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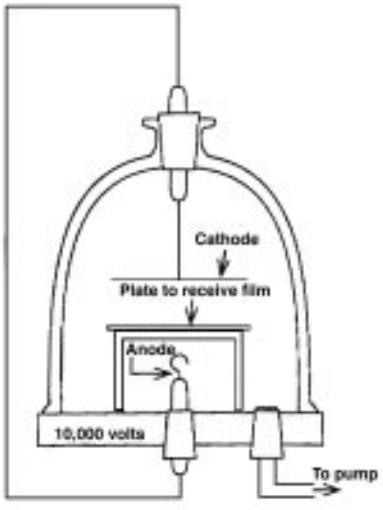
A Concise History Of Vacuum Coating Technnology

Part I: Prior to WWII (1940)

Before the mid-1930s, many techniques for vaporizing material and depositing coatings in vacuum had been demonstrated; however, they remained mostly laboratory curiosities. This was mainly because of the lack of good vacuum materials and systems. In the mid-1930s, improvements in materials, techniques and equipment led to the development of commercial applications of vacuum deposition for zinc-metallized paper for paper capacitors for the electronics industry, reflector coatings for mirrors and lighting and antireflection coatings for optics. The advent of World War II led to a dramatic increase in the use of vacuum coatings.

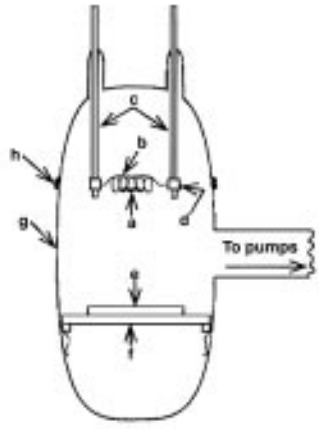
The deposition of coatings in a vacuum environment was known for a long time before the process was used commercially. Vacuum deposition of a coating consists of a source of the material to be deposited, transport of the material through a low-pressure gaseous (or plasma) environment and condensation on a substrate. In some cases, the depositing material reacts with the gaseous environment, or a co-deposited material, to form a coating of a chemical compound, such as a nitride or carbide (reactive deposition). The source of the material can be a solid or liquid surface that is vaporized (physical vapor deposition, or PVD), from a chemical vapor precursor (subatmospheric chemical vapor deposition, or SA-CVD), from a chemical monomer generally in plasma (plasma polymerization) or from a combination of processes (hybrid deposition process). In PVD, the principal vaporization techniques are thermal evaporation/sublimation, sputtering and arc vaporization.

Columnist's Note: *This is Part 1 of a three-part series.*



a.

Apparatus for the production of mirrors by (a) cathode sputtering. "This method for the preparation of reflecting surfaces is particularly useful as a process for half-silvering and for depositing metals other than silver. ... For joint grease, a special solution of crude rubber and lard was made. ... A 10,000-volt transformer furnishes the current; and it is advisable, although not absolutely necessary, to rectify the current."



b.

Apparatus for the production of mirrors by (b) evaporation of metal. "This method of deposition has not been widely tested, and its possibilities are, therefore, little known, but it would seem to be especially valuable for small work where films of any volatile substance are required. ... The glass gube may be made entire, then cracked off at (h) and subsequent sealings be accomplished with sealing wax."

Figures and quotes are from the Bureau of Standards Circular #389, "The Making of Mirrors by the Deposition of Metal on Glass," January 1931.

Arc vaporization in vacuum was first reported by Hare (1939). Grove (1852) and Pulker (1858) first reported vaporization by sputtering. Electric discharge vaporization of wires was first reported by Faraday (1857). Plasma polymerization of organic monomers was reported by deWilde (1874) and Thenard (1874). Sputter deposition of films was reported by Wright (1877) and film deposition by thermal evaporation (from a crucible) by Nahrwold (1887) and Pohl and Pringsheim (1912). Vacuum pyrolysis of hydrocarbon vapors to form carbon films was reported by Sawyer and Mann (1880), and the hydrogen reduction of WCl_4 to form tungsten films was reported by de Lodyguine (1897).

To deposit a solid film in a vacuum by PVD processes, it is necessary to reduce the gas pressure to the extent that collisions in the gas phase do not produce gas-phase nucleation and "soot," rather than a solid film. This requires a pressure of less than about 0.0001 atmospheres. That vacuum

could be attained with some early "mercury piston" pumps. By 1880, Edison had achieved a "good" vacuum of about 10^{-6} atmospheres, as measured by a McLeod vacuum gauge (McLeod, 1874) using a combination of Geissler (1858) and Sprengel (1865) glass mercury piston pumps, chamber heating ("flaming") and cold traps. This level of vacuum was necessary to prevent oxygen from burning out the carbon filaments used in the production of the first light bulbs (Edison, 1879).

Another requirement is to reduce the gaseous contaminant level in the deposition environment to a level that is acceptable. Contamination can affect both the deposited film material and the material in the vaporization source. Before 1940, the principal non-fluid vacuum gauges were the Piriani (Piriani, 1906), thermocouple (Voege, 1906), bourdon (Lorenz, 1917) and cold cathode ionization (Penning, 1937) gauges. The concept of the viscosity (molecular drag) gauge (Hogg, 1906) and capacitance manometer gauge (Olsen & Hirst, 1929) were known, but not well developed.

In the best early vacuum systems, the glass vacuum chamber was fused to the glass vacuum pump and fusion-sealed ("tipped off") when the desired vacuum was attained. This procedure was acceptable for the production of light bulbs and early studies involving vacuum and plasmas, such as the gas-discharge tubes (Crookes, 1879), X-ray tubes (Rontgen, 1895), discovery of the electron (Thompson, 1898) and the triode electron tube (DeForest, 1906). The procedure was not amendable to depositing films on substrates in any commercial quantity. The use of cold traps to keep mercury from the processing chamber was improved by the use of liquefied air (1885) and the development of a means for its storage in a vacuum-insulated vessel (Dewar, 1892). The development of the mercury diffusion pump (Gaede, 1913; Langmuir, 1916) allowed good vacuums to be attained more easily than with the mercury piston pumps. The replacement of mercury by refined low-vapor-pressure hydrocarbon oils (Burch, 1928; Hickman, 1929) in the diffusion pumps allowed the elimination of cold traps in many applications. In some cases, there was not valve in the system—only an optical baffle between the vacuum pump and the processing chamber. This made for a slow cycle time, because the oil diffusion pump had to heat up and cool down on each cycle.

A major obstacle to producing vacuum-deposited films was the lack of accessibility to the vacuum chamber. Greases, waxes and oiled leather were common vacuum sealants but, because of their high vapor pressures, did not allow heating the vacuum chamber enough to achieve the good vacuum necessary for thermal evaporation in a demountable system. The figure shows a sputtering chamber and a vacuum evaporation chamber as published in the Bureau of Standards Circular #389, "The Making of Mirrors by the Deposition of Metal on Glass" (January 1931), along with some excerpts describing the processes. Low-vapor-pressure greases and waxes were introduced by Burch in 1929 (Apiezon waxes and greases), but it was not until the mid-1930s that fairly reliable, nonpermanent (breakable) "bakeable" vacuum seals came into use and allowed good vacuums and repetitive easy access to the vacuum chamber. One of these was the lead-wire "corner seal" described by Strong in 1938. Neoprene ("artificial") rubber was invented by DuPont in 1933, and molded seals of this material began to be used in the late 1930s.

Before the 1930s, sputter deposition was the most widely used vacuum coating process. Edison, for example, patented a process for sputter deposition of films on the masters for wax phonograph cylinders in 1904. Sputtering could be used for vacuum coating because it is a low-temperature vaporization process that does not require a very good vacuum for the deposition of non-reactive materials. The low temperature avoided vaporization of oils, greases and waxes used for sealing and minimized reaction of the deposited film material with gaseous contaminants.

Thermal evaporation, on the other hand, is a high-temperature process where the radiant heat from the vaporization source heats the chamber and associated seals. Gaseous contaminants react with the molten source material, as well as the depositing film material. After about 1930, with the advent of better seals, better vacuum pumps and evaporation from tungsten filaments (Ritschl, 1928; Strong, 1929), most films were deposited by thermal evaporation. Ruhle described the use of an electron beam for thermal evaporation in 1940, but e-beam evaporation for vacuum coating did not become commonplace until the early 1950s. In 1938, Strong published his book, *Procedures in Experimental Physics* (Prentice-Hall), which discussed many aspects of vacuum technology and film deposition of that period.

Deposition of chemically reactive materials in a partial pressure of a reactive gas can produce films of a compound material (reactive deposition), but early films formed this way were of poor quality. Reactive evaporation was first reported by Soddy in 1907, and reactive sputter deposition was studied by Berraz in 1933. Also in 1933, Overbeck advanced the idea that oxide films could be deposited for optical coatings; numerous papers on the subject followed.

In 1930, Pfund evaporated metals into a poor vacuum to form very fine particles by gas phase nucleation (gas evaporation). A layer of ultrafine particles of gold (black gold "smoke") is still used as a very efficient infrared-radiation absorber. This technique is used today to form "nanoparticles" of a variety of materials.

After the 1930s, the primary disadvantage of sputtering was that most materials of interest could be deposited by thermal evaporation faster and cheaper. The fundamental phenomena of sputtering was studied by Guntherschutzer in the 1920s and 1930s, who established that the vaporization by sputtering was non-thermal process caused by momentum transfer from high-energy bombarding ions. An effect that later had a major impact on sputtering was the use of magnetic and electric fields to confine electrons, which was reported by Penning in 1936. In the late 1960s and early 1970s, the "Penning effect" was used to enhance the ionization in the low-pressure plasmas utilized for sputtering (magnetron sputtering). Resurgence of sputter deposition came in the early 1970s with the advent of various high-rate magnetron sputtering configurations.

Theories on the nucleation of depositing atoms on surfaces began with Frenkel in 1923. It was not until diffraction of electrons passing through a thin film was discovered by Thompson in 1928—and appropriate analytical techniques were developed—that the use of transmission electron microscopy (TEM) was applied to atomic nucleation by Basset, Menter and Pashley (1959). Before the 1930s, it was known that the properties of a material formed by vacuum deposition could vary significantly from the properties of the material in wrought form. Around 1935, scientists began studying the growth morphology of vacuum-deposited films using optical microscopy (Andrade, 1935; Da & Martindale, 1935). It was not until about 1965 that the development of the scanning electron microscope (SEM) allowed comprehensive structure-morphology studies of thick, atomistically deposited coatings.

The era of consumer use of vacuum coating technology began in the mid-1930s when three developments led to its rapid expansion. The first was the deposition of antireflection (AR) coatings on glass lenses. The second was the discovery of the self-healing effect in zinc-metallized paper capacitors used in electronics, and the third was the development of aluminum metallization for telescope mirrors.

Naturally formed and chemically formed AR coatings on optical lenses had been known for some time prior to the 1930s (Fraunhofer, 1817). Vacuum-deposited AR coatings allowed the use of better AR-coating materials for single-layer AR coatings (Strong, 1936; Bauer, 1934). In 1939, Cartwright & Turner reported the use of two-layer AR coatings and patented the use of MgF_2 for AR coatings in 1940. A common way of depositing the AR films was to initiate a glow discharge in the deposition chamber and begin the evaporation 10 min or so after the glow had been extinguished—this was their vacuum gauge. The glow discharge in air also cleaned the glass substrates (Bauer, 1934; Strong, 1935) and desorbed vapors from the chamber walls (Campbell, 1921). Film thickness was determined by visually observing the color change of the transmitted or reflected radiation. Optical interference measurements of film thickness were first made by Wiener in 1897, but it was not until after the War that optical interference measurements were used for *in situ* process monitoring and control in optical coating systems.

Web coating is a deposition process whereby a film is deposited onto a roll of flexible material (web) that is unrolled and re-rolled in a vacuum (web-coating or roll-coating). Web coating was used to sputter-deposit silver on cloth (Germany, 1933) and gold on glassine (waxed paper) to make foil (Kurz, 1934; Whiley, 1934). Metallized paper, using thermal evaporation, was an important material for making electrical capacitors for electronic applications. It was found that if arcing took place in a zinc-metallized paper-foil capacitor, the zinc film melted away from the discharge path and did not create a short (Bosch Co., 1935). This "self-healing" effect was important to making paper capacitors on a commercial scale.

Before 1930, reflective surfaces on mirrors were primarily produced by chemical reduction in an aqueous solution to form a silver coating, and sputtering was used to deposit other mirror materials, such as platinum (Bureau of Standards Circular #389). In the mid-1930s, aluminum metallization by thermal evaporation in vacuum for astronomical mirrors had been well developed (*e.g.*, J. Strong aluminum-metallized the 100-in. Palomer telescope mirror in 1935 using multiple evaporation filaments). This rapidly led to aluminum reflector films in sealed-beam headlights (Wright, 1937), which first appeared on production automobiles in 1940.

By the end of the 1930s, small contract coating businesses began to emerge in the U.S. One of these, Evaporated Metal Films of Ithica, NY, founded in 1936, is still in business and is being run by the descendents of the founder. Many large optical companies began their optical coating departments during World War II. P&SF