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88 – Observation of Charge Separation Along $BiFeO_3$ 109^0 Domain Walls by Using Low-convergence Angle 4-dimensional Scanning Transmission Electron Microscopy

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Ferroelectric oxides have become a prototypical example of functional materials, attracting considerable interest in both fundamental research and device engineering. These materials often form domain walls (DWs) which are quasi-2D boundaries separating domains that differ in the orientation of their spontaneous polarization. DWs play an important role in determining many material properties such as stability[1], conductivity and photovoltaic activity[2], and they can be created, erased, and reconfigured by external electric fields[3], making them appealing as active elements in future nanoelectronic devices. Although, observation of the electric field in large scale polarization structures has been developed[4], the direct observation of charge distributions that is induced by local polarization states at large scale is still lacking. In this work, we report the observation of charge separation along $BiFeO_3$ (BFO) 109^0 DWs by using low-convergence angle 4-Dimensional scanning transmission electron microscopy (4D-STEM), the structures and polarizations are studied based on cross-sectional STEM.

Low-convergence angle 4D-STEM was performed on a BFO thin film with 50 nm thickness on $TbScO_3$ (TSO) substrate. A convergence angle of 2.4 mrad was used so that the diffraction disks are separated and the electron probe is larger than 1 unit cell. The electric field can be mapped by calculating the shift of the center diffraction disk because it relates to the change of the electron beam momentum and is negatively proportional to the local electric field. The charge mapping is then derived by differentiating the electric field based on Gauss's law. **Figure 1b** shows that the electric field is enhanced on the 109^0 DWs and points normal to the DWs. The corresponding charge map in **Figure 1c** shows that positive and negative charges are populated on the sides of the domain wall. To understand this charge separation, the Fe displacement is measured in the 109^0 DW areas. The cross-sectional atomic resolution STEM image in **Figure 2a** shows the intersections of two 109^0 DWs with the TSO surface. The Fe in-plane displacement in regions b and c are measured and plotted in **Figure 2b and c**, respectively, revealing an average displacement of ~ 15 pm in the domains but only ~ 5 pm on the DWs. This means that the polarization dipole is weaker on the DW and results in a displacement discontinuity. Such displacement discontinuity may induce unbalanced charge in the local DW area because the weaker polarization dipole at the DW is not able to fully compensate the negative and positive charge that is produced by the dipoles in the two adjacent unit cells, respectively (shown schematically in **Figure 1a**). As a result, the unbalanced positive charges will locate along the left side of the 109^0 DW while the unbalanced negative charges stay on the right side, forming an electric field across the DW and pointing to the right.

In conclusion, we have demonstrated a direct observation of charge separation along BFO 109^0 DW by using low-convergence angle 4D STEM, which is capable for resolving the features of electric field and charge density at lower magnifications. The displacement measurement shows the charge separation is induced by the displacement discontinuity on 109^0 DW. This work demonstrates a method for directly observing electric fields and charges at large scale, improving our understanding of emergent phenomena from nanoscale ferroelectric structures, and thus facilitating the development of ferroelectric-based nanodevices in information and energy technologies.

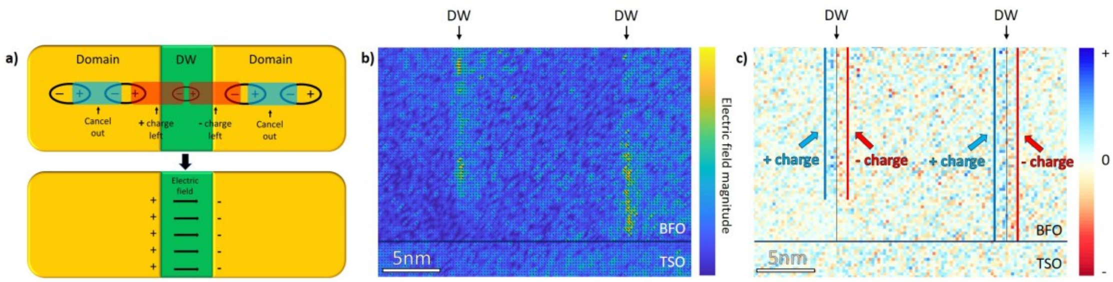

Figure 1. Figure 1. 109^0 DW model and low-convergence angle 4D STEM results. (a) Schematic of a 109^0 DW with displacement discontinuity. (b) Electric field and (c) charge density mappings are collected by using low-convergence angle 4D STEM.

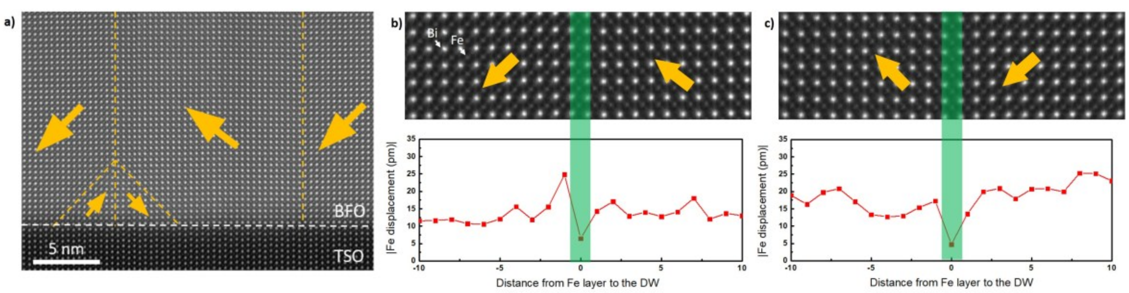

Figure 2. Figure 2. 109^0 DWs and displacement measurements (a) Cross-sectional HAADF STEM image. (b) & (c) Fe in-plane displacement measurements in the regions labeled as b and c in (a), respectively.

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