

## Materials Designed to Produce Dense Layers

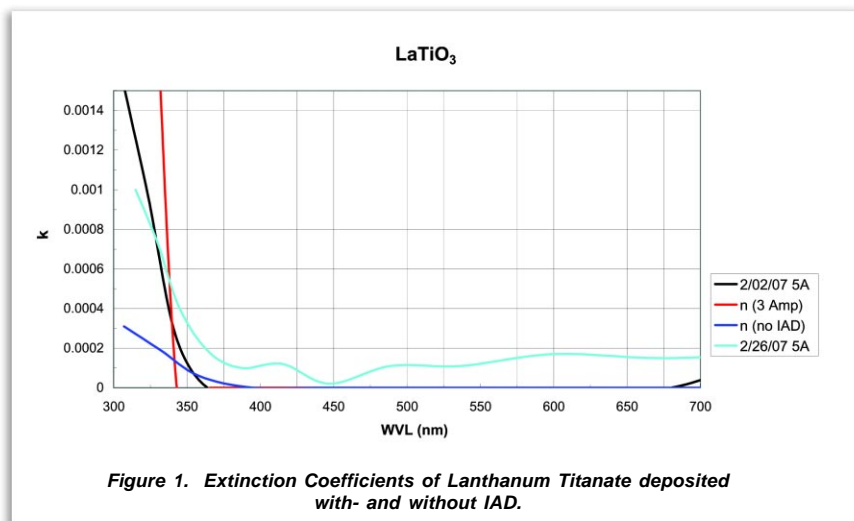
CERAC *Coating Materials News* (CMN) has frequently discussed the development of new optical coating materials designed from the mixture of a host material and an additive. In contrast to thin films deposited from pure materials, layers of these alternate “designed” materials are generally amorphous and more densely packed. This is because the short-range order that is characteristic of pure materials and evidenced as microcrystalline column growth structure, is absent in the modified material.

Thin film layers deposited by electron-beam or resistance-heated evaporation, and by sputtering, do not grow with a crystal structure. Because the condensation / growth process provides low mobility energy, arriving adatoms nucleate in a statistically random manner. Ordered lattice structure over millimeter ranges that characterizes crystal growth is absent. Instead, microcrystalline elements having short-range order often at the ~100 nanometer scale compose the microstructure of PVD film layers. We loosely describe this microstructure as “amorphous” (glassy), and the solid film as a matrix rather than a crystal lattice. This partially structured order affects the optical and physical properties of optical and non-optical films because of the presence of discontinuities and volume voids that can be centers of interaction with light and with external environmental influences. For example, deposited films generally exhibit higher absorption than the crystal form of the parent material. External influences that produce unstable properties include mechanical force, chemical reaction, or simply non-reactive absorption of water vapor into pores. It is therefore the goal of thin-film materials suppliers and coaters to promote the growth of layers that more completely achieve homogeneous and amorphous structure. One approach to achieving this is to deliberately introduce impurities or disrupting compositions that prevent long-range crystalline order. Another is to impact the growing film with high energy to produce high mobility of adatoms. Past CMN issues have covered both approaches in many pages of discussion.

## Examples of Designed Materials

Starting materials composed by admixing 5-10 wt% of an appropriate material to a host material improves the evaporation behavior and the optical and durability properties of the coated layer over those for a pure starting material. When the admixture is pre-conditioned preceding evaporation, surface melting rather than sublimation generally occurs, eliminating or reducing the emission of particulates (spitting) and out-gassing. Typical improvements that result with “doped” materials are volume densification resulting in higher and more uniform refractive indices, greater environmental stability, higher strength and hardness, and often higher laser damage thresholds. We discuss first a novel material that is actually a stoichiometric compound composed of two high-index materials, rather than a “doped” mixture.

In designing improved evaporation materials, the emphasis has been on high-index materials. There are a greater number of high – medium index materials available to work with, each having specific advantages. For example, Titania ( $\text{TiO}_2$ ) and Niobia ( $\text{Nb}_2\text{O}_5$ ) have the highest indices for the visible range, ~2.2, but begin to absorb below ~450 nm, rendering them useless for UV laser applications. Hafnia ( $\text{HfO}_2$ ) and Zirconia ( $\text{ZrO}_2$ ) are useful for UV coatings, but their indices, ~1.9 – 2.0, require a greater number of high-low index pairs in high reflection coating designs. CERAC has been working on improved evaporation materials that are based on additives.



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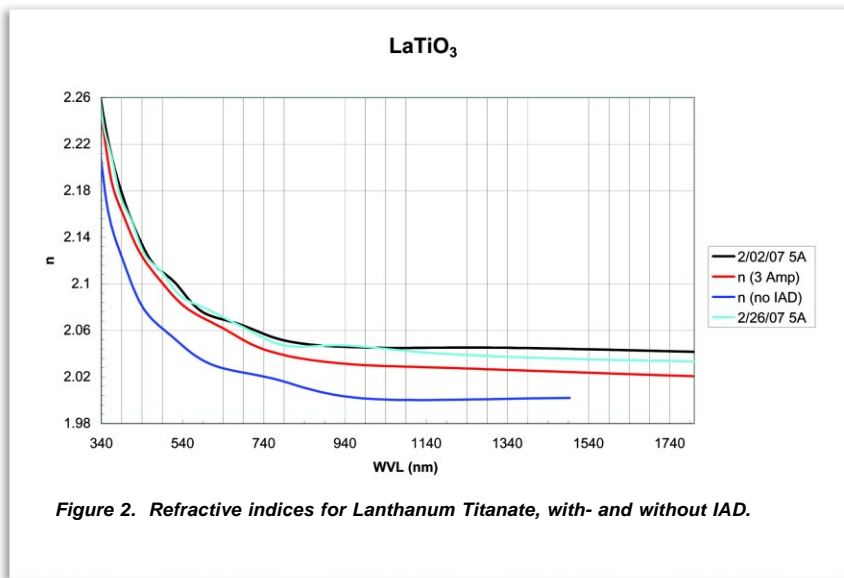
Since the trend has been the application of Ion Assisted Deposition to exploit IAD's advantages for increasing packing density, adhesion, and hardness, we present data from IAD evaluations. Refractive index, extinction coefficient, and physical thickness are derived from transmission spectra of layers 500 to 700 nm thick deposited on fused silica substrates. Substrate temperature is 200° to 275°.

## Lanthanum Titanate

We present a high-index material that, by design, has many advantages over  $TiO_2$ ,  $Ta_2O_5$ , and other high-index materials. The compound, Lanthanum Titanate ( $LaTiO_3$ ) has an index at 550 nm of 2.06 (2.09 with IAD), and very low absorption to wavelengths below 350 nm. By contrast,  $TiO_2$  layers  $k$  (extinction coef.) values are ~5 times higher. Figure 1 (page 1) shows the  $k$  values for  $LaTiO_3$  layers deposited with and without IAD. IAD increases the  $k$  values, a typically observed phenomenon with all materials.

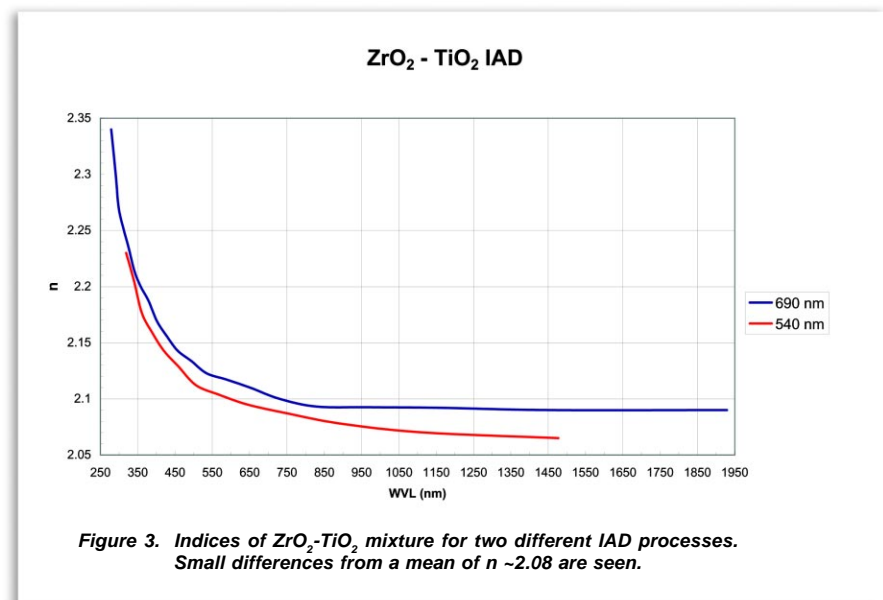
Figure 2 shows the refractive indices for the same depositions as for Figure 1. The repeatability of index for different depositions is evident. The coatings show low index dispersion and low absorption in the visible and to near-IR wavelengths to the limit measured: 2400 nm.

$LaTiO_3$  source material melts, and conditioning by e-beam sweeping for several minutes prepares the charge for evaporation with minimum outgassing and spitting. New material can be added to the melt for subsequent evaporations.



## Zirconium Oxide - Titanium Oxide

This combination of materials displays an index near 2.1 when IAD is used. Figure 3 shows the index dispersion curves for two different IAD processes and two thicknesses. Absorption does not reach  $k \sim 0.001$  until wavelength 350 nm, making this material useful to shorter wavelengths than pure  $TiO_2$ . The mixture fuses to form a smooth evaporation surface during e-beam conditioning.



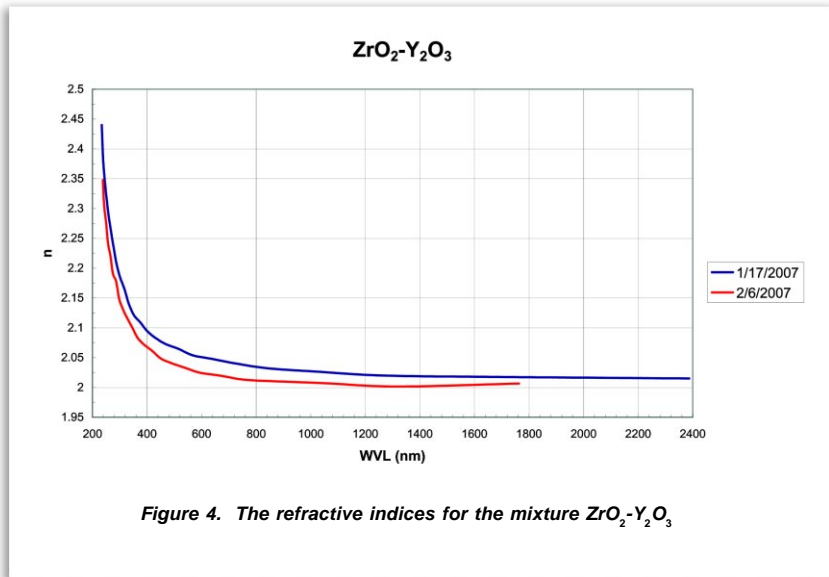


Figure 4. The refractive indices for the mixture  $ZrO_2-Y_2O_3$

### ZrO<sub>2</sub> Stabilized with Y<sub>2</sub>O<sub>3</sub>

Ytria is one of the materials often used to improve the hardness and density of compatible oxide compounds. It operates to promote amorphous growth. Both Zirconia and Ytria are known as very hard materials; both also have good transparency into the UV. Zirconia characteristically representative of other refractory materials (Hafnia is another example), often grows layers with an inhomogeneous index depth profile. The presence of Ytria promotes a more even structure. Therefore, the combination should produce improved optical and mechanical properties over the sepa-

rate pure materials. The addition of a small percentage of Ytria does not lower the index of the combination much below that for pure Zirconia. Figure 4 shows the refractive index for two depositions made using IAD at different times. There is an apparent decrease in index by ~0.03, or 1.5%, for the second deposition.

The films show *k* values <0.001 to wavelengths as short as 250 nm, even with IAD, demonstrating that the transparency for the altered material is preserved well into the UV region.

### Conclusions

The designed materials provide several advantages over pure evaporation materials. Consistent optical properties are produced and improved durability is achieved. In many cases, little sacrifice is introduced in the value of the refractive index by the additive.

To learn more about these “designed” materials or other optical coating materials, please contact CERAC at [ceracinfo@beminc.com](mailto:ceracinfo@beminc.com).

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