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Atomic Level Structural Modulations at the Negatively Charged Domain Walls in $BiFeO_3$ Films

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Rhombohedral multiferroic $BiFeO_3$ (BFO) possesses various kinds of domain walls (DWs) which feature 109°, 180° and 71° configurations, respectively. Depending on the orientations of DWs, the dipole configurations beside DWs can either be 'head-to-tail', 'head-to-head' or 'tail-to-tail' which then introduce zero, net positive or net negative bound charges at the DWs, respectively. Since the finding of novel DW conduction in BFO, several emergent phenomena at DWs are confirmed, such as electrically tunable conductance, enhanced photovoltage and magnetoresistant effect [1-3]. Particularly, charged DWs (CDWs) in BFO exhibit electrically controlled photo-detection property which implies non-volatile optoelectronic memory applications [3]. In addition, these CDWs are also known to exhibit pinning effects on the movement of DWs and thus induce polarization fatigue in BFO memories. Although a charge-accumulation driven T phase was identified at a 71° CDW with 'head-to-head' polarizations [4], atomic-scale mapping of tail-to-tail CDWs in BFO films is still so incomprehensive that the physical insights of the CDW phenomena are known little.

In our recent study, BFO thin films are epitaxially grown on $SrTiO_3$(STO) (001) and $GdScO_3$(GSO) $(110)_{orthorhombic}$ single-crystal substrates by pulsed laser deposition (PLD). The choice of the STO substrate is to introduce CDW by making use of the four-fold symmetry of the cubic structure in STO. The BFO films grown on GSO are further buffered with an epitaxial and conducting $SrRuO_3$(SRO) layer which promotes an introduction of 71° CDW through surface-compensating. Transmission electron microscopic samples are made by slicing, gluing, grinding and final ion milling with a Gatan PIPS 691. Aberration-corrected scanning transmission electron microscopic (AC-STEM) images are recorded using the high-angle angular dark-field (HAADF) detector on FEI Titan G2 60-300kV microscopy equipped with a high-brightness field-emission gun, double Cs correctors, and a monochromator operating at 300kV. The probe convergence is 25 mrad which yields a probe size of less than 1Å. Before quantitative analysis, HAADF-STEM images are performed by fast Fourier transform (FFT) filtering using only a low-pass annular mask (slightly more than the resolution limit of the image). The atomic position is determined by two-dimensional Gaussian fitting of the individual atomic intensity profile of the STEM image using Matlab [5]. Two dimensional mapping of lattice spacing, lattice rotation and Fe sub-lattice displacement were also carried out using Matlab and Gatan DigitalMicrography software.

Using aberration-corrected scanning transmission electron microscopy (STEM), negatively CDWs are systematically investigated in BFO films, with their structures being directly mapped on the atomic scale. 109°, 180° and 71° CDWs on (100) plane and a 109° CDW on (110) plane, with tail-to-tail dipole configurations, are thus revealed. Both the atomic structural details and sub-lattice ferroelectric ion displacements of these CDWs are quantitatively studied using aberration corrected HAADF-STEM with sub-angstrom precision. Lattice spacing *Lx* and lattice rotation *Ry* at the CDWs of (100) type show one-dimensional modulations where alternate lattice expansions and clockwise/anticlockwise rotations are clearly imaged, which differ remarkably from both uncharged domain walls (UCDWs) and positively CDW with head-to-head polarizations in BFO reported previously. These findings are expected to broaden our understanding on DW structures as well as the effect of bound charges on structural stabilities of DWs [6,7].

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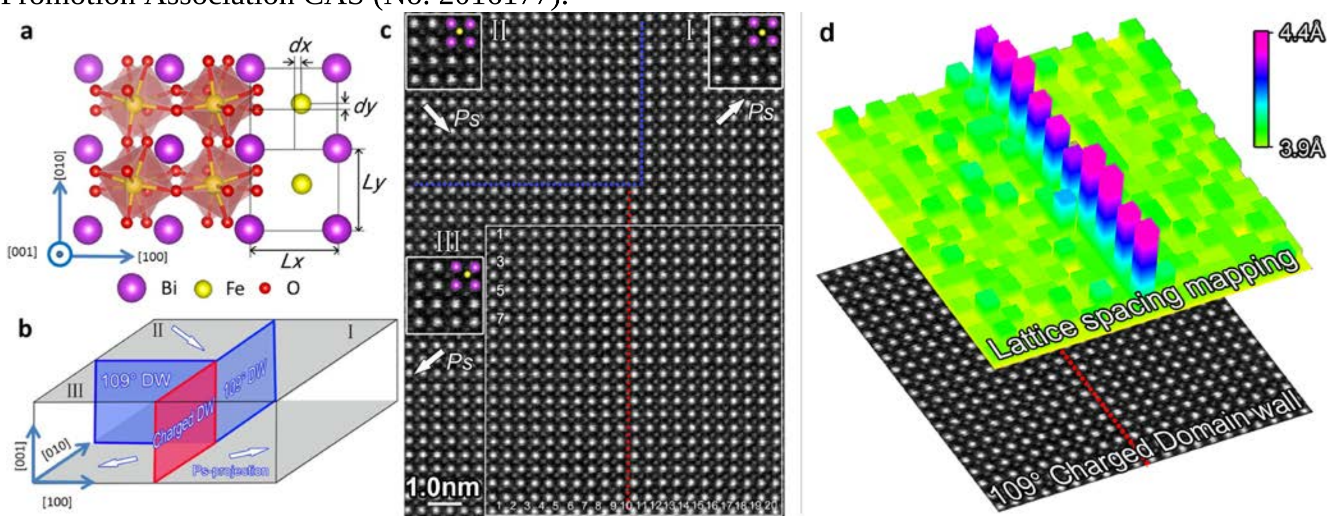

Figure 1. Illustration of 109° CDW of (100) type. (a) Atomic model of multiferroic BFO projected along [001] direction where Bi, Fe and O are represented by violet, yellow, and red spheres, respectively. *dx* and *dy* are components of sub-lattice displacement vectors of Fe sub-lattice D_F (from Bi sub-lattice center to Fe sub-lattice) in horizontal and vertical directions. *Lx* and *Ly* are the lattice spacing in horizontal and vertical directions. (b) Illustration of intersection of three domains Ⅰ, Ⅱ and Ⅲ, the white arrows are the *Ps* projections of the corressponding domains along [001] direction. The blue planes are 109° UCDWs of (100) type. The red plane is 109° CDW of (100) type. (c) A HAADF image of domain intersection projected along [001]. The 109° UCDWs of (100) type is marked by blue dotted lines. A red dotted line indicates the 109° CDW of (100) type. The insets are the enlarged images of the corresponding area (violet: Bi, yellow: Fe). The white arrows are the *Ps* projections. The square frame is the area used for analyzing the lattice variations and Fe sub-lattice displacements. (d) Atomic-level 1D modulation is demonstrated at the negatively charged domain walls in $BiFeO_3$ thin films. All the 109º, 180º, and 71º charged domain walls of (100) type reveal similar 1D modulations in terms of alternate lattice expansions and clockwise/counterclockwise lattice rotations [6].

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