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Growth of homoepitaxial $SrTiO_3$ thin films by molecular-beam epitaxy

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We report the structural properties of homoepitaxial (100) $SrTiO_3$ films grown by reactive molecular-beam epitaxy (MBE). The lattice spacing and x-ray diffraction (XRD) rocking curves of stoichiometric MBE-grown $SrTiO_3$ films are indistinguishable from the underlying $SrTiO_3$ substrates. Off-stoichiometry for both strontium-rich and strontium-poor compositions (i.e., $Sr_{1+x}TiO_{3+\delta}$ films with $-0.2<x<0.2$) results in lattice expansion with significant changes to the shuttered reflection high-energy electron diffraction oscillations, XRD, and film microstructure. The dependence of lattice spacing on nonstoichiometry is smaller for MBE-grown films than for homoepitaxial (100) $Sr_{1+x}TiO_{3+\delta}$ films prepared by pulsed-laser deposition or sputtering. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3117365]

Homoepitaxial growth is a standard way of assessing the ability of a thin film growth technique to make a material. Although this approach has been widely used to assess a multitude of techniques for the growth of semiconductors, it was largely bypassed in the drive to make thin films and heterostructures of complex oxides, e.g., oxide superconductors. Now, decades later, studies of homoepitaxial films of complex oxides are beginning to emerge with surprising results. For example, homoepitaxial $SrTiO_3$ films grown by pulsed-laser deposition (PLD) have been found to have compositions differing significantly from the stoichiometric targets from which they are ablated,[1,2] to have extended lattice constants[1–3] that get even more extended following oxygen annealing,[1,2] and even to be ferroelectric at room temperature[4] in striking contrast to unstrained (bulk) $SrTiO_3$ itself which is not ferroelectric at any temperature. Only when grown with a very narrow range of laser fluence and ablation area do PLD-grown $SrTiO_3$ films appear to be stoichiometric with bulk lattice constants.[2] Studies for homoepitaxial $SrTiO_3$ films made by sputtering show similar features.[5] The defect structure of highly nonstoichiometric homoepitaxial $SrTiO_3$ films grown by PLD has been studied.[6] Here we study the structural properties of homoepitaxial $SrTiO_3$ films grown by reactive molecular-beam epitaxy (MBE), including the effect of changes in stoichiometry ($-0.2<x<0.2$) on the structural properties of the resulting homoepitaxial $Sr_{1+x}TiO_{3+\delta}$ films.

250 unit-cell-thick $Sr_{1+x}TiO_{3+\delta}$ films, approximately 100 nm in thickness, were grown on (100) $SrTiO_3$ substrates in a Veeco 930 oxide MBE system at a substrate temperature of 650 °C in a background pressure of 5.0×10^{-7} Torr of molecular oxygen. Two sets of five films were grown with one set being grown in the additional presence of ~10% ozone. The compositions of the $Sr_{1+x}TiO_{3+\delta}$ films ranged from $-0.2<x<0.2$. A Ti-Ball™ was used as the titanium source[7] and an effusion cell supplied strontium. Both sources were shuttered to deposit alternating monolayer doses of SrO and TiO_2.[8] Shutter times were initially set based on flux measurements made using a quartz crystal microbalance, and then precisely tuned by optimizing shuttered reflection high-energy electron diffraction (RHEED) intensity oscillations during deposition on a calibration sample immediately prior to the growth of the sample sets.[8,9] These shuttered RHEED oscillations differ from typical RHEED growth oscillations and are more similar to the behavior seen in migration-enhanced epitaxy.[10] A set of films was also grown using true codeposition with both shutters being open for the duration of the growth. The strontium and titanium elemental source fluxes were approximately 3×10^{13} atoms/(cm^2 s), corresponding to shutter times of about 20 s and a film growth rate of 6 Å/min. Substrates were prepared using a termination recipe that provides a TiO_2-terminated starting surface.[11] Growth temperature was verified by optical pyrometry. The film structure, including out-of-plane lattice constant, was examined by x-ray diffraction (XRD) using a high-resolution Philips X'Pert Pro MRD diffractometer with a PreFix hybrid monochromator on the incident side and triple axis/rocking curve attachment on the diffracted side. The microstructure of the film was further analyzed using a 200kV FEI Tecnai F20-ST scanning transmission electron microscope (STEM). To increase signal to noise and ave3rage out the scan noise, up to 6 successive images, each recorded at 8 microseconds per pixel, were cross-correlated and averaged.

Figures 1(a) and 1(b) show the shuttered RHEED intensity as a function of time for the 01 streaks along the [011] azimuth at the beginning and middle of the growth of a 100 nm thick stoichiometric film of (100) $SrTiO_3$. The shuttered RHEED oscillations are stable and maintain intensity throughout the duration of the entire film deposition indicating both full monolayer dosage and 1:1 stoichiometry.[8] Optimizing these oscillations is done prior to growth on a calibration sample by tuning computer-controlled shutter times.

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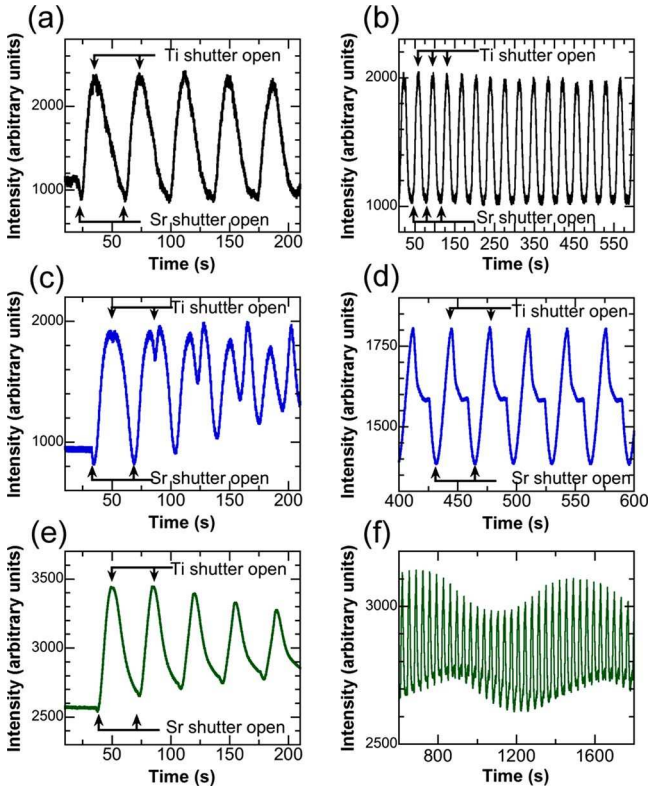

FIG. 1. (Color online) Shuttered RHEED oscillation behavior at the beginning [(a), (c), and (e)] and middle [(b), (d), and (f)] of the growth process of $Sr_{1+x}TiO_{3+\delta}$ films with stoichiometric composition (x=0) [(a) and (b)], ~10% strontium excess (x=0.1) [(c) and (d)], and ~10% strontium deficiency (x=−0.1) [(e) and (f)].

Film composition was verified by Rutherford backscattering spectrometry (RBS). While there is some overlap in the signal, determining the homoepitaxial film composition from the substrate using RBS is possible and results confirm that all off-stoichiometric films are within 5% of the expected compositions based on shutter time adjustments. Stoichiometric homoepitaxial films had less than a 1% difference in composition from the substrate.

RHEED oscillations from a $Sr_{1+x}TiO_{3+\delta}$ film with x =0.1 is displayed in Figs. 1(c) and 1(d). In the excess strontium case the intensity reaches a maximum and then starts to decrease before the strontium shutter is closed and the titanium shutter is opened. Following the start of growth [Fig. 1(c)] this maximum occurs earlier in time for each subsequent layer before the strontium shutter is closed. This case eventually results in stable oscillations [Fig. 1(d)] of a different form to that of the stoichiometric x=0 case. Similar behavior is observed during the strontium cycle when the strontium excess is increased to x=0.2, except the intensity goes down further after reaching its maximum before the closing of the strontium shutter.

Figures 1(e) and 1(f) are of a strontium deficient film x=−0.1. In this situation, the strontium shutter closes and the titanium shutter opens before the RHEED intensity reaches a maximum. This causes the peak maxima to decrease in intensity over time. During each cycle the strontium shutter is closed earlier than in the preceding oscillation. This eventually results in a beat frequency with a long period due to the accumulation of insufficient monolayer doses of strontium. Strontium-deficient films with even lower x had correspondingly shorter periods for this oscillation envelope.

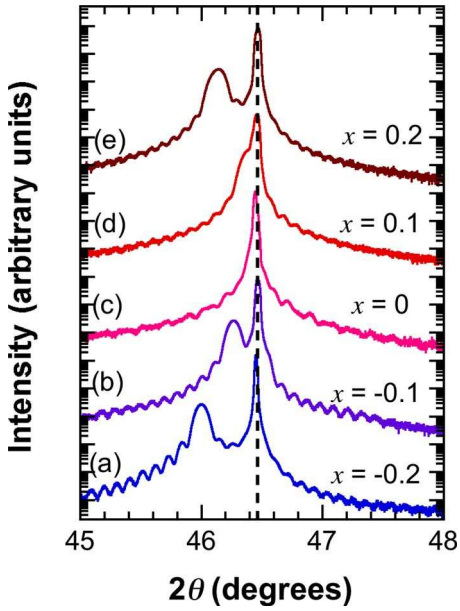

FIG. 2. (Color online) Out-of-plane XRD data taken around the 200 peak of $Sr_{1+x}TiO_{3+\delta}$ films with x=−0.2 (a), −0.1 (b), 0 (c), 0.1 (d) and 0.2 (e). The vertical dashed line marks the 200 peak of the (100) $SrTiO_3$ substrate.

As shown in Fig. 2, the nonstoichiometric films exhibit XRD peaks distinct and slightly offset to lower 2θ from the substrate peaks while the stoichiometric film peaks are indistinguishable from the substrate peaks. Intensity oscillations corresponding to the ~100 nm film thickness around film peaks are present in all films, including stoichiometric films, indicating smooth interfaces between the film and substrate, but also suggesting differences between deposited film and substrate. The deviation between the 2θ position of the film peak and the substrate peak increases as film composition diverges from stoichiometric. The in-plane lattice spacing of the $Sr_{1+x}TiO_{3+d}$ films were determined from XRD measurements of the 101 film peaks in combination with the out-of-plane spacing determined from h00 peaks.[12] In all cases the in-plane lattice spacing was identical (within experimental error) to the underlying substrate. Figure 3 is a plot of the out-of-plane lattice constant as a function of strontium excess for the MBE-grown films in this work and those deposited by other growth methods.[2,5,6] All methods see an expan-

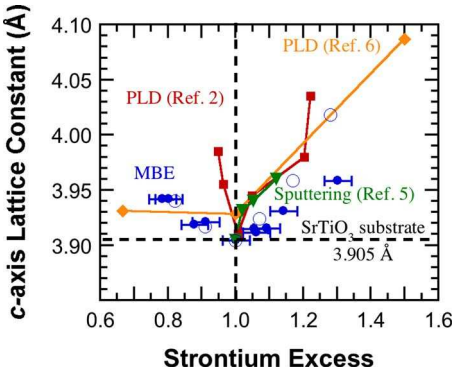

FIG. 3. (Color online) Comparison of out-of-plane lattice constant as a function of strontium excess x in $Sr_{1+x}TiO_{3+\delta}$ for sets of homoepitaxial films grown by MBE, PLD (Ref. 2 and 6), and rf magnetron sputtering (Ref. 5). The circles are from films grown by MBE in this study. The open circles were grown by codeposition, while the closed circles were grown by alternately shuttered monolayers.

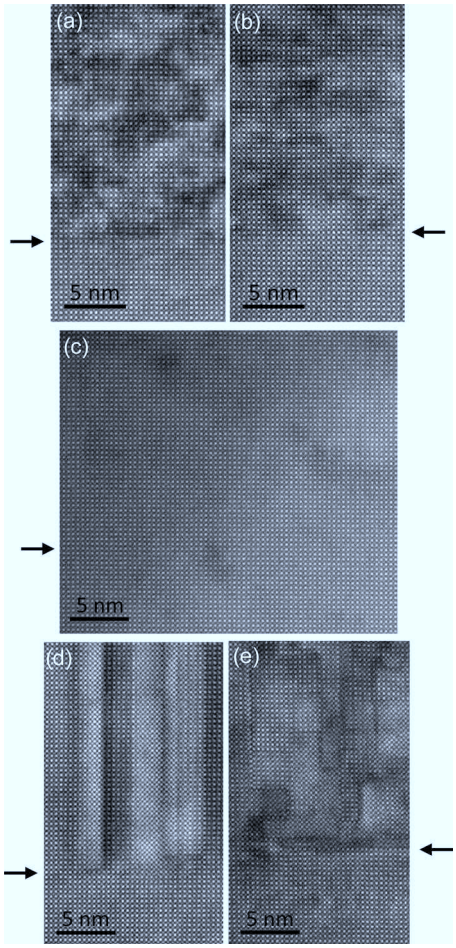

FIG. 4. STEM images of the interface between the (100) $SrTiO_3$ substrate and film for $Sr_{1+x}TiO_{3+\delta}$ films with $x=-0.2$ (a), -0.1 (b), 0 (c), 0.1 (d), and 0.2 (e). An arrow indicates the interface.

sion of the lattice constant corresponding to the degree of off-stoichiometry. The largest lattice expansions occurred in films where PLD was the growth technique. Despite the MBE films being grown in low oxygen pressures (5×10^{-7} Torr), the lattice expansion was not measurable for the stoichiometric cases due to the overlap between film and substrate peaks. All nonstoichiometric film results show an expansion of the out-of-plane lattice constant regardless of growth technique or whether the films are excess or deficient in strontium. Strontium deficient MBE-grown films showed similar lattice expansion independent of whether they were deposited by true codeposition or alternately shuttered monolayers. For the strontium excess case, the codeposited films grown by MBE had larger lattice expansions than the films grown by alternately shuttered monolayers.

Figure 4 shows scanning transmission electron microscope (STEM) images of the set of five $Sr_{1+x}TiO_{3+\delta}$ films grown in the presence of 10% ozone in order of increasing strontium off-stoichiometry x increasing from -0.2 to 0.2. The film microstructure seen is in general agreement with the microstructure seen in off-stoichiometric films prepared by PLD (Ref. 6) where excess SrO is incorporated as Ruddlesden–Popper planar faults[13] and films deficient in strontium have a more disordered structure. The same features are visible despite the films in this study being much closer to stoichiometric composition. When the sample is deficient in strontium, the film appearance is visibly disordered from the lack of strontium throughout the film, as shown in Figs. 4(a) and 4(b). The film and the substrate for the stoichiometric film, where $x=0$, are nearly indistinguishable [Fig. 4(c)]. For the strontium excess case, where $x=0.1$ [Fig. 4(d)], the Ruddlesden–Popper planar faults[13] appear as columns in the film. When the strontium excess reaches a higher value, $x=0.2$ in Fig. 4(e), the planar faults no longer appear as columns but take on a mosaic structure similar to the $x=0.5$ case in Suzuki *et al.*[6]

The precise control over composition provided by the MBE growth process for homoepitaxial $SrTiO_3$ films allows for the examination of slight deviations in film composition on film structure. These results highlight the sensitivity of $SrTiO_3$ film structure and out-of-plane lattice constant to even small changes in stoichiometry. Other material systems likely exhibit similar sensitivity to composition. The shuttered RHEED intensity behavior during the growth of off-stoichiometric films was shown to have unique forms for both the strontium excess and strontium deficient cases. The presence of ozone during growth had no observable effect on the out-of-plane lattice constant measurement by XRD or film microstructure observed by STEM. XRD film peaks are indistinguishable from substrate peaks for the stoichiometric homoepitaxial films.

Under optimized conditions sputtering, PLD, and MBE growth methods are able to achieve stoichiometric films with lattice constants close to bulk $SrTiO_3$. For a given amount of off-stoichiometry, however, the MBE growth process is able to deposit films much closer in lattice constant to bulk $SrTiO_3$ than films grown by higher energy growth methods such as PLD. If it is challenging to reproduce the structure and properties of the substrate when growing homoepitaxial films by a growth technique, then it becomes all the more important that additional care be taken with the growth and characterization of heteroepitaxial films.

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