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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 (τ_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_2films. 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 ^oC.

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

Granqvist 1990). The change in optical properties can be in the form of absorption, transmittance, reflectance or scattering. The change can be either within the visible or beyond visible spectrum (Granqvist et al 2010). Windows with optical coatings that can adjust their optical properties in response to dynamic needs are called 'smart windows' (Lampert and Granqvist 1990, Greenberg 1994).

Vanadium dioxide (VO_2) 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 τ_c of ≈ 68 °C (Morin 1959). VO_2 is technologically important due to its ability to undergo a reversible metal-to-semiconductor phase transition. The conversion of the low temperature monoclinic phase VO_2 to the high temperature rutile phase VO_2 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 VO_2 is semiconductor and infrared transparent at room temperature, but above τ_c VO_2 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 VO_2 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 VO_2 thin films, namely, optical, electrical and structural are improved. The τ_c of VO_2 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 VO_2 thin films geared to obtain both improved luminous transmittance and lowered transition temperature.

Materials and Methods

Thin films ofVO_2, tungsten doped vanadium dioxide (VO_2:W) and aluminium and tungsten co-doped vanadium dioxide (VO_2: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 (O_2, 99.9% purity) into the chamber at the rates of 75 and 6.6 – 7.2 ml_n/min, respectively. The optimum oxygen rate was 7.0 ml_n/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^{-3} mbar. VO_2, VO_2:W and VO_2: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 VO_2: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.

VO_2 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 $\lambda = 2500$ nm, the wavelength at which VO_2 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 VO_2 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, VO_2, VO_2:W, VO_2:W:Al1, VO_2:W:Al2, VO_2:W:Al3 and VO_2:W:Al4 for the two phases of VO_2 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 VO_2 films. The best being the one co-doped with two aluminium pellets (VO_2: W:Al2). This film had the highest transmittance peak of 54% at $\lambda = 729$ nm. The results agree with those reported by Granqvist et al. (2010). Generally the transmittance measurements in the wavelength range $250 \le \lambda \le 729$ nm both below and above the transition temperature, show monotonous increase in transmittance with wavelength. At room temperature, the transmittance of undoped VO_2 film rises sharply from ~ 0% at 250 nm to a peak of 44% at $\lambda = 658$ nm, the VO_2: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.

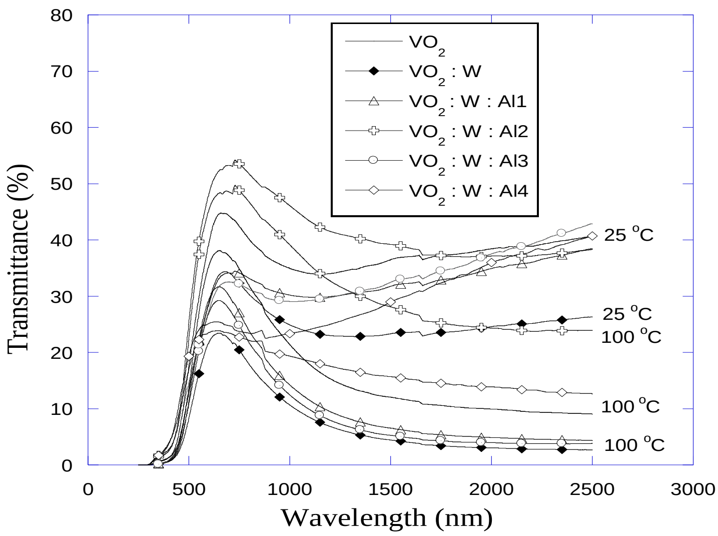

Figure 1: Spectral transmittance for VO_2, VO_2:W, VO_2:W:Al1, VO_2:W:Al2, VO_2:W:Al3 and VO_2:W:Al4 thin films at 25 °C and 100 °C.

Table 1: Peak transmittance for VO_2 based thin films as derived from Figure 1

Sample	λ (nm) at which the transmittance (*T*) peak occur at 25 °C	% *T* peak at 25 °C	λ (nm)at which the transmittance (*T*) peak occur at 100 °C	% *T* peak at 100 °C
VO_2	658	44.7	654	38
VO_2:W	680	34.3	656	23.4
VO_2:W:Al1	729	34.4	647	31.6
VO_2:W:Al2	729	54.1	729	49.7
VO_2:W:Al3	683	37.6	700	32.0
VO_2:W:Al4	638	25.4	652	23.8

The strong suppression of reflectance, *R* (λ, T) as shown in Figure 2 is a contributing reason for the higher transmittance in the visible region. The results show that *R* (λ, T) in the low temperature semiconducting phase for VO_2:W is suppressed from a peak value of 35% film at λ = 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 λ = 475 to 6% at λ = 640 nm. Generally, all the films had reflectance values monotonically increasing in the wavelength (λ) range 250 to ≈ 500 nm and decreasing in the wavelength (λ) range 500 < λ < ~ 650 nm. At λ = 2500 nm, the reflectance of VO_2:W:Al is much lower, at ≈ 41% in the metallic phase compared to ≈ 54% for undoped VO_2 films.

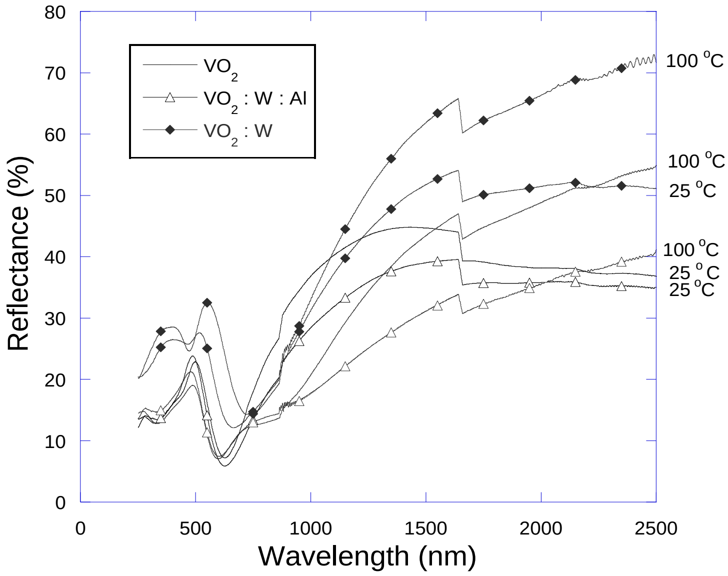

Figure 2: Reflectance spectra of VO_2, VO_2:W and VO_2:W:Al thin films showing suppression in the visible region of the solar spectrum as a result of co–doping.

Integrated luminous, solar transmittance and modulation

Integrated luminous transmittance (T_{lum}), solar transmittance (T_{sol}), luminous modulation (ΔT_{lum}) and solar modulation (ΔT_{sol}) values were of particular interest in this study for practical applications of VO_2 based films, particularly for smart windows applications. T_{lum} and T_{sol} values of the optical properties were obtained from equation 1:

$$X_i(\theta,\tau)=\frac{\int_a^b \varphi_i(\lambda)X(\theta,\lambda,\tau)\partial\lambda}{\int_a^b \varphi_i(\theta,\lambda)\partial\lambda} \quad (1)$$

where the integral is evaluated from a = 0.385 to b = 0.76 µm for luminous transmittance and from a = 0.25 to b = 2.5 µm 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*, $\varphi_{lum}(\lambda)$ is the spectral sensitivity of the light-adapted human eye in the wavelength range of 0.385 to 0.76 µm, and φ_{sol} is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon).

Transmittance modulation, ΔT_{lum} and solar modulation (ΔT_{sol}) values are obtained from:

$$\Delta T_{lum} = T_{lum,l} - T_{lum,h} \quad (2)$$

and

$$\Delta T_{sol} = T_{sol,l} - T_{sol,h} \quad (3)$$

where l and h denote low and high temperature corresponding to semiconductor and metallic phases of VO_2 thin films, respectively.

Calculations for $T_{lum,}$ and T_{sol} were done based on the ASTM G173-03 reference spectra derived from SMARTS v. 2.9.2 taken in the wavelength range 385 ≤ λ ≤ 760 and 280 ≤ λ ≤ 2500 nm, respectively. The calculations show that the VO_2:W:Al2 film exhibited high integrated luminous transmittance ($T_{lum,\ l}$ = 39.3%, $T_{lum,\ h}$ = 36.6%) and luminous modulation (ΔT_{lum} = 2.6%, from $T_{lum,\ l}$ = 39.3% to $T_{lum,\ h}$ =

36.6%), compared to VO_2 ($T_{lum,\,l}$ = 30.3%, $T_{lum,\,h}$ = 26.8%) and its luminous modulation (ΔT_{lum} = 3.4%, from $T_{sol,\,l}$ = 30.3% to $T_{sol,\,h}$ = 26.8%). Solar transmittance, T_{sol}, of VO_2:W:Al2 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:Al2 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 ΔT_{lum} across the metal-insulator transition, MIT, effectively influences the ΔT_{sol} (Gao et al. 2011). For instance, ΔT_{sol} increased by 6.8%, from 9.1% for undoped VO_2 films to 15. 9% for VO_2:W:Al2 films. On the other hand, doping with W decreased the ΔT_{sol} by 2.6% from 9.1% for undoped films to 6.5% for W doped films. Furthermore, VO_2:W:Al2 films had the highest solar modulation compared to the other co-doped films, with ΔT_{sol} being 15.9% compared to 2.85% for VO_2:W:Al1 films, 10.9% for VO_2:W:Al3 and 6.6% for VO_2:W:Al4 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 λ = 2500 nm for VO_2:W, VO_2:W:Al1, VO_2:W:Al2, VO_2:W: Al3 and VO_2:W:Al4 thin films. From these figures, transition temperatures were determined. The VO_2 film has the highest τ_c of ≈ 68 °C compared to 32 °C, 42.6 °C, 61.3 °C, 61.1 °C and 47 °C for VO_2:W,VO_2:W:Al1, VO_2:W:Al2, VO_2:W:Al3 and VO_2:W:Al4 thin films, respectively.

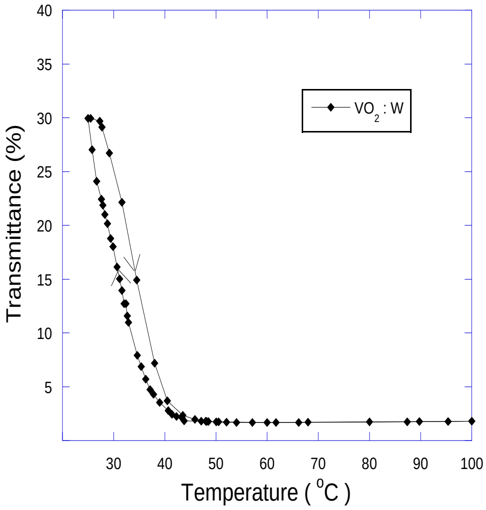

Figure 3a: Transmittance as a function of temperature for tungsten doped vanadium dioxide thin film at λ = 2500 nm.

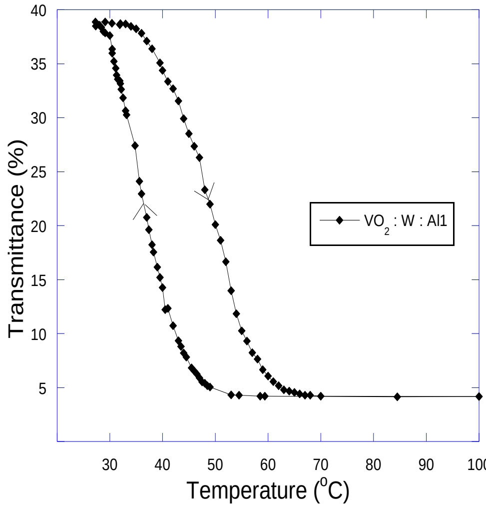

Figure 3b: Transmittance as a function of temperature for VO_2:W:Al1 thin film at λ = 2500 nm.

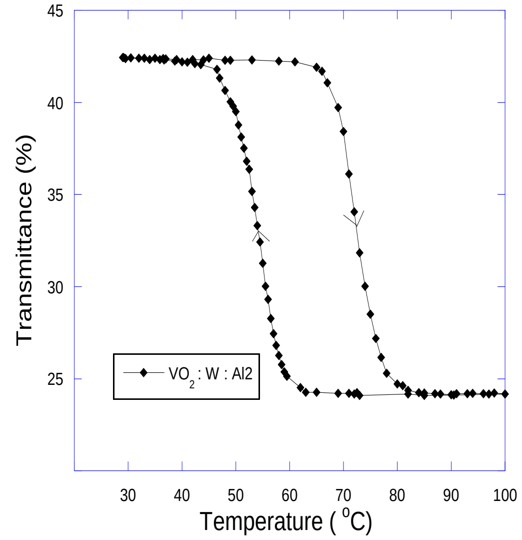

Figure 3c: Transmittance as a function of temperature for VO_2:W:Al2 thin film at λ = 2500 nm.

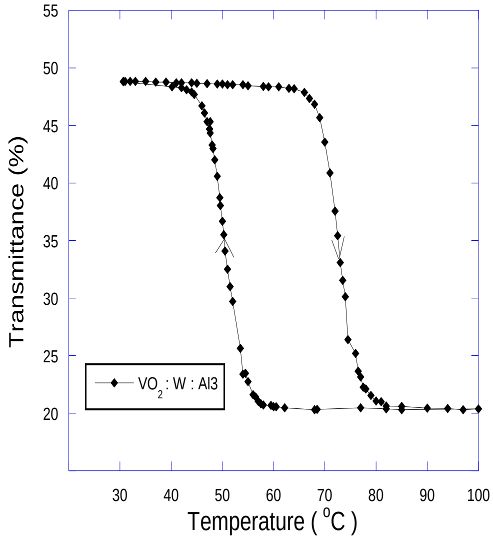

Figure 3d: Transmittance as a function of temperature for VO_2:W:Al3 thin film at λ = 2500 nm.

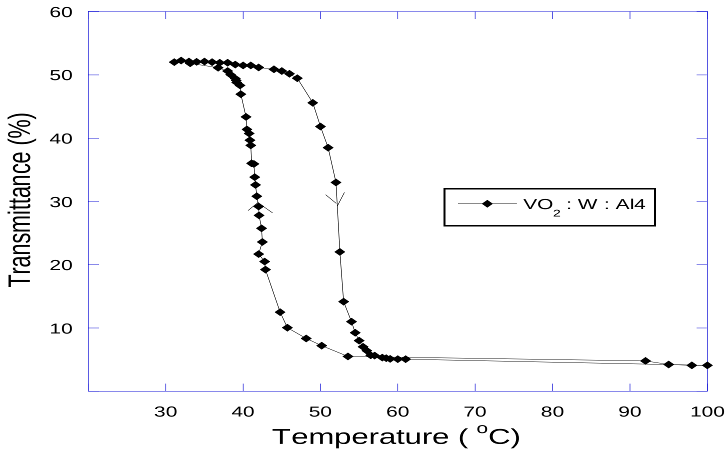

Figure 3e: Transmittance as a function of temperature for VO_2:W:Al4 thin film at λ = 2500 nm.

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).

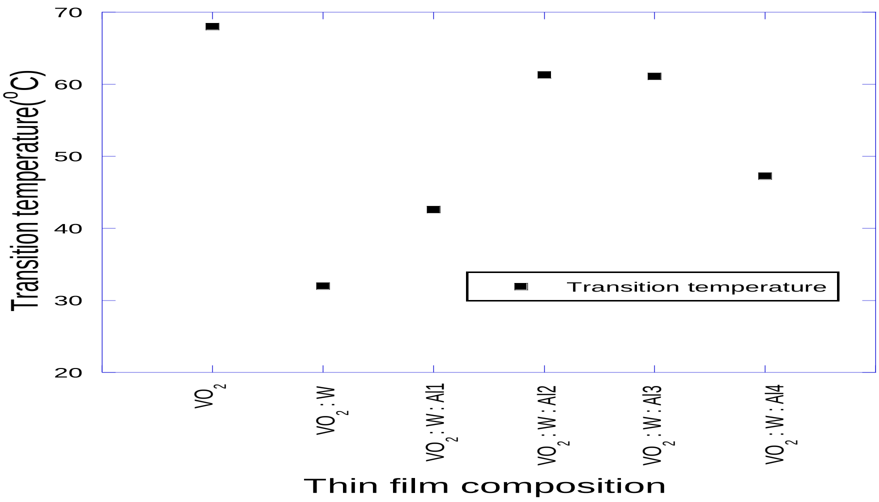

Figure 4: Variation in transition temperature for 150 nm thick VO_2 based thin films deposited at 450 °C, showing decrease in τ_c in VO_2: W: Al films as compared to undoped VO_2 film.

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_2film.

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References

Béteille F and Livage J 1998 Optical switching in VO_2 thin films. *J. Sol-Gel Sci. Technol.* 13(1): 915-921.

Chain EE 1991 Optical properties of vanadium dioxide and vanadium pentoxide thin films. *Applied Optics*, 30(19): 2782-2787.

Gao Y, Kang L, Chen Z and Luo H 2011 Solution to Processing of Nanoceramic VO_2 Thin Films for Application to Smart Windows. In: Masude Y (ed) *Nanofabrication*. InTech 167-198.

Gentle A and Smith GB 2007 Dual metal–insulator and insulator–insulator switching in nanoscale and Al doped VO_2. *J. Phys. D. Appl. Phys.* 41(1): 015402.

Granqvist CG 1990 Window coatings for the future. *Thin Solid Films* 193: 730-741.

Granqvist CG, Mlyuka NR and Niklasson G A 2010 Thermochromic material and fabrication thereof. International patent publication number WO 2010/039067 A1.

Greenberg CB 1983 Undoped and doped VO_2 films grown from $VO(OC_3H_7)_3$. *Thin Solid Films* 110: 73-82.

Greenberg CB 1994 Optically switchable thin films-A review. *Thin Solid Films* 251: 81-93.

Jin P and Tanemura S 1994 Formation of thermochromism of VO_2 films deposited by RF magnetron sputtering at low substrate temperature. *Jpn. Appl. Phys.* 33: 1478-1483.

Kato K, Song PK, Shigesato Y and Odaka H 2001 Thermochromic non–doped and W–doped VO_2 films heteroepitaxially grown on glass substrate using ZnO polycrystalline films as buffer layers. *Proc. SPIE, Solar and Switching Materials* 4458: 261-267.

Kivaisi RT and Samiji ME 1999 Optical and electrical properties of vanadium dioxide films prepared under optimized RF sputtering conditions. *Sol. Energy Mater. Sol. Cells* 57: 141-152.

Lampert CM and Granqvist CG 1990 Large-Area Chromogenics: Materials and Devices for Transmittance Control. Volume IS 4. SPIE-The International Society for Optical Engineering, Bellingham, WA United States.

Livage J 1999 Optical and electrical properties of vanadium oxides synthesized from alkoxides. *Coordinat. Chem. Rev.* 190: 391-403.

MacChesney JB and Guggenheim HJ 1969 Growth and electrical properties of vanadium dioxide containing selected impurity ions. *J. Phys. Chem. Solids* 30: 225-234.

Mlyuka N and Kivaisi RT 2006 Correlation between optical, electrical and structural properties of vanadium dioxide thin films. *J. Mater. Sci.* 41(17): 5619-5624.

Mlyuka NR 2003 *Structural stability of vanadium dioxide under different ambient conditions*, MSc Thesis, University of Dar es Salaam, Tanzania.

Morin F 1959 Oxides which show a metal-to-insulator transition at the Neel temperature. *Phys. Rev. Lett.* 3(1): 33-34.

Msomi V 2008 *Vanadium dioxide thermochromic thin films correlation between microstructure, electrical and optical properties*, MSc Thesis, University of Zululand.

Msomi V and Nemraoui O 2010 The influence of deposition temperature on vanadium dioxide thin films microstructure and physical properties. *S. Afr. J. Sci* 106(11-12): 1-4.

Mlyuka NR 2010 Vanadium *dioxide based thin films: enhanced performance for smart window applications*, PhD Thesis, University of Dar es Salaam, Tanzania.

Rogers KD 1993 An X–ray diffraction study of semiconductor and metallic vanadium dioxide. *Powder Diffraction* 8(4): 240-244.

Sobhan MA, Kivaisi RT, Stijerna B and Granqvist G 1996 Thermochromism of sputter deposition $W_XV_{1-X}O_2$ films. *Sol. Energy Mater. Sol. Cells*. 44: 451-455.

Soltani M, Chaker M, Haddad E, Kruzelecky RV and Margot J 2004 Effects of Ti–W codoping on the optical and electrical switching of vanadium dioxide thin films grown by a reactive pulsed laser deposition. *Appl. Phys. Lett.* 85(11): 1958-1960.

United Nations Environment Programme (UNEP) 2007, Buildings and Climate Change: Status, Challenges and Opportunities, Paris, France.

Verleur WH, Barker AS and Berglund CN 1968 Optical properties of VO_2 between 0.25 and 5 eV. *Phys. Rev.* 172(3): 788-798.