

Properties of Thin Film Layers for Optical Applications: A Tutorial

It is well known that the material properties of thin film layers of compounds and single elements grown from a vapor-condensation process differ substantially from their bulk form. Considered from a remote point of view, the structural disorder, defect density, impurity inclusion, stoichiometric composition difference, and low packing density differences between the film- and bulk-states might lead one to conclude that it is impossible to achieve useable and reproducible optical and mechanical properties for the material in the form of a thin film. We know from experience that the reality is that the technology of the deposition of materials at sub- μm film thicknesses enables the industry to routinely produce controlled film properties for many applications.

To help appreciate the complexity of coating deposition technology, we present an outline of the numerous variables associated with thin film deposition that must be considered at the level appropriate to the final application. More discussion is given in Ref [1]. It is clear that many of the variables are coupled, and it is generally impossible to isolate a specific independent variable.

The unique properties of the 'film structure' state are characterized by the following qualities:

- Optical properties
 - Transparency (absorption)
 - Refractive index (dispersive values and homogeneity)
 - Scatter (surface roughness/ volume defects)
- Mechanical properties
 - Adhesion (to substrate or adjacent layers)
 - Cohesion (within the film)
 - Stress (compressive or tensile)
 - Packing density (porosity)
 - Micro hardness (indenter)
 - Wear resistance (abrasion and scratch)
- Chemical / environmental resistance
 - Influence of humid atmosphere (on optical & mechanical properties)
 - Solubility
 - Cleanability
- Laser damage resistance
 - Damage threshold value (CW vs pulse: duration and repetition rate)
 - Wavelength dependence
 - Electric field distribution

The listed qualities of a thin film layer are determined by the following film microstructure parameters:

- Morphology (crystalline or amorphous)
- Grain size
- Composition
- Packing density
- Morphological homogeneity
- Layer interface nature (abrupt / graded)

Those film parameters are in turn determined by deposition technique parameters:

- Vapor species energetics (thermal: ~ 0.1 eV; E-beam ~ 1 eV; sputtering $\sim 1-10$ eV).
- Deposition atmosphere composition (reactive species, density)
- Substrate temp. / electrical bias (influences nucleation coverage, growth structure)
- Surface condition (cleaning chemistry, ion / plasma scouring, nucleation layer)
- Growth rate (function of: pressure, energy, substrate temperature, etc).

Previous *CMN* issues have discussed the above aspects as related to specific materials and applications. The specific problem of refractive index depth-inhomogeneity is discussed on the following pages.

Optical Inhomogeneity: Occurrences and Cures

Some film layers exhibit a variation in refractive index with depth. The variation can be large enough to cause the deposited film to differ significantly in performance from design predictions. The problem is especially troublesome for the case of achieving minimum reflectance with AR coatings in general, and for high-energy laser coatings in particular. Figure 1 shows this effect for a QW-HW-QW design that uses $n_1 = 1.67$ for the first layer, $n_2 = 2.22$, and $n_3 = 1.43$ (black curve). When the index of the middle layer is changed in steps from 2.22 to 2.14 to 2.11, the loss in performance is as shown by the colored curve.

Materials most likely to exhibit this problem are metal oxides that require evaporation temperatures in

excess of $\sim 2000^\circ\text{C}$. Materials evaporated by thermal evaporation using E-beam or resistance-heating are more likely to exhibit this problem. The effect is apparently not as severe for sputter-deposited films or with the use of other high-energy deposition techniques such as ion-beam vaporization, ion plating, or ion bombardment (IAD). Optical index inhomogeneity has been reported for several common materials, including: CeO_2 , HfO_2 , Sc_2O_3 , and ZrO_2 [2,3]. Index inhomogeneity, Δn , is the difference between the

value of refractive index at the substrate / film interface and that at the air interface, and can be either a positive or negative value depending on whether the index is decreasing or increasing away from the substrate. The Δn can be as large as 0.18 for Sc_2O_3 and 0.28 for ZrO_2 . Optical inhomogeneity is detected through the observation that the transmittance or reflectance values of a single layer do not equate to those of the uncoated substrate at the half-wave optical thickness wavelengths. Fluoride compounds as well as oxide compounds can exhibit the effect.

The causes are believed to be two in nature: structural growth pattern and crystal state. In the former, the columns that form the film have large base diameters at and near the substrate, whose widths decrease with increasing film thickness. Thus, the density of the layer decreases along the height of the tapered

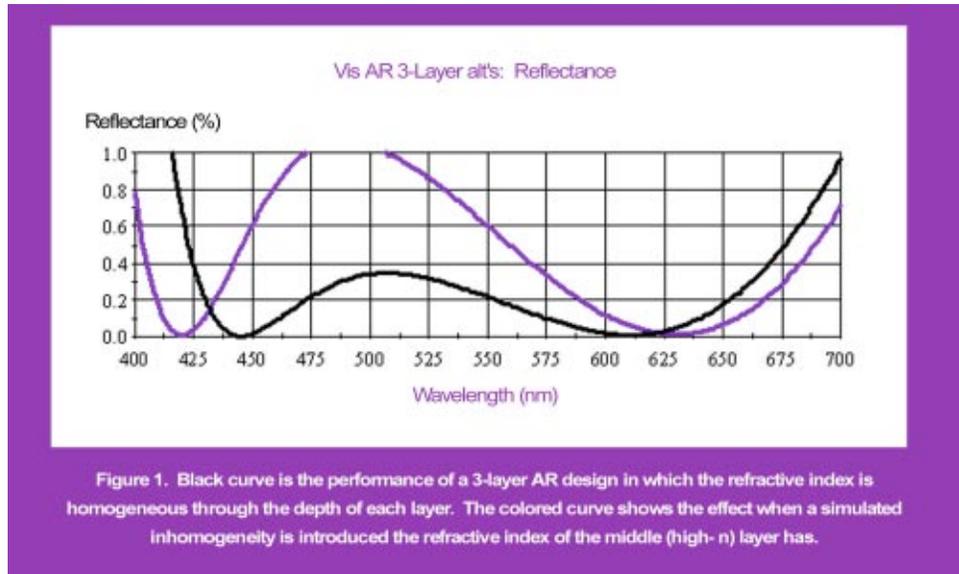


Figure 1. Black curve is the performance of a 3-layer AR design in which the refractive index is homogeneous through the depth of each layer. The colored curve shows the effect when a simulated inhomogeneity is introduced the refractive index of the middle (high- n) layer has.

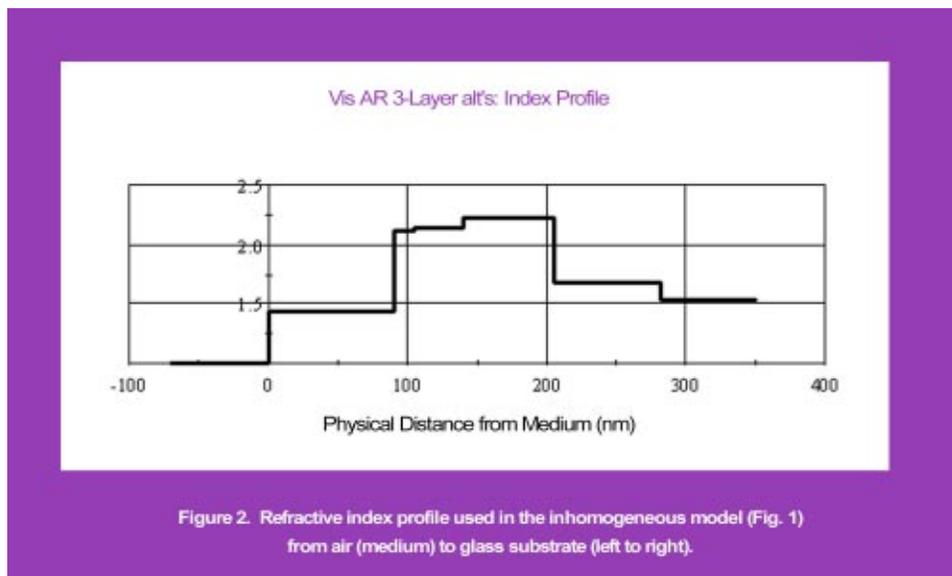


Figure 2. Refractive index profile used in the inhomogeneous model (Fig. 1) from air (medium) to glass substrate (left to right).

continued on page 3

continued from page 2

columns producing a reduction of index. This 'porosity' can approach 30% in oxide compounds and 50% in fluoride compounds, and has impacts on mechanical and chemical durability as well as on optical inconsistencies. The second cause for index inhomogeneity is a thickness-dependent change in crystal state along the growth axis of the film. Mixed and evolving phases have been observed in the oxide materials mentioned, particularly ZrO_2 . The presence of multiple crystal states can also result in instability of optical and mechanical properties at high operating temperatures. Crystal-form transformations can occur, producing physical dimensional and stress quality and quantity modification. Similarly, column structures can reassemble at high temperatures with the same results. The source of inhomogeneous optical properties in fluoride-compound layers is most likely their columnar micro-structure. The attendant porosity of evaporated fluoride-compound layers is evidenced by the change in optical thickness (refractive index) observed as they adsorb and desorb atmospheric water.

Generally both mechanisms that cause optical inhomogeneity are concurrently present in a thin film layer, but one might dominate over the other depending on material and deposition conditions. In the case of ZrO_2 , multiple crystal phases are present in a film deposited on room-temperature substrates, with the monoclinic phase dominating. When raised to higher temperature, phase transformation occurs, specifically tetragonal at $1000^\circ C$ and to cubic at $\sim 1580^\circ C$. On substrate temperature $300^\circ C$, the cubic phase

nucleates and grows first, and as the layer thickness increases the monoclinic phase overcomes the cubic and the upper thicknesses are predominately monoclinic phase. Both the difference in refractive index and the difference in crystal structure contribute to the optical inhomogeneity observed [2]. Volume changes of 3 – 6% have been observed between crystal phase transitions. This behavior model might also explain the effect in the other high-temperature metal oxides mentioned above.

Materials That Produce Homogeneous and Stable Film Layers

One solution to the problem is to employ materials with constrained phase transformation properties. This is accomplished by substituting for the pure compound a composite consisting of a small percentage of a mutually soluble compound admixed with the host material. Two methods have been employed to achieve these mixtures: co-evaporation or co-sputtering and the evaporation of a solid solution of the composite mixture. The latter method is convenient and more cost-effective since it is a simple substitution of materials.

The advantages of mixture-composite were discussed relative to improving UV laser damage thresholds in a previous issue of *CMN* [4]. As reported, in addition to improving laser damage threshold such new-material mixtures produce better optical homogeneity, and smoother, denser and harder films. The stable, dense fluoride-compound mixture materials, IRX™ and IRB™ for applications from $\lambda \sim 250$ nm to $10 \mu m$, were discussed in another *CMN* [4]. Examples of stabilized high-index mixtures ($n = 2.1$) composed of

ZrO_2 & TiO_2 (CERAC Z-1077) and ZrO_2 & MgO (Z-1092) are available from CERAC. Experience with Z-1092 shows very good homogeneity ($\Delta n < 0.02$, the limit of detectability) and index 2.1 at $\lambda = 550$ nm for film thicknesses ~ 3000 Å. For mid-index ($n = 1.7$) layers, a ternary mixture (M-1126) is a material that produces smooth, high-temperature tolerant films.

CERAC Coating Materials News is a quarterly publication of CERAC, inc.
P.O.Box 1178
Milwaukee, WI 53201-1178
Phone: 414-289-9800
FAX: 414-289-9805
web: www.cerac.com
e-mail: marketing@cerac.com

Editor:

Russ De Long
Manager, Advanced Technologies Group
CERAC, inc.

Principal Contributor:

Samuel Pellicori
Pellicori Optical Consulting
P.O. Box 60723
Santa Barbara, CA 93160
Phone/FAX: 805-682-1922
e-mail: pellopt@silcom.com

For a free subscription to *CMN*, please E-mail your name and address to marketing@cerac.com or send us a fax at 414-289-9805.

Guest articles or topic suggestions are welcome. Questions and comments can be e-mailed to marketing@cerac.com or faxed to 414-289-9805.

An electronic version of this publication can be accessed from the **Technical Publications** page of the CERAC web site at www.cerac.com. From there, link to the *CMN Archives* to view back issues. Printed copies of issues earlier than vol. 6 can be obtained, while supplies last, by contacting CERAC.

©Copyright 2003, CERAC, inc.

Coating Materials News

CERACTM
Incorporated

P.O.Box 1178
Milwaukee, WI 53201-1178
USA

PRSRT STD
U. S. POSTAGE
PAID
MILWAUKEE, WI
PERMIT NO. 2418

CMN

References

1. Karl H. Guerther, Appl. Opt. V23, 3612 (1984).
2. R. E. Klinger and C. K. Carniglia, Appl. Opt. V24, 3184 (1985).
3. J. P. Borgogno, F. Flory, P. Roche, B. Schmitt, G. Albrand, E. Pelletier, and H. A. Macleod, Appl. Opt. V23, 3567 (1984).
4. CERAC Coating Materials News V8, Issue 2, April-June 1998.
5. CERAC Coating Materials News V5, Issue 11 Jan-Mar 1995.

**Visit CERAC at Semicon
West-Wafer Processing,
July 14-16 at the
Moscone Center in
San Francisco.**

**We'll be in
booth number 6782,
located in North Hall.**