Structural and optical properties of tungsten-doped vanadium dioxide films*

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Thin films of tungsten (W)-doped thermochromic vanadium dioxide (VO_2) were deposited onto soda-lime glass and fused silica by radio frequency magnetron sputtering. The doped VO_2 films were characterized by X-ray diffraction, optical transmittance measurement, and near field optical microscopy with Raman spectroscopy. X-ray diffraction patterns show that the (011) peak of W-doped thermochromic VO_2 film shifts to a lower diffraction angle with the increase of W concentration. The optical measurements indicated that the transmittance change (ΔT) at wavelength of 2500 nm drops from 65% (ΔT at 35 °C and 80 °C for undoped VO_2 film) to 38% (ΔT at 30 °C and 42 °C for the doped VO_2 film). At the same time, phase transition temperature drops from 65 °C to room temperature or lower with the increase of W concentration. Near field optical microscopy image shows that the surface of W-doped VO_2 film is smooth. Raman results show that the main Raman modes of W-doped VO_2 are centered at 614 cm^{-1}, the same as that of undoped VO_2, suggesting no Raman mode changes for lightly W-doped VO_2 at room temperature, due to no phase transition appearing under this condition.

Keywords: tungsten-doped vanadium dioxide, thermochromic, magnetron sputtering

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1. Introduction

A thin film of vanadium dioxide (VO_2) undergoes a first order transition from a semiconducting state to a metal state at 68 °C accompanied by the steep change of opto-electronic properties.[1] Compared with all of the other vanadium oxides, VO_2 thin film has the nearest phase transition temperature (T_t) to room temperature. Moreover, T_t could decrease to or below the room temperature by doping high valance metal ions, such as tungsten, molybdenum, tantalum, etc., into the VO_2 films, which makes it very suitable for fabricating smart windows, infrared (IR) detectors, and high speed switches.[2–4] VO_2 thin films were deposited by many methods, such as sol–gel,[5] sputtering,[6–9] pulse laser deposition,[10] atmospheric pressure chemical vapor deposition,[11] etc. Sol–gel and sputtering are much more efficient to fabricate large-area uniform VO_2 thin films. There are also many methods to dope W into VO_2 thin films partially determined by the deposition methods of VO_2 thin films.[5,11–14] In the case of sputtering, one method is simultaneously sputtering V and W targets into Ar/O_2 atmosphere for W-doped VO_2 films,[14] the other one is preparing W-doped vanadium oxide films by reactive sputtering of a V–W (1.6 at% W) alloy target.[13] In a dual target configuration, it is easy to control the tungsten concentration in the VO_2 films, however, two dependent systems are needed to control the sputtering of targets, which leads to a high cost. In a V–W (1.6 at% W) alloy target configuration, it is difficult to change tungsten concentraion in VO_2 films by tuning sputtering parameters only. If various tungsten concentration V–W targets have to be used, the cost of materials will increase dramtically.

To reduce the cost, we introduce a method to prepare W-doped VO_2 thin films in this study. Only the V metal (whose diameter is 54 mm) with a small amount of tungsten wires was used as a target to fabricate the uniform W-doped VO_2 films. We found that it was convenient to control the tungsten content in VO_2 films by changing the number of tungsten wires at the glowing zone. This is very important for reducing the cost of materials when large scale production of VO_2 films is carried out in industry.

2. Experimental details

Thin films of VO_2 and W–VO_2 were deposited in an argon/oxygen atmosphere by radio frequency (RF) magnetron sputtering. Before the film deposition, the sputtering chamber was evacuated down to a pressure of about 1×10^{-3} Pa using a turbomolecular pump. Then the argon/oxygen gas with a typical purity of 99.999% was introduced into the sputtering chamber. The vanadium had a purity of 99.9%, tungsten wire on the target, and soda-lime glasses and fused silica with a temperature of about 580 °C were used as the target, the dopant, and substrates, respectively. Typical deposition pa-

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rameters were as follows: the ratio of oxygen to argon was 0.8%∼1.2%; the total sputter gas pressure was 1.0 Pa; RF power was 120 W.

Conventional X-ray diffraction (XRD) measurement was performed by means of RINT 2400 with monochromatized Cu Kα radiation. The transition spectra of the samples were measured by a spectrometer (BIORAD FTS 6000) in the infrared (IR) region. The Raman spectra were acquired at room temperature using near field optical microscopy with Raman measurement.

Thin films of pure VO_2 and W–VO_2 on various substrates were prepared at the same oxygen partial pressure of 10 mPa while the total pressure of Ar/O_2 is 1 Pa. The W–VO_2 film measured by X-ray photoelectron spectroscopy is $W_{0.014}V_{0.986}O_2$.

3. Results and discussion

The structure and properties of VO_2 films doped with titanium, $Ti_xV_{1-x}O_2$, are stable when x changes from 0 to 1,[15] which is different with that of W-doped VO_2 films. The structure and properties of W-doped VO_2 film are stable if the quantity of tungsten is small. Otherwise, they will be unstable and colored stripes will show up on the sample several days later.

By controlling the content of tungsten carefully, W-doped VO_2 thin films have been successfully deposited onto various substrates. Figure 1 shows the XRD patterns for VO_2 and W–VO_2 films deposited onto soda-lime glass. As shown in Fig. 1, the strong peaks in both patterns correspond to the (011) diffraction of the monoclinic VO_2. The XRD peaks of curve a corresponding to 27.88°, 39.80°, 42.25°, and 57.28° are attributed to the (011), (020), (210), and (022) planes of vanadium dioxide film, respectively. The XRD peaks of curve b centered at 27.75°, 37.10°, 39.80°, 55.34°, and 57.28° are attributed to the (011), (200), (020), (220), and (022) planes of vanadium dioxide film, respectively. The inset of Fig. 1 plots the XRD patterns of the above two samples with 2θ ranging from 25° to 31° which shows that the main (011) peak shifts to a lower diffraction angle when the vanadium dioxide film is doped with tungsten and the distance between neighbor (011) planes, d_{011}, increases with the increase of the doping level according to Bragg's law, $d\sin\theta = k\lambda$, where $k = 1$, λ is the wavelength of X-ray, θ is the diffraction angle and d is the distance between the neighbor planes. We suggest that the compressive stress in the (011) plane influences the increase of d_{011}, which will induce a tensile stress along the [011] direction. It is well known that when vanadium dioxide changes from a semiconducting state to a metal state, its volume will expand by 1% of its original volume. Therefore, this tensile stress will be helpful to the phase transition occurring at the lower temperature. We attribute the decrease of T_t of W-doped VO_2 film to the shifting of (011) peaks to the lower diffraction angles.

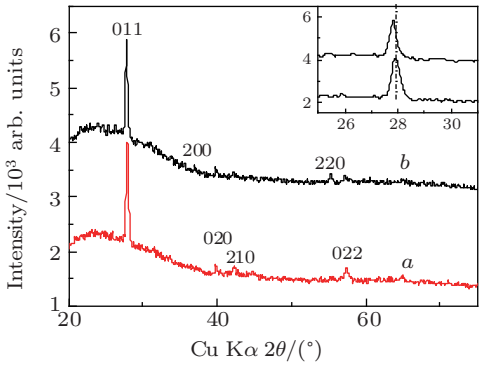

Fig. 1. (color online) XRD patterns of VO_2 film (curve a, red) and W–VO_2 film (curve b, blank). The inset is the XRD patterns with 2θ ranging from 25° to 31°.

The transmittance for W-doped VO_2 films versus the wavelength at different test temperatures are shown in Fig. 2. It can be seen that the transmittance in the whole wavelength changes little at temperatures ranging from 46 °C to 42 °C, the transmittance changes with temperature at a rate of about 1%/°C at the wavelength of 2500 nm. However, the transmittance changes obviously at the temperature ranging from 42 °C to 40 °C, its change rate increases clearly up to 2%/°C at 2500 nm. The transmittance changes rapidly at 2500 nm at the temperature ranging from 40 °C to 30 °C, the transmittance changes with temperature according to 3%/ °C. The transmittance as a function of the temperature at the wavelength of 2500 nm for W-doped has been drawn in Fig. 3. For comparison, the temperature-depend transmittance at 2500 nm for undoped VO_2 films deposited on fused silica and soda-lime glass has also been plotted. The phase transition temperature T_t of W–VO_2 film deposited on soda-lime glass is about 35 °C in Fig. 2, and the T_t of VO_2 films deposited on soda-lime glass and fused silica are 63 °C and 69 °C, respectively. The reason for the changing of T_t of VO_2 films on various substrates can be found in our previous paper.[16]

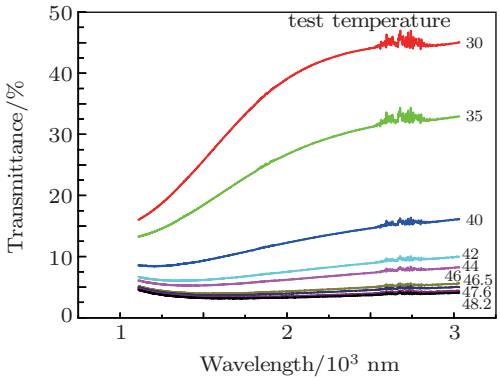

Fig. 2. (color online) Transmittance as a function of wavelength at different temperatures for W–VO_2 film.

Raman spectra were used to confirm the presence of monoclinic VO_2, as well as W-doped VO_2.[17–19] Piccirillo *et al.* reported that the Raman spectrum of doped VO_2 film, such as $V_{0.9825}W_{0.0175}O_2$, is the same as the spectrum assigned to the

monoclinic VO_2, and the spectrum also shows no sign of carbon contamination determined by the peak at 1355 cm^{-1} in the films.[17] From the curves *a* and *b* of Fig. 4, it can be seen that all the signals detected and marked in the spectra are the same, and the carbon contamination in both films is not obvious. The major peaks of the spectra of both films are centered at 223, 260, 303, 392, and 614 cm^{-1}, respectively, which is in agreement with the literature data reported elsewhere.[19] No other vanadium oxide is present and the Raman spectrum of monoclinic VO_2 is almost the same as that of W-doped VO_2. We point out that impurities such as W ions instead of V ions do not change the structure of VO_2 significantly. Although the ratio of vanadium to oxygen slightly deviates, the stoichiometric VO_2 would dramatically influence the peak positions of Raman spectra. This is probably due to the W ions instead of V ions located in the lattice spots of monoclinic VO_2 which, despite a slight distortion, does not mechanically breakdown the structure, so that the vibration modes of both W-doped VO_2 and undoped VO_2 remain unchanged.

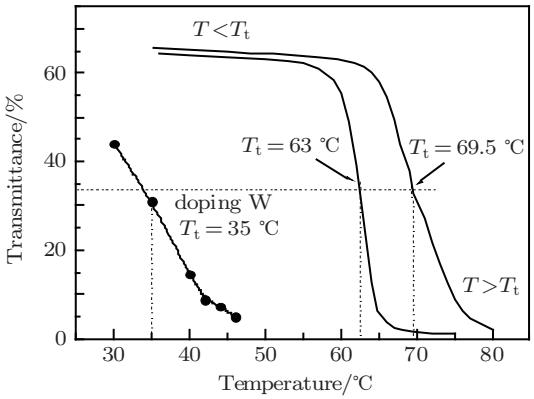

Fig. 3. Transmittance at wavelength 2500 nm versus temperature for W–VO_2 (phase transition temperature $T_t = 35$ °C) and undoped VO_2 ($T_t = 63$ °C) films on the soda-lime glass, and for undoped VO_2 film ($T_t = 69.5$ °C) on the fused silica.

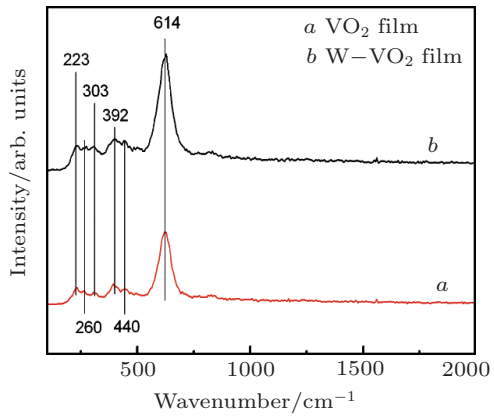

Fig. 4. (color online) Raman spectra of VO_2 film (curve *a*, red) and W–VO_2 film (curve *b*, blank).

4. Conclusion

We present a study on the structural and optical properties of pure and W-doped vanadium dioxide films. We have shown that an increase in tungsten content in the film results in a slight shift of the diffraction angle towards a lower angle.

Upon going through semiconductor–metal transition, the transmittance of the doped VO_2 film does not drop as dramatically as that of the pure VO_2 film. The transmittance change of the doped VO_2 film is about 38% (ΔT at 30 °C and 42 °C) at 2500 nm, while that of the pure VO_2 film is about 65% (ΔT at 35°C and 80°C).

We have shown that Raman spectra of both doped and undoped VO_2 films are nearly the same. We suggest that although W ions alternating V ions located in the lattice spots of monoclinic VO_2 distort the lattice slightly, they do not induce phase transition. Therefore, the vibration modes of W-doped VO_2 and undoped VO_2 are the same.

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References

[1] Kivaisi R T and Samiji M 1999 *Sol. Energy Mater. Sol. Cells* **57** 141
[2] Granqvist C G 2007 *Sol. Energy Mater. Sol. Cells* **91** 1529
[3] Wang H C, Yi X J, Chen S H, Huang G and Xiao J 2004 *J. Infrared Millim. Wave* **23** 99 (in Chinese)
[4] Wang H C, Yi X J, Li Y 2005 *Opt. Commun.* **256** 305
[5] Chae B G, Kim H T, Yun S J, Kim B J, Lee Y W, Youn D H and Kang K Y 2006 *Electrochem. Solid-State Lett.* **9** C12
[6] Jin P and Tanemura S 1994 *Jpn. J. Appl. Phys.* Part 1 **33** 1478
[7] Lee M H and Cho J S 2000 *Thin Solid Films* **365** 5
[8] Wang X J, Liang C J, Guan K P, Li D H, Nie Y X, Zhu S Q, Huang F, Zhang W W and Cheng Z W 2008 *Chin. Phys. B* **17** 3512
[9] Luo Z F, Wu Z M, Xu X D, Wang T and Jiang Y D 2010 *Chin. Phys. B* **19** 106103
[10] Soltani M, Chaker M, Haddad E and Kruzelesky R V 2006 *J. Vac. Sci. Technol. A* **24** 612
[11] Manning T D and Parkin I P 2004 *J. Mater. Chem.* **14** 2554
[12] Jin P, Nakao S and Tanemura S 1998 *Nucl. Instrum. Method Phys. Res. B* **141** 419
[13] Jin P, Tazawa M, Ikeyyama M, Tanemura S, Macak K, Wang X, Olafsson S and Helmersson U 1999 *J. Vac. Sci. Technol. A* **17** 1817
[14] Romanyuk A, Steiner R, Marot L and Oelhafen P 2007 *Solar Energy Material and Solar Cell* **91** 1831
[15] Kakiuchida H, Jin P and Tazawa M 2008 *Thin Solid Films* **516** 4563
[16] Wang X J, Xu J J, Fei Y J, Li D H, Li T J, Nie Y X, Feng K A and Wu N J 2002 *Jpn. J. Appl. Phys.* Part 1 **41** 312
[17] Piccirillo C, Binions R and Parkin I P 2007 *Chem. Vap. Deposition* **13** 145
[18] Piccirillo C, Binions R and Parkin I P 2008 *Thin Solid Films* **516** 1992
[19] Parker J C 1990 *Phys. Rev. B* **42** 3164