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Thermochromic characteristics of WO_3-doped vanadium dioxide thin films prepared by sol–gel method

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Abstract

Thin films of tungsten-doped vanadium oxide were fabricated on an alumina substrate by spin coating technology. A V_2O_5 solution was prepared by an inorganic sol–gel method, which was a fairly cheap and effective process. As-coated V_2O_5 films turned to VO_2 films during heat treatment in a reducing gas flow. Non-doped VO_2 film exhibited the best switching property of 4.0 orders of magnitude of electrical resistance and a small hysteresis of approximately 5 °C width. Tungsten in VO_2 led to a diffuse phase transition and weak jump of electrical resistivity. A reduction of the transition temperature by 15.5 °C/mol was observed for the tungsten doping in this study.

Keywords: A. Films; C. Electrical properties; E. Thermal applications; Thermochromic

1. Introduction

Global warming is receiving worldwide attention, and means to alleviate its harmful consequences are much in focus. Major changes in energy technology will be necessary, and will impact the global economy [1]. Intelligent window coatings respond to an external stimulus with increasing sophistication on an 'as needed' basis, this includes thermochromic coatings. Thermochromic window coatings offer new possibilities for achieving energy efficiency in windows.

The most widely studied thermochromic material is VO_2, which is characterized by a semiconductor-to-metal transition occurring from a reversible change in the crystalline structure as a function of the temperature [1–4]. This change has been observed in transition-metal oxides such as Ti_2O_3, Fe_3O_4, Mo_9O_{26} and in several Magneli phases of vanadium oxide, V_nO_{2n-1}. Among them, VO_2 has been received most attention because of the large reversible change of electric, magnetic, and optical properties at temperatures around 68 °C, which is, compared with the other materials, nearest to room temperature. During the semiconductor–metal transition, the optical properties of vanadium dioxide are characterized by a sharp decrease in optical transmission in the infrared spectrum. This is coupled with an increase in its resistivity. Because of this anomalous behaviour, vanadium dioxide has been presented as an attractive thin film material for electrical or optical switches [5], optical storage [6], laser protection, and solar energy control for windows [7].

For practical use, however, it is necessary in most cases that the transition temperature be reduced to near the ambient, and efforts have been made to reduce it by doping with metals such as W, Nb, Mo, and Ta or non-metals such as F and P [8,9]. The hysteresis profile associated with the transition depends on the microstructure and crystallinity. Tungsten has been shown to be the most effective dopant ion in reducing the metal–semiconductor transition of VO_2, it can optimally lower the T_c to about 25 °C at 2 at.% loading [10]. A quite precise relationship between transition temperature and the W concentration has been reported for the $V_{1-x}W_xO_2$ films deposited by dual-target sputtering, which gave a T_c reduction efficiency of 24 °C/at.% W [11].

Tungsten-doped VO_2 films have been previously prepared by sol–gel [2], physical vapour deposition methods [12] and CVD; both atmospheric pressure [13,14] and aerosol-assisted

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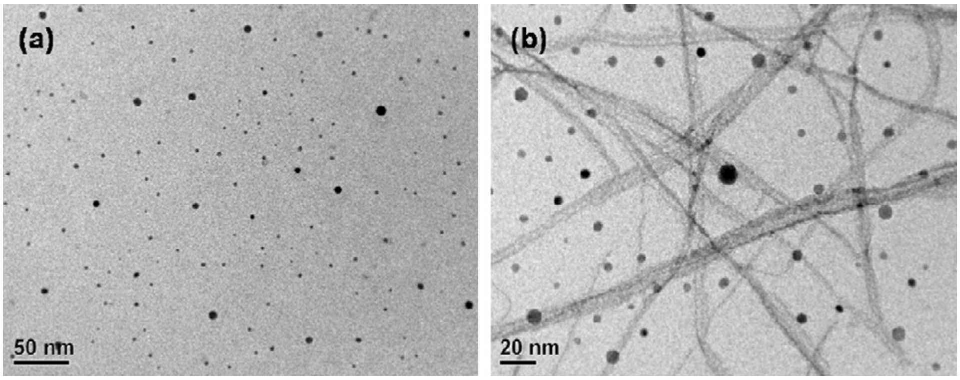

Fig. 1. TEM images of the dispersed V_2O_5 nano-particles in solution: (a) pH 2.3 and (b) pH 3.5.

[15]. No work has, however, been reported on tungsten-doped VO_2 films by an inorganic sol–gel method (a quenching method), which is fairly effective for preparing pure VO_2 thin film [16]. In this study, the electrical properties of tungsten-doped vanadium oxide ($V_{1-x}W_xO_2$) films prepared by an inorganic sol–gel method were investigated.

2. Experimental

Thin films of tungsten-doped vanadium oxide were coated on alumina substrate. The compositions of these films were prepared with $x = 0$, 1, 2 and 3 mol%. Reagent grade (>99.0% purity) V_2O_5 and WO_3 were used as starting materials. In a typical experiment, 13 g of V_2O_5 and WO_3 powder mixture were put into a Pt crucible and melted at 800–900 °C for 10 min in air. The molten liquid was quickly poured into distilled water and then a brownish V_2O_5 sol, which included a lot of precipitates, was formed. Three steps filtration was performed to eliminate the precipitates. First, large precipitates were eliminated using a centrifugal separator with 3000 rpm for 10 min. The first filtrated solution was passed through 1 μm filter paper and then 0.8 μm filter paper was used to obtain the final V_2O_5 solution.

In the present investigation, V_2O_5 thin films were deposited on alumina substrates by spin coating technology. Using 50 μl pipette, 10 μl of the stock solution was placed on the surface of the substrate and spun with 2500 rpm speed for 60 s in order to spread the solution on the entire surface of the substrate. Thicker films were prepared by repeating this process. The films were dried at 80 °C for 10 min. Lastly, the dried V_2O_5 films were heat-treated at different temperatures ranging from 400 to 600 °C at the rate of 10 °C/min for 0.5–2 h in $90N_2/10H_2$ mixed gas flow (reduced atmosphere) in order to obtain a VO_2 phase.

The pH of the solution was measured by pH-meter (CG842, SCHOTT, German). To evaluate the phase formation of the VO_2, the X-ray diffraction (XRD) was used (D/MAX-2500V, RIGAKU, Japan). The morphology of the films was observed using scanning electron microscope (SEM, JSM-6700F, JEOL, USA). The resistivities were measured using multimeter (Keithley 2010, USA) and transmittance measurements were performed on a UV–Vis spectrophotometer (V-570, JASCO, Japan) between 200 and 1300 nm. The TEM experiment was carried out on a JEM-4010 (JEOL Ltd., Japan) operated at 200 kV.

3. Results and discussion

V_2O_5 melt was dispersed in water during a quenching process. The pH of these solutions after quenching and filtering was in the range of 2.5–2.8. To improve the stability of the solution, the effect of pH on the stability was observed with adding nitric acid. The V_2O_5 solution was most stable in the range from pH 2.2 to 2.5. When the pH was higher than 2.5, the solution rapidly changed to gel due to its instability. Fig. 1 shows TEM images of the dispersed V_2O_5 nano-particles in solution. The nano sized particles were well dispersed and their sizes were 5–10 nm (Fig. 1(a)), and gelation occurred in a high pH solution as shown in Fig. 1(b).

The as-coated V_2O_5 films turned to VO_2 films, which successfully switched upon heating through the transition temperature, during heat treatment in a reducing gas flow. A monoclinic VO_2 phase was obtained after heat treatment at 500 °C for 1 h. Further thermal treatment at a higher temperature or for a longer time led to more-reduced vanadium

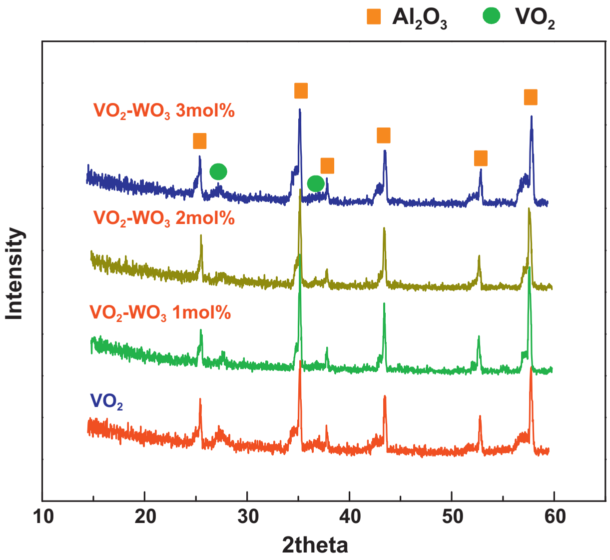

Fig. 2. XRD patterns of VO_2 thin film on alumina substrate with WO_3 contents.

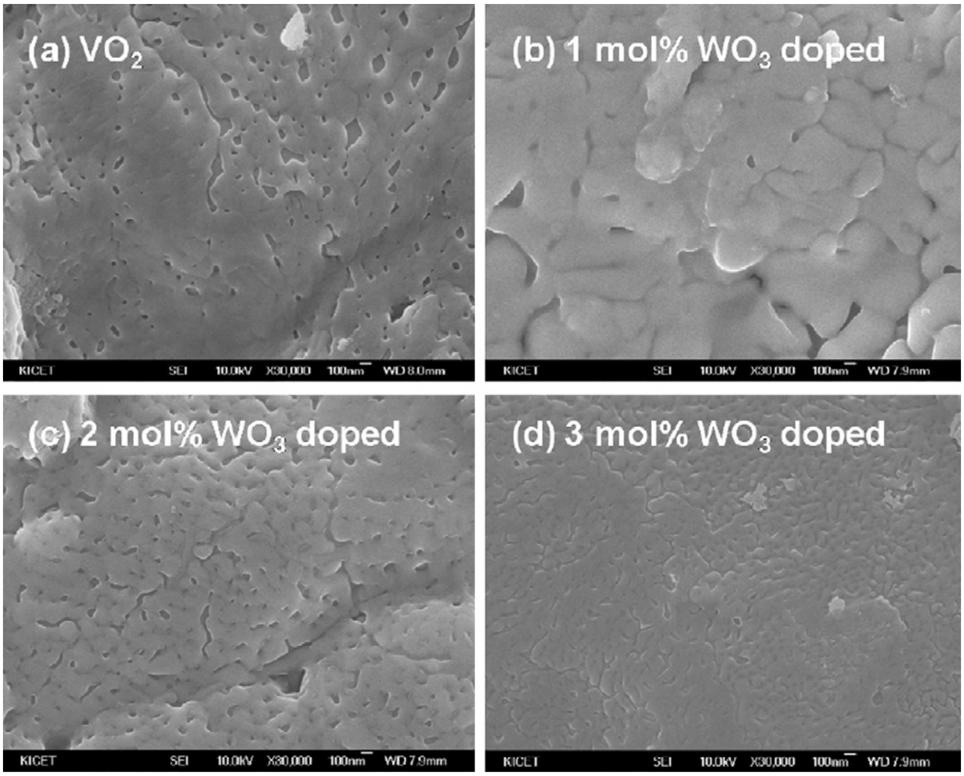

Fig. 3. The surface microstructures of VO_2 thin films with the following WO_3 contents: (a) pure VO_2, (b) 1 mol% WO_3, (c) 2 mol% WO_3 and (d) 3 mol% WO_3.

oxides, such as V_2O_3. Fig. 2 shows the XRD patterns of vanadium oxide films with WO_3 contents. The peak at 27.8° corresponding to the (0 1 1) plane diffraction of the monoclinic phase confirms that the vanadium oxide films on substrates are monoclinic VO_2. Other square-marked peaks in Fig. 2 are attributed to the alumina substrate. No peaks corresponding to WO_3 were observed because a solid solution of tungsten in VO_2 could be formed with tungsten ions substituting for some of the vanadium ions in the lattice. This is the reasonable situation for tungsten to have an affect on the thermochromic switching temperature of the VO_2 thin films. If WO_3 was segregated from the VO_2 matrix as a second phase, these composites would be expected to show no reduction in the transition temperature [17].

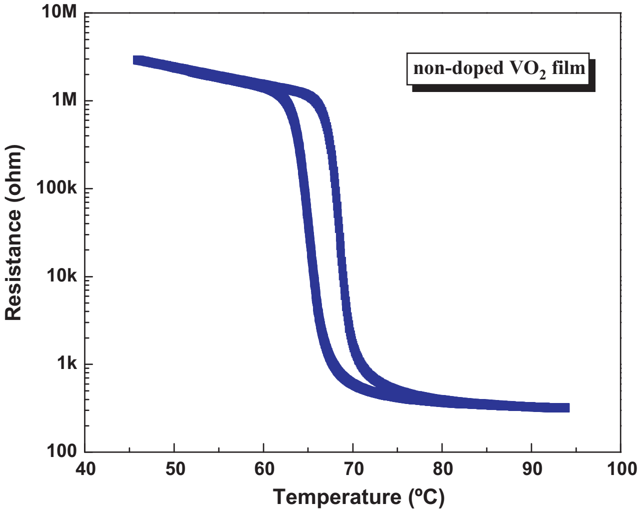

Fig. 4. Resistance of non-doped VO_2 thin film as a function of temperature.

Fig. 3 shows the surface micrographs of VO_2 thin films containing 0, 1, 2 and 3 mol% WO_3. The films consisted of small grains and a lot of pores. It is obvious that WO_3 addition in the VO_2 composition led to a significant change in the average grain size and pore size. The average grain size of the VO_2 films increased from 300 to 1000 nm with the addition of 1 mol% WO_3. However, it is evident from these SEM micrographs that the addition of more than 1 mol% WO_3 resulted in a decrease in the average grain size.

Electrical measurements were performed in the 20–100 °C temperature range. A typical hysteresis cycle was observed. The resistivity of VO_2 thin film dropped rapidly above the transition temperature and the insulating state was recovered upon cooling. Fig. 4 shows the electrical resistivity switching of the non-doped sample. Non-doped VO_2 film exhibited the best switching property of 4.0 orders of magnitude of electrical resistivity as the temperature was cycled through the phase transition. Compared to films obtained by the other techniques [12–15], the electrical transition of the non-doped film was sharper and characterized by a small hysteresis of approximately 5 °C in width. This switch in resistivity was noticeable more abrupt than the other sample, and such sharpness of transition is usually interpreted as indicating the film is close to the exact stoichiometry of VO_2 [18].

The extent of the reduction in thermochromic transition temperature could be related to the tungsten content of the film as shown in Fig. 5. A reduction of the transition temperature by

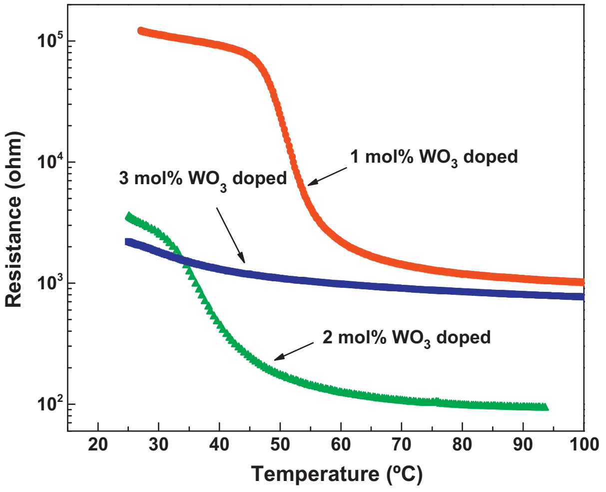

Fig. 5. Temperature dependence of the resistance of tungsten-doped VO_2 thin.

15.5 °C/mol was observed for the tungsten doping. With an increasing tungsten content, the width of phase transition broadened fairly and the jump of resistivities of the tungsten-doped films were somewhat lower than that of pure VO_2 film, that is, tungsten doping led to a diffuse phase transition and weak jump of electrical resistivity.The semiconductor–metal transition of the vanadium oxides is influenced very strongly by the stoichiometry of the oxides and by doping. An increase of the oxygen content gives rise to a reduction of the transition temperature with a simultaneous reduction of the change in resistivity [19]. When W^{6+} substitutes V^{5+}, the defect chemistry can be described as follows:

$$[\text{case 1}]\quad WO_3 \xrightarrow{VO_2} W_V^{\bullet} + e' + \frac{1}{2}O_2 \tag{1}$$

$$[\text{case 2}]\quad 2WO_3 + V_O^{\bullet\bullet} \xrightarrow{2VO_2} 2W_V^{\bullet} + 5O_O + \frac{1}{2}O_2 \tag{2}$$

In case 1, the W^{6+} substituted into the V^{5+} site leads to generation of free electrons to neutralize the total charge. The reduction of room temperature resistance with tungsten content could be appropriately explained by a reaction, attributed to these electrons. In case 2, the oxygen of WO_3 occupies an oxygen vacancy in the VO_2 matrix. As a result, the decrease of the concentration of the oxygen vacancy could contribute to large interplannar distance and low transition temperature. However the change of room temperature resistance could not be explained by the reaction because the concentration of a charge carrier was constantly maintained. Ye et al. [17] reported that a large interplannar distance results from the ionic size difference between W^{6+} (0.6 Å) and V^{5+} (0.46 Å). Large ion (W^{6+}) leads to increases of lattice parameters and decreases of lattice distortion. Thus we assume that the reaction of case 1 is a more valid mechanism than that of case 2 in the tungsten-doped VO_2 material.

4. Conclusions

Thin films of tungsten-doped vanadium oxide were coated on an alumina substrate by spin coating technology. The V_2O_5 solution was prepared by an inorganic sol–gel method and was most stable in the range from pH 2.2 to 2.5. As-coated V_2O_5 films turned to VO_2 films during heat treatment in a reducing gas flow. A monoclinic VO_2 phase was obtained after heat treatment at 500 °C for 1 h. The non-doped VO_2 film exhibited the best switching property of 4.0 orders of magnitude of electrical resistivity. Compared to films obtained by the other techniques, the electrical transition of the films prepared by the inorganic sol–gel method was sharper and characterized by a small hysteresis of approximately 5 °C in width. This switch in resistivity is noticeably more abrupt than the other sample, and such sharpness of transition is usually interpreted as indicating the film is close to the exact stoichiometry of VO_2. A reduction of the transition temperature by 15.5 °C/mol was observed for the tungsten doping. Tungsten in VO_2 led to a diffuse phase transition and weak jump of electrical resistivity. The transition temperature could be expected to shift to room temperature (25 °C) by doping 2.7 mol% WO_3.

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