

Effects of microstructure and nonstoichiometry on electrical properties of vanadium dioxide films

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Voided growth structures of sputter-deposited films affect strongly their optical and electrical properties. Vanadium dioxide is an interesting material to study effects of film microstructure and nonstoichiometry on electrical properties because its phase transition makes it possible to investigate electrical behavior both in a semiconducting phase and in a metallic phase. We have deposited vanadium oxide films with different vanadium/oxygen ratios for substrate temperatures between 250 and 550 °C by dc reactive magnetron sputtering. The resistivity ratios between a semiconducting phase and a metallic phase are limited to 10^3 order by voided boundaries and oxygen vacancies. The voided boundaries are defined by columnar structure and agglomerated grain growth. The results emphasize the necessity of a combination of deposition to obtain the film with a favorable structure and postdeposition annealing to control the film stoichiometry.

I. INTRODUCTION

For polycrystalline or amorphous thin films, microstructure is a critical incident in order to obtain films with favorable properties. Voided growth structure is a result of poor diffusion of atoms on the substrate or film surface. An established growth structure model was proposed by Thornton.¹ As a result of the voided growth structure, it is generally found that electrical properties of a metal film with voided structures are similar to those of semiconductors, because of the current flow across the oxidized intergrains which induces a negative temperature coefficient of resistance. The void structure increases the film resistivity by one or two orders relative to the bulk resistivity. In reactive sputtering, reactive gas pressure is a crucial factor to determine the film structure.

From the viewpoint of studying the effects of the film microstructure and nonstoichiometry on electrical film properties, VO_2 is an interesting material because of its semiconductor-to-metal transition. The transition is a result of the phase transition from monoclinic to tetragonal rutile structure. Above the transition temperature, vanadium dioxide behaves as a metal, and below the transition temperature it behaves as a semiconductor. This interesting feature makes it possible to discuss the effects of the film microstructure and nonstoichiometry on film properties both in the metallic and semiconducting phases.

A generally accepted transition model was given by Goodenough.² A transition resistivity ratio obtained for a single crystal VO_2 is 10^5 , and transition temperature is $\sim 67^\circ\text{C}$.³ The transition resistivity ratio and transition temperature are strongly affected by degree of nonstoichiometry.^{4,5}

We have reported that VO_2 films have been obtained for a narrow range of O_2 injection rates by dc reactive sputtering and that the films yield resistivity ratios during the transition of as high as 5×10^3 . By comparing the resistivity data of the obtained films to those of a single crystal, we concluded that oxygen vacancies raised the carrier density, thereby decreasing

the semiconducting phase resistivity by one order, and that voided boundaries of columnar structures were the origin of the high metal phase resistivities.⁶

In this study, we deposited vanadium oxide films on fused silica glass substrates for substrate temperatures T_s between 250 and 550 °C, in order to investigate effects of substrate temperature on film properties. By introducing F_M (deposition flux intensity) as a control parameter, VO_2 films with several different vanadium/oxygen ratios have been obtained.

II. FILM DEPOSITION

Sputtering source was a 12.7-cm-diam. vanadium metal target (99.997%, Teledyne Wah Chang). The substrates were $25 \times 25 \times 1$ mm fused silica plates (Heraeus Quartz, Type T-08). The working gases were Ar (99.999%) and O_2 (99.998%), which were injected separately through Tylan type FC-260 mass flow controllers. The total pressure was measured with an MKS type 310BHS capacitive manometer. Apparatus was described elsewhere⁶ in detail. Although we used the oxygen injection rate as a control parameter in the previous study, it was not enough to control film stoichiometry because, as mentioned above, the range of oxygen injection rate (partial pressure) to obtain VO_2 films was very narrow and because film properties were too sensitive to the oxygen partial pressure within the range of VO_2 . In order to perform more detailed study near stoichiometry it is advantageous to use one of the variables that undergo a large variation in the transition region of the reactive sputtering, as a control parameter. Candidates were pressure change after the discharge ignition, vanadium emission line intensity, and deposition flux intensity F_M , measured by a quartz-crystal rate monitor.

The F_M was selected as a control parameter in this study, since it was convenient and had a good reproducibility. The region of the F_M used was about 1×10^{-7} – 1.6×10^{-7} g/cm² s. The rate monitor was mounted adjacent to the sub-

strates, and there was no difference in the deposition flux intensities between the two positions. The deposition flux was controlled by changing the sputtering current from 1.96 to 2.06 A continuously while other conditions were kept constant during a deposition [P_{O_2} (prior to ignition) = 0.60 mTorr and $P_{Ar} = 2.00$ mTorr for the pumping speed of 230 l/s for O_2 at the deposition conditions]. The P_{O_2} of 0.60 mTorr was found to be the critical value for VO_2 after depositions for P_{O_2} between 0.56 and 0.62 mTorr. F_M was only a control parameter in an empirical sense since both V and O content could vary as the current changes. A high incident flux yielded a higher V/O ratio in the flux, resulting in the oxygen deficit films. Changing the sputtering current was more controllable than changing the oxygen injection rate because the sputtering current affected the ion flux to the target which changes F_M directly, while the O_2 flow rate affected the O flux to both target and chamber wall, that may induce a time delay to achieve a steady state. Thickness of deposited films ranged from 250 to 500 nm. Resistivity was measured by the van der Pauw method. Resistivity transition ratio was defined by ratios of resistivities measured at 20 and 120 °C.

III. FILM PROPERTIES

In Fig. 1 the phases detected by x-ray diffraction measurement are shown. It should be noted that the second phase may not be detected by x-ray diffraction measurement because of a detection limit of the measurement. Higher substrate temperatures yielded a wide region of the incident flux where VO_2 were obtained. VO_2 films obtained were all (011) oriented. At the lower end of the incident flux, films were mixtures of VO_2 and V_6O_{13} or V_4O_9 . At the higher end, films were amorphous and might be mixtures with Magneli phases (V_nO_{2n-1}), whose existence reduced crystallinity of the films. At 250 °C, all films were amorphous. Those results agree with the results obtained by Griffiths *et al.*⁴

Figure 2 shows typical resistivity hysteresis curves of films with different degrees of nonstoichiometry. It is clear that

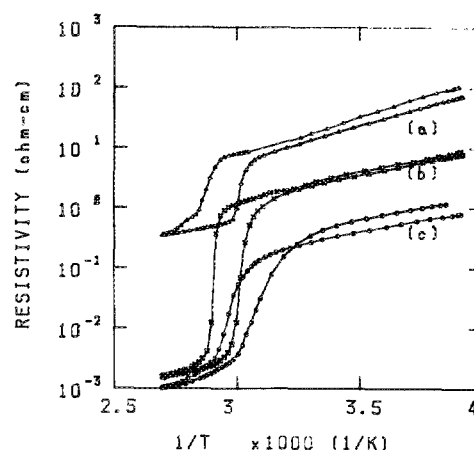


FIG. 2. Typical resistivity hysteresis curves for films with different degrees of nonstoichiometry: (a) O rich, (b) optimized V/O ratio, and (c) V rich.

the degrees of nonstoichiometry affect transition magnitudes and temperatures. The film providing the largest transition magnitude is expected to have an optimum V/O ratio. Although several analysis methods such as Auger electron spectroscopy (AES), mass analysis have been attempted in order to determine the degree of nonstoichiometry, accuracy is limited to > 5% for a V/O ratio of 0.5; that is not enough to estimate the degree of nonstoichiometry.

Figure 3 shows the resistivity ratios for several values of the incident flux and substrate temperature. The largest ratio was obtained at a substrate temperature of 400 °C. Single-phase VO_2 films exhibit resistivity ratios of $\sim 10^3$ except films deposited at 500 and 550 °C and low F_M . Although at 550 °C VO_2 films were obtained over a wide range of the incident flux, the film deposited at a low oxygen incident flux yields a very small magnitude of the resistivity transition.

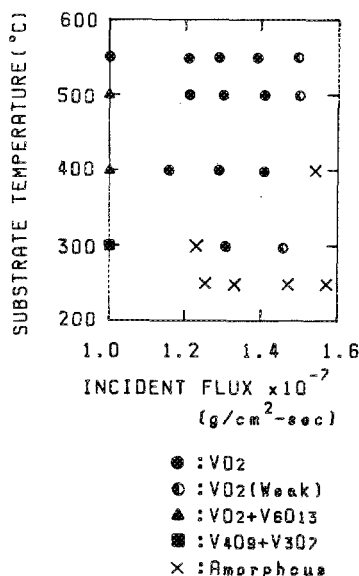


FIG. 1. Phases identified by x-ray diffraction measurement as a function of substrate temperature and incident flux intensity.

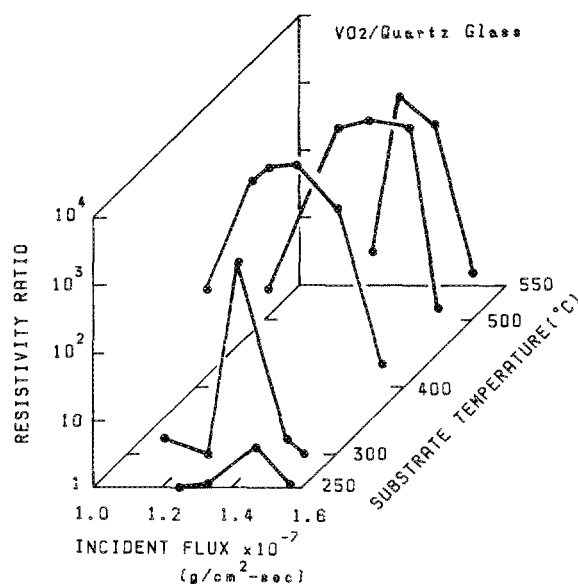


FIG. 3. Resistivity ratios for substrate temperature and incident flux intensity.

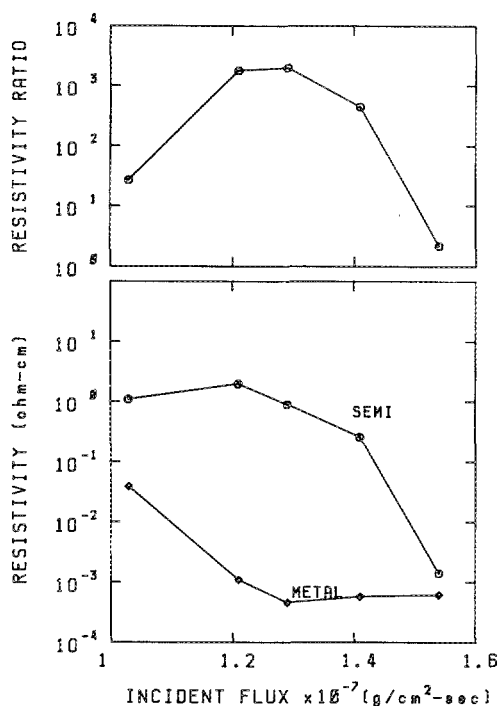


FIG. 4. Resistivity variation and ratios of the films deposited at 400 °C. Resistivities were measured at 20 °C for the semiconducting phase and at 120 °C for the metallic phase.

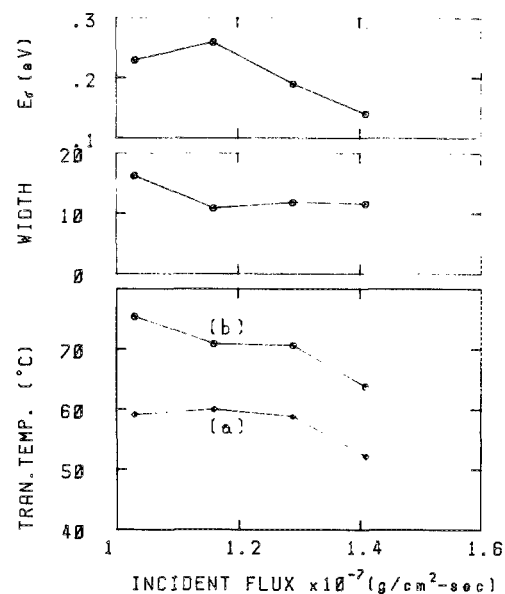


FIG. 5. Transition temperature, hysteresis width, and activation energy for conductivity in the semiconducting phase as a function of incident flux intensity. Curve (a) shows transition temperatures on the increasing temperature side and (b) transition temperature on the decreasing temperature side.

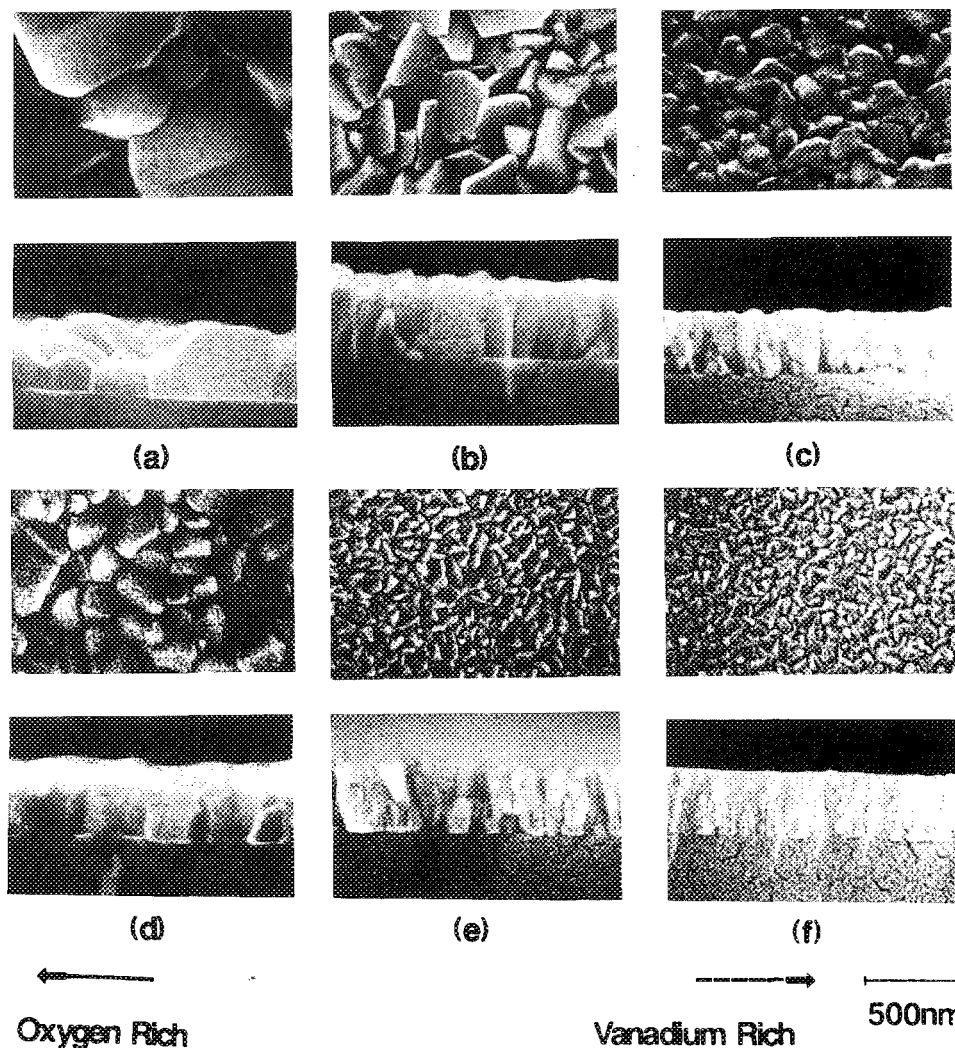


FIG. 6. Scanning electron micrographs of films deposited at substrate temperatures of 400 and 550 °C for different incident flux intensities. The coating thickness were nominally 400–500 nm thick. Films (a)–(c) were identified as VO_2 by x-ray diffraction measurement and deposited at a substrate temperature of 550 °C and incident flux intensities of 1.0×10^{-7} , 1.3×10^{-7} , and 1.5×10^{-7} g/(cm² s), respectively. Film (d) was a mixture of VO_2 and V_6O_{13} and deposited at 400 °C and an incident flux intensity of 1.0×10^{-7} g/(cm² s). Film (e) was VO_2 , and deposited at 400 °C and 1.3×10^{-7} g/(cm² s). Film (f) was VO_2 deposited at 400 °C and 1.5×10^{-7} g/(cm² s).

Even the film deposited at 250 °C, which was amorphous, provided a transition resistivity ratio.

Metallic phase and semiconducting phase resistivities of films deposited at a substrate temperature of 400 °C are shown in Fig. 4. The resistivities were measured at 20 °C for the semiconducting phase and at 120 °C for the metallic phase. Lower values of the incident flux increase resistivities both in metallic and semiconducting phases, and consequently resistivity ratios are kept nearly the same at values of 10^3 . At the low end of F_M , the resistivities decrease because of the existence of V_6O_{13} second phase which is metallic at room temperature. Also the low oxygen film exhibits low resistivity possibly because of the existence of Magneli phases which are metallic at room temperature.

Transition temperature and hysteresis width, both defined at the midpoint of the transition, are also influenced by degrees of nonstoichiometry (Fig. 5). Oxygen-deficit films yield low transition temperatures. A film with a large resistivity ratio has a large activation energy for conductivity. The reduction of the transition temperature agrees with Goodenough's suggestion (addition of extra electrons will reduce the transition temperature).²

Scanning electron microscopy (SEM) investigation revealed interesting structures of the films. Figure 6 shows SEM micrographs of VO_2 , and mixtures of VO_2 and V_6O_{13} deposited at 400 and 550 °C. A film deposited at high values of the incident flux, namely, with oxygen deficit, possessed a columnar structure with a feature size of 100 nm or less [Fig. 6(c)]. A higher substrate temperature of 550 °C yielded larger grain size. Lower F_M yielded large, crystallized grains with grain sizes of ~ 400 nm [Fig. 6(a)]. In particular, at 550 °C film microstructures were very sensitive to the incident flux, namely, ratios between oxygen and vanadium in the flux.

IV. DISCUSSION

The x-ray diffraction measurements suggest that higher substrate temperatures increase the range of the incident flux where VO_2 films were deposited. In addition evidence of high crystallization was shown by SEM investigation. However, high substrate temperatures did not yield high transition resistivity ratios. The semiconducting phase and metallic phase resistivities suggest discussion of the problem. As shown in Fig. 4, the metal phase resistivities of the films are $\sim 10^{-3} \Omega \text{ cm}$ in high F_M and increase in F_M . The semiconductor phase resistivity increases as F_M decreases. Consequently, the resistivity ratios were limited to $\sim 10^3$ all over the region of VO_2 single phase.

As shown in the SEM pictures, there is an influence of the nonstoichiometry and existence of the second-phase V_6O_{13} on the film structure. V_6O_{13} has a lower melting point (T_m

$= 940 \text{ K}$)⁷ than VO_2 ($T_m = 1800 \text{ K}$).⁷ In particular, the films obtained at 550 °C yielded highly faceted, large grains. The substrate temperature of 550 °C ranged $T/T_m = 0.5$ for VO_2 (zone 2 for Thornton's model). In this region the importance of surface diffusion is enhanced, since the width of columnar structure grains was seen to increase with T/T_m .¹ Furthermore the temperature gives a T/T_m value of 0.9 for V_6O_{13} , where bulk diffusion dominates film growth. In our case of VO_2 , the high oxygen ratio of the films accelerated the formation of wide, faceted columnar grains, providing poor connection on the top half of the film, possibly because the existence of V_6O_{13} enhanced diffusion of atoms, which was required for the film growth. This grain growth is believed to increase resistivities, especially metallic phase resistivities, for oxygen-rich films deposited at 500 and 550 °C, although there may be an overestimation of the resistivity since the surface roughness of the films yields larger film thickness. (Average thickness was used to calculate resistivity.)

Thus, in order to lower the metallic phase resistivity of oxygen-rich films, it is required to suppress the formation of agglomerated grain growth. In the sputter deposition, however, it seems to be difficult to control film structure and stoichiometry simultaneously. Therefore, as previously suggested,⁶ postdeposition would be an effective method to obtain a high resistivity ratio.

In conclusion, although high substrate temperatures spread the region where VO_2 films are deposited, the resistivity ratio has not been improved because of the existence of highly crystallized grains with poor connection. Growth structure is very sensitive to the change of the incident flux intensity even within a region where single-phase VO_2 films were obtained. The results emphasize the necessity of postdeposition annealing to obtain a high resistivity ratio.

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