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Low-temperature synthesis of thermochromic vanadium dioxide thin films by reactive high power impulse magnetron sputtering

Asim Aijaz, Yu-Xia Ji *, José Montero, Gunnar A. Niklasson, Claes G. Granqvist, Tomáš Kubart

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden

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ABSTRACT

Thermochromic (TC) vanadium dioxide thin films provide means for controlling solar energy throughput and can be used for energy-saving applications such as smart windows. One of the factors limiting the deployment of VO_2 films in TC devices is the growth temperature τ_s. At present, temperatures in excess of 450 °C are required, which clearly can be an impediment especially for temperature-sensitive substrates. Here we address the issue of high τ_s by synthesizing VO_2 thin films from highly ionized fluxes of depositing species generated in high power impulse magnetron sputtering (HiPIMS) discharges. The use of ions facilitates low-temperature film growth because the energy of the depositing species can be readily manipulated by substrate bias. For comparison, films were also synthesized by pulsed direct current magnetron sputtering. Structural and optical characterization of VO_2 thin films on ITO-coated glass substrates confirms previous results that HiPIMS allows τ_s to be reduced from ~500 to ~300 °C. Importantly, we demonstrated that HiPIMS permits the composition and TC response of the films to be tuned by altering the energy of the deposition flux via substrate bias. An optimum ion energy of 100 eV was identified, which points at a potential for further reduction of τ_s thereby opening new possibilities for industrially-relevant applications of VO_2-based TC thin films. Weak TC activity was observed even at $\tau_s \approx 200$ °C in HiPIMS-produced films.

1. Introduction

Vanadium dioxide (VO_2) exhibits a reversible phase transition at a "critical" temperature $\tau_c \approx 68$ °C from a semiconducting and monoclinic state at $\tau < \tau_c$ to a metallic-like and tetragonal state at $\tau > \tau_c$, where τ denotes temperature [1]. Thin films of VO_2 possess thermochromic (TC) properties and display significant near-infrared (NIR) transmittance at $\tau < \tau_c$ and NIR reflectance at $\tau > \tau_c$ and are therefore of interest for energy-efficient windows regulating the throughput of solar energy in accordance with dynamic needs [2,3]. A number of challenges have to be overcome in order to make VO_2-based thin films practically useful for windows [4]: (i) τ_c should be decreased to the vicinity of room temperature as can be done by tungsten doping [5], (ii) the luminous transmittance should be increased which is possible by magnesium doping [6,7], (iii) the solar energy modulation at τ_c should be boosted as can be achieved by nanostructuring [8,9] and (iv) the further oxidation towards V_2O_5 should be impeded which can be accomplished by protective over-layers [10]. Another important parameter, which the present study focuses on, is the substrate temperature τ_s required for crystalline VO_2 thin film deposition. In the case of standard magnetron sputtering such as direct current magnetron sputtering (DCMS) and radio frequency magnetron sputtering (RFMS), $\tau_s > 450$ °C is typically required to obtain VO_2 films with good TC properties [9]; this temperature is undesirably high and prohibitive for low-cost web coating on temperature-sensitive substrates.

Low-temperature synthesis of metal-oxide thin films has been demonstrated by employing highly ionized deposition fluxes [11,12]. In this way, the energy input into the growing film can be significantly enlarged and readily controlled by electric fields. Highly ionized deposition fluxes also facilitate control over phase formation and resulting film properties [11,12]. The ionized fraction of the deposition fluxes in standard magnetron sputtering is typically few percent [13], and therefore low-temperature film synthesis using these methods is challenging.

High power impulse magnetron sputtering (HiPIMS) is a variant of magnetron sputtering wherein a very high ionization level of the sputtered material is achieved [13,14]. Low-frequency operation in HiPIMS with a duty cycle of 1–5% is typical which leads to 2–3 orders-of-magnitude higher electron densities than in standard sputtering and to corresponding increases in the

* Corresponding author.
E-mail address: yuxia.ji@angstrom.uu.se (Y.-X. Ji).

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ionization of the deposition fluxes [13,15]. Other advantages of HiPIMS are its compatibility with existing magnetron sputtering systems and its scalability.

Fortier et al. [16] reported deposition of TC VO_2 thin films using HiPIMS at $\tau_s \approx 300$ °C. Films with greater than 60% NIR transmission modulation at a wavelength λ of 2500 nm were deposited onto glass without any nucleation-promoting "seed" layer. This first report [16] is very encouraging, but more work is needed in order to further reduce τ_s and identify deposition conditions compatible with polymer substrates.

An important parameter when synthesizing films using highly ionized deposition fluxes is the selection of energy for the depositing species. Manipulating the energy—for example by varying the substrate bias potential—facilitates control over film structure and phase formation, and an optimum energy could also lead to reduction in growth temperatures [17,18]. We therefore synthesized V oxide thin films by use of HiPIMS and investigated the effect of ion energy during film growth on the structural and optical properties as well as on τ_s. RF biasing of the substrate, as used by Fortier et al. [16], is difficult to control in combination with HiPIMS, and therefore we deposited films onto electrically conducting ITO (In_2O_3:Sn) coated glass substrates. In order to establish a correlation between deposition conditions and ensuing properties of VO_2 films, we investigated the discharge current characteristics using different gas compositions. Discharge characteristics suitable for VO_2 film growth were identified by analyzing the waveforms of the discharge current.

The composition and crystallinity of the V oxide films were investigated for growth temperatures in the $200 < \tau_s < 500$ °C range and for different energies of the deposition flux, controlled by a substrate bias potential. Furthermore we studied optical properties with regard to visible light ($400 < \lambda < 700$ nm) and NIR radiation ($700 < \lambda < 2500$ nm). We also probed the structural properties of the films. For comparison, we investigated discharge characteristics and properties of films deposited by pulsed direct current magnetron sputtering (pDCMS).

2. Experimental details

Experiments were performed in a cylindrical (height 400 mm, diameter 460 mm) vacuum chamber (Kurt J. Lesker CMS-18) equipped with a load-lock and evacuated through a cryopump (CTI CryoTorr 8). The base pressure was kept below 10^{-5} Pa. Argon and oxygen, both of 99.9995% purity, were introduced into the chamber at flow rates ϕ_{Ar} and ϕ_{O_2}, respectively, set by mass-flow controllers. We used $\phi_{Ar} = 50$ sccm and $0 \le \Theta \le 0.28$, where the oxygen fraction is $\Theta \equiv \phi_{O_2}/(\phi_{Ar}+\phi_{O_2})$. Ar was injected near the target whereas O_2 was introduced into the chamber by use of a gas distribution ring around the substrate holder. The importance of the "gas geometry" for VO_2 deposition was highlighted in an earlier study [9]. The working pressure was adjusted via a throttle valve, and the total pressure was kept constant at 0.53 Pa. A 6-mm-thick and 100-mm-diameter circular vanadium disk (99.995%) was employed as a sputter target.

The HiPIMS power to the target was supplied via a SPIK 1000 A pulsing unit (Melec) fed by an Advanced Energy Pinnacle DC power supply. The pulsing unit was controlled by an arbitrary-function generator (Tektronix AFG 3200) and was capable of generating rectangular-shaped unipolar voltage signals. The discharge current I_D and voltage U_D were monitored by use of current and voltage transducers and were recorded on an Infiniium (DSO 9064 A) digital oscilloscope. The HiPIMS power was supplied with a pulse frequency of 500 Hz and a pulse on-time of 100 μs that resulted in a duty cycle of 5%. An average power of 600 W was used during all experiments, as calculated from values of I_D and U_D. The pDCMS power to the target was supplied by an Advanced Energy Pinnacle Plus power supply with a pulse frequency of 100 kHz and a pulse off-time of 1.6 μs. The average power was 600 W for all pDCMS experiments, which is the same as for HiPIMS.

Vanadium oxide films were deposited onto Si(100) and ITO-coated glass substrates placed 180 mm from the target on a rotatable substrate holder set at 20 rpm. Transparent and electrically conducting ITO-coated glass substrates with a sheet resistance of 60 Ω were employed to facilitate the use of substrate bias. Furthermore, it has recently been shown that ITO promotes crystallization of VO_2 and leads to a broadened process window for sputter deposition [19]. Vanadium oxide films were deposited by HiPIMS at $200 < \tau_s < 500$ °C. Substrates were heated by a backside radiative heater. A bias potential U_B was applied at the substrate holder for controlling the ion energy using another Advanced Energy Pinnacle Plus power supply with a pulse frequency of 250 kHz and a pulse off-time of 0.5 μs. U_B was varied between the floating potential U_{fl} and −200 V. Film thickness d was determined by x-ray reflectivity (XRR) using a Philips X'Pert diffractometer operating in reflection configuration and using CuK_α radiation at a wavelength of 0.154 nm. Specifically, d was determined by fitting XRR data to curves generated by the X'Pert reflectivity program [20]; details on this method are given elsewhere [21]. The V oxide films reported on below were confined to the $50 < d < 120$ nm range.

Film crystallinity and structure were investigated using the same diffractometer but operating in grazing incidence x-ray diffraction (XRD) configuration and scanning over $10 < 2\theta < 80°$. Structural properties were also inferred from Raman spectroscopy, using a Renishaw inVia Raman microscope with a solid-state laser ($\lambda = 532$ nm), and by recording surface topographies using a scanning electron microscope (Merlin, Carl Zeiss).

Spectral optical transmittance $T(\lambda)$ of the V oxide films was recorded on a Perkin-Elmer Lambda 900 spectrophotometer with integrating sphere and using a sample holder with a heater around the edges of the sample. The TC behavior was probed by measuring $T(\lambda)$ at $300 < \lambda < 2500$ nm for $\tau < \tau_c$ and $\tau > \tau_c$, specifically for ~20 and ~90 °C.

3. Results

3.1. Characterization of the HiPIMS process

We first characterized the deposition process by analyzing the HiPIMS discharge current and voltage with respect to Θ. Fig. 1a shows time-dependent waveforms of I_D and U_D for the HiPIMS conditions under which the VO_2 films were prepared, and corresponding waveforms for the metal-mode (without oxygen) are presented for comparison. The peak current density is ~0.5 A/cm^2 and leads to a peak target power density of ~0.5 kW/cm^2, which is about two orders-of-magnitude higher than that obtained under pDCMS conditions. The HiPIMS process was operated with substantially higher discharge current densities than the pDCMS process, but the average target power densities were the same, i.e., ~7.5 W/cm^2. The waveform and the peak value of I_D at the VO_2 operation point are clearly different for the oxide mode (oxidized sputter target surface) and the metal mode (for pure Ar atmosphere). In the metal mode, I_D exhibits a fast initial rise, reaches a maximum at ~50 μs and then decays until the end of the pulse. In the oxide mode, on the other hand, I_D continues to increase until the end of the pulse. The peak value of I_D is ~30% higher in the oxide mode than in the metal mode.

In order to elucidate this change in the waveform of I_D, we investigated the gradual modification in the shape and peak value