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Journal

Applied Physics Letters, 98

Author

Stemmer, Susanne

Publication Date

2011

Peer reviewed

Determining ferroelectric polarity at the nanoscale

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(Received 25 October 2010; accepted 6 January 2011; published online 1 February 2011)

Position averaged convergent beam electron diffraction (PACBED) in scanning transmission electron microscopy is shown to be capable of determining the direction of ferroelectric polarity at the nanoscale. We show that PACBED patterns of ferroelectric materials such as PbTiO_3 and BaTiO_3 are sensitive to both unit cell distortion and the absolute direction of polarity within the unit cell. It is shown that the polarity can be determined even in cases where real-space high-resolution transmission electron microscopy would not be capable of resolving the atomic displacements. The method is applied to determine the direction of polarization in an epitaxial BaTiO_3 film. © 2011 American Institute of Physics. [doi:10.1063/1.3549300]

The properties of ferroelectric materials depend on the orientation, stability, magnitude, and spatial arrangement (domain patterns) of the ferroelectric polarization, the dynamics of which determine the ferroelectric response. Several methods have been developed to locally characterize the orientation of the ferroelectric polarization. Piezoresponse force microscopy allows for the study of domains on surfaces at the nanometer scale^{1,2} but cannot be easily used to study the polarization within embedded structures such as superlattices or parallel plate capacitors. X-ray diffraction³ and Raman spectroscopy⁴ do not have the spatial resolution to map polarity locally on the nanometer scale. While transmission electron microscopy has been used for the analysis of ferroelectric domain patterns in bulk materials⁵ and thin films,^{6–8} determining the absolute direction of polarity (such as across 180° domain boundaries) is challenging when the atom displacements that cause noncentrosymmetry are small, such as in BaTiO_3 . Convergent beam electron diffraction (CBED) can determine the absolute polarity of noncentrosymmetric crystals.^{9–12} The typical beam size in CBED is on the order of 10 nm, which limits its utility for examining nanoscale variations of the ferroelectric polarization. In this letter, we show that a scanning transmission electron microscopy (STEM) based diffraction technique, position averaged convergent beam electron diffraction (PACBED), allows for the direct determination of the polarity direction in ferroelectric materials at the nanoscale.

The PACBED technique¹³ uses a scanned, highly coherent, and angstrom-sized electron probe in STEM to form patterns that exhibit a high sensitivity to specimen thickness and tilt as well as crystal structure polarity. The method is compatible with the electron optical settings and specimen thicknesses used in STEM imaging, and can thus be performed in parallel with atomic resolution imaging. The spatial resolution is given by the area over which the probe is scanned, which can be as small as a unit cell. For the PACBED experiments, a 90 nm thick film of BaTiO_3 was grown by hybrid molecular beam epitaxy (MBE)¹⁴ on a

(001) SrTiO_3 substrate. Cross-section samples were prepared by wedge polishing to electron transparency. A FEI (Hillsboro, Oregon) Titan 80–300 kV S/TEM operating at 300 kV was used in STEM mode with a convergence semiangle of 9.6 mrad, i.e., the same settings that are used for atomic resolution high-angle annular dark-field (HAADF) imaging with this microscope.^{15,16} PACBED patterns were recorded along [100] by incoherently averaging coherent zone-axis CBED patterns by rapidly scanning the STEM probe while recording the pattern on a charge coupled device (CCD) camera.¹³ Typically, the acquisition time for one PACBED pattern was around 4 s. The scanned area from which the PACBED pattern was acquired was $\sim 5 \times 5$ unit cells. PACBED patterns of tetragonal BaTiO_3 and PbTiO_3 were simulated using the absorptive Bloch wave method, which takes into account the influence of thermal diffuse scattering on the Bragg beam amplitudes.¹³ Unit cell parameters for the simulations were taken from Refs. 17 and 18.

Figure 1(a) shows a simulated PACBED pattern of PbTiO_3 . The unit cell and direction of polarization are shown in Fig. 1(b). The Bragg disk separation allows for distinguishing the a and c axis, respectively, of the tetragonal unit cell. Specifically, the ± 020 disks [outlined in Fig. 1(a)] are well separated due to the smaller a lattice parameter ($a = 3.902$ Å), whereas the ± 002 disks overlap ($c = 4.156$ Å). Thus, by recording PACBED patterns across an area of interest, changes in the unit cell orientation can be mapped, i.e., as may occur across 90° domains. Moreover, the PACBED patterns allow for determining the absolute direction of the polarization within the domains, including across 180° domain boundaries. As can be seen from Fig. 1(c), the pattern intensity is asymmetric in the top and bottom lobes along 00 l within a practical range of thicknesses. The observed pattern asymmetry results from the noncentrosymmetry of PbTiO_3 (space group $P4mm$). The lobe with the greater intensity and reduced contrast (bottom lobe) coincides with the direction of the polarization. PACBED patterns can thus distinguish between unit cell distortions (which affect the Bragg disk separation) and polarity. For example, a cubic film that is coherently strained to a substrate may exhibit a tetragonal distortion of the unit cell but may not necessarily be polar. Specifically, PACBED pattern

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FIG. 1. (Color online) (a) Simulated PACBED pattern of 15.2 nm thick PbTiO_3 along $[100]$. Solid red circles outline the $002/020$ -type Bragg disks. (b) Schematic showing the orientation of the PbTiO_3 unit cell relative to the PACBED pattern with the direction of polarization indicated by the arrow. (c) Magnified images of the lobes from the regions indicated by white rectangles in (a) for different thicknesses. The range of image intensities has been adjusted to accentuate the asymmetry.

simulations of PbTiO_3 in the space group $P4/mmm$, which is tetragonal and centrosymmetric, show a symmetric intensity distribution.

To explore the sensitivity of PACBED patterns to even smaller polarizations, patterns of BaTiO_3 were simulated. In BaTiO_3 , the Ti positions are offset by only 4 pm relative to the c -axis midplane. This is beyond the capability of determining polarization in high-resolution images, even with aberration corrected microscopes.⁶ Figure 2(a) shows a simulated PACBED pattern for BaTiO_3 and Fig. 2(c) shows the bottom and top lobes magnified for different thicknesses. As with PbTiO_3 , the polar nature of the unit cell causes the intensity within the bottom lobes ($00\bar{2}$ disk) to be increased relative to the top lobe, and the increased intensity coincides

FIG. 2. (Color online) (a) Simulated PACBED pattern of 15.2 nm thick BaTiO_3 along $[100]$. (b) Schematic showing the orientation of the BaTiO_3 unit cell relative to the PACBED pattern with the direction of polarization indicated by the arrow. (c) Magnified images of the lobes from the regions indicated by white rectangles in (a) for different thicknesses. The range of image intensities has been adjusted to accentuate the asymmetry.

FIG. 3. (Color online) (a) Experimental and simulated PACBED patterns of an ~ 15.2 nm thick BaTiO_3 sample. (b) Comparison of the top and bottom lobes [see white rectangles in (a)] in experiment and simulation. Image contrast and brightness have been adjusted to accentuate the asymmetry. Arrows in (a) and (b) indicate features apparent only in the lobe pointing in the direction of polarization. Note that the patterns in this figure are rotated by 180° relative to those in Fig. 2.

with the direction of polarization [Fig. 2(c)]. Also note that in addition to differences in intensity, the contrast in the lobes is asymmetric (also, see arrows in Fig. 3), which allows for additional (and perhaps even easier) visual identification of the direction of polarization using PACBED than the intensities alone.

Figure 3(a) shows an experimental PACBED pattern of the epitaxial BaTiO_3 film and the corresponding simulated pattern. The agreement between experiment and simulation is very good. As can be seen from the magnified lobes shown in Fig. 3(b), the asymmetry allows for the determination of the polarity in the 5×5 unit cell film region from which the pattern was recorded. Here, the direction of polarization is along the surface normal and pointing away from the substrate surface, i.e., the Ti are displaced away from the substrate.

It should be noted that care must be taken to minimize specimen tilt relative to the incident beam for correct interpretation of the PACBED patterns in terms of specimen polarity. Specimen tilt modifies the intensity distribution across PACBED patterns.¹³ If the tilt is greater than about 1 mrad, then small polarities such as in BaTiO_3 can no longer be distinguished by visual inspection. Even if tilt is present, the polarization direction can be extracted in most cases.¹⁹ However, as discussed in Ref. 13, tilts as small as 1 mrad can be detected and corrected using PACBED. As also discussed in Ref. 13, the interpretation is insensitive to aberrations of the microscope, including C_s . For example, a large defocus will simply contain patterns averaged over many unit cells rather than disrupt or change the pattern.

In summary, we have demonstrated that PACBED allows for the determination of specimen polarity in ferroelectric materials even when the polarity is smaller than what can be measured using real-space imaging techniques. The method can also be applied to nonferroelectric polar materials such as GaN. Because an angstrom-sized probe is used, the technique can be applied to layers in superlattices that are on the order of a few unit cells thick or to nanostructures, provided

that specimen drift is sufficiently small during the acquisition of the pattern. When combined with *in situ* heating, electric field, or straining capabilities, the method allows for real-time analysis of domain switching and nucleation.

The research at UCSB was supported by DOE Basic Energy Sciences (Grant No. DE-FG02-02ER45994) and SRC (Grant No. 1997.001). N.J.W. also thanks the Intel Foundation/SRCEA for a graduate fellowship. The work made use of the UCSB MRL Central facilities supported by the MRSEC Program of the National Science Foundation under Grant No. DMR-0520415. L.J.A. acknowledges the support by the Australian Research Council.

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- ¹⁹See supplementary material at <http://dx.doi.org/10.1063/1.3549300> for an example of PACBED patterns of BaTiO₃ with tilt.