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Epitaxial growth and electronic structure of LaTiO$_x$ films

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LaTiO$_x$ films have been grown on (001) perovskite oxide substrates by pulsed-laser deposition. Both single-phase perovskite LaTiO$_3$ and layered La$_2$Ti$_2$O$_7$ films could be stabilized by varying the oxygen partial pressure and substrate temperature during growth. We have obtained a crystallographic and electronic phase diagram for LaTiO$_x$ films, demonstrating the ability to vary the titanium valence from 3+ to 4+ in thermodynamically unfavorable growth conditions by utilizing interface energies. © 2002 American Institute of Physics. [DOI: 10.1063/1.1481767]

The physical properties of La$_{1-x}$Sr$_x$TiO$_3$ evolve from a semiconductor to an antiferromagnetic insulator as the formal titanium valence varies from 4+ to 3+ with substitutional doping. For a broad range of intermediate valences, a good metal is formed, and this system is currently studied as a prototypical example of the development of a Mott–Hubbard gap as the 3$d^1$ configuration at half filling is approached. In the field of oxide electronics, this is an important materials family, since SrTiO$_3$ is a common substrate and doped SrTiO$_3$ is a high-mobility metallic layer, while modulating the correlation gap of LaTiO$_3$ makes it a candidate for novel electronic devices.

The synthesis of stoichiometric bulk LaTiO$_3$ is quite difficult, primarily due to the extremely reducing conditions necessary to stabilize Ti$^{4+}$. For instance, the thermodynamic phase stability of Ti$_2$O$_3$ requires an oxygen partial pressure ($P_{O_2}$) below $10^{-10}$ Torr at typical growth temperatures. Pulsed-laser deposition (PLD) is potentially suitable for controlling the oxidation process during metal-oxide thin-film growth. The metal-oxide in the bulk target can be reduced during burst ablation with short laser pulses, and the oxidation process on the surface of the growing film generally involves not only bulk thermodynamics (temperature and $P_{O_2}$), but also surface oxidation kinetics and interface energies.

In this letter, we report a systematic study controlling the crystalline phase of LaTiO$_x$ films grown on perovskite substrates. As a function of $P_{O_2}$ during growth, either perovskite LaTiO$_3$ or the layered compound La$_2$Ti$_2$O$_7$ is formed. The microstructure of the films reflects the competition between the bulk thermodynamic oxidative state, which favors La$_2$Ti$_2$O$_7$, and the interface energy, which favors LaTiO$_3$. We demonstrate the ability to control the Ti valence between 4+ (ferroelectric band insulator La$_2$Ti$_2$O$_7$) and 3+ (Mott insulator LaTiO$_3$) far from thermodynamic limits.

LaTiO$_x$ films were grown in an ultra-high-vacuum chamber (Pascal) by PLD, using a single-phase La$_2$Ti$_2$O$_7$ polycrystalline target grown by solid-state reaction processing in air. Single-crystal (001) SrTiO$_3$ and LaAlO$_3$ substrates were used to grow 2000 Å films at temperatures between 650 and 950 °C, as measured by a pyrometer. A KrF* excimer laser with a repetition rate of 5–10 Hz was used for ablation, with a laser fluence at the target surface of ~1.7 J/cm$^2$. The target–substrate distance was 45 mm, and $P_{O_2}$ was varied between 0.1 and $10^{-10}$ Torr, as monitored by a residual gas analyzer on the chamber. After the growth, the temperature was lowered at a constant rate of 50 °C/min, keeping $P_{O_2}$ constant.

Reflection high-energy electron diffraction (RHEED) intensity oscillations of the specular spot were observed at the beginning of the growth for all deposition experiments carried out on SrTiO$_3$ at growth temperatures below 850 °C and $P_{O_2} \leq 1 \times 10^{-4}$ Torr. Regular oscillations typically disappeared after 6–10 periods, and the pattern showed weak streaks and broad diffraction spots after the initial growth, indicating a roughening surface. With $P_{O_2} \geq 1 \times 10^{-4}$ Torr, twinned streaks with a slight tilting from the surface normal were observed for the films assigned to be La$_2$Ti$_2$O$_7$, as discussed below. From the film thickness measured by Rutherford backscattering spectroscopy (RBS), the observed RHEED oscillation period is found to correspond to the growth of one perovskite unit cell (~4 Å).

The epitaxial structure of the films grown both on SrTiO$_3$ and on LaAlO$_3$ in one deposition run showed essentially the same characteristics. Figure 1(a) shows the 2θ x-ray diffraction (XRD) pattern of a film grown at 970 °C in $P_{O_2} = 2 \times 10^{-4}$ Torr on SrTiO$_3$. The film is determined to be the (~210) orientation of monoclinic La$_2$Ti$_2$O$_7$ (a = 13.01 Å, b = 5.54 Å, c = 7.81 Å, β = 98.7°). La$_2$Ti$_2$O$_7$ is derived from the perovskite structure by considering four unit-cell-thick [110] perovskite layers connected by crystallographic shears in the [100] direction, which incorporate the extra oxygen. From the epitaxial relation between the distorted TiO$_6$ octahedral lattice in La$_2$Ti$_2$O$_7$ with respect to the (001) perovskite lattice, the crystallographic angle between (~210) La$_2$Ti$_2$O$_7$ and (001) SrTiO$_3$ is 4.52°. Consequently, the higher-index peaks of the film are not seen for a scan aligned on axis with the SrTiO$_3$ substrate [Fig. 1(a), upper curve]. By tilting the substrate by 4.5° off axis from the surface normal along the SrTiO$_3$(100) direction, the intense La$_2$Ti$_2$O$_7$ film peaks [labeled as aligned to layer in Fig. 1(a)] are recovered.
The film is twinned across the ⟨100⟩ direction of the substrate; therefore, ⟨−210⟩ peaks have fourfold symmetry as shown by an in-plane φ scan for the same sample [Fig. 1(b)]. Similar XRD patterns were obtained for other films grown at $P_{\text{O}_2} \approx 2 \times 10^{-4}$ Torr. Figure 1(c) shows the $\theta$–2θ XRD pattern of a film grown at 700 °C in $P_{\text{O}_2} = 5 \times 10^{-9}$ Torr on LaAlO$_3$. The film shows strong peaks aligned with the substrate, assigned to be the perovskite-phase LaTiO$_3$ (00$l$) where $l$ is the Miller index for the pseudocubic lattice.

Figure 2 compares annular dark-field images of two films obtained by scanning transmission electron microscopy (JEOL 2010F). Figure 2(a) shows a La$_2$Ti$_2$O$_7$ film, viewed parallel to the SrTiO$_3$ substrate [100] zone axis, displaying the characteristic layered structure along the perovskite $|$[110]$|$ directions. The different orientation grains, arising from the fourfold orientation degeneracy discussed in Fig. 1(a), are clearly seen. A Fourier transform of Fig. 2(a) [inset to Fig. 2(a)] reproduces the 4.5° tilt from the substrate normal observed in Fig. 1(a). Figure 2(b) shows a higher-magnification view of a single grain. The observed layered structure is well reproduced by the inset simulation of La$_2$Ti$_2$O$_7$, viewed along a projection that is $(\beta - 90)°$ from the $c$-axis. This is consistent with the orientation relationship determined by XRD.

Figure 2(c) shows a LaTiO$_3$ film grown on SrTiO$_3$. Although the film clearly retains the perovskite structure of the substrate near the interface, a high density of $|$[110]$|$ faults develops, driven energetically to achieve the equilibrium oxidative state of Ti. All of the film structures shown in Fig. 2 can be considered members of the homologous series $A_{n+1}B_{n+1}O_{3n+5}$, $0 \leq n \leq \infty$, where $n = 3$ corresponds to La$_2$Ti$_2$O$_7$ and $n = \infty$ corresponds to LaTiO$_3$. Unlike other perovskite-derived phases such as Ruddlesden–Popper phases, in this structural series, the valence states of cations $A$ and $B$ change with $n$. The $|$[110]$|$ faults in Fig. 2(c) correspond, therefore, to locally raising the oxidative state of Ti. The stacking faults seen in La$_2$Ti$_2$O$_7$, indicated by arrows in Fig. 2(b), can be considered $n = 4$ La$_5$Ti$_4$O$_{17}$ interlayers, for which the Ti valence is slightly less than 4+. The structure of the LaTiO$_3$ film is quickly dominated by the interface energy and oxidation kinetics at the growing interface, as we do not observe further evolution of the film structure above ~10 perovskite unit cells.

Film composition was determined from RBS and x-ray photoelectron spectroscopy (XPS). XPS was performed in a separate analysis chamber (Perkin Elmer PHI5800) after quick ex-situ transfer from the growth chamber, using an Al $K\alpha$ x-ray source with an escape angle of 45°. The surface La to Ti ratio was found to be, typically, 0.99±0.02, reflecting stoichiometric transfer of the target cation species. RBS measured
measurements using a 2 MeV Ar beam were used to estimate film stoichiometry, using the La to Ti ratio obtained from XPS. This was necessary to resolve the signal overlap of the film and substrate elements Ti and O. Simulation of the random yield spectra performed assuming the composition of La:Ti:O = 1:1:x yielded values of x = 3.5 ± 0.15 and 3.0 ± 0.1 for films identified as La₂Ti₂O₇ and LaTiO₃, respectively. The channeling yield along the substrate [001] direction was quite poor, 85% for La₂Ti₂O₇ and 56% for LaTiO₃, reflecting the microstructure revealed in Fig. 2.

Evaluation of the Ti valence, as well as refining the oxygen stoichiometry, by XPS was unsuccessful due to the tendency of the surface of the film to further oxidize upon exposure to air. In order to measure the Ti valence accurately in the bulk of the film, electron energy-loss spectroscopy (EELS) measurements were performed in the electron microscope. The sample thickness was chosen so that surface states produce a negligible fraction of the transmitted signal. Figure 3 shows Ti L₂,₃ edge EELS spectra taken from LaTiO₃ and La₂Ti₂O₇ films, as well as the SrTiO₃ substrate. The close agreement of the La₂Ti₂O₇ and the SrTiO₃ spectra confirms the 4+ oxidative state of Ti in La₂Ti₂O₇. A core-level shift of ~1.2 eV is clearly seen for LaTiO₃, indicating a Ti³⁺ valence state. The observed Ti L₂,₃ edge features in the EELS spectra closely match the Ti 2p x-ray absorption spectra reported for La₁₋ₓSrₓTiO₃ in bulk.¹¹

Figure 4 summarizes our results in a phase diagram for LaTiO₃ films grown in this study. The boundary between LaTiO₃ and La₂Ti₂O₇ is located at a constant line of P₀₂ ~ 1 × 10⁻⁴ Torr. The films assigned to La₂Ti₂O₇ always showed insulating properties, while LaTiO₃ displayed increasingly metallic behavior with decreasing P₀₂. Hall-effect measurements show electron carrier densities varying from 10¹⁹ to 10²² cm⁻³ across this range, resulting from the known propensity of LaTiO₃ to accommodate significant oxygen off-stoichiometry.²,₁² Our results for films grown on (001) perovskite substrates can be contrasted with work on (110) substrates,¹³ in which the different orientations pro-

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FIG. 3. Ti L₂,₃ electron energy-loss spectra taken from the LaTiO₃ film, La₂Ti₂O₇ film, and SrTiO₃ substrate with ~0.7 eV energy resolution.

FIG. 4. Growth phase diagram of oxygen partial pressure vs growth temperature for 200Å-thick LaTiO₃ films. Samples indicated by closed circles and closed squares were evaluated to be LaTiO₃ and La₂Ti₂O₇, respectively. Dashed circle indicates the optimal growth condition for LaTiO₃.