

## Coating Techniques and Influential Factors

### Deposition Science

A large variety of deposition techniques are available for the production of thin film layers for optical, mechanical, chemical, and decorative applications. Our readers are familiar with the common PVD techniques electron beam and resistively-heated evaporation as well as magnetron and ion-beam sputtering. The deposition technique chosen depends on several factors: the application (optical vs. mechanical, for example), the production volume capacity (batch vs. in-line), and the economics (equipment costs and lot size). We discuss the recommended combinations of materials and deposition technique in this edition.

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### Electron-Beam Evaporation

Because of its high evaporation rates relative to sputtering and the ability to evaporate refractory compounds as well as metals, e-beam evaporation is the most popular technique for many materials. This technique is especially appropriate for reactively depositing metal oxide compounds such as Titania, Tantalum, Hafnia, Alumina, Silica, etc. or corresponding metal nitride compounds. The starting material is often in a reduced oxidation state, lending some electrical conductance to the evaporating surface and thus enabling a constant rate free of arcing to be established. Highly insulating materials such as oxidized compounds can accumulate an electrical charge that results in arcing that can have two undesirable consequences: disruption of the rate, and emission of particulates. Depending on the preparation of the starting form, some oxide compounds melt, others sublime.

Evaporation proceeds in a partial pressure of oxygen to compose a fully oxidized film; the addition of energized ions (oxygen and argon in IAD) promotes the oxidation reaction. Reactive e-beam deposition is applied for all oxide compounds because in the process of evaporation, oxygen is released and removed by the vacuum system. Re-oxidation

can occur on the substrate surface or in the vapor stream either in proximity to the e-gun or in the path between source and substrate. Oxygen can be supplied near the e-gun, to the chamber volume away from the pump opening, or through an ion source. In the latter case, the oxygen is ionized and activated, thus promoting the oxidation reaction. Substrate conditions such as surface reactivity and temperature influence the recombination rate. At high background pressures, water vapor or residual gasses reside on the surface and thus compete for the substrate chemical bond. High substrate temperature or scrubbing with ions can remove some of the condensed gasses as a pre-cleaning step.

Nitride compounds that mostly find application in mechanical (tribological) and decorative color applications rather than optical applications can be deposited by evaporating the parent metal and then introducing activated nitrogen. Reactive sputtering of the metal in a nitrogen plasma is the preferred deposition method because of its speed and covering ability on non-planar surfaces.

High substrate temperature has other influences on film growth and microstructure: it can inhibit film

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## Mechanical Stress in Coatings

It is not possible to discuss materials and deposition processes without considering the mechanical nature of the film layer (in concert with its optical properties). We have covered some aspects of film stress in previous CMN articles, and refer the reader to recent discussions [2], and to publications by Georg N. Strauss [3].

Substrate temperature, deposition rate, deposition energy, microstructure, and environment all influence the intrinsic stress that a thin film experiences. The stress value generally increases with film thickness, but there are exceptions to this behavior. Thermal expansion coefficient differences influence the extrinsic stress value. Intrinsic stress that is tensile exerts a contraction force parallel to the substrate surface and can result in a concave curvature. The opposite is observed with compressive stresses that produce convex curvature of the coated substrate. Visible signs of the release of tensile stress are “mud flat” patterns where irregular pieces of the coating crack apart and might curl concavely with the edges lifted from the substrate. A film whose compressive stress force exceeds the bond to the substrate will delaminate from the substrate surface.

Generally speaking, fluoride compounds grow films that possess tensile stress. Metal-oxide films may exhibit either compressive or tensile stress, however, and this behavior is exploited to balance the opposing stresses and result in a low- or zero-stress multi-layer coating. The origin of film stress is not completely understood, but the growth mechanics model seems to provide basic insight into the problem. The

initial nucleation of the film material on the substrate is energy- and surface mobility-dependent. For conditions favorable for high adatom mobility, the following model is accepted. Adatoms first attach to the substrate and subsequent adatoms build islands around them. The attachment points might be surface defects, for example. As the film grows along the surface in two-dimensions, voids between the islands might not be completely filled, and as the film grows in thickness, columns with spaces between them dominate the microstructure, encouraged by self-shadowing. Stress begins as compressive and transitions to tensile as the islands coalesce and form discrete grain boundaries. Interaction between the surfaces of these columns is believed to result in tensile stress in the film. As film thickness increases, the columns (grains) grow, and large grain sizes produce low stresses, while the opposite is true for small grain sizes. As the film becomes continuous, the stress tends toward the compressive sign. This explains the observed reversal in stress sign with film thickness. For conditions of low surface mobility, the film retains a net tensile stress value.

External conditions can alter the stress balance. A common phenomenon is the absorption and desorption of moisture in a film whose packing density is relatively low. Control of film stress and stability requires control of the deposition parameters mentioned above, but two additional techniques are available. Both techniques apparently operate by discouraging or destroying the columnar growth preference. One technique was discussed in CMN many issues ago,

and consists of supplying foreign “contaminant” atoms to deactivate the forces between the columns by attaching to the grain boundaries. “Doping” materials with small percentages of compatible materials accomplishes this effect. CERAC’s CIROM®-IRX and modified  $MgF_2$  materials, for example are based on this phenomenon. These fluoride mixtures can be grown to greater thicknesses than the pure parent materials, and are amorphous with a high packing density.

The other approach is to bombard the growing film with energetic particles, either inert argon or reactive oxygen (or mixtures of both). The energy dissipated in the microstructure in effect breaks up the columnar crystalline growth tendency and can change tensile to compressive stress and even balance the resultant stress to zero.

Strauss tabulates the stresses for materials deposited by various techniques. Summarizing from his paper, silica films are generally in compressive stress with values that vary over a factor of 2 to >10 depending on process. Ion plating produces the highest compressive stress. Titania films are tensile from reactive evaporation, and compressive if sputtered. Alumina films are compressive unless, again, they are deposited by reactive evaporation. Tantalum and niobium films tend to be in compression.

Through experience, the optical coater learns the deposition conditions and layer combinations that minimize the resultant stresses within a coating and between the coating and the substrate.

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growth in the case of selenides and sulfides, or beneficially increase packing density and bond strengths in the case of fluoride compounds. These are but two factors that establish the so-called temperature-dependent “sticking coefficient”. Cooling the chamber walls or including a cooled surface area encourages the condensation of water vapor during evacuation, essentially increasing the sticking coefficient for water (cryo-pumping). When the chamber interior is exposed to the atmosphere, however, the walls ideally should be heated to discourage the collection of water vapor.

**Resistively Heated Evaporation**

While fluoride and sulfide / selenide compounds can be evaporated by e-beam, their evaporation temperatures are significantly lower than those for oxide compounds, and very low e-gun power must be used to avoid excessive rates and/or decomposition. Selenides and sulfides naturally dissociate during evaporation, and recombine at the substrate if conditions are favorable. E-beam evaporation is too aggressive for those compounds, and resistively heated sources are recommended. The same is true for fluoride compounds that generally melt and are best evaporated from an open boat source. Fluoride compounds do not dissociate unless exposed to high-energy ions. Therefore, they are not suitable for IAD or sputtering techniques unless the fluorine component is restored reactively from a supplied gas flow.

Coating designs that include combinations of layers of oxide and

fluoride compounds require both e-beam and resistively-heated sources. The oxygen supplied for the oxide layers must be pumped away and the pressure reduced to near  $10^{-6}$  Torr range for the fluoride layers. This is a lengthy procedure, but when the lowest possible reflectance is required for AR coatings for wavelengths between  $\sim 400$  nm and  $\sim 5$   $\mu$ m, for example,  $MgF_2$  is used as the outermost layer in place of  $SiO_2$  because the index of  $MgF_2$  is lower. For durability reasons and to avoid chamber contamination, the other layers for these wavelengths are oxide compounds (rather than ZnS or ZnSe).

Nearly all the commonly used metal oxide compounds absorb at wavelengths  $>8$   $\mu$ m, and ZnS or ZnSe are used as the high-index component at the longer wavelengths. The low index component will be a fluoride compound.

Recent editions of CMN can be consulted for further detail [1].

**References**

1. CMN: V11, Issue 4 Dec 2001; V12, Issue 1 March 2002.
2. CMN: V13, Issue 1 March 2003; V15, Issue 2 June 2005.
3. Georg N. Strauss, “Mechanical Stress in Optical coatings” in *Optical Interference Coatings* by N. Kaiser and H. K. Pulker, eds, Springer Series in Optical Sciences 88 (2003)

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