

REVIEW

Thin films for solar control applications

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The excessive use of heating systems in cold climates and air conditioning systems in hotter climates is resulting in the extensive use of electricity in order to maintain such systems. This in turn leads to the greater use of fossil fuels and higher emissions of carbon dioxide and other pollutant gases. The growing amount of carbon dioxide emissions is contributing to the problem of global warming, hence increasing the need for alternative technologies to heating and air conditioning systems.

One such alternative is the production of thin films which can be used as window glazing coatings to construct ‘smart windows’. These windows have the greatest use within constant climates. In cold climates, windows with high solar transmittance and low thermal emittance are needed; this allows sunlight into the building to brighten the room but stops heat from escaping thus warming the room. In constantly hot climates, materials that are transparent in the visible region but reflective in the infrared, such as thin metallic coatings, can be used to ensure that the inside of the building remains cool.

These solar control coatings, however, pose a problem in varying climates such as in northern and central Europe. For these cases, materials that have altering properties owing to external surroundings could be the solution. These ‘chromatic’ materials include several categories, such as photochromic glasses and polymers, thermochromic metal oxides and electrochromic materials.

This review will begin with a discussion as to the chemistry behind the solar control coatings and chromic materials including ambient radiation and the ideal of a black-body object. It will then look in depth at each class of these chromic materials considering experimental results and theoretical insight as well as production techniques and applications.

Keywords: solar control; thin film; thermochromism; electrochromism; photochromism

1. Introduction

The world’s energy consumption is continuously increasing and this creates a heavy demand for renewable energy sources to be developed. The emission of carbon dioxide and other pollutant gases is posing a problem not only to the

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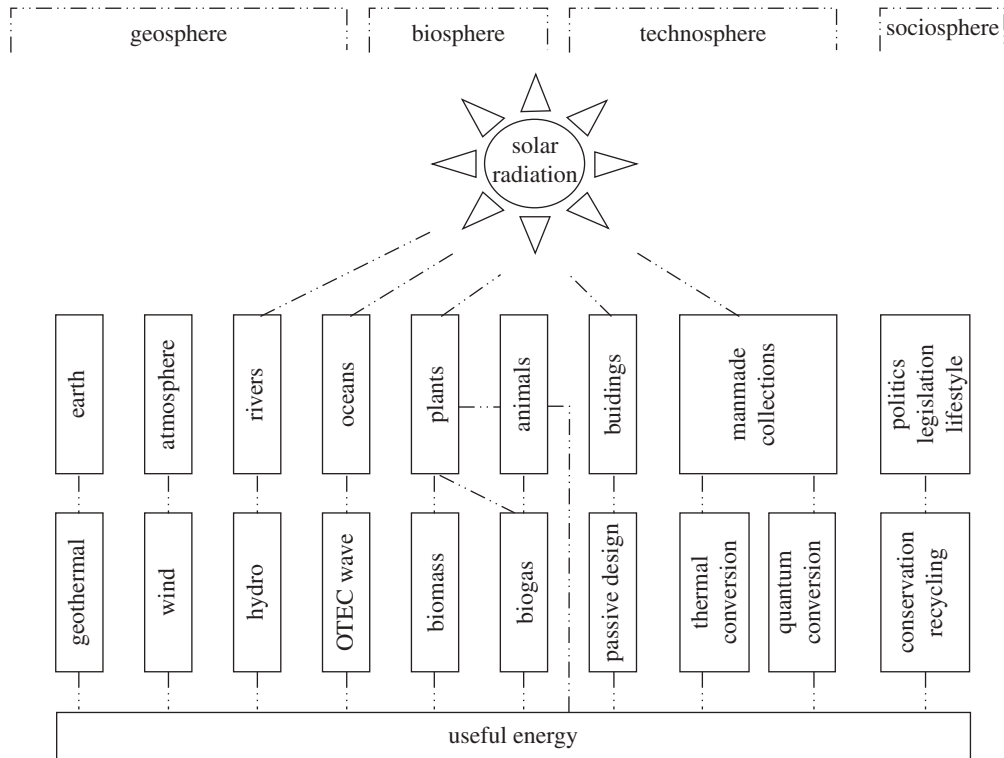


Figure 1. Systematic diagram of the conservation of solar energy (diagram adapted from Granqvist 1991). OTEC, ocean thermal energy conversion.

environment but also to human health as well (Granqvist 2007). This coupled with the increase of the general standard of living has shown an increase of the reliance of renewable sources worldwide. There have been many suggestions for renewable energy sources; however, the source which shows the greatest promise is solar energy. Figure 1 shows a schematic of renewable energy conservation of solar energy.

Buildings are said to be responsible for about 40 per cent of the world's total annual energy consumption owing to the excessive use of lighting, air conditioning and heating (Omer 2008). A way in which this can be reduced is to use thin film coatings on building glazing in order to limit the amount of solar radiation entering or black-body radiation leaving a building. Transparent conducting oxides (TCOs) and thin metallic coatings are useful in solar applications because they are transparent in the specific range of 400–700 nm (Granqvist 1991, 2007). As a consequence of their metallic properties, they reflect in the infrared but absorb in the ultraviolet. If the reflectance occurs in the interval of $3000 < \lambda < 50\,000$ nm, i.e. the range for thermal radiation at ambient temperature, the emission of heat is hindered. If reflectance occurs at $700 < \lambda < 3000$ nm, then visible transmission is combined with solar energy as well as low thermal emittance. Another important class of materials for 'solar control' applications is those that show chromogenic properties. By consideration of

ambient temperature, solar materials can be designed in order to achieve the desired properties (Granqvist 1991). These include materials with high electrical conductivity and the combination of high solar absorbance or transmittance with low thermal emittance; these properties are useful for low-emittance windows coatings. Materials with high transmittance of ultraviolet radiation but the complete blockage of infrared solar radiation can be used for solar control windows. Solar control and low emittance are only practical in climates that do not vary much from season to season. However, in parts of the world where there are changeable climates such as the United States, Japan and Northern Europe, the use of chromogenic materials can be used for ‘smart windows’ as their properties allow them to adapt to the changing environment and provide an energy benefit all year round (Granqvist 2007).

This review discusses the way in which solar control, low emittance and chromic materials work as energy saving window coatings, with reference to a number of experimental results. Section 2 includes the theory behind the mechanism of the films, taking into consideration the development of ‘low-emittance’ coatings and heat mirrors. The rest of the review concentrates solely on the recent work on chromic materials. Section 3 gives an in depth discussion on thermochromic materials, focusing on vanadium oxide thin films; electrochromic thin films, in particular nickel, and tungsten oxide thin films in §4; photochromic materials are then talked about in §5 and the review ends with some concluding thoughts and a discussion of future prospects of chromic materials as thin films for solar control applications.

2. Principles and background theory to solar control coatings

(a) *Ambient radiation*

Solar energy materials work on the basis of controlling the flow of ambient radiation in our environment (Granqvist 2007).

Ambient radiation is split into four components which are shown in figure 2. The first and most fundamental property of this radiation arises because all matter emits electromagnetic radiation. This leads to the concept of an ideal black body which has a radiation spectrum known as Planck’s spectrum, derived from the quantum nature of the radiation (Granqvist 1981). Figure 2*a* shows such spectra corresponding to four different temperatures within the range of $2000 < \lambda < 100\,000$ nm. The thermal black-body radiation from a real body can be determined by multiplying Planck’s spectrum by a wavelength-dependent emittance which is in the interval of zero to 1. It can be seen from figure 2 that these spectra are bell-shaped and have a maximum at 10 000 nm, which is displaced towards shorter wavelengths as the temperature rises. The next component of ambient radiation which is of importance is the solar radiation. The solar spectrum corresponding to radiation outside the earth’s atmosphere is shown in figure 2*b*. This lies in the range of $250 < \lambda < 3000$ nm and thus does not overlap with the wavelength of black-body radiation, making it possible to obtain surfaces with completely different properties with respect to black-body and solar radiation. As most energy-related applications occur at ground level, atmospheric absorption is also very important. Figure 2*c* corresponds to the

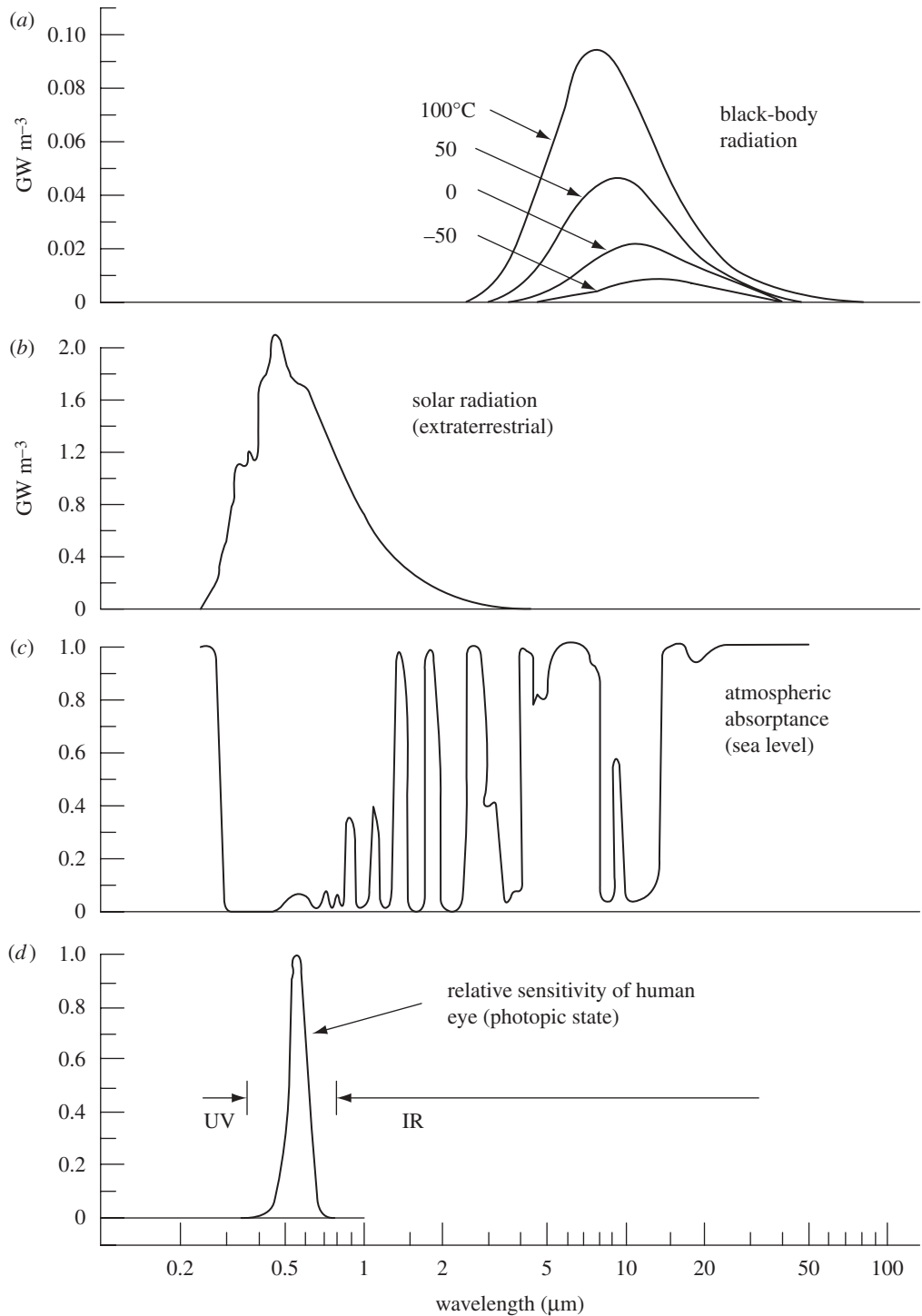


Figure 2. Spectra showing (a) black-body radiation for four different temperatures, (b) solar irradiation outside the earth's atmosphere, (c) typical absorptance across the atmospheric envelope, and (d) relative sensitivity of the human eye (adapted from [Granqvist 1991](#)).

typical atmospheric absorption spectrum at the levels of the earth's surface. What is clear from this spectrum is that not only is solar radiation being transmitted through the atmosphere but there is also an 'atmospheric window' at $8000 < \lambda < 13\,000$ nm, permitting the transmittance of black-body radiation. Figure 2*d* shows the spectra corresponding to the reactive sensitivity of the human eye in its light-adapted state, which occurs in the interval of $400 < \lambda < 700$ nm with a maximum at 555 nm, indicating that a large amount of solar energy is in the invisible infrared region. If the spectra shown in figure 2*a, b, d* are then averaged, luminous, solar or thermal values significant to the respective optical properties are obtained and written as X_{lum} , X_{sol} and X_{therm} , where X is T (transmittance), R (reflectance), A (absorbance) or E (emittance). Hence, figure 2 shows that ambient radiation is spectrally selective (restricted to precise and distinct wavelengths), which is an important factor for solar energy materials. Another crucial selectivity to consider is the angular selectivity. This is a consequence of the fact that different angles may apply for different types of radiation. As well as selectivity, two fundamental relationships must be considered:

$$A(\lambda) + R(\lambda) + T(\lambda) = 1, \quad (2.1)$$

where A , R and T are absorptance, reflectance and transmittance, respectively, and

$$A(\lambda) = E(\lambda), \quad (2.2)$$

where E is the emittance, i.e. the fraction of black-body radiation which is emitted at the wavelength λ (usually $\lambda > 3000$ nm).

(b) Solar thermal surfaces

A surface that facilitates the conversion of solar radiation into useful heat should possess two important properties. The first is that it should have high absorptance (i.e. low reflectance) and low emittance (i.e. high reflectance) for thermal radiation. This can also be written as

$$R(\lambda) = 0 \quad \text{for } 300 < \lambda < 3000 \text{ nm} \quad (2.3)$$

and

$$R(\lambda) = 1 \quad \text{for } 3000 < \lambda < 50\,000 \text{ nm}. \quad (2.4)$$

In order to obtain a spectrally selective solar absorbing surface, various design principles and physical mechanisms can be used; six of these are shown in figure 3.

Figure 3*a* illustrates a material which has appropriate intrinsic optical properties which are ideal for solar control materials; however, there are few materials which actually exhibit this property and further work needs to be done in order to develop these materials further. Figure 3*b* shows an example of a semi-conductor metal tandem, which gives the required spectral selectivity by the absorption of short-wavelength radiation in a semiconductor which has a band gap of 0.6 eV. It also has low- E_{therm} owing to the metal also on the surface. However, the disadvantage with this surface is that useful semiconductors usually have large refractive indexes, which results in high reflection losses and creates a need for an extra antireflection coating that is effective in the solar range. Multi-layer coatings shown in figure 3*c* consisting of

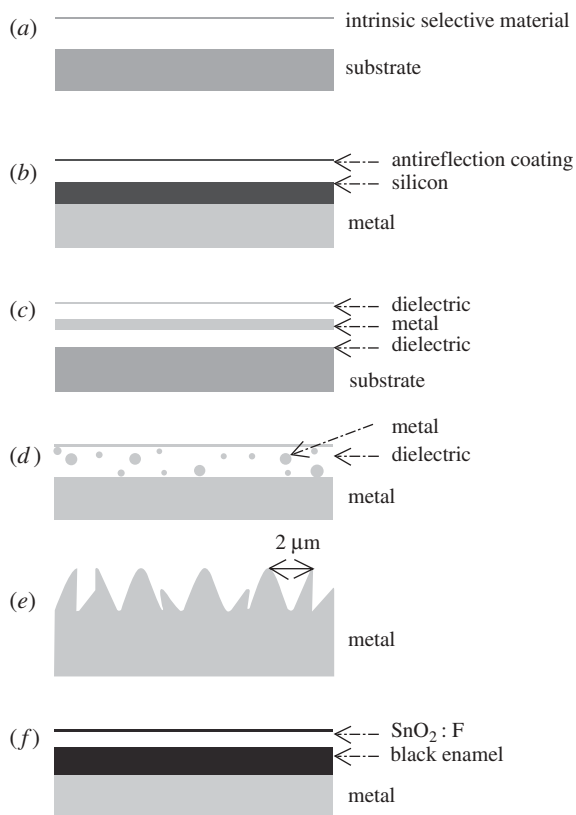


Figure 3. A schematic of six different coatings and surface treatments for selective absorption of solar energy (diagram adapted from Granqvist 1991).

dielectric/metal/dielectric (D/M/D) alternation can be made into very efficient selective solar absorbers. Those coatings with Al₂O₃ and Mo as the dielectric and metal, respectively, have been shown to have good properties, and can be produced on a large scale using vacuum coating technology. Figure 3*d* illustrates a metal/dielectric-composite-metal tandem, which contains nanoparticles in a dielectric host. This design is flexible and the choice of materials, film thickness, particle concentration, grading and the shape and orientation of the particles all affect the optimization of the spectral selectivity. Numerous reflections against metal dendrites which are 2000 nm apart can produce high A_{sol} in textured metal surfaces, shown in figure 3*e*. However, the low- E_{therm} is unaltered by this treatment owing to the fact that relevant wavelengths are much larger than the dendrite separation. Ultimately, figure 3*f* shows a selectively solar-transmitting film on a black-body-like absorber, which can be used to import spectral selectivity (Granqvist 1991).

These design principles and physical mechanism have been the basis of a number of thin films coated on metallic substrates. Nickel pigmented anodic alumina (Andersson *et al.* 1980) is the most well-understood coating and is commercially produced by AC anodization of an aluminium sheet in dilute phosphoric acid followed by AC electrolysis in a NiSO₄ bath (Granqvist 1991).

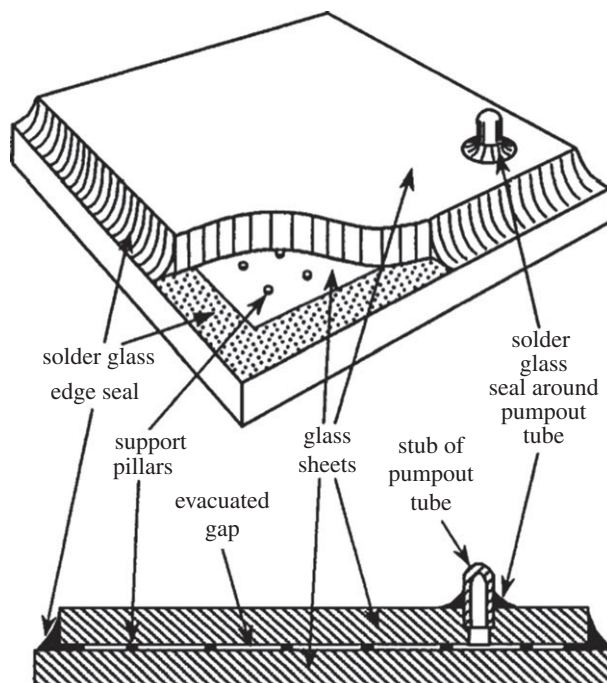


Figure 4. A schematic of vacuum glazing (adapted from Ng *et al.* 2003).

(c) *Thin films for window glazing: static properties*

The fundamental function of architectural windows is to supply visual connection between the inside and outside of buildings. However, practically, thermal energy leaves or enters the building via the windows, leading to the need of heating and air conditioning. A solution to this could be to coat the window glass exposed to the air with thin films that have low- E_{therm} . As well as low- E_{therm} , T_{lum} has to be large (at least 60%) and the solar radiation which contains infrared radiation not needed for vision can be prevented from entering the building by using a thin film with low transmittance at $700 < \lambda < 3000$ nm. These requirements have led to the production of low-emittance coatings (low-E) which are transparent at $300 < \lambda < 3000$ nm and reflecting at $3000 < \lambda < 100\,000$ nm, and ‘solar control coatings’ that are transparent at $400 < \lambda < 700$ nm and reflecting at $700 < \lambda < 3000$ nm. A well-known use of low-E coatings are in ‘vacuum glazing’, which has been researched extensively during the last several years (Fischer-Cripps *et al.* 1995; Garrison & Collins 1995; Lenzen & Collins 1997; Collins & Simko 1998). These consist of two or more sheets of low-E coated glass that have been separated by support pillars (Fang *et al.* 2007), as shown in figure 4. The edges of the glass are then sealed hermetically together and a high and stable vacuum is produced in between the films (Lenzen & Collins 1997). A vacuum is required in order to stop heat transfer between the two glass panes by gaseous conduction or convection (Collins & Simko 1998). The role of the low-E coatings is to reduce the amount of radiative heat that transfers from the glass sheets.

The first successful method for producing vacuum glazing was done in 1989 (Fang *et al.* 2007); however, this used a contiguous solder glass edge seal that could only be formed at temperatures exceeding 450°C. This was problematic because at such temperatures tempered glass and many soft low-E coatings begin to degrade. This created the need for only hard low-E coatings to be used for glazings that were sealed using solder glass edge seals. Recently, a method for producing an edge seal at low temperatures (less than 200°C) has been developed by Fang *et al.* (2007) and a heat transfer coefficient of less than $1 \text{ W m}^{-2} \text{ K}^{-1}$ for the centre of glass of the vacuum glazing has been accomplished. The vacuum state in these windows obviously needs to be preserved over long periods of time (Granqvist 2007), and studies into the effects of carbon dioxide, carbon monoxide and water vapour have been carried out (Ng *et al.* 2003, 2005; Minaai *et al.* 2005). It has been shown that $\text{SnO}_2 : \text{F}$ coatings are the most useful for the use of vacuum glazing (Mbise *et al.* 1997). Another way in which energy efficiency can be attained is by the use of angular selective thin films on window coating (Smith *et al.* 1998).

(i) *Spectrally selective thin films: heat mirrors*

In order to obtain energy-efficient glass windows in warm climates, window glass can be coated with spectrally selective coatings which transmit almost all visible radiation and reflect all infrared radiation. Hence, an ideal energy-efficient window in a warm climate should have $T = 1$ and $R = 0$ for the visible region (i.e. $400 < \lambda < 700 \text{ nm}$) and $T = 0$ and $R = 1$ for the infrared region ($700 \text{ nm} < \lambda$) (Köstlin & Frank 1982). This can be achieved by using a three-layer system of (D/M/D) on a glass substrate (Köstlin & Frank 1982; Fu *et al.* 1997; Durrani *et al.* 2004; Al-Shukri 2007; Kawasaki *et al.* 2008). Such films have been fabricated via a number of experimental techniques such as plasma ion assisted deposition (PIAD) (Al-Shukri 2007), evaporation (Durrani *et al.* 2004) and physical vapour deposition (PVD) (Fu *et al.* 1997) using $\text{TiO}_2\text{--Ag--TiO}_2$, ZnS--Ag--ZnS and $\text{WO}_3\text{--Ag--WO}_3$ systems (Fu *et al.* 1997; Al-Shukri 2007). Experimental results on the overall optical performance of these films have shown close agreement with results predicted by computer simulations (Al-Shukri 2007), shown in figure 5.

It has also been shown that all oxide–metal–oxide mirrors degrade during heating as a result of the silver layer in the oxide environment; however, to improve this Cu block layers are used to protect silver against oxidation. In those heat mirrors composed of TiO_2 and MgF_2 films, the silver film is not directly surrounded by oxide layers and so exhibit excellent optical and environmental properties (Fu *et al.* 1997). Other systems which have also been investigated are Zn/Al and Zn/Ag systems (Zhang *et al.* 1996). Heat mirrors have also been constructed for cold climates, these include (D–M–D) layers on glass $\text{TiO}_2\text{--Ag--TiO}_2$, ZnS--Ag (or Al)– ZnS , ZnS--Ag--ZnS and tin-doped indium oxide, coatings on glass.

(d) *Thin films for window glazing: dynamic properties*

In environments where the ambient temperature is not constant, a more dynamic approach to window coatings is needed. This has led to the recent work of ‘chromogenic’ materials (Lampert 1998; Granqvist 2003). Thin films which exhibit properties such as photochromism (TiO_2 - and MoO_3 -based films, Granqvist 1981), thermochromism (VO_2 , Morin 1959; Manning *et al.* 2002) and

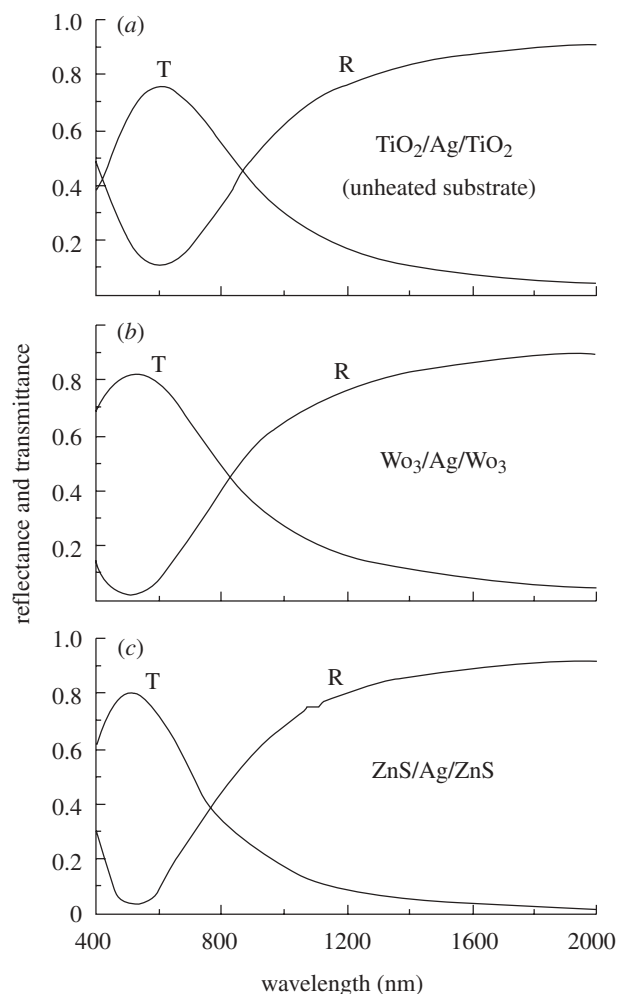


Figure 5. Graphs of the measured reflectance and transmittance of D/M/D on glass (adapted from Al-Shukri 2007).

electrochromism (NiO , WO_3 , Lampert 1993; Bouessay *et al.* 2005) have been in the forefront of this work. These oxide-based thin films have now been produced through various experimental techniques and used as glass coatings. Each of these different types of chromogenic materials will be discussed further in subsequent sections of this review.

3. Thermochromic coatings for thin films

Thermochromic materials are those where some optical property reversibly changes with temperature. Such a change affects the amount of both ultraviolet and infrared radiation allowed to pass through the glass. As the temperature of the glass is increased the amount of infrared transmittance decreases (Granqvist 1990). Figure 6 demonstrates qualitatively how thermochromic glazing coatings work.

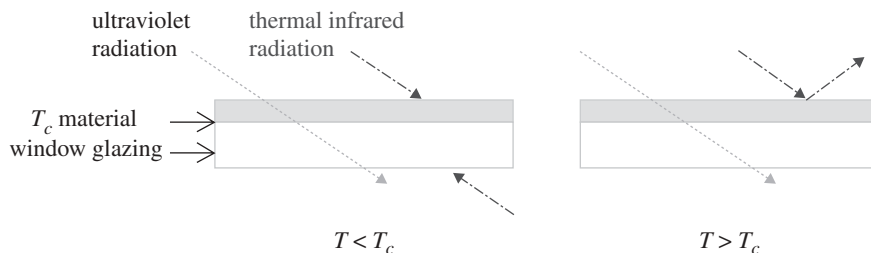


Figure 6. Schematic of the mechanism of thermochromic materials.

Many transition metal oxides such as Ti_2O_3 , V_2O_3 , V_2O_5 , VO , VO_2 (Morin 1959) and V_6O_{13} (Manning *et al.* 2002) can be used as thermochromic glazing coatings; however, there has been particular interest in vanadium (IV) oxide as it has the closest transition temperature (T_c) to room temperature and so shows the most promise.

(a) Vanadium (IV) oxide thin films

(i) Metal-to-semiconductor transitions (MST)

A single crystal of vanadium (IV) oxide has a transition temperature, T_c , of 68°C , at which there is a phase change from monoclinic to tetragonal rutile (Béteille *et al.* 1997). This temperature is significant because below this value the material becomes transparent to both the visible and the infrared regions of the electromagnetic spectrum, which in turn heats the building. By contrast, above the T_c , different properties are observed; the material becomes metallic in nature and remains transparent in the visible region but becomes reflective in the infrared region. As a result, less thermal radiation heats the inside of the building. This effect has been investigated extensively since the 1950s (Manning *et al.* 2002) but the exact nature of the transition at this temperature is still ambiguous. The work of Barker *et al.* (1966) displayed the transition as a sudden change of resistance, and so it was thought that the nature of the transition was metallic \leftrightarrow antiferromagnetic, and hence called a metal-to-insulator transition. However, following further research in the properties of thermochromic materials, the transition is now believed to be metallic \leftrightarrow semiconducting and renamed as a metal-to-semiconductor transition (MST) (MacChesney & Guggenheim 1969).

In order to enhance the understanding of the MST, Goodenough (1971) explored the line band structure of the two phases of vanadium (IV) oxide and presented it as a schematic energy band as shown in figure 7.

Goodenough (1971) postulated the idea that the MST was a result of an antiferroelectric transition in the vanadium (IV) oxide, whereby the V–V pairing in the tetrahedral phase becomes more energetically stable once cooled to the monoclinic arrangement. Following this, he discussed the idea of the presence of two transition temperatures, T_c as a result of the antiferroelectric distortion and T'_c resulting from a crystallographic distortion (Parkin *et al.* 2008). Eyert (2002) built upon the idea by Goodenough by using functional theory in correspondence to the local density approximation.

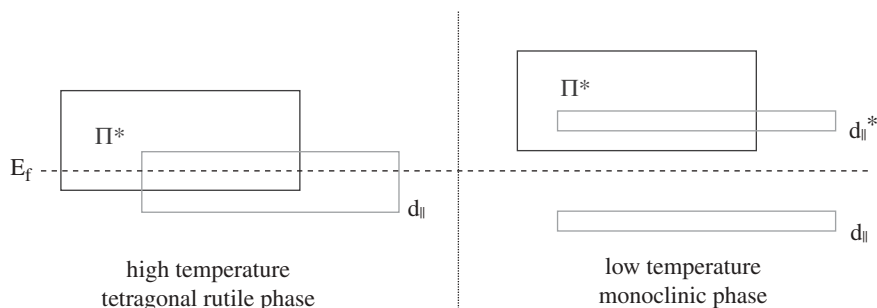


Figure 7. An energy band for both phases of vanadium (IV) oxide, where the $d_{||}$ orbital is the result of V–V pairs that occur from the overlap of dx^2-y^2 atomic orbital (diagram adapted from Eyert 2002).

Vanadium (IV) oxide thin films have been investigated extensively as the metal-to-semiconductor temperature is the closest to room temperature. However, this is also a disadvantage, as this temperature is still too high to be used effectively to regulate ambient temperature of about 18–25°C. In order to overcome this problem, dopants can be introduced into the coating and lower the transition temperature. Dopants can increase or decrease the T_c depending on a number of factors.

(ii) Dopants

Dopants with atomic radii larger than the vanadium (IV) ion cause a decrease in the transition temperature, T_c , and those with smaller ionic radii increase T_c ; however, changes in the transition temperature are only evident when large concentrations of the dopants are integrated into the crystal structure (MacChesney & Guggenheim 1969). Other factors such as dopant charge (Phillips *et al.* 1987) and variation of electron carrier density (Pierce & Goodenough 1972) also affect the transition temperature. Dopants which are high-valence metal ions such as tungsten (VI) and niobium (V) in sufficient amounts can decrease the transition temperature to approximately room temperature, 25°C, whereas low valence ions such as aluminium (III) or chromium (III) increase the transition temperature (Parkin *et al.* 2008).

Goodenough (1971) invoked a more in-depth discussion about the effect of dopants to the structure using X-ray diffraction. He considered the presence of a second semi-to-conducting phase between the monoclinic and tetragonal phase. This phase has an orthorhombic structure for low-valence dopant ions and a rutile structure for high-valence dopant ions.

Tungsten has proven to be the most useful dopant as less than 2 at.% reduces the transition temperature of vanadium (IV) oxide to the ideal temperature for window coatings of 25°C (Jin *et al.* 1998). This is typically by 25°C per at.%. This decrease in T_c by tungsten is caused by the substitution of a vanadium (IV) ion with a tungsten (VI) ion, which occurs because of the charge-transfer mechanism. This can be explained by either the insertion of extra electrons into the vanadium d-band (Jin *et al.* 1998) or by the fact that the tungsten ion has a larger ionic radius than vanadium. The efficiency of tungsten to reduce T_c can be shown schematically in figure 8.

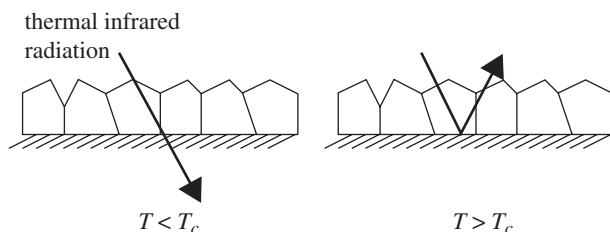


Figure 8. Qualitative diagram of the mechanism of tungsten thermochromic materials (diagram adapted from Jin *et al.* 1998).

Furthermore, a dopant which has shown to decrease the transition temperature of vanadium (IV) oxide is titanium (up to 5 at.%) (Béteille *et al.* 1997). If more than 5 at.% of Ti is added, this causes the high temperature states to become less reflective in the infrared region. There are a number of other dopants that are doped into vanadium (IV) oxide. Gold decreases the transition temperature; however, if high concentrations are used in the rutile high temperature phase the material becomes less far infrared reflecting (Jin *et al.* 1998). Other dopants which have been found to decrease the transition temperature of vanadium (IV) oxide are molybdenum, which lowers it by 11°C per at.% and niobium, which lowers T_c by 6°C per at.% (Greenberg 1983; Hanlon *et al.* 2003). Fluorine has also been shown to reduce the transition temperature to 20°C but it not suitable to use as a window coating as it causes an increase to the hysteresis width of the thermochromic transition (Jin *et al.* 1998). On the other hand, iron has been shown to decrease the T_c of vanadium (IV) oxide (Phillips *et al.* 1987) at a rate of -6°C per at.% Fe up to 1.4 at.% Fe. Above this concentration of Fe, the T_c of vanadium oxide begins to increase, remaining unchanged after 3 at.% Fe.

(iii) Deposition technologies of pure and doped vanadium (IV) oxide thin films

Thin films of vanadium (IV) oxide are usually prepared within the range, 10–1000 nm (to maintain suitable levels of transmittance), and are preferred to single crystals as they are able to withstand films stresses that result from cycling between the two structural phases during the metal-to-semiconducting transition, resulting in cracks and dissolution of single crystals (Parkin *et al.* 2008). Three main technologies have been employed to prepare thin films: PVD; sol–gel spin and dip coating and chemical vapour deposition (CVD).

Physical vapour deposition

This method usually involves the presence of a plasma created in a reduced pressure atmosphere of either inert or reactive gases or a mixture of the two. Molecules are energetically removed from a target. Subsequently, these ions then go on to remove molecules from the solid raw material and deposit them as thin films. The composition of the films can be easily varied by monitoring the number of molecules initially removed, the number of seed gases present in the chamber and/or by the size of the host material. PVD methodologies include laser ablation, RF magnetron sputtering, ion beam sputtering, DC magnetron sputtering and evaporation (Cui *et al.* 2008; Parkin *et al.* 2008).

Sol-gel and dip coating

The sol-gel dip coating methodology involves the submersion of a substrate in a solution of metal alkoxides, with a controlled rate of removal. The layer is allowed to dry or age and gelatinize; this is followed by a heat treatment to remove the solvent and form a network of metal oxygen bonds from the metal oxide precursors. Depending on the processing conditions, the sol-gel method can be used to obtain continuous films (with a variety of different thicknesses) or nanoparticles. Additionally the method is not limited to dip coating, once the sol has been generated it may be applied by dropping or spinning onto the substrate. The sol-gel method allows for the facile introduction of dopants; precursors are added in the required quantity and dispersed as the sol is generated and are incorporated into the final product. A number of starting materials have been used to produce vanadium (IV) oxide films; the most common are the metal alkoxides vanadyl tri (iso-propoxide) and vanadyl tri (tert-amyl oxide) (Parkin *et al.* 2008). A number of dopants have been introduced into vanadium (IV) oxide using sol-gel methods, such as gold (Cavanna *et al.* 1999), tungsten and molybdenum (Takahashi *et al.* 1996, 2001), all of which have been shown to lower the thermochromic transition temperature.

Chemical vapour deposition

Vanadium (IV) oxide thin films have also been obtained by CVD (Greenberg 1983). It must be noted that there can be difficulties associated with controlling the stoichiometry of metal oxides produced. This method has much more potential in large-scale industrial production (Parkin *et al.* 2008). One way in which thin films have been produced is via low pressure metal-organic chemical vapour deposition (MOCVD), where an organometallic such as vanadyl tri (isobutoxide) $\text{VO}(\text{O-i-BU})_3$ is used as a precursor (Takahashi *et al.* 1989). An alternative starting material is the β -diketone complex, vanadyl acetylacetonate (Sahana *et al.* 2002a). Depositions were carried out on $\alpha\text{-Al}_2\text{O}_3$ substrates at relatively low temperatures, such as 380°C , in O_2 , N_2 and N_2 and H_2O atmospheres (Barreca *et al.* 1999). Also, vanadium acetylacetonate $\text{V}[\text{C}_5\text{H}_7\text{O}_2]_3$ has been used in a spray pyrolysis process in a controlled atmosphere to produce vanadium oxide films (VO_2 , V_2O_3 and V_2O_5) (Sahana *et al.* 2002b).

Vanadyl acetylacetone has been used to prepare VO_2 (B) that was subsequently annealed under argon at 550°C to convert it from the meta-stable phase to the metallic rutile phase (Barreca *et al.* 1999). Atmospheric pressure chemical vapour deposition (APCVD) has been used to produce thin films directly (Parkin *et al.* 2008). The APCVD method is carried out in a number of steps, and the process can be shown qualitatively in figure 9.

A much preferred precursor of vanadium tetrachloride and water at $400\text{--}555^\circ\text{C}$ can be used to produce thin films of vanadium oxides, V_2O_5 , VO_2 , VO_x ($x = 2.00\text{--}2.50$) and V_6O_{13} (Manning *et al.* 2002). Another precursor often used in the APCVD method is VCl_4 . Both VCl_3 and VCl_4 are suitable precursors for the APCVD experiment as they are volatile liquids, which results in easy transportation to the reaction site by a hot, inert carrier gas (Parkin *et al.* 2008) (figure 10).

The most recent method of CVD investigated to produce vanadium (IV) oxide films is a method that combines aerosol-assisted (AA) and APCVD (Binions *et al.* 2008). This hybrid technique has been used to dope gold nanoparticles into vanadium (IV) oxide films, using vanadyl acetylacetonate and auric acid

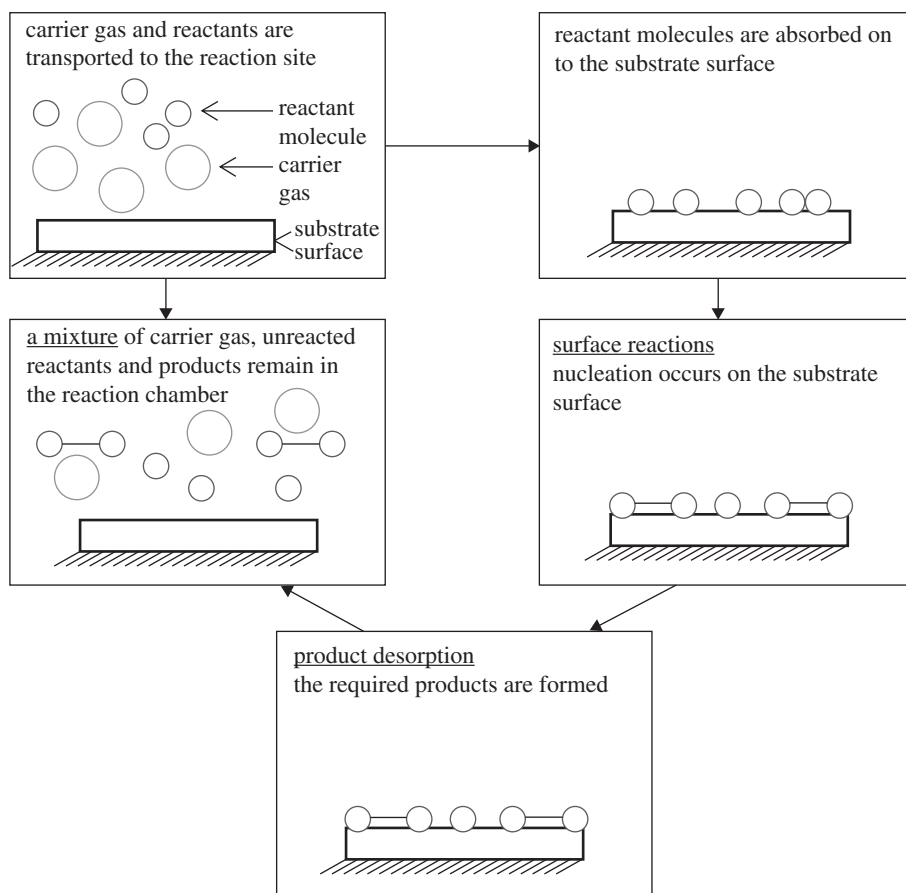


Figure 9. Qualitative diagram of the steps involved in the atmospheric pressure chemical vapour deposition (diagram adapted from [Parkin *et al.* 2008](#)).

in methanol with colloidal gold suspensions ([Ung *et al.* 2002](#); [Klimnov 2004](#)). Like the APCVD method, atmospheric pressure is used in the reaction chamber; however, this is coupled with the aerosol flow. The insertion of gold dopants led to the production of a variety of blue and green films, as opposed to the yellow/brown colour normally associated with vanadium (IV) oxide ([Binions *et al.* 2008](#)).

Ultraviolet visible spectroscopy indicated that this colour was the result of the presence of a surface plasma resonance (SPR) band associated with the gold nanoparticles ([Walters & Parkin 2009](#)). The ratio of gold to vanadium atoms in the film influenced the strength and position of the SPR band. The colour of the film is dependent on the position of this SPR band, which is influenced by three factors: the interparticle distance, particle size and the relative index of the host matrix ([Ung *et al.* 2002](#); [Klimnov 2004](#)). There are numerous advantages to hybrid CVD. The first is that it can produce films which are of various colours, the thermochromic properties of the vanadium films produced are similar to those grown by APCVD; unlike sol-gel techniques this method is a single-step process which easily produces films that have good surface coverage with a variety of thickness and varied dopant levels ([Binions *et al.* 2008](#)). Further work is being

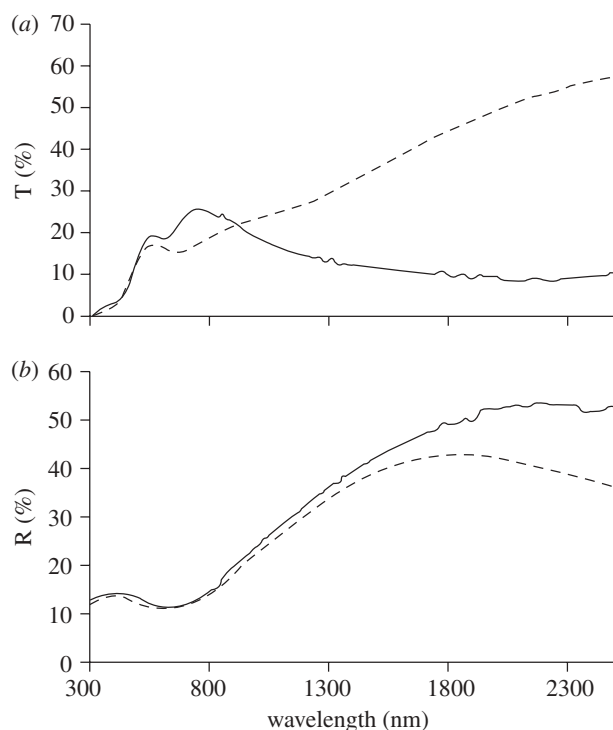


Figure 10. Graphs show (a) transmission and (b) reflectance spectra of typical gold-doped vanadium dioxide samples deposited using the combined system over 15 min at a temperature of 525°C (adapted from Binions *et al.* 2008). Straight line, hot; dashed line, cold.

carried out in order to develop this technique using a wider variety of dopants and nanoparticles.

4. Electrochromic thin films

This section is included as the electronic supplementary material.

5. Photochromic coatings for thin films

Photochromism is the reversible photocolouration of a single chemical species between two states having distinguishably different absorption spectra, which results from the effects of electromagnetic radiation in at least one particular direction (Minkin 2004; Saleh Abdel 2006)



Consequently, a photochromic material is one which undergoes a reversible colour change in response to light (Ohko *et al.* 2003). Figure 11 shows a transmittance spectrum for initial, coloured and bleached states of mesoporous tungsten oxide.

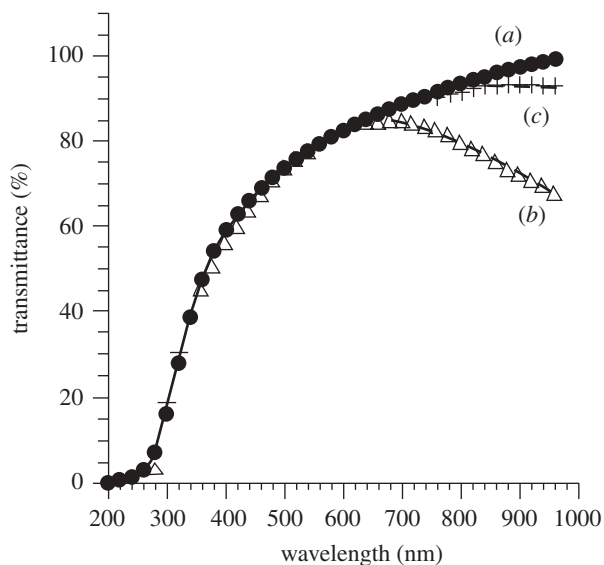


Figure 11. Transmittance spectra for the (a) initial, (b) coloured and (c) bleached states of mesoporous tungsten oxide (adapted from Lai *et al.* 2005).

Traditional photochromic materials respond in a monochromatic way, in which it only displays one colour; therefore in order to generate multi-coloured photochromism, a number of different materials or filters need to be used (Ohko *et al.* 2003). Accomplishing multi-coloured photochromism in simple materials would mean that photochromic devices could be used in a wide range of applications, especially as smart windows.

There are many different types of chromogenic materials, with the most extensively studied being photochromic glass and polymers (Granqvist 1990). Thin films based on TiO (Naoi *et al.* 2004, 2005; Kelly & Yamashita 2006), MoO₃ (He & Yao 2003) and WO₃ (Avendaño *et al.* 2003; He *et al.* 2003; Poirier *et al.* 2006) have been studied for photochromic properties.

Each of these transition metal oxides mentioned above have all been recently discovered as having multi-colour photochromic properties. Each one will be discussed in turn.

(a) Multi-colour photochromism of titanium oxide thin films

The relatively new phenomenon of multi-colour photochromism has been reported in TiO₂ films loaded with silver nanoparticles by photocatalytic reaction under ultraviolet light. Under visible light, usually from a Xe lamp with a band pass filter (full width half maximum, 10 nm) or laser is used, the initial brownish-grey films change to almost the same colour as that of the incident light. The photochromism can then be reactivated by sufficient irradiation of the colour film by ultraviolet radiation (figure 12).

In order to produce silver and TiO₂ nanocomposites (Ag–TiO₂) films, a non-porous TiO₂ film is treated with AgNO₃ so the Ag⁺ is absorbed (Ohko *et al.* 2003). However, under ultraviolet light, electrons in the valence band of TiO₂ are

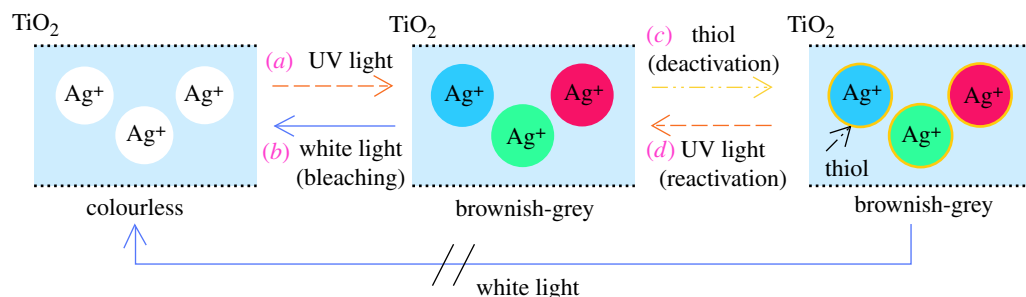


Figure 12. Schematic for photochromism of the (a,b) Ag-TiO₂ film and (c) deactivation, and (d) reactivation of the photochromism (diagram adapted from Naoi *et al.* 2005).

excited to the conduction band, which consequently results in the formation of holes. The excited electrons of TiO₂ are responsible for the reduction of the Ag⁺ ions to Ag nanoparticles, and also the oxidation of water (Naoi *et al.* 2004, 2005). Additionally, as a consequence of the Ag nanoparticle plasma resonance effects, an adsorption band visible over the entire optical spectrum is given. The presence of a spectral hole results in the transmitted colour having the same wavelength of that which was used to irradiate the Ag nanoparticles originally. This causes a decrease in the optical extinction peak together with a blue shift in the plasmon resonance for the photoexcited Ag nanoparticles (Walters & Parkin 2009).

The brownish-grey colour of the films is a result of the deposition of Ag nanoparticles with various shapes and sizes in the nanopores of the TiO₂ films (Naoi *et al.* 2004, 2005). The absorption peak wavelength of Ag nanoparticles shifts from about 400 to 500 nm as the particle size decreases from 2 to 70 nm (Kleemann 1968; Russell *et al.* 1987), also increasing the refractive index of the matrix causes a red shift in absorption. As most of the Ag particles are deposited in the nanopores of the TiO₂ film, this may affect and result in the variety of the shapes and sizes of the Ag particles, this effect is known as the 'moulding effect'. This may give rise to particles with an arrangement of absorption wavelength, which occurs in the broad visible adsorption ranging from 350 to over 700 nm of the Ag-TiO₂ films. If the Ag-TiO₂ films are irradiated with a coloured light, for example, green, the film will no longer absorb green light but reflects it instead; this coupled with the fact that all other colours are absorbed, the film consequently looks green. As well as this effect, irradiation with coloured light causes an 'absorption hole' to be formed, and absorption at around the excitation wavelength decreases. These holes could arise because the electrons of Ag nanoparticles are excited only when they are irradiated with the light of their resonance wavelength. The excited electrons are then accepted by oxygen in the air and this causes the Ag nanoparticles to oxidize to colourless Ag⁺ ions. Consequently, only the light of the excitation wavelength is reflected or transmitted, while the lights of the other wavelength are absorbed by the remaining particles, hence the colour of the excitation wavelength appears. The chromogenic properties of these can be improved by the simultaneous irradiation of Ag deposition with ultraviolet and blue light to repress the formation of anisotropic Ag particles (Ohko *et al.* 2003; Naoi *et al.* 2004, 2005).

(b) *Photochromism of molybdenum oxide thin film*

Photochromism in molybdenum oxide films (MoO_3) is the result of the formation of electron hole pairs by the increase of energy of the excitation light above the band gap (E_g) of MoO_3 . This results in the change of optical absorption and MoO_3 films change from colourless to blue (He & Yao 2003). The photochromic properties of MoO_3 films have led to the increased interest of their use in applications such as erasable optical storage devices and smart windows.

Amorphous molybdenum oxide films have been shown to display more efficient photochromic response than crystalline film (Scarminio *et al.* 1997) or single crystals (Tubbs 1974). The amorphous film has a perovskite-like type structure which consists of corner-sharing MoO_6 octahedra (Carcia & McCarron III 1987; Ramans *et al.* 1987; Granqvist 1994) and has been produced by a number of techniques. The most common way of producing these films is by thermal evaporation from a resistive source (Deb & Chopoorian 1966; Deb 1968; Rabalais *et al.* 1974; Yao *et al.* 1990, 1992; Chudnovskii *et al.* 1992). Vacuum evaporation is the standard technique; however, evaporation under slightly reactive conditions (Ramans *et al.* 1987) and flash evaporation (Julien *et al.* 1995) have also been used. RF sputtering from targets of Mo and MoO_3 (Carcia & McCarron III 1987; Scarminio *et al.* 1997) and DC planar magnetron sputtering from a Mo target (Jankowski & Schrawyer 1990) have also been carried out. CVD (Abdellaoui 1988; Cross & Schrader 1995) and sol-gel-related techniques (Yanovskaya *et al.* 1990; Zhang *et al.* 2001) are also major techniques used to produce MoO_3 films. There are a number of mechanisms which have been suggested to account for the photochromism in MoO_3 films. The first is the colour-centre model explained by Deb (1968). This explanation involves the formation of defects (i.e. oxygen vacancies) in the oxide and of F-centres (positively charged vacancies, which result from the absence of a negatively charged ion from a particular point in an ionic solid), which capture photogenerated electrons. These trapped electrons can be excited into the empty conduction band, leading to transitions that range from the near-infrared to the visible region. Consequently, the blue colour of the films arises from this absorption in the red region (He & Yao 2003).

The next mechanism to consider is the model of double insertion/extraction of ions and electrons developed by Faughnan *et al.* (1975). This was initially developed to describe electrochromism in WO_3 (Chatten *et al.* 2005); however this has now been accepted as an appropriate way of describing the photochromism in transition metal oxides, especially MoO_3 and WO_3 . Ultraviolet irradiation leads to the formation of electrons and holes, which react with the protons (necessary for coloration) from water molecules on the surface of the as-prepared film. Following this, the protons can diffuse into the MoO_3 lattice, owing to the electric field generated by the remaining electron in the film (figure 13). The oxygen radicals can then occupy the vacancy sites inside the sample or alternatively escape as molecular oxygen into the atmosphere (He *et al.* 2001). Injection of the photogenerated electron into the conduction band of MoO_3 causes the formation of hydrogen molybdenum bronze, $(\text{H}_x\text{Mo}_x^{\text{V}}\text{Mo}_{1-x}^{\text{VI}}\text{O}_3)$, which turns the film blue owing to intervalence charge transfer from the newly formed Mo^{5+} to adjacent Mo^{6+} (He & Yao 2003).

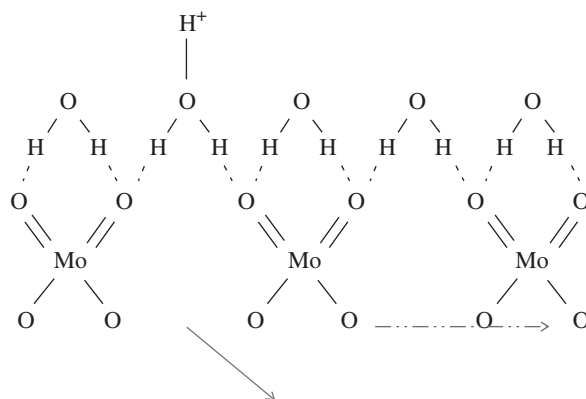


Figure 13. Schematic to show the diffusion of protons in the MoO_2 thin film during the photochromic process (diagram adapted from He & Yao 2003).

The third model proposed for the mechanism of photochromism in MoO_3 films is the small-polaron theory (Gerard *et al.* 1977; Schirmer *et al.* 1977). This model has similarities to the intervalence charge transition model; however, in this model it is thought that incident photons are absorbed by small polarons and the optical absorption of coloured oxide films is the result of the small-polaron transitions hopping between two neighbouring non-equivalent sites of molybdenum. The performance of photochromic properties of molybdenum oxide can be affected in various ways. The method in which the films are prepared strongly affects their optical properties (Galyamov *et al.* 1990). Oxygen affects the stability of the molybdenum species and causes gradual degradation of the colour of the films over time. The degree of coloration is also greatly dependent on the amount of available protons which are able to be incorporated into the MoO_3 lattice. Water, alcohol and organic acid have all been found to affect the photochromic properties of MoO_3 (He & Yao 2003).

(c) Photochromism of tungsten oxide thin films

In 1973, Deb reported the first photochromic properties of $\alpha\text{-WO}_3$, since then WO_3 has been investigated extensively for use in applications such as information display device and smart windows (Oi *et al.* 1982; Xu *et al.* 2000; Avellaneda *et al.* 2001). For the application of smart windows, the electrochromic properties of WO_3 can be used; however, an electrochromic device requires an external voltage in order to control the electrochromic behaviour, whereas photochromic devices do not. In order to promote a colour change in photochromic devices, only radiation is needed (Avellaneda & Bulhões 2003), which acts as a great advantage over an electrochromic device. Exposure of amorphous as-prepared WO_3 thin film to ultraviolet radiation causes an intense blue or brown coloration, which can be characterized by a strong absorption band in the visible and near-infrared region (Deb 1973). The colour change was found to be caused by the reduction of W^{6+} atoms to W^{5+} and/or W^{4+} followed by the formation of the so-called tungsten bronzes (H_xWO_3) (Gazzinelli & Schirmer 1977; Temmink *et al.* 1990).

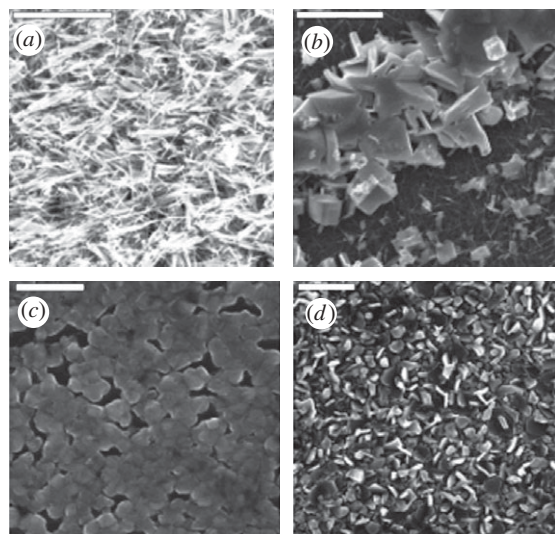


Figure 14. SEM of films deposited from (a) WCl_6 and ethanol at 625°C , (b) WCl_6 and methanol at 625°C , (c) WCl_6 and ethanoic acid at 62°C and (d) WCl_6 and water at 625°C (Blackman & Parkin 2005).

In 1980, Gavriluk *et al.* first reported photochromism in polycrystalline WO_3 thin films deposited by thermal deposition *in vacuo*. More recently, in 2003, Avellaneda and Bulhões studied thin films of WO_3 and $\text{WO}_3 : \text{X}$ (where $\text{X} = \text{Ti}$, Nb , Ta and Zr) deposited by dip coating. They found that the sufficiency in photochromism of these films was related to the thickness and the heat treatment temperature of the films. They found that the sample of $\text{WO}_3 : \text{Zr}$ (with three layers) heated at 120°C showed the best photochromic responses, even though all amorphous films showed photochromic effects.

DC magnetron sputtering method was also used by Georg *et al.* (2000*a,b*) to deposit WO_3 films. The most recent method to be used is APCVD, by Blackman & Parkin (2005). They studied the reaction of WCl_6 with a number of different reactants (ethanoic acid, ethanoic anhydride, ethyl ethanoate, methanol, ethanol, 2-propanol, 2-methyl-2-propanol and water) on glass substrates. They found that all the film deposited were monoclinic WO_3 ; however, various morphologies led to considerable differences in the gas sensitive properties of the films, although the photochromic properties were not examined (Blackman & Parkin 2005) (figure 14).

6. Conclusion

This review has discussed the technology of solar control low-E and chromogenic materials for the applications of solar control. Of all these technologies, solar control and low-E materials are the most established. These are materials based on spectral selectivity; however, angular selectivity materials propose the need for further research and development. Solar control and low-E materials

are materials which are sufficient to use as thin film on window glassing in climates which are constant. In those climates which vary, there is a greater need for chromogenic materials. At present, most of the research has been carried out on chromogenic materials whose optical properties change according to temperature (thermochromic), external voltage (electrochromic) and radiation (photochromic). Currently, thin films have been used in many applications; however, bulk materials such as photochromic glasses and polymers, thermochromic polymers and polymer-based cloud gels offer other possibilities. The most interesting, so far, has been in the applications of electrically controlled electrochromic smart windows. These windows offer the possibility of combining comfort for the occupants of the building with the growing need of energy efficiency (see figure 15 in the electronic supplementary material). Photochromic thin films also pose as a possible contender for smart windows as these work in a similar way to an electrochromic device; however, an external voltage is not required. Radiation is used to change the colour of these films and set photochromic properties within them. The most promising thermochromic material for window glazing is vanadium (IV) oxide, owing to its relatively low transition temperature of 68°C; however, this is still not low enough for it to be actually used on a larger scale. The introduction of some particular dopants lowers the T_c to a suitable temperature. Of all the chromogenic materials, the ones which show most promise are electrochromic thin films. Electrochromic technology can be coupled with facilities to direct daylight deeply into buildings by the use of light guides (see figure 16 in the electronic supplementary material). Electrochromic foil technology can also be used with membrane architecture to create lightweight buildings with little embedded energy. Building upon this idea, huge membranes which allow the flow of visible light and solar energy to be controlled and optimized can be developed. A possible drawback with regard to this new technology is the availability of the resources needed in order to produce these coatings. One must not forget that this will be a large-scale production of new technology and issues such as accessibility of the raw materials needed should be considered. Nevertheless, the current energy situation and future issues, such as population growth and increased standard of living, will inevitably demand a safe and affordable solution to the shortage of fossil fuel and environmental effects such as global warming. Chromogenic technology and thin film materials will play an important role in finding the appropriate solution.

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