CERAC, incorporated: The Ongoing Commitment to VIS/IR and IR Coating Materials, May 1, 2007.

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For more than 40 years, CERAC, incorporated has been a steady contributor to the industry as both a supplier and as a partner in the development and customization of optical coating materials. CERAC has continued to support the industry through the production of Thorium Fluoride and yet continues to innovate with new and improved coating materials for VIS/IR and IR applications. In the past two years we have combined our materials manufacturing knowledge with investment in new process technology from principle reactions to melting/forming routes to provide more service to this intensely competitive segment. For VIS/IR segment new products in the TiO_2 family and $LaTiO_3$ have added process stability and enhanced productivity. For the burgeoning IR segment, our YF_3 is proving versatile and effective and is joined by a new CVD ZnS for thermal or e-beam evaporation. Finally, the continued need for a ThF_4 replacement and far IR designs has resulted in a completely new YbF_3. Our new material has less surface area and a more conventional coating material look and feel with high performance. We hope this paper and our high quality discussions in CMN show our commitment and dedication to this market and our ability to continue to provide innovative solutions.

The Titanium Oxides

With the general characteristics of dense granules for e-beam evaporation – resulting in adherent films with useful transmission from 400nm to 12000 nm with an index in excess 2.4 at 500nm, the titanium oxides are a staple for VIR/IR designs. The problem is that all the competing sub-stoichiometric phases (i.e. $TiO_{1.98}$, TiO_2, Ti_3O_5, Ti_4O_7) are competition for valuable process stability. To satisfy the demands of the VIS/IR –with designs ranging from 3 layers to over 60, we have historically offered many of these sub-phases as finished goods for our customers to build processes taking their tools, training, temperature control, gas control, beam utilization and ion assistance capabilities into account while meeting their customers' needs.

Taking a departure from our classical offering of precipitated and press/reacted then sintered products, we have added two new products and one new compound to the market based on 1) process stability and turn-around, 2) process stability and contamination and 3) stable index and/or elevated index at specific wavelengths.

Electron-Beam TiO_2 ($TiO_{1.9}$)

For the past two years, CERAC, incorporated has been rolling out products created in E-Beam equipment. Our custom long-throw, high power e-beam furnace is producing variants of TiO_2 based finished EB cones and EB pieces for direct evaporation. The EB cones (T-5003) are made to fit directly into the copper crucible or a customer supplied/specified crucible. A specially formulated cold-pressed TiO_2 starting material (less dense than our standard T-1192, 3-6mm) allows for uniform melting without inclusions at a specific structure (*see figure 1a, b*) defined by interaction with customer. The different structures of the cone can allow more consistent utilization of the material and permit potential additional coating power without spatter for those looking to keep the index high throughout long designs.

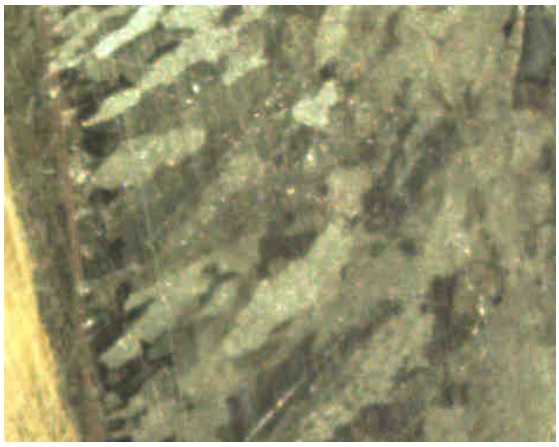

Figure 1a - EB cone with highest Heat Transfer configuration.

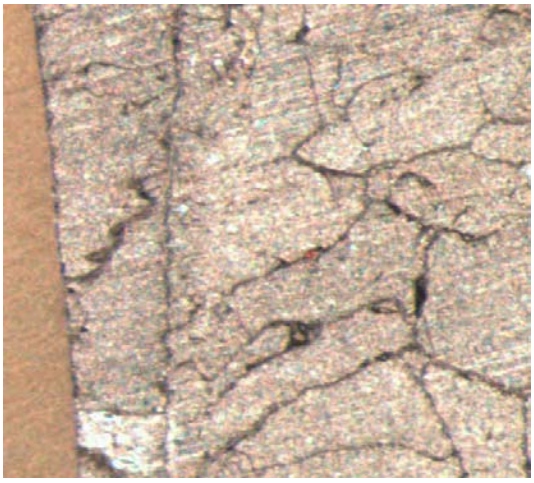

Figure 1b - EB cone with lowest Heat Transfer configuration.

The EB cones are dense and sturdy with very low moisture sensitivity and come individually sealed –ready for use. The lack of dust – as from the classical sintered granules- reduces embedded contamination. The drop-in design minimizes turn-around, pump-down to coating time and provides Process Engineering with a stable platform for refilling with anything from white pieces, to sintered Ti_xO_y options to our melted EB pieces (T-5503 1-5mm) for the most stringent applications.

Ti_3O_5 – Crystalline

CERAC, incorporated recognizes that many may feel that the preparation of their TiO_2 or cost effective sintered Titanium Oxide is a strong part of their process. In addition, some applications are perfectly satisfied with a partially conductive, low dust sub-stoichiometric granule material. After years of offering a sintered Ti_3O_5 CERAC, incorporated now offers a true crystalline Ti_3O_5 (T-2100 1-4mm 3N) material with lower dusting and reduced pump-down to coat time to work with the EB cones as a refill material or in addition/instead of the EB pieces.

Being a true Titanium oxide (Ti_3O_5 crystalline) has the general characteristics of dense granules for e-beam evaporation – resulting in adherent films with useful transmission from 400nm to 12000nm with an index up to 2.4 at 500nm for VIS/IR designs.

As with other non-sintered Ti_3O_5 variants –CERAC Ti_3O_5 crystalline yields durable films but minimizes contamination due to its inherent durability in transport, the pocket, and the ease of melting. Whereas TiO_2 must be iteratively melted to get the long run length mass, Ti_3O_5 crystalline offers a fraction of the preparation time due to the minimized surface area compared to a sintered product. Sintered sub-stoichiometric Titanium oxides can “boil” out of the pocket and sometimes have periods of high fluctuation in degassing behavior which cause unwanted rate variation and/or adsorption due to film density discontinuities. When choosing between TiO_2, sintered Ti_3O_5 or other less dense phases like Ti_2O_3 – without good IAD or a good dynamic recipe – too much can be left to the operator or specification to handle. In these cases, crystalline Ti_3O_5 can be a good option before trying EB cones for your application.

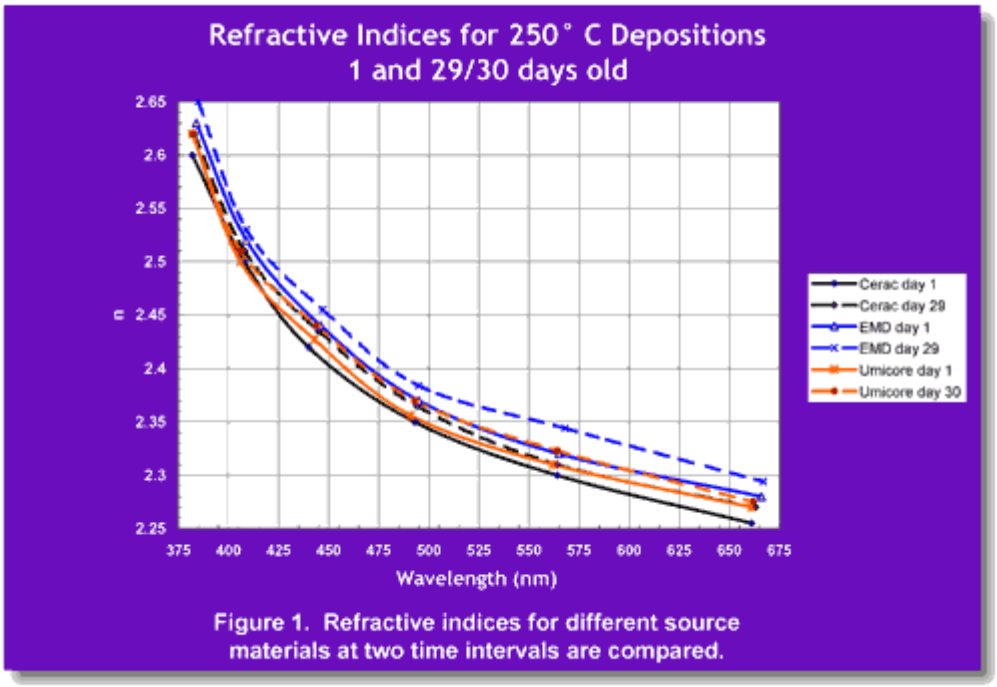

Figure 2 EB Cone, EMD TiO_2(S) and Umicore Ti_3O_5 Compared*
Base pressure 2 x 10^{-5} Torr; Deposition partial pressure: 1.0 to 1.5 x 10^{-4} Torr.
Rate: 2.9 to 3.1 A / s, substrate 250C

*As reported by Samuel Pellicori (Pellicori Optical Consulting @ pellopt@cox.net) "*Study of Titanium Oxides: Comparison with CERAC Pre-Melted Cones*," on December 20, 2004 and later in **CMN** Article "*Pre-Melted TiO2 Deposition Results*"- Volume 15, Issue 1 on March 2005 (www.cerac.com – Technical Publications, CMN Archives)

As shown in *Figure 2*, using the EB cones does not necessarily mean a process shift. This is especially important for VIS/IR filters with excessive layer counts which need index stability for the length of the run. Where the full features of EB cones may not be needed, further testing showed that CERAC, incorporated Ti_3O_5 crystalline can be a drop in analog for EMD TiO_2(S) and Umicore Ti_3O_5 (*view CMN article online or contact Pellicori Optical Consulting*). However, the added customization, versatility and process/efficiency improvements offered by these maturing new products can offer the customer more than just an option but a platform for greater Process Engineering controls.

$LaTiO_3$ – Lanthanum Titanate

Sometimes the customer has the advantage of being able to narrow their requirements to optimum performance from 325nm to 4000nm. For this case, CERAC, incorporated combined a new chemistry with its most advanced densification technology to arrive at a new $LaTiO_3$ (NP-122-03 1-4mm 3N) coating material. $LaTiO_3$ has the general characteristics of dense granules for e-beam evaporation for adherent films in the VIS/IR optimized for < 4000nm. Over this range, the index is in range of 2.0 -2.1 at 550nm with and without IAD (*see Figure 3*). Since this material is not a mixture the index is stable through long coating runs and subsequent refills with $LaTiO_3$. In addition, the uniform melting and lack of sub-phase competition (as with the Ti_xO_y system) means that evaporation is stable and less prone to spitting and rate fluctuation.

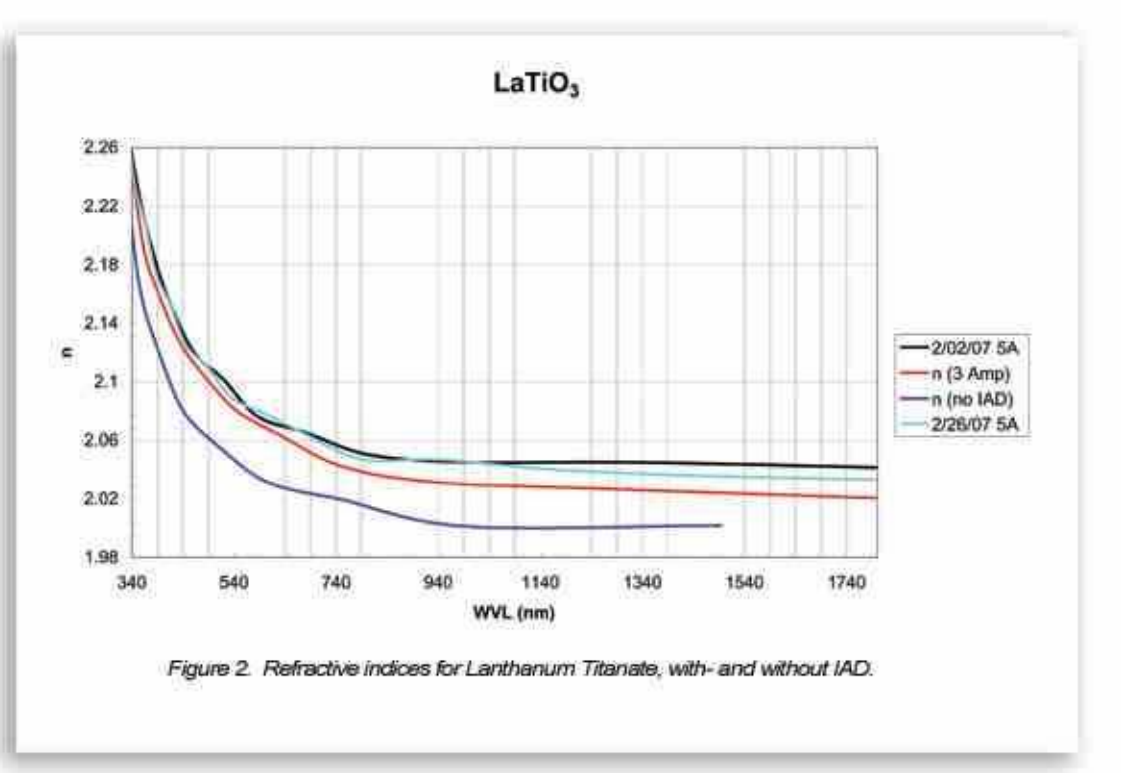

Figure 3 $LaTiO_3$ - With and Without IAD

w/o IAD prep at 1 E-05 Torr – and substrate 200° C and 1 E-04 Torr O2 pressure at 2 Å / s rate*
w IAD and substrate 200° C and 1.4 E-05 Torr O2 pressure, rate 3 Å/s. Ion voltage 180 at 5 A current.*

*As reported by Samuel Pellicori (Pellicori Optical Consulting @ pellopt@cox.net) "*LaTiO3 Evaluation*," on February 6, 2006 and "*LaTiO3 Deposited with IAD*" on February 22, 2006 and later in **CMN** Article "*Materials Designed to Produce Dense Layers*"- Volume 17, Issue 1 on March 2007 (www.cerac.com – Technical Publications)

For IR color-filters and even for coating on polymers the $LaTiO_3$ material can give a 2.0 index at substrate temperatures less than that of classical TiO_2 processes. Additionally the influence of the La on the Ti_xO_y system enables superior performance to TiO_2 below 400nn. Finally, whereas one fights high extinction coefficients with TiO_2 (even without IAD) and stressed films for high layer counts (with Ta_2O_5), $LaTiO_3$ offers stable index, IAD feasibility and simplified reloading sensitivity than the classical TiO_2 processes. Similar to our other new Engineered materials, EB TiO_2 and Ti_3O_5 crystalline this new CERAC $LaTiO_3$ enables our customers to build processes taking their tools, training, temperature control, gas control, beam utilization and ion assistance capabilities into account while meeting their customers' needs.

The Far IR

We understand the need for IR replacements for our ThF_4 radioactive coating material. In addition, the needs of the far IR take many companies out of their comfort zone for run length, chamber contamination and sometimes mixes co-deposition, multiple coating techniques in the same chamber (e-beam and thermal) or increased risk due to use of different stations for the same production part.

Over the past two years, our improved YF_3 (Y-1049 3-12mm 3N) pieces have helped push the envelope of YF_3 fit-for-use on the upper end of its range (9000 to 15000 nm) and has enabled reload upon reload with manageable water band interference or excessive decomposition when e-beam deposited. While IRX and IRB remains the staple for thermal process replacement for ThF_4, YF_3 continues to gain in the increasingly common e-beam platform routes.

Of course the increasing use of e-beam technology with YF_3 for the far IR quickly demonstrated that even the highest purity ZnS or most heavily engineered ZnS still had excessive SOx emissions or S/ Zn deficiencies. Weak ZnS bonds or excess S made utilization of the requisite amount of ZnS difficult to support from a housekeeping and operator satisfaction/S.H.E. perspective. To that end CERAC Incorporated developed a CVD ZnS (400nm to 14000nm with good adhesion to ZnSe, and Ge) that is tightly bound and available as cubes or pieces (Z-2072 3/8" 4N cubes or Z-2026 2-12mm 4N pieces). The price and performance of this material has been so good and SOx emissions so manageable that these products have proven themselves for both Specialty Optics and for Large Area Coatings. The CERAC Incorporated CVD ZnS has been a success in both thermal and e-beam platforms alike.

YbF_3 - Ytterbium fluoride

Over the past two years more and more IR designs are being tried by more and more companies. 1-3µm. 3-5µm and 3-12µm designs are increasingly sought after by both consumer and traditional military markets. To meet the demand, CERAC, incorporated developed a new YbF_3 suitable for E-beam evaporation and with a much more conventional look and feel as a coating material. The difficult chemistry and atypical growth characteristics which make it an interesting option of far IR designs has also prevented its wide-scale use. The < 1mm crystallites were difficult to manage in the pocket, produced dust contamination and also the high surface area made it difficult to suppress the water bands normally associated with fluorides at 2.7 and 6.2 µm and even on Ge substrates useful transmission through 12µm and beyond was difficult to achieve repeatedly.

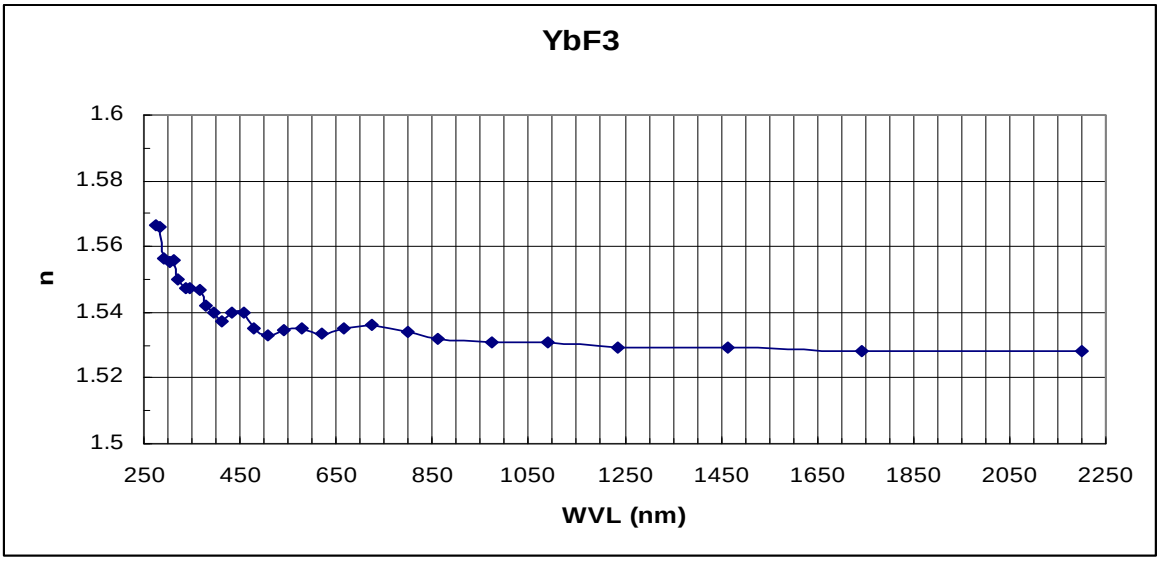

Figure 4 CERAC YbF_3 (Y-1051) Index vs Wavelength (VIS/IR) 11-14-05

Refractive indices on Ge for 14 kÅ film of YbF3 deposited at 160° C and pressure <2 E-05 Torr at >8A/sec*

*As reported by Samuel Pellicori (Pellicori Optical Consulting @ pellopt@cox.net) "*YbF3 Material Evaporation Evaluation*," on November 14, 2005 and "*YbF3 Material Evaporation Evaluation – NP-19105*" on April 13, 2006 and "*YbF3 Material Evaporation Evaluation – YM 5050005*" on April 23, 2006.

After reworking the principle reaction and utilizing several different densification technologies CERAC, incorporated now offers YbF_3 (Y-1051 3-12mm 3N) granules to the marketplace. Starting in November of 2005, Pellicori Optical Consultants performed 3 complex designed experiments on fused silica and Germanium substrates to prove the material. With more experiments to come and a future CMN article to follow it was shown that this YbF_3 evaporates without out-gassing and evaporates at a consistent rate without spitting. These tests showed refractive VIS/IR indices around ~1.52 – 1.53 and furthermore, the water-bands were less conspicuous and the hard, adherent films had useful spectral range from ~270 nm to +12 μm.

SUMMARY

CERAC, incorporated continues to demonstrate its dedication to the Specialty Optics marketplace by continued improvement and new product innovation and testing. Our reworking of principle reactions, and acquisition/utilization of novel melting/forming routes has resulted in EB TiO_2, Crystalline Ti_3O_5, $LaTiO_3$ and YbF_3 for the VIS/IR and far IR marketplace. Our commitment to continuous improvement has proved invaluable as our new CVD ZnS is versatile, cost effective and offers superior performance from Specialty Optics to Large Area Specialty Coatings. Our Process Improvement and stringent manufacturing guidelines has improved our YF_3 to achieve broad performance on EB platforms for designs well into the IR region. Our new materials offer less surface preparation, more versatility and high performance to an Industry reliant on Process Engineering. We hope this paper and our continued dedication to fresh and challenging CMN articles keep CERAC, incorporated at the forefront of customer and industry directed innovation. CERAC, incorporated offers a special thanks to Samuel Pellicori and the partners of Pellicori Optical Consulting for their dispassionate testing and reporting on the submitted materials.