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This issue of *Coating Materials News* explores three topics. We begin with a discussion on mechanical properties of optical films, continued from previous issues. The second section presents the advantages of high-index Niobia films. Finally, the deposition of Fluoride compounds using IAD and IBS instead of thermal evaporation is discussed.

Mechanical Stress Compensation in Multilayers

We have discussed the sources of strain and stress in deposited layers and in multi-layer coatings composed of layers of differing stress values [1]. Silicon dioxide is the low-index component of essentially all optical coatings for UV through Mid- IR coatings, and is generally in compressive stress. High-index partners are often compressive also, but their stress can be changed toward the direction of tensive under some deposition conditions.

Large values of intrinsic coating stress can cause cracking and crazing, bowing of thin substrates, phase non-uniformity, and even layer or substrate separation. Compressive and tensive stresses behave oppositely, as illustrated in Figure 1. Table 1 lists some oxide-compound materials and their relative stress characters. We remind the reader that it is possible to manipulate the tension in a layer by varying such deposition parameters as substrate temperature and rate with evaporation, and background pressure and deposition energy in the case of IAD evaporation and sputtering. Many sputtered oxide compounds are compressively stressed. Post deposition thermal annealing can also alter stress. Some materials, Titanium dioxide in particular, change crystalline state and stress level when exposed to high temperatures. All fluoride compound films are tensive in nature, and the magnitude of the stress can change with ambient humidity level if the films are not densely packed. This humidity absorption phenomenon is also present with some oxide films, but can be defeated by the use of high-energy deposition processes such as IAD and sputtering.

Films of the metals Cr, Ni, Ag, stainless steel, Cu and Al are generally in tension, while films of Nb, Ti, and Zr are in compression [3]. This knowledge is applied to design and fabricate dielectric-metal multi-layers that exhibit near zero net stress.

Table 1. Common Optical Oxide-Compound Materials and Their Typical Stress Nature

Material	Stress Character
Silicon Dioxide	Low
Aluminum Oxide	High
Tantalum Pentoxide	Medium
Titanium Dioxide	High, variable
Niobium Pentoxide	Compressive or tensive
Zirconium Oxide	High
Hafnium Oxide	High
Yttrium Oxide	Medium-high

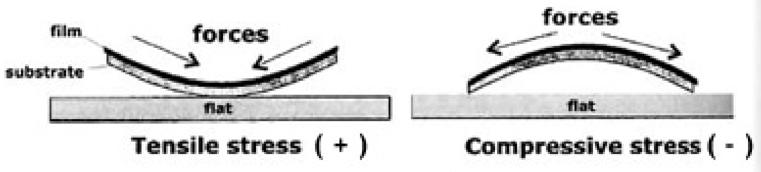

Figure 1. Stress deformation of thin substrates [2].

An example of this using this technique for the fabrication stress-compensated mirrors on thin substrates is described [3]. The special case involved sputter deposition of high reflectivity visible spectrum mirrors on 30 μm thick silicon MEM optics. The multilayer design consists of High- and Low-index layers, with the L being necessarily silicon dioxide. Candidate materials with the highest values of refractive index include Tantalum pentoxide, Titanium dioxide, and Niobium oxide. Niobia can be efficiently sputtered by reactive d.c. magnetron from a Niobium metal target. Virtually all oxide film materials grow with compressive stress. High-energy deposition procedures such as high ion energy IAD or high bias voltage during sputter deposition, result in densely compacted films with high indices, but also with high compressive stress. Increasing the substrate temperature above ~250° C increases the compressive stress of Niobia, but has little effect on Silica layers. The combination multi-layer dielectric stack design consisting of Silica and Niobia layers will therefore have resultant compressive stress. To

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achieve stress compensation and low total accumulated stress, a companion material is needed that possesses opposing tensive stress.

While it is possible to lower intrinsic stress by operating with the substrate unbiased, and for some sputtered oxides even reverse the sign, the range is available is not sufficient to compensate for the large total compressive stress that the oxide compound layers introduce. In the case of sputtered niobia, increasing the substrate bias voltage has a very strong influence on stress level, and can change it from slightly tensive to -1200 MPa as voltage is changed from 0 to -400 V [3]. Few other deposition parameter variations are available to influence layer stress. Compressive stress can be reduced by increase the pressure during reactive metal sputtering until a pressure threshold is reached beyond which the stress reaches a constant value. A higher background concentration of gas results in ion energy dissipation by collision. Then a trade between the values of low packing density and low stress must be decided. The researchers building the low stress mirror were able to use a metal layer under the dielectric stack to solve the problem [4]. From the metals mentioned, they chose chromium as the stress-balancing film component deposited directly on the silicon substrate. Complete stress balance to net zero was not possible. However, the compressive multilayer was designed using appropriate thicknesses of niobia and silica layers to limit the stress within a value that could be mostly compensated by the Cr layer and exhibit stable properties.

Niobium Pentoxide

Nb_2O_5 is a high index film that has a relatively high sputtering rate from a metal target under reactive conditions. It can also be rf sputtered from an oxide target at lower rates. The films are transparent from ~350 nm to longer than 2000 nm, and are hard and scratch resistant. As a replacement for Titania (TiO_2) films, Niobia films grow with fewer and more stable crystalline phase states. Index curves for e-beam deposited films with and without IAD are shown in Figure 2. The starting material was a pre-melted plug (produced by CERAC). The substrate temperature was ~200° C. Shown as the lower curve, films that were air baked at 400° C for 2 hrs and showed no change from the pre-bake condition. The addition of IAD resulted in a significant increase in index as seen in the upper curve, and insignificant change in extinction coef (not shown). IAD values of n are comparable in magnitude with those of TiO_2.

Sputtered layers whose indices fall between the two curves of Figure 2 have been reported to change form from amorphous to crystalline after annealing in air at 500° C for 24 h accompanied by only a small increase in index [5]. By contrast, two additional crystalline forms can co-exist or be transformed upon heating hotter than 400° C. Niobia has advantages over Titania for both evaporation and sputtering processes.

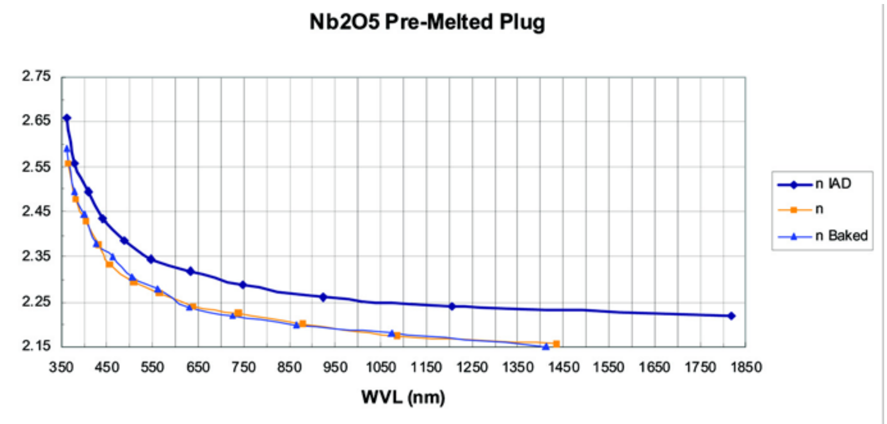
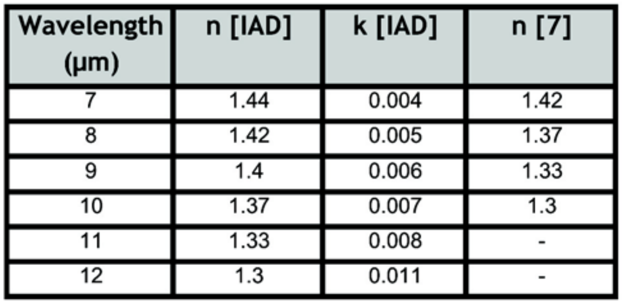


Figure 2. Index values for Niobium Pentoxide deposited by e-beam, with and without IAD

IAD of Yttrium Fluoride

We normally do not consider adding IAD to the deposition of fluoride films for fear that the high energy ions will break fluoride bonds and result in absorption. With the loss of fluorine, optical absorption can increase when stiochiometric ratio is lower than that of the starting compound, or when some fluorine is replaced by oxygen creating an oxy-fluoride. An extensive study employing IAD with YF_3 film deposition was done in which temperature, ion energy, energy density, pressure, packing density, and other parameters were varied. Comparison was made with IBS and e-beam evaporated film results [6].

YF_3 is one of several low-index materials – all fluoride compounds—that are in use or suggested as replacements for ThF_4 layers for coatings that transmit to the LWIR region, 8-10μm [7, 8]. As is true of many fluoride compounds, Yttrium fluoride films exhibit water absorption bands at wavelengths 2.9-3.2 μm and 6.0-7.4 μm, and intrinsic absorption above 10 μm. The depths of the water bands are influenced by the packing density and nano-structure of the film layer. Since fluorides as a group tend to grow with columnar structure, packing densities are generally low, typically 80-90% of bulk. Low packing density results in low refractive index value. Deposition parameters that can be used to increase packing density are: high substrate temperature, low pressure, high condensing energy and/or externally applied energy from impinging ions, and low growth (incidence) angle. In our previous work, we reported that AlF_3, HfF_4, and IRX™ films exhibited lower or comparable water absorption band depths than YF_3. That unaided e-beam work was done on substrates held at 250° C and rates approaching 20 Å/s. [7]. Under these conditions, surface mobility energy was supplied by the high substrate tem-



Wavelength (µm)	n [IAD]	k [IAD]	n [7]
7	1.44	0.004	1.42
8	1.42	0.005	1.37
9	1.4	0.006	1.33
10	1.37	0.007	1.3
11	1.33	0.008	-
12	1.3	0.011	-

Table 2. Optical Constants Yttrium Fluoride with IAD [4] and Without

perature, and the high deposition rate partially offset the need for higher vacuum. The IAD process provides high mobility energy and compacting forces, negating the need for high substrate temperature.

YF_3 can be evaporated from a boat using resistance heating or by e-beam. Parameters that produce high optical quality films are: high substrate temperature (=150°C), low process pressure (<10e-5 Torr), and medium to high rate (~10 Å/S). IAD is a technique for increasing packing density as a result of the energy transfer of impacting ions, and provides the benefits of maximizing refractive index and minimizing water absorption. Disadvantages are increased absorption and intrinsic tensive stress. At least two deterministic parameters interact in opposition when using the IAD technique. Pressure must be higher as Ar^+ or ions of another working gas are generated to supply the momentum, and control of substrate temperature can be lost if a hot wire filament is used for beam neutralization. Current (ion) density decreases as substrate distance increases. Some amount (1-2%) Ar is incorporated in the film. The researchers also sputtered a YF_3 target using a high-energy Kaufman ion source, and obtained a high packing density with the Y/F ratio of 2, and consequent high absorption.

The results of e-beam and IAD deposition processes show promise of producing optical quality films. With the above conditions present, we can compare the two. For straight e-beam evaporation / deposition, the highest index value at 800 nm wavelength was 1.50 for substrate temperature 150° C. This temperature also produced the highest film density. Water bands were present. When IAD is introduced, the operating pressure is 10X higher and the substrate temperature was reported to be 25° C. Refractive index, *n*, and extinction coef, *k*, increased with increased voltage (170 V) and current (4A). The water bands disappeared. The films retained good transparency, low *k*, to >10 µm, but show absorption at visible wavelengths where a compromise between *n* and *k* is required. Some of the IR values achieved with IAD [6] are listed in Table 2 along with some values from e-beam depositions at temperature ~175° C.

We can conclude that YF_3 can be deposited at low substrate temperatures using IAD. The refractive indices achieved will be higher, and water absorption lower than when pure e-beam deposition is used.

Lanthanum and Magnesium Fluorides by IBS

These fluorides represent the High- and Low index layer materials for wavelengths to ~150 nm. High index oxide materials that might be paired with SiO_2 absorb below 200 nm, leaving fluoride materials as the only choice for these VUV and DUV wavelengths. Applications include photolithography of nano-scale features and coatings for high-energy UV laser optics. In a joint effort at evaluating deposition techniques, a publication by a group of European countries compared the film properties deposited by resistance heated and e-beam evaporation with ion-beam sputtered films of LaF_3 and MgF_2 [10]. IBS of the films was done in a reactive atmosphere by rf from hot-pressed targets. Substrate temperatures were 60° C for IBS and 300° C for evaporation. Refractive indices at 200 nm were 1.42 for MgF_2 and 1.66 for LaF_3. The deposition rates for evaporated films were, respectively, 0.8 nm/s and 0.4 nm/s. The rates by IBS were 0.04 nm/s.

IBS films were smoother (see micrographs in ref 10) and exhibited no nano-structure indicating very high packing density, while the evaporated films exhibited the columnar structures typical for fluorides. Comparing the stress levels as measured for films on silicon substrates, the IBS films were highly compressive (-910 for MgF_2 and -1180 for LaF_3) while total stresses for the evaporated films were tensive and in the range 200 to 385. The authors concluded that IBS produces fluoride films of a quality suitable for VUV and DUV applications.

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A subsidiary of Williams Advanced Materials Inc.
P.O.Box 1178
Milwaukee, WI 53201-1178
Phone: 414-289-9800
FAX: 414-289-9805
web: www.cerac.com
e-mail: ceracinfo@beminc.com

Editor:
David Sanchez
Sr. Materials & Applications Scientist
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@cox.net

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CERAC™ incorporated
P.O.Box 1178
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