

Domain Engineering for Enhanced Ferroelectric Properties of Epitaxial (001) BiFeO₃ Thin Films

By Ho Won Jang, Daniel Ortiz, Seung-Hyub Baek, Chad M. Folkman, Rasmi R. Das, Pdraic Shafer, Yanbin Chen, Christofer T. Nelson, Xiaoqing Pan, Ramamoorthy Ramesh, and Chang-Beom Eom*

Multiferroic BiFeO₃ has attracted great interest due to its promising application to magnetoelectric devices.^[1–3] In addition, the high remanent polarization and piezoelectric response of BiFeO₃ thin films, which are comparable to those of conventional Ti-rich lead zirconia titanate, suggested BiFeO₃ as a strong candidate for lead-free nonvolatile memories.^[4] BiFeO₃ has a rhombohedral perovskite structure with pseudocubic lattice parameters $a_r = 3.96 \text{ \AA}$ and $\alpha_r = 0.6^\circ$.^[5] Due to this low symmetry, (001)-oriented epitaxial BiFeO₃ films possess the rhombohedral distortion along one of the four (111) crystallographic directions of the pseudocubic perovskite unit cell.^[6] Thus, eight possible polarization (ferroelectric) variants, which correspond to four structural (ferroelastic) domains, may form in the films, leading to complex domain patterns with both {100} and {101} twin boundaries.^[6,7] Such a complex domain structure can deteriorate the ferroelectric response of the system by external electric field, and complicates the examination of the coupling between magnetic and ferroelectric order parameters in BiFeO₃.^[3] Recently, several studies have shown that high-quality (001)-oriented BiFeO₃ thin films with two-variant stripe domains can be achieved by using miscut^[8] and orthorhombic^[9,10] substrates. However, the clear identification of the origin of the stripe domains in BiFeO₃ thin films has not yet been reported. Furthermore, correlating the ferroelastic domain structures of BiFeO₃ thin films with the ferroelectric properties is a critical, yet missing link between materials properties and device performance.

In this communication, we report the origin of the ferroelastic domain variant selection in (001) BiFeO₃ films on miscut (001) SrTiO₃ substrates with coherent SrRuO₃ bottom electrodes, and its effect on the ferroelectric properties of the films. To our best

knowledge, this is the first report that ferroelectric switching behavior and leakage current in BiFeO₃ films are simultaneously improved by domain engineering. For the demonstration of the domain variant selection in BiFeO₃ films by substrate miscut, the SrTiO₃ substrate was chosen to have either 0.05° or 4° miscut toward the [100] direction, which corresponds to the downhill miscut direction. Since the step width of the 0.05° miscut substrate (~460 nm) is much larger than that of the 4° miscut substrate (6 nm), the effects of the substrate on the strain relaxation and domain structure can be resolved using both substrates (in this letter we call 0.05° miscut *exact* and 4° miscut *miscut*, for convenience). Atomic force microscopy (AFM) and reciprocal space mapping (RSM) using high-resolution X-ray diffraction (HRXRD) show that the *miscut* substrate leads to step-flow growth and two-variant strip domains in the BiFeO₃ film. In contrast, the *exact* substrate causes 3D island-growth and four-variant domains. Combined with transmission electron microscopy (TEM) and piezoelectric force microscopy (PFM) results, it is suggested that both the preferential distortion of unit cells and the complete step-flow growth induced by the substrate anisotropy are the origins of the formation of the two-variant stripe domains in (001) BiFeO₃ films. Finally, the polarization–electric field (P – E) hysteresis loop and leakage-current measurements allow us to find that two-variant stripe domains provide complete ferroelectric switching in BiFeO₃ thin films with low leakage current.

The growth mode of the epitaxial BiFeO₃ film can be clarified by monitoring the change of surface morphology with increasing film thickness. AFM images were obtained before and after the deposition of BiFeO₃ films on both *exact* and *miscut* (001) SrTiO₃ substrates with coherent SrRuO₃ bottom electrodes, as shown in Figure 1. The surface of the 100 nm thick SrRuO₃ on the *exact* substrate is atomically smooth with one unit cell high (4 Å) steps (Fig. 1a). The terrace width is ~500 nm, which is consistent with the miscut angle of 0.05°. After the deposition of BiFeO₃ on top of SrRuO₃ bottom electrode, the 100 nm thick BiFeO₃ film on the *exact* substrate exhibits many protrusions and holes (Fig. 1b). The propagation of atomic steps is randomly oriented, as indicated by white arrows. With increasing thickness to 400 nm, the film shows a much rougher surface with big islands (Fig. 1c), consistent with the 3D island-formation growth mode.^[11]

In contrast, completely different surface morphology can be observed in BiFeO₃ films on the *miscut* substrate. The AFM image of the SrRuO₃ bottom electrode shows the periodic steps (Fig. 1d), originating from step bunching due to the small terrace width. The actual terrace width (140 nm) is much larger than the

[*] Prof. C. B. Eom, Dr. H. W. Jang, D. Ortiz, S. H. Baek, C. M. Folkman, R. R. Das

Department of Materials Science and Engineering
University of Wisconsin
Madison, WI 53706 (USA)
E-mail: eom@engr.wisc.edu

P. Shafer, Prof. R. Ramesh
Department of Physics and Department of Materials Science and Engineering
University of California
Berkeley, CA 94720 (USA)

Dr. Y. B. Chen, C. T. Nelson, Prof. X. Q. Pan
Department of Materials Science and Engineering
University of Michigan
Ann Arbor, MI 48109 (USA)

DOI: 10.1002/adma.200800823

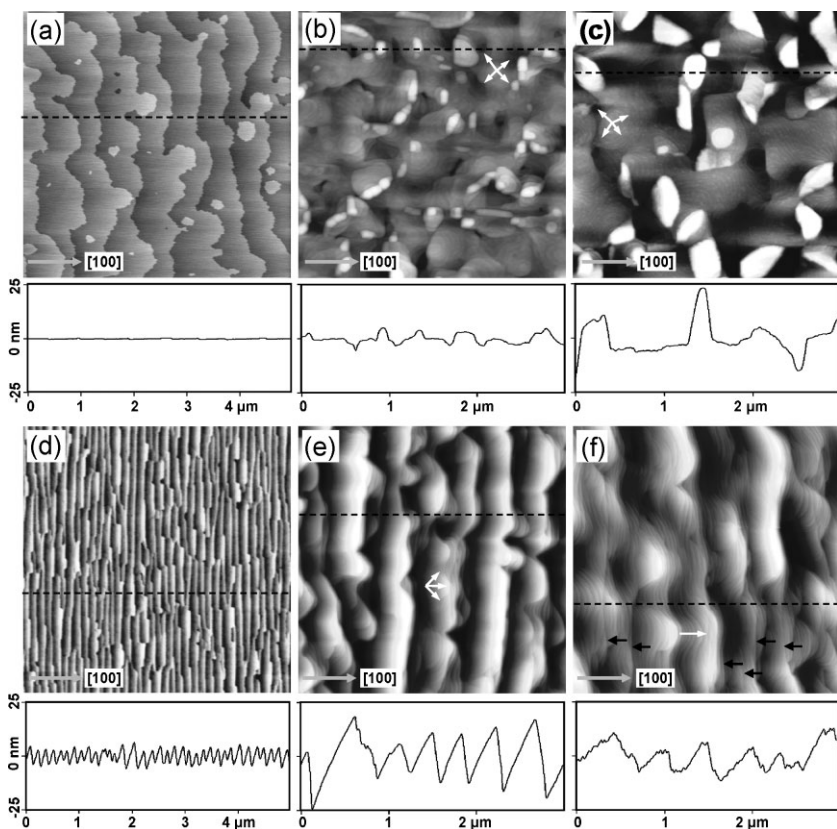


Figure 1. AFM images of a,d) before and after b,e) 100 nm and c,f) 400 nm thick BiFeO₃ films on a–c) *exact* and d–f) *miscut* SrTiO₃, with coherent 100 nm thick SrRuO₃ bottom electrodes. The white arrows indicate the directions of step propagation. The line profiles were obtained across the dotted lines in the corresponding images. The black arrows in f) indicate domain boundaries.

estimated value based on the miscut angle (6 nm), due to step bunching. After the deposition of BiFeO₃, the 100 nm thick BiFeO₃ film displays terraces 500 nm wide (Fig. 1e), which means that step bunching also happens during the growth of BiFeO₃ on the *miscut* substrate. The atomic steps propagate along the miscut direction. As the film gets thicker, the film surface gets smoother, and the flat terraces fade away with the formation of a number of small steps along the miscut direction (Fig. 1f). Note that the thicker film still exhibits a surface morphology of the step-flow growth mode^[11] without formation of 3D islands. The step-flow growth of BiFeO₃ was also reported using orthorhombic DyScO₃ substrates.^[9]

In order to determine the domain structures and the crystallographic distortion of each domain with respect to the substrate miscut direction, BiFeO₃ films were investigated using the HRXRD RSM technique. Figure 2 shows RSM patterns around SrTiO₃ 013 reflections for BiFeO₃ films 400 nm thick on *exact* and *miscut* SrTiO₃. The single narrow peak for SrRuO₃ 013_p reflections indicates that the SrRuO₃ layers on both substrates are single-domain. Since the crystal structure of SrRuO₃ is cubic at the BiFeO₃ growth temperature (690 °C),^[12] the surface of the SrRuO₃ layer is crystallographically identical to that of the underlying SrTiO₃ substrate. This indicates that the SrRuO₃ bottom electrodes have no additional effect on the growth of

BiFeO₃. In contrast to the SrRuO₃ bottom electrodes, BiFeO₃ films show broad peaks with different shapes compared with the substrate. Analysis on the RSM patterns suggested that the BiFeO₃ film on *exact* SrTiO₃ has four domains (Fig. 2a), but clearly exhibits only two domains on *miscut* SrTiO₃ (Fig. 2c). The BiFeO₃ film on *exact* SrTiO₃ shows the same intensity for each domain, whereas that on *miscut* SrTiO₃ displays two different peak intensities. The RSM pattern around the 0 $\bar{1}$ 3 SrTiO₃ reflection (not shown here) revealed that the peak intensities of both BiFeO₃ domains on *miscut* SrTiO₃ are exactly reversed after rotating the film by $\Phi = 180^\circ$, indicating the equal amount of both domains in the film. According to Streiffer et al.,^[6] there are four structural domains of a rhombohedral phase, r_1 , r_2 , r_3 , and r_4 . Using these notations, we can identify all domains of both BiFeO₃ films, as shown in Figure 2b and d. Note that the BiFeO₃ film on *miscut* (001) SrTiO₃ has the rhombohedral distortion only along the [100] direction (distortion angle $\alpha_m = 0.65^\circ$), while that on *exact* SrTiO₃ has the distortion along both [100] and $[\bar{1}00]$ directions ($\alpha_e = \pm 0.4^\circ$). These results provide direct evidence that the miscut substrate significantly affects the domain structure of the BiFeO₃ film. The peak width of BiFeO₃ film along the $0k0$ direction is much narrower in the film on *miscut* SrTiO₃, indicating the improvement of crystalline quality in BiFeO₃ films by using that substrate. Details on the crystal symmetry and domain structure of the

BiFeO₃ films on *exact* and *miscut* (001) SrTiO₃ substrates will be discussed elsewhere.^[10]

In the cross-sectional views of a (001) rhombohedral film along [100] direction by Streiffer et al.,^[6] r_1/r_2 or r_3/r_4 pairs form {100} twin boundaries, and r_1/r_4 or r_2/r_3 pairs form {101} twin boundaries. It suggests that a film with all four r_1 , r_2 , r_3 , and r_4 domains can have both {100} and {101} twin boundaries, but a film with only two domains will have one preferred boundary orientation. This is consistent with our experimental results. Figure 3a and c show cross-sectional TEM images of 600 nm thick BiFeO₃ films on *exact* and *miscut* (001) SrTiO₃, respectively. The film on the *exact* substrate shows irregular domains with both {100} and {101} twin boundaries. In contrast, the film on the *miscut* substrate exhibits periodic domains with {101} twin boundaries, namely stripe domains. Corresponding domain configurations for both films are identified and schematically presented. The width of stripe domains is determined to be 200~250 nm for 400~600 nm films,^[13] which is consistent with the spacing between domain boundaries parallel with the nonmiscut direction seen in the AFM image in Figure 1f. It is clear that the BiFeO₃ film on the *exact* substrate has four polarization variants (Fig. 3a), and the BiFeO₃ film on the *miscut* substrate has two polarization variants (Fig. 3c). The in-plane PFM images confirm four variants in the

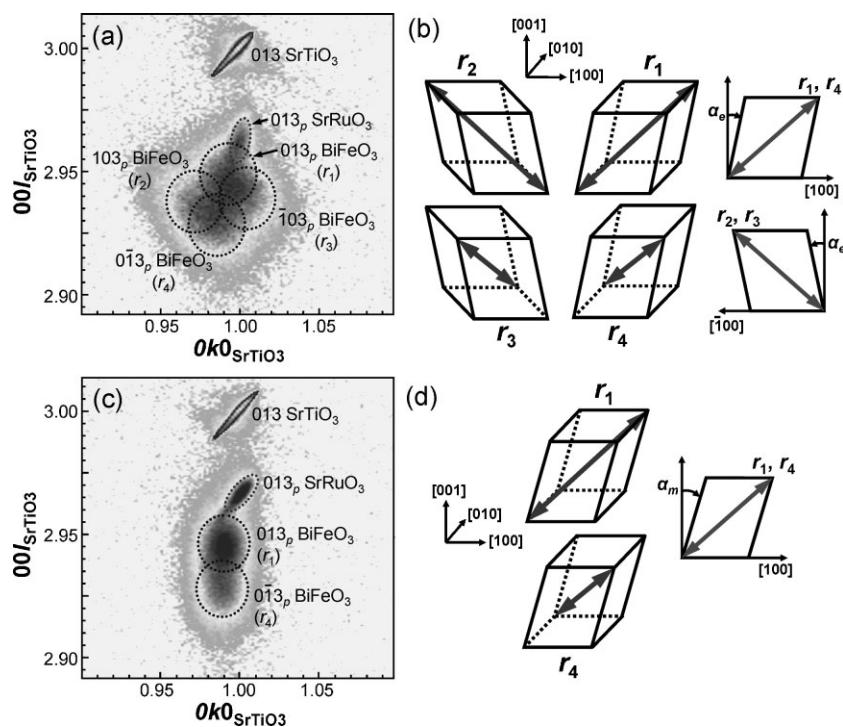


Figure 2. RSM images around 103 SrTiO₃ reflections for BiFeO₃ films 400 nm thick on a) *exact* and c) *miscut* SrTiO₃. Subscript *p* represents pseudocubic setting. The schematics describe b) four structural domains in the film on the *exact* substrate and d) two domains in the film on the *miscut* substrate. The black arrows indicate the polarization direction of each domain in the unit cell and the (010) plane. α_e ($= 0.4^\circ$) and α_m ($= 0.65^\circ$) are the rhombohedral distortion angles.

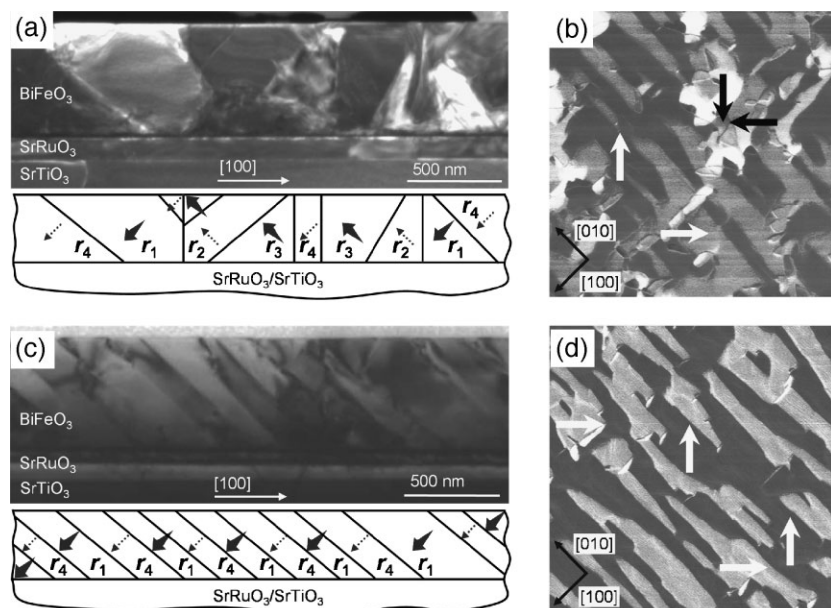


Figure 3. Cross-sectional TEM images of BiFeO₃ films 600 nm thick on a) *exact* and c) *miscut* SrTiO₃. In-plane PFM images ($4 \mu\text{m} \times 4 \mu\text{m}$) of BiFeO₃ films 40 nm thick on b) *exact* and d) *miscut* SrTiO₃ were obtained with an ac bias of $3 V_{pp}$ at 6.39 kHz. The arrows in each PFM image represent directions of in-plane polarization, indicating four variants on *exact* SrTiO₃ and two variants on *miscut* SrTiO₃.

BiFeO₃ film on *exact* SrTiO₃ (Fig. 3b) and two variants in the BiFeO₃ film on *miscut* SrTiO₃ (Fig. 3d).

It was observed that an 800 nm thick BiFeO₃ film on *miscut* substrate still has only two variants. This fact suggested that the elastic-strain energy in BiFeO₃ films on *miscut* substrates are effectively relieved without forming additional domain variants (*r*₂ and *r*₃). There are two competing mechanisms for strain relaxation, namely surface roughening and crystallographic tilt by dislocation multiplication.^[14] The AFM images clearly indicate that the BiFeO₃ films on *exact* SrTiO₃ exhibit strain relaxation by surface roughening. However, there was no surface roughening in the BiFeO₃ films on *miscut* SrTiO₃. Thus, we measured the crystallographic tilt of BiFeO₃ films respective to the SrRuO₃ bottom electrodes using RSM patterns around 002 SrTiO₃ reflections along two orthogonal directions (*miscut* and *nonmiscut* directions), as shown in Figure 4a. As expected, there is no film tilt along the [010] direction (*nonmiscut* direction) because the *miscut* angle does not exist for the films to tilt against the substrate. However, the tilt of the films along the [100] direction (*miscut* direction) is significant. The highly strained 20 and 50 nm films have negative tilt angles, due to the intrinsic tilt mechanism described by Nagai,^[15] in which a compressively strained coherent film tilts away from the surface normal due to lattice mismatch on the surface steps of the *miscut* substrate, as shown in the inset of Figure 4a. With increasing film thickness, the film tilts toward the direction normal to the surface, reducing the angle between this and the [001] direction of the film (Fig. 4b). This positive tilt is evidence of preferential dislocation nucleation, which corresponds to strain relaxation in the film to relieve its total elastic energy.^[14] It should be noted that the tilt of the BiFeO₃ films is observed along the *miscut* direction, and not in the *nonmiscut* direction.

The tilting of BiFeO₃ films along the [001] direction is attributed to the anisotropic strain relaxation in the films on *miscut* substrates. Figure 4c and d show the in-plane and out-of-plane lattice parameters of BiFeO₃ films on *exact* and *miscut* SrTiO₃ as a function of film thickness. With increasing film thickness, the in-plane lattice parameters increase and the out-of-lattice parameters decrease, due to the relaxation of biaxial compressive strains. As the film thickness increases, the films on *exact* SrTiO₃ display almost identical variation in in-plane lattice parameters along [100] and [010] directions (Fig. 4c). In contrast, the films on

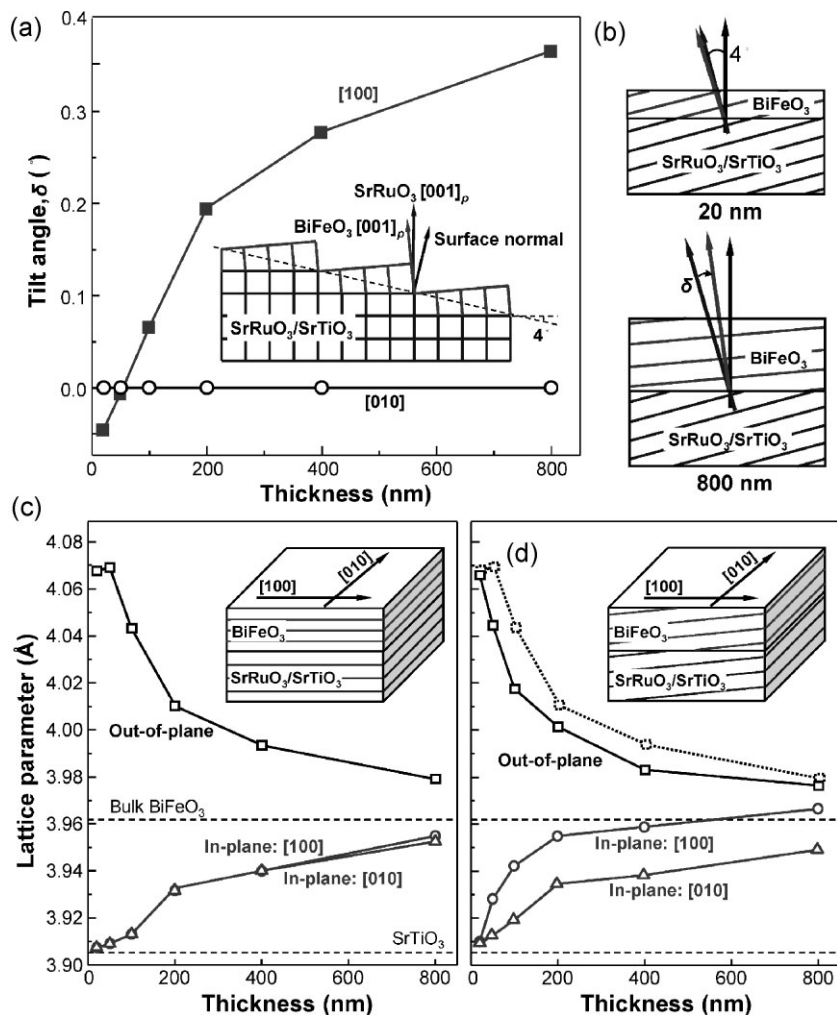


Figure 4. a) Tilt angle as a function of film thickness for BiFeO₃ films on *miscut* SrTiO₃ substrate with SrRuO₃ bottom electrodes. The inset is a schematic for the negative tilting of coherent BiFeO₃ films on the *miscut* SrRuO₃/SrTiO₃ substrate. b) Schematic diagrams for the change of the tilt angle for the BiFeO₃ films with thickness. Pseudocubic lattice parameters were measured as a function of film thickness for BiFeO₃ films grown on c) *exact* and d) *miscut* SrTiO₃. The dotted line in d) represents the out-of-plane lattice parameter of the BiFeO₃ film on *exact* SrTiO₃.

miscut SrTiO₃ show faster in-plane strain relaxation along the *miscut* direction ([100] direction) than along the non*miscut* direction ([010] direction) (Fig. 4d). Thus, the overall strain relaxation is faster in the films on *miscut* SrTiO₃. This result confirms the in-plane anisotropy of the *miscut* substrate, which has also been observed in the tilting of the crystallographic planes and in the AFM images.

Based on these experimental results, the origin of ferroelastic domain variant selection in epitaxial (001) BiFeO₃ films by the *miscut* substrate is described as follows. On the *exact* substrate, the terrace width is too large for BiFeO₃ to grow in a step-flow growth mode. As a result, 3D islands are formed. As the film gets thicker, the shear strain in the film, induced by the rhombohedral symmetry of BiFeO₃, should be relieved by the rhombohedral distortion of the unit cells. Since the film has biaxially isotropic strain, the rhombohedral distortion occurs randomly, and is

described as distortions along both [100] and $\bar{1}00$ directions in the (010) plane. As seen in Figure 5a, r_1 and r_4 are twins with the (101) plane, and r_1 and r_2 with the (100) plane. As a result, all four r_1 , r_2 , r_3 , and r_4 domains are formed in the film {101} and {100} twin boundaries. It is easily speculated that r_2 or r_3 domains are formed preferentially to the 3D islands, creating {100} boundaries. On the *miscut* substrate, the small terrace width drives BiFeO₃ to adopting a complete step-flow growth mode. This prevents the formation of 3D islands for r_2 or r_3 domains, because the rhombohedral distortion toward the step edge is not energetically favorable, as shown in Figure 5b. Furthermore, the *miscut* substrate drives the films to tilting along the [100] direction (Fig. 4a), which corresponds to the preferential rhombohedral distortions to the downhill *miscut* direction, as shown in Figure 5b. In other words, the *miscut* substrate removes from the film the degree of freedom of having rhombohedral distortions for r_2 and r_3 . Consequently, r_1 and r_4 stripe domains with (101) twin boundaries are formed in the film.

The effects on the ferroelectric properties of BiFeO₃ films can be explored by measuring P - E hysteresis loops. The domain selection by the *miscut* substrate greatly affects the ferroelectric switching behavior of BiFeO₃. The 400 nm thick BiFeO₃ film on *miscut* SrTiO₃ exhibits perfect square-like P - E loops (Fig. 6a). The remanent polarization (P_r) value is measured to be $64 \pm 2 \mu\text{C cm}^{-2}$. Compared with the P_r of bulk single-crystal BiFeO₃ ($\sim 60 \mu\text{C cm}^{-2}$),^[16] it is concluded that complete domain switching is obtained from the BiFeO₃ films with the two-variant stripe domains. The higher P_r values of the films than those of BiFeO₃ bulk single-crystal can be attributed to the strain-induced polarization rotation.^[17] In contrast, the 400 nm thick

BiFeO₃ film on *exact* SrTiO₃ displays an unclosed and slanted loops at the lower frequency, and drastically lower P_r values of $43 \pm 5 \mu\text{C cm}^{-2}$ (Fig. 6b). The slanted loop indicates the nonuniformity of the domains, in that each one in the film has a different coercivity. This suggests that some of domains are very hard to switch with applied field, leading to the lower P_r . As seen in TEM and PFM images, more uniform and ordered ferroelectric (ferroelastic) domains are seen for films on *miscut* than on *exact* substrates, contributing to a square-like loop rather than a slanted P - E loop. To confirm the significantly different switching behaviors between both films, pulsed-polarization measurements were carried out as functions of applied field and pulse width. Figure 6c shows the switching polarization (ΔP) as a function of electric field. The saturated ΔP values for both films are in excellent agreement with the $2P_r$ value from the P - E loops, clarifying the reduced P_r in the film on *exact* SrTiO₃. From

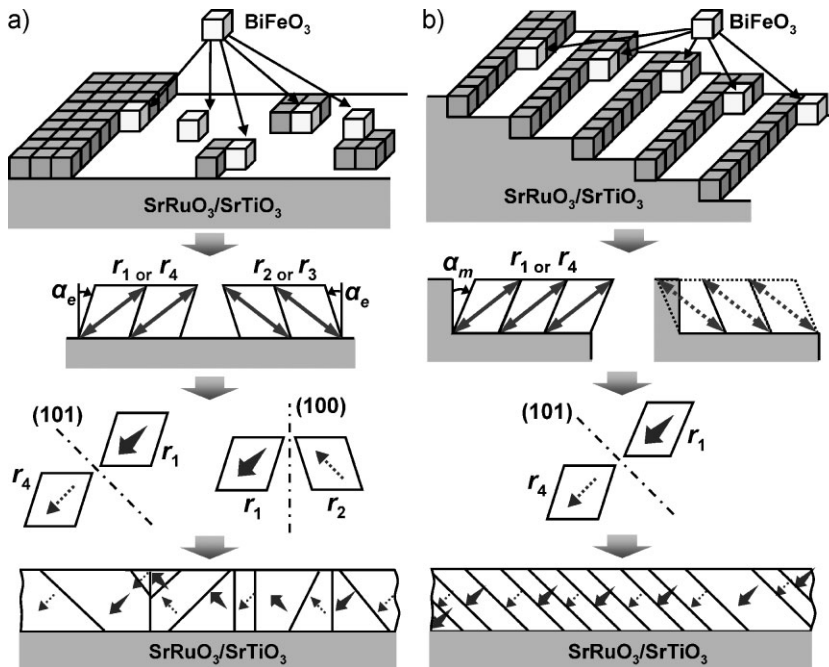


Figure 5. Schematic drawings for the initial growth, domain selection, formation of domain boundaries, and final structure for BiFeO₃ films on a) *exact* and b) *miscut* SrTiO₃ substrates with SrRuO₃ bottom electrodes. The formation of r_2 and r_3 domains is prohibited in BiFeO₃ films on *miscut* SrTiO₃ substrates, because the rhombohedral distortion for r_2 and r_3 is mechanically unfavorable.

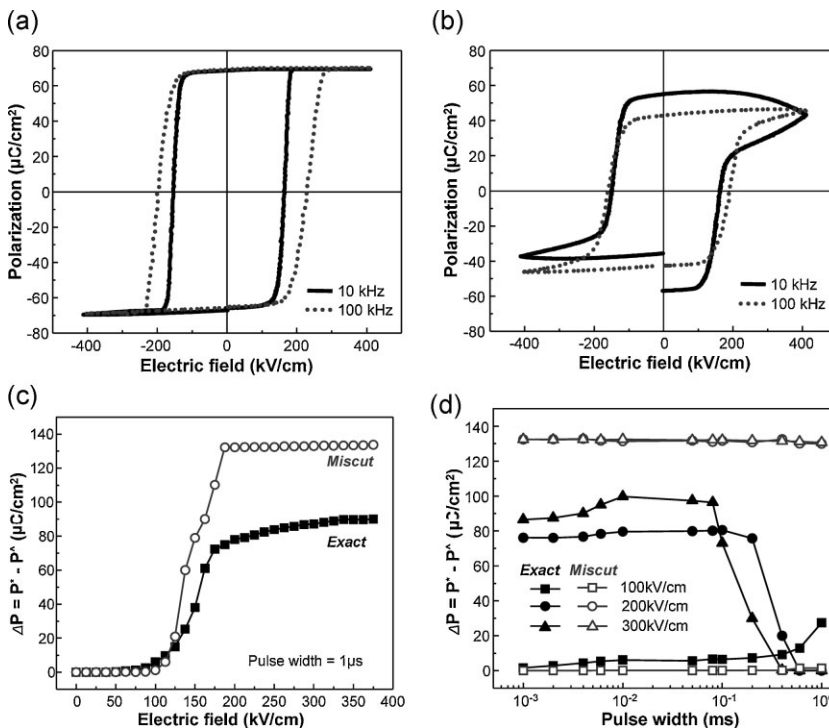


Figure 6. P - E hysteresis loops of BiFeO₃ films 400 nm thick on a) *miscut* and b) *exact* SrTiO₃ at room temperature. Switching polarization (ΔP) as a function of c) applied electric field and d) pulse width for BiFeO₃ films 400 nm thick on *miscut* and *exact* SrTiO₃.

starting to increase to saturating, the ΔP of the film on *miscut* SrTiO₃ shows a narrower and abrupt transition, whereas that of the film on the *exact* SrTiO₃ shows a more gradual transition, consistent with the difference in the shape of P - E loops (square-like vs. slanted). With increasing the pulse width from 1 μ s to 1 ms, the ΔP of the film on *miscut* SrTiO₃ remained constant at 132 μ C cm⁻² at 200 and 300 kV m⁻¹. However, the film on *exact* SrTiO₃ shows different ΔP values at 200 and 300 kV m⁻¹, and a stark contrast when ΔP becomes zero with pulses approaching 1 ms at 200 and 300 kV m⁻¹. This means that the film does not switch at all with long pulse widths.

Significant reduction in leakage current density is found in BiFeO₃ films on *miscut* SrTiO₃. Figure 7a shows leakage current density as a function of applied electric field for 400 nm thick BiFeO₃ films on both *exact* and *miscut* SrTiO₃. The film on the *exact* substrate displays a leakage current density around 2×10^{-3} A cm⁻² at 100 kV cm⁻¹, which is comparable to the previously reported values between 5×10^{-1} and 5×10^{-3} A cm⁻² at 100 kV cm⁻¹.^[18-20] Note that the leakage current density is reduced by two orders of magnitude for the film on the *miscut* substrate. The leakage current density of 3×10^{-5} A cm⁻² at 100 kV cm⁻¹ is the lowest value ever reported for BiFeO₃ films.^[21] Current-time measurements were carried out to examine current relaxation in both films, as shown in Figure 7b. The leakage current for the film on the *miscut* substrate stabilizes in 10 ms, whereas the current relaxation for the film on the *exact* substrate is very slow, and does not stabilize even in 100 ms, implying that the film has a lot of free charge carriers with oxygen vacancies, resulting in high leakage current levels and slow current relaxation times.^[22]

We believe there are two possible mechanisms for the origin of the higher leakage current in BiFeO₃ films on *exact* SrTiO₃, namely i) domain structure and ii) nonstoichiometric point defects. The first mechanism operates through the notion that 109° domain walls are dominant leakage paths rather than the bulk matrix, as shown in Figure 7c. According to Streiffer et al.,^[6] a rotational deformation of opposite sense about the (010) direction in adjacent domains is required to bond the vertical 109° domains to the substrate, which is not necessary for the 71° domains with (101) twin boundaries to be bonded to the substrate. This additional deformation can cause the width of the 109° domain walls to be larger and generate charge carriers near the walls. In addition, the 109°

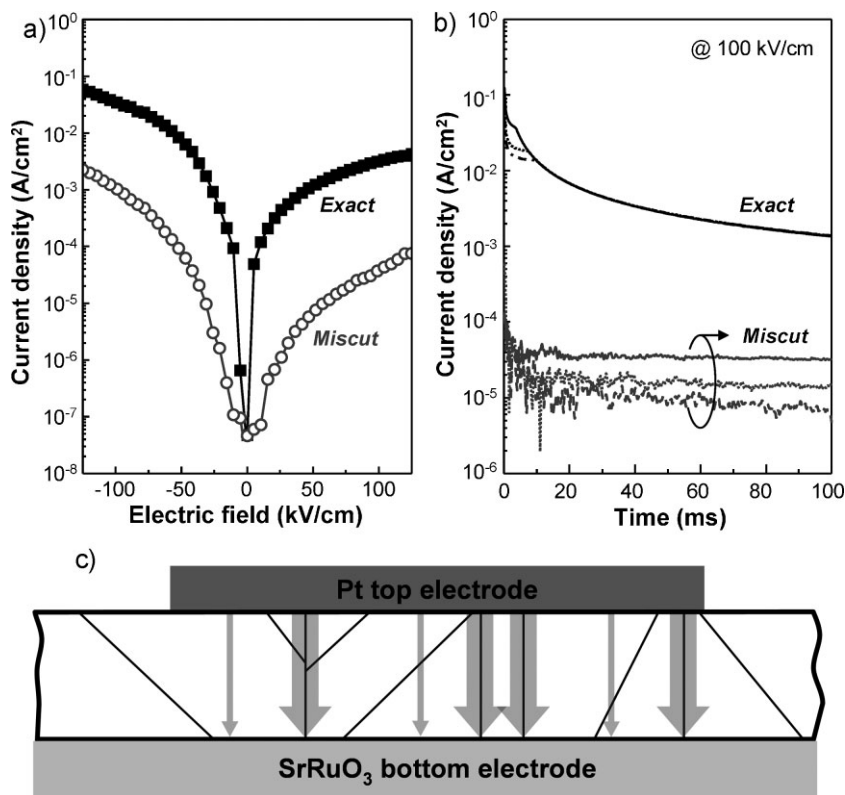


Figure 7. a) Current–voltage characteristics of BiFeO₃ films 400 nm thick on *exact* and *miscut* SrTiO₃. The measure time for each point was 100 ms. b) Current–time characteristics of BiFeO₃ films 400 nm thick on *exact* and *miscut* SrTiO₃. c) Schematic drawing for leakage paths in BiFeO₃ film 400 nm thick on *exact* SrTiO₃. The arrows represent leakage current through the film, showing that the vertical 109° domain walls are dominant leakage paths rather than the bulk matrix.

domain wall is parallel to the electric field. Thus, the 109° domain wall can become a predominant leakage path in the film on *exact* SrTiO₃, leading to the high leakage current.

The second mechanism operates through the notion that the bulk matrix is the dominant leakage path rather than domain walls. Although BiFeO₃ films on *exact* as well as *miscut* SrTiO₃ are stoichiometric, with a Bi/Fe 1:1 ratio, and have no secondary phases, there is the possibility of formation of point defects, such as oxygen vacancies, in the films. It is generally accepted that the *miscut* substrate leads to the formation of preferential domains and the stabilization of stoichiometric phases.^[23] The longer step width on *exact* SrTiO₃ means longer time for adapted atoms to reach the step edge and crystallize. The relatively volatile bismuth adatoms can evaporate from the film surface during the growth, and thus bismuth and oxygen vacancies are formed in the films after growth. As a result, those nonstoichiometric point defects spread out in the films, leading to the large leakage current. Detailed studies on the high leakage current on *exact* SrTiO₃ are currently underway.

In epitaxial (001) BiFeO₃ films, polarization switching occurs with the formation of both ferroelectric and ferroelastic domain walls.^[7] According to Wicks et al.,^[24] grain boundaries in Pb(Zr_xTi_{1-x})O₃ thin films impede domain-wall movement, and are able to nucleate domains that are opposite to those generated by an electric field. From this, we believe that 109° domain walls contribute to the reduction in P_r due to incomplete switching for

BiFeO₃ films on *exact* substrates. The domain-wall motions for polarization switching can be delayed and impeded by the larger walls between 109° domains, resulting in incomplete switching with the applied electric field. At very high electric fields, nonswitchable domains can be switched, and then complete switching can be obtained. However, at such high fields, the leakage current through the vertical 109° domain walls and/or bulk matrices becomes predominant, and thus complete switching cannot be obtained. For this same reason, the films do not switch with the long pulse widths in Figure 6d. A recent study on PFM of (011) BiFeO₃ films showed that 109° domain switching is less stable and less electrically controllable than 71° domain switching, partially supporting our suggestion.^[25]

In conclusion, we have demonstrated the selection of domain-structure variants in epitaxial BiFeO₃ films, and consequently achieved significant improvement in ferroelectric switching behavior and leakage current by employing miscut in cubic (001) SrTiO₃ substrates. BiFeO₃ films on *miscut* SrTiO₃ have a step-flow growth and a preferential rhombohedral distortion toward the miscut direction. This result indicates that both the substrate anisotropy and the step-flow growth of BiFeO₃ are the origins of the two-variant stripe domains in BiFeO₃ films. Square-like P - E loops and very low leakage current densities are obtained from these BiFeO₃ films. In contrast, BiFeO₃ films on *exact* SrTiO₃ exhibit low P_r values and high leakage currents. From this, we suggest that 109° domain walls prevent the complete ferroelectric switching of (001) BiFeO₃ domains and act as dominant leakage paths in the four-variant BiFeO₃ films, whereas the intrinsic ferroelectric properties of BiFeO₃ can be observed from two-variant BiFeO₃ films with 71° domain walls.^[26] The dependence of ferroelectric properties on domain-wall configuration opens the exciting opportunity to investigate the correlation between domain walls and the antiferromagnetic order in BiFeO₃. We believe that such domain engineering can be very useful for growing high-quality BiFeO₃ films on cubic (001) Si substrates for device applications^[27] and more generally for heterostructures with rhombohedral thin films, such as Pb(Zr_xTi_{1-x})O₃, Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃, La_{1-x}Sr_xMnO₃, and LaAlO₃.

Experimental

Epitaxial (001) BiFeO₃ films were grown by off-axis radio-frequency (rf) magnetron sputtering on 0.05 and 4° miscut (001) SrTiO₃ substrates^[8]. Prior to the deposition of the BiFeO₃ films, an epitaxial 100 nm thick SrRuO₃ bottom electrode was deposited by 90° off-axis rf magnetron sputtering^[28]. The thicknesses of the BiFeO₃ films were varied from 20 to 800 nm. The surface morphology and piezoelectric properties of BiFeO₃/SrRuO₃ heterostructures were investigated using a DI Multimode AFM system^[7]. A commercially available high-resolution four-circle X-ray

diffractometer (D8 Advance, Bruker A×S) was used in HRXRD-RSM measurements. TEM studies were carried out on a Philips CM12 operated at 120 kV with a high-angle ($\pm 60^\circ$) double-tilt holder, and on a JEOL 3011 ultrahigh-resolution TEM operated at 300 kV with a point-to-point resolution of 0.17 nm. Pt top electrodes (100 μm in diameter) were patterned to measure the ferroelectric properties using a Radiant PFH100 ferroelectric measurement system.

Acknowledgements

The authors gratefully acknowledge the financial support of the National Science Foundation through grants ECCS-0708759, 0425914, the Office of Naval Research through grant N00014-05-1-0559, and the Department of Energy under grant DE-FG02-07ER46416. The corresponding author wants to thank Paul Evans for helpful discussions.

Received: March 25, 2008

Revised: August 20, 2008

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