1390
doi:10.1017/S1431927613008945
Microsc. Microanal. 19 (Suppl 2), 2013
© Microscopy Society of America 2013

Polarization and Charge Density Distribution in Highly Strained Mixed Phase $BiFeO_3$ Studied by STEM and Electron Inline Holography

Yoon Ah Shin[1], Kyung Song[1], Kanghyun Chu[2], Chang-Su Woo[2], Chan-Ho Yang[2] and Sang Ho Oh[1*]

[1.] Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea
[2.] Department of Physics, KAIST, Daejeon 305-701, Korea

Morphotropic phase boundaries (MPBs) in complex oxides exhibit unexpectedly large responses to electric or electromagnetic stimulus, as exemplified by large dielectric response and photon-induced conduction [1]. Recent studies showed that MPBs can be derived in strained bismuth ferrite ($BiFeO_3$, BFO) thin films by the lattice misfit strain imposed by a substrate [2]. For example, the compressive misfit strain imposed by $LaAlO_3$ (001) substrate on BFO film (-4.5%) is known to result in the pseudomorphic growth of a tetragonal-like monoclinic phase (T-BFO). Compared with the bulk BFO, this T-BFO phase is characterized by shorter in-plane but larger out-of-plane lattice parameters. When the film thickness increases over a certain value (~50 nm), a rhombohedral-like monoclinic phase (R-BFO) evolves to relax the misfit strain, forming a mixture of R-/T- phases in a stripe pattern (Fig. 1a). The boundaries of the two phases revealed a typical MPB-like characteristic with exhibiting notably enhanced optoelectronic responses in photocurrent measurements. Polarization rotation has been believed as an inherent characteristic of MPBs and thus responsible for the enhanced photocurrent, suggesting that the MPBs are most likely charged. We aimed to verify the charged boundary model based on polarization rotations, and to investigate how this is related to the strains in the BFO films.

The polar displacement of cations, i.e. displacement of Fe atom from the centrosymmetric position of Bi cage, was determined quantitatively on STEM Z-contrast images with unit cell resolution (Fig. 2). Although the obtained Fe-displacement map is not necessarily identical to the polarization map, it can, at least, provides an idea about the spatial distribution of polarization vector. Inline electron holography experiments were carried out to determine the charge density across the phase boundaries using the sub-electron-volt-sub-angstrom-microscope (SESAM) (Carl Zeiss NTS) equipped with a monochromated 200 kV field emission gun and in-column MANDOLINE filter.

Inline electron holography results showed that the total charge density was several times higher in the regions close to the phase boundaries and also to the interface with LAO substrate than the interior of each T- and R-phase (Fig. 1b). Interestingly, the charge distribution at the R/T phase boundaries was asymmetric, only high (positive in sign) at the one side of the R-phases, i.e. obtuse angle corner with the interface (Fig. 1c). Referring to the Fe-displacement map shown in Fig. 2b, the polar rotation across the obtuse angle boundary might lead to the buildup of positive bound charges due to incomplete cancellation of dipole moment of each phase; although the polar displacement vectors are aligned in a sort of head-to-tail configuration, the magnitude of polarization in T-phase is 1.5 times larger than that of R-phase, so that the positive polarization charge of T-phase outweighs the negative charge of R-phase. This phenomenon appears to be enhanced by the lattice strain as it was confirmed that the charge density decreases and eventually vanishes along the boundary near the free surface of BFO film, where the strain is usually relaxed due to the thin foil effect of TEM sample. Spatial distribution of polarization and associated charge density and their relationship with the lattice strain will be discussed more thoroughly in comparison with the strain map obtained by dark-field inline electron holography.

https://doi.org/10.1017/S1431927613008945 Published online by Cambridge University Press

References:

[1] T. Asada and Y. Koyama, Phys. Rev. B. **75** (2007), p. 214111-1.
[2] R. J. Zeches *et al*, Science **326** (2009), p. 977.

[3] The authors acknowledge funding from the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant 2010-0005834, 2011-0029406).

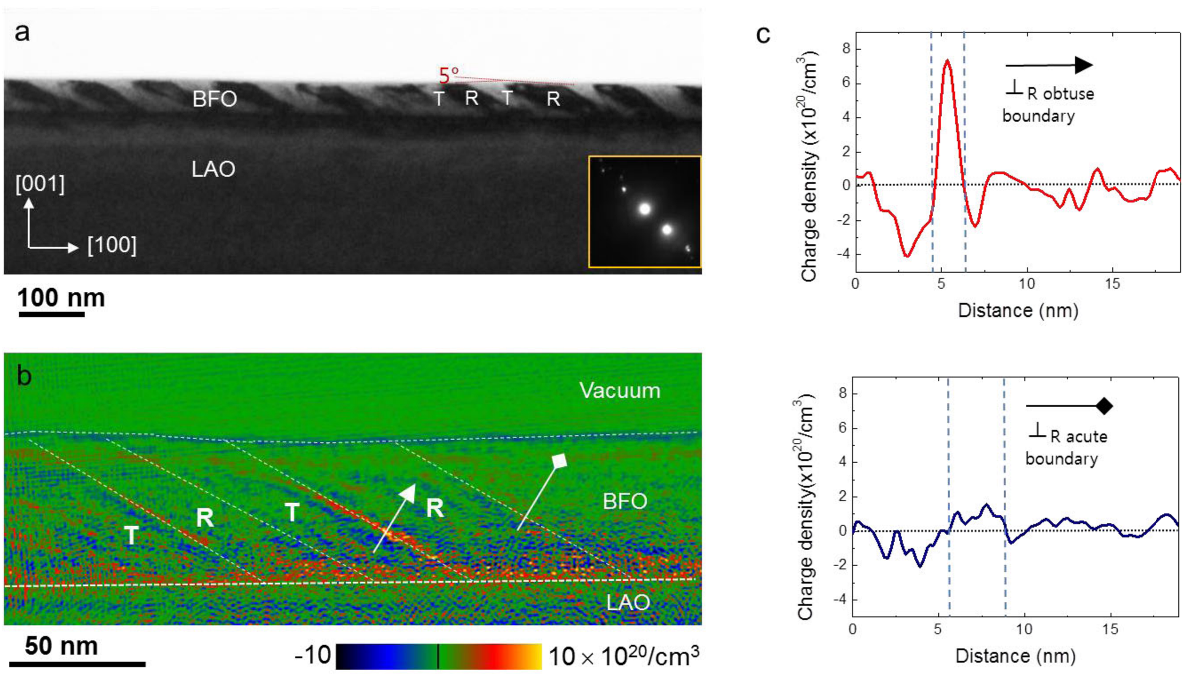

Figure 1. a. TEM image showing a strained $BiFeO_3$ film consisted of mixed phases on $LaAlO_3$ (001) substrate. b. Charge density map obtained from the phase information reconstructed by applying inline electron holography. c. Box averaged profile of the charge density across the obtuse (arrow in b) and the acute (diamond arrow) boundary.

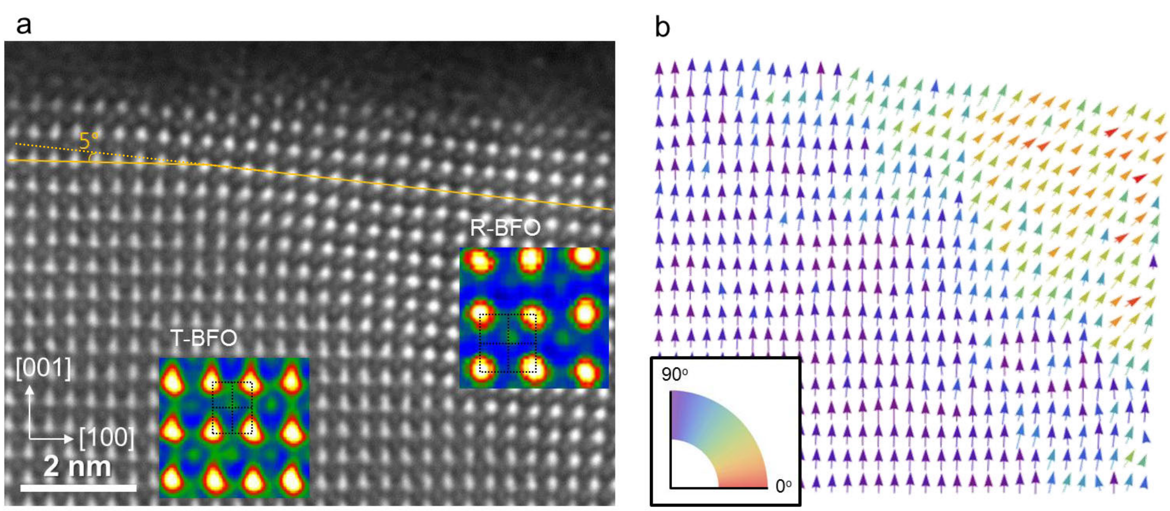

Figure 2. a. HAADF-STEM image of mixed phase BFO. b. Fe-displacement vector map. The map reveals head-to-tail configuration and also the rotation of polarization across the T-/R- phase boundary.

https://doi.org/10.1017/S1431927613008945 Published online by Cambridge University Press