Value-Added Flat-Glass Products for the Building, Transportation Markets, Part 2
An overview of value-added solar glass, solar and heat reflective coating on glass and the new category of self-cleaning glass products is provided.

M. Arbab, L.J. Shelestak and C.S. Harris
Glass Technology Center, PPG Industries Inc., Pittsburgh, Pa.

The first part of this two-part series on value-added flat-glass products focused on product requirements and online and off-line coating deposition manufacturing processes. It also included a discussion about flat-glass composition. This part of the series presents an overview of value-added products.

Coated Glass Products for Energy Efficiency
Low-emissivity (low-E) and solar control coatings are spectrally selective thin-film stacks that are deposited on float glass. Either chemical vapor deposition (CVD) or physical vapor deposition (PVD) is used for deposition. In general, the CVD-coated products are harder and chemically more durable. The sputter-deposited coatings have better spectral selectivity.

The reflectance and transmittance of several coatings as a function of wavelength have been determined (Figs. 5(a) and (b)). These coatings are usually designed to have high transmittance and neutral color to meet currently accepted aesthetic requirements. To select the glass pane for optimum energy efficiency, the local climate for the entire year should be taken into account.

Minimizing winter heat loss should be balanced against desirable passive solar heating in northern climates, particularly for south-facing windows, and air-conditioning requirements during summer. More than 94% of the thermal energy from bodies at 21°C (a typical indoor temperature in winter) is emitted in the 5–40 µm region of the electromagnetic spectrum (thermal radiation range). Uncoated glass is a high-emissivity material. It absorbs and reemits heat in this region (emissivity = 0.84). In contrast, a conductive coating on glass reflects this thermal radiation and has low emissivity.

Most commercial CVD low-E coatings consist of transparent conductive oxides (TCO) that are good reflectors in the thermal radiation range (emissivity = 0.2). A prime example of such a coating is fluorine-doped tin oxide (F:SnO$_2$), which is an n-type semiconductor. SnO$_2$ can be deposited in the tin bath under atmospheric conditions from tin-bearing organometallic compounds, e.g., monobutyltin chloride.

Generally, higher conductance of the coating results in a lower emissivity for the product. Therefore, at a given conductivity, the film should be thick enough to meet the emissivity requirement for its intended use. F:SnO$_2$ has a relatively high index of refraction (~2.0) compared with glass (1.5). At a typical thickness of $\geq$100 nm, F:SnO$_2$ can impart high reflectance and undesirable color to the glass product. Therefore, the glassmaker inserts an optical thin-film stack between the functional F:SnO$_2$ film and the glass substrate for color suppression.

An innovative approach is to use a mixed-metal oxide layer, e.g., a mixture of oxides of tin and silicon. The composition of the layer continuously varies between relatively pure SiO$_2$ at the glass surface to SnO$_2$ at its interface with the conductive layer. This results in a layer with a graded index of refraction that changes from ~1.5 to ~2.0. Therefore, well-defined optical interfaces that cause optical interference in the coating are eliminated.

An optical model of such a thin-film stack demonstrates that a low-emissivity coating with neutral color and decreased total reflectance can be designed. A more usual solution to this problem, which also is practiced in the industry, is the use of several thin-film layers.
with varying indexes of refraction. These layers and the conductive SnO₂ film result in destructive interference of visible light in reflection. F:SnO₂ or other similar conductive transparent oxides that are nonabsorbing in the visible spectrum are not effective in reflecting the solar IR radiation. Other conductive oxides that are more absorbing, e.g., Sb:SnO₂, can be incorporated into the coating stack to decrease solar heat load through a glass window. These oxides also may result in absorption of visible light and lower visible transmittance.²¹

An alternative group of products that have either low-E properties, solar heat load reduction properties, or both, consists of sputter-deposited thin films. These coatings often consist of metal and metal compound layers. The most widely used commercial examples of these coatings are silver based. Silver is a highly effective mirror in the solar and thermal ranges of IR radiation. However, silver reflects visible light and, relative to the conductive transparent oxides, is soft and nondurable. To overcome these deficiencies, multilayer stacks have been designed. One or more silver layers are sandwiched between thin films of transparent dielectric metal compounds.²²

These dielectric layers are usually chosen from a group of metal oxides or nitrides, including ZnO, SnO₂, SiO₂ and TiO₂ or Si₃N₄. These films function as optical interference layers. They also must provide chemical and mechanical durability to silver-containing thin-film stacks by stabilizing silver and acting as buffer layers.²² The coating stack then consists of repeating units of dielectric–silver–dielectric, where the silver layer is generally ~10–15 nm thick.

Depending on their place in the stack and their index of refraction, the dielectric layer thickness can vary between several and 100 nm. The silver-based coatings nevertheless remain more prone to mechanical damage than the CVD films discussed earlier. However, as has been demonstrated (Figs. 5(a) and (b)), the solar performance of these coatings is superior to tinted glass and CVD-coated low-E glass products. Similarly, these coatings offer the lowest emissivity available among all highly transparent coated products, with neutral color.²² For example, a double silver layer stack²³ has an emissivity of <0.04.

Total value of the product to the customer must be considered, e.g., solar-performing glass. In choosing the most appropriate product, either for an office building or an automobile, the designer (or engineer) chooses from several options of tinted glass or IR-reflective coatings, or a combination thereof. This choice is driven by several considerations and constraints, including aesthetics or appearance, heating and air-conditioning requirements, daylighting preferences, occupant comfort and security, wireless communication requirements, and material cost.

For example, tinted glass can provide distinct transmit-
ted colors to match the rest of the car body or affect the appearance of the car interior. The glass also must effectively absorb solar radiation and be relatively simple to fabricate and use, at comparatively low cost. On the other hand, tinted glass windows absorb heat. However, tinted glass can decrease occupant comfort and result in more heat buildup in buildings or parked cars than solar-reflective glass. High-electrical-conductivity silver-based coated glass has excellent solar performance and sheet resistance of <3 Ω/square. Therefore, it can function as a radio antenna or a resistive heater for deicing the car windshield. However, this conductance may decrease wireless signal transmission into and out of the vehicle.

The glass supplier has to be sensitive to all these customer needs and offer a product portfolio that agrees with its own business strategy. The designer then specifies the product to the glazing fabricator. During fabrication, glass usually undergoes the process steps of cutting, edging, washing, tempering or bending, and laminating or incorporating in an insulated glass unit. The overall process must be economically acceptable to the fabricator and the designer. Thus, the product has to be process robust: it must be sufficiently hard and amenable to glass tempering or bending.

In the case of the PVD-coated products, traditionally, the glass supplier cuts to size, bends or tempers the glass pane, coats it and then sends it to the fabricator. This has been economically unacceptable to the fabricator. The long lead time for ordering the glass and the extra cost of coating bent or tempered glass limit the flexibility of the fabricator to respond adequately to the needs of the downstream manufacturer of the OEM products. Therefore, the flat-glass industry has developed coated glass products that can be postcut and heat processed by the fabricator. This has required new materials, coating processes and stack designs for the multi-silver-layer stacks, as described elsewhere. Thus, total value in this case results from the ability to choose the product with the right performance for a given end use at acceptable price. It also results in the ability of the fabricator to process the product economically and without unnecessary dependence on production schedule at the flat-glass supplier factory.

There are several other large-area coated-glass products for applications other than automobile or architectural markets. For example, in the aircraft industry, TCO coatings, e.g., In:SnO2 (ITO), are used for airplane deicing or opacity to radar signal. Also, TCO-coated low-iron glass is used as a substrate for large-area photovoltaic applications. However, in comparison with the architectural and automotive markets, the volume of glass used in these applications is small.

### Self-Cleaning Glass

The self-cleaning window was introduced during 2001. The self-cleaning window is the newest category of window since the introduction of low-E solar reflective coatings during the early 1980s. The self-cleaning window is based on the photocatalytic and photoinduced hydrophilic properties of a durable film of TiO2. There are other products that can be applied to a glass surface to make the glass easier to keep clean or that protect the glass surface from contamination. However, the self-cleaning category of products is unique. The coating is actively involved in a chemical reaction that breaks down organic material on the glass surface.

The photocatalytic property of TiO2 causes the breakdown of organic material on the film surface. The electron–hole pair formation in TiO2 is induced by a photon of energy. It is followed by oxidation reactions that attack organic materials in a series of steps to clean the TiO2 surface.

The photocatalytic properties of TiO2 gained interest during the fuel crisis of the 1970s. At that time, TiO2 was being explored for its water-splitting properties to produce hydrogen gas. This later prompted interest in using TiO2 coatings for self-cleaning surfaces. The anatase form of TiO2 is a semiconductor with a bandgap of 3.2 eV. Therefore, light with wavelengths <387 nm, i.e., the UV range of solar spectrum, is needed to create the electron–hole pairs.

Another property of TiO2 is UV-induced hydrophilicity. This property manifests itself by the contact angle of a drop of water on the TiO2 surface that is in the superhydrophilic regime (<5°) when exposed to UV light. This property of TiO2-coated glass is what is most obvious to the consumer. It is the visual effect of water, from rain or spray, wetting out on the window, rather than forming drops. Windows with self-cleaning glass wet out dramatically compared with ordinary glass windows when sprayed by water (Fig. 6).

The sheeting of water on a self-cleaning glass surface after outdoor exposure is clearly evident when com-
pared with the beading of water on the surface of ordinary clear float glass. The water on the self-cleaning glass surface is not easily visible, because it is spread out as a uniform thin sheet. This visual effect also results in a cleaner-looking window, because water spotting is eliminated on the dry glass. This hydrophilic effect is supported by the photocatalysis that prevents oily hydrophobic dirt buildup, which would spoil the observed wetting behavior.

UV-induced hydrophilicity of a TiO₂ film has been quantified (Fig. 7). The contact angle of water on the surface of a TiO₂-coated glass has been compared with that on the top-side of a piece of standard soda–lime–silica float glass. The samples are exposed to simulated solar UV light (UVA340 bulbs with a 28 W/m² irradiance level at the sample surface). The contact angle is measured periodically. The contact angle of the TiO₂-coated glass has an initial value of ~40°. However, the value quickly decreases to 5° within 2 h of UV exposure. The contact angle for the standard glass starts out small, which is expected for a mostly SiO₂-based material. However, the contact angle increases over time as naturally occurring organic compounds condense on the surface from the air.

The mechanism for the photocatalytic properties for TiO₂ have been well documented. However, the mechanism for the photo-induced hydrophilicity is less well understood. One proposed mechanism is the reaction of photogenerated holes with bridging oxygen species at the TiO₂ surface to form defect sites. Dissociative adsorption of water occurs at these defect sites. This results in an increase in hydroxyl groups at the coating surface, which render the surface superhydrophilic. Detailed surface analysis work is being done on single-crystal TiO₂ to further investigate this interesting property.

The contact angle on the regular glass surface does not change. The stearic acid does not degrade under these conditions without the aid of a photocatalyst. The combination of the photocatalytic and UV-induced hydrophilicity are necessary to bring about the self-cleaning function to a window. However, a third property, durability, also is needed to bring value to the customer and the consumer.

The film and its function must endure handling during window manufacturing and installation. However, it also must survive outdoor exposure over a period of ≥10 years. Therefore, TiO₂-based self-cleaning glass products are deposited using an on-line CVD process, as described in preceding sections.

The aesthetics of the TiO₂-coated glass also are important. The residential market, in particular, requires that value-added glass products do not vary too far in appearance from that of windows made with regular glass. This requirement is a challenge for TiO₂-coated glass because of the high index of refraction of TiO₂ (2.3–2.5 at 550 nm). Sufficiently thick TiO₂ films on glass can be highly reflective. Interference effects result in strong coloration as the film thickness increases. This
aesthetic challenge can be managed using thin TiO\textsubscript{2} films. For example, a 20 nm thick film results in a first surface luminous reflectance value of \textasciitilde20\%. This value is much higher than that for regular glass (8\%). However, the neutral, slightly blue reflected color of the coated glass gives a pleasing bright appearance to the windows when they are installed, which adds to the overall clean look.\textsuperscript{32}

The high index of TiO\textsubscript{2} also can be countered using optical layers—transparent thin films of appropriate optical thickness—between the glass and the TiO\textsubscript{2}. These layers act to suppress the strong interference color of thicker TiO\textsubscript{2} films. For example, this optical layer can be a single $\lambda/4$ homogenous film with an index of refraction between that of the TiO\textsubscript{2} and the glass. Such approaches need to be chosen with care to balance the cost and manufacturing complexity with the overall appearance and performance of the product.

The use of self-cleaning glass continues to grow in the marketplace. There is always a drive to find other applications for this type of product, such as expanding the use of the TiO\textsubscript{2}-coated glass to automotive and building interiors. These applications have unique challenges: the amount of the necessary UV light available to drive the photocatalytic and hydrophilic functions, and the requirements for durability and appearance. Self-cleaning glass is new to the marketplace. However, as the consumer becomes more familiar with its function, the possibilities and demands for such a product will continue to grow.

**Preferred Glazing Material**

Glass remains the preferred glazing material because of its lower cost and superior properties. However, new competition is arising from advances in other areas, particularly in polymer technology and nanomaterials. Examples include hard-coated plastic car windows, energy-absorbing nanoparticles in transparent polymer–ceramic composite films and multilayer polymer thin-film stacks for IR reflection. At the same time, these and other developments in materials science also have created exciting new opportunities for flat-glass products. In particular, new developments in nanotechnology, where the glass technologist has for centuries taken advantage of the special optical properties of nanoparticles, offer promising new routes to adding function to glass and its surface.

Total value to the customer will continue to determine the success of new value-added flat-glass products. A recent market study\textsuperscript{33} predicts a 50% growth in the total world demand for flat glass in the first decade of this millennium. This coincides with an unprecedented increase in global production capacity. Most of the growth has occurred in Asia, which already has resulted in serious price competition in the industry. Energy and fuel efficiency, safety, comfort and aesthetics continue to drive flat-glass product innovation.

Sophisticated customers participate in leading the research and development effort in the flat-glass arena. A customer-driven product strategy ensures that the limited marketing and research and development resources are focused on market needs. This focus can result in more emphasis on incremental developments at the expense of game-changing technologies. The industry must consider this risk, particularly in the face of the cost challenge from the low-labor-cost economies. Therefore, in our higher-cost environment, we cannot depend on exclusivity and long product life cycles. Rather, a multidisciplinary approach to continuous innovation in products and manufacturing excellence is a must.

**Editor’s Note**


**References**


\textsuperscript{23}Solarban® 60 Coated Glass, PPG Industries, Pittsburgh.


\textsuperscript{26}A. Fujishima and K. Honda, Nature (London), 238, 37 (1972).


\textsuperscript{33}“World Flat Glass,” Industry Study 1589, The Freedomia Group, Cleveland, Ohio, 2002.