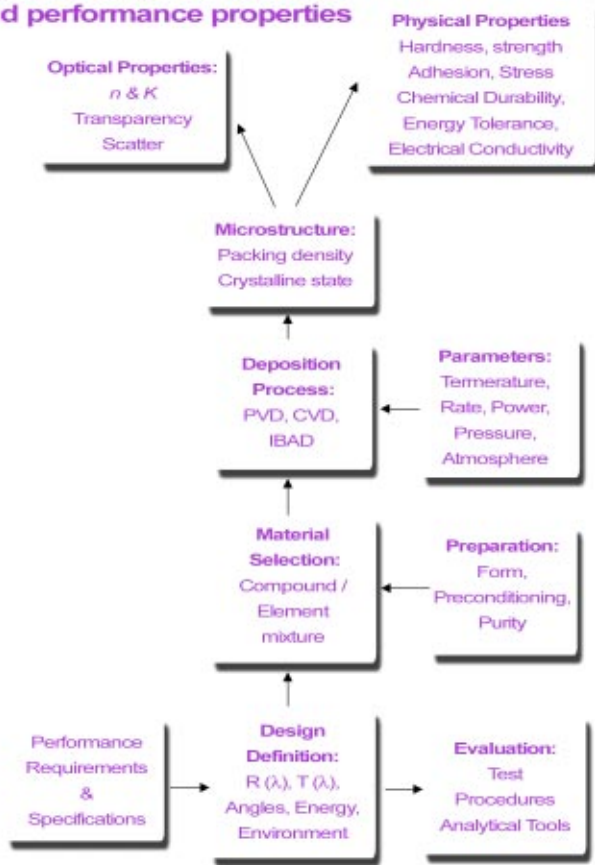


Tutorial on Properties of Thin Film Layers for Optical Applications - PART II

The June, 2003 issue of *Coating Materials News* (CMN) presented an outline of the tutorial subject matter that forms the details of the coating process; in this issue we continue discussion of the items in that outline. Figure 1 illustrates the interdependent steps involved in the process of depositing optical coatings [1]. For example, the choice of coating material is influenced by design requirements that include the following properties: optical, mechanical, chemical, energy density, and electrical. Material preparation and form are selected according to the available or preferred deposition process and its parameters. The latter are responsible for the microstructure that, in turn, determines the optical and mechanical properties of the film layer.

Figure 1: The thin-film layer deposition process and performance properties



The Deposition Technology

We had previously broken the technology for optical applications into three categories:

- Characteristic properties of materials in their thin-film state
- Deterministic quantities as related to film microstructure
- The influences of the deposition parameters on film properties

The discussion begins with the material selection and the characterization of deposited layers. The intended application of the coating will contain the specification of the transmission or reflection wavelength range, the mechanical and durability values and their evaluation as defined by US MIL Standards or ISO international standards, and perhaps laser damage threshold testing. The spectral transmission range is determined by the absorptions of the individual coated layers. The extinction coefficient, k , must generally be < 0.001 , but exceptions to this rule-of-thumb exist for low and high-power applications where k can be $>$ or < 0.001 , respectively. Titanium dioxide is a commonly used material for wide-band AR and some filter coatings for the visible region because it has a high refractive index and can be sputter- or e-beam deposited. However, TiO_2 exhibits sufficiently high band-gap absorption below ~ 475 nm that significant losses in transparency affect its performance, especially in multi-layer designs. Titania also exhibits water-band absorption near and above 900 nm, making it unusable for WDM and other high layer count filters and laser coatings. Alternatively Ta_2O_5 does not suffer from these problems and is the recommended substitute for more demanding coatings that operate in the range ~ 400 nm to ~ 2000 nm. Narrow-bandpass Vis-NIR filters and WDM filters in the 1550 nm region are composed of tantalum and silica layers, the latter typically

Physical and Chemical Durability

Among factors that limit the mechanical and chemical durability of thin film materials are the layer packing density and morphology. These structural factors are influenced by the deposition technique. Layer composition is, of course, of high importance if the desired index and transparency are to be obtained. Oxide-compound deposition requires the presence of excess oxygen, often in activated species, to compensate for oxygen loss or to reactively compose the final desired oxidation state. Fluoride compounds require high vacuum to achieve high purity and low absorption. Thus the production of a coating design that includes oxide and non-oxide compounds without creating cross contamination requires a more complicated coating procedure. It should be apparent even from this limited discussion that all the parameters involved in growing thin film layers are interrelated, and that the development of a coating for a particular application is a complex multi-step process.

The mechanical properties of a coating, namely adhesion, hardness, and abrasive wear resistance, are determined by the microstructure morphology and the nature of chemical bonds. Films with low packing density are structurally weak, exhibit poor wear resistance, and absorb and desorb water and other gaseous materials. Packing density is determined by the energetics of the deposition process and to some degree the nature of the chemical bonding that is established within the layer. Sputtering, ion plating, and the inclusion of a supplemental ion source are high-energy deposition techniques that produce compact layers. CMN has reported on an economical alternate method for achieving dense, stable layers, namely through the development of mixed compound materials available from CERAC. In this approach, low concentrations of foreign ('dopant') materials in the deposited layer discourage the growth of large grain morphology and favor amorphous or small grain structures, both of which are dense by nature. These film layers exhibit extraordinary stability to moisture-induced spectral (changing index) shifts and greater layer smoothness (lower scatter) and better strength (cohesion) and adhesion. Mixed-material films having predetermined fixed or controllable refractive index can be grown by co-evaporation or co-sputtering sources with high- and low-indices, or by varying the reactive gas composition. An application of this advanced deposition technology is the production of narrow-band filters or graded-index AR coatings. Control of the material composition requires continuous monitoring and control of rates and gas composition.

Mechanical Stress Issues

Mechanical stress effects can assume a variety of forms, including increased optical scatter from microscopic crazing, macroscopic cracking, and partial or complete adhesion failure between layers or at the substrate. Stress associated with a thin film layer can originate within the layer or at the layer interface with another material. In the later case, differences in thermal expansion coefficient need to be considered; similarly, differences in mutual chemical bonding can impose a structural mismatch. Therefore, it is important to select materials with compatible thermal expansion coefficients when possible, especially when the finished product is to be exposed to large or rapid temperature excursions. Because of this requirement,

the available selection of stable glasses provides more suitable substrate choices than fused silica, whose TCE is the smallest existing.

Generally a microstructure composed of large microcrystalline grains is in a state of higher internal stress than is an amorphous or small-grained microstructure. Such structure often exhibits a columnar growth form that tapers to smaller diameter from the bottom to top of the layer. This is form due to shadowing during layer growth, and represents a mechanically weak structure. Further, coarse grains can have large inter-grain spaces that are open to permeation of gas (water) vapor. Condensation of water on internal walls will change the stress

state, at times resulting in film crazing, cracking, or catastrophic breakage and adhesion separation. Deposition temperature is a parameter that influences the film morphology, particularly grain size. Temperature also affects the relative stress between coating and substrate, as noted above. Many oxide and fluoride coating materials require a substrate temperature near or greater than 200° C to achieve the desirable mechanical and optical properties we have been discussing. Their intrinsic layer stresses can be either compressive or tensile, depending on material and microstructure and substrate temperature. Metals generally are under tensile stress, while compounds can be of either nature. For example, ti-

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tania, alumina, and fluoride-compound films are generally in tension, while silica films are in compression. Thus the pair TiO_2 / SiO_2 can produce a low stress multi-layer within a certain substrate temperature range, generally lower than that required for single layers. Control of the stress nature can be exerted by the deposition process to some degree, with sputtering having the most versatility in controlling the sign of the stress through variation of pressure and power and at lower substrate temperature than E-beam or thermal evaporation. To add to the complexity of stress prediction and management, the intrinsic stress of some materials has been observed to change as a function of the following variables: water or impurity absorption at grain boundaries, layer thickness, crystalline state, and condensation incidence angle. Examples are, respectively, MgF_2 , ZnS and ZrO_2 . Silicon monoxide film stress can be altered from tensile to compressive by adding a partial pressure of water vapor during growth. The accumulation of impurity atoms or ions that are larger than the film atoms can reduce tensile stress. This is the premise behind the ability of 'doped' MgF_2 and products such as CIROM[®]-IRX and CIROM[®]-IRB to be capable of being grown to thicknesses far greater than the pure host materials. Thickness dependence is the result of morphological changes in columnar structure. Metals, especially inert examples, show less dependence on thickness than oxide compounds possess. Crystalline state changes can be caused by source temperature changes with time, as in the case of E-beam evaporation. Films grown at large incidence angles tend to have higher tensile stress and lower volume density.

Substrate Surface Preparation

Other factors that affect layer microstructure and its dependent properties are substrate surface condition. The preparation of the surface for deposition is different for glass, polymer, and semiconductor substrates. Surface conditioning consists of one or more of the following procedures: removing adsorbed molecular contamination that causes the surface to be chemically or electrically inert, generating reactive but incomplete chemical bonds in the substrate surface, increasing surface area, depositing a reactive layer that stimulates nucleation of the arriving adatoms, or establishing energetic physical bonding such as inter-diffusion mixing (sometimes attributed to mutual solubility). The adhesion mechanism with most metals is the formation of an interfacial oxide bond. This is especially applicable to reactive metals such as aluminum, titanium, and chromium. It is also true for oxide compounds of those metals, silicon oxides, and tin oxide and ITO. Metal that form hard oxide films also generate the strongest bonds to silicate surfaces because of the presence of oxide bonds in those surfaces.

Cleaning with the use of high-energy ions or with a reactive plasma accomplishes similar results. The reactive plasma might be a low-energy glow discharge or the discharge of a sputtering system. High energy transferred to the surface might physically scour condensed contaminants or chemically alter them. Surface bonds might be activated setting up a surface that initiates the nucleation of reactive compounds. Depending on the material to be deposited, the reactive plasma should contain oxygen for oxide compounds or nitrogen for nitrides. Different polymer substrate compositions require either reactant to produce surface bonds.

Deposition Rate Effects

Deposition and growth rate affects layer morphology and stress because it determines the concentration of included impurity atoms/molecules from the residual atmosphere in the coating chamber. These gases might be the ubiquitously present water from evaporation chamber tooling and walls or from the plasma gas composition in a sputtering chamber. IAD processes also raise the chamber

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CERAC Coating Materials News is a quarterly publication of CERAC, inc.
P.O.Box 1178
Milwaukee, WI 53201-1178
Phone: 414-289-9800
FAX: 414-289-9805
web: www.cerac.com
e-mail: marketing@cerac.com

Editor:

Russ DeLong
Manager, Advanced Technologies Group
CERAC, inc.

Principal Contributor:

Samuel Pellicori
Pellicori Optical Consulting
P.O. Box 60723
Santa Barbara, CA 93160
Phone/FAX: 805-682-1922
e-mail: pellopt@silcom.com

For a free subscription to CMN, please E-mail your name and address to marketing@cerac.com or send us a fax at 414-289-9805.

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Coating Materials News

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numbering >50 pairs. Silica is the low-index mate for multi-layer designs, as we see below.

Nearly all multi-layer coating designs will be optimum in terms of layer count and optical performance when the maximum index ratio between high- and low-index materials is used. More high-index materials are available than low-index, and the choices for the visible range are restricted to silicon dioxide ($n = 1.45$) and magnesium fluoride ($n = 1.36$) as the most commonly used stable compounds. Environmental instability, particularly abrasive wear resistance and water vapor interaction, limit the usefulness of other candidate low-index compounds, even in some cases fluoride compound layers.

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pressure above deep vacuum, supplying ambient gas. Some energetic plasma / ion or high substrate temperature processes reduce the percentage of included gases by driving them out of the film. A balance is reached, but some gas is still included in the pores of the film. High gas inclusion can lead to weak, unstable films. It can also influence grain size, tending to prevent large grain growth in some materials. In addition to mechanical influences, gas inclusion can detrimentally affect performance in the UV and in high-energy laser applications.

This has been a brief outline of the complex subject of optical coating deposition technology. The reader is

referred to past issues of CERAC *Coating Materials News* for greater detail on the topics addressed.

References

1. Reprinted from CERAC's article "**Thin Film Coatings: Applications and Materials**" in The Photonics Design & Applications Handbook, 2003 edition p. H-348; Laurin Publishing.