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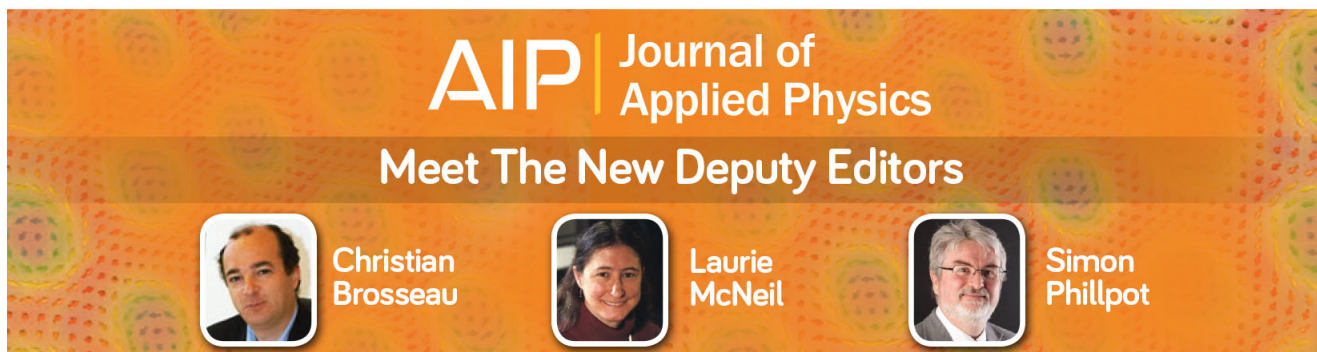
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The role of SrRuO₃ bottom layer in strain relaxation of BiFeO₃ thin films deposited on lattice mismatched substrates

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The present study deals with BiFeO₃ and SrRuO₃ thin films deposited on large lattice mismatched substrates like LaAlO₃, MgO, and SrTiO₃. The 80 nm thickness BiFeO₃ films deposited directly on LaAlO₃ substrate are highly constrained, while those on SrTiO₃ substrate are only somewhat constrained. The BiFeO₃ films deposited with 50 nm SrRuO₃ bottom layer are fully relaxed on all the three substrates. The separate SrRuO₃ layers deposited under identical conditions on these substrates are also found to be relaxed. These films exhibit different morphological features in accordance with strain relaxation process. The BiFeO₃ thin films show characteristic low magnetic moment resulting from antiferromagnetic ordering irrespective of substrate induced strain. © 2011 American Institute of Physics. [doi:10.1063/1.3564940]

Invention or renaissance of materials with new functionalities is central concern of materials science research. After superconductivity and spintronic phenomena, multiferroic has become a topic of scientific interest owing to its potential for a variety of applications.¹ BiFeO₃ (BFO) has been heralded as a lead-free material with effective electrical as well as magnetic switching above room temperature. It is multifunctional character has been further enhanced with presence of photovoltaic^{2,3} and photostriction⁴ phenomena. The recent advances in using ferroelectric ultrathin films for spin polarization⁵ and tunneling devices⁶ have fuelled further interest in exploring new frontiers of BiFeO₃ and related materials. The scientific sensation created by Wang *et al.*⁷ through report on effect of epitaxial strain in BiFeO₃ thin films still continues. Highly strained or structurally modified BFO thin films were fabricated using lattice mismatched substrates.^{8,9} Alternatively, tensile strain is also reported to affect ferroelectric behavior of BFO thin films.¹⁰ Recently, Lee *et al.* reported observation of simultaneous ferroelectric and ferromagnetic behavior in EuTiO₃ thin films using epitaxy and substrate-induced strain as effective tools.¹¹ Epitaxial strain induced multiferroicity has also been predicted theoretically in SrMnO₃ compound.¹² Our recent study on strain engineered BFO thin films clearly demonstrated nanoscale switching and electric field driven structural phase transition.¹³ While studying ferroelectric behavior of such strained films, an important issue resides with the conducting buffer layer used between the ferroelectric thin film and the substrate. In addition, magnetic behavior of strained films is interesting to study on its own.

For practical purpose, ferroelectric films are often deposited on electrically conducting substrates or with conducting bottom layer. The film-electrode interface plays an

active role in governing film properties as switching is initiated at the interface.¹⁴ We have reported that SrRuO₃ (SRO) bottom electrode is a more convenient choice than conducting Nb:SrTiO₃ (STO) substrates for ferroelectric switching of BFO thin films.¹⁵ Similarly, Chu *et al.* have reported evolution of ferroelectric domains with thickness of SRO bottom layer.¹⁶ The deposition of a conducting bottom layer, such as SRO, is essential for ferroelectric studies even though the BFO films are deposited on strain inducing substrates. One important aspect, unexplored in detail so far, is masking of substrate effect by the intermediate SRO layer. Here we present a systematic account of deposition of BFO films on various substrates with and without SRO layer. We also deposited SRO films independently under identical conditions. The strain effect is clearly observed in BFO films deposited directly on the substrate, whereas those with SRO bottom layer are unstrained. The magnetic ordering of BFO films remains unaffected by substrate-induced strain.

Pulsed laser deposition technique with 248 nm KrF excimer laser was used for deposition of several SRO and BFO films, as reported elsewhere.^{15,17} We used ultrasonically cleaned LaAlO₃ (LAO), STO, and MgO substrates. The characterization techniques employed in the present work were x-ray diffraction (X'pert Pro, Phillips), Atomic Force Microscope (Nanoscope IV, Digital Instruments), Superconducting Quantum Interference Device magnetometer (Quantum design).

The x-ray diffraction patterns for various combinations of film-substrate heterostructures are shown in Fig. 1. The out-of-plane lattice parameters determined for these samples are given in Table I. The 80 nm BFO films directly deposited on LAO substrate are highly constrained as evident from shifting of the (002) peak and large value (4.65 Å) of out-of-plane lattice parameter. The 50 nm SRO and top BFO films deposited on LAO substrate are relaxed with lattice parameter values approaching the respective bulk values. Similarly,

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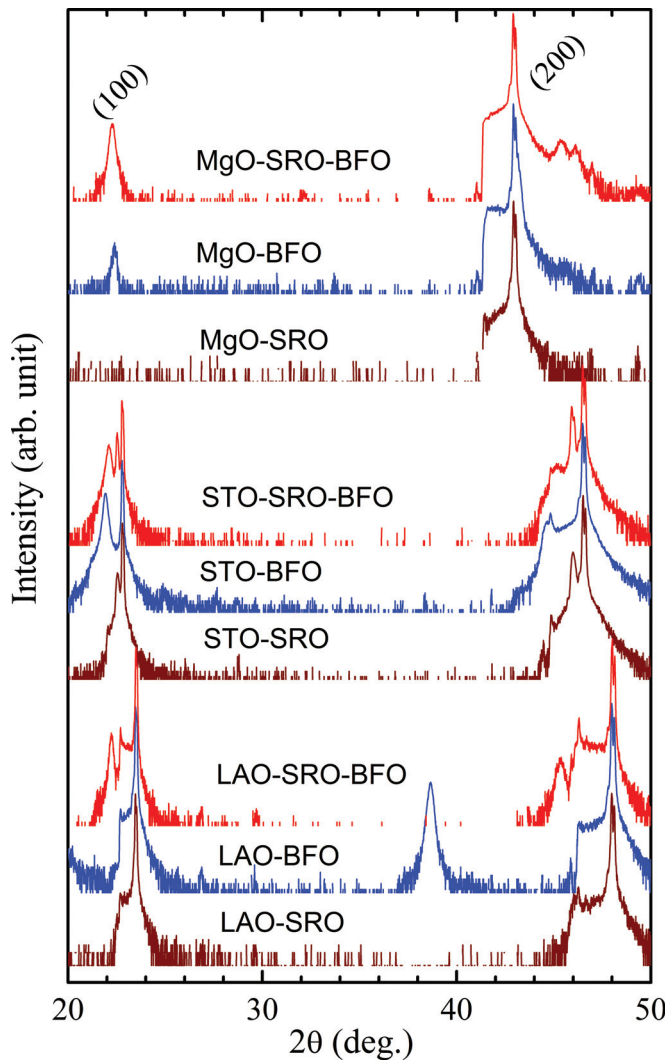


FIG. 1. (Color online) X-ray diffraction patterns for SRO, BFO, and SRO-BFO thin films deposited on LAO, STO, and MgO substrates.

on STO substrate, BFO films are moderately constrained whereas SRO films and SRO-BFO hetero-structure are relaxed. On MgO substrate tensile strain is expected on both the films because of the large mismatch. However, all films prefer to grow in a relaxed mode.

The structural response of SRO and BFO films to substrate-induced strain is quite different. This may be partly

TABLE I. Out-of-plane lattice parameters and surface roughness of the films.

Substrate	Thin film	Lattice parameter (\AA)	RMS roughness (nm)
LaAlO ₃	SRO	3.92	2.24
	BFO	4.65	–
	SRO-BFO	3.99	1.34
SrTiO ₃	SRO	3.93	1.64
	BFO	4.05	–
MgO	SRO-BFO	4.00	1.87
	SRO	–	1.29
	BFO	3.97	–
	SRO-BFO	3.99	1.93

due to lower lattice mismatch for SRO (3.6%) than BFO (4.3%) with LAO. In addition, bulk structure is orthorhombic (space group Pbnm; $a = 5.56 \text{ \AA}$, $b = 5.53 \text{ \AA}$, and $c = 7.84 \text{ \AA}$) for SRO¹⁸ and rhombohedral (space group R3c; hexagonal lattice parameters $a = 5.58 \text{ \AA}$, and $c = 13.90 \text{ \AA}$) for BFO.¹ Theoretically, BFO can undergo 9% volume change for strain-induced isosymmetric transition from rhombohedral to tetragonal phase.¹⁹ The structural change is manifested by polar displacement and oxygen octahedral tilt.²⁰ On LAO substrate, the BFO structure exhibits giant polar out-of-plane displacement due to in-plane compression. On STO substrate, the in-plane compression is moderate, which causes slight elongation of out-of-plane lattice parameter. On the other hand, SRO films do not exhibit any structural

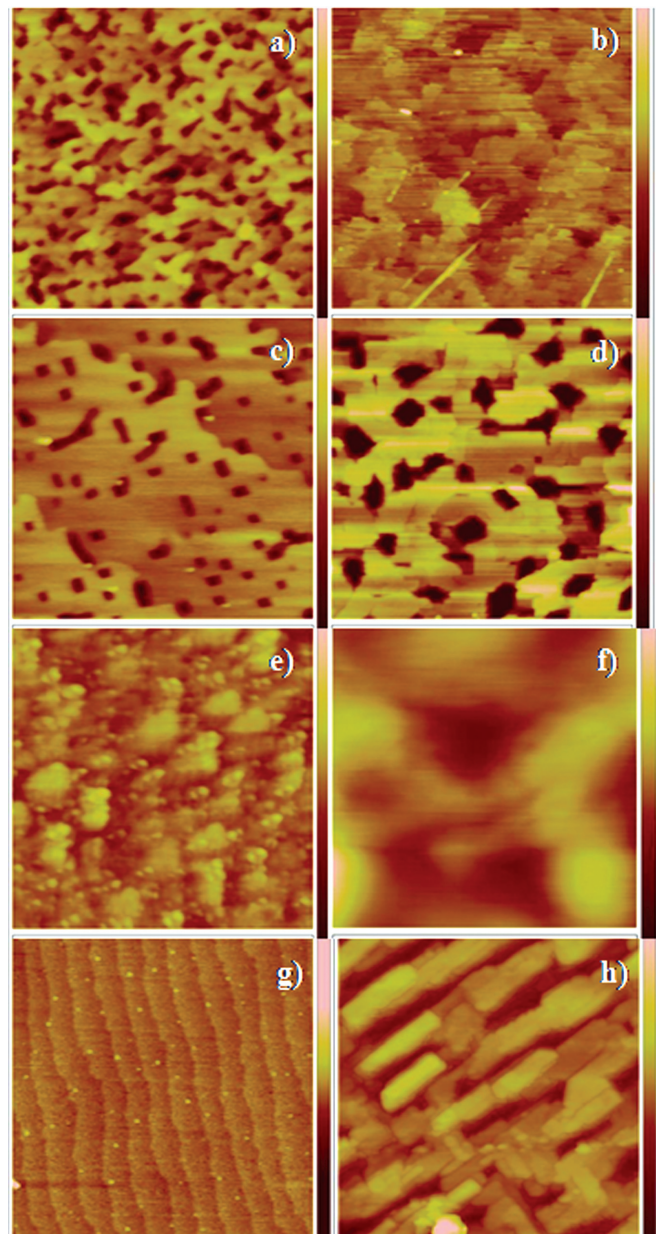


FIG. 2. (Color online) The surface topography scans of $2 \times 2 \mu\text{m}$ area with height scale of 20 nm for (a) LAO-SRO, (b) LAO-SRO-BFO, (c) STO-SRO, (d) STO-SRO-BFO, (e) MgO-SRO, (f) MgO-SRO-BFO, (g) HF-treated STO-SRO, and (h) HF-treated STO-SRO-BFO samples.

changes.²¹ On the basis of density functional theory, Zayak *et al.* have reported that [110]-oriented SRO films may have monoclinic symmetry while [001]-oriented SRO films do not undergo structural changes at any reasonable value of strain.¹⁸ Therefore, relaxation of strain for SRO films on different substrates may be through misfit dislocation formation. BFO and SRO likely have different defect chemistry under the influence of strain as BFO undergoes structural change and SRO does not.

The surface morphology of these films is shown in Fig. 2 and values of corresponding surface roughness are given in Table I. An island growth with plateletlike grains is observed for SRO films deposited on LAO substrate [Fig. 2(a)]. A similar growth mode and features are sustained for BFO films deposited on top of SRO layer, as shown in Fig. 2(b). A change in morphology of SRO and SRO-BFO films deposited on STO substrate is seen in Figs. 2(c) and 2(d). Lower strain from STO substrate than LAO substrate may result in proficiency of 3D grain growth. Clear evidence of spherical grain growth is observed in Figs. 2(e) and 2(f) for SRO and SRO-BFO films deposited on MgO substrates. For comparison, we have shown in Figs. 3(g) and 3(h), AFM images of SRO and SRO-BFO films deposited on step-surfaced (HF-treated) STO substrates. In this case, films grow in step-flow growth mode with a propensity for step bunching.²² It is noteworthy that SRO films deposited on different substrates are structurally invariant. However, difference in lattice mismatch or associated strain induces relaxation through variable tendency of misfit dislocation formation. As a result, growth mode remains the same but microstructure differs.

The magnetic behavior, i.e., variation of total magnetic moment with applied magnetic field, for BFO films deposited on LAO, STO, and MgO substrates is shown in Fig. 3. All the samples showed predominant diamagnetic characteristics arising from the dominant substrate contribution. This means that the contribution of magnetic moment of BFO film is very small as expected from antiferromagnetic ordering.^{1,23} The substrate-induced strain seems to have minimal effect on magnetic behavior of BFO films. This is an important observation as strain was considered an effective tool to enhance magnetic moment or magneto-electric coupling in multiferroic materials.⁷ Our observation is in agreement with experimental data of strained/relaxed BFO thin films²⁴ and recent first principle-based theoretical study.²⁵ It is well known that bulk rhombohedral BFO has G type antiferromagnetic ordering. Under large compressive strain, G type and C type are nearly degenerate.¹⁹ For C type, neighboring magnetic moments are ferromagnetically aligned in out-of-plane direction. However, the out-of-plane Fe distance is large in high strain regime, which reduces the magnetic coupling strength in that direction.¹⁹ Therefore, strain does not impart significant change in resultant magnetic moment.

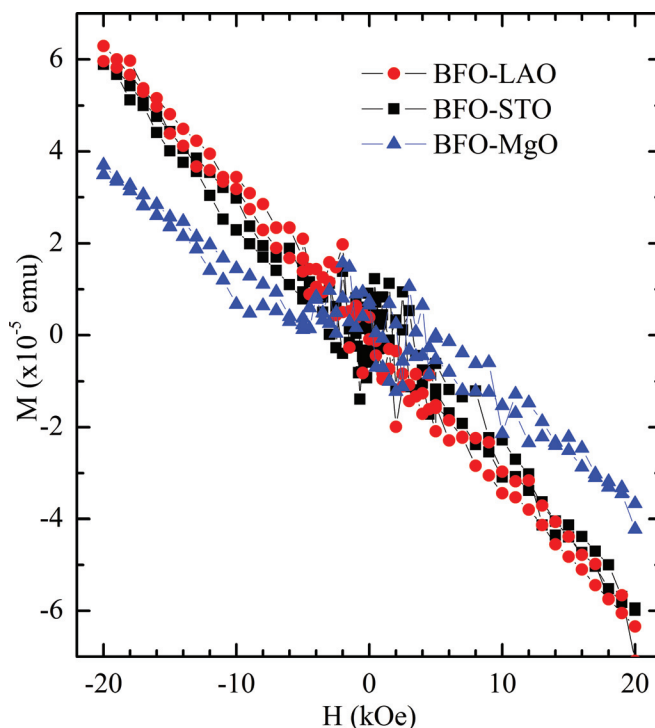


FIG. 3. (Color online) The variation of the total magnetic moment with applied magnetic field for BFO films deposited on LAO, STO, and MgO substrates.

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