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DURABLE INNOVATIVE SOLAR OPTICAL MATERIALS--THE INTERNATIONAL CHALLENGE

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Durable Innovative Solar Optical Materials -
The International Challenge

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Abstract

A variety of optical coatings are discussed in the context of solar energy utilization. Well known coatings such as heat mirrors, selective absorbers, and reflective films are covered briefly. Emphasis is placed on the materials limitations and design choices for various lesser known optical coatings and materials. Physical and optical properties are detailed for protective antireflection films, fluorescent concentrator materials, holographic films, cold mirrors, radiative cooling surfaces, and optical switching films including electrochromic, thermochromic, photochromic, and liquid crystal types. For many of these materials research is only now being considered, and various design and durability issues must be addressed.

Introduction

Optical coatings play a vital role in solar energy conversion. A number of well known coatings can be classified as heat mirrors, selective absorbers and reflective materials. But there remain numerous less known films and materials that have significant consequence to solar energy development. The deployment of such films in active and passive solar energy conversion, photovoltaic, energy efficient windows, and mixed designs offers improvement in efficiency and allows new designs to be introduced. It is the function of this study to expand the horizon of innovation by considering new materials, concepts, and techniques that can manipulate solar energy as a form of heat, light, and electrical power. Specific coatings and materials will be covered under individual sections. Such materials are not without shortcomings. The solution to materials science and design problems is the responsibility of a number of scientists and engineers working in many countries and various fields. It is their commitment that will further this technology.

Figure 1. Spectrum of solar radiation (airmass 2) shown with three blackbody spectral distributions (-30°C, 40°C, 100°C). Superimposed is the idealized selective reflectance of a heat mirror or solar-selective absorber.

Figure 2. Reflectance of various antireflection treatments for glass.
Transparent conductive films

Transparent conductive coatings can be utilized for four major applications in solar energy conversion. They can be used as low-emittance coatings for windows and solar collectors, as electrodes for photovoltaic and photoelectrochemical cells, and as active elements in heterojunction and oxide photovoltaics. The use of heat mirrors for architectural windows and for solar collectors is discussed extensively elsewhere. The relationship between the solar spectrum, blackbody spectra, and idealized selective reflectors is shown in Figure 1. Heat mirrors fall into two classes based on design: single-layer doped semiconductors, and metal/dielectric interference films. Examples of the former are SnO:F, In2O3:Sn, Cd2Sn4, and CdO. Illustrative systems of the latter might be based on TiO2/metal, Al2O3/metal, or ZnS/metal alternations. Photovoltaics and photoelectrodes can utilize only single-layer materials having high electrical conductivity. Several reviews cover the properties of doped transparent semiconductors.

Active materials research areas center around deposition processes and materials microstructural-property relationships. Development of cost-effective techniques to deposit such films on glass and plastic film materials is of major concern. Eliminating post-annealing treatments, to increase conductivity, would reduce expense. Improvement in chemical dip coating processes and understanding of hydrolysis (CVD) chemistry as it relates to film properties through deposition parameters are important research areas. Further development of plasma-assisted physical vapor deposition (PVD) is critical to room-temperature deposition on thin plastic film substrates. Lower deposition temperatures along with near-atmospheric pressures should be utilized for refined coating processes. An understanding of doping and defect properties in semiconductor films is necessary, with emphasis on durability and stability. There is also room for basic materials research of new binary and ternary compounds including boride, nitride, oxide, and carbide systems which may be better suited to simple deposition. Existing high-rate, large-scale deposition techniques for heat mirrors should be examined carefully for cost-effectiveness.

Solar absorbers

Solar absorber research is dominated by studies on selective surfaces and paints. Absorbers for solar collectors have been one of the most active research fields in solar coatings in the last few years. This work has produced a better understanding of one of the most popular coatings, black chrome. Its chemistry, microstructure, degradation lifetime, and thermal limitations have been explored in detail. Studies of chemical conversion and native oxide coatings have uncovered new absorbers. The development of stick-on solar absorber foils has allowed versatility in solar designs. The study of high-temperature selective absorbers is quite challenging. Large-scale, high-temperature conversion requires an absorber material which will remain stable and have consistent properties under high solar flux and cyclic temperature extremes. One promising coating is the refractory metal-oxide, graded-index coating in which simple materials composition variation is responsible for the graded optical index. The development of a selective spray-on or dip paint is also an area of active research. The challenge is to find a binder material that is devoid of infrared absorption bands within the region of the absorber's blackbody operating temperature response. This binder must be sufficiently strong to withstand the operational environment. Spraying or dipping techniques also must be optimized to assure consistency and uniformity of properties.

Refractor materials

Refractor materials for solar energy uses fall into two distinct categories: front-surface and backsurface. They also differ according to method of deposition of the metallic aluminum, silver, or alloy layer and whether the host material is flexible. Front-surface mirrors suffer from abrasion, atmospheric corrosion, and delamination. A protective, durable overcoating material is required. For second-surface mirrors produced by the wet chemical process there is a lack of understanding of the various interfacial chemical reactions. For example, certain mirrors degrade rapidly while others last for several years. For both types of reflectors an understanding of the stability between metal/polymer and metal/glass mirrors is a significant issue. Dirt and dust can be responsible for considerable decline of efficiency of reflector surfaces. Techniques to limit dusting and washing of surfaces need to be devised. Many of these concerns were addressed at a recent solar materials workshop.

Antireflective and protective overcoatings

Antireflective coatings, if designed with proper compounds, can also serve as durable overcoating materials. For photovoltaics, some polymeric and elastomeric protective coatings can be effective antireflective materials if the coating is thin enough, although protective coatings are generally used in thick-film form. Popular protective materials are silicones, fluorocarbons, halocarbons, and acrylic resins. One major need is to develop a coating that serves both protective and antireflective functions. Some polymers having a low refractive index (n) can antireflect glass (n = 1.5) and other high-index plastics. Dispersions of fluorinated ethylene propylene (n = 1.34) can be used for this purpose. Polyvinyl fluoride (n = 1.46) can be antireflected by dipping in aceto phenone. Graded-index films present a versatile range of coatings having refractive indices that are not readily found. Fluorosilicic acid can give a graded-index,
antireflective coating to glass. (See Figure 2.) It primarily roughens the surface by etching out small pores, in nonsilica regions.\textsuperscript{16,15} Silica coatings deposited from sodium silicate or colloidal silica can be used for acrylic, polycarbonate, and several glasses. A film for polyethylene terephthalate (polyester) and glass materials has been devised.\textsuperscript{17,18} The coating is made from a steam-oxidized aluminum film; this processing causes a needle-like structure of aluminum hydroxide [Al(OH)] to form. A polyester film treated in this fashion can serve in glazing applications where solar transmission must be optimum.\textsuperscript{19} (See Figure 3.) Inorganic thin films have been used for a wide range of single and multiple interference coating applications. Compounds such as MgF\textsubscript{2}, CeO\textsubscript{2}, CeF\textsubscript{3}, SiO\textsubscript{2}, SiO\textsubscript{2}, and TiO\textsubscript{2} in various combinations have been used for antireflection applications. Other than the traditional PVD techniques, a number of oxides can be dipcoated onto optical substrates. Coatings of hot hydrolysed metal alkoxides can be polycondensed, forming oxides of Al, In, Si, Ti, Sr, Sn, Pb, Ta, Cr, Fe, Ni, Co, and some rare earths.\textsuperscript{20} A similar method known as the sol-gel process has formed mixed TiO\textsubscript{2}-SiO\textsubscript{2} antireflective films on silicon and black chrome. Diamond-like (\textit{I} - carbon) transparent coatings have been used for antireflective films. They are formed from plasma decomposition of hydrocarbons and ion beam deposition.\textsuperscript{22} Coatings of about \( n = 1.9 \) can be made which are suited to photovoltaics.

\begin{center}
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Hemispherical transmission of antireflected 3M Sungain polyester film compared to uncoated substrate.}
\end{figure}
\end{center}

\begin{center}
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Spectral transmittance for COIL greenhouse cold mirror.}
\end{figure}
\end{center}

\textbf{Cold-mirror and spectral splitting coatings}

Cold-mirror coatings are selective transmission films having optical properties directly opposite to those of the heat mirror. Cold mirrors exhibit high reflectance in the visible region and transmit highly in the infrared. Generally such coatings are all-dielectric, for example ZnS/MgF\textsubscript{2} and TiO\textsubscript{2}/SiO\textsubscript{2} hard-layer films.\textsuperscript{23} These coatings are useful for separating light and heat and might be utilized in a combined thermal-photovoltaic system. Another application for these films is for greenhouses.\textsuperscript{24} Plants require only a range of wavelengths 0.3 - 0.75 microns; the remainder of the solar spectrum is unused. This extra portion can be separated as heat and used to warm the greenhouse. A baffle-type greenhouse utilizing both cold-mirror and reflective coatings is illustrated in Figure 4.

Spectral splitting coatings are used to separate the solar spectrum into various bands of wavelengths. These bands are matched to a particular photovoltaic response.\textsuperscript{25} A system might consist of a series of cold mirrors where the transition from reflecting to transmitting moves to longer wavelengths for each successive spectral splitting cell. In this way the solar spectrum could be partitioned from high to low energies. A series of heat mirrors could also be used, but the solar spectrum would be partitioned from low to high energy as the heat-mirror transition wavelength became shorter.

\textbf{Fluorescent concentrator materials}

The principle of fluorescent concentrators consists of a transparent plate which has been doped with fluorescent dye molecules. Incident light corresponding to the fluorescent absorption will be captured and emitted isotropically. Due to the index of refraction difference between the plate and surrounding media, a large fraction of light will be trapped and transmitted to the edges of the plate by total internal reflection. By silvering some of the edges, a greater amount of light can be funneled to a favored edge where tuned photovoltaics, for example, may be placed. The amount of light guided in a plate to that lost by transmission out of the sheet, according to \( G = (n - 1)^2 / n \), is 75\% for a sheet with \( n = 1.5 \). By using multiple plates various portions of the solar spectrum can be utilized. For each level of collector plate a higher absorption level is used so the innermost plate absorbs the highest energy. With the use of a backup mirror reemitted energy can be absorbed by lower-energy fluorescent levels. (See Figure 5.) The advantages of using a fluorescent plate for concentration are that the concentration ratio is high (100 - 100), the concentrator works even in low insolation or diffuse sky conditions, and no tracking of the sun is required.
Also, there is less heat dissipation in photovoltaic systems and high efficiency at low insolation levels. For thermal collectors using fluorescent concentrators, efficiencies of 42-59% have been estimated. For purely photovoltaic conversion overall efficiency of 32% for a four-plate system has been calculated. 

![Figure 5. Fluorescent concentrator design showing hypothetical absorption and emission spectra.](image)

![Figure 6. Spectral reflectance of 1 micron SiO/Al film for radiative cooling. Idealized properties are shown by broken line.](image)

Materials for fluorescent concentrators have favored polymethyl methacrylate (PMMA) for converting wavelengths shorter than 1 micron. Good materials for the infrared need to be devised as glazings for cover plates. Fluorescent dyes need to be custom tailored for solar collectors as they have been for lasers. The dyes should have high quantum efficiency and low self-absorption with absorption and emission spectra well separated in energy. Many existing dyes have overlapping spectra. Dyes need to be chemically resistant to UV decomposition. New materials can be used such as ligands containing rare earth ions and mixed organic systems with nonradiative energy transfer between different molecules. The types of fluorescent materials used for experimentation fall into the category of rare-earth doped laser glass and laser dyes. Rhodamine 6G in PMMA has $\lambda_a = 525 \text{ nm}$ $\lambda_e = 575\text{ nm}$ and ED2 Ne-doped glass has $\lambda_e = 500-900\text{ nm}$ $\lambda_a = 1060\text{ nm}$. A dye-doped fluorescent thin film could also be devised as a substrate coating. This design could minimize reabsorption by the dye. Furthermore, a broader coverage in tailoring the dye emission spectrum can be obtained by mixing dye materials in such a way that one emission band corresponds to the absorption band of another. Rhodamine 6G and Coumarin 6 dyes have been used in this fashion.

**Radiative cooling materials**

The earth naturally cools itself by radiative transfer through high-transmission windows in the atmosphere to the cold troposphere. This effect is most noticeable on clear nights. A significant atmospheric window occurs from 8-13 microns wavelength. One could conceivably design an upward-facing surface which would emit over this wavelength range. A material would have to have high reflectance for 0.3-50 microns, excluding the 8-13 microns region. In the 8-13 micron region the material would have to have a very low reflectance or high emittance. It is theoretically possible for such a surface to reach 50 °C below ambient, with typical temperatures about 15 °C below ambient. Temperatures below the dew point should be avoided.

Materials used for radiative cooling include SiO/Al (see Figure 6) and polymer-coated metals. Polymers such as polystyrene (PVC), polyvinylfluoride (PVF, Tedlar), and poly-4-methylpentene (TPX) have been suggested. A radiative cooling device can also consist of two separate materials, a selective cover and an emitter. Infrared emitters are easy to find, but the selective cover is a challenge. Materials like polyethylene with coatings of TiO or dispersions of TiO have been experimented with. The overall field of radiative cooling has just recently regained interest. Materials need to be designed that not only satisfy the optical requirements but are also resistant to weathering and solar degradation. For the materials investigated thus far, the emittance of the coatings need to be optimized to take full advantage of the 8-13 micron window. Finally, methods of coupling these surfaces with heat-transfer media need to be devised.

**Optical shutter materials**

Optical shutter materials or devices can be used for energy-efficient windows or other passive solar uses. An optical shutter offers a drastic change in optical properties under the influence of light, heat, or electrical field or by their combination. The change can be, for example, a transformation from a material that is highly solar transmitting to one which is reflecting either totally or partly over the solar spectrum. A lesser choice might be a film which converts from highly transmitting to highly absorbing. In application an optical shutter coating could control the flow of light and/or heat in and out of a...
building window, thus performing an energy management function. Depending upon design such a coating device could also control light and thermal levels for lighting, heating, and cooling functions. Generally, this idea represents future research and design areas. Phenomena of interest to optical shutters are electrochromic, photochromic, thermochromic, and liquid crystal processes.

**Electrochromic devices**

Electrochromism is exhibited by a large number of materials both inorganic and organic. The electrochromic effect is of current research interest mainly because of its application to electronic display devices. However, the use of electrochromic devices for windows has been addressed. The electrochromic effect, in essence, is a material which exhibits intense color change due to the formation a colored compound. This compound is formed from an ion insertion reaction induced by an instantaneous applied electric field. The reaction might follow: \( \text{MO}_x + y\text{A}^{+} + ye^{-}\rightarrow \text{A}_y\text{MO}_x \).

There are three categories of electrochromic materials: transition metal oxides, organic compounds, and intercalated materials. The materials which have gained the most research interest are \( \text{WO}_3, \text{MoO}_3, \) and \( \text{IrO}_x \) films. These compounds, among other transition metal oxides, are the subject of a timely review. Organic electrochromics are based on the liquid viologens, anthraquinones, diphthalocyanines, and tetraphthalfulvalenes. With organics, coloration of a liquid is achieved by an oxidation-reduction reaction, which may be coupled with a chemical reaction. Intercalated electrochromics are based on graphite and so are not useful for window applications.

A solid-state window device can be fabricated containing the elements shown in Figure 7: transparent conductors (TC), an electrolyte or fast-ion conductor (FIC), counter electrode (CE), and electrochromic layer (EC). Much research is needed to develop a usable panel, better electrochromic materials with high cycle lifetimes, and short response times. Certainly fast-ion conductors and electrolytes also require study.

![Figure 7. Model of solid-state electrochromic cell.](image)

![Figure 8. Example of spectral transmittance for photochromic glass showing light and dark responses.](image)

**Photochromic materials**

Photochromic materials change their optical properties or color with light intensity. Generally, photochromic materials are energy-absorptive. Basically, the phenomenon is the reversible change of a single chemical species between two energy states, having different absorption spectra. This change in states can be induced by electromagnetic radiation. Photochromic materials have been reviewed. Probably the best known is photochromic glass used in eyeglasses and goggles. Photochromic materials are classified as organics, inorganics, and glasses. Within the organics are stereoisomers, dyes, and polynuclear aromatic hydrocarbons. The inorganics include \( \text{ZnS}, \text{TiO}_2, \text{Li}_2\text{N}, \text{HgS}, \text{HgI}_2, \) and \( \text{HgCN}_3, \) and alkaline earth sulfides and titanates, with many of these compounds requiring traces of heavy metal or a halogen to be photochromic. Glasses that exhibit photochromism are Hackmanite, Ce, and Eu doped glasses (which are ultraviolet sensitive), and silver halide glasses (which include other metal oxides). The silver halide glasses color by color-center formation from an \( \text{AgCl} \) crystalline phase. The typical response for a photochromic glass is shown in Figure 8.

For windows, development work is needed to utilize commercially available silver halide glasses. Other deposition of such glasses as film compounds requires more research for possible utilization as films and suspensions in polymeric materials.
Reversible thermochromic materials

Many thermochromic materials are used as nonreversible temperature indicators, but for an optical shutter one can consider only the reversible materials, although their actual cyclic lifetime is limited by nonreversible secondary reactions. Organic materials such as spiropyans, anils, polyvinyl acetal resins, and hydroxides are examples of thermochromism. Inorganic materials include HgI₂, AgI, Ag₂HgI₄, Cu₂HgI₄, SrTiO₃, Cd₃P₃Cl, and Copper, Tin, and Cobalt, complexes. Research areas are fairly wide open; some work is suggested on compounds which exhibit both photo and thermochromism. Identification of limiting reactions, development of film materials, and polymeric and glassy dispersions are necessary.

Liquid crystals

Liquid crystals are actively used for electronic and temperature displays. The greatest part of research has gone into these areas. Liquid crystals can be in one of three structural organic mesophases: smectic, nematic, or twisted nematic (cholesteric). The most widely used is the twisted nematic. From a materials standpoint liquid crystals are based on azo-azoxy, esters, biphenyls, and Schiff bases. Also passive liquid crystal films can be solidified into solid films by polymerization, giving preset optical properties. A liquid crystal in the form of a light valve could be used to modulate transmittance and reflectance of light entering the cell. Unlike the electrochromic device, a liquid crystal would require continuous power to stay reflective. Both cost and fabrication must be considered for large-area optical shutters.

Holographic and interferometric films

Holography consists of the recording of two reflected, coherent beams interferometrically from a physical object. An analogous technique using interferometric noncoherence could be used to construct thin films which are light-concentrating, reflecting or redirecting in a wavelength-selective manner. As a hologram requires coherent light (a laser) to reconstruct the image, this analogous method could utilize a non-coherent light source like the sun. The holographic phase and amplitude pattern needed for solar uses could be generated by computer, once given a mathematical model of the spatial distribution required.

Holographic recording materials can be photographic emulsions (phase and amplitude holograms), photo polymers, thermoplastic xerography, and dichromatic gelatin, which are useable for all phase-only holography.

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References

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