Solar energy materials for thermal applications: A primer

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ABSTRACT

Solar energy materials have properties that are tailored to the characteristics of the electromagnetic radiation in our natural surroundings, specifically its spectral distribution, angle of incidence and intensity. This tailoring can be made with regard to solar irradiation, thermal emission, atmospheric absorption, visible light, photosynthetic efficiency and more. Solar energy materials can be of many kinds, e.g., metallic, semiconducting, dielectric, glassy, polymeric, gaseous, etc. In particular, thin surface coatings of solar energy materials may exhibit the desired properties in their own right or may yield such properties when backed by an appropriate substrate. This article surveys a number of topics related to thermal applications such as solar thermal converters, transparent thermal insulators, devices for radiative cooling by exposure to the clear sky, and windows and glass facades with static or dynamic properties. The purpose of the present paper is to provide a bird's eye view over a wide class of materials of rising importance rather than giving detailed accounts of highly specialized topics.

1. Introduction

Solar energy materials for thermal applications have optical properties that make them well adapted for utilizing solar energy and for reaching energy efficiency, especially in the built environment [1,2]. This class of materials is of growing importance, which is connected with the fact that energy production today (2018)—and for decades to come—is dominated by the burning of fossil fuels with accompanying massive injection of carbon dioxide into the air. Specifically, the CO_2 concentration has risen from ~315 ppm at the end of the 1950s so that it now exceeds ~400 ppm, with no change of this trend yet in sight [3]. It is widely understood that growing amounts of atmospheric CO_2 lead to global climate change and rising sea levels [4] and that there are numerous secondary and often harmful side effects. Another important trend of significance for solar energy materials is the rapid growth of the global population [5] and its ongoing accumulation in mega-cities [6] whose local climate is altered and often considerably warmer than in surrounding rural regions [7].

Solar energy materials for thermal applications can be prepared and used in many ways, and here are some glimpses of the contents of this paper, with *italicized* key technologies and terms: *Solar thermal collectors* for hot fluid production make use of surfaces that are strong absorbers of solar energy, and energy efficiency is obtained via low thermal emittance, i.e., high reflectance for wavelengths where thermal radiation takes place [8,9]. These solar absorbers are often put behind *transparent convection shields* that let through solar irradiation. A key property of materials for thermal solar energy is frequently *spectral*

selectivity, which means that the optical properties must differ qualitatively among different wavelength ranges. Spectral selectivity can also be employed for *energy efficient glazing*—a term referring to buildings and embracing both windows and glass facades—either for obtaining good thermal insulation together with high solar energy inlet or for having good transmittance of visible light together with minimum solar energy ingress [2,10]. Other kinds of spectral selectivity can be used to accomplish "*radiative cooling*" under a clear sky, and temperatures lying much below those of the ambient air can be obtained by exploiting surfaces that emit radiation at wavelengths for which the atmosphere is transparent while the same surfaces exhibit low absorptance at other wavelengths [2]. Materials with *strongly angular-dependent optical properties* [11] yield alternative options for optimizing solar energy utilization. For example, such materials can be employed in glazing—even non-vertical—to achieve high transmittance along near-horizontal lines-of-sight and low transmittance at off-horizontal angles [12]. The materials mentioned so far are characterized by static properties, but there are also many solar-energy-related uses of "chromogenic" materials [13] whose properties can be varied and adjusted to changing properties of their surroundings. *Electrochromic* and *thermochromic* materials, and devices based on them, are especially significant and provide roads toward future architecture with "dynamic" buildings able to combine high energy efficiency with excellent indoor comfort and convenience [14–16]. The characteristic property of these materials is that the absorptance or reflectance can be altered by insertion and extraction of electrical charge or by temperature changes. Many of the solar energy materials for thermal applications make good use of
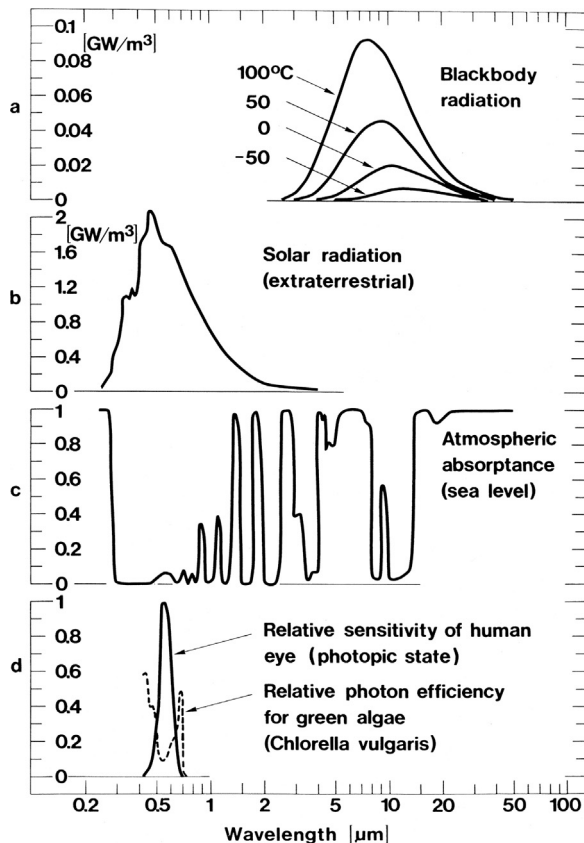

Fig. 1. Spectra for (a) black-body radiation at four temperatures, (b) solar radiation outside the earth's atmosphere, (c) typical absorptance vertically across the full atmosphere, and (d) relative sensitivity of the human eye and relative photosynthetic efficiency for green plants [20].

thin surface coatings (*thin films*) backed by transparent or reflecting substrates, and thin film deposition technology is important. A "primer" on the latter topic was published some years ago [17] and can be viewed as a companion to the present article.

It should be emphasized that solar energy materials are of importance not only for thermal applications, which this tutorial paper is focused on, but also have numerous non-thermal applications related to photovoltaics [18], cleaning of water and air by solar-driven photocatalysis [19] and, in general, for solar-energy-effected chemical reactions. Furthermore it should be noted that this article does not list more than a tiny fraction of the references to work on solar energy materials for thermal applications, but an attempt has been made to include broad-coverage review papers, with the object of providing general overviews, as well as a selection of recent papers in order to give some flavor of ongoing endeavors. When appropriate, references are to books and book chapters which, arguably, are less ephemeral than journal publications.

2. The radiation around us: a look into Nature's rule-book for solar energy materials

Fig. 1 gives a unified presentation of the electromagnetic radiation of our ambience [20]. Most fundamental is *thermal radiation*, which is emitted by everything around us and by ourselves. This radiation is conveniently introduced via the ideal black-body whose spectrum—known as the Planck spectrum—is defined once the temperature is specified. Planck's law is a consequence of the quantum nature of radiation. Panel (a) in Fig. 1 illustrates such spectra pertaining to four temperatures. The vertical scale states power per unit area and wavelength increment (hence the unit GWm^{-3}). The spectra appear bell-

shaped and lie in the $2 < \lambda < 100 \mu m$ range of wavelengths. The peak in the spectrum moves toward shorter wavelength as the temperature rises; the peak is at ~10 μm for room temperature. The actual thermal radiation from a material is obtained by multiplying the Planck spectrum by a numerical factor, known as the emittance, which is less than unity. The emittance is wavelength dependent for all real materials.

Panel (b) in Fig. 1 shows a spectrum for *solar radiation* outside the earth's atmosphere. This radiation displays a bell-shape defining the sun's surface temperature, which is ~5500 °C. It should be noted that the solar spectrum is confined to $0.25 < \lambda < 3 \mu m$, which implies that there is virtually zero overlap with thermal radiation. Therefore one can have surfaces with properties that are completely different for thermal and solar radiation. The integrated area under the solar spectrum gives the "solar constant" ($1353 \pm 21 \ Wm^{-2}$). This is the maximum power density on a surface perpendicular to the sun if there is no absorption or light scattering in the atmosphere.

Solar energy conversion systems are normally at ground level, and it is obviously interesting to contemplate how *atmospheric absorption* affects solar irradiation and net thermal emission. Panel (c) of Fig. 1 shows a characteristic absorption spectrum vertically across the full atmosphere under typical clear-sky conditions. This spectrum is complex and contains bands with high absorption—mainly due to water vapor, carbon dioxide and ozone—and bands with high transparency. Most of the impinging solar energy can reach the ground, and only some ultraviolet ($\lambda < 0.4 \mu m$) and infrared ($\lambda > 0.7 \mu m$) radiation is absorbed. Maximum power density at right angles to the sun is ~1000 Wm^{-2}. Thermal radiation from surfaces under a clear sky is strongly absorbed, except within the $8 < \lambda < 13 \mu m$ interval where the transmittance is large as long as the humidity is not too high.

Finally, panel (d) of Fig. 1 shows two highly relevant biological properties. The solid curve illustrates the relative *sensitivity of the human eye* under daylight conditions; the bell-shaped curve is in the $0.4 < \lambda < 0.7 \mu m$ range with a peak at $0.55 \mu m$. It is evident that much of the solar energy is invisible infrared radiation. The dashed curve indicates *photosynthetic efficiency* and demonstrates that plants use light with about the same wavelengths as those perceived by the human eye.

Fig. 1 proves an important feature of ambient radiation, namely its *spectral selectivity*. In other words, the radiation around us is confined to specific and often well-defined wavelength intervals. There is also another type of selectivity—*angular selectivity*—since different angles may be characteristic for different types of radiation. For example, solar radiation mostly comes from angles that are far above the horizon, while visual contact between persons and their surroundings generally is of most concern at near-horizontal lines-of-sight. Finally and importantly, ambient radiation varies with time during the day and between seasons; it thus displays *temporal variability*. These three characteristic features of ambient radiation will be referred to frequently in the following text.

3. Transmitting and reflecting materials

3.1. Principles

Consider electromagnetic radiation incident on a material. One part of this radiation may be transmitted, a second part is reflected, and a third part is absorbed. Energy conservation dictates that, for each wavelength, one has

$$T(\lambda) + R(\lambda) + A(\lambda) = 1, \tag{1}$$

where T, R and A denote transmittance, reflectance and absorptance, respectively. There is also another fundamental relationship that follows from energy conservation, namely

$$A(\lambda) = E(\lambda), \tag{2}$$

where E is emittance, i.e., the fraction of the black-body radiation (cf.

Fig. 1a) that is emitted at each wavelength. This relationship is known as Kirchhoff's Law and is significant mainly for $\lambda > 3\,\mu m$.

It is often convenient to average spectral data over the eye's sensitivity, over a solar spectrum (usually accounting for atmospheric absorption at an off-zenith angle), or over a black-body emittance spectrum (for a specified temperature). One then obtains what are known as *luminous*, *solar* and *thermal* properties; these properties are referred to as X_{lum}, X_{sol} and X_{therm}, respectively, with X being T, R, A or E.

3.2. Glass

Glass can be used in different ways in the context of solar energy materials: to protect against undesired impact from the environment, to suppress heat transfer due to gas convection, and as substrate for surface coatings (thin films). Glass can have various properties [21,22] but float glass, which is generally is used for glazing in buildings [23,24], is highly standardized. Float glass has great uniformity, and its flatness is on the scale of a few atoms. This flatness is a consequence of the production technology in which the glass solidifies on top of molten tin. Float glass is available in a wide range of thicknesses, typically 1.5–25 mm. Recent developments have led to much thinner flexible glass with thicknesses down to 25 μm. The scale of flat-glass production in the world is, stunningly, on the order of 10^{10} m^2/year and growing.

The middle curve in Fig. 2 shows spectral transmittance of a 6-mm-thick standard float glass pane at wavelengths of interest for solar radiation. A characteristic transmittance minimum can be seen at $\lambda \approx 1\,\mu m$ and is due to optical absorption in iron oxide. This glass has a greenish tint—most apparent when viewing the edge of a pane—which decreases T_{lum} typically on the level of some percent. Different amounts of iron oxide are available in special float glass, and Fig. 2 indicates that low-iron glass exhibits very high values of T_{lum} and T_{sol} and has significant transmittance also for ultraviolet radiation. Iron-rich glass limits T_{sol} while T_{lum} remains rather large; such glass looks distinctly green.

Each interface between air and glass leads to reflectance of about 4% for the $0.4 < \lambda < 2\,\mu m$ spectral range, which implies that the maximum transmittance of a glass pane is ~92%. Glass absorbs strongly at $\lambda > 3\,\mu m$, and E_{therm} is commonly stated to be ~84% which, however, may be an overestimation [25].

Photochromic glass darkens under ultraviolet light irradiation from the sun and bleaches in the absence of this irradiation [26]. Highly reversible photosensitivity is normally achieved by adding metal halides—particularly silver halide—to the vitreous glass matrix, and other additives are important as well. Fig. 3 reports T_{lum} as a function of time for darkening and bleaching of photochromic glass. Darkening is relatively fast and the glass has reached ~80% of its full range after one minute. However, bleaching progresses at a much slower pace and is still not complete after an hour. Photosensitivity is mostly confined to the $0.4 < \lambda < 1.0\,\mu m$ range, and the modulation of T_{lum} is much
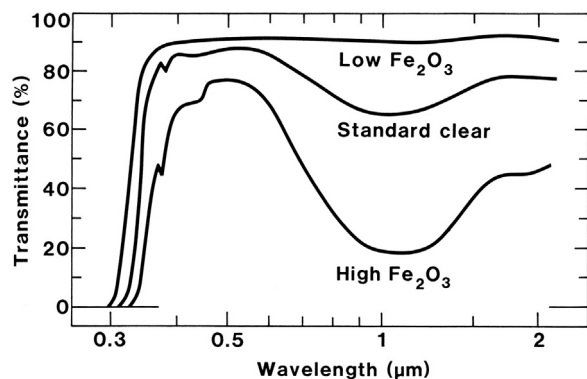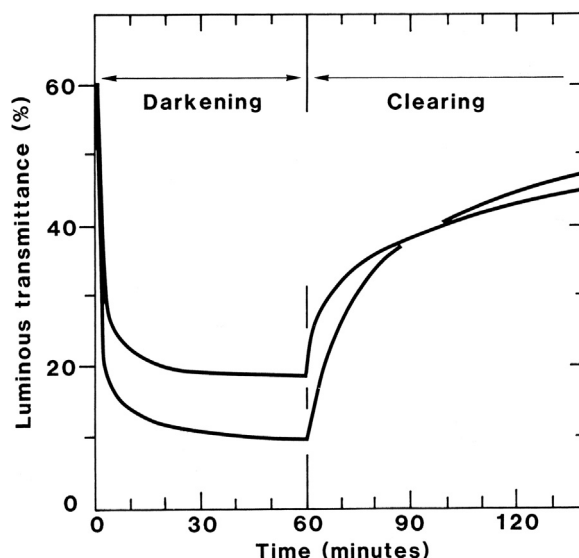

Fig. 3. Luminous transmittance versus time for two plates of photochromic glass [1].

larger than the modulation of T_{sol}. Photosensitivity has no influence on reflectance and emittance. Manufacturing issues have so far hampered large-scale production of photochromic glass.

3.3. Polymers

Many polymers are transparent and can replace glass, at least in principle. However, polymers normally degrade more easily than glass and hence have fewer applications. Polyethylene terephthalate (PET) foil should be noted and can serve as a flexible and inexpensive substrate for thin films of various kinds. Another alternative is ethyltetra-fluoroethylene (ETFE) [27,28], which is used in some contemporary buildings (typically stadiums and function halls); this material is noteworthy for its very low value of A_{sol}.

Photochromism is well known in polymers [29], and detailed information is at hand for spirooxazine in a host of cellulose acetate butyrate. Coloration dynamics is similar to that for photochromic glass, but bleaching proceeds faster for the polymer and occurs in ~20 min. More rapid dynamics, with coloration and bleaching times of the order of one minute, is possible in dyed ormosils [30]. In most cases, the photo-induced effects are confined to T_{lum}; they become less prominent at elevated temperature.

Polymeric lamination materials [31] are of interest, and laminated glass may be used for safety, sound protection and other purposes. Such glass usually employs a layer of polyvinyl butyral (PVB) sandwiched between glass panes and bonded to glass under heat and pressure. PVB laminate serves as an efficient absorber of ultraviolet light, and the transmittance at $\lambda < 0.38\,\mu m$ is almost nil for a layer thickness of ~1 mm. Ethylene-vinyl acetate (EVA) is an alternative to PVB.

3.4. Metals

Metal surfaces can provide high values of R_{lum} and R_{sol}, for example in mirrors of various kinds, and for giving low E_{therm}. Fig. 4 shows spectral reflectance for five different metals [32]. The largest magnitudes of R_{lum} and R_{sol} are provided by Ag and Al, and these metals are employed—in bulk form or as thin films backed by substrates—in numerous solar-energy-related applications. Surface protection of such surfaces is normally required to achieve long-term durability. Au has significant absorption at $\lambda < 0.5\,\mu m$, which accounts for its golden color, whereas other corrosion resistant metals—such as Cr, Rh, W or Pt—tend to have undesirably low reflectance in most of the solar range. All good metals can provide low values of E_{therm}.
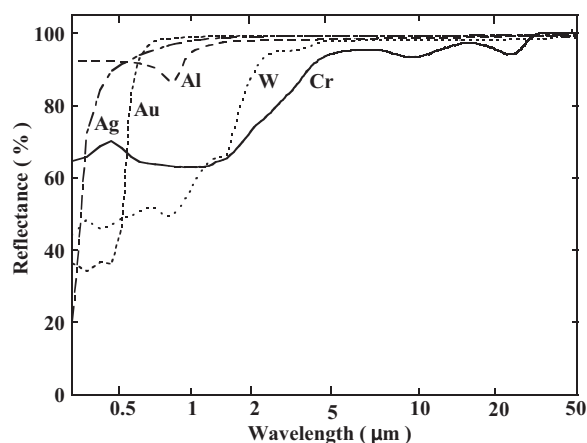

Fig. 2. Spectral transmittance of float glass with three amounts of iron oxide in the form of Fe$_2$O$_3$ [1].

Fig. 4. Spectral reflectance for surfaces of several metals [1].

Fig. 5. Spectral reflectance of a standard (STD) fiber cement specimen and after painting with cool brown and conventional brown paint [49].

3.5. Composite materials, especially for the built environment

A single material is often not good enough for efficient utilization of solar energy, and composites are frequently required. These composites can be of many types and consist of two or more superimposed layers, i.e., a *multilayer*, often including metals and dielectrics. The optical properties can be understood in detail from well-established theory, given that the properties of the individual layers are known [33]. Numerous cases of multilayer coatings will be mentioned below; for example they are used for energy efficient windows (Section 8.2). Particles embedded in matrices constitute another wide class of composite materials. If the particles are much smaller than the wavelengths of interest (typically particles with diameters much smaller than λ/10) one speaks of a *nanoparticle composite* whose optical properties can be understood as an average over the properties of the constituent materials. Light scattering is insignificant in this case. The averaging is described by effective-medium theory [34] and must account for the concentration, shape and orientation of the nanoparticles. For example, nanoparticle composites are usually employed in coatings for spectrally selective solar absorbers (Section 6.2). If the *particle composite* contains larger structural units (typically having diameters greater than 0.1 μm), the material exhibits substantial light scattering. The optical properties can be modeled [35–37], though seldom with high accuracy, in the case of practical solar energy materials. Paint stands out as an important example of the latter class of materials [38] and comprises inorganic or organic pigments in an organic binder. Surfaces of cementitious materials are another example.

Concrete and paint, as well as other composites, are widely used in the built environment, and some further comments on these materials are in order here. In particular, current trends towards a warmer climate and growing effects of urban heat islands, referred to in the Introduction, make it urgent to implement ways to avoid excessive temperatures in the built environment [39,40]. Cooling of pavements and roofs, in particular, have gained interest recently and is essential since together they may account for as much as ~60% of the area in many cities [41]. Cooling can be accomplished by increasing the albedo ("whiteness") via the addition of light-colored aggregates and/or solar reflecting coatings to concrete or asphalt [42–44], and permeable pavements or walls may be useful by allowing evaporation of water. "Green roofs" with various kinds of vegetation are efficient both for cooling and for water management [45]. Energy-efficient temperature levelling can be achieved by organic and inorganic composite phase-change materials integrated in the building structure [46,47].

Spectrally selective paints allow high reflection of solar radiation while providing desirable visible colors; they can utilize pigments, coated metal flakes, or plasmonic nanoparticles [2,48]. Fig. 5 reports the reflectance of a fiber cement roofing plate in as-prepared state and
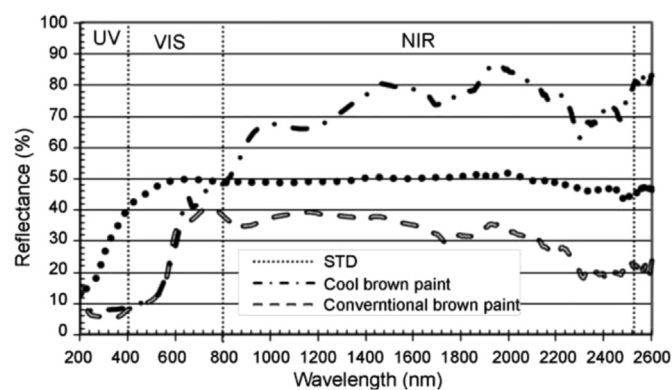
after being coated with "cool light brown" paint and its conventional counterpart [49]. Clearly the "cool" paint has much larger reflectance in the $0.8 < λ < 2.5$ μm range, which implies that it does not get heated as much as the standard paint by solar irradiation.

4. Thin films

4.1. Deposition technologies

Surface treatments can change the optical properties of the underlying material and make surfaces better adjusted to the requirements set by the ambient radiation (cf. Fig. 1). Subsequent sections of this paper, which discuss specific types of solar energy materials, contain many examples of this. The technological field is huge [50–57], and nothing but the most commonly used methods are mentioned below. Some more detail is given in the companion "primer" referred to above [17].

Sputter deposition is widely used to produce highly uniform coatings on glass, metals, polymers, etc. In essence, a plasma is established in an inert and/or reactive gas kept at low pressure, and energetic ions in the plasma remove material from a solid plate or tube of the raw material of the film (the "target") and deposit these atoms on an adjacent surface (the "substrate"). *Evaporation* can be an alternative to sputter deposition; here the raw material of the film is heated in vacuum, and vapor of this material is condensed and deposited on a substrate. Other technologies can be applied without using vacuum: For example, *sol–gel deposition* involves immersion of a substrate in a chemical solution, withdrawal at a controlled rate, and subsequent heat treatment; the chemical solution may also be applied by spraying or spinning. *Chemical vapor deposition* uses heat to decompose a vapor of a "precursor" chemical in order to create a thin film of a desired composition. Electrochemical techniques include *cathodic electrodeposition* from a chemical solution and *anodic conversion* of a metallic surface—especially of Al—to form an oxide. Several other techniques can be used, especially for research and development work.

Large-area thin-film deposition is often essential, and production capacities on the scale of square kilometers per year may be required for solar energy materials. This productivity can be accomplished, in particular, with in-line coaters working with sputter deposition [53] and with roll-to-roll coaters for flexible substrates, particularly comprised of PET foil [58,59].

4.2. Antireflection treatments

Antireflection treatment, for example to reach high values of T_{lum} through glass, can be achieved by the application of a thin film with a refractive index that 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). Only a few
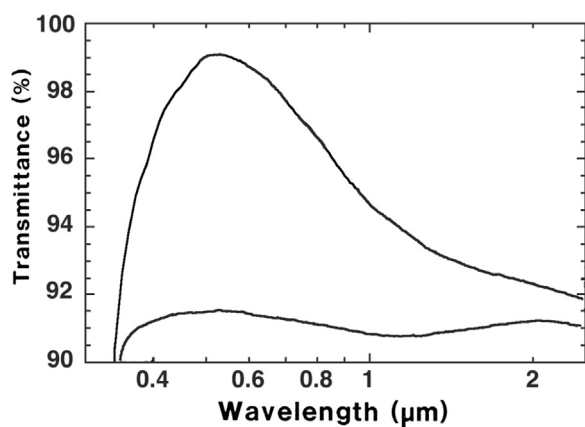
Fig. 6. Spectral transmittance of a glass plate before (lower curve) and after (upper curve) being coated on both sides by antireflecting thin films of porous silica [1].
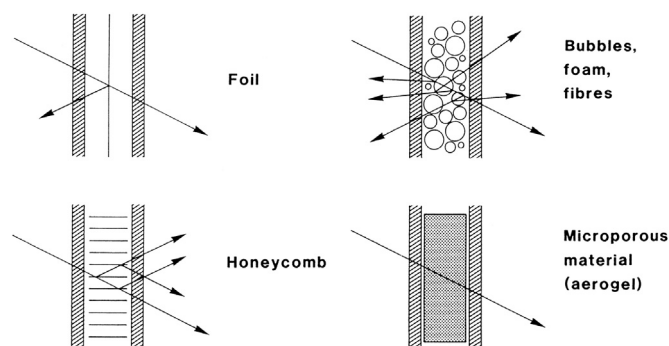

Fig. 7. Principles of four kinds of solid transparent insulation materials positioned between glass panes. Arrows indicate light rays. Reflections at glass surfaces are not shown [1].

materials are able to have the desired low refractive index and simultaneously provide good durability. Fig. 6 shows an example of a glass plate which has both of its surfaces coated with a thin film of porous silica [60]. It is apparent that T_{lum} is higher than 99% in the middle of the luminous spectrum. Other antireflection treatments include thin films of magnesium fluoride or aluminum oxy-fluoride, porous or micro-structured surface layers prepared by liquid or vapor etching of glass [61], and sub-wavelength surface structuring [62].

Simple antireflection treatments can diminish the reflectance only within rather narrow wavelength ranges, but if a low magnitude of R_{sol} is demanded it is necessary to use a multilayer film with judiciously selected thicknesses and refractive indices. Furthermore, antireflection is efficient only for a specific range of incidence angles for the light, but several kinds of more advanced designs can improve the situation [63].

5. Transparent thermal insulation

5.1. Principles

Heat transfer takes places via the added effects of *radiation*, *convection* and *conduction* [64,65]. Efficient applications of solar energy materials often require that this transfer is diminished. Radiative transfer can be lowered by use of surfaces with small values of E_{therm}. Convection, which is important for gases, can be diminished by confining the gas to cells with linear sizes of ~1 cm or less or, alternatively, by decreasing the gas pressure. Conductive heat transfer, finally, can be minimized by appropriate constructions incorporating materials with low heat conductivity.

5.2. Solid materials

There are numerous types of solid materials for thermal insulation [66,67]. Fig. 7 shows four kinds of transparent materials, specifically flexible polymer foils; polymer honeycomb materials; bubbles, foam, and fibers; and inorganic micro-porous materials such as silica aerogel [68]. Capillary structures ensue if the honeycomb cross-section is small in comparison with the cell length. Foils and aerogels can be virtually invisible, while honeycombs, bubbles, foam and fibers yield some reflection and scattering and therefore impede direct transmittance; only the former group of materials is of interest if unperturbed vision is needed, which is the case for most glazing. The other transparent insulation materials can be applied in translucent walls as well as thermal solar collectors. The materials can be used in vertical, horizontal or inclined positions depending on application.

Flexible PET foil can be suspended and divide a thick gas slab into ~1-cm-thick layers with lowered convection, and thin films can be used to adjust T_{lum} and T_{sol} and to minimize E_{therm} (these aspects are covered

in detail below). Analogously, macro-porous materials—typically of polystyrol, polyamide, polyvinylchloride or polycarbonate—can yield gas-filled cells that are sufficiently small to almost remove heat transfer by convection. The heat transfer coefficient of the honeycombs, capillaries, bubbles, foam and fibers is typically 1 W m^{-2} K^{-1} for a thickness of 10 cm [69,70].

Silica aerogel can be manufactured by supercritical drying of colloidal silica gel under high temperature and pressure [71–74]. The material comprises ~1-nm-diameter silica particles that are interconnected and form a sparsely packed structure with pore sizes of 1–100 nm. The relative density can be as low as a few percent of the bulk density. The materials can be prepared as translucent granules or as transparent tiles with some haze [75,76]. Fig. 8 shows spectral transmittance through a 4-mm-thick tile. The low transmittance at short wavelengths is caused by optical scattering. Heat transfer below 1 W m^{-2} K^{-1} can be obtained in 1-cm-thick slabs of aerogel under favorable conditions, specifically by positioning the slab between surfaces with low E_{therm} and at low gas pressure.

5.3. Gases

Heat transfer between two surfaces depends on the intervening gas and can be lowered by using a gas different than air. This is common in modern glazing, which is based on hermetically sealed constructions (known as "insulated glass units", IGUs) [10,77,78]. Heat transfer across a common 1.2-cm-wide gas slab is diminished by some ~10% if air is replaced by Ar or CO_2, and greater effects can be reached with Kr and Xe. The relative influence of the gas filling is increased to about ~20% if radiative heat transfer is decreased by having surfaces with low magnitudes of E_{therm}. Infrared-absorbing gases can diminish heat transfer, but limited availability of suitable gases makes this possibility less important [79]. Some improvement of thermal properties can be
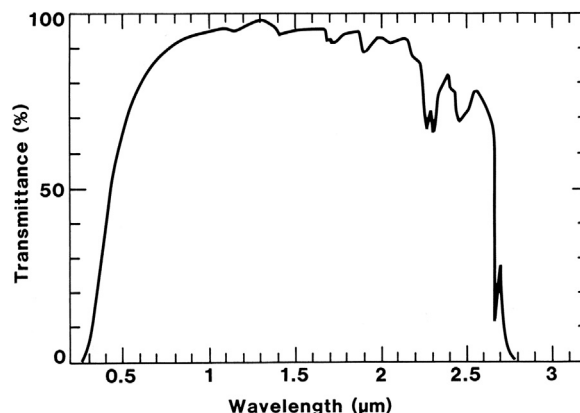

Fig. 8. Spectral transmittance of a 4-mm-thick silica aerogel tile [1].

combined with sound insulation by use of SF_6 gas.

Finally, minimum heat transfer can be obtained by removing the gas, which means that both conduction and convection are absent [80]. In practical "vacuum glazing", the mechanical strength must be sufficient to allow vacuum, which requires inconspicuous spacers.

6. Solar thermal converters

6.1. Principles

Solar collectors are used for photo-thermal conversion of solar energy to produce hot fluid or hot gas [81,82]. These devices can be of different types: most common are roof-top collectors with flat-plate absorbers or with absorbers positioned inside evacuated glass tubes. A third collector type uses linear parabolic trough reflectors that direct solar radiation towards tubular collectors and are used for power production, and a fourth type employs a field of individually steered plane mirrors to concentrate solar radiation onto a centrally located absorber on a tower. Efficient conversion takes place when the solar-absorbing surface is in good thermal contact with the fluid or gas and when thermal losses to the ambience are minimized. For most applications, the absorber must be placed behind a stiff solar-transparent cover, and a transparent thermal insulation material may be integrated in the design. The back and sides of the solar collector should be thermally well insulated. The most critical component for efficient photo-thermal conversion is the solar absorber surface, which must have a large value of A_{sol}. Its radiative heat losses should be minimized, which demands low E_{therm}. The absorber is non-transparent, and the requirements above can be expressed as an ideal spectral reflectance according to

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

and

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

Here λ_c denotes a "critical" or "cut-off" wavelength between 2 and 3 μm depending on the solar collector's operating temperature (cf. Fig. 1). Eqs. (3) and (4) stand out as a clear example of spectral selectivity as a means to create an optimized solar energy material for thermal applications.

Several design principles and physical mechanisms can be employed to create a solar absorbing surface with spectral selectivity; Fig. 9 shows six of them schematically [8]. Most straight-forward would be to use a material with appropriate *intrinsic optical properties*, but there are few materials of this kind and this approach has not been successful. *Semiconductor–metal two-layer structures* can provide the desired spectral selectivity by absorbing short-wavelength radiation in a semiconductor whose band-gap corresponds to a wavelength of ~2 μm and achieving low E_{therm} via an underlying metal. The semiconductors of interest have

large refractive index, which leads to pronounced reflection losses and hence diminish A_{sol} so that elaborate antireflection treatments are needed. *Metal–dielectric multilayer films* represent another possibility and can be tailored so as to reach efficient selective absorption of solar energy. *Multilayers containing metal–dielectric nanocomposites, dielectrics and metals* are of considerable interest. The composite has metal nanoparticles embedded in a dielectric host, often being an oxide, and is frequently referred to as a ceramic–metal ("cermet") material. This latter design principle offers much flexibility, and optimization of the spectral selectivity can be made with regard to selection of constituent materials, film thickness, nanoparticle concentration and grading with depth, and shape and orientation of nanoparticles. The nanoparticles are much smaller than any wavelengths relevant to solar or thermal radiation, and the composite constitutes an "effective medium" whose optical properties lie in between those of the metal and dielectric [34,83–85]. *Textured metal surfaces* can exhibit high values of A_{sol} through multiple reflections against metal dendrites separated by ~2 μm while a low E_{therm} is rather unaffected by this texturing since the relevant wavelengths are much larger that the dendrite separation [86]. Finally, *selectively solar-transmitting films on blackbody-like absorbers* can display spectral selectivity.

6.2. Spectrally selective thin films

A number of spectrally selective thin films, coated onto metal substrates by one of the thin film technologies discussed in Section 4.1, have been developed in the past, and some of these films are commercial products. These films normally exploit several of the design principles and physical mechanisms mentioned above.

Electrochemical techniques have been employed for decades to make spectrally selective surfaces suitable for flat-plate solar collectors. Typical surfaces have electrodeposited films containing Cr or Ni (known as "black chrome" and "black nickel", respectively) with complex compositions. Another technique is based on anodic conversion of Al, to produce a porous surface layer, followed by electrolysis to precipitate Ni particles in the pores [87]. The solid curve in Fig. 10 shows $R(\lambda)$ for such a film; $A_{sol} \approx 96\%$ and $E_{therm} \approx 15\%$ at 100 °C are typical for this type of surface. Durability has been modeled in detail [8].

Electrochemical methods necessitate that large quantities of environmentally hazardous chemicals are handled, and thin film techniques based on deposition in vacuum are in principle more environmentally benign [2,88]. The dotted curve in Fig. 10 illustrates $R(\lambda)$ for a sputter-deposited Ni-based thin film; the design includes an antireflection layer to enhance A_{sol}. These data yield $A_{sol} \approx 95\%$ and
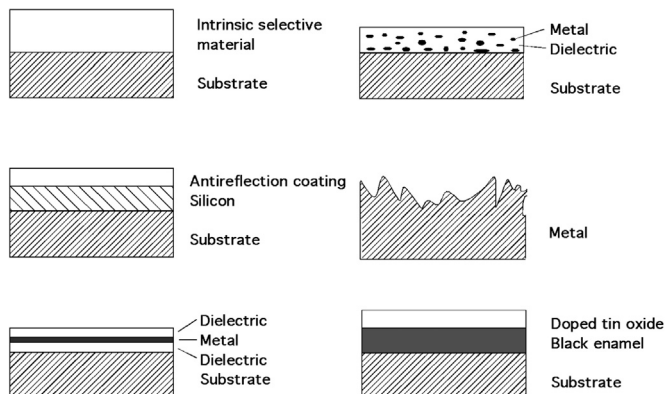
Fig. 9. Cross-sectional schematic designs of six types of thin films and surface treatments for selective absorption of solar energy [1].

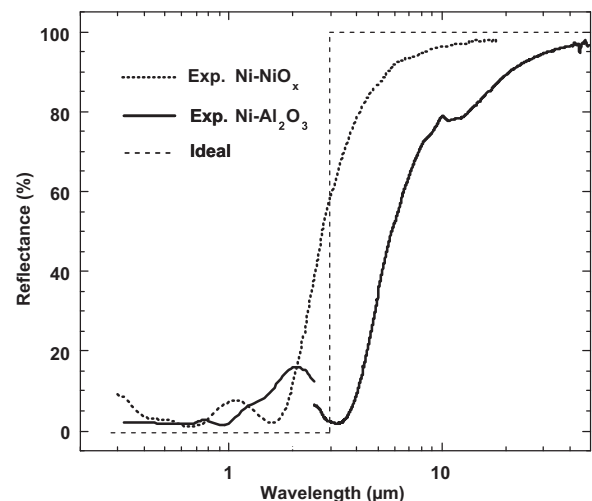**Fig. 10.** Spectral reflectance for two kinds of selectively solar absorbing surfaces. Dashed lines indicate ideal performance [1].

$E_{therm} \approx 10\%$ at 100 °C. A trend is to move towards multilayer sputter-deposited coatings, which allow considerable further optimization of the spectral optical properties [9,89,90]. These films can be used for various types of solar collectors, including concentrating ones. Non-black solar absorbers have attracted recent interest; coloration entails an inevitable loss of A_{sol} by a few percent, which can be tolerated since the absorber may more readily satisfy architectural demands [91].

Deposition from chemical solution has been forwarded to produce Ni–Al$_2$O$_3$ "cermet" coatings that contain more Ni than the pigmented anodic alumina mentioned above. The chemically deposited coatings therefore can be thinner and reach $A_{sol} \approx 97\%$ along with $E_{therm} \approx 5\%$ [92].

Advanced selectively solar-absorbing surfaces have been developed for solar-thermal power generation. The appropriate absorbers can be based on ceramics [93] or use sputter deposition to produce complex multilayer structures for example incorporating graded Mo oxide films, antireflection treatment, and emittance-suppressing Mo films [94]. Generally speaking it is more important to maximize A_{sol} than to minimize E_{therm} for this application [95].

6.3. Spectrally selective paints

Paints have an obvious asset in that they can be applied by generally available techniques. Typically a strongly absorbing pigment, such as FeMnCu-based oxide, is mixed with an infrared-transparent polymeric binder such as a silicone or a siloxane [96]. The paint is applied as a 2–3 μm thick layer on a metallic substrate with low E_{therm}. Characteristic performance data are $A_{sol} \approx 90\%$ and $E_{therm} \approx 30\%$, i.e., not as good as for thin films. Lowering the paint's emittance requires thinner coatings with higher pigment concentration and leads to problems with adherence and durability. Thickness-insensitive spectrally selective paint can be made by incorporating metallic flakes in the binder [97].

7. Radiative cooling

7.1. Principles

The atmosphere can be transparent to thermal radiation in the $8 < \lambda < 13$ μm "window" range, as demonstrated in Fig. 1, and this effect can lead to radiative cooling of surfaces facing the sky [2,98,99]. The resource for this cooling has been evaluated via detailed calculations, which showed that the cooling power for a blackbody can be as large as 80–120 W m^{-2} depending on atmospheric conditions, if the radiating surface is at ambient temperature [100]. Considering nothing but radiation exchange, the surface can drop to 14–26 °C below air temperature. Assuming a non-radiative heat transfer equal to 1 W m^{-2} K^{-1}, maximum temperature decrease is predicted to be 10–20 °C.

The temperature decrease can be augmented if radiation exchange occurs solely in the atmospheric "window", which requires surfaces with infrared-selective emittance. The ideal reflectance is

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

and

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

Further temperature decrease is possible via aperture control to ensure that radiation exchange occurs mainly in the zenith direction [101]. If cooling should take place also during the day, it is desirable to maximize R_{sol}. Calculations have demonstrated that infrared-selective surfaces can yield cooling powers between 60 and 95 Wm^{-2} depending on the conditions in the atmosphere [100,102]. A maximum temperature decrease of 26–60 °C with nothing but radiation exchange, and of 18–34 °C for a non-radiative heat influx of 1 W m^{-2} K^{-1}, have been calculated. Spectral selectivity is hence imperative for reaching very low temperatures.

7.2. Materials

Spectral selectivity in approximate accordance with Eqs. (5) and (6) has been achieved recently with Si$_3$N$_4$/a-Si bilayers and with oxide multilayer coatings backed by metal [102,103] as well as by use of surface-phonon resonance in SiC and/or SiO$_2$ nanoparticles embedded in a polymer foil backed by Ag [104,105]. Practical tests with an optimized cooling device (shaded from direct sunlight) demonstrated an average temperature reduction by as much as 37 °C during a full day–night cycle [102]. Earlier work employed less optimized ~1-μm-thick silicon oxide and oxynitride films backed by Al [106,107] and by aluminized polymer foil. Another option is to use confined gas layers of NH$_3$, C$_2$H$_4$, C$_2$H$_4$O, or mixtures of these, with thicknesses of a few centimeters [108].

Practical tests of radiative cooling have mostly used devices in which the cooling surface, or the gas, was positioned under a convection-suppressing infrared-transparent shield. Plates of ZnSe have appropriate optical properties [102] but may be restricted to small-area installations. High-density polyethylene foil can be employed conveniently but needs stiffening so as not to induce forced-convection heating due to mechanical movements caused by wind [109], and favorable properties have been found also with polyethylene meshes [110]. Furthermore, it appears feasible to devise infrared-transparent personal clothing for improved comfort in warm climates [111]. For the case of radiation-cooled gases, the coolant can be circulated through the space between the cover shield and the backing, and subsequent heat-exchange may provide a continuous source for cooling.

Radiative cooling is also possible without the use of convection shields, and foil materials that are strongly scattering for solar radiation and strongly emitting in the 8–13 μm range can serve as tarpaulins that prevent overheating of underlying material during the day even in full sunlight [112]. Actual cooling in full daylight has been demonstrated with advanced cooling designs employing multilayer polymer stacks [113] as well as with the SiO$_2$–polymer composite foils mentioned above [105].

Radiative cooling can be used to condense water from the atmosphere [114,115], and measurements have shown that significant amounts can be obtained even under adverse climatic conditions. The water-condensing material can be comprised of polymer foil pigmented by white TiO$_2$ and BaSO$_4$ [114].

8. Coatings for glazing: static properties

8.1. Principles

Architectural glazing is challenging from an energy perspective [2,24]. Its primary function is to give visual contact between indoors and outdoors as well as daylighting, and therefore glazed areas must not be too small. A consequence of this fact is undesired energy flows with excessive thermal energy exiting or entering buildings via their glazing, which leads to needs for energy guzzling heating and cooling. The architectural trend is to increase glazing areas rather than decreasing them, so the energy issue related to glazing may be exacerbated in the future.

The radiation part of the heat transfer can be diminished via thin films with low E_{therm} which, in a multi-pane glazing, should face one of the enclosed air (or gas) spaces [2,10,116]. The heat transfer across a vertically mounted window can then drop from ~3 to ~1.5 W m^{-2} K^{-1} for double-pane glazing and from ~1.8 to ~1.0 W m^{-2} K^{-1} for triple-pane glazing when one of the panes has a coating with low E_{therm}. It is obvious that T_{lum} must be large for these films. The infrared part of the solar radiation—which transports energy through the glazing but is not seen by the eye—can be cut off by a thin film with high reflectance at $0.7 < \lambda < 3$ μm. The films are electrically conducting and hence appropriate as transparent electrodes for electrochromic (cf. Section 9.1) and photovoltaic devices.

These requirements have led to the development of two different types of thin films. One of them is known as "low emittance coating" ("low-*E* coating") and ideally characterized by

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

and

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

whereas the other type is called "solar control coating" and ideally characterized by

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

and

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

Another, principally different, approach to create energy efficiency is to invoke angular selective thin films on glass [12,117]. This technique benefits from the fact that the indoors–outdoors contact through a glazing normally involves more or less horizontal lines-of-sight, while solar irradiation emerges from a small element of solid angle high up in the sky during most of the day, at least if cloudiness is not too strong. In principle, it is possible to combine spectral and angular selectivity.

8.2. Spectrally selective metal-based thin films

Very thin films of metals can display optical properties that are not too distant from those in Eqs. (7)–(10), and calculations for extremely thin bulk-like films of the coinage metals Ag, Au and Cu demonstrate that large magnitudes of T_{lum} and T_{sol} can be combined with low values of E_{therm} [118]. However, such films cannot be prepared on substrates of glass or polymers but, instead, the growing thin film goes through a series of distinct phases and a well-defined contiguous electrically conducting film with low E_{therm} requires a thickness of ~10 nm at which point T_{lum} and T_{sol} are no larger than ~50% [119]. Most of the transmittance loss is caused by reflectance at film interfaces, which implies that the transmittance can be enhanced if the metal film is put between dielectric layers serving, essentially, for antireflection purposes.

Ag exhibits the best optical properties, and Ag-based films are most commonly used. Au and Cu tend to produce films with some coloration, which is undesired for many architectural applications. TiN have optical properties similar to those for Au [120], while ZrN is more similar to Ag [121]. The dielectric layer can be comprised of many materials, such as Bi_2O_3, SnO_2, TiO_2, ZnO and ZnS. The multilayer structure may also include corrosion-impeding layers, for example Al_2O_3, as well as extremely thin interfacial layers for boosting the contiguity of the metal film(s). Depending on film thicknesses, it is possible to optimize T_{lum} or T_{sol} while E_{therm} remains low, which implies that low-*E* as well as solar control coatings can be prepared from metal-containing multilayer structures. These types of coatings are used for glazing on a huge scale internationally; on some markets they are the norm rather than the exception, whereas uncoated glazing continues to dominate elsewhere.

Fig. 11 reports $T(\lambda)$ and $R(\lambda)$ for a commercial Ag-based solar control coating on float glass [122]. Metal-based films must be used under protected conditions, typically in IGUs. Film thicknesses are small enough to avoid iridescence (rainbow-like exhibition of color) which is generally undesirable for glazing.

8.3. Spectrally selective doped-semiconductor-based and dielectric thin films

Doped oxide semiconductor coatings with wide optical band gaps are alternatives to the spectrally selective metal-based films [123,124]. The most commonly investigated and used materials are In_2O_3:Sn (known as ITO) [125], SnO_2:F (known as FTO) [126], SnO_2:Sb [126], and ZnO:Al (known as AZO) [127]; another material with similar properties is TiO_2:Nb [128]. Many other possible materials can be
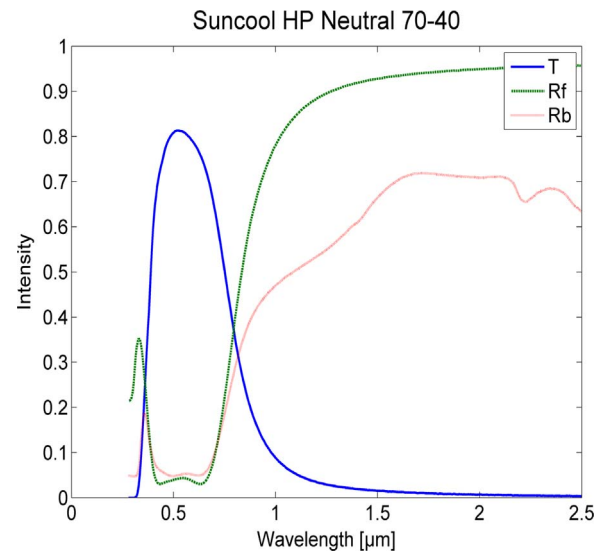

Fig. 11. Spectral transmittance *T* and reflectance from the front (coated) side (R_f) and the back side (R_b) for a commercial Ag-based coating on glass. The spectral data correspond to $T_{lum} \approx 80\%$ and $T_{sol} \approx 41\%$ [122].

found among ternary and quaternary oxides and among mixtures of the mentioned oxides. Nevertheless, the binary oxides stated above remain popular. These oxides do not have identical properties but In-based ones have the lowest E_{therm}, Sn-based oxides have highest durability, while Zn-based oxide is commonly used for some specific applications (such as transparent electrical contacts in solar cells). The films are electrically conducting and have a minimum resistivity of ~10^{-4} Ω cm for optimized ITO. However, it is notoriously difficult to reach these properties, which typically require thermal treatment at ~300 °C or above. High-rate deposition is possible for ITO [129].

Fig. 12 shows $T(\lambda)$ and $R(\lambda)$ for a commercial SnO_2:F-based coating on float glass [122]. The properties are appropriate for low-*E* applications while solar control is inadequate since it is not possible to reach sufficient reflectance at $0.7 < \lambda < 3 \text{ } \mu m$. The doped semiconductor oxides are hard and corrosion resistant, and they can be used on glass surfaces exposed to ambient air. The practically useful thicknesses exceed ~0.2 μm, which means that thickness variations—which may be hard to avoid under practical manufacturing conditions—can lead to iridescence.

The refractive index of the doped oxide semiconductors is ~2 with

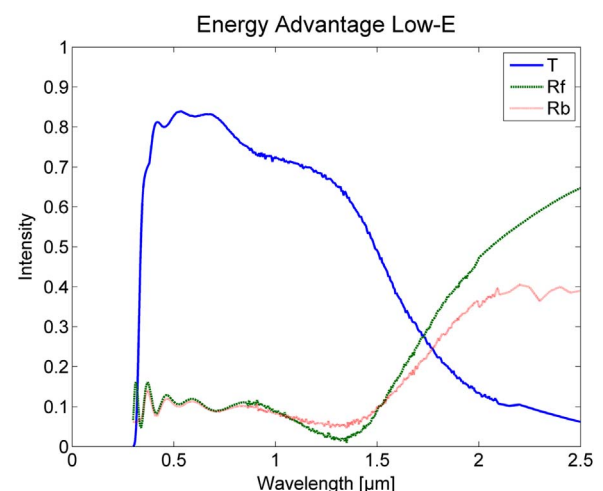**Fig. 12.** Spectral transmittance *T* and reflectance from the front (coated) side (R_f) and the back side (R_b) for a commercial SnO_2:F-based coating on glass. The spectral data correspond to $T_{lum} \approx 83\%$ and $T_{sol} \approx 71\%$ [122].

regard to luminous radiation, which limits T_{lum} to ~80%. Higher transmittance can be reached by antireflection treatment, and T_{lum} can even be marginally larger than for uncoated glass. The antireflection layer lowers E_{therm} by a few percent, which is insignificant for most applications [130].

Polymer foils with many thin alternating layers can achieve interesting optical properties. If the difference in refractive index among the layers, as well as the number of layers, is large enough it is possible to reach high reflectance in a prescribed range, as can be understood from multi-layer optics, whereas E_{therm} remains large. Multilayer foils of this type can be prepared by efficient co-extrusion.

8.4. Other transparent conducting coatings

Recent research and development on transparent conductors has given numerous alternatives to thin films of metals and oxides. One of the most widely studied types is carbon-based transparent conductors, specifically based on carbon nanotubes [131] or graphene [132]. Meshes of metal-based nanowires, often comprised of silver, are another option; they can be made cheaply by wet chemistry and can be deposited onto substrates by "simple" methods including electro-spraying and brush-painting [133]. Meshes can have excellent electrical properties, but the sizes of the individual wires tend to produce some diffuse light scattering which may curtail glazing-related applications whereas scattering may be advantageous in, for example, solar cells. Furthermore, some organic materials can be employed as transparent conductors and can be produced by low-cost printing [134]. Hybrid transparent conductors, combing two or more of the mentioned options, have attracted interest recently. Finally, macroscopic metal meshes, grids and arrays can be of some interest albeit they may produce undesired optical effects.

It is difficult to compare and assess the entire gamut of transparent conductors with regard to specific applications, and many properties have to be studied and evaluated such as direct optical transmittance and haze, electrical conductivity, durability, mechanical performance and cost.

8.5. Angular selective thin films

Glazing can be rendered energy efficient also by exploiting strong angular properties, as already noted [12,117]. Fig. 13 serves to illustrate this feature and reports data computed for a five-layer stack of thin films comprising two 12-nm-thick Ag films positioned between
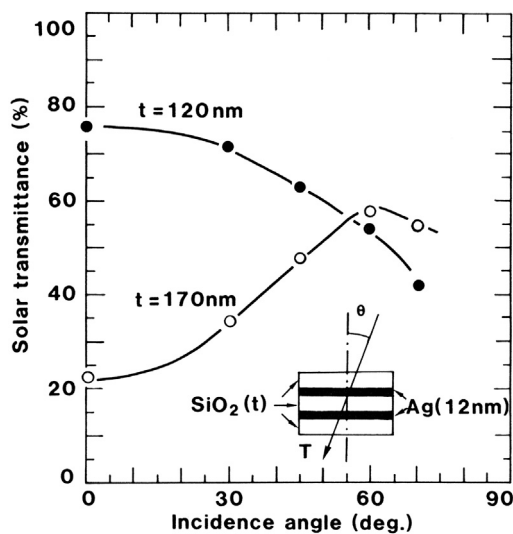
Fig. 13. Solar transmittance for thin films of SiO$_2$/Ag/SiO$_2$/Ag/SiO$_2$ as a function of SiO$_2$ thickness (t) and incidence angle (θ) [1].
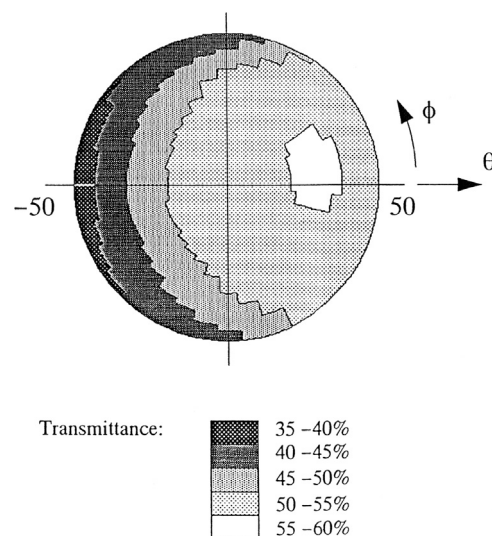
Fig. 14. Polar diagram for luminous transmittance through an obliquely evaporated Cr-based thin film; data are given as a function of incidence angle (θ) and azimuthal angle (φ) [136].

three 120-nm-thick or 170-nm-thick SiO$_2$ films. Pronounced angular effects are evident at the larger of these thicknesses; T_{sol} is 23% for light with normal incidence but as high as 58% when the incidence angle is 60 degrees.

The transmittance shown in Fig. 13 looks symmetrical with regard to the film's surface normal. However, it is also possible to achieve angular properties that are strongly different at equal angles of the two sides of the normal by using films with strongly inclined columnar nanostructures [135]. Fig. 14 reports a polar plot of T_{lum} for a Cr-based film prepared with the incident flux arriving at the substrate with almost glancing angle [136]. The columnar features underlying angular selectivity then create an array slanted towards the evaporated flux. Appropriate deposition techniques, and properties of thin films prepared by them, have been described in detail [11,137]. Coatings of this type may be of interest for inclined glass louvres and yield high see-through transmittance while partially blocking direct solar radiation during most of the day. Car windscreens can be another application.

9. Coatings for glazing: dynamic properties

9.1. Principles

Windows and glass facades with variable optical properties have been architects' desire for many years [24]. Such products have recently emerged on the market; they make use of "chromogenic" materials [13], especially those with electrochromic properties. The present section treats electrochromic, gasochromic, thermochromic and photochromic coatings, and glazing based on those; this ordering is intended to reflect the coatings' level of technical maturity. Photochromic glass and polymers were discussed in Sections 3.2 and 3.3, respectively.

9.2. Electrochromic thin films and devices

Electrochromic devices can modulate T_{lum} and T_{sol} under the action of a low voltage [14,138,139]. Hence they are able to control the amount of energy that enters through a "smart" glazing and lower the need for air conditioning in cooled buildings [140,141]. The energy efficiency provided by this technology can be substantial given that the control strategy is appropriate. Furthermore, transmittance control can diminish glare and provide better indoor environment. Absorptance rather than reflectance is normally modulated so that the electrochromic
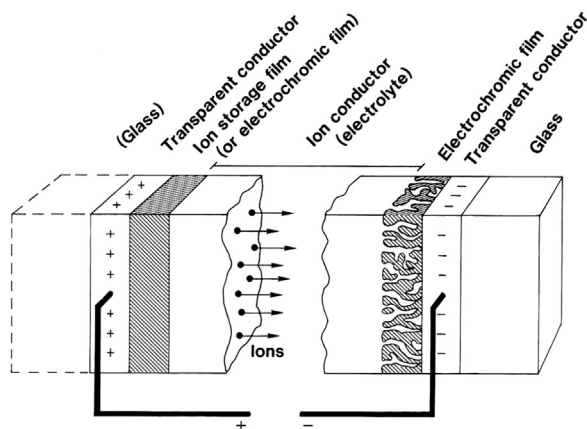
Fig. 15. Design of a generic electrochromic device; arrows indicate transport of positive ions in an electric field [138].
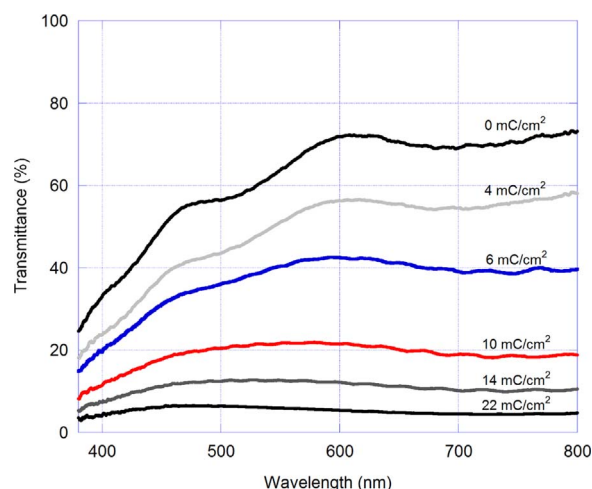

Fig. 16. Spectral transmittance through an electrochromic foil with thin films of W-based and Ni-based oxides. Data are reported for the shown amounts of charge transfer [145].

glazing tends to heat up in its low-transparent state, which has to be accounted for in practical constructions. In principle, it is feasible to modulate E_{therm}, and variable-emittance surfaces can be used for temperature control of space vehicles and for infrared camouflage [142,143].

Fig. 15 shows a generic electrochromic five-layer device and introduces basic design features and types of materials [138]. The principle similarity to an electrical battery should be noted. The central part of the device is a purely ionic conductor (electrolyte), either a thin film or a polymer; it should be a good conductor for small ions such as H^+ or Li^+. The electrolyte joins an electrochromic film and a counter-electrode film. For a transparent device, the counter-electrode should stay non-absorbing irrespective of its ionic content or should be electrochromic in a sense opposite to that of the base electrochromic film. The central three-layer structure is positioned between transparent electrical conductors, normally consisting of doped oxide semiconductors such as those discussed in Section 8.3; they are backed by glass or PET foil. The application of a few volt between the transparent conductors—for example by use of solar cells—causes ions to be shuttled into or out of the electrochromic film(s) whose optical properties are then modified so that the overall optical transmittance is altered. In principle, the voltage is needed only when the transmittance is changed, i.e., electrochromic glazing can exhibit open-circuit memory and hence be energy efficient. The time for transitioning between high and low transmittance is mainly governed by the electrical resistance of the transparent conductors. Today's "smart" glazing, with areas of square meters, takes some ten minutes for changing from transparent to moderately dark, which permits the eye to light-adapt. Smaller electrochromic devices can change their optical properties much faster.

Many materials and design issues are of interest for practical electrochromic "smart" glazing. Electrochromism is found in many organic [144] and inorganic [14,138,145] materials, the latter mainly being transition metal oxides. Organic electrochromic materials are predominantly modulating T_{lum}, and they tend to degrade under intense ultraviolet irradiation; hence they are of less interest than the inorganic materials for applications as solar energy materials. Thin films based on WO_3 are employed as the base electrochromic layer in almost all devices investigated and implemented until now; the properties can be optimized by admixture of oxides such as MoO_3 and TiO_2 [146]. However, there are many alternatives for the counter electrode, and good results have been found for oxides based on Ce, Ir, Ni and V; other designs have used $KFe^{3+}Fe^{2+}(CN)_6$ ("Prussian Blue"). Ni-oxide-based films have been studied in particular detail [147,148]. There are many alternatives also for the central electrolyte; it can be an adhesive polymer with high ionic conductivity or, in an all-solid-state design, an oxide layer allowing easy diffusion of Li^+. The electrolyte can be functionalized, and nanoparticles of a transparent conducting oxide

such as ITO can decrease T_{sol} without changing T_{lum} significantly [149]. Fig. 16 shows optical performance for a laminated PET-based electrochromic foil device with films based on WO_3 and NiO [145]. It is evident that T_{lum} can be modulated over a wide range.

Several alternative approaches to the basic electrochromic device in Fig. 15 have been studied over the years and some have been commercialized [14]. They include suspended particle devices [150], metal hydrides [151], polymer-dispersed liquid crystals [152], reversible electroplating [153], and constructions based on variable plasmonic absorption in transparent conducting oxide nanoparticles [154].

9.3. Gasochromic thin films and devices

Gasochromic thin films can be an alternative to electrochromic devices, with specific pros and cons [155,156]. Glass is coated with WO_3 and an extremely thin surface layer of catalytic Pt. The coated side of the glass is in contact with a gas that is confined in an IGU. Changing the amount of H_2 in contact with the thin film makes it possible to incorporate variable amounts of H^+, and the transmittance is then modulated in analogy with the functioning of an electrochromic device.

9.4. Thermochromic thin films and thermotropic materials

Thermochromism offers another possibility to modulate T_{sol} and achieve energy efficient glazing. By far the most widely studied thermochromic oxide material is VO_2, which exhibits a structural transition at a "critical" temperature below which thin films are semiconducting and relatively non-absorbing in the infrared and above which they are metallic and infrared reflecting [16,157]. However, VO_2 must be modified to be practically useful: specifically, the "critical" temperature should be changed from the bulk value of 68 °C to the vicinity of room temperature which can be accomplished by doping preferably with W [158], T_{lum} should be improved which can be done by adding some Mg [159], the modulation of T_{sol} should be enhanced which can be achieved in layers with VO_2 nanoparticles dispersed in a transparent matrix ("nanothermochromism") [160], and oxidation resistance must be created by a protective over-coating [161].

Fig. 17 shows the most important properties of VO_2 thin films and nanoparticles and reports that the infrared transmittance of a VO_2 film can be significantly higher in the low-temperature semiconducting state than in the high-temperature metallic state. A layer containing VO_2 nanoparticles displays a larger value of T_{sol} than a corresponding thin film and, importantly, T_{sol} decreases sharply in the high-temperature state as a consequence of a strong surface-plasmon-induced transmittance minimum in the $0.7 < \lambda < 2$ µm wavelength range. The
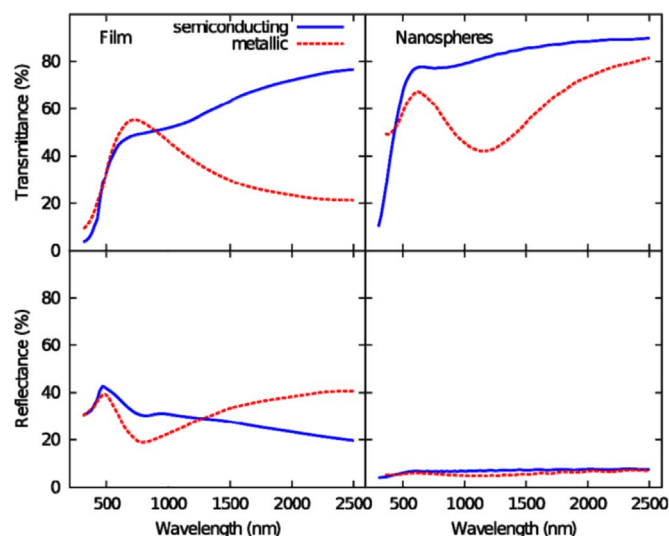
Fig. 17. Spectral transmittance (upper panels) and reflectance (lower panels) for a 50-nm-thick coating of VO_2 (left-hand panels) and for a layer consisting of a dilute dispersion of VO_2 nanospheres, having an equivalent VO_2 thickness of 50 nm, in a medium mimicking transparent glass and polymer (right-hand panels) [16].

corresponding influence on T_{lum} is minor. It seems that work during recent years has changed thermochromism from being mainly a curiosity with regard to glazing into a viable option [15,162].

There are still other possibilities to vary T_{lum} as a function of temperature. They include color-neutral thermochromic layers and laminates based on organic materials [163–165], arrangements comprising "Christiansen filters" [166], as well as thermotropic [163,164,167] and photothermotropic [168] "cloud gels" that may be positioned between glass panes. These gels are polymers, and "clouding" (transition to a diffusely scattering state) can occur at a "critical" temperature as a result of reversible thermochemical dissolution and thermally induced modification in the lengths of the polymer molecules.

9.5. Photochromic thin films

Thin films of oxygen-containing yttrium hydride have been studied relatively recently; they are capable of giving optical absorption in the full wavelength range of solar energy upon exposure to ultraviolet and visible light [169,170]. Thin films of MoO_3 and WO_3, as well as hybrid materials incorporating these, also show some photochromism [171]; it is strongest for infrared radiation, which is consistent with the properties of electrochromic and gasochromic thin films of these materials.

10. Conclusions and perspectives

It should be patently clear from this survey article that there are many types of solar energy materials for thermal applications. They are in different stages of development and range from an early explorative phase all the way to mature technology. Ongoing and future research will widen the scope of these materials, but how? An answer must be a subjective matter and can only reflect the authors' experiences and visions. This is how this final section should be read.

Solar collectors for producing hot water or air are widely used today. Spectrally selective absorber surfaces have been developed and refined during decades, and numerous surfaces of this kind are produced industrially. Their properties approach theoretical limits. Manufacturing technologies seem to have shifted in favor of vacuum-based methods with small environmental footprint. Apart from high-performance solar absorbers, which must look black, there are ongoing developments of somewhat less efficient colored surfaces which lend themselves well to integration in ordinary architecture. Such surfaces

might be applied by painting and similar low-cost technologies. A parallel development trend concerns solar absorber coatings for very high temperatures and devised for solar-thermal production of electrical power

Technologies for cold roofs and walls are finally being developed and will undoubtedly lead to better living conditions in hot regions of the world.

Radiative cooling by using the clear sky as a heat sink remained a strangely unexplored field for decades, but keen interest is currently growing worldwide. Further materials development will be instrumental in order to develop practical systems for passive cooling, and selectively emitting surfaces as well as infrared-transparent convection shields are required. Radiatively cooled water-collecting surfaces have attracted very scant attention despite their unquestionable significance.

In the industrialized countries of today, some 30–40% of the primary energy is used for heating, cooling, lighting and ventilation of buildings and for electrical appliances of various kinds [172]. However, the built environment offers a large potential for "passive" solar energy utilization, and it is evident that solar energy materials are crucial. Coatings on glass are of particular importance. In some countries, coated float glass is used in multiple-pane glazing with almost no exception, whereas much less advanced glazing is employed elsewhere. Coatings with static properties—for providing "low-E" or "solar control"—are produced with mature technologies, well known to glass manufacturers and unlikely to be improved more than marginally in the future. These coatings are either based on ~0.01 μm thick silver or ~0.2 μm thick doped tin oxide. It is probable that these materials will continue to be used in the future owing to their excellent properties and the large investments in existing manufacturing technology.

Coatings for glazing can combine spectral selectivity with angular dependent properties, but these coatings are usually optimized only for light at normal incidence [173]. Multilayer designs with angular performance tailored to specific building sites and orientation are options for the future. Angular selectivity remains a possibility that needs further exploration, including for angular-selective thermal emission.

Glazing with adjustable optical properties has long been a Holy Grail in "high-tech" architecture [24]. Such glazing can be developed by harnessing many different techniques and using electrochromic, thermochromic, gasochromic and photochromic materials. Multifunctional glazing involving two or more of these chromogenic features—perhaps together with energy production, photocatalytic air cleaning, etc.—is an interesting possibility awaiting further development.

Electrochromic "smart" glazing is, in the authors' opinion, especially significant and has a potential to give user-adapted operation. Such glazing enables a combination of increased indoor comfort for the occupants of the building (less glare and thermal stress) and large energy efficiency (especially lowered air cooling load). Products of this kind are currently (2018) proving themselves on the market. Cost is an issue, but current developments of manufacturing technology, such as roll-to-roll coating of polymer foil, open avenues towards cheap products [174]. Considering the combined blessings of comfort and energy savings—as well as recent advances in technology and business opportunities—one may envisage the introduction of electrochromic "smart" glazing on a massive scale, possibly making such glazing the norm rather than the exception in analogy with how glazing with static surface-coated glass currently is the standard on a number of markets.

Thermochromics has made great strides recently and may be ready for implementation in glazing both as a stand-alone technology and in conjunction with electrochromics.

An attempt to look into the future can only be subjective, as noted above. However, certain global trends will continue to affect and stimulate research on solar energy materials for decades to come. These trends include a growing population which will increase the need for safe and affordable energy to meet its needs and aspirations, global climate change driven by CO_2 emission due to energy production,

agglomeration of people in mega-cities with associated effects on human health and micro-climates, and progressive depletion of raw materials which will make it increasingly important to rely on abundant and non-critical resources.

For better or worse, fossil fuels will be with us for many years. Atomic fission is fraught with safety issues, and abundant energy from atomic fusion—touted for many decades—is likely to remain conjectural. But solar energy is gradually supplementing and replacing fossil and nuclear sources of energy, and further materials research and development is the key to success in this sea-change.

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