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Coating Materials & Processes for the Long-Wave Thermal Band

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In the last issue of Coating Materials News, the partial spectral overlapping applications of coating materials as the spectrum is traversed from visible (VIS) to infrared (IR) wavelengths was discussed. That overlap only pertained to wavelengths to ~5µm, and was satisfied by oxide and fluoride compounds. Longer wavelengths require different materials that exhibit low absorption. Additional properties are ease of deposition, available starting forms and conditioning, and the mechanical properties of the deposited film layers. First, we will review the IR spectrum.

Sensing and Imaging Objects by Solar Irradiation

Solar spectral emission conforms to ~6000 K black body radiation that peaks near 450 nm and supplies energy for human and animal vision as well as vegetation processes. Solar energy dwindles to smaller values as longer wavelengths are approached. The human eye has a spectral response between ~380 to 720 nm, with its photopic response peaking at 550 nm for bright light (daylight) and ~520 nm for scotopic response at low light level (moon light). CCD and CMOS camera sensors based on Silicon are filtered to mimic the RGB photopic response. Regions beyond the Near-Infrared are called Short Wavelength Infrared (SWIR) in wavelengths 1 to 3 µm (1000 to 3000 nm) and Mid-Wavelength Infrared (MWIR) for 3000 to 5500 nm. Long-Wavelength Infrared (LWIR), the “thermal band,” is between ~7 and ~11 µm. A set of black body curves is shown in Figure 1.

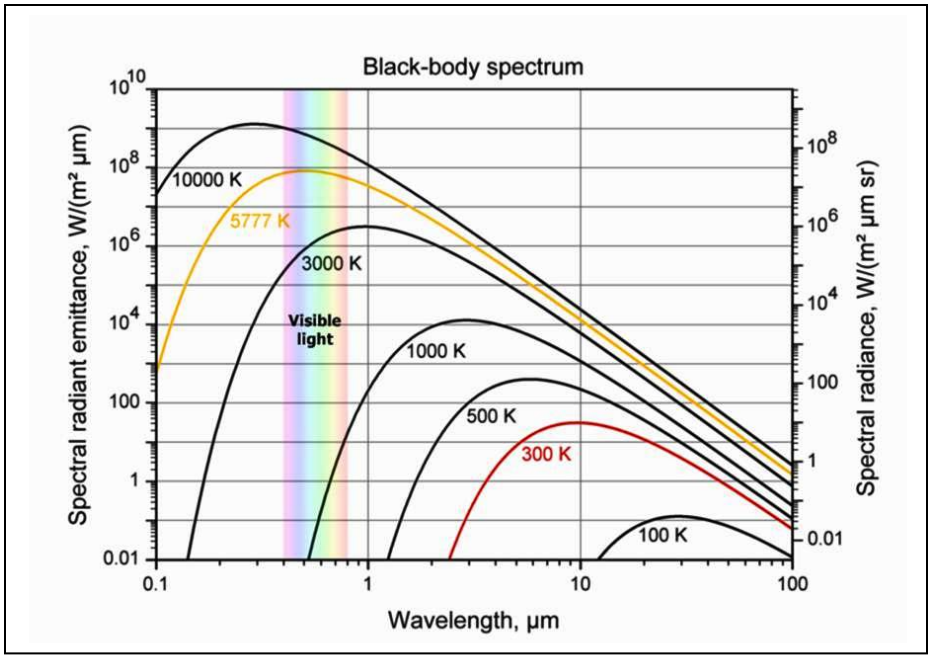

Figure1. Spectral emission of Black Body curves of different temperatures. (Wikipedia Commons)

To be able to “visualize”, i.e., detect, monitor and image IR wavelengths, requires sensors with spectral responses at wavelengths longer than ~700 nm. Near-IR wavelengths can be sensed with silicon, VOx, GaAs and similar composition detectors. Objects can be viewed by reflected solar energy to wavelengths ~3 µm using sensors made of different semi-conductor materials.

At wavelengths longer than ~4 µm, solar reflected energy is very slight. Objects can be detected and imaged by their IR thermal emission which follows a black body curve that is determined by temperature as shown in Figure 1. Reflected solar energy is many orders of magnitude lower than emission at SWIR, MWIR and LWIR wavelengths. Radiation from sources near room temperature or 290 K (~20^{o} C) peak near 10 µm. The human body is a thermal emitter at 310 K or 37^{o} C, whose emission curve peaks at 9.6 µm. Water vapor in the atmosphere has spectral absorption bands between transparent windows (see Figure 2) which may pose significant design limitations. The MWIR window between ~3 and ~5 µm includes the CO_2 band at 4.2 µm which is important to environmental studies. The LWIR window between ~8 and 14 µm – the “thermal band”- is open to the radiation of BB temperature near 9 µm. Therefore, it is ideal for sensing living bodies and other objects, whether natural or man-made.

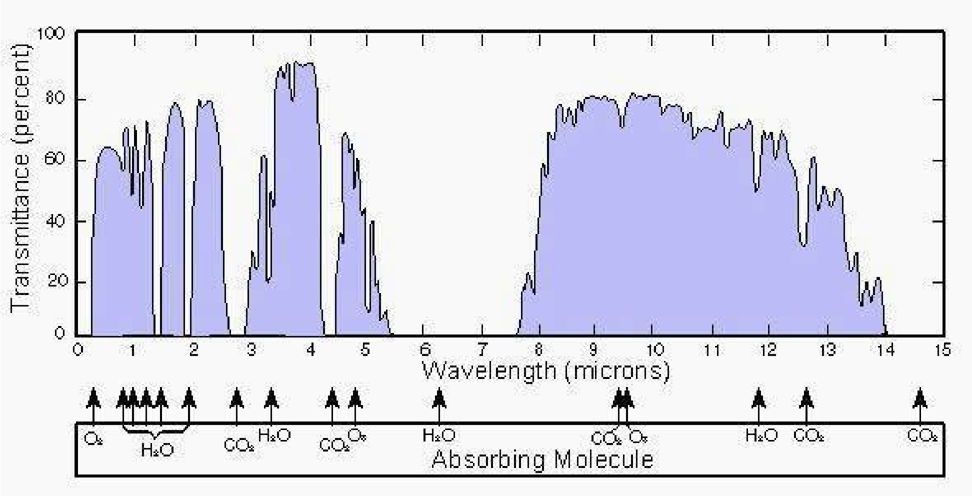

Figure 2. Colored regions are the transmitting windows of atmospheric transmission (WikipediaCommons)

Applications of Thermal Imaging

Imagers that operate in the MWIR and LWIR wavelength bands have multiple applications in remote sensing. Among them are monitoring of natural resources, such as weather, cloud cover, fog and smoke detection, energy utilization efficiency plus other uses such as medical diagnosis and more.

Materials Used in Thermal IR Coatings

Heavy-element compounds such as ZnSe, ZnS, CdTe and others are transparent to LW (longer wavelength) energy in the thermal IR band. They are combined with semi-conductor materials such as Ge, Si, GaAs, etc, to compose the respective Low- index and High-index components (coating materials and substrates) of multi-layer coating designs that cover wavelengths >~7µm.

H/L repetitions are used in multi-layer stacks to achieve desired spectral response. Designs can be generated that use a higher H/L index ratio by using a fluoride with Ge. For example, index of Ge ~4.0 / index of fluoride ~1.35. Fewer layers are required, and edge slopes will be steeper, with a higher H/L ratio. The problem with that layer combination, however, is that layers of fluoride compounds do not adhere well to Ge and other semi-conductors. An intermediate layer material is required between layers to guarantee adhesion. That adherence layer can be a thin layer of an oxide compound such as MgO, Y_2O_3, or HfO_2. The design and the deposition process become more complicated when including interlayers. The oxide introduces some optical absorption in the LWIR region. The thickness is ~10 nm, depending on materials and temperature, and absorption is therefore very small.

Comparing two stable, durable LWIR coating combinations, Ge and ZnSe combination with a H/L ratio ~1.7, and Ge/ZnS, H/L ~ 1.8, the ZnS ratio is slightly larger. However, the ZnSe stack transmits longer wavelengths than ZnS. General design functions range from AR with fewer than 7 layers to band-pass filters, edge filters, and beam dividers with more than 20 layers. All require a higher level of attention to substrate, coating, annealing and pocket loading density and process stability. More detail will be provided further in the article about potentially key materials differences that need to be accounted for in the highest performance coatings.

In perhaps the most prolific and growing application – Anti-reflective (AR) coatings - a low index material is required as the final layer for best efficiency. Specific fluoride compounds satisfy that index requirement. Fluoride layers have indices ≤1.4 near 10-µm wavelength. Some begin absorption. The thickness for the last layer of an AR is near QW, which for an AR in the 8 – 12 µm region is ~1800 nm. Fluoride compounds grow with high tensile stress, which is high enough at those thicknesses (typically > 1000 nm) to self-destruct by breaking into cracks that might compromise adhesion to the substrate or promote stress.

This is tendency is even more critical in applications where the H/L multi-layer uses many fluoride layers in the design. Some solutions to this problem are: the use of a mixture of fluorides, altering the deposition temperature and rate, low-energy IAD, and dividing the thick layer into thinner sections with a very thin different material interspersed. The last suggestion has the drawback of increasing the effective index of the last layer, thereby reducing the effectiveness of the AR. The goal of the materials and process variations is to modify the tendency of fluoride materials to grow in columnar form rather than with a homogenous morphology. The open-structure columnar micro crystals possess high structural stress and void volume which allow water vapor to penetrate and alter both mechanical and optical properties. Among those optical properties is resistance or durability to high-energy laser radiation.

Deposition properties

E-beam is generally used to deposit the materials used to produce LWIR coatings. Some, for example Zinc Sulfide (ZnS) and Zinc Selenide (ZnSe), can be deposited by resistance-heated evaporation. This is the preferred process for compounds that can be dissociated by the more energetic E-beam technique. Challenges with thermal boat heat radiation and material capacity for longer IR band-pass runs, may make multi-pocket E-beam approaches attractive. ZnS dissociates into Zn and S during evaporation, and these elements recombine at the substrate if temperature and the evaporation rate are favorable. The film layers can be grown to be larger and thicker, and have a columnar microstructure. Germanium (Ge) deposited film quality, in particular its optical absorption, is dependent on evaporation rate and substrate temperature. Because ZnS (ZnSe) and Ge layers are typically combined to build IR multilayers, a compromise substrate temperature, ~175^{o} C, is needed that will result in high quality coatings. As the low index, Fluorides can benefit from higher temperatures or even some ion energy. However, care must be taken in pocket maintenance (packing density and refill material) and in avoiding oxygen contamination in order to minimize absorption resulting from oxygen substitution for fluorine in the fluoride compound.

High IR Index Materials - Processing & Preparation for Deposition

We have discussed IR material developments in previous CMN articles. The focus was primarily on the low index fluoride coating materials related to the importance and challenges associated with 10.6um laser optics and general replacements for the radioactive ThF_4. However, with the high index materials, especially those that are common as substrates as well as the actual thin film material, there are differences in typical supply chain, manufacturing techniques and risk. These “dual use” high index materials, namely Germanium, Zinc Sulfide and Zinc Selenide, have key manufacturing differences that have posed challenges in recent years. Because of this, they deserve further consideration beyond the classic reasons why a material is chosen as a coating material or as a substrate for a given design or application.

Germanium (Ge)

Perhaps the most important fact about Germanium is that unlike its period table comrade Silicon, it is not found abundantly in its dominant oxide state. Conventional Ge metal is produced from Zinc smelting concentrates, Copper/ Lead sulfurous minerals or from coal combustion by-products. Just as with single crystal Silicon however, this brittle metal is pulled from a melt with a seed crystal and then zone-refined to 5N + purity. In optical components and evaporation sources, the substrates/granules can be single crystal, polycrystalline or amorphous. Each type can have dramatically different costs and pocket behavior.

Furthermore, to prepare evaporation materials, rods can be drawn and crushed or droplets can be formed that may negate shards and hand-sizing for refills of the crucibles. In addition, substrates, starter charges and IR optics are typically diamond-turned due to fragility. High purity materials can be doped which may have unintended consequences for deposition approaches. As hyper-spectral IR designs, which may have a visible or NIR bandpass requirement, Ge is replaced with hot or hot isostatic-pressed CVD ZnSe and ZnS.

In recent years, China has dominated the principle production of germanium concentrates, thus also refinement and metal production, which may be at risk with geopolitical or change control sensitive applications. Amorphous workable chalcogenide glasses are promising replacements for Ge substrates but remain difficult to form and challenging to coat due to adhesion issues. As coating material, chalcogenide glasses are showing promise in semiconductor devices but their composition is difficult to control and more absorbable compared to pure Ge in IR designs.

Zinc Sulfide (ZnS)

Zinc sulfide has a long previous history in manufacturing as a pigment and phosphor as IR coatings came of age. Over the years, different products were made with different levels of sulfur ranging from deficient to excessive which helped/hindered the use for increasingly complex IR designs. Until recently, vacuum condensation from the elements on a cold trap produced superior results for different forms of thermal evaporation. Advancing chemical vapor deposition (CVD) technology resulted in condensed production of increasingly thick plates of ZnS (and ZnSe).

In general today, a plate is condensed and crushed into pieces, or cut into cubes for evaporation. However, the high demand for “substrate-grade” material requires additional processing to remove water and enhance density and transmission. The subsequent hot press or hot isostatic process adds to the cost, but yields benefits to evaporative coatings. Hot-pressed ZnS powders are important for IR coatings utilizing thermal deposition approaches where the very high density ZnS CVD would promote hot spots in the metal or cause excessive sulfurous wear on costly Tantalum or Molybdenum consumables. One critical downside to ZnS thin films is the dramatic reduction of its sticking coefficient at elevated temperatures. Substrate temperatures exceeding ~175 ^{o}C can result in physical thickness errors or undesirable spectrum shift.

Zinc Selenide (ZnSe)

As a substrate, ZnSe is a CVD billet much like CVD ZnS. However, subsequent processing isn’t automatically favored as it is with ZnS, which tends to heal its stoichiometry under intense pressure and heat. While great care is taken during the CVD process itself, it is rumored that inadequate argon (Ar) recycle, together with the high vapor pressure of Se and the potential retention of the toxic H_2Se reactive gas (either at grain boundary or as exterior sludge), requires even more diligence and expertise to refine into standard coating and bulk substrate materials. It is for this reason that, unlike ZnS, substrate-grade ZnSe and evaporation-grade ZnSe are different in the sense that substrate-grade undergoes engineered refinement and is remediated to a higher purity and density standard not common for typical coating materials. In recent years, the number of high quality supply sources of evaporation materials and substrates has declined. This may be due to the rather limited region of specialty of ZnSe in10.6µm optics; however, that is a growth area due to lasers in manufacturing.

Summary

In the last issue of Coating Materials News, we discussed the complex IR spectrum and key non-fluoride high and low index materials critical to growing MWIR and LWIR wavelength bands applications. It is at these longer wavelengths that different forms of even the same materials can have critical processing, use and spectral nuances. These factors must be taken into consideration beyond the simple cost or nameplate transmission profile. In all cases, how well the film will perform - spanning from anti-reflection or multi-spectrum bandpass coatings - requires careful consideration of absorption, stress and yield. By reviewing key differences between material manufacturing methods and some process considerations, we hope to raise awareness of factors that enable our industry to meet industry challenges for years to come. Whether in the arena of remote sensing, atmospheric studies, night vision, military & defense, lasers in manufacturing, medical diagnostics, and many more applications under development.

Coating Material Solutions

Since 1964, Materion Advanced Materials has led the global industry by supplying the highest quality thin film coating materials for a broad range of industries and applications. We offer comprehensive technical expertise, scope of products, customized inorganic chemical compositions and strong customer relationships.

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