# Observation of Strong Polarization Enhancement in Ferroelectric Tunnel Junctions

Linze Li,<sup>†</sup><sup>®</sup> Xiaoxing Cheng,<sup>‡</sup> Thomas Blum,<sup>○</sup> Huaixun Huyan,<sup>†</sup> Yi Zhang,<sup>†</sup> Colin Heikes,<sup>§</sup> Xingxu Yan,<sup>†</sup><sup>®</sup> Chaitanya Gadre,<sup>○</sup> Toshihiro Aoki,<sup>∥</sup> Mingjie Xu,<sup>∥</sup> Lin Xie,<sup>⊥</sup> Zijian Hong,<sup>‡</sup> Carolina Adamo,<sup>#</sup> Darrell G. Schlom,<sup>#,∇</sup> Long-Qing Chen,<sup>‡</sup> and Xiaoqing Pan<sup>\*,†,∥,○®</sup>

<sup>†</sup>Department of Chemical Engineering and Materials Science, University of California - Irvine, Irvine, California 92697, United States

<sup>‡</sup>Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, United States

<sup>O</sup>Department of Physics and Astronomy, University of California - Irvine, Irvine, California 92697, United States

<sup>§</sup>NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

<sup>II</sup>Irvine Materials Research Institute (IMRI), University of California - Irvine, Irvine, California 92697, United States

<sup>1</sup>National Laboratory of Solid State Microstructures and College of Engineering and Applied Sciences, Nanjing University, Nanjing, Jiangsu 210093, China

<sup>#</sup>Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, United States

<sup>∇</sup>Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, United States

**Supporting Information** 



**ABSTRACT:** Ferroelectric heterostructures, with capability of storing data at ultrahigh densities, could act as the platform for next-generation memories. The development of new device paradigms has been hampered by the long-standing notion of inevitable ferroelectricity suppression under reduced dimensions. Despite recent experimental observation of stable polarized states in ferroelectric ultrathin films, the out-of-plane polarization components in these films are strongly attenuated compared to thicker films, implying a degradation of device performance in electronic miniaturization processes. Here, in a model system of BiFeO<sub>3</sub>/La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>, we report observation of a dramatic out-of-plane polarization enhancement that occurs with decreasing film thickness. Our electron microscopy analysis coupled with phase-field simulations reveals a polarization-enhancement mechanism that is dominated by the accumulation of oxygen vacancies at interfacial layers. The results shed light on the interplay between polarization and defects in nanoscale ferroelectrics and suggest a route to enhance functionality in oxide devices.

**KEYWORDS:** Ferroelectric tunnel junctions, ultrathin films, polarization enhancement, oxygen vacancies, transmission electron microscopy

As the demand for scaling nonvolatile memories down to only a few nanometers continues to increase, heterostructures based on ferroelectric oxides have emerged as promising candidates to meet the requirements of low power consumption, fast write speed, large read/write cycle endurance, high density, and multilevel functionalities.<sup>1,2</sup> One prototype device that has recently drawn considerable interest is the ferroelectric tunnel junction (FTJ), in which an ultrathin

 Received:
 May 7, 2019

 Revised:
 July 27, 2019

 Published:
 September 11, 2019

ferroelectric film is sandwiched between two electrodes. Its conductance is dominated by electronic tunneling through the ultrathin film and can be modulated by reversing the ferroelectric polarization with an applied electric field.<sup>3-4</sup> Two different device configurations are frequently adopted in practical FTJ devices. While the bottom electrode is usually an epitaxial conductive buffer layer embedded between an insulating substrate and the ferroelectric layer, the top electrode can be either a second conductive layer deposited above the ferroelectric film or just a conductive probe that can move arbitrarily at the free surface of the film.<sup>3,6</sup> The latter case is particularly attractive for nanodevice applications, as it allows the domain structures in the ferroelectric film to be manipulated facilely and controllably by the mobile probe and thus permits an ultrahigh density of storage bits to be written.

To gain a fundamental understanding of the polarization structures in FTJ, a number of theoretical and experimental studies have explored the polarized states in ferroelectric thin films with varying thicknesses.<sup>7–12</sup> A general observation is that with reduced film thickness, the out-of-plane polarization is inevitably suppressed due to enhanced depolarization effects. In some systems, a "critical thickness", below which the ferroelectric polarization is eliminated, also exists. For example, using electrical measurements, Kim et al. observed significantly reduced polarization in BaTiO<sub>3</sub> thin films between two metallic SrRuO<sub>3</sub> electrodes when the films are <10 nm in thickness.<sup>7</sup> From first-principles calculations Junquera and Ghosez showed that BaTiO<sub>3</sub> thin films between two SrRuO<sub>3</sub> electrodes lose their ferroelectricity when their thicknesses are below a critical value of ~2.4 nm.<sup>8</sup> Using piezoresponse force microscopy (PFM) Maksymovych et al. detected weak signals of ferroelectric switching in BiFeO3 ultrathin films grown on La0.7Sr0.3MnO3 electrodes and predicted that the critical thickness lies in the range from 1 to 2 nm.9 With in situ optical second harmonic generation (ISHG), De Luca et al. monitored the evolution of polarization states during the layerby-layer growth of both BaTiO<sub>3</sub> and BiFeO<sub>3</sub> films on SrRuO<sub>3</sub> electrodes and found that ferroelectricity in both films does not emerge until the films are more than 4 unit cells in thickness.<sup>11</sup>

This observed polarization attenuation or annihilation in ferroelectric ultrathin films would in principle lead to degraded performance in FTJ devices, but numerous groups have reported very high tunnel electroresistance (TER) measured from fabricated FTJ devices. Specifically, TER values as large as  $6.0 \times 10^8$  % are reported in a four-unit-cell BaTiO<sub>3</sub>-based FTJ device,<sup>13</sup> and TER of ~2700% is reported in a two-unit-cell BiFeO<sub>3</sub>-based FTJ device.<sup>14</sup> Such measured giant TER requires a significant and switchable out-of-plane polarization in the ferroelectric ultrathin layer of the FTJ device. Therefore, although extensive research activity has been devoted to the technical exploration and fundamental understanding of FTJ systems, a gap still exists between the optimization of device configurations and the probing of polarization structures in nanosized ferroelectrics. In particular, electrical measurements of the polarization-field loops in ferroelectric ultrathin films are complicated by leakage or tunneling currents. Measurements with PFM can only provide indirect, semiquantitative estimates of the polarization and can be affected by several artifacts related with topographical features, background signals, or nonpiezoelectric effects.<sup>15</sup> In situ SHG is conducted during film growth at elevated temperatures and thus cannot directly reflect the room-temperature properties of ferroelectric films.

First-principle calculations often must ignore local defects that may dominate the responses of real materials. It is thus necessary to experimentally explore possible mechanisms of polarization enhancement in ferroelectric ultrathin films, at the atomic scale, to make full use of the technological potential of FTJ devices.

Recent advances in aberration-corrected scanning transmission electron microscopy (STEM) have opened exciting opportunities for probing materials structures with subangstrom-level precision and have made it possible to directly measure the spatial distribution of polarization displacement vectors in a ferroelectric crystal at atomic scale.<sup>16</sup> Using a polarization mapping technique based on atomic-resolution STEM, stable polarized states have been directly observed in tetragonal PbTiO<sub>3</sub> and Pb( $Zr_{0.2}Ti_{0.8}$ )O<sub>3</sub> films with only a few unit cells in thickness or tetragonal-like (T-like) BiFeO3 films with thicknesses down to a single unit cell.<sup>17-19</sup> Their polarization strength, however, is still greatly reduced compared to thicker (>5-10 nm) tetragonal PbTiO<sub>3</sub> or  $Pb(Zr_{0,2}Ti_{0,8})O_3$  films, or *T*-like BiFeO<sub>3</sub> films, respectively.<sup>17,18,20</sup> Enhanced polarization states stabilized by surface impurity defects have also been observed in 2 nm-thick BiFeO<sub>3</sub> film.<sup>21</sup> Nevertheless, the strong polarization-defect interaction makes the polarization stable only when it is pointing to the defect, and therefore the enhanced polarization state is almost certainly nonswitchable. Here, we use aberration-corrected STEM to exam the polarization structures in a model system of ferroelectric heterostructures composed of ferroelectric BiFeO<sub>3</sub> films and La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> bottom electrodes. We show that, contrary to previous measurements in ferroelectric films, the magnitude of the out-of-plane polarization component in the BiFeO<sub>3</sub> films does not decrease monotonically with the reduced film thickness, but instead presents an asymmetric behavior for the two opposite polarized states. While the polarization strength in the upward polarized domains is reduced with decreasing film thickness, the polarization strength in the downward polarized domains is surprisingly enhanced to a great extent. This occurs with a concomitant rhombohedral-like-to-tetragonal-like structure transformation in the BiFeO<sub>3</sub> film when its thickness reaches below a critical value of ~2 nm. Our STEM analysis coupled with electron energy-loss spectroscopy (EELS) and phase-field simulations reveal the critical nature of oxygen vacancy accumulation at the BiFeO<sub>3</sub>/La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> interface, which produces a strong built-in field that can lead to the observed changes of polarization structures.

BiFeO<sub>3</sub> is a room-temperature multiferroic exhibiting coupled ferroelectric ( $T_{\rm C} \sim 1103$  K) and antiferromagnetic ( $T_{\rm N} \sim 650$  K) order.<sup>22–24</sup> Structures of epitaxial BiFeO<sub>3</sub> films are correlated to the misfit strain imposed by their underlying substrates. BiFeO<sub>3</sub> films with moderate tensile or compressive (<  $\sim$  4.5%) strain are usually monoclinically distorted, but closely resemble the bulk rhombohedral phase, and are therefore referred to as "rhombohedral-like (R-like)" structures.<sup>25</sup> In pseudocubic unit cells of the R-like structure (Figure 1a), the oxygen octahedra and the central Fe cation are displaced from their respective positions at the face and body centers, giving rise to a large spontaneous polarization (~100  $\mu$ C cm<sup>-2</sup>) along the  $\langle 111 \rangle_{PC}$  directions,<sup>22-24,26,27</sup> where the PC subscript represents pseudocubic indices. Under a large compressive epitaxial strain exceeding ~4.5%, BiFeO<sub>3</sub> can also be stabilized into a monoclinic structure that is *T*-like.<sup>25</sup> In the T-like structure (Figure 1a), the Fe atom is five-coordinated,



**Figure 1.** Polarization structures in BiFeO<sub>3</sub> thin films. (a) Atomic models of the pseudocubic structures of rhombohedral-like (*R*-like) and tetragonal-like (*T*-like) BiFeO<sub>3</sub>. Polarizations are shown by light green arrows. (b) HAADF STEM image of a BiFeO<sub>3</sub> thin film viewed in cross-section along the  $[100]_{PC}$  zone axis. The overlaid brown and blue balls mark the Bi and Fe atom columns, respectively. The **D**<sub>FB</sub> vector, defined as the atomic displacement in the image plane of the Fe cation from the center of the unit cell formed by its four Bi neighbors, is opposite to the polarization vector (**P**). The black arrows indicate a uniform downward polarization. (c) Out-of-plane components of  $-\mathbf{D}_{FB}$  vectors  $(|-\mathbf{D}_{FB}|_2)$  as a function of BiFeO<sub>3</sub> (BFO) film thickness in upward and downward polarized domains.

forming an oxygen square-pyramidal that is displaced from the center of the pseudocubic unit cell. This gives rise to a large polarization (~150  $\mu$ C/cm<sup>2</sup>) oriented along the out-of-plane direction.

In this work, a series of  $(001)_{PC}$  oriented BiFeO<sub>3</sub> thin films with thicknesses ranging from 1.2 to 20 nm are grown on  $(110)_O$  TbScO<sub>3</sub> substrates (where the O subscript represents orthorhombic indices) with the insertion of 20 nm thick La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> buffered electrodes grown by molecular-beam epitaxy (MBE).<sup>28</sup> The BiFeO<sub>3</sub> films were grown using the absorption controlled MBE growth method described previously<sup>29,30</sup> with an Fe:Bi ratio of ~5:1 in a 5  $\times$  10<sup>-6</sup> Torr background pressure of distilled ozone ( $\sim 80\% \text{ O}_3$ ). Using aberration-corrected high-angle annular dark-field (HAADF) STEM imaging, atomic-scale structures within a BiFeO<sub>2</sub> thin film can be directly visualized, and the polarization displacement vector within each pseudocubic unit cell can be measured. For example, in the HAADF STEM image shown in Figure 1b, a vector,  $D_{FB}$ , can be defined as the atomic displacement in the image plane of the Fe cation from the center of the unit cell formed by its four Bi neighbors and can be directly measured by fitting the atomic columns as twodimensional (2D) Gaussian peaks to locate their centers and record their offsets.<sup>16</sup> This D<sub>FB</sub> vector, as the dominant manifestation of the ferroelectric polarization in BiFeO<sub>3</sub>, points toward the center of the negative oxygen charges and thus is exactly opposite to the polarization component in the image plane. Therefore,  $-D_{FB}$  vectors can be used to estimate the polarization and are called polarization vectors.

Mapping of polarization vectors in the BiFeO<sub>3</sub> films show that the polarization in most of the film is pointing downward, toward the bottom electrode, which can be partially attributed to the downward built-in field induced by the Schottky junction at the BiFeO<sub>3</sub>/La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> interface.<sup>31</sup> Atomicresolution energy dispersive spectroscopy (EDS) mapping shows a Fe-O<sub>2</sub> termination layer at the BiFeO<sub>3</sub>/ La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> interface (Figure S1), which also favors a downward polarization in the BiFeO<sub>3</sub> layers grown above.<sup>10</sup> On the other hand, upward polarized domains are also frequently observed, indicating the formation of multiple stable polarization states and thus the switchability of the BiFeO<sub>3</sub> films. To estimate the change of the out-of-plane polarization strength in the BiFeO<sub>3</sub> films, we averaged local polarization vectors across the film thickness in upward and downward



Figure 2. Atomic structures in a 10 nm-thick BiFeO<sub>3</sub> film. (a–c) A HAADF STEM image (a) of a downward polarized domain at the interface region and corresponding maps of  $-\mathbf{D}_{FB}$  vectors (b) and out-of-plane lattice parameter over in-plane lattice parameter ratios (*c/a* ratios) (c) overlaid on the same HAADF STEM image. (d–f) A HAADF STEM image (a) of a upward polarized domain at the interface region and corresponding maps of  $-\mathbf{D}_{FB}$  vectors (b) and c/a ratios (c) overlaid on the same HAADF STEM image. (g–j) Changes of out-of-plane components of  $-\mathbf{D}_{FB}$  vectors (l– $\mathbf{D}_{FB}|_{z}$ ) (g), *c/a* ratios (h), EELS Fe L<sub>3</sub>/L<sub>2</sub> ratios (i), and integrated O K-edge intensities (j) across the BiFeO<sub>3</sub>/ La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (BFO/LSMO) interface.



**Figure 3.** Phase-field simulations of polarization structures in a 10 nm-thick BiFeO<sub>3</sub> film. (a–d) Plot of charge density (a), electric field (b), polarization vectors in a downward polarized domain (c), and polarization vectors in an upward polarized domain (d). The yellow dashed lines indicate the BiFeO<sub>3</sub>/La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> interface. (e) Distribution of out-of-plane polarization (*Pz*) in the 10 nm-thick BiFeO<sub>3</sub> film in a 5 nm region above the BiFeO<sub>3</sub>/La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> interface.

polarized domains, respectively, in each BiFeO<sub>3</sub> film. In Figure 1c, we plot the average magnitude of the out-of-plane polarization vectors  $(|-D_{FB}|_{z})$  as a function of the film thickness. The observed polarization attenuation with the reduced film thickness in the upward polarized domains is commonly expected as a result of an enhanced depolarization field arising from interface boundary conditions.<sup>8</sup> However, the anomalous polarization enhancement with the reduced film thickness in the downward polarized domains is counterintuitive and directly opposite to the correlation between ferroelectric polarization and film thickness reported in previous studies.<sup>7-12</sup> Based on an assumed linear relationship between the ferroelectric polarization  $(P_S)$  and the  $-D_{FB}$ vectors,<sup>16</sup> the out-of-plane polarization strength is estimated to be 59 uC/cm<sup>2</sup> in the 20 nm BiFeO<sub>3</sub> film and increases to 72 uC/cm<sup>2</sup> and 105 uC/cm<sup>2</sup> in the 5 and 1.2 nm BiFeO<sub>3</sub> films, respectively.

To explain the asymmetric trends observed for the two opposite polarization states, it is necessary to examine the atomic-scale polarization distribution in the BiFeO<sub>3</sub> films. We first show the results of a 10 nm BiFeO<sub>3</sub> film, in which typical R-like crystal structures are observed. The HAADF STEM images and corresponding maps of polarization vectors and lattice parameters of two local regions across the BiFeO<sub>3</sub>/ La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> interface with upward and downward polarization states are shown in Figure 2a-c and d-f, respectively. By averaging the data from each lattice layer, the change of the lattice parameters and the magnitude of out-of-plane polarization vectors  $(|-D_{FB}|_z)$  for the upward and downward polarized domains is plotted in Figure 2g,h, respectively. The most remarkable feature is a change of both polarization and lattice parameters at the interfacial region in the BiFeO<sub>3</sub> film that extends four-unit cells from the interface. While the polarization vectors are clearly attenuated at the interfacial region of the upward polarized domain (Figure 2e), no apparent polarization suppression is observed at the interfacial region of the downward polarized domain (Figure 2b), and instead, the local polarization vectors there slightly rotate into the out-of-plane direction. As a result, the magnitudes of outof-plane polarization vectors at the interfacial region in the upward polarized domain are significantly reduced, but those in the downward polarized domain are slightly enhanced (Figure 2g). In contrast, the mapping results in Figure 2c,f,h similarly show an increase in the out-of-plane lattice parameter over in-plane lattice parameter ratio (c/a) at the interfacial regions of both domains.

The changes of polarization and lattice structures at the interfacial regions could be correlated to local variations of chemical profiles and oxidation states across the BiFeO<sub>3</sub>/ La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> interface, as evidenced by our EELS study. Figure 2i,j shows average profiles of the  $L_3/L_2$  ratios for the Fe and Mn L<sub>3.2</sub>-edges and average profiles of the integrated O Kedge intensities, respectively, where similar trends are observed for the two interface regions with opposite polarization orientations. By comparing the measured  $L_3/L_2$  values to the reference values marked with the yellow (Fe) and blue (Mn) bands (Figure 2i), the changes of the cations' valence states can be estimated.<sup>32</sup> While away from the interface, Fe and Mn have valence states of  $\sim +3$  that are close to the bulk value; lower valence states of both elements are observed within the interfacial layers that include three unit cells above and one unit cell below the interface. In the corresponding EELS spectra shown in Figures S2 and S3, the L3 peaks of both Fe and Mn shift to lower-energy positions at the interfacial region, which is also an indication of local valence decrease of these transition metals. The reduction of cation valences in perovskites is usually associated with strong local accumulation of oxygen vacancies, which is indeed consistent with the apparent oxygen depletion at the interfacial layers, as revealed by the profiles of the O K-edge intensities in Figure 2j. A reduced cation valence in general leads to an increased radius of cations and thus to a lattice expansion in perovskite oxides.<sup>33-35</sup> In epitaxial thin films, as the in-plane lattice parameters are constrained by the substrate, the lattice expansion mostly occurs through the out-of-plane elongation. In fact, formation of oxygen vacancies at heterostructure interfaces has been observed in several different ferroelectric systems, and it has been shown that these vacancies can cause local out-of-plane lattice elongation.  $^{32,36-38}$  This is consistent with our finding of enhanced c/a ratios at the interfacial regions of the 10 nm-thick BiFeO<sub>3</sub> film (Figure 2c,f,h).

To further illustrate the effects of interfacial oxygen vacancies, in Figure S4 we show the maps of polarization vectors and lattice parameters across a local  $BiFeO_3/La_{0.7}Sr_{0.3}MnO_3$  interface with downward polarization, in which strong accumulation of oxygen vacancies is not observed according to EELS analysis of transition-metal valences and O intensities (Figures S4 and S5). Of note, such a type of interface has been rarely observed in our  $BiFeO_3$  films, as the dominant type shows a much stronger oxygen vacancy accumulation as discussed above. Here, the polarization strength gradually reduces from the inner region of the

## **Nano Letters**

BiFeO<sub>3</sub> film to the interface (Figure S4b,d), and the c/a ratios at the interfacial regions are not apparently enhanced compared to the inner film (Figure S4c,e). Through the comparison between the two types of interfaces, the critical effects of interfacial accumulation of oxygen vacancies on the polarization structures can be deduced. Such interface effects become more prominent as the film thickness decreases. In the case of a 5 nm BiFeO<sub>3</sub> film, this leads to an overall polarization enhancement/suppression in the downward/upward polarized domains, respectively (Figure S6).

Phase-field simulations allow the effect of the charge distribution induced by the accumulation of oxygen vacancies at the interfacial region to be studied. Such accumulation of oxygen vacancies should results in a positively charged layer of several unit cells in thickness in the semiconducting BiFeO<sub>3</sub> film above the interface, and consequentially an atomically thin, negatively charged, free charge compensation layer at the surface of the metallic La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> film. In a simulated 10 nm BiFeO<sub>3</sub> film on a La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> substrate, we applied positive charge densities ranging from  $0.26 \times 10^9 \text{ C/m}^3$  to 2.08  $\times 10^9$  C/m<sup>3</sup> at a 2 nm-thick interfacial layer in the BiFeO<sub>3</sub> film above the interface and maintained a total zero net charge across the heterojunction by applying corresponding negative charge densities ranging from  $-1.3 \times 10^9$  C/m<sup>3</sup> to  $-1.04 \times$  $10^{10} \text{ C/m}^3$  at the surface of the La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> layer. In Figure 3c,d, the calculated stable polarization structures with a charge density of 0.78  $\times$  10<sup>9</sup> C/m<sup>3</sup> at the interfacial layer of the BiFeO<sub>3</sub> film show apparent polarization suppression at the interfacial region of the upward polarized domain and polarization enhancement at the interfacial region of the downward polarized domain, whereas the polarization in the upper portion of the film remains mostly unperturbed. This situation is most consistent with the experimental observation in Figure 2. The origin of the changes of polarization structures is the built-in electric field (Figure 3b) introduced by the charge distribution (Figure 3a) at the interfacial layers. The phase-field simulations thus confirm the important role of the electrostatic boundary conditions at the interface in both polarization states.

The situation for the coupling between accumulation of oxygen vacancies and lattice distortion in BiFeO<sub>3</sub> is further complicated by possible phase transformations. Previous firstprinciples calculations show that the presence of oxygen vacancies greatly reduces the energy difference between the rhombohedral and tetragonal phases of BiFeO<sub>3</sub> lattices and can thus facilitate the structural transformation.<sup>32</sup> In our system, we observed a R-like-to-T-like structural transformation in the BiFeO<sub>3</sub> lattice when the film thickness is reduced to 2.4 nm in thickness. Figure 4a-c and d-f shows the mapping results of an upward polarized domain and a downward polarized domain in the 2.4 nm-thick BiFeO<sub>3</sub> film, respectively. In the downward polarized domain, the polarization vectors are very large in magnitude and generally point in the out-of-plane direction, and the lattice structure shows an out-of-plane elongation with enhanced c/a ratios. In the upward polarized domain, the out-of-plane polarization components are dramatically reduced, and thus the overall polarization vectors are generally pointing in-plane. However, the local lattice structure still presents an out-of-plane elongation, indicating that the accumulation of oxygen vacancies, rather than the polarization rotation, should the driven force for the observed lattice elongation. In Figure S7, we show the polarization in the 2.4 nm-thick film is electrically switchable by piezoelectric

Letter



**Figure 4.** Atomic structures in a 2.4 nm-thick and a 1.2 nm-thick BiFeO<sub>3</sub> film. (a–c) A HAADF STEM image (a) of a downward polarized domain at the interface region of the 2.4 nm-thick BiFeO<sub>3</sub> film and corresponding maps of  $-\mathbf{D}_{FB}$  vectors (b) c/a ratios (c) overlaid on the same HAADF STEM image. (d–f) A HAADF STEM image (d) of an upward polarized domain at the interface region of the 2.4 nm-thick BiFeO<sub>3</sub> film and corresponding maps of  $-\mathbf{D}_{FB}$  vectors (e) c/a ratios (f) overlaid on the same HAADF STEM image. (g–i) A HAADF STEM image (g) of a downward polarized domain at the interface region of the 1.2 nm-thick BiFeO<sub>3</sub> film and corresponding maps of  $-\mathbf{D}_{FB}$  vectors (h) c/a ratios (i) overlaid on the same HAADF STEM image.

force microscopy (PFM). With the film thickness further decreasing, the *T*-like structure is also maintained in a 1.2 nm-thick  $BiFeO_3$  film (Figure 4g–i), where we only observed large polarization vectors that are pointing downward.

In conclusion, in ferroelectric BiFeO<sub>3</sub> thin films grown on  $La_{0.7}Sr_{0.3}MnO_3$  bottom electrodes, we have observed a strong out-of-plane polarization enhancement, with a concurrent rhombohedral-like-to-tetragonal-like structure transformation, that occurs along with a reduction of the BiFeO3 film thickness. We propose that this polarization enhancement and corresponding structural transformation is caused by the accumulation of oxygen vacancies at the BiFeO<sub>3</sub>/ La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> interfaces, which tends to play a more dominant role as the thickness of the ferroelectric film continues to shrink. Our observation can reconcile multiple prior studies by resolving the discrepancy that very high tunnel electroresistance can be measured from fabricated ferroelectric tunnel junctions, but only attenuated polarization has been previously observed in ferroelectric ultrathin films. Our results also call for a careful examination of the role of defectpolarization coupling in ferroelectric films with multifunctional properties. Further study of such coupling may allow the polarization-mediated functionalities to be tuned by modulating the spatial distribution of oxygen vacancies in ferroelectric films, either during material synthesis by adjusting growth parameters or post-synthesis through applying external stimuli. These developments could contribute to establishing the

design paradigm for next-generation ferroelectric-based reconfigurable electronic nanodevices.

# ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.9b01878.

Film growth; transmission electron microscopy; phase-field simulations; and discussion on PFM results (PDF)

## AUTHOR INFORMATION

## **Corresponding Author**

\*E-mail: xiaoqinp@uci.edu.

## ORCID 💿

Linze Li: 0000-0001-5362-8991 Xingxu Yan: 0000-0001-7991-4849 Xiaoqing Pan: 0000-0002-0965-8568

#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The experimental work was mainly supported by the Department of Energy (DOE) under grant DE-SC0014430 (L.Z.L., T.B., H.H, X.X.Y., C.G., T.A., M.J.X., L.X., and X.Q.P.). The TEM work was conducted at the Irvine Materials Research Institute at University of California, Irvine. The theoretical work at the Pennsylvania State University was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award FG0207ER46417 (X.X.C., Z.J.H., and L.Q.C.). Calculations at the Pennsylvania State University were performed on the Cyberstar Linux Cluster funded by the National Science Foundation through grant OCI0821527. The work at Cornell University was supported by the National Science Foundation (Nanosystems Engineering Research Center for Translational Applications of Nanoscale Multiferroic Systems) under grant number EEC-1160504 (C.H., C.A., and D.G.S.). This work was performed in part at the Cornell Nanoscale Facility, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (grant ECCS-1542081).

#### REFERENCES

(1) Scott, J. F. Applications of modern ferroelectrics. *Science* 2007, 315, 954–959.

(2) Hu, J. M.; Duan, C. G.; Nan, C. W.; Chen, L. Q. Understanding and designing magnetoelectric heterostructures guided by computation: progresses, remaining questions, and perspectives. *Npj Computational Materials* **2017**, *3*, 18.

(3) Garcia, V.; Fusil, S.; Bouzehouane, K.; Enouz-Vedrenne, S.; Mathur, N. D.; Barthelemy, A.; Bibes, M. Giant tunnel electroresistance for non-destructive readout of ferroelectric states. *Nature* **2009**, *460*, 81–84.

(4) Gajek, M.; Bibes, M.; Fusil, S.; Bouzehouane, K.; Fontcuberta, J.; Barthelemy, A. E.; Fert, A. Tunnel junctions with multiferroic barriers. *Nat. Mater.* **2007**, *6*, 296–302.

(5) Velev, J. P.; Burton, J. D.; Zhuravlev, M. Y.; Tsymbal, E. Y. Predictive modelling of ferroelectric tunnel junctions. *Npj Computational Materials* **2016**, *2*, 16009.

(6) Garcia, V.; Bibes, M. Ferroelectric tunnel junctions for information storage and processing. *Nat. Commun.* **2014**, *5*, 4289.

(7) Kim, Y. S.; Kim, D. H.; Kim, J. D.; Chang, Y. J.; Noh, T. W.; Kong, J. H.; Char, K.; Park, Y. D.; Bu, S. D.; Yoon, J. G.; Chung, J. S. Critical thickness of ultrathin ferroelectric  $BaTiO_3$  films. *Appl. Phys. Lett.* **2005**, *86*, 102907.

(8) Junquera, J.; Ghosez, P. Critical thickness for ferroelectricity in perovskite ultrathin films. *Nature* **2003**, *422*, 506–509.

(9) Maksymovych, P.; Huijben, M.; Pan, M. H.; Jesse, S.; Balke, N.; Chu, Y. H.; Chang, H. J.; Borisevich, A. Y.; Baddorf, A. P.; Rijnders, G.; Blank, D. H. A.; Ramesh, R.; Kalinin, S. V. Ultrathin limit and dead-layer effects in local polarization switching of BiFeO<sub>3</sub>. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 014119.

(10) De Luca, G.; Strkalj, N.; Manz, S.; Bouillet, C.; Fiebig, M.; Trassin, M. Nanoscale design of polarization in ultrathin ferroelectric heterostructures. *Nat. Commun.* **2017**, *8*, 1419.

(11) Fong, D. D.; Stephenson, G. B.; Streiffer, S. K.; Eastman, J. A.; Auciello, O.; Fuoss, P. H.; Thompson, C. Ferroelectricity in ultrathin perovskite films. *Science* **2004**, *304*, 1650–1653.

(12) Rault, J. E.; Ren, W.; Prosandeev, S.; Lisenkov, S.; Sando, D.; Fusil, S.; Bibes, M.; Barthelemy, A.; Bellaiche, L.; Barrett, N. Thickness-Dependent Polarization of Strained BiFeO<sub>3</sub> Films with Constant Tetragonality. *Phys. Rev. Lett.* **2012**, *109*, 267601.

(13) Xi, Z. N.; Ruan, J. J.; Li, C.; Zheng, C. Y.; Wen, Z.; Dai, J. Y.; Li, A. D.; Wu, D. Giant tunnelling electroresistance in metal/ferroelectric/semiconductor tunnel junctions by engineering the Schottky barrier. *Nat. Commun.* **2017**, *8*, 15217.

(14) Yoong, H. Y.; Wang, H.; Xiao, J.; Guo, R.; Yang, P.; Yang, Y.; Lim, S. T.; Wang, J.; Venkatesan, T.; Chen, J. Tunneling electroresistance effect in ultrathin BiFeO<sub>3</sub>-based ferroelectric tunneling junctions. *Appl. Phys. Lett.* **2016**, *109*, 242901.

(15) Seol, D.; Kim, B.; Kim, Y. Non-piezoelectric effects in piezoresponse force microscopy. *Curr. Appl. Phys.* 2017, *17*, 661–674.
(16) Nelson, C. T.; Winchester, B.; Zhang, Y.; Kim, S. J.; Melville, A.; Adamo, C.; Folkman, C. M.; Baek, S. H.; Eom, C. B.; Schlom, D.

G.; Chen, L. Q.; Pan, X. Q. Spontaneous vortex nanodomain arrays at ferroelectric heterointerfaces. *Nano Lett.* **2011**, *11*, 828–834.

(17) Gao, P.; Zhang, Z. Y.; Li, M. Q.; Ishikawa, R.; Feng, B.; Liu, H. J.; Huang, Y. L.; Shibata, N.; Ma, X. M.; Chen, S. L.; Zhang, J. M.; Liu, K. H.; Wang, E. G.; Yu, D. P.; Liao, L.; Chu, Y. H.; Ikuhara, Y. Possible absence of critical thickness and size effect in ultrathin perovskite ferroelectric films. *Nat. Commun.* **2017**, *8*, 15549.

(18) Zhang, S. R.; Zhu, Y. L.; Tang, Y. L.; Liu, Y.; Li, S.; Han, M. J.; Ma, J. Y.; Wu, B.; Chen, Z. H.; Saremi, S.; Ma, X. L. Giant Polarization Sustainability in Ultrathin Ferroelectric Films Stabilized by Charge Transfer. *Adv. Mater.* **2017**, *29*, 1703543.

(19) Wang, H.; Liu, Z. R.; Yoong, H. Y.; Paudel, T. R.; Xiao, J. X.; Guo, R.; Lin, W. N.; Yang, P.; Wang, J.; Chow, G. M.; Venkatesan, T.; Tsymbal, E. Y.; Tian, H.; Chen, J. S. Direct observation of roomtemperature out-of-plane ferroelectricity and tunneling electroresistance at the two-dimensional limit. *Nat. Commun.* **2018**, *9*, 3319. (20) Rossell, M. D.; Erni, R.; Prange, M. P.; Idrobo, J. C.; Luo, W.;

Zeches, R. J.; Pantelides, S. T.; Ramesh, R. Atomic Structure of Highly Strained BiFeO<sub>3</sub> Thin Films. *Phys. Rev. Lett.* **2012**, *108*, 047601.

(21) Xie, L.; Li, L. Z.; Heikes, C. A.; Zhang, Y.; Hong, Z. J.; Gao, P.; Nelson, C. T.; Xue, F.; Kioupakis, E.; Chen, L. Q.; Schlom, D. G.; Wang, P.; Pan, X. Q. Giant Ferroelectric Polarization in Ultrathin Ferroelectrics via Boundary-Condition Engineering. *Adv. Mater.* **2017**, *29*, 1701475.

(22) Zavaliche, F.; Yang, S. Y.; Zhao, T.; Chu, Y. H.; Cruz, M. P.; Eom, C. B.; Ramesh, R. Multiferroic BiFeO<sub>3</sub> films: domain structure and polarization dynamics. *Phase Transitions* **2006**, *79*, 991–1017.

(23) Chu, Y. H.; Martin, L. W.; Holcomb, M. B.; Ramesh, R. Controlling magnetism with multiferroics. *Mater. Today* **2007**, *10*, 16–23.

(24) Catalan, G.; Scott, J. F. Physics and Applications of Bismuth Ferrite. *Adv. Mater.* **2009**, *21*, 2463–2485.

(25) Christen, H. M.; Nam, J. H.; Kim, H. S.; Hatt, A. J.; Spaldin, N. A. Stress-induced R-M-A-M-C-T symmetry changes in BiFeO<sub>3</sub> films. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, 83, 144107.

#### **Nano Letters**

(26) Das, R. R.; Kim, D. M.; Baek, S. H.; Eom, C. B.; Zavaliche, F.; Yang, S. Y.; Ramesh, R.; Chen, Y. B.; Pan, X. Q.; Ke, X.; Rzchowski, M. S.; Streiffer, S. K. Synthesis and ferroelectric properties of epitaxial BiFeO<sub>3</sub> thin films grown by sputtering. *Appl. Phys. Lett.* **2006**, *88*, 242904.

(27) Kubel, F.; Schmid, H. Structure of a ferroelectric and ferroelastic monodomain crystal of the perovskite BiFeO3. *Acta Crystallogr., Sect. B: Struct. Sci.* **1990**, *46*, 698–702.

(28) Adamo, C.; Ke, X.; Wang, H. Q.; Xin, H. L.; Heeg, T.; Hawley, M. E.; Zander, W.; Schubert, J.; Schiffer, P.; Muller, D. A.; Maritato, L.; Schlom, D. G. Effect of Biaxial Strain on the Electrical and Magnetic Properties of (001) La0.7Sr0.3MnO3 Thin Films. *Appl. Phys. Lett.* **2009**, *95*, 112504.

(29) Smith, E. H.; Ihlefeld, J. F.; Heikes, C. A.; Paik, H. J.; Nie, Y. F.; Adamo, C.; Heeg, T.; Liu, Z. K.; Schlom, D. G. Exploiting kinetics and thermodynamics to grow phase-pure complex oxides by molecular-beam epitaxy under continuous codeposition. *Physical Review Materials* **2017**, *1*, 023403.

(30) Mundy, J. A.; Heikes, C. A.; Grosso, B. F.; Ferenc Segedin, D.; Wang, Z.; Goodge, B. H.; Meier, Q. N.; Nelson, C. T.; Prasad, B.; Kourkoutis, L. F.; Ratcliff, W. D.; Spaldin, N. A.; Ramesh, R.; Schlom, D. G. A high-energy density antiferroelectric made by interfacial electrostatic engineering. arXiv e-prints, 2018. https://arxiv.org/ftp/ arxiv/papers/1812/1812.09615.pdf.

(31) Nelson, C. T.; Gao, P.; Jokisaari, J. R.; Heikes, C.; Adamo, C.; Melville, A.; Baek, S. H.; Folkman, C. M.; Winchester, B.; Gu, Y. J.; Liu, Y. M.; Zhang, K.; Wang, E. G.; Li, J. Y.; Chen, L. Q.; Eom, C. B.; Schlom, D. G.; Pan, X. Q. Domain dynamics during ferroelectric switching. *Science* **2011**, 334, 968–971.

(32) Kim, Y. M.; Morozovska, A.; Eliseev, E.; Oxley, M. P.; Mishra, R.; Selbach, S. M.; Grande, T.; Pantelides, S. T.; Kalinin, S. V.; Borisevich, A. Y. Direct observation of ferroelectric field effect and vacancy-controlled screening at the  $BiFeO_3/La_xSr_{1-x}MnO_3$  interface. *Nat. Mater.* **2014**, *13*, 1019–1025.

(33) Mi, S. B.; Jia, C. L.; Heeg, T.; Trithaveesak, O.; Schubert, J.; Urban, K. Heterostructures of  $BaTiO_3$  bilayer films grown on  $SrTiO_3$  (001) under different oxygen pressures. *J. Cryst. Growth* **2005**, *283*, 425–430.

(34) Cai, H. L.; Wu, X. S.; Gao, J. Effect of oxygen content on structural and transport properties in  $SrTiO_{3-x}$  thin films. *Chem. Phys. Lett.* **2009**, 467, 313–317.

(35) Enriquez, E.; Chen, A. P.; Harrell, Z.; Dowden, P.; Koskelo, N.; Roback, J.; Janoschek, M.; Chen, C. L.; Jia, Q. X. Oxygen Vacancy-Tuned Physical Properties in Perovskite Thin Films with Multiple Bsite Valance States. *Sci. Rep.* **2017**, *7*, 46184.

(36) Catrou, P.; Tricot, S.; Delhaye, G.; Le Breton, J. C.; Turban, P.; Lepine, B.; Schieffer, P. Effect of oxygen vacancies at the Fe/SrTiO<sub>3</sub> (001) interface: Schottky barrier and surface electron accumulation layer. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2018**, 98, 115402.

(37) Matsuo, H.; Kitanaka, Y.; Inoue, R.; Noguchi, Y.; Miyayama, M. Cooperative effect of oxygen-vacancy-rich layer and ferroelectric polarization on photovoltaic properties in BiFeO<sub>3</sub> thin film capacitors. *Appl. Phys. Lett.* **2016**, *108*, 032901.

(38) Matsuo, H.; Kitanaka, Y.; Noguchi, Y.; Miyayama, M. Strong interaction between ferroelectric polarization and oxygen vacancy in BiFeO<sub>3</sub> thin film capacitors. *J. Ceram. Soc. Jpn.* **2016**, *124*, 634–638.