

Amorphous thermochromic VO₂ coatings grown by APCVD at low temperatures

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ABSTRACT

Vanadium dioxide coatings were grown on SnO₂-precoated glass substrates by atmospheric pressure chemical vapor deposition using vanadyl (V) triisopropoxide at temperatures $\leq 450^\circ\text{C}$. X-ray diffraction indicated the presence of metastable phase for the as-grown samples at 350 and 400°C, while well-defined monoclinic vanadium dioxide phase was shown at 450°C as derived by Raman spectroscopy. The different phases of vanadium dioxide affected the coating's morphology presenting long grains with irregular size and shape turning to flattened structures composed with grains of uniform dimensions as the temperature increased from 350 to 450°C. The best reversible behavior was at 64°C with hysteresis width of 15°C and a change in transmittance of 21 % for the as-grown coating at 450°C. The significance of achieving thermochromic vanadium dioxide at temperatures $\leq 450^\circ\text{C}$ by a chemical procedure without post-treatment reduction and oxidant source is highlighted. Copyright © 2015 VBRI Press.

Keywords: APCVD; vanadium dioxide; monoclinic; thermochromicity.

Introduction

A lot of attention is given to responsive coatings because they can regulate a comfortable living environment, while saving energy consumed for appropriate lighting or air conditioning [1]. A typical example is the thermochromic vanadium dioxide (VO₂) coating that modifies its behavior in response to temperature. Above a certain temperature called transition temperature (T_c), it presents a transition from the monoclinic to the rutile phase (a metal-to-semiconductor transition (MST)), that is reversible and takes place at 68°C [2]. A change in the physical properties is also detected on passing through the MST transition; the monoclinic phase behaves as a semiconductor and does not reflect much solar energy, whereas the rutile phase is a semimetal and shows higher electrical conductivity and reflectance particularly in the infrared range [3]. In practical terms, for $T < T_c$, the solar radiation will be transmitted keeping the interior of the building warm, while for $T > T_c$, part of the energy from the sun will be reflected. In this way, the heat gain from the solar radiation will be high in winter and low in summer reducing the need for cooling and heating, respectively.

As with many coatings, chemical vapour deposition (CVD) routes are more attractive for the production of vanadium oxides on glass than other conventional techniques, since the stoichiometry and the morphology of the oxides can simply be controlled by tuning the vapour flows in the coating zone [4, 5]. In addition, the simplicity of CVD, particularly when performed at atmospheric pressure (APCVD), would make such a process compatible with in-line glass manufacturing processes. Towards this direction, vanadium chlorides [6-8], alkoxides [9], acetyl acetonates [10, 11] and various oxovanadium reagents [12] have been used as vanadium sources.

In this work, we report the APCVD of vanadium dioxide coatings on SnO₂-precoated glass substrates using vanadyl (V) triisopropoxide as a single precursor [13-15]. Based on work previously reported [16], the growth of thermochromic layers at temperatures lower than 450°C without post-treatment reduction and oxidant source is investigated. This is one of the simplest CVD route that has not been studied before to the best of our knowledge. The correlation of the vanadium dioxide phases with the thermochromic parameters including T_c , hysteresis width

and the percentage changes in transmittance (below and above T_c) is studied.

Experimental

Materials

The vanadyl (V) triisopropoxide ($\text{VO}(\text{OC}_3\text{H}_7)_3$, 96 %) was purchased by Alfa Aesar (Germany) without further purification. The substrates used during all APCVD experiments were commercial SnO_2 -precoated glass supplied by Uniglass (Greece), all of dimensions 2 cm x 2 cm x 0.4 cm. Prior to coating, they were cleaned with H_2O and detergent, rinsed thoroughly with H_2O and deionised H_2O , and allowed to dry.

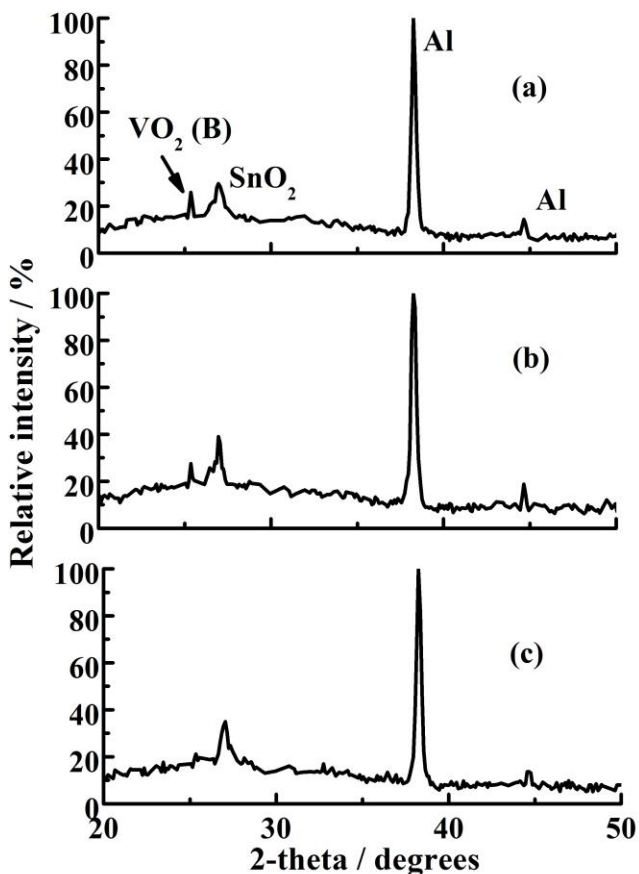


Fig. 1. XRD of APCVD vanadium oxide coatings at 350 (a), 400 (b) and 450°C (c) using 0.5 L min^{-1} N_2 flow rate through the vanadium precursor's bubbler for 150 min.

Method

The APCVD reactor used in this work was consisted of a cold-wall reactor connected to an arrangement of stainless-steel heated pipes, valves and bubblers [16-17]. The vanadium precursor was placed in a bubbler at 50°C. The carrier gas was N_2 , which was passed through the apparatus during the experiments. The total gas flow rate was kept at 12 L min^{-1} , while the one through the vanadium precursor's bubbler was at 0.5 L min^{-1} . The deposition temperatures were 300, 350, 400 and 450°C for a period of 150 min.

X-ray diffraction (XRD) measurements were carried out in a Siemens D5000 Diffractometer for 2-theta = 20.0-50.0°, step size 0.02° and step time 30 s°. Raman analysis was performed in a Nicolet Almega XR micro-Raman

system operating at a Raman shift range of 150-700 cm^{-1} using a 514 nm laser line. Morphology analysis was done on a Jeol JSM-7000F field-emission scanning electron microscope (FE-SEM). In this case, samples were over-coated with a thin film of gold in order to make them more conductive. The transmittance measurements were carried out in a Perkin-Elmer Lambda 950 spectrophotometer over the wavelength range of 250-2500 nm at 25 and 90°C [16]. Finally, transmittance-temperature studies were performed using a tungsten-halogen lamp with an interference filter at $1500 \pm 20 \text{ nm}$ and a temperature controller to adjust the temperature between 30 and 90°C.

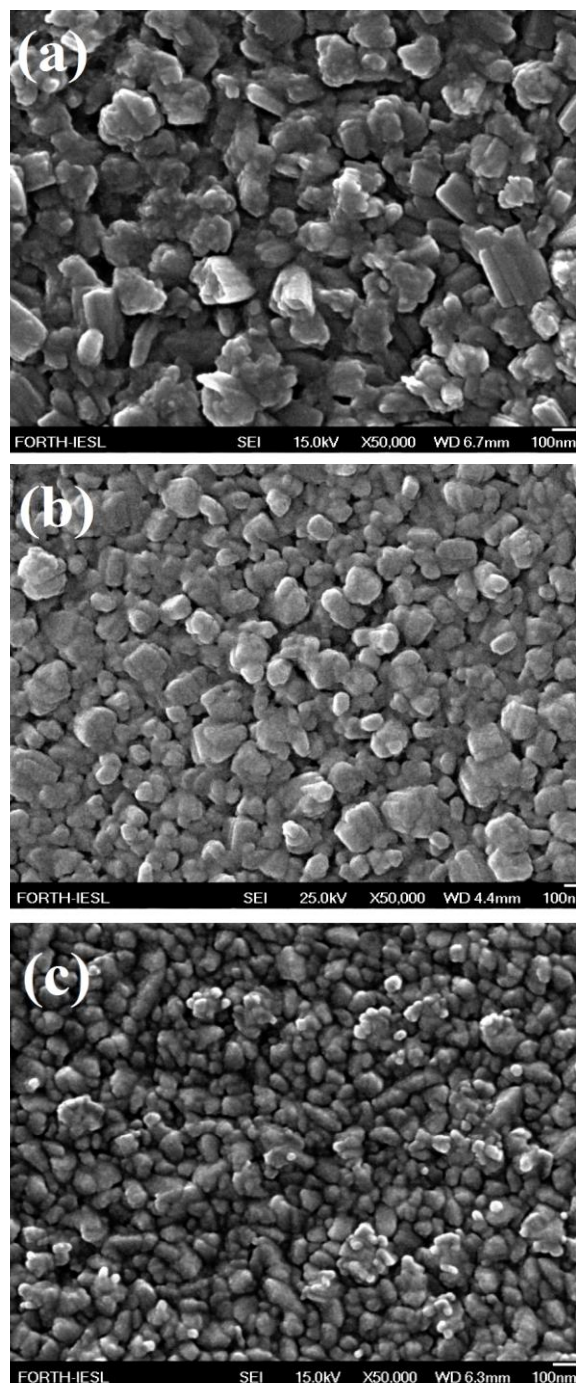


Fig. 2. FE-SEM images of vanadium oxide coatings grown at 350 (a), 400 (b) and 450°C (c) using 0.5 L min^{-1} N_2 flow rate through the vanadium precursor's bubbler for 150 min.

Results and discussion

The coatings prepared in the APCVD reaction of VO (OC_3H_7)₃ passed the Scotch tape test (removal of an X shaped piece tape [3]) and were resistant in H₂O and acetone. In addition, they all had similar properties (structural, morphological and thermochromic (transition temperature, hysteresis width and change in transmittance)) after approximately six months, indicating their stability with time. Finally, there was no deposition at 300 °C, hence this sample was not further characterized.

Fig. 1 displays the XRD patterns of vanadium oxide coatings deposited on SnO₂-precoated glass substrates for 0.5 L min⁻¹ N₂ flow rate through the vanadium precursor's bubbler at 350, 400 and 450 °C. In all patterns, one peak is indicated at 26.5° with Miller index (110) due to the underlying substrate [18] and two peaks at 38.3 and 45.6° due to the Al holder. The coating grown at 350 °C presents one additional peak at 25.3° with Miller index (110) due to the metastable phase of VO₂ (VO₂ (B)) [19], which becomes weaker as the substrate temperature increases at 450°C.

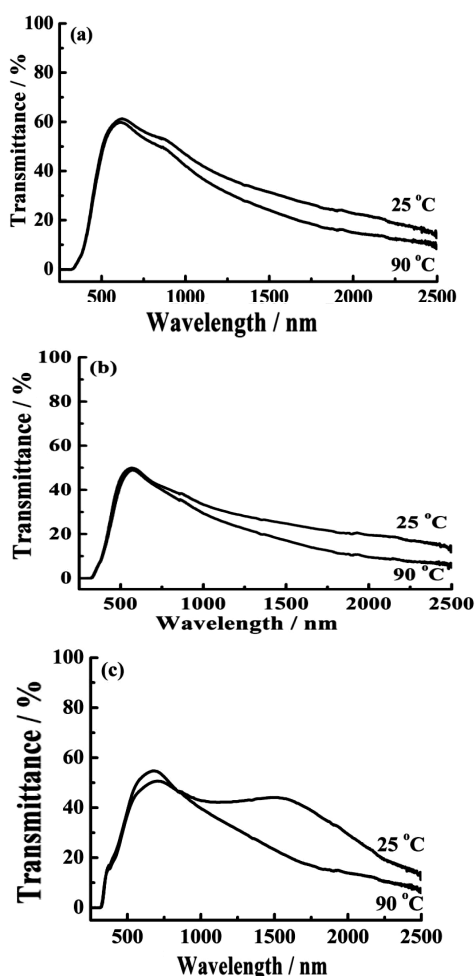


Fig. 3. Transmittance spectra at 25 and 90°C of the vanadium oxide coatings grown at 350 (a), 400 (b) and 450°C (c).

Raman spectroscopy measurements were also performed in all samples indicating the presence of monoclinic VO₂ only for those grown at 450°C. The data

was similar with the one reported previously [16]. The Raman spectra for the other samples did not show appreciable signal, a response that can be attributed to their dark color, which most likely resulted in a reduction of light scattering to a level that was below the detection limit of our instrument [20].

Although, XRD analysis gave no indication of crystalline vanadium dioxide at 450°C, Raman study revealed the presence of monoclinic VO₂ suggesting that they are mainly amorphous retaining however a short-range crystalline ordering [21].

FE-SEM measurements were performed on vanadium oxide coatings prepared at different substrate temperatures to study their effect on surface morphology (**Fig. 2**). At 350°C, long grains with irregular size and shape are formed having different directions with respect to the substrate. As the growth temperature increases to 400 and 450°C, the surface morphology becomes flattened, and grains of uniform size and shape are finally formed at 450°C. These images demonstrate that coatings morphology depends on the phase of vanadium oxide, which in turn is affected by the substrate temperature.

The thermally induced reversible transition at 25 and 90°C of all coatings is shown in **Fig. 3**. It is observed that they all display the properties required for thermochromic applications even if they are amorphous or they present the metastable VO₂ phase. From the data observed in **Fig. 3**, the percentage changes in transmittance are 6, 10 and 21 % for 350, 400 and 450°C respectively.

Furthermore, the hysteresis width and the transition temperature of the coatings were studied through the change in transmittance with temperature at 1500 nm as shown in **Fig. 4**. These values were determined through a plot of $d(\text{Transmittance})/d(\text{Temperature})$ –Temperature [22]. Hence, the T_c and the hysteresis width of the samples grown at 350, 400, 450 °C were calculated to be 63 and 22 °C, 62 °C and 20 °C, 64 °C and 15 °C. The hysteresis width of the 450 °C (15 °C) was comparable with the one reported in previous work [6] and the continuous polycrystalline VO₂ [23, 24].

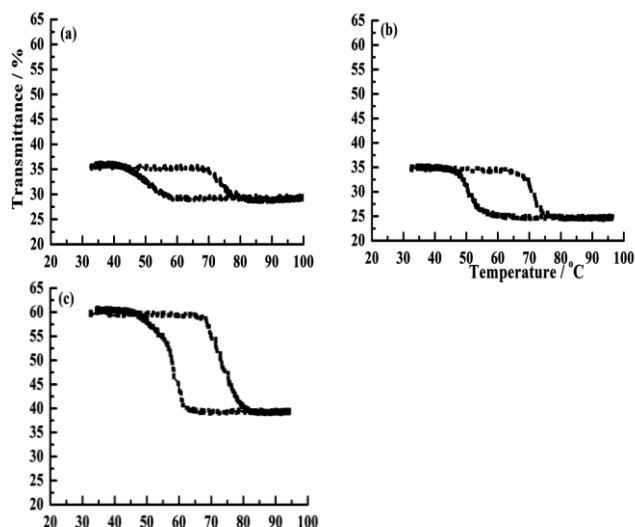


Fig. 4. Transmittance-temperature studies at 1500 nm of the vanadium oxide coatings grown at 350 (a), 400 (b) and 450 °C (c).

It is observed that the highest change in transmittance and the narrowest hysteresis width are at 450°C indicating that the presence of monoclinic VO₂ based on Raman analysis is an important factor affecting these parameters. Additionally, since the hysteresis width is due to nucleation barriers such as grain boundaries and voids, the microstructure of the coatings, which is different for each sample as evident from SEM images, can affect the width [25].

Conclusion

Metastable and monoclinic VO₂ coatings were grown at 350, 400 and 450°C, respectively using an APCVD reactor as derived from XRD and Raman analysis. The different vanadium dioxide phases affected the surface morphology of the coatings presenting long grains with irregular size and shape turning to flattened structures composed with grains of uniform dimensions from 350 to 450°C. The best reversible behavior corresponds at a T_c of 64°C, hysteresis width of 15°C and a change in transmittance of 21 % for the as-grown monoclinic VO₂ at 450°C.

This paper has considered the possibility to isolate VO₂ phases depending on the growth temperature without post-treatment reduction and an oxidant source. We may then say that this APCVD approach can further decrease the large-scale production cost leading in advances for solar energy control applications. In our laboratories, we have also studied the doping process under these conditions, which will be reported in a future publication.

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