SVC Topics

Donald M. Mattox, Technical Director • Society of Vacuum Coaters
71 Pinon Hill Place N.E. • Albuquerque, NM 87122
505/856-7188 • FAX: 505/856-6716 • www.svc.org

A Concise History Of Vacuum Coating Technology

Part 2c: 1940–1975

Coating Characterization

The transmission electron microscope had its beginnings in 1928, when Busch pointed out that electrons could be focused using electric and magnetic fields. Davisson and Germer discovered electron diffraction from surfaces in 1927, and Thompson demonstrated the diffraction of electrons through a thin gold film in 1928. In the following years, analytical techniques were developed that allowed the use of transmission electron microscopy (TEM) to be applied to atomic nucleation and the microstructure of deposited thin films (Bassett, Menter & Pashley, 1959; Pashley 1963).

A major contribution to the physical characterization of deposited coatings was the scanning electron microscope (SEM), which was first commercially available in 1965 (Cambridge Scientific Instruments, Mark 1). This instrument was an outgrowth of a research instrument described by Zworykin, Hillier and Snyder (1942), who recognized that secondary electrons could be used for imaging surfaces. The SEM allowed visualization of the topography of substrate surfaces and coatings, as well as the fracture-surfaces of fractured film-substrate couples. The use of the SEM allowed the structure-morphology studies of thick, atomistically deposited coatings (Movchan & Demschishin, 1969; Mattox & Kominiak, 1972; Bunshah & Junz, 1972; Thornton, 1977).

A major problem with characterizing deposited films and coatings is that they are often less than fully dense. This affects their electrical resistivity, dielectric properties (Weaver, 1962), optical constants, environmental stability, hardness and other properties. Hardness measurement of deposited coatings were made by Palatnik, Federov and Il’inski in 1962. They measured the hardness of 40-micron-thick copper films using standard hardness-measuring techniques. The hardness of thinner films was affected too much by the substrate to yield reliable results. Reliable hardness measurement of thin films awaited the development of microindentation hardness tests in the early 1980s.

Residual film stress can be a major factor in the adhesion and stability of vacuum-deposited films and coatings. Stress in films had been studied as early as 1877 by Mills on chemically deposited films and by Stoney (1909) on electrodeposited coatings. Major studies of stress in vacuum coatings began in the early 1950s (Hoffman, Daniels & Crittenden, 1954; Murbach & Wilman, 1953; Turner, 1951) using a variety of techniques. Hoffman reviewed the early stress-measurement work in the book, *Thin Films* (1963). It was established that film stress could vary with a number of deposition parameters, such as film thickness, angle-of-incidence of the depositing atoms, substrate temperature, residual reactive gases, etc. In the early 1970s, it was shown that high-energy particle bombardment during deposition ("atomic peening") could introduce high compressive stresses into the depositing film (Mattox & Kominiak, 1972; Hoffman & Thornton, 1977).

In the early 1960s, methods for testing the adhesion of films to surfaces began to be formalized (Benjamin & Weaver, 1960), but the techniques were mostly qualitative and gave relative values, at best.

Process Monitoring & Control

Before 1948, the proper film thickness for optical multilayer film "stacks" was determined visually. In 1948, instrumented optical transmission was used by Dufour for in-process control of optical properties, and the technique was well developed by 1959 (Steckelmacher, Parisot, Holland & Putner). Early deposition rate monitors used vacuum microbalances or ionization-based rate monitors. Sauerbrey (1959) was the first to measure the mass of deposited material using the frequency change of a quartz-crystal oscillator. By the early 1960s, quartz crystal monitors for control of film deposition were well established.

Applications

World War II provided a major impetus to the use of vacuum coatings, particularly as applied to antireflection coatings and mirrors. During WWII, MgF_2 replaced CaF_2 in antireflection coatings (Cartwright & Turner, 1940) and the advantage of post-deposition baking of MgF_2 films to improve their durability was demonstrated (1941). In Germany, aluminum mirrors were over-coated with evaporated silicon monoxide, followed by an air bake to improve the durability of their mirror surfaces (Hass, 1939). Semitransparent, electrically conductive gold coatings on glass were developed for aircraft window defrosting during WWII. The process of glow discharge cleaning of optical surfaces before coating was well established by the beginning of WWII. During the war, many companies, such as Bausch and Lomb, developed vacuum coating departments, and these efforts continued after WWII. In 1947, the 200-in. Palomar telescope mirror was metallized with aluminum, using 350 separate evaporator filaments.

Optical-coating design rapidly produced many types of bandpass filters, selective reflectors (such as heat mirrors), and other specialized coating systems. Heat mirror (IR-reflecting) coatings were proposed as early as 1922 (Hoffman patent). These efforts accelerated after the publication of the book, *Optical Properties of Thin Solid Films*, by O.S. Heavens in 1955, as well as numerous articles in the series of books, *Physics of Thin Films,* beginning in 1963, originally edited by Georg Hass and Rudolf E. Thun.

Invention of the transistor by Shockley, Bardeen & Brattin (1947) led to the deposition of vacuum coatings for contacts and thin layers in semiconductor device fabrication. Semiconductor device and integrated circuit processing introduced some new requirements to PVD processing. Multilayer and complex metallization structures needed to be developed to serve several functions, such as adhesion to a surface, electrical conductivity, etchability (to form a conductive pattern), corrosion resistance (resistance to corrosion during subsequent processing), resistance to electromigration, resistance to stress-voiding, bondability (for wire bonding or soldering), etc. In addition, as surface features on devices became smaller, the ability to deposit a conformal coating with no pinholes or voids became more difficult.

The introduction of integrated circuits in the early 1950s led to the use of vacuum coatings for electrical interconnection and electrical components, such as thin film resistors, as described in the book, *Thin Film Technology,* by Robert M. Berry, Peter M. Hall and Murray T. Harris in 1967. The production of semiconductor devices required the deposition of electrodes by vacuum coating. Aluminum and gold were used, but the requirement of subsequent high-temperature processing limited their application. In addition, aluminum was susceptible to electromigration problems under high-current-density conditions, stress-voiding after PSG encapsulation by PECVD processing, and the "purple plague" (Philofsky, 1970) after wire bonding to gold wire. Multilayer metallizations were developed, such as Ti-Pd-Au, which resisted corrosion during subsequent wet-chemical etching (Speight & Bill, 1973). A major problem was getting good coverage ("filling") over surface features.

NASA was formed in 1958 and led the way in developing tribological coatings—particularly solid-film lubricants (Spalvins & Buckley, 1967; Spalvins, 1969). They vacuum-deposited both low-shear metal lubricants, such as ion-plated silver, and sputter-deposited compound lubricants, such as MoS_2. Ion-plated, low-shear, metal-coated bearings have become the standard coating for rotating anode bearings in X-ray tubes. NASA also developed solar-control coatings for heat management on spacecraft (Hass, Drummeter & Schach, 1959). The energy crisis of the mid-1970s increased the interest in coatings for energy conservation and efficiency.

Vacuum (PVD) cadmium plating for corrosion protection was developed in the mid-1950s to avoid hydrogen embrittlement of high-strength steels encountered when using electroplated cadmium. "Vac cad" plating began to be used on military-aircraft components in late 1957 (MIL-C-8837—ASG, June 1958). In the mid-1960s, ion-plated aluminum replaced electroplated nickel for corrosion protection of uranium in reactor applications (Mattox & Bland, 1967; Bell, 1970). In 1967, Schick rf sputter-deposited a chromium coating on razor blades* for corrosion protection.

In 1968, an ion-plating technique was developed using a rotating cage at a negative potential to contain small parts without having to make direct electrical contact to the parts (Mattox & Rebarchik; McCrary, 1968, Carpenter & Klein, 1968; Steube [patent] 16 December 1975). The process is analogous with "barrel plating" in electroplating. McDonnell

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* *Krona-Chrome™ razor, Schick Corp.*

Douglas Corporation utilized this technique for coating metal fastners with aluminum for the aerospace industry and called the process “ivadizing,” then later, ion vapor deposition (IVD), by which name it is still known in the aerospace industry (MIL-C 83488.)

The aerospace industry also provided other coating requirements. These included the corrosion/erosion protection coatings on engine turbine blades, thin foils of metal alloys that were difficult to roll, and thin-walled, freestanding shapes of exotic metals. An interesting metallurgical application was the ion plating of very adherent silver films to beryllium for subsequent low-temperature/low-pressure diffusion bonding (McLeod & Ma, 1974).

The first use of vacuum coating for decorative purposes was probably by sputter-depositing silver on cellophane web material in 1941 by Hy-Sil of Boston, MA. Aluminum metallizing of webs by thermal evaporation was used to produce radar chaff during WWII (beginning about 1941). After WWII, many entrepreneurs entered the vacuum coating business and developed various types of decorative coatings. Some of the most popular decorative metallizations (sometimes called “junk coating” or “vacuum metallizing”) utilized a reflective aluminum coating on a surface with a colored semitransparent topcoat that could be textured. If the substrate surface was rough, as with a zinc die-cast material, it could be flow-coated with a polymer to provide a smooth surface (base coat) before the vacuum metallization. All types of polymers were coated for decorative purposes (Rampelberg & Scharnberg, 1961). A major concern is to cover three-dimensional objects by the proper racking, fixturing and movement at a low unit cost. A topcoat provides the durability, so adhesion of the vacuum metallization was generally not a major concern.

Vacuum coating for decorative purposes was first employed in the auto industry as a second-surface coating on clear plastics for decals in the early 1950s. In 1956, Ford began using first-surface coated plastics with a topcoat for interior decorative purposes in its 1957 production cars. In 1975, Chevrolet released for production a magnetron sputter-deposited, chrome-coated plastic grill for its Caprice automobile. In 1966, “stick-on” metallized window film was developed by 3M. Decorative coatings using compound coatings such as TiN were not considered until the late 1970s (Zega, Kornmann & Amignet, 1977).

Metallizing of paper and polymers for packaging probably began with the metallization of paper for cigarette packing to replace lead foil. Metallized webs for packaging have continually developed and are a major aspect in keeping food fresh. With the energy crisis of the early 1970s, the use of deposited films and coatings for energy generation and energy conservation became a potentially important industry by the mid-1970s (Mattox, 1976).

In 1975, vacuum coatings on tool surfaces to increase their hardness and wear resistance (Carson, 1975) and thermal control coatings on architectural glass were just starting to be developed. Transparent and semi-transparent electrically conductive oxide coatings on glass had been prepared since the mid-1960s, but it was not until the late 1970s that such coatings were commercially deposited on polymer webs. (*To be continued.)*

P&SF

Bibliography

Vacuum Deposition of Thin Film, Leslie Holland, Chapman & Hall, 1956.

Optical Properties of Thin Solid Films, O.S. Heavens, Butterworth, 1955.

Handbook of Thin Film Technology, edited by L.I. Maissel & R. Glang, McGraw-Hill, 1970.

Thin Film Phenomona, Kasmura L. Chopra, McGraw-Hill, 1969.

Thin Films, American Society for Metals, 1964.

Structure and Properties of Thin Films, edited by C.A. Neugebauer, J.B. Newkirk & D.A. Vermilyea, John Wiley & Sons, 1959.

Physics of Thin Films (series), 1963 —, Academic Press.

Thin Film Technology, Robert M. Berry, Peter M. Hall, and Murray T. Harris, Van Nostrand-Reinhold, 1967.

The Properties of Glass Surfaces, L. Holland, John Wiley & Sons, 1964.