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doi:10.1017/S143192761301026X
Microsc. Microanal. 19 (Suppl 2), 2013

Atomic Structure and Properties of Charged Domain Walls in $BiFeO_3$ Films

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Ferroelectric domain walls have been studied for more than 50 years and are now attracting increasing interest due to their unique properties and novel functionalities that are different from bulk materials.[1] A ferroelectric domain wall can become electronically active, as a result of a "head-to-head" or "tail-to-tail" polarization configuration. Such domain walls carrying net bound charge can have distinct properties from uncharged domain walls, such as a metallic conductivity.[2] In this work, we show that charged domain wall (CDW) in the rhombohedral-like (R-like, as shown in Figure 1a left) $BiFeO_3$ thin films can possess a tetragonal-like (T-like, as shown in Figure 1a right) crystal structure, which induces the formation of nano-domains with novel polarization states and unconventional domain walls in nearby regions.

Figure 1b shows a diffraction contrast TEM image taken from a cross-sectional specimen of a 20 nm thick $BiFeO_3$ film grown epitaxially on an insulating (110) $TbScO_3$ substrate. The 180° domain walls occur typically paired with 109° ones to form triangular 109°/180° domain wall junctions. Above the junction near the free surface of the $BiFeO_3$ film, a CDW is observed. The atomic structure of the CDW is studied by high angle annular dark field (HAADF) imaging using National Center for Electron Microscopy's TEAM0.5 instrument with a point-to-point resolution of 0.5 Å. The HAADF image is further processed to obtain mapping of the lattice parameter and the atomic displacement of Fe cations from the center of four Bi neighbors, ($\mathbf{D_{FB}}$). The electric polarization is proportional to $-\mathbf{D_{FB}}$.[3] Figure 1c shows the spatial distribution of $-\mathbf{D_{FB}}$ overlaid on the HAADF image. A "head-to-head" polarization configuration is clearly seen above the triangular junction and an inclined 71° CDW forms. Interestingly, the polarization rotates gradually from <111> directions beside the CDW to the out-of-plane orientation at the CDW. The lattice parameter mapping also shows a local increase of the c/a ratio at the CDW. These results suggest the formation of a T-like structure at the CDW, surrounded by the regular R-like phase. The T-like CDW also leads to changes in polarization states in surrounding regions. As seen in Figure 1c and d, below the T-like CDW, a nano-domain with a pseudocubic structure, with an in-plane oriented polarization, occurs. As a result, unconventional 54.7° neutral domain wall and 125.3° CDW are observed, which are different from the generic 71°, 109°, and 180° domain walls in rhombohedral perovskite ferroelectrics.

In conclusion, using sub-Å resolution HAADF imaging and polarization analysis, we have shown that charged domain wall (CDW) in rhombohedral $BiFeO_3$ thin films can possess different crystal structure and electric polarization state from those in the bulk, and induces the formation of unconventional nano-domains and domain walls in nearby regions. T-like CDW and 125.3° CDW observed here may provide metallic conduction channels in the film, since the accumulation of compensating free charge that screen the bound charge at the CDW can in

principle intriguer an insulator-metal transition. Furthermore, the T-like CDW and its surrounding R-like regions form a nano-region with "R-T" structure mixture, which may provide new mechanisms for the electrical switching of thin films.

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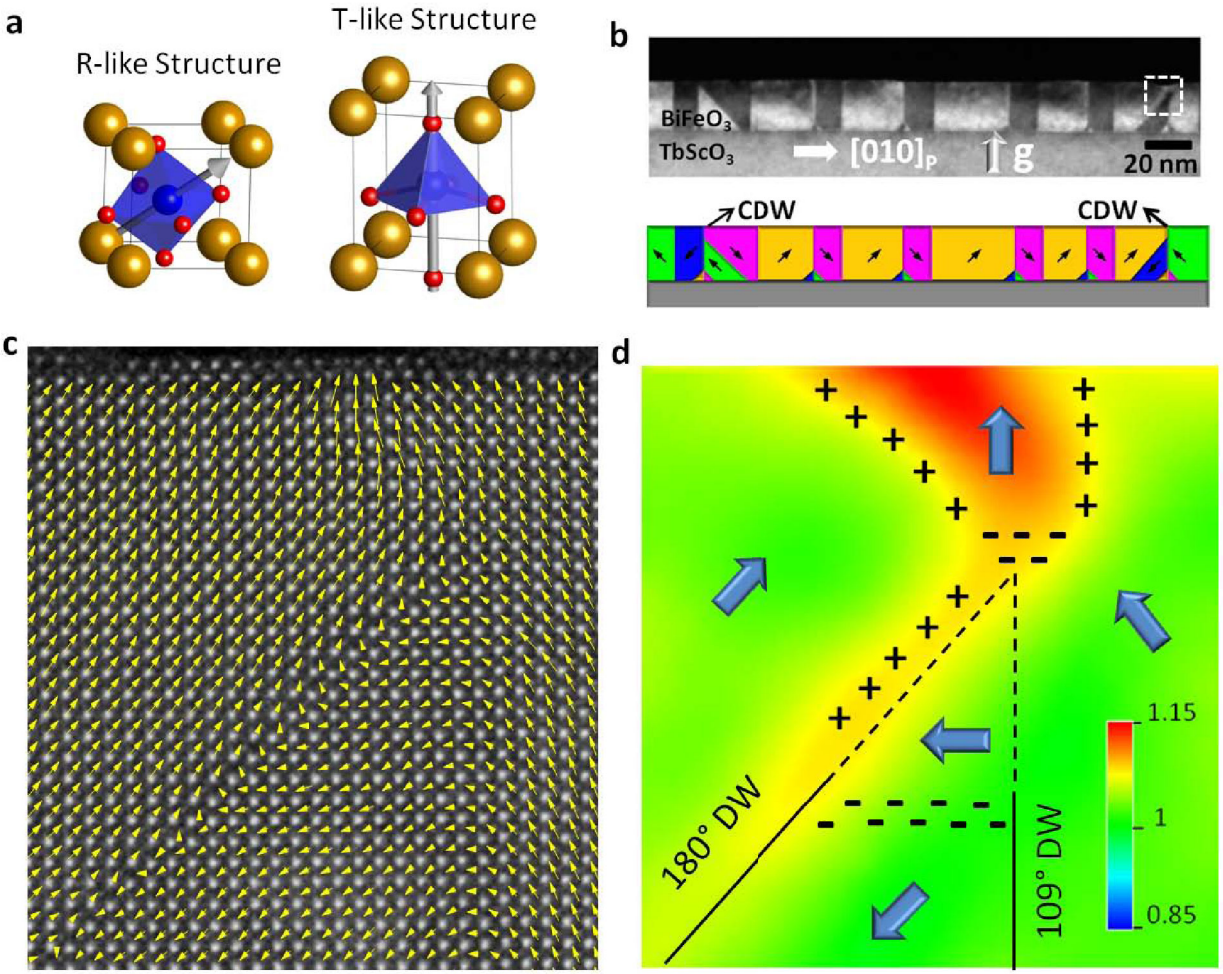

Figure 1. (a) Atomic models of the rhombohedral-like and tetragonal-like structures of $BiFeO_3$. (b) Cross sectional dark field TEM image of domain patterns of 20 nm thick $(001)_P$ $BiFeO_3$ film on $(110)_O$ $TbScO_3$ substrate (P denotes pseudocubic and O denotes orthorhombic), with the corresponding schematic domain configuration shown below. (c) Plot of the $-\mathbf{D}_{FB}$ vectors ($\mathbf{D}_{FB}$ is the atomic displacement in the image plane of the Fe cation from the center of four Bi neighbors, and $-\mathbf{D}_{FB}$ is proportional to the polarization) overlaid on HAADF image of a 109°/180° domain wall junction near the free surface of the $BiFeO_3$ film. (d) The corresponding color map of the c/a ratios. The polarization orientation and bound charge are indicated schematically.

https://doi.org/10.1017/S143192761301026X Published online by Cambridge University Press