

Comment on “Epitaxial BiFeO₃ Multiferroic Thin Film Heterostructures”

Wang *et al.* (1) recently reported multi-ferroic behavior, with ferromagnetic and ferroelectric polarizations that are both large at room temperature, in thin strained films of BiFeO₃ (BFO). Although at room temperature, bulk BFO is ferroelectric (2) and antiferromagnetic (3–5), Wang *et al.* (1) reported that a 70-nm film shows both an enhanced ferroelectric polarization (90 μC cm⁻²) and a substantial magnetization (1 μ_B/Fe). This remains the only report of a robust room-temperature multiferroic and suggests the potential for novel devices that exploit the anticipated strain-mediated magnetoelectric coupling between the two ordered ground states. In this Comment, we argue that epitaxial strain does not enhance the magnetization and polarization in BiFeO₃.

Like Wang *et al.* (1), we grew BFO films on 50-nm underlayers of SrRuO₃ (SRO) on SrTiO₃ (001) substrates (STO). In addition, we used plain STO and conducting 0.2% atomic Nb-doped SrTiO₃ substrates (Nb-STO). Both BFO and SRO films were grown by pulsed laser deposition with a KrF excimer laser (248 nm, 1 Hz, target-substrate distance = 8 cm). BFO films were grown (670°C, 8 Pa O₂, 1.6 J cm⁻²) using a Bi-rich target of Bi_{1.2}FeO₃, because Bi is volatile (6). SRO films were grown (650°C, 9 Pa O₂, 1.7 J cm⁻²) using a stoichiometric target. The growth rate for both BFO and SRO was 10 Å/min. After deposition, films were cooled at 5°C/min to 400°C in 40 kPa oxygen, annealed for 1 hour, and then cooled to room temperature at 8°C/min.

The crystalline quality of our films was investigated with high-resolution x-ray diffraction (Fig. 1). The reciprocal space maps show that the BFO and SRO in-plane lattice parameters are equal to the STO lattice parameter of 3.905 Å, consistent with coherently strained films. It should be noted that Wang *et al.* (1) performed their calculations of saturation polarization using the bulk SRO lattice parameter of 3.935 Å for the BFO in-plane lattice parameter. In our work, BFO films as thin as 40 nm gave equivalent x-ray results, but 300-nm BFO films were found to be relaxed. All coherently strained films showed a root-mean-square surface roughness of 2 nm, as determined by atomic force microscopy.

BFO film stoichiometry was determined from quantitative energy dispersive x-ray spec-

trosopy in a thick (~400 nm) film grown at a laser repetition rate of 2 Hz. The Fe:Bi ratio was found to be unity, within the error of the technique of a few percent. The Fe oxidation state was investigated for BFO/STO samples

grown at 1 Hz and 2 Hz with x-ray photoelectron spectroscopy. All samples behaved similarly; a representative scan of the Fe 2p line is shown in Fig. 2. The position of this line is expected to be 711 eV for Fe³⁺ and 709.5 eV for Fe²⁺, and the position of the satellite is expected at 719 eV for Fe³⁺ and 716 eV for Fe²⁺ (7). From Fig. 2, we deduce that the oxidation state of Fe in our BFO/STO films is Fe³⁺ and that there is no evidence for Fe²⁺ within a resolution of a few atomic percent.

To verify that our BFO films are insulating and ferroelectric, we performed piezoresponse microscopy (8) on BFO/Nb-STO and

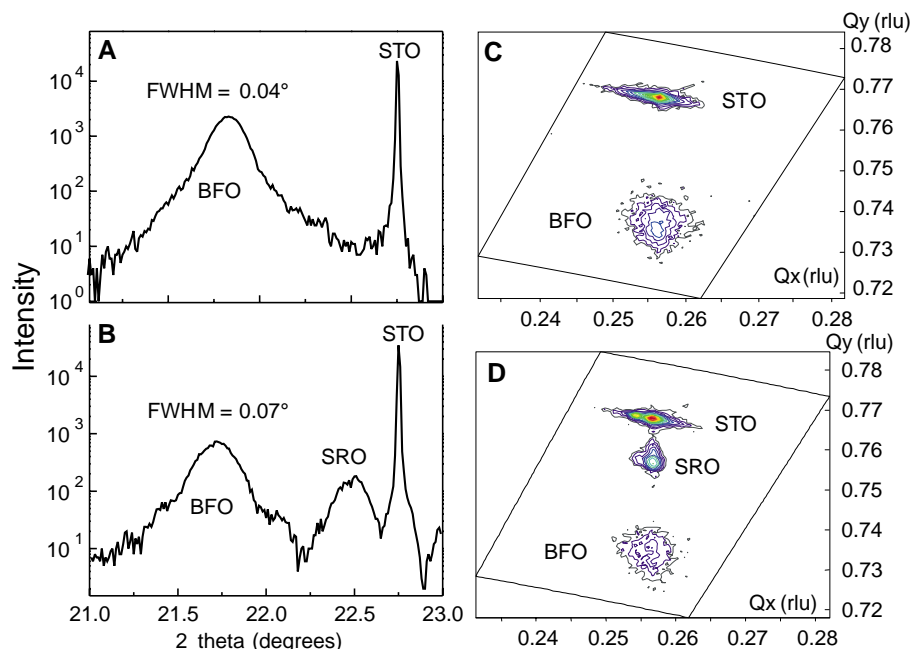


Fig. 1. Ω-2θ scan of the (001) pseudocubic reflection for (A) BFO(80 nm)/Nb-STO and (B) BFO(90 nm)/SRO(50 nm)/STO. The corresponding reciprocal space maps of the (013) pseudocubic reflections are shown in (C) and (D). Reciprocal lattice units (rlu) Q_x and Q_y are equal to the inverse lattice spacing. All in-plane film lattice parameters can be seen to be equal to the STO lattice parameter of 3.905 Å. The BFO out-of-plane lattice parameter in both samples is 4.07 Å, and the corresponding value for SRO is 3.95 Å.

Fig. 2. X-ray photoelectron spectrum of the Fe 2p lines for BFO(40 nm)/STO.

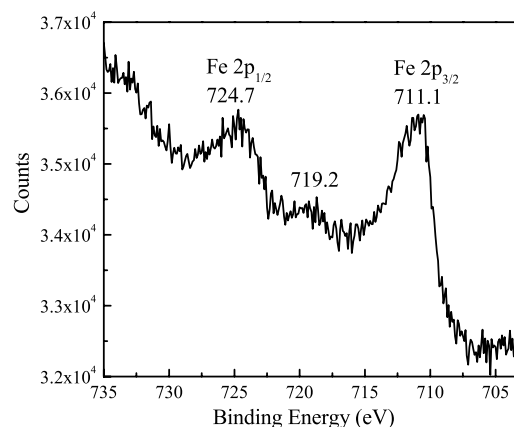
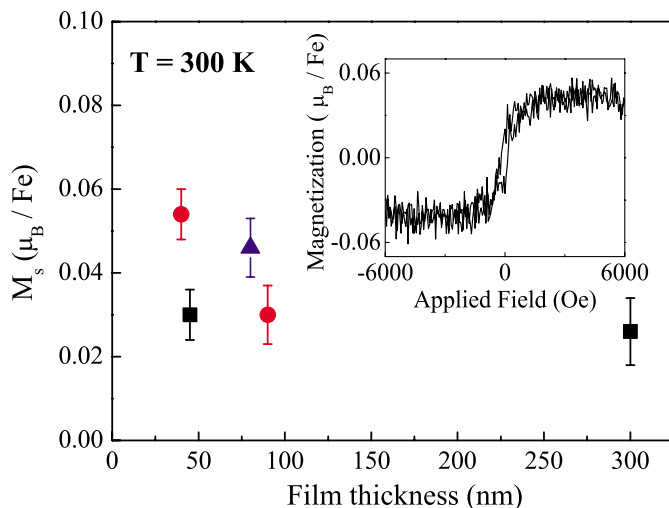


Fig. 3. Saturation magnetization M_s of BFO films versus film thickness. Black squares, BFO/STO; red circles, BFO/SRO(50 nm)/STO; blue triangle, BFO/Nb-STO. The inset shows a typical hysteresis loop. Magnetometer axis in-plane and parallel to STO [100]. Before taking magnetic measurements, we used emery paper to grind away silver dag from the sides and undersides of the substrates to eliminate spurious magnetic signals that we attribute to material originating from the heater block.



BFO/SRO/STO, and impedance spectroscopy using sputter-deposited Pt on BFO/Nb-STO. The former technique confirmed ferroelectric switching. The latter technique showed our films to be low-loss (2% loss tangent in 10 kHz to 1 MHz) and nonconducting (resistivity $>10^{10}$ Ωcm). The high-temperature conductivity data showed an activation energy of 1.03 ± 0.05 eV, compatible with only a small concentration of oxygen vacancies (9, 10). In agreement with the literature (11), the effective dielectric constant (10 kHz to 1 MHz) was found to be 70 ± 2 at ambient temperature, increasing to ~ 375 at 550 K.

Magnetic measurements were taken at room temperature with a Princeton Measurements Corporation (Princeton, NJ) vibrating sample magnetometer. In Fig. 3, we plot saturation magnetization M_s as a function of BFO film thickness. BFO films both with and without the SRO underlayer behave similarly, which precludes any substantial magnetic contribution from SRO. All BFO films show an essentially thickness-independent M_s that is less than $0.06 \mu_B/\text{Fe}$, which rules out the strain-enhanced magnetization inferred by Wang *et al.* (1). Indeed, strain should not modify antiferromagnetic exchange interactions between singly occupied $\text{Fe}^{3+} 3d$ orbitals. We note that density functional calculations (12) of unstrained BFO suggest a local magnetization of around $0.05 \mu_B/\text{Fe}$, consistent with the findings presented here.

The small M_s that we observed is reminiscent of bulk behavior (3–5). The large value observed by Wang *et al.* (1) could arise as a result of a substantial Fe^{2+} fraction. If this fraction were 50%, then $M_s = 0.5 \mu_B/\text{Fe}$, and the composition would be $\text{BiFeO}_{2.75}$. However, this mixed-valent system with oxygen vacancies would be expected to possess an electrical resistivity that is orders of magnitude lower than the figure of $\sim 10^9 \Omega\text{cm}$ stated in (1). In this scenario, the reported increase of polarization with decreasing film thickness (1) could be an experimental artifact. Regarding the polarization (50 to $60 \mu\text{C cm}^{-2}$) of the thicker (200 nm) films measured by Wang *et al.*, although it is larger than the value recorded (2) in a poor-quality bulk sample ($6 \mu\text{C cm}^{-2}$), it is, in effect, not epitaxially enhanced with respect to unstrained polycrystalline films ($40 \mu\text{C cm}^{-2}$) (13). Therefore, we conclude that ferroelectric polarization is not enhanced by strain in BFO films. Indeed, calculations that supersede those presented by Wang *et al.* show $90 \mu\text{C cm}^{-2}$ in unstrained BFO (14).

We conclude that an increased thickness-dependent magnetization is not an intrinsic property of fully oxygenated and coherently strained epitaxial BFO films that exhibit a high electrical resistivity. If it is only possible to achieve substantial magnetization values in deoxygenated BFO, then the applications potential is reduced, because an

increased electrical conductivity will be detrimental to ferroelectric performance.

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