Effects of Aluminium and Tungsten Co-Doping on the Optical Properties of VO$_2$ Based Thin Films

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Abstract

Aluminium and tungsten co-doped vanadium dioxide (VO$_2$:W:Al) thin films were deposited by DC reactive magnetron sputtering technique. In this work we report on the effects of aluminium and tungsten co–doping on the optical properties of vanadium dioxide (VO$_2$) based thin films with a view of combining both increased luminous transmittance (T$_{lum}$) and lowered transition temperature ($\tau_c$). The effect of aluminium and tungsten co-doping on semiconductor-metal transition of vanadium dioxide films was investigated and compared with tungsten doped and undopedVO$_2$-films. Spectral transmittances of the films were obtained using Shimadzu SolidSpec-3700 DUV UV-VIS-NIR spectrophotometer. The results revealed that the transmittance of tungsten and aluminium co–doped vanadium dioxide using two Al pellets showed a peak at about 54% in the visible spectral range with fairly good switching characteristics and a transition temperature of 61 °C.

Keywords: Transition temperature, luminous transmittance, tungsten-aluminium co-doping, vanadium dioxide

Introduction

The excessive use of heating systems on cold climate and air conditioning systems in warm climate results in extensive use of electricity in order to maintain such systems. This situation calls for new technologies for energy generation and energy conservation in industry, transportation and building sectors. The building sector is of particular importance, since according to comprehensive study by the United Nations Environment Programme, it accounts for 30 to 40% of the primary energy used in the world (UNEP 2007). This energy is spent mainly on heating, cooling, lighting and ventilation.

Energy efficiency fenestration materials and devices have the potential to decrease the energy expenditure in buildings (Granqvist 1990, Lampert and Granqvist 1990). Chromogenic materials are of much interest for energy saving as they are able to change their optical and electrical properties when subjected to a change in environment (temperature, light, pressure, etc.) (Greenberg 1983, Jin and Tanemura 1994, Granqvist et al. 2010). The most important chromogenic materials are electrochromic, photochromic and thermochromic. Electrochromic materials are the ones which when incorporated in multi-layer devices are able to vary the optical properties by electrical charging and discharging. Photochromic materials are the ones colouring under light irradiation and bleaching in the dark. Materials whose optical, electrical and structural properties depend on temperature are called thermochromic materials (Lampert and
Vanadium dioxide (VO₂) has held the attention of researchers since 1959, when F. J. Morin first observed its remarkable metal-to-insulator transition upon cooling or heating through a critical temperature τc of ≈ 68 °C (Morin 1959). VO₂ is technologically important due to its ability to undergo a reversible metal-to-semiconductor phase transition. The conversion of the low temperature monoclinic phase VO₂ to the high temperature rutile phase VO₂ is associated with changes in electrical conductivity and optical properties especially in the near-infrared region (Morin 1959, Verleur et al. 1968, Rogers 1993). The VO₂ is semiconductor and infrared transparent at room temperature, but above τc VO₂ becomes metallic and infrared reflecting (Chain 1991, Livage 1999, Msomi and Nemraoui 2010). Vanadium dioxide thin films have been revealed from many studies as one of the potential materials for fabrication of practical smart windows (Kivaisi, and Samiji 1999, Mlyuka 2003, Mlyuka 2010). So far, all these investigations did not result in producing VO₂ films which sufficiently accomplish the demand for practical applications, particularly, demand for high transmittance in the visible spectral range and a transition temperature near room temperature. The challenge would be overcome if the thermochromic properties of doped VO₂ thin films, namely, optical, electrical and structural are improved. The τc of VO₂ films have been reported to be lowered by several techniques such as tungsten (W), molybdenum (Mo), niobium (Nb) or rhenium (Re) doping or by introduction of stress (Kato et al. 2001), but these dopants showed lowered optical contrast (Sobhan 1996, Béteille and Livage 1998). Doping with elements known to form wide band gap oxides, e.g., Mg, Al and Ti, could yield improved transmittance (Mlyuka 2010, Soltani et al 2004, Gentle and Smith 2007). This paper reports the recent results on determining the combined effects of Al and W co-doping of VO₂ thin films geared to obtain both improved luminous transmittance and lowered transition temperature.

**Materials and Methods**

Thin films of VO₂, tungsten doped vanadium dioxide (VO₂:W) and aluminium and tungsten co-doped vanadium dioxide (VO₂:W:Al) were deposited by DC reactive magnetron sputtering in an argon/oxygen atmosphere using Balzers BAE 250 coating unit. The films were made from metallic targets of V, V-W alloy and V-W alloy stuck with aluminium pellets. V target was 99.9% pure, 5.1 cm in diameter and 0.6 cm thick. The alloy target had percentage composition of 99% vanadium and 1% tungsten. Prior to film deposition the sputtering chamber was evacuated down to a base pressure of ≈ 3 × 10⁻⁶ mbar. The substrates in the chamber were heated to a temperature of about 450 °C before introducing sputtering gas (Ar, 99.999% purity) and reactive gas (O₂, 99.9% purity) into the chamber at the rates of 75 and 6.6 – 7.2 ml/min, respectively. The optimum oxygen rate was 7.0 ml/min for the best films. The deposition time and power were fixed at 25 minutes and 200 W, respectively. The working pressure was about 5.8 - 6.1 × 10⁻² mbar. VO₂, VO₂:W and VO₂:W:Al thin films were deposited on well cleaned normal soda lime glass substrates. KLA-Tencor Alpha Step IQ surface profiler was used to measure film thicknesses.
To obtain VO₂:W:Al thin films, a number of high-purity, 99.99% aluminium pellets were cut into pieces with diameter, length and mass of 6 mm, 5 mm and 0.32 g, respectively. Those sizes and mass were optimum for the switchable films. The metal pieces were placed at the centre, over the tungsten doped vanadium (V:W) target surface so that both elements could be co-sputtered allowing a homogeneous dispersion of the dopant elements in the film. In order to obtain films with different aluminium concentrations, the numbers of aluminium pellets were varied. The maximum number able to produce switchable film within one run was four.

VO₂ based thin films transmittance and reflectance were measured using Shimadzu SolidSpec-3700 DUV UV-VIS-NIR and Perkin Elmer Spectrum BX FT-IR spectrophotometers with a locally made sample heating cell capable of heating the samples from room temperature (≈ 25 °C) to 100 °C. Spectral transmittance and reflectance were measuring at near normal angle of incidence in the UV-Vis-near-infrared (NIR) range, from 250 to 2500 nm wavelength, below and above the transition temperature. The determination of the transition temperature was carried out by evaluating the optical transmittance change with temperature at a given NIR wavelength, in this case at λ = 2500 nm, the wavelength at which VO₂ displays maximum contrast in transmittance across the metal semiconductor transition. The phase transition temperatures were estimated by determining the average between temperatures at midpoint of the transmittance–temperature curve during heating and cooling cycles.

Results and Discussion
Transmittance and reflectance of VO₂ based thin
The optimum film thickness for all samples was found to be 150 nm. Figure 1 shows the spectral transmittance curves of six samples, VO₂, VO₂:W, VO₂:W:Al1, VO₂:W:Al2, VO₂:W:Al3 and VO₂:W:Al4 for the two phases of VO₂ based thin films, the semiconductor phase at 25 °C and metallic phase at 100 °C.

The analysis revealed that the co-doped samples have higher transmittance in the visible region compared to W doped and undoped VO₂ films. The best being the one co-doped with two aluminium pellets (VO₂:W:Al2). This film had the highest transmittance peak of 54% at λ = 729 nm. The results agree with those reported by Granqvist et al. (2010). Generally the transmittance measurements in the wavelength range 250 ≤ λ ≤ 729 nm both below and above the transition temperature, show monotonous increase in transmittance with wavelength. At room temperature, the transmittance of undoped VO₂ film rises sharply from ~ 0% at 250 nm to a peak of 44% at λ = 658 nm, the VO₂:W reaches a peak of 34% at 680 nm. The spectral transmittance data are generally comparable to those obtained by other researchers (Mlyuka 2003, Mlyuka and Kivaisi 2006, Msomi 2008). From the transmittance spectral in Figure 1, it is observed that the films exhibit clear thermochromism especially in the near infrared part of the spectrum, where large contrast in transmittance between the two phases is observed. The transmittance peak values for the six samples at 25 °C and 100 °C as per Figure 1 are shown in Table 1.
Figure 1: Spectral transmittance for VO$_2$, VO$_2$:W, VO$_2$:W:Al1, VO$_2$:W:Al2, VO$_2$:W:Al3 and VO$_2$:W:Al4 thin films at 25 °C and 100 °C.

Table 1: Peak transmittance for VO$_2$ based thin films as derived from Figure 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ (nm) at which the transmittance ($T$) peak occur at 25 °C</th>
<th>% $T$ peak at 25 °C</th>
<th>$\lambda$ (nm) at which the transmittance ($T$) peak occur at 100 °C</th>
<th>% $T$ peak at 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_2$</td>
<td>658</td>
<td>44.7</td>
<td>654</td>
<td>38</td>
</tr>
<tr>
<td>VO$_2$:W</td>
<td>680</td>
<td>34.3</td>
<td>656</td>
<td>23.4</td>
</tr>
<tr>
<td>VO$_2$:W:Al1</td>
<td>729</td>
<td>34.4</td>
<td>647</td>
<td>31.6</td>
</tr>
<tr>
<td>VO$_2$:W:Al2</td>
<td>729</td>
<td>54.1</td>
<td>729</td>
<td>49.7</td>
</tr>
<tr>
<td>VO$_2$:W:Al3</td>
<td>683</td>
<td>37.6</td>
<td>700</td>
<td>32.0</td>
</tr>
<tr>
<td>VO$_2$:W:Al4</td>
<td>638</td>
<td>25.4</td>
<td>652</td>
<td>23.8</td>
</tr>
</tbody>
</table>

The strong suppression of reflectance, $R$ ($\lambda$, $T$) as shown in Figure 2 is a contributing reason for the higher transmittance in the visible region. The results show that $R$ ($\lambda$, $T$) in the low temperature semiconducting phase for VO$_2$:W is suppressed from a peak value of 35% film at $\lambda = 550$ nm to about 16% at the same wavelength for VO$_2$:W:Al. For the co-doped films reflectance in the visible region varies from 23% at $\lambda = 475$ to 6% at $\lambda = 640$ nm. Generally, all the films had reflectance values monotonically increasing in the wavelength ($\lambda$) range 250 to $\approx$ 500 nm and decreasing in the wavelength ($\lambda$) range 500 $< \lambda < \approx$ 650 nm. At $\lambda = 2500$ nm, the reflectance of VO$_2$:W:Al is much lower, at $\approx$ 41% in the metallic phase compared to $\approx$ 54% for undoped VO$_2$ films.
Integrated luminous, solar transmittance and modulation

Integrated luminous transmittance ($T_{\text{lum}}$), solar transmittance ($T_{\text{sol}}$), luminous modulation ($\Delta T_{\text{lum}}$) and solar modulation ($\Delta T_{\text{sol}}$) values were of particular interest in this study for practical applications of VO$_2$ based films, particularly for smart windows applications. $T_{\text{lum}}$ and $T_{\text{sol}}$ values of the optical properties were obtained from equation 1:

$$X_i(\theta, \tau) = \frac{\int_a^b \varphi_i(\lambda) X(\theta, \lambda, \tau) d\lambda}{\int_a^b \varphi_i(\theta, \lambda) d\lambda}$$

where the integral is evaluated from $a = 0.385$ to $b = 0.76$ $\mu$m for luminous transmittance and from $a = 0.25$ to $b = 2.5$ $\mu$m for solar transmittance, $X$ is average transmittance, $(Ts + Tp)/2$ or average reflectance, $(Rs + Rp)/2$ for s and p-polarized light (Mlyuka 2010), $i$ denotes lum or sol, $\varphi_{\text{lum}}(\lambda)$ is the spectral sensitivity of the light-adapted human eye in the wavelength range of 0.385 to 0.76 $\mu$m, and $\varphi_{\text{sol}}$ is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon).

Transmittance modulation, $\Delta T_{\text{lum}}$ and solar modulation ($\Delta T_{\text{sol}}$) values are obtained from:

$$\Delta T_{\text{lum}} = T_{\text{lum},l} - T_{\text{lum},h}$$

and

$$\Delta T_{\text{sol}} = T_{\text{sol},l} - T_{\text{sol},h}$$

where $l$ and $h$ denote low and high temperature corresponding to semiconductor and metallic phases of VO$_2$ thin films, respectively.

Calculations for $T_{\text{lum}}$ and $T_{\text{sol}}$ were done based on the ASTM G173-03 reference spectra derived from SMARTS v. 2.9.2 taken in the wavelength range 385 $\leq \lambda \leq$ 760 and 280 $\leq \lambda \leq$ 2500 nm, respectively. The calculations show that the VO$_2$:W:Al2 film exhibited high integrated luminous transmittance ($T_{\text{lum}, l} = 39.3\%$, $T_{\text{lum}, h} = 36.6\%$) and luminous modulation ($\Delta T_{\text{lum}} = 2.6\%$, from $T_{\text{lum}, l} = 39.3\%$ to $T_{\text{lum}, h} =$

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Figure 2: Reflectance spectra of VO$_2$, VO$_2$:W and VO$_2$:W:Al thin films showing suppression in the visible region of the solar spectrum as a result of co–doping.
36.6%), compared to VO$_2$ ($T_{\text{hun}} = 30.3\%$, $T_{\text{hun,h}} = 26.8\%)$ and its luminous modulation ($\Delta T_{\text{hun}} = 3.4\%$, from $T_{\text{sol,h}} = 30.3\%$ to $T_{\text{sol,h}} = 26.8\%)$. Solar transmittance, $T_{\text{sol}}$, of VO$_2$:W:Al$_2$ film in both low and high phases are larger than those of VO$_2$ thin film. The results show that solar modulation of VO$_2$:W:Al$_2$ thin film is also larger compared to that of VO$_2$ thin film.

In view of the fact that solar energy in the visible region has a peak at 550 nm, the $\Delta T_{\text{sol}}$ across the metal-insulator transition, MIT, effectively influences the $\Delta T_{\text{sol}}$ (Gao et al. 2011). For instance, $\Delta T_{\text{sol}}$ increased by 6.8% from 9.1% for undoped VO$_2$ films to 15.9% for VO$_2$:W:Al$_2$ films. On the other hand, doping with W decreased the $\Delta T_{\text{sol}}$ by 2.6% from 9.1% for undoped films to 6.5% for W doped films. Furthermore, VO$_2$:W:Al$_2$ films had the highest solar modulation compared to the other co-doped films, with $\Delta T_{\text{sol}}$ being 15.9% compared to 2.85% for VO$_2$:W:Al$_1$ films, 10.9% for VO$_2$:W:Al$_3$ and 6.6% for VO$_2$:W:Al$_4$ films.

**Effect of aluminium and tungsten co-doping on the hysteresis and transition temperature of the VO$_2$ thin films**

Figures 3(a) – (e) show the temperature-dependent transmittance at $\lambda = 2500$ nm for VO$_2$:W, VO$_2$:W:Al$_1$, VO$_2$:W:Al$_2$, VO$_2$:W:Al$_3$ and VO$_2$:W:Al$_4$ thin films. From these figures, transition temperatures were determined. The VO$_2$ film has the highest $\tau_c$ of $= 68^\circ$C compared to $32^\circ$C, $42.6^\circ$C, $61.3^\circ$C, $61.1^\circ$C and $47^\circ$C for VO$_2$:W, VO$_2$:W:Al$_1$, VO$_2$:W:Al$_2$, VO$_2$:W:Al$_3$ and VO$_2$:W:Al$_4$ thin films, respectively.

**Figure 3a:** Transmittance as a function of temperature for tungsten doped vanadium dioxide thin film at $\lambda = 2500$ nm.

**Figure 3b:** Transmittance as a function of temperature for VO$_2$:W:Al$_1$ thin film at $\lambda = 2500$ nm.
There is evidence that for the co-doped films, the transition temperature is lower compared to undoped VO$_2$ film as seen in Figure 4. The reduction in transition temperature with increasing doping level of aluminium in VO$_2$ based thin films have been also reported by Gentle and Smith (2007) while other authors reported rising transition temperature with increasing Al doping level (MacChesney and Guggenheim 1969, Mlyuka 2010).
Figure 4: Variation in transition temperature for 150 nm thick VO$_2$ based thin films deposited at 450 °C, showing decrease in τ, in VO$_2$: W: Al films as compared to undoped VO$_2$ film.

Conclusion
Thermochromic VO$_2$ thin films were successfully synthesized by DC reactive magnetron sputtering. From a practical point of view, aluminium and tungsten co-doped VO$_2$ films exhibit promising characteristics with regard to optical transmittance and switching properties. Application of the VO$_2$:W:Al2 coating enhances the transmittance in the visible spectral range to more than 54%. With VO$_2$:W:Al2 the reversible phase transition occurs at 61 °C, compared to 68 °C for undoped VO$_2$ film.

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