Influence of ambient atmosphere on metal-insulator transition of strained vanadium dioxide ultrathin films

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The effect of ambient atmosphere on metal-to-insulator transition (MIT) in strained vanadium dioxide (VO_2) ultrathin films (7–8 nm) grown epitaxially on TiO_2 (001) single crystal substrate by pulsed laser deposition was investigated by varying the ambient oxygen pressure and substrate temperature with the intention being to control arbitrarily the MIT events of strained VO_2 ultrathin films, including the MIT temperature and the resistivity change. When reducing the ambient oxygen pressure, the MIT temperature remained almost constant, whereas the change of resistivity during MIT tended to be smaller. Contrary, varying the substrate temperature resulted in the variation of the MIT temperature with keeping the abruptness of transition. The lower the substrate temperature, the lower the MIT temperature, and in addition the MIT temperature ~290 K with keeping the abrupt change of resistivity is found to be the lowest compared with previously reported values. The reduction of the MIT temperature was found to correlate with shortening c-axis length when decreasing the substrate temperature, indicating the significant strain effects. Thus these results highlight that controlling appropriately the ambient atmosphere enables us to modulate arbitrarily the MIT events of strained VO_2 thin films near room temperature. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2345600]

INTRODUCTION

Vanadium dioxide (VO_2) exhibits a metal-to-insulator transition (MIT) at 341 K, accompanied by the structural change from a high-temperature tetragonal structure (metal) to low-temperature monoclinic structure (insulator).[1–6] Since the MIT occurs relatively near room temperature (RT), switching devices and sensors[7–17] working at RT would be possible and promising by utilizing the MIT. In across the transition, the drastic change in electrical resistivity and optical transmittance occur. In particular, the variation of electrical resistivity is reported to be $\Delta R = 10^5 \ \Omega$ cm for single crystal[18] and $\Delta R = 10^3 - 10^4 \ \Omega$ cm for typical thin films.[19,20] In addition, the abrupt resistivity change was found to occur within the width of transition less than 0.1 K for single crystal.[21] If it were possible to control arbitrarily such MIT events for desired applications, the availability of possible VO_2 based devices and sensors would be expanded. There have been much interests in modifying the MIT events in both bulk and thin films.[22–29] Especially the thin film form would be desirable in terms of the practical applications. For example, the MIT events of VO_2 thin films were investigated by varying the oxygen pressure,[22–24] temperature[25] during deposition process, and the lattice mismatch with substrates.[26–29] One of the important issues on these investigations is that the MIT temperatures are more or less the same as the bulk value of ~341 K, which is clearly higher than RT. Although doping W or Nb into VO_2 was found to be effective to reduce the MIT temperature,[30–32] the resistivity change during MIT tended to be broader for such doped

systems, indicating the difficulty of maintaining the abrupt change of resistivity across MIT. More recently, Hiroi and co-workers[33,34] have succeeded to modify the MIT temperature of VO_2 thin films grown on TiO_2 (001) single crystal substrate to be near RT with keeping the abrupt transition. A tensile strain received from the TiO_2 substrate, in which the in-plane lattice mismatch is 0.86%, plays an important role on modifying the MIT temperature. In a similar mechanism to bulk single crystal being applied hydrostatic pressure,[35] shortening V–V chain in c axis stabilizes a high-temperature metal phase, resulting in decreasing the MIT temperature. As such the controllability of MIT temperature by utilizing a tensile strain received from the substrate seems to be powerful in comparison with the use of hydrostatic pressure from a viewpoint of the practical applications. In addition, since the MIT temperature modified was found to be just above 300 K and modifying the MIT temperature below 300 K with keeping the abrupt transition was unfeasible,[34] further controllability of the MIT temperature down to lower temperature is strongly desired. Although generally an ambient atmosphere during the crystal growth affects significantly the MIT events of VO_2 thin films, knowledge in the context with such ambient atmosphere effects on strained VO_2 thin films is still scarce. Investigating systematically such effects would enable the MIT events of strained VO_2 thin films to be controlled arbitrarily near RT, which will contribute to the realization of VO_2 based device applications in the future. These backgrounds motivated us to investigate the effects of ambient atmosphere for strained VO_2 ultrathin films (7–8 nm) deposited on TiO_2 (001) single crystal substrate.

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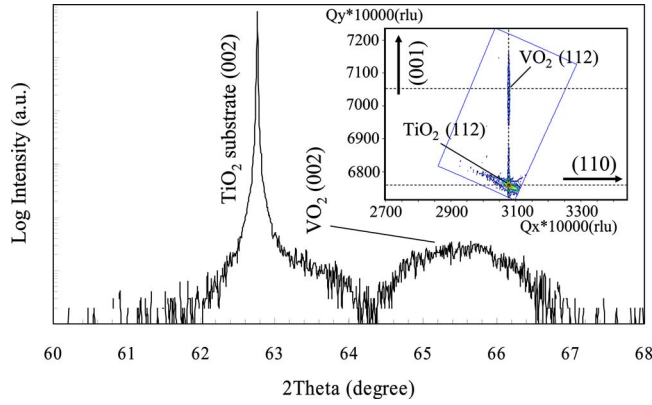
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FIG. 1. Typical XRD pattern of VO_2 ultrathin film deposited on TiO_2 (001) single crystal substrate. The inset figure shows the reciprocal space map data performed around the (112) peak.

FIG. 2. Temperature dependence in resistivity of VO_2 films deposited at 593 K of the substrate temperature varying ambient oxygen pressure.

EXPERIMENT

Epitaxial VO_2 thin films were grown on TiO_2 (001) single crystal substrate (lattice mismatch: 0.86%) by pulsed laser deposition (ArF excimer, $\lambda = 193$ nm) with varying the oxygen pressure and the temperature during film growth in order to investigate the effects on strained VO_2 thin films. The crystal structure of TiO_2 substrate is rutile same as with the high-temperature metal phase of VO_2. Since the *a*-axis length of VO_2 bulk is shorter than that of TiO_2 with the lattice mismatch of 0.86%, epitaxial VO_2 thin film receives a tensile strain along the *a* axis, resulting in shortening the *c*-axis length. V_2O_5 pellet was used as a target, which was obtained by milling V_2O_3 (99.9% pure) powder for 1 h and then sintered at 773 K for 20 h. Subsequently, the samples were reground for 4 h and then calcined at 683 K for 50 h. During the deposition, the oxygen pressure (P_{O_2}) and the substrate temperature (T_s) were ranging from 0.01 to 5 Pa and from 477 to 696 K, respectively. The thickness of the films fabricated was controlled to be 7–8 nm, measured by a surface profilometer. The deposition rate was about 1.2 Å/min. After deposition, the films were cooled down to 300 K in 30 min under the same oxygen pressure. The crystal structures were characterized by four-axis x-ray diffraction (XRD) measurement. The electrical properties of the films were evaluated by a four probe method using physical property measurement system (PPMS) (Quantum Design).

RESULTS AND DISCUSSION

The typical XRD pattern of VO_2 films on TiO_2 (001) single crystal substrate grown at $T_s = 643$ K and $P_{O_2} = 1$ Pa is shown in Fig. 1. Two significant peaks were observed. The lower angle peak is indexed to TiO_2 (002) substrate and the higher angle peak is due to tetragonal VO_2 (002) thin film. Other peaks were not observed, indicating that the prepared film is (001) oriented single phase. In addition, the epitaxy of the film can be clearly seen in the inset figure of Fig. 1, which shows the reciprocal space map around (112) peak. Figure 2 shows the temperature dependence of resistivity of films grown under various oxygen pressures ranged from 0.01–1 Pa with 593 K of the substrate temperature. In this figure, no remarkable change in the MIT temperature was
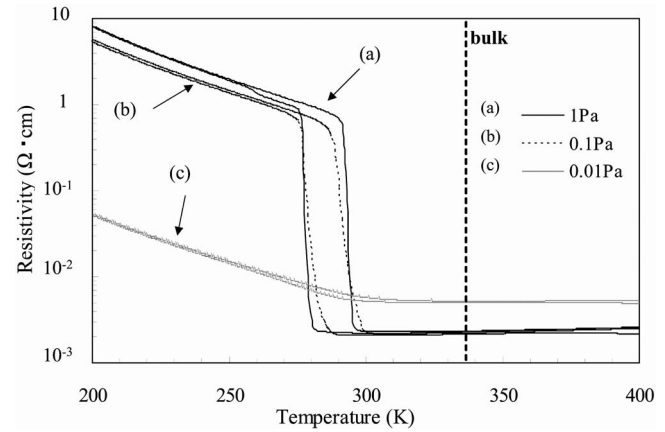
found even in decreasing the ambient oxygen pressure, indicating that the effect of the ambient oxygen pressure in the presence of tensile strain is not so significant in terms of the modification of the MIT temperature. In other words, the presence of oxygen vacancies does not modify the MIT temperature. Contrary the abruptness of resistivity change during MIT tended to be smaller when decreasing the ambient oxygen pressure. In addition, the resistivity in the low-temperature insulator phase decreased as decreasing the ambient oxygen pressure. These trends on the MIT events when varying the ambient oxygen pressure were confirmed to be similar for films grown at different temperatures. Data of the magnitude of the resistivity change ratio (above and below the transition temperature) for films grown at various substrate temperatures are shown in Fig. 3. As can be seen, the abrupt change of resistivity was found for temperature conditions above 543 K. Since below 543 K the crystallinity tends to be worse, clear MIT has not been observable. Thus the ambient oxygen pressure affects mainly the abruptness of resistivity change during MIT in strained VO_2 thin films. Although oxygen vacancies are closely related to such effects, it is generally quite difficult to measure precisely the oxygen content within oxide films grown on oxide substrates. Such oxygen vacancies may result in intermediate
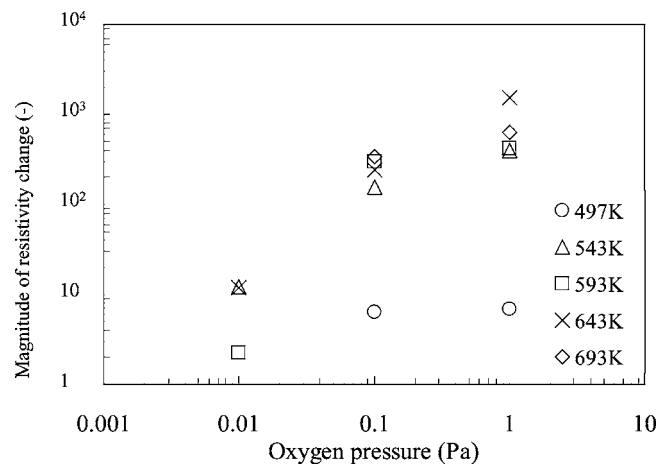

FIG. 3. Effect of ambient oxygen pressure on the magnitude of resistivity change ratio for VO_2 films grown at various ambient temperatures.
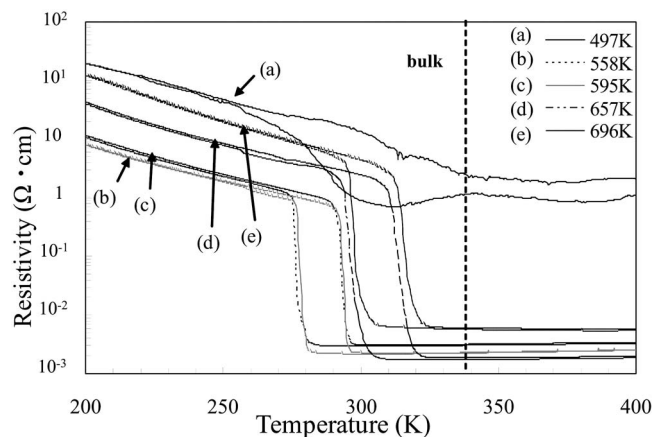
FIG. 4. Effect of ambient temperature on the temperature dependence of resistivity. All films are grown at 1 Pa of the oxygen pressure.

FIG. 5. Dependences of ambient temperature on the MIT temperature (in the left *y* axis) and on the magnitude of resistivity change (in the right *y* axis). The inset figure shows the relation between the MIT temperature and *c*-axis length.

compositions between VO_2 and V_2O_3, which are well known as "Magnéli phases" with a chemical formula V_nO_{2n-1} ($3 \leq n \leq 9$) exhibiting the wide variety of electrical properties.[36] However, in the phase equilibrium the formation of Magnéli phases seems to be thermodynamically unstable within the range of ambient atmospheres used in this study.[36] Considering the ambient atmosphere during depositions, $VO_{2-\delta}$ in which the MIT tends to be broader as the crystallinity tends to be less[23] rather than the presence of Magnéli phases seems to be responsible for the dependence of ambient oxygen pressure on the MIT events. These results highlight that reducing the ambient atmosphere results in decreasing the abruptness of resistivity change during MIT but does not modify the MIT temperature near RT in the presence of strain effects.

Figure 4 shows the effect of substrate temperature on the temperature dependence of resistivity. All these films were fabricated at 1 Pa of the oxygen pressure and the temperature was varied from 497 to 696 K. Except the case of 497 K, the abrupt change of resistivity was observed and maintained for the temperature range. It was found that the lower the substrate temperature, the lower the MIT temperature. It was reported that decreasing the substrate temperature resulted in not only the reduction of MIT temperature but also loosing the abruptness of resistivity change during MIT.[25] Our experimental trends clearly differ from those of previous reports in terms of the abruptness of resistivity change, indicating the high quality of films fabricated herein since the abruptness of resistivity change is known to be closely related to the crystallinity and the stoichiometry.[37] In fact, the MIT temperature of ~290 K with keeping the abrupt change of resistivity seems to be the lowest in the literatures as far as we are aware. The MIT temperature was taken as the midpoint between the start and finish temperatures of the transition during the heating process. Figure 5 shows the MIT temperature and the abruptness of resistivity change as a function of the substrate temperature. Clearly the substrate temperature affects significantly the MIT temperature with keeping the abruptness of resistivity change unlike the case of the ambient oxygen pressure. A correlation between the MIT temperature and the *c*-axis length when varying the substrate temperature is shown in the inset figure of Fig. 5.
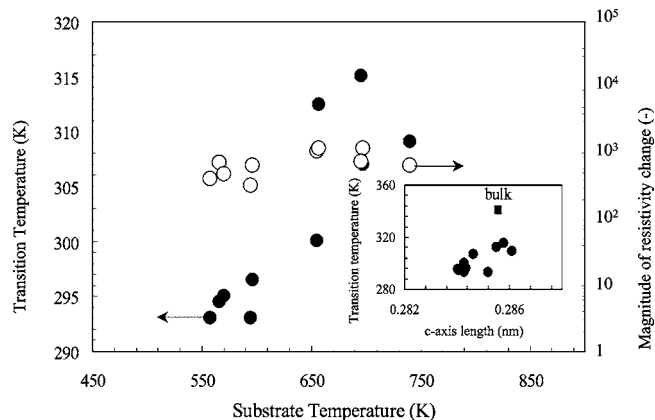
The MIT temperature decreased with decreasing the *c*-axis length, i.e., shortening the V–V distance and also stabilizing the metallic phase, which is qualitatively consistent with previous results although the abruptness of resistivity change was not maintained in their experiments.[33,34] Since in general as the substrate temperature tends to increase the film structure tends to be the bulk crystal structure even in the presence of strain effects due to thermal stabilization, the dependence of the substrate temperature on the *c*-axis length can be solely interpreted in terms of the difference of strain relaxation effects. Thus controlling appropriately the substrate temperature enables us to modify the MIT temperature via changing the *c*-axis length with keeping the abruptness of transition.

CONCLUSION

The effect of ambient atmosphere on metal-to-insulator transition (MIT) in strained vanadium dioxide (VO_2) ultrathin films (7–8 nm) grown epitaxially on TiO_2 (001) single crystal substrate was investigated with the intention being to control arbitrarily the MIT events of strained VO_2 ultrathin films, including the MIT temperature and the abruptness of transition. When reducing the ambient oxygen pressure, the MIT temperature remained almost constant, whereas the abruptness of resistivity change during MIT tended to be smaller. Contrary, varying the substrate temperature resulted in the variation of the MIT temperature with keeping the abruptness of transition. The lower the substrate temperature, the lower the MIT temperature, and in addition the MIT temperature ~290 K with keeping the abrupt change of resistivity is the lowest compared with previously reported values. The reduction of the MIT temperature was found to correlate with shortening *c*-axis length when decreasing the substrate temperature, indicating the significant strain effects. Thus controlling appropriately the ambient atmosphere enables us to modulate the abruptness of the MIT events of strained VO_2 thin films near RT.

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