Stripe domain structure in epitaxial (001) $BiFeO_3$ thin films on orthorhombic $TbScO_3$ substrate

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We have analyzed the ferroelastic and ferroelectric domain structure of high crystalline quality (001) $BiFeO_3$ films on orthorhombic (110) $TbScO_3$ substrates. Two domains were present in stripes separated by (010) vertical boundaries, with spontaneous polarizations in adjacent domains rotated by 109°. The striped morphology was caused by nucleation of only two *ferroelastic* domains on the low symmetry $GdFeO_3$-type substrate. Domain engineering through substrate symmetry is an important finding for rhombohedral ferroelectric epitaxial thin films. The stripe pattern with vertical walls may be useful for extracting domain wall contributions to magnetism and electrical transport properties of $BiFeO_3$ materials. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3152009]

Epitaxial thin films of the rhombohedral multiferroic bismuth ferrite ($BiFeO_3$) have been considered for lead free *ferroelectric* random access memories because of high remnant polarization (approximately 100 $\mu C/cm^2$ along the [111] direction) and for spin valve devices that rely on room temperature magnetoelectric coupling between the polarization and antiferromagnetism.[1,2] So far, most epitaxial structures have consisted of $BiFeO_3$ deposited on $SrRuO_3$ conducting oxide electrodes on $SrTiO_3$ single crystals or Si with a $SrTiO_3$ template.[3,4] Typically, the orientation and vicinality of the $SrTiO_3$ determines the structural properties of the $BiFeO_3$ film including orientation and domain structure.[5,6] Although strong epitaxial effects have been realized for $BiFeO_3$ overlayers on cubic $SrTiO_3$ substrates, few reports address domain configurations on other types of substrates. To obtain a more general description of epitaxial induced changes from bulk $BiFeO_3$, experimental investigation of more than one type of underlying substrate and electrical boundary condition are required.

In this letter, we report the domain structure of high crystalline quality epitaxial (001) pseudorhombohedral $BiFeO_3$ films grown on orthorhombic $(110)_o$ $TbScO_3$ single crystal substrates (subscripts *o* and *p* denote orthorhombic and pseudocubic indexes, respectively). The approximate relationship between pseudocubic and orthorhombic indices is shown at the bottom of Fig. 1. $TbScO_3$ was chosen because of its very close lattice match with $BiFeO_3$ (<−0.3%). Before deposition of the films, the $TbScO_3$ substrates were annealed at 1100 °C for 3 h in O_2 resulting in atomically flat surfaces with unit cell high steps. Multiple $BiFeO_3$ films with thickness between 200 and 800 nm were deposited by off-axis radio frequency magnetron sputtering at 690 °C.[3] The fact the growth temperature is below the paraelectric to *ferroelectric* transition temperature ($T_c \sim 840$ °C) strongly influences the final *ferroelastic* domain structure. Specifically, films on (001) cubic substrates may have up to four *ferroelastic* domains,[7] however, the domains in $BiFeO_3$ on orthorhombic $TbScO_3$ were highly aligned, with the presence of only two *ferroelastic* domain variants. In this letter, we focus on $BiFeO_3$ films that exhibited *vertical domain walls* (VDWs) between adjacent domains (other domain wall configurations will be reported separately). The origin of this domain pattern anisotropy is the accommodation of only two specific $BiFeO_3$ spontaneous shear distortions by nonequal in-plane lattice parameters of the orthorhombic substrate.

The *ferroelastic* domain structure was characterized with atomic force microscopy (AFM) and transmission electron microscopy (TEM). Figure 2(a) is an AFM image of a $BiFeO_3$ film on $TbScO_3$ substrate showing a corrugated sur-

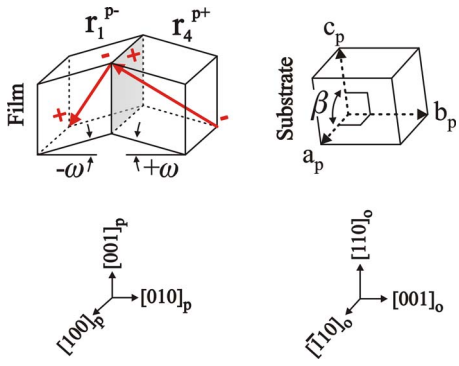

FIG. 1. (Color online) The 3D schematic indicating the as-grown *ferroelastic* and *ferroelectric* domain structure of the film. P_s is represented by red arrows for two domain variants r_1 and r_4 and shaded area represents $(010)_p$ domain wall. The domains are tilted oppositely by $\pm\omega$. The substrate is represented with an orientation matched monoclinic unit cell. All angular distortions are exaggerated for clarity. Beneath are approximately collinear orthorhombic and pseudocubic coordinates systems.

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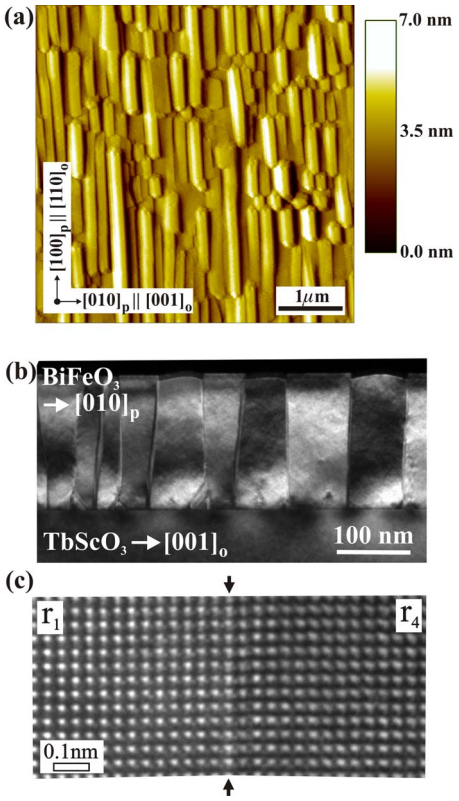

FIG. 2. (Color online) AFM topography (a) of a $BiFeO_3$ film on $TbScO_3$ substrate and a dark field TEM cross section (b) of the $BiFeO_3$ film on $TbScO_3$ substrate. A high resolution image is shown of a vertical domain boundary (c) (marked with arrows).

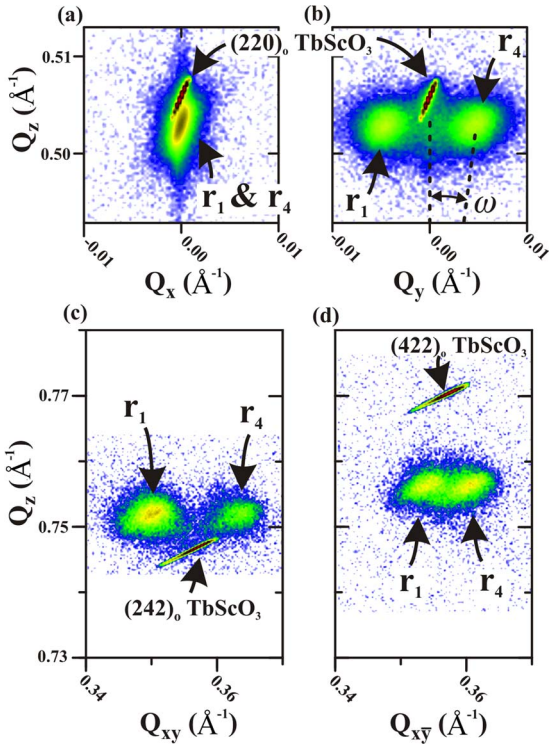

FIG. 3. (Color online) Detailed RSM maps near the $TbScO_3$ 220_o and $BiFeO_3$ 002_p reflections at two orthogonal in-plane sample orientations [$\varphi=0°$ (a) and $\varphi=90°$ (b)]. The angle ω is a measure of domain tilting due to domain wall coherency. Below are two $\{113\}_p$ off-axis RSMs measured at $\varphi=45°$ (c) and at $\varphi=135°$ (d).

face topography where the direction traversing peak to valley is $[010]_p \| [001]_o$. Cross-sectional TEM revealed that the corrugated surface morphology was due to the underlying domain structure. Figure 2(b) is a dark field TEM image of a $BiFeO_3$ overlayer on $TbScO_3$ substrate where the in-plane direction is $[010]_p \| [001]_o$. Vertical lines are clearly observed at a spacing ~80 nm and are intersections of $(010)_p \| (001)_o$ type VDWs with the $(100)_p$ cross-sectional plane. High resolution TEM shows coherency across the boundary near one vertical wall indicated by arrows in Fig. 2(c). Combining TEM and AFM observations suggests the presence of only two *ferroelastic* domains (instead of the four observed on cubic substrates).[7] These *ferroelastic* domains are labeled r_1/r_4 as shown on either side of the VDW in Fig. 2(c).

Next, the crystallography of this stripe domain pattern was investigated with high-resolution x-ray reciprocal space mapping (RSM), obtained on a four-circle Cu $K\alpha$ x-ray diffractometer equipped with a four-bounce monochromator. Since well-defined crystallographic tilting of the constituent domains are associated with VDWs,[7,8] RSMs or rocking curves of any $00L_p$ reflection at two in-plane orientations of the sample (i.e., $\varphi=0°$ and $\varphi=90°$) distinguish the morphology of the VDWs by particular splittings of the diffraction peaks from the domains. Specifically, three possible situations exist: splitting is observed only as a rotation about $[100]_p \| [1\bar{1}0]_o$ (stripe-$(010)_p$ VDWs), splitting is only about $[010]_p \| [001]_o$ (stripe-$(100)_p$ VDWs), or splitting is in both directions (mixed VDWs). Experimentally, only the out-of-plane $BiFeO_3$ 002_p reflection shown in Fig. 3(b) ($\varphi=90°$) exhibited peak splitting and no splitting was observed in Fig. 3(a) ($\varphi=0°$). Therefore, rotation and localized domain tilting was about $[100]_p$ corroborating the $(010)_p$ VDW geometry, consisting of only a single domain pair. The strength of the tilting was $\omega=-0.5°$ and $+0.5°$ for r_1 and r_4 the domains, respectively.

The domain structure, lattice parameters and symmetry of the $BiFeO_3$ on $TbScO_3$ were examined with off-axis RSM. Figures 3(c) and 3(d) are the RSM data from the two accessible $\{113\}_p$ reflections ($\varphi=45°$ and $\varphi=135°$, respectively) in the asymmetric Bragg–Brentano geometry. Each RSM contains reflections from the substrate and film, with calibration to the substrate. The high crystalline quality of the $BiFeO_3$ film leads to clear peak separation. This allowed the *ferroelastic* domain pattern and unit cell geometry to be fit by a simulated diffraction pattern. Results matched the r_1 and r_4 *ferroelastic* domain variants observed with TEM. The symmetry matched the bulk pseudorhombohedral with $\alpha_r=89.4\pm0.1°$.[9,10] The average pseudorhombohedral in-plane lattice parameter was slightly strained −0.24% to 3.955 ± 0.01 Å and the out-of-plane lattice parameter was elongated to 3.973 ± 0.005 Å consistent with a small compressive in-plane stress (bulk $BiFeO_3=3.964$ Å).[9,10]

The fact that the measured spontaneous rhombohedral distortion of $BiFeO_3$ ($90°-\alpha_r=0.6°\pm0.1°$) matches well with the measured tilting angle ($+\omega=0.5°\pm0.1°$) of the domain pattern in Fig. 3, suggests that the VDWs have little or no distortion within our detection limits, which matches well with the result from high resolution TEM [Fig. 2(c)].

Using the above structural data in conjunction with out-of-plane piezoresponse force microscopy (PFM) measurements, a three-dimensional arrangement of the r_1 and r_4 *ferroelectric* domains was constructed (Fig. 1). PFM mea-

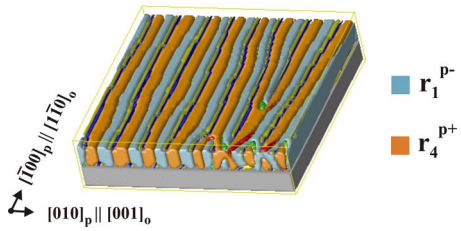

FIG. 4. (Color online) Phase field simulation of $BiFeO_3$ on $TbScO_3$ exhibiting the same stripe-$(010)_p$ vertical domain walls observed experimentally.

sured out-of-plane polarization (not shown). Two states were observed having up (+) and down (−) components of the spontaneous polarization (P_s). When additionally assuming P_s is coincident with the long axis of the *ferroelastic* unit cell, two *ferroelectric* domains with polarization directions 109° rotated can be defined. Figure 1 schematically represents a *ferroelectric* domain structure that is consistent with our RSM and PFM measurements. This alternating polarization points to an absence of a net charge at the substrate and air interfaces of the $BiFeO_3$ film.[7]

Since low substrate symmetry is known to strongly influence other epitaxial systems,[11] its affect on the $BiFeO_3$ stripe-(010) VDW morphology was investigated. Instead of an orthorhombic unit cell, the $TbScO_3$ substrate was defined by a simplified monoclinic unit cell (calculated from the bulk orthorhombic),[12,13] where a_p=3.9530 Å, b_p=3.9574 Å, c_p =3.9530 Å, and β=87.24° (see Fig. 1). Therefore, the $(110)_o$ $TbScO_3$ surface is rectangular with b_p (along $[001]_o$) about 0.1% longer than a_p (along $[\bar{1}10]_o$). However, measuring the effect of this anisotropy with respect to in-plane lattice parameters is beyond the limits of our RSM measurements.

To circumvent this problem, the experimental *ferroelectric* domain pattern (Fig. 1) was compared to a phase field simulated *ferroelectric* pattern for a $BiFeO_3$ film on a rectangular insulting surface.[14,15] As previously established,[8] there is no critical thickness for spontaneous rhombohedral shear strain making it unlikely that a fully commensurate $BiFeO_3$ film on the orthorhombic substrate is possible. Furthermore, for $BiFeO_3$ on $TbScO_3$, the strain relaxation should be anisotropic where the simulation included a high level of strain relaxation (ε_{11}=−0.001) for the highest misfit direction along a_p and a low level of strain relaxation (ε_{22} =−0.010) for the lowest misfit direction along b_p. This is the same as the experimental situation where the smallest lattice misfit and hence the largest residual strain are expected along $[010]_p \| [001]_o$. The result of the simulation is depicted in Fig. 4 where two *ferroelastic* domains (r_1/r_4) are present. Additionally, the *ferroelectric* domain morphology mimics the experimental result with stripe-$(010)_p$ VDWs where the domains are labeled r_1^{-p} and r_4^{+p} consistent with previous notation. Therefore, the low in-plane symmetry of the orthorhombic substrate drives an anisotropic *ferroelastic* domain pattern. Within this *ferroelastic* framework, vertical domain walls are generated to neutralize the net charging effects present with nonvertical boundaries.[7]

In conclusion, the domain structure of $(001)_p$ $BiFeO_3$ on orthorhombic $(110)_o$ $TbScO_3$ was determined for films consisting of stripe domains separated by $(010)_p$ VDWs. X-ray analysis showed that the two domains were oppositely tilted ($\pm\omega$) due to coherency of the vertical domain walls. RSM determined that the $BiFeO_3$ symmetry is rhombohedral and that the formation of the two *ferroelastic* domains in the stripe pattern was driven by the rectangular $(110)_o$ surface of the $TbScO_3$ substrate common to all $GdFeO_3$-type crystal structures. Besides utilizing the periodic VDW geometry, this finding is important for understanding the influence of substrate symmetry on domain patterns and growth of rhombohedral ferroelectrics such as $BiFeO_3$ and high Zr content $Pb(Zr_xTi_{1-x})O_3$.

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