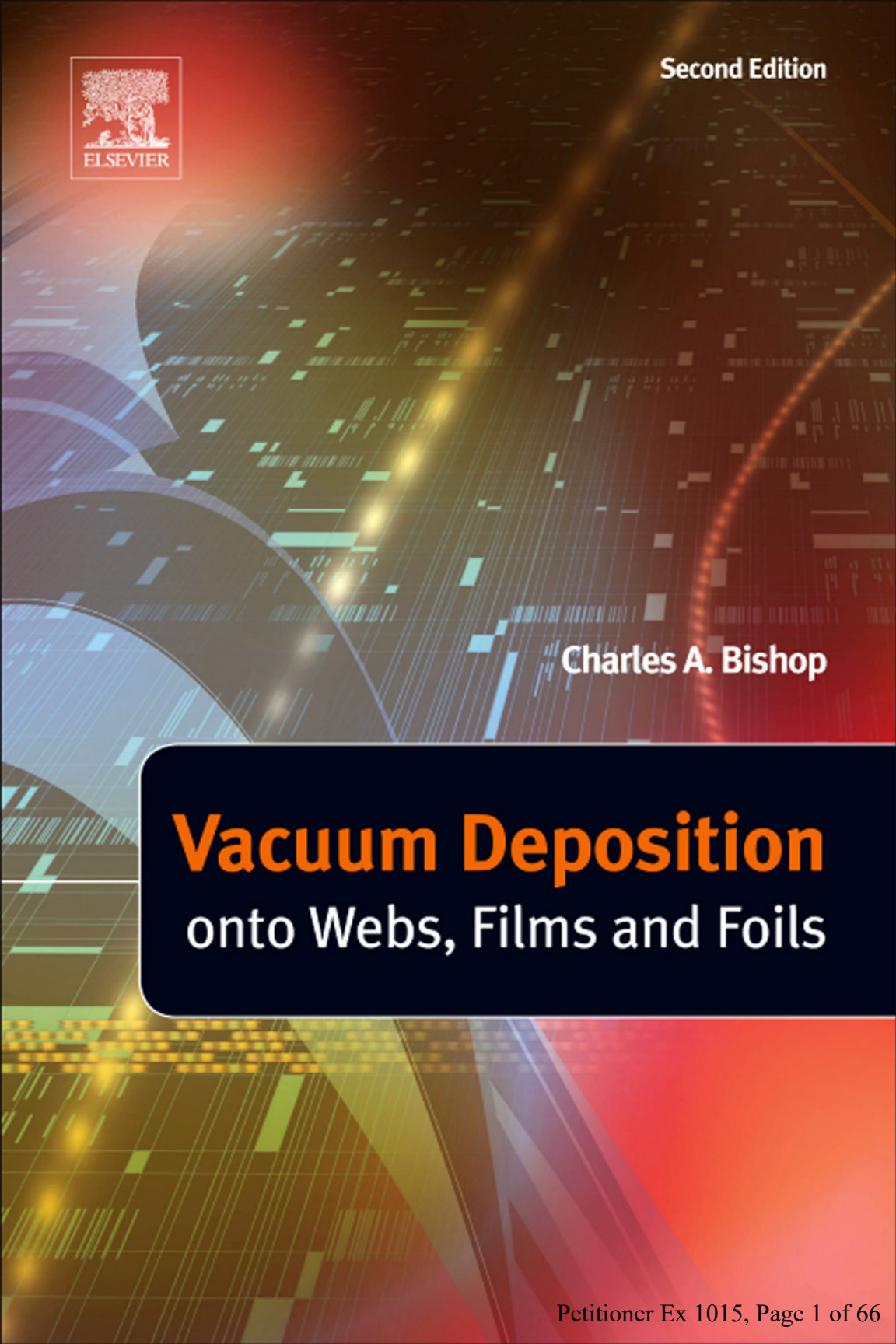

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Vacuum Deposition onto Webs, Films, and Foils

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Vacuum Deposition onto Webs, Films, and Foils

Second Edition

Charles A. Bishop

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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

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Part I

Vacuum Basics

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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

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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:

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

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

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)

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

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

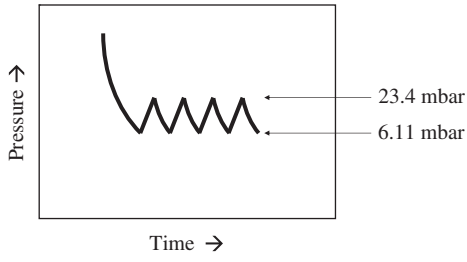

Figure 1.1 Schematic of a system with a characteristic water leak showing the cycling between the two saturated vapor pressures of ice and water.

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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:

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

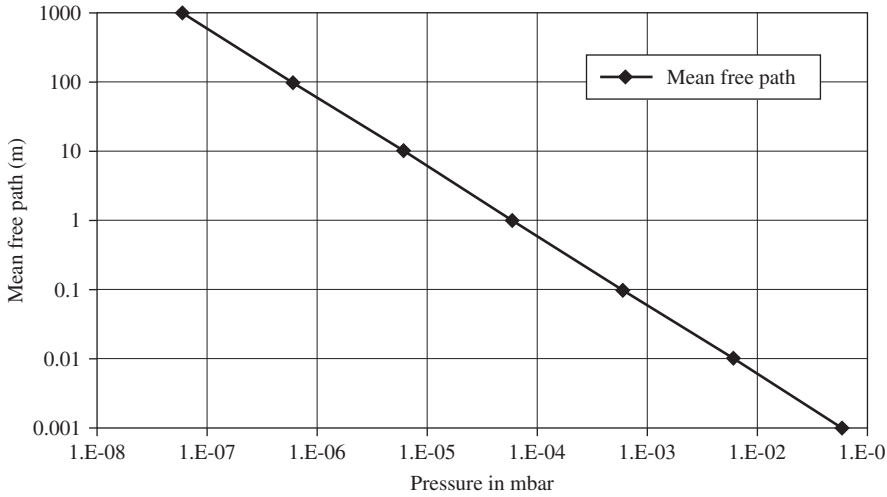

Figure 1.2 The mean free path (mfp).

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.

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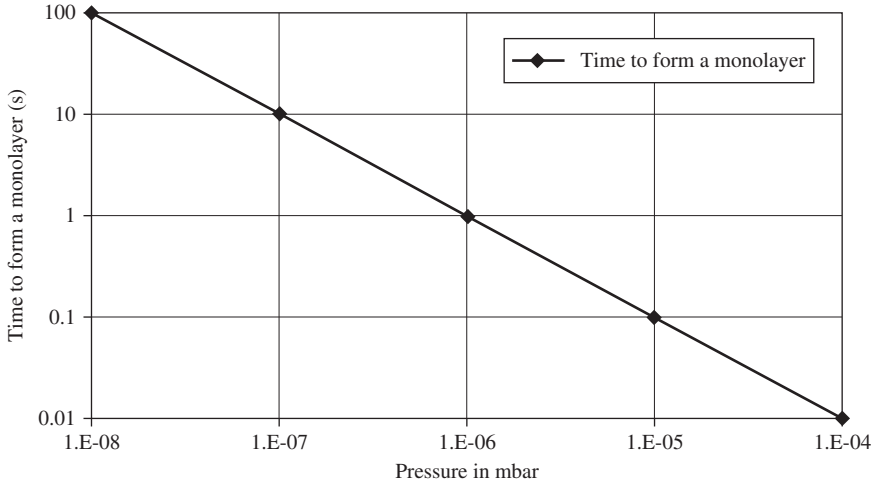

Figure 1.3 The time taken to form a monolayer in vacuum.

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

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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

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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.

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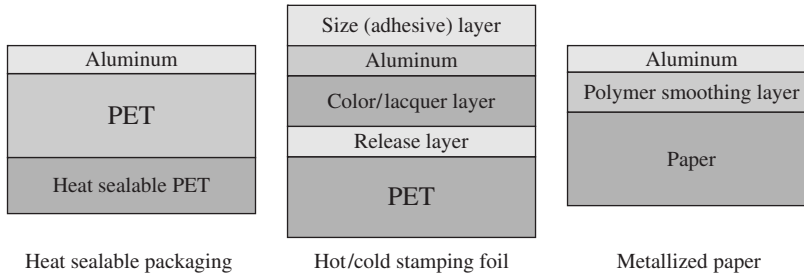

Figure 2.1 Schematics of some different aluminum metallized structures.

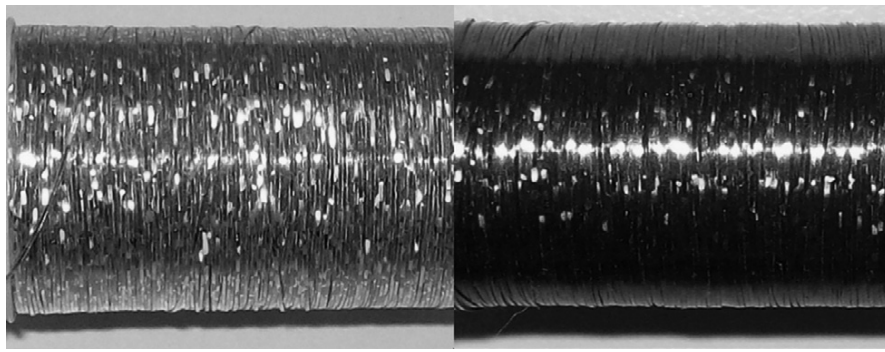

Figure 2.2 An example of metallized holographic thread; the left-hand thread is plain metallized and the right-hand one is blue lacquered.

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.

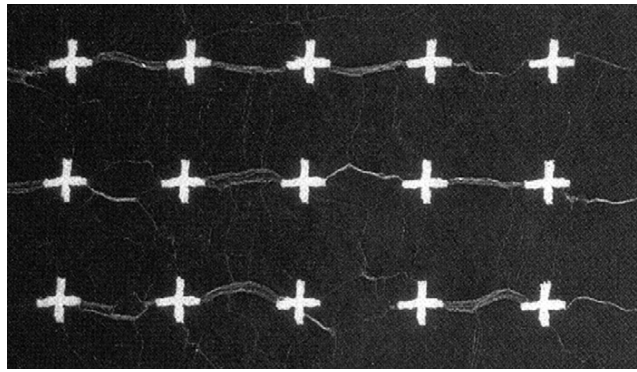

Figure 2.3 An example of a simple fused susceptor metallized film as produced by an in-vacuum pattern printing method [2, 3]. Photograph courtesy of Paper, Film & Foil Converter [6].

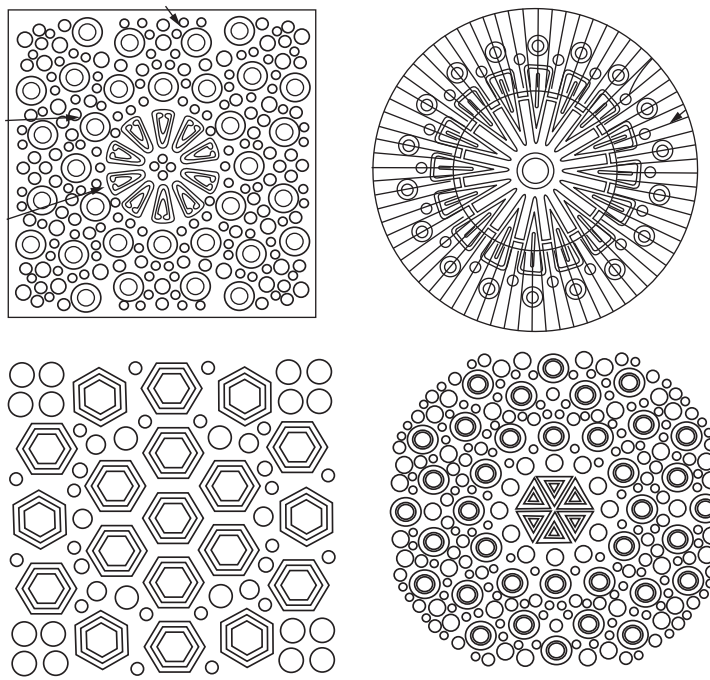

Figure 2.4 Some of the more complex patterns that are used for the antenna-type microwave susceptors [4]. The different shapes and sizes of antenna couple different proportions of the microwave energy and so heat different areas of the food at different rates and/or to different temperatures.

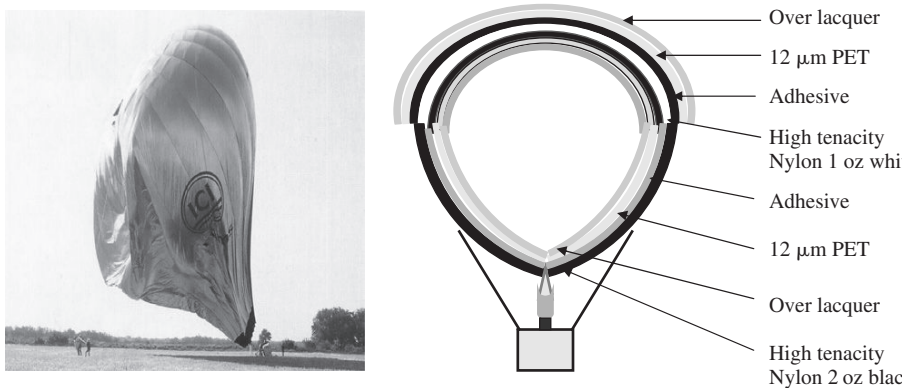

Figure 2.5 Metallized polyester laminated to make the envelope for balloons [8, 9]. Photograph courtesy of DuPont-Teijin Polyester Films (ex ICI Polyester Films).

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

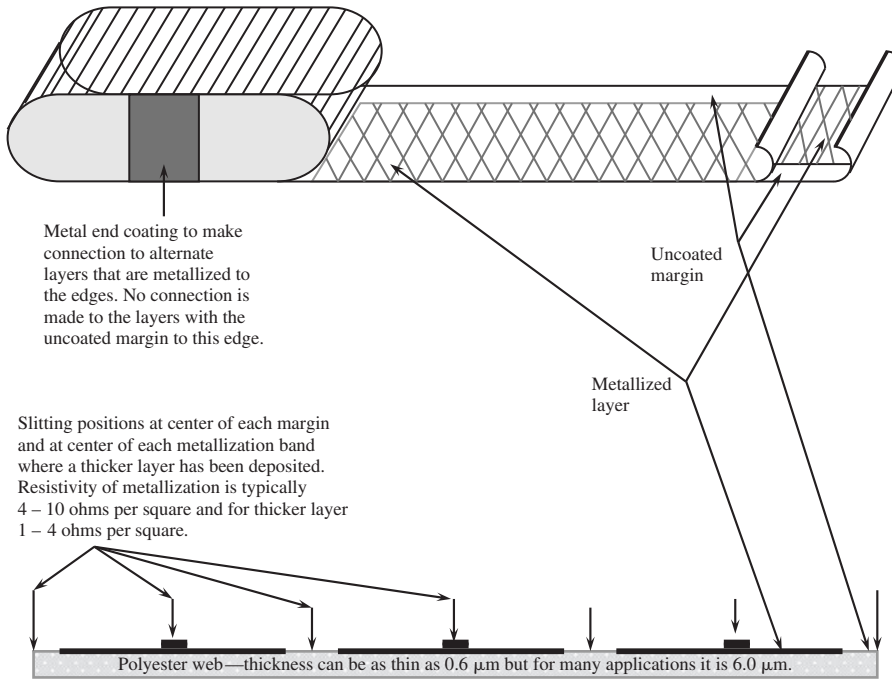

Figure 2.6 A schematic of the construction of a capacitor from thin metallized polyester.

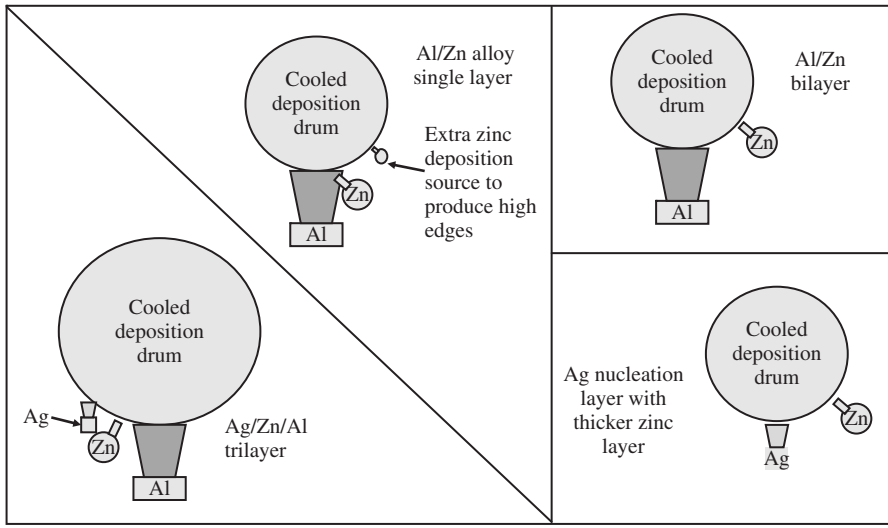

Figure 2.7 Schematics of the different system options for the manufacture of capacitors containing more than one layer.

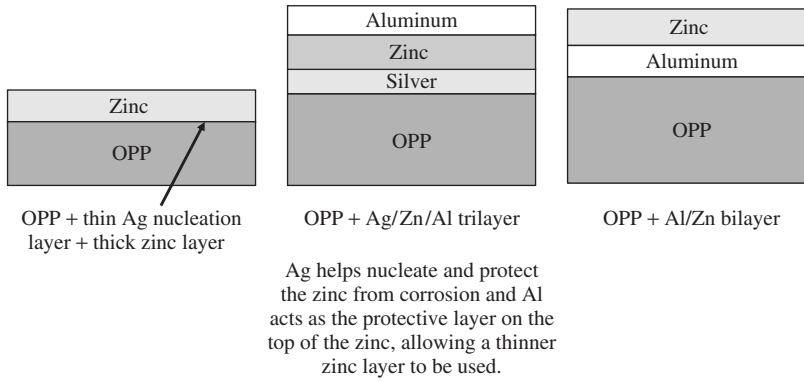

Figure 2.8 Schematics of the structure of various capacitors containing more than one layer.

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].

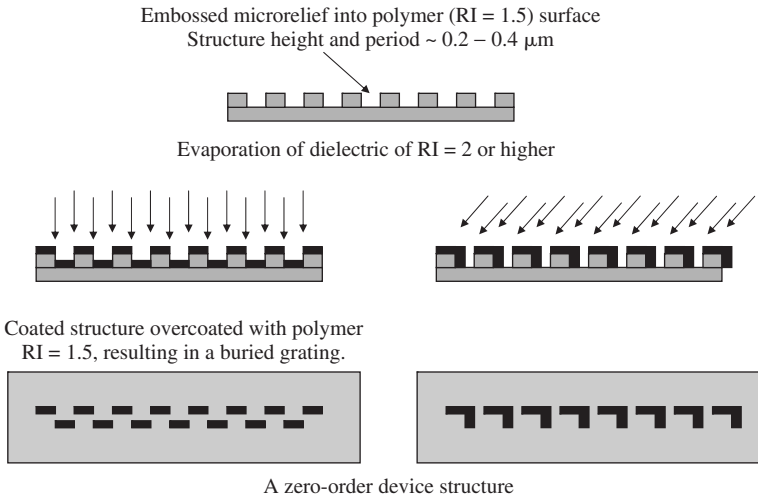

Figure 2.9 A schematic of a zero-order diffraction device.

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.

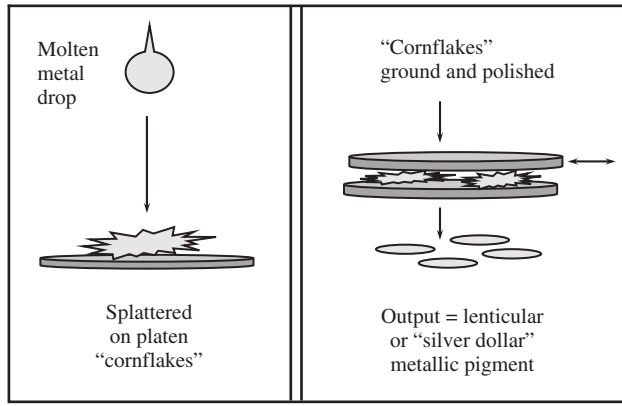

Figure 2.10 A schematic of the production of "cornflakes" (left) and lenticular flakes (right) that are commonly used in metallic inks and paints.

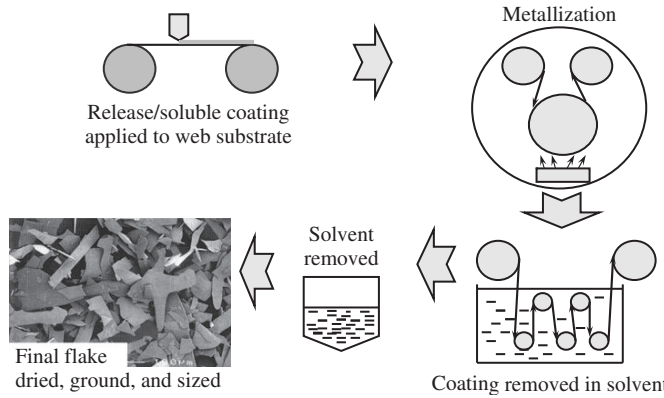

Figure 2.11 The production process of the vacuum deposited super flat bright aluminum flake pigment.

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.

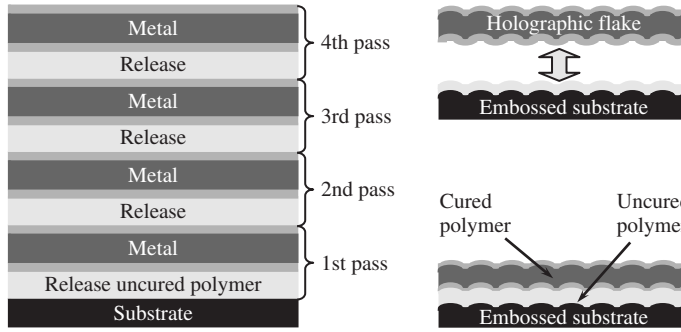

Figure 2.12 A schematic of a method of improving the production efficiency of metallic flakes and also using the same process producing embossed holographic pigment [39].

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

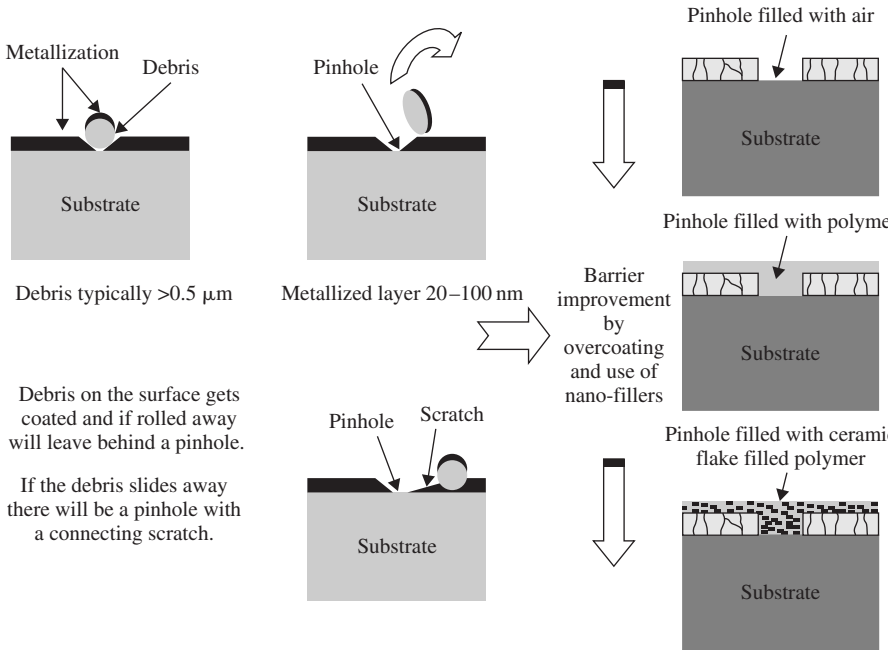

Figure 2.13 The cause of pinholes in vacuum deposited coatings and the way that an overcoating and use of nanoflake filler can improve the barrier performance [40].

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.

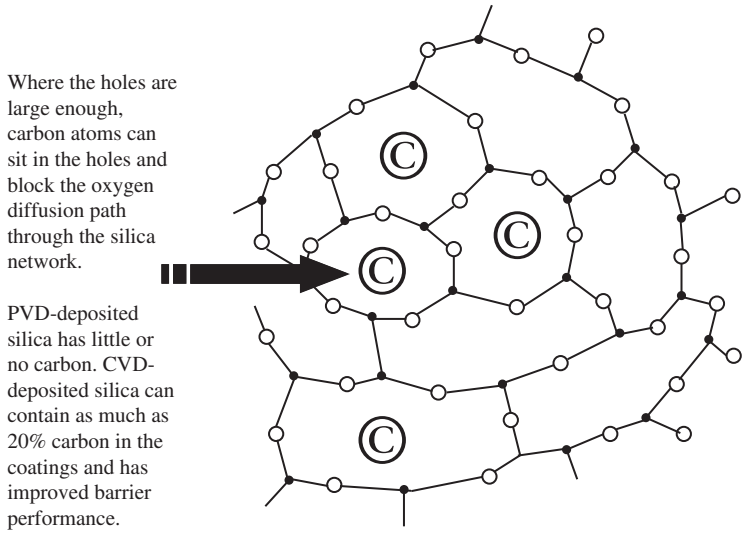

Figure 2.14 A schematic of the silica network.

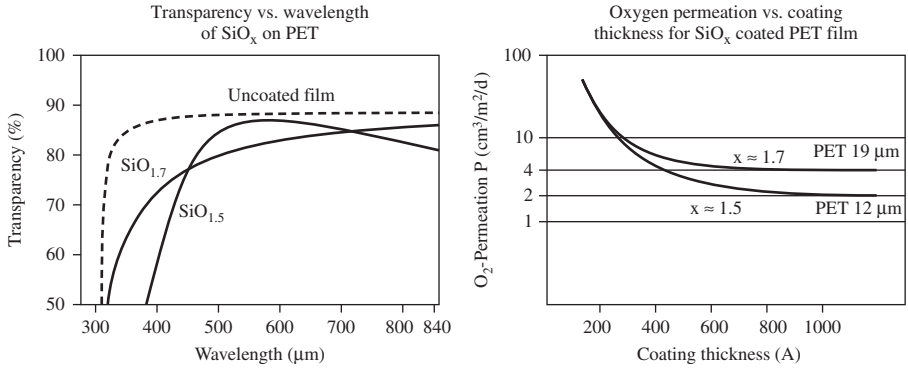

Figure 2.15 Graphs showing stoichiometry versus transparency and oxygen permeation versus coating thickness [48,50]. Courtesy of SVC [49].

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.

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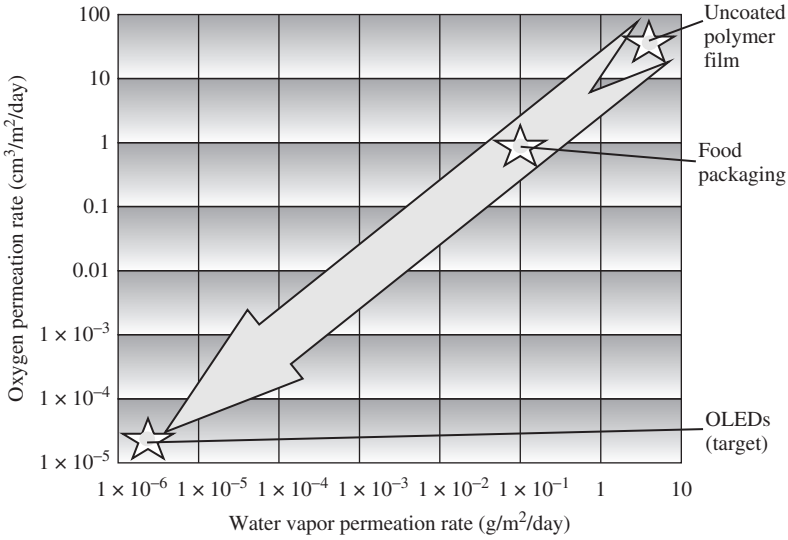


Figure 2.16 Barrier performance of uncoated polymers, coated polymers for food packaging, and the target for OLED ultrabarrier materials.

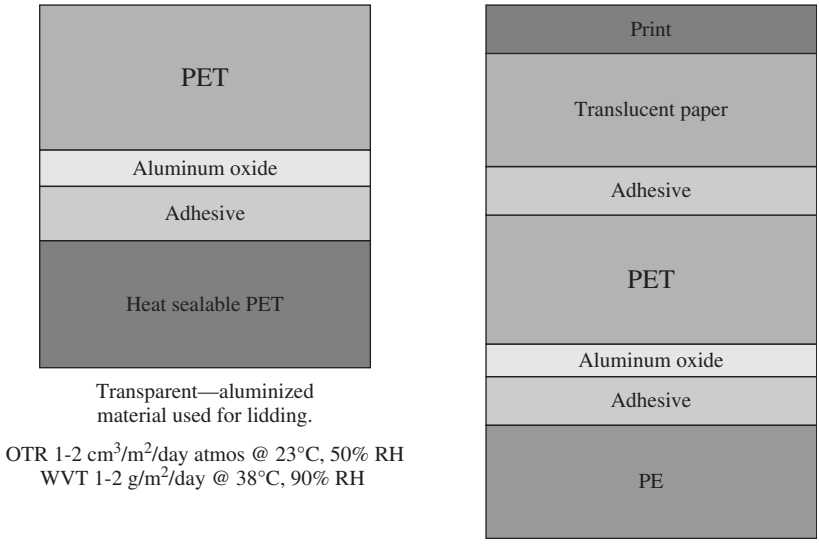


Figure 2.17 Schematics of laminate barrier packaging materials.

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).

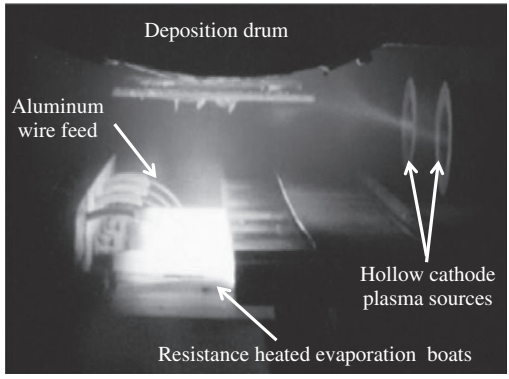
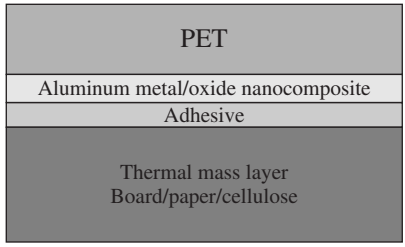


Figure 2.18 A picture courtesy of Fraunhofer FEP Dresden showing a hollow cathode secondary plasma source for the oxidation of evaporated aluminum to produce alumina.



Semitransparent—aluminized
material used as microwave susceptor

OTR <2 cm^3/m^2/day atmos @ 23°C, 50% RH
WVTR <1 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
RESISTANCE UNIFORMITY	(+/−10)*	(+/−10)*	≤ 100	(+/−10)*	(+/−10)*	%	(ILLUMINANT-C)
TRANSMISSION (Tvis)**	≥ 85	≥ 85	≥ 85	≥ 80	≥ 60	%	

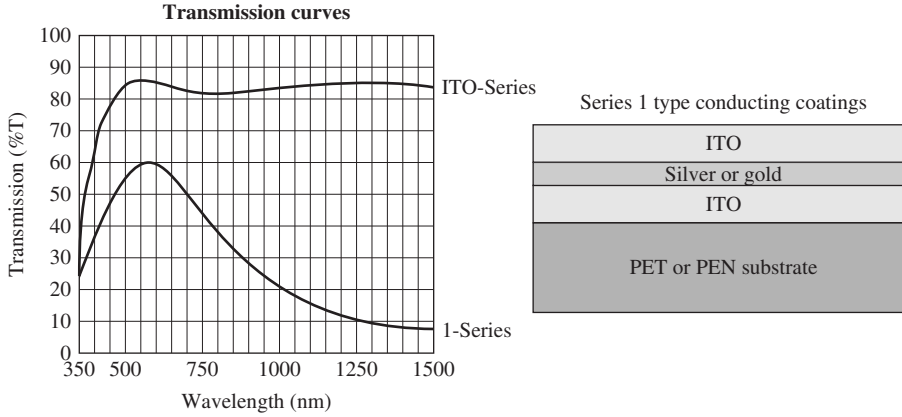


Figure 2.20 A graph comparing two ITO coatings and a table of some properties [68]. Graph and table courtesy of Flex Products Inc., a division of JDSU.

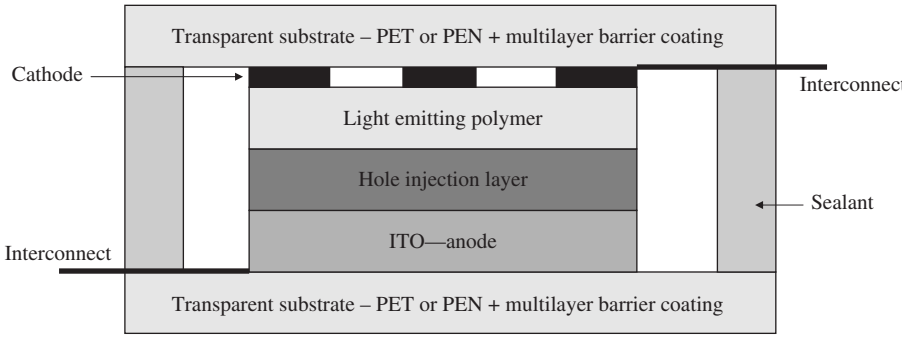


Figure 2.21 A schematic of an organic light emitting device (OLED).

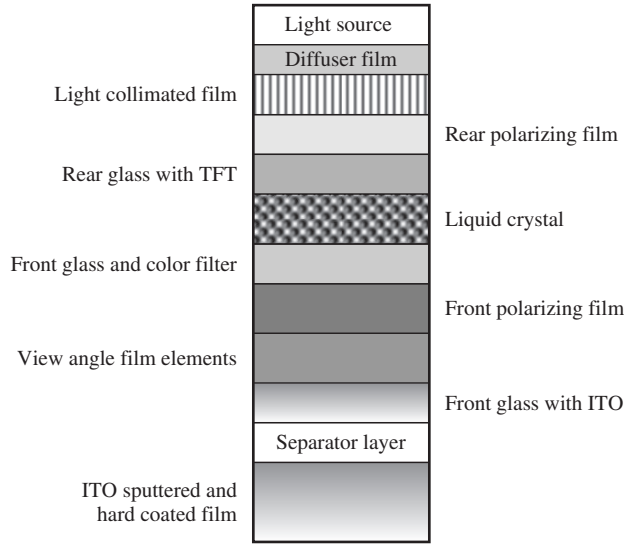


Figure 2.22 A schematic of an active matrix touch panel liquid crystal display.

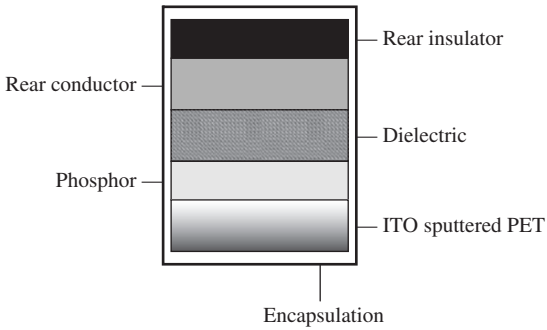


Figure 2.23 A schematic of an electroluminescent display.

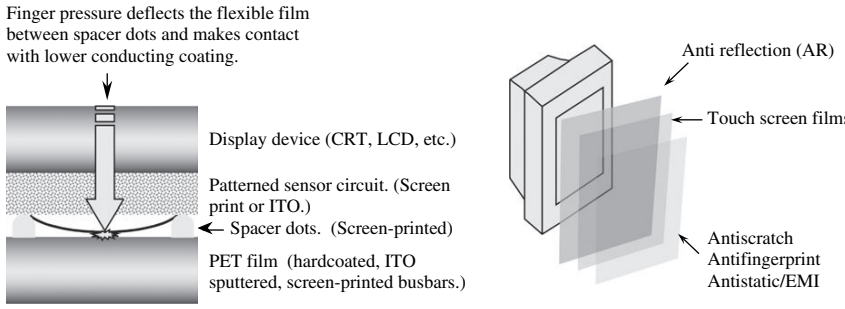


Figure 2.24 A schematic of a touch panel—as used with other layers for providing an active but also protective screen for the front of displays.

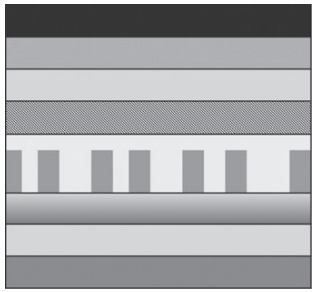


Figure 2.25 A schematic of the construction of a plasma display.

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

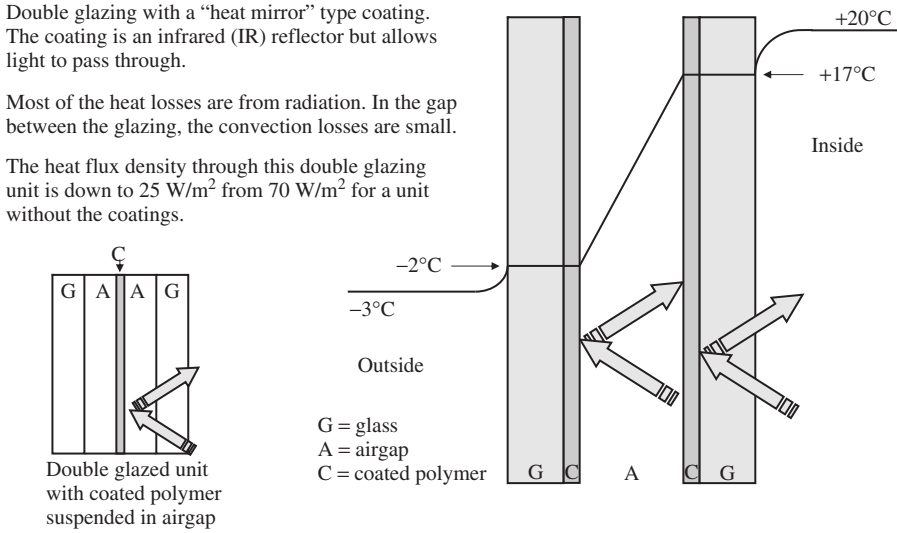


Figure 2.26 A schematic of a low E-type coating [99].

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.

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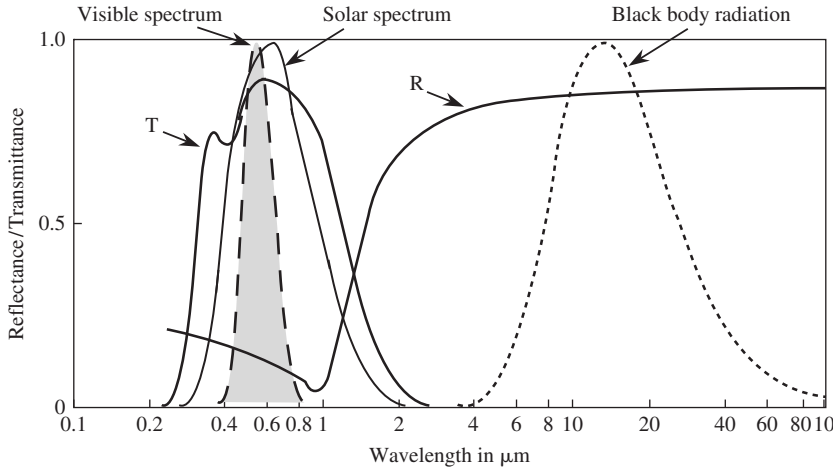

Figure 2.27 Reflection and transmission for an ITO coating overlaid on the solar spectrum, visible spectrum, and black body radiation.

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

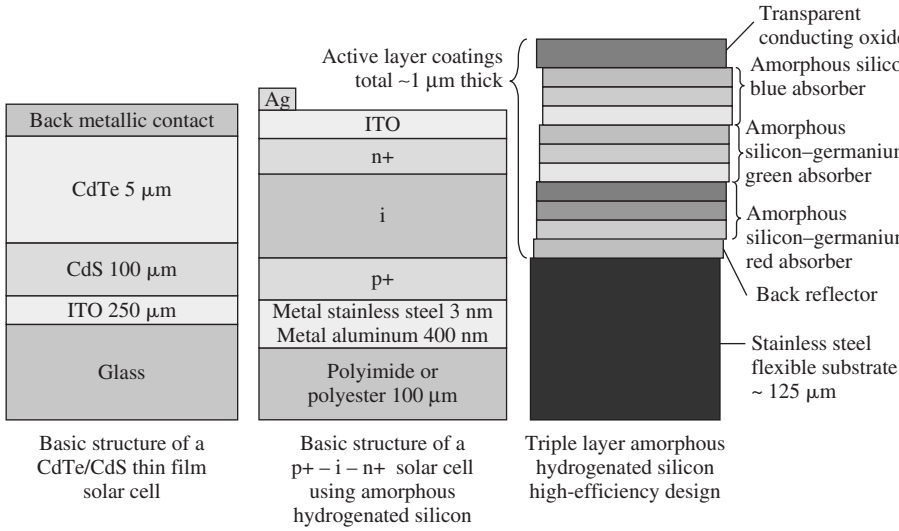

Figure 2.28 Two simple cell designs: the right-hand one aimed at vacuum deposition onto polymer substrates.

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.

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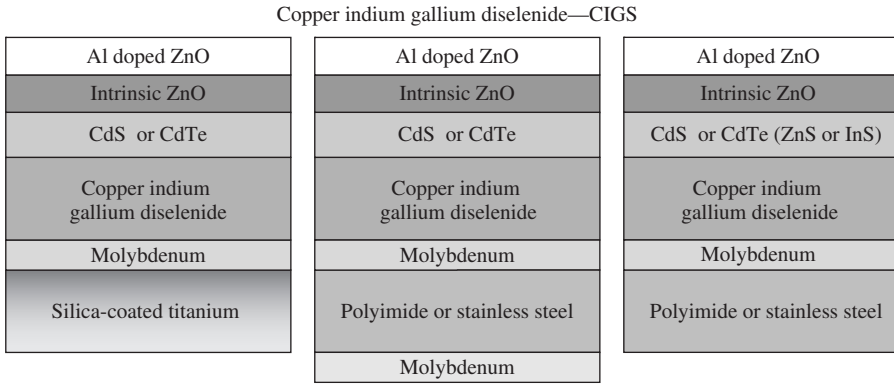


Figure 2.29 Some of the alternative structures possible on different flexible substrates.

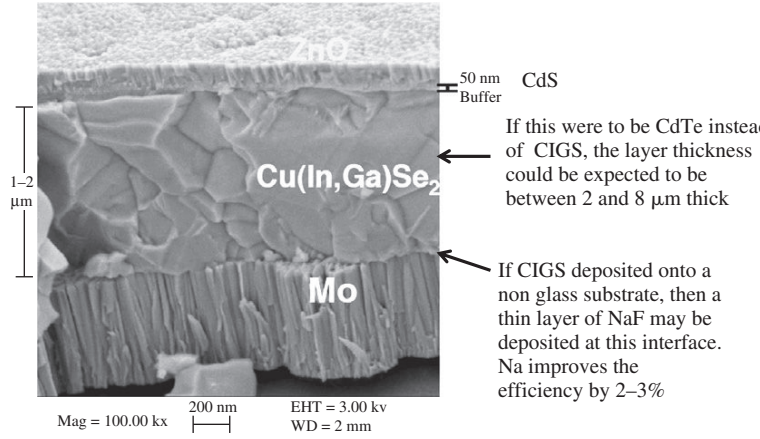


Figure 2.30 A micrograph of a CIGS solar cell structure. Courtesy of Ayodhya N. Tiwari, EMPA.

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	–

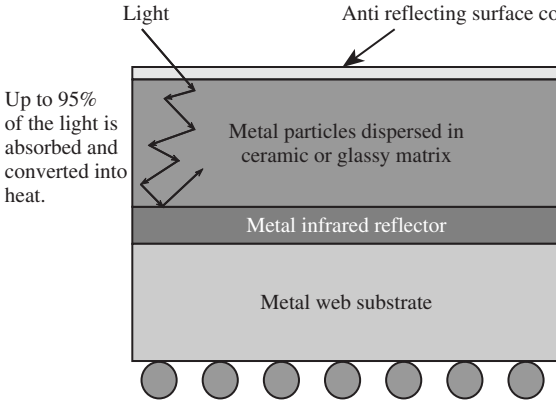


Figure 2.31 A schematic of the structure of a solar absorber.

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.

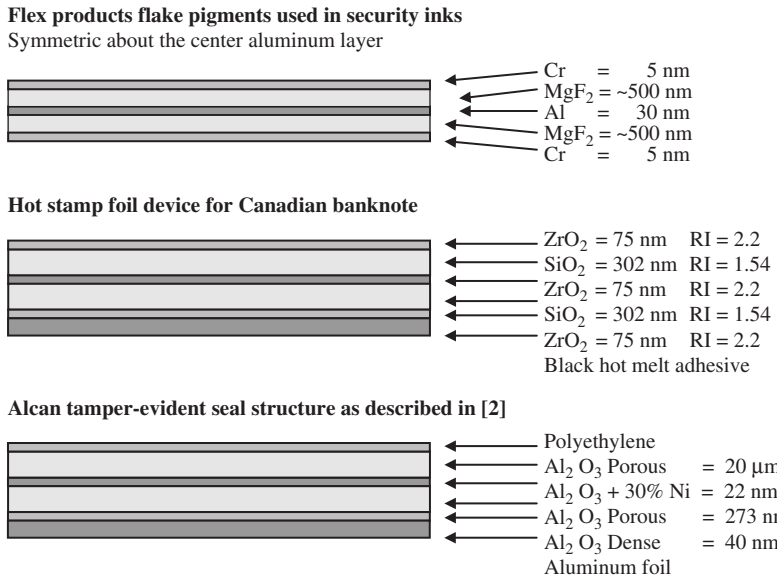


Figure 2.32 A schematic of three different optical variable devices.

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).

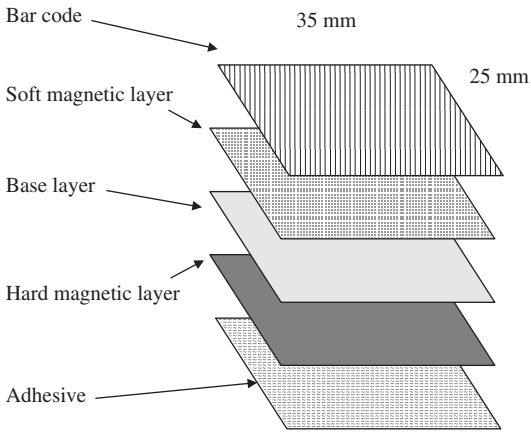


Figure 2.33 A schematic of the construction of a more conventional EAS magnetic security tag.

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

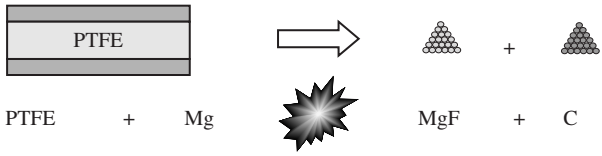
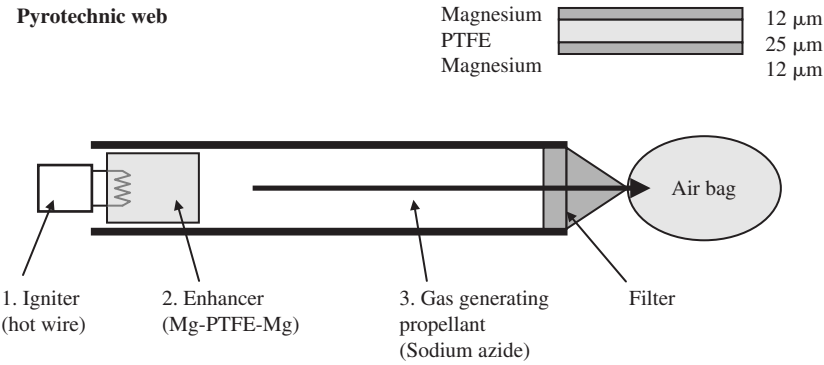


Figure 2.34 The reaction produces benign reaction products as powder.



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.

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