Control of Crystal-growth of VO₂ Films Fabricated by Excimer Laser Assisted Metal Organic Deposition

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1. Introduction

Vanadium dioxide (VO₂) exhibits a metal-insulator (MI) transition at around 341 K, accompanied by a dramatic change in electrical property [1], thus it is useful for thermal sensors. For applications, it is indispensable to induce the transition at around room temperature. In order to control the transition temperature, the epitaxial films are effective, since the transition temperature is affected by expansion and compression of a VO₂ crystal along c-axis [2]. The epitaxial films are generally prepared by gas-phase deposition processes, but these processes are high cost. On the other hand, chemical solution process is low cost and easy, but heat-treatment at 500 °C under controlled oxygen partial pressure needs to be carried out. It is desirable that the VO₂ thin films can be fabricated at low temperature for industrial applications. In this study, we demonstrated the low-temperature fabrication of VO₂ films on (001) TiO₂ by metal organic excimer laser assisted deposition (ELAMOD) and the control of epitaxial growth by the pre-heated temperature.

2. Experiment and results

Exprimental

Vanadium (V) organic solution was spin-coated onto the substrate, and pre-heated at 300 or 500 °C under air. The film was then irradiated by a KrF excimer laser ($\lambda = 248$ nm) at room temperature. The obtained films were characterized by X-ray diffraction (XRD), infrared (IR) absorption and transmission electron microscope (TEM) measurements.

Results and Discussion

When the film pre-heated at 500 °C was irradiated by the laser under 250 Pa, polycrystalline as well as epitaxial VO₂ phases were formed (Fig. 1 (a)). The film pre-heated at 500 °C was amorphous with crystallized V₂O₅ phase. It is suggested that the epitaxial phase was grown through the amorphous phase, while the polycrystalline phase was grown from the crystalline phase formed by the pre-heating at 500°C. When the film pre-heated at 300 °C was irradiated by the laser under the same conditions (250 Pa), no VO₂ phase was formed. On the other hand, the film pre-heated at 300 °C was irradiated by the laser under air, a single phase of the epitaxial VO₂ film was successfully obtained as shown in Fig. 1 (b). Based on the IR and TEM observations,

the film pre-heated at 300 $^{\circ}$ C was amorphous phase containing organic compounds. Accordingly, oxygen atmosphere would be effective for the photo-decomposition of the organic compounds. Furthermore, in the case of the film pre-heated at 300 $^{\circ}$ C with no crystallized phase, the

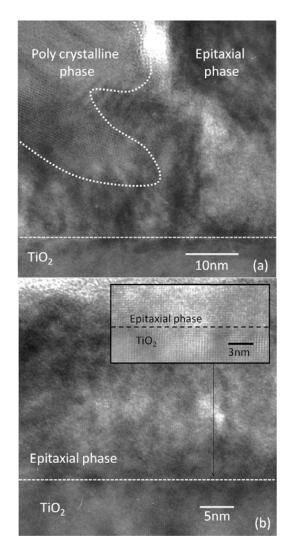


Fig. 1 $\,$ TEM images of the VO_2 thin films by using ELAMOD after pre-heating at (a) 500 and (b) 300 $^{\rm o}C$

epitaxial phase only was grown through amorphous phase with no growth of polycrystalline phase.

Fig. 2 shows the temperature dependence of the resistivity of the VO₂ films at the thickness of 25 nm. The MI transition temperature (T_{MI}) was determined as a midpoint of the temperature at which the resistivity rapidly changed on heating. The T_{MI} of the irradiated films after pre-heating at 500 and 300 °C were 306 K and 294 K, respectively. XRD patterns showed that the lattice parameter c of the two films were almost same at 0.284 nm (cf. that of bulk is 0.286 nm [1]). When the VO₂ film was epitaxially grown on (001) TiO₂ substrates in tetragonal form, the c-axis length of the film was decreased due to different lengths of a- (or b-) axis between the film and substrate. In the previous work, the T_{MI} of the epitaxial VO₂ film which was 0.284nm in the c-axis length was about 290 K [2]. In comparison with the result, the T_{MI} of the irradiated films after pre-heating at 500 °C was higher. It is thought that the T_{MI} of polycrystalline phases in the film was close to that of bulk because of no tensile stress, so the film containing polycrystalline phases in epitaxial phase would transform at higher temperature. On the other hand, the T_{MI} of the irradiated films after pre-heating at 300 °C was corresponding with the above-mentioned result, indicating that the MI transition was dominated only by c-axis length due to a single phase of the epitaxial VO_2 film.

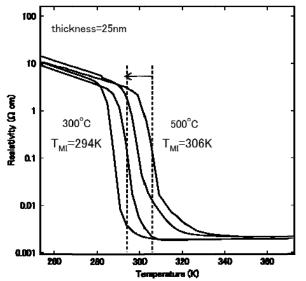


Fig. 2 The temperature dependence of the resistivity of the VO₂ films by using ELAMOD after pre-heating at 500 and 300 °C

3. Conclusions

 VO_2 epitaxial films have been fabricated on (001) TiO₂ substrates by the ELAMOD process. It is found that the structure of the obtained films would be affected by that of the films before the irradiation. When the amorphous film pre-heated at 300 °C was irradiated by a KrF laser at room temperature, the single phase of epitaxial VO_2 film was successfully formed by the irradiation. The T_{MI} of the obtained film was sifted at room temperature due to the

epitaxial single phase. Therefore, the ELAMOD process is found to be effective for low-temperature fabrication of epitaxial VO_2 films and be advantageous in term of process cost.

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