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Application of Vacuum Coating Technology

A vacuum is an environment where the gas pressure is less than the ambient. A plasma is a gaseous environment in which there are enough ions and electrons for there to be appreciable electrical conductivity. Vacuum coating is the deposition of a film or a coating in a vacuum (or low-pressure plasma) environment. Generally, the term is applied to processes that deposit atoms (or molecules) one at a time, such as physical vapor deposition (PVD), low-pressure chemical vapor deposition (LP-CVD) or plasma-enhanced CVD (PECVD).

In PVD processes, the material being deposited comes from the vaporization of a solid or liquid surface. In CVD and PECVD processes, the material being deposited comes from a chemical vapor precursor species that is decomposed by reduction or thermal decomposition in the gas and on a hot surface.

In some cases, the material being deposited reacts with the gaseous environment or a co-deposited species to form a film of a compound material such as an oxide, a nitride, a carbide or a carbonitride. In CVD processing, the use of a plasma to fragment the chemical vapor precursor in the vapor phase allows the decomposition or reduction processes to proceed at lower temperatures than with thermal activation alone.

PECVD can be performed at pressures as low as those used in PVD processing (low-pressure PECVD or LP-PECVD), where the precursor vapor is mainly decomposed in the plasma. In some cases, a hybrid deposition process of PVD and LP-PECVD is used to deposit alloys, composites or compounds. An example is the metal carbonitrides

where the carbon comes from a chemical vapor precursor such as acetylene—the nitrogen from a gas—and the metal from evaporation, sputtering or arc vaporization of a solid or liquid surface.

Applications

Electrically Conductive Films

Metal films are the most common electrical conductor films. The metal films may be used as “blanket” metallizations, which completely cover the surface or can be formed into discrete conductor lines (“stripes”) by masking the substrate during deposition, or by subsequent photolithographic etching processes. Conductor lines are used in hybrid microcircuit technology and in the manufacture of semiconductor devices. Often, the electrical conductors are multilayer films (stacks) where each layer has a function. For example, the conductor film stack might have the composition: glass-Ti-Pd-Cu-Au. The Ti is the “glue” layer, the Pd gives corrosion resistance, the Cu is a good, inexpensive electrical conductor and the Au gives corrosion protection. Deposited metal conductors in “vias” are used in establishing electrical contacts between different layers in semiconductor device manufacturing. Blanket metallization is used to provide electromagnetic interference (EMI) and radio frequency interference (RFI) shielding on structures such as the plastic cases for cellular phones, electrodes for rigid and flexible capacitor electrodes and surfaces for radar “chaff.”

Metal nitride, carbide and silicide films are generally electrically conductive (Si_3N_4 and AlN are important exceptions). In some applications, films of these refractory

materials are used to provide diffusion barriers between materials. In semiconductor metallization, for example, aluminum or gold electrode material will diffuse into the silicon during subsequent high-temperature processing. An electrically conductive titanium nitride film deposited on the silicon surface before the metal electrode is deposited will prevent the diffusion. Metal nitrides, such as titanium nitride (TaN), are used as thin-film resistor materials. Generating stable, electrically conductive, non-rectifying, metal-semiconductor contacts of conductive metals or compounds is an important aspect of semiconductor device fabrication. Non-transparent, electrically conductive oxides, such as Cr_2O_3 , PbO and RuO_4 , are used as electrodes in high-temperature oxidizing atmospheres.

Superconductors are materials that have close to zero electrical resistivity below some critical temperature (T_c). Low- T_c ($<10\text{ K}$) superconductors are often metals. A typical high T_c ($>50\text{ K}$) superconductor material is a mixture of oxides (Y-Bi-Cu oxides or YBCO). High- T_c superconductor thin films are often deposited by laser ablation in a vacuum.

Transparent Electrical Conductors

Transparent conductive oxide (TCO) films, such as In_2O_3 , SnO_2 , ZnO and an alloy of indium oxide and tin oxide (ITO), have numerous applications—such as heaters on windows for defrosting, antistatic coatings on display screens, electrodes on flat panel displays and electro-chromic devices, and electrodes on both flexible (resistive screen) and rigid (capacitive screen) touch screens. Electrical resistivity for the TCO films can vary from greater than 1,000

ohms per "square" to less than 10 ohms per "square" with good optical transmission.

Electrical Insulators

Electrically insulating films are used to electrically isolate conducting components in semiconductor devices, and as a dielectric layer in capacitors. Common insulator film materials are SiO_2 , Al_2O_3 , Ta_2O_5 , Si_3N_4 and AlN . Interposing a thin oxide film between a metal film and a semiconductor allows the formation of the technologically important metal-oxide-semiconductor (MOS) semiconductor device. Thick coatings of SiO_2 , with its low coefficient of thermal expansion, can be rf sputter-deposited. Insulating layers of SiO_2 , Si_3N_4 and glass are deposited by PECVD for encapsulating conductor stripes in semiconductor processing.

Optical Films

Optical films, usually multilayer film "stacks," are films that affect the optical transmission or reflection of a surface. They are generally alternating layers of materials having high (Ge, Si, TiO_2 , ZrO_2 , SiO_2 , CeO_2) and low (MgF_2 , SiO_2) indices of refraction. A major application is the antireflection (AR) coatings on lenses. Optical film stacks can be used as optical filters. Neutral density or gray filters reduce the light intensity equally for all wavelengths: broadband filters affect the transmission of radiation over a wide wavelength range, while narrow or monochromatic filters affect transmission over a very narrow wavelength region. An example of a broadband filter is an "edge filter" that "cuts off" the UV emitted by a mercury vapor lamp. The color filters used in photography and in optical projectors are examples of narrow-band filters. Some film stacks are a special type of optical film that has a color related to the angle-of-observation. These films are called optically variable image displays (OVIDs) or holographic imaging. These OVID films are used as security devices to prevent counterfeiting. These films are an outgrowth of the interference-colored films used for decorative films and, when pulverized, as pigments.

Thermal Control Coatings

The composition of the thermal control coatings on windows differs

with the end result desired. If the objective is to keep solar radiation from entering through the window, a multilayer film of glass- TiO_2 -Cr- TiO_2 may be used (solar control coating). If the objective is to keep heat in the room, a thin film of silver can be used to reflect 85–95 percent of the low-temperature infrared radiation back into the room (low-E coating). One such "double-E-coating" is glass- ZnO -Ag-(Ti)- ZnO -Ag-(Ti)- ZnO - TiO_2 . The ZnO provides an anti-reflective coating.

Other types of thermal-control coatings are used to absorb solar radiation (solar absorbers). Some coatings adsorb solar radiation without emitting infrared radiation (selective solar absorbers), while others have a high emissivity to enhance cooling by radiation. Thermal barrier coatings are used to reduce the thermal transport from a hot environment to the substrate. Zirconium oxide (ZrO_2) stabilized with CaO, MgO and/or Y_2O_3 is used as a thermal barrier coating on aircraft engine turbine blades.

Reflector Coatings

Metal films are widely used for reflector surfaces. Silver is often used when corrosion is not a problem, such as for "back-surface" mirrors. Aluminum can be used either as a front-surface or back-surface reflector. Aluminized front-surface reflectors, such as headlight reflectors, are often over-coated with protective polymer film (topcoat). Chromium is used on front-surface reflectors when corrosion is a problem, even though its reflectivity in the visible is not as good (60%) as that of aluminum (>90%). Reflector films are used in numerous commonly encountered applications, such as on compact discs for video and music storage, lamp reflectors and visual mirrors, such as the rearview mirror for cars. In some cases, multilayer films, similar to multilayer optical films, are used to selectively reflect certain wavelengths and not others. Examples are "cold mirrors" that reflect the visible radiation but not the infrared wavelengths, and "heat mirrors" that reflect the infrared but not the visible. Heat mirrors are used to raise the internal temperature of halogen lamps. Cold mirrors are used to reduce heating by stage lighting.

Packaging

Barrier coatings are used on flexible polymer films and paper for food packaging to reduce the water vapor transmission rate (WVTR) and the oxygen transmission rate (OTR) through the paper or polymer film. The most common vapor barrier coating material is aluminum, which is deposited on rolls of polymer film (web), then supplied to "convertors" that fabricate the metallized film into the packaging. In some cases, the metal coatings are deposited on a surface, then transferred to the packaging film, often by "hot stamping." Aluminum films are used on polymer helium-filled balloons to reduce the loss of helium. Transparent vapor barrier coatings are desirable in any instances. Layers of SiO_2 , by reactive evaporation and PECVD, and composite coatings of (SiO_2 :30% Al_2O_3) by e-beam co-evaporation are used to form transparent barrier layers. The composite coating material is more dense and flexible than the SiO_2 or Al_2O_3 deposited material alone.

Decorative & Decorative/Wear Metallization for strictly decorative purposes is a large market. Applications vary from coating polymer webs—which are then converted to decorative use, such as with balloons and labels—to metallization of 3-D articles, such as sports trophies, zinc die cast and molded polymer decorative fixtures, and cosmetic containers. These coatings often consist of a reflective aluminum coating that is deposited on a smooth base coat, then over-coated with a dyed lacquer to give the coating the desired color and texture, and also some corrosion and wear resistance. In some applications, in addition to the decorative aspects of the coating, the coating is required to withstand wear. Titanium nitride (TiN) is gold-colored and titanium carbonitride (TiC_xN_y) can vary in color from gold to purple to black, depending on the composition. Zirconium nitride (ZrN) has the color of brass and is much more wear- and scratch-resistant than brass. Decorative/wear coatings are used on door hardware, plumbing fixtures, fashion items, marine hardware and other applications.

Hard Coatings

Hard coatings are often called metallurgical coatings and are a type

of tribological coating. The hard coatings are used to increase the cutting efficiency and the operational life of cutting tools, and to maintain the dimensional tolerances of components used in applications where wear can occur, such as injection molds. In addition, the coatings can act as a diffusion barrier where high temperatures are generated by motion between surfaces, or corrosion protection in aggressive environments.

There are various classes of hard coating materials. They include: ionically bonded metal oxides (Al_2O_3 , ZrO_2 and TiO_2), covalently bonded materials (SiC , B_4C , diamond, diamond-like carbon [DLC], TiC , AlN , CrC , mixed carbide, nitride and carbonitride compound alloys, and cubic boron nitride) and some metal alloys (CoCrAlY , NiAl , NiCrBSi). In some cases, the hard coating may be a layered structure.

Hard coatings are also used to minimize fatigue-wear, such as is found in ball bearings. Wear-resistant coatings may also be applied to surfaces where there is a light or periodic load. For example, hard coatings are deposited on plastics to improve scratch-resistance. Applications are on molded plastic lenses and plastic airplane canopies. In some cases, the wear coatings, such as SiO_2 or Al_2O_3 , may be applied to already hard surfaces—such as glass—to increase the scratch-resistance. DLC coatings, for example, are being used on new razor blades.

Electrically Active Films

Doped silicon films are used in semiconductor devices, and these films are often deposited by a very sophisticated PVD evaporation technique called molecular beam epitaxy (MBE), or the CVD technique of vapor phase epitaxy (VPE). Amorphous silicon for solar cells is deposited by PECVD on webs and rigid substrates.

Electro-chromic films, which change optical transmission on the application of a voltage, depend on the diffusion of a mobile species in the film under an electrical field. Films of a material such as selenium can become electrically charged when exposed to light. Such films are used to hold the toner in photocopying machines.

Magnetic Storage Media

Magnetic materials are classified as “hard” or “soft,” depending on how hard it is to magnetize, demagnetize or “switch” the magnetic field. Soft magnetic materials, such as the permalloys (Fe :40-80% Ni) and garnet ($\text{Y}_2\text{Fe}_5\text{O}_{12}$) are used in memory storage devices where the data is changed often. Hard magnetic materials such as Fe_3O_4 , Co:Ni:W , Co:Re , Gd:Co and Gd:Tb:Fe are used in more permanent recording media (e.g., audiotapes). Various techniques are used to define the magnetic domains that act as the storage sites.

Corrosion Protective Coatings

Protection from an aggressive chemical environment can be accomplished in several ways. The surface can be coated with an inert material; with a material that forms a protective surface after reacting with the environment; or with a material that will be sacrificially removed to protect the underlying material. Tantalum, platinum and carbon are inert in many chemical environments. Carbon coatings, for example, are used on metals that are implanted in the human body to provide biocompatibility.

Chromium, aluminum, silicon and the MCrAlY (where M is Ni , Co , Fe) alloys will react with oxygen to form a coherent protective oxide layer on the surface. If the metal ions (Fe , Cu) diffuse more rapidly than the oxygen through the oxide, a thick oxide will form on the surface. If the oxygen diffuses more rapidly through the oxide than metal ions (Al , Si , Ti , Zr —the “valve” metals), oxidation will occur at the interface and a thin oxide will be formed. The MCrAlY alloy coatings are used as protective coatings on aircraft engine turbine blades. Cr:Pt coatings are used as protective coatings on razor blades. Cadmium, aluminum and Al:Zn alloys are used as galvanic sacrificial coatings on steel. Vacuum Cd -plating has the advantage over electroplated cadmium in that there is no possibility of hydrogen embrittlement of high-strength steel when vacuum coating processes are used.

Solid Film Lubricants

NASA pioneered the use of vacuum-deposited, thin-film solid lubricants. The lubricants are of two types: the

low-shear metal lubricants—such as silver and lead—and the laminar-shearing compound materials—such as MoS_2 . The low-shear metal lubricants are used in high-torque applications, such as on the bearings of the rotating anodes in X-ray tubes. The low-shear compound materials are used in mechanical-bearing applications in vacuum, and where liquid lubricant “creep” can be a problem. Because only a very thin film is needed for lubrication, the application of the solid lubricant film does not result in significant changes of dimensions.

Freestanding Structures

Freestanding structures are made by depositing a coating on a surface (mandrel), then separating the coating from the mandrel surface or dissolving the mandrel. The technique is useful for fabricating very thin structures, complex surfaces, or foils or sheets of materials that are hard to deform by rolling. Examples are beryllium windows used for X-ray transmission, boron thin-wall cones for high-frequency audio speakers, and Ti-V-Al metal alloy foils.

Base Coats for Electroplating

Materials that are difficult to electroplate because of rapid oxide formation can have an adherent base coat applied by PVD processes, and then the coating can be built up by electro-deposition. Examples are plating on titanium, uranium and zirconium, where a base coat of a material like nickel or copper is applied by a PVD process before the electroplated coating is built up.

Polymer Films

There is increasing interest in depositing polymer films in vacuum. These films can be formed by condensation of a monomer, followed by e-beam or UV curing to polymerize the monomer. Organic and inorganic films can be formed by plasma polymerization of a monomer. The monomer precursor can yield a carbon-, silicon- or boron-based polymer material often containing hydrogen, chlorine or fluorine. The films can be partially oxidized by having some oxygen in the plasma. Fluorine-containing films are used to form hydrophobic surfaces. P&SF