One of the main goals of Coating Materials News (CMN) is to provide information on advances in thin-film material development and processes. This information often takes the form of process refinements reported either from direct experience or from work in progress reports that appear in current literature. This issue first briefly reviews the current three most commonly applied deposition technologies for oxide thin films, then discusses material choices for optical applications. Finally, we offer more specifically, deposition parameters related to titanium dioxide layers that are the workhorse of optical coatings for the visible region.
High Refractive Index Materials for Optical Applications

Optical coatings generally are composed of low-index layers coupled with high-index layers. Examples are all types of AR coatings, bandpass and edge filters, and high reflection coatings. For many filters, using a high index ratio, \( n_H : n_L \) simplifies the design and deposition complexity because with a higher ratio, the band of reflected wavelengths is wider and the number of layers smaller for a hot or cold mirror, for example. In the Visible and Near-IR region, 400 nm to 1100 nm, the material pair that has the maximum index ratio is TiO\(_2\) and MgF\(_2\), with \( n_H / n_L = 1.73 \) at 550 nm. We are considering hard coatings and therefore exclude soft coatings that might have a higher ratio, specifically, ZnS (\( n = 2.4 \)) and the soft, water sensitive cryolite compositions (\( n = 1.35 \)). The all-oxide combination, TiO\(_2\)/SiO\(_2\) has the next highest ratio, 1.62. The optical properties and their values: index \( n \) and absorption \( k \), determine a material’s suitability for optical applications. For MgF\(_2\) and SiO\(_2\), these values are useful over wavelengths from <200 nm in the UV to beyond 2000 nm in the NIR. The same cannot be said for all candidate high-index metal oxide compound partners since they either have a bandgap absorption starting near 400 nm or another type of absorption in the NIR (outside the visible range). This is the case for TiO\(_2\), which begins to absorb near 450 nm wavelength. Listed in Table 1 are high index oxide compounds deposited either with E-beam, E-beam + IAD, or sputtering, and their approximate ranges of low absorption.

The availability of high-index materials transparent below \( \sim 300 \) nm wavelength is limited to those listed, creating a challenge for UV coating manufacture.

The achieved refractive index of a layer is a strong function of deposition process and of the particular deposition parameters within a process. It is possible to create a film index greater than that of the bulk material despite the fact that films are never fully dense. This artifact results when the \( k \) value, the extinction coefficient, is not zero, indicating incomplete oxidation. Absorption in this case, shows up at the short wavelengths and sometimes the film can be used successfully at near-IR wavelengths. Some materials, TiO\(_2\) for example, form bonds with OH or are slightly oxygen deficient and exhibit slight absorption at wavelengths >900 nm where most oxides are free of absorption. This problem with TiO\(_2\), prevents its use for WDM filters in the 1300 – 1600 nm region. Such filters have as many as 60 high-index layers. Ta\(_2\)O\(_5\) is used instead.

An example of process-dependent index is shown in Figure 1, where TiO\(_2\) deposited by e-beam alone and e-beam with IAD shows an index difference \( \sim 0.16 \) [1]. The e-beam alone films were deposited at substrate temperatures near 300° C; the higher index IAD films at 50 to 175° C. Even higher indices have been reported with ion-beam sputter deposition and ion or plasma plating [2], both being very high energy processes. In the latter cases, and to some degree with sputter deposition, more of the rutile form of titanium dioxide is present compared with the lower index anatase form.

Since TiO\(_2\) is so important a material for optical coatings, process development for the optimum deposition parameters continues. The starting material might be Ti metal or one of the many sub-oxidation state forms from TiO to Ti\(_3\)O\(_5\). If one were sputtering TiO\(_2\), the starting material would naturally be Ti metal sputtered in a reactive plasma containing oxygen. What is the most technology ready starting material for e-beam deposition? This question has been the subject of many studies. In a recent study [1], it was concluded that the sub-oxides Ti\(_2\)O\(_3\) and Ti\(_3\)O\(_5\) are preferred. They both melt under e-beam and thus yield more homogeneous film layer indices and good mechanical properties, even with low temperature conditions continued on page 3

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Index at 550 nm</th>
<th>Transparency Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>2.31 E-B; 2.35 sput; 2.47 IAD</td>
<td>450 – 10,000 nm</td>
</tr>
<tr>
<td>Nb(_2)O(_5)</td>
<td>2.25 E-B; 2.32 sput.</td>
<td>400 – 10,000?</td>
</tr>
<tr>
<td>Ta(_2)O(_5)</td>
<td>2.04 – 2.10 E-B</td>
<td>400 – 10,000</td>
</tr>
<tr>
<td>HfO(_2)</td>
<td>1.93 – 1.97 E-B</td>
<td>250 – 10,000</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>2.05 E-B; 2.22 sput.</td>
<td>270 – 7,000</td>
</tr>
</tbody>
</table>
produce a distributed spectrum of low energy, high current-density beam that is effective for maximum oxidation. The IAD process may be added to resistance-heated or E-beam deposition equipment to achieve denser, more stable film layers on glass, or polymer substrates where high substrate temperatures cannot be used.

Sputter Deposition

CMN has discussed the techniques and merits of sputter deposition in many past issues. There are many variations of AC or RF and DC sputtering techniques. DC techniques involve the sputter removal of metal atoms which are subsequently oxidized in an energetic plasma of an oxygen / Ar mixture that is established between the target and the substrate. The substrate might be biased with respect to the target to accelerate ionized species and thus produce dense layer growth. AC techniques permit the use of a compound target. Higher deposition rates are generally achieved starting with metal targets that are also less expensive than compound targets.

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References


Figure 1. Refractive indices of e-beam deposited TiO$_2$ alone and with IAD [1].

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depositions on polymer ophthalmic lenses. Consistent properties from run to run from the same source charge are not obtained with the other oxidation states because they do not melt and sequential evaporations change the composition of the source material. This problem is not experienced with Ti$_2$O$_3$ and Ti$_3$O$_5$.

The deposition parameters suggested for TiO$_2$ layers using the preferred starting compositions are: O$_2$ pressure ~2 E-04 Torr; rate 5 A/s; temperature 250° C; container: Molybdenum liner.

The refractive index is ~10-15% lower on unheated substrates, as is the case for ophthalmic AR coatings, which are deposited at lower temperatures because of the lower packing density. An increase will be seen as the film absorbs water from the air. This change must be allowed for in the design and deposition process of the production environment.

Using these suggestions, it is possible to develop an optimal deposition process for TiO$_2$ without undertaking a research project.
While sputtered films are deposited in relatively high pressure conditions, they are generally denser and more adherent than E-beamed films because the higher energy of deposition overcomes surface contamination barriers and micro-crystalline forces that would normally tend to aggregate adatoms in a low-energy column form. Furthermore, stress, microstructure and grain size can be controlled by varying the bias energy and O\textsubscript{2} /Ar pressure parameters. For example, the relative amounts of the various crystal phases in materials such as ZrO\textsubscript{2} and TiO\textsubscript{2} can be controlled. These crystal phases possess different stress levels and microcrystalline sizes and orientations, leading to mechanical as well as optical (index) inhomogeneities. Sputtering permits deposition onto low-temperature substrates such as polymers. Millions of square meters of polymer substrates intended for window laminations in display, architectural and automotive window applications are coated each year in sputter roll (web) coating systems.