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Ultra Violet Coating Technology: Materials and Processes

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Optical coatings that perform in the UV at wavelengths shorter than ~350 nm require materials with low absorption. Fluoride compounds are exclusively required for wavelength shorter than ~200 nm, labeled the Deep UV (DUV) region. This article outlines the application of fluoride compounds to satisfy special coating requirements in the DUV spectral region, and the materials and processes involved for manufacturing and depositing these critical materials.

As discussed in previous *Coating Materials News* [1], the UV is divided into three regions. Using terms relevant to biological activity, "UVA" is the Near-UV consisting of wavelengths 400 – 320 nm; "UVB" is between 320 and 280 nm; and "UVC" from 280 nm to 200nm, shortward of which is the DUV region.

Metal oxide compounds that are used in visible through shortwave IR applications are not suitable for high performance UV optical coatings because they possess absorption at UV wavelengths - with a few exceptions. The exceptions are the low-and medium refractive index oxides SiO_2 and Al_2O_3 that can be used to ~200 nm. The high-index HfO_2 is useable to ~225nm [2]. These oxide materials have alternate chemistry, or a limited number of stable sub-stoichiometric states, or high oxygen mobility which opens the door for some custom-coating materials. When manufacturing fused silica, the chemical route to the principle oxide is essentially eliminated and the result is a glass that can be further refined into high quality substrates as well as coating materials critical for UV and NIR intense photonics. This glass will also have the bonus of being without detrimental grain boundaries, trapped gases and pocket instability.

In the case of Al_2O_3, a slightly sub-stoichiometric state is desirable. Unlike other oxides that lose much oxygen upon evaporation, aluminum oxide by its nature is content to share localized oxygen atoms and densify into a very useful melted plug. This property is advantageous in depositing the oxidized thinner ¼ wave layers in the UV region. Considering the high-index UV candidates, HfO_2, while expensive due to its nuclear industry extraction genesis, has an extraordinary oxygen mobility which can be harnessed to deposit durable dielectric layers that transmit from the UV to the SWIR. In addition, contrary to its periodic table partner ZrO_2, there are no catastrophic phase changes and an increasing number of reactive processes ranging from the full oxide to the pure metal.

Applications of UV-Coated Optics

UV coatings include, among others, anti-reflective (AR), high-reflecting, bandpass, and beam-dividing designs. Common applications are lithographic patterning of semiconductor electronics, ophthalmic corrective surgery equipment, medical forensic diagnosis and treatment instruments, solar and high-energy physics, germicidal equipment, UV LIDAR, and others.

Common application of UV coatings - laser surgery equipment.

Deep UV lithography applies excimer lasers at UV wavelengths 248nm (KrF), 198nm (Hg), 193nm (ArF) and 157nm (F2) in patterning features of ever-decreasing dimension to produce high area densities for computer memory and other components. DUV coatings must handle high-energy photons without degrading over the millions of repetitions required to produce high-density data storage devices such as compact discs, solid-state memories, and in multi-exposure technologies to produce integrated circuits (ICs) critical for autonomous vehicles, artificial intelligence (AI) and deep learning. Storage density is inversely proportional to the wavelength dimension. Lithography at Extreme UV wavelengths as short as 57nm and 13nm is also being developed to advance data storage capacity according to Moore's law. Materials for making reflective optics used at those Extreme UV wavelengths consist of dozens of sputter-deposited thin layers of metals such as Molybdenum (Mo) alternately combined with Silicon (Si).

Deposition Processes: Film Quality and Morphology

In the UV region where high-intensity lasers are used, purity and microstructure are more important than they are at Visible to IR wavelengths. Purity is controlled by the materials preparation and deposition technique. Microstructure is dependent on process energy. Both parameters can influence the nature and density of film defects. Defects occupy three categories: chemical, eg. composition and impurity concentration; nano-structural, eg. morphological and packing density; and atomic displacement.

The deposition process energy determines physical and optical properties of coated layers. Low-energy processes produce porous, crystalline microstructures that have unstable optical and mechanical behavior. High-energy processes involving direct bombardment during growth of energetic ions as with IAD, or energetic plasmas in the sputter process, promote high compaction density. High-energy layers will grow with an amorphous morphology that is desirable because of its high structural packing density. Our previous technical paper discusses film growth morphology as related to deposition energy [3].

The variety of deposition processes specific to fluoride compounds is more limited than those employed for oxide deposition. Moderating the decomposition of the fluoride compound, especially in high-energy deposition techniques using fluorine-containing make up gasses, is difficult or even hazardous. Micro-meter sized source ejecta and dust, distributed by pumping turbulence or electro-static charging, are the primary causes for low laser-induced damage thresholds (LIDT). Materials that melt generate fewer ejected particles than those that sublime. Tooling and chamber walls must be cleaned to remove dust and deposits that can spread to substrates. Resistance-heated (RH) thermal evaporation is the primary process to avoid material compositional changes and particulate spatter often associated with e-beam evaporation. RH and e-beam deposition, while low-energy processes, grow coatings that possess high resistance to laser damage. This is primarily because they produce fully oxidized layers with lower particulate emanation and contamination within or on the layer. Higher energy processes such as sputter deposition, ion beam deposition and most ion-assisted approaches can create absorption by several means: partial dissociation of the fluoride molecule, evolution and entrapment of filament or emitter contaminants, or radicalization of surface species. Sputter plasma energies produce lower particulate densities but can result in partial dissociation of fluoride compounds. Decomposition will result in absorption that compromises the survivable functionality of laser coatings, especially at deep UV laser wavelengths.

The high photon energies associated with UV optics require special consideration of the parameters: material purity, defects and deposition process energy. The energies of UV photons of wavelength shorter than 400nm to 200nm range from ~3 to 6 eV. Resistance to damage is critical for UV LIDAR coatings exposed to millions of pulses of high-intensity 355nm light (the third harmonic of YAG 1064nm laser). Laser-induced damage thresholds (LIDT) decrease in the presence of morphological defects and other sites where absorption can increase. Structural defects, impurities, and especially particles can act as centers for absorption and initiate consequent damage. These imperfections are particularly significant when the high-energy excimer lasers with 6 -8 eV energy are present. Therefore, in order to ensure high LIDT, special attention is required in the preparation, vaporization and deposition of the coating materials that are used in high-energy environments. Those environments include not only the high-energy applications already mentioned, but also the space environment in which climate-monitoring, communications, and military satellites operate. Particulate and ionizing radiation is potentially damaging to coatings, as discussed in Materion technical paper Coatings Used in Space [4].

As previously mentioned, the optimum deposition energy for fluorides is somewhere between high-energy IAD and low-energy thermal evaporation. High-energies tend to dissociate fluoride compounds resulting in absorption. Low-energy sources produce low density fluoride structures. An alternative to energy supplied by ions, heating substrates to high temperatures (>250° C) promotes dense morphology by supplying kinetic energy for high surface mobility. Without high energy, the film grows columnar micro-structures with a high proportion of void volume that is weak and absorbs/desorbs water in humid/arid environments. Structural inhomogeneities in fluoride micro-structures are noted in a study where substrate temperatures varied between 25° and 300° C. Substrates at ~200° C produced the best compromise in structure and hardness. MgF_2 and LaF_3 grow columnar structures. LiF and CaF_2 grow granular structures [5].

While reactive sputtering tends to favor oxide and nitride compounds, on the industrial scale there are often calls to use IBS and RF sputtering for fluoride compounds due to the theoretical advantages of high uniformity and amorphous dense films. While several fluorides have been made into sputtering targets, the targets themselves often fail due to thermal load. The tendency for decomposition of the fluoride species can further deteriorate the target, poison the growing film or increase heating of the substrate. The use of make-up oxygen can work for designs in the UV but substitution of oxygen for fluorine causes excessive UV absorption. Even if this is of no optical consequence, post-processing steps such as etching or lift-off can complicate complex opto-microelectronic lithographic applications.

Preparation of Coating Materials

The preparation of the oxide and fluoride compounds used in UV coatings includes elimination of contaminants that can introduce absorption. The nature (chemistry) and concentration of the impurities is an important consideration in the material preparation that starts with the raw material and requires monitoring the purity concentration during synthesis and sizing. Impurities that increase absorption in the UV and lower LIDT include oxides of metals such as Fe, Ni, Cr and neighboring atoms that can be introduced from the reaction, drying, and sizing and handling steps. More complex impurity compositions that are left over from principle extraction can be much harder to control and have dramatic consequences on melt behavior.

For most fluoride compounds, common materials that depress the melting point such as Na and Ca, can lead to spitting, excessive heating or physical thickness variability through rate changes. For dielectric oxide~~s~~ materials, the most critical impurities are S, V and Ti, Zr and Nb. Here the stability of the dielectric compound itself may be linked to packing density and phase. For high LiDT and long cycle UV applications, stress in the film can be the limiting factor for the fluoride portion of the design. In general, it has been demonstrated that the minor presence (<5%) of a similar “impurity” fluoride is not detrimental to the optical performance of fluoride coatings. In some mixed fluoride preparations, notably MgF_2 and CeF_3, the “impurity atom” serves to reduce the tensile stress that fluoride layers typically exhibit. The low percent “doping” mentioned discourages columnar microcrystalline growth. When considering mixtures, the composition of the starting material (oxidation state) stoichiometry of components, miscibility and compatibility must be considered to maximize stability during short quarter-wave deposition times and very thin layers typical to the DUV.

Critical coatings for Deep UV and other high-power UV laser coatings continue to push purity standards past 4-9s toward 5-9s. As seen with UV MgF_2, this super high purity level requires sophisticated thermal management from evaporation to condensation. These factors ultimately lead to the recent development of LiF as an alternative to UV grade MgF2 (with equivalent index to ~130nm) where lower deposition temperatures, lower stress and a stable melt pool are desired. The other key DUV material that has been processed to higher purity to enhance performance is LaF_3, which provides a higher index. AlF_3 and GdF_3 are alternate high-performance DUV materials that have experienced improved cost and availability through expanded production capacity. A couple of features about AlF_3 that can be exploited include its tendency to sublime and the possibility of forming an in-situ outermost oxide layer.

UV materials and their applicable spectral regions

UV Region	**UV**	**Deposition**	**Deep UV (DUV)**	**Deposition**
Wavelengths (nm)	**220-400**		**220-150**	
Materials	SiO2	e-beam	MgF2	RH, melts
	Al2O3	e-beam	LaF3	RH, e-beam
	MgF2	RH, melts	GdF3	RH
	HfO2	e-beam	AlF3	Rh, e-beam
	ZrO2	e-beam	LiF	RH, e-beam

Table 1. Materials usable in short-wave UV regions.

What is the Recommended Deposition Process for Fluorides?

With film growth, morphological and material properties in mind, what is the best deposition process for fluoride films? The answer has as a determinate parameter the intended application for the fluoride coatings. Application variables include low vs. high intensity (laser), humid vs. arid environments and protected vs. abrasive conditions. Tensile stress buildup in fluorides limits its thickness, therefore, process parameters such as substrate temperature, deposition rate, and material preparation are key to growing thick, low stress strong film layers.

General deposition parameters for most fluoride compounds are: select the material and its purity as required for the wavelength and flux density; substrate temperature ~250^{0} C; rate ~10 Å/s; pressure ~10 e-6 Torr. Premelt the source material if possible. Deposit using RH or e-beam as opposed to higher energy techniques.

In Summary

The discussion conveys the importance of fluoride materials for coatings, including their initial preparation and ultimate deposition processes and taking into account current and future applications. Materion produces a broad range of fluoride compositions for coatings with up to 99.999% purity levels.

References

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