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Journal
Applied Physics Letters, 90(10)

ISSN
0003-6951

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Publication Date
2007-03-05

Two-dimensional mapping of triaxial strain fields in a multiferroic $BiFeO_3$ thin film using scanning x-ray microdiffraction

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The dramatically enhanced polarizations and saturation magnetizations observed in the epitaxially constrained $BiFeO_3$ BFO thin films with their pronounced grain-orientation dependence have attracted much attention and are attributed largely to the constrained in-plane strain. Thus, it is highly desirable to directly obtain information on the two-dimensional 2D distribution of the in-plane strain and its correlation with the grain orientation of each corresponding microregion. Here the authors report a 2D quantitative mapping of the grain orientation and the local triaxial strain field in a 250 nm thick multiferroic BFO film using a synchrotron x-ray microdiffraction technique. This direct scanning measurement demonstrates that the deviatoric component of the in-plane strain tensor is between 5 10^{-3} and 6 10^{-3} and that the local triaxial strain is fairly well correlated with the grain orientation in that particular region

Multiferroic ferroelectromagnets[1] that display simultaneous magnetic and polarization orderings have stimulated intense scientific and technological interest.[2-7] Among the many ferroelectromagnets, rhombohedral $BiFeO_3$ space group *R*3*c* is known to be the only perovskite material that exhibits multiferroism at room temperature with its ferro- electric Curie point of 850 ° C and antiferromagnetic Néel temperature of 370 ° C.[8] Thus, $BiFeO_3$ BFO is currently considered to be the prime candidate for future device applications.

Recently, Wang *et al.*[2] fabricated epitaxial pseudotetragonal BFO films having a remanent polarization P_r almost an order of magnitude higher than that of bulk BFO by applying a strong compressive stress imposed by the bottom $SrRuO_3$ electrode. Though there are some controversial arguments,[9] the dramatically enhanced polarization and saturation magnetization in the distorted pseudotetragonal BFO thin film[2] are attributed largely to the constrained strain in the heteroepitaxially grown film layer.[2,10-13] In addition to this critical role of epitaxial film[-13] strain on the enhanced polarization and magnetization,[2,11] it has been reported that the value of P_r is highly susceptible to the grain orientation in a given BFO thin film.[10]

In view of these, it is very important to directly obtain information on the two-dimensional 2D distribution of lat- tice strain and its correlation with the grain orientation of each corresponding microregion. The strain around ferro- electric domains has been observed by using various tech- niques including transmission electron microscopy,[14] atomic force microscopy,[15] and synchrotron scanning x-ray microdiffraction S-XRMD .[16] However, only S-XRMD allows us a direct measurement of the strain fields around local ferroelectric domains or grains. Rogan *et al.*[16] carried out S-XRMD study using a $BaTiO_3$ single crystal. In spite of its importance, however, no direct measurement of the strain field in a multiferroic material has been performed prior to the present study. Here we report a first-of-its-kind 2D quan- titative mapping of the grain orientation and local triaxial strain field in a BFO thin film using S-XRMD technique. This measured deviatoric component of the local triaxial strain i.e., lattice distortion was correlated with the grain orientation in that particular region.

Pulsed laser deposition PLD was employed to prepare a BFO thin film on a 001 plane of $SrTiO_3$ STO . To examine the effect of the grain orientation on the local in-plane strain tensor, we have intentionally fabricated a BFO film with more than one grain orientation. Thus, the deposition conditions used in the present study were somewhat different from those used in the fabrication of 001 -oriented pseudotetragonal epitaxial BFO films.[11] The main differences are 1 the target composition, $Bi_{1.05}FeO_3$, 2 the deposition temperature, 675 ° C, and 3 the oxygen partial pressure, 100 mTorr.

The x-ray diffraction XRD pattern indicated that the film was preferentially 001 oriented with some minor reflection peaks mostly from 101 reflection. As presented in Fig. 1, the pole figure confirms that the BFO thin film on 001 STO is preferentially grown along the 001 direction. However, one cannot ignore other grain orientations, especially 101 -type orientations. The degree of 001 -type preferred orientation, as estimated using the Lotgering orienta-

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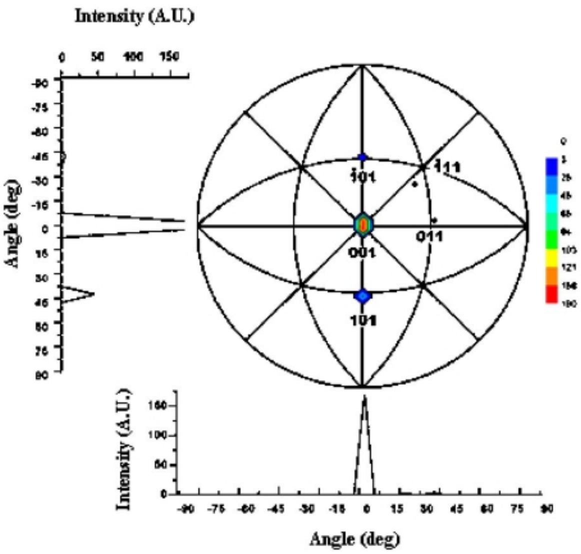

FIG. 1. Color online Pole figure of the 250 nm thick BFO film showing 001 -preferential growth.

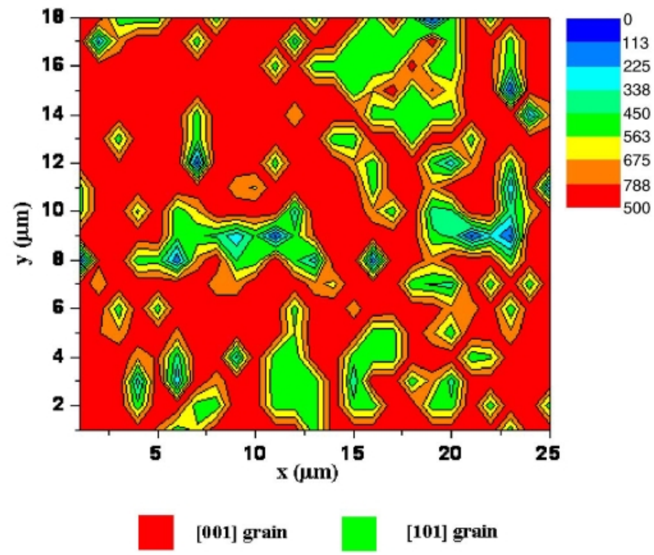

FIG. 2. Color online Two-dimensional mapping of the grain orientation in the 250 nm thick BFO film on 001 STO. The step size used in the present S-XRMD experiment is 1 m, and the total scanned area is 25 18 m². In the figure, *x* and *y* denote two orthogonal in-plane directions.

tion factor,[17] is 75%. Polarized Raman scattering of the 500 nm thick 001 preferentially oriented BFO film by employing the side-view *Y ZZ Y* scattering configuration confirmed the three mode frequencies of the transverse optical A_1 TO phonons for the tetragonal *P*4*mm* BFO Ref. 18 at 136, 168, and 212 cm^{-1}.

The polarization-electric field *P-E* curves of the 250 nm thick film capacitor fabricated on the bottom electrode structure of $SrRuO_3$ 50 nm / STO showed that the net switching polarization $2P_r$ measured at 1 kHz with E_{max}= ± 400 kV/ cm is 62 C / cm². The *M-H* curves of the present PLD-grown BFO film with a mixed grain orientation were very similar to those of the 001 -oriented epitaxial pseudotetragonal BFO film having the same thickness of 250 nm.[19]

We now seek for detailed information on the spatial distribution of lattice distortions and its correlation with the grain orientations at each corresponding microregion in a constrained BFO film. For this purpose, the S-XRMD experiment was conducted on beamline 7.3.3 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The energy of the polychromatic x-ray beam was between 5 and 14 keV, and the beam cross section was measured to be around 1 1 m². A more detailed description of the beamline can be found in Ref. 20.

The data were analyzed with the x-ray microdiffraction analysis indexing software XMAS which adopts nonlinear least-squares refinement.[20] Geometrical calibration parameters were determined by using a single-crystal unstrained STO sample with its lattice parameter *a* of 3.905 Å. The grain orientation, i.e., *hkl* -peak indexing, of each scanned area pixel was determined by having the XMAS code search for proper sets to compare the theoretical scattering vector based on the local spin-density approximation[2] LSDA with the scattering vector from the experimental Laue reflection. Because the exact atomic positions for the present thin-film BFO phase with *P*4*mn* tetragonal symmetry are not known, the computed atomic positions and lattice parameters a = 3.935 Å and c = 3.998 Å based on the LSDA Ref. 2 were adopted in the computation of the theoretical scattering vector.

Exact values of the local strain tensor were obtained from the transformation matrix which in turn was evaluated from the unit-cell parameters of each scanned position and the input unstrained unit-cell parameters obtained from the LSDA result. Because the deviatoric strains involved the changes in the angles between atomic planes, the deviatoric tensor was evaluated from the angular displacements of the Laue spots in an experimental Laue pattern. In this way, the crystal orientation and the triaxial deviatoric strain tensor

$_{xx}$ were obtained for every scanned position. The accuracy of measuring the deviatoric strain tensor i.e., lattice distortion depends on the number of Laue reflections used in the strain refinement.[21,22] In the present S-XRMD study, we evaluated the deviatoric strain tensor by employing more than 72 Laue reflections. According to Valek,[22] the uncertainty of our measurement of the deviatoric strain tensor is estimated to be essentially zero.

Figure 2 presents the 2D mapping of grain orientation, as

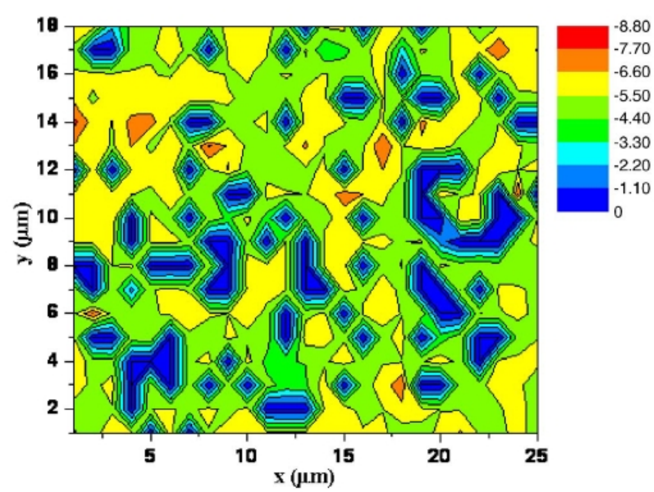

FIG. 3. Color online Two-dimensional spatial distribution of the deviatoric component of the in-plane residual strain in the 250 nm thick BFO film on 001 STO. Exact values of the local in-plane strain tensor, i.e., 1 / 2 $_{xx}$ + $_{yy}$, were obtained from the unit-cell parameters of each scanned position and the input unstrained unit-cell parameters.

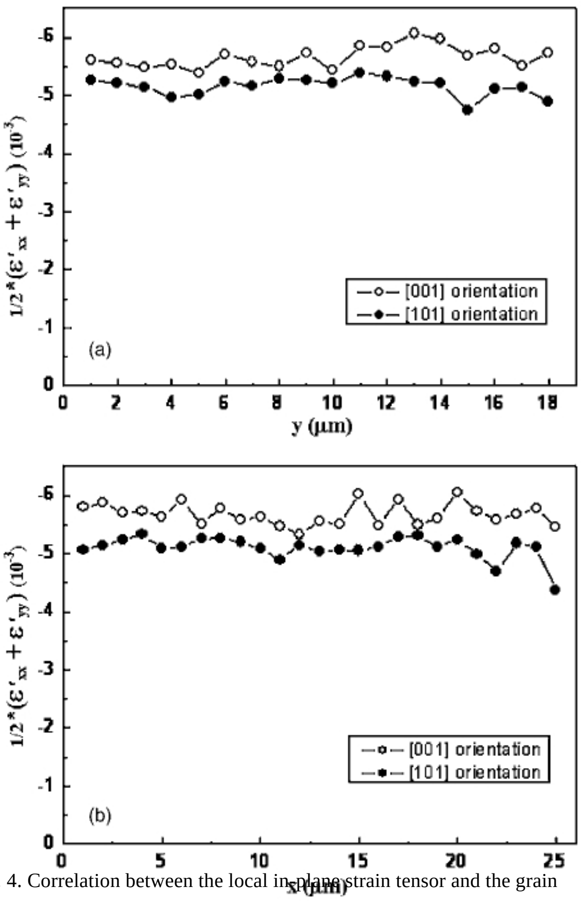

FIG. 4. Correlation between the local in-plane strain tensor and the grain orientation. a *x*-integrated average of the deviatoric component of the in-plane strain tensor for the two different grain orientations, plotted as a func- tion of *y*. b *y*-integrated average of the deviatoric component of the in- plane strain tensor for the two different grain orientations, plotted as a function of *x*.

obtained using the method of S-XRMD. The red-colored re-gion denotes the 001 -oriented grains, whereas the green-colored regions scattered in the matrix of 001 -oriented grains represent the 101 -oriented grains. Besides these two major orientations, a negligible portion of the scanned area actually corresponds to the grains with higher *hkl* indices, ¯mostly 111 . This region is marked with a deep blue color. The *hkl* indexing of each scanned microregion 1 1 m^2 indicates that 65% of the scanned area in Fig. 2 consists of 001 -oriented grains and 20% corre-sponds to 101 -oriented grains. These estimates exclude the yellow- and orange-colored transition regions located be-tween the 001 - and 101 -oriented domains.

Figure 3 represents a 2D spatial distribution of the de-viatoric component of the in-plane residual strain tensor. We have plotted the sum of $_{xx}$ and $_{yy}$ instead of $_{xx}$ or $_{yy}$ alone since 1 / 2 $_{xx}$ + $_{yy}$ i.e., $-1/2_{zz}$ is the most ap-propriate measure of the in-plane strain, where *z* denotes the out-of-plane direction which is normal to *x* and *y*. Various colors shown in the right-hand-side column of Fig. 3 repre-sent different values of the deviatoric strain tensor $-1/2_{zz}$ 10^{-3}. Thus, the maximum observed in-plane residual strain is as large as -8.8 10^{-3}. Comparing the in-plane strain mapping Fig. 3 with the 2D distribution of grain orientations Fig. 2 , one can notice that the lattice distortion is more pronounced in the region of 001 -oriented grains in general.

A quantitative correlation between the local in-plane strain tensor and the grain orientation can be made by plot- ting the in-plane strain tensor along any of the two orthogo- nal in-plane directions. Figure 4 a shows the *x*-integrated average of the deviatoric component of the in-plane strain tensor for the two major grain orientations, plotted as a func- tion of *y*. Similarly, Fig. 4 b presents the grain-orientation dependence of the *y*-integrated average of the in-plane strain tensor for various locations of *x*. As presented in Fig. 4, the residual strain of the 001 -oriented grain is consistently larger than that of the 101 -oriented grain throughout the whole region, showing a fairly good correlation between these two structural parameters. The present S-XRMD result is also consistent with the recent report[10] obtained by using conventional XRD that the monoclinically distorted BFO film heteroepitaxially grown on 001 STO is under more significant epitaxial constraint than the film grown on 101 STO.

This work was supported by the Korea Science and Engineering Foundation KOSEF under Contract No. R01-2005-000-10354-0. The authors thank B. C. Valek for his assistance in performing x-ray microdiffraction experi- ments at the Advanced Light Source ALS , Lawrence Berkeley National Laboratory LBNL , USA. The ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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