Lawrence Berkeley National Laboratory
Recent Work

Title
INNOVATIVE SOLAR OPTICAL MATERIALS

Permalink
https://escholarship.org/uc/item/5rk82887

Author
Lampert, C.M.

Publication Date
1983-03-01
Presented at the International Society for Optical Engineering (SPIE) Technical Symposium and Exhibit, Los Angeles, CA, January 25-29, 1982; and to be published in Optical Engineering

INNOVATIVE SOLAR OPTICAL MATERIALS

C.M. Lampert

March 1983

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

INNOVATIVE SOLAR OPTICAL MATERIALS

Carl M. Lampert
Materials and Molecular Research Division

and

Energy Efficient Buildings Program
Lawrence Berkeley Laboratory
University of California
Berkeley CA 94720

MARCH 1983

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.
Innovative Solar Optical Materials

Carl M. Lampert

Materials and Molecular Research Division and Energy Efficient Buildings Program, Lawrence Berkeley Laboratory, University of California, One Cyclotron Road, Bldg. 62-235, Berkeley CA 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

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 four major ways in solar energy conversion: 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. Other work has extensively discussed the use of heat mirrors for architectural windows and solar collectors and for solar collectors. The relationships among the solar spectrum, blackbody spectra, and idealized selective surface are shown in Figure 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 $\text{SnO}_2:F$, $\text{In}_2\text{O}_3:Sn$, and $\text{Cd}_2\text{SnO}_4$. Their spectral properties are shown in Figure 2. Systems employing the latter might be based on $\text{TiO}_2$/metal, $\text{Al}_2\text{O}_3$/metal, or $\text{ZnS}$/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.

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. Eliminating post-annealing treatments, to increase conductivity, would reduce expense. Improvement in chemical dip coating processes, and 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 near-atmospheric 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 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.

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 Figure 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 $E_{ir} = 0.0$. 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 selected solar absorbers, black chrome, textured Mo-Al$_2$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 $e = 0.11$, and for thickness-insensitive paints the values $a_s = 0.90$ and $e = 0.30$ 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 sufficiently strong 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 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. Silicones, 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 aceto-phenon.

Graded-index films represent a range of coatings having uncommon refractive indices. Fluorosilicic acid can give a graded-index, antireflective coating to glass (see Figure 4). It roughens the surface by etching out small pores in nonsilica regions.24,25 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.26,27 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 optimum28 (see Figure 5).

Inorganic thin films have been used for many types of single and multiple interference coatings. Compounds such as MgF₂, CeO₂ CeF₂, SiO, 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 hydrolysed metal alkoxides can be polycondensed, forming oxides of Al, In, Si, Ti, Fr, Sn, Pb, Ta, Cr, Fe, Ni, Co, and some rare earths.29 A similar method, known as the sol-gel process, has formed mixed TiO₂-SiO₂ antireflective films on silicon and black chrome.30 Diamond-like (1 - carbon) transparent coatings have been used for antireflective films. They are formed from plasma decomposition of hydrocarbons and ion beam deposition.31 Coatings of about n = 1.9 are suited to photovoltaics.
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/MgF$_2$ and TiO$_2$/SiO$_2$ 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 microns; the remainder of the solar spectrum is unused. This extra portion can be separated for heat to warm the greenhouse. A baffle-type greenhouse utilizing both cold-mirror and reflective coatings is illustrated in Figure 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 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.

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 light guided in a plate to that 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, re-emitted energy can be absorbed by lower-energy fluorescent levels (see Figure 7). The advantages of using a fluorescent plate for concentration are that the concentration ratio is high (10-100), 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 that use fluorescent concentrators, efficiencies of 42-59% 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 micron. 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 $W_a = 500-900 \text{ nm}$, $W_e = 1060 \text{ nm}$. 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 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 8-13 microns wavelength. One could conceivably design an upward-facing surface that would emit over this wavelength range. The material used would need high reflectance for 0.3-50 microns, excluding the 8-13 microns region. In the 8-13 micron region the material would need 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 and Si₃N₄/Al (see Figure 8) and polymer-coated metals. Polymers such as polyvinylchloride (PVC); polyvinylfluoride (PVF, Tedlar); and poly-4-methylpentene (TPX) have been suggested. 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 emittances of the coatings need to be optimized to take full advantage of the 8-13 micron 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 which is reflective either totally or partly 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 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 \(\text{A}\) 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 \(\text{WO}_3\), \(\text{MoO}_3\), and \(\text{IrO}_x\) films. These compounds, among other transition metal oxides, are the subject of a timely review.\(^40\) Organic electrochromics are based on the liquid viologens, anthraquinones, diphthalocyanines, 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 so are not useful for window applications.

A solid-state window device can be fabricated; an example of one configuration is shown in Figure 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 Figure 8.\(^41\) 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.\(^1\)\(^2\)\(^3\)\(^4\) 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 stereoisomers, 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 Figure 8.

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 spiropyrans, anils, polyvinyl acetal resins, and hydrozides are examples of
thermochromism. Inorganic materials include HgI₂, AgI, Ag₂HgI₄, Cu₂HgI₄, SrTiO₃, Cd₂P₃Cl, 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. 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 absorptance 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. 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. ACKNOWLEDGEMENT

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


Figure 1. Spectrum of solar radiation (airmass 2) shown with four blackbody spectral distributions (−30°C, 40°C, 100°C, 300°C). Superimposed is the idealized selective reflectance of a spectrally sensitive surface (heat mirror or selective absorber).
Figure 2. Spectral normal transmittance and reflectance of heat-mirror coatings based on SnO$_2$:F, In$_2$O$_3$:Sn and Cd$_2$O$_4$, all on substrates. The properties of these films are: SnO$_2$:F ($T_s = 0.75$, $E_{IR} = 0.15$); In$_2$O$_3$:Sn ($T_v = 0.9$, $E_{IR} = 0.15$); Cd$_2$SnO$_4$ ($T_s = 0.86$, $E_{IR} = 0.12$).
Figure 3. Four examples of selective absorbers. The black chrome surface has $A_s = 0.95$, $E_{IR} = 0.07$ (1000°C). Textured Mo-Al$_2$O$_3$ cermet has $A_s = 0.992$, $E_{IR} = 0.2$ (500°C). The nickel-pigmented Al$_2$O$_3$ has $A_s = 0.93$, $E_{IR} = 0.10$.\textsuperscript{19}
Figure 4. Reflectances of various antireflection treatments for glass.
SPECTRAL TRANSMITTANCE FOR 3M POLYETHYLENE TEREPTHALATE FILMS

Hemispherical transmittance of antireflected 3M Sungain polyester film compared to uncoated substrate. 27
Figure 6. Spectral transmittance of OCLI greenhouse cold mirror.33
Figure 7. Fluorescent concentrator design showing hypothetical absorption and emission spectra.
Figure 8. Spectral reflectance of 1 micron SiO/Al and Si₃N₄/Al film for radiative cooling. Idealized properties are shown by short broken line.
Solid State Electrochromic Cell

Figure 9. Model of solid-state electrochromic cell.
Figure 10. Transmission characteristics of crystalline and amorphous WO₃ films colored by injection of 10⁶/cm² charge and Li⁺ ions.
Figure 11. Example of spectral transmittance for photochromic glass showing light and dark responses.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.