CERAC™ incorporated

Coating Materials News

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IAD Effects on Materials Properties

CERAC is continually exploring and developing new and improved materials for the optical coating industry. Materials useable from the UV to the Far IR spectral regions have been produced for applications that range from eyeglass AR coatings, high-energy laser applications in medical and industrial instruments, transparent conductive coatings for displays and energy-conserving windows, filters, mirrors, and general filters and decorative coatings. We have discussed in these pages how higher deposition energy than available from straight resistance-heated or electron-beam evaporation is required in the production of hard, durable, environmentally stable coatings for all of the above application examples. In this issue, we begin to include results achieved when high-energy ion bombardment accompanies evaporation. We have discussed the advantages provided by Ion Assisted Deposition many times. Briefly summarized, IAD provides added kinetic and reactive energy that results in physically denser (close to bulk density), fully oxidized, low-stress thin film layers. Ion assisted layers are stronger cohesively and adhesively and harder than straight E-beam or resistance-evaporation processes. IAD depositions do not require heated substrates, making them safe processes for polymer and other heat-sensitive substrates. Producers of optical coatings have adopted IAD as a routine quality improvement process for those reasons. The new preparations of metal oxide compounds that CERAC has been developing recently exhibit improved optical and physical improvements when deposited using IAD, and some of the results are presented in this and subsequent issues as evaluation of different materials continues.

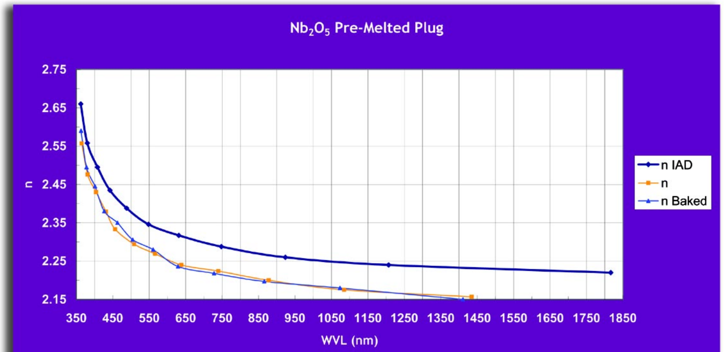

Figure 1. Niobia deposited from a pre-melted form by e-beam, with and without IAD at Substrate Temperature 200° C

Niobium Pentoxide

Nb_2O_5 is a hard material with one of the highest refractive indices in the Vis-NIR regions. While it is often sputter deposited, e-beam evaporation has been problematical because of the tendency to grow with incomplete stiochiometric oxidation, resulting in appreciable absorption. Typically the films needed to be air baked to achieve complete oxidation. The newly available pre-melted plug-form of CERAC Niobia has been evaluated. The deposition parameters for Figure 1 were: substrate temperature 200° C, rate 3 Å/s, partial pressure of oxygen 1.8 E-04 Torr, IAD: 180 V, 5 A. In Figure 1, the refractive index dispersion curves are presented for as-deposited, air-baked, and IAD film layers ~450 nm thick. Figure 1 shows that air-baking of this form does not increase the index values, apparently full oxidation had been achieved without this post-process step. However, the addition of IAD increases the index values significantly. The interpretation is that the index increase is the result of an increase in packing density. A slight lowering in short-wave absorption over the air-baked process step was noted for the IAD sample. A set of depositions of Nb_2O_5 in pre-melted plug (C) and broken pieces (A) forms were made at 100° C using IAD to compare with depositions at 200° without IAD but with air-baking at 400° C for 2 hrs. The rate was again 3 Å/s. Figure 2 suggests that the higher temperature during deposition is still needed to achieve high packing density with Niobia, and comparable results are obtained at 200° with and without IAD. The difference in index is >3%.

Lanthanum Titanate

CERAC $LaTiO_3$ is a special material with the high index properties of TiO_2, but with denser film microstructure and friendlier process behavior. We have evaluated the deposition process and film characteristics for as-deposited and IAD procedures. The material evaporates smoothly with no evident spitting or spatter of outgassing. Figure 3 pre-

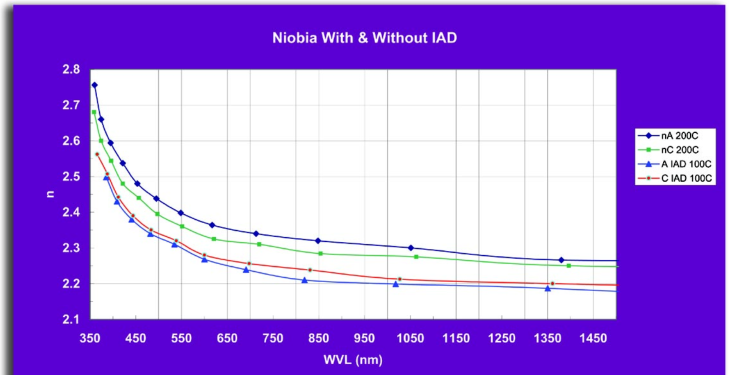

Figure 2. Niobia depositions compared for 200° C and 100° C and with and without IAD

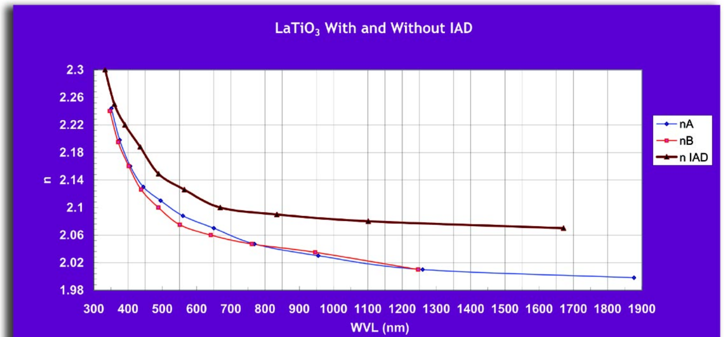

Figure 3. Lanthanum Titanate refractive indices for as-deposited and IAD processes

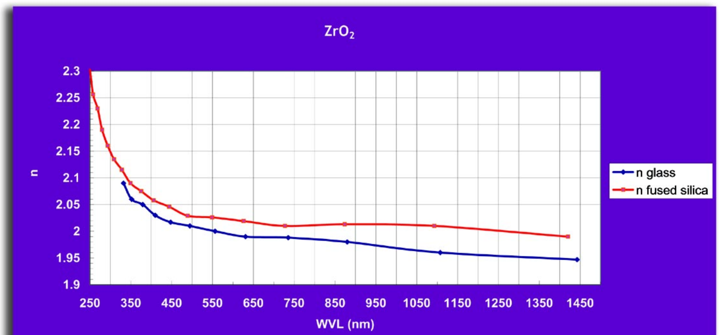

Figure 4. Zirconia Depositions on fused silica and glass substrates (no IAD).

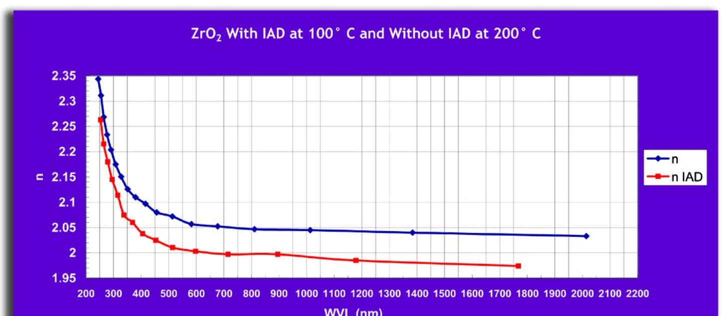

Figure 5. Zirconia at two substrate temperatures and IAD conditions.

sents the results for two different starting forms deposited by e-beam, and for the addition of IAD to the deposition. For the IAD deposition, the pressure of O_2 was 1.4 E-05 Torr, rate 3 Å/s, and substrate 200° C. Ion voltage: 180 at 5 A current.

Zirconia

Zirconia is a useful material because of its great hardness and high UV transmission and laser damage threshold. Historically, evaporated ZrO_2 layers grow with an inhomogeneous stratification in refractive index, creating problems for optical coating designs and manufacturing consistency. The problem arises from the very high temperature required for evaporation and the tendency for multiple crystal phases to develop within the different temperature gradients in the e-beamed area. CERAC has processed a number of Zirconia preparations in the development of starting materials that minimize that effect and provide friendly evaporation properties (low outgassing and spitting). The results shown in Figure 4 were for a black tablet starting form deposited using parameters: 1 E-04 Torr oxygen; substrate temperature 200° C; and rate 3 Å/s, thickness 540 nm. The substrates, glass and fused silica, were cleaned immediately before deposition with a high-energy ion beam for 3 minutes.

The slightly higher indices for the fused silica substrate might result from the smoother surface of the silica compared with glass. Absorption does not become significant until near 250 nm wavelength, where k ~0.001. Therefore this material is useable into the UV to at least 200 nm. The dispersion in index between 450 nm and at least 1500 nm is small, an advantage for certain types of coating designs. No evidence of index inhomogeneity was observed, in spite of performing the deposition without IAD or at the relatively low 200° substrate temperature. (Inhomogeneity is signified by the appearance of irregular and inconsistent HW and QW values of spectral transmittance. For example, if the HW values are not equal to the values of the uncoated substrate, and absorbance is zero, an index gradient is present).

The optical properties produced from a pre-melted plug of Zirconia were evaluated both with and without IAD. The pre-melted form eliminates spitting and outgassing, and is ready to evaporate without further conditioning. Figure 5 presents the results of a 500 nm thick film deposited at 200° C substrate temperature without IAD and a 450 nm thick film deposited at 100° C substrate temperature with IAD. The difference in index between the low and high temperatures is 1% at the long wavelengths and 1.4% at 300 nm. The significance of this set of depositions is that nearly the same optical performance can be achieved at a lower temperature with IAD as at the higher temperature without IAD. Evaluations of the film deposited at 200° C with IAD are in process for comparison with these results. Notice the smooth dispersion curves that this preparation of ZrO_2 achieves.

Tantalum Pentoxide

Ta_2O_5 is a favorite high index material that has superior optical behavior to TiO_2 in that it exhibits lower water absorptions in the near-IR. It is used for WDM filters and other high quality applications. The curves of Figure 6 show the results of depositing Ta_2O_5 with IAD. The common deposition parameters were: Substrate temperature: 200° C, Rate: 2.5 Å/s, Pressure 1.5 x 10^{-4} Torr, Thickness: ~5500 Å. Material "C" was pellet form and material "D" was a pre-melted cone form.

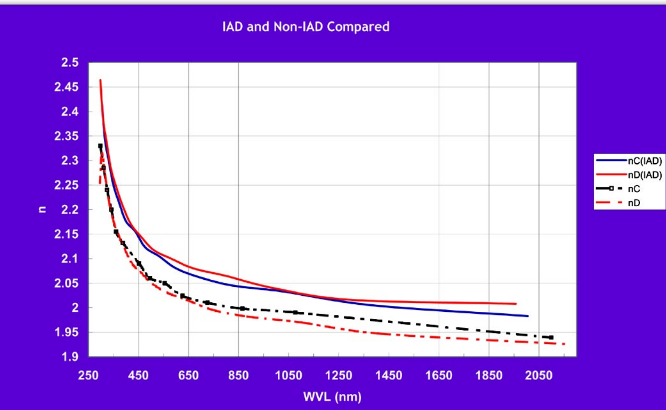

Figure 6. The increase in refractive index when IAD is used with Tantala depositions.

Hafnium Dioxide

Hafnia is used in laser damage-resistant coatings for the UV region, and in thin layers has transmission into the IR as far as 10 mm. The following recent result of the evaluation of CERAC UV grade Hafnia materials are for different evaporation rates without IAD and with IAD. The deposition parameters were: pressure 1.8 E-05 Torr, substrate temperature 200° C, rates were varied 2.5 – 7.5 Å/s.

An interesting dependence of the indices of Hafnia on evaporation rate is demonstrated in figure 7. The indication from Figure 7 is that the deposition rate must be ≥ 5 Å/s to achieve maximum index values. The lower rate apparently entraps more background gas, lowering the packing density.

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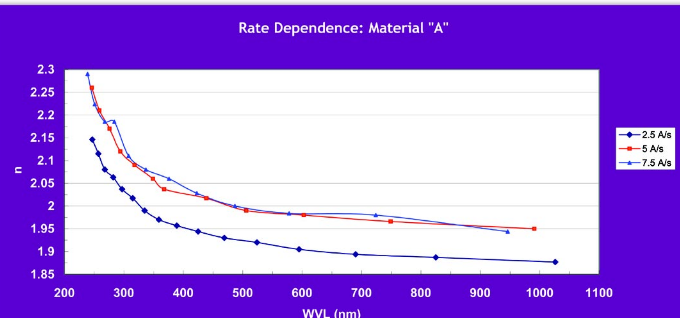

Figure 7. Depositions of Hafnia at different rates (no IAD)

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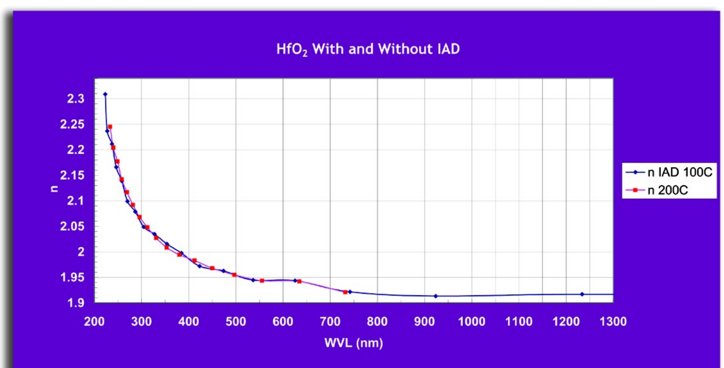

Figure 8. Hafnia deposited at two temperatures with and without IAD

Looking now at the effects of IAD, the plots in Figure 8 show that the same indices are obtained when IAD is used with substrate temperature 100° C as for the case without IAD, but at temperature 200° C, both at the rate 2 Å/s. IAD energy has compacted the microstructure and raised the index from the low values of the blue curve of Figure 7. However, the k value at l240 nm is ~2 x higher with the low temperature deposition.

Future editions of CMN will report on more material studies.

CERAC will be exhibiting at the following upcoming trade shows:

- **Society of Vacuum Coaters (SVC)**
  April 24-25,
  Washington, DC,
  Booth# 1100

- **Optatec**
  June 20-23,
  Frankfurt, Germany
  Booth# E21, Hall 3.0