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Suppression of mixed-phase areas in highly elongated BiFeO₃ thin films on NdAlO₃ substrates

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Mixed-phase areas are produced in highly elongated BiFeO₃ (BFO) thin films as a consequence of strain relaxation. A (001) neodymium aluminate (NdAlO₃; NAO) substrate ($a \sim 3.747$ Å) prominently suppresses the strain relaxation effect and prevents the formation of mixed-phase regions. This creates a pathway to the thick, quasipure, highly elongated phases required for magnetoelectric applications. We characterize the crystal structure, the interface between film and substrate, the surface morphology, and the ferroelectric domain structure of BFO films on NAO substrates and compare them with those of films on typical lanthanum aluminate substrates. The underlying mechanisms are discussed based on the intriguing nature of phase competition in bismuth ferrite phases using first principles density functional calculations for the misfit strain-dependent total energy.

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I. INTRODUCTION

Multiferroics, which involve the coexistence of ferroelectricity and magnetism, have been extensively studied due to fundamental interest in their multiple order parameters and potential applications in magnetoelectric devices.¹⁻⁴ In particular, bismuth ferrite (BiFeO₃; BFO) has received a great deal of attention because it is both ferroelectric and magnetic at room temperature with a large electric polarization ($P_r \sim 90 \mu\text{C cm}^{-2}$) along the $\langle 111 \rangle$ direction.⁵⁻⁹ Bulk BFO is a rhombohedrally distorted perovskite with a space group of $R3c$ and a pseudocubic lattice parameter of $a \sim 3.96$ Å.¹⁰ The high-quality epitaxial growth of the normal BFO phase (R-BFO) has been extensively explored using several single crystal substrates with relatively well-matched lattice parameters, such as SrTiO₃ ($a \sim 3.905$ Å) and DyScO₃ ($a \sim 3.946$ Å).¹¹⁻¹⁴

It has recently been discovered that a highly elongated phase of bismuth ferrite can be stabilized when BFO films are grown on (001) lanthanum aluminate (LaAlO₃; LAO) ($a \sim 3.789$ Å) or (110)_o yttrium aluminate (YAlO₃; YAO) ($a \sim 3.69$ Å) due to misfit strain.^{15,16} Although careful structural analysis indicates that the crystal symmetry is not tetragonal, but rather monoclinic with a polarization on a monoclinic c - a plane, the unit cell has a high tetragonality ($c/a \sim 1.26$), such that this highly elongated phase is often described as “tetragonal-like” BiFeO₃ (T-BFO). The synthesis and properties for the phase have been extensively studied.¹⁷⁻²⁵ Clearly, a greater than 10% elongation along the c -axis direction compared with R-BFO would induce significant changes in most physical properties. The magnetic transition temperature (T_N) is suppressed to near room temperature¹⁷⁻¹⁹ and ferroelectric polarization reorients concomitantly at the T_N , accompanied by a monoclinic to monoclinic structural transition.^{17,18} The T-BFO phase has been theoretically predicted to show giant ferroelectric polarization of around $150 \mu\text{C/cm}^2$, and its ferroelectric properties have been explored based on mixed-phase

samples.^{26,27} However, the polarization value of the pure T-BFO phase sample has not yet been confirmed experimentally. Additional systematic investigation of these promising new multiferroics is required for ferroelectric and magnetoelectric applications. In this regard, thick, pure T-BFO films are helpful in measuring various physical properties that require a large thickness or a large sample volume. Unfortunately, if the film thickness exceeds ~ 40 nm, mixed-phase areas consisting of several competing BFO phases occur, probably due to strain relaxation.¹⁵ Although the morphotropic phase boundary in the mixed-phase area is an interesting issue, the appearance of these mixed-phase areas prevents the elucidation of the newly discovered T-BFO phase. Our work thus focuses on obtaining a relatively thick, pure T-BFO phase.

II. EXPERIMENTAL METHODS

BFO thin films were grown on (001) NAO and (001) LAO single crystal substrates using pulsed laser deposition with a KrF excimer laser ($\lambda = 248$ nm). The laser fluence was $\sim 1.2 \text{ J cm}^{-2}$ and the repetition rate was 10 Hz. A BFO target with 10% bismuth excess was used to compensate the bismuth volatility. During growth, the substrates were maintained at a temperature of 650 °C with an oxygen pressure of 100 mTorr. Once growth had ceased, oxygen gas with a pressure of 500 Torr was added and the samples were cooled to room temperature at a rate of 10 °C/min.

The crystal structures of the thin films were analyzed using an x-ray diffractometer (D/MAX-2500, Rigaku) with a 18-kW source and a Cu K α line ($\lambda \sim 1.5406$ Å). The film thicknesses were obtained by analyzing the Kiessig fringes around a (001) diffraction peak. Optical reflectance with a light ($\lambda \sim 632.8$ nm) was also used as a complement to determine the film thickness (ST4000, K-MAC). Reciprocal space maps (RSMs) for the BFO film (56.2 nm in thickness) on NAO

were carried out at beamline 3A at the Pohang Light Source, Pohang Accelerator Laboratory. Monochromatic light with a wavelength of 1.126 Å was used for the (002) reflection. For the (103) RSM, we used a wavelength of 1.425 Å so that the (103) film peaks were located within a measurable range. A similar structural analysis was carried out independently by Singapore Synchrotron Light Source, and similar results were obtained.

For the transmission electron microscopy (TEM), cross-sectional specimens of a 60-nm-thick BFO film were prepared using the standard procedure of cutting, gluing, mechanical polishing, and ion milling. The ion milling process was performed on a Precision Ion Polishing System (PIPS, model 691, Gatan) with an incident ion angle of 5° and an accelerating voltage of 3 kV using liquid N₂ to cool the stage. The TEM investigations were carried out on a JEOL2100F (FEG) electron microscope operated at 200 kV. The selective area electron diffraction (SAED) pattern was indexed based on the pseudocubic unit cell.

The surface morphology and ferroelectric domain structure were measured using a Digital Instruments Nanoscope-V Multimode scanning probe microscope with commercially available Ti/Pt coated Si tips (MikroMasch). The tip was oriented and swept along a $\langle 100 \rangle$ crystal axis to sensitively discriminate four variant $\langle 110 \rangle$ in-plane polarizations. All of the data were measured under ambient conditions at room temperature.

We performed the density-functional calculations using the Vienna *ab initio* simulation package (VASP)²⁸ with the projector augmented-wave method (PAW)²⁹ and the generalized gradient approximation (GGA)³⁰ plus the Hubbard U approach. We used the default VASP potentials (Bi_d, Fe_pv, O), a $3 \times 3 \times 3$ Monkhorst-Pack k -point mesh, and a 500 eV cutoff. The on-site Coulomb interaction (U) was 2 eV, which is known to be appropriate for BFO.³¹ The G -type antiferromagnetic order of the Fe ions was also considered

in the calculations. The initial structures were built to be pseudotetragonal. The monoclinic distortion was ignored due to negligible energy changes compared with the misfit strain effect. We relaxed the atomic positions and the c -axis lattice parameter for the strained films.

III. RESULTS

A. Crystal structure

We grew BFO films of different thicknesses on key NAO substrates and reference LAO substrates using pulsed laser deposition. We explored the crystal structure of the BFO films using x-ray diffraction. Normal x-ray θ - 2θ scans provided information on the crystal orientation in an out-of-plane direction and the corresponding lattice parameter. As Fig. 1(a) shows, the BFO films on the LAO substrate experienced a 001 T-BFO peak with Kiessig fringes. Films thicker than 45 nm showed an additional diffraction peak at $2\theta \sim 21^\circ$. It has been reported that such peaks originate from the new strain state of BFO, especially in the mixed-phase areas.^{32,33} In contrast, the BFO films on the NAO substrates did not exhibit the additional diffraction peak for all of the thicknesses. Because the pseudocubic lattice parameter of NAO is ~ 3.747 Å, which is very close to that of the LAO of ~ 3.789 Å, and the crystal structure of LAO and NAO share the same rhombohedral perovskite (space group: $R\bar{3}c$),^{34,35} the different tendencies observed in the x-ray diffraction are quite unexpected and indicate that the phase competition of BFO is highly sensitive to misfit strain.

The position of the (001) T-BFO peaks tended to move to a lower 2θ angle for the films on the LAO substrates and to a higher 2θ angle for the films on the NAO substrates with increasing thickness. This reveals valuable information regarding the strain state of T-BFO films. The T-BFO phase is a metastable phase that can be stabilized through the misfit strain. This metastable phase has a characteristic lattice

FIG. 1. (Color online) Thickness dependence of the c -axis lattice parameters of T-BFO. (a) X-ray θ - 2θ scans of the BFO films grown on NAO and LAO substrates. (b) The c -axis lattice parameters of the T-BFO phases presented as a function of the BFO film thicknesses for the films grown on NAO and LAO substrates. The c -axis lattice parameters are calculated from the positions of the (001) diffraction peaks. The error bars are estimated from the full width at half maximum of each (001) peak.

parameter that induces the lowest free energy under no external strain. Our observations indicate that the in-plane lattice parameter of a strain-free T-BFO phase should be between ~ 3.747 Å (NAO) and ~ 3.789 Å (LAO). This finding is also supported by theoretical work based on the density functional calculation, which subsequently explained. The c -axis lattice parameter extracted from the position of the peaks is summarized in Fig. 1(b). Based on the thickness dependence of the c -axis lattice parameter, we conclude that the T-BFO on NAO was compressively strained, whereas the T-BFO on LAO was tensilely strained. It is worth noting that the c -axis lattice parameters of the T-BFO on the two substrates differed by ~ 0.8 Å, which is approximately twice the difference of the in-plane lattice parameter of NAO and that of LAO.

FIG. 2. (Color online) Reciprocal space maps for the BFO film (56.2 nm in thickness) grown on NAO substrate. (a) HL scan around (002) reflections. (b) Twin structure of the NAO substrate displayed by HK scan at $L = 2$. (c) HL scan around (103) reflections. The RSMs are plotted on logarithmic scales.

To investigate the structural coherence between the film and the NAO substrate, we measured reciprocal space maps (RSMs) using a synchrotron source. The reciprocal lattice unit (r.l.u.) is defined as $2\pi/3.747$ Å $^{-1}$. The NAO substrate has structural twins that produce peak splits in a transverse direction in the RSMs. We chose the left twin peak in the (002) RSM as the criterion for sample alignment [Fig. 2(a)]. To gain more insight into the twin structure of the NAO substrate, we measured an HK-scan of the (002) peak [Fig. 2(b)]. The twin angle was determined to be $\sim 0.72(\pm 0.05)^\circ$, which was estimated from the split along the H (or K) direction of the (002) NAO peak. To obtain the structural information along the in-plane direction, we performed an HL-scan for the (103) reflection, as shown in Fig. 2(c). The (103) peak of the NAO was detected at the expected pseudocubic position. The peak of the BFO film was located on a truncation rod along the L direction with the characteristic M_c phase of T-BFO, indicating that the T-BFO film had grown quasicohently. In the RSMs, we detected some weak and broad impurity peaks between the NAO peak and the T-BFO peak. This is not attributable to the mixed-phase areas, as it does not have the highly ordered feature detected in the mixed-phase areas of BFO/LAO.^{32,33} The impurity peak detected at $L = 1.88$ is attributable to the R-BFO, as mentioned in Ref. 33. Nevertheless, we maintain that the R-BFO peak is not derived from the mixed-phase areas. The mixed-phase areas involve a morphotropic phase boundary in which several competing phases, including R-BFO and T-BFO, appear alternately on a scale a few tens of nanometers in length. The ordering structure within the mixed-phase areas produces peculiar features in the RSMs. In addition to the R-BFO peak, it is known that the T-BFO peak should have two satellite peaks along the transverse direction (H direction) and another triclinic peak at $L \sim 1.8$.³³ The detection of only the R-BFO peak without the other characteristics of mixed-phase areas indicates that while the mixed-phase areas were prominently suppressed in the BFO on NAO substrate, some R-BFO segregation occurred elsewhere. The R-BFO peak can be attributed to the epitaxial breakdown often observed in thick films, which produces phase segregation on a much larger length-scale.³⁶ The surface

FIG. 3. (Color online) Cross-sectional transmission electron microscopy at the interface between the pure T-BFO film and the NAO substrate. (a) HRTEM image. (b) SAED pattern. Yellow (red)-colored spots represent the diffraction peaks of the NAO substrate (T-BFO film).

FIG. 4. (Color online) Surface morphologies of the BFO films grown on LAO and NAO substrates. (a) Surface morphologies of BFO films grown on LAO substrates. As the film thickness increased, the mixed-phase areas indicated by dark contrast expanded. Each AFM image is supplemented by a histogram to show the height distribution. The thinnest film shows a pure T-BFO phase and a step terrace structure. The thicker films have mixed-phase areas and thus the histograms have double-peak shapes that are fitted to two Gaussian curves for quantitative analysis of the areal fraction. (b) Surface morphologies of BFO films grown on NAO substrates. None of the films with different thicknesses showed any mixed-phase areas, but rather exhibited smooth surfaces as a result of having only a quasipure T-BFO phase. Single-Gaussian fits are applied to all of the associated histograms because they have no shoulder peak. (c) A high-resolution AFM image over a $1 \mu\text{m} \times 1 \mu\text{m}$ area for a representative BFO film (42 nm in thickness) on NAO. (d) Areal fraction of the mixed-phase regions for the film grown on LAO, calculated by fitting the two-Gaussian peaks. The error bars are estimated from the standard error of each fit parameter in the two-Gaussian function. The films analyzed by a single-Gaussian fit are assigned a zero value for the fraction and no error bars are shown. (e) The mixed-phase regions of the BFO/LAO fall in and the dips become deeper in proportion to the thickness of the BFO film. The scale bars represent $1 \mu\text{m}$.

morphology did not reveal any mixed-phase areas, as subsequently discussed.

B. Cross-sectional transmission electron microscopy

The quasicoherent growth of the T-BFO film was again confirmed by high-resolution transmission electron microscopy

(HRTEM) and selective area electron diffraction (SAED) measurements (Fig. 3). The results reveal that the BFO film grew epitaxially on the NAO substrate, with orientation relations of (001) BFO// (001) NAO and [010] BFO// [010] NAO. Lattice parameters of $a = 0.375 \text{ nm}$ and $c = 0.47 \text{ nm}$ were determined from high-resolution images and SAED patterns using the

FIG. 5. (Color online) Film thickness dependence of the BFO films' ferroelectric domain structures on the NAO substrates (left) and on the LAO substrates (right). For each sample, both ferroelectric domain structures along an out-of-plane direction and an in-plane direction were measured simultaneously using piezoresponse force microscopy (PFM) scanning in the $\langle 100 \rangle$ crystalline direction. Fine stripe domain structures along the $\langle 110 \rangle$ crystal axis occurred over the T-BFO regions, except for the mixed-phase areas. None of the samples show contrast in the out-of-plane PFM image. This represents the same polarization direction along the out-of-plane direction, which is typical due to a self-poling effect induced by different top-down interfaces. The scale bars indicate $1 \mu\text{m}$. The Fourier transformed results of the in-plane PFM images are displayed nearby on logarithmic scales. The domain width can be estimated from the satellite peak position along the $\langle 110 \rangle$ direction. The size of the k spaces is $(\frac{2\pi}{5 \mu\text{m}} \times 128) \times (\frac{2\pi}{5 \mu\text{m}} \times 128)$.

NAO substrate as the calibration standard. In the SAED patterns, in addition to the fundamental Bragg reflections of the BFO and NAO, extra super-lattice spots were clearly observed. The spots lying on the (00 l) ($l = \pm 1/2, \pm 3/2, \dots$) planes may have arisen from the antiphase tilting of oxygen octahedra about the pseudocubic [111] axis.³⁷

C. Surface morphology

Using the crystal structural studies as a background, we investigated the surface morphology of the T-BFO films. As Fig. 4(a) reveals, the surface morphology of the BFO films grown on the LAO substrates had an atomically flat surface with a step terrace structure, indicating that they had grown in step flow mode. The dark contrast regions corresponding to areas located at relatively lower heights expanded with increasing film thickness, as shown in the surface morphology images of the BFO/LAO films. These regions correspond to mixed-phase areas where several competing BFO phases, including T-BFO and R-BFO, appear alternately on a scale of a few tens of nanometers in length.¹⁵ To analyze the areal fraction of the mixed-phase areas quantitatively, we plotted histograms to give a visual impression of the surface height distribution, fitted to two Gaussian curves that represent the T-BFO region and the mixed-phase areas, respectively. As the film thickness increased, the mixed-phase areas became larger and the two peaks separated, implying that the depth of the mixed-phase areas was systematically increasing. BFO films thinner than ~ 40 nm mainly consisted of the T-BFO phase, whereas the mixed-phase areas continued to grow and reached a surface coverage of more than 40% at a thickness of ~ 90 nm [Fig. 4(d)]. The depth of the mixed-phase areas increased in proportion to the film thickness, with the depth corresponding to approximately $\sim 2\%$ of the film thickness [Fig. 4(e)].

The mixed-phase areas could not be removed from the thick films on the LAO substrate. However, the BFO grown on the NAO substrate showed the prominent suppression of mixed-phase areas for the whole thickness series, which is consistent with the previous x-ray diffraction results. Figure 4(b) shows the surface morphology of the T-BFO films on NAO. The typical mixed-phase region is not observed. The surface roughness is small at ~ 2.8 Å for the 42-nm-thick film on NAO and its high-resolution surface morphology image exhibits fine step terrace structures [Fig. 4(c)].

D. Piezoresponse force microscopy

We now report the ferroelectric domain structure of the BFO thin films on the LAO and NAO substrates. We measured both the out-of-plane and in-plane components of ferroelectric polarization simultaneously with the surface morphology using piezoresponse force microscopy. Unlike the normal R-BFO, the T-BFO phase had a projected polarization onto the (001) surface that pointed in four variant $\langle 100 \rangle$ directions because the polarization existed on a c - a mirror plane.¹⁷ Assuming a typical head-to-tail stripe domain structure, we expect the stripe domain walls to align along the $\langle 110 \rangle$ direction.³⁸ Indeed, the measured images of the ferroelectric domains (Fig. 5) show the expected stripe domain structure. Systematic investigations of the thickness effect of the domain width are presented in Fig. 6.

FIG. 6. (Color online) Double logarithmic plot of stripe domain width versus film thickness. From the Fourier transformed images of the in-plane PFM results, an average domain width (half period) perpendicular to the $\langle 110 \rangle$ direction was extracted as a function of film thickness. Because the typical domain width (w) grew with increasing film thickness (t), in accordance with $w \propto t^\gamma$, a least-squares linear fit was carried out in the log-log plot. The exponent (γ) was determined to be ~ 1 for the NAO case.

The domain widths were obtained through careful Fourier transform analyses. The NAO substrate produced a linear curve in the double logarithmic plot of domain width (w) as a function of BFO film thickness (t). Because the domain width is known to follow a power law ($w \propto t^\gamma$),³⁹ we determined the scaling factor (γ) by performing a least-squares fit. The scaling factor is $\gamma \simeq 0.96 \pm 0.08$ for BFO/NAO. However, it is relatively hard to determine the average domain width for thick BFO/LAO films through Fourier transform analysis because interference between the mixed phase and domain structure prevents clear ordering peaks from forming in the k space. It is noteworthy that the domain width of T-BFO/NAO is narrower than that of T-BFO/LAO for the same film thickness. Moreover, because of the dense stripe domain structure, it is hard to determine the domain width of the ~ 20 -nm-thick film within experimental resolution, although linear extrapolation of the fitting curve predicts it to be in the order of 10 nm.

IV. DISCUSSION

We now discuss why the NAO substrate can only stabilize the quasipure T-BFO phase in terms of the misfit strain-dependent total energy. We performed first principles calculations to investigate the total energy of the T-BFO and the R-BFO. We used tetragonal unit cells because the monoclinic tilt affects the free energy by a few meV per formula unit, which is tiny compared with the effect of the misfit strain.⁴⁰ In the first principles calculation, the in-plane lattice parameters are fixed, whereas the c -axis lattice parameter and the atomic positions of the elements inside the unit cell are relaxed. The results are in good agreement with recent theoretical findings.^{15,41,42} The free energy as a function of the misfit strain is plotted in Fig. 7. The theoretical calculation for the R-BFO results in the minimum energy at an in-plane lattice parameter value of ~ 4 Å. The

FIG. 7. (Color online) Density functional calculation results for the phase competition between T-BFO and R-BFO. (a) Total energy per formula unit with respect to the ground state is presented as a function of the substrate lattice parameter. It is assumed that the films are fully strained to the substrates and that the in-plane lattice parameters of the strained films are the same as those of the substrates. The NAO substrate provides an in-plane lattice parameter of 3.747 Å on which the T-BFO is considerably more stable than R-BFO and coherent growth can be realistically achieved. (b) c/a ratios plotted as a function of the substrate lattice parameter. For the R-BFO phase with an in-plane lattice parameter of less than 3.85 Å, the local minimum is barely stabilized due to the interference of the T-BFO phase. Given such highly compressive strains, the c -axis lattice parameter is fixed under the constraint of volume conservation while the atomic positions are relaxed.

calculation is consistent with the known pseudocubic lattice parameter of bulk BFO (~ 3.96 Å). The T-BFO phase has the lowest energy at an in-plane lattice parameter value of ~ 3.76

Å. The free energy shows a nearly quadratic dependence on the misfit strain centered at the strain-free lattice parameter. The quadratic curvature predicts that the T-BFO structure has a larger elastic constant in the in-plane direction compared with the R-BFO. The relatively higher elastic constant of the T-BFO is reasonable because the T-BFO has a much shorter in-plane lattice parameter and shorter bond length along the in-plane direction, which could possibly lead to a larger in-plane stiffness. The key finding is that only a small range of the in-plane lattice parameter around ~ 3.76 Å allows the metastable T-BFO phase to stabilize. Furthermore, a value of ~ 3.8 Å for the in-plane lattice parameter results in comparable free energy between T-BFO and R-BFO, where a mixed phase can appear. This situation exactly corresponds to the behavior of the BFO films grown on the LAO substrate. With the YAO substrate, both phases of T-BFO and R-BFO were too heavily strained. Accordingly, we expect that a fully strained film would be unstable on the YAO substrate. The observation of mixed-phase areas¹⁵ may be due to a certain relaxation of the large misfit strain. Recently, a layered perovskite LaSrAlO₄ substrate ($a \sim 3.756$ Å; $c \sim 12.636$ Å) was used to grow T-BFO films, but it also produced the typical mixed-phase areas. Although it has a similar lattice parameter to NAO, the layered perovskite substrate seems not to be directly comparable with standard perovskite substrates, possibly due to initial strain relaxation at large half-unit-cell steps. T-BFO films on a layered substrate are reported to be tensilely strained, unlike the films grown on the NAO substrates in this study.⁴³

V. CONCLUSION

In summary, we grew BFO films on NAO and LAO substrates and characterized their crystal structures through x-ray diffraction, reciprocal space maps, and high-resolution transmission electron microscopy. The surface morphology and ferroelectric domain structure were explored using piezoresponse force microscopy. We found that the NAO substrate prevents the formation of mixed-phase areas, whereas the LAO substrate produces such areas. This finding provides guidance for the growth of thick quasipure T-BFO films for magnetoelectric and ferroelectric applications. The underlying physics are discussed based on phase competition, which is justified by the density functional calculation of the misfit strain-dependent total energy.

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