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ARTICLE

A Synthesis of Pure Monolayer VO_2 Films with High Visible Transmittance

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ABSTRACT

Thermochromic VO_2 thin film was synthesized on glass slide substrates by reactive RF magnetron deposition ($T_{dep} = 450$ °C) following annealing ($T_{ann} = 400$ °C). The method of synthesis results in the formation of preferred orientation vanadium dioxide with acicular nano-structure. The transmittance of monolayer VO_2 thin film reaches to 67% in the visible light region. This study provides a novel method to improve visible transmittance of VO_2 thin films, which boosts their practical applications in smart windows.

KEYWORDS: Vanadium Dioxide, Sputtering, Preferred Orientation, Visible Transmittance.

1. INTRODUCTION

In the past few decades, metal oxide thin films have attracted increasing attention,[1–5] specially V-based oxide.[6–7] Among the metal oxide thin films, Vanadium dioxide with the reversible metal-insulator phase transition (MIPT) exhibits large changes in infrared optical property. The nature of this transition was related to the crystal structure transformation from monoclinic to tetragonal at a critical temperature (T_c) of 68 °C.[8] The MIPT near room temperature makes VO_2 (M/R) a promising candidate for potential applications as an energy-efficient thermochromic smart window for solar heat control.[9] If VO_2 is used in applications like smart windows, the visible transmittance should exceed 60%.[10–11] However, the visible transmittance values reported for VO_2 thin films are quite low, and the transmittance maximum in the visible region (380–780 nm) has been reported to be ≈50%,[12–13] 42%,[14] 45%,[15] or less than 40%.[16–20]

Many methods have been investigated in an effort to improve the visible transmittance for VO_2 thin films. Fluorine (F) doping can enhance the visible transmittance of VO_2 thin films,[21] but the maximum transmittance achieved was only 55% for a 80 nm thick film, and this value of transmittance is not sufficient for smart window applications. Deposition of an antireflection film is an efficient way to increase the visible transmittance. Such films either suppress the reflectance or shift the transmittance peak to the low wavelength,[22–23] but this procedure has to increase the material consumption and the processing complexity. In this communication, we have prepared pure monolayer VO_2 film with high visible transmittance.

2. EXPERIMENTAL DETAILS

The VO_2 thin film has been deposited onto glass slide substrates by reactive RF magnetron sputtering of pure metallic vanadium target (99.99%) in O_2–Ar gas mixture. The deposition chamber was pumped down to about 9×10^{-4} Pa, and then glass slide substrates were heated to target temperature (heating power was 3.5 W) before the gas inflow. In order to prepare high visible light transmittance of vanadium dioxide thin film, firstly the vanadium target was sputtered for 10 min in order to remove target material surface impurities, secondly passed O_2 into the mixing chamber, and finally started sputtering deposition.

After many experiments, we found that the optimum deposition parameters were O_2/Ar 1%, sputtering pressure 1.4 Pa, magnetron power 135 W, and the substrate temperature close to 450 °C. After deposition, the films were cooled down to 150 °C in the vacuum chamber. The deposited film was annealed at 400 °C for 4 h in N_2 for their further crystallization.

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 Cu K_α wavelength ($\lambda = 0.15406$ nm). The thickness and surface morphology of VO_2 thin films were measured with CSPM 5500 scanning probe microscope system.

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3. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of the films of as-deposited and annealing. As shown in Figure 1(a), one diffraction ($2\theta = 20.04°$) peak which matches to V_2O_5 phase (JCPDS 52-0794) is observed. However, as it is shown in Figure 1(b), the films after annealing exhibit two diffraction peaks that match to monoclinic VO_2 phase (JCPDS 43-1051). The observed diffraction peaks at 2θ values of 18.30 and 37.08° correspond to the [100] and [200] planes of monoclinic VO_2 phase, respectively. It is to be noted that no other vanadium oxide phases are formed, and the exclusive formation of single-phase VO_2 films has been realized. This fact explicitly indicates on monoclinic VO_2 phase formation with preferred orientation. The average crystallite size is calculated about 35 nm by the Scherrer analysis of VO_2 thin film.

The MIPT in the film was studied by the measurements of temperature dependences of electrical resistivity (using the standard four point probe technique). Figure 2 shows the changes in electrical resistance of VO_2 thin films as a function of temperature by using the heating and cooling. For the VO_2 film after annealing, transition from a semiconductor to metal phase is accompanied with the change in resistance. The MIPT temperature of VO_2 thin film was obtained from the following equation: $T_{\text{MIPT}} = (T_{\text{heating}} + T_{\text{cooling}})/2$, where T_{heating} denotes the temperature of maximum resistance rate of change in the heating process, T_{cooling} is the temperature of maximum resistance rate of change in the cooling process. So it is concluded that the MIPT temperature of VO_2 thin film is 63 °C, which is close to theoretical value 68 degrees.

Figure 3 shows the AFM image of as-deposited film and film after annealing. As shown in Figure 3(a), the surface of VO_2 thin film was actually composed of rectangular nano-particles which were random distribution before annealing. And from Figure 3(b), the VO_2 thin film after annealing became denser and the particles became smaller.

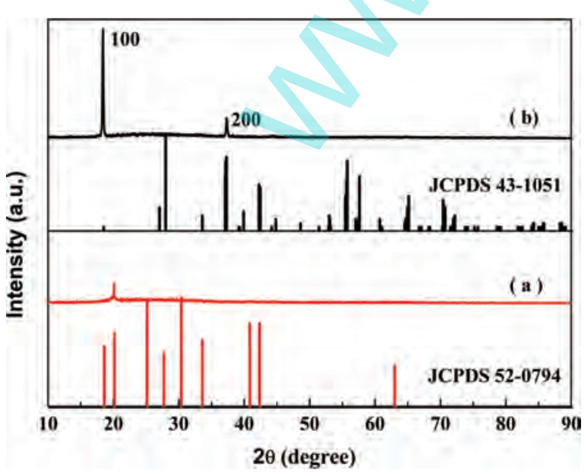

Fig. 1. X-ray diffraction of vanadium oxide thin films: (a) X-ray diffraction of as-deposited film; (b) X-ray diffraction of film after annealing.

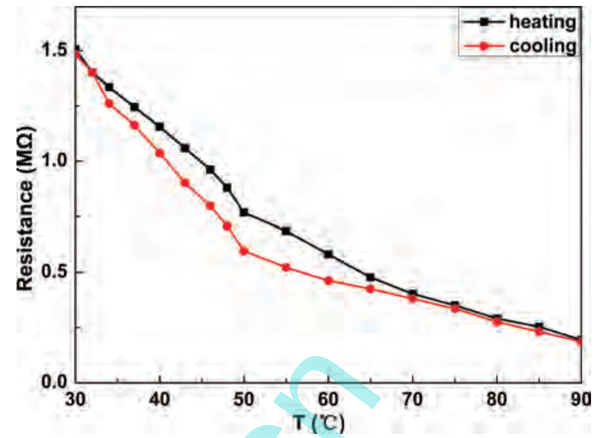

Fig. 2. Temperature dependence of the resistance for VO_2 thin film after annealing at heating and cooling.

Especially, the particle size became relatively homogenous (about 30 nm diameter), and acicular nano-particles were observed. Moreover, the film thickness after annealing was measured by Imager 4.7 software, and it was about 100 ± 10 nm.

Figure 4 shows the transmittance of VO_2 thin film within the range of 200 to 900 nm at room temperature.

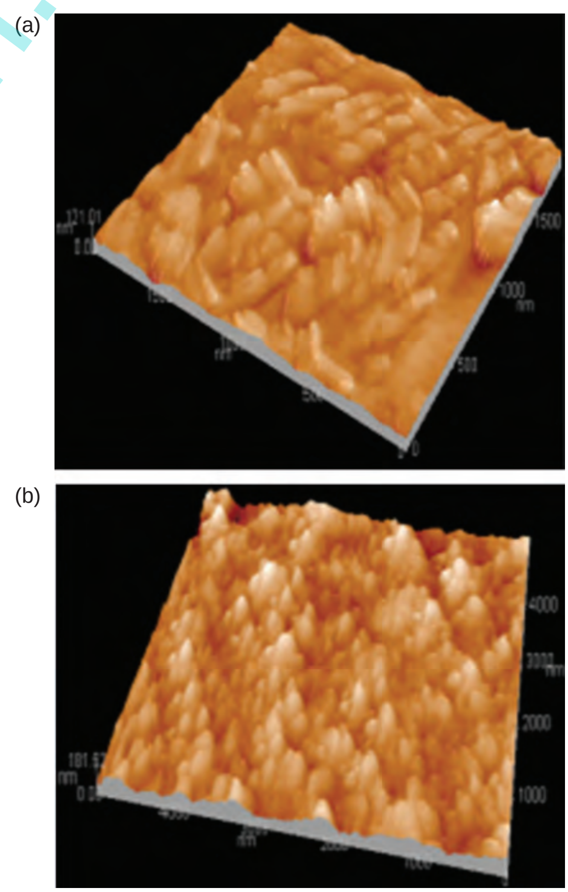

Fig. 3. Vanadium oxide thin films AFM image: (a) the AFM image of as-deposited film; (b) the AFM image of film after annealing.

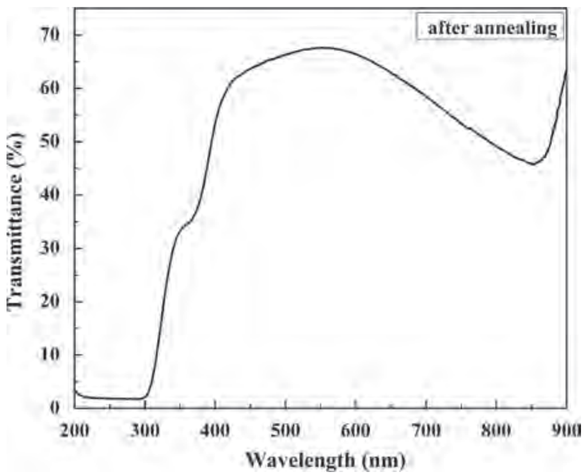

Fig. 4. Spectral transmittance of VO_2 thin film after annealing.

It can be seen that the ultraviolet transmittance is low ($<4\%$), and the visible light transmittance is quite high. Integrated luminous (T_{lum}, 380–780 nm) values were obtained from the following equation: $T_{\text{lum}} = \int \varphi_{\text{lum}}(\lambda) \times T(\lambda)d\lambda / \int \varphi_{\text{lum}}(\lambda)d\lambda$, where $T_{(\lambda)}$ denotes transmittance at wavelength λ, φ_{lum} is the spectral sensitivity of the light-adapted eye. It is necessary to notice that the visible light transmittance of the VO_2 thin film after annealing is 67%, which is relatively high in comparison with the films in Refs. [24–25]. In our opinion, it is caused by the preferred orientation of crystal faces and acicular nano-particles, but the reasons must be investigated further in detail.

4. CONCLUSION

In conclusion, the VO_2 thin film with preferred orientation was prepared by the two processes which were deposition and annealing. The VO_2 thin films are preferential growth at [100] and [200] planes. Furthermore, the visible light transmittance has reached to 67% for a 100 ± 10 nm thick film, and meets the requirement of practical application in the smart windows.

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References and Notes

1. H. Y. Li, J. S. Wang, J. S. Wu, and Y. C. Du, *Mater. Focus* 1, 39 (**2012**).
2. F. Liu and D. F. Xue, *Mater. Focus* 1, 112 (**2012**).
3. K. Y. Li, H. Chen, and D. F. Xue, *Mater. Focus* 1, 121 (**2012**).
4. F. Liu, J. Liu, and D. F. Xue, *Mater. Focus* 1, 160 (**2012**).
5. K. Y. Li, P. C. Yan, and D. F. Xue, *Mater. Focus* 1, 169 (**2012**).
6. J. Liu, H. Xia, D. F. Xue, and L. Lu, *J. Am. Chem.* 131, 12086 (**2009**).
7. J. Liu, Y. C. Zhou, J. B. Wang, Y. Pan, and D. F. Xue, *Chem. Commun.* 47, 10380 (**2011**).
8. F. J. Morin, *Phys. Rev. Lett.* 3, 34 (**1959**).
9. I. P. Parkin and T. D. Manning, *J. Chem. Educ.* 83, 393 (**2006**).
10. M. A. Sobhan, R. T. Kivaisi, B. Stjerna, and C. G. Granqvist, *Sol. Energy. Mater. Sol. Cells* 44, 451 (**1996**).
11. C. S. Blackman, C. Piccirillo, R. Binions, and I. P. Parkin, *Thin Solid Films* 517, 4565 (**2009**).
12. T. D. Manning, I. P. Parkin, M. E. Pemble, D. Sheel, and D. Vernardou *Chem. Mater.* 16, 744 (**2004**).
13. W. Burkhardt, T. Christmann, S. Franke, W. Kriegseis, D. Meister, B. K. Meyer, W. Niessner, D. Schalch, and A. Scharmann, *Thin Solid Films* 402, 226 (**2002**).
14. P. Jin and S. Tanemura, *Jpn. J. Appl. Phys. Part I* 33, 1478 (**1994**).
15. P. Jin, G. Xu, M. Tazawa, and K. Yoshimura, *Appl. Phys. A: Mater. Sci. Process* 77, 455 (**2003**).
16. R. Balu and P. V. Ashrit, *Appl. Phys. Lett.* 92, 021904 (**2008**).
17. R. Binions, G. Hyett, C. Piccirillo, and I. P. Parkin, *J. Mater. Chem.* 17, 4652 (**2007**).
18. I. Takahashi, M. Hibino, and T. Kudo, *Jpn. J. Appl. Phys. Part I* 40, 1391 (**2001**).
19. T. D. Manning and I. P. Parkin, *J. Mater. Chem.* 14, 2554 (**2004**).
20. D. Vernardou, M. E. Pemble, and D. W. Sheel, *Chem. Vap. Deposition* 13, 158 (**2007**).
21. K. A. Khan and C. G. Granqvist, *Appl. Phys. Lett.* 55, 4 (**1989**).
22. P. Jin, G. Xu, M. Tazawa, and K. Yoshimura, *Appl. Phys. A: Mater. Sci. Process* 77, 455 (**2003**).
23. G. Xu, P. Jin, M. Tazawa, and K. Yoshimura, *Sol. Energy Mater. Sol. Cells* 83, 29 (**2004**).
24. N. R. Mlyuka, G. A. Niklasson, and C. G. Granqvist, *Sol. Energy Mater. Sol. Cells* 93, 1685 (**2009**).
25. N. R. Mlyuka, G. A. Niklasson, and C. G. Granqvist, *Appl. Phys. Lett.* 95, 171909 (**2009**).