<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Nanoscale phase mixture in uniaxial strained BiFeO3 (110) thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Liu, Huajun; Yang, Ping; You, Lu; Zhou, Yang; Fan, Zhen; Tan, Hui Ru; Wang, Junling; Wang, John; Yao, Kui</td>
</tr>
<tr>
<td><strong>Date</strong></td>
<td>2015</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10220/38751">http://hdl.handle.net/10220/38751</a></td>
</tr>
<tr>
<td><strong>Rights</strong></td>
<td>© 2015 American Institute of Physics (AIP). This paper was published in Journal of Applied Physics and is made available as an electronic reprint (preprint) with permission of American Institute of Physics (AIP). The published version is available at: [<a href="http://dx.doi.org/10.1063/1.4930049">http://dx.doi.org/10.1063/1.4930049</a>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.</td>
</tr>
</tbody>
</table>
Nanoscale phase mixture in uniaxial strained BiFeO3 (110) thin films
Huajun Liu, Ping Yang, Lu You, Yang Zhou, Zhen Fan, Hui Ru Tan, Junling Wang, John Wang, and Kui Yao

Citation: Journal of Applied Physics 118, 104103 (2015); doi: 10.1063/1.4930049
View online: http://dx.doi.org/10.1063/1.4930049
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/118/10?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Enhancement of piezoelectric response in Ga doped BiFeO3 epitaxial thin films
J. Appl. Phys. 117, 244107 (2015); 10.1063/1.4923217

Microstructure and ferroelectric properties of epitaxial cation ordered PbSc0.5Ta0.5O3 thin films grown on electroded and buffered Si(100)

Magnetic and structural properties of BiFeO3 thin films grown epitaxially on SrTiO3/Si substrates

Composition and temperature-induced structural evolution in La, Sm, and Dy substituted BiFeO3 epitaxial thin films at morphotropic phase boundaries
J. Appl. Phys. 110, 014106 (2011); 10.1063/1.3605492

Piezoresponse and ferroelectric properties of lead-free [ Bi 0.5 ( Na 0.7 K 0.2 Li 0.1 ) 0.5 ] Ti O 3 thin films by pulsed laser deposition
Nanoscale phase mixture in uniaxial strained BiFeO₃ (110) thin films

Huajun Liu,1,2 Ping Yang,3 Lu You,4 Yang Zhou,4 Zhen Fan,2 Hui Ru Tan,1 Junling Wang,4 John Wang,2,a) and Kui Yao1,a)

1Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 2 Research link, Singapore 117602
Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575
Singapore Synchrotron Light Source (SSLS), National University of Singapore, 5 Research Link, Singapore 117603
School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798

(Received 17 June 2015; accepted 23 August 2015; published online 9 September 2015)

A strain-induced nanoscale phase mixture in epitaxial BiFeO₃ (110) films is investigated. High resolution synchrotron x-ray diffraction shows that a monoclinic M₂ phase (orthorhombic-like, with a c/a~1.01) coexists as the intermediate phase between monoclinic M₁ phase (tetragonal-like, with a c/a~1.26) and monoclinic M₃ phase (rhombohedral-like, with a c/a~1.00), as the film thickness increases from 10 to 190 nm. Cross-sectional transmission electron microscopy images reveal the evolution of domain patterns with coexistence of multiple phases. The different ferroelectric polarization directions of these phases, as shown by piezoelectric force microscopy, indicate a strong potential for high electromechanical response. The shear strain ε₁₃ is found to be a significant driving factor to reduce strain energy as film thickness increases, according to our theoretical calculations based on the measured lattice parameters. The nanoscale mixed phases, large structure distortions, and polarization rotations among the multiple phases indicate that (110)-oriented epitaxial films provide a promising way to control multifunctionalities of BiFeO₃ and an alternative direction to explore the rich physics of perovskite system. © 2015 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4930049]

I. INTRODUCTION

Nanoscale phase mixture and large structural distortion have led to extraordinary functionalities in many materials with perovskite structure for wide device applications. Strong piezoelectric responses, which are applied for various electromechanical sensors and actuators, often come from solid solutions with intimate coexistence of mixed phases, for example, the rhombohedral and tetragonal phases in solid solutions with intimate coexistence of mixed phases, often come from perovskite systems at morphotropic phase boundaries (MPBs). The origin of large electromechanical response is often a result of polarization rotation under external electric field, which is facilitated by the coexistent phases at MPBs. A recent work on pure PbTiO₃ demonstrates that MPB can also be induced by high pressure, suggesting an alternative route other than tuning chemical compositions. Most recently, a strain driven MPB has been identified in BiFeO₃ (BFO) epitaxial thin films grown on (001) LaAlO₃ (LAO) substrates with a large compressive strain of ~4.5%. The mixed tetragonal-like and rhombohedral-like monoclinic phases give rise to large electric field induced strain over 5%. The phase transitions and mechanism of large electromechanical response of this MPB in BFO films with (001) orientation have been a focus of recent studies. In addition, these nanoscale mixed phases also exhibit interesting magnetic property and multiferroic phase transitions around room temperature.

Our previous work has shown a uniaxial nature of strain in (110)-oriented BFO film on LAO substrates, where only one in-plane lattice along pseudocubic [001]pc direction is strained by substrate misfit strain. A uniaxial strain of ~4.5% induces a ferroelectric BFO tetragonal-like phase with a giant c/a~1.24 and a large angle between twin domains of ~26°. In this work, nanoscale phase mixture has been investigated by varying the film thickness of BFO epitaxial thin films on (110)-oriented LAO substrates. A monoclinic M₂ phase (orthorhombic-like, with a c/a~1.01) of BFO is found by high resolution synchrotron x-ray diffraction to coexist with monoclinic M₁ phase (tetragonal-like, with a c/a~1.26) and monoclinic M₃ phase (rhombohedral-like, with a c/a~1.00) as the film thickness increases. Ferroelectric polarization rotation among monoclinic M₁, M₂, and M₃ phases is demonstrated with piezoelectric force microscopy (PFM). The domain evolutions of these nanoscale mixed phases are revealed by high resolution transmission electron microscopy (HRTEM). Theoretical calculations show that the decrease in the shear strain ε₁₃ is the significant factor to reduce elastic energy as the film thickness increases. The nanoscale mixed phases discovered in this work provide an alternative direction, using uniaxial strain instead of biaxial strain, to understand the rich physics of BFO system and a promising new route to control its multifunctional properties.

---
a)Authors to whom correspondence should be addressed. Electronic addresses: msewangj@nus.edu.sg and k-yao@imre.a-star.edu.sg.
II. EXPERIMENTAL DETAILS

Epitaxial BFO films were deposited directly on LAO substrates with (110) orientation by RF sputtering. The film thickness was varied from 10 nm to 190 nm by changing sputtering time. The crystal structures were investigated by using high resolution synchrotron x-ray diffractometry at the x-ray development and demonstration beamline of Singapore Synchrotron Light Source. HRTEM is employed to study the domain patterns (Philips CM300 FEG). Ferroelectric domain structure was studied by a commercial atomic force microscope system (Asylum Research MFP-3D).

III. RESULTS AND DISCUSSION

θ-2θ x-ray diffraction patterns show interesting thickness-dependent evolution of BFO diffraction peak from a single peak at film thickness of 10 nm to several peaks at 60 and 190 nm (Figure 1). No secondary phase or other orientations are observed, indicating an epitaxial growth of BFO films in (110) orientation. To study the detailed crystal structures of BFO (110) films with different thicknesses, reciprocal space mappings (RSM) are measured by using high resolution synchrotron x-ray, along H direction in Figure 2 and K direction in Figure 3. Note that the reciprocal space lattice with H, K, and L directions are defined on the real space lattice of (110)-oriented LAO substrate with $a_{sub} = 2.68 \AA$ along $[-110]_{pcc}$ direction, $b_{sub} = 3.79 \AA$ along $[001]_{pcc}$ direction, $c_{sub} = 2.68 \AA$ along film surface normal direction $[110]_{pcc}$, $\alpha_{sub} = \beta_{sub} = \gamma_{sub} = 90^\circ$, which is called NEW lattice in the following discussions to differentiate from the pseudocubic lattice. Figure 2 shows the $(001)_{HLL}$ and $(-102)_{HLL}$ RSM along the in-plane H direction. In $(001)_{HLL}$ RSM in Figure 2(a), a single diffraction spot is observed for BFO film with thickness of 10 nm, indicating a single phase. The two symmetric peaks around the main peak are observed for BFO film with thickness of 60 nm, indicating a multiple phase. The three symmetric peaks around the main peak are observed for BFO film with thickness of 190 nm, indicating a multiple phase.

FIG. 1. x-ray diffraction θ-2θ scans of BFO (110) films grown on LAO single crystal substrates with thicknesses of 10 nm, 60 nm, and 190 nm.

FIG. 2. Reciprocal space mappings around $(001)_{HLL}$ and $(-102)_{HLL}$ for BFO (110) films with thicknesses of 10 nm (left column (a), (d)), 60 nm (middle column (b), (e)), and 190 nm (right column (c), (f)), respectively. H, K, and L are indexed in LAO substrate lattice with $a_{sub}$, $b_{sub}$, and $c_{sub}$ along $[-110]_{pcc}$, $[001]_{pcc}$, and $[110]_{pcc}$, respectively.
diffraction peaks in Figure 2(a) are modulation peaks, whose origin will be discussed later. Interestingly, two diffraction spots and three diffraction spots are observed for BFO films with thickness of 60 nm and 190 nm in Figures 2(b) and 2(c), respectively. This suggests that a single BFO phase develops into a coexistence of two phases and then three phases as the strain relaxes with increased film thickness. In the \((H/L)RSM\), two diffraction spots with the same \(H\) are observed in Figure 2(d) for BFO film with thickness of 10 nm, corresponding to a pair of twins with twin angle of \(\sim 26^\circ\). Based on the reciprocal space vector method developed recently,\(^{20}\) the precise lattice parameters of the film can be determined. The lattice parameters of this phase in NEW lattice is \(a = 3.003 \text{ Å}, \ b = 3.790 \text{ Å}, \ c = 2.985 \text{ Å}, \ \beta = 77.0^\circ, \ \alpha = \gamma = 90^\circ\). In order to compare with other reports in (001) oriented film, the lattice parameters are converted to pseudocubic unit cell with \(a_{pc} = 3.731 \text{ Å}, \ b_{pc} = 3.790 \text{ Å}, \ c_{pc} = 4.684 \text{ Å}, \ \beta_{pc} = 89.6^\circ, \ \alpha_{pc} = \gamma_{pc} = 90^\circ\) (The conversion between the NEW lattice and pseudocubic lattice is illustrated in Figure 7). This phase is referred as monoclinic M1 phase (tetragonal-like, with \(c/a \sim 1.26\)), because it is very close to the tetragonal BFO phase although the real symmetry is monoclinic. For BFO film with thickness of 60 nm, four diffraction spots are observed in Figure 2(e), in which two of them are at similar positions compared with monoclinic M1 phase of 10 nm film and two new peaks occur at L value between 1.8 and 1.9. These two new peaks correspond to another pair of rotated twins with small twin angle of \(\sim 0.8^\circ\). This new phase that appears at 60 nm has pseudocubic lattice parameters of \(a_{pc} = 4.048 \text{ Å}, \ b_{pc} = 3.790 \text{ Å}, \ c_{pc} = 4.105 \text{ Å}, \ \beta_{pc} = 89.8^\circ, \ \alpha_{pc} = \gamma_{pc} = 90^\circ\), which are very close to an orthorhombic lattice, but the real symmetry is monoclinic. This phase is named as monoclinic M2 phase (orthorhombic-like, with \(c/a \sim 1.01\)) throughout this work. Orthorhombic BFO phase has previously been theoretically predicted and recently experimentally studied in tensile strained (001) films.\(^{21,22}\) For BFO film with thickness of 190 nm, five diffraction spots are observed in Figure 2(f), in which four of them are from monoclinic M1 (tetragonal-like) and monoclinic M2 (orthorhombic-like) phases. The fifth peak at L = 1.9 corresponds to a new phase, with pseudocubic lattice parameters of \(a_{pc} = 3.964 \text{ Å}, \ b_{pc} = 3.790 \text{ Å}, \ c_{pc} = 3.964 \text{ Å}, \ \beta_{pc} = 89.6^\circ, \ \alpha_{pc} = \gamma_{pc} = 90^\circ\), which are close to bulk BFO lattice except that \(b_{pc}\) is constrained by substrate. This phase is named monoclinic M3 (rhombohedral-like, with \(c/a \sim 1.00\)) phase throughout this work. Figure 3 shows the (001) and (0–12) RSM along the other in-plane [001] direction. In (0–12) RSM in Figures 3(d)–3(f), the positions of BFO spots are the same as the substrate, regardless of film thicknesses and phases. This shows
In summary, a single monoclinic M1 phase is identified for BFO film with thickness of 60 nm, a large portion of the area shows no polarization signal (brown color) in in-plane PFM along [−110]pc direction for BFO film with thickness of 60 nm and 190 nm, respectively. The islands grow wider and connect with each other and the surfaces of these films are still not flat. Both Figures 4(e) and 4(h) show the monoclinic M1 (tetragonal-like) phase BFO grows at the interface between film and substrate. Away from the interface, monoclinic M2 phases (orthorhombic-like) can be observed to coexist with monoclinic M1 phases (tetragonal-like), as shown in Figures 4(f) and 4(i).

Figure 5 shows the cross-sectional TEM images along the in-plane [001]pc direction. In contrast to the [−110]pc direction in Figure 4, the films are continuous and the surfaces are flat, as shown in Figures 5(a)–5(c) for all three samples. The high resolution images in Figures 5(d) and 5(e) suggests a coherent growth across the interface for film thickness of 60 and 190 nm, in consistence with the x-ray diffraction result in Figure 2. Therefore, TEM data reveal an island growth along [−110]pc direction with coexistence of multiple phases, while a coherent growth along [001]pc direction.

With the understanding on the thickness-dependent phase transition for the nanoscale phase mixture of BFO (110) films, the ferroelectric polarization directions are studied by PFM, as shown in Figure 6. The topographic images, Figures 6(a), 6(e), and 6(i), show that the films are grown as stripes along [001]pc direction, due to the anisotropic nature of uniaxial strain from the substrate, agreeing well with cross-sectional TEM images in Figures 4 and 5. For BFO film with thickness of 10 nm, the projection of ferroelectric polarization into in-plane [−110]pc direction has two opposite orientations, as shown by the purple and yellow color in the in-plane PFM in-phase image in Figure 6(b), which corresponds to the pair of twins of monoclinic M1 phase (tetragonal-like) BFO. No in-plane PFM signal (brown color) is detected along [001]pc direction in Figure 6(c). Out-of-plane PFM shows a single downward orientation of polarization in Figure 6(d). Provided that the piezoresponse magnitude is proportional to the polarization magnitude, combining both in-plane and out-of-plane PFM images enables 3D reconstructions of the polarization vectors. The polarization vector for monoclinic M1 phase (tetragonal-like) is thus oriented within the vertical plane and close to the pseudocubic cpc direction, as shown in Figure 7. For BFO film with thickness of 60 nm, a large portion of the area shows no polarization signal (brown color) in in-plane PFM along [−110]pc direction, Figure 6(f), in addition to the purple and yellow color domains. These areas with no signal are due to the existence of monoclinic M2 phase (orthorhombic-like) at this thickness. The in-plane PFM
along [001]_pc direction and out-of-plane PFM images did not change as compared to the film with thickness of 10 nm. Therefore, the polarization vector for monoclinic M2 phase (orthorhombic-like) is oriented downward along the film surface normal direction, with almost no in-plane projections, as shown in Figure 7. For BFO film with thickness of 190 nm, most of the area shows no polarization signal (brown color) in in-plane PFM along [-110]_pc direction, Figure 6(j). This indicates that the fraction of monoclinic M1 phase (tetragonal-like) decreases while monoclinic M2 phase (orthorhombic-like) increases as the film thickness increases, agreeing well with RSM results. The polarization direction for monoclinic M3 phase (rhombohedral-like) is along body diagonal direction of pseudocubic lattice, with in-plane orientation along [00–1]_pc direction, as shown by the circle in Figures 6(k) and 7. In summary, the polarization vector, tilted toward the pseudocubic c_pc direction in monoclinic M1 phase (tetragonal-like) for thin films, rotates within the vertical plane towards the surface normal direction in monoclinic M2 phase (orthorhombic-like) and towards body diagonal direction for monoclinic M3 phase (rhombohedral-like) for thick films. Rotation of ferroelectric polarization direction facilitated by the coexistence of the multiple phases can potentially lead to large electromechanical response.

Based on the x-ray diffraction, TEM, and PFM data, a schematic structure model for BFO monoclinic M1, M2, and M3 phases is drawn in Figure 7. It is obvious that the β angle of the NEW lattice (Table I) changes dramatically from ~77° of monoclinic M1 phase (tetragonal-like) to ~89° of monoclinic M2 phase (orthorhombic-like) and ~90° of monoclinic M3 phase (rhombohedral-like), which is the most significant difference between the different phases of BFO.

![Figure 5. TEM images of BFO (110) thin films with thickness of 10 nm (a), 60 nm (b), and 190 nm (c).](image1)

![Figure 6. PFM images of BFO films with thickness of 10 nm (a)–(d), 60 nm (e)–(f), and 190 nm (g)–(l).](image2)
identified in this work. The strain energy change can be estimated by strain and stress matrix.23,24 Most of previous theoretical studies, however, assumed an elastically isotropic nature of the films, which does not consider the effect of crystal symmetry on elasticity.25–28 Here, we employ the stiffness tensor $C$ with monoclinic symmetry to calculate the stress from strain.29 As an estimation here, we ignore the effect of lattice parameter change on the tensor $C$ in our calculations for these three monoclinic phases. The three orthogonal axes for the strain tensor are defined as $x$ along $[−110]_{pc}$ direction, $y$ along $[001]_{pc}$ direction and $z$ along film surface normal direction $[110]_{pc}$. Therefore, the lattice parameters in NEW lattice are used to calculate strain, as shown in Table I. As the film surface is stress free, the out of plane components in stress matrix, $σ_{33}$, $σ_{23}$ and $σ_{32}$ should be zero.30 The strain components $ε_{12}$ and $ε_{23}$ are also zero, due to the fact that $α = γ = 90°$. Thus, we have

\[
\begin{bmatrix}
σ_{11} \\
σ_{22} \\
σ_{12}
\end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} \\
C_{12} & C_{22} & C_{23} \\
C_{13} & C_{23} & C_{33}
\end{bmatrix} \begin{bmatrix} C_{00} & 0 & 0 \\
0 & C_{00} & 0 \\
0 & 0 & C_{00}
\end{bmatrix} \begin{bmatrix} ε_{11} \\
ε_{22} \\
ε_{12}
\end{bmatrix}.
\]

(1)

TABLE I. Lattice parameters of BFO phases in NEW lattice, $x$ and $y$ angles are $90°$. Strain $ε_{11}$ and $ε_{13}$ are calculated by $ε_{11} = \frac{a_{pc}}{a_{bulk}} = \frac{a_{pc}}{a_{pc}}$, $ε_{13} = \frac{b_{pc}}{b_{pc}} = \tan(90° − β)$ using the lattice parameters in NEW lattice. The bulk BFO lattice parameter in this NEW lattice setting is $a = c = 2.800 Å$, $b = 3.960 Å$.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Phases</th>
<th>$a(Å)$</th>
<th>$b(Å)$</th>
<th>$c(Å)$</th>
<th>$β$ (deg)</th>
<th>$ε_{11}$</th>
<th>$ε_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$M_1$</td>
<td>3.003</td>
<td>3.790</td>
<td>2.985</td>
<td>77.0</td>
<td>0.07</td>
<td>0.23</td>
</tr>
<tr>
<td>60</td>
<td>$M_1$</td>
<td>2.943</td>
<td>3.790</td>
<td>2.936</td>
<td>77.3</td>
<td>0.05</td>
<td>0.22</td>
</tr>
<tr>
<td>190</td>
<td>$M_1$</td>
<td>2.888</td>
<td>3.790</td>
<td>2.877</td>
<td>89.2</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>$M_2$</td>
<td>2.966</td>
<td>3.790</td>
<td>2.952</td>
<td>77.0</td>
<td>0.06</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>$M_3$</td>
<td>2.853</td>
<td>3.790</td>
<td>2.880</td>
<td>89.1</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>$M_5$</td>
<td>2.794</td>
<td>3.790</td>
<td>2.812</td>
<td>90.0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

It can be further simplified as $C_{11} ≫ C_{12} ≈ C_{13} ≈ C_{15}$, $C_{22} ≫ C_{12} ≈ C_{23} ≈ C_{25}$, $ε_{13} ≫ ε_{11}$, $ε_{22}$, $ε_{33}$.31–33 Therefore, the stress components

\[
σ_{11} ≈ C_{11} · ε_{11} + C_{15} · ε_{13},
\]

(2)

\[
σ_{22} ≈ C_{22} · ε_{22} + C_{25} · ε_{13},
\]

(3)

\[
σ_{12} = 0.
\]

(4)

The elastic energy can be calculated as

\[
e = \frac{1}{2} [ε_{11}^2 + (C_{15} · ε_{11} + C_{15} · ε_{13}) · ε_{13} + ε_{22}^2].
\]

(5)

As $ε_{22}$ does not change for all phases, the terms that reduce elastic energy as film thickness increases are normal strain $ε_{11}$ and shear strain $ε_{13}$, with the latter term playing a significant role, as shown in Table I. Note that elastic strain is a $3 × 3$ symmetric tensor with six independent components.34 Most of previous studies, however, focused only on varying the biaxial strain in (001)-oriented films, where two in-plane normal strains $ε_{11} = ε_{22} = ε_{m}$ are tuned simultaneously, while out-of-plane normal strain $ε_{33}$ and shear strains $ε_{ij}$ are free.35,36 Tuning biaxial strain alone has already shown rich physics in oxide thin films, such as the complex temperature- and thickness-dependent phase diagram observed in highly strained BFO (001) films.13 Considering the six dimensional space of elastic strain, there is plenty of room to explore novel ways of elastic strain engineering by changing one component at a time or a combination of several components at the same time. Tuning shear strains $ε_{ij}$ or in-plane normal strain $ε_{ij}$ uniaxially would lead to unique promising possibilities, with fundamentally different mechanisms from biaxial strain case, to engineer physical and chemical properties of thin films.

It should be noted that previous theoretical calculation shows that inducing structural softness in regular multiferroics is able to obtain very large magnetoelectric effects.37,38 The magnetoelectric coefficient comprises three parts,
IV. CONCLUSION

In summary, BFO (110) epitaxial thin films on LAO substrates with varied thickness from 10 to 190 nm were investigated. High resolution synchrotron x-ray diffraction shows a phase transition with the increased thickness, from a single monoclinic $M_1$ phase (tetragonal-like) to a coexistence of two phases, monoclinic $M_1$ (tetragonal-like) and another monoclinic $M_2$ (orthorhombic-like) phase, and finally to mixture of three phases, monoclinic $M_1$ (tetragonal-like), monoclinic $M_2$ (orthorhombic-like), and monoclinic $M_3$ phase (rhombohedral-like). Cross-sectional high resolution transmission electron microscopy further reveals the evolution model of the domain patterns as film thickness increases. The $\beta$ angle (in the NEW lattice) changes dramatically from $\sim 77^\circ$ of monoclinic $M_1$ phase (tetragonal-like) to $\sim 89^\circ$ of the monoclinic $M_2$ phase (orthorhombic-like) and $\sim 90^\circ$ of monoclinic $M_3$ phase (rhombohedral-like). The shear strain $\epsilon_{13}$, directly related to this $\beta$ angle, is found to be a significant driving factor to reduce strain energy according to our theoretical calculations based on the measured lattice parameters. Ferroelectric polarization direction rotates among the different phases, as shown by piezoelectric force microscopy. The nanoscale mixed phases, large structure distortions, and polarization rotations among the multiple phases indicate that (110)-oriented films provide a promising new way to control multifunctionalities of BFO and an alternative direction to investigate the rich physics of perovskite system.

ACKNOWLEDGMENTS

This work was supported with facilities and a research Project No. IMRE/13-2P1107 at IMRE.