

In-Situ Cross-Sectional Switching of Multiferroic BiFeO₃ Thin Films

C.T. Nelson^{*}, P. Gao^{*}, J. Jokisaari^{*}, B. Winchester^{**}, Y. Gu^{**}, C. Heikes^{***}, A. Melville^{***}, C. Adamo^{***}, S.H. Baek^{****}, C. . Folkman^{****}, C.B. Eom^{****}, D.G. Schlom^{***}, L.Q. Chen^{**}, X.Q. Pan^{*}

^{*}Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109

^{**}Department of Materials Science and Engineering, Penn State University, University Park, PA 16802

^{***}Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853

^{****}Department of Materials Science and Engineering, University of Wisconsin, Madison, WI 53706

The ferroelectric BiFeO₃ has garnered much attention as a single-phase multiferroic, possessing coupled ferroelectric and antiferromagnetic ordering. Many applications of such ferroelectric materials rely on the repeatable switching between ferroelectric states under an applied field. BiFeO₃ is a particularly complicated case as it possesses a large number of polarization states (eight), and only a subset of switching between them results in a reorientation of the antiferromagnetic ordering. Magneto-electric heterostructures which rely on the exchange interaction between the antiferromagnetic BiFeO₃ and a ferromagnetic material [1, 2] at the interface therefore require deterministic control of ferroelectric switching. Specifically, a change of the antiferromagnetic order occurs only if there is a change of the polarization axis, that is ferroelastic 71° or 109° switching [3]. In this work we use in-situ TEM to study such switching in a (001) oriented BiFeO₃ thin film.

BiFeO₃ is a rhombohedral ferroelectric with polarization along one of the <111> directions. Fig. 1a shows an as-grown single-domain region of a 100 nm BiFeO₃ film used for this study with the polarization axis oriented upward as indicated by the arrow. The unit cell corresponding to this polarization along [111] is shown alongside. Ferroelectric switching is carried out by applying a bias between a tungsten surface probe and an epitaxial 20 nm La_{0.7}Sr_{0.3}MnO₃ (LSMO) bottom electrode (dark layer in Fig. 1a), in a setup shown schematically in Fig. 2a. In this work BiFeO₃ films were grown on insulating (110) TbScO₃ single crystal by molecular beam epitaxy. Ferroelectric switching was performed using *in situ* transmission electron microscopy (TEM) in a JEOL 2010F. The resulting domain structures were characterized *in situ* by diffraction contrast TEM and *ex situ* using atomic resolution Z-contrast imaging on the TEAM 0.5, a Cs corrected FEI Titan operating at 300kV.

Our study of cross-sectional switching reveals a variety of interface and depth dependant phenomenon. Although the peak external field occurs at the film surface directly beneath the probe (Fig. 2b) the built-in electric field of the Schottky junction between the metallic LSMO layer and semiconducting ferroelectric layer induces nucleation at the bottom interface. The nucleated domains are metastable, forming an array at the interface until a critical bias is reached (Figs. 3c-e), whereupon the film beneath the tip undergoes 71° switching to form a large single domain. In the case of Fig. 3, ferroelastic switching has occurred at the BiFeO₃ bottom interface. However, there are a number of scenarios where ferroelectric switching is confined to the interface or, in contrast, fails to propagate to the interface which could prove deleterious to ferroelectric heterostructure applications.

In conclusion, we have studied real-time ferroelectric switching in a BFO / LSMO heterostructure cross section. We find that reliable switching at the interface is impeded by the formation of a

frozen polarization interface layer and by pinning of the propagating domain walls. Furthermore we observe unusual switching phenomenon that deviates from the expected kinetic models.

References:

- [1] Y.H. Chu et al. *Nature Materials*, **7** (2008) 478.
 [2] S.M. Wu et al. *Nature Materials*, **10** (2010) 756.
 [3] C. Ederer and N.A. Spaldin, *Physical Review B*, **71** (2005) 060401.
 [4] This work was supported through DOE grant DoE/BES DE-FG02-07ER46416, NSF grant DMR-0820404 (PG), and DOE grant DE-AC02-05CH11231 (NCEM user facilities)..

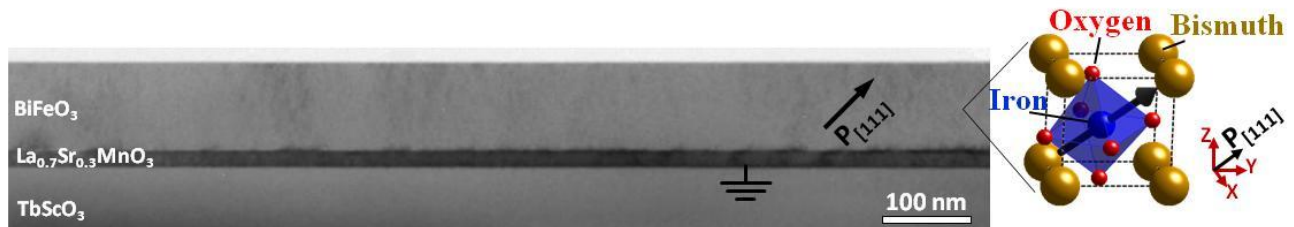


FIG 1. As grown film: Bright-field TEM image of the 100 nm BiFeO₃ film on a 10 nm LSMO buffer electrode. The polarization in this region is shown schematically at right.

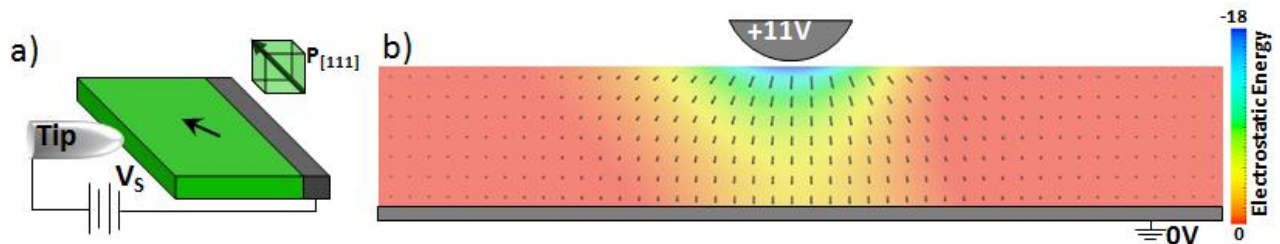


FIG 2. Sample Geometry: (a) An electric field is applied across the film in a TEM cross section using a positionable SPM tip. (b) The electrostatic energy in the film from applied field.

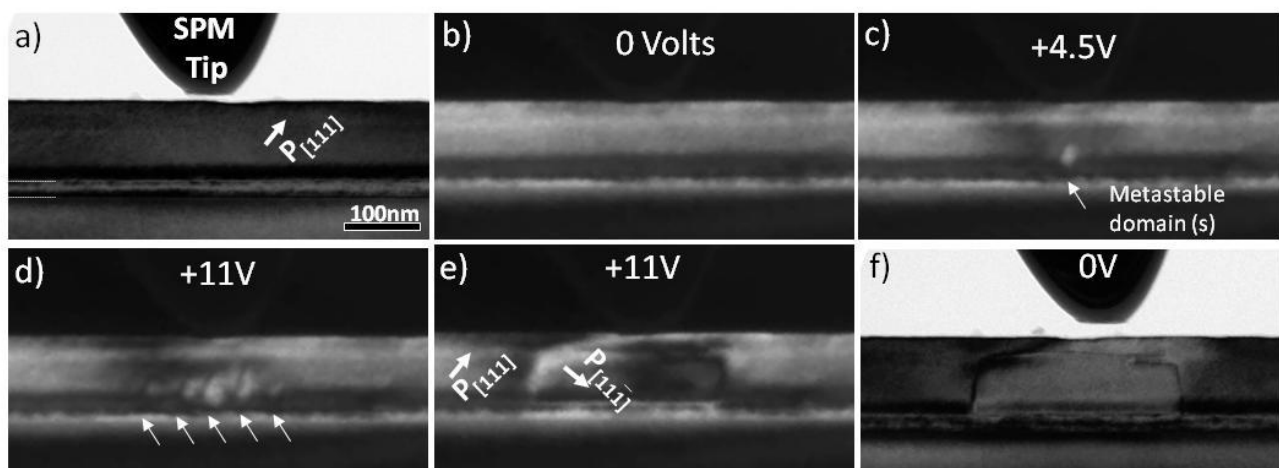


FIG 3. Ferroelectric switching: The initial domain structure with the SPM tip at the sample surface shown in bright field (a) and dark field (b). Nucleation occurs at the bottom electrode (c) at $\sim +4.5$ V. This expands into an array of such domains (d) before they merge into a large single domain (e). (f) The domain structure remains relatively unchanged after the bias is removed.