



The Abdus Salam
International Centre for Theoretical Physics


United Nations
Educational, Scientific
and Cultural Organization


International Atomic
Energy Agency



**Workshop on "Physics for Renewable Energy"
October 17 - 29, 2005**

301/1679-3

**The Radiation Around Us & How it can be
used: Review of Solar Energy Materials"**

**C. Granqvist
The Angström Laboratory
Uppsala University
Sweden**

THE RADIATION AROUND US, AND HOW IT CAN BE USED: Review of Solar Energy Materials

Claes G. Granqvist, Uppsala University, Sweden

Abstract

Solar energy materials have properties tailored to meet requirements set by the spectral distribution, angle of incidence, and intensity of the electromagnetic radiation prevailing in our natural surroundings. Specifically, the optimization can be performed with regard to solar irradiation, thermal emission, atmospheric absorption, visible light, and photosynthetic efficiency. Materials for thermal and electrical conversion of solar energy in man-made collectors, as well as for energy-efficient passive design in architecture, are typical examples. This article reviews solar energy materials with emphasis on thermal applications of a variety of kinds. Electrical applications are given a more cursory exposition, the reason being that a systems perspective—rather than a materials perspective—is most fruitful in this case. [This article is based on C G Granqvist, “Solar Energy Materials”, *Adv. Mater.* **15**, 1789-1803 (2003)].

Solar energy materials have optical properties that make them well suited for solar energy utilization and for obtaining energy efficiency mainly in the built environment (1). The desired properties are often achieved by having a suitable surface coating on a transparent or non-transparent (absorbing or reflecting) substrate. Surface coating technology is therefore vital for many solar energy materials. Solar collectors for hot water production use absorbers whose surfaces are strongly absorbing for solar energy, whereas energy efficiency is achieved by having low thermal emittance (i.e., high reflectance for wavelengths corresponding to thermal radiation) (2). These selective absorbers need to be positioned under a convection shield that is transparent to solar radiation. The key property for thermal utilization of solar energy is often spectral selectivity, implying that the optical properties are radically different in different wavelength ranges. Spectral selectivity can be used also in energy efficient fenestration, either for achieving good thermal insulation combined with high solar energy throughput (“low-emittance” windows) or for combining good transmittance of visible light with minimized solar energy inflow (“solar control” windows) (3). Furthermore, improved thermal insulation is possible with silica aerogels, transparent honeycomb materials, etc (4). Spectral selectivity of other kinds can be exploited for radiative cooling, and temperatures significantly below those of the ambience can be achieved for surfaces that emit thermal radiation toward the clear sky at wave-lengths for which the

atmosphere is transparent while the surface has low absorptance at other wavelengths (5). Cooling, or at least prevention of over-heating, is possible even in the day provided that the materials have a high reflectance for solar energy. Materials with strongly angular dependent properties offer other possibilities to optimize with regard to solar energy; for example these materials can be used in windows—even inclined ones—in order to achieve high transmittance along a near-horizontal line of sight and a low transmittance for significantly off-horizontal angles (6).

The materials mentioned thus far have static properties, but there are also numerous solar-energy-related applications for “chromogenic” materials (7) whose properties can be regulated. Electrochromic materials and devices based on such are of particular significance and open avenues to future architecture with buildings that are able to combine high energy efficiency with superior indoor comfort (8,9). The characteristic feature of these materials is that their absorptance can be changed, reversibly and persistently, by the insertion and extraction of electrical charge. Photochromic and thermochromic materials give other options. Solar energy materials are of importance also for the purification of water and air by exploiting photo-catalysis (10), and more generally for solar-driven chemical reactions. The present article is an update on a previous one published in 2003 (11).

1. Ambient Radiation: The Basis for Solar Energy Materials

Figure 1 introduces the electromagnetic radiation of our ambience in a unified manner (12). The most fundamental property of this radiation ensues from the fact that all matter emits electromagnetic radiation, which is conveniently introduced by starting with the ideal black-body whose emitted spectrum—known as the Planck spectrum—is uniquely defined if the temperature is known. Planck’s law is a consequence of the quantum nature of the radiation. Part (a) in Fig. 1 depicts such spectra for four temperatures. The vertical scale denotes power per unit area and wavelength increment (hence the unit GWm^{-3}). The spectra are bell-shaped and confined to the $2 < \lambda < 100 \mu\text{m}$ wavelength range. The peak in the spectrum is displaced toward shorter wavelength as the temperature goes up. At room temperature, the peak lies at about $10 \mu\text{m}$. Thermal radiation from a material is obtained by multiplying the Planck spectrum by a numerical factor—the emittance—which is less than unity. In general, the emittance is wavelength dependent.

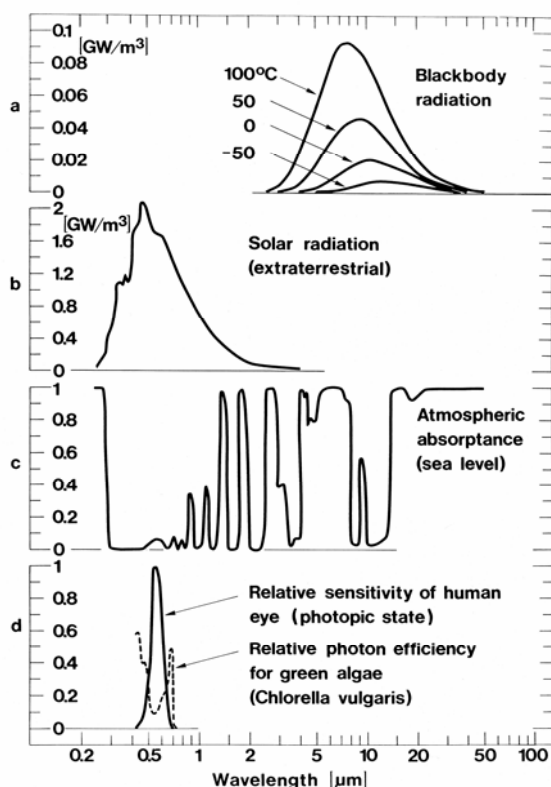


Figure 1. Spectra for (a) black-body radiation pertaining to four temperatures, (b) solar radiation outside the earth’s atmosphere, (c) typical absorptance across the full atmospheric envelope, and (d) relative sensitivity of the human eye and relative photosynthetic efficiency for green algae. From (12).

Part (b) of Fig. 1 reproduces a solar spectrum for radiation just outside the earth’s atmosphere. The curve has a bell shape and defines the sun’s surface temperature ($\sim 6000 \text{ }^\circ\text{C}$). It is important to observe that the solar spectrum is limited to $0.25 < \lambda < 3 \mu\text{m}$, so that there is almost no overlap with the spectra for thermal radiation. Hence it is possible to have surfaces with properties being entirely different with regard to thermal and solar radiation. The integrated area under the curve gives the “solar constant” ($1353 \pm 21 \text{ Wm}^{-2}$); this is the largest possible power density on a surface oriented perpendicular to the sun in the absence of atmospheric extinction.

Most solar energy conversion systems are located at ground level, and it is of obvious interest to consider to what extent atmospheric absorption influences solar irradiation and net thermal emission. Part (c) of Fig. 1 illustrates a typical absorption spectrum vertically across the full atmospheric envelope at clear weather conditions. The spectrum is complicated and comprises bands of high absorption—caused mainly by water vapor, carbon dioxide, and ozone—as well as bands of high transparency. It is evident that most of the solar energy can be transmitted down to ground level, and only parts of the ultraviolet ($\lambda < 0.4 \mu\text{m}$) and infrared ($\lambda > 0.7 \mu\text{m}$) radiation are strongly damped. The maximum power density perpendicular to the sun is about 1000 Wm^{-2} . Thermal radiation from a surface exposed to the clear sky is strongly absorbed except in the $8 < \lambda < 13 \mu\text{m}$ range, where the transmittance can be large provided that the humidity is not too large.

Part (d) of Fig. 1 illustrates two biological conditions of relevance for solar-energy-related applications. The solid curve shows the relative sensitivity of the human eye in its light-adapted (photopic) state; the bell-shaped graph extends across the $0.4 < \lambda < 0.7 \mu\text{m}$ interval and has its peak at $0.555 \mu\text{m}$. Clearly a large part of the solar energy comes as invisible infrared radiation. The dashed curve indicates that photosynthesis in plants makes use of light with wavelengths in approximately the same range as those for the human eye, which is relevant for greenhouse applications.

Figure 1 shows an important fact about the ambient radiation: that it is spectrally selective, *i.e.*, confined to specific and usually well defined wavelength ranges. This property is of large importance for most types of solar energy materials, as discussed below. Another type of selectivity—known as angular selectivity—results from the fact that different angles may apply for different types of radiation; for example, solar radiation comes from a point far from the horizon during most of the day, whereas the visual contact between a person

and his or her surroundings is often at near-horizontal lines-of-sight.

This article covers a number of solar energy materials and attempts to show their state-of-the-art. References are mainly to reviews, although some other key papers are listed as well. Earlier work in this field, up to 1990, was covered in earlier treatises (1,13).

2. Transmitting and Reflecting Materials

2.1 Fundamentals

When electromagnetic radiation impinges on a material, one fraction can be transmitted, a second fraction is reflected, and a third fraction is absorbed. Energy conservation yields, at each wavelength, that

$$T(\lambda) + R(\lambda) + A(\lambda) = 1 \quad (1)$$

where T , R , and A denote transmittance, reflectance, and absorptance, respectively.

Another fundamental relationship, also following from energy conservation and referred to as Kirchhoff's Law, is

$$A(\lambda) = E(\lambda) \quad (2)$$

with E being the emittance, *i.e.*, the fraction of the black-body radiation (*cf.* Fig. 1(a)) that is emitted at the wavelength λ . It is evident that Eq. (2) is of relevance mainly for $\lambda > 3 \mu\text{m}$.

It is frequently convenient to average the spectral data over the sensitivity of the eye, over a solar spectrum (with or without account for atmospheric effects), or over a black-body emittance spectrum (for a specific temperature). One then obtains luminous, solar, or thermal values pertinent to the respective optical property; they are denoted X_{lum} , X_{sol} , and X_{therm} , with X being T , R , A , or E .

2.2 Glasses

Glass can be used for protection against an unwanted environmental impact, for convection suppression, and as a substrate for surface coatings (normally referred to as "thin films"). Glass can exhibit a variety of properties (14), but float glass, used in a great majority of windows in buildings, is a highly standardized product (15). It is characterized by uniformity and flatness almost on the atomic scale. The latter feature is an outcome of the production process in which the molten glass is solidified on a surface of molten tin. The middle curve in Fig. 2 shows the spectral transmittance of 6-mm-thick standard float glass within the wave-

length range relevant to solar radiation. A characteristic absorption feature at $\lambda \approx 1 \mu\text{m}$, due to the presence of Fe oxide, limits T_{sol} to some noticeable extent.

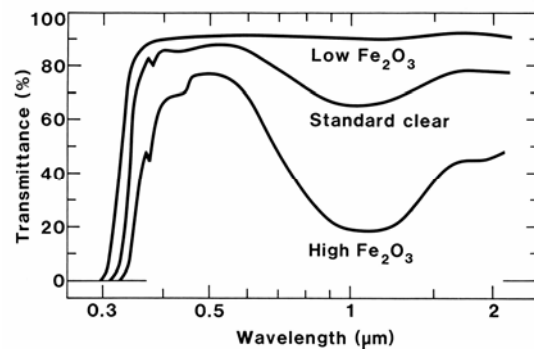


Figure 2. Spectral transmittance for float glass with three different amounts of Fe_2O_3 . From (1).

Special float glass is available with varying amounts of Fe oxide (15). Figure 2 shows that low Fe content leads to glass with very high T_{lum} and T_{sol} , and with substantial transmittance also in the ultraviolet. Glass with a large Fe content limits T_{sol} while T_{lum} remains rather large; such glass has a distinctive greenish tint.

The reflectance of each interface between glass and air is about 4 % in the $0.4 < \lambda < 2 \mu\text{m}$ range, implying that the maximum transmittance for a glass pane is 92 %. Glass is strongly absorbing for $\lambda > 3 \mu\text{m}$, and E_{therm} is as large as about 87 %.

Laminated glass may be used for safety and other reasons. This glass comprises a layer of polyvinyl buteral sandwiched between two glass panes and bonded to the glass under heat and pressure. The laminate is an efficient absorber of ultraviolet light, and the transmittance at $\lambda < 0.38 \mu\text{m}$ is almost zero for a layer thickness of the order of 1 mm.

Photo-chromic glass is able to darken under irradiation of ultraviolet light from the sun and clears in the absence of such irradiation (16). Fatigue-free photo-sensitivity is normally accomplished by adding metal halides—particularly silver halide—to the vitreous matrix of the glass. A number of other additives are important as well. Figure 3 shows T_{lum} as a function of time for darkening and clearing of two photo-chromic glass plates. Darkening progresses rapidly and has reached about 80 % already after one minute. Clearing is much slower, though, and is still incomplete after one hour. The photo-sensitivity occurs almost entirely in the $0.4 < \lambda < 1.0 \mu\text{m}$ interval, and hence the modulation of T_{lum} is much more pronounced than the modulation of T_{sol} . Photosensitivity exerts no effect on the reflectance or on E_{therm} .

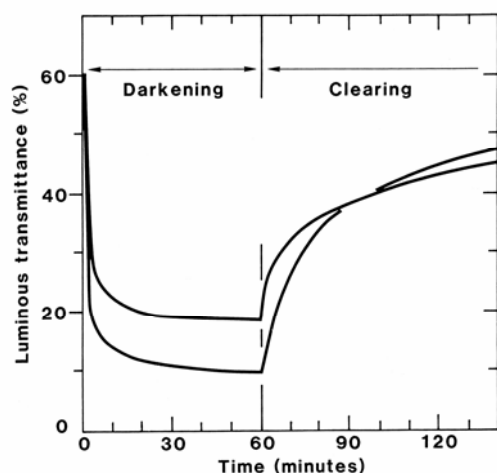


Figure 3. Luminous transmittance vs. time for two photochromic glasses. From (1).

2.3 Polymers

Many polymers are transparent and can, in principle, replace glass. However, polymers degrade more easily than glass and hence have fewer applications. Polyester foil deserves special mention since it can serve as a flexible and inexpensive substrate for thin films of many different kinds, transparent as well as reflecting. Such foils, suspended between glass panes, are used in practical window constructions. Another alternative, used in some contemporary building projects, is ethyl tetra fluoro ethylene. This material is virtually non-absorbing for solar radiation.

Photo-chromism is known in a number of polymers (17), and detailed information is available for spiro-oxazine in a host of cellulose acetate butyrate. The coloration dynamics are similar to those for photochromic glass, but the bleaching is faster for the polymer and takes place in about 20 minutes. The photo-effects are limited to T_{lum} ; they vanish at elevated temperatures.

2.4 Metals

Metal surfaces can be used to accomplish high R_{lum} and R_{sol} , for example in mirrors of various types, or for providing low E_{therm} . Figure 4 shows spectral reflectance for five different metals (18,19). The highest values of R_{lum} and R_{sol} are found in Ag and Al, and these metals are used—in bulk form or as thin films supported by substrates—in several solar-energy-related applications. Surface protection of such surfaces is normally needed to obtain long term durability. More corrosion resistant metals, such as Pt or Rh, are somewhat less reflecting. All of the metals can yield a low magnitude of E_{therm} .

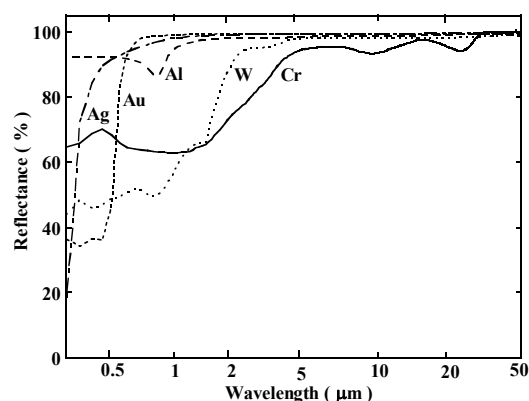


Figure 4. Spectral reflectance for some metal surfaces. From (11)

3. Thin Films

3.1 Deposition technology

Surface treatments can be used to modify the optical properties of the underlying material and make it better adapted to the requirements set by the ambient radiation (*cf.* Fig. 1). Subsequent sections, devoted to specific types of solar energy materials, contain many examples of this. Thin film deposition is particularly important (20-24). This is a vast technological field (25-29), and only the most common methods are mentioned here. Typical film thicknesses are 0.1 to 1 μm .

Sputter deposition is widely used to make uniform coatings on glass, polyester, metal, etc. Essentially a plasma is set up in a low pressure of inert and/or reactive gases, and energetic ions in the plasma dislodge material from a solid plate of the raw material of the film (known as the “target”) and deposit these atoms as a uniform film on an adjacent surface (the substrate) (30-33).

Evaporation can be an alternative to sputtering. Here the raw material of the film is heated in vacuum so that a condensing vapor can transfer material to the substrate at a sufficient rate (34,35).

Other technologies can be applied without recourse to vacuum: For example, sol-gel deposition involves immersion of a substrate in a chemical solution, withdrawal at a controlled rate, and subsequent annealing (36). Alternatively, the chemical solution can be applied by spray coating. Chemical vapor deposition uses heat to decompose a vapor of a “precursor” chemical to produce a thin film of a desired composition (37,38). Electrochemical techniques include cathodic electro-deposition from a chemical solution (39) and anodic conversion of a

metallic surface—especially of Al—to form a porous oxide (40). Numerous alternative techniques exist as well.

3.2 Antireflection Treatment

Antireflection treatment, for example to obtain high T_{lum} through glass, can be accomplished by the application of a layer whose refractive index is close to the square root of the refractive index of the underlying glass (*i.e.*, 1.23) and with a thickness corresponding to a quarter wavelength for visible light (*i.e.*, ~100 nm). The requirement on the refractive index can be combined with good durability only for a few materials. Figure 5 shows an example of a glass slab whose two surfaces have been coated with a layer of porous silica obtained via sol-gel technology (41). It is seen that T_{lum} exceeds 99 % in the middle of the luminous spectrum. Other antireflection treatments of practical interest include thin films of aluminum oxy-fluoride (42,43) or magnesium fluoride, porous or micro-structured surface layers produced by liquid or vapor etching of glass (44,45) or silicon (46), and application of a layer serving as a sub-wavelength surface relief grating (47).

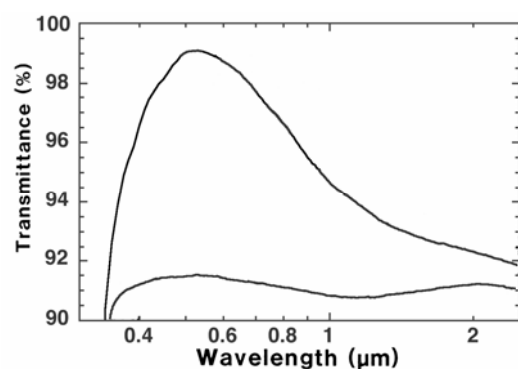


Figure 5. Spectral transmittance of a glass plate coated on both sides by anti-reflecting thin films of porous silica. After (41).

Simple antireflection treatments are able to decrease the reflectance within a rather narrow wavelength range, but if a low magnitude of R_{sol} is required one could use a multilayer film with carefully adjusted refractive indices and thicknesses. It should be noted that antireflection is efficient only for a specific range of incidence angles for the light, especially for the case of multilayer films.

4. Transparent Thermal Insulation

4.1 Principles

Heat transfer occurs via the additive effects of radiation, convection, and conduction (48,49). Cutting back this transfer is of concern for many different applications of solar energy. Radiation transfer can be diminished by having surfaces with low values

of E_{therm} . Convection—which is of interest for gases—can be lowered by breaking up the gas into cells with dimensions of the order of 1 cm or less (or, possibly, by decreasing the gas pressure), and conduction heat transfer can be minimized by suitable constructions using low-conducting materials.

4.2 Solid materials

Figure 6 shows four types of solid transparent insulation materials including flexible polymer foils; polymer honeycomb materials; bubbles, foam, and fibers; and inorganic microporous materials such as silica aero-gels (4). If the honeycomb cross-section is small compared to the cell length, one may speak of a capillary structure. Foils and aero-gels can be almost invisible to the eye, whereas honeycombs, bubbles, foam, and fibers cause reflection and scattering and hence a limited direct transmittance; only the former group of materials is of interest when unperturbed vision is a demand—such as in many windows—while the other materials find applications in translucent wall claddings and solar collectors. The materials can be used in vertical, horizontal, or inclined positions depending on the type of application.

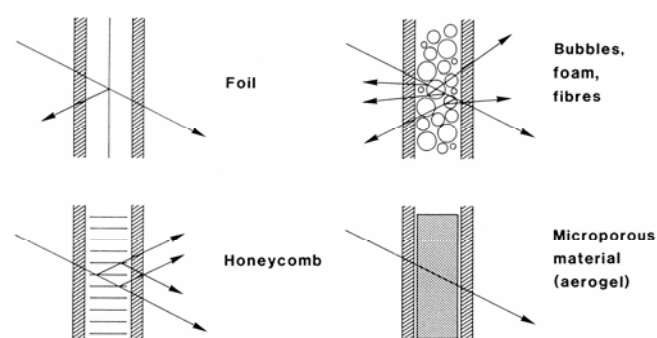


Figure 6. Principles of four different types of solid transparent insulation materials placed between glass panes. Arrows signify light rays. Reflections at the glass surfaces are not shown. From (1).

Flexible polyester foils can be suspended to break up a thick gas slab into ~1-cm-thick layers with diminished convection, and thin films can be applied to adjust the magnitudes of T_{lum} and T_{sol} , and to minimize E_{therm} (these aspects are covered below). Similarly, the macro-porous materials—typically made of polystyrol, polyamide, polyvinyl-chloride, or polycarbonate—produce gas filled cells of a sufficiently small size to practically eliminate convection. A characteristic value of the heat transfer of the honeycombs, capillaries, bubbles, foam, fibers is $1 \text{ Wm}^{-2}\text{K}^{-1}$ for a material thickness of 10 cm (50,51).

Silica aero-gel can be made by super-critical drying of colloidal silica gel under high temperature and high pressure (52,53). The ensuing material consists of ~ 1 -nm-diameter silica particles interconnected so that a loosely packed structure with pore sizes of 1 to 100 nm is formed. The relative density can be as low as a few percent of the bulk density. The material can be produced as translucent granules or as transparent tiles with a certain degree of haze (54,55). Figure 7 shows spectral transmittance through a 4-mm-thick tile (56). The low transmittance at short wavelengths is partly due to optical scattering. A heat transfer lower than $1 \text{ Wm}^{-2}\text{K}^{-1}$ can be achieved in 1-cm-thick slabs of aero-gel under favorable conditions (positioning between surfaces with low E_{therm} and at low gas pressure).

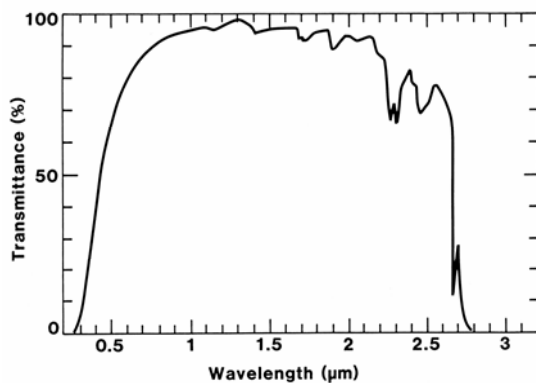


Figure 7. Spectral transmittance of a silica aero-gel tile. From (1).

4.3 Gases

The heat transfer between two surfaces can be lowered by use of a gas different than air, as is common in modern fenestration technology involving hermetically sealed glazing units (3,57). The heat transfer across a typical 1.2-cm-wide gas slab is diminished on the $\sim 10\%$ level if air is replaced by Ar or CO_2 , while larger effects are found with Kr or Xe. The relative role of the gas filling is enlarged—in practice to the $\sim 20\%$ level—if the radiation component to the heat transfer is decreased by the use of surfaces with a low E_{therm} .

Infrared-absorbing gases can diminish the heat transfer across a given distance, but the limited availability of suitable gases makes this possibility less interesting (58). Among other options related to gases, one can note that some improvement of the thermal properties can be combined with sound insulation by the use of SF_6 gas. Finally, minimized heat transfer can be achieved by eliminating the gas, so that both the conduction and convection components vanish (59). Obviously, the mechanical strength of the device must be sufficient to allow vacuum. This leads to the requirement of inconspicuous spacers for “vacuum windows”.

5. Solar Thermal Converters

5.1 Principles

Photo-thermal conversion of solar energy, to produce hot fluid or hot air, takes place in solar collectors (60,61). Efficient conversion requires that a solar absorbing surface is in thermal contact with the fluid or gas, and that thermal losses to the ambience are minimized. For most applications, the absorber should be positioned under a transparent cover, and a transparent thermal insulation material may be used as well. The back and sides of the solar collector should be well insulated using conventional techniques. The most critical part for the photo-thermal conversion is the actual solar absorber surface, which obviously should have maximum A_{sol} . Its radiation heat losses should be minimized, and this requires low E_{therm} . The absorber is non-transparent, and the above conditions can be rewritten in terms of an ideal spectral reflectance as

$$R(\lambda) = 0 \quad \text{for } 0.3 < \lambda < \lambda_c \text{ } \mu\text{m} \quad (3)$$

$$R(\lambda) = 1 \quad \text{for } \lambda_c < \lambda < 50 \text{ } \mu\text{m} \quad (4)$$

where λ_c denotes a “critical” wavelength lying between 2 and 3 μm depending on the temperature (*cf.* Fig. 1). Clearly this is one example of how spectral selectivity is used to obtain optimized properties of a solar energy material.

A number of different design principles and physical mechanisms can be used in order to create a spectrally selective solar absorbing surface. Six of these are shown schematically in Fig. 8 (2,62-67). The most straight-forward would be to use a material with suitable intrinsic optical properties. There are few such materials, though, and this approach has not been particularly fruitful. Semiconductor-metal tandems can give the desired spectral selectivity by absorbing short-wavelength radiation in a semiconductor with a band-gap corresponding to a wavelength of $\sim 2 \mu\text{m}$ and having low E_{therm} as a result of the underlying metal. The pertinent semiconductors all have large refractive indices, which tend to give strong reflection losses and diminish A_{sol} , implying that complex anti-reflection treatments must be invoked. Multilayer-metal tandems can be tailored so that the thin film stack becomes an effective selective absorber of solar energy. Metal/dielectric composite-metal tandems contain metal nano-particles in a dielectric (often oxide) host. The composite is often referred to as a “cermet”. This design principle offers a large degree of flexibility, and the optimization of the spectral selectivity can be made with regard to the choice of constituent materials, film thickness,

particle concentration and grading, as well as the shape and orientation of the particles. The particles are much smaller than any relevant wavelengths of solar (or thermal) energy, and the composite behaves as an “effective medium” with properties intermediate between those of the metal and the dielectric (68-72). Textured metal surfaces can produce a high A_{sol} by multiple reflections against metal dendrites that are $\sim 2 \mu\text{m}$ apart, while the low E_{therm} is rather unaffected by this treatment since the relevant wavelengths are much larger than the dendrite separation. Finally, selectively solar-transmitting films on black-body-like absorbers can be used to impart spectral selectivity. The relevant thin films will be discussed below.

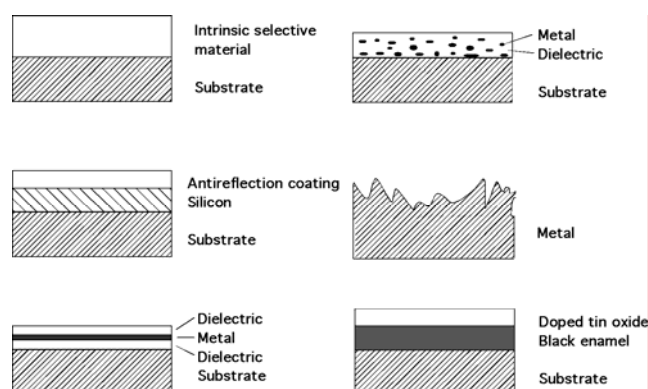


Figure 8. Cross-sectional schematic designs of six types of thin films and surface treatments for selective absorption of solar energy. From (2).

5.2 Spectrally selective thin films

A number of thin films, coated onto metallic substrates by one of the thin film technologies discussed above, have been developed in the past, and some of these have reached commercialization. These films normally exploit several of the design principles and physical mechanisms mentioned above.

Electrochemical techniques have been used for several decades to make spectrally selective surfaces—suitable for flat-plate solar collectors—based on electrodeposited films containing Cr or Ni (referred to as “black chrome” and “black nickel”, respectively) of complex compositions. Another technique employs anodic conversion of Al, to make a porous surface layer, followed by electrolysis to precipitate out Ni particles inside the pores (73). The solid curve in Fig. 9 illustrates a spectral reflectance curve; $A_{\text{sol}} \approx 96\%$ and $E_{\text{therm}} \approx 15\%$ at 100°C are typical performance data. The durability of these films has been modeled in detail (2,67).

The electrochemical techniques involve the handling of large quantities of environmentally hazard-

ous chemicals, and this has led to a trend towards thin film techniques based on deposition in vacuum (74-76). The dotted curve in Fig. 9 shows a spectrum for an optimized sputter-deposited film based on Ni; the design includes an antireflection layer which boosts A_{sol} . These data correspond to $A_{\text{sol}} \approx 95\%$ and $E_{\text{therm}} \approx 10\%$ at 100°C . Other sputter-deposited and evaporated films of practical use include a number of “cermet” with stainless steel and metal nitride (77-78), and compositionally graded films containing chrome oxide and chrome nitride (79). These films can be used for different types of solar collectors, including concentrating ones.

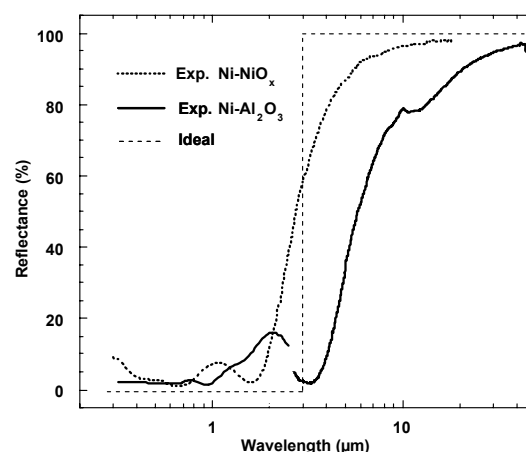


Figure 9. Spectral reflectance for two types of selectively solar absorbing surfaces. Dashed lines indicate the ideal performance. From (11).

Deposition from chemical solutions has recently been used to produce Ni-alumina “cermet” coatings. They contain larger Ni fractions than the Ni pigmented anodic alumina referred to above. Therefore the coatings can be considerably thinner and achieve $A_{\text{sol}} \approx 97\%$ together with $E_{\text{therm}} \approx 5\%$ (80).

Advanced selectively solar-absorbing surfaces have been developed for solar thermal power stations with parabolic trough reflectors and tubular solar collectors. The absorber surfaces used in this case employ sputter deposition to manufacture a complex multilayer film stack incorporating graded Mo/oxide films, antireflection treatment, and an emittance-suppressing Mo film on the stainless steel tube serving as a substrate (81). These absorbers have $A_{\text{sol}} \approx 97\%$ and $E_{\text{therm}} \approx 17\%$ at 350°C .

5.3 Spectrally selective paints

Paints have an obvious advantage in the fact that they can be applied by commonly available techniques. Typically, a strongly absorbing pigment—for example an oxide of FeMnCu—is mixed in an infrared-transparent polymeric binder such as a

silicone or a siloxane (82). The paint is applied in a 2 to 3 μm thick layer onto a metallic substrate with low E_{therm} . Characteristic data are $A_{\text{sol}} \approx 90\%$ and $E_{\text{therm}} \approx 30\%$; they are not as good as for the thin films. Possibilities to prepare thickness-insensitive spectrally selective paints by including metallic flakes in the binder may lead to interesting products in the future. Visibly colored solar absorbing surfaces—which may be desirable for aesthetic reasons—can be obtained by relaxing the requirement on A_{sol} somewhat.

6. Radiative Cooling

As shown in Fig.1, the atmosphere can be transparent to thermal radiation in the $8 < \lambda < 13\ \mu\text{m}$ “window” range. This effect can lead to radiation cooling of surfaces oriented towards the sky (5). The resource for this cooling has been evaluated through detailed calculations showing that the cooling power for a black-body surface is 80 to 120 Wm^{-2} , depending on the atmospheric conditions, when the surface is at ambient temperature (83). If nothing but radiation exchange is considered, the surface can decrease to 14 to 26 $^{\circ}\text{C}$ below the air temperature. In the presence of a non-radiative heat transfer equal to $1\ \text{Wm}^{-2}\text{K}^{-1}$, the maximum temperature drop is expected to be 10 to 20 $^{\circ}\text{C}$. Practical tests, using a multi-stage radiation cooler placed under an exceptionally dry atmosphere, demonstrated that a temperature decrease as large as $\sim 33\ ^{\circ}\text{C}$ could be achieved in practice by purely passive means.

The temperature drop can be enhanced if radiation exchange takes place only within the atmospheric “window”. This calls for surfaces with infrared selective emittance, whose ideal reflectance is

$$R(\lambda) = 1 \text{ for } 3 < \lambda < 8\ \mu\text{m} \text{ and } 13 < \lambda < 50\ \mu\text{m} \quad (5)$$

$$R(\lambda) = 0 \text{ for } 8 < \lambda < 13\ \mu\text{m}. \quad (6)$$

If cooling should take place also in the day, it is desired to have a maximum $R(\lambda)$ for $0.3 < \lambda < 3\ \mu\text{m}$. Calculations have shown that infrared-selective surfaces can have a cooling power between 60 and 95 Wm^{-2} depending on the atmosphere. A maximum temperature drop of 26 to 60 $^{\circ}\text{C}$ with nothing but radiation exchange, and of 18 to 34 $^{\circ}\text{C}$ when the non-radiative heat influx is $1\ \text{Wm}^{-2}\text{K}^{-1}$, have been predicted. The significance of spectral selectivity for reaching low temperatures is hence evident.

Spectral selectivity, approximately according to Eqs. (5) and (6), has been achieved with $\sim 1\ \mu\text{m}$ thick silicon oxide and oxynitride films backed by Al (84,85) and by some aluminized polymer foils.

Another possibility is to use confined gas slabs of NH_3 , C_2H_4 , $\text{C}_2\text{H}_4\text{O}$, or mixtures of these, with thicknesses of a few centimeters (86). In both cases the low reflectance in the atmospheric “window” range is associated with molecular vibrations, and the high reflectance outside this range is caused by the Al.

Practical tests of the cooling ability of these materials have been carried out with devices in which the cooling surface, or the gas, is located under an infrared-transparent convection shield. High-density polyethylene foil has suitable optical properties but requires stiffening in order not to cause convection heating due to mechanical movements caused by wind (87). Using a radiation cooled gas, the coolant can be circulated and heat exchanged so that it provides a continuous source for cooling under the clear sky. Pigmented foil materials that are strongly scattering solar radiation and absorbing in the 8 to 13 μm range can serve as self-cooling tarpaulins even during the day (88,89).

Radiation cooling can be used for condensation of water from the atmosphere (90,91). Preliminary measurements have demonstrated that significant amounts can be collected even under unfavorable conditions (during drought months in a semi-desert part of Tanzania). The material used in this case was a 0.4-mm-thick polymer foil pigmented by white TiO_2 and BaSO_4 (90).

7. Solar Cells

Solar cells are used for converting solar radiation to electricity. Generally speaking, a device perspective—rather than a materials perspective analogous to the one put forward elsewhere in this article—is most convenient, and hence the exposition below is kept brief. Detailed discussions of solar cells, including some materials aspects, can be found elsewhere (92-99).

In principle, all that is needed to generate electricity is an excited state or states, into which a carrier can be excited from a ground state by photon absorption, and some means of extracting or supplying carriers to or from these states. There are many options but, despite much research and development during decades, the attention has been focused almost entirely only on a few of these.

Silicon is an excellent material for solar cells and is by far the most widely used one (99,100). It is non-toxic, very abundant, and has a well established technological base due to its ubiquitous uses in microelectronics. Essentially, a slab or film of Si is n -doped and p -doped in its two surface regions, and

this structure is positioned between a transparent front electrode arrangement and an opaque metallic back electrode. The device is supported by glass or a polymer foil. The Si can be of three types: crystalline (cut from a single crystal ingot), polycrystalline (made from a multi-crystalline ingot or prepared by “ribbon growth”), or amorphous and hydrogenated (typically a $\sim 0.3\text{-}\mu\text{m}$ -thick film made by glow discharge deposition of a silane gas). High photoelectric conversion efficiency demands low reflection losses, which can be achieved by an anti-reflecting film or—in the case of a single-crystalline material—by using anisotropic etching to make a pyramid-type texturing.

Compound semiconductors of the III-V type (101)—based on GaAs, (Al,Ga)As, InP, or (In,Ga)P—can show high efficiency as well as good resistance to ionizing radiation; they are costly, though, and mainly used for space applications. Among the II-VI compounds (102-104), CdTe and Cd(S,Te) are known for their robust manufacturability and are of interest for ground-based solar cells, although environmental concerns regarding large-scale use of a technology including Cd should not be overlooked. Among the I-III-IV₂ compounds (104-106), CuInSe₂, Cu(In,Ga)Se₂, and Cu(In,Ga)(S,Se)₂ are notable for their possibility to reach high photo-thermal conversion efficiencies in thin film solar cells. Numerous other materials—including organic ones (107,108)—and approaches to solar cells are possible, and many other compound semiconductors can well turn out to have favorable properties. Some of those may find applications in thermophotovoltaicity, *i.e.*, cells operating with thermal irradiation (109-111). Others can be used in tandem cells, encompassing superimposed cells with optical band-gaps that are large on the exposed surface and gradually shrink towards the underlying substrate.

Alternatively, photo-electrochemical techniques can be employed to generate electricity, and studies of nano-crystalline dye cells are popular at present (112-114). These cells absorb light in the dye molecules—normally containing a Ru-based compound—coated onto nano-crystals of TiO₂. The nano-structured material is usually made by colloidal technology, but other technologies, such as sputter deposition, is currently emerging (115). Electrons are excited in the dye and can flow into the conduction band of the adjacent *n*-type TiO₂. The electron is transferred to a transparent front surface electrode, through the load, and to a counter electrode having a thin layer of Pt. Here it reduces triiodine to iodide, which then diffuses to the dye molecules and reduces them back to their original state. Sealing and durability are issues that need to be resolved before widespread applicability is possible. Also the fact that the fundamental functioning

principles remain obscure hampers rapid progress (116).

Generally speaking, solar cells lose efficiency when they become warm. It is therefore of interest to devise cells and cell systems that minimize the heating. One possibility is to use external surfaces which reflect at wavelengths shorter than those corresponding to the bandgap (useful for photo-electric conversion) onto the solar cell while absorption prevails at longer wavelengths. Mirrors of SnO₂-coated Al have been developed for this purpose (117).

One aspect of today’s solar cell technology requires particular attention as it proliferates, *viz.*, global availability of the raw materials (118). Ga, Se, and Ru are all rare in the earth’s crust. Indium is also widely believed to be rare, but recent assessments indicate that the global availability is about as large as that of Ag (119).

8. Coatings for Glazings: Static Properties

8.1 Principles

Architectural windows and glass facades are problematic from an energy perspective (15). Their primary function—to provide visual contact between indoors and outdoors, as well as daylighting—must be kept in mind, though, so that window areas are not made too small. In a practical situation, there are often unwanted energy flows with too much thermal energy leaving or entering the building via the window, with a concomitant demand for space heating and cooling; furthermore excessive solar energy may be admitted, which puts additional demand on air conditioning. Present architectural trends tend to increase the window areas, so that the energy issue may become even more pressing in the future.

The radiation part of the heat transfer can be controlled by thin films with a low E_{therm} which, in a multiply-glazed window, should face one of the confined air (or gas) spaces (3,57). In this way the heat transfer across a vertically mounted window can drop from ~ 3 to $\sim 1.5 \text{ Wm}^{-2}\text{K}^{-1}$ for double glazing and from ~ 1.8 to $\sim 1.0 \text{ Wm}^{-2}\text{K}^{-1}$ for triple glazing. Obviously, T_{lum} must be large for these films. The infrared part of the solar radiation—which transmits energy through the glazing but is not needed for vision—can be stopped by a thin film having low transmittance at $0.7 < \lambda < 3 \mu\text{m}$.

These demands have led to the development of two types of thin films, known as “low emittance coatings” (“low-E”) ideally characterized by

$$T(\lambda) = 1 \text{ for } 0.4 < \lambda < 3 \mu\text{m} \quad (7)$$

$$R(\lambda) = 1 \text{ for } 3 < \lambda < 50 \mu\text{m} \quad (8)$$

and “solar control coatings” ideally characterized by

$$T(\lambda) = 1 \text{ for } 0.4 < \lambda < 0.7 \mu\text{m} \quad (9)$$

$$R(\lambda) = 1 \text{ for } 0.7 < \lambda < 50 \mu\text{m} \quad (10)$$

The spectral selectivity inherent in these relationships is of course idealized.

Another, principally different, way to achieve energy efficiency is to use angular selective thin films on the glass (6,120). In this way it is possible to take advantage of the fact that the indoors-outdoors contact across a window normally occurs along near-horizontal lines-of-sight, whereas solar irradiation comes from a small element of solid angle high up in the sky during most of the day. It is also possible to combine spectral and angular selectivity.

8.2 Spectrally selective thin films

Very thin metal films can have properties resembling those in Eqs. (7) to (10). Calculations for extremely thin bulk-like films of Ag, Au, and Cu predict that large values of T_{lum} and T_{sol} can be combined with low values of E_{therm} (121). However, such films cannot be made on glass or polyester. Rather the thin film goes through a number of distinct growth phases, and large-scale coalescence into a metallic state with low E_{therm} requires thicknesses exceeding 10 nm, and then T_{lum} and T_{sol} are limited to about 50 % (122). Most of the transmittance loss is due to reflectance at the film interfaces, implying that the transmittance can be boosted by embedding the metal film between dielectric layers serving, essentially, for antireflection purposes.

Ag has the best optical properties and is used in most applications. Au and Cu tend to produce colored films that are undesired for many architectural applications. TiN can serve as a replacement for Au (123). The dielectric layer can be of several different kinds, such as Bi_2O_3 , SnO_2 , TiO_2 , ZnO , and ZnS . The multilayer structure may also include corrosion-impeding layers, such as Al_2O_3 . Figure 10 illustrates $T(\lambda)$ for three types of thin films based on $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ and deposited onto glass. Depending on the film thicknesses, it is possible to optimize T_{lum} or T_{sol} , while E_{therm} is invariably low. Thus low-E coatings as well as solar control coatings can be made from metal-based thin films. Much of the glass that is used in modern windows and glass facades employ sputter-

deposited films based on Ag (15). These films can only be used under protected conditions, such as in insulated glass units. The film thicknesses are small enough that iridescence—*i.e.*, a rainbow exhibition of colors—is not a problem.

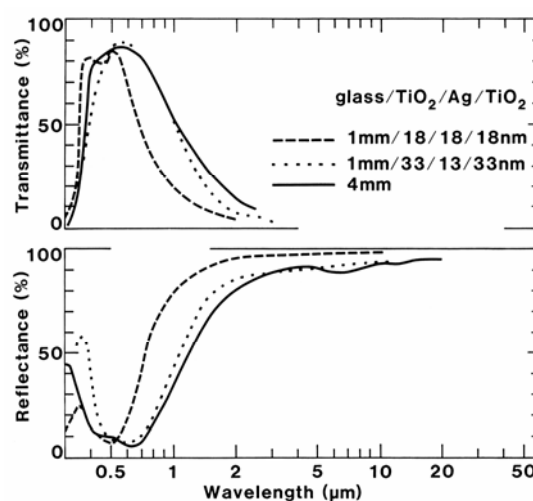


Figure 10. Spectral transmittance and reflectance for glass having thin films based on $\text{TiO}_2/\text{Ag}/\text{TiO}_2$. Thicknesses are given for two of the film stacks. From (1).

Doped oxide semiconductor coatings offer an alternative to the spectrally selective metal-based films just discussed (124,125). The most useful materials are $\text{In}_2\text{O}_3:\text{Sn}$ (126,127), $\text{SnO}_2:\text{F}$ (128), $\text{SnO}_2:\text{Sb}$ (128), and $\text{ZnO}:\text{Al}$ (129). A recently discovered material with similar properties is $\text{TiO}_2:\text{Nb}$ (130). Many other options can be found among the ternary and quaternary oxides as well as among mixtures of the mentioned oxides. Nevertheless, the binary oxides listed above have remained popular. The In-based oxide has the lowest E_{therm} , the Sn-based oxides are most durable, whereas the Zn-based oxide is most popular for some applications (such as in many solar cells). The films are electrically conducting with a minimum resistivity of $\sim 10^{-4} \Omega\text{cm}$ for optimally prepared $\text{In}_2\text{O}_3:\text{Sn}$ (127, 131). Achieving such properties is notoriously difficult, though, and typically requires thermal treatment at $\sim 300^\circ\text{C}$ or above. High-rate deposition appears feasible for $\text{In}_2\text{O}_3:\text{Sn}$ (132). Today’s production of In is small, and most of it is used in $\text{In}_2\text{O}_3:\text{Sn}$ films for display-related applications.

Figure 11 shows $T(\lambda)$ and $R(\lambda)$ in the full $0.3 < \lambda < 50 \mu\text{m}$ range for 0.2- μm -thick films of $\text{In}_2\text{O}_3:\text{Sn}$ (126). The parameter denoted n_e is the density of free electrons, which is directly associated with the amount of Sn doping; in practice this amount is of the order of a few percent. The data in Fig. 11 were computed from a fully quantitative theoretical model of heavily doped semiconductors and gives a clear representation of the salient features developing upon increased doping: an onset of high reflect-

tance in the near-infrared (*i.e.*, a lowering of E_{therm}), band-gap widening tending to enhance T_{sol} , and disappearance of phonon-related absorption features in the thermal infrared (approximately at $20 < \lambda < 30 \mu\text{m}$). The doped semiconductor oxides can be very hard and resistant to corrosion, and they can be applied on glass surfaces exposed to the ambience. The practically useful thicknesses are larger than $\sim 0.2 \mu\text{m}$, implying that thickness variation—which may be difficult to eliminate in practical manufacturing—can lead to aesthetically displeasing iridescence.

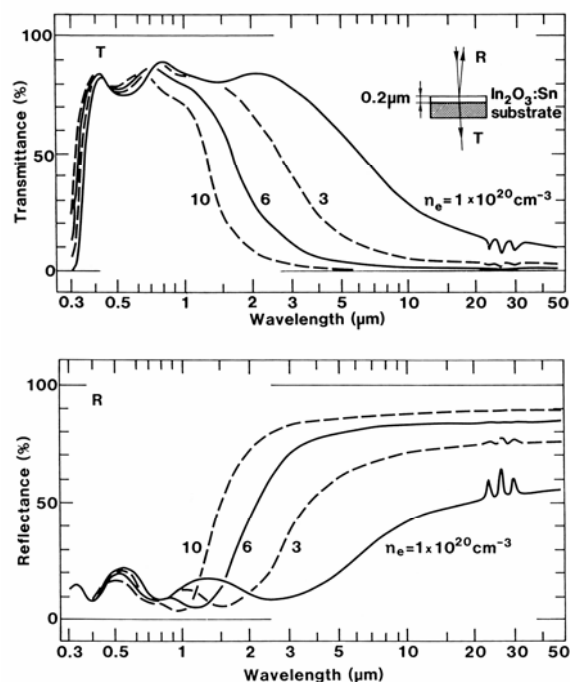


Figure 11. Spectral transmittance (T) and reflectance (R) computed from a fully quantitative model for the optical properties of $\text{In}_2\text{O}_3:\text{Sn}$, using the shown values of film thickness and free-electron density (n_e). From (126).

The refractive index of the doped oxide semiconductors is about 2 for luminous radiation, which tends to limit T_{lum} to $\sim 80\%$. Higher transmittance values can be obtained by antireflection treatment, and T_{lum} can then even exceed the value for uncoated glass. The antireflection layer lowers E_{therm} , but on an insignificant level of a few percent only (133).

8.3 Angular selective thin films

Pronounced angular properties can be used to invoke energy efficiency for glazings, as mentioned above (6,120). Figure 12 illustrates this feature as computed for a five-layer stack of thin films, specifically with two 12-nm-thick Ag films embedded between three SiO_2 films with 120 or 170 nm thickness. Strong angular effects prevail at the

larger of these thicknesses, and T_{sol} is 23 % for normally incident light and as large as 58 % at an incidence angle of 60 degrees.

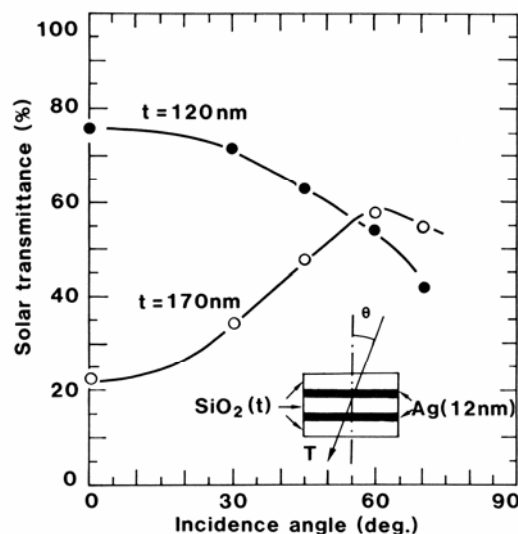


Figure 12. Solar transmittance for thin films of $\text{SiO}_2/\text{Ag}/\text{SiO}_2/\text{Ag}/\text{SiO}_2$ as a function of SiO_2 thickness (t) and incidence angle (θ). From (1).

The data in Fig. 12 are symmetrical around the surface normal of the film. However angular properties that are distinctly different at equal angle on the two sides of the normal can be obtained by the use of films with inclined columnar microstructures (134). Figure 13 shows a polar plot of T_{lum} recorded for a Cr-based film prepared by evaporation under conditions so that the incident flux arrived at the substrate at an almost glancing angle (135). The columns needed for the angular selectivity then tend to form an array inclined in the direction towards the evaporated flux. Sputter deposition can also be used for making angular selective films (136).

9. Coatings for Glazings: Dynamic Properties

Windows and glass facades with variable properties have been the architect's dream for years (15). Such products are now becoming possible by exploiting "chromogenic" materials (7,137). This section discusses electrochromic devices, which are being used in practical windows, albeit as yet on a small scale. A range of other options for dynamic fenestration is then covered more superficially.

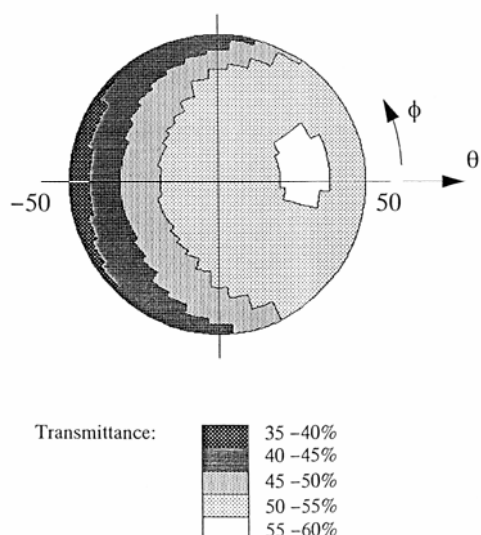


Figure 13. Polar plot of luminous transmittance through an obliquely evaporated Cr-based thin film. Data are given as a function of incidence angle (θ) and azimuthal angle (ϕ). From (135).

9.1 Electrochromic devices

Electrochromic devices are able to vary their throughput of visible light and solar radiation upon electrical charging and discharging using a low voltage (8,138). Thus they can regulate the amount of energy entering through a “smart window” so that the need for air conditioning in a cooled building becomes lessened (9,139). The energy efficiency inherent in this technology can be large, provided that the control strategy is adequate. Additionally, the transmittance regulation can impart glare control as well as, more generally, user control of the indoor environment. The absorptance, rather than the reflectance, is modulated so that the electrochromic devices tend to heat up in their low-transparent state, which has to be considered in a practical window construction. Modulation of E_{therm} is possible in principle, though, and developments of variable-emittance surfaces for temperature control of space vehicles, as well as for other applications, are in progress (140-142).

Figure 14 shows an electrochromic five-layer prototype device that introduces basic design concepts and types of materials (8). A principle kinship to an electrical battery is noteworthy. The central part of the construction is a purely ionic conductor (*i.e.*, an electrolyte), either a thin film or a polymer laminate material; it must be a good conductor for small ions such as H^+ or Li^+ . The electrolyte is in contact with an electrochromic layer and a counter electrode. For a transparent device, the latter must remain non-absorbing irrespective of its ionic content, or it should exhibit electrochromism in a sense opposite to that of the base electrochromic film. This three-layer configuration is positioned between transpa-

rent electrical conductors, normally being doped oxide semiconductors of the kinds discussed above; they are backed by glass or polyester foil. By applying a voltage of a few volts between the outer layers—conveniently obtained from solar cells (143)—ions can be shuttled into or out of the electrochromic film(s) whose optical properties are thereby modified so that the overall optical performance is changed. The voltage needs to be applied only when the transmittance is altered, *i.e.*, the electrochromic devices exhibit open-circuit memory. The time for going between bleached and colored states is largely governed by the electrical resistance of the transparent conducting films. Today’s “smart windows”, with areas of the order of a square meter, require some ten minutes for changing from a bleached state to a moderately colored state. Smaller devices can display much faster dynamics, though.

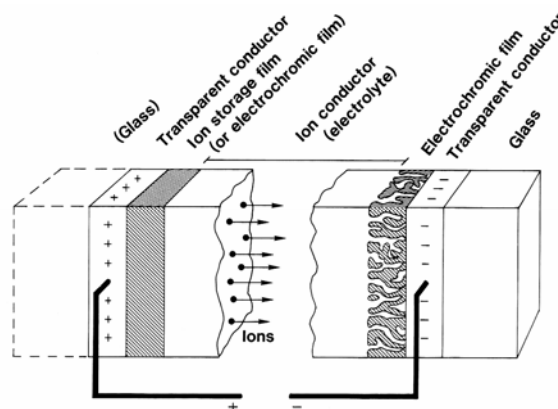


Figure 14. Basic design of an electrochromic device, indicating transport of positive ions under the action of an electric field. From (8).

There are many materials and design issues for practical electrochromic “smart windows”. Electrochromism is found in numerous organic and inorganic materials, the latter mainly being transition metal oxides (8,144-146). Films of WO_3 are used as the base electrochromic layer in almost all devices studied until now. However, many options exist for the counter electrode, with good results having been documented for oxides based on Ce, Co, Ir, Ni, and V, while other designs have used $\text{KFe}^{3+}\text{Fe}^{2+}(\text{CN})_6$ (known as “Prussian Blue”). Additions of Al and Mg to oxides of Ir or Ni can enhance the bleached-state transmittance of the devices, which is important for architectural applications (146,147). In the case of Ir oxide, the additions lead to significant cost reduction. Many alternatives exist for the central electrolyte, which can be an adhesive polymer with high ionic conductivity or—in an all-solid-state approach with superimposed thin films—a hydrous layer of Ta_2O_5 , ZrO_2 , or SiO_2 serving as a conductor for H^+ .

Figure 15 illustrates the optical performance of a laminated polyester-based electrochromic foil device comprising films based on WO_3 and NiO in bleached state and after maximum coloration (139,148). It is seen that T_{lum} can be modulated between 74 and 7%. There is a tradeoff between durability and maximum coloration, though, and a minimum T_{lum} of some 30% may be more adequate for practical applications. Lower T_{lum} s are possible, though, and values below 5% can be reached.

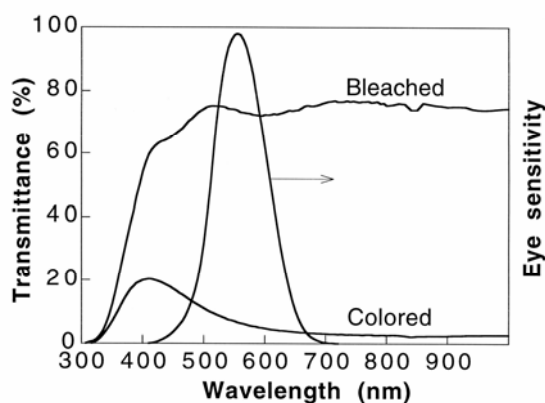


Figure 15. Spectral transmittance through an electrochromic foil including thin films of W-based and Ni-based oxides. Data are shown for fully bleached and colored states. From (148).

9.2 Alternative chromogenic technologies

“Gasochromic” thin films represent an alternative to the electrochromic devices, with specific pros and cons (149). Glass is coated with a WO_3 -based thin film having an extremely thin surface layer of catalytically active Pt. The coated side of the glass is in contact with the gas confined in a carefully sealed double-glazed window. By changing the amount of H_2 in contact with the thin film, it is possible to insert a variable amount of H^+ and the transmittance is then modulated in analogy with the case of the electrochromic device.

Among the many other possibilities to control T_{lum} and T_{sol} electrically, one should note suspended particle devices and phase dispersed liquid crystal devices (150). They have much swifter dynamics than the electrochromic ones but require higher voltages. Rapid technological progress, as well as the proprietary nature of much basic information, makes a detailed comparison of the various techniques futile.

Thermochromism represents another possibility to control T_{sol} in order to create energy efficiency in buildings (151,152). The most interesting material is a thin film based on VO_2 ; it undergoes a structural transition at a certain “critical” temperature τ_c below which the material is semiconducting and relatively non-absorbing in the infrared, and above

which it is metallic and infrared reflecting (153). Figure 16 shows typical data on $T(\lambda)$ above and below τ_c . Bulk-like VO_2 has $\tau_c \approx 68^\circ\text{C}$, which obviously is too high for buildings applications, but τ_c can be decreased to room temperature by additions such as Mo, Nb, or W (154,155).

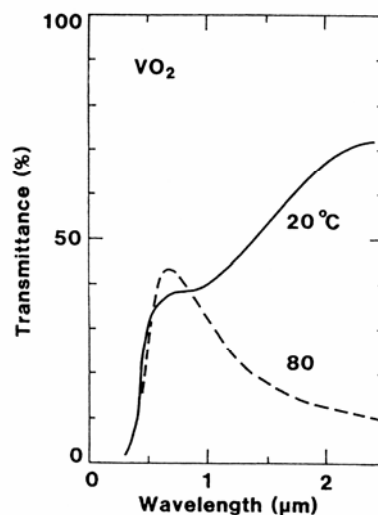


Figure 16. Spectral transmittance through a thermochromic VO_2 film at two temperatures. From (154).

Still another possibility to vary T_{lum} as a result of temperature changes is found among the “cloud gels”, which may be interposed between the panes in a double-glazed window. These are polymers for which “clouding”—*i.e.*, transition to a diffusely scattering state—can set in above a certain τ_c due to a reversible thermochemical dissolution and a thermally induced modification in the lengths of the polymer molecules (156,157).

10. Solar Photocatalysis

Photocatalytically active surfaces can cause the breakdown of organic molecules as well as microorganisms adsorbed on these surfaces under the action of solar irradiation (10,158,159). Thus hazardous or otherwise unpleasant pollutants in air or water can be decomposed into tasteless, odorless, or at least less toxic compounds. Well known photocatalysts are oxides of Cd, Ce, Fe, Sb, Sn, Ti, W, Zn, and Zr, with most work having been devoted to TiO_2 with a crystal structure of the anatase type. The latter oxide is able to use ultraviolet light only. Photocatalytic degradation of water pollutants by use of solar energy or artificial ultraviolet irradiation have been widely investigated (160-163). Deodorization is another possibility, and, for example, a double-glazed window may be transformed into a photo-catalytic reactor with an

outer ultraviolet-transparent pane (*cf.* Fig. 2) and an inner pane with a TiO₂ film.

It may be an advantage to employ not only ultraviolet light but also the less energetic but more abundant visible light for inducing photocatalysis, and transition metal additions to the oxides mentioned above (164), as well as nitrogen, carbon, and fluorine incorporation (165-170), are able to widen the spectral range for photocatalysis.

Photocatalytic decomposition of water into hydrogen and oxygen has been investigated for many years, but this process has turned out to be difficult to accomplish efficiently using solar irradiation (159). Present research includes studies of thin film semiconductor electrodes as well as colloidal solutions of noble-metal-loaded oxide catalysts of many kinds. For gas phase studies, the catalysts have sometimes been covered with NaOH or Na₂CO₃. Sonophotocatalysis, entailing ultrasonic irradiation of the catalyst, can improve the efficiency of water splitting.

11. Conclusions and Futures Perspectives

Many types of solar energy materials are in existence, as discussed in this article. They are in very different stages of development, ranging from established technology, in some cases, to an early explorative phase. The implications of all this work with regard to future developments must be a subjective matter, reflecting one person's experiences and visions. This is how this final part should be interpreted.

The material is presented under four headings, the first being solar energy materials for creating a benign indoor climate in buildings; then follow discussions of solar heating and solar electricity, and some concluding thoughts. Strict boundaries do not exist between the materials-related topics, but the division gives a practical way to organize an extensive material.

11.1 Materials for a benign indoor climate in buildings

Making rational use of energy in the built environment has a large potential for "passive" solar energy applications, thereby yielding large savings of fossil and nuclear fuels. In the industrialized countries, typically 40 % of the energy goes into heating, cooling, lighting, and ventilation of buildings, and to electrical appliances of various kinds. It is obvious that improved solar energy materials could be used to alleviate the situation. Coatings on glass are

of particular importance. In some countries, surface coated glass is employed in double- and multiple-pane windows almost without exception, whereas much less advanced fenestration prevails elsewhere. Irrespective of the detailed situation, coatings with static properties—for providing "low-E" or "solar control", as discussed in Chapter 8—is currently a mature technology, well known to the flat glass manufacturers and unlikely to undergo more than minor improvements in performance. The coatings are either based on ~0.02 μm thick silver or ~0.2 μm thick doped tin oxide. It can be expected that these materials will continue to be used in the future owing to their excellent properties and the large investments in existing manufacturing technology.

The coatings mentioned above combine spectral selectivity with angular dependent properties but are usually only optimized for light with normal incidence. Hence multilayer designs with angular performance tailored to a specific building site and orientation represent options for the future. Angular selectivity, as defined in Sec. 8.3, remains a possibility to be further explored.

Windows with tunable optical properties have long been something of a Holy Grail in "high-tech" architecture. These can be developed using many different approaches involving photochromic, thermochromic, electrochromic, and "gasochromic" materials, as discussed in Chapters 2 and 9. Presently, thin films are used in many cases, but bulk materials such as photochromic glass and polymer and polymer-based cloud gels also offer other, although more remote, possibilities. Electrically regulated electrochromic "smart windows" are, in the author's opinion, particularly interesting in view of their potential to provide user-related operation. Such windows make it possible to combine increased indoor comfort for the occupant of the building (less glare and thermal stress) with large energy efficiency (especially lowered air conditioning load in cooled spaces). Hence there is a strong incentive for their introduction. Durability, optical switching speed, and size constraints constitute an interrelated problem complex which is not fully solved today. However consensus is growing that a satisfactory solution can be achieved. Cost is another concern, but recent progress in manufacturing technology (such as roll-to-roll coating of polymer foil) opens new avenues towards inexpensive products. It should be realized that electrochromism is an enabling technology of relevance for a vast number of applications so there may be multiple roads towards devices eventually used in buildings. Contemplating the combined blessings of comfort and energy savings, the recent advances in technology, and the undeniable business opportunities, it may not be far fetched to envisage a

gradual introduction of electrochromic “smart windows” on a large scale within a few decades—perhaps leading to such windows being the norm rather than exception, in the same way that fenestration with surface coated glass is today the norm for a number of markets. An alternative to electrochromics is “gasochromics”, which relies on exchange of oxidizing and reducing gases and leads to a simple coating configuration but a complex control system.

Solar-driven photocatalysis for cleaning of water and air is a relatively unexplored field, but one with many interesting possibilities. The future of this technology is still uncertain but research is being pursued vigorously, especially in Japan and China.

11.2 Heating and cooling

Solar collectors are in widespread use today. The selectively absorbing surface has been gradually developed and refined during more than two decades, and several such surfaces are industrially viable. The properties are close to the theoretical limits. Manufacturing technologies are now gradually shifted away from electrochemistry-based ones, such as plating or chemical conversion, to vacuum-based alternatives with lower potential environmental impact.

Apart from high-performance solar absorbers, which of course must look black, somewhat less efficient, colored surfaces, which lend themselves well to integration in ordinary architecture, are being developed. Such surfaces can be applied expediently by painting and similar technologies.

Radiative cooling by using the clear sky as a heat sink is, in the author’s opinion, a strangely unexplored field in which materials development can be instrumental. Selectively emitting surfaces, as well as infrared-transparent convection shields, are required. Water-collecting surfaces have attracted even less attention despite their undeniable importance.

11.3 Solar cells

Solar cells for electricity generation are attracting much attention today, not the least among the general public. The cost of solar electricity is still an order of magnitude larger than the cost of conventionally generated electricity, and it is also much higher than for electricity produced by wind and waves. Nevertheless there is no doubt that solar electricity will play an increasing role in off-grid situations and as building components offering special and desired architectural expressions.

Concerning materials, silicon is by far the most widely used absorber at present. Thin film cells, especially those incorporating Cu(In,Ga)(Se,S)_2 ,

may have cost benefits but also involve manufacturing difficulties and materials of unknown long-term availability. The technological persistence of Si in solar cells brings to mind microelectronics, in which this particular material continues to be used despite the existence of other possible options.

A reasonable projection is that the development of solar electricity, as for the case of solar heating, will progress along two paths: one leading to devices with an ever-increasing performance requiring stacked or graded cells based on inorganic materials and capable of using a large part of the solar spectrum, and another path leading to very inexpensive cells with a lower performance and perhaps based on organic materials.

11.4 Some concluding thoughts

An attempt to look into the future is subjective at best, as emphasized above. Nevertheless, some global trends will continue to influence and spur the research on solar energy materials for decades to come. Among these trends are a growing population, which will boost the demand for safe and affordable energy to fulfill its needs and aspirations; a continuing agglomeration of people in mega-cities, which has important effects on human health as well as on micro-climates tending to aggravate the effects of a general global warming; and a progressive depletion of raw materials, which will make it increasingly needed to employ abundant ones. The role of solar energy materials in promoting public health is likely to move from today’s relative obscurity into clear light in the future as devices for air and water cleaning are developed. Solar energy can also be used for maintaining anti-septic surfaces. Dedicated materials research may conceivably lead to solar-driven photocatalysis of water, releasing hydrogen that can be used as a fuel.

Fossil fuels will not run out for many years, but their use is rightly curtailed by environmental concerns—pollution-related and others. Abundant energy from atomic fusion will remain conjectural at least for decades. But solar energy will continue to flow and to be ready for harnessing in the service of mankind to an extent that is limited only by our ingenuity.

References

- [1] C. G. Granqvist, editor, *Materials Science for Solar Energy Conversion Systems*, Pergamon, Oxford, UK, 1991.
- [2] E. Wäckelgård, G. A. Niklasson, and C. G. Granqvist, in *Solar Energy: The State of the Art*, edited by J. Gordon, James & James, London, UK, 2001, Chapter 3, pp. 109-144.

- [3] K. G. T. Hollands, J. L. Wright, and C. G. Granqvist, in *Solar Energy: The State of the Art*, edited by J. Gordon, James & James, London, UK, 2001, Chapter 2, pp. 29-107.
- [4] W. Platzer and V. Wittwer, in C. G. Granqvist, *Materials Science for Solar Energy Conversion Systems*, Pergamon, Oxford, UK, 1991, Chapter 3, pp. 44-69.
- [5] C. G. Granqvist and T. S. Eriksson, in *Materials Science for Solar Energy Conversion Systems*, edited by C. G. Granqvist, Pergamon, Oxford, UK, 1991, Chapter 6, pp. 168-203.
- [6] G. W. Mbise, D. Le Bellac, G. A. Niklasson, and C. G. Granqvist, *J. Phys. D: Appl. Phys.* **30**, 2103 (1997).
- [7] C. M. Lampert and C. G. Granqvist, editors, *Large-Area Chromogenics: Materials and Devices for Transmittance Control*, The International Society for Optical Engineering, Bellingham, U.S.A., 1990, Vol. IS4.
- [8] C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier, Amsterdam, The Netherlands, 1995 (reprinted 2002).
- [9] A. Azens, E. Avendaño, J. Backholm, L. Berggren, G. Gustavsson, R. Karmhag, G. A. Niklasson, A. Roos, and C. G. Granqvist, *Mater. Sci. Engr. B* **119**, 214 (2005).
- [10] A. Fujishima, K. Hashimoto and T. Watanabe, *TiO₂ Photocatalysis*, Bkc Tokyo, Japan, 1999.
- [11] C. G. Granqvist, *Adv. Mater.* **15**, 1789 (2003).
- [12] C. G. Granqvist, *Appl. Opt.* **20**, 2606 (1981).
- [13] C. G. Granqvist, *Spectrally Selective Surfaces for Heating and Cooling Applications*, The International Society for Optical Engineering, Bellingham, U.S.A., 1989, Vol. TT1.
- [14] H. Bach and N. Neuroth, editors, *The Properties of Optical Glass*, Springer, Berlin, Germany, 1995.
- [15] M. Wigginton, *Glass in Architecture*, Phaidon, London, UK, 1996.
- [16] H. J. Hoffman, in *Large-Area Chromogenics: Materials and Devices for Transmittance Control*, edited by C. M. Lampert and C. G. Granqvist, The International Society for Optical Engineering, Bellingham, U.S.A., 1990, Vol. IS4, pp. 86-101.
- [17] N. Y. C. Chu, in *Large-Area Chromogenics: Materials and Devices for Transmittance Control*, edited by C. M. Lampert and C. G. Granqvist, The International Society for Optical Engineering, Bellingham, U.S.A., 1990, Vol. IS4, pp. 102-120.
- [18] J. H. Weaver, C. Krafka, D. W. Lynch, and E. E. Koch, *Physik Daten / Physics Data: Optical Properties of Solids*, Fachinformationszentrum Energi, Physik, Mathematik GmbH, Karlsruhe, Germany, 1981, Vol. 18.
- [19] E. D. Palik, editor, *Handbook of Optical Constants of Solids*, Academic, San Diego, U.S.A., 1997.
- [20] A. Thelen, *Design of Optical Interference Coatings*, McGraw-Hill, New York, U.S.A., 1989.
- [21] J. A. Dobrowolski, in M. Bass, editor-in-chief, *Handbook of Optics*, second edition, McGraw-Hill, New York, U.S.A., 1995, Vol. 1, Chapter 42, pp. 42.1-42.130.
- [22] J. D. Rancourt, *Optical Thin Films: User Handbook*, SPIE Press, Bellingham, U.S.A., 1996, Vol. PM37.
- [23] H. K. Pulker, *Coatings on Glass*, second edition, Elsevier, Amsterdam, The Netherlands, 1999.
- [24] H. J. Gläser, *Large Area Glass Coating*, von Ardenne Anlagentechnik GmbH, Dresden, Germany, 2000.
- [25] L. I. Maissel and R. Glang, editors, *Handbook of Thin Film Technology*, McGraw-Hill, New York, U.S.A., 1970.
- [26] J. L. Vossen and W. Kern, editors, *Thin Film Processes*, Academic, New York, U.S.A., 1978.
- [27] R. F. Bunshah, J. M. Blocher, Jr., T. D. Bonifield, J. G. Fish, P. B. Ghatge, B. E. Jacobson, D. M. Mattox, G. E. McGuire, M. Schwartz, J. A. Thornton, and R. C. Tucker, Jr., *Deposition Technologies for Films and Coatings*, Noyes, Park Ridge, U.S.A., 1982.
- [28] D. L. Smith, *Thin-Film Deposition*, McGraw-Hill, New York, U.S.A., 1995.
- [29] J. E. Mahan, *Physical Vapor Deposition of Thin Films*, Wiley, New York, U.S.A., 2000.
- [30] B. Chapman, *Glow Discharge Processes*, Wiley, New York, U.S.A., 1980.
- [31] J. J. Cuomo, S. M. Rossnagel, and H. R. Kaufman, editors, *Handbook of Ion Beam Process Technology*, Noyes, Park Ridge, U.S.A., 1989.
- [32] M. Konuma, *Film Deposition by Plasma Techniques*, Springer, Berlin, Germany, 1992.
- [33] K. Wasa and S. Hayakawa, *Handbook of Sputter Deposition Technology*, Noyes, Park Ridge, U.S.A., 1992.
- [34] L. Holland, *Vacuum Deposition of Thin Films*, Chapman & Hall, London, UK, 1956.
- [35] R. Glang, in L. I. Maissel and R. Glang, editors, *Handbook of Thin Film Technology*, McGraw-Hill, New York, U.S.A., 1970, Chapter 1, pp. 1.3-1.130.
- [36] L. C. Klein, editor, *Sol-Gel Optics: Processing and Applications*, Kluwer, Dordrecht, The Netherlands, 1994.
- [37] C. E. Morosanu, *Thin Films by Chemical Vapour Deposition*, Elsevier Science, Amsterdam, The Netherlands, 1990; *Thin Films Science and Technology*, Vol. 7.
- [38] H. O. Pierson, *Handbook of Chemical Vapor Deposition: Principles, Technology, and Applications*, second edition, Noyes, Park Ridge, U.S.A., 1999.
- [39] F. A. Lowenheim, in J. L. Vossen and W. Kern, editors, *Thin Film Processes*, Academic, New York, U.S.A., 1978, Chapter III-1, pp. 209-256.
- [40] S. Wernick and R. Pinner, *The Surface Treatment and Finishing of Aluminium and Its Alloys*, fourth edition, Draper, Teddington, UK, 1972, Vols. 1 and 2.
- [41] P. Nostell, A. Roos, and B. Karlsson, *Thin Solid Films* **351**, 170 (1999).
- [42] G. L. Harding, *Solar Energy Mater.* **12**, 169 (1985).
- [43] G. L. Harding, I. Hamberg, and C. G. Granqvist, *Solar Energy Mater.* **12**, 187 (1985).
- [44] K. J. Cathro, D. C. Constable, and T. Solaga, *Solar Energy* **32**, 573 (1984).
- [45] G. K. Chinyama, A. Roos, and B. Karlsson, *Solar Energy* **50**, 105 (1993).
- [46] C. C. Striemer and P. M. Fauchet, *Appl. Phys. Lett.* **81**, 2980 (2002).
- [47] A. Gombert, W. Glaubitt, K. Rose, J. Dreiholz, C. Zanke, B. Bläsi, A. Heinzl, W. Horbelt, D. Sporn, W. Döll, V. Wittwer, and J. Luther, *Solar Energy* **62**, 177 (1998).
- [48] R. Siegel and J. R. Howell, *Thermal Radiative Heat Transfer*, second edition, McGraw-Hill, New York, U.S.A., 1981.
- [49] W. M. Rohsenow, J. P. Hartnett, and, E. N. Ganić, editors, *Handbook of Heat Transfer Fundamentals*, second edition, McGraw-Hill, New York, U.S.A., 1985.
- [50] W. J. Platzer, *Solar Energy* **49**, 351 (1992).
- [51] W. J. Platzer, *Solar Energy* **49**, 359 (1992).
- [52] J. Fricke, editor, *Aerogels*, Springer Proceedings in Physics, Springer, Berlin, 1986, Vol. 6.
- [53] J. Fricke, *Sci. Am.* **258** (5), 92 (1988).
- [54] K. Duer and S. Svensen, *Solar Energy* **63**, 259 (1998).

- [55] M. Reim, W. Körner, J. Manara, S. Korder, M. Arduini-Schuster, H.-P. Ebert, and J. Fricke, *Solar Energy* **79**, 131 (2005).
- [56] P. H. Tewari, A. J. Hunt, J. G. Lieber, and K. Lofftus, in *Aerogels*, edited by J. Fricke, Springer Proceedings in Physics, Springer, Berlin, 1986, Vol. 6, pp. 142-147.
- [57] C. G. Granqvist, in *Materials Science for Solar Energy Conversion Systems*, edited by C. G. Granqvist, Pergamon, Oxford, 1991, Chapter 5, pp. 106-167.
- [58] T. S. Eriksson, C. G. Granqvist, and J. Karlsson, *Solar Energy Mater.* **16**, 243 (1987).
- [59] R. E. Collins and T. M. Simko, *Solar Energy* **62**, 189 (1998).
- [60] G. L. Morrison, in *Solar Energy: The State of the Art*, edited by J. Gordon, James & James, London, UK, 2001, Chapter 4, pp. 145-221.
- [61] G. L. Morrison, in *Solar Energy: The State of the Art*, edited by J. Gordon, James & James, London, UK, 2001, Chapter 5, pp. 223-289.
- [62] B. O. Seraphin, in *Solar Energy Conversion: Solid-State Physics Aspects*, edited by B. O. Seraphin, Springer, Berlin, Germany, 1979, Topics in Applied Physics, Vol. 31, Chapter 2, pp. 5-55.
- [63] M. M. Koltun, *Selektivnye Opticheskie Poverkhnosti Preobrazovatelei Solnechnoi Energii*, Izdatel'stvo "Nauka", Moscow, Soviet Union, 1979 [*Selective Optical Surfaces for Solar Energy Converters*, Allerton, New York, U.S.A., 1981]
- [64] O. P. Agnihotri and B. K. Gupta, *Solar Selective Surfaces*, Wiley, New York, U.S.A., 1981.
- [65] G. A. Niklasson and C. G. Granqvist, *J. Mater. Sci.* **18**, 3475 (1983).
- [66] R. A. Buhrman, in *Advances in Solar Energy: An Annual Review of Research and Development*, edited by K. W. Böer, Plenum, New York, U.S.A., 1986, Vol. 3, pp. 207-282.
- [67] G. A. Niklasson and C. G. Granqvist, in *Materials Science for Solar Energy Conversion Systems*, edited by C. G. Granqvist, Pergamon, Oxford, 1991, Chapter 4, pp. 70-105.
- [68] A. Sievers, in *Solar Energy Conversion: Solid-State Physics Aspects*, edited by B. O. Seraphin, Springer, Berlin, Germany, 1979, Topics in Applied Physics, Vol. 31, Chapter 3, pp. 57-114.
- [69] R. A. Buhrman and H. G. Craighead, in *Solar Materials Science*, edited by L. E. Murr, Academic, New York, U.S.A., 1980, pp. 277-317.
- [70] A. Ignatiev, in *Solar Materials Science*, edited by L. E. Murr, Academic, New York, U.S.A., 1980, pp. 151-170.
- [71] G. A. Niklasson and C. G. Granqvist, *J. Appl. Phys.* **55**, 3382 (1984).
- [72] G. A. Niklasson and C. G. Granqvist, in *Contribution in Cluster Physics to Materials Science and Technology*, edited by J. Davenas and P. M. Rabette, Nijhoff, Dordrecht, The Netherlands, 1986, pp. 539-600.
- [73] Å. Andersson, O. Hunderi, and C. G. Granqvist, *J. Appl. Phys.* **51**, 754 (1980).
- [74] M. Lazarov, R. Sizmann, and U. Frei, *Proc. Soc. Photo-Opt. Instrum. Engr.* **2017**, 345 (1993).
- [75] E. Wäckelgård and G. Hultmark, *Solar Energy Mater. Solar Cells* **54**, 165 (1998).
- [76] S. Zhao and E. Wäckelgård, *Solar Energy Mater. Solar Cells*, to be published (2005).
- [77] Q.-C. Zhang, *J. Phys. D: Appl. Phys.* **31**, 355 (1998).
- [78] Q.-C. Zhang, K. Zhao, B.-C. Zhang, L.-F. Wang, Z.-L. Chen, D.-Q. Lu, D.-L. Xie, Z.-J. Zhou, and B.-F. Li, *J. Vac. Sci. Technol. A* **16**, 628 (1998).
- [79] W. Graf, R. Brucker, M. Köhl, T. Tröscher, V. Wittwer, and L. Herlitze, *J. Non-Cryst. Solids* **218**, 380 (1997).
- [80] T. Boström, G. Westin, and E. Wäckelgård, to be published.
- [81] M. Lanxner and Z. Elgat, *Proc. Soc. Photo-Opt. Instrum. Engr.* **1272**, 240 (1990).
- [82] Z. C. Orel, *Solar Energy Mater. Solar Cells* **57**, 291 (1999).
- [83] T. S. Eriksson and C. G. Granqvist, *Appl. Opt.* **21**, 4381 (1982).
- [84] C. G. Granqvist and A. Hjortsberg, *J. Appl. Phys.* **52**, 4205 (1981).
- [85] T. S. Eriksson and C. G. Granqvist, *J. Appl. Phys.* **60**, 2081 (1986).
- [86] E. M. Lushiku and C. G. Granqvist, *Appl. Opt.* **23**, 1835 (1984).
- [87] N. A. Nilsson, T. S. Eriksson, and C. G. Granqvist, *Solar Energy Mater. Solar Cells* **12**, 327 (1985).
- [88] T. M. J. Nilsson, G. A. Niklasson, and C. G. Granqvist, *Solar Energy Mater. Solar Cells* **28**, 175 (1992).
- [89] Y. Mastai, Y. Diamant, S. T. Aruna, and A. Zaban, *Langmuir* **17**, 7118 (2001).
- [90] T. M. J. Nilsson, *Optical Scattering Properties of Pigmented Foils for Radiative Cooling and Water Condensation: Theory and Experiment*, unpublished Ph. D. Thesis, Chalmers University of Technology, Göteborg, Sweden, 1994.
- [91] M. Muselli, D. Beysens, J. Marcillat, I. Milimouk, T. Nilsson, and A. Louche, *Atmospheric Res.* **64**, 297 (2002).
- [92] A. L. Fahrenbuch and R. H. Bube, *Fundamentals of Solar Cells*, Academic, New York, U.S.A., 1983.
- [93] L. D. Partain, editor, *Solar Cells and Their Application*, Wiley, New York, U.S.A., 1995.
- [94] R. H. Bube, *Photovoltaic Materials*, Imperial College, London, UK, 1998.
- [95] S. K. Deb and B. Sopori, in *Handbook of Thin Film Devices*, edited by M. H. Francombe (Academic, New York, U.S.A., 2002), Vol. 2, pp. 311-362.
- [96] M. A. Green, in *Solar Energy: The State of the Art*, edited by J. Gordon, James & James, London, UK, 2001, Chapter 6, pp. 291-355.
- [97] M. A. Green, *Solar Cells: Operating Principles, Technology, and System Applications*, second edition, Bridge Printery, Sydney, Australia, 2002.
- [98] G. P. Smestad, *Optoelectronics of Solar Cells*, SPIE Press, Bellingham, U.S.A., 2002, Vol. PM115.
- [99] A. Goetzberger, J. Luther, and G. Willeke, *Solar Energy Mater. Solar Cells* **74**, 1 (2002).
- [100] A. Goetzberger, C. Hebling, and H.-W. Schock, *Mater. Sci. Engr. R* **40**, 1 (2003).
- [101] I. Iles and Y. C. M. Yeh, in *Solar Cells and Their Applications*, edited by L. D. Partain, Wiley, New York, U.S.A., 1995.
- [102] T. L. Chu and S. S. Chu, *Solid-State Electronics* **38**, 533 (1995).
- [103] V. Meyers and R. W. Birkmire, *Progr. Photovoltaics Res. Appl.* **3**, 393 (1995).
- [104] A. Romeo, M. Terheggen, D. Abou-Ras, D. L. Bätzner, F.-J. Haug, M. Kälin, D. Rudmann, and A. N. Tiwari, *Prog. Photovoltaics Res. Appl.* **12**, 93 (2004).

- [105] M. A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Schwartzlander, F. Hasoon, and R. Noufi, *Progr. Photovoltaics Res. Appl.* **7**, 311 (1999).
- [106] B. Stanbery, *Crit. Rev. Solid State Mater. Sci.* **27**, 73 (2002).
- [107] J. Nelson, *Current Opinions Solid State Mater. Sci.* **6**, 87 (2002).
- [108] J.-M. Nunzi, *Comptes Rendues Phys.* **3**, 53 (2002).
- [109] T. J. Coutts, *Renewable Sustainable Energy Rev.* **3**, 77 (1999).
- [110] T. J. Coutts, *Solar Energy Mater. Solar Cells* **66**, 443 (2001).
- [111] H. Yugami, H. Sasa, and M. Yamaguchi, *Semicond. Sci. Technol.* **18**, S239 (2003).
- [112] A. Hagfeldt and M. Grätzel, *Chem. Rev.* **95**, 49 (1995).
- [113] A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.* **33**, 269 (2000).
- [114] A. Zaban, in *Nanocrystalline Metals and Oxides: Selected Properties and Applications*, edited by P. Knauth and J. Schoonman, Kluwer, Dordrecht, 2002, pp. 209-224.
- [115] M. Gómez, J. Lu, E. Olsson, A. Hagfeldt and C. G. Granqvist, *Solar Energy Mater. Solar Cells* **64**, 385 (2000).
- [116] H. Tributsch, *Coord. Chem. Rev.* **248**, 1511 (2004).
- [117] M. Mwamburi, E. Wackelgard, A. Roos, and R. Kivaisi, *Appl. Opt.* **41**, 2428 (2002).
- [118] B. A. Andersson, *Progr. Photovoltaics. Res. Appl.* **8**, 61 (2000).
- [119] U. Schwartz-Schampera and P. M. Herzig, *Indium: Geology, Mineralogy, and Economics*, Springer, Berlin, Germany, 2002.
- [120] G. B. Smith, S. Dligatch, R. Sullivan, and M. G. Hutchins, *Solar Energy* **62**, 229 (1998).
- [121] E. Valkonen, A. Roos, and C.-G. Ribbing, *Solar Energy* **32**, 211 (1984).
- [122] G. B. Smith, G. A. Niklasson, J. S. E. M. Svensson, and C. G. Granqvist, *J. Appl. Phys.* **59**, 571 (1986).
- [123] Y. Claeson, M. Georgson, A. Roos, and C.-G. Ribbing, *Solar Energy Mater.* **20**, 455 (1990).
- [124] D. S. Ginley and C. Bright, *MRS Bull.* **24** (8), 15 (2000).
- [125] P. P. Edwards, A. Porch, M. O. Jones, D. V. Morgan, and R. M. Perks, *Dalton Trans.* (19) 2995 (2004).
- [126] I. Hamberg and C. G. Granqvist, *J. Appl. Phys.* **60**, R123 (1986).
- [127] A. Hultåker and C. G. Granqvist, *Thin Solid Films* **411**, 1 (2002).
- [128] B. Stjerna, E. Olsson, and C. G. Granqvist, *J. Appl. Phys.* **76**, 3797 (1994).
- [129] Z.-C. Jin, I. Hamberg, and C. G. Granqvist, *J. Appl. Phys.* **64**, 5117 (1988).
- [130] Y. Furubayashi, T. Hitosugi, Y. Yamamoto, K. Inaba, G. Kinoda, Y. Hirose, T. Shimada, and T. Hasegawa, *Appl. Phys. Lett.* **86**, 252101 (2005).
- [131] F. O. Adurodiya, H. Izumi, T. Ishihara, H. Yoshiooka, M. Motoyama, and K. Murai, *Vacuum* **67**, 209 (2002).
- [132] T. Minami, I. Ida, and T. Miyata, *Thin Solid Films* **416**, 92 (2002).
- [133] E. Hammarberg and A. Roos, *Thin Solid Films* **442**, 222 (2003).
- [134] G. W. Mbise, G. A. Niklasson, and C. G. Granqvist, *J. Appl. Phys.* **77**, 2816 (1995).
- [135] S. Palmer, G. W. Mbise, G. A. Niklasson, and C. G. Granqvist, *Solar Energy Mater. Solar Cells* **44**, 397 (1996).
- [136] D. Le Bellac, G. A. Niklasson, and C. G. Granqvist, *J. Appl. Phys.* **78**, 2894 (1995).
- [137] C. M. Lampert, *Mater. Today* (3), 28 (2004).
- [138] P. M. S. Monk, R. J. Mortimer, and D. R. Rosseinsky, *Electrochromism: Fundamentals and Applications*, VCH, Weinheim, Germany, 1995.
- [139] A. Azens and C. G. Granqvist, *J. Solid State Electrochem.* **7**, 64 (2003).
- [140] E. B. Francke, C. L. Trimble, J. S. Hale, M. Schubert, and J. A. Woollam, *J. Appl. Phys.* **88**, 5777 (2000).
- [141] M. G. Hutchins, N. S. Butt, A. J. Topping, J. Galleo, P. Milne, D. Jeffrey, and I. Brotherston, *Electrochim. Acta* **46**, 1983 (2001).
- [142] A.-L. Larsson and G. A. Niklasson, *Mater. Lett.* **58**, 2517 (2004).
- [143] C. M. Lampert, *Solar Energy Mater. Solar Cells* **76**, 489 (2003).
- [144] C. G. Granqvist, *Solar Energy Mater. Solar Cells* **60**, 201 (2000).
- [145] C. G. Granqvist, E. Avendaño, and A. Azens, *Thin Solid Films* **442**, 201 (2003).
- [146] A. Azens and C. G. Granqvist, *Appl. Phys. Lett.* **81**, 928 (2002).
- [147] E. Avendaño, A. Azens, G. A. Niklasson, and C.G. Granqvist, *Solar Energy Mater. Solar Cells* **84**, 337 (2004).
- [148] C. G. Granqvist, *Smart Mater. Bull.* (10), 9 (2002).
- [149] A. Georg, W. Graf, R. Neumann, and V. Wittwer, *Solid State Ionics* **127**, 319 (2000).
- [150] P. G. Montgomery, Jr., in *Large-Area Chromogenics: Materials and Devices for Transmittance Control*, edited by C. M. Lampert and C. G. Granqvist, The International Society of Optical Engineering, Bellingham, U.S.A., 1990, Vol. IS4, pp. 577-606.
- [151] G. V. Jorgenson and J. C. Lee, in *Large-Area Chromogenics: Materials and Devices for Transmittance Control*, edited by C. M. Lampert and C. G. Granqvist, The International Society of Optical Engineering, Bellingham, U.S.A., 1990, Vol. IS4, 142-159.
- [152] J. H. Day and R. D. Wilett, in *Large-Area Chromogenics: Materials and Devices for Transmittance Control*, edited by C. M. Lampert and C. G. Granqvist, The International Society of Optical Engineering, Bellingham, U.S.A., 1990, Vol. IS4, 122-141.
- [153] S. M. Babulanam, T. S. Eriksson, G. A. Niklasson and C. G. Granqvist, *Solar Energy Mater.* **16**, 347 (1987).
- [154] M. A. Sobhan, R. T. Kivaisi, B. Stjerna and C. G. Granqvist, *Solar Energy Mater. Solar Cells* **44**, 451 (1996).
- [155] T. D. Manning, I. P. Parkin, M. E. Pemble, D. Sheel, and D. Vamardou, *Chem. Mater.* **16**, 744 (2004).
- [156] H. R. Wilson and W. Eck, *Solar Energy Mater. Solar Cells* **31**, 197 (1993).
- [157] W. Eck, H. R. Wilson, and H.-J. Cantow, *Adv. Mater.* **7**, 800 (1995).
- [158] D. Y. Goswami, in *Advances in Solar Energy: An Annual Review of Research and Development*, edited by K. W. Böer, American Solar Energy Society, Boulder, U.S.A., 1995, Vol. 10, pp. 165-209.
- [159] M. Kaneko and I. Okuda, editors, *Photocatalysis: Science and Technology*, Springer, Berlin, Germany, 2002.
- [160] D. Bahnemann, *Solar Energy* **77**, 445 (2004)

- [161] S. Devipriya and S. Yesodharan, *Solar Energy Mater. Solar Cells* **86**, 309 (2005).
- [162] P. Fernández, J. Blanco, C. Sichel, and S. Malato, *Catalysis Today* **101**, 345 (2005).
- [163] A. V. Vorontsov, D. V. Kozlov, P. G. Smirnotis, and V. N. Parmon, *Kinetika i Kataliz* **46**, 203 (2005) [*Kinetics Catalysis* **46**, 189 (2005)].
- [164] M. Iwasaki, M. Hara, H. Kawada and S. Ito, *J. Colloid Interface. Sci.* **224**, 202 (2000).
- [165] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, *Science* **293**, 296 (2001).
- [166] S. U. M. Khan, M. Al-Shahry, and W. B. Ingler, Jr., *Science* **297**, 2243 (2002).
- [167] K. Nukumizu, J. Nunoshige, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen, *Chem. Lett.* **32**, 196 (2003).
- [168] T. Lindgren, J. M. Mwabora, E. Avendaño, J. Jons-son, A. Hoel, C. G. Granqvist, and S.-E. Lindquist, *J. Phys. Chem. B* **107**, 5709 (2003).
- [169] G. Romualdo Torres, T. Lindgren, J. Lu, C. G. Granqvist, and S.-E. Lindquist, *J. Phys. Chem. B* **108**, 5995 (2004).
- [170] J. M. Mwabora, T. Lindgren, E. Avendaño, T. F. Jaramillo, J. Lu, S.-E. Lindquist, and C. G. Granqvist, *J. Phys. Chem. B* **108**, 20193 (2004).