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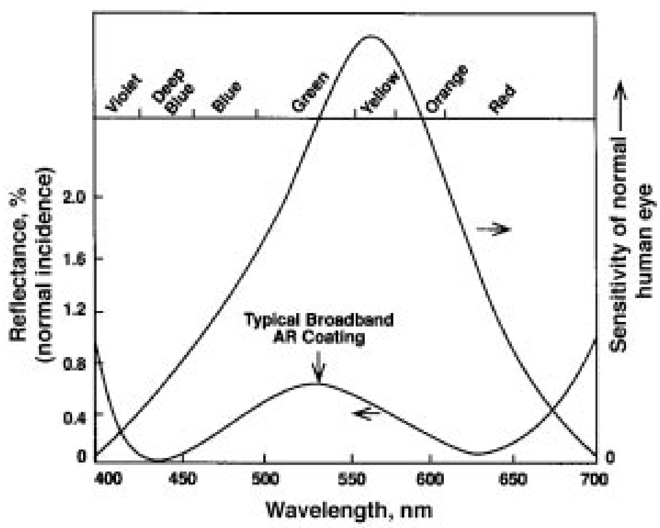
PVD Processes: Ophthalmic Coatings

Ophthalmic lenses are used in eyewear for a number of purposes. They may be used to correct vision, protect the eye from unwanted radiation (*e.g.*, sunglasses) or debris (safety glasses), or for a combination of purposes (prescription sunglasses). Until recently, lenses have been made of glass, but now various plastics are the most common lens materials. In 1997, 90 percent of eyewear were plastic. Plastic material is desirable because of its light weight and high impact resistance; however, it is also soft and easily scratched compared to glass. There are many polymer formulations used for ophthalmic lenses but polycarbonate is one of the most widely used.

In some cases, the lens material can provide the desired function. In others, however, coatings are necessary to achieve the desired effect. Coatings are also used to make the lenses more functional, so as to improve their optical transmittance, scratch resistance, or ability to be cleaned or to retain fluids on the surface (contact lenses). Coatings are also used to make the eyewear more marketable by making them distinctive or otherwise more attractive.

To improve scratch resistance, a hard polymer coating—such as an acrylic—can be applied to the plastic lens. This is the most inexpensive coating and the acrylates have good adhesion to polycarbonates. Blends of acrylates can be used to increase the toughness of the coating. The abrasion resistance of the acrylates can be improved by the addition of siloxanes to the blend, which will oxidize to form surface SiO_x-type structure when exposed to air. Tinting dyes and UV absorbers can be incorporated into the blend.

Another type of abrasion-resistant coating uses thermally curing organosiloxanes, which provide organic bonding to the plastic and oxidize to form significant concentrations of SiO_x in the organic matrix to provide scratch-resistance. The properties of the SiO_x/organic composite are determined by the extent of oxidation. The higher the organic content, the higher the fracture toughness, but the lower the hardness. The scratch resistance can be increased by the addition of colloidal (10-30 nm) silica particles to the blend. Surface oxidation also increases the scratch resistance.



Effect of a four-layer AR coating on reflectance and the spectral sensitivity of the human eye.

Plasma-enhanced chemical vapor deposition (PECVD) using organosilanes is increasingly being used to deposit scratch-resistant coatings on plastics. In PECVD, the plasma fragments the vapor precursor molecules, allowing cross-linking and deposition at lower temperatures than with thermal curing. Common organosilanes used for PECVD are hexamethyldisiloxine (HMDS) and tetraethyl ortho silicate (TEOS). The addition of N_2O, oxygen or water vapor to the plasma allows oxidation of a portion of the deposited material. By controlling the amounts, the degree of oxidation—and so the properties of the material—can be varied through the coating. The more the oxidation, the harder and less flexible the film. The surface of the PECVD coating can be made either hydrophobic (water-hating) or hydrophilic (water-loving). Oxidized surfaces are hydrophilic and surface groups containing fluorine or carbon create a hydrophobic surface. This condition is important to the contamination and cleaning of surfaces, as well as the retention of fluids as a lubricant. PECVD technology has the advantage that it can be incorporated into an in-line system along with the PVD processes necessary to deposit antireflection (AR) coatings. Other materials, such as diamond-like carbon (DLC), are being evaluated for application as scratch-resistant coatings.

Multilayer AR coatings are applied to lenses to increase their optical transmission and, in some cases, to limit the transmission of ultraviolet radiation, which can harm the eye. Antireflection results from the reflections from the interfaces between layers of thin films on a substrate. A coating with a thickness that is a quarter-wavelength of light with a refractive index equal to the square root of the refractive index of the substrate will yield an AR coating. This is difficult to achieve on plastics that have a low index of refraction. CR39, a common lens plastic, has an index of refraction of 1.5, requiring a film material with an index of refraction of 1.22 in order to get AR properties. No such film material exists.

For this reason, AR coatings on plastics require thin-layer film "stacks" of high-index (TiO_2-2.3, ZrO_2-2.1) and low-index (SiO-1.55 to 2.0, SiO_2-1.46, MgF_2-1.35) inorganic materials. If the deposited film material is less than fully dense, the index of refraction will be lower than that indicated.

Polycarbonate plastic, another common plastic lens material, has an index of refraction of 1.59. The AR coating stack can reduce the reflectance losses to less than a few percent for radiation at normal incidence (higher at oblique incidences). The figure shows the reflectance of a typical four-layer AR coating and the sensitivity of the normal human eye. The residual reflectance gives the surface a yellow-green, blue-green or bluish tint when viewed at normal incidence. Note that the transmittance is decreasing rapidly in the ultraviolet (<400 nm).

Inorganic multilayer AR ophthalmic coatings are usually applied to lenses by the physical vapor deposition (PVD) processes of vacuum evaporation or increasingly reactive magnetron sputter deposition. In the case of plastic lenses, the deposition temperature should be kept low (<60 °C preferably) in order to avoid continued curing reactions or secondary reactions that would create an unstable polymer surface during deposition.

High deposition temperatures can also increase the problem of residual stress in the films because of differences in coefficient of thermal expansion (CTE) between the film materials and the substrate material. For example, CR39 has a CTE of about 1 x 10^{-4} °C^{-1} while SiO_2 has a CTE of 8 x 10^{-6} °C^{-1}. High residual film stress can lead to long-term adhesion and crazing problems.

In both vacuum evaporation and magnetron sputter deposition, the substrate temperature can be kept low. In vacuum evaporation, several materials can be sequentially deposited from one e-beam evaporator using a multi-"pocket" crucible source. In reactive sputter deposition, a separate sputtering target is used for each film composition.

In both cases, the deposited film material may have an index of refraction that differs from that of the bulk material, either as a result of the film being less than fully dense or because the composition is slightly "off." For this reason, the "stack" transmission (which depends on each film thickness and its index of refraction) is measured and controlled during the deposition process. This is done by measuring the optical transmission of the film during deposition and comparing it with the desired value—when the desired transmission is achieved, that deposition is terminated and the next begins. Generally, this measurement is easier to make in the large processing chambers associated with vacuum evaporation than with sputter deposition, where the chambers are generally small. Historically, most AR coatings have been deposited by vacuum evaporation.

Eyewear can be subjected to extreme conditions of mechanical and thermal stress. It is important that the coatings adhere to the lenses under these conditions. Adhesion of oxygen-active film material to glass lenses is rather easily attained, but adhesion to plastics, such as CR39 or polycarbonate, is more difficult. The difference in the mechanical properties of the plastic substrate and the hard coating puts high stress on the interface during shock or deformation.

In the case of plastics, base coats are often applied to increase the adhesion of subsequent AR coating material. Sometimes, to improve adhesion, the polymer surface is activated by an oxygen plasma treatment prior to film deposition or a very thin layer (5-10 nm) of chromium (Cr or Cr_xO_y) is used as a "glue layer" for the AR coating stack. In some cases, "topcoats" are applied to the AR coating stack to provide a hydrophobic surface that resists contamination and makes the surface easy to clean.

The market for AR ophthalmic coatings is already large in Europe and Asia and is rapidly increasing in the United States. New developments in the technology center on PECVD processing and integrating several types of processes (hybrid processing) into in-line deposition systems. The AR Council of America is in the process of generating standards for AR ophthalmic coatings. P&SF