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Low-temperature rf sputtered VO_2 thin films as thermochromic coatings for smart glazing systems

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ABSTRACT

VO_2 is a material of great interest due to its excellent thermochromic properties. In this work, Vanadium dioxide (VO_2) films were deposited on commercial SnO_2-coated glass by the rf magnetron sputtering technique, at the low deposition temperature of T_{sub} = 300 °C. The effect of thickness and oxygen content in Ar–O_2 plasma on the thermochromic properties were studied. In specific, it was found that the critical transition temperature (Tc) remained constant, while the width of transmittance hysteresis loop (ΔT_C) was slightly decreased as thickness was increased from 35 nm to 260 nm. In addition, solar/transmittance modulation (ΔTr_{sol}) was increased by about 6%, while luminous transmittance (Tr_{lum}) was decreased almost 30%, with thickness. Furthermore, as the oxygen content in the plasma ranged from 2% to 4%, both T_C and ΔT_C increased about 4 °C, while ΔTr_{sol} and Tr_{lum} showed a slight increase of 1% and 3%, respectively. Finally, ZnO antireflective coatings of thicknesses from 22 to 100 nm were deposited on VO_2 thermochromic films by dc magnetron sputtering technique at room temperature, in an effort to enhance the luminous transmittance. As a result, an increase in Tr_{lum} of over 8%, with a 30 nm ZnO film was observed, while ΔTr_{sol} was increased by about 1%, independent of the ZnO thickness, while both T_C and were unaffected by the presence of ZnO antireflective coating.

1. Introduction

Thermochromic materials have attracted the interest of the research community during the last decades, as they can be used as coatings on smart windows, in order to regulate the interior temperature in buildings (Fazel et al., 2016; Kuhn, 2017; Long and Ye, 2014). VO_2 is by far the most well studied thermochromic material, because its critical transition temperature (T_C = 68 °C) is the closer to room temperature (Goodenough, 1971) of any counterparts. At this critical temperature, VO_2 undergoes a semiconductor to metal transition (SMT) which is accompanied by structural and optical changes (Goodenough, 1971). For temperatures below T_C, VO_2 is a semiconductor, exhibiting a monoclinic (M1 phase) structure (space group $P2_1/c$) and high transmittance in the infrared (IR) region, while for temperatures higher than T_C it is a metal, with a tetragonal rutile (R phase) structure (space group $P4_2/mnm$) and poor IR transmittance (Kiri et al., 2010). This transition can be attributed either on a strongly correlated electrons interaction (Mott-Hubbard transition) or on electron–phonon interactions, known as the Peierls transition (Okazaki et al., 2006; Wentzcovitch et al., 1994).

In the past, a number of diverse deposition techniques such as Atmospheric Pressure Chemical Vapor Deposition (Vernardou et al., 2014), sol-gel (Beck et al., 1993; N. Wang et al., 2013), hydrothermal synthesis (Long et al., 2015), PLD (Jian et al., 2013) and dc or rf sputtering (Gagaoudakis et al., 2016; Melnik et al., 2012; Panagopoulou et al., 2015; Zhang et al., 2014) have been employed in order to grow thermochromic VO_2 thin films. Among them, rf sputtering is an appropriate technique to produce VO_2 films with good thermochromic properties and high homogeneity suitable also for large scale production purposes. A great variety of substrates such as glass (Luo et al., 2016), Si (Luo et al., 2013) or sapphire (Nag et al., 2013) have also been used to deposit thermochromic VO_2 films. In addition, SiO_2 (Batista et al., 2011), TiO_2 (Martens et al., 2014), ZnO (Panagopoulou et al., 2015) or some other metal oxides (Koo et al., 2013; Zhu et al., 2016), have been used as buffer layers. The use of a buffer layer may decrease the deposition temperature and improve the thermochromic properties of the VO_2 films as the structural similarity of those metal oxides facilitates the formation of thermochromic VO_2. Another way to modify the thermochromic properties of VO_2 is by doping with specific metals.

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It was found (Chen et al., 2012; Tazawa et al., 1998; X.-J. Wang et al., 2013; Zhou et al., 2012) that doping VO_2 films with tungsten (W) leads to a decrease of T_C of about 23 °C per 1 at.%, while doping with Mg enhances luminous transmittance of thermochromic VO_2 films (Gagaoudakis et al., 2016; Li et al., 2013; Panagopoulou et al., 2016). An alternative way to increase luminous transmittance is by depositing an antireflective coating of metal oxide, such as TiO_2 (Mlyuka et al., 2009; H. Wang et al., 2013), ZnO (Zhou et al., 2016b) or other materials (Kang et al., 2011; Xu et al., 2004).

In the present work, thermochromic VO_2 films were deposited by rf sputtering technique, on SnO_2 precoated glass substrates (Pilkington K-Glass), commercial available for windows applications. The substrate temperature of 300 °C, applied was one of the lowest referred to in the literature by this technique (Dai et al., 2008; Melnik et al., 2012; Sun et al., 2017; Zhang et al., 2016). The effect of thickness and the content of oxygen in the Ar-O_2 plasma mixture on the resulting thermochromic properties were studied, showing a clear dependence upon these parameters. Finally, antireflective coatings of ZnO with various thicknesses were deposited on VO_2 films by dc sputtering technique at room temperature. It is known (Xu et al., 2004) that the refractive index of ZnO is between the optimum values to act as an antireflective coating for VO_2, while ZnO also acts as a protective layer against oxidation of VO_2 with antibacterial properties (Zhou et al., 2016b). The dependence of the thermochromic properties on the antireflective coating thickness is also presented. Thus, in this study it is shown that the combination of the lowest growth temperature with the application of an AR coating (30 nm ZnO) is shown to lead to a significant increase (8%) of luminous transmittance.

2. Experimental details

Thermochromic VO_2 films were growth by rf magnetron sputtering, using a Nordiko RFG2500 system with a 6 in. diameter vanadium (V) metal target (99.95% pure). The films were deposited on pieces of Si wafer for thickness measurements and on commercial Pilkington K-Glass substrates (4 mm thick float glasses) coated with a 60 nm SnO_2 film, known as low emissivity (Low-e) glasses, at the low substrate temperature of 300 °C. All substrates were initially cleaned by acetone and isopropanol for 5 min under ultrasonic and washed with nanopure water before dried by pure N_2 gas. The sputtering power was set at 400 W, while the total pressure during deposition was kept at 5 mTorr. Deposition duration was varied in order to grow films with thickness between 35 nm and 260 nm. Moreover, the oxygen content in the Ar-O_2 plasma mixture was varied from 2% to 4%. Finally, ZnO antireflective (AR) coating with thickness 22–100 nm were deposited on the thermochromic VO_2 films by dc magnetron sputtering method. For this, an Alcatel dc magnetron sputtering system, using a 6 in. diameter zinc (Zn) metallic target (99.999% pure), was employed. The base pressure before deposition was less than 0.75×10^{-6} mTorr, while during deposition the total pressure was kept constant at 6 mTorr. The sputtering current and voltage were 0.25 A and 280 V, respectively. The oxygen content in the plasma was 100% and deposition took place at room temperature. In order to measure their thickness, a Corning 1737F glass with a piece of Al tape to create a step was also placed in the Alcatel sputtering chamber. All thicknesses were measured by a Veeco Dektak 150 profilometer.

The structure of the VO2 films was examined by X-ray Diffraction (XRD) technique using a Rigaku RINT-2000 system with Cu Kα X-rays. For VO2 films deposited on K-Glass, the Grazing Incident-XRD (GI-XRD) method was employed (θ = 1°, 2θ = 20–60°), in order to minimize the SnO_2 diffraction peaks, while for the bare K-Glass the θ / 2θ method was used. Furthermore, the desired thermochromic VO_2(M) phase was confirmed by Temperature-dependent Micro-Raman spectroscopy, using a T64000 Jobin-Yvon system assorted by a 514.5 nm Ar^+ laser.

The thermochromic properties of films were also investigated by studying the transmittance spectrum from room temperature (RT) to elevated temperature. For this, a Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer, operating at λ = 250–2500 nm, with a homemade heating stage attached, was used. Temperature was controlled by a temperature controller, while a thermocouple on contact with film surface monitored the temperature. Transmittance spectrum was recorded at 25 °C (RT) and 90 °C, that were well below and above the usual critical transition temperature (T_C = 68 °C) for bulk VO_2. At these two temperatures, the IR transmittance variation (ΔTr_{IR}) at λ = 2000 nm defined as the difference of transmittance between RT and 90 °C was obtained.

$$\Delta Tr_{IR}(\%) = Tr_{IR}\ (25°C)\ (\%) - Tr_{IR}\ (90^{\circ}C)\ (\%) \quad (1)$$

The integrated luminous transmittance (Tr_{lum}, 350–750 nm) and solar transmittance (Tr_{sol}, 250–2500 nm) were obtained from the measured spectra, using the following equation:

$$Tr_i = \frac{\int \varphi_i(\lambda) * Tr(\lambda) d\lambda}{\int \varphi_i(\lambda) d\lambda} \quad (2)$$

where Tr(λ) denotes the transmittance at wavelength λ, i denotes luminous (lum) or solar (sol) for calculations, φ_{lum} is the standard luminous efficiency function for photopic vision (Wyszecki and Stiles, 2000), and φ_{sol} is the solar irradiance spectrum for an air mass of 1.5 (corresponding to the sun standing 37° above the horizon) ("ASTM G173-03 Standard Tables of Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on a 37° Tilted Surface," 2003). Thus, the solar transmittance modulation defined as

$$\Delta Tr_{sol}\ (\%) = Tr_{sol}\ (25°C)\ (\%) - Tr_{sol}\ (90^{\circ}C)\ (\%) \quad (3)$$

and the variation of luminous transmittance between RT and 90 °C defined as

$$\Delta Tr_{lum}\ (\%) = Tr_{lum}\ (25°C)\ (\%) - Tr_{lum}\ (90^{\circ}C)\ (\%), \quad (4)$$

were calculated. Moreover, in order to determine the critical transition temperature (T_C), the hysteresis loop of transmittance at λ = 2000 nm during heating (1.5 °C/min) and cooling was measured. By plotting the derivative of transmittance (dTr/dT) versus temperature for both procedures and fitting a Gaussian curve, the transition temperatures T_1 and T_2 were calculated for heating and cooling, respectively. Then, the critical transition temperature (T_C) was obtained as

$$T_C = \frac{T_1 + T_2}{2}, \quad (5)$$

while the transmittance hysteresis loop width as

$$\Delta T_C = T_1 - T_2. \quad (6)$$

Finally, the Full Width at Half Maximum (FWHM), denoted as ΔT_H, of the above mentioned Gaussian curves for heating ($\Delta T_{H,\ h}$) or cooling ($\Delta T_{H,\ c}$) was defined by the sharpness of each transition, respectively, indicating how abrupt the phenomenon is, since low ΔT_H leads to more abrupt transition.

3. Results and discussion

3.1. Structural characterization

The XRD patterns of the VO_2 films with thickness 120 nm and 260 nm grown at 3% O_2 in Ar-O_2 plasma, deposited on K-Glass substrates are presented in Fig. 1. It can be seen that both films exhibit a polycrystalline structure with the two characteristic peaks at 2θ = 27.8° and 2θ = 39.7°, corresponding to the VO_2 (0 1 1) and (0 0 2) characteristic directions, respectively (JCPDS card no. 44-0252). In addition, for the thicker film one may identify two more characteristic peaks at 2θ = 44.6° and 2θ = 55.5°Corresponding to the (0 1 2) and (2 2 0) directions, respectively. However, the low intensity of the VO_2 diffraction peaks can be attributed to the low deposition temperature (Dai et al., 2008), as 300 °C is at the low temperature limit at which the