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A novel wet process for the preparation of vanadium dioxide thin film

S. DEKI, Y. AOI, A. KAJINAMI
Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Rokkodai-cho, Nada-ku, Kobe 657, Japan

Thin films of vanadium oxide have been prepared from an aqueous solution system of (V_2O_5–HF aq.) with the addition of aluminium metal by a novel wet-preparation process which is called liquid-phase deposition (LPD). From X-ray diffraction measurements, the as-deposited film was found to be amorphous and it was then crystallized to V_2O_5 by calcination at 400 °C under an air flow. In contrast, the monoclinic VO_2 phase was obtained when the deposited film was calcined under a nitrogen atmosphere. The deposited film showed excellent adherence to the substrate and was characterized by a homogeneous flat surface. The deposited VO_2 film exhibited a reversible semiconductor–metal phase transition around 70 °C and its transition behaviour depended on the way in which the film was prepared.

1. Introduction

Transition metal oxides possess a number of interesting optical and electrical properties. Therefore, they are widely used as inorganic functional materials in many fields of application. As thin films, they will find application in many electrical and optical devices.

Generally, the preparation methods of metal oxide thin films can be classified into two groups. One group includes dry processes, such as vacuum evaporation, sputtering and chemical vapour deposition. The other group includes wet processes, such as dipping or spin coating of some suitable precursors. Recently, these processes have been widely applied to prepare many metal oxide thin films. However, there are several engineering problems associated with these processes. For the former methods, a special apparatus is required for the deposition of films, whereas it has been found that conventional wet processes are not suitable for coating the surface of substrates with a large surface area and/or complex morphology.

A new process, which overcomes some of these problems, has been developed. This process is called the liquid phase deposition (LPD) process [1, 2]. In this process, thin films of metal oxide can be deposited directly on to the immersed substrate. Use is made of the ligand exchange equilibrium reaction between the metal fluoro-complex ion and metal hydroxide or metal oxide in aqueous solution. The addition of boric acid or aluminium metal as a scavenger for F^- will shift the chemical equilibrium. In this process, thin films of metal oxide or metal hydroxide can be deposited directly from the liquid phase without the use of special equipment. Hence this process is easy to apply to various kinds of substrates with a large surface area and complex surface morphology.

In the present study, we have attempted to deposit thin film of vanadium dioxide, VO_2, from an aqueous solution by the LPD method. VO_2 is known to have a reversible thermally induced semiconductor-to-metal phase transition around 68 °C. Electrical conductivity and infrared reflectivity increase abruptly when going through the transition temperature [3, 4]. The crystal of VO_2 undergoes a first-order phase transition from a low-temperature monoclinic structure to a high-temperature tetragonal structure [5]. In order to avoid the deterioration by volume change during the transition, the use of VO_2 in the form of thin film is proposed [6]. Thin films of VO_2 have been prepared by a variety of techniques such as reactive sputtering [7, 8], reactive evaporation [9], chemical vapour deposition [6, 10, 11] and sol-gel processes [10, 12, 13]. In these methods, precise control of the deposition atmosphere is necessary, because of the narrow stability range of the phase [14], in order to obtain a stoichiometric VO_2 film.

In this paper, we report a novel and very simple process for the synthesis of thin films of VO_2 by the LPD process. Electrical properties of the deposited VO_2 films are also described.

2. Experimental procedure

2.1. Liquid-phase deposition process

Vanadium (V) oxide (Nacalai Tesque Inc.) was supersaturated in 5% aqueous solution of hydrofluoric acid (Hashimoto Chemical Corp.). The concentration of the vanadium ion was 0.384 mol dm^{-3}. This solution was then diluted to 0.15 mol dm^{-3} of vanadium ions with distilled water, and then supplied to the treatment solution. Non-alkali glass (Corning, no. 7059) was used as a substrate. After degreasing and washing ultrasonically, the substrate was immersed into the treatment solution and kept suspended vertically. Then 99.98% aluminium metal plate, which acts as

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a free F^- ion scavenger, was placed around the suspended substrate, and the solution was maintained at 30 °C for 40 h. After 40 h, the sample was taken out of the treatment solution, washed with distilled water and dried at room temperature. Calcination of the deposited films was carried out at various temperatures under an air flow or a nitrogen atmosphere.

2.2. Characterization and electrical properties of the deposited film

X-ray diffraction of the deposited film was measured by using a Rigaku RINT-2100 diffractometer with a thin film attachment and using CuK_α radiation. Infrared (IR) absorption spectra of the deposited films were measured with an A-302 IR spectrophotometer (Japan Spectroscopic Co. Ltd) over the region 5000–330 cm^{-1}. The surface morphology of the film was observed by scanning electron microscopy (SEM) (Hitachi, S-2500).

In order to clarify the dissolved species in the treatment solution, the ultraviolet–visible (UV–VIS) spectrum of the solution was measured with a UVIDEC 660 (Japan Spectroscopic Co. Ltd) over the region 910–310 nm with an acrylic cell.

The transition behaviour observed in the electrical conductivity values of the deposited VO_2 film was measured using a conventional two-probe method. Silver paste was coated in a coplanar geometry to serve as the electrodes. The sample was located on a temperature-controlled electric heater plate, and heated at a rate of 2 °C min^{-1} in a heating cycle. In the cooling cycle, a spontaneous decrease in the temperature value was adopted. The transition temperature, (T_t), is taken as the temperature at which the midpoint of the conductivities at 40 and 90°C in a heating cycle occurs after cycling three to four times through T_t.

3. Results and discussion

3.1. Preparation and characterization of the film

After treatment for several tens of hours, a brownish film was deposited on the substrate. The deposited film showed excellent adherence to the substrate. At the bottom of the reaction cell, a brownish powder was observed which was similar to the deposited film.

Fig. 1 shows the X-ray diffraction patterns for the deposited films which were calcined at various temperatures under an air flow. It can be seen that the as-deposited film and the films calcined at 100 and 200 °C were amorphous without any significant diffraction peaks. However, the films calcined above 300 °C were crystalline. Diffraction peaks assigned to V_3O_7 and V_2O_5 were observed for the film calcined at 300 °C, while diffraction peaks of V_2O_5 were observed for the film calcined at 400 °C. V_3O_7 is a mixed oxide, one of the intermediates formed by oxidizing from V(IV) to V(V), consisting of VO_2 and V_2O_5.

IR spectra of the deposited films are shown in Fig. 2. Broad absorption bands were observed for the as-deposited film and the films calcined at 100 and 200 °C. The IR spectrum of the as-deposited film showed an absorption band at 970 cm^{-1}. This band shifted towards the higher energy side with increasing values of the calcining temperature. For the films calcined at 300 and 400 °C, the shifted band was observed at 1020 cm^{-1}, which is assigned to the V–O stretching mode of vanadium oxide [15, 16]. This result indicates that the V–O bond length of the as-deposited film and the films calcined at low temperatures is longer than that of the films calcined at 300 and 400 °C. The IR spectra for the film calcined at 300 and 400 °C also showed absorption bands at 820 and 620 cm^{-1}, which are assigned to the V–O–V deformation mode of vanadium oxide [15, 16]. The broadening of the absorption bands for the as-deposited film and the films calcined at low temperatures indicates a wide distribution of the bond length between the vanadium ion and oxygen.

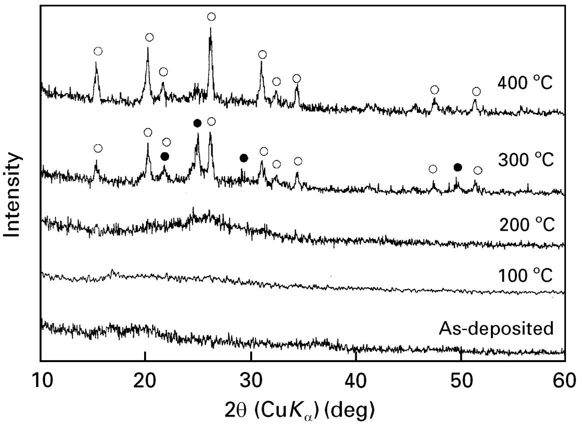

Figure 1 X-ray diffraction patterns of the deposited films calcined at various temperatures for 1 h under air flow. (○) V_2O_5, (●) V_3O_7.

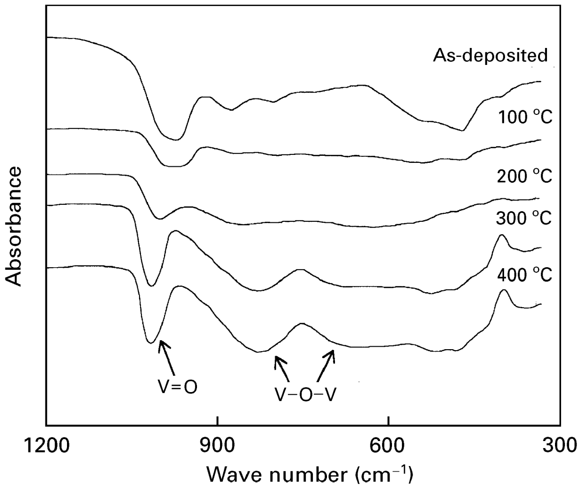

Figure 2 IR absorption spectra of the deposited films calcined at various temperatures for 1 h under air flow.

These X-ray diffractions and IR spectra indicate that the as-deposited film was mainly composed of vanadium ions in the reduced state, that is V^{4+}, and it was oxidized and crystallized during the calcination under an air flow.

In order to clarify the mechanism of deposition, soluble species in the treatment solution were investigated by UV–VIS absorption spectroscopy. Fig. 3

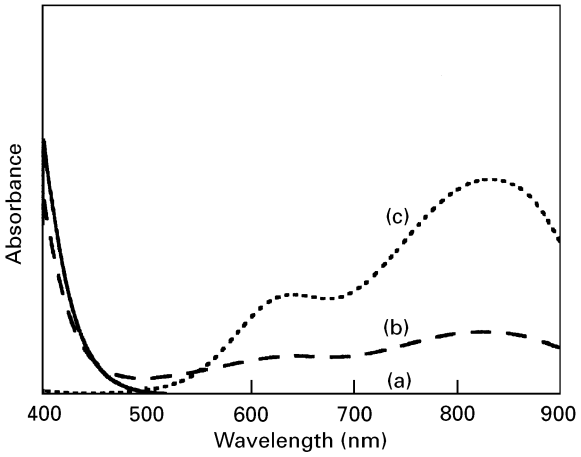

Figure 3 UV–VIS spectra of the treatment solution (a) before and (b) after 2.5 min and (c) 15 min addition of aluminium metal.

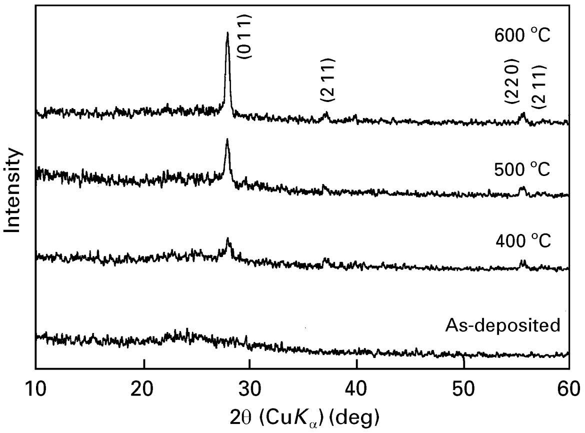

Figure 4 X-ray diffraction patterns of the deposited films calcined at various temperatures for 1 h in a nitrogen atmosphere.

shows UV–VIS absorption spectra of the treatment solutions before and after addition of aluminium metal. The spectrum of the treatment solution before the addition of aluminium has an absorption edge which rises at 500 nm, and no other absorption bands were observed. The absorption band below 500 nm was assigned to a charge transfer band of the complex ion of V^{5+} [17]. After the addition of aluminium, the spectrum can be seen to change. The absorption band below 500 nm decreased gradually with time and disappeared completely after 15 min, and two kinds of absorption bands were observed in the VIS region. The absorption bands at 630 and at 830 nm were assigned to the $^2B_2 \rightarrow {}^2B_1$ transition and $^2B_2 \rightarrow {}^2E(I)$ transition of vanadyl ion, VO^{2+} [18], respectively. From these results, it is concluded that the vanadium ion in the initial treatment solution was V^{5+} and it was reduced to V^{4+} by the addition of aluminium which behaves as a F^- scavenger. In the treatment solution, VO^{2+} is co-ordinated by fluorine ions, and forms a fluoro-oxy complex ion, $[VOF_n]^{2-n}$. In addition, following the F^- ion releasing reaction, the film deposition process takes place

$$[VOF_n]^{2-n} + xH_2O \rightleftharpoons [VOF_{n-x}(OH)_x]^{2-n} + xHF \qquad (1)$$

The ligand exchange equilibrium Reaction 1 is shifted to the right-hand side by the addition of aluminium metal which reacts with the F^- ion. Finally, the dehydration reaction occurs forming $[VO(OH)_n]^{2-}$ which is generated in the ligand exchange reaction of $[VOF_n]^{2-n}$, and then the deposition of vanadium oxide occurs.

It has been demonstrated that a VO_2 film can be obtained by calcination of the deposited film under an inert atmosphere. When the deposited film was calcined in a nitrogen atmosphere, a greenish film was obtained. Fig. 4 shows the X-ray diffraction patterns of the deposited films which were obtained by the calcination at various temperatures in a nitrogen atmosphere for 1 h. The monoclinic VO_2 phase was observed for the film calcined above 400 °C. No other crystalline phases can be detected from X-ray diffraction data. Diffraction peaks of VO_2 became intense and the full-width at half-maximum of the diffraction peaks became narrow with increasing calcining temperature, indicating that the crystallinity of the VO_2 film was advanced with increasing calcining temperature. The diffraction from the (0 1 1) plane of monoclinic VO_2 for the deposited film is particularly intense compared with a randomly oriented powder of VO_2. These results indicate that the deposited film is partially oriented in the [0 1 1] direction. Similar phenomena are observed for thin films of VO_2 prepared by other methods, such as chemical vapour deposition [10] and sol–gel procedures [12].

Scanning electron micrographs of the deposited films calcined in a nitrogen atmosphere are shown in Fig. 5. The films were composed of particles. The particle sizes were several tens of nanometres in diameter for the film calcined at 400 °C, and around one hundred nanometres for that calcined at 500 °C. The surface microstructure of the film calcined at 600 °C is different from the other two: large particles about 150–300 nm in diameter were observed on the underlying small particles. A scanning electron micrograph of the cross-section of the deposited film which was calcined at 500 °C in a nitrogen atmosphere is shown in Fig. 6. The film exhibits a homogeneous flat surface and the thickness is ~500 nm.

3.2. Electrical properties of the LPD–VO_2 film

Electrical measurements were performed on the deposited VO_2 films obtained by the calcination at 400 and 500 °C in a nitrogen atmosphere. The film obtained by the calcination at 600 °C showed very high resistivity values of more than $30\,M\Omega\,sq^{-1}$. These high values may be due to the formation of some insulator phases, even though X-ray diffraction of the film showed only the peaks of VO_2, or alternatively the resistance of the sample may be dominated by the high resistance of the crystallite boundaries.

Typical transition behaviour of the electrical resistivity is shown in Fig. 7, where it can be seen that the resistivity value fell abruptly around 70 °C. A heating–cooling hysteresis of about 10 °C was observed.

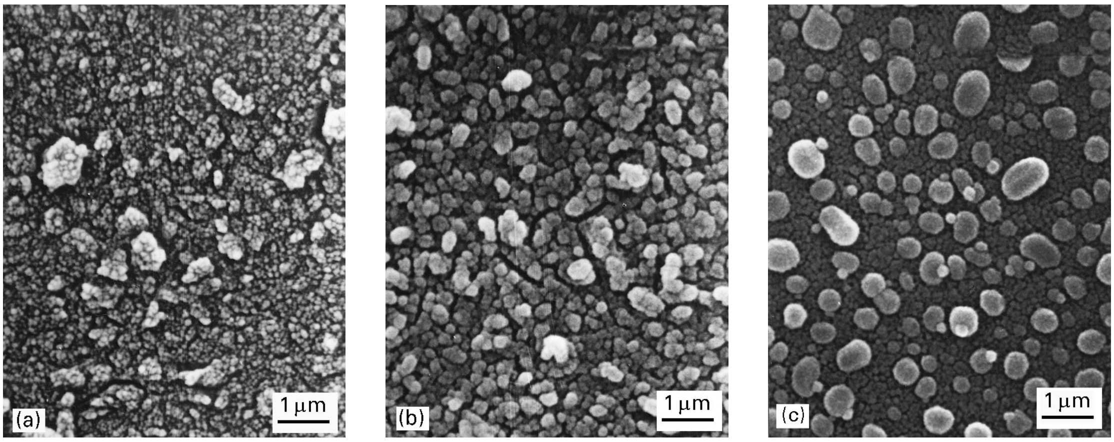

Figure 5 Scanning electron micrographs of the deposited films calcined at various temperatures for 1 h in a nitrogen atmosphere. (a) 400 °C, (b) 500 °C, (c) 600 °C.

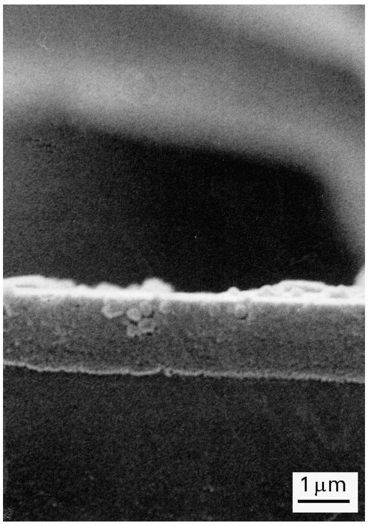

Figure 6 Scanning electron micrograph of the cross-section of the deposited films calcined at 500 °C for 1 h in a nitrogen atmosphere.

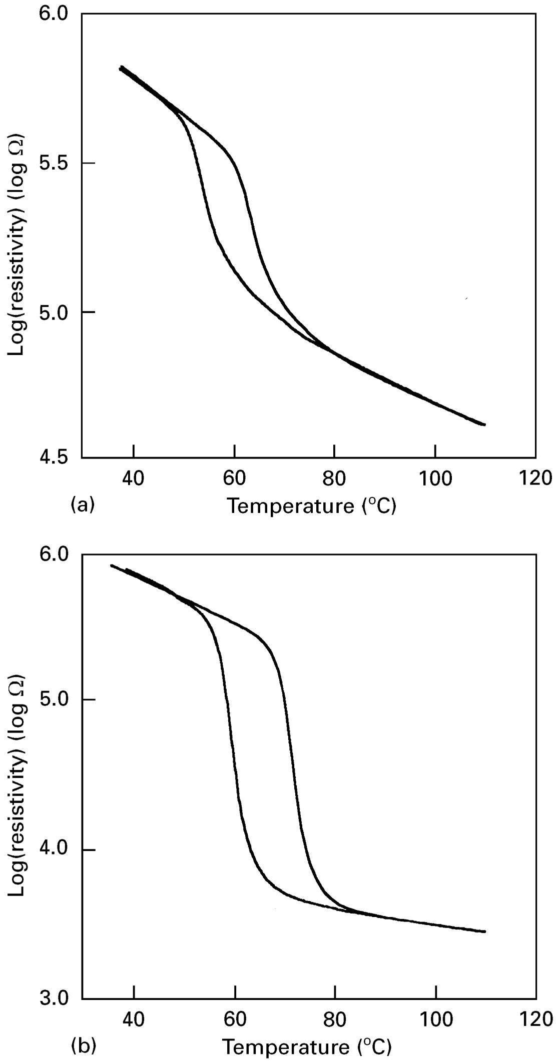

Figure 7 Typical transition behaviour in electrical resistivity of the LPD–VO_2 films calcined at (a) 400 °C and (b) 500 °C.

The change in resistivity with temperature for the film obtained by the calcination at 500 °C was sharper than that obtained by the calcination at 400 °C. The transition temperature, (T_t), the ratio of the conductivity at 90 and 40 °C, and the activation energy of conduction for below and above T_t for the film obtained under several preparation conditions, are summarized in Table I. The transition temperature for the film obtained by the calcination at 400 °C was lower than that obtained by the calcination at 500 °C, and the ratio of the resistivity for the film obtained by the calcination at 400 °C was smaller than that obtained by the calcination at 500 °C. Begishev *et al.* [19] and Griffiths and Eastwood [14] indicate that the transition behaviour depends on both structural and compositional factors. The broadening of the transition behaviour for the film obtained by the calcination at 400 °C is attributed to an inhomogeneous distribution of transition temperature in the deposited film because of the spatial inhomogeneity in the distribution of the factors leading to change in transition temperature [19]. The film obtained by the calcination at 400 °C was deficient in crystallinity in comparison with that obtained by the calcination at 500 °C, thus it remained a much more amorphous phase. The existence of the substantial amorphous phase caused the broadening of the transition behaviour. The crystal imperfection also affects the transition temperature. It is clear from Table I, that the transition temperatures for the films obtained by the calcination at 400 °C were lower by about 10 °C than those

TABLE I Preparation conditions of the LPD–VO_2 films and the electrical conductivity data

Reaction time (h)	Calcining temperature (°C)	Transition temperature (°C)	σ_{90}/σ_{40}	Activation energy (eV)	
				$T < T_t$	$T > T_t$
40	400	65.2	10	0.26	0.22
40	500	72.4	200	0.32	0.14
70	400	66.2	90	0.29	0.14
70	500	76.4	450	0.34	0.12

obtained by the calcination at 500 °C. This is also explained by the differences observed in crystallinity between the film obtained by the calcination at 400 and at 500 °C. In addition, compositional factors are also important in accounting for the differences in the transition temperatures. The non-stoichiometry of the material, which is, for example, caused by the presence of V^{3+} or V^{5+} ions, has an influence on the transition temperature. It is reasonable to assume that the LPD–VO_2 film is non-stoichiometric, although exact compositions of the deposited films have not been determined. The non-stoichiometry of the film depends on the preparation conditions; therefore, the transition temperature changes due to changes in the preparation conditions of the film.

In the high-temperature state, a single crystal of VO_2 or high-quality oriented VO_2 films, exhibit a positive temperature coefficient of resistivity, characteristic of metallic behaviour [3, 9, 20]. In the LPD–VO_2 films, the temperature coefficients of resistivity were all negative in the high-temperature state. These results indicate that the LPD–VO_2 films were non-stoichiometric and/or the existence of some other semiconductor phases of vanadium oxide. In the low-temperature state, that is, semiconductor state, a linear Arrhenius behaviour was observed, which provides a measure of the activation energy of conduction. The values of the activation energies of conduction, which are reported to be sensitive to the film stoichiometry [21, 22], for the LPD–VO_2 films, are in the range 0.26–0.34 eV, which is consistent with the range of reported values [20, 23].

4. Conclusion

The LPD process was applied to the preparation of thin films of vanadium oxide. These films have been deposited on to the immersed substrate from the aqueous solution system of (V_2O_5–HF aq.) with the addition of aluminium metal by using the ligand exchange equilibrium reaction. The deposited film showed excellent adherence to the substrate and a homogeneous flat surface. The as-deposited film was amorphous and contained reduced-state vanadium ions. By calcination under an air flow, the film crystallized and oxidized to a mixture of V_3O_7 and V_2O_5 at 300 °C, and to V_2O_5 at 400 °C. The monoclinic VO_2 phase was obtained when the film was calcined in a nitrogen atmosphere above 400 °C. This VO_2 film was partially oriented in the [0 1 1] direction. No other phases were detected from the X-ray diffraction measurements.

The VO_2 film exhibited metal–semiconductor transition around 70 °C accompanied by a heating–cooling hysteresis of about 10 °C. The transition temperature and sharpness of the transition behaviour depended on the preparation conditions of the film. The transition temperature for the film obtained by the calcination at 500 °C was higher than that obtained at 400 °C, but the ratio of the conductivity for below and above the transition temperature was larger than that obtained at 400 °C.

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