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HiPIMS-deposited thermochromic VO_2 films on polymeric substrates

S. Loquai, B. Baloukas, O. Zabeida, J.E. Klemberg-Sapieha, L. Martinu*

Department of Engineering Physics, Polytechnique Montreal, Montreal, Quebec, Canada

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ABSTRACT

Thermochromic vanadium dioxide, VO_2, is a semi-conductor of major interest for energy control applications. Generally, the fabrication of high-quality VO_2 films requires a high deposition temperature over 400 °C which limits its large scale implementation as well as its compatibility with temperature-sensitive substrates. In this work, we demonstrate the deposition of thermochromic VO_2 thin films on flexible polymer substrates using High Power Impulse Magnetron Sputtering (HiPIMS); this process is known for its high degree of ionization, high plasma density and hence high ion flux towards the substrate that allows one to deposit crystalline films at lower temperatures in comparison with conventional sputtering techniques. We first describe the optimization approach of the HiPIMS process followed by the optical performance study of the resulting VO_2 films on Kapton polyimide substrates. The films deposited at temperatures as low as 275 °C are then analyzed by means of temperature-resolved spectrophotometry, XPS, ERD, RBS, Raman spectroscopy and spectroscopic ellipsometry. Optimized films show an infrared modulation $\Delta T_{2500\ \mathrm{nm}}$ of up to 50% with a transition temperature T_c close to the bulk temperature of 68 °C.

1. Introduction

Traditional glass windows, with their low thermal insulation properties, represent an energetically weak point of a building. This leads to undesirable energy gains and losses which need to be compensated by additional cooling or heating. In fact, in developed countries, temperature control in buildings by temperature management is estimated to account for more than 30% of the primary energy consumption [1]. Only in the US, the portion of this sector in the total consumption has increased from 34% in 1980 to 41% in 2010 [2]. The currently commercialized and popular solution is the installation of low emissivity (low-e) windows that offer passive heat transfer insulation leading to a decrease in the energy budget due to heating and cooling. However, in regions with distinct seasons, particularly in continental climates, the possibility of using dynamic (active) glazings for heat transfer control is expected to further reduce energy consumption. For a recent review on fenestration applications, see [3].

A particularly attractive option is the use thermochromic (TC) materials. Defined by a capacity to change their optical properties as a function of temperature, TC materials can be used to provide variable infrared transmittance. First reported by Morin in 1959 [4], these materials were highly explored in the late 1980s [5], with a regain of interest in the late 2000s. Of all the possible choices, vanadium dioxide, VO_2, has always been the main material considered for high performance TC systems in smart window applications for the simple reason that it possesses an intrinsic transition temperature, T_c, of 68 °C which is closer to room temperature than other inorganic TC materials. In its low temperature state ($T < T_c$) VO_2 displays a semi-conductor monoclinic crystaline phase with a high infrared (IR) transmission, and in its high temperature state ($T > T_c$), a metallic rutile crystalline phase with a lower IR transmission. Consequently, the induced transmission variation in the 1–20 μm spectral range is of interest for heat control applications. For example, transmission variations of up to 61% at a wavelength of 2.5 μm have been reported [6,7].

While of great interest, the commercial application of VO_2 films still faces multiple challenges which are being addressed by different researchers. First of all, the 68 °C transition temperature needs to be reduced closer to room temperature – this can be achieved by doping with W and other metals [7]. Similarly, the relatively low luminous transmittance, around 40% for conventional 60–80 nm VO_2 thick films, and the unpleasant greenish tint can both be addressed by doping [8], or by the addition of anti-reflection layers [9]. Finally, high performance VO_2 films require high deposition temperatures above 400 °C [10] that are not compatible with temperature-sensitive substrates. The latter problem represents the main motivation of the present study.

* Corresponding author.
E-mail address: ludvik.martinu@polymtl.ca (L. Martinu).

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It has recently been demonstrated that high-quality VO_2 films can be deposited at temperatures as low as 300 °C by using High Power Impulse Magnetron Sputtering (HiPIMS) [6,11]. Furthermore, the HiPIMS process results in high ionization of the sputtered material [12,13] that offers an opportunity to fine tune the ion bombardment energy and flux towards the substrate, thus leading to a better control of the film growth and of the resulting microstructure [14]. For example, it has been shown that by using HiPIMS dense and crystalline films of TiO_2 can be obtained at temperatures as low as room temperature [15], and that the use of HiPIMS in its reactive mode can lead to a reduction of hysteresis effects [16].

In the present work, we demonstrate the possibility to deposit high performance TC VO_2 films onto plastic substrates using HiPIMS. Specifically, we apply this approach to two types of flexible Kapton polyimides, namely the traditional yellow-colored Kapton HN as well as a new transparent and colorless Kapton CS. We first describe the optimization strategy of the HiPIMS process with respect to the optical performance criteria of the resulting films. The quality of the TC VO_2 layers is then examined by complementary chemical and structural analysis techniques, and we confirm that the films are highly crystalline and stoichiometric. The results suggest that roll-to-roll deposition of VO_2 films is indeed possible, thus opening new application opportunities such as lamination with glass for retro-fitted smart windows.

2. Experimental methodology

2.1. Substrates and deposition process

Two types of polyimide substrates were used throughout this study, namely a 50.8 μm thick yellow-colored Kapton HN and a 25.4 μm thick clear Kapton CS polyimide foil. Kapton HN is commercially available from E.I. du Pont de Nemours and Company (DuPont for short). Its ultimate temperature is 450 °C, and it is suitable for operation at temperatures in the 250–350 °C range. The Kapton CS substrate is a prototype colorless polyimide film manufactured by the same company. Due to its larger elastic modulus, we chose a 25.4 μm thick foil in order to obtain a similar rigidity as the Kapton HN. The ultimate temperature for Kapton CS is estimated at 350 °C, thus limiting the deposition to a lower temperature range. Additionally, glass and silicon substrates were added during deposition in order to allow for a comparison of the deposition rates and of the film properties.

The VO_2 films were deposited in a turbomolecularly pumped magnetron sputtering system [6] equipped with a 4-inch-diameter pure vanadium target (99.5%). The cathode was powered by a SIPP2000 HiPIMS power supply made by Melec GmbH. The current and voltage waveforms were monitored with a Tektronix DPO3014 digital oscilloscope using high current and high voltage probes. The substrates were placed on a copper plate at a distance of 15 cm from the target, and the substrate temperature (T_s), controlled by a radiative heater from the back side, was adjusted between room temperature (RT) and 400 °C. T_s was measured prior to plasma ignition using a thermocouple in contact with the substrate's surface. We estimate the T_s measurement precision to be about ±5 °C for all of our depositions. Indeed, the plasma process may provide additional heating by way of ion bombardment, fast neutrals' impacts and radiation from both the plasma and the target. While we did not quantify this increase of temperature, it should be similar to more conventional sputtering techniques at comparable average powers as reported by Cormier [17] and Lundin [18]. Also note that the temperature sensitivity of the substrates acted as probes as their physical properties would have been severely affected by a significant temperature increase.

The VO_2 film fabrication was optimized in three stages: a) by depositing VO_2 onto conventional borosilicate glass (B270), b) by the application of the pre-optimized process parameters to coat polyimide substrates, and c) by applying a TiO_2 seed layer on top of the polyimide; indeed, it is known from the literature that rutile TiO_2, in correspondence with rutile VO_2, has a similar lattice parameter which promotes the growth of crystalline VO_2 [19,20]. The films themselves were deposited in four steps: (i) the substrate was heated until it reached the desired stable temperature, (ii) the vanadium cathode was exposed to a HiPIMS discharge in pure argon and pre-cleaned for 5 min, (iii) oxygen was then introduced into the chamber and the discharge was left to stabilize for 10 min in order to obtain a steady reactive sputtering regime. During this stage, a radio-frequency power supply connected to the substrate holder was turned on in order to pretreat and clean the substrates. (iv) Finally, the target shutter was opened for deposition.

After optimization, the process parameters applied for all depositions were as follows: an argon working pressure of 9.7 mTorr (1.30 Pa), a pulse length of 45 μs, a pulse frequency of 200 Hz, and a pulse peak voltage of 900 V. The average discharge power was approximately 350 W, which is comparable to the one used in traditional RF and DC magnetron sputtering processes. Under these conditions, the deposition rates measured on the Si substrate was 0.32 Å/s. The final film thickness values were between 40 nm and 80 nm.

The radiofrequency (RF) power applied to the substrate holder produced a plasma which provided a stabilizing effect on the HiPIMS discharge as well as additional energy to the growing films by ion bombardment during the time-off period. The self-induced negative bias V_b was set at −200 V between the individual HiPIMS pulses. This value dropped to −30 V during each pulse. The process parameters for the deposition of VO_2 films and TiO_2 seed layers are summarized in Table 1 and Table 2.

2.2. Film characterization

Normal incidence spectral transmittance of the samples deposited on polyimide and on glass substrates was measured at different temperatures using a Perkin Elmer Lambda 1050 spectrophotometer for wavelengths between 250 nm and 2500 nm. A custom-made heat cell was used to gradually heat the samples from 25 °C to 90 °C at a controlled rate of 1°/min. Using the recorded spectral transmittance vs. temperature curve, the transition temperature could be assessed by using the inflection point of the measured temperature dependence (minimum of the first-derivative) for the heating phase (T_{up}) and the cooling phase (T_{down}). The transition critical temperature was then determined by simply averaging T_{up} and T_{down} as $T_c = \frac{T_{up}+T_{down}}{2}$.

The optical constants (n and k) of the films and substrates were determined from spectroscopic ellipsometry measurements using a RC2 ellipsometer from J.A. Woollam Co., Inc. The ellipsometric

Table 1
Deposition parameters for thermochromic VO_2 films and TiO_2 seed layers.

	VO_2	TiO_2
Target diameter [cm]	10.2	7.6
Pressure [mTorr](Pa)	9.7 (1.3)	4.0 (0.67)
O_2 to Ar ratio [%]	3.9 to 5.6	20
Average target power [W]	300–380	350
Average target power density [W/cm^2]	4.0–4.8	2
Target voltage [V]	900	412
Frequency [Hz]	200	DC
Pulse length [μs]	45	n/a
Film thickness [nm]	40–80	10