Review

Transparent conductors as solar energy materials: A panoramic review

Claes G. Granqvist*

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden

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This Review is dedicated to the memory of Godfrey W. Mbise, whose research was instrumental for the development of angular selective transparent conductors discussed in Section 4.

Abstract

Transparent conductors (TCs) have a multitude of applications for solar energy utilization and for energy savings, especially in buildings. The largest of these applications, in terms of area, make use of the fact that the TCs have low infrared emittance and hence can be used to improve the thermal properties of modern fenestration. Depending on whether the TCs are reflecting or not in the near infrared pertinent to solar irradiation, the TCs can serve in “solar control” or “low-emittance” windows. Other applications rely on the electrical conductivity of the TCs, which make them useful as current collectors in solar cells and for inserting and extracting electrical charge in electrochromic “smart windows” capable of combining energy efficiency and indoor comfort in buildings. This Review takes a “panoramic” view on TCs and discusses their properties from the perspective of the radiative properties in our ambience. This approach leads naturally to considerations of spectral selectivity, angular selectivity, and temporal variability of TCs, as covered in three subsequent sections. The spectrally selective materials are thin films based on metals (normally gold or titanium nitride) or wide band gap semiconductors with heavy doping (normally based on indium, tin, or zinc). Their applications to energy-efficient windows are covered in detail, experimentally as well as theoretically, and briefer discussions are given applications to solar cells and solar collectors. Photocatalytic properties and super-hydrophilicity are touched upon. Angular selective TCs, for which the angular properties are caused by inclined columnar nanostructures, are then covered. A discussion of TC-like materials with thermochromic and electrochromic properties follows in the final part. Detailed treatments are given for thermochromic materials based on vanadium dioxide and for electrochromic multi-layer structures (incorporating TCs as essential components). The reference list is extensive and aims at giving an easy entrance to the many varied aspects of TCs.

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Keywords: Transparent conductor; Thin film; Solar energy; Energy efficiency

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*Tel.: +46 18 471 3067; fax: +46 18 500 131.
E-mail address: claes-goran.granqvist@angstrom.uu.se

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1. Introduction

Future energy supply and energy security will demand revolutionary advances in technology in order to maintain or forward today’s (2007) general standard of living and economic prosperity [1]. Faced with high and rising energy prices, limitations in energy supply, and growing concerns about climate changes and their environmental- and health-related effects, the magnitude of the problems may seem daunting. For example, it has been stated that the warming and precipitation trends due to anthropogenic climate change during the past 30 years already claim over 150,000 human lives annually [2,3]. These changes are also expected to be accompanied by more common and/or extreme events such as heatwaves, heavy rainfall, and storms and coastal flooding; there is also a risk that nonlinear climate responses will lead to even more and rapid climate changes such as breakdown of the ocean “conveyor belt” circulation, collapse of major ice sheets, and/or release of large quantities of methane at high latitudes thus leading to intensified global warming [4].

Furthermore, the urgently needed advances in energy technology must take place for an increasing population, whose growing concentration in mega-cities leads to “heat islands” which tend to aggravate the warming [5] and increase the urban cooling load by up to 25% compared to the case of the surrounding rural areas [6]. By 2050, there will be some ten billion people in the World. Energy must be available to them all, and it has to be clean. New technologies are urgently needed to accomplish this. Some of these technologies—mainly related to efficient solar energy utilization and to energy savings in the built environment—will be discussed in this Review.

Before proceeding one should contemplate how large and important the energy sector is for Society. Currently (2007), the total global energy consumption of oil, coal, natural gas, nuclear and hydropower, etc., is estimated to be some 10,000 million ton oil equivalents per year [7]. This corresponds to around 6700 billion USD, which in fact might be greatly underestimated since only primary sources are accounted for. To put this number in perspective, one could note that it is about ten times larger than the total value of the biotechnology market, including everything from pharmaceuticals to medicine. The economics of renewable energy and energy savings is a challenging subject, fraught with risks but also noteworthy for its new opportunities [8].

Where do the transparent conductors (TCs), which this Review is about, enter into this large scenario? How can they contribute to meeting “The Terawatt Challenge” discussed in a recent article in which the ten most serious global concerns were listed with “energy” at the head [1]? As discussed below, the TCs—oxides as well as non-oxides—can indeed play an important role both for energy generation and for energy saving.

A basic reason why TCs are of concern is that they can show transparency in a limited and well-defined range, normally encompassing visible light in the 0.4<\lambda<0.7\mu m wavelength interval. In the infrared (IR) their metallic property leads to reflectance and at sufficiently short wavelengths, in the ultraviolet (UV), they become absorbing due to excitations across an energy gap. If the
reflectance is in the range for thermal radiation, i.e., $3 < \lambda < 50 \mu m$ at normal temperature, the emission of heat is impeded. If reflectance prevails at $0.7 < \lambda < 3 \mu m$, covering the IR part of the solar spectrum which carries about 50% of the solar energy, one can combine visible transmittance with rejection of a large part of the solar energy and at the same time have low thermal emittance. It is then obvious that TCs have a number of diverse applications in the fields of solar energy utilization and energy efficiency. Other applications of TCs emerge from their electrical conductivity, which enables their use as current collectors in solar cells and as transparent electrodes for charging and discharging of electrochromic smart windows, etc. Clearly the TCs can be viewed as “solar energy materials”, whose properties have been given a bird’s eye perspective in recent articles [9–11]. Parts of this Review can be viewed as elaborations on these earlier papers.

The applications of TCs, hence, can rely on their spectral selectivity, as clear from the discussion above. Other possible uses emerge from the angular properties of the radiation that surrounds us, specifically by the fact that one can take advantage of the Sun’s passage over the vault of heaven to have different performances for midday and dawn or dusk. Still other applications ensue from the fact that ambient radiation or human needs vary during the day and season, so that solar energy and/or visible light ideally should be admitted or rejected as a function of time.

This Review is organized as follows: Section 2 presents an overview of the radiation that prevails in our natural surroundings with the main object of defining the types of spectral and angular selectivity that are of interest for solar energy and energy efficiency. Also introduced are materials with variable optical properties, known as “chromogenic” materials [12], whose usefulness for energy savings in buildings is discussed. Primers on thin-film-coating technology and on the materials capable of serving as substrates for the coatings are included too. Then follow discussions of TCs with tailored spectral selectivity, angular dependence, and temporal variability in Sections 3–5, respectively. Regarding spectral selectivity, most attention is devoted to architectural windows and glass façades, which require TCs for admitting and reflecting visible light, solar energy, and thermal radiation in different wavelength regions. Special attention is devoted to noble-metal-based films, which are commonly used on today’s windows, and n-doped wide band gap oxide semiconductor films with particular consideration of In$_2$O$_3$:Sn. Theoretical and experimental data are given for the spectral optical properties. The possible use of TCs to avoid or modify the condensation of water on windows is also discussed, as are applications to “vacuum glazings”, photovoltaic cells, and thermal solar collectors. Angular selectivity is given a shorter presentation with focus on obliquely deposited metal-based films having inclined columnar nanostructures. Materials and devices enabling temporal variability attract much current interest, and this part of the Review covers photochromic, thermochromic, and gasochromic options. In-depth discussions are given for thermochromic VO$_2$-based films and for oxide-based electrochromics. Concerning the latter, the discussion embraces, in particular, general device design, discussions of WO$_3$ and NiO films, and data on foil-type devices incorporating these two materials. The Review is concluded with an outlook towards some future possible materials and applications of TCs in Section 6.

The aim is to give a “panoramic” view on TCs, including those that may be of interest in forthcoming technologies, and to give an easy entrance to recent literature. The latter ambition has led to the incorporation of an extensive and detailed reference list covering, in particular, the most recent work.

2. Foundations for solar energy materials

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

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

where $T$, $R$, and $A$ denote transmittance, reflectance, and absorbance, respectively. Another fundamental relationship, also ensuing from energy conservation and referred to as Kirchhoff’s Law, is

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

with $E$ being emittance, i.e., the fraction of the blackbody radiation that is given off at a particular wavelength. Eq. (2) is of practical relevance mainly for $\lambda > 3 \mu m$.

2.1. Spectral and angular selectivity of ambient radiation

Fig. 1 introduces the electromagnetic radiation of our ambience in a unified manner [13]. The most fundamental property of this radiation stems from the fact that all matter sends out electromagnetic radiation, which is conveniently introduced by starting with the ideal blackbody 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 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 GW m$^{-2}/C0$). The spectra are bell-shaped and confined to the $2 < \lambda < 100 \mu m$ range. The peak in the spectrum is displaced toward shorter wavelength as the temperature goes up, which is referred to as Wien’s displacement law. The peak lies at about $10 \mu m$ for room temperature. 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 a function of $\lambda$.

Part (b) of Fig. 1 reproduces a solar spectrum for radiation just outside the Earth’s atmosphere. The curve
has a bell shape, which defines the Sun’s surface temperature (≈6000 °C). It is important to observe that the solar spectrum is limited to 0.25 < λ < 3 μm, 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 ± 21 W m⁻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, taken with the widest meaning of this term, 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 during 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 UV (λ < 0.4 μm) and IR (λ > 0.7 μm) radiation are strongly damped. The maximum power density perpendicular to the sun is about 1000 W m⁻². Thermal radiation from a surface exposed to the clear sky is strongly absorbed except in the 8 < λ < 13 μm range, called the “atmospheric window”, where the transmittance can be large provided that the humidity is not too high.

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 < λ < 0.7 μm interval and has its peak at 0.555 μm. Clearly a large part of the solar energy comes as invisible IR 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.

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) [14,15]. One then obtains luminous, solar, or thermal values pertinent to the respective optical property; they are denoted Xₜₐₜₜₜₜ, Xₜₐₜₜₜₜ, and Xₜₐₜₜₜₜ, with X being T, R, A, or E.

Fig. 1 emphasizes that ambient radiation is spectrally selective, i.e., confined to specific and usually well-defined wavelength ranges. This property is of large importance with regard to TCs used for energy-related applications, as discussed next in Section 3. Another type of selectivity—known as angular selectivity—originates 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 as further discussed in Section 4.

2.2. The potential of chromogenic technologies

The well-known fact that the ambient properties vary during the day or season makes it of interest to use “chromogenic” materials, capable of changing their properties [12]. The purpose can be to create energy efficiency in order to admit solar energy if there is a heating demand or to reject solar energy if there is a cooling demand. Considering such “smart” fenestration, there is also a “human dimension” related to comfort, implying a desire to experience good lighting, avoid discomfort though glare, and prevent thermal stress. Obviously the notion of “comfort” is a subjective one even if quantification is possible to some extent [16–19]. Another aspect concerns skin protection (and, in general, materials protection) [20]. The key question at present is the magnitude of the energy efficiency inherent in the ability of a material to vary its
optical properties. It is a complicated and multi-dimensional one as will become apparent.

The first line of reasoning is intuitive and simplistic [21–23]: it considers a cooling situation. The solar energy falling onto a vertical surface, such as a window, each year is set to 1000 kWh m⁻². This can serve as a nominal value, whereas more correct numbers for South-facing/North-facing/horizontal surfaces are 850/350/920, 1400/450/1700, and 1100/560/1800 kWh m⁻² for Stockholm (Sweden), Denver (USA), and Miami (USA), respectively. Half of this, 500 kWh m⁻², corresponds to visible light. This number is used in the analysis below since IR radiation can be reflected off—at least in principle—by use of a spectrally selective surface that does not exhibit variable transmittance. If the transparency can be altered between 7% and 75%—which is by no means unlikely with electrochromic technology as discussed in Section 5—the difference between having the window constantly colored and constantly bleached is 340 kWh m⁻². The next issue is then to consider when the “smart” window should be colored and when it should be bleached. With occupant presence as a basis for the control strategy, the question is when a room is in use—or, more precisely, the fraction of the solar energy that can enter when nobody is present. Considering that a normal (office) room is empty during weekends, holidays, and vacations, early mornings and late afternoons (when the Sun is near the horizon), etc., it is probably a conservative estimate that 50% of the energy can enter the room when there is no one to look through the window. Hence, the estimate yields that 170 kWh m⁻² is the amount of energy saved annually by adopting the given control strategy.

Is this energy savings significant or not? To answer this question, one may note that 17% is a typical value for the photoelectric conversion efficiency of today’s best solar cells and thin-film sub-modules devised for terrestrial applications [24]. Thus, these solar cells would be able to generate 170 kWh m⁻² in the example given above. Of course the analogy between energy savings in “smart” windows and energy generation in solar cells is not tied to the choice of the incident solar energy being 1000 kWh m⁻², but applies generally irrespectively of the orientation of the surface under consideration. The “smart” window saves thermal energy, but if a cooling machine—operating with an efficiency of 300%, say—runs on electricity generated with an efficiency of 33% then the analogy becomes perfect. This latter consideration implies that one has a “national scenario” for the energy, with a “Coefficient-of-Performance” equal to unity.

Simulations of energy use in buildings in principle can be employed to calculate savings regarding cooling load, peak demand, lighting energy, etc. Other important issues concern occupant satisfaction and acceptance. These various aspects have been investigated recently with the object of providing realistic estimates of the potential of the “smart” windows technology [25–28]. Specifically, calculations for a standard office module with well-defined size, window area, lighting demand, occupancy, equipment and appliances, etc., showed that the energy savings potential was considerable for the cooling load [25,26,29]. The studied office block was oriented with one façade facing South and one facing North and the simulations were performed with climate data applicable to Rome (Italy), Brussels (Belgium), and Stockholm (Sweden). When using “smart” windows instead of conventional static solar control windows, the energy for space cooling, on an annual basis, could be reduced by as much as 40–50%. The amount of saved energy is obviously climate dependent. In moderately warm climates, such as those of Brussels and Stockholm, the number of days with very high outdoor temperature is relatively small but the energy required for balancing excessive solar energy inflow nevertheless is substantial, and an interesting result of the simulations was that the cooling power could be reduced so that air conditioning might be completely avoided when “smart” windows were used. Substantial energy savings appeared also in another recent study [27,28], which also pointed at a number of important subjective assets of the technology [30]. The strategy for controlling the “smart” windows is of obvious importance and has been the subject of a number of recent studies [27,28,31–38].

The examples above were chosen to correspond to cooling of buildings. This choice is appropriate since the energy for air-cooling is steadily rising and takes a growing share of the energy used in the built environment. The energy spent in buildings presently amounts to about 40% of the energy expenditure in the EU and corresponds to roughly 4% of the Gross National Product [5,39]. As pointed out recently [40,41], air conditioning and refrigeration becomes increasingly important for the peak electricity demand; it has risen by an average of 17% per year in the EU between 1995 and 2003 [42]. A further indication of the pressing demand for new and efficient cooling techniques is that more than half of the electricity consumption in households in some major Chinese cities is for air conditioning, refrigeration, and water cooling [43]. In an extreme climate, such as that of Kuwait [44], more than 75% of the electrical peak load is currently used for air conditioning, largely as a result of current building practices [45].

2.3. Thin-film deposition technologies

The TCs used for solar energy and energy efficiency are normally thin films, with thicknesses between 10 nm and 1 μm, backed by transparent or non-transparent substrates. Consequently thin-film deposition and thin-film optics are of much importance; they are discussed in numerous books and tutorial texts [46–51]. Deposition constitutes a vast technological field [52–57], and only the most common methods are mentioned here.

Sputter deposition is widely used to make uniform coatings on glass, polymers, metals, 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 or cylinder 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) [58–61]. Fig. 2(a) shows the principle for coating sheet glass by this technique; the panes are transported in and out of deposition chambers via load locks so that the process is continuous. Evaporation can be an alternative to sputtering. Here, the raw material of the film is heated in vacuum so that a vapor transfers material to the substrate at a sufficient rate [62,63]. Systems for sputtering and evaporation are normally set up so that the deposition flux hits the substrate at a more or less normal angle, but angle-resolved sputtering is possible even for large areas [64]; such techniques are of interest for applications requiring angular selectivity, as further discussed in Section 4. Sputtering and evaporation are often referred to jointly as “physical vapor deposition” or “PVD”.

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 heat treatment [65,66]. Alternatively, the chemical solution can be applied by spray coating. Chemical vapor deposition (CVD) uses heat to decompose a vapor of a “precursor” chemical to make a thin film of a desired composition [67,68]. Plasma-enhanced CVD is particularly suited for optical coatings [69]. A variety of the CVD technique is called spray pyrolysis; a fluid containing the precursor is then sprayed onto a hot substrate. This method is used on a large scale for deposition of tin oxide-based films on hot glass, either in a separate process as indicated in Fig. 2(b) or continuously onto the hot glass as it comes out from the float glass production and is transferred to the cooling stage. Electrochemical techniques include cathodic electrodeposition from a chemical solution [70] and anodic conversion of a metallic surface—especially of Al—to form a porous oxide [71]. Numerous alternative techniques exist as well [72].

Web coating of flexible substrates can be used to make films on very large surfaces. Fig. 3 illustrates one variety in which the web is transferred to a chilled drum where the deposition takes place by sputtering or any other suitable technique, and where the coated web is then collected on a take-up roll [73]. The whole process can take place inside a vacuum chamber. Optical coatings on plastics have been surveyed recently [74].

So far the techniques that have been described are best suited for coating non-patterned surfaces. However, masking is possible in order to produce patterns; alternatively etching or some other subtractive technique can be made to obtain a desired configuration. Rather than obscuring or subtracting material it is also possible to use an additive process, such as printing with an appropriate ink containing (nano)particles, normally followed by heat treatment to remove unwanted binder substances. Recent advances in printing technology, as well as the great amount of contemporary work on large-scale fabrication of nanoparticles, makes it likely that printing-related techniques will gain increased popularity in the future.
2.4. Substrates for transparent conductors, and their antireflection treatment

It is suitable to include some information on substrate materials for coatings of TCs. The most widely used substrate is glass. It can exhibit a variety of properties [75], but float glass is a highly standardized product [76]. Float glass is characterized by uniformity and flatness almost on the atomic scale, which is important for its usefulness as a substrate for thin-film deposition. The flatness is an outcome of the production process in which the glass melt is solidified on a surface of liquid tin. The middle curve in Fig. 4 shows the spectral transmittance of 6-mm-thick standard float glass within the wavelength range relevant to solar radiation. A characteristic absorption feature at \( \lambda \approx 1 \) \( \mu \text{m} \), due to the presence of Fe oxide, limits \( T_{\text{sol}} \) to some noticeable extent. Special float glass is available with varying amounts of Fe oxide [76]. Fig. 4 shows that low Fe content leads to glass with very high \( T_{\text{lum}} \) and \( T_{\text{sol}} \), and with substantial transmittance also in the UV. Glass with a large Fe content limits \( T_{\text{sol}} \) while \( T_{\text{lum}} \) remains rather large; such glass has a greenish tint, which becomes increasingly distinct at large thickness. The reflectance of each interface between glass and air is about 4% in the 0.4 \( \mu \text{m} \) range, implying that the maximum transmittance for a glass pane is 92%. Glass is strongly absorbing for \( \lambda > 3 \) \( \mu \text{m} \), and \( E_{\text{therm}} \) is as large as about 87%.

Polymers are also of much importance as substrates for TCs, and transparent polymers can, in principle, replace glass. However, polymers degrade more easily than glass and hence have fewer applications; photodegradation, photooxidation, and photostabilization of polymers are a vast field of research [77–80]. Polyethylene terephthalate (PET) foil deserves special mention since it can be suspended between glass panes and used in practical window constructions. Another application of coated foil is in “window film” for upgrading the performance of existing fenestration. An alternative to PET is polyethylene napthalate (PEN) and fluoro carbon plastics.

Laminated glass may be used for safety and other reasons. Such glass normally has a layer of polyvinyl buteral (PVB) sandwiched between two glass panes and bonded to the glass under heat and pressure. The laminate is an efficient absorber of UV light, and the transmittance at \( \lambda < 0.38 \) \( \mu \text{m} \) is almost zero for a layer thickness of the order of 1 mm. Transparent electrically conducting glue based on conducting polymers was described recently [81].

Both for glass and polymers it is possible to modify the optical properties by incorporation of nanoparticles or ions. Noble metal particles give absorption at visible wavelengths, whereas particles with lower electron densities, such as heavily doped oxide semiconductors, display absorption peaks at longer wavelengths [82]. A particularly interesting situation, with rather high \( T_{\text{lum}} \) and moderately low \( T_{\text{sol}} \), can be achieved with LaB\(_6\) nanoparticles dispersed in PVB [83]. This is a result of the unusual electronic structure of LaB\(_6\) [84].

Antireflection (AR) coating of glass and polymers is often of interest for boosting the performance of devices for solar energy and energy efficiency. For example, contemporary fenestration uses at least double-glazing, and the overall value of \( T_{\text{lum}} \) and \( T_{\text{sol}} \) are limited by reflections at the various interfaces. To obtain high \( T_{\text{lum}} \) through glass one can apply a layer whose refractive index is close to the square root of the refractive index of the underlying substrate (i.e., 1.23) and with a thickness corresponding to a quarter wavelength for visible light (i.e., \( \approx 100 \) nm). By coating both sides of a glass pane with self-assembled silica nanoparticle films it is possible to obtain \( T_{\text{lum}}>99\% \) in the middle of the luminous spectrum [85,86]. This is illustrated in Fig. 5 [85]. Excellent AR properties have been obtained also with graded-index silica films made by oblique angle deposition [87]; this technique is further discussed in Section 4.1. Other AR treatments of interest include thin films of nanoporous organosilicates [88], AlO\(_x\)F\(_y\) [89,90] or MgF\(_2\), porous or micro-structured surface layers produced by liquid or vapor etching of glass.

![Fig. 4. Spectral transmittance for float glass with three different amounts of Fe\(_2\)O\(_3\). From Granqvist [72].](image1)

![Fig. 5. Spectral transmittance of a glass plate coated on both sides by antireflecting thin films of porous silica. Replotted from Nostell et al. [85].](image2)
[91,92] or Si [93], and layers serving as a sub-wavelength surface relief gratings [94].

Simple AR treatments are able to decrease the reflectance within a rather narrow wavelength range, but if broadband AR is required one could use multi-layer films with carefully adjusted refractive indices and thicknesses; they can be designed using several different strategies [95–99]. Normally an AR coating is efficient only for a specific range of incidence angles for the light, especially for the case of multi-layer configurations, but wide-angle AR coatings are possible for narrow wavelength ranges [100,101]. Recently AR treatments invoking a combination of graded index layers and layers with fixed refractive index have been investigated computationally as well as experimentally in order to specify coatings combining low reflectance in the full visible wavelength range and with low reflectance in a wide angular interval [102–105].

3. Applications based on spectral selectivity

Spectrally selective TCs can be used in different ways as discussed below. By far the largest applications are in architectural windows and glass façades, which are dealt with in detail in Sections 3.1–3.7. After some general considerations in Section 3.1, there are discussions of single-layer and multi-layer metal-based films in Sections 3.2 and 3.3, respectively. Doped oxide-based films are then covered; an introduction is given in Section 3.4, and this is followed by theoretical considerations and empirical data for, in particular, In$_2$O$_3$:Sn films in Sections 3.5 and 3.6, respectively. A brief discussion of TCs in “vacuum glazings” is given in Section 3.7. Another, less well known, use of TCs is for preventing water from condensing on windows; this is treated Section 3.8. Self-cleaning and super-hydrophilicity are discussed briefly in Section 3.9. Solar cells require transparent electrodes as covered in Section 3.10. Finally, some possibilities with regard to TCs in thermal solar collectors are put forward in Section 3.11.

Architectural windows and glass façades are problematic from an energy perspective [76]. Their primary function—to provide unmitigated visual contact between indoors and outdoors, as well as day-lighting—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 buildings via their windows, with concomitant demand for space heating and cooling. Present architectural trends are to increase the window areas, so that the energy issue may become even more pressing in the future.

Thin films of TCs can alleviate the situation, and their ability to provide spectral selectivity is already used to a large extent for new windows. On some markets, the penetration of this technology is currently almost total, whereas the market share is smaller elsewhere. Given the obvious need to diminish the energy consumption on a global scale, the technology can only be expected to grow.

The enormity of the market is obvious; the current production of float glass—used almost without exception in modern fenestration—is about four billion m$^2$ per year [106]. Coating even a small portion of this with TCs makes architectural and automotive windows by far the largest field of applications for TCs, completely outsizing other presently much discussed applications such as displays and transparent electronics.

3.1. Two principles for energy-efficient windows: “low-E” and “solar control"

The radiation part of the heat transfer can be controlled by thin films with low $E_{\text{therm}}$, which, in a multiply glazed window, should face one of the confined air (or gas) spaces [72,107]. In this way the heat transfer across a vertically mounted window can drop from ~3 to ~1.5 Wm$^{-2}$K$^{-1}$ for double glazing and from ~1.8 to ~1.0 Wm$^{-2}$K$^{-1}$ for triple glazing. Obviously, $T_{\text{hum}}$ must be large for these films. The IR 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 two types of thin films, known as “low emittance coatings” (“low-E”) characterized by

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

$$R(\lambda) = 1 \quad \text{for} \quad 3<\lambda<50\mu\text{m} \quad (4)$$

and “solar control coatings” characterized by

$$T(\lambda) = 1 \quad \text{for} \quad 0.4<\lambda<0.7\mu\text{m}, \quad (5)$$

$$R(\lambda) = 1 \quad \text{for} \quad 0.7<\lambda<50\mu\text{m}. \quad (6)$$

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

In order to go below the heat transfer values mentioned above it is necessary to diminish also non-radiative (conductive and convective) heat transfer, which is possible in evacuated “vacuum glazings”. A heat transfer coefficient less than 0.2 Wm$^{-2}$K$^{-1}$ has been estimated for a triple vacuum glazing [108]. The requirements of TCs in such devices are discussed briefly in Section 3.7 below.

3.2. Metal-based thin films for energy-efficient windows: single-layer films

Very thin films of free-electron-like (“noble”) metals have been used as TCs and transparent heat reflectors at least since the early 1950s [13,109,110]. They can have properties to some extent resembling those in Eqs. (3)–(6) and hence provide a good starting point for development, and in principle a very thin layer of Cu, Ag, or Au is the simplest way to accomplish a TC and transparent IR reflector [111–113]. Alternative materials are TiN and ZrN [114–119] as well as Pt [120] and Al [121]. The nitrides are notable for their hardness and durability [122].
Thin Ag films stand out as the superior option as a result of their low value of $A_{\text{lum}}$. The other metals exhibit some, usually unwanted, short-wavelength absorption at $\lambda < 0.5 \mu m$ for Cu, Au, and the nitrides (hence their color), and at $\lambda \approx 0.8 \mu m$ for Al. Chemical and mechanical ruggedness is an issue for the metal-based TCs—much more than for the oxide TCs to be discussed in Sections 3.4–3.6 below—and laboratory experiments as well as field tests show that they are only suited for application on surfaces facing cavities in double-glazed windows. The films are sometimes referred to as “soft coats” and are normally applied by high-rate magnetron sputtering.

The idealized performance of a metal-based thin film is readily computed using established techniques [123,124] by representing it as a plane parallel slab of thickness $t$. The metal is uniquely characterized by two parameters—known as the optical constants or the complex dielectric function—pertinent to a uniform bulk-like material. Fig. 6 shows computed results of $T_{\text{lum}}$, $T_{\text{sol}}$, $R_{\text{sol}}$, and $E_{\text{therm}}$ as a function of $t$ for Ag [112]. It is found that $t = 5 \text{ nm}$ yields an impressive set of data, specifically with $T_{\text{lum}} = 85\%$, $T_{\text{sol}} = 74\%$, and $E_{\text{therm}} = 8\%$. A glass with such a thin film would constitute an excellent low-$E$ glazing. Unfortunately, however, extremely thin noble metal films deposited onto glass cannot be represented as plane parallel slabs, as will be considered next.

When a metal such as Cu, Ag, or Au is deposited onto glass or some other dielectric material the film goes through a series of rather well defined “growth stages” [113,125–128]. This is illustrated in Fig. 7, where the pertinent structures and thickness scales are also shown. Initially, tiny metallic nuclei are formed at certain sites on the substrate [129,130]. Continued deposition makes the nuclei grow via surface diffusion and direct impingement. Fractality concepts can be used to understand aspects of this growth [131]. The metal islands that are then formed have elliptical shapes—as seen by electron microscopy—with both major and minor axes obeying log-normal distribution functions, as can be reconciled with a statistical model for island coalescence [132]. Progressing coalescence growth leads to larger and more irregular islands. The growing film then passes through “large-scale coalescence”, meaning that an extended metallic network is formed [133]. Subsequent deposition makes the voids between the metallic paths become smaller and increasingly regular. The void structure can in itself be conducive to $T_{\text{sol}}$, particularly in the near-IR [134]. A close to uniform layer with atomically flat grain tops may ultimately be formed [135]; the surface roughness can be as small as 0.4 nm for Au films sputter deposited onto float glass under optimized conditions [136]. Some vacancies and small voids may be difficult to evade, though [137]. The corresponding structures are illustrated in Fig. 7 with metal shown as black. Prior to large-scale coalescence, the islands are ~10 nm in size.

It is now evident that a model of the film based on a plane parallel slab can only be adopted for the later growth stages. However, effective medium theories [138,139] can be used to describe the optical properties of island structures [140–142] as well as void structures [113] and theories can be used also for the cross-over stage at large-scale coalescence [143] where the optical properties are gradually shifted from being associated with localized surface plasmons to extended plasmon–polaritons [144,145]. The theory for nanoparticulate matter can be refined by considering “spill out” of the electronic density outside the nanoparticle as well as coupling to the electronic environment [146]. These models are not of central importance to TCs, though, and thus they are not discussed further here.

The thickness scale appropriate for representing the growth stages depends on many parameters, such as deposited species, substrate material, presence of (artificially added) nucleation centers, substrate temperature, vacuum condition, electrical fields, etc. Fig. 7 indicates two typical scales referring, respectively, to conventional
evaporation (c.e.) and to ion-assisted evaporation (i.a.); the latter uses an optimized flow of energetic Ar⁺ ions. Such ion bombardment is known to lead to grain growth [147]. Sputter deposition may be represented by an intermediate thickness scale. The most important conclusion of the discussion above is that noble metal films are reasonably uniform only at thicknesses above 10 nm, which is far beyond the optimal thickness for an idealized uniform film (cf. Fig. 6).

The internal structure of a thin film can comprise grains of different sizes and connectivity depending on the deposition conditions; these features are often discussed in terms of “zone models” of which there are several varieties that are more or less able to capture the specifics of one or another thin-film deposition technology [148–156]. Computer modeling can be used to understand the evolution of the “zones” [157,158]. It has been predicted from theory that linear grain growth is expected if the thin-film deposition rate is constant [159]. Texture normally develops jointly with grain growth [160].

It is now possible to appreciate experimental data on spectral optical properties of noble metal films as a function of thickness. Fig. 8 shows measured reflectance and transmittance for conventionally evaporated Ag films [111,112]. At t = 6 nm one observes that $R_{\text{therm}}$ is low, implying that $E_{\text{therm}}$ is high. This can be reconciled with the occurrence of an island structure; if the layer were continuous then $E_{\text{therm}}$ would have been low as inferred from Fig. 6. It appears that a continuous Ag layer is formed only at $t > 9$ nm. These films yield high IR reflectance combined with significant $T_{\text{lum}}$ and hence are of interest for low-E windows. As expected, $T_{\text{lum}}$ and $T_{\text{sol}}$ decrease with increasing film thickness.

The tendency for thin metal layers to form non-uniform structures at small thicknesses gives a significant limitation to their performance as TCs and transparent IR reflectors. Prescribing high reflectance at long wavelengths—i.e., low $E_{\text{therm}}$—one is confined to $T_{\text{lum}} < 50\%$ and $T_{\text{sol}} < 40\%$ for evaporated films [111]. Somewhat superior properties, with $T_{\text{lum}} \approx T_{\text{sol}} < 60\%$, can be achieved with ion assisted deposition [113] or special sputter technology [161]. If a higher transmittance is required—as is frequently the case for architectural windows and glass façades—one must use multi-layer coatings as considered next in Section 3.3.

The properties of optically thick metal films with nanoholes (smaller that the wavelength) have attracted interest recently following the remarkable observation of extraordinary light transmission through metallic sub-wavelength hole arrays, which does not obey classical optical theory [162,163]. The effect is illustrated in Fig. 9 showing transmittance through Au films with the indicated nanostructures; the holes are 0.25 μm in diameter and have a lattice constant of ~2 μm. An extraordinary transmittance peak centered at $\lambda \approx 615$ nm stands out clearly [164]. Peak transmission levels up to 39% have been reported recently [165]. Multiple transmission bands can be created with periodic arrays of nanohole apertures [166], and maxima and minima of transition spectra can be suppressed by adequate nanohole arrangements so that the transmittance can be tailored to different needs [167]. Much of the experimental work has been done on films of Ag and Au. The transmittance may not be sufficient for most energy-related applications, but the phenomenon nevertheless deserves some attention here since it may affect $T_{\text{lum}}$ and $T_{\text{sol}}$ for non-continuous metal films. The effect has been interpreted in different ways [168–175]. The initial explanation [169,176], in terms of surface plasmon polaritons, has been given strong support through near-field optical measurements in recent work [164,165,177]. Strong polarization effects can occur if the
holes’ cross-sections are non-circular [178–180]. Results have been recorded recently for different film thicknesses [181], different hole symmetries [182], double nanoholes [183], and holes surrounded by surface corrugations [184].

Nanostructured Ag films with voids have been discussed in terms of extraordinary light transmittance, and it was demonstrated that the enhancement effect could be effectively turned off by a dielectric surface layer [185,186]. Thermal radiation through nanoholes also shows unexpected and novel features, and the flux is not proportional to the fourth power of the temperature—as for Planck radiation (cf. Fig. 1a)—but rather to the eighth power [187].

3.3. Metal-based thin films for energy-efficient windows: multi-layer films

The limitations in $T_{\text{lum}}$ and $T_{\text{sol}}$ in reasonably uniform noble metal films are largely due to reflectance at their surfaces, and consequently it is possible to boost the transmittance by adding layers that serve, effectively, to antireflect the metal. One is then led to dielectric/metal and dielectric/metal/dielectric multi-layers. Dielectrics with high refractive indices—such as Bi$_2$O$_3$, In$_2$O$_3$, SnO$_2$, TiO$_2$, ZnO, and ZnS—give the largest enhancement. It is possible to optimize for low-$E$ or solar control trough proper selections of the film thicknesses.

Fig. 10 compiles measured transmittance spectra for TiO$_2$/Ag/TiO$_2$ films on glass [72]. These data are characteristic for what one can accomplish by using the three-layer design. It can be inferred that $T_{\text{lum}} > 80\%$ and $E_{\text{therm}} < 20\%$ are obtainable for all of the coatings. The dashed curve pertains to the coating with maximum IR reflectance; it yields $T_{\text{sol}} \approx 50\%$ and $R_{\text{sol}} \approx 42\%$. The dotted curve corresponds to $T_{\text{sol}} \approx 67\%$ and $R_{\text{sol}} \approx 26\%$. The solid curve was measured for a commercial coating on float glass of the type represented by the middle curve in Fig. 2; this coating has $T_{\text{lum}} \approx 87\%$ and $T_{\text{sol}} \approx 72\%$. Work has been reported recently also on ZnS/Ag/ZnS [188,189], ZnO/Ag/ZnO [190–192], and ZnO/Cu/ZnO [193,194].

Fig. 11 illustrates the joint development of electrical and optical properties in a three-layer film of ZnO(20 nm)/Ag/ZnO(20 nm) [192]. The sheet resistance $R_{\text{S}}$ is given; it is defined by $R_{\text{S}} = \rho / t$ where $\rho$ is the resistivity. The stated transmittance corresponds to its maximum value. Clearly $t < 4\ nm$ yields poor electrical properties while $t > 8\ nm$ produces poor optical properties. The optimum is at $t \approx 6\ nm$, where one finds $R_{\text{S}} \approx 3\ \Omega$. Additional data on ZnO/Ag/ZnO films have been reported elsewhere [190,191].

A thin-film design which in principle can give very low resistivity is In$_2$O$_3$:Sn/Ag/In$_2$O$_3$:Sn [195–202]. In this case, all of the constituent layers are electrically conducting and a resistivity as low as $1.7 \times 10^{-4}\ \Omega\ cm$, together with $T_{\text{lum}} > 80\%$, has been obtained on a polymer substrate [200]. Corrosion at the interface between Ag and In$_2$O$_3$:Sn can be diminished if the Ag is alloyed with Pd, Au, or Cu [202].

Coatings of the type TiO$_2$/TiN/TiO$_2$ have been studied as well [116,117,203–206]. Fig. 12 shows data from a recent study of a three-layer stack with the TiO$_2$ layers being 35 nm thick and the TiN layer being 22 nm [206]. The top layer of TiO$_2$ can render this type of coating photocatalytically active and super-hydrophilic, as discussed further in Section 3.9 below. A very thin Ti interlayer between the TiN and the outer TiO$_2$ layer improved the heat insulating performance noticeably and also influenced the photocatalytic activity favorably [206].

The examples above were selected to illustrate principles rather than today’s (2007) commercial products. In fact, Ag-based thin films for energy-efficient fenestration are now highly optimized, and a very large number of products with specified thermal, solar, and luminous (including
color) properties are available on the market. Some of these products use multi-layers that go far beyond the three-layer concept and may include as many as seven layers, with two metal films. It is remarkable that these TCs have been on the market for decades, and the pertinent investigations of In oxide [213–215], and films of this material and of Sn oxide were shown to have excellent electrical and optical properties about 1965[216,217]. It appears that all of this work was motivated by potential technical applications. Transparent conducting oxides (TCOs) have been subjected to a very large number of investigations for several decades, and the pertinent literature embraces many thousand papers and is virtually impossible to penetrate in its entirety.

The most widely used and studied n-type TCOs are based on Zn, In, and Sn (and sometimes Cd). Doping is accomplished either by adding a higher-valent metal, by replacing some oxygen with fluorine, or by oxygen vacancies. The fundamental band gap is wide enough to allow very low magnitudes of $A_{\text{lum}}$ and $A_{\text{ext}}$, and doping is feasible to a level high enough to render the materials IR reflecting and electrically conducting. The onset of reflectance lies in the near IR, implying that the oxides can have a small $E_{\text{therm}}$ and thereby serve as low-$E$ coatings. However, the material is less useful for solar control, the main reason being that the doping cannot be brought to a sufficiently high level, at least not without considerable difficulty. A specific advantage of the TCOs, compared to their noble metal-based counterparts, is the chemical and mechanical stability, which allows their use on glass surfaces exposed to the ambience; the oxide films are sometimes referred to as “hard coats”. Several reviews of TCOs have been published recently [208,218–223].

A resistivity of $10^{-8}\Omega cm$ is often quoted as a number characterizing optimized films of In$_2$O$_3$:Sn (known as Indium Tin Oxide or ITO), ZnO:Al (AZO), and ZnO:Ga (GZO), even if lower resistivities were sometimes claimed already in the 1980s for ITO [224,225]. Recent investigations of ITO films have demonstrated resistivities between 7.2 and $8 \times 10^{-5}\Omega cm$ and free carrier densities as high as $2.5 \times 10^{21} cm^{-3}$ [226–234]. Films of AZO with $\rho \approx 8.5\times 10^{-5}\Omega cm$ [235] and of GZO with $\rho \approx 8.1 \times 10^{-5}\Omega cm$ [236,237] have been reported. It seems that pulsed laser deposition is particularly apt for making TCOs with exceptionally low resistivity. Other work from 2005 and later, demonstrating resistivities between 1 and $6 \times 10^{-4}\Omega cm$, has been reported for ITO [226,238–249], ITO:ZnO [250,251], ITO:Ti [252], In$_2$O$_3$ [242,253,254], In$_2$O$_3$:ZnO (IZO) [248,255–259], In$_2$O$_3$:Ti [260–262], In$_2$O$_3$:Mo [242,260,263–266], In$_2$O$_3$:Ga [267], In$_2$O$_3$:W [260,268], In$_2$O$_3$:Zr [260], In$_2$O$_3$:Nb [260], In$_2$–Sn,Mn$_2$O$_3$, with M being Zn or Cu [269], AZO [237,241,270–288], ZnO:(Al,F) [289], GZO [290–297], ZnO:B (BZO) [260,298], ZnO:Ga [297], Zn$_{0.95}$Mg$_{0.05}$O:Ga [299], and (Zn,Mg)O:P [300]. Bilayer films of ZnO/ZnO:Al showed lower resistivities than single-layer ZnO:Al films [301]. The properties of ZnO-based films made by sputtering have been reviewed [302] as have the properties of IZO [303]. All resistivity data lie inside the intrinsic limits of the electrical conductivity of TCOs formulated some time ago [304]. For completeness we note that other dopants can lead to ferromagnetism, which has been seen in ITO:Fe [305], SnO$_2$:Co [306], In$_2$O$_3$:Ni [307], In$_2$O$_3$:Sn,Ni [307], ZnO:Mn [308], ZnO:Co [309–311], and other similar materials. Attempts have been made to boost the properties of ITO by small additions of Ag [312–316]; such films could have lowered $\rho$, but $T_{\text{lum}}$ decreased if the Ag content was excessive. A resistivity of $8.2 \times 10^{-5}\Omega cm$ was stated for the most conducting films; they displayed $T_{\text{lum}} \approx 50\%$ [315].

Thin-film TCO preparation is usually very sensitive to deposition conditions. In the case of ITO sputtering, for example, the properties of the target—such as its density—are important for the films [317] as are the composition and conditions of the plasma [246] and the distribution of the
sputter gases [240]. The sintering technique is essential for ITO and In$_2$O$_3$ targets [318–325]. An addition of ozone to the sputter gas can lead to a desirable oxidation enhancement [326]. Post-deposition annealing is commonplace to enhance the optical and electrical properties, and studies have been made specifically for grain growth in SnO$_2$ [327]. Recently it was demonstrated that electrical current flow through an ITO film can lead to annealing [328]. There are many other possibilities to modify the properties of ITO, and it has been shown that a single top layer of monodisperse SnO$_2$:F nanoparticles can increase the carrier density in the bilayer by as much as 30% [329,330]. Bombardment with high-energy heavy ions was found to contribute to enhanced conductivity in AZO films [331,332]. High deposition rate is usually needed for practical manufacturing of ITO films; a rate of 650 nm min$^{-1}$, together with $\rho \approx 7.5 \times 10^{-4}$ Ω cm, has been reported recently for sputtering [234].

The critical nature of the thin-film preparation conditions is evident from Fig. 13, which shows scanning electron micrographs of an ITO film deposited by DC magnetron sputtering onto a substrate at ambient temperature and subsequently annealed at 200 °C for 1 h in air (panel a) and of such a film deposited onto a substrate kept at 200 °C (panel b) [333]. The film morphologies are strikingly different although both films were treated at the same temperature.

SnO$_2$-based films are commonly prepared by spray pyrolysis or CVD and are then capable of yielding excellent properties as TCOs. These techniques normally operate at high temperature, but ozone-assisted deposition can decrease the substrate temperature to ~100 °C and yet give SnO$_2$:F films with $\rho \approx 10^{-7}$ Ω cm [334]. Concerning techniques operating at even lower temperature, SnO$_2$-based films with $\rho \approx 10^{-3}$ Ω cm have been prepared by sputtering [335,336] and spin coating [337].

GZO deserves some special attention since it is capable to serve as a TCO with UV transparency limited by a band gap as wide as ~5 eV [338–340]. This opens possibilities to transmit radiation appropriate for photocatalysis, as further discussed in Section 3.9 below. ZnO-based films are known to be sensitive to humidity ensuing from reactions of water molecules with oxygen vacancies. However, the moisture resistance of GZO can be very significantly improved if the “dopant” level is ~10%, i.e., much larger than in typical TCOs. Fig. 14 indicates that the resistivity can show less than 3% change over 2000 h at a temperature of 85 °C and a humidity of 85% if the Ga “doping” is 12.4 wt% [341]. This film had $\rho \approx 1.3 \times 10^{-3}$ Ω cm and $T_{\text{lum}} \approx 80\%$. Special off-axis sputtering was used to avoid bombardment of energetic species and led to film growth with random c-axis orientation.

Fig. 13. Scanning electron micrographs for an ITO film sputter deposited at ambient temperature and annealing post-treated at 200 °C (a) and for a similar film sputter deposited onto a substrate kept at 200 °C (b). Note that the magnifications were different for the two images, as indicated by the horizontal bars. From Betz et al. [333].

Fig. 14. Relative change of resistivity for ZnO:Ga films with the shown amounts of Ga as a function of time during ageing at elevated temperature and humidity. From Nakagawara et al. [341].
for improving the adherence of a TCO film to a polymer substrate, though [345]. Nevertheless, despite a number of difficulties concerning the fabrication of TCOs on polymers, deposition at low substrate temperatures onto PET is feasible, as was first demonstrated already in the late 1970s and early 1980s [346,347]. AZO films with resistivities between 5 and $6 \times 10^{-4} \Omega \text{cm}$ were reported in 1987 [348]. More recent work on ITO yielded resistivities between 3 and $5 \times 10^{-4} \Omega \text{cm}$ [349–353], while In$_2$O$_3$–ZnO films have shown $\rho \sim 5 \times 10^{-4} \Omega \text{cm}$ [354]. SnO$_x$ films on PET were found to have a resistivity that was about an order of magnitude higher [355]. Superior conductivity, down to $\sim 10^{-4} \Omega \text{cm}$, has been stated for doped CdO and ZnO bilayers on PET, thereby surpassing data for the other TCOs, but these films have some absorption at the blue end of the luminous spectrum [356]. ITO films have been prepared also on PEN [357,358], polycarbonate (PC) [359], and on high-temperature stable flexible transparent polyimide substrates [360]. GZO films on PEN yielded $\rho \sim 5 \times 10^{-4} \Omega \text{cm}$ [361], and similar results have been reported for ITO on PC [362–365], poly-methyl methacrylate [366] and polyethersulfone [367], IZO on PET and PC [368], and for In$_2$O$_3$–ZnO–SnO$_2$ on PET [369]. AZO and SnO$_2$:Sb films with $\rho \sim 2 \times 10^{-4} \Omega \text{cm}$ have been deposited onto flexible polypropylene adipate [370,371]. Beneficial effects have been observed of a ZnO “buffer” layer on PC [372] and of SiO, SiO$_2$, or SiON “buffer” layers on PET [353,356].

Patterning of ITO is possible with several strategies, and recent work has demonstrated successful applications of reaction and diffusion processes initiating from hydrogel stamps [373], laser patterning [374], and UV curing imprint lithography on PET [375]. The plastics have some gas permeability, which may be a problem for some devices; however, an ITO coating is known to serve as a very efficient gas barrier [376].

Still other alternatives for making n-type TCOs may appear in the future, such as TCOs based on TiO$_2$ [377–379]. In particular, TiO$_2$:Nb is metallic in reduced state [380,381]. Carbon nanotube layer is another emerging possibility, and the same may be true for 12CaO·7Al$_2$O$_3$ (a high-alumina cement). The latter two materials are discussed further in Section 6.1.

TCOs which are strongly p-doped, rather than n-doped as those discussed above, were first reported for CuAlO$_2$ in 1997 [382]. These TCOs are of much current interest owing to their potential applications in optoelectronic devices [383–385]. Future applications in energy-related technology are possible though rather undeveloped as yet [386]. Representative recent data on p-type TCOs have been reported on ZnO:N [387–393], ZnO:(N,In) [387,394,395], ZnO:Ag [396,397], ZnO:As [398–401], ZnO:(N,As) [402], ZnO:Sb [403], ZnO:P [404–407], ZnO:Li [408–410], ZnO:(N,Na) [411], (Zn,Mg)$_2$O$_3$ [300,412], Zn$_{1-x}$Mg$_x$:O:Sb [413], In$_2$O$_3$:Ag [414], In$_2$O$_3$:Zn [415], oxidized Sn$_{0.8}$In$_{0.2}$ [416], NiO:Li [417], Cu$_2$O–NiO [418]; on numerous delafossite structures of the general type ABO$_2$ with A being (Ag, Cu) and B being (Co, Al, Fe, Ga, Sc) [419–422]; and on oxychalcogenides such as LaCuOS: Mg [423], Sr$_{1-x}$Na$_x$FCuS [424], and SrF$_{1-x}$O$_x$CuS [424]. ZnO:P can be p-doped and n-doped depending on the deposition conditions [407], and ZnO:As as well as (Zn,Mg)O can be transformed from n-doped to p-doped by thermal treatment [400,412]. NiO:Li showed increasing p-type conductivity and decreasing optical transmittance in proportion to the amount of Li [417]. The research on p-type TCOs is evolving rapidly and is characterized by a certain lack of consistency regarding physical data; this can be seen as a reflection of the difficulty to prepare reproducible samples. A resistivity of $\sim 10^{-4} \Omega \text{cm}$ has been reported for ZnO-based films [387].

3.5. Doped oxide-based thin films for energy-efficient windows: theoretical considerations

The electromagnetic properties of doped oxides, above the Mott critical density [425,426], are conveniently discussed in terms of additive contributions to the complex dielectric function from valence electrons, free electrons, and phonons [427,428]. They influence the optical properties of the oxides in different wavelength regions as shown schematically in Fig. 15, applying to ITO [429]. Essentially, the heavy doping leads to n-type conduction and Sn$^+$ ions. Going from short to long wavelengths it is found that interband absorption prevails at $\lambda < 0.3 \mu\text{m}$ due to excitations across the fundamental band gap denoted $E_g$. This band gap is shifted towards shorter wavelengths as a consequence of the free electrons entering states at the bottom of the conduction band of In$_2$O$_3$. This feature is conveniently described in terms of the Burstein–Moss effect [430,431], but the underlying physics is considerably more complex than what can be captured in a rigid band model, and a quantitative theoretical description must include many-body representations of ion–ion and electron–electron scattering [432]. The theory has been developed in particular detail for ZnO-based materials and was found being (Ag, Cu) and B being (Co, Al, Fe, Ga, Sc) [419–422]; and on oxychalcogenides such as LaCuOS: Mg [423], Sr$_{1-x}$Na$_x$FCuS [424], and SrF$_{1-x}$O$_x$CuS [424]. ZnO:P can be p-doped and n-doped depending on the deposition conditions [407], and ZnO:As as well as (Zn,Mg)O can be transformed from n-doped to p-doped by thermal treatment [400,412]. NiO:Li showed increasing p-type conductivity and decreasing optical transmittance in proportion to the amount of Li [417]. The research on p-type TCOs is evolving rapidly and is characterized by a certain lack of consistency regarding physical data; this can be seen as a reflection of the difficulty to prepare reproducible samples. A resistivity of $\sim 10^{-4} \Omega \text{cm}$ has been reported for ZnO-based films [387].

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**Fig. 15.** Survey over fundamental physical processes and mechanisms for In$_2$O$_3$:Sn films. $E_g$ is fundamental semiconductor band gap, $\hbar \omega_p$ is plasma energy, and $\hbar \omega_{ph}$ is phonon energy. From Hamberg and Granqvist [429].
to agree well with experimental data for AZO [433,434]. Recent work showed that this theory could account for band gap widening in GZOs (whereas, surprisingly, it did not fit data for AZO) [435]. The band edge is of the Urbach type (i.e., logarithmic) [436]; there are several possibilities why this may be the case [429], one of them related to the effect of the Sn\(^+\) impurities. From a practical point of view it is advantageous that the band gap widening is so strong that the “Urbach tail” at the band gap plays very little role for the optical properties in the solar range and no role whatsoever in the luminous range.

Continuing the discussion around Fig. 15, the free electrons lead to onset of reflectance at a “plasma energy”, denoted \(h\omega_p\), somewhat beyond 1 nm in the near IR. The electrons are scattered against several different kinds of centers; in the luminous wavelength range it seems that grain boundaries predominate, whereas ionized impurities, i.e., Sn\(^+\), are important at longer wavelengths. These impurities become screened by the free electron plasma to an extent that increases gradually in the near IR and is fully developed in the thermal IR. This gradual onset is advantageous with regard to applications and it leads to larger transmittance than would have been the case if the screening would have been fully developed already at the plasma energy. Phonon effects come into play far into the thermal IR, indicated schematically by \(h\omega_{ph}\). They can be represented as Lorenzian peaks added to the dielectric function. In practice, they are of little concerns since they are swamped in the effects of the free electron plasma.

It is now clear that the free electron plasma is of overriding importance in the wavelength range of relevance for solar energy applications and energy efficiency. Free electron theory is a very well understood subject, originally developed already in the 1950s [437] and subsequently modified to account for exchange and correlation [438–440]. The theory can be quantitatively compared with experimental data, most conveniently in terms of the complex dynamic resistivity \(\rho(\omega) = \rho_1(\omega) + i\rho_2(\omega)\) which is directly related to the optical constants and the dielectric function. This representation is suitable since \(\rho_1 \approx \omega^2\), where \(s\) depends on the type of scattering that dominates [441]. Specifically, \(s = -\frac{1}{2}\) for ionic impurities represented by a Coulomb potential, \(s = -2\) or \(-1\) for dislocations represented by a charged monopole or dipole line, respectively, \(s = \frac{1}{2}\) for a short-ranged neutral defect described by a \(\delta\)-potential, \(s = \frac{1}{4}\) or \(-\frac{1}{4}\) for acoustic phonons with deformation potential coupling or piezoelectric coupling, respectively, and \(s = -\frac{1}{4}\) for optical phonons with polar coupling. Empirical data are consistent with \(s = -\frac{5}{4}\), implying that point-like ionized impurities are dominating the free electron scattering beyond the plasma wavelength [429,442]. This is an important result since it shows that the analyzed films are indeed optimized in the sense that their performance is largely governed by the type of scattering that is inherent in the doping mechanism, and the properties cannot be expected to be significantly improved by some conceivable post-treatment such as annealing to improve the crystalline order. The frequency-dependent scattering also shows that the classical Drude model [218,443] cannot be used for detailed quantitative work unless a frequency-dependent mean scattering time or mean free path is invoked. The theoretical model outlined above is applicable not only to ITO films but also nanoparticles of this material [444–447].

Having a quantitative theoretical model for the optical properties of ITO makes it possible to calculate the optical properties in detail as discussed next [429,448]. Fig. 16 reports \(R(\lambda)\) and \(T(\lambda)\) in the full range covering luminous, solar, and thermal properties for an ITO film with \(t = 0.2 \mu m\) and backed by a substrate having a refractive index 1.5. The latter value is appropriate for glass with low Fe content in the visible and near IR, or a foil of a polymer such as PET. In subsequent calculations the substrate was represented by the dielectric function for amorphous SiO\(_2\) [449–451], and the ITO was specified by a free electron density \(n_e\) in the \(10^{20} \leq n_e \leq 3 \times 10^{21}\) cm\(^{-3}\) range. Fig. 16 shows band gap widening, onset of reflectance at a wavelength which scales with \(n_e\), and a gradual disappearance of phonon-induced structure. It appears that the best low-E coating is obtained for \(n_e \approx 6 \times 10^{20}\) cm\(^{-3}\), and that one would expect to have a very good solar control coating at \(n_e \approx 3 \times 10^{21}\) cm\(^{-3}\). The latter value may be difficult to realize in practice, although data that are not too far off have been reported [226–234], as mentioned above.

![Fig. 16. Spectral normal reflectance R and transmittance T computed from a quantitative theoretical model for the optical properties of In\(_2\)O\(_3\):Sn. The shown values of electron density \(n_e\) and film thickness \(t\) were used. From Hamberg and Granqvist [429].](image-url)
The spectral data can be used to calculate $T_{\text{lum}}$, $R_{\text{lum}}$, $T_{\text{sol}}$, $R_{\text{sol}}$, and $E_{\text{therm}}$ in order to assess the applicability of ITO films for energy-efficient fenestration [429]; data are given in Figs. 17–20. Fig. 17 shows $T_{\text{lum}}$ and $R_{\text{lum}}$ for ITO films with four thicknesses and $10^{20} \leq n_e \leq 3 \times 10^{21} \text{cm}^{-3}$. At $n_e < 10^{21} \text{cm}^{-3}$ one finds $75 \leq T_{\text{lum}} \leq 85\%$ and $10 \leq R_{\text{lum}} \leq 20\%$ with the actual magnitudes being strongly influenced by optical interference. When $n_e$ increases there is a tendency for $R_{\text{lum}}$ to decrease while $T_{\text{lum}}$ is more erratic. Fig. 18 is the counterpart for $T_{\text{sol}}$ and $R_{\text{sol}}$, showing that $T_{\text{sol}}$ decreases and $R_{\text{sol}}$ increases as $n_e$ goes up. This is an effect of the plasma wavelength gradually moving into the solar spectrum. At $n_e \leq 5 \times 10^{20} \text{cm}^{-3}$ one observes $R_{\text{sol}} \approx 13\%$ independently of $t$. Fig. 19 deals with $E_{\text{therm}}$ and displays results for ITO backed by a substrate with a refractive index 1.5 (solid curves) and a substrate simulating glass (dotted curves). Generally speaking $E_{\text{therm}}$ drops when $n_e$ and $t$ increase, which is a consequence of the increased number of free electrons. It is found that substrate emission is important for $n_e \leq 5 \times 10^{20} \text{cm}^{-3}$ but negligible above this value as long as $t > 0.2 \mu\text{m}$; these latter films have $E_{\text{therm}} \approx 15\%$ for $n_e \approx 10^{21} \text{cm}^{-3}$.

Figs. 17–19 show that ITO films are useful for energy-efficient windows. The actual performance of a window with such a film depends also on a number of other factors such as heat conduction and convection [107], which largely falls outside the scope of this Review. However,
some general conclusions can be drawn. To that end it is appropriate to fix $E_{\text{therm}}$ at a low magnitude. It is not meaningful to decrease it to the extreme \[452\], though, since non-radiative heat transfer always plays a role. Fig. 20 shows computed results for $E_{\text{therm}}$ set to 15\%, 20\%, and 25\% and gives $T_{\text{sol}}$ as a function of $t$. Requiring $E_{\text{therm}} = 15\%$ one cannot exceed $T_{\text{sol}} \approx 70\%$, which is undesirably low for many applications in architecture. However, limiting the requirement to $E_{\text{therm}} = 20\%$ one can have $T_{\text{sol}} \approx 78\%$, and at a still larger $E_{\text{therm}}$ the solar transmittance can be marginally higher. Optimum data for low-$E$ applications can be obtained for $t = 0.2 \mu m$ and $4 \leq n_e \leq 6 \times 10^{20} \text{cm}^{-3}$; spectral data for such a film were shown in Fig. 16 above.

Fig. 20 illustrates one way of optimizing a TC for applications. Other, simpler methods have been suggested, and a convenient figure of merit, which is sometimes used to distinguish between different thin films, is $T_{\text{lum}}^{10}/R_{\perp}$ \[453,454\].

3.6. Doped oxide-based thin films for energy-efficient windows: some empirical results

The optimization of the TCO film in Fig. 20 did not consider $T_{\text{lum}}$, which obviously is a property of the greatest importance for a window. However, here one can resort to AR coatings analogously with the case of noble metal-based TCs. Figs. 21 and 22 show, respectively, experimental data on $T(\lambda)$ in the luminous range and $R(\lambda)$ in the main part of the thermal range for a thin ITO film with and without an AR coating of AlO$_x$F$_y$ or MgF$_2$ and backed by glass \[429,455,456\]. Fig. 21 illustrates two important features: (i) after AR treatment the transmittance of the coated glass is larger than for the uncoated glass and hence there is no grounds for the common claim that a low-$E$ coating must limit the luminous performance, and (ii) the interference effects are diminished which makes the AR-treated glass less prone to show iridescence than the glass with only ITO. The AR coating degrades the thermal performance to some extent, as illustrated in Fig. 22 which shows $R(\lambda)$ at 45° incidence angle for s- and p-polarized light. The effect of the MgF$_2$ is not noticeable for
s-polarization, whereas the p-polarized reflectance displays a dip at \( \lambda \approx 17 \mu m \) consistent with the dielectric function of MgF₂. Considering the effect on \( E_{\text{therm}} \) one can conclude that this parameter is not increased by more than a few percent as a result of the AR treatment. Another AR coating for ITO is indium-tin oxyfluoride, sometimes called ITOF [457]; it is obviously convenient since it can be made from the same starting material as the ITO film itself. The same holds true for SnO₂:F films as AR treatments for SnO₂-based films [458].

The discussion above has been confined to In₂O₃:Sn. However, this is less of a restriction than one may first think since detailed experimental and theoretical studies—analogous to the one reported on above—have been given for SnO₂:F and SnO₂:Sb [335] and for AZO [433,459]. All of the thin-film techniques mentioned in Section 2.3 can be used for making TCOs. In that section it was remarked that thin-film fabrication using nanoparticle deposition rather than atomistic, molecular, ion-based, or solution-based deposition might become of increasing importance in the future. A recent study [444–446, 460,461] specifically considered ITO films made from nanoparticles prepared by a wet chemical technique. A dispersion of these particles was spin coated and the ensuing film was annealed. Fig. 23 shows some data on \( R \) and \( T \) for \( \lambda < 30 \mu m \); they are consistent with \( T_{\text{ therm}} \approx 90\% \) and \( E_{\text{ therm}} \approx 70\% \). A detailed analysis of the structural, electrical, and optical properties showed that the individual nanoparticles had \( \rho \approx 2 \times 10^{-4} \Omega \cdot \text{cm} \)—i.e., a resistivity comparable with that in the best films made by conventional techniques—but the film only had \( \rho \approx 10^{-2} \Omega \cdot \text{cm} \). Investigation of temperature-dependent resistivity gave clear evidence for hopping conduction [426], specifically related to fluctuation-induced tunneling [462,463] between \( \mu m \)-size clusters of internally connected nanoparticles. It is then obvious that a densification of the particulate ITO films is needed in order to boost \( \rho \) and produce a magnitude of \( E_{\text{ therm}} \) that would be of interest for applications related to solar energy and energy efficiency.

Nanoparticle-based deposition has been reported recently also elsewhere for ITO [447,464–470] and SnO₂:F [329,330], and properties have been reported for constituent nanopowders [471–476]. A recent study showed that aggregated ITO particles could be transformed into a colloidal solution, stabilized by addition of poly(vinyl pyrrolidone), and cast onto PET to form an electrically conducting, mechanically hard, and translucent material [477].

### 3.7. Low-emittance coatings for “vacuum glazings”

As pointed out in Section 3.1, exceptionally good thermal insulation can be achieved in “vacuum glazings”. Essentially they comprise glass panes separated by tiny support pillars that do not significantly obstruct the view. The space between the panes is evacuated and permanently sealed. Low-E coatings are essential in order to obtain good thermal properties. This technology has been discussed in detail during the last several years [478–483], and special investigations have been performed for the role of low-E coatings [484], heat conduction through the pillars [485], temperature-induced stress [486,487], and effects of different frames [488,489]. “Vacuum glazings” are available as commercial products [490]. The heat transfer coefficient, not too close to the edges, can be \( \sim 0.4 \text{ W m}^{-2} \text{K}^{-1} \) for double glazing [491] and \( \sim 0.2 \text{ W m}^{-2} \text{K}^{-1} \) for triple glazing [108].

The ability to maintain good vacuum during extended periods of time is of obvious concern, and water vapor desorption during heating and carbon oxide desorption during solar irradiation have been investigated lately [492–494]. Most of the desorption must emerge from the TCOs, specifically from SnO₂:F coatings, whose nanostructure therefore is critical for the successful use of “vacuum glazings”.

### 3.8. Doped tin oxide-based thin films for avoiding radiative cooling

The atmosphere can be transparent to thermal radiation in the \( 8 < \lambda < 13 \mu m \) “window” range, as shown in Fig. 1(c). This effect can lead to radiation cooling of surfaces oriented towards the sky [495–498], an effect that is well known and with a venerable history for climatization and ice production especially in the Middle East and North Africa [499,500]. 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 W m\(^{-2}\), depending on the atmospheric condition, when the surface is at ambient temperature [501]. If nothing but radiation exchange is considered, the surface can drop to 14–26°C below the air temperature. In the presence of a non-radiative heat transfer equal to 1 W m\(^{-2}\) K\(^{-1}\), the maximum temperature drop is expected to be 10–20°C. Practical tests have given clear evidence for radiative cooling of rigid plates in collector devices of different types [495,502–511], gases [495,512,513], and flexible foils [514,515]. Cooling of blackbody-like surfaces under cover

![Fig. 23. Spectral normal transmittance \( T \) and near-normal reflectance \( R \) for an In₂O₃:Sn film made from sintered nanoparticles. Note the scale change at 2.5 \( \mu m \). Replotted from Ederth et al. [444,445].](image-url)
plates that are opaque to solar radiation but transparent in the atmospheric “window” were discussed recently [516]. In an exceptionally dry atmosphere it was found that a temperature decrease as large as $\Delta T \approx 33 \, ^\circ C$ could be achieved in practice by purely passive means [517,518].

Radiative cooling is in fact a ubiquitous phenomenon, although its dependence on the IR transmittance of the atmosphere has not always been clearly understood. The cooling manifests itself in water condensation during clear nights on surfaces exposed to the sky [519]. This is particularly noticeable on sky-facing windows and originates from the fact that the glass, which is a poor heat conductor and has limited heat capacity, can drop below the dew point before most other objects in the surrounding do so, implying that water condensation—with or without frost formation—takes place. Frost covered car windscreenes are well known in cold climates [520] and water condensation on architectural windows and glass façades is a growing concern owing to the introduction of glazed units with good thermal insulation [521]. A way to practically eliminate the condensation is to avoid radiative cooling, which can be done if the exposed glass surface has a coating with a low emittance in the $8 < \lambda < 13 \, \mu m$ interval. This is the case for the materials discussed in Sections 3.2–3.6 above. If one further requires good chemical and mechanical durability, the favored material is doped SnO$_2$, normally prepared by spray pyrolysis onto hot, solidifying float glass. One may note for completeness that a low emittance in the $8 < \lambda < 13 \, \mu m$ range can be obtained also via the “Reststrahlen” effect in BeO [522–524], but this oxide is not electrically conducting and therefore falls outside the scope of this Review.

Figs. 24 and 25 illustrate the practical usefulness TCO coatings on car windscreens [520] and architectural windows [525], respectively. The “anticondensation” property is compatible with a very thin top coating, for example an AR layer, as apparent from the discussion around Fig. 22.

Deicing and demisting are obviously possible by heating, using electrical power supplied to a TCO coating on glass. Electrical power can be used also for space heating, if there is a need for such, and for maintaining the impact strength of glass (for example in windows of airplane cockpits).

3.9. Comments on photocatalytic properties, self-cleaning, and super-hydrophilicity of transparent conductors

The possibility of using TiO$_2$ films in conjunction with TCs (mentioned in Section 3.3) and the current interest in the wetting of glass surfaces (discussed in Section 3.8) warrant some brief discussion of photocatalysis and related effects in TiO$_2$-based thin films. Photocatalytically active surfaces can cause breakdown of organic molecules as well as microorganisms adsorbed on these surfaces under the action of solar irradiation [526–534]. Thus, hazardous or otherwise unpleasant pollutants 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 anatase-type crystal structure. The latter oxide is
able to use UV light only owing to the width of the band gap. The photocatalytically active surfaces normally are comprised of nanocrystalline structural units, but polymer incorporated TiO$_2$ is another option [535].

Deodorization is possible, which in principle allows the use of natural light, rather than some energy-consuming air cleaning device, to purify indoor air. Representative recent work in this area has been reported for volatile organic compounds (VOCs) [536–541], NO$_x$ [531,536,537,542,543], sulfur compounds [536,537,544–546], toluene [547,548], benzene [549], acetone [550,551], chloroethylene [544,552], formaldehyde [553], acetaldehyde [554–556], 2-propanol [557], methanol [558], and ammonia [559]. Selective oxidation of CO in the presence of H$_2$ is another possibility [531]. TiO$_2$ coatings are also active for photocatalytic breakdown of bacteria [560–564]. Plasma processing is a viable technology for boosting the photocatalytic activity of TiO$_2$ [565], and incorporation of noble metal particles can have a similar effect [566,567]. An applied potential can be used for enhancing the photocatalytic efficiency [568,569]. Photocatalytic surfaces are usually backed by glass or metal, but coatings onto flexible PET, having a protective surface layer of SiO$_2$, has demonstrated photocatalytic elimination of trichloroethylene [570]. Coated fluorocarbon foils have also been studied recently [571]. The photocatalytic layer can exhibit a dual function and serve also as AR treatment of an underlying glass [572].

The photocatalysts tend to loose some of their efficiency over time, in particular under operation as air cleaners. The phenomenon, although well known, is not frequently reported in the literature. There may be several reasons for the degradation, one of them being a change in the electronic properties of the TiO$_2$-based layer [573]. It is noted for completeness that non-stoichiometric Ti oxides can have excellent properties as thermoelectric converters, and the “power factor”—defined as $z^2/\rho$, where $z$ is the Seebeck coefficient—is the largest so far reported for an oxide [574].

It may be an advantage to employ not only UV light but also the less energetic but more abundant visible light for photocatalysis, and dopants have been added to TiO$_2$ for that purpose in order to modify the spectral absorption range. There is much recent work in particular for nitrogen doping to form TiO$_2$–xN$_x$ [539,548,552,575–590], and other dopants that have been studied include C [591,592], S [593], (C,N) [594], (F,N) [595,596], Cu [597], Zn [598], Zr [599], Ni [600], Co [601], and (Fe,N) [602]. A further admixture of WO$_3$ was able to enhance the photocatalytic activity still further [603].

The photocatalytic surfaces exhibit photo-induced super-hydrophilicity, meaning that water droplets spread more or less evenly over the surface so that light scattering tends to be insignificant. Thus the water is not visible and, furthermore, drying-related contamination residues do not appear, which can be a considerable asset from a practical point of view. Representative recent work on super-hydrophilicity has been reported for films of TiO$_2$ [555,604–616], TiO$_2$:Ni [600], layered TiO$_2$/SiO$_2$ [617], TiO$_2$:Si$_2$O$_3$ [617–619], TiO$_2$:Si [620], WO$_3$ [621], layered TiO$_2$:WO$_3$ [622], TiO$_2$:WO$_3$ [623], TiO$_2$:xN$_x$ [624,625], ZnO [615], and InTaO$_4$ [615]. Most investigations have been made on films coated onto glass substrates, but PC substrates have been studied recently too [626].

Self-cleaning by use of super-hydrophobicity—alogously with the features of the lotus leaves—represents another possibility for surfaces having nanoscale roughness [627,628]. The super-hydrophobic property has been documented recently also with multi-walled carbon nanotubes [629] and with coatings made by discharge decomposition of polydimethyl-siloxane [630]. Transition between super-hydrophobicity and super-hydrophilicity, depending on UV irradiation, has been reported for rough TiO$_2$-based surfaces [572], TiO$_2$:Ni films [631], and layers of SnO$_2$ nanorods [632].

### 3.10. Doped oxide-based thin films for solar cells

Solar cells are used for converting solar radiation to electricity. Detailed discussions can be found in several recent reviews [633–645]. 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 intense research and development during decades—the attention has been focused on only a few of these. One common feature is that the side exposed to the sun must have a current collecting arrangement, either a metallic pattern, a TCO film, or a combination of these.

For solar cells made of thin films it may be advantageous to have a scattering—sometimes called “milky”—TCO which can make the average path length for light in the absorber longer than for a non-scattering film [646,647]. This can be so both for a “substrate cell” with the TCO facing the sun and for a “superstrate cell” for which the solar radiation passes through the substrate before it reaches the TCO. Wet etching of sputter deposited AZO films has been studied several times for this purpose [646,648–652]. Fig. 26 shows the development of roughness when a film is treated in 0.5% HCl [652]. The etched film has a roughness of the order of 1 µm, which is advantageous since maximum scattering occurs when the roughness is comparable with the wavelength of the light. The detailed deposition conditions are important for the roughness evolution, as has been documented for AZO [653–655] and GZO [656]. This is illustrated in Fig. 27, which shows the haze—i.e., the diffuse transmittance divided by the total transmittance—at three wavelengths for AZO films made at different oxygen partial pressures in the sputter plasma [652]. Clearly there is an optimum pressure. The scattering is highest at the shortest wavelength.

Silicon is an excellent material for solar cells and is by far the most widely used one [641,657,658]. It is non-toxic, very abundant, and has a well-established technological base.

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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 foil of metal or polymer. 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 film made by glow discharge deposition of silane gas). High photoelectric conversion efficiency demands low reflection losses, which can be achieved by an AR film or—in the case of a single-crystalline material—by using anisotropic etching to make pyramid-type texturing. For single crystalline and polycrystalline cells it is conventional to have metallic “fingers” as current collectors, whereas TCO layers—normally based on SnO₂—are used for thin-film devices. A thin layer of TiO₂ can serve as a protection against hydrogen radical exposure inherent in some techniques for making amorphous silicon solar cells [659,660].

Compound semiconductors of the III–V type—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 [661–663], 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 [663–665], CuInSe₂, Cu(In,Ga)Se₂, and Cu(In,Ga)(S,Se)₂ are notable for their possibility to reach high photoelectric conversion efficiencies in thin-film solar cells. The sulfur-containing films seem to allow cheaper techniques for film preparation than the selenide-containing ones, which is of considerable interest for applications [666]. Numerous other materials—including organic ones [667–669]—and approaches to solar cells are possible, and many other compound semiconductors may well turn out to have favorable properties. Some of those may find applications in thermo-photoelectricity, i.e., cells operating with thermal irradiation [670–672]. Others can be used in tandem cells, encompassing superimposed cells with optical band gaps that are large on the solar-exposed surface and gradually shrink towards the underlying substrate. The current collector is frequently a film of AZO, but other TCOs may work as well. In particular ZnO:B has been put forward as a superior material suitable for large-area deposition and characterized by great hardness [260,298,673]. Deposition rates up to ~3 nm s⁻¹ have been reported recently in work using vacuum arc plasma evaporation [298]. Recent work has shown that carbon nanotubes may replace the TCO in organic solar cells [674–678].

Alternatively, photo-electrochemical techniques can be employed to generate electricity, and studies of nanocristalline dye cells are popular at present [679–683]. These
cells absorb light in dye molecules—normally containing a Ru-based compound—coated onto nanocrystals of TiO₂. The nanostructured material is usually made by colloidal technology, but other methods, such as sputter deposition, are currently emerging [684–686]. 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. It reduces tri-iodine 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 [687]. Record solar–electrical conversion efficiencies of 11.1% and 7.2% were reported recently for rigid [688] and flexible [689] devices, respectively. The TCO is normally SnO₂-based; the film is rough, which contributes to the ability to absorb the dye. TCs made from carbon nanotube layers have been demonstrated recently [690].

Transparent photovoltaic cells may be of interest for see-through applications. Thin-film devices with amorphous silicon, as well as nanocrystalline dye cells, can show some transparency, and another possibility can be realized by using superimposed n-type and p-type TCOs. Thus a ZnO/CuAlO₂/ITO structure was able to demonstrate a photovoltaic effect [691].

In solar cell systems it is possible to make use of selectively reflecting mirrors, which, ideally, reflect only radiation with energies above the band gap of a solar cell towards this cell. Such an arrangement prevents excessive heating of the solar cell and thereby boosts its efficiency. The long-wavelength radiation may be used to advantage in a solar thermal system. Selectively reflecting mirrors can be produced by using a TCO layer backed by a metal, and the properties may be further optimized by having a dielectric layer between the TCO and the metal. A detailed study of such a system—comprising SnO₂:F, Al₂O₃, and Al—was recently carried out theoretically and experimentally [692–694]. The alumina was made by anodizing the Al.

Thermal radiation can be used to generate electricity in thermo-photovoltaic devices, as mentioned above. It is advantageous to put a spectrally selective filter in between the emitter and the photocell, and TCOs can be used for this application. Computations to show the effect of such a filter were presented recently [695]; they were based on the simplified Drude model which, as discussed above, is not fully adequate but nevertheless serves as an approximation.

3.11. Doped oxide-based thin films for solar collectors

Solar collectors use photo-thermal conversion of solar energy to produce hot fluid or hot gas [696,697]. 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. Multi-layer coatings on the cover can render it somewhat colored, which may facilitate solar collector integration in architecture [698,699]. The back and sides of the solar collector should be well insulated, which can be accomplished by conventional techniques. The most critical part for the photo-thermal conversion is the actual solar absorber surface, which obviously should have a large A₂₆. Some deviation from the maximum A₂₆ may be desirable since it can lead to an aesthetically desirable color [700–702]. The radiation heat losses should be minimized, and this requires low E₆₇. A number of design principles and physical mechanisms can be used in order to create such a spectrally selective solar absorbing surface, as discussed in an extensive literature [9–11,703–709]. TCOs can, in principle, be applied in two different ways: to serve as a heat reflector that brings radiation from the hot absorber surface back to the same, and as a top coating on a non-selective black absorber. The latter approach was attempted in some early work on solar absorbers based on black enameled surfaces [710], but it has not gained popularity.

Mg–Ti hydrides can show a strongly absorbing state depending on their hydrogen content. The absorption is caused by a two-phase nanostructure, thus making this material principally similar to most other coatings for selective absorption of solar energy [711]. By varying the hydrogen content it was possible to change A₂₆ between 87% and 32% while the absorbing state displayed E₆₇ ~10% [711]. These properties may make the hydrides of interest for solar collectors based on cheap temperature-sensitive plastics. Further discussion of metal hydrides is in Section 5.1.

4. Applications based on angular selectivity

Pronounced angular properties can be used to accomplish energy efficiency as pointed out above. Section 4.1 discusses general principles for obtaining angular selectivity, either with optical properties being symmetrical around the surface normal or with different optical properties on the two sides of the surface normal. Section 4.2 then treats experimental data focused on Cr films prepared with physical vapor deposition arranged so that the incident flux has an oblique angle to the surface normal.

4.1. General considerations

For a window it may be advantageous to have small transmittance for solar radiation coming from a point high up on the vault of heaven—thereby avoiding overheating—whereas the transmittance along a near-horizontal line-of-sight is high so that unmitigated visual contact can be maintained through the window. If the window is vertical, the situation is simple, at least in theory, and a TC coating
will be able to bring advantages. A single metal film has the desired property to some extent. Spectral and angular selectivity hence can go hand in hand for vertical windows.

However, the situation is more complicated for inclined windows such as those commonly used in atria and in transparent blinds; car windscreen is another common example. In this case it is possible to use coatings including two or more metal layers to create an angular dependence that is qualitatively different from that in a coating with a single metal layer. Fig. 28 illustrates this for the case of a five-layer configuration with two 12-nm-thick continuous Ag layers and three SiO₂ layers [72,712]. When the SiO₂ thickness is 170 nm, $T_{\text{sol}}$ goes from $\sim \text{23\%}$ at normal incidence to as much as $\sim \text{58\%}$ at 60° angle of incidence. When the SiO₂ thickness is 120 nm there is a monotonic decrease of $T_{\text{sol}}$ with increasing angle, much as expected in a coating with a single Ag layer. Clearly the metallic films render the coatings electrically conducting, i.e., they are TCs.

The coating type illustrated in Fig. 28 cannot be used universally. Considering the case of a window inclined at 45°, one would like to have high transmittance at 45° on one side of the window’s normal but low transmittance at 45° on the other side of the normal. This cannot be obtained with homogeneous thin films, but it is possible if the metal film has a nanostructure with directional selectivity, as considered next. In general, coatings of this type can exhibit different electrical, magnetic selectivity, as considered next. In general, coatings of this type can exhibit different electrical, magnetic, mechanical, etc., properties [87,734–778]; “sculptured films” is a term sometimes used. The structure can be modeled by Monte Carlo techniques, molecular dynamics, and “ballistic” deposition, as well as by continuum theories [779]. Essentially the limited mobility of the condensed atoms produces a “self-shadowing” effect, which manifests itself in columnar film growth. Fig. 29 illustrates this effect schematically from simulations of random depositions of two-dimensional hard discs (“atoms”) onto a smooth substrate at the angle $\alpha$ [780]. The effect of different adatom mobilities was included in the simulation. Clearly the “film” develops inclined nanostructures with more or less “crystallinity” depending on the adatom mobility (i.e., “temperature”). Simulations have been carried out also in other work [781–785], and they have been extended in various ways so as to encompass binary systems [786], local ordering in alloys [787], stress effects [788], density [789], column orientation [790], void formation [137], nodular and “tree-like” features [791,792], topography coverage [793–797], microchannel surface area enhancement [798], grain boundaries [799], and zone diagrams [800]; effects related to ion bombardment [801–803], cluster-beam deposition [804], and thermal spikes [788] have been modeled as well. Three-dimensional features have been studied [805–808], including grain growth [809]. The self-shadowing is able to produce quasi-periodic nanostructures [766]. The results from the ballistic deposition can be reconciled with theoretical scaling arguments [810–811]. A recent detailed study proved that self-shadowing indeed is the dominant effect for nanostructure creation, but other effects are not totally insignificant [812].

The limited mobility of the adsorbed atoms is critical [813], and if this parameter is enhanced by having the substrate at a high temperature the growth can be radically different and lead to whiskers [814]. Post-growth annealing.

Fig. 28. Solar transmittance for thin films of SiO₂/Ag/SiO₂/Ag/SiO₂ as a function of SiO₂ thickness $t$ and incidence angle $\theta$. From Mbise et al. [712].
can change the nanostructure though maintaining some of its fundamental features [815]. Magnetic data indicate that discontinuous metallic underlayers can promote oblique columnar growth [719,720], but this possibility does not appear to have been explored with regard to optical properties.

Another recently investigated method for making thin films with oblique columnar structures starts with granular films made by codeposition of metallic and dielectric materials. In particular, interest has been in Au-SiO₂ films, whose optical properties have been investigated in considerable detail [816,817]. Heavy ion irradiation, with impingement from an off-normal direction, is able to change the shapes of the incipient gold particulates so that they become elongated in the direction of the ion beam [818,819].

4.2. Data on obliquely deposited Cr films

Films with oblique columnar nanostructures can exhibit angular selectivity and be of interest for energy efficiency [820–823]. Particularly detailed data are available for Cr films made by oblique angle deposition [824–828]. Fig. 30 shows a scanning electron micrograph of the cross section of a film prepared by evaporation with \( \alpha = 75^\circ \). A pronounced columnar structure is clearly seen with \( \beta = 40 \pm 5^\circ \).

Measurements of polarization-dependent optical transmittance, \( T_s(\theta, \lambda) \) and \( T_p(\theta, \lambda) \), were performed on such films with the light beam incident at an angle \( \theta \) to the film’s normal and in the incidence plane (spanned by this normal, the direction of the evaporated flux, and the column direction). Data were taken for \( -64^\circ < \theta < +64^\circ \), with positive angles taken to be on the same side of the normal as the deposition direction and the column orientation. It is necessary to consider s- and p-polarized light separately; the transmittance pertinent to unpolarized light is then the arithmetic mean of the two values. Fig. 31 shows data for \( T_s(0, \lambda), T_s(\pm 55^\circ, \lambda), T_p(0, \lambda), \) and \( T_p(\pm 55^\circ, \lambda) \) for a film with \( t = 45 \) nm evaporated at \( \alpha = 85^\circ \). The curves display pronounced angular selectivity with the transmittance increasing monotonically with wavelength in the displayed solar range. It is found that \( T_s(-55^\circ, \lambda) = T_s(+55^\circ, \lambda) < T_p(0, \lambda) \) and \( T_p(-55^\circ, \lambda) < T_p(0, \lambda) < T_s(+55^\circ, \lambda) \), i.e., selectivity is confined to the p-polarized component, as expected from theory [821]. Fig. 32 illustrates \( T_{s,\text{lum}}(\theta) \), \( T_{p,\text{lum}}(\theta) \), and \( T_{u,\text{lum}}(\theta) \), where “u” denotes unpolarized
light, at \(-64^\circ < \theta < +64^\circ\) for the same film as in Fig. 31. Expectedly, \(T_{\text{s,lum}}(\theta)\) is symmetrical around \(\theta = 0\), whereas \(T_{\text{p,lum}}(\theta)\) is strongly angular selective. \(T_{\text{u,lum}}(\theta)\) varies from \(-0.3\) to \(-0.7\) when \(\theta\) goes from \(-64^\circ\) to \(40^\circ\). The maximum transmittance occurs at an angle \(\theta_{\text{max}}\). It was found that \(\theta_{\text{max}} \approx \beta\), implying that the column orientation coincides with the direction for maximum transmittance.

Data were recorded not only with regard to the incidence plane but also for other directions. A polar representation of \(T(\theta, \varphi, \lambda)\), where \(\varphi\) is the azimuthal angle, is then appropriate; \(\varphi = 0\) and \(180^\circ\) correspond to the incidence plane. Measurements were taken with laser light at \(\lambda = 543\) nm and a photodetector matched to the eye’s sensitivity. Fig. 33 shows data for the same film as above. The transmittance is illustrated by way of a gray scale with five 5%-wide intervals. The asymmetry between the left- and right-hand halves of the diagram provides striking evidence of angular selectivity for monochromatic as well as for luminous light, whereas the good agreement between the upper and lower halves of the diagrams indicates the symmetry expected from the geometrical features of the obliquely evaporated films. The lines representing \(\varphi = 0\) and \(180^\circ\) can be directly compared with data in Fig. 32.

The degree of angular selectivity is conveniently specified by plotting \(T_{\text{u,lum}}(+60^\circ)/T_{\text{u,lum}}(-60^\circ)\) versus \(T_{\text{u,lum}}(+60^\circ)\).
Data for three evaporated Cr films are shown in Fig. 34. The same figure also shows results for Cr films, Al-oxide-based films, and Ti-oxide-based films made by oblique angle sputtering. It is noteworthy that films made by evaporation show larger selectivity than films made by sputtering, a fact that can be reconciled with the higher directionality of the deposition flux in the former case. Fig. 34 also contains some literature data. Analogous results are available also for Fe films.

5. Applications based on temporal variability (chromogenics)

The variability of the weather conditions during the day and season makes it interesting to create energy efficiency by use of materials whose properties can be changed depending on external conditions, as discussed in Section 2.2, and windows and glass façades with variable properties have been the architects' dream for years. Such functionality is now becoming possible by exploiting "chromogenic" materials, some of which can be classified as TCs. The exposition below gives an overview over chromogenics in Section 5.1 and then provides in-depth analyses of thermochromic VO₂-based films in Sections 5.2 and 5.3 and on electrochromic materials and devices in Sections 5.4–5.6.

5.1. Brief survey of chromogenic materials and devices

There are several categories of chromogenic materials. The most widely known are probably photochromic glasses [838] and polymers [839–841], which have existed for decades; they darken under UV irradiation and bleach in the dark. Photochromism has been studied recently in thin films based on TiO₂ [842–845], MoO₃ [846], WO₃ [621,847–850], and WO₃ with various oxide admixtures [847,851,852]. Bulk glass composed of NaPO₃–BaF₂–WO₃ with addition of Sb₂O₃ and Na₂O is another recently discovered photochromic material [853]. These materials do not show electrical conduction, though, and will not be discussed further here.

Another class of materials consists of thermochromic ones; their optical properties change reversibly when the temperature is altered [854,855]. A number of transition metal oxides show strong thermochromism owing to metal–insulator transitions taking place at a well-defined "critical" temperature τ_c [856,857]. Materials based on VO₂ are of particular interest since τ_c lies in reasonable vicinity of a comfort temperature; thin films comprising this oxide are discussed in Sections 5.2 and 5.3 below. Thermochromic "cloud gels" represent another option; these are polymers for which "clouding"—i.e., transition to a diffusely scattering state—can set in above τ_c due to reversible thermochemical dissolution and thermally induced modification in the lengths of the polymer molecules [858–861]. These gels are not electrically conducting. A somewhat related approach uses the "Christiansen effect" with a temperature-independent fibrous material immersed in a matrix having a strongly temperature-dependent refractive index [862].

A problem with the photochromic and thermochromic materials with regard to many applications is that they do not allow operator control, a feature that is found among the electrochromic (EC) materials [863–866]. An EC device includes TCs for inserting or extracting charge in the EC materials, whose optical properties thereby are changed. The device hence can be viewed as a variable-transmittance electrical conductor and IR reflector.

There are several other chromogenic categories as well, embracing materials with solvatochromism (caused by solvent polarity), ionochromism (caused by ions), halochromism (caused by change in pH), tribochromism (caused by mechanical friction), piezochromism (caused by mechanical pressure), and others [867]. None of these types of materials need consideration here.

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Considering electro-optical effects, there is a plethora of options that can be used more or less successfully in devices. A consideration of these technologies with regard
to energy-related applications must include aspects such as dynamical range in the modulation of $T_{\text{lum}}$ and $T_{\text{sol}}$, the speed of the modulation in window-size apertures, open-circuit memory (i.e., whether electrical power is needed to maintain a colored or bleached state), long-term durability under operating conditions, transparency level in failure mode, device manufacturability, potential cost for mass fabrication, etc. Such considerations lead to a focus on inorganic EC devices incorporating oxide layers serving as anode and cathode in the same sense as in an electrical battery; they are discussed in detail in Sections 5.4–5.6.

EC devices can be made also with organic films, rather than oxide films, but the former are prone to show degradation under UV irradiation and hence are less likely candidates for energy-related applications. Representative recent work on organic ECs has been done on devices incorporating various polymers such as polyaniline (PANI) [868–871], poly(pyrrole) [872], monomeric pyrrole [873], viologens [874–876], bipyridinium [877], poly(3,4-ethylene-dioxythiophene) (PEDOT) [878–883], polystyrene sulfonate (PSS) and PEDOT [869,884], PANI and PEDOT [885], PANI and 4,4’-diaminodiphenyl sulfone (DDS) [886], poly(3-methylthiophene) (PmeT) and PEDOT [887], poly(2-acrylamido-2-methyl-1-propane sulfonate) (PAMPS) and PEDOT [888], PEDOT and dicyanocyclopentadiene (DFC) [889], polyamides [890–892], triarylamino derivatives [893], and other polymers [894–901] and organic–inorganic hybrids [902–904]. The list is not complete but serves to illustrate the current dynamics of the field of research. Multiple color capability can be achieved [905–909], and it may well be that such organic EC devices will be able to establish themselves as displays—i.e., exactly in the nice where the inorganic EC devices failed to gain acceptance in the mid 1970s—and in data storage [910]. Transmittance/reflectance switching for microwave wavelengths has been investigated for composites based on PEDOT [911]. Fibrous- and textile-type devices are feasible [912,913]. A combination of electroluminescence and electrochromism has been demonstrated in polymer-based devices [914]. Devices of the type VO$_2$/TiO$_2$/ITO are able to act as all-optical switches due to photo-oxidation of VO$_2$ under laser irradiation as well as electro-optical switches by application of a voltage between the VO$_2$ and the ITO films [915]. Materials comprising TiO$_2$ nanoparticles and PEDOT-PSS show photo-induced electrical conductivity [916]. Electrofluorescence is possible in tetrazine derivatives [917].

Among the numerous alternative technologies capable of electrically modulating the optical properties, special mention should be made of solution- and gel-based EC redox systems enabling optical absorption as a current is drawn through them and transparency in the absence of a current; such materials are successfully used in automatically dimming rear view mirrors for automobiles since almost 20 years years [918]. The working substance in these devices is believed to be 5,10-dihydrido-5,10-dimethylphena-

zine monomer, which has been discussed in the literature [919,920]. This type of compounds is of potential toxic or otherwise hazardous nature [921,922], which is one reson why alternatives are of interest. Other options are given by materials incorporating liquid crystals [923–927], suspensions of rod-like particles [928], electrically adjustable “cloud-gels” [929], and reversible electroplating systems [930–932]. Rapid technological progress, as well as the proprietary nature of much basic information regarding several technologies for light modulation, makes a detailed comparison of various techniques difficult.

The oxides that display electrochromism are also “gascosomeric”, meaning that if their gaseous ambience is changed between oxidizing and reducing the optical transmittance is modulated; this has been studied recently in devices with films based on MoO$_3$ [933], V$_2$O$_5$ [934], NiO [935,936], and WO$_3$ [937–944]. A thin catalytic layer of Pt is usually incorporated to facilitate the gaschromic effect. The oxides remain electrically non-conducting. For completeness we note that optical properties can also be modified by ion-bombardment [945] and gamma irradiation [946] of oxide films. The relevant literature on the mentioned oxides is much larger than indicated above, though, and encompasses numerous investigations of similar films for sensing applications (of gases and liquids), thin-film batteries, fuel cells, super-capacitors, (photo/electro)catalysis, photo-induced hydrophilicity, etc. NiO films have been widely studied for a variety of magnetic applications (such as spintronics). Some of these analogies have been emphasized lately [947]. A survey of this vast literature is outside the scope of this Review.

Changing the gaseous ambience of certain metal hydrides modulates their optical properties, which can shift between transparent and reflecting with an intermediate strongly absorbing state. In principle a modulation of $R_{\text{sol}}$ may be superior to a modulation of $A_{\text{sol}}$ since heating is less pronounced in a practical fenestration-related application. Much work has been done recently on reflectance modulation and associated effects in hydrides of Y [948,949], Gd nanoparticles [950], Mg-rare earths [951], and Mg-transition-metals [952–959]. The intermediate absorbing state can be used for application to thermal solar energy, as mentioned in Section 3.10 above, as well as for optical hydrogen sensing [960]. The comparatively small range of the optical modulation as well as the limited long-term durability has so far curtailed the usefulness of the hydrides with regard to energy-related applications [959]. Switchable microwave properties have been observed in Y hydride [961]. Electrochemical insertion and withdrawal of hydrogen is capable of yielding effects analogous to those shown under gas exposure [962,963].

5.2. Thermochromic vanadium dioxide films: basics

Thermochromism in VO$_2$ was first reported in 1959 [964]. This material has been discussed for window applications since the early 1980s [965–967], and it has received resurgent interest recently [968–973] among other
things owing to the possibilities to achieve some energy efficiency of windows and glass façades through comparatively simple coatings. The same type of coating can be deposited onto polymer substrates [974]. Thermal IR detection is another area where VO₂ films are of interest [975–977].

VO₂ undergoes a first order structural transformation from a semiconducting, non-magnetic, and relatively IR transparent state with monoclinic structure below τ_c to a metallic, paramagnetic, and IR reflecting state with tetragonal structure above τ_c. The underlying physics of the metal–insulator transition has been much debated for many years; it has been described as predominantly Peierls-like [978–980], Mott–Hubbard-like [981–984], or going beyond these notions [985,986]. There is a sizeable current literature on this subject, which, however, is not central to the purpose of this Review. In geometrical terms, the main difference between the two states in VO₂ is that the monoclinic structure exhibits V atoms that dimerize and twist with regard to their positions in the tetragonal structure. This transition can be highly repeatable in a thin film, whereas single crystals of VO₂ tend to disintegrate during structural transformations. The change of structure can happen in the picoseconds to femtoseconds range [987–993], but in a practical window application it is limited by the heat capacity of the substrate. High frequency measurements have shown that the transition takes place via a gradual growth of metallic domains in the VO₂ film [994]. A window with a VO₂ coating has a T_{sol} that drops when heated to above τ_c, i.e., the window is in principle capable of automatically controlling the inflow of radiant energy to maintain a predetermined indoor temperature. A detailed investigation of the optical properties was presented recently for VO₂ films above and below τ_c [995].

In order to be of practical interest, τ_c must be close to a comfort temperature of about 20 °C. Crystals of VO₂ are characterized by τ_c=68 °C, which clearly is too high. However, other transition metal oxides, including many vanadium-oxide-based ones, have τ_s that are much further off from a comfort temperature and are therefore less likely candidates as starting points for developing thermochromics as a means to accomplish energy efficiency [857]. The existence of a very large number of vanadium-oxide-based phases [996,997]—sometimes referred to as Magnéli phases and denoted V_{2n}O_{2n−1}—calls for accurate process control with regard to thin-film fabrication.

Fig. 35(a) shows a typical example of data for a VO₂ film above and below τ_c [998]. Very similar data have been reported elsewhere [999]. T_{lum} is undesirably low for most applications to fenestration, but superior data with T_{lum} ~ T_{sol} up to about 45% have been recorded recently for epitaxial films grown on sapphire (0 0 0 1) [1000,1001]. The near-IR optical properties are strongly temperature dependent—a feature that is further accentuated in the thermal IR—while the luminous properties are rather independent of temperature. However, a careful study revealed that for t<50 nm the low-temperature phase exhibits lower T_{lum} than the high-temperature phase, whereas the situation is reversed at larger thicknesses [1001]. The film in Fig. 35(a) was made by sputter deposition onto a glass plate heated to ~400 °C, but similar results can be achieved with other thin-film techniques involving similar substrate temperatures. Particularly facile techniques use thermal oxidation of metallic vanadium layers [1002,1003] or thermal reduction in

![Fig. 35](https://example.com/fig35.png)

**Fig. 35.** Spectral transmittance of sputter deposited films of VO₂ (a) and W_{0.03}V_{0.96}O₂ (b) measured at the shown temperatures, i.e., below and above τ_c. From Sobhan et al. [998].
5.3. Thermochromic vanadium dioxide-based films: towards practical applications in energy-efficient fenestration

It is possible to decrease $\tau_c$ in a VO$_2$-based material by replacing some of the vanadium by another metal. Tungsten addition to make films of W$_x$V$_{1-x}$O$_2$ has been investigated in several studies [915,965,966,969,998,1010–1023], and other dopants that have received attention are Mo [965,1013,1024–1029], Nb [966,1028,1030], Cu [1031], W+Ti [1032,1033], and W+F [1034]. Some dopants, such as Fe, can increase $\tau_c$ [1035]. Tungsten is most efficient for decreasing $\tau_c$, and Fig. 36 illustrates this parameter versus doping level $x$, showing that a few atomic percent of W is all that is needed to reach the vicinity of a comfort temperature [998]. The relationship between $\tau_c$ and $x$ is linear to within experimental uncertainties, which is consistent with literature data for bulk crystals [1036,1037]. Fig. 35(b) shows spectral transmittance data for a W$_x$V$_{1-x}$O$_2$ film with $x = 0.032$. The value of $T_{\text{lum}}$ may be somewhat enhanced by the addition of W, but the effect is not large. It was found recently that thin sputter deposited polycrystalline “buffer” layers of ZnO can improve the thermochromic performance of VO$_2$ and W$_x$V$_{1-x}$O$_2$ films [1021,1038,1039]; adequately doped layers of this type may also contribute to give a low $E_{\text{therm}}$ irrespectively of the temperature (cf. Sections 3.4–3.6). VO$_2$ films on Si$_3$N$_4$-coated silica showed $\tau_c$ as low as 34°C [977]. VO$_2$–SiO$_2$ composites made by different techniques have been reported to display enhanced $T_{\text{lum}}$ and broad metal–insulator transitions as a result of the silica addition [1040–1044], and VO$_2$–TiO$_2$ composites have shown decreased $\tau_c$ [1045]. Recent data indicate that $\tau_c$ is in the range 30–40°C can be obtained in VO$_2$ films comprised of nanoscale grains [1046], thus emphasizing that details of the deposition process are important for the magnitude of $\tau_c$ [1047]. VO$_2$ combines to some extent electromagnetism and thermochromism, and $\tau_c$ can be modified by Li incorporation, though not to any larger degree [1048].

Another way to influence $\tau_c$ is to replace some of the oxygen by fluorine [1049,1050]. Fig. 37 shows spectral transmittance data consistent with $T_{\text{lum}} \approx 28\%$ irrespective of temperature and $T_{\text{sol}}$ ranging from 35% at 25°C to 28% at 70°C. The thermochromic transition is rather smooth around $\tau_c \approx 52°C$. The fluorination definitely enhances $T_{\text{lum}}$ as apparent from Fig. 38, showing data for films of different thicknesses with and without fluorine. The effect is on the scale of several percent, which is a clear improvement although $T_{\text{lum}}$ may still be undesirably low for many applications. The reflectance is expected to be essentially wavelength independent to long wavelengths, which is a general feature of systems near a metal-insulator transition [121,1051,1052].

Still another method to influence $\tau_c$ and $T_{\text{lum}}$ is via mechanical stress induced by a suitable substrate, by an overlayer, or by a combination of both [967,1011,1053]. Specifically, data recorded on glass coated with 50 nm of VO$_2$ and 110 nm of SnO$_2$ yielded $\tau_c \approx 49°C$ together with $T_{\text{lum}} \approx 45\%$ and $T_{\text{sol}} \approx 53\%$ at 25°C, and $T_{\text{sol}} \approx 46\%$ at

![Fig. 36. Thermochromic transition temperature $\tau_c$ versus tungsten content in sputter deposited W$_x$V$_{1-x}$O$_2$ films. The line was drawn as a fit to the data points. From Sobhan et al. [998].](image)

![Fig. 37. Spectral transmittance for a sputter deposited film of VO$_2$F$_x$ measured at the shown temperatures. From Khan et al. [1049].](image)
80 °C; a substrate with only the VO₂ layer had \( T_{\text{lum}} \approx 35\% \). VO₂ films deposited on TiO₂ (0 0 1) had their \( T_c \) decreased to about room temperature [1054,1055]. Metallic buffer layers are able to suppress \( T_c \) to some extent as well[1047]. Clearly a top layer can also serve as AR treatment [967,1046,1053,1056–1058]. An AR layer of TiO₂ on top of VO₂ was shown capable of yielding \( T_{\text{lum}} \approx 49\% \) [1058], whereas an optimized ZrO₂ layer on VO₂ led to \( T_{\text{lum}} \approx 50.5\% \) [1059]. TiO₂ can also yield desirable multifunctionality and serve as a photocatalytic, self-cleaning, and super-hydrophilic layer, as discussed in Section 3.9. Bilayers with strongly UV absorbing CeO₂ on top of VO₂ have been investigated[1060]. The electrical properties are also significantly affected by strain [1061–1064] and by ion bombardment [1065,1066].

Radiative cooling (cf. Section 3.8 above) in combination with a thermochromic film may lead to a spontaneously cooled surface with built-in temperature stabilization. This was demonstrated in simulations and some experiments for a system comprising a black-body-like substrate with a \( V_{1-x}W_xO_2 \) film overcoated with 1 μm of SiO, where the latter film is capable of emitting radiation in the “atmospheric window” at 8–13 μm [1020,1067,1068]. This emission does not cover the full “window”, though, [1069] and better results might have been obtained with a film of silicon oxynitride [450,495,1070].

5.4. Electrochromic oxide-based films and devices: introduction

Electrochromic materials were brought to public attention in the late 1960s and early 1970s through seminal work on WO₃ [1071,1072]. Early applications were sought in information displays, but they did not stand up to the then rapidly developing liquid-crystal-based technology. The focus of much of the research on electrochromics was changed during the first part of the 1980s when it was realized that the technology might be capable of achieving energy efficiency in buildings [1073]. The concept of a “smart window” was coined [1074] and captured the attention of researchers as well as the general public. Stable electrochromism in NiO was first reported in 1986 and was investigated in depth during the subsequent few years [1075–1079]. Considering the energy scene of the early 2000s, it is hardly surprising that “smart windows” technology experiences considerable market pull for applications in buildings [1080,1081] and automobiles [1082]. EC materials and technology have been reviewed several times [863–865,1083–1087].

EC technology is introduced in Fig. 39, which illustrates a standard device construction and allows basic features and operating principles to be introduced conveniently. The design embodies five superimposed layers on one substrate or positioned between two substrates in a laminate configuration. The substrates are normally made of glass or flexible polymer foil. Possibilities to incorporate textile materials have been mentioned [913]. The central part of the five-layer construction is a pure ion conductor (i.e., electrolyte), which can be organic (an adhesive polymer) or inorganic (often based on an oxide film). The ions should be small in order to be mobile; protons (H⁺) or \( \text{Li}^+ \) are normally preferred, but \( \text{Mg}^{2+} \) has received some interest lately [1088–1091]. Electrolytes based on PVB—i.e., a standard polymer for glass lamination—has been used in some recent work [1092]. The ion conductor is in contact with an EC film (WO₃ being a typical example) capable of conducting electrons as well as ions. On the other side of the ion conductor is a film serving as ion storage, ideally with EC properties complementary to those of the first EC film (NiO being a typical example as further
discussed below). This central three-layer structure is positioned between TCO films; the best material in terms of optical and technical properties—or at least by far the most well-known one—is ITO, but the other TCOs discussed in Sections 3.4–3.6 can be used as well. SnO2-based TCOs are well suited for window-size devices on glass substrates [1093]. Metal-based layers such as ZnS/Ag/ZnS [188,189] and even carbon nanotube layers [1094] have been mentioned but not investigated in detail for EC applications. Symmetrical devices, incorporating two WO3 or two IrO2 films, have been studied with the object of shedding light on degradation modes [1095].

When a voltage of the order of one volt is applied between the TCOs, ions are shuttled between the ion storage film and the EC film. The electrons extracted from or injected into the TCOs then alter the optical absorption. A reversal of the voltage, or short-circuiting, brings back the original properties. The coloration can be halted at any intermediate level so that the device exhibits open-circuit memory. This implies that the optical changes take place only when charge is moved, which is an important feature for a device designed for energy savings applications. The voltage level is convenient for powering via photovoltaics [106]. Integrated devices with electrochromic WO3 films and TiO2-based dye sensitized solar cells (cf. Section 3.10) are able to provide “self powering” [1096–1098]. The EC devices can be non-scattering, i.e., their light scattering level can remain below the one perceived by human eyes [1099,1100]. Provided that the film deposition is made with an oblique angle of the deposition flux, it is possible to invoke some angular selectivity [1101]. A metallic pattern can be deposited to assist in the charge insertion and extraction, and work related to EC devices has been reported recently for patterning using line printing [1102], screen printing [1103], inkjet printing [1104], and electroless technique [1105]; a conventional shadow mask together with physical vapor deposition is another option. Additional layers can be used in order to diminish the reactivity between the electrolyte and the adjoining oxide layers [1106,1107]. As pointed out above, WO3 films have been used in the great majority of the device-oriented work, but recent research on Nb2O5-based devices has demonstrated some unusual features such as multicolor capability [1108]. The five-layer design in Fig. 39 is used in most work, but other and principally simpler arrangements—such as “monolithic” ones—may be feasible too [1109,1110].

It is apparent that the EC device can be viewed as an electrical battery with its charging state manifested as optical absorption. Transfer of battery-type work to the field of electrochromics has been attempted [1111–1113], but much remains to be done to fully exploit the analogies of the two technologies. In particular, it appears that work on long-term-durable batteries should be possible to transfer to the field of electrochromics.

Recent work has been reported for EC oxides based on W, Mo, Ir, Ti, V, Ni, and Nb. Some fifty to a hundred scientific and technical articles are currently published per year; those from the period 2002–2005 and confined to thin films have been listed recently [1114–1116]. Representative work beginning in 2005 has been published for films based on WO3 [849,943,946,1117–1152], WO3–MoO3 [1129–1130, 1153,1154], WO3–TiO2 [1155–1157], WO3–Ta2O5 [1158–1160], WO3–Fe2O3 [1161], WO3–P [1139], nanocomposites of WO3–Au [1162] and WO3–Pt [1163], multi-layers of WO3–Chitosan [1164] and WO3–TiO2–Chitosan [1165], Na0.2Mo3W1−xO3·2H2O [1166], WO3 doped with bipyridine [1167], metal containing hexagonal tungsten bronze [1166,1168]; MoO3 [1088–1091,1128–1130,1153,1154, 1169,1170]; IrO2 [1171–1174], IrO2–MoO3 [1175,1176], IrO2–Ta2O5 [1174]; TiO2 [1177,1178], TiO2–V2O5 [1179]; V2O5 [1180–1183], V2O5:Ta [1184]; NiO [1185–1193], NiO–TiO2 [1194,1195], NiO–Ta2O5 [1196–1198], NiO–Co2O3 [1198], Cu,Ni1−xO [1199], polyethylene oxide-doped NiO [1200]; and Nb2O5 [1201,1202]. Fluorination may have some beneficial effects on the EC performance [1203]. Nanocrystalline WO3 films with good EC properties have been made by a templating technique [1204]. Work on films comprising nanofabricated structural units has appeared recently, specifically based on WO3 nanoparticle [1205] and nanowires [1206], WO3–H2O nanorods [1207]; TiO2 nanotubes [1208,1209]; and V2O5 nanorods [1210] and nanowires [1211]. Applications of electrochromic WO3 in tunable photonic band gap materials have been explored lately [1212,1213].

Work related to EC devices has been carried out also on CeO2-containing materials, which are capable of serving as fully transparent counter electrodes. In particular, data have been reported recently for CeO2 [1214–1216], CeO2–SiO2 [1217], CeO2–TiO2 [1214,1218–1224], CeO2–TiO2–ZrO2 [1225], CeO2–ZrO2 [1220,1226,1227], and CeO2–HfO2 [1227]. CeO2:F is another option [1228].

The EC oxides can be divided into two main groups; those based on W, Mo, Ti, and Nb color under charge insertion and are referred to as cathodic EC materials, whereas oxides of Ir and Ni color under charge extraction and are called anodic EC materials; V oxide is of intermediate nature and displays features of weak cathodic and anodic coloration in different wavelength regions. Among inorganic non-oxides, one notes that hexacyanometallates—i.e., compounds of the general type MX[M’(CN)6]n−, where M and M’ are transition metal ions with different valencies—can exhibit pronounced anodic electrochromism [1229–1231]. Most of the thin-film deposition techniques reported in Section 2.3 can be used for the oxides, whereas the hexacyanometallates normally are prepared by electrodeposition.

A clear impression from the survey of the most recent literature referred to above is that much interest is currently focused on electrochromic WO3 and NiO, and that sputtering and sol–gel deposition stand out as particularly relevant owing to their capability of yielding mixed oxide films. Therefore these materials will be considered in some more detail next.
5.5. Electrochromic oxide-based films and devices: WO₃ and NiO films

Electrochromic WO₃ is normally termed “amorphous”, implying that no clear features are discerned in X-ray diffraction. On an atomic scale, the structure comprises corner-sharing WO₆ octahedra with a spread in bond angles and bond lengths [863]. The bonding is predominantly ionic although with a significant covalent contribution [1232,1233]. The structural features regarding stoichiometric, substoichiometric, overstoichiometric, and ion intercalated amorphous WO₃ have been given a schematic though consistent interpretation recently [1234]. Upon heating, the films transform in the sequence monoclinic→orthorhombic→hexagonal [1235,1236]. Electron–phonon interaction is strong so that structural rearrangement occurs easily, and doubly charged (W–W)₁₀⁺ complexes form readily [1237] in accordance with the Anderson electron pairing mechanism [1238]. The valence band is largely composed of O 2p orbitals while the conduction band derives mainly from W 5d orbitals [856,1239]. The electronic structure has been studied recently using surprisingly simple chronopotentiometry and taking a rigid-band model to represent the effect of ion intercalation [1240–1242]. Combining the chronoa-thermometry with electrical conductivity data it became apparent that the electronic states are localized far up in the conduction band [1241–1243]. When ions are intercalated into the W oxide, the charge compensating electrons enter these localized states. Hence the optical absorption underlying the EC effect would be best described as due to transitions between occupied and empty localized conduction band states. As to the specific optical absorption mechanism, poly-crystalline W oxide can be described in terms of polaron absorption [1244,1245], which is consistent with recent temperature-dependent angle-resolved photoemission data for NaₓWO₃ [1246]. However, the situation is less clear for the amorphous material, and a traditional polaronic model [1247–1249] has been questioned in recent quantum chemical modeling [1250]. The fact that the optical absorption does not increase linearly with intercalation level has led to the notion of “site saturation” [1251], whose extension to the case of transitions between three kinds of states—corresponding to W⁴⁺, W⁵⁺, and W⁶⁺—has provided a new model and new insights into the EC absorption in amorphous W oxides up to high intercalation levels [1150,1252]. A reflecting state is possible in sufficiently crystalline ion containing W oxide; it can be represented by free electrons in the conduction band [1253–1255].

Electrochromism in NiO is less well understood than in WO₃. NiO is an insulator with an onset of absorption at 3.1 eV and an absorption peak at 4.3 eV [1256–1258]; this is consistent with recent first-principles calculations of the quasiparticle excitation spectrum [1259]. Oxygen deficiency can lead to in-gap states about 0.5 eV below the Fermi level [1260]. Generally speaking, however, there is no consensus regarding the detailed electronic structure of NiO despite decades of investigations [1261]. The knowledge of NiO films has advanced considerably recently particularly for sputter deposited films [1262–1268]. In overall terms, as-deposited films are characterized by oxygen excess, low density (high porosity), and small grain size. The grain surface is richer in oxygen than the bulk. Independently of the color condition, there are always Ni atoms in valence states 2+ and 3+, but the number of Ni³⁺ ions increases upon coloration. A NiO structure was found by X-ray diffraction for films in all color conditions, while a presence of other Ni-based phases—such as Ni(OH)₂, Ni₂O₃, and NiOOH—was inferred from other data. This indicates that the coloration process is a surface phenomenon, most likely occurring in the outer parts of the grains. In the beginning of an electrochemical cycling sequence, a number of cycles are required for the charge capacity to reach its maximum value and stabilize. X-ray photoemission results were consistent with a transformation of the over-stoichiometric hydrated Ni oxide to hydroxide and oxy-hydroxide phases on the grain surfaces. The amount of oxygen in the films increased by ~10% through intercalation of hydroxyl groups occurring simultaneously with intercalation of protons from the electrolyte. Electrochemical data [1266] suggested crystallization of the hydroxide and oxy-hydroxide phases during the initial intercalation cycles. The electrochemical coloration occurs solely by proton intercalation in stabilized films, with the oxygen content in the films being equal under bleached and colored conditions. Proton extraction was consistent with the “Bode scheme” [1269,1270] originally developed for batteries. However, this scheme does not explain the 2+ to 3+ valence change for nickel belonging to the NiO phase upon coloration, and an extension was suggested to account for these results [1268]. Because the coloration is a surface effect and the bulk remains NiO independently of the film being bleached or colored, one can argue that—after the transformation of the Ni(OH)₂ to NiOOH—the change of the NiO to Ni₂O₃ may take place at the interface between the NiO and the Ni oxy-hydroxide.

5.6. Electrochromic oxide-based films and devices: flexible foils

After having examined the basic properties of WO₃ and NiO films above, it is appropriate to turn to devices incorporating such films. Rigid, glass-based devices of this kind have been reported on in a number of studies [1106,1271–1284], and recently work has been carried out on flexible PET-based devices [1285–1287] and flexible organics-based devices [878,879] sometimes with an origin in plastic lithium battery technology [1288]. Some results from PET-based devices will be briefly discussed here. The main reason for using a flexible substrate is that roll-to-roll coating can be employed—rather than coating of large rigid substrates—which is a cost-cutting measure. Electrochromic WO₃ absorbs mainly in the red end of the visible
spectrum whereas NiO absorbs mainly in the blue end, and jointly they tend to give a neutral gray color in the dark state, a feature that is advantageous for most architectural applications [76]. Sputter deposited NiO films display some unwanted absorption at short wavelengths, but this feature can be alleviated by adding a second oxide to the Ni oxide. If the additive has a larger band gap than Ni oxide, such as MgO and Al₂O₃, the result will be a widened band gap for the mixed oxide and hence a lowered absorption of blue light [1265]. A similar beneficial effect exists in Ir oxide [1174,1289], which is another anodically coloring EC oxide. Mg-doping is able to widen the band gap also in ZnO, as seen from calculations [1290].

Successful device assembly requires that the EC film and counter electrode are appropriately precharged, which is a demanding task in a manufacturing situation. However, W oxide can be efficiently precharged in H₂ during sputter deposition [1291] and Ni oxide can be discharged by post-treatment in O₃ [1292,1293]. These foils were then laminated together by using a polymeric electrolyte [1294] using roll-pressing under heating. Fig. 40 illustrates the high transmittance of the electrolyte [1295]; it was put on an UV transparent quartz substrate, and the measurement shows that absorptance prevails only at λ<0.3 μm, which is outside the range where the PET and the ITO film are transparent. Hence, the electrolyte is exceedingly well protected from radiation which otherwise might have tended to degrade it. The edges of the double foil were sealed, electrical contacts were attached, and the EC device was ready for testing and use. Cycling between colored and bleached states took place using trapezoidal voltage pulses between −1.6 and +1.5 V, respectively; the precise voltage range was adjusted automatically to compensate for varying temperatures.

Fig. 41 shows the transmittance at three wavelengths for cycling with one full color-bleach cycle each 200 s [1295]. The optical modulation is pronounced, especially for mid-luminous and red light. Most of the changes take place within a few tens of seconds after application of the pulse, but the coloration has not reached saturation even after several minutes. Fig. 42 reports on the transmittance in fully colored and bleached states after cycling in the same way as in Fig. 41 [1286]. The foils are seen to change between a high level of about 70% and a low level of 35 to 40% at a mid-luminous wavelength, which is in agreement with data in Fig. 41. The span between the colored and bleached states remains practically unchanged for 5000 cycles. This by no means represents the maximum achievable number of cycles, though. Lower transmittance levels, down to 25% or considerably less in the colored state, could be reached for longer coloration times. The devices have open-circuit memory, which is an asset since electrical power must be drawn only to effect changes in the optical properties. Fig. 43 illustrates the mid-luminous transmittance for a device colored to a transmittance equal to 20% [1286]. The transmittance has increased only marginally after a time as long as 160 h, and hence there is no “trickle current” and no need for “refresh” charging to keep the EC foil dark during an extended period of time. This is a considerable asset not the least for automotive applications, in which the available amount of electrical charge is highly limited.

Quality measures for EC devices are of obvious interest. Long-term testing is an option, ideally under some type of accelerated yet reliable conditions [1084,1296], but there is a clear need for other, faster techniques. One possibility may be offered by low-frequency current noise [1297], which was investigated recently in a device of the type discussed above [1298]. Fig. 44 shows experimental current power spectral density Sᵦ as a function of current I at a frequency f of 700 Hz during the final stage of discharging of an EC device. It is found that Sᵦ(f)≈I². The most interesting feature of Fig. 44 is that the amplitude of Sᵦ was increased after cycling of the EC device so as to deliberately
cause some degradation manifested in irreversible coloration. The result is hardly surprising since current noise of \(1/f\) type is a well-known tool for monitoring the reliability of electronic [1299–1303] and ionic [1304] devices such as batteries [1305], sensors, and transducers [1306]. \(1/f\) noise is also able to provide information on corrosion processes [1307–1311].

The work reported above has demonstrated EC devices—in particular flexible EC foils—with sufficient optical modulation range, dynamics, and durability for making them interesting with regard to a number of energy-related and other applications, especially “smart” windows for uses in buildings and automobiles. Consumer products, such as visors for motorcycle helmets, may be another option and the EC device leads to diminished facial warming, which is an important issue with regard to comfort and hence riding safety [1312].

Detailed technical information on practical EC devices is rarely found in the literature but some examples of devices were reported recently [1092,1313–1315] and a computational feasibility study has been presented for automotive EC windows [1082]. It is important to realize that the “smart” windows can fulfill different goals as discussed above in Section 2.2: they can provide improved indoor comfort by being able to prevent glare and thermal discomfort for the users of the building or automobile, and simultaneously they can provide large energy savings through a lowered cost for air cooling. The “smart” windows technology is thus able to yield environmental benefits, and in this context it is important to have environmental assessments regarding EC glazing production, as reported recently [1316,1317]. Economic aspects of the technology have been modeled [1318] as well as diverse applications issues [1319–1321] including net energy performance of EC skylights [1322].

The discussion of EC devices has dealt with absorptance changes in order to modulate \(T_{\text{lum}}\) and \(T_{\text{sol}}\). In principle a modulation of \(E_{\text{therm}}\) is possible, but this requires either that a crystalline WO\(_3\) film is exposed to the ambience or that the layers in the device between an IR reflecting substrate and the ambience are IR transparent. This can be accomplished to some extent [1283,1288,1323–1327].
but the relevance to solar energy and energy savings is uncertain.

6. Concluding remarks and futures issues

6.1. Materials

Are there new and promising TCs for energy-related applications appearing at the horizon? One such possibility is indeed offered by carbon nanotube layers, especially single-walled ones consisting of one layer of the hexagonal graphite lattice rolled to form a seamless cylinder with a radius up to a few nanometers [1328,1329]. There are several different methods for preparing such nanotubes on a variety of substrates. They can be dissolved in a solvent and then applied by dipping [1330], spraying [1331], spin coating, printing [1332], or electrodeposition [1333,1334]. The ensuing layer is a network of “bundled” nanotubes; a typical example is shown in Fig. 45 [1332]. Alternatively, growth can take place with a minimum of substrate interaction on porous silicon, i.e., under clean conditions [1335]. Individual nanotubes can be as long as several centimeters. The nanotubes are of two types: metallic and semiconducting with conductivities comparable to those of Cu and Si, respectively. The individual nanotubes are separated by barriers for fluctuation assisted electron transfer from one tube to the next [1336,1337]. Limitations in heat transfer from metallic nanotubes can lead to unusual effects such as negative differential resistance upon heating [1338]. The optical transparency is high in the visible and IR. Fig. 46 displays sheet resistance as a function of transmittance at λ = 0.55 μm [1332]; the curve represents a theoretical expression [1332]. Quantitatively similar data have been reported in recent work on organic light-emitting diodes with carbon nanotube electrodes [1339]. Other studies of the optical and electrical properties have been presented elsewhere [1340–1347]. Composites incorporating carbon nanotubes are of interest too [1348,1349]. It is apparent that the properties cannot yet fully match those of the best TCOs, but advantages regarding cost can outweigh this limitation depending on application. In the future, nanotube layers with a higher fraction of the metallic variety, and perhaps means to diminish the intertube barriers, can lead to better performance. A few examples of uses of carbon nanotube layers in devices with a bearing on energy applications have been noted above; they concern TCs for organic solar cells [674–678], for dye-sensitized solar cells [690], and for organic EC devices [1094]. TCs based on multi-walled carbon nanotubes have attracted some interest recently [1350]. Chemical functionalization of carbon nanotubes is presently of much interest and may give new avenues to process and assemble tubes and to adjust and optimize their electrical and optical properties [1351,1352]. Recently it has been discovered that cycloaddition functionalizations can preserve or control the conductivity of carbon nanotubes [1353].

A newly discovered class of TCOs is based on 12CaO·7Al2O3 (often denoted C12A7), i.e., a well-known insulating oxide of much use in high-alumina cements [1354]. It is characterized by a cage structure with two formula units (12 cages) per unit cell. Its empirical formula may be written [Ca24Al28O64]4++2O2−; the free oxygen ions give charge neutrality and are located inside the cages. Hydrogen can be incorporated by a reaction according to O2−(cage)+H2(atm)→OH−(cage)+H+(cage). After hydrogen incorporation the unit cell has two cages occupied by OH−, two occupied by H+, and eight empty ones. The
hydrogen incorporation produces no apparent change in the optical and electrical properties of the material, but subsequent UV irradiation induces two optical absorption bands. The color is persistently changed from white to green, and the conductivity is increased by as much as ten orders of magnitude by a process involving $H^0 \rightarrow H^+ + e^-$ [1355]; the material can be described as an electride. Films were made by pulsed laser deposition onto MgO followed by annealing at 800 °C and hydrogen treatment at 1200 °C [1356]. The electromagnetic properties have been subject to a number of detailed investigations, and it has been documented that the optical absorption is due to inter- and intra-cage electron transitions [1357] and electrical conductivity due to variable range or polaron hopping of photoexcited electrons between neighboring cages [1358–1361]. Other studies have elucidated the formation of oxygen radicals [1362] and the pertinent band structure [1363]. Substitution with Mg to form $Ca_{12-x}Mg_xAl_{14}O_{33}$ has been reported in recent work [1364] showing that $x = 1$ can give $\rho \sim 10\Omega \text{cm}$, which is about a factor four larger than for $x = 0$.

The $12CaO \cdot 7Al_2O_3$ type TCOs are very interesting for several reasons. They are based solely on some of the most abundant elements and offer a new method to accomplish optical transmittance and electrical conductivity. Thus far the properties are not good enough to allow applications to solar energy and energy efficiency, but the fundamental notions behind the electromagnetic properties of the electrides conceivable can be developed to more useful materials. Thin-film manufacturing presently involves high temperature treatment, and alternative fabrication routes are needed.

### 6.2. Applications

The TCOs—given a generous definition—have a multitude of applications with regard to solar energy and energy efficiency, as discussed in detail above. They are in very different stages of development, ranging from established technology for example with regard to spectrally selective solar-control and low-emittance windows in buildings, to an early applications phase such as for some chromogenic materials enabling temporal variability of the transmittance, to an explorative phase such as for angular selective nanostructured materials. 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 these final sections should be interpreted.

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 industrialized countries, typically 40% of the energy goes into heating, cooling, lighting, and ventilation of buildings, and to electrical appliances of various kinds, as noted in Section 2.2. It is obvious that improved materials could be used to alleviate the situation, and coatings on glass and PET foil are of particular importance. In some countries, surface coated glass is employed in new 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—currently represent mature technologies, well known to the flat glass manufacturers and unlikely to undergo more than minor improvements in performance. The coatings are either based on $\sim 0.02 \mu m$ thick silver or $\sim 0.2 \mu m$ 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. TC coatings on the exposed outer side of windows can almost eliminate water condensation which may otherwise occur under certain climatic conditions; this represents a new field of application which is compatible with self-cleaning induced by a very thin $TiO_2$-based outer layer. TC coatings could also be used on the inside of windows for buildings and vehicles, where they can serve as reflectors for thermal radiation and avoid what is sometimes referred to as “cold radiation”, i.e., the coatings can reflect thermal radiation from a human body back to the same body.

The coatings mentioned above combine spectral selectivity with angular-dependent properties but are usually only optimized with regard to light with normal incidence. Hence multi-layer designs with angular performance tailored to a specific building site and orientation represent options for the future. Angular selectivity 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. Presently, thin films are used in many cases, but bulk materials such as photochromic glasses and polymers, thermochromic polymers, and polymer-based cloud gels also offer other, although more remote, possibilities. Electrically regulated EC “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). Therefore, there are strong incentives 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 major concern, but recent progress in manufacturing technology—such as roll-to-roll coating of polymer foil—appears to open 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 EC “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. Pixelation can lead to glass facades serving as information media or to surfaces with specific artistic expressions.

The EC technology may be combined with facilities to direct daylight deeply into buildings by use of light-guides. By equalizing the light level in a room, the eye—which tends to adjust to the brightest illumination—does not perceive deeper regions as disturbingly dark and hence there is less need for artificial lighting. Similar notions, though employing a Venetian blind system, have been discussed recently [1365,1366]. Generally speaking, the EC technology leads to new vistas in daylighting, which is generally regarded as superior to artificial lighting by giving better task performance, improved visual comfort, and positive mood effects, especially if glare problems are eliminated [1367]. Particularly beneficial effects have been observed concerning student performance in daylit schools [1368] and increased sales in daylit stores [1369].

On the speculative side, membrane architecture [1370,1371] may be merged with EC foil technology in order to allow lightweight buildings with little embedded energy. These notions are perfectly in tune with “intelligent buildings” [1372] and “smart skins” [1373]. One can envisage huge membranes allowing the flow of visible light and solar energy to be controlled and optimized. The possibilities offered by such membranes—although then based on glass technology—were in fact pointed out more than 50 years ago by the great visionary Buckminster Fuller [1374]. Perhaps this grand vision will come true one day—thanks to electrochromics.

A concern with regard to applications is the availability of the raw materials needed for the different types of TCO coatings. This concern has become acute owing to the rapid price increase of indium during the first part of the 2000s. The situation does not seem to be entirely clear today (2007), and on one hand it has been stated that the global availability of indium is ample and about as large as that of silver [1375], but it has also been claimed that the availability is much too low to allow widespread deployment of indium-containing thin-film solar cells [1376]. Whatever view will turn out to be correct, resource availability is definitely an important aspect for large-scale TC-related applications—as it is for any other large-scale implementation of new technology—and one may wonder whether there are new options emerging. In the author’s view there are, and carbon nanotubes may have a large potential—though it is difficult to assess at present. Possibly thin films of such nanotubes could lead to a revolution in TC applications.

Solar-driven photocatalysis for air cleaning is a relatively unexplored field, but one with interesting possibilities to provide benign indoor conditions without excessive and energy intensive air handling. The future of this technology is still uncertain but research is being pursued vigorously, especially in Japan. Combinations with TCs are interesting and point towards multifunctionality as an important feature for future developments.

Solar cells for electricity generation are attracting much attention today. The cost of solar electricity is still an order of magnitude higher than the cost of conventionally generated electricity. 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. The availability has been a limiting factor in the early 2000s, but the introduction of cheaper “metallurgical grade” silicon is likely to alleviate this situation. Thin-film cells, especially those incorporating Cu(In,Ga)(Se,S)2, may have cost benefits but also involve manufacturing difficulties. 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. TCs are of great importance for many solar cells, and cheaper materials and deposition processes will remain of importance.

Much of the pioneering work on the TCs was made in Europe in the 1950s and, in a few cases, even earlier. The metal-based thin films are currently undergoing fine tuning and cost optimization in large industrial operations in most parts of the world. The work on TCOs moved, to a considerable extent, to Japan in the 1980s and 1990s, and such work is now pursued vigorously throughout South-East Asia. The US has started to compete with this research and development, and more recently Europe has woken up to a new start on TCOs. The current domination of research in countries such as Japan, China, Korea, and Taiwan is obvious from the list of references to this Review. In particular work based on nanoscience as a basis for TCs is strong in that region, which is consistent with general trends for the nanofield [1377]. The overwhelming part of this work is presently motivated by potential applications to transparent electronics and display devices—which in a large perspective are marginal compared to the energy-related ones as emphasized in the Introduction. Indeed solving the energy situation is a sine qua non for the other work!

6.3. 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 TCs for energy-related applications for decades to come. Among these are a growing population, which will boost the demand of 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.

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, and energy savings will be ever more important. The transparent conductors have an important role to play in this sea-change of energy technology.

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