Low temperature rf-sputtered thermochromic VO_2 films on flexible glass substrates

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Abstract

The high deposition temperature of the order of 400 ºC and more is requirement for the growth of the thermochromic phase of vanadium dioxide (VO_2), limits the type of substrates that one may grow them on only to rigid ones. In this work, thermochromic VO_2 films were successfully deposited on flexible Corning® Willow® glass substrates, without the use of a buffer layer, by rf sputtering at a substrate temperature of 300 ºC, one of the lowest for this technique ever reported. The critical transition temperature of 80 nm thin films was T_c = 50.7 ºC, transmittance hysteresis width was ΔT = 12.1 ºC, while the modulation of the transmittance at λ = 2000 nm measured at 25 ºC and 90 ºC was around 36%, leading to a solar modulation of ΔTr_{sol} = 5%. In addition, an increase in transmittance at λ = 600nm (visible region) of 4% was observed before and after heating, while integrated luminous transmittance remained almost constant at Tr_{lum} = 34%. The thermochromic and luminous characteristics of the VO_2 films deposited on flexible glass are comparable to those deposited on rigid glass substrates. The deposition of thermochromic VO_2 film on flexible glass substrates by sputtering technique opens up a new window for thermochromic applications on flexible substrates. Copyright © 2017 VBRI Press.

Keywords: Thermochromic VO_2, rf sputtering, flexible glass substrate, low deposition temperature.

Introduction

Chromogenics are materials which change their optical properties due to an external stimulation, such as light (photochromic materials), voltage (electrochromic materials) or temperature (thermochromic materials) [**1**]. Among them, thermochromic materials are of great interest since they can be used as coatings for smart windows in energy saving buildings, in order to regulate the internal temperature [**2**, **3**]. VO_2 is the most well studied thermochromic material because its critical transition temperature (T_c) is the closest to room temperature [**4-6**]. In specific, VO_2 undergoes a first-order semiconductor to metal transition (SMT) at a critical transition temperature (T_c) of 68 ºC, which can be attributed either to strong electron correlations (Mott-Hubbard transition) or to electron-lattice correlations (Peierls transition) [**5**, **7-8**]. Below T_c it is an insulator, having a monoclinic structure and high transmittance in infrared irradiation, while above T_c it turns to metal, with a rutile structure and high reflectance in infrared [**9**]. In addition, during this procedure the visible transmittance remains constant [**10**].

Various deposition techniques such as APCVD [**11**], sol-gel [**12**], PLD [**13**], dc or rf sputtering [**9**, **14-17**] etc., are used to growth thermochromic VO_2. Among them rf sputtering is a widely-used technique in order to growth films of high quality and homogeneity, even in large scale. Thermochromic VO_2 films can also be deposited on a wide range of rigid substrates such as glass [**13**, **18**], Si [**18**], sapphire [**19**], while in some cases a buffer layer of SnO_2 [**20**, **21**], ZnO [**21**], or other metal oxides [**22**] may be used to obtain VO_2 with improved thermochromic properties. However, depositing thermochromic VO_2 on flexible substrates is of great interest and remains a challenge for application in retrofitting in buildings as well as other potential applications that a flexible substrate may be used like consumers electronics, automobiles etc. The relative high substrate temperature (over 300 ºC) which is normally required to produce the VO_2 phase by sputtering technique [**14-16**], works as a barrier for depositions on flexible substrates such as polyethylene terephthalate (PET) and polyethylene-naphthalate (PEN). This could be probably achieved only by methods applying chemical solution processes [**23**, **24**] by which, initial VO_2 produced in powder form and fired at high temperatures undergoes a specific treatment that turns it into a film, however with less uniformity comparable to that produced by sputtering. In this work, thermochromic VO_2 films were deposited on flexible Corning® Willow® glass substrates for first time, without the need of buffer layer, using the rf sputtering technique, at a substrate temperature of 300 °C which is one of the lowest reported in the literature [**17**, **25**]. The thermochromic properties of the VO_2 films were similar to those produced on rigid glass substrates with or without a buffer layer.

Experimental

VO_2 films were growth by rf sputtering technique, using a vanadium metal target (8'' dia. x 0.250'', purity 99.95%). The total pressure during deposition was kept at 5 mTorr, while sputtering power was 400 W. The O_2 content in Ar / O_2 plasma was 1% and the substrate temperature was 300 °C, selected as the optimum conditions to produce thermochromic VO_2. The films were deposited on flexible Corning® Willow® glass, using the rf sputtering deposition technique. The thickness of flexible glass was 0.2 mm, while that of VO_2 films was around 80 nm as verified by both a-step profilometer and Field Emission Scanning Electron Microscopy (FE-SEM) measurements. Film structure was examined by X-Ray Diffraction (XRD) technique using a Panalytical X' Pert Diffractometer system with Cu K_α X–Rays. Grazing Incidence XRD (GIXRD) method with $\theta = 0.5^o$ and $2\theta = 10^o - 80^o$ was employed to take the diffraction pattern of the film. From X-Ray Diffraction pattern, the grain size was calculated using Scherrer's formula

$$D(nm) = \frac{0.9 \cdot \lambda}{B \cdot \cos\theta_B},$$

where, λ=0.154 nm is the wavelength of X-Rays corresponding to Cu Ka edge, B the full width half maximum at 2θ and $\theta_B = \theta$.

Additionally, the presence of thermochromic VO_2 phase was confirmed by Temperature – dependant Micro – Raman spectroscopy using a T64000 J-Y system. The surface morphology was investigated by FE-SEM (Jeol 7000), operating at 15 keV.

Thermochromic properties of VO_2 films were studied by recording the transmittance at elevated temperatures, using a Perkin Elmer Lambda 950 UV/VIS/NIR spectrophotometer at λ = 250 – 2500 nm with a homemade heating stage. A thermocouple was in contact with film surface to measure the temperature and a temperature controller was used to control heating by a step of 1.5 °C / min. Transmittance spectra were taken at room temperature (25 °C) and at 90 °C, which is well below and well above T_c of the material. By using these spectra, both variation of IR transmittance at λ = 2000 nm (ΔTr_{IR}) and visible transmittance (Tr_{vis}) were calculated. The former defined as the difference in transmittance at λ = 2000 nm between 25 °C and 90 °C, while the latter is defined as the transmittance of the film at λ = 600nm. Moreover, integrated luminous transmittance (Tr_{lum}, 350–750 nm and solar transmittance (Tr_{sol}, 250–2500 nm) were obtained from the measured spectra, using the equation.

$$Tr_i = \frac{\int \varphi_i(\lambda) \cdot Tr(\lambda)}{\int \varphi_i(\lambda)},$$

where, $Tr(\lambda)$ 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 [**26**], and φ_{sol} is the solar irradiance spectrum for an air mass of 1.5 (corresponding to the sun standing 37 ° above the horizon) [**27**]. From this, the solar modulation is defined as the difference $\Delta Tr_{sol} = Tr_{sol}(25^oC)\text{-}Tr_{sol}(90^oC)$, of integrated solar transmittance between 25 °C and 90 °C.

Finally, by taking the transmittance hysteresis loop at λ = 2000 nm, between 25 °C and 90 °C, both critical transition temperature (T_c) and width of transmittance hysteresis loop (ΔT) were extracted. In particular, by plotting the derivative of transmittance (dTr/dT) versus temperature for heating and cooling procedure and by fitting a Gaussian curve, the transition temperatures (T_1) and (T_2) were calculated, respectively. Thus, the critical temperature (T_C) is defined as $T_C = (T_1+T_2)/2$ and the width of transmittance hysteresis loop defined as $\Delta T = T_1\text{-}T_2$.

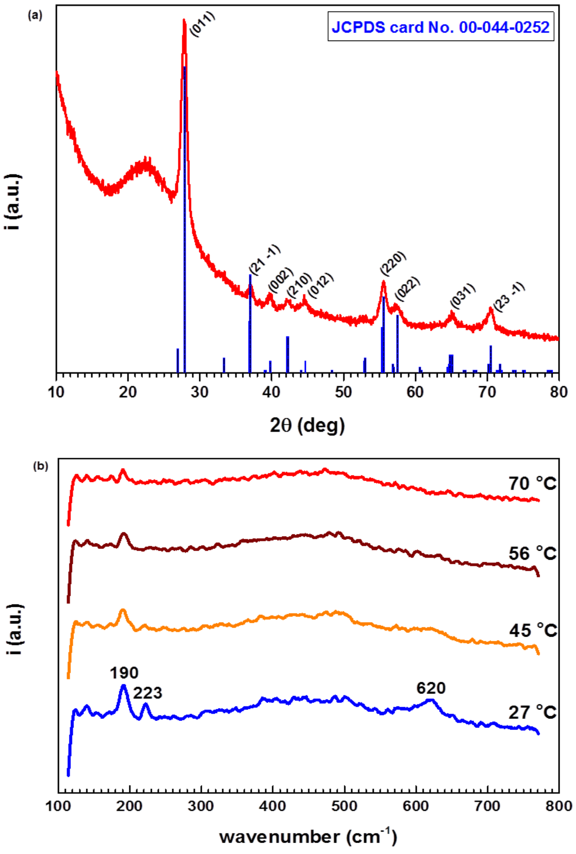

Fig. 1. (a) XRD pattern and (b) T – dependent Raman measurements of a 80 nm VO_2 thermochromic film deposited on flexible Corning® Willow® glass substrate.

Results and discussion

All VO_2 films were polycrystalline as revealed by XRD analysis presented in (**Fig.1a**). According to this, a preferable growth orientation of the (011) plane, which is characteristic for VO_2 and corresponds to $2\theta = 27.77^{o}$ (JCPDS card No. 44025) was obtained. Using Scherrer's formula, grain size was calculated and found to be D = 10.2 nm which is one of the lower values referred to the literature [**28**, **29**]. The presence of thermochromic VO_2 was verified by T-dependent micro Raman spectroscopy (**Fig.1b**). The spectrum was recorded gradually elevating the temperature from RT to 70 ^{o}C and back to RT [**21**]. Peaks of 190 and 223 cm^{-1} correspond to V-V vibration modes, while that of 620 cm^{-1} corresponds to V-O vibration modes and are the monoclinic VO_2 signatures [**25**].

Furthermore, the decrease of 190 cm^{-1} peak intensity upon heating is an indication of the phase transition of VO_2 from low temperature, monoclinic, to high temperature, tetragonal rutile, for which the enhanced symmetry leads to the disappearance of the 223 and 620 cm^{-1} Raman phonon modes [**30**] at around 50 ^{o}C. However, a more accurate account of the film's T_C evaluation based on the transmittance hysteresis loop is presented above.

The surface morphology of the films was examined by SEM, an image of which is presented in (**Fig.2**). It can be seen that films' surface is very smooth with small grains, in agreement with XRD measurements.

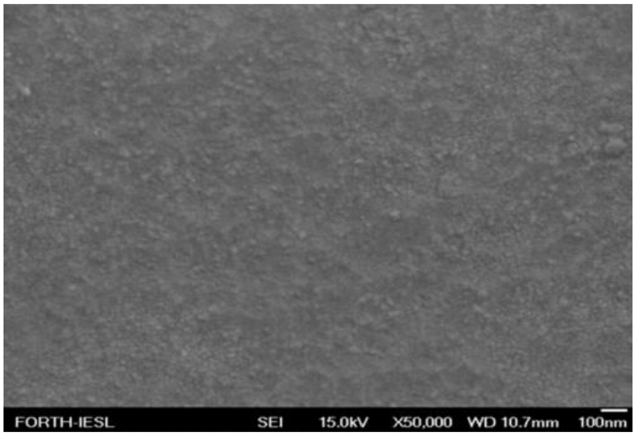

Fig. 2. SEM image of a 80 nm VO_2 thermochromic film deposited on flexible Corning® Willow® glass substrate.

In (**Fig. 3a**), the transmittance at T = 25 ^{o}C and T = 90 ^{o}C, of the 80 nm VO_2 film deposited on flexible glass is presented. It can be clearly seen that the film exhibits a thermochromic behavior having an IR transmittance variation at $\lambda = 2000$ nm of $\Delta Tr_{IR} = 36\%$ (from 48% at RT to 12% at 90 ^{o}C) resulting to a modulation of the integrated solar transmission $\Delta Tr_{sol} = 5\%$, which is a typical value for undoped VO_2 films, deposited on various rigid substrates with or without a buffer layer, as it can be seen in **Table 1**. The corresponding transmittance hysteresis loop at $\lambda = 2000$ nm is presented in (**Fig. 3b**), from which the critical transition temperatures T_1 and T_2 during heating and cooling, respectively, were calculated and found to be 56.8 ^{o}C and 44.7 ^{o}C. The former is in good agreement with the value extracted by the above mentioned T-dependent micro Raman spectroscopy (**Fig. 1b**) where the peaks corresponding to VO_2 disappeared at 56 ^{o}C, during heating from RT to 70 ^{o}C. The width of the transmittance hysteresis loop ΔT was 12.1 ^{o}C, while the critical transition temperature T_c was 50.7 ^{o}C, which is 18 ^{o}C below that is calculated for a single crystal of VO_2.

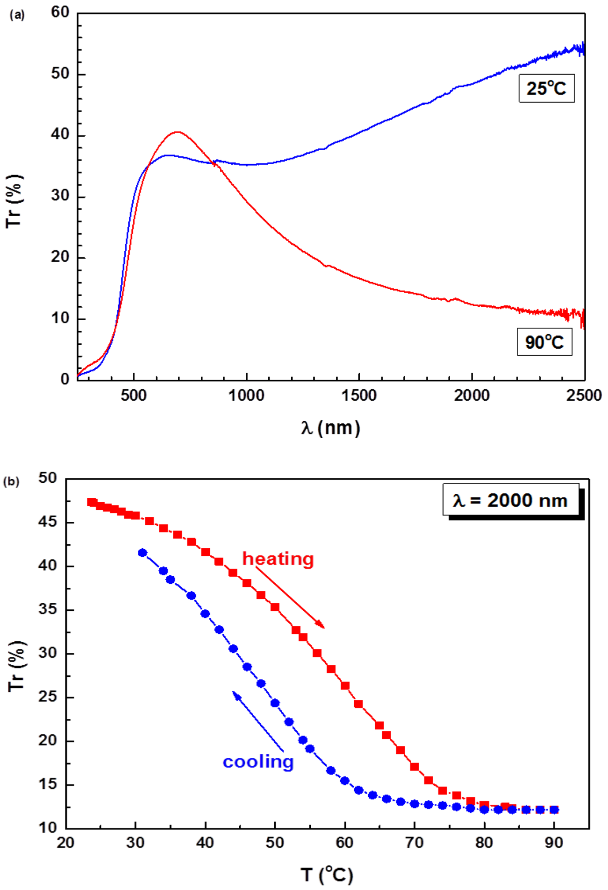

Fig.3. (a) Transmittance spectra at different temperatures and (b) transmittance hysteresis loop at $\lambda = 2000$ nm, of a 80 nm VO_2 thermochromic film deposited on flexible Corning® Willow® glass substrate.

Taking into account that the films were not doped and were grown at low deposition temperature without further annealing, such a low T_c can be attributed to the inherent small crystallite size and the resulting increased mechanical internal stresses. This is in agreement with Suh *et al.* [**31**] who reported that T_c is size-dependent. Moreover, these values are close enough to those calculated by Melnik *et al.* [**17**] for VO_2 films deposited on rigid glass at 200 ^{o}C, however, followed by post-deposition annealing at 300 ^{o}C. Evidence, that the small grain size leads to transmittance hysteresis width slightly over 10 ^{o}C, has also been reported recently by Zhang *et al.* [**32**]. It is known [**29**] that small crystallite size implies high density of grain boundaries resulting in more defects that can cause a distortion by lowering the distance between V-V pairs and as a consequence lower energy is needed in order to change the crystallographic phase from monoclinic to tetragonal rutile structure thus decreasing the critical transition temperature. On the other hand, the lack of sharp transmittance hysteresis loop can be also attributed to defects that make the transition difficult, and slow the propagation of transition during heating and cooling procedure. Finally, a slight increase of 4% at λ = 600 nm for the visible transmittance was observed (rising up to 40%); however the integrated luminous transmittance was slightly decreased from 34.14% at 25 °C to 33.71% at 90 °C. This is in agreement with results from Xu *et al.* [**33**], reporting that the integrated luminous transmittance (Tr_{lum}) is thickness dependent and that Tr_{lum} for films with thickness over 50 nm decreases after heating.

Table 1. Thermochromic and optical properties of undoped VO_2 films deposited on various glass substrates referred in literature. T_c is the critical transition temperature, ΔT is the width of transmittance hysteresis loop, Tr_{lum}, is the integrated luminous transmittance at 25 °C and ΔTr_{sol} is the solar modulation.

deposition technique	**substrate**	**T_C (°C)**	**ΔT (°C)**	**ΔTr_{sol} (%)**	**Tr_{lum} (%)**	**Ref.**
rf sputtering	Flexible Glass	50.7	12.1	5	34	**this work**
rf sputtering	SiO_2/Glass	57	15.8	6.3	30.1	[**22**]
rf sputtering	SnO_2/Glass	55.7	8.2	5.2	36.2	[**20**]
rf + dc sputtering	Glass	59	3	12.8	24.7	[**34**]
Sol-Gel	Glass	62.5	5	4.54	10.06	[**12**]
hydrothermal	Plastic (PET)	55.9	8.7	13.6	29.2	[**24**]

To summarize, this was a first successful attempt to deposit undoped VO_2 on flexible glass, at low substrate temperature of 300 °C, using rf sputtering technique. Both thermochromic and luminous characteristics of the films were comparable with those deposited on rigid or plastic substrates with post annealing, as it can be seen in **Table 1**. In specific, VO_2 films on flexible substrate have lower T_C and higher luminous transmittance than films deposited on rigid or other substrates. However, width of transmittance hysteresis loop is over 10 °C, while solar modulation is lower than the others. These variations between films deposited in different substrates can be attributed to different thickness, grain size or deposition temperature.

Conclusion

Thermochromic VO_2 films were deposited directly on flexible glass substrate for first time, at a low substrate temperature of 300 °C, with no post-deposition annealing. Films found to be polycrystalline, with small crystallite size of 10 nm. The thermochromic behavior of the films was verified by both T-dependent micro Raman spectroscopy and transmittance measurements upon heating. They exhibited a low critical transition temperature of T_c = 51 °C, while the width of transmittance hysteresis loop was ΔT = 12 °C. Both values were attributed to the small crystallite size, due to the low deposition temperature. Additionally, IR transmittance variation (ΔTr_{IR}) at λ = 2000 nm was decreased by 36% upon heating, leading to a modulation of integrated solar transmission ΔTr_{sol} = 5%, as a consequence of film thickness and grain size too. Finally, integrated luminous transmittance Tr_{lum} was almost unaffected maintaining a value of around 34%, thus demonstrating the potential of using these thermochromic films of low deposition temperature on flexible substrates for smart windows applications. A comparison with previous works on thermochromic VO_2 deposited on rigid glass or plastic substrates was done, resulting that flexible substrate is an appropriate candidate in order to deposit thermochromic VO_2 films.

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Author's contributions

Conceived the plan: GK, EA, EG, VB, YR, DT; Performed the expeirments: EG, GM, IK, MP; Data analysis: EG; Wrote the paper: EG. Authors have no competing financial interests.

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