Solar Energy Materials & Solar Cells 160 (2017) 217–224

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

HiPIMS-deposited thermochromic VO_2 films with high environmental stability

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

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

ARTICLE INFO

Keywords:
High power impulse magnetron sputtering
Vanadium dioxide
Thermochromism
Durability
Environmental stability

ABSTRACT

A comparative study of the environmental stability of high power impulse magnetron sputtered (HiPIMS) and radio frequency magnetron sputtered (RFMS) thermochromic vanadium dioxide thin films in a highly oxidizing environment has been performed. We observe that RFMS-deposited VO_2 films quickly transform into V_2O_5 at 80 °C and 100% relative humidity while HiPIMS-deposited films retain their thermochromic behaviour at least three times longer. Following a thorough analysis of the films, this increase in performance is ascribed to the films' higher density and larger average grain size. The results indicate that the HiPIMS process provides sufficient durability for VO_2 films without the need for a diffusion barrier used in typical everyday conditions. Still, when a 35 nm thick SiN_x diffusion barrier is added on top of the HiPIMS VO_2 films, the thermochromic device shows less than 5% loss in thermochromic performance following extended accelerated ageing.

1. Introduction

Additional control of the thermal transfer properties of architectural glass through the implementation of smart windows is one of the most important avenues presently being explored to decrease the energy consumption of buildings [1]. In this respect, vanadium dioxide (VO_2), with its thermochromic (TC) properties, is a promising material. Indeed, VO_2 presents a reversible metal-to-insulator transition at a critical temperature T_C of 68 °C accompanied by a large modulation of its infrared (IR) transmission. Specifically, in the low temperature state ($T < T_C$), VO_2 is a semiconductor with a monoclinic crystalline structure which is transparent to IR whereas in the high temperature state ($T > T_C$), it presents a metallic-like rutile (tetragonal) crystalline phase with a low transmission in the IR due to a combination of increased absorption and reflection. For these reasons, this makes VO_2 one of the strongest candidates for smart windows [1] as well as for smart radiator devices for satellites [2,3].

For decades now, work has mostly concentrated on modifying the fundamental characteristics of VO_2 to compensate its application drawbacks such as changing its natural greenish tint by doping [4], decreasing the T_C closer to room temperature through doping [5], and increasing its luminous transmission through the implementation of VO_2-based interference filters [6], or by the dilution of VO_2 in the form of nanoparticles in a dielectric matrix (so-called nanothermochromics [7]).

However, there remains another important challenge associated with VO_2: its environmental instability. Indeed, vanadium oxide naturally transforms by a progressive oxidation process into the more stable V_2O_5 which, moreover, is well known to be soluble in water. Specifically, in the presence of oxygen, VO_2 will slowly transform into the intermediate oxides of V_6O_{13} and V_3O_7, before finally reaching the V_2O_5 phase [8].

The implementation of VO_2 thin films in ambient and humid water-containing environments thus leads to a relatively quick decrease in their TC performance. A typical way to protect a material from water and oxygen is obtained by the addition of an overlying diffusion barrier such as Al_2O_3, HfO_2, SiN_x, etc. In the specific case of VO_2, Saitzek *et al.* studied the effect of cerium oxide CeO_2 [9] on top of VO_2 in the context of variable infrared emissivity applications. They reported that the non-protected films displayed a dendritic growth formation on the surface following a 6-month exposure to ambient air at room temperature; however, the resulting loss in performance was not measured. Transparent and conductive ZnO:Al coatings were also studied by Kang *et al.* [10] to enhance the performance of VO_2 in the visible and near-infrared ranges by increasing its luminous transmittance and solar transmittance variation by interference effects. Samples were subjected to a rapid thermal annealing at 450 °C in an ambient atmosphere: once again, non-protected VO_2 films oxidized in less than 400 s and possessed no TC activity. Protected coatings presented a different oxidation degradation mechanism with the formation of an overlying $Zn_2V_2O_7$ intermix-layer that, according to the authors, protects the sample from further oxidation. Finally, Ji *et al.* [11,12] focused solely on the protection of VO_2 against degradation by the addition of a 10–150 nm thick Al_2O_3 film. The authors showed that a

* Corresponding author.

http://dx.doi.org/10.1016/j.solmat.2016.10.038
Received 17 August 2016; Received in revised form 20 October 2016; Accepted 22 October 2016
Available online 31 October 2016

minimum thickness of 30 nm is sufficient to protect VO_2 against humid environments (80 °C and 100% R.H.) for up to 120 h.

In the present work, we study the impact of high power impulse magnetron sputtering (HiPIMS [13]) on the stability of VO_2 thin films. Indeed, HiPIMS is known for its high ionization rate of sputtered particles both in metallic and reactive processes [14] while also enabling hysteresis-free reactive sputtering [15,16]. The large flux of sputtered particles can also be used to provide additional energy to the growing film leading to a higher density without the incorporation of gaseous species thus suppressing mechanical stress [17]. Correspondingly, HiPIMS has also been shown to result in the deposition of polycrystalline films at lower temperatures [18]. This has in fact been successfully implemented and demonstrated for the deposition of high performance thermochromic VO_2 on glass [18,19] and polymers [20] at temperatures as low as 275 °C, a temperature significantly lower than the typically required 400–500 °C.

In order to demonstrate the beneficial impact on the environmental stability of HiPIMS-deposited VO_2 films, we compare the optical performance of films fabricated under comparable conditions by HiPIMS and by radio-frequency magnetron sputtering (RFMS). Contrary to the above-mentioned articles, we not only study the effect of exposing VO_2 to an aqueous environment in terms of its optical performance, but also systematically evaluate the resulting structural and chemical changes in the films. Finally, an additional SiN_x diffusion barrier is also added to protect against oxidation, and its impact on the degradation dynamics between unprotected and protected coatings is evaluated. Interestingly, protected RFMS samples show degradation kinetics similar to unprotected HiPIMS samples. Our results suggest that HiPIMS deposition of VO_2 offers an attractive alternative to the deposition of an additional oxidation barrier in the case of mildly oxidizing environments.

2. Methodology

2.1. Film deposition

In this study, vanadium oxide and silicon nitride films were deposited in an ultra-high vacuum multi-magnetron process chamber (CMS-18, Kurt J. Lesker Co., Ltd.). The magnetron guns were equipped with 3 in. (7.62 cm) targets of pure vanadium (99.999%) and of boron-doped silicon (0.02–0.05 Ω cm). The substrates were 2 mm thick 5×5 cm B270 glass from S.I. Howard Glass Co., Inc. During deposition, substrates were rotated to ensure good thickness uniformity (≤3% variation).

Both HiPIMS (HiP3, Ionautics/Solvix) and RFMS (13.56 MHz, SEREN) power supplies were used to deposit the VO_2 films, while silicon nitride films were deposited by RFMS. Experimental conditions for each type of layer were independently optimized, and the resulting deposition parameters are summarized in Table 1.

The substrates were first inserted into the deposition chamber through a load lock, and the system then pumped down to a base pressure of 5×10^{-8} Torr (6×10^{-6} Pa). They were then heated by infrared lamps to a surface temperature of 350 °C and plasma cleaned for 20 min at a RF bias of 100 V using an 80:20 $Ar:O_2$ mixture at 20 mTorr (2.6 Pa). Subsequently, they were covered with a 35 nm diffusion barrier of SiN_x (see Table 1 for deposition conditions) to suppress the possible and undesirable diffusion of dopants coming from the glass itself [21].

Vanadium oxide films were then deposited by HiPIMS or RFMS using the conditions summarized in Table 1. In both cases the deposition rate was about 0.6 nm/min. Finally, half of the samples were covered with a 35 nm diffusion barrier layer of SiN_x. Note that all sample architectures were deposited on three B270 substrates simultaneously to ensure sample homogeneity, and then cut into four 2.5 cm×2.5 cm squares for a total of 12 samples in anticipation of the ageing tests.

Table 1
Deposition parameters for VO_2 and SiN_x films.

	VO_2		SiN_x
Source	**HiPIMS**	**RFMS**	**RFMS**
Pressure [mTorr]	5		3
O_2 flow [sccm]	2	4	0
$O_2(N_2)$:Ar ratio [%]	6.3	13.5	40
Average power [W]	450		350
Target voltage [V]	600	200	212
Pulse frequency [Hz]	200	N/A	N/A
Pulse length [μs]	45	N/A	N/A
RF Bias [V]	−180	−180	0
Typical film thickness [nm]	35	35	35
Substrate temperature [°C]	350 °C	350 °C	350 °C

2.2. Film ageing and characterization

Sample ageing was conducted in a temperature-controlled glass container kept at a constant temperature of 80 °C and saturated water vapour (~100% relative humidity). One sample was kept as a reference and the 11 other samples were then aged for different amounts of time (at 12-h intervals). The first ageing experiment was conducted for a total of 52 h with 4 types of samples, namely HiPIMS-deposited VO_2 samples with and without a SiN_x top layer, and RFMS-deposited VO_2 samples with and without a SiN_x top layer. The second (longer) ageing test was then run for 144 h (6 days) with a smaller batch of unprotected HiPIMS-deposited VO_2 samples.

The thickness and optical constants of the as-deposited films were obtained from spectroscopic ellipsometry measurements between 250 nm and 1700 nm and between 45° and 75° using a RC2 ellipsometer from J.A. Woollam Co., Inc. The ellipsometric data (Ψ and Δ) were assessed using the *CompleteEase* software package also from J.A. Woollam Co., Inc. The SiN_x was modelled with a Cody-Lorentz oscillator while the VO_2 was modelled using a combination of Tauc-Lorentz and Gaussian oscillators. A detailed description of the VO_2 model can be found in our previous articles [18,20]. Knowledge of the optical constants obtained by ellipsometry allowed us to predict the thermochromic performance of VO_2 as a function of the film thickness using the *OpenFilters* software [22].

The crystalline structure and chemical signature of the VO_2 films were assessed by Raman spectroscopy using a Renishaw *INVIA* system equipped with holographic filters and a 514 nm excitation wavelength. Scans were performed from 180 cm^{-1} to 1050 cm^{-1} using an 1800 line/mm grating. X-ray diffraction (XRD) measurements were carried out in the θ-2θ mode from 15° to 65° at a grazing angle of 1° using a Bruker *D8-Discover* diffractometer equipped with a Linkseye CCD accumulation-detector. The diffraction patterns were then evaluated using the *DIFFRACT.EVA* software package from Bruker.

Normal incidence spectral transmittance (T) of the samples was measured at different temperatures using a Perkin Elmer *Lambda 1050* spectrophotometer for wavelengths between 250 nm and 2500 nm. The data was recorded at 25 °C and 90 °C, below and above vanadium dioxide's transition temperature, T_C, using a custom-made heat cell. Time-resolved measurements of the transition speed were obtained by placing the coating directly onto a 90 °C hot plate while measuring the transmission at 2500 nm.

The stress in the coatings was evaluated using a Tencor *FLX-2900* which measures the change in the radius of curvature of a substrate before and after the addition of a thin film. The internal stress can then be calculated using the well-known Stoney equation. VO_2 films were deposited onto 60 μm thick rectangular glass strips coated with a chromium film on their backside to increase the sample's reflectivity and thus measurement accuracy. Additionally, these substrates were also coated with SiN_x and pre-characterized before and after annealing