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Origin of suppressed polarization in BiFeO₃ films

J. W. Park,¹ S. H. Baek,¹ P. Wu,² B. Winchester,² C. T. Nelson,³ X. Q. Pan,³ L. Q. Chen,² T. Tybell,^{1,4} and C. B. Eom^{1,a)}

¹Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA

²Department of Materials Science and Engineering, Penn State University, University Park, Pennsylvania 16802, USA

³Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA

⁴Department of Electronics and Telecommunications, Norwegian University of Science and Technology, 7491 Trondheim, Norway

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We have studied the origin of suppressed remanent polarization in 4-variant BiFeO₃ by correlating microscopic observations of ferroelectric/ferroelastic domain structures and ferroelectric measurements of (001) epitaxial BiFeO₃ thin films with 2- and 4-ferroelastic domain variants. Piezoelectric force microscopy revealed that domain wall pinning was the cause of the reduced polarization observed in 4-variant BiFeO₃. Using repetitive switching, the unswitched domains were completely switched and the remanent polarization reached a value comparable to 2-variant BiFeO₃. These results demonstrate that control of ferroelastic domains in rhombohedral systems is necessary in order to obtain high performance and reliable ferroelectric and magnetoelectric devices. © 2010 American Institute of Physics. [doi:10.1063/1.3506902]

Multiferroic BiFeO₃ (BFO) has attracted attention because of its potential application in nonvolatile memory technology and magnetoelectric devices.^{1–5} BFO has a rhombohedral perovskite structure with pseudocubic lattice parameters $a_r=3.96$ Å and $\alpha_r=0.6^\circ$.⁶ Due to the low symmetry of the unit cell, BFO films have four possible structural (ferroelastic) variants (r_1 , r_2 , r_3 , and r_4) and eight possible polarization (ferroelectric) variants (r_1^+ , r_1^- , r_2^+ , r_2^- , r_3^+ , r_3^- , r_4^+ , and r_4^-).⁷ This implies a complex domain and a twin structure with different domain walls, such as $\{101\}$ twin 71° , $\{100\}$ twin 109° , and $\{h\ k\ l\}$ (where, $\pm h \pm k + l = 0$) twin 180° domain walls.^{7,8}

The electrical properties of single-domain BFO epitaxial films are superior to those of multidomain epitaxial films.^{9,10} Recently, there has been focus on the possibility of using domain engineering to control the properties of BFO films—for example, by using vicinal substrates.^{9,11} Jang *et al.*⁹ reported that epitaxial 2-variant (001) BFO films on vicinal substrates exhibit superior ferroelectric and leakage properties compared to 4-variant (001) BFO films on exact (001) substrates. There has also been focus on the properties of the domain walls themselves.^{12,13} For example, Seidel *et al.*¹² recently reported room-temperature electrical conduction through 109° and 180° ferroelectric domain walls in (110) BFO films, and suggested that there is a correlation between domain wall conductivity and structurally driven changes in both the electrostatic potential and the local electronic structure of the domain wall.

In spite of these efforts, microscopic evidence of domain wall contributions to macroscopic ferroelectric properties and polarization switching is scarce. In this study, we report microscopic observations of suppressed polarization switching in domain-controlled epitaxial (001) BFO films through a

combination of local piezoelectric force microscopy (PFM) and macroscopic electrical measurements.

In order to study the contributions of domain walls and their configuration to polarization switching, we prepared epitaxial BFO films with two different domain structures. Vicinal (001) SrTiO₃ (STO) substrates, having 4° and 0.2° miscut toward the $[100]$ direction, were used (for convenience, we will call 4° miscut “high-miscut” and 0.2° miscut “low-miscut”). Prior to the deposition of the BFO films, 50 nm thick epitaxial SrRuO₃ (SRO) bottom electrodes were deposited by pulsed-laser deposition. From atomic force microscopy (AFM) analysis, both SRO bottom electrodes were found to exhibit periodic step-terrace structures; however, they were found to have different terrace widths. On the high-miscut STO, the SRO shows a step height of ~ 7.2 nm and a terrace width of ~ 120 nm, and on the low-miscut STO, a step height of ~ 3.4 nm and a terrace width of ~ 830 nm were obtained. Four-circle high-resolution x-ray diffraction (HRXRD) analysis confirmed that the SRO films on both the high- and low-miscut STO are fully coherent with the substrate and have the same out-of-plane (OP) lattice parameters (3.955 Å). Hence, only the different terrace widths of the SRO bottom electrodes affect the growth dynamics of BFO films.

After deposition of SRO, 600 nm thick epitaxial (001) BFO films were deposited by off-axis radio-frequency sputtering.^{14,15} HRXRD reciprocal space mapping (RSM) revealed that the BFO film on the high-miscut STO has a 2-variant ferroelastic domain structure [Fig. 1(a)], whereas the BFO film on the low-miscut STO has a 4-variant domain structure [Fig. 1(b)]. Both types of BFO films have the same OP-lattice parameters of ~ 3.98 Å.

Figure 1(c) shows polarization-electric field (P-E) hysteresis curves for both the 2- and 4-variant BFO films. The 2-variant BFO film exhibits a remanent polarization (P_r) value of ~ 64 $\mu\text{C}/\text{cm}^2$, whereas the 4-variant BFO film shows a lower P_r value of ~ 40 $\mu\text{C}/\text{cm}^2$. The origin of this

^{a)}Author to whom correspondence should be addressed. Electronic mail: eom@engr.wisc.edu.

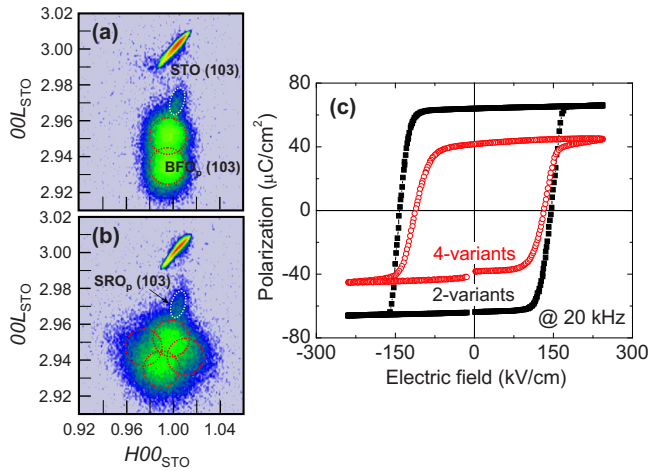


FIG. 1. (Color online) HRXRD RSM patterns of epitaxial (001) BFO films on (a) high-miscut and (b) low-miscut STO substrates. The BFO film on high-miscut STO is 2-variant, whereas the BFO film on low-miscut STO is 4-variant ferroelastic domain structure. (c) P-E hysteresis curves of epitaxial (001) BFO films with 2- and 4-variant ferroelastic domains. The size of Pt top electrode is 200 μm in diameter.

P_r suppression was investigated by PFM analysis. Figures 2(a)–2(c) display OP-PFM images of the 2-variant BFO film. Before PFM switching [Fig. 2(a)], all ferroelectric domains corresponded to down-polarization¹¹ and in-plane (IP)-PFM data (not shown here) showed a stripe-shaped domain structure consistent with a 2-variant ferroelectric/ferroelastic domain structure.⁹ The combination of IP-PFM and OP-PFM images also revealed that the BFO film consisted of only 71° domain walls.¹⁶

To switch the polarization, a dc bias voltage was applied between the AFM tip and the SRO bottom electrode. After

applying -10 V [Fig. 2(b)], all ferroelectric domains were switched to an up-polarization state. In addition, by subsequently applying $+10$ V [Fig. 2(c)], all domains switched back to the initial down-polarization state. The region in Fig. 2(c) still showing up-polarization is caused by a small off-set of the square written with $+10$ V as for the -10 V; hence, complete reversible switching was obtained.

On the other hand, the 4-variant BFO film exhibits a completely different switching behavior. Before PFM switching [Fig. 2(d)], the OP-PFM image shows both up- (dark regions) and down- (bright regions) polarized domains, and IP-PFM images revealed a mosaic-like domain structure, indicating 8-ferroelectric variants (4-ferroelastic variants). By combining the OP-PFM and IP-PFM images, it was found that both the 109° and 180° domain walls, as well as the 71° domain walls, coexist in the 4-variant BFO film.

By applying -10 V to the tip [Fig. 2(e)], all ferroelectric domains were switched to up-polarization state, as for the 2-variant BFO film. After applying $+10$ V [Fig. 2(f)], some regions were not switched back to the initial state. From a comparison of PFM images before [Fig. 2(d)] and after [Fig. 2(f)] the PFM switching experiments, it was found that the unswitched (=pinned) regions mainly corresponded to up-polarization and were surrounded by the 109° and 180° domain walls. In Fig. 2(f), the regions surrounded by white solid lines correspond to the unswitched regions. Some of the unswitched regions (green solid lines) were in a down-polarization state before the experiments.

Repeated bipolar voltage-pulses effectively de-pin the domain walls. Figure 3(a) shows P-E loops for a 4-variant BFO film. After 41 000 cycles, the P_r reaches almost the same value as for 2-variant BFO films. To investigate a possible change in domain configuration after pulse-switching,

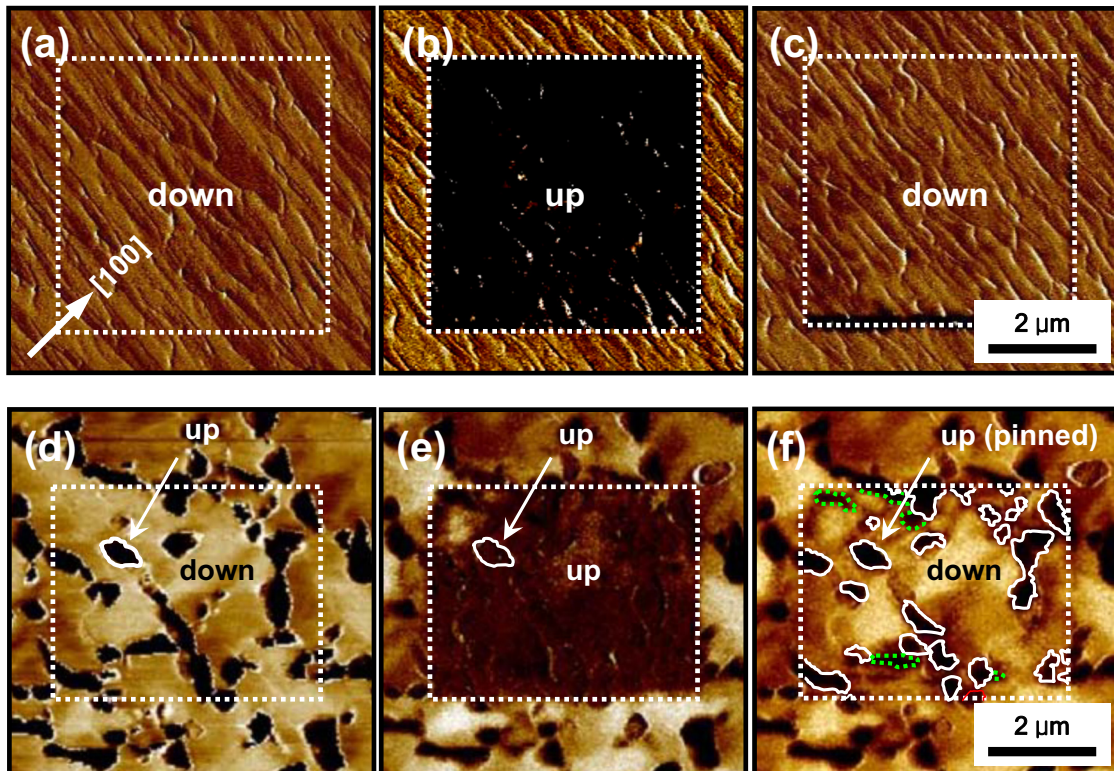


FIG. 2. (Color online) OP-PFM images of [(a)–(c)] 2-variant and [(d)–(f)] 4-variant BFO films. [(a) and (d) Before and after PFM switching by [(b) and (e)] -10 V and [(c) and (f)] $+10$ V. Dark and bright regions represent up- and down-polarization components, respectively. Solid lines and dot lines in (f) indicate pinned domains [white circles in (d) and (e) indicate the up-pinned domains as an example].

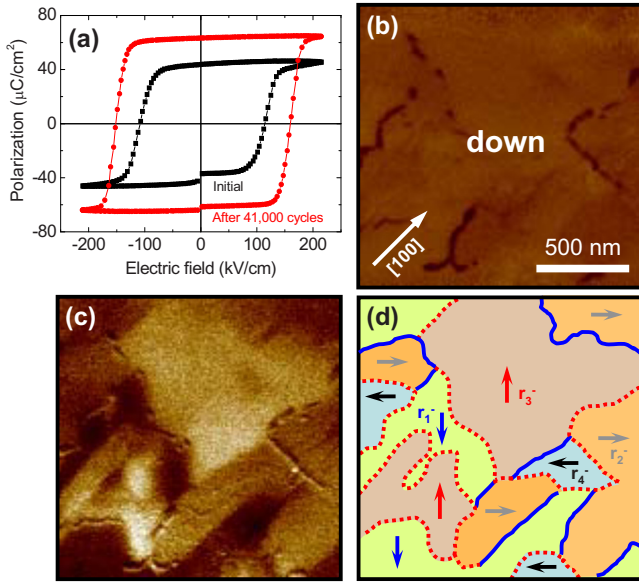


FIG. 3. (Color online) (a) P-E hysteresis curves of 4-variant BFO films before and after 41 000 switching cycles. (b) OP-PFM and (c) IP-PFM images of 4-variant BFO film after complete switching by voltage-pulse. (d) Detailed domain wall analysis of (c).

the 4-variant BFO film was observed by PFM after cycling more than 41 000 times—ending on a positive voltage bias at the top electrode—and removing the Pt top-electrode. As shown in Fig. 3(b), the OP-PFM data reveals a homogeneously down-polarized area, indicating that all domains have been switched. However, the IP-PFM image [Fig. 3(c)] still exhibits a random 4-variant ferroelectric domain structure (r_1^- , r_2^- , r_3^- , and r_4^-). A detailed analysis of the domain structures, based on IP data taken at different scan directions, revealed that both the 71° and 109° domain walls are present.

Figure 4 depicts the variation in the P_r value of BFO films as a function of switching cycles. The 2-variant BFO film does not show breakdown over 4×10^5 cycles, whereas the 4-variant BFO film breaks down after $\sim 1 \times 10^5$ cycles. We have measured many capacitors on several 2- and 4-variant samples. All devices on 4-variants BFO samples showed similar breakdown behaviors before 1×10^5 cycles. However, all capacitors on 2-variants BFO samples did not show any breakdown behavior over 4×10^5 cycles.

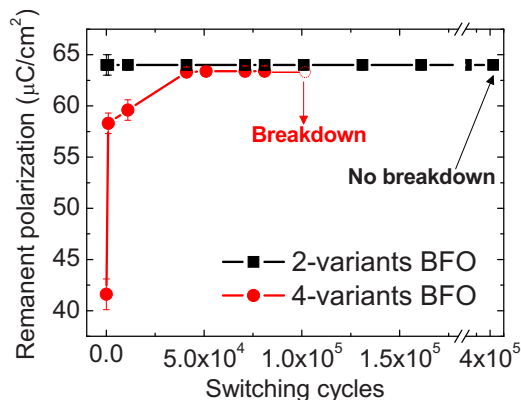


FIG. 4. (Color online) Breakdown behaviors of 2- and 4-variant BFO films. The voltage-pulse used for cycle test is ± 16 V, 1 kHz frequency and 0.5 ms width.

Generally, 109° domain walls consist of ferroelectric domains with opposite OP-polarization components (r_1^+/r_2^- or r_3^-/r_4^+) due to charge neutrality.⁷ Therefore, we suggest that the presence of 109° domain walls in Fig. 3(c) is attributed to charged defects compensating for the charge non-neutrality. One possibility is that repeated switching randomizes the defect distribution, possibly pinning the domain walls in the as grown films, effectively lowering the defect density at the domain walls and, hence, leading to complete switching. It is well known that charged defects can act as leakage paths, which can induce a breakdown,¹⁷ and it is possible that the 109° domain walls in the 4-variant BFO film after repeated switching act as breakdown sites.

In conclusion, we have investigated the origin of suppressed P_r in 4-variant BFO films. Our results microscopically demonstrate that the suppressed polarization switching of 4-variant BFO film is due to pinned ferroelectric domains. The remanent polarization of the 4-variant BFO could be enhanced by repeated switching, which effectively de-pins the domain walls. The results show that careful control of the domain wall structure is important to reducing early breakdown, and the data can be used as guide for the future improvement of reliable ferroelectric and magnetoelectric devices in low symmetry material systems.

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