Elastic relaxation and correlation of local strain gradients with ferroelectric domains in (001) BiFeO₃ nanostructures

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(Received 22 April 2011; accepted 9 June 2011; published online 1 August 2011)

We report an elastic relaxation and increase in local strain variation correlated with ferroelectric domains within epitaxial BiFeO₃ thin film nanostructures fabricated by combined electron-beam and focused ion-beam nanolithography. Nano-focused x-ray diffraction microscopy provided new insights into the relationship between film strain and ferroelectric domains in nanostructures, namely: (i) an out-of-plane (C-axis) elastic relaxation of as much as $-1.8\% \Delta c/c$ in a BFO film-based nanostructure relative to the planar film lattice constant; (ii) an out-of-plane rotation trending from the center towards all released edges of the nanostructure; and (iii) an increase of inter-domain strain variation within the nanostructure of approximately 10 times the inter-domain variation found within the planar film, correlated with ferroelectric domain boundaries as confirmed by piezoresponse-force microscopy. These results indicate that the release of in-plane BFO/SRO mismatch strain in a planar film is taken up by the local ferroelectric domain structure after patterning, resulting in greatly increased mechanical strain gradients within the structure. © 2011 American Institute of Physics. [doi:10.1063/1.3605594]

The single-phase multiferroic BiFeO₃ (BFO) material is a ferroelectric antiferromagnet with a large polarization ($P_r \sim 90$ μ C/cm²) and high Curie ($T_C \sim 1100$ K) and Néel ($T_N \sim 640$ K) temperatures.¹ The coexistence and relative robustness of ferroelectric (FE) and antiferromagnetic (AF) order parameters make BFO thin films an attractive candidate for a variety of device applications, which exploit one or both degrees of ordering.¹⁻³ Much of the recent work has focused on investigating conditions of film growth that can be manipulated to optimize one type of ordering independently of the other⁴ or by creating domain structures that enhance the coupling strength between the FE/AF ordering.⁵ We report here that patterning of BFO thin films into nanostructures produces a strong elastic relaxation of the entire nanostructure and an increase in local strain variation correlated with ferroelectric domain boundaries within the nanostructure, as observed by nano-focused x-ray diffraction microscopy (nano-XRD) performed at the Hard X-ray Nanoprobe Beamline (HXN) operated by the Center for Nanoscale Materials (CNM) and X-ray Science Division at the Advanced Photon Source (APS). These results indicate that varying the size and geometry of lithographed BFO nanostructures directly affects both the local c/a ratio and the local interdomain mechanical energy. This suggests that future nanoscale applications based on multiferroic properties relating to either ferroelectric polarizability⁴ or domain energetics⁵ can potentially harness patterning effects to enhance device performance.

Bulk BFO has a rhombohedral distorted perovskite structure (R3c) with a ferroelectric polarization along the [111] direction. There are eight possible polarization orientations in a pseudocubic (001) oriented film corresponding to $\pm P_r$ variants along the four cubic diagonal ([111]) directions. This domain structure can lead to both ferroelectric (180°) and ferroelastic (71° and 109°) switching in BFO films grown on (001) oriented SrTiO₃ (STO).⁶ Fabrication of thin film-based ferroelectric nanostructures, where the constraint of the surrounding planar film is eliminated, can significantly alter the elastic properties of the thin film heterostructures, leading to increased ferroelastic domain wall motion as shown previously for Pb(Zr_xTi_{1-x})O₃ nanostructures.⁷

For this study, an epitaxial (35 nm) BFO/(70 nm) SrRuO₃ (SRO) thin film heterostructure was grown on a (001)-oriented STO substrate following procedure described elsewhere.⁸ Nanostructures were fabricated with lateral dimensions ranging from 1 μ m to 500 nm, using combined electron-beam lithography and focused ion-beam (FIB) nanopatterning, with the BFO nanostructure regions protected from ion-beam tails using a removable tungsten (W) mask layer (Figs. 1(a)–1(f)).⁹ Nanolithography induces an asymmetric release of the in-plane lattice constraint at the top of the nanostructure, while the bottom interface is still matched to the SRO in-plane lattice constant (Fig. 1(g)), depending on pattern size and geometry.

Scanning nano-XRD measurements were performed at the CNM/APS HXN beamline, similarly to previous measurements of bulk ferroelectric domain structures.¹⁰ A hard x-ray Fresnel zone plate was used to focus 10 keV x-rays to ~40 nm FWHM beam spot. The sample was rotationally aligned on the BFO (002)_c crystallographic direction Bragg condition in a horizontal diffraction geometry. Spatially resolved diffraction maps were made with 2D lateral X-Y

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FIG. 1. (Color online) Schematic diagram of two-step lithography process utilizing a nanopatterned tungsten (W) film as a protective layer. Spincoated double layer electron resist on (a) $BiFeO_3/SrRuO_3/SrTiO_3$, (b) electron beam lithography, (c) sputter-deposition of a W layer, (d) lift off of the resist layer, (e) FIB lithography, and (f) chemical removal of the W layer. (g) Schematic showing the rotation and strain of the out-of-plane lattice vector due to asymmetric in-plane expansion of the BFO film when the planar film constraint is removed from the sides of the nanostructure upon fabrication.

scans of the beam position across the sample with a smallest lateral step of 10 nm, using an optomechanical nanopositioning system described elsewhere.^{11,12} Diffracted x-rays were collected using a CCD area detector with 13 μ m × 13 μ m pixels placed at a distance of 70 cm from the sample, resulting in angular pixel size of 0.001° × 0.001°. This technique allows for non-invasive, non-destructive strain imaging of thin film nano-heterostructures with minimal sample preparation and beam interaction effects.

A scanning electron microscopy (SEM) image of multiple patterned BFO nanostructures is shown in Figure 2(a) and the results of a corresponding nano-XRD diffraction intensity and rotation map are shown in Figures 2(b)-2(d). The sample scattering angle was matched to the (002) diffraction condition of the larger BFO nanostructures in the scan,



FIG. 2. (Color online) Overview scan of multiple patterned BFO devices showing nano-XRD results [(b)-(d)] and a reference SEM image (a). The BFO (002) diffracted x-ray intensity is shown in (b), the 2θ center of mass variation (COM) in (c), and the χ COM variation in (d). A rotation of the out-of-plane lattice vector (C-axis) from the center of each object towards all released edges is indicated by the left-right/blue-red angular (COM) distribution of 2θ (c) and the up-down/blue-red angular COM distribution of χ (d).

which causes an apparent reduction of intensity in the smaller nanostructures due to a generally higher elastic relaxation that shifts the Bragg diffraction condition outside of the incident angle spread of the focusing optic. The angular center of mass position of the outgoing x-ray radiation within the scattering plane (2θ) and transverse to the scattering plane (χ) are shown in Figures 2(c) and 2(d), respectively. A generally smooth rotation of the [002] lattice vector from the center of each nanostructure towards all released edges is indicated by the blue-red left-right distribution of the x-ray in-plane diffracted angular position in Fig. 2(c) and the blue-red down-up distribution in the out-of-plane diffracted angular position in Fig. 2(d). Due to the incident angle spread of the focusing optic, the change in 2θ angular position at a fixed scattering angle convolutes with both lattice strain and with lattice vector rotation (see Fig. 1(g)), as revealed by the sharp streaks underlying the left-right trend on several of the nanostructures in Fig. 2(c) and required more detailed analysis for quantitative lattice mapping (see Fig. 4).

A comparison of a fixed-angle nano-XRD map for a planar BFO film and a nanostructure is shown in Figure 3. The nanostructure exhibits generally a lower diffraction intensity (Fig. 3(d)), a higher 2θ value (Fig. 3(e)), and a greater 2θ and χ variance (Figs. 3(e) and 3(f)) when compared to the planar film (Figs. 3(a)-3(c)). The higher 2θ value indicates that the nanostructure has a generally smaller out-of-plane lattice constant consistent with the expectation of elastic release of in-plane clamping stress. The average domain size indicated by the 2θ and χ variance (~250 nm laterally in this case) is comparable between the planar film and the nanostructure, but the magnitude of the 2θ variation increases as much as ~10× within the nanostructure. This suggests that the underlying ferroelectric domain structure of the BFO film may not change substantially during the lithographic



FIG. 3. (Color online) Overview of x-ray diffraction scan, comparing a single patterned BFO nanostructure [(d)-(f)] with the unpatterned planar film [(a)-(c)]. The BFO (002) x-ray diffraction signal from the nanostructure exhibits a generally lower intensity, higher 2θ value, and increased 2θ and χ variance in comparison with the unpatterned planar film (common linear scale bars are included for comparison). The average domain size indicated by this variance is comparable between the nanostructure and the planar film regions.



FIG. 4. (Color online) Results of nanofocused x-ray diffraction lattice mapping in a single 500 nm BFO nanostructure [(b)-(d)] compared to the ferroelectric domain structure observed via PFM (a). Repeated 2D lateral scans were taken while varying the sample angle across the BFO (002) rocking curve, from which (b) the integrated intensity, (c) out-of-plane lattice strain, and (d) out-of-plane lattice (C-axis) rotation were extracted. The lattice constant of the film in the nanostructure is relaxed relative to the planar film by a strain value of as much as $-1.8\% \Delta c/c$, with a strain distribution that generally corresponds to the ferroelectric domain structure (shown in (a)).

steps but, instead, accommodates the out-of-plane elastic relaxation and C-axis rotation within the existing structure, greatly increasing the inter-domain elastic strain gradients.

A quantitative mapping of the out-of-plane lattice parameter and lattice vector rotation within a 500 nm \times 500 nm square nanostructure is shown in Figure 4. This figure shows a composite map taken while varying the sample scattering angle across the BFO (002) diffraction condition for the nanostructure, explicitly accounting for a convolution of lattice rotation and strain within the incident angle spread of the focusing optic. The individual maps were registered using Fe fluorescence and then used to extract a per-pixel rocking curve with integrated intensity shown in Fig. 4(b). The detector 2θ position relative to an absolute lattice constant was calibrated at 10 keV using Si line powder diffraction and verified with the substrate STO (002) reflection prior to the experiment. We observed that the out-of-plane lattice parameter is strained within the nanostructure by as much as -1.8% $\Delta c/c$ relative to the planar film lattice constant (4.077 Å). The internal distribution of this strain (Fig. 4(c)) generally corresponds to the ferroelectric domain pattern obtained using PFM (Fig. 4(a)). The observed strain variation across domain walls within the nanostructure (up to $0.5\% \Delta c/c$) is increased by as much as $\sim 10 \times$ relative to variations in the planar film. This is consistent with expectations of elastic patterning release generated by removal of in-plane clamping stress from the surrounding film – the maximal release is found near the edges of the nanostructure, where the lattice constant nearly approaches that of bulk BFO (bulk BFO 3.965 Å). We also observed that the out-of-plane lattice vector exhibits a smooth rotation away from the center of the nanostructure towards all released edges (see Fig. 4(d)), consistent with previous discussion.

In summary, epitaxial BFO nanostructures were studied by nano-XRD with sub-50 nm spatial resolution. Comparison of the BFO (002) diffraction maps from a patterned nanostructure and the planar film regions shows that elastic relaxation induced by removal of the film surrounding the BFO nanostructure leads to an enhanced variation in the local strain and lattice rotation fields across the entire structure. Internal strain gradients within the nanostructure are increased by up to $\sim 10 \times$ relative to the planar film and are correlated with ferroelectric domain boundaries as observed by PFM. These results indicate that direct manipulation of both local ferroelectric polarizability and local inter-domain mechanical energy is feasible via nanoscale patterning of multiferroic BFO thin films. These results have significant implications for future use of sub-micron lateral scale multiferroic heterostructures in the fabrication of high-density FeRAMs and other micro- and nanoelectronic devices exploiting the multiferroic properties of BFO films.

Work in the Materials Science Division and use of the Advanced Photon Source and the Center for Nanoscale Materials were supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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