

Thermochromic Properties of VO₂ Thin Films Derived from Thermal Reduction of Sol-Gel Deposited V₂O₅

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Abstract Vanadium dioxide (VO₂) thin films were prepared by thermal reduction of vanadium pentoxide (V₂O₅) films and thermochromic properties of the films were investigated. V₂O₅ films were prepared by dip-coating glass substrates at different withdrawal speeds of 5, 10, 15, and 20 mm/min. The as-deposited V₂O₅ films were annealed at different temperatures of 450, 500, 550 and 600°C in an inert environment of flowing argon gas under normal atmospheric pressure. The as-deposited V₂O₅ films were gray in color and the films changed color to golden yellow after annealing. UV-VIS-NIR spectrophotometry and sheet resistance probe were used to evaluate performance of the films. The result shows that a withdrawal speed of 5mm/min and annealing temperature of 500°C produced homogeneous VO₂ films with luminous transmittance close to the desired transmittance threshold for day-lighting. This was attributed to reduced thickness and crystallization resulting to low absorption by VO₂. Results showed that 500°C was threshold for obtaining crystalline VO₂ films. UV-VIS-NIR analysis revealed solar modulation ability of 5.2%, large transmittance change of over 35°C in the IR region and hysteresis loop of 6.0°C when going through phase transition between 25°C and 90°C. Temperature dependence of sheet resistance revealed semiconductor to metal transition behavior change of 2 orders of magnitude across transition temperature. The film showed semiconductor to metal transition temperature of 61.2°C lower than the classical value of 68°C and was attributed to crystalline structure of the films. This simple solution process followed by thermal reduction makes the VO₂ potentially useful in smart window application.

Keywords: vanadium dioxide, transition temperature, near-infrared-radiation, luminous transmittance, solar modulation ability and crystallinity

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1. Background

VO₂ undergoes a fully reversible semiconductor-metal transition (SMT) at a temperature of 68°C, coupled with a structural phase transition (SPT) between monoclinic VO₂ (M) phase and rutile VO₂ (R) phase [1,2]. To take advantage of interesting functions, due to temperature-dependent switching, VO₂ has been used in various applications for sensing and in optical communications such as infrared bolometers, photonic crystals and its application as a switchable window glazing for energy efficient application has also been discussed for decades [3, 4]. Thin film coatings of doped multilayer VO₂ on building glazing to limit the amount of solar radiation entering and thermal radiation leaving a building have so far been demonstrated [4]. As a marvelous thermochromic material, vanadium dioxide (VO₂) holds a great promise for application in smart devices due to its semiconductor-to-metal transition (SMT) which is an active response to external temperature stimuli of near infrared irradiation [5].

Sol-gel method has a number of advantages in obtaining thin films which include good control over the stoichiometry, low cost, large area deposition, feasibility of doping and lower synthesis temperature to obtain the crystalline films [10]. Among the process that use chemical precursors to deposit thin films, the more utilized are dip-coating and spin coating. In this process, a specified substrate is dipped in a uniform solution, after that it is withdrawn from solution, dried, and heat-treated. Unfortunately, the disadvantage of polymeric precursor method for preparation of thin films is the appearance of cracking caused by development of stress during the thermal treatment used for the decomposition of the polymeric solution and formation of the ceramic film. In general appearance of cracks is lower in thinner films as the adhesion on the interface film-substrate is higher and lateral shrinkage of the film is suppressed [11]. When critical value of thickness is reached, the cracks cannot be avoided. To obtain crack free films, it is necessary to control the parameters including characteristics of the solution such as viscosity, condition of heating and withdrawal speed [11,12]. In this paper VO₂ films were

produced by thermal reduction of V_2O_5 in an inert atmosphere of flowing argon gas under normal atmospheric pressure and whose optical and electrical properties were investigated. The objective of this work is to investigate the potential of VO_2 dioxide thin film as a smart material to control solar radiation in built environment among other applications and give way for further research on improvement.

2. Experimental Procedure

1g of V_2O_5 powder was dissolved in hydrogen pentoxide (H_2O_2 , 30% wt, 100 ml) at room temperature of $27^\circ C$ in a glass beaker while stirring to ensure uniform solubility. Since the reaction is exothermic, H_2O_2 was added at a rate of 10 cm^3 every 30s while stirring. The stirring continued while oxygen gas was released until a clear orange-yellow solution (decavanadic acid) was formed. After the orange-yellow color appeared gelation started and lasted until a red-brown gelatinous flocculate was formed ($V_2O_5 \cdot nH_2O$). The gel was allowed to age for 24 hours in the open glass beaker under ambient temperature to form a homogeneous dark red gel.

Before deposition, glass substrates measuring 2cm by 2cm were cleaned successively in detergent, acetone (purity 99.5 %), ethanol (99.5% pure) and deionized water sequentially for 5 minutes in each step. After rinsing with distilled water, glass substrates were dried with pressurized warm air before dehydrating them on a hot. Dipping of the substrate in the gel was done at a constant speed to ensure homogeneous wetting of the surface. After dipping was over, the substrate was held inside the gel for 5 minutes to allow sufficient interaction of coating gel with substrate surface for complete wetting. Sets of substrates were withdrawn at different constant speeds of 5 mm/min, 10 mm/min, 15 mm/min and 20 mm/min to entrain a uniform thickness thin film. The deposited films were allowed to dry in air at room temperature for 1 hour.

V_2O_5 films were annealed inside a horizontal tube furnace with inside inert atmosphere under normal atmospheric pressure with argon gas flowing at a rate of 100 sccm. After samples were placed in the furnace, argon was pumped at a rate of 300 sccm for 10 minutes to drive out oxygen and then lowered to 100 sccm during heat treatment. A sample coated at a withdrawal speed of 10mm/min was annealed at $450^\circ C$ for 30 minutes. The furnace was then allowed to cool naturally at a rate of $5^\circ C/min$ until the temperature reached $100^\circ C$. The furnace was then allowed to cool naturally to room temperature after which the samples were retrieved from the furnace for analysis. The same procedure was repeated for other samples annealed at 500, 550 and $600^\circ C$.

2.1. Characterization of Samples

To determine optical properties, the transmittance spectrum was measured using UV-VIS-NIR spectrophotometer equipped with a custom-built heating unit. The measurements were performed in the wavelength range 250-2500 nm at sample temperature between $25^\circ C$ and $90^\circ C$. The optical spectrum data obtained was used to determine integral transmittance for UV-transmittance

($T_{uv\ 200-380}$), luminous transmittance ($T_{lum\ 380-780\text{ nm}}$) and solar transmittance ($T_{sol\ 250-2500\text{ nm}}$) which are vital in evaluating films performance.

Sheet resistance (R_{\square}) method through four point probe technique was used to detect the switching of the VO_2 film from semiconductor state to metallic state as the temperature of the sample was varied from below to above critical temperature (τ_c) at a rate of $2^\circ C/min$, a rate which enabled the detection of transition temperature. Sheet resistance was used to determine the SMT temperature (τ_c) and the hysteresis width as well as judging the crystallinity and stoichiometry of the films.

The integral visible transmittance ($T_{lum\ 380-780\text{ nm}}$) and solar transmittance ($T_{sol\ 240-2600\text{ nm}}$) were obtained based on the measured spectra using equation 1.

$$T_i = \int \left(\frac{\phi_i(\lambda)T(\lambda)d\lambda}{\phi_i(\lambda)d\lambda} \right) \quad 1$$

Where $T(\lambda)$ denotes transmittance at wavelength λ , i denotes *lum* or *sol* for calculations, ϕ_{lum} is standard luminous efficiency function for the photonic vision and ϕ_{sol} is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon).

Solar transmittance modulation ability (ΔT_{sol}) determines the efficiency of a thermochromic material in modulating solar radiation and was determined using equation 2.

$$\Delta T_{sol} = T_{sol}(\tau < \tau_c) - T_{sol}(\tau > \tau_c) \quad 2$$

Where T_{sol} refers to solar transmittance, τ is variable temperature and τ_c is transition temperature.

3. Results and Discussion

3.1. Optical Properties

The optical spectra of the various films obtained at $25^\circ C$ and $90^\circ C$ within the 250-2500 nm wavelength range are plotted in Figure 1 (a). At two temperatures, $25^\circ C$ and $90^\circ C$, the luminous transmittance is independent of temperature whereas the infrared transmittance is strongly dependent on temperature. The films are absorbing in the ultra violet region and they start to transmit in the visible range. The solar transmittance at $25^\circ C$ and $90^\circ C$ increases steadily toward long wavelengths for the *as-deposited* and $450^\circ C$ annealed film since the films transmit both visible light and infrared wavelengths. Films annealed at $450^\circ C$ showed no IR modulation since they had not yet crystallized to convert to VO_2 hence it showed no thermochromism.

Annealing temperature influences changes in luminous transmittance of VO_2 films as well as IR modulation [9]. The low temperature ($25^\circ C$) phase of films annealed at $450^\circ C$ had a maximum transmittance of about 30.5 % at the peak of visible light, while it was 54 % for film annealed at $500^\circ C$, 43 % for film annealed at $550^\circ C$ and 38.8 % for film annealed at $600^\circ C$. Decrease in transmittance is attributed to increase in roughness and grain size resulting to decrease in band-gap as the annealing temperature was increased from $500^\circ C$ to $600^\circ C$ for crystalline films. Decrease in band-gap results to increase in absorption of photon energy hence low transmittance for higher annealing temperature [11]. From

the representative spectrum in Figure 1 (a), it is observed that the NIR transmittance decreased significantly by raising the temperature above the transition temperature which indicates that thermochromism was achieved for films annealed at 500°C, 550°C and 600°C. With these optical properties the color of the films annealed at 500°C, 550°C, and 600°C was golden yellow [13] (typical color for M/R phase VO₂). However, the 450°C annealed film and the as-deposited film remained grey in color. The observed shift of the absorption edge from 320 nm before annealing to 380 nm after annealing in the UV region also justified change in color between as-deposited films and annealed films. These changes were in accordance with changes reported for VO₂ thin films [9,11,13]. The transmittance changes in the IR region for 500°C, 550°C and 600°C at 2500 nm were 42°C, 26.8°C and 19.4°C respectively after raising the temperature above transition temperature. From Figure 1 (b) decrease in UV transmittance for the annealed films is elucidated which is one of the design goals of the smart windows. The figure also shows the NIR transmittance for the samples

measured at 25°C and 90°C as well as the percent reduction in NIR after elevating the temperature from 25°C, to 90°C. From the Figure 1 (b), it is shown that NIR transmittance for 500°C annealed sample decreased by 65% (from 59% to 38.5%). As the annealing temperature was increased to 550°C and 600°C, the NIR reduction decreased to 56.5% (from 47.5% to 20.7%) and 48% (from 42 to 22.6%) respectively. 500°C was realized as the optimum annealing temperature in terms of low UV transmittance, relatively high luminous transmittance at 580 nm and NIR modulation at $\lambda = 2500$ nm for the synthesis method used. Annealing temperature of 500°C has been reported as the optimum temperature for VO₂ films synthesized through sol-gel method [14].

The withdrawal speed dependence of the optical properties of VO₂ films obtained by annealing at the realized optimum temperature of 500°C is shown in Figure 2(a). Variation of the withdrawal speeds had significant effects on the films transmittance after annealing, owing to the fact that withdrawal speed dictates uniformity and thickness of the films.

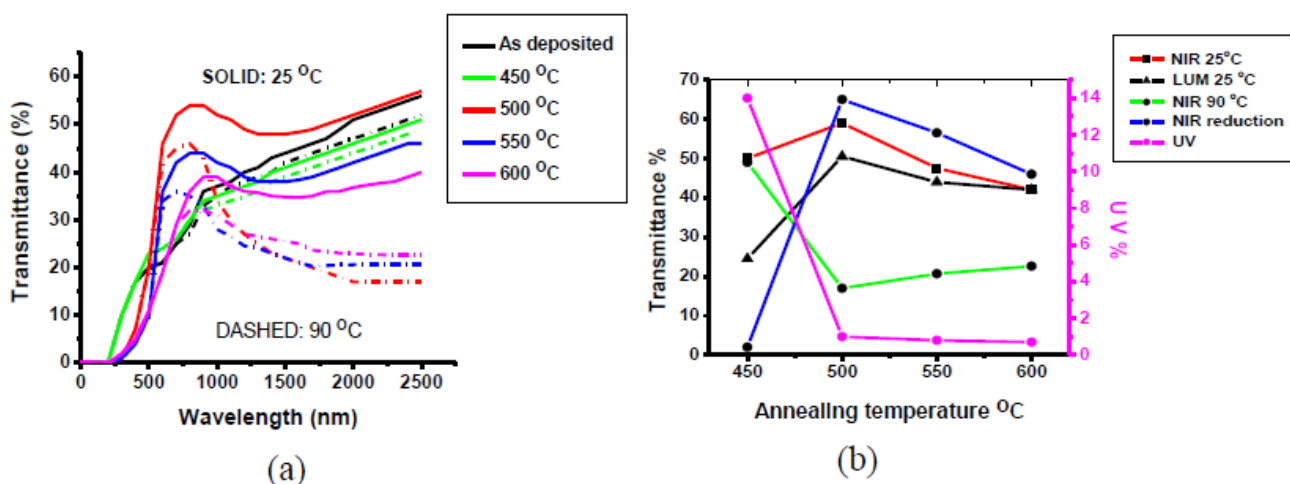


Figure 1: (a) UV-VIS-NIR transmittance spectra of V₂O₅ films for as-deposited film and annealed at different annealing temperatures (b) UV, luminous and NIR transmittance for VO₂ samples with respect to annealing temperature

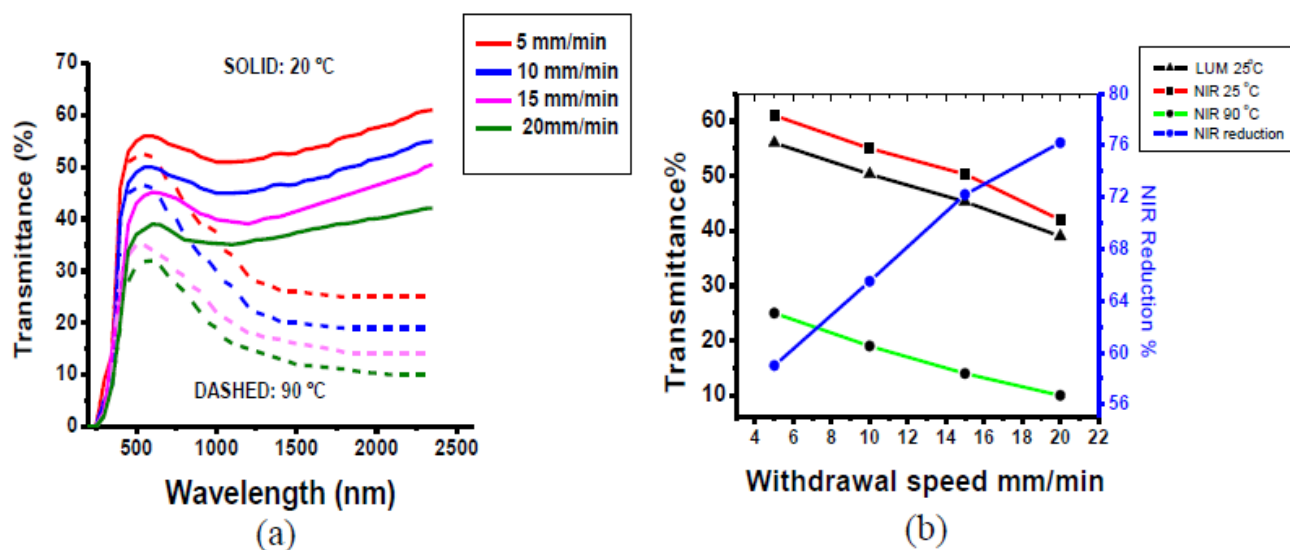


Figure 2: (a) UV-VIS-NIR transmittance spectra of VO₂ films obtained by dip-coating at different withdrawal speeds and annealing at a common temperature of 500°C. (b) Luminous transmittance, NIR transmittance and NIR reduction percentage with respect to withdrawal speed

The visible transmittance decreased distinctively with increasing withdrawal speed, which was mainly attributed to increased absorption of VO₂ due to increased thickness of the film as withdrawal speed increased [11,13]. Analysis from Figure 2 (b) shows that sample film produced at a withdrawal rate of 5 mm/min had luminous transmittance of 56 % at the peak of visible wavelength while those produced at 10 mm/min, 15 mm/min and 20 mm/min had transmittances of 50.3 %, 45.3 % and 39 % respectively.

NIR reduction increased with increase in withdrawal speed as it is depicted in Figure 2 (b), however higher NIR reduction in films produced at higher withdrawal speed °C occurred at the expense of low luminous transmittance. From Figure 2 (b) it is shown that NIR decreased by 59% (from 61 to 25 %), 65.5 % (from 55 to 19%), 72.2% (from 50.3 to 14%) and 76.2% (from 42 to 10%) for withdrawal speeds of 5mm/min, 10 mm/min, 15 mm/min and 20 mm/min respectively. Withdrawal speed of 5 mm/min gave best results of thin films in this study in terms of minimal cracks depicted by lower electrical resistance and luminous transmittance close to the desired transmittance threshold for day-lighting. The films had characteristics similar to those reported for VO₂ films deposited on amorphous substrates [15,18].

3.2. Electrical Properties

The electrical properties in terms of sheet resistance dependence on temperature within the range 25-110°C, for films annealed at different temperatures are as shown in Figure 3(a). The films annealed at 450°C presented highest resistance values which varied from 1.4×10^5 to $1.2 \times 10^5 \Omega/\text{sq}$ with increasing temperature from 25°C to above 90°C respectively.

This is attributed to lack of crystallinity and presence of unconverted V₂O₅ coexisting with other vanadium oxides other than VO₂ in the film which deteriorated the electrical and also optical switching properties associated with semiconductor-metal phase transition [8,17]. The film annealed at 500°C showed drop of resistance at near 68°C, which is the typical property of crystalline VO₂ thin film. Lowest resistance values, from 1.3×10^5 to $1.2 \times 10^3 \Omega/\text{sq}$ at 25°C and 90°C respectively revealed crystallinity of the films. This resistance drop is equivalent to 2 orders of magnitude across the transition temperature which is a typical behavior for VO₂ films deposited on amorphous substrates [18]. The switching behavior with narrowest hysteresis evident at this annealing temperature was attributed to improved crystallinity and stoichiometry of the VO₂ phase. The dual semiconductor/metal nature of the VO₂ can be attributed to the difference in electronic band structure which shows strong V 3d and O 2p band overlapping and separating, above and below the transition, respectively, associated with the atomic rearrangement between the low temperature monoclinic and the high temperature rutile phase [5,8,18]. Films annealed at 550°C and 600°C revealed wider hysteresis, transition temperature above 68°C and increased resistance values varying from 1.33×10^5 to $6.1 \times 10^3 \Omega/\text{sq}$, compared to the film annealed at 500°C with temperature

increasing from 25°C to 90°C. These deteriorated thermochromic properties were attributed to poor crystallinity (coarse and increased grain size films) resulting to degradation of VO₂ to other oxides which lack thermochromic properties [13,19]. Grain size is viewed as an important factor in controlling transition temperature [13,19,20]. From Figure 3(b), the transition temperatures were 63°C, 79.2°C and 80.1°C while hysteresis were 9.1°C, 15.2°C and 16.4°C for 500°C, 550°C and 600°C respectively and the films had been synthesized at a withdrawal speed of 10 mm/min during optimization of annealing temperature.

Electrical resistance was also affected by withdrawal speed during deposition in response to the resulting thickness of the films as shown in Figure 4(a). Resistance increased with increase in thickness contrary to expectations. This is attributed to presence of cracks whose size and density increased with increase in thickness thus increasing the effect of structural discontinuity in the films hence carrier mobility is reduced in thicker films [11,21]. Similar phenomena have been reported in indium tin oxide films and Molybdenum-doped zinc oxide thin films [12,21]. Films produced at a withdrawal speed of 5 mm/min revealed best results in terms of lowest transition temperature and narrowest hysteresis. Thinner films have small and less cracks thus continuity is promoted hence higher conductivity [11]. Therefore, above the critical thickness for cracks to occur, thinner films are less resistive than thicker films. In this research our lowest withdrawal speeds may have given thicknesses above the critical thickness considering that below critical thickness, resistivity decreases with increase in thickness [11,21]. This is attributed to difference in activation energy which depends on compactness of grains to enhance electrical contacts. Therefore thicker films may have lower activation energy than thinner films hence they have higher resistance [22].

The withdrawal speed also affected the transition temperature as well as the hysteresis width. The variations of transition temperature and hysteresis width with withdrawal speed during coating are shown in Figure 4 (b). The transition temperatures were 61.3°C, 63°C, 67.4°C and 72°C while the hysteresis width was 6.0°C, 9.1°C, 9.5°C and 10.1°C for films synthesized at a withdrawal speed of 5 mm/min, 15 mm/min and 20 mm/min respectively and annealed at a common temperature of 500°C. The analysis shows that transition temperature and hysteresis width increased with increase in withdrawal speed. This is attributed to larger grain size as the thickness of the films increased and also increase of cracks density as the thickness increased may have resulted in increased transition temperature and hysteresis width due to numerous transition points and hysteresis loops whose totality blurred and broadened the switching [19]. Sample film synthesized at a withdrawal speed of 5 mm/min had lowest transition temperature and hysteresis width. This film may have had less cracks and smaller crystals resulting to improved crystallinity. Higher number of grain boundaries (smaller grain size) provides a greater number of nucleating defects which in turn reduces transition temperature and hysteresis loop [13].

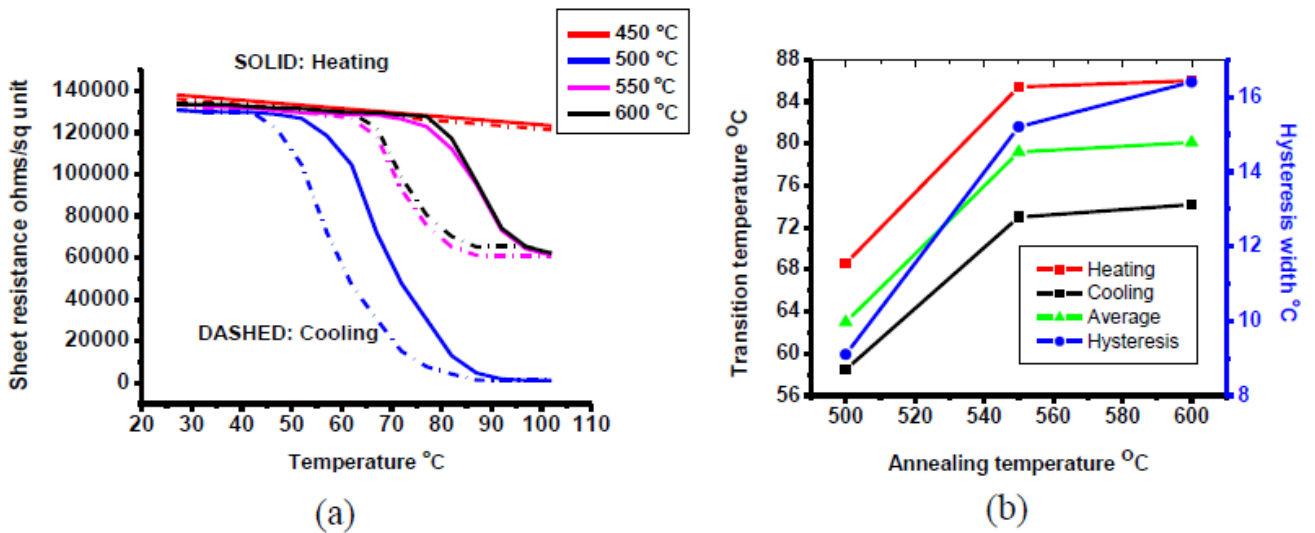


Figure 3: (a) Temperature dependent sheet resistance of films annealed at different annealing temperatures but same withdrawal speed of 10mm/min. (b) Plot of hysteresis width and transition temperature against annealing temperature

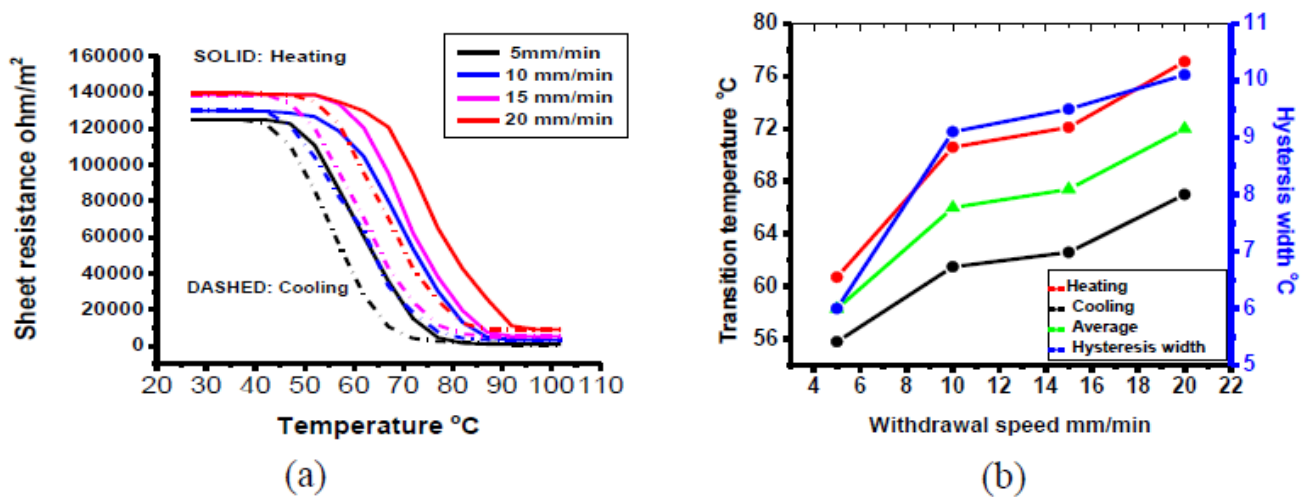


Figure 4: (a) Temperature dependent sheet resistance of films deposited at different withdrawal speeds and annealed at the same temperature of 500°C. (b) Plot of hysteresis width and transition temperature against withdrawal speed

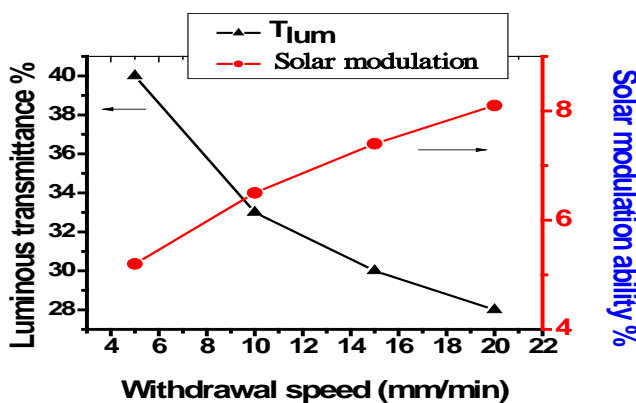


Figure 5: Showing the variation between the luminous transmittance and solar modulation ability for the films synthesized at different withdrawal speeds and annealed at the same optimum annealing temperature of 500°C

Thermochromic performance of the films obtained by withdrawal speed of 5 mm/min and annealing temperature of 500°C is elucidated in Figure 5 (a) in terms of trade-off between luminous transmittance and solar modulation

ability. Integral luminous transmittance (T_{lum}) and solar transmittance (T_{sol}) were calculated using equation 1 [3], while the solar modulation ability (ΔT_{sol}) was calculated using equation 2 [18]. The analysis shown in Figure 5 (a) elucidates that luminous transmittance decreased with increase in dip-coating withdrawal speed which depicts increase in thickness. This is attributed to increased absorption by VO_2 as thickness increased [11,13].

Contrary to luminous transmittance, solar modulation ability (ΔT_{sol}) increased with increase in dip-coating withdrawal speed. This is attributed to increased NIR modulation as thickness increased with increase in withdrawal speed. Thicker films have higher density of free carriers which result in increased reflectance of low energy photon in the IR region [21]. All solar modulation abilities obtained were less than 10% similar to majority of reported solar modulation abilities [13,23,24,25]. However, modulation ability of below 10% is not efficient enough for energy-saving function. This calls for more work to be done to find out how to improve solar modulation ability past 10%. Multilayer structures have been reported to improve balance between luminous

transmittance and solar modulation to 54 % and 16.1 % respectively [24]. Nanoparticles have also been reported to improve the trade-off between the two parameters [25]. Trade-off between luminous transmittance and solar modulation ability is vital in evaluating films performance. From Figure 5, the balance between luminous transmittance and solar modulation ability were as follows: 5 mm/min (40 %, 5.2%), 10 mm/min (32.9%, 6.5%), 15 mm/min (30%, 7.4 %) and 20 mm/min (28%, 8.1%) respectively. The withdrawal speed of 5 mm/min gave the best balance between the two parameters for the method of fabrication used.

4. Conclusion

The pure VO₂ thin film was successfully obtained by thermal reduction of V₂O₅ thin film at 500°C for 30 min under inert atmosphere with argon flowing at 100 sccm. The films showed comparable solar modulating ability and luminous transmittance to those previously reported and had metal-to-insulator transition temperature (τ_c) of 61.2°C, lower than that of typical value of 68°C. Deposition withdrawal rate of 5 mm/min followed by annealing at 500°C produced crystalline films with minimal cracks, sharper transition and relatively large transition amplitude with good luminous transmittance. The obtained films have outstanding thermochromic properties. The resistance of obtained film can change by 2 orders of magnitude, which is very promising in commercial energy saving windows. There is a possibility of better window performance if the films are deposited on a crystalline surface like graphene, FTO, sapphire etc. Luminous transmittance of 55% or more and solar modulation ability of over 10 % are required for practical smart windows in buildings.

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