Growth and infrared switching properties of deposited VO$_2$ films at various sputtering power with a VO$_2$ target by RF magnetron sputtering

N Muslim$^1$, Y W Soon$^1$ and N Y Voo$^1$

$^1$ Physical and Geological Sciences, Faculty of Science, Universiti Brunei Darussalam, Jalan Tungku Link, Gadong BE 1410, Brunei Darussalam
E-mail: noormariah.muslim@ubd.edu.bn, noormariahmu219@gmail.com

Abstract. In this work, structural and morphological properties as well as phase transition temperature and hysteresis width of VO$_2$ thin films grown with a VO$_2$ target by RF magnetron sputtering were studied under the influence of relatively low sputtering power of 80 – 140 W. It was observed that as sputtering power increased, the crystallinity of the films improved with the presence of obvious diffraction peaks of VO$_2$, and a slight increase in the average crystallite and grain sizes of the films. The deposited films revealed a slight change in infrared transmittance during heating and cooling cycles. Films deposited at sputtering power of 140 W exhibited the lowest Tt of 60.5 °C with a hysteresis width of 41.0 °C.

1. Introduction
Vanadium dioxide or Vanadia (VO$_2$), due to intelligent thermochromic properties, has received a great attention over the last few decades. The properties make it very beneficial for the electrochemical energy storage, smart windows as well as aerospace and microelectronics industries [1-2]. However, studies on optical properties such as infrared transmittance, and surface properties such as morphology, topography and crystal structure, of VO$_2$ thin films are crucial for those applications [3-4]. Many investigations on preparations and developments of VO$_2$ thin films have been reported [5]. For example, studies on surface and optical properties of direct-current (DC) [6-7] and radio-frequency (RF) [8-9] magnetron sputtered VO$_2$ thin films have been investigated. VO$_2$ films have also been prepared using RF magnetron sputtering to study its structural, morphological, optical and thermochromic properties for the application of solar control coatings [10]. Meanwhile, VO$_2$ thin films deposited with high sputtering power of 330 – 400 W by RF magnetron sputtering have also been studied [11]. Control of sputtering power was highly significant to achieve high purity monoclinic VO$_2$ films. In addition, at such high sputtering power of 400W, target poisoning happened due to a chemisorption of oxygen on the surface of the target causing a reduction in deposition rate and film thickness with large grain size, and an increase in formation of defects. Thus, this leads to films with porous structure [12]. Hence, in order to prevent porous films, this present work will study depositions of VO$_2$ films at low sputtering power to ensure pores filled during the film depositions.

This work will investigate the influence of low sputtering power of 80 – 140 W on structural, morphological and infrared switching properties of VO$_2$ films grown with a VO$_2$ target by RF magnetron sputtering, which has not been considered yet.
2. Details of experiments

2.1. Preparation of films
The method for preparing VO₂ films was reported as in our previous papers [6,10]. VO₂ films were prepared on Corning 2947 glass substrates by RF magnetron sputtering using a high purity VO₂ target (99% purity) of 76 mm diameter and 5 mm thickness. The substrates were ultrasonically cleaned with ethanol for about 15 min and rinsed with distilled water. The substrates were then blow-dried using high purity nitrogen gas (99.9% purity), and screwed onto a substrate holder in the sputtering chamber. Commercial high purity argon, Ar (99.9% purity) was supplied into the chamber as the sputtering gas. The sputtering chamber was evacuated to 10⁻⁴ Pa by a turbomolecular pump that was backed by a mechanical pump. The Ar gas flow was kept constant at a gas flow rate of 40 sccm by a mass flow controller. Before depositing VO₂ onto the substrates, Pre-sputtering of the VO₂ target in Ar atmosphere was performed for 10 min to eliminate any oxide layers and impurities. The substrates were rotated at 10 rpm throughout the film deposition in order to get films with uniform thickness. The film thickness during deposition was maintained at 50 nm and monitored using a quartz crystal thickness meter with 1 Angstrom (Å) resolution reliably supplied by Inficon (Model SQM-160). During sputtering, the chamber pressure and substrate temperature were 10⁻¹ Pa and 500 °C, respectively. The films were grown on the substrates at various sputtering power of 80 – 140 W.

2.2. Characterization of films
A surface profilometer (Alpha-Step IQ) was employed to ensure film thickness of the deposited VO₂ films by applying a stylus force of 0.03 N with measurement accuracy of ± 1.5 nm. Crystal structure of the films was analyzed by grazing incidence X-ray diffraction (GIXRD) on a Shimadzu XRD-7000 using monochromatic high-intensity Cu Kα (λ = 1.54056Å) radiation operated at 40 kV and 30 mA. GIXRD patterns of the films were detected in the range of 2θ = 20 – 40° and an incident angle of 1.0 ° at a scanning rate of 2 °/min. Surface morphology was studied by field-emission scanning electron microscopy (FE-SEM) using a JEOL JSM-7610F field-emission scanning electron microscope. The infrared switching properties, i.e. phase transition temperature and hysteresis width in infrared region, were recorded using a CARY 5000 UV-Vis-NIR spectrophotometer (Agilent Technologies) assembled with a SPECAC 4000 Series™ high stability temperature controller. The temperature-dependent transmittance spectra were taken at a wavelength of 2.5 μm with temperature varied from room temperature of 25 °C to 100 °C.

3. Results and discussion

3.1. Crystal structure
The GIXRD patterns of the VO₂ thin films deposited at sputtering power of 80 – 140 W are detected as shown in figure 1. It could be seen that all films have an obvious diffraction peak at 2θ = 27.9 ° of monoclinic VO₂(M) phase. Thus, it can be deduced that the deposited films have a prominent peak of VO₂(M) corresponding to (011) orientation plane. The peak enhanced with increasing sputtering power. As the sputtering power stepped-up from 100 to 140 W, another peak appeared at 2θ = 29.2 ° of metastable VO₂(B) phase. When the sputtering power was 80 W, the deposition rate was 0.72 nm/min. The films were found to have low film crystallinity as seen from the low peak intensity. This was also reported by Ahmadipour et al. [13], in which the low sputtering power leads to very low formation energy which was insufficient to cause production of a high crystalline thin film. As the sputtering power rose up to 140 W, the deposition rate seemed to increase up to 1.32 nm/min. This might be due to more energetic particles bombarded with high driving energy and settled on suitable lattice sites resulting in high film crystallinity [14]. In addition, the average VO₂ crystallite size can be estimated using the (011) crystallite orientation and Scherrer formula. The average crystallite size of the films at sputtering power of 80, 100, 120 and 140 W was 14.9, 25.6, 39.0 and 43.1 nm, respectively. It has also been reported by several studies that enhancement of crystallite size was obtained by increasing the RF sputtering power [13,15-16].
Figure 1. GIXRD patterns of monoclinic VO$_2$(M) and metastable VO$_2$(B) thin films at sputtering power of 80 – 140 W.

3.2. Surface morphology

Figure 2 represents the FESEM images of the films at sputtering power of 80 – 140 W. Spherical-like grains in VO$_2$(M) phase are grown on the film surface with a slight increment in the grain size of the VO$_2$ as the sputtering power increased. Irregular and dark areas, which indicate deep and wide trenches, are seen on the surface of the films grown at sputtering power of 80 W. As the sputtering power stepped-up, from 100 to 140 W, uniform grain distributions are observed on the film surface. It has been reported that, at high sputtering power, more ionized Ar gas particles bombarded on the VO$_2$ target, and hence more energetic target atoms are dominant causing the formation of nuclei on the film surface [14,16]. Thus, this indicates more sites for growth of the grains. In other words, when the energetic atoms implanted into the surface of the films, this induced a thermal effect in the substrate [11]. This will cause the grain size to increase and the defect density to decrease with elevating sputtering power.

Figure 2. FESEM images of VO$_2$ thin films grown at sputtering power of 80 – 140 W.
3.3. Temperature-dependent transmittance spectra

Figure 3 exhibits transmittance spectra measured in heating and cooling cycles at a wavelength of 2.5 \( \mu \text{m} \) for the films prepared at various sputtering power. Hysteresis loops could also be obviously observed. According to Luo et al. [11], grain size could influence the hysteresis width. When the films have bigger grain size, the hysteresis width will be narrower. Particularly, the transition temperature of the VO\(_2\) films was reported to correlate with microstructures such as defect density and grain boundary of the films [11]. By increasing sputtering power, the defect density could be reduce and lower transition temperature could be achieved. In addition, Table 1 shows the infrared switching properties i.e. phase transition temperature and hysteresis width, of the prepared films in infrared region with respect to the figure 3. Infrared transmittance of the films varied with sputtering power at the measured wavelength. The film deposited at 80 W showed a slightly high transmittance than the other films. The Tt of the films prepared at 80 W is 65.5 °C with a hysteresis width of 57.0 °C; while that of the films deposited at 100 W is 69.5 °C with a hysteresis width of 43.0 °C; and the films deposited at 120 W is 65.0 °C with a hysteresis width of 44.0 °C. The lowest Tt of 60.5 °C with a narrowest hysteresis width of 41.0 °C was observed for the films prepared at sputtering power of 140 W. This might due to high crystallinity with larger average crystallite size of the VO\(_2\) films sputtered at sputtering power of 140 W. Furthermore, the nonmonotonic variation of transition temperature against sputtering power obtained in this study was also reported in a study whereby VO\(_2\) films prepared at sputtering power of 330 – 400 W [11].
4. Summary

The influence of relatively low sputtering power on several properties of VO$_2$ thin films prepared with a VO$_2$ target by RF magnetron sputtering were analysed. This study also showed the ability of the technique employed to control sputtering power in order to obtain desired VO$_2$ thin films. As sputtering power increased, the film crystallinity enhanced revealing diffraction peaks of VO$_2$, and a slight increase in the average crystallite sizes. A slight change in infrared transmittance of the deposited films during heating and cooling cycles was observed. By increasing sputtering power, the average crystallite and grain sizes of the films rose which contributes to narrow hysteresis width. In addition, the enhancement in sputtering power resulted in lower transition temperature due to decrease in defect density. Among the prepared films, films prepared at sputtering power of 140 W have the lowest Tt of 60.5 °C with a hysteresis width of 41.0 °C.

5. References

[1] Prasadam V P, Bahlawane N, Mattelaer F, Rampelberg G, Detavernier C, Fang L, Jiang Y, Martens K, Parkin I P and Papakonstantinou I 2019 Materials Today Chemistry 12 396.
[2] Liu M, Su B, Tang Y, Jiang X and Yu A 2017 Advanced Energy Materials 7 1700885.
[3] Strelcov E, Davydov A V, Lanke U, Watts C and Kolmakov A 2011 ACS Nano 5 3373.
[4] Ho H C, Lai Y C, Chen K, Dao T D, Hsueh C H and Nagao T 2019 Applied Surface Science 495 143436.
[5] Muslim N, Soon Y W, Lim C M and Voo N Y 2018 IOP Conf. Series: Materials Science and Engineering 409 012016.
[6] Muslim N, Idris M N S M, Soon Y W, Chou Chau Y F, Lim C M and Voo N Y 2018 IOP Conf. Series: Materials Science and Engineering 409 012025.
[7] Fang B, Li Y, Tong G, Wang X, Yan M, Liang Q, Wang F, Qin Y, Ding J, Chen S, Chen J, Zheng H and Yuan W 2015 Optical Materials 47 225.
[8] Reddy I N, Sreedhar A, Shim J and Gwag J S 2019 Journal of Electroanalytical Chemistry 835 40.
[9] Sullivan M, Son T V, Beaudoin N and Haché A 2015 Optics Communications 356 395.
[10] Muslim N, Soon Y W and Voo N Y 2019 IOP Conf. Series: Materials Science and Engineering 538 012022.
[11] Luo Y Y, Pan S S, Xu S C, Zhong L, Wang H and Li G H 2016 Journal of Alloys and Compounds 664 626.
[12] Zhang X, Ren W, Kong W, Zhou Q, Wang L, Bian L, Xu J, Chang A and Jiang C 2018 Applied Surface Science 435 815.
[13] Ahmadipour M, Ayub S N, Ain M F and Ahmad Z A 2017 Materials Science in Semiconductor Processing 66 157.
[14] Li S, Jiao S, Wang D, Gao S and Wang J 2018 Journal of Alloys and Compounds 753 186.
[15] Srinivas K, Manivel Raja M, Sridhara Rao D V and Kamat S V 2014 Thin Solid Films 558 349.
[16] Lu Y M, Hwang W S, Liu W Y and Yang J S 2001 Materials Chemistry and Physics 72 269.

Acknowledgments

This research study was financed by the Brunei Research Council (S&T 17), and Universiti Brunei Darussalam Block Grant (UBD/RSCH/1.4/FICBF(b)/2019/020).