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Growth of high-quality SrTiO₃ films using a hybrid molecular beam epitaxy approach

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A hybrid molecular beam epitaxy approach for atomic-layer controlled growth of high-quality SrTiO₃ films with scalable growth rates was developed. The approach uses an effusion cell for Sr, a plasma source for oxygen, and a metal-organic source (titanium tetra isopropoxide) for Ti. SrTiO₃ films were investigated as a function of cation flux ratio on (001) SrTiO₃ and (LaAlO₃)_{0.3}(Sr₂AlTaO₆)_{0.7} (LSAT) substrates. Growth conditions for stoichiometric insulating films were identified. Persistent (>180 oscillations) reflection high-energy electron diffraction oscillation characteristic of layer-by-layer growth were observed. The full widths at half maximum of x-ray diffraction rocking curves were similar to those of the substrates, i.e., 34 arc sec on LSAT. The film surfaces were nearly ideal with root mean square surface roughness values of less than 0.1 nm. The relationship between surface reconstructions, growth modes, and stoichiometry is discussed. © 2009 American Vacuum Society. [DOI: 10.1116/1.3106610]

I. INTRODUCTION

Titanates with the perovskite and related structures are among the most important complex oxides, exhibiting properties as diverse as ferroelectricity, superconductivity, and strongly correlated Mott–Hubbard-type insulator characteristics. Low energetic, high-purity techniques such as molecular beam epitaxy (MBE) have the potential to produce epitaxial perovskite films with low intrinsic defect concentrations and atomic-layer control. Oxide MBE growth of cation and oxygen stoichiometric perovskite titanate films has, however, proved challenging. Oxides such as SrTiO₃ have no wide “MBE growth window” in which the cation stoichiometry is self-regulating and thus their growth requires precise flux control.^{1,2} Furthermore, the low vapor pressure of Ti severely limits growth rates in MBE from high temperature effusion cells or sublimation sources.^{3–5} These sources also suffer from flux instabilities in oxidizing growth environments.⁴ Typical growth rates in SrTiO₃ MBE are between 0.1 and 0.7 nm/min.^{6–9} Low growth rates severely limit practically achievable film thicknesses needed for film characterization and in device structures. Higher growth rates are achieved with electron beam evaporators, but the inherent instability of these sources requires flux monitoring and feedback control.^{5,10}

In this article, we report on a novel hybrid approach for the growth of stoichiometric SrTiO₃ films that combines chemical beam, solid source MBE, is capable of scalable growth rates and produces films of excellent structural quality. This hybrid MBE approach uses an effusion cell for Sr, a rf plasma source for oxygen, and a metal-organic source, titanium tetraisopropoxide [Ti(OC₃H₇)₄ or TTIP], for Ti. Advantages of the metal-organic source include a vapor pressure that is orders of magnitude higher than solid Ti (Refs. 11

and 12) and a beam flux that should be relatively unaffected by the presence of oxygen in the growth chamber.¹²

II. EXPERIMENT

Epitaxial SrTiO₃ films were grown on (001) SrTiO₃ and on (001) (LaAlO₃)_{0.3}(Sr₂AlTaO₆)_{0.7} (LSAT) substrates in a MBE system (GEN 930, Veeco Instruments) with a base pressure of 10⁻¹⁰ torr. The lattice mismatch between SrTiO₃ (*a*=3.905 Å) and LSAT (*a*=3.868 Å) is -0.9%. Selected substrates were pretreated in a rapid thermal annealing furnace at 1100 °C in oxygen for 2 min. This treatment caused the substrate surface to exhibit well-defined regular terraces with one unit cell step height. The substrates were ultrasonically cleaned in acetone, isopropanol, and de-ionized water before and after deposition of a Ta backing layer, which served to improve the heat transfer between heater and substrate. Samples were baked in the entry/exit chamber at 200 °C for 2 h, followed by annealing in the growth chamber at 700 °C for 20 min. Each substrate was cleaned in an oxygen plasma for 20 min using a rf plasma source operated at 250 W and a constant beam equivalent pressure (BEP) of 5 × 10⁻⁶ torr. Titanium tetraisopropoxide (99.999%, Sigma-Aldrich, USA) was supplied by thermal evaporation from a bubbler that was connected through a gas inlet system to the growth chamber. No carrier gas was used. Strontium was supplied from a low temperature effusion cell. No Sr flux instability over time was observed, consistent with reports in literature that Sr sources are relatively stable at intermediate oxygen pressures.¹³ A series of samples was grown at different TTIP to Sr flux ratios by varying the TTIP BEPs between 2 × 10⁻⁶ and 3 × 10⁻⁶ torr and the Sr BEPs between 4.8 × 10⁻⁸ and 8.0 × 10⁻⁸ torr. The substrate temperature was 700 °C (measured using an Ircon Modline 3 pyrometer) and the oxygen BEP was 5 × 10⁻⁶ torr for all films. The plasma was left on during cooling until the sample reached a temperature of 250 °C.

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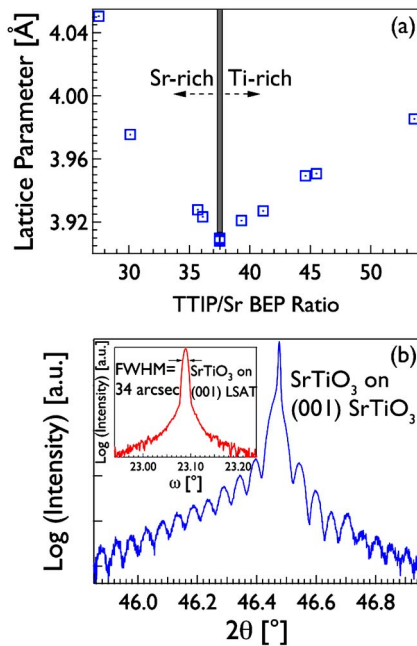


FIG. 1. (Color online) (a) Out-of-plane lattice parameter as a function of TTIP/Sr BEP flux ratio for SrTiO₃ films grown on (001) SrTiO₃. (b) High-resolution x-ray diffraction 2θ - ω scan of the 002 reflection of a SrTiO₃ film grown on (001) SrTiO₃ showing good overlap between film and substrate reflection and thickness fringes. The film was grown with TTIP and Sr BEPs of 2.1×10^{-6} and 5.6×10^{-8} torr, respectively. The film thickness is ~ 200 nm. The inset shows a ω -scan of the 002 reflection of a SrTiO₃ film (thickness of ~ 140 nm) grown on (001) LSAT under the same conditions. The ω -FWHM is 34 arc sec (0.0095°).

Reflection high-energy electron diffraction (RHEED) was used to monitor the growth *in situ*. Films were characterized *ex situ* using on-axis high-resolution x-ray diffraction 2θ - ω and ω -scans with a Philips X'Pert Panalytical MRD Pro thin-film diffractometer equipped with a duMond-Hart-Partels Ge(440) incident beam monochromator. All films were epitaxial with a cube-on-cube orientation relationship with the substrates. RHEED intensity oscillations were used to determine the film thickness, which were calibrated using x-ray reflectivity measurements of SrTiO₃ on LSAT. Growth rates were as high as 3.3 nm/min and could easily be further increased by using higher Sr and TTIP fluxes. Atomic force microscopy (AFM) in tapping mode was used to investigate the surface morphology. The electrical resistivity of the films was measured in a four-point probe configuration with Ti contacts deposited by electron beam evaporation.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the out-of-plane lattice parameter of a series of homoepitaxial SrTiO₃ films grown with different TTIP/Sr flux ratios. The film lattice parameter was strongly correlated with cation stoichiometry, similar to what has been observed for pulsed laser deposited films.¹⁴ The lattice parameter corresponded to that of bulk SrTiO₃ for a TTIP/Sr flux ratio of 37.5. Good overlap between film and substrate reflections was achieved for this flux ratio [see Fig. 1(b)], consistent with a stoichiometric film. The film lattice param-

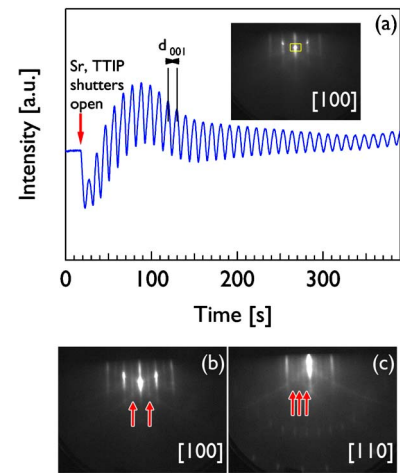


FIG. 2. (Color online) (a) RHEED intensity of the specular spot as a function of time for a SrTiO₃ film grown on SrTiO₃ with TTIP and Sr BEPs of 2.1×10^{-6} and 5.6×10^{-8} torr, respectively. The RHEED oscillations persist for >180 cycles. The inset shows a RHEED pattern of the SrTiO₃ substrate along the [100] azimuth during oxygen plasma cleaning. (b) RHEED patterns along the [100] azimuth and (c) along the [110] azimuth taken after growth at a substrate temperature of 160 °C, showing $\frac{1}{2}$ order and $\frac{1}{4}$ order reflections, respectively.

eter increased for nonstoichiometric films, independent of whether they were Ti or Sr rich. The thickness oscillations seen for the homoepitaxial film are most likely due to a small offset between the film and the substrate, as may be caused by surface contamination or adsorbates not removed during heating of the substrate. The thickness oscillations corresponded to a thickness of ~ 180 nm, which is somewhat less than that determined from the RHEED oscillations (~ 200 nm). Detailed high-resolution x-ray diffraction simulations are underway to determine the magnitude of the offset.¹⁵ No oscillations were observed in x-ray reflectivity measurements for any of the films (stoichiometric or nonstoichiometric) grown on SrTiO₃ substrates. Because SrTiO₃ substrate possesses a significant mosaic, leading to wide x-ray rocking curves,⁸ the films' rocking curve widths were determined on structurally more perfect LSAT substrates. The inset in Fig. 1(b) shows a ω -scan of a 140 nm thick stoichiometric SrTiO₃ film on (001) LSAT. The full width at half maximum (FWHM) of the 002 SrTiO₃ reflection was 34 arc sec, which was similar to that of the LSAT substrate. No measurable electrical conductivity was observed for the stoichiometric SrTiO₃ films.

Figure 2(a) shows the time dependent RHEED intensity oscillations observed during the growth of a stoichiometric film. Oscillations in RHEED are characteristics for a layer-by-layer growth mode yielding atomically smooth films (see below).¹⁶ Similar to what has been reported in literature,^{10,17} each oscillation corresponded to one unit cell of SrTiO₃, as confirmed by x-ray reflectivity measurements. Although RHEED oscillations have been widely reported on in SrTiO₃ MBE, most recent studies have focused on approaches in which at least one of the cation fluxes was shuttered, causing a periodic change in surface termination.^{2,7,18} In contrast, the

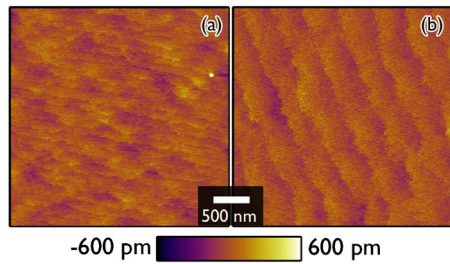


FIG. 3. (Color online) (a) AFM image of a stoichiometric SrTiO₃ film on SrTiO₃ that showed the (2×1) surface reconstruction after growth. The rms roughness is 0.086 nm and the film thickness is ~ 200 nm. (b) AFM image of a SrTiO₃ film on LSAT. The rms roughness is 0.072 nm and the film thickness is 140 nm. Both films were grown using the stoichiometric parameters. The AFM image area is $3 \times 3 \mu\text{m}^2$.

oscillations observed in the coevaporation approach used here likely reflect changes in the surface morphology. Remarkably, the oscillations persisted for a long time on both LSAT and SrTiO₃ substrates. For example, more than 180 oscillations were observed for a stoichiometric film on SrTiO₃. In most systems, RHEED oscillations dampen after a relatively short period of time because the growth proceeds simultaneously in different layers, causing a loss in coherence. Persistent RHEED oscillations in (nonshuttered) MBE have been reported for several systems: in particular, homoepitaxial Si,¹⁹ Pt,²⁰ and in one study of SrTiO₃.¹⁰ Persistent layer-by-layer growth could be an indication of a low step-edge barrier.²¹ Furthermore, it has been suggested that surface reconstructions promote layer-by-layer growth.²² RHEED oscillations are, however, a dynamical diffraction phenomenon¹⁶ and further studies are required to understand them in this system.

Similar to (001) SrTiO₃ single crystal surfaces,^{23–27} surface reconstructions were observed both during and after growth. During growth, both the stoichiometric and Sr-rich films showed $\frac{1}{2}$ order reflections along $\langle 110 \rangle$, corresponding to a $c(2 \times 2)$ reconstruction. No surface reconstructions were observed for the Ti-rich films. Thus the results are not consistent with previous reports, in which 2×2 reconstructions along $\langle 100 \rangle$ and $\langle 110 \rangle$ were considered to be a signature of Ti-rich or Sr-rich films, respectively.^{6,7} Since all films (stoichiometric and nonstoichiometric) showed persistent RHEED oscillations, no obvious correlation with specific surface reconstructions could be established. After growth and cooling, RHEED showed $\frac{1}{2}$ order reflections along $\langle 100 \rangle$ for the stoichiometric films, i.e., the reconstruction changed to (2×1) with domains [Fig. 2(a)]. The film surfaces on both substrates were atomically flat with terraces [Figs. 3(a) and 3(b)]. The root mean square (rms) surface roughness values were less than 0.1 nm. Given the stepped morphology of the final surface, further investigations are needed to determine if a transition to step-flow mode occurs. For some stoichiometric films additional $\frac{1}{4}$ order reflections along $\langle 110 \rangle$ were seen after growth [see Figs. 2(b) and 2(c)], corresponding to a $c(4 \times 4)$ reconstruction. Films exhibiting the $c(4 \times 4)$ reconstructions showed a surface network pattern (not shown)

not seen in the films with only the (2×1) reconstruction. The nonstoichiometric films showed nanocrystallites on the surface, which were occasionally also observed for the stoichiometric films similar to observations on bulk SrTiO₃ surfaces²⁶ and films grown by solid source MBE.⁹ The density of these crystallites increased with the degree of nonstoichiometry.

In summary, we have shown that a hybrid MBE growth approach allows for the growth of stoichiometric insulating SrTiO₃ films with scalable growth rates and excellent structural quality, as evidenced by the very narrow rocking curves and nearly ideal surfaces. Further studies are required to understand why RHEED oscillations persisted for long periods and to determine if step-flow growth also partially occurred. Future studies are also underway to determine the residual carbon concentration from the metal-organic precursor as a function of growth conditions (oxygen pressure and substrate temperature). For example, our previous studies of metal-organic MBE of TiO₂ have shown that oxygen aids in the breakdown of the precursor;¹² thus the oxygen pressure may influence the carbon content. Finally, the hybrid MBE approach should also be of interest for other perovskite titanates or complex oxide films with constituents that have a low vapor pressure.

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