Lattice Relaxation in Epitaxial BaTiO$_3$ Thin Films

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We have investigated the out-of-plane lattice relaxation related to the ferroelectric transitions in epitaxial BaTiO$_3$ (BTO) films using synchrotron X-ray diffraction. Under either compressive strain or tensile strain, there is evidence for two structural phase transitions as a function of temperature. The transition temperature $T_C$ is a strong function of strain, which can be as much as 100 K above the corresponding $T_C$ in bulk. Under compressive strain, the tetragonality of BTO unit cell implies that the polarization of the first ferroelectric phase is out-of-plane, while under tensile strain, the polarization is in-plane. The transitions at lower temperature may correspond to the $aa \rightarrow r$ or $c \rightarrow r$ transitions, following the notations by Pertsev et al. The orientations of the domains are consistent with theoretical predictions.

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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, ferroelectricity, and variable dielectric constants. These properties can be quite different in thin films versus nominally similar bulk crystals. The primary reasons for the property changes are believed to be strain and defects.\cite{1}

Bulk BrTiO$_3$ (BTO) undergoes three phase transitions at 393 K, 278 K and 183 K, from cubic paraelectric phase at high temperature to three ferroelectric phases at lower temperature, with tetragonal, orthorhombic and rhombohedral symmetries, respectively. At each transition the lattice parameters change drastically. Thus in bulk, the lattice parameters can be used to identify the phase transitions. In strained BTO films, theoretical calculations based on either first-principles method or Landau-Devonshire-type thermodynamic theory predict that there are two successive phase transitions for many values of film strain.\cite{2,3,4,5,6,7} The high-temperature, paraelectric-to-ferroelectric transition has been identified by electrical measurements.\cite{8,9} However, lattice parameter measurements on epitaxial BTO films have not been consistent. Terauchi et al reported that both the out-of-plane and in-plane lattice parameters increase linearly with temperature from 15 K to 800 K, with no indications of the transitions.\cite{2} On the contrary, recent experiments revealed that the temperature dependence of the lattice parameters do show slope changes associated with the ferroelectric transition.\cite{10,11}

Experimental evidence for the transition at lower temperature has not been reported for BTO films. This may be because this transition involves only a slight change in the orientations of the polarization, thus the signature is too subtle for electrical measurements or Raman scattering. Inspired by the recent experimental observations and theoretical results\cite{12} and our understanding on other perovskite film systems,\cite{13,14} we have pursued an investigation of the temperature dependence of the lattice parameters of BTO films at lower temperatures. We show that an accurate lattice parameter measurement does reveal a lower temperature phase transition for BTO films. The structural evidence is consistent with the phase transitions predicted by theory.

BTO films were grown on (001) KTaO$_3$ (KTO, $a = 3.989$ Å) and (001) MgO ($a = 4.213$ Å) single crystal substrates by pulsed laser deposition. The films, with thickness of about 400 Å on KTO and 500 Å on MgO, show excellent epitaxy with mosaics around 0.2°. X-ray diffraction measurements were carried out at beamline X22A and X22C at the National Synchrotron Light Source, Brookhaven National Laboratory. The angular resolution with a graphite (002) analyzer was less than 0.006' FWHM for an (0 0 2) peak, as measured from the substrates. The temperature scans were carried out in a high temperature capable Displex with a base temperature near 15 K and a maximum of 800 K. The temperature control was within ±0.5 K.

At room temperature, BTO in the tetragonal phase is almost coherent with KTO substrate, with in-plane lattice parameters of 3.995 Å and out-of-plane 4.041 Å. On MgO, since the lattice mismatch is too large, the BTO is relaxed, with in-plane lattice parameters 4.029 Å and out-of-plane 3.996 Å. The misfit strain is defined as $\epsilon_m = (a_f - a_0)/a_f$, where $a_f$ is the measured in-plane lattice parameters, and $a_0$ the equivalent cubic cell constant of free BTO crystal. Here the measured $a_f$ corresponds to the effective substrate lattice parameters $b^*$ used in theoretical calculations. A positive or negative strain means the film is stretched in-plane or compressed in-plane, respectively. Since the misfit strain is calculated based on $a_0$ instead of the real bulk value, even though BTO and KTO have similar in-plane lattice parameters at room temperature, the BTO film on KTO substrate is under a -0.28% (compressive) strain. The BTO film on MgO has a tensile strain of 0.57%.

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FIG. 1: Lattice parameters of BTO films on KTO and MgO substrates. The curve for bulk MgO is shifted for comparison with in-plane BTO data. Bulk BTO data from Ref. [16]. Bulk KTO data (dashed-line in upper panel) from Ref. [17]. Bulk MgO data from Ref. [18].

In this report, we choose a coordinate system such that the axis normal to the film surface is the \( c \) axis. The definitions of the possible phases follow Pertsev’s notation.[5]

Fig. 1 shows the temperature dependence of lattice parameters for both BTO/KTO and BTO/MgO samples. We observed two turning points in each out-of-plane lattice parameter curve. For BTO/KTO sample, the two temperatures are at \( T_1 \approx 500 \) K and \( T_2 \approx 250 \) K. For BTO/MgO sample, \( T_1 \approx 450 \) K and \( T_2 \approx 200 \) K. The first turning points at higher temperature may correspond to the paraelectric-to-ferroelectric transitions. The transition temperature \( T_1 \) is much higher than the \( T_C \) in BTO bulk. The transitions at lower temperature, \( T_2 \), may correspond to the \( c \rightarrow r \) or \( aa \rightarrow r \) transitions as predicted by theories. As expected and shown in BTO/MgO case, the in-plane lattice parameters of the BTO films vary smoothly over the entire temperature range studied with no changes connected to the phase transition. These in-plane parameters track the substrate lattice and neither MgO nor KTO has a structural phase transition at these temperatures.

For the ferroelectric transition, the primary order parameter is the spontaneous polarization \( P \), which is not accessible by X-ray diffraction. A secondary order parameter for the high temperature transition is the tetragonality of the unit cell, and that can be evaluated by X-ray diffraction. For films, in order to maintain the convention of labelling the out of plane axis as \( c \), the definition of tetragonality is a little different for the compressive and tensile cases. For compressive strain, the out-of-plane \( c \) is larger, so the tetragonality \( \gamma = (c/a) - 1 \). For tensile strain, in-plane lattice parameters are larger, thus \( \gamma = (a/c) - 1 \). For the lower temperature transition, and for all transitions in films, the appropriate secondary order parameter would be the change in slope of \( \gamma \); \( \gamma \) itself is not zero above the critical temperature in any of these cases. The temperature dependence of the tetragonality of our films are shown in Fig. 2. \( \gamma \) from bulk BTO is shown as a reference.

Analyzing \( \gamma \) gives insight into the transition in several ways. Particularly for BTO on MgO, the transitions are more clearly seen. The figure makes clear that adjusted for the different orientation of the long axis, the transitions in the two films are similar though with different critical temperatures. Above the first tuning point \( T_1 \), the tetragonality decreases smoothly. Below \( T_1 \), the slopes of the out-of-plane lattice parameters change to allow for a marked increase in \( \gamma \). This increasing tetragonality ought to reflect the internal polarization as in the bulk. For the \( c \) phase in BTO/KTO, the polarization drives \( c \) axis longer to increase tetragonality. Interestingly, under tensile strain, although the lattice parameters cannot increase along the polarization direction

FIG. 2: Tetragonality of unit cell in BTO films suggests second order transitions. The two turning points in both curves may indicate the onsets of polarization along different directions. Note that the definitions of tetragonality are slightly different for compressive strain and tensile strain conditions. Bulk data are derived from Ref. [16] and shows clearly first order transitions.
(in-plane), the BTO still manages to increase the tetragonality by shrinking the out-of-plane lattice. Below the $T_2$, the trend of $c$ lattice parameters changes again, so that the tetragonality is smaller. This is consistent with the theoretical picture that the $r$ phase is emerging.

In bulk BTO, all the phase transitions are first order, as indicated by the appreciable discontinuities in lattice parameters. But in epitaxial films, as illustrated by the secondary order parameter, the phase transition becomes second order. We see that the combination of strain and lattice constraint imposed by epitaxy with the substrate lowers the order of the phase transitions and broadens the transition width.

In the $c$ phase, both the polarization and the 4-fold axis of the tetragonal unit cell are out-of-plane, so the two in-plane axes are identical. Thus the $c$ phase is always single domain. The tensile strain case is more complicated. The polarization has in-plane components. If $ac$ phase exists, the $a$ axis can then be distinguished from $b$ axis due to polarization and there may be a difference in the length of the $a$ and $b$ axes. We would expect twin domains with an in-plane misalignment near 90°. If $aa$ phase or $r$ phase exists, the two in-plane axes will be identical, so the two in-plane lattice parameters must be the same. Structurally there should be only one domain, though internal polarization may be along different diagonals. Thus a peak split in in-plane direction may serve as an indication to identify what phase is present.

By using reciprocal spacing mapping, we examined the domain structure in BTO/MgO sample. Through the whole temperature range we probed, there is no peak splitting observed. This indicates that the $aa$ phase is the likely state between $T_1$ and $T_2$. Note that this $aa$ phase is slightly different from the orthorhombic phase found in bulk. In bulk, the pseudo-cubic unit cell for orthorhombic phase is elongated along one face diagonal direction, which is the natural consequence of the polarization. The $aa$ phase, however, has a square in-plane lattice due to the substrate constraint.

This result supports the predictions in Ref. [2, 3, 4] that $p$, $c$, $aa$ and $r$ phases are presented while $ac$ phase is unlikely. As an example, in Fig. 3 we compare our data with the strain phase diagram calculated by Pertsev et al. [5]. While we have only a limited number of experimental data on this phase diagram, several points are brought to light. The general layout of the phase diagram, including both the specifically predicted phases and the rough critical temperatures, is consistent with our experimental observations. While the $T_C$s agree fairly well with theory in a qualitative sense, quantitative agreement is present only for compressive strain. For tensile strain, our data show a substantially smaller change in $T_C$ versus the unstrained case than predicted in Ref. [4]. The calculation of Lai et al. in Ref. [2] shows better agreement with the data for positive strain. Another phase diagram obtained through first-principles method shares the same topology despite a shift in temperatures. However, we note that there is a large lattice mismatch between BTO and MgO and these films are not coherently grown.

There are some aspects of the predicted phase diagram that we cannot yet corroborate. We do not have enough data to verify that a tetra-critical point, sometimes called a phase point, occurs near zero strain. It may be that the smaller than predicted change in spread of critical temperatures for tensile strain indicates that this phase point is either at larger strain values, as suggested in Ref. [2], or that the structure of the phase diagram near zero strain is more complicated than predicted. These questions require further study.

In summary, epitaxial BTO films were grown on KTO and MgO substrates to induce compressive strain and tensile strain, respectively. Through temperature dependence of the lattice parameters, two phase transitions can be identified in each sample. The tetragonality analysis implies that the orientations of the spontaneous polarization are consistent with theoretical predictions.

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