Switching Properties and Phase Transition Mechanism of Mo^{6+}-Doped Vanadium Dioxide Thin Films *

XU Shi-Qing(徐时清)[1], MA Hong-Ping(马红萍)[2], DAI Shi-Xun(戴世勋)[1], JIANG Zhong-Hong[1](姜中宏)

[1]*Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800*

[2]*Department of Mechanical and Electrical, Zhejiang University of Science and Technology, Hangzhou 310012*

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Using V_2O_5 and MoO_3 powders as precursors, a novel preparation method, i.e., the so-called inorganic sol-gel, is developed to synthesize Mo^{6+}-doped vanadium dioxide (VO_2) thin films. The structure, valence state, phase transition temperature and magnitude of resistivity change are characterized by x-ray diffraction, x-ray photoelectron spectroscopy and the four-point equipment. The results show that the main chemical composition of doped thin films was VO_2, the structure of MoO_3 in doped thin films did not change, and the phase transition temperature of doped thin films was obviously lowered with the increasing MoO_3 doped concentration, but the magnitude of resistivity change was also decreased. However, so long as MoO_3 doped concentration was not more than 5 wt.%, the magnitude of resistivity change of doped thin films still reached more 2 orders. The analysis show that MoO_3 dissolved in crystal structure of VO_2 formed the donor defect MO_v^x and then reduced the forbidden-band width, which lowered the phase transition temperature. Consequently it was widened applications of the VO_2 thin films.

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Single crystal vanadium dioxide (VO_2) has attracted more interests because it undergoes a phase transition at approximately 68°C from a semiconductor to a metal. The phase transition exhibits a marked change in switching properties and is accompanied by a change in optical properties.[1−4] Thermal expansion causes damage to the single crystal during repeated cycling through the transition, but VO_2 thin films are more tolerant to repeat heating and cooling. Thus, VO_2 thin films have been extensively studied and a wide variety of applications have been proposed, e.g., temperature sensing devices,[5] optical switching devices,[6,7] modulator and polarizer of submillimetre wave,[8] optical data storage medium,[9] variable reflectance mirrors,[2] and energy-conserving coatings for windows.[1] However, it is required in most cases that the phase transition temperature of VO_2 thin films be reduced to near the ambient, thus great efforts have been made in order to lower the phase transition temperature for practical applications.

It is well known from the literature that the phase transition temperature of VO_2 thin films can be modified by doping.[7,10−17] It decreases with high-valent cations (Nb^{5+}, Ta^{5+}, W^{6+}) that generate a donor-like defect, whereas it increases with low-valent cations (Al^{3+}, Cr^{3+}, Fe^{3+}) that generate an acceptor-like defect. There have been reported on the metal doping of VO_2 thin films, e.g., by means of sputtering,[12,18] high-energy ion implantation,[19] by introducing dopants to the precursors[20] and sol-gel methods.[11,21] Due to the advantages of high purity, homogeneity, stoichiometry, and the ease of doping, the sol-gel processing has become one of the best approaches to prepare doped VO_2 thin films on the silica glasses substrates.[15,22] However, the sol-gel method uses expensive and usually unstable vanadium alkoxides as precursors. To avoid this disadvantage, we have developed a new preparation method to synthesize doped VO_2 thin films based on a quenching method. It is called the inorganic sol-gel method in which the former uses vanadium alkoxides as precursors, whereas the latter uses V_2O_5 and MoO_3 powders as precursors.[2,5] In this Letter, we report on the doping of inorganic sol-gel VO_2 thin films on the silica glasses substrates using V_2O_5 and MoO_3 powders as precursors, and we investigate the effect Mo^{6+} ions on switching properties of VO_2 thin films and phase transition mechanism.

The doped thin films were prepared by using the highly pure (99.9%) chemicals of V_2O_5 and MoO_3 powders. The chemical composition of precursors was $(100 - x)$ V_2O_5 − $x$$MoO_3$ (where x = 1.0, 2.0, 3.0, 4.0, and 5.0 wt.%). The mixture of the constituent chemicals put into a ceramic crucible were melt at 800–900°C for 20–30 min in an ambient atmosphere, and then the molten liquid was quickly poured into distilled water at room temperature. The brownish mixture sol of V_2O_5 and MoO_3 were formed in water while the molten liquid was being poured. Silica glasses were used as substrates. The substrates were dipped into the mixture sol and then pulled out at a low speed while the doped V_2O_5 sol thin films were formed on the substrates using the mixture sol. The doped V_2O_5 sol thin films were dried at ambient

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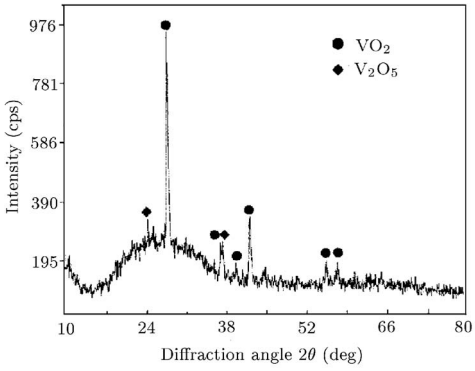


Fig. 1. x-ray diffraction pattern of the sample containing MoO_3 of 3 wt.%.

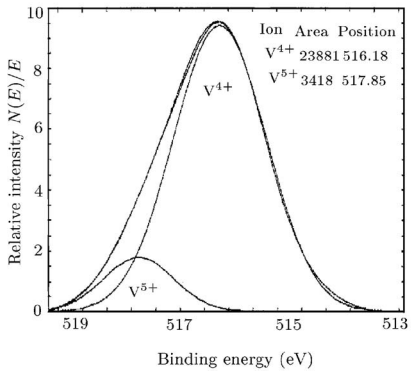


Fig. 2. Separated V $2p_{3/2}$ peaks of the sample containing MoO_3 of 3 wt.% (V $2p_{3/2}$ peak of the sample at binding energy 517.1 eV, V $2p_{3/2}$ peak of V(IV) at binding energy 516.18 eV, V $2p_{3/2}$ peak of V(V) at binding energy 517.85 eV).

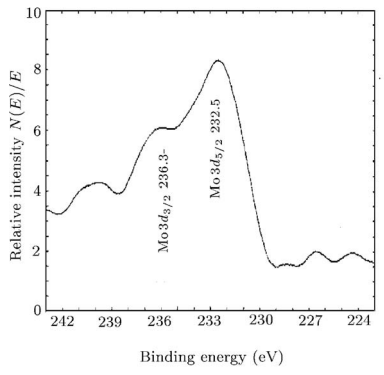


Fig. 3. Mo $3d$ peaks of the sample containing MoO_3 of 3 wt.%.

temperature for two days to obtain Mo ion doped V_2O_5 gel thin films. Thicker thin films can be obtained by repeating this process. Then Mo ion doped V_2O_5 gel thin films were put into a vacuum furnace, heated at 500 ± 10°C for 10 h. The heating rate was 3–4°C/min. The vacuum chamber was fed with low-pressure air, and pressure was 1–5 Pa. The resulting doped thin films were obtained after cooling from the heat treatment temperature.

The structure of the samples was determined by x-ray diffraction (XRD) using a P/max-3C (Japan) diffractometer and Cu K_α radiation. The valence state of vanadium was studied by x-ray photoelectron spectroscopy (XPS) using an Escalab 220-IXL spectrometer. The electric resistance of doped thin films was measured as a function of temperature, and tested by using a four-points equipment associated with a Hewlett Packard HP 3456 A multimeter, and coupled with an automated control temperature (rate 2°C/min) by using a Peltier device.

Figure 1 shows the XRD patterns of the sample containing MoO_3 (3 wt.% of MoO_3). The thin films thickness is about 600 nm. The strong peaks of monoclinic VO_2 are seen and a few peaks of V_2O_5 are also observed, compared with the standard pattern stored in the computer of the XRD system, no other vanadium oxide was detected. However, MoO_3 is not also discovered in the XRD pattern of the sample, which is due to the fact that the MoO_3 in doped thin films as the solute donor forms solid-solution phases with VO_2. The raw surface XPS spectra of the sample containing MoO_3 (3 wt.% of MoO_3) are also characterized by XPS, as shown in Figs. 2 and 3. Figure 2 shows that peak V$2p_{3/2}$ of the sample can be separated into V^{4+} peak and V^{5+} peak at 516.18 eV and 517.85 eV, respectively. In Fig. 2 the area presents the ratio of V ion in different valences, V^{4+} and V^{5+}, so it can conclude that the composition proportion of V^{4+} in the sample is about 87.55% through area calculation. Figure 3 shows the Mo_{3d} peaks of the samples. According to standard binding energy of MoO_3, it is known that there is a little MoO_3 in the sample, and the existence form of Mo ion in VO_2 thin films is Mo^{6+}.

The effects of MoO_3 doped concentration on the phase transition temperature and the magnitude of resistivity change are shown in Figs. 4 and 5, respectively. With the increasing MoO_3 doped concentration, it can be seen from the figures that the phase transition temperature is obviously lower, but the magnitude of resistivity change and is also decreased. When MoO_3 doped concentration is 5 wt.%, the phase transition temperature of doped thin films is lowered to about 30°C, and the magnitude of resistivity change reaches two orders more, so it can be satisfied for the switching properties of doped thin films and it is widened for applications of VO_2 thin films.

From the result of XPS, it is known that the structure of MoO_3 in VO_2 thin films does not change and the existence form of Mo ions in VO_2 thin films is Mo^{6+}. Because of the replacement of parts V^{4+} position by Mo^{6+} ions, the structure of the resulting doped thin films is $V_{1-x}Mo_xO_2$. When VO_2 thin films are doped with Mo^{6+}, the impurity defect $Mo_v^{\cdot\cdot}$ is formed in the crystal structure of VO_2 thin films. The impurity defect $Mo_v^{\cdot\cdot}$ is equivalent to bivalent positive ion relaxedly bound up two electrons, namely, corresponding to $Mo_v^{\cdot\cdot} + 2e$. The effective charge sign was denoted by Mo_v^x. The ionization process of electron from Mo_v^x is given by[23]

$$Mo_v^x + E_D \rightarrow Mo_v^{\cdot\cdot} + 2e. \quad (1)$$

Actually the doping of Mo^{6+} ions in VO_2 thin films plays the same role with the donor defect Mo_v^x, the negative charge ionized from the donor,defect Mo_v^x

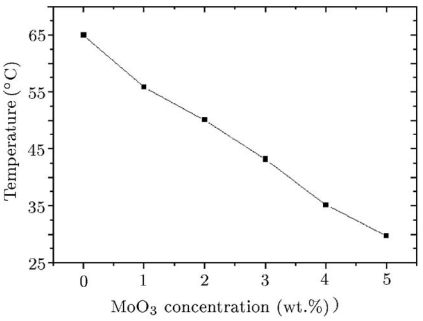


Fig. 4. Effect of MoO_3 concentration on the phase transition temperature of the samples.

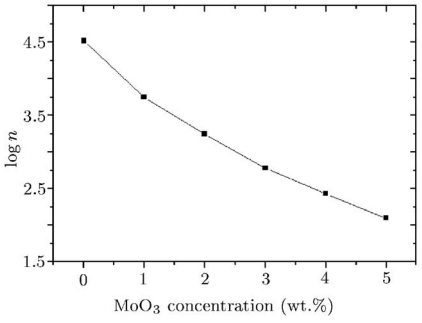


Fig. 5. Effect of MoO_3 concentration on the magnitude of resistivity change of the sample with (before phase transition)/(after phase transition).

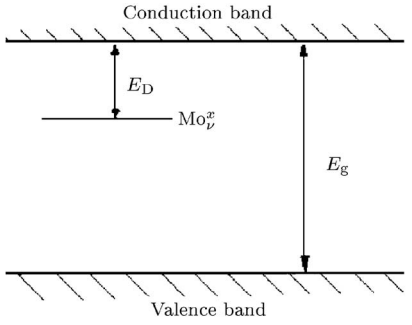


Fig. 6. Schematic diagram of local energy levels formed in the VO_2 thin films by doping with MoO_3.

situates on the formed local energy level in the forbidden band which locates at the bottom of conduction bands, which reduces the forbidden-band width, as shown in Fig. 6. The switching properties of VO_2 thin films are changed as a result of redundant negative charge, which matches with Mo^{6+} that was excited and transitted to conduction band at low temperature, so it make the phase transition temperature lower. Because different concentrations of Mo^{6+} in the VO_2 thin films will induce different amount of the donor defects Mo_v^x, the phase transition temperature is lowered with increasing MoO_3 doped concentration. However, the switching properties of VO_2 thin films are determined by characteristics of the crystal structure of VO_2 in essence. Although the dissolved MoO_3 in the VO_2 thin films changes the energy level structure of VO_2, the change of the VO_2 crystal structure produced by Mo^{6+}, namely the donor defect Mo_v^x formed in the VO_2 crystal structure has an adversely effect on the process of electron transition, so it is evident that the resistance of electron transition be augmented, which is the reason that the magnitude of resistivity change is reduced with the increasing MoO_3 doped concentration.

In conclusion, using V_2O_5 and MoO_3 powders as precursors, we have prepared high quality Mo^{6+}-doped VO_2 thin films by an inorganic sol-gel method. The main chemical composition of doped thin films is VO_2, the structure of MoO_3 in the VO_2 thin films does not change from the result of XPS. The phase transition temperature of Mo^{6+} doped VO_2 thin films is obviously lowered with the increasing MoO_3 doped concentration, although the magnitude of resistivity change is also decreased, when the MoO_3 doped concentration is 5 wt.%. The phase transition temperature is lowered to about 30°C, and the magnitude of resistivity change reaches 2 orders more. Therefore, it can still well satisfy with application need of switching properties of VO_2 thin films and it is widened for VO_2 thin films in application ranges.

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