Crystal Structure, Surface Topography, Surface Morphology and Optical Properties of DC Magnetron Sputtered VO₂ Thin Films using VO₂ Target

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Abstract. Vanadium dioxide (VO₂) thin films were deposited at room temperature on Corning 2947 glass substrates by direct current (DC) magnetron sputtering with a high purity VO₂ target. Crystal structure, surface topography, surface morphology and optical properties of the deposited VO₂ thin films were investigated. The deposited films exhibited a single orientation of (110) with a crystallite size of 41.3 nm as confirmed by the X-ray diffraction analysis and Scherrer formula, respectively. From the surface topography analysis, the film surface had root mean square surface roughness of ~6.8 nm and consisted of round-shaped grains. Similarly, from the surface morphology analysis, spherical-like grains were observed on the surface of the deposited VO₂ thin films with estimated average grain size of 34.2 nm. The deposited thin films showed high transmittance and low reflectance in the visible and near-infrared wavelength regions at room temperature. In addition, from the optical transmittance against temperature measurements, only a few transmittance variation and a slight change in hysteresis loop were detected during heating and cooling between room temperature and 100 °C. Hence, the deposited VO₂ thin films were found to exhibit lack of phase transition.

1. Introduction
Vanadium Dioxide (VO₂) thin films have been intensively studied over the last decade to the point where the thin films were discovered as materials with distinctive characteristics such as temperature-dependent properties, for a wide range of applications for instance intelligent coatings for architectural glazing. However, accessibilities of deposition techniques to grow stoichiometric VO₂ thin films are still crucial.

Deposition techniques that have been employed to deposit VO₂ thin films include atmospheric pressure chemical vapour deposition [1,2], reactive pulsed laser deposition [3], magnetron sputtering [4-5] and solution-based techniques. Despite, among those techniques, magnetron sputtering techniques with vanadium (V) target are very popular and become the process of choice for preparations of VO₂ thin films. For instance, in 1996, direct current (DC) magnetron sputtering was chosen, and employed to fabricate stoichiometric VO₂ films at sputtering power of 250 W applied on a V target with working pressure of 1.0 Pa, substrate temperature of 400 °C, Ar gas flow of 88.9 % and O₂ gas flow of 11.1 % [6]. The films exhibited transition temperature (Tt) at 65 °C where changes in structural and optical properties of the films were observed. Additionally, Batista et al. [7] investigated several depositions of single phase of monoclinic (M) VO₂ films by using DC magnetron sputtering.
with substrate temperature of 450 °C and various parameters such as O\textsubscript{2}/Ar gas flow ratio, sputtering power, DC current supply and working pressure. Moreover, according to Cui et al., VO\textsubscript{2} films were also successfully deposited with a V target at working pressure of 1.0 x 10\textsuperscript{-3} Pa, DC power of 160 W and different substrate temperature ranging from room temperature to 400 °C, as well as different O\textsubscript{2} partial pressure of about 9 to 20 % [8]. Mlyuka et al. reported depositions of VO\textsubscript{2} thin films with different film thicknesses (i.e. ranging from 25 to 120 nm) at substrate temperature of 450 °C, Ar/O\textsubscript{2} flow ratio of 10.7 and working pressure of 12.3 Pa [9]. The deposited films exhibited T\textsubscript{c} at 60 °C. Meanwhile, Ji et al. studied growth of VO\textsubscript{2} thin films at O\textsubscript{2}/Ar flow ratio of 0.05, working pressure of 1.2 Pa, sputtering power of 172 W and substrate temperature 380 °C with film thickness of ~80 nm [10]. Luo et al. conducted a study on depositions of nanocrystalline VO\textsubscript{2} thin films at low temperatures with different film thickness (i.e. 60 to 197 nm) by using DC magnetron sputtering and in-situ annealing process [11]. Furthermore, polycrystalline VO\textsubscript{2}(M) thin films were prepared at working pressure of ~12.3 Pa, Ar/O\textsubscript{2} flow ratio of ~19, sputtering power of 210 W and substrate temperature of 450 °C [12]. In addition, Melnik et al. reported depositions of polycrystalline VO\textsubscript{2}(M) thin films at working pressure of 0.4 Pa, sputtering power of 70 W, substrate temperature of 200 °C and annealing process at 300 °C in air [13]. Besides, depositions of stoichiometric VO\textsubscript{2} films were also studied on various substrates. For example, Lafort et al. researched the depositions of single polycrystalline VO\textsubscript{2} thin films with film thickness of 100 to 200 nm on stainless steel substrates at working pressure of 1.3 x 10\textsuperscript{-4} Pa, DC power of 200 W, Ar flow rate of 20 sccm, O\textsubscript{2} flow rate of 4.5 sccm and substrate temperature of 480 °C [14]. In addition, nanostructured VO\textsubscript{2} films were deposited on amorphous glass slides with a V target at substrate temperature of 100 °C, DC current 0.3 A, O\textsubscript{2}/Ar flow ratio of 3.2 % and in-situ annealing process at 350 °C in O\textsubscript{2} ambient for 25 min [15]. According to Zhang et al., DC sputtered VO\textsubscript{2} thin films were successfully deposited on K9 glass substrates and in-situ annealed at low temperature with different annealing time [16]. VO\textsubscript{2} thin films deposited on soda lime glass substrates were also reported at working pressure of 0.5 Pa, O\textsubscript{2} flow rate of 1.6 sccm, Ar flow rate of 40 sccm, substrate temperature of 200 °C and sputtering power of 110 W with negative bias voltage of -160 V [17]. Nevertheless, among those depositions, the application of DC magnetron sputtering and VO\textsubscript{2} target for depositions of VO\textsubscript{2} thin films is unexplored.

Hence, this work aims to study the structural, morphological and optical properties of VO\textsubscript{2} thin films deposited by using a DC magnetron sputtering and a VO\textsubscript{2} target at room temperature.

2. Experimental Details

2.1. Film Preparation
A VO\textsubscript{2} target (99.9 % purity) with a diameter of 76.2 mm and thickness of 3.0 mm was used to prepare VO\textsubscript{2} thin films on Corning 2947 glass substrates by using a DC magnetron sputtering technique. Before depositions, the glass substrates were cleaned in an ultrasonic bath with ethanol for 15 min, rinsed with distilled water, dried by blowing dry nitrogen gas of 99.9 % purity, and mechanically clamped to the substrate holder in the sputtering chamber. The sputtering chamber was evacuated to 8.0 x 10\textsuperscript{-4} Pa by a turbomolecular pump. A commercial Ar (99.9 % purity) was supplied as the sputtering gas and controlled by a mass flow controller to a flow rate of 30 sccm. Then, the VO\textsubscript{2} target was pre-sputtered in Ar atmosphere for 10 min to remove any impurities. The film thickness during depositions was monitored with an Inficon Model SQM-160 quartz rate/thickness meter. To ensure a uniform film thickness, the substrates were rotated at 10 rpm during film depositions. The thickness of the deposited VO\textsubscript{2} thin films was 100 nm. During sputtering, the working pressure and DC supply were maintained at 0.8 Pa and 160 mA, respectively with substrate temperature of room temperature.

2.2. Film Characterization
Film thicknesses were measured by a surface profilometer (Alpha-Step IQ) with a stylus force of 0.03 N (3.0 mg) and measurement accuracy of ± 1.5 nm. The structural property of the prepared films was studied by X-ray diffraction (XRD) on a Shimadzu XRD-7000. The XRD patterns were obtained

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using monochromatic high-intensity Cu Kα (λ = 1.54056Å) radiation operated at 40 kV and 30 mA. The patterns were recorded at a scanning rate of 2°/min in the range of 2θ = 20 – 50° and an incident angle of 1.2°. The surface topography of the films was determined by an atomic force microscopy (AFM) on a commercial Nanos (CSM Instruments). The measurements were performed in the contact tapping mode whereby the load force on the cantilever was maintained at 2.0 nN in order to apply a constant force on the samples. The surface morphology of the films was analyzed by field-emission scanning electron microscopy (FE-SEM) using a JEOL JSM-7610F field-emission scanning electron microscope. The optical properties of these films were measured using a CARY 5000 UV-Vis-NIR spectrophotometer (Agilent Technologies) equipped with a SPECAC 4000 Series™ high stability temperature controller. The measurements were taken in the wavelength range of 350 – 2500 nm for the optical transmittance, and 300 – 800 nm for the optical reflectance. The scanning rate was 250 nm/min.

3. Results and Discussion

3.1. Crystal Structure of the Deposited VO₂ Films

Fig.1 (a) shows the XRD diffraction pattern of the VO₂ thin films deposited on glass substrates using DC magnetron sputtering and VO₂ target at room temperature. It could be seen that there is only one obvious diffraction peak at 2θ = 25.3° (as magnified in Fig.1 (b)) which is a characteristic of VO₂ phase of (110) plane, as confirmed with the standard ICDD2016: card no. 01-071-0042. The (110) crystallite orientation was used to estimate crystallite size of the deposited films by using the Scherrer formula. The estimated crystallite size of the deposited VO₂ thin films was 41.3 nm.

3.2. Surface Topography of the Deposited VO₂ Films

Fig.2 (a) display the AFM images of the deposited VO₂ thin films which were used to analyze surface topography and surface roughness of the films. The images were acquired using a scan area of 4 µm². The study of surface topography of the films from the AFM images was carried out by

![Figure 1](image1.png)

**Figure 1.** (a) XRD patterns of the deposited VO₂ thin films. (b) presents magnified details of (a).

![Figure 2](image2.png)

**Figure 2.** AFM (a) 2D- and (b) 3D- images with a scan area of 4 µm² of the upper surface of the deposited VO₂ thin films.
assuming the dark regions represent areas with zero or near zero height value along the Z scale (positive direction) and the bright regions represent higher areas i.e. the top of bulging grains. The surface of the films was composed of round-shaped grains. The root mean square surface roughness of the films was detected to be ~6.8 nm.

3.3. Surface Morphology of the Deposited VO$_2$ Films

Fig.3 represents the FE-SEM image of the deposited VO$_2$ thin films under a magnification of x 200,000 with an accelerating voltage of 2.0 kV. The surface of the films appeared smooth and uniform. VO$_2$ grains were grown in spherical shape with the estimated average grain size of 34.2 nm. Similar surface morphology was also observed by Zhang et al. [18] whereby nanostructured VO$_2$ films were prepared on glass substrates by reactive DC magnetron sputtering with a vanadium metallic target. In addition, Batista et al. [7] reported that VO$_2$(M) would appear as spherical-like grains whereas very flat and no particular features were detected to be in VO$_2$(B) phase and elongated grains were found to be in V$_2$O$_5$ phase. Hence, the surface morphology of the deposited films correspondingly featured the surface topography obtained on the AFM analysis.

Figure 3. FE-SEM image of the deposited VO$_2$ thin films recorded at a magnification of x 200,000.

3.4. Optical Properties of the Deposited VO$_2$ Films

Fig.4 shows the optical transmittance spectra (in the wavelength range of 350 – 2500 nm) of the deposited VO$_2$ thin films at room temperature and 100 ºC, i.e. on the semiconducting and metallic states, respectively. The deposited VO$_2$ films exhibited high transmittance in the visible and near-infrared wavelength regions. This was suggested due to the surface of the films. Cui et al. [8] reported that the VO$_2$ thin films prepared at room temperature showed relative smooth surface and very compact structure resulting in low surface roughness, hence leads to low light-scattering loss and high transmittance. Moreover, only a slight decrease in the transmittance of the films from room temperature to 100 ºC was detected.

Figure 4. Optical transmittance spectra of the deposited VO$_2$ thin films at room temperature (RT) and 100 ºC.

Figure 5. Optical transmittance at a fixed wavelength of 1500 nm as a function of temperature for the deposited VO$_2$ thin films.

Figure 6. Optical Reflectance spectrum of the deposited VO$_2$ thin films measured at room temperature.
The curves of the optical transmittance at a fixed wavelength of 1500 nm during heating and cooling for the deposited VO$_2$ thin films are shown in Fig. 5. Only a few transmittance variation within the temperature range could be measured. In other words, only a slight change in the hysteresis loop was observed. As a result, lack of phase transition was present [19].

Furthermore, Fig. 6 represents the optical reflectance spectrum of the VO$_2$ thin films, which was only measured at ambient temperature in air. As observed, the optical reflectance was about 16 % at 400 nm in the visible region and around 11 % at 800 nm in the near-infrared region. The low reflectance of the films could be attributed to the smooth surface and low surface roughness of the films based on the surface morphology and surface topography analyses, respectively.

4. Conclusion

VO$_2$ thin films were successfully deposited on glass substrates by using DC magnetron sputtering with a VO$_2$ target at room temperature. X-ray diffraction pattern of the deposited VO$_2$ thin films displayed a single orientation of (110). In addition, with the help of the Scherrer formula, a crystallite size of about 41.3 nm was obtained. Spherical-like grains were observed on the surface of the films with the root mean square surface roughness of ~6.8 nm and the estimated average grain size of 34.2 nm obtained from the surface topography and surface morphology analyses, respectively. From optical properties analyses, the deposited thin films showed high transmittance and low reflectance in the visible and near-infrared wavelength regions at room temperature. Moreover, only a small change in the transmittance and the hysteresis loop were found during heating and cooling between room temperature and 100 °C. Subsequently, as demonstrated, DC magnetron sputtering with a high purity VO$_2$ target is also a good alternative technique for the fabrication of VO$_2$ thin films. Hence, further studies on depositions of VO$_2$ thin films using DC magnetron sputtering with a VO$_2$ target are in progress in order to improve the properties of the films, especially crystallinity and hysteresis behavior of the films.

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