Growth of \(a\)-axis Textured Pulsed Laser Deposited VO\(_2\) Nanostructures on Glass Substrate

M Thiam\(^1\), BD Ngom\(^{1,2,3,4,*}\), O Sakho\(^1\), NM Ndiaye\(^{1,5}\), M Chaker\(^2\), N Manyala\(^4\), AC Beye\(^1\)

\(^1\)Laboratoire de Photonique et Nano-Fabrication, Groupe de physique du Solide et Sciences des Matériaux (GPSSSM), Faculté des Sciences et Techniques Université Cheikh Anta Diop de Dakar (UCAD) B.P. 25114 Dakar-Fann Dakar (Senegal)

\(^2\)Institut National de la Recherche Scientifique Centre – Énergie Matériaux Télécommunications 1650, Boul. Lionel Boulet, Varennes (Québec) J3X 1S2

\(^3\)UNESCO-UNISA Africa Chair in Nanosciences/Nanotechnology, College of Graduate Studies, University of South Africa (UNISA), Muckleneuk Ridge, P O Box 392, Pretoria 2000, South Africa

\(^4\)Nanosciences African Network (NANOAFNET), iThemba LABS, National Research Foundation of South Africa, 1 Old Faure Road, Somerset West 7129, Western Cape, South Africa

\(^5\)Department of Physics, SARChI Chair in Carbon Technology and Materials, Institute of Applied Materials, University of Pretoria, Pretoria 2001, South Africa

\(*\)Corresponding author: bdngom@gmail.com

Abstract

Vanadium dioxide thin film nanostructures were synthesized by pulsed laser deposition on soda lime glass at a substrate temperature of 600°C and an oxygen ambient pressure of 15 mTorr. The effect of cooling pressure on the crystalline orientation of VO\(_2\) nanostructures was investigated. As the cooling oxygen pressure is increased, the VO\(_2\) nanostructures exhibit sharp \(a\)-axis diffraction peaks, showing the growth of \((1\ 0\ 0)\) oriented VO\(_2\) on glass, which is characteristic of the VO\(_2\) monoclinic phase and implies that pure highly \(a\)-axis textured VO\(_2\) was formed. We found that the growth mechanism and substrate–film interaction play important roles in the development of these well-textured films via the formation of an interlayer of SiO\(_2\).

Keywords: crystal growth, crystal morphology, vapor phase epitaxy, grain growth, growth models, pulsed laser deposition

Cite This Article: M Thiam, BD Ngom, O Sakho, NM Ndiaye, M Chaker, N Manyala, and AC Beye, “Growth of \(a\)-axis Textured Pulsed Laser Deposited VO\(_2\) Nanostructures on Glass Substrate.” American Journal of Nanomaterials, vol. 6, no. 1 (2018): 24-33. doi: 10.12691/ajn-6-1-3.

1. Introduction

Thermochromic materials [1] are characterized by semiconductor-to-metal transition occurring from a reversible change in their crystalline structure as a function of temperature and voltage [2,3]. This change has been observed in several phases of vanadium oxides. Vanadium dioxide is a promising candidate for memristive, switchable optical and metamaterial applications [4,5,6]. Under temperature stimulus, it has a metal-to-insulator electronic transition (MIT) along with an allotropic transition from monoclinic VO\(_2\) (M) to a tetragonal rutile VO\(_2\) (R) lattice [7-12]. 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 for 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. PVD films showing good thermochromic properties are usually grown as VO\(_2\) (R) at around 600°C. This growth temperature should result in Zone I or Zone II growth according to the structure zone diagram of single-phase PVD films proposed by Barna and Adamik [13] and Petrov et al. [14] as well Adamik et al [15].

Zone I is characterized by adatom exchange between grains, which results from adatom mobility. This process is controlled by competitive grain according to Adamik et al [15]. This growth finally gives a columnar-like morphology, in which the grains have an increasing or decreasing lateral diameter along the growth directions. According to Adamik et al [15] some of these grains do not extend through the whole thickness of the film.

Zone II is characterized by a morphology that is influenced by bulk diffusion, where there is broadening of grain size distribution. In this process the energetically preferable grains grow in lateral directions at the expense of the other less preferable grains, and the grain boundaries remain parallel to the growth direction [13,14,15]. This phenomenon is also referred to as grain boundary migration, and it results in the scaling of the lateral grain size with film thickness [13,14,15].

The excellent agreement between theory and experiments regarding the growth of metal oxides nanostructures has yielded strong evidence for efficient controlled growth under low interfacial tension conditions. It has also created great expectations for the future development of nanomaterial devices and the optimization of their physical properties. Moreover, when thermodynamic stabilization is achieved, not only is the size tailored to requirements but also both the shape and the crystallographic
structure may be controlled. This controlled crystallographic structure has important implications and quite often modifies the physical properties of materials.

The change of texture in thin films growth is a process governed by surface and interface energy. This process is determined mainly in the developmental stages of film formation when the ratio of surface interface to volume is high. Consequently for different substrates, the surface conditions can have a huge impact on the texture progression of films grown on them.

According to Adamik et al. [15], there are two mechanisms of texture development, which can be considered, and known as restructuring and competitive growth of crystals. Where in the competitive growth of crystals, small randomly oriented crystals form on the substrate and the texture change occurs after the film has become continuous. The small grains that develop initially randomly orient the structure of the film while growing and the texture changes by the competitive growth of crystals with different orientations. As a result of this process the film has an inhomogeneous structure along its thickness [15]. Consequently, the substrate does not influence this kind of texture evolution [15]. The development of texture through restructuring begins when the grains initially amalgamate, a stage related to grain boundary migration [13,14,15]. This process is governed by the temperature and condition of the grain boundaries [15,16]. The main driver is the surface energy and the substrate−film interface energy as previously mentioned.

Following work on controlling the crystallographic structure of VO₂, Garry et al. [17] reported on a-axis textured VO₂ thin films deposited on R-plane sapphire; they observed all the (1 0 0) planes of VO₂. They suggested that all the peaks observed resulted from stress developed on the interface between the substrate and the film. Chiu et al. [18] reported on VO₂ thin films deposited on a glass substrate and also on a 5 nm thick ZnO buffer layer deposited on a glass substrate, both at 500°C. They found that when a VO₂ film was deposited directly on glass substrates, polycrystalline VO₂ films formed on the amorphous substrate surface and showed a preferential orientation along the (0 1 1) plane located at 27.87° in the X-ray diffraction (XRD) chart. When VO₂ thin films were deposited under 5.33 and 6.67 Pa O₂ pressure on a 5 nm thick ZnO buffer, a polycrystalline randomly oriented VO₂ thin film formed, and only VO₂ (0 1 1) peaks located at 27.90° were observed. Their results reveal that b-axis oriented VO₂ film can be prepared under 1.33 Pa O₂ ambient using a c-axis oriented ZnO buffer. They reported [18] that the structure of VO₂ thin films deposited on the ZnO buffer was more sensitive to O₂ pressure during deposition. Even though the O₂ pressure was controlled within the range in which the pure VO₂ phase could be formed on a c-cut sapphire and glass substrate, the crystalline orientation of the VO₂ thin films was drastically changed and formed the interface layer between VO₂ and ZnO. In their work Chiu et al. [19] also proved that single-crystal substrates are effective in obtaining VO₂ thin films with a narrow hysteresis width, but they are expensive and difficult to prepare on a large scale.

This communication reports on the control of the synthesis of a-axis oriented and nanosized VO₂ at a substrate temperature of 600 °C by pulsed laser deposition (PLD) on soda-lime glass substrate without any catalyst. Soda-lime glass is used in everyday products and devices such as solar cells, household mirrors, automobile glass, and architectural building windows. Therefore, the focus of our investigation is an interesting topic in thin film growth for cost-effective optical applications, as the physical properties of the films will depend strongly on their texturation.

2. Experimental Details

Films were deposited on soda-lime glass substrate held at a temperature of 600°C in 15 mTorr pure oxygen pressure for a deposition time of 45 minutes. An excimer laser, wavelength of 248 nm, fluence of 1.7 J/cm², repetition rate of 10 Hz, and 30 ns pulse duration, was incident on the V metal target. The substrate−target distance was kept at 65 mm and the laser was focused to ablate the off-center of the rotating target. After deposition the samples were cooled at different oxygen pressures ranging from vacuum to 50 mTorr at a cooling rate of 25°C/min.

XRD data of the samples produced were collected on a laboratory D8 ADVANCE powder diffractometer in Bragg-Brentano geometry, operated at 40 kV and 40 mA using a Cu Kα1 radiation.

The XRD patterns of the samples were recorded in the range (2θ = 12°−80°) using a step size of 0.02° and a counting time of 20 s per step, in each case without moving the sample. The instrumental profile was obtained experimentally by collecting the diffraction data of a standard Al₂O₃ powder, fitting them with pseudo-Voigt functions and parameterizing the trends of the full width at half maximum (FWHM), as well as the shape parameters as functions of 20 according to the Caglioti expression implemented in the PM2K software [20]. Qualitative phase analysis (search match) was done using the PANalytical Xpert Highscore plus software employing the ICDD PDF database.

The whole powder pattern modeling (WPPM) method [21] implemented in the PM2K software [20] was employed for the microstructural analysis. In addition to the peak intensities, unit cell parameters and Chebyshev coefficients polynomial background, the microstructure parameters refined are the log-normal standard deviation (σ), log-normal mean (µ) and log-normal distribution of cuboidal crystalline domain size.

The surface morphology was characterized via a Nova NanoSEM 230 scanning electron microscope (SEM) in secondary electron mode to investigate the surface morphology of the films after deposition. High-resolution transmission electron microscopy (HRTEM) using a field emission gun with an accelerating voltage of 200 kV in a TECNAI F20 FEGTEM was employed to ascertain the crystallinity of the structures of the interface layer. Raman spectroscopy data on the synthesized samples were collected using a T64000 micro-Raman spectrometer from HORIBA Scientific (Jobin Yvon Technology), equipped with a triple monochromator system to eliminate contributions from the Rayleigh line. All the samples were analyzed with a 514 nm argon excitation laser (12 mW at laser exit to avoid thermal effects) and a X50 objective with recording times ranging from 120 s and a resolution of 2 cm⁻¹.
3. Results and Discussion

Figure 1 shows the XRD patterns characteristic of VO₂ thin films deposited on soda-lime glass substrate and cooled down to room temperature at a rate of 25 °C/min at different oxygen pressures ranging from vacuum to 50 mTorr. The patterns show peaks due to the VO₂ thin layer at angles of 18.48, 27.97, 37.18, 39.98, 55.72 and 57.048°. 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), (2 1 1) and (0 2 2) planes respectively. It can be seen that the four samples present similar diffraction patterns and that the only difference lies in the relative intensity of the diffraction peaks. As the oxygen pressure increases, the intensity of the (1 0 0) and (2 0 0) diffraction peaks increases, while the intensity of the (0 1 1) peak decreases. This indicates an enhancement of the texture of the VO₂ thin films along the (1 0 0) plane with the increasing oxygen pressure. This is clearly shown in Figure 2 in which the intensity of the (0 1 1) peak relative to the (1 0 0) peak is plotted as a function of cooling pressure. However, in most cases only the (2 0 0) and (4 0 0) peaks appear with a preferential orientation along the (0 1 1) plane or b-axis orientation [17,18,19,22,23].

The preferential orientation along the (1 0 0) plane in our samples is not clearly understood. Garry et al. [17] reported the same phenomena; they observed all the (h 0 0) planes of VO₂ thin films deposited on R-plane sapphire but not on glass substrate, and suggested that the observation of all the peaks might be due to stress developed at the interface between the substrate and the film.

Compared with the standard data (JCPDS No. 43-1051), the relative intensity of the (1 0 0) peak for the VO₂ samples was stronger than those of the other peaks to an extraordinary degree as shown in Figure 2, indicating that the (1 0 0) planes are probably the preferred growth direction of the VO₂ nanorod-like crystals. This is illustrated by the evolution of the crystallite size obtained using the well-known Debye Scherrer formula, as presented in Figure 3C and Figure 3D. Figure 3A and Figure 3B show the evolution of the d-spacing as a function of the cooling pressure along the (1 0 0) and (0 1 1) planes respectively. Fig. 3A shows a continuous, almost linear decrease of the d-spacing along the (1 0 0) plane, which may suggest that the films are under strain during growth along the (1 0 0) direction. No peaks of any other phases or impurities were observed at any oxygen cooling pressure beyond 30 mTorr, demonstrating that VO₂ nanostructures with high purity could be obtained using the present synthetic process, where the control of the cooling pressure served in a manner similar to an in situ annealing process.
The extra peaks in some of the samples indicated by (*) for cooling pressures less than 30 mTorr may correspond to the presence of minor phases and/or impurities. Lu et al. [24] in their work on VO$_2$ deposited on glass substrates reported two peaks at $2\theta = 12.1$ and $2\theta = 29.1$, indicating the presence of a small amount of Na$_x$V$_2$O$_5$ ($0.3 < x < 1.0$) phase in the VO$_2$ films. Wang et al. [25] strongly concluded that sodium ions would diffuse from a soda-lime substrate to the film surface when sputter was performed at a high substrate temperature (580°C in their experiment). However, more investigations are needed to reach a definite conclusion on this particular point.

Figure 4 shows the evolution of the room temperature lattice parameters as a function of the cooling pressure. The reported values agree with those of the monoclinic structure of VO$_2$ (JCPDS No. 43-1051). The cooling pressure is seen to have opposite effects when one looks at its influence on the “c” and “b” lattice parameters, while its effect on the “a” lattice parameter is to cause a slight increase before dropping again at 50 mTorr of oxygen cooling pressure.

Figure 3. Evolution of: (a) the $d_{100}$-spacing; (b) the $d_{001}$-spacing; (c) the crystallite size along the (100) plane; (d) the crystallite size along the (0 1 1) plane as a function of the cooling oxygen pressure.
Figure 4 illustrates the log-normal distribution of the cuboidal crystallite domain size obtained using the whole powder pattern modeling (WPPM) method. It can be seen that the average cuboidal crystallite domain size increases linearly with the oxygen cooling pressure (see Figure 5B).

To investigate the origin of the observed preferential orientation and texturation in our VO$_2$ thin films, we used HRTEM for monitoring and analyzing the interface between the substrate and the VO$_2$ film and to further backup our observations. Figure 6 is a typical HRTEM image showing the analysis of the lattices in the interlayer between the substrate and the film. It can be seen that the d-spacing is about 5.57 Å, as indicated by two parallel lines in the inset to the figure, which correspond to the (1 1 0) plane of the SiO$_2$ monoclinic crystals (JCPDS No. 76-1805). This indicates that the glass substrate has gone through a surface crystallization process since the substrate temperature deposition was higher than its transition temperature, reported to be around 575°C. Therefore it appears that a crystalline layer of SiO$_2$ developed on the surface of the substrate before the film was deposited and this induced elementary atomic processes. This can also account for the global effects of the atomic processes on the structure evolution in that it created the structural preconditions for the VO$_2$ texturation to take place [15].
Figure 5. (a) Log-normal distribution of the cuboidal crystallites; (b) evolution of the average cuboidal crystallite size as a function of the cooling oxygen pressure from WPPM.

Figure 6. HRTEM lattice analysis of the VO₂ films and substrate interface layers.
Figure 7. (a) EDX spectrum taken on the surface of the substrate (Inset: SEM image showing the interface between the VO$_2$ film and the substrate; the yellow dotted square shows where the EDX were taken); (b) EDX spectrum taken on the surface of the film (Inset: SEM image showing the interface between the substrate and the VO$_2$ film; the yellow dotted square shows where the EDX were taken).

Figure 8. Raman spectrum of the VO$_2$ thin film cooled at different oxygen pressures.
To further investigate the origin of the preferential orientation and the texturation, we conducted high-resolution scanning electron micrograph (HRSEM) imaging of the interface between the substrate and the VO$_2$ films deposited, as well as energy-dispersive X-ray spectroscopy (EDX) on the substrate and the VO$_2$ films. Figure 7a and Figure 7b present the EDX surface analysis of the substrate and the film surfaces respectively, with the insets to both figures showing the SEM images corresponding to the spots where the measurements were taken. These figures demonstrate V, O and other elements, such as Na, coming from the substrate when the EDX spectra were measured on the VO$_2$ films, which is clearly reported in Figure 7b, while the formation of SiO$_2$ is supported by the EDX results reported in Figure 7a. These results shed light on the extra peak marked (*) which could be attributed to the formation of a SiO$_2$ interface layer.

Figure 8 shows the room temperature Raman spectrographs of the VO$_2$ films deposited on the soda-lime glass substrate and cooled to room temperature at different oxygen pressures. All the VO$_2$ thin films exhibit the same Raman bands, as reported in the Table 1, except for the band around 295 cm$^{-1}$, which is observed clearly only on the sample cooled at 50 mTorr. Fig. 8 clearly shows that, three sharp peaks at around 142, 254 and 268 cm$^{-1}$, and a boarder peak at 507 cm$^{-1}$ dominate the spectrum. The 507 and 417 cm$^{-1}$ bands are attributed to a V-O-V stretching mode, consistent with the medium range order. The mode at 254 cm$^{-1}$ is a V-O-V bending mode, and the bands at 295, 218–208 and 144 are the external modes. The modes observed around 417 and 268 cm$^{-1}$ shown by the dotted yellow circles in the figure correspond to SiO$_2$ breathing modes [26,27]. This concurs with the observations from the HRTEM and EDX results and hence confirms the interface layer formation of SiO$_2$.

The positions of the major Raman peaks observed here are in agreement with those of stoichiometric VO$_2$ reported by Cheng et al. [28] and Parker [29]. However, when the oxygen cooling pressure is increased, the major peaks are shifted. This is in agreement with the result of surface oxidation of VO$_2$ reported by Parker [29]. Therefore we further confirmed that surface oxidation occurred when the VO$_2$ films were cooled in an oxygen atmosphere, becoming oxygen-rich when the cooling oxygen pressure was increased.

The observed variation of the surface morphology of the VO$_2$ nanostructures with oxygen pressure as reported in Figure 9 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 VO$_2$. This follows the so-called “active fundamental structure-forming phenomenon” which is well known in materials science and solid-state physics (nucleation, crystal growth, grains growth). The nanostructures observed at different cooling oxygen pressures are certainly related to the so-called “restructuring mechanism” [15] as we have described above. This is supported by the evolution of crystalline grain growth along the preferential structural growth path, which is the (1 0 0) plane. The morphology and the growth direction of these nanograins indicate that the surface crystallization starts off in a preferential direction. These results can be correlated with the SEM results as it can be seen in Figure 9 that the growth of some of the nanorods takes place parallel to the substrate surface, in the same structural plane (1 0 0) which is the preferential direction of plane growth suggested by the XRD results.

It is common knowledge that the growth of thin films proceed through successive stages characterized by precise processes of structure evolution, such as nucleation, island growth, merging of islands, formation of polycrystalline islands and channels, development of a continuous structure and thickness growth [13,14,15]. The development of the structure in polycrystalline thin films is a very complex process and displays different features in different stages of film growth [15].

Table 1. Raman spectrum data of the VO$_2$ thin film at 300 K as a function of the cooling oxygen pressure

| Vacuum | 15mTorr | 30mTorr | 50mTorr | Chun Cheng and al. [32] 300 K | Shell Model |
|--------|---------|---------|---------|----------------------------|-------------|
| 117    | 117     | 117     | 119     | _                          | _           |
| 142 Ag | 142 Ag  | 142 Ag  | 144 Ag  | 144 Ag                     | 185 Bg      |
| 218 Ag | 214 Ag  | 211 Ag  | 208 Ag  | 192 Ag                     | 201 Ag      |
| _     | _       | _       | _       | 224 Ag                     | 225 Ag      |
| 255 Bg | 255 Bg  | 255 Bg  | 254 Bg  | 260 Bg                     | 254 Ag      |
| 268 Bg | 268 Bg  | 268 Bg  | 269 Bg  | _                          | _           |
| _     | _       | _       | _       | 309 Bg                     | 303 Ag      |
| _     | _       | _       | _       | _                          | 331 Bg      |
| 417 Ag | 417 Ag  | 417 Ag  | 417 Ag  | _                          | _           |
| _     | _       | _       | _       | 392 Ag                     | 405 Bg      |
| _     | _       | _       | _       | _                          | 420 Ag      |
| _     | _       | _       | _       | 440 Bg                     | 451 Ag      |
| _     | _       | _       | _       | _                          | 451 Bg      |
| 508 Ag | 508 Ag  | 507 Ag  | 507 Ag  | 497 Ag                     | 487 Bg      |
| _     | _       | _       | _       | _                          | 501 Ag      |
| _     | _       | _       | _       | _                          | 500 Ag      |
| _     | _       | _       | _       | 615 Ag                     | 586 Ag      |
| _     | _       | _       | _       | _                          | 682 Ag      |
| _     | _       | _       | _       | _                          | 722 Bg      |
| _     | _       | _       | _       | _                          | 732 Ag      |
| _     | _       | _       | _       | _                          | 829 Bg      |
Consider the structure development of real polycrystalline thin films; the effects of the deposition parameters on the structure and the appearance of particular structural features, it can be concluded that a comprehensive description of the formation of these particular structural features is possible by following the basic structure-forming phenomena well known in materials science and solid-state physics (nucleation, crystal growth, grain growth) [13,14,15,30,31,32,33,34]. These processes are composed of elementary atomic processes, and can account for the global effects on the structure evolution [15]. Imperatively the atomic processes are governed directly not only by the temperature, but also by the structural conditions characteristic of the actual growth stage (structural preconditions include, for example, the formation of an interlayer) [15].

It must be emphasized that by considering the fundamental structure formation phenomena, both the evolution of the size and morphology of the grains, and the orientation of the crystals can be described. The present results are supported by both SEM images and XRD, and the evolution of the crystalline growth parameters along the (1 0 0) plane shows that the growth mechanism involved here is restructuring texturation.

4. Conclusion

In this paper we have reported how the cooling of VO$_2$ thin film samples after deposition at different oxygen pressures affects the crystal structure, grain size and shape of VO$_2$ grown via the pulsed laser deposition technique on soda-lime glass substrate. A detailed description of the growth mechanisms and the substrate-film interaction is given. Results on the surface morphology, the grain boundary structure and the texturation are also presented. This study has shown that a-axis textured VO$_2$ can be grown on glass owing to the formation of an interface layer of SiO$_2$ which results from nucleation at a substrate temperature of 600°C.

Acknowledgments

We are grateful for financial support from the World Federation of Scientists, INRS (Canada), and the NANOAFNET. We also wish to thank iThemba LABS and the EMT-INRS for the use of their facilities.

References

[1] BJ Kim, YW Lee, BG Chae, SJ Yun, SY Oh and HT Kim, «Temperature dependence of the first-order metal-insulator transition in VO$_2$ and programmable critical temperature sensor», Appl. Phys. Lett. 90 (2007) 023515.
[2] HT Kim, BG Chae, DH Youn, SL Maeng, G Kim, KY Kang and YS Lim, Mechanism and observation of Mott transition in VO$_2$-based two- and three-terminal devices, New. J. Phys. 6 (2004) 52.
[3] FJ Morin, Oxides Which Show a Metal-to-Insulator Transition at the Neel Temperature, Phys. Rev. Lett. 3 (1959) 34.
[4] IN Zheludev, The Road Ahead for Metamaterials, Science 328 (2010) 582.

[5] T. Driscoll, H-T Kim, B-G Chae, M Di Ventra and DN Basov, Phase-transition driven memristive system, Appl. Phys. Lett. 95 (2009) 043503.

[6] W Huang, X Yin, C Huang, Q Wang, T Miao and Y Zhu, Optical switching of a metamaterial by temperature controlling, Appl. Phys. Lett. 96 (2010) 261908.

[7] BD. Ngom, M. Chaker, I. G. Madiba, S. Kamlichi, N. Manyala, O. Nenraoui, R. Madjo, A. C. Beye and M. Maaza, "Competitive Growth Texture of Pulse Laser Deposited VO₂ Nanostructures on Glass Substrate", Acta Materialia Volume 65, 15 February 2014, Pages 32–41

[8] AS Barker Jr., HW Verleur, HJ Guggenheim, Infrared Optical Properties of Vanadium Dioxide Above and Below the Transition Temperature, Phys. Rev. Lett 17 (1966) 1286.

[9] PJ Fillingham, Domain structure and twinning in crystals of vanadium dioxide, J. Appl. Phys. 38 (1967) 4823.

[10] JB Goodenough, the two components of the crystallographic transition in VO₂, J. Solid. State. Chem. 3 (1971) 490.

[11] MM Qazilbash, KS Burch, D Whisler, D Shrekenhamer, BG Chae, H.T.Kim and D.N.Basov, Correlated metallic state of vanadium dioxide, Phys. Rev. B. 74 (2006) 205118.

[12] MM Qazilbash, AA Schafgans, KS Burch, SJ Yun, BG Chae, BJ Kim, H.T.Kim, D.N.Basov, electrodynamic of the vanadium oxides VO₂ and V₂O₃, Phys. Rev. B. 77 (2008) 115121.

[13] PB Bara, M Adamik, fundamental structure forming phenomena of polycrystalline films and the structure zone models, Thin Solid Films 317 (1998) 27.

[14] I Petrov, PB Bara, L Hultman and JE Greene, microstructural evolution during film growth, J. Vac. Sci. Technol. A 21 (2003) S117.

[15] M. Adatnik, P.B. Barna “Role of underlayers in the development of evolutionary texture in polycrystalline thin films” Surface and Coatings Techntology 80 (1996) 109-112.

[16] GJ Kovacs, D Burger, I Skorupa, H Reuther, R Heller and H Schmidt, effect of the substrate on the insulator–metal transition of vanadium dioxide films, J. Appl. Phys. 109 (2011) 063708.

[17] G Garry, O Durand and A Llordereau, structural, electrical and optical properties of pulsed laser deposited VO₂ thin films on R- and C-sapphire planes, Thin Solid Films. 453–454 (2004) 427-430.

[18] T-W Chiu, K Tonooaka and N Kikuchi, influence of oxygen pressure on the structural, electrical and optical properties of VO₂ thin films deposited on ZnO/glass substrates by pulsed laser deposition, Thin Solid Films. 518 (2010) 7441-7444.

[19] T-W Chiu, K Tonooaka and N Kikuchi, Growth of b-axis oriented VO₂ thin films on glass substrates using ZnO buffer layer, Appl. Surf. Sci. 256 (2010) 6834-6837.

[20] M Leoni, T Confrontea and P Scardi, PM2K: a flexible program implementing Whole Powder Pattern Modelling, Z. Kristallogr. Suppl., 23 (2006) 249-254.

[21] P Scardi and M Leoni, whole powder pattern modelling, Acta. Cryst. A58 (2002) 190-200.

[22] Li Jian and J Dho, anomalous optical switching and thermal hysteresis behaviors of VO₂ films on glass substrate, Applied. Phys. Lett. 99 (2011) 231909.

[23] A Kaushal, N Choudhary, N Kaur and D Kaur, VO₂-VO₃ nanocomposite thin films synthesized by pulsed laser deposition technique, Appl. Surf. Sci. 257 (2011) 8937-8944.

[24] S Lu, L Hou and F Gan Surface analysis and phase transition of gel-derived VO₂ thin films, Thin Solid Films, 353 (1999) 40-44.

[25] X-J Wang, C-J Liang, K-P Guan, D-H Li, Y-X Nie et al, Surface oxidation of vanadium dioxide films prepared by radio frequency magnetron sputtering, Chinese. Phys. B. 17 (2008) 3514.

[26] P Gillet, A Le Cleach, and M Madon High-temperature raman spectroscopy of SiO₂ and GeO₂ Polymorphs: Anharmonicity and thermodynamic properties at high-temperaturesJ. Geophys. Res. 95 (1990) 21635-21655.

[27] RJ Hemley, pressure dependence of Raman spectra of SiO₂ polymorphs: alpha-quartz, coesite and stishovite, in: MH Manghnani, Y Syono (Eds.). High-pressure Research in Mineral Physics, Tokyo/Washington DC: Terra Scientific Publishing Co, (1987) 347-360.

[28] C Cheng, K Liu, B Xiang, J Suh and J Wu, ultra-long, free-standing, single-crystalline vanadium dioxide micro/nanowires grown by simple thermal evaporation, Appl. Phys. Lett. 100 (2012) 103111.

[29] JC Parker, raman scattering from VO₂ single crystals: A study of the effects of surface oxidation, Phys. Rev. B. 42 (1990) 3164.

[30] JF Pócza, A. Barna, PB Barna, I Pózsgai, G Radvózzi: in-situ electron microscopy of thin film growth, Proc. 6th Int. Vacuum Congress, Kyoto (1974), Jap. Journal of Applied Physics, Supplement 2, (1974) Part 1, 525-532.

[31] P.B. Barna, G. Radvózzi, F.M. Reicha: Surface growth topography of grain boundaries in Al thin films, Vacuum 38. (1988), 527-532.

[32] M. Menyhard, L. Uray, Grain boundary segregation produced by grain boundary movement, Scripta Metall. 17 (1983), p.1195.

[33] L. Uray and M Menyhard, the segregation of iron in tungsten, Phys. Status. Solidi. A 84 (1984) 65-72.

[34] PB Barna, M Adamik, growth mechanisms of polycrystalline thin films, in: FC Matacotta, G Ottaviani (Eds.), Science and Technology of Thin Films. Singapore: World Scientific Publications. (1995).