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Transmission Electron Microscopy Study of Domain Structures in Multiferroic $BiFeO_3$ Thin Films

C. T. Nelson[1], Y. Zhang[1], C. M. Folkman[2], C. B. Eom[2], and X.Q. Pan[1]

[1]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109
[2]Department of Materials Science and Engineering, University of Wisconsin, Madison, WI 53706

The ferroelectric $BiFeO_3$ is the subject of considerable contemporary research as it is a rare example of a room temperature single-phase multiferroic making it attractive for use in novel magnetoelectric devices. Ferroelectric properties such as the polarization of $BiFeO_3$ thin films are sensitive to their domain structure[1]. Furthermore, both experimental measurements and theory have shown that the domain walls of $BiFeO_3$ are electrically conducting[2], which suggests that tailoring the domain pattern is not only important to optimize ferroelectric properties but that domain walls themselves can be directly utilized to realize novel devices. In this work we examine the self-assembling long-range domain patterns formed by (001) $BiFeO_3$ thin films.

$BiFeO_3$ is a rhombohedral ferroelectric with polarization along one of the <111> directions. The unit cell corresponding to a polarization along $[\bar{1}11]$ is shown in Fig. 1a. The four unique <111> axes correspond to four ferroelastic variants, r_1-r_4, illustrated in Fig. 1b. Streiffer et al.[3] have predicted that (001) oriented films will spontaneously form two types of ferroelastic twin structures: a striped pattern of 109° rotated domains with vertical domain walls (Fig 2a) or a striped pattern of 71° rotated domains with inclined domain walls (Fig 2b).

In this work $BiFeO_3$ films were grown on insulating (110) $TbScO_3$ single crystal substrates at 690 °C by off axis *rf*-magnetron sputtering. This is below the Curie temperature of 830 °C for $BiFeO_3$ so the sample does not undergo a phase transition after deposition. Characterization of the domain structure was performed by transmission electron microscopy (TEM) using a JEOL 3011. Samples were prepared by mechanical polishing followed by argon ion milling.

TEM shows that the $BiFeO_3/TbScO_3$ films are free of dislocations owing to the small <–0.2% lattice mismatch between $TbScO_3$ and $BiFeO_3$. Both the predicted 109° and 71° domain structures are observed in the $BiFeO_3/TbScO_3$ materials system. Dark-field TEM micrographs show the 109° and the 71° stripe pattern in Figs. 3a and 3b, respectively. Selected area diffraction (SAD) patterns along the [010] direction of both films confirm the presence of only r_1 and r_4 ferroelastic variants (SAD pattern inset in Fig 3a). The [100] axis SAD pattern inset in the 109° domain structure shows a distinct split in the *00l* peaks indicating a canting of these planes while the vertical (010) domain wall planes are coplanar. The dark field image in Fig. 3b is formed from the split *004* peak resulting in strong bright/dark contrast between the r_1 and r_4 variants. In contrast, the [100] SAD pattern of the 71° structure shows canted (h00) planes and coplanar (00*l*) planes (not shown here). Since it lies orthogonal to the 109° structure, the domain walls are viewed edge on along the [100] axis. In this projection the r_1 and r_4 domains are isostructural, thus the only strong contrast in the dark field image is from the domain wall itself and from the strain fields. These canted planes show a relaxation to the predicted rhomobhedral domain structures but without the formation of any dislocations.

References:

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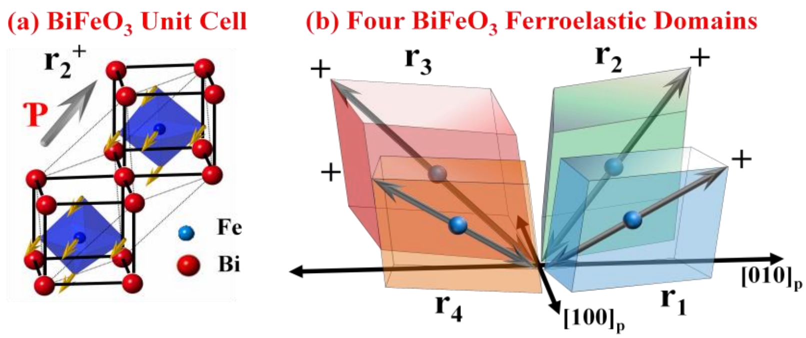

Figure 1. (a) Bulk rhombohedral $BiFeO_3$ structure. **(b)** The four ferroelastic variants of the pseudo-cubic unit cell.

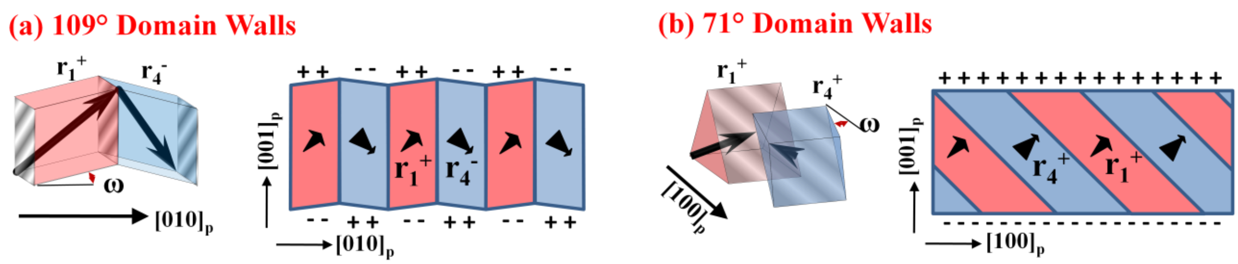

Figure 2 (a) Striped r1/r4 domain pattern with vertical 109° domain walls. **(b)** Striped r1/r4 domain pattern with inclined 71° domain walls.

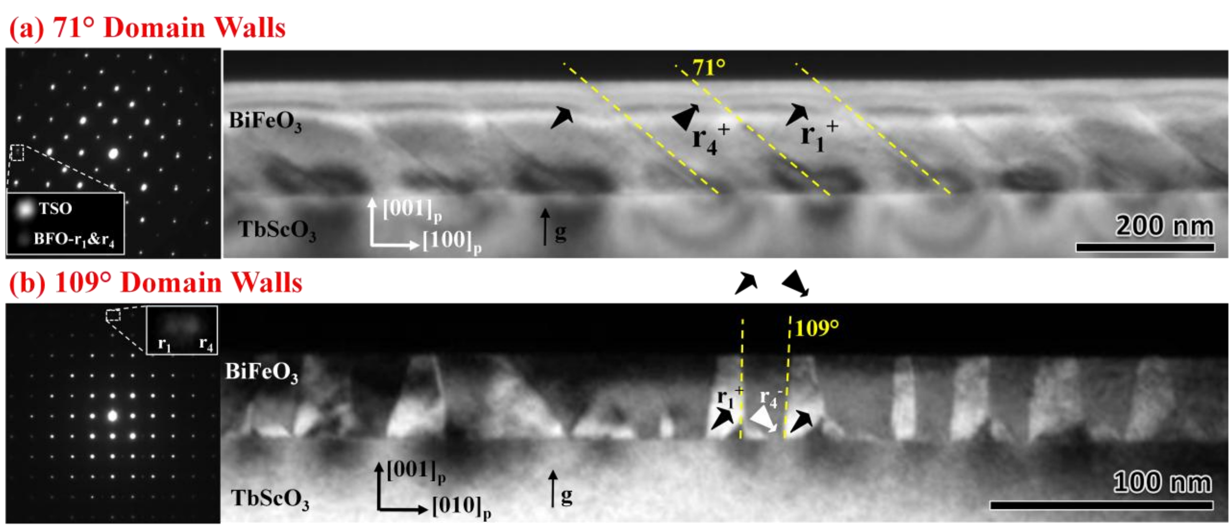

Figure 3 (a) Dark-Field TEM micrograph of the 71° domain pattern viewed along [010] direction with the corresponding SAED pattern at left indicating the presence of only r_1/r_4 ferroelastic domains. Several inclined 71° domain walls are highlighted. **(b)** Dark field TEM image of the 109° domain pattern with several vertical 109° domain walls highlighted. Inset SAED pattern shows the canting of the (00*l*) peaks.

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