

*This issue of CMN is focused on materials properties. It begins by outlining the primary properties that are desirable in a typical optical coating material. A preliminary report on CERAC's latest material improvement – pre-melted titanium dioxide—is presented. These topics are followed by discussions on achieving mechanical and optical stability in selected coating materials, and on the theory of thin film growth.*

## What Properties Are Required in an Evaporation Material?

For a material to be suitable for evaporation and use in depositing thin films for optical applications, whether by resistance-heating or electron beam-heating, it must possess specific properties. As an illustration we have constructed a relative comparison listing of the properties of three fluoride-based low-index materials that are popular for IR coatings: ThF<sub>4</sub>, IRX<sup>TM</sup> and YF<sub>3</sub>. These materials exhibit high transparency that extends from UV to IR wavelengths, and are used in multilayer AR and high reflectors requiring high damage thresholds to laser irradiation, and in edge filters, bandpass filters, and polarizers. Articles discussing IRX<sup>TM</sup> in greater depth can be found in past issues: CMN V3, Issue 3 (1994) and V4(5), Issue 1 (1994).

The properties considered include the vaporization and condensation behaviors of the starting material, and the optical, chemical and mechanical durability of the deposited film. Some coating applications require survivability with retention of their physical properties when exposed to severe mechanical stresses such as high-speed rain drop impact, sand erosion, and salt fog tolerance. Other coatings must perform after continual exposure to weather and experience variable humidity and temperature conditions and perhaps mild abrasion in everyday use. Coatings for IR laser applications, particularly the CO<sub>2</sub> 10.6 μm line, require high laser damage thresholds to irradiation. The fluorides chosen to illustrate material properties (Table 1) are used in laser applications and in wide-band AR coatings operating to 11+ μm.

## CERAC Pre-Melted TiO<sub>2</sub> Lives up to Expectations

In CMN Volume 14 / Issue 2 (June 2004), we described the introduction of pre-melted forms of popular oxide compounds. An evaluation program is underway that is comparing evaporation-ready pre-melted CERAC oxide compounds with material compounds supplied by other manufacturers. Preliminary results are reported here for the TiO<sub>2</sub> materials; a more complete report will appear in a future issue of CMN.

CERAC's objective in producing pre-melted oxide compounds is to provide ready-state materials, i.e., pre-conditioned forms, that eliminate the typical lengthy preparation time for deposition. One form that is especially beneficial is the cone-shape intended for common crucible or E-gun pocket. Production of TiO<sub>2</sub> film layers has always required the cyclic process of melting down the pieces of the starting compound, cooling, breaking vacuum, adding material on top of the melted slug, and repeating the steps until the crucible is filled with melted and outgassed material ready for deposition. For most oxide-compound materials supplied in piece or pressed tablet forms, this process requires at least 3 hours of **continued on page 2**

**Table 1. Comparison of Properties of Three IR Fluoride Materials**

Property	ThF <sub>4</sub>	IRX <sup>TM</sup>	YF <sub>3</sub>	Comments
Index at λ 5 μm	1.45	1.47	1.46	
Index at λ 10.6 μm	1.30	1.43	1.34	
Absorption at 10.6 μm for 1 QWOT	0.06	≤0.8	0.12	Coherent Auburn Group
Evaporation Behavior	Sublimes, some spitting	Melts; smooth, no spitting or outgassing	Melts, spits	
Evap Rate (A/s)	15	Smooth up to 20	15	
Substrate Temp. °C	175	150-225	175-200	
Humidity Stability	Small effect	Excellent	Good	
Scratch Resistance	Soft	Very good	Good	
Solubility	Slight	Insoluble	Insoluble	
Form/Density	Columnar	Amorphous	Columnar	Very low scatter
IR Water Bands?	Yes	Shallow	Yes	High Temp. reduces depths
Spectral Stability	Moderate	Good: little moisture shift	Moderate	
Stress	Relatively low	Low in thick layers	Low	

## Achieving Low Mechanical Stress in Thin Film Layers

Thin film layers that have high tensile or compressive stress in relation to their substrates are vulnerable to mechanical failure that may take many forms, ranging from increased scatter due to micro-cracking to catastrophic flaking and peeling. In general, fluoride films grow with tensile stress while the stress in oxide-compound films can range from compressive to tensile, depending on many parameters. CMN previous issues have treated the subject of stress in thin-film layers: CMN V1, Issue 3 (1991); V2, Issue 3 (1992); and V11, Issue 4 (2001). Low-stress mixtures of oxide compounds were discussed in CMN V2, I3 (1992) and V8, I4 (1998). New information was presented at the Tucson 2004 Optical Interference Coatings Meeting that deserves review.

Zirconium dioxide is a material with exceptional hardness, moderately high refractive index and high transparency from ~300 nm to ~11 μm, thus is useful in optical and tribological coatings. Layers of pure  $ZrO_2$  share a common characteristic with many refractory compounds: they exhibit inhomogeneous refractive index depth profiles, resulting in difficulties in applications such as efficient AR coatings. The origin of

this stress is known to be the presence of multiple or unstable crystalline forms throughout the layer.

The effects of the thermal history on residual stress in  $ZrO_2$  layers on glass were studied by monitoring the evolution of crystallinity using XRD [1]. Stress was measured in films that were deposited by E-beam on substrates at temperatures between room and 350° C. The room temperature films were then annealed in air for 1 hour at temperatures 200° C, 300° C and 400° C. For films deposited at room temperature to 190° C, the residual stress was tensile: 64 and 14 MPa, respectively. At 260° C the stress became -46 MPa compressive; and at 350° C it increased to -150 MPa. Films deposited at room temperature changed from tensile to increasing values of compressive as the annealing temperature was increased, reaching -240 MPa at 350° C. XRD showed evolving crystallinity from amorphous for films with thermal histories below 200° C to monoclinic and tetragonal at the higher temperatures. The densities and residual compressive stresses of the high-temperature films increase in correspondence with contraction of the microstructure with crystallization.

Materials composed from mixtures are often used to overcome some of the problems associated with refractory materials because the additive thwarts the growth of multiple crystal phases and promotes better homogeneity or in some cases amorphicity. In laser applications where heating in the  $ZrO_2$  layers might produce phase transformations among the possible crystal states, the mechanism that results in superior threshold performance for the mixture is presumed to be that specific additives prevent crystalline transformation from cubic at temperatures below the melting point.

In mixture with  $Y_2O_3$ ,  $ZrO_2$  E-beam-deposited films exhibit high damage thresholds to XeCl (308 nm) excimer laser radiation [2]. Sputter  $ZrO_2$  targets containing  $SiO_2$  (available from CERAC) produce increased stability [CMN V4(5), I1 (1994)]. Zirconium oxide and hafnium oxide targets stabilized with  $Y_2O_3$  are also available from CERAC for producing layers of superior mechanical and optical properties than pure oxides of the primary compounds.

## Achieving Spectrally Stable Layers

We have often discussed another source of instability somewhat different from the problem of mixed crystalline phases, that due to film porosity. If a film layer does not possess high packing density, its internal void volume can absorb water, causing its optical path length to increase as the effective index of the layer increases. This phenomenon will result in spectral shifting as the film humidifies and dries out [3]. In evaluating the spectral shift due to moisture adsorption and desorption in an edge filter made from metal oxides, a simple test was demonstrated in 1988 for revealing this reversible effect that used dry nitrogen impinging on the coating to dehydrate it.

Researchers reported at the Tucson conference a hydrolysis reaction between moisture and the silica network in  $SiO_2$  layers [4]. A multi-layer high-reflector QW structure for  $\lambda$  1200 nm consisting of  $HfO_2$  and  $SiO_2$  was E-beam deposited at <100° C substrate temperature. It was found that after 3 years at room environment ~45% RH, the  $SiO_2$  thickness increased from 217 nm to 228 nm (+5.1%) and its index de-

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### CERAC Pre-Melted $TiO_2$ , from page 1



$TiO_2$  rod, cones & pieces

chamber time. This non-productive use of vacuum chamber time has been reduced to <30 minutes melt time with the new CERAC pre-melted forms.

We compared the preparation / evaporation behavior, and mechanical and optical properties of the CERAC pre-melted crucible-cone form with Umicore  $Ti_3O_5$  granules and EMD Chemicals Titanium Ox "S" granules.

Different film thicknesses were deposited on different substrate materials at two temperatures by E-beam without IAD or any other energetic assist. The granular form of the materials required 3 hours of preparation to make a 25 cm<sup>3</sup> plug with sufficiently low outgassing and spitting to permit deposition. The CERAC pre-melted cone was ready for deposition after only 30 minutes of heating. The spectral and abrasion (tape pull, cheesecloth and eraser tests per MIL-C 48497) properties of the final films were essentially identical. The future report will provide analysis of the data including refractive indices.

The objective of achieving virtually identical performance with the more convenient pre-melted evaporation-ready form made by CERAC has been demonstrated. Evaluation work will continue using other popular metal-oxide compounds.

## And Now for Some Theory on Film Growth

It is clear that the optical and mechanical properties of materials condensed to thin solid film layers are different from those of the bulk parent materials. Efforts to understand the growth mechanisms that produce the deposited films and their peculiar characteristics have been underway since the first thin films were grown. The subject is a complex one because many factors are involved; two key ones are: surface substrate energy and arriving adatom energy. Certainly the chemical or reactive nature of the vapor species and the presence of additional gaseous species are important, and other variables need to be considered in the whole picture. Ultimately the goal is to develop growth structure models that permit prediction of the properties of deposited film layers. [7]

The ideal thin film layer would be either a single crystal or possess an amorphous structure. The growth process from a physical vapor inevitably produces disordered films that contain high defect and impurity densities. Therefore, real films have a disordered polycrystalline microstructure with contaminants and other defects concentrated at the boundaries between the crystallites. In the cases of compound deposition, stoichiometry can be incorrect, leading to absorption or changes in electrical properties (in transparent conducting layers). Further, the film structure is in a metastable state, and in the presence of sufficient thermal or chemical energy can restructure to obtain permanently altered optical and mechanical properties. This can occur with coatings that are exposed to high energy laser radiation, high operating temperatures, and even conditions of high humidity.

Thin-film growth models are based on an evolutionary progression that starts with nucleation on the substrate, assumes three-dimensional growth of isolated islands that eventually coalesce, and finally grown in thickness to form a continuous layer. The conditions for nucleation and subsequent growth are dependent on the kinetic energy of the arriving adatoms and on the substrate surface energy. The latter is highly influenced by the atomic-level condition of the surface: the presence of contamination layers reduces the energy available for the generation of bonds, whether chemical or

physical. It is not generally appreciated that the deposition atmosphere contains a high density of what should be considered "impurities". These consist of residual water molecules, hydrocarbons, other organic and inorganic molecules degassing from the walls, and from the evaporation source, etc. These impurity species impinge on the substrate at rates comparable to that of the arriving adatoms, thus they are included within the growing film layer and are responsible for the internal defects and disorder and instability of the layer. Those impurities that are insoluble in the host material migrate to the grain boundaries where they are loosely bound in a metastable structure. Soluble impurities form part of the film matrix and can actually stabilize the film. Examples of the former are water in fluoride- or oxide-compound films and argon in sputtered films. Examples of the latter are mixtures of coating materials that are deliberately "doped" with soluble additives, and include IRX™, and hafnia and zirconia and other oxides mixed with 10-20% yttria, as discussed above.

Nucleation and continuous growth can be encouraged by conditioning the substrate surface. We review some of the methods previously presented in past CMN issues. High substrate temperatures promote mobility through increased surface energy. However, high temperatures can create high intrinsic and thermal mismatch stresses and perhaps even deform or damage the substrate. Therefore, low temperature processes are being developed, especially for coating polymers. Removal of adsorbed water and organics can be accomplished with low energy discharges such as the traditional glow-discharge. Removal of bound species such as oxides can be done using higher-energy heavy Ar ions from an ion gun or pre-sputter step. Surface energy can be further changed by depositing suboxides of reactive metals and compounds. Typical examples are Cr, NiCr, Pd (for gold adhesion), Ti, etc. Compounds include suboxides of Ti, Ta, Cr, Y, etc. In reality, the precursor metal layers (of thickness <10 nm) react with the residual oxygen always present in the atmosphere and form suboxides with unsatisfied bonds. The suboxides are especially valuable for silicate substrates such as glass, but are also useful with some IR materials. In the case

of some polymers, treatment with energetic nitrogen ions is beneficial in creating active surface bonds.

Adatom energy can be increased by co-bombarding the growing film with energetic (10-100 eV) ionized evaporant species and Ar ions. High quality films can be deposited by sputtering because the energies are several eV as opposed to <0.2 eV in electron-beam evaporation. Each of these deposition techniques has its own influence on film structure and therefore resultant properties. Ion-assisted deposition (IAD) produces dense films whose stress levels can be high unless special steps are taken. IAD also tends to produce substoichiometric oxide and fluoride compound

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### **Theory on Film Growth from page 3**

compositions with absorption that for general optical applications might not be acceptable, and is intolerably high for high-energy laser applications. E-beam coatings, on the other hand exhibit high laser damage resistance, but they are somewhat porous and thus can be unstable in varying humidity environments. Sputtered films are dense, but their stress levels need to be controlled, and the argon content might be problematical in some applications. The latest modifications in deposition employ higher adatom energy processes in attempts to simultaneously improve all film optical and mechanical qualities; they include reactive ion plating and high energy plasmas. To date, no process has solved all the problems, and coating engineers are forced to make compromises in adopting techniques that appear to be suitable for their current specific coating needs. The availability of coating materials with improved consistency removes one of the variables that plague optical thin-film deposition and growth.

### **Achieving Spectrally Stable Layers from page 2**

creased ~1.6%. The researchers concluded that the porosity decrease of the film matrix is responsible for the index decrease. Any aging effects that the HfO<sub>2</sub> layers might be responsible for were not considered, but probably should be explored in future investigations. Other researchers reported that silica hydrolysis induces a shift in mechanical stress from compressive to tensile [5, 6].

The deposition process for widely used SiO<sub>2</sub> low-index films and other oxides should be capable of producing layers with as high a packing density as possible in order to discourage unstable optical and mechanical properties. The porosity and thus the magnitude of the moisture-induced shift can be reduced by deposition at high substrate temperature, but not eliminated. Densification to the degree that the spectral shift is reduced to <~1 nm is generally accomplished by employing energetic processes such as IAD or some plasma-assisted technique.

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