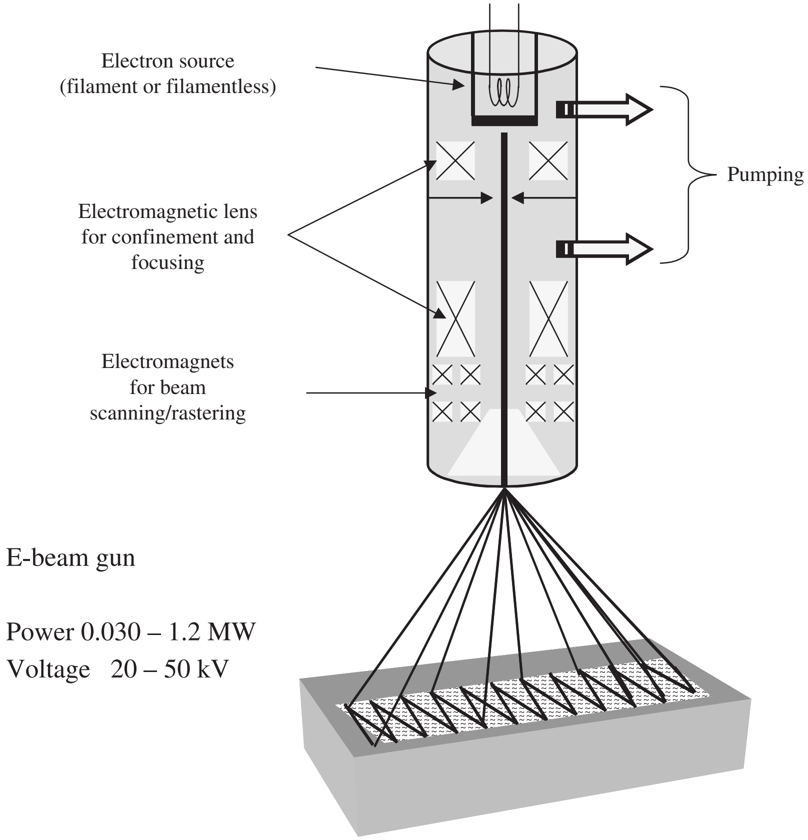


Figure 15.1 A schematic of a basic electron gun design. In reality, the electron stream would be bent to allow the evaporant to have an uninterrupted path to the deposition drum. This figure also does not show the secondary electron trap that is essential for systems depositing onto polymer webs. Further examples can be seen in Refs. [2,3].

by gas collisions, and hence in high-powered guns, it is common for the filament area of the e-beam gun to have its own pumping system.

The power to the filament can be either AC or DC. With such high currents being used, a magnetic field is created by the current flowing through the wire, and this will affect the electron emission. When using DC to power the filament, because the current flow remains in the same direction, there will be a permanent offset to the beam direction because the electrons escaping the filament surface have been influenced by the magnetic field. When using AC power, this offset will be in opposite directions for each half of the power cycle. This means that DC e-beams tend to be tighter and more precise beams than AC ones that tend to be broader beams.

The quantity of electrons emitted depends on the current passed through the filament, the temperature achieved, and the work function along with other factors.

Figure 15.2 A 2.5 m wide twin electron beam evaporation system showing the two electron guns angled down and in to the source crucible. Photograph courtesy of Applied Materials

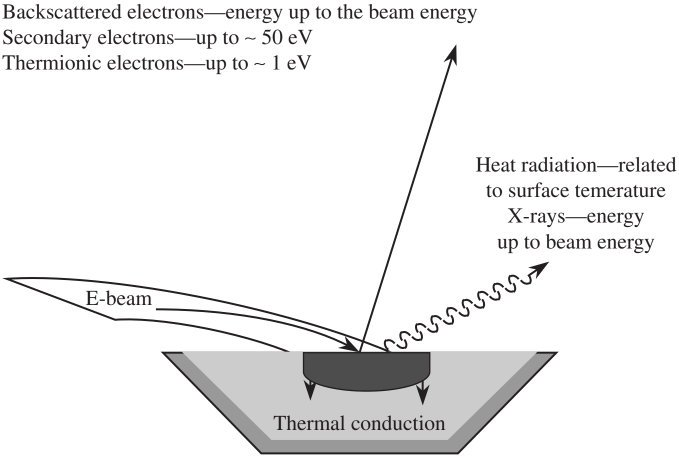


Figure 15.3 A schematic showing the interactions that occur as the electron beam hits the source material.

These three factors are all dependent on the material chosen as the filament. One of the common choices of material is tungsten. This is the same as is used in the construction of light bulbs and the same problems can occur. At an elevated temperature and for a prolonged period of time, there can be significant grain growth of the crystals within the filament. This can reach the point where the diameter of the filament is taken up by a single crystal. When this crystal meets the next crystal, there will be a concentration of impurities, and this will cause an increased resistance and failure of the filament. To slow down this effect, tungsten filaments are doped with thorium.

Many high-power systems now have a separate compartment for the e-beam filament. This chamber can be isolated from the rest of the system, thus allowing fast access for filament changes.

The electrons are essential to this process; however, they can also cause problems. It is essential that the electrons either hit the source material or are captured elsewhere. When the e-beam hits the source, it will also generate some secondary electrons [5]. Any of the lost electrons from the e-beam and all of the secondary electrons need to be captured by an electron trap [6,7]. If this is not done, they may well hit the substrate, and, in some cases, this can generate electrets that remain in the web and can cause the web to block. (Blocking is where the web cannot be easily separated once wound up. In this case, the electrostatic forces are large enough to effectively stick the web layers together.)

One source of failure of e-beam systems is due to arcing, which is often caused by oxide buildup [8,9].

15.2 E-beam Control

The anode provides the acceleration to the e-beam. The acceleration voltage can be as high as 35 kV. Once this beam has been produced, it can be focused and manipulated in the same way a cathode ray tube operates using electromagnetic sweep coils.

There are many styles of e-beam guns (Figs. 15.4 and 15.5). In some, the beam is pointed straight at the source material, and the beam sweep coils are used to

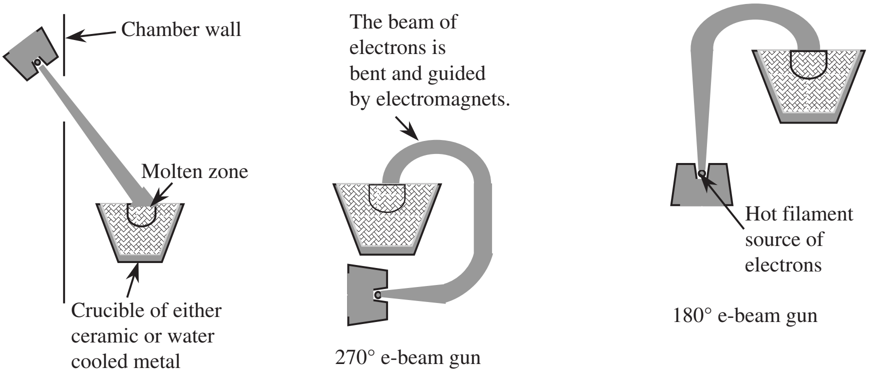
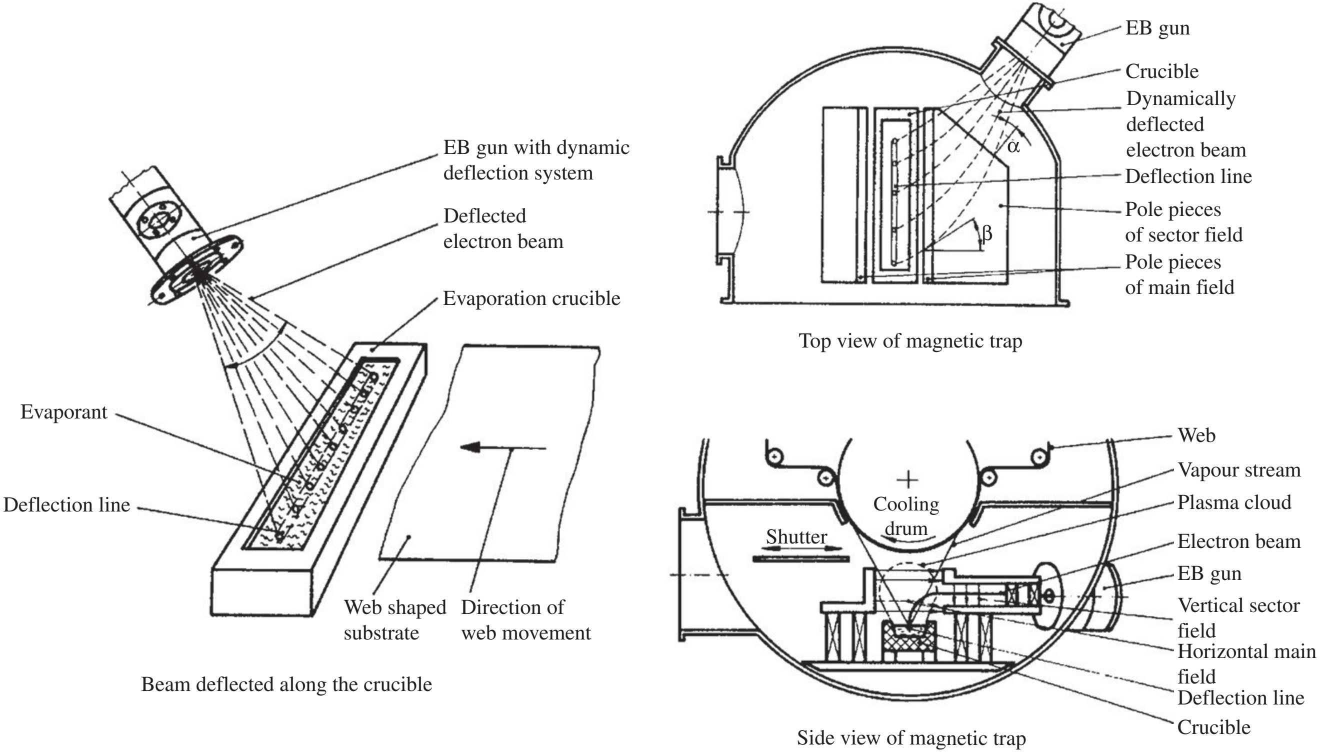


Figure 15.4 Schematics showing several different sources with different electron paths.



Beam deflected along the crucible

Top view of magnetic trap

Side view of magnetic trap

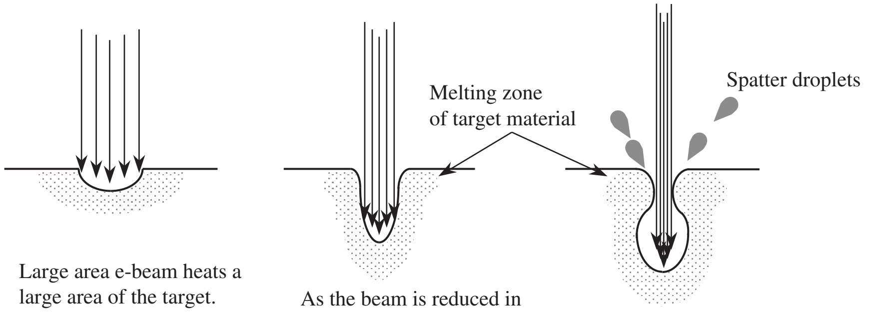
Figure 15.5 Further details of a large area source heated by a powerful scanning electron beam, the system is based on the Pierce-type gun. Diagrams courtesy of Manfred von Ardenne Research Institute [6,11,12].

move the beam around across the whole surface to provide a large area rather than a point source [1]. In others, the e-beam is bent round through as much as 270° into the source crucible. These tend to be operated as point sources and several can be used side by side to coat a larger width of web in exactly the same way as with the multiple resistance boats.

In the same way that resistance-heated evaporation sources can be arrayed as a series to coat wide webs, so too can small e-beam systems be similarly arranged [10]. In this way, it is possible to dispense with any scanning system on each of the e-beam guns. This can make the uniformity of heating and stability of deposition rate better than for a single scanned source.

These large-scale sweeping e-beams are extremely powerful and can be damaging to the source material if used incorrectly. Source material can be in a variety of forms from powder through to solid billets. The source material may be anything from a good to a bad thermal conductor. If a high-power e-beam hits a powder hard, it can blow all the powder out of the crucible. If it hits a powder compact hard, it may warm up pockets of gas trapped in the block and blow the block apart. Similarly for a poor thermal conducting material, the thermal stresses can be enough to break the material into pieces. On softer materials if the beam is not moved around fast enough, it may evaporate a pit where the walls then fall in and the molten mass is spat out (Fig. 15.6).

The options that are available to control the e-beam are the power, the beam shape (diameter), the raster pattern, and the residence time. Materials with a poor thermal conductivity may be heated up slowly by building up the power slowly. In addition, the beam can be defocused and moved across the whole surface, thus bringing the whole of the surface up to the desired temperature at the same time. To evaporate a high melting point metal, it may be necessary to keep the beam more tightly focused to attain the high temperature and to limit the size of the

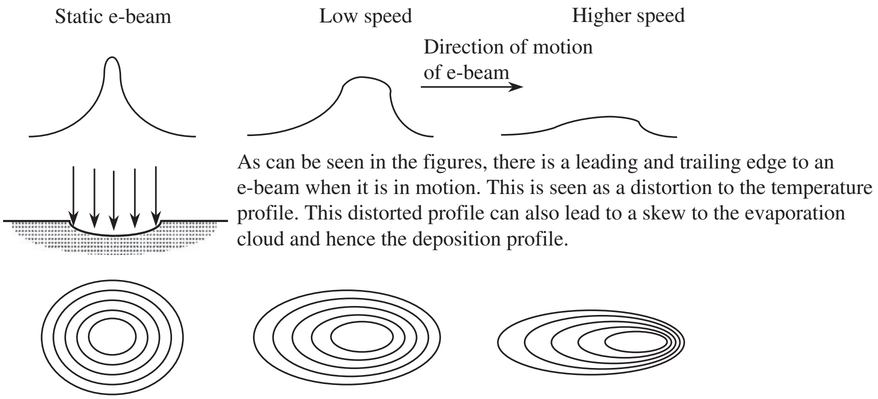


Large area e-beam heats a large area of the target. With beam movement a large volume of material can be raised to the evaporation temperature with little or no spatter.

As the beam is reduced in area the current density is raised and the beam starts to "drill" a deeper pit in the target surface.

If the beam area is reduced too much the depth of the pit is so great that the walls at the surface fall inward and become molten, throwing up droplets known as spatter.

Figure 15.6 Details of how the electron beam can be a source of spits [4].



As can be seen in the figures, there is a leading and trailing edge to an e-beam when it is in motion. This is seen as a distortion to the temperature profile. This distorted profile can also lead to a skew to the evaporation cloud and hence the deposition profile.

Figure 15.7 Details of how an electron beam shape can be affected by the scanning motion [13].

molten pool by limiting the raster pattern. On linear e-beam systems, where a single e-beam has to heat up as much as a 1 m wide source, the beam has to sweep rapidly from one side of the crucible to the other to try to keep all the material at the same temperature and in so doing keep the evaporation rate constant across the full crucible width. As there are greater heat losses at the ends of the crucible, it is common to compensate for this by increasing the beam residence time at each end. In so doing, it is also possible to give a small increase in evaporation rate, enabling an increase in the deposition that not only compensates for the end losses but also improves the deposition profile.

Care also needs to be taken when moving the e-beam; it is possible that the evaporant will, instead of being symmetric about a line normal to the surface, be skewed off at an angle as shown in Fig. 15.7. In most cases, this is not significant, but where a mixture of sources is being used, it is possible to have the sources mechanically positioned on the same centerline but for the coatings to be deposited each about a different centerline. This is the result of different scanning speeds producing different amounts of skew for different materials. Once identified, the beam can usually be repositioned for one source to compensate and bring the deposits together in full overlap.

15.3 Power Supply

The power supply for e-beam guns must be able to do more than supplying a highly stabilized voltage and current. The nature of the power that is involved means that the supplies have to be well protected from arcing.

The emission circuit is reliant on a very high stability source and a current-sensing resistor to ensure a constant electron emission current. The acceleration voltage also uses a constant voltage control circuit, thus keeping everything as stable as possible.

The raster coils have sinusoidal or sawtooth waveforms as well as the basic beam direction controls. For mixed materials, the beam can be scanned in predetermined patterns with slow or stationary points such as those at the ends of the crucible and quicker points across the center of the crucibles [14].

15.4 Crucibles and Feed Systems

Water-cooled copper crucibles are expected to be in direct contact with the source material. Alternatively, other materials may be used where the crucible is allowed to get hot too. Cold crucibles can take 75% of the power used away in the cooling water. Hot crucibles have the problem that after the deposition cycle, they may take a long time to cool and thus delay the process cycle. They may also be prone to thermal cracking that can lead to molten material leaking and causing other maintenance problems. The problem is a difference in the rate of thermal expansion of the source material and the crucible. The crucible may also be porous, and the molten source material may infiltrate the ceramic surface. When the source and the crucible cool, any difference in contraction rates will tend to cause the two different materials to move relative to each other. If the source material has bonded to the crucible, this can restrict the movement and cause other mechanisms of stress relief such as cracking.

There are many variations of design that allow for replenishment of the source material [4] (Fig. 15.8). There are water-cooled crucibles where the source material is fed up as a solid rod through the base of the crucible and into the molten source. The feed of the rod is aimed at keeping the liquid level constant. Others have used an annulus crucible with the e-beam directed into the crucible at one point and directly opposite fresh material is fed into the annulus and the annulus keeps slowly rotating. Another alternative is for pellets to be added to the molten pool periodically.

All of these require the crucible type and the e-beam control to be optimized to suit the different materials.

It is possible to deposit alloys, although with web coaters the number of components may be limited. A common method is to have two parallel crucibles and a single e-beam gun that moves between each source keeping both evaporating (or subliming) [15]. The alloy composition can be varied by controlling the residence time on each crucible and hence the individual deposition rates.

15.5 System Design

One of the first choices to be made is in deciding whether to use a series of small crucible e-beam sources or to go for a single large sweeping beam e-beam source.

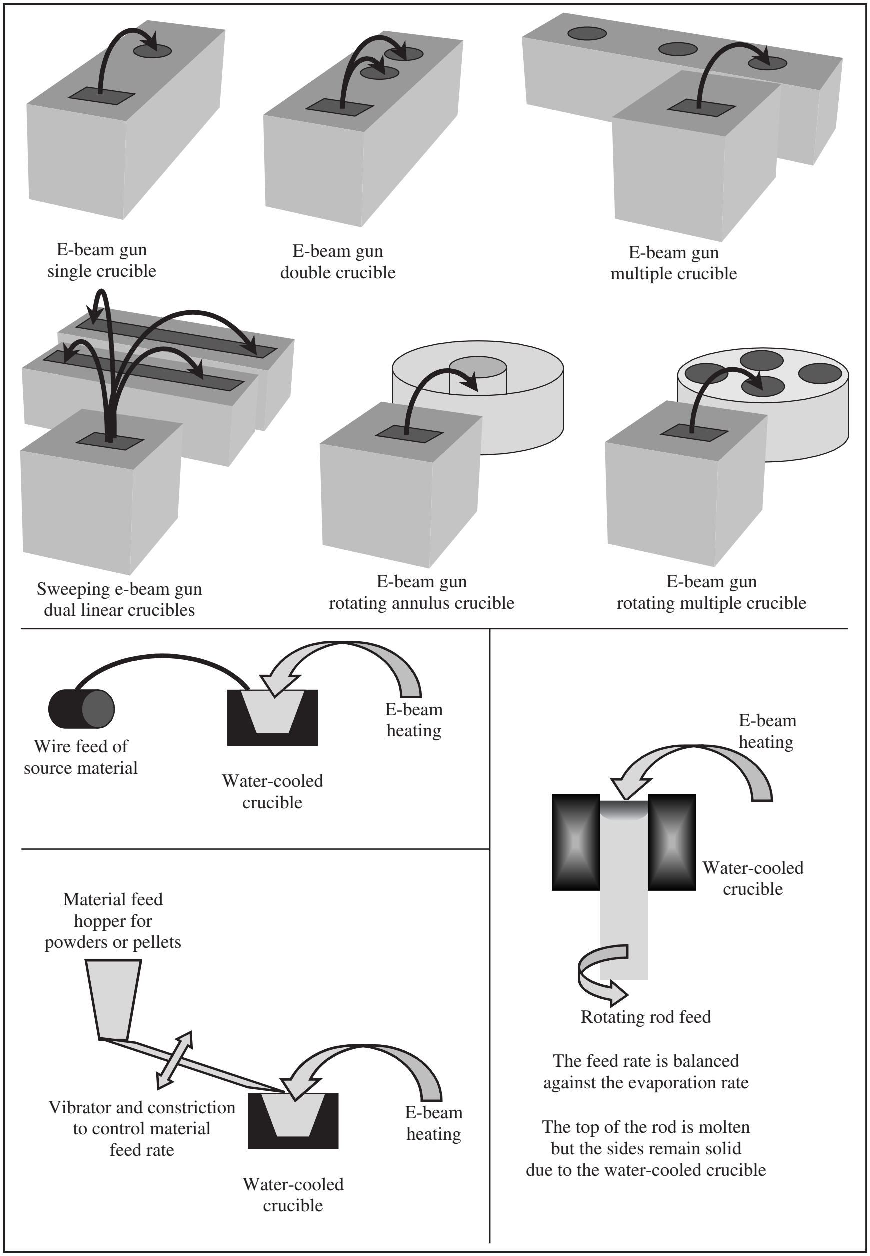


Figure 15.8 Details of a number of crucible types and the three most frequently used feed systems.

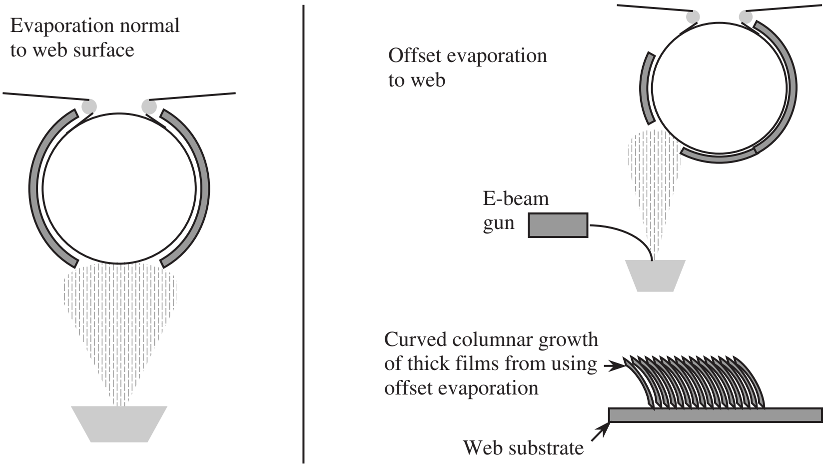


Figure 15.9 A schematic showing deposition normal to the cooled deposition drum and also offset deposition that can alter the growth pattern of the coating [16].

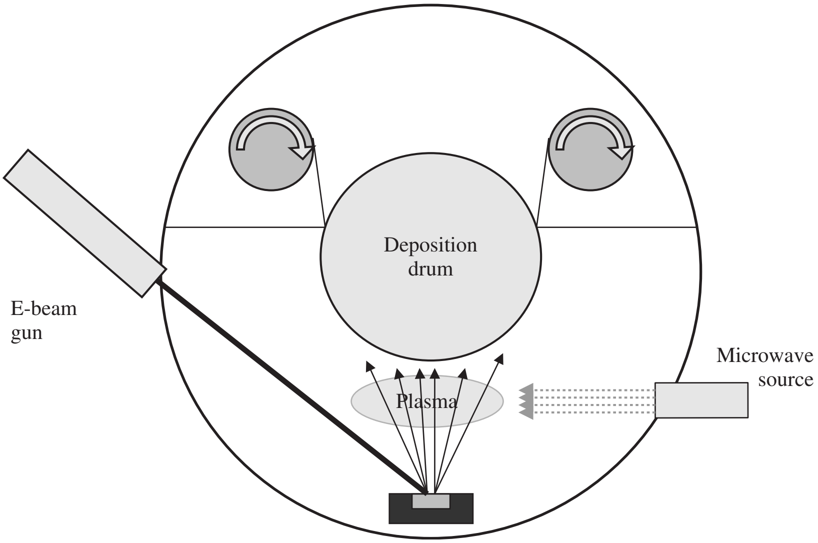


Figure 15.10 A schematic showing the layout of a plasma-enhanced electron beam deposition system.

The individual sources have the same options as resistance-heated evaporation boats in that they can be set in a line or staggered in two lines [10]. The deposited material will be an integration of all the fluxes. The advantage can be that the sources can be placed under the deposition drum and, if necessary, quite far from the vessel walls. These individual e-beam guns may have to operate at a higher pressure as the filaments are within the main vessel and are not often separately pumped.

The sweeping e-beam source system tends to have the deposition drum sited near to one side of the vessel. The e-beam gun is sited on one side of the vessel and aimed at the crucible directly under the deposition drum [17].

In the schematic in Fig. 15.9, the crucible is offset from the drum centerline in order to use the curved columnar structure of the growing film to aid adhesion.

Another option is to add an additional plasma to densify the coating and to improve the adhesion [18,19]. In Fig. 15.10, the additional plasma is generated using a microwave source, but it could also be a triode, arc, magnetron, or other source.

As with other deposition systems, there are benefits to pretreating the web with a plasma treatment prior to deposition [20].

References

[1] Hill RJ. Physical vapor deposition. 2nd ed. Berkeley, CA: Temescal; 1986. Part no. T-0186-6001-1.

[2] Schiller S, et al. Processing and instrumentation in PVD techniques. Vakuum-Technik 1986;35(4):35−54.

[3] Schiller S, et al. Electron beam processing in metallurgy. In: Proc. IX international vacuum congress and V international conference on solid surface; 1983.

[4] Schiller S, et al. Electron beam coating. In: Sudarshan TS, editor. Surfacing technologies handbook. New York: Marcel Dekker; 1988.

[5] Schiller S, et al. High-rate electron beam evaporation. Thin Solid Films 1983;110:149−64.

[6] Schiller S, Neumann M. Application of EB line evaporators for web coating. In: Proc. 1st international vacuum web coating conference; 1987. p. 113−28.

[7] Schiller S, et al. Capabilities of electron beam evaporation for the deposition of compounds. In: Proc. 4th international vacuum web coating conference; 1990. p. 138−58.

[8] Gevelber M, et al. Improving rate control in electron-beam evaporated optical coatings: the role of arcing and controller tuning. In: Proc. 47th annual technical conference of Society of Vacuum Coaters; 2004. p. 395−400.

[9] Thiede A, et al. New type of high voltage power supply for electron beam web coaters. In: Proc. 46th annual technical conference of Society of Vacuum Coaters; 2003. p. 149−53.

[10] Matteucci JS. Electron beam evaporation and D.C. magnetron sputtering in roll coating. In: Proc. 30th annual technical conference of Society of Vacuum Coaters; 1987. p. 91−104.

[11] Pierce JR. Theory of design of electronic beams. New York: Van Nostrand Inc.; 1954.

[12] Schiller S, Neumann M. High rate electron beam evaporation for roll coating. In: Proc. conference EB melting and refining; 1984.

[13] Schiller S, et al. Evaporation of alloying elements in EB melting—possibilities and influence. In: Proc. conference EB melting and refining; 1984.

[14] Schiller S, et al. Some remarks about our new developments in high-power EB gun technique. In: Proc 5th annual conference on E-beam melting and refining; 1987. p. 111–30.

[15] Ohya T, et al. A ceramic (SiO_2-Al_2O_3 mixture) coated barrier film by electron beam evaporation. In: Proc. 43rd annual technical conference of Society of Vacuum Coaters; 2000. p. 368–72.

[16] Hoffmann G, et al. Electron beam web coating—technology and applications. In: Proc. 42nd annual technical conference of Society of Vacuum Coaters; 1999. p. 425–9.

[17] Walsh TB. High output electron beam metallizing roll coater for packaging applications. In: Proc. 30th annual technical conference of Society of Vacuum Coaters; 1987. p. 111–7.

[18] Heinss J-P, et al. Enhanced surface properties of metallic sheets by high-rate electron beam evaporation. In: Proc. 40th annual technical conference of Society of Vacuum Coaters; 1997. p. 157–62.

[19] Schiller S, et al. Plasma-activated high-rate deposition of oxides on plastic films. In: Proc. 37th annual technical conference of Society of Vacuum Coaters; 1994. p. 203–10.

[20] Lohwasser W. Large scale electron beam web coating not only for packaging. In: Proc. 43rd annual technical conference of Society of Vacuum Coaters; 2000. p. 362–7.

16 Thermal Evaporation

The bulk of aluminum evaporation is done by passing a current through an intermetallic boat, thus heating it up and simultaneously feeding a wire of aluminum against the hot surface of the boat. The aluminum, on touching the surface, melts, and, if the wire feed rate is high enough, forms a pool of molten aluminum that steadily evaporates. A series of these boats are arranged in a line across the width of the web that results in a coating of somewhere between ±5% and ±20% uniformity depending on geometry.

The same basic technology is used for the evaporation of aluminum at narrow web widths onto polymer film as thin as 0.6 μm used for capacitors and through to very wide systems as shown in Fig. 16.1 that would be used on 12 μm thick polymer films for packaging applications. For the wider machines, there are more boats at the same spacing to cover the wider film and each with their own wire reel and feed system and thickness monitoring head.

16.1 Boats

Molten aluminum is highly corrosive, and the refractory materials do not make cheap or robust evaporation boats. The most commonly used materials for the resistance boats are the intermetallic mixtures.

There is a choice of either a two- or a three-phase intermetallic mixture that offers the right mixture of resistivity and corrosion resistance [1−6]. The two-phase mixture consists of boron nitride and titanium diboride. The three-phase mixture contains aluminum nitride.

Titanium diboride has low electrical resistivity and is easily wet by the aluminum.

Boron nitride has high electrical resistivity and also possesses good thermal shock resistance and ease of machining.

Aluminum nitride is added for its thermal conductivity and electrical resistance performance.

The typical boat lifetime is only about 15 hours. Figure 16.2, of service life versus resistivity, depends on many factors but is based on an average of the temperature of operation and wire feed rate into the boat [7].

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00016-7

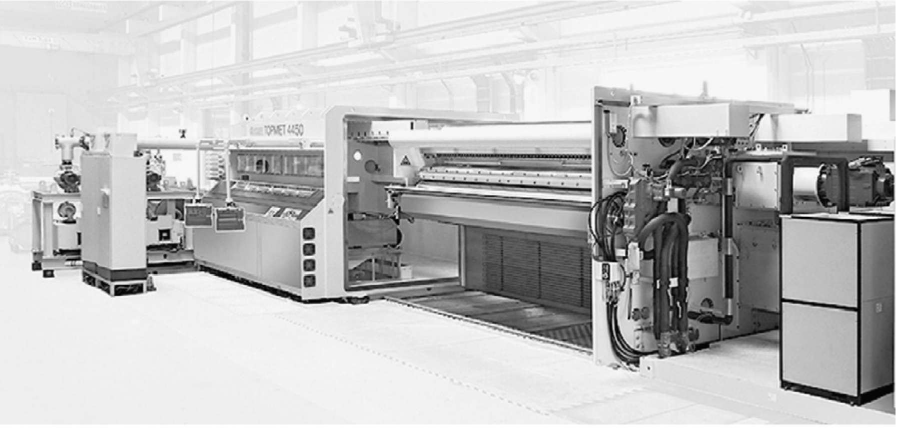


Figure 16.1 Photograph of one of the largest aluminum metallizers of 4.45 m wide and capable of running at 1250 m/min. Photograph courtesy of Applied Materials.

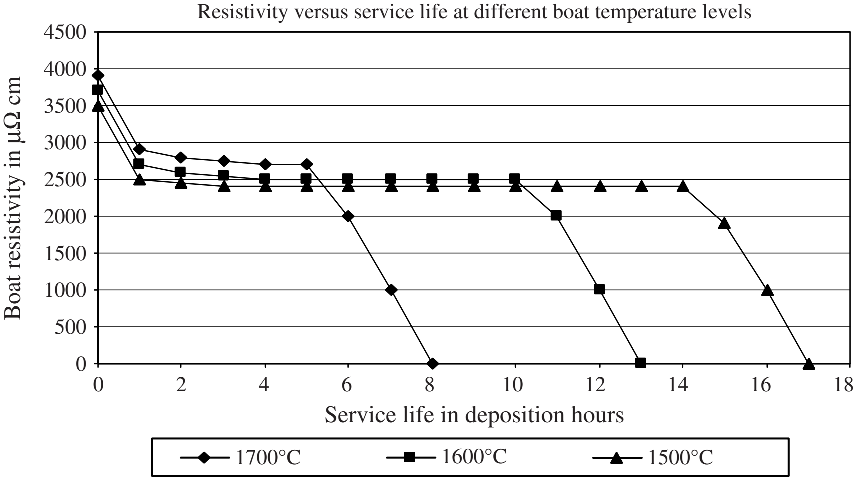


Figure 16.2 Graph of resistivity versus service life for resistance-heated evaporation boats operating at different temperatures. Reprinted from Mount EM, III, editor. Metallizing technical reference. 3rd ed. Fort Mill, South Carolina: Association of Industrial Metallizers, Coaters and Laminators (AIMCAL); 2001, with permission.

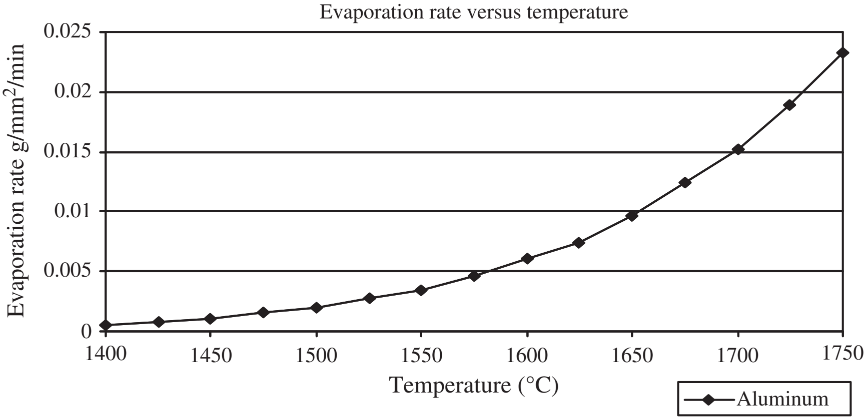
If the boat is driven harder, using a higher temperature and higher wire feed rate, the lifetime can fall below 10 hours. Similarly if the boats are run slightly cooler and the wire feed rates are lower, the boat life can exceed 20 hours.

The trade-off is a higher cost in boats versus a slightly higher rate of metallized roll production.

Some of the problems of boat life results from decisions made at the time the system was designed and built. The deposition efficiency of many systems is poor at around 35%. Increasing the cooled deposition drum diameter can raise this figure to 50% or greater. Systems with larger deposition drum and higher material collection efficiency are more easily able to deposit high optical density coatings. The larger drum also spreads the heat load over a larger area and is also less likely to suffer winding problems. With the higher deposition efficiency, the boats can be driven at a lower power for the same deposition thickness as could be achieved by one of the lower efficiency systems where the boats are driven harder at a higher temperature and corresponding lower boat life. The penalty for the larger drum is that the cost to build a system will be slightly higher.

It is also true to say that systems with more efficient design are also often run with high boat temperatures to try to squeeze a little more productivity out of the system (Fig. 16.3).

The aluminum is supplied as a wire that is directed to feed into the boat at a shallow angle touching the boat surface toward the middle of the boat. Ideally, the feed rate is sufficient to keep the molten pool of aluminum at a constant size and depth. In this way, the wire melts as it feeds into the molten pool rather than as it



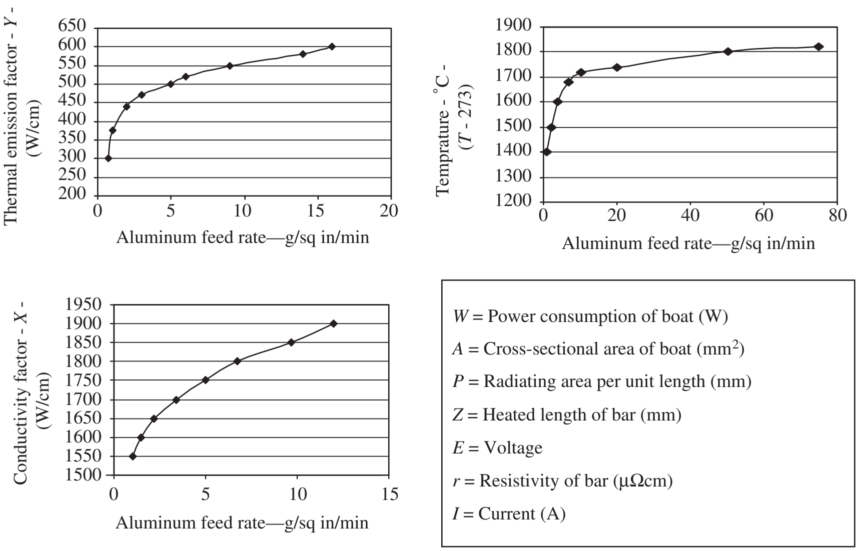
At 1500°C Boat life taken as baseline
At 1600°C Boat life ~ = ¾ of life at 1500°C
At 1700°C Boat life ~ = ½ of life at 1500°C

Figure 16.3 Graph of the evaporation rate versus evaporation boat temperature. Reprinted from Mount EM, III, editor. Metallizing technical reference. 3rd ed. Fort Mill, South Carolina: Association of Industrial Metallizers, Coaters and Laminators (AIMCAL); 2001, with permission.

rubs against the boat surface. The more the wire rubs against the boat surface, the deeper the groove it will erode into the surface locally, changing the resistivity of the boat. This erosion and changed resistivity will cause a local change in the temperature of the boat, and the molten pool will no longer be as uniform as when the boat is new. The ultimate result of the erosion can be the failure of the boat in service.

The operating procedure for the boats can also affect the boat lifetime [8]. Taking care in heating the boats on first use and on finishing deposition can extend the boat lifetime (Fig. 16.4).

Boat manufacturers offer recommendations on the “break-in” or “burn-in” heating procedure. This initial heating is slower than for subsequent use and is to ensure that the boats are free of any residual volatiles and/or moisture. Any absorbed moisture or residual volatiles when heated rapidly can change to a gas with a huge change in volume. This change to a gas may create a high pressure and



W = Power consumption of boat (W)
A = Cross-sectional area of boat (mm^2)
P = Radiating area per unit length (mm)
Z = Heated length of bar (mm)
E = Voltage
r = Resistivity of bar (μΩcm)
I = Current (A)

Power	Voltage	Current
$W = X\frac{A}{Z} + YP$	$E = \frac{W}{I}$	$I = 1000\left(\frac{W.A}{(3.7\,r\,.\,Z)}\right)$

Over the life of a boat the voltage will drop by 60–70% and the current will increase by 40–50%.
The lifetime of boats, also depends on the temperature and deposition rate.

Figure 16.4 Graphs of the performance of resistance-heated evaporation boats [9]. Reprinted from Archibald P. and Parent E. Source evaporant systems for thermal evaporation. Solid State Technol. 1976;19: 32−40, with permission from PennWell Corporation.

prematurely crack the boat while heating slowly allows more time for the gas to diffuse out and reduce any pressure buildup. This preconditioning is to try to ensure that the aluminum, when it is fed into the boat, will fully wet the surface.

At the end of the evaporation process, they also recommend that the aluminum feed is stopped and the heating is continued until the whole boat surface is free from aluminum. Aluminum tends to migrate into any pores in the powder compact boat. If this aluminum is not evaporated out, the differential contraction on cooling can cause microcracking of the surface that can be easily eroded, which will lead to a reduced boat lifetime.

It is also recommended that up to 5 minutes is given for the boats to cool down naturally, from their operating temperature of around 1400–1500°C, before the air is admitted into the system. Generally, the advice given is to wait until the temperature is below 600–700°C. At this temperature, the boats will no longer be glowing red and so this lower temperature is referred to as below the "black heat" temperature.

The boats need to have a high-quality electrical contact in order to pass current through the boat to heat it up. As the boat heats up, it will expand and so provision must be made to maintain the contact but allow for movement. The difference in the materials means that there is a difference in the coefficient of thermal expansion. If the holder and boat were to be rigidly connected, the boat would, most likely, be overstressed by this load and its lifetime would be reduced. Originally, allowance for movement was done by pressing the boats into a slot in a copper busbar with a carbon-loaded conducting paper used between the two to help get a tight fit but still allow movement. In more recent times, this technique has been replaced by using spring-loaded end connectors. The boats simply push against the spring as they heat and expand, which, if anything, improves the electrical contact. The end contacts are usually water cooled, and so the springs do not suffer from thermal aging. The end connectors also enable more of the length of the boats to be heated to a uniform temperature that can then be used for evaporation.

It is still essential to maintain full contact between the boat and the busbar surface. Any misalignment will result in uneven heating and reduced deposition uniformity and reduced boat lifetime.

The power that is fed into the boats disappears in three ways: 33% is lost through radiation, 33% through thermal conduction, and 33% is used in the evaporation of the aluminum metal [10] (Fig. 16.5).

The 33% that is lost through radiation is lost from all surfaces. Simplistically, it can be thought of as 50% downward and 50% upward (Fig. 16.6). The radiation that is emitted upward can be absorbed by the web and is a significant part of the heat load that has to be controlled.

It may be worth considering what happens to the heat emitted downward. If this were to be reflected back onto the boat, it ought to be possible to reduce the energy required to achieve any given temperature. Potentially, this could be as much as 15% of the power consumption of the boats. In reality, there will already be some heat reflected back toward the boats albeit inefficiently, and so only a proportion of the energy might be saved.

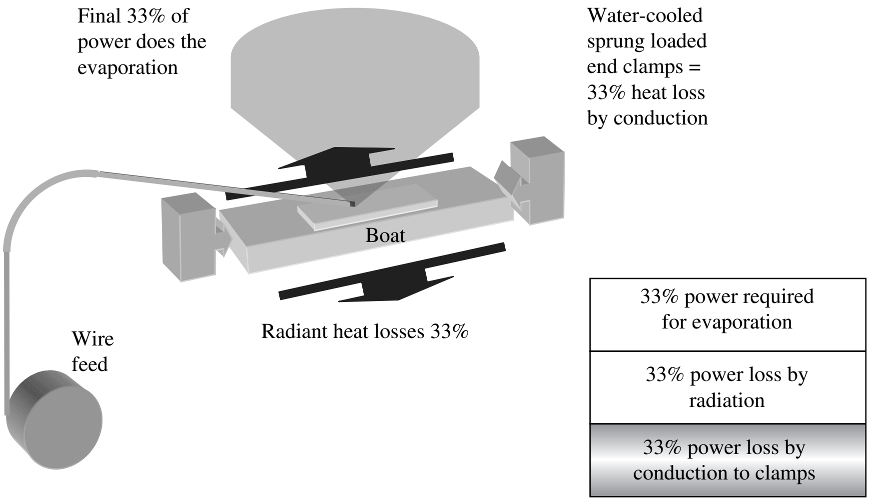
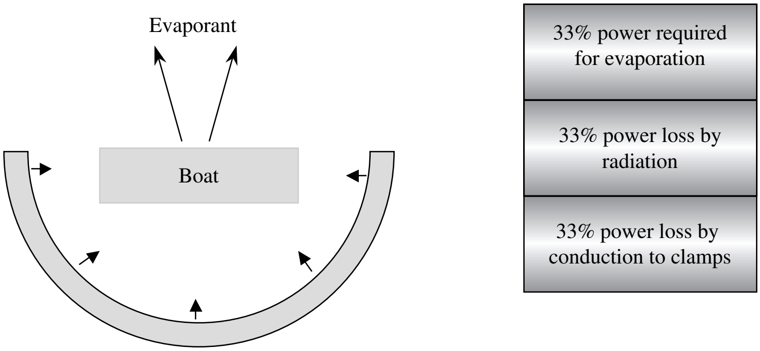


Figure 16.5 A schematic of a resistance-heated evaporation source indicating where the power gets used.



50% of radiation loss is downward.

If this could be reflected back onto the boat there is the potential for an energy saving of up to 15%.

This process is quite dirty and so using bright reflectors to reduce the radiant heat losses is not very effective. Boat design has had only a marginal improvement on power use.

Figure 16.6 A schematic showing approximately where the power goes.

A practical difficulty may be the cleanliness of the process. If one looks into a metallizer below the evaporation sources, it is frequently an extremely dirty area. It is not easily accessible and so is infrequently cleaned. Thus, to get the benefits of reflecting the heat back to the boat would require a redesign of this area or the sources to make it much more easily cleaned so that more efficient heat-reflecting surfaces could be easily and properly maintained. In these days of energy efficiency, this might still be a cost-effective measure worth considering.

Boats are available in several different designs [11] (Fig. 16.7). The basic boat is a rectangular block with a shallow depression machined into the surface. The aluminum is fed along the centerline and is aimed to meet the boat surface at between one third and halfway down the boat length. The aim is for the aluminum to wet the surface and substantially fill the depression.

This is shown schematically in Fig. 16.8. If too much aluminum is fed into the source, the increasing thermal mass will cool the boat and the evaporation rate will drop.

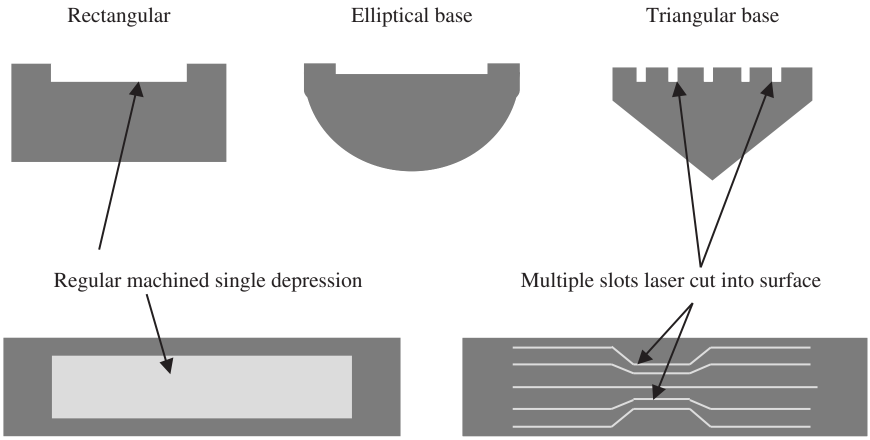


Figure 16.7 A schematic of some of the different boat designs available.

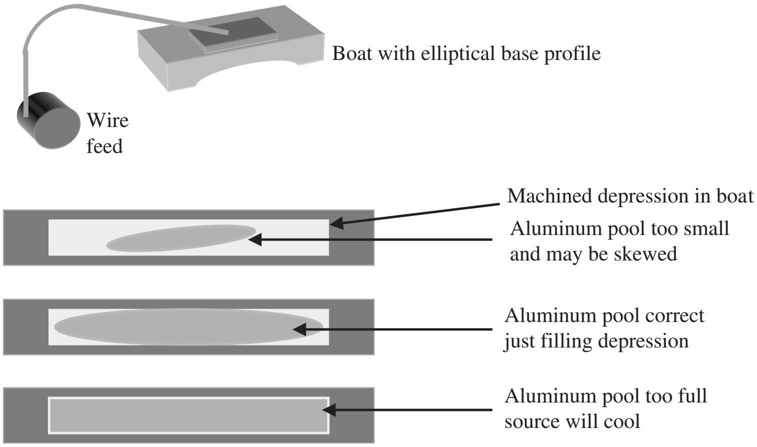


Figure 16.8 A schematic showing what can happen to the aluminum pool in a crucible.

Conversely, if too little aluminum is fed into the pool, it will shrink in size and the boat will heat up and spitting will increase.

Variations on this include having the mass of the boat reduced by making the underside of the boat profile elliptical or triangular. This is claimed to reduce the power requirement and improve the temperature profile, increasing the performance by around 10%.

Another variation is to not have the single machined depression in the top surface but to have a series of slots instead. It is claimed that this allows the aluminum to wet out the surface at a lower temperature and hence allow deposition to commence sooner than with the single depression version. It is also claimed that the improved wetting leads to less spitting and bending and results in an extended source lifetime.

The choice of supplier of boats can also affect the productivity. Some of the lower cost boats do not have the performance of the higher cost boats. The reason for the different lifetimes can be dependent on the quality of the powder compact process and the grain size of the powders used. The coarser grained boats tend not to last as long as corrosion and erosion occur more rapidly and hence some of the cheaper boats may represent a false economy.

A schematic of a boat and how the boat will wear in use due to the binder being dissolved and the turbulence in the molten pool scouring the surface is shown in Fig. 16.9. This leads to changes in the boat composition locally, which results in changes in temperature and electrical conductivity. Also shown is the region at the

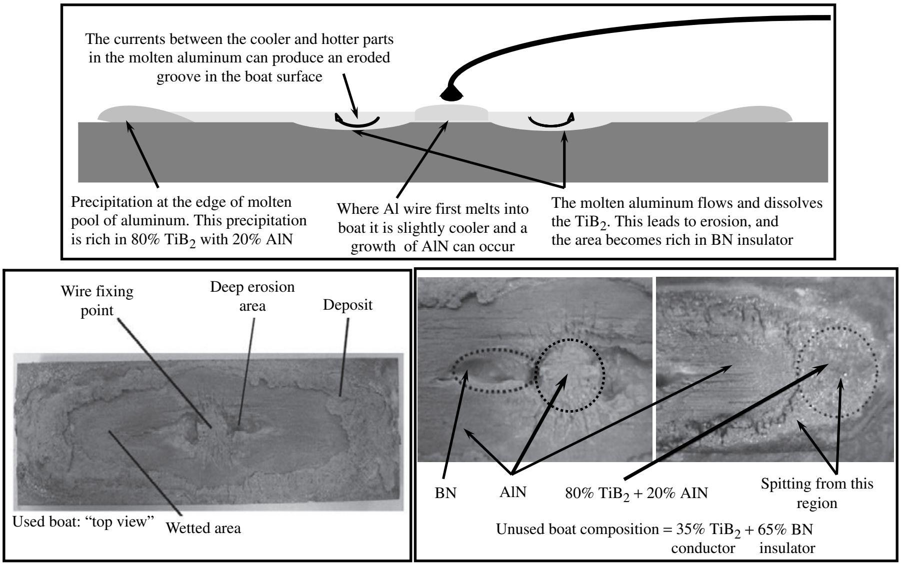


Figure 16.9 Erosion and corrosion of resistance-heated boats. Photographs courtesy of Kennametal Sintec Keramik GmbH [12].

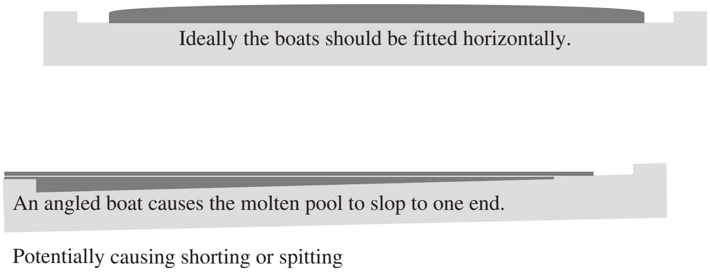


Figure 16.10 A schematic showing the necessity of fitting the boats perfectly level.

ends of the boat where the molten pool surface crud also collects and can become a source of source spitting.

One aspect that is generally assumed is that the vacuum system is level and that the fixings and location parts for the boats are also level (Fig. 16.10). It becomes very noticeable if the boats are not mounted level as the molten pool will not sit uniformly in the depression in the boat. If the molten pool does not sit level, there may be a tendency for some of the aluminum to overflow the depression and there will probably be an increased tendency for spitting.

The boats have to have current passed through them so that they will heat up. As they heat up, the boats will expand, and this expansion has to be allowed for in making the electrical contact. The connection has to have some flexibility. One method used to achieve this is to pack the gap between the clamp and boat with a conducting carbon-loaded paper. Not only does this compressed paper allow for some movement, but it can also accommodate some damage to the clamps. Clamps, if they do not have a good and even contact to the boat, can develop hot spots that may also lead to arcing. This arcing can, in turn, lead to melting the clamp surface and may cause pitting and other surface defects. These defects can, in turn, cause a problem with making a good connection to the next boat that is installed. The surface should be checked before loading a new boat and if sharp defects are found, these should be removed or smoothed. It is not economic to keep replacing clamps that have minor pits in the surface and so the use of the carbon-loaded paper helps extend the lifetime of the clamps by improving contact to the damaged surfaces (Fig. 16.11).

Although the carbon-loaded conducting paper can be used to improve the contact, it is still essential to ensure that the basics of good clamping are still observed, otherwise boat failures will become commonplace (Fig. 16.12).

16.2 Wire Feeding

Modern metallizers can be expected to coat 50 km of web, or more, of up to 4.45 m widths at a speed of 1250 m/min at an optical density of 2.0 or more.

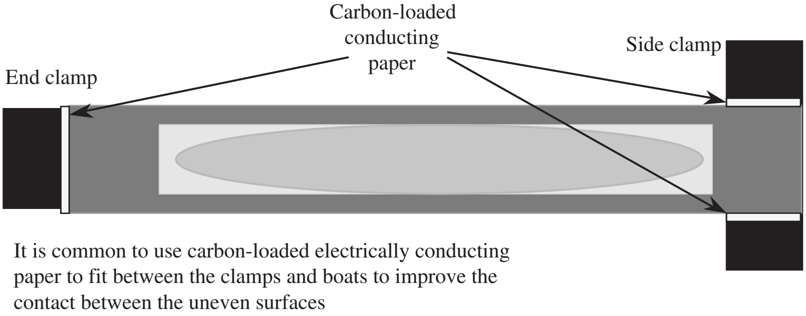


Figure 16.11 A schematic of the use of carbon-loaded conducting paper to aid making good electrical connection between clamps and evaporation boats.

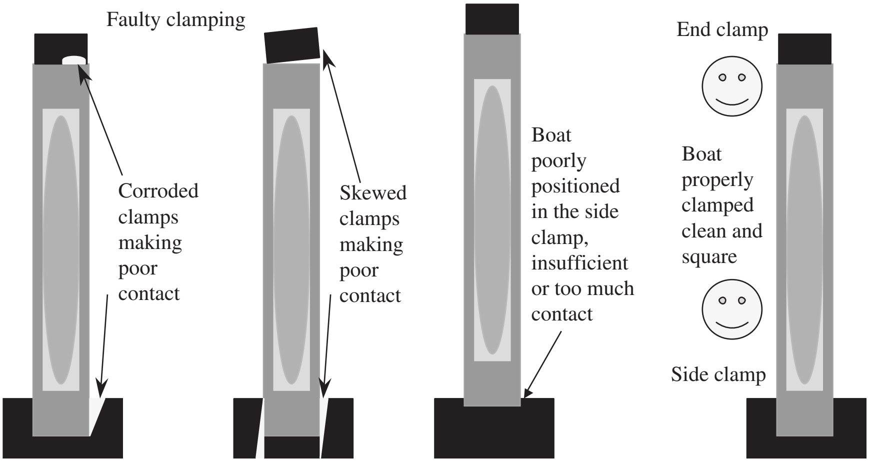


Figure 16.12 A schematic showing the possible mechanical faults that can cause heating and boat lifetime problems.

Allowing for a collection efficiency of 50%, this could require approximately 7.0 kg of aluminum per boat. It would be quite a slow process to heat the whole quantity of aluminum up from the start of the process. The technique adopted is to heat up a boat and to feed the aluminum gradually into the boat for evaporation. There are various methods of feeding material. Common ones include vibrating powders or pellets into a crucible or rod feeding through a water-cooled crucible into a molten pool from underneath. The one that has been adopted for aluminum is a wire feed where a drum of aluminum wire is gradually uncoiled and pushed into the molten pool on the surface of the boat.

The control of this technique has been improved over time. Initially, all the drums of wire were located along the same shaft, and thus if the rate of wire feed was increased for one boat, it was increased for the others too.

Figure 16.13 A schematic showing the indentations that may be caused by knurled drive wheels leading to aluminum pool fluctuations.

The first step forward was to use slipping electromagnetic clutches on each drum feed so that they could be independently controlled. The electromagnetic clutches were controlled by a series of pulses, and by varying the duration of the pulse, the rate of feed could be controlled. This system works well up to winding speeds of around 800 m/min, above which the speed of response of the clutches was a limiting factor. The slow nature of the response could cause the feed to oscillate between slightly too fast and slightly too slow. This caused the molten pool size to increase and decrease slightly with a subsequent increase in the rate of spitting from the wetting and de-wetting of the boat surface around the perimeter of the pool (Fig. 16.13).

The latest change has been to use a stepper motor drive to each of the wire feeds that enables a much higher precision and faster response to be achieved [10]. The stepper motors have a set of windings that receive a series of high-voltage pulses that cause the shaft to rotate by a fixed angular amount per pulse. The stepper motors have a high torque output and high precision so that given a signal the shaft will be rotated a fixed amount very quickly without any need for any feedback to check the position. The high voltage signal is also unaffected by electromagnetic interference and so the quality of the control is good too. Typically, the stepper motors have 400 pulses per revolution of the shaft and so an angular motion of less than 1° per pulse.

It is possible to achieve a speed control to the wire feed of ±0.02%. This precision control ensures that the pool size can be kept constant, thus minimizing spitting.

16.3 Wire

The wire used for feeding can vary in composition, diameter, and hardness [7]. There is a trade-off to all of these features. The wire needs to be thick to have a good volume to surface area ratio. All aluminum is easily oxidized in atmosphere, and so to minimize the amount of oxide, it is preferable to maximize the volume to surface ratio. The limit to this is that the wire has to be flexible enough to be curved down to the boats. If the wire is thick, it needs to have been softened more to enable it to be bent round and to enter the boat easily without causing too much erosion. The older the wire, the greater the thickness of the oxide, and so more oxide crud will build up on the molten pool leading to more spitting. The oxide

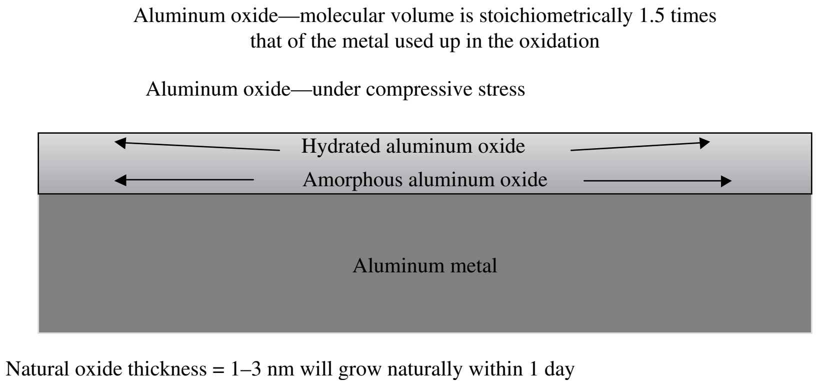


Figure 16.14 A schematic of the oxidation of aluminum.

that forms on the aluminum, as shown schematically in Fig. 16.14, is of higher density than the metal (metal ~ 2.7 g/cm^3, aluminum oxide ~ 4 g/cm^3) but to accommodate the oxygen atoms has to take up a larger volume and so the oxide is in compression which can help reduce the rate of further oxygen diffusion and oxidation of the remaining aluminum. This means that the initial oxide forms very quickly, but the oxidation rate will decrease with increase in oxide thickness. Thus, it is preferable to use freshly made or at least polished and cleaned wire to help minimize the surface oxide layer thickness and so reduce the crud produced on the molten pool and so reduce spitting.

The higher purity grades of aluminum will produce less crud in the molten pool that can be a source of spitting (see section below). The higher the purity of the wire, the greater the manufacturing cost. This is because there needs to be additional processing to soften the wire after drawing to the final diameter that will result in a higher cost [1]. The higher purity can also give a better boat life. These costs need to be balanced against the quality of the product required, the amount of spitting and hence pinholes that are acceptable, and also against the boat life that can be achieved.

Another aspect of choosing the wire diameter relates to the coating thickness required and the wire feed rate available. Figure 16.15 shows a graph of the feed rates required to deliver different coating rates for some different wire diameters.

Aluminum wire used for evaporation is usually 99% pure or better. The code used for specifying aluminum is usually four digits long. The first digit generally is a “1” and specifies the 99% purity, the second digit is used when there is specific control of one particular impurity, and the final two digits are the same as the two digits to the right of the decimal point indicating the minimum aluminum content; that is, 1199 would indicate a 99.99% pure aluminum wire (Table 16.1).

The wire can be supplied in different states of hardness. If the wire is fully annealed or soft tempered, it is graded “O” and if it is fully hardened by strain hardening to 75%, it is graded H18. In between these two extremes are quarter

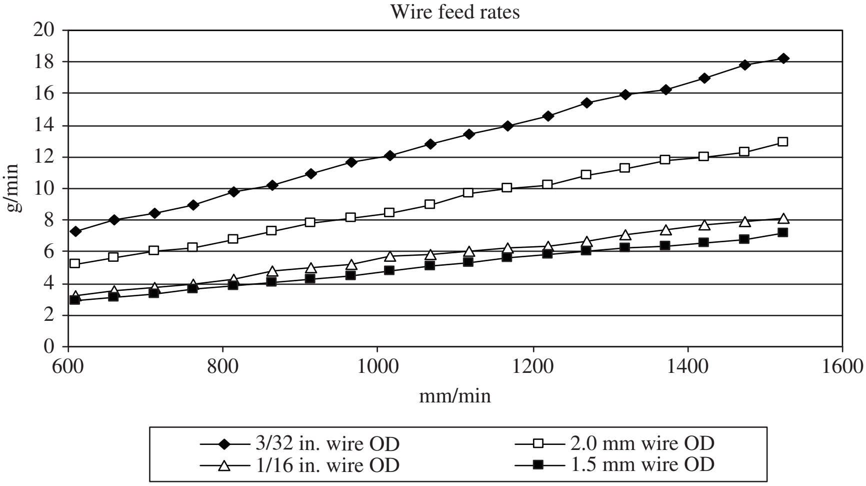


Figure 16.15 Graph of wire feed rates for different diameter wires to deliver different coating rates. Reprinted from Mount EM, III, editor. Metallizing technical reference. 3rd ed. Fort Mill, South Carolina: Association of Industrial Metallizers, Coaters and Laminators (AIMCAL); 2001, with permission.

Table 16.1 A Typical Table Showing Aluminum Purity and Code Numbers and the Wire Temper and Codes

Alloy/Impurity	**1100**	**1350**	**1188**	**1199**
Silicon (Si)	0.95 Si + Fe	0.1	0.06	0.006
Iron (Fe)	0.05–0.20	0.4	0.06	0.006
Copper (Cu)	0.05	0.05	0.005	0.006
Manganese (Mn)		0.01	0.01	0.002
Magnesium (Mg)			0.01	0.006
Chromium (Cr)		0.01		
Zinc (Zn)	0.10	0.05	0.02	0.006
Titanium (Ti)			0.01	0.002
Others	0.15	0.1	0.01	0.003
Aluminum (Al)	99.00	99.5	99.88	99.99

Alloy 1100 = first digit means minimum 99% Al; second digit refers to any special content control; third and fourth digits refer to the % purity of Al following the decimal point.

Wire Temper Designation

O	Soft temper—annealed after working to final dimension
H12	Strain hardened to a point 1/4 tensile strength between “O” and H18
H14	Strain hardened to a point 1/2 tensile strength between “O” and H18
H16	Strain hardened to a point 3/4 tensile strength between “O” and H18
H18	Hard temper—fully hard—strain hardening ~75%

hard H12, half hard H14, and three-quarter hard H16. The temper determines how easily the wire can be bent from the drum of wire round to the boat. As the wire approaches the boat, it will be heated and may sag and so some temper may be advantageous, particularly if the distance between guide and boat is large.

16.4 Spitting and Pinholes

The aim is to have the aluminum evaporating at a consistent rate. Unfortunately, there are several factors that can prevent this happening. The aluminum quality is one of the factors. Ideally, the aluminum would be 100% pure and the surface would be free from oxide. The reality is that neither is true. The choice of wire can affect the process. A larger diameter of wire will have a better volume to surface ratio but will be stiffer and more difficult to handle. This higher stiffness may cause more severe erosion to the boat leading to earlier boat failure. A finer diameter wire will be more easily handled, but there will be a much higher surface area and so the volume to surface area will be lower. The surface area is a factor because the surface of the aluminum will oxidize and the boat will not evaporate the oxide. This oxide will tend to collect around the edges of the molten pool. This mixture of metal and oxide can be moved about as the pool size is changed, and the wetting characteristics will be different from pure, clean metal. This can mean that some material gets flash evaporated off the surface. This very rapid flash evaporation can carry with it some of the debris from the pool edges, and this will be incorporated in the thin film coating. On occasions, some of this debris will be incandescent. This debris can be a cause of coating defects. The incandescent material may be energetic enough to burn a hole through the web. Debris with less energy may simply be a cause of pinholes particularly because of poor adhesion where the debris can be moved away during winding leaving behind pinholes of uncoated web. The oxide is likely to be very hard and can also induce scratches into the freshly coated surface (Fig. 16.16).

If the pool is expanding in size and the boat is hot enough, the pool may not wet the new surface of the boat that it covers. The aluminum will bead and may spit causing quite large spots of aluminum to be deposited [10]. An analogy would be adding water to a very hot surface where the water may be seen to bead up and bounce around on the surface and spit without wetting the surface. As the surface cools, the water will then wet out the surface and the spitting will stop.

Pinholes are seen by placing the coated material over a light box as described in Chapter 8 (Section 8.2). Unless the pinholes are examined in detail using optical or electron microscopy and possibly using one of the chemical surface analytical tools, it is impossible to determine the source of the pinhole. The largest source of pinholes is from residual debris being present on the substrate surface before coating and being moved afterward. The other sources of pinholes such as source spitting, volatilization of oligomers, or pickoff tend to be a minor cause of pinholes in comparison.

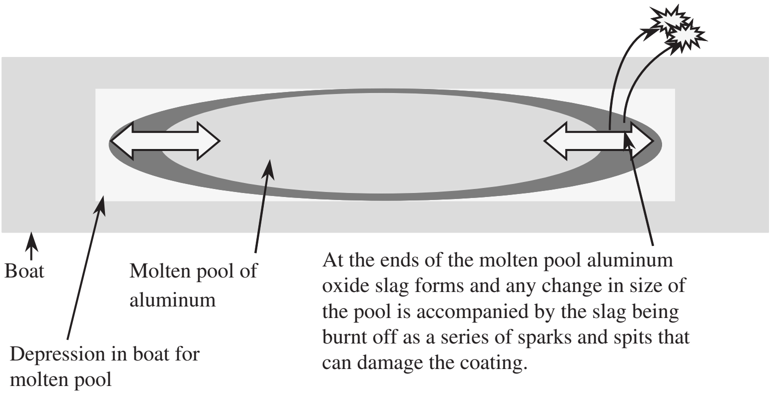


Figure 16.16 A schematic of material spitting from a resistance-heated boat evaporation source.

16.5 Thin Film Measurement

There are two main techniques that are used for measuring the performance of the deposited thin film coating. One measures the optical transmittance in the visible, usually expressed as the optical density. The other measurement is of the electrical conductivity or resistivity of the thin film coating.

Both these methods have limitations as described in sections 16.5.1, 16.5.2 and 16.5.3 and so other methods have been used to more accurately determine the true coating thickness. This includes scanning transmission electron microscopy (STEM) where a small sample of the coated film is mounted in a polymer block and a thin sliver is shaved off by a microtome and this sample is then examined. The STEM micrographs can be measured directly against the STEM system calibration to give the coating thickness. Other techniques can be used, such as weighing a coated sample and then etching off the aluminum and then reweighing the sample and calculating the thickness of a uniform coating as a result of the weight difference from the aluminum removed by the etching. This assumes a fully dense coating, which we know the coating cannot be, and so an educated guess needs to be used about the coating density. Anything less than 100% density of the coating results in an increase in the coating thickness for any given weight of aluminum. This means that this technique will always have some uncertainty about the thickness results and so larger error bars than for the STEM measurements.

16.5.1 Optical Density

The opacity of a coating is a measure of light that is incident on the coating divided by the amount of light that is transmitted [13–16]. In metallizing, this is more usually expressed as the optical density (OD) of the coating where OD is opacity expressed as a logarithm to base 10.

$$\text{Opacity} = \frac{\text{Incident light}}{\text{Transmitted light}} \quad \text{Transmittance} = \frac{\text{Transmitted light}}{\text{Incident light}}$$

$$\text{Opacity} = \frac{1}{T}$$

$$\text{Optical density} = log_{10}\text{opacity} = log_{10}\frac{1}{T}$$

Typically, operators will have a conversion table from where they measure the OD but will quote the coating thickness off the chart. As the metal is opaque and the aluminum oxide is transparent, they contribute different amounts to the light blocking with the metal being the dominant factor and the alumina contributing very little. This means that the thickness taken from the conversion tables may be for the equivalent metal thickness rather than the true coating thickness that would include both metal and oxide layer thickness.

16.5.2 Resistance Monitoring

It is possible to measure the resistance or conductivity of a thin film coating by using two front surface contacting rolls in the winding system and taking measurements through these rolls. In this case, there may be problems as the rolls have to be isolated to ensure that the measurements are purely a measurement of the coating conductivity and not via some other leakage path. The second problem is to maintain a low resistivity contact to a roller that by its nature is rotating. This can be done using hard carbon or copper brushes, but these can give resistance problems over time.

The more common and elegant solution is to use a noncontact measurement technique [17–20]. This is done using an eddy current monitor. The construction of this type of monitor can vary, but essentially there is a coil, which is used to generate a high-frequency magnetic field from a radio frequency (RF) supply, placed close to the web. If the thin film coating is conducting, there will be a change in frequency and a loss of signal intensity that can be detected. The changes in frequency and intensity are dependent on the material, thickness, and structure that combine to define the conductivity. There are two ways of arranging the source and detector. One is to have them placed directly opposite each other when the web is in free span. The other is to combine the source and detector within the same body and place this unit close to the metallized side of the web. The transmitter unit does not require the web to be any precise distance away from the source or sensor; it simply has to pass somewhere between them. The single sensor is sensitive to web distance away from the head. Any change of distance will affect both the signal and detector and so it is usual to site this unit at a position where the web is passing around a roller. In order not to affect the signal by the conductivity of the roller, these rolls are made of a nonconducting material such as fiberglass.

The eddy current monitors can be susceptible to changing thermal conditions, and this can cause the signal to vary for material of the same conductivity. To eliminate this source of error, these monitors need to have some inbuilt temperature compensation system.

The eddy current device measures the average conductivity from an area under the monitoring head. The size of the head and the area it takes the signal from can be varied to some extent. It is common to use a series of heads to measure the conductivity of a web. There can be of the order of 25—30 boats on the most popular width metallizers and as many as 56 on the widest machines [21]. The coating quality is required to be as good on larger machines as it is on smaller machines; this has led to the use of one head directly in line with each boat. This then allows for the output from each eddy current monitor to be the control signal for the boat that it is in line with.

In exactly the same way that the optical monitor is more sensitive to the opaque metal than to the transparent oxide, the eddy current monitor only measures the electrical performance of the conducting coating and not any insulating coating. So the same problem occurs with the eddy current monitor in that it is sensitive to changes in the metal coating thickness but cannot measure the total coating thickness. So, once again the oxide thickness contribution to the total thickness is ignored and hence conversion tables that ignore the oxide thickness component will give a coating thickness that relates only to the metal thickness.

16.5.3 Errors in OD and Eddy Current Measurements Used for Coating Thickness

There has always been some question about the true thickness of the aluminum coatings deposited. The aluminum coating will oxidize and the aluminum oxide is transparent as opposed to the opaque aluminum metal and so the proportion of oxide will affect the OD measurement. Similarly, the aluminum metal is conducting, but the aluminum oxide is an insulator and so there will also be an effect on the eddy current resistivity measurement. This means that both the online measurement techniques are actually measuring only the metal component of the coating thickness. As the oxidation of the metal continues throughout the lifetime of the coating, the coating thickness if measured by either of these two methods will also change with time. As the rate of oxidation can be affected by the nucleation and growth of the coating and hence the coating density and surface roughness, it is no surprise that using what appears to be an identical process on two different vacuum coating systems can produce coatings that are measured as having two different thickness coatings as the oxide thickness may be different.

It is easy to think of this oxide layer as being very thin, such as 1—3 nm, and to ignore it, but as the aluminum coating thickness is also thin, the oxide can represent a significant proportion of the total coating thickness. It was reported that measuring the OD in-line during metallization and immediately after venting the system, there could be a reduction of OD of more than 40% showing a significant amount of oxidation [22]. This high change in OD is because the coating is so thin. The oxide thickness that grows is similar irrespective of how thick the metal coating is, and so for a coating of 10 nm or 10 μm, the oxide thickness after a day would be expected to be of the order of 1−3 nm on the surface of either coating. There may be small variations due to differences in crystal growth and surface roughness, but essentially the oxide growth will be similar. What was not considered at the time, but more recent work [23,24] has proven, is that the oxidation of the aluminum layer is on both sides of the aluminum metal as shown in the micrograph in Fig. 16.17. This micrograph clearly shows that the expected 1−3 nm surface oxidation is present at both the metal/polymer interface and the metal/air surface. This micrograph shows the total oxide thickness to be close to 7 nm range with a 29 nm thick aluminum coating giving an oxide thickness of the order of 20% of the total thickness. The implication of this is that to achieve a particular OD for a customer, a much thicker coating needs to be applied in the metallizer to allow for the metal oxidizing over the time before the customer receives the coating web and measures it.

The longer the delay between vacuum metallizing and the final use, the greater the difference in the measured OD during metallizing and the OD that will be present in the final product. Also, the higher the storage temperature and humidity, the greater the oxidation rate expected. As OD is used in the light barrier calculations to determine the shelf life of products that can undergo photodegradation, it can be important to know the rate of oxidation to be able to predict the final performance and prevent customer returns.

This detailed work [23,24] examined coatings after aging and produced new plots of the OD versus coating thickness for the metal and for the metal with oxide layer included, as shown in Fig. 16.18.

It is encouraging that the metal component of the thickness compares well to the theoretical optical model giving a confidence in the quality of the measurements.

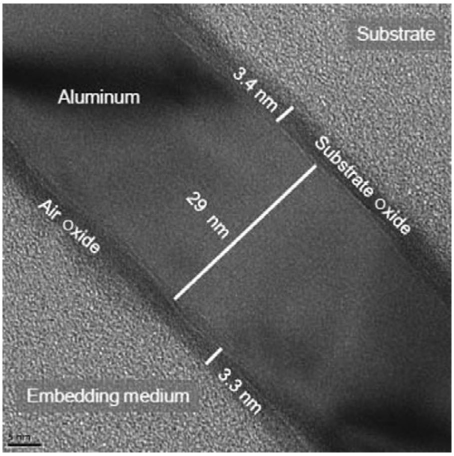


Figure 16.17 Scanning transmission electron micrograph of an aluminum metallized coated polymer film showing oxide growth on both sides of the metal coating [23]. TEM courtesy of Don McClure, 3M Corporate Research Laboratory.

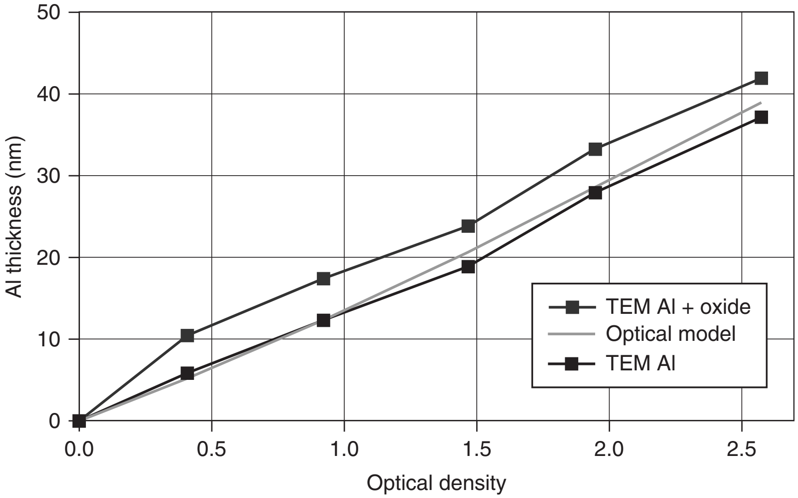


Figure 16.18 Graph of aluminum coating thickness versus optical density showing the theoretical performance from an optical model, the metal thickness, and the metal thickness complete with oxide layers as measured using the scanning transmission electron microscope [24].

The graph also shows the oxide thickness to be similar for any thickness of aluminum coating.

The relationship between the OD and resistivity was also plotted, and it was shown that the results can be fitted to the same curve irrespective of aging time, which, as both are affected by the loss of aluminum, might have been expected, and this is shown in Fig. 16.19. The regression of the data results in a polynomial curve fit where:

$$Y = 2.4425(X)^{-0.6535} \quad R^2 = 0.9979$$

with OD = Y and sheet resistance = X.

Using a combination of the above two graphs, it is now possible to plot both the OD and the sheet resistance against the as-measured coating thickness onto polymer films. Using the evidence of the oxide growth thickness, it is also possible to estimate the excess thickness of aluminum that needs to be deposited in order to deliver an optical or electrical resistance performance that can meet customer requirements after it may have been in storage or transit for some weeks.

16.6 Power Supplies and Control

The power supplies to the boats are controlled initially by setting either the voltage or power to a particular value and allowing the current to each boat to vary to suit

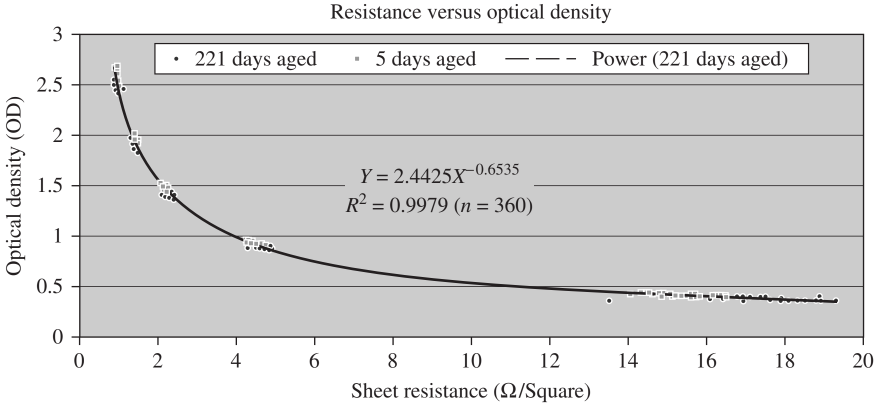


Figure 16.19 Plot of optical density versus sheet resistance for metallized sample aged 5 and 221 days [23]. Graph courtesy of GVE Ltd.

the boat resistance. This has the effect that if the molten pool increases in size, the resistance will fall and the current will increase raising the temperature and increasing the evaporation rate. This stabilizes the growth of the molten pool. Similarly, if the molten pool reduces in size, the resistance will increase and the current drawn falls again bringing the evaporation pool back to equilibrium.

The eddy current resistance monitors or light transmission monitors, which can be converted to optical density, can be used as a supply measurement converted to a thickness that can then be used to adjust the wire feed rate that in turn controls the pool size [19] (Fig. 16.20). The power supply will either react to the changing boat resistance or the power supply can be programmed to also take the information from the resistance monitors so that at the same time the wire feed rate is changed, the current is similarly changed so that the time to respond to any change in the volume of aluminum being fed into the molten pool is minimized.

The power supplies have thyristor control, but a feature of the power supplies has been that the power is pulsed even though the thermal mass of the resistance-heated boat appears to be constant. It has been found that this pulsing can stress the boats and reduce the lifetime and so modern supplies have been developed to reduce this pulsing effect [25].

16.7 Coating Uniformity

Each of the evaporation boats is considered to be a point source of deposition material. The deposition profile from a point source is based on a cosine law, and this will become narrower as the rate increases [26–29].

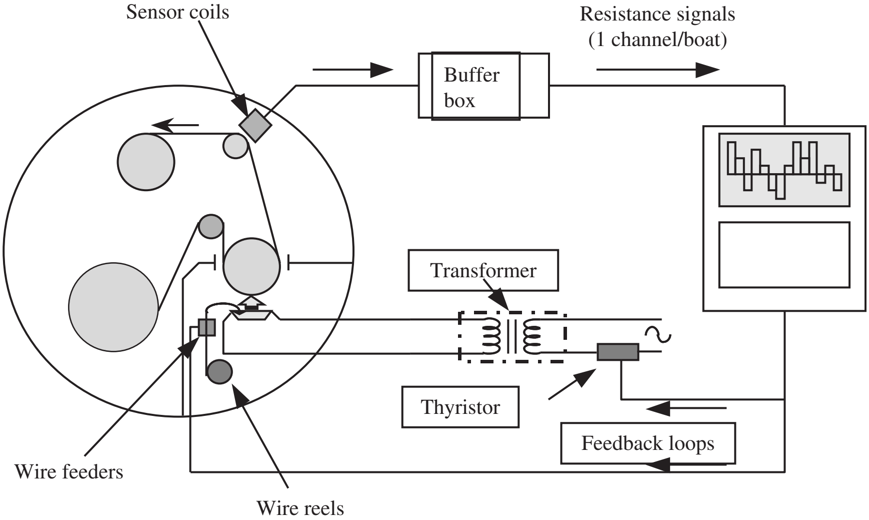


Figure 16.20 A schematic of the automated control loop for thermal evaporation.

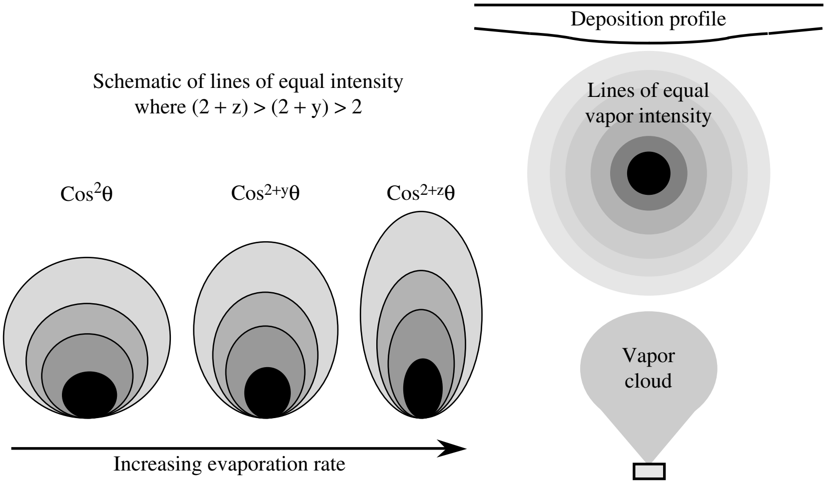


Figure 16.21 A series of diagrams showing how the deposition profile changes with increasing deposition rate.

The profile of the deposition flux will depend not only on the deposition rate but also on the shape of the molten pool. Thus, a pool that only partially fills the boat will have a different profile to the one that is run where the boat is fuller (Fig. 16.21). Each of these individual profiles will overlap the adjacent source profiles and so the final coating profile will be the summation of all the profiles.

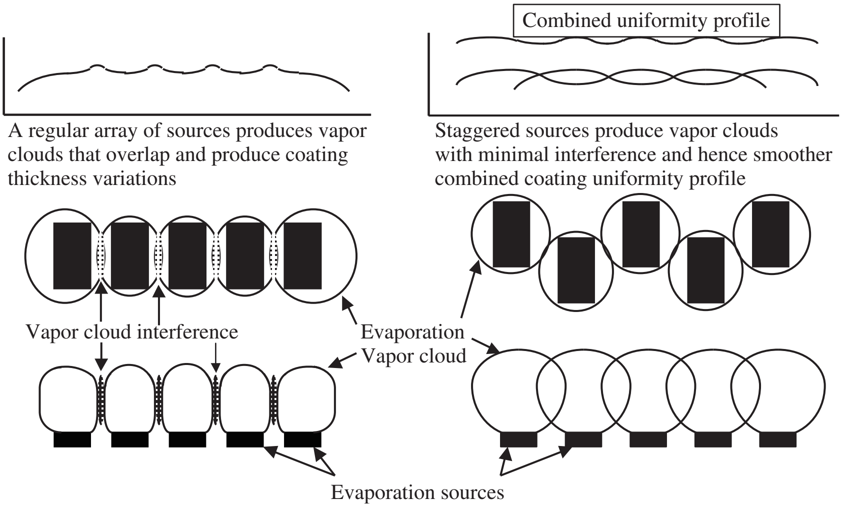


Figure 16.22 A schematic showing the variation in deposition profile for a single series of deposition boats and the improvement available when two sets are used in combination.

There is a limit to how near evaporation sources can be to each other, and an improved profile has been obtained by staggering the sources as shown in Fig. 16.22.

It has also been shown that within the boat the molten pool forms an asymmetric elongated area as the evaporation source rather than a symmetric circular point source. Hence, having the boats skewed to the machine direction can take advantage of this asymmetry, and this has also been claimed to aid smoothing out the coating variations.

To further improve the deposition uniformity, a profile shield can be used to smooth out the high spots in the deposition profile (Fig. 16.23). This will reduce the collection efficiency of the material.

One difficulty with controlling uniformity is when changing conditions. As the power changes, the vapor cloud shape changes, and so the uniformity will change as the amount of overlap of adjacent clouds varies. The same variation will occur when using shaped profile shields. The shape that has been optimized for one particular power setting and wire feed, which fixes the deposition rate, will have the wrong profile for other power settings.

The other thing that can change with deposition rate is the collection efficiency. As the power increases and the flux profile narrows, more material will be collected on the substrate, increasing the material collection efficiency (Fig. 16.24). However, this may well be at the cost of reduced uniformity. As the boat separation is limited because of the problems of electrical interaction, there can be only limited overlap of the deposition flux, and so at higher powers the uniformity will get worse.

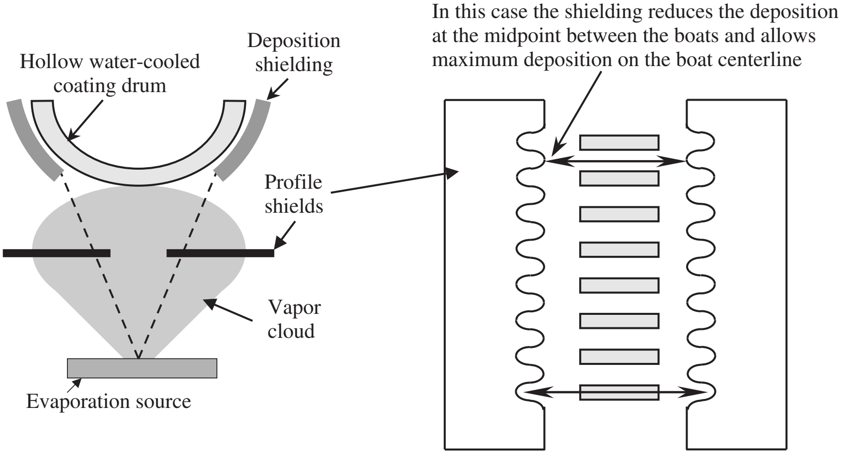


Figure 16.23 A schematic of the use of profile shielding to improve deposition uniformity.

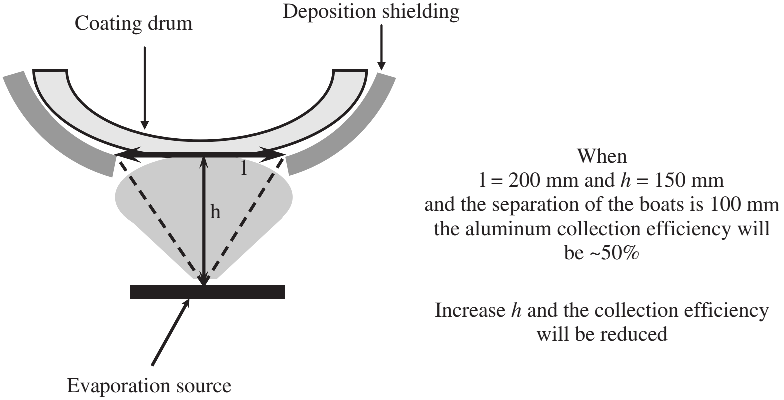


Figure 16.24 A schematic describing the collection efficiency.

The collection efficiency is also a function of power, positioning of the shields, and source to substrate distance. To improve the deposition efficiency, it would be required to move the hot evaporation boats closer to the deposition drum. This usually causes a problem with overheating the substrate. This then leaves the alternative of moving the source farther away combined with a larger deposition drum. This makes use of the same angle of collection as would be obtained with a source close to the deposition drum. The advantage of using more distant sources is that the heat load can be spread over more of the deposition drum for the same deposition rate. A disadvantage of having a large source to substrate distance is that unless the vacuum is maintained at a low pressure, an increased proportion of the

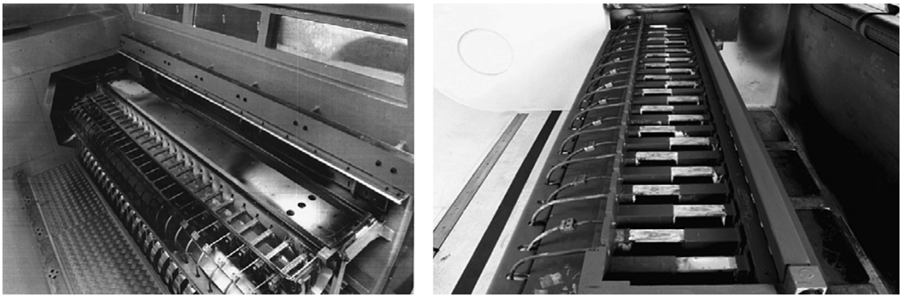


Figure 16.25 Photographs of systems showing the basic arrangement for a single set of boats on the left and a staggered double set on the right. Photograph courtesy of Bobst-General Vacuum Equipment.

depositing material may be scattered and either lost to the shields or hitting the substrate at a low angle and probably having poor adhesion. Spreading the deposition shields too wide also allows the depositing material to meet the substrate at a low angle such that the growth is porous or rough and so the specular reflection is reduced. Thus, there will always be some of the collection efficiency lost to keep the reflection high.

The photograph on the left of Fig. 16.25 shows the typical arrangement for a single row of evaporation boats with the wire feed from below through guide tubes. In this case, the boats are close together with no skew angle or staggered second row.

The wire is often fed through a tube, and the curve of the tube helps to bend the wire down toward the boats. To stop the tubes becoming blocked by the evaporated vapor condensing in the tube, they are sited some distance away and in an area of low deposition rate. This does mean that it may be hard to direct the wire into the exact center of the molten pool at a precise distance from one end. This can be one disadvantage of the use of a staggered row of boats. Half of the boats will be farther away from the wire feed guides and so the precision of wire feed can be less good than for the closer boats (Figs. 16.26 and 16.27).

16.8 Coating Strategy

When coating, it is important to have a strategy for what to do if there is a boat failure. Boat failures are frequent enough that sooner or later one will occur during a deposition run.

There are differing strategies for managing the boats. Some operators will use every boat through to failure. Others will replace the boats after a set number of hours without waiting for them to fail. The latter strategy will give a more consistent product, but the costs will be higher.

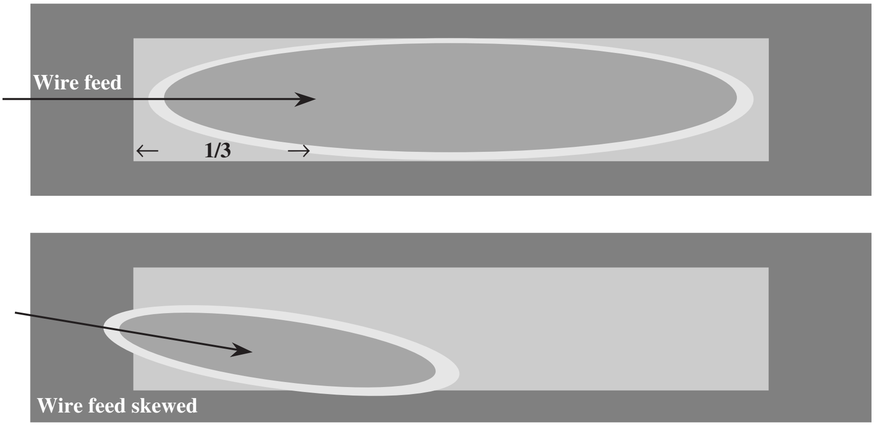


Figure 16.26 A schematic showing the ideal position of the wire feed.

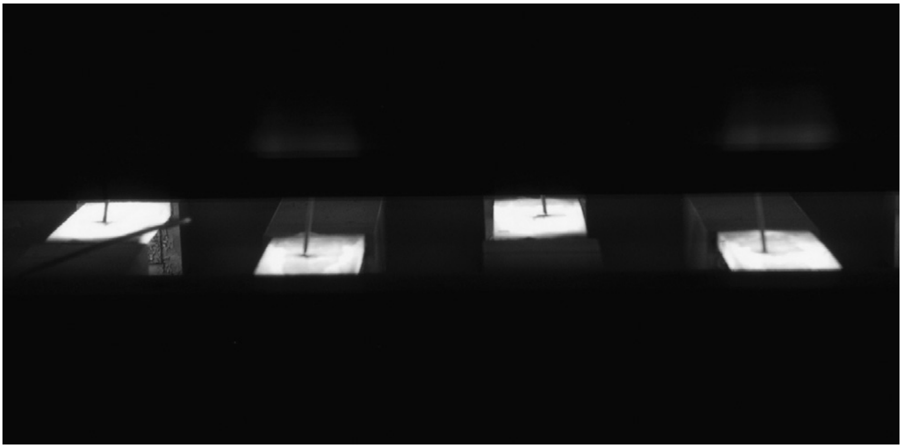


Figure 16.27 Photograph of some wire-fed resistance-heated evaporation boats in action. *Note*: The wire feed is not perfectly in the center of all boats, but the molten pool fills the boat acceptably. Photograph courtesy of Bobst-General Vacuum Equipment.

If there is a boat failure during the deposition cycle, it is possible to increase the evaporation rate from the boats on either side of the failed boat to compensate for the dip in coating thickness opposite the failed boat. Even with this compensation there will still be a dip in the coating profile, but for many applications there will be sufficient deposition to make some saleable product. The boats next to the ones with increased power may need to be reduced in power slightly to compensate for the two boats operating with the higher power.

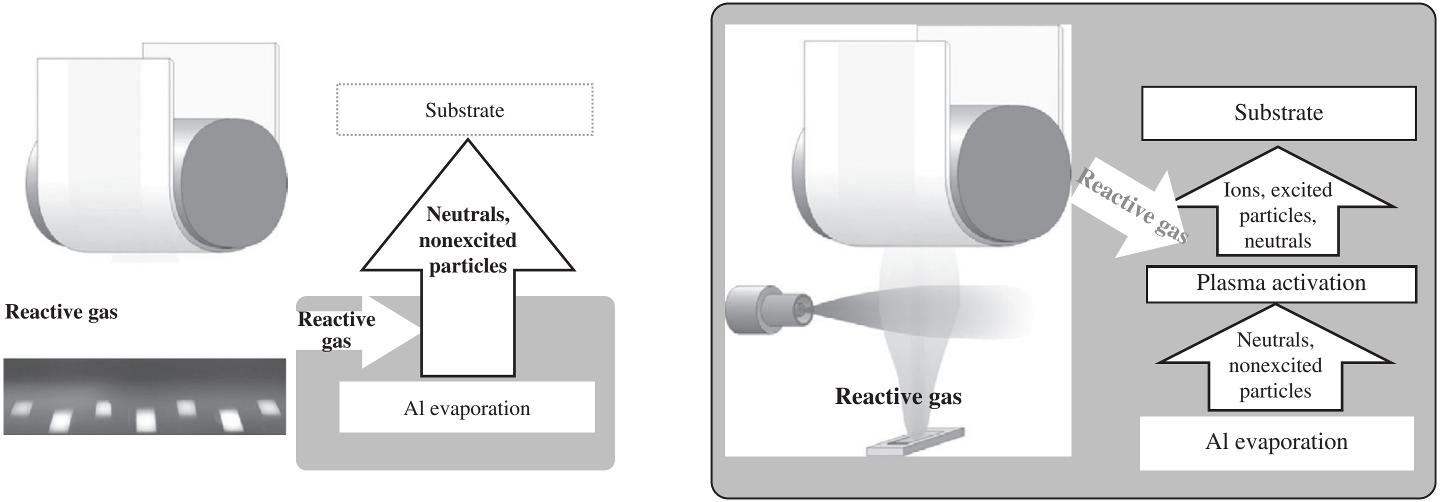
When replacing boats, it is important to use boats from the same batch as boats from different batches are likely to have slightly different resistances and will run differently. If boats of different resistances are used together, there are likely to be occasions when, as the boats age, the available power range is reached, and thus the evaporation rate will become limited and no longer matched to the output of the others.

16.9 Reactive Thermal Evaporation of Aluminum Oxide

Aluminum oxide has for many years been on the list as a suitable transparent barrier material, but the limiting factor has always been the cost of depositing a good barrier layer [30−32]. Depositing the coating was not a problem as there was suitable technology available, but this tended to be more expensive than resistance-heated evaporation that made the cost of deposition prohibitive to anything except niche markets. Transparent barrier coatings are often based on transparent ceramic materials with high melting points, and typically these would have been deposited using electron beam gun sources. The deposition rate of the oxides also tended to be slower than for the metal and so the lower process speed coupled to a higher capital cost made the final film cost significantly higher. Over the last 20 years or so, the costs have reduced, closing the gap from more than ten times higher to around two to three times higher than metallized film, but this still did not compete well enough to generate the expected market growth that had been predicted.

One option that has been developed is that of oxidizing the coating in a standard metallizer. One company took the idea of using a standard metallizer and finding a method of oxidizing the aluminum deposited [33−36]. Although this may sound easy as the aluminum is receptive to oxidation, it can be difficult to control well. The oxygen can oxidize not only the growing coating but also the molten aluminum pool, which can slow down the rate of evaporation [37]. There is also a high induced magnetic field because of the high current passing through the evaporation boats, and an unwanted plasma can form causing problems with instrument interference. Once process problems such as this are suitably controlled, the process can run and produce transparent barrier coatings at only a slight premium over that of aluminum metal coatings. Once one company found this simple approach could be made to work, others followed with their own variations [38−41]. One that has been documented and included in the references uses an additional plasma that increases not only the process reactivity but also the coating adhesion and densifies the depositing coating. The two versions are shown in the schematics in Fig. 16.28. This becomes a trade-off as the plasma sources and power supply become a significant capital cost and increased running cost and so the product cost will be higher than that of the more simple systems that do not have the additional plasma (Figs. 16.29 and 16.30).

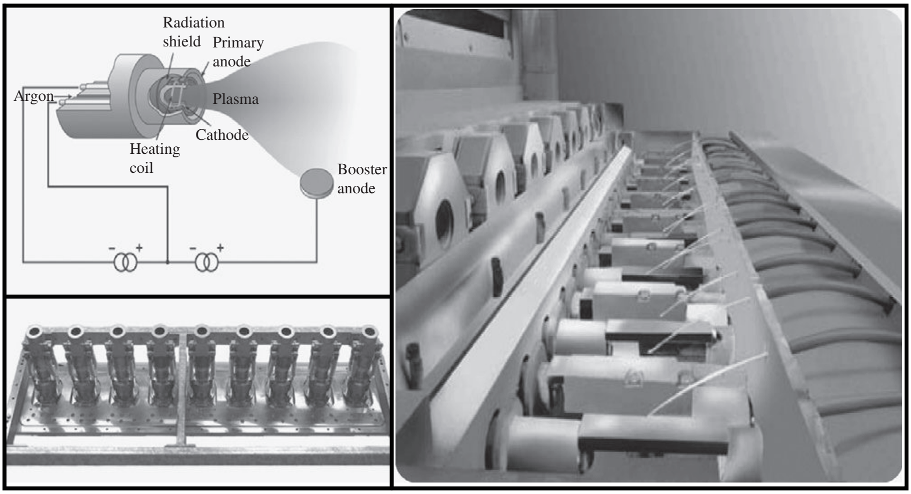
The coatings deposited with the plasma enhancement are expected to have improved barrier properties as the densification reduces the size and density of



Evaporation of Al + oxygen inlet = AlOx on substrate

New advanced process developed by and up scaled with the Fraunhofer FEP in Dresden

Figure 16.28 Schematics of the addition of oxygen to the aluminum evaporation process to produce aluminum oxide. On the left-hand side without any additional plasma and on the right-hand side with an activation plasma. Schematics courtesy of Applied Materials.



On left-hand side is a detailed view of the hollow cathode plasma unit with the schematic on the right-hand side showing how it is positioned relative to the resistance-heated evaporation sources. AlOx process proven for web speed up to 8 m/s and coating length 50,000 m

Figure 16.29 Schematics on the top left-hand side showing a detailed view of the hollow cathode plasma unit with below an assembly of nine sources ready to be installed in a metallizer. The right-hand side photograph showing how the cathodes are positioned relative to the resistance-heated evaporation sources for an AlO*x* process proven for web speeds up to 8 m/s and coating length 50,000 m in a TopMet™ system. The right-hand side photograph courtesy of Applied Materials.

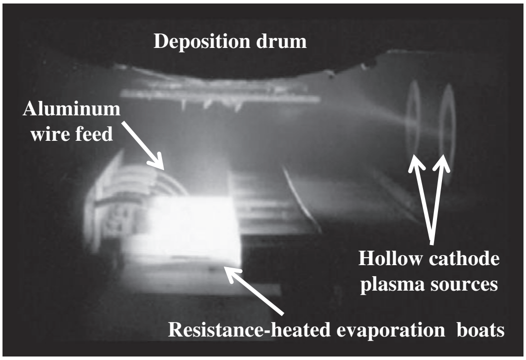
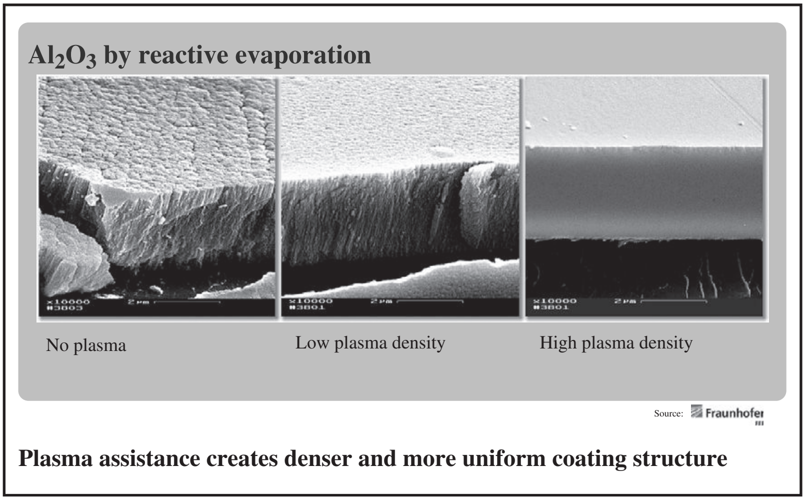


Figure 16.30 Photograph of a deposition process in progress showing the plasma-enhanced deposition system. Photograph courtesy of Fraunhofer FEP, Dresden as presented at AIMCAL conference [40].

some types of coating defects [42]. This improvement also means the increased process costs have to be balanced against the improved barrier performance. As with all plasma densification processes, this needs to be done with care to prevent an increase in coating stress that would result in the film curling during downstream processing. An example of the improvement in coating density is shown in



Plasma assistance creates denser and more uniform coating structure

Figure 16.31 Micrographs showing the change in coating density with the application of the plasma. Images courtesy of Applied Materials and micrographs courtesy of Fraunhofer FEP, Dresden.

Fig. 16.31 where the coating deposited without any plasma can be seen to have a rougher surface topography with cracks, and from the side the cracks run down the columnar growth. In comparison, the micrograph on the right-hand side shows the coating to be denser and without the structural defects that reduce the barrier performance. Note that these coatings are approximately 2.5 μm thick and so are considerably thicker than those that would be used for barrier coatings, but they are used here to highlight the ability of the plasma-enhanced evaporation process to densify the coating and reduce the structural defects.

References

[1] d'Ouville T, et al. The effects of boat and wire parameters on boat life and coating in vacuum metallization of an OPP web. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 125−31.

[2] Ruisinger B, et al. Evaporation boats—investigations on the electrical properties. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 84−7.

[3] Ruisinger B, Mossner B. Evaporation boats—properties, requirements, handling and future requirements. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 335−8.

[4] Fletcher DA. Evaporation boats—latest developments improve metallizing performance and economics. In: Proc. 31st annual technical conference of the Society of Vacuum Coaters; 1988. p. 267−73.

[5] Zoeliner H. Resistance heated ceramic evaporation boats. In: Proc. 27th annual technical conference of the Society of Vacuum Coaters; 1984. p. 1−4.

[6] Mitchell R, et al. Influencing barrier properties by optimising aluminium wire and evaporation boats. In: Proc. 10th international conference on vacuum web coating; 1996. p. 134−45.

[7] Mount EM, III editor. Metallizing technical reference. 3rd ed. Fort Mill, SC: Association of Industrial Metallizers, Coaters and Laminators (AIMCAL); 2001.

[8] Gibson CD, Kohnken KH. Intermetallic evaporator boats. In: Proc. 3rd international conference on vacuum web coating; 1989. p. 121−30.

[9] Archibald P, Parent E. Source evaporant systems for thermal evaporation. Solid State Technol 1976;19:32−40.

[10] Baxter I. Advance resistance deposition technology for productive roll coating. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 197−204.

[11] Evaporation boats—key to performance. Sales literature evaporation boats/e-05.02-1, www.wacker.com.

[12] Nuernberger M. Changes to an IMC evaporator during aluminium evaporation. In: Proc. AIMCAL fall technical conference and 21st international conference on vacuum web coating; 2007.

[13] Gale MT, et al. A simple optical thin film deposition monitor using LEDs and fibre optics. J Vac Sci Tech 1982;20(1):16 −20.

[14] Maissel LI. Electrical properties of metallic thin films. In: Maissel LI, Glang R, editors. Handbook of thin film technology. New York: McGraw-Hill; 1983, 0 07 039742 2 [Chapter 13].

[15] US 3935458 patent. Method for monitoring the surface resistivity of metallized film. Peters DW; 1976.

[16] Casey F, Broomfield AA. An optical profile monitor with zoom capabilities for web coaters. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 383−6.

[17] Zelisse JK. Accurate modelling of eddy current sensors for square resistance and thickness measurements. In: Proc. 5th international conference on vacuum web coating; 1991. p. 135−43.

[18] Duesbury P. A heuristic approach to temperature compensation in non-contact resistance meters for vacuum roll coaters. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 232−5.

[19] Brandenberg J, et al. Experiences of operating a closed-loop feedback system on a vacuum web coater. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 94−9.

[20] Scarr JM, Zelisse JK. A new topology for thickness monitoring eddy current sensors. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 228−31.

[21] www.appliedmaterials.com/products/assets/rolltoroll/topmet_brochure.pdf TopMet™ Brochure 2009. p. 4.

[22] Walters GJ. Microwave susceptors: aluminium versus alloy coatings, optical density versus direct resistivity measurements. In: Proc. 33rd annual technical conference of the Society of Vacuum Coaters; 1990. p. 153−56.

[23] Copeland NJ, Astbury R. Evaporated aluminium on polyester: optical, electrical, and barrier properties as a function of thickness and time (Part I). In: Proc. AIMCAL annual conference and 24th international conference on vacuum web coating; 2010.

[24] McClure DM, Copeland NJ. Evaporated aluminum on polyester: optical and electrical properties as a function of thickness (Part II). In: Proc. AIMCAL annual conference and 24th international conference on vacuum web coating; 2010.

[25] Loebig G, et al. A new advanced power supply for resistance heated evaporation boats, used in standard roll coaters. In: Proc. 43rd annual technical conference of the Society of Vacuum Coaters; 2000. p. 401−3.

[26] Meinel J, et al. Dynamics and efficiency aspects in the evaporator zone of vacuum metallizers. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 191−6.

[27] Pasqui A, et al. High rate deposition on new high speed aluminium roll coaters. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 185−9.

[28] Swisher RL. Distribution patterns of coatings from small sources onto webs moving over drums. In: Proc. 7th international conference on vacuum web coating; 1993. p. 64−9.

[29] Casey F, Ellis GH. Deposition uniformity and visual appearance in high speed web coaters. In: Proc. 10th international conference on vacuum web coating; 1996. p. 123−32.

[30] Felts J. Transparent gas barrier technologies. In: Proc. 33rd annual technical conference of the Society of Vacuum Coaters; 1990. p. 184−93.

[31] Krug TG. Transparent barriers for food packaging. In: Proc. 33rd annual technical conference of the Society of Vacuum Coaters; 1990. p. 163−9.

[32] Chahroudi D. Transparent glass barrier coatings for flexible film packaging. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 130−4.

[33] Kelly RSA. Development of clear barrier films in Europe. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 312−7.

[34] Kelly RSA. Development of aluminium oxide clear barrier films. In: Proc. 37th annual technical conference of the Society of Vacuum Coaters; 1994. p. 144−9.

[35] Kelly RSA. Transparent barrier coatings for films. In: Proc. AWA conference metallized papers and films—Europe. Paper IX; February 2002.

[36] Web barrier packaging material. European patent application EP0437946 1990.

[37] Kobayashi T, et al. Reactive vacuum vapour deposition of aluminium oxide thin films by an air-to-air metallizer. J Vac Sci Technol A 2006;24(4):939−45.

[38] Schiller S, et al. How to produce Al_2O_3 coatings on plastic films. In: Proc. 7th international conference on vacuum web coating; 1993. p. 194−219.

[39] Schiller S, et al. Al_2O_3 layers on plastic films—ways to get high deposition rates. In: Proc. 8th international conference on vacuum web coating; 1994. p. 173−90.

[40] Schiller N, et al. Innovative clear barrier technology for the packaging industry. In: Proc. AIMCAL technical conference and 22nd international conference on vacuum web coating; 2008.

[41] Gunther S, et al. Innovative transparent barrier for packaging. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 727−9.

[42] Schiller N, et al. Transparent barrier coatings on polymer films. In: Proc. AIMCAL technical conference and 23rd international conference on vacuum web coating; 2009.

17 Radiant-Heated, Induction-Heated, and Other Sources

It is not always possible or convenient to use a resistance-heated boat. Some materials interact with the source boat, others are not suitable for wire feeding. In these cases, alternative methods of heating may be used.

An advantage of using a radiant-heated crucible is that the crucible can be made to be as wide as the web. The outlet nozzle or nozzles can be optimized to maximize the coating uniformity. There is also no reason why the enclosed crucible should not operate with the vapor cloud within the crucible at a higher pressure than the deposition zone pressure. In this way, the deposition flux can be made to jet out of the nozzle, and there is no reason why the deposition direction has to be upward. It can be arranged in any direction. In this way, the deposition zone can be extended around the deposition drum, spreading out the heat load and thus increasing the total deposition that can be achieved in a single pass (Fig. 17.1).

17.1 Radiant-Heated Sources

In this method, the material to be deposited sits in a crucible and the crucible is heated from an adjacent heat source. Typically, this will be a resistance-heated rod. The rod is usually malleable enough to be shaped to conform to the shape of the crucible. This allows extra heating to be applied to the ends of the crucible where the heat losses are greatest, thus compensating for the loss and allowing the whole crucible to be held more easily at a constant temperature.

It is common for the radiant-heated crucibles to be the full width of the web to be coated, and therefore, so long as the temperature is constant, the deposition rate will be uniform across the whole width and the corresponding deposition uniformity will be equally as good [3].

Typically, these sources are referred to as linear or slot sources. The most common use of these sources is for the deposition of zinc for capacitors and then zinc sulfide as a high refractive index transparent material for holograms [4–8].

Work was done to try to use these sources for the deposition of transparent barrier coatings based on silica. The sources used carbon crucibles, and the heating

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00017-9

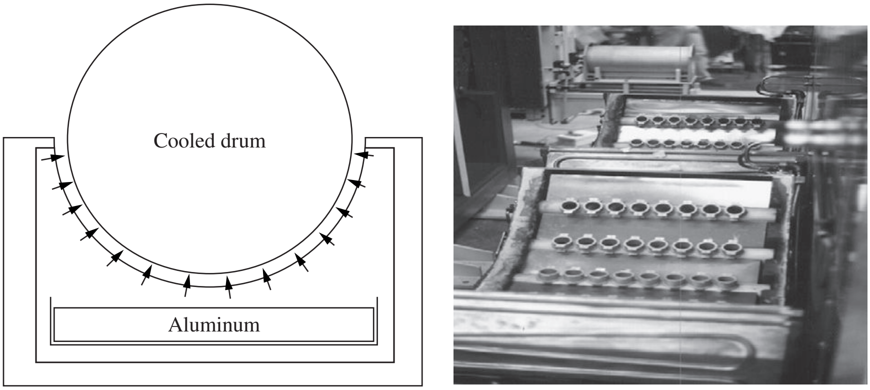


Figure 17.1 A diagram of a distributed evaporation source and a photograph of a pair that were installed for the high-rate deposition of a thick metal coating onto a polymer web [1,2].

and deposition rate were acceptable. However, the problem area for the process was the rate of cooling of the source. It took several hours for the source to cool to an acceptably low temperature that was considered safe enough to open the vessel to recharge the crucible. This made the whole process uneconomic. In one case, this problem was solved by use of a forced gas quenching system [9].

The use of these linear slot sources has been proposed as the next generation of sources for the metallization process [10]. It has been calculated that the rate achieved with one of the sources, for depositing magnesium, had the equivalent deposition rate for aluminum that would have required a winding speed of 2000 m/min, approximately double the current operating speeds.

One such source was developed for an air-to-air machine that was close to 2 m in length. This source successfully achieved lifetimes of around 120 hours by making the crucible material very dense with very low porosity to protect it against the aluminum corrosion [11].

A variation of this was more recently used to deposit alumina transparent barrier coatings by adding an oxygen gas feed into the depositing aluminum from the rewind side of the deposition zone [12].

17.1.1 Polymer Sources

Over the last few years, there has been an increased interest in the vacuum deposition of polymers for both smoothing and protective overcoatings. The advent of organic light-emitting polymers that are suitable for evaporation has further increased the interest [13—15]. The polymers tend to be evaporated at relatively low temperatures, and tantalum plate heaters have been used to give large areas of radiant heat to the crucibles. There is still the problem of balancing the end losses to get the very high uniformity required for these materials. These evaporators are now available as off-the-shelf items suitable for retrofitting into existing systems [16].

The smoothing layers need not have the thickness quite so precisely controlled, although even here reproducibility and consistency is required. The thickness of these coatings tends to be a couple of orders of magnitude thicker than the light-emitting polymers, and hence the deposition rate becomes of increasing importance. It has been suggested that to get stability, at high rates of deposition, the surface area of the evaporation material needs to be a minimum of six times the area of the deposition nozzle where the vapor exits. This ensures the vapor pressure builds up within the source and the vapor mixes and evens out any variations. The exiting vapor then jets toward the substrate and this also helps to minimize scatter of the vapor. It has also been suggested that the temperature uniformity needs to be within 1°C across the whole source. In addition, to control the rate well at high speeds, the overall temperature control needs to be better than 1°C.

In evaporating polymers, it is important to choose the correct polymer. Some polymers break down with the heat and either polymerize in the retort or fractionate and produce coatings with inferior properties. The aim is to evaporate complete "mer" units, and once condensed on the substrate, stabilize them by cooling back to a solid or cross-linking them to some required level.

A common problem for all of these sources is the material capacity. The sources have sufficient capacity to contain all the evaporant or they have a feed mechanism. Commonly, the sources are designed to have sufficient capacity for at least one complete production roll of material that may be as long as 40 km. This may be easier than it initially looks because as the sources can be distributed around the deposition drum, by using the source exit nozzles to direct the vapor at the deposition drum, there can be many sources each with a fraction of the total charge in each.

The alternative is to feed the source that is much more difficult than it first appears. Most sources operate best if there is an increase in pressure within the source so that the vapor jets to the substrate. This pressure will also push the vapor out through any hole that is being used to feed the source. It is assumed that the material will melt and that there is a molten pool for the feedstock to go in. Generally, the feed material remains solid until it hits the molten pool where it is melted; this means that the feed hole and beyond are below the material melting point and hence any escaping vapor may condense on the surfaces and, over time, block the feed hole. If the hole is made larger, then more vapor will escape and the source efficiency goes down and the cleaning time goes up.

If the material sublimes, the problems are worse, because for a wide web source, the feed would need to either have some kind of transport method within the source or have multiple feeds down the length of the source to maintain the source uniformity.

The sources that have a molten pool also have a uniformity issue and that is where the feed meets the molten pool, the source will be locally cooler than the rest of the source. This too needs careful designing to maintain the high uniformity that the source offers.

Hence, with all the difficulties of feeding these sources, it is much more common for them to instead contain a fixed charge of material. When a fixed charge of material is used, then at the same time the substrate rolls are changed the source has to be replenished.

One area where research is still needed for these sources to be more universally used is in the choice of crucible material. Metals such as aluminum become corrosive when molten and so the choice of crucible material is critical. The mass of the crucible needs to be low in order for it to give a fast thermal response. Balanced against this is the aim that the crucible ideally needs to be reused to keep the cost of consumables down. There are many material and construction options available to develop the crucible technology, but until there are more sources in use to justify the developmental costs, this will remain an area of potential weakness.

With the likes of the Climate Change Levy imposed in some countries, as an additional tax on power consumption, there is a driving force to make machines more efficient. The radiant-heated slot sources can be made to be >95% material efficient and also more power efficient than other sources. Thus, it is likely that more of these sources will be developed over the next few years.

Another aspect of the radiant-heated source is that unless the heating elements are insulated in the direction away from the crucible, most of the input energy will be spent heating the system rather than the crucible. Under vacuum, there is little or no heat transferred by convection or conduction. The majority of the heat is transferred by radiation. The radiant heat is emitted from the whole heating element surface in all directions. Using radiation shields to reflect back the heat or at least to restrict the losses enables most of the heat to be focused on the crucible. This both improves heat-up times and minimizes the operating energy.

17.2 Radiation Shields

The radiation shields are often plain sheets of thin metal separated by fine coils of metal. The principle of use is that the heat that is absorbed will raise the temperature of the sheet and it will be reradiated from the sheet of metal [17]. The heat radiated from the thin sheet will be radiated from all surfaces and so 50% will be radiated back toward the source and 50% on toward the next sheet metal acting as a radiation shield (Figs. 17.2 and 17.3).

The same will occur with the next sheet; hence, the heat loss will be reducing with each sheet. The bulk of the heat is transferred by radiation, although whatever is used to keep the shields separate could act as a thermal bridge and provide a route for thermal conduction. A spiral of wire is often used to provide the separation because the coil provides a very small contact area but enough mechanical strength to keep the shields separate.

Often a high-temperature thin material such as molybdenum is used for the shielding. There can be problems of distortion of the shields from the thermal cycling and residual stress. In the design of the source, care also needs to be taken

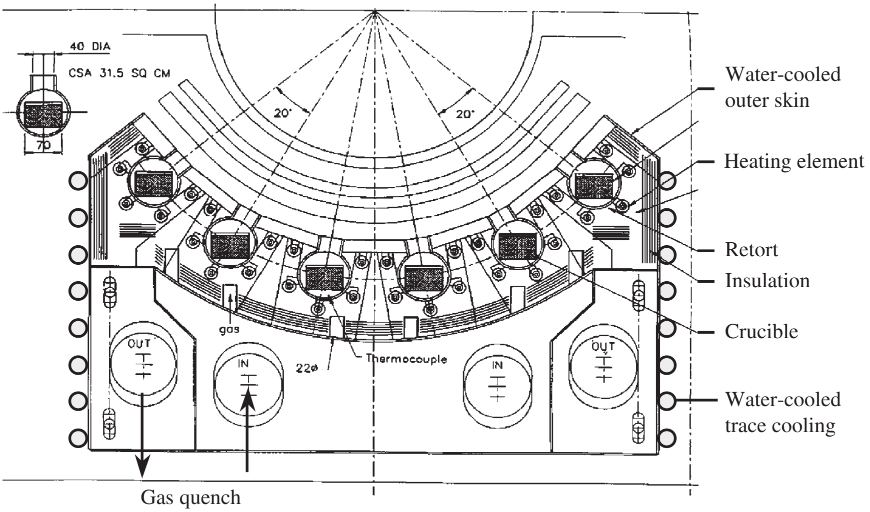


Figure 17.2 A diagram of a six-crucible radiant-heated deposition source.

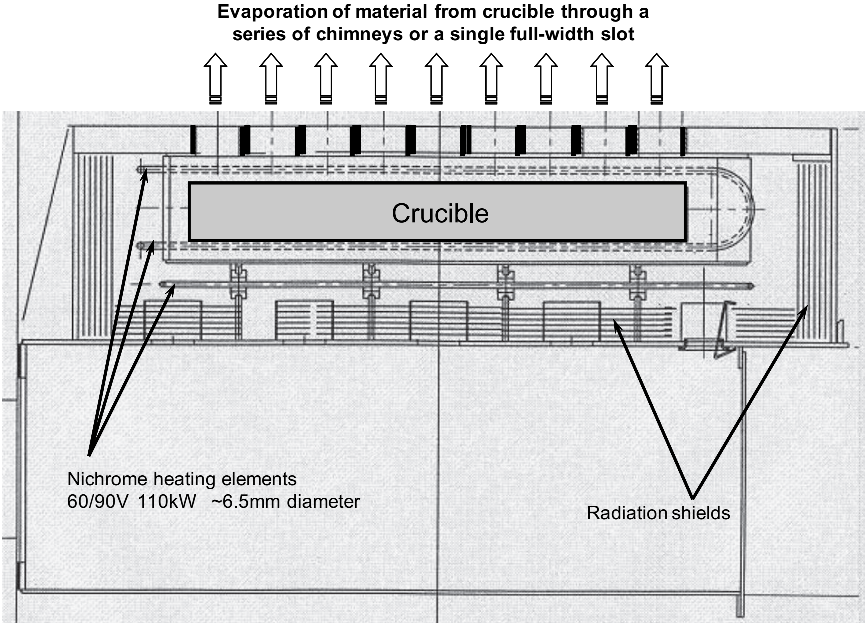


Figure 17.3 A further diagram showing more details of the slot source construction

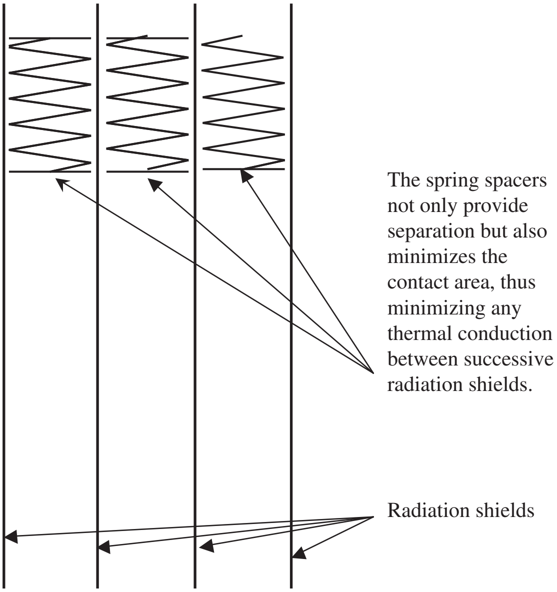


Figure 17.4 A schematic showing the construction of radiation shields.

to allow quick access to the source for repair and replenishment without causing any thermal short leading to a cold spot and distortion to the deposition uniformity.

Figure 17.2 shows six retorts each containing a crucible, with the retorts heated by radiant heat from nichrome heating elements that are placed in a serpentine pattern around the retorts. There is radiation shielding to the base and walls to minimize the heat losses.

There can be a tendency for the radiation shields to buckle and warp with the thermal cycling. This is due to the relaxation of the residual stresses of the worked metal and also any constraints that are put on the shields during the thermal cycle. There must be ample space to allow for the free movement of the shields as they expand with the heat. On occasions, this can lead to a conflict in that any gaps will allow for a higher heat loss. Overlapping shields can offset this problem. Another problem for the shields is that the thermal cycling can increase the rate of oxidation of the metal, and over time this can lead to the loss or failure of the shields. Using a more inert material such as molybdenum that is more stable at elevated temperature can help but there is a cost penalty for this. The shields can also become brittle after much thermal cycling and so designing out the need to move the shields once positioned is also advantageous.

17.3 Induction-Heated Sources

These can be thought of as alternatives to electron beam sources in that they tend to be circular crucibles or pots [18,19]. They often have sufficient material loaded into them to complete a single deposition cycle without the need for replenishing the crucible. Where they are used on a more continuous basis, the circular design allows for a rod feed from the base of the crucible.

The principle of operation is that the crucible containing the deposition material is located concentrically in the center of a water-cooled circular coil of copper tube. The coil is powered by a medium frequency RF source (250 Hz−25 kHz) and an eddy current is produced down the centerline of the coil, which will induce a magnetic field. The changing polarity by the RF power supply produces an oscillating magnetic field that vibrates the molecules, thus heating the material in the crucible [17−21] (Figs. 17.5 and 17.6).

This type of source has been used in several machines in Japan for the deposition of silica for barrier applications. As with electron beam and resistance boat evaporation systems, the induction source system has multiple crucibles arranged across the web width, and the deposited coating thickness profile is similarly dependent on the temperature and area of each source along with the spacing of the individual sources.

In theory, it is possible to have shaped sources, but the most popular appears to be circular sources. I am only aware of one large system that has a linear source [11]. As with any RF source, care should be taken to ensure that the system is suitably screened to stop stray power heating other nearby components.

The crucibles are insulated using a ceramic fiber cloth as used in vacuum furnace design. This type of insulation can be patched and repaired adding to the durability, hence it can be regarded as quite robust and tolerant to spits of metal.

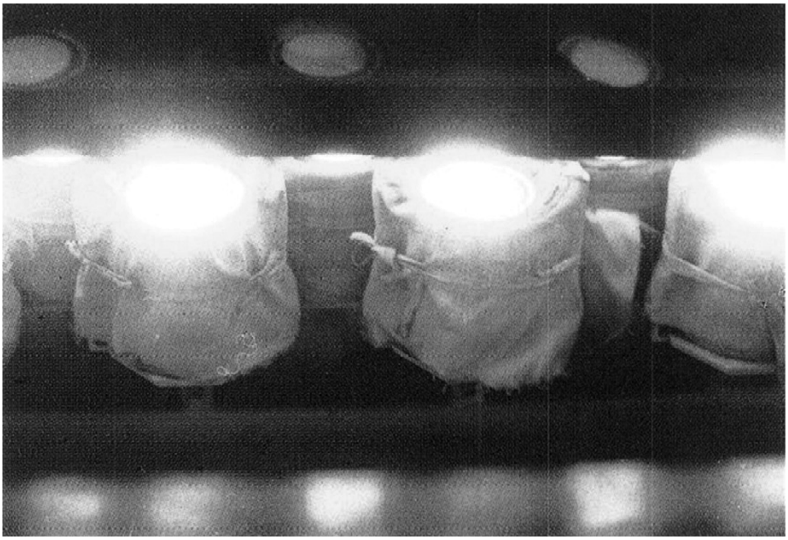


Figure 17.5 A photograph from a ULVAC vacuum coater that shows some induction-heated sources in action. The induction coils are hidden from view by the heat-insulating fabric wrapped around each source.

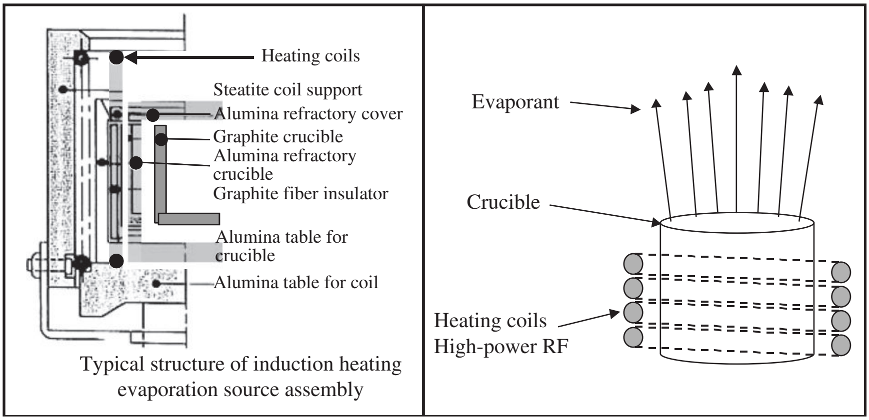


Figure 17.6 A diagram of the construction including some of the typical materials used along with a schematic of the basic layout of an induction-heated evaporation source.

Induction heating is a very rapid method of heating material. Magnetic materials heat more rapidly than nonmagnetic ones, and materials of higher resistivity heat faster than those of lower resistivity.

Induction heating has the same limitations as other methods. When the deposition material is porous and gas can be trapped within the material, it is possible to heat the material too quickly and for the gas to expand and explode the material. The thermal cycling problems are also similar and the cooling speed of the sources is also similar. The advantage of induction-heated sources over e-beam is that induction heating power supplies are simpler and hence cheaper. The improved uniformity available from a sweeping e-beam source tends to override the cost arguments.

Comparing the induction-heated sources to resistance-heated sources, it is claimed that the aluminum-metallized film produced using the resistance-heated technology is cheaper and more cost effective. This comparison has probably not been tested for many years. Originally, the boat life for the induction-heated crucibles was only around five batches or rolls. The reason for the crucible failure was that the aluminum had a tendency to creep and migrate into the pores of the crucible. When the crucibles were then cooled, there would be a differential contraction between the bulk crucible material, usually carbon, and the aluminum-containing surface. This surface would then be under stress and tend to spall. Developments have improved the lifetime of the newer crucibles to around 120 hours [11]. These are thus, on average, lasting three times longer than the resistance-heated intermetallic boats. This might suggest it is worth reviewing this technology. The method used to extend the life of the crucibles was to deposit alumina into the pores in the crucibles, thus preventing the aluminum access to the pores. What is surprising is that similar coating technology has not been used to extend the life of the resistance-heated boats.

Where the induction-heated source wins is for the ability to deposit so many other materials. Being able to swap out crucibles to change materials makes them very flexible although not many systems use this ability.

Systems have been built that are used for the deposition of silica thin film coatings for use in transparent barrier applications.

17.4 Magnetic Levitation Aluminum Deposition Source

A novel evaporation system for the deposition of aluminum onto strip steel has been developed [23,24]. As molten aluminum is corrosive, the idea was that suspending the molten aluminum by magnetic levitation would eliminate this problem and reduce the cost of replacing crucibles or resistance-heated boats. By enclosing the source and only allowing the vapor out directed toward the substrate, the material collection efficiency could be optimized. A material utilization of >99% was achieved onto strip steel in production. The enclosed source enables the pressure in the source to be increased so that the vapor mixes and is equalized, enabling the deposition to be uniform across the width of the web. This source, because the molten pool is freely suspended in space and the vapor is enclosed, also enables the exit slot and hence the deposition to be in any orientation and not just vertically upward.

The aluminum still has to be fed to the molten levitation zone, and this could be a source of the vapor exiting and possibly blocking the feed entry similar to the wire feed problems in resistance-heated evaporation systems.

17.5 Jet Vapor Sources

Jet vapor sources have been evaluated for some time and come in a variety of different configurations [25–28]. The common idea is that the material source is separated from the deposition part of the source by a volume where the vapor pressure of the material can be raised. This serves several purposes. Collecting the vapor in a volume helps equalize the pressure and so ensures that even from a point source there will be a uniform exiting flux of material giving uniform coating thickness on the substrate. The volume and gas mixing also allows more than one source to be combined, enabling alloy deposition to take place [27,29]. The exiting slot or nozzle can be constricted so that the vapor expands as it exits, and this adiabatic expansion cools down the vapor. The aim is to have the jet of vapor stick to the substrate and not to bounce off. As will be seen in the schematic in Fig. 17.7, although it is desired that the vapor will not bounce off the substrate, a proportion will bounce off. To combat this, a hot shroud is used so that the material that has

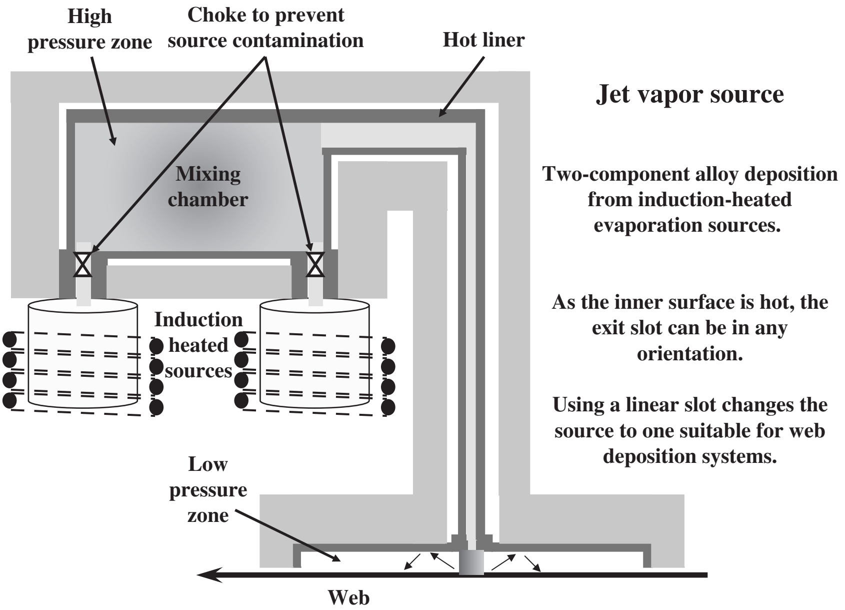


Figure 17.7 A schematic of a two-component jet vapor source with induction-heated sources [29].

bounced off the cool substrate will then hit a hot surface where the sticking coefficient will be low, and it will bounce off the hot surface and so have a second chance of sticking to the substrate.

Figure 17.7 shows a couple of induction-heated sources, this is purely an example. Almost any source of vapor can be used so long as each vapor supply line can be provided with a choked orifice to ensure that the supply does not become contaminated with the other vapor.

The attraction of this type of source is that there is the potential of having a very high material utilization. As with the magnetic levitation source and the distributed or slot sources, it is possible to arrange the deposition exit nozzles at any angle, and so it is possible to spread out the deposition around the deposition drum. Because of the enclosed nature of the source, it is possible to reduce the deposition losses to very small amounts giving very high, $>99\%$, material utilization. This sounds so good that the question is why has everyone not switched to this type of source, and the answer is usually a mixture of materials, source feeding, and source cooling problems. With aluminum, there is still the problem of molten aluminum being corrosive and so any source and the hot surface need to be compatible with aluminum at high temperature while still retaining their mechanical performance. Similarly for other deposition materials, the source materials need to be compatible. If long deposition runs are envisaged, there is still the question of do you heat up the whole inventory of deposition material or do you feed the source in some way?

If you feed the source, the aperture is a potential leak of the depositing material; if the conductance gap is small, it can be blocked by the escaping vapor condensing, or if the conduction gap is larger, then a large amount of vapor will escape. If the whole inventory of material is loaded into the source, the source size and crucible capacity will have to be larger than if it is continuously fed. The source is enclosed and generally is insulated to prevent it being a significant heat load to the substrate and to reduce the power requirements to maintain the temperature. However, this insulation also means the source can be slow to cool down and this can cause significant problems in obtaining suitable manufacturing cycle times as the cooling of the source becomes a significant proportion of the deposition cycle.

It is possible to increase the jetting effect by adding a gas feed to the enclosed volume and so increase the pressure within the source [30]. This enhances the pressure difference, and both gas and source material will jet out of the orifices faster than without the gas feed.

17.6 Molecular Beam Epitaxy Sources

This might appear to be an odd place to be talking about molecular beam epitaxy (MBE) sources as they are more associated with semiconductor device manufacturing. MBE sources should only be considered as high-stability deposition sources. Over many years, the design and manufacturing has been refined and improved so that the temperature stability has been improved and the source lifetime or periods between maintenance have been extended. Part of the evolution toward making the source design robust has been the symmetry of the source. MBE sources are circular with the heat distributed uniformly around the source. The materials for the source and shields are cut or machined and annealed to stabilize them. When coupled to a good quality stable power supply, the temperature of the source can be maintained to a fraction of a degree. Multiple MBE sources can be used for codeposition [31].

If you consider that resistance-heated evaporation boats are simply an array of individual sources set out in a line, then it is not surprising that setting out a series of MBE sources can be done to enable the MBE sources to be used for web coating. This is most useful when the stability of the deposition rate is critical. In photovoltaic deposition, where multiple material deposition is required and a precise control of the stoichiometry is also required through the coating thickness, this type of source becomes an option. In many system designs, the deposition zone is longer than for other processes, and as the substrate temperature is heated, it enables the substrate to be coated as a free span rather than around a deposition drum. This means that there is space to have sequential arrays of MBE sources of different materials to allow for the gradation of the depositing material. The MBE sources may not be ideal for high-rate deposition of rolls of material, but the basic design information can be utilized as a starting point for customized deposition sources for high-rate sources for photovoltaic materials.

References

[1] Fonseca JJ, Gorton W. A novel roll coater for double sided heavy deposition of magnesium onto PTFE films. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 64−70.

[2] Bishop CA, et al. Vacuum web coating. EP 0 652 302 patent; 1995.

[3] Hartwig E, Krug T. Food packaging films utilizing non metallic and glass-like barriers. In: Proc. speciality plastics conference; 1991.

[4] Hartwig E, et al. New developments and future trends in vacuum web coating. In: Proc. 31st annual technical conference of the Society of Vacuum Coaters; 1998. p. 75−84.

[5] Lackey Jr DE. A versatile web coater with multiple source capability. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 145−51.

[6] Vacuum web coating of capacitor films and paper with Al/Zn composite layers. Publicity Literature 13-230-02 3/10/89 Leybold.

[7] Vacuum web coaters for capacitor films. Publicity Literature 13-130-02 5/5/87.

[8] Glang R. Vacuum evaporation. In: Maissel LI, Glang R, editors. Handbook of thin films technology. New York: McGraw-Hill; 19830 07 039742 2 (reissue) [chapter 1].

[9] Bishop CA, et al. Evaporator for vacuum web coating. EP 0 652 303 patent; 1995.

[10] Bishop CA. Slot sources: a suitable replacement for resistance-heated boats in aluminium metallizers. In: Proc.46th annual technical conference of the Society of Vacuum Coaters; 2003. p. 580−5.

[11] Taguchi T, et al. Air-to-air metallizer: design and operational data. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 135−40.

[12] Kobayashia T, et al. Reactive vacuum vapor deposition of aluminum oxide thin films by an air-to-air metallizer. J Vac Sci Technol A 2006;24(4):939−45.

[13] van Slyke S, et al. Linear source deposition of organic layers for full colour OLED. SID Symp Digest Tech Pap 2002;27(2):886−9.

[14] Hoffman U, et al. New in-line machine concept for OLED manufacturing. SID Symp Digest Tech Pap 2002;27(3):891−3.

[15] Spahn RG. Source for thermal physical vapor deposition of organic electroluminescent layers. US 6 237 529 patent; 2001.

[16] LADS linear thermal evaporators for organics. Kurt J. Lesker Co. Available from: http://www.lesker.com.

[17] Warrington RO, Powe RE. The transfer of heat by natural convection between bodies and their enclosures. Int J Heat Mass Transfer 1985;28(2):319−30.

[18] Yadin E Andreev Y. Zinc and magnesium vapor generators in a steel strip coating system. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 39−42.

[19] Yadin E. Deposition of coatings or free foils of sublimating metals. In: Proc. 40th annual technical conference of the Society of Vacuum Coaters; 1997. p. 390−3.

[20] Tada I, et al. Comparison of evaporation sources for vacuum web coaters. In: Proc. 32nd annual technical conference of the Society of Vacuum Coaters; 1989. p. 131−49.

[21] Miyabayashi T, et al. Recent advances on the world largest 122 inch vacuum web coater aimed at cast polypropylene (CPP) films. In: Proc. 3rd international conference on web coating; 1989. p. 2−23.

[22] Ames I, et al. Crucible type evaporation source. Rev Sci Inst 1966;37:1737−8.

[23] Baptiste L, et al. Electromagnetic levitation: a new technology for high rate physical vapour deposition of coatings onto metallic strip. Surface Coat Technol 2007;202

(4–7):1189–93; In: Proc. 34th international conference and metallurgical coatings and thin films; 2007.

[24] Van Westrum S, et al. Method and device for coating a substrate. US patent 7 323 229; January 29, 2008.

[25] Yadin E. Deposition of coatings or free foils of sublimating metals. In: Proc. 40th annual technical conference of the Society of Vacuum Coaters; 1987. p. 390–3.

[26] Yadin E, Andreev Y. Zinc and magnesium vapor generators in a steel strip coating system. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1989. p. 39–42.

[27] Zijp JP, et al. High rate evaporation of alloys. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 390–3.

[28] Rebrov AK, et al. The supersonic jet deposition of metal-polymer films, in particular for antimicrobial applications. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 192–7.

[29] Schmitz B, et al. Integration of jet vapor deposition (JVD) in steel industry. In: Proc. 3rd international symposium on vacuum coating of metal strips and sheets VaCMeSS 2005. Dresden, Germany; September 29–30, 2005.

[30] Schweitzer MO, et al. Deposition of a thin film on a substrate using a multi-beam source. European patent EP 0839925A2 (filing date 29 October 29, 1997.

[31] Available from: http://www.tfp.ethz.ch/AnnualReports/jb2004-2005.pdf. p. 1–31.

18 Chemical Vapor Deposition/ Polymerization onto Webs

The basic process comprises feeding a precursor gas into a vacuum plasma. The plasma has energetic particles and the precursor gas is fragmented. Some of the molecules hit and condense on the substrate surface. The polymer webs have to be kept reasonably cool, and so thermally activated chemical vapor deposition (CVD) tends not to be used, instead plasma-enhanced CVD is preferred.

Once molecules hit the substrate surface, there are five steps to film growth (Fig. 18.1):

1. Adsorption, including condensation and desorption
2. Lateral diffusion
3. Surface reaction
4. Nucleation
5. Growth and film formation

Not included in the list, but of equal importance, is the assumption that there is sufficient throughput of gas to give adequate arrival of the different components. Of similar importance is the exhausting of the by-products speedily enough so that they do not slow down or poison the process [2].

There has been a lot of experimentation to investigate what sort of plasma can be used to deposit coatings [3–15]. RF, DC glow discharge, microwave, ECR, and other magnetically enhanced plasmas are used in a wide variety of system geometries. The frequency of the RF plasma varies from low to medium to high and on to microwave [16–22]. All work to some extent, although some lend themselves to a linear geometry more than others and so are preferred for web processes.

18.1 Substrate Temperature

Raising the substrate temperature increases the number of adsorbed molecules that are desorbed and increases the speed and distance of lateral diffusion of the molecules on the surface.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00018-0

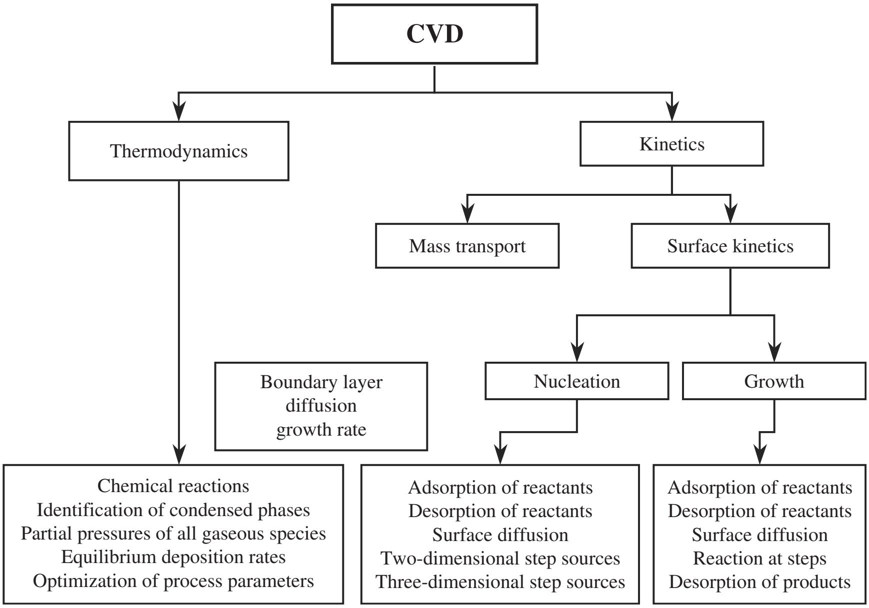


Figure 18.1 A diagram of what happens in a CVD process [1].

18.2 Power

Increasing the RF power has the effect of increasing the ionization, plasma potential, and plasma volume. This leads to increased dissociation of the precursor gas and an increase in the substrate self-bias.

18.3 Pressure

Increasing the pressure increases the reactant gas density, gas diffusion times, and system residence times. It also decreases the molecular mean free path, gas flow velocity, and plasma volume.

18.4 Substrate Bias

Increasing the negative DC bias increases the ion bombardment of the substrate and growing film. This increased bombardment leads to removal of any loosely bonded atom/molecule and thus an increase in the film adhesion. The removal of loosely bonded material also means that the growing film will be denser and there is likely to be an increase in polymer cross-linking.

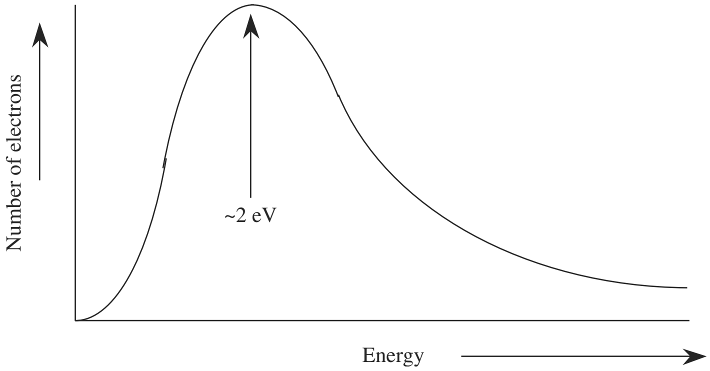


Figure 18.2 Typical electron energy distribution available within the plasma.

Table 18.1 Some of the Bond Strengths and Energy Available Within a Plasma

Bond	**Bond Strength (eV)**	**Species**	**In Plasma Energy (eV)**
C−C	6.3	Electrons	1−30
C−Si	4.7	Ions	0.025−1
C−O	11.2	Metastables	0−30
O=CO	5.5	Vis−UV photons	1−30
O−O	5.2		
O−Si	8.3	If the substrate is insulating and charges up, the ions may be accelerated into the substrate surface with higher energy (10−100 eV).	
Si−Si	3.4		
H−OH	5.2		
H−O	4.4		
H−H	4.5		
H−CH_3	4.5	It can be seen that the plasma has more than enough energy to break bonds and thus fragment precursor chemical vapors.	
H−CH_2	4.8		
H−CH	4.4		
H−C	3.5		

Figure 18.2 shows that only a proportion of the electrons have sufficient energy to make bond-breaking collisions. Changing the bias will change this proportion and hence will change the effect on a complex precursor molecule. Increasing the energy will provide more bond breaking and smaller fragments.

Table 18.1 shows that it is possible for molecules impacting the surface to break bonds easily, producing dangling bonds available for molecules to attach to them. The molecules, if impacting each other within the plasma, have the energy to break any of the precursor bonds, thus generating fragments.

It is worth bearing in mind that the plasma deposition process will be depositing the coating not only on the substrate, where it is wanted, but also on other surfaces.

If the coating is nonconducting, then this is likely, over a period of time, to change the characteristics of the plasma. As with the reactive sputtering of dielectrics, there can be the problem of the disappearing anode. In one process, the anode is run at red heat and with a gas purge to prevent deposition [31].

18.5 Fluorinated Plasma Polymerization

There is an interest in depositing fluorinated coatings to give low-energy surfaces that are hydrophobic. These are used in applications such as drug delivery systems to ensure all the drug is supplied and none remains behind coated on the polymer surfaces. It is also possible to provide rubbing surfaces with some lubricity with a polytetrafluoroethylene-type coating.

The fluorinated polymer depositing plasmas have some additional trends.

18.5.1 Power

Increasing the power will initially lead to an increase in deposition because of an increase in the CF_2 content. This increased deposition is balanced by an increase in the self-biasing, and thus increased substrate bombardment. As power is increased, the deposition rate will increase to a point at which both the increased deposition and the etching will be in balance. Any further increase in power will result in a decrease in deposition rate.

18.5.2 Substrate Bias

The substrate bias can be self-generating such as when insulating substrates are immersed in an RF plasma. As the substrate bias is increased, the bombardment of the substrate and growing film increases. This improves the adhesion and the densification of the growing film. However, in fluorinated polymers it can also lead to a reduction in the fluorine content. This results in the growing polymer becoming harder with the increased carbon content and also the water drop contact angle being reduced along with the hydrophobicity.

18.5.3 Substrate Temperature

Increasing the substrate temperature can lead to an increase in film densification and more efficient removal of loose surface atoms or molecules. This has the same effect as raising the substrate bias, and the fluorine:carbon ratio can be reduced.

18.6 Carbon—Fluorine Plasmas

Carbon—fluorine plasmas are used for etching semiconductor devices at least as much as, and possibly more than, for the deposition of fluorinated polymers by plasma-enhanced CVD [23].

There are several commonly used precursors such as:

Tetrafluoromethane	CF_4
Hexafluoroethane	C_2F_6
Octafluorocyclobutane	c-C_4F_8

Plasmas can break down these precursors, producing fragments.

$$CF_4 + e^- \rightarrow CF_3^+ + F + 2e^-$$

Many of these fragmenting collisions generate free fluorine. Free fluorine is the most active etchant.

CF, CF_2, CF_3 are all active depositing fragments

CF_4 and C_2F_6 both tend to be stable species within the plasma. They are more difficult to fragment further into more active species and so do not lead to deposition.

Adding hydrogen helps the deposition process and reduces the etching process, giving an overall net increase in deposition rate. Hydrogen-to-fluorine bonds are stronger than the weak fluorine-to-fluorine bonds.

$F + H \rightarrow HF$ is a rapid process
$CF_3 + H \rightarrow CF_2 + HF$ is a rapid process
$CF_2 + H \rightarrow CF + HF$ is a slow process

In this process, the CF_3 content reduces and the CF_2 content increases. The free fluorine combines with the hydrogen, reducing the etching. The loss of the free fluorine also stops the recombination back up to higher-mass fragments. Overall, this leads to an increase in the proportion of CF_2 within the plasma and thus an increase in the deposition rate.

Oxygen will combine with carbon, and this can lead to an increase in the free fluorine that results in increased etching. The CF and CF_2 content of the plasma decreases with increased oxygen content. Oxygen can also react with the substrate surface directly acting as an etchant too. Hence, a small quantity of oxygen can give a step change in etch rate.

These plasmas have been used to produce controlled hydrophobic or hydrophilic surfaces for medical applications [24].

18.7 CVD of Barrier Coatings

There are a number of different PECVD coatings that can act as barrier films. These include silica, melamine, and carbon films of various stoichiometries deposited by a variety of methods [25−38].

Figures 18.3 and 18.4 depict the basic process for depositing an SiO_x-type coating onto polymer web to improve the moisture and oxygen barrier performance [31].

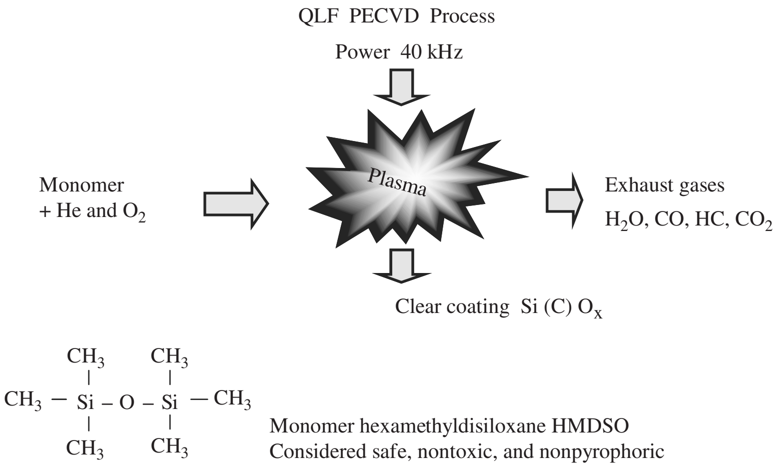


Figure 18.3 Details of the quartz-like-film (QLF) deposition process.

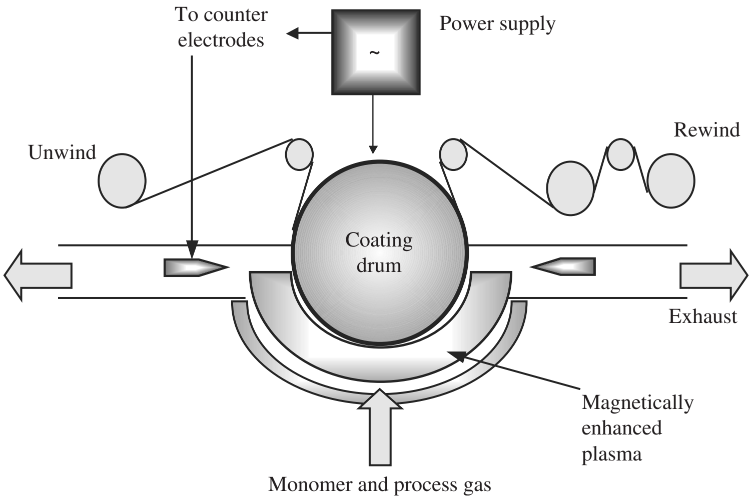


Figure 18.4 A schematic of the QLF process.

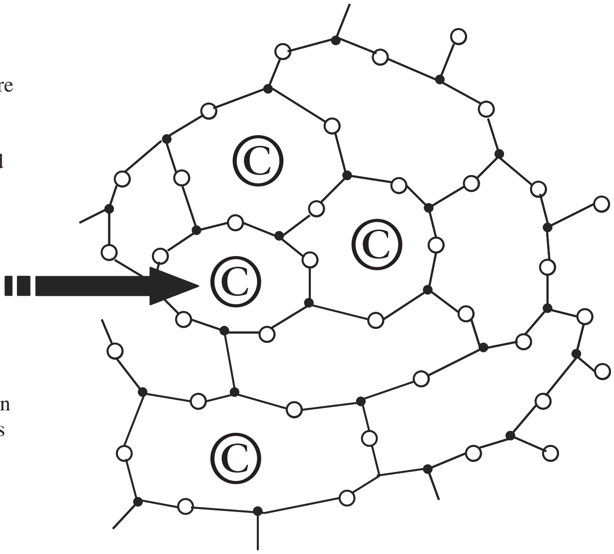
Although the coating contains significant amounts of carbon, it is referred to as silica. Depending on the process conditions, the carbon content can be as high as approximately 20%. It is this carbon content that is believed to give the different barrier performance for oxygen and water vapor. Thus, the tuning of the process, which is done to get a better oxygen barrier or to optimize the coating for water vapor barrier, is to a large extent controlling the carbon content of the silica.

This process also has the plasma enhanced using magnets. This is very similar to magnetron sputtering in that the magnetic enhancement makes the plasma denser in the deposition zone. This denser plasma results in the speeding up of the decomposition process and concentrating the coating onto the substrate.

This particular process has been easily done for many years but has never achieved the expected market size because the costs have never quite matched the requirements. Hence, this process needs all the aids possible to increase the deposition rate in order to increase the winding speed and bring down the unit costs of the product.

The carbon atoms are believed to sit in the holes within the silica network which is thought to prevent the holes acting as pores through which the oxygen or water vapor migrates (Fig. 18.5).

As can be seen from Table 18.2, the CVD process is cheaper than the e-beam process. However, both are higher than the organic coatings they are expected to replace. In some countries, a number of solvent-coated products are banned and the vacuum-coated products are seen to be environmentally preferable. A combination



Where the holes are large enough, carbon atoms can sit in the holes and block the oxygen diffusion path through the silica network.

PVD-deposited silica has little or no carbon. CVD-deposited silica can contain as much as 20% carbon in the coatings and have improved barrier performance.

Figure 18.5 A schematic of the silica network and the believed potential sites where the carbon can fit [39].

Table 18.2 Relative Costs of Different Coated Films

System	Oxygen (cm^3/m^2/day)	Moisture (g/m^2/day)	Price (£/ton)	Price Including PET (£/m^2)	Price Excluding PET (£/m^2)
Opaque film					
Aluminum foil	<1	<1			
Metallized PET	<1	<1	3500	6	3
Uncoated PET	50 +	20 +	1800		3
Transparent film					
PVdC	6–8	6–8	3300		
EVOH	2–5	Very high	5000	9	6
Al_2O_3	1	1	4500	8	5
SiO_x (e-beam)	1	1	5000	9	4.5 to >5.5
$SiCO_x$ (QLF)	<2	<2	4500	8	3.5–4.5
Melinex PET D888	1	20	4500	8	5
Melamine (CVD)	1			8	4–5

PET, polyethylene terephthalate; PVdC, polyvinylidine chloride; EVOH, ethylene vinyl alcohol; Melinex, trade name of PET; D888, development grade no. 888; QLF, quartz-like film.

of the performance and clean image has enabled the coatings to gain a strong foothold in the market even though the costs are higher than the market would wish.

There continues to be development work aimed at reducing the coating costs coupled to performance improvements. The aim is to make the vacuum coating route the preferred manufacturing process. If this occurs, there will be a massive expansion in the market requirements and an order of magnitude change in the number of systems required worldwide.

18.8 Atmospheric Plasma Deposition

This technology started out by being an improvement over corona treatment of polymer surfaces. There can be a problem with corona treatment as the plasma produced can break down and arcs can form, which can damage the substrate including piercing polymer webs. Starting with a vacuum plasma and increasing the pressure toward atmospheric pressure can result in problems. The mean free path between collisions is reduced, and this can quench the ionization process as the electrons undergo too many collisions and lose energy. To compensate for this, the strike voltage and the operating voltage have to be increased. This higher voltage has the side effect that the plasma is much more likely to form arcs. Arcing is unwanted, as this concentrates the energy into a tiny spot that then has a very high current density and can be very damaging to the surface. Designs of atmospheric plasmas include DC, low-frequency AC, RF, and microwave power supplies [40–49]. Probably the most common of these is the RF atmospheric plasmas, operating at 13.56 MHz. The high mobility of the electrons along with the field reversal of the RF supply is being used to suppress the tendency of the plasma to arc. It is also common for helium to be included as another method of quenching arcs. As the helium breaks down at a substantially lower voltage than other gases, this allows the operating voltage to be lowered, thus reducing the propensity to arc. However, this can be regarded as a disadvantage, as helium then becomes a high-cost consumable gas.

Once a stable atmospheric plasma had been obtained, it was only a short step to then consider adding other gases to take the process from only carrying out surface treatment to being capable of deposition of coatings [50–63]. The attraction is that by eliminating the vacuum system, the coating costs would be significantly reduced. The expectation is that by using a readily available power supply rather than a specifically designed supply, the cost of the power supply would be reduced, and by more carefully designing the web system and enclosing it and recirculating the gas, it is possible to reduce the cost of the helium consumable gas. In some systems, the plasma can also reach the back surface of the web, and so this too needs a redesign to limit any deposition to the front surface only. This technology appears to offer some potential to produce lower-cost deposition but is still in the scale-up and development phase.

References

[1] Park J-H. Chemical vapor deposition. Surface engineering series Vol. 2 ASM International, Materials Park, OH 2001 ISBN 0-87170-731-4.

[2] Mucha JA. Mechanisms in plasma etching. In: IPAT workshop on semiconductor technology: thin film production and properties; 1986. p. 143–52.

[3] Beamson G, et al. Modification of surfaces and surface layers by non equilibrium processes. Physica Scripta 1988;T23:249–57.

[4] Roth JR. Industrial plasma engineering. Vol 2—Applications to nonthermal plasma processing. Institute of Physics. Bristol and Philadelphia 2001. ISBN 0-07503-0545-2.

[5] Wertheimer MR, Moisan M. Comparison of microwave and lower frequency plasmas for thin film deposition and etching. J Vac Sci Technol A 1985;3(6):2643–9.

[6] Claude R, et al. Comparison of microwave and lower frequency plasmas for plasma polymerisation. Appl Phys Lett 1987;50(25):1797–9.

[7] Claude R, et al. Comparison of microwave and lower frequency plasmas for plasma polymerisation. Plasma Chem Plasma Process 1987;7(4):451–64.

[8] Boudreau M, et al. Electron cyclotron resonance chemical vapor deposition of silicon oxynitrides using tris(dimethylamino)silane. Appl Phys Lett 1993;63:3014–16.

[9] Madocks J. High rate PECVD source for flexible substrates. In: Proc. 46th annual technical conference of the Society of Vacuum Coaters; 2003. p. 137−42.

[10] Outten CA, et al. Development of antireflection coatings using microwave plasma-enhanced chemical vapor deposition. In: Proc. 46th annual technical conference of the Society of Vacuum Coaters; 2003. p. 181−4.

[11] da Silva Sobrihno AS, et al. Transparent barrier coatings on PET by single- and dual-frequency PECVD. In: Proc. 41st annual technical conference of the Society of Vacuum Coaters; 1998. p. 115−20.

[12] Izu M, et al. Roll-to-roll RF PECVD machine for a-Si for solar cell manufacturing. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 120−3.

[13] Angus JC, et al. Carbon thin films. In: Mort J, Jansen F, editors. Plasma deposited thin films. CRC Press; 1986 ISBN 0-8493 5119-7 [chapter 4].

[14] Biederman H. Polymer films prepared by plasma polymerisation and their potential application. Vacuum 1987;37(3/4):367−73.

[15] Ouellette RP, et al. Low-temperature plasma technology applications. Electrotechnology, Vol 5. Ann Arbor Science. Ann Arbor, MI. 1980 ISBN 0-250-40375-7.

[16] Wyslouzil W, Kashyap S. Single sided microwave applicators for sealing cartons. J Microw Power 1985;267−72; Also US patent 3 764 768; October 9, 1973.

[17] Ji T-R, Gerling J. A versatile microwave plasma applicator. J Microw Power Electromagn Energy 1988;23(1):3−10.

[18] Sauve G, et al. Slotted microwave field applicator for the generation of long uniform plasmas. J Microw Power and Electromagn Energy 1988;28(2):123−31.

[19] Rotman W, Oliner AA. Asymmetrical trough waveguide antennas. IRE Trans. Antenna Propag 1959;7:153−62.

[20] Rappaport CM, Morgenthaler FR. Localized hyperthermia with electromagnetic arrays and the leaky-wave troughguide applicator. IEEE Trans. Microw Theory Tech 1986; MTT-34(5):636−43.

[21] Sauve G, et al. Sustaining long linear uniform plasmas with microwaves using a leaky-wave (troughguide) field applicator. IEEE Trans Antenna Propag 1995;43(3):248−56.

[22] Weissfloch CF, Wertheimer MR. Apparatus and method for plasma generation and material treatment with electromagnetic radiation. US patent 3 814 983; 1974.

[23] d'Agostino R. Summary abstract: mechanisms of polymerisation in discharges of fluorocarbons. J Vac Sci Technol A 1985;3(6):2627−8.

[24] Palmers J. A new alternative for better modification of medical surfaces and textiles. In: Proc. Medtec; 1999.

[25] Madocks J, et al. Packaging barrier films deposited on PET by PECVD using new high density plasma source. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 672−3.

[26] Wocjik J, Mascher P. The influence of the deposition conditions on the optical and compositional characteristics of SiO_x thin films deposited by ECR-PECVD. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 687−90.

[27] Martinu L, Poitras D. Plasma deposition of optical films and coatings: A review. J Vac Sci Technol A 2000;18(6):2619−45.

[28] Moser EM, et al. Hydrocarbon films inhibit oxygen permeation through plastic packaging material. Thin Solid Films 1998;317:388−92.

[29] Bouchet J, et al. Novel multifunctional organo-silane based barrier coatings on polymers. Poster presentation 8. In: Proc. 46th annual technical conference of the Society of Vacuum Coaters; 2003.

[30] Rochat G, et al. Cohesive strength and oxygen permeability of PECVD-based coatings on semicrystalline polymers. In: Proc. 46th annual technical conference of the Society of Vacuum Coaters; 2003. p. 50−5.

[31] Smith AW, et al. PECVD of SiOx barrier films. In: Proc. 45th annual technical conference of the Society of Vacuum Coaters; 2002. p. 525−9.

[32] Komada M, et al. Novel transparent gas barrier film prepared by PECVD method. In: Proc. 43rd annual technical conference of the Society of Vacuum Coaters; 2000. p. 352−6.

[33] Leterrier Y, et al. Durability of thin PECVD SiO_x coatings on polymer films. In: Proc. 41st annual technical conference of the Society of Vacuum Coaters; 1998. p. 429−33.

[34] Fayet P, et al. Growth mode of PECVD SiO_x barrier coatings on polyethylene terephthalate. In: Proc. 14th vacuum web coating conference; 2000. p. 169−74.

[35] Sacher E, et al. Moisture barrier properties of plasma-polymerized hexamethyldisiloxane. In: Proc. applied polymer symposium on plasma chemistry. J Appl Poly Sci 1984; 38:163−71.

[36] Lewis JS, Weaver MS. Thin-film permeation-barrier technology for flexible organic light-emitting devices. IEEE J Sel Top Quantum Electron 2004;10(1):45−57.

[37] Felts TJ. Commercial-scale application of plasma processing for flexible polymeric substrates: from laboratory to production. In: Proc. 5th vacuum web coating conference; 1991. p. 239−59.

[38] d'Agostino R, Claprico V. Process and mechanisms of deposition of plasma polymers. In: Proc. 8th vacuum web coating conference; 1994. p. 19−32.

[39] Weston GF. Material for ultrahigh vacuum. Vacuum 1975;25(11/12):469−84.

[40] Kanazawa S, et al. Stable glow plasma at atmospheric pressure. J Phys D: Appl Phys 1988;21:838−40.

[41] Okazaki S, et al. Appearance of stable glow discharge in air, argon, oxygen and nitrogen at atmospheric pressure using a 50 Hz source. J Phys D: Appl Phys 1993;26: 889−92.

[42] Tendero C, et al. Atmospheric pressure plasmas: a review. Spectrochimica Acta part B 2006;61(1):2−30.

[43] Kunhardt EE. Generation of large-volume, atmospheric-pressure nonequilibrium plasmas. IEEE Trans Plasma Sci 2000;28(1):189−200.

[44] Massines F, et al. Experimental and theoretical study of a glow discharge at atmospheric pressure controlled by dielectric barrier. J Appl Phys 1998;83(6):2950−7.

[45] Roth JR, et al. Experimental generation of a steady-state glow discharge at atmospheric pressure. In: Proc. 19th IEEE international conference on plasma science [paper # 5P21]. Tampa, FL, June 1−3, 1992. p. 170−1.

[46] Liu C, Roth JR. Characteristics of a steady-state, low power glow discharge at atmospheric pressure. APS Bull 1992;37(6):1563.

[47] Roth JR, et al. The physics and phenomenology of one atmosphere uniform glow discharge plasma (OAUGDP) reactors for surface treatment applications. J Phys D: Appl Phys. 2005;38(4):555−67.

[48] Roth JR, et al. Treatment of metals, polymer films and fabrics with a one atmosphere uniform glow discharge plasma (OAUGDP) for increased surface energy and directional etching. Acta Metallurgica Sinica 2001;14(6):391−407.

[49] Balcon N, et al. Pulsed RF discharges, glow and filamentary mode at atmospheric pressure in argon. Plasma Sources Sci Technol 2007;16:217−25.

[50] Sawada Y, et al. Synthesis of plasma-polymerized tetraethoxysilane and hexamethyldisiloxane films prepared by atmospheric pressure glow discharge. Phys D: Appl Phys 1995;28:1661−9.

[51] Salge J. Plasma-assisted deposition at atmospheric pressure. Surf Coat Technol 1996;80:1−7.

[52] Thyen R, et al. Plasma-enhanced chemical-vapour-deposition of thin films by corona discharge at atmospheric pressure. Surf Coat Technol 1997;97:426−34.

[53] Goossens O, et al. Application of atmospheric pressure dielectric barrier discharges in deposition, cleaning and activation. Surf Coat Technol 2001;142−144:474−81.

[54] Schmidt-Szalowski K, et al. Thin films deposition from hexamethyldisiloxane and hexamethyldisilazane under dielectric-barrier discharge (DBD) conditions. Plasmas Polym 2000;5(3−4):173−90.

[55] Ward LJ, et al. Atmospheric pressure glow discharge deposition of polysiloxane and SiO_x films. Langmuir 2003;19(6):2100−14.

[56] Baránková H and Bárdoš L. Atmospheric plasma technology for coating. In: Mattox DM and Mattox VH editors. 50 Years of Vacuum Coating Technology, Society of Vacuum Coaters, Albuquerque, NM, 2007, [chapter 19]. ISBN: 978-1-878068-27-9.

[57] Dowling DP, et al. Influence of substrate to source distance on the properties of siloxane coatings deposited using an atmospheric plasma jet system. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 297−302.

[58] Albaugh J. Characterisation of nano-coatings deposited using an aerosol assisted atmospheric pressure plasma jet technology. In: Proc. 51st annual technical conference of the Society of Vacuum Coaters; 2008. p. 550−3.

[59] Twomey B, et al. Evaluation of the mechanical behaviour of nanometre-thick coatings deposited using an atmospheric pressure plasma system. In: Proc. 50th annual technical conference of the Society of Vacuum Coaters; 2007. p. 58−63.

[60] Premkumar PA, et al. Large area SiO_2 films deposition by atmospheric pressure plasma enhanced chemical vapour deposition (AP-PECVD): growth mechanisms by surface characterization. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 311−4.

[61] Johnson KW, et al. Atmospheric pressure plasma deposition of transparent conductors—tailoring precursor chemistries. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 327−32.

[62] O’Neill L, et al. Coatings generation and control of wide area, homogenous atmospheric pressure glow discharges for industrial coating applications. In: Proc. 49th annual technical conference of the Society of Vacuum Coaters; 2006. p. 658−63.

[63] Dowling DP, et al. Deposition of functional coatings using an in-line atmospheric pressure plasma apparatus. In: Proc. 48th annual technical conference of the Society of Vacuum Coaters; 2005. p. 214−8.

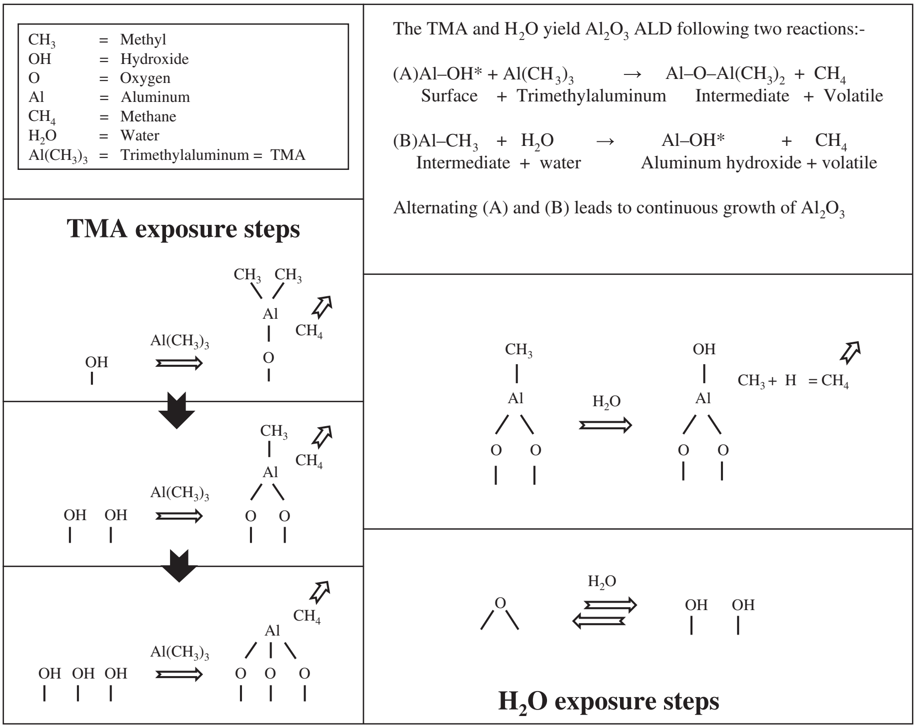
19 Atomic Layer Deposition

The technique of atomic layer deposition (ALD) has been around for many years [1]. It can be regarded as a special type of chemical vapor deposition (CVD). The process that consists of introducing a precursor gas that will attach to all surfaces as a monolayer is known as chemisorption. Once the whole surface is covered by a monolayer of the first gas, saturation is said to have been reached. The excess gas is pumped away and a second gas is introduced that also condenses and is chemisorbed on top of the first layer. There is a reaction or decomposition that converts the first and second precursors into the desired coating [2,3] as a saturated surface reaction. The excess second gas is pumped away and then the whole process can be repeated to deposit a second monolayer. This sequence can be repeated as many times as necessary to deposit the desired total coating thickness. The deposition process steps for the deposition of aluminum oxide by using trimethylaluminum and water as the process gases are shown in Fig. 19.1. The methyl groups take the hydrogen from the hydroxide to make volatile methane that leaves the surface and is removed during the purge cycle.

One of the attractive features of ALD as a process is that the coating deposited is conformal with the substrate surface. Conformal means that the coating follows the surface contours so that there is the same thickness of coating over the whole surface irrespective of surface roughness or defects. This is highlighted in Fig. 19.2, which shows how evaporation or other limited area fixed position sources can result in surface features or contamination being shadowed as the substrate enters or exits the deposition zone. This can lead to a reduced thickness or no coating at all in the shadowed areas and a concomitant loss of barrier performance. The covalent bonding of the ALD coatings gives good adhesion. This process has been used by the semiconductor industry, as the conformal coating can coat the sides and bottom of trenches equally as well as the top surfaces. It has also been used to smooth glass surfaces, reducing the surface cracks that can lead to premature failure of the glass [4]. This conformal nature makes this coating process interesting, as it looks as if it has the potential to reduce the number of coating defects that are caused by substrate effects.

As a process it is relatively simple. So long as there is sufficient gas introduced, the surface will be coated with a monolayer of material. If too much gas is introduced, the process is wasteful but the coating thickness will not have changed, as it

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00019-2



CH_3 = Methyl
OH = Hydroxide
O = Oxygen
Al = Aluminum
CH_4 = Methane
H_2O = Water
$Al(CH_3)_3$ = Trimethylaluminum = TMA

The TMA and H_2O yield Al_2O_3 ALD following two reactions:-

(A) $Al\text{–}OH^* + Al(CH_3)_3 \rightarrow Al\text{–}O\text{–}Al(CH_3)_2 + CH_4$
Surface + Trimethylaluminum → Intermediate + Volatile

(B) $Al\text{–}CH_3 + H_2O \rightarrow Al\text{–}OH^* + CH_4$
Intermediate + water → Aluminum hydroxide + volatile

Alternating (A) and (B) leads to continuous growth of Al_2O_3

Figure 19.1 An example of the reactions for the ALD of an aluminum oxide coating using trimethylaluminum and water for the two exposure steps.

will still only deposit a monolayer of material. So long as there is a suitable purge and the second gas is introduced in sufficient quantity, the reaction will take place and the first coating layer will be completed. Thus, the controls do not necessarily have to be of high precision to produce high-precision coatings. The coating thickness uniformity is not an issue, as each layer is conformal and only one monolayer thick. This is not to say that the deposition process does not have quirks. As the gas coats every surface, it will also coat surfaces other than the substrate, and this can include the system all the way through to the pumps. Thus, high-capacity filters are required to protect the pumps from accumulation of powder. The use of dry pumps is preferred, but these still need good filtration. The surfaces will start to flake when coatings reach the order of 10 μm, and so there is plenty of potential within any roll-to-roll coater for the generation of particles from flaking. So although the coatings may be conformal, there is still the possibility of particles becoming incorporated in the coatings.

One of the other inputs to the ALD process is often substrate temperature. The temperature can be used to aid thermal decomposition of the gases applied. The substrate temperature is an important control parameter. If the substrate temperature is too low, the reaction may be slowed down, whereas if the temperature is too

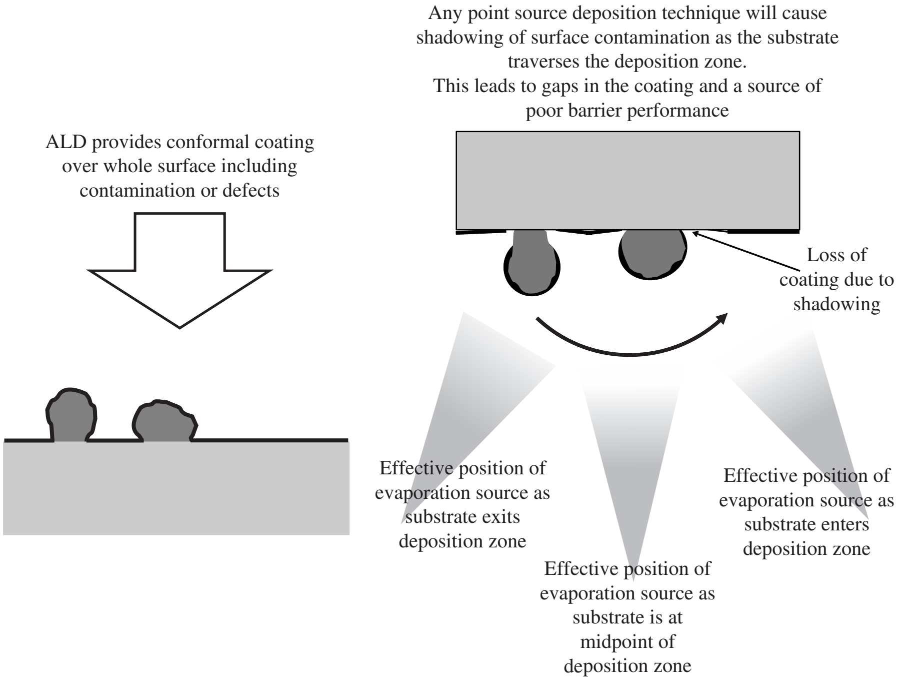


Figure 19.2 A schematic comparison between the conformal coating from atomic layer deposition and the more common evaporation process highlighting the shadowing of contamination that causes coating defects in the evaporation process and the lack of these defects in coatings produced by ALD.

high, the chemicals may desorb from the surface without reaction. There is usually a window between these two states that defines the production conditions [5].

Recently, the ALD process has been developed to make it possible to deposit coatings onto rolls of polymer film [6−15]. The first two of these papers describe two quite different approaches to the design of equipment for the roll-to-roll ALD.

The first of these two designs has taken the idea of making a compact delivery system that could be multiplied to make it easier to build up the coating thickness. This is shown schematically in Fig. 19.3, where the polymer film is wound through and sequentially exposed to the first precursor gas, then the excess gas is pumped away, and this is followed by a buffer gas and then the second gas is introduced, followed by the excess gas being pumped away. Using the right manifold design, the gas introduction can be made to be uniform across the full width of the film. This design came from the semiconductor end of the industry and the work was designed for producing multilayer electronic coatings. Using multiple deposition heads and gas delivery systems makes it a high-precision but a predicted higher-cost system than the other approach, which is shown in Fig. 19.4.

In Fig. 19.4, the polymer film is wound in a serpentine geometry so that the film repeatedly passes through a zone with gas 1, then through a buffer zone and

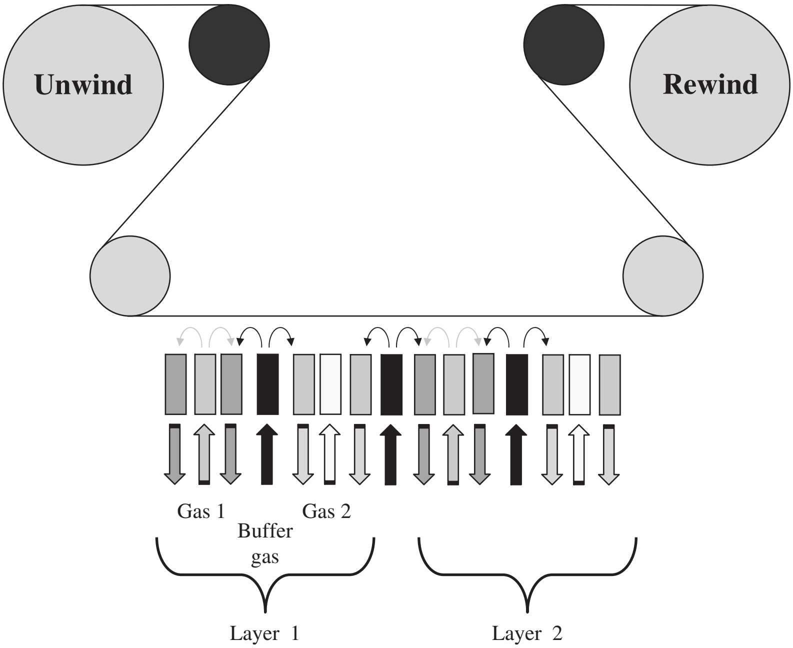


Figure 19.3 A schematic of a multiple-source roll-to-roll ALD process.

then through gas zone 2 and back through the buffer zone. This cycle is repeated multiple times to build up the coating thickness. The simplicity of this system is that there is only a single feed for each gas, and this makes the cost lower. This design has been used for barrier coatings during the development. As with the other design, there is still more development work to be done before this becomes a major competitor for the production of barrier coatings. The existing design has what could be seen by different users as either a disadvantage or an advantage. As the gas sticks to all surfaces, it means that the gas sticks to both the front and back surfaces of the film and so the coating grows on both surfaces. This is fine if you want a coating on both surfaces and the barrier looks to be good, but part of the improvement is because some of the pinholes are offset and there is a more tortuous diffusion path. It is possible to engineer the system to limit the back surface deposition, but care is needed to make sure that no film damage is done in using static masking.

This is certainly a deposition process for the future once the roll-to-roll process has been proven to be robust and has been fully optimized [16]. Even at this early stage, it is promising enough that it is being evaluated for deposition onto solar cells [17] as well as for barrier layers for everything from ultra barriers for OLEDs [18–20] to adding barrier layers for rolls of paper. Part of the interest is because the process looks to be simple enough that it is believed to have the potential to reduce the transparent barrier costs because of reduced system capital costs.

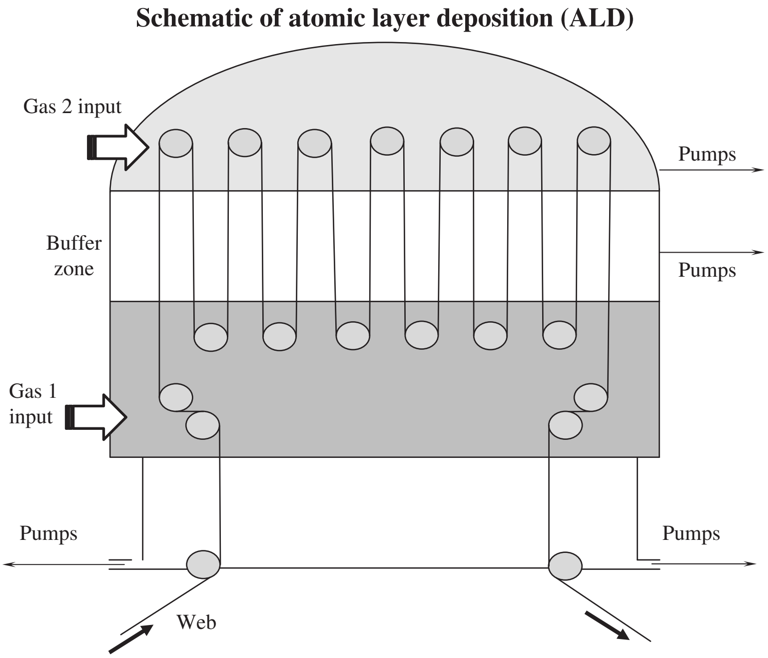


Figure 19.4 A schematic of an ALD process using winding geometry to build up the coating thickness.

As with CVD, the economics of this does also depend on having the appropriate gaseous precursors and at a reasonable cost. This also means that the precursor gases need to be in the low-hazard category, otherwise the gas-handling costs or pumping costs increase significantly. There has even been work done using an atmospheric ALD process [22,23] that offers an even greater opportunity to reduce costs.

References

[1] Suntola T, Antson J. Method for producing compound thin films. US patent 4058430; 1977.

[2] Sneck S. High capacity atomic layer deposition for industrial coating applications. In: Proc. 50th annual technical conference of Society of Vacuum Coaters; 2007. p. 36−8.

[3] Sneck S. Atomic layer deposition in mass production of optical coatings. In: Proc. 51st annual technical conference of Society of Vacuum Coaters; 2008. p. 413−6.

[4] Rajala M, et al. Increasing the glass cracking resistance by atomic layer deposition. ICCG7, June 15, 2008; p. 7−12.

[5] George SM. Atomic layer deposition: an overview. Chem Rev 2010;110(1):111−31.

[6] Levy DH. Spatial atomic layer deposition: high quality films on continuous substrates. In: Proc. AIMCAL fall technical conference and 23rd international conference on vacuum web coating; 2009.

[7] Barrow WA. Roll-to-roll ALD deposition of Al_2O_3 barrier layers on PET. In: Proc. AIMCAL fall technical conference and 23rd international conference on vacuum web coating; 2009.

[8] Cameron D. Towards a roll-to-roll ALD process. In: Proc. 5th Mikkeli international industrial coating seminar (MIICS). Finland: Mikkeli; March 17−19, 2010.

[9] Maula J. Latest developments in large scale ALD coating. In: Proc. 5th Mikkeli international industrial coating seminar (MIICS), Finland: Mikkeli; March 17−19, 2010.

[10] Heller CMA, et al. Systems and methods for roll-to-roll atomic layer deposition on continuously fed objects. US patent application no. 2007/0281089, World patent application no. WO/2008/057625.

[11] Ellinger CR, et al. Process for atomic layer deposition. US patent application no. 2009/0081842.

[12] Yudovsky J. Gas distribution system for cyclical layer deposition. US patent application no. 2004/0067641.

[13] Levy DH. Process of atomic layer deposition. US patent application no. 2007/0238311 and 2007/0228470.

[14] Visintin S, Golfetto E. An air-to-air feed through for vacuum coating of films. In: Proc. 3rd annual technical conference of the Society of Vacuum Coaters; 2010. p. 138−41.

[15] Sneck S, et al. Low cost large area moisture barriers by atomic layer deposition. In: Proc. 53rd annual technical conference of the Society of Vacuum Coaters; 2010. p. 296−302.

[16] Dickey ER, Barrow WA. Optimization of cycle elements for increased throughput in roll-to-roll atomic layer deposition. In: Proc. 53rd annual technical conference of the Society of Vacuum Coaters; 2010; p. 558−64.

[17] Wang J-C, et al. Highly efficient flexible inverted organic solar cells using atomic layer deposited ZnO as electron selective layer. J Mater Chem 2010,;20:862−6.

[18] Ghosh AP. Apparatus and method for encapsulating an OLED formed on a flexible substrate. US patent 6888172 2005.

[19] Groner MD, et al. Gas diffusion barriers on polymers using Al_2O_3 atomic layer deposition. Appl Phys Lett 2006;88(5):051907-3.

[20] Carcia PF, et al. Ca test of Al_2O_3 gas diffusion barriers grown by atomic layer deposition on polymers. Appl Phys Lett 2006;89(issue):031915-3.

[21] Kääriäinen TO, et al. Atomic layer deposition of metal oxide films as diffusion barriers on flexible packaging materials. In: Proc. 53rd annual technical conference of the Society of Vacuum Coaters; 2010. p. 93−7.

[22] Levy DH, et al. Oxide electronics by spatial atomic layer deposition. J Display Technol 2009;5:484−94.

[23] Fyson JR, et al. Fabrication of a patterned interference filter array deposited by an atmospheric pressure vapour deposition technique. e-J Surf Sci Nanotechnol 2009;7:284−9.

20 Magnetron Sputtering Source Design and Operation

In the design and operation of sputter source deposition systems, there are many aspects of the sputter sources that tend to get overlooked. It is worth delving into some aspects of the design and building of the sources to understand how the source operates and which features can affect the process.

The planar sputtering source with no magnetic enhancement has a high loss of electrons and so a poor ionization efficiency. The result of this is that the power supply to drive the source needs to deliver the required current at around 2 kV. The use of magnets enables trapping of the electrons close to the sputtering target. The electrons stay within the plasma for a considerably longer time and hence the chance of making ionizing collisions is very much greater. This increase in ionizing efficiency results in a denser plasma capable of carrying a much higher current at a significantly lower voltage. Thus, magnetron power supplies are capable of delivering a higher current at voltages less than 1 kV. The facility for 1 kV, or greater, is available for striking the plasma after which the voltage required is often in the range 500−750 V.

The sputtering rate is proportional to power and so the magnetron sputtering sources have significantly higher sputtering rates (10 nm/s/kW) than the nonmagnetron sources (<1 nm/s). This means that for most, if not all, roll-to-roll coating systems, only planar magnetron sputtering sources would be considered if sputtering were the chosen route to follow. As such, only magnetron sources will be described here.

20.1 DC Planar Magnetron Sputtering Source

Sputtering was first noticed when a potential was applied between two plates in a vacuum of around 20 Pa (150 mT). There was a glow discharge produced, and it was noticed that around the cathode the glass vessel became coated with the cathode material [1]. The plasma created contained ions and electrons; under the applied potential, the ions were accelerated to the cathode and the electrons to the anode [2]. The heavier ions when hitting the cathode eject material off the surface and it is this material that deposits to form the thin film coating [3−5]. This basic process has been developed to increase the efficiency and the deposition rate

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00020-9

of the process. Increasing the plasma density allows higher currents to be used with the resultant increase in the deposition rate. This can be done using an electron source to supply more electrons as in the case of triode sputtering systems [6,7] or by constraining the electrons using magnetic fields. As with any magnet, the magnetic material has a north and a south pole, and these are effectively linked by magnetic field lines to complete a magnetic circuit.

The magnetron circuit has the arrangement as shown in Figs. 20.1 and 20.2. The target material is placed across the front surface and the field lines trap the electrons near to the target surface. The target is also a cathode and hence there is a crossed electric and magnetic field, so there will also be a drift motion of electrons into the paper [7—10]. The magnets are arranged such that the electron drift path returns back to the starting point. This produces the characteristic plasma over the target surface and results in the racetrack erosion of the target (Fig. 20.3).

The maximum erosion is where the magnetic field lines are parallel to the target surface. The electrons spiral around and along the magnetic field lines. As the electrons approach the cathode surface, the negative charges repel and so the electrons are reflected back along the field lines. If the electrons undergo a collision, they will be knocked either closer or farther from the target surface. A proportion of them will be knocked far enough away that they are lost from the confined volume. All plasmas will have equilibrium of electrons generated to electrons lost. Modifying the magnet strength or the position of the poles will affect the magnetic field and change this equilibrium. At any given pressure, this equilibrium will define the voltage and current relationship of the magnetron source. The spiraling of the electrons along with them being reflected back and forth along the field lines means the electrons have a long average residence time in the plasma and a better chance of undergoing an ionizing collision.

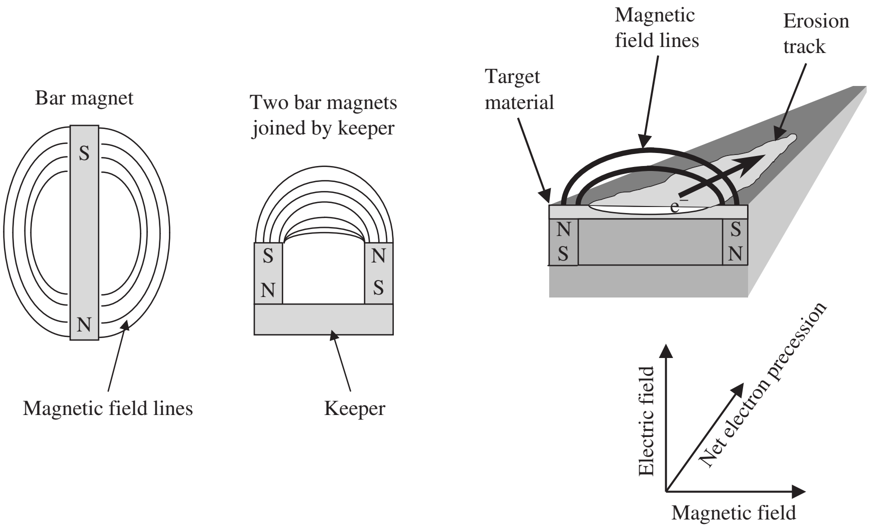
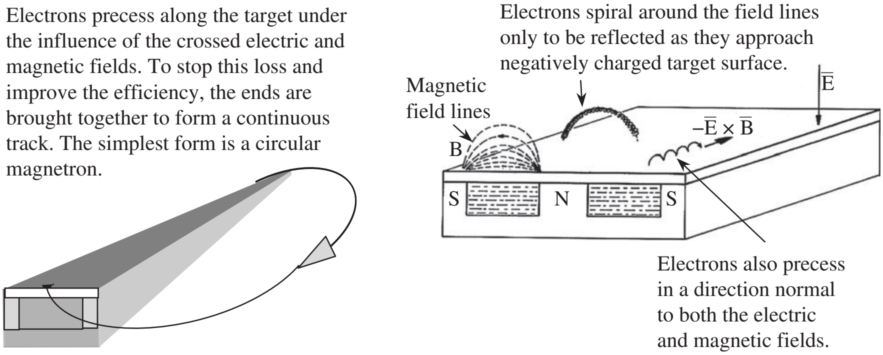


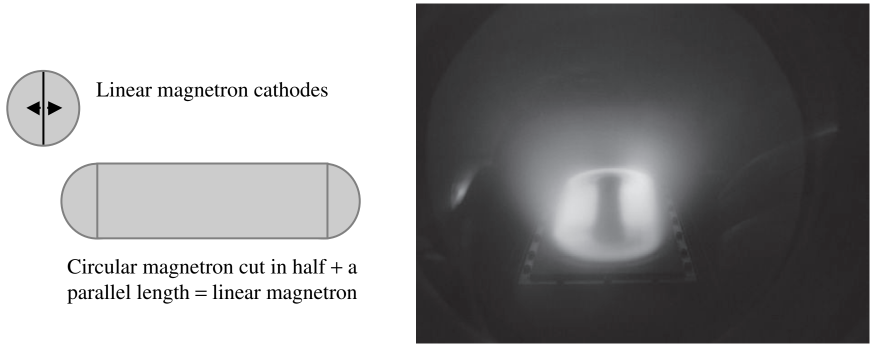
Figure 20.1 A schematic showing the field lines for different magnetic configurations.


Electrons precess along the target under the influence of the crossed electric and magnetic fields. To stop this loss and improve the efficiency, the ends are brought together to form a continuous track. The simplest form is a circular magnetron.

Electrons spiral around the field lines only to be reflected as they approach negatively charged target surface.

Electrons also precess in a direction normal to both the electric and magnetic fields.

Figure 20.2 A schematic showing how the magnets can be arranged to confine the electrons and so make a magnetron source.


Linear magnetron cathodes

Circular magnetron cut in half + a parallel length = linear magnetron

Figure 20.3 A schematic showing how a circular magnetron is extended to make a linear magnetron and a photograph of such a device in use. Photographs of large systems are used in the advertising literature of most of the major machine manufacturers [11].

Figures 20.4, 20.5 and 20.6 show different configurations of magnetron. Figure 20.4 has three cross sections with the top one (a) being the simplest design, and it can be seen that the erosion profile is a “v” shape. The material efficiency of this design is poor and may only be around 35%. The second design (b) shows how altering the position of the pole pieces modified the erosion profile of the target. This results in widening the erosion track and increasing the material efficiency to greater than 50%.

The third design (c) has the target sitting between the poles and shows the best material efficiency. This design, with deeper poles and the target material directly between the poles, has been used commercially for the sputtering of aluminum for coating compact discs. This has achieved a material efficiency of greater than 80%.

One of the trade-offs that is made in designing magnetrons is in the complexity of the shape and clamping of the target material. The first design is very simple and the targets require minimum machining. The second design requires more

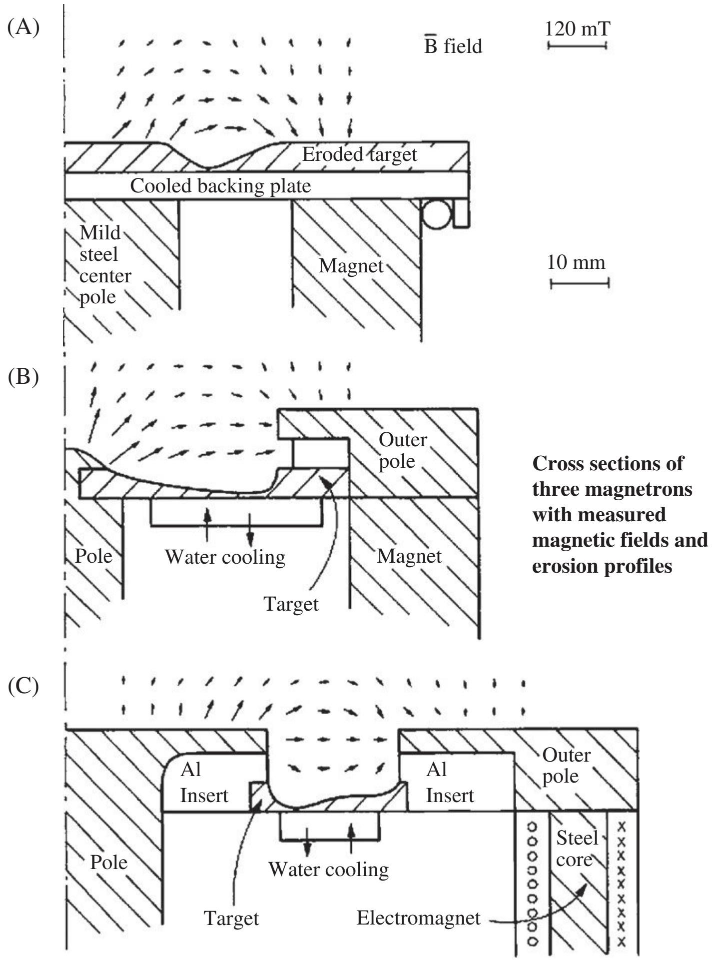
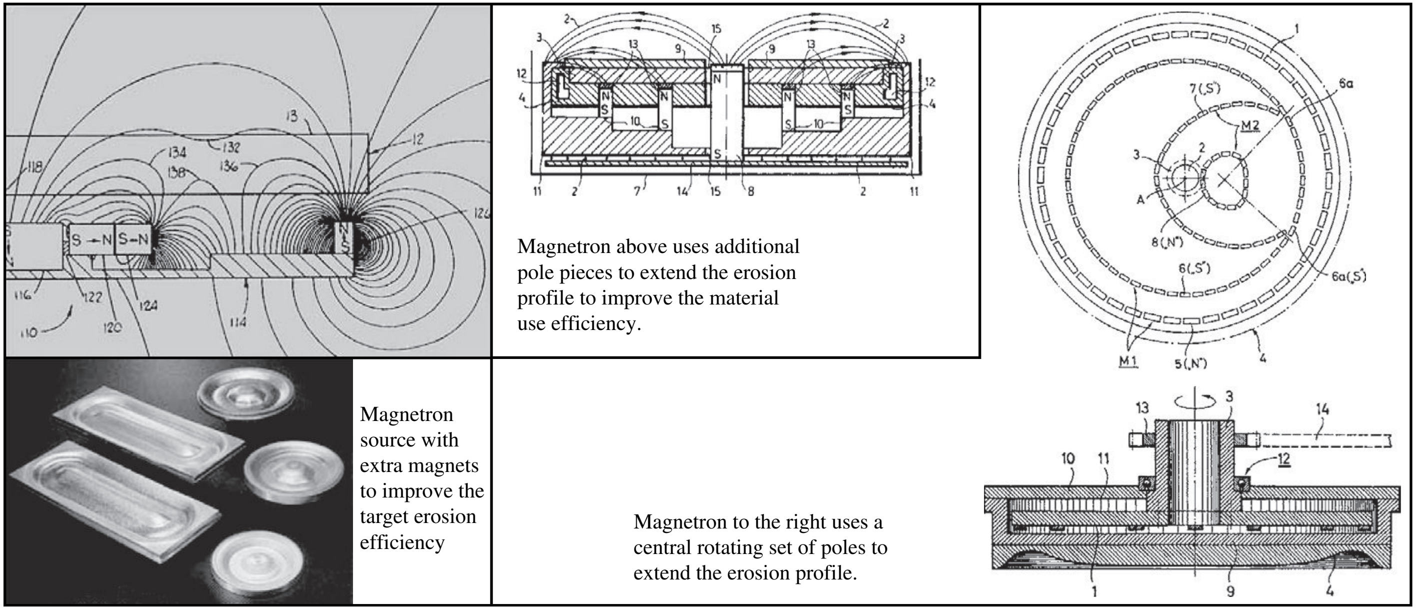


Figure 20.4 A schematic showing how changing the position and strength of the magnetic pole pieces can affect the field lines and hence erosion profile [12].

machining of the targets, and replacing the targets is more complex and takes longer. The cost of using each design will depend on the cost of the target material and the cost of downtime of the production machine. In some cases material efficiency is insignificant, whereas in others it is critical to the economics of the process.

The third design also shows the use of an electromagnet that allows for modifications of the field strength.

There are many ways of building magnetrons and different options on placing the magnets to alter the magnetic field and hence erosion track. A few examples are shown in Figs. 20.5 and 20.6 [13–23].

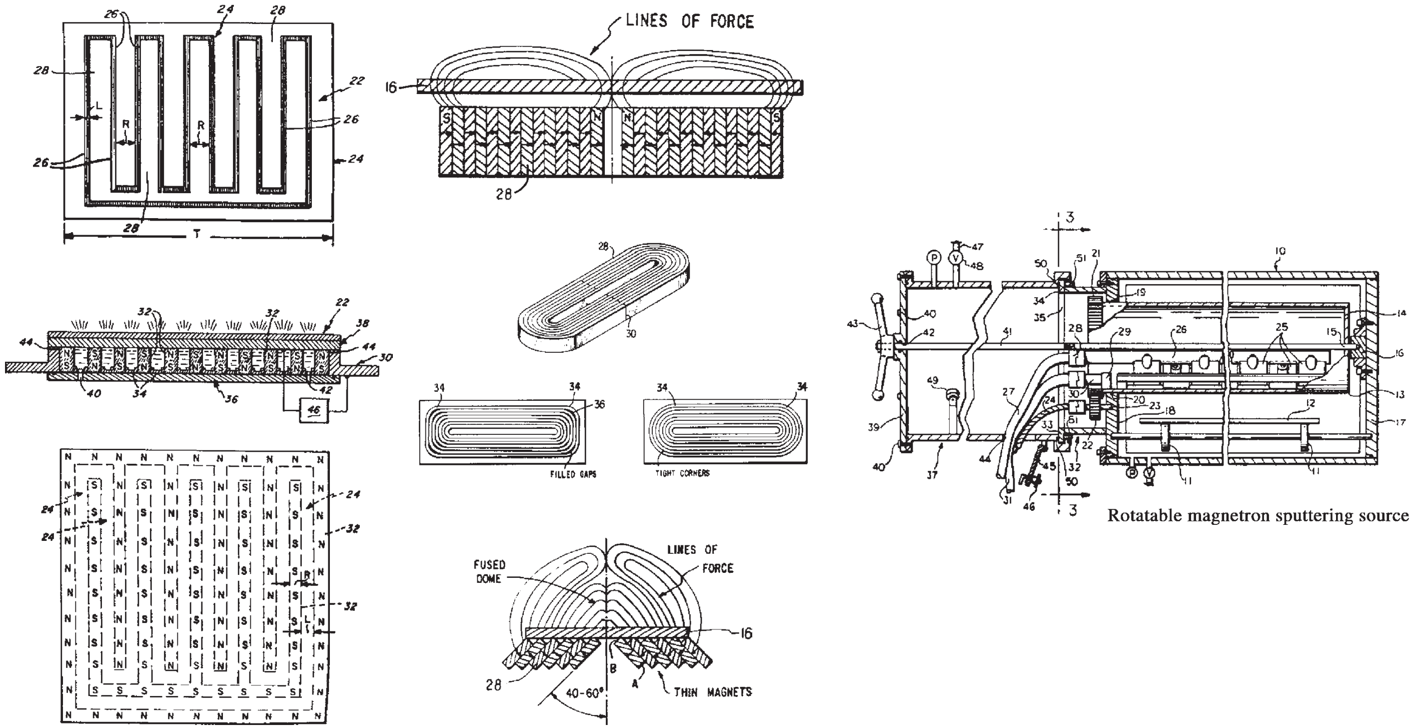


Magnetron above uses additional pole pieces to extend the erosion profile to improve the material use efficiency.

Magnetron source with extra magnets to improve the target erosion efficiency

Magnetron to the right uses a central rotating set of poles to extend the erosion profile.

Figure 20.5 Examples of different designs of magnetrons.



Rotatable magnetron sputtering source

Figure 20.6 Further examples of different magnetron designs including a schematic of the basic design of a rotatable magnetron that has proved popular in the large glass coating systems [24].

Figure 20.7 A photograph of a rotatable magnetron cathode. Courtesy of Applied Materials.

Other options are to move the target or the magnets to improve the erosion profile. The most widely used version of this technique is the rotatable magnetron design where the target is a cylinder and rotates around the rest of the magnetron design [25−30]. This boosts the material efficiency of a design that would otherwise be less than 50% up to 80% or better. This is shown in the right-hand side of Fig. 20.6. There is still the trade-off of the cost of producing cylinders of the target material against the higher material efficiency and possibly a higher deposition rate.

The rotatable magnetrons (Fig. 20.7) were developed to enable magnetic materials to be sputtered more effectively. A magnetic target material could short out the magnetic field. The target material can only be used at a thickness where the magnetic field strength is large enough to have some residual field, projecting beyond the target material to enable the magnetron to still operate. If the target were too thick, it would contain all the magnetic field and the source would revert to a plain diode-sputtering source with the need for a higher operating pressure and voltage and lower deposition rate. Using targets that were thin enough to allow continued operation as a magnetron gave the problem that the targets were eroded through very quickly needing frequent changes. This was not cost-effective. The move to rotatables allowed thin targets to be used, but because the erosion was spread across the whole of the cylinder circumference, the target lifetime was significantly extended, making the process viable.

Rotatables can also be used for web cleaning. If the web is passed around the target tube, using the tube as a roller, the web then becomes the new front surface of the target and will be sputtered. This gives a high-power physical etch of the web surface.

A novel design has recently been demonstrated that uses a remote plasma and an electromagnet that erodes the whole target surface without a racetrack. This gives much higher target erosion than conventional designs. This design is also ideally suited for sputtering magnetic materials. Initially, the design was only for a circular design of source, but recent developments have enabled a linear source to be used with similar success [31,32].

20.2 Balanced and Unbalanced Magnetron Sputtering

It has been seen how the magnetic field can be used to control the erosion track of the sputtering target. The magnetic field can also be used to control the bombardment that the substrate is subjected to. If the magnetic material and flux are matched, between the center pole and the outer pole, then most of the field lines that exit the surface at one pole will re-enter the surface at the other pole. This is known as a balanced magnetron. In effect, this maximizes the capture of electrons within the plasma and minimizes substrate bombardment. However, it is possible to mismatch the magnetic flux between the poles such that there are field lines that take the electrons away to bombard the substrate. This will give some substrate heating and bombardment during growth such that the thin film structure will be modified [33−39].

In Fig. 20.8, the right-hand photograph is of a 100 mm diameter unbalanced magnetron sputtering titanium metal. It can be clearly seen from the ionized material that there is a jet of electrons streaming from the center of the target. This energetic material was sufficient to carbonize the polymer web in a fraction of a second.

In polymer web coating, most applications need to have the heat loading of the polymer web minimized and so it is more likely that balanced sputtering cathodes are used.

A consideration needs to be given in the situation where more than one cathode is used in close proximity [40−43]. The cathodes could be built identically or they could have the magnets with the opposing polarity. All will work as sputtering sources; however, there is a choice of whether the two cathodes are magnetically coupled or not.

Figure 20.9 shows what happens when a non identical pair is used. This allows the stray field lines from one cathode to link to the adjacent cathode. This means that one cathode could collect electrons lost from other adjacent cathodes.

If the two magnetrons were identical, the electrons from both would be forced away by the field repulsion and there would be some increase in substrate bombardment. This pair would operate at a slightly higher voltage because of the overall greater loss of electrons.

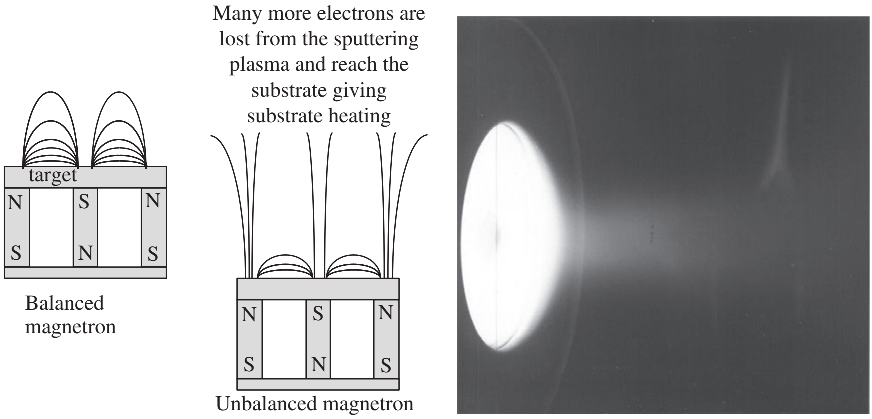


Figure 20.8 A schematic showing the difference between a balanced and an unbalanced magnetron and a photograph of an unbalanced magnetron in operation.

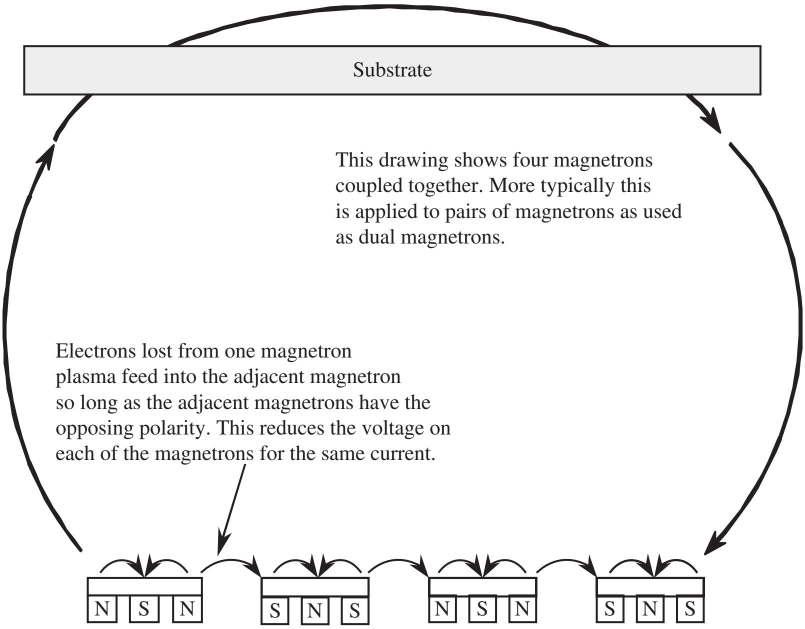


Figure 20.9 A schematic showing how adjacent magnetrons can couple together via fringing field lines.

20.3 Anodes

Another of the forgotten topics when the design of a system is considered relates to the anodes. To be able to sputter the target material, the magnetron source has an applied potential applied between it and an anode. This can be a specific anode, which may or may not be linked in some way to the chamber, which is allowed to float with respect to earth potential, or to an earth [44–47]. It is possible to have some peculiar electrical faults if there is not a properly established earth somewhere for the system. It is common to strap the chamber down to the earthing strip and to then use the chamber as the anode to the sputtering cathodes.

One of the problems that can occur during sputtering and, in particular, reactive sputtering is that the anode surface becomes coated [48–54]. This deposited material is likely to change the conductivity, and in the case of dielectrics, the surface will become insulating. Once the surface becomes insulating, the surface charge builds up and thus the anode disappears. The anode may then move somewhere else, thus changing the plasma. It is possible to use, as part of the magnetron design, an anode that is sited in an area where there is very restricted deposition. Even so, it is a good policy to clean the anode regularly to maintain the conductivity (Fig. 20.10).

In some very large magnetron designs, there is provision for a series of switchable anodes. The idea is that each of the anodes is used in turn for a short period of

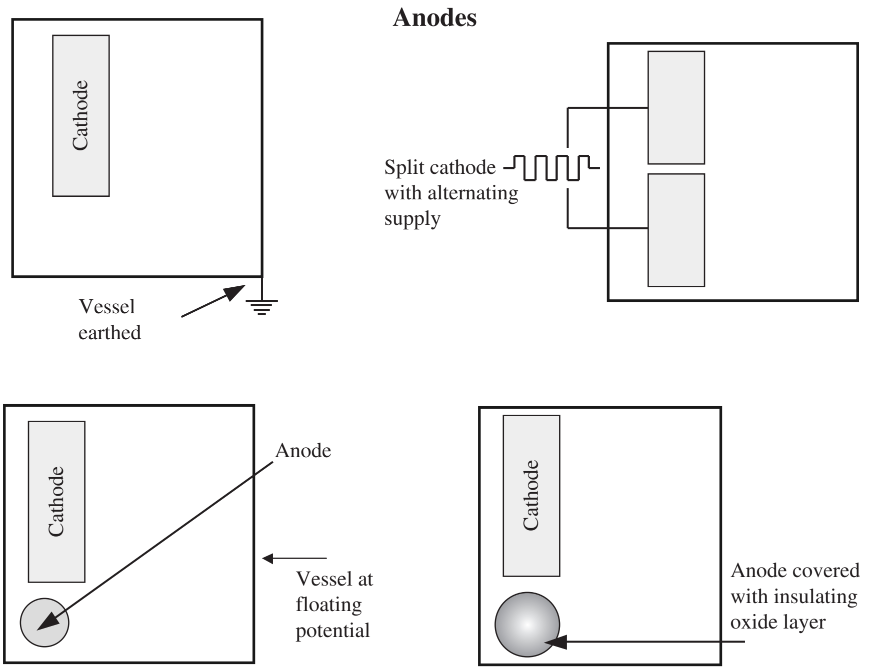


Figure 20.10 The above schematic shows four scenarios. The split cathode is attractive because it does not have the problem of the disappearing anode.

time. These anodes are of small surface area and the power passing through such small anodes causes them to heat up sufficiently to prevent deposition onto them. The need for a series of anodes is to share out the load and prevent the anodes melting, and the switching is performed fast enough that the plasma averages the position of the anodes such that it is equivalent to there being an anode the full length of the cathode.

Not controlling where the anode is within the system can mean that the plasma shape, density, and characteristic change as it moves between anodes. This may be seen as changes in the voltage and current. These changes could result in differences in the deposition produced.

It is always better to define parameters rather than have them as unknown variables.

20.4 Radio Frequency Sputtering

DC sputtering works well for conduction target materials but not for insulators. If a DC power supply is applied to a magnetron sputtering source with an insulating target, what happens is that the target is initially negatively charged and the ions are attracted to the surface starting the sputtering process. Now the target as it is initially bombarded by ions charges up the front surface and the nonconducting nature of the target stops the charge being dissipated. The charged front surface then acts to repel further ion bombardment of the surface and sputtering stops.

One method to improve the deposition rate from basic radio frequency (RF) sputtering has been to dope any nonconducting target to make it conducting enough to be able to use a medium-frequency switched-mode DC supply.

The basic RF process for the sputtering of dielectrics was to apply an RF power supply across the system [55—64]. This supply alternates the polarity of the applied power and the surfaces alternate between charging and discharging. There is a difference in the mass between the ions and electrons. The lighter electrons are much more mobile than the heavier ions. The electrons bombard the target much more than the ions. This results in the target surface building up a net negative charge and hence there is a net ion bombardment and sputtering can take place.

The downside of this is that for at least half the cycle, there is no sputtering, and so the deposition rate from RF sputtering cathodes is always low compared to sputtering from a DC metal cathode reactively. The trade-off that is often given is that it is easier and cheaper to sputter by RF than to do battle and control all the variables that can affect the reactive process when sputtering DC from the metal cathode.

20.5 Arcing and Control of Arcs

Arcing can be a problem and this tends to be much more so for reactive processes or when operating at high current densities.

The magnetron sources operate in the abnormal glow discharge region of the curve labeled “A” in Fig. 20.11. To get the maximum deposition possible from a

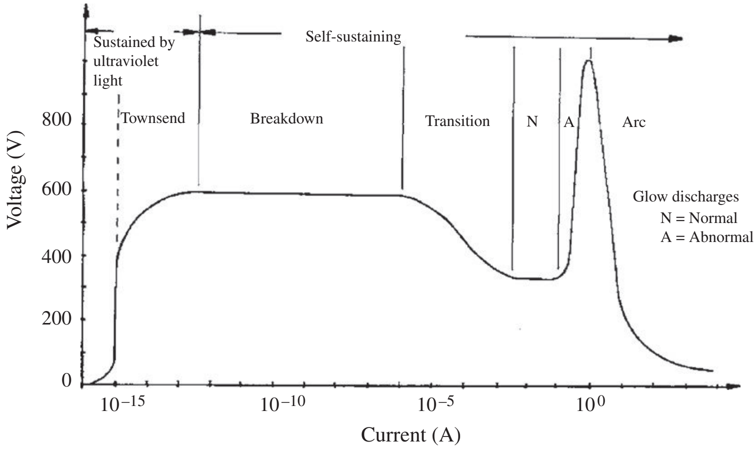
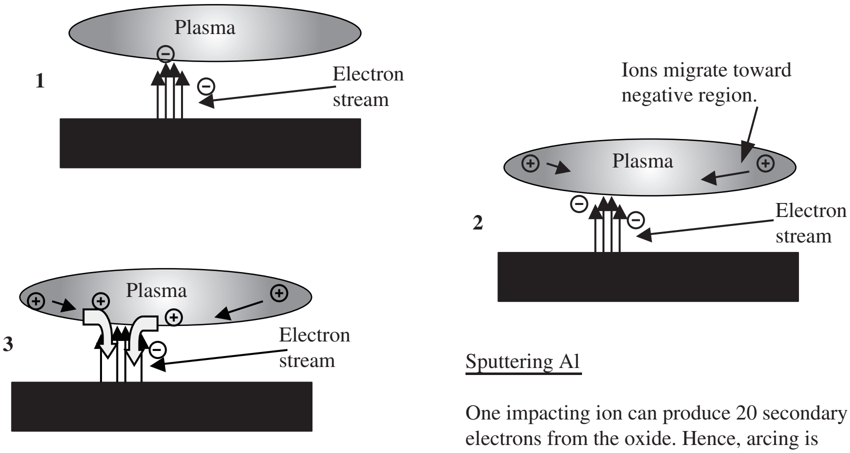


Figure 20.11 The graph showing the voltage versus current for a plasma.



Ions stream down and form arc.

Sputtering Al

One impacting ion can produce 20 secondary electrons from the oxide. Hence, arcing is a common problem.

Figure 20.12 A schematic of the steps that occur as an arc is started.

cathode, there is a tendency to drive the cathodes hard and so work toward the top of the abnormal part of the curve. This means that even a quite small perturbation to the plasma can move the characteristic over the voltage hump and into the avalanche process and so to form an arc. This voltage peak makes it impossible for the process to recover. It is only by extinguishing the arc that the magnetron sputtering abnormal plasma can be re-established [65−86]. During an arc, the whole of the plasma is focused on a single point with a lower voltage and much higher current density characteristic. Arcs can be established in a few microseconds. Arcs can be started by several mechanisms (Fig. 20.12).

Essentially, there needs to be a perturbation of the plasma caused either by heating or by some electronic charging of the surface. This localized charge on the target causes the ions to migrate through the plasma. This localized increased plasma allows the current to short between the plasma and the cathode in the form of an arc. These three steps are shown schematically in Fig. 20.12. The arc heats the target very rapidly, and this produces evaporation of the target material and also the emission of many more secondary electrons both of which allow the arc to be sustained very easily. Common sources of arc initiators are defects on the target surface. These can be either physical defects or inclusions in the target surface. If an inclusion sputters at a slower rate, then the metal around the defect is removed and a spike that concentrates the electric field around or onto the tip is left. Physical defects can be within the target material or can form on the surface by oxidation, from backscattered deposits or debris that falls on the cathode and that heats up from the bombarding ions. The backscattered material is not thermally well connected to the cooled target surface and so heats up more than the surface as a whole and may become a thermionic emitter. Some materials are worse than others for a propensity to arcing. In the case of aluminum, one of the worst, the oxide can emit

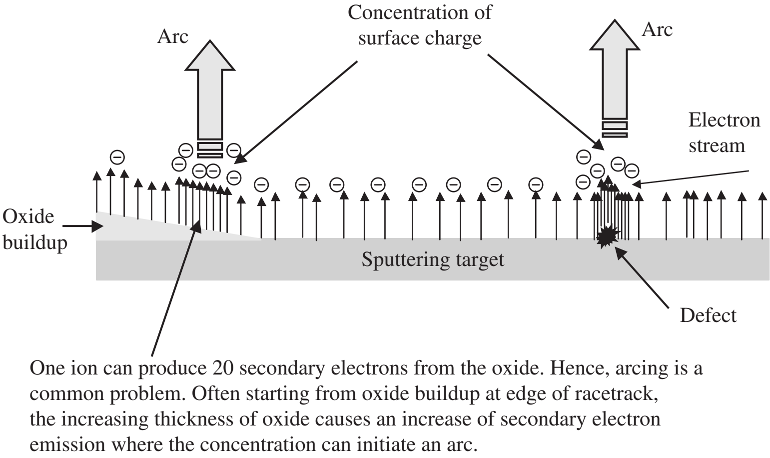


Figure 20.13 A schematic showing possible arcing sources on a magnetron target.

as many as 20 secondary electrons from the impact of one ion. Hence, at the periphery of the erosion track is a region of oxide buildup where even small defects can result in arcs.

Most metals oxidize and it is common for targets to suffer from considerable arcing until the oxide layer has been cleaned off the target at the start of sputtering (Fig. 20.13). It has been shown that an insulating film on a cathode under ion bombardment has a highly reduced strike potential for starting an arc. It is around 34 V for the insulating film but more than 6 kV for the metal surface.

The magnetron sources have the advantage of the presence of the magnetic field, which tends to make the arc move because of the electron precession caused by the crossed magnetic and electric fields. This has the benefit that the arc is dissipating the energy over more of the surface than if it were fixed in one spot. If the arc is to sit in one spot, the target at that spot would rapidly become molten, with the molten area increasing the longer the arc is sustained. The evaporation rate from this molten pool is sufficient that it effectively provides a metal vapor that produces a local high-pressure region helping the arc to continue in the same place. The arc, if it forms, has such a large energy associated with it that, in many cases, the defect that caused the arc to initiate is blown off the surface. If this happens, then when the arc is extinguished, it is unlikely to re-form from the same point (Fig. 20.14).

Modern power supplies monitor the voltage and current and can sense when an arc is forming. When this happens, the current is stopped and the arc decays and is extinguished at which point the current can be reapplied. If the source of the arc, such as a particle or molten pool, still remains, then it is possible that the arc will try to re-form and the sequence of cutting the current, reapplying the power, sensing the arc, and cutting the power will occur for a number of cycles. Some power supplies can produce a high-voltage pulse to try to blow off any particle-type defect

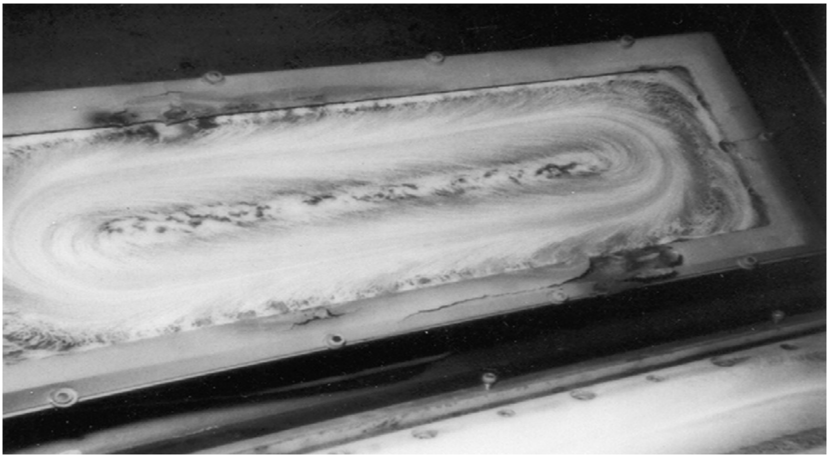


Figure 20.14 A photograph of a magnetron sputtering target that suffered badly from arcing.

that caused the repeat arc. There can also be the problem that if an arc has established, the temperature can have been raised enough to start thermionic emission sufficient to initiate another arc at the same site. Thus, the speed of sensing and cutting the power is many times faster than the speed at which the power can be reapplied.

Another feature that the more modern supplies have is that once they sense an arc is forming, they reverse the polarity and power the arc off rather than waiting for the normal decay of the arc following cutting the power. This makes the quenching process faster, and as there was less energy that could have heated the defect site, there is less likelihood of re-establishing the arc by thermionic emission.

The problem of the oxide formation on the periphery of the erosion track causing arcs has also been addressed. The dual magnetron, whereby two magnetrons are placed side by side, enables each magnetron to act in turn as the cathode and the anode. In the anode cycle, the surface that has become charged in the cathode cycle is neutralized. In this way, the surface charge never reaches a point at which there is sufficient field emission to initiate an arc (Fig. 20.15).

Other choices that are then presented are of a sinusoidal cycling of power between the two cathodes or to have the higher rate from a switched square wave (Fig. 20.16).

These switched-wave power supplies also offer the option of having two dissimilar elements in the two cathodes and to then sputter alloys [87]. It is then possible to change the duty cycle to change the alloy composition.

A further modification of these switched-mode power supplies is that the square wave supply can be applied to a single cathode, with most of the cycles being conventional polarity with a very short reversal of polarity used to discharge the dielectric surfaces. This is a proactive way of reducing the arcing of a cathode

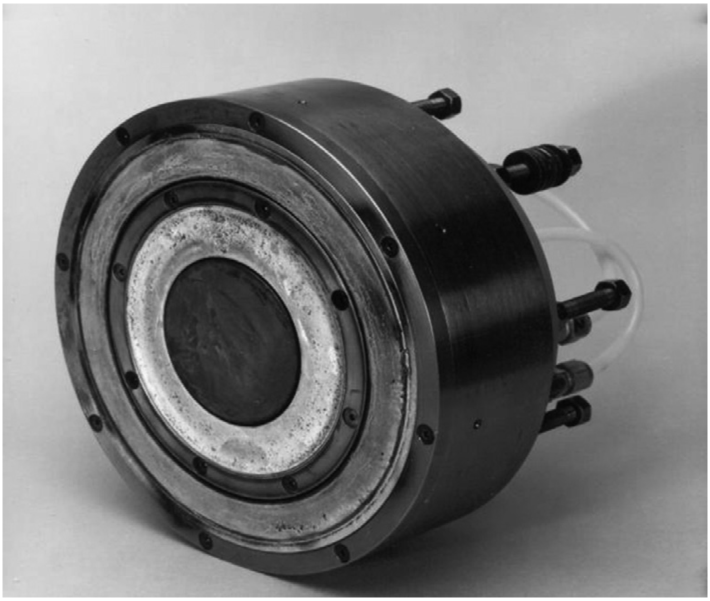


Figure 20.15 A photograph of a double circular magnetron as used to investigate different alloy compositions showing the targets after some use.

This system utilizes a plasma emission monitor to control the reactive sputtering process using fixed reactive gas flow and pressure and controlling the process by varying the sputtering power.

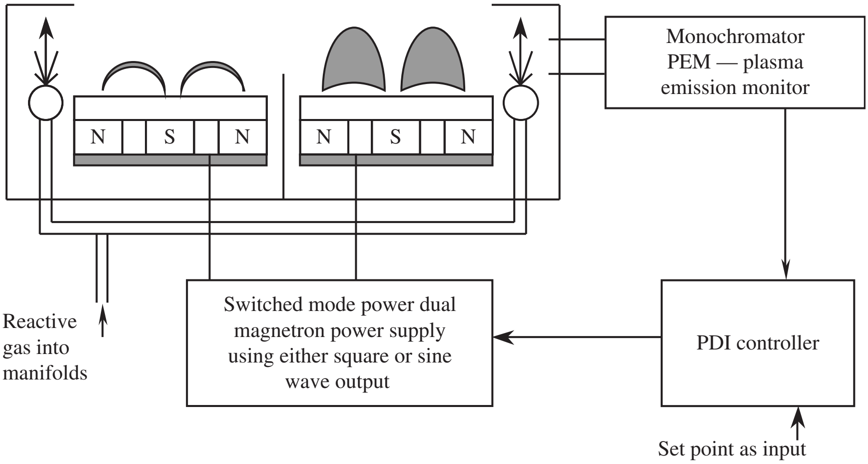


Figure 20.16 The figure shows a dual cathode with plasma emission monitor and control for reactive processes.

rather than waiting for the arcs to happen and then trying to react quickly. The duty cycle can be set such that there is very little power and hence rate lost, which is more than compensated for by the reduction in the number of arcs.

This reduction in arcing becomes critical in the deposition of transparent conducting oxides. The product is price sensitive and will become more so in future and hence has to be deposited as fast as possible. This tends toward sputtering by DC from the metallic targets that, over time, have an increasing number of arcs due to oxide building up at the edges of the erosion track.

When an arc occurs, this severely disrupts the stoichiometry of the growing coating that destroys the electrical conductivity. It may also take from a few seconds to minutes to recover the same conductivity. The web passing under the cathodes at this time is scrap but it is part of the roll of material. Either this has to be marked at the time of deposition as poor-quality material or it has to be rewound and marked at a later date. The customer then has to use either a variety of different length rolls or a single roll with intermittent good- and poor-quality material. Hence, for this very sensitive material, it is essential that the process is as stable as possible, and this is where the added cost of proactive arc reduction is of cost benefit. Coupled to this has to be quick and precise control of the gases. Monitoring the process in real time can give the quickest control signal even if the eventual response of the gases has a time lag. The most direct measurement of the process is by the plasma emission monitor [88–95].

The effectiveness of these power supplies has made it such that they are applied to systems to help them recover from poor design. If a system is designed with too little pumping such that during reactive deposition there is a hysteresis loop and the reactive process is inherently unstable, then it is possible to hide the problem by the use of one of these power supplies.

While it will allow reactive sputtering to be done and it will be faster than sputtering from a poisoned target, it will still be worse than having an inherently stable process. There would still be an advantage of using this type of supply on an inherently stable process in that it would still provide proactive arc management. The inherently stable system will recover from arcs but more slowly, and so these supplies give the extra stability and speed of recovery, further adding to the product quality.

20.6 Water Cooling

It has been estimated that as much as 75% of the input power to the magnetron source needs to be taken away by water cooling [96,97].

The water cooling serves several purposes. The primary use is to cool the target that is heated by the ion bombardment. This bombardment raises the front surface temperature of the target that is a source of radiant heat to the substrate. Cooling the back surface of the target reduces the radiant heat load (small as it is) and also prevents the target melting. In the case of some of the lower melting point materials, the target thickness is often limited by the thermal conductivity of the material.

If the thermal conductivity is poor, it means that the heat cannot be removed very efficiently, and hence there would be a large thermal gradient through the material thickness. If the target were too thick, this could mean the front surface could melt while the back surface would still be at the water temperature. An example of this is indium metal targets.

Targets that are brittle (e.g. chromium) or very soft (e.g. indium) would not be able to easily withstand the thermal or mechanical stress without problems of cracking or deformation. Brittle materials cracking or soft materials flowing can lead to water leaks, and so for these materials it is preferable to bond the targets onto a backing plate.

There are various methods of bonding, but if the target is to have the highest power density applied, it is essential that the bonding is done to a high standard. Many target suppliers will examine the bond to confirm that there are no gaps in the weld or solder that could produce a hot spot and sputtering problems.

Even with materials that are not brittle or soft, most users will prefer to have some form of separation between the target and water cooling. More details of the various options are given in the next chapter (Section 21.6).

It is possible to directly water cool the target, but the risk is that if the target erosion goes too deep, it will break through to the water and create a leak into the system. This can be managed by knowing the precise erosion rate and plotting it against the number of deposition hours and, using a suitable safety factor, stopping the process for a target change.

The other components of the magnetron source it is essential to keep cool are the magnets. There are many different magnets and combinations of magnets used in the design of modern magnetron sources. The most widely used is still likely to be ferrites, although more recently the use of samarium cobalt and neodymium iron magnets has enabled many more designs to be utilized. Most of the magnets are painted or otherwise sealed to prevent corrosion, and they are, in many cases, in direct water contact. The ferrites have a gradual loss of performance with increasing temperature, whereas the rare earth magnets have a more sudden magnetic failure if a critical temperature is exceeded. Thermally cycling magnets also leads to a decline in magnetic performance.

Most users of magnetron sources buy them and never check the magnetic performance on receipt of the source and periodically throughout their operating lifetime. It is likely that if they did, they would see that there would be an initial rapid decline in performance, followed by a smaller but steady decline with time. If at any time the magnetron suffered from a water-cooling failure, low flow, or anything else resulting in an excessive temperature rise, then there could again be a rapid drop in performance. Ferrites have a lower magnetic performance but are more tolerant of temperature and on cooling recover most of the performance back. The rare earths are more stable until the critical temperature is exceeded and then most of the power is permanently lost.

I am aware of only one user, with 3 m long and multiple cathodes on their production system, who, once per month, demagnetized and then remagnetized their cathodes as a way of ensuring a more consistent performance.

If we look at what happens during powering up a cathode, we can see that at any given pressure there will be an initial voltage and current. If the cathode is allowed to remain at the same setting, there will be a change in the voltage and current. Some of this will be caused by the cathode surface being cleaned of oxide and coming to some equilibrium state with regard to metal and oxide covered proportions. This change in surface state means that the secondary electron emission will change and hence the plasma density will change. If the power is turned up, the voltage and current will change, and again if there is time for the system to stabilize, there will be change in the electrical parameters. The magnetron cathode will also move toward some thermal equilibrium. The front surface of the target will be the hottest surface, with the deepest part of the racetrack the hottest region of the target. As the target is clamped to the body of the magnetron source, there is thermal conduction of this heat not only through the target to the cooling water behind but also to the rest of the body of the cathode. Depending on the design of the magnetron, the magnets may or may not be in direct contact with the target and also directly water-cooled. The magnets will rise in temperature and, depending on the materials and configuration, this may cause small changes decreasing the magnetic field that will result in additional electron losses. The net result of this would be a higher voltage needed to maintain the same current (Fig. 20.17).

As the temperature is raised, the efficiency of the magnetron declines and it is possible to reach a situation when all the increase in power results only in an increase in voltage. This indicates that there is insufficient cooling of the magnets.

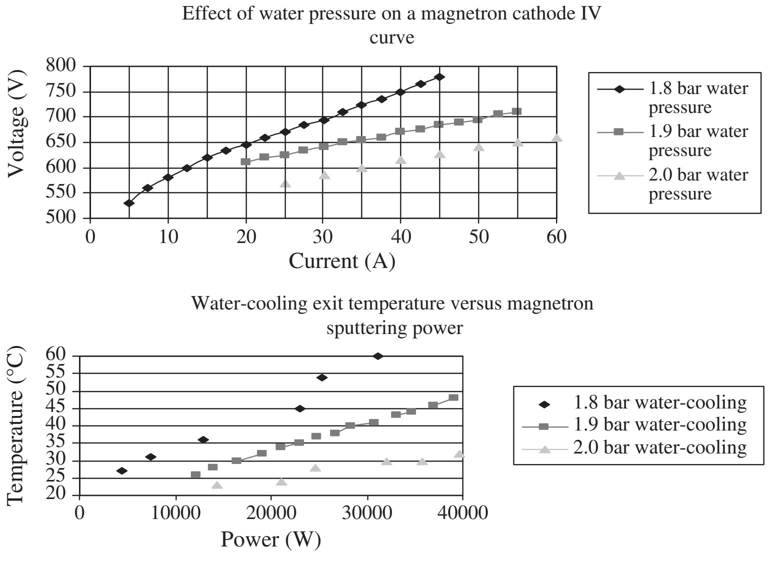


Figure 20.17 Graphs showing the effect of cooling water pressure on the available magnetron power and voltage.

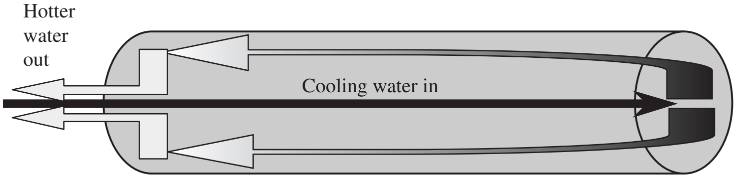


Figure 20.18 A schematic showing the potential problem of a temperature gradient on very long magnetrons.

The difficulty for large magnetrons of 3 m, or more, in length is to cool the whole of the target uniformly. If water is introduced at one point on the racetrack and passes round the whole of the racetrack before it exits, then the target at the exit point will be significantly hotter than at the entry point. This will be reflected in a difference in the magnetron characteristics that may result in different deposition rates. If water enters at one end and is extracted at the other end, this will give a different deposition rate between each side of the web, and for a reactive process, this would mean a different stoichiometry and coating performance. The longer the cathode or the higher the temperature difference, the greater the nonuniformity (Fig. 20.18). It is common for larger cathodes to have divided water paths to minimize the temperature gradients.

This is where the rotatable magnetrons can have a significant advantage over the planar magnetrons. The water cooling of the targets does not have to take place only behind the racetrack. The cylindrical nature of the target means that most of the cylinder can be in contact with the water, allowing the cooling to take place over a much larger surface area. This allows the target to operate at a much lower temperature than an equivalent planar. There is still the issue of having a thermal gradient from one end of the cathode to the other, but if the temperature is kept lower, this effect is reduced. Again, a divided water path can assist in minimizing thermal gradients.

What is important to all systems is to measure and record the water flow and input and exit temperatures as a matter of routine. It is common for there to be temperature fluctuations of the cooling water depending on the season. Frequently, there are other variations caused by having a water supply shared with other production equipments. This means that there can often be wide variations in both the flow and the temperature of the water, which, in turn, will affect the performance of the cathode. These variations may only be minor and irrelevant for some metallization processes; however, for other more sensitive processes, where stoichiometry control is critical, these parameters need to be tied down.

20.7 End Effects

Figure 20.19 shows how the deposition thickness falls off at the ends of a sputtering source.

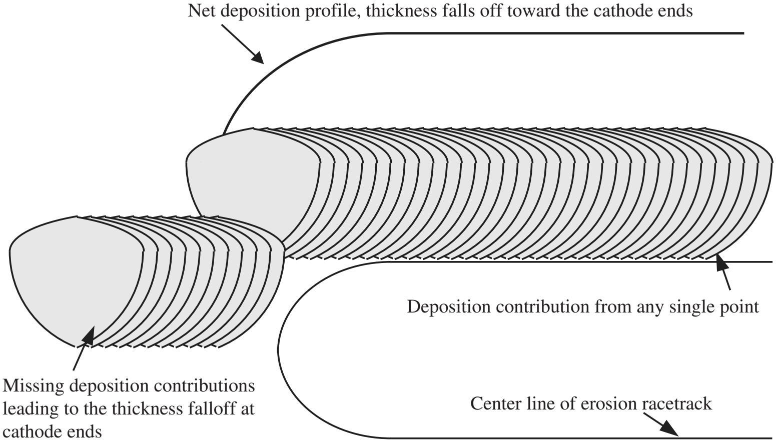


Figure 20.19 A schematic showing the drop-off of deposition rate at one end of a linear magnetron.

Magnetic field strength and position can be changed at the ends to try to compensate for the deposition falloff. The problem with this can be that with the increased erosion the target is worn through faster at the ends than at the rest of the target and this results in an overall reduction in efficiency of material use.

For web coaters, it is common to have cathodes that extend beyond the edge of the web. Typically, this extra length of cathode is one to two times the end erosion track radius (see Fig. 20.19).

20.8 Troubleshooting Magnetron Sputtering Sources

The common problems with sputtering sources can be grouped into failures in service and failure to restart following servicing.

Occasionally, there may be a design-related failure. One design philosophy was to never have a water-to-vacuum seal but instead to have a water-to-air seal followed by an air-to-vacuum seal. One result of this philosophy was that it was possible to have a small water leak for some time without it showing up in the cathode performance. Along with this, the mixture of materials in the construction and electric fields meant that an electrochemical cell formed and the corrosion of components was quite rapid. In fact, the water leak was eventually detected due to a component failure due to corrosion. This type of failure becomes very much more expensive than having a more simple design that allows the use of a water-to-vacuum seal. The water-to-vacuum seal, when it begins to fail, will have an immediate effect that is very obvious (Fig. 20.20).

Figure 20.20 A photograph showing the corrosion products, the white foam-like material, that has overgrown the "O" ring.

20.8.1 Failures in Service

This section covers problems such as surface oxidation causing arcing, loss of sputtering performance (rate), or loss of plasma.

If the process is reactive, then the target surface can oxidize. This oxide needs to be cleaned off prior to starting the process. This cleaning brings the target to a metal surface and a consistent starting point. From this common starting point, the reactive gas can be fed in, and a reproducible process point should then be achievable. If the oxide is not cleaned off, it may be that a high rate process can never be achieved because the reactive gas can be arriving faster than the oxide is removed.

Arcing can be due to a long-term accumulation of oxide creeping in from the edges. This oxide can reach thicknesses where it is nonconducting and then charges up disrupting the plasma and initiating arcs. This type of arcing could be reduced by the use of a switched-mode power supply to ensure the target surface was regularly discharged.

More severe arcs or even a loss of plasma altogether can be caused by flakes of material, either from the source or more likely from accumulated stray coating from deposition shields, falling onto the cathode surface or shorting out the cathode to the adjacent earthshields.

This type of catastrophic failure can rarely be fixed under vacuum. The exception is where a current surge is used on a sputtering source that heats and explodes the flake of material. This disintegration of the flake removes the short. This rarely works and is not to be recommended. The safer and more usual option is to open the system up and clean the source thoroughly.

Other reasons for loss of performance can be down to changes in services, such as loss of water pressure or flow. This can cause the temperature of the body of the magnetron source and, more particularly, the front surface of the sputtering target to rise. The rise in temperature of the front surface of the target can result in a change in the secondary electron emission, thus changing the voltage/current characteristic of the plasma and hence sputtering rate. The body of the sputtering source can also be a problem, depending on the thermal stability of the magnets. Magnets can change performance with temperature which usually means that, as they heat up, the magnetic strength declines. As the magnetic strength declines, the number of electrons captured by the magnetic field falls and then the voltage/current characteristic changes and the sputtering rate falls.

20.8.2 Failures Following Servicing

Many of these failures relate to errors during reassembly. The magnetron sputtering source design will determine how simple a target change is to achieve. Also, it will determine how frequently the source requires a more major overhaul.

Common problems are water leaks from joints that do not seat properly or have not been tightened sufficiently.

Magnets are either damaged by careless handling or even assembled in the wrong magnetic orientation. Magnets wrongly assembled may allow the plasma to be struck but run in an unstable manner, or it may not even allow the plasma to be struck because the magnetic path guides a sufficient number of electrons out of the racetrack.

Where arcing has occurred, it is essential to clean away any tracks to make sure there are no sharp edges, which could act as electron concentrators or, in the case of tracks on insulators, could be a conductive track that would act as a short circuit.

References

[1] Grove WR. On the electrochemical polarity of gases. Phil Trans Roy Soc London 1852;142:87−101.

[2] Wehner GK, Anderson GS. The nature of physical sputtering. In: Maissel L, editor. Handbook of thin film technology. McGraw-Hill; 1983 ISBN 0 07 039742 2 [chapter 3] Application of sputtering to the deposition of films; chapter 4, Maissel LI and Glang R. (reissue).

[3] Guentherschultze A. Cathodic sputtering—as analysis of the physical processes. Vacuum 1953;3(4):360 −374.

[4] Westwood WD. Glow discharge sputtering. Prog Surf Sci 1978;7:71−111.

[5] Greene JE. Epitaxial crystal growth by sputter deposition: applications to semiconductors. Part 1. CRC Crit Rev Solid State Matl Sci 1984;11(1):47−97.

[6] Ectertova L. Physics of thin films. 2nd ed. Plenum; 1986 ISBN 0 306 41798 7.

[7] Adachi R, Takeshita K. Magnetron sputtering with additional ionization effect by electron beam. J Vac Sci Technol 1982;20(1):98−9.

[8] Thornton JA, Penfold AS. Cylindrical magnetron sputtering. In: Vossen JL, Kern W, editors. Thin film processes. Academic Press, Inc.; 1978 ISBN 0 12 728250 5 [chapter II-2].
[9] Chapin JS. The planar magnetron. Res Dev 1974;25(1):37–40.
[10] Chapin JS. Sputtering process and apparatus. US patent 4 166 018; 1979.
[11] Versatility in thin-film technology. Airco coating technology promotional literature ASP1045M688; 1986.
[12] Thornton JA. Magnetron sputtering: basic physics and application to cylindrical magnetrons. J Vac Sci Technol 1978;15(2):171–7.
[13] Spencer AG, et al. The design and performance of planar magnetron sputtering cathodes. Vacuum 1987;37(3/4):363–6.
[14] Ferenbach D, Muller J. Magnetron sputtering cathode for vacuum coating apparatus. US patent 4 746 417; 1988.
[15] Class WH, et al. Magnetron sputtering target and cathode assembly. US patent 4 198 283; 1980.
[16] Boys DR. Sputter coating source having plural target rings. US patent 4 761 218; 1988.
[17] Morrison CF. Planar magnetron sputtering device. US patent 4 162 954; 1979.
[18] Morrison CF. Planar magnetron sputtering device. US patent 4 180 450; 1979.
[19] Garrett CB. Planar magnetron sputtering device. US patent 4 444 643; 1984.
[20] Kertesz G, Vago G. Penning sputter source. US patent 4 282 083; 1981.
[21] Penfold AS, Thornton JA. Electrode type glow discharge apparatus. US patent 3 884 793; 1975.
[22] Lamont Jr LT. Sputter target for use in a sputter coating source. US patent 4 457 825; 1984.
[23] Munz W-D, Wolf H. Method and means for controlling sputtering apparatus. US patent 4 426 264; 1984.
[24] Hill RJ, Nadel SJ. Coated glass: applications and markets. Fairfield, CA: BOC Coating Technology; 1999 ISBN 0-914289-01-2.
[25] Aichert H, et al. Magnetron cathode for sputtering ferromagnetic targets. US patent 4 572 776; 1986.
[26] Innis DT. Method and apparatus for changing sputtering targets in a magnetron sputtering system. US patent 4 519 885; 1985.
[27] McKelvey HE. Cathodic sputtering apparatus. EP 0 134 559; 1985.
[28] Wrigth M, Beardow T. Design advances and applications of the rotatable cylindrical magnetron. J Vac Sci Technol A 1986;2(3):388–92 Pt. 1.
[29] Kovilvila R. Sputtering apparatus and method. CA patent 1 239 115; 1988.
[30] Zega B. Cylindrical magnetron sputtering cathode, as well as sputtering apparatus provided with such cathodes. EP 0 045 822; 1982.
[31] Hockley PJ, et al. High density plasma deposition. In: Proc. 48th annual technical conference of the Society of Vacuum Coaters; 2005. p. 125–30.
[32] Hockley PJ, et al. A remote plasma sputter process for high rate web coating of low temperature plastic film with high quality thin films and insulators. In: Proc. AIMCAL fall annual conference and 19th international conference on vacuum web coating; 2005.
[33] Window B, Savvides N. Charged particle fluxes from planar magnetron sputtering sources. J Vac Sci Technol A 1986;4(2):196–202.
[34] Window B, Savvides N. Unbalanced DC magnetrons as sources of high ion fluxes. J Vac Sci Technol A 1986;4(3):453–65.
[35] Savvides N, Window B. Unbalanced magnetron ion-assisted deposition and property modification. J Vac Sci Technol A 1986;4(3):504–8.
[36] Munz W-D. Current industrial practices. The unbalanced magnetron: current status of development. Surf Coat Technol 1991;48:81–94.

[37] Kelly PJ, et al. Novel materials by unbalanced magnetron sputtering. Mater World 1993;March:161−5.

[38] Teer DG. Magnetron sputter ion plating. US patent 5 556 519; 1996.

[39] Kelly PJ, Arnell RD. Magnetron sputtering: a review of recent developments and applications. Vacuum 2000;56:159−72.

[40] Munz W-D, et al. A new concept for physical vapor deposition coating combining the methods of arc evaporation and unbalanced-magnetron sputtering. Surf Coat Technol 1991;49:161−67.

[41] Munz W-D, et al. A new method for hard coatings: ABS™ (arc bond sputtering). Surf Coat Technol 1992;50:169−78.

[42] Shidoji E, et al. A comparative study of an unbalanced magnetron with dielectric substrate with a conventional magnetron through the use of hybrid modelling. Plasma Sources Sci Technol 2001;8:621−6.

[43] Sieck P. Effect of anode location on deposition profiles for long rotatable magnetrons. In: Proc. 37th annual technical conference of the Society of Vacuum Coaters; 1994. p. 233−6.

[44] Gillery FH, Criss RC. Anode for magnetic sputtering apparatus. US patent 4 478 702; 1984.

[45] Gillery FH, et al. Anode for magnetic sputtering of gradient films. US patent 4 744 880; 1988.

[46] Sieck PA, et al. Anode structure for magnetron sputtering systems. US patent 5 683 558; 1997.

[47] Sieck PA, et al. Magnetron sputtering methods and apparatus. EP 0 674 337 A1; 1995.

[48] Belkind A, et al. Reactive sputtering using a dual-anode magnetron system. In: Proc. 44th annual technical conference of the Society of Vacuum Coaters; 2001. p. 130−5.

[49] Scholl R, et al. Anode problems in pulsed power reactive sputtering of dielectrics. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 169−75.

[50] Glocker DA. An estimate of potentials developed on coated anodes during pulsed DC reactive sputtering. In: Proc. 43rd annual technical conference of the Society of Vacuum Coaters; 2000. p. 87−90.

[51] Sieck P. Active control of anode current distribution for D.C. reactive sputtering of SiO_2 and Si_3N_4. Surf Coat Technol (Switzerland) 1994;68/69:794−8.

[52] Belkind A, Jansen F. Anode effects in magnetron sputtering. Surf Coat Technol 1998;99:52 −59.

[53] Scholl R, et al. Problems and solutions in reactive sputtering of dielectrics. In: Proc. 13th international conference on vacuum web coating; 1999. p. 153−64.

[54] Brauer G, et al. New approaches for reactive sputtering of dielectric materials on large scale substrates. J Non-Cryst Solids 1997;218:19 −24.

[55] Jackson GN. R.F. Sputtering: a review. Thin Solid Films 1970;5:209−46.

[56] Butler HS, Kino GS. Plasma sheath formation by radio-frequency fields. Phys Fluids 1963;6(9):1346−55.

[57] Tsui RTC. Calculation of ion bombarding energy and its distribution in RF sputtering. Phys Rev 1968;168(1):107−13.

[58] Lau SS, et al. Temperature rise during film deposition by RF and DC sputtering. J Vac Sci Technol 1972;9(4):1196−202.

[59] Savas SE, et al. Dummy load technique for power efficiency estimation in RF discharges. Rev Sci Instrum 1986;57(7):1248−50.

[60] Kohler K, et al. Plasma potentials on 13.56-MHz RF argon glow discharges in a planar system. J Appl Phys 1985;57(1):59−66.

[61] Steinbruchel Ch, et al. Diagnostics of low-pressure oxygen RF plasmas and the mechanism for polymer etching: a comparison of reactive sputter etching and magnetron sputter etching. IEEE Trans Plasma Sci 1986;PS-14(2):137−44.

[62] Norstrom H. Experimental and design information for calculating impedance matching networks for use in RF sputtering and plasma chemistry. Vacuum 1979;29(10):341−50.

[63] Gill MD. Sustaining mechanisms in RF plasmas. Vacuum 1984;34(3/4):357−64.

[64] Brouk V, Heckman R. Stabilizing RF generator and plasma interactions. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 49−54.

[65] Scholl R. A new method of handling arcs and reducing particulates in DC plasma processing. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 405−8.

[66] Anderson GL, et al. Circuit for detecting and diverting an electrical arc in a glow discharge apparatus. US patent 5 241 152; 1993.

[67] Christie DJ, et al. A novel pulsed supply with arc handling and leading edge control as enabling technology for high powered pulsed magnetron sputtering HPPMS. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 113−8.

[68] Rettich T, et al. Arc management in DC and MF generators for large area coating systems. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 237−40.

[69] Anderson GL. A new technique for arc control in DC sputtering. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 325−9.

[70] Segers A, et al. Arc discharges in the reactive sputtering of electrical insulating dielectrics. In: Proc. 45th annual technical conference of the Society of Vacuum Coaters; 2002. p. 30−5.

[71] Blondeel A, De Bosscher W. Arc handling in reactive DC magnetron sputter deposition. In: Proc. 44th annual technical conference of the Society of Vacuum Coaters; 2001. p. 240−5.

[72] Koski K, et al. Surface defects and arc generation in reactive magnetron sputtering of aluminium oxide thin films. Surf Coat Technol 1999;115:163−71.

[73] Milde F, et al. Experience with high power DC supplies with fast arc suppression in large area coating. In: Proc. 44th annul technical conference of the Society of Vacuum Coaters; 2001. p. 375−81.

[74] Scholl RA. Advances in arc handling in reactive and other difficult processes. In: Proc. 37th annual technical conference of the Society of Vacuum Coaters; 1994. p. 312−6.

[75] Sellers JC. Asymmetric bipolar pulse DC—an enabling technology for reactive PVD. In: Proc. 39th annual technical conference of the Society of Vacuum Coaters; 1996. p. 123−6.

[76] Grove T. Arcing problems encountered in sputter deposition of aluminium. In: Proc. 29th annual technical conference of the Society of Vacuum Coaters; 1986. p. 214−23.

[77] Blondeel A, De Bosscher W. Arc handling in reactive DC magnetron sputter deposition. In: Proc. 44th annual technical conference of the Society of Vacuum Coaters; 2001. p. 240−5.

[78] Scholl RA. Process improvements for sputtering carbon and other difficult materials using combined AC and DC process power. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 391−4.

[79] Scholl RA, et al. Problems and solutions in reactive sputtering of dielectrics. In: Proc. 13th international conference on vacuum web coaters; 1999. p. 153−64.

[80] De Bosscher A, et al. Global solution for reactive magnetron sputtering. In: Proc. 3rd international conference on coatings on glass; 2000. p. 59−76.

[81] Rettich T, Wiedemuth P. MF, DC and pulsed DC in the use of large area coating applications on glass. In: Proc. 3rd international conference on coatings on glass; 2000. p. 97−105.

[82] Brauer G, et al. Mid frequency sputtering—a novel tool for large area coating. Surf Coat 1997;94–95:258–62.

[83] Schneider JM, Sproul DM. Reactive pulsed DC magnetron sputtering and control. In: Glocker DA, Shah SI, editors. Handbook of thin film process technology. Bristol and Philadelphia: Institute of Physics; 1998; Section A5.1.

[84] Este GO, Westwood WD. AC and RF reactive sputtering. In: Glocker DA, Shah SI, editors. Handbook of thin film process technology. Institute of Physics; 1998; Section A5.2.

[85] Schatz DS. The MDX^{TM} as a strategic tool in reducing arcing, 1985; Grove TC. Arcing problems encountered during sputter depositing of aluminium, 1986; Harpold J, Scholl RA. How Advanced Energy$^{®}$ MDX^{TM} products manage arcs, 1993; Scholl RA. Power supplies for pulsed power technologies: state-of-the-art and outlook, 1999. Applied Energy Industries Inc. application notes.

[86] Sellers J. Asymmetric bipolar pulsed DC. ENI$^{®}$ technical note, 1985; Using the RPG generator. ENI$^{®}$ technical note; 1996.

[87] TwinMag—the art of coating—the new generation of sputtering technology. Leybold systems sales literature 014.5.60.22.052.02 3.09.96 (+ others).

[88] Schiller S, et al. Fully automated control of reactive sputtering processes in web coaters by integrated PEM stabilisation. In: Proc. 1st international conference on vacuum web coating; 1987. p. 54–61.

[89] Greene JE. Optical spectroscopy for diagnostics and process control during glow discharge etching and sputter deposition. J Vac Sci Technol 1978;15(5):1718–29.

[90] Strumpfel J, et al. Production of optical multilayers on webs for AR application by means of reactive dual magnetron sputtering. In: Proc. 11th international conference on vacuum web coating; 1997. p. 279–89.

[91] Fraval RH, Angus R. A novel optical spectrum analyser for plasma process monitoring. CEP Consultants Ltd Edinburgh, London; 1986 Proc. IPAT workshop ‘semiconductor technology—thin film production and properties’; June.

[92] Cilia M, et al. Optical emission spectroscopy study of the radio-frequency magnetron discharge used for the fabrication of X-ray multilayer mirror. Thin Solid Films 1998;312(1/2):320–6.

[93] Schiller S, et al. Application of plasma emission spectroscopy for process control in reactive D.C. high-rate plasmatron sputtering. Thin Solid Films 1983;108: Proc. international conference met coatings apl; 1983.

[94] Enjouji K, et al. The analysis and automatic control of a reactive D.C. magnetron sputtering process. Thin Solid Films 1983;108:1–7.

[95] Rossnagel SM, Saenger KL. Optical emission in magnetrons: nonlinear aspects. J Vac Sci Technol A 1989;7(3):968–71.

[96] Hill RJ. Physical vapor deposition. Temescal A division of the BOC Group, Inc., Berkeley, CA 94710. 2nd ed. 1986; Part no. T-0186-6001-1.

[97] Vossen JL, Kern W. Thin film processes. Academic Press; 1978 ISBN 0-12-728250-5.

[98] Westwood WD. Sputter deposition. American Vacuum Society, NY 10017; 2003; HB-2.

21 Magnetron Sputtering Source Design Options

Most of us simply buy a magnetron from a supplier or system manufacturer without necessarily understanding the subtleties of the design. Some magnetron suppliers now offer a service of exhibiting a model of their design showing magnetic field, erosion pattern, and predicted coating uniformity and deposition rate [1,2]. Not all magnetron suppliers are the same nor are their designs, and so it is worth trying to understand some of the compromises that might have to be made between designs.

The first task is to decide on your aims. This includes not only the specification but also those that affect the marketing strategy.

Some of the questions that you might think about asking might be as follows:

- Do you want to produce a “me too” design and price it at a “me too” price?
- Do you want to produce the “best” magnetron for each application, customizing the design with the concomitant price implications?
- What type of magnetron do you wish to design? That is, is it a design with the maximum target utilization, maximum deposition rate, minimum target cost, minimum web damage, minimum cathode build cost, minimum arc rate, maximum deposition uniformity, and DC and/or RF use?

Some of these features are mutually exclusive. The simplest cathode to build will not have the best target utilization. To spread out the magnetic fringing fields to get the target utilization will make the magnet positioning more complex. To get the minimum target cost will mean no target machining costs, and to clamp this in place is more complex than if machining the target and clamping it directly. Minimizing the arc rate will mean using a dual magnetron type of source that again will be more complex than using a single source.

There will be some other options that need a decision to be taken, such as:

Single or dual magnetron?
Including an anode or not?
Balanced or unbalanced magnetic confinement?
Fixed or variable magnetic performance?
Internal or external mounting for the source?
Direct or indirect cooling?
Single or multiple materials?

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00021-0

With multiple magnetrons are they magnetically linked or not?
Planar or rotatable?

Some of the issues in the above list are discussed to highlight what options are available and how the performance is affected.

21.1 Single or Dual Magnetron Sputtering Source

When sputtering from a target, there will be parts of the surface that are not sputtered or sputtered at a very slow rate. There will be backscattered material that will attach to the surface, and when the sputtering rate is slower than the deposition rate, there will be an accumulation of this material. This material is often powdery and can become a source of arcs. The metal deposited will be oxidized and will be poorly conducting and hence can charge up and become a good arc initiator (Fig. 21.1).

The dual source uses a pair of magnetrons placed adjacent to each other. Both cathodes are of the same metal. A common power supply is switched between the two targets making each, in turn, the cathode and the anode. This ensures that any powdery, usually oxidized, nonconducting material that accumulates around the racetrack edges and that is charged up due to the ion bombardment will then be discharged by the electron bombardment in the next half cycle. Thus, the neutralization on each half cycle prevents the charge from building to a point where an arc will be initiated, thus the propensity to arcing is minimized.

21.2 Anode Included or Not

This choice is complex. Many systems rely on the whole of the system (chamber and fittings) being the anode to the magnetron cathode. The anode is prone to changing during the process. As the anode surface becomes coated and oxidized, the effective area of the anode changes. This change in area can change the anode

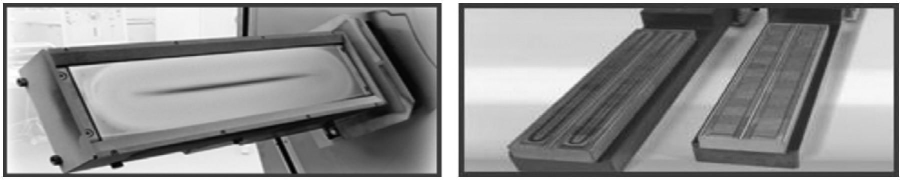


Figure 21.1 On the left-hand side is a single planar magnetron source and on the right-hand side a pair of dual magnetron sputtering sources, with the one on the right being new and that on the left having been used and showing the erosion racetracks.
Photographs courtesy of Applied Materials.

potential and hence can make changes to the plasma density. These changes are often small and would not be noticed for many operating hours, if at all.

One of the options of greater interest is to have a specific anode that is separate to the system earth. The aim of this is to make the magnetron plasma better defined and more reproducible. It does, however, rely on being able to keep the anode clean. This is problematic in that anodes close to the cathode will also get scattered sputtered material and the arrival rate will be of the same order as that of the contaminating gases such as oxygen or water. Hence, the depositing material will most likely be nonconducting.

There are a number of different strategies for keeping the anode clean. This has relatively simple solutions such as switching between separate anodes or by choosing the anode shape to be small and pointed so that the end heats and/or melts, thus preventing deposition on the hot surface. A slightly more complex system requires feeding a gas through the anode so that the net gas flow is from the anode, and this reduces any contaminating deposition onto the anode.

21.3 Balanced or Unbalanced Magnetic Fields

It is possible to design the magnetic circuit in a variety of different ways. If the design is such that the electrons are well confined and the electron losses are minimized, the design is thought of as balanced. Alternatively, if the design is chosen where some of the electrons are collimated and allowed to escape to bombard the substrate, the design is said to be unbalanced. The well-confined version will operate at a lower voltage, for the same operating current, than the less well-confined one.

It is more common, where the deposition is onto polymer webs, to require the system to be balanced to minimize the heat load on the web. When the substrate can tolerate the higher bombardment and heat load, the unbalanced design gives the advantage of depositing the coating at a higher temperature and with increased bombardment without the need to invest in a secondary plasma.

21.4 Fixed or Variable Magnetic Performance

There are magnetrons in which changes can be made to the magnetic field without having to rebuild the magnetron.

One simple version of this was where the magnetic keeper plate linking the outer and inner magnetic poles could be pulled away from the magnets. As the keeper was moved away from the magnets, the front field strength above the target fell and the plasma moved away from the cathode surface. The sputtering rate fell but the plasma bombardment of the substrate increased. Thus, the coating growth rate fell but the substrate temperature and the thin film density increased.

Another variable magnetic performance technique was used to increase the target utilization. This was done by oscillating the center pole piece making the racetrack move, widening the overall racetrack, and thus increasing the amount of the target sputtered.

A third option to enable a change in the magnetic performance is by the use of electromagnets. By passing a large current through a coil of wire, it is possible to induce a magnetic field down the axis of the coil. By placing a suitable bar down the axis, the magnet can be used as part of the magnetic circuit of a magnetron source. Using multiple coils distributed around a magnetron, the magnetic performance of either the inner, outer, or both coils can be modified. This allows the balanced or unbalanced operation to be changed during the deposition process.

This can have advantages in that it is possible to maintain the same magnetic performance every time even if the permanent magnets are slowly changing with use. The difficulty is in measuring the performance to provide the most suitable feedback.

21.5 Internal or External Fitting

This is a relatively simple option. The internal fitting magnetron can be sited anywhere inside the vacuum vessel. The external fitting magnetron has an integral flange that mates up with the outside wall of the vessel and the cathode pokes through a hole in the vessel wall facing inward into the center of the vessel.

The external fitting makes the positioning of the cathodes quite limited and the system design may then be limited to having the vessel wall concentric to the deposition drum. The internal magnetron design option is more versatile but requires water-cooling connections made within the vacuum vessel. These connections are regarded as a potential source of leaks and downtime.

A compromise design is to have semi-rigid water connections where the pipes pass through a vacuum seal, and the joint, where most of the disconnections are made, can then be sited outside of the vacuum system. This minimizes, but does not eliminate, the risk of leaks.

21.6 Direct or Indirect Cooling

There is a choice of cooling the target directly or indirectly. Some materials dictate the choice because they are either too weak or too brittle to risk using them with direct cooling. Direct cooling means that the cooling water is in direct contact with the back face of the target material that is being sputtered from the front face. Indirect cooling is where the water cools a metal plate and the target material is in contact with the cooled plate. This can be done in different ways. One way is to use a very thin deformable metal membrane that is of a tough material such as stainless steel. The water pressure will press the stainless steel sheet hard onto the back face of the sputtering target. Variations of this can be to provide crushable packing between the stainless steel membrane and the target. This crushable metal allows for variations in the pressure of contact between the target and the metal membrane. Sometimes this crushable material is a lead solder. The theory is that if the contact is poor and a hot spot develops, the solder will melt and immediately the thermal contact and heat transfer coefficient will improve and the temperature will fall and the solder will solidify. Another way is to weld or solder the target material onto a backing plate and then to directly cool the backing plate. The soldering guarantees the good thermal contact. The backing plate is often made of a material that has a high thermal conductivity such as copper.

The use of backing plates, such as in the case where the target material is brittle, can be essential. The thermal shock of having a high level of ion bombardment creating a high front surface temperature with a cold back surface temperature can easily fracture brittle materials. Added to all of this would be the pressure difference between the water-cooling pressure on one side of the target and vacuum on the other side helping to bend the target.

The argument against direct water cooling the target is that if the erosion of the racetrack is taken too far then the water pressure will be too much and the water will break through into the vacuum and cause a major process shutdown. The reality is that the breakthrough is quite slow and there are indications from the pressure gauges that give ample warning of the problem beginning to occur. The alternative view is that if the erosion had instead gone through to the backing plate, there would be no water leak to the system; however, the roll of product just completed would potentially all be scrap. Depending on the product, the contamination of the coating by partially sputtering the backing plate may cause it all to fail the quality control. Thus, the cost would be at least as much as a system shutdown because of a water leak. Backing plates take up space and move the front surface of the target further away from the magnetic confinement. This can be seen as the voltage and current characteristic being different at the start of using a target to the characteristic just before it fails. This will happen with most designs but is more exaggerated the further away the front surface is. Eliminating the backing plate either enables a thicker target to be used or helps reduce changes in performance from the varying magnetic field over the target's lifetime. For materials such as indium tin where the thermal conductivity is poor, the target thickness can be the limiting factor in the deposition rate. Adding a backing plate will reduce the deposition rate, and, to such a cost-sensitive process, this will increase production costs. The cost of bonding targets to backing plates should also not be ignored as the bonding and verification of quality can be a significant part of the target cost.

21.7 Single or Multiple Materials

There is an option of depositing alloys using concentric or parallel cathodes. Once upon a time the cathodes needed to be electrically isolated and independently powered. Now, with the availability of switched power supplies, it is possible to alternate between the two materials and change the waveform or period for each of the materials to control the alloy composition.

21.8 Linked or Isolated Cathodes

If there is more than one cathode sited close together, there is a choice of either running the cathodes completely separate to each other or linking them magnetically.

If both of the cathodes have north poles as the outer magnet then the fringing fields will repel each other and the plasmas from each of the magnetrons will remain isolated.

If one of the cathodes has a north pole as the outer magnet and the other has a south pole as the outer magnet, the fringing fields of the two cathodes will link together. This means that some of the electrons lost from one of the magnetrons will be gained by the linked adjacent plasma and vice versa. This also means that both the plasmas will operate at a lower voltage for the same current setting compared to if the poles had been identical and the electrons lost to both plasmas.

This linking of the plasmas does tend to mean the plasmas will be stretched and larger than the disconnected case.

21.9 Cost Implications

The cost of the magnetron and the cost of the targets can be a feature of the design.

The simplest and hence cheapest target, of any given material, is a plain flat sheet of the target material. The target material needs to be clamped to the magnetron body, and for a plain sheet of material, this requires a clamping ring. The clamping ring has to overlap the target to apply pressure to hold the target, and so the material under the clamp cannot be sputtered and hence the material utilization goes down.

The next simplest target design is to drill holes in the target material and bolt the target down directly. This requires counterbored holes to allow for the bolt heads to be sunk below the target surface. The bolts should not be sputtered to prevent contamination of the coating and so the bolts are outside the racetrack, and this again makes the material utilization poor.

Another common occurrence is to also bolt the target down the center too. This is to prevent the target from bowing out under the combined forces of water pressure, vacuum, and bending due to thermal gradients. These bolts also are usually designed to be in a zone that is not sputtered, making the target utilization worse.

The next simplest type of target is where the plain target material is bonded onto a backing plate, and it is the backing plate that is machined to be clamped to the magnetron. The backing plates can be reusable by unsoldering the old target and soldering on a new target.

The final group of targets are those that are machined to complex shapes. The utilization of the complex shape can be very high (>80%, even on some designs >90%), but this high value tends not to include the material that was machined away in making the target in the first instance. The machining costs can be very high for some of the more difficult materials.

For a very expensive target material and where it is costly to recover the remains of a used target, it may be preferable to aim for a design with a very high material utilization. For the cheap target materials, it may be more cost effective to have a simple design that has a very fast target change time and is inherently cheap to manufacture but with only a modest target utilization.

It may be a selling point to show comparisons of the two types showing the capital cost and revenue cost for a low- and high-cost target material, demonstrating the difference in economics.

21.10 Coating Uniformity

There are different ways of gaining coating uniformity across the web/foil. The simplest by far is to build the magnetron longer than the web width. Ideally, the web width will be approximately the same length as the parallel part of the racetrack, and the semicircular ends of the racetrack will overlap the web. This again makes the target utilization worse.

Typically, where the racetrack curves round at the magnetron ends, the track narrows and deepens and the resultant deposition rate falls off. Unless the magnetron target is significantly longer than the web width and so overlaps the web edges there will be no contribution to the deposition from beyond the web width and so there will be a fall off of the coating thickness towards the web edges. This is analogous to the fall in deposition rate above the end resistance-heated boat.

The methods of increasing the rate at the magnetron ends are to move the magnets further apart and increase the strength slightly. This effectively widens the racetrack back out again. Sometimes the magnets are also arranged to spread the racetrack at the ends to make the overall shape of the racetrack more like a dog-bone shape. This increases the deposition rate above the ends, but as there is no additional deposition from wider out, it balances out to being similar to that above the more central parallel region. The downside of this modification at the magnetron ends is that the erosion may be faster and the target may need to be changed earlier because the ends have eroded away before the central zone. The advantage of this type of modification is that the magnetron length can be made nearer to the web width.

A simpler modification is to shield the deposition to block off some of the deposition from the central region while allowing the maximum deposition from the ends. This will bring down the overall running speed of the process and will affect the annual output from the machine. This, again, is where a cost model is needed to check out the implications of such changes.

21.11 Magnets

The choice of magnets, to some extent, depends on the magnetic field shape that is required and the design of the pole pieces. The cheapest and simplest designs may well be adequately produced using ferrites only. Where modification of the field shape is required using compact higher power magnets such as SmCo or NdFeB to increase the field strength from a reduced volume of magnetic material. Typically, for a high-power magnetron, the maximum field between the poles will be of the order of 30 mTesla (300 G).

It must be borne in mind that the performance of the magnets varies with material. Magnetrons built using only ferrites will age and perform at elevated temperatures differently than those built using other or mixed magnet types.

Magnets may be permanently damaged if overheated above the Curie temperature. Above the Curie temperature, all the magnetic performance is lost. However, before the Curie point is reached, there will be a smaller loss in performance that is recoverable on cooling. A loss in performance will mean an increase in the loss of electrons and hence the magnetron will operate at a higher voltage for the same current. Ferrites will have a loss of 10% at 50°C, 20% at 100°C, and on to 100% at 450°C. AlNiCo is much less with only 1% loss at 100°C.

With any change in operating power, the bulk temperature of the magnetron will change. Depending on where the magnets are positioned will govern whether they are well cooled or will operate at a higher temperature than the bulk temperature. Ideally, the water cooling will be sufficient to limit the bulk temperature rise to only a few degrees and the magnets will be maintained at the bulk temperature. This will then help to maintain the magnet's performance for a prolonged period of operation.

This sensitivity to temperature is often just put down to the process taking time to stabilize. The voltage drifting upward may be due to the changing shape and size of the erosion racetrack but could also be from the magnet temperature progressively increasing.

A further factor, which may be worth considering in the purchase of magnets, is the strength of magnets as received. The Magnetic Materials Producers Association (MMPA) allows for a 20% variation in the magnetic energy from the published values for a grade of material. Thus, the performance of magnetrons could be expected to vary even for the same design with magnets from the same source.

One user, who became concerned about the varying performance, over time, of their production magnetrons and of never being quite certain what performance to expect, used to demagnetize and remagnetize the cathodes once per month as part of a routine maintenance program. This was a huge investment in both downtime and the additional equipment, as they had to be able to stabilize the magnetic performance of 3 m long cathodes. This cost was deemed to be an overall cost benefit because of the improvements in product reproducibility.

This sensitivity of the magnets to thermal damage also impacts the cooling of the cathodes. The cooling cannot be left to chance and so needs to be interlocked to the power supplies, thus preventing power being applied without sufficient cooling being present. This interlock should be on the exhaust of the magnetron. If on the supply side there is always the possibility of a leak between the interlock sensor and the magnetron, and if there is a leak after the interlock sensor on the exhaust, then at least the magnetron is protected.

It is also a good policy to have all exhaust coolant temperatures measured independently for each magnetron. I have seen systems where, to save on costs, a common sensor is used after the individual exhausts have been merged into a single outlet. This use of a common sensor will not properly protect any individual magnetron that has a temperature problem.

21.12 Planar or Rotatable?

Planar magnetrons can have a buildup of backscattered material that collects at the edges of the racetrack and can be a source of arcing. In reactive processes, where a metal is sputtered but the compound produced might be a dielectric, this collection of granular material can charge up locally, distorting the electric field and initiating arcs.

Rotatable magnetrons have the same fixed magnetic arrangement, but instead of having a fixed flat target material in front of the magnets, the target material is in the form of a cylinder that slowly rotates past the magnetic poles. In this way, the target material moves through the magnetic field and so the backscattered material is cleaned off during each revolution. As there is no buildup of material, the propensity of the target to arc is reduced.

As the cylinder of material to be sputtered spends in the order of 80% of the time being cooled, it is usually possible to use a higher current density for rotatable magnetron cathodes than for planar magnetron cathodes. This can also mean that thicker targets can be used for rotatable magnetron cathodes as the front surface is only periodically bombarded and heated and so the average peak surface temperature is lower than that on a similar sized planar.

Rotatable magnetron cathodes have achieved an early popularity for two particular types of materials. One is magnetic materials where the magnetic material shorts out the magnetron magnets and can cause the magnetron to revert to operating as a simple diode cathode. So long as the magnetic material is thin enough that the material is magnetically saturated, the excess magnetic field will allow the source to continue to operate as a magnetron. This meant that targets were made out of very thin material and there was a high downtime because the targets had to be changed frequently. With the rotatable magnetron, the target thickness would have to be the same but as the cylinder had a surface area more than five times that of the planar and the erosion was around the whole circumference of the target tube, the lifetime was at least five times longer than that for a planar. This reduced the downtime and increased productivity significantly. The second class of materials that used the rotatable magnetron design was that of expensive target materials such as gold. As the erosion of the rotatable target was around the whole circumference, the target utilization was of the order of 80% compared to 35% for some planar magnetron sources. Again, the longer target lifetime as well as the higher material utilization efficiency was an economic advantage that more than offset the higher capital cost of the rotatable magnetron sources.

More recently, using the combination of a rotatable magnetron source design and coupling a pair of sources to make a dual rotatable source has been favored. The dual rotatable offers a long target lifetime, higher power density, and faster deposition rate along with minimizing the target arcing and eliminating the problem of the disappearing anode. This gives this type of source a significant advantage in manufacturing where the production yield is a critical economic factor.

21.13 Power Supply Choices

To some extent the choice of which type of power supply to use may be dictated by the type of magnetron source being used and the material to be sputtered. As with all choices, it is preferable to choose the simplest and most economic power supply that is fit for purpose. If sputtering a conducting metal and depositing the metal onto the substrate, choosing a DC source can be the most cost-effective choice.

If, however, the same metal is to be sputtered reactively to deposit a compound onto the substrate and the compound is nonconducting, then there can be a problem of arcing and so the simple DC source may not be good enough. Adding an arc management system to the DC power supply that can detect the formation of an arc and quench the arc before reintroducing the power is one option. Alternatively, using a switched-mode power supply where for most of the time the power supply operates at one polarity but for a short time the polarity is switched to the opposite. This switching to the opposite polarity is used to discharge any accumulated charge that might have built up on any of the backscattered material at the edges of the racetrack. By neutralizing the charge, it reduces the possibility of this backscattered material becoming a source of arcing.

If the target material is nonconducting, then it may require a radio frequency (RF) power supply. RF power supplies can have problems in matching and on occasions can cause interference problems with other instrumentation. As the RF supply is, in effect, only sputtering the target for half of the supply cycle, the sputtering rate is considerably lower than that for an equivalent DC power supply. These reasons make using an RF power supply a less preferred option. For some materials, it is possible to dope the target material to change it from being an insulator to being a semiconducting material in which case it is then possible to use a DC supply to sputter the material.

Where a dual magnetron sputtering source is used, a medium frequency power supply is used with each magnetron source being alternately the cathode and then the anode.

A recent development has been the use of high-power impulse magnetron sputtering (HIPIMS) power supply. This supply uses a very high pulse of power for a very short period of time. This very high pulse of power not only sputters the target material but it changes the level of ionization from ~10% to ~90% [2]. This changes the nucleation and growth of the growing coating. The average power for a complete cycle is the same as for other supplies but the electronics for being able to control the pulse duration and peak power makes them a more expensive power supply option. In roll-to-roll systems, the winding speed is usually low enough and the speed of pulsing fast enough that the coating is deposited uniformly. Indications are that for the same average power, the heat load to the substrate is reduced, which could help for heat-sensitive substrates [3]. Although initial work has shown promise, there has not been sufficient manufacturing done on roll-to-roll systems to make it clear where these supplies have the greatest advantage to justify the cost.

References

[1] Monaghan D, et al. Optimizings putter processes via 3D magnetic and plasma simulations. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 9–12.

[2] Williams S, et al. Novel cylindrical magnetron design for enhancing rotatable web technology. In: Proc. AIMCAL annual technical conference and 23rd international vacuum coating conference; 2009.

[3] Hala M, et al. Time- and space-resolved optical emission spectroscopy study of reactive HIPIMS discharges. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 228–33.

[4] Barker PM, et al. Low temperature HIPIMS deposition of AZO coatings on polymeric web. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 691–95.

22 Reactive Sputter Deposition: Setup and Control

There are three main problems relating to reactive sputtering: target poisoning, which leads to arcing; the disappearing anode; and the hysteresis of the reactive process that is particularly bad with underpumped systems [1,18]. Different strategies were adopted to reduce the effects of these problems. This included separating the inert and reactive gas introduction in an attempt to reduce the target poisoning [2]. An extension of this was to deliberately use the deposition of material onto the nearby shields as a getter pump to help stabilize the process [3–6]; use buffer zones between adjacent reactive processes to reduce the cross contamination and control the gas flow dynamics [7,8]; develop more sophisticated automatic feedback control and higher speed gas control to help prevent a runaway situation thus enabling control of a reactive process in what would usually be regarded as an unstable region [9–12,32].

22.1 Target Preconditioning

There are two types of preconditioning. First, there is the preconditioning of alloy targets. Initially, targets have to have sputtered away some of the faster sputtering component (or components) to bring the surface composition to a balance. Once the sputtering surface has reached the balance composition, the system will then deposit a reproducible alloy from the alloy target [13]. The second preconditioning is to remove any buildup of compounds formed since the last time the target was used. In particular, metal targets that oxidize easily and are used for reactive deposition require to be cleaned back to a metallic state before the reactive process is started. This should be carried out in an atmosphere of pure argon. This brings the target surface back to a known starting point. The surface including the racetrack and the target when fired up will oxidize and will initially have the characteristic of an oxide target. As sputtering cleans away the surface oxide the voltage will change, indicating the appearance of the metal surface. The voltage will stabilize once the whole of the sputtering surface becomes metallic. The higher the power used to clean the surface, the faster the surface will return to the metallic state.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00022-2

If the power used is too low, the rate of oxidation will match the erosion rate and the surface will never be cleaned of oxide. Once the voltage has stabilized, the desired power, current, voltage, gas flows, and pressure can be set for the desired reactive process to commence.

Electron beam sources also may require preconditioning. As they cool, they too may oxidize and the surface may need to be cleaned of oxide before stable evaporation/sublimation may start. There is often a need for this to be done slowly or gently by using only a small thermal load. Using too high power too early may cause violent spitting from the surface. In the case of small volume crucibles, this can result in the whole charge of material being ejected from the pot.

22.2 Control Options

The aim in reactive deposition is to control the deposited film composition. The composition depends upon the ratio of the metal arrival rate to the reactive gas arrival rate. These two are not independent variables and so either can be controlled.

Keep metal arrival rate constant	change the reactive gas flow constant current control
Keep reactive gas flow constant	change the metal arrival rate constant power control constant voltage control constant current control

22.3 Hysteresis Loop

The difference in sputtering rates of the metal and oxide surface gives rise to a hysteresis loop. Starting with a metal surface, if an oxidizing gas is fed into the system, some of the reactive gas will be consumed by the growing coating and some will be pumped away. The growing coating is not only on the surface of the substrate but also on any surface that receives some of the metal flux sputtered from the target. This will include some material that is back scattered onto the sputtering target surface. Some reactive gas will hit the target directly and will oxidize the surface. Within the racetrack this will very quickly be removed, but on the edges of the racetrack the removal rate will be slower. At some point the oxidation rate will be faster than the removal rate and from here outward will build up an oxide layer on the surface. If the oxygen partial pressure is increased, this point where the oxide starts to form will encroach further into the racetrack. The effect of this will be that less metal is sputtered, effectively reducing the gettering of oxygen by the reduced amount of growing coating. This will in turn increase the partial pressure of oxidizing reactive gas, thus accelerating the process. This is shown schematically in Fig. 22.1.

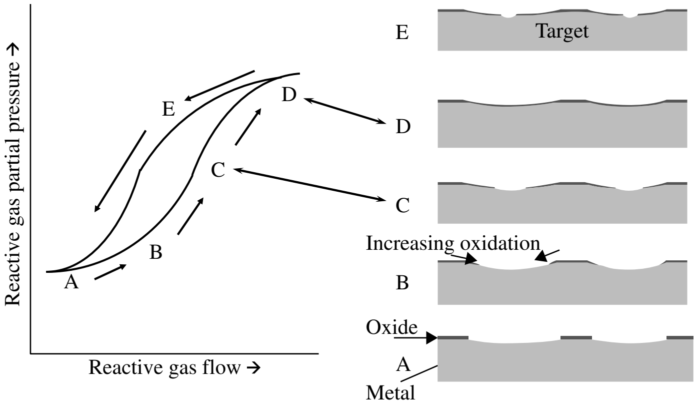


Figure 22.1 Schematics showing the relationship between target surface oxidation and the hysteresis loop in the sputtering characteristics.

In Fig. 22.1, A represents the target surface when only a small amount of oxidizing gas is introduced. The thick line represents the oxide layer. At B, there has been an increase in nitrogen partial pressure and the oxide has encroached further across the target. By the time C is reached, the process is not in control and very soon the surface reaches point D where the whole target surface is oxidized. By cutting off the reactive gas supply, the target surface will begin to reduce the oxide thickness and eventually the sputtering will break through to bare metal. This will occur at the point of greatest erosion at the bottom of the racetrack and will spread outward until the target reaches the new equilibrium against the flow of nitrogen.

Most systems expected to perform reactive processes are underpumped for performing this reactive process. It is possible to compensate for this problem by putting additional baffles and shields into the system. All too often these are carried out to reduce the deposition rate to the point where the pumping speed dominates the process again to allow for stable deposition. The better solution has to be to provide the correct pumping speed to match the available deposition rate. This process has been well documented and once the instability was understood it enabled better monitoring and control methods to be developed [14—29,33].

22.3.1 Constant Metal Rate, Variable Reactive Gas Flow

Ideally the sputtering will take place using the inert argon gas and the reactive gas will be completely consumed by the film growing on the substrate. In reality, there is metal deposited on other surfaces than the substrate; the surface of the cathode is metallic and clean and hence very reactive and so may have a higher sticking coefficient than other surfaces. The reactive gas cannot be confined to only being available to the substrate surface and will be available to all other surfaces too. To make sure that enough gas is available at the substrate, there will always need to be an excess of the reactive gas and this will be seen as a partial pressure.

One of the common techniques for controlling the reactive process is to control the mass flow of reactive gas from the total pressure. The sputtering rate is made constant using constant current control. If the inert gas flow is constant giving a constant pressure, the reactive gas is introduced to the level that gives a small increase in the total pressure. This total pressure is made the set point and the flow of reactive gas is allowed to vary as required by the growing film.

It is possible to minimize the required excess of reactive gas by increasing the reactivity of the gas by ionizing it before introducing it into the deposition zone. It can also be minimized by system design. If the system is designed such that the inert gas flows uniformly across the target material and the reactive gas flows uniformly across the substrate in the deposition zone, this too will minimize the excess reactive gas.

A more sophisticated control system is using a plasma emission monitor to look at the colored plasma emission lines and to use them to control the process. This is a much more expensive method of controlling the reactive gas, but it is much more sensitive and gives a direct measurement of what is happening in the plasma in real time. The plasma emission monitor needs to be set to look across the plasma fairly close to the front surface of the magnetron. The plasma intensity drops off with distance from the cathode surface and so the strongest signal is available near to the surface. The fiber optics need to be shielded from the deposition. This is usually achieved by placing a tube at the end of the fiber. This sampling from a distance and from a narrow capture angle will reduce the signal intensity. A method of compensating for any variations in plasma or signal intensity to find the ratio of the two of the plasma lines. The signal intensity changing for both lines will not affect the ratio, whereas a change in the metal sputtering rate or the reactive gas flow rate would affect only one of the lines and the ratio would be changed.

In this system, the metal rate is again set at a constant and the reactive gas flow is increased to the point where the desired film is produced. At this point the intensity of two of the plasma lines, for the metal and reactive gas component in the plasma, are monitored and the reactive gas is controlled to keep the ratio of the two lines constant.

22.3.2 Constant Reactive Gas Flow, Variable Metal Rate

This uses fixed gas flows and controls the arrival rate of the metal at the substrate. The same plasma emission monitor can be used to control the power to the cathode, enabling the ratio of the two lines to be kept constant.

The cheaper option is to use the pressure to act as the control trigger for the power supply. Again the gas flows are made constant and then the power supply is set to voltage or power control.

In constant voltage control, if there is a fall in the pressure, the natural response would be for the pressure to rise while the current remained constant or alternatively for the current to fall while the voltage remained constant. As the voltage is fixed, the latter happens and the current drops and that causes the demand for the reactive gas to fall. This excess reactive gas will then increase and the pressure will return to the set point. The reverse of this would happen if there were to be a pressure increase.

In constant power, if there is a fall in pressure, the voltage is not constrained and so can rise but the power is constrained and so there is a corresponding drop in current to keep the power constant. Thus, the effect is the same as for constant voltage but there may be a difference in sensitivity in some circumstances.

22.4 Monitors

Critical to all types of control is a suitable monitoring tool. Monitoring the coating on the web after the deposition zone works well for metallizing where the coating speed is up to 1000 m/min. In this case, the monitoring takes place within a second of the deposition. In contrast, for reactive processes, where the coating speed is often around 1 m/min, it is likely to be many seconds or even minutes before the coating might show the process having gone out of control. Thus, for reactive processes, it is common to use either a sensitive pressure monitor or the plasma to provide the control information. Even when using the faster and more direct monitors, the information given still needs to be related back to the coatings that are produced. Monitoring the quality of the coating can provide information about where to set the control set point and indicate any slow long-term process drift that would also need to be corrected.

The most popular options for fast monitoring are using an amplified and offset pressure signal from a Baratron or Pirani gauge, to use the output from a mass spectrometer, a plasma emission monitor, or a lambda oxygen partial pressure monitor. The mass spectrometer needs to have a separate pumping system to get the sensitivity and speed of response and is not as adaptable as the plasma emission monitor. Both the mass spectrometer and the plasma emission monitor can be used as diagnostic tools for troubleshooting process problems. The use of a pressure gauge provides a simple control signal only and hence is robust and cheap but is not as sensitive or flexible as the other systems.

The chart recorder trace in Fig. 22.2 is from an amplified and offset output from a Pirani gauge. The sensitivity was such that a 0.1% change in partial pressure of

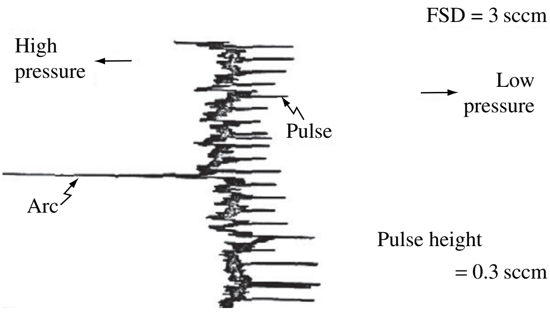


Figure 22.2 A chart recorder trace of an amplified and offset output from a Pirani gauge [18] showing the effect of the pressure fluctuations caused by the high-pressure side pressure reduction valve pulsing.

reactive gas could easily be detected. As the rubber flap valve opened and closed on the gas cylinder pressure reduction valve, a pressure spike was produced that passed through the mass flow controller into the vacuum system. This type of pressure change would not be noticed in most vacuum systems. In this case because of the amplification, caused by the highly reactive nature of the reactive sputtering of titanium, plus the careful monitoring of the pressure, the pulses were seen. If the process was to be pushed to the limit and there were insufficient pumping, these pulses would have been enough to tip the process over from sputtering metal to sputtering oxide. With enough pumping the system would be insensitive to these pulses.

22.5 Time Constants

The time constants within the system are also worth noting. There will be a time constant for pumping the main volume of the system out. There is likely to be a longer time constant for gas in the reactive gas manifold to be pumped away. This can mean that corrections made in the gas flow are exaggerated because of the delay in seeing the response. It may be that the length of the pipe after the control valve, the diameter of the pipe, and any constriction in the introduction nozzles mean that the system cannot react fast enough to be able to maintain a steady pressure but instead the pressure cycles up and down slightly.

It is assumed that there is a symmetry about the web centerline for the gas feed and pumping system. If the gas is fed from one side or if the pumps are hung off one end of the system, it will be virtually impossible for there to be a common equilibrium point for both ends of the cathode. Asymmetric pumping or gas feed can be compensated for by use of switched mode dual magnetrons. This will be a higher cost magnetron and power supply and the deposition rate will be lower than that achievable by having the designed in symmetry.

Hence in the system design it is worth trying to maximize the natural system uniformity. This requires a design to minimize the gas distribution pipe lengths and gas volume while keeping the gas manifold nozzle sizes as large as possible.

22.6 Pumping

The time constants will be increased if the pumping system is throttled and at the same time the sensitivity of the system to variations in the excess reactive gas will correspondingly increase. Hence, the process will be more stable if the pumps are fully open. If the diffusion pump backing line pressure looks to be high, where the diffusion pump becomes close to stalling, it is worth considering increasing the capacity of the backing pump, rather than restricting the pumping by the use of throttle valves.

The pumping system needs to be large enough so that it dominates the process. If the growing film pumps the reactive gas faster than the pumps, the process will be inherently unstable. This can be compensated for by the use of pulsed gas flow, pulsed power supplies, and additional shuttering. These processes reduce the deposition rate.

Figure 22.3 shows the benefit of increasing the pumping speed. The system on the right has the higher pumping speed and has no region of instability.

There is a simple cycle that leads to instability [14]:

Increasing reactive gas pressure→Reduced reactive gas consumption→Surplus reactive gas→Increasing reactive gas pressure

The aim is to have sufficient pumping such that any increase in surplus reactive gas will be pumped away rapidly and not result in a significant pressure rise (Fig. 22.4).

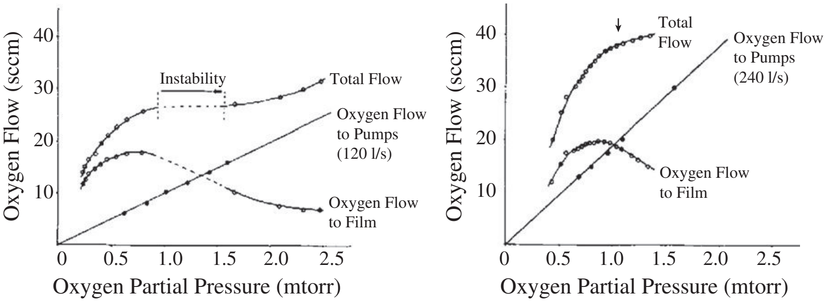


Figure 22.3 Two graphs of different pumping characteristics of the same vacuum system but using different pumping speeds [15].

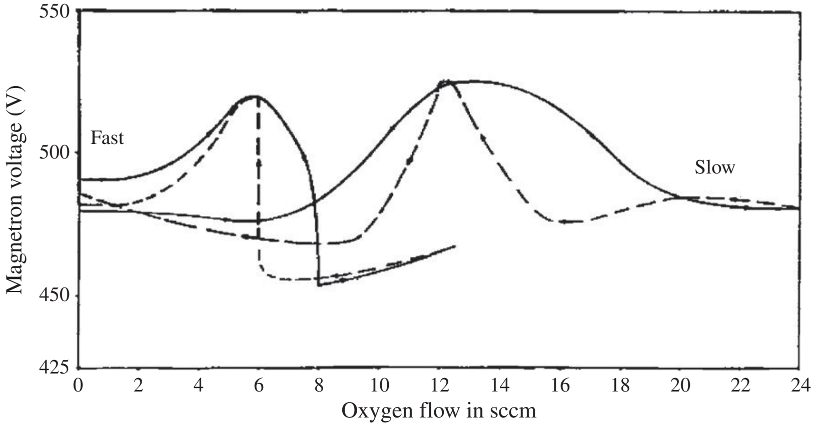


Figure 22.4 A graph showing how the hysteresis loop can be affected by the rate of change of gas input to the system [18].

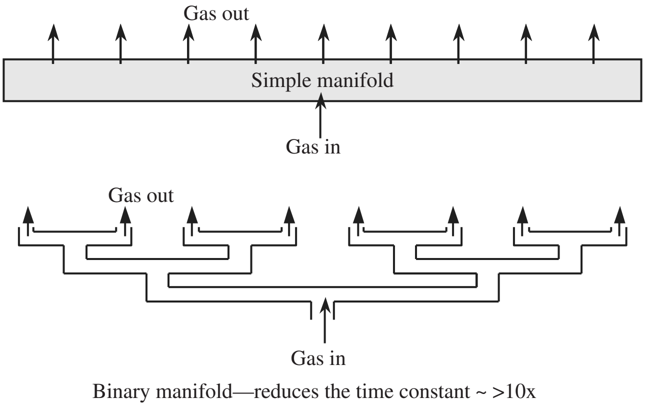


Figure 22.5 A schematic of two different types of gas manifold the choice of which can affect the time constant to the system significantly [30–32].

Another variable can be the rate of change of the gas feed. It is possible to increase the gas flow faster than the system comes to equilibrium. Unless the time constant is known for each of the component parts of the system, the acceptable rate of change will be something of a guess. Ideally the time constant will be as low as possible such that the changes to the gas flow can be equally as responsive. A good analysis of this has been done, providing details of how to define the manifold size including exit holes and spacing [33] (Fig. 22.5).

22.7 Control of Arcs

Arcs are caused by defects in the target surface or accumulations of nonconducting backscattered material on the target surface. These defects cause localized electric field concentrations that can attract additional ions to a point in the plasma above the defect causing the plasma to breakdown and short to the target [34–36]. When this happens, all the current passes through this short and the current density on the surface of the target produces localized melting of the target. The molten spot evaporates and increases the pressure in that localized area, that in turn encourages the high current to remain in the spot. Once arcs are established, it may be difficult to extinguish them. Although the arc is operating, the reactive process will have been thrown into confusion. Either the mass flow controllers or the power supplies will try to compensate for the new conditions. In the mean time, the coating deposited onto the substrate will be out-of-spec. Thus, it is essential to eliminate arcs wherever possible and to control and extinguish those that do occur as speedily as possible.

The arc control features were developed over some time. Initially the power supplies had a sensor circuit that detected an arc had occurred and simply switched off the power and after a short time reintroduced the power. Although this worked to an extent, a number of arcs were either large enough or originated from a defect that remained in place and so when the power was reintroduced immediately reverted back to the arc mode. On some supplies it was possible to send a power surge to try to blast off any defects to stop this happening. The next stage of development was to actively suppress the arc by reversing the polarity of the power. This was aimed at limiting the energy that went into the arc and hence limiting the temperature and thus preventing the arc from re-establishing quite so easily. Most modern switched mode power supplies have arc suppression as a standard feature.

Then came a change in philosophy. This was to not just wait for the arc to start but to actively work to prevent an arc starting. So now there are two aspects of arc control; the first is to stop the arcs from occurring in the first place and the second is to react quickly to those that do occur. The prevention usually involves discharging any built-up charge from the surface of the cathode by switching the polarity of the supply for a fraction of a second on a regular basis. This prevents the charge from building up on the insulating backscattered material and thus stops the field concentrations from occurring. This pulsing works effectively but does not prevent the problem of the disappearing anode where a nonconducting surface builds up on the anode making it ineffective. The sputtering process continues but the plasma may become distorted and the process uniformity may be lost. Using a pair of magnetrons connected side by side to the power supply, so that at any one time one would be the anode and the other the cathode and on reversing the polarity each target alternates as the anode and cathode, minimizes this problem. Hence, it is common to have pairs of magnetrons working together with a pulsed or medium-frequency power supply. If an arc occurs, the system senses this and again switches the polarity of the supply to effectively quench the arc and then controllably reinstates the power. This allows time for the arc site to cool and limits any possible evaporation of material and hence stops any localized pressure rise, which would make the arc more easily re-established when the power is reintroduced [37—46].

Even if the pumps are fast enough that there is no hysteresis in the sputtering process, it is still worth using a switched mode or medium-frequency power supply and pairs of magnetrons as a positive method of controlling (reducing) arcing. This will lead to a higher capital cost, but it will give a higher quality and more reproducible product.

22.8 RF Sputtering

With RF sputtering, there is not the option of voltage or current control for the cathode. In this case, all that is left is to use the constant power mode for the cathode and use the excess partial pressure control for the reactive gas flow.

Simplistically the target will only be sputtering for half of the cycle and so it will at best be half the sputtering rate of DC sputtering. Coupled with this is the need for a very good earth as well as good shielding to prevent interference of other electronic equipment. Grounding is not exclusively an RF source problem, although it may be more noticeable when using an RF source. All systems have, of course, to comply with electrical safety standards. What occasionally gets overlooked is when adding items to a vacuum system there may be nonconducting vacuum seals that may also electrically isolate items. Also, a good earth for DC is not necessarily a good earth for an RF source [47]. There can also be the problem of tuning the system. I would suspect anyone who has had to try to install, set up, and sputter material using RF has had problems, at times, with getting the tuning optimized. All of this has made RF sputtering almost a last resort source for deposition.

The major advantage of RF sputtering is to be able to sputter nonconducting materials. This usually does not require any reactive gas input. Occasionally, some materials do undergo some dissociation and may need some reactive gas to help recover stoichiometry but this cannot result in target poisoning and hence there is not the same control issue as with DC reactive sputtering from metallic targets.

To some extent the use of pulsed switched mode power supplies allows for the sputtering of nonconducting materials without the need to use RF. These power supplies reverse the polarity for a small fraction of the duty cycle; thus, for the large part of the cycle the material will be DC sputtered. The change in polarity is to discharge the surface using the more mobile electrons, thus preventing arcing. The doping of targets is also much more common and this too reduces the need for RF sputtering.

22.9 Other Processes

Reactive deposition is not restricted to sputtering; sputtering has the problem of the hysteresis loop that can give some process problems. Other deposition processes do not exhibit this hysteresis loop and it has been shown that the deposition process may only have a limited operating window if the desired property films are to be produced. There is an interest in the low-cost deposition of aluminum oxide coatings using a modified conventional aluminum metallizer. Oxygen is added to the system at an appropriate point in the process and the highly reactive growing coating is oxidised. This will still have competing processes of the aluminum growing on both the system shields and the substrate, and the pumping of the oxygen is divided between all the growing coatings and the system pumps. The aluminum oxide coatings are required to be transparent with an improved oxygen and water vapor barrier performance. It has been shown that by adding an additional plasma to the process, using hollow cathode guns that increase the reactivity of the depositing material, the process window for oxygen flow can be extended where the barrier performance and transparency remain within the desired specification [48].

References

[1] Scholl R, Belkind A. Problems and solutions in reactive sputtering of dielectrics. In: Proc. 13th international conference on vacuum web coating; 1999. p. 153–64.

[2] Schiller S, et al. Different properties of reactively DC sputtered chromium-silicon-oxide films with variation of target-to-substrate coupling. In: Proc. 7th international conference on ion and plasma assisted techniques (IPAT). CEP Consultants, Edinburgh; 1989. p. 124−9.

[3] Maniv S, et al. High rate deposition of transparent conducting films by modified reactive planar magnetron sputtering of Cd_2Sn alloy. J Vac Sci Technol A 1981;18(2):195−8.

[4] Belkind A, Wolfe J. Enhancement of reactive sputtering rate of TiO_2 using a planar and dual rotatable cylindrical magnetrons. Thin Solid Films 1984;248(2):163−5.

[5] Westwood WD. Reactive sputtering: introduction and general discussion. In: Glocker DA, Shah SI, editors. Handbook of thin film process technology. Institute of Physics, Bristol; 1998 Section A5.0.

[6] Howson RP, Spencer AG. Self-pumping in high rate reactive sputtering. In: Proc. 32nd annual technical conference of the Society of Vacuum Coaters; 1989. p. 40−47.

[7] Advanced vacuum web coating trends reviewed. Paper, Film & Foil Converting 1989; April:70−72.

[8] Buschbeck W, et al. Vacuum design for mixed-mode sputtering roll coaters. In: Proc. 30th annual technical conference of the Society of Vacuum Coaters; 1987. p. 127−34.

[9] Schiller S, et al. Reactive D.C. high-rate sputtering as production technology. Surf Coat Technol 1987;33:405−23.

[10] Howson RP, et al. The importance of gas flow in reactive sputtering. In: Proc. 8th international conference on ion and plasma assisted techniques (IPAT). CEP Consultants, Edinburgh; 1991. p. 340−5.

[11] Schiller S, et al. Progress in the application of the plasma emission monitor in web coating. In: Proc. 2nd international conference on vacuum web coating; 1988. p. 124−38.

[12] Hmiel AF. Partial pressure control of reactively sputtered titanium nitride. J Vac Sci Technol A 1985;3(3):592−5.

[13] Wehner GK. Sputtering of multicomponent materials. J Vac Sci Technol A 1983;1(2):487−90.

[14] Spencer AG, et al. Pressure stability in reactive magnetron sputtering. Thin Solid Films 1988;138:141−9.

[15] Spencer AG, Howson RP. Dynamic control of reactive magnetron sputtering: A theoretical analysis. Thin Solid Films 1988;138:129−36.

[16] Spencer AG, et al. Design and use of a vacuum system for high rate reactive sputtering of TiO_2/TiN/ TiO_2 solar control films. Sol Energy Mater 1988;18:87−95.

[17] Spencer AG, et al. Pressure stability in reactive magnetron sputtering. In: Proc. international conference on ion and plasma assisted techniques (IPAT). CEP Consultants Ltd., Edinburgh; 1987. p. 1−6.

[18] Bishop CA. The deposition of coatings onto polymer substrates by planar magnetron sputtering [PhD thesis]. Loughborough University, UK; 1986.

[19] Penfold AS. The influence of pump size on D.C. reactive sputtering systems. In: Proc. 29th annual technical conference of the Society of Vacuum Coaters; 1986. p. 381−403.

[20] Berg S, et al. Modelling of reactive sputtering of compound materials. J Vac Sci Technol A 1987;5(2):202−7.

[21] Larsson T, et al. A physical model for eliminating instabilities in reactive sputtering. J Vac Sci Technol A 1988;6(3):1832−6.

[22] Berg S, et al. Predicting thin-film stoichiometry in reactive sputtering. J Appl Phys 1988;63(3):887−91.

[23] Carlsson P, et al. Reactive sputtering using two reactive gases, experiments and computer modelling. J Vac Sci Technol A 11(4):1534−39.

[24] Serikawa T, Okamoto A. Effect of N_2−Ar mixing on the reactive sputtering characteristics of silicon. Thin Solid Films 1983;101(1):1−6.

[25] Kadlec S, et al. Hysteresis effect in reactive sputtering: a problem of system stability. J Phys D 1986;19(9):L187.

[26] Okamoto A, Serikawa T. Reactive sputtering characteristics of silicon in an Ar−N_2 mixture. Thin Solid Films 1986;137(1):143−51.

[27] Sproul WD. High rate reactive sputtering process control. Surf Coat Technol 1987;33:73−81.

[28] Bellido-Gonzalez V, et al. Flexible reactive gas sputtering process control. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 44−8.

[29] Ershov A, Pekker L. Model of DC magnetron reactive sputtering of the silicon target in Ar-O_2 gas mixtures. In: Proc. 39th annual technical conference of the Society of Vacuum Coaters; 1996. p. 279−84.

[30] Theil JA. Gas distribution through injection manifolds in vacuum systems. J Vac Sci Technol A 1995;13(2):442.

[31] Bartzsch H, Frach P. Modelling the stability of reactive sputtering processes. In: Proc. 7th international conference on plasma surface engineering; 2000.

[32] Milde T, et al. Gas inlet systems for large area linear magnetron sputtering sources. In: Proc. 44th annual technical conference of the Society of Vacuum Coaters; 2001. p. 204−9.

[33] Spencer AG. High rate reactive magnetron sputtering [PhD thesis]. Loughborough University, UK; 1989.

[34] Grove T. Arcing problems encountered in sputter deposition of aluminium. In: Proc. 29th annual technical conference of the Society of Vacuum Coaters; 1986. p. 214−23.

[35] Blondeel A, De Bosscher W. Arc handling in reactive DC magnetron sputter deposition. In: Proc. 44th annual technical conference of the Society of Vacuum Coaters; 2001. p. 240−45.

[36] Scholl RA. Advances in arc handling in reactive and other difficult processes. In: Proc. 37th annual technical conference of the Society of Vacuum Coaters; 1994. p. 312−6.

[37] Scholl RA. A new method of handling arcs and reducing particulates in DC plasma processing. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 405−8.

[38] Scholl RA. Process improvements for sputtering carbon and other difficult materials using combined AC and DC process power. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 391−4.

[39] Scholl RA, et al. Problems and solutions in reactive sputtering of dielectrics. In: Proc. 13th international conference on vacuum web coating; 1999. p. 153−64.

[40] De Bosscher A, et al. Global solution for reactive magnetron sputtering. In: Proc. 3rd international conference on coatings on glass; 2000. p. 59−76.

[41] Rettich T, Wiedemuth P. MF, DC and pulsed DC in the use of large area coating applications on glass. In: Proc. 3rd international conference on coatings on glass; 2000. p. 97−105.

[42] Brauer G, et al. Mid frequency sputtering—a novel tool for large area coating. Surf Coat 1997;94−95:258−62.

[43] Schneider JM, Sproul DM. Reactive pulsed DC magnetron sputtering and control. In: Glocker DA, Shah SI, editors. Handbook of thin film process technology. Institute of Physics, Bristol; 1998 Section A5.1.

[44] Este GO, Westwood WD. AC and RF reactive sputtering. In: Glocker DA, Shah SI, editors. Handbook of thin film process technology. Institute of Physics; 1998 Section A5.2.
[45] Scholl RA, et al. Applied energy application notes. The MDX™ as a strategic tool in reducing arcing; 1985. Arcing problems encountered during sputter depositing of aluminium; 1986. How Advanced Energy® MDX™ products manage arcs; 1993. Power supplies for pulsed power technologies: state-of-the-art and outlook; 1999. Advanced Energy Industries Inc., Fort Collins, CO 80525.
[46] Sellers J. Asymmetric bipolar pulsed DC. ENI® Tech. Note; 1985. Sellers J. Using the RPG generator. ENI® Tech. Note; 1996.
[47] Advanced Energy® grounding application notes; 1991. Introducing power supplies and plasma systems. Tech. Note 33; 1992.
[48] Gunther S, et al. Innovative transparent barrier for packaging. In: Proc. 52nd annual technical conference of the Society of Vacuum Coaters; 2009. p. 727−9.

Part IV

System Issues

23 Machine Specification and Build Issues—Risk Analysis—Process

We start by making the assumption that we are working with a worse-case scenario. Someone has had an idea for a new product and has to take it forward through to production. The process has not been done before and hence the production machine cannot be an off-the-shelf design. Even for a fairly standard metallizer, it is probably a 1 year-long task, from the point of writing a machine specification and choosing a supplier, to accepting the machine on site [1].

It is common to underestimate the time required to get to the point of production. So many of the items included in the timeline appear on the critical path but are controlled by others who may not be working to the same deadlines or with the same enthusiasm.

History shows that for most projects the time from idea to production is greater than 3 years and for many cases is often more than 4 years (Fig. 23.1). Some of this time is the actual time taken to do the initial research and development. However, very frequently a lot of time is lost from the point where the decision is made to take the process through to production.

The other aspects of developing a new product are to make sure there is a market for it and that the market is ready to accept it when it becomes available [2]. It is essential that market plans are developed in parallel with each and every new product [3−5]. If there is a lack of a market, it may be developed or the project stopped.

23.1 Risk Analysis: Process

It is common for processes developed on a small vacuum system to be scaled up without any thought to the possibility of failure of the process.

Quite often a process would have been developed to a point where the envisioned product could be produced. However, the process would not have been optimized. In demonstrating the “proof of principle” of the process, any variations in the process and the product outcome would usually have been ignored as being due to the lack of control available on the system. There are two possible sources of the

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00023-4

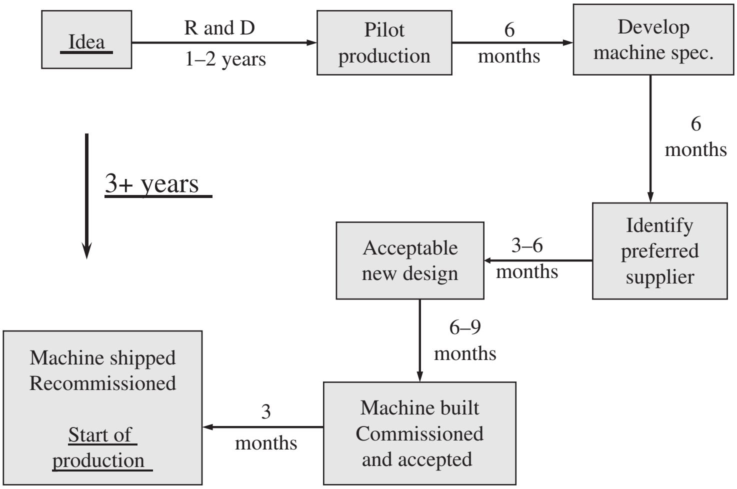


Figure 23.1 A typical timeline showing the time from idea to production.

variations. The first is that the variations are due only to the lack of control. The second possibility is that the variations are caused by a variable or a number of variables that not only are not being controlled but are also not even known about. If the process is not well understood, changes that are made during scale-up could be damaging if not catastrophic to the process.

Reducing the risk is cheaper before the system is built than after it is built. After it is built, the costs of not running production are far higher than the cost of additional development before the system is designed and built. It is also cheaper to build the system with the correct process than it is to try to modify it once it has been built.

The risks may be small, such as for the deposition of a metal from an evaporation source. There is a body of information that is already available about a number of evaporation sources and on systems that have been built up to 4 m in width. Hence, most of the information can be pieced together or calculated. The same is not true when it comes to the deposition of a multilayer optical stack to be deposited in a single pass. There may be information about each of the individual materials but not necessarily about the deposition of several of the materials sequentially. If the fastest possible production rate is required, it would be usual to try to run multiple processes in the same substrate pass. If the process is done reactively from the metals, the reactive process of each layer may have an effect on the adjacent depositions. If the multilayer stack requires a mixture of metals and oxides the problem increases. The sources need to be matched in deposition speed to allow for the correct thickness of coating to be deposited at the common winding speed. The sources need to be isolated from each other to prevent contamination from each other and the system needs to be symmetric to give the best possible chance for coating uniformity.

Using Table 23.1 and multiplying each of the risks will give an indication of the scale of the risk. No doubt other factors can also be included, such as geographic location, where language, time zones, and availability will affect the risk level.

System complexity × Process risk × Choice of manufacturer risk = Total risk

As with all risk analysis there are judgments required. What is the true risk of the process? It is common that the person operating the process in the laboratory believes that there is no risk because they have got it to work. This is not the same as having all the information to make the process universally transferable to any other machine. The choice of a manufacturer is also a judgment; seeing machines built does not necessarily mean they have been optimized or are reliable. A company that is long established is no proof of current quality. These choices and assessments need to be taken dispassionately and objectively.

Table 23.1 A Simple Method of Risk Analysis

	Scale-Up Risks	
System Complexity	**Process Risk**	**Manufacturer Risk**
1 Basic metallizing	1 Established process	1 Established manufacturer + proven experience with specials
2 Metallizing + plasma clean		
3 Single layer oxide deposition	3 New process, known materials and established system design	3 Young co. built some machines inc. one special, proven basic skills
4 Single layer oxide + plasma clean		
5 Single drum metal + oxide		
6 Single drum metal + oxide + plasma		
7 Two drum mixed metal + oxide	7 New process, known materials, new system design, some background info	7 Young co. limited experience, built some machines but still learning
8 Two drum metals + oxides + plasma		
9 Multi source + multidrum, one-pass multilayer mixed metals + oxides		
10 Air-to-air multidrum + multisource mixed metals and oxides	10 Untried process, new materials, radical system design, limited background info	10 New co. first machine hungry for the work but unproven skills

Part of the use of trying to do a risk analysis is to make everyone think about the whole process of system purchase. It can also highlight areas where a piece of extra work will significantly reduce the risk. It can also highlight risks that cannot be reduced and hence need to be monitored throughout to make sure that problems are found at the earliest opportunity.

There are ways that these risks can be minimized. It is usually not practical to take a process that has been developed as a series of single depositions and to build a small-scale single pass process. This is regarded as too expensive and time-consuming. What can be done is to use the development system to look at the process sensitivities. First, a "design of experiments" matrix can be used to optimize the individual processes and look at the stability of the process. If all the system parameters can be linked to a data logger, the information can be analyzed further using chemometrics.

Chemometrics is a technique of analyzing data, looking at the natural excursions of parameters during a normal operation of the system. Using mathematical techniques such as principal component analysis (PCA), hierarchical cluster analysis (HCA), known nearest neighbors (KNN), and soft independent modeling of class analogy (SIMCA), it is possible to extract much more information. Typically, this type of analysis would pick out the primary variables and would highlight where insufficient control was available; also the minor variable would be shown along with any interactions. This may confirm only the expected variables, but it may also show up sensitivities that could potentially be damaging to the process that previously had been overlooked. The more information that can be gathered and analyzed and the more closely the final process can be tested, the lower the risks involved.

The above risk analysis is applied to the process initially. It is worth repeating the risk analysis on the project as a whole and in this way the financial implications can be assessed [6].

23.2 Mistake-Proofing or Fool-Proofing

Mistake-proofing developed out of the drive for higher productivity and quality in the 1970s and 1980s in Japan [7,8]. It was found that if something could be assembled wrongly then sooner or later it would be. This assembly error could cause process problems and the final result would be loss of product. In an attempt to eliminate this source of lost product, it was aimed to eliminate any assembly ambiguities.

If we take a new look at a metallizer with the idea of mistake-proofing in mind, we can find areas where there are weaknesses. If we look at the machine assembly first and then move on to the process, looking at where it is possible for an operator or a mechanic to make an error, we can then try to design out that possibility.

In production lines this may mean that there is often a sensor included that checks whether the task has been completed correctly. This may be too expensive as a mistake-proofing tool for metallizers in which system costs are very price sensitive. The more simple things that can be carried out are where a component needs to have a particular orientation the design is made in such a way that it can only be assembled in the correct orientation. Parts such as flanges can be modified easily by adding a dowel and slot eccentric to the clamping bolts, one on each of the mating surfaces. In any other position other than opposite each other the flange will not mate with the other surface because the dowel will hold it off the surface. This type of arrangement can be used on anything that has to be mounted either within or onto the outside of the vessel. Other parts may require more thought and invention. In metallizers the most common parts to be removed and reassembled are the shields around the deposition source. It is becoming more common for these to be exchanged and so it is worth checking if these can be misassembled and how this problem might be designed out.

Currently, this is not a huge problem in vacuum deposition systems. In the future, it is expected that processes will be much cleaner than is currently in common practice. This will require much more extensive cleaning between deposition runs, which in turn will require a greater number of easily removed shields and components. Consequentially there will be an increased chance of assembly errors unless the fittings have been designed based on the mistake-proofing philosophy.

23.3 Project Management

Another potential area of weakness can be in the project management. Often the scientists or engineers who develop the initial idea are expected to take the project through to production. This may not be the most effective use of resources. Unless the people are well trained and good at project management, the project will suffer. Many people end up learning about project management on-the-job with the machine purchase and build being part of their first project to manage, or where the project is orders of magnitude bigger than anything they have done before. This inexperience becomes one of the risks to be considered in the risk management of the project.

Included in the project may be an assessment of the impact of the new process on the company. There may well be an increase in size including recruitment, training, and location of the increase in staff numbers. There will also be an increasing requirement for power, water, and other facilities to be prepared for along with all the other smaller details such as increased inventory and waste products [9]. All of these can get lost with most of the focus being on the arrival of a new machine.

As with all project management, it is essential to know what items are on the critical path and to monitor the progress of these items very closely to ensure they do not slip. This is not a trivial task. Many suppliers delay telling any bad news for as long as possible, and it is often the case that the first time the project manager knows an item has slipped is after the deadline. The fact that an item is on the critical path means that it is unlikely that the time lost can be recovered elsewhere unless some slack time has been built into the program. Suppliers often include hidden slack because they expect there will be some slip on their part of the timeline. If, however, there have been hard negotiations to reduce the design and build times, to get the shortest time to manufacture, it may be that all their built-in slack time has already been removed.

Frequently, machine suppliers are from across the world to their customers and another evaluation has to be made about how well they will be able to work together. In this electronic age it is possible through e-mail and video conferencing to still have daily project meetings, if required, throughout the design phase to clarify new concepts or confirm and accept modifications. This can reduce the delays in either posting drawings back and forth or having to move people around the world to have frequent face-to-face meetings. However, this requires a positive attitude on both sides and if there is any culture or personality clash, the long distance between supplier and customer can make project management very difficult.

Overall it is cheaper to spend the money and to get good professional project management than to have the much higher expense of the machine being late.

23.4 Safety

Another area that tends to get reviewed later than it ought to is safety. It is always harder and more costly to have to modify the machine after it is built than to design the safety features from the start. It is worth bringing in all kinds of people such as operators, cleaners, the maintenance staff, and the scientists to review the design and operation of the process at the time of writing the specification. This ought to be repeated with the final drawings before they are accepted and again a more hands-on review should be made during commissioning and acceptance. Even at that late stage it is going to be easier to make a modification at the machine builders than it is to wait until it is in production.

23.5 Costs

There are two aspects to this, the cost of the system and the operational cost of the process.

In the same way that time is always underestimated, so too cost is often underestimated. Typically, the cost of the project is 40% more than the basic machine cost and this assumes there is the infrastructure to accept the machine. If a new site has to be prepared, the costs can be several times the cost of the machine.

The other aspect of costs is the cost model that is used to determine the cost of the product and the expected profit from manufacturing [10,11]. This will not be a static model but will get updated as the quality of the information improves. The accuracy of the model will improve as the process is modified and the machine design is modified toward the final optimized process and design at which point the most accurate predictions of process and machine efficiency will be produced.

23.6 Machine Specification

There are different levels of machine specification. Early in the project there may be a single-page specification that outlines the basic aim of the process. This is because the basic process is known but not necessarily all the details are known or understood. As more R&D is done and more experience gained of making a product, it will be possible to provide a more detailed specification. This may be used to help sort out the potential machine suppliers before the final specification is issued from the top two or three machine suppliers.

The final specification will typically include details such as the scope of the specification and liability, process description, machine description, mechanical requirements, electrical requirements, control requirements, acceptance trials, packing and shipping, installation, commissioning, maintenance, spares, and training.

23.7 Maintenance and Spares

This is the less glamorous part of the machine specification but is one that can be every bit as important for the overall machine operational efficiency.

There will need to be discussions around what the maintenance philosophy will be [12]. This can range from no maintenance until the machine stops running through to a comprehensive preventive maintenance schedule. There will need to be thought given to the inventory of spares that will be carried. As can be seen in the trend in Fig. 23.2, it is possible to have a very large inventory cost, which will minimize production losses but does not necessarily make economic sense.

The machine supplier is likely to be able to draw up a series of lists. One of these will have the regularly used items such as “O” rings used on seals that are regularly broken. A second list may be where there are items included that history would suggest are the most likely parts to fail in service. A final list would be the most comprehensive one, which might include high-cost spares such as spare pumping units.

These spares lists not only need the items listing but also the part number and lead time to deliver in the event of needing a spare. This becomes important when trying to decide on which items to include in any spares inventory. Another part of the equation is the cost per hour of the downtime of the system.

There will be some items on long delivery that are cheap and, if not available, will stop the machine running and so can easily be identified as being required. The problem items are the ones that are high cost and have long delivery times and which are machine critical but are seldom a problem. This again is a problem of managing risk. A high-risk strategy is to carry no spares. A low-risk strategy for

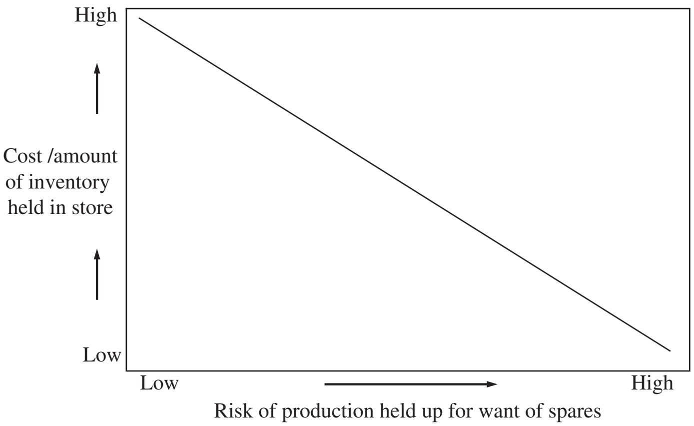


Figure 23.2 Trade-off of cost of inventory against lost production.

the machine is to carry a spare for everything but this becomes a high risk for the business because the profitability will be low. There is no simple answer to this problem and much of it depends upon the machine productivity and the product profitability.

Another consideration to be made when drawing up a specification is in the choice of items such as gauges and pumps. If you are already in possession of a system, it is useful to have the same components on both systems so that the spares inventory can be minimized. This can include having the common roughing pumps of sufficient size to pump both systems with enough spare capacity to be able to take out one pump for maintenance without having to stop production on either system. This would allow for a program of planned maintenance to be done on the pumps with no loss in production. In many systems the need for large roughing pumps is purely to achieve a fast turnaround time. An alternative method of achieving this is to have a large vacuum tank that is continuously pumped and to use this to assist in the roughing of a system, allowing for smaller pumps to be used for the backing of the high vacuum pumps. This type of system also allows for planned maintenance with uninterrupted production.

References

[1] Fletcher DA. Guidelines for purchasing, installing and commissioning a vacuum web coater. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 220–23.
[2] Comer AM. Bringing new products to the market place. In: Proc. 12th international conference on vacuum web coating; 1998. p. 14–23.
[3] Cooper RG. Winning at new products. London: Kogan Page; 1988. ISBN 1 85091 769 8.
[4] Meyer MH, Lehnerd AP. The power of product platforms. New York: The Free Press; 1997. ISBN 0 684 825805.

[5] McDonald MHB. Marketing plans—how to prepare them: how to use them. 2nd ed. Oxford: Butterworth-Heinemann Ltd; 1989. ISBN 0 7506 01078.

[6] Raugei P. Evaluation of technology risk in vacuum coating equipment decisions. In: Proc. 10th international conference on vacuum web coating; 1996. p. 164−8.

[7] Lievens D. Engineering aspects of building a sputtering facility. In: Proc. 7th international conference on vacuum web coating; 1993. p. 140−50.

[8] Shingo S. Zero quality control: source inspection and the Poka-Yoke system. Translated by Productivity Press. Cambridge MA; 1986.

[9] Poka-Yoke—improving quality by preventing defects. Nikkan Kogyo Shimbum Ltd. and Factory Magazine, Eds. Translated by Productivity Press. Cambridge, MA; 1988.

[10] Misiano C, et al. Optical coatings on roll-to-roll coaters by reactive deposition. In: Proc. 11th international conference on vacuum web coating; 1997. p. 132−7.

[11] Jaran JR. The economics of the vacuum roll coating process. In: Proc. 2nd international conference on vacuum web coating; 1988. p. 27−34.

[12] Boswarva IM, et al. Some experiences in maintaining a vacuum roll coater system for 24 hours-a-day production and high levels of availability. In: Proc. 5th international conference on vacuum web coating; 1991. p. 260−90.

24 Heat Load on the Webs/Foils

24.1 Introduction

All deposition processes provide a heat load onto the substrate. Although it does not matter whether the web is cooled or heated prior to the deposition process, the management of the heat load is a critical factor in most processes.

The primary heat load is the latent heat of condensation, which is the energy lost when the condensing atom stops moving about on the surface and nucleates and cools. The other sources of energy tend to be source dependent. Resistance-heated boats run at 1400°C, and the whole boat radiates heat, which is seen by the substrate [1]. The magnetron sputtering sources tend to run much cooler and so do not radiate as much of a heat load. They do, however, have energetic species in the plasma that are a source of heat load [2–4]. The resistance-heated boats do not produce these energetic particles. Electron beam guns fall somewhere in between the above two sources. The crucible is often cooled, and it is only the molten pool that radiates heat, making them similar to the resistance-heated sources. However, they also produce some secondary electrons that can bombard the substrate, although this is much less than for the sputtering sources [5].

There can be an additional source of heating in some reactive processes, such as the oxidation of aluminum. The chemical reaction of converting aluminum metal to aluminum oxide is an exothermic reaction and liberates heat. In some aluminum deposition processing, the whole metal layer is converted to oxide, rather than the surface oxidation of only the top few monolayers, and thus the heat liberated by this conversion, in addition to the other heat sources, can be of significance. It is possible for this oxidation process to continue beyond the deposition process and, in some cases, the roll temperature can continue to rise after metallization has been completed and the roll removed to storage [6].

In production, it is usual for the process to be run at the maximum possible speed. In many processes, the rate-limiting step is the ability of the web to handle the heat. The process has an energy balance, where the deposition source is the initial source of heat and the cooled deposition drum is the heat sink (Fig. 24.1). The heat transfer coefficient between the polymer web and the cooled deposition drum is most often the rate-limiting factor.

As the process is in a vacuum, the heat transfer is through direct contact between the web and the drum. The number of points of contact is dependent on

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00024-6

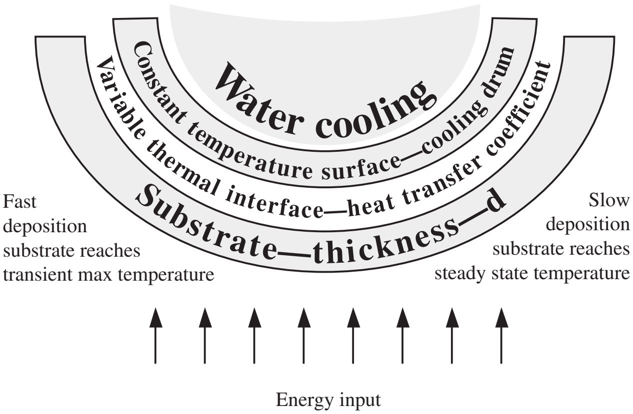


Figure 24.1 A schematic of the critical area of energy balance, the polymer web to cooled deposition drum interface.

the surface roughness of the deposition drum and the polymer web. The surface roughness of the polymer web is often determined by the addition of fillers that are added to make the polymer web more easily handled.

What has been established is that the heat transfer coefficient is material dependent, and this has been found to relate to the water content of the polymer. The water vapor present on the reverse surface of the polymer acts as a heat transfer medium between the polymer and the deposition drum, increasing the heat transfer coefficient. This process has been improved by using the idea of having a heat transfer medium added between the web and deposition drum. In this way, rather than relying on the water content of the polymer, the quantity of which can be a variable, a gas is injected between the web and the drum as the former is brought into contact with the latter. The gas will leak out of the edges over a period of time but, if the process speed is high enough, will remain long enough to improve the heat transfer coefficient while the web is under intense heat load through the deposition zone.

Polymer webs have a limited heat capacity before the heat relaxes the bonds such that the polymer will shrink. Hence, it is common to aim to balance the heat load with an equal amount of cooling [7].

Metal foils are commonly thought to be less in need of cooling. This may not entirely be true. It is common for foils to be contaminated with oils from the previous manufacturing processes. Even after washing or pickling, these oils can still be present deep within the grain boundaries of the metal foil. The effect of heat for these oils is to migrate to the surface, leading to coating blemishes and loss of adhesion. It is common to use high-power plasma etch or sputter etch to clean out this residual oil before deposition. This high-power clean can raise the temperature of the foil by several hundred degrees and this can affect any heat treatment already given to the foil. Hence, there can be a need to control the temperature even with metal foils.

There is a balance between using the heat to give better adhesion and maintaining the substrate properties. It is also worth bearing in mind that in many processes a steady state will never be reached. Over the years, there have been several studies that discuss and model the behavior of polymer webs in vacuum [1−15].

24.2 Cooling Webs

The most common form of cooling is done using a liquid-cooled deposition drum. This can be extended by using pre- or postdeposition cooled rolls. Although it is often referred to as water cooling, it is common for the liquid to be a mixture of water and ethylene glycol (antifreeze). This mixture allows the refrigeration unit to take the temperature down to around −20 to −30°C or lower. If the process increases the web temperature by 100°C, this would take the substrate to 120°C from a starting point of room temperature. Reducing the starting temperature by 40−50°C will, at best, reduce this peak temperature to 70−80°C. This rule of thumb only applies if there is sufficient time with the web in contact with the drum for the temperature of the web to reach equilibrium with the drum. The same also applies with the web temperature as it leaves the drum being dependent on the peak temperature and the time it remains in contact with the drum following the end of the deposition zone.

The web, once it is in intimate contact with the deposition drum, will start to cool down to match the drum temperature. If there is enough time and a sufficiently high heat transfer coefficient between the first contact to the drum and the start of the deposition zone, the web will reach the same temperature as the drum. This makes the precooling very speed dependent. In slow processes, such as most sputtering processes, the web will reach the drum temperature easily, but for faster metallizing speeds, there will be insufficient time, even with a high heat transfer coefficient, for the web to reach equilibrium. As the web progresses across the deposition zone, the web temperature will rise because the rate of heat arrival at the front surface is faster than the rate of cooling at the back surface. Once the web moves beyond the deposition zone, the cooling continues and the web temperature falls.

Again, depending on the time spent in contact with the drum, postdeposition will determine whether the web is above, at, or below room temperature as it leaves contact with the drum. Figure 24.2 shows the web starting temperature as being 20°C, falling to 5°C with precooling, then rising to 110°C and finally falling to 50°C with postcooling. Some materials can exhibit problems if rewound too hot. The rewound roll can shrink on cooling and put damage into the roll such as blocking of the web. Where it is necessary to rewind at a temperature close to ambient, it has been known for additional cooled postdeposition rolls to be included. In Fig. 24.2, the temperature profile has the additional cooling of a postdeposition roll included. If the plot were to continue to include another roll before the web reaches the rewind, it would show further falls in temperature with the web approaching ambient.

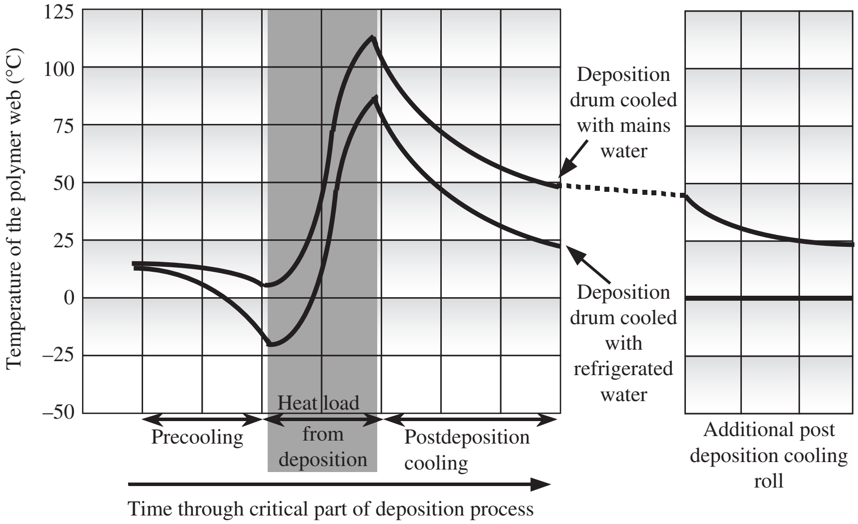


Figure 24.2 The web temperature profile from pre- to postdeposition drum.

Occasionally, this is not enough, and an additional controlled temperature roll has to be supplied. A cold roll will attract condensation when the system is brought back to atmospheric pressure. A hot roll will contract on cooling and can cause other problems such as crushed cores as well as transverse shrinking, distorting the roll. So, it is better to aim for ambient temperature.

24.3 Free Span Deposition

A number of problems that arise from the changes in polymer web temperature are seen as winding defects. One development that was aimed at eliminating some of the web-handling problems was to not have the web in contact with a cooling drum at all during deposition but instead to coat the web in free span. In this case, there are pre- and postdeposition cooled rolls. This system does without the cooling during the deposition, and so the temperature rise during deposition will be a maximum. This will limit the maximum quantity of metal that can be deposited in a single deposition. This process can have the advantage of allowing the deposition to take place all the way to the web edges without any need for edge shields to protect any deposition drum. This can reduce the shielding necessary and so be a way of increasing the material deposition efficiency as well as reducing the scrap as there is no need to slit off the uncoated edge.

Where the substrate is tolerant to high temperature, such as metal foils or polyimide films, the web may be preheated and then the heat loss from the hot substrate be balanced against a distributed deposition heat load. The difficulty here is still about managing the heat load. If the film entering the deposition zone is already at the desired deposition temperature, the depositing coating will increase the temperature, and although the back surface can be used to radiate heat away, if necessary to a cooled surface, it is common for the substrate to still increase in temperature throughout the deposition zone as it is easier to add heat than to lose it.

24.4 Heated Substrates

Instead of using a coolant passing through the deposition drum to extract heat from the substrate, it is possible to use a hot liquid such as oil to increase the deposition drum temperature and so increase the substrate temperature. This method of increasing the web temperature has the advantage that it can be uniform and it limits the heat to a small section of the winding path. However, it is not without problems. The greater the temperature change that is being given to the substrate, the more the substrate will want to expand, and as the substrate is held hard onto the deposition drum, there is a risk of the substrate wrinkling due to the transverse compressive load from the combination of thermal expansion and in-line tension.

Where high temperatures are required, the substrate may be heated so that there is a free-span region between heating stages to allow the transverse expansion to be accommodated. Similarly, if the substrate is heated in free span using radiant heaters, this problem may be reduced. It may still be necessary to use spreader rolls to assist the transverse expansion to be accommodated such as before it is wrapped around a deposition drum.

Beyond the deposition zone and rewind roll, it is preferable for the substrate to be returned to ambient temperature, and this can often be more of a challenge than heating. This is not because of a problem of web handling but simply because removing heat is a slower process than adding. Many processes want to minimize the number of contact rolls and so cannot easily use contact with cooled rolls as a method of extracting the heat. Radiating to cooled surfaces often looks on paper as if it will work well, but it tends not to work as well in practice. One significant problem is the quality of the cooled surfaces, which cannot be maintained, and so the original performance cannot be maintained. The surface roughness and emissivity will change with contamination or oxidation, which means that the surface no longer absorbs as much heat, and so the substrate will not lose heat as quickly and will wind hotter. It is very difficult to isolate these cooling surfaces so that they do not degrade, although it requires little effort to maintain the cooling efficiency of any in-contact rolls. In other words, cooling techniques have been suggested such as using cold gas or liquid jets directed against the back surface of the substrates. In this case, the jets of liquid as they hit the substrate are heated and convert to a gas and so provide cooling. The gas simply increases in temperature on contacting the substrate. The difficulty of this type of cooling is managing the volumes of gas that would be required to bring the substrate temperature down. Not only would this require considerable pumping but also there is the difficulty in preventing the high gas load adversely affecting the deposition process.

24.5 Potential Winding Problems

There are the usual winding problems that can occur on winding systems in vacuum just the same as winding systems in air [16]. Here, we will concentrate on those additional ones that appear to be highlighted during the deposition process. If we look at the most commonly used system, where the web is in contact with a cooled drum during deposition, we can see how stress in the web can create coating/web defects.

The web is wrapped around the deposition drum and a tension is pulled on the web. This tension means that the web is held hard against the drum (Fig. 24.3).

We look at the transverse direction first. The web will already have a compressive stress because of the machine direction tension. As the web is cooled by the drum, it wants to contract but is held in place by the friction between the web and the drum. When the web is exposed to the heat load it will be in compression, due to wanting to expand but being constrained by the contact pressure produced by the applied tension. Once the web passes beyond the deposition zone and the web is cooled, the compressive force is reduced back to the point where, at ambient temperature, the stress returns to zero.

In the machine direction, it is slightly different. There is an initial tensile stress. If the web were not pinned by the contact pressure, the tension would increase in the precooling zone because of the web contraction. In the deposition zone, it would expand due to thermal expansion that would tend to relieve the tension and the final postdeposition cooling would return the tension back toward the starting condition.

Where things start to go wrong is where the contact pressure is insufficient to pin the web to the drum. Any movement in the transverse direction can be catastrophic. When the web is in the deposition zone and the web wants to expand but is constrained, the coating will be uniform across the web. If the tension is too low and the contact pressure is overcome by the polymer expanding, there is nowhere for the polymer to go other than outward, thus losing contact with the drum. This is shown schematically in Fig. 24.4.

This problem can start out as a narrow buckle, but as contact is lost with the cooling drum the web temperature will locally increase, making the thermal

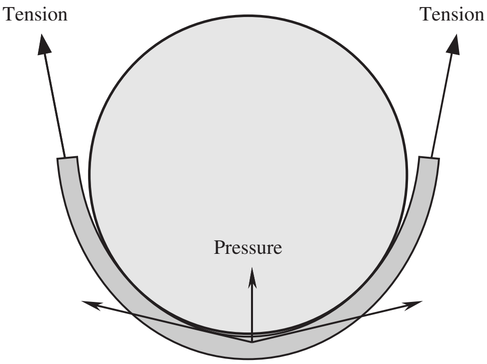


Figure 24.3 A schematic of web tension around the deposition drum.

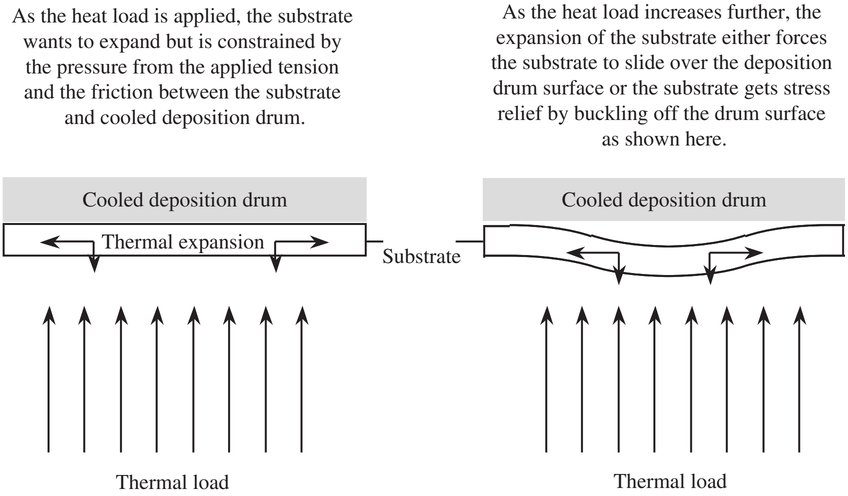


Figure 24.4 A schematic of how a buckle forms.

expansion greater and tending to increase the width of the buckled web [17—23]. The coating material will have a slightly reduced thickness on the web not in contact with the drum because of the increased surface area and slightly reduced sticking coefficient. Thus, when the web is inspected, lines can be seen down the length of the web. These are known as tramlines or wrinkles.

If tramlines are seen to be starting, it may be possible to stop them by increasing the tension to increase the contact pressure and increasing the pinning action on the web. This may not always be possible. The tension applied is commonly around 10%, or lower, of the yield strength of the polymer at the maximum temperature the web reaches.

24.6 Characteristic Winding Problems Associated with Too Much Heat

24.6.1 Tramlines

As described above, a combination of too much heat and lack of tension allows buckling of the web in the machine direction. Often a number of lines are formed that are parallel to each other, hence the term tramlines.

These tend to occur more easily in thinner and softer substrates. If the tramlines are parallel and exactly oriented in the machine direction, they are most likely caused by heat and low tension alone (Fig. 24.7). If the tramlines are angled to the machine direction but are regular, there may also be some roller misalignment too. If the tramlines are angled and irregular, they may also be related to some contamination.

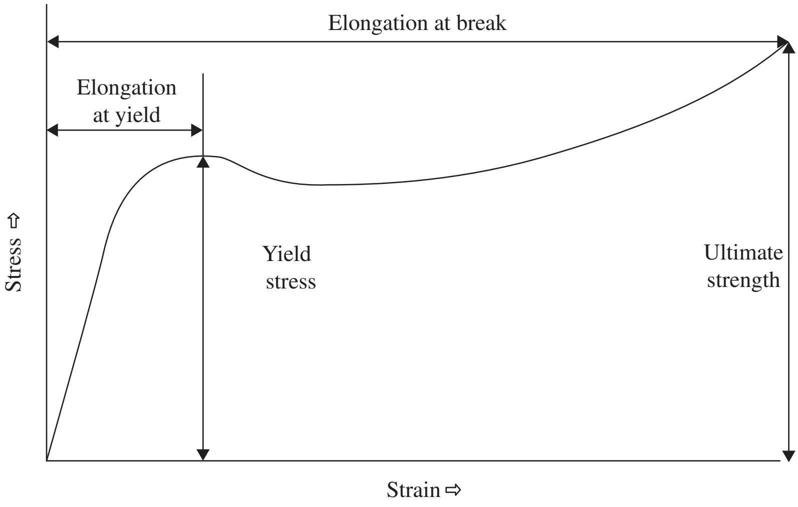


Figure 24.5 A typical stress/strain curve for a polymer web.

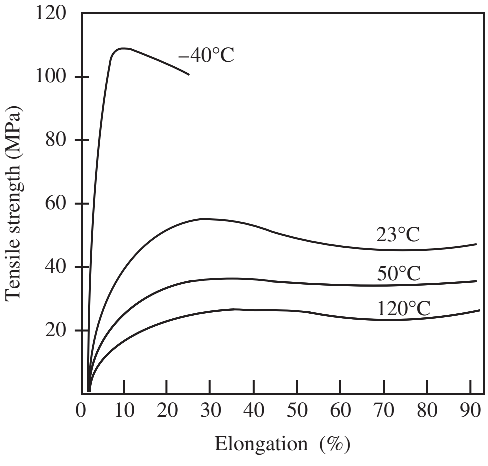
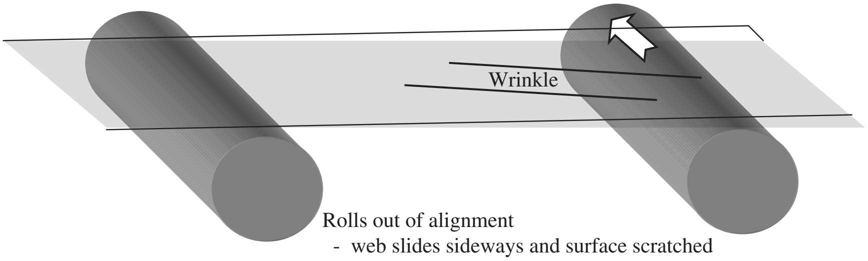


Figure 24.6 A schematic showing the fall in tensile performance of the polymer web with increasing temperature.

It is possible to model the winding and heat load to the web to estimate when it will be at risk of having tramlines formed [24,25], which can be worth doing as, when down-gauging film thickness, a process that does not wrinkle the original web may wrinkle the thinner web simply because of the different combination of thickness, stiffness, tension, heat load, and speed.

24.6.2 Ballooning

This is an exaggerated form of tramlines. The buckled web overheats enough so that the volume of the web that is no longer in contact with the drum continues to



Rolls out of alignment
- web slides sideways and surface scratched
  - this will also tend to cause wrinkles

Also not helped by large distances between rolls

Figure 24.7 A schematic showing how wrinkles form due to roll misalignment.

grow and the web balloons off the drum. This tends to be more of a problem with thicker and stiffer webs and those that have a higher water content. As the web heats up, the water vapor outgases from the polymer surface. On the back of the web, the water vapor has nowhere to go other than to increase the volume by separating the web from the drum.

24.6.3 Shrinking

If the web has been oriented and the temperature is raised enough, there will be some memory to the polymer and it will try to shrink [26]. Some polymers are heat stabilized to minimize this shrinkage, and it may well be controlled to a fraction of 1% at 100°C, whereas others will shrink much more than this at temperatures well below 100°C.

If the temperature is raised too much, it may reach a point where the yield point, which falls with rising temperature, is exceeded and the polymer extends in the machine direction (Figs. 24.5 and 24.6). There will be a concomitant shrinkage in the transverse direction. This can be seen in the rewind roll where the edge quality looks poor due to the variable polymer width.

24.6.4 Polymer Melting and Web Breaks

An extreme case of shrinkage is where the temperature continues to increase and the tension is sufficient to snap the web. It is worth noting that not all polymers melt; high-temperature substrates such as polyimide may oxidize and decompose rather than melt. This is a slower failure process and so it is often possible to exceed the recommended maximum use temperature in vacuum systems. This is because as the amount of available oxygen in the vacuum is limited, the decomposition is much slower than that at atmospheric pressure. There have been occasions where polyimide has been used at more than 100°C above the recommended maximum use temperature without any apparent problem.

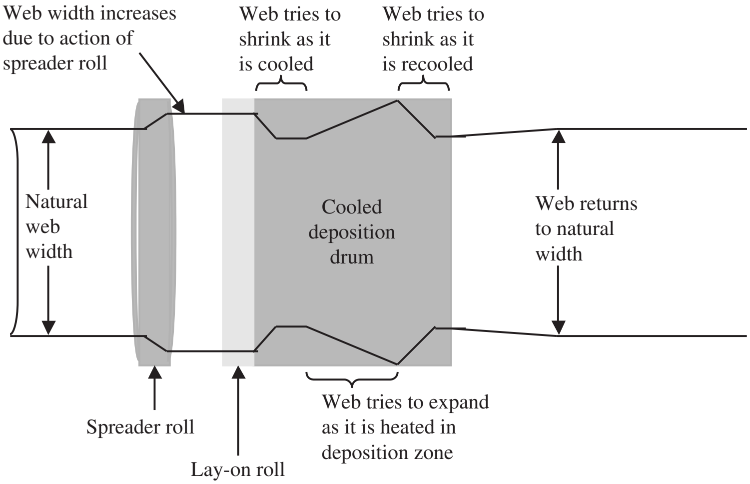


Figure 24.8 A schematic showing how the web width will be changing through the process. Ideally, the width on the rewind roll will be equal to the unwind width.

24.7 Heating Webs

There are some processes that have to be run with a heated substrate to ensure the coating produced has the desired crystal structure. Obviously, this requires a substrate that allows a higher working temperature. The methods of heating the web include the use of radiant heaters, or a scanned e-beam (in the case of metal substrates) before the web reaches the deposition zone and/or heating the web on the drum by using a heated liquid instead of a cooling liquid.

This adds a different problem to the deposition process. Once the coating has been deposited at high temperature, it will cool back to ambient as too will the substrate. The coating and substrate are likely to have different thermal expansion coefficients so that as they cool they will contract at different rates. This will add a stress at the coating−substrate interface and may also be seen as a curvature of the coated substrate as a result of the stress in the coating. High stress can cause interfacial adhesion failure or, if the adhesion is good enough, can cause either buckling or cracking in the coating.

Edge masking is done to prevent the deposition drum from being coated. The aim is to have the mask close to the drum and the web so that the mask only overlaps the web by a small amount (Fig. 24.9). If the mask is too close, the deposited coating during deposition can be sufficient to touch the web and cause scratches to the web or worse be a cause of web breaks. If the gap between the mask and the web is too great, scattered material can travel down the gap and coat the drum and so the overlap needs to be increased. So time is spent to make sure these shields are robust and do not distort and are shaped to minimize the chance of any buildup of coating touching the web.

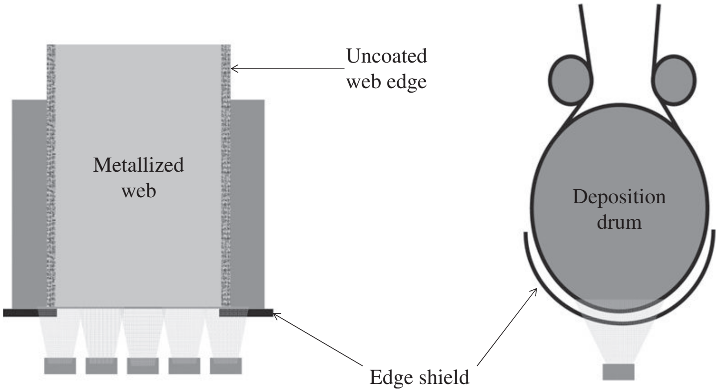


Figure 24.9 A schematic showing the cold web edge caused by edge masking.

These edge masks do give an additional problem to the winding of the webs in that they cause the web to have a different heat load beneath the mask to the rest of the web. So in the case of a standard metallizer that has a cooled deposition drum the edges of the web will be cooled all the time they are in contact with the deposition drum, whereas the rest of the web will initially be cooled but then, in the deposition zone, will be rapidly heated to a peak temperature before leaving the deposition zone and being cooled once more. So in the region of the deposition zone, the edges will have the web being cooled and wanting to contract and the rest of the web wanting to expand due to the heat load from the depositing material and radiant heat from the deposition source. Thus, the edges will take more tension than the rest of the web, which will be under reducing tension as the web expands. This is shown schematically in Fig. 24.10 where it is important to note that the graphs of tension are idealized and they take no account of the variations that might be present in the web, such as gauge profile variations.

For a standard metallizing process where the drum is cooled to, for example, $-20°C$ and the peak temperature reaches 80°C, there will be a peak difference of 100°C between the edges and the rest of the web. This would represent a difference in web length in the machine direction of approximately 0.4 mm between the longer heated section and the shorter cooled edges, assuming a deposition zone of 0.25 m. There will be a similar temperature difference for any process where the edges are shielded. So for some of the higher temperature materials that are heated, rather than cooled, the web or foil will still have the additional heating from the deposition process and the edges will still be shielded from this heat load and so there will still be a temperature difference and hence a tension difference. If the tension is being reduced, the heat transfer coefficient could be falling and so the substrate cooling reduced, and this could lead to wrinkling of the area of the web being deposited on or even ballooning of the web. The cooled edge, at the higher tension, will be held harder onto the deposition drum and so this will increase the resistance to any transverse movement. The transverse thermal expansion across the central

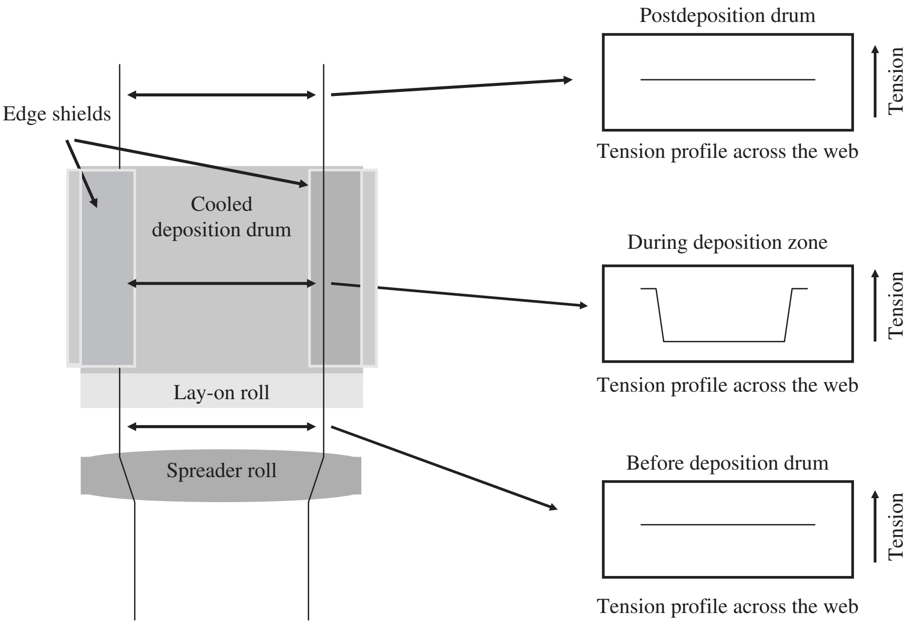


Figure 24.10 A schematic highlighting the variation in tension across the web width in the deposition zone because of the shorter cold edges caused by the edge shields.

heated region of the web will be seen as a compressive force for which the stress release mechanism is wrinkling.

24.7.1 Outgassing

Many webs contain moisture absorbed both on the surface and within the bulk of the polymeric web [27]. This water vapor can be both a help and a hindrance. The web surface when exposed to the vacuum will have the surface water vapor removed, albeit slowly. As the surface is denuded of water vapor, more is diffused out from the bulk of the polymer to repopulate the surface with more water vapor [28]. This surface water vapor can affect the quality of the depositing coating. The deposition of transparent conducting coatings is particularly sensitive to this problem and so pretreatment such as outgassing [29,30] or outgassing and a blocking or sealing layer has been used to improve the quality of these coatings. Metallized coatings too have been shown to be affected by the water vapor content [6].

Figure 24.11 shows that the rate of outgassing can be increased if the temperature of the web is increased. If we look at the distance between the unwind roll and the deposition drum in each system along with the winding speed, it will give the time available for outgassing before the coating deposition. If we take the distance between the unwind roll and the deposition drum as being 2 m, we have a time of 12 seconds at a winding speed of 10 m/min or 0.2 seconds for a winding speed of

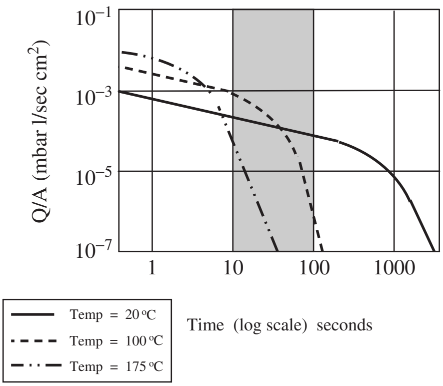


Figure 24.11 Outgassing of thick polymer film at different temperatures.

600 m/min. If we look at the shaded area in Fig. 24.11, we can see that it needs more than 10 seconds when the web temperature is taken up to 175°C to have a significant impact on the outgassing rate, or closer to 100 seconds if the polymer is taken to 100°C. This indicates that there is insufficient time for full outgassing for a standard winding system and single-pass process. The web needs to be wound through the system either several times or a couple of times at a slower speed and higher temperature to fully outgas the polymer web. What slows down the outgassing process is the diffusion rate of water within the bulk polymer. Heating increases the diffusion rate through the bulk polymer. Plasma treatment is one method of speeding up the removal of the surface water vapor and also heating up the substrate. Usually, the residence time is only a fraction of a second, which is insufficient time for water to diffuse out from the center of the film, which could take minutes [31]. Hence, by the time the web reaches the deposition zone, there may once again be some water vapor present at the web surface.

It is worth noting that the time taken to outgas any film will depend on the amount of absorbed water, which, in turn, will depend on the storage conditions and possibly the location in the world. Some locations have seasons where the humidity is 100%, and so unless the film is stored in humidity-controlled conditions, the film will absorb considerably more moisture than where local conditions are much drier. This will make the preconditioning time much longer than that for films with lower moisture content. Figure 24.12 shows how the moisture uptake can vary with relative humidity. Different manufacturers or different grades of polyimide may have different absorption characteristics as too will other polymers [33,34].

The choice of how much time and heating can be used to prepare the substrate will be determined by the potential added value available from the final coated product. Thus for metallized film, there is little cost available and so generally nothing is done beyond the plasma treatment used to increase adhesion helping clean the surface to be coated. For electronic applications, including photovoltaics that use transparent conducting coatings, there is often more added value available and so some processes include heating and winding the roll through one or more times before depositing the coating.

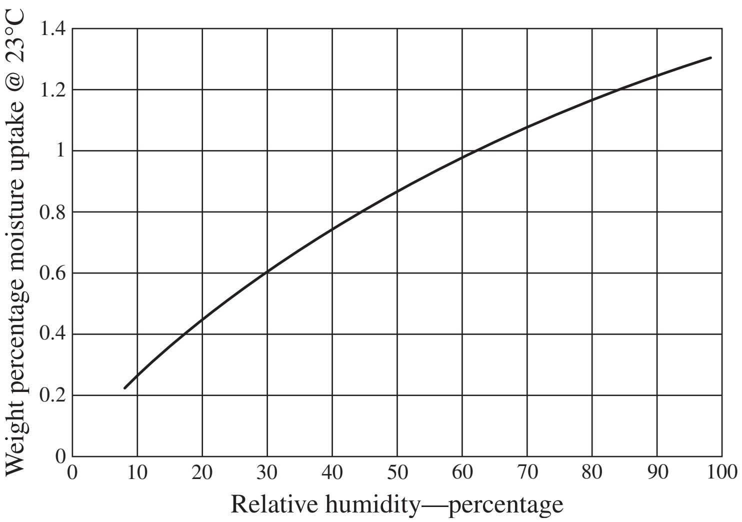


Figure 24.12 A graph showing the relationship between relative humidity and the percentage moisture absorption for Kapton E [32].

References

[1] Baxter IK. Effective film temperature control for vacuum web coaters. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 106–20.

[2] Class W, Hieronymi R. The measurement and source of substrate heat flux encountered with magnetron sputtering. Solid State Technol 1992;December:55–61.

[3] Lau SS, Mills RH. Temperature rise during film deposition by RF and DC sputtering. J Vac Sci Technol 1972;9(4):1196–202.

[4] Thornton JA, Lamb JL. Substrate heating rates for planar and cylindrical-post magnetron sputtering sources. Thin Solid Films 1984;119:87–95.

[5] Schiller S, et al. Progress in high rate electron beam evaporation of oxides for web coating. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 278–89.

[6] Ahmed NAG, Ellis GH. The influence of water content on temperature rise in metallized polypropylene films. In: Proc. 40th annual technical conference of the Society of Vacuum Coaters; 1997. p. 350–3.

[7] Hendricks WC, Diffendaffer PA. Web thermal modelling for vacuum coating processes. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 134–9.

[8] Blackwell JK, Knoll AR. Thermal profiles and model for various webs heated in vacuo by IR. In: Proc. 32nd annual technical conference of the Society of Vacuum Coaters; 1989. p. 91–9.

[9] Blackwell JK, Knoll AR. Web temperature profiles and thermal resistance measurements of roll sputtered copper and chromium onto polyimide films. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 169–73.

[10] Blackwell JK, et al. DC glow effects on web temperatures. In: Proc. 33rd annual technical conference of the Society of Vacuum Coaters; 1990. p. 194−9.

[11] Taylor A. Practical solutions to web heating problems. In: Proc. 7th international conference on vacuum web coating; 1993. p. 107−19.

[12] Affinito J, et al. Web substrate heating and thermodynamic calculation method for Li film thickness in a thermal evaporation system. In: Proc. 44th annual technical conference of the Society of Vacuum Coaters; 2001. p. 492−7.

[13] Roehrig M, et al. Vacuum heat transfer models for web substrates: review of theory and experimental heat transfer data. In: Proc. 43rd annual technical conference of the Society of Vacuum Coaters; 2000. p. 335−41.

[14] Taylor A, Lievens D. Flexible substrates for sputtering. In: Proc. 11th international conference on vacuum web coating; 1997. p. 238−48.

[15] Uyama H, et al. Thermal behaviour of plastic substrate during deposition. In: Proc. 14th international conference on vacuum web coating; 2000. p. 63−71.

[16] Roisum D. Wrinkling of thin webs. In: Proc. 41st annual technical conference of the Society of Vacuum Coaters; 1998. p. 406−11.

[17] Clow H. A model for thermal creasing and its application to web handling in roll to roll vacuum coaters. In: Proc. 32nd annual technical conference of the Society of Vacuum Coaters; 1989. p. 100−3.

[18] Wales JLS, Clow H. Model for thermal creasing in roll to roll vacuum metallising. In: Proc. 2nd international conference on vacuum web coating; October 1988. p. 204−14.

[19] McCann MJ, Jones DP. Web coating dynamic and wrinkling model. In: Proc. 41st annual technical conference of the Society of Vacuum Coaters; 1998. p. 412−7.

[20] McCann MJ, et al. Buckling or wrinkling of thin webs off a drum. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 638−43.

[21] Schwarz W, Wagner W. Thermal limitations in roll coating processes. In: Proc. 28th annual technical conference of the Society of Vacuum Coaters; 1985. p. 28−41.

[22] Benson RC, et al. Simulation of wrinkling patterns in webs due to non-uniform transport conditions. In: Proc. 2nd international conference on web handling; OSU, 1993.

[23] Chiu HC, et al. Mechanical and thermal wrinkling of polymer membranes. In: Proc. ASME winter annual meeting; 1993.

[24] McCann MJ, et al. The power of simple models used on complex processes. In: Proc. AIMCAL fall conference and 24th international conference on vacuum web coating; 2010.

[25] TopVac vacuum deposition software module. Rheologic. Available from: http://www.rheologic.co.uk.

[26] Behaviour of Mylar under heat and stress. DuPont films information note (1M) 9.94 - H-36633; 1994.

[27] Roehrig M, et al. Vacuum heat transfer models for web substrates: review of theory and experimental heat transfer data. In: Proc. 43rd annual technical conference of the Society of Vacuum Coaters; 2000. p. 335−41.

[28] Gebele T, et al. Substrate heat load and cooling in PVD-web coaters. In: Proc. AIMCAL fall technical conference and 17th international conference on vacuum web coating; 2003.

[29] Noda K, et al. Characterization of Sn-doped In_2O_3 film on roll-to-roll flexible plastic substrate prepared by DC magnetron sputtering. Jpn J Appl Phys 2003;42:217−22.

[30] Schwartz E. Roll to roll processing for flexible electronics. MSE 542: flexible electronics, Cornell University; May 11, 2006. p. 1−24.

[31] Song S, Placido F. Effect of gas release from polymer surfaces during microwave plasma pre-cleaning on the adhesion of metal films. In: Proc. 51st annual technical conference of the Society of Vacuum Coaters; 2008. p. 574−8.

[32] Eichstadt AE. Structure-property relationships and adhesion in polyimides of varying aliphatic content. PhD thesis, Virginia Polytechnic Institute and State University; 2002. p. 98.

[33] Upilex S data sheet. Version: 031105, Available from: http://www.ube.de/index.html.

[34] McClure DJ. Polyimide film as a vacuum coating substrate. In: Proc. AIMCAL fall technical conference and 23rd international conference on vacuum web coating; 2009.

25 Process Variables

25.1 Drum Surface Roughness

The drum surface roughness determines the number of contact points per unit area. The greater the number of contact points, the greater the heat transfer.

Typically, a 1-microinch mirror finish is required. There is no point in obtaining this quality of finish if it is not maintained well. This means that operators need to be trained to understand why scraping the surface with a screwdriver is an inappropriate way of cleaning and how a damaged surface can lead to web wrinkles.

25.2 Polymer Surface Roughness

It is relatively easy to manufacture polymer webs with a high-quality smooth finish. However, if both sides of the polymer are equally smooth, the polymer will block when wound in vacuum. The reason for this is that in vacuum there is no air to act as a lubricant to help the polymer web to move over the preceding layer during winding.

To solve this problem, it is common to find one side of the polymer rougher than the other. The smooth side is the side that gets coated and hence the rough side would be the one in contact with the deposition drum. The method of obtaining the roughness is often by inclusion of fillers into one side of a coextruded polymer (Fig. 25.1).

The difference in number and size of fillers can be one of the reasons why different manufacturers' equivalent grades handle differently. This can be particularly true in the deposition zone where differences in roughness and friction can be the factors that cause one film to wrinkle and another to emerge without wrinkles.

The heat transfer coefficient is dependent on the area of contact between the polymer and the drum; hence, the size, shape, and frequency of the fillers are significant.

This also shows why having dust-free webs is important. If the web cannot lie flat onto the drum surface in intimate contact, then the area of loss of contact is the potential start of tramlines [1] (Fig. 25.2).

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00025-8

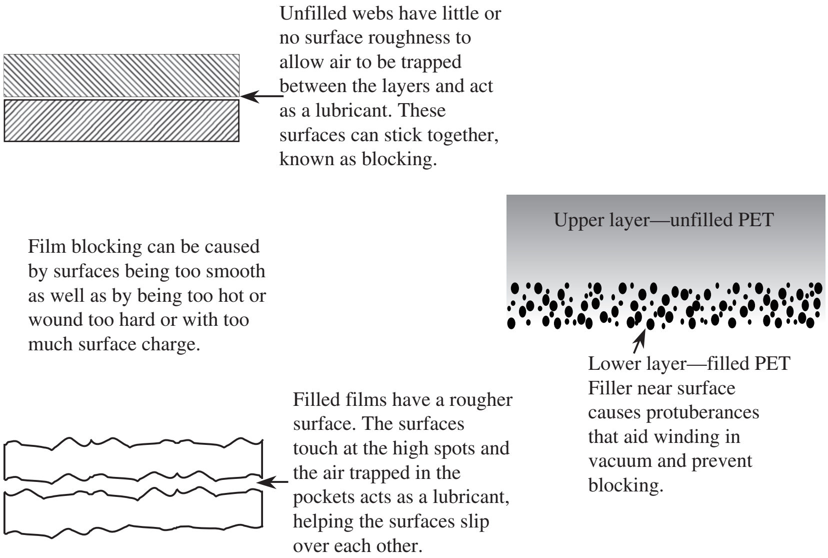


Figure 25.1 A schematic showing how fillers can change the surface roughness and thus prevent blocking problems.

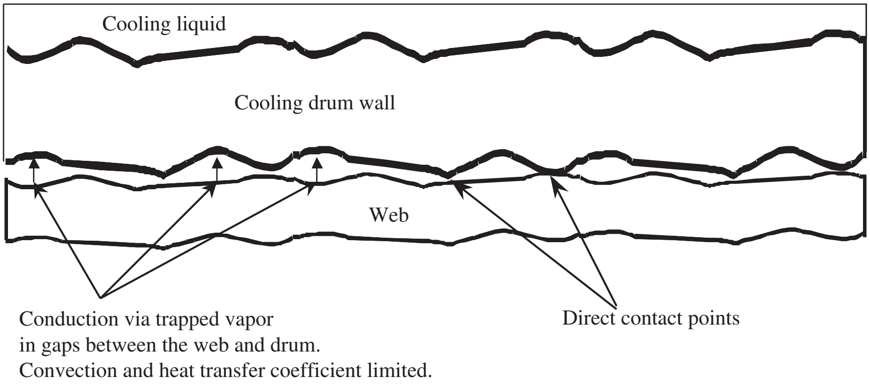


Figure 25.2 A schematic of the web to deposition drum interface.

25.3 Material Properties

The thicker the polymer, the greater the thermal capacity. This means that for very thin coatings, the rate of cooling may be less important.

$$\text{The heat absorbed } (Q) = \text{Unit mass} \times \text{specific heat} \times \text{temperature rise}$$
$$\text{The unit mass } (m) = 1 \times 1 \times \text{thickness} \times \text{density}$$

Typical specific heat for PET ~ 1.35 J/g/°C
Typical density for PET ~ 1.4 g/cm^3
Thermal conductivity for PET ~ 1.6×10^3 J/cm/sec/°C
Typical modulus for PET ~ 4.5×10^4 kg/cm^2 at 25°C
Typical modulus for PET ~ 1.4×10^4 kg/ cm^2 at 100°C
Typical thermal expansion coefficient for PET ~ 2×10^{-5} per °C

The rule of thumb is that PET expands 0.2% per 100°C
Thermal conduction through the film = (Q)

$$(Q) = \frac{\text{Thermal conductivity } (k) \times \text{area} \times \text{temperature difference through the film}}{\text{thickness } (d)}$$

Different polymers have different glass transition temperatures, specific heats, coefficients of thermal expansion, density, modulus, etc. These will affect the maximum allowable operating temperature, the tension applied, and the winding speed.

25.4 Deposition Rate and Winding Speed

The deposition rate and the winding speed are often linked. For a coating of the same thickness but different winding speed, the heat load per unit time will change. Also, the residence time in the deposition zone will be different, hence the total load from the radiant heat source and the peak temperature will be different [2].

In most cases, there is a requirement to deposit the coating as fast as possible because this gives a higher quality coating and the cost of coating is lower.

25.5 Water Content of Polymer

The limiting factor in cooling the web is the heat transfer coefficient. The heat transfer coefficient is a difficult parameter to measure and hence the value is often inferred from other measurements. Measuring the water inlet and exit temperatures, the final web temperature in the roll, the coating thickness, and the winding speed can be done more easily. Thus, the heat transfer coefficients quoted can vary quite widely. More recently, it was shown that the heat transfer coefficient was not totally dependent on the conduction through the high spot contact points. It was proposed that the rest of the heat transfer was being done by conduction through convection through gas trapped between the web and the drum. As the process is being run in vacuum, the source of this gas was taken to be residual moisture from the web that was still being outgassed. The heat load hitting the front surface would increase this outgassing rate. The outgassing from the front surface would be pumped away. There would be outgassing from the back, but this gas would be trapped in the voids between the polymer and deposition drum contact points.

There are polymers that do not absorb moisture, and these have a lower heat transfer coefficient than those that do. The ones that do absorb moisture will have a heat transfer coefficient that is an uncontrolled variable (Fig. 25.3).

The amount of water they contain will depend on the history of manufacture to that point (Table 25.1). The humidity on the day they were manufactured will help define the water content. This may be modified if the roll is rewound. In this case, the humidity at the time of rewinding and additionally the humidity and time spent in storage will together define the water content. When in the vacuum system, the surface layer of water will be pulled out during the initial unwinding. The gas load seen when pumping the vacuum system will depend on the water content in the bulk polymer which, in turn, will affect the diffusion rate and determine the continued outgassing rate.

Modern PET films can now be produced with the moisture content down at 0.15% [3]. However, this is not necessarily achieved for all grades, and the age and

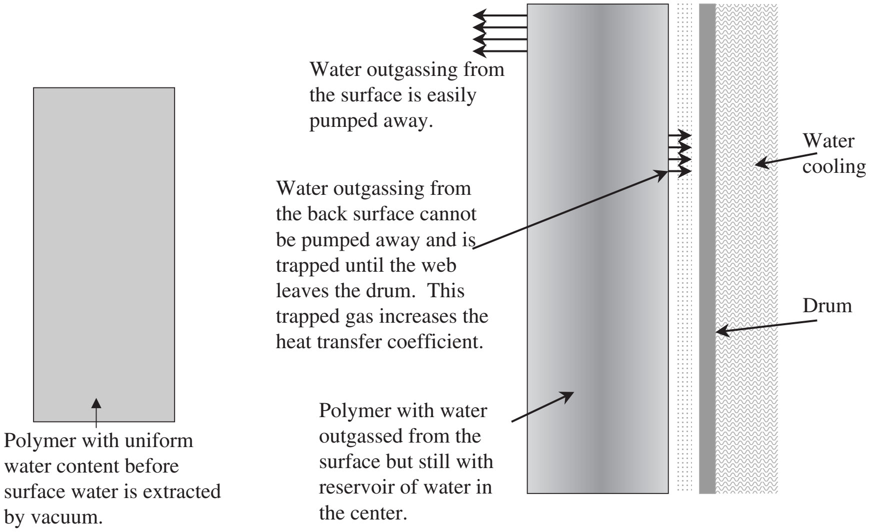


Figure 25.3 A schematic of the moisture content of polymer webs.

Table 25.1 Details of the Possible Moisture Content of a Number of Materials

Polymer Type		Maximum Water Absorption (% by weight)
Polyethylene terephthalate	(PET)	0.15–0.6
Polyethylene		0.02
Polyvinyl chloride	(PVC)	0.2
Polytetrafluoroethylene	(PTFE)	∼0

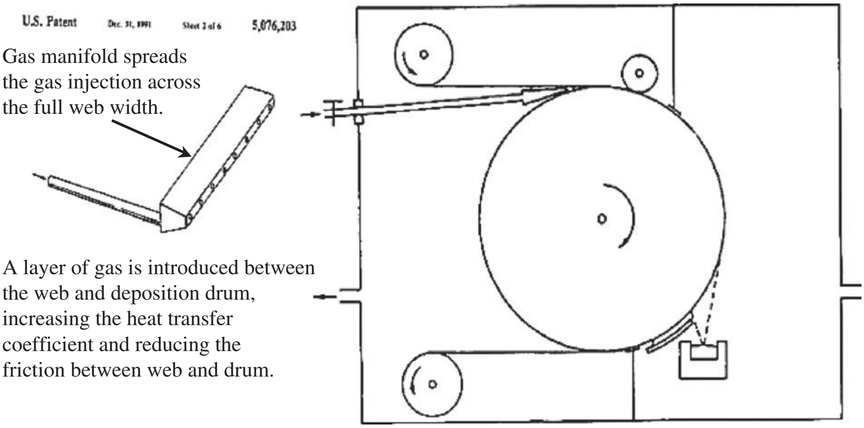
storage conditions can also affect the amount contained when the roll reaches the vacuum system.

A development that uses this phenomenon, as a method for maximizing the heat transfer coefficient, was first tried in the deposition of thick magnetic films by e-beam deposition. The process was to deliberately inject gas behind the web at the point where the web meets the deposition drum [4–7] (Fig. 25.4). The effect was that the web floated on the trapped gas layer. Not only did the gas increase the heat transfer coefficient, allowing a higher deposition rate, but it also allowed the web to move to adjust for the dimensional changes due to thermal expansion. This minimized the propensity of the web to wrinkle.

Figure 25.5 shows how the coefficient of friction is reduced by the increasing gas flow to the injection wedge [4]. Also, it shows that the faster the web winds, the less the gas required to achieve a particular coefficient of friction.

The injected gas picks up heat each time it hits the hot substrate surface and loses heat each time it hits the cooled refrigerated drum surface (Fig. 25.6). There will be a pressure differential between the center of the web and the edge of the web where the gas is lost to the system. This highlights one of the potential problems with this technology. The gas injected behind the web as it leaks out at the edges increases the pressure in the deposition zone. If this is added as a process modification, this may affect the structure of the growing film. Ideally, the pumping system is sized to manage this gas load during deposition and there is a suitable flow path for the escaping gas to reach the pumps easily.

To overcome this problem, the gas should be injected through channels and holes in the drum surface so that throughout the time the web is in contact with the drum, the gas is always being introduced between the web and the drum [8]. This allows the process to be used for both slow winding speeds and narrow web widths.



Gas manifold spreads the gas injection across the full web width.

A layer of gas is introduced between the web and deposition drum, increasing the heat transfer coefficient and reducing the friction between web and drum.

Figure 25.4 Diagram of one of the patents taken out for this gas wedge technology [4].

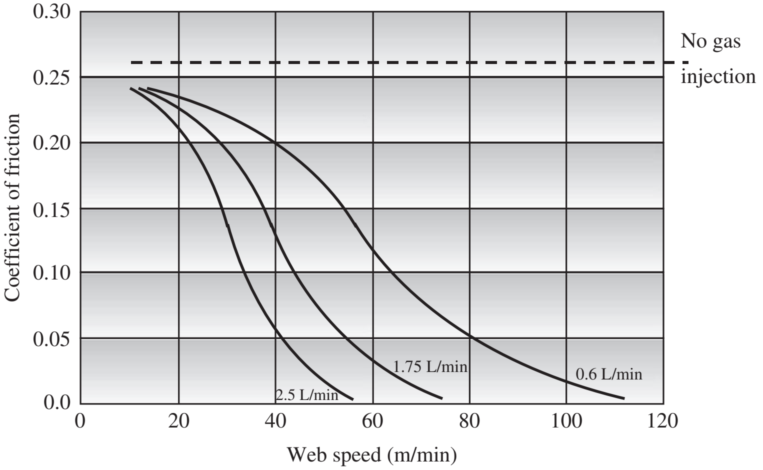


Figure 25.5 A graph of the change of friction with different gas injection rates.

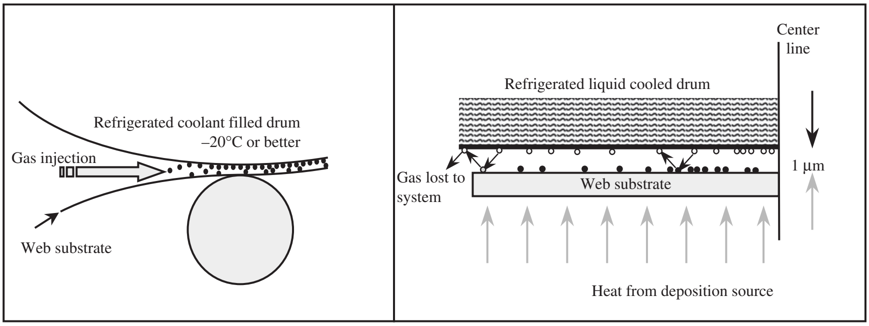
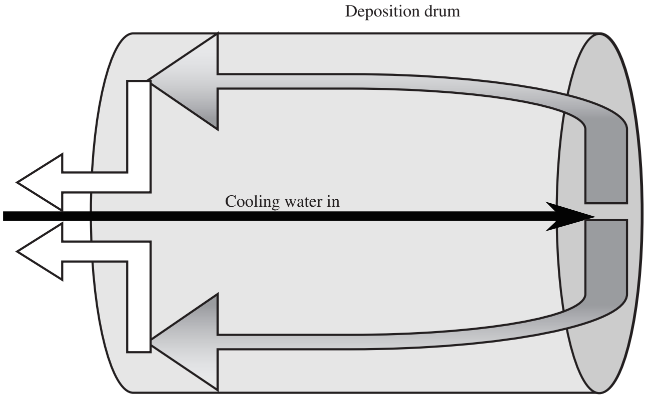


Figure 25.6 Schematics of the introduction of gas to aid heat removal.

25.6 Drum Temperature

The drum temperature is often assumed to be whatever the cooling system temperature has been set to. In reality, that temperature may only be seen by part of the drum. The design of the drum will determine the cooling path for the liquid. In some designs, the liquid is pumped to one end of the drum where it returns down a spiral tube around the drum's inner surface (Fig. 25.7). This leads to the drum being cooler on one edge than the other. Obviously, as the web coaters become wider, this temperature difference becomes greater, and alternative liquid paths have to be designed to minimize this effect. One strategy has been to have multiple spirals but with an extended spiral so that the liquid is moved from one end of the drum to the other more quickly. Others have used spray bars to spray the upper



The temperature of the coolant increases as the liquid moves from one end of the drum to the other and exits back to the refrigeration unit. Hence, there is a thermal gradient across the drum.

Figure 25.7 A schematic of the potential thermal gradient in a deposition drum.

inner surfaces with cooled liquid, and the liquid runs down the wall and collects in the bottom of the drum and the overflow is recirculated. This type of cooling process leads to a very heavy drum. For wide rolls, which have to be driven to high speeds, the mass makes inertia a problem when trying to start and stop the rotation quickly.

It is common to lower the cooling temperature to allow a further increase in deposition rate. Lowering the temperature can reduce the outgassing from the back surface of the web that would reduce the conduction component of the heat transfer coefficient. This could mean that the additional cooling might not gain as much of an advantage as was expected.

25.7 Single or Double Side Coating

If the web is to be metallized on both sides, it is noticeable that the heat transfer coefficient is different and higher for coating the first side compared to the second side.

The first side has a polymer to drum interface whereas the second side has a metal coating to drum interface [9]. The web will also reach a higher temperature during the second side deposition due to the heat being reflected back through the polymer web from the metallic coating on the first side. This means that more heat may be absorbed by the polymer and correspondingly less transferred to the cooled deposition drum.

This lower heat extraction rate and higher radiant heat adsorption usually mean that the speed of deposition for the second side is lower than for the first side. It has been referred to as being anywhere up to four times slower to coat the second side. This figure has been passed around by word of mouth with limited measured details to support this figure, although the second side deposition is definitely slower. Where both sides are deposited in a single pass, the process winding speed will be determined by the maximum temperature reached by the web in the second side part of the process.

25.8 Source Type

The total heat load can have up to four components: condensation heat load, radiation, energetic particles, and chemical reaction heat. The contribution that each component makes depends on the source type.

The deposition of metal from resistance-heated boats has only a contribution from the latent heat of condensation and the radiant heat from the sources. This is the easiest calculation to make. When using an e-beam source, there is the additional problem of estimating the contribution from the charged particles. Different designs of e-beam source will produce different quantities of secondary electrons that can bombard the substrate. Similarly, magnetron sources can be built to be balanced or unbalanced as well as with different strength magnets that will affect the amount of particle bombardment of the substrate.

25.9 Heat Load Calculations

The total specific heat load on a web/foil $= \frac{Q_{\mathrm{total}}}{A}$ where A = coating area.

$$\frac{Q_{\mathrm{total}}}{\mathrm{A}} = \frac{Q_{\mathrm{c}}}{\mathrm{A}} + \frac{Q_{\mathrm{r}}}{\mathrm{A}} + \frac{Q_{\mathrm{p}}}{\mathrm{A}} + \frac{Q_{\mathrm{o}}}{\mathrm{A}}$$

Where Q_{c} = condensation heat load
Q_{r} = radiation heat load
Q_{p} = charged particle heat load
Q_{o} = chemical reaction heat load

The condensation heat load (Q_{c})

$$\frac{Q_{\mathrm{c}}}{\mathrm{A}} = \gamma \times \frac{t \times v}{l}$$

Where $\gamma = \text{condensation parameter } (\text{J/m}^3)$
$t = \text{coating thickness (m)}$
$v = \text{winding speed (m/s)}$
$l = \text{coating length (m)}$

The condensation parameter γ is dependent on the specific enthalpy h_v of its vapor and the solid density of the deposit ρ:

$$\gamma = \mathrm{h_v} \times \rho$$

Thus, for the deposition of 25 nm of aluminum at 600 m/min (10 m/s) with a coating zone of 0.25 m, the condensation heat load would be:

$$\frac{Q_c}{A} = \gamma \times \frac{t \times v}{l} = 3.8 \times 10^{10} \times \frac{25 \times 10^{-9} \times 10}{0.25} = 38 \ \text{kW/m}^2$$

Where γ for aluminum $= 3.8 \times 10^{10}$

The radiation heat load (Q_r):

$$\frac{Q_r}{\mathrm{A}} = \phi \ \varepsilon_s \varepsilon_d \sigma (T_s^4 - \mathrm{T_f^4})$$

Where $\varepsilon_s = \text{emissivity of source}$
$\varepsilon_d = \text{emissivity of deposited film}$
$\phi = \text{the view factor from the film to the heat source}$
$\sigma = \text{Stephan–Boltzman constant} = 5.67 \times 10^{-8} \text{W/m}^2/\text{K}^4$

The emissivity of the deposited film changes during deposition from approximately 0.9, the emissivity of the polymer film, down to an emissivity of 0.04 for metals such as Al, Cu, or Ag.

Typically, for a resistance-heated source, running at a temperature of 1400°C and with a source to substrate distance of 0.2 m, one would expect the radiant heat load to be around 3 kW/m^2. This is approximately 10% of the condensation heat load.

The radiant heat load may increase with deposition time. The surrounding deposition shields will also be subject to radiation heating as well as having a condensation heat load, and unless the shields are efficiently cooled, they will heat up and start to radiate. It is unlikely that these will reach a steady state where heat losses equal the heat input, and so there will be a steady rise in temperature and hence radiation from the shields. Again, this will be small in comparison with the red hot boats, but it all adds to the heat load on the web.

25.9.1 The Energetic Particle Heat Load

This heat load depends so much on design that it is hard to calculate. Polymer webs that are particularly sensitive to heat load generally require that the magnetron design is of the balanced type so that the escaping electrons are not directed at the substrate as they would be with an unbalanced design [10–12]. Where it has been found experimentally, by looking at the difference between measured load and the input from condensation and radiation heat load, it has been estimated that the energetic particle energy is also of the order of 10% of the condensation heat load [13–15]. In magnetron sputtering, rather than trying to measure each component part of the heat load to enable the total heat load to be established so that they can then size the cooling capacity for the deposition drum, it is common to use a figure between 2% and 8% of the input power as the total heat load [16,17]. If the magnetron to substrate distance is reduced so that the substrate encroaches into the plasma, the heat load will increase because of the increased substrate bombardment.

25.9.2 The Chemical Reaction Heat Load

Less work has been done on this source of heat load. It is always expected to be low, and in cases where only surface oxidation occurs, it is ignored as being insignificant. Where the whole coating is exothermically oxidized, it is possible to calculate, from the mass of metal and thickness of coating, the energy given up during the conversion of the metal to oxide, using thermodynamics.

25.9.3 Web Temperature

During deposition, the web is heated from the front side and cooled from the back side by the cooled deposition drum. When the time taken to traverse the coating zone is 1 second or greater, the film temperature will have reached a steady state. The steady state temperature difference between the film surface and the cooling drum is defined by the web thickness, the thermal conductivity, and the heat transfer coefficient between the web and the drum:

$$T_{\mathrm{wf}} - T_{\mathrm{d}} = \left(\frac{d_{\mathrm{f}}}{\lambda_{\mathrm{f}}} + \frac{1}{\alpha}\right)\frac{Q}{A}$$

where T_{wf} = temperature of front surface of web
T_{d} = temperature of the drum
d_{f} = web thickness
λ_{f} = thermal conductivity of web
α = heat transfer coefficient

If the above equation is used and the results plotted out, the critical parameter is shown to be the heat transfer coefficient.

The thermal load is taken up partly by the thermal capacity of the web, which is largely dependent on the thickness, and the heat dissipated to the cooling drum.

It can be seen that for thin films, there will be little heat capacity, and so most of the heat has to be transferred to the cooling drum.

It is common to wind webs at up to 1000 m/min, and this means that the residence time in the deposition zone is considerably less than the 1 second that would allow steady state conditions to be reached. In practice, a long deposition zone should be aimed for. With the short residence time, the maximum temperature will be lower than if the steady-state temperature had been reached. This is calculated from the following formula:

$$\delta_T = \frac{Q_{\text{total}}}{\mathrm{A} \cdot \alpha \cdot s}\left[1 - \exp\left(\frac{-\alpha \cdot s}{\mathrm{d_f} \cdot \rho_{\mathrm{f}} \cdot \lambda_{\mathrm{f}}}\right)\right]$$

where δ_T = the difference in web temperature from entering the deposition zone to leaving it.

s = the residence time of the web in the deposition zone (l/v)

ρ_{f} = polymer web density

25.10 Heat Transfer Coefficient

This is often the most critical parameter but is often an unknown quantity, and, as there is no way of monitoring it, it is most likely degrading as the deposition drum ages.

The heat transfer coefficient is made up of two components. The first is the thermal conduction through the points of contact of the polymer web and drum. This is measurable by heating a web in contact with a drum and measuring the cooling liquid temperature rise carefully. This is done in vacuum and the polymer is outgassed for several hours to ensure that there is no outgassing from the back surface of the web.

The second part of the heat transfer coefficient is through conduction through any trapped gas between the polymer web and the cooled drum. This is much more difficult to measure directly and is often inferred from the total heat transferred less the contribution by thermal conduction.

$$\alpha = \alpha_{\text{contact}} + \alpha_{\text{gas}}$$

where α_{contact} = thermal conductance through points of contact

α_{gas} = thermal conductance by convection through trapped gas

Typically, the $\alpha_{\text{contact}} = \sim 100\,\mathrm{W/m^2 \cdot K}$ This is for a contact pressure of approximately 10^4 N/m^2 (100 mbar)

The value for α_{gas} is much more variable. It depends on the outgassing rate from the polymer, which in itself depends on temperature and moisture content.

In addition, once there is gas present, the pressure of the gas will determine the efficiency of heat transfer by convection. If the pressure is too low, the mean free path between collisions is too long to efficiently transfer the heat. Hence, the pressure has to be sufficiently high to make the mean free path shorter than the polymer web to drum separation.

The gas conductance can be calculated using the following formula:

$$\alpha_{\text{gas}} = \frac{c}{b+\lambda}$$

where c = thermal conductivity of the gas assuming $\lambda \ll b$
b = the effective thickness of the gas layer
λ = the mean free path at the pressure of the gas

Typically, the $\alpha_{\text{gas}} = 200 - 1000\ \text{W/m}^2 \cdot \text{K}$

The range given for the heat transfer coefficient is partly an indication of the difficulty in measuring this value accurately. Typically, the other parameters are determined and the heat transfer coefficient value is then inferred to balance the equations. Additionally, because it is possible to inject gas behind the web and so increase the gas layer thickness and the heat transfer efficiency, this has extended the heat transfer coefficient range upward. There is an agreement from some of the magnetic tape manufacturers that a figure of 800 $\text{W/m}^2 \cdot \text{K}$ has been achieved in some systems. Thus, for a temperature rise of the web of 100°C, the heat flow to the drum may be of the order 10 kW/m^2 for the contact conductance but of the order 80 kW/m^2 for the gas conductance. Radiation heat transfer is negligible $\sim$0.1 kW/m^2. As it is so low compared to the other heat transfer mechanisms and also because the other mechanisms have such a large range of possible errors, the contribution of the radiation heat load may be less than the size of these value errors and hence is often neglected from consideration.

References

[1] McCann MJ, et al. Buckling or wrinkling of thin webs off a drum. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 638–43.
[2] Beccaria C, et al. Improvement in the vacuum coaters design for high quality products. In: Proc. 33rd annual technical conference of the Society of Vacuum Coaters; 1990. p. 128–39.
[3] DuPont Mylar product literature. Available at http://www.dupont.com/packaging/products/films.
[4] Clow H, et al. Coating apparatus for thin plastic webs. Application serial no 07/254088 [filed 10:6:1988, now abandoned]. Continued as application no 626,320—US patent 5 076 203. 31 Dec 1991.
[5] Krug T. Apparatus and method for cooling films coated in a vacuum. US patent 5 395 647. 7 March1995.

[6] Casey F, et al. Vacuum metallising using a gas cushion and an attractive force. UK patent GB 2 326 647. 30 Dec 1998.

[7] Bishop CA, McCann MJ. An investigation of the limitations of the heat transfer mechanism when using a gas wedge between the web and drum. In: Proc. 48th annual technical conference of the Society of Vacuum Coaters; 2005. p. 626−30.

[8] Yadin E, Pipkevich G. Improvement of web heat condition by the deposition drum design. In: Proc. 50th annual technical conference of the Society of Vacuum Coaters; 2007. p. 749−53.

[9] McCann MJ, Cox ER. Process modelling of a novel double-sided vacuum coating system. In: Proc. 40th annual technical conference of the Society of Vacuum Coaters; 1997. p. 338−42.

[10] Window B, Savvides N. Charged particle fluxes from planar magnetron sputtering sources. J Vac Sci Technol A 1986;4(2):196−202.

[11] Window B, Savvides N. Unbalanced dc magnetrons as sources of high ion fluxes. J Vac Sci Technol A 1986;4(3):453−65.

[12] Savvides N, Window B. Unbalanced magnetron ion-assisted deposition and property modification. J Vac Sci Technol A 1986;4(3):504−8.

[13] Thornton JA, Lamb JL. Substrate heating rates for planar and cylindrical-post magnetron sputtering sources. Thin Solid Films 1984;119:87−95.

[14] Schwarz W, Wagner W. Thermal limitations in roll coating processes. In: Proc. 28th annual technical conference of the Society of Vacuum Coaters; 1985. p. 28−41.

[15] Class W, Hieronymi R. The measurement and sources of substrate heat flux encountered with magnetron sputtering. Solid State Technol December 1982. p. 55−61.

[16] Gebele T, et al. Substrate heat load and cooling in PVD web coaters. In: Proc. AIMCAL annual technical conference and 17th vacuum web coating conference; 2003.

[17] RJ Hill, editor. Physical vapor deposition. Temescal; 1986, p. 143. Code T-0186-6001-1.

26 Mechanical Design

Most of us design systems based on experience. This tends to mean that each new system is very similar to the previous one with some minor modifications aimed at reducing the problems that the last machine had. This approach has some merit in that if every time we started with a blank sheet of paper and ignored all the good things about previous designs, we would be repeating an assortment of mistakes.

There are some aspects of design, that I see repeatedly, which are detrimental to the process that in many cases, once the system is built, cannot be rectified without a complete system rebuild. The most common pair of problems, by far, are for reactive processes where most systems are (a) underpumped and (b) the pumping is not uniform.

Part of the advantage of roll-to-roll coating is that the web moving across the sources gives the opportunity for good coating uniformity in the down-the-web orientation. There is then a struggle to get similar uniformity of coating in the across-the-web orientation. Often there are elaborate shields and source designs made to aid across-the-web uniformity, but little may have been done with respect to the pumping performance and uniformity (Fig. 26.1). Let us now look at these two aspects of the process.

26.1 Pumping

Consider the deposition of an oxide layer such as titania. The metal sputters at a rate almost 20 times faster than that of the oxide. Hence, it might be expected that using a reactive process, to sputter at the high metal rate and to add the oxygen from the process gas, would be the preferred process. Titanium, because of its reactivity, is very sensitive to the oxygen available, and the sputtering rate is affected by minute variations in the ratio of oxide to metal present on the target. If there is insufficient pumping, it shows itself as a hysteresis loop where the target is quick to oxidize but slow to clean back to metal. This does not need to be the case; the hysteresis loop is the only evidence that the process zone is insufficiently pumped [1,2]. Once the system exhibits a hysteresis loop, it is the titanium that dominates the design and operation of the process. The development of some of the modern power supplies that allow pulsing was aimed at recovering some of the deposition speed lost because of operating with a system that exhibits a hysteresis loop.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00026-X

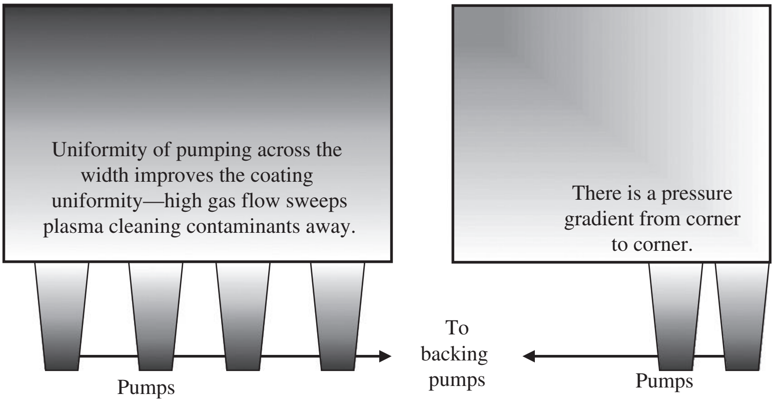


Figure 26.1 A schematic of the pressure gradient produced from nonuniform pumping. Many large vessels are pumped via the end plate, which would maximize this gradient.

Essentially, the system needs to pump faster than the growing coating for no hysteresis loop to be produced. More pumping means a higher capital cost as well as a higher process gas throughput that increases the operating costs slightly. This trades off against more precise, faster, and stable deposition. Set against systems that are currently built, this could look as if the system has too much pumping. Consider the situation of the design and build of a production machine put out to tender. There is always likely to be some nervousness, on the part of the company submitting their design, that if they include sufficient pumping, the system cost will be too high, which could lead to the loss of the order. It is easier to reduce the pumping to look more typical and to bring the price down to make it more competitive. The process can always be made to work to some extent irrespective of the design; however, it will be far from optimized. The use of a more sophisticated power supply and the use of pumping shields will compensate albeit at a reduced deposition rate.

High pumping also has other benefits. The high gas throughput means that the reactive gas partial pressure excess can be minimized. Also the high gas throughput means that the process zone is continuously being swept such that there is less buildup of contaminant gases and particles.

26.2 Nonuniform Pumping

There is a continuing trend of ever-increasing coating quality and uniformity. With roll-to-roll coaters having good down-the-web uniformity, the focus has always been on improvements to across-the-web uniformity. The advent of linear sources of all types, rectangular magnetron sputtering sources, linear evaporation sources, linear ion guns, and sweeping e-beam linear sources, have contributed toward improved coating uniformity. When using reactive processes, the deposition source represents only half of the process. If the pumping and reactive gas feed are not equally as uniform as the deposition source, there can be no expectation of delivering uniform deposition in either thickness or stoichiometry. This is shown schematically in Fig. 26.2.

I am sure all of us have seen systems where the pumps are hung off the end plate rather than distributed across the width of the system. There can be many reasons for this, such as keeping the system at one operating level, having more space on that end plate, and being able to use a more standard vessel design repeatedly.

For vacuum metallizing where the deposition was of aluminum metal, there was not perceived to be a need for uniform pumping across the width. However, more recently, systems have been modified for the introduction of oxygen for deliberately oxidizing the aluminum coating to make transparent barrier coatings. This means that the asymmetric pumping has the potential to make this a more difficult process to control.

On systems where some attempts have been made to distribute the pumping across the width, either by use of a manifold or by a multiplicity of pumps, it tends to be limited to the deposition zone. If there is not similar uniform pumping on all zones, within the vessel there will be nonuniformity of conductance between zones. This too will create pressure and throughput differences.

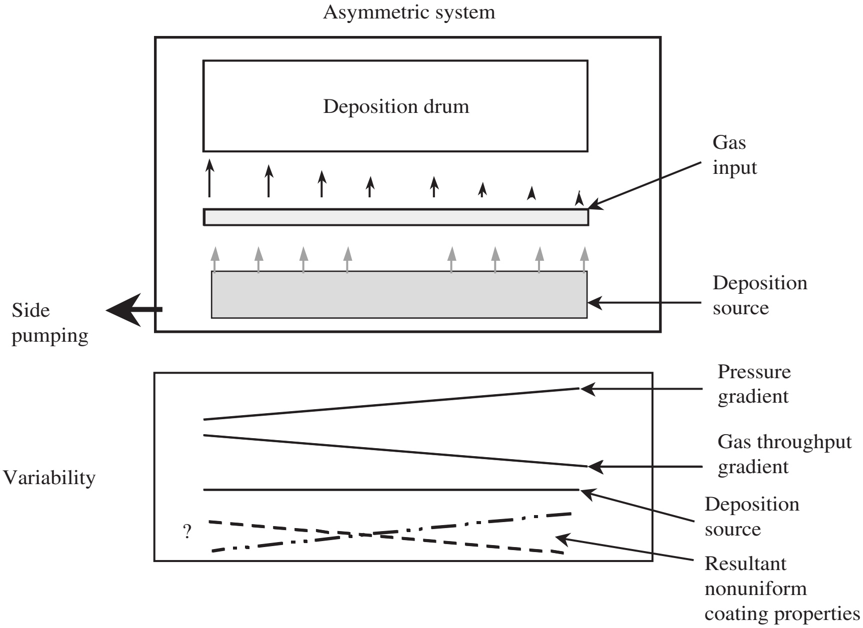


Figure 26.2 A schematic showing the effect of nonuniform pumping on the resulting deposited film variability.

Similarly, within any one zone there is a tendency to add components without regard to how they might disrupt the reactive deposition process. Included in this would be the use of cryocoils. These are often mounted against vessel walls without any consideration to the effect they might have on the pressure gradients generated across the vessel.

On other systems, a skewed distribution of gas input is done as an attempt to balance the reactive gas against the nonuniform pumping. This is only a fix and is usually difficult to optimize. Attacking the root cause by providing uniform pumping that enables uniform reactive gas input to be used will make the optimization of the process easier. This is shown schematically in Fig. 26.3.

It is worth comment that in 1976 a linear diffusion pump was patented [3]. The idea is simple if you regard a linear magnetron sputtering cathode as being a circular cathode cut in half with a parallel section placed between the two halves, the same principle can be applied to the diffusion pump, as per Fig. 26.4. Thus, there is no reason why roll-to-roll systems cannot be built with symmetry either side about a centerline down the web.

Oxide deposition is usually the rate-limiting step in any multilayer deposition process. If all the layers are deposited in a single pass, all the other processes will be restricted to match that of the slowest. If we take titania as a desired coating,

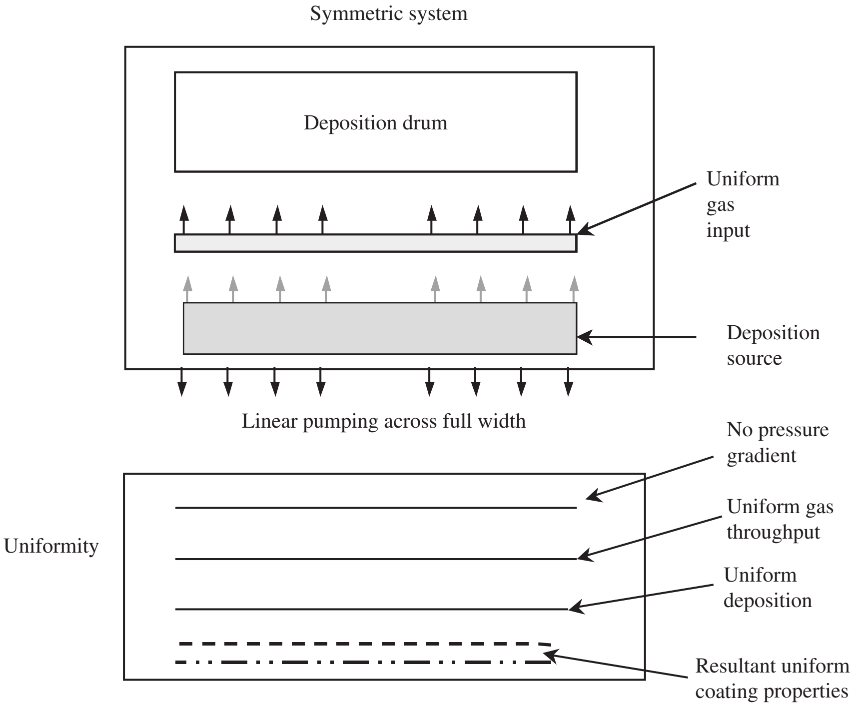


Figure 26.3 A schematic showing the effect of uniform pumping on the resulting deposited film with reduced variability.

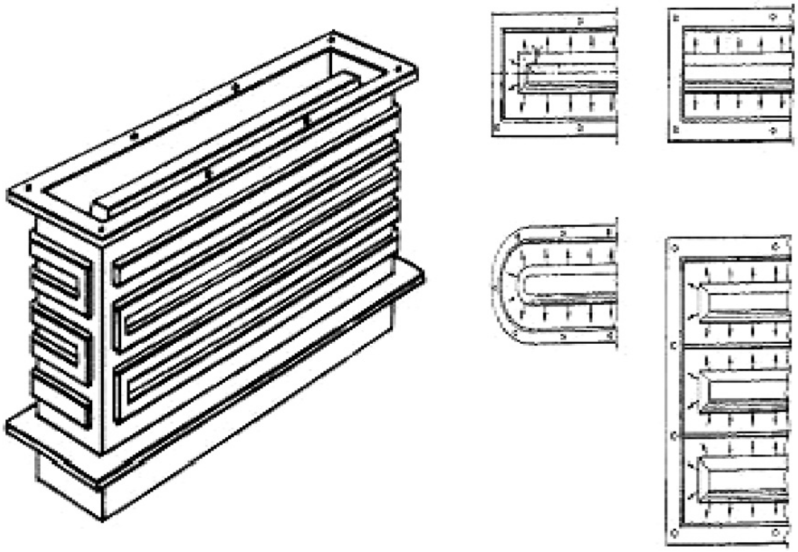


Figure 26.4 Diagrams taken from patent of linear diffusion pump design [3].

sputtering titania from the oxide is as much as 20 times slower than reactively sputtering from the metal. If we can work from the metal, we can speed up the whole process. Use of all the techniques that have been developed such as a pulsed power supply, customized shielding, separated gas inputs, etc. would have better improved the deposition rate than sputtering from an oxidized target. If, however, we eliminate the hysteresis loop, we can still make a significant further improvement on the deposition rate.

If we consider the implications that making any process improvements will have on the final production costs we can usually see more cost benefit. Taking as a baseline case, if we have a roll length of 10,000 m and a web speed of either 10 or 100 m/min, the deposition time will be 1000 or 100 minutes, respectively. If by using the extra pumping to eliminate the hysteresis loop we get a rate improvement of a factor of two times, the winding speed can be doubled and so the deposition time will be halved. The extra pumping will also mean a reduced pumping time down to the starting base pressure. Thus, doubling the deposition rate will not quite double the production output.

This is very simplistic, but it can be seen that for a reactive deposition process, which is invariably the rate-limiting step in any multilayer process, any increase in deposition rate must be worthy of consideration. As the pumping, typically, represents only a small fraction of the total machine build costs, for a roll-to-roll coating system, doubling or tripling the pumping to speed up the reactive deposition process is still likely to represent a worthwhile investment.

The symmetry of the system design needs to cover all components (Fig. 26.5). The cooled drum ideally needs to be cooled such that there is no thermal gradient across the drum. This is not critical for most coatings; however, for transparent

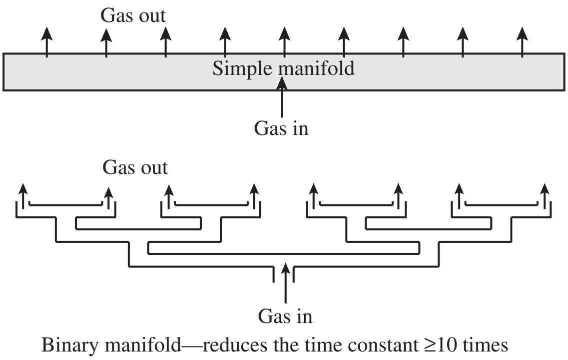


Figure 26.5 A schematic showing two different gas manifold designs.

conducting coatings the conductivity can be sensitive to the temperature of deposition and hence there could be a conductivity gradient unless the drum temperature is kept uniform.

The magnetron sputtering sources also need to be cooled symmetrically. Again, if they are not, they will have different secondary electron emissions and the local plasma density will be different.

The gas input not only needs to maintain the uniformity but also requires to have the time constant minimized. This is done by trying to minimize the gas distribution pipe lengths and gas volume while keeping the gas manifold nozzle sizes as large as possible [1,4−6].

26.3 Shields

26.3.1 Deposition Shields

All deposition sources deposit material not only onto the substrate but also elsewhere in the system. Because the system is static, the buildup of stray coating material could be huge if not controlled and so it is usual to use deposition shields to collect the stray material. These shields can then be periodically exchanged or cleaned much more easily than if the vacuum system had to be cleaned with all the nook and crannies.

It is essential to organize regular cleaning of any vacuum system. The stray coating will not be as densely packed as the coating normal to the deposition source. This porosity will give the coating a massive surface area, which can take up moisture whenever the system is brought up to atmospheric pressure. This adsorbed moisture can significantly slow down the pumping of the system.

In the worst cases, this can raise the base pressure by over an order of magnitude and aluminum coatings can be oxidized and appear golden rather than silver.

One aim of the deposition shields is to collect as much stray deposition as possible onto flat surfaces. The flat surfaces can make cleaning much easier. It is important to try to avoid exposed nuts and bolts that can become welded together by the deposited material and difficult to undo when the shields need to be removed for cleaning.

Consideration needs to be given to the cleaning of the shields. It is common to use a carbon or titanium diboride slurry to paint onto the shield. This slurry when dried acts as a controlled interfacial release layer. This prevents the coating sticking to the shield too well and speeds up the coating removal from the shield. Commonly, hammers, chisels, and wire brushes are used to clean the shields. This needs some care and the correct safety equipment. It is not unknown for the freshly exposed surfaces to rapidly oxidize. With some materials, such as aluminum, this is an exothermic reaction, and there can be flashes and fires. Thus, personal protective equipment is essential as well as good housekeeping to prevent the buildup of debris that could be ignited and form a more serious fire.

The use of these release layers need careful control. It is important to avoid any of the coating exploding off during the deposition process. This can occur because of the buildup of differential stresses reaching the point where the interface fails and the coating breaks off.

Alternative methods are used in some industries, such as chemical etching [7,8]. This process can involve depositing a layer onto the shields that acts to stop the etching process once the collected coating has been removed. This tends to be a more expensive cleaning process because there are the chemical etching baths to be maintained and the disposal also tends to be more expensive.

Another method is to use aluminum foil to cover the permanent shielding. It is often perceived that the aluminum foil is more easily removed and replaced than permanent shields.

It is possible to use quick-release fastenings to help minimize the time to remove the shields. Using a second set to replace them with will also minimize the downtime. This method can be more expensive initially, but over a period of time it will usually be cheaper.

26.3.2 Protective Shields

It has long been noticed that when the vacuum system is vented to atmosphere and during the time the system is left standing during roll changes and/or maintenance, there is the generation of significant levels of debris. This debris can settle on the top surface of the stationary deposition drum and winding rolls. This can lead to additional debris being transferred via any front surface rolls onto the web that can result in coating defects.

Another source of web contamination can be due to small quantities of diffusion pump oil that can backstream during the time the system is close to the base pressure. The mean free path will be long at these low pressures and the oil molecules will bounce around from surface to surface. Any roll that is in line-of-sight with the deposition pump will have the most oil hitting the surface. The sticking coefficient will to some extent depend on the temperature.

Again, the oil can not only be catastrophic if it sticks to front surface rolls but it can also cause problems if it deposits on any roll as the back surface will eventually come into contact with the front surface as the web is rewound.

The cooled deposition drum can have a higher sticking coefficient and it may be more noticeable if the oil is present in larger amounts.

Both of these problems may be offset by use of some protective shielding to limit the settling of debris and limit the area available to oil molecule collisions.

26.3.3 Conductance Shields

It is common practice to separate as much of the winding system from the deposition area as possible. The simplest method of achieving this is to put a plate across to divide the two zones leaving a very narrow gap for the substrate to pass through to travel between the two zones. This type of conductance shield does allow the winding system to operate at a pressure of up to a couple orders of magnitude higher than the deposition zone. Care needs to be taken that the conductance gap is wide enough so that the web does not catch on the edge and suffer surface damage. It also needs to be small enough to maintain the pressure differential.

The other consideration is that the better the pressure separation, the harder it will be to pump one side out from the other and so the pumping will need to be designed with this in mind.

As the conductance shield has to separate the deposition zone from the winding, there is the potential problem that the conductance plate will become coated with stray vapor. This coating can progressively close the gap and so there may be a coating collection shield to protect the conductance shield. This protective shield needs to be easily removed for cleaning.

26.3.4 Profile Shields

Profile shields are corrective items that are used to improve the uniformity profile of the depositing coating. Unfortunately, these shields are shaped for specific deposition conditions. This means that if the deposition conditions were changed, the shape would need to be changed to suit. Generally, it is inconvenient to keep changing these shields and so often a compromise is made and a single-shaped shield is used for all conditions.

Profile shields are most frequently included as an additional shield over and above the regular conductance and protective shields. They too are subject to deposition and need regular cleaning, otherwise the accumulation of coating will further restrict the deposition to the substrate. As the shield is designed to block the regions of maximum deposition, the speed of accumulation will be greatest. The accumulation will vary with deposition rate and thus the shape will change accordingly, making the deposition uniformity profile change with time.

As shown in Fig. 26.6, the shield shape, for correcting variations in the coating uniformity from a magnetron sputtering target, is much more simple than is needed for a coating deposited from resistance-heated boats, where there is a maximum

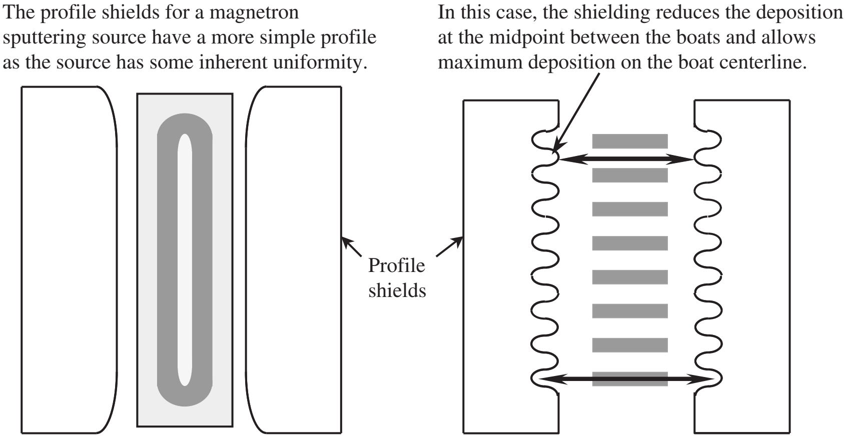


Figure 26.6 A schematic showing the different shape types for profile shields for a sputtering source (left) and a resistance-heated evaporation boat system (right).

and minimum to be smoothed for every boat. The magnetron source has a parallel section between the two half-circle ends to the racetrack and this parallel section has inherent uniformity; thus the profile is usually only required to correct for the end effects.

References

[1] Spencer AG. High rate reactive magnetron sputtering [PhD thesis]. Leicestershire, UK: Loughborough University; 1989.

[2] Penfold AS. The influence of pump size on D.C. reactive sputtering systems. In: Proc. 29th annual technical conference of the Society of Vacuum Coaters; 1986. p. 381−403.

[3] Maltagliati MM, Redi P. FR 2310482 French patent. Perfectionnements aux pompes a vide a diffusion. May 4, 1976; Maltagliati MM, Redi P. Einstufige oder mehrstufige Diffusionspumpe. German patent DE 2619411. May 6, 1976.

[4] Theil JA. Gas distribution through injection manifolds in vacuum systems. J Vac Sci Technol A 1995;13(2):442.

[5] Bartzsch H, Frach P. Modelling the stability of reactive sputtering processes. In: Proc. 7th international conference on plasma surface engineering; 2000.

[6] Milde T, et al. Gas inlet systems for large area linear magnetron sputtering sources. In: Proc. 44th annual technical conference of the Society of Vacuum Coaters; 2001. p. 204−9.

[7] Sasaki YT. A survey of vacuum material cleaning procedures: a subcommittee report of the American Vacuum Society Recommended Practices Committee. J Vac Soc Technol A 1991;9(3):2025−35.

[8] Mattox DM. Substrate fixturing and cleaning. Vac Technol Coat 2002;September:24−5.

27 Winding Webs in Vacuum

Winding webs in vacuum is different than winding webs at atmospheric pressure for the obvious reason that in vacuum there is, in effect, no air. The effect of this is that there is no boundary layer of air to be dragged along by the web to act as a lubricant when the web travels over rolls. There is also no air to become entrained as the web is rewound into a roll. Without this air layer, the rewound roll will always be harder wound as compared to air wound webs. This is true even with only a small amount of tension used on the web during rewinding. Also without this air, acting as a lubricant, there is the opportunity for microscratches to be put into the web and/or coating as the web travels over rolls in hard surface-to-surface contact. The lack of air and hard roll will mean that, once rewound in vacuum, any web profile problems will become clearly apparent.

It has often been said that a good winding system can help minimize the problems caused by poor quality film, whereas a poor winding system is likely to add additional winding problems.

27.1 System Design

In general, the manufacturer building the vacuum system will design the appropriate winding system. The vacuum system will often be separated into two separate zones, the winding zone and the deposition zone. One aim tends to be to minimize the chamber volume and so the winding system will be made as compact as possible. In many cases, the winding zone volume is dictated by the maximum roll diameter, remembering that there needs to be clearance for both the unwind roll and, once the web has been transferred, the rewind roll.

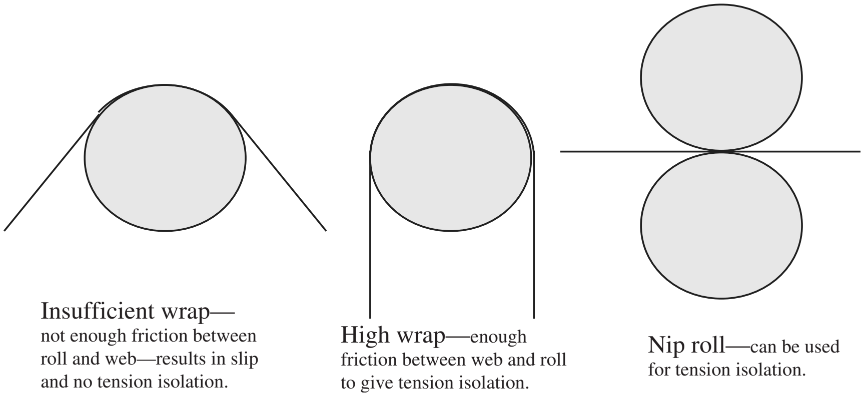
Provision has to be made for some space for any plasma treatment before the deposition zone and a measurement system to be included after the deposition zone. If the plasma treatment is very aggressive, it may be expected to put a lot of heat into the web and so it might require a cooled roll. There will also be decisions about whether the process will include a gas injection system to insert gas between the web and cooled deposition drum and if there is to be a spreader and lay-on roll included.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00027-1

Once these decisions have been made, a provisional web path can be mapped out. This will then allow an assessment to be made on the composition of the drive system. The simplest system will be to use three driven rolls, the unwind, rewind, and deposition drum. However, this should be regarded as the bare minimum and it is more typical to have five or more drives. With the three-drive system there is the limitation that as the unwind and rewind rolls control the tension of the web around the deposition drum, it can lead to rewinding rolls harder than preferred. Winding rolls with too much tension can result in the polymer web blocking [1]. Blocking is where layers of polymer web do not slip over each other easily and under certain conditions may stick together and it may be difficult, or even impossible, to unwind. If the tension is reduced, to make the rewind roll softer, the reduced tension around the deposition drum can limit the deposition rate, as the web is more likely to buckle under heat load as it is pulled less hard against the deposition drum. It is common to use a nip roll against the deposition drum on the unwind side of the system to prevent the unwind roll and rewind roll from fighting against each other. Without this isolation, a correction on one drive can cause a correction on the other, which then causes a correction back on the first drive. In some cases, this can result in a runaway situation with an increasing ferocity of oscillation that at worst can result in a web break. Hence, tension isolation is a critical feature in any winding system (Fig. 27.1).

The three driven roll design was superseded by a four driven roll design with a high wrap capstan roll separating the different tension zones. The next development was to do the same on both sides of the deposition drum and the five driven roll design became the standard one used for metallizers (Fig. 27.2).

A winding system that utilizes more driven rolls would allow the tensions in different parts of the system to be isolated from each other. Thus, it then becomes possible to have a high tension around the deposition drum without the possibility of pulling too hard on the unwind roll and suffering from slip in the roll, causing


Insufficient wrap—not enough friction between roll and web—results in slip and no tension isolation.

High wrap—enough friction between web and roll to give tension isolation.

Nip roll—can be used for tension isolation.

Figure 27.1 A schematic of tension isolation options.

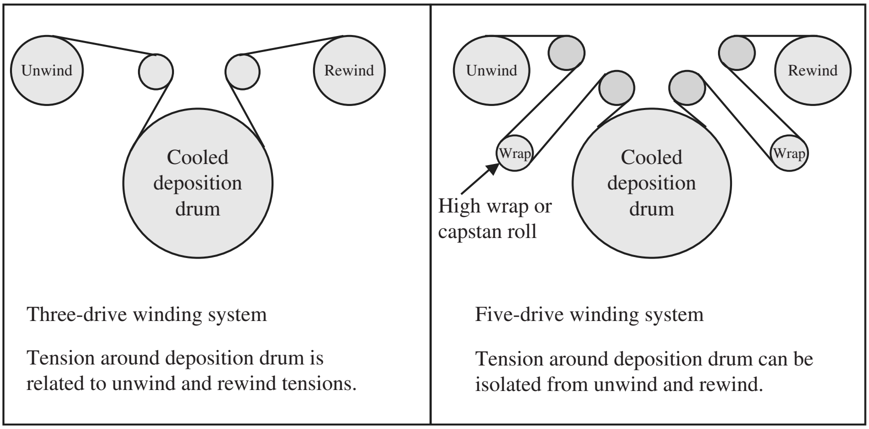


Figure 27.2 Schematics of simple three- and five-drive winding systems. In the five-drive system, the dark rolls are driven and the others would have load cells to monitor the tensions.

web damage through surface scratching, as well as reducing the tension after the deposition zone in preparation for the rewind.

If the plasma deposition is included in the winding zone and requires a cooled roll, it may be that this will require independent tension control too. This may further increase the number of driven rolls.

The tension can be isolated by use of nip rolls or high wrap or capstan rolls (Fig. 27.1). The high wrap capstan rolls are to be preferred as they cause less damage into the web. If there is any web profile variation, the nip roll is also more likely to show these up as wrinkles in the substrate. If nip rolls are used, at least one of the rolls needs to be crowned so that any roll deflection is compensated for and the web will run through with equal nip across the full width [2]. This does require the nip roll pressure to be correct as too little or too much pressure will result in uneven pressure across the web width. The high wrap rolls require the friction between the web and the roll to limit the tension that can be transferred past the high wrap roll. If the contact length between the roll is too short the tension will continue beyond the roll, but if the contact length is long the tension may be independent on either side.

Different webs will have different friction coefficients and so changing materials may change the winding characteristics [3]. Thus, what would be an adequate wrap for a polyester or polypropylene web is unlikely to be sufficient for a polytetrafluoroethylene web. It is also often seen that two rolls are used with a large amount of wrap in preference to a nip roll; these are known as “S” wrap rolls. Similarly, any rolls that are driven purely by contact with the web will also be dependent upon the friction between the substrate and roll. The lower the friction between the roll and web, the greater the potential for the web to slip over the roll and cause scratches.

In reality, there will be a number of additional rolls in the winding system for the positioning of the plasma treatment zone around a cooled roller and after the deposition drum for the coating measurement system. What is aimed for is to minimize the number of front surface rolls after the deposition zone. This will help to minimize defects as it will minimize the possibility of surface scratches into a newly deposited and often soft coating.

The use of more drives also allows for rewinding with a changing tension as the diameter of the roll increases while keeping the tension around the deposition drum constant. The rewind tension can be varied in many ways using taper tension, where the tension is reduced with increasing diameter to a designed tension profile or where a simple constant torque method is used [4].

There are many development systems or new process pilot production systems or full production systems that have special requirements that need to be accommodated. There have always been the so-called "specials" where the system is in some way out of the ordinary, but these have been relatively few in number. This is changing, particularly with the advent of the vacuum deposition of photovoltaic materials. There is not a standard deposition process, even for the same nominal material. An example of this would be the copper indium gallium diselenide (CIGS) material that can be evaporated or sputtered, and within sputtering it can be sputtered from elemental or alloy targets. Using the same CIGS example, the substrate has not been standardized either and both metal foils and high temperature polymer films have been used. As many of the companies depositing these materials believe that their process has some technical advantage, they all tend to a customized system. This growth in the solar industry has led to a large growth in the building of special systems.

Some materials are deemed sensitive to surface damage and so to protect them from slip damage within the roll they have paper interleaving. This interleaving needs to be removed before the deposition process and may need to be replaced following the deposition process as part of the rewind process. This would then require additional drives for winding up a roll of interleaving material and unwinding another roll.

The schematics shown in Fig. 27.3 are of winding systems that have been designed with a film or coating that has a surface sensitive to damage. The right-hand side schematic shows a basic design where the substrate material is unwound, passes through the whole of the process, and is rewound without any front surface contact with any rolls. As shown at the rewind end of the web path, if the roll positions are chosen well, it is still possible to use a high wrap roll and so isolate the tensions between the unwind, process, and rewind. Substrates and coatings only really get damaged if there is movement of the surface against another surface such as a roll. If there is no relative movement of the two surfaces, there is no reason for damage to occur. However, where temperatures are rising and falling by large amounts and the tension on the web may not be under complete control, there may easily be movement and so having no front surface roll contact can become important. This can be made worse if the process is one where dust or debris can be produced as any debris trapped between the web or coating and the roller has the

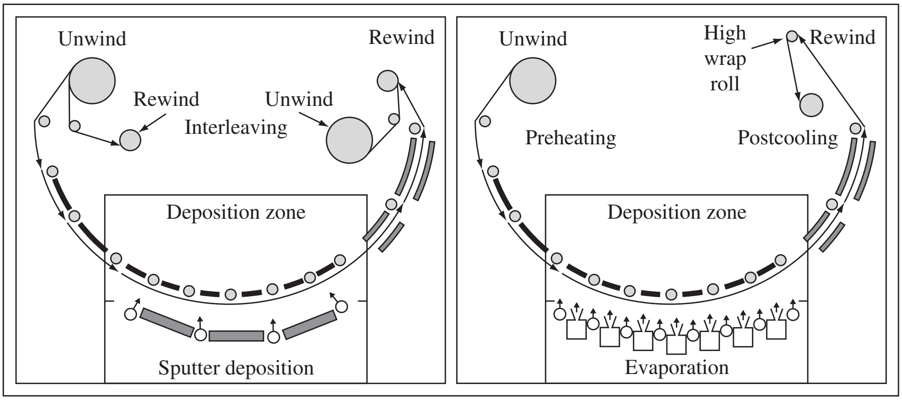


Figure 27.3 Winding systems designed to have no front surface contact rolls. The left-hand system also includes interleaving of the supply and finished roll.

potential to scratch the surface. Many of these processes for the deposition of photovoltaics take place at a high temperature, and as it is much harder to cool a web than it is to heat, it often results in the rewind being done on a hot roll. The hot roll, as it cools, is likely to suffer from movement as the layers contract and so, despite the winding path having no front surface rolls, it is feasible that damage still occurs. Hence, the option shown on the left-hand side of Fig. 27.3 where the design uses paper interleaving as a method of protecting the web and coating surface. The idea behind this is that the paper is always going to be softer than either the web or the coating and possibly can allow debris to become embedded in the paper rather than rolling or sliding around and damaging the surface. As many CIGS coatings are deposited onto precoated substrates, the roll may enter the system with interleaving already present and this has to be removed before the web is processed. Once the processing has been completed, another layer of paper needs to be inserted. The schematic has been simplified but as the interleaving needs to be tension controlled, it needs to have a separate drive.

As with all other parts of the system, the aim is to produce the simplest possible winding system that will work well for the application. Hence, if it is believed that the tension is going to be under complete control throughout the process and that there is little chance of any slip between the substrate and any rolls, designing a system with no front surface contact rolls is not really necessary. If this level of control is believed not to be possible, not having front surface rolls may be a wise precaution. To increase the complexity, and expense both in capital and running costs, by including interleaving should only be done if it can be proved to be necessary.

There is the occasional requirement to deposit a coating on both sides of the substrate. This can be done on a basic roll-to-roll system by coating one side and then opening the chamber and rethreading the same roll, but with the substrate the other way up so that the second side gets coated. The disadvantages of this method are that the substrate gets handled twice and so it might be expected for more defects to be generated and the productivity of the system is half of that of a system that could coat both sides in a single path. Figure 27.4 shows a typical web path that could be used to coat both sides of a material in a single pass. It does depend on the substrate type, coating material, coating thickness, and hence the heating load as to the full design of the system. This figure shows the web being coated on each side as it passes around two separate deposition drums. On the first drum, the coating will coat one side, and in the figure "x" has been added to allow you to follow the surface around to the second deposition drum where you can see the marked surface becomes the backside of the substrate and hence the second side becomes coated. If the coating is very thin and the heat load can be controlled well, it is possible to simply have two deposition sources facing each other and the web to pass between the two sources in free span. This is shown as a second double-side coating applied in the sputtering chamber following the first double-side coating that is applied by evaporation in the larger first deposition zone. This schematic also shows a load lock at the end of the process. This particular system design was used to manufacture pyrotechnic material; although the supply unwind roll could be large, the rewind roll could only be of limited size because of the nature of the product. Using the load lock, the process time was improved as the main chamber could be sealed off and kept under vacuum and also the sources kept hot while a roll was removed and a new roll started. This reduced the down time as the source did not need to be cooled and reheated and also the main chamber did not need to be vented and repumped. This same approach can be used on CIGS systems using a load lock for the supply as well as product rolls. As some of the CIGS vessels are large, it can be beneficial to adopt this design approach so that the largest volume part of the system does not have to be vented and pumped so frequently.

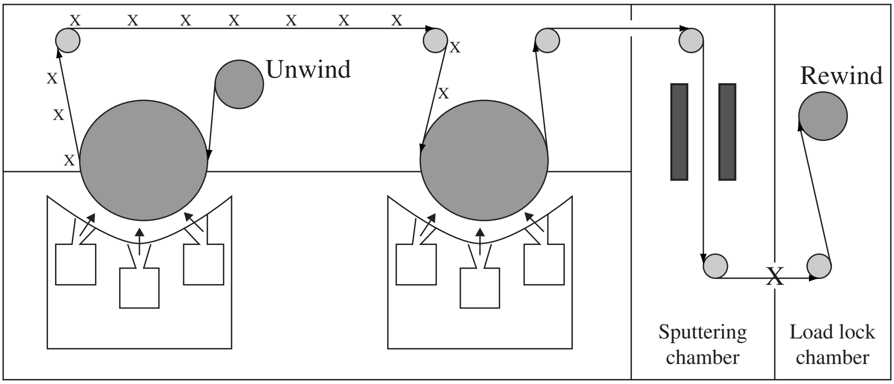


Figure 27.4 A schematic of a winding system showing a web path allowing double-side deposition as a single-deposition pass process. The schematic also shows a system load lock to enable an exchange of rewind rolls without having to open the main vacuum chamber.

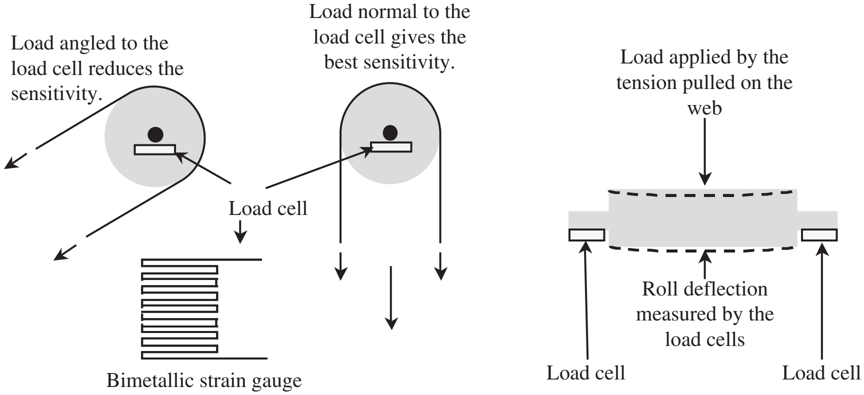


Figure 27.5 A schematic of the load cell orientation to the applied load.

27.2 Tension Measurement: Load Cells

The most conventional method of measurement of tension is the use of load cells [5]. A load cell utilizes a bimetallic strain gauge and it monitors the bending of the roll under loading. Usually these are used in pairs, one at each end of the roll.

The load cells are most sensitive if positioned so that the orientation of the load is normal to the orientation of the load cell. The cell will still work in other orientations but will be less sensitive. This is shown schematically in Fig. 27.5.

27.3 Alignment and Spacing

The roll alignment starts with the machining of the end plates for the winding system. It is common for the end plates to be clamped together and the bearing housings to be machined out together. In this way the rolls should be in perfect alignment so long as the end plates are positioned correctly and then clamped in position well. Often large diameter spacer bars are used to make sure the end plates are correctly spaced and are not likely to move or twist.

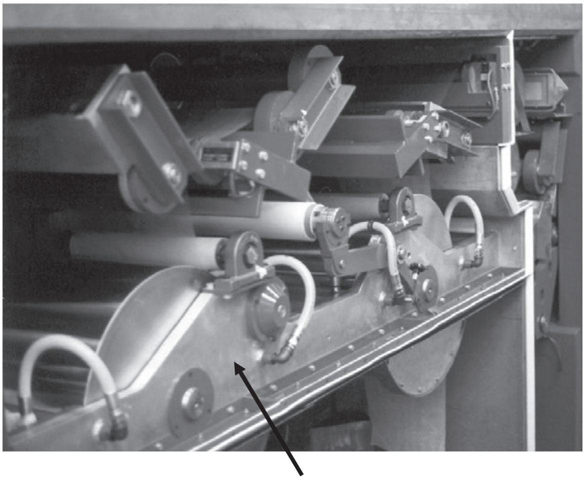
The alignment of the system needs to be done very accurately for all rolls and this includes both the unwind and rewind rolls. The aim should be to have all rolls aligned with a run out of less than 40 μm/m both axially and in plan view [2,6]. The alignment may be adjusted on most systems and so may be worth checking periodically. It is common to lock rolls in position and hence there ought to be little need to make frequent checks of the alignment unless one or more rolls have been changed. Alignment can be done from roll to roll; however, bear in mind that errors can be cumulative and so checking back to a reference roll to make sure there is no systematic error is then essential. The roll to use as a reference should be the one that is likely to be disturbed least. The deposition drum does not necessarily make a good reference roll as it may be taken out for periodic cleaning, polishing, or replating. The alignment can be checked using techniques including lasers or engineering slip blocks [7]. More recently a technique, using gyroscopes in each of the three axes, has been developed that looks to be a more precise method of measuring rolls [8,9]. This technique is not available for everyone to do for themselves but requires hiring the company who developed the technique to do the work, as the gyroscope mechanism is similar to that used in guidance systems and so the hardware is regarded as a security issue that has to be managed carefully. The gyroscopes are sensitive to displacement and so once the measuring head is placed at one point on a reference roll it can then measure and store this base position and then every other roll can be measured as a displacement relative to this one point. The combination of the precision as well as not requiring the rolls to be in line-of-sight of each other makes this extremely useful.

Small systems potentially can have a problem where a cantilever design of winding system is used. In this design the rolls are on shafts that have double bearings that are aimed at preventing roll movement when under tension. These cantilevered winding systems work well for most tensions and few have any winding problems; however, if very high tensions are used it is possible to flex the rolls, and the substrate at the free end of the rolls can lose some tension and this can lead to some winding problems. Some compromise on the cantilever design by using a lattice frame that can locate bearings for each roll. This frame, sometimes called a “spider”, usually has many access holes and is by no means a full end plate; it purely keeps the rolls at a constant distance from each other when the web is under high tension. The wider the web the more the rolls can be distorted and so cantilevered winding systems are generally only used for webs of up to 0.5 m and if high tensions are to be used this width may be reduced to 0.3 m or a spider frame added to give additional stability. An example of the use of this stabilizing frame is shown in Fig. 27.6 which shows a double-side double-deposition drum winding system of approximately 0.5 m width. Although the tension used for this process was not necessarily high, the substrate material had poor stability and so it was thought that the extra stability was required.

Alignment ought to present no difficulties for most of the rolls. Ones that potentially could be problematic are the unwind and rewind rolls. This brings the quality of the cores to the fore along with the mechanism chosen to locate the cores. Obviously, precision metal or polymer cores would be the ideal but would cost much more than cardboard cores. The precision cores also require much more logistical control as they have to be provided to the supplier and retrieved from the customers.

Thick webs are easier to handle than thin ones as the thicker film stiffness simplifies the web handling [10] with the stiffness varying with the cube of the thickness. As such, the alignment for a winding system for thin films is much more critical than for thick films. In general, for very thin webs the distance between rolls should be no greater than the web width.

It is possible to use guidance systems to correct for wander but it is preferable not to include such methods [11]. Spreader rolls are the one correction method that



Support “spider” end frame to support free end of cantilever winding system

Figure 27.6 A photograph of a cantilevered double-deposition drum winding system showing the additional “spider” spacer plate used to maintain the roll separation.

is frequently included [12—15]. These are usually placed immediately prior to critical events such as just before the web connects with the deposition drum or before rewinding, the idea being to take out any wrinkles [16,17]. Care needs to be taken on the choice of spreader as changing the web thickness can cause some spreaders to put wrinkles into thin webs where the roll works well for thicker webs [6].

The rolls can never be accurately aligned if they are not machined to tight tolerances or not circular in cross section. If there is any machining error, such as the roll being lobed or tapered, the web will always wind badly irrespective of how well it might be aligned. Again the weakest link to the winding system is the unwind and rewind rolls where there is the greatest possibility for error. This all starts again with the choice of core material. The higher the designed winding speeds, the more critical the precision needs to be so that the core is truly cylindrical and remains so following use [18].

Not only is the roll cylindrical nature critical to good alignment and winding but so also is the roll design. The rolls must be designed so that they do not suffer from excessive bending as this deflection may be equivalent to misalignment [19].

Having produced high-quality rolls and aligned them precisely with good quality cores, it will still be possible to have highly visible winding problems. The one item there is little control over is the polymer web. Not only is the uniformity of the web thickness an issue but also there are other things that need some consideration such as the stress profile within the roll. In particular, for biaxially stretched polymer substrates there will be a different stress profile depending on where the roll is cut, the center or edge, out of the mill roll [20].

As a way of eliminating mild variations and allowing consistently good winding, some prefer to use rolls with a slightly concave surface that provides some spreading action [6].

27.4 Materials

The initial thought might be that metal rolls would be used throughout but this is not necessarily the case. To increase the friction of the high wrap capstan rolls, they may be covered with a polymer surface. The eddy current resistance monitors are often placed to measure the coating as the web passes over the roll so that the web is precisely located at a fixed distance from the measurement head, which improves the signal quality. However, to measure the coating conductivity, the roll has to be made from a nonconducting material. In the case of in-line ellipsometry, a low-reflectivity roll may be beneficial. Of the rest of the rolls, there is a choice of using solid rolls or hollow rolls. The deposition drum will be hollow to allow for the use of the coolant to keep the drum surface cold, and to give a high thermal conduction and low corrosion the choice of materials and design can affect the performance. In the future, there are likely to be an increasing number of other processes included in the vacuum system, such as polymer coating, printing, and embossing, and these too will require other considerations on the roll materials used.

Another factor that needs to be considered is the inertia of the rolls. As the process speed increases, this has to be considered more critically. Rolls that are not driven would scratch the web surface if, every time the web speed were changed, the nondriven rolls continued at the previous speed because of the roll inertia [3]. The trend is to build larger machines that not only can wind faster but also can start with larger diameter and width and hence heavier rolls. This increasing size and speed will impact most on the winding system because of the problems of roll inertia in starting to increase the speed to the metallizing speed very quickly and uniformly. Similarly, the inertia will play an important role in any emergency-stop procedure if the machine is to halt quickly without snapping the web. The aim always is to stop the web almost instantaneously but still to be able to restart it afterwards. This again will be more critical on the thinner webs than the thicker ones. As machines have increased in size, both in width (the current widest metallizer is 4.45 m wide) and the length of material they can handle has also increased, the material issues can become more critical. A core that will adequately support a standard length roll at 2 m width may well be crushed or bend with a quadruple length of material at 4.45 m width. This tends to mean that higher strength lightweight materials need to be used where cardboard, for cores, or steel, for rollers, has traditionally been used.

There are reviews of materials used for rolls [21,22] but these need to be used with care because they generally are for atmospheric winding systems and each of the materials needs to be considered for use in vacuum where outgassing may be a concern. Over time, many items will heat up and some of the roll materials will contain materials that may exude out and be a source of contamination.

In addition to these polymeric materials there are materials such as fiberglass and carbon fiber reinforced composites that can be used for rolls. These have low inertia, and if the fiber reinforcement is designed well they can also have a very low deflection for very wide rolls. Needless to say these materials represent a much higher cost than the more traditional materials. Although the use and design of these rolls is not a new idea as they have been used in other industries for some time, they are relatively new for the vacuum metallizing industry.

27.5 Other Related Items and Materials

There are bearings that also need to be considered. They have to be as free running as possible, particularly for the nondriven rolls that rely on the friction from the web to turn them. Any resistance will cause the rolls to slip and this can put scratches into the web surface. It is common to receive bearings packed with grease. This can cause a couple of problems, of which the first is that the grease may not be vacuum compatible and the second is that if the grease is packed with a sealed cover any trapped gas inside may act like a permanent leak. Often bearings that will be internally mounted will be cleaned out and solvent washed and then very lightly greased with a vacuum compatible oil to give minimum resistance.

The external bearings can still be oil lubricated with an oil dashpot to top up the bearings as required. The leadthrough for each driven shaft will also need to be a vacuum seal and rotating. These can be of the oil type, although many now use the more expensive ferrofluidic seals [23].

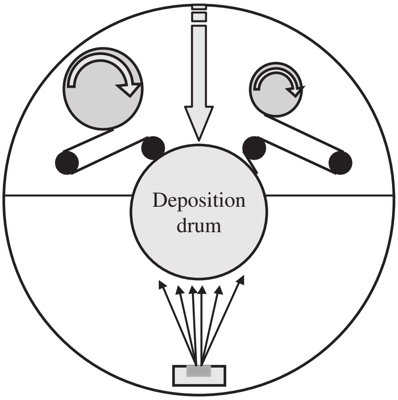
One of the aims of a good winding system is to be able to wind any web at the fastest possible deposition rate at the fastest possible winding speed without any damage to the web. Tramlines are often an indication that the process is working on the limit. The heat load is sufficient to make the web expand enough so that the web buckles off the deposition drum. This buckling limit may be lowered by the effect of having some debris trapped between the web and the deposition drum. The effect of this debris is to lift the web off the surface, which allows the web locally to become hotter and expand further (see Chapter 23). The web also is no longer having the compressive load transmitted along the plane parallel to the drum surface; the web is already bent and so the resistance to buckling is reduced. Thus, it becomes even more important to prevent any debris from getting trapped between the deposition drum and the web. One regular source of this type of debris is the vessel at atmospheric pressure. The sources are likely to be replenished, the deposition shields cleaned or exchanged, the rolls changed and a new core fitted along with a myriad of other activities, all of which may stir up dust or debris into the atmosphere. This debris will also be settling out from the atmosphere onto all horizontal upward facing surfaces.

Table 27.1 shows that many particles will get settled onto these surfaces in the 10 to 15 minutes in which a metallizer may be opened between production cycles.

Figure 27.7 shows a schematic of a system showing how airborne debris can easily settle out onto the deposition drum during the downtime when the winding system may well have been extracted from the vacuum chamber to allow easy access and roll replacement. Thus, it is worth having protective shields to protect

Table 27.1 Settling Rates for Airborne Particulates

Diameter of Particles (microns)	Velocity of Settling	
	(ft/min)	(mm/s)
1	0.007	0.0004
5	0.2	0.0109
10	0.59	0.0323
60	21.3	1.1644



When the system is stationary, dust/debris can fall onto the top of any roll.

The critical ones are those not covered by any polymer web.

Once the winding is started, the debris will be wound into the web and carried forward through the system contaminating the whole substrate.

Figure 27.7 A schematic of the areas prone to dust settling when the system is up at atmospheric pressure.

the critical surfaces from this source of contamination. This would include the deposition drum and any other rolls in the winding system, with those before the deposition zone more critical than those after. These shields do not have to be permanent and fixed as part of the winding system but may be temporary ones that are put in place immediately the system is opened to the atmosphere.

Although this is shown for the deposition drum, the same is also true for any exposed roller or part of the web surface that is exposed. The debris settling out before the deposition drum can get trapped between the web and deposition drum and cause buckling of the web and tramlines. This debris is not guaranteed to stay with the web as it can become stuck to the deposition drum and hence has the potential to start another wrinkle on every revolution. The greater the amount of debris in the reverse surface of the web and that settles out during the downtime, where there is usually system cleaning, the greater the probability of this type of defect occurring. This is another area where a tack roll, to ensure the deposition drum and any other exposed rolls stays dust-free, would be a cost-effective addition.

27.6 Substrates: Thermally and Dimensionally Variable

It is convenient to think of the webs as dimensionally stable materials, but they are anything but this. The roll length and width will hopefully be the same after completing the coating process as they were before the process. We look more closely at the deposition zone, the most critical part of the winding system. If we plot what the web would do if it could slip easily on the deposition drum, we get a schematic as shown in Fig. 27.8. What we see in the figure is the web reaching a spreader roll where the width is increased as the web is laid onto the deposition drum. The deposition drum is cooled and there may be a temperature difference of around 60°C. This cooled deposition drum will rapidly cool the web to the same temperature, causing the web to shrink and so get narrower. Following this the web enters the deposition zone where the temperature may rise by more than 120°C. Thus, the web will try to expand and increase in width. There is the postdeposition zone also on the deposition drum, and a further rapid cooling and shrinking of the web. If the wrap is sufficient, the web temperature may leave the drum lower than ambient temperature. However, it is more typical that the web leaves the deposition drum above ambient temperature as shown in Fig. 27.9. Thus, over the rest of the winding system, the web will be gently returning to close to ambient temperature and original dimensions.

Ideally, the web wants to be rewound with a temperature close to ambient. If it is not at a similar temperature once it leaves the vacuum chamber it will change dimensions on the fully wound roll, which can cause the roll to have layers trying to move against each other and thus introducing damage. Hot rolls are also more

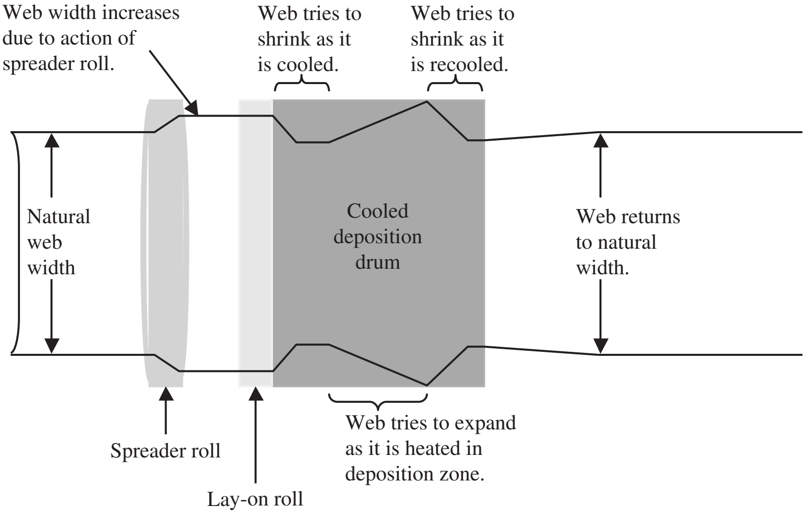


Figure 27.8 A schematic of what the web would do if allowed to freely move on the deposition drum surface. In reality, it is pinned by the applied tension and so will be under permanent stress although of different signs at different points in the process.

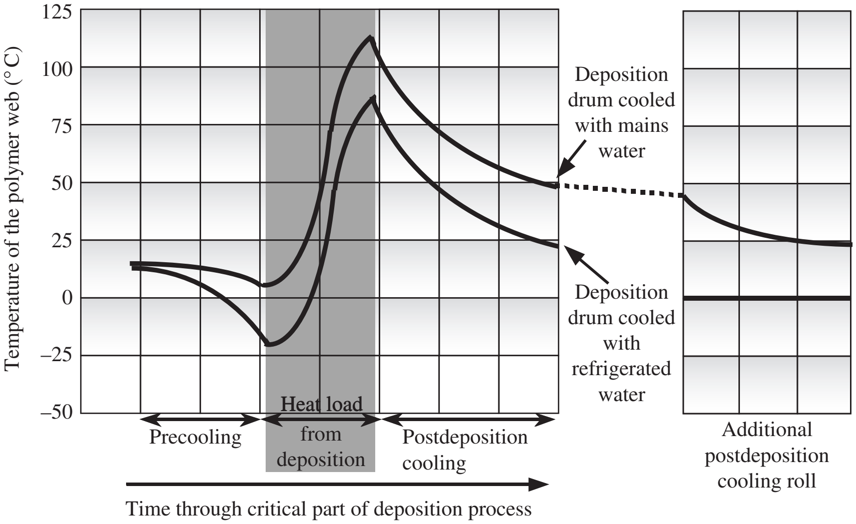


Figure 27.9 A schematic of the polymer web temperature on the deposition drum, including a postdeposition cooled roll.

likely to block and thin aluminum coatings to oxidize to a greater depth than cold ones. Where this is a problem, the postdeposition cooled rolls may be used [24].

Figure 27.12 shows the changing substrate width assuming the web to be unconstrained. In reality, the pressure exerted by the web onto the deposition drum, because of the tension pulled on the web, as shown in Fig. 27.11, along with the coefficient of friction between the web and drum, resists any movement of one against the other. What does change is the stress in the transverse direction that changes from tensile to compressive and back to tensile as the web goes through the temperature changes of cooled, heated, and cooled again, respectively.

27.6.1 Wrinkles

There have been several strategies for trying to prevent tramlines starting. The most common one is to pull more tension onto the web. This has a couple of potential problems, of which the first is that as the polymer web heats up the tensile performance falls dramatically as shown in Fig. 27.10. So it is possible to pull more tension and all that occurs is the elastic limit of the polymer is exceeded and a permanent elongation is put into the web. This also does not remove the problem as the elongation, if anything, will ease the contact pressure.

A more radical proposed strategy is to reduce the tension in the web so that it makes it easier for the web to slide over the drum and expand as required. Unfortunately, this strategy only works in some exceptional circumstances, and in most cases the reduced contact pressure also means a reduced heat transfer coefficient that makes the web temperature higher and the required expansion greater.

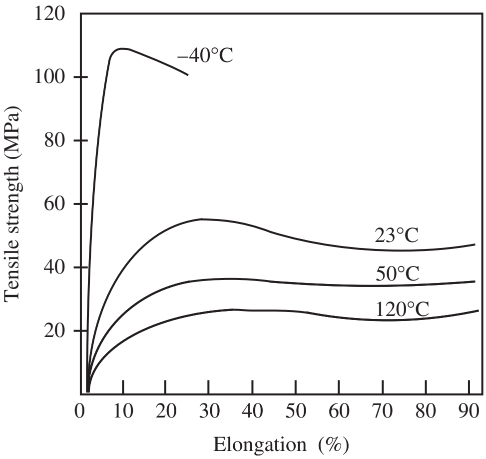


Figure 27.10 The polymer tensile performance as it changes with heat.

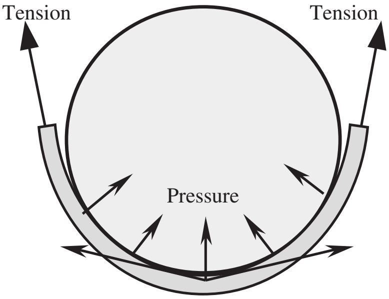


Figure 27.11 A schematic of the pressure exerted on a roll by web tension.

The most recent strategy has been to inject a gas between the web and the drum as a way of both increasing the heat transfer coefficient and also reducing the coefficient of friction as shown in Fig. 27.12. The improved heat transfer coefficient means that the peak temperature reached should be reduced and the reduced coefficient of friction allows the web to move over the drum more easily. Thus, either would reduce the propensity for tramlines and so this technique offers the greatest benefit of the different strategies.

This strategy is often negated because as there is an improvement in the heat transfer coefficient, it allows the deposition rate, coating thickness, and/or winding speed to be increased to the point where the process is back on the knife-edge of starting a wrinkle.

The problems of wrinkling and winding have been investigated and modeled for many years [25−35]. Some of the work has included the use of gas injected between the web and the drum [36−40].

In setting the tension level to apply to the web around the deposition drum, it is reasonable to assume that the temperature would rise enough and that the tensile performance would change as shown in Fig. 27.10. Polyester loses two thirds of its performance by the time the web reaches 120°C. Thus, using a tension that loads the web to approximately 10% of the yield strength is regarded as a good starting

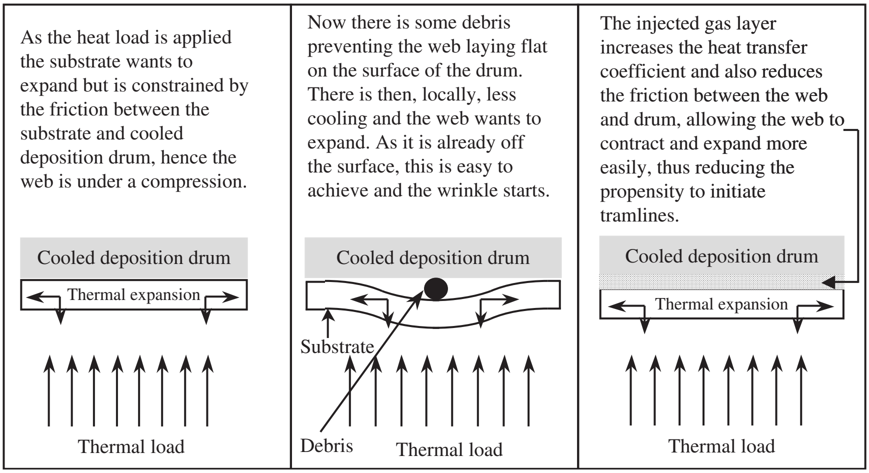


Figure 27.12 A schematic of the web stresses under heating.

point. This is reasonable for those polymers that are heat sensitive. The polymers that have been developed because of their high-temperature performance can start with a much higher tension. It is worth bearing in mind that 25 μm PET with 18 g/mm stretches 0.15% at room temp. This is at the low end of applied tension and this stretching will increase with temperature.

Figure 27.12 also shows the effect that debris trapped between the web and the deposition drum might have. The debris prevents the web from laying flat down on the drum surface. Instead it forms a "tent" over the debris. The shape of this tent is likely to be distorted by the differential stress between the tensile stress in the machine direction and the compressive stress in the transverse direction. This tent of polymer is no longer cooled by the deposition drum and so will be heated to a higher temperature than the surrounding polymer that remains in contact with the drum. This higher temperature will cause the tent to expand and so it will try to increase in size. This is shown schematically in Fig. 27.13, where it can be seen that the elongated tent in the machine direction has the potential to become the defect that initiates a wrinkle. The larger the debris, the easier this method of wrinkles starting will be. Hence, keeping the deposition drum clean can help minimize wrinkles as too can cleaning the back surface of the web of any particulate contamination.

It is difficult to know when trying to develop a process what might happen in production and where wrinkling might or might not occur. Recently, some work has been done to develop a software package that allows many of the "what-if" experiments to be tried, such as doubling the speed or increasing the deposition rate, and one of the outputs of the model is a warning that the web might be moving into a range of instability where wrinkling is a risk [41,42]. This software uses much of the information contained in the references used here along with additional information and compare the model to real production systems.

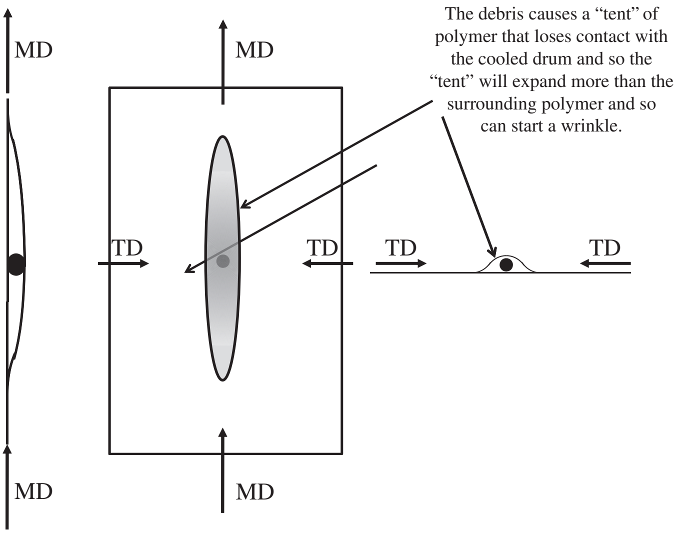


Figure 27.13 A schematic of how debris between the web and the deposition drum can help to initiate a wrinkle.

27.7 Safety

Winding systems have competing requirements in many aspects of the design. The safety requirements vary from country to country and customer to customer, with those with the most stringent requirements usually offering the greatest challenge. On the one side is the need to thread the web quickly and easily and on the other side is the need to not have operators injured because they have been caught and threaded into the system too. Thus, operators often want to be able to wind the web in air to assess the winding performance of troublesome rolls. They also often want to look for problem areas of the winding system and try to track down faults. In threading the system, if for any reason they have lost the leader web (the leader web being a length of web deliberately left threaded through the system to attach the new web onto, to make threading it easier), they may want to have the driven rolls turning so they can stick the new web to them to help draw material through. The danger of this is that many of the gaps are small and if the operator or the operator’s clothing gets caught in the system, the operator can be injured before anything stops the motors. To this end, many systems have strict limitations on operating any motors except under vacuum. Others try to protect the operators in other ways such as by adding finger guards that prevent even fingers reaching the roll surfaces where there are potential nipping or trapping points in the system. This can make threading more time-consuming but without doubt it is safer for the operators.

This type of protective shielding can also make the whole system much more difficult to clean and so some thought has to be given to the shielding to make sure that deposition shields protect as much of the areas that are difficult to clean as possible.

27.8 Key Points on Winding

1. Thin webs need rolls to be more accurately aligned.
2. Thin webs need rolls to be closer together, less free span.
3. When aligning rolls, start from the roll that will be least disturbed.
4. An alignment target should be a “run out” of no more than 40 μm/m.
5. A rule of thumb for tension. Run at $<10\%$ of the web yield strength.

   Note: This means the yield strength at the temperature reached in the deposition zone.
6. Nip rolls can damage the web (if web is not perfectly clean). Thus, there is a trade off and tension isolation can be achieved by an “S” wrap which takes up more space but may be less damaging to sensitive webs/products; the nip roll does the same job but is more compact but potentially damaging.
7. The tension will be taken first by the shortest and/or thickest part of the web. Sufficient tension needs to be pulled such that all the web width is in tension to ensure intimate contact around the cooled deposition drum.
8. A good winding system can minimize the problems caused by poor-quality film. A poor winding system can only add additional winding problems.
9. Typical tensions: for 12 μm PET 20–40 kg/m, for 30 μm OPP 5–12 kg/m; 25 μm PET with 18 g/mm stretches 0.15% at room temperature (see Note below Point 10)
10. Roll deflection should be less than 0.015% of the roller width to avoid the roll acting as a spreader roll and being a possible cause of wrinkles.

It is worth noting that when tension is talked about it can be in a variety of different forms. The tension can be quoted as the total force pulled on the web and be in kilograms. The same tension can be divided by the width of web and quoted as kilograms per meter (g/mm) (this is often quoted as pounds per linear inch (pli)). The tension can also include the film thickness and be quoted in kilograms per meter per micron.

When changing the thickness of the film, it is worth noting that once the film gets above a certain thickness the inherent stiffness of the film means that the applied tension can be reduced below the calculated value and the web would still be expected to wind well. However, as the tension can also affect the contact pressure between the web and the deposition drum, which can affect the heat transfer coefficient, it is often preferable to keep the tension high.

A typical starting tension would be approximately 10% of the yield stress. This is a good starting tension but it can be modified as desired. Reducing tension can be advantageous during the metallization process as the above calculation is for the modulus of elasticity as measured at room temperature. The value is likely to be reduced at an elevated temperature and so reducing the tension may be desirable.

Care needs to be taken in reducing the tension as this can result in a reduction of the heat transfer coefficient between the polymer web and the chilled deposition drum and this can result in an increase in web temperature and further change in the polymer mechanical performance.

Hence, any calculated or suggested value should only be used as a guideline.

References

[1] Pasqui A, Raugei P. Mega—a new design concept for aluminium metallizers. In: Proc. 8th international conference on vacuum web coating; 1994. p. 68−80.

[2] Hawkins WE. Vacuum coater thread path design using basic web handling principles and techniques. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 430−32.

[3] Schwarz W. Design aspects of vacuum web coaters—high speed web handling. In: Proc. 32nd annual technical conference of the Society of Vacuum Coaters; 1989, p. 156−160.

[4] Taylor KA, Pan CHT. Mechanics of web transport systems for vacuum metallization. In: Proc. 29th annual technical conference of the Society of Vacuum Coaters; 1986. p. 136−167.

[5] Montalvo III WW, Alf CG. Tension and web control in vacuum coaters (metallizers). In: Proc. 6th international conference on vacuum web coating; 1992. p. 35−44.

[6] Roisum DR. Wrinkling of thin webs. In: Proc. 41st annual technical conference of the Society of Vacuum Coaters; 1998, p. 406−11.

[7] Walker TJ. When rollers fight, webs lose. Paper, film and foil converter 2004;April:26.

[8] Sasikumar A. Measuring the roll parallelism in the laminating/coating industry using inertial alignment equipment. In: Proc. AIMCAL fall technical conference and 21st international conference on vacuum web coating. 2007.

[9] Hegde D. A return on investment of a roller alignment survey. In: Proc. AIMCAL fall technical conference and 22nd international conference on vacuum web coating. 2008.

[10] Hawkins WE. Web stability and alignment requirements. Paper, film and foil converter 1998;March:28.

[11] Hawkins WE. Controlling your web from beginning to end −part II. Paper, film and foil converter 2001;January:52−5.

[12] Weiss HL. Various web-control devices minimize wrinkling problems. Paper, film and foil converter 1989;October:104−47.

[13] Weiss HL. Installing roller devices can prevent web wrinkling. Paper, film and foil converter 1989;November:131−4.

[14] Weiss HL. Web spreaders help prevent wrinkling in nipping unit. Paper, film and foil converter 1994;March:68−71.

[15] Taylor A. Practical solutions to web heating problems. In: Proc. 7th international conference on vacuum web coating; 1993. p. 107−119.

[16] Hawkins WE. Under the layon roll: the genesis of MD wrinkles. Paper, film and foil converter 1998;June:32.

[17] Hawkins WE. Winder considerations: web spreading at laydown. Paper, film and foil converter 1998;October:28.

[18] Hawkins WE. Winding technology – Part II: the role of the core. Paper, film and foil converter 1999;September:32.

[19] Nadolney DB. Taming the wild web: part I. Paper, film and foil converter. March 1997, 35–37.

[20] Hawkins WE. Web stability: film structure affects web behavior. Paper, film and foil converter 1998;May:28.

[21] D'Armour MR. Roller compound choice key performance factor. Paper, film and foil converter. November 1989, 74–78.

[22] Polston WR. Elastomeric rollers: how to maximise performance. Paper, film and foil converter 1999;April:98–112.

[23] Moskowitz R, Howe W. Magnetic liquid vacuum seals and feedthroughs. In: Proc. 17th annual technical conference of the Society of Vacuum Coaters; 1974. p. 41–7.

[24] Baxter IK. Effective film temperature control for vacuum web coaters. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 106–20.

[25] Clow H. A model for thermal creasing and its application to web handling in roll to roll vacuum coaters. In: Proc. 32nd annual technical conference of the Society of Vacuum Coaters; 1989. p. 100–3.

[26] Wales JLS, Clow H. Model for thermal creasing in roll to roll vacuum metallising. In: Proc. 2nd international conference on vacuum web coating; October 1988. p. 204–14.

[27] McCann MJ, Jones DP. Web coating dynamic and wrinkling model. In: Proc. 41st annual technical conference of the Society of Vacuum Coaters; 1998. p. 412–7.

[28] McCann MJ, et al. Buckling or wrinkling of thin webs off a drum. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 638–43.

[29] Schwarz W, Wagner W. Thermal limitations in roll coating processes. In: Proc. 28th annual technical conference of the Society of Vacuum Coaters; 1985. p. 28–41.

[30] Benson RC. Simulation of wrinkling patterns in webs due to non-uniform transport conditions. In: Proc. 2nd international conference on web handling OSU; 1993.

[31] Chiu HC, et al. Mechanical and thermal wrinkling of polymer membranes. ASME winter annual meeting; 1993.

[32] Behaviour of Mylar under heat and stress. DuPont Films information note (1M) 9.94 1994 H-36633.

[33] Hendricks WC, Diffendaffer PA. Web thermal modelling for vacuum coating processes. In: Proc. 38th annual technical conference of the Society of Vacuum Coaters; 1995. p. 134–9.

[34] Roehrig M, et al. Vacuum heat transfer models for web substrates: review of theory and experimental heat transfer data. In: Proc. 43rd annual technical conference of the Society of Vacuum Coaters; 2000. p. 335–41.

[35] Uyama H, et al. Thermal behaviour of plastic substrate during deposition. In: Proc. 14th international conference on vacuum web coating; 2000. p. 63–71.

[36] Clow H, et al. Coating apparatus for thin plastic webs. Application serial no. 07/254,088 filed October 6, 1988, now abandoned; continued as application no. 626,320—US patent 5 076 203.

[37] Krug T. Apparatus and method for cooling films coated in a vacuum. US patent 5 395 647. March 1995.

[38] Casey F, et al. Vacuum metallising using a gas cushion and an attractive force. UK patent GB 2326647. December 1998.

[39] Bishop CA, McCann MJ. An investigation of the limitations of the heat transfer mechanism when using a gas wedge between the web and drum. In: Proc. 48th annual technical conference of the Society of Vacuum Coaters; 2005. p. 626–30.

[40] Yadin E, Pipkevich G. Improvement of web heat condition by the deposition drum design. In: Proc. 50th annual technical conference of the Society of Vacuum Coaters; 2007. p. 749−53.

[41] McCann MJ, et al. The power of simple models used on complex processes. In: Proc. AIMCAL fall conference and 24th international Conference on vacuum web coating; 2010.

[42] TopVac. Vacuum deposition software module, rheologic. Available from: http://www.rheologic.co.uk

28 Machine Building Trends

28.1 Metallizers

If one looks back at metallizers of 10 or 20 years ago and then at the current design of metallizers, it is possible to extrapolate the progress and hence it is possible to get a rough idea of what specifications might be needed in the future.

Typically, the winding speeds have increased and are currently around 1000 m/min (Fig. 28.1). Hence, in the future they are likely to need to be quicker. Looking at similar industries, papermaking used to be at 1000 m/min several years ago, and they have now progressed to over 2000 m/min. It may be that there is some technology or learning already done in the paper industry that would shortcut some problems and make the 2000 m/min metallizer available sooner rather than later. If the winding speed increases, there has been a requirement for increases in roll length. This allows the proportion of machine uptime to downtime to remain constant as the winding speed increases further gaining an increase in productivity.

Similarly, the width of metallizers has increased and recently 3.5- and 4.45-m-wide machines were sold (Fig. 28.2). The polymer web manufacturers have gone for the economies of scale and are now up to at least 8 m width on PET film and 10-m-wide on OPP film. I would expect that there is a case for producing metallizers that will accept full width film rolls, hence a threefold increase in width.

Another trend has been the requirement for an increase in the coating uniformity (Fig. 28.3). This was ±10%, but more recently ±5% has become common and some are even claiming ±2% from evaporation boats. This would suggest the trend is heading toward ±1% or better within 10 years.

One of the more global trends is that of reducing waste and increasing efficiency (Fig. 28.4). Some of this would come naturally from increasing the machine width where the edge effects are a smaller proportion of the reel and hence the waste is reduced. However, the evaporation sources are still only about 50% material efficient and the boats wear out every 12–20 hours. Increasing the width of the metallizers would mean using as many as 50 boats to cover the width. Each boat has a different characteristic and lifetime. This would suggest that there needs to be a change in source design to improve the material efficiency to >95% and increase the source robustness and lifetime, as well as spreading the deposition further round the deposition drum to enable the speed increases. Using suitable insulation may also reduce the power requirements, making a better energy-efficient system.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00028-3

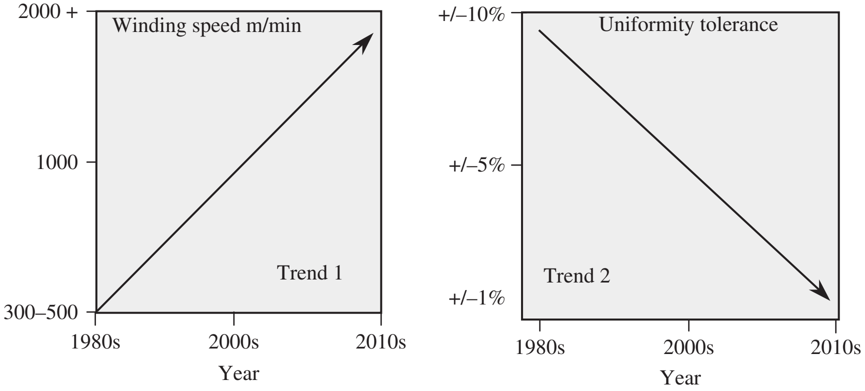


Figure 28.1 An indication of some system trends.

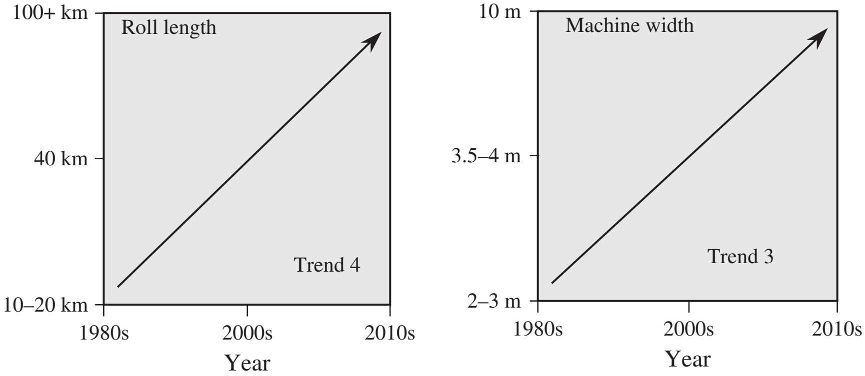


Figure 28.2 An indication of some more system trends.

A further indication of this trend is in the introduction of the Climate Change Levy (CCL), which was introduced in the UK on April 1, 2001. This puts an additional charge onto the power used with lower rates being available for the likes of LPG compared to electricity. Depending on the country and the agreements made, there will be a range of energy-saving requirements from none at all to the most stringent. It is unlikely that world production is going to move to only those countries that allow inefficient machines. What is more likely is that at least one manufacturer is going to see a more energy-efficient machine as a selling feature. If this can be proved to reduce the cost of manufacture, it will be advantageous irrespective of the country of operation taxes.

A slightly more difficult trend to spot is that of cleanliness. Many of the web-based products have had a requirement for improved substrate cleanliness, but this

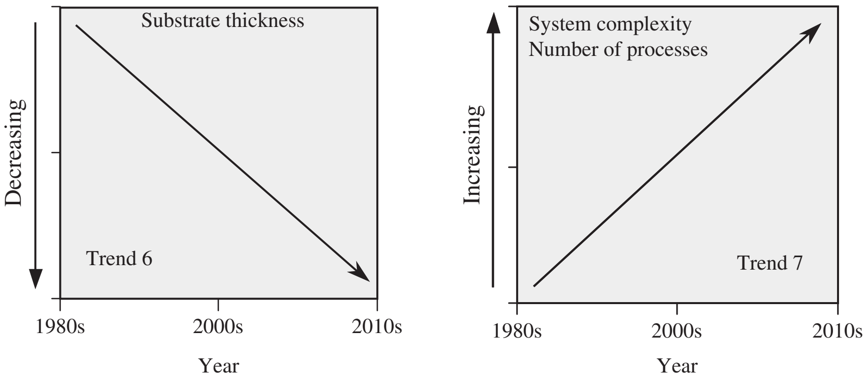
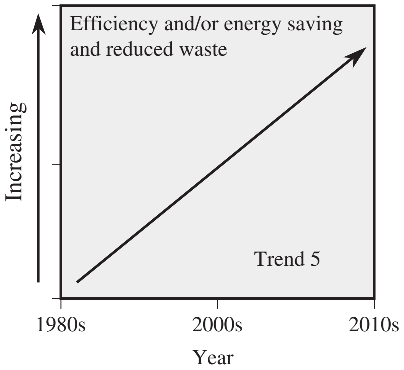


Figure 28.3 Trends for substrate downgauging and system complexity.



Energy efficiency
Climate Change Levy (CCL)

• Electricity	0.43 p/kWh	
• Coal	0.15 p/kWh	(1.17 p/kg)
• Natural gas	0.15 p/kWh	
• LPG	0.07 p/kWh	(0.96 p/kg)

- VAT will be charged on the levy.
- Levy applied in UK from April 1, 2001.

Figure 28.4 The trend showing the increasing requirement for energy saving.

has not been matched by any improvement by the suppliers. This has resulted in the metallizers adopting their own strategies to improve the web performance to become an acceptable product. In packaging, the improved barrier performance of metallized web was made by double-side metallizing and/or laminating.

The display industry is large enough that many companies want to be able to sell their products into what is seen as a very large and lucrative market. The barrier requirements for the display industry will force the web suppliers, if they want to sell into this large market, to improve the substrate cleanliness. Similarly, vacuum systems can be designed to reduce the generation of debris during operation and cleaning. Where cleaning substrates becomes limited because of the small size of the debris, a suitable deposition system for coating a polymer over the remaining smaller sized debris will be developed. These developments, initially made for the high technology applications, will then become available to the wider metallizing industry, which will progressively improve the performance of the metallized film such as for food packaging applications. I fully expect this to become the new standard process over the next few years (see Box 28.1).

Box 28.1 Machine Specification 2015

- Web width 10 m
- Roll length 100 km
- Winding speed 2000 m/min
- Coating uniformity ±1%
- 97 + % material efficiency
- 97 + % uptime/productivity
- No pinholes

Another aspect of taking energy and cost out of the process is that it is not cost-effective to ship rolls of substrate around the country or even from country to country. It would make more economic sense to have the metallizers next to the film-making plant. There were early attempts at this around 15 years ago including putting air-to-air machines close to film lines. These could still be run as batch coaters, but by using flying splices they could coat several rolls without breaking vacuum.

These complex air-to-air systems did more to highlight the problems, risks, and costs of building such systems, and would appear to have frightened off anyone else from repeating the experiment.

One would have thought that the benefit of such systems is that they do provide the learning necessary to improve the system design. The development of long-life aluminum slot sources was addressed, but despite the advantages this does not appear to have been converted to use in more conventional metallizers [1—3].

Looking at other industries that produce commodity items, we can see that the successful companies have all gone down the route of consolidation. They followed this by then investing in the largest, widest, and fastest machines to become the lowest cost producer. As yet, this consolidation has not yet happened to the metallizing industry, although there are many smaller metallizing companies suffering as their profitability has been reduced by rising substrate prices and there continues to be the expectation by large customers that prices will continue to be reduced. This would make the industry look to be ripe for consolidation.

28.2 Speciality Vacuum Coaters

This is a much more difficult segment. Speciality products may be defined as being made in smaller quantities at higher profit margins, so the lower volumes mean that, by their nature, there are far fewer speciality machines built. In turn, this means that looking for trends is much more difficult, if not impossible.

What has been discussed recently is the current market for speciality film products, the opportunities for the future, and hence the expectations for the design of future machines [4—8]. The current enthusiasm running through the industry for future opportunities is for nanotechnology. This is an all-embracing word that allows everyone to include a whole raft of possible products into the definition. The one thing that draws the information together is that all the nanotechnology products are, by their nature, very small. This means that for many of them many thousand products can be produced per square meter and therefore many millions can be produced per roll. (For 1 cm × 1 cm square, there would be 10,000 devices per square meter and for a 1000 m roll, there would be 10 million devices per roll.) This requires a very speedy market introduction and uptake for any new product to generate sufficient demand to keep a vacuum coating machine fully occupied.

The net result of this type of calculation has been that there has been a general feeling that the next generation of speciality machines should be narrow web machines. In this context, narrow web means anything about 300−650 mm wide. These machines would be expected to have multiple sources distributed around either a single or a double deposition drum system depending on the product mix and number of coating materials required. In some cases, designing a system flexible enough to utilize interchangeable deposition sources, might reduce the number of coating stations and allow a single deposition drum, reducing the overall system costs.

Despite the narrow width of these machines, the costs are not too different from that of wider machines of 1 m and above. This is because of the complexity and the fact that most of the high-cost items are still required. It has always been that extra width has been a relatively low-cost option.

An advantage of these systems has to be that there will be no scale-up issues. The production machine is exactly the same as the research and development machine, thus any process will be fully developed on the correct machine.

In the case of the newer metallized and transparent barrier coatings, there is a move to deposit a polymer planarization layer, to cover up the surface defects, prior to vacuum depositing the coating. In some cases, this is done off-line within a clean room, and in other cases, it is done in the vacuum system directly before the coating zone. With the trend for an ever-increasing size of display and because of the weight of opinion, encouraging a move toward polymer-based displays instead of the traditional glass-based displays, the quality of coating has improved. This improvement is nowhere near as much as will be required in the future if the process is to match the production yields that are currently being achieved on glass substrates.

Hence, it is early days, but I would expect the surface quality to improve steadily for some years to come along with more options in the method of achieving this goal.

References

[1] Hartwig EK, et al. Air-to-air metallizer—suitability and profitability. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 152−61.

[2] Taguchi T, et al. Air-to-air metallizer: design and operational data. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 135−40.
[3] Taguchi T, et al. Air-to-air metallizer. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 424−6.
[4] Bishop CA. Possible future trends for aluminium metallizing. In: Proc. 47th annual technical conference of the Society of Vacuum Coaters; 2004. p. 615−9.
[5] Kukla R, et al. Multiprocess roll-to-roll web coater: first results. In: Proc. 48th annual technical conference of the Society of Vacuum Coaters; 2005. p. 617−22.
[6] Mahl GOB. High tech web/roll coating system for R and D and production. In: Proc. 39th annual technical conference of the Society of Vacuum Coaters; 1996. p. 323−6.
[7] Technical sales literature—"OptiLab" and/or "MultiLab." General Vacuum Equipment Ltd. Available from: http://www.bobstgroup.com.
[8] Kukla R, et al. New modular roll-to-roll PVD web coater for cleanroom production. In: Proc. 48th annual technical conference of the Society of Vacuum Coaters; 2004. p. 174−8.

29 System Design

There are many issues that need to be considered in any system design. In this chapter, I have tried to highlight the need to consider the subject holistically considering the widest possible view of a "system." Personally, I would include the materials supply and any downstream processes in my holistic view because the substrate and any pretreatments can affect the process and the resultant product. Also, variations in the process, while it may produce a product within a desired specification, may also generate variations in any downstream process. If the following downstream process is to be carried out by a customer, then you may, or may not, know of all their problems and so believe that the product is consistent and reproducible, even when it is not.

I am sure that many of us have suffered from a supplier changing their manufacturing process and not disclosing the fact. Nominally, the product meets the same specification and so it is deemed not necessary to inform customers of the changes. However, it is sometimes the case that some of the required functionality of the substrate may never have been described in the specification, This requirement may only come to light once the changes in the manufacturing process have changed this functionality and the same has been highlighted as a problem in the vacuum deposition process.

To be on the safer side, we need to understand the processes both upstream and downstream of our own process so that we fully understand the implications of any process changes.

This is another case of trying to find out as much about the whole process and analyzing the results in as much detail as possible as a method of better specifying the system.

29.1 System Choices

When presented with a proof-of-principle process, which has to be scaled up, it is worth looking at all the design options, listing the pros and cons of each option, and iterating toward a design. This will include choosing between continuous and batch process, the type and quantity of pumping, the type and number of deposition sources, free span or the number of deposition drums, single or multiple deposition passes, and many other options.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00029-5

Box 29.1 The Problems of Scale-up

Proof of principle → → → → → → Production

bigger, more, faster, cheaper

geometry change, deposition rate change, maybe source type change, heat load change, etc. . .change

This is a process change and increased risk

It is unlikely that a process can be scaled up by the simple means of making everything larger and hence the process may get modified inadvertently during the scale-up. A change often occurring but often overlooked is that of the time constants. Where gas has to be introduced into the system, the fact of simply having a larger size vacuum chamber will increase the length of the gas pipes and hence will change the time constant. Where there is a feedback control system, this may not operate in the same way because of the slower response to gas flow changes (Box 29.1).

Often marketing information will add some constraints such as web width, standard roll lengths, and target costs that can impact the design. Systems have been built where, between the proof-of-principle stage and the production machine, the type of source has been changed to increase the deposition rate by orders of magnitude. This was done to achieve a required cost with the assumption that the material deposited would be identical to the material produced in the laboratory. This proved to be problematic as the coating properties did not match those produced at the lower deposition rate. The increased deposition rate changed the crystal size and coating density that further changed the physical performance of the coating, taking it outside the desired parameters. Where possible, any process change proposed during scale-up ought to be investigated first so as to minimize the risk in case any change implemented is detrimental to the product.

Many of the choices may be straightforward, whereas others may bring forward problems, some of which may not be immediately apparent. The greater the number of changes, the greater the risk. If such large changes are required, it is well worth repeating the proof-of-principle stage with the new process to confirm that a product can still be made. This may not be possible if no machine has been built that can reproduce the process. Thus, it is a challenge to test out as many parts of the process as possible to bring the risk down.

Another common oversight is the variability of samples produced when developing a process or a product. It is a common problem to assume that variability is acceptable for coatings produced from a research or development machine. This may, or may not, be true. The variability may be due to poor control of one or more parameters in the system. This poor control may, or may not, be a known limitation of the process. By accepting that coatings can be variable, it may be that there are unidentified factors that are affecting the coating. These unknown factors

Box 29.2 Managing Risks

Risk is associated with “unknowns”

Convert as many “unknowns” to “knowns”

Analyze existing data in great detail to minimize the number and extent of “unknowns”

If product from pilot machine is variable

– Either	poor control	→ small risk
– Or	unidentified factor/s	→ BIG risk

Scale-up changes that are not tested = BIG risk

may, or may not, be critical to the process, and as these are unknown cannot be specified properly during the scale-up. Hence, this changes the problem from a small risk for known poor control to a high risk (Box 29.2).

This is not a trivial topic in that many investment decisions are made by non-technical people, and they often want to see, in addition to the economic case, a presentation of the risks. They want to feel comfortable that potential problems have been thought about and assessed, and some action plan has been considered.

Not everything needs to be developed inhouse or even within the industry. It is always worth looking toward other industries and cherry-picking the best of their techniques. There are various methods for helping in evaluating processes. Apart from the “design of experiments” (DoE) [1] matrices for experimentation, there are also methods of systematic analysis to find the optimal choice of equipment [2,3].

It is always worth doing a “sanity check” by looking back to see if the process has been tried before and, if so, what the outcomes were. This is not a method of quashing ideas but is a method to maximize the benefits of previous learning. Sometimes an idea is ahead of the technology available to deliver it and as the technology progresses it changes from not being possible to becoming possible. Hence, it is always worth reviewing earlier work.

There are some design philosophies that are regularly raised but rarely adopted. An example of a common idea that gets raised periodically is to minimize the cycle downtime by the continuous operation of a roll-to-roll air-to-air coating system as opposed to the lower productivity of a batch process. If we look at this in more detail, we will see some of the problems encountered.

29.2 Batch Versus Air-to-Air Processing

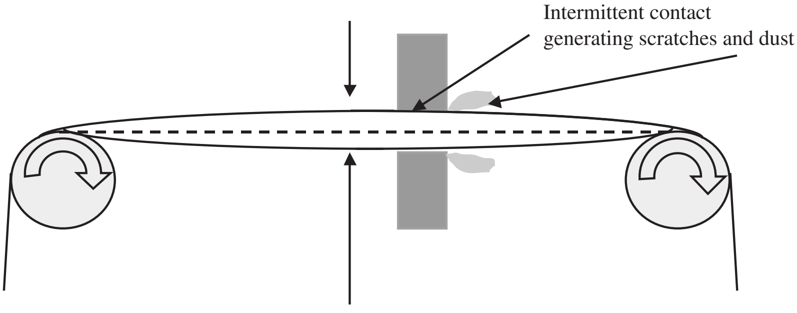
One of the visions was to have a metallizing machine at the end of a film line so that the whole output of a film line was metallized. This will cut out all the intermediate handling, thus reducing costs and some film losses. Some film lines run in campaigns that can last for several weeks and sometimes months.

There have been a small number of air-to-air systems built and all have had serious manufacturing problems such that the productivity has been worse than that of operating a batch process. There are a number of reasons that explain why this has happened.

The air-to-air process aims at unwinding and rewinding the web in air and feeding the web through a series of narrow slots into a series of vacuum chambers [4−6]. Each successive chamber is at a lower pressure until the process pressure is reached at which the coating can be applied and then the web passes through a second series of chambers to bring the web back to atmospheric pressure.

The first observation is that this requires many more rolls and winding motors as well as a larger overall chamber with much more pumping than a comparable batch process. The increased number of rolls increases the chances of scratching of the web through debris lodged on a roll or a slight sticking of a roll. As the web enters the first vacuum chamber, the air also enters through the slot and it enters the vacuum chamber at something approaching the speed of sound. This high-speed rush of turbulent air makes the web flutter (Fig. 29.1). This web fluttering needs to be controlled or suppressed because if fluttering is allowed to occur it too can result in surface scratches as the web contacts a surface during the fluttering. If the fluttering gets too bad it is possible to start a web tear that can progress to a web break. A web break can be more catastrophic on an air-to-air machine because the system is often more complex and the downtime to vent the system, clean it out, rethread the web, and pump the system back out is often much longer than the more simple equivalent batch machine. The propensity to flutter can be reduced by keeping the spacing of rollers to a minimum, particularly where the web has to pass through a slot.

The slot required is either fixed and needs to be large enough to take the web splice or is adjustable to allow for widening the slot for the splice and then closing



Flutter—amplitude brings web in contact with static item causing scratching and debris generation. Flutter frequency is a resonance- and machine-dependent phenomenon.

Figure 29.1 Schematic of web flutter.

it down for the next length. This in itself is a batch process and usually requires slowing the process down to minimize wasted film.

Another problem that occurred was in the deposition zone. Typically, a metallizer has a material maximum collection efficiency of around 50%. This means that the other 50% of the material is falling on the vacuum system furniture, the shields, shutter, drum, and vessel walls. However, this is not an issue in a batch process because the shields are cleaned or exchanged in each deposition cycle. In the early air-to-air systems, there was no facility for cleaning the shields. Over the prolonged process time, the coating growth was built sufficiently to encroach on the coating apertures. The coating reached a thickness that resulted in closing the gap between the deposition drum and shields to the point where the accumulated coating started scratching the web.

The fix to this problem was to heat the shields to prevent the metal condensing on the shields; however, this increased the radiant heat load that the web was subjected to causing the deposition rate to be reduced and the winding speed to be reduced. As the winding speed could then no longer be matched to the film line output, a decision needed to be made to either reduce the speed of the film line or convert the air-to-air process to an off-line process. Running a film line more slowly is uneconomic; hence, the systems were converted to off-line processes requiring the film to be wound and stored before being metallized. This damaged the system efficiency and increased the coating costs.

Even with improved material efficiency and an increased metal wire inventory, the system could not be run for weeks without opening for cleaning and maintenance. Thus, the air-to-air machines ended up being converted to batch machines as a solution to the problems but, without being designed as batch systems, they were not efficient batch machines either.

This is not to say that the idea is not viable in all cases. Many processes do not require a high winding speed, and the substrate can be thicker than is typically used for packaging applications, which, perhaps, gives a greater degree of tolerance thus allowing use of an air-to-air process. A recent development system [7] uses a narrow slot in combination with a tacky roll cleaning system and a proprietary dynamic sealing system to reduce the number of differential pressure chambers. This further reduces the amount and cost of pumping. It remains to be seen if this will develop into a viable production process or will have speed, web width, or other limitations such that it will remain only as an interesting development system.

29.3 Source Choices

All too frequently, the choice of source is made for the wrong reasons. Rather than selecting the source specifically for its characteristics and performance, it is often chosen purely because it was the source used in the development machine. In other cases, products have been made slowly in the laboratory, and when specifying a new production machine the opportunity was taken to speed everything up as well as looking to incorporate economies of scale. Thus, the source is chosen simply because it is of the lowest cost or has the fastest deposition rate without giving any thought to whether it can still deliver the desired coating.

Sometimes it can be helpful to fill in a matrix of source types and their relative performance, such as shown in Table 29.1.

Table 29.1 attempts to compare the three broad groups of deposition sources. As might be expected, this is difficult and arguments can be made that some entries are wrong for some specific materials or processes. In sputtering, it states that compounds may be produced with difficulty but there are some materials that can be produced easily although they may not be deposited at the fastest rate or with the optimum properties. Indium tin oxide may fall into this category as it is possible to RF sputter from a compound target and deposit a transparent conducting coating. However, this will be at a fraction of the deposition rate and with a lower electrical performance than can be achieved by sputtering from a metallic target in a reactive mode but the reactive sputtering process is much more difficult to control. Similarly, in evaporation, it states that alloys are difficult to make but scanning electron beam systems have been used with separate crucibles where a different

Table 29.1 Relative Performance of Different Sources

Sputtering	**Evaporation**	**Chemical Vapor Deposition**
Stable deposition rate	Unstable deposition rate	Coating composition may change with changing deposition rate
$\sim$10 nm/s	$\sim$100–1000 nm/s	$\sim$100–1000 nm/s
Dense stable coatings	Columnar structure to coatings, plasma/ion assistance increases coating density	Higher substrate temperature leads to denser inorganic coatings
Different materials need target change	Different materials easy with multiple/exchange crucibles	New materials need new precursor gas
Compounds may be difficult	Alloys are difficult to make	Changes in chemistry are possible with changes in process balance
Alloys sputter true from alloy targets		
Easy to scale using linear cathodes	Relatively easy to scale with sweeping e-beam guns	More difficult to scale—chemistry may change with scale
High voltages	Very high voltages	Precursors may be toxic/pyrophoric
Coatings can be stressed	Coatings can include damage from source spitting	

Box 29.3 Heat Load from Different Sources

Evaporation boat
Heat of condensation + radiant heat load (+ chemical reaction heat load)

Electron beam
Heat of condensation + radiant heat load + energetic species
(+ chemical reaction heat load in reactive processes)

Magnetron sputtering
Heat of condensation + energetic species + radiant heat load
(+ chemical reaction heat load in reactive processes)

Box 29.4 Relative Costs and Performance of Different Sources

Resistance-heated evaporation
Cheapest for aluminum
Limited number of materials can be evaporated from boats

Electron beam
Similar cost to sputtering but faster deposition rate
Less precise—thick engineering coatings

Magnetron sputtering
High cost—similar to electron beam systems
High precision—optical coatings—multilayers

residence time on each crucible has allowed different evaporation rates enabling alloy deposition. Again this is possible but not necessarily easy to achieve. So, this table should be used as a very coarse guide to choosing a possible source but ideally backing up the choice with other information about the specific materials and process options to confirm the choice. As we will see below, there are other factors that will also influence the choice of deposition source.

In comparing sources, there are a number of things that need to be considered because these will affect other parts of the system design. The choice of source could be limited by the choice of substrate. In some cases, substrates are extremely heat sensitive and it becomes essential to minimize the heat load. In other cases, the heat load is inconsequential, and the cost per unit area is the most critical consideration (Boxes 29.3 and 29.4).

In choosing the source, there may be limitations in the source orientation. If the source is an evaporation source then they are typically sited at the base of the vacuum system and evaporate upward. Thus, if a multilayer coating is required this may require multiple deposition drums. A trade-off might be made to use a slower sputtering source but one which can be sited in any orientation so that a number of

Box 29.5 Orientation of Sources

Upward deposition only
E-beam
Induction sources
Resistance-heated evaporation

Any orientation
Sputtering
Enclosed radiant-heated evaporation
Arc—filtered arcs
CVD

Box 29.6 Relative Cost of Pumping

Atmospheric deposition cheaper than vacuum deposition

Roughing pumps cheaper than high vacuum pumps

Diffusion pumps cheaper than turbomolecular or cryopumps

Simple solutions are cheaper than complex ones

sources can be used around a single deposition drum. This may result in a lower cost system but with a slower deposition rate (Box 29.5).

Machine suppliers will want to be competitive when quoting for systems. It has been known that in order to trim the costs, the pumping system will be minimized. While this may achieve the required base pressure, it may reduce process tolerance or flexibility. Any small leak or insufficient cleaning may adversely affect the performance more quickly than where there is some amount of additional pumping capacity. Hence, it is important to make sure that a system has enough pumping for all envisioned processes. The other side of the coin is that when specifying a vacuum system, it has also been known for systems to be overspecified for the desired process. The end result of this would be that a more expensive pumping system would have to be included that would not benefit the process at all (Box 29.6).

29.4 Summary

Designing and specifying a vacuum system requires a methodical approach if mistakes are to be avoided (Box 29.7). Initially, it will be possible to start with a draft specification where some choices can be made and fixed. However, this initial specification ought then to be reviewed to check that any choices made do not impinge on other parts of the design.

Box 29.7 Process Considerations

Single layer—multilayer (single or multipass)
Single side—double side coating
Metal or reactive deposition—symmetry
Source type—sputtering, evaporation, etc.
Surface texture—embossing
In-vacuum release—or not
Planarization or protective overcoats—or not

Box 29.8 System Types to Review

Pre-layers or patterning + deposition
Air-to-air machines
Loadlocks
Multidrum−multizone

Single product or universal machine
Cost and risk management

Initially, the information available for the draft specification will be based on the materials used, process, and the desired product. Beyond this, the more information that is available about the process tolerance and/or any material interactions, the more detail that can be included in the draft specification (Box 29.8).

The more complex the process, the greater the care that needs to be exercised. If it is intended to deposit more than one coating in the same deposition pass then they need to be compatible processes. This is particularly true if one layer is a metal and the other is a compound deposited by a reactive process. Problems can arise if the reactive process interacts with the metal coating. One must bear in mind that the speed of the process will be only as fast as the slowest of the processes. Where the deposition sources are different, it becomes important to make adequate provision for any differences in pressure requirements. The system has to be designed with the lowest pressure requirement in mind and using suitable baffling or conductance gaps to isolate different zones (Box 29.9).

Armed with the initial specification there may be other sources of information input, such as a target volume output, that have to be considered. Once the specification has been through one or more iterations, it may be worth reviewing how the process compares to the original laboratory process. If there are many changes, it may be worth evaluating the risk of the scale-up and initiating some further work to reduce this risk prior to developing the system.

Box 29.9 Considerations for Multilayer Coatings

Lowest pressure process
Pumping is designed for this process

Slowest deposition process
Process speeds must be compatible

Heat load to substrate

Box 29.10 System Contents to Review

Deposition rate
Coating structure and performance
Source type
Pretreatment—plasma, e-beam, heat
Single or multilayer
Single side or double side deposition
Single or multipass
Monitoring
Coating uniformity and symmetry
Gas flow and conductance
Zone plates, shielding, and differential pumping
Pumpdown time and speed
Reactive processes
Cleaning and process contamination

Over and above the process, there will also be other considerations relating to the design such as those listed in Boxes 29.10 and 29.11. Again, if any of these considerations instigate further changes, another review needs to be made to make sure the process has not been affected.

Inevitably as a process grows from a laboratory process through to a pilot and then to a full production process, other influences are brought to bear on the design process. It is common to model the production process to be able to look at the effects of increasing or decreasing the speed, roll length, width, downtime, substrate thickness, coating thickness, etc. At some point before the system supplier is set to producing a design, it is well worth doing a review of all the data and the specification produced, sometimes referred to as a "sanity check." This is another part of reducing the risks of a new design. Included in the data checklist is a check on all the "known" facts. This sounds daft but is well worth doing. I have seen a model that has optimized the output from a system that was based on the width of substrate that was larger than anyone was able to produce. If this had not been checked, then building the machine would have been possible but as it would have

Box 29.11 Other System Considerations

Safety
Ergonomics
Interactions—sources—gases
Cleaning—downtime
Space
Future upgrades
Obsolescence

to run with a narrower substrate the shielding would have had to be re-made and the efficiency of the sources would have been lower and the productivity of the machine against the model would never have been realized.

Another aspect that needs to be checked and assessed is the availability and price of supply materials. Some of the deposition materials are believed to be running out [7–9] and so the price is expected to rise significantly. The earth's crust has a finite amount of material, of which much is inaccessible either deep under the sea or in high mountains or in hostile environments or countries. Estimates have been made of the amount of various elements that are thought to be available and, at the current rate of use, how quickly we would run out of them. This is open to large errors, as mining companies or countries do not always want the precise volumes to be publicized. Some materials are in countries where trading is difficult and erratic. The amount of material that is, or could be, recycled is also not well known. All of this can lead to large errors. Besides there is also the problem that energy costs are rising and so the cost of extraction and processing is also rising and the process is open to errors. One of the more widely discussed cases is that of indium where the current usage is greater than the amount being mined. Indium is mined as a by-product and so the decision to mine is usually dependent on the price of the dominant element in the ore. As indium is used in transparent conductors for displays, including flexible displays, and for the transparent conductor for photovoltaics as well as within the photovoltaic material copper indium gallium diselenide, the very rapid growth of each of these two (displays and photovoltaics) markets has caused the stockpiles to diminish. The benefit in such a case is that users are much more careful to recycle the exhausted sputtering targets but there is still a shortage of indium. Thus, looking at the future scenario, it is very difficult to predict the price of indium as it depends on various conditions, such as finding new sources to mine and whether China allows exporting of indium without restriction.

Thus, it is well worth including as part of the modeling an evaluation of the sensitivity of the product to a rise in price of the supply materials. Already some companies have announced their decision not to use indium because they cannot guarantee the supply of indium for the lifetime of their production facility.

So, modeling can be a powerful tool if used properly, but it still requires correct and high-quality information to give the best results. It can be used well to make sure that any new process has a chance of becoming profitable and that the risk is not too high for a poor return.

The benefits of minimizing risks before any machine is built cannot be stressed enough. Once a machine has been built, it is much harder and expensive to redevelop the process on the production machine. This is worth highlighting to all the team members for any new machine purchase. The perceptions of team members may differ. I have known accountants who believe that once a specification has been produced the delivered system will be turnkey and will be in production within days; whereas, the engineers in the same team believed they would be lucky to get the system producing anything in less than three months, let alone production. Most systems are delivered with a given functionality and the process is the responsibility of the system purchaser. This means that usually the system purchaser takes most of the risk unless they have taken out the risk by experimentation, development, or modeling sufficiently to fully understand the process and to minimize the process development time on the production machine.

References

[1] Barrentine LB. An introduction to design of experiments: a simplified approach. ASQ Quality Press, Milwaukee, WI 1999. ISBN 0873894448.

[2] Saaty TL. The analytic hierarchy process. McGraw-Hill; 1980.

[3] Arbel A, Shapira Y. A decision framework for evaluating vacuum pumping technology. J Vac Sci Technol A 1986;4(1):230–6.

[4] Hartwig EK, et al. Air-to-air metallizer: suitability and profitability. In: Proc. 34th annual technical conference of the Society of Vacuum Coaters; 1991. p. 152–61.

[5] Taguchi T, et al. Air-to-air metallizer: design and operational data. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 135–40.

[6] Taguchi T, et al. Air-to-air metallizer. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 424–6.

[7] Visintin S, Golfetto E. An air-to-air feedthrough for vacuum coating of films. In: Proc. 53rd annual technical conference of the Society of Vacuum Coaters; 2010. p. 613–5.

[8] Gordon RB, et al. Metal stocks and sustainability. Proc Natl Acad Sci USA 2006;103 (5):1209–14.

[9] Earth's natural wealth: an audit by David Cohen New Scientist, Issue 2605, 23 May 2007. p. 34–41.

[10] Bishop CA. Dwindling resources – or how to make a molehill out of a mountain. Vac Technol Coat 2009;December:49–52.

30 Hazards

Hazards represent a potential cost, either through an injury to an operator or loss of production. Accident prevention is often regarded as a cost but ought to rather be regarded as a cost benefit. A small outlay in prevention can prevent a larger cost in compensation, fines, sick pay, loss of production, etc.

Everything can be viewed as a potential hazard and so there also needs to be a modicum of common sense applied when assessing all the aspects of the vacuum deposition process [1,2]. Some products, such as pyrotechnics, need additional consideration during their manufacture, and these will often have additional requirements [3].

30.1 Risk Assessment

It is possible to get carried away with accident prevention and to imagine all kinds of disaster scenarios. One way of doing a risk assessment is to take each possible hazardous action and look at and score the likelihood of occurrence, the degree of possible harm, frequency of exposure, and number of people involved. These results are then multiplied together. The results will fall on a scale ranging from negligible risk through to unacceptable risk.

Using the scores as shown in Fig. 30.1, any process can be assessed. Figure 30.2 shows a trapping hazard in a winding system. The scores given are used for example only and should not be regarded as exact. Different systems may score differently.

This type of risk assessment is not foolproof in that for some actions there will be a difference of opinion on the precise score of each item (Fig. 30.3). There will also be a judgment as to what is an acceptable level of risk. For items that fall into the unacceptable risk level category, it is easy to make the decision to review the process and make changes. Items that fall into a lower category, such as significant risk, are more difficult to make decisions on. It is probably impractical to bring everything down to the negligible risk category, but it may be possible to achieve this but not cost-effectively (Fig. 30.4).

Hazards fall into many different categories; mechanical, electrical, thermal, chemical, and ergonomic would be one way to group them.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00030-1

Likelihood of occurrence (LO)

0	Impossible	Cannot happen under any circumstances
0.1	Most unlikely	Possible only under extreme circumstances
0.5	Highly unlikely	Though possible
1	Unlikely	But could occur
2	Possible	But unusual
5	Even chance	Could happen
8	Probable	Not surprised
10	Likely	Only to be expected
15	Certain	No doubt

Frequency of exposure (FE)

0.1	Infrequently
0.2	Annually
1	Monthly
1.5	Weekly
2.5	Daily
4	Hourly
5	Constantly

Degree of possible harm (DPH)

0.1	Scratch/bruise
0.5	Laceration/mild ill health effect
1	Break—minor bones or minor illness (temporary)
2	Break—major bone or major illness (permanent)
4	Loss of one limb/eye or serious illness (temporary)
8	Loss of two limbs/eyes or serious illness (permanent)
15	Fatality

Number of persons at risk (NP)

1	1–2 persons
2	3–7 persons
4	8–15 persons
8	16–50 persons
12	>50 persons

Figure 30.1 Descriptions and scores that help score the different parts of the formula.

$$\mathrm{LO} \times \mathrm{FE} \times \mathrm{DPH} \times \mathrm{NP} = \mathrm{HRN}$$

HRN = Hazard rating number

LO = Likelihood of occurrence

FE = Frequency of exposure

DPH = Degree of possible harm

NP = Number of persons at risk

Example

Trapped fingers between rolls

LO × FE × DPH × NP
Even chance × daily × minor break × 3–7 persons

5 × 2.5 × 1 × 2 = 25 = significant risk

Score chart

Hazardous rating number (HRN)	Risk level
0–1	Negligible
1–5	Very low
5–10	Low
10–50	Significant
50–100	High
100–500	Very high
500–1000	Extreme
1000+	Unacceptable

Figure 30.2 A simple formula for making a risk assessment calculation.

The adequate training of personnel and detailed safe operating instructions are other items that could be added to the risk equation. Where either one or both are missing, the risk of accidents increases. Operators are more likely to take short-cuts where no instructions are available or where no training is given.

Good system design can be used to take out many of the risks. If the risk analysis is done before or during the design stage, any safety items can be built into the

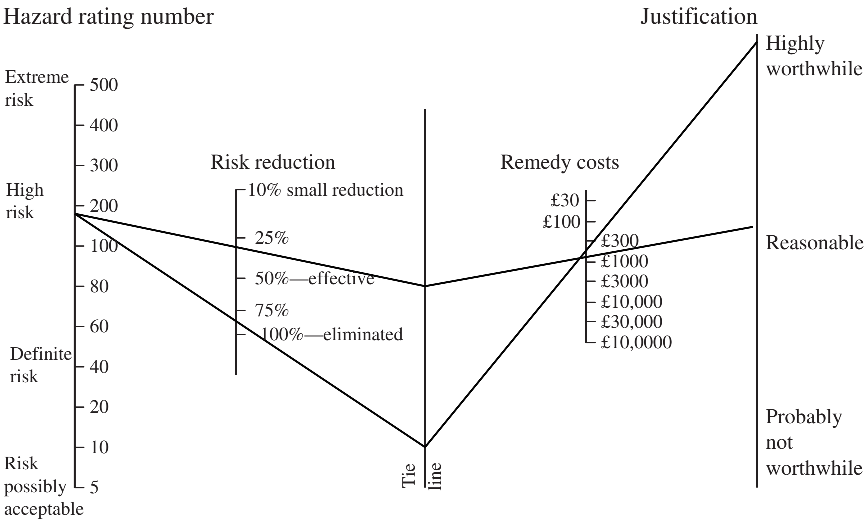


Figure 30.3 A method of helping to look at the cost benefit of reducing risk.

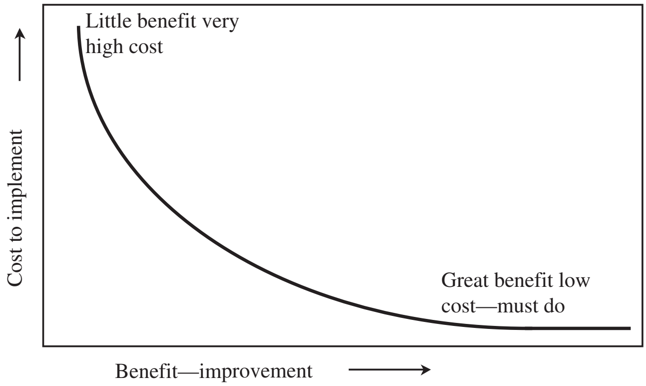


Figure 30.4 Cost−benefit graph that can help clarify decisions.

system at the least cost. If the risk analysis is done at a later stage, any items that have to be retrofitted can result in a higher cost. Hence, starting the risk analysis sooner rather than later is the preferred option.

30.2 Mechanical

Within this category, the type of hazard can be put under some other headings such as trapping or crushing, cutting, weight, bumping, tripping, falling, explosion/implosion, etc.

All vacuum systems have a method of opening the system. Large vacuum coaters often have a large door to the system that presents some hazards. If the door moves back on a track, there is the possibility of a trapping hazard if a person is in the way of the door wheels as it moves. There is the crushing hazard if a person gets a finger trapped as the door closes. On a large system, there is also the possibility of closing the door with an operator still within the system as it closes. All of these possibilities have happened in the past.

As the web is transported by a system of rolls, it too can provide a trapping hazard. The aim is to produce a design that is easy to thread and maintain but which is safe for operators to use. It is too easy to guard against all the eventualities to the point where it is virtually impossible to use the system. If it is made too difficult to use, there will always be someone who will try to bypass the difficulty and hence compromise the safety measure.

Hence, the aim is to have designs that are intrinsically safe wherever possible, and with simple and manageable safety precautions wherever not.

Large vacuum systems will often contain large components. This may well mean that many items could be too heavy for safe manual lifting, thereby requiring assisted lifting or automated systems. Automated systems can often be cost-effective for routine events, such as roll changes, that occur after each deposition cycle. This same problem may also occur with the routine maintenance of the equipment. Here, the occurrence may only be an annual event and a permanent feature may not be justified. In this instance, to make the process easier and safer, it might only require the provision of adequate space to enable a forklift truck or similar temporary lifting implement to be brought in to assist the operation.

Large systems also tend to have different working levels, with staging around either the system or the pits. These provide a large source of possible hazards, particularly of the bumping, tripping, and falling types. Access around the system is often quite limited, and where items only require occasional maintenance or replacement, it is common to have very poor access with many hazards with low harm levels (injuries would be bruises). Even here, it is possible to reduce, though not eliminate, the problem cost effectively by using cushioning on sharp edges.

Systems will usually have viewports to allow a view of the process in operation. These viewports need to be constructed of suitable materials. It is common for the window glass to be laminated with a polymer film. This is done so that, in the event of a failure of the glass under vacuum, the glass does not splinter and cause injury either during the event or during the subsequent cleaning operation.

30.3 Electrical

There are a variety of electrical hazards. The process is likely to require not only a high-power electrical supply but also high-pressure cooling water. These two items are also likely to be situated in close proximity to each other. The possibility of leaks in the water-cooling system is moderately high and, particularly within the vacuum system, there may be only limited protection of the electrically live surfaces.

This is another case where there needs to be plenty of thought that goes into the use of the protection and interlocks that are used. I have seen systems that have had so many interlocks that at times it has been difficult to get enough of the system running to find the problems that were stopping the rest of the process working.

The use of radio frequency supplies can cause a number of problems, often relating to earthing of the system. It is common to strap one side of the power supply to the system as an earth. The system may not be sufficiently well earthed for such RF supplies and it may in fact be floating with respect to earth. I have come across systems that I could touch and see sparks because of insufficient or poor earthing.

30.4 Thermal

This type of hazard falls into two categories: high-temperature hazards and low-temperature hazards. The high-temperature hazards are from the likes of the diffusion pump heaters and hot oil, the deposition sources, or uncooled shielding. The low-temperature hazards are where cryocooling is used. Liquid nitrogen is pumped through some cold traps, and unless the supply and return lines are well insulated, there can be very cold surfaces that are exposed and can give a cold burn.

In general, these are well-known hazards and are easily predicted and protected against.

30.5 Chemical

This hazard can be more difficult to predict and defend against. A number of deposition processes are reactive processes and may use a variety of precursors [4]. Often it is not quite known how these materials will react with each other in fine detail, what is known is what the resultant coating and main by-products are like. The process takes place in a confined vessel and so there is little chance of exposure to the operators. Typically, the exhaust for the process would be just a pipe into the atmosphere (Fig. 30.5).

This is increasingly becoming an unacceptable practice, usually on environmental grounds [5]. This means that the use of exhaust cleaning by processes such as incineration or wet scrubbers is becoming commonplace for many more systems [6]. If incineration is to be used, the aim should be that the incineration temperature exceeds 1300°C to ensure that all PCBs (polychlorinated biphenyls) and dioxins are completely broken down. Incineration above 1300°C will allow the exhaust to be bubbled through a water scrubber and vented to atmosphere. At anything less than 1300°C, there need to be permissions for the release of toxins into

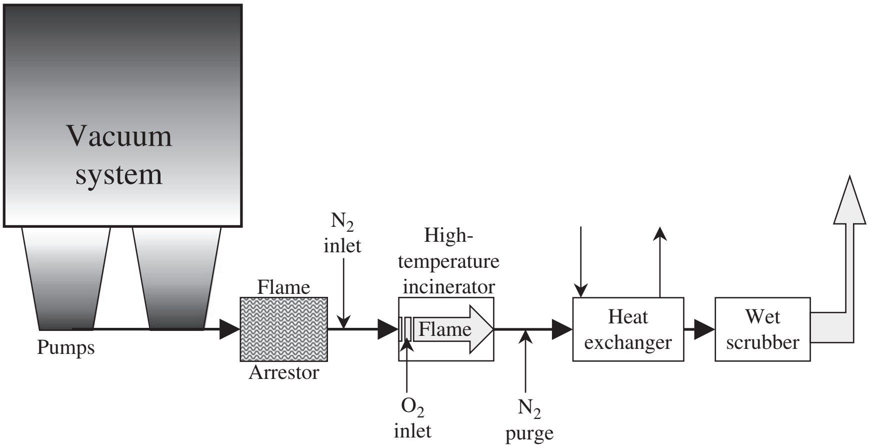


Figure 30.5 A schematic of one option for cleaning up the exhaust gases [7].

the atmosphere, or other more complex scrubbing systems need to be used to prevent these toxins being released.

Other chemical processes that are less acceptable now than previously would include cleaning using solvents. Depending on both country and local restrictions, the range of acceptable solvents is more restricted and different. Some of the need for cleaning can be removed by suitable design, particularly in the area of shielding.

30.6 Material Interactions

Other more rare chemical hazards are the ones that appear as a result of interactions between materials. There have been explosions in vacuum systems due to the deposition of thin film metals (aluminum) onto a mild steel vessel. The inside of the vessel had a thin oxide layer and the thin aluminum coating gave an intimate contact between the two materials that make up a thermite reaction. However, generally, there is insufficient energy for this reaction. Coupled to this, many vessels are now painted on the inside to provide a smoother and more easily cleaned surface. What is usually seen is the rapid oxidation of the aluminum. The aluminum surface is new and not fully oxidized, and so it will oxidize. This oxidation is an exothermic reaction, and if the mass of the aluminum flake is small, the increase in temperature can raise to the point of autoignition. These are the sparks that can often be seen. If a large quantity of material is oxidized, at the same time the heat rise may be enough for a larger amount of material to provide a flash. The quantities of material are, in general, small, and so other than a quick flash, it is likely that there would be little damage other than giving the operators a fright. There is the potential for something worse if not guarded against. Other problems have been caused by the rapid oxidation of thin metallic coatings. If the coating is too thin to transport away the heat generated by the exothermic reaction, the coating may reach a temperature at which the metal coating will burn. On one system, this reaction happened, but the problem was only seen after the deposition of the titanium coating was completed. The heat generated from the burning metal progressively heated the water-cooling pipes within the vessel to the point where they melted, and this led to a major water leak.

Where this type of material is being produced, some have adopted the technique of deliberately oxidizing as many of the surfaces as possible in a controlled manner. The way this was done was to introduce a small quantity of oxygen into the vessel to start the oxidation process and then immediately pumping the vessel back down to a low pressure. This cycle was repeated a number of times, with the pressure raised each time closer toward atmospheric pressure. By this means if any material catches fire, the following pumpdown back to a low pressure would extinguish the fire. Thus, when the system will finally be brought to the atmosphere, the surfaces should be quiescent.

30.7 Deposition Material and By-products

The aim is to deposit a known hazardous material such as selenium as part of the deposition process of the copper indium gallium diselenide (CIGS) material for the photovoltaic market. The selenium has a high vapor pressure and so is usually present as a vapor through which the other materials deposit onto the substrate and incorporate some of the selenium. The selenium will migrate to other parts of the vacuum deposition system and deposit on most other surfaces. As the hazard of selenium is well known, the appropriate personal protective safety equipment can be easily identified.

The real hazards are those that are hard to identify. Chromium is one such material, as the deposition process can produce different forms of chromium of which chromium VI is a potent carcinogen. It is extremely difficult to prove, for certain, that chromium VI is not produced. It is possible to take samples of the coated material from the substrate, from stray deposition onto shields, and even from powder from the bottom of the chamber. The analysis of these powders will almost certainly confirm that no chromium VI is present. However, there are usually some caveats such as that the analysis technique could alter the form of chromium, or that over time there might have been changes to the sample, or that in a finer form such as from airborne dust there might be chromium VI present that is not found in the sample tested. All of this leads back to the risk analysis of judging how probable any of these scenarios might be. The difficulty is that if the judgment is wrong, a life could be at risk because the chromium VI is so dangerous.

This is why it is so important to review all materials and the possible interactions or reactions that might be possible and to make a judgment on the likelihood that each reaction might occur. If there is any doubt, the safest course is to assume that the reaction can occur and to take the appropriate precautions.

30.8 Hazardous Gases

Gases can be placed into four general types: benign, toxic, pyrophoric, or flammable. There are three areas that need consideration: the supply, the process, and the exhaust. The supply gas may be benign but may be partially decomposed in the process to become more hazardous within the reaction vessel and through the pump to the exhaust. Other hazardous supply gases may end up as benign gases when they reach the exhaust.

An assessment needs to be made to determine if a gas is hazardous. A gas can be hazardous:

A. By itself
B. Because the process decomposes the gas into a hazardous by-product
C. Because the gas mixes and combines into another hazardous compound
D. Because the gas reacts with other materials such as the pump oils or sealing greases
E. Because of an abnormal concentration of the gas into the ambient air

A. Gases that are, of themselves, hazardous are well known and the procedure for the safe handling, storage, and supply are well documented.

E. The abnormal concentration of gas into the ambient air is also common, although rarely is it identified as a problem. Imagine a large vacuum system that is vented using, instead of air, dry nitrogen. When the vessel is first opened, the atmosphere in the vessel is 100% nitrogen, and hence it would suffocate an operator who breathed the atmosphere for too long. It is worth noting that breathing air with as little as 18% oxygen content can lead to oxygen deficiency in the blood, leading to brain damage. Hence, there is often a reliance on the general air movement to disperse the nitrogen and to dilute it.

Another possible asphyxiation hazard is where there is a pit associated with the large vacuum system. Often to allow the main vessel to be at floor level, the diffusion pumps are mounted such that they need to be positioned over a pit. The heating elements are on the base of the diffusion pump, and to replace the heating element, it is necessary for the maintenance engineer to enter the pit. If the process requires an inert gas, such as argon, there is likely to be a supply pipe fairly close to the pit. If the supply line were to leak, the argon, because it is heavier than air, would tend to accumulate in the pit. Thus, the engineer could be entering a hazardous area. This is particularly dangerous because neither does the gas have any odor nor can it be seen. This type of hazard requires that the problem has been thought about beforehand and the appropriate oxygen level monitor and alarm located in the pit along with a safe operating procedure adopted and suitable training given.

D. Another incidence of an explosion problem was in the use of oxygen as a reactive gas [8]. Pure oxygen was used, and the thin oil film on the blades of the rotary pump under mechanical load and the pure oxygen led to an explosion.

The use of 100% oxygen is common for plasma-treating polymers or in plasma etching materials. Mineral oils that can be used on pumps are combustible. It is preferable to use an inert synthetic fluid or a dry pump when using high oxygen concentrations. In many cases where only a small proportion of oxygen is used within the process, there is the assumption that this will always be the case. A simple precaution of using a gas ballast of nitrogen to dilute the oxygen prior to it entering the roughing pumps is to negate the problem. This does, however, have the disadvantage that any operator error or a failure of the diluent supply could allow 100% oxygen to be pumped. One fail-safe method is to use the dry pump or the inert synthetic fluids even on what appear to be acceptable oxygen levels so that in the event of a gas failure or operator error the system remains safe. Other methods such as the monitoring and interlocking of parts of the process can be used such that a failure of any one aspect would shut the whole process down. These systems need to be thoroughly thought through to be robust against all eventualities.

It is worth noting that oxidation and combustion can occur or be supported by gases other than oxygen. All oxidizing gases such as fluorine, nitrous oxide, and nitrogen dioxide, to name but three, will support combustion.

B & C. The above problems are known about and the process can take account of them. The more difficult hazard to defend against is the unknown one. When developing a new process, it is worth looking at every material used in the process and the possible interactions with all materials it will come in contact with. It is also worth bearing in mind that in some circumstances some of these interactions will happen at elevated temperatures and possibly in highly reactive atmospheres.

In a reactive process, it will be possible to produce many different exhaust compounds. Many may be unstable and short lived, some may be toxic, others benign, and many will have no toxicity data available. Using published data and assuming all potential combinations can be achieved, it is possible to systematically look at what compounds might be produced and identify if there are any particularly hazardous ones included in the list. If the process is new, it may be possible to check out the process, using a mass spectrometer, in order to see which of all the possible compounds are really produced and in what proportions. This check can also be repeated at the exhaust port. A check on the level of hazard for these compounds will then allow the appropriate protection to be adopted.

Again, there has to be a judgment on how far to try to identify everything that can be produced and under what circumstances and what may be assumed, and the appropriate level of protection required.

30.9 Cold Traps and Cryopumps

Cold traps and cryopumps can be hazardous, especially in systems used for research and development.

Cold traps and cryopumps work by condensing gases onto a suitably cold surface. The condensing gas can trap other gases that do not condense within the growing solid layer. A process may consist of several individual processes that are carried out sequentially. Each process may use different gases or gas mixtures, and each may be totally safe. Consider the solid layer condensed on the cold surface; it will be like the geological strata with layers from each of the different parts of the process. Now consider what happens during the regeneration of that cold surface. The surface is heated and the solid converts into gas. The heating process is done quickly, and in this instance, there is no sequential evolution of the gases but everything will vaporize off the surfaces at the same time and be mixed and pumped together. This has been known to cause problems. Thus, in reviewing a process, it should be done holistically and not piecemeal in order to look at the widest range of possible interactions.

R&D systems can be particularly susceptible to this type of problem. It may be days or weeks between each regeneration cycle and there may be many people using the equipment. In this case, it is all too easy to overlook the full history of the pump and inadvertently mix incompatible gases.

30.10 Cleaning Hazards

The cleaning of vacuum systems represents a regular exposure of operators to potential hazards.

The bringing of the vacuum system back to atmospheric pressure using air will allow any coatings that wish to oxidize to do so. As mentioned in Section 30.6, on material interactions, this can lead to heating and possible flashes or fires. This possible hazard is also present during cleaning. Often coatings are scraped off shields or abraded using wire brushes or powered wire brushes. This abrasion process generates a couple of problems. One is the production of fresh surfaces that can again, depending on the material, oxidize. This is potentially a higher level of hazard as the material is now in fine particulate form where it is often more easily heated and ignited. If a lot of dust were produced, the worst case would be that an ignition could lead to an explosion of the dust.

The second problem is that the dust generated is an inhalation hazard and the operators need to be protected [9,10]. Vacuum cleaners may be used to reduce the dust levels but they need to be explosion proofed because of the fine particulate nature of the material. Depending on the level and toxicity of the materials being cleaned, the operators need to use either dust masks or respirators.

The other common problem when cleaning surfaces relates to the use of solvents in confined spaces. To wipe over and clean surfaces, such as the deposition drum and rollers, will produce a large quantity of vapor that may become an asphyxiation hazard or explosion hazard. The type of solvent allowed and requirements for personal protective equipment depend on the country and local regulations.

30.11 Ergonomic and Miscellaneous

The ergonomic hazards are where the nature of the process or design of the machine has created a hazard. An example of this would be a lifting hazard where the process or product requirements have been tending to larger machines, and to service the machines, heavier items have to be lifted and moved that can bring an increased risk. Earlier generations of the same type of system might have smaller and lighter items, but as the systems get larger and heavier the same jobs of routine maintenance that could be done without lifting aids now ought to have the lifting aids included as standard. Another problem, particularly on special machines, is one of access. To get a compact vacuum system, in order to minimize the pumping requirements, can mean that the access to components that need regular or routine maintenance is poor. This can put the operator at risk of injury because of poor body position and/or an increased chance of bumping his head. These are simple issues that need some thought during the design phase.

Very large vacuum systems have the additional problem that it is possible for a person to work inside the vacuum system to repair or clean components. This gives the possibility of closing and evacuating the vessel with the person trapped inside. In one system where this happened, hammers on chains were welded near to the vessel windows to allow an occupant to break the window in case of such an event. In other systems, I have seen emergency stop cords fitted. Elsewhere, lockout or tagout procedures are adopted.

Large machines have the problem that many people may be working on the machine at the same time. It is hard to know where everyone is all the time and so audible and visual alarms are often used with major events such as opening and closing the vessel.

Hazop (hazardous operation) reviews are becoming more common even with smaller companies. This is where the system and process are reviewed with contributions from the design, manufacture, and operations and maintenance teams. The aim is to confirm that the process is safe and that the design of the system is safe and also that it can be operated and maintained safely. Where hazards are present and cannot be designed out, a safe operating procedure must be written out. This process takes place in five or six stages, with the first review being done before the design phase is completed. The final review takes place after 12 months of production has been completed. This acts as a check that nothing has been missed in transferring the process from the development phase to production and that any procedures that had been implemented, which had been envisioned during the earlier reviews, were still considered appropriate.

References

[1] Beavis LC, et al. Vacuum hazards manual. 2nd ed. American Vacuum Society, New York, NY 10017 monograph series M:1. ISBN 0 88318 261 0.

[2] Poley N. Safety considerations in vacuum deposition systems. In: Proc. 24th annual technical conference of the Society of Vacuum Coaters; 1981. p. 25−9.

[3] Merrifield R. Safe handling requirements during explosive, propellant and pyrotechnic manufacture. Health and safety executive. Specialist inspector reports, No. 31; November 1991.

[4] Hammond ML. Safety in chemical vapor deposition. Solid State Technol 1980;23 (12):104−9.

[5] Duval P. Problems in pumping aggressive, poisonous and explosive gases. Vacuum 1988;38:651−8.

[6] Handling fumes from integrated circuit manufacture. European semiconductor design and production; March/April 1987, p. 42−4.

[7] O'Hanlon JF, Fraser DB. American Vacuum Society recommended practices for pumping hazardous gases. J Vac Sci Technol A, 6, 3, 1226−54.

[8] Weikel TD, Yuen NN. Vacuum pump explosion study. US Navy report AD763370 NAEC-GSED-60; August 1972.

[9] EH40/98 Occupational exposure limits. Health and Safety Executive; 1998. ISBN 0 7176 1474 3. HSE Books, Sudbury, UK.

[10] Barlow WJ. Aluminium and dust management in a metalizing facility—safety and regulatory concerns. In: Proc. AIMCAL fall conference and 23rd international conference on vacuum web coating; 2009.

31 Troubleshooting

The basics of troubleshooting are the same whether it be troubleshooting poor vacuum, the process, or coating adhesion.

In troubleshooting, one of the real dangers lies in trying to solve the wrong problem. This is why it is essential to ask questions and trust as little as possible without verification. It is all too easy to leap to easy conclusions. An example of this that I have seen happen is as follows.

A poor base pressure was immediately thought to be caused by a leak. On the previous cycle, everything was OK and as per many previous cycles. The immediate reaction was to assume a leak and to attach a leak detector. Many hours were spent searching the system for leaks. With large or complex systems, the number of joints could be huge, and this could have taken more than a few hours, in some cases many days. Over the hours, no leaks were found. The problem of the poor base pressure was not due to a leak but was eventually found to be due to the diffusion pump oil level being too low and the pump performance falling off rapidly.

The experience of this type of problem suggests to produce a simple list of actions that can be used to troubleshoot most problems:

1. Confirm the problem is real.
2. Question everything—trust nothing—do not jump to conclusions—wait for information—do not assume anything.
3. Use all the senses.
4. Review history—compare with the normal operation cycles.
   Ask the question—"What has changed since the last successful cycle?"
5. Be systematic (checklists can help).
6. Review the process and include learning for future use.

31.1 Troubleshooting Vacuum

Take, for instance, a vacuum system in which there is no vacuum. There are two possibilities: the first is that there is no vacuum and the second is that there is some vacuum, but the information telling you there is no vacuum is wrong or missing.

Let us look at this situation in the context of a typical problem.

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00031-3

Presented with a system that appears to have no vacuum, the first step is to confirm that the information is correct. Ideally, any system should have sufficient gauges to be able to confirm what any one gauge reads. This does not necessarily mean a duplication of gauges. When roughing the vessel, there would be a gauge on the main chamber, but there should also be another gauge on the roughing line. The gauge on the roughing line also provides a measurement of the backing pressure during the time the vessel is being pumped by the diffusion pump. Using the second gauge, it is possible to compare the pressure being read by the gauge when the system is being pumped normally and on the occasion when no vacuum is indicated. If the readings of the roughing line gauge are similar, the indication is that the main vessel gauge is faulty. If the reading on the roughing line gauge is very high, it supports the main vessel gauge and suggests that there is either no or little vacuum in the vessel.

This leads to the next "tool" in troubleshooting, which is to use all of your senses to aid the diagnosis.

Let us continue with the "no vacuum" problem. Having used the second gauge to confirm the lack of vacuum, the next step is to look for the reason. Simplistically either the system is being pumped but has an enormous leak or the system is not being pumped. So the next step is to check on the pumps. The troubleshooters can use their own senses to answer several questions.

Listen to the sounds of the system. Are the pumps working or silent; if the pump is working, is the sound normal? If the sound and the backing pressure are normal, it may be that a valve has failed to open. If the pump sound is louder than normal, it is likely to be working harder, and a high backing pressure will be indicated. If this is the case, it is more likely that the system is being pumped, but there is a large leak. If the backing pumps have a belt drive, then when a load is applied if there is a screech from the belts this would indicate a slipping belt drive. Also listen to the main chamber door opening; it may be that there is a whistling sound indicating that there is a large air leak into the chamber. Often, such noises are only audible close to the system and are unheard at the control desk where the noise of the pumps and other equipment can mask the sound.

Smell the area near the pumps. If there are belt-driven pumps and a smell of burning rubber, it could be that the drive belts are slipping. Other smells that might indicate problems are from overheated paint (from the painted outer casing of equipment) or overheated oils.

Looking at the system can also provide clues. If the belt drive is slipping, it may have generated debris from the slipping belt, which may be visible after a more detailed inspection. Also look at the oil levels and the oil color. Falling levels will cause a drop off in pumping performance. A change in the color of the roughing pump oil from a transparent straw or light brown color to an opaque yellow milky appearance is an indication of an oil/water emulsion having formed. This may be an indication of a water leak, a very large air leak, or a long-term lower level water load problem.

If we assume that, from the information gleaned from the above checks, it has been possible to identify that the system is at the point of pulling some vacuum we can move to trying to pump the system down. However, if we also find that not all the problems have been eliminated and the indication is that the system is still not performing as expected, then we have to continue the checks.

Most modern systems include a data-logging package and also a diagnostic package as part of the control system [1]. These can provide a useful and convenient method of comparing different process cycles. Commonly, they will show the operational state of pumps, valves, and motors in a schematic diagram, with the data logger recording the precise details of voltages, currents, powers, and any measurement outputs.

This leads to the question that can be asked, “What has changed or is different from the previous cycles?” An example would be if the source has been changed, that is, a sputtering target change or a new set of resistance-heated boats. Another example would be if there were other equipment changes, that is, a new set of deposition shields fitted, etc.

If data-logging systems are not available, there are some simple things that can be done to help diagnose problems when they occur. Timing the process to various critical points is quite easy to do and can be very illuminating.

The aim is still the same, that is, to match what is happening in the problematic pumpdown with data from a “normal” cycle. This means recording, saving, and plotting data manually so that it can be used for comparison.

A common method of determining the health of the pumping system is to calculate the time the system takes to reach particular pressure points. Typically, there will be some variation from cycle to cycle. However, a sudden worsening (slowing) of the times to reach the desired pressure points indicates a problem. This may be due to a leak, a faulty valve, or a problem with the pumps and needs other questions answered as outlined earlier. A progressive worsening of the times is often an indication of a buildup of stray coating onto the shields and other vessel furniture that massively increases the surface area, allowing for a greater absorption of moisture each time the vessel is brought to atmospheric pressure.

As can be seen from the preceding text, the process is not difficult but does need to be systematic and thorough [2]. If you are troubleshooting a process that you do not usually operate, it is well worth involving the operator in the process. Typically, many of the operators will automatically be listening and watching the system and will be the ones to first spot a problem in operation. Thus, questioning the operators in detail ought to be one of the early parts of the questioning process.

A final thing to do is to record the troubleshooting process so that it can be used to learn from and to help refine the process for possible future use and for training purposes.

31.2 Troubleshooting Process

Troubleshooting a process appears to be more difficult than troubleshooting a lack of vacuum. Typically, there will be more things that can go wrong and affect the process. The approach, however, stays the same. First, verify the given information and define the problem. Then, systematically go through the process and question what has changed between a good process cycle and the problem process cycle.

Included in this would be the use of the senses as in "Does the system sound, look, or smell the same?"

It is well worth bearing in mind that the changes may not be just within the vacuum system. There may be external changes such as a change in substrate or source supplier, a change in the weather or season, or a change in the operators of the system.

An example of this would be when there was an increase in the number of pinholes in the metallized film. This was eventually traced back to the polymer web supplier who, in turn, traced it back to a particular batch of material run during the time in the season when the pollen count was high. The warmer weather meant that the film line operators opened the factory doors to let through a cool breeze to make the process hall more tolerable. Carried on the breeze was a high level of pollen. All polymer webs attract dust, debris, and pollen out of the air because of electrostatic charging. The result was a higher level of contamination that was eventually seen as the increase in pinholes by the metallizer.

This example demonstrates the benefit of looking at the process as a whole and not just thinking about the vacuum deposition process in isolation.

31.3 Troubleshooting Winding Problems

There are some common problems that are seen in winding films in vacuum [3]. The first is when the unwind roll telescopes during the pumpdown sequence. This occurs invariably as a result of the roll being wound too soft. Too much air will be trapped between the layers of film such that when it is pumped out in the vacuum system, the roll is very loose and the layers will slip sideways.

Sometimes, the rolls have been deliberately wound soft to hide other film manufacturing problems such as a poor thickness profile.

If there is a poor thickness profile, this will be highlighted and may cause rewind problems with a very hard band at the thick area of the film width that can, in some cases, be permanently deformed because it is taking all the tension.

If, under gentle or low tension, flutes or wavy edges appear, it is an indication that the film is not of uniform length, and therefore it will wind with uneven tension across the width [4]. In most instances, this may not be a problem. However, if the deposition process is running on the limit of the acceptable thermal load, this tension variation will be a likely source of any wrinkling appearing in the deposition zone.

Wrinkling of the film in the deposition zone is the other most common problem. The cause of this is the film being heated by the deposition process and wanting to expand but being constrained by the friction between the film and the deposition drum. This puts the film in compression, and when this reaches a critical point, the film will buckle off the drum and a wrinkle start.

Where a process has previously been running well and then suddenly, with a different roll of material running through, wrinkles appear, it may be due to a number of causes. It is worth checking whether there has been a change in the supplier of the material. Different manufacturers of so-called standard grade rolls will have different proprietary treatments or coatings that may have changed the surface energy and number of contact points between the film and the deposition drum, thus changing the slip coefficient. The different suppliers may also produce film with different levels of residual moisture content within the film, thus changing the heat transfer coefficient. Either of these two factors could make a difference to the onset of wrinkling. Another factor that could change the onset point of wrinkling is the drum-cooling performance. If the drum is cooled by the factory cold water supply, it may be that the incoming water temperature is higher than usual and so the cooling capacity has been reduced, and therefore the temperature of the film web has been increased. Similarly, even if a chiller unit cools the deposition drum, it may be that the chiller is not bringing the recycled coolant back to a common low temperature, but the temperature is gradually increasing with the same result of allowing the film web temperature to increase. The increase in film web temperature will result in the film wanting to expand more than previously, and hence the compressive stress is increased and the tendency to buckle and start a wrinkle is increased.

Tension variations can be caused by a variety of different problem roll types. A roll wound up with too much tension can have some random slip that will be seen as a sudden relaxation of tension, followed by the tension snapping back on. If the tension is oscillating, this would suggest a regular mechanical problem such as either the unwind or rewind roll being eccentric. Where the tension is changing, a shear stress can be produced that can result in a lateral movement.

When bow rolls are used and these are incorrectly set, the tension will be uneven across the web and this may be seen as bagginess of the web. Similarly, bagginess can be caused by the deflection of the rolls by running with very high tensions.

Occasionally, if there are larger differences in tension in different parts of the winding path, there may be creases generated just after the web relaxes when the tension is eased around a capstan roll after a high-tension region.

If a problem recurs, it may be worth winding the web through the system at atmospheric pressure and looking for the location in the process where the problems are occurring. It is always worth checking the web material to confirm the profile is good and free from thick spots.

As with any other problem, it is worth systematically checking through the winding path looking for where possible variations might occur. In most aluminum metallizers, it is common to use a spreader roll immediately before the deposition drum to give the web some transverse tension, and then as the web contacts the deposition drum the temperature changes. Soon after the web has contacted the cooled deposition drum, it will then enter the deposition zone where the front surface is hit by a large amount of heat. This all works while the spreading, cooling, and heat load are uniform across the web, but the reality is often different. Most webs being coated around a deposition drum will have an edge shield to protect the drum from becoming coated, which means the web actually has cooled edges, which will make the edges shorter and so take more tension than the rest of the web that is heated. A similar problem can occur for webs that have to be heated to achieve high-temperature deposition. In these cases, the webs need to be heated, and it becomes important that the heating is uniform across the whole width. Also if the web is being heated between rolls, the thermal expansion of the web needs to be accommodated such as by using a spreader roll following any heating. The web will still be under tension and so there will be a transverse compressive force and that, coupled with the thermal expansion, will lead to wrinkling unless the web is spread enough. Again, if the hot substrate is shielded in any way during the deposition zone, either around a deposition drum or free span, the differential heat load will potentially cause winding problems unless suitably balanced and managed. This may all work well while the incoming web is reasonably well balanced along the machine direction centerline, but if the web is imbalanced because of a gauge band, poorly slit edge, or asymmetric residual stress, this will be highlighted during heating or cooling and the deposition zone where wrinkles can be created.

If the winding problems are on every roll, it is worth suspecting the alignment of the winding system. Normally, once the system is built and aligned, there is little that goes wrong to cause the appearance of winding problems. If a roller has been changed or if a bearing has dried out and started to wear, then this can mean that the alignment of that roll has been affected. If the system has a cooled or heated deposition drum, this can also be a source of change. I have known an unforeseen set of circumstances where the result was damage to a cooled deposition drum. A series of decisions culminated in the liquid inside the drum freezing and expanding forcing the end wall of the drum to buckle. Where there are deliberate temperature changes, it is often also possible that there may be an operator error or system failure and an unscheduled or larger-than-expected temperature change. Any temperature change may or may not result in a distortion that may affect the winding alignment. Other than these unforeseen or maintenance-related changes, the winding quality will be defined by the basic winding design principles that have been applied [5—7]. If there is any doubt about the alignment of the winding system, then it needs to be checked out and ideally as precisely as possible. It is possible to use a gyroscopic based system [8,9] to check every roll not only for the quality of the individual roll in terms of being cylindrical and concentric but also with respect to every other roll in the winding system.

31.3.1 Electrostatic Charge

This aspect of winding has often been forgotten as the winding system is hidden within the vacuum chamber, and so operators do not tend to see any sparking or receive as many shocks.

Any two dissimilar materials when brought into contact will try to bring the mating surfaces into equilibrium [10—13]. This is done using the movement of electrons that adjust to make one surface positively charged and the other one negatively charged. When the materials are separated, the two surfaces will retain the charge.

If the material is conducting and connected to earth, it will allow a current to flow and the charge to be neutralized. With a good dielectric material, this mechanism is not possible and so the charge can be carried on the surface.

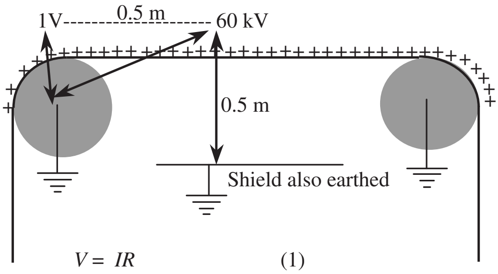
If the polymer is wound over a metal roll, the system acts as a capacitor with the charge on the surface and with the associated surface potential increasing as it moves away from the conducting roll. Thus, the measured surface charge will be a maximum midway between rolls.

In this way, a surface charge of 1 $\mu C/m^2$ would have a surface potential of 1 V around the roll, whereas by the time it is 0.5 m away from the roll, it would be 60 kV as shown schematically in Fig. 31.1.

One effect of an electrical charge on a surface is that it can work as an electrophoretic collector [14]. This can be used as a method of reducing the effects of dust generated inside the vacuum chamber by using strategically placed electrophoretic collectors. Unfortunately, the polymer web, because it gets charged, as described earlier, also acts as a collector. As most metallizers do not include any electrophoretic collectors, there is no competition for any debris and so it is likely that contamination of the web is possible.

One possible countermeasure that is included on many metallizers, although few would think of it as such, is plasma cleaning. The plasma will help to neutralize any surface charge, or to be more accurate to limit the charge as the web passes through the conducting plasma. Although we think of the plasma cleaning being in a discrete zone, this is simply because this is where the high-intensity light emission part of the plasma is visible. In reality, the plasma extends elsewhere throughout the whole vessel and so will help reduce the charge throughout the winding system.

Another concern in metallizing webs that have charged up is the cumulative effect that the alternating layers of metal and polymer can make on the rewound roll. The capacitance of the roll will not change much as more metallized web is



As the distance increases from the roll and/or from other earthed surfaces, the potential increases as per equations (2) and (3).

$$V = IR \qquad (1)$$

$$Q = CV \qquad (2)$$

$$C = EE_oA/d \qquad (3)$$

V = Voltage
I = Current
R = Surface resistance
Q = Charge on the capacitor
C = Capacitance between web and earth
E = Relative permittivity
E_o = Permittivity of free space
A = Area
d = Separation of surfaces

Figure 31.1 Triboelectric charging of polymer web over metal rolls.

added but more and more charge will be added. This can run to several hundred kilovolts. This can reach levels where, if an operator approaches the roll, they can act as a conductor to earth. In this case, a spark will be generated if the distance between the operator and the roll is small enough. These are not generally harmful by themselves, but the reaction they produce, as the operator involuntary reaction is to rapidly pull away, can cause injury.

A simple precaution is to have an earthing wand available to discharge the web.

Other problems that are associated with the charging of the web are when the electric charge becomes buried within the polymer. This electric charge results from high-energy electrons being embedded in and below the surface of the bulk polymer. These are called electrets. This will only happen with deposition processes where high-energy electrons are produced such as magnetron sputtering or, more usually, electron beam deposition.

These electrets produce a positive charge on the surface to offset the interior negative charge of the electrets. This surface charge can help to stick the next layer of the web onto the surface by electrostatic pinning. In the extreme, these charges can cause a roll of film to “block” and become unwindable. Most electron beam systems are now built with electron traps to catch any stray secondary electrons that might cause this type of problem.

On some occasions, a charge is deliberately added to the web as a method of holding it hard to a surface such as just before a cooled roll or deposition drum [15,16]; this process is known as electrostatic pinning. Care may be needed in choosing the correct charge level. If the web is already charged, it may need little or no extra charge adding; however, if the web has a plasma cleaning station nearby, the added charge may be neutralized to some extent and be less effective than expected.

31.4 Troubleshooting Adhesion

The first thing to check is that the assumed plane of failure is the correct plane of failure. It is all too common to assume that the interface is the problem, whereas it may easily be a problem of cohesive failure due to skin effects in the polymer bulk.

Ideally using one of the surface analytical techniques to determine the true nature of the materials on each surface at the plane of failure will confirm the failure as being either cohesive or adhesive [17].

It is also worth remembering that most polymer surfaces are pretreated, and so although they are nominally called PET or OPP, they may chemically be entirely different.

If it is not possible to carry out any surface analysis, a simpler alternative is to test the surface energy of the material at the plane of failure. If both surfaces have the same surface energy, it may indicate that they are made up of the same material and thus the failure is cohesive. If the surface energies are different, it is more indicative of adhesive failure.

If it is adhesive failure, then raising the surface energy of the substrate is widely used to increase the adhesion.

If failure is patchy, then it may be that there is some form of surface contamination. It is worth looking for patterns in case there is a contaminant such as oil that is being transferred via rollers. If the contaminant is being transferred via the rollers, it will be seen that the spots of poor adhesion will be regularly spaced and can be related back to the roller circumference.

As with all processes, the quality of supply of material is a key factor. Changing supplier even for a nominally equivalent grade of substrate polymer may give rise to differences in the end product. This may be because of the differences in pretreatments or polymer chemistry recipes between manufacturers. Even with a common source of polymer substrate, downstream converters will differ in the quality of hygiene and handling and may result in differences in levels of pinholes and contamination.

If many different suppliers are used, then implementing quality control of the incoming material is often cheaper than producing a variable inferior product and having to quality check the outgoing material.

Sometimes the adhesion problem only shows at a later stage in manufacturing such as by delamination of the final structure and sometimes this might be delayed and only appear after a few weeks or months after manufacture. In some cases, this delamination can result from small defects or poor adhesion at the interface where air or moisture can reside. This air or moisture will change volume with temperature, and there will be a force acting to spread apart the two surfaces. As the coated material is not a perfect barrier, more air or moisture can diffuse through to fill any increase in volume and again a change in temperature will further force the surfaces apart. This thermal cycling will progressively expand a tiny defect into a large area delamination. This will occur only where there is insufficient adhesion in the first instance. The rate of the original defect growing into a delamination problem will depend on the adhesion as well as on the rate and magnitude of thermal cycling.

In some other cases of delamination, the solvent contained in the adhesive can react with some other component in the substrate and a gas such as hydrogen may be evolved, and this too can force surfaces apart and provide the driving force for delamination.

In these cases, the troubleshooting of the cause of the delamination requires questions to be asked more widely because it requires a knowledge not only of the substrate and vacuum deposition process but also of the chemicals and processes downstream of the vacuum coating process. It also requires a knowledge of the temperature and humidity of the material in storage and in final use to be able to evaluate whether there has been a possible detrimental thermal cycling of the material.

31.5 Troubleshooting—Loss of Barrier

This is another problem that can appear immediately after vacuum deposition or may appear somewhere downstream. As the barrier performance is defect dominated, it all starts with the quality and cleanliness of the substrate but can also be affected by any pretreatment and how the vacuum-coated material is handled in any or all downstream processes. The material may also be affected by how long it is stored before being used downstream following vacuum deposition.

Here, the starting point is to determine what might have been changed between the good and bad product to determine the most likely cause of an increase in the amount of defects. If the barrier material is opaque, then a simple check of putting good and bad materials onto a light box and comparing the amount of pinholes between materials is a good start. As has been explained earlier, pinholes are the most common source of loss of barrier. A difference in the number of pinholes can be caused by a difference in debris levels on the substrates, but there are other possible causes also. A substrate with a constant amount of debris contamination may show different levels of pinholes because of a different amount of contact and movement following vacuum coating. A difference in rewinding tension may make one roll slip more than another and the one with the greatest amount of slip would be expected to have more pinholes than the one with less slip. A higher tension may also increase the amount of pickoff, which also is a source of pinholes and would add to the number of pinholes created by the coating and movement of debris. Similarly, for two rolls of the same substrate, there can be a difference in the contamination level if one roll is handled immediately after vacuum metallizing and the other is stored for a day. It could be expected that the one used immediately could have a higher level of pinholes than the one stored for a day. As aluminum can take a little time to build up a sufficient amount of protective oxide, the one that is used immediately can be more prone to debris causing more damage than the one that has the thicker protective oxide surface layer. So although it is easy to check on pinhole levels, it may not be as easy to determine why rolls differ in performance without having information from the whole manufacturing process. Downstream of the vacuum deposition process the web might be handled several times, and as stretching the web can cause cracking of the coating, this too can be a source of loss of barrier. This is often expected as in the calculations of barrier performance requirements some companies will include a barrier fallback factor in their calculations to allow for handling causing defects and a reduction in barrier performance. A change in the amount of coating cracking can be a reflection of a change in adhesion performance with coatings with a lower adhesion cracking at lower strains than those with a higher adhesion.

31.6 Troubleshooting—Common Problems and Diagnostic Tools

Having established the basics of identifying the true nature of the problem, by questioning everything and comparing the problematic process with previous good process cycles, the next section gives a brief description of some of the more common problems that might be encountered.

A way of categorizing these common problems is to look at them in the context of each different source type along with the most common topic of adhesion or more precisely the loss of adhesion.

As there is a limit to troubleshooting process problems with only the standard process instrumentation, there will also be some comment on the use of residual gas analyzers (RGAs) and optical emission spectrometers (OEMs).

31.7 Thermal Evaporation by Resistance-Heated Boats

The common problems are coating uniformity, short boat lifetimes, and spitting and/or pinholes.

31.7.1 Uniformity

As the spacing of the boats is fixed, there will be a basic deposition profile [18–21] and any other variations in uniformity are usually related to inconsistencies in the boat temperature, puddle size and shape, or the wire feed. The temperature can be different from boat to boat. If all boats are running at the same power setting, the uniformity will be expected to vary, as all boats will have a unique resistivity and will need to be powered to a different level to give the same deposition rate. The precise power to each boat, and hence deposition rate, is usually fine tuned using a series of deposition monitors. These monitors are arranged in lanes, either one in line with each boat or one between each pair of boats.

The boat temperature can also vary if the clamping of the boat is not even, as shown in Fig. 31.2. If the clamps are worn, damaged, or corroded or if the boat has been overclamped and damaged causing crumbling of the ceramic, there will be

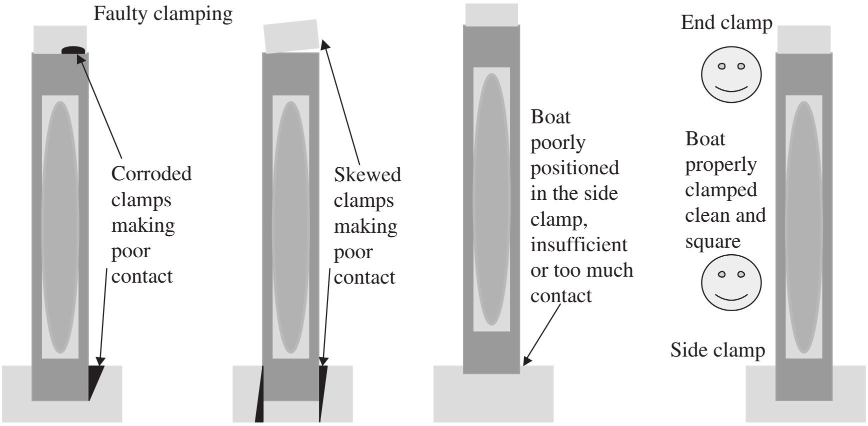


Figure 31.2 Some common mechanical faults that can affect the boat temperature and hence the pool formation and deposition profile.

areas of different resistance causing local differences in the boat temperature. These differences in temperature will cause differences in the puddle shape and deposition rate and profile that can lead to coating nonuniformity.

Also, if the wire feed is not positioned correctly but is offset, as shown later in the text (Fig. 31.3), the puddle shape can again be affected causing the deposition profile to be skewed that, in turn, can lead to coating nonuniformity. Similarly, if the wire feed is not at a uniform rate, the size of the puddle will vary and the deposition will vary accordingly. This can be differentiated from other nonuniformity problems because it is a down-the-web nonuniformity rather than an across-the-web nonuniformity that the other problems tend to produce.

Short boat lifetimes can also result from the clamping problems as shown earlier (Fig. 31.2). They can also be due to poor conditioning. Most boat suppliers have a recommended procedure for the first use of the boats that limits the rate of temperature rise and then soaks the boat at a high temperature for a time before the wire is first fed into the boat. If the heating is too fast, the thermal changes can cause localized cracking in the ceramic, producing resistance variations.

Short boat lifetime may also be related to the boat supplier. The different suppliers use different powder qualities in purity, size, and material composition. Hence, boats from different manufacturers may have the same starting resistivity but may perform differently and last for different lifetimes. The very cheap sources of boats may well have a larger ceramic grain size that will have a different wetting, hardness, and erosion performance. Typically, these may only have half the lifetime of the finer-grained denser ceramics used in the higher-cost boats.

Another factor that can reduce the lifetime is whether the boats are driven harder than normal so that they have to be run hotter with a higher wire feed rate.

Spitting, spatter, and the resulting pinholes tend to be related to changes in the puddle size, and hence any of the above reasons for variations in puddle size, such as wire feed variations or resistivity variations, may cause not only nonuniformity but also sudden bursts of spitting. The spitting may be seen directly if someone is

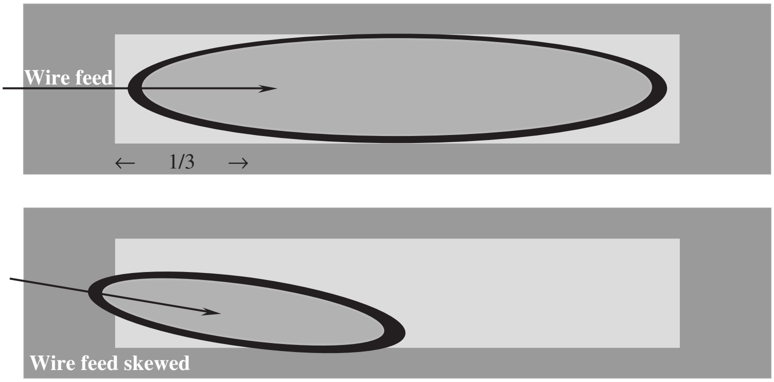


Figure 31.3 A schematic showing how a crooked wire feed can affect the pool position, shape, and size and hence the coating uniformity.

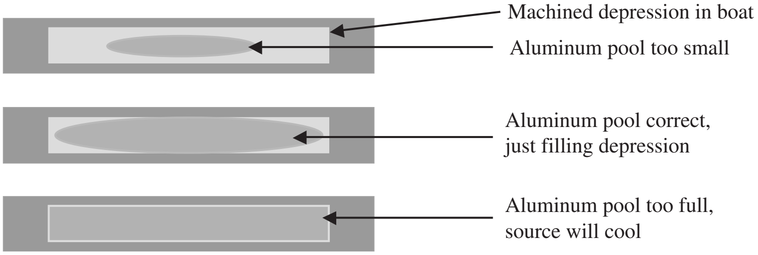


Figure 31.4 A schematic showing the optimum pool position and size to give the best uniform deposition.

looking at the boats at the time it occurs. Much of the material as it spits will be hot enough to be incandescent and to be visible. If not observed during the process, the coated product will have sudden increases in the number of pinholes seen in transmission. The source of these spits is the collection of the oxide slag at the edges of the puddle. When the puddle size is constant, the wire as it enters the puddle and melts will uniformly disperse the oxide from the outer surface of the wire across the surface of the puddle where some will be evaporated and the rest will migrate to the edges and collect there. If the puddle size increases, the oxide-rich edge will be pushed onto a fresh hotter surface that will tend to send a shower of oxide up. As the puddle contracts, there will be fewer spits, and so if the puddle size oscillates with some regularity, there will be these pulses of pinholes seen at regular intervals down the web.

The aim is to fill the boat with the molten aluminum puddle and then to maintain the size of the puddle as shown in the middle schematic in Fig. 31.4.

31.8 Electron Beam Deposition

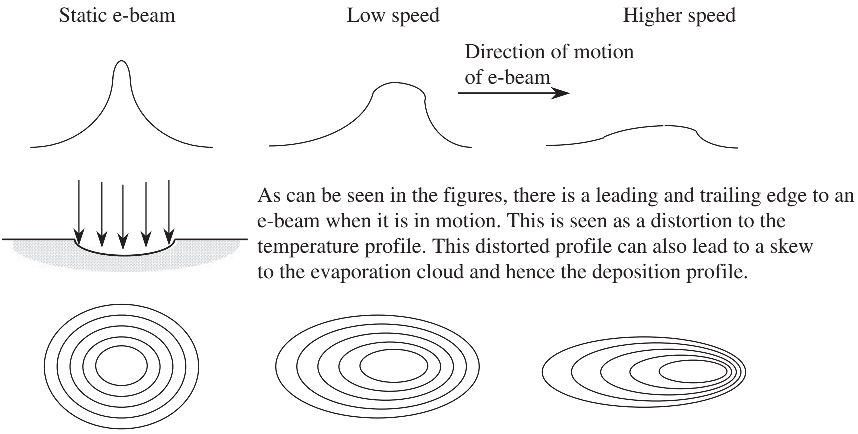
The common problems associated with electron beam deposition are short filament lifetime, deposition nonuniformity, and spatter.

Many electron beam guns use a resistance-heated wire filament as the source of electrons. This filament is very similar to an electric light bulb filament and has the same basic problems. The filament has to be run very hot and this leads, over a prolonged time, to grain growth that eventually will lead to a high-resistance grain boundary causing overheating and failure. At the grain boundaries, there is oxidation of the metal and this oxidation increases the local resistivity and can act as a hot spot. Hence, the filaments are sensitive to oxygen. Thus, if the filaments start to have a short lifetime, it is worth looking for a worsening of the vacuum level during the process or a source of an increase in oxygen content. The other reason for a short lifetime is in the handling of the filament and the initial thermal cycling. If the filament is fitted under stress and/or the first thermal cycle is too rapid, the thermal distortion can lead to an accelerated grain growth and localized hot spot giving premature failure.

The electron beam can be controlled to give different beam diameters and hence a range of different heating intensities. The beam may also be moved around the crucible, which also changes the heating pattern. When the electron beam moves, the intensity profile does not remain constant and concentric but can become skewed. This is shown schematically in Fig. 31.5.

The uniformity of heating of the source material depends on the material's thermal conductivity, the rate of beam movement, and the beam intensity and focus. Locally, the point where the electron beam hits the source material will have the highest deposition rate, just for that moment. The beam is moved quickly over as large an amount of the source surface as possible. This is done in order to keep the average temperature as uniform as possible and hence the deposition rate as uniform as possible. In wide web coaters, that use the large electron beam guns sweeping a crucible as wide as 1 m, there can sometimes be patterns that are seen on the coated web that relate back to the scanning pattern of the electron beam. In smaller coaters that use multiple small electron beam guns, the uniformity variations may be more associated with differences between adjacent guns and this needs to be corrected with reference to the deposition monitors in the same way as for the resistance-heated boat process.

There are some materials that can also make nonuniformity more likely. An example would be the materials that sublime, that is, the materials evaporate from the solid without converting to a liquid first. These materials are often irregular in shape and hence the surface area may well vary hugely as too will the impact angle of the electrons as they arrive at the uneven surface. Thus, maintaining a constant sublimation rate from each crucible can be difficult. It is common to use an



As can be seen in the figures, there is a leading and trailing edge to an e-beam when it is in motion. This is seen as a distortion to the temperature profile. This distorted profile can also lead to a skew to the evaporation cloud and hence the deposition profile.

Temperature distribution profile and distortion due to speed of motion of beam

Figure 31.5 A schematic showing how movement and speed of movement can affect the electron beam shape and temperature profile.

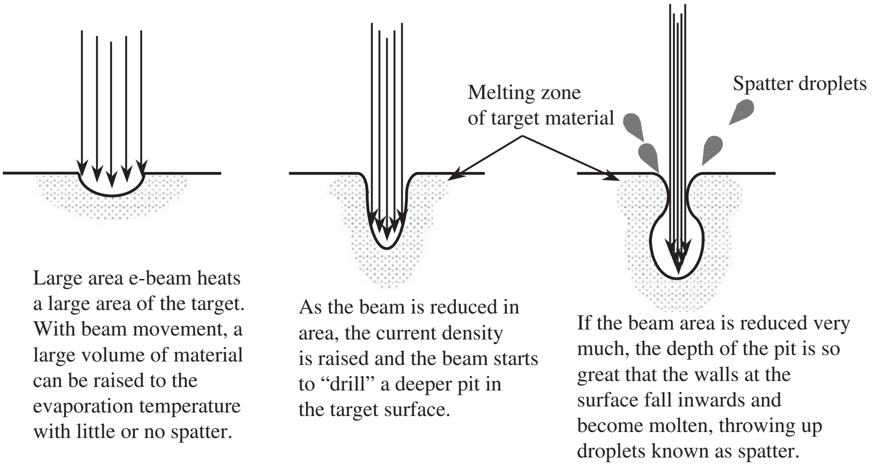


Figure 31.6 A schematic showing how an electron beam can be the source of molten droplets that can cause coating defects.

expanded diffuse beam to average out the heating over as much of the available surface as possible to minimize these temperature differences.

Spatter is another problem that relates to the electron beam shape and intensity. If the beam is too narrow and intense, it will melt and penetrate the material surface more than if it is a broad and lower-intensity beam. If the beam penetrates too far into the material, the surrounding material at the surface, that has been melted, will fall in on the beam and the energy will be sufficient to evaporate collections of molecules rather than individual molecules. If these collections are large enough, they will be seen as droplets or spatter. This is shown schematically in Fig. 31.6.

There is a tendency for this to happen more during initial heating of the evaporant and it will only occur with materials that melt.

Materials that sublime can also be seen to spit. The cause of this tends to be the heating of trapped gas within the material that creates enough internal stress to explode and throw out material. This can occur from any material if it contains trapped gas and so the first heating of any material is usually more sensitive than subsequent heating cycles.

In general, when spitting problems occur, corrective actions such as broadening the beam, moving it more rapidly to even out the heating, and possibly reducing the intensity will all help to reduce the problem.

31.9 Magnetron Sputtering

This process probably has the most opportunity for problems that require troubleshooting, particularly where a reactive process is used. This is not necessarily because the process is any more complex but more because the products are technically more sophisticated with tighter tolerances that tend to highlight any process variations.

31.9.1 Magnetron Plasma Does Not Light Up

This may be simply because the electrical connection has not been made, or because there is an electrical short. The electrical short may be due to some stray deposition material that has built up to a sufficient thickness where it is able to flake off the shield. These flakes may then be able to make an electrical connection between the shield and the magnetron cathode.

It may also happen following cleaning when some of the material cleaned off has fallen down between the close-fitting earth shield and the cathode. The electrical connection may be poor and this may not show up even if the resistance between the cathode and earth is checked before the system is pumped. Often, it may be that the disturbance caused by pumping the system down will dislodge some material that makes the short between the magnetron and earth.

Another cause of the plasma failing to light is that the magnetron has been stripped down for cleaning and the magnets have been assembled wrongly so that the magnetic circuit is incomplete. I have seen this happen a number of times. With some magnetron designs, the magnets are not held in place well and can flip over while being assembled, and it is sometimes hard to be sure that they have remained in the correct orientation throughout reassembly. It is possible to buy a sheet of material that has little ferrites encapsulated that can be used to check the magnetic field. This is usually a sheet of green polymer where the change in direction in the magnetic field gives rise to a color contrast, with the polymer appearing either black or green depending on the field direction. Hence by laying the sheet over the magnetron, it is possible to check the continuity of the field. Any magnet that is in the wrong orientation will immediately be seen by the change in color contrast.

This is a very simple visual technique. The same thing can also be checked by the use of a Hall probe connected to digital voltmeter. The Hall probe would be moved around the edge of the racetrack recording the field strength and polarity.

31.9.2 Falling Deposition Rate or Large Voltage Drift During Deposition Cycle

Often, much attention is paid to the control of mass flow of gases, the system pressure, and the power to the magnetron sputtering source. However, one parameter that often gets overlooked is the water cooling to the magnetron-sputtering source. The flow, pressure, or inlet temperature may vary and the performance of the source may vary because of this. If the temperature of the magnetron rises, the magnetic field strength may be reduced. This reduces the effectiveness of the magnetic confinement of what is in effect an electron trap. This results in a loss of electrons and this, in turn, reduces the plasma density. The reduced plasma density will give rise to a raised voltage, reduced current, and reduced sputtering rate still at the same constant pressure and mass flow.

A more subtle change that may take place and cause a long-term drift of the plasma characteristics may be due to a disappearing anode. Many systems do not have a well-defined anode and those that do may lose it as the effective anode because of stray coating building up a dielectric on the surface. It is assumed that the vessel is at earth potential and that it is acting as the anode to the cathode. This may or may not be true. If there is no defined earth, the system will find its own earth and if this anode becomes insulated by a buildup of dielectric material, the effective anode will then move to the next most appropriate surface. This can change the shape and characteristics of the plasma.

In many cases, these changes are small compared with other changes and so are ignored. In large systems with cathodes several meters long and depositing a dielectric in a reactive process from a metal cathode, the changes can be critical to producing the correct stoichiometry coating. In these large systems, it is regarded as important enough to provide active anodes that are kept at red heat to prevent any stray deposition and ensure that the anode stays clean, active, and in the same position throughout the deposition process.

31.9.3 Arcing

There are two common sources of arcs. If the cathode is new, and arcing starts immediately after the magnetron is fired up, then the arcs may be caused by small amounts of physical damage to the surface or an oxide surface that has yet to be cleaned back to the metal. This arcing can be minimized by preparing the target surface before it is attached to the magnetron. If there is a heavy oxide buildup on the surface, machining the surface to clean it up or even filing or abrading the surface will quickly remove the oxide and get the magnetron started more easily. After the initial cleaning of the surface, or even if the target does not require cleaning, it is worth feeling the surface to check that there are no raised defects on the surface and that all the target edges are smooth. If the surface has been hit and there is a raised sharp edge, it must be polished back to smooth it out. Similarly, if the target edges are sharp, it is worth rounding them off.

Any point or sharp edge will act as a concentration point for the electric field and this concentration can cause a concentration of electrons in the plasma just above the surface. This draws the ions in the plasma to the same point, and the plasma density if locally increased allows more current to flow and further exaggerates the effect. This process continues to the point where an arc will form. The arc suppression circuits in the more modern power supplies will limit the arcing to all but the major arcs. Following the power supply shutting down due to a major arc if, on re-establishing the power to the magnetron, the arc immediately reforms, it may be as a consequence of one of these sharp projections remaining intact. Sometimes, the arc will remove the offending sharp point and normal sputtering can be resumed. Hence, it is well worth cleaning and smoothing any new target surface before use as a preventive measure.

Arcing that starts within the process cycle may occur as a result of the process. If the process is to reactively sputter a nonconducting oxide from a metal target, then this can, over a period of time, result in the target arcing. Around the edges of the racetrack on the target, there will be a region where the backscattered material will be deposited at a rate slightly higher than that at which the surface is being sputtered. The net result is that there will be a buildup of poorly adhered, nonconducting material. This material will charge up distorting the electric field and start arcs. On a few occasions, these arcs will clear the offending material, but most of the time it is an indication that the target is ready for a clean.

If this is a regular process, it might be worth looking at the option of replacing the single cathode with a dual cathode. This is where the two cathodes are linked, with one acting as the cathode and the other as the anode for each half cycle and then the polarity is reversed for the second half of each cycle. In this way, the anode is always kept clean and the sputtering target generally only gets a buildup of conducting material around the edges so that the start of arcing is delayed and greater productivity is achieved before the targets need cleaning.

Other sources of arcing are usually accompanied by other telltale signs such as the pressure has risen due to a pump problem or a system leak. Similarly, if there is some change in the balance of the process gases such that there is a sudden increase in the reactive gas, this can result in arcing. These cases will all have other information available such as a pressure rise or mass flow change before the arc was triggered. If the changes occur after the arc begins, they may only be a reflection of the arc having occurred. These changes may only be easily identified if suitable data logging has been taking place during the process, allowing suitable graphical outputs to be viewed to aid the troubleshooting process.

References

[1] Beccaria A, et al. Integral computer control of roll to roll coaters. In: Proc. 35th annual technical conference of the Society of Vacuum Coaters; 1992. p. 100–4.

[2] Vibert PD. Troubleshooting vacuum pumping systems. In: Proc. 43rd annual technical conference of the Society of Vacuum Coaters; 2000. p. 27–33.

[3] Taylor A. Practical solutions to web heating problems. In: Proc. 7th international conference on vacuum web coating; 1993. p. 107–19.

[4] Roisum D. Wrinkling of thin webs. In: Proc. 41st annual technical conference of the Society of Vacuum Coaters; 1998. p. 406–11.

[5] Hawkins WE. Vacuum coater thread path design using basic web handling principles and techniques. In: Proc. 42nd annual technical conference of the Society of Vacuum Coaters; 1999. p. 430–2.

[6] Montalvo WW III, Alf CG. Tension and web control in vacuum web coaters (metallizers). In: Proc. 6th international conference on vacuum web coating, Reno, Nevada; 1992. p. 35–44.

[7] Taylor KA, Pan CHT. Mechanics of web transport systems for vacuum metallization. In: Proc. 29th annual technical conference of the Society of Vacuum Coaters; 1986. p. 136–67.

[8] Sasikumar A. Measuring the roll parallelism in the laminating/coating industry using inertial alignment equipment. In: Proc. AIMCAL Fall technical conference and 21st international conference on vacuum web coating; 2007.

[9] Hegde D. A return on investment of a roller alignment survey. In: Proc. AIMCAL Fall technical conference and 22nd international conference on vacuum web coating; 2008.

[10] Clow H. Electrostatic charging of polymeric films in vacuum roll coaters. In: Proc. 3rd international conference on vacuum web coating; 1989. p. 97−107.

[11] The control of static charges on film. Information Note MX IN48. 4th ed. ICI Polyester Films; 1986.

[12] Davies DK. The generation and dissipation of static charge on dielectrics in a vacuum. In: Proc. static electrification conference; 1967. p. 29−36.

[13] Griffiths JA, Lander JR. Packaging and static electricity. Packaging 1988; February:29−36.

[14] Rappe G. The electrophoresis effect as a method to remove airborne and surface contaminants. In: Proc. 32nd annual technical conference of the Society of Vacuum Coaters; 1989. p. 19−23.

[15] Casey F, et al. Vacuum metallising using a gas cushion and an attractive force. UK patent GB 2326647; 1998.

[16] Tsai PP-Y, et al. Theory and techniques of electrostatic charging of melt-blown nonwoven webs. TAPPI Journal 1998;January:274−8.

[17] DiNardo NJ. The application of surface analysis techniques to adhesion at metal−polymer interfaces. In: Proc. 5th international conference on vacuum web coating; 1991. p. 35−58.

[18] Meinel J, et al. Dynamics and efficiency aspects in the evaporator zone of vacuum metallizers. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 191−6.

[19] Pasqui A, et al. High rate deposition on new high speed aluminium roll coaters. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 185−9.

[20] Baxter I. Advanced resistance deposition technology for productive roll coating. In: Proc. 36th annual technical conference of the Society of Vacuum Coaters; 1993. p. 197−204.

[21] Casey F, Broomfield A. Metallizing—shining through. Converting Today 1991; September:21−7.

This page intentionally left blank

32 Final Thoughts

Hopefully, this book has highlighted why it is necessary to look at the process holistically.

Taking a holistic view of the process helps during developing or troubleshooting the process. It is worth noting that over and above the holistic view is the more global view that looks wider than the upstream and downstream processing. This global view includes many more factors that can affect the business or investment decisions and can include technology and social and legal trends. Of these, the ones that tend to be of immediate interest are the technology developments and trends. In developing any new process or product, it is important to periodically review available technologies and do a SWOT (strengths, weaknesses, opportunities, threats) analysis to make sure the development remains relevant.

There should be no illusions—there can be as many threats to the business as there are opportunities.

Currently, there are developments in conducting polymers, printing technology, atmospheric processing, and, more recently, atmospheric atomic layer deposition that will be a threat to some vacuum web coating processes in years to come.

An example of taking a global view could be for the solar energy industry where the conversion of sunlight into electricity can be done by high-cost, high-efficiency or by low-cost, lower-efficiency solar cells. Currently, single-crystal or polycrystalline silicon devices are available, which are manufactured using semiconductor processing techniques or amorphous silicon, CdTe, CIS, or CIGS solar cells that are manufactured using roll-to-roll web processing. The roll-to-roll manufactured solar cells are cheaper to manufacture than the crystalline silicon devices but with a lower efficiency. These roll-to-roll based devices are expanding manufacturing rapidly. The threat to all these vacuum deposition based products is the printing of solar cells where all the processing is done at atmospheric pressure, enabling a further reduction of manufacturing costs.

Another industry that has a similar dynamic is the display industry. In the same way that web coating is currently challenging coatings-on-glass, the new developments of printed all-polymer electronics will challenge the vacuum web-coated products.

In both the display and photovoltaic industries, as they have progressed so too has the need for more effective ultrahigh barrier materials. Since the first edition of

Vacuum Deposition onto Webs, Films, and Foils. DOI: 10.1016/B978-1-4377-7867-0.00032-5

this book, these have moved from being in research and development laboratories to production, although this is still on a limited scale and the products are high cost. This makes the continued development to improve the barrier performance at lower cost the target for the next few years but with the incentive of many tens of millions of square meters of material required each year.

This changing market makes the speciality vacuum web coating industry quite different from the metallizing industry. As the markets come and go, it forces the vacuum web coating industry to remain dynamic and to always be prepared to change. This does not make systems cheap to build, and often the products are made on systems that are less than ideal. These systems have to be used because, for a developing business, a customized system would almost certainly be prohibitively expensive.

Where the solar industry was prepared to buy in some coatings from these toll coating companies for their early production runs, they want to buy an optimized dedicated system for full-scale production so that the throughput can be maximized and costs minimized.

Set against this large-scale manufacturing is the latest fashionable topic of nanotechnology. Some of these products can have the whole of the world's production carried out in a very short time on a small web coater that in previous times would have been regarded as a research machine. This can make the economics of building a dedicated system difficult, unless the added value of the final product is large enough to be able to underutilize a dedicated vacuum system.

Where I hope that this book has been useful is in encouraging everyone to research and develop products and processes in more detail to minimize any scale-up risks. My expectation of the way in which systems will have to develop, in order to cope with increasing integration of processes and demands for very high process efficiency, is in improvements in monitoring and control developed from an increasing amount of detailed process understanding. It is still disturbing to find that moving a process from one system to another, all too often, results in a different end product. Thus, it is necessary to redevelop the process on the new machine in order to produce a product identical to that produced on the first system.

To be able to manufacture systems that include any turnkey processes, it is necessary to have an improved, more fundamental, understanding of the processes and, where there are multiple processes, it is necessary to understand the process interactions. Some of this may occur by cherry-picking the best knowledge from other industries. It is common to restrict our search for solutions to our problems to only within the same industry. This blinkered approach can be very limiting and can mean that developments are repeated unnecessarily.

There are plenty of examples of other industries that wind materials faster or have more difficult or complex processes, that can provide us with information to help improve our understanding, and thus improve our system design and process management.

A current example can be in the transfer of the printing technology. This technology helps to upgrade the in-vacuum patterning process. This improvement enables designs to be produced in-register with other parts of the multilayer structure. The next generation of systems will have this option available, thus helping in the manufacture of more sophisticated security labels that couple the metallization pattern to other aspects of the label such as the holographic image. This will also enable in-register multilayer coatings for electronics to be developed too.

I hope that you will agree that all these changes continue to provide a future for vacuum-deposited coatings onto webs, foils, and films, which is both interesting and challenging.

Index