Interface effect on metal-insulator transition of strained vanadium dioxide ultrathin films

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The interface effects on the metal-insulator transition (MIT) of strained VO_2 ultrathin films grown epitaxially on TiO_2 (001) single crystal substrate were investigated. Varying the surface conditions of TiO_2 substrate, such as the roughness and the surface reconstructions, produced the remarkable changes in the MIT events of VO_2 thin films, including the transition temperature and the abruptness. The presence of the surface reconstructions was found to be detrimental for applying effectively strain effects due to the strain relaxation in the *c* axis of VO_2 thin films. The abrupt MIT in strained VO_2 thin films, deposited on the substrate without such detrimental surface reconstructions, was successfully maintained down to around 5 nm film thickness. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2424321]

INTRODUCTION

Vanadium dioxide shows the structural phase transition from a metallic high temperature tetragonal structure to an insulative low-temperature monoclinic structure.[1–6] Since the temperature of the metal-insulator transition (MIT) is 341 K relatively close to room temperature (RT), switching devices and sensors working at RT are expected by utilizing the MIT events.[7–17] Across the MIT the abrupt change in electrical resistivity occurs.[18] Since the bulk MIT temperature, 341 K, is higher than typical RT, various approaches including doping and strain effects have been suggested to control the MIT temperature.[19–29] Among them, the tensile strain effects induced by the lattice mismatch with the single crystal substrate seem to be powerful. For example, the MIT temperature of VO_2 thin films grown on TiO_2 (001) single crystal substrate was successfully modified to be close to RT with keeping the abrupt transition.[26–29] Although the strained interface between the film and the substrate surely plays an important role on the transport properties of VO_2 thin films, knowledge regarding such interface effects on strained VO_2 thin films is still scarce. In addition, it would be invaluable to understand the critical thickness in the context with such interface effects on the transport properties of strained VO_2 thin films, where the abrupt MIT can be maintained. Although previous investigations reported the disappearance of the abrupt MIT below 25 nm (Ref. 22) using sapphire substrate with relatively large lattice mismatch (4.49%), the critical thickness of strained VO_2 thin films deposited on TiO_2 substrate with relatively small lattice mismatch (0.86%) has not been reported. Thus this study aims to clarify the interface effects on the MIT events of strained VO_2 ultrathin films (3–15 nm) deposited on TiO_2 (001) single crystal substrate.

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EXPERIMENT

VO_2 thin films were grown on TiO_2 (001) single crystal substrate by pulsed laser deposition (ArF excimer, $\lambda = 193$ nm) with the oxygen pressure of 1 Pa and the substrate temperature of 643 K.[26–29] The *a*-axis length of VO_2 bulk (0.4554 nm) is shorter than that of TiO_2 (0.4593 nm) with the lattice mismatch of 0.86%, resulting in a tensile strain along the *a* axis for VO_2 thin film and also shortening the *c*-axis length.[26–29] The surface treatment of TiO_2 substrate was performed by immersing into HF aqueous solution (pH=5.0) and annealing at 1173 K, as reported elsewhere.[30–34] V_2O_5 pellet was used as the target material. The thickness of the films fabricated was varied from 3 to15 nm. The thickness was measured by surface profilometer. The deposition rate was about 2.0 Å/min. After deposition, the films were cooled down to 300 K in 30 min under the same oxygen pressure. The surface structures were characterized by atomic force microscopy (AFM) (JEOL JSPM 4200). 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

Figure 1 shows the surface morphology images of surface treated TiO_2 substrates. (a), (b), and (c) images are the mechanical polished substrate, the substrate with HF treatment and annealing for 1 h, and the substrate with HF treatment and annealing for 6 h, respectively.[32,33] The rms roughnesses were 0.133 nm for (a), 0.422 nm for (b), and 0.779 nm for (c). The surface reconstructions can be clearly seen in the image of high temperature annealed substrate (c). In fact, similar reconstructions on TiO_2 (001) single crystal have been reported previously,[30–34] in which the presence of TiO_2 (110)-(1×2) structure was identified.[34] The step and terrace structures were found in image (b) with slight surface

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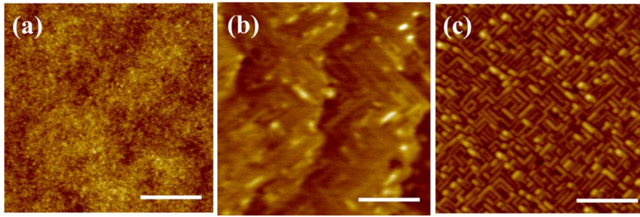

FIG. 1. AFM images of the surface morphology of surface treated TiO_2 (001) substrates. The scale bar in each image is 200 nm. (a) Mechanical polished surface, (b) Annealed surface at 900 °C for an hour, and (c) annealed surface at 900 °C for 6 h.

reconstructions. Such surface reconstructions and the step and terrace structures were not observed for substrate (a). Using these substrates, the interface effect on the transport properties of VO_2 thin films was investigated, as shown in Fig. 2. The film thickness was set to be 8 nm. It can be seen that the presence of surface reconstructions systematically increased the MIT temperature. Since the MIT temperature of VO_2 is known to strongly correlate with the *c*-axis length, the variation of the *c*-axis length was shown in the inset. As can be seen, the longer the *c*-axis length, the higher the MIT temperature. Thus the presence of surface reconstructions enhances the strain relaxation at the interface layers. This presumably indicates the presence of grain boundaries at the interface layers due to the surface reconstructions with the roughness. In such boundaries, the stress received from the substrate might be partially released, resulting in longer the *c*-axis length as shown in the inset of Fig. 2. As such, the surface reconstructions on TiO_2 (001) substrate are detrimental for applying effectively the strain effects to VO_2 thin films. Figure 3 shows the film thickness dependence on the transport properties of VO_2 thin films deposited on the TiO_2 substrate without surface reconstructions. Below 5 nm, an increase of the MIT temperature with disappearing abruptness was observed. However, the MIT abruptness, which is often referred as the crystallinity index of VO_2,[35] was almost maintained down to the critical thickness, as seen in the inset. In fact, the critical thickness in this study seems to be

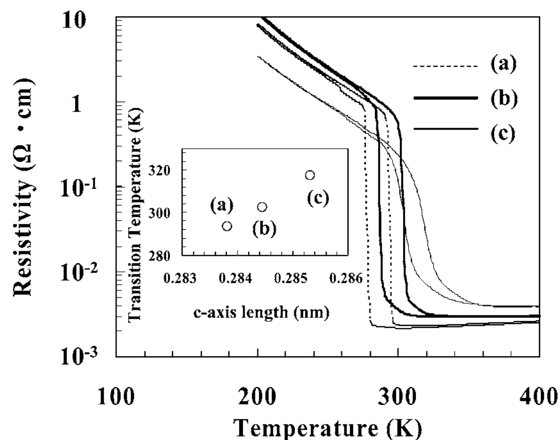

FIG. 2. Interface effects on the transport properties of VO_2 thin films. The thickness of the films is 8 nm. The inset figure shows the correlation between the MIT temperature and the *c*-axis length. In both figures, (a) mechanical polished surface, (b) step and terrace surface, and (c) reconstructed surface.

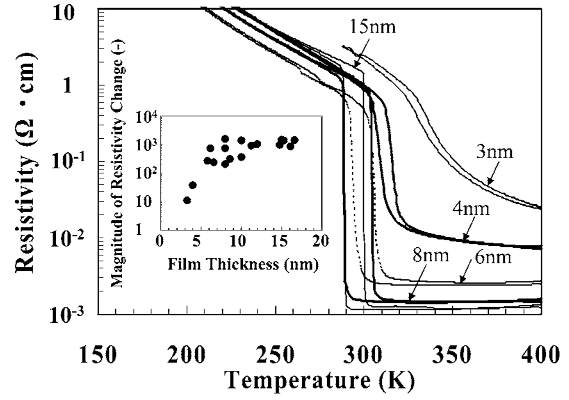

FIG. 3. Effect of film thickness on temperature dependence of resistivity of the VO_2 thin films on flat TiO_2 substrate. The inset figure shows the film thickness dependence on the magnitude of resistivity change ratio.

much lower than values reported previously using sapphire substrate 25 nm thick.[22] Thus these results highlight that the interface effect via the surface reconstructions plays an important role on the transport properties of strained VO_2 ultra thin films.

CONCLUSION

The interface effects on metal-insulator transition (MIT) of strained VO_2 ultrathin films grown epitaxially on TiO_2 (001) single crystal substrate were investigated. Varying the surface conditions of TiO_2 substrate, such as the roughness and the surface reconstructions, produced the remarkable change in the MIT events of VO_2 thin films, including the transition temperature and the abruptness. The presence of the surface reconstructions was found to be detrimental for applying effectively strain effects via the strain relaxation in the *c* axis of VO_2 thin films. The abrupt MIT in strained VO_2 thin films was successfully maintained down to 5 nm film thickness.

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