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# X-ray Absorption Fine-Structure Determination of Interfacial Polarization in SrTiO<sub>3</sub> Thin Films Grown on Si(001)

J. C. Woicik<sup>1,\*</sup>, F. S. Aguirre-Tostada<sup>2</sup>, A. Herrera-Gomez<sup>2</sup>, R. Droopad<sup>3</sup>, Z. Yu<sup>3</sup>, D. Schlom<sup>4</sup>, E. Karapetrova<sup>5</sup>, P. Zschack<sup>5</sup> and P. Pianetta<sup>6</sup>

<sup>1</sup>National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

<sup>2</sup>CINVESTAV-Queretero, Apartado Postal 1-798, Queretaro 76001, Mexico

<sup>3</sup>Physical Sciences Research Labs, Motorola, 2100 East Elliot Road, Tempe, Arizona 85284, USA

<sup>4</sup>Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA

<sup>5</sup>University of Illinois, APS-UNICAT, Argonne National Laboratory, Argonne, IL 60439, USA

<sup>6</sup>Stanford Synchrotron Radiation Laboratory, Stanford, CA 94309, USA

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## Abstract

Polarization-dependent X-ray absorption fine structure together with X-ray diffraction have been used to study the local structure in SrTiO<sub>3</sub> thin films grown on Si(001). Our data indicate that an interfacial polarization of the SrTiO<sub>3</sub> layer by the Si substrate results in a tetragonal distortion of the SrTiO<sub>3</sub> unit cell.

At room temperature, SrTiO<sub>3</sub> (STO) exemplifies the ideal, cubic perovskite structure [1]. It is formed by placing Sr<sup>+2</sup> atoms at the corners of a cube, a Ti<sup>+4</sup> atom at the cube center, and O<sup>-2</sup> atoms at the face centers, in perfect octahedral coordination with the Ti<sup>+4</sup> atom, as shown in Figure 1a. STO is often referred to as an “incipient” ferroelectric because it exhibits quantum paraelectric behavior below 4°K in which the ferroelectric phase transition is suppressed by the non-vanishing zero-point motion of the ions [2]. It also possesses a competing, anti-ferroelectric distortion at 105°K that involves the rotation of the oxygen octahedra coupled with a small, <0.01%, tetragonal *c/a* distortion [3]. Additionally, it is well known that strain induces ferroelectricity in STO at liquid-helium temperatures [4], and a recent theoretical study has suggested that the “mismatch” strain imposed on a thin STO layer when grown on a substrate with a dissimilar lattice constant can lead to ferroelectricity at room temperature [5].

To examine the effects of epitaxial strain on thin STO films, films with thicknesses of 40 Å, 60 Å, 80 Å, and 200 Å were grown on Si(001) substrates using molecular-beam epitaxy. Details of the sample preparation have been given elsewhere [6]. Near and extended X-ray absorption fine-structure data were collected at the Ti K edge. All data were recorded at room temperature. The data were recorded by monitoring the Ti K fluorescence using a single-element SiLi detector. The absorption data were collected with the polarization vector of the synchrotron radiation aligned both parallel and perpendicular to the Si(001) surface. In addition, the X-ray absorption spectrum from finely ground STO powder was recorded in transmission; it was used as the phase and amplitude standard to determine the Ti–O bond lengths within the films.

In order to characterize the strain state of the STO films, high-resolution X-ray diffraction measurements were performed. Figure 2 shows the results of the diffraction experiment for both the parallel (in-plane) and perpendicular (out-of-plane) lattice constants of the STO films. Notably is the observation that the lattice constant in the in-plane direction; i.e., the lattice constant parallel to the STO/Si interface, is significantly larger than the

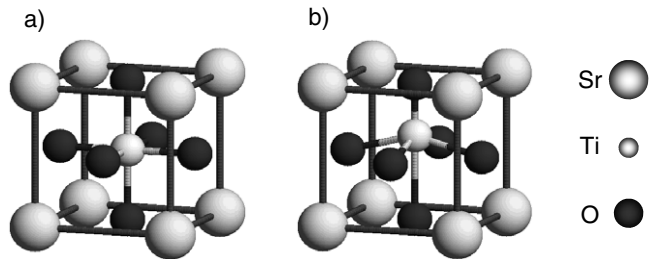


Fig. 1. STO unit cell. a) Cubic. b) Tetragonal.

bulk STO lattice constant. This effect is due to the different thermal expansion coefficients of STO and Si. It has been observed for GaAs on Si hetero-epitaxy and results from the relaxation of the film at growth temperature [7]. Even more surprising, however, is that the out-of-plane lattice constant of the thinner films becomes larger than the corresponding in-plane lattice constant with a *c/a* distortion approaching  $\sim 0.33$ . This distortion is close to the *c/a* distortion observed for the tetragonal, ferroelectric phases of BaTiO<sub>3</sub> ( $\sim 1\%$ ) [8].

Figure 3 shows the Ti K X-ray absorption near-edge spectra from the thin films studied. The main edge occurring near 4980 eV is associated with dipole transitions from the Ti 1s to the Ti 4p conduction-band levels. The first two features occurring below the edge are associated with dipole-forbidden transitions from the Ti 1s to the crystal-field split Ti 3d states that have a splitting of  $\sim 2.1$  eV, as we have indicated in the figure [9]. Our data show a

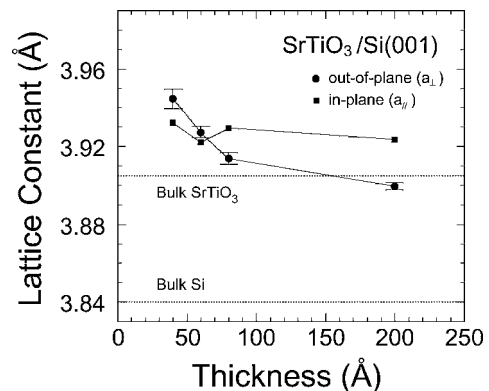


Fig. 2. Perpendicular lattice constants of the 40 Å, 60 Å, 80 Å, and 200 Å STO films as determined by X-ray diffraction. The dotted line shows the cubic lattice constant of STO.

\*E-mail: woicik@bnl.gov

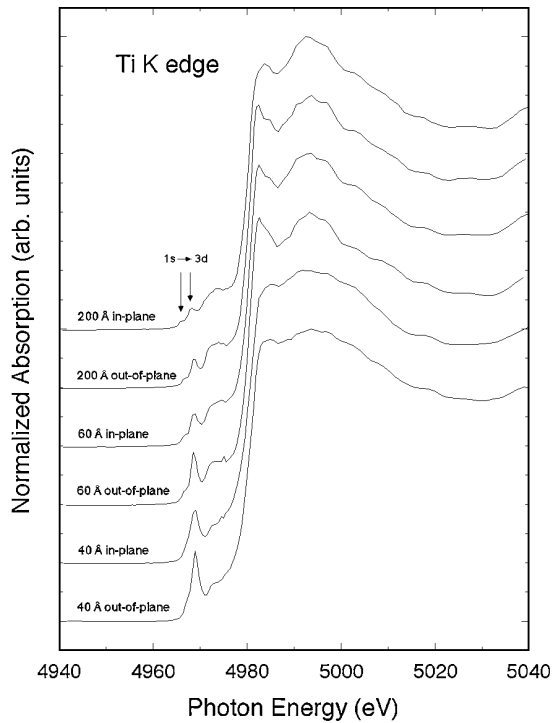


Fig. 3. Ti K pre-edge spectra from the thin STO films recorded with the polarization vector in-plane and out-of-plane. The data have been normalized to equal edge jump.

large increase in the intensity of the second but not the first Ti K pre-edge feature with increasing strain. In crystals that possess an inversion center, the d states that are even with respect to inversion are symmetry forbidden from mixing with the p states that are uneven. In crystals that lack an inversion center, this symmetry restriction is lifted, and the p states are allowed to mix with the d states making 1s transitions to the second of the two pre-edge features dipole allowed [9, 10]. The intensity of the second pre-edge feature therefore has been correlated with the loss of inversion symmetry that accompanies ferroelectricity in the perovskite structure [11]. Consequently, these data suggest that the presence of the STO/Si interface results in the polarization of the STO layer. As evidenced by the data from the thicker films, this polarization decreases away from the interface, and it is likely caused by the ionic rearrangement of the first STO layer.

To quantify the extent of this distortion, we now examine our extended X-ray absorption fine-structure data. The Ti-O radial shell was modeled with the phase and amplitude standards obtained from the STO powder. The results of the modeling for the 60 Å film are shown in Figure 4. The top panel (a) shows the fit to the data from the film recorded with the polarization vector in-plane, and the middle panel (b) shows the fit to the data recorded with the polarization vector out-of-plane, both assuming a single Ti-O bond length. Clearly, a beat occurs in the out-of-plane data near  $k = 7 \text{ \AA}^{-1}$  that is not modeled by a single Ti-O distance. Our analysis using two Ti-O distances (c) finds the Ti-O bond length to be split by  $0.22 \pm 0.06 \text{ \AA}$  along the Si[001] surface-normal direction. (We note that due to the limited data range attainable from such thin films, only the coordination numbers and bond lengths were fit.)

It is interesting to compare our determination of the splitting of the Ti-O distance to that determined by neutron scattering for the tetragonal, ferroelectric phase of  $\text{BaTiO}_3$  [12]. This distortion

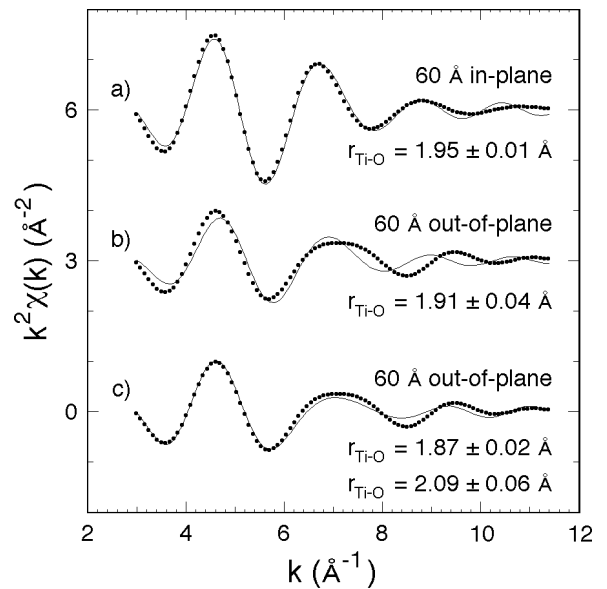


Fig. 4. Fits to the Fourier-filtered, first-shell contributions to the  $k^2$ -weighted fine structure from the 60 Å film using the phase and amplitude functions obtained from the STO powder. The dots are the data points of the backtransform, and the solid lines are the fits. a) In-plane data using one Ti-O distance. b) Out-of-plane data using one Ti-O distance. c) Out-of-plane data using two Ti-O distances.

results in three distinct Ti-O bond lengths, one within the contracted a plane,  $r_{\text{Ti-O}} = 2.00 \text{ \AA}$ , and two along the elongated c axis,  $r_{\text{Ti-O}} = 1.83 \text{ \AA}$  and  $r_{\text{Ti-O}} = 2.20 \text{ \AA}$ . These bond lengths compare with our determination of the in-plane,  $r_{\text{Ti-O}} = 1.95 \pm 0.01 \text{ \AA}$ , and out-of-plane,  $r_{\text{Ti-O}} = 1.87 \pm 0.02 \text{ \AA}$  and  $r_{\text{Ti-O}} = 2.09 \pm 0.06 \text{ \AA}$ , Ti-O bond lengths within the strained STO film.

Our model of the strained STO tetragonal unit cell is shown in Figure 1b. The model possesses three distinct Ti-O bond lengths (one within the contracted a plane and two along the expanded c axis) concomitant with the loss of inversion symmetry around the central Ti ion. The intrinsic relationship between strain, polarization, and chemical hybridization had been observed experimentally.

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