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Atomic-scale Mechanisms of Defect-Induced Retention Failure in Ferroelectric Materials

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The ease of reversibly switching the spontaneous polarization of a ferroelectric with an applied electric field has made this material attractive for application of high-density nonvolatile memories. One of the major challenges impeding this application, however, has been the so-called "retention failure" phenomenon – a self back-switching process of the written polarization that can lead to data loss. An understanding of the atomic-scale mechanism of the retention failure process is thus necessary to engineer reliable ferroelectric devices. Here, using *in situ* transmission electron microscopy (TEM), we report direct observation of polarization back-switching induced by non-stoichiometric defects that commonly exist in ferroelectrics. Our results of atomic-resolution scanning transmission electron microscopy (STEM) show a novel mechanism of the retention failure process, revealing that the process is induced by the strong atomic interaction between the defects and the surrounding domains.

$BiFeO_3$ (BFO) thin film of 50 nm in thickness with 8 nm thick $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) bottom electrode was grown on $LaAlO_3$ substrate by pulsed laser deposition. In this film, BFO possesses a tetragonal-like (*T*-like) structure (Fig. 1a) in most regions, and a large density of non-stoichiometric defects is observed within the 15 nm thick region above the BFO/LSMO interface. Local switching was performed upon applying a bias between a tungsten surface probe and the LSMO bottom electrode (Fig. 1b). The bias was linearly increased from 0 to 10 V during 20s and then removed. A plot of the measured switched domain area versus time during the switching and back-switching process is shown in Fig. 1c. Corresponding selected TEM images in Fig. 1d show the formation of a large "up" polarized domain in the "down" polarized matrix during the initial 0 to -10 V ramp and back-switching to a much smaller stable domain pinned by defects after the removal of the bias. To understand the underlying mechanism of the back-switching process, atomic resolution high-angle annular dark-field (HAADF) STEM was performed to image a polarized BFO region interacting with a defect, as shown in Fig 2a. Atomic displacements of Fe cations from the center of four Bi neighbors for BFO, which are proportional to the polarization, [1] are measured and shown in Fig. 2b. Due to a strong atomic interaction between the BFO and the defect, significantly enhanced out-of-plane polarizations were observed for the first BFO lattice layer that is in direct contact with the defect. Such strong interaction would cause a large downward built-in field pointing to the defect and thus destabilize the "up" polarized written domain and cause retention failure.

In conclusion, using *in situ* TEM combined with atomic resolution STEM, we have shown a strong interaction between ferroelectric polarizations and the non-stoichiometric defects, which

can cause a large built-in field, leading to local polarization enhancement and destabilizing written domains. Our results provide new insights into the critical role of defects on domain configurations and dynamics and suggest a new route to design ferroelectric devices through defect engineering.

References:
[1]. Li, L., et al., Nano Letters, 2013. **13**(11) 5218-5223.
[2]. The authors gratefully acknowledge the financial support through DOE grant DoE/BES DE-FG02-07ER46416.

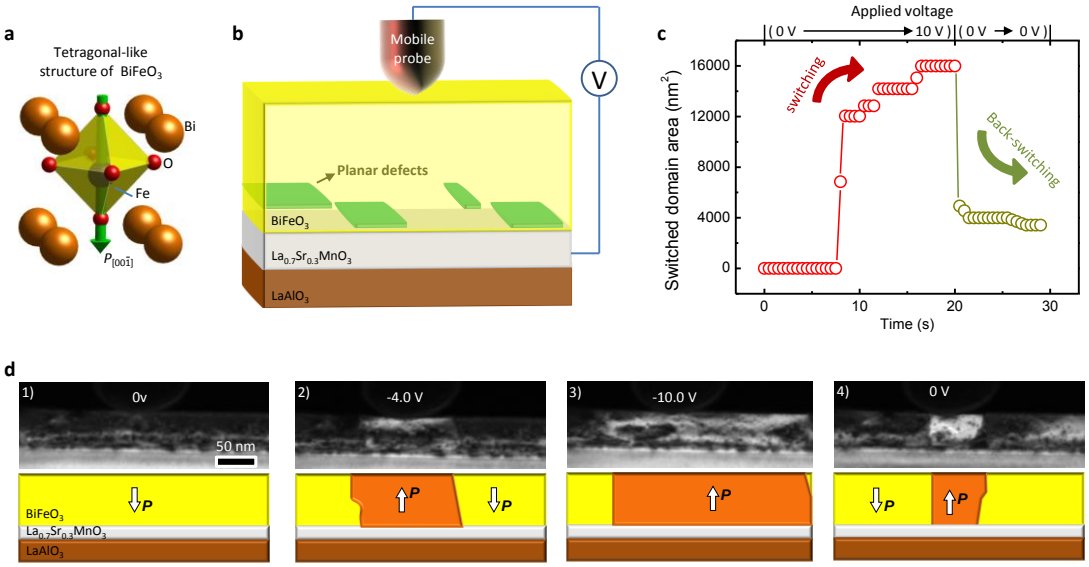

Figure 1. (a) Atomic models of the tetragonal-like structure $BiFeO_3$. (b) Schematic of *in situ* TEM experimental set-up. (c) Plot of the measured switched domain area versus time extracted from an *in situ* TEM video. (d) A chronological TEM image series showing the evolution of a written "up" polarized domain in a "down" polarized matrix.

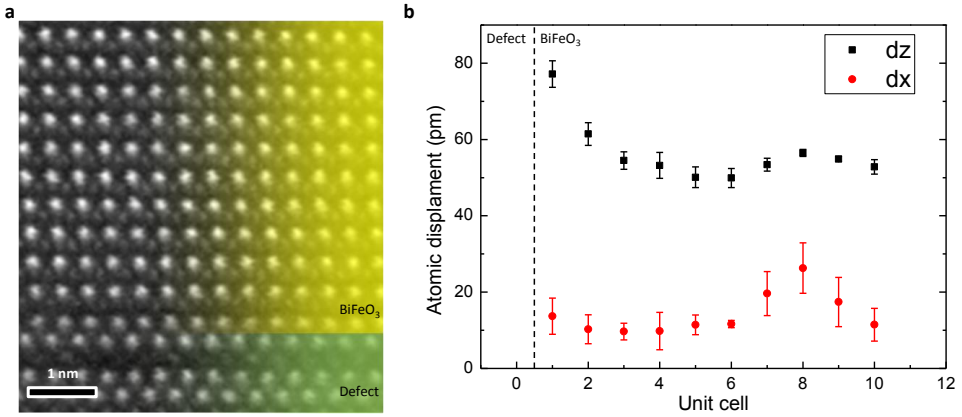

Figure 2. (a) A HADDF STEM image of a polarized BFO region that is in contact with a planar non-stoichiometric defect. (b) Plot of the measured atomic displacements (dz: out-of-plane atomic displacement, dx: in-plane atomic displacement) of Fe cations from the center of four Bi neighbors for BFO atomic structures shown in (a).