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Thermochromic amorphous VO_2 coatings grown by APCVD using a single-precursor

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ABSTRACT

This work reports the growth of thermochromic amorphous vanadium dioxide coatings on SnO_2-precoated glass substrates by atmospheric pressure chemical vapor deposition using vanadyl (V) triisopropoxide as single-precursor at 450 °C. The best reversible transition behavior was at 65.5 °C as derived from the transmittance–temperature measurements. This finding is discussed in terms of variations in microstructure occurring during the different nitrogen flow rate studies. We show that the thermochromic behavior of the oxides is determined by the presence of well-defined monoclinic vanadium dioxide.

1. Introduction

The thrust of research and development for windows and in general light control systems is to find cost-efficient means that can follow changing circumstances and allow “right” amount of light and heat without losing the outside view. Thermochromics is a class of windows called “smart windows”, which absorb or reflect near infrared (NIR) from solar radiation as a function of temperature, while allowing most of sunlight to pass through the window, without any external stimulus provided by the user [1]. Among more than 10 polymorphs of vanadium dioxide (VO_2), only the monoclinic VO_2 phase is a typical thermochromic material, which is known to undergo a reversible metal-to-semiconductor transition associated with a structural phase transformation from monoclinic to tetragonal at a critical temperature (T_c) [2,3]. Chemical vapor deposition (CVD) has already been used for the production of VO_2 at temperatures ≥ 450 °C [1,4–10], which increases the probability of other vanadium oxides (such as V_2O_5, V_6O_{13}, and VO_x) nucleation and enhances mechanical stresses due to different values of thermal expansion coefficients for oxide and substrate [11]. As a consequence, the development of a simple method for integrating VO_2 coatings into thermochromic windows is of immediate interest.

In this work, we report the atmospheric pressure CVD (APCVD) of amorphous VO_2 coatings on SnO_2-precoated glass substrates using vanadyl (V) triisopropoxide [4,8,12] as a single-precursor for the first time to the best of our knowledge. This approach has several advantages over the conventional CVD methods: 1) The coatings are grown at atmospheric pressure, which can then be compatible with high-volume glass manufacturing lines. 2) The precursor is a liquid with high vapor pressure 38.6 Pa at 45 °C, which makes it highly desirable for handling reasons. Precursor decomposition over time, irreproducible delivery rates and transport of unknown species are avoided. 3) The use of this single-precursor simplifies operations e.g. by removing the, commonly necessary, oxygen source which is usually provided either in the form of pure gas or from an extra bubbler through H_2O or alcohol. In addition, the V–O bond is present in a single molecular entity, which enhances the formation of the oxide at low temperatures while control over the particle size, size distribution and film homogeneity becomes easier [13,14].

2. Experiment

The APCVD reactor used in this work was an in-house design as reported previously [5,6]. The vanadium source was the vanadyl

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(V) triisopropoxide ($VO(OC_3H_7)_3$) (96%, Alfa Aesar) precursor. It was placed in a bubbler at 50 °C, while the gas lines were kept at 60 °C to avoid any condensation. The carrier gas was nitrogen (99.9%), which was passed through the reactor during all depositions. The nitrogen flow rate passing through the vanadium bubbler was 3, 3.5 and 4 L min^{-1}, while the total flow rate in all experiments was kept at 12 L min^{-1}. The substrates were commercial SnO_2-precoated glass (Uniglass, Greece), all of dimensions 2 cm × 2 cm × 0.4 cm. 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 in air. The deposition period was 30 min and the growth temperature was set at 450 °C. Once the deposition time was complete, the reactor temperature controller was turned off and the substrate allowed cooling at a temperature of 100 °C under an atmosphere of nitrogen. Then, it was removed from the reactor, handled and stored in air.

X-ray diffraction (XRD) measurements were carried out in a Siemens D5000 Diffractometer for $2\theta = 10.00–50.00°$, step size 0.02° and step time 30 s/°. Raman spectroscopy was performed in a Nicolet Almega XR micro-Raman system using a 514 nm laser line at an incident intensity of 10 mW μm^{-2}, i.e. low enough to prevent any structural change to either the coating or the underline substrate. The morphology of the samples was evaluated using a Jeol JSM-7000F field-emission scanning electron microscope (FE-SEM). Samples were over-coated with a thin film of gold prior to analysis to prevent charging. 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. An aluminum temperature cell controlled by temperature controller and K-type thermocouple was used to manipulate the sample temperature. Transmittance–temperature studies were performed using a tungsten–halogen lamp with an interference filter at 1500 ± 20 nm and a temperature controller to adjust the temperature between 25 and 90 °C with a heating and cooling rate of 5 and 4 °C min^{-1}. Finally, the coating's thickness was estimated using a profilometer A-step TENCOR. Prior to measurements, a step was formed by etching the vanadium oxide coatings off the SnO_2-precoated glass substrate in 1:3, H_2O_2 (30%):HCl for 40 s up to 2 min depending on the thickness of each coating. Tin dioxide remained intact after this procedure and the thickness was deduced from the measured step height.

3. Results and discussion

The amorphous vanadium dioxide coatings were grown using $VO(OC_3H_7)_3$ as a single-precursor at 450 °C for various nitrogen flow rates through the vanadium bubbler. A general observation was that there was no efficient deposition for flow rates < 4 L min^{-1}, a finding that is in agreement with the growth rates estimated, i.e. being ca. 3 and 0.7 nm min^{-1} for 4 and 3 L min^{-1}, respectively. The growth rate was calculated from the deposition time and the coating's thickness as determined from the profilometer. This behavior may be due to the increased collision rate of the species in the gas-phase with those adsorbed on the substrate at the highest incoming flow resulting in higher vanadium oxide species concentration. Furthermore, there was no coating's deposition above 450 °C possibly due to the vanadium oxide decomposition [15] or pathways, which reduces precursor concentration [16]. Since, film decomposition does not occur for this system, it is suggested that at 475 and 500 °C (the highest temperatures studied), the precursor pre-reacts with existing vanadium species in the gas phase. Further evidence of this pre-reaction is the observed lack of deposition even at 450 °C upon N_2 flow rate increase through the vanadium bubbler (i.e. 4.5 L min^{-1}). Furthermore, decreasing the total flow rate (i.e. < 12 L min^{-1}) and the deposition time (i.e. < 30 min) generally resulted in the formation of vanadium oxide phases other than VO_2. This is possibly due to the increase in the residence time of the reaction gas in the hot zone of the reactor, which may enhance those reactions, which lead to the formation of the other vanadium oxide phases, over those which lead to VO_2 formation. All coatings passed the Scotch tape test (removal of an X shaped piece of sticking tape [1]) and were resistant to H_2O and acetone. Furthermore, the samples presented similar structural, morphological and thermochromic properties after storage for six months indicating long term stability under environmental conditions.

In order to accomplish the growth of thermochromic VO_2, SnO_2 was chosen as a substrate for two main reasons. The first reason is related to the similar crystalline structure of SnO_2 and rutile phase VO_2, which can promote crystallinity of the oxide [17]. Hence, it would be very interesting to investigate whether SnO_2 may act as a template for the growth of VO_2 with a rutile lattice, as observed in the case of the oxide deposited on titanium dioxide, which has also a rutile-type structure [18]. Another reason is related to the higher activities and selectivities in oxidation reactions of V_2O_5/SnO_2 compared with SnO_2 alone. This was attributed to the effect of SnO_2 to easily remove the terminal oxygen of V=O surface species in the catalysts.

A proposed mechanism of VO_2 growth under CVD conditions may possibly be given as follows [4]:

$$VO(OC_3H_7)_3 \rightarrow VO_2 + C_3H_8 + 2C_3H_6O + (1/2)H_2 \qquad (1)$$

It is assumed that the vanadyl (V) triisopropoxide initially decomposes into V_2O_5 as a solid layer on the substrate and propanol in the gas phase. Based on the literature, the propanol reacts on the V_2O_5 surface to produce propylene and acetone. Then, as sites become increasingly occupied or blocked by hydrogen and/or hydroxyl species, propylene production decreases and propane formation becomes evident [19]. Thus, it might be expected that the O:V ratio would be lowered as a result of the reducing conditions. In order to verify this assumption, the analysis and discussion of the coatings' characteristics are indicated below.

Fig. 1 shows a representative XRD pattern of the coatings as inset indicating one peak at 26.5° with Miller index (110) due to the underlying substrate [20] and two peaks at 38.3° and 45.6° due to the Al holder. This behavior shows that the coatings were largely amorphous. This pattern does not alter after 6 months as shown in Fig. 1 from the similarity between the two curves (difficult to distinguish between the solid and the dot line).

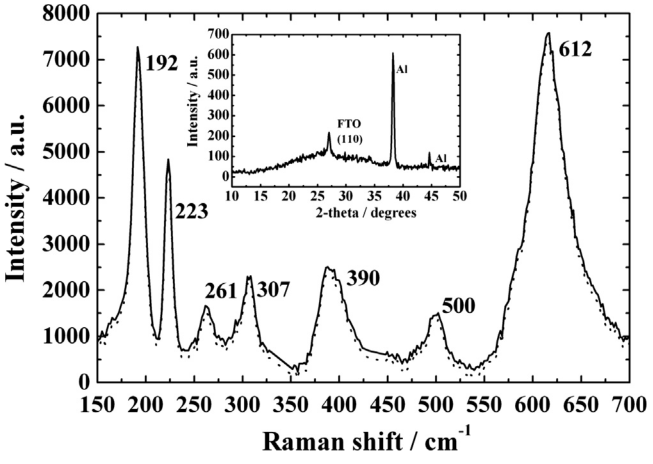

Fig. 1. XRD (inset) and Raman spectra of APCVD monoclinic VO_2 coating using N_2 flow rate through the vanadium bubbler of 4 L min^{-1} at 450 °C before (solid line) and after six months (dot line).