

## Reviewing Advances in Coating Materials and Processes

From the premier issue of *Coating Materials News* 15 years ago, we have attempted to review and summarize for our readers current advances in our technology. The growing application of optical coatings and the higher demands placed on them by state-of-the-art developments have encouraged pace-keeping development of coating materials and their deposition technologies. Emerging industries producing display screens, digital image projection systems, energy conservation in automobile and architectural windows, and others have placed challenging demands on the thin-film coating industry. We can add to that list highly specialized precision filters for telecom, commonplace AR coatings on eyeglasses, anti-counterfeiting coatings on currency, and colored decorative finishes on household appliances. Medical and military requirements continue to push the requirements envelope.



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Professional meetings, symposiums, and publications report many of the advances, but it is safe to speculate that proprietary and trade secret developments in private industry might equal or exceed the volume of publicly distributed information. Coating practitioners, while motivated to stay current with the state of their art, are busy people and must often be satisfied to accept summaries of the advances in progress. One goal of *CMN* is to acquaint our readers with new developments.

## Progress in Coating Materials Science

A major accomplishment in materials engineering is the demonstration that pre-melted forms of many oxide compounds provide processing advantages over tablets and piece-forms, without sacrificing optical performance. The elimination of the need to process multiple melts and venting to build a solid, non-spitting, non-outgassing evaporation source saves valuable chamber time and assures better repeatability of coating properties [1].

Mixtures of oxide and fluoride compounds continue to provide advantages over "pure" materials, and in some cases, produce improvements approximating high-energy deposition techniques. Specifically, densely packed, amorphous growth from mixed composites produces film layers with

## Coatings on Polymer Optics

Glass and metal surfaces present few coating problems, but the unique chemical and physical properties of polymers present a number of coating challenges. Polymer optics are continually replacing glass optics in a number of applications: critical (medical, scientific, military) as well as commercial. The list of polymeric materials used in the optical industry includes: polycarbonate (PC), polymethyl methacrylate (PMMA), polyethylene-terephthalate (PET), acrylic (AC), polyether sulphone (PES) and polyetherimide. The ophthalmic industry is a large supplier of AR-coated lenses [3], the computer and entertainment industries consume large volumes of metallic coatings on polycarbonate for DVD and CD recording, and architectural thermal-control coatings are made of coated plastic PET films laminated into the window. Reasons for the increasing use of polymer AC and PES optics include the ease of molding high volumes of precision lenses, lower coat and weight, and simplicity of mounting. Display panels are often made using PES, PET or PC coated with a sputter-deposited AR design that includes a transparent conductive layer of ITO. The ITO layer can act as an RFI shield or touch contact circuit. The refractive indices of polymers used in optical components range from ~1.4 to 1.64 (polyetherimide), and surfaces require anti-reflection coatings in many devices. Polymer components are also used as substrates for mirrors and colored parts, the latter requiring multi-layers of dielectric coating.

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**Table 1**

Optical Application	Index (550 nm)	Material Mixture	Reference, CERAC item
Hard, wear –resistant films, 250 to 2000+ nm	~2.1	ZrO <sub>2</sub> + soluble glass formers	CMN V7, Issue 2 (1997)
Hard, wear –resistant films, 450 to 2000+ nm	2.1	ZrO <sub>2</sub> + TiOx	Z-1079, Z-1092
Tribological,	1.7	MgO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	CMN V8, Issue 4 (1998), M-1126
High temp., wear resistant	2	ZrO <sub>2</sub> -MgO	CMN V8, Issue 2 (1998), Z-1077, Z-1078
Excimer laser; High temp	1.8	ZrO <sub>2</sub> -Y <sub>2</sub> O <sub>3</sub>	CMN V14, Issue 4 (2004)
Hard, UV transparent	2	HfO <sub>2</sub> - Y <sub>2</sub> O <sub>3</sub>	CMN V14, Issue 4 (2004)
Wear (abrasion) resistance	2	SnO- ITO	
High laser damage threshold	1.9	ZrO <sub>2</sub> -SiO <sub>2</sub>	CMN V4, Issue 1 (1994)

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high environmental stability and improved optical mechanical and chemical durability. It has been established that stability of crystalline phase of many refractory oxides can be achieved over a high temperature range by adding a few wt-% of another oxide compound such as yttria to form a solid solution. While co-evaporation of two oxide compounds from separate evaporation sources is useful in establishing the optimum mixing ratio, and can be used in production, pre-mixed material preparations are more convenient. Films deposited from the mixture possess greater hardness, higher homogeneous refractive indices, smoother surfaces, and lower stress than the pure host material as a result of the uniform and stable crystalline state and higher packing density [2]. Optimum optical properties such as highest refractive indices with low absorption and scatter and high resistance to water absorption were demonstrated with CeO<sub>2</sub> - SiO<sub>2</sub> composite films [2].

Mixtures designed for e-beam evaporation for tribological or high-temperature exposure coating are proving useful in optical applications. Many of these are based on ZrO<sub>2</sub> or Y<sub>2</sub>O<sub>3</sub>, materials that are inherently hard in pure form, as the host material. Table I lists some applications that benefit

from the use of specific mixed materials deposited by e-beam; sputter targets are available for some materials (only transparent materials are included). Only high- and medium-index materials are listed because the choice for the low index is mostly limited to silica, which in pure form or doped with alumina grows with a dense glass form. More discussion of the materials listed can be found in the reference column.

**Progress in Deposition Techniques**

E-beam and sputter deposition are the basic production processes used in the industry. The refractory oxide compounds and their mixtures require the high thermal energy of an electron beam to reach their evaporation temperatures, often 2000° C. Alternatively, sputter processes produce sufficiently high energy to move material from the target to condense on the substrate. Some of the material mixtures mentioned are available in sputter-target form.

E-beam evaporated species have low energies (<10 eV) upon impingement at the substrate surface, therefore the kinetic energy available for high mobility on the surface is marginal. Free mobility insures dense surface coverage in two dimensions before isolated islands

appear and grow into sparsely populated columns with resultant large void volume between them. Limited mobility and line-of-sight adatom arrival contribute to the growth of the self-shadowing columnar open microstructure that pure oxide compounds often exhibit. The relationship between energy and growth microstructure was illustrated in Figure 1 of CMN V13, Issue 3 (Sept. 2004). The presence of foreign species admixed with the host oxide interferes with crystalline growth and encourages denser microstructure. Ion assisted deposition (IAD) is a process enhancement that produces dense, hard, adherent films, and has been incorporated in commercial coating production for at

least 10 years. Energies in IAD approach hundreds of eV and a high ratio of energetic ion-to-species can be achieved with high current densities. The transfer of kinetic energy throughout the growing structure results in the dissipation of singular growth structures, thus encouraging dense, random microstructure. Varieties of IAD equipment are available to accomplish the same basic function: to provide added energy for increasing layer packing density through increased surface energy and momentum transfer.

Sputter deposition is a high-energy process that also results in hard, dense film layers. Many variations in sputter techniques have been developed; the primary differences in technique are adapted to sputtering metals vs dielectric compounds. The process pressure in sputtering is higher than for E-beam evaporation, as a result the growth is not line-of-sight, and a more random structure grows that exhibits relatively high density. By varying sputter parameters, large or small crystals can be grown, and stress can be controlled. Energies are generally lower than can be achieved by IAD. Sputtering is easily adapted to high volume, large area, automated production. We have discussed IAD and sputter deposition extensively in previous issues of CMN.

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Several properties peculiar to polymer surfaces require different considerations and techniques to achieve stable, adherent optical coatings [4]. The high water absorption (up to 0.45%), low temperature limit ( $<125^{\circ}\text{C}$ ), high thermal expansion compared with the coating materials ( $\sim 2X$ ), non-reactive surfaces, and low hardness are the more important issues that must be accommodated. When we attempt to apply typical coating techniques to plastics, failures appear in the forms of: high stress and water content leading to poor coating adhesion and short-term physical stability, surface figure deformation from excessive process temperatures, and process instabilities from out gassing of water and additive / plasticizer components.

The coating deposition process and the materials used must be engineered to accommodate the diffusion of water and the thermal properties associated with polymers. Either can result in adhesion loss: the first by weakening the bond between polymer and coating interfaces; the latter by the presence of stress due to thermal coefficient mismatch. Chemical hardcoats are applied to the surfaces of eyeglass lenses and data disks, and their characteristics also become part of the coating process. Often this treatment reduces the chemical and physical mismatch presented by the bare polymer surface. Sputter deposition is used to deposit low-e window coatings for thermal control. Such coatings consist of thin silver between dielectrics and often ITO to reflect the IR. Large area roll-to-roll coaters produce millions of sq. meters annually. E-beam systems produce the majority of ophthalmic coatings; when augmented with IAD, substrate temperatures can be kept low. Both techniques employ energetic ions and are low temperature processes.

Proper surface preparation is necessary to obtain adherent and stable coatings. Some techniques were discussed earlier in CMN [3]. For many polymers, a  $\sim 20\text{ \AA}$  deposit of Cr provides a good nucleation and adhesion precursor. The Cr metal converts to  $\text{CrO}_x$  which actively binds to the following  $\text{TiO}_2$  layer. More vigorous pre-treatments consist of

plasma-surface interactions that clean and create chemical bond energy to which an oxide or metal can strongly adhere (surface activation). The plasma can be created in an oxygen or nitrogen atmosphere, as required for the polymeric materials involved. More recently, plasma-enhanced CVD has been applied to polymer coating because the process permits control of the plasma-surface interactions resulting in stronger bonds, and because can it be used to generate graded-index films and thus rugate filters [4] employed on visors as a countermeasure to laser blinding. Energetic N or O ion plasmas and UV exposure modify the polymer surface and create a denser and harder interphase layer  $<0.5\text{ mm}$  thick. Present in this interlayer are reactive cross-linked and functional groups that can chemically bond to oxide and metal depositions. The PECVD process is more efficient at producing these active groups than classical PVD because of the dense plasma and higher energies involved.

The most popular coating materials for polymers such as PC are  $\text{TiO}_2$  (index = 2.2) and  $\text{SiO}_2$  ( $n = 1.45$ ). This couple adheres well and can satisfy most designs for AR and filter coatings. Ophthalmic coaters also use mixed high- and low-index materials based on titania and silica that were developed for lower stress and low temperature deposition. As new applications for polymeric materials appear, new and improved coating material combinations will be developed for them. It is clear that the solution for stable and durable coatings on plastics requires close interaction between the chemistry of the polymer and the entire coating process.

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