Atomic Structure of $PbTiO_3$ Films Grown on $SrTiO_3$

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Introduction

Ferroelectric thin films display a variety of interesting properties. A detailed understanding of these properties is of considerable scientific and technological interest. In this report, we present detailed images of thin $PbTiO_3$ films epitaxially grown on $SrTiO_3$ substrates using a newly developed x-ray method called coherent Bragg rod analysis (COBRA) [1, 2]. This method uses measured x-ray diffraction intensities along the substrate-defined Bragg rods to calculate the complex scattering factors (CSFs) and provides the real-space, 3-D electron density (ED) by Fourier transforming the CSFs into real space. The method is generally applicable to systems that are periodic in two dimensions, a-periodic in the third, and commensurate with the underlying substrate. It also provides detailed structural information on systems that are only partially periodic in two dimensions and are nonuniformly strained or locally incommensurate with the substrate. Unlike high-resolution transmission electron microscopy, the method does not depend on correctly guessing a structural model. It provides the positions of all the atoms, including oxygen, with a resolution of about ±0.1 Å and is nondestructive.

Methods and Materials

We investigated three samples. Samples 1 and 2, with nominally four and nine $PbTiO_3$ unit cells, were measured at room temperature (RT). Sample 3, with nominally nine unit cells, was measured at 180°C. All samples were grown by using a vertical-flow metal-organic chemical vapor deposition (MOCVD) growth chamber mounted on a horizontal-diffraction-plane, z-axis goniometer located at BESSRC beamline station 12-ID-D of the APS. The $PbTiO_3$ films were grown epitaxially on $SrTiO_3$ (001) substrates, as described previously [3]. Films were typically deposited at ~700°C and a total pressure of 10 Torr (P_{O2} = 2.5 Torr). Samples 1 and 2 were subsequently slowly cooled down to RT in about 24 h and measured *ex situ*. Sample 3 was cooled to 180°C in roughly 5 h and measured *in situ*. All the films considered in this study were thin enough to remain perfectly lattice-matched with the $SrTiO_3$.

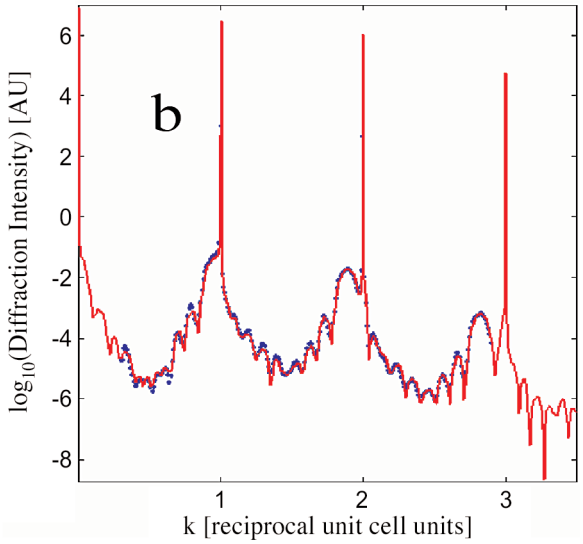

FIG. 1. The normalized diffraction intensity along the [1 1 k_z] line in reciprocal space. Blue dots indicate experimental data. Red line indicates data calculated from the COBRA-calculated electron density.

The measurement setup is described in detail in Ref. 1. The measurements were performed on undulator insertion device beamlines at the APS at sector 7 (MHATT-CAT) and sector 20 (PNC-CAT). The measurements were carried out in the range $|k|_x$, $|k|_y$ <3.5; 0.5 k_z < 3.5 given in reciprocal unit cell units. The number of symmetry-independent Bragg rods within this range is 10. This takes into account the square symmetry of the system. Because of the geometrical limitations of the experimental setup, the [3 3 k_z] Bragg rod was not measured. An example of the diffraction intensities along the [1 1 k_z] Bragg rod for sample 2 is shown in Fig. 1. The quality of the data is very good. The ratio between the smallest and largest contributions of the film that can be accurately measured is at least 4 orders of magnitude, and the error in the intensity ratio at different points within the same Bragg rod or on different Bragg rods is a few percent.

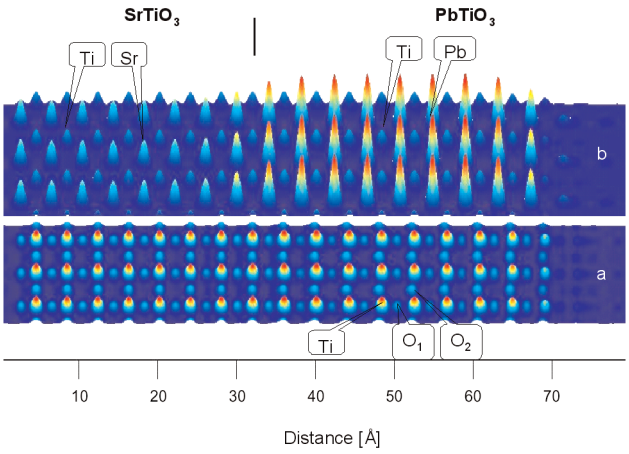

FIG. 2 The electron density on planes perpendicular to the surface. In a, the plane goes through Ti, O_1, and O_2 atoms. In b, the plane goes through Sr, Pb, and O_1 atoms.

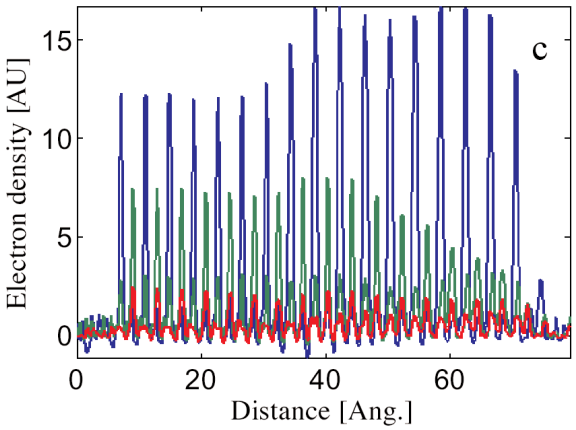

FIG. 3. The electron density as a function of perpendicular distance along the Pb-Sr line (blue), the Ti-O_1 line (green), and the O_2 line (red).

Sample 3 was measured *in situ* at 180°C by using the MOCVD chamber described above. A moderately high energy (24 keV) was used in order to penetrate the 2-mm-thick quartz walls of the chamber, and the incidence angle was 1°. Because of access limitations of the sample chamber, only three Bragg rods were measured: (2 2 k_z), (3 0 k_z), and (3 1 k_z).

The analysis started with a reference model that consisted of a $SrTiO_3$ substrate and a $PbTiO_3$ film. All the atoms in this model occupied centro-symmetric positions. We used COBRA to calculate the complex scattering factors along the Bragg rods and Fourier transformed them into real space to obtain the 3-D ED of the interface region and the film. We then used this newly obtained ED to construct a new model and repeat the above procedure. This procedure converged after six iterations. We used this ED to calculate the normalized diffraction intensities that the ED would give rise to, and we compared them to the experimentally measured ones. An example of this comparison is shown in Fig. 1. As can be seen, the agreement is very good and is typical for all three samples and all Bragg rods measured.

Results and Discussion

An example of the ED on a plane perpendicular to the surface of sample 2 is shown in Fig. 2. Notice that the atoms on the $SrTiO_3$ side occupy centro-symmetric positions. On the other hand, on the $PbTiO_3$ side, the Ti atoms are displaced to the left relative to the Pb atoms, and the oxygen atoms are displaced to the left relative to the Ti atoms. This means that the $PbTiO_3$ film is in a single domain state, polarized in the "c" direction. Sample 1 is also in a single domain state, polarized in the "c" direction, with the polarization vector pointing away from the substrate. On the other hand, the structure of the $PbTiO_3$ film in sample 3 at 180°C has a different structure. This can be seen in Fig. 3. Notice that the ratio between the ED peak intesities of Pb and Sr is much less than the tabulated ratio of 77:37. This is because the Pb peaks are split, indicating that the Pb has two folded positions. Close to the top of the film, the Ti atoms behave in a similar way. This means that the film consists of two domains; in one, with the Pb atoms are displaced upward; in the second, they are displaced downward. These results are consistent with the findings of Streiffer et al. [4]. We evaluated the atomic displacements and the splitting quantitatively by fitting a Gaussian to each peak in the ED. Also, where necessary, we fitted two Gaussians to determine the splitting of the folded structure. The results are shown in Fig. 4. The displacement of the oxygens relative to the Pb in samples 1 and 2 is about 0.6 Å. In contrast, the splitting in sample 3 is only 0.4 Å, meaning that the displacement of the Pb atoms relative to the oxygens is about 0.2 Å — much less than at RT.

It should be emphasized that the COBRA-calculated ED shows that the structure is distorted in spite of the fact that in the initial reference model, the atoms occupied centro-symmetric positions. The results presented here show that COBRA is a very powerful method that provides a very detailed atomic structure of thin films. In the perovskites, it provides the atomic positions deep inside the film and at the interface with an accuracy of about 0.1 Å.

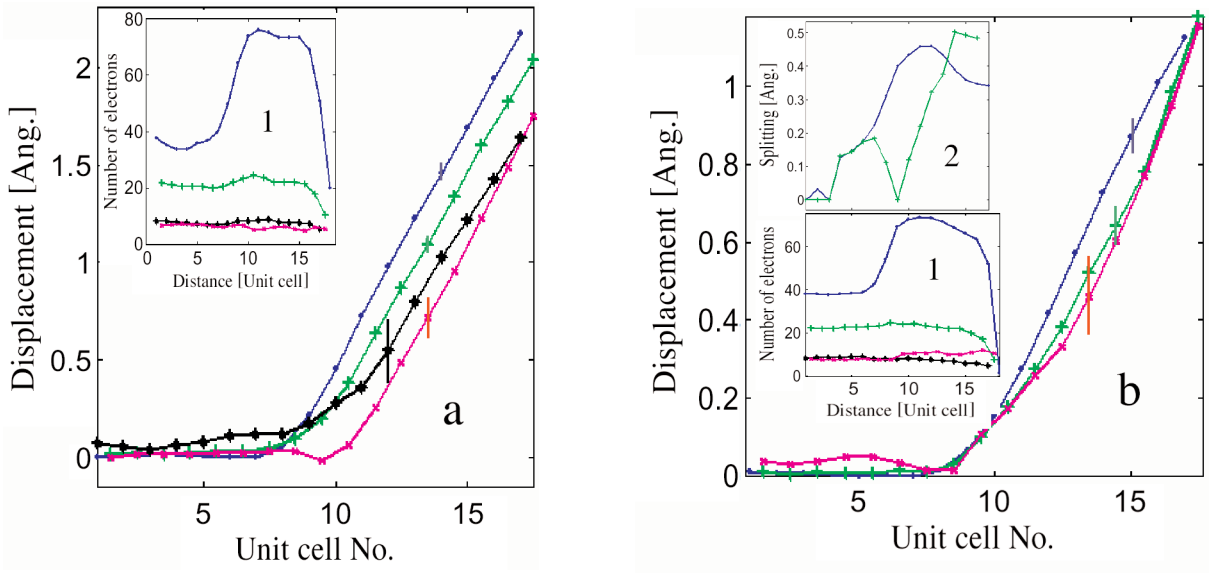

FIG. 4. The displacement of the atoms relative to the atoms of an ideal reference $SrTiO_3$ lattice. Sr and Pb = dots, Ti = plus signs, O_1 =x's, and O_2 = asterisks. Sample 1 is shown in a; sample 2 is shown in b. Inset 1 shows the scattering factor as a function of vertical distance. Inset 2 shows the splitting of the Pb and Ti folded positions.

Acknowledgments

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