Physical Vapor Deposition: The Technical Process With a Relatively Short Past & a Long, Exciting Future

By Donald M. Mattox

When it comes to physical vapor deposition processes, Don Mattox is P&SF's resident expert. Normally, he serves readers monthly as the columnist for "SVC Topics," but he responded to giving an extended overview in this issue. As the technical director of the Society of Vacuum Coaters in Albuquerque, NM, Mattox is highly qualified to give special industry insight on where PVD has been—and where it's going.

Q. What are some of the recent developments in PVD processing technologies?

A. This is one thing that never ceases to amaze me. Every few years there is a new technique or equipment that comes available and allows new processes and products to be developed. In the last couple of years, the use of pulsed DC sputtering and biasing has allowed dielectric films to be deposited at very high rates. Also, films formed by sequential deposition and reaction every few atomic layers are being used. In the past 10 years, magnetron sputtering has become the premiere PVD vaporization technology, even though I am sure that thermal evaporation still leads the way in the total film-area deposited. Many of these technologies depend on the development of new equipment, so the equipment manufacturers are often in the lead in introducing new technologies and equipment to the industry.

PVD Coating Markets

Q. What are some of the markets for PVD coatings that have opened up recently?

A. In the past few years, the decorative coating of three-dimensional functional articles has really increased. These coatings provide not only a decorative coating, but are protective as well. For example, in the high-end market for door hardware and plumbing fixtures, the item was gold-plated with a lacquer topcoat. The problem was that the lacquer was often removed with cleaning, and the gold was easily scratched. Now there are several companies offering gold-looking titanium-nitride- (TiN)-coated products that have a high wear resistance. Zirconium-nitride (ZrN) provides a wear-resistant, brass-looking coating.

The coating of cutting tools with PVD processing is a large new market. Even simple drills are now coated to improve their performance, as well as to increase their sales appeal. The increased wear life is very

Vacuum coatings can enhance beauty and wear in many decorative applications, such as door hardware. Photo courtesy of Baldwin Hardware Corporation, Reading, PA.

important in applications where the object to be coated has a high cost, such as an injection mold for plastics, or where failure creates product loss or a long down-time, such as in computer-controlled machining of a complicated surface. The thin nature of PVD coatings allows dimensional tolerances to be maintained after coating.

In the past 20 years, the coating of architectural glass for energy control has become a major industry. Initially, the coatings were applied by vacuum evaporation, but now they are deposited by sputter deposition. The coating of plastic films (webs) with transparent heat-reflecting coatings has allowed the development of very energy-efficient windows, in which the coated web is positioned between two panes of glass.

Q. What are some of the future markets for PVD coatings?

A. The decorative and protective coating markets are opening up rapidly. This is particularly true where the two objectives can be combined to give a higher quality, longer-lasting product. Protective coatings applied by PVD processing will become an important market. For example, the use of aluminum as a corrosion-protective coating is a steadily growing market.

The use of passive and active films in devices such as flat panel displays and photochromic windows and mirrors is going to be a growing market. The PVD processes allow a wide range of designs. These include multilayers of materials and the gradation of material properties in a single layer. For example, one gold decorative coating application uses 25 alternating layers of gold and titanium-nitride to form a decorative and protective layer. The item is sold as gold-plated. Composition control allows a variety of products. An example is the deposition of a mixed titanium-nitride-carbide layer, where the color can range from gold to violet to gray to black, depending on the composition.

PVD has a place as an alternative to electroplating in depositing simple films. Its advantage is pollution control associated with the deposition is not a major problem. It is interesting to note that PVD-coated products can pose a problem with waste disposal and recycling. Aluminum-coated plastics, for example, cannot be recycled as easily as uncoated plastics.

This door hinge exhibits a decorative functional finish. (Photo courtesy of Gold Star Coatings, Inc.)

Future Developments

Q. What do you see in the future for PVD processing?

A. The demands on PVD processing seem to be increasing all the time. Both new requirements and new markets are driving the development of equipment and processes. The ability of PVD processing to form complex single- and multicomponent layers provides an unlimited opportunity for application.

New technologies bring new requirements. PVD coating of plastics, for example, has allowed the use of plastics to reduce the weight of automobiles while still retaining the appearance of a metallic surface. The packaging industry has some major requirements for new PVD coatings. In the past, aluminum films have provided a good moisture permeation barrier film for flexible packaging. The consumer, however, can't see the contents, and from a marketing standpoint, that is not desirable. What would be desirable is a transparent barrier layer.

Also, in microwave heating, using aluminum film packaging, the aluminum film is heated and acts as an oven for the contents. In many cases, it would be desirable to heat the contents directly, which requires a dielectric barrier layer, such as an oxide.

In many cases, companies are being forced into considering PVD processing because of the possibility that their competitors will develop new products and take over market share, either because of lower cost, better performance or an environmental concern. There are a number of applications in the medical field, for example, where a vacuum must be maintained in an optically transparent container for a long period of time. This is now done with a glass container, for which disposal is difficult. If a plastic container with a gas barrier layer could be developed, it would probably take over a lot of the market share for this type of container, because it could be easily incinerated.

Q. What are some areas for development of PVD coatings?

A. A major goal in the rigid packaging industry is to develop an optically transparent, low-permeation coating for plastics. This coating would keep gases out and vapors in. This would allow the use of plastic containers to replace heavy glass ones. This coating would be deposited on a molded three-dimensional object, such as a bottle. Uniformly coating a bottle at a high rate and low cost will require significant equipment and process development.

In the future, I think that we will see more in-line, one-at-a-time processing lines where several processes are integrated into a single line. The aluminum coating of compact music discs (CDs), for example, started out by molding the discs, then mounting them into a fixture that holds several hundred discs and then coating the discs by vacuum evaporation. Now individual discs are molded, transferred to the coating chamber and coated by sputter deposition at a rate of one every three seconds or less in a continuous processing line.

Cleaning and contamination control are major factors in obtaining reproducible processing, and this is a continuing area of interest. In the semiconductor industry, for example, where particulate contamination is a major concern, it is proposed that most of the contamination occurs in the deposition system and not in the processing ambient. This has inspired a major effort on the part of equipment manufacturers to develop contamination-free processing equipment. New developments in turbopumps, using magnetic levitation instead of mechanical bearings and adding molecular drag stages, have allowed the development of virtually oil-free, high vacuum pumping for situations in which contamination is a problem. Cleaning processes, such as plasma cleaning, that can be integrated into the deposition equipment are of interest, as is integrating the cleaning line with the deposition system in order to avoid recontamination in the processing ambient.

The development of PVD process monitoring and control equipment and techniques will be important in utilizing PVD techniques for sophisticated processing. Atomic adsorption spectroscopy techniques, for example, developed in conjunction with fusion reactor technology, are just becoming available to the PVD community. These techniques allow the non-intrusive monitoring and control of sputtering rates.

Film Properties

Q. What determines the properties of a PVD film?

A. There are no handbook values for the properties of PVD films. The film properties are determined by a number of factors, such as substrate surface roughness, the angle-of-incidence of the depositing atoms, the chemical reaction between the substrate surface and the depositing atoms (nucleation and interface formation), the deposition process used, the deposition conditions, etc. In addition, there may be postdeposition treatments that can be used to modify the film properties.

To obtain specific properties in a film, an understanding is required of the bulk properties of the film material and the factors that affect the film growth. Where the film is deposited by reactive deposition, the properties are a function of the film composition. Probably the main film property that affects all the film properties is density. Generally, the deposited film is less than fully dense, and special techniques must be used to densify the film, either during film deposition or by subsequent processing, in order to approach bulk properties. For example, the complex corrosion/erosion coatings that are applied to aircraft turbine blades by sputter deposition are shot-peened after deposition to densify the film and seal pinholes in the coating.

Adhesion is affected by the interfacial reactions and the residual film stress, which are dependent on the deposition parameters. Pinholes in the film are often determined by surface roughness and particulate contamination on the substrate surface.

The thickness for PVD films ranges from several hundred atomic layers (1000 Å) needed for optical reflectance and diffusion barriers to several microns (about 1/50 of the thickness of the human hair) for wear-resistant coatings. The properties of the film can vary with the thickness.

Q. What is the best way to determine what PVD process is the best for a specific application?

A. To make that determination requires a knowledge of published information, a knowledge of what affects film properties and what others are doing. In some cases, there is no simple answer. In coating door hardware and plumbing fixtures, for example, some people use sputter deposition, some use arc vaporization, and a few use a combination of both. In some cases, portions of the decision may be simple. In all cases I know of in the PVD deposition of high-performance hard coatings, some version of ion plating is used (that is, during deposition there is concurrent bombardment by energetic ions to promote chemical reaction and densification). Mostly, the decision on which process is best is based on testing of components coated by equipment manufacturers or contract coaters.

Many equipment suppliers will provide turnkey operations, in which they develop the process and the equipment to meet your specifications, and tell you which button to push. This can lead to problems in manufacturing. In addition to knowing which button to push, one must understand the equipment, the process and what affects film properties.

Vacuum Coating & PVD

Q. What is meant by the terms "vacuum coating" and physical vapor deposition?

A. The term "vacuum coating" means that the coating process is done in a vacuum (*i.e.*, under a pressure less than the local atmospheric pressure). This is not very definitive, because just about every coating technique has some version that is done in a vacuum. These include low-pressure plasma spray, low-pressure chemical vapor deposition, and even electroplating.

Physical vapor deposition (PVD) processes are those film deposition processes in which the coating material, or some portion of it, is vaporized from a solid or liquid surface, transported through a low-pressure gaseous environment, and condensed on a surface that is called a *substrate*. If the depositing material reacts with the gaseous ambient or co-deposited species, the process is called a "reactive deposition process." Reactive deposition processes are used to deposit oxide, nitride and carbide films of materials.

Q. What are the most common vaporization techniques in PVD processing?

A. The highest volume vaporization technique is thermal evaporation, usually from a liquid surface. There is probably more aluminum evaporated than any other material. Physical sputtering, where atoms are ejected from a solid surface by momentum transfer from a high-energy bombarding ion, is used extensively. Arc vaporization, which uses a high-current, low-voltage arc to evaporate and ionize material, is becoming an important vaporization technique.

Q. What gas pressures are used for PVD processing?

A. PVD processes typically use gas pressure (vacuum) below about 10^{-4} atmospheres. At that vacuum, atoms can travel from the course to the substrate without a significant number of collisions and deposit with little contamination from residual gases. At pressures above about 10^{-4} atmospheres, the atoms will combine in the gas during the transport process to form "soot," which gives a poor film. The lower the pressure in the system, the less the possible effects of gaseous contamination on the depositing film material. Typical vacuum evaporation processes will use a gas pressure of about 10^{-8} atmospheres.

Q. What is a "plasma" used in PVD processing?

A. A plasma is a gaseous atmosphere that contains an appreciable number of ions and electrons so that it acts as an electrical conductor, even though often the neutral atoms far outnumber the ions (a "weakly ionized plasma"). The plasma supplies the ions that can be accelerated in an electric field to cause sputtering, and also activates reactive gas species in order to enhance reactive deposition processes. Plasmas used in PVD processes are typically at a gas pressure of about 10^{-6} to 10^{-5} atmospheres.

Q. What is the ion plating process?

A. In ion plating, the growth of the depositing film is modified by concurrent bombardment by atomic-sized energetic particles. This bombardment densifies the film and promotes chemical reaction, in the case of reactive deposition. The bombardment can also induce compressive stresses that can be used to offset the tensile stresses that are often introduced into high-modulus films during growth. The ions used for bombardment are usually extracted from a low pressure by a negative bias on the substrate surface. In some cases, the ions are formed in an "ion gun." ***P&SF***

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