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Self-assembly and properties of domain walls in BiFeO$_3$ layers grown via molecular-beam epitaxy

ABSTRACT

Bismuth ferrite layers, $\sim$200-nm thick, are deposited on SrRuO$_3$-coated DyScO$_3$(110)$_o$ substrates in a step-flow growth regime via adsorption-controlled molecular-beam epitaxy. Structural characterization shows the films to be phase pure with substrate-limited mosaicity ($0.012^\circ$ x-ray diffraction $\omega$-rocking curve widths). The film surfaces are atomically smooth (0.2 nm root-mean-square height fluctuations) and consist of 260-nm-wide [1011]$_o$-oriented terraces and unit-cell-tall (0.4 nm) step edges. The combination of electrostatic and symmetry boundary conditions promotes two monoclinically distorted BiFeO$_3$ ferroelectric variants, which self-assemble into a pattern with unprecedentedly coherent periodicity, consisting of 145 $\pm$ 2-nm-wide stripe domains separated by [001]$_o$-oriented 71$^\circ$ domain walls. The walls exhibit electrical rectification and enhanced conductivity.

I. INTRODUCTION

The control of topological textures within the lattice, charge, and spin order parameters of multiferroic materials offers the possibility to realize emergent behaviors that transcend the functionality of any spatially uniform host material. Indeed, ferroelectric domain walls are already employed in various applications spanning nonlinear optics, nanoelectronics, and nonvolatile memories.

Epitaxial layers of the room-temperature multiferroic BiFeO$_3$ are a well-established material platform for hosting domain walls with functional properties. To date, the overwhelming majority of BiFeO$_3$ films are produced using far-from-equilibrium growth techniques incorporating ion irradiation during film growth, including magnetron sputter deposition$^7$ and pulsed-laser deposition.$^8$ When uncontrolled, ions spawn unintended defects impacting domain wall morphology and properties.$^9,10$ Molecular-beam epitaxy, in contrast, provides an alternative synthesis approach which employs thermalized molecular fluxes.$^{11,14}$ Near-equilibrium growth regimes free from the bombardment of energetic ions$^{11}$ are expected to engender subtler defect profiles,$^{14}$ desirable for the fabrication of nonlinear optical elements as well as for understanding leakage mechanisms in nonvolatile ferroelectric-based memories.

In this letter, we employ molecular-beam epitaxy$^{11,14}$ to grow commensurately strained BiFeO$_3$/SrRuO$_3$/DyScO$_3$(110)$_o$ epitaxial heterostructures (the $o$ subscript designates orthorhombic indices in the nonstandard $Pbnm$ setting) and demonstrate the self-assembly of
ferroelectric BiFeO$_3$ domain walls with unprecedentedly long-range order. The walls exhibit the combination of enhanced conductivity and electrical rectification. We anticipate that the results discussed here may prove useful for improving the fabrication of nonlinear optical and nano electronic devices.

II. RESULTS

A. Film growth

BiFeO$_3$/SrRuO$_3$/DyScO$_3$(110)$_o$ heterostructures are grown without breaking vacuum in a Veeco GEN10 molecular-beam epitaxy system with a chamber base pressure of 1 × 10$^{-8}$ Torr using deposition conditions summarized in Table I. For SrRuO$_3$ growths, ruthenium is supplied in abundance with a ruthenium-to-strontium flux ratio of J$_{Ru}$/J$_{Sr}$ < 2. At a growth temperature of 780 °C, the excess ruthenium oxidizes forming volatile RuO$_2$ species which continuously desorb from the growth surface resulting in single-phase SrRuO$_3$ layers. BiFeO$_3$ is grown in an oxidant comprised chiefly of oxygen (and 20% oxygen). This approach, which represents an evolution of increasing oxidation environments, helps to suppress the formation of oxygen vacancies, responsible for engendering mobile electrons and ensures the oxidation of bismuth. Additionally, high bismuth-to-iron flux ratios (J$_{Bi}$/J$_{Fe}$ ∼ 16) are employed to compensate the loss of volatile BiO$_2$ species at the high homologous growth temperature utilized (Ts ∼ 650); the desorption of bismuth oxides during BiFeO$_3$ deposition is analogous to that of ruthenium oxides during SrRuO$_3$ growth. Although multiple films were grown and all findings presented here (and in the supplementary material) are obtained from a single film, for which Rutherford back scattering spectrometry results yield a film bismuth-to-iron molar ratio equal to 0.98 ± 0.07. The deposition of stoichiometric layers, containing equal concentrations of bismuth and iron, combined with long diffusion lengths for surface adatoms promote films with long-ranged crystallographic and ferroic order.

B. Film structural perfection

The structural perfection of BiFeO$_3$ layers deposited on SrRuO$_3$-coated DyScO$_3$(110) substrates is established using the combination of x-ray diffraction (XRD), atomic force microscopy (AFM), and scanning transmission electron microscopy (STEM). An XRD θ–2θ scan (see Fig. S1 of the supplementary material) collected between 10 ≤ 2θ ≤ 110° using Cu K$_a$ radiation (wavelength λ = 0.15406 nm) exhibits only 00$l_p$ film and hh0$_o$ substrate reflections (the p subscript refers to pseudocubic indices); the absence of additional reflections evince a phase-pure single crystalline film.

Figure 1(a) highlights diffracted intensity oscillations near DyScO$_3$ 110$_o$, which result from the interference of x-rays reflected at BiFeO$_3$ and SrRuO$_3$ interfaces. Measured intensities are accurately reproduced by simulations based on a heterostructure with atomically sharp interfaces, pseudocubic out-of-plane lattice parameters $a$, of 0.3991 (BiFeO$_3$), 0.3942 (SrRuO$_3$), and 0.3939 nm (DyScO$_3$), film thicknesses of 217 (BiFeO$_3$) and 23 mm (SrRuO$_3$), and a thickness-limited film out-of-plane mosaic coherence. The in-plane mosaic coherence length, $\sim$2 μm, is determined from the full-width-at-half-maximum (FWHM) value of the BiFeO$_3$ peaks, indicative of atomically sharp interfaces. The coordinates on (b) and (c) refer to the axes of the DyScO$_3$ heterostructure described in this letter. The growths are carried out using molecular-beam epitaxy in an adsorption-controled regime. $T_s$ are substrate temperatures, estimated using a thermocouple in the vicinity of, but not in direct contact with, the growth surface. $P$ are partial pressures during deposition of an oxidant comprised of approximately 20% O$_2$ and 80% O$_3$, produced by controllably degassing ozone-infused silica beads. $J_{J_{Bi}}$ and $J_{J_{Fe}}$ are molecular fluxes, measured using a calibrated quartz-crystal microbalance. $T_{J_{Bi}}$ and $T_{J_{Fe}}$ are effusion cell temperatures (Ru is supplied from an electron-beam source). $R$ are film growth rates.

<table>
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<th>$T_s$</th>
<th>$P$</th>
<th>$J_{J_{Bi}}$</th>
<th>$J_{J_{Fe}}$</th>
<th>$T_{J_{Bi}}$</th>
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<tr>
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<td>3.1</td>
<td>6.7</td>
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FIG. 1. Structural perfection of a commensurate BiFeO$_3$/SrRuO$_3$ heterostructure grown on DyScO$_3$(110)$_o$. (a) XRD θ–2θ intensities (purple) agree with simulation results (gray) based on an ideal heterostructure. Overlapping BiFeO$_3$ 001$_p$ (purple) and DyScO$_3$ 011$_o$ (gray) $\omega$-rocking curve scans (inset) attest to a high substrate-limited film structural perfection; full-width-at-half-maxima values for film and substrate peaks are both 0.012° (43 arc sec), corresponding to in-plane mosaic coherence lengths $\sim$2 μm. (b) Surface height modulations, as measured via AFM, establish an atomically smooth film surface with unit-cell-tall (0.4 nm) step edges. Lattice-resolution STEM images collected along the [110]$_o$ zone axis demonstrate commensurate and abrupt (c) BiFeO$_3$/SrRuO$_3$ and (d) SrRuO$_3$/DyScO$_3$ interfaces. The coordinates on (b) and (c) refer to the axes of the DyScO$_3$ substrate.
001, reflection (0.0122 = 43 arcsec), measured along [001], using ω-rocking curve scans [Fig. 1(a), insert]. The FWHM value measured for the BiFeO₃ reflection is the same as that for the underlying DyScO₃ and demonstrates that the film structural perfection is limited by the intrinsic mosaicity of the substrate.

From lattice-resolution STEM images obtained along the [110] zone axis near BiFeO₃/SrRuO₃ [Fig. 1(c)] and SrRuO₃/DyScO₃ [Fig. 1(d)], we find atomically abrupt heterostructure interfaces with commensurate pseudo cube-on-cube crystallographic stacking: BiFeO₃[001]∥SrRuO₃[001]∥DyScO₃[110][001].

APM height images, including Fig. 1(b), evince smooth surfaces (0.2 nm root-mean-square height fluctuations) over macroscopic distances (≥20 μm) with motifs including unit-cell-tall (0.4 nm) step-edges oriented parallel to BiFeO₃[110] and DyScO₃[111], 260-nm-wide [111],-oriented terraces (0.09° miscut), and shallow islands (areal density ≤10⁶ cm⁻²). The latter, through analyses of in situ reflection high-energy electron diffraction (RHEED) patterns (see Fig. S2 of the supplementary material), are determined to form during the layer-by-layer growth of SrRuO₃.

C. Symmetry breaking and wall self-assembly

To investigate the breaking of cubic symmetries and the emergence of topological features within BiFeO₃, we perform XRD reciprocal space maps (RSM), lateral (LPFM), and vertical (VPFM) piezoforce microscopy (PFM), and bright-field transmission electron microscopy (BF-TEM).⁵⁵ RSM analyses carried out about film peaks reveal that the BiFeO₃ 103 and 113 family of reflections are split into doublets and triplets [Fig. 2(a)], consistent with monoclinically distorted pseudocubic unit cells that have been sheared along [110].³⁵ The descent in symmetry from the cubic perovskite to the monoclinic structure is accompanied by polar (111) domain walls in our as-grown BiFeO₃[Fig. 2(b)], cross-sectional VPFM [Fig. 2(c)], and cross-sectional BF-TEM micrographs [Figs. 2(d) and 2(e)] show that the domain walls in our as-grown BiFeO₃ layers self-assemble into a periodic quasi-one-dimensional stripe array along DyScO₃[001] with inter-wall separations measuring 145 ± 2 nm. The walls are found to be inclined ∼45° relative to the surface normal [Figs. 2(c)–2(e)], in agreement with geometric considerations for 71° walls (the wall type is labeled based on the angle formed between polarization vectors in adjacent domains) residing on [110] planes. In previous work, it was shown that the inclination angle and the wall type can be controlled by changing boundary conditions and film thicknesses; similarly, the wall orientation can be tuned through the application of biaxial in-plane strain from (100) for 1.5% ≤ m ≤ 0.3% to (110), for m = 3.6%, in which m is the lattice mismatch between the BiFeO₃ film and the underlying substrate.⁵⁶–⁵⁸

The stripe domains are occasionally seen to terminate within the film, giving rise to one-dimensional topological defects analogous to dislocations [the dotted circle in Fig. 2(b)]. Despite the one-dimensional array of self-assembled domain walls with unprecedented long-range perfection, in agreement with cross-sectional BF-TEM findings, (d) and (e). The coordinates on (b) and (e) refer to the axes of the DyScO₃ substrate.
defect that we observe in a ≥ 20 µm field of view, the structural perfection of the pattern realized here represents the most well-ordered self-assembled array of ferroelastic domain walls produced to date.35,36,46–48

D. Electrical properties of walls

The electrical properties of the BiFeO3/SrRuO3/DyScO3(110), heterostructure are investigated using conductive AFM (c-AFM), by grounding the bottom SrRuO3 electrode and rastering a biased tip in contact with the sample surface while recording through-layer currents. Typical results, shown in Figs. 3(a)–3(d), establish that no current flows for biases \( V_b \leq 1 \) V (detectable current limit ∼1pA). In the \( 2 \leq V_b \leq 3 \) V regime, the current is preferentially emitted at domain walls, where the conductivity is two to ten times higher than at domains [see the current histogram in Fig. 3(e)]. At a bias of \( V_b = 4 \) V, the corresponding electric field across the film, 180 kV/cm, exceeds the coercive field of bismuth ferrite, ∼170 kV/cm.34 As a consequence, c-AFM images acquired under these conditions, including Fig. 3(d), contain contributions from both resistive and displacement currents as a result of domains being locally poled.

Macroscopic current-voltage \( I(V) \) measurements, obtained by integrating the c-AFM measurements over a \( 5 \times 5 \) µm² area, Fig. 3(f), highlight the existence of rectifying behavior, agreeing with previous reports.9,10 The enhanced conduction at 71° domain walls can be understood to result from a combination of effects which include a reduction in the BiFeO3 conduction band energy and an accumulation of intrinsic defects,21,47 including double-donor23 oxygen vacancy states, near the walls. The asymmetric response, which produces the rectifying behavior, is attributed to the combination of dissimilar emission barrier heights across the film/electrode and film/tip interface as well as to the presence of an out-of-plane film polarization which breaks up/down symmetry.49 For the measurement conditions employed, Joule heating is estimated to cause a temperature rise of only ∼0.03 K; for reference, electric fields are expected to trigger breakdown in perovskite oxides only above ∼2000 kV/cm,50 five to ten times larger than the largest values applied here.

III. CONCLUSIONS

The ability to produce ordered walls with well-ordered periodicity, as demonstrated here, could have immediate technological implications. For example, domain walls are already lithographically introduced into commercial nonlinear crystals to help satisfy momentum conservation in three-photon interactions. These processes, which include sum frequency generation and parametric down conversion, are essential for up-converting laser frequencies as well as entangling photons for quantum computation. Being able to produce arrays of walls which self-assemble into high-fidelity patterns could provide a bottom-up alternative for the fabrication of such nonlinear optical elements. Additionally, the perfection of the patterns realized here reflects an intrinsically low concentration of defects. The realization of films with low defect density are necessary to produce energy efficient memories with ferroic orders that can be easily switched at low coercive fields without wall pinning. Finally, the 71° domain walls are shown to simultaneously exhibit enhanced conductivity and electrical rectification—attributes which are desirable for emerging nanoelectronic applications, including domain wall memories.3

SUPPLEMENTARY MATERIAL

Additional film characterization, including XRD \( \theta - 2\theta \), RHEED, and VPFM, is provided in the supplementary material.

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REFERENCES

in addition to the two parallelograms, the unit cell also projects as a square, giving diagonals. When projected on [100], the resulting unit cells have the shape of parallelograms, which emphasizes the square symmetry.

rather than shift can be understood to arise from a superposition of both these reasons. The fact that the Bragg peak to shift closer to the origin. The lengthening of the major diagonal in real space moves the corresponding diffraction peak farther from the origin in diffraction space. Conversely, the lengthening of the major diagonal rather than shift can be understood to arise from a superposition of both these reasons. The fact that the Bragg peak to shift closer to the origin. The lengthening of the major diagonal in real space moves the corresponding diffraction peak farther from the origin in diffraction space. Conversely, the lengthening of the major diagonal rather than shift can be understood to arise from a superposition of both these reasons.

The monoclinic deformation changes the lengths of the ideal cubic perovskite lattice vectors, the resulting unit cells have the shape of parallelograms, which emphasizes the square symmetry.

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Supplementary Material

FIG. S1. XRD θ-2θ scan between 10 to 110° collected from a BiFeO$_3$/SrRuO$_3$/DyScO$_3$ heterostructure grown via adsorption-controlled ozone molecular-beam epitaxy. The peaks observed correspond to the 00\_p family of film and substrate reflections.

FIG. S2. RHEED patterns collected in situ following the deposition of (a) SrRuO$_3$ and (b) and (c) BiFeO$_3$. (a) and (b) are obtained along [100]$_p$ azimuth; (c) is acquired along [110]$_p$. The arcs demarcate regions where the specular condition is satisfied, i.e. where the incident and scattered electron beams form the same angle with the sample surface.

Figures S2(a) and S2(b) are RHEED patterns collected in situ along the [100]$_p$ azimuth following the growth of SrRuO$_3$ and BiFeO$_3$ layers, respectively. The streaked reflections in Fig. S2(a) are consistent with the layer-by-layer growth of SrRuO$_3$ and results from the formation of shallow islands on atomic terraces. The spots in Fig. S2(b) and S2(c) indicate that the growth of BiFeO$_3$ proceeds in a step-flow mode, promoting wide terraces.

FIG. S3. (a) VPFM and (b) AFM height image of a pattern generated by modulating the probe bias by ±15 V as a tip was rastered across the sample surface. The blue and green regions in (a) correspond to BiFeO$_3$ out-of-plane ferroelectric polarizations components which point towards and away from the SrRuO$_3$ bottom electrode. The coordinates on (a) and (b) refer to the axes of the DyScO$_3$ substrate.

Figure S3(a) is a plan-view VPFM image of a ferroelectric domain pattern generated by modulating the bias on a probe as it was rastered across the sample surface; Figure S3(b) is the corresponding AFM contact-mode height image showing the changes associated with the ferroelastic domain structure. These results demonstrate our ability to control the ferroelectric and ferroelastic order parameters of our BiFeO$_3$/SrRuO$_3$/DyScO$_3$ heterostructures. Note that the region imaged in Figs. S3(a) and S3(b) includes the region shown in Fig. 1(b).