Mg doping of thermochromic VO_2 films enhances the optical transmittance and decreases the metal-insulator transition temperature

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Thermochromic films of $Mg_xV_{1-x}O_2$ were made by reactive dc magnetron sputtering onto heated glass. The metal-insulator transition temperature decreased by ~3 K/at. %Mg, while the optical transmittance increased concomitantly. Specifically, the transmittance of visible light and of solar radiation was enhanced by ~10% when the Mg content was ~7 at. %. Our results point at the usefulness of these films for energy efficient fenestration. © *2009 American Institute of Physics*. [doi:10.1063/1.3229949]

Thermochromic VO_2 films transmit more solar radiation below a "critical" temperature τ_c than above this temperature. As shown in this letter, Mg doping of VO_2 enhances the luminous transmittance T_{lum} and lowers τ_c, thus demonstrating that such films are interesting for windows of energy efficient buildings.

Worldwide, 30%–40% of all primary energy is used in buildings, and well insulated envelopes as well as radiation control of window apertures are keys to energy efficiency and associated CO_2 abatement.[1] Optimized radiation control requires chromogenic materials,[2] and thermochromic coatings are interesting options either for stand-alone uses, because a single coating can be applied, or for boosting the performance of electrochromic "smart windows."[3]

VO_2 is a well studied thermochromic material.[4] Bulk VO_2 is monoclinic and insulating at $\tau < \tau_c$ and is tetragonal and metallic at $\tau > \tau_c$, where τ is temperature and $\tau_c \approx 68$ °C.[5] The nature of the metal-insulator transition (MIT) has been much debated, but recent work indicates a Mott transition.[6–8] Doped bulk oxides, denoted $M_xV_{1-x}O_2$, can have lowered τ_c (with M being W^{6+}, Mo^{6+}, Ta^{5+}, Nb^{5+}, and Ru^{4+}) or increased τ_c (with M being Ge^{4+}, Al^{3+}, and Ga^{3+}).[9] Dopants with a valency 2+, such as Mg^{2+}, apparently have not been investigated before.

$M_xV_{1-x}O_2$ films have shifted τ_c, as in the bulk, but the transition temperatures are also influenced by thickness and stress.[10,11] There has been much recent work on $W_xV_{1-x}O_2$ focused on films made by techniques suitable for large area depositions such as reactive dc magnetron sputtering,[12] chemical vapor deposition,[13,14] and sol-gel deposition.[15] It has been found that a few percent of W can decrease τ_c to 20 to 25 °C, i.e., to a comfort temperature suitable for practical fenestration. However, the requirement of a high relative modulation of the transmittance at τ_c has invariably limited T_{lum} to <40%, which in general is too low.[4]

Our $Mg_xV_{1-x}O_2$ films were made by reactive dc magnetron sputtering onto substrates of glass (and simultaneously onto carbon plates for compositional analysis) from 5-cm-diameter targets of V (99.5%) and Mg (99.99%). After evacuation to 0.4 mTorr, Ar and O_2 (both 99.997%) were introduced via mass-flow-controlled regulators so that the Ar/O_2 ratio was ~19 and the total pressure was ~92 m Torr. Cosputtering took place at powers being 210 W and 0–29 W for the V and Mg targets, respectively. The substrates were kept at 450 °C, and the target-substrate separation was 13 cm. Deposition rates, via sputtering time and thickness d by surface profilometry, were 0.083 nm/s from V and 0–0.008 nm/s from Mg.

Spectral normal transmittance $T(\lambda,\tau)$ was measured for 300 nm $< \lambda <$ 2500 nm and 20 °C $< \tau <$ 120 °C as described before.[11] Figure 1(a) refers to VO_2 and $Mg_{0.072}V_{0.928}O_2$ films with $d = 50 \pm 5$ nm. The VO_2 film displays expected thermochromism.[4,11] Importantly, Mg doping yields a significantly larger value of $T(\lambda,\tau)$ for $\lambda < 600$ nm at both temperatures. Quantitative enhancements were evalu-

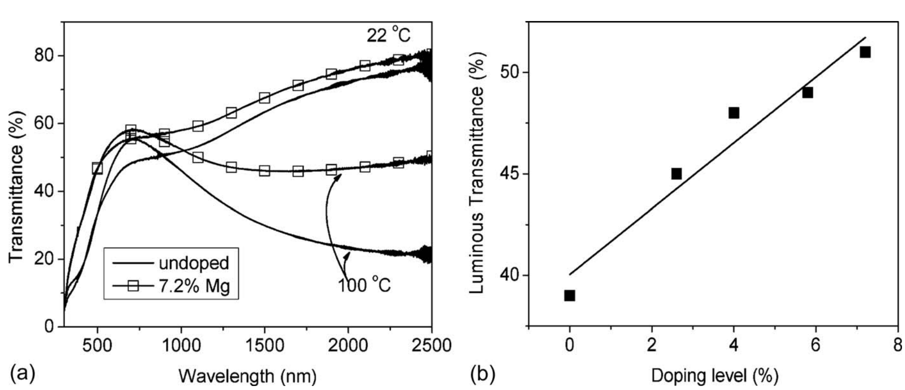

FIG. 1. Spectrophotometric transmittance at two temperatures (a) and T_{lum} vs x at room temperature (b) for 50-nm-thick $Mg_xV_{1-x}O_2$ films. The line in the latter panel is solely to guide the eye.

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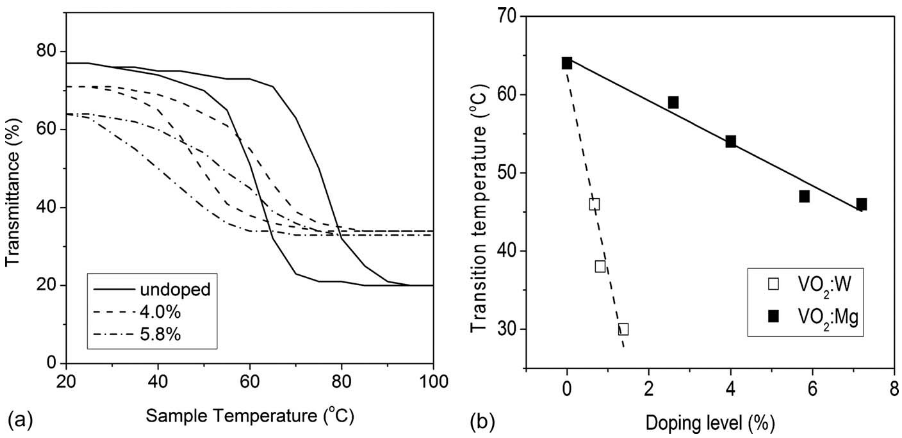

FIG. 2. Transmittance at $\lambda = 2300$ nm vs temperature (a) and τ_c vs x (b) for 50-nm-thick VO_2 and $Mg_xV_{1-x}O_2$ films. The latter panel also contains data for $W_xV_{1-x}O_2$ films; the lines are solely to guide the eye.

ated for the luminous (lum) and solar (sol) transmittance, defined by

$$T_{\text{lum,sol}}(\tau) = \int d\lambda \varphi_{\text{lum,sol}}(\lambda) T(\lambda,\tau) \Big/ \int d\lambda \varphi_{\text{lum,sol}}(\lambda), \quad (1)$$

where φ_{lum} is the spectral sensitivity of the light-adapted eye[16] and φ_{sol} is the solar irradiance spectrum for air mass 1.5 corresponding to the sun standing 37° above the horizon.[17] The spectral ranges used in the evaluations were 385 nm $< \lambda <$ 760 nm and 300 nm $< \lambda <$ 2500 nm for T_{lum} and T_{sol}, respectively. Figure 1(b) shows, for $\tau < \tau_c$, that the T_{lum} increases from 39% to ~51% when x goes from 0 to 7.2 at. %Mg. Corresponding T_{lum} for $\tau > \tau_c$ lay between 43% and ~52%, and corresponding T_{sol} for $\tau < \tau_c$ and $\tau > \tau_c$ lay between 45% and ~54% and between 41% and ~50%, respectively.

We inferred τ_c from $T(\lambda,\tau)$ at $\lambda = 2300$ nm. Figure 2(a) shows data for films of VO_2, $Mg_{0.040}V_{0.960}O_2$, and $Mg_{0.058}V_{0.942}O_2$, taken for temperatures increasing and decreasing by ~10 °C/min. The MIT is hysteretic and shifted toward lower temperatures when x is increased; the transmittance change then became less pronounced, whereas the width of the transition remained rather unchanged. Taking $\tau_c = (\tau_{c1} + \tau_{c2})/2$, where 1 (2) refers to increasing (decreasing) temperature, at half of the transmittance change one obtains the data in Fig. 2(b). Clearly τ_c decreases linearly by ~3 K/at. %Mg. This can be compared with our data for $W_xV_{1-x}O_2$ for which τ_c drops by ~25 K/at. %W.[18] Our data are not accurate enough to tell whether the decreases in τ_c are strictly proportional to the doping content.

Structural characterizations were made by x-ray diffraction (XRD). Figure 3 displays results for films of 50-nm-thick VO_2 and 100-nm-thick $Mg_{0.058}V_{0.942}O_2$ at $\tau = 22$ °C. The former film shows multiple diffraction peaks consistent with monoclinic VO_2. The $Mg_{0.058}V_{0.942}O_2$ film has a less distinct XRD pattern, but the features—excepting the tiny peak at $2\Theta \approx 18°$—agree with a monoclinic structure as might be expected from data in the literature.[19]

Elemental compositions were inferred from Rutherford backscattering spectrometry (RBS) and x-ray photoemission spectroscopy (XPS). Figure 4(a) shows RBS data for a $Mg_xV_{1-x}O_2$ film backed by carbon from which $x = 0.058 \pm 0.015$ was obtained from a simulation routine based on the SIMNRA program[20] which iteratively produces a least-squares fit to the experimental spectrum subject to ion scattering and energy loss equations (indicated by the curve). The absolute errors are significant because of the low signal-to-background ratio of the Mg feature. However, relative errors are much smaller, and therefore the trends seen in Fig. 1(b) and Fig. 2(b) are well established. The RBS data also verified that the O/V atom ratio was 2 to within simulation errors and gave unambiguous evidence for Mg, Ar, and Si, as well as for C ensuing from the substrate. A small peak is due to Ar, presumably incorporated during film growth via sputtering, and there is also some contribution—of unknown origin—due to Si.

Consistent compositional data for $Mg_xV_{1-x}O_2$ films on glass, shown in Fig. 4(b), were obtained from XPS and displays the Mg 2s feature whose intensity grows in proportion to x.

Summarizing, we have shown that $Mg_xV_{1-x}O_2$ films displayed thermochromism with a luminous transmittance that went up by ~10% and a metal-insulator transition temperature that dropped to ~45 °C in proportion to x as this parameter increased from zero to 0.07. Mg is the first dopant with this combined effect on VO_2, and our work hence makes thermochromic window coatings a more viable alternative for energy efficient fenestration than with previously known materials. The lowered luminous absorption makes it very interesting to make multilayer films of the type $D/Mg_xV_{1-x}O_2/D$ and $D/Mg_xV_{1-x}O_2/D/Mg_xV_{1-x}O_2/D$, where D is a dielectric material, in order to create induced transmittance as well as favorable angular properties; films of the latter type—though with $x=0$—have been investigated recently.[21] Finally, we note that Mg doping is capable of increasing the transmittance also in electrochromic Ni-oxide-

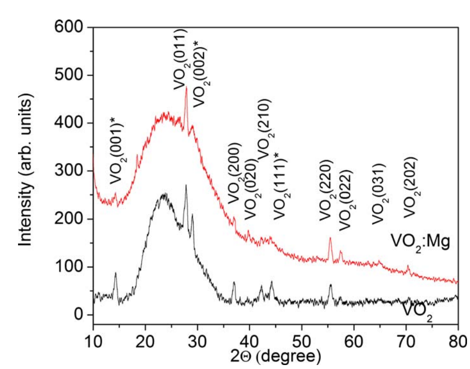

FIG. 3. (Color online) XRD data for $Mg_xV_{1-x}O_2$ films with $x=0$ and $x = 5.8$ at. %. The peaks are designated by the pertinent crystallographic planes as obtained from Refs. 27 and 28 (an asterisk designates data from the latter file). The broad peak at a diffraction angle $2\Theta \approx 23°$ originates from the glass substrate.

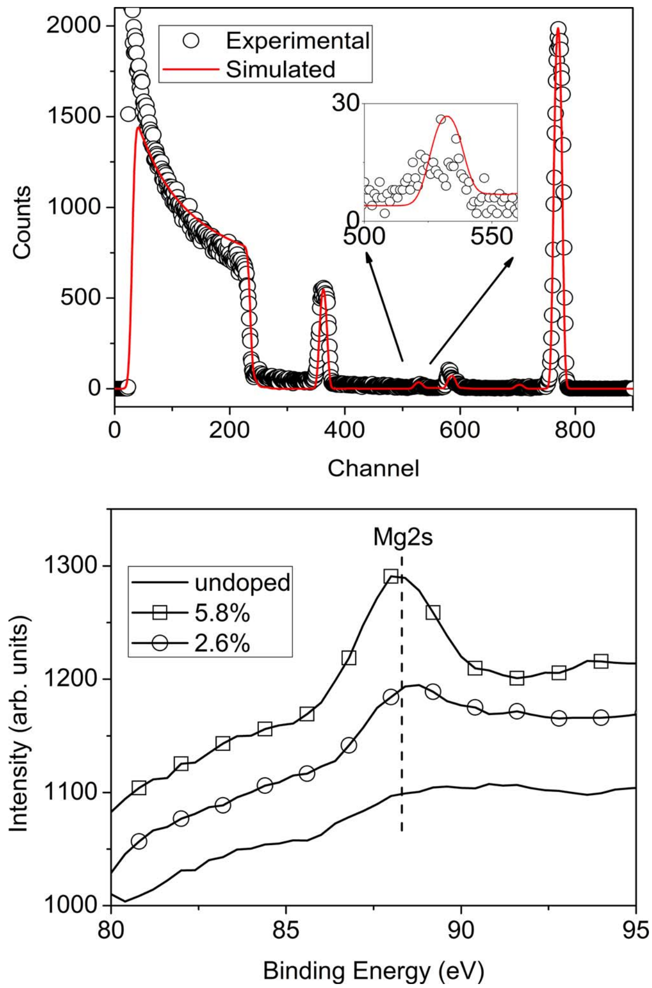

FIG. 4. (Color online) Data from RBS (a) and XPS (b) for 50-nm-thick $Mg_xV_{1-x}O_2$ films. The RBS results, taken at the Uppsala University Tandem Laboratory, are denoted by circles and model results are indicated by the curve. The film contains the shown elements and the part showing the Mg feature is magnified. XPS data were recorded with a SCIENTA ESCA 300 spectrometer.

based films[22] and in ZnO films and nanoparticles.[23–25] Band-gap widening in $Mg_xZn_{1-x}O$ has been modeled recently in *ab initio* calculations[26] and it is conceivable that a similar approach can account for $Mg_xV_{1-x}O_2$.

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