doi:10.1017/S143192761301163X
Microsc. Microanal. 19 (Suppl 2), 2013

Atomic Structure of Surface Dielectric Dead Layer in $BiFeO_3$ Thin Film

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Surface dielectric dead layer in ferroelectric perovskite thin films was suggested as an explanation for decrease in effective polarization as the film thickness decreases; however, whether the dead layer exists as a distinct structural feature has long been a subject of scientific debate [1, 2]. Significant progress towards understanding the origin of the dead layer was achieved by atomistic simulations [3], which predict that the dielectric dead layer is an inherent phenomenon, and the magnitude of the associated adverse effects is determined by the details of interface bonding [4]. Recent study of $BiFeO_3$ (BFO) single crystal has demonstrated that within the first few nm of its surface the bulk symmetry appears broken, and out-of-plane lattice parameter appears elongated, forming a charge-depleted layer [5]. However, the details of the atomic structure of the surface layer, including the behavior of the order parameter fields such as polarization, strain, and octahedral tilt, remain unaddressed. Here, we report atomic structure of the surface dielectric dead layer in BFO thin film and uncover associated order parameter changes occurring at the surface layer using quantitative aberration-corrected scanning transmission electron microscopy (STEM) combined with EELS.

Figure 1a shows annular dark field (ADF) STEM image for the BFO thin film grown on $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) on $SrTiO_3$ (STO) substrate; the enlarged image of the BFO surface is given in Fig. 1b. The two left graphs (Fig. 1c and d) represent the associated changes in polarization and lattice spacing. Only out-of-plane component of polarization (observed as Fe displacement, Fig. 1c) seems to be non-zero in this area of the film. The lattice spacing is very stable at 4.1 ± 0.07 Å (Fig. 1d) up to the last two unit cells. Strikingly, the structural order parameters (including oxygen octahedral tilts (not shown)) show dramatic changes in the the first two atomic layers nearest the surface (Fig. 1a and b). A substantial contraction (~30%, 2.8 ± 0.12 Å) of the Bi-Bi interatomic distance is observed in the topmost layer accompanied by a dielectrically dead state (no off-centering of Fe observed), while the first second layer exhibits sudden increase of both Fe cation displacement (Fig. 1c) and Bi-Bi interatomic distance (Fig. 1d). Our results directly demonstrate that the dead layer in the BFO thin film is confined within these two surface atomic layers, which is much smaller than the thickness predicted from the mesoscopic measurements of the single crystal BFO [5]. The electronic and chemical properties at the surface layer were further probed by electron energy loss spectroscopy (EELS). Results of the EELS analysis, as well as additional examples of dead layer behavior will also be presented.

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[6] Research supported in part by the U.S. Department of Energy (DOE), Basic Energy Sciences (BES), Materials Sciences and Engineering Division (AYB, YMK, SVK), and through a user project supported by ORNL's Shared Research Equipment (ShaRE) User Program (YMK, AYB), which is also sponsored by DOE-BES.

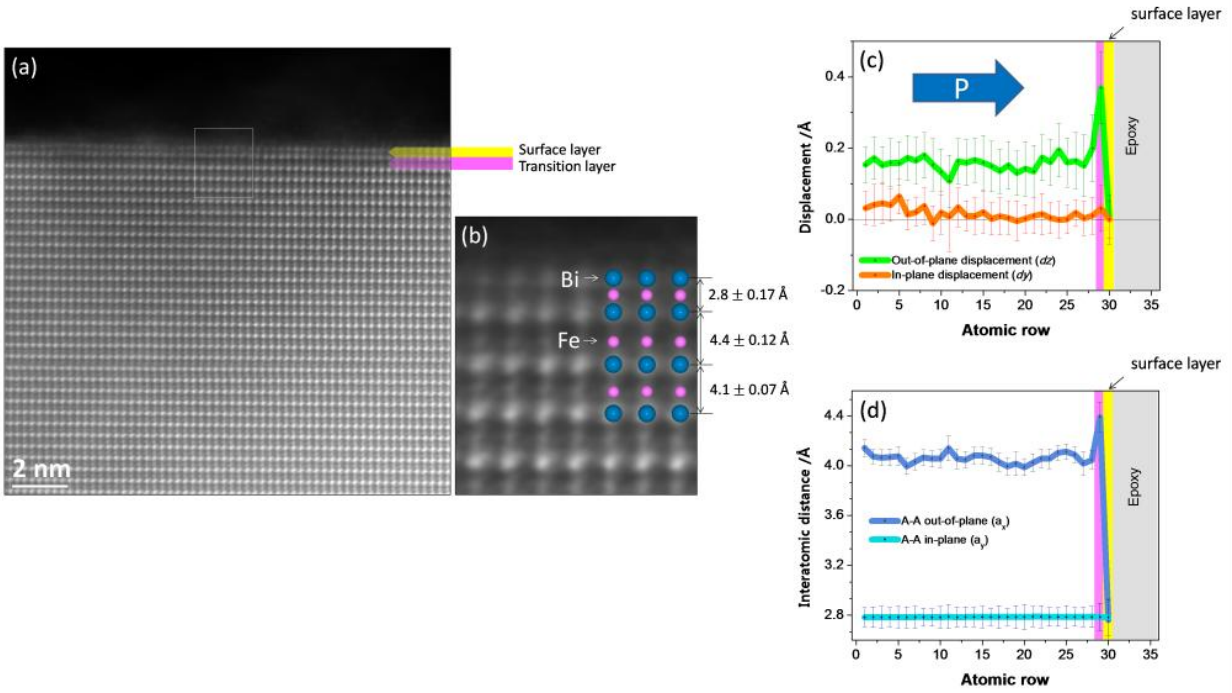

Figure 1. (a) ADF STEM image of the $[110]_{pc}$ (pseudocubic) oriented BFO films (50 nm) grown on LSMO (5 nm)/STO substrate. The first surface layer (showing substantial out-of-plane contraction) and the second transition layer (showing out-of-plane expansion) just inside of the surface layer are marked by yellow and pink bands, respectively. (b) Enlarged image of the BFO surface structure marked by a rectangle with white solid line in **a**. (c) Out-of-plane and in-plane Fe displacement profiles. (d) Profiles of Bi-Bi interatomic distance in the BFO structure for both out-of-plane and in-plane directions.

https://doi.org/10.1017/S143192761301163X Published online by Cambridge University Press