A thermochromic low-emittance coating: Calculations for nanocomposites of In_2O_3:Sn and VO_2

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Calculations based on the Bruggeman effective medium theory were applied to thin films comprising a heavily doped wide band gap semiconductor (specifically In_2O_3:Sn (ITO)) and VO_2. Films with ~20 vol. % of VO_2 can combine a 10% thermochromic modulation of the solar energy throughput with a luminous transmittance of 50%–60% and low thermal emittance. The maximum thermochromic modulation is ~13% and occurs at ~35 vol. % VO_2. Coatings of ITO-VO_2 are of interest for energy efficient fenestration. © *2011 American Institute of Physics*. [doi:10.1063/1.3641869]

This letter presents calculations to show that it is possible to devise coatings that combine high luminous transmittance with low thermal emittance—as required for having minimum heat transfer between two glass panes—and a temperature-dependent modulation of the solar energy throughput. The latter functionality is accomplished through VO_2 nanoparticles and hence builds on our prior work on "nanothermochromics."[1,2]

An energy efficient window should incorporate at least two panes and have a minimum of thermal transfer between them. For uncoated glass, about half of the heat is transferred between the panes by radiation while the rest occurs by gas conduction and convection.[3] The radiative component can be minimized by a transparent low-emittance coating, and one of the most widely used types of materials for this purpose is based on heavily doped wide band gap semiconductors.[3] In a practical case, the materials are SnO_2:F, In_2O_3:Sn (i.e., indium tin oxide, known as ITO), or ZnO:Al.[3] These materials combine superior luminous transmittance T_{lum} in the $0.4 < \lambda < 0.7$ μm wavelength range with moderately low thermal emittance E_{therm} for $3 < \lambda < 50$ μm.

The near-infrared interval, at $0.7 < \lambda < 3$ μm, carries about half of the solar energy and, ideally, should be transmitted into a building if there is a heating demand, whereas it should be reflected if there is a need for space cooling. Thermochromism offers possibilities to do this, and VO_2 is a thermochromic material whose potential for energy efficient fenestration has been discussed for decades.[3,4] In the bulk, it is monoclinic and insulating for $\tau < \tau_c$ and is tetragonal and metallic-like at $\tau > \tau_c$, where τ denotes temperature and $\tau_c \approx 68\,°C$.[5] In order to be of practical interest for windows, it is necessary to decrease τ_c to the vicinity of room temperature, to maintain a high enough T_{lum}, and to have a sufficiently large drop of the solar energy transmittance, denoted ΔT_{sol}, at τ_c. The first requirement can be met by doping, most effectively by tungsten.[6] The latter two requirements have been problematical for many years, but recent work of ours[1] has demonstrated by computation that a VO_2-based material consisting of nanoparticles, rather than being a thin film, boosts both T_{lum} and ΔT_{sol} and makes thermochromic fenestration a much more likely proposition than before.

Coatings combining low thermal emittance, irrespectively of the temperature, and thermochromism have only rarely been discussed in the past. However, recent work by Kang *et al.* showed data on VO_2 films with a top layer of extremely thin Pt (Ref. 7) or ZnO:Al.[8] The best films of this kind showed a modest combination of $T_{\text{lum}} \approx 46\%$, $\Delta T_{\text{sol}} \approx 4\%$, and $E_{\text{therm}} \approx 0.3$. In this present work, we take another, and in our view better, approach and investigate a heavily doped wide band gap semiconductor incorporating VO_2 nanoparticles. Specifically, we use ITO, which has an unsurpassed combination of high T_{lum} and low E_{therm} among the doped wide band gap oxides.[3]

Our calculations consider a random mixture of nanoparticles comprised of VO_2 and ITO. The structural units are taken to be spherical and much less than λ so that an effective medium model applies for the average optical properties. Assuming that the VO_2 and ITO units are topologically equivalent, it is appropriate to employ the Bruggeman theory[9,10] to get the effective dielectric function, denoted ε^{BR}, from

$$f\,\frac{\varepsilon_{VO_2} - \varepsilon^{BR}}{\varepsilon_{VO_2} + 2\varepsilon^{BR}} + (1-f)\,\frac{\varepsilon_{ITO} - \varepsilon^{BR}}{\varepsilon_{ITO} + 2\varepsilon^{BR}} = 0, \qquad (1)$$

where ε_{VO2} and ε_{ITO} are the dielectric functions of the two components and f is the "filling factor" (i.e., volume fraction) of VO_2. It should be noted that the Bruggeman theory allows us to include optical effects of the percolation threshold in our computations.

We used $\varepsilon_{VO2}(\lambda,\tau) \equiv \varepsilon_{VO2,1}(\lambda,\tau) + i\varepsilon_{VO2,2}(\lambda,\tau)$ from previous work on reactively sputter deposited 50-nm-thick VO_2 films.[11] These data are taken to be independent of particle size since the mean free paths of the electrons present for $\tau > \tau_c$ are comparable with interatomic distances,[12,13] implying that VO_2 can be described as a "bad metal" above τ_c.[14] For ITO, we used $\varepsilon_{ITO}(\lambda) \equiv \varepsilon_{ITO,1}(\lambda) + i\varepsilon_{ITO,2}(\lambda)$ based on measurements on high-quality films prepared by reactive *e*-beam evaporation.[15] No dependence on particle size was invoked that is justified by the fact that the mean free path of the free electrons in high-quality ITO, which is governed by

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ionized impurity scattering in the infrared, is as short as ~5 nm (while it increases progressively towards shorter wavelengths).[15]

Spectral and temperature dependent-transmittance $T(\lambda,\tau)$ and reflectance $R(\lambda,\tau)$ were computed from $\varepsilon^{BR}(\lambda,\tau)$ at $300 < \lambda < 2500$ nm using standard formulas[16] for thin film optics of a single layer on a glass substrate. Figure 1 shows data for composites of VO_2 and ITO in which the ITO mass thickness was kept constant at 200 nm and the VO_2 mass thickness was varied so that the composite attained the shown values of f, ranging from 0.1 to 0.5. Clear evidence for thermochromism is seen in $T(\lambda,\tau)$ and $R(\lambda,\tau)$ irrespectively of the wavelength. It is found that $R(\lambda,\tau)$ increases monotonically for $\lambda > 1$ μm and reaches ~60% at $\lambda = 2.5$ μm when the VO_2 phase is metallic. The data for $\tau < \tau_c$ and for films with low filling factors are fully consistent with earlier evaluations of the spectral reflectance for 200-nm-thick ITO films;[15] the latter films yielded $E_{\text{therm}} \approx 0.2$. An addition of VO_2 clearly makes E_{therm} larger, but the composite films nevertheless can serve as low-emittance coatings especially for the lower VO_2 fractions.

Wavelength-integrated luminous (lum) and solar (sol) transmittance—denoted $T_{\text{lum}}(\tau)$ and $T_{\text{sol}}(\tau)$, respectively—were derived from

$$T_{\text{lum,sol}}(\tau) = \int d\lambda\, \varphi_{\text{lum,sol}}(\lambda) T(\lambda,\tau) \Big/ \int d\lambda\, \varphi_{\text{lum,sol}}(\lambda), \qquad (2)$$

where φ_{lum} is the spectral sensitivity of the light-adapted human eye[17] and ϕ_{sol} is the solar irradiance spectrum for air mass 1.5 (the sun at 37° above the horizon).[18] The modulation of the solar energy transmittance is of particular relevance for energy assessments; it is defined by

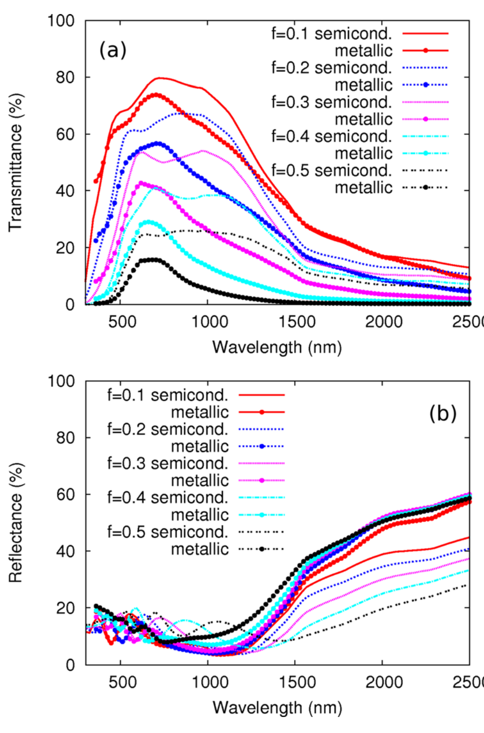

FIG. 1. (Color online) Spectral transmittance (a) and reflectance (b) computed for ITO-VO_2 composites as discussed in the main text. The VO_2 volume fraction is denoted f. Results are shown for $\tau < \tau_c$ (semiconducting VO_2) and for $\tau > \tau_c$ (metallic VO_2).

$$\Delta T_{\text{sol}} = T_{\text{sol}}(\tau < \tau_c) - T_{\text{sol}}(\tau > \tau_c). \qquad (3)$$

Figure 2 illustrates T_{lum} and T_{sol} for $\tau < \tau_c$ and $\tau > \tau_c$ as well as ΔT_{sol} as a function of the VO_2 fraction from spectral data of the kind shown in Fig. 1. Expectedly, T_{lum} and T_{sol} decrease progressively when f is increased. The integrated transmittance is higher for $\tau < \tau_c$ than for $\tau > \tau_c$; the differences are rather similar for T_{lum} and for T_{sol}, which indicates that the thermochromism is not confined to the near infrared but takes place in the entire solar range. It is inferred that $\Delta T_{\text{sol}} = 10\%$ occurs for $f \approx 0.196$ and is compatible with $T_{\text{lum}} \approx 59.7\%$ at $\tau < \tau_c$ and $T_{\text{lum}} \approx 51.1\%$ at $\tau > \tau_c$. ΔT_{sol} displays a broad maximum of ~12.8% for $f \approx 0.35$, which is close to the value where the VO_2 units start to percolate in the Bruggeman model.[3]

The main result of this study is to show by computation that luminous transmittance, low thermal emittance, and a substantial thermochromic modulation of the solar energy throughput are compatible in films comprising a mixture of a heavily doped wide band gap semiconductor and a

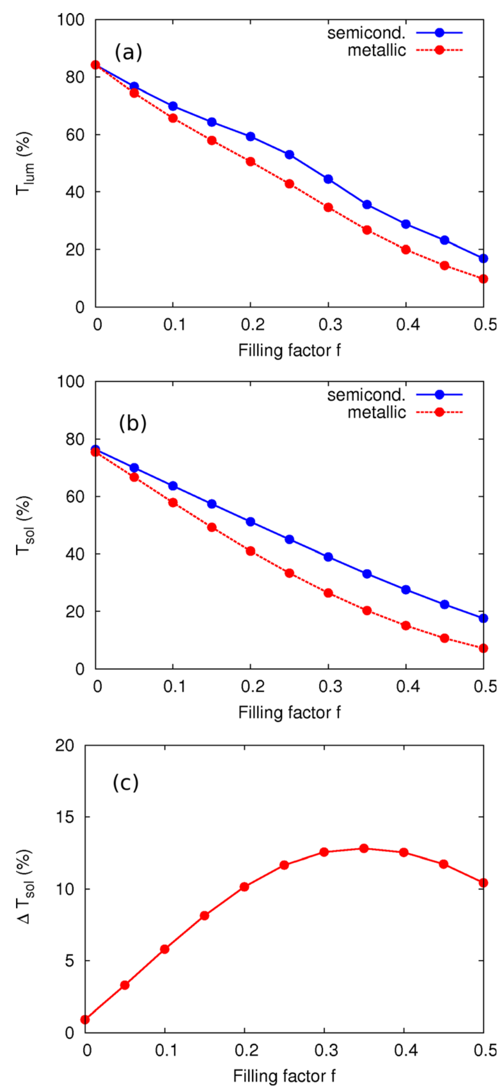

FIG. 2. (Color online) Wavelength-integrated luminous (a) and solar (b) transmittance, and thermochromic modulation of the solar energy throughput (c), computed as a function of the VO_2 fraction f for ITO-VO_2 composites. Results are shown for $\tau < \tau_c$ (semiconducting VO_2) and for $\tau > \tau_c$ (metallic VO_2). Circles indicate the data and connecting lines were drawn for convenience.

thermochromic VO_2-based material. Using $W_xV_{1-x}O_2$ (Ref. 6) or $Mg_yV_{1-y}O_2$,[19] rather than pure VO_2, can decrease τ_c and, for the case of Mg doping, also increase T_{lum}. Practical realizations of ITO-VO_2 composite films were demonstrated through very recent work[20] in which polyvanadates were combined with solution-derived ITO nanoparticles; however, the thermochromism of such films has not yet been reported.

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[1]S.-Y. Li, G. A. Niklasson, and C. G. Granqvist, J. Appl. Phys. **108**, 063525 (2010).
[2]S.-Y. Li, G. A. Niklasson, and C. G. Granqvist, J. Appl. Phys. **109**, 113515 (2011).
[3]G. B. Smith and C. G. Granqvist, *Green Nanotechnology: Solutions for Sustainability and Energy in the Built Environment* (CRC, Boca Raton, FL, 2010).
[4]C. G. Granqvist, Sol. Energy Mater. Sol. Cells **91**, 1529 (2007).
[5]F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).
[6]J. B. Goodenough, J. Solid State Chem. **3**, 490 (1971).
[7]L. Kang, Y. Gao, Z. Chen, J. Du, Z. Zhang, and H. Luo, Sol. Energy Mater. Sol. Cells **94**, 2078 (2010).
[8]L. Kang, Y. Gao, H. Luo, J. Wang, B. Zhu, Z. Zhang, J. Du, M. Kanehira, and Y. Zhang, "Thermochromic properties and low emissivity of ZnO:Al/VO_2 double-layered films with a lowered phase transition temperature," Sol. Energy Mater. Sol. Cells (in press), doi: 10.1016/j.solmat.2011.06.047.
[9]D. A. G. Bruggeman, Ann. Phys. **24**, 636 (1935).
[10]G. A. Niklasson, C. G. Granqvist, and O. Hunderi, Appl. Opt. **20**, 26 (1981).
[11]N. R. Mlyuka, G. A. Niklasson, and C. G. Granqvist, Phys. Status Solidi A **206**, 2155 (2009); the optical constants for VO_2 are expected to be weakly thickness dependent, but the effect is not a dramatic one as evidenced from the fact that τ_c was 63 °C in 2-nm-thick films and 68 °C at 50 nm [J. Ma, G. Xu, L. Miao, M. Tazawa, and S. Tanemura, Jpn. J. Appl. Phys. **50**, 020215 (2011)].
[12]K. Okazaki, S. Sugai, Y. Muraoka, and Z. Hiroi, Phys. Rev. B **73**, 165166 (2006).
[13]A. Gentle, A. I. Maaroof, and G. B. Smith, Nanotechnology **18**, 025202 (2007).
[14]M. M. Qazilbash, K. S. Burch, D. Whisler, D. Shrekenhamer, B. G. Chae, H. T. Kim, and D. N. Basov, Phys. Rev. B **74**, 205118 (2006).
[15]I. Hamberg and C. G. Granqvist, J. Appl. Phys. **60**, R123 (1986). Data on $\varepsilon_{ITO}(\lambda)$ are given in that paper for films with different values of the electron density n_e; specifically, we used results for $n_e = 6.2 \times 10^{20}$ cm^{-3} (Fig. 21) which, for the computations presented in this letter, are indistinguishable from the results for n_e being 7.5 to 8×10^{20} cm^{-3} (Fig. 22).
[16]M. Born and E. Wolf, *Principles of Optics*, 7th ed. (Cambridge University Press, Cambridge, UK, 1999).
[17]G. Wyszecki and W. S. Stiles, *Color Science: Concepts and Methods, Quantitative Data and Formulae*, 2nd ed. (Wiley, New York, 2000).
[18]ASTM G173-03: Standard Tables of Reference, Solar Spectral Irradiances: Direct Normal and Hemispherical on a 37° Tilted Surface, *Annual Book of ASTM Standards* (American Society for Testing and Materials, Philadelphia, PA, USA, 2008), Vol. 14.04, available at http://rredc.nrel.gov/solar/spectra/am1.5.
[19]N. R. Mlyuka, G. A. Niklasson, and C. G. Granqvist, Appl. Phys. Lett. **95**, 171909 (2009).
[20]A. Llordes, A. T. Hammack, R. Buonsanti, R. Tangirala, S. Aloni, B. A. Helms, and D. J. Milliron, J. Mater. Chem. **21**, 11631 (2011).