Strain induced ferroelectric distortion in SrTiO$_3$ thin films on Si: experiment and theory

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Introduction

The epitaxial growth of metal oxides on silicon opens the possibility of incorporating many of their unique electronic properties with silicon-device technology. As an example, SrTiO$_3$ grown commensurately on Si(001) is a strong candidate for ferroelectric memory and ferroelectrically confining quantum dots. Additionally, it has recently been shown that the biaxial strain imposed on the perovskite unit cell through hetero-epitaxial growth may be used to engineer both its electronic and structural properties [1].

Methods and Materials

SrTiO$_3$ films were grown on Si(001) by molecular beam epitaxy (MBE) using an oxide MBE system equipped with Sr and Ti metal effusion cells [2]. X-ray diffraction data were collected at the UNICAT beamline facility 33BM of the Advanced Photon Source using a 4-circle diffractometer and a Si(111) crystal analyzer at 9 keV [2]. High resolution, polarization dependent, x-ray absorption fine structure data were collected at the Ti *K* edge on NIST beamline X23A2 and at the Ti *L* edge on NIST beamline U7A, both at the National Synchrotron Light Source.

Results and Discussion

Figure 1 shows the measured *c/a* ratios for 5 monolayer (ML) and 10 ML SrTiO$_3$/Si(001) thin films as a function of in-plane compressive strain. The in-plane lattice constant for the 5 ML film is found equal to the lattice constant of the Si substrate (coherent epitaxial growth), but the in-plane lattice constant for the 10 ML film exhibits partial relaxation (critical-thickness behavior). Clearly, the *c/a* ratios for both films are much larger than the lattice constants predicted by the elastic constants of bulk SrTiO$_3$. In fact, the experimentally determined expansion of the perpendicular lattice constant exceeds the prediction of elastic theory by nearly 100 %. This expansion is consistent with a *c*-axis oriented, strain induced, room temperature ferroelectric distortion in the SrTiO$_3$ films at this level of in-plane compressive strain [1].

It is well known that a polarization in a thin film oriented normal to the surface generates a depolarizing electric field, which, if not screened, will push the ions to an unpolarized state. In order to understand the screening mechanism that allows the polarization within the ultrathin films studied here, we performed first-principles density-functional theory calculations of the entire SrTiO$_3$/Si(001) system using the generalized-gradient approximation (GGA) and projector-augmented wave functions as implemented in VASP [2]. All calculations were performed on slabs with five layers of Si and

five layers of SrTiO$_3$; the Si dimers are bonded to oxygen at the interface and passivated with ½ ML of Sr. The resulting SrTiO$_3$/Si(001) structure is shown in Fig. 2(a). This structure is the most stable structure found by first principles calculations; consequently, it is the ideal structure by which to study the possible polarization mechanisms for the SrTiO$_3$/Si(001) interface.

We find that the optimal calculated structure of the ideal system with no defects or adsorbates has a *c/a* ratio much smaller than the experimentally observed *c/a* ratio and close to the value predicted by elastic theory (see Fig. 1). This structure has nothing to screen a ferroelectric polarization and indeed we find that it is unpolarized.

As the films are likely to contain defects (primarily oxygen vacancies), and XPS measurements performed at NIST beamline X24A at the National Synchrotron Light Source find strongly bound OH adsorbates on the surface of these films that have been exposed to air, we also include oxygen vacancies and both H$_2$O and OH adsorbates in our calculations. With oxygen vacancies, we find OH adsorbates are energetically favored over H$_2$O adsorbates, the film polarizes with an enhanced *c/a* ratio, and this enhanced *c/a* ratio is in agreement with the experimentally determined *c/a* ratio of the film (see Fig. 1). This structure is shown in Fig. 2(b). The O vacancies at the interface assume a positive charge while the OH adsorbates on the surface become negative. Clearly, it is the combination of both vacancies and adsorbates that provides the required screening to compensate the electrostatic depolarization field and allow the system to polarize and expand by the observed amount in the *z* direction.

In order to determine whether or not the theoretical model of Fig. 2 accurately predicts the local ferroelectric structure of SrTiO$_3$ films, theoretical calculations of the Ti *K* and Ti *L* x-ray absorption near edge structure were performed using a Bethe-Salpeter treatment of the excited density of states and the x-ray absorption transition-probability matrix elements that include core-hole and multiplet effects with the atomic coordinates generated for infinite, coherently strained SrTiO$_3$ films by GGA. Fig. 3 shows the experimental data and Fig. 4 shows the results of the theoretical calculations.

Agreement is found with the dipole-enhanced *p-d* hybridization feature of the *K* edge that occurs at 4970 eV. This feature is a signature of the ferroelectric transition as it is strictly dipole-forbidden in octahedral symmetry and is therefore indicative of

the off-center displacement of the Ti ions. Agreement is also found with the reduction in crystal-field splitting between the metal $3d$ orbital derived t_{2g} and e_g states that results from the tetragonal distortion of the TiO_6 octahedral cage. Underestimation by theory of both the intensity of this transition and the reduction in crystal-field splitting, however, suggests that the real films are more ferroelectrically polarized than predicted by the infinite GGA model. External electric fields generated by adsorbates and vacancies are known to be present in these films and are a likely cause of the additional polarization.

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2) J.C. Woicik, H. Li, P. Zschack, E. Karapetrova, P. Ryan, C.R. Ashman, and C.S. Hellberg, Phys. Rev. B **73**, 024112 (2006).
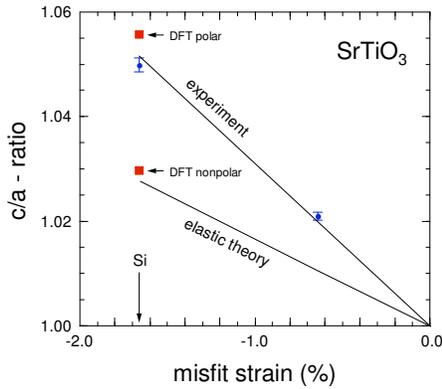
Fig. 1. Measured *c/a* ratio for 5 ML (fully strained) and 10 ML (partially relaxed) SrTiO$_3$ films grown on Si(001) as a function of in-plane misfit strain. Also shown are the predictions of elastic theory and the results of the density functional theory calculations for the polar and nonpolar structures.
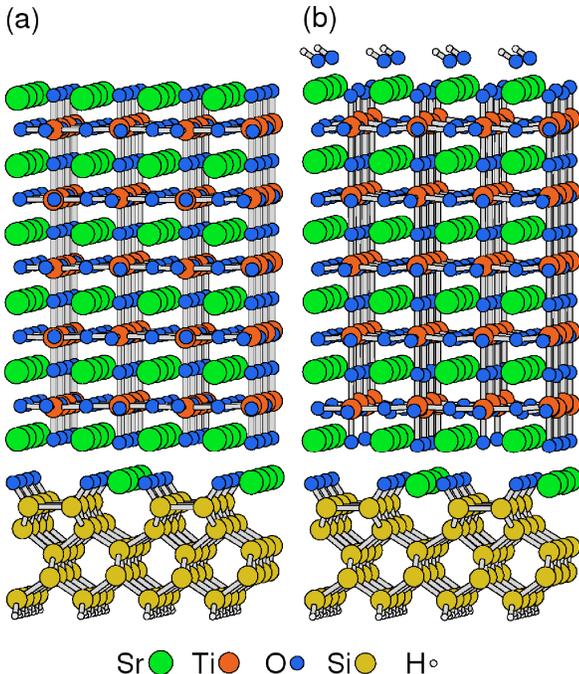
Fig. 2. First principles density-functional theory calculations of the ideal 5 ML SrTiO$_3$/Si(001) system.
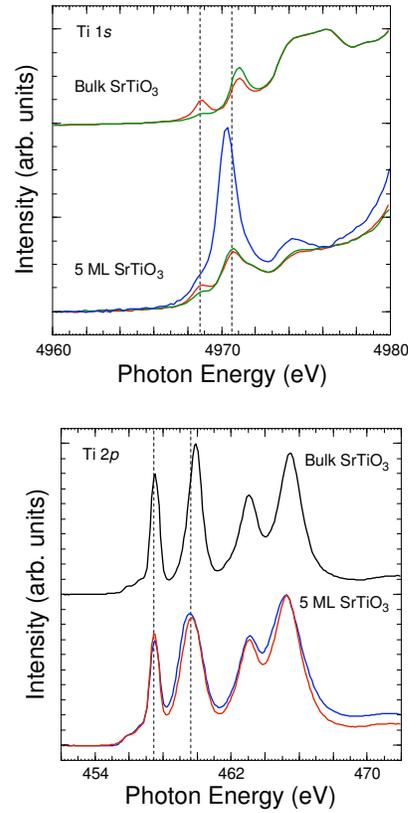
Fig. 3. Polarization dependent Ti *K* (top) and Ti *L* (bottom) x-ray absorption fine structure spectra for the 5 ML SrTiO$_3$/Si(001) film.
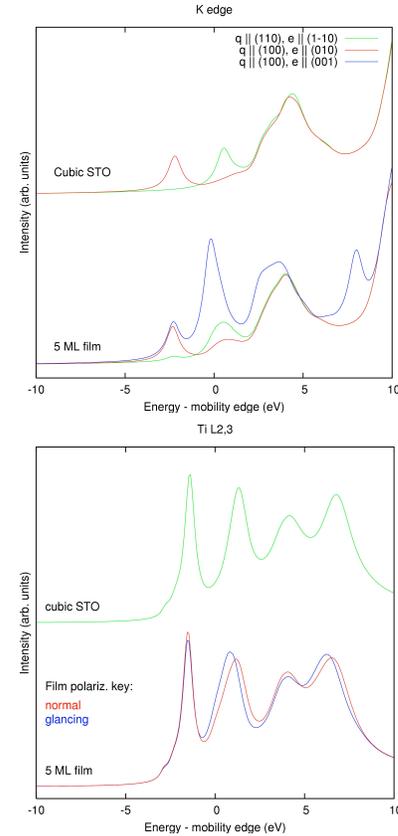
Fig. 4. Theoretical calculations of the Ti *K* (top) and Ti *L* (bottom) x-ray absorption fine structure spectra.