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Common Deposition Techniques

Electron-beam

The most common deposition technique for metal-oxide film materials is electron-beam evaporation because their temperatures are generally in excess of ~1200°C. Some oxides, notably SiO (1100°C) and ITO (600°C), can be evaporated using resistance heating. With the exception of the common materials: Al_2O_3 and SiO_2, metal oxides require a partial pressure of oxygen in the range of 0.5 to 20 E^{-5} Torr and deposition rates 2 to 5 Å/s at substrate temperatures of 200 – 250°C. These conditions promote complete oxidation and the correct stiochiometry of the oxide compound, which is important for producing the desired physical properties of the film layer such as refractive index, transparency, and mechanical durability. Demands in critical applications such as imaging, displays, high ophthalmic AR coatings, laser applications, etc. require that thin film layers also possess the following properties: stable optical and mechanical/chemical properties and low light scatter. Unfortunately, e-beam deposited films grow with a columnar microstructure, meaning that there are sub-microscopic voids in the structures of the layers. This under-dense structure can and will absorb moisture and other gaseous-state materials, and in doing so, change in all of the above desired properties. Such films can have high scatter properties and sometimes high stress. Changes in optical properties with environmental exposure are evidenced by shifts in performance wavelength of filters and in reflection value for AR coatings. Mechanical degradation may take the form of loss of adhesion, strength, or hardness because the grain sizes are large and loosely bound. For these reasons, other, more energetic forms of film deposition and growth were developed. When more energy is made available, either in the form of the momentum of the arriving adatoms or surface and species activation, the adatoms have the mobility to find sites to nucleate on and to grow with a more compact and finer grain structure. High substrate temperatures assist with the surface mobility, but not necessarily with densification. Often surface energy barriers are present if atomic contamination is present on the surface or if the surface is otherwise chemically inert.

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.

Ion-Assisted Deposition, IAD

In this technique, kinetic energy is supplied by a beam of ionized Ar atoms that are directed onto the growing film. Momentum transfer of energy at values of 10 to 100's eV discourages columnar growth, thus densifying the layer. IAD films are harder, smoother, and exhibit more stable optical properties than E-beam films. A percentage of oxygen is mixed with argon to produce films with complete stiochiometry and low optical absorption in this process. The quality of the IAD film is influenced by the energy of the incident ions and their density. Ion sources with grids are designed to direct a narrow energy spectrum beam toward the substrates for maximum density; gridless ion sources

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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 ~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_2O_5 is used instead.

Table 1

Metal Oxide	Index at 550 nm	Transparency Range
TiO_2	2.31 E-B; 2.35 sput; 2.47 IAD	450 – 10,000 nm
Nb_2O_5	2.25 E-B; 2.32 sput.	400 – 10,000?
Ta_2O_5	2.04 – 2.10 E-B	400 – 10,000
HfO_2	1.93 – 1.97 E-B	250 – 10,000
ZrO_2	2.05 E-B; 2.22 sput.	270 – 7,000

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 ~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_3O_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_2O_3 and Ti_3O_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

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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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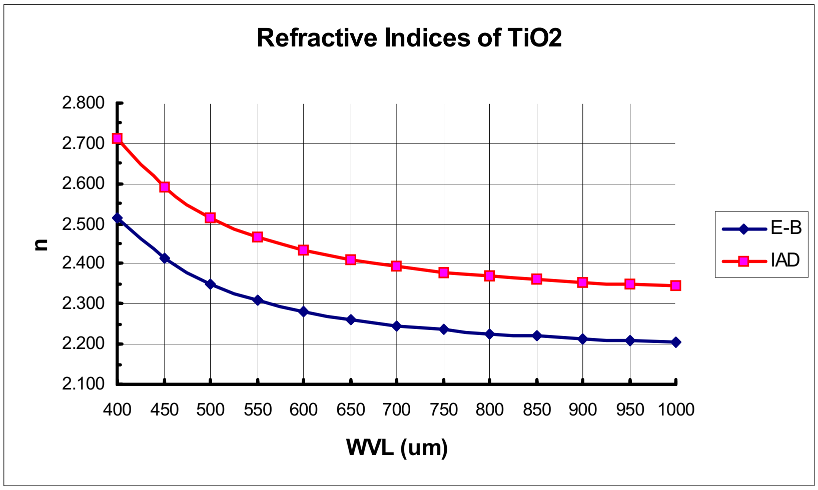

Figure 1. Refractive indices of e-beam deposited TiO_2 alone and with IAD [1].

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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_2O_3 and Ti_3O_5.

The deposition parameters suggested for TiO_2 layers using the preferred starting compositions are: O_2 pressure ~2 E-04 Torr; rate 5 Å/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 temparatures 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.

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While sputtered films are deposited in relatively high pressure conditions, they are generally denser and more adherent that 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_2 /Ar pressure parameters. For example, the relative amounts of the various crystal phases in materials such as ZrO_2 and TiO_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.