The Evidence of Giant Surface Flexoelectric Field in (111) Oriented BiFeO₃ Thin Film

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Supporting Information

ABSTRACT: In this work, the surface structure of a single-domain epitaxial BiFeO₃ film with (111) orientation was investigated by in situ grazing incidence X-ray diffraction and X-ray reflectivity. We found that a large strain gradient exists in the surface region (2-3 nm) of the BiFeO₃ film. The strain gradient is approximately 10^7 m^{-1} , which is 2 or 3 orders of magnitude larger than the value inside the film. Moreover, we found that a surface layer with a lower electron density compared with the underlying BiFeO₃ layer exists on the surface of BiFeO₃ film, and this layer exhibits an irreversible surface structure transition occurs at 500 K, which should be associated with the surface flexoelectric field. We considered that this large strain gradient is originated from the surface depolarization field of ferroelectrics. Our results suggest a coupling between the surface structure and the flexoelectricity and imply that the surface layer and properties would be controlled by the strain gradient in ferroelectric films.



KEYWORDS: Surface layer, ferroelectric thin films, X-ray diffraction, flexoelectrics, microstructure

1. INTRODUCTION

In ferroelectric thin films, there has been significant progress in epitaxial strain engineering to control and enhance the ferroelectric order. Strain coupling to electrical polarization enables functionalities that are crucial for a range of applications.^{1–4} Recently, strain gradients have also been highlighted due to the discovery of the coupling between strain gradients and polarization.^{5–7} This property is called "flexoelectricity", which was experimentally observed in 1968.⁸ Although flexoelectricity is more general, it was ignored for decades because the flexoelectric coefficient is quite small $(10^{-10}-10^{-11} \text{ m}^{-1})$ and elastic deformation in most solids is therefore limited.^{9,10}

However, recently this situation has begun to change. Strain gradients can be enhanced at the nanoscale level.¹¹ A strain gradient as large as 10^5-10^6 m⁻¹ can be produced in ferroelectric epitaxial thin films. Experimental studies showed that flexoelectricity can have a considerable impact on ferroelectric and piezoelectric properties, and flexoelectricity can be used to control the direction and magnitude of the spontaneous ferroelectric polarization using the electric field resulting from a strain gradient field.¹² At the same time, flexoelectricity can affect the domain configuration and imprint,¹³ the dielectric constant,^{14,15} the continuous rotation of the spontaneous polarization direction,¹⁶ the polarization

switching by a mechanical force,¹⁷ and the unusual coupling between electronic transport and the mechanical strain gradient.¹⁸

In this work, most of the large strain gradient originates from interface strain in epitaxial films due to the lattice mismatch of the epitaxial ferroelectrics with the substrate. However, the present work shows that a large strain gradient also exists in the surface region (several nanometers) of single-domain epitaxial BiFeO₃ (BFO) films. The strain gradient is approximately 10^7 m^{-1} , which is 2 or 3 orders of magnitude larger than the value inside the film. Moreover, we show that a surface layer exists on the BFO film, and an irreversible surface structure transition at 500 K is found to be associated with flexoelectricity.

2. EXPERIMENTAL SECTION

The BFO film was deposited on a single crystal $SrTiO_3$ (111) (STO) substrate with a $SrRuO_3$ (SRO) bottom electric layer by pulsed laser deposition (PLD) equipped with reflection high-energy electron diffraction (RHEED). The substrate temperature was maintained at 610 °C and the oxygen partial pressure was maintained at 10 Pa during the deposition process. The thickness of the BFO film used in this

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Figure 1. Out-plane RSM around (111) reflection (a) and asymmetric (221) reflection (b) of (111) oriented BiFeO₃ films; (c) OP-PFM and (d) IP-PFM phase image of (111) oriented BiFeO₃ film.

study is approximately 300 nm. The detailed deposition conditions have been described elsewhere.¹⁹ The microstructure was characterized at the beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) with a wavelength of 1.2387 Å. The ferroelectric domain structure was studied by a commercial scanning probe microscope (MFP-3D, Asylum Research, U.S.A.) in vector PFM mode. The Raman spectra were measured using a spectrometer (Bruker Senterra) with a 514 nm laser line as the excitation source.

3. RESULTS AND DISCUSSION

The X-ray diffraction curve of the BFO thin film is shown in Figure S1 of the Supporting Information. The (111) reflections from the films are observed in addition to the substrate and SRO peaks, indicating that the BFO film is of a single phase and well oriented. From the Bragg law, the out-of-plane lattice constant of the BFO film was obtained as 4.01 Å. The Raman spectra at room temperature (shown in Figure S2 of the Supporting Information) indicate an rhombohedral phase (Rphase) symmetry of the film. Because of the existence of the SRO buffer layer, a small lattice mismatch is achieved, and the R-phase is easier to form in this condition.

Figure 1a shows the reciprocal space mapping (RSM) around the (111) reflection of STO substrate. Figure 1a shows that the BFO RSM spot has almost the same Q_x values as those of the SRO/STO substrate, indicating that the (111) plane of the BFO film is parallel to the SRO/STO substrate and the BFO film is grown coherently on the SRO/STO substrate. To further characterize the crystal structure of the BFO film, we collect the RSM around the asymmetric (221) reflection of STO, as illustrated in Figure 1b. We found that BFO (221) and STO (221) have different values of Q_{xy} indicating that the two layers have different in-plane lattice parameters. Therefore, the strain from the substrate should be partly released. Moreover, it can be clearly observed from Figure 1 that the single peak structure of BFO was observed in the RSMs of (111) and (221), indicating that a rotated twinning structure or BFO lattice structural domains do not exist.

The single domain structure in the film is also confirmed by piezoresponse force microscopy (PFM). Figure 1c,d shows the out-of-plane PFM (OPP) and in-plane PFM (IPP) images of the (111) BFO film. Normally, the ferroelectric polarization in a rhombohedra BFO can have four orientations along the cube diagonals and can have eight polarization variants. However, as shown in Figure 1c,d, only one contrast can be observed, suggesting that the film is predominantly of the downward single domain state with an orientation perpendicular to the surface. This type of domain structure of BFO (111) also has been reported, 20,21 and the domain structure can be controlled by strain and orientation.

To further explore the detailed structure of the BFO, we perform grazing incidence X-ray diffraction (GID) experiments on the sample in in-plane $[1\overline{10}]$ and $[11\overline{2}]$ directions. The geometry of the experiment has been presented in the Figure S3 of the Support information. Using this technique, depth-



Figure 2. (a) The variation of in-plane $(1\overline{10})$ and $(11\overline{2})$ lattices with incidence angle of 0.2°. (b) In-plane RSM around $(1\overline{10})$ reflection of BiFeO₃ films at incidence angle of 0.2°.



Figure 3. Fitting result with eq 1 (a) and eq 3 (b). (c) The strain gradient along the in-plane $[11\overline{2}]$ direction. (d) The local amplification figure of panel c.

dependent structure information can be obtained because as the incident angle of the X-ray beam is less than the critical angle, the penetration depth of the X-ray becomes on the order of nanometers.^{22,23} The X-ray critical angle on the BFO film is 0.25° . The in-plane interplanar spacings, as determined from the (002) and (110) diffraction peaks at different incident angles, are plotted in Figure 2a. We found that with decreasing penetration depths, the interplanar spacings of the (111) oriented film in both the [110] and [112] directions are increased. Because the lattice constant of BFO is larger than that of SRO and STO, the internal BFO should suffer compressive stress, and the strain is gradually released from the interface to the surface, which is consistent with the above analysis of the RSM. Figure 2b shows the in-plane RSM around the $(1\overline{10})$ reflection of BFO at an incidence angle of 0.2° . The single peak structure still existed in the surface region, implying that the surface region is also in a single domain state, which is similar to the internal BFO. As shown in Figure 2a, the in-plane lattice constant in the surface region has an approximately 0.4% expansion. Given that BFO in the surface region must be coherent with the internal lattice, therefore, a strong uniaxial strain should exist in the surface region. To evaluate the strain state in the film, we estimate the strain gradient from the GID data as a function of the distance z from the film surface. According to a general model for the strain profile, ^{13,24,25} the strain u(z) in epitaxial thin films can be expressed as follows

$$u(z) = u_0 + u_1 \cdot e^{-\alpha(t-z)}$$
(1)

In this equation, u(z) means the strain normal to the surface, u_0 , u_1 , and α are constants, t is the thickness of the film, and z is the distance from the film surface. Therefore, the strain gradient can be estimated using eq 2.

$$\frac{\partial u(z)}{\partial z} = 2 \frac{\partial \overline{u(z)}}{\partial z} + z \frac{\partial^2 \overline{u(z)}}{\partial z^2}$$
(2)

where u(z) is the averaged strain obtained from the GID data. Figure 3 shows the linear—log plot of average strain profile, and we found the profile cannot be well fitted with eq 1 because the simulated curve has large differences from the original data, as shown in Figure 3a. Therefore, we assumed that the strain of the surface and the bulk were different and followed different exponential relationships, a surface item has to be added to this equation. We fitted our data with eq 3 and had a good fitting result, as shown in Figure 3b.

$$u(z) = u_0 + u_1 \cdot e^{-\alpha 1(t_1 - z)} + u_2 \cdot e^{-\alpha 2(t_2 - z)}$$
(3)

where u_0 , u_1 , u_2 , α_1 , and α_2 are constants, t_1 and t_2 are the thickness of the surface layer and bulk of the film, and z is the distance from the film surface. The strain gradient along the inplane $[11\overline{2}]$ direction is shown in Figure 3c; the strain gradient along the in-plane $[1\overline{10}]$ direction is shown in Figure S4 of the Support information, almost identical to that shown in Figure 3c.

From the fitting results, we found that the surface region exhibits a large strain gradient, approximately 4×10^7 m⁻¹, and by increasing the depth the strain gradient reduced sharply from 4×10^7 m⁻¹ (1.7 nm) to 0 m⁻¹ (3.3 nm). The strain gradient inside the film has a small value as expected due to the existence of the SRO buffer layer. As the depth increased from 3.4 to 100 nm, the strain gradient reduced from -7×10^4 to -1.8×10^2 m⁻¹. The strain gradient near the interface should have originated from the interface lattice mismatch. Because of the small lattice mismatch between BFO and SRO, BFO near the interface is almost strained with SRO/STO, and the interface strain is gradually relaxed with the increasing thickness of the BFO layer, which leads to the reduced strain gradient with the increasing depth in the range of 3.4–100 nm.

Using the above experimentally obtained values of the surface strain gradient, we could estimate the flexoelectric fields $E_{\rm s}$ using eq 4^{5,26}

$$E_{\rm s} = \frac{e}{4\pi\varepsilon_0 a} \times \frac{\partial u}{\partial z} \tag{4}$$

where *e* is the electronic charge, ε_0 is the permittivity of free space, *a* is the lattice constant, and $\frac{\partial u}{\partial z}$ is the strain gradient. Therefore, the E_s in the surface region is calculated to be 145.3 MV m⁻¹. This estimated magnitude of the flexoelectric field is comparable to that of the coercive field of BFO,²⁷ which should have considerable effects on the surface microstructure and phase transition characteristics and will be described in the following section separately.

Figure 4 shows the X-ray reflectivity (XRR) profile of the sample measured in air. To present the interference fringes



Figure 4. XRR of the (111) oriented BiFeO₃ film. Inset: the EDP.

more clearly, we also plotted the reflectivity data as $R \cdot Q_{z}^{4}$ vs Q_{z} in Figure 4, where R is the reflectivity, $Q_r = 4\pi \sin \theta / \lambda$ is the vertical wave-vector transfer. A broad bump can be observed between 0.2 and 0.25 $Å^{-1}$, indicating that a surface structure is present on top of the film with an electron density that is different from that of the underlying BFO layer. By simulating the XRR profile using the matrix formalism corrected by a Croce–Nevot factor 28,29 and the electron density profile (EDP) obtained from the fitted data shown in the inset of Figure 4, we obtained a surface layer thickness of approximately 2.3 nm with an average electron density of 1.8 e^{-/A^3} , which is slightly smaller than that beneath the BFO layer $(2.06 \text{ e}^{-}/\text{Å}^3)$. According to the simulation, two surface layers are necessary for the best fitting, and this double surface layer structure has also been described in our previous work.³⁰ The surface layer should be associated with the surface relaxation due to the large surface flexoelectric field while the top skin layer of about several angstroms should be due to the defect with lack of Bi.³¹⁻³³ However, the two layers have only slight differences in electron density. Therefore, the double-layer structure also can be considered to be one combined surface layer with a lower electron density in this paper. We believe that the giant surface flexoelectric effect may contribute to the surface layer.

The surface of ferroelectrics has been extensively studied, and the surface layer can exhibit various structures and electric properties. Watanabe et al. investigated the structure of BaTiO₃ (BTO) single crystals and found an intrinsic surface electron layer formed at the surface of the ferroelectric.³⁴ Hofer et al. studied the surface of BFO and showed a surface strip domain structure.³⁵ In our previous work, we showed that a surface relaxation layer existed in BTO and BFO surfaces.^{30,36}

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However, the origin and the precise thickness of this layer are still not very clear. In this paper, we first reveal that the giant flexoelectric field exists in the surface region, which should contribute to the formation of a surface layer approximately 2-3 nm thick.

The phase transition of the BFO film is investigated by variable temperature GID. The lattice parameters of the inplane BFO $(11\overline{2})$ obtained from the evolution of the Bragg peaks as a function of temperature are shown in Figure 5.



Figure 5. In-plane interplanar spacing in $[11\overline{2}]$ direction dependence with temperature at grazing incidence angle of 0.05° (a) and 0.4° (b). Red and blue arrows mean increase and decrease of temperature, respectively.

Curves (a) and (b), respectively, show the lattice parameters of the BFO measured at an incident angle of 0.05 (surface sensitive) and 0.4 (bulk sensitive). During the heating process from 30 to 500 °C, we observed that curve (a) is a straight line caused by the thermal expansion of BFO, while curve (b) deviates weakly from the linear evolution at approximately 250-300 °C, clearly indicating that the surface phase transition occurred. This phase transition can be defined as the "flexoelectric field-induced phase transition". Because of the existence of the large surface flexoelectric field, the surface electrostatic potential is changed and, thus, corresponds to varied surface dipoles.^{37,38} Therefore, in contrast to the bulk phase transition of BFO at approximately 900 °C (shown in Figure S5 of the Supporting Information), a surface phase transition at a lower temperature can be induced by the modified surface polarization state. Similar phenomena have also been reported in electric field induced phase transitions of ferroelectrics.^{39–42} However, because the surface layer only has a thickness of several unit cells, it is difficult to determine the phase structure after the phase transition; however, we expect it must be a high symmetry phase according to the phase diagram of the BFO bulk.

Moreover, as shown in Figure 5, at the cooling process the curve of the *d*-value becomes linear and similar to curve (b), which indicated that the structural transition of the surface layer may not be irreversible. To verify this, we compared the inplane interplanar spacing in the $[11\overline{2}]$ direction dependence on the incidence angle at room temperature before and after the variable temperature experiments. As shown in Figure 6a, the interplanar spacing of $(11\overline{2})$ at the lower incident angles is decreased whereas that at higher incident angles has almost no change, implying that a strain relaxation behavior occurs after the variable temperature process. We also calculated the strain gradient profiles before and after the variable temperature experiments, and the results are shown in Figure 6b. We found that after the annealing process, the strain gradients of both the surface and the bulk are reduced, and the surface layer that contained a large strain gradient became thinner (2.3 nm). Furthermore, we compared the XRR results before and after the variable temperature experiments (shown in Figure S6 of the Supporting Information). The XRR results show that the thickness of the surface layer decreases from 2.3 to 1.8 nm and the electron density increases to a value near to that of the underlying BFO layer, which exhibits a relaxation behavior, consistent with the strain analysis results. Combining the above results, we assume that the irreversibility of the phase transition is due to the release of the surface and interface strain at high temperatures.⁴³ Therefore, when the temperature is decreased to room temperature, the original surface phase cannot be recovered due to the change of the total strain state of the film.

Now, we discuss the origin of the giant surface flexoelectric field. In the surface of ferroelectrics, the macroscopic electrics can generate a large depolarization field when they are



Figure 6. (a) In-plane interplanar spacing in $[11\overline{2}]$ direction depend with incidence angle at room temperature before and after the variable GID experiments. (b) The strain gradient along the in-plane $[11\overline{2}]$ direction before and after the variable GID experiments. Inset: the local amplification figure of panel b.

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unshielded. This field has been considered a dominant controlling factor of the ferroelectric structure and properties.⁴⁴ The depolarization field is expected to enhance the surface or interface lattice distortion. Sepliarsky investigated the interface of PbTiO₃ (PTO) ultrathin films on STO.⁴⁵ They found that atomic displacements across the film-substrate interface are crucial for the stabilization of the ferroelectric state in films that are a few unit cells thick. Jia studied the interface of the PTO/ SRO surface and interface structure and found that the decreased polarization in the surface of PTO⁴⁶ was due to the reduced tetragonal distortion. In our case, we observed an increased in-plane lattice constant in the surface laver. According to the Poisson's ratio, the out-of-plane lattice constant will be shrunk and the decreased (111) polar axis should exhibit reduced polarization in the surface region. Furthermore, the lattice distortion can also be proven by the lower electron density surface layer with XRR. Because of the atomic displacement in the surface layer, a large surface flexoelectric field is induced to neutralize the depolarization field energy. As a result, the ferroelectric monodomain state is stabilized.

In addition, the above analysis implies that the flexoelectric field should have a comparable value to the depolarization field. In fact, the depolarization field in an individual system is hard to estimate due to the complex electron boundary conditions and domain structure.^{47,48} In the research by Kim,⁴⁹ the value of the depolarization field can be determined experimentally from an applied external field that stops the net polarization relaxation. According to our results, we found a direct method to estimate the depolarization field by measuring the surface flexoelectric field. This will be helpful for understanding and controlling the surface characterization with ferroelectric polarization.

4. CONCLUSIONS

In conclusion, the surface structure and phase transition is investigated in this work. We found that a large strain gradient exists in the surface region (2-3 nm) of the BFO film by in situ GID measurements. The strain gradient has a value approximately 10^7 m^{-1} , which is 2 or 3 orders of magnitude larger than the value inside the film. Moreover, we found that the giant surface flexoelectric field can significantly affect the surface microstructure of the BFO film. We show that a surface layer exists on the BFO film, and an irreversible surface structure transition at 500 K is found to be associated with flexoelectricity. The large strain gradient is found originate from the depolarization field of ferroelectrics.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b15162.

Additional figures and references (PDF)

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Notes

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