Thickness dependence of electronic phase transitions in epitaxial V$_2$O$_3$ films on (0001) LiTaO$_3$

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Single crystal epitaxial thin films of V$_2$O$_3$ were grown on (0001) LiTaO$_3$ by pulsed laser deposition. X-ray diffraction and atomic force microscopy data show that the deposits were initially pseudomorphic, that they underwent plastic relaxation at a critical thickness of $\approx$16 nm, and that relaxation is accompanied by the development of surface roughness, increasing with deposit thickness. These effects lead to changes in electrical properties of the films as a function of temperature. As film thickness increases the properties go from insulator-insulator to metal-insulator, then metal-metal transitions. The thickest films ($>200$ nm) remained metallic over the temperature range of the measurements. © 2008 American Institute of Physics.

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Vanadium sesquioxide (V$_2$O$_3$) typifies material systems exhibiting a metal-to-insulator transition (MIT) as a function of temperature, pressure, and doping concentration. At an ambient pressure of 1 atm, V$_2$O$_3$ transforms from a rhombohedral paramagnetic metal to a monoclinic antiferromagnetic insulator phase upon cooling to 160 K, with a jump in the resistivity of about seven orders of magnitude. This behavior has stimulated extensive theoretical and experimental research on V$_2$O$_3$. Various methods have been devised to grow high-quality V$_2$O$_3$ thin films, both for samples to study the physics of the MIT in thin films and as the basis for potential sensing and actuation devices. While such films can be produced using pulsed laser deposition (PLD), this is usually done using a V$_2$O$_3$ target while exerting careful control of deposition conditions to give V$_2$O$_3$ deposits. In a recent paper we have reported the synthesis of high-quality epitaxial V$_2$O$_3$ films on $\{11\bar{2}0\}$ and (0001) sapphire ($\alpha$-Al$_2$O$_3$) substrates via PLD using a powder-pressed pure V$_2$O$_3$ target in an evacuated deposition chamber. The films on (0001) $\alpha$-Al$_2$O$_3$ displayed a MIT at $T$=180 K compared to $T$=160 K in single-crystal V$_2$O$_3$. The films on $\{11\bar{2}0\}$ $\alpha$-Al$_2$O$_3$, however, showed an insulator-to-insulator transition at $T$=186 K. For films on (0001) $\alpha$-Al$_2$O$_3$ the in-plane and out-of-plane strains were determined via x-ray diffraction (XRD) to be $\varepsilon_1=\varepsilon_2=-0.22\%$ and $\varepsilon_3=-0.13\%$, respectively. In films on $\{11\bar{2}0\}$ $\alpha$-Al$_2$O$_3$, there existed an anisotropic in-plane strain state with $\varepsilon_1=1.20\%$ and $\varepsilon_2=-1.15\%$. The variations in the phase transformation characteristics and in the resistivities of these films were thus attributed to different levels of strain and commensurate changes in the film morphologies.

In this letter, we present a study on the role of film thickness and internal strain on the electrical properties of V$_2$O$_3$ thin films deposited by PLD from V$_2$O$_3$ targets onto (0001) LiTaO$_3$ substrates. Such substrates have been used previously for the epitaxial deposition of V$_2$O$_3$, and the magnitude of the isotropic in-plane misfit (3.9%) is similar to that for growth on (0001) $\alpha$-Al$_2$O$_3$ ($-4.1\%$), although this is of the opposite sign.

V$_2$O$_3$ thin films were deposited onto (0001) LiTaO$_3$ substrates using a KrF pulsed excimer laser with a wavelength of 248 nm, an energy of 240 mJ/pulse, a pulse length of 20 ns, and a repetition rate of 6 Hz. The laser was focused on a powder-pressed stoichiometric V$_2$O$_3$ target rotating at 35 rpm. The laser fluence was estimated at about 2.8 J/cm$^2$, and this gave a growth rate of about 0.08 – 0.16 nm/s. The substrates were rotated at 20 rpm during deposition to promote homogenous growth of the films. The details of the fabrication of the target and of the deposition parameters have been presented elsewhere. Portions of the substrate were masked to enable the thickness of the film $h$ to be measured using atomic force microscopy (AFM) at the edge of the masked region. Films with $h=12$–406 nm were grown in this study.

A general area detector diffraction system diffractometer was used to collect XRD patterns from each of the films, and these patterns confirmed that the deposits were single-crystal epitaxial films. The conventional XRD spectra obtained from the films with $h=12$, 87, 200, 370, and 406 nm are shown in Fig. 1. These $\theta$–$2\theta$ scans were collected with the source and detector inclined equally to the substrate surface normal. As expected, the spectra contain only (0001) peaks from the substrate and deposit, except for the 370 nm film whose spec-

FIG. 1. (Color online) XRD patterns of V$_2$O$_3$ thin films on $c$-LiTaO$_3$ substrates of different thicknesses ranging from 12 to 406 nm.

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The surface morphology of the films was evaluated using AFM and in all cases the rms surface roughness $R$ was <2.5 nm. Four examples of AFM images are shown in Figs. 2(b)–2(e). All of the images showed self-similar morphologies with the exception of the 370 nm film, which exhibited a secondary surface deposit. These deposits appeared as three sets of laths, 1 μm long by 0.2 μm across lying parallel to (1120) in the surface: the {1120} peak in the XRD spectrum from this film presumably arises from these laths. The values of $R$ are plotted against $h$ in Fig. 2(a) and it is clear that the roughness only starts to increase after the onset of plastic relaxation, whereupon $R$ increases linearly with $h$. The development of surface roughness with deposit thickness as a secondary relaxation mechanism after misfit dislocation introduction has been well documented for epitaxial semiconductors and it seems likely that the roughening observed here occurs by similar processes.

Electrical resistance measurements were performed using a Displex system equipped with a LAKESHORE temperature controller software package. The Van de Pauw and standard four-point probe methods were used to measure the in-plane transport properties of all the films as a function of temperature over the range 10–340 K. Figure 3(a) is a plot of the temperature dependence of resistivity for each of the films. Four different types of electrical transitions were observed, as highlighted in Fig. 3(b). Such transitions have been reported previously in V$_2$O$_3$ films on other substrates, but we observe here all four types of transitions in the same film-substrate system.

The thinnest film ($h=12$ nm) displays an insulator-insulator transition (IIT) (type 1), where the resistivity increases with decreasing temperature down to $\sim220$ K followed by a jump of approximately two orders of magnitude. Films with $h=24$ and 35 nm exhibit the expected MIT (type 2). There is a decrease in the resistivity with decreasing...
temperature down to \(\sim 190\) K followed by a jump of approximately three orders of magnitude. We note that this transition occurs at a temperature \(\sim 30\) K higher than bulk \(\text{V}_2\text{O}_3\) and the change in the resistivity at the phase transformation is four orders of magnitude smaller. The 46 nm sample shows a metal-metal transition (MMT) (type 3), where there is a linear decrease in resistivity with decreasing temperature down to \(T \approx 128\) K followed by a small jump in resistivity. For temperatures lower than 72 K, the sample displays typical metallic behavior with a decrease in the resistivity as the temperature is lowered further. Thicker films (\(h > 80\) nm) demonstrated only metallic (M) (type 4) behavior over the whole temperature range with no indication of a phase transformation.

One of the interesting aspects of the data shown in Fig. 3(a) is that the insulating phases in \(\text{V}_2\text{O}_3\) are systematically eliminated with increasing film thickness. The high temperature insulating phase observed in the thinnest film (\(h=12\) nm), which displays the IIT behavior, disappears as \(h\) is increased, resulting in an MIT in the films with \(h=24\) and 34 nm. The low temperature insulating phase observed in 12, 24, and 34 nm thick films vanishes with further increases in \(h\), leading to the emergence of a MMT in the 46 nm thick film. In films with \(h=87–406\) nm, we see that a metallic phase is stabilized and the resistivity of the films decreases linearly as a function of temperature down to the temperature limit of our measurement system (10 K). The observed behavior follows a systematic order that can be summarized as IIT \(\rightarrow\) MIT \(\rightarrow\) MMT \(\rightarrow\) M with increasing \(h\). The plot of the room temperature (RT=25 °C) resistivity as a function of \(h\) is shown in Fig. 4. The resistivity values of the films decrease with increasing \(h\), further demonstrating the stabilization of a metallic phase.

The IIT in the thinnest film is most likely due to the high in-plane tensile stresses. The compressive out-of-plane strain [Fig. 2(a)] calculated from the XRD data (Fig. 1) is consistent with a pseudomorphic film in biaxial tensile tension parallel to the substrate surface. As such, the in-plane interionic distances will be larger, leading to a separation of the \(a_{1g}\) and \(e_{g}(\pi)\) bands and hence the insulating behavior above the phase transformation temperature. The overlap of these bands in bulk \(\text{V}_2\text{O}_3\) results in metallic behavior above the MIT. After the onset of strain relaxation at \(h=15–20\) nm as confirmed by XRD, the in-plane tensile strains are greatly reduced and the expected MIT transition is observed in the 24 and 34 thick films. However, the absence of a phase transformation and the stabilization of the metallic phase in thicker films is a very surprising finding. Shifts in the MIT temperature and stabilization of the metallic phase have been observed in other PLD-deposited \(\text{V}_2\text{O}_3\) films.\(^{19,21}\) One would expect that with an increase in \(h\) and a commensurate relaxation of the epitaxial stresses, the thicker films would assume the properties of the bulk. Previous reports show that completely relaxed \(\text{V}_2\text{O}_3\) films on (0001) \(\alpha\)-\(\text{Al}_2\text{O}_3\) tend to display the typical MIT of bulk \(\text{V}_2\text{O}_3.\)

We note that all electronic phase transformations in bulk \(\text{V}_2\text{O}_3\) can be suppressed by the application of a hydrostatic pressure of about 23 kbar or by doping with Ti [for \((\text{V}_{1-x}\text{Ti}_x)\text{O}_3\) with \(x > 0.05\), the antiferromagnetic insulator phase is completely suppressed].\(^{22}\) Defects have highly localized short-range stress fields. In films with a dense misfit dislocation substructure and surface undulations, one could imagine that these stress fields would overlap, creating very thin “layers” at the film-substrate interface and at the surface with a different strain state than the rest of the film. The observed behavior in the thicker films might thus be related to specific defect microstructures that generate localized conditions equivalent to the application of a hydrostatic pressure in bulk. We are currently conducting a detailed microstructural analysis of the \(\text{V}_2\text{O}_3\) films on both (0001) \(\text{LiTaO}_3\) and (0001) \(\alpha\)-\(\text{Al}_2\text{O}_3\) in an attempt to identify the differences in defect structure that might lead to the contrasting electronic behavior.

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