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UV Coatings: Materials and Applications

Thin film coatings for the spectral region shortward of the visible range require special considerations with regard to materials. Wavelengths shorter than 400 nm, the ultraviolet wavelength region, have many uses in science and technology. Depending on the specific discipline, the small wavelengths or high energies of UV have application in fluorescence diagnostics, germicidal equipment, corneal surgery, high-energy astronomy and physics, gas species detection, lithography of circuits, and other laser optics. Deep UV lithography requires performance at the ArF excimer wavelength 193 nm and the F_2 wavelength 157 nm. Absorption, surface and bulk morphology defects, impurities, and microstructure are properties that determine the limits of performance, and in the case of laser optics, resistance to damage. These properties are more critical at the higher energies (>3 eV) and smaller wavelengths of UV for both bulk and thin film materials. In the case of absorption, many materials have energy gaps near or greater than 3 eV, and thus are absorbing. This is the case for most oxide compounds, silica and alumina being the most common exceptions. AR and filter coating designs require a high- and low-index combination. The high index would normally be supplied by an oxide compound; the low index by silica or a fluoride compound. Generally the high-index oxide compounds begin to absorb as wavelengths approach 300 nm. Some, like titania absorb as long as 450 nm. Therefore, when a thin-film coating design is needed for use at wavelengths below ~350 nm, the number of candidate oxides is quite limited.

In this issue of CERAC Coating Materials News (CMN), we discuss two divergent, but pertinent topics in the coating industry. The push for higher density semi-conductor devices requires smaller circuit features. These can only be obtained by reducing the wavelengths of the photolithographic mask features used to create the circuits. Line widths decrease in proportion to the wavelength of the light used to expose the features. Optical components and their coatings are being forced to operate at wavelengths below 400 nm and into the deep UV region. For the popular deposition technique, magnetron sputtering, causes of common sputtered film defects in relation to target preparation are discussed.

We shall examine the available thin-film materials and their preferred deposition processes in this issue. Past issues [1, 2] have discussed several UV materials. The first referenced issue listed the candidate high- and low-index materials usable below 300 nm wavelength including the optical and mechanical advantages of mixtures or composite materials; the second discussed how e-beam deposition of MgF_2 produces superior low damage films in excimer laser applications. New information is continually being published that CMN reviews for its readers, for example, the June Applied Optics contains some interesting papers presented at the 8th Topical Meeting on Optical Interference Coatings held 15-20 July 2001.

The bandgap energy is the energy needed for an electron to transition from a material's valence band to its conduction band, causing absorption of light. The corresponding extinction coefficient, k and its increase at shorter wavelengths, imposes a limit to the useful transmission range of the thin film material. We assume that the practical maximum k value (acceptable limit depends on application and total thickness of the absorbing layers) is ~0.07 where the transmittance of a QW optical thickness would be reduced by 10%, and list the approximate wavelength limits for some UV materials in Table 1. These were derived from models that were fitted to ellipsometric [3] and transmittance data [4].

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Some Notes on Sputter Deposition: Defects and Targets

Deposition of metal, dielectric, and alloy films by sputtering is a common volume production process for flat panel display screens (thin film transistor LC devices), thermal control architectural windows (web coated polymer films for lamination to glass), tribological surfaces, CD & DVD production, magnetic data storage media, etc. Some of these applications, namely data storage and TFT display panels, can tolerate only the smallest defects at very low spatial density. Particulate sizes, for example, must be less than 100 nm to prevent head crashes in high-density disk data storage systems. In addition to low defect density, sputtered films must have low mechanical stress to prevent micro-cracking than can, for example in conducting films, lead to increased sheet resistance. Micro-cracks can also absorb water and present variable resistance depending on atmospheric humidity conditions. Film stress can be controlled by varying power and pressure parameters during sputter deposition. The preparation of the sputtering target has the primary influence on the particulate deposition in the deposited film layer. CMN Issues 3 & 4, 1992 discussed the sputtering process and control of stress and available special purpose mixed targets.

Sputter targets are produced according to the material, metals and alloys are vacuum melted to remove gaseous impurities that might form oxide compounds and then cast or rolled into target shape. Some metallic and ceramic materials are first reduced to fine powder and cold-pressed, finally sintered into a solid form. Some ceramic materials must be hot pressed from powders of a critical size distribution. Mixed-material sputtering targets are also produced by CERAC for use in printer head coatings, magnetic data recording layers, thin film resistors, wear-resistant coatings, transparent-conducting coatings, and other optical and electro-optical applications. Mixed target processing requires special attention to prevent the formation of multiple phases. Processes include pre-reaction and homogenization before the hot-pressing formation.

The main sputtered film mechanical defects affecting film performance are particulate accumulation and nodule growth. A number of causes have been identified for these defects, and these will be briefly discussed. Further info is provided in Ref. 7. Target purity is important because, for example, partially oxidized materials imbedded in a metal target will sputter at a different rate than the metal, probably charge up, be ejected, and deposit on the substrate. At the substrate, film growth around the particulate might proceed in the form of nodule growth. The nodule can become a protrusion above the surface of the film or can dislodge, producing a pinhole. Depending on the application from the earlier list, these film defects can range in effect from acceptable to disastrous (TFT LC and data disks). Metal targets for semiconductor applications should have purities ranging from 4 to five 9's %. Impurities containing alkali compounds are especially problematical because of ion formation that can 'dope' the film and alter its resistance.

Sputter targets for optical, electrical, and decorative applications can have purities in the 2 to four 9 % range. Metals that readily form oxides often contain points or regions of oxidized material that will sputter at a different rate, again forming particulate projectiles. The local erosion features can differ from the target surface as a whole, and roughness can occur. The increase in surface area encourages oxidation ('surface poisoning') and will require surface regeneration by etching to restore the sputtering rate. Pointed cones formed can be points of arcing, which again will dislodge material.

As described above, the target manufacture process depends on the material. Dielectric, ceramic, and mixed-material targets are compressed into a solid form, but the bulk density is often between 90 and 99%. The presence of void volume influences sputter rate, film resistance, and defect rate.

Non-metal targets must be bonded to a metal cooling plate to prevent overheating during sputtering. Considerations for successful bonding include the thermal expansion coefficients of the target, binding, and cooling plate materials, and their mutual conductivities (including thicknesses). Solder is often used as the binder, but epoxies may work for some combinations. Failure due to thermal mismatching or overheating might take the form of microcracks or catastrophic cracking and debonding. Either situation creates a run-away heating profile. A typical example is an ITO target. The power handling capacity is greater when bonded to a titanium or molybdenum cooling plate than when bonded to a copper plate because the thermal coef. Matching is closer.

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Table 1 UV Materials Properties

Material	AlF_3	Al_2O_3	GdF_3	HfO_2	LaF_3	MgF_2
Wvl (nm)	~130	170	140	200	<150	130
n 157 nm	1.44	2	1.8	2.3@200	1.81	1.47
k 157 nm	0.003	0.3	0.004	~0.01“	~0.006	0.002
Ref.	4	3	4	5	3	4

The deposition technique also influences the performance of UV coatings, especially those used with excimer lasers. With the support of the European commission, a group of European researchers studied the properties of MgF_2 and LaF_3 to wavelengths as short as 120 nm [5]. These materials present a promising layer pair for coatings at or shorter than 193 nm wavelength. The refractive indices at 193 nm are for MgF_2 1.42 – 1.44 and for LaF_3 1.67 – 1.70. Deposition techniques: resistance heated (RH) and e-beam (EB) heated evaporation and ion-beam sputtering (IBS) were compared for micro-structural and optical properties, specifically index, stress, and scatter. In agreement with previous studies that reported higher damage thresholds for RH deposited MgF_2 [2, and Protopapa, et al, J. Vac. Sci. Technol., A 19(2), Mar/Apr 2001], the thermal processes produce superior films compared to IBS. IBS films of both MgF_2 and LaF_3 possess 2 times higher stress and higher UV absorption due to incomplete stoichiometry, but are smoother. The IBS microstructure is more uniform, consisting of smaller grains of uniform size distribution throughout the depth of the layer. RH and EB films grow with a columnar form whose grain size increases toward the surface of the film. The less compact, larger structure scatters more than the IBS deposition. The higher energy of IBS can also result in a reduction of the fluorine content, leading to higher UV absorption. Replacement with adventitious oxygen has been observed to also increase UV absorption. The lowest scatter was observed with EB MgF_2 on super polished CaF_2 substrates, but MgF_2 presented the highest scatter when deposited on super polished fused silica substrates. The same tendency is observed for the LaF_3 films. EB layers exhibited the lowest scatter in spite of their roughness tendency to be greater than that of the IBS depositions. In fact, no simple relationship exists between roughness and total backscatter because of the complex nature of the growth process of thin films which includes such factors as the nature of the chemical bond between substrate and film, interface layers, microstructure variations through the film layer depth, adatom and surface energies etc. The authors of the work conclude that IBS films exhibit the lowest surface roughness but high backscatter, highest refractive index, high stress, and homogeneous microstructure compared to films deposited by thermal evaporation techniques. Higher laser damage thresholds are predicted for the thermal processes than for IBS depositions of these fluorides.

UV materials must have very low levels of transition metal impurities or other elements that absorb in the UV. Levels must be below 0.5% and in some cases below 0.1% by weight. A different paper [6] demonstrated the importance of eliminating contamination from the ion source structure when depositing UV films. Construction materials containing Ni, Cr, Mo, W, and Fe caused significant absorption below 300 nm wavelength, while Ti did not. Ti has a lower sputtering rate than the other metals. This precaution also applies to the container (liner) used in EB evaporation. A straying beam striking the liner can contaminate the deposition. The metal grids and neutralizer filament wire in ion-beam sources can be sputtered in ion-beam assisted sources causing UV absorption. Finally, carbon from the coating chamber is an ubiquitous contaminant.

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