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

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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 = 3.96 Å and αr = 0.6.[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 BeFeO3 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, 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 (4Å) 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
estimated value based on the miscut angle (6 nm), due to step bunching. After the deposition of BiFeO$_3$, the 100 nm thick BiFeO$_3$ film displays terraces 500 nm wide (Fig. 1e), which means that step bunching also happens during the growth of BiFeO$_3$ 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 BiFeO$_3$ was also reported using orthorhombic DyScO$_3$ substrates.$^{[9]}$

In order to determine the domain structures and the crystallographic distortion of each domain with respect to the substrate miscut direction, BiFeO$_3$ films were investigated using the HRXRD RSM technique. Figure 2 shows RSM patterns around SrTiO$_3$ 013 reflections for BiFeO$_3$ films 400 nm thick on exact and miscut SrTiO$_3$. The single narrow peak for SrRuO$_3$ 013$_p$ reflections indicates that the SrRuO$_3$ layers on both substrates are single-domain. Since the crystal structure of SrRuO$_3$ is cubic at the BiFeO$_3$ growth temperature (690 $^\circ$C)$^{[12]}$, the surface of the SrRuO$_3$ layer is crystallographically identical to that of the underlying SrTiO$_3$ substrate. This indicates that the SrRuO$_3$ bottom electrodes have no additional effect on the growth of BiFeO$_3$. In contrast to the SrRuO$_3$ bottom electrodes, BiFeO$_3$ films show broad peaks with different shapes compared with the substrate. Analysis on the RSM patterns suggested that the BiFeO$_3$ film on exact SrTiO$_3$ has four domains (Fig. 2a), but clearly exhibits only two domains on miscut SrTiO$_3$ (Fig. 2c). The BiFeO$_3$ film on exact SrTiO$_3$ shows the same intensity for each domain, whereas that on miscut SrTiO$_3$ displays two different peak intensities. The RSM pattern around the 013 SrTiO$_3$ reflection (not shown here) revealed that the peak intensities of both BiFeO$_3$ domains on miscut SrTiO$_3$ 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 BiFeO$_3$ films, as shown in Figure 2b and d. Note that the BiFeO$_3$ film on miscut (001) SrTiO$_3$ has the rhombohedral distortion only along the [100] direction (distortion angle $\alpha_{\text{miscut}} = 0.65^\circ$), while that on exact SrTiO$_3$ has the distortion along both [100] and [\bar{1}00] directions ($\alpha_c = \pm 0.4^\circ$). These results provide direct evidence that the miscut substrate significantly affects the domain structure of the BiFeO$_3$ film. The peak width of BiFeO$_3$ film along the $\tilde{0}k\tilde{0}$ direction is much narrower in the film on miscut SrTiO$_3$, indicating the improvement of crystalline quality in BiFeO$_3$ films by using that substrate. Details on the crystal symmetry and domain structure of the BiFeO$_3$ films on exact and miscut (001) SrTiO$_3$ substrates will be discussed elsewhere.$^{[10]}$

In the cross-sectional views of a (001) rhombohedral film along [100] direction by Streiffer et al.$^{[10]}$, $r_1/r_2$ or $r_3/r_4$ pairs form {100} twin boundaries, and $r_2/r_3$ or $r_3/r_4$ 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 BiFeO$_3$ films on exact and miscut (001) SrTiO$_3$, 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~$\sim$ 250 nm for 400~$\sim$ 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 BiFeO$_3$ film on the exact substrate has four polarization variants (Fig. 3a), and the BiFeO$_3$ film on the miscut substrate has two polarization variants (Fig. 3c). The in-plane PFM images confirm four variants in the
BiFeO$_3$ film on *exact* SrTiO$_3$ (Fig. 3b) and two variants in the BiFeO$_3$ film on *miscut* SrTiO$_3$ (Fig. 3d).

It was observed that an 800 nm thick BiFeO$_3$ film on *miscut* substrate still has only two variants. This fact suggested that the elastic-strain energy in BiFeO$_3$ 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 BiFeO$_3$ films on *exact* SrTiO$_3$ exhibit strain relaxation by surface roughening. However, there was no surface roughening in the BiFeO$_3$ films on *miscut* SrTiO$_3$. Thus, we measured the crystallographic tilt of BiFeO$_3$ films respective to the SrRuO$_3$ bottom electrodes using RSM patterns around 002 SrTiO$_3$ 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 BiFeO$_3$ films is observed along the *miscut* direction, and not in the *nonmiscut* direction.

The tilting of BiFeO$_3$ 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 BiFeO$_3$ films on *exact* and *miscut* SrTiO$_3$, as a function of film thickness. With increasing film thickness, the in-plane lattice parameters increase and the out-of-plane parameters decrease, due to the relaxation of biaxial compressive strains. As the film thickness increases, the films on *exact* SrTiO$_3$ display almost identical variation in in-plane lattice parameters along [100] and [010] directions (Fig. 4c). In contrast, the films on...
SrTiO3 show faster in-plane strain relaxation along the miscut direction ([100] direction) than along the nonmiscut 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 on the miscut SrTiO3 substrate is described as distortions along both [100] and [010] directions in the (010) plane. As seen in Figure 4a, r1 and r4 are twins with the (101) plane, and r1 and r2 with the (100) plane. As a result, all four r1, r2, r3, and r4 domains are formed in the film {101} and {100} twin boundaries. It is easily speculated that r2 or r3 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 r2 or r3 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 r2 and r3. Consequently, r1 and r4 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 ± 2 μC cm⁻². Compared with the P_r of bulk single-crystal BiFeO3 (~60 μC cm⁻²), 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. 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 ± 5 μC 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.
starting to increase to saturating, the $\Delta P$ of the film on miscut SrTiO$_3$ shows a narrower and abrupt transition, whereas that of the film on the exact SrTiO$_3$ 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 $\mu$s to 1 ms, the $\Delta P$ of the film on miscut SrTiO$_3$ remained constant at 132 $\mu$C cm$^{-2}$ at 200 and 300 kV m$^{-1}$. However, the film on exact SrTiO$_3$ shows different $\Delta P$ values at 200 and 300 kV m$^{-1}$, and a stark contrast when $\Delta P$ 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 BiFeO$_3$ films on miscut SrTiO$_3$. Figure 7a shows leakage current density as a function of applied electric field for 400 nm thick BiFeO$_3$ films on both exact and miscut SrTiO$_3$. The film on the exact substrate displays a leakage current density around $3 \times 10^{-5}$ A cm$^{-2}$ at 100 kV cm$^{-1}$, which is comparable to the previously reported values between $5 \times 10^{-5}$ and $5 \times 10^{-4}$ 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 $3 \times 10^{-5}$ A cm$^{-2}$ at 100 kV cm$^{-1}$ is the lowest value ever reported for BiFeO$_3$ 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 BiFeO$_3$ films on exact SrTiO$_3$, 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°
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. 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. According to Wicks et al.,[24] grain boundaries in Pb(Zr, Ti)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 P1 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 filed. 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 (001) 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 P1 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, Ti)O3, Pb(Mg1/3 Nb2/3)O3-PbTiO3, La1–xSr1-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
differometer (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 (±60°) 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 nm in diameter) were patterned to measure the ferroelectric properties using a Radiant PFH100 ferroelectric measurement system.

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