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ABSTRACT
We systematically investigate the role of defects, introduced by varying synthesis conditions and by carrying out ion irradiation treatments, on the structural and ferroelectric properties of commensurately strained bismuth ferrite Bi$_x$Fe$_{2-x}$O$_3$ layers grown on SrRuO$_3$-coated DyScO$_3$ (110)$_o$ substrates using adsorption-controlled ozone molecular-beam epitaxy. Our findings highlight ion irradiation as an effective approach for reducing through-layer electrical leakage, a necessary condition for the development of reliable ferroelectrics-based electronics.

I. INTRODUCTION
BiFeO$_3$ crystalizes in a rhombohedrally distorted perovskite structure (space group #161, R$_3$c) and exhibits the combination of ferroelectricity and spin-canted weak ferromagnetism. At room temperature, the polar and magnetic order parameters are coupled. As a result, when ferroelectric domains are poled, magnetic moments reorient deterministically. Voltage-controlled magnetism is important for enabling low-power spintronic devices that operate efficiently and independently of current-based switching mechanisms, including Oersted induction and spin-transfer torque. Utilizing BiFeO$_3$ for practical voltage-controlled spintronics, however, requires overcoming reliability challenges currently limiting ferroelectric-based devices. Key among these is reducing through-film leakage.

In this letter, we investigate the influence of growth conditions and postdeposition ion-irradiation treatments on the composition, structure, and ferroelectric properties of epitaxial Bi$_x$Fe$_{2-x}$O$_3$ layers grown via adsorption-controlled ozone molecular-beam epitaxy. Structural characterization reveals that stoichiometric films, for which bismuth and iron concentrations are equal (i.e., $x \approx 1.00$), exhibit the highest crystalline and ferroelectric domain perfection. The leakage characteristics of these high-quality layers are found to be similar to defective layers grown near the single-phase field boundaries (i.e., $x \neq 1.00$). Through film leakage is dramatically reduced by irradiating both stoichiometric and nonstoichiometric samples with He$^+$ ions.

II. FILM GROWTH
Bi$_x$Fe$_{2-x}$O$_3$ layers are grown to a thickness of $\approx 200$ nm on SrRuO$_3$-coated (110)$_o$-oriented DyScO$_3$ substrates (o subscripts denote orthorhombic indices in the nonstandard Pbnm setting) via adsorption-controlled molecular-beam epitaxy in a Veeco GEN10
system (base pressure $P_{\text{base}} = 1 \times 10^{-8}$ Torr $= 1.3 \times 10^{-6}$ Pa). SrRuO$_3$ is selected as an epitaxial bottom electrode$^{1}$ due to its relatively low electrical resistivity (170 $\mu$Ом-cm at room temperature)$^{12}$ and lattice match with the DyScO$_3$ substrate (lattice mismatch $m = 0.6\%$). The SrRuO$_3$ electrodes are deposited as described in Refs. 12 and 13 to thicknesses of $\approx 20$ nm. Bi$_{1-x}$Fe$_2$O$_3$ films are grown subsequently without breaking vacuum at growth temperatures $T_g$ between 550°C and 650°C, estimated using a thermocouple in indirect contact with the growth surface.

Iron (99.995% pure) and bismuth (99.9999% pure) are simultaneously$^1$ supplied to the growth surface from effusion cells operating at temperatures near 1250°C and 650°C, respectively. Iron fluxes are fixed at $J_{Fe} = 2.4 \times 10^{10}$ cm$^{-2}$ s$^{-1}$, yielding bismuth ferrite deposition rates of 1.1 nm/min; bismuth fluxes are varied between $J_{Bi} = 4.8 \times 10^{10}$ cm$^{-2}$ s$^{-1}$ and $3.8 \times 10^{10}$ cm$^{-2}$ s$^{-1}$, corresponding to $J_{Fe}/J_{Bi}$ flux ratios spanning 2 through 16. High bismuth fluxes ($J_{Bi}/J_{Fe} \gg 1$) promote the incorporation of bismuth into the growing film, compensating for the desorption of volatile Bi$_2$O$_3$ species.$^{21}$

Elemental oxygen is supplied via atmospheric mixtures consisting of 20% O$_2$ and 80% O$_3$. The deposition pressure is maintained at $1 \times 10^{-2}$ Torr (1.3 $\times$ 10$^{-3}$ Pa), corresponding to an equivalent ozone flux of $J_O = 10^{16}$ cm$^{-2}$ s$^{-1}$. The use of strong oxidants,$^{12,19}$ and high ozone fluxes ($J_O/J_{Fe} \approx 500$) suppress the formation of oxygen vacancies, which engender mobile electrons.$^{21}$

### A. Structure and composition

Initial film growth experiments focus on determining the effects of incident flux ratios $J_{Bi}/J_{Fe} \leq 16$ and deposition temperatures $550°C \leq T_d \leq 650°C$ on the composition and structure of the Bi$_{1-x}$Fe$_2$O$_3$ layers grown on SrRuO$_3$/DyScO$_3$(110)$_o$.

Figure 1(a) is a variability chart showing film bismuth fractions $x$ vs incident metal flux ratios $J_{Bi}/J_{Fe}$ and deposition temperatures $T_d$. The broken lines connect points grown at the same temperature $T_d$. Diffuse and coherent labels refer to RSM peak shapes [see the inset in (b)]. (b) $J_{Bi}/J_{Fe}$ vs $T_d$ parameter space governing the adsorption-controlled growth of Bi$_{1-x}$Fe$_2$O$_3$ layers via ozone molecular-beam epitaxy. White regions denote phase-pure layers; blue and red areas indicate mixed-phase films with Fe$_2$O$_3$ and Bi$_2$O$_3$ inclusions, respectively; striped (non-striped) regions identify regimes where RSMs carried out about Bi$_{1-x}$Fe$_2$O$_3$ 002 reflections (inset) display diffuse (coherent) peak shapes. The dimensions of the RSMs are $0.08 \times 0.13$ nm$^{-2}$. (c) XRD $\theta$-2$\theta$ diffracted intensities near 002$_d$ film and substrate reflections from Bi$_{1-x}$Fe$_2$O$_3$ layers. (d) Corresponding film out-of-plane lattice parameters $a_{\parallel}$ vs bismuth fractions $x$.

Deposition temperatures and bismuth fluxes, the fundamental film reflections display diffuse features; at higher $T_d$ and $J_{Bi}/J_{Fe}$ values, the peaks exhibit coherent profiles. In the remainder of this letter, we focus on the latter set of films, for which the structural quality is superior.

Figure 1(c) shows diffracted $\theta$-2$\theta$ x-ray intensities collected near 002$_d$ film and substrate peaks from Bi$_{1-x}$Fe$_2$O$_3$ layers (p-subscripts denote pseudocubic indices) grown along the isoflux $J_{Bi}/J_{Fe} = 16$ and isothermal $T_d = 650°C$ lines. As the film bismuth fraction $x$ is increased, film reflections shift to slightly lower 2$\theta$ values, resulting in out-of-plane lattice parameter values $a_{\parallel}$ which grow linearly with composition $x$ [Fig. 1(d)].$^{29}$ The variation in $a_{\parallel}$ values suggests a changing concentration of point defects within the films.

### B. Surface and domain morphology

The combination of reflection high-energy electron diffraction (RHEED) and atomic force microscopy (AFM) is employed to investigate the surface morphology of epitaxial Bi$_{1-x}$Fe$_2$O$_3$ layers deposited on SrRuO$_3$-coated DyScO$_3$(110)$_o$ substrates. Figures 2(a)–2(j) are in situ RHEED patterns collected along (100)$_p$ and (110)$_p$ azimuths as a function of film bismuth fractions $x$ between 0.90 and 1.07; corresponding ex situ AFM topography maps are shown in Figs. 2(k)–2(o).
Stoichiometric Bi$_x$Fe$_{2-x}$O$_3$ layers with $x = 0.99$ exhibit electron reflection patterns characterized by circular spots. The spots lie on half-circles [double arcs, Figs. 2(c) and 2(b)] on which the specular condition is satisfied. Both the position and shape of the spots indicate two-dimensional step-flow growth—a conclusion which is corroborated by AFM height maps [e.g., Fig. 2(m)], which consist of atomically smooth surfaces (root-mean-square surface fluctuations $\rho_{\text{rms}} = 0.2$ nm) with well-defined terraces and unit-cell-tall step edges.

Increasing $x$ to 1.05 causes the reflected spots to elongate vertically into streaked ellipses [ovals, Fig. 2(d)]. Concurrently, sixth-order stripes [rectangles, Fig. 2(g)] as well as split Kikuchi lines [arrows, Fig. 2(d)] also appear. Together, these features suggest reconstructions of surface atoms and broadening of surface widths following the formation of mosaic blocks. Surface topographies are determined via AFM [Fig. 2(n)] to consist of shallow fractal-like features, yielding a surface roughness of $\rho_{\text{rms}} = 0.9$ nm.

For higher bismuth fractions of $x = 1.07$, arrays of bulk diffraction spots are observed [squares, Figs. 2(e) and 2(f)]. Bulk diffraction is a hallmark of three-dimensional growth and occurs when glancing electrons penetrate through surface protrusions. Such features are visible in AFM height images, including Fig. 2(o), and are attributed to Bi$_2$O$_2$$_5$ grains. The protrusions also lead to rough surfaces for which $\rho_{\text{rms}} = 11.0$ nm, exceeding the roughness values obtained here for stoichiometric bismuth ferrite layers by an order of magnitude.

Systematic changes in the morphologies of the layers are also observed for bismuth-deficient layers. RHEED and AFM images collected from Bi$_x$Fe$_{2-x}$O$_3$ films with $x = 0.95$ exhibit half-order spots [rectangles, Fig. 2(q)] indicating doubling of surface unit cells and shallow islands characteristic of the layer-by-layer growth in the presence of limited adatom diffusivity across step-edge barriers [2–7] [Fig. 2(f)]. For films with $x = 0.90$, bulk diffraction spots are detected in RHEED patterns [squares, Figs. 2(a) and 2(f)] and pits are observed in AFM height maps [Fig. 2(k)]. The surface roughness for bismuth deficient layers spans $\rho_{\text{rms}} = 2.7$ nm ($x = 0.95$) through $7.4$ nm ($x = 0.90$).

Collectively, the direct- and Fourier-space analyses establish a rich morphological phase diagram in which topographical features vary systematically and depend sensitively on film composition. This makes RHEED a sensitive in situ monitor for characterizing the growth of Bi$_x$Fe$_{2-x}$O$_3$ layers in real time.

C. Ferroelectric properties

Figures 2(p)–(t) are lateral piezoforce microscopy (PFM) images showing ferroelectric domain morphologies of Bi$_x$Fe$_{2-x}$O$_3$ layers grown as a function of the film bismuth fraction $x$. Stoichiometric layers with $x = 0.99$ exhibit bimodal contrast variations corresponding to two ferroelectric domain variants [Fig. 2(t)], in agreement with prior reports. The domains assemble into one-dimensional stripes with remarkable long-range order and an in-plane periodicity along [001]$_o$ of $\lambda_{[001]} = 296 \pm 20$ nm. Increasing $x$ to 1.05 and 1.07 progressively disrupts the uniformity of the stripe pattern. Concurrently, array periodicities decrease to $\lambda_{[001]} = 245 \pm 32$ ($x = 1.05$) and $235 \pm 44$ nm ($x = 1.07$). Increased disorder and reduced domain widths are also observed with decreasing $x$ in bismuth deficient layers; in these cases, $\lambda_{[001]} = 260 \pm 38$.
(x = 0.95) and 213 ± 42 nm (x = 0.90). Because of the increased pattern disorder observed near the single-phase field boundary, we hypothesize that pattern irregularities are due to lattice imperfections, including the cluster of point defects which accommodate film nonstoichiometry. The varying domain periods reflect an interplay between polar stiffness and depolarization effects. 8–11 Near x = 0.99, polar stiffness reduces domain wall densities by penalizing the regions containing rapidly varying polarization. Conversely, near the single-phase field boundaries, depolarization effects dominate, suppressing stray fields by bringing domain walls closer together.

The ferroelectric properties of the Bi$_{2}$Fe$_{2-x}$O$_{3}$ films are quantified using metal-ferroelectric-metal capacitor structures. Platinum top electrodes, in the form of 40-μm-diameter circles, are defined lithographically. Polarization P vs electric field E measurements are performed by applying trains of bipolar triangular pulses to the devices at a frequency of 10 kHz using a Precision Multiferroic Tester (Radiant Technologies, Inc.).

In the as-deposited state, the films display pronounced leakage which impede ferroelectric poling. Leakage in bismuth ferrite arises from a combination of factors, including domain-wall conductivity as well as electron and hole donor defects such as oxygen vacancies and Fe$^{2+}$-based complexes. 12,13 Ion irradiation was recently demonstrated as a successful avenue for increasing the resitivity of leaky ferroelectrics. 14–19 We adopt a similar strategy and bombard our patterned structures with 3.0 MeV He$^{2+}$ ions. At this energy, the ions penetrate to a mean depth of ~15 μm, damaging the film lattice but preserving the film chemistry.

Figure 3(a) shows P(E) curves obtained as a function of irradiation doses D between 0.3 × 10$^{15}$ and 1 × 10$^{16}$/cm$^{2}$ from a stoichiometric Bi$_{2}$Fe$_{2}$O$_{3}$ film grown with x = 0.99. In contrast to P(E) curves measured from as-deposited heterostructures [for reference, also shown in Fig. 3(a)], devices irradiated with D ≥ 0.3 × 10$^{15}$/cm$^{2}$ exhibit clear signatures of ferroelectricity, manifested in the form of hysteresis loops. For 0.3 × 10$^{15}$ ≤ D ≤ 1 × 10$^{15}$/cm$^{2}$, small residual leakage causes the hysteresis loop to be open, but increasing D further causes the loops to close completely, reflecting progressively decreased leakage. The suppression of leakage in irradiated layers is attributed to the formation of carrier scattering and trapping defects. 17

Figure 3(a) also demonstrates that, as irradiation doses are increased, ferroelectric coercive fields grow from E$_{c}$ = 0.15 MV/cm (D = 0.3 × 10$^{13}$/cm$^{2}$) to 0.90 MV/cm (1 × 10$^{16}$/cm$^{2}$), following the exponential relationship E$_{c}$ = 0.14e$^{0.19}$ (here, the units for E$_{c}$ and D are MV/cm and 10$^{15}$/cm$^{2}$, respectively). Measured E$_{c}$ values are comparable to those reported for epitaxial BiFeO$_{3}$ films deposited on SrRuO$_{3}$/DyScO$_{3}$(001) 15 and SrTiO$_{3}$/Nb(001) 16 but are larger than the 0.08 MV/cm value obtained for free-standing bismuth ferrite membranes, for which domain walls move unobstructed by epitaxial strain. 17 The larger coercive fields of irradiated devices are attributed to the formation of domain-wall-pinning defects.

Hysteresis loops measured from Bi$_{2}$Fe$_{2-x}$O$_{3}$-based devices 17 bombarded with 3 × 10$^{15}$ ions/cm$^{2}$ are presented as a function of film bismuth fractions x in Fig. 3(c). Remanent polarizations are approximately constant at 62 ± 6 μC/cm$^{2}$, independent of the bismuth fraction. This is consistent with a spontaneous polarization of P$_{s}$ = 107 ± 10 μC/cm$^{2}$ along (111)$_{c}$, the polarization direction in bismuth ferrite. As x is increased, however, coercive fields E$_{c}$ vary substantially, decreasing from 0.57 (x = 0.90) to 0.31 MV/cm (x = 0.99) before rising to 0.35 MV/cm (x = 1.05). The reduced E$_{c}$ values observed near stoichiometry are consistent with the lower defect concentration and higher structural perfection of these films (see Fig. 2).

When cyclically poled, bismuth ferrite layers exhibit fatigue-induced failure. The mechanisms responsible for fatigue are diverse: conducting filaments form causing electrical shorts, 20 charge injection at ferroelectric/electrode interfaces suppresses domain nucleation, 21,22 and pinned domains grow in size. 23 To characterize the endurance of our Bi$_{2}$Fe$_{2-x}$O$_{3}$ layers and determine n, the number of polarization cycles tolerated before breakdown, we employ a 10 kHz rectangular waveform with variable bias amplitudes between ±0.35–0.65 MV/cm to ensure complete poling during testing. Figure 3(d) shows n as a function of the film bismuth fraction x. For bismuth-rich films with x = 1.05, repeated poling leads to breakdown above 3 × 10$^{5}$ cycles. As x is decreased, n grows exponentially to 6 × 10$^{5}$ (x = 0.99) and 4 × 10$^{6}$ (x = 0.90). The observed n values are typical of ferroelectric capacitor structures in which at least one of the electrodes is a metal 24 and can be enhanced by exclusively employing epitaxial conducting oxide electrodes. 25 The combination of oxide electrodes, ion irradiation, and bismuth deficient films thus provides an avenue for prolonging the reliability of Bi$_{2}$Fe$_{2-x}$O$_{3}$ capacitors.

III. CONCLUSIONS

Commensurately strained Bi$_{2}$Fe$_{2-x}$O$_{3}$ layers grown on SrRuO$_{3}$-coated DyScO$_{3}(110)$_{c}$ substrates using adsorption-controlled ozone molecular-beam epitaxy are employed to investigate the role of
defects, introduced by varying synthesis conditions and by per-
forming postgrowth ion bombardment, on the chemical com-
position, structural characteristics, domain morphology, and ferroelec-
tric attributes of bismuth ferrite. Within the explored ranges of
growth temperature 550 °C ≤ T ≤ 650 °C and incident bismuth-to-
iron flux ratios 2 ≤ \( \frac{I_{Bi}/I_{Fe}}{x} \) ≤ 16, a single-phase field with bismuth fractions \( x \) spanning 0.90 through 1.07 is established. The varying film compositions are accompanied by topographical features that include pits (\( x = 0.90 \)), mounds (\( x = 0.95 \)), terraces (\( x = 1.00 \)), fractals (\( x = 1.05 \)), and protrusions (\( x = 1.07 \)); each feature produces unique diffraction signatures in RHEED suitable for monitoring film growth in real time.

Film polarization morphologies generally consist of two domain variants arranged in stripe patterns. Pattern perfection and geometry depend sensitively on point defect profiles, with the widest domain widths and most periodic structures occurring near stoichiometry (\( x \approx 1.00 \)). In the as-deposited state, all films display excessive leakage which impedes ferroelectric poling but when tested using fabricated 40-μm-diameter platinum-capped capacitor structures. By performing postgrowth ion irradiation treatments, leakage is suppressed, yielding closed polarization-vs-field hysteresis loops. Remanent polarizations are constant at \(-60 \mu \text{C/cm}^2\) and independent of film composition; coercive fields are reduced near stoichiometry, where the bismuth and iron concentra-
tion are equal. Bismuth deficiency is demonstrated as an avenue for enhancing the endurance of Bi\(_2\)Fe\(_2\)O\(_5\)-based ferroelectric devices.

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The absolute uncertainty in measured out-of-plane lattice parameters is 0.0004 nm.

Equilibrium polarization morphologies \( u(r) \) can be understood by minimizing a free energy functional comprised of three essential terms,

\[
\mathcal{L}[u(r)] = \int \mathcal{G}[u(r)] + \mathcal{D}[u(r)] + \mathcal{U}[u(r)] \, dr,
\]

where \( \mathcal{G}[u(r)] = |\nabla_u u(r)|^2 \) represents the order parameter stiffness by associating an energetic cost with the magnitude of the field gradient \( |\nabla_u u(r)| \), \( \mathcal{D}[u(r)] = u(r) \cdot \int (\nabla_r \otimes \nabla_r') \mathcal{G}(r - r') u(r') \, dr' \)

is a nonlocal dipole-dipole interaction which acts, through \( \mathcal{G}(r - r') \), the Green function of the Laplacian, to suppress stray \( u(r) \) fields, and \( \mathcal{U}[u(r)] \) is the potential energy function of the order parameter, describing crystalline anisotropy. The interplay between the order parameter stiffness, which penalizes the formation of domain walls, and the nonlocal interactions, which encourages the formation of domains, determines the equilibrium width of domains and, consequently, the periodicity of ferroelectric domain patterns.