Strain relaxation during *in situ* growth of $SrTiO_3$ thin films

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We report a real-time observation of strain relaxation during *in situ* growth of $SrTiO_3$ thin films by measuring the in-plane lattice constant at the film surface using reflection high-energy electron diffraction. The initial misfit strain in the $SrTiO_3$ film is tensile on MgO and compressive on $LaAlO_3$ as expected from the lattice mismatches between the film and the substrates. Strain relaxation begins immediately after the deposition starts, but is not complete until the film thickness reaches 500–2500 Å depending on the substrate and the deposition temperature. The strain relaxation at the growth temperature influences the film strain at room temperature, which is compressive for both substrates for thin $SrTiO_3$ films.
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Strain in ferroelectric thin films plays a significant role in influencing their dielectric properties, which are important for electronic applications.[1–3] Strain can result from the lattice mismatch[2] and the thermal expansion mismatch[4,5] between the film and the substrate. Defects such as oxygen vacancies can also affect the strain in the films.[6] The evolution of strain during *in situ* growth and subsequent cooling is a complex process, and a clear understanding of the nature of strain in ferroelectric thin films is of both scientific and technological significance. In this letter, we present an *in situ* reflection high-energy electron diffraction (RHEED) study of strain in $SrTiO_3$ (STO) films during growth at around 800 °C on substrates of different lattice and thermal expansion mismatches. We were able to monitor the variation of strain in real time as the STO film was deposited, and we found that the strain relaxes completely when the film reaches a thickness of 500–2500 Å. The strain relaxation at the growth temperature also impacts the room temperature strain, which depends on the densities of misfit dislocations in the films.

STO thin films were deposited by an *in situ* reactive coevaporation technique described previously.[7,8] A pocket heater[9,10] was used which has a high-oxygen-pressure (20 mTorr) pocket for oxidation of the deposited film and an opening to the high-vacuum ($\sim 10^{-5}$ Torr) chamber where the evaporation sources are located. Ti and Sr were evaporated by electron-beam and from a Radak cell, respectively. Single crystal substrates were rotated continuously between the open area and the oxidation pocket at a rotation frequency of 5 Hz. The substrate temperature studied in this work was from 750 to 850 °C. Quartz crystal monitors were used to measure and control the evaporation rates of Sr and Ti in order to maintain the stoichiometry of the deposited film. *In situ* RHEED, with a synchronization procedure described previously,[8,10] was used to measure the in-plane lattice constant of the deposited film, which is inversely proportional to the spacing between the reciprocal lattice rods (streaks) in the RHEED image. Strain derived from the in-plane lattice constant was monitored as a function of the film thickness. This technique has been used during growth of thin films of semiconductors,[11–13] metals,[14,15] and to a lesser extent oxide thin films.[16]

The substrates used in this study were MgO (room-temperature lattice constant $a = 4.216$ Å) and $LaAlO_3$ (LAO), ($a = 3.79$ Å). Since the room-temperature lattice constant of STO is $a = 3.905$ Å, one expects the misfit stress in the STO films to be tensile on MgO and compressive on LAO. The coefficient of thermal expansion of STO[17] is smaller than that of MgO[18] and larger than that of LAO.[19] Therefore, when cooled from the deposition temperature around 800 °C to room temperature, one expects a compressive stress from MgO and a tensile stress from LAO on the STO films due to the thermal expansion mismatch.

In Fig. 1, the strain in our STO films at the deposition

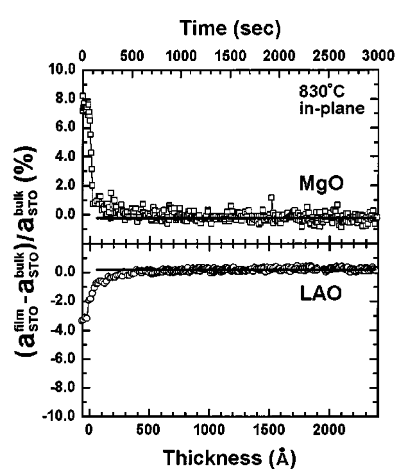

FIG. 1. Strain in STO films on MgO and LAO substrates at the deposition temperature of 830 °C as a function of film thickness. The in-plane lattice constant of the film a_{STO}^{film} is derived from the RHEED measurement during the film growth.

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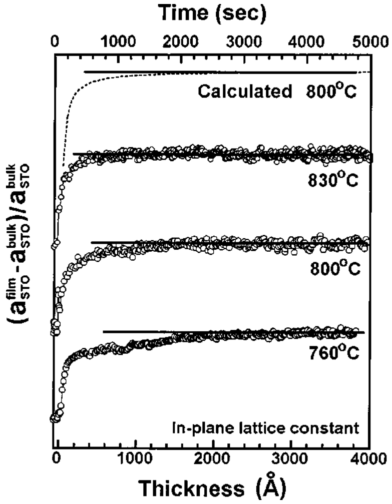

FIG. 2. Strain in STO films on LAO substrates as a function of film thickness and the deposition temperature. Also plotted is a theoretically predicted curve for strain relaxation by misfit dislocations taking into account only the lattice constant mismatch between the film and the substrate at 800 °C.

temperature of 830 °C, expressed as $(a_{\mathrm{STO}}^{\mathrm{film}}-a_{\mathrm{STO}}^{\mathrm{bulk}})/a_{\mathrm{STO}}^{\mathrm{bulk}}$, is plotted as a function of the STO film thickness for MgO and LAO substrates. We calculate the in-plane lattice constant of the film $a_{\mathrm{STO}}^{\mathrm{film}}$ using the RHEED spacing before the STO deposition as a reference, which measures the lattice constant of the substrate, which in turn is calculated from the thermal expansion properties of the substrates.[18,19] The lattice constant of the bulk STO $a_{\mathrm{STO}}^{\mathrm{bulk}}$ is calculated from the room temperature value and the thermal expansion of STO.[17] As expected, the initially deposited film is under a tensile strain of 7.5% on MgO and a compressive strain of −3% on LAO due to the lattice mismatches with the substrates. The strain decreases in magnitude immediately and saturates to nearly zero at ~500 Å, beyond which the lattice constant becomes that of bulk STO. This indicates a process of strain relaxation through the generation of misfit dislocations. Due to the large lattice mismatches, the critical thickness that marks the start of strain relaxation is very small for both substrates. The majority of the strain is relaxed quickly, but the complete strain relaxation takes place much more slowly until ~500 Å has been deposited at a temperature of 830 °C.

The rate of strain relaxation depends on the deposition temperature. In Fig. 2, the results for 760, 800, and 830 °C are shown for deposition onto LAO substrates. Again, the strain changes from −3% to near zero which is indicated by the horizontal lines. The strain relaxes much more slowly when the deposition temperature is reduced. The thickness of complete strain relaxation increases from ~500 to ~2500 Å when the deposition temperature changes from 830 to 760 °C. This is because less thermal energy is available at lower deposition temperatures to overcome the kinetic barrier for dislocation formation.[20] Also plotted in Fig. 2 is a theoretically predicted curve for strain relaxation by misfit dislocations taking into account only the lattice constant mismatch between the film and the substrate at 800 °C.[21] A general agreement is found between the calculated curve and the experimental curves. However, the theory predicts little temperature dependence of the strain relaxation in contradiction to the experimental results, which demonstrates that the kinetic barrier is important when considering strain relaxation through dislocations.

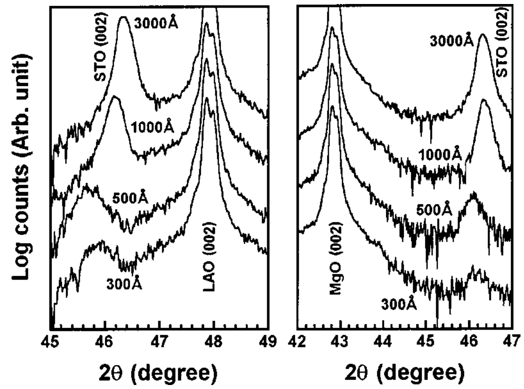

FIG. 3. Room temperature x-ray θ–2θ scans near the (002) peak for a series of STO films grown at 830 °C on LAO (left panel) and MgO (right panel) substrates with different thicknesses.

The room-temperature lattice constants of the STO films were measured by x-ray diffraction. Because the in-plane lattice constant is difficult to measure for very thin films, only the out-of-plane lattice constant was measured for most of the samples. Figure 3 shows the θ–2θ scans near the (002) peak for STO films of different thicknesses grown at 830 °C on LAO (left panel) and on MgO (right panel) substrates. The peak shifts when the film thickness increases, indicating a change of the lattice constant with the film thickness. The out-of-plane lattice constant as a function of the STO film thickness is plotted in Fig. 4. Qualitatively, the same thickness dependences are found for both substrates despite the differences in the misfit and thermal mismatches between LAO and MgO. At large thicknesses, the out-of-plane lattice constant is about the same as the bulk value. For small film thicknesses a large rise occurs with a maxima at a thickness of about 500 Å. The enlarged out-of-plane lattice constant appears to be related to the misfit dislocations, because 500 Å is about the film thickness where the complete strain relaxation occurs at 830 °C (see Fig. 1). Before the strain is completely relaxed, more and more dislocations are being generated to relieve the misfit strain when the film thickness increases. After the strain completely relaxes, further increase in the film thickness reduces the volume fraction of the film having misfit dislocations. This trend coincides with that shown in Fig. 4.

Larger lattice constants in STO thin films than in bulk STO have been widely reported.[6–8,22–24] This has often been

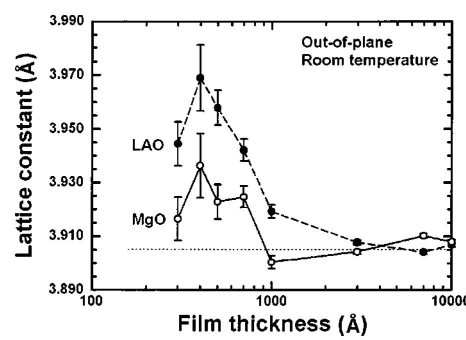

FIG. 4. Room temperature out-of-plane lattice constant as a function of film thickness for STO films grown at 830 °C on LAO and MgO substrates.

attributed to oxygen vacancies in the films because the lattice constant increases with oxygen deficiency[6,22,23] and the volume of a vacancy in ionic solids is in general larger than the atomic volume of the missing ion,[25] although one report shows an independence of the lattice constant on the oxygen vacancy concentration in reduced polycrystalline STO.[26] Off-stoichiometic Sr/Ti ratios have also been used to explain the larger lattice constants in STO films.[8,24] However, the Sr/Ti ratio in our films was controlled to within 1% of stoichiometry as determined by energy dispersive x-ray measurements, and it is too small to explain the large enhancement of the lattice constant. The result in Fig. 4 links the density of misfit dislocations to the enlarged lattice constant. Tarsa *et al.* have shown that the strain in STO films becomes more compressive with larger out-of-plane lattice constants.[6] The large increases in the lattice constants in Fig. 4, therefore, indicate an increased compressive strain in the STO films at small film thicknesses for both substrates. This contradicts expectations from both lattice and thermal expansion mismatches and indicates the importance of misfit dislocations in determining the film strain.

The thicknesses of complete strain relaxation and the deposition temperatures studied in this work are well within the commonly used ranges for ferroelectric thin films.[1,3,5,27,28] It is known that the details of the deposition conditions as well as the film thickness have dramatic effects on the film properties. Our result suggests that this may be related to the state of strain and the misfit dislocations in the films. The technique described in this work allows for the observation of strain relaxation in real time during growth, which is a valuable tool for understanding the misfit strain and its evolution during and after the film growth. Further, it can be applied not only to ferroelectric films but also to films of other oxides such as high temperature superconductors and colossal magnetoresistive manganites, and in heterostructures of these oxides.

In conclusion, *in situ* RHEED measurement during STO film growth reveals that—although the critical thickness is very small on both LAO and MgO substrates—complete misfit strain relaxation does not occur until the film thickness reaches 500–2500 Å. The film strain at room temperature is influenced by the strain relaxation at the growth temperature through misfit dislocations. In thin films with high densities of misfit dislocations, an increased compressive strain is found for both substrates despite the differences in their lattice and thermal expansion mismatches with STO.

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