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Growth of *a*-axis oriented vanadium dioxide polycrystals on glass substrates

Yushen Zhang, Rui Wang *, Zhaozhong Qiu, Xiaohong Wu *, Yang Li

Department of Chemistry, Harbin Institute of Technology, Harbin 150001, China

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ABSTRACT

Vanadium dioxide (VO_2) polycrystals on glass substrates were synthesized by radio frequency magnetron sputtering method. The VO_2 polycrystals exhibit sharp *a*-axis diffraction peaks, characteristics of the VO_2 monoclinic phase, which can imply that highly *a*-axis textured VO_2 was formed. The characteristics of the electronic transition and hysteresis of the phase transition are described in terms of the morphology and grain boundary structures. The sharpness of the transition and the hysteresis upon heating and cooling are found to be strong functions of the crystal structure and microstructure (grain size and shape).

1. Introduction

Bulk VO_2 undergoes a fully reversible metal to insulator transition (MIT) at a critical temperature T_c (68 °C), which was first reported by Morin in 1959 [1]. Actually, this fascinating transition is a first order phase transformation from monoclinic (space group P21/c, M) to tetragonal (space group P42/mmm, R) symmetry [2], accompanied by noteworthy reversible jumps in electrical resistance, optical transmittance and reflectance in the infrared region. These features make VO_2 suitable for applications in thermo-chromic coating [3,4], ultrafast switching devices [5], sensors and micromechanical systems [6], etc.

The desired properties of VO_2 thin films are high resistance, reflectance change during phase transition and a narrow hysteresis width. It has been proven that using single crystal substrates is effective to obtain VO_2 thin films with a large electrical during phase transition and a narrow hysteresis width because metal–insulator domain wall propagation of highly oriented VO_2 is faster. Orientation control is an interesting topic in thin film growth; highly oriented VO_2 films have been obtained on sapphire and TiO_2 single crystals [7–9]. It is found that the conductivity exhibits a variation of more than four orders of magnitude for the highly (100) texture of VO_2 thin films and only three orders of magnitude for the highly (010) texture of sample with a hysteresis behavior upon heating and cooling through the transition [9]. However, to the best of our knowledge, the work concerning the synthesis of *a*-axis oriented VO_2 thin films on glass substrates has rarely been reported. In our previous work, we reported the high visible transmittance of preferred orientation vanadium dioxide with acicular nano-structure on glass slide substrates [4]; however, the MIT characteristics of these VO_2 films are negligible. Therefore, in the present work, we report the successful preparation of *a*-axis oriented VO_2 films with the obvious MIT characteristics.

2. Experimental

VO_2 thin films were deposited on glass substrates, from radio-frequency reactive sputtering technique, using a V_2O_5 target of diameter of 49 mm. The distance between the substrate and the target for sputtering was 80 mm. The vacuum chamber was evacuated to 9.0×10^{-4} Pa and then back-filled with a mixture of Ar and oxygen to a certain total gas pressure. Ar and oxygen were pre-mixed in a small chamber at a positive pressure before being led into a vacuum chamber to maintain a sputtering pressure.

It was found that the optimum deposition parameters were 1% of O_2 in Ar at a total gas pressure of 1.2 Pa, RF magnetron power 120 W, and the substrate temperature close to 450 °C. After deposition, the films were cooled down to the room temperature in the vacuum chamber. The deposited films were further annealed at 450 °C in N_2 for VO_2 polycrystals.

The crystalline structures of the films were tested by X-ray diffraction at room temperature. X-ray diffraction (XRD) was carried out using D/Max – rb rotating anode X-ray diffractometer with the CuKα wavelength ($\lambda = 0.15406$ nm). The surface morphology and cross-section image of VO_2 thin films were respectively

* Corresponding authors.

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measured with CSPM 5500 scanning probe microscope system and Hitachi S-570 scanning electron microscopy.

3. Results and discussion

Fig. 1 shows the XRD spectra of the films of as-deposited and annealing. As shown in Fig. 1(a), one diffraction ($2\theta = 19.96°$) peak which matches to V_2O_5 phase is observed. However, as it is shown in Fig. 1(b), the patterns show peaks due to thin layers at angles of 18.36°, and 37.15° which are very similar to values reported in [9,10]. Following the calculated pattern description of the monoclinic structure of VO_2, these peaks can be indexed as the reflections on the (100) and (200) planes thus showing the highly oriented growth of these films. The preferential orientation along the (100) plane of the VO_2 films deposited on soda–lime glass substrate is not clearly understood and has not been reported in the literature so far. Garry et al. [9] reported on *a*-axis textured VO_2 thin films deposited on R-plane sapphire and suggested that the cause could be a stress developing on the interface between the substrate and the film. Ngom et al. [10] also studied that the crystalline orientation of VO_2 thin films deposited on glass substrate, the crystalline orientation of the VO_2 thin films was drastically changed because of the formation of an interface layer between the VO_2 and a soda–lime glass substrate. As a result, under their experimental conditions the (011) and (020) peaks of the VO_2 appeared in addition to the (100) and (200) peaks.

Fig. 2 illustrates the AFM images showing the influence of nitrogen annealing on the surface morphologies of films and the related cross-section image after annealing. As can be seen, the as-deposited film exhibits a smooth and compact surface, consistent

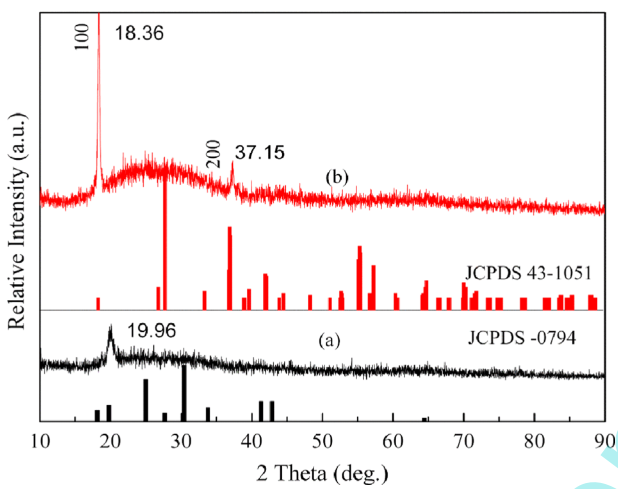

Fig. 1. XRD patterns of films: (a) before annealing and (b) after annealing.

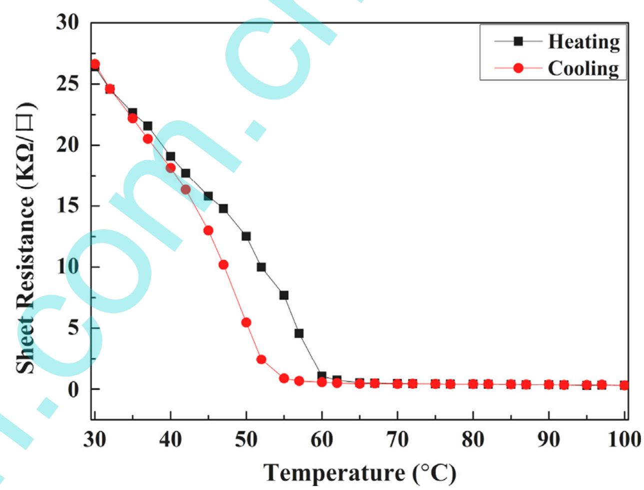

Fig. 3. Temperature dependence of sheet resistance of *a*-axis oriented VO_2 thin film at heating and cooling.

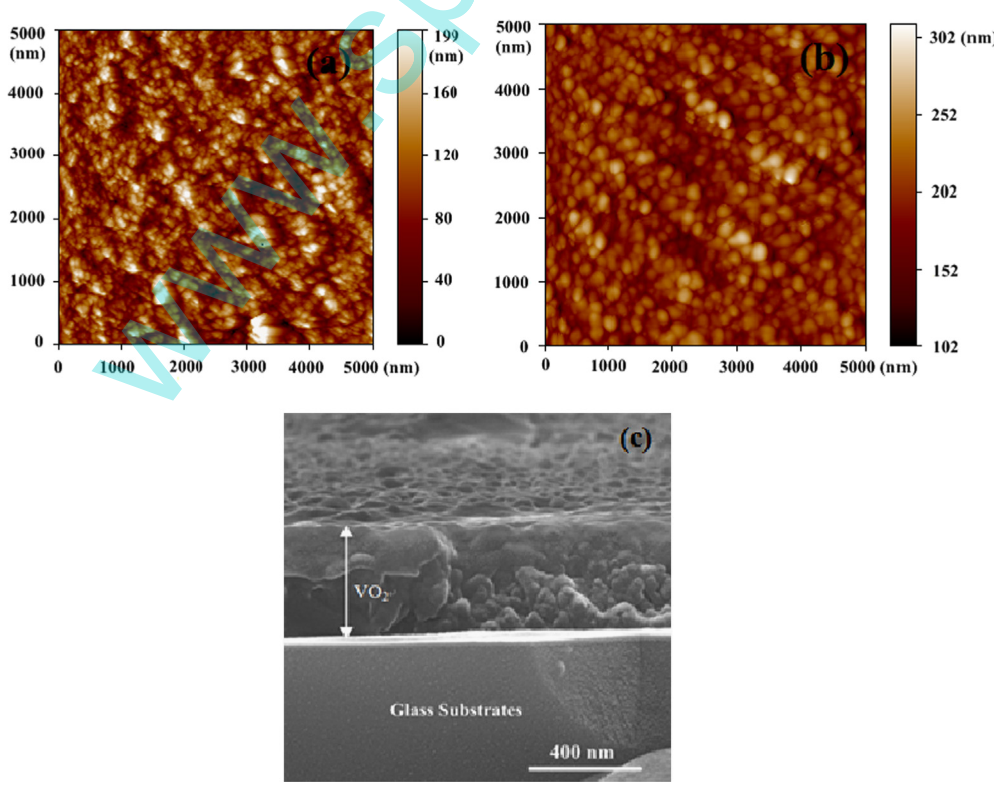

Fig. 2. AFM images of films: (a) before annealing; (b) after annealing and (c) the related cross-section after annealing (SEM).

with the weak diffraction peak of as-deposited film. After having been annealed in nitrogen, fine particles (100 nm) are observed at the surface. The related cross-section image shows that the film has a thickness of about 400 nm with a compact structure. Combining the data with the XRD result, it is suggested that the VO_2 is grown on the glass substrate with the preferred orientation along *a*-axis.

Fig. 3 shows the change in electrical resistance of synthesized films as a function of temperature by using the heating and cooling cycles. For crystalline VO_2 films, transition from a semiconductor to metal phase is accompanied with the change in specific resistance by two orders of magnitude. The hysteresis loop width of VO_2 thin films is 8 °C. These results have the same magnitude as VO_2 grown on a TiO_2 single crystal. They are also close to VO_2 grown on sapphire substrate because the VO_2 thin films are highly preferentially *a*-axis oriented and the crystallinity has been improved.

The MIT temperatures at heating and cooling were 58 and 50 °C, respectively. Transition parameters were defined by the method described in the paper [11]. It is necessary to notice that these MIT temperatures are much less than those mentioned in papers devoted to undoped VO_2 films (typical values of T_t is 68 °C) [11]. This peculiarities are not related with doping the films during deposition or/and annealing [12,13]. T_t decrease can be related with small sizes of crystallites. It was reported in [14] that for VO_2 films with the crystallite size 12–18 nm the MIT temperature is ~55 °C. For our films, the values of average grain size and T_t are very similar to values reported in [14]. Decrease in mechanical stresses in a film, due to low temperatures of formation, also promotes reduction of T_t [4].

4. Conclusions

VO_2 polycrystals were deposited on soda–lime glass substrates by using RF-magnetron sputtering technique in which the control of post-deposition parameters enhances the quality of the films' structure. XRD data suggest that the VO_2 thin films exhibited a highly (100) texture. However, it was found that a recrystallization process took place after annealing, which led to a preferential growth along the *a*-axis of the monoclinic VO_2. The sharpness and the hysteresis width, ΔT, of T-dependent insulator-to-metal hysteretic phase transition were our most immediate and relevant indicators of the quality of the deposited *a*-axis oriented VO_2 on glass substrate.

Acknowledgments

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