

Thermochromic vanadium oxide thin films: Electronic and optical properties

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Abstract. Vanadium dioxide, VO_2 , is a widely studied thermochromic material with potential applications in energy efficient window technology. It undergoes a first-order metal-to-insulator transition, accompanied by a crystal structure transformation from monoclinic to tetragonal rutile, at a critical temperature of 68 °C. Below this temperature, VO_2 is semiconducting and infrared transmitting whereas it is metallic and infrared reflecting above the transition temperature. However, in order to achieve significant thermochromic switching, the luminous transmittance of thin films will typically be less than 50%. Here we report on recent research to improve the luminous transmittance as well as the transmittance change at the transition temperature. We systematically evaluate the effect of antireflection coatings, doping with Mg and the performance of coatings comprising thermochromic nanoparticles in a transparent matrix. The last option is shown to give the best performance and holds great promise for practical applications.

1. Introduction

Modern buildings have large windows and glass facades in order to give desired indoors–outdoors contact as well as good day-lighting. These glazings are often detrimental to the energy efficiency of the building and let in or out too much energy. This needs to be compensated for by indoor space cooling or heating, depending on the season. In particular, the need for cooling has increased dramatically in recent years. Chromogenic glazings—based on thermochromism or electrochromism—can regulate the inflow of visible light and solar energy between widely separated limits and hence achieve good energy efficiency [1]. Whereas electrochromic smart windows are beginning to appear on the market, the thermochromic option has so far been little used in practical applications. However, thermochromic smart windows have potential advantages in terms of simplicity of operation and have been intensively researched in recent years.

There are two types of thermochromic materials: inorganic and organic. The inorganic ones are transition metal compounds, but of those only vanadium dioxide, VO_2 , exhibits a switching temperature in the vicinity of room temperature [2]. The switching takes place in the near infrared (NIR) and infrared wavelength regions from a low temperature transmitting state to a high temperature reflecting state. There also exist a large number of organic polymer-based thermochromic materials [3]. In particular, the ligand-exchange systems may be promising for niche applications. They switch mainly in the visible wavelength range from a low-to-medium absorbing state to a highly absorbing



state as the temperature increases [3]. For completeness we mention also thermotropic materials [3], whose working principle is a temperature-dependent change of optical scattering.

In this paper we review recent developments in the field of inorganic thermochromic coatings with emphasis on doped vanadium dioxide coatings and VO_2 nanoparticles.

2. Optical properties of vanadium dioxide films and nanoparticles

Vanadium dioxide, VO_2 , is of particular interest since its optical properties change at a temperature that is not too far from room temperature [2]. Specifically, the switching in VO_2 occurs between a low-temperature phase with semiconducting properties and a high-temperature phase with metallic-like conductivity. The switching temperature is around 68°C and exhibits significant hysteresis. Vanadium dioxide has been attracting attention with regard to fundamental research as well as window applications for many years; see [4–6] and references therein.

A thin film of VO_2 exhibits a large NIR transmittance at low temperatures and a low transmittance at high temperatures, as illustrated in figure 1. The left-hand panels show spectral transmittance $T(\lambda)$ (upper) and reflectance $R(\lambda)$ (lower) for a 50-nm-thick VO_2 film in the wavelength range corresponding to solar radiation. It is clearly seen that $T(\lambda)$ is much larger in the semiconducting state than in the metallic state—*i.e.*, below and above the phase change temperature—for wavelengths $\lambda > 1\ \mu\text{m}$.

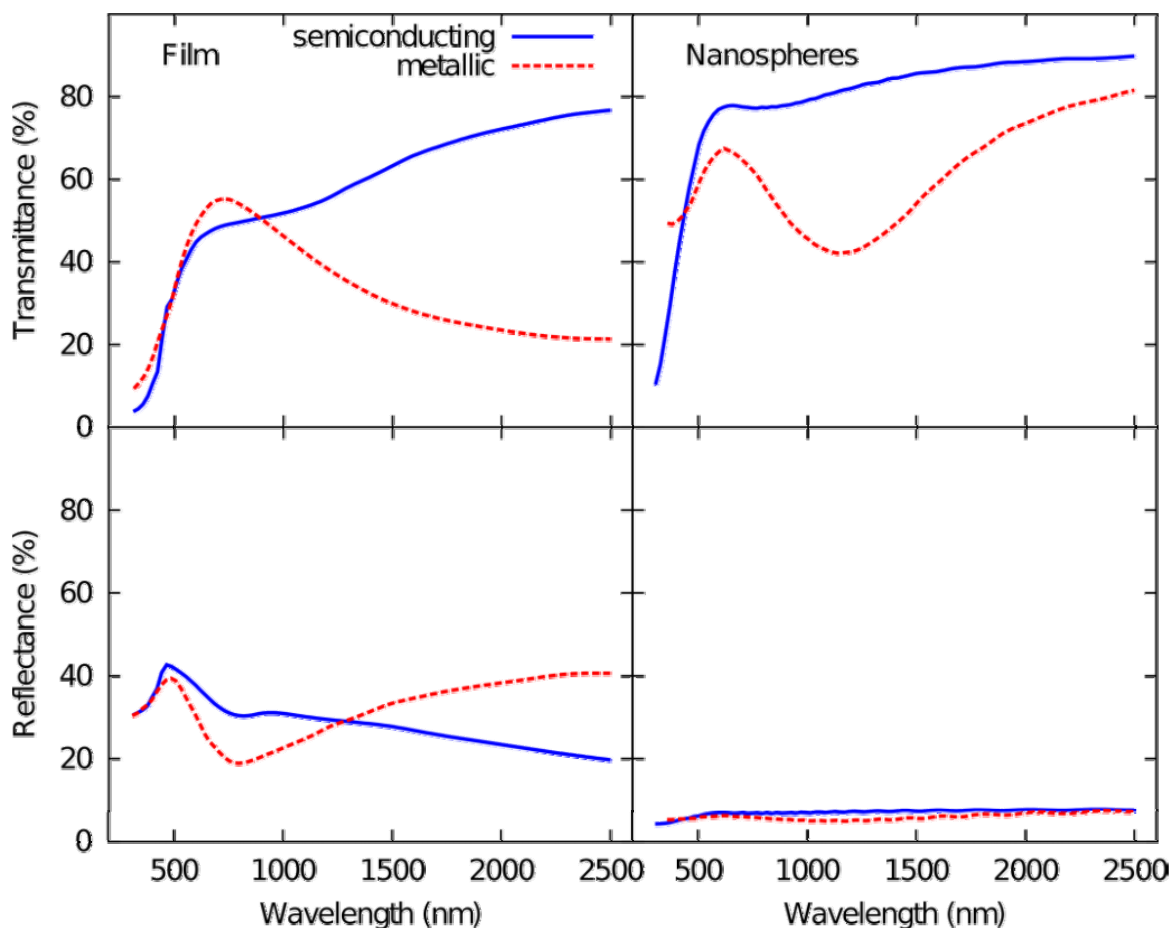


Figure 1. Spectral transmittance (upper panels) and reflectance (lower panels) for a sputter deposited 50-nm-thick thermochromic VO_2 film (left-hand panels) and as computed for a layer consisting of a dilute dispersion of VO_2 nanospheres, with an equivalent VO_2 thickness of 50 nm, in a medium mimicking typical transparent polymers (right-hand panels).

The difference in $T(\lambda)$ between low and high temperature grows with increasing wavelength. It is also observed that the change in reflectance is considerably lower. However, $R(\lambda)$ increases monotonically towards long wavelengths, as expected for a metallic state. Hence a glazing with a thermochromic VO_2 film lets in significantly more energy at low temperature than at high temperature [7].

The right-hand panels in figure 1 show the computed spectral transmittance and reflectance for a layer of VO_2 nanospheres in a matrix. The material was taken to be a 5- μm -thick layer of a transparent medium, with properties representative of typical polymers, containing 1 vol.% of well dispersed VO_2 nanospheres with diameters much less than any relevant wavelength. This choice of parameters gives an equivalent VO_2 thickness of 50 nm, which makes the data for the nanospheres and the film straightforward to compare. It is seen that the nanoparticle composite is less reflecting and more transmitting than an equivalent thin film having the same amount of VO_2 . In the metallic state, a pronounced absorption occurs around a wavelength of approximately 1200 nm. Hence the switching in the composite is from a low-temperature transmitting state to a high-temperature NIR absorbing state. The conduction band electrons in the metallic phase of VO_2 are confined within the nanoparticles and give rise to localized plasma resonance absorption. This is the physical reason for the thermochromism of VO_2 nanoparticles [8].

We now consider the implication of these properties for applications in energy-efficient fenestration. We can identify three major challenges for practical implementation of thin films of VO_2 on glazings [8]:

(i) The shift between the semiconducting and metallic states takes place at a switching temperature τ_c of about 68°C, which obviously is too high for buildings-related applications.

(ii) The visible transmittance is only about 40–50 %, which is too low for most practical window applications. Of course, a film thinner than 50 nm would be more transparent, but such films have a smaller change of the solar energy transmittance between the semiconducting and metallic states.

(iii) The transmittance switching is strong only for wavelengths far out in the NIR, at which the solar irradiation is quite weak. This limits the solar energy modulation to below 10%, which is too small to be of much practical interest.

Issue (i) is straightforward to resolve. Replacing a few per cent of the vanadium atoms with tungsten to make $\text{W}_x\text{V}_{1-x}\text{O}_2$ films can decrease the transition between the semiconducting and metallic states to room temperature as illustrated in figure 2 [9]. Doping with Mg gives a similar effect, but the drop of the transition temperature is smaller in this case.

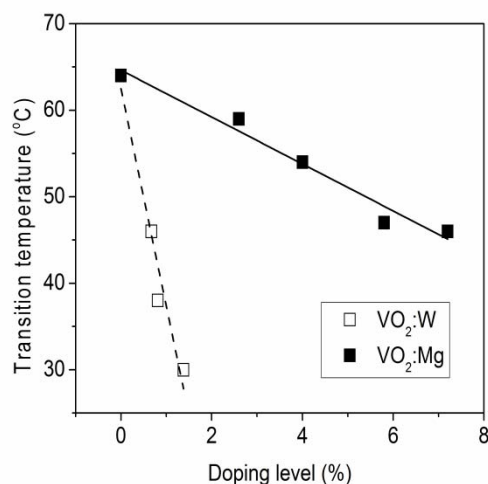


Figure 2. Temperature for the transition between semiconducting and metallic states in thermochromic thin films of $\text{W}_x\text{V}_{1-x}\text{O}_2$ and $\text{Mg}_y\text{V}_{1-y}\text{O}_2$, where x and y are referred to as “doping level” and lines were drawn for convenience. From [9].

Issue (ii) is associated with optical absorption at short wavelengths, which is clearly seen in figure 1. This absorption is due to the fact that VO₂ has a rather small optical band gap, of the order of 1.6 to 1.8 eV [10], between the *O2p* and π^* bands [11]. This band gap can be made larger by adding a dopant, for example magnesium. The addition of Mg displaces the transmittance edge at ~500 nm towards shorter wavelengths, but it also decreases the transmittance change between the semiconducting and metallic states at long wavelengths [9]. It was shown that the luminous transmittance goes from 39 to 51% when the Mg content is increased from zero to 7.2% [9]. The short wavelength transmittance shift is indeed due to a widening of the optical band gap, as clarified recently for Mg_yV_{1-y}O₂[10]. However, widening of the fundamental band gap does not completely solve the problem of low visible transmittance. Vanadium dioxide also exhibits a smaller band gap, of the order of 0.5 eV, between a split-off *Vd_{||}* band and the π^* band [11]. Electronic transitions between these two bands give rise to a low optical absorption in the wavelength range between the two band gaps, which ultimately limits the visible and NIR transmittance. However, it is seen in figure 1 that the material containing nanospheres is considerably more transparent than the corresponding film.

It can be realized from figure 1 that the limited modulation of the solar energy transmittance between the semiconducting and metallic states in VO₂ can be improved by using a layer containing VO₂ nanoparticles rather than a continuous VO₂ film. The optical switching takes place at shorter wavelengths in the nanocomposite than in the homogeneous film. The main part of the switching occurs between 700 and 1500 nm in the case of a nanocomposite, which is a region where the solar NIR radiation has an appreciable intensity. The localized plasma resonance is almost ideally located for solar control. Calculations have shown that the solar energy modulation can be increased up to 20% [12,13]. In addition, the particle size should be of the order of 20 nm or less in order not to produce too large optical scattering (“haze”) [14].

3. Experiments and calculations

3.1. Sample preparation and characterization

Thin films of Mg-doped and pure VO₂ were prepared on glass and carbon substrates by reactive DC magnetron sputtering in a deposition system based on a Balzers UTT 400 unit. Co-sputtering was performed from 5-cm-diameter targets of vanadium (99.5%) and Mg (99.9%) onto substrates kept at ~450 °C. More than forty samples were grown to thicknesses in the range 40 < *d* < 100 nm at a rate of ~0.06 nm/s.

The value of *d* was measured with a Bruker Dektak XT profilometer and was further confirmed with optical analysis.

The elemental compositions of samples deposited on carbon substrates were evaluated using Rutherford backscattering spectrometry (RBS) with 2 MeV ⁴He ions backscattered at an angle of 170°. Data were then extracted from analyses based on iterative least-square fitting to experimental spectra by use of the SIMNRA program [15]. More detailed information on the experimental procedures has been presented elsewhere [16].

Spectral and temperature-dependent normal transmittance *T*(λ, τ) and near-normal reflectance from the surface side *R_s*(λ, τ) and back side *R_b*(λ, τ) of the samples were measured using a single-beam spectrophotometer devised for absolute measurements and a Perkin–Elmer Lambda 900 double-beam spectrophotometer equipped with a BaSO₄-coated integrating sphere.

Data were recorded in the wavelength range 300 < λ < 2500 nm; measurements were performed at room temperature and ≈ 100 °C. Optical constants were obtained by simulating the complex dielectric functions $\epsilon = \epsilon_1 + i\epsilon_2$ with oscillator models and fitting the experimental data on *R_s*, *R_b* and *T* to calculated spectra using commercial software [17]. The optical constants for a large number of VO₂ and VO₂:Mg films were subsequently used to compute the performance limits of thermochromic thin films and nanoparticle composites, as detailed below.

3.2. Calculations of optical properties

Calculations based on Fresnel's equations [18] were used to derive $T(\lambda, \tau)$ for VO₂-based thin films with thicknesses $0 < d < 200$ nm and backed by glass plates characterized by a refractive index 1.5. The input data were the optical constants for all our samples.

In order to model the optical properties of nanocomposite layers, we must first obtain the effective dielectric function of the nanocomposite. The modelling considers VO₂ nanoparticles embedded in a polymer-like dielectric medium characterized by the dielectric constant $\epsilon_m = 2.25$ (refractive index 1.5). The optical properties of such a composite layer can be described with effective medium theory, assuming nanoparticle sizes that are much smaller than the wavelength. In the same manner as in earlier work [12], we derive an effective dielectric function ϵ^{MG} from Maxwell–Garnett theory [19] according to

$$\epsilon^{MG} = \epsilon_m \frac{1 + \frac{2}{3} f \alpha}{1 - \frac{1}{3} f \alpha} \quad , \quad (1)$$

where f represents the filling factor (*i.e.*, volume fraction) of VO₂ particles and is taken to be 0.01 for the dilute material of present interest. The parameter α is given for spherical particles by

$$\alpha = \frac{\epsilon_p - \epsilon_m}{\epsilon_m + \frac{1}{3}(\epsilon_p - \epsilon_m)} \quad , \quad (2)$$

where ϵ_p is the dielectric function of the VO₂ particles. Finally ϵ^{MG} for VO₂-polymer composites with different Mg contents was used as an input for computations of $T(\lambda, \tau)$ and $R(\lambda, \tau)$. These calculations used Fresnel's equations in the same way as for thin films. The layer thickness for the nanocomposites was varied in the 0 – 20 μ m range to enable comparison with data for films containing the same amount of VO₂-based material and shown above.

3.3. Performance criteria

The performance of VO₂ thin films and nanoparticle composite layers were characterized in terms of their wavelength-integrated luminous and solar transmittance. These properties were obtained from

$$T_{\text{lum, sol}}(\tau) = \int d\lambda \phi_{\text{lum, sol}}(\lambda) T(\lambda, \tau) / \int d\lambda \phi_{\text{lum, sol}}(\lambda) \quad , \quad (3)$$

Where ϕ_{lum} is the spectral sensitivity of the light-adapted human eye [20] and ϕ_{sol} is the solar irradiance spectrum for air mass 1.5 (the sun at 37° above the horizon) [21]. The thermochromic performance, and its relevance for energy efficient fenestration, was specified by T_{lum} for $\tau < \tau_c$ and $\tau > \tau_c$, T_{sol} for $\tau < \tau_c$ and $\tau > \tau_c$, and ΔT_{sol} defined by

$$\Delta T_{\text{sol}} \equiv T_{\text{sol}}(\tau < \tau_c) - T_{\text{sol}}(\tau > \tau_c). \quad (4)$$

In the following, we will primarily use the parameters T_{lum} and ΔT_{sol} to compare the performance of thermochromic thin films and nanocomposites.

4. Results and performance limits

Figures 3 and 4 display computed data on the luminous transmittance in the low-temperature semiconducting state and on ΔT_{sol} , respectively, as a function of Mg content. Data for VO₂:Mg thin films with thickness 50 nm and for VO₂: Mg nanocomposites having an equal amount of vanadium

based oxide are compared side-by-side. It is seen that the luminous transmittance is significantly higher for the nanocomposites than for the homogeneous films. An increase of T_{lum} due to the addition of Mg is observed for both films and nanocomposites. Qualitatively similar results were obtained for the metallic phase of VO_2 as well [16]. In addition, figure 4 shows that ΔT_{sol} is limited to approximately 0.07 for the VO_2 films but can reach as much as 0.2 for the nanocomposites. This parameter exhibits the highest values for pure VO_2 and is decreasing with increasing Mg content. Overall, the nanocomposites display much improved luminous transmittance and solar energy modulation as compared to homogeneous VO_2 thin films.

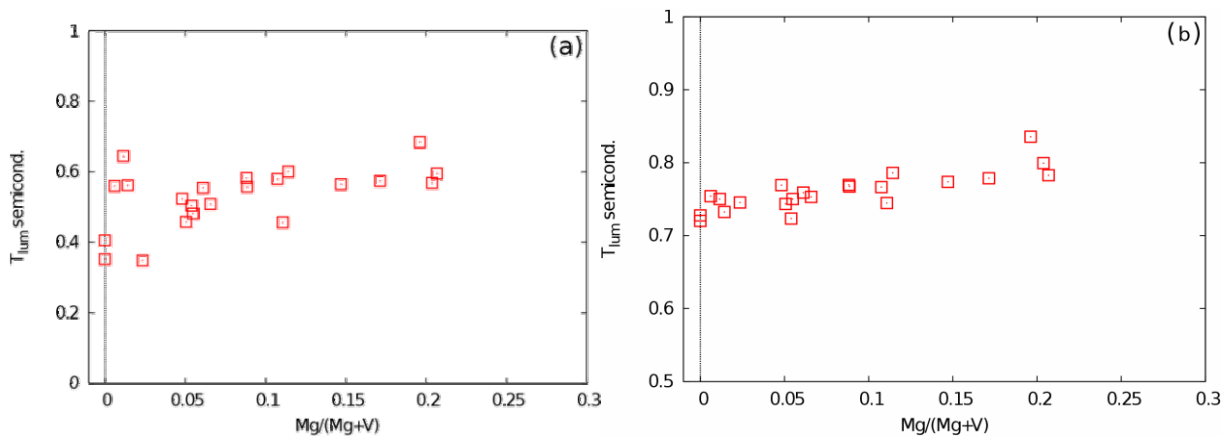


Figure 3. Luminous transmittance T_{lum} for 50-nm-thick films of undoped and Mg-doped thermochromic VO_2 (panel a) and for 5- μm -thick nanocomposite layers containing 1 vol.% of undoped and Mg-doped thermochromic VO_2 (panel b) as a function of Mg/(Mg+V) atom ratios. From [16].

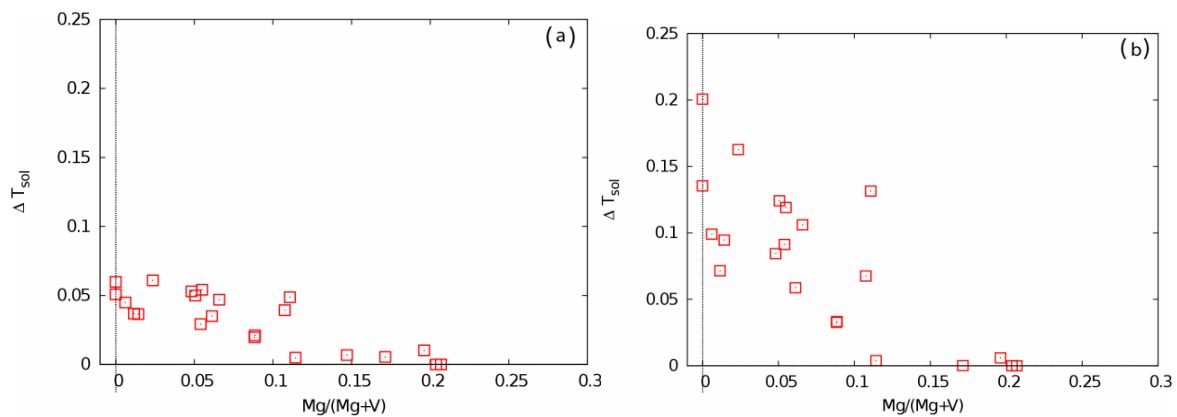


Figure 4. Solar energy transmittance modulation ΔT_{sol} for 50-nm-thick films of undoped and Mg-doped thermochromic VO_2 (panel a) and for 5- μm -thick nanocomposite layers containing 1 vol.% of undoped and Mg-doped thermochromic VO_2 (panel b) as a function of Mg/(Mg+V) atom ratios. From [16].

It is evident that various combinations of luminous transmittance and solar energy modulation can be accomplished in different VO_2 -based materials. Figure 5 (from ref. [16]) presents an overview over the current state-of-the-art. This figure is based on a much more detailed set of computations than those presented above, as well as on published experimental data. Pure VO_2 films give rather low

values for both T_{lum} and ΔT_{sol} , but the situation can be improved by antireflection (AR) coatings. Particularly good properties have been obtained with multilayers of TiO_2 and VO_2 [22, 23]. Mg-containing VO_2 films, especially those with a low amount of Mg, have superior properties, which can be boosted by antireflection. However, the best performance is achieved with VO_2 nanoparticles which, for example, can display $\sim 60\%$ luminous transmittance combined with more than 20% solar energy modulation. Interestingly, Mg-containing nanoparticles do not yield better performance than nanoparticles of pure VO_2 . The reason for this seems to be that the Mg partly decreases the solar modulation, as shown above, to an extent that is not compensated by the better transmittance at shorter wavelengths.

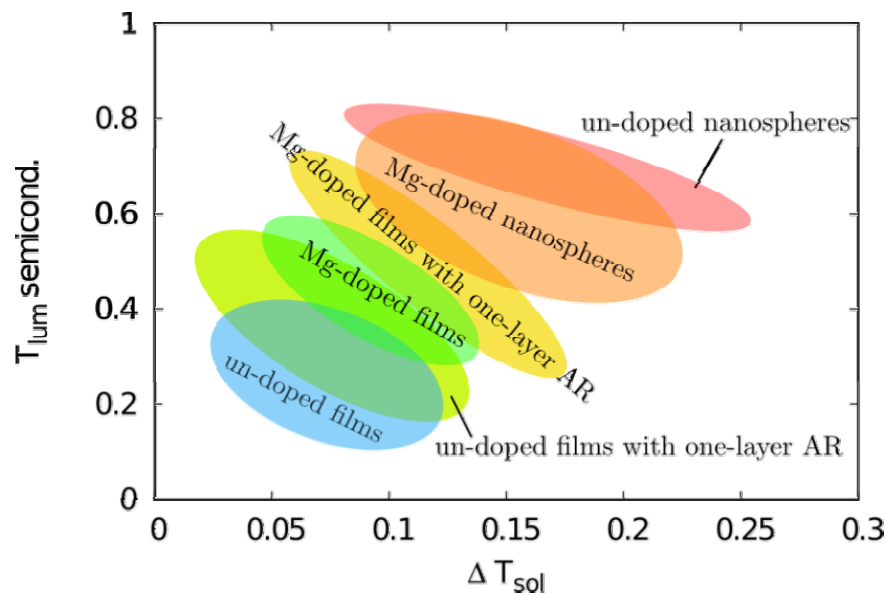


Figure 5. Schematic illustration of performance limits of the shown VO_2 -based materials with regard to window applications. Specifically shown are luminous transmittance T_{lum} for semiconducting films and particles, and solar energy transmittance modulation ΔT_{sol} for thin films—including antireflection (AR) coated ones—and dilute nanoparticle composites. From [16].

5. Conclusions

We have given a comprehensive review on thermochromic VO_2 -based materials with regard to applications in energy efficient windows. The optical constants of sputter deposited undoped and Mg-doped VO_2 films were used in model computations for optical properties of undoped and Mg-doped VO_2 films and dilute nanoparticle composite layers with different thicknesses. It was found from computational results that Mg-doped VO_2 films with $\text{Mg}/(\text{Mg} + \text{V}) < 0.06$ and judiciously chosen thicknesses can have much improved luminous transmittance and somewhat improved solar energy modulation compared to pure VO_2 films. Modelling of nanoparticle composites suggested that undoped VO_2 nanoparticles are more favourable than Mg-doped ones. The nanocomposites displayed superior values of both luminous transmittance and solar energy modulation and are of prime interest for applications in energy-efficient smart windows. The technological challenges related to the large-scale production of VO_2 -based nanocomposites are great, though. VO_2 nanoparticles can be produced by a variety of chemical and physical methods but they must be incorporated into a passivating matrix material to prevent oxidation of the particles. The possibility to produce VO_2 particles [24, 25] and composites [26] by sputtering is particularly interesting in this respect, since sputtering is a potentially upscalable technology.

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