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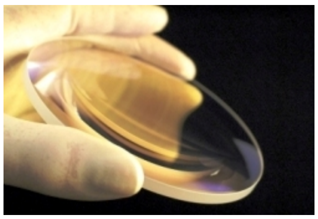
TECHNICAL PAPER

Optical Coatings for Harsh Environments

"Survival of the Fittest"

Author: Samuel Pellicori

Materion Coating Materials News



Optical coatings have thicknesses smaller than the thickness of the finest human body hair. Despite this miniscule size, there are applications that demand from them durability and resistance to harsh external forces. Coatings used in terrestrial & space, scientific, commercial, communication, NASA/NOAA, military, and medical applications can suffer potentially damaging or catastrophic failure in their operational environments. The following discusses the environmental challenges faced and how these micrometer-thin layers are designed to be able to survive and function over long-exposure lifetimes.

Terrestrial Applications

In terrestrial applications, thin-film coatings are required to operate and survive in environments that include high humidity, temperature swings, abrasive sand and high-velocity rain impacts, salt water exposure and organic solvent immersion. In previous issues of Coating Materials News (CMN), we have discussed the deposition processes and materials that produce coatings that exhibit the required resistance to these environmental stresses. Briefly, we learned that high-energy deposition processes are employed to produce thin-film layers with morphology that possesses high packing density, low stress, and correct chemical composition. Such deposition processes include ion-assist (IAD), magnetron sputtering (MS), ion-beam sputtering (IBS), atomic layer deposition (ALD), and variations on these techniques.

The PVD processes, IAD, MS, and IBS produce durable film layers by supplying high kinetic and reactive energy to the condensing vapor species, so they grow film layers that are dense enough to prevent the permeation of water and other liquids and vapors that can alter physical and optical properties. Simultaneously, chemical stoichiometry, such as oxidation state, is completed to further stabilize optical properties. As frequently discussed, oxide compounds produce the hardest, stable films, and are used when stability is essential.

Consumer Abuse

A common example of exposure to potentially damaging environments includes the handling of eyewear. Before being qualified for consumer use, ophthalmic AR coatings must undergo hot / cold water soaking, salt water immersion, and moderate abrasion. After purchase, the user subjects these coatings to further abrasive abuse and cleaning in the uncontrolled conditions of daily wear. Because they are designed for careless handling, these coatings resist scratching, peeling, solvent dissolution, and crazing. Layers of metal oxides such as TiO_2 and SiO_2 are routinely deposited using energetic IAD processes to apply durable AR coatings onto millions of polymer eyewear, goggles, and windscreens.

Effect on Thermal Imagers in Abrasive Environments
Another application was developed particularly for the IR windows on thermal imagers. Imager windows are routinely exposed to the abrasive forces of blowing sand and high-velocity rain. Impacting particles and raindrops cause surface pitting that results in increased scatter and the weakening of the window. These windows are often coated with diamond-like carbon (DLC), which also serves to reduce reflection losses. While DLC is very hard and somewhat brittle, it extends the operational life of these imagers for jet craft, naval applications, and even automobiles. Adhesion can work well for Ge and Si windows, but ZnSe requires additional materials for adequate adhesion.

Figure 1 shows the reflection of a single layer of DLC on the IR window materials Ge, Si, and ZnSe, that transmit the thermal IR band between wavelengths 8 and 11 µm. *Figure 1* also shows the reflectance of a QW of DLC on IR substrate materials. Zero reflectance is obtained when the refractive index of the QW layer is equal to the square root of the substrate. Index of DLC is 2, Ge = 4, Si = 3.4, and ZnSe = 2.4. For critical applications such as those used in NASA and DoD instruments, the residual reflection is excessive, and multi-layer AR designs are used. A single-layer AR is not efficient over the thermal IR band, 8 to 12 µm; multi-layer designs are used to meet typical requirement of ~1% Ravg over the band. To accomplish this average, Materion's low-index materials YbF3 and YF3 are used as replacements for ThF_4.

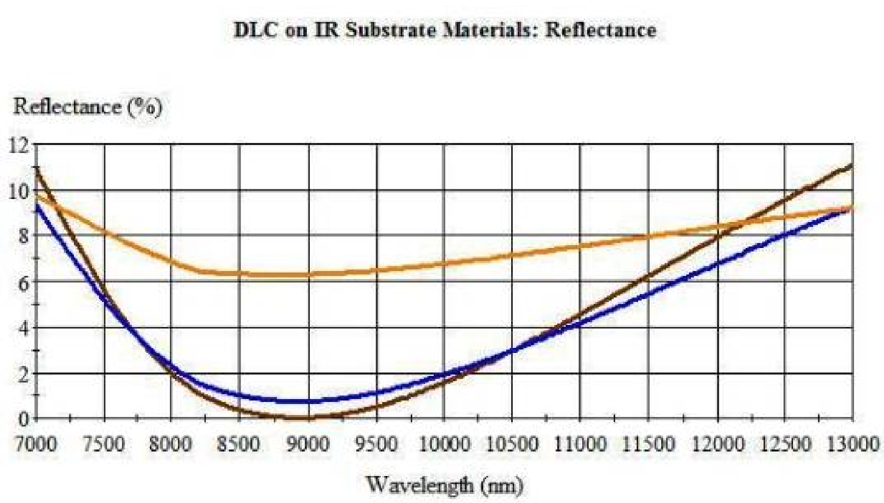


Figure 1. Reflectance of a QW of DLC on Ge (brown curve), silicon (blue), and ZnSe (orange).

The design of these wide-band AR coatings that can tolerate abrasive and impact exposure involves engineering development that considers the mechanical forces and stresses that could result in crazing, cracking, adhesion loss, and scatter due to surface abrasion. Previous issues of CMN have discussed approaches and techniques involved in the engineering of composite materials and layers that provide the necessary hardness while balancing or re-distributing stress to introduce resilience to impact forces [1].

Space Applications
The space environment imposes a different set of stressors than the terrestrial environment. Optical instruments have been flown above the Earth's atmosphere since the beginning of the space age. Even before rocket vehicles became available, instruments had to survive and operate in the low-pressure, low-temperature conditions of high altitude balloon flights.

Earth's atmosphere prevents UV at wavelengths shorter than ~290 nm, and also some low energy particulate radiation, from reaching the terrestrial surface. Optical instruments operating in low-to-high Earth orbits, as well as planetary missions into deep space, must resist the effects of hard vacuum, zero humidity, ionizing, particulate & UV radiation, micro-meteorite impact, and atomic oxygen erosion. In low Earth orbit (LEO), the international space Station (ISS) at an altitude of 350 to 400 km continually flies through a plasma consisting of atomic oxygen and ionizing particles such as solar protons, as well as solar UV. An additional concern is the damaging electrostatic discharge (ESD) of accumulated electrical charge.

Communication, broadcast, GPS navigation, earth resources, weather and climate monitoring instruments and reconnaissance systems operate in Mid-Earth Orbits (MEO) at 2,000 to 20,000 km altitude, see *Figure 2*. These environments, geosynchronous orbit (GEO) at 36,000 km altitude, and deep space missions to planets, comets and asteroids, are all exposed to higher energy ionizing protons and trapped electrons as well as UV radiation.

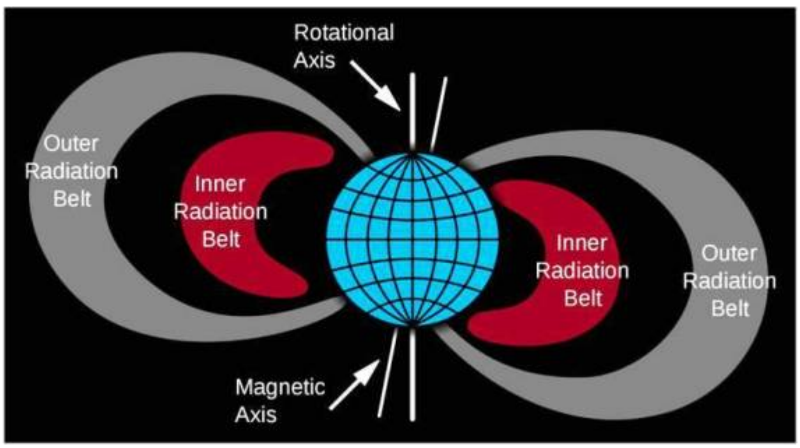


Figure 2. The radiation belts surrounding Earth contain different high energy particles. These plus solar protons and UV constitute hazards to space-borne instruments. (Courtesy: European Space Agency Center for Electronic Imaging).

The many square km of solar cells that power these instruments are continually exposed to solar UV, ionizing particulate radiation and micrometeorite impacts. Thin-film optical coating materials and processes have been developed that are used in solar cell cover coatings and are stable enough to last for many years in the space environment [2, 3]. These UVR/AR coatings reflect the damaging region of the UV spectrum while efficiently transmitting the useable wavelengths of the solar spectrum between ~320 nm and ~1700 nm. The wider spectral sensitivity of the next-generation four- (and larger number) junction solar cells will produce even higher power. The UVR/AR coating also provides conductivity to prevent ESD that can result in damage due to arcing.

Interaction with ionizing radiation, such as high-energy solar steady-state and flare-event protons, poses the threat of loss of optical performance in coatings. A key example is the gradual loss of electrical power generation due to radiation-induced damage of solar cells as their protective coatings darken with increased exposure time.

In discussing coatings that are stable to space radiation exposure, we include the modeling of the radiation damage as a function of material composition and physical path in order to determine their thresholds to energetic particulate radiation [4]. It is important to calculate the scattering range of protons vs penetration depth into the thickness of the coating for different types of coating and optical materials. Energetic particles such as protons and electrons interact with the atoms in materials. The most intense interaction is with atoms having heavy nuclei and large numbers of electrons. The common high refractive index coating materials, TiO_2, Ta_2O_5, Nb_2O_5, and HfO_2 fall into this category. The low-index multi-layer partnering material, SiO_2, has a lower interaction cross-section.

Figure 3 following shows the scattering cross-section of 100 keV protons as a function of penetration depth in a high reflector coating for 1064 nm. Ionization is produced along the penetration path (*Figure 3*) as the energy of the protons is dissipated, and damage is created in the coating layers.

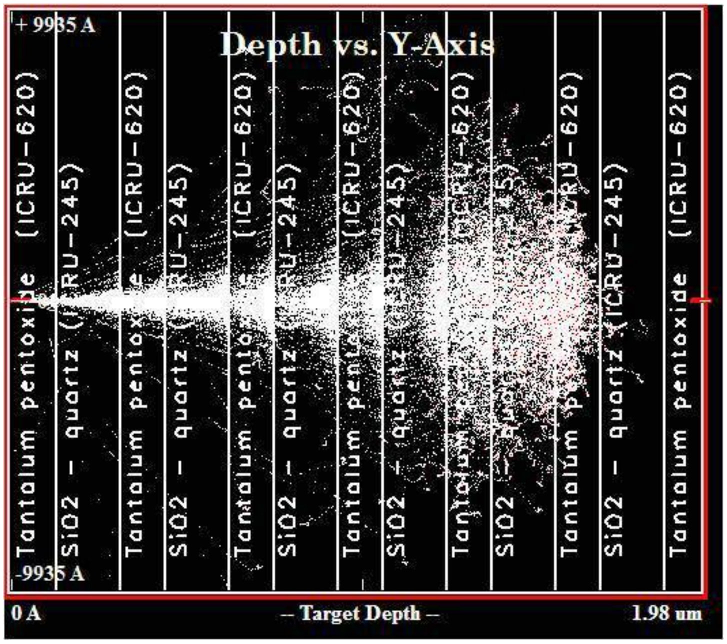


Figure 3. The stopping range of 100 keV protons in a HR design occurs ~85% through the coating. Protons of a lower energy would be stopped and produced damage in the first several layers.

In *Figure 4 below*, the density of ionizing collisions and accompanying damage vs depth is plotted. In the case of the example shown, the HR would exhibit a severe reduction in performance when irradiated by 100 keV protons because they are stopped deeply within the coating, and all their energy has been deposited and created damage.

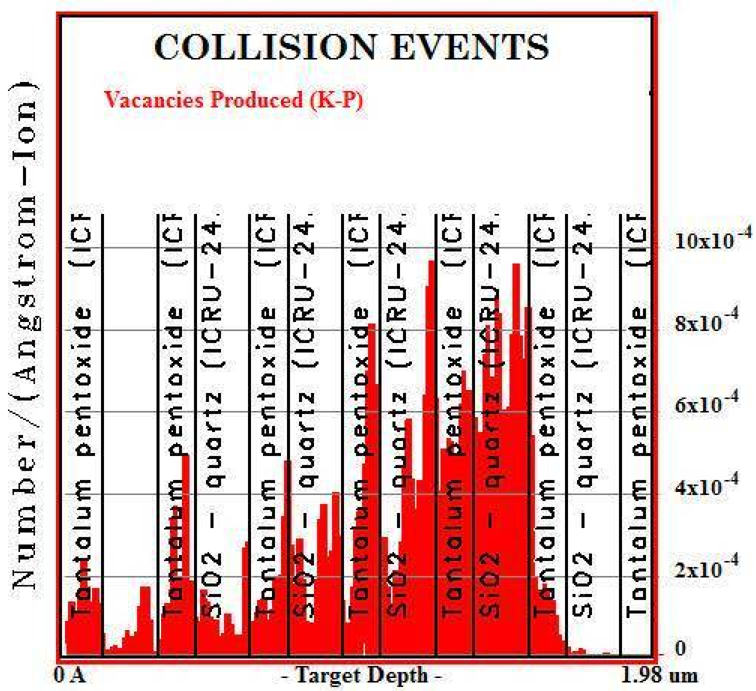


Figure 4. Collisions increase as the energy of the protons is dissipated along their path.

Lower energies would only damage the first few layers. An operational stress that is imposed on some coatings is to check for high-energy laser radiation. Previous CMNs have discussed this topic in detail and outlined how pulse width, repetition rate, and power density of high-power lasers affect coatings differently. In the femtosecond pulse range, coatings are damaged by the vaporization and ionization of materials; for longer pulse widths, localized melting can occur. The particular coating materials and their deposition processes play a defining role in determining the laser-induced damage threshold (LIDT). Damage is often initiated at sites with defects that might be the locations of microscopic particulates, microstructural growth defects, surface contamination, micro-cracks, etc.

Summary

We have seen how coating materials with thickness 1/25th of that of a human hair are expected to be strong enough to withstand overt physical stresses as well as more subtle stress exposures. We described how environmental durability is influenced by the management of deposition processes and materials. For questions about optical coatings and Materion thin film products and services, contact David A. Sanchez, Sr. Materials & Applications Scientist, David.Sanchez@Materion.com.

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Principal Contributor
Samuel Pellicori, Pellicori Optical Consulting, Santa Barbara, CA
Phone: 805.682.1922, Email: pellopt@cox.net