

Effect of substrate temperature on the structure and the metal insulator transition in pulsed laser deposited VO_2 films on soda lime glass

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Abstract In this paper, we report the effect of soda lime substrate deposition temperature (T_s) on the crystal structure and the metal insulator transition of VO_2 thin films. Samples were deposited at substrate deposition temperature ranging from 450 to 600 °C by pulsed-laser deposition and characterized by x-ray diffraction and UV–VIS spectrophotometer. At a substrate temperature of 550 °C, the VO_2 (100) reflection dominate the spectrum showing a change in crystalline grains orientation. The highest transition temperatures of 74 °C with the lowest hysteresis width of 11 °C were obtained on the same sample grown at a substrate deposition temperature of

500 °C and also corresponding to the largest grains size of a value of 350 nm.

Keywords Crystal growth · Grains Growth · Texturation · Phase transition · Pulsed Laser deposition

Introduction

Vanadium dioxide (VO_2) has attracted much attention in recent years because it is well known to have a temperature driven metal to insulator transition (MIT) around a critical temperature (T_{MIT}) of 68 °C [1]. This MIT is accompanied by a transformation of crystallographic structure, from monoclinic at temperatures below T_{MIT} to tetragonal at temperatures above T_{MIT} . This first order phase transformation is characterized by a small lattice distortion along the c-axis, which results in pairing of the vanadium atoms and a distinct band structure in each phase. In the insulating phase, a monoclinic distortion of the lattice by a pairing of the V atoms induces a change in the V-O hybridization, resulting in a rise of the π^* band above the Fermi energy and a splitting of the $d_{||}$ band with one above and the other below the Fermi level. The optical band gap between the $d_{||}$ valence and π^* conduction bands is obtained as 0.7 eV in the insulating phase, to which the $\pi^*-d_{||}$ correlation energy contributes partially. Contrary, in the metallic phase $d_{||}$ and π^* are the lowest-energy bands near the Fermi level and they overlap [1, 2]. The phase transition behaviors of deposited VO_2 films are often investigated for practical use. The transition temperature and the hysteresis width are generally the criteria qualifying of deposited VO_2 material. A lower phase transition temperature is favorable for device applications such as smart window [3]. The narrow hysteresis films width (1–5 °C) implies good switching properties and can be used for IR radiation control in smart

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windows, in light modulators while a broad hysteresis width is used for optical data storage [4, 5]. In terms of the energy efficiency, and because of its, as mentioned promising technological applications for IR radiation control, this thermochromic VO_2 compound has sparked a large research effort especially in its thin film configuration. Many efforts have been undertaken to deposit suitable VO_2 thin films by reactive sputtering, pulsed laser ablation, evaporation, chemical vapor deposition techniques, oxidation of deposited metal films and sol–gel techniques [6–11]. In addition to a requirement for an accurate optimization to obtain the correct VO_2 polycrystalline structure due to the multiple V electronic valences and its high affinity with oxygen [12], it is challenging to synthesize large thermochromic VO_2 based coatings, with such techniques. While the cost effective sol–gel synthesized VO_2 coatings exhibit a relatively good IR modulation, they do not possess long term age stability. The excellent agreement between theory and experiments has yielded strong evidence for efficient growth control of metal oxide nanostructures; it has also produced great expectation for the future development of nano-materials devices and the optimization of their physical properties. Moreover, when the thermodynamic stabilization is achieved, not only is the size tailored but also the shape as well as crystallographic structure maybe controlled. This controlled crystallographic structure has an important bearing and quite often modifies the physical properties of materials. In the high quality single crystalline form of VO_2 the MIT occurs at the critical temperature of 340 K and has a narrow hysteresis, but in physical vapor deposited (PVD) films the critical temperature, the width of the hysteresis loop, and the amplitude of the MIT depend strongly on the film morphology and stoichiometry as well as structural defects. PVD films showing good thermochromic properties are usually grown as VO_2 (R) at around 600 °C. A. Ilinski et al. [13] reported, the metal–semiconductor phase transition depend on the grain size and exhibit a hysteresis (20–30 °C) in the polycrystalline films. R. Lopez et al. [14], report the enhanced hysteresis (greater than 35 °C) in the semiconductor-to-metal phase transition of VO_2 precipitates formed in SiO_2 by ion implantation. Te-Wei Chiu et al. [15], reported that it has been proven the single crystal substrates is effective to obtain VO_2 thin films with a narrow hysteresis width but they are expensive and difficult to prepare on large scale.

This communication reports on the synthesis of a-axis oriented and nanosized VO_2 at different substrate temperature by pulsed laser deposition (PLD) on soda lime glass substrate without any catalyst. To our knowledge, soda-lime glass is used in everyday products and devices such as solar cells, household mirrors, automobile glass, and architectural building windows. Therefore, ours focus investigation is an interesting topic in thin film growth for optical application in a cost effective way as the physical properties of the films will depend strongly on their texturation.

Experimental details

The films were deposited on the substrate held at temperatures ranging from 450 to 600 °C at deposition time of 45 min. A KrF excimer laser, wavelength of 248 nm, fluence of 1.7 J/cm², repetition rate of 10 Hz, was incident on target of pure V metal. The soda lime–target distance was kept at 65 mm. The cooling temperature soda lime was done with 50 °C/min. The deposition was carried out in an oxygen atmosphere at a pressure 15 mTor. X-ray diffraction (XRD) patterns using an AXS Bruker diffractometer equipped with a position sensitive detector determined the crystalline structure. The films morphology was characterized via scanning electron microscopy (SEM). The metal insulator transition was investigated in the wavelength of ultraviolet–visible–near infrared region using a CECIL 2000 spectrophotometer incorporated with Peltier thermoelectric heating and cooling stage. The light source, detector and sample holder are designed to fit within a dark box that has a cover. The spectrophotometer was allowed to create a baseline which removes background from the data to be collected. The beam of light is directed to the sample and the detector detects the amount of light transmitted through the sample. The data was generated and captured by the computer and temperature measurements were recorded. The data collected was used in our work to study the metal insulator transition.

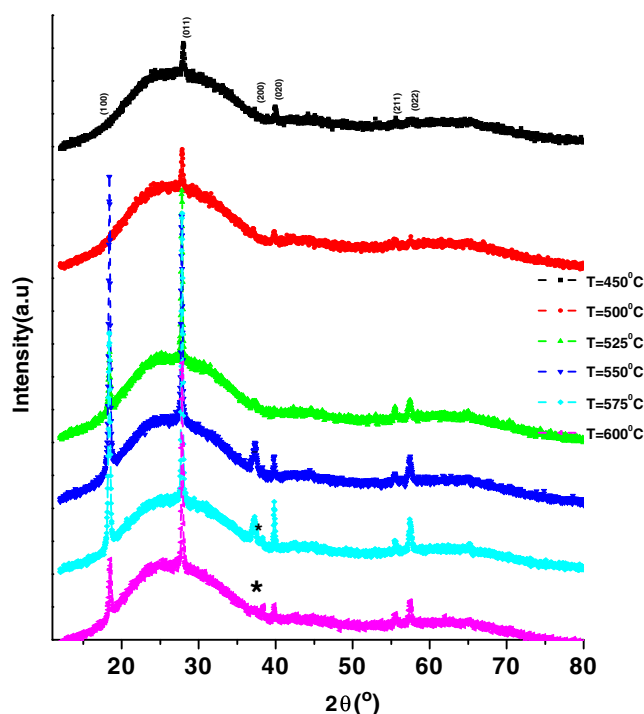


Fig. 1 XRD of VO_2 monoclinic (JCPDS 43-1,051) thin films deposited by pulsed laser deposition on glass at different substrate deposition temperatures (T_s)

Results and discussion

The XRD profile of the VO₂ thin films deposited on soda lime glass substrate at different substrate deposition temperatures (Ts) is shown in Fig. 1. The prominent Bragg reflections are occurring around $2\theta=18.42^\circ$ and $2\theta=27.08^\circ$ corresponding respectively to (100) and (011) diffraction planes, along with four other weak diffraction peaks viz. (200), (020), (211), (211) which confirms the monoclinic VO₂ polycrystalline nature of the film (JCPDS 0,043–1,051). Fig. 1. Shows that the VO₂ (011) reflection emerges from a broad structure. The broad structure may suggest the existence of a disordered phase of VO₂. The

XRD spectra of the films deposited at substrate deposition temperatures of above 500 °C exhibited the same behaviour as that of the film deposited at below 500 °C with an additional Bragg reflection at $2\theta=18.42^\circ$, corresponding to VO₂ (100) reflection of the VO₂ monoclinic phase. At a substrate deposition temperatures below and above 550 °C, the grains are preferentially oriented along the VO₂ (011) reflection, but for the specific substrate deposition temperature of 550 °C, the VO₂ (100) reflection dominate the spectrum showing a change in crystalline grains orientation. The appearance of this new VO₂ (011) reflection is a clear indication of the deterioration of the orientation of the crystalline VO₂ grains with an increase in temperature.

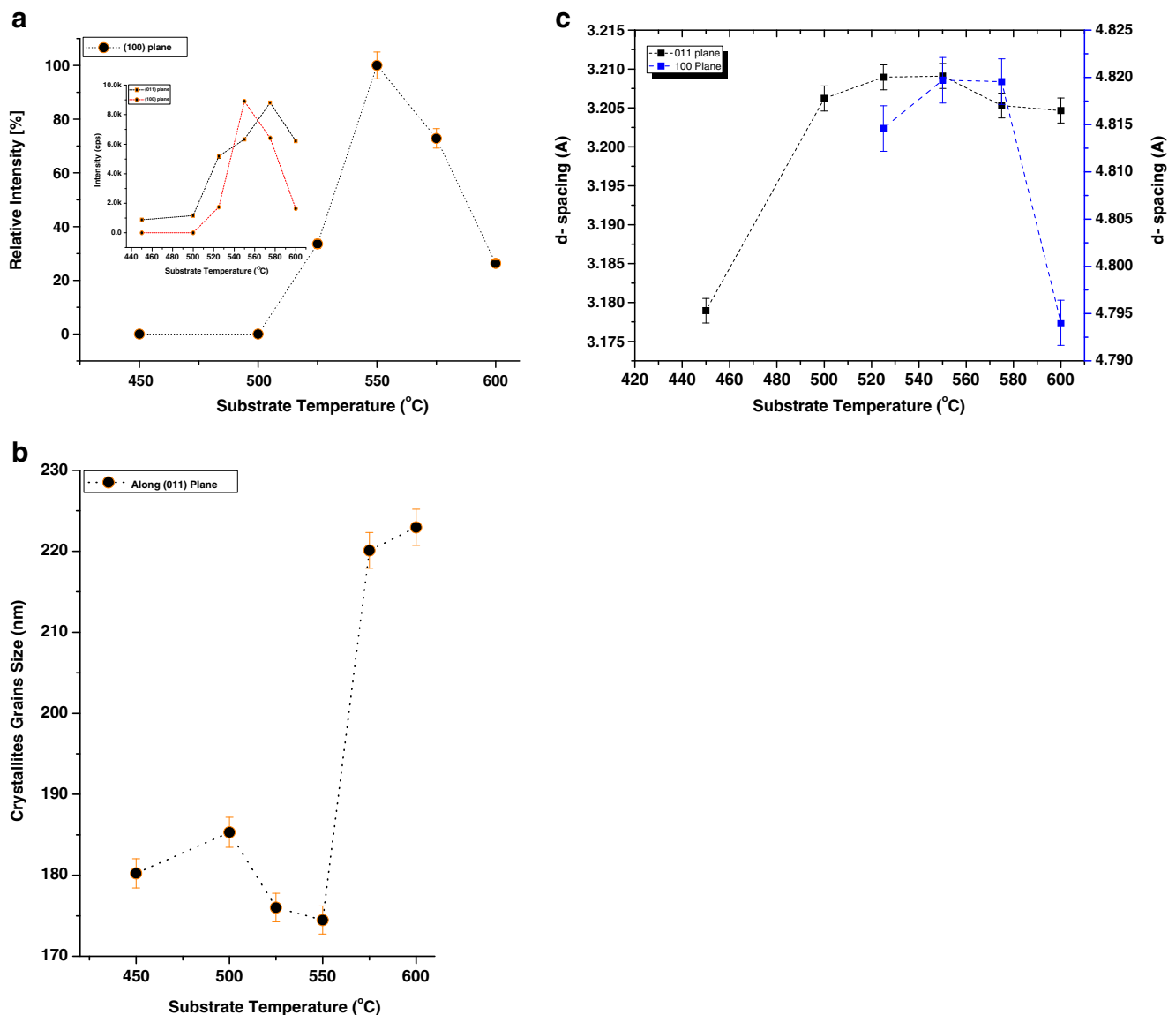


Fig. 2 a. Relative Intensity of the (100) reflection of VO₂ with respect to the (011) plane of pulsed laser deposited VO₂ thin films as function of substrate deposition temperature. Inset: evolution of the intensity of both reflections as function of substrate deposition temperature. b: Crystallites

size along (011) plane of pulsed laser deposited VO₂ thin films as function of substrate deposition temperature. c: Evolution of the d-spacing along the VO₂ (011) and VO₂ (100) of pulsed laser deposited VO₂ thin films as function of substrate deposition temperature

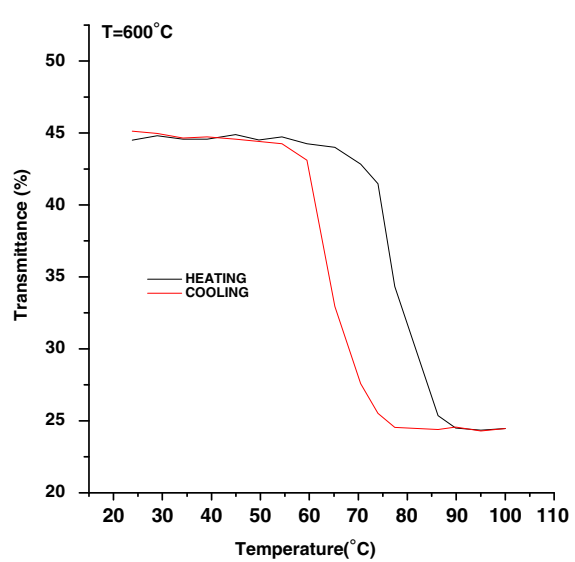
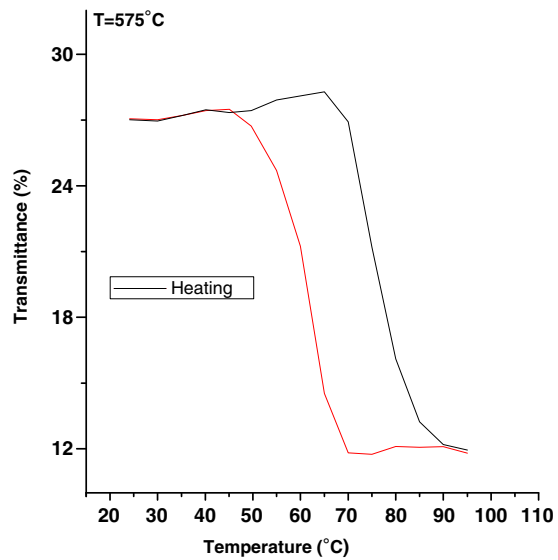
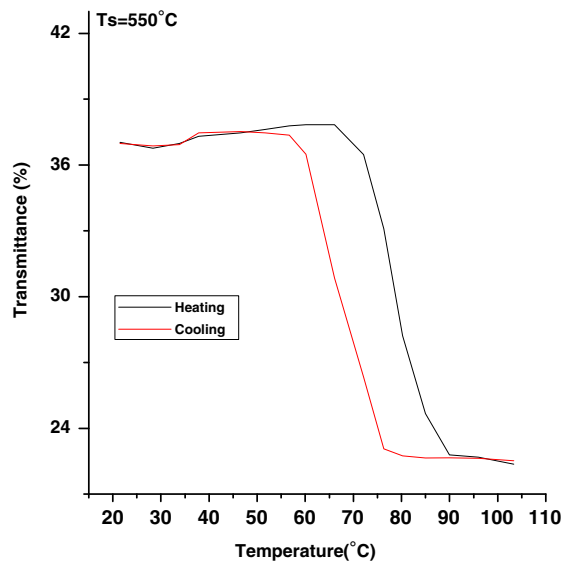
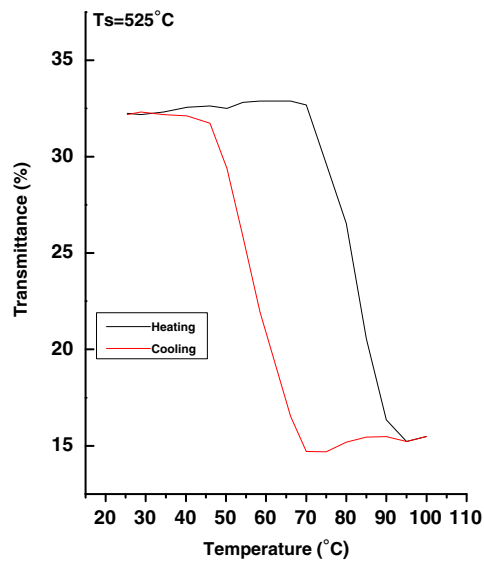
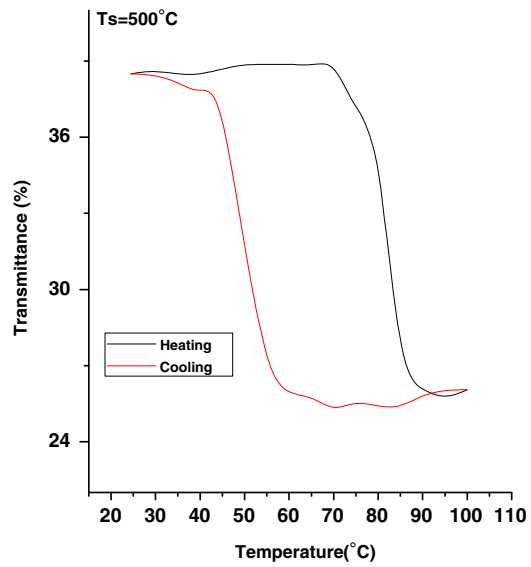
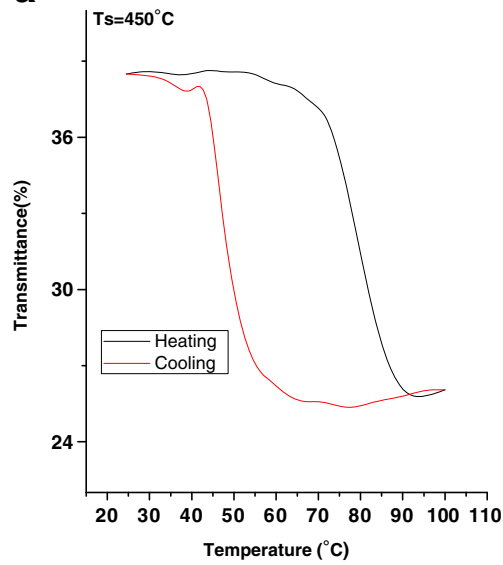
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Fig. 3 a. Thermal hysteresis loops of transmittance at wavelength of 1,100 nm of pulsed laser deposited VO₂ thin films as function of substrate deposition temperature. **b:** First derivative curves for thermal hysteresis loops of transmittance at wavelength of 1,100 nm of pulsed laser deposited VO₂ thin films as function of substrate deposition temperature. **c:** Variation of transition temperature of pulsed laser deposited VO₂ thin films as function grains sizes obtained from SEM images (Fig. 3). **d:** Variation of hysteresis width of pulsed laser deposited VO₂ thin films as function grains sizes Inset: Evolution of the grains sizes as function of substrate deposition temperature

Compared with the standard data, the relative intensity of (100) reflection (ref: Fig. 2a), of the VO₂ thin films reaches a maximum at the temperature of 550 °C, indicating that VO₂ (100) plane is most probably the preferred growth direction of the VO₂ (M1) nano-grains at a substrate deposition temperature of 550 °C.

In addition to the VO₂ (100) Bragg reflection which appears within the increase of the substrate deposition temperature, the patterns of the films deposited at temperature higher than 550 °C, show the emergence of a new Bragg reflection at $2\theta = 38.23^\circ$, which was identified and attributed as the (0,006) reflection of V₂O₃ by Zhou et al. in their work [16]. However, a qualitative phase analysis (search match), using the PANalytical X'pert Highscore Plus software with the ICDD PDF database has showed that the only closest phase that could probably much the peak indicated by * is Na_{1.80}V₂O₅ (400) (JCPDS 0,020–1,167). Therefore we could speculate that this reflection at $2\theta = 38.23^\circ$ also could indicate the presence of small amount of Na_{1.80}V₂O₅ phase in the thin films on soda-lime glass substrates, resulting from a diffusion of Na⁺ into thin films from substrates at high substrate temperature. It is interesting to note that this small impurity does not affect the thermochromic properties of the VO₂ films. S. Lu et al. [17],

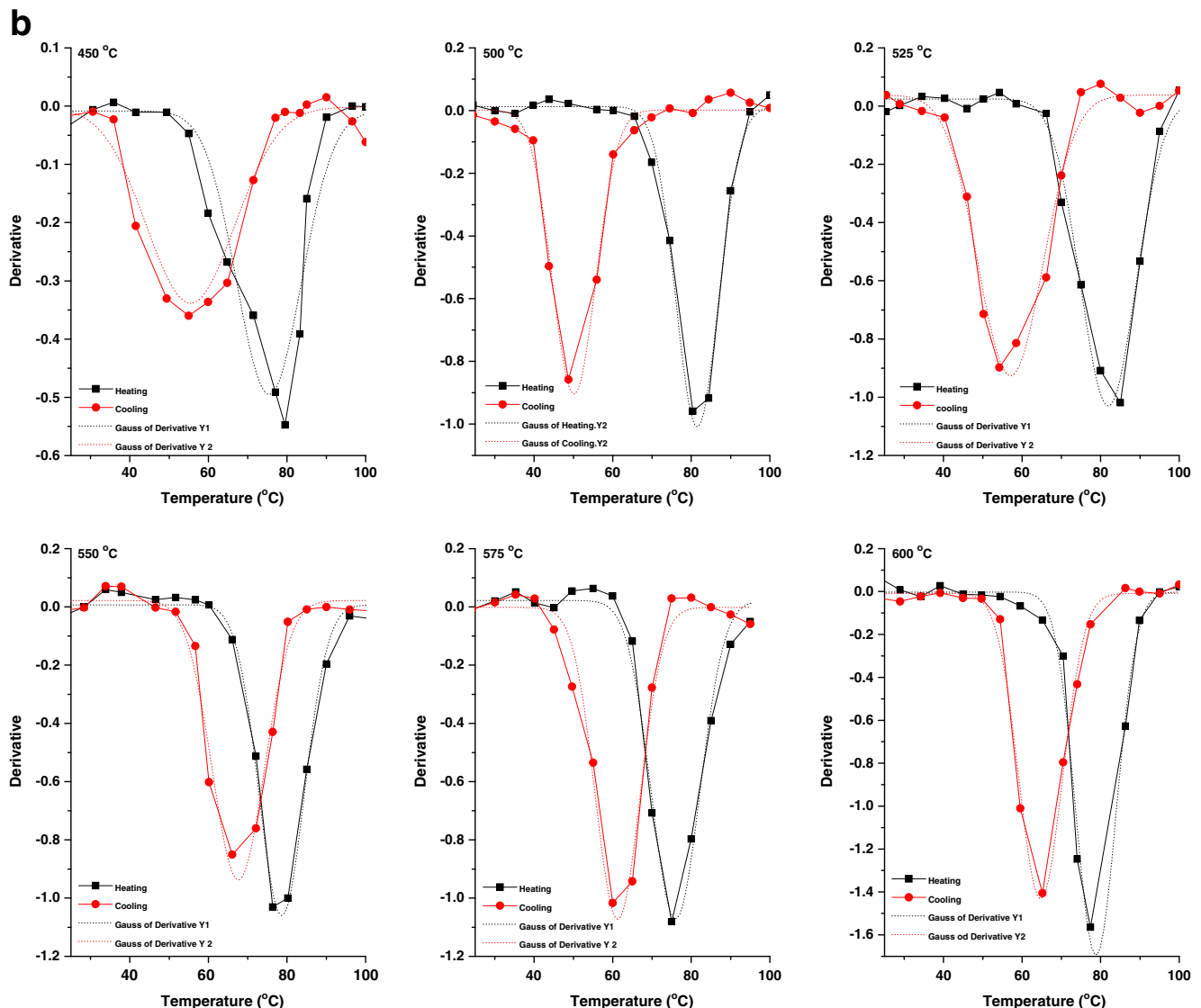


Fig. 3 (continued)

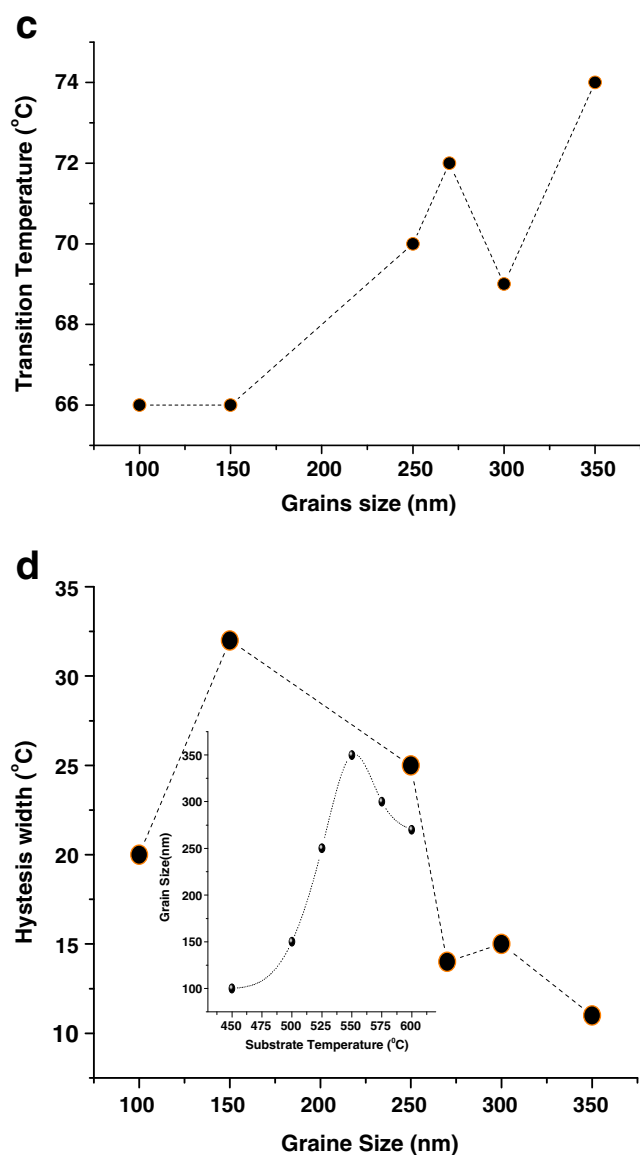


Fig. 3 (continued)

reported the same-like impurity with two small peaks at angle of $2\theta=12.1^\circ$ and $2\theta=29.1^\circ$ indicating the presence of small amount of $\text{Na}_x\text{V}_2\text{O}_5$ phase in the films on soda-lime-silica glass substrates, which resulted from the diffusion of Na into the films. Wang Xue-Jin et al.: [18], strongly concluded that sodium ions would diffuse from soda-lime substrate to film surface when sputter performed at high substrate temperature (580°C in their experiment), which was in agreement with other authors who claimed that VO_2 film could not be deposited on soda-lime glass because of sodium contamination. Therefore we could suggest that at a substrate temperature of 575°C and beyond, the peak at $2\theta=38.23^\circ$ indicate the presence of $\text{Na}_{1.80}\text{V}_2\text{O}_5$ phase in the thin films on soda-lime glass substrates, and is resulting from a diffusion of Na^+ into thin films from substrates high substrate temperature.

Figure 2b shows the influence of deposition temperature on the VO_2 crystallites along VO_2 (011) plane, which correlates well with the influence of the deposition temperature on the intensity of the peak VO_2 (011). Fig. 2c report on the evolution of the d-spacing as function of the substrate deposition temperatures, it can be seen that the effect of the deposition temperature is the same on both VO_2 (011) and (100) planes, the increase in substrate temperature induced an increase in d-spacing from 450 to 550°C before dropping down. It can be noted that the $d_{(100)}$ -spacing dropped four time faster than that of the $d_{(011)}$ -spacing at a substrate temperature of 550°C and beyond. We suggest that this can be due to the substrate thermal treatment around its transition temperature of 575°C .

To investigate the effect on grain size thermo-optical properties and the metal insulator phase transition in VO_2 films deposited on soda lime, the transmittance measurements were carried while heating and cooling the sample at different temperatures and the average grains size was obtained from the SEM images using image-J software. Figure 3a shows the thermal hysteresis loops of the optical transmittance (T_r) at a fixed wavelength of $1,100\text{ nm}$ for VO_2 thin films deposited at different temperatures. We see qualitatively different hysteresis shapes for the films deposited with different substrate temperatures as shown in Fig. 3a. The transition temperature during heating (T_H) or cooling (T_C) is defined by the minimum of derivative T_r curve. The transition temperature of the films is defined as the average of transition temperature of the heating and the cooling; $T_{\text{MIT}}=(T_H+T_C)/2$, while the hysteresis width (ΔT) is defined as the absolute difference between the T_C and T_H . The results obtained for the transition temperature and the hysteresis loop, are plotted respectively in Fig. 3b and c as function of the average grains size obtained from SEM images. In Fig. 4 we report on the 2D SEM images surface of the VO_2 thin films deposited with different substrate temperature. As shown in the inset of Fig. 3c, the average grains size obtained from SEM images, increase with the deposition substrate temperature from 450 to 550°C and drops at substrate temperature beyond 550°C substrate deposition temperature.

From Table 1, we can see that the T_H for all the samples is quite larger than that of bulk single-crystal VO_2 . However, all the three samples prepared at substrate temperature between 450 and 525°C , show a very large ΔT because their T_C (50 – 57°C) in addition to their higher T_H , are far lower than that of bulk VO_2 . As reported in Fig. 3b the transition temperature increases with the increase in grains size and drops at a grains size of 300 nm corresponding to the sample grown at a substrate temperature of 575°C and then increase again. It is interesting to notice that, the obtained values for the transition temperature for the samples prepared at substrate temperature between 450 and 525°C are similar to the value of bulk single crystal of VO_2 , but for higher substrate temperature from 550 to 600°C there is a shift towards a higher temperatures with an

exception for the sample grown at a substrate temperature of 575 °C, which its transition temperature correspond almost exactly to the transition temperature of the single crystal of VO₂.

J. B. Kana Kana et al. [19] have reported high substrate temperature induced anomalous phase transition temperature shift in sputtered VO₂ thin films on corning glass. They have observed an increase in the transition temperature from 70 to 80 °C when the substrate temperature varies from 450 to 600 °C. In their results, a the substrate temperature range of 450–500 °C led to a transition temperature of 70 °C similar to the bulk single crystal this is in agreement with our results. While a higher substrate temperature from 550 to 600 °C led to a transition temperature of 75 and 80 °C, respectively and these values are closer to our reported values but a little bit higher and this may be due to the difference in glass substrate type used. As reported by J.B. Kana Kana et al. [19], the major two effects that could led to this higher VO₂ transition temperature are a slight stoichiometry deviation and or a possible diffusion of some element from the glass substrate to the films such as Al, Na or Ca. As suggested from the XRD profile (Fig. 1), there may be a diffusion of Na in to the VO₂ films and

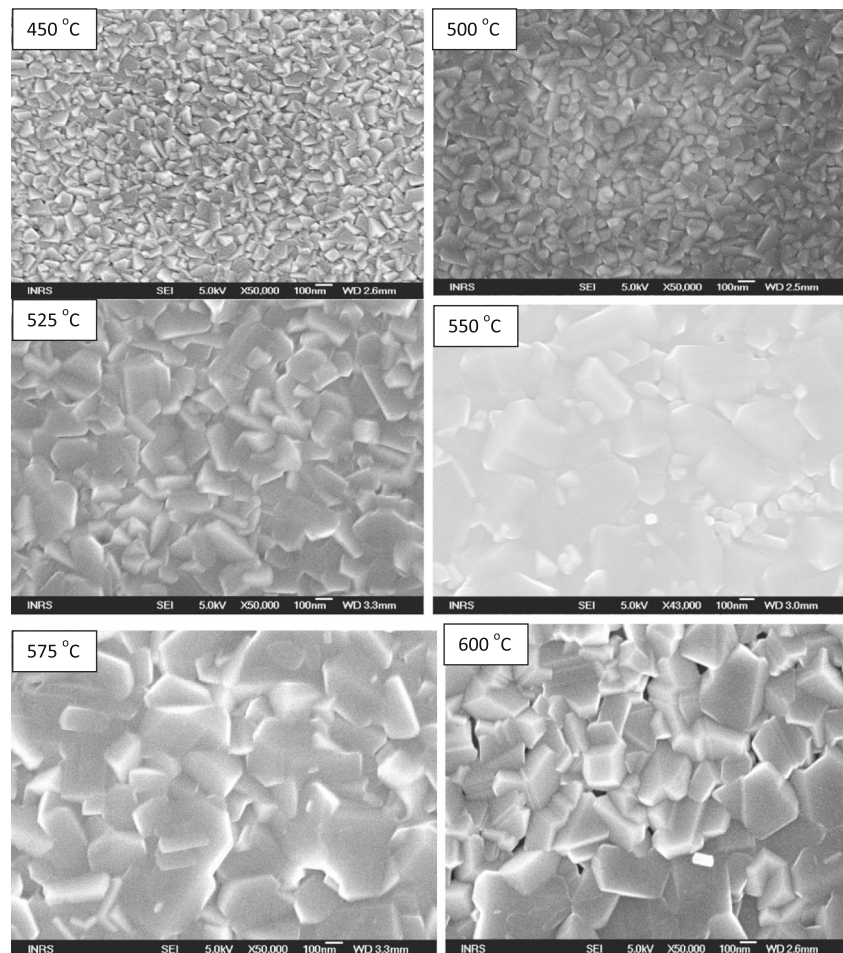
Table 1 Variation of the Transition temperature during the heating (T_H) and cooling (T_C) of pulsed laser deposited VO₂ thin films as function of substrate deposition temperature

Substrate Temperature (°C)	450	500	525	550	575	600
T _H (°C)	76	82	82	79	76	79
T _C (°C)	56	50	57	68	61	65

a formation of N_{1.80}V₂O₅ (400) (JCPDS 0,020–1,167), this would explain why we have observed higher transition temperature above a substrate temperature of 550 °C, but does not account for the sample grown at a substrate temperature of 575 °C. This anomaly seen for the sample of 300 nm of grains size corresponding to a substrate temperature of 575 °C in our results compared to the obtained trend by J. B. Kana Kana et al. [19], may be related to some effect induced by the substrate glass transition temperature reported to be around 575 °C during the growth of the films.

The increase of the hysteresis width in our samples as function of the grains sizes, is in agreement with the reported values by A. Ilinski et al. [13] and J. B. Kana Kana et al. [19] and R. Lopez et al. [14], we notice an increase of hysteresis

Fig. 4 SEM images of pulsed laser deposition VO₂ as function of deposition temperature



width from 20 to 32 °C for a grain size of 100 and 150 nm respectively and after that there is a continuous decrease of the hysteresis width with the increase in grains sizes that lead to a value of 11 °C for a grains size of 350 nm corresponding to the sample grown at a substrate temperature of 550 °C. The decrease in Hysteresis width with the increase in grains sizes in our results agreed with the reported values [13, 19]. But it is quite interesting to see that the samples prepared at a substrate temperature range of 450–525 °C (specially for a substrate temperature of 500 °C corresponding to a grain size of 150 nm), have a T_{cooling} lower than the other samples this explains why the hysteresis is larger. It have been reported that the thermo-optical properties of VO₂ rise from the competing effect of grains sizes, dislocations, nucleation defects, grains boundaries and crystal imperfections. In previous studies in the literature, such low T_C was also observed in VO₂ films or particles with different morphologies. The isolated bar-like VO₂ particles show a low T_C of about 35 °C as reported by R. Lopez et al. [14] while individual spheroidal VO₂ nanoparticle shows a T_C that is as low as 25 °C and misshapen VO₂ nanoparticle with the same volume shows a T_C of about 50 °C in the work done by E. U. Donev et al. [20]. Porous nanostructured VO₂ films obtained by Y.J. Xu et al. [21] show a low T_C in the range of 38.5–43.2 °C while VO₂ films with the “flower” like microstructure deposited on Nb-doped SrTiO₃ substrate by Y.J. Cui et al. [22] shows a T_C of about 54.5 °C. The low T_C of VO₂ films indicates that the MIT upon cooling undergoes a significant lagging. In other words, as reported also by H. Zhang et al. [23], the deposited films would require large additional driving forces in order to change from tetragonal to monoclinic phase. This could be attributed to the lack of nucleating defects and the large interfacial energies, which are determined by the characteristics of the particles in the deposited films, namely the small grain size resulting from low substrate deposition temperature. The smaller the grain size, the smaller the density of nucleating defects [23–25].

Conclusion

VO₂ thin films were deposited on soda lime glass substrate by pulsed laser deposition. The effect of the substrate temperature during deposition on the structure and the metal insulator transition were systemically investigated by means of XRD, SEM and UV–Vis spectrophotometer. It was found that the temperature of the substrate influence, the structure, the morphology evidently and consequently the Metal-Insulator phase transition. When substrate temperature was 550 °C, a change in VO₂ (100) preferential orientation could be obtained. Interestingly a larger ΔT was obtained for a grain size of 150 nm for the sample prepared at a substrate temperature of 500 °C and this was explained as a result of low transition temperature when the film have to go under crystallographic phase

transition from tetragonal to monoclinic. This could be attributed to the lack of nucleating defects and the large interfacial energies, which are determined by the characteristics of the particles in the deposited films, namely the small grain size resulting from low substrate deposition temperature.

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