

**VANADIUM DIOXIDE THERMOCHROMIC THIN FILMS CORRELATION
BETWEEN MICROSTRUCTURE, ELECTRICAL AND OPTICAL
PROPERTIES**

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DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

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ABSTRACT

Thermochromic thin films of vanadium dioxide (VO_2) were successfully prepared using two physical vapour deposition methods namely Pulsed Laser Deposition (PLD) and Inverted Cylindrical Magnetron Sputtering (ICMS). We used these two techniques in order to comparatively study the effect of deposition temperature on VO_2 thin films microstructure, electrical and optical properties. Prior to the deposition, we first optimized the deposition conditions for both techniques. Optimized conditions were then used to systematically study the effect of substrate temperature, ranging from 350°C to 550°C , on the microstructure and the switching properties of VO_2 thermochromic thin films. All films prepared by PLD were observed to be crystallized, giving a first peak at 27.87° corresponding to (011) plane indicating the existence of VO_2 [5,9,13,18,21]. We also observed (by Debye Sherrer's formula) that the film grain size increases with the increase in substrate temperature. AFM was employed so as to study the surface roughness. We observed the electrical and optical properties for VO_2 behaviour using four point probe and UV-VIS spectrophotometer.

The same procedure used for characterizing VO_2 thin film synthesized by PLD was also repeated for ICMS results. The films deposited by ICMS were also found to be crystallized, showing strong texturation corresponding to (011) plane indicating VO_2 existence [5,12,13,18,21]. We observed that optical and electrical properties exhibited by VO_2 thin films are almost the same with substrate temperature increase. ICMS technique appears to be a better technique to as compared to PLD to synthesize or deposit high quality films which would show clear substrate temperature dependence as it appears to be important effect in the study.

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Ngibonga amaSomi wonke ngokungivumela ngiqhubekele kuleli zinga lemfundo.

*“Nomndayi, Phingoshe, Gcogcobane, Nina enehla ngomzungulu wasala
wabola, nime nje boSingila”*

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CHAPTER 1

INTRODUCTION

Materials application depends on their behaviour at different environmental conditions. In general, most of the materials change their properties due to the change in environmental conditions which normally affect the performance of material. There are some materials that change colour due to external factors; those materials are known as chromic materials.

There are materials which change colour due to temperature change, known as thermochromic materials, others change colour due to light, known as photochromic, others change colour due to pressure, and known as piezochromic etc. These materials are applied in various ways like, thermochromic materials are applied in window coating, laser protection, optical and electrical switching etc. Thermochromism occurs by means of rearrangements of the molecular structure of a material, as a result of change in temperature [1].

For window coating application, a thin film of a thermochromic material on an exterior window could modify its reflectance properties, dependant on outside ambient temperature. The solar radiation that is not able to pass through the window when it is in its darkened state must be either reflected or absorbed. In a cooling dominated application, the window would pass all or part of the visible radiation incident on the window. Incident solar radiation, that is not transmitted, is absorbed or reflected. Absorption will cause significant heating of the window if left to stagnate in a coloured state under conditions of high irradiance [2, 3].

Temperature increase in the window will give rise to a radiant heat source adjacent to the room, potentially leading to thermal discomfort, and will impose additional demands on the temperature stability of the materials used in the smart window. Effective thermochromic window coatings would respond to this heating by increasing their reflectance and compensating for the increased heating by reflecting more heat away. Such intelligent coatings could be used in a countless applications including windscreens of automobiles, sunscreens and greenhouses. The development of such coatings will lead to large savings in energy costs (e.g. power to air conditioning units) and environmental benefits (e.g. reduced CO₂ emissions).

This work is focusing mainly on thermochromic material called vanadium dioxide.

Vanadium dioxide is a material which undergoes a reversible semiconductor-to-metal transition at 68°C [4]. Vanadium dioxide has a monoclinic structure below transition temperature and become tetragonal above transition temperature [5]. It has narrow band gap (0.65 eV) below transition temperature [6, 7]. The transition of VO₂ is accompanied by abrupt change in the electrical resistivity and optical transmittance [6-8]. VO₂ has a very low transmittance in the infrared region during metallic phase but has higher transmittance in the infrared region during semiconducting phase. The transition temperature (68 °C) of this material can be lowered or increased using dopants (e.g. tungsten, molybdenum, etc) depending on the application purpose.

This material belongs to complicated vanadium-oxygen system as shown in Figure 1. This system is complex due to the multivalent vanadium ion but also contains a very wide range of ordered and disordered defect structures [9]. These defect structures result in the large range of stoichiometry of vanadium oxides and the existence of the

homologous series of separate oxides with the general formula V_nO_{2n-1} between V_3O_5 and VO_2 [9].

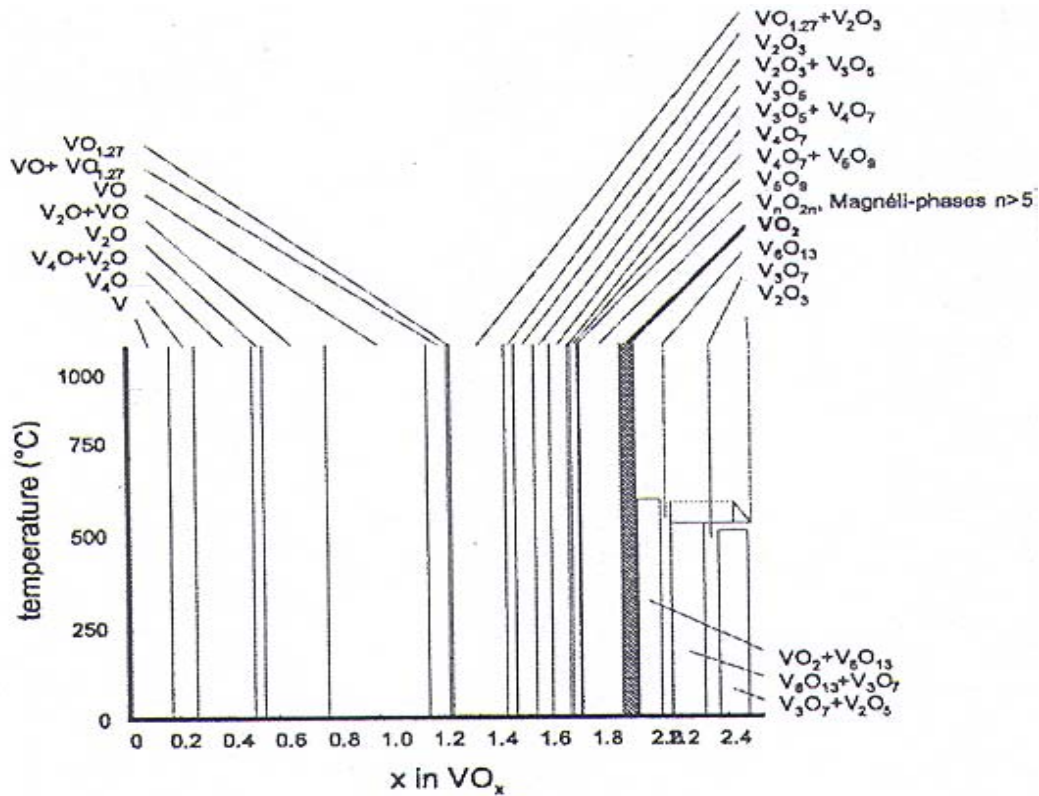


Figure 1: Vanadium-oxygen system [9].

There are many materials which are transiting like iron sulphide and others. The main problem with them is that they behave above room temperature (above 100°C). VO_2 has been chosen because its anomalous behaviour happens below 100°C . In this work, Pulsed Laser Deposition (PLD) and Inverted Cylindrical Magnetron Sputtering (ICMS) techniques have been utilized to deposit VO_2 on soda lime glass substrates with different substrate temperature in order to study the effect of substrate temperature on the microstructure, electrical and optical properties of the film, which is the main aim of the study.

The whole write-up consists of chapter 1 which gives an introduction on VO₂. Chapter 2 gives background on thermochromism and an aim of this work. Techniques that have been used in this work are briefly explained under Chapter 3. Chapter 4 gives explanation on how the deposition and the characterization techniques were used. Chapter 5 discuss and compare the results from both techniques. At the end a conclusion of the work is given in Chapter 6.

CHAPTER 2

LITERATURE SURVEY ON VO₂

The thermochromism of VO₂ was discovered by F.J. Morin in 1959 [5]. VO₂ has a monoclinic structure at temperature below transition temperature and it is infrared transparent. In the semiconducting phase, VO₂ has a high transmittance due to the low free carrier concentration. The free carrier concentration increased in the metallic phase, therefore, the transmittance in the IR decreased.

VO₂ thin film is reddish-brown in the semiconducting state and become greenish-blue in the metallic state. At temperature above the critical temperature, each vanadium atom is located at the center of an oxygen tetrahedron. At lower temperature, the structure is distorted as vanadium atoms pair up and are alternately displaced from the center of oxygen [12]. The transformation in VO₂ is of shear type, with a slight atomic displacement and a small dilation (0.044%) accompanying the phase change [13].

The electrical and optical properties of the films depend mostly on the stoichiometry and the microstructure, as well as the levels of residual stress caused by the deposition technique [13]. The dependence phenomena are due to crystallinity of the film. The film morphology is affected by the thickness of the film (see Figure 2.2). The increase in film surface roughness due to thickness increase leads to the transition temperature decreases [12]. An increased number of atoms distributed randomly at grain boundaries and/or large surface/interface ratio for a very thin VO₂ film, may damage the zigzag chains of V-V pairs characteristic of the low temperature phase, resulting in the destabilization of the low temperature phase and therefore the decrease in

transition temperature [11]. The film thickness also affects the transmittance, as the thickness increase transmittance decreases.

When the film thickness is less than 100 nm, the transmittance of the metallic phase exceeds that of a semiconducting phase near the infrared region, while for those films thicker than 100 nm, the transmittance of the semiconducting phase exceeds that of metal phase (see Fig 2.1).

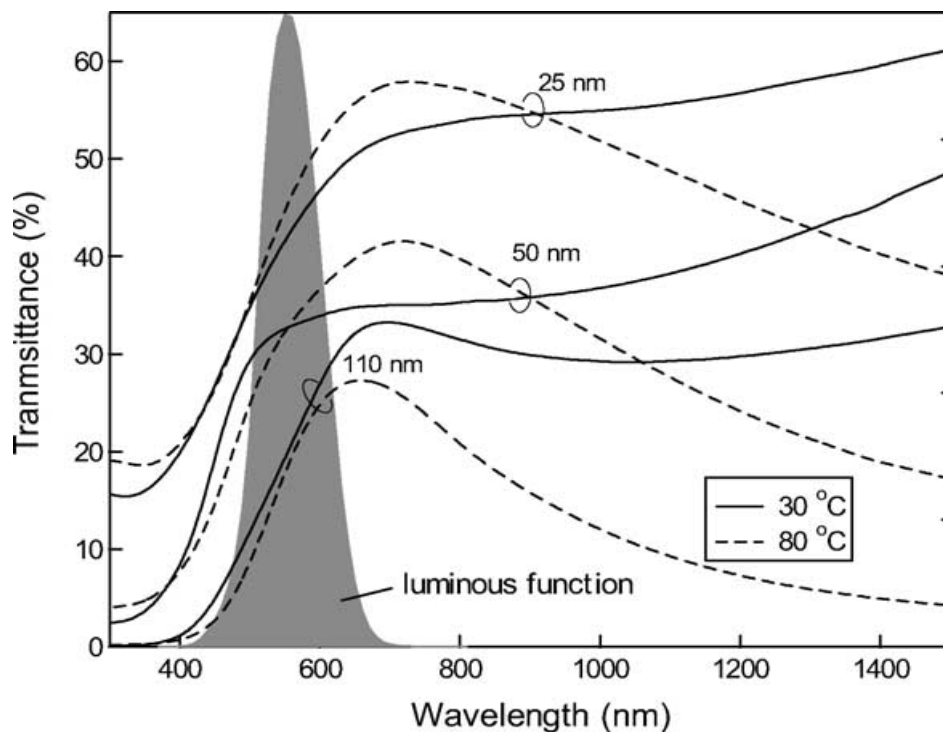


Figure 2. 1: Transmittance of 25-110 nm of VO₂ respectively .The dashed and solid lines symbolize metallic and semiconducting state of the films, respectively [12].

The electrical and the optical properties for VO₂ thin film (synthesized by PLD) does not depend on the nature of substrates [15]. Various deposition methods have been developed to produce VO₂ thin films. These include physical vapour deposition (reactive sputtering, reactive evaporation and laser ablation), chemical vapour deposition (CVD), sol-gel techniques and controlled oxidation and reduction [3-8].

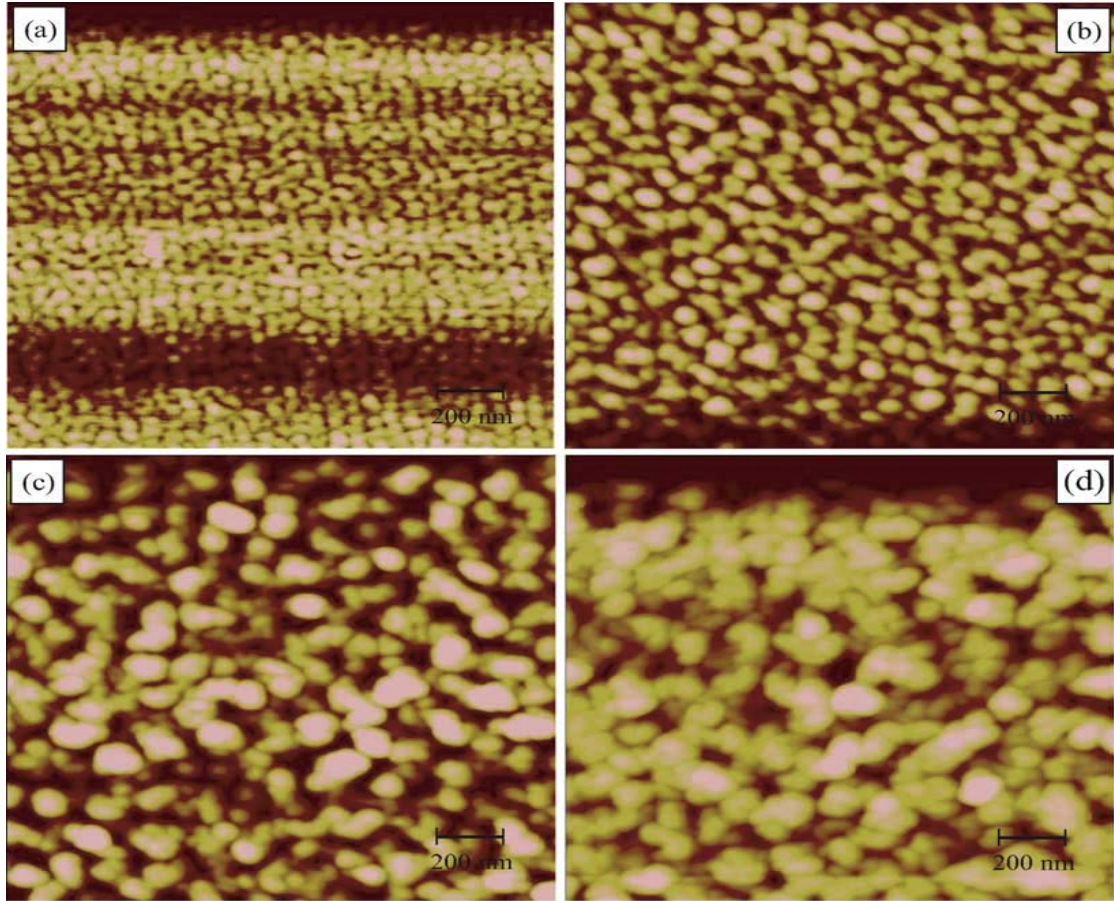


Figure 2. 2: AFM images of VO₂ films with thickness of (a) 10 nm, (b) 50 nm, (c) 100 nm, and (d) 150 nm [12].

During the semiconductor-to-metal-transition, the optical properties of vanadium dioxide are characterized by a sharp decrease in optical transmission in the infrared spectrum. Because of this anomalous behaviour, vanadium dioxide has been presented as an attractive thin film material for electrical and optical switches, optical storage, laser protection, and solar energy control for windows space satellites [5-6].

Vanadium dioxide has been studied in various ways using various deposition techniques as mentioned above. VO₂ has been doped with various dopants in order to increase or decrease the transition temperature i.e. tungsten, molybdenum, lithium,

hydrogen etc. According to the Tang et al. [14] model, the incorporation of dopant atoms leads to the loss of $V^{4+}-V^{4+}$ pairs, which are essential for the crystal structure of the semiconducting phase.

The loss of these homopolar $V^{4+}-V^{4+}$ bonds are caused by the incorporation of the dopants, as electrons are injected from the donors into the Vanadium 3d valence band, resulting in the transformation of V^{4+} to V^{3+} ions via charge transfer. Thus doping elements destabilise the semiconducting phase, and consequently lower the semiconducting to metal transition temperature. VO_2 has been doped with tungsten and fluorine in order to decrease the transition temperature to room temperature, with the purpose of applying it to smart windows [15].

The pure VO_2 thermochromism was compared with the W and F doped VO_2 . The AFM results show the effect of dopants in the surface of VO_2 thin films (see Figure 2.3). The introduction of 1.8 at% W on VO_2 thin film decreases the crystal size of the film. The surface roughness decreases with the increase of tungsten as a dopant hence the VO_2 quality decreases [15]. Burkhardt et al. [15] reported that doping VO_2 with tungsten only affect the transition temperature, whereas doping with fluorine affect the transition temperature and the absorption edge. To achieve a colourless appearance for VO_2 films, the optical absorption edge has to be shifted towards shorter wavelengths in order to sustain blue part of the visible light [15].

The higher the concentration of fluorine the higher the absorption edge shifts. The effect of F doping depends on the presence of tungsten in VO_2 . If the film is only

doped with F, the transmittance of the metallic phase converges towards the high transmittance of the semiconducting phase as the F content is increased [15].

Concerning the consequences for the VO_2 film, the two effects are contrasting i.e. F and W dopants. Doping with fluorine implies the stabilisation of the semiconducting phase whereas doping with tungsten implies the stabilisation of the metallic phase.

VO_2 has been doped with lithium so as to increase the transmittance and blue shifts the absorption edge. The transmittance successfully increased but the layers changed the colour from brown to bluish due to the lithium content. The switching efficiency for VO_2 doped with lithium become poor and the luminous transmittance increases [9]. VO_2 lithium doped causes higher transmittance but lower transition temperature. The increase in lithium content in the film of VO_2 leads to the increase in transmittance but the thermochromism decreases.

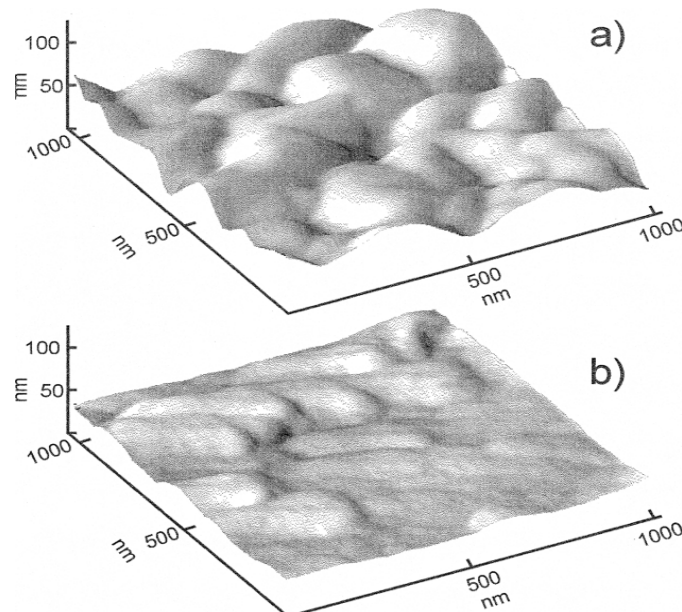


Figure 2. 3: AFM images of $1000 \times 1000\text{-nm}^2$ area of VO_2 films: (a) undoped grown at 800 K substrate temperature; (b) doped with 1.8 at. % W grown at 800K [15].

VO₂ thin films have been synthesized using many techniques as mentioned above. Each technique has its own effect on the synthesized film like stress. PLD, RF magnetron sputtering, Chemical Vapour Deposition etc has been used several cases in synthesizing VO₂. There is a recent technique that has been developed in synthesizing VO₂, known as rf-inverted cylindrical magnetron sputtering [16]. It is defined as the supplementary exceptional way to engineer nano-system at high deposition rates onto complex shapes substrates.

This technique has been used to synthesize thermochromic VO₂. JBK Kana et al. [16] has deposited VO₂ at different deposition time using the ICMS. The VO₂ film thickness increases with the increase in deposition time, hence the average grain size increases with time. The increase in peaks intensity (Figure 2.4) with time which indicates the volume decrease and hence the increase in film grain size with time [16].

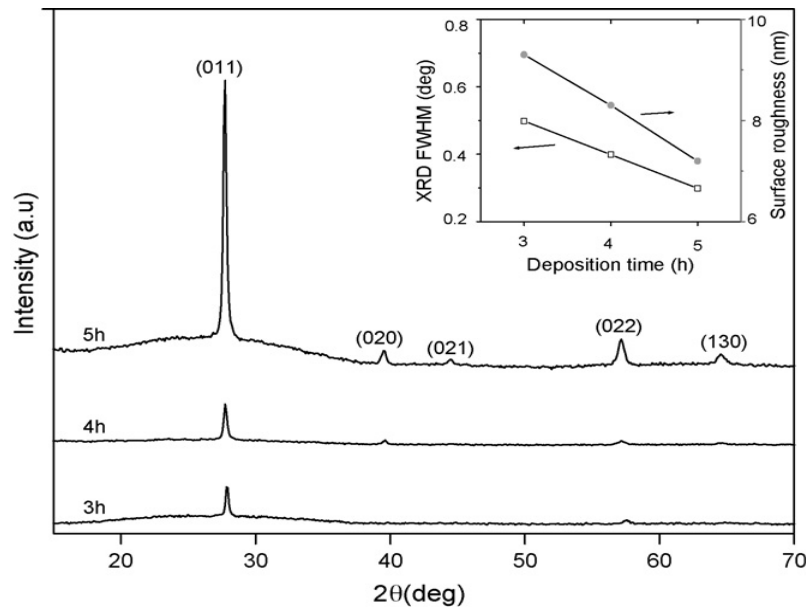


Figure 2. 4: XRD patterns of VO₂ thin films at different deposition time [16].

The transition temperature also decreases with the increase in film thickness (see Figure 2.5).

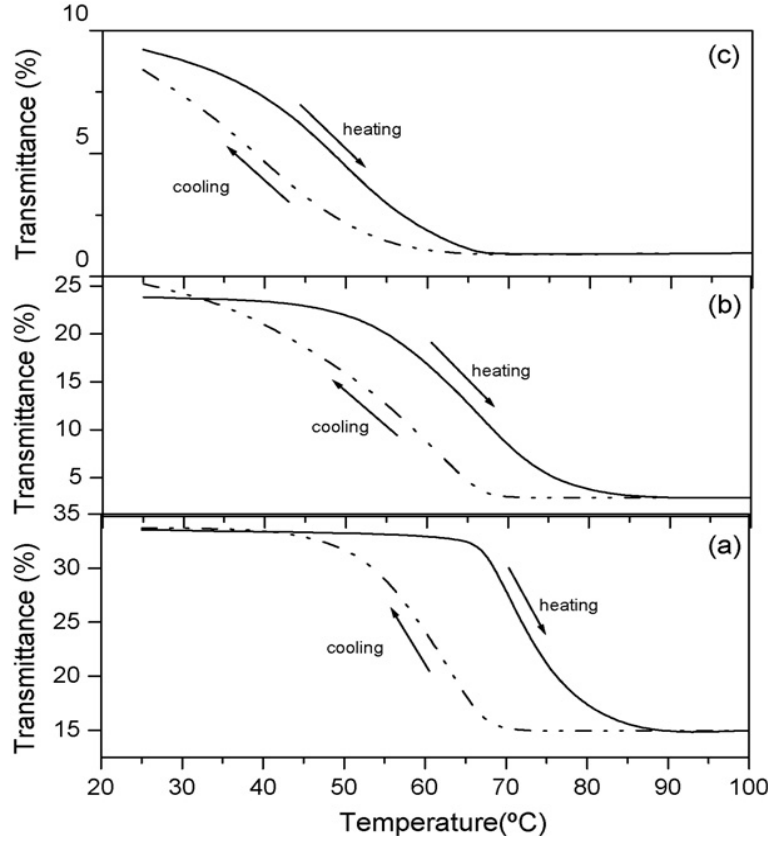


Figure 2. 5: Transmittance at wavelength of 1100 nm of VO₂ thin film as a function of temperature at different deposition time: (a) 3h; (b) 4h; (c) 5h [16].

The transition temperature decreases with the increase in deposition time which indicates the film thickness increment (see Figure 2.5). From the literature, it was presented that the optical transmittance for VO₂ could be decreased or increased by the dopants. It was reported from the literature that the deposition time affect the transition temperature. The increase in deposition time leads to the increase in film thickness [18]. It was also reported that oxygen pressure is the critical parameter to obtain pure VO₂ [19]. It has been reported from literature that VO₂ thin film gives the first strongest peak at (011) plane [5,12,13,18,21].

Two deposition techniques have been employed in developing VO₂ thin film i.e. Inverted Cylindrical Magnetron Sputtering (ICMS) and Pulsed Laser Deposition (PLD). As vanadium dioxide is difficult to synthesize because of the many other stable vanadium oxides. Various depositions have been done so as to optimize the deposition condition of the systems. The optimized conditions were fixed but the substrate temperature was varied. The films obtained on both techniques were then comparatively studied.

CHAPTER 3

PREPARATION AND CHARACTERIZATION

TECHNIQUES: PRINCIPLES AND INSTRUMENTATION

As it was mentioned in the previous chapter, vanadium dioxide is difficult to synthesize because of many other stable phases of vanadium oxides. In the present study, inverted cylindrical magnetron sputtering and pulsed laser deposition were used to deposit VO₂. The deposited films were characterized by using different techniques. X-ray diffraction was employed for the structural characterization. The roughness of the surface was scanned by atomic force microscopy.

Rutherford backscattering spectroscopy was utilized to examine the stoichiometry and the thickness of the films. The optical properties of the films were investigated by the UV-VIS spectroscopy. In this chapter, the principles and the instrumentation of these techniques are briefly described.

3.1 Pulsed laser deposition (PLD)

PLD is a thin film deposition technique where a high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the desired composition. The PLD system used in the present work (see Figure 3.1) consist of convex lens which was used to focus a laser beam from the laser generator into the chamber. It also has a gas inlet which was used to introduce oxygen gas inside a chamber.

The oxygen pressure was monitored by a computer. It also has a heated substrate holder that was used to hold a substrate and vary its temperature using the computer

software. It has a five rotating target holders to hold targets. Multiple targets can be loaded inside the chamber on a rotating holder, which can be used to sequentially expose different targets to the laser beam, thereby enabling the in-situ growth of heterostructures without opening the chamber.

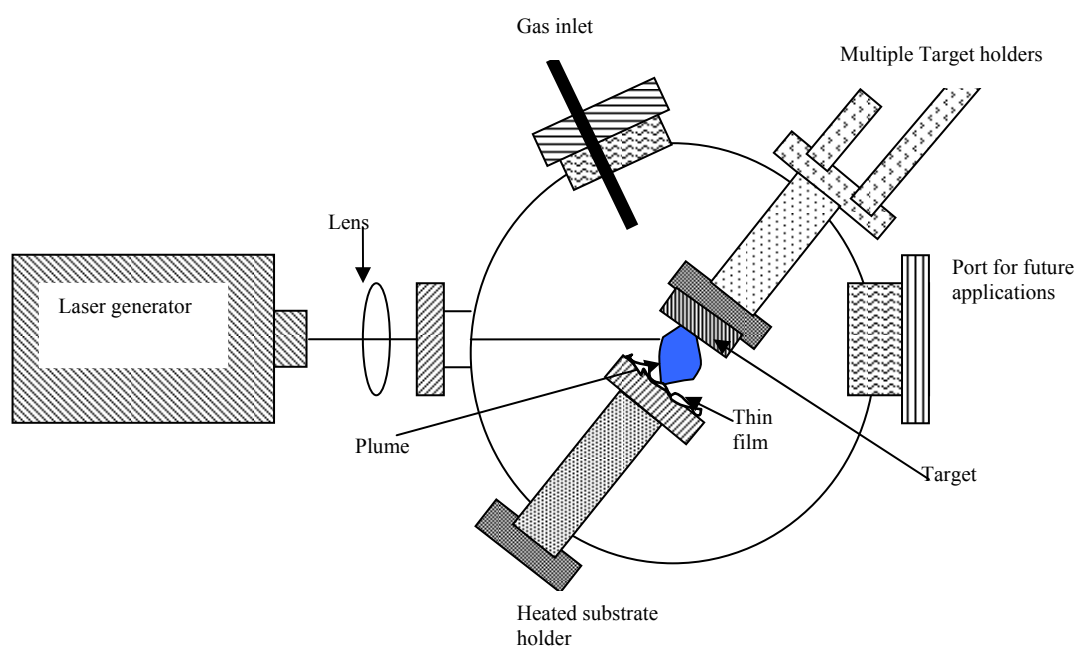


Figure 3.:1 The schematic sketch of the Pulsed laser deposition system.

The positioning of the target was also controlled using computer software. The substrate holder is in line with the target holder. Lastly, it has a port that is reserved for future applications. The PLD system used in this work functioned as follows; a laser beam (with a known energy) was directed from laser generator to a vanadium metal target.

The interaction of the pulsed laser beam with the target produced a blue plume (see Figure 3.1) of vanadium atoms that were transported towards a heated substrate placed in line with the plume. Vanadium atoms reacted with oxygen atoms to form a

certain vanadium oxide which was controlled by the amount of oxygen introduced inside the chamber.

3.2 Inverted Cylindrical Magnetron Sputtering (ICMS)

Inverted cylindrical magnetron sputtering is a supplementary exceptional way to engineer nano-systems at high deposition rates onto complex shapes substrates. This system (shown in figure 3.2) consists of cylindrical ring vanadium metal target with a circular magnet enclosed behind the target. The ring magnets are there for enhancing the electron path.

Since the electron path is not on a straight line due to magnetic field, the collision probability of an electron with ions is high, therefore the plasma is enhanced. The target was highly negatively charged so as to attract ions to knockout the surface atoms of the target. The substrate holder is fitted with a nichrome heater which can bring the substrate temperature up to 700°C.

The vacuum chamber was fitted with two gas inlets to introduce a mixture of Argon and oxygen gases for reactive sputtering. The chamber was evacuated using a diffusion pump backed by rotatory pump. The gas flow was controlled with a leak valve and the pressure inside the chamber was monitored by Penning and Pirani gauges. A Dressler Cesar RF power generator was used as a power supply. The Ar gas was introduced inside the chamber and it gets ionised by electrons from the plasma since the plasma is composed of electrons and ions. Ionized Ar gas is what forming plasma.

Since Ar is ionised it get attracted by the surface electrons of the vanadium target. When a vanadium surface was bombarded with Ar ions, surface atoms of vanadium target were partly scattered backward due to collisions between the surface atoms and the Ar ions. This phenomenon was called sputtering.

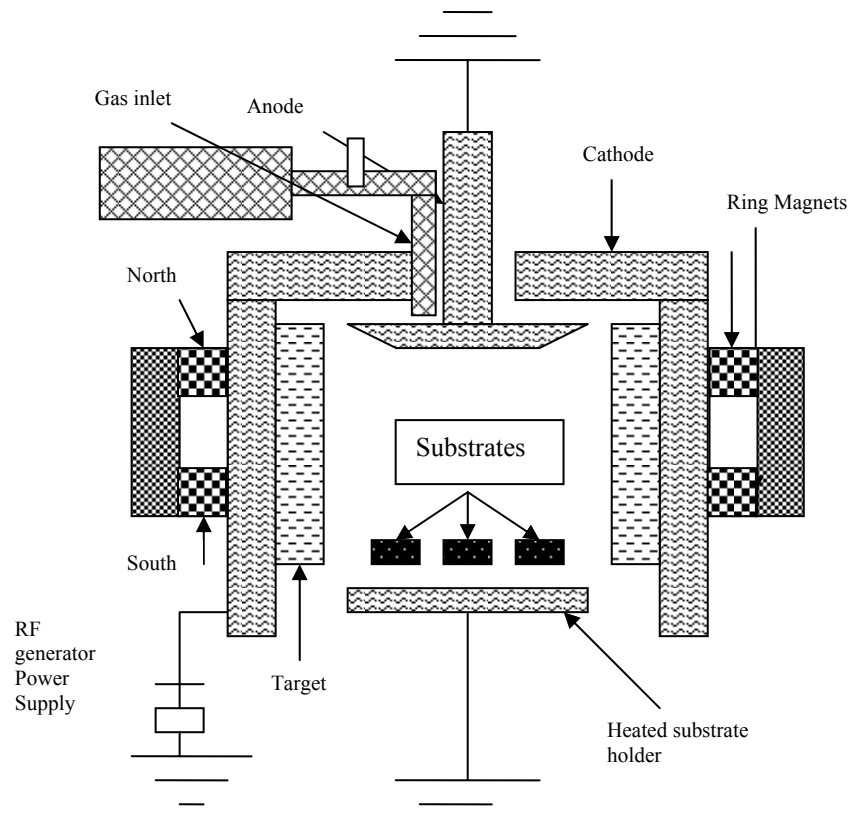


Figure 3. 2: Inverted Cylindrical Magnetron sputtering deposition system.

The front surface of the cathodes was covered with the vanadium target to be sputtered. The substrate was placed on the anode. The sputter chamber was filled with the sputter gas (Ar). The glow discharge is maintained under the application of the voltage between the electrodes.

The Ar^+ ions generated in the glow discharge are accelerated towards the cathode (target). The bombardment of the target by these energetic positive ions causes the removal of target atoms. These target atoms deposit on the substrate so the thin film is formed. In this process, no chemical reaction happens between Ar gas and the target atoms. However, oxygen was added as a reactive gas in chamber besides Ar, and then oxygen gas reacted with target atoms forming a compound layer on the substrate.

3.3 Characterization techniques

3.3.1 X-Ray Diffraction spectroscopy (XRD)

XRD is a powerful non-destructive technique for characterization of crystalline materials [19,32]. It provides the information on the structure, phase, preferred crystal orientation (texture) and other structural parameters, such as average grain size, strain and crystal defects.

When a monochromatic X-ray beam with wavelength λ , on the order of lattice spacing d , is projected onto a crystalline material at an angle θ , X-ray diffraction peaks are produced by constructive interference of monochromatic beam scattered from each set of lattice planes at specific angles. Constructive interference gives the diffraction peaks according to Bragg's law,

$$2d \sin \theta = n\lambda. \quad (3.1)$$

By varying the angle θ , the Bragg's Law condition is satisfied by different d -spacings in polycrystalline materials. Plotting the angular position and intensities of the

resultant diffracted peaks of radiation produces a pattern, which is the characteristic of the material. The full width at half maximum (FWHM) of the peak, $\Delta(2\theta)$ (in radians), is a measure of the grain size b in a polycrystalline film or the mosaic blocks in an epitaxial layer, as described by Scherrer's formula:

$$b = \frac{0.89\lambda}{\Delta(2\theta) \cdot \cos(\theta)} \quad (3.2)$$

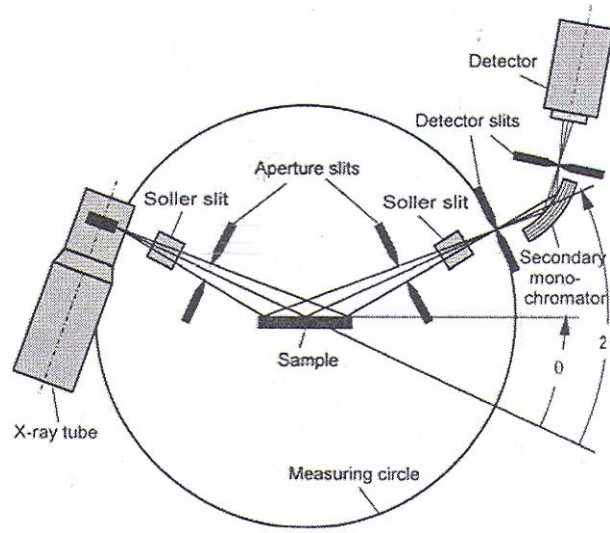


Figure 3. 3: Schematic representation of Bragg-Brentano diffractometer.

Figure 3.3 shows the schematic representation of a standard Bragg-Brentano diffractometer, with the $\text{Cu K}\alpha$ ($\lambda = 0.15418 \text{ nm}$) radiation and a scintillation detector. The X-ray tube was typically operated at a voltage of 40 kV and a current of 20 mA. In this work, one scan mode, θ - 2θ scan, was used for structural characterization. The detector rotated twice as fast and in the same direction around the diffractometer axis as the sample.

This technique is also called locked-coupled scan. In θ - 2θ scan, the reflections from the planes parallel to the substrate surface were detected. This allowed us to determine

the orientation along the growth direction of an (epitaxial or polycrystalline) films with respect to the substrate .

3.3.2 Atomic Force Microscopy (AFM)

The principles on how the AFM works are very simple. An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. Tips are typically made from Si_3N_4 or Si, and extended down from the end of a cantilever. The nanoscope AFM head employs an optical detection system in which the tip is attached to the underside of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever. As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a dual element photodiode.

The photodetector measures the difference in light intensities between the upper and lower photodetectors, and then converts to voltage. Feedback from the photodiode difference signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample.

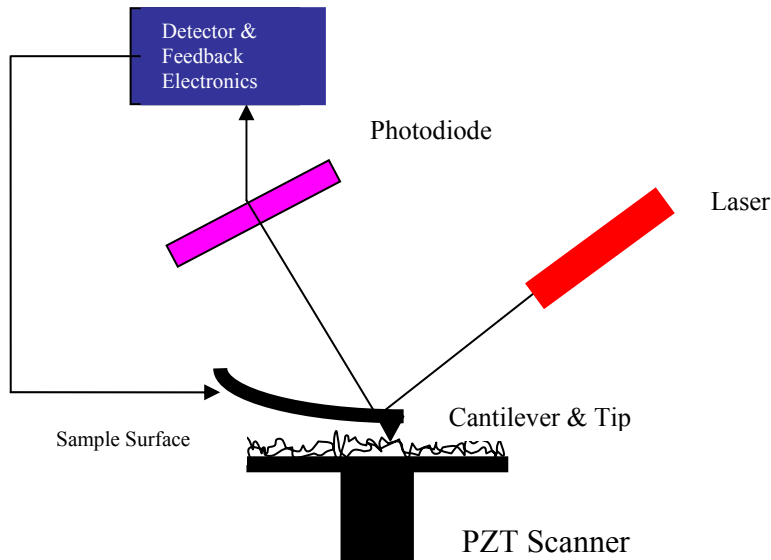


Figure 3. 4: The schematic diagram of Atomic Force Microscopy.

In this work, the primary purpose of using AFM (shown in figure 3.4) was to quantitatively measure surface roughness (average surface roughness, R_a). The AFM has scanners that are used to translate either the sample under the cantilever or the cantilever over the sample. By scanning in either way, the local height of the sample was measured. Three dimensional topographical maps of the surface were then constructed by plotting the local sample height versus horizontal probe tip position.

3.3.3 Rutherford Backscattering Spectroscopy (RBS)

Rutherford back-scattering spectroscopy is one of the most frequently used techniques for quantitative analysis of composition, thickness and depth profiles of thin solid films. In RBS, a beam of monoenergetic ions, usually He^+ or He^{++} with typical energy of 0.5 to 2.5 MeV, is directed at target, and the energies of ions which are scattered

backwards are analyzed. In the back-scattering collision, energy is transferred from the impinging particle to the stationary target atom.

Figure 3.5 shows the collision kinematics between a projectile atom (M_p , Z_p) and a target atom (M_r , Z_r) in RBS. The energy ratio between the projectile energy E_1 after collision and the energy E_0 before collision, derived from binary collision theory, is

$$K = \frac{E_1}{E_0} = \left[\frac{M_r \cos \theta + (M_r^2 - M_p^2 \sin^2 \theta)^{1/2}}{M_r + M_p} \right]^2 \quad (3.3)$$

The energy ratio E_1/E_0 , called the kinematic factor K , shows that the energy after scattering depends on the mass M_p of the projectile, the mass M_r of the target atom, and the scattering angle θ (i.e. the angle between incident and scattered beams). If M_p , E_0 and θ are known, M_r may be determined and the target element is identified.

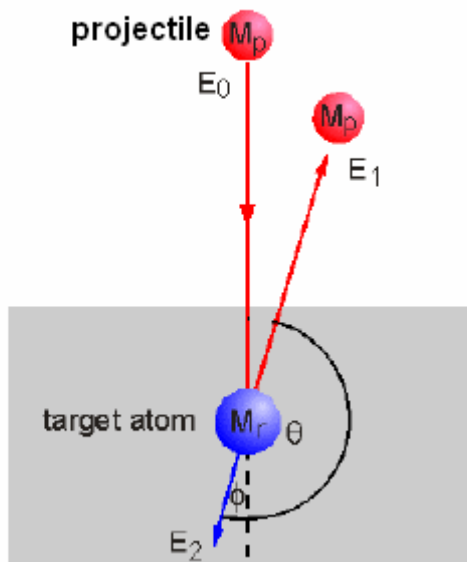


Figure 3. 5: Collision kinematics between a projectile atom M_p and a target atom M_r in RBS [9].

For an ion beam with the total number Q of ions impinging on a target, the number, Q_r , of ion backscattered from target atoms and registered in the detector gives the concentration of the corresponding element. It is given by:

$$Q_r = Q N_r \sigma_r \Delta\Omega \quad (3.4)$$

Where N_r is the areal density of target atoms in the sample (atom cm^{-2}), σ_r the differential scattering cross-section ($\text{cm}^2 \text{ sr}^{-1}$) and $\Delta\Omega$ is the solid angle for the detector.

The differential scattering cross-section describes the probability of a projectile being scattered by a target atom through an angle, θ , into a solid angle, $\Delta\Omega$, centered about θ . If the interaction potential between the projectile and the target atom during scattering is given by Coulomb potential, the cross-section is given by the Rutherford formula:

$$\sigma = \left(\frac{Z_p Z_r e^2}{16\pi\epsilon_0 E_0} \right)^2 4 \frac{\left[\left(M_r^2 - M_p^2 \sin^2 \theta \right)^{\frac{1}{2}} + M_r \cos \theta \right]^2}{M_r \sin^4 \theta \left(M_r^2 - M_p^2 \sin^2 \theta \right)^{\frac{1}{2}}} \quad (3.5)$$

For a compound film $A_m B_n$, the composition can be calculated from Eq. (3.4) to be:

$$\frac{n}{m} = \frac{N_B}{N_A} = \frac{Q_B \sigma_A}{Q_A \sigma_B} \quad (3.6)$$

The energy of the backscattered ion is given by Eq. (3.3) only for scattering by an atom at the target surface. In RBS, however, the ion beam penetrates the target and an ion might be backscattered by target atoms at any point along its path, as shown in Figure 3.6. In the energy region used for RBS the ion trajectory is a straight line (apart from the backscattering collision) along which the ions lose energy primarily through excitation and ionization of atomic electrons (electronic energy loss).

The energy loss per unit path length, dE/dx , is called the stopping power. These additional energy losses broaden the peak to be observed in an RBS spectrum of thin film. In this method, projectiles scattered by angles larger than 90° are analyzed. Because projectiles with mass M_p can only be backscattered from a target atom with mass M_r if $M_p < M_r$, light projectiles such as protons and He ions are usually used in RBS. High back-scattered energies and large backscattering cross-section are observed due to heavy target atoms. RBS is, therefore, well suited for the analysis of heavy target elements, but its sensitivity for light elements is poor. This difference in energy can then quantify the amount of a particular element in the sample [18,31].

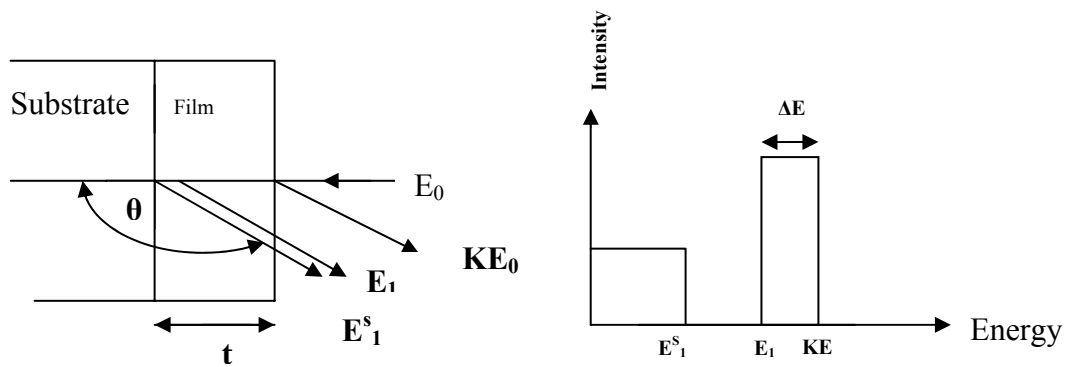


Figure 3. 6: Schematic representation how the depth corresponds to different energy signals.

3.3.4 Four Point Probe

The four point electrical probe is a very versatile device used widely in physics for the investigation of electrical phenomena [25-30]. When a simple measurement of the electrical resistance of a test sample is performed by attaching two wires to it, one inadvertently also measures the resistance of the contact point of the wires to the sample. Typically the resistance of the point of contact (called contact resistance) is far smaller than the resistance of the sample if one has good contacts between the sample and the wires used, and can thus be ignored. However, when one is measuring a very small sample resistance, especially under variable temperature conditions, the contact resistance can dominate and completely obscure changes in the resistance of the sample itself.

The effects of contact resistance can be eliminated with the use of a four point probe. A schematic of a four point probe is shown in Figure 3.7 below. In this diagram, four wires (or probes) have been attached to the test sample. A constant current is made to flow the length of the sample through probes labelled 1 and 4 in the figure. If the sample has any resistance to the flow of electrical current, then there will be a drop of potential (or voltage) as the current flows along the sample, for example between the two wires (or probes) labelled 2 and 3 in the figure. The voltage drop between probes 2 and 3 can be measured by a digital voltmeter. The resistance of the sample between probes 2 and 3 is the ratio of the voltage registering on the digital voltmeter to the value of the output current of the power supply.

The high impedance of the digital voltmeter minimizes the current flow through the portion of the circuit comprising the voltmeter. Thus, since there is no potential drop across the contact resistance associated with probes 2 and 3, only the resistance associated with the semiconductor between probes 2 and 3 is measured.

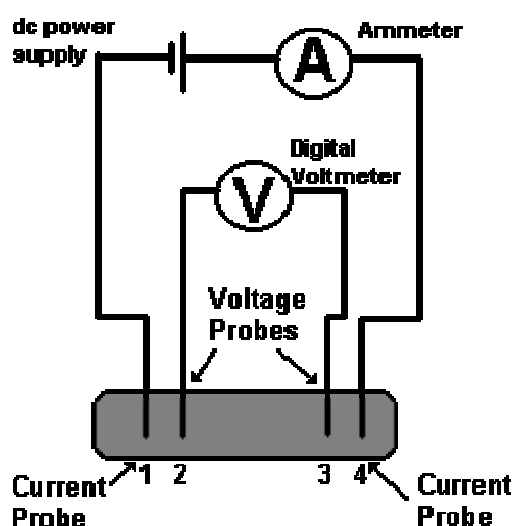


Figure 3. 7: Schematic diagram of the four point probe.

3.3.5 UV-Vis-Spectrophotometer

The UV/Vis spectrophotometer that was used in this work consists of a light source a sample holder fitted with a heating stage, a detector, and a data acquisition computer [24,31]. The sample holder is located between the light source and the detector. The light source, detector and sample holder are designed into a dark box which has a cover preventing unwanted light to interfere with the laser beam during experimentation.

The spectrophotometer was allowed to create a baseline which removes background from the data to be collected. The beam light was directed to the sample and the detector detects the amount of light that is transmitted through the sample.

The data was generated and captured by the computer. The measurements were taken with respect to temperature. The wavelength range of the spectrophotometer used in this work was 200-1100 nm. The data collected was used to plot the graphs of transmittance as a function of wavelength. The UV-VIS spectra were used to investigate the optical switching property of the deposited vanadium oxide films.

CHAPTER 4

DEPOSITION TECHNIQUES.

As mentioned in chapter 2, VO₂ has been synthesized using various techniques including those used for this study. According to our knowledge, no one has done the comparative study on VO₂ quality synthesized by PLD and ICMS techniques. G. Xu et al. [12] have used rf magnetron sputtering to deposit VO₂ by varying the power keeping the other parameters constant. Chae et al [17] deposited VO₂ at different pressures and keeping other parameters constant by using the PLD system.

The present work focus on VO₂ deposition by ICMS and PLD system by varying the substrate temperature but keeping optimal pressure constant, aiming to describe (in comparison) the effect of substrate temperature on VO₂ thin films microstructure, electrical and optical properties. The influence of the substrate temperature on the microstructure, electrical and optical properties of VO₂ thin films is reported in chapter 5.

4.1.1 VO₂ deposition using PLD

Soda lime glass was used as substrate for VO₂ deposition for both techniques (PLD and ICMS). Three types of lasers were available in the laboratory (see Table 4.1). The KrF excimer laser (Lambda-Physik) with the wavelength of 248 nm was used to ablate vanadium metal target. Several deposition steps were made trying to optimize the deposition condition (see Table 4.2).

A laser beam with an energy density of 1~2.05 J/cm² was focused on the target surface at a repetition rate of 10 Hz. The distance between target and the substrate was kept to 5 cm. The initial pressure of oxygen used was 200 mTorr. The substrate temperature was kept at 400°C while the oxygen pressure was decreased so as to find the optimal pressure for obtaining thermochromic VO₂. The pressure was found to be 15 mTorr. The oxygen pressure is a critical parameter for synthesizing VO₂. Prior to the deposition, the substrates were cleaned with an ultrasonic procedure to remove the possible residual contaminants on their surfaces; the target was pre-ablated by placing a shutter in front of a substrate for several minutes so as to remove the contaminants that might occur on the surface of the target.

The substrates were cleaned using the following procedure: methanol, acetone, trichloroethylene, acetone, methanol and finally deionised water. Thereafter, the samples were submerged in a 20% solution of hydrofluoric acid. The substrates were then placed in the chamber and the VO₂ films were deposited under the optimal pressure of oxygen at different substrate temperature ranging from 350°C to 450°C.

Before each deposition, the PLD system was allowed to evacuate to the low pressure of the order of 10⁻⁶ mbar in order to remove all the gases that might occur inside the chamber. After each deposition, the sample was slowly cooled to the room temperature under the same deposition conditions as that used for growth of the films.

Table 4. 1: Lasers used for PLD.

Wavelength	Power	Class	OD Required	Description
1064 nm	250 mJ,10 ns,10 Hz	IV	5	Continuum laser
248 nm	300 mJ,30 ns, 50 Hz	IV	5	LP Excimer laser(KrF)
193 nm	300 mJ,30 ns,250 Hz	IV	5	LP Excimer laser(ArF)

4.1.2 Deposition parameters

In this section, all thin films were deposited for 2 hrs and the vanadium plate was used as a target, if not stated especially. Table 4.2 shows the deposition parameters that were used for film preparation by PLD. During the optimization of deposition parameters, the temperature was kept constant (400°C) and the working oxygen gas pressure was tuned until the deposited vanadium oxide films exhibited a good thermochromic property.

Table 4. 2 : PLD deposition parameters

Base Pressure (mbar)	Working Pressure (mTorr)	Gas	Working Temperature (°C)	Energy (mJ)	Energy Density(J/cm ²)	No. Pulses	Rep. Rate(Hz)	Film checked by UV-Vis
1.1×10^{-7}	200	O ₂	400	230	1.96	30000	10	V ₂ O ₅
1.2×10^{-7}	130	O ₂	400	217	1.85	60000	10	V ₂ O ₅
3.36×10^{-7}	97.3	O ₂	400	240	2.05	60000	10	V ₂ O ₅
1.60×10^{-7}	1.3	O ₂	400	220	1.88	60000	10	V ₂ O ₅
1.1×10^{-7}	13	O ₂	400	224	1.91	60000	10	V ₂ O ₅
5×10^{-5}	15	O ₂	350	210	1.79	60000	10	VO ₂
5×10^{-5}	15	O ₂	400	210	1.79	60000	10	VO ₂
5×10^{-5}	15	O ₂	450	210	1.79	60000	10	VO ₂

4.2 VO₂ deposition using ICMS

The vacuum chamber was evacuated by a diffusion pump backed by rotary pump down to 10^{-6} mbar. A Dressler Cesar RF power generator was switched on so as to start the plasma. A mixture of Argon and oxygen that was used as the working gas for enhancing plasma and oxygen as a reactive gas, were let into the sputter chamber. For all deposition process a mixture of Ar (90%) and oxygen (10%) was introduced in the chamber at a pressure of 8×10^{-3} mbar followed by high purity of Ar (99.99%) at a pressure of 10^{-2} mbar. The above deposition conditions were known to be the optimal to produce good quality for VO₂ hence no other vanadium oxide observed.

The substrate temperature was varied from 450°C to 550°C. The temperature 450 °C was the minimum temperature to obtain crystalline VO₂ in our sputtering system. For all deposition, time and power were fixed at 2 hrs and 70 W respectively (see Table 4.3).

Table 4. 3: ICMS deposition parameters.

Background pressure(mbar)	5×10^{-5}	2×10^{-5}	5×10^{-5}	10^{-5}
Substrate Temperature	450°C	500°C	550°C	450°C
Total Working Pressure(Ar+O ₂)	8×10^{-3} mbar	8×10^{-3} mbar	8×10^{-3} mbar	8×10^{-3} mbar
Partial Pressure(O ₂)	10^{-2} mbar	10^{-2} mbar	10^{-2} mbar	10^{-2} mbar
RF Power(Forward)	70W	70W	70W	70W
RF Power(Reflected)	0W	0W	0W	0W
Voltage bias of target	170V	168 V	173 V	181 V
Dep. Time	2hrs	2hrs	2hrs	2hrs
In all deposition vanadium plate was used as a target.				

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 The PLD results

As mentioned before, the optimal deposition conditions (for PLD) were fixed but the substrate temperature was varied from 350°C to 450°C. The effect of the substrate temperature on microstructure, electrical and optical properties is reported. The film structure, surface roughness, thickness, electrical and optical properties are discussed.

5.1.1 The film structure

In this section we investigate by means of X-ray diffraction (XRD) the effect of the substrate temperature on the crystallinity of the VO₂ thin films.

The XRD spectra (scanned from 20 and 70°) of the VO₂ thin films deposited by PLD at different substrate temperatures are shown in Figure 5.1. The scan was taken at room temperature, in the semiconducting phase of VO₂ (monoclinic structure). The films exhibit a polycrystalline structure whose peaks matches the single phase of monoclinic VO₂ (PDF file number 44-0225) without the indication of other vanadium oxide phases.

All the films deposited at temperature ranging from 350-450°C were found to be crystallized. The reflection planes with their corresponding values of 2theta are tabulated in table 5.1. In general, the peak broadening and intensity depend on the size of the grains and the degree of crystallinity, respectively [16]. All the films show a

first peak at 27.87° corresponding to (011) plane indicating the existence of VO_2 [5,9,12,13,16,18,21]. The XRD spectra of the film deposited at substrate temperature of 350°C shows Bragg reflections at 2θ equal to 27.87° and 57.91° corresponding respectively to (011) and (022) reflections of the VO_2 monoclinic phase. Since no other clear x-ray peaks are observed, the grains of VO_2 films deposited at 350°C are in fact highly oriented with crystallographic (011) planes. We observed that the (011) reflection emerges from a broad structure. This broad structure may suggest the existence of disordered phase of VO_2 .

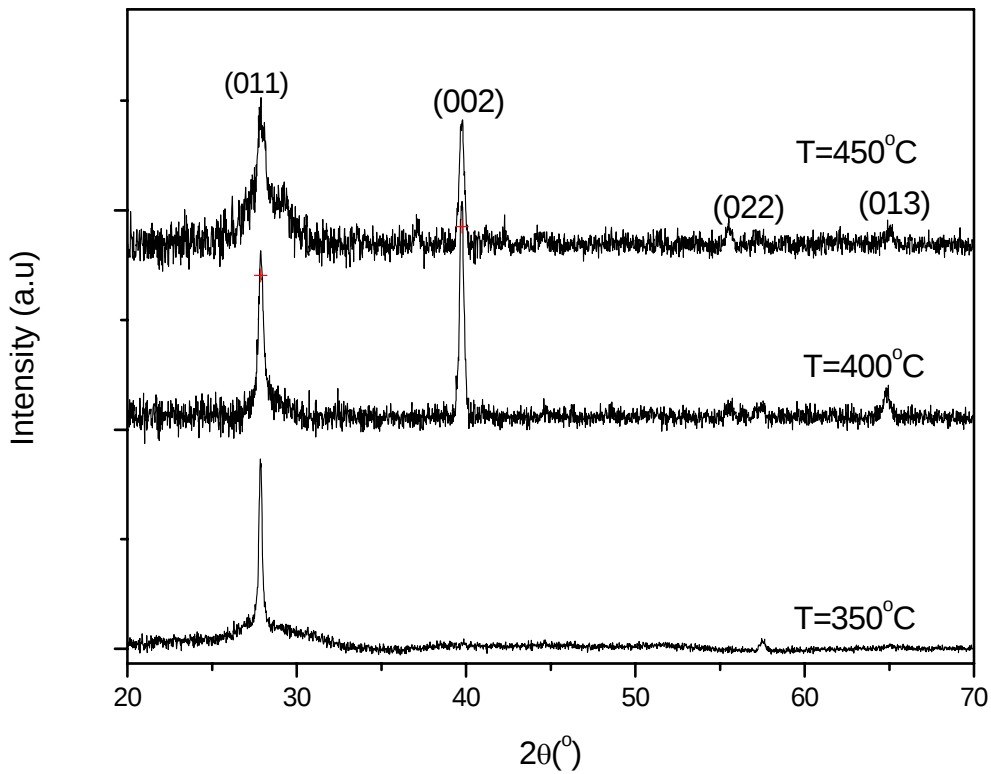


Figure 5. 1: X-ray diffraction pattern of VO_2 deposited by PLD at different temperatures.

Table 5. 1: X-ray diffraction results

Temperature ($^{\circ}\text{C}$)	2θ ($^{\circ}$)	Phase	Plane
350, 400, 450	27.87	VO_2	(011)
400, 450	39.75	VO_2	(002)
400, 450	64.90	VO_2	(013)
450	57.91	VO_2	(022)

The films deposited at substrate temperature of 400 $^{\circ}\text{C}$ and 450 $^{\circ}\text{C}$ exhibit similar XRD patterns. In addition to the (011) peak the patterns show the emergence of new peaks at $2\theta = 39.75$ and 64.90 corresponding respectively to the (002) and (013) reflections. The appearance of new reflections is a clear indication of the deterioration of VO_2 grains orientation.

Moreover the XRD spectra of the film deposited at 450 $^{\circ}\text{C}$ shows some extra unknown reflections, which might suggest the presence of secondary phase of vanadium oxide.

Debye's formula (see appendix) was used to estimate the grain sizes using the (011) peak.

The estimated values were then used to plot a graph shown in figure 5.2. The graph was used to observe the effect of substrate temperature on the grain size. The increase in substrate temperature leads to the increase in grain size. It is suggested that above 450 $^{\circ}\text{C}$, the film could give more phases. It is clear that the crystallinity evolves with substrate temperature.

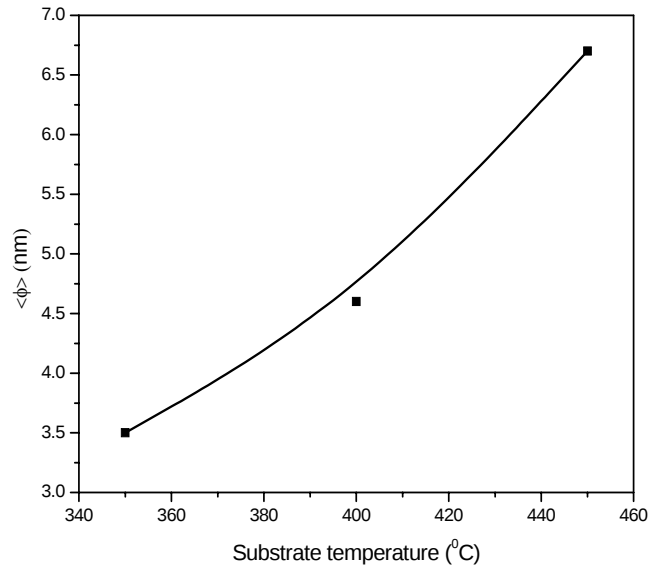


Figure 5. 2: Grain size vs. substrate temperature graph.

5.1.2 Film surface topography

The roughness of the films was investigated using atomic force microscopy and the Nanoscope software was used to calculate the root mean square roughness (R_q).

Figures (5.4-6) shows the surface topography of the VO_2 thin films deposited by PLD. The topography of the films was taken at room temperature in semiconducting phase VO_2 . The surface average roughness values are listed in Table 5.1. The results reveal that R_a is not the same for the film deposited at substrate temperatures of 350°C and 400°C, but shows an abrupt increase from the film deposited at 450°C. This roughness variation is suggested to be caused by the change in grains orientation.

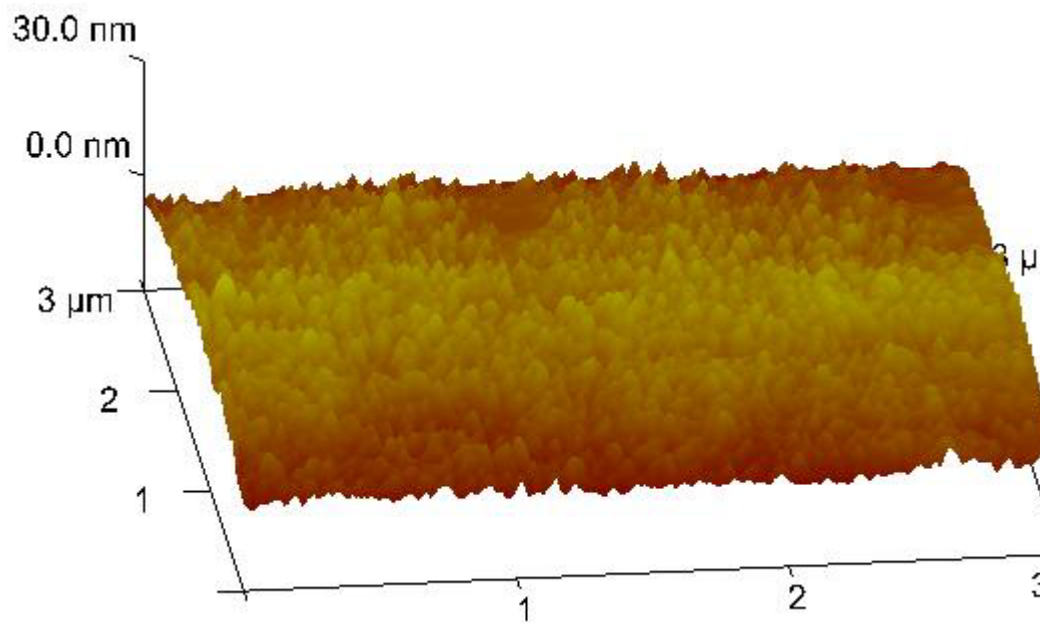


Figure 5. 3: The surface morphology for VO₂ thin film deposited by PLD at 350°C.

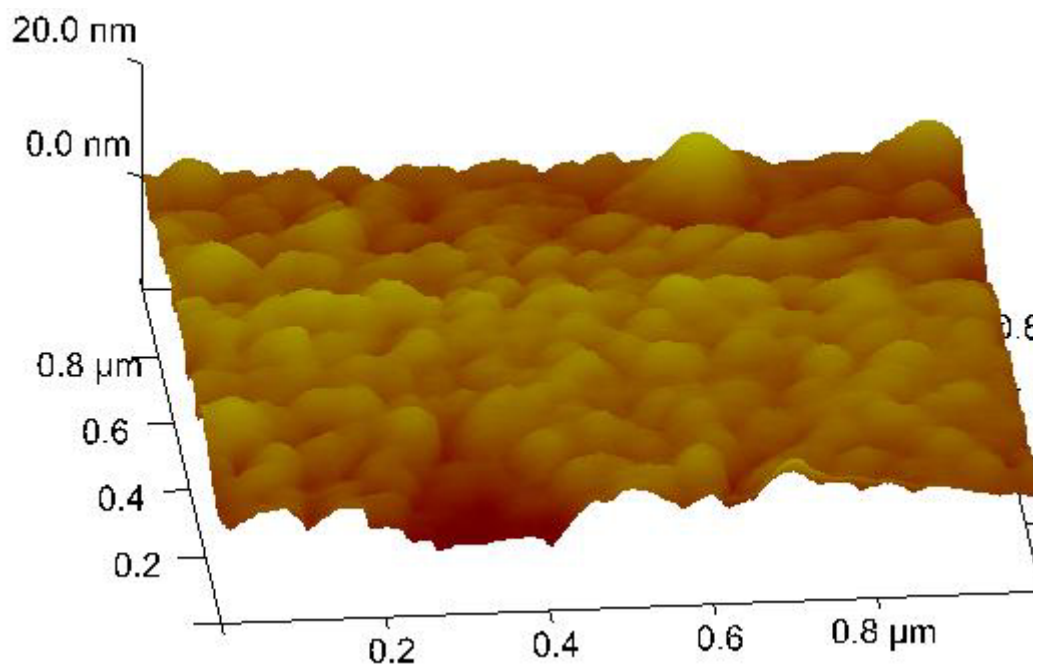


Figure 5. 4: The surface morphology for VO₂ thin film deposited by PLD at 400°C.

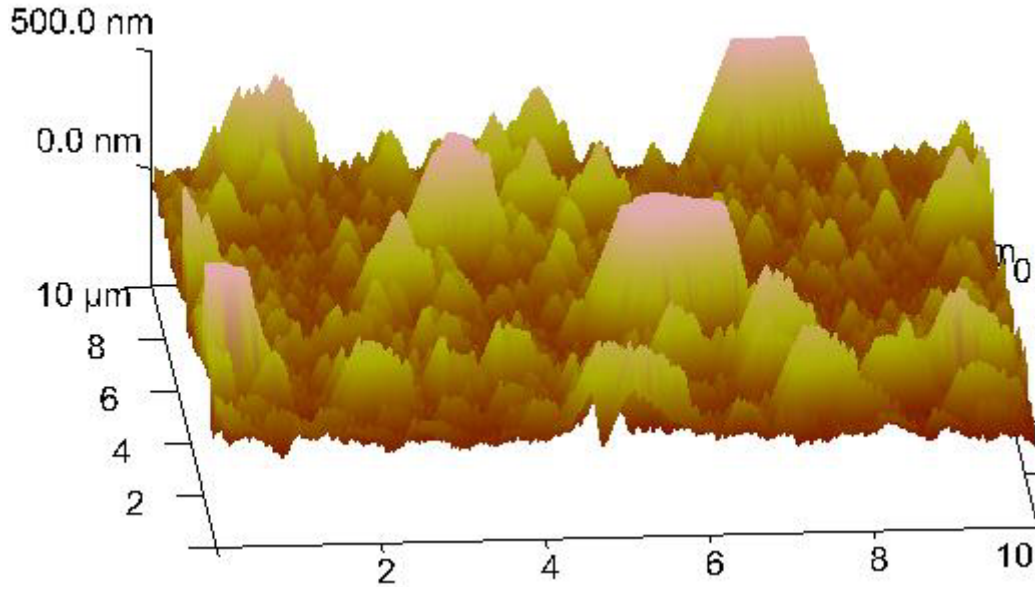


Figure 5. 5: The surface morphology for VO₂ thin film deposited by PLD at 450°C.

Table 5. 2: The surface roughness, R_a , of the film.

Substrate Temperature (°C)	Surface roughness, R_a , (nm)
350	2.54
400	1.50
450	68.20

5.1.3 Rutherford Backscattering Results

RBS has been used to estimate the film thickness using the XRUMP simulation software. The thickness was checked with respect to the substrate temperature. The film on glass substrate was checked for thickness but not the film stoichiometry because the glass is composed of oxygen, so it can be difficult to see if the oxygen is

from the film or from the glass. Silicon substrate is normally used to find the stoichiometry of the VO₂ thin film.

The RBS spectra of the VO₂ film on the soda lime glass substrate deposited by PLD is shown in Figure 5.6. The figure shows how the thickness was estimated using XRUMP simulation software. The estimated values are tabulated in table 5.2. The RBS results indicated that there was no contamination during the film deposition. The other elements appearing on the simulation are from the glass substrate. The results also revealed that for our optimized conditions, the thickness is almost the same with the increase in substrate temperature. However, the film thickness variation is suggested to be caused by the slight variation of the laser beam energy of the PLD system during the film deposition. The RBS results reveal that the substrate temperature does not affect the film thickness.

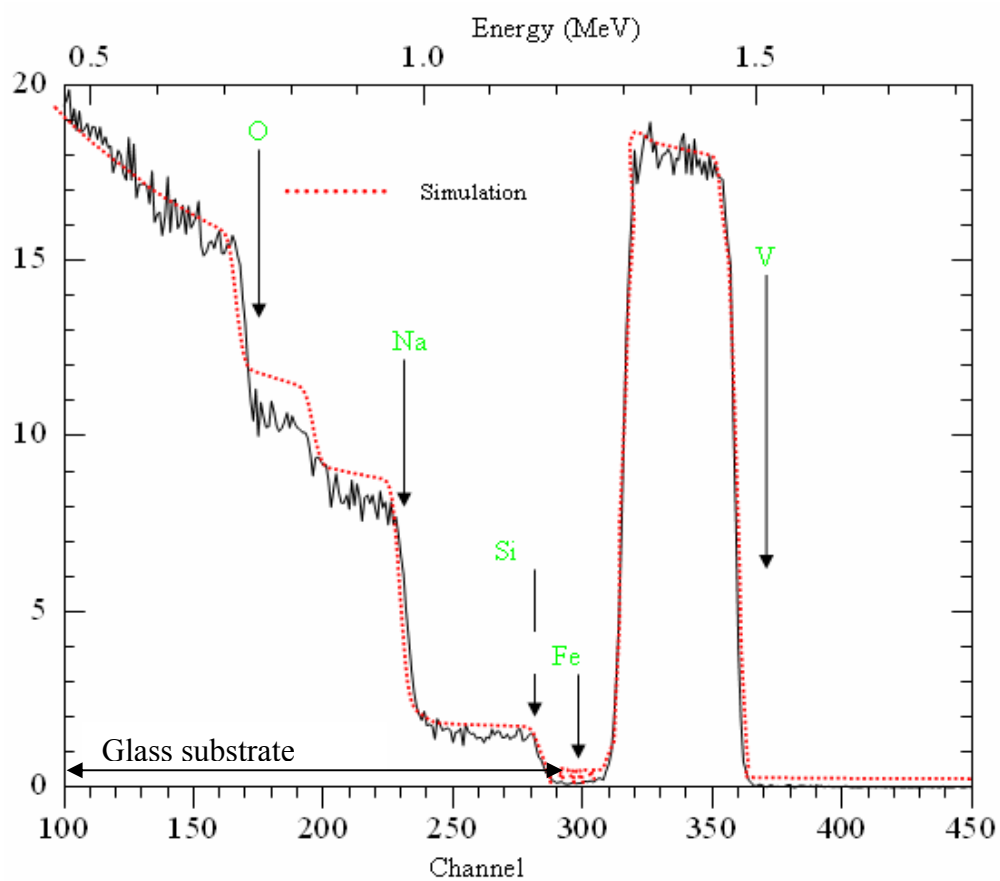


Figure 5. 6: The fitted spectrum for VO₂ on a soda lime glass deposited by PLD.

Table 5. 3: The estimated values of film thickness from XRUMP simulation.

Substrate temperature (°C)	Film thickness (nm)
350	131
400	143
450	167.3

5.1.4 Thermochromic properties of the film

The following results are the results which indicate the thermochromism of the film deposited at different substrate temperatures. The results were obtained using the UV-VIS-Spectrophotometer (Ultraviolet-visible spectrophotometer is an instrument used to measure the intensity of light passing through the sample).

Figure 5.7 shows the film optical transmittance (%) as a function of wavelength (nm) of the films deposited by PLD techniques. The film thermochromism was observed and the spectral transmittance of low temperature (25°C) semiconducting phase and high temperature (100°C) metal phase were showing a sharp contrast in the infrared region (IR). The results reveal that the contrast is decreasing with the increase in substrate temperature.

The estimation of the optical transmission switching efficiency for the film is given by the difference of the transmittance of the film at room temperature (semiconducting phase) and the transmittance at high temperature (metallic phase) in the near infrared region. The highly oriented VO₂ film obtained at 350°C, exhibits the high optical transmittance efficiency. The films deposited at 400 and 450°C exhibit lower optical transmittance. This indicates that the optical transmittance depends on the grains alignment in the film.

Figure 5.8 show the hysteresis loops of the transmittance as a function of temperature (at a fixed wavelength of 1100 nm) for the films of VO₂ prepared by PLD techniques. The transition temperature is defined as the center of the derivative curve. The width of the hysteresis is defined as the difference between the transition temperature of the

heating and the cooling cycle of the hysteresis loop. The results show that the VO₂ thin films prepared by PLD are having almost the same hysteresis width of ~10°C.

The transition temperatures of the films are shown in Table 5.3. The results reveal that the increase in substrate temperature leads to the decrease in transition temperature. This indicates that the transition temperature does not depend only on the film thickness but also on the film crystallinity [9,11,12,13,16,18,21]. The highly oriented VO₂ film deposited at 350 °C, has higher transition temperature than these other two that are poorly crystallized.

The hysteresis sharpness, shape, width, position and switching ratio depend on the quality of VO₂ (i.e. crystallinity, stoichiometry etc.), the substrate type and its crystallographic orientation and the film thickness [13]. The highly oriented VO₂ film obtained at 350°C, exhibits higher optical transmittance and has a sharp hysteresis indicating good optical properties. This is in agreement with J.B. Kana Kana et al. results [16] which show that the grains arrangement plays an important role in the optical properties of the film.

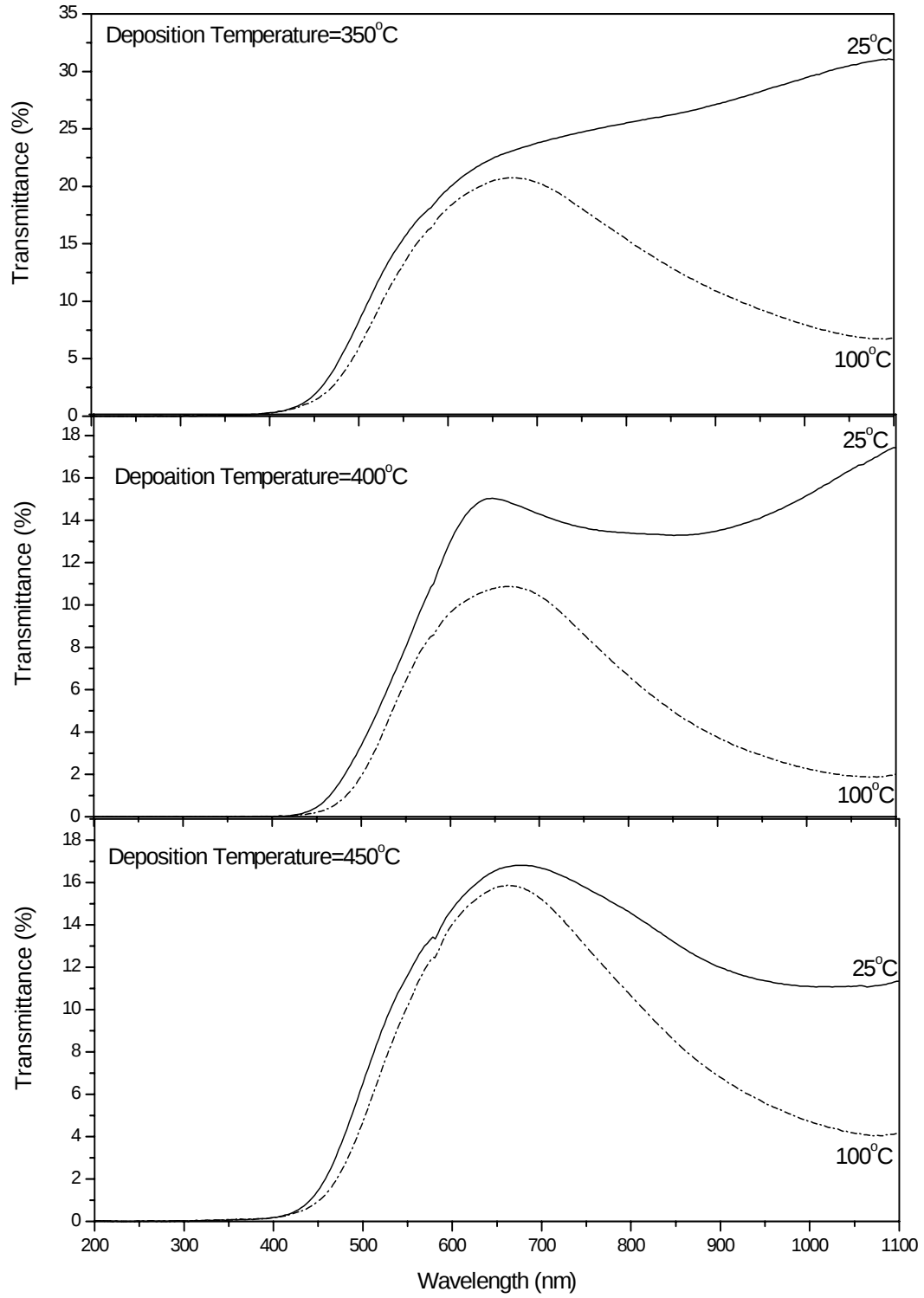


Figure 5. 7: Optical transmission as a function of wavelength for VO₂ thin films deposited by PLD at different substrate temperature. The solid and dashed lines indicate the semiconducting and metallic states of the films, respectively.

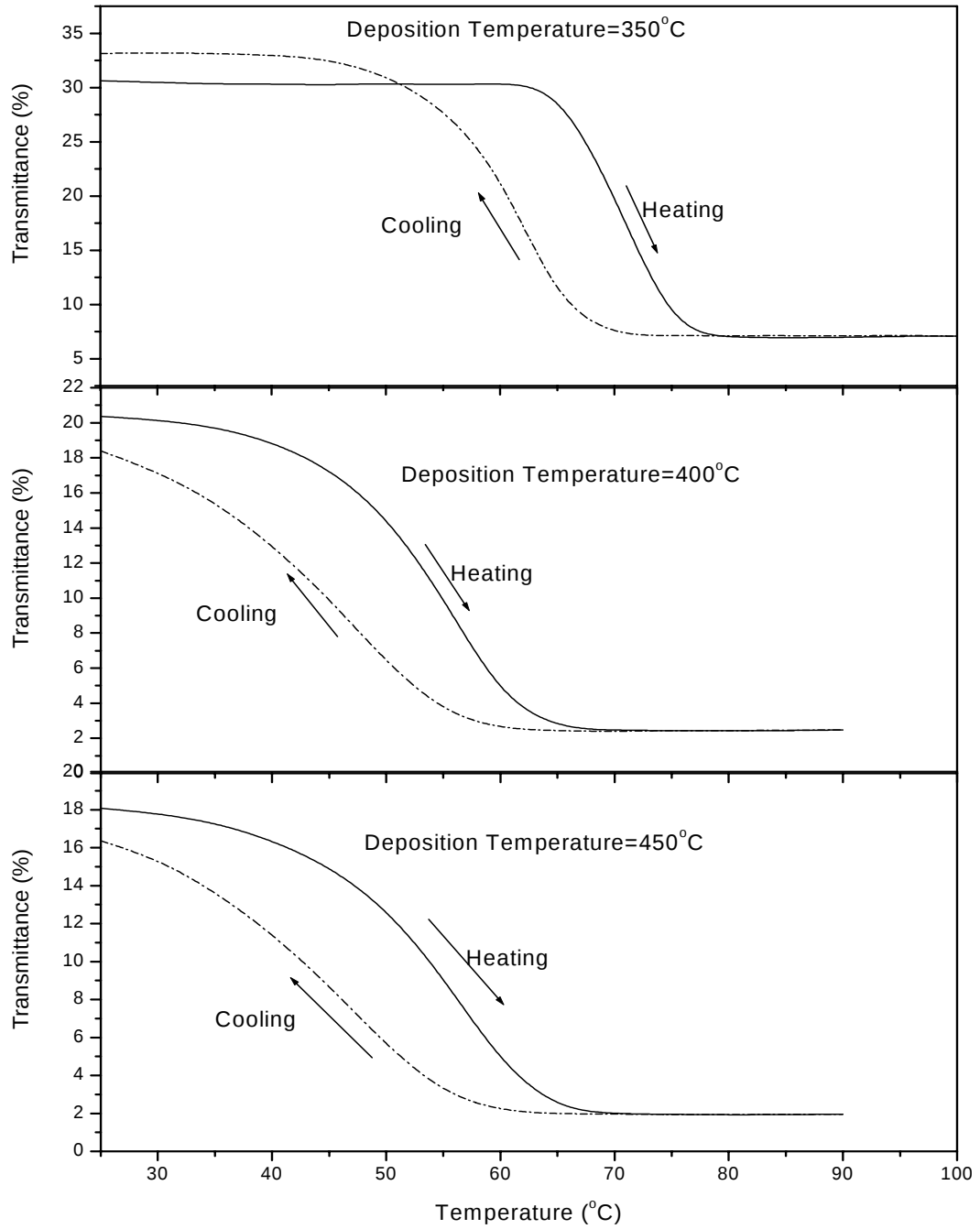


Figure 5. 8: Optical transmission as a function of temperature at wavelength of 1100 nm for VO₂ thin films deposited by PLD at different substrate temperature.

Table 5. 4: The transition temperature as function of substrate temperature results.

Substrate temperature (°C)	Transition temperature (°C)
350	70
400	54
450	51

5.1.5 Electrical measurements of the film

The following section describes the electrical properties of the film deposited at different substrate temperatures.

Figure 5.9 shows the resistance hysteresis loops of VO₂ thin films deposited at substrate temperature of 350°C, 400°C and 450°C. The oriented film deposited at 350°C, exhibits a sharp transition in electrical resistance near 68 °C which is a definitive confirmation of formation of thermochromic VO₂. The drop in the electrical resistance is about three orders of magnitude which is similar to the one observed in high quality polycrystalline VO₂ thin films but less than that reported for single bulk crystal of VO₂ (five orders of magnitude) [3]. The sharpness of the transition is determined by the arrangement of the grains in the film. The film with the similar grain arrangement has the same grain boundaries and exhibit high electrical switching properties. The heating and cooling curves diverge, indicating a temperature hysteresis. Defining the temperature hysteresis width as the difference between the temperature at the midpoint of the transition region of heating and cooling curves, a hysteresis width of 10°C is observed. This large hysteresis of VO₂ film compared to that observed in single bulk VO₂ crystal (2°C), may have its origin in the extrinsic

stress created during deposition by the difference in thermal expansion coefficient between the VO₂ film and the substrate.

The films deposited at 400°C and 450°C exhibit the same behaviour in terms of electrical switching. The transition is sluggish and shifts toward lower temperature near 54 °C. The drop in the electrical resistance is about two orders of magnitude. Both films exhibit a temperature hysteresis width of about 10 °C which is the same as for 350°C. The decrease in the sharpness of the transition profile and the magnitude of the drop in the electrical resistance is caused by the random arrangement of the grains in the film hence leads to different grain boundaries. The increase in substrate temperature affected the microstructure of the film which led to the decrease in electrical and optical properties.

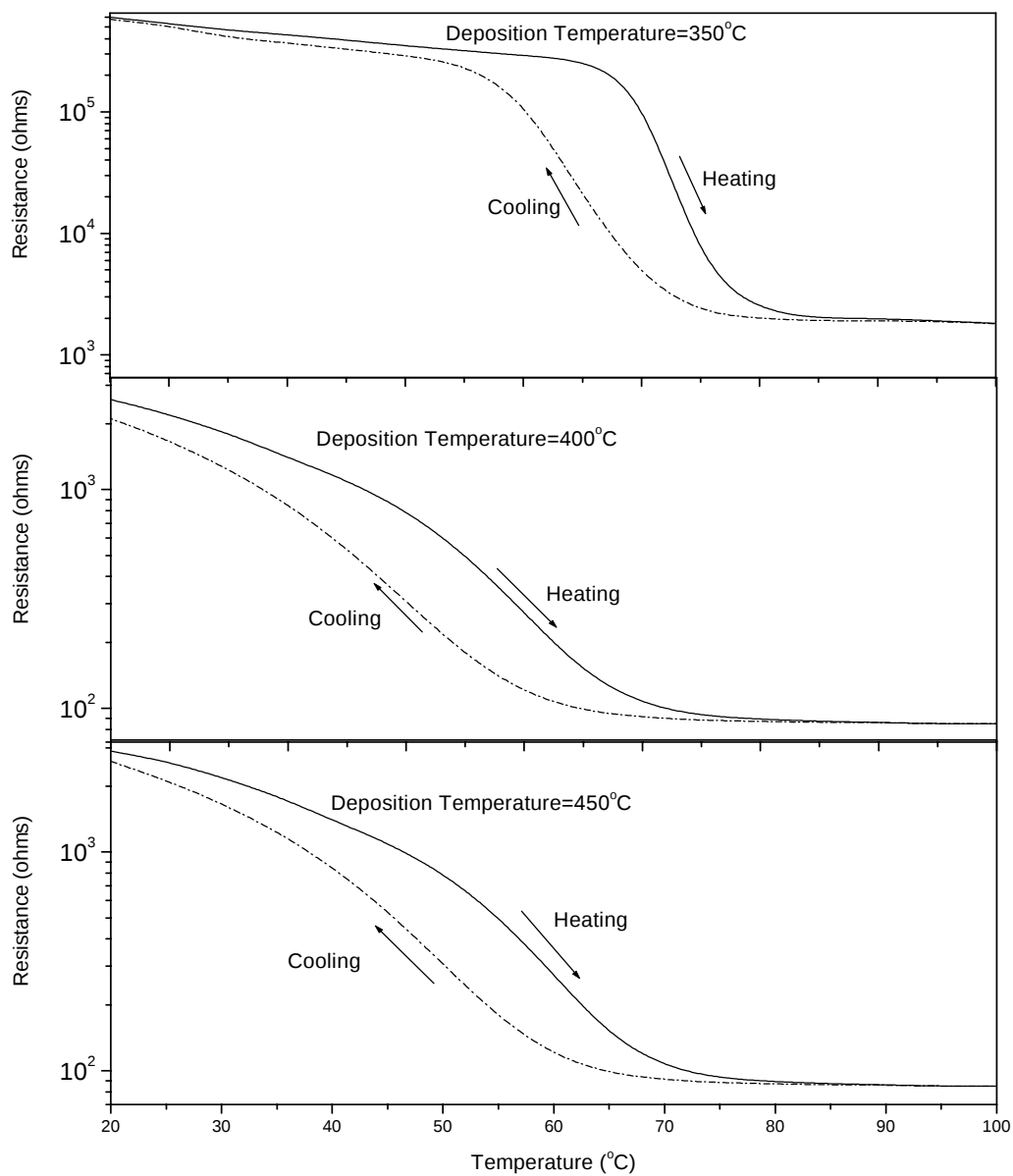


Figure 5. 9: Change of electrical resistance as function of temperature of VO_2 thin films deposited by PLD at different substrate temperatures.

5.2 Summary and conclusion

The effect of substrate temperature on the VO₂ film has been investigated. We investigated that the increase in substrate temperature gives rise to the increase of grain size and also give rise to deterioration of grains orientation (texture). We also observed that hysteresis width is another factor which determines the quality of VO₂ thin film. The good VO₂ thin film is the one with small hysteresis width and visa versa. In our case, an oriented VO₂ thin film deposited at 350°C appeared to exhibit good quality characteristics. We observed that the optical and electrical properties of the film decrease with the increase in substrate temperature which is suggested to be caused by the change in grains orientation. It is clear that the grains orientation improves the electrical and optical switching of VO₂ thin films.

5.3 The ICMS results

The following results are the results that were obtained from ICMS technique whereby the optimized deposition conditions were fixed but varying the substrate temperature from 450°C to 550°C. The film structure, surface roughness, thickness, electrical and optical properties are discussed.

5.3.1 The film structure

In this section we investigate by the means of X-ray diffraction (XRD) the effect of the substrate temperature on the crystallinity of the VO₂ thin films.

The XRD spectra (scanned from 20 to 70°) of the VO₂ thin films deposited by ICMS at different substrate temperatures are shown in Figure 5.10. The scan was taken at room temperature, in semiconducting phase of VO₂ (monoclinic structure). The films exhibit a polycrystalline structure whose peaks matches the single phase of monoclinic VO₂ (JCPDS 044-0225) without showing the indication of other vanadium oxide phases.

All the films deposited at temperature ranging from 450 to 550°C were found to be well crystallized. The reflection planes with their corresponding values of 2θ are tabulated in table 5.5. All the films show a first peak at (011) plane indicating the existence of VO₂ [5,9,12,13,16,18,21]. The XRD spectra of the film deposited at substrate temperature of 450°C shows Bragg reflection at $2\theta = 27.72^\circ$ corresponding to (011) reflection of the VO₂ monoclinic phase. Since no other x-ray peaks are observed, the grains of VO₂ films deposited at 450°C are in fact highly oriented with crystallographic (011) planes. We observed that the (011) reflection emerges from a broad structure. This broad structure may suggest the existence of disordered phase of

VO₂. The XRD spectra of the film deposited at substrate temperature of 500⁰C exhibit almost the same behaviour as the film deposited at 450⁰C. The film deposited at substrate temperature of 550⁰ C exhibit similar XRD patterns. In addition to the (011) peak the patterns show the emergence of new peaks at $2\theta = 57.63^\circ$ and 65.61° corresponding respectively to the (220) and (022) reflections. The appearance of new reflections is a clear indication of the deterioration (disordered) of grains orientation when the temperature increases.

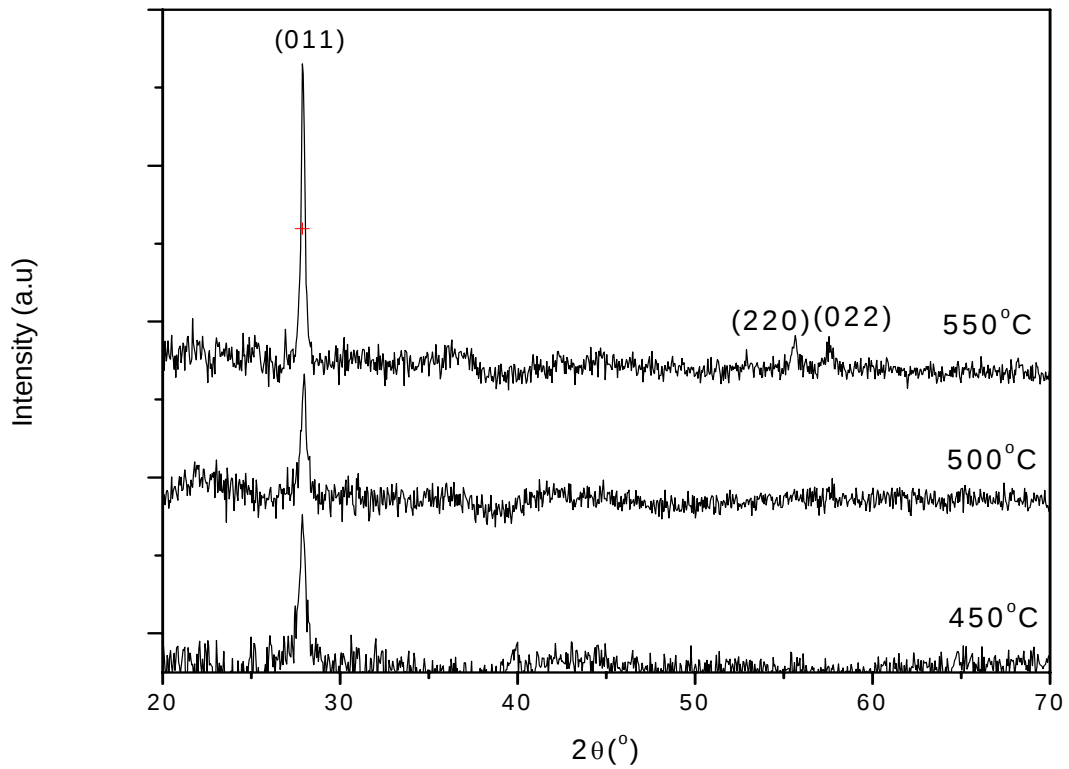


Figure 5. 10: XRD patterns for VO₂ at different substrate temperature deposited by ICMS.

The peak at (011) reflection was used to estimate the average grain size. The average grain size was estimated using the Debye's formula. The estimated values were then used to plot the graph shown in figure 5.11. The graph was used to observe the effect of substrate temperature on the grain size. The increase in substrate temperature leads

to the increase in grain size. It is clear that the crystallinity of the film is affected with substrate temperature increase.

Table 5. 5: X-ray diffractions results

Temperature ($^{\circ}\text{C}$)	2θ ($^{\circ}$)	Phase	Plane
450, 500, 550	27.72	VO_2	(011)
550	57.63	VO_2	(220)
550	65.61	VO_2	(022)

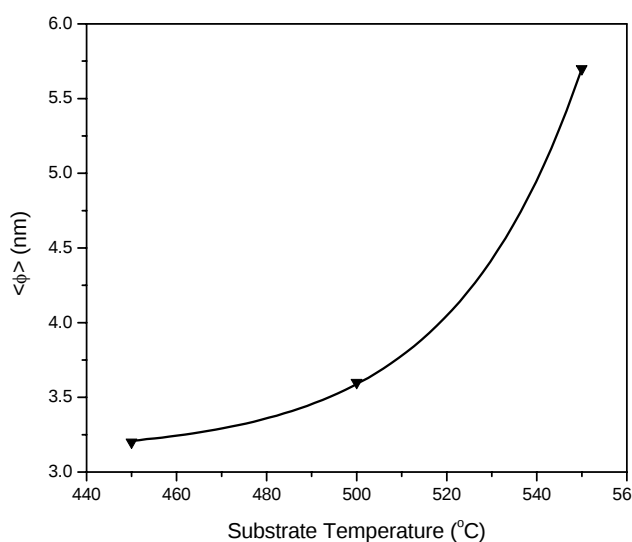


Figure 5. 11: Grain size vs. substrate temperature

5.3.2 Film surface topography

The roughness of the film was confirmed using atomic force microscopy and the Nanoscope software was used to calculate the root mean square roughness (R_q).

Figure (5.12-14) shows the surface topography of the VO_2 thin films deposited by ICMS at different substrate temperatures. The topography of the films were taken at room temperature, semiconducting phase of VO_2 . The results show that the film

surface roughness increases with the increase in substrate temperature. This is confirmed by the average roughness, R_a , of the surface (see Table 5.4). The film deposited at substrate temperature of 450°C shows two peaks on the surface which is suggested to be the dust that was on the surface of the film during the surface scan. The surface roughness increment with substrate temperature agrees with XRD results.

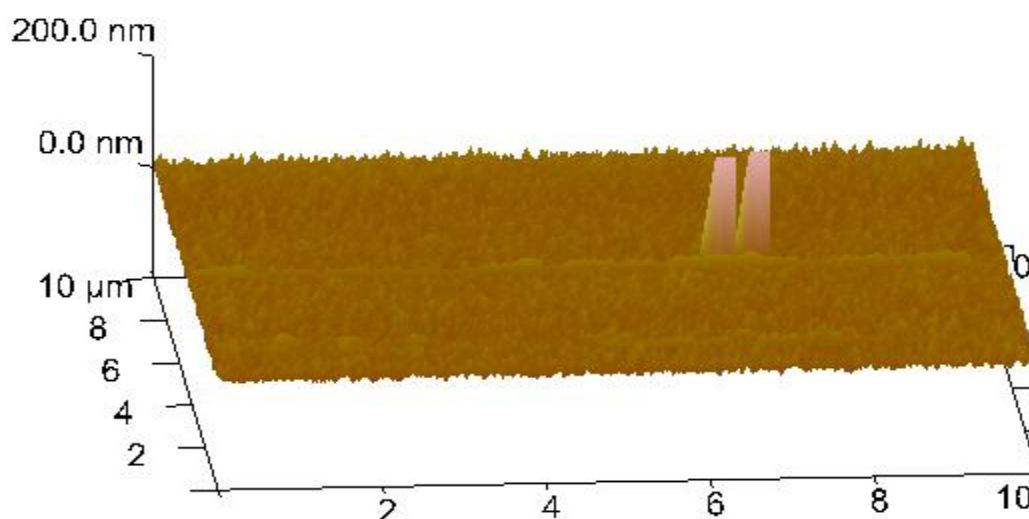


Figure 5. 12: AFM results for VO_2 thin film synthesized by ICMS at substrate temperature of 450°C .

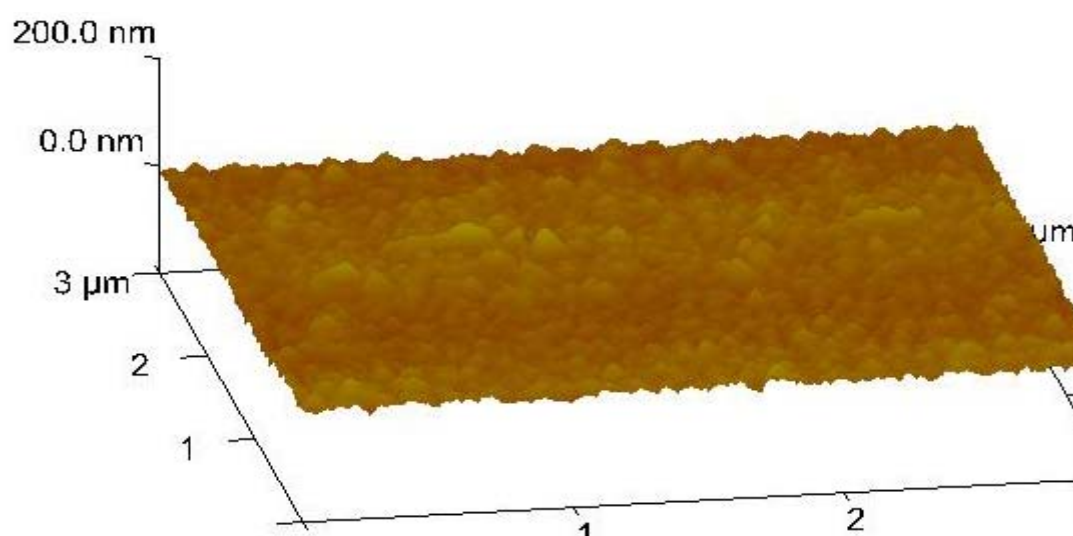


Figure 5. 13: AFM results for VO_2 thin film synthesized by ICMS at substrate temperature of 500°C .

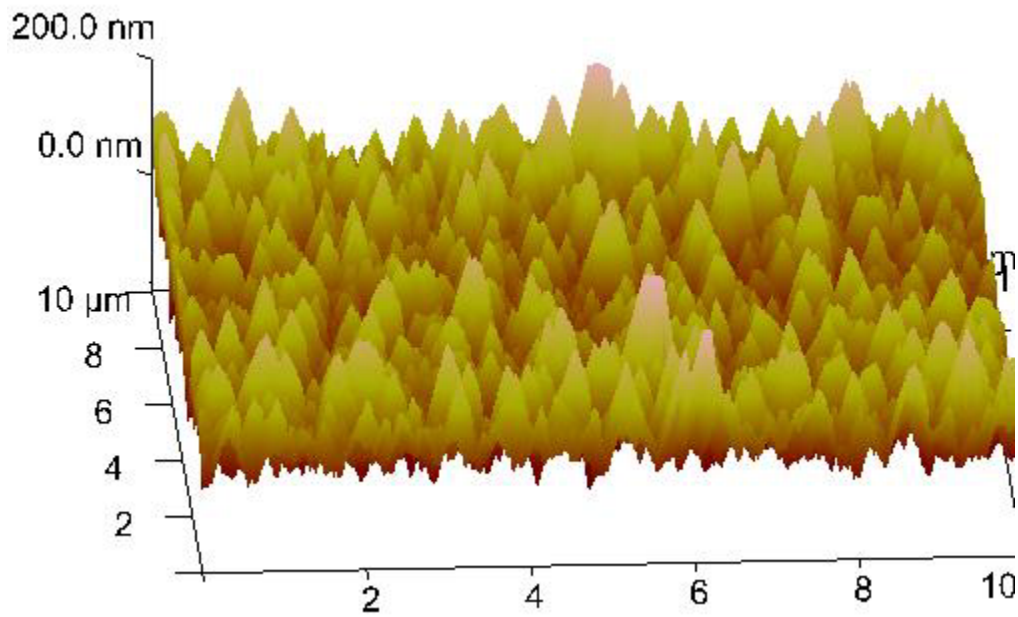


Figure 5. 14: AFM results for VO₂ thin film synthesized by ICMS at substrate temperature of 550°C.

Table 5. 6: The surface roughness, R_a (average roughness) results.

Substrate Temperature (°C)	Surface roughness, R_a , (nm)
450	5.44
500	6.41
550	35.5

5.3.3 Rutherford Backscattering

RBS has been used to investigate the thickness using the XRUMP simulation. The thickness was checked with respect to the substrate temperature. The glass substrate was used to check the film thickness and the silicon substrate was also used to check the film stoichiometry.

Figure 5.15 exhibits the RBS spectra of the VO₂ film on the soda lime glass substrate deposited by ICMS. The film thickness for VO₂ deposited by ICMS is almost the same for 450°C, 500°C and 550°C, respectively. The simulation revealed that the film thickness has a least variation in film thickness with the increase in substrate temperature which is suggested to be caused by inaccuracy of the system. The RBS results indicated that there was no contamination during the film deposition. The observed other peaks are from the glass substrate as indicated. The simulation also reveal that the vanadium to oxygen ratio was found to be 1:1.7.

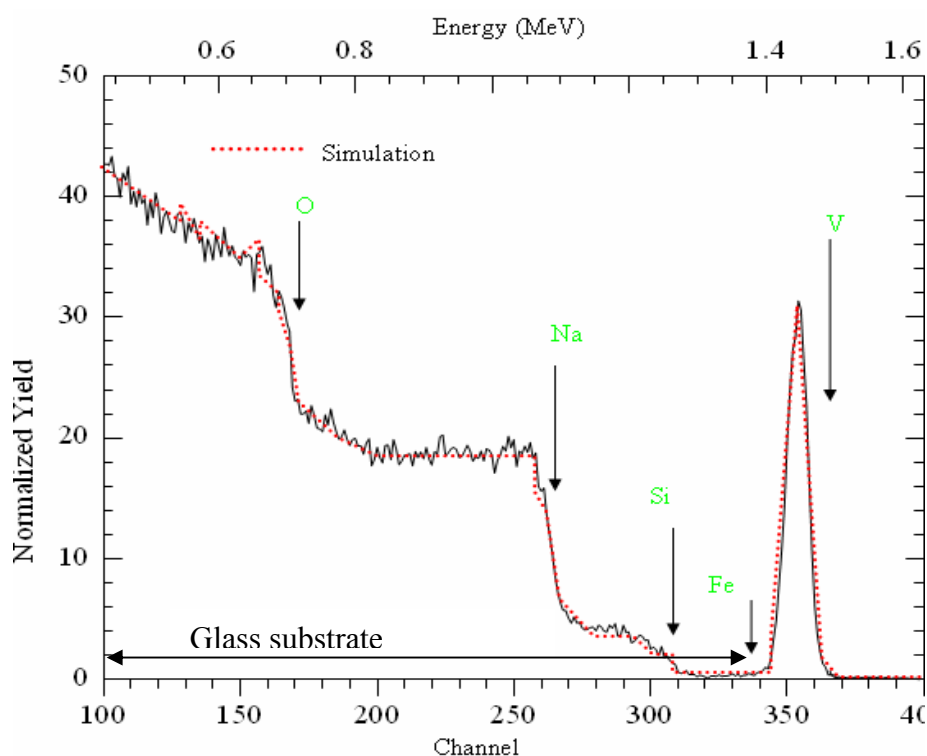


Figure 5. 15: The fitted spectrum for VO₂ on a soda lime glass deposited by ICMS.

Table 5. 7: The values of film thickness from XRUMP simulation.

Substrate temperature (°C)	Film thickness (nm)
450	50.3
500	61.7
550	93.4

5.3.4 Thermo-chromism of the film

The following results are the results which indicate the thermo-chromism of the films deposited at different substrate temperatures. The results were obtained using the UV-VIS Spectrophotometer.

Figure 5.16 shows the film optical transmittance (%) as a function of wavelength (nm) of the VO₂ thin films deposited by ICMS techniques. The film thermo-chromism was observed and the spectral transmittance of low temperature (25°C) semiconducting phase and high temperature (100°C) metal phase were showing a sharp contrast in the infrared region (IR).

The metallic phase exceeds the semiconducting phase in the infrared region for all the films which indicate that the film is less than 100 nm as demonstrated by G. Xu et al. [14]. The highly oriented VO₂ film obtained at 450°C, exhibits higher transmission switching efficiency than the films obtained at 500 and 550°C. Figure 5.17 show the hysteresis loops of transmittance as a function of temperature (at a fixed wavelength of 1100 nm) for thin films of VO₂ prepared by ICMS technique.

The hysteresis width of the films deposited at a substrate temperature of 450°C is approximately 5°C. The other films obtained at 500 and 550°C have the same hysteresis width of approximately 10°C. The transition temperatures are shown in Table 5.8. All the films have the same hysteresis sharpness which indicates the similar grain arrangement (from XRD results). The transition temperature of the films is slightly decreasing with the substrate temperature increase. This slight decrease is suggested to be caused by the random arrangement of the grains in the film deposited at 550°C. It is clear that the grains alignment affect the transition temperature.

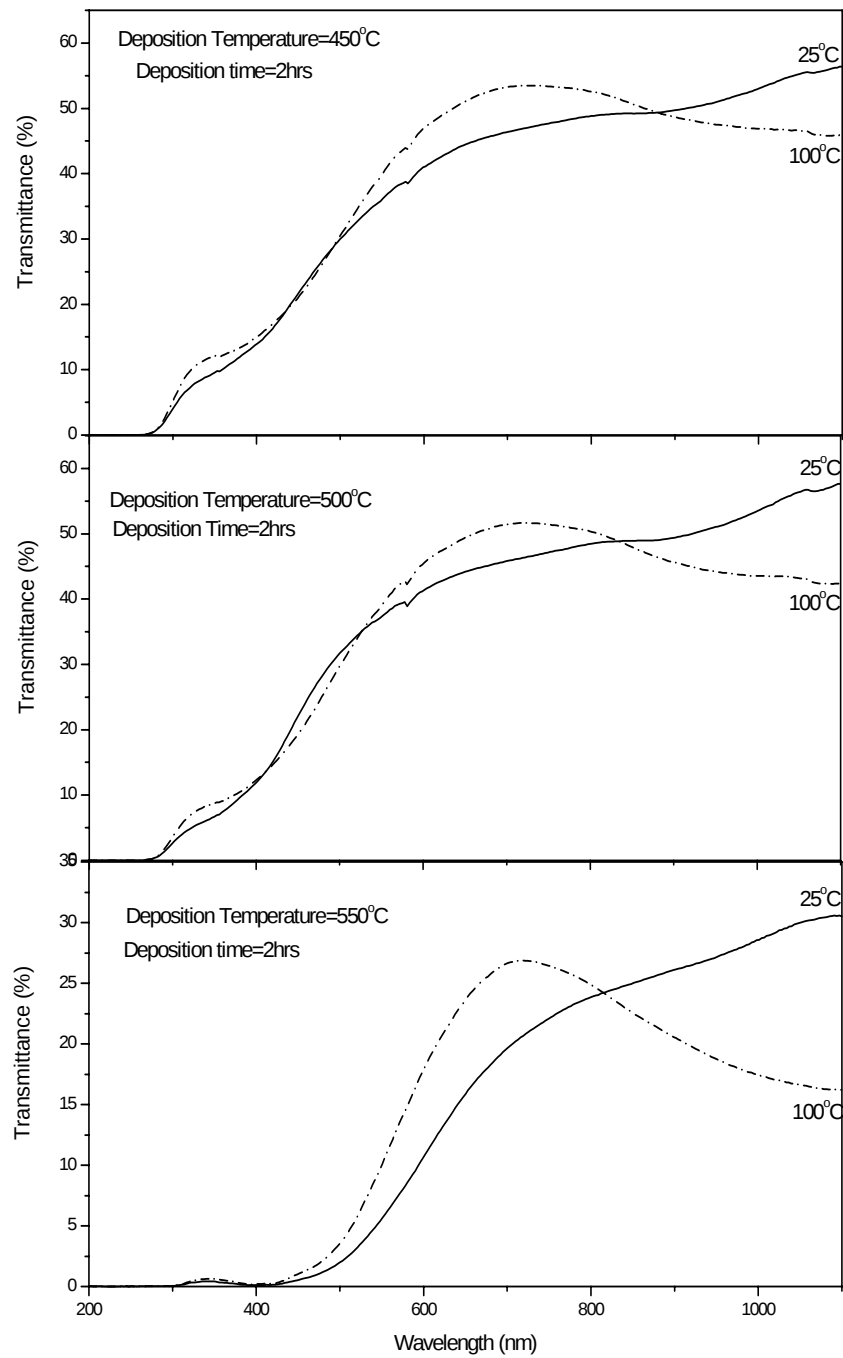


Figure 5. 16: The optical transmission as a function of wavelength for VO₂ thin films deposited by ICMS at different substrate temperatures. The solid and dashed lines symbolise the semiconducting and metallic states of the films, respectively.

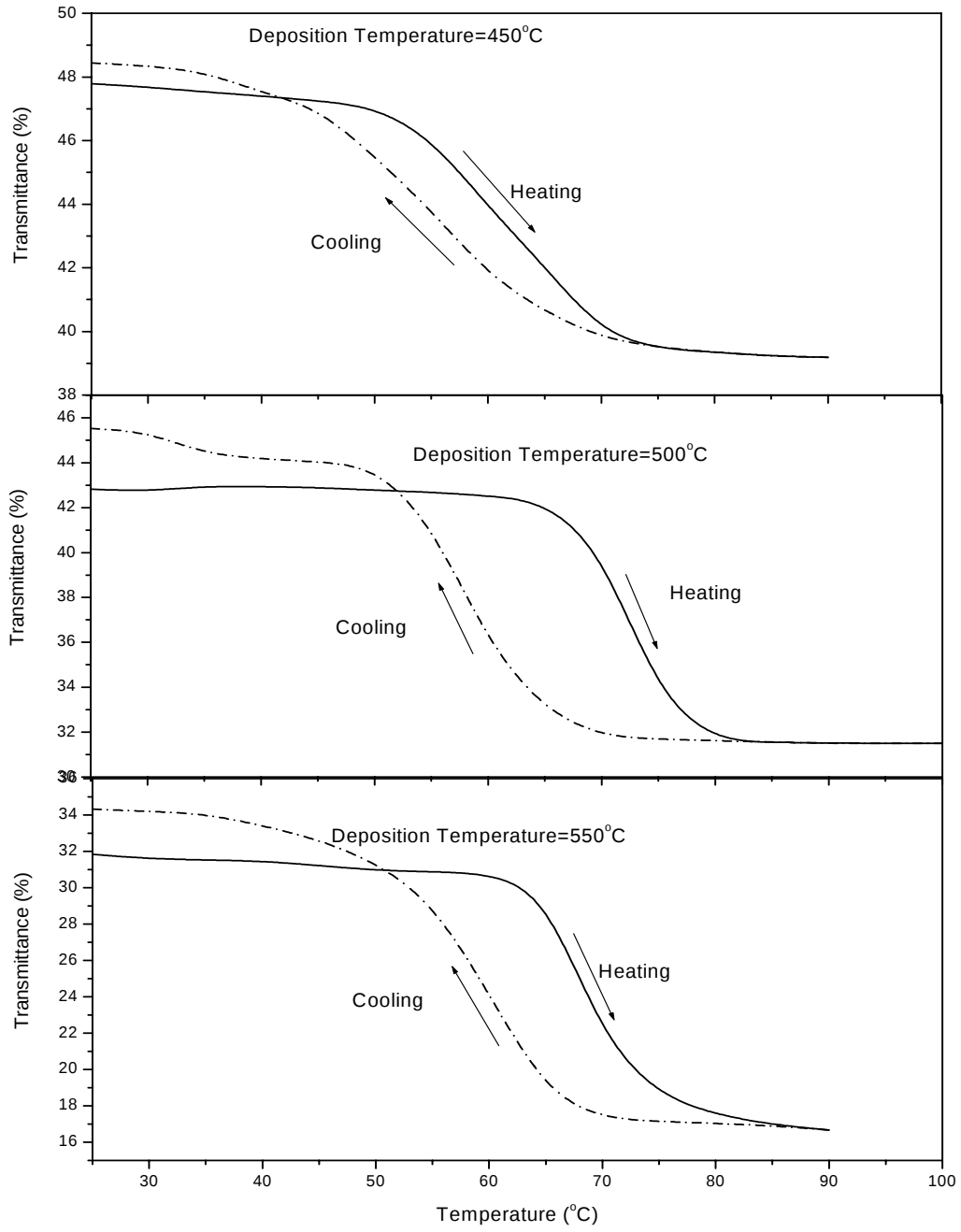


Figure 5. 17: The optical transmission as a function of temperature at wavelength of 1100 nm for VO₂ thin films deposited by ICMS at different substrate temperature.

Table 5. 8: The transition temperature as a function of substrate temperature results.

Substrate temperature (°C)	Transition temperature (°C)
450	66
500	70
550	65

5.3.5 Electrical measurements of the film

The following results are the analysis of the electrical properties of the film deposited at different substrate temperature.

Figure 5.18 shows the resistance hysteresis loops of VO₂ thin films deposited at substrate temperature of 450°C, 500°C and 550°C. The oriented film deposited at 450°C, exhibits a sharp transition in electrical resistance near 68 °C which is a definitive confirmation of formation of thermochromic VO₂. The drop in the electrical resistance is about four orders of magnitude which is similar to the one observed in high quality polycrystalline VO₂ thin films but less than that reported for single bulk crystal of VO₂ (five orders of magnitude) [3]. The temperature hysteresis width is approximately equal to 10°C. This large hysteresis of VO₂ film compared to that observed in single bulk VO₂ crystal (2°C) [3], may have its origin in the extrinsic stress created during deposition by the difference in thermal expansion coefficient between the VO₂ film and the substrate.

The films deposited at 500°C and 550°C exhibit the same behaviour in terms of electrical switching. The transition is sluggish and shifts toward lower temperature

near 66 °C. The drop in the electrical resistance is about three orders of magnitude. Both films exhibit a temperature hysteresis width of about 10 °C. The decrease in the sharpness of the transition profile and the magnitude of the drop in the electrical resistance is caused by the random arrangement of the grains in the film hence leads to different grain boundaries. The increase in substrate temperature affected the microstructure of the film which led to the decrease in electrical and optical properties.

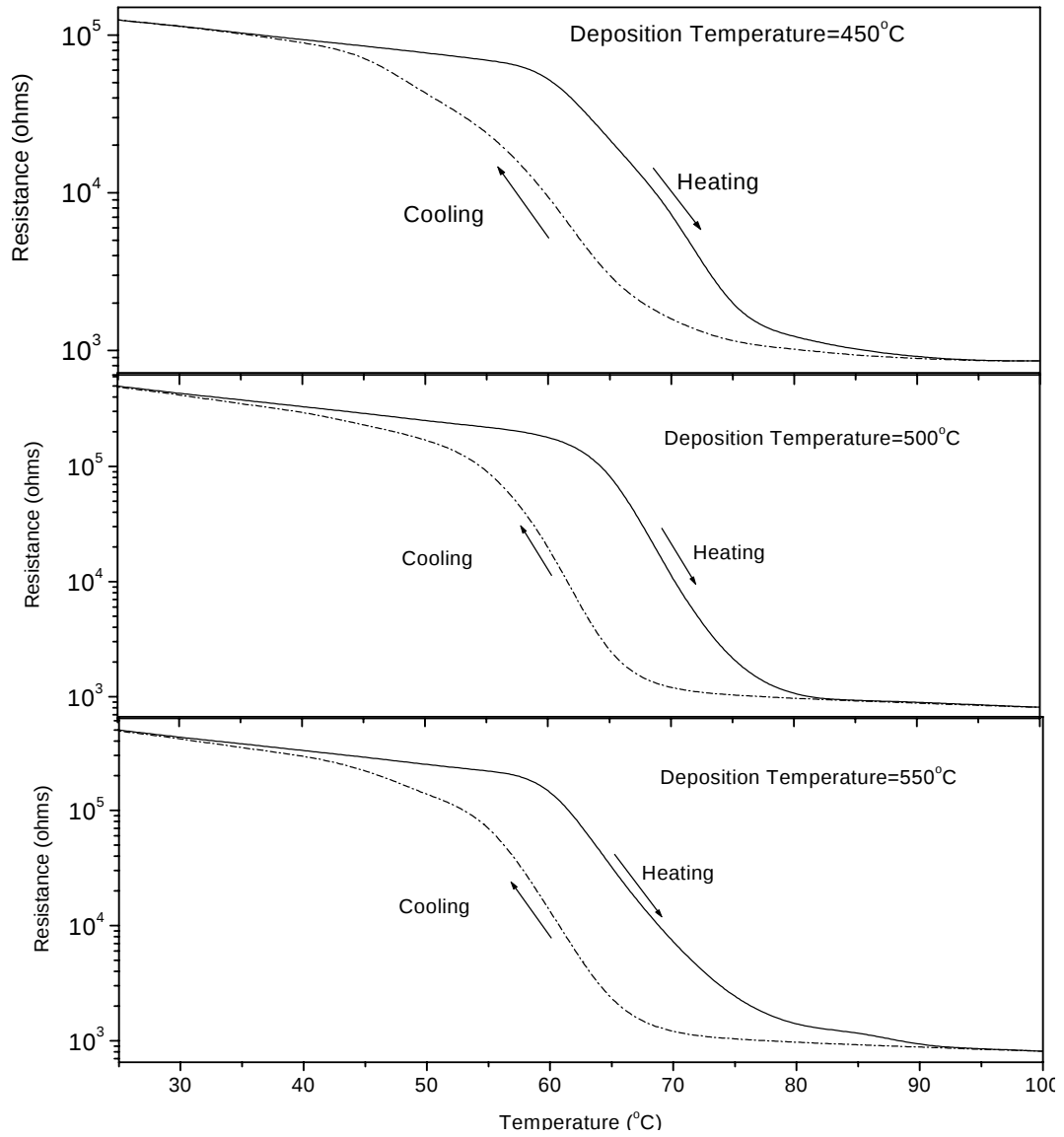


Figure 5. 18: The resistance as a function of temperature at a wavelength of 1100 nm for VO_2 thin films deposited by ICMS at different deposition temperature.

5.4 Summary and conclusion

We observed almost the same behaviour on the microstructure of the film deposited by PLD. The film thickness is almost the same. The hysteresis sharpness and resistance variation are almost the same hence showing similar electrical quality. The optical properties (transition temperature) were found to be varying with substrate temperature increase hence showing inconsistency with the XRD results. According to PLD findings, the grains orientation determines the quality of the film. Random orientation of grains leads to the decrease in film quality. The film deposited at 550⁰C was expected to exhibit poor quality of the film because of difference in grains orientation observed. The inconsistent is suggested to be caused by the error during the film characterization. The results proved that the microstructure correlates with the electrical and optical properties of the film.

5.5 Comparative discussion

We observed almost similar effect of the substrate temperature on the film deposited by PLD and ICMS. The films deposited by PLD show a drastic change in film microstructure with substrate temperature increase whereas films deposited by ICMS show trivial change in microstructure. The XRD results from both techniques showed clearly that the crystallinity evolves with substrate temperature.

The films from both techniques show an increase in surface roughness with the increase in substrate temperature which indicated the increase in grain size of the film. The films from both techniques show almost constant thickness with the increase in

substrate temperature. The films synthesized by the PLD show a decrease in optical transmittance with the increase in substrate temperature whereas the films deposited by ICMS show a fluctuation in optical transmittance with the increase in substrate temperature.

The films deposited by ICMS show a good electrical properties which is consistent with the XRD results whereas the films synthesized by PLD show poor electrical properties with the increase in substrate temperature. We observed an obvious correlation between microstructure, electrical and optical properties of the film. It is suggested that one should use ICMS technique in order to find the effect of substrate temperature in the film of VO₂.

CHAPTER 6

CONCLUSION

Vanadium dioxide thin films were successfully synthesized under optimized condition on soda lime glass by PLD and ICMS. The film synthesized by both techniques comparatively studied. We observed similar effect of substrate temperature on the film deposited by both techniques. The substrate temperature does not affect the film thickness. The study revealed that the increase in substrate temperature affect the grains alignment in the film. The XRD results revealed that the increase in substrate temperature leads to the increase in grain size hence peak width decrease. The electrical and optical properties show dependence in the microstructure of the film. The random alignment of the grains in microstructure of the film leads to the decrease in electrical and optical properties of the film. We observed that microstructure correlates with the electrical and optical properties of VO₂ thin films.

For future purposes, the substrate temperature range should be increase so as to find if there is a change or if there are other phases to be formed. The techniques should be in a good working condition (technically) in order to obtain good and comparative results. The results proved that to do such comparative study, one must be consistent to make comparison.

APPENDICES

APPENDIX A

Phase identification by x-ray diffraction

A.1 Plane Spacings

The value of d , the distance between adjacent planes in the set (hkl), may be found from the following equations.

Cubic:
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal:
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal:
$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

Rhombohedral:
$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

Orthorhombic:
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Monoclinic:
$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

Triclinic:
$$\frac{1}{d^2} = \frac{1}{V^2} (S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

In the equations for triclinic crystals,

V=volume of the unit cell (see its calculation below)

$$S_{11}=b^2c^2\sin^2 \alpha$$

$$S_{22}=a^2c^2\sin^2 \beta$$

$$S_{33}=a^2b^2\sin^2 \gamma$$

$$S_{12}=abc^2 (\cos \alpha \cos \beta -\cos \gamma)$$

$$S_{23}=a^2bc (\cos \beta \cos \gamma -\cos \alpha)$$

$$S_{13}=ab^2c (\cos \gamma \cos \alpha -\cos \beta)$$

C.2 Cell volumes

The following equations give the volume V of the unit cell.

Cubic: $V=a^3$

Tetragonal: $V=a^2c$

Hexagonal: $V = \frac{\sqrt{3}a^2c}{2}$

Debye Scherer's formula for calculating the average grain size:

$$\langle \phi \rangle = \frac{0.9\lambda}{FWHM \cos \theta}$$

λ is the wavelength that is read from the XRD data for vanadium dioxide.

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