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ADVANCED OPTICAL MATERIALS FOR ENERGY EFFICIENCY AND SOLAR CONVERSION

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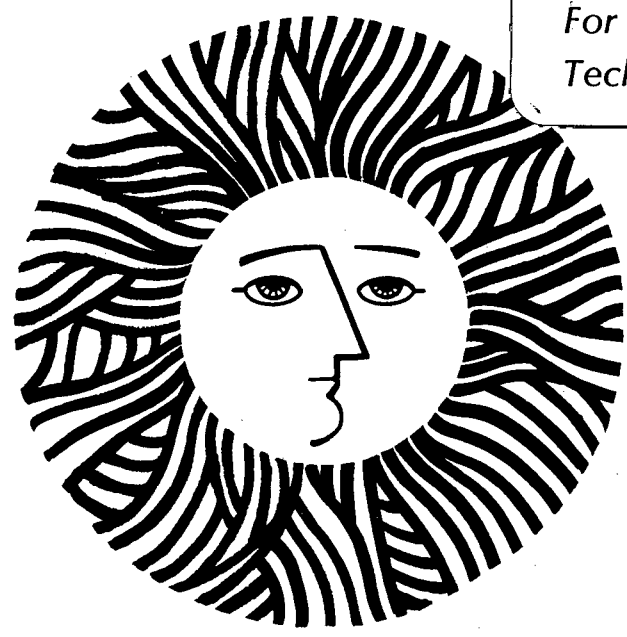
Presented at the Advanced Course on Solar Energy, International Institute for Advanced Studies, Caracas, Venezuela, June 21-July 2, 1982; and to appear as a chapter in Advanced Solar Materials, to be published by Plenum New York, 1982

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Carl M. Lampert

June 1982

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ADVANCED OPTICAL MATERIALS FOR ENERGY EFFICIENCY
AND SOLAR CONVERSION

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ABSTRACT

Materials science properties of optical materials and coatings are discussed for a broad range of solar conversion and energy efficient uses. Coatings for windows and solar collectors--known as heat mirrors, selective absorbers and antireflection films--are covered in detail. The use of Drude theory to model heat mirrors is also discussed. Both Maxwell-Garnett and Bruggeman effective medium theories are related to bound theory for composite films. Other coatings and materials discussed include reflectors, fluorescent concentrator materials, holographic films, transparent insulation, cold mirrors, radiative cooling surfaces and optical switching films for windows. Application and use of each coating in various passive, active and photovoltaic conversion designs are also covered.

ADVANCED OPTICAL MATERIALS FOR ENERGY EFFICIENCY
AND SOLAR CONVERSION

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INTRODUCTION

Optical materials and coatings play an important role in determining the efficiency of solar conversion processes. At present the best known coatings are heat mirrors, selective absorbers and reflector materials. There are, however, many less known coatings and materials, some of which are under current research and development. Since they are of significant consequence to solar conversion and energy conservation, they will be included in this work. These films and materials are known as antireflective coatings or treatments, fluorescent concentrator materials, holographic films, cold mirrors, radiative cooling surfaces, optical switching films and transparent insulation materials. The use of such films and materials improves the efficiency and stimulates innovation in passive and active solar energy conversion, photovoltaics, energy efficient windows and many hybrid designs. The present study is intended to instruct readers on the properties of solar energy materials, their function, as well as advantages and limitations. It is also intended to expand the horizons of solar invention by considering new materials, techniques and concepts that can manipulate solar energy into the forms of heat, light and electrical power. The material stability requirements for effectively collecting and transmitting solar energy are extremely demanding. This combined with the need for inexpensive production methods creates a very broad area for innovative scientific research. The solution to materials science and design problems are the responsibility of a number of scientists, engineers and educators working in many countries and in numerous fields. It is their strong commitment to solar energy that will further advance this energy source.

BASIC THEORY

The optical engineering properties that are of primary interest for most solar materials are transmittance, (T) reflectance, (R) absorptance (A) and emittance (E). These properties characterize how a particular coating or a material interacts with incident energy. Furthermore, these qualities can be related to intrinsic materials properties such as the index of refraction (n) and extinction coefficient (k). Also all these properties have a spatial, wavelength or temperature dependence. Formally, the spectral transmittance (T_w) is the ratio of incident radiation transmitted through a medium at wavelength (w), to that of the total incident radiation at w.

The spectral reflectance, (R_w) is the ratio of incident radiation reflected from the medium at w, to the total incident radiation at w. The spectral absorptance (A_w) is the ratio of incident radiation absorbed in the medium at w, to the total incident radiation at w. A relationship between these quantities allows for conservation of energy:

$$A_w + R_w + T_w = 1 .$$

The thermal emittance ($E(T)$) is defined as the ratio of emitted radiation from a surface at Temperature (T), to corresponding blackbody radiation at T. The spectral quantities of A_w, E_w are equivalent provided the measurements are taken at the same temperature and under the same conditions.

$$A_w(T) = E_w(T).$$

In practice these properties are best represented as integrated values. Total solar absorptance can be defined as :

$$A_s = \frac{\int_{0.3}^{2.5} A_w I_w dw}{\int_{0.3}^{2.5} I_w dw}, w \text{ in microns,}$$

where (I_w) is defined as the solar irradiance at (w) at some air mass. For a selective absorber $T_w = 0$ and A_w can be defined from reflectance measurements as:

$$A_w = 1 - R_w.$$

Similar integrations can be made for R_s , and T_s . The total thermal emittance, $E_T(T)$ can be defined as:

$$E_T(T) = \frac{\int_1^{100} E_w(T) B_w(T) dw}{\int_1^{100} E_w(T) dw}, \quad w \text{ in microns,}$$

where $B_w(T)$ is the radiation intensity (given by the Planck function) for a blackbody at temperature T , the same temperature of the object being measured. For heat mirrors and other transparent coatings the visible transmittance is important. Although much reported data is cited as visible transmittance, it is usually only averaged data and not integrated, T_v is defined as follows:

$$T_v = \frac{\int_{0.39}^{0.77} T_w P_w dw}{\int_{0.39}^{0.77} P_w dw}, \quad \text{where } w \text{ is in microns.}$$

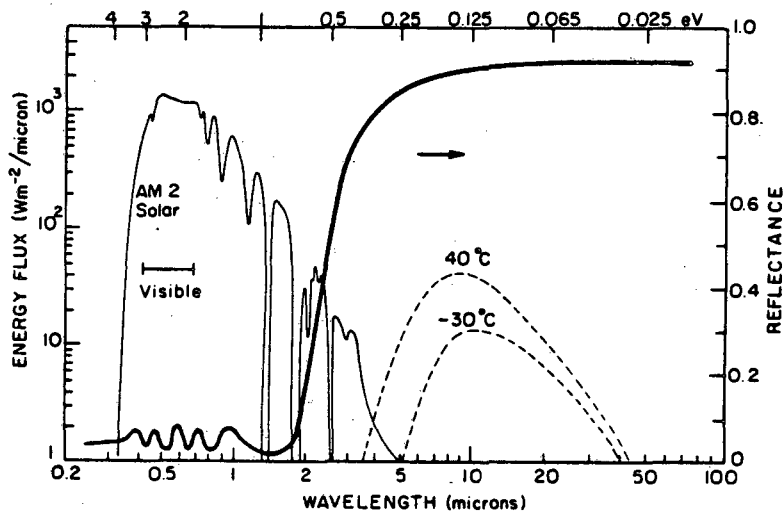
In this case the distribution function is the photopic or specular eye response distribution, (P_w). This distribution is Gaussian in nature and peaks in the green wavelengths (0.55 microns).

TRANSPARENT HEAT MIRRORS

Heat mirror coatings play a significant role in solar thermal conversion,¹ transparent insulation for architectural windows² and photovoltaic conversion³. In this work a heat mirror is defined as a coating which is predominately transparent over the visible wavelengths (0.3 - 0.77 microns) and reflective in the infrared (2.0 - 100 microns). Over the near infrared (0.77 - 2.0 microns) the coating may exhibit combined properties depending upon design or application requirements. Figure 1 shows an example of an idealized heat mirror response superimposed on solar and blackbody radiation spectra. Heat mirrors for windows derive their usefulness from their low emittance (or high reflectance in the infrared). The lower the emittance, the less the magnitude of radiative transfer by the window. The emittance of glass is $E_T = 0.84$; many plastics have high emittance values also. Two scenarios can be invoked to demonstrate the usefulness of single glazed heat mirrors

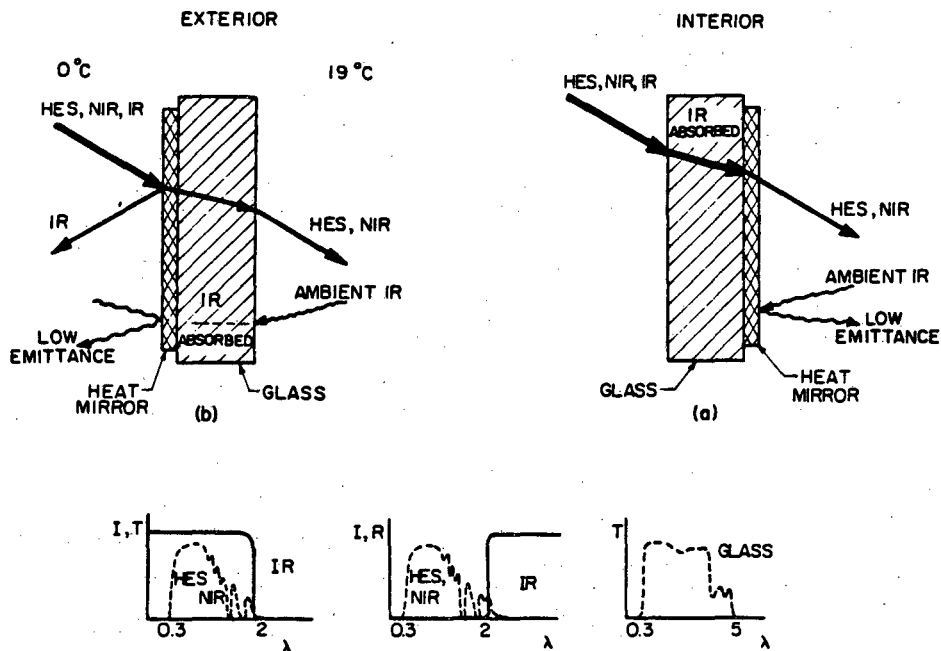
in buildings². The first scenario, depicted in Figure 2 represents winter heating where solar gain is important to reduce the heating load in a building. The optimum heat mirror for this function would transmit both solar visible and near infrared to about 2-3 microns, the cut-off wavelength for glass. The thermal infrared would be reflected back into the building. In this process the majority of the solar energy could be utilized for passive solar gain and daylighting.

A second scenario can be treated as a cooling load reducing heat mirror, where all infrared energy is reflected to reduce air conditioning loads. This type of heat mirror is depicted in Figure 3. The coating allows only transmission of visible energy through the window, with the remainder of the wavelengths reflected. A heat mirror alters only the radiative character of a window; the effects of convective and conductive heat losses must be taken into account, too. Window orientation, climate and building type are important factors in choosing the exact combination of optical properties the heat mirror is to have. A film with adjustable properties might be the best solution.



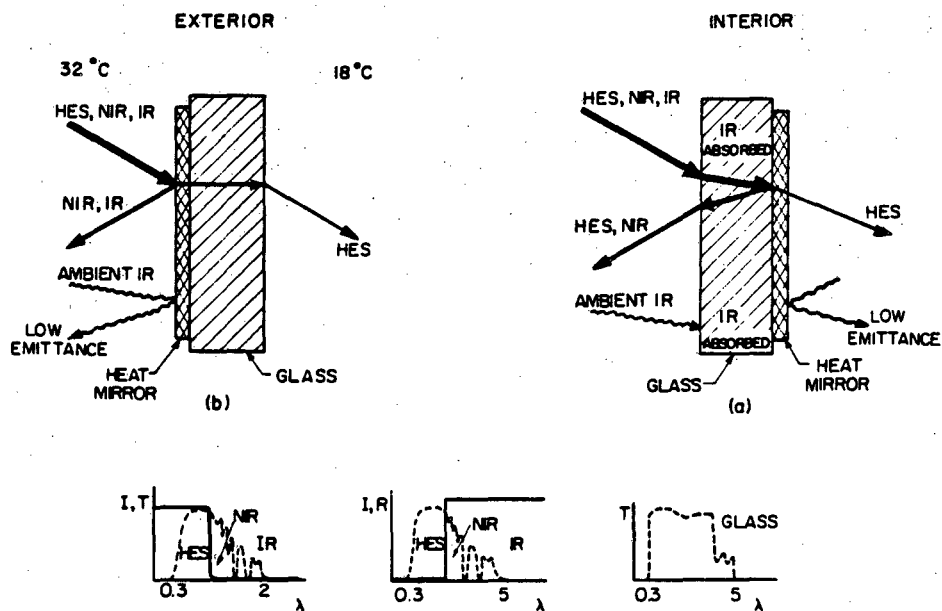
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Figure 1. Solar spectrum (air mass 2) with two blackbody spectra (40°C-30°C). Superimposed is the idealized reflectance of a SnO₂:F heat mirror coating.



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Figure 2. Schematic of heating-load heat mirror properties. Lower drawings depict optical properties of coating and substrate.



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Figure 3. Schematic of cooling-load heat mirror properties. The exterior placement is subject to convection losses which can lessen the benefit.

Examples of multiple glazed heat mirrors are shown in Figure 4. Here both a double and triple glazed window are shown. One design depicts a heat mirror coating on plastic. Deposition of heat mirrors on glass and plastic substrates are of significant importance. One fits well into conventional glass coating processes, the other is a refined extension of the metallizing process for plastics. By use of a computer model, thermal conductance (U) values have been derived for various types of glazings. This data is shown in Figure 5. A nonglass insulated wall has $0.3 \text{ W/m}^2\text{K}$ (R-19) to $U = 0.6 \text{ W/m}^2\text{K}$ (R-11).

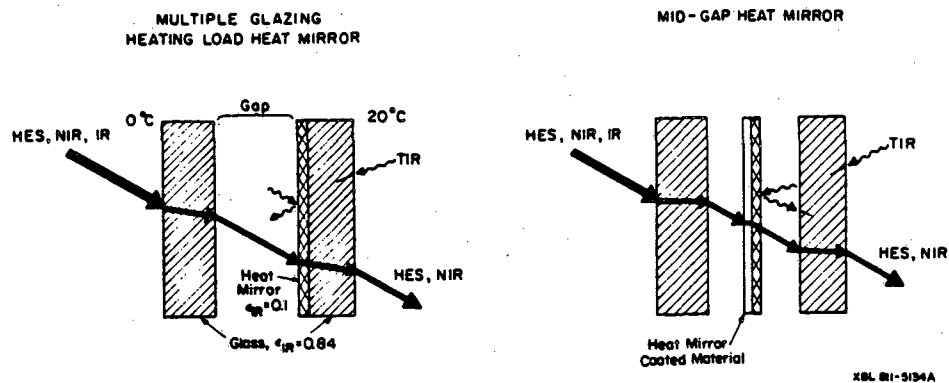
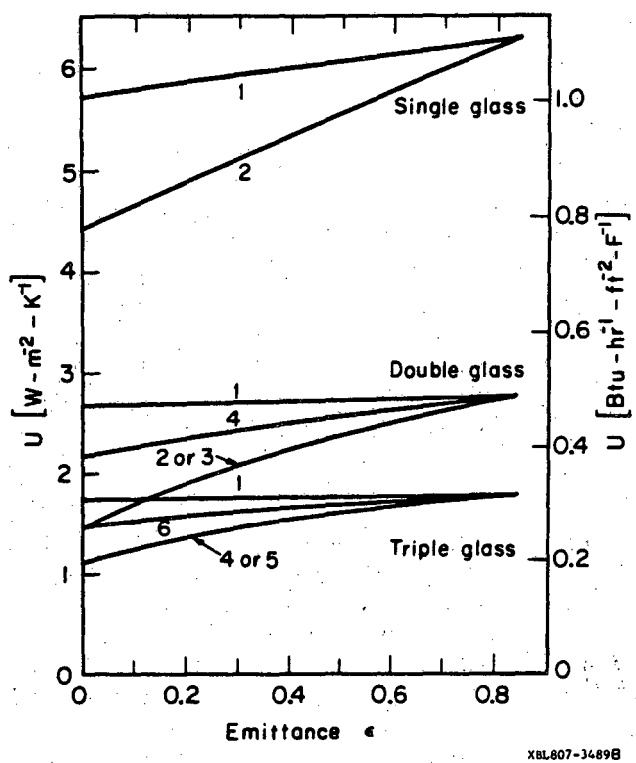


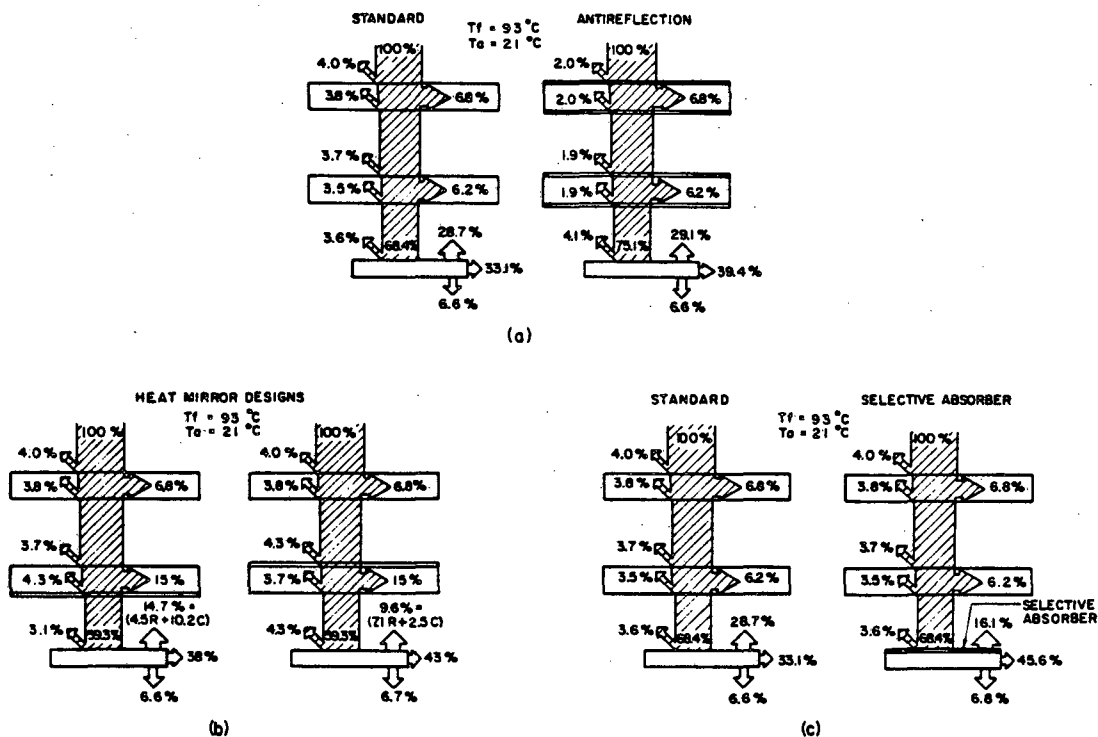
Figure 4. Double and triple glazed windows incorporating heat mirrors.



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Figure 5. Computer-modeled thermal conductance (U) for various window designs⁴ using ASHRAE Standard winter conditions ($T_{out} = -18^{\circ}C$, wind speed = 24 km/hr). The effect of lowering the emittance of a single surface by the addition of a heat mirror coating is shown. The surfaces on which the coating appears are given as consecutive numbers, starting from the outside surface, labeled 1. Airgap is 1.27 cm.

A heating load heat mirror could also be used for solar thermal collectors as an alternative to selective absorbers. But, in this case the heat mirror could be used with a nonselective absorber. One modification of this heat mirror is to shorten the transition or cut-off reflectance wavelength, which would be more suitable for higher operating temperatures of solar collectors. The result of using a heat mirror coating on a double glazed flat plate collector are shown in Figure 6. Also shown for comparison, is the effect of using a selective absorber and antireflective coatings.⁵ These coatings will be discussed in subse-



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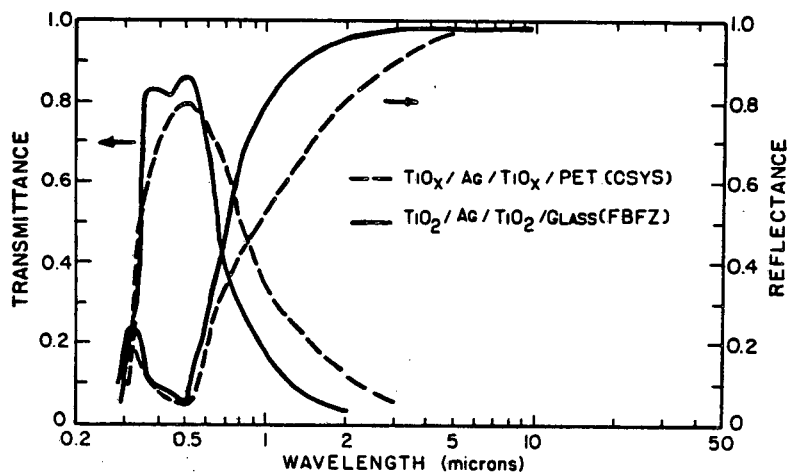
Figure 6. The effect of various coatings upon collector efficiency⁵ for a flat plate collector operating at 93°C under ambient of 21°C. The notation R stands for reflection losses, and C stands for convection losses.

quent sections. Transparent conductors as heat mirrors can be physically deposited (PVD) on glass and plastic by vacuum evaporative and sputtering techniques. Methods including chemical vapor deposition (CVD) and polycondensation of organometallics have been limited mostly to glass. The thermal and chemical stability of the substrate are significant in determination of the proper deposition technique and conditions. With CVD the secondary and competing reactions must be suppressed by control over reaction kinetics and knowledge of system thermodynamics. Also, thermal durability and property stability of substrate and film is significant for long life designs. Heat mirror films can be classified into two categories: multilayer dielectric/metal based films such as $\text{Al}_2\text{O}_3/\text{Ag}$, $\text{ZnS}/\text{Cu}/\text{ZnS}$ and $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ and single layer semiconductors (highly doped) such as $\text{In}_2\text{O}_3:\text{Sn}$ and $\text{SnO}_2:\text{F}$. There is considerable growing interest in both multilayer and semiconductor heat mirrors in Europe, North America, USSR, East Germany and Japan. Further information on heat mirrors is contained in a number of excellent works.^{2,3}

Multilayer Heat Mirror Films

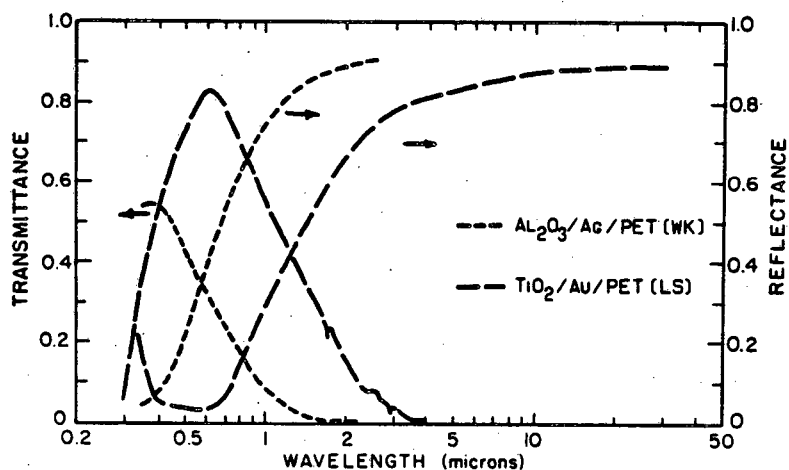
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Metal films less than approximately 100 Å thick exhibit partial visible and solar transparency. Dielectric overlayers serve to both protect and to partly antireflect the metal film in the visible region, thereby increasing transmission. Generally though, further protection is required of the metal/dielectric film as it is quite thin and vulnerable to corrosion and abrasion. The design of the appropriate dielectric type and thickness is detailed elsewhere.⁶ The dielectric film when used to overcoat a metal, must exhibit high infrared transmittance in order to preserve the infrared reflectance of the metal. Example systems² are SiO_2/M , polymer/M, $\text{Al}_2\text{O}_3/\text{M}$, $\text{Bi}_2\text{O}_3/\text{M}$, $\text{Bi}_2\text{O}_3/\text{M}/\text{Bi}_2\text{O}_3$, $\text{ZnO}/\text{M}/\text{ZnO}$, $\text{TiO}_2/\text{M}/\text{TiO}_2$ and $\text{ZnS}/\text{M}/\text{ZnS}$ where M is a metal of Ag, Al, Au, Cu, Cr, Ni and Ti. Additional designs include X/M and X/M/X where X is an appropriate semiconductor or polymer. Infrared transparent polymers of polyethylene, polyvinylidene chloride, polyacrylonitrile, polypropylene and polyvinyl fluoride might be used for this application. Multilayer films have an advantage over the doped semiconductors of broad wavelength tunability. Some selected multilayer films on glass and plastic substrates⁷⁻¹⁰ are shown in Figures 7 and 8. Detailed property data on these films is shown in Table 1. Extensive data on D/M/D coatings is covered elsewhere.² Durability improvement of multilayer films still remains an important research area for the material scientist. Three United States manufacturers of multilayer heat mirror coated windows have had their products reviewed recently.¹¹ The companies covered are Southwall of Palo Alto, CA, and Airco Temescal of Concord, CA in conjunction with Guardian Industries of Carleton, MI.



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Figure 7. $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ coating on polyethylene terephthalate⁷ (PET) and glass^{8,2},



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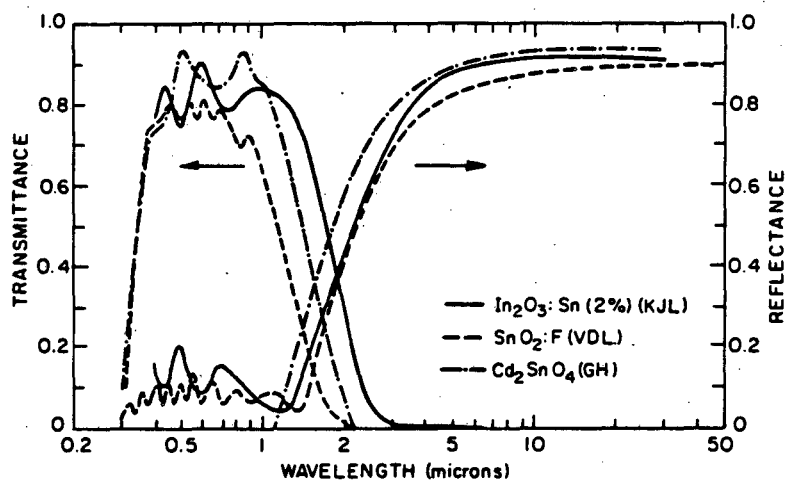
Figure 8. Dielectric/metal coatings on PET.^{9,10}

TABLE I
Multilayer Heat-Mirror Films

Material	$\text{Al}_2\text{O}_3/\text{Ag}$	$\text{TiO}_2/\text{Au}/\text{PET}$	$\text{TiO}_2/\text{Ag}/\text{TiO}_2$	$\text{TiO}_x/\text{Ag}/\text{TiO}_x$	$\text{ZnS}/\text{Ag}/\text{ZnS}$
Deposition tech.	Ion Beam Sputt.	e-Beam Evap. & Chemical Dep.	RF Sputter	Chemical Dep. & Vac Evap.	Vac. Evap.
Sheet Resist. (ohm/sq)	-	10	-	-	10
Thickness (angstroms)	-	-	180/180/180	270/150/270	520/100/770
T_{vis} (ave) or T_{s}	0.47, 5 μm	0.80	0.84	~0.75	0.68
R_{ir} or (E_{ir})	0.93, 2.5 μm	0.87	0.99, 10 μm	0.98, 5 μm	(0.06)
Reference	9	10	8	7	23

Doped Semiconductor Films

Certain doped semiconductors can exhibit high infrared reflectance due to the proper combination of high mobility, ($>10 \text{ cm}^2/\text{V sec}$) carrier concentration (10^{20} - 10^{23}), effective mass and lattice relaxation frequency. Materials science details are outlined elsewhere¹². The best known transparent semiconductors are $\text{SnO}_2:\text{F}$, $\text{SnO}_2:\text{Sb}$, $\text{In}_2\text{O}_3:\text{Sn}$ and Cd_2SnO_4 . Characteristic spectral transmission and reflectance is shown detailed in Figure 9 for research grade films on glass.¹³⁻¹⁵ The transmission of these films can be increased by etching microgrids in the coatings.¹⁶ Obtaining a reproducible high quality commercial coating is considerably more difficult than making research grade films. Present techniques need to be improved to deposit these coatings on polymeric substrates.^{17,18} Specific examples of these films are shown in Figure 10. Table 2 lists the physical properties of selected doped semiconductor films. Detailed information on deposition process is enumerated elsewhere.^{2, 12} There are other promising heat mirror materials. They include some of the rare earth oxides, borides, transition metal nitrides, carbides and selected ternary systems. Although little knowledge has been obtained optically about these materials, they are known to exhibit Drude-like electrical conduction. Also, graded index and surface textured heat mirror coatings remain to be developed. They show promise of improved solar transmission characteristics.



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Figure 9. Spectral normal transmittance and reflectance of heat mirror research-grade film on glass based on $\text{In}_2\text{O}_3:\text{Sn}$, $\text{SnO}_2:\text{F}$ and Cd_2SnO_4 .¹³⁻¹⁵

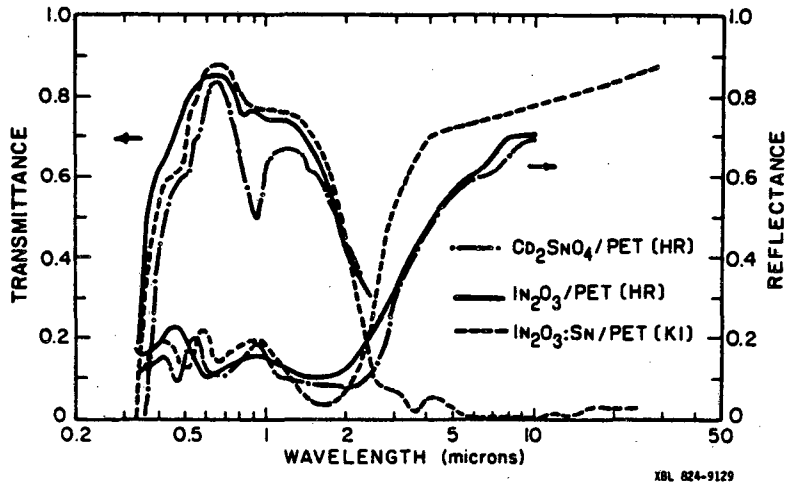


Figure 10. Spectral normal transmittance and reflectance of single-layer heat mirror coatings deposited on polyethylene terephthalate.

TABLE 2
Selected Heat-Mirror Films

Material	SnO ₂ :F	Cd ₂ SnO ₄	In ₂ O ₃ :Sn	In ₂ O ₃ :Sn
Deposition tech.	Spray Hydro. 500-570°C	RF Sputt. Anneal 420°C	Spray Hydro.	RF Sputt. etched microgrid
Sheet Resist. (ohm/sq)	4	26-43	15-20	3
Thickness (microns)	1.0	< 0.3	-	0.35
Mobility (cm ² /V-sec)	37	-	-	-
Carrier Density (cm ⁻³ x 10 ²⁰)	4.4	-	15	-
T _{vis} (ave) or (T _s)	(0.75)	(0.86)	-0.9	(0.90, AM2)
R _{ir} or (E _{ir})	(0.15)	(0.12, 77°C)	0.85	0.83, 10um
Reference	15	14	13	16

TABLE 2 (continued)

Material	Cd ₂ SnO ₄ /PET	In ₂ O ₃ /PET	In ₂ O ₃ :Sn/PET
Deposition tech.	REACT DC Sputt. & RF BIAS	REACT DC Sputt. & RF BIAS	REACT RF Sputt.
Sheet Resist. (ohm/sq)	24	30	<30
Thickness (microns)	0.28	0.34	0.5
Mobility (cm ² /V-sec)	30	29	-
Carrier Density (cm ⁻³ x 10 ²⁰)	3.4	2.1	-
T _{vis} (ave) or (T _s)	-0.65	-0.78	0.8
R _{ir} or (E _{ir})	0.7, 10um	0.7, 10um	0.8, 10um
Reference	17	17	18

Theory of Drude-Like Coatings

Both highly doped semiconductors and thin metal films are linked by the conductive metal-like properties described by classical Drude theory.²⁴ In this theory, a well defined plasma edge characterizes the material. It occurs due to excitation of free carriers by incident electromagnetic radiation. Since the charge carriers are actually moving in a potential field of the crystal, an effective mass (m^*) must be used. The effective mass is defined as:

$$m^* = m_r m_e ,$$

where m_e is the rest mass and m_r is the relative mass of the charge carriers in the field. The complex dielectric constant is related to the optical constants by:

$$\epsilon = \epsilon_1 - \epsilon_2 = (n - ik)^2 ;$$

$$\text{where } \epsilon_1 = n^2 - k^2 \text{ and } \epsilon_2 = 2nk.$$

For a Drude-like reflector, the dielectric constant can be expressed in terms of (V/V_p) and (Y/V_p) as follows:

$$\epsilon_1 = \epsilon_b \left[1 - \frac{1 + \left(\frac{Y}{V_p}\right)^2}{\left(\frac{V}{V_p}\right)^2 + \left(\frac{Y}{V_p}\right)^2} \right],$$

$$\epsilon_2 = \epsilon_b \left[\frac{Y}{V_p} \left(1 + \left(\frac{Y}{V_p}\right)^2 \right) / \frac{V}{V_p} \left(\left(\frac{V}{V_p}\right)^2 + \left(\frac{Y}{V_p}\right)^2 \right) \right],$$

where ϵ_b is the dielectric constant associated with bound carriers (at very high frequency) and Y is the relaxation frequency, $Y = e/um_e$, u is the carrier mobility, and e is the electron charge. The damped plasma frequency (v_p) is derived as:

$$v_p = (Ne^2/e_b e_0 m^*)^{1/2} - Y^2,$$

where N is the carrier density and e_0 is the dielectric constant of air. From this theory, n and k can be extracted in terms of frequency (W). Reflectance in air (normal-specular) can be derived by:

$$R = \frac{((n-1)^2 + k^2)}{((n+1)^2 + k^2)}.$$

The theoretical reflectance for a highly doped transparent is shown in Figure 1. The Drude-modeled reflectance agrees well with that obtained

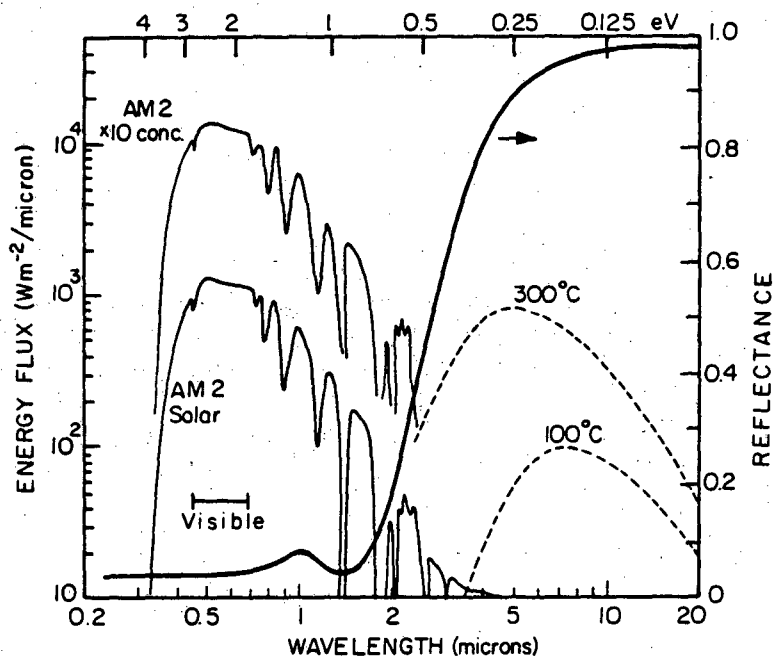
by experimental doped semiconductor films. One should note that in the Drude equation as $V \gg v_p > Y$, n becomes constant and $k \rightarrow 0$, indicating that the material is transparent at short wavelengths and for $V \ll Y < v_p$, $n = k$ are about equal and large in magnitude, indicating a high reflectance.

SOLAR SELECTIVE ABSORBERS

Absorbers for collectors have been one of the most active materials science research fields over the last several years. There are two categories of absorbers, selective and nonselective. The selective absorber has optical properties which vary greatly from one spectral region to another. The selective absorber or selective surface efficiently captures solar energy in the high intensity visible and the near-infrared spectral regions while exhibiting poor infrared radiating properties. This characteristic is depicted in Figure 11. In contrast a nonselective absorber, such as ordinary black paint has a flat spectral response and loses much of its absorbed energy by reradiation. The optimum characteristics of a solar absorber are high solar absorptance and a minimum emittance (or maximum reflectance) in the infrared wavelengths. The exact transition wavelength is determined by application, solar concentration and operating temperatures. Examples of concentrating collector designs are shown in Figure 12. Solar selectivity can be obtained by a variety of methods. These techniques consist of intrinsic solar selective materials, optical trapping surfaces, semiconductor/reflector tandems, composite coatings, multilayer thin films and quantum size effects. Significant reviews have been written about solar absorbers, giving insight and detail beyond the scope of this work.^{1, 25-29} A selected group of solar selective absorbers are outlined in Table 2 after Herzenberg and Silberglitt.²⁶

Intrinsic Absorbers

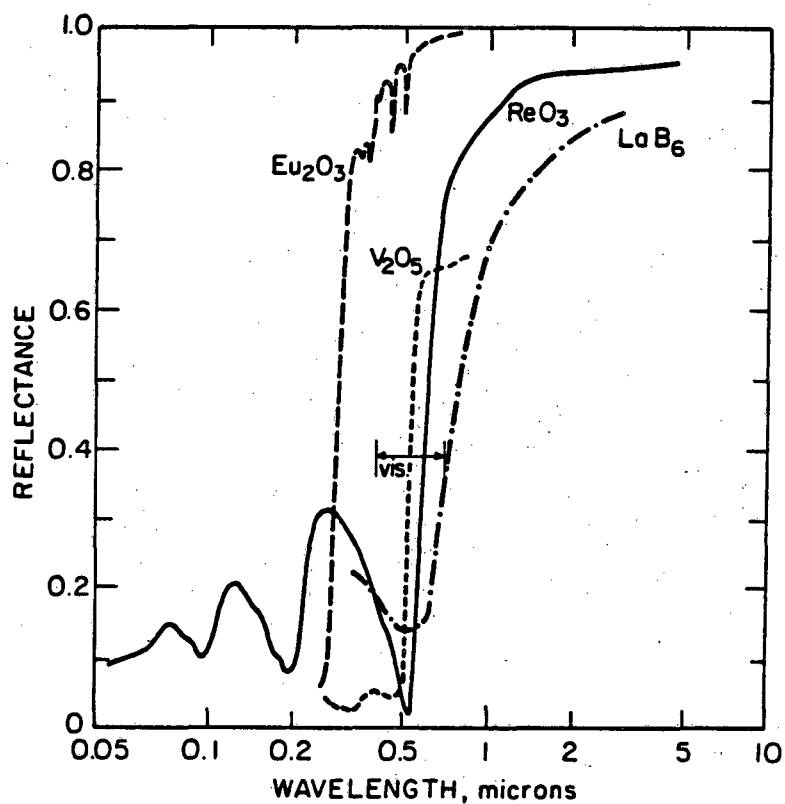
No known natural compound or material exhibits ideal solar selectivity. However, there are some materials which show wavelength selectivity to some degree. Possibly, synthetic materials could be fabricated once enough knowledge is obtained to design and predict fairly complex electronic structures and their relationships to the necessary optical properties. Both transition metals and heavily doped semiconductors exhibit at least one desirable absorber characteristic. Unfortunately, metals exhibit a plasma edge too early in the solar spectrum to be good absorbers. Semiconductors tend to be good absorbers but exhibit transmission in the infrared. These differences have resulted in the



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Figure 11. Wavelength relationship between a characteristic black chrome solar selective surface in terms of reflectance, to that of solar energy and blackbody spectra.

use of tandem absorbers. Materials such as (Cu_2S , HfC , ZrB_2 , Mo:MoO_3 , Eu_2O_3 , V_2O_5 , ReO_3 , LaB_6 (as shown in Figure 13) have reasonably intrinsic selective reflectance. Here, too, the dominant transition takes place too early in the solar spectrum for a good absorber. Also, the absorptance and transmittance properties are not well characterized. Lanthanum hexaboride may be a good heat mirror, since it has fair visible transmittance.

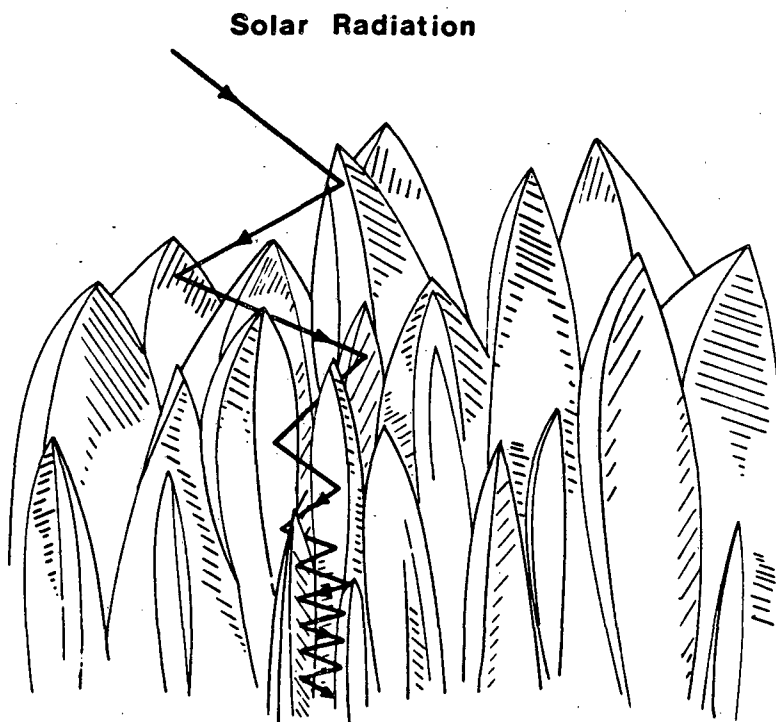


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Figure 13. Spectral reflectance of various oxides showing intrinsic wavelength sensitivity.¹²

Optical Trapping Surfaces

It is possible to roughen surfaces so they will enhance absorption geometrically in one wavelength region but appear smooth in another. This technique is possible since the high energy solar spectrum is distributed far enough in wavelength away from the thermal infrared spectra. Materials can be grown as dendrites, rough crystallites or surface roughened to form optical trapping surfaces as in Figure 14. These dendritic materials do not require a high intrinsic absorption as they rely upon multiple reflection and partial absorption to give a large effective absorption. Materials such as NiAl_x , W, Mo, Ni, Cu, Fe, Co, Mn, Sb and stainless steel have been grown as dendrites or textured by sputter etching.^{1,31,58} Texturing of surfaces is also an excellent method to antireflect other types of absorbers. This has been done with great success with the $\text{Mo-Al}_2\text{O}_3$ composite absorber.⁵⁴

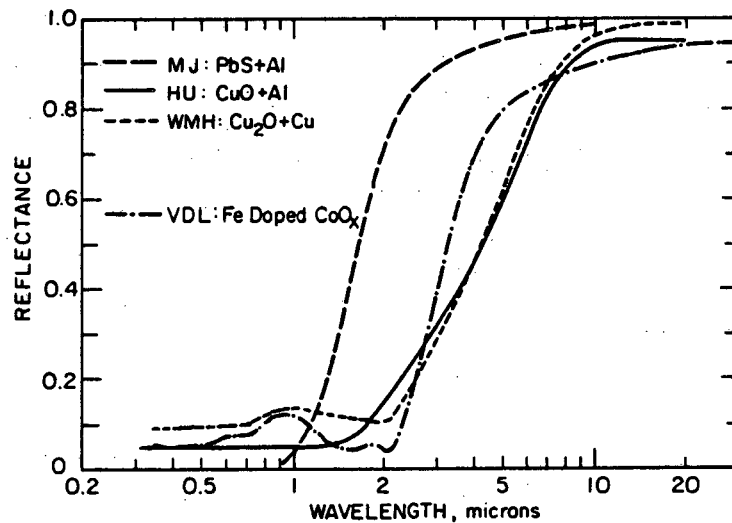


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Figure 14. Dendritic selective surface.

Semiconductor/Metal Tandems

Semiconductor coated metals provide complementary functions as a spectrally selective surface. The semiconductor provides high absorptance in the high energy solar region and becomes transparent beyond its absorption edge in the infrared. In the infrared the underlying metal layer gives the tandem or metallic reflectance as low emittance. A simple tandem is an oxidized metal. Usually the natural thickness of oxide is not optimum or is not stable in operation. Many chemical conversion processes are used to oxidize metals.¹ Metals like stainless steel, copper and titanium have been oxidized. Other tandems can be made with deposits of oxides on a variety of metals. Examples are shown in Figure 15. High temperature absorbers can also be designed such as the Si/Ag absorber stable to 500°C.²⁷ Tandem absorbers can be made by simple chemical conversion, electrochemical, chemical vapor deposition (CVD) and physical vapor deposition processes (PVD) (sputtering and evaporation). Composite coatings can also be used as the absorber portion of tandem absorbers.



X BL 792-57888

Figure 15. Reflectance of various tandem absorbers PbS/Al⁵⁹, CuO/Al⁶¹, Cu₂O/Cu⁶⁰, CoO_x:Fe/Ni.¹⁵

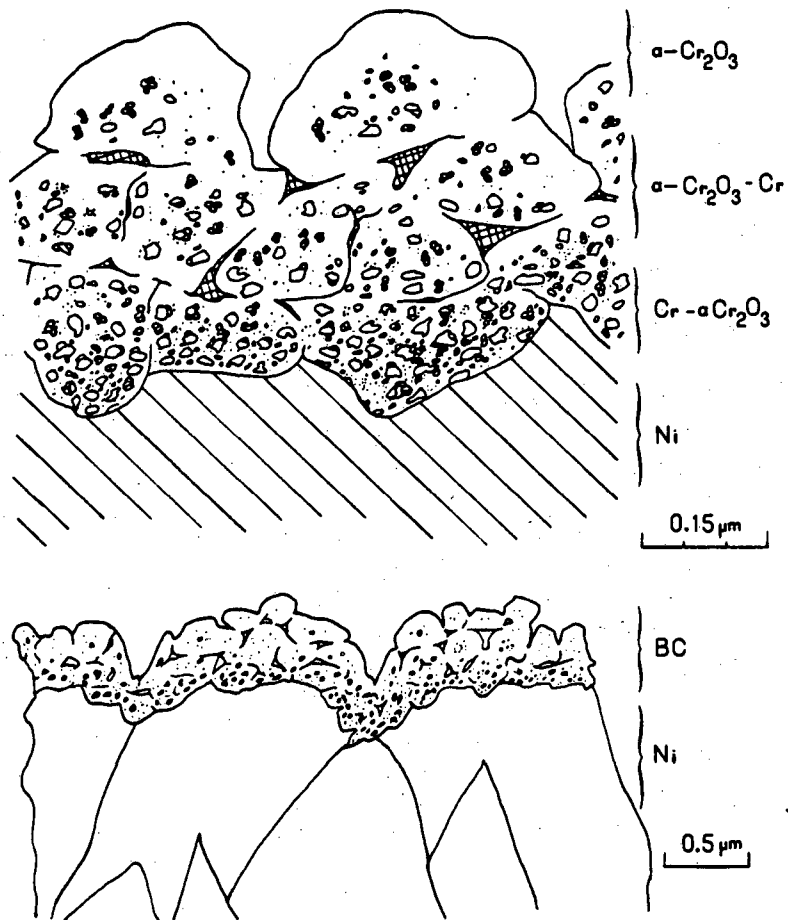
Metal-Dielectric Composite and Graded Coatings

Composite coatings consists of two or more components graded and interdispersed in a film. These components are usually phase separated. Reflective scattering can take place purely by the geometry of imbedded surface particles. Resonant scattering is dependent upon particle size, shape and the effective index of refraction with respect to the surrounding media. Both Mie and Maxwell-Garnett theory describe the role of sub-wavelength particles as resonant scatters.⁶² An example of a complex composite material is the well known black chrome absorber depicted in Figure 16. This coating consists of a predominately oxide region which grades to an Cr_2O_3 -Cr region which is responsible for solar absorption. Infrared properties are derived from a deeper metallic chromium region coupled with a metallic substrate.⁶³⁻⁶⁶ Further research on black chrome has been reviewed elsewhere²⁶. Other types of composites range from Ni- Al_2O_3 , Zn-ZnO, Cr- Cr_2O_3 , Pt- Al_2O_3 , Mo- Al_2O_3 and metal carbides. Many of their properties are detailed in Table 3. Composite coatings black chrome, NiCrO_x , Cr- CrO_x have been deposited on thin metal films for stick-on applications.^{39, 55, 57} The spectral characteristics of black chrome and Cr- Cr_2O_3 cermet coatings are shown in Figure 17.

Electrodeposited black nickel has a very interesting structure. By changing plating parameters during deposition, layers of ZnS and NiS can be formed on top of a metallic substrate. This absorber shows a combination of tandem and multilayer interference effect. The reflectance for the two varieties is shown in Figure 18. Multilayer effects will be discussed in a subsequent section. It is important to note that in a number of cases combined effects in a single absorber may make a superior design, although a more complicated one.

Of theoretical interest regarding tandem absorbers is the theory of Quantum Size Effects (QSE).⁷⁹ QSE occurs in thin film for metals, perhaps less than 10-20 Å for metals and 500 Å for degenerate semiconductors. QSE relates the influence of the geometrical dimensions of the sample to that of distribution of electron states. This distribution can be optimized by size effects to interact strongly with incident electromagnetic radiation. A combination of a QSE material and a reflector metal layer can result in a tandem absorber. QSE has been experimentally verified for InSb/Al, InSb/Ag⁷⁹.

Two effective medium theories that can be used to describe composite solar absorbers are Maxwell-Garnett Theory^{69, 70} and Bruggeman Theory⁷¹.



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Figure 16. Schematic cross-section of black chrome.⁶⁴ Three distinct regions are shown in the as-plated structure:

1. Top layer of amorphous or fine crystalline Cr_2O_3 .
2. Intermediate area of metallic Cr in Cr_2O_3 .
3. Bottom layers, consisting principally of Cr and Ni substrate.

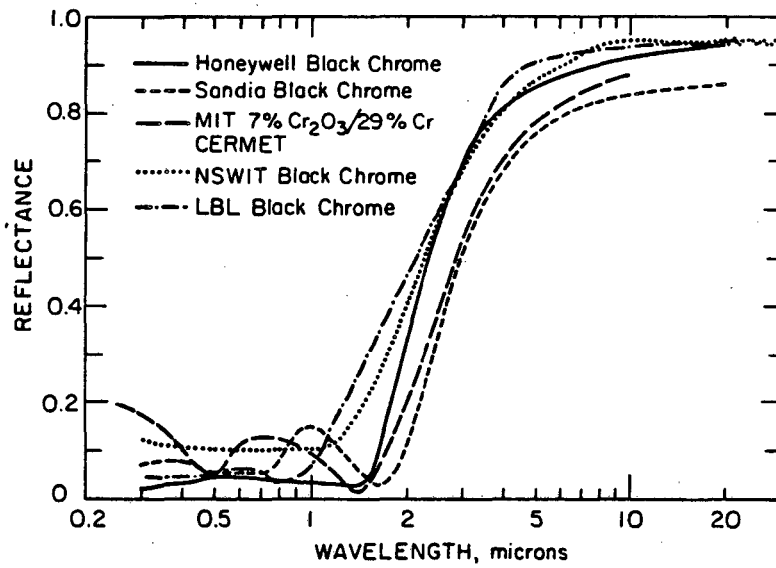
TABLE 3: PROPERTIES OF SELECTIVE ABSORBERS²⁶

Absorber ¹	Type	Deposition Technique	Maturity ²	A_s	E(°C)	Stability ³ °C	Estimated Commercial Cost (US\$/ft ²) ⁴	Ref.
Copper	Textured	Sputter etch	1	.9-.95	.08-.11	300(air)		31
SS	Textured	Sputter etch	1	.9-.96	.22-.26	350(air)		31
Ni	Textured	Sputter etch	1	.9-.95	.08-.11 (27)	250(air)		31
ZrB ₂ /Si ₃ N ₄	Intrinsic	CVD	1	.93	.08-.09 (102)	500(air)		30
Cr-Cr ₂ O ₃ (black chrome)	Graded Composite	Electroplating	5	.92-.97	.04-.06 (100)	400(air)	coating:0.85 foil:1.50	32-34
Cr-Mo-Cr ₂ O ₃	Graded Composite	Co-electroplating	1	.96-.97		400(air)	> black chrome	35
Ni-Al ₂ O ₃ / Al ₂ O ₃	Graded Composite	Anodic Oxidation	5	.92-.97	.1-.26 (65)	300(air)		36
Zn-ZnO	Graded Composite	Anodic Oxidation	1	.98	.18(100)	<300(air)		37
Cu ₂ O-CuO-Cu	Composite/Tandem	Anodic Oxidation	1	.95	.34(100)	130(air)	.25	38
NiO-Ni-Cr/ NiCrO _x	Graded Composite	Chemical Conversion	5	.97-.99	.07-.1 (100)	250(air)	foil:.80	39, 57
SS-C	Graded Composite	Reactive Magnetron Sputtering	3	.94	.03-.1 (100)	300(vacuum) 200(air)	.5	40
SS-C (on rough sputtered copper)	Textured Composite	Reactive Mag.Sput.	3	.9	.04(67)	450 (vacuum)	.5	41
SS-SSO _x /SSO _x	Anti-Refl. Composite	Reactive Mag. Sput.	1	.89-.93	.08(20)	150(air)		42
Cr-Al ₂ O ₃	Graded Composite	Dual Source Mag. Sput.	1	.92	.09(20)			42
Mo-MoO ₂ / Si ₃ N ₄	Composite/ Intrinsic	CVD	1	.91	.11(500)	500(vacuum) 300 (air)		43
Tellurium	Textured Tandem	Angled Vapor Deposition	1	.92	.03			47
a-Si/Si ₃ N ₄	AR Tandem	CVD	1	.75	.08(500)	500(air)		48

TABLE 3: PROPERTIES OF SELECTIVE ABSORBERS²⁶

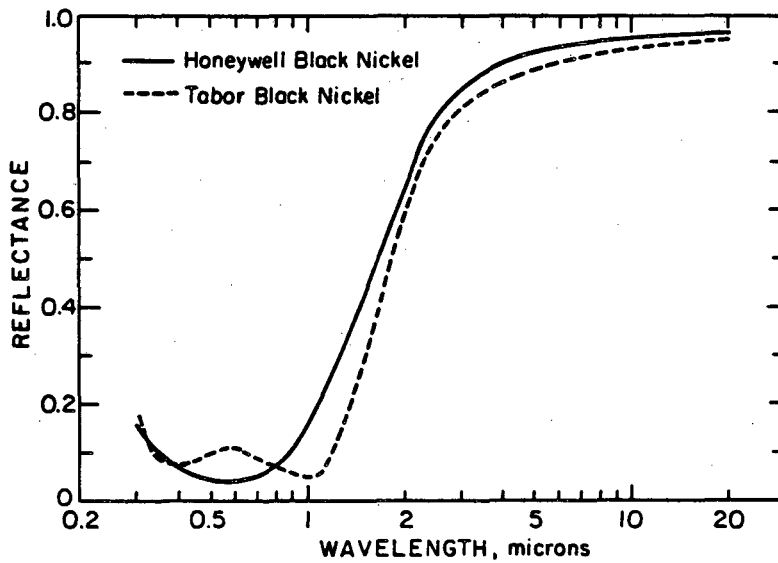
Absorber ¹	Type	Deposition Technique	Maturity ²	α_s	E(°C)	Stability ³ °C	Estimated Commercial Cost (US\$/ft ²) ⁴	Ref.
Cu ₂ S	Tandem	Chemical Spray Dep'n	1	.89	.25(100)	130 (air)	.25	49
CoO	Textured Grd'd Tand.	Electropl'd Co: Heat Oxd'n	1	.98	.2(100)	425(air)		50
CoO-FeO ₃ -Co ₃ O ₄	Textured Tandem	Electropl'd Co: Heat Oxd'n	1	.9	.07(100)	300(air)		51
Ge-CaF ₂	Semicond. ins Dielec.	Sputtering	1	.65-.72	.01-.1 (100)			52
Ge	Textured Tandem	Rf Sputt. H ₂ O ₂ etching	1	.98-.99	.58			53
AMA (M-Cr)	3-layer	Re-Mag-Sput.	3	.95	.12(20)	300(air)	.2-.5	45
AMA (M-Ni)	3-layer	Re-Mag-Sput.	3	.91	.08(20)	350(air)	.2-.5	45
AMA (M-Ta)	3-layer	Re-Mag-Sput.	3	.89	.12(20)	300(air)	.2-.5	45
Proprietary	3-layer	Elect.B. Evap.	3	.92-.96	.05-.08	250(air)	foil: .7-.8	26
Al ₂ O ₃ /Pt-Al ₂ O ₃ /Al ₂ O ₃	3-layer Composite	Rf Mag. Sput.	3	.91-.93	.08-.1 (20)	>600(air)	1 (on Cr)	45
Al ₂ O ₃ /Mo-Al ₂ O ₃ /Mo	Composite	Co evap.	1	.99	0.2(500) 0.08(200)	750(vac)		54
ZrC _x /ZrCr-CrO _x	Tandem Composite on Al foil	RF Sputt. react. evap.	3	.93	0.25	625 (vac)		55
			3	.9	0.05	175		55
Ni-C	Composite	Sputtering	1	.8	0.028-0.035 (150)			56
NiN _x	Tandem	Sputtering	1	.84	0.039 (150)			56

Notes: ¹ Absorber layers are separated by a/. Constituents of composite layers are separated by a -.
² Maturity of absorber coatings: 5 commercial, 3 development, 1 research
^{3,4} Temperature stability and commercial cost for most absorbers are not well known.
 Costs are in US \$ (1981).



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Figure 17. Reflectance for different types of selective black chrome absorbers.^{1, 67, 68}



XBL 783-478

Figure 18. Spectral reflectance for black nickel.^{77,78}

Maxwell-Garnett Theory

The Maxwell-Garnett Theory (MG) is employed to help elucidate the absorption properties of extremely fine particles in a solid matrix. The MG theory was developed from Mie Scattering Theory, which describes the scattering properties of spherical particles larger than those which could be handled by Rayleigh theory. The original MG theory treated isolated spherical metal particles in a dielectric matrix. Also, it was assumed that the particles exhibited identical properties to the bulk metal, which is oversimplified. The MG theory was further developed to take a random distribution of particles characterized by a metal filling factor (f) and simple particle shapes.^{62,72} The diameter (d) of the particles is small compared to the film dimensions and wavelengths (λ), so $d < 0.1\lambda$.

Historically, the MG theory has been used to describe the color obtained from colloidal suspension of metal in glass, and currently used to predict the properties of uniform ultrafine particulate solar absorbers.⁷²

In general, a homogenous isotropic material is optically characterized when the refractive index and the extinction coefficient are known as a function of all wavelengths of interest.

Consider a medium composed of metal spheres suspended in a vacuum. There are N spheres per unit volume. Each sphere behaves like an electric dipole with dipole moment \bar{P} in an applied external field \bar{E} . The external field is the sum of the field due to the incident light or energy \bar{E}_1 plus contributions from other dipoles, as expressed in the following relationship:

$$\bar{E} = \bar{E}_1 + \frac{4}{3} \bar{P} .$$

Where \bar{P} due to N individual dipole moments per unit volume is given as:

$$\bar{P} = Np = Na^3 \left[\frac{(e - 1)}{(e + 2)} \right]$$

The complex dielectric constant is given as ϵ and is defined as:

$$\epsilon = (n - ink)^2 = \epsilon_1 + i\epsilon_2 .$$

The wavelengths of interest for solar energy applications are orders of magnitude larger than the particle sizes, showing that the optical properties should be discussed in terms of a spatially averaged dielectric

constant:

$$\bar{e} = \bar{e}_1 + i\bar{e}_2$$

To use the Maxwell Garnett theory, the fill factors of metal to matrix ratio must be ≤ 0.2 . Otherwise, corrections have to be made for retardation effects. The Maxwell-Garnett theory gives:

$$\bar{e} = e_d \frac{1 + \frac{2}{3} fa}{1 - \frac{1}{3} fa},$$

where (a) is the polarizability factor; for metal spheres particles in dielectric:

$$a = \frac{(e_m - e_d)}{e_d + Q(e_m - e_d)}, \quad Q = \frac{1}{3},$$

e_m = the complex dielectric constant for the metal;

e_d = the dielectric constant for the oxide.

Q = the total depolarization factor

Also \bar{e} can be expressed as:

$$\bar{e} = \frac{e_d [2e_d(1-f) + e_m(2f+1)]}{e_d(f+2) + e_m(1-f)},$$

The above equation can be expressed in its symmetric form:

$$\left[\frac{\bar{e} - e_d}{\bar{e} + 2e_d} \right] = f \left[\frac{e_m - e_d}{e_m - 2e_d} \right]$$

Bruggeman Effective Medium Theory

In the Bruggeman Theory (BR) an inhomogeneous two phase material is treated as a system of spherical particles. These particles are comprised separately of pure phase A and pure phase B. The theory solves for the local electric field around a typical two phase element, embedded in an effective medium. In the BR Theory first-order scattering shall vanish on the average; that is, all field fluctuations will average to zero. In this fashion, a self consistent local field is equivalent to the choice of an active medium such that the average single site scattering is zero. Considering a metal-oxide system, the

effective medium permeability results as:

$$\bar{e} = e_{\text{ox}} \frac{(1 - f + \frac{1}{3}fa)}{(1 - f - \frac{2}{3}fa)} ;$$

where (a) for spheres is:

$$a = \frac{(e_m - \bar{e})}{e + \frac{1}{3}(e_m - \bar{e})},$$

and e_{ox} = dielectric permeability of oxide;
 e_m = dielectric permeability of metal
 \bar{e} = effective dielectric permeability
 f = chromium fill factor.

Also, the above expression can be seen in its symmetric form:

$$f \left[\frac{e_m - \bar{e}}{e_m + 2\bar{e}} \right] = (f - 1) \left[\frac{e_{\text{ox}} - \bar{e}}{e_{\text{ox}} + 2\bar{e}} \right]$$

Effective Medium Bound Theory

A range of effective medium theories including various microstructured shape effects in cermet systems can be bounded by mathematical theory. An effective dielectric function within bounds can be calculated with only knowledge of separate dielectric functions for phase A and B volume fractions. This can be done regardless of their geometrical configuration. ⁷⁴⁻⁷⁶ The bounds can be developed using the function $F(s)$ which is defined as ⁷⁵:

$$F(s) = (e_d - \bar{e})/e_d \text{ and,}$$

$$s = e_d / (e_d - e_m) .$$

The bounds can be derived using the parametric representation, as: ⁷⁴⁻⁷⁵

$$F_e(s) = \frac{f(s - s_0)}{[s - s_0(s - \frac{1}{3}(1-f))]} \text{ for } \frac{2}{3} < s_0 < 1$$

and

and

$$F_f(s) = \frac{f(s - s_0)}{(s - s_0)(s - \frac{1}{3}(1-f)) - \frac{2}{3}(1-f)(1-s_0)} \quad \text{for } \frac{2}{3} < s_0 < 1$$

Both $F_e(s)$ and $F_f(s)$ represent arcs which intersect on the complex F plane. The area bounded represents allowed values of \bar{e} . Their intersection points are exactly the MG theory result. If percolation is considered for the metal (or phase A) then $F_f(s)$ becomes:⁷⁶

$$F_{fa}(s) = \frac{1}{s} \frac{f(s - s_0)(s - \frac{2}{3}) - fs_0(1 - s_0) / 3(1 - 2s_0)}{(s - s_0)(s - 1 + f/3) - fs_0(1 - s_0) / 3(1 - 2s_0)}$$

$$\text{for } 0 < s_0 < \frac{1}{3} ,$$

If the dielectric (or phase B) percolates, then $F_f(s)$ becomes:

$$F_{fb}(s) = \frac{f(s - s_0)}{(s - s_0)(s - \frac{1}{3} - (1-f)s_0(1 - s_0) / 3(2s_0 - 1))}$$

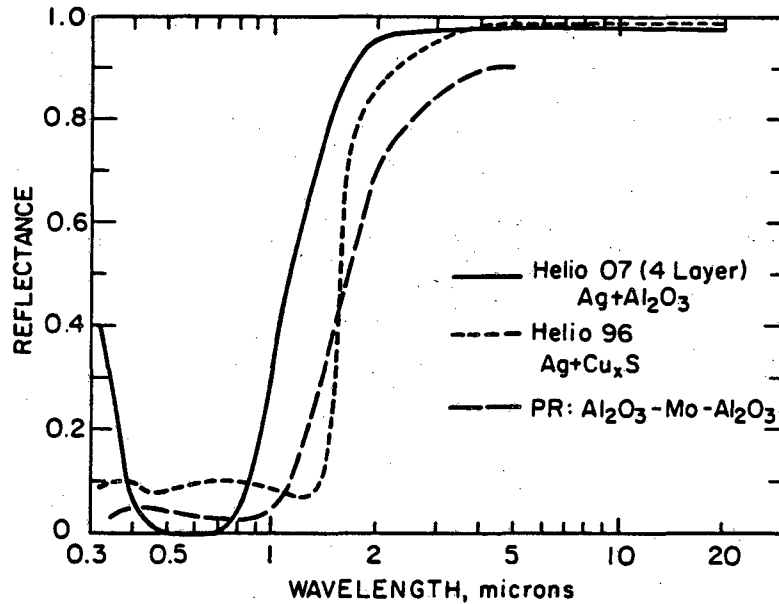
$$\text{for } \frac{2}{3} < s_0 < 1 .$$

Graphical representations showing the relationship between these bounds and various effective medium theories are detailed elsewhere.⁷⁶

Multilayer Absorbers

Multilayer thin films can make excellent solar absorbers. Dielectric/metal/dielectric combinations known as interference stacks behave like selective filters for energy absorption. The desired effect of an interference stack is to capture energy between metal-dielectric alternations. Specific solar wavelengths are absorbed by multiple reflection in the layers. Other wavelengths not of the absorption, or tuning frequency of the multilayer films are reflected. For solar energy absorption a broad band filter is required. Thin films are generally produced by CVD or PVD processes. Example film responses are shown in Figure 19. The disadvantage with most multilayer coatings is that they are fairly expensive to fabricate compared to a single layer process. These coatings can also suffer from interdiffusion and corrosion at elevated temperatures and humidity. In spite of all this, stable multilayer coatings do exist like that of the $\text{Al}_2\text{O}_3/\text{M}/\text{Al}_2\text{O}_3$ design.⁷³ The metal layer in these coatings is typically 50-100Å thick to appear semi-transparent to incoming radiation. The dielectric layers

need not be intrinsically absorbing to solar radiation since this three layer structure behaves as a resonant cavity tuned to a band of solar wavelengths. A novel multilayer coating has been devised by D.C. anodization of aluminum.³⁶ The coating is made by phosphoric acid anodization followed by an A.C. electrolysis of a nickel pigmenting bath. The structure of this coating consists of porous Al_2O_3 with the lower portion of the pores filled with bundles of needle shaped nickel particles. A thin Al_2O_3 barrier layer protects the aluminum substrate.



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Figure 19. Reflectance for example multilayer absorbers of the dielectric/metal type. Also included is the $\text{Al}_2\text{O}_3\text{-Mo-Al}_2\text{O}_3$ high temperature absorber.⁷³

Absorber Paints

If a thermally resistant, property stable paint could be developed which offered the solar selectivity of the black chrome for a low cost, the solar coating industry would be revolutionized. Up to this time a highly selective paint does not exist. There are a few who exhibit partial solar selectivity and are commercially available. Others, however are still in the research stage. A listing of a number of nonselective paints is given elsewhere. Three approaches can be taken in designing a selective paint. One makes the paint coating very thin so the low infrared emittance of the metal substrate dominates the infrared. Notice that a metal substrate is specified. For passive applications such as Trombe walls the substrate would probably be concrete or brick and this type of paint would not be selective. The major problem with thickness sensitive paints is their binder material. This is usually a polymer, which exhibits dominant infrared absorption bands. This absorption increases the infrared emittances of the paint. To remedy this either a special polymer must be devised or an inorganic system be used. Another approach to the paint is to use a coated metal flake in the composition. In this way the selective effect is created as a distributed tandem, with each particle serving as an individual tandem absorber; recent research has documented this effect⁴⁴. A third approach is to use an intrinsic absorber materials such as ZrB_2 and disperse it in a low absorbing binder. The final concept relies upon both development of the intrinsic absorber and binder. A few selected properties of selective absorber paints are detailed in Table 4.

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. To model radiative cooling one must first consider a surface radiating towards the sky. A simplified radiation balance can be used to determine idealized radiative cooling power in the absence of convective and conductive heat transfer effects.⁸¹ The radiative cooling power (P) is given by:

$$P = bE_s(T_s^4 - T_a^4) + E_{sc}(1 - E_{ac}) \int_8^{13} B_w(T_a) dw ,$$

TABLE 4 SELECTIVE ABSORBER PAINTS

All data taken from manufacturers product literature or research reports, accuracy or completeness has not been verified.

<u>Type</u>	<u>Highest Operating Temp. in Air.</u>	<u>$\frac{A_s(T)}{E_{ir}(T)}$</u>	<u>Ref.</u>
Soot/polyurethane alkyd	>70-100°C	0.90, 0.30 (100°C)	46
Thurmalox Silicone based	537°C	0.96, 0.52 (84°C)	Dampney Co. Everett, MA
Solkote-Hi/Sorb	880°C	0.95, 0.44	Solec Princeton, NJ
Fe, Mn, Cu oxides + silicone	200°C	0.9 , 0.31 (100°C)	44
Fe, Mn, Cu oxides and silicone epoxy	200°C	0.9 , 0.31 (100°C)	44
Fe, Mn, Cu oxides +* /Al flake and silicone	>600°C	0.91-0.93, 0.8-0.1 (20°C)	44

*Thickness insensitive

where

w = wavelength in microns.

E_s = hemispherical emittance of the cooling surface.

b = Stefan Boltzmann constant.

T_s = Temperature of the cooling surface

T_a = Temperature of the atmosphere

E_{ac} = Average hemispherical emittance of atmosphere from 8-13 microns

E_{sc} = Average hemispherical emittance of the surface from 8-13 microns.

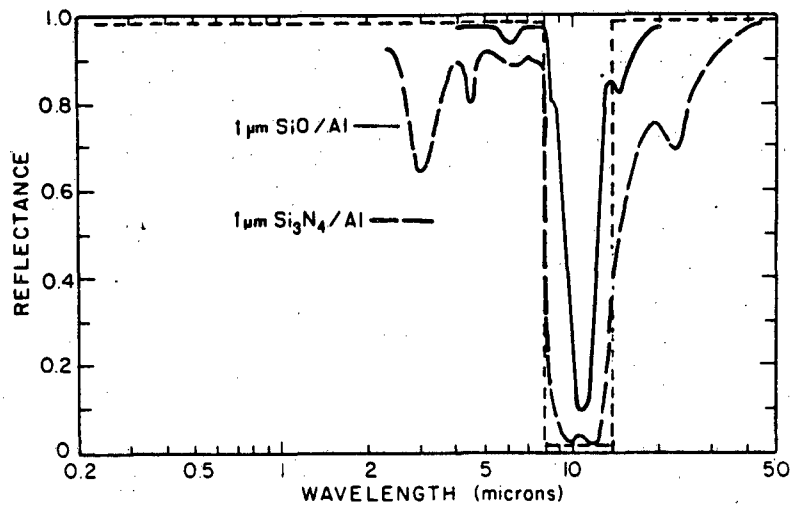
E_{ac} is given by:

$$E_{sc} = \frac{\int_8^{13} B_w(T_a) E_s dw}{\int_8^{13} B_w(T_a) dw}, \quad E_{ac} \text{ can be defined in a similar manner.}$$

As a figure of merit the largest cooling temperature differential requires that E_{sc}/E_s be maximum and that the cooling power at near ambient is governed by E_{sc} .

This implies that 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. The cooling power is about $< 100 \text{ W/m}^2$ at near ambient.

Solid-state materials used for radiative cooling include SiO/Al, Si₃N₄/Al (see Figure 20) and polymer-coated metals.⁸¹ Polymers such as polyvinylchloride (PVC), polyvinylfluoride (PVF, Tedlar), and poly-4-methylpentene (TPX) have been suggested.⁸² 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 Te or dispersions of TiO₂ have been experimented with. 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.



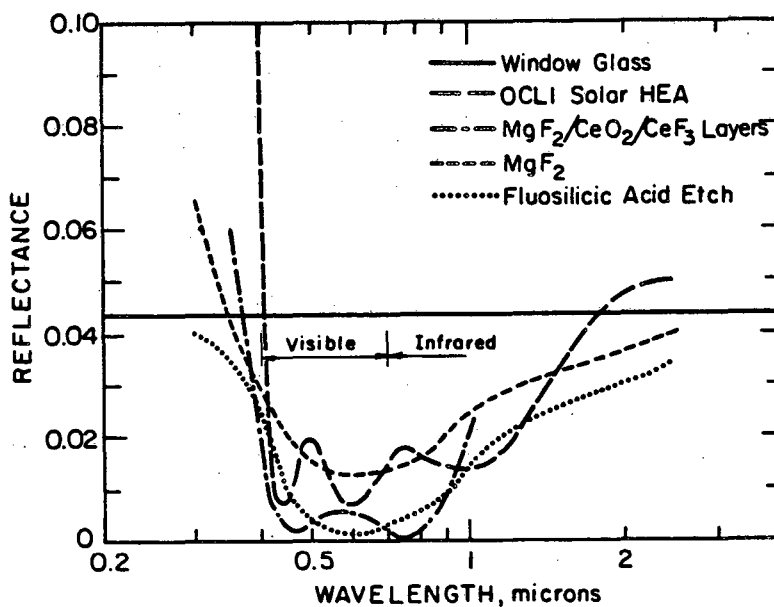
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Figure 20. Spectral properties of radiative cooling tandem of 1 micron SiO/Al and $\text{Si}_3\text{N}_4/\text{Al}$. Ideal properties are shown by short dashed line.

ANTIREFLECTIVE FILMS

Antireflective coatings, if designed properly, 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 acetophenon. 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 21.) It primarily roughens the surface by etching out small pores, in non-silica regions.^{82,83} Silica films deposited from sodium silicate or colloidal silica can be used for acrylic, polycarbonate, and several

glasses. A treatment for polyethylene terephthalate (polyester) and glass materials has been devised.⁸⁴⁻⁸⁵ The coating is made from a steam-oxidized aluminum film; this processing causes a needle-like structure of aluminum hydroxide $[AlO(OH)]$ to form. A polyester film treated in this fashion can serve in glazing applications where solar transmission must be optimum.⁸⁶ (See Figure 22.) Inorganic thin films have been used for a wide range of single and multiple interference coating applications. Compounds such as MgF_2 , CeO_2 , CeF_3 , SiO , SiO_2 , and TiO_2 in various combinations have been used for antireflection applications. Other than 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 transition metals, refractory metals and some rare earths.⁸⁷ A similar technique known as the sol-gel process has formed mixed TiO_2 - SiO_2 antireflective films on silicon⁸⁸ 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.⁸⁹ Coatings of about $n = 1.9$ can be made which are suited to photovoltaics. However, the absorption properties of i-carbon films must be reduced before they can be utilized for optical applications.



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Figure 21. Specular reflectance for a number of antireflection treatments on glass.¹

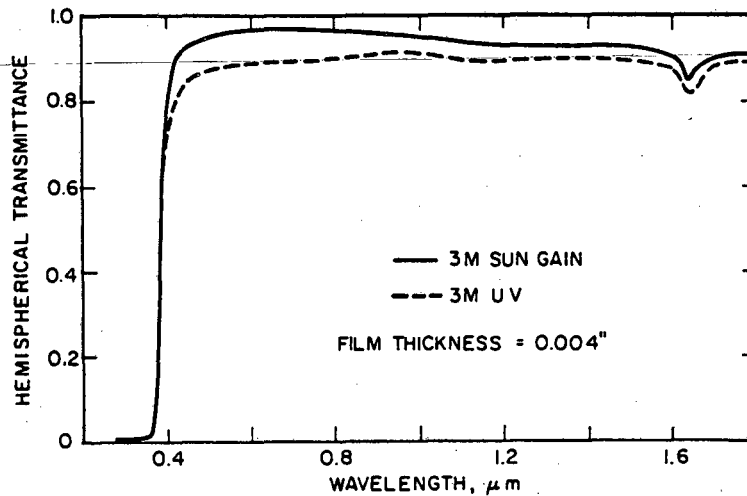


Figure 22. Hemispherical transmission of antireflected 3M Sungain polyester film compared to the uncoated substrate.⁸⁵

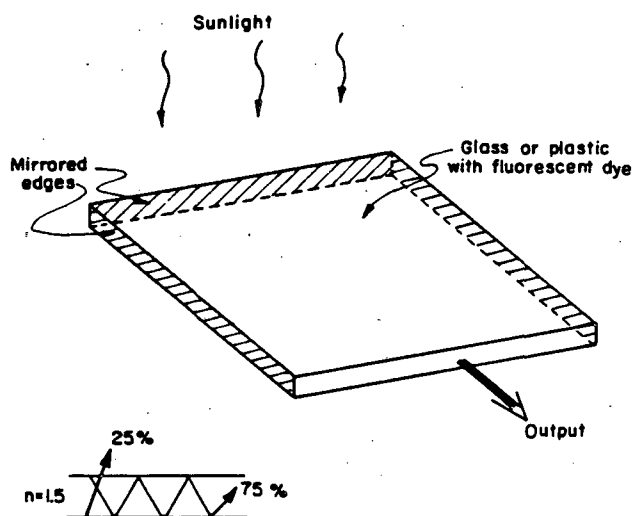
REFLECTOR MATERIALS

Reflector materials consist of a metal reflector on a substrate either in a front surface or back surface configuration. They can differ according to the method of metallic deposition, be it either, silver aluminum on an alloy reflector. The substrate material can be flexible or rigid.

Front surface mirrors offer the best initial optical reflectance but suffer from abrasion and atmospheric corrosion and delamination. Application of a durable overcoating material is required. Second surface mirrors are conventionally produced by a wet chemical process. For mirrors made with this process, there is considerable lack of understanding of various interfacial reactions and degradation mechanisms that can occur with time. A recent workshop addressed many of these issues.⁹⁰ Methods of protecting the backside of second surface mirrors including ion plated and electroless nickel coatings have been investigated.⁹¹ Also more durable reflector layers for second surface mirrors have been devised by sputtering, evaporation and decomposition of organometallic resins.⁹² 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.

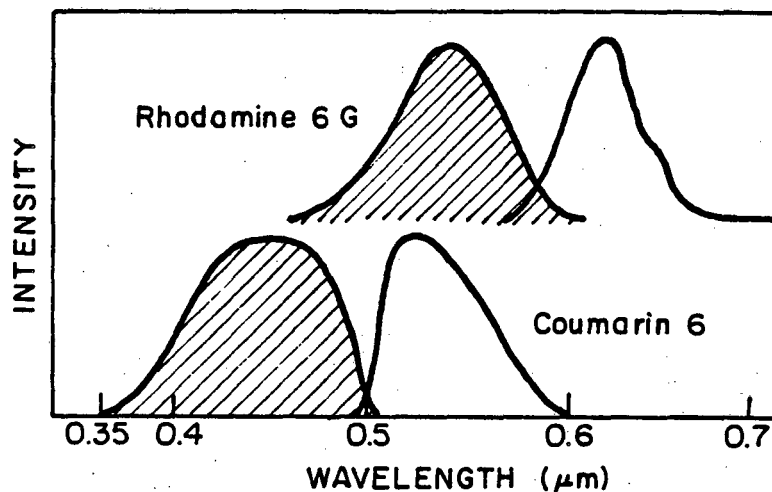
FLUORESCENT CONCENTRATORS

Fluorescent materials can be used to down-convert or alter spectrally incident radiation, concentrate and guide it along the plane of the material. This process is shown schematically in Figure 23. A fluorescent concentrator consists of a transparent plate (of polymer or glass) which has been doped with fluorescent dye molecules. Depending upon the dyes used, various spectral compositions can be obtained. A combination of coupled dyes is depicted in Figure 24. Incident light corresponding to the fluorescent absorption of the dye will be captured and emitted isotropically. Because of the index of refraction difference between the plate and surrounding media, a large portion of light will be trapped and guided to the edges of the plate by total internal reflection. One edge can be favored by silvering the other three edges (see Figure 23). At this favored edge a photovoltaic⁹³ or photothermal collector⁴⁴ can be placed. One of the unique advantages of this system is it will collect diffuse, low insolation radiation without solar tracking. Other advantages are there is less heat dissipation in



XBL821-5089

Figure 23. Schematic representation of a fluorescent concentrator showing how light can be guided along the plane of the material.



XBL 821-5085

Figure 24. Spectra of coupled fluorescent dyes. Absorption wavelengths are crosshatched. Emission spectra are shown spectrally downshifted.

photovoltaics and high efficiency at low insolation levels. Concentration ratios for these systems can be fairly high (10-100). The collection efficiency of this system is dependent upon a number of factors. The loss due to light leaving the collector through the boundary planes by fluorescence for a single plate is given by:

$$L = \frac{1 - (n^2 - 1)^{1/2}}{n},$$

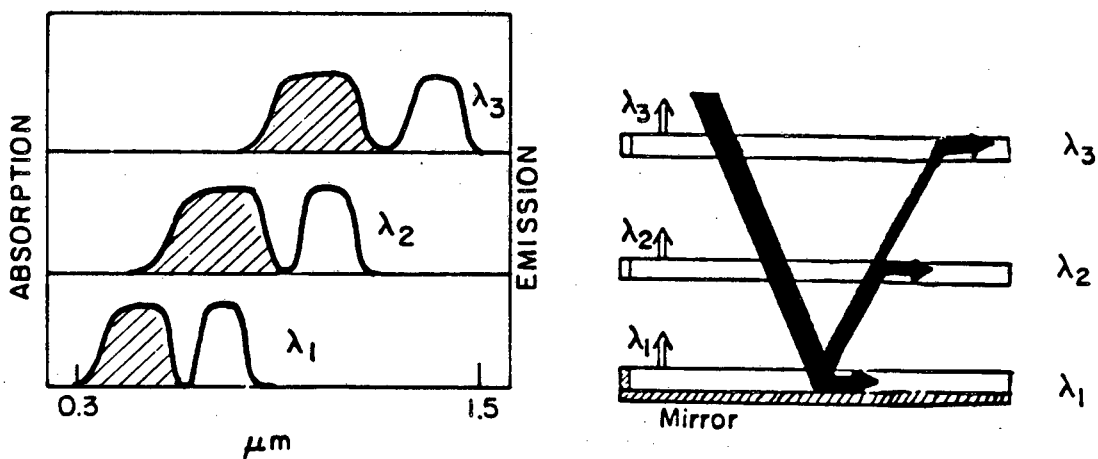
where n is the index of refraction of the collector plate. If $n = 1.5$, $L = 0.255$, if $n = 2$, $L = 0.134$. This equation implies that n should be as large as possible to minimize loss. But another process is important, that of external reflection loss which implies a low n . This loss is given by the Fresnel equation. As a result the total optical loss of the system is given by:

$$L_T = \frac{1 - 4(n^2 - 1)^{1/2}}{(n + 1)^2}.$$

A minimum occurs at $n = 2.0$, $L_T = 0.23$. If we consider the role of the dye and its associated properties than an overall concentrator efficiency (n_c) can be derived.

$$n_c = n_f n_q n_g n_e n_s ,$$

where n_f is defined as the quantum efficiency of the fluorescent dye; n_q is the efficiency due to fluorescent emission beyond the limiting angle of total internal reflection; n_g is efficiency due to collector geometry (absorption); n_e is the energy conversion efficiency due to the Stokes wavelength shift associated with fluorescence and finally n_s is the loss of the long and short wavelength tails of the solar spectrum. For thermal collectors using fluorescent concentrators operational efficiencies of 42-59% have been estimated. For photovoltaic systems operating efficiencies of 32% for a four glazing plate system has been estimated.⁹³ By using multiple plates various portions of the solar spectrum can be collected. Each level of collector plate down has a higher absorption energy so that the innermost level absorbs the highest solar energy. A backup mirror is used on the lowest level to reflect unused energy to the upper lower energy fluorescent levels. This action is seen in Figure 25.



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Figure 25. Three-stage fluorescent concentrator depicting peak wavelengths for each stage.

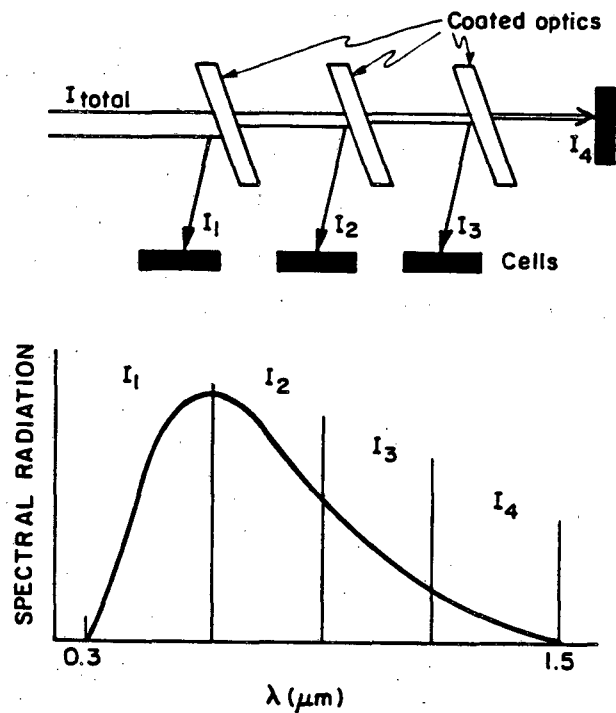
Current research on fluorescent concentrators has favored polymethyl methacrylate (PMMA) and rare earth doped glasses as host materials for the dye. Its high optical transmission property is good to about 1 micron. For a variety of glazing uses there is a need to devise durable glazing materials which can maintain transparency further into the infrared. Dyes that are used for experimentation have not been specifically tailored for solar uses. Experimental collectors generally use laser dyes. Dyes need to be developed with high quantum efficiency, with separated emission spectra with low self absorption. One of the most severe requirements for the dyes is they be UV stable in the PMMA matrix. It is possible that new materials such as ligands containing rare earth ions and non radiative coupled organic systems may offer greater stability. Furthermore, it may be possible to make a polymer based fluorescent thin film which by index matching could couple energy into a substrate material. This design could minimize reabsorption by the dye. Emission - absorption coupled dyes may offer a wide variety of solar collection and energy redistribution possibilities.

SPECTRAL SPLITTING AND COLD MIRROR FILMS

Spectral splitting coatings are used to divide the solar spectrum into various broadband regions. In this fashion various regions can be tailored to particular photovoltaic or photothermal needs⁹⁵. A simple design utilizing a heat mirror might be used to separate heat and light from the solar spectrum. The infrared energy could be used for photothermal uses and the high energy visible could be used for a photovoltaic. Photovoltaics will operate more efficiently if infrared heating is eliminated. Expanding this idea further a system depicted in Figure 26 could result, for an all photovoltaic system. If heat mirrors with different spectral characteristics were used, the solar spectrum could be partitioned from low to high energy as the heat mirror transition wavelength become shorter.

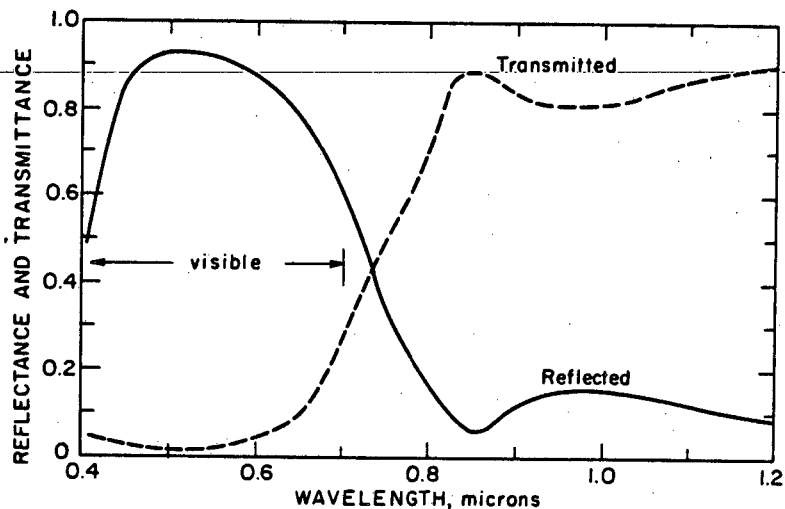
A coating known as a cold mirror could also be employed for spectral splitting. A system might consist of a series of cold mirrors where the transition from reflecting to transmitting moves to longer wavelengths for each successive cell as shown in Figure 26. The cold mirror has the opposite spectral response to that of the heat mirror. It exhibits high reflectance in the visible region and transmits highly in the infrared. Cold mirrors are generally all dielectric interference films. Material systems such as ZnS/MgF_2 and TiO_2/SiO_2 have been devised.⁹⁶ Spectral characteristics of a commercial film as shown in Figure 27. An application for this film is for greenhouses⁹⁷. Plants require only a range of

wavelengths 0.3 - 0.75 microns, the remainder of the solar spectrum is unused. This remainder can be utilized as heat to warm the greenhouse indirectly. A baffle type greenhouse is depicted in Figure 28. Heat mirrors can also be used in this fashion.⁹⁸



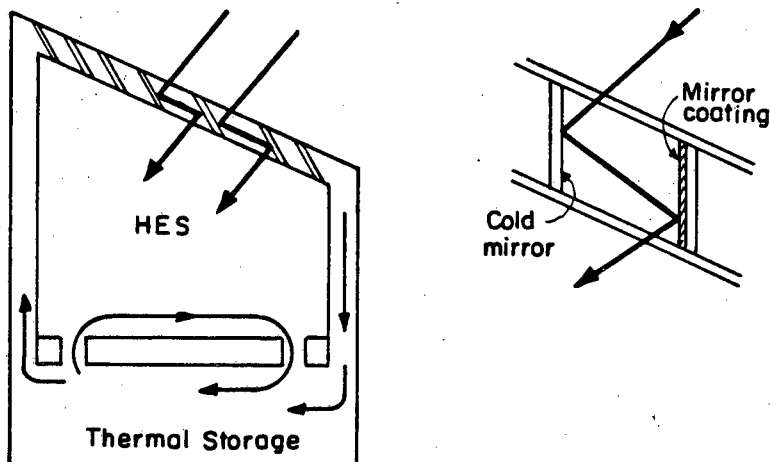
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Figure 26. Spectral splitting scheme for photovoltaics.



XBL783-4709

Figure 27. Cold mirror coating for greenhouse baffle collector. 97



XBL821-5091

Figure 28. Selective baffle greenhouse using cold mirror coatings to separate heat from visible energy. The roof is made of air cells that circulate heated air to the thermal storage. In this fashion the solar spectrum is divided to suit both needs without an added collector area.

TRANSPARENT INSULATION MATERIAL

One of the major drawbacks of conventional windows is their high thermal loss characteristics compared to other building elements. As discussed previously, surface treatments and modified window design can do much to solve this shortcoming. Another approach is to develop a highly transparent material which, by virtue of its bulk properties, has low thermal conductivity. Research on one such material, known as silica aerogel, has begun. This material has a microstructure of bonded fine silica particles surrounded with high porosity volume. Since the particles are smaller than a wavelength of visible light, they are not visibly scattering. The thermal conductivity of such a material is better than still air with optical properties similar to silica glass except for $n \sim 1$. This material has been modeled optically by Rayleigh Theory⁹⁹. Silica aerogel is made by producing a colloidal silical gel from hydrolysis and polycondensation reaction. This gel is solidified in place by supercritical drying. The disadvantages of aerogel is that it must be protected from shock and moisture. It is possible to form aerogel between two sheets of glass to make a window. For a window of aerogel (20 mm thick) the thermal conductance (U), is calculated⁹⁹ to be about $1\text{W/m}^2\text{K}$ (R-5). For a double glazing without the aerogel (20mm spacing) $U = 2.8 \text{ W/m}^2\text{K}$ (R-2). The solar hemispherical transmission properties for aerogel are $T_g = 0.67$ (20mm thick) $T_g = 0.9$ (5mm thick).

OPTICAL SWITCHING MATERIALS AND DEVICES

There are various physical processes which can be used for the regulation of incident solar energy and in glare buildings. Optical switching materials or devices can be used for energy efficient windows or other passive solar uses. The basic property of an optical shutter is, it offers a radical change in optical properties upon a change in light intensity, spectral composition, heat, electrical field or injected charge. This optical change can be manifested in a transformation from highly transmitting to reflecting either totally or partly over the solar spectrum. The purpose of such a device would be to control the flow of light and/or heat in and out of a building window, according to an energy management scheme. This device could also control lighting and heating levels for energy load functions. In general, the idea of an optical shutter is a scientific possibility based on a future research and design idea. Phenomena of interest as optical switching processes can be classified as either discrete mass movement or collective particle movement. Discrete mass movement includes ion and localized electron motion (photorefractive, chromogenic and redox reactions),

also ion and delocalized electron population changes (reversible electrodeposition). Collective particle movement includes gas or vacuum deformable membranes, and adjustable diffraction gratings as one category and liquid crystals and electrophoresis processes as another.

Only selected physical processes will be covered here. Chromogenic reactions known as photochromism, thermochromism and electrochromism will be discussed along with holographic and liquid crystals.

Photochromic Materials

Photochromic materials alter their optical properties 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.^{100,101} Probably the best known photochromic material is photochromic glass for 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 ZnS, TiO₂, Li₃N, HgI₂, HgCNS, 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). Of all the photochromic materials the bulk of the information is on the alkali-halide glasses. The silver halide glasses transform by color-center formation from an AgCl crystalline phase. The typical response for a photochromic glass is depicted in Figure 29.

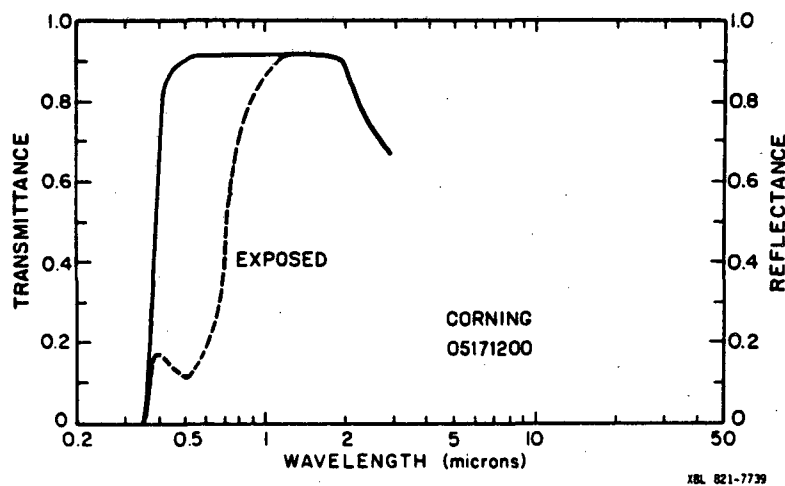


Figure 29. Example light and dark transmission spectra for Corning photochromic glass.¹⁰⁵

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

Thermochromic Materials

Many thermochromic materials are used as nonreversible temperature indicators. For an optical shutter one must consider only the reversible materials, although their actual cyclic lifetime is limited by nonreversible secondary reactions. Organic materials such as anils, spiropyrans, polyvinyl acetal resins, and hydrozides are examples of thermochromism. Inorganic materials include AgI , HgI_2 , Ag_2HgI_4 , HgI_4 , SrTiO_3 , $\text{Cd}_3\text{P}_3\text{Cl}$, and Copper, Cobalt, and Tin complexes.¹⁰² 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.

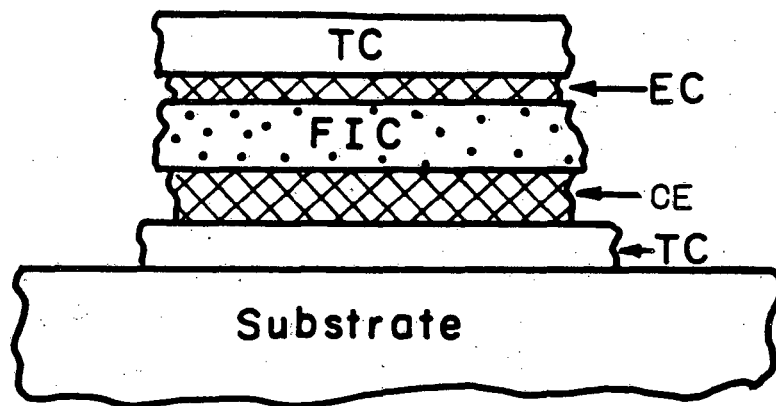
Electrochromic Materials and Devices

Electrochromism is exhibited by a large number of materials both inorganic and organic. The electrochromism 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.¹⁰³ The electrochromic effect, in essence, is a material which exhibits intense color change due to the formation a colored compound. The reaction might follow: $\text{MO}_x + y\text{A}^+ + ye \leftrightarrow \text{A}_y\text{MO}_x$ for cathodic materials.

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 WO_3 , MoO_3 , and IrO_x films. These compounds, among other transition metal oxides, are the subject of a timely review.¹⁰⁴ 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 continuing the layers shown in Figure 30: 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 solid electrolytes also require study.



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Figure 30. Schematic structure of a solid-state electrochromic device.

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.¹⁰⁶ 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 conventional hologram requires coherent light (a laser) to reconstruct the image, this analogous method could utilize a non-coherent light source like the sun (like a white light hologram). 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 materials¹⁰⁷ can be photographic emulsions (phase and amplitude holograms), photo-polymers, dichromatic gelatin, and thermoplastic xerography, which are useable for all phase-only holography.

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