

Commonalities between UV and IR Materials

Breaking the Spectral Overlap Rules

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The choice of materials employed in coating designs is primarily differentiated by the operating wavelength range. The available materials are, however, not strictly segregated to either short- or long-wavelength candidates, but overlap exist in spectral range applicability. That wavelength overlap permits the designer to deviate from the common set of coating materials in many cases, thereby providing process flexibility.

General Examples of Material Spectral Overlap

In general, materials that transmit IR do not transmit short wavelengths, and vice-versa. This “rule” applies primarily to the high-index materials. Examples are Ge, Si and ZnSe that transmit from the near-IR to LWIR. At the shorter Vis – UV wavelengths, oxide materials are transparent. However, some oxide compounds can be used at UV as well as the MWIR wavelengths. Their longest range is limited to approximately 3000 nm wavelength. Fluoride compounds are the exceptions; they transmit from UV (~200 nm) to LWIR (~11 μm).

The only available low index oxide compound, SiO_2 , is transparent between ~220 nm to ~5000 nm, covering UV to MWIR wavelengths. So, combinations of SiO_2 with the high-index component consisting of Ta_2O_5 , TiO_2 , Nb_2O_5 , or HfO_2 are commonly used for visible-NIR coating designs. HfO_2 may be used in UV coatings. Tantalum pentoxide, Ta_2O_5 , is transparent between ~320 nm and ~4000 nm, thus providing the high-index component covering visible to MWIR wavelengths. Titanium oxide and Nb_2O_5 are other high-index candidates that have sufficiently low absorption between ~450 and ~5000 nm to be used in multi-layer designs. Materials with an intermediate index are Al_2O_3 and SiO and can be used up to ~5 μm wavelength applications. Coatings for wavelengths between ~3 μm and 5 μm can take the advantage of the high index ratio provided by combining Ge and SiO .

The Special Role Played by Fluoride Compounds

At wavelengths shorter than ~220 nm, no high-index oxide compounds exist that possess sufficiently low absorption that can be used in multi-layer designs. The low-index layer component for longer and

shorter coverage requires a fluoride compound such as MgF_2 , LiF or AlF_3 . These fluoride compounds are used for wavelengths as short as ~ 150 nm, with LiF having acceptable transparency to ~ 130 nm. The challenge for deep UV fluoride coatings is that their refractive indices are similar, restricting the H/L index ratio to smaller values. The consequence is that many more layers are needed to make high and partial reflector as required for excimer laser applications. Among the DUV fluorides, LaF_3 and GdF_3 have the higher indices, and are combined with the lower index layers of MgF_2 , LiF and AlF_3 .

Fluoride compounds provide the required low index outer layer of high-efficiency wide-band AR coatings for visible coatings. MgF_2 and Cryolite can be combined with high-index oxide layers and since they melt before vaporizing, they can be used when high abrasive durability is not required. When greater durability is required, as with eyewear and commercial AR on displays and instrument panels, SiO_2 is substituted for the outermost layer. Wide-band AR coating designs for the LWIR region require the lowest index material for their outer layer. Recently, a set of low-index, low-absorption non-radioactive compounds have become popular replacements for ThF_4 . Special mixtures such as Materion’s IRX™ and IRB™ were formulated as low-stress, low-absorption substitutes that can be evaporated by resistance-heating or E-beam. They are less common because the single compounds YF_3 and YbF_3 can be evaporated by E-beam and have been adopted for this application. Other materials used in the 8 – 12 μm region are listed in Table 1.

Material	ThF_4	YF_3	YbF_3	IRX™	IRB™	LaF_3	AlF_3	HfF_4
Absorp. in QW at $10\mu m^*$ (%)	~ 1	2-5	~ 1	2-3	~ 3	5-10	Low-none	none
n,k at $\lambda 10 \mu m$	1.35, 0.001	1.35, 0.002	1.42	1.4, 0.006	1.35	1.4, 0.004	1.3, 0.04	1.35, 0.002
Water band depths*	low	low	signif.	low	Low+	signif.	low	signif
Humidity stability	Good-	good	good	good	OK	good	good	good
Abrasion durability*	good	Fine scratches	good	good	fair	good	good	good
Stress related thickness limit (μm)	~ 2	~ 2	>2	>2	>2.5	>2	>2	>2
Melt or sublimate	S	M	M	M	M	S	S	S

Table 1. Properties of alternate Fluoride compounds for LWIR region compared with Thorium Fluoride.

The physical properties of fluoride compounds impose limitations peculiar to IR wavelengths; these have also been discussed in [previous CMNs](#). To be effective in producing the lowest reflection in a multi-layer AR coating for the 8 to 12 μm region, the outer layer of the coating must have the lowest possible index material. This corresponds to a QW at 10 μm with a physical thickness of 1860 nm (index 1.34). Fluoride layers build with a columnar rather than amorphous nano-structure that exhibits high tensile stress. This

generally limits their cohesive and adhesive integrities to a smaller thickness of approximately 1200 nm. Fluoride compounds also exhibit water absorption bands near wavelengths of 2.9 and 6.1 μm , whose depth is related to volume packing density. With a packing density of around 0.8-0.9, fluoride layers are also fragile and not able to pass the MIL-STD severe abrasion (eraser rub) test. Some techniques to reduce stress and water incorporation are based on densifying the growth morphology of the layers. They include alternating with thin layers of another material, co-doping deposition with a second material, and low-energy ion bombardment. The ion energy needs to be low enough to not severely dissociate the fluorine from the compound. For UV applications, IAD is not used because even slight dissociation introduces unacceptable absorption. A high substrate temperature, when not limited by other materials, may also reduce the depth of the water absorption bands if they appear within the spectral bands of interest. Figure 1 shows the IR transmittance of YbF₃ layers at a 1500 nm thickness deposited at different rates, and demonstrates the effect of that process parameter on the depth of the water bands.

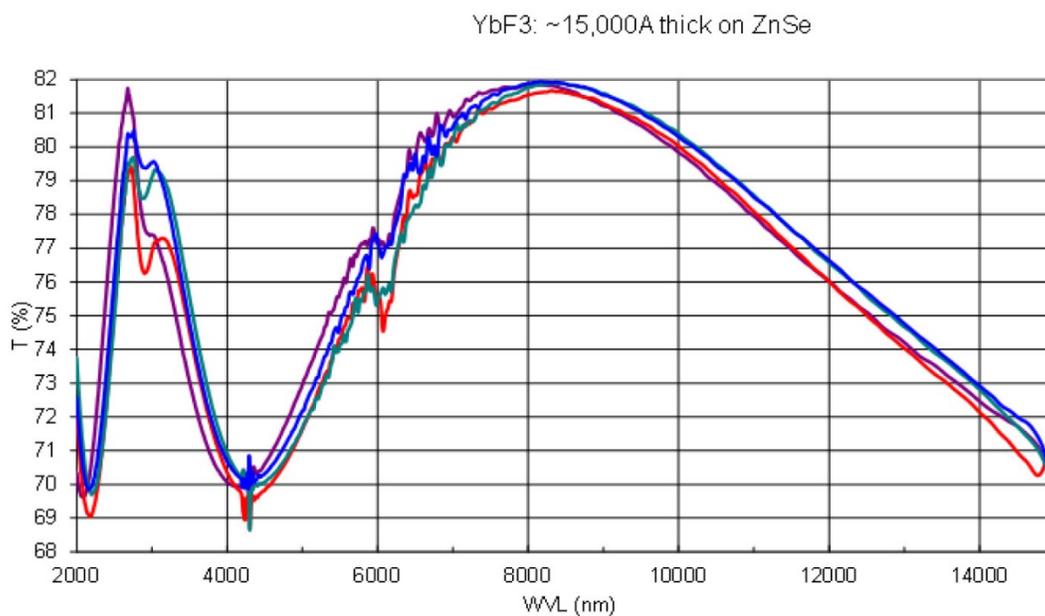


Figure 1. Transmittance of YbF₃ layers by E-beam deposition with substrate temperature of 150° C and rates of 10 to 20 Å/s. The higher rates reduce water-band depth.

Process Considerations

Intended application, deposition process technology and economy of usage play an important role in all material choices and combinations. The application might require multi-layer coatings that exhibit wear and impact abrasion resistance, stability in humid and salty environments, stability to a wide range or thermal conditions, insolubility or laser irradiation. In some cases, high-quality materials are required to

be optimally prepared for critical applications, such as UV and laser coatings for medical and space applications.

UV coatings require very low concentrations of impurities, such as the transition metals, to provide minimum absorption at short wavelengths. High-energy laser coatings require low impurity concentration and special deposition processes to eliminate nano-structural defects that can lower damage thresholds. Preparation to reduce impurity species to low ppm levels separates high optical coating materials from materials that do not require exceptionally stringent properties. UV and laser coating materials have a purity of 4-9s or 5-9s. Vis and SWIR materials for non-laser applications can tolerate 3-9s and 4-9s purity. Acceptable IR materials might be 3-9s purity. The nature of the impurity is important, as mentioned above. In the case of fluorides and other materials that deposit with a porous or columnar nano-structure, some types of impurity subvert that form and promote amorphous morphology. The form in which the material is prepared or pre-processed is a factor that is relevant to sputter targets as well as to evaporation materials. Thus, oxide and fluoride compound starting forms can be optimized for specific ranges of granular particles or be pre-melted. In the case of oxides, starter sources that are prepared in a specific sub-oxide state produce the smoothest evaporation or sputtering rate during reactive deposition processes. These physical properties are determined by deposition process technology parameters such as energy, interrelated pressure and rate values. [Previous CMNs](#) contain discussions of additional process measures including specifically engineering the nano-morphologies, such as volume packing density, and structural and compositional defects designed to eliminate low quality film layers. Materion Advanced Materials supplies [fluorides](#) and [oxides](#) in a variety of forms including [pre-melts](#), targets, pieces and powders.

Material and deposition process research continues to improve the quality of the ubiquitous thin-film optical coating.

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