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Thermochromic VO_2 thin films deposited by HiPIMS

J.-P. Fortier, B. Baloukas, O. Zabeida, J.E. Klemberg-Sapieha, L. Martinu *

Department of Engineering Physics, École Polytechnique de Montréal, P.O. Box 6079, Montreal, Quebec H3C 3A7, Canada

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ABSTRACT

Thermochromic VO_2 windows have the potential of managing heat transfer in an efficient way. However, several problems such as a high transition temperature ~68 °C and high deposition temperatures (over 400 °C) limit their applicability. We present a novel approach for the fabrication of thermochromic VO_2 films in which High Power Impulse Magnetron Sputtering (HiPIMS) is used for deposition. Indeed, HiPIMS is known for its high ionization degree of sputtered species that allows one to control the evolution of the film microstructure by ion bombardment. The optical and other physical properties of the obtained HiPIMS VO_2 coatings are first presented. Based on spectrophotometry, ellipsometry, AFM, SEM, TOF-SIMS, Raman spectroscopy and XRD results, we show that it is possible to deposit dense stoichiometric crystalline VO_2 films at lower substrate temperatures (300 °C) compared to other approaches. These films exhibit a high infrared modulation ($\Delta T_{2500\ nm}$ of 61% between 30 °C and 90 °C), low surface roughness (R_{rms} under 10% of total thickness for films approximately 100 nm thick), and lower transition temperatures than the bulk material (T_c down to 50 °C for thicker films).

1. Introduction

In a worldwide effort to limit global warming, energy-efficient technologies such as smart windows are being proposed as one possible solution to reduce energy consumption [1]. Currently, low-emissivity (low-e) windows are widely in use to control solar input. However, their passive nature offers low versatility in environments where the climate varies from season to season [1]. Therefore, future opportunities are seen in active technologies such as electrochromic, photochromic and thermochromic glazings.

Thermochromic VO_2 coatings, which have been studied for several decades [2], are of growing interest for window applications since the material behaves as a self-tunable infrared (IR) filter [3]. VO_2 films are also under consideration for optical switching and smart radiator devices [4,5]. At ambient temperatures, the material is characterized by a monoclinic structure, which exhibits semiconducting properties and a considerable IR transparency. Above a critical temperature T_c of 68 °C, the bulk oxide reorganizes and adopts a tetragonal lattice, leading to a metallic-like behavior and high IR reflectivity [6].

Current drawbacks surrounding the commercialization of VO_2 include a high transition temperature, high deposition temperatures, a low visible transmittance and an unattractive color [6]. Some of these issues have recently been addressed; mainly, the T_c has been lowered to more convenient temperatures by doping with tungsten or other elements such as Mo, F and Nb [6], whereas the low transmittance has been improved with the use of interference or Mg doping [6,7]. The greenish color of VO_2 has also been modified by Au doping [3]. These solutions, which have yet to be optimized and possibly combined, appear promising for future commercial applications [2]. Yet, despite this progress, there is still one remaining issue which complicates large scale production, that is the high deposition temperature of typically over 400 °C which is required for the formation of crystalline thermochromic VO_2 [6]. Indeed, this issue also includes other aspects such as temperature uniformity over large surfaces as well as substrate heating and cooling procedures. The present work is thus primarily motivated by the prospects of decreasing the film deposition temperature, possibly to values that would allow one to apply thermochromic VO_2 coatings on sensitive substrates such as flexible polymers.

In this context, we specifically investigate the use of High Power Impulse Magnetron Sputtering (HiPIMS). Indeed, recent studies on HiPIMS suggest that one can obtain denser crystalline films compared to conventional direct current or radio-frequency magnetron sputtering (dcMS or rfMS) due to the very high ionization degree of the sputtered material [8]. In addition, HiPIMS is particularly suitable for reactive deposition due to a possibility of suppressing the hysteresis effects caused by target poisoning [9]. Since sputtered metal atoms are highly ionized, their ion bombardment energy and ion flux toward the substrate can be

* Corresponding author. Tel.: +1 514 340 4099; fax: +1 514 340 3218.
E-mail address: ludvik.martinu@polymtl.ca (L. Martinu).

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controlled by substrate biasing, which then influences the film growth and the resulting microstructure. Consequently, due to this additional energy, substrate heating can be lowered.

Using the HiPIMS deposition approach, we demonstrate the fabrication of dense stoichiometric VO_2 films at low substrate temperature (300 °C), while achieving an optical transmission difference at 2500 nm between the isolating (30 °C) and the metallic (90 °C) states of 61% and maintaining an optical transmission of about 40% in the visible region.

2. Experimental methodology

2.1. Deposition process

VO_2 films were fabricated using a turbomolecularly pumped magnetron sputtering system [10] equipped with a HiPIMS *Huettinger HMP 2/1* power supply. B270 substrates (5 cm × 5 cm) were placed at a distance of 15 cm from the target and were heated by a conduction heater from the back side to a surface temperature of 300 °C or less. The substrate surface temperature was measured before plasma ignition using a thermocouple firmly touching the substrate surface. We estimate the precision of these measurements to be about ±5 °C for all our HiPIMS-deposited films. Additional heating due to the plasma process (bombardment by ions and neutrals as well as radiation coming from the target and the plasma zone) can also possibly contribute to a further increase of the substrate temperature. We have not quantified this effect; however, taking into account that the present average power densities are similar to other more traditional sputtering processes we can consider this effect as comparable. Also note the relatively large target-to-substrate distance of 150 mm which will limit the samples exposure to additional heating. A continuous wave radio frequency (13.56 MHz) power was applied at the substrate holder in order to facilitate HiPIMS plasma ignition and favor ion bombardment. The resulting bias voltage was −200 V between the individual HiPIMS pulses. Optical emission spectroscopy (OES) measurements were performed using an optical fiber probe installed in the deposition chamber to collect plasma emission approximately 5 cm above the target. Although not shown here, OES was used as a tool to monitor the intensities of sputtered species to optimize the process, and to assure its reproducibility. The current and voltage waveforms were monitored with the help of a *Tektronix TDS2014B* digital oscilloscope.

The deposition process of the VO_2 films proceeded in three steps: (i) A 4-inch-diameter pure vanadium target (99.5%) was exposed to a HiPIMS discharge with an average power of 875 W and pre-cleaned in pure argon for 5 min. (ii) During the target conditioning phase, oxygen was introduced into the chamber and the discharge was left to stabilize for approximately 10 min in order to obtain a steady reactive sputtering regime. (iii) Once such a regime had been reached, the target shutter was opened for deposition. The optimized discharge characteristics were as follows: a working pressure of 10 mTorr, an oxygen-to-argon flow ratio of 0.06 at a pulse length of 45 μs, a pulse frequency of 200 Hz and a pulse peak voltage of 900 V. Under these conditions, a deposition rate of 0.8 ± 0.1 Å/s was obtained. A systematic study of the effect of different discharge parameters on the properties of VO_2 films will be the subject of a separate publication.

2.2. Film characterization

Normal incidence spectral transmittance (T) of VO_2 films was obtained at different temperatures using a *PerkinElmer Lambda19* spectrophotometer for wavelengths ranging from 400 nm to 2500 nm. A home-made heat cell was used to control the samples' temperature between 25 °C and 90 °C. The samples were first gradually heated and then cooled to ambient temperature. Once the hysteresis curve was obtained, the transition temperature could be determined by placing a horizontal line at $T = T_{minimum} + 0.5\Delta T_{2500\ nm}$ and positioning the transition temperature at the half-width of the hysteresis curve at that point (see Fig. 8).

The optical constants (n and k) of the films were determined from spectroscopic ellipsometry measurements. Ellipsometric data (Ψ and Δ) were acquired for wavelengths between 400 and 1700 nm using a *J.A. Woollam Co. RC2* ellipsometer. The measurements were performed at low and high temperature states (30 °C and 90 °C) using a heat cell mounted on the *RC2*. The spectral characteristics were extended to 2500 nm for the low temperature state using an *IR VASE* ellipsometer (also from the *J.A. Woollam Co.*). Modeling was performed using a combination of *WVASE32* and *CompleteEASE* (*J.A. Woollam Co.*) software packages.

The ellipsometric model used to fit the Ψ and Δ values was relatively simple: it consisted of a 2 mm thick B270 glass substrate, followed by the VO_2 coating and a Bruggeman effective medium approximation (EMA) layer to simulate surface roughness. Multiple oscillators were required to replicate the experimental data. Specifically, for both low and high temperature modeling, a general oscillator function consisting of a Tauc–Lorentz and Lorentz oscillators for the UV absorption, and an additional Lorentz oscillator for the IR absorption was sufficient to obtain a good fit. In addition, an infrared pole, which represents contributions to the real part of the dielectric permittivity by oscillators outside the measuring range, was also applied to fine tune the model in the IR. Note that in order to increase the accuracy of the model, the ellipsometric data were also combined with transmittance measurements extending to 2500 nm.

An *ION-TOF SIMS IV* time-of-flight secondary ions mass spectrometry system was used to obtain the compositional profiles of the films as a function of depth. The measurements were performed in the negative ion mode with Cs etching atoms to study the sputtered negative ions. The microstructure was assessed using X-ray diffraction (XRD) measurements at a grazing angle of 1° using a *Philips X'Pert* diffractometer. The surface topography and phase as well as the roughness of the coatings were determined by atomic force microscopy (AFM) using a *Digital Instruments Dimension 5000* apparatus. AFM images were acquired in air at room temperature in the tapping mode. Phase imaging was applied to evaluate surface homogeneity. A *Raman Renishaw RM3000* spectrometer equipped with a 514.5 nm Ar laser was used for chemical bond analysis. Finally, to measure the thickness and examine the microstructure of the samples, film cross-sections were observed with a *JEOL JSM-7600TFE* field emission scanning electron microscope (SEM). In order to limit charging effects, samples were coated with carbon prior to observation.

In this work, most of the film characteristics are reported for 75 and 185 nm thick coatings. While the former one exhibits the highest IR modulation and the best thermochromic performance, the latter one was deposited in order to better observe the growth trends and surface topography during the AFM measurements.

3. Results and discussion

3.1. Microstructure and composition of the HiPIMS VO_2 films

The HiPIMS deposited VO_2 films were found to be polycrystalline. The XRD pattern of the 75 nm sample shown in Fig. 1 indicates the presence of (011) oriented crystals at $2\theta = 27.8°$ characteristic of monoclinic VO_2 (JCPDS card 44-0252). No peaks belonging to V_2O_5 or other crystalline forms of VO were detected.