

## Pre-Melted TiO<sub>2</sub> Deposition Results

In the last issue, we published a note announcing the performance of the new pre-melted form of TiO<sub>2</sub> offered by CERAC. The results of a study commissioned by CERAC and conducted independently by Pellicori Optical Consulting were recently summarized in a presentation at Photonics West. In this issue, more detailed results of the evaluation tests are presented. Multiple depositions of each material made under evaporation conditions as identical as possible are evaluated for their:

- Evaporation behavior
- Spectral properties (refractive index and absorption values)
- Index homogeneity
- Index reproducibility
- Temporal stability
- Mechanical durability

All depositions were made under identical parameters on polished glass, fused silica and silicon substrates to permit spectral evaluation between ~350 nm and 2000 nm. Deposition conditions for all evaporations were:

- Substrate temperature: 250° C and 175° C.
- Base pressure 2 x 10<sup>-5</sup> Torr; Deposition partial pressure: 1.0 to 1.5 x 10<sup>-4</sup> Torr.
- Rate: 2.9 to 3.1 Å / sec.
- Consistent pre-evaporation conditioning, heating, and cooling times.

All depositions were made without ion assistance, i.e., straight e-beam evaporation. The materials were placed directly in the hearth of the e-beam gun. Adhesion and abrasion testing was also done on these substrates. The Ti<sub>x</sub>O<sub>y</sub> source materials used were purchased from the vendors, except for those provided by CERAC. They were:

1. CERAC Ti<sub>3</sub>O<sub>5</sub> pieces 1-4 mm (NP-127-03)
2. CERAC TiO<sub>2</sub> pieces 1-5 mm (WT-5503)
3. CERAC 15 cc fused cone of TiO<sub>2</sub> (WT-5003-15cc) Batch W500162-12A.

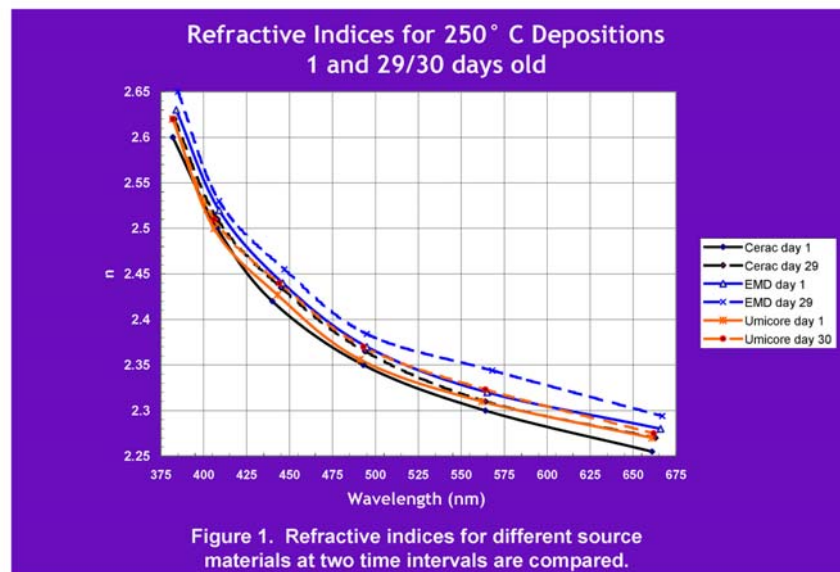
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## Transparent Conductive Oxides: ITO Replacements

Transparent conductive oxide coatings (TCO), especially ITO the favorite, have been discussed frequently in past issues [1]. In a recent article, we discussed some of the industry concerns with ITO, namely the availability of Indium and the resultant impact on cost, and its toxicity [2]. One alternate material with useable electrical and optical properties especially for photo-voltaic applications is Cadmium stannate. However, the toxicity of Cd presents a problem. Consequently, alternate TCOs are sought.

Research into alternates to ITO and Cd<sub>2</sub>SnO<sub>4</sub> continues, and recent developments based on ZnO and SnO<sub>2</sub> show promise. Zinc stannates (ZnSnO<sub>3</sub> and Zn<sub>2</sub>SnO<sub>4</sub>) exhibit higher optical transparency but several orders lower electrical conductivity than ITO and Cadmium stannates. Films of SnO<sub>2</sub>-ZnSnO<sub>3</sub> of varied relative concentrations were deposited by simultaneous magnetron sputtering of targets of ZnO and ZnO<sub>2</sub>:3 wt.% Sb<sub>2</sub>O<sub>5</sub> doping [3]. The content of the cation Zn determines the conductivity of the amorphous film; higher concentrations of Zn lower the resistivity and decrease the carrier concentration. When the composition was SnO<sub>2</sub>-ZnSnO<sub>3</sub>, the minimum resistivity of 4-6 x 10<sup>-2</sup> Ω cm was reached. ITO films typically have a resistivity ~10<sup>-4</sup> Ω cm. Zinc stannate films deposited at 350° C show higher transmission near 1350 nm than films deposited at 250° C. In TCOs, mobile electrons are responsible for n-type conductivity. The conduction electrons are supplied by donor sites associated with

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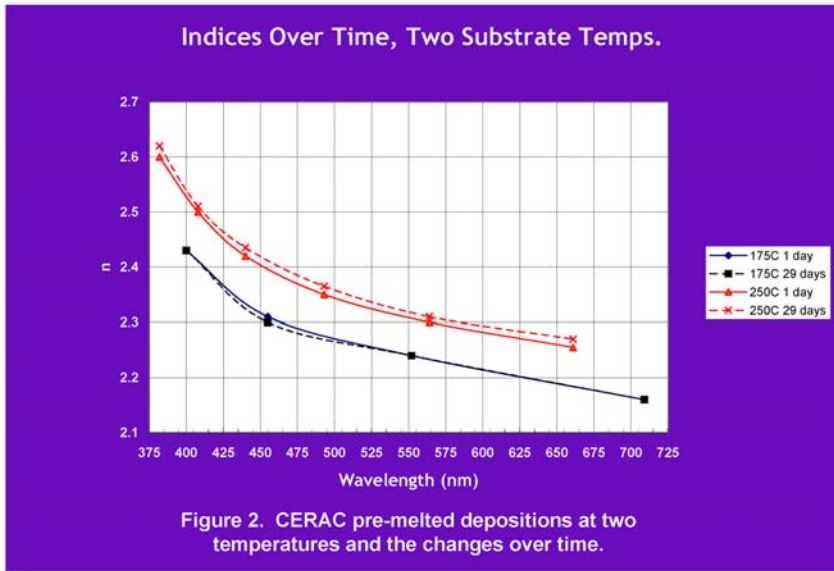


Figure 2. CERAC pre-melted depositions at two temperatures and the changes over time.

- EMD Chemicals Titanium Dioxide “S” granules 1-4 mm. Consisting of 70 wt. % TiO<sub>2</sub> and 30 wt. % TiO. (116828)
- Umicore Ti<sub>3</sub>O<sub>5</sub> granular 0.7 – 3.5 mm (0489459).

Spectral transmittances were measured, and the QW and HW optical positions (wavelengths and T values) were determined by the spectrophotometer’s software and printed on the chart. These data were used in Macleod Thin Film Program to determine the refractive index, extinction coefficient, and physical thickness. The routine uses an envelope method to fit the transmittance values knowing the transmittance of the uncoated substrate material. Checks of the reproducibility of the curves using the solved optical constants lent confidence in the accuracy and repeatability of the method. The ultimate accuracy is affected by the spectrophotometer’s program for finding the inflection points in the curve. The accuracy decreases at the long-wave features which are relatively flat rather than sharply curved as they are for short-waves. The final accuracy is felt to be within 0.01 in refractive index and <5 nm in physical thickness.

The behaviors of the CERAC particulate and cone forms follow.

**CERAC TiO<sub>2</sub>:** No spitting, but outgases for first run. Requires a little more O<sub>2</sub> than fused cone. Approximately 3 hours required to melt into a uniform plug.

**CERAC Ti<sub>3</sub>O<sub>5</sub>:** Good behavior: no spitting or outgassing. Same time required to build a plug.

**CERAC TiO<sub>2</sub> Fused Cone:** Easiest to use, smooth rate. No spitting or outgassing, lowest need for additional O<sub>2</sub> compared with the other materials in the study. Ready for deposition after <30 minutes of heating.

A shift in index with time due to moisture absorption is an indication of film packing density. Titania films are known to assume a porous microstructure under low-energy deposition conditions such as we used, i.e., e-beam without IAD. Spectral dispersion of refractive index for the EMD, Umicore and CERAC fused cone are

shown in Figure 1.

It is seen that the curves closely follow the same dispersion and water absorption trends, with relatively close values. Values for the EMD sample are ~1% higher near wavelength 1000 nm, an insignificant difference in thin film designs. Examination of the spectral transmittance curves revealed that all the films deposited with good index homogeneity. This was indicated by the return of the T values to the same value at the QW and HW points where the film is not absorbing. An inhomogeneous index profile with depth can result in the T value exceeding that of the uncoated substrate at the HW points and reaching different values at subsequent QW points.

As explained earlier, the packing density of a film influences the index stability of the deposit. As water is absorbed in the pores, the index increases. Generally, this increase is reversible, and to avoid this instability, high temperatures or ion bombardment (IAD process) is applied during film growth. Figure 1 shows the shifts for the films 29 or 30 days after an initial spectral trace for film layers 400 nm thick. Since all films had been exposed to the atmosphere for at least one day, they did not start at zero water content. What is revealed is how the shift progressed over time. Comparing the materials at wavelength ~495 nm, each showed an increase in n of 0.014. Thus the packing densities of all materials are the same: none is less porous than the other.

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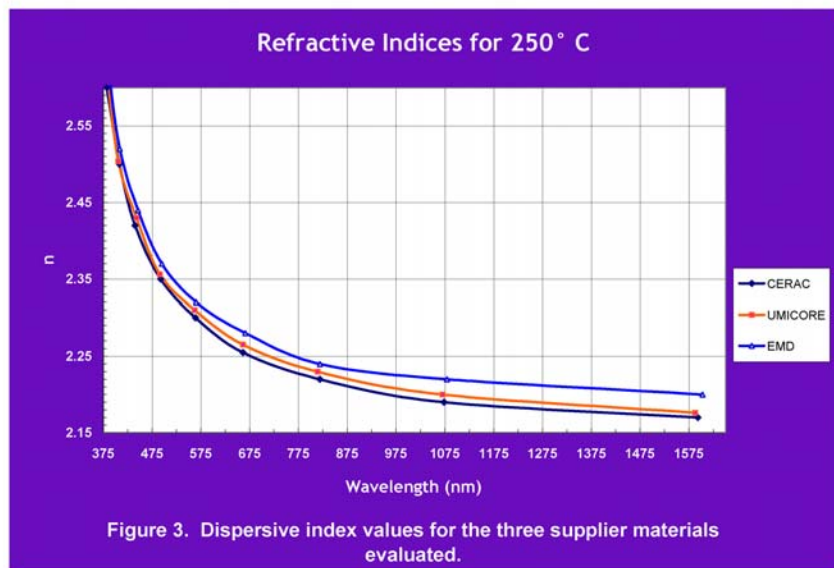


Figure 3. Dispersive index values for the three supplier materials evaluated.

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The substrate-temperature dependence of index is well known. Figure 2 shows results for temperatures 175° C and 250° C, and the change over time. An increase in index is shown, as expected. A real, but small, change in index is evidenced for the two substrate temperatures, indicating similar packing densities.

We present a plot extending to 1575 nm wavelength in Figure 3 for the indices of the materials supplied by the three vendors. The results are very close between the materials.

Table 1 lists the dispersive constants for the CERAC cone form of TiO<sub>2</sub> for wavelengths from the visible to 1600 nm. The measured data were fitted to a smooth curve.

Wvl (nm)	n	Wvl (nm)	n
400	2.54	675	2.25
425	2.47	700	2.25
450	2.42	750	2.25
475	2.38	800	2.24
500	2.36	850	2.24
525	2.34	900	2.23
550	2.32	950	2.22
575	2.3	1000	2.21
600	2.29	1200	2.2
625	2.28	1400	2.19
650	2.26	1600	2.18

**Table 1. Indices deposited from CERAC Pre-melted TiO<sub>2</sub> cone.**

The conclusion is that the new CERAC pre-melted form of TiO<sub>2</sub> material performs as well as particulate forms, but provides the major advantage of saving pre-processing time — <30 minutes vs 3 hours — in the coating chamber, thus reducing non-productive chamber time. This can translate to savings ranging from \$200-\$600 per coating run.

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oxygen vacancies or excess metal ions, Sn<sup>+</sup> ions in the case of ITO.

ZnO films have some advantages over SnO<sub>2</sub> films, one being the desirable etching properties when forming electrode patterns. However, pure ZnO TCOs are unstable at high temperatures. Doping ZnO with Al, “AZO”, improves its electrical and optical performance, and at relatively low expense. There are three sputter-deposition methods used for generating AZO films: co-sputtering Al and ZnO targets, sputtering of a mixed Al<sub>2</sub>O<sub>3</sub>-ZnO target, co-sputtering Zn and Al metal targets reactively. Reactive sputtering of metal targets produces higher deposition rates, but as we have described in past issues, the final properties of the film are strongly influenced by substrate temperature, argon and oxygen gas pressures, power, and Al content. Work using magnetron reactive sputtering of metal targets of different Zn/Al ratios with deposition parameters as dependent variables was reported [4]. We summarize the major findings. The optimum concentration of Al in the target is 1.5 wt %. At concentration above and below this value mixed crystal orientations appear, producing rougher surface texture. The lowest stress, lowest resistivity, highest Hall mobility, and highest visible transmission were obtained at substrate temperatures near 250° C. This is ~100° lower than the temperature normally used to deposit ITO TCO films. It appears that AZO films have good potential for replacing ITO films.

Another study of doped ZnO films used vacuum arc plasma evaporation to overcome deposition uniformity problems encountered by magnetron sputtering of Zn targets [5]. During reactive sputtering, sputter rates can be influenced by the presence and spatial distribution of ZnO formed on the target by oxygen impinging on its surface. The vacuum arc plasma deposition does not suffer from this problem and produces more uniform films. The targets used were either ZnO + Al<sub>2</sub>O<sub>3</sub> (AZO) or ZnO fragments composed of sintered powders of ZnO and Al<sub>2</sub>O<sub>3</sub>. The aluminum content in the films was changed by changing the concentration of an Al dopant gas, Aluminum acetylacetonate, Al(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub>

introduced during evaporation. It was found that the carrier concentration increased as the concentration of Al was increased to 10%, and the resistivity correspondingly decreased, reaching ~10<sup>-4</sup> Ω cm. Ga doping (GZO) has reportedly also achieved resistivities approaching those of ITO.

The ZnO and SnO<sub>2</sub> systems look promising as lower cost replacements for ITO, and we’ll surely hear more about them in the near future.

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