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Thermochromic vanadium oxide coatings grown by APCVD at low temperatures

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Abstract

Amorphous vanadium dioxide coatings were deposited on SnO_2-precoated glass substrates at 400 ^oC by atmospheric pressure chemical vapor deposition for various vanadium precursor flow rates. The coatings were characterized by X-ray diffraction, Raman spectroscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. Their thermochromic performance has been found to be independent on the vanadium (V) triisopropoxide flow rates. All vanadium dioxide films present a reversible transition behavior at 68 ^oC as derived from the transmittance studies.

Keywords: Atmospheric pressure chemical vapor deposition; Vanadium dioxide; Thermochromics; Transition temperature.

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1. Introduction

A lot of attention is given to materials, which can respond in a desired way to an external stimulus (i.e. temperature). As such, thermochromic VO_2 coatings exhibit a reversible semiconductive state to a metallic state at a critical temperature called transition temperature (T_c), while maintaining visible transparency (Morin, 1959; Nag et al., 2008).

Chemical vapor deposition (CVD) routes are attractive for the production of VO_2 on glass, since the characteristics of the materials can be simply controlled via the growth temperature and the vapor flow in the coating zone (Manning et. al., 2004; Vernardou et. al., 2006). In addition, the simplicity of CVD, particularly when performed at atmospheric pressure (APCVD), makes such a process compatible with in-line glass manufacturing processes.

The aim of this work is to study the effect of vanadium (V) triisopropoxide ($VO(OC_3H_7)_3$) vapor carrier gas flow rate on the structure, morphology and thermochromic behavior of the coatings grown at 400 ^oC by APCVD.

2. Experimental

The APCVD reactor used in this work is an in-house design and consists of a cold-wall reactor connected to an arrangement of stainless-steel heated pipes, valves and bubblers as reported previously (Vernardou et. al., 2006; Vernardou et. al., 2007; Vernardou et. al., 2011). $VO(OC_3H_7)_3$ bubbler was heated at 50 ^oC, while the gas lines were kept at 60 ^oC to avoid any condensation. The carrier gas was nitrogen, which was passed through the reactor during all depositions. The vanadium oxide growth was performed at 400 ^oC for vanadium precursor flow rate of 2.5, 3, 3.5 and 4 $l.min^{-1}$. The deposition time for all samples was 30 min. The substrates used during the APCVD experiments were commercial SnO_2-precoated glass (Uniglass, Greece), all of dimensions 2 x 2 x 0.4 cm^3. Prior to deposition, all substrates were cleaned with H_2O and detergent, rinsed thoroughly with H_2O and deionised H_2O, and allowed to dry.

X-ray diffraction (XRD) measurements were carried out in a Siemens D5000 Diffractometer for 2θ = 10.00-60.00 ^{o}, step size 0.02 ^{o} and step time 30 $s/^o$. Raman spectroscopy was done in a Nicolet Almega XR micro-Raman system using a 473 nm laser. Fourier transform infrared spectroscopy (FTIR) was performed in a Bruker IFS 66v/S spectrometer at a resolution of 4 cm^{-1}, sample and background scan time of 30 scans in the mid-IR region. Surface characterization was accomplished in a Jeol JSM-7000F field-emission electron microscope. The transmittance was measured using a Perkin-Elmer Lambda 950 UV-Vis spectrophotometer in the region of 300-1100 nm at 25 and 90 ^oC. Finally, transmittance/temperature studies were fulfilled at 1100 nm.

3. Results and Discussion

The coatings produced during the APCVD reaction of $VO(OC_3H_7)_3$ were green, adhesive and passed the Scotch tape test. They were insoluble in water and common organic solvents. Higher vanadium precursor flow rates led to better coating uniformity and coverage over the whole substrate surface. This behaviour may be due to the increased collision rate of the species in the gas-phase with those adsorbed in the substrate resulting in higher vanadium species concentration. By increasing the precursor flow rate from 2 to 4 $l.min^{-1}$, the thickness of the coatings raised as indicated from the respective decrease in transmittance by half (not shown here).

3.1. Structure

XRD patterns of the as-deposited coatings showed only the peaks of SnO_2 (Tao et. al., 2000) related with the substrate (not shown here) indicating that the films are amorphous. On the other hand, Fig. 1 (a) presents a representative monoclinic VO_2 Raman spectrum of the samples grown using different $VO(OC_3H_7)_3$ flow rates at 400 ^oC. The Raman band at 616 cm^{-1} results from the stretching modes of the V-O-V bridging bonds, while the other bands at 222, 263, 308, 385 and 479 cm^{-1} are attributed to bending motions of the vanadium-oxygen bonds. In addition, a representative FTIR spectrum of the coatings is shown in Fig. 1 (b). The modes located at 508 (Botto, et. al., 1997) and 540 cm^{-1} (Subba Reddy, et. al., 2009) are associated to the edge-shearing vanadium-oxygen stretching and V-O-V octahedral bending modes respectively, both corresponding to vanadium dioxide. It is observed for all samples that there are not peaks either at 820 and 1020 cm^{-1} or at wavenumbers higher than 1100 cm^{-1} indicating that the samples do not contain V_2O_5 (Culea, et. al., 1984; Ramana, et. al. 1997) and the vanadium precursor is completely decomposed (Schraml-Marth, et. al., 1990) under these growth conditions.

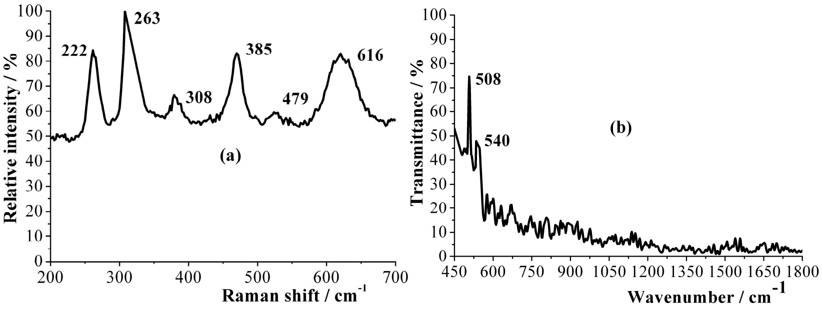

Fig. 1. **(a)** Raman and **(b)** Fourier transform infrared spectra of the vanadium oxide coating grown on SnO_2-precoated glass at 400 ^oC for $VO(OC_3H_7)_3$ flow rate of 3.5 $l.min^{-1}$.

3.2. Morphology

Fig. 2 presents the field-emission scanning electron microscopy (FE-SEM) images of the substrate (inset) and the vanadium oxide coating grown using $VO(OC_3H_7)_3$ flow rate of 3.5 $l.min^{-1}$. It is observed that the oxide morphology follows closely that of the substrate suggesting that the deposited layer is relatively smooth. One may then say that the vanadium oxide has a promotable epitaxial growth on SnO_2 surface (Atrei, et. al., 2002; Zhang, et. al., 2011).

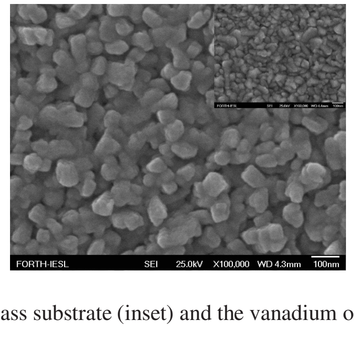

Fig. 2. FE-SEM images of the SnO_2-precoated glass substrate (inset) and the vanadium oxide coating grown on SnO_2-precoated glass using $VO(OC_3H_7)_3$ flow rate of 3.5 $l.min^{-1}$.

3.3. Thermochromic behavior

The reversible transition performance during heating and cooling was measured for all samples using the transmittance spectroscopy. Fig. 3 (a) presents the transmittance spectra at 25 (below T_c) and 90 °C (above T_c) of the coating grown using $VO(OC_3H_7)_3$ flow rate of 3.5 $l.min^{-1}$. It is seen that, despite the fact that the coating is not crystalline, the transmittance decreases at 90 °C in the region of 750-1100 nm due to its thermochromic behavior.

The T_c value of the coating was also monitored by studying the change in transmittance as a function of temperature at 1100 nm (Fig. 3 (b)). The T_c (based on the centre of the hysteresis loop) (Vernardou et. al., 2006) and the hysteresis loop width were found to be 68 and 25 °C respectively. This transition could be repeatedly cycled up to three times without any detectable changes in T_c or sample degradation.

It is shown that the precursor flow rate is not the critical factor to influence the thermochromic characteristics of the coatings since the transition temperature, the hysteresis loop width and the change in transmittance (at 90 °C) are similar among all samples.

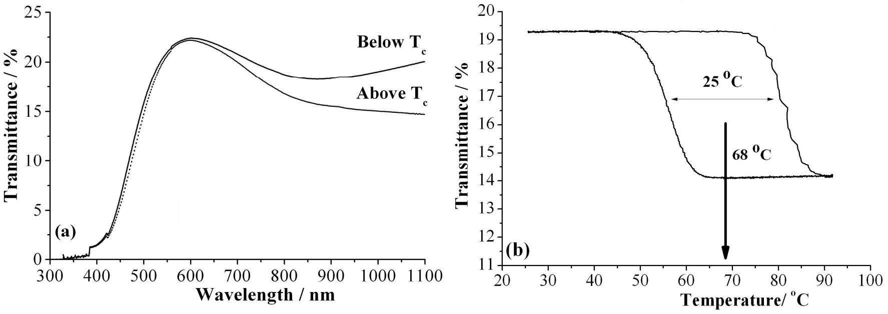

Fig. 3. (a) Transmittance spectra for the vanadium oxide sample at 25 °C (below T_c) and 90 °C (above T_c) over the region of 300-1100 nm, deposited using $VO(OC_3H_7)_3$ flow rate of 3.5 $l.min^{-1}$. (b) Transmittance at 1100 nm against temperature of the vanadium oxide sample. The direction of cycling is also indicated.

4. Conclusions

Amorphous VO_2 coatings were grown using an APCVD reactor at 400 °C for various $VO(OC_3H_7)_3$ flow rates. It is indicated that the vanadium precursor flow rate does not affect the structure, morphology and thermochromic characteristics of the samples. All dioxides present a stable transition performance with time having a T_c of 68 °C.

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