



# Effects of thickness on the nanocrystalline structure and semiconductor-metal transition characteristics of vanadium dioxide thin films

Zhenfei Luo <sup>a,b,\*</sup>, Xun Zhou <sup>a,b,\*</sup>, Dawei Yan <sup>b</sup>, Du Wang <sup>a,b</sup>, Zeyu Li <sup>a,b</sup>, Cunbang Yang <sup>b</sup>, Yadong Jiang <sup>c</sup>

<sup>a</sup> Terahertz Research Center, China Academy of Engineering Physics, Mianyang Sichuan 621900, People's Republic of China

<sup>b</sup> Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang Sichuan 621900, People's Republic of China

<sup>c</sup> State Key Laboratory of Electronic Thin Films and Integrated Devices, School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, People's Republic of China

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## ABSTRACT

Nanocrystalline vanadium dioxide (VO<sub>2</sub>) thin films were grown on glass substrates by using reactive direct current magnetron sputtering and *in situ* thermal treatments at low preparation temperatures ( $\leq 350$  °C). The VO<sub>2</sub> thin films were characterized by grazing-incidence X-ray diffraction, field emission scanning electron microscope, transmission electron microscopy and spectroscopic ellipsometry (SE). The semiconductor-metal transition (SMT) characteristics of the films were investigated by four-point probe resistivity measurements and infrared spectrometer equipped with heating pads. The testing results showed that the crystal structure, morphology, grain size and semiconductor-metal transition temperature ( $T_{\text{SMT}}$ ) significantly changed as the film thickness decreased. Multilayer structures were observed in the particles of thinner films whose average particle size is much larger than the film thickness and average VO<sub>2</sub> grain size. A competition mechanism between the suppression effect of decreased thickness and coalescence of nanograins was proposed to understand the film growth and the formation of multilayer structure. The value of  $T_{\text{SMT}}$  was found to decrease as average VO<sub>2</sub> grain size became smaller, and SE results showed that small nanograin size significantly affected the electronic structure of VO<sub>2</sub> film.

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## 1. Introduction

Vanadium dioxide (VO<sub>2</sub>), a transition-metal compound, undergoes a reversible first-order semiconductor-metal transition (SMT) at a critical temperature  $T_{\text{SMT}} \sim 68$  °C [1]. Below  $T_{\text{SMT}}$ , VO<sub>2</sub> has a monoclinic structure and exhibits semiconducting properties, while above  $T_{\text{SMT}}$ , it becomes a metal with a tetragonal rutile structure. Associated with the SMT are abrupt changes in resistivity, optical transmittance or reflectance covering from visible to terahertz region. These fascinating features make this material a promising candidate for numerous practical applications such as ultrafast optical switches [2], field-effect transistors [3], memory metamaterials [4], etc.

VO<sub>2</sub> is a prototypical strongly correlated electron material. Because of the strong electronic correlations, the electronic structure of VO<sub>2</sub> is sensitive to internal, structurally related factors such as particle size [5,6], dimensional effect [7], structural imperfections [8,9], etc. This implies that interesting physical properties and functionalities of VO<sub>2</sub> can be obtained by changing its microstructures or nanostructures. However, it is a challenging task to precisely control the microstructure of VO<sub>2</sub>

because of the complexity of vanadium-oxygen system. Although chemical preparation methods such as chemical vapor deposition, solution-based synthesis have been regarded as preferred approaches to prepare VO<sub>2</sub> with various morphologies (e.g. nanoparticles, nanorods and nanowires), some physical preparation methods [5,10,11] have been developed for the growth of nanostructured VO<sub>2</sub> in past decade. For example, R. Lopez et al. [5] fabricated VO<sub>2</sub> nanoparticle arrays by a combination of ion beam lithography, pulsed laser deposition and thermal oxidation. Y. Wang et al. [10] grew the film of aligned VO<sub>2</sub> nanorods by rapidly heating a vanadium sheet to 900 °C using a current of 65 A. I.S. Kim et al. [11] increased yield and uniformity of VO<sub>2</sub> nanobeam growth via two-step physical vapor transport process.

Preparation temperature and film thickness are two important parameters for VO<sub>2</sub> thin film preparation using physical methods. Generally, relatively high preparation temperature is critical to grown single crystal VO<sub>2</sub> films with large grains [12], while relatively low temperature synthesis techniques are preferred for the growth of VO<sub>2</sub> films with fine grains [12,13]. By properly controlling film thickness, one can change the crystal structure, grain size, morphology as well as physical properties of VO<sub>2</sub> film [14–16]. For example, D. Brassard et al. [14] decreased average VO<sub>2</sub> grain size by decreasing film thickness and found that the amplitude of SMT decreased when the average VO<sub>2</sub> grain size decreased. G. Xu et al. [15] investigated the effects of thickness

\* Corresponding authors at: Terahertz Research Center, China Academy of Engineering Physics, Mianyang Sichuan 621900, People's Republic of China.

E-mail addresses: [zhfuo8@yahoo.com](mailto:zhfuo8@yahoo.com) (Z. Luo), [zx\\_zky@yahoo.com](mailto:zx_zky@yahoo.com) (X. Zhou).

ranging from 3 to 150 nm on the optical properties of VO<sub>2</sub> films. It was revealed that  $T_{\text{SMT}}$  was reduced and the film surface became smoother with decreasing film thickness. X. Wei et al. [16] reported that with the increase in film thickness, sheet resistance decreased, temperature coefficient of resistance increased and the SMT became obvious for the sputter-deposited VO<sub>2</sub> films. Although the correlations between the film thicknesses and properties of VO<sub>2</sub> films have been repeatedly observed by researchers, further studies are required to better understand the cause of these correlations. In this work, we prepared the nanocrystalline VO<sub>2</sub> thin films by using reactive direct current magnetron sputtering and *in situ* thermal treatments at low preparation temperatures ( $\leq 350$  °C). The relatively low preparation temperature shows advantages including high degree of control, high reproducibility and good uniformity over a large area for the growth of film. Then we investigated the microstructures and SMTs of the VO<sub>2</sub> thin films with different thicknesses, and, in particular, analyzed the relationships between them.

## 2. Experimental details

Carefully cleaned amorphous K9 glass substrates were loaded into the deposition chamber of a planar magnetron sputtering apparatus, and the chamber was evacuated to a base pressure lower than  $2 \times 10^{-3}$  Pa using a turbo molecular pump backed up by a mechanical pump. Then the substrate temperature was set to be 100 °C. Before deposition, the surface of vanadium target (99.99%) was sputter-cleaned by pure Ar (99.999%, flux of 98 sccm) plasma for 10 min. After that, O<sub>2</sub> (99.9999%, flux of 1 sccm) was introduced to mix with Ar gas, and the O<sub>2</sub>/Ar flow ratio (O<sub>2</sub>/Ar = 1/98) was kept at a constant. The direct current power was ~85 W. Reactive sputtering deposition was performed with the intraplanar rotation of substrate holder to improve the uniformity of film growth. The as-deposited films were *in situ* annealed at 350 °C in the ultrapure O<sub>2</sub> ambient after the deposition. For all the experiments, the experimental conditions (e.g. annealing pressure and annealing time) were identical except for the sputtering times, which were 30, 25, 20, 15 and 10 min to prepared films with average thicknesses [measured by using spectroscopic ellipsometry at room temperature (RT = 24 °C) (see in Section 3.4) of 197, 176, 128, 87, and 60 nm, respectively.

The crystal structures of films were characterized by grazing-incidence X-ray diffraction (GIXRD, Philip X Pert MPD with copper X-ray source ( $\lambda = 1.5406$  Å), calibrated with respect to the peak position of an Si calibration standard,  $2^\circ$  X-ray incidence angle, in  $\theta$ - $2\theta$  configuration). Field emission scanning electron microscope (FE-SEM, Hitachi S4800 with operating voltage of 3 kV) and transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN with operating voltage of 200 kV) were employed to characterize the surface and cross-sectional morphologies, respectively. The values of resistivity ( $\rho$ ) and near-infrared transmittance at the wavelength of 2.5  $\mu\text{m}$  were measured by using four-point probe resistivity measurements (SZ-82) and infrared spectrometer (WGH-30), respectively. Electronic structures were analyzed by spectroscopic ellipsometry (SE, Sentech SE850 operating in the wavelength range of 300–2300 nm corresponding to the photon energy range of 0.53–4.13 eV).

## 3. Results and discussion

### 3.1. Crystal structures

The GIXRD spectrum collected from  $10^\circ$  to  $70^\circ$  are given in Fig. 1. The results indicate that the polycrystalline structures of the films have multiple orientations of monoclinic VO<sub>2</sub>, namely, (100), (011), (200), (020), (210), (021), (102), (211), (022) and (013). The peak assigned to the orientation (100) disappears when the film thickness is smaller than 176 nm, while a peak at about  $12.3^\circ$  corresponding to an inter-planar spacing of 0.720 nm appears [probably due to the other vanadium oxide phases with higher oxygen contents (V<sub>3</sub>O<sub>7</sub> or/and  $\beta$ -V<sub>2</sub>O<sub>5</sub> according to the powder diffraction file: PDF No.71–1591, and PDF No.45–1074, or

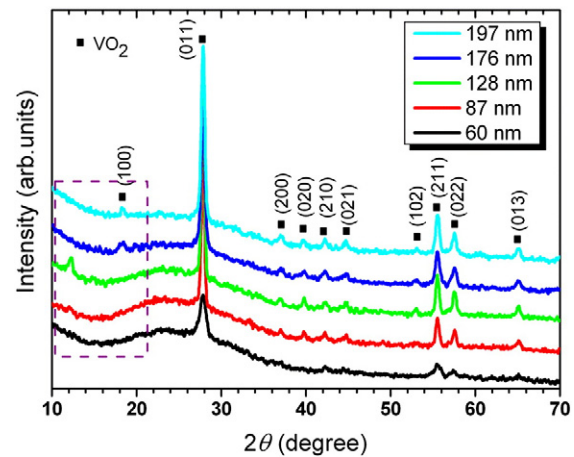


Fig. 1. (Color online) GIXRD patterns of the films. The broad diffraction peak at about  $15^\circ$ – $35^\circ$  is attributed to the amorphous structure of glass substrate.

see in Ref. [17–19]). In addition, the diffraction peaks become obviously weak and broad when the thickness decreases to 60 nm.

To have a further investigation of the VO<sub>2</sub> grain growth in the films, the average VO<sub>2</sub> grain sizes ( $d$ ) were estimated by using Scherrer formula according to the diffraction peak positions and full-width at half-maximum values (FWHMs, after subtraction of instrumental broadening) of the predominant orientations (011) and (211). The  $d$  values versus film thicknesses are  $d_{197\text{ nm}} = 29.2 \pm 2.1$  nm,  $d_{176\text{ nm}} = 25.1 \pm 2.7$  nm,  $d_{128\text{ nm}} = 34.4 \pm 1.6$  nm,  $d_{87\text{ nm}} = 33.5 \pm 1.5$  nm and  $d_{60\text{ nm}} = 13.4 \pm 0.4$  nm.

### 3.2. Surface and cross-sectional morphologies

Fig. 2 shows the surface morphologies of the VO<sub>2</sub> films. As can be seen, the 192- and 176-nm-thick films exhibit porous features with cracks, while the other three show relatively dense grain distribution and no crack (even if they were observed in a larger field of view, not shown here). The 128- and 87-nm-thick films contain plenty of particles whose sizes are much larger than the values of film thicknesses, whereas the particle sizes of other three films are much smaller than the values of film thicknesses. In addition, the average VO<sub>2</sub> grain sizes determined by the XRD results are much smaller than the average film particle sizes obtained by FE-SEM for the 128- and 87-nm-thick films. To reveal the microstructure of the large film particle, cross-sectional TEM measurements were made for the 128-nm-thick film, and the results are given in Fig. 3. One can observe that the film particles have multilayer structures and the layer-thickness ranges from 3 to 13 nm. These observations allow us to infer that the relatively small average VO<sub>2</sub> grain sizes obtained from the XRD patterns are related to the multilayer structure of the large film particles.

Furthermore, the relationships between the film thickness, the average film particle size ( $D$ ) and the average VO<sub>2</sub> grain size ( $d$ ) was investigated, as illustrated in Fig. 4. Fig. 4(a) shows that the thickness dependence of  $d$  value exhibits a similar variation with that of  $D$  value: the  $D$  (or  $d$ ) value first decreases, then increases and then again decreases when the thickness decreases. In general, the surface energy favors the suppression of grain growth due to the shrinking of film thickness [14,16,20,21]. Thus, it seems that a monotonic variation of grain size against thickness is more understandable than that we observed here. In fact, the nonmonotonic variation of grain size against thickness can be explained by the competition between the suppression effect of decreased thickness and the coalescence of nanograins during the annealing process. As the thickness decreases from 197 to 176 nm, the nanograins become smaller because of the dominant suppression effect of decreased thickness. For this case, although the activity of nanograins is enhanced owing to the grain size reduction, the

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