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Interaction between Ferroelectric Polarization and Defects in $BiFeO_3$ Thin Films

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Nanoscale impurity defects, with structures different from host materials, are known to commonly exist in functional complex oxides as a result of slight stoichiometry fluctuations that occur during material growth. Local perturbations induced by these defects, such as charge, strain, and atomic interaction, could have a profound effect on the physical properties of oxide nanomaterials. A direct correlation of the defects to the material functionalities, however, are often hampered by the lack of a fundamental understanding of the microscopic mechanisms underlying the coupling between the defects and the host lattice. Here, with a combination of atomic-scale STEM and *in situ* TEM, we perform a systematic study of atomic-scale polarization structures and microscopic domain-switching processes in the prototypical multiferroic $BiFeO_3$ thin films to explore the interaction between ferroelectric polarization and defects.

Fig. 1a shows the polarization distribution in a 2 nm $BiFeO_3$ film grown on $TbScO_3$ substrate based on atomic-resolution HAADF STEM imaging. An array of island-like monolayer defects, several unit-cells in length along the horizontal direction, are observed at the surface of the $BiFeO_3$ film. The polarizations in this film are either very large in magnitude pointing in the out-of-plane direction forming *tetragonal*-like (*T*-like) "*c*-type" domains, or significantly attenuated with multiple directions forming "*a*-type" domains. And at the transition regions between the *c*-type and *a*-type domains, *rhombohedral*-like (*R*-like) structures with polarization pointing to the diagonal of the pseudocubic unit-cell can be observed. While the *c*-type domains are located right below the surface defects, the *a*-type domains exist at local regions without defects on the surface. This alternating *c*-/*a*-type domain structures can also be seen in the maps of the out-of-plane components of the polarization vectors ($-\boldsymbol{D}_{FB}^{(z)}$) (Fig. 1b) and the *c*/*a* ratios (Fig. 1c), where significantly enhanced out-of-plane polarizations and *c*/*a* ratios are observed in the *c*-type domains. Fig. 2 shows the polarization distribution surrounding a charged linear defect embedded in a $BiFeO_3$ film grown on $TbScO_3$. A pair of polarization half vortex and half antivortex structures at the two edges of the linear defect are produced as a result of the formation of a "head to head" polarization configuration above and below the defect. In addition, our *in situ* TEM results show that in presence of the nanoscale defects, the stability of newly created domain can be dramatically altered as well.

In conclusion, we have discovered a strong interaction between the ferroelectric polarization and nanoscale defects. These defects can lead to polarization enhancement in ultrathin $BiFeO_3$ films, challenging the long-term understanding that the ferroelectric polarization is inevitably suppressed under reduced dimensions. They can also stabilize novel polarization topologies or mixed-phase structures, which could be useful for nanoelectronic or nanoelectromechanical applications. These results indicate that engineering nanoscale defects could be a new route for tuning ferroelectric properties [3].

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[3] The author gratefully acknowledges the financial support by the Department of Energy (DOE) under grant DESC0014430.

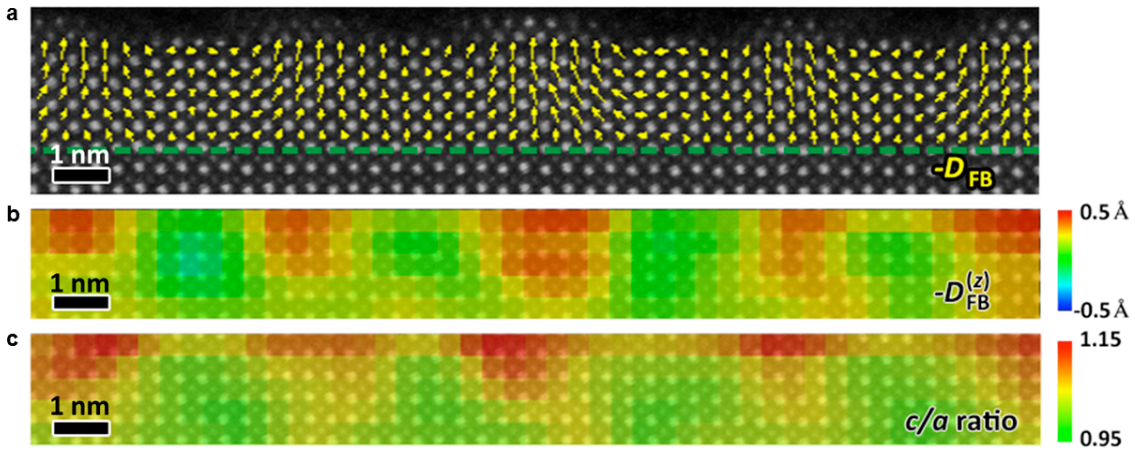

Figure 1. Distribution of polarization and strain in an ultrathin $BiFeO_3$ film. HAADF STEM image of the ultrathin $BiFeO_3$ film overlaid with **(a)** map of polarization vector ($-\boldsymbol{D_{FB}}$, which is defined as the atomic displacement of the Fe cation from the center of the unit cell formed by its four Bi neighbors), **(b)** $-\boldsymbol{D_{FB}}^{(z)}$ map (out-of-plane component of $-\boldsymbol{D_{FB}}$ vector), **(c)** *c*/*a* ratio (out-of-plane over in-plane lattice parameter ratio) map of the film. The green dashed line in (a) mark the position of the $BiFeO_3/TbScO_3$ interface.

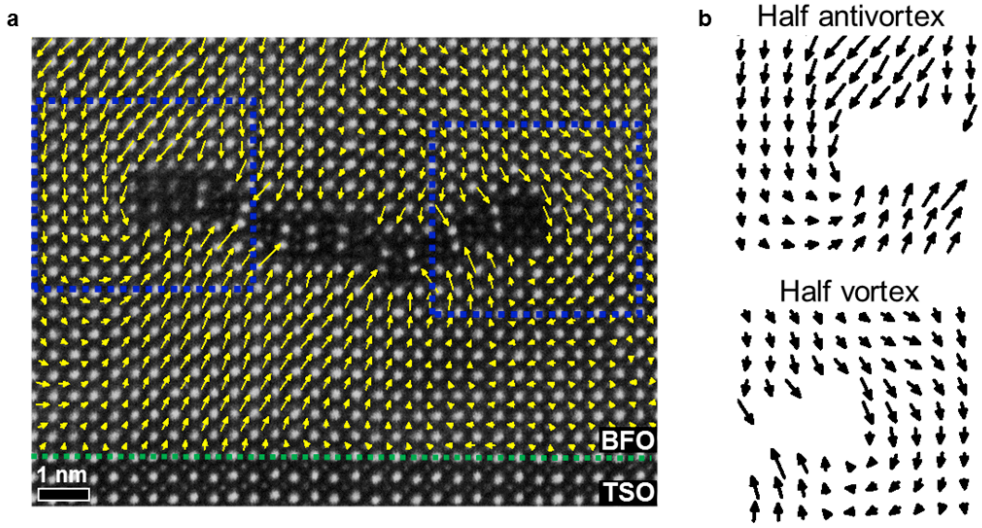

Figure 2. Polarization maps of half vortex and antivortex induced by a charged linear defect in a $BiFeO_3$ thin film. **(a)** HAADF STEM image of a defect above the $BiFeO_3/TbScO_3$ interface, where the polarization vectors ($-\boldsymbol{D_{FB}}$) are overlaid on the $BiFeO_3$ lattice. **(b)** Magnified map of the polarization vectors in the two different nanoregions highlighted by the blue rectangles in (a). The polarization distribution within these two regions presents novel half vortex/antivortex patterns.

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