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Large tensile-strain-induced monoclinic M_B phase in BiFeO₃ epitaxial thin films on a PrScO₃ substrate

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Crystal and domain structures, and ferroelectric properties of tensile-strained BiFeO₃ epitaxial films grown on orthorhombic (110)_o PrScO₃ substrates were investigated. All films possess a M_B -type monoclinic structure with 109° stripe domains oriented along the $[\bar{1}10]_o$ direction. For films thicknesses less than ~40 nm, the presence of well-ordered domains is proved by the detection of satellite peaks in synchrotron x-ray diffraction studies. For thicker films, only the Bragg reflections from tilted domains were detected. This is attributed to the broader domain size distribution in thicker films. Using planar electrodes, the in-plane polarization of the M_B phase is determined to be ~85 $\mu\text{C}/\text{cm}^2$, which is much larger than that of compressive-strained BiFeO₃ films. Our results further reveal that the substrate monoclinic distortion plays an important role in determining the stripe domain formation of the rhombohedral ferroic epitaxial thin films, which sheds light on the problem of understanding elastic domain structure evolution in many other functional oxide thin films as well.

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I. INTRODUCTION

Epitaxial strain is recognized as an effective parameter to modify the structure and tune many physical properties of functional oxide thin films.¹ Among the functional oxides, BiFeO₃ (BFO) provides good opportunities for tunable functionalities through its rich strain-temperature related phase diagram because of the inherent coupling among elastic, electric, and magnetic order parameters.² For this reason, the effect of strain in BFO epitaxial thin films has received considerable attention, leading to several interesting theoretical predictions and experimental verifications in strained BFO films.^{3–9} At room temperature, bulk BFO possesses a rhombohedrally distorted perovskite structure with space group $R3c$ having pseudocubic lattice parameters, $a = 3.965 \text{ \AA}$ and $\alpha = 89.4^\circ$.¹⁰ (Pseudocubic index is used throughout this paper unless otherwise specified.) When BFO film is epitaxially grown on low-mismatch single-crystal substrate with equal in-plane lattice parameters, its symmetry is lowered to monoclinic due to the in-plane biaxial strain.^{11,12} There are three different types of monoclinic ferroelectric phases, namely, M_A , M_B , and M_C , following the notation of Vanderbilt and Cohen.¹³ Among them, the M_A and M_B phases belong to the space group Cm (or Cc), and the M_C phase belongs to Pm (or Pc). The differences between the M_A and M_B phases lie in the magnitudes of their monoclinic lattice parameters and consequently their polarization components corresponding to the pseudocubic unit cell: For the M_A , $a_m/c_m < \sqrt{2}$, and $P_x = P_y < P_z$, whereas for the M_B , $a_m/c_m > \sqrt{2}$, and $P_x = P_y > P_z$. (Subscript m denotes monoclinic indices.) The orientation of the polarization vector is, respectively, along $[uuv]$ ($u < v$), $[uuv]$ ($u > v$), and $[u0v]$ in the monoclinic M_A , M_B , and M_C phases. As shown in Fig. 1, these low-symmetry monoclinic phases could act as structural bridges linking the tetragonal (T), rhombohedral (R), and orthorhombic (O) phases, and

the monoclinic symmetry allows the polarization vector to be unconstrained within a certain symmetric plane.¹⁴ Therefore, the polarization in the monoclinic phase could continuously rotate in the symmetric plane under an external stimulus, such as electric field,¹⁵ pressure,¹⁶ or epitaxial strain.^{4,17} Such symmetry-allowed polarization rotation has been proposed to be responsible for the high piezoelectric response of ferroelectric monoclinic phases.¹⁸ Recent experiments have demonstrated a phase transition sequence of $R \rightarrow M_A \rightarrow M_C \rightarrow T$ with increasing compressive strain in (001)-oriented BFO epitaxial thin film,^{7,19} and the compressive-strain-stabilized, highly distorted tetragonal-like M_C phase could coexist with rhombohedral-like M_A phase, forming a morphotropic phase boundary with the potential of enhanced ferroelectric and piezoelectric responses.⁵

In comparison to the extensive reports on the effect of compressive strain in BFO epitaxial films, the tensile-strain effect is less investigated. One reason is that most commercially available perovskite single-crystal substrates have in-plane lattice parameters smaller than that of bulk BFO. Recent phenomenological calculations predicted that a tensile strain larger than ~1.5% could induce an orthorhombic O phase whose polarization vector lies along the in-plane $[110]$ direction.^{5,20–22} In contrast, more recent first-principles calculations reported that the orthorhombic phase transition only occurs at a tensile strain larger than 5%.^{23,24} However, the rhombohedral R phase might not transform directly to the orthorhombic O phase as there is a bridging monoclinic M_B phase between R and O . Experimental verification of the existence of the M_B phase and tensile-strain-induced phase transition/polarization rotation could now be done using the new, rare-earth scandate PrScO₃ (PSO) single-crystal substrate which has an orthorhombic structure with lattice constants $a_o = 5.780 \text{ \AA}$, $b_o = 5.608 \text{ \AA}$, and $c_o = 8.025 \text{ \AA}$.²⁵ (Subscript o denotes orthorhombic indices) The orthorhombic unit cell

FIG. 1. (Color online) Sketch of the relationship between T , O , R , and three M phases. T , R , O , and M represent tetragonal, rhombohedral, orthorhombic, and monoclinic phases, respectively. Arrows represent the directions of the spontaneous polarization P .

can be related to a tilted pseudocubic (monoclinic) unit cell through the following relationships:

$$a = \frac{c_o}{2} = 4.013 \text{ \AA}, \quad b = c = \frac{\sqrt{a_o^2 + b_o^2}}{2} = 4.027 \text{ \AA},$$

$$\alpha = 2 \arctan \frac{b_o}{a_o} = 88.3^\circ, \quad \beta = \gamma = 90^\circ.$$

It is important to note that the $(110)_o$ -oriented PSO substrate has the largest in-plane pseudocubic lattice parameters among all commercially available perovskite single-crystal substrates. PSO could impose tensile strains of 1.2% and 1.6% along the $[001]_o$ and $[\bar{1}10]_o$ directions respectively, in BFO films. Therefore, PSO was chosen as the substrate for investigating the effect of tensile strain in BFO films in this work.

Here, we report a detailed structure characterization of the tensile-strained BFO films with various thicknesses grown on PSO single-crystal substrates, and determine the role of substrate monoclinic distortion on the domain formation in the tensile-strained BFO films. We also demonstrate that the tensile strain induces a rotation of the spontaneous polarization toward in-plane direction by directly measuring the in-plane polarization of the films.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

BFO films with thicknesses ranging from 8 to 110 nm were deposited by pulsed laser deposition (PLD) on $(110)_o$ -oriented PSO substrates. The deposition temperature and the oxygen pressure were 700 °C and 100 mTorr, respectively.^{7,26} High-resolution x-ray diffraction (HRXRD) measurements were performed at the Singapore Synchrotron Light Source (SSLS). The diffraction data were plotted in reciprocal lattice units (r.l.u.) of the PSO substrate defined by the monoclinic unit cell (1 r.l.u. = $2\pi/4.013 \text{ \AA}^{-1}$ for H direction, 1 r.l.u. = $2\pi/4.027 \text{ \AA}^{-1}$ for K and L directions). H , K , and L are reciprocal space coordinates. The thickness of the BFO film was calibrated by x-ray reflectivity (XRR).²⁷ The surface morphology and piezoelectric force microscopy (PFM) investigations were carried out on an Asylum Research MFP-3D atomic force microscope (AFM). In-plane ferroelectric hysteresis loops were measured at a frequency of 1 kHz using a Precision LC ferroelectric tester (Radiant Technologies) on planar electrode

FIG. 2. (Color online) (a) L scan along $(00l)$ for a 20-nm BFO film grown on PSO. (b) A typical AFM topographic image of the film. (c) Out-of-plane, and (d) in-plane PFM images of the BFO film.

devices, where Pt electrodes were patterned on top of the BFO films.^{17,27} Transmission electron microscopy (TEM) was done in a JEOL 2100F microscope at 200 kV.

III. RESULTS AND DISCUSSION

Figure 2(a) displays a typical L scan (specular $\theta - 2\theta$ scan) of a 20-nm-thick BFO film. Only the $00l$ peaks of the PSO substrate and the BFO film are detected, indicating phase-pure and epitaxial growth. The thickness fringes apparent near the BFO diffraction peaks indicate the high quality of the films. The out-of-plane c lattice parameter calculated from the $00l$ peaks is $\sim 3.89 \text{ \AA}$, which is smaller than the bulk value of BFO due to the Poisson's effect arising from the in-plane tensile strain. The c lattice parameter determined from the $00l$ Bragg reflections for all film thicknesses did not vary signifying that the tensile strain is retained even in the thicker films. Figure 2(b) is a typical AFM topographic image of a 50-nm film showing a smooth film surface. Both out-of-plane [Fig. 2(c)] and in-plane PFM [Fig. 2(d)] images, taken with the cantilever along $[110]$, show a striplike contrast over large areas. Such stripe domain patterns with domain walls along the $[\bar{1}10]_o$ direction, and the corrugated film surface, are typical features of 109° periodic domain configuration in rhombohedral BFO films (note that we still use notation of 109° domains in bulk BFO although the real angle between polarizations of neighboring domains in epitaxial films is strain dependent).^{28–32}

It is known that with PFM technique it is hard to provide sufficient resolution to detect domain structure in ultrathin ferroelectric films because of the weak piezoelectric response and fine domain feature of the ultrathin films. On the other hand, synchrotron x-ray scattering is a powerful technique to probe the crystal and domain structures of ferroic ultrathin films.^{33–36} The different cation shift within each domain gives

FIG. 3. (Color online) KL reciprocal space mappings around (a) (002) and (b) (0 $\bar{1}$ 3); and HL reciprocal space mappings around (c) (002) and (d) (1 $\bar{1}$ 03) of a 13-nm-thick BFO film.

rise to different unit cell structure factors. If the domains are well ordered, the difference in the structure factors between adjacent domains leads to satellite peaks at specific reciprocal lattice vectors which have a component parallel to the relative polar shift direction.^{33–39} Therefore, analysis of the distribution and orientation of the satellite peaks by HRXRD could provide additional information regarding the domain wall orientation and polar symmetry in ferroelectric thin films.^{33,34} We embark on such an exercise here.

Figure 3 shows the specular and off-specular reciprocal space mappings (RSMs) for a 13-nm film obtained by synchrotron HRXRD. As evident in Figs. 3(a) and 3(b), only two Bragg spots with identical K values from the substrate and the film are detected in the (OKL) zone when the incident x-ray beam is along the $[\bar{1}10]_o$ direction, indicating that there is no tilt between the $(00l)$ planes of the film and the substrate along the $[\bar{1}10]_o$ direction and the film is coherently strained. When the incident x ray is aligned parallel to the $(001)_o$ direction, satellite peaks appear with equal spacing in reciprocal space in both (002) and ($\bar{1}$ 03) mappings as is clear in Figs. 3(c) and 3(d). This implies that the satellite peaks are not from Bragg reflections of tilted domains, but are from periodic domain modulation. The presence of satellite peaks in the $(00L)$ and $(OK0)$ (see Supplemental Material²⁷) zones indicates that spontaneous polarization in the tensile-strained

FIG. 5. (Color online) KL reciprocal space mappings around (a) (002) and (b) (0 $\bar{1}$ 3); and HL reciprocal space mappings around (c) (002) and (d) (1 $\bar{1}$ 03) of a 93-nm-thick BFO film.

film has both out-of-plane as well as in-plane components. This eliminates the possibility of the structure belonging to the orthorhombic aa phase with purely in-plane polarization.^{33,34} The possible domain structure, that is 109° stripe domains with walls along the $[\bar{1}10]_o$ direction, is illustrated in Fig. 4(a). Furthermore, it is found that the BFO (0 $\bar{1}$ 3) reflection has a larger L value than the BFO (003) and (013) counterparts (diffraction data not shown here). Then, the α angle of the BFO pseudocubic unit cell must deviate from 90° , and the pseudocubic unit cell is tilted along the $[\bar{1}10]_o$ direction by an angle of $\delta = 90 - \alpha_{\text{BFO}} = \arctan \frac{L_{0\bar{1}3} - L_{013}}{2} \sim 1.6^\circ$. That is, the α angle of the BFO unit cell follows the monoclinic distortion of the substrate, as shown in Fig. 4(b). Previous phenomenological modeling showed that all eight polarization variants in rhombohedral BFO remain degenerate even under a large substrate-induced in-plane anisotropic strain.⁴⁰ Therefore, we suggest that the domain degeneracy is probably broken by the monoclinic distortion propagated from the substrate, rather than by the in-plane anisotropic strain, leading to two-variant stripe domains with net shear direction along the substrate monoclinic distortion direction.

Figure 5 shows RSMs for a 93-nm-thick BFO film. The diffraction data of the film show no peak splitting in the (OKL) zone but splitting occurs in the (HOL) zone, a feature similar to that reported in BFO films with 109° domains grown on

FIG. 4. (Color online) (a) (Left) Schematic of 109° -like periodic stripe domains, and (right) the $(00l)$ associated peak positions of the film (black circles) and the substrate (red circle) in reciprocal space. (b) Side view along $[001]_o$ of the twined domain.

FIG. 6. (Color online) H scans around BFO (00 l) for (a) 13-, (b) 36-, and (c) 93-nm films. (Dashed lines are guides to the eyes.)

other rare-earth scandate substrates with relatively smaller lattice parameters.^{29,30,32} Peak splitting occurring only in the ($H0L$) zone can be attributed to the generation of two Bragg diffraction peaks from two tilted structural variants, where the (00 l) plane is tilted by an angle of $\sim \pm 0.4^\circ$ in [001]_o with respect to the substrate surface. Combining all diffraction information one could show that a monoclinic phase of BFO with derived lattice parameters of $a_m = 5.741(7)$ Å, $b_m = 5.634(7)$ Å, $c_m = 3.884(3)$ Å, $\beta_m = 89.29(7)^\circ$, could explain all the observed structural information (subscript m denotes monoclinic indices).²⁷ The fact $c_m < b_m/\sqrt{2} < a_m/\sqrt{2}$ indicates that the monoclinic phase is a M_B -type structure. The polarization in the M_B phase lies within the (1 $\bar{1}$ 0) plane and tilts away from the [111] direction, towards the in-plane [110] direction.⁷ To attain the theoretically predicted, *orthorhombic aa* phase, further tilt of the polarization vector down towards the in-plane direction is necessary. Therefore, a larger tensile strain is required to achieve such tilting of the polarization vector and stabilize the orthorhombic phase.^{23,24}

In-plane H scans (rocking curves) around the 00 l BFO reflections were done to understand the origin of the diffraction intensity distribution and structural evolution with film thickness. Figure 6 displays the H -scan curves for different diffraction orders of films. As clear in Figure 6(a), the 13-nm-thick film exhibits satellite peaks with equal spacing up to the second order in all reflections, indicating that the domains are well ordered with a very narrow size distribution. It is important to note that the central zero-order peak with

$H = 0$ originates from the modulation structure, i.e., 0th order of the satellite peak.³⁵ The intensity of the Bragg peak is hidden by the satellite peaks. At intermediate film thickness of ~ 35 nm, satellite peaks and Bragg peaks are simultaneously observed as evident in Fig. 6(b). Only the first-order satellite peaks are visible in this figure, indicating that the domains are less ordered and thus have a larger size distribution than those in the 13-nm-thick film. The spacing ΔH between the satellite peaks yields the domain modulation periodicity D in the real space. And it is found that D increases with increasing film thickness for films thicker than ~ 10 nm; for instance, $D = 0.4013 \text{ nm}/\Delta H \approx 20$ and ≈ 45 nm for the 13- and 36-nm BFO film, respectively. With further increasing film thickness, as shown in Fig. 5(c), for a 93-nm-thick film, the spacing between the two tilted peaks increases with the diffraction order L , suggesting that two distinct Bragg diffraction peaks originate from the tilted domains. The absence of clear satellite peaks in the thick films indicates that the domain size distribution in these films is wide and scattered.

The domain structures of the films were further examined using TEM. Figure 7(a) is a typical plan-view TEM image of an 8-nm-thick film. A stripelike domain pattern with walls along the $[\bar{1}10]_o$ direction, clear in the TEM image of the 8-nm film, was also observed in thicker films by PFM. Figure 7(b) shows cross-sectional dark-field TEM images of a 20-nm-thick film. Domains with alternating dark and bright contrasts separated by vertical (001)_o domain walls are observed proving the presence of 109° domain pattern in the film. The domain widths

FIG. 7. (Color online) (a) Typical plan-view bright-field TEM image of an 8-nm-thick BFO film. (b) Cross-sectional dark-field TEM images of a 20-nm-thick film. (c) SAED pattern taken from the interface between the BFO film and the PSO substrate. (d) SAED pattern taken from the top area of the BFO film; the splitting on high-order reflection spots is indicated by arrows.

FIG. 8. (Color online) Field-dependent variation of in-plane P - E loops of 50-nm BFO films grown on PSO and SrTiO₃ substrate when the electric field is applied along the [010] direction.

ranged from 6 to 24 nm and the average size of the domains is between 11 and 14 nm, which is close to half of the modulation periodicity determined from the HRXRD data. Figures 7(c) and 7(d) show two typical selected-area electron diffraction (SAED) patterns taken from the interface area and the top area of the film viewed along the $[\bar{1}10]_o$ or $[010]_c$ zone axis. From the pattern, the orientation relationship of the film and the substrate can be determined to be $(001)_c$ BFO// $(110)_o$ PSO and $[010]_c$ BFO// $[\bar{1}10]_o$ PSO. The diffraction pattern in Fig. 7(d) shows the splitting on high-order reflection spots, indicated by arrows. Such splitting is consistent with the existence of two ferroelastic variants (r_1 and r_4) in the films revealed by PFM and XRD studies.

We have studied in-plane domain switching and also directly measured in-plane polarization hysteresis loops of compressively strained BFO films using planar electrode devices and remnant hysteresis measurements.^{17,41} Here, in-plane polarization of the tensile-strained films is determined using the same method. Figure 8 shows in-plane P - E loops of 50-nm film grown on PSO. The loops are well saturated and rectangular in shape. It is clear that the in-plane polarization value and coercive field of the M_B phase obtained in the film on PSO are much larger than those of the compressive-strained film on SrTiO₃. The remnant polarization ($P_{E//[010]}$) of the M_B phase obtained in the film on PSO is $\sim 60 \mu\text{C}/\text{cm}^2$ for E lying along [010], which is in good agreement with the polarization value calculated by first-principle calculations for the film under the same tensile strain.²⁴ Considering that

the spontaneous polarization in the monoclinic M_B phase is constrained within the $(1\bar{1}0)$ plane, therefore, the in-plane polarization in each individual domain is along $\langle 110 \rangle$ and the net in-plane polarization of stripe domains is the sum of their resolved components in $\langle 100 \rangle$. Thus, the in-plane polarization (P_{in}) of each domain in the M_B phase is then $P_{in} = \sqrt{2}P_{E//[010]} \sim 85 \mu\text{C}/\text{cm}^2$, which is much larger than that in compressive-strained films.¹⁷ Such a large in-plane polarization in the tensile-strained film is probably due to the fact that the tensile strain induced a rotation of spontaneous polarization toward the in-plane $[110]$ direction, and thus has a larger in-plane projection.

IV. CONCLUSION

In summary, we have determined that tensile-strained BFO films grown on $(110)_o$ PrScO₃ single-crystal substrates have the unit cell symmetry of the monoclinic M_B phase and consist of stripe domains separated by 109° domain walls. Films with thickness less than 40 nm contain well-ordered nanodomains which give distinct satellite peaks in synchrotron HRXRD. Satellite peaks are not clearly observed in thicker films because the domain sizes are larger and their size distributions are broader. We also suggest that the substrate monoclinic angle plays an important role in determining the stripe domain formation of rhombohedral BFO thin films. Furthermore, by directly measuring the in-plane polarization of the M_B phase, we found that the large tensile strain induces the rotation of the spontaneous polarization toward the in-plane direction and gives rise to a large in-plane polarization component of $\sim 85 \mu\text{C}/\text{cm}^2$.

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