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Investigation of Thermochromic and Optical Properties of VO_2 Thin Films Derived from Thermal Reduction of V_2O_5 Deposited on Graphene

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Abstract Vanadium dioxide has been of interest for thermochromic smart windows to control the near infrared radiation (NIR), but suffers limitations due to high transition temperature, low luminous transmittance and low solar modulation ability. In this paper, we report on low switching temperature and improved balance between luminous transmittance and solar modulation ability of VO_2 derived from thermal reduction of sol-gel deposited vanadium pentoxide (V_2O_5) on graphene. Thermal reduction of vanadium pentoxide (V_2O_5) was done in an innert atmosphere of flowing argon gas under normal atmospheric pressure. The optical properties of thermally reduced films were investigated using UV-VIS-NIR spectrophotometer while transition temperature was determined by measuring sheet resistance as a function of temperature. The films revealed semiconductor to metal transition after investigation. An analysis of transmittance showed an improved NIR switching efficiency of 46.86% for VO_2 on graphene compared to 41.79 for VO_2 on bare glass. Resistance drops corresponding to 2 and 3 orders of magnitude for VO_2/glass and VO_2/graphene /glass respectively were realized. VO_2 film on graphene/glass substrate had a transition temperature of 55.4 ^oC lower than 61.2^oC for VO_2 on bare glass substrate. The low Semiconductor-Metal Transition (SMT) temperature and the enhanced trade-off between luminous transmittance and solar modulation ability are noted to emanate from the increased crystallinity and nano-scale crystallites of VO_2 films enhanced by graphene matrix. The results reveal that graphene enhanced solar modulation ability and lowered transition temperature through structural ordering and nanoscale reduction of VO_2 crystallites.

Keywords: *Vanadium dioxide, graphene, transition temperature, smart window, near infrared radiation*

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1. Introduction

VO_2 undergoes a fully reversible semiconductor-metal transition (SMT) at a temperature of about 68°C, coupled with a structural phase transition (SPT) between monoclinic VO_2 (M) phase and rutile VO_2 (R) phase [1,2]. To take advantage of interesting functions due to temperature–dependent switching, VO_2 has been used in various applications for sensing and in optical communications such as in IR bolometers, photonic crystals and its application as a switchable window glazing for energy efficient application has also been discussed for decades [3,4]. However the practical use of VO_2 for energy efficient windows has long been hampered by low luminous transmittance, low solar modulation ability and high transition temperature [5]. Again growth of VO_2 films on amorphous substrates like glass does not easily enhance crystallinity at relatively low annealing temperatures [6]. The microstructure and properties of VO_2 films exhibit strong dependence upon the substrates as well as the buffer layers used. By varying the substrates used, the crystallization behavior (amorphous, polycrystalline or epitaxial film), transition temperature and hysteresis width of VO_2 films can be regulated. To date, buffer layers of SiO_2, ZnO, SiNx, RuO_2, TiO_2 and doping metals (V, W, Fe and Ni**)** have been used [4,7]. Graphene, which is recognized as a zero-gap semiconductor (namely, a semimetal), is a two dimensional (2D) hexagonal honeycomb structure and possesses excellent carrier mobility $\approx 200000\ cm^2\ V^{-1}\ S^{-1}$ and thermal conductivity $\approx 5.0 \times 10^3\ W\ m^{-1}\ K^{-1}$ [8]. Based on its unique properties, one can expect that graphene has a potential to act as a functional buffer layer. However, it is still a mystery how a graphene layer will influence the microstructure and properties of VO_2 films, which needs to be investigated to elucidate its effects as a buffer layer. Graphene has an advantage of high optical transmission, thermal stability and mechanical flexibility. Graphene serves to aid the formation of densely interlinked VO_2 nanocrystals [9]. A higher density of grain boundaries (smaller grain size) provides a greater number of nucleating defects which in turn reduces

transition temperature. Similarly a higher number of grain boundaries reduce hysteresis width, that is, the difference between transition temperature in heating and cooling [5,9,10]. Moreover, the defects in VO_2 nanoparticles can act as nucleation sites of the phase transition [10]. It has been reported that, sharp SMT accompanied by narrow hysteresis width is aided by stoichiometric VO_2 [11]. As a result of epitaxial growth, stoichiometry for graphene supported VO_2 is expected to be universal across the VO_2 film thickness. It has also been reported that, the magnitude of change in resistance and the narrowness of the hysteresis are indicators of how close the stoichiometry is to 1: 2 for VO_2 [10,11]. Graphene aids the reduction of VO_2 crystals size to nanoscale which then makes the phase transition temperature to reduce. Depression of phase transition temperature is also attributed to high thermal conductivity of graphene which ensures efficient transfer of heat from graphene to VO_2 [9]. By taking advantage of a tunable localized plasmon resonance in metallic state VO_2 nanoparticles, the optical absorption at $\tau > \tau_c$ can be shifted to a shorter wavelength in the near infrared range where the solar intensity is high, thereby improving the modulation of solar transmittance (ΔTsol) through put. It has been reported that nanothermochromics works very well indeed, and the luminous transmittance and solar transmittance modulation can be significantly improved [5,10]. In this study, VO_2 thin film is coated on bare glass and again on graphene supported by glass substrate. The films were analyzed in terms of thermochromic, electrical and optical properties using sheet resistance and UV-VIS-NIR spectrophotometry. This work is geared towards investigation of effect of graphene on thermochromic properties of VO_2 derived from thermally reduced sol gel deposited V_2O_5 on graphene.

2. Experimental Procedure

1 g of V_2O_5 powder was dissolved in hydrogen peroxide (H_2O_2, 30%, 100 ml) at room temperature 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 30 s while stirring. The stirring continued while oxygen gas was released until a clear orange-yellow solution was formed. After the orange-yellow color appeared gelation started and lasted until a red-brown gel was formed ($V_2O_5.2H_2O$). The gel was allowed to age in the open glass beaker under ambient temperature to form homogeneous dark red gel.

Before deposition, glass samples measuring 2cm by 2cm were cleaned successively in detergent, acetone, ethanol and distilled water. The glass substrates were rinsed using distilled water then dried with pressurized warm air before dehydrating them on a hot plate. Dip coating method was used to coat the samples by dipping the substrate in the gel at a constant speed of 10 mm/min to allow and ensure homogeneous wetting of the surface. After dipping was over, the substrate was held inside the gel for 5 min to allow sufficient interaction of the gel with substrate surface for complete wetting. The substrates were withdrawn at a constant speed of 5 mm/min to entrain a uniform thickness thin film. The deposited films were allowed to dry in air at ambient temperature for 1 hour before subjecting them to annealing at a temperature of 500°C.

After the Samples were placed in a horizontal tube furnace, argon gas was pumped into the furnace at a rate of 300 sccm for 10 min to drive out air and then lowered to 100 sccm during heat treatment. After annealing, the furnace was allowed to cool naturally where the cooling rate was controlled at 5°C/minute until the temperature reached 100°C. The furnace was then allowed to cool naturally to room temperature after which the samples were retrieved from the furnace for analysis.

To determine optical properties, transmittance spectrum was measured using UV-VIS-NIR spectrophotometer (JascoV-530) equipped with a custom-built heating unit. The measurements were performed in the wavelength range 250-2500 nm at sample temperature below and above critical temperature (transition temperature). Optical performance was done using simulated solar irradiation of 1000W/m^2 (AM 1.5) for the UV, luminous light and IR regions individually. The integrated luminous transmittance and solar transmittance were calculated using equation 1while the solar modulation ability of the films was calculated using equation 2. The measured parameters in the optical characterization were also used to evaluate thermochromic performance of the films.

$$T_i = \int \left(\phi_i(\lambda) T(\lambda) d\lambda / \phi_i(\lambda) d(\lambda) \right) \quad (1)$$

Where T(λ)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.

The corresponding domains of integration were 280-400 nm, 400-780 nm and 750-2500 nm for UV, luminous light and IR regions respectively.

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

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

Electrical properties were analyzed through sheet resistance (R_s). 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°C/min. The 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. Determination of magnitude of change in sheet resistance (R_s) between the temperature driven states of VO_2 was a good indicator of the achievement of crystalline VO_2.

3. Results and Discussion

3.1. Optical Properties

The transmittance spectrum for VO_2 on bare glass and VO_2 on graphene buffer layer as a function of wavelength (250-2500nm) above and below transition temperature are as shown in Figure 1. The impact of the composition and structure on the optical properties was very clear from the

UV-VIS-NIR spectrophotometry measurements. The transmittance at 25°C increases steeply towards long wavelengths whereas it decreases at 90°C. This is attributed to the increase in IR-reflecting behavior of the high temperature metallic phase.

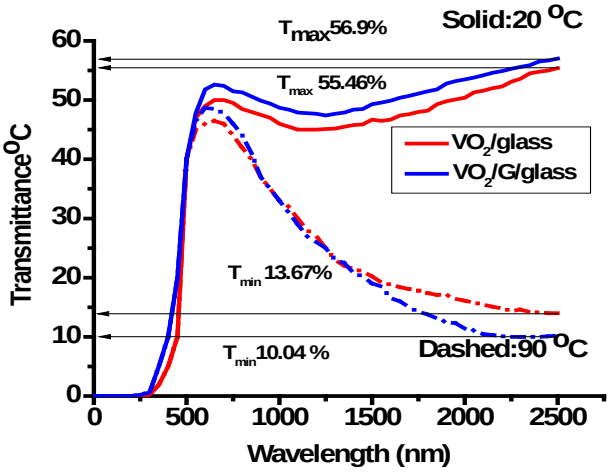

Figure 1. Transmittance spectra of VO_2 on bare glass and on monolayer graphene

According to the transmittance spectra, optical properties are significantly different from each sample. Thermochromic property of VO_2 are more pronounced in graphene supported sample than in graphene free sample, where NIR modulation was revealed in the two samples when the transmittance of the films where measured at 25°C and 90°C. The switching efficiencies were 41.79% and 46.86% for VO_2/glass sample and VO_2/graphene/glass sample respectively. Higher switching efficiency of VO_2 on graphene is attributed to nanocrystalline structure of VO_2 enhanced by graphene matrix [9]. Coarse structure with large crystals of VO_2 on bare glass may have caused scattering of light in the visible region resulting to lower transmittance [10]. In addition, reduction of crystal size to nano-scale resulted to increase in band-gap. Increased band gap caused less changes in the free carriers transitions (low absorption) resulting to higher transmittance of the semiconductor phase of VO_2 on graphene [11]. Graphene serves to aid formation of highly interlinked VO_2 nanocrystals [9]. By taking advantage of a tunable localized plasmon resonance in metallic state VO_2 nanoparticles, the optical absorption (at $\tau > \tau_c$) can be shifted to a shorter wavelength in the near infrared range where the solar intensity is high, thereby improving the modulation of solar transmittance (ΔT_{sol}) through put [5]. It has been reported that nanothermochromics works very well indeed, and the luminous transmittance and solar transmittance modulation can be significantly improved [5,12].

3.2. Sheet Resistance Measurements

The results showing variation of sheet resistance with temperature for VO_2 thin films on glass and VO_2 thin films on mono-layer graphene measured using four point probe are demonstrated in Figure 2. A two-step decrease in sheet resistance (two points of inflexion) was observed in the heating loop for both samples, as reported earlier [14]. VO_2/graphene/glass sample exhibited a sharp resistance drop from 1.20×10^5 to 1.2×10^2 Ω/sq. compared to VO_2/glass sample which dropped from 1.25×10^5 to 1.2×10^3 Ω/sq. Such resistance drops corresponds to about 2 and 3 orders of magnitude for VO_2/glass and VO_2/graphene /glass respectively. Less sharp resistance drop for VO_2 on bare glass could be as a result of presence of large number of microscopic crystals each characterized by its own hysteresis loop, which resulted to blurred and broadened switching [15]. From the literature, this can be attributed to lack of enhancement towards better crystallinity because of the amorphous nature of glass and common soda lime glass that may have diffused into the VO_2 film resulting to $Na_xV_2O_5$ material that lacks the thermochromic properties that makes VO_2 an attractive material for smart windows and other applications [12]. This characterization elucidates that the average (between cooling and heating) which gives the transition temperature were 61.2°C and 55.4°C for VO_2/glass and VO_2/graphene/glass respectively. Hysteresis for VO_2/glass and VO_2/ graphene followed the same trend at 6.2°C and 5.0°C respectively as shown in Figure 2.

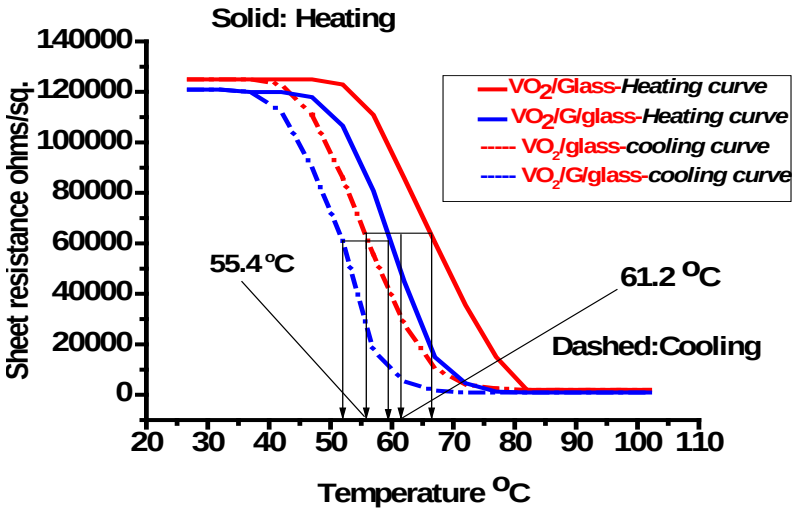

Figure 2. NIR switching and hysteresis loops for VO_2 films on bare glass and on monolayer graphene, measured using four point probe

Under wider perspective, depression of phase transition and hysteresis width have several attributes; structural ordering, strain, doping with other transition metals and scaling to nano-scale dimensions [6,7,9,16]. Factors such as grain size, residual stress, percent crystallinity and impurities can affect the transition temperature substantially [12]. Since the VO_2 preparation described here does not use any transition metal, we attribute reduction of the phase transition temperature to the effect of graphene buffer layer on reduction of VO_2 crystal to nanoscale.

The graphene support behaves as an electron donor and provides electrons for VO_2, which can thus increase the electron density in the VO_2 film and modify the electronic structure of VO_2 [17,18]. Thus, such an increase in electron density in the VO_2 film, especially upon light irradiation, will consequentially distabilize the semiconductor phase of the thermochromic VO_2 film on the basis of the theory of Zylbersztejn and Mott, in which the SMT of the VO_2 is shown to be a Mott-Hubbard transition and driven by the increase in electron density. Therefore, once the electron density reaches a critical value, the SMT can be triggered and a metal phase can be generated [17,19]. Based on these analyses, the SMT of the thermochromic VO_2/graphene/glass film may be triggered at a relatively lower temperature than that of VO_2/Glass. In addition, with the high thermal conductivity reported for graphene, the efficient heat transfer from graphene to VO_2 may account for depression of SMT temperature.

4. Conclusion

The transition temperature of VO_2 thin films has been reduced using graphene as a buffer layer. This was revealed by sheet resistance measurements where VO_2 film on graphene/glass substrate had a transition temperature of 55.4°C lower than 61.2°C for VO_2 on bare glass substrate. The trade-off between the luminous transmittance and solar modulation ability improved substantially to 40% and 6.3% respectively with a remarkable improvement on ΔT_{sol} by 21.1% for VO_2/graphene films. This improvement is attributed to epitaxial growth of VO_2 film on graphene. Thus, graphene demonstrated a potential of being used as a buffer layer to enhance thermochromic and optical properties of VO_2 for applications such as in sensors, electrical switches, energy saving windows and other nano technology devices.

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