Anomalous Phase Transition in Strained SrTiO$_3$ Thin Films

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We have studied the cubic to tetragonal phase transition in epitaxial SrTiO$_3$ films under various biaxial strain conditions using synchrotron X-ray diffraction. Measuring the superlattice peak associated with TiO$_6$ octahedra rotation in the low temperature tetragonal phase indicates the presence of a phase transition whose critical temperature is a strong function of strain, with $T_C$ as much as 50K above the corresponding bulk temperature. Surprisingly, the lattice constants evolve smoothly through the transition with no indication of a phase change. This signals an important change in the nature of the phase transition due to the epitaxy strain and substrate clamping effect. The internal degrees of freedom (TiO$_6$ rotations) have become uncoupled from the overall lattice shape.

Perovskite films have received a great deal of interest lately due to the potential for creating working technologies based on a variety of interesting properties such as high-$T_C$ superconductivity, colossal magneto-resistivity, ferro-electricity, and variable dielectric constants. These properties can be quite different in thin films versus nominally similar bulk samples. The primary reasons for the changes in properties are believed to be strain and defects. There is also an emerging theoretical effort to treat the effects of strain. To understand the mechanisms for these changes we must be able to conduct detailed microscopic measurements of the atomic and electronic structure.

SrTiO$_3$ (STO) is a nearly ferroelectric material with a large dielectric nonlinearity and low dielectric loss at cryogenic temperature, making it ideal for tunable microwave devices. STO is also a good model system for studying structural phase transitions. Bulk STO crystals are cubic at room temperature, with space group Pm3m(O$_h^1$), but become tetragonal, space group I4/mcm(D$_{4h}^{18}$), below about 105K. This phase transition involves the rotation of TiO$_6$ octahedra and has been featured historically in the study of structural phase transitions as the classic example of a soft-mode phase transition. The unit cell of the tetragonal phase has a volume four times that of the cubic unit cell, with approximate unit cell of $\sqrt{2}a \times \sqrt{2}a \times 2a$, where $a$ is the lattice parameter of cubic unit cell. In this paper we describe the tetragonal phase as pseudo-cubic, in order to compare the structure before and after the phase transition. In this pseudo-cubic frame, the tetragonal phase has additional superlattice peaks at half integer index positions. These superlattice peaks disappear as the temperature is raised through the tetragonal-cubic phase transition.

In the bulk, the deviation from cubic symmetry is directly related to the rotation angle of the TiO$_6$ octahedra. This rotation angle has been identified as the order parameter for this phase transition. Correspondingly, the intensities of the superlattice peaks are proportional to the square of the order parameter and can be used to track the phase transition.

For a second-order structural phase transition, usually the volume of the unit cell changes smoothly through the transition temperature, but lattice parameter versus temperature curves have a sudden change in slope. This is the case for bulk STO. For epitaxial films the in-plane lattice parameters are subject to lateral restraint from the substrate and therefore do not have the freedom to change as in bulk. In this paper we show that for epitaxial films of STO the lattice parameters are indeed constrained though this does not completely inhibit the occurrence of the soft-mode phase transition. The strains do change both the transition temperature and the nature of the transition.

The films studied were STO films grown on (001) LaAlO$_3$ (LAO) single crystal substrate with SrRuO$_3$ (SRO) buffer layers. The samples were grown using the Pulsed Laser Deposition technique with details described elsewhere. X-ray diffraction implies excellent epitaxy with average mosaics around 0.2 degrees and no detectable misoriented regions. Several different measurements of films grown in the same system under the same conditions have been reported elsewhere. All of the samples were of the type STO/SRO/LAO with variations of either the STO or SRO thickness. The main study consisted of STO films with thickness varying from 50 to 1000nm on a SRO-buffer layer 350nm thick. A secondary study investigated STO films 200nm thick on SRO buffer layers with thickness from 0 to 350nm. X-ray diffraction measurements were carried out at beamline X22A at the National Synchrotron Lights Source at Brookhaven National Laboratory. X22A has a bent Si(111) monochromator, giving a small beam spot and fixed incident pho-
ton energy of 10 keV. The longitudinal resolution with a Si(111) analyzer was at least 0.001Å⁻¹ (HWHM) for an (0,0,2) peak, as measured from the LAO substrate. Below room temperature the sample was cooled in a closed cycle refrigerator with a temperature control of ±0.5°C.

We choose the coordinate system such that the axis normal to the film surface is the c axis. Like bulk STO, all of our STO films have extra half-integer superlattice peaks at low temperature. The intensity of these peaks decreases as the temperature rises and the peaks vanish at 130−170K for different samples. Thus the STO films also have a phase transition with similar symmetry change as seen in the bulk. Fig. 1 shows an example of such a superlattice peak for a [1000nm STO / 350nm SRO] sample. In the first panel are raw data scans through the (1/2, 1/2, 7/2) peak at some representative temperatures. The presence of a superlattice peak for SRO is a result of its structural phase transition occurring at ~800K. The STO and SRO peaks are well resolved and the STO peak intensity decreases with increasing temperature. Fig. 1 panel (b) is a summary plot of the peak intensity versus temperature. Compared to the bulk, the intensity versus temperature curve is shifted towards higher temperature. The intensity does not fall abruptly to zero but includes a tail that extends to higher temperature. This indicates that the phase transition is rounded and occurs over a range of temperature. This rounded transition is most likely due to the presence of a range of local strains within the film. Due to the rounding of the transition, we need to derive a method for extracting the average T_C. We extrapolate the linear portion of the curve between 10% to 40% maximum intensity and define the transition temperature as where this line crosses the zero intensity. The use of a linear function is justified by the data itself as well as previous work that has found a power law coefficient b very close to one for this phase transition in bulk samples[9]. While this method may produce T_C too high by a few degrees (<5K), it allows for an accurate comparison of T_C between different films. We believe we can determine ΔT_C to about 0.5K.

For samples with a 350nm SRO buffer layer and varying STO thickness, T_C increases monotonically with in-plane strain as shown in Fig. 2(a), and in more detail in Fig. 2(b). The difference, ΔT_C, is about 14K (or ΔT_C/T_C~10%) between the 1000nm STO sample and 50nm sample although the in-plane strain at room temperature measured by glancing incidence x-ray diffraction (not shown) only changes from 0.01% to 0.23%. The thinner film, with greater strain, has the higher T_C, while thicker film has T_C close to the bulk value. Thus the
structural phase transition is very sensitive to the biaxial strain caused by the lattice mismatch at the interface, with the ratio \((\Delta T_C/T_C)/\varepsilon \sim 45\), where \(\varepsilon\) is the in-plane strain.

We also studied a series of samples with the same 200nm STO layer but varying the thickness of SRO buffer layer. Here we observed even larger effect of strain on \(T_C\), as shown in Fig. 2(c). In this case the largest strains and the largest shifts in \(T_C\) appear for SRO buffer layers of intermediate thickness. We believe this is due to the complexity of the SRO domain structure. The highest \(T_C\) is in the sample with a 20nm SRO buffer layer. In this case, \(T_C\) is shifted about 30K above the STO film on a 350nm buffer and about 40K above the most bulk like of our films [1000nm STO / 350nm SRO]. Clearly the overall rise in \(T_C\) can be quite large. Further detail will be given in a follow up paper \[10\], that also includes a discussion of the temperature-strain phase diagram which has been theoretically predicted \[11\].

Although from the presence of the superlattice peaks we can see that there is a phase transition near 130K, the out-of-plane lattice constants evolve smoothly through the transition temperature with no indication of the transition. This is illustrated in Fig. 3 for the 200nm STO / 350nm SRO film. The variation in lattice constant is merely the thermal expansion with no indication of a phase transition. This is obviously different from the bulk STO where a sudden slope change is clearly seen at 105K \[12\]. We ascribe this effect to the clamping effect of the substrate upon the film. The film in-plane lattice parameters are not free to move to their bulk equilibrium values because they are tied to the substrate lattice. Our experiments show that the overall film is tetragonal at all temperatures measured. However this doesn’t prevent the TiO\(_6\) octahedra from rotating and ordering leading to a reduced symmetry phase. In fact the tetragonal cell shape seems to favor the rotation of TiO\(_6\) octahedra, stabilizing the lower symmetry phase and enhancing \(T_C\).

It is a remarkable that the phase transition in the STO films involves a lowering of the internal symmetry due to TiO\(_6\) octahedra rotations without a change in the unit cell size and shape. This unique phase transition manifests a decoupling of the internal degree of freedom of TiO\(_6\) rotation and the external degree of freedom of the unit cell dimensions. Such a difference between the nature of structural phase transitions in epitaxial films and bulk materials may occur in many situations and should be considered in analyzing a variety of results.

Raman scattering experiments on similar films have studied the temperature dependence of the structural R modes, which are Raman active only below \(T_C\) \[13\]. In bulk STO these phonons disappear at 105K, while in thin films their intensity vanishes at about 120\(\pm 5\)K. The mode is detectable in Raman upon the doubling of the unit cell thus folding this mode back to the zone center. This change is dependent upon the rotation of the octahedra and not the presence of a tetragonal unit cell. In contrast, dielectric measurements show obvious thickness dependence and the temperature range over which the dielectric constant is tunable by an electric field is vastly increased versus the bulk \[6\]. The empirical evidence suggests that this behavior is connected to the presence of a tetragonal unit cell.

A review of the literature reveals that a similar effect may exist in BaTiO\(_3\) (BTO) films. Bulk BTO has a series of phase transitions at 183K, 278K and 403K, at each of which the lattice constants change drastically. All of the lower temperature phases are ferroelectric. In contrast, lattice parameter measurements of epitaxial films show no abrupt changes in either the \(a\) or \(c\) constant, which both increase roughly linearly with temperature from 15K to 800K \[14\]. However, it appears from electrical measurements that the ferroelectric phase transition still occurs in similar BTO films on a Pt/MgO substrate \[15\] \[16\]. Ferroelectricity is due to the shift of the position of the Ti ion with respect to the O octahedron surrounding it, not the cubic to tetragonal change in the unit cell. Thus ferroelectricity is due to the internal degree of freedom of the phase transition. The ferroelectric transition in BTO films seems to be another example of an epitaxy strain and substrate clamping effect that permits a phase transition in the internal atomic arrangements (ferroelectricity) but does not allow external dimension changes.

It appears that the decoupling of the internal and external aspects of a phase transition in films is not universal. One example is NdNiO\(_3\). Both bulk and films of this material have a metal-insulator transition around 200K. Recent x-ray diffraction measurements on epitaxial films of NdNiO\(_3\) on LaAlO\(_3\) have shown that the out of plane lattice constant exhibits a sudden change at the transition \[17\]. Further experiments are ongoing to try to determine what makes the two transitions fundamentally different with respect to the clamping effect of the substrate and the relaxation of the overall unit cell dimensions.

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