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Coating Materials News

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Introduction: Improvements in Materials for Thin Film Coatings

The historically driven motivation for these CMN communications is to convey advances and improvements that are being developed in coating materials and processes. Many PVD processes have been developed and are available to the coater of optical thin films. Improvements in the optical and mechanical properties of the film layers has required the introduction of high energy techniques to replace traditional evaporation and sputtering. Imparting high adatom and surface energies to the deposition and growth process results in films with greater packing density, lower stress, and stronger adhesion. These properties are required in the production of stable coating layers. Deposition process enhancements include the addition of high-energy ion bombardment evaporation and ion beam sputtering (IAD, IBS), and energetic plasma environments such as present in plasma ion assisted and magnetron sputtering (PIAD, MS) and variations.

However, only a few new compound materials have been introduced in the past two decades. Niobium Pentoxide comes to mind as a high-index material that until recently was unexploited. Niobia can be evaporated by E-beam to produce high index layers, ~2.3 at 550 nm. Adding IAD increases the indices [1]. A high sputter rate can be achieved, and the layers are homogeneous and dense with relatively high stress. Requirements for UV coatings have forced the use of expensive materials such as HfO_2 and Sc_2O_3. In the category of non-oxide materials, readers of CMN are acquainted with our discussions of replacements for Thorium Fluoride with non-radioactive materials such as YF_3, YbF_3, IRX™, LaF_3, etc. IRX™ has a mixture composition. Layers of Fluoride compounds often grow a porous structure composed of coarse columns. Environmental instability and high tensive stress are common characteristics attributed to this microstructure. The mixture prevents these defects from occurring.

Material Mixtures Revisited

Concurrent with deposition process advances are improvements in materials preparation and deposition. In this approach, emphasis is redirected toward improving material properties rather than deposition techniques. Admixing a small weight-% of a chemically similar or mutually soluble material to deliberately disrupt the growth microstructure is a technique applied to oxide compound starting materials as well as to fluoride materials such as IRX™ [2]. Improvements in mechanical and optical properties have resulted, therefore this approach is justified for further development. Figure 1 outlines the process.

The simplest procedure is to physically mix the foreign additive during the preparation of the starting material. The preparation is then evaporated as a single component. Alternatively, the admixture can be achieved by co-evaporation or co-sputtering from two separate sources. Stress, index and even laser damage threshold can be controlled by varying the relative deposition rates of the two sources. Because magnetron and ion-beam sputter deposition processes provide better control, better reproducibility is possible compared with evaporation. We discussed the basic mechanisms of stress development and modification using evaporation and sputtering in the March CMN [3, 4] and briefly introduced mixing results using IBS [4]. In the 2010 Optical Interference Conference, a German organization of 12 small / medium industries and 3 research facilities known as TAILOR is investigating the development and comparative properties of mixtures and deposition techniques [5, 6]. The group is exploring and developing nano-composited layers synthesized from ternary compounds. Their goal is to optimize materials for integration into industry for custom optical applications. We discussed ternary compounds composed of ZrO_2 + MgO + Al_2O_3 (CERAC M-1126) and the superior stability properties in [7, 8]. CERAC $LaTiO_3$ is another example of a high index material that grows with low stress and high mechanical and environmental stability [3].

One set of materials related to UV coatings for 400-200 nm are composed of HfO_2 with Al_2O_3 or ZrO_2 added. The high index of HfO_2 and its UV transparency are major advantages; however inhomogeneous growth leading to inconsistent optical properties is a disadvantage. Admixing other oxides reduces the tendency toward inhomogeneity, as we have discussed previously. The typical porous / crystalline structure of the Hafnia is reduced and becomes homogeneous and dense with an increased laser damage threshold.

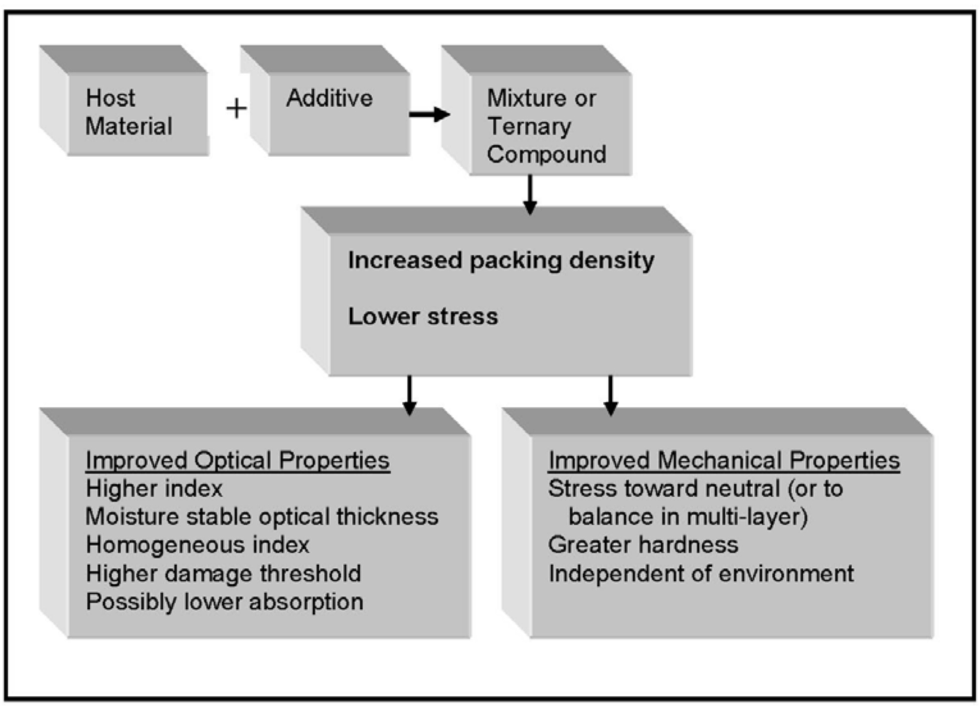

Figure 1. Outline of Property Improvement Resulting from Mixing to Form New Materials.

The Ideal High-Index Material

Multi-layer coatings are designed using combinations of a low-index materials and high-index layers. The choices of low-n materials are limited: SiO_2 for UV and Visible designs and fluoride compounds for IR coatings. As a coating system, the layers must possess transparency, i.e. low absorption, low mechanical stress, and environmental (moisture) stability. High index and moisture stability are produced when the film has high packing density, i.e. low void volume or low porosity. Until recently, the mechanisms responsible for the mechanical and optical properties of high-index layers were not understood. Procedures necessary to achieve these desirable properties were therefore unknown. It was known that films deposited by IAD, PIAD, sputtering, IBS, and ion plating each exhibit different packing densities and therefore different stress level. For example, the stress in ion plated films is so large because density equals bulk values that IP can be used only for special applications. Sputtering permits some control of density and stress by variations in pressure. Denser and homogeneous microstructures absorb less moisture than porous structures, and therefore are more stable to temperature and environmental moisture exposure.

The German TAILOR group has published work that correlates porosity with stress, index, and stability [9]. By employing deposition techniques with different energies, films of HfO_2 Ta_2O_5, Nb_2O3, and SiO_2 were evaluated using TEM, index, roughness, stress and moisture shift measurements. External indicators suggest microstructure. For example, Hafnia films are rougher than Tantala, Niobia and Silica films because their structure is polycrystalline. The high-energy techniques IP and PIAD produce smoother films than MS or EB. Tantala, Niobia, and Silica films are also denser than Hafnia films. The researchers then proceeded to relate moisture stability to pore size and population density. For all depositions except IP, Hafnia exhibited the largest water content and moisture shift. Niobia showed the lowest, except for the MS layer. Nearly all the deposition techniques created tensive stress in the high-n layers and compressive stress in the Silica layers. IP produced very high compressive stress. PIAD tended compressive.

The proven but perhaps unexpected relationship between stress, index, and stability requires a causative explanation. An analytical model was developed that relates these properties to pore size and open/closed nature [10]. Some results of the model are: larger pores tend to produce larger tensive stress, open pores produce a negative moisture shift while closed pores do not result in a shift. A large population of pores is associated with larger open pore size. Closed pores prohibit the exchange of water between the bulk of the film layer and the external medium. There is an optimum fraction of pore density necessary to provide a balance between optical and mechanical properties. A low volume of small pores is necessary to maintain high index. Size range ≤ 2 nm provides a good balance between index, stability, and stress level. High energy deposition does not lead to the best properties because pore size and population are virtually extinguished, but rather moderate to low energy processes are favorable. Thus optimum operating parameters for PIAD, EBIAD and MS with these properties in mind are the preferred deposition techniques. Achievement of optimum film properties is strongly correlated to the absence on minimization of the moisture shift, since that is an indirect indication of the nature of the pore component.

The Future

Addressing the weak link in the production of high quality thin optical films, namely the materials component, is appropriate. After a more thorough research effort, mating the optimum material preparation with a chosen deposition process will lend consistency to the industry by reducing production complexity and variability.

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