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Effects of W^{6+} Doping on Structure and Electrical Property of VO_2 (A) Thin Film

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Abstract. Thin films composed of high pure VO_2 (A) doped W^{6+} ions were successfully prepared by an inorganic sol-gel method. The effects of W^{6+} ions doping on the structure, surface morphology and electrical property the films were investigated. The results show that the solution of W^{6+} ions distorted the lattice of VO_2 (A) film, and made the lattice parameter *d* increase. With W^{6+} ions concentration increase, the grain size of the film increased, and the grain shape became rod or block from sphere. The film resistance decreases sharply, near one magnitude with the W^{6+} doping concentration increase from 0 to 0.75 at%. And W^{6+} doping made the film *TCR* close to zero from a negative value, the film change to metal from semiconductor.

Introduction

Vanadium dioxide (VO_2) is an interesting electron material that exhibits a reversible first order phase transition from a low temperature semiconductor phase to a high temperature metal phase at a critical temperature around 68 °C, which can be manipulated to a human-comfortable temperature by doping other ions[1]. The phase transition could be triggered not only by temperature, but also by electric field light, and pressure[2],. The phase transition accompanied with abrupt several orders of magnitude changes in optical and electrical properties[3]. All these properties make VO_2 a promising candidate for a variety of applications, such as smart windows[4], infrared uncooled bolometer, optical and electrical switching[5], sensor devices, modulators and memory devices[6].

There are some methods to prepared VO_2 film, such as Sol-Gel[7], CVD[8], sputtering[9], pulsed laser deposition, thermal reduction, and so on[10]. These methods have their own advantages and disadvantages. Sol-gel method is a simple and mature technology. It is easy to control the thickness of the membrane, and doping other ions can be easily realized by adding salt or alcohol salt to the precursor solution. Therefore, Sol-Gel is chosen to prepare the films in this paper.

Compared with the VO_2 (M), the VO_2 (A) and VO_2 (B) are rarely reported. Oka et al.[11] confirmed that VO_2 (A) is a metastable phase and the mechanism of VO_2 (A) transformation into VO_2 (B) was also proposed. Xie et al[12] investigated that the phase transition between VO_2 (A) and VO_2 (B) using hybrid density functional theory calculation and crystallographic VO_2 topology analysis. And all theoretical analyses reveal that VO_2 (A) is a thermodynamically stable phase and has lower formation energy compared with the metastable VO_2 (B). But Li et al[13] thought that VO_2 (A) was a metastable phase, and the high quality single crystalline metastable phase VO_2 (A) ultra-long nanobelts were synthesized with hydrothermal method using inorganic V_2O_5 sol as precursor and polyethylene glycol as both surfactant and reducing agent. They found that electrical transport measurement of a single VO_2 (A) nanobelt presented a relative low hoping activation energy of 0.28 eV. Zhu et al[14] prepared pure VO_2 (A) nanorods and W^{6+} doped VO_2 (A) nanorods using a facile high temperature mixing method under hydrothermal conditions, and they found that the phase transition temperature of the pure VO_2 (A) was 154.75 °C, and the pure VO_2 (A) showed good thermochromic properties and optical-switching characters. When a small amount of W^{6+} was doped, VO_2 (A) will be transformed into other polymorphic forms, which indicates that the crystal structure of VO_2 (A) is highly sensitive to a limited doping.

No matter what VO_2 (A) is a metastable state or a thermodynamically stable phase, the pure VO_2 (A) films and W^{6+} doped VO_2 (A) films were successfully prepared by using inorganic sol-gel method, the effect of W^{6+} doping on structure and electrical property of W^{6+} doped the VO_2 (A) thin film were investigated.

Experimental

Preparation of VO_2 (A) Thin Films

W^{6+} doped VO_2 (A) films were prepared by the inorganic sol-gel method. 3.5 g of vanadic anhydride powder (V_2O_5, AR, 99.99%) and a certain amount of ammonium tungstate ($(NH_4)_{10}W_{12}O_{41}\cdot xH_2O$, AR, 99.99%) were mixed and ground in an agate mortar. Next, the mixture was put into a ceramic crucible, heated to 800 °C lasting 10 min to get uniform melt, and then the melt was poured into 300 ml deionized water at room temperature. In the process of melting, V_2O_5 and ammonium tungstate underwent hydrolysis and polycondensation reaction to form a colloid. After vigorous stirring for 2 h, a deep brownish sol was obtained. The sol was aged for 24 h before filtering, and a precursor was formed. The V/W atomic ratio is 0 at.%, 0.25 at.%, 0.5 at.%, 0.75 at.%.

The quartz glasses were selected as substrates. These substrates were pretreated in ethanol, dilute sulfuric acid, and aqueous ammonia to remove the organic contaminations and cations which were found on the surface of the substrates. The films were deposited on quartz glass substrates using dip coating, and then the films were dried in the oven at 80 °C for 5 min to remove the residual moisture. The process was repeated three times to increase the thickness. The films' thicknesses ranged from 400 to 500 nm. After the above treatment, the W^{6+} doped V_2O_5 thin film was obtained.

The Annealing Processes

The annealing treatment process has great influence on the microstructure and properties of the W^{6+} doped V_2O_5 thin film. In the annealing processes, the annealing temperature of the samples increased from the room temperature to 350 °C at a rate of 1 °C/min in the nitrogen atmosphere (purity > 99.99%), and then the annealing temperature remained at 350 °C for 120 min. Next, the annealing temperature increased to 500 °C at a rate of 15 °C/min, and then lasted for 45 min. Finally, the samples cooled to room temperature naturally. The pure VO_2 (A) film and W^{6+} doped VO_2 (A) films were obtained. The brief schematic flow of the annealing processes is shown in Fig.1.

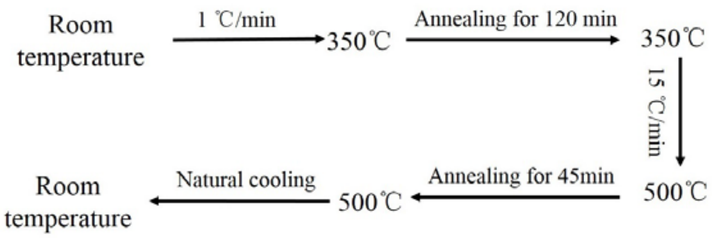

Fig. 1 The brief schematic flow of the annealing processes.

Characterization

The crystal structure of the film was characterized by X-ray diffraction using a Rigaku D/MAX-2500 diffractometer in its reflection mode with Cu Kα (k= 0.154 nm) radiation. The surface morphologies of the films were observed with a Hitachi S-4800 FE scanning electron microscope. The electrical property of the film was tested with the standard four point probe technique.

Results and Discussion

The Structures of W^{6+} Doped the VO_2 (A) Films

To investigate the structure of the W^{6+} doped VO_2 (A) films, the XRD patterns of these films are showed in Fig.2 (a). The peaks at 2θ = 14.881°, 29.922° and 45.516° correspond to (110), (220), and (330) respectively, which matches well with the JCPDS No. 42-0876 (a=0.845 nm, b=0.845nm, c=0.7686 nm) indexing to tetragonal VO_2 (A) with the space group *P42/ncm* (138). It suggests that these films have a pure VO_2 (A) structure with high crystalline preferential orientation on the substrate. From Fig.2 (b), the diffraction peaks deflected to the small angle direction with the increasing of W^{6+} concentration. According to the equation $\lambda=2d\sin\theta$, when λ is constant, a smaller value of θ corresponds to a larger value of *d*. Therefore, it is indicated that the W^{6+} might enter the VO_2 lattice. The radius of V^{4+} is 0.058 nm, and the radius of W^{6+} is 0.062 nm, the difference between the radii of these ions, Δr, is < 15%, therefore, the W^{6+} ions probably displaced V^{4+} ions in the lattice, and the lattice parameter *d* increases with the W concentration. Therefore, the W^{6+} ions dissolved into the vanadium dioxide well.

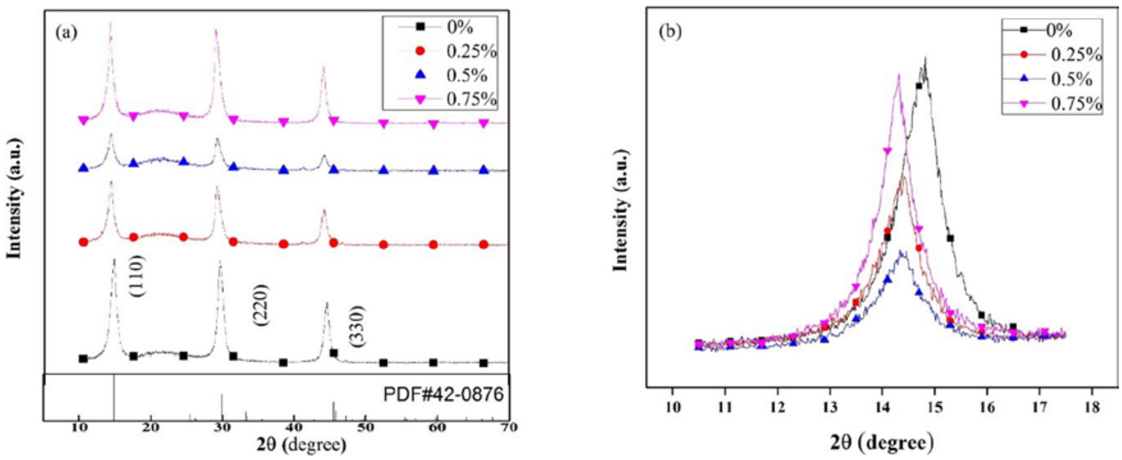

Fig. 2 (a) The XRD patterns of W^{6+} doped VO_2 (A) thin films
(b) (110) diffraction peaks of VO_2 films with W^{6+} doping.

The Surface Morphologies of W^{6+} Doped VO_2 (A) Films

Fig.3 shows the surface morphologies of these films doped with different concentration of W^{6+}. It seems that the all pure VO_2 (A) films consist of homogeneous and continuous granules, which are compact without obvious pore. And with the increase of W^{6+} concentration, these films' granules gradually transit from spheres to rods and even blocks gradually, and the size of the granules continues to increase, see Fig. 3(b)-3(d). When W^{6+} concentration is increased to 0.75 at%, the surface of the film becomes rod-like structure. This may due to the agglomeration of grains resulting from the annealing process. The solution of W^{6+} ions into VO_2 grain cells makes lattice distortion, and increase the grain the surface energy, which would promote grains' growing up and agglomeration.

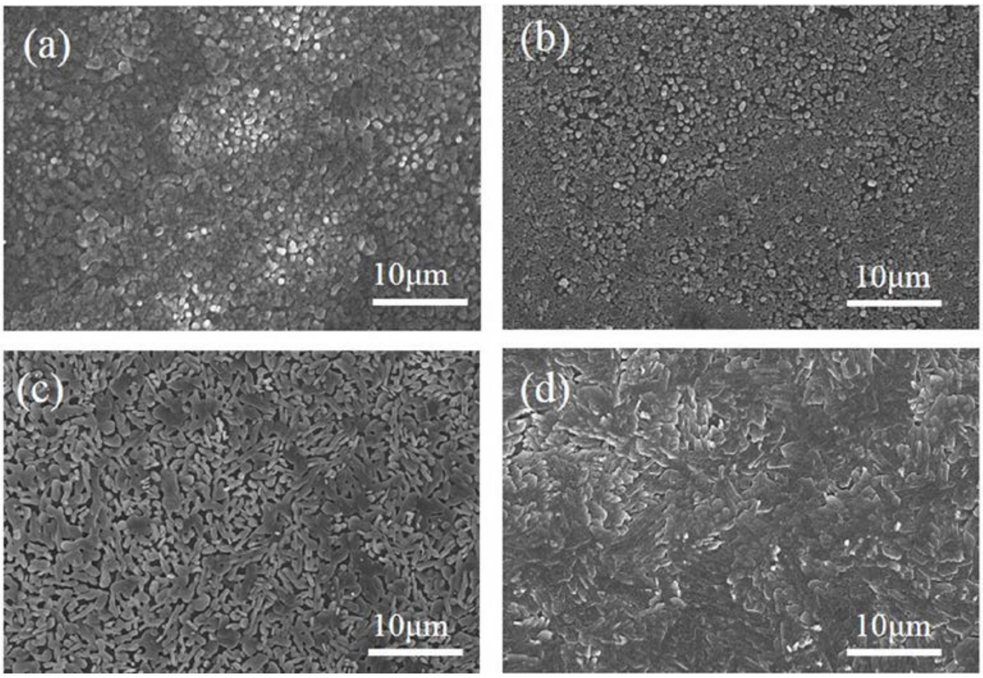

Fig. 3 The effect of W^{6+} doping concentration on the film's surface morphology
(a) 0 at%, (b) 0.25 at%, (c) 0.5 at%, (d) 0.75 at%

Electrical Property of W^{6+} Doped VO_2 (A) Film

The effect of the W^{6+} doping concentration on the resistance of VO_2 (A) film is shown in Fig. 4. It can be seen that the resistance of each thin film decreases linearly with the temperature increase, which is just was one of the typical characteristics of the VO_2 (A) phase. This could be attributed to the carrier density increase with the temperature. Some electrons in the semiconductor could break free from the shackles of the atomic nucleus, and become free electrons with the temperature increases. Moreover, the film resistance decreases sharply, near one magnitude with the W^{6+} doping concentration increase from 0 to 0.75 at%. In other words, W^{6+} ions could improve the conductivity of VO_2 (A) thin film.

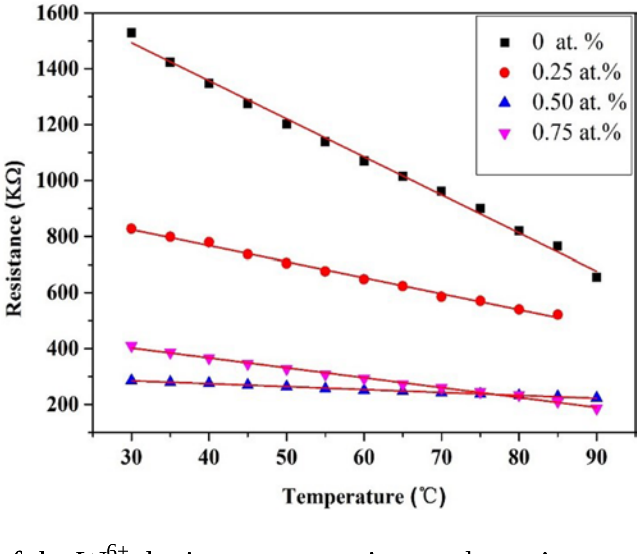

Fig. 4 The effect of the W^{6+} doping concentration on the resistance of VO_2 (A) films

The temperature coefficient of resistance (*TCR*) is definite as *TCR*=*dR*/(*R*·*dT*). And the *TCRs* of the VO_2 (A) films are listed in table 1. Fig. 5 shows the effect of W^{6+} concentration on the film TCR clearer. It is very clear that *TCR* increases quickly with the W^{6+} concentration increase. That is to say, W^{6+} doping made *TCR* close to zero from a negative value, the film change to metal from semiconductor.

Table 1 The *TCRs* of different W^{6+} concentration doped VO_2 (A) films.

W^{6+} concentration	0 at%	0.25 at%	0.5 at%	0.75 at%
dR/dT	-13.61	-5.70	-1.047	-0.997
TCR	-0.72%/°C	-0.56%/°C	-0.32%/°C	-0.2%/°C

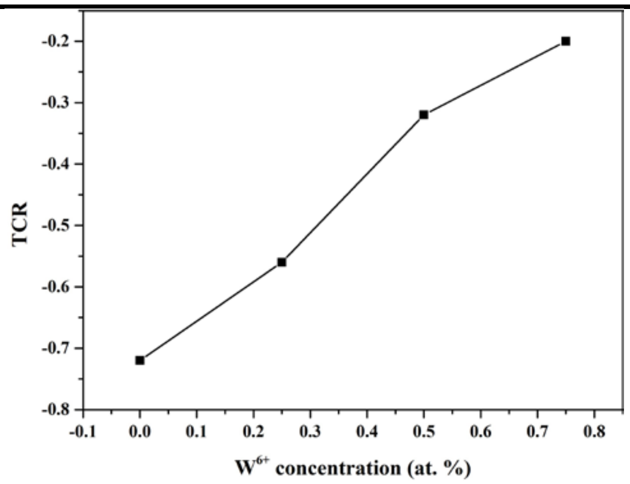

Fig. 5 The effect of the W^{6+} doping concentration on *TCR* of VO_2 (A) films

This could be explained as the following. W^{6+} ions in the lattice of VO_2 film could donate two extra free electrons, which would enter the localized energy levels near the bottom of the conduction band and decrease the band gap. Doping W^{6+} not only provides free electrons but also results in a region of dense energy levels, in which the difference in energy between any two levels is very small. Therefore, more W^{6+} ions doped VO_2 (A) film could have a lower resistance and a bigger *TCR*. On the other hand, W^{6+} in the VO_2 (A) film could make a large quantity of defects, such as large crystal lattice distortions, vacancies, dislocations, and impurity centers, the carrier density of VO_2 (A) film increases gradually, so the resistance of VO_2 (A) film decreases.

Conclusion

Thin films composed of high pure VO_2 (A) doped W^{6+} ions were successfully prepared by the inorganic sol-gel method. The effects of W^{6+} ions doping on the structure, surface morphology and electrical property the films were investigated.

(1) The solution of W^{6+} ions distorted the lattice of VO_2 (A) film, and made the lattice parameter *d* increase.

(2) With W^{6+} ions concentration increase, the grain size of the film increased, and the grain shape became rod or block from sphere.

(3) The film resistance decreases sharply, near one magnitude with the W^{6+} doping concentration increase from 0 to 0.75 at%. And W^{6+} doping made the film *TCR* close to zero from a negative value, the film change to metal from semiconductor.

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