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Vanadium Oxide Film Growth onto Various Buffer Layers Deposited by RF Magnetron Sputtering

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Vanadium oxide films were deposited by RF magnetron sputtering onto a silica glass substrate or silica glass substrates coated with various metal thin film buffer layers. V_2O_5 film was deposited without some buffer layers, however, VO_2 film was deposited onto V and W buffer layers under the V_2O_5 film deposition condition. From the surface morphology analysis by AFM measurements, it was proved that nucleation density was increased by presence of V or W buffer layer. When VO_2 film deposited onto W buffer layer, transition temperature of the deposited film was fallen down.

Keywords: metal - Insulator transition, vanadium oxide, buffer layer, reactive sputtering, surfactant

1. Introduction

Metal - Insulator transition temperature T_t of VO_2 is 68°C, and it could be used as a smart window by means of VO_2 coating on a glass [1-7]. This is the reason why VO_2 bulk or films had been widely studied. T_t of VO_2 could be fallen down by addition of cations (for example Mo, W, ···) which forms a solid solution [8]. VO_2 film coating on glass has been tried by sputtering method [5,7], however, the stoichiometry of vanadium oxide is very difficult to be controlled and the reproducibility was far from satisfactory.

In previous study, we deposited vanadium oxide films by RF magnetron sputtering [9], and the deposition rate of the VO_x films as a function of oxygen flow ratio deposited at substrate temperature of 400°C is shown in Fig. 1. When oxygen partial flow ratio was higher than that of the transition region, V_2O_5 films were deposited. Transition region indicates the region that deposition rate changes abruptly. V_2O_3, VO_2, and V_4O_9 films were deposited by controlling the oxygen partial flow ratio within the transition region, but the VO_2 deposition condition were very narrow region of oxygen partial flow ratio and high substrate temperature.

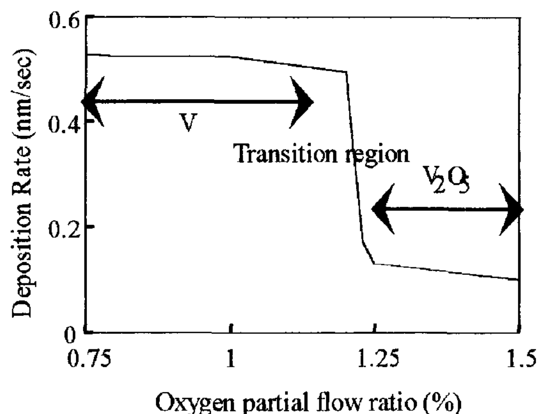

Fig. 1. The deposition rate of VO_x films as a function of the O_2 partial flow rate.

In this paper, vanadium oxide films were deposited either on a silica glass or onto those coated with various metal thin films as a buffer layer in-vacuum [10]. When vanadium oxide films were deposited onto Ti, V, Fe, Ni, W and Pt buffer layer, VO_2 film was deposited under wide partial Oxygen pressure region. When VO_2 films were deposited onto W buffer layer, the T_t of the deposited VO_2 film was fallen down.

2. Experimental details

Vanadium oxide thin films were deposited by RF magnetron sputtering using an ANELVA SPF-332H with a 3 inch-diameter 99.7% metallic V target. Vanadium oxide films were deposited onto silica glass substrates, or also deposited onto metal V, W, Ti, Fe, Au, Ag, and Pt thin film and the thickness of buffer layer films were about 10nm. Deposition of vanadium oxide films onto V, W, Ti, Fe, buffer layer were carried out in-vacuum. The substrate temperature was

400°C. The total sputtering pressure during growth of a film was 1 Pa of Ar and O_2 mixture gas and the O_2 / Ar ratio was 1.5%. The RF power applied to the cathode was 100W, and these conditions were maintained during the deposition.

The structures of the films were characterized by X-ray diffraction (XRD) measurement using a diffractometer RIGAKU RINT 2100. The surface morphologies of the deposited films were observed by an AFM with JEOL JSTM-4200D/A/S. When the AFM measurements were carried out, the chamber of the AFM instrument was evacuated down to 10^{-3} Pa. Visible and near infrared (wave length is 350 nm to 2500 nm) absorption spectra were measured with a spectrometer HITACHI U-3410. Concentration of various metal as a buffer layer vs V was observed by an XPS depth measurement with Phi Quantum 2000.

3. Results

The XRD profiles of vanadium oxide films onto silica glass, V and W metal thin films are shown in Fig. 2. The crystal structure of the film deposited onto a silica glass substrate was V_2O_5. When vanadium oxide films were deposited onto V or W buffer layer under the same condition, the VO_2 films were obtained, and crystalinity of VO_2 film deposited onto V buffer layer was higher than the one deposited onto W buffer layer.

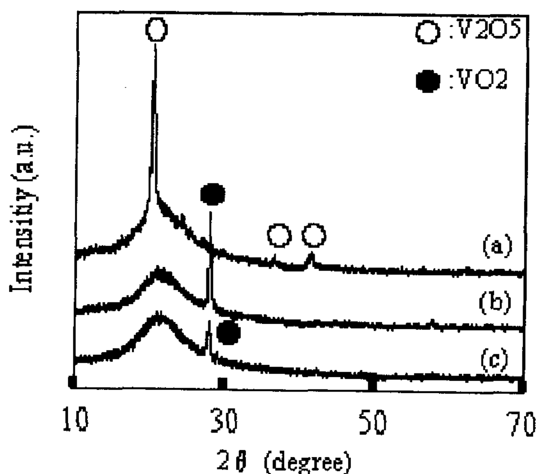

Fig. 2. The XRD patterns of the VO_x films deposited onto (a)silica glass, (b)V buffer layer, (c) W buffer layer.

Figure 3 shows the transmittance of these films at two regions of the temperature T, specifically at T_t (transition temperature) > T~20°C (close to a room temperature), and T_t < T~80°C. The transmittance of infrared region was higher for the low temperature semiconducting phase than for the high temperature metallic phase. Thus, it was obvious that the obtained VO_2 films in this study indicated a thermochromic property.

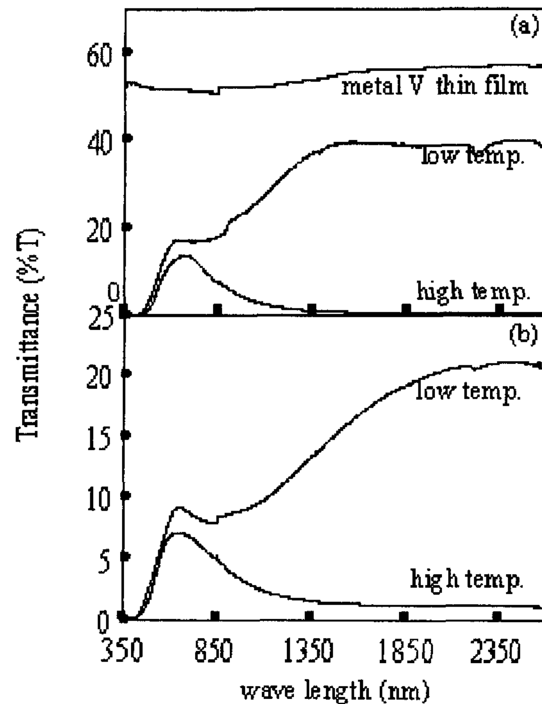

Fig. 3. Optical transmittance spectra for a VO_2 film (thickness: 150nm) deposited onto (a) V buffer layer and (b) W buffer layer.

Utilizing the absorption property of near infrared (wave length was 2000 nm), the transition temperature T_t of a VO_2 film was determined, as shown in Fig. 4 [11]. T_t of the sample which was deposited onto the V buffer layer was about 68°C and it was the same value of reported one [7]. T_t of the VO_2 film which was deposited onto W buffer layer was 53°C, and T_t of the sample was 15°C lower than the reported value [7]. To compare with a VO_2 film deposited onto a V buffer layer, the decrease in T_t was caused by the formation of solid solution of W into VO_2 film. W / V ratio was expected about 0.005 from the result of the transition temperature of the deposited VO_2 film onto the W buffer layer [7].

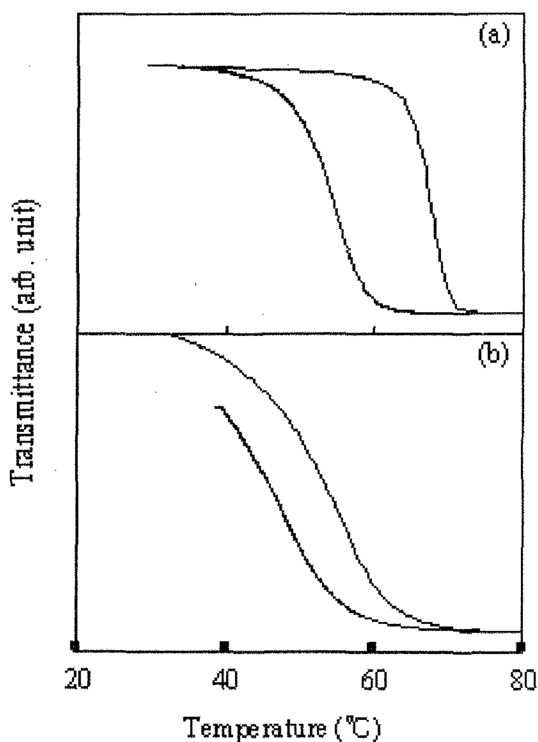

Fig. 4. Transmittance change (wave length was 1500nm) as a function of temperature for the VO_2 film deposited onto (a) V buffer layer and (b) W buffer layer.

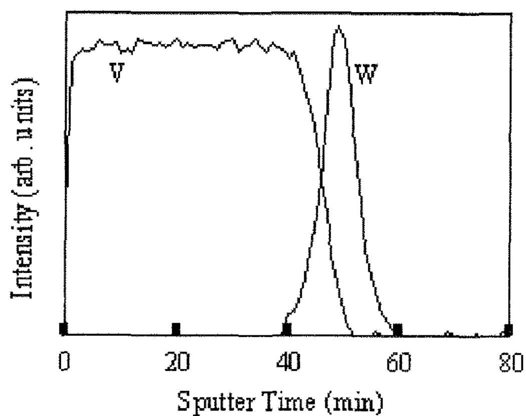

Fig. 5. The depth profiles of XPS signals for each element of W / V in the film.

W / V ratio of depth profile for the obtained vanadium oxide film is shown in Fig. 5 [12]. A few W atoms were observed in the vanadium oxide layer, however, W /V ratio could not be determined. W atoms did not exist on the film surface, i.e., surfactant effect was not observed.

4. Discussion

VO_2 films were deposited easily by the presence of V or W buffer layers. About these phenomena, various discussions could be considered. One is vanadium metal as a buffer layer reacted with oxygen in the career gas and VO_2 nucleus could be formed under the vanadium oxides deposition condition (considered only the case of the film deposited with vanadium buffer layer), thus, VO_2 film grew onto VO_2 nucleus. The others are that nucleation of VO_2 can occur easily on the W or V buffer layer, or reduction of the deposited vanadium oxide films is occur by various metal buffer layer taking in oxygen from the deposited oxide film.

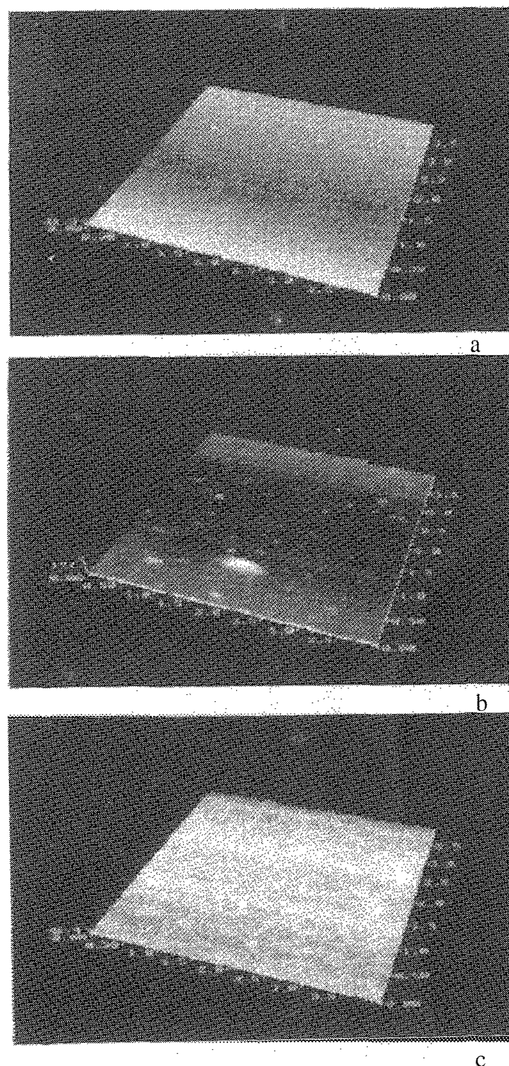

Fig. 6. The AFM images ($4\mu m \times 4\mu m$) of the vanadium oxide films deposited onto (a) a V buffer layer and (b) a W buffer layer and (c) a silica glass substrate.

Table 1. The Structure of the deposited films onto various buffer layers.

Metal	Ti	Fe	Ni	Cu	Ag	Pt	Au
Composition	VO_2	VO_2	VO_2	V_3O_7, V_2O_3	V_6O_{11}, (VO_2)	VO_2	V_5O_9

From the equilibrium oxygen pressure figure of V-O system, the pressure of the equilibrium oxygen partial pressure to form VO_2 is about $10^{-5} \sim 10^{-2}$ Pa under 400°C [13], thus, the previous discussion could be applied to this case.

AFM observations were carried out for these films, and the AFM photographs are shown in Fig. 6. The grain sizes of vanadium oxide onto V or W buffer layer was smaller and more homogeneous than the grain seize of vanadium oxide onto silica glass, and it was expected that VO_2 homogeneous nucleation was occurred onto V or W buffer layer. Thus, the later consideration could be also applied to this case.

Vanadium oxide films were deposited onto Ti, Fe, Ni, Cu, Au, Ag, and Pt buffer layer with the same condition. The structure of the obtained vanadium oxide films onto various buffer layers are shown in Table 1. Mixed phases were observed for the deposited films onto Ag, and a single phase of VO_2 could not be deposited onto Cu, Ag and Au buffer layer. Melting point of Ti, Fe, Ni and Pt are high, and of Cu, Au and Ag are not very high. The surfactant effect was observed in the films onto low melting point material buffer layers. Vanadium oxide films were deposited onto the buffer layer which was low melting point, this buffer layer material moved to the film surface, therefore, this effect prevented to be formed and grown a VO_2 film.

Vanadium oxide films were also deposited onto various oxide buffer layers (V_2O_5, FeO, ⋯)or substrates (TiO_2 single crystal, soda lime glass, ⋯) under the same condition, and V_2O_5 films were deposited onto them. When vanadium oxide film was deposited onto metal buffer layer, reduction of deposited vanadium oxide film was caused.

5. Conclusion

Vanadium oxide films were deposited onto various buffer layers under the V_2O_5 deposition condition, VO_2 films were deposited onto Ti, V, Fe, Ni, W, and Pt buffer layer. It is assumed that T_t of the VO_2 film deposited onto a W buffer layer was decreased because of W diffusion into the obtained VO_2 film. When vanadium oxide films were deposited onto the buffer layer which was low melting point, this buffer layer material moved to the film surface and VO_2 film could not be obtained. When vanadium oxide film was deposited onto metal buffer layer, nucleation on of low oxidation number of vanadium oxide and reduction of deposited vanadium oxide film were caused.

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