

Effect of Oxygen Deposition Pressure on the Structure and the Metal Insulator Transition in Pulsed Laser Deposited VO₂ Films on Soda Lime Glass

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Abstract Vanadium dioxide thin films nanostructures were synthesized by pulsed laser deposition on soda lime glass at a substrate temperature of 600°C and the effects of the oxygen deposition pressure on the crystalline structure and the phase transition characteristics of VO₂ nanostructured films were investigated. The structure and microstructure of the films have been examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Results indicate that the crystal structure of the films is strongly sensitive to the oxygen deposition pressure; exhibiting sharp a-axis diffraction peaks, showing a texturation along (1 0 0) plane. A detailed description of the growth mechanisms and the substrate–film interaction is given, and the characteristics of the electronic transition and hysteresis of the phase transition are described in terms of the morphology, grain boundary structure and crystal orientation. The sharpness of the transition and the hysteresis upon heating and cooling are found to be strong functions of the crystal structure and microstructure (grain size).

Keywords: B. Crystal growth, A. Optical Material, A. Thin Films, C. X-ray Diffraction, D. Phase Transition

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1. Introduction

Large number of transition metal oxides and sulphides are semi-conducting and metallic at low temperatures and high temperatures, respectively [1]. In vanadium oxide compounds categorized as Mott insulators, this semi-conducting / metal phase transition is a first-order type as observed in V₂O₃, V₃O₅, V₄O₇, VO₂ [2]. The fascinating properties and wide range applications of vanadium oxides family, especially in thin film form, have attracted considerable interest [3]. Vanadium dioxide (VO₂), which is part of the several vanadium oxide phases such as the Magneli (V_nO_{2n-1}) and Wadsley phases (V_{2n}O_{5n-2}), is studied widely due to its abrupt change of reflectance in the infrared range near room temperature [4,5].

Vanadium dioxide (VO₂) manifests a femtosecond 1st order semiconductor/metal transition (SMT) at a temperature T_{SMT} ~ 68°C. At temperatures higher than the

critical temperature which is T_{SMT} ~ 68°C, it transforms to a narrow gap (0.7 eV) [6,7]. Below T_{SMT}, the semiconductor VO₂ exhibits a monoclinic structure, with lattice constants a ~0.575 nm, b~0.4526 nm and c~0.5383 nm. Above T_{SMT}, the metallic behavior is characterized by a tetragonal rutile-type structure, with lattice constants a~0.455nm and c~0.285 nm. This tetragonal rutile (P₄₂/mm) structure has chains of edge-shared VO₆ octahedral along the c-axis and the V–V distance along the chains is 0.2851 nm. In the semiconducting monoclinic (P21/c) crystal structure, the dimerized vanadium atoms have alternate V–V distances of ~0.2619 and ~0.312 nm [4].

As a consequence of such a femtosecond electronic/crystallographic and reversible SMT phase transition, the optical dielectric constant and thus the refractive index of VO₂ exhibits a temperature modulation, which translates in a large reversible optical properties. This singular and unique property of VO₂ makes it a multifunctional optical candidate of choice for smart windows applications, optical switching devices, field effect transistors, ultrafast

tunable nano-plasmonics and optical limiting devices as well as ultrafast opto-electronic gates among others. Through this reversible SMT near room temperature, VO₂ is considered also as a material having high potential for various applications other than thermochromic smart coatings, which include electronic switches and thermal sensors [8,9,10].

The nature of the electronic and structural phase transition has been a matter of research and debate for over three decades with many recent experiments shedding additional light on the issue [11]. But during this period the hysteretic nature of VO₂ has received much less attention. The hysteresis nature and mechanism in VO₂ are still open questions, which are interesting from a basic research point of view and might provide both information regarding the SMT mechanism and hysteresis in general in VO₂. It is also of vast importance from a technological aspect. For example, for optical memory-type applications, a large hysteresis is needed, while a small hysteresis is preferable in VO₂-based room-temperature bolometers for UV detectors. So, understanding the origin of the hysteresis can lead to a better control of its properties as reported by J.-G. Ramírez et al. [11]. The VO₂ thermal hysteresis characteristics are found to vary between samples grown under different conditions and resulting samples conditions, growth temperature, choice of substrate, as well as growth atmospheric pressure [11]. And film thickness and grain size respectively [11].

There are many reports on controlling the transition temperature of VO₂ thin film, either by doping [12,13] or applying stress [14,15]. Due to the small compositional differences between the numerous phases of vanadium oxide, VO₂ preparation requires a stringently controlled process that provides the desired oxygen stoichiometry and correct crystalline structure. Consequently, oxygen pressure is a critical parameter in growing the films [16]. In search of such a process, VO₂ films have been produced by a number of methods, including DC and RF reactive magnetron sputtering [8,17,18], reactive ion-beam sputtering [19,20], reactive evaporation [21,22], chemical vapor deposition [23,24], pulsed laser deposition (PLD) [2,3,25], electrochemical (anodic) oxidation [26,27] and sol-gel processes [28,29]. Given the requirement for accurate optimization to obtain the correct VO₂ polycrystalline structure, and due to the numerous electronic valences of vanadium and its high affinity for oxygen, it is challenging to synthesize large thermochromic VO₂-based coatings using such techniques. PLD has been found to be efficient and cost effective technique to produce, large amounts of thermochromic coatings. This technique is known for its rational fabrication of smart and functional high-quality metal oxide particulate thin films and coatings. Some of the synthesis methods have produced amorphous or quasi-amorphous films; others have produced polycrystalline films, and still others have produced oriented epitaxial films. The resultant films structures vary, depending on the crystallographic relationship between the growing VO₂ and the substrate, as well as on other factors, such as the growth temperature [30] and oxygen pressure.

In this paper we report on PLD-grown thin films, with a-axis orientation, influenced by the oxygen deposition pressure. It was determined that the manner of growth of

a-axis oriented VO₂ thin films on a glass substrate has a direct bearing on the characteristics of these films. As the hysteresis nature and mechanism in VO₂ are still an open question, which is interesting from a basic research viewpoint. This contribution will shed light on the effect of oxygen deposition pressure on the structural and micro-structural properties of the VO₂ thin films and consequently on its hysteresis characteristics and transition temperature.

2. Experimental Details

The VO₂ thin films were deposited using pulsed laser ablation deposition on a soda lime glass substrate maintained at a temperature of 600°C. The oxygen deposition pressure was varied from 3 to 15 mTorr to prepare various samples. The deposition time was set and maintained at 45 minutes corresponding to a deposition rate of 1,78 nm/min. This gives a thickness of 80 nm for each sample. We used a KrF excimer laser of wavelength of 248 nm, which has been focused onto the rotating target metal vanadium. The laser fluence was maintained at 1.7J/cm² and the repetition rate at 10 hertz, and 30 ns of pulse duration. The target-substrate distance was maintained at 6 cm. After deposition all samples were cooled in a vacuum with a cooling rate of 50°C/min. The crystallographic structure of thin films of VO₂ was characterized and confirmed by the technique of X-ray diffraction using a Bruker D8 diffractometer model powder Bragg-Brentano geometry. The intensity of the direct beam is obtained using a variable tube current of 40 kV and 40 mA with Cu radiation of wavelengths K α_1 length. The goniometer comprises a set up with N -1 Vantec detector and filter 4 degrees of Soller slit and providing narrow symmetrical profiles instrumental (PI) to the desired angular range. The spectra of X-ray diffraction of the samples were recorded in the range ($2\theta = 12^\circ$ - 80°) using in each case a step size of 0.02° and a count time of 20 s per step without moving the sample. The instrumental profile was obtained experimentally by collecting diffraction data of a standard Al₂O₃ powder by fitting with pseudo-Voigt functions and setting changes on the value of the width at half height. A Scanning electronic microscope (SEM) SEM 230 Nano secondary electron mode was used for analysis of the surface morphology of the films after deposition and the UV-Vis-NIR spectroscopy data of the VO₂ samples were collected in the wavelength range of 350 – 1100 nm using a CECIL 2000 Spectrophotometer incorporated with Peltier thermoelectric heating and cooling stage.

3. Results and Discussions

Figure 1a shows the XRD patterns characteristics of VO₂ thin films deposited on soda-lime glass substrate at different oxygen deposition pressures ranging from 3 mTorr to 15 mTorr, and cooled down to room temperature at a rate of 50°C/min in vacuum after deposition. The patterns show peaks due to the VO₂ thin layer at angles of 18.48°, 27.97°, 37.18°, 39.98° and 55.72° and a broad peak due to the glass substrate at an angle around 20°. Following the

calculated pattern description of the monoclinic structure of VO₂ (JCPDS No: 43-1051), these peaks can be indexed as the reflections on the (1 0 0), (0 1 1), (2 0 0), (0 2 0) and (0 2 2) planes respectively. After a qualitative phase analysis (search match) carried out using the PANalytical X'pert Highscore plus software employing the ICDD PDF database, no additional peaks due to others impurities were observed. It should be noted that although the multiple valence states of vanadium ions lead to several vanadium oxide phases such as Magneli phases (V_nO_{2n-1}) and Wadsley phases (V_{2n}O_{5n-2}), no other peak corresponding to any other vanadium oxide phases mentioned is present

in the XRD spectra, indicating the exclusive formation of single-phase VO₂ films on the glass substrate.

However it can be seen that the sample prepared with an oxygen pressure of 3 mTorr is completely amorphous with the broad peak around 20° coming from the substrate, while the other samples prepared in the range of 5 to 12 mTor of oxygen pressure, present the same XRD patterns with a preferential orientation along the <1 0 0> direction. The sample prepared with an oxygen pressure of 15 mTorr presents the very same characteristic of monoclinic VO₂ that is usually reported into the literature with a preferential growth along the <0 1 1> direction.

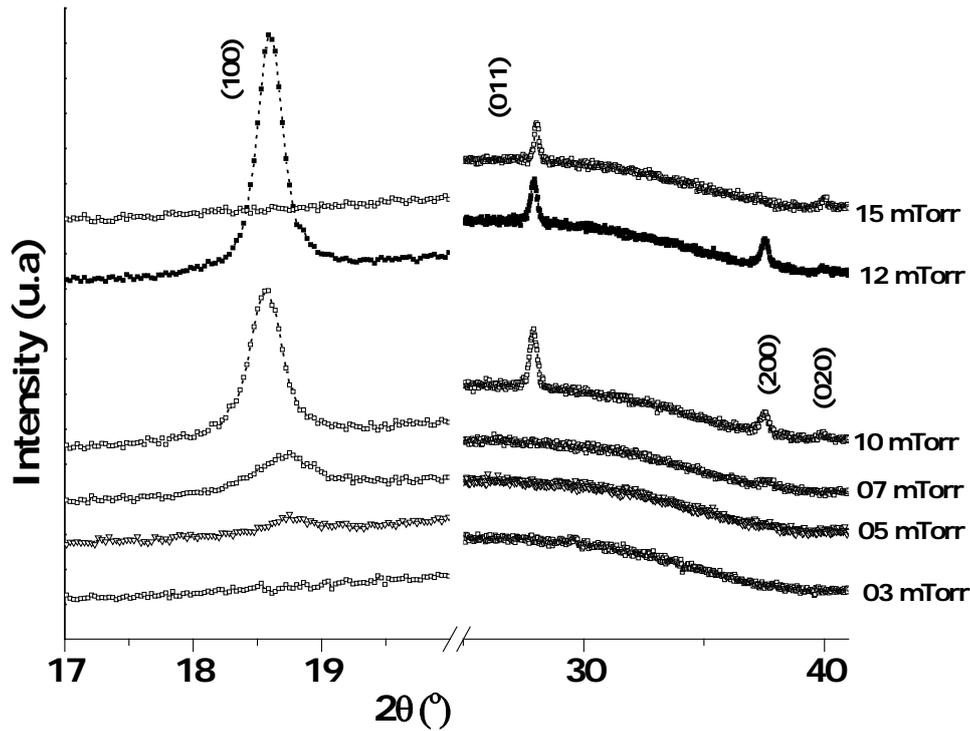


Figure 1a. XRD patterns characteristic of VO₂ thin films deposited at different oxygen pressures on soda-lime glass substrate and cooled down to room temperature at a rate of 50°C/min in vacuum

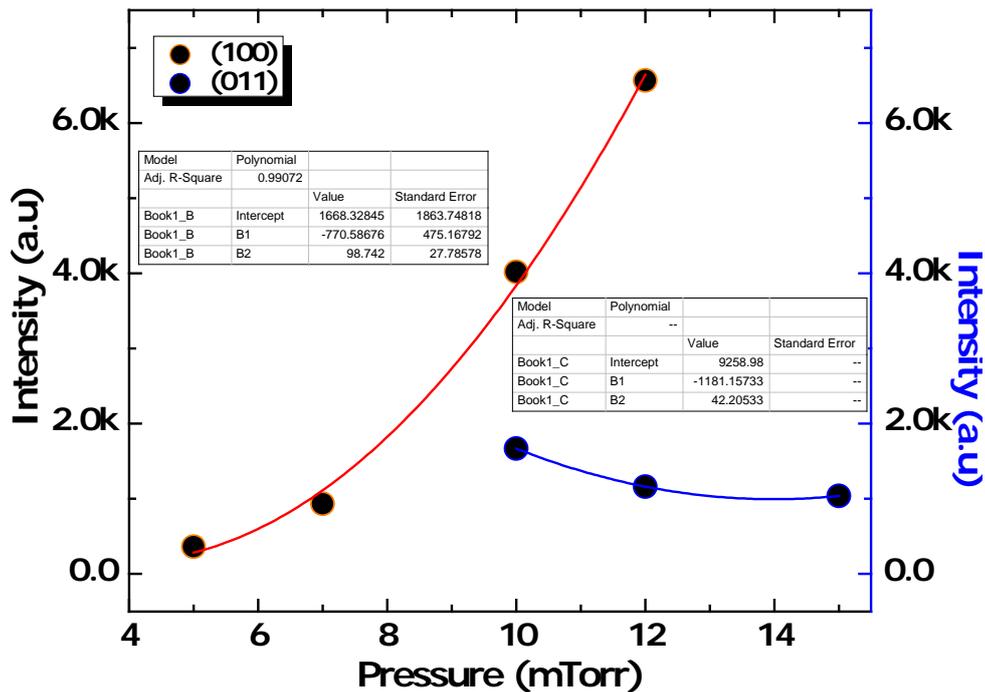


Figure 1b. Evolution of the intensity of the VO₂ (0 1 1) and (1 0 0) peak as a function of the deposition oxygen pressure

In an attempt to study and try to understand the mechanism that govern the preferential structural growth of our reported VO_2 (1 0 0), we have look at the evolution of the intensity of the (0 1 1) plane with respect to the (1 0 0) plane, as a function of oxygen deposition pressure and it is shown in Figure 1b. When the oxygen pressure increases, it is observed that the intensity of the reflection coming from the (1 0 0) diffraction plane increases, while the intensity of the (0 1 1) diffraction plane decreases. These observations indicate an enhancement of the texture of the VO_2 thin films along the $\langle 1\ 0\ 0 \rangle$ direction within the increasing of oxygen pressure. It should be noted that mostly reported work on the structural properties of VO_2 on glass show only a preferential growth along the $\langle 0\ 1\ 1 \rangle$ direction. But recently a report by Ngom et al, [29], whom worked out the crystal structure and morphology of vanadium dioxide (VO_2) nanostructures, showed a preferential orientation of VO_2 along the $\langle 1\ 0\ 0 \rangle$ direction. They have synthesized their VO_2 thin film by pulsed laser deposition on soda-lime glass substrate in pure oxygen at a pressure of 15 mTorr by controlling the cooling rate of

the substrate from $5^\circ\text{C}/\text{min}$ to $25^\circ\text{C}/\text{min}$ after deposition in vacuum.

On the work done by Ngom et al., the presented results, as supported by both their SEM and XRD findings, and specially by the evolution of the crystalline growth along the (1 0 0) plane, showed that the growth mechanism that can be considered is the competitive texturation to explain the origin of the structural preferential growth along the VO_2 (1 0 0) plane.

As shown in Figure 1b, it should be noticed that a “growth competition” is not the a better explanation of the origin of the preferential orientation since as the oxygen pressure increases, it is observed that the intensity of the reflection coming from the (1 0 0) diffraction plane increases, while the one of the (0 1 1) diffraction plane decreases. At maximum oxygen deposition pressure of 15 mTorr there is a restructuring and a change in the preferential orientation. Therefore there should be another mechanism that govern the preferential orientation along (1 0 0), which is not really very understand because of lack of enough information.

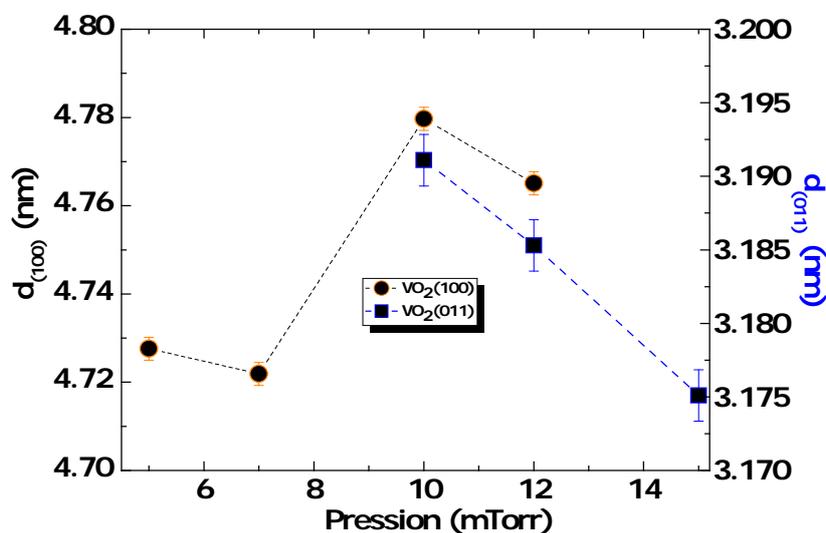


Figure 1c. Evolution of: the $d_{(100)}$ -spacing and the $d_{(011)}$ -spacing; as a function of the deposition oxygen pressure

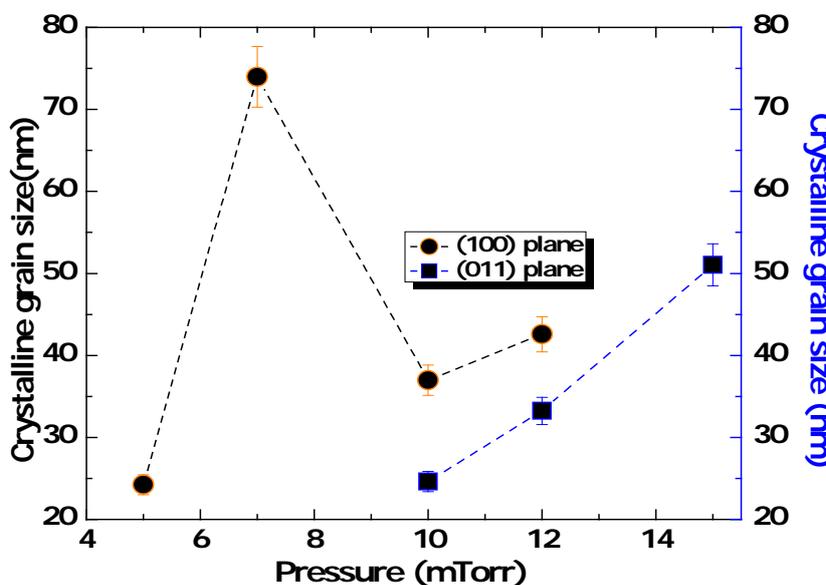


Figure 1d. Evolution of the crystallite size along the (100) and the crystallite size along the (0 1 1) planes respectively as a function of the deposition oxygen pressure

Figure 1c show the evolution of the d-spacings as a function of the deposition pressure along the (1 0 0) and (0 1 1) planes respectively. The reported values for the d-spacings agree with those of the monoclinic structure of VO₂ (JCPDS No. 43-1051). Figure 1c shows a continuous, almost linear decrease of the d-spacing along the (0 1 1) plane, which may suggest that the films are under strain during growth along the (0 1 1) direction. This is illustrated by the evolution of the crystallite size obtained using the well-known Debye Scherrer formula, as presented in Figure 1d. While the crystalline grains size follow a linear trend along the (0 1 1) plane it is not the case along the (1 0 0).

The observed variation of the surface morphology as reported in Figure 2, of the VO₂ nanostructures with

oxygen pressure, may be due to the nucleation of the glass substrate, which occurs at around 575°C and is followed by the process of crystallization of the VO₂ [30]. Increasing the pressure up to 12 mTorr leads to preferential crystal growth along the (1 0 0) plane, while longitudinal grain growth leading to very well-dispersed nanorods-like edge shapes are taking off parallel to the surface of the substrate are observed. At a pressure of 15 mTorr grains dominate the surface morphology and there is a complete change on surface morphology, which can be correlated to the XRD results. In Figure 2, the SEM images of the films prepared at 3mTorr and 5mTorr there is some cracks, the origin of this, can be discussed in terms of films stress.

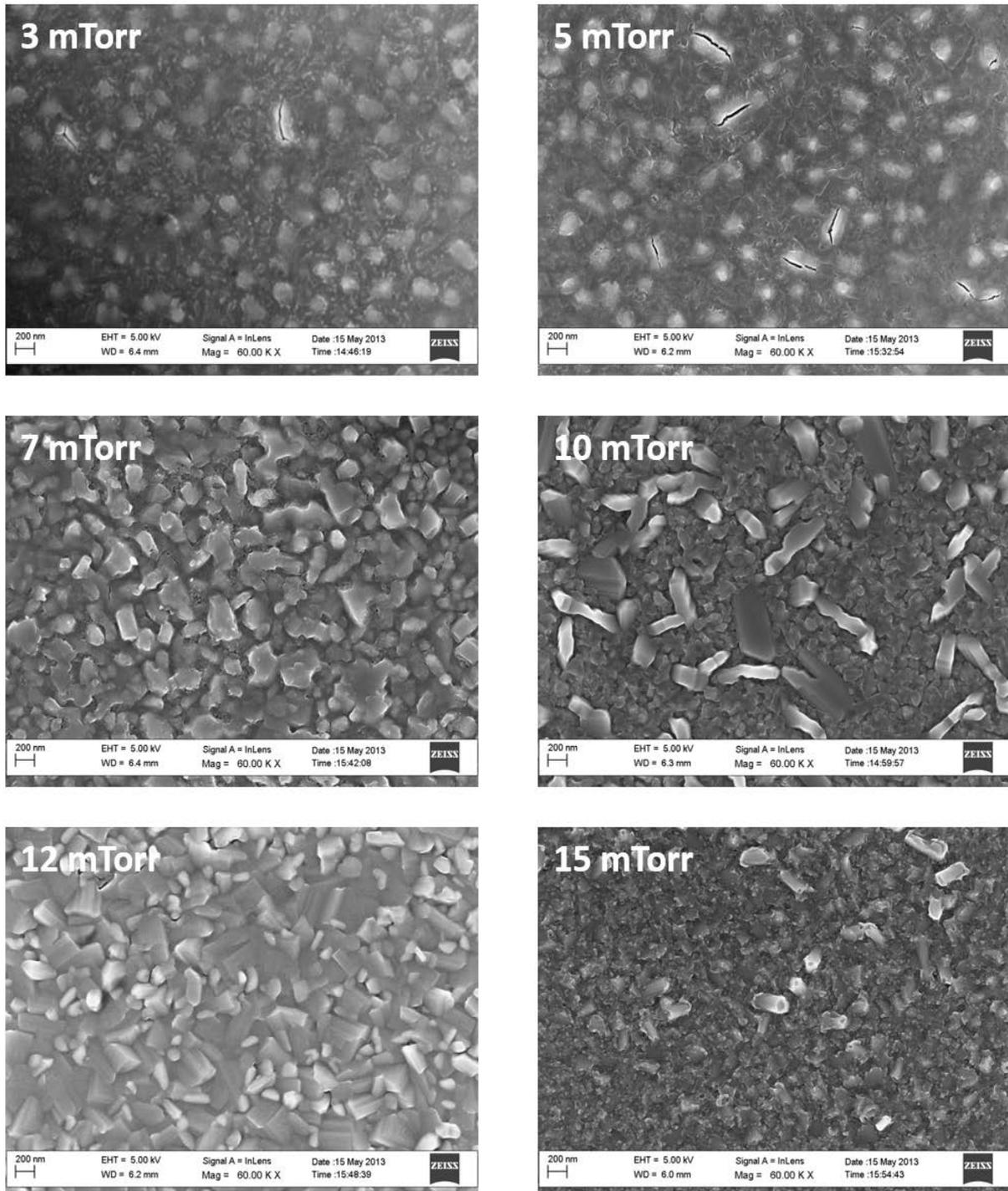


Figure 2. 2D SEM images of the VO₂ thin film samples as a function of the deposition oxygen pressure

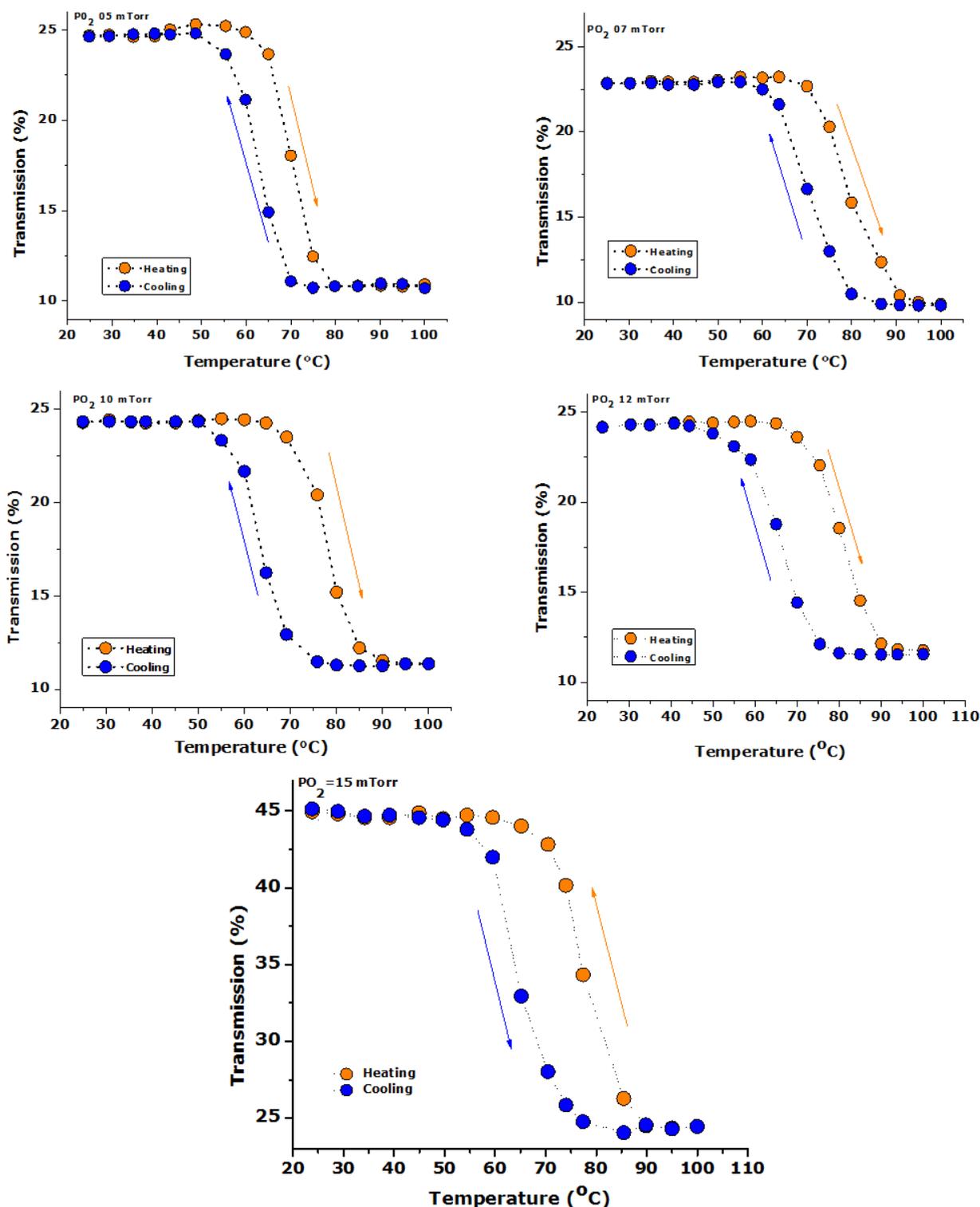


Figure 3a. Optical transmittance (%) hysteresis loop vs. temperature of VO₂ thin films deposited on a soda-lime glass substrate at different deposition oxygen

To investigate the effect of deposition pressure on the thermo-optical properties and the SMT phase transition characteristics in the VO₂ films deposited on soda lime, the transmittance measurements were carried while heating and cooling the sample at different temperatures from room temperature to 100°C. Figure 3a shows the thermal hysteresis loops of the optical transmittance (Tr) at a fixed wavelength of 1100 nm for VO₂ thin films deposited at different oxygen pressure. We see qualitatively different hysteresis shapes for the films for different oxygen

pressure as shown in Figure 3a.

To evaluate the transition temperature and the hysteresis width as functions of the deposition pressure, derivatives of the transmittance (Tr) and its temperature dependence (dTr/dT) were extracted for the VO₂ thin films at different temperatures. A plot of (dTr/dT) was obtained from the transmittance (Tr)–temperature (T) data for each sample. The maximum temperatures corresponding to (dTr/dT) were defined as the phase temperatures in the heating and cooling cycles, T_{Heating} and T_{Cooling} , respectively.

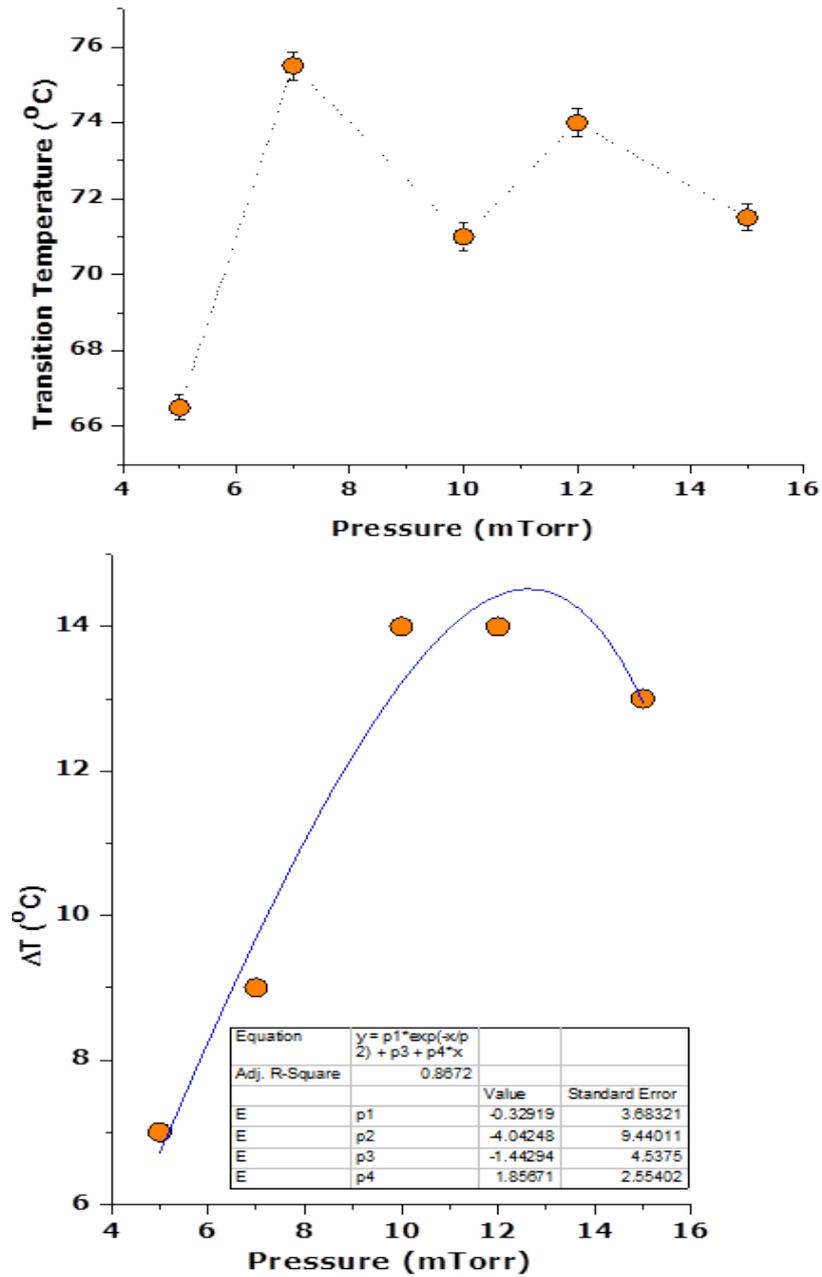


Figure 3b. Evolution of the hysteresis and transition temperature characteristics of VO₂ thin films deposited on a soda-lime at different deposition oxygen pressure

The SMT temperature (T_{SMT}) was defined as

$$T_{SMT} = (T_{Heating} + T_{Cooling}) / 2.$$

The hysteresis width can be defined by

$$\Delta T_{SMT} = T_{Heating} - T_{Cooling}.$$

We can observe that the transition temperature follows the same trend as the crystalline size along the (1 0 0) plane of the VO₂, within the increase of the deposition pressure. The Highest transition temperature was obtained at the higher crystalline sizes. This is to demonstrate how the crystalline grains sizes affect the transition temperature, but seems to be contradicting with what have been reported in the literature so far. Suh et al. [31] undertook a careful study of the SMT transition of VO₂ films on (1 0 0) silicon substrates as a function of annealing time and found that

the microstructure of the films changed from nanocrystalline nearly amorphous to crystals with a diameter of 200 nm. In the early stages, the film showed that as the grain size increased, the SMT decreased, but hysteresis continued to increase. The changes of the thermo-optical properties of VO₂ thin films are usually explained as results of the competing effects between grains size, nucleation defects, grain boundaries and crystal imperfections [32,33]. Therefore the differences in the morphologies and crystal orientations of the films lead to the distinctive SMT characteristics seen in the curves of Figs 3b but not only because of the variation in crystal grain sizes.

J. B. Kana Kana et al [16] have reported high substrate temperature induced anomalous phase transition temperature shift in sputtered VO₂ thin films on corning glass. They have observed that at higher substrate temperature from 550 to 600°C led to a transition temperature of 75°C 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 [15], the major two effects that could lead 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. This would explain why we have observed higher transition temperature at higher crystal grain sizes, which may be related to some effect induced by the substrate glass transition temperature reported to be around 575°C during the 600°C thin films growth since thickness of the samples are the same.

As reported in fig. 3b it is interesting to notice that the hysteresis width increase linearly with the increase in deposition pressure with a smallest width of 7°C obtained at a deposition pressure of 5 mTorr and a maximum of 14°C obtained at a deposition pressure of 12 mTorr. While the sample prepared at a deposition pressure of 15 mTorr, which presents the preferential orientation along (0 1 1) plane of VO₂ gave a hysteresis of 13°C. These values agree with the usual reported values into the literature for such (0 1 1) oriented VO₂ [34,35]. The smaller hysteresis of the films is obtained at lower oxygen pressure and this could be explained by the texture obtained at this oxygen pressure as reported in Figure 1a.

4. Conclusion

In this paper we have reported on the deposition and characterization of VO₂ thin film samples, to study how the deposition oxygen pressures affects the crystal structure, grain size and shape of VO₂ grown via the pulsed laser deposition technique on soda-lime glass substrate. Results on the surface morphology, the texturation is also presented. This study has shown that a-axis textured VO₂ can be grown on glass owing at a substrate temperature of 600°C at an oxygen deposition pressure lower than 15 mTorr. And that the thermo-optical properties of the films are very sensitive to the crystal preferential orientation.

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