Deterministic Switching in Bismuth Ferrite Nanoislands

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Supporting Information

ABSTRACT: We report deterministic selection of polarization variant in bismuth BiFeO₃ nanoislands via a two-step scanning probe microscopy procedure. The polarization orientation in a nanoisland is toggled to the desired variant after a reset operation by scanning a conductive atomic force probe in contact over the surface while a bias is applied. The final polarization variant is determined by the direction of the inhomogeneous in-plane trailing field associated with the moving probe tip. This work provides the framework for better control of switching in rhombohedral ferroelectrics and for a deeper understanding of exchange coupling in multiferroic nanoscale heterostructures toward the realization of magnetoelectric devices.

KEYWORDS: Bismuth ferrite, multiferroics, nanoislands, polarization switching, scanning probe microscopy.
77 the symmetry of the field experienced by the material, so that
78 the final state adopted is strongly influenced by the direction of
79 the in-plane component of the trailing field. Trailing fields have
80 been employed to control domain writing with a certain degree
81 of success for a range of materials,18−20 including BFO.21−23
82 Control of predefined stripe domain patterns21 and of
83 ferroelectric polarization22 has been achieved; however, the
84 influence of the surrounding matrix in continuous ferroelectric
85 films has led to problems in retention at the nanoscale level. A
86 higher degree of control has been obtained in two-variant
87 films with polarization selection in submicron areas remaining stable
88 for the duration of the experiment.23

The investigation of deterministic polarization switching in
89 BFO has not been previously performed on free-standing
90 nanoislands although device miniaturization would require an
91 understanding and verification of the phenomenon in this kind
92 of geometry. There could even be advantages to switching in
93 patterned media, as reduced lateral dimensions have been
94 demonstrated to improve retention.17

In this Letter, we present PFM investigations concerning
96 polarization switching in BFO nanoislands by predominantly
97 [001] oriented electric fields. We demonstrate that submicron
98 lateral size and limited constraint from surrounding material
99 can allow polarization to be effectively toggled among any of
100

Figure 1. Topography (a), line profile (b), and schematic diagram (c) of the patterned portion of the BFO film in which nanoislands of BFO have been produced.

Figure 2. Topography (a); vertical PFM phase (b); lateral PFM phase with cantilever axis along [0\(\overline{1}\)0] (c) and [\(\overline{1}\)00] (d) of a portion of milled area. Domain color map with different polarization orientations inferred from vector PFM (e) with three-dimensional and top-view planar color coding (left) and a magnified image of the domain configurations in two islands from a different region of the machined area (f). A topographic mask has been superimposed onto the PFM images and vector PFM maps in order to identify the island positions. Inset diagrams in (c) and (d) represent cantilever orientation with color coding for lateral PFM image interpretation.
the four variants pointing toward the bottom electrode, a feat not achieved in previous research. Each polar orientation is selected after a “reset” operation via the raster scanning direction of the scanning probe microscopy (SPM) probe. With the aid of electric field simulations, we demonstrate that the operation is made possible by the inhomogeneous electric fields generated at the PFM probe-tip; a transverse field is confined to a small volume at the edges of the tip–sample contact area that allows the in-plane component of the polarization to be controlled during the out-of-plane switching procedure. Moreover, we report that a quadrupole configuration is stabilized by switching the polarization toward the top surface of the BFO nanoislands; in previous studies on continuous films, this dipole pattern had been highly unstable. Experiments were performed on BFO islands fabricated from a parent (001) BFO thin film (30 nm) grown by pulsed laser deposition on SrTiO$_3$ with a 30 nm SrRuO$_3$ buffer layer as a bottom electrode. Details on film growth are described elsewhere. Fabrication of the islands from the BFO parent film was performed by a mask-assisted focused ion beam (FIB) milling procedure, which has been demonstrated to produce islands that retain their ferroelectric properties with minimal fabrication-induced damage. The milling procedure yielded a milled square area (5 $\times$ 5 $\mu$m$^2$) containing a number of BFO islands about 400 nm in diameter and 25 nm in height (Figure 1).

Investigations to reveal domain configurations were performed by vector PFM, which allows identification of polarization variants by consecutive scans of the same area with the probe cantilever oriented along two orthogonal axes. The parent film has a striplike ferroelectric domain configuration (top areas in Figure 2a–e) with a predominance of variants with downward out-of-plane components (i.e., polarization vectors pointing toward the bottom electrode). The initially observed domain configurations in the nanoislands are clearly inherited from the parent film (because the BFO ferroelectric Curie temperature ($T_c$ $\sim$ 1100 K) is not exceeded during any step of the fabrication procedure (Figure 2e). Piezo-hysteresis loops measured over a virgin area of parent film and the middle of an island (Figure S1) confirm preservation of
ferroelectricity with minimal change in imprint resulting from the island patterning process.

Switching experiments were performed using PFM, scanning the grounded probe over the surface of the island under investigation while the bottom electrode was biased (Figure 3a,b). The expected control over the switched polar orientation is understood by considering the inhomogeneous nature of the electric field in the proximity of the PFM probe, combined with its movement. Application of an out-of-plane electric field across rhombohedral (001) BFO leads to reversal of the out-of-plane component of polarization with four available variants nearly energetically equivalent. The field generated between the PFM probe and the bottom electrode has an inhomogeneous normal component in the volume underneath the contact area, and a radial transverse component around it. When the probe is not moving, the normal field induces out-of-plane polarization reversal and in-plane polarization reorientation with opposite senses either side of the contact area.

Removal of the field leads to an energetically unfavorable charged domain wall, which encourages relaxation of domains into a different configuration, determined by mechanical and electrostatic boundary conditions. Selection between the available variants can be achieved by moving the probe over the surface, hence breaking the symmetry of the transverse field. The moving probe creates a virtual “trailing field”, the direction of which is opposite to its movement (Figure 3). Slow raster axis scanning along [100] or [010] leads to a multidomain configuration, as two out of the original four ⟨111⟩ polar variants are still energetically equivalent under the influence of the trailing field. On the other hand, slow raster axis scanning along [110] or [110] breaks the symmetry in favor of only one of the available four variants and hence selects it.

Reversal of as grown island out-of-plane polarization from downward to upward requires a positive direct current (dc) bias (typically +6 V). Irrespective of the slow raster axis direction used during poling, the resulting island domain configuration is...
always multidomain (Figure 4b–d) with out-of-plane components upward. Three-dimensional domain mapping reveals a quadrupole or antivortex pattern (Figure 4e,f) often results. This may be of interest for the investigation of topological patterns.29–32

The virgin domain configuration displaying downward polarization (Figure 2b) and the measured imprint both in films and islands (Figure S1) indicate efficient polarization screening at the bottom interface, rendered possible by free carriers in the electrode.33,34 On the other hand, at the top surface and sidewalls of the island screening is not as efficient, and depolarizing fields are inevitable, which contribute to the multidomain state found when polarization points upward.35

Following polarization reversal by positive bias (which for brevity we will refer to as the "reset" operation), scanning with negative dc bias (typically −6 V) induced domain configurations that were almost entirely dependent on the slow raster axis direction used. Poling with the probe scanning along [100] or [010] led to multidomain configurations (Figure S3) similar to the striplike configurations resulting from switching experiments on BFO film surfaces where all polarization variants are allowed.31 However, poling with the slow raster axis along the surface projection of one of the polar axes (Figure 2a), yielded domain configurations with almost a single domain variant (Figure 5a). All four polarization variants with downward out-of-plane components could be selected. For instance, poling with slow raster scan axis along [110] creates an island with a predominant [111] polar orientation (Figure 5a, bottom-right image). Analysis of domain populations (Figure 5b) show deterministic selection of the desired variant on at least 70% of the area of the island. Notably, areas not displaying the selected variant are mostly located at island sidewalls; sidewalls have been subjected to an ion dose during the fabrication procedure, and it is known that this can affect the ferroelectric properties of the material. When only the very top surface of the island is considered, then at least 90% of the domains observed are seen to be deterministically selected, while less control occurs at the sidewalls (Figure S8).

The procedure is repeatable, reproducible, and leads to domain configurations with good retention (Figure S9). Islands can be switched among any of the four down-state variants after a "reset" operation by applying negative dc bias combined with a suitable slow scan direction. It has to be noted that application of negative bias on an island with out-of-plane component already downward (i.e., without previous "reset" biasing) does not induce any domain reconfiguration. Hence, it can be inferred that the influence of the trailing field can only be realized in conjunction with reversal of the out-of-plane polarization.

In order to gain more insight as to the nature of the "trailing field" responsible for the deterministic selection of polarization variants, we considered the electric field in the system using finite element modeling (Quickfield). The film thickness was set to 40 nm with bias applied from the bottom electrode and, considering the rhombohedral structure of BFO, we assumed an isotropic dielectric permittivity with a set value of ε = 100.35,36 We modeled the PFM conductive probe in contact with the surface as a 10 nm top capacitor. This was consistent with a tip–surface contact diameter in the "strong indentation regime" (the ideal condition for performing PFM).36 The outcome of the simulation is displayed in Figure 6, showing a field distribution with a relatively homogeneous normal component (Figure 6a) as well as distinct localized transverse components (Figure 6b). Fringing fields at the edges of the tip–sample contact are clear. Figure 6c shows that the transverse fields at the surface can be relatively intense but decrease rapidly away from the surface (Figure 6c, open symbols). High transverse field components therefore seem to be confined into small volumes at the edges of the contact area.

Even assuming transverse fields high enough to reorient the in-plane polarization component when used as a trailing field, this would take place only in a confined volume very close to the surface. Any possible transverse field-driven reorientation...
In conclusion, switching to obtain specific polarization variants in (001) BFO nanoislands has been experimentally demonstrated. We have shown that each of the four available variants with out-of-plane components pointing downward can be independently selected depending on the sense of the "trailing" field associated with a moving PFM tip. Electric field modeling reveals the presence of high transverse fields within small volumes at the edges of the probe-surface contact area and it appears to be these fields that are responsible for polar variant selection, during the out-of-plane polarization reversal process.

This work demonstrates that a higher degree of control on functional properties can be achieved in nanostructures, due to reduced dimensionality and the lack of constraint from surrounding matrix material. Selection of polarization variants will be of use for verification of electric field driven magnetization switching in BFO-based multiferroic heterostructures with nanoscale lateral size, and therefore the research may contribute toward the realization of magnetoelectric memories.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b02311.

Piezo-hysteresis loops; full piezoresponse force microscopy data for Figures 4 and 5; domain population analysis; piezoresponse force microscopy imaging for additional switching experiments; retention data (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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■ REFERENCES

(2) Kleemann, W. Physics 2009, 2, 105.

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■ NOTES

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373 (22) Bea, H.; Ziegler, B.; Bibes, M.; Barthelemy, A.; Paruch, P. J. 
374 
Phys.: Condens. Matter 2011, 23 (14), 142201.
376 Nanotechnol. 2015, 10 (7), 614–618.
377 (24) Johann, F.; Morelli, A.; Biggeman, D.; Arredondo, M.; Vrejoiu, 
381 (26) Morelli, A.; Vrejoiu, I. Epitaxial Ferroelectric Nanostructures 
382 Fabricated by FIB Milling. In FIB Nanostructures; Wang, Z. M., Ed.; 
383 Lecture Notes in Nanoscale Science and Technology; Springer 
385 (27) Rodriguez, B. J.; Gruverman, A.; Kingon, A. I.; Nemanich, R. J.; 
390 104 (20), 207602.
392 (10), 4200–4205.
394 132902.
396 Bhattacharya, S.; Chen, L. Q.; Chu, Y.-H.; Lin, I.-N.; Kalinin, S. V.; 
398 (33) Chu, Y.-H.; He, Q.; Yang, C.-H.; Yu, P.; Martin, L. W.; Shafer, 
400 (34) Grossmann, M.; Lohse, O.; Bolten, D.; Boettger, U.; Wasel, R. J. 
406 (37) Horcas, I.; Fernández, R.; Gómez-Rodríguez, J. M.; Colchero, J.; 