

Room-temperature epitaxial growth of V_2O_3 films

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Herein we report the room-temperature epitaxial growth of V_2O_3 films by laser molecule beam epitaxy. X-ray diffraction profiles show the room-temperature epitaxial V_2O_3 films orient in the [110] direction on $\alpha-Al_2O_3$ (0001) substrates. Atomic force microscopy measurements reveal that the ultra-smooth surfaces with root-mean-square surface roughness of 0.11 nm and 0.28 nm for 10-nm-thick and 35-nm-thick V_2O_3 film, respectively. X-ray photoelectron spectroscopy results indicate the V^{3+} oxidation state in the films. Typical metal-insulator transition is observed in films at about 135 K. The resistivities at 300 K are approximately 0.8 m Ω cm and 0.5 m Ω cm for 10-nm-thick and 35-nm-thick V_2O_3 film, respectively.

room-temperature epitaxy, V_2O_3 , metal-insulator transition

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1 Introduction

Vanadium sesquioxide (V_2O_3) is an interesting material because of a typical metal-insulator transition (MIT), as observed by Foëx [1]. Strong electron correlation leads to the complex interplay of structural, magnetic and transport properties in V_2O_3 system. At room temperature, pure V_2O_3 has a corundum structure, and is a paramagnetic metal (PM). When the temperature is cooled across critical temperature (about 160 K), it undergoes a first-order transition, in which the crystal structure transforms from rhombohedral to monoclinic [2], and it transits into an antiferromagnetic insulating (AFI) phase with a remarkable characteristic as the electrical resistivity increases by ~ 7 orders of magnitude [3]. Therefore, V_2O_3 has been studied as a prototype of MIT materials, and has focused theoretical [4,5] and experimental [6–8] research interest.

Thin film of V_2O_3 is a good system to exploring the physical nature of MIT. It is difficult to prepare pure-phase

V_2O_3 film because of the existence of diverse oxidation states of vanadium [9]. Pulsed laser deposition and magnetron sputtering are commonly employed to prepare V_2O_3 film [10,11]. Herein we note that V_2O_3 can be epitaxially grown on sapphire substrates by means of laser molecule beam epitaxy (Laser-MBE), even though the substrate temperature remains at room temperature during the deposition. The room-temperature epitaxial film not only can avoid surface deterioration effectively, but also exhibits the intrinsic properties of V_2O_3 material itself, and the room-temperature epitaxy process shows good reproducibility, because of the absence of thermal treatment.

2 Experimental

V_2O_3 thin films were prepared on $\alpha-Al_2O_3$ (0001) substrates by Laser-MBE method [12]. A vanadium plate (purity >99.99%) was employed as target. Commercial c -plane $\alpha-Al_2O_3$ substrates were annealed in air at 1200°C for 2 h beforehand to obtain step-and-terrace surface structure. The

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distance between target and substrate was fixed at 60 mm. The beam of a XeCl excimer laser ($\lambda=308$ nm) was focused on the vanadium target with an energy density of 1.5 J/cm^2 at 2 Hz. The background pressure of the growth chamber was pumped to 1×10^{-5} Pa. Oxygen pressure was maintained at 1×10^{-3} Pa and the substrate temperature was kept at room temperature ($\sim 25^\circ\text{C}$) during entire preparation process. The growth rate of V_2O_3 film on sapphire substrate was estimated to be about $1.5 \text{ \AA/min}$.

The surface structure of the films were studied with *in situ* reflection high-energy electron diffraction (RHEED) and with *ex situ* atomic force microscopy (AFM). The thickness was obtained by a step profiler. The crystal structure was characterized by X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation. The oxidation states of V in the films were analyzed by using X-ray photoelectron spectroscopy (XPS) with $\text{Mg K}\alpha$ radiation. The resistance measurements were performed by standard four-terminal method using a Physics Property Measurement System (PPMS).

3 Results and discussion

The thicknesses of as-prepared films are measured to be 10 nm and 35 nm by a step profiler. A typical RHEED pattern of the V_2O_3 film is shown in the inset of Figure 1 recorded after the growth. The bright and sharp diffraction streaks indicate the well crystallization and smooth surface. Figure 1 shows the XRD θ - 2θ scanning profiles of V_2O_3 films. Except for the XRD peak ascribed to $\alpha\text{-Al}_2\text{O}_3$ substrate, only diffraction peaks at approximately $2\theta=36.2^\circ$ and 77.0° are recorded, which can be fully indexed as rhombohedral V_2O_3 (110) and (220) planes (JCPDS PDF card 85-1411). This indicates that V_2O_3 films grow along [110] direction. It

is reported that V_2O_3 is more inclined to grow in [001] direction on high-temperature $\alpha\text{-Al}_2\text{O}_3$ (0001) substrates [10,11,13], rather than [110] direction. The formation of [110]-oriented V_2O_3 films in this work may be resulted from the relatively low thermal energy provided by unheated substrates and the ultra-smooth surface of the annealed sapphire substrates. In addition, there is not any diffraction signal from either randomly oriented grain or impurity phase in the XRD curves, revealing that the as-grown V_2O_3 films have highly pure crystal phase. On the basis of RHEED and XRD measurements, we can conclude that the room-temperature epitaxy of V_2O_3 (110) film on $\alpha\text{-Al}_2\text{O}_3$ (0001) substrate is confirmed.

Figures 2(a) and (b) display the two-dimensional (2D) AFM images of the room-temperature epitaxial V_2O_3 films in a $2 \mu\text{m} \times 2 \mu\text{m}$ area. The cross section profiles corresponding to the solid line in the AFM images are also pre-

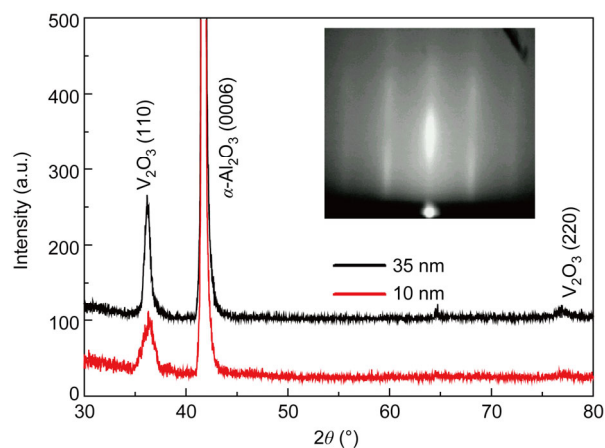


Figure 1 (Color online) XRD profiles of 10-nm-thick and 35-nm-thick V_2O_3 films on *c*-plane $\alpha\text{-Al}_2\text{O}_3$ (0001) substrates. The inset is a RHEED pattern for the V_2O_3 film.

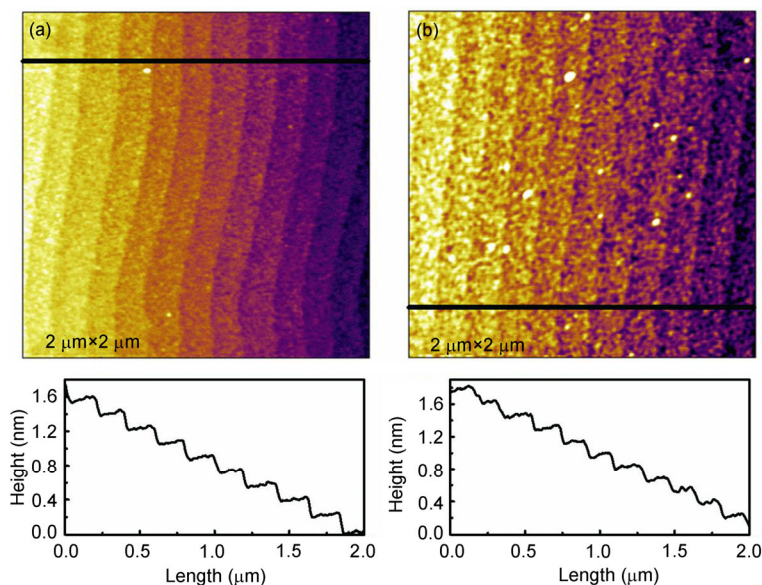


Figure 2 (Color online) AFM images and corresponding height profiles of V_2O_3 films with thickness of (a) 10 nm and (b) 35 nm.

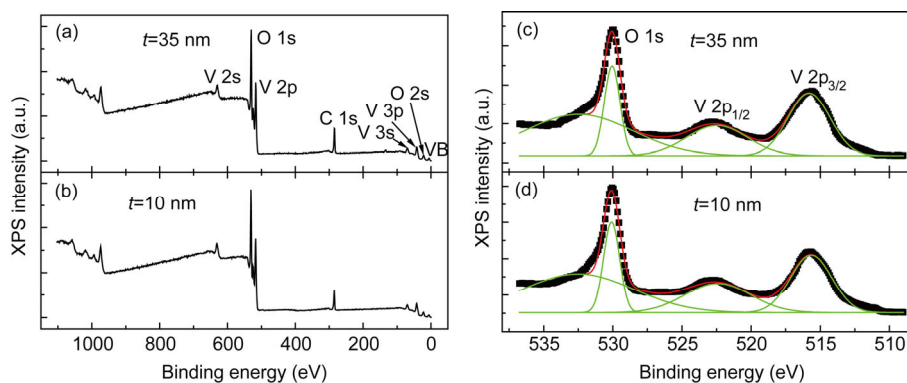


Figure 3 (Color online) XPS wide scan spectra for V_2O_3 films with thickness of (a) 35 nm and (b) 10 nm. (c) and (d) are XPS spectra of V 2p and O 1s core levels in 10 nm and 35 nm film, the dot lines are experimental data, and the solid lines are fitted results by Gauss lines.

sented in Figure 2. One can clearly observe the step and terrace morphologies on the surface of the films. The corresponding root-mean-square (Rms) surface roughness within a $2\ \mu\text{m} \times 2\ \mu\text{m}$ area are calculated to be 0.11 nm and 0.28 nm for 10-nm-thick and 35-nm-thick V_2O_3 film, respectively, which indicates that the room-temperature epitaxial V_2O_3 films have ultra-smooth surfaces. It is to be expected that the room-temperature epitaxial V_2O_3 films can maintain the step and terrace structures of the annealed $\alpha\text{-Al}_2\text{O}_3$ substrates consistently for the repressed surface deterioration.

To determine the chemical component of the samples, XPS wide scan surveys were performed on both room-temperature epitaxial V_2O_3 films. Figures 3(a) and (b) show two typical wide scan spectra for vanadium oxides. The photoelectron peaks of the main elements, V, O and C can be seen clearly. The C 1s peak, taken at 284.8 eV, which was used as binding energy (BE) reference. Figures 3(c) and (d) display the spectra of V 2p and O 1s core level, the dotted lines representing the experimental data, and the solid lines representing the fitted results. It is found that the shapes of the two curves are quite consistent. The fitted BE values of V $2p_{3/2}$ are 515.9 eV and 515.7 eV for 10-nm-thick and 35-nm-thick V_2O_3 film, respectively. The line width is determined as a full width at half maximum (FWHM), which are measured to be 3.2 eV and 3.1 eV for 10-nm-thick and 35-nm-thick V_2O_3 film, respectively. These measured values are in good agreement with the reported values of V^{3+} in V_2O_3 [9,10,13,14–17]. The BEs of O 1s peak were fitted to be 530.1 eV, which falls within the range of 530–530.5 eV reported elsewhere for V_2O_3 [14].

As mentioned above, phase transition is one of the most critical intrinsic characteristics of V_2O_3 which often reflected in the variation of resistance. Figure 4 plots the temperature-dependent resistance of the room-temperature epitaxial V_2O_3 films in temperature range of 10–300 K, measured in the process of both cooling and heating. Thermal hysteresis is observed in the two samples, which indicates a first order phase transition. The critical temperature is determined to

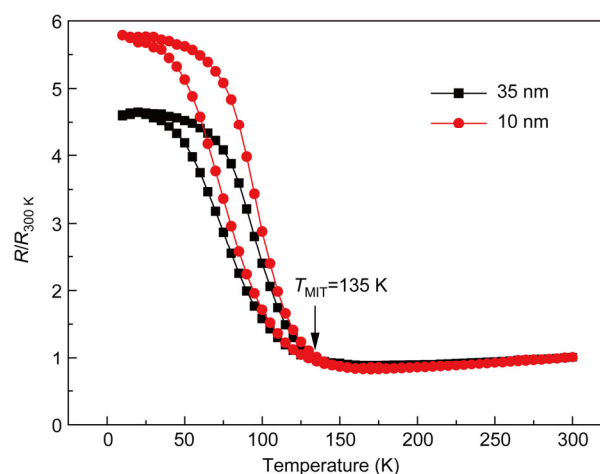


Figure 4 (Color online) Temperature dependence of the resistance of V_2O_3 films, measured in both cooling and heating process.

be about 135 K. At high temperature, the films exhibit a metallic state; but they transit into insulating state when the temperature decreases below the critical point characterized by abrupt jump of resistance. It should be noted that the resistance increases by only 1 order of magnitude as the temperature decreased. This is much less than the reported 7 orders of magnitude for bulk V_2O_3 [1,18]. A similar phenomenon has also been observed in thermal-processed V_2O_3 films as discribed elsewhere [19,20]. Epitaxial strain and size effect may be responsible. The values of resistivity for 10-nm-thick and 35-nm-thick V_2O_3 film are 0.8 m Ω and 0.5 m Ω cm at 300 K, and 4.6 m Ω and 2.4 m Ω cm at 10 K.

4 Conclusions

The V_2O_3 epitaxial films were grown on *c*-plane $\alpha\text{-Al}_2\text{O}_3$ substrates using Laser-MBE with a substrate temperature of 25°C. This approach appeared to more straightforward and simple, and showed good reproducibility because of the nonparticipation of thermal process. RHEED pattern and

AFM images indicate the atomic-scale smooth surfaces. The epitaxial relationship can be confirmed as $[110]\text{V}_2\text{O}_3\| [0001]\text{Al}_2\text{O}_3$. XPS measurements reveal the V^{3+} oxidation state in the films. Electrical resistance measurements show the films undergo a typical MIT at approximately 135 K. These results demonstrate that epitaxial V_2O_3 films grown at room temperature have as-expected ultra-smooth surfaces, as well as exhibit natural properties of V_2O_3 . Apparent applications in electrode materials for smooth surfaces and conductivity can be seen in room-temperature epitaxial V_2O_3 films.

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