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PFM and TEM Characterization of Polarization in Ferroelectric BFO under Changing Mechanical Constraints

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Ferroelectric oxides, particularly multiferroic bismuth ferrite (BFO), have attracted much attention for applications in a new generation of devices such as nonvolatile memories and piezo-actuators. In these materials, ferroelectric domain structure and properties are closely coupled with mechanical strain and the domain structure depends sensitively on both mechanical and electronic contributions with both charged defects and strains both having a strong influence.

Scanning probe microscopy (SPM) techniques, most notably piezoresponse force microscopy (PFM), and transmission electron microscopy (TEM) have emerged as primary methods for characterizing ferroelectric domain microstructures. SPM methods are surface-only and have a resolution limit on the order of a few nanometers, and there are difficulties in obtaining quantitative results as the true tip geometry is not known. TEM has long been used where the highest possible resolution is required, with sub-angstrom resolution limit and chemical sensitivity through EELS and EDS. In this work we utilize both techniques to characterize ferroelectric thin films with two primary objectives: to follow changes in domain structure during sample preparation, and to combine these observations on the same sample to give a more complete picture of the ferroelectric structure.

TEM and high-resolution aberration-corrected STEM, combined with PFM were used to examine the evolution of polarization domain structure with respect to defects and a change in the mechanical boundary conditions on BFO thin films. (001) oriented BFO thin films were grown by molecular beam epitaxy on (110) $TbScO_3$. Cross sections were prepared by mechanical polishing followed by argon ion-milling for both all specimens. Films were characterized by JEOL 2010F, 3011, and 2100F and the TEAM0.5 FEI titan (TEM), and the Bruker Dimension Icon SPM.

PFM images in Fig. 1 show the surface topography and phase, and the cross-section of a 400 nm thick BFO sample where a complex structure composed of 109° domains transitioning to inclined 180° domains exits. This complex structure likely produces charged domain walls that must be compensated. A change in the mechanical boundary conditions occurs during sample thinning, which results in a reorganization of the polarization structure to the more commonly observed vertical 109° degree domain structure. The pure 109° domains extended through the film in the thin region, while in a slightly thicker area the previous domain structure persists. Aberration-corrected STEM examination of this film (Fig. 3) shows the presence of extended chemical defects approximately 100 nm from the substrate interface, where the domain structure changes in PFM images. There is an interplay, then, between the mechanical constraints and the electric and structural effects of the defects, where the defects may pin the 109° domains and compensate charge stabilizing the 180° domain structure. Here we examine the reorganization of a complex defect stabilized domain structure driven by a change in strain by complimentary piezoresponse force and aberration-corrected transmission electron microscopies.

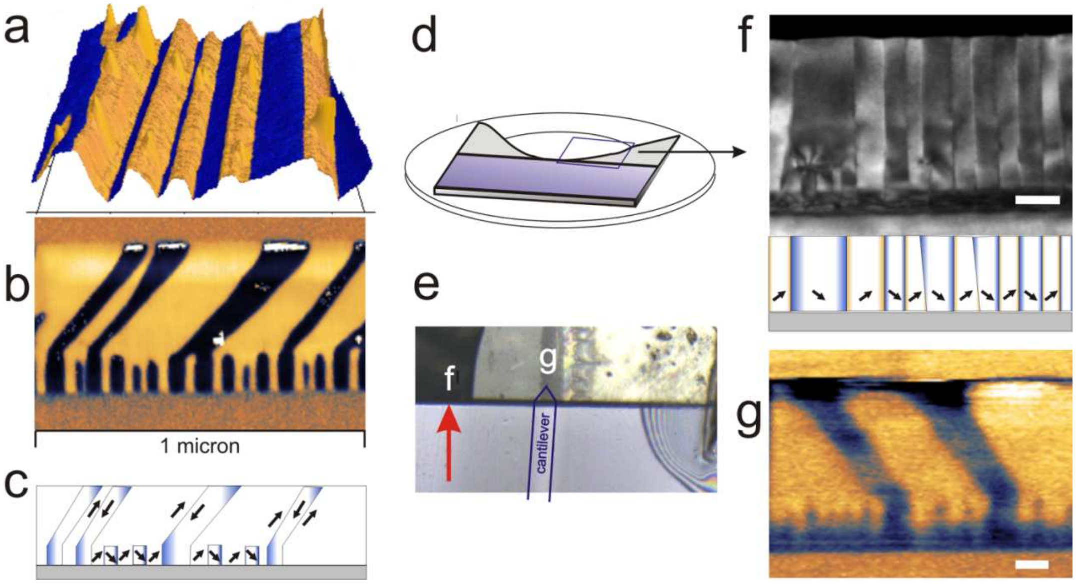

FIG 1. (a) PFM phase overlain on sample topography of the sample surface showing topographic steps corresponding with 180 domain walls (b) PFM phase of a cross-section of the same sample showing the complex native domain structure of the film (c) schematic of polarizations in (b). (d) and (e) show a schematic and optical image of the TEM specimen from which images (f) and (g) were taken. (f) is a DF image of the thin region of the specimen where the domain structure has been completely altered during thinning. The polarization is noted schematically beneath the image. (g) PFM of a slightly thicker region of the same specimen. The scale bars are 100 nm in both images. At a thickness between points (g) and (f), the domain structure is completely altered. PFM taken over the entire interface of a cross section at various stages during thinning appeared as in (e)

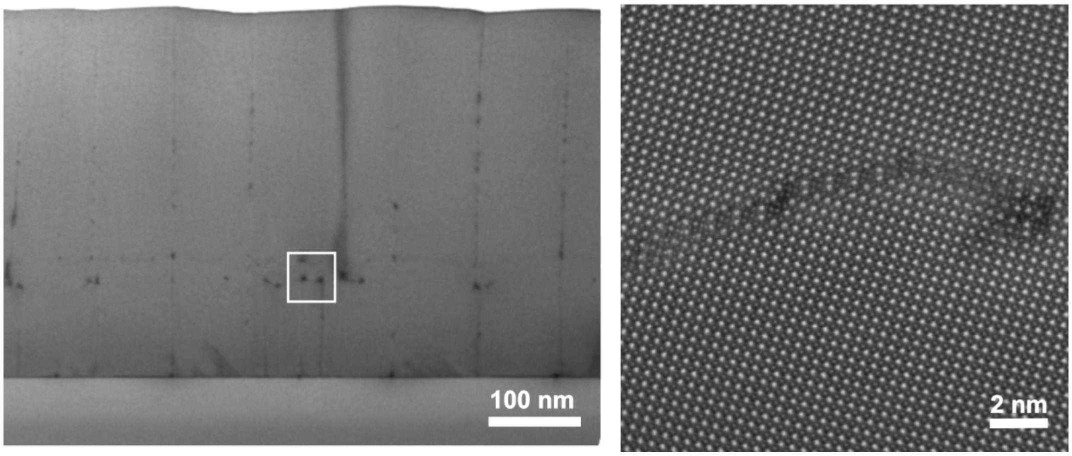

FIG 2. ABF STEM image of 400 nm BFO film with a 109 degree domain structure and showing extended linear defects about 100 nm from the substrate interface. The inset is a HAADF image of the defect site where a layer of Bi atoms is missing from the structure. These defects may stabilize the original domain structure of the film, depicted in Fig. 1.