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## Ferroelectric Distortion in SrTiO<sub>3</sub> Thin Films on Si(001) by X-Ray Absorption Near-Edge Spectra: Experiment and First-Principles Calculations

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*Ti K and Ti L<sub>2,3</sub> x-ray absorption fine-structure near-edge spectra of SrTiO<sub>3</sub> thin films grown coherently on Si(001) reveal the presence of a ferroelectric (FE) distortion at room temperature. This unique phase is a direct consequence of the compressive biaxial strain achieved by coherent epitaxial growth.*

The cubic perovskite SrTiO<sub>3</sub> is a classic example of a system with two coupled instabilities. At room temperature it is cubic, but at 105K it undergoes an antiferrodistortive (AFD) transition involving staggered rotation of the TiO<sub>6</sub> octahedra and a sub-percent *c/a* distortion. The system also verges on but does not become ferroelectric (FE) at low temperature. Early literature suggested that the FE transition is suppressed by zero-point motion, but more recent work has found that the FE distortion is suppressed by the interaction between the FE polarization and the AFD order parameter. The biaxial strain imposed on SrTiO<sub>3</sub> thin films by hetero-epitaxial growth has also been shown to have dramatic affect on its structural phase diagram.

Here we report a spectroscopic structural study of strained SrTiO<sub>3</sub> grown coherently on Si(001). We report on the splitting, geometric dependence, and chemical hybridization of the Ti 3*d* states by Ti K x-ray absorption near-edge spectra. It is found that strain allows the FE distortion at room temperature, and the local atomic geometry of this distortion is well modeled by first-principles calculations. The evidence presented here

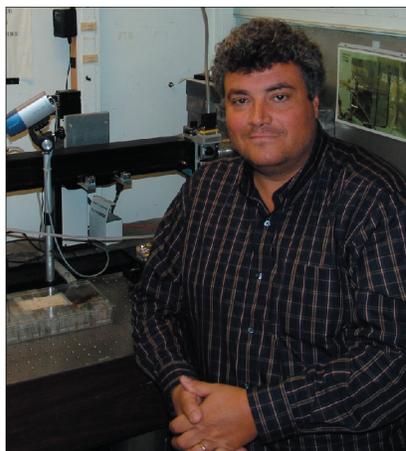
for a *c*-axis oriented FE distortion in compressively strained SrTiO<sub>3</sub> thin films grown coherently on Si(001) opens the possibility of producing FE devices on Si using appropriate growth conditions and strain engineering.

We studied a 5 monolayer (ML) SrTiO<sub>3</sub> thin film, which has an in-plane lattice constant equal to the lattice constant of the Si(001) 1x1 surface-unit cell (3.840 Å) and an out-of-plane lattice constant equal to 4.031±0.01 Å, giving *c/a* = 1.050±0.003 as determined by x-ray diffraction. As the lattice constant of cubic SrTiO<sub>3</sub> is 3.9051 Å,

this film has the largest in-plane compressive strain (1.66 %) reported to date for epitaxial perovskite thin-film growth.

**Figure 1a** shows the ideal cubic perovskite structure of SrTiO<sub>3</sub>. To understand the observed *c*-axis expansion and possible consequences of strain on the local atomic geometry in the thin film, we performed density-functional theory (DFT) calculations of tetragonally distorted SrTiO<sub>3</sub> on Si(001) using the generalized-gradient approximation and projector-augmented wave functions as implemented in VASP.

**Figure 1b** shows the theoretically optimized structure within the 5 ML SrTiO<sub>3</sub> film. Elongation along the *c* axis is evident, as are the FE distortion (displacement of the Ti atoms along *c*) and the AFD rotation of the TiO<sub>6</sub> octahedra. The actual atomic positions are shown. The resulting increase of *c* in the optimized structure gives *c/a* = 1.058, in agreement with experiment. This anomalous increase in *c* results from the macroscopic polarization and its coupling to strain that simultaneously allows the coexistence of both the FE and AFD distortions.



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**Figure 2a** shows the Ti K x-ray absorption near-edge spectra for the SrTiO<sub>3</sub> thin film. The data are plotted for different sample geometries relative to the incident synchrotron-beam wave-vector **q** and synchrotron-beam polarization-vector **e** and have been normalized to equal edge jump. We also show results for single-crystal cubic SrTiO<sub>3</sub>. All data were collected at room temperature.

In cubic materials, the intensity of dipole transitions is invariant with respect to **q** and **e**. As shown by their sensitivity to sample geometry, the first two peaks of the bulk SrTiO<sub>3</sub> spectra are dipole-forbidden transitions of the Ti 1s electrons to the Ti 3d-derived t<sub>2g</sub> (d<sub>xy</sub>, d<sub>yz</sub>, and d<sub>zx</sub>) and e<sub>g</sub> (d<sub>3z<sup>2</sup>-r<sup>2</sup></sub> and d<sub>x<sup>2</sup>-y<sup>2</sup></sub>) unoccupied molecular orbitals. The energy difference between the two peaks in the bulk SrTiO<sub>3</sub> spectra is 2.2 eV, which represents the crystal-field splitting. This splitting results from the different orbital overlap between the Ti 3d orbitals and the ligand 2p orbitals that are strong functions of symmetry. These transitions appear sharp, rather than band-like, because of excitonic interaction between the Ti 1s core hole and electron in the Ti 3d levels.

The situation is very different for the tetragonally distorted SrTiO<sub>3</sub>

thin film with  $c/a=1.050\pm 0.003$ . The simplest reduction in symmetry of the TiO<sub>6</sub> molecular point group is O<sub>h</sub> to D<sub>4h</sub>, which lifts the triple degeneracy of the t<sub>2g</sub> levels and the double degeneracy of the e<sub>g</sub> levels.

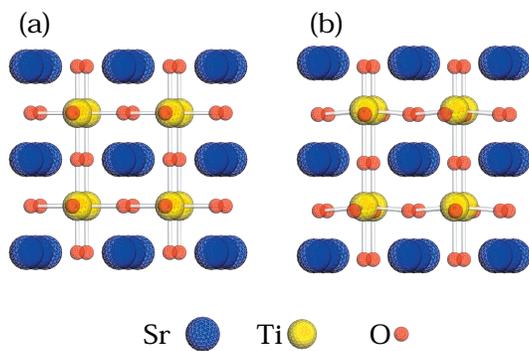
Not only is this reduction to D<sub>4h</sub> symmetry apparent in the data that show significant shifts and splitting of the 1s → t<sub>2g</sub> and 1s → e<sub>g</sub> transitions relative to cubic SrTiO<sub>3</sub>, but a large increase in the intensity of the 1s → 3d<sub>3z<sup>2</sup>-r<sup>2</sup></sub> transition is also observed. This enhancement in absorption indicates the further reduction to C<sub>4v</sub> symmetry that results from the relative displacement of Ti along z, making the transition dipole-allowed via 3d<sub>3z<sup>2</sup>-r<sup>2</sup></sub>-4p<sub>z</sub> hybridization. This hybridization is parity-forbidden in both the O<sub>h</sub> and D<sub>4h</sub> point groups that have inversion symmetry, but it is energetically favored in C<sub>4v</sub> symmetry that breaks inversion; it allows the strong distortion of the Ti atom found in **Figure 1b** and the resulting shorter apical Ti-O bond demonstrated essential for ferroelectricity.

To associate the spectral changes with the local structural distortions found by DFT of **Figure 1**, we calculated Ti K near-edge spectra for cubic SrTiO<sub>3</sub> and the 5 ML film.

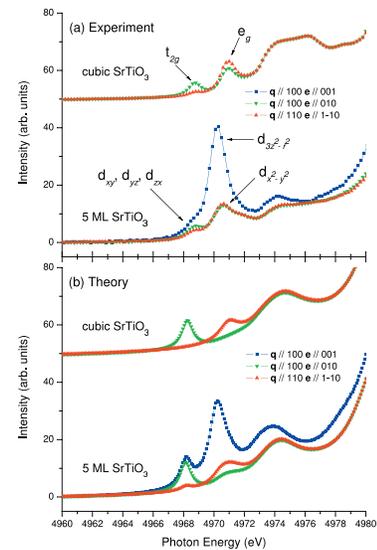
For bulk SrTiO<sub>3</sub>, we assumed the cubic perovskite structure with  $a = 3.9051 \text{ \AA}$ . For the film, we considered a bulk crystal with the theoretically predicted local atomic geometry found in **Figure 1b**.

**Figure 2b** shows the theoretical Ti 1s spectra using a Bethe-Salpeter treatment. All features of the electronic structure and their differences in cubic SrTiO<sub>3</sub> vs. the thin film are reproduced in the theoretical calculations: shifting and splitting of the Ti 3d levels, the decrease of t<sub>2g</sub> and e<sub>g</sub> in-plane angle-dependence, and enhancement of the 1s → 3d<sub>3z<sup>2</sup>-r<sup>2</sup></sub> transition. C<sub>4v</sub> symmetry allows Ti 3d<sub>yz</sub>-4p<sub>y</sub>, 3d<sub>xz</sub>-4p<sub>x</sub>, 3d<sub>3z<sup>2</sup>-r<sup>2</sup></sub>-4p<sub>z</sub>, and 4s-4p<sub>z</sub> hybridization.

Such close agreement between the theoretical spectra and experiment confirm the accuracy of DFT in predicting the local atomic coordinates of this strain-induced FE distortion. This is an important result that substantiates the use of DFT calculations in the strain engineering of FE and other devices, and it should have increasing impact as devices based on thin films of these materials find their way into industrial applications.



**Figure 1:** (a) Structure of cubic SrTiO<sub>3</sub>. (b) Structure of tetragonally distorted SrTiO<sub>3</sub> on Si(001) as calculated by DFT. The structure in (b) reveals both the AFD and FE distortions.



**Figure 2:** (a) Ti K spectra for cubic SrTiO<sub>3</sub> and a 5 monolayer (ML) SrTiO<sub>3</sub> thin film grown coherently on Si(001). (b) Theoretical spectra using the structures from Figure 1 (see text).