Controlling the Sun’s Energy With Thin Film Coatings

Introduction
The sun delivers 1.36 kW/m² at the Earth’s surface. This “free” clean energy powers solar and wind electricity generators, sea waves, and solar water heaters. Chlorophyl uses blue wavelengths to produce plant nutrients while reflecting near-IR energy that produces unwanted heating. Millions of square meters of architectural glass control the heating of indoor space - and this is where thin film coatings play an important role. This article will discuss the use of coatings that selectively absorb and reflect different portions of the solar irradiance spectrum, and the deposition processes used for their manufacture.

Figure 1. Spectrally selective coatings are used to make optical art. Plate with graticulated multi-layer oxide compounds coating resulting in a stress-textured coating (by T. Ives). Squares are multilayer green reflectors on textured glass. Bottom of “Jack in the Pulpit” blown glass vase with chemical thin film, in the style of Louis Comfort Tiffany (Lundberg Studios). Photo by Samuel Pellicori, 2012.

Spectrally Selective Coating Functions
Visible light has wavelengths between ~400 nm and ~700 nm. Window glass transmits visible and IR energy to wavelengths as long as ~2.7µm (2700 nm). This spectral range includes about half of the solar radiation, the other half is at longer IR wavelengths. A significant portion of solar IR energy at wavelengths >700 nm is transmitted by glass and is responsible for heating the interior of a building or automobile. While the transmission of IR energy is desirable in colder climates, in warm climates it imposes the need for interior cooling. At wavelengths where glass does not transmit, it absorbs. Thus, at wavelengths longer than 2.7 µm, high absorption causes the glass to heat up and become a black body radiator at 300 K, with maximum radiation near 10 µm.
Thin-film coatings have been developed for architectural and automotive glass that selectively transmit visible light to interior space while reflecting IR energy that will either escape from, or be transmitted to, the interior space. The control of the flow of solar energy in both directions enables the reduction of heating demands for cold climates and of cooling demands for warm climates, thereby reducing reliance on non-solar based energy sources.

Three function-related types of spectrally selective solar control coatings have been developed and are in use world-wide. They include passive and active constructions:

- Visible-transmitting, IR heat reflecting
- High- / low-emissivity coatings
- Electrochromic and thermochromic coatings that modulate the reflection of IR energy

### The table classifies the functions and their designs:

<table>
<thead>
<tr>
<th>Function</th>
<th>Requirement</th>
<th>Coating Design</th>
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</thead>
<tbody>
<tr>
<td>Visible transmitting/ IR Reflecting</td>
<td>Transmit ~400 nm to ~700 nm, Reflect &gt; ~700 nm</td>
<td>Dielectric / metal / dielectric</td>
</tr>
<tr>
<td>Heating / cooling</td>
<td>Transmit or absorb &lt;2700 nm, Reflect / emit &gt;2700 nm</td>
<td>Oxide semiconductors: Transparent conducting oxides (TCO)</td>
</tr>
<tr>
<td>Radiative cooling</td>
<td>Emit &gt;2700 nm</td>
<td>Ceramic absorber</td>
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#### Visible-Transmitting, Heat Rejection Coatings

A dielectric/ thin metal / dielectric design is used for architectural, automotive and aircraft windows. The metal layer is sandwiched between dielectric layers to both enhance the visible transmission and protect the metal from environmental corrosion and scratching. A typical design consists of a DMD structure, where the dielectrics induce transmission in the otherwise highly reflecting metal layer by index matching over the visible band of wavelengths. Outside this band, the metal reflects the long wavelength energy. This design is effective in excluding the transmission of heat energy into a living space while admitting visible light. The transition interval between transmitted and reflected wavelengths can be steepened by doubling the design to DMDDMD, where the dielectric layers are QW thickness. A typical design is: 300 Å TiO₂ / 130 Å Ag / 300 Å TiO₂. Visible transmission and IR reflection are both ~80%. This film is characterized by having low solar absorptivity, \( \alpha \), and high IR reflectivity or low emissivity, \( \varepsilon \), and windows are called “low-e” coated glass.

Variations on this design are in use by different large area coaters of architectural glass. Curved windshields are also coated using sputtering and shaped targets or movable glass holders. Some manufacturers bend the windshield to shape after coating. The TCO ITO is a favorite coating because it provides the spectral properties as well as the possibility of defrosting by conducting an electrical current, and does not require patterning as wire heaters do.

The coatings are deposited on sheets of glass in a large area sputter coating system or on polymer film in a continuous roll coating system. Sputter processes using planar and cylindrical magnetron targets are employed in in-line glass and roll-to-roll polymer film coaters. The polymer film is later laminated to rigid glass window sheets. Metals commonly used are copper, silver, and Titanium Nitride (gold colored) and the TCO ITO. In layers as thin as 10 nm, they transmit some visible light and reflect highly in the IR. Metals of the typical thickness used do not form continuous thin film layers unless the conditions of the surfaces on which they are
deposited are properly conditioned. This process involves the choice of dielectric underlayer and the deposition energy. Oxide compounds such as Titanium Dioxide and Zinc Oxide are typical. More detailed information on sputter targets follows in a later section titled “Sputter Targets for Large Area Coatings.” Sputtering processes are also discussed in previous CMN issues [1]. CMN newsletter.

Lighting and Heating Coatings with Heat Barrier Properties
These coatings passively transmit visible light and solar IR while reflecting 300 K blackbody radiation. The application is to heat interior space while preventing the heat from escaping by radiation through the window. Retention of the heat reduces the need for space heating during cold weather. TCOs like In$_2$O$_3$:Sn (ITO), SnO$_2$:Sb, SnO$_2$:F and others transmit visible to ~1500 nm and reflect all longer wavelength energy. We have discussed ITO and other TCOs in several past issues of the CMN Newsletter. TCOs have a refractive index near 2. Bare ITO is very resistant to scratching and other environmental exposure effects, and transmission can be increased by the addition of a layer of SiO$_2$.

Electrochromic and thermochromic Coatings
Unlike the previous types of selectively controlling coatings, electro- and thermo-chromic coatings are not passive coatings, but require an electric current or applied heat to cause a change in reflection and transmission. Such coatings find application where there is need to control visual or IR transmission. Visible light transmission can be modulated between ~80% and ~10% as required to maintain comfortable interior lighting under varying external lighting conditions. The coatings operate by controlling the concentration of ions injected or extracted from metal oxides in the electrochromic layer. A high concentration of ions produces high reflection. The electrochromic layer is sandwiched between ITO layers that conduct electrons into it as a function of the applied voltage. Typical materials are WO$_3$ for visible light and Ni(OH)$_2$ for the IR.

Thermochromic materials respond to temperature changes. VO$_2$ is a commonly used material, but its visible transmission is lower than WO$_3$. Variations are generated by replacing some of the O by F.

Selectively Absorbing Coatings for Solar Heating
By increasing the absorption of solar energy which is maximum in the visible region of the spectrum, surface temperatures can be raised for water and air heating. Simultaneous control of the emissivity of the coating reduces the loss of heat by radiation from the surface. Thus, the film has high solar absorptivity, $\alpha$, and low IR emissivity, $\varepsilon$. The function is to collect and retain heat for transfer to a circulating medium such as a gas or fluid. Such coatings are black in appearance, but reflective in the thermal IR region. Examples are: vacuum deposited or sputtered films of nickel-silicon oxide, Cr/ Cr$_2$O$_3$, and sub-oxide Titania / Ti films.

A fluid at the focal point of multiple mirrors on a solar farm is heated to high temperature and used to generate electricity. Another application based on this principle is seen on the roofs of Middle-East residential dwellings - the ubiquitous solar water heater. Black paint may be used as the absorber, but it has neither the low emissivity nor the environmental stability that thin-film coatings provide.
In the previous passages, we have addressed the application of thin film coating materials that serve to more efficiently use available solar energy for lighting and heating and thereby reduce our reliance on fossil fuels and their attendant effects on climate change.

As mentioned in the previous section “Visible-Transmitting, Heat Rejection Coatings”, more information on sputter targets follows. Materion Advanced Chemicals provides a wide variety of materials for large area thin film coatings and manufactures sputtering targets across a variety of materials and alloys to support energy-efficient glass applications.

**Sputter Targets for Large Area Coatings**

Large area coatings employ large targets that can be cylindrical or planar in configuration. TCO and oxide-compound targets such as ITO, i-ZnO, TiOx, TiOxNb, ZnSn and others, are manufactured by spraying or pressing techniques. Metal targets such as Al, Ag, NiV are cast and have higher densities than materials that are sprayed or hot pressed.

Commercial Cylindrical target manufacture is commonly done by the following four techniques (with their attendant limitations).

A. Cold press/sinter, Hot press and HIP (hot isostatic press) collars are the most common, but require specialty bonding and backing tube considerations. Density is a strong function of starting powder size and particle characteristics. Dense targets are fragile - especially for semiconductors or ceramics. Powder metal parts often have low (compared to cast) heat transfer, that can cause melting or composition issues.

B. Cast, machine-to-large cylinder, extrude-to-long cylinder in use and under development, generally have the best grain structure and composition. These types of cylindrical targets offer the best strength, density and thermoelectric properties. Some pure metals and some compounds just don't "flow"/"deform" well or they sag; these require more specialty processing as in C or D below.

C. Casting directly to a backing tube is very common, but is very limited in grain and composition control. Due to differential cooling related to heat transfer issues during manufacture and use, front-to-back uniformity issues limit deposition rate and power density. This approach requires good reproducibility and control to produce robust alloys or highly pure metals.

D. Spray-to-tube (plasma or thermal spray) is a very common and well-known process. Sources for the spray can be pure or alloy wire as well as complex atomized or agglomerated powders. Limitations, such as low material utilization, weak lateral strength and limited run time, vex this approach. However, sometimes this allows the capability of alloys and mixtures to be made that would simply not be possible by casting. Similarly, without collars on a backing tube, the monolithic design can be critical if only for high value coatings due to target thickness or deposition power limitations.

Planar targets have the advantage of being produced by any of the above techniques. Casting and rolling produces a large output of high density targets of well-behaved alloys and pure metals. Simple hot pressing, while offering low cost of market penetration, is limited by throughput; but purity and sputterability can be maximized for a given powder/system.

**Summary**
We have briefly discussed the application of thin film coating materials that serve to more efficiently use available solar energy for lighting and heating and thereby reduce our reliance on fossil fuels and their attendant effects on climate change. Also, the role of sputter targets in producing coatings.

Materion Materials
Materion Advanced Chemicals, formerly CERAC, Inc., has a worldwide reputation for supplying the highest quality specialty inorganic materials since 1964. We provide materials for use in thin film coating deposition processes that produce products that absorb and reflect solar irradiance. For more information, view Solar Applications.

References

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