Ferroelectric domain wall pinning at a bicrystal grain boundary in bismuth ferrite

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The ferroelectric polarization switching behavior at the 24° (100) tilt grain boundary (GB) in an epitaxial multiferroic $BiFeO_3$ bicrystal film is studied using piezoresponse force microscopy (PFM). The PFM amplitudes across positively and negatively poled GB regions suggest the presence of a frozen polarization component at the interface. The switching experiments demonstrate that the GB attracts the domain wall and acts as a pinning center. The PFM results are compared with conductive atomic force microscopy and spectroscopy, which suggest domain wall pinning at the GB can be partially attributed to increased conductance at the GB. © *2008 American Institute of Physics*.
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Polarization switching in ferroelectric materials underpins the operation of ferroelectric-based nonvolatile random access memories and data storage devices.[1,2] Domain dynamics in ferroelectric materials is controlled by the presence and density of local defects such as point defects, dislocations, and grain boundaries that act as pinning centers for moving domain walls. The development of piezoresponse force microscopy (PFM) in the past decade has provided a powerful tool for imaging ferroelectric domain structure at the $\sim$10 nm level,[3] enabling studies of domain wall dynamics on the nanoscale. Domain wall geometry in epitaxial films has provided information on dominant disorder types,[4,5] and numerous studies of polarization switching in polycrystalline and epitaxial ferroelectric films have demonstrated preferential domain wall pinning at grain boundaries[6] and ferroelastic domain walls,[7] respectively. In an early work, Gruverman *et al.*[8] observed the relationship between domain dynamics and conductivity at interfaces. However, in most studies, the exact type of the interface formed between individual grains has been unknown, precluding the relationship between grain boundary (GB) type and its role on polarization switching to be established. Here, we study local ferroelectric domain behavior in the vicinity of a 24° tilt GB in a multiferroic $BiFeO_3$ (BFO) (001) bicrystal.

Epitaxial multiferroic BFO (200 nm) was deposited on a conductive $SrRuO_3$ (50 nm) bottom electrode layer on a bicrystal (0°,24°) (001) $SrTiO_3$ substrate (CrysTec) by pulsed laser deposition (PLD).[9] Growth of $SrRuO_3$ and BFO by PLD on a bicrystal $SrTiO_3$ substrate is epitaxial and follows the structure of the substrate, including the continuation of GB through the film. The PFM imaging and polarization switching experiments were implemented on a Veeco Nanoman V atomic force microscope (AFM) using Au–Cr coated Si tips (Micromasch) (spring constant $k\sim 40$ N/m). Conductance imaging was performed on an Asylum Research MFP-3D AFM using Pt–Ir coated Si tips (Olympus, Electri-Lever) (spring constant $k\sim 2$ N/m).

The topography of the GB region is illustrated in Fig. 1(a). The topography is found to be inhomogeneous along the length of the GB due to variations in the height and location of a topographic feature (referred to as *ridge*). This ridge feature ($\sim$500 nm in width) can be on either (or both) side(s) of the GB [in Fig. 1(a), the GB is to the left of the ridge]. The ridge height generally does not exceed 10 nm, and the ridge and pores represent the dominant topographic defect types on the bicrystal surface. In these studies, topographic variations along the ridge were found to have a significantly weaker effect on polarization behavior than the GB per se. Hence, the observed anomalies of polarization behavior are interpreted here as the result of the GB rather than a topographic contrast.

To address the effect of the GB on polarization switching, a square region was first switched uniformly in one direction (+8 V applied to the tip). Then, while a slightly smaller area was scanned, an opposite dc bias was applied [from −1 to −8 V in 1 V increments (1 Hz scan, 256 lines, 1 V increment per 32 lines)] to determine if the GB affected switching bias. The resulting PFM amplitude and phase images are shown in Figs. 1(c) and 1(d), respectively. The images illustrate that switching in this direction is only weakly affected by the presence of the GB. Note that in the PFM amplitude image [Fig. 1(c)], the GB is associated with reduced ($\sim$20%) PFM amplitude compared to the free surface. The switching in the opposite direction is illustrated in Figs. 1(e) and 1(f). In this case, the region was first switched uniformly with a −8 V bias, and subsequently backswitched during the application of an incrementally increasing positive voltage (1 Hz scan, 256 lines, 1 V increment per 32 lines). Switching at the GB is initiated slightly earlier than in the surrounding material [Fig. 1(f)]. At the same time, the PFM amplitude within the GB region coincides with that of the free surface. These observations suggest the presence of a

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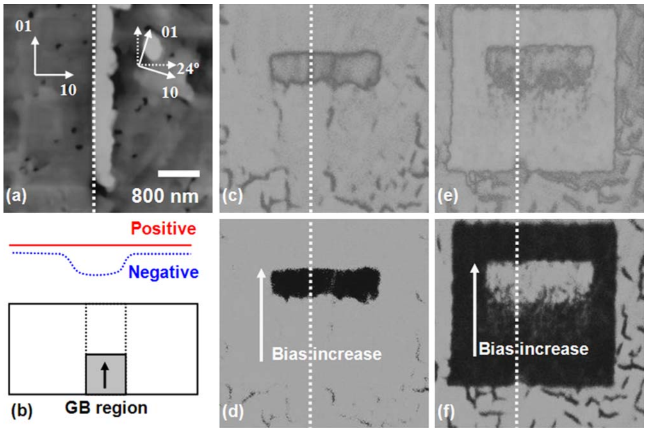

FIG. 1. (Color online) (a) Topography and (b) schematic of GB cross section. Red and blue lines in (b) represent the piezoresponse signal. [(c) and (d)] PFM amplitude and phase images, respectively, of a region switched uniformly with positive tip bias and backswitched with an increasing negative bias. [(e) and (f)] PFM amplitude and phase images, respectively, of a region switched with a negative bias and backswitched with an increasing positive bias. Scales are (a) 30 nm, [(c) and (e)] 3 mV, and [(d) and (f)] 360°. The dashed white lines indicate the location of the GB. In [(d) and (f)], bright (dark) contrast corresponds to an out-of-plane polarization component, which points toward (away from) the substrate.

positive frozen polarization component or strong built-in field at the GB region. This component affects the PFM amplitude profile across the interface, as illustrated in Fig. 1(b), in agreement with the experimental data, and also shifts the corresponding nucleation biases. From comparison of the magnitudes of the PFM signal,[10] the thickness of the frozen layer near the GB can be estimated as ~20 nm.

To elucidate the role of the GB on domain wall motion, we have performed single-point bias-pulse experiments.[11–14] In these, a square region was uniformly poled by −8 V, and pulses of opposite polarity were applied at several locations near the GB. Topographic and piezoelectric images obtained after pulses of 7 V for 10 s and 8 V for 3, 15, and 20 s have been applied are shown in Figs. 2(a)–2(c). Notably, unlike domain switching in lithium niobate,[11,12] the radius of the switched domain depends only weakly on the pulse duration, making comparison of domains created with different pulse magnitude and duration possible. While the domain shape is often irregular (presumably due to the presence of defects), in the vicinity of the GB the domains adopt a characteristic shape, developing "necks" that extend ["attract" in Fig. 2(d)] toward the GB. A segment of the domain wall coincides with the GB. This demonstrates the presence of an attractive force between the domain wall and the GB. Despite applying 8 V, 30 s pulses [at locations indicated with white "x" marks in Figs. 2(d)–2(f)] in closer proximity to the GB in an existing domain [Figs. 2(d)–2(f)] and in a pristine location [Fig. 2(e)], the domain was not observed to grow across the GB, suggesting it is pinned by it, as indicated in Fig. 2(d). Similar behavior was observed for negative pulses.

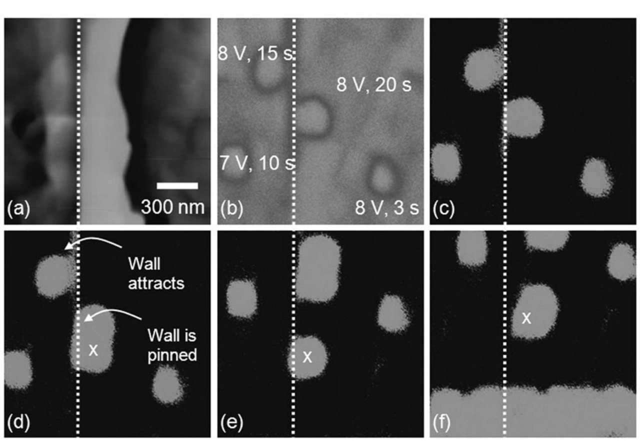

FIG. 2. (a) Topography and [(b) and (c)] PFM amplitude and phase images, respectively, of a region switched with a negative bias and backswitched in several locations by positive dc-bias pulses. [(d)–(f)] PFM phase images following the application of additional dc-bias pulses. Scales are (a) 10 nm, (b) 3 mV, [(c)–(f)] 360°. Images (c)–(f) are compensated for a phase offset. The dashed white lines indicate the location of the GB. White "x" marks in [(d)–(f)] indicate the location of the tip during the application of additional bias pulses.

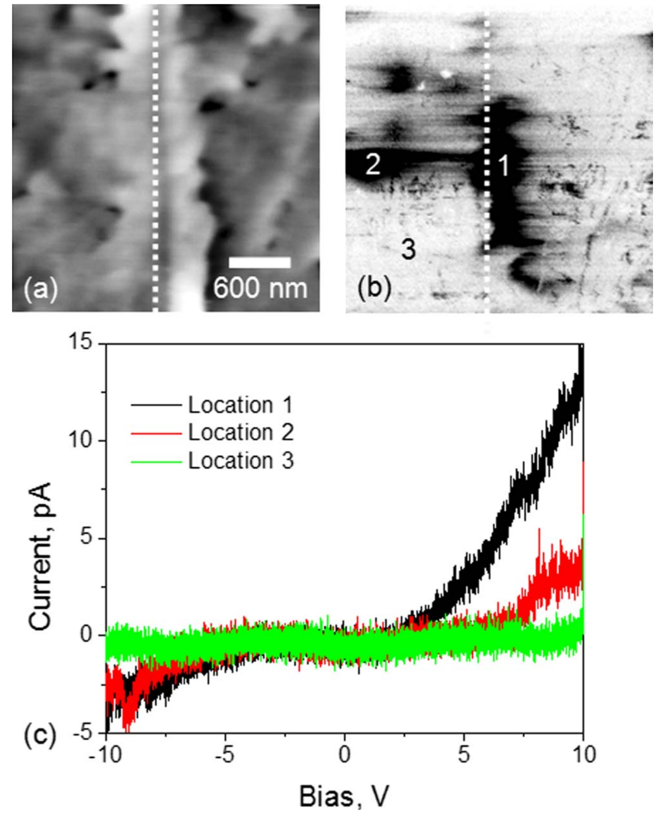

FIG. 3. (Color online) (a) Topography, (b) current image, and (c) selected current-voltage curves. Scale for (b) is ~15 pA. The dashed white line in (a) indicates the location of the GB. The dark contrast in (b) is indicative of increased leakage.

To complement PFM studies and develop insight into the pinning mechanism, transport properties of the interface were probed by conductive AFM, as shown in Figs. 3(a) and 3(b). The film and GB region are shown to have a number of conductive locations, presumably associated with dislocations.[15] Note the increased conductivity along most of the length of the GB. Corresponding current-voltage curves measured at and near the GB are presented in Fig. 3(c), illustrating early onset of conductivity (at ~3 to 4 V) at the GB. At biases required for polarization switching, the GB is essentially conductive, suggesting that minimization of the depolarization energy for a domain wall pinned at the GB may contribute significantly to the pinning mechanism.

To summarize, domain wall motion on a well-defined 24° tilt GB in a BFO (001) bicrystal is studied using the combination of PFM, domain writing experiments, and conductive AFM. The comparison of PFM amplitudes on positively and negatively polarized GB regions indicates the presence of a region with a frozen positive polarization component. The GB is shown to attract a domain wall and act as a pinning center. The symmetry of the pinning behavior with respect to wall polarity suggests the pinning is unrelated to the frozen polarization component. The high conductivity of the GB at biases below those required for wall motion suggests the GB conductivity can contribute to domain wall pinning by reducing the effective potential acting on the wall and also minimizing the depolarization energy for a domain wall pinned at the interface.

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