

## Strain Phase Diagram and Domain Orientation in SrTiO<sub>3</sub> Thin Films

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SrTiO<sub>3</sub> thin films were used as a model system to study the effects of strain and epitaxial constraint on structural phase transitions of perovskite films. The basic phenomena revealed will apply to a variety of important structural transitions including the ferroelectric transition. Highly strained SrTiO<sub>3</sub> films were grown on different substrates, providing both compressive and tensile strain. The measured strain-temperature phase diagram is qualitatively consistent with theory; however, the increase in the phase transition temperature is much larger than predicted. Because of the epitaxial strain and substrate clamping, the SrTiO<sub>3</sub> lattice is tetragonal at all temperatures. The phase transitions involve only changes in internal symmetry. The low temperature phase under tensile strain has a unique structure with orthorhombic *Cmcm* space group but a tetragonal lattice, an interesting consequence of epitaxial constraint.

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An important area of research in recent years has been to understand exactly why the properties of epitaxial films differ from related bulk materials, and to learn how to use these differences to engineer desirable properties. Effects due to strain in films are often thought of as analogous to those of high pressure experiments. The main differences are (1) the stress in films is typically biaxial rather than hydrostatic or uniaxial, (2) films are subject to the additional constraint from the substrate, (3) films can have much larger strains than is usually achievable in pressure cells, and (4) films are easier to work with for many experiments and applications. Ferroelectricity in strained perovskite films has been a particularly noteworthy topic of study. For example, recent experiments have shown strain-induced ferroelectricity in SrTiO<sub>3</sub> (STO) films, and huge changes in the ferroelectric transition temperature  $T_C$  in both SrTiO<sub>3</sub> and BaTiO<sub>3</sub> (BTO) films under strain [1,2]. Other notable results include large changes in the metal-insulator transition temperature of RNiO<sub>3</sub> films under strain [3] and reports of increasing the transition temperature of La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> under compressive strain [4–7].

In this Letter, we present a systematic investigation of the structural phase transition in epitaxial STO films with varying degrees of both compressive and tensile strain. This transition is not ferroelectric, though it has been described by the same theory as used for the ferroelectric transition in STO [8] and referenced in the works above. We construct a strain-temperature phase diagram for this transition with several data points over a wide range of strain. The observed enhancement of the structural phase transition temperature,  $T_s$ , is much greater than predicted by theory, though in many aspects the theoretical predictions are qualitatively correct. We also note that in some cases the film structures have unique symmetry not possible in a free bulk system.

We chose the antiferrodistortive structural phase transition in STO as a model system for phase transitions in

epitaxial films. The principal advantage of this system is that both the primary and secondary order parameters are directly accessible through x-ray diffraction measurements [9], as explained below. This is in contrast to the ferroelectric phase transition in materials such as BTO where the primary order parameter is the polarization, which is best detected by electrical measurements. However, these phase transitions are similar in many ways: the variation of lattice constant is a secondary order parameter for both, changes in critical temperature with strain vary in a similar manner, and similar domain orientations are present in the low symmetry phases.

Bulk STO crystal is cubic at room temperature, with space group  $Pm\bar{3}m$ . Below 105 K it becomes tetragonal with  $I4/mcm$  symmetry. This phase transition involves the rotation of TiO<sub>6</sub> octahedra, and the rotation angle has been identified as the order parameter for this phase transition [10]. In terms of the pseudocubic unit cell, the tetragonal phase has additional superlattice peaks at half-integer index positions. The intensities of the superlattice peaks are proportional to the square of the order parameter and can be used to track the phase transition. A secondary order parameter is the tetragonality, which in the bulk is coupled to the octahedra rotation.

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 [11,12]. For epitaxial films the in-plane lattice parameters are subject to lateral constraint from the substrate and therefore do not have the freedom to change as in bulk. In previous studies we have discussed the effect of strain and substrate clamping on several film systems, noting that this substrate clamping effect is often described in too simplistic a manner [9,13].

The STO films studied were grown on four kinds of substrates: SrLaAlO<sub>4</sub> (SLAO), LaAlO<sub>3</sub> (LAO),

(LaAlO<sub>3</sub>)<sub>0.3</sub>(Sr<sub>2</sub>LaTaO<sub>6</sub>)<sub>0.7</sub> (LSAT) and KTaO<sub>3</sub> (KTO). All substrates are  $\langle 001 \rangle$  oriented single crystals. The mismatch between STO and these substrates ranges from  $-3.82\%$  for SLAO to  $+2.15\%$  for KTO. Pulsed laser deposition (PLD) was used to grow the films. The energy density of the KrF excimer laser was about  $1 \text{ J/cm}^2$ . The films were grown at  $720^\circ\text{C}$  in  $100 \text{ mTorr O}_2$ , with thickness ranging from  $7 \text{ nm}$  to  $90 \text{ nm}$ . X-ray diffraction showed excellent epitaxy with average mosaics around  $0.1$  degrees and no detectable misoriented regions.

X-ray diffraction measurements were carried out at beamline X22A at the National Synchrotron Light Source, Brookhaven National Laboratory. X22A has a bent Si(1 1 1) monochromator, giving a small beam spot and fixed incident photon energy of  $10 \text{ keV}$ . The angular resolution with a graphite (0 0 2) analyzer was less than  $0.006^\circ$  FWHM 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  $\pm 0.5 \text{ K}$ .

Table I shows the lattice parameters of STO films on various substrates by measuring several Bragg peaks at room temperature. The random measurement errors in lattice parameters are less than  $0.00005 \text{ nm}$ , though systematic errors may be larger. The in-plane biaxial strain is defined as  $\epsilon = (a_{\parallel} - a_0)/a_0$ , where  $a_0$  is the lattice parameter of bulk STO ( $0.3905 \text{ nm}$ ), and  $a_{\parallel}$  is the average of the lattice parameters along two in-plane axes in the strained films. On KTO substrate, we obtained very large tensile strain in  $7 \text{ nm}$  STO film. The in-plane lattice parameters are almost equal to KTO value, resulting in an in-plane strain of  $+2.03\%$ . The out-of-plane lattice parameter shrinks to  $0.3878 \text{ nm}$ . The  $20 \text{ nm}$  sample shows partial relaxation, with in-plane strain of  $+1.7\%$ .

The films on LSAT substrates show the largest compressive strain. Because of the small mismatch between STO

TABLE I. Lattice parameters and in-plane strains of STO films on different substrates. The in-plane lattice parameters of substrates are: SLAO –  $0.3756 \text{ nm}$ , LAO –  $0.3790 \text{ nm}$ , LSAT –  $0.3868 \text{ nm}$ , and KTO –  $0.3989 \text{ nm}$ . For bulk STO  $a = 0.3905 \text{ nm}$ .

STO Thickness	Substrate	STO Lattice Parameters (nm)			In-plane Strain <sup>a</sup>
		$a_1$	$a_2$	$c$	
7 nm	SLAO	0.3887		0.3921	$-0.46\%$
35 nm	SLAO	0.3886		0.3934	$-0.49\%$
10 nm	LAO	0.3884		0.3922	$-0.54\%$
90 nm	LAO	0.3888		0.3935	$-0.44\%$
7 nm	LSAT	0.3864		0.3924	$-1.04\%$
35 nm	LSAT	0.3871		0.3951	$-0.86\%$
7 nm	KTO	0.3984	0.3878 <sup>b</sup>	0.3984	$+2.03\%$
20 nm	KTO	0.3971	0.3879 <sup>b</sup>	0.3973	$+1.72\%$

<sup>a</sup>positive – tensile strain, negative – compressive strain.

<sup>b</sup> $a_2$  axis is out of plane for films under tensile strains.

and LSAT, even the  $35 \text{ nm}$  film is pseudomorphic with LSAT. Unfortunately, LSAT exhibits face-centered-cubic-type ordering [14], which results in additional peaks at half-integer positions. This makes following the STO superlattice peaks impossible. Because of the large mismatch, even very thin films on SLAO or LAO substrates are already partially relaxed by forming misfit dislocations. The residual compressive strain within the STO layer is around  $-0.5\%$  for both substrates. Since the lattice mismatch between LAO and STO is smaller, the density of misfit dislocations in STO/LAO samples is lower than that in STO/SLAO samples. Thus the phase transitions in  $10 \text{ nm}$  and  $90 \text{ nm}$  STO/LAO samples were investigated.

The tetragonality,  $(c/a) - 1$ , of the STO unit cell does not change dramatically through the whole temperature range. This is consistent with our previous observations [9,13]. The tetragonality in all our films is considerably larger than in bulk. In addition, we observed a surprising phenomenon: the tetragonality of STO films under compressive strain increases with increasing film thickness. This is contrary to the usual expectation for strain relaxation of epitaxial films. We believe this is related to the large deviation of unit cell volume of very thin films from that of bulk, which has also been observed in another film system [15]. Under compressive strain, the unit cell volume of very thin films is considerably smaller than in bulk, while thicker films have unit cell volume closer to bulk, with the difference largely accommodated through out-of-plane lattice relaxation.

Figure 1 shows the temperature dependence of one of the half-integer superlattice peaks associated with the low temperature phase of STO. Results from several different films are shown. The STO films also have a phase transition with similar internal symmetry change as seen in the

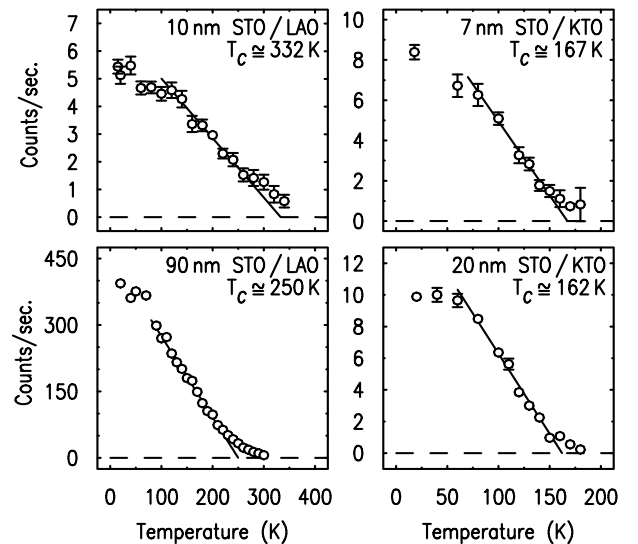


FIG. 1. Temperature dependence of STO superlattice peak intensities, showing  $T_s$  for different samples. For LAO (KTO) substrate, the strain in STO is compressive (tensile).

bulk. The transition temperature is enhanced under conditions of both tensile and compressive strain. A much larger enhancement is present for compressive strain. The presence of rounded transitions, as seen most clearly for 90 nm STO/LAO, is due to nonhomogeneous strain distribution caused by defects such as misfit dislocations.

The tetragonal bulk phase of STO (space group  $I4/mcm$ ) is characterized by the rotation of the  $\text{TiO}_6$  octahedra around the  $c$  axis. The appropriate selection rules denote some peaks such as  $(1/2\ 1/2\ 7/2)$  as forbidden, while  $(1/2\ 7/2\ 1/2)$  and  $(7/2\ 1/2\ 1/2)$  peaks are permitted. We can use the selection rules to determine the domain orientation in the films. However, in the following, we continue to follow the standard practice of denoting the direction normal to the surface as  $\langle 0\ 0\ 1 \rangle$ . We refer to the unique tetragonal axis as merely the axis of rotation. Figure 2 shows the relevant peaks for one of the STO films on LAO, the standard case for compressive strain. The  $(1/2\ 1/2\ 7/2)$  peak is missing. This indicates that the axis of rotation coincides with the normal to the plane. This is not surprising since in bulk STO, the axis of rotation is longer than the others. In the case of compressive strain, epitaxial strain forces the out-of-plane axis to be longer than the in-plane axes. Further, this means that the films are single domains and have a space group  $I4/mcm$  as in the bulk. The high temperature phase does differ from the bulk in that it is tetragonal rather than cubic, thus having space group  $P4/mmm$ . The phase transition in this case is from a high temperature, high symmetry tetragonal phase ( $P4/mmm$ ) to a low temperature, low symmetry tetragonal phase ( $I4/mcm$ ).

The films under tensile strain have a somewhat more interesting morphology. All peaks of the type  $(1/2\ 1/2\ 7/2)$ ,  $(1/2\ 7/2\ 1/2)$ , and  $(7/2\ 1/2\ 1/2)$  are present. This indicates at least two domain orientations. Because of the tensile strain, and the fact that the rotation axis is the longer in the bulk, the most likely orientations are with the rota-

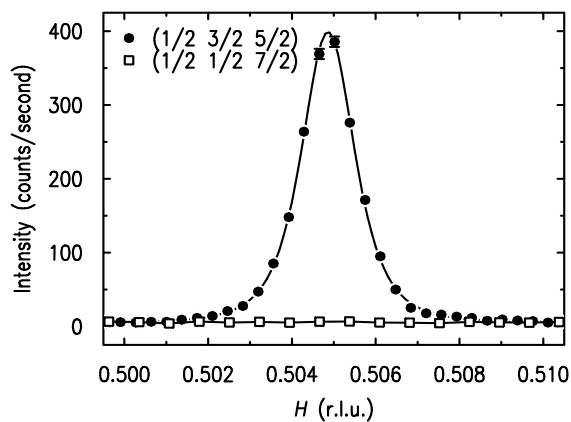


FIG. 2. The presence of  $(1/2\ 3/2\ 5/2)$  peak but not  $(1/2\ 1/2\ 7/2)$  peak at 20 K in 90 nm STO/LAO sample proves that the unique axis  $c$  of STO film is out of plane.

tion axis along each of the primary in-plane directions. Thus there is a  $90^\circ$  twin structure. As far as we can measure, the two in-plane lattice constants remain identical regardless of the orientation of the rotation axis. Thus we have a very unique morphology for the low temperature phase. The most likely space group is orthorhombic  $Cmcm$ . This space group is a subgroup of  $I4/mcm$ , but lacks the fourfold axis. It also permits unequal dimensions along all three directions. The lattice itself appears to be tetragonal in that  $c \approx a_1 \neq a_2$  for each domain in the twin structure. This situation is fundamentally allowed since the space group refers only to symmetry operations and not the shape of the unit cell itself. The existence of a phase with an orthorhombic space group but a tetragonal lattice is an interesting consequence of strain and substrate clamping. We do not believe that such a situation is possible in a free crystal. In this case the phase transition is from the same high temperature, high symmetry tetragonal phase ( $P4/mmm$ ) to a low temperature, orthorhombic phase ( $Cmcm$ ).

The orientation of the unique axis  $c$  below  $T_s$  is quite similar to the ferroelectric polarization in the recently reported electric measurements on similar films [1]. Similar symmetry considerations will apply. It is also possible that in STO the two phase transitions are intimately coupled; thus it will be interesting to investigate the relationship between the two.

Our data allow us to construct the strain phase diagram for STO thin films. The new  $T_s$  points reported in this Letter extend the range of strain considerably in both compressive and tensile directions, as shown in Fig. 3, where high symmetry tetragonal, low symmetry tetragonal, and orthorhombic phases are labeled HT, LT, and LO, respectively. For tensile strain, the experimental data show rapid increase of  $T_s$  over the small strain regime. Then  $T_s$  stabilizes at about 160–170 K for larger strain up

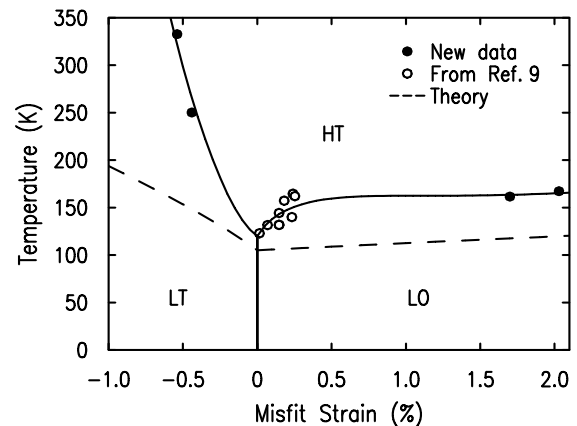


FIG. 3. Structural phase diagram of strained STO. The theoretical prediction from Ref. [8] is shown as dashed lines for comparison. Solid lines are from a fitting to experimental data [16].

to 2%. For compressive strain, the  $T_s$  increase rapidly even for relatively small strain. A 0.5% compressive strain results in a  $T_s$  over 200 K higher than bulk value, reaching room temperature region.

A theoretical investigation of this phase transition in epitaxial films has been performed by Pertsev *et al.* [8]. Our data correspond to the structural part of their phase diagram, designated by Pertsev as HT/SO and HT/ST transition, while Ref. [1] reflects the ferroelectric part. Our result is qualitatively consistent with the theory in many aspects. The domain structures we measured for both compressive and tensile strain were predicted correctly. In addition, the general trend in the variation of the transition temperature with strain occurs much as predicted. The  $T_s$  rises for both strains, though compressive strain causes a much larger increase than does tensile strain. The major difference between the data and theory is that the magnitude of the rise in  $T_s$  is much larger than predicted. In addition, the shape of the actual  $T_s$  versus strain curves deviates from the nearly-linear prediction.

We have analyzed this result in terms of the theory of Pertsev *et al.*, where  $T_s$  is calculated from the relationship  $\beta_i^* = 0$  using Eq. (3) in Ref. [8]. Trying to fit the data to this form but allowing the materials parameters to float would result in unreasonable values of the elastic constants. It is possible that a more complicated coupling term must be included in a proper theory. However, we note that the amount of strain in our films is much larger than is achieved in measurements of bulk elastic constants. For such large strains, the elastic response may no longer be linear. We would expect that compression would become more difficult at large strains but tension easier, due to the fundamental nature of atomic interactions. It appears that such variation of the elastic constants would allow for an expression similar to Pertsev's to match our data [16], though a proper theory needs to be constructed.

In conclusion, highly strained SrTiO<sub>3</sub> films were obtained on different substrates. Under compressive strain, the phase transitions in STO films are from high symmetry tetragonal to low symmetry tetragonal, while under tensile strain, the transitions are from high symmetry tetragonal to orthorhombic. The effects of strain and substrate clamping induces structures in epitaxial films that are not possible for bulk materials. The structural phase transition temperature  $T_s$  is enhanced by both compressive strain and tensile strain. Many aspects of the strain-temperature phase dia-

gram are well described by current theory though improvements are necessary to describe the magnitude of the increase in transition temperature.

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