Innovative solar optical materials

Carl M. Lampert
Lawrence Berkeley Laboratory
University of California
Materials and Molecular Research Division
and
Energy Efficient Buildings Program
Berkeley, California 94720

Abstract. A variety of optical coatings are discussed in the context of solar energy utilization. Well-known coatings such as transparent conductors (heat mirrors), selective absorbers, and reflective films are surveyed briefly. Emphasis is placed on the materials' limitations and on use of lesser-known optical coatings and materials. Physical and optical properties are detailed for protective antireflection films, cold mirrors, fluorescent concentrator materials, radiative cooling surfaces, and optical switching films including electrochromic, thermochromic, photochromic, and liquid crystal types. For many of these materials, research has only recently been considered, so various design and durability issues need to be addressed.

Keywords: solar energy; optical coatings; heat mirrors; selective absorbers; optical switching films; solar collectors.

Optical Engineering 23(1), 092-097 (January/February 1984).

CONTENTS

1. Introduction
2. Transparent conductive films
3. Solar absorbers
4. Reflector materials
5. Antireflective and protective overcoatings
6. Cold-mirror and spectral-splitting coatings
7. Fluorescent concentrator materials
8. Radiative cooling materials
9. Optical shutter materials
  9.1. Electrochromic devices
  9.2. Photochromic materials
  9.3. Reversible thermochromic materials
  9.4. Liquid crystals
10. Acknowledgment
11. References

1. INTRODUCTION

Optical coatings are very important for solar energy conversion. There are a number of well-known coatings: heat mirrors, selective absorbers, and reflective materials. There are also less well-known films and materials that can influence solar energy development. Using such films for active and passive solar conversion, photovoltaics, energy efficient windows, and mixed applications can improve efficiency and lead to new designs. This study considers new materials and techniques for using solar energy for heating, lighting, and electric power. The materials are not without shortcomings; the solutions to problems must come from scientists and engineers in many countries and fields.

2. TRANSPARENT CONDUCTIVE FILMS

Transparent conductive coatings can be used in three major ways in solar energy conversion: as low-emittance coatings (heat mirrors) for windows and solar collectors, as electrodes for photovoltaic and photoelectrochemical cells, and as active elements in heterojunction and oxide photovoltaics. Other work has extensively discussed the use of heat mirrors for architectural windows$^{1-3}$ and for solar collectors.$^{4-6}$ The relationships among the solar spectrum, blackbody spectra, and idealized selective surface are shown in Fig. 1. The ideal properties for heat mirrors are solar transmittance $T_s = 1.0$ and infrared emittance $E_{IR} = 0.0$. The transition wavelength is determined by the specific application of the film. Heat mirrors fall into two classes based on design: single-layer doped semiconductors and metal/dielectric interference films. Examples of the former are SnO$_2$:F, In$_2$O$_3$:Sn, and Cd$_2$SnO$_4$.$^{7-9}$ Their spectral properties are shown in Fig. 2. Systems employing the latter might be based on TiO$_2$/metal, In$_2$O$_3$:Sn/metal, Al$_2$O$_3$/metal, or ZnS/metal alternations. Photovoltaics and photoelectrodes can use only single-layer materials that have high electrical conductivity. Several reviews cover the properties of doped transparent semiconductors.$^{10-12}$

Current materials research centers around deposition processes and microstructural-property relationships. Development of cost-effective techniques to deposit films on glass and plastic is a major concern.$^{13-15}$ Eliminating postannealing treatments to increase conductivity would reduce expense. Improvement in chemical dip coating processes, and an understanding of chemical vapor deposition chemistry as it relates to film properties through deposition parameters, are also important research areas. Further development of plasma-assisted physical vapor deposition (PVD) is vital to room-temperature deposition on thin plastic substrates. Lower deposition temperatures and pressures should be used 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 research on new binary and ternary compounds including boride, nitride, oxide, and carbide.

Invited Paper S124 received Nov. 12, 1982; revised manuscript received June 3, 1983; accepted for publication June 16, 1983; received by Managing Editor July 5, 1983. This paper is a revision of S124-30 which was presented at SPIE conference on Optical Coatings for Energy Efficiency and Solar Applications, Jan. 28-29, 1982, Los Angeles. The paper presented there appears (unrefereed) in SPIE Proceedings Vol. 324.

© 1984 Society of Photo-Optical Instrumentation Engineers.
3. SOLAR ABSORBERS

Solar absorber research is dominated by studies on single and tandem selective surfaces and paints. The reflectance properties of an idealized selective surface are shown in Fig. 1. A selective absorber, unlike a heat mirror, is totally absorbing in the solar wavelength region. Idealized properties are solar absorptance $A_s = 1.0$ and infrared emittance $E_r = 0.0$. The transition wavelength is determined by the operating temperature of the collector. Absorbers for solar collectors have been actively researched during the past few years. Figure 3 shows the properties of the following selected solar absorbers: black chrome, textured Mo-Al$_2$O$_3$, black copper, and Ni-pigmented Al$_2$O$_3$. Research has led to a better understanding of a number of coatings; one of the most popular coatings is 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 increased versatility and upgraded solar designs.

The study of high-temperature selective absorbers is quite challenging. Large-scale, high-temperature conversion requires an absorber material that remains stable and maintains consistent properties under high solar flux and cyclic temperature extremes. One promising coating is the refractory metal-oxide, graded-index coating; simple composition variation is responsible for its graded optical index.

The development of a selective spray-on or dip paint is also an area of active research. For absorber paints having silicone binders, values have been obtained experimentally for controlled thicknesses of $A_s = 0.92$ and $E_r = 0.11$, and for thickness-insensitive paints the values $A_s = 0.90$ and $E_r = 0.30$ have been obtained. The challenge is to find a binder material that is devoid of infrared absorption bands in the region of the absorber's blackbody operating temperature. This binder must be sufficient to withstand the operational environment. Spraying or dipping techniques also must be optimized to assure consistent and uniform properties.

4. REFLECTOR MATERIALS

Reflector materials for solar energy uses fall into two categories: front-surface and back-surface reflectors. They also differ according to the method of deposition of their metallic aluminum, silver, or alloy layer and whether or not the host material is flexible. Front-surface mirrors suffer from abrasion, atmospheric corrosion, and delamination. A protective, durable overcoating material is required. We do not understand various interfacial chemical reactions of second-surface mirrors produced by the wet chemical process. 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 in reflector surface efficiency. Techniques need to be devised to limit dusting and washing of surfaces. Many of these concerns were addressed at a recent solar materials workshop.

5. ANTIREFLECTIVE AND PROTECTIVE OVERCOATINGS

Antireflective coatings, if designed with appropriate compounds, can also serve as durable overcoating materials. For photovoltaics some polymeric and elastomeric protective coatings can be effective antireflective materials if they are thin enough, although protective coatings are generally used in thick-film form. Silicons, fluorocarbons, halocarbons, and acrylic resins are popular protective materials. One major need is for a coating that serves both protective and antireflective functions. Some polymers that have 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 serve this purpose. Polyvinyl fluoride (n = 1.46) can be antireflected by dipping in acetylphenone.

Graded-index films represent a range of coatings having uncommon refractive indices. Fluorosilicate acid can give a graded-index, antireflective coating to glass (see Fig. 4). It roughens the surface by etching out small pores in nonsilica regions. Silica coatings deposited from sodium silicate or colloidal silica can be used for acrylic, polycarbonate, and several glasses. A film has been devised for polyethylene terephthalate (polyester) and glass materials. The coating is made from a steam-oxidized aluminum film; this process produces a needle-like structure of aluminum hydroxide [AlO(OH)]. A polyester film processed in this fashion can serve in glazing applications where solar transmission must be optimum (see Fig. 5).

Inorganic thin films have been used for many types of single and multiple interference coatings. Compounds such as MgF₂, CeO₂, CeF₃, SiO₂, SiO₂, and TiO₂ in various combinations have been used for antireflection applications. As well as being deposited by the traditional PVD techniques, a number of oxides can be dip-coated onto optical substrates. Coatings of hot hydrolyzed metal alkoxides can be polycondensed, forming oxides of Al, In, Si, Ti, Fr, Sn, Pb, Ta, Cr, Fe, Ni, Co, and some rare earths. A similar method, known as the sol-gel process, has formed mixed TiO₂-SiO₂ antireflective films on silicon and black chrome. Diamond-like (i—carbon) transparent coatings have been used for antireflective films. They are formed from plasma decomposition of hydrocarbons and ion beam deposition. Coatings of about n = 1.9 are suited to photovoltaics.

6. COLD-MIRROR AND SPECTRAL-SPLITTING COATINGS

Cold-mirror coatings are selective transmission films the optical properties of which are opposite to those of heat mirrors. Cold mirrors exhibit high reflectance in the visible region and transmit highly in the infrared. Generally such coatings are all-dielectric, for example ZnS/MgF₂ and TiO₂/SiO₂ hard-layer films. These coatings are useful for separating light and heat and might be used in a combined thermal-photovoltaic system. These films can also be used for greenhouses. Plants require wavelengths ranging from only 0.3 to 0.75 μm; the remainder of the solar spectrum is unused. This extra portion can be separated for heat to warm the greenhouse. A baffletype greenhouse utilizing both cold-mirror and reflective coatings is illustrated in Fig. 6.

Spectral-splitting coatings are used to separate the solar spectrum into bands of wavelengths. These bands are matched to a particular photovoltaic response. A system might consist of a series of cold mirrors where the transition from reflecting to transmitting moves to longer wavelengths with each successive spectral-splitting cell. In this way the solar spectrum would 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.

7. FLUORESCENT CONCENTRATOR MATERIALS

A fluorescent concentrator consists of a transparent plate that has been doped with fluorescent dye. Incident light corresponding to the fluorescent absorption is captured and emitted isotropically. Since the indices of refraction between the plate and surrounding media are different, a large fraction of light is trapped and transmitted to the edges of the plate by total internal reflection. By silvering some of the edges, a greater quantity of light can be funneled to a favored edge to connect with tuned photovoltaics, for example. The proportion of guiding in a plate that is lost by transmission out of the sheet is 75% for a sheet having n = 1.5. Multiple plates can utilize various portions of the solar spectrum. For each level of collector plate, a higher absorption level is used so that the innermost plate absorbs the highest energy. With a back-up mirror, remitted energy can be absorbed by lower-energy fluorescent levels (see Fig. 7). The advantages of using a fluorescent plate for concentration are that the concentration ratio is high (10 to 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 sys-
tems and high efficiency at low insolation levels. For thermal collectors that use fluorescent concentrators, efficiencies of 42 to 59% have been estimated. For purely photovoltaic conversion, overall efficiency of 32% has been calculated for a four plate system. 35,36

Fluorescent concentrators have generally used polymethyl methacrylate (PMMA) to convert wavelengths shorter than 1 μm. Materials suitable for converting 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 energies from the absorption and emission spectra well separated. 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 that show 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 peak absorption and emission wavelengths of \( W_a = 525 \text{ nm} \), \( W_e = 575 \text{ nm} \), and ED2 Ne-doped glass has \( W_a = 500 \) to 900 nm, \( W_e = 1060 \) 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 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. 37

8. RADIATIVE COOLING MATERIALS

The earth naturally cools itself by radiative transfer through high-transmission windows that lead from the atmosphere to the cold troposphere. This effect is most noticeable on clear nights. A significant atmospheric window occurs from 8 to 13 μm wavelength. One could conceivably design an upward-facing surface that would emit over this wavelength range. The material used would need high reflectance for 0.3 to 50 μm, excluding the 8 to 13 μm region. In the 8 to 13 μm region, the material would need very low reflectance or high emittance. It is theoretically possible for such a surface to reach 90°C below ambient, with typical temperatures about 15°C below ambient. 38 Temperatures below the dew point should be avoided.

Materials used for radiative cooling include SiO/Al and Si₃N₄/Al (see Fig. 8) and polymer-coated metals. Polymers such as polyvinyl chloride (PVC), polyvinyl fluoride (PVF, Tedlar), and poly-4-methylpentene (TPX) have been suggested. 38 A radiative cooling device could 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 such as polyethylene with coatings of Te or dispersions of TiO₂ have been experimented with. The overall field of radiative cooling has just recently received attention. Materials need to be designed to satisfy optical requirements and resist weathering and solar degradation. For the materials investigated so far, the emissivities of the coatings need to be optimized to take full advantage of the 8 to 13 μm window. Finally, methods need to be devised to couple these surfaces with heat-transfer media.

9. OPTICAL SHUTTER MATERIALS

Optical shutter materials or devices can be used for energy-efficient windows or other passive solar uses. An optical shutter undergoes a drastic change in optical properties under the influence of light, heat, electrical field, or their combination. The change can be, for example, a transformation from a material that is highly solar transmittant to one that is reflective either totally or partially over the solar spectrum. A less attractive choice might be a film that 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, performing an energy management function. Depending on design, such a coating could also control light and thermal levels to provide lighting, heating, and cooling. Generally, this idea is ripe for research and design. Phenomena of interest to optical shutters are electrochromic, photochromic, thermochromic, and liquid crystal processes.

9.1. Electrochromic devices

Electrochromism is exhibited by a large number of materials, both inorganic and organic. The electrochromic effect is of current research interest primarily because of its application to electronic display devices. However, the use of electrochromic devices for windows has been addressed. 39 The electrochromic effect, in essence, occurs in a material that exhibits intense color change due to the formation of a colored compound. This compound is formed from an ion-insertion reaction induced by an instantaneous applied electric field. The reaction might follow: \( 
\text{MO}_x + y\text{A}^+ + ye \rightarrow A_y \text{MO}_x \), where \( \text{MO}_x \) is a metal oxide and \( A \) is an ion or proton.

There are three categories of electrochromic materials: transition metal oxides, organic compounds, and intercalated materials. The materials that have received most attention are WO₃, MoO₃, and IrO₂ films. These compounds, among other transition metal oxides, are the subject of a timely review. 40 Organic electrochromics are based on the liquid viologens, anthraquinones, diphenyleneamines, and tetrathiafulvalenes. 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, therefore, are not useful for window applications.

A solid-state window device can be fabricated; an example of one configuration is shown in Fig. 9. The layers are transparent conductors (TC), an electrolyte or fast-ion conductor (FIC), counter electrode (CE), and electrochromic layer (EC). The spectral characteristics of an electrochromic device are shown in Fig. 10. 41 Much research is needed to develop a usable panel, better electrochromic materials with high cycle lifetimes, large-scale deposition techniques, and durability to the solar environment. Thin-film ion-storage layers and ion-conductive layers also require study.
9.2. Photochromic materials

Photochromic materials change their optical properties or colors in response to 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.\(^{41,42}\) Probably the best-known is photochromic glass used in eyeglasses and goggles. Photochromic materials are classified as organics, inorganics, and glasses. Included with the organics are sterioisomers, dyes, and polynuclear aromatic hydrocarbons. The inorganics include ZnS, TiO\(_2\), Li\(_3\)N, HgS, HgI\(_2\), HgCNS, and alkaline earth sulfides and titanates. Many of these compounds require 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 defect formation from an AgCl crystalline phase. The typical response for a photochromic glass is shown in Fig. 11.

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

9.3. 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 cyclic lifetimes are limited by nonreversible secondary reactions. Organic materials such as spiropyran, anilis, and polyvinyl acetal resins are examples of thermochromism. Inorganic materials include HgI\(_2\), AgI, Ag\(_2\)Hgl\(_4\), Cu\(_2\)Hgl\(_4\), SrTiO\(_3\), and copper, tin, and cobalt chemical complexes. Research areas are fairly wide open; some work is suggested on compounds that exhibit both photo- and thermochromism.\(^{43}\) Identification of limiting reactions, development of film materials, and polymeric and glassy dispersions are necessary. These materials may also be useful in controlling the selective absorber degradation that occurs by stagnation from overheating. Thermochromics may be added to a solar absorber to alter solar absorbance or thermal emittance when a certain temperature is reached.

9.4. Liquid crystals

Liquid crystals are widely used for electronic and temperature displays, the areas in which most research has occurred. 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.\(^{44}\) From a materials standpoint, liquid crystals are based on azo-azoxy, esters, biphenyls, and Schiff bases. 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 an electrochromic device, a liquid crystal would require continuous power to stay reflective. Both cost and fabrication must be considered for large-area optical shutters.

10. ACKNOWLEDGMENT

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Building Energy Research and Development, Building Systems Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

11. REFERENCES

11. V. A. Baum and A. V. Sheklen, Geliotekhnika 4, 50(1968).