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PVD Technology: A Tutorial

The deposition of thin film layers from the vapor phase is accomplished through several techniques. We review the physical vapor deposition (PVD) techniques and equipment that are in common use in the high-volume production of coatings that find application in the optical, display, decorative, tribological, and energy-generating /saving industries. Specific PVD processes and coating materials have been developed and optimized for the specific application. Coating materials are classified as dielectric compounds, metals, alloys, or mixtures. The same material can exhibit different optical, electrical, and mechanical properties depending on the deposition process. Titanium oxide is a unique example of a metal oxide compound that, depending on deposition process parameters, can be made into film layers that are: transparent, electrically conductive, chemically reactive to light and bio-agents, chemically inert, or exhibit spectrally selectively absorption. The dependent parameters are starting composition, oxidation state, crystalline structure and packing density.

PVD techniques used in production are basically two in nature: thermal evaporation by resistively heating or by using an electron-beam heating, and sputtering, a non-thermal process. Variations and additions are made to the basic PVD techniques to permit different coating materials and substrate types to be accommodated. Process additions designed to alter the growth nano-structure or composition of the film through control of the dependent variables listed above include bombardment of the growing film by high energy inert- or / and reactive ions, substrate heating, atmosphere composition and partial pressure, rate, and vapor incidence angle. A further important variable contribution to the nucleation and self-assembling growth structure of the condensing adatoms, that we have discussed frequently, is the condition — both chemical and physical — of the substrate surface.

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Visit www.cerac.com for product data sheets on many of the materials listed in this edition.

Table 1. Sputtered materials: targets and reactive gas composition, and common applications.

Deposited Material	Target	Plasma Gas	Coating Application
Al_2O_3	Aluminum	O_2	Optical, tribological
SiO_2	Silicon	O_2	Optical low n
Si_3N_4	Silicon	N_2	Electronic insulator
SiO_xN_y	Silicon	N_2 & O_2	Electronic insulator
SiOx	Silicon	O_2	O_2 and H_2O barrier
SiC	Silicon	C_xH_y	Tribological
Si	Silicon	Argon	Optical IR, high n
Ta_2O_5	Tantalum	O_2	Optical high n
TiO_2	Titanium	O_2	Optical high n
Nb_2O_5	Niobium	O_2	Optical high n
ZrO_2	Zirconium	O_2	Optical high n
Y_2O_3	Yttrium	O_2	Optical mid n, tribological
HfO_2	Hafnium	O_2	Optical, electronic
AZO	Al:ZrO_2	O_2	TCO
ITO	Sn:In_2O_3	O_2	TCO
TiN, CrN, ZrN, BN, HfN	Ti, Cr, Zr, B, Hf	N_2	High temperature tribological
TiC, HfC, WC, TaC	Ti, Hf, W, Ta	C_xH_y	High temperature tribological

Evaporation Processes

Resistance-heated (RH) sources are constructed of metal containers that can be open and boat shaped, or closed as with a baffle box and exit opening. The type of source used, and its metal (or surface lining) depends on whether the material melts when heated or sublimes. Refractory metals (Ta, Mo, W) and ceramic or graphite crucibles are used to form sources. Since most fluoride compounds melt, an open container is often used, and evaporation proceeds from a large melted area. If the material sublimes, as do sulfide and selenide compounds and some oxide compounds, a baffled box source is used that emits the vapor. Materials that require high temperature (>~1000° C) to vaporize, such as refractory oxide compounds and refractory metals, require the higher temperature of a focused electron beam source (E-B). Nearly any material that can be evaporated by RH can be evaporated by E-B; however, the power (high voltage) must be lowered for fluoride compounds for example, to prevent dissociation. Metals such as aluminum, gold, and copper have lower evaporation temperatures than dielectrics and RH is generally used. Oxide and nitride compounds generally require the presence of a reactive atmosphere to recompose the compound or to establish the correct composition of the film. A partial pressure of the appropriate gas, deposition at the appropriate rate and substrate temperature all influence film composition. More information is contained in the Photonics Handbook article, "Materials for Optical Coating Deposition: a Wide Selection is Available", and accompanying Data Tables that provide deposition parameters for specific materials [1]. Technical data sheets are also available on the CERAC web site [2].

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PVD is a line-of-sight process, where the vapor stream profile is approximately a cosine distribution, provided that the mean free path (MFP) of the evaporant molecules is larger than the scattering depth of the residual atmosphere. At a pressure of 1 e-05 Torr (0.01 Pa), the MFP is 1 m. The distance between the substrate and source must be less than the MFP to prevent loss of rate due to excessive scatter by the resident gas background. To achieve uniform thickness deposition over a large substrate area requires special geometrical considerations. The substrates are typically in motion through the plume distribution to provide random time and area sampling. Substrate tooling is rotated in planetary motion to accomplish uniformity. Various shapes of occluding masking might be added to fine tune the thickness uniformity. Monitoring of thickness can be done indirectly using a quartz crystal oscillator or directly with an optical monitor. Coating systems are now available that can automatically execute a multilayer coating design and control the thicknesses through the monitoring system.

Metals and sub-oxides can be starting materials for depositing oxide compounds in reactive deposition. Stoichiometric composition of the oxide can be achieved, but the mechanical properties of the layer are poor because the nano-structure is not dense, but instead contains a large volume of voids. Arriving adatom energy is a few tenths of an eV, and competes with the surface free energy of the substrate as affected by the presence of gas and other contaminant bonds. Low kinetic energy results in low surface mobility and island-form condensation instead of uniform surface coverage and growth. Ionization of a partial pressure oxygen or of the evaporant species produced in an energetic plasma or with the use of an ion source for ion-assisted deposition (IAD) supplies higher energies. The IAD source ionizes and accelerates argon and oxygen ions toward the substrates. Reactive oxygen completes the oxide compound, and energetic Ar+ ions compact the growing film to increase its packing density. Ion energies of hundreds of eV are possible with IAD sources. In some processes, the substrate or its holder can have a bias with respect to the source that accomplished the same purpose, but at lower energies.

Other forms of PVD for optical applications include pulsed laser deposition (PLD) and atomic layer deposition (ALD). PLD has the advantages of preserving the composition of the starting material for a large variety of compositions. It has not found use in high volume production due to small area coverage and expensive laser accessories. ALD is not based on evaporation, but on chemically reacting precursor gases under temperatures of 200° C or hotter. It has the advantages of producing dense films and consistent repeatable composition and predictable thickness without the need for real-time monitoring. The deposition rate is extremely slow, however.

Sputter Deposition

Evaporation processes are based on vaporizing a material by heating it beyond its melting or subliming temperature. In sputter deposition, atoms of materials are dislodged by impact of ions, atoms or other particles that are created in an energetic plasma when the kinetic energy of these particles exceeds the binding energy of the target surface. The basic sputter technique is configured as a diode with a plasma discharge between the anode and cathode. Figure 1 shows the basic configurations for sputtering techniques. The cathode target material can be of nearly any composition, for example, insulators, metals, and alloys and can be sputtered to deposit solid thin films of predetermined composition. Oxide and nitride compounds can be reactively sputtered from metal targets using a DC plasma; targets composed of dielectrics, ceramics, and targets with low electrical conductance are sputtered using one of the many variations of RF sputtering. Table 1 (page 1) lists commonly sputtered films used in a variety of applications, and their target and gas plasma components. Argon is generally the working gas and a reactive component gas is added to determine the final composition of the sputtered film.

The addition of concentrated magnetic fields near the target increases the deposition rate and distribution ("magnetron sputtering") by increasing the density of the plasma and power density on the target surface. Energies are 1-10 eV for classical sputter deposition, about a factor of 10 greater than R-H or E-B energies. A beneficial consequence is that sputtered films are denser than evaporated films; a negative is higher compressive stress that for some applications needs to be reduced through process optimization. Alloys of materials can be sputtered with preservation of the starting composition, unless the sputter yields of the two materials differ significantly from each other. In spite of such differences, the target can be conditioned to control the composition of the deposited film.

Recently, high-and mid- frequency pulsed power is used to generate high sputtering rates, and dual magnetrons have been configured to mix two different materials to create films with entirely new properties. Alternatively, in the ion beam sputtering technique (IBS), a remote source producing ions of energies of hundred's is directed toward the target. The energy and mass of the impacting particles determines how many target atoms are sputtered. Because the sputtering process is very repeatable, thickness control is done by controlling power and deposition time. When sputtering from targets that react with oxygen or nitrogen, greater stability of rate and composition is achieved using an optical emission controller that maintains a chosen oxidation state as indicated by its line emission intensity.

The pressure in the sputtering chamber is three orders of magnitude higher than that for evaporation, consequently scatter due to collisions is very high and spacing between target and substrate is reduced to a few centimeters. A beneficial consequence of the scatter at the high pressures is that the distribution can more easily be made to conform to non-planar shapes. Discussions containing more detail on the many aspects of sputter deposition processes have appeared in previous CMN issues [3].

Summary

This brief tutorial is intended to introduce the novice to thin film deposition by the basic PVD techniques. The state of the technology of deposition equipment and coating materials is well developed, but minor variations continue to improve both. Accurate self-controlled coating systems for volume production of coated items are now available through commercial order. This has been made possible through the development of stable coating materials and process monitoring.

References

1. The Photonics Directory Handbook published by Laurin Publishing.
2. www.cerac.com.
3. CERAC Coating Material News V2, Issue 4 (1992), V6, Issue 3 (1996), V8 I4 (1998), V9 I2 (1999), V11 I4 (2001), V12 I 1 (2002), V12 I2 (2002), V13 I1 (2003), V13 I 4 (2003), V16 I2 (2006)

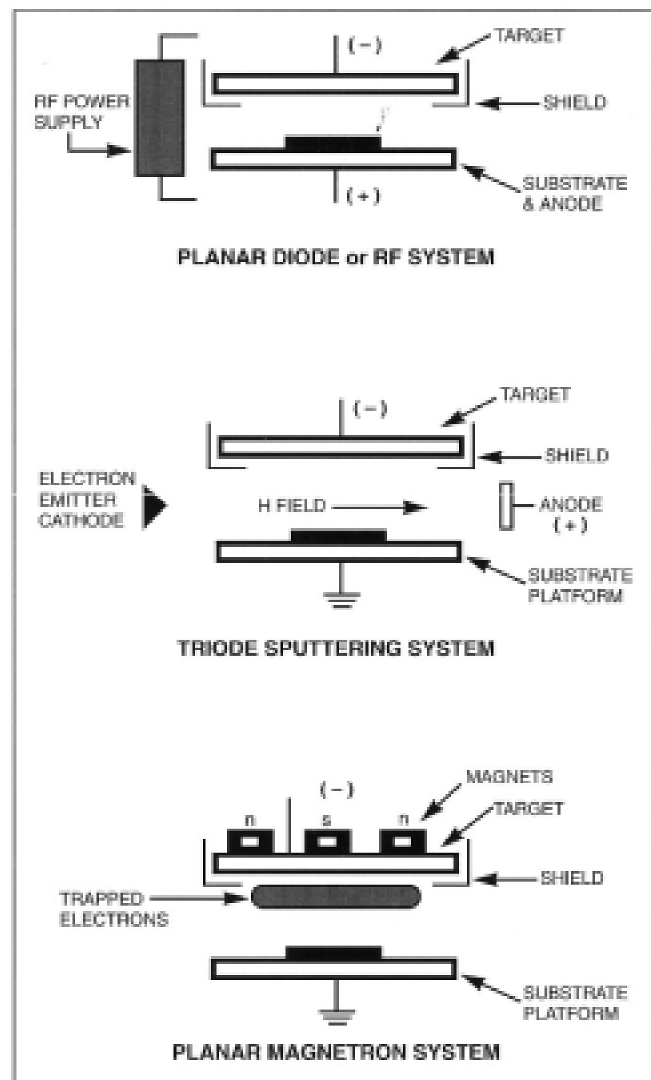

Figure 1. Sputtering Systems

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