Atomic Structure and Switching Dynamics of Charged Domain Walls in Multiferroics

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Charged domain walls (CDWs) in ferroelectrics, as a result of "head-to-head" or "tail-to-tail" polarization configurations, play a critical role in controlling the atomic structure, electric, photoelectric and piezoelectric properties of ferroelectric materials. The accumulation of compensating free charge that screen the bound charge at the CDW can in principle intriguer an insulator-metal transition. In this work, we show that CDWs in the rhombohedral-like (R-like) $BiFeO_3$ thin films possess a tetragonal-like (T-like) crystal structure, and that the CDW can be manipulated by applying electric field, leading to switching of the electrical resistance of the ferroelectric film.

An epitaxial 20 nm thick $BiFeO_3$ film with a 20 nm thick $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) bottom electrode was grown on (110) $TbScO_3$ substrates by reactive molecular-beam epitaxy. 71° CDWs were observed above/below triangular 109°/180° domain wall junctions. The CDW was studied by high angle annular dark field (HAADF) imaging using the TEAM0.5 instrument with a point-to-point resolution of 0.5 Å. The HAADF image was processed to obtain mapping of the lattice parameter and atomic displacement of Fe cations from the center of four Bi neighbors ($\mathbf{D_{FB}}$). The electric polarization is proportional to $-\mathbf{D_{FB}}$. Fig. 1a shows the spatial distribution of $-\mathbf{D_{FB}}$ overlaid on the HAADF image. A CDW with "head-to-head" polarization configuration is seen above the triangular junction. Interestingly, the polarization rotates gradually from <111> directions beside the CDW to an out-of-plane orientation at the CDW. Lattice parameter mapping (Fig. 1b) 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. Applying a positive voltage results in shrinkage of the triangular domain and thus formation of a CDW with "head-to-head" polarization configuration (Fig. 2a-c). A subsequent low reading voltage (Fig. 2d) does not change the domain configuration and the reading current suggests a conductive state. Applying a sufficiently large negative voltage results in expansion of the triangular domain and annihilation of the CDW (Fig. 2e-g). After the CDW is erased, the reading I-V curve (Fig. 2h) suggests that the ferroelectric film returns to its insulating state.

In summary, we have found stable charged domain walls in $BiFeO_3$ thin films, which possess crystal structures different from the bulk film due to local charge compensation and polarization rotation. The CDW can be written and erased by applying electric field, and the resulting states with and without CDWs are found to have different electrical resistance, suggesting a route to engineer ferroelectric devices.

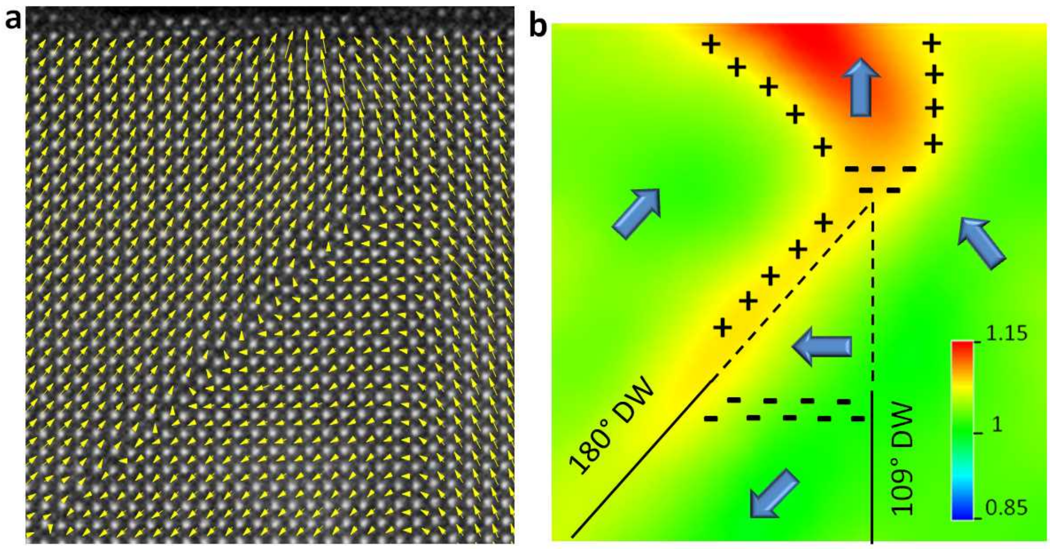

FIG. 1. (a) Plot of the **-D$_{FB}$** vectors overlaid on HAADF image of a 109°/180° domain wall junction near the free surface of the 20 nm thick $BiFeO_3$ film. (b) The corresponding color map of the c/a ratios. The polarization orientation and bound charge are indicated schematically.

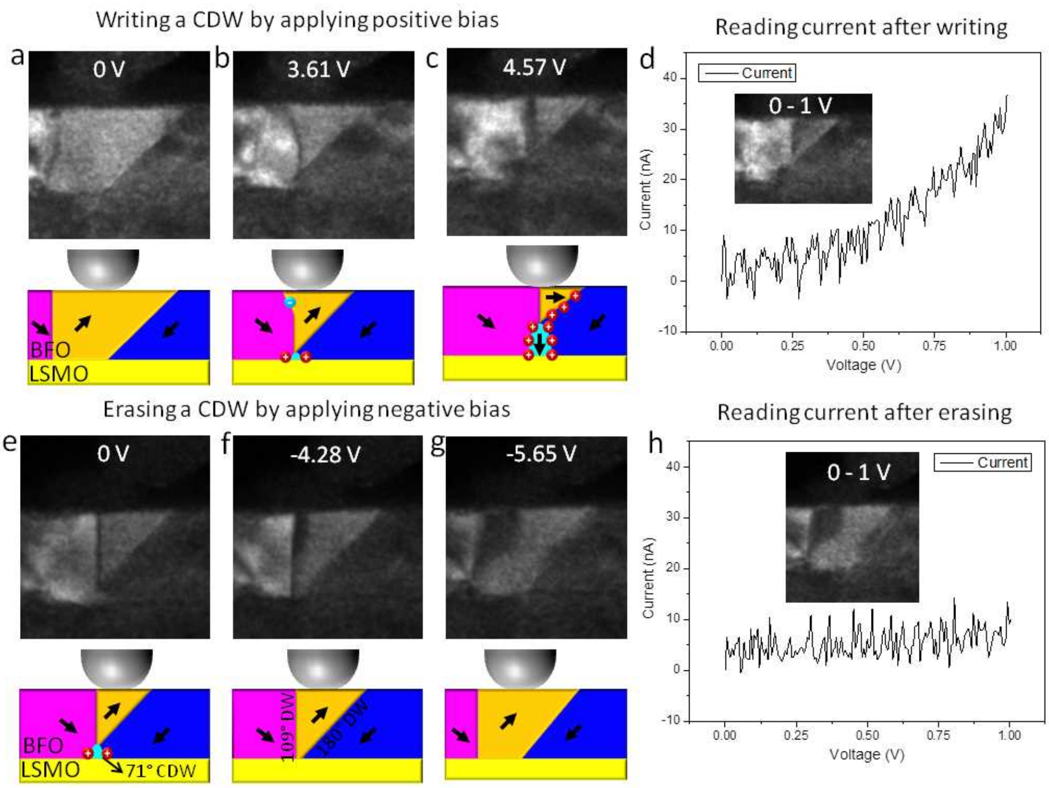

FIG. 2. (a)-(c) Dark-field diffraction contrast TEM images extracted from a video showing writing a CDW by applying a positive bias ramp. (d) Current measured by applying a low reading voltage after writing. (e)-(g) Dark-field diffraction contrast TEM images extracted from a video showing erasing a CDW by applying a negative bias ramp. (d) Current measured by applying a low reading voltage after erasing.