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Krishnan, P. S. S. R., Arredondo, M., Saunders, M., Ramasse, Q. M., Valanoor, N., & Munroe, P. (2011). Microstructural analysis of interfaces in a ferromagnetic- multiferroic epitaxial heterostructure. *Journal of Applied Physics*, 109(3), [034103]. <https://doi.org/10.1063/1.3531992>

Published in:
Journal of Applied Physics

Document Version:
Publisher's PDF, also known as Version of record

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Microstructural analysis of interfaces in a ferromagnetic-multiferroic epitaxial heterostructure

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(Received 26 August 2010; accepted 26 November 2010; published online 2 February 2011)

We report a study on multiferroic bismuth ferrite (BiFeO₃, BFO)-ferromagnetic lanthanum strontium manganese oxide (La_{0.7}Sr_{0.3}MnO₃, LSMO) epitaxial interfaces by scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) and energy-filtered transmission electron microscopy (EFTEM). Epitaxial (001) oriented LSMO/BFO heterostructures were fabricated on a (001) strontium titanate (SrTiO₃, STO) substrate using pulsed laser deposition (PLD). Different cooling conditions to room temperature (rapid or slow) were used to investigate the effect of fabrication conditions on the structural quality of the interfaces. The combined analysis of bright field transmission electron microscopy imaging, STEM-EDS and EFTEM data reveals that the LSMO-BFO heterostructure interface is free from any defects but the phases are chemically interdiffused over a length scale of ~ 4 nm. © 2011 American Institute of Physics.

[doi:10.1063/1.3531992]

I. INTRODUCTION

Ferroelectric and ferromagnetic materials are traditionally used in applications such as storage media, capacitors, sensors, optoelectronic devices and actuators.¹ Multiferroic² materials, which possess both ferroelectric and ferromagnetic ordering, have generated significant interest. The simultaneous presence of switchable ferroelectric and ferromagnetic ordering in a single phase material leads to additional functionality in which ferroelectric polarization can be used to switch magnetization and ferromagnetic ordering can be used to switch the electric polarization.^{3,4} Combining multiferroic and ferromagnetic materials in a thin film epitaxial heterostructure form provides a novel method for controlling the electron spin polarization through the lattice polarization.⁵ While the idealized model of a chemically sharp interface between the oxide films can provide invaluable insight into the properties of these structures, there is mounting evidence that complex interfacial phenomena such as local nonstoichiometry, interdiffusion,⁶ and charge imbalance^{7,8} occur widely. Understanding the chemical and physical significance of these phenomena will lead to improved and novel device designs,^{9,10} and it is essential that they be suitably characterized to achieve the best possible device performance.¹¹ These systems not only offer new avenues for applications in novel storage media and spintronics¹² but also possess a rich and diverse range of fundamental physical phenomena due to the interactions between both materials systems.

Doped manganite perovskite, LSMO, has attracted considerable interest mainly due to its high Curie temperature

($T_c \sim 370$ K)¹³ and colossal magnetoresistance (CMR) properties. It has been widely investigated as a suitable candidate for ferromagnetic electrodes. In addition to having a close lattice parameter match with other perovskite substrates such as STO, the observation of CMR above room temperature¹⁴ in LSMO has increased scientific interest in this new system.

A number of studies have been performed investigating BFO-based tunnel junction devices,¹⁵ as well as nanoscale domain engineering of BFO thin films (with different electrodes),^{16–18} but a detailed investigation of the LSMO-BFO interface is just emerging.^{19,20} In addition to this, the fabrication of ultrathin (5–20 nm) phase pure epitaxial multiferroic (BFO) thin films is a very challenging task considering the narrow growth window for bismuth-based films.²¹ In this paper we report the interfacial investigation of epitaxial, phase pure ferromagnetic-multiferroic interfaces. The ferromagnetic, multiferroic and substrate materials forming the heterostructure were selected to have a very small lattice mismatch. Pulsed laser deposition (PLD), a technique that is capable of producing high quality stoichiometric films,²² was used to fabricate the heterostructure. The PLD processing conditions, such as laser energy, laser frequency, deposition temperature, oxygen partial pressure, cooling rate, and atmosphere were optimized to improve the epitaxy and phase purity of the heterostructure. An array of analytical microscopy techniques, such as scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS), energy filtered transmission electron microscopy (EFTEM), and STEM-electron energy loss spectroscopy (STEM-EELS) were carried out. Combined analysis of the interfaces using these methods revealed an interdiffusion across the heterostructure over distances in the range of 4–7 nm.

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TABLE I. Summary of (thickness and cooling conditions) STO-LSMO-BFO heterostructure specimens reported in the article.

Specimen ID	Thickness		Cooling conditions (after high temperature deposition cooling up to room temperature)
	LSMO (nm)	BFO	
LS50BF20SC	~50	20–22	Slow (5 °C/min, 240 min)
LS50BF12FC	~50	10–12	Fast (20 °C/min, 90 min)
LS50BF35FC	~50	~35	Fast (20 °C/min, 90 min)

II. EXPERIMENTAL METHODS

Multiferroic BFO with a rhombohedral structure and a lattice constant (a_r) of 0.396 nm (Ref. 23) and ferromagnetic LSMO, a rhombohedral perovskite with a lattice constant (a_r) of 0.387 nm, were selected to form the multiferroic-ferromagnetic heterostructure. (001) STO with a lattice parameter of 0.390 nm was used as a substrate to fabricate the LSMO-BFO heterostructure. The reported crystal structures and lattice constants are at room temperature.

Prior to deposition all the targets were sanded at room temperature and preheated at the deposition pressure. The target-substrate distance was a constant 10 cm for all the depositions. The LSMO bottom layer was deposited first at an oxygen partial pressure of 100 mTorr and deposition temperature of 750 °C. A LSMO (Praxair, USA) target with 6.1 g/cc density and purity of 99.9% was used. The laser energy was ~ 1.8 – 2.0 J/cm² with a repetition rate of 7 Hz. The BFO top layer was deposited subsequently at an oxygen partial pressure of 2 mTorr and 700 °C. A BFO (Praxair, USA) with 7.3 g/cc density and 99.9% purity was used as a target. A deposition pressure of 2 mTorr was used to avoid the presence of parasitic phases such as Fe₂O₃. For this layer the laser energy density was 1.6 J/cm² with a repetition rate of 10 Hz. The STO-LSMO-BFO heterostructure was then cooled in the oxygen-rich pressure of 200 Torr. In the LS50BF20SC specimen (see nomenclature in Table I) a strontium ruthenate (SRO) protective top coating was deposited at room temperature under high vacuum (1.5×10^{-6} Torr).

The interfacial investigation was carried out for the specimens described in Table I. The acronyms used to identify the specimens are LS—LSMO, BF—BFO, SC—slow cooling, FC—fast cooling and the numerical values give the corresponding film thicknesses. The faster and slower cooling rates are 20 °C/min and 5 °C/min, respectively.

Using a faster cooling rate allows us to minimize the holding time of the STO-LSMO-BFO heterostructure at a high deposition temperature. Prolonged exposure of volatile BFO to high temperatures can result in the breakdown of BFO into parasitic phases such as Bi₂O₃, α -Fe₂O₃, and γ -Fe₂O₃.²⁴ Reducing the high temperature exposure time will not only inhibit the possibility of any dissociation reactions but also likely improve the quality of the interface by the reduced time for mobility of atoms across the interface.

X-ray diffraction (XRD) was carried out using a Pan Analytical MRD, in θ -2 θ mode for a scan angle ranging between 15° and 90° and atomic force microscopy (AFM)

TABLE II. Pre-edge and postedge energy used for EFTEM mapping.

Element	Pre-edge 1 (eV)	Pre-edge 2 (eV)	Postedge (eV)	Filter slit width (eV)
Ti	421	441	466	20
O	494	514	547	20
Mn	605	625	655	20
Fe	678	693	716	15
La	782	812	847	30

studies were carried out in a Multimode AFM (Digital Instruments). Cross-sectional TEM specimens for LS50BF20SC, LS50BF12FC samples were prepared by using a dual beam focused ion beam microscope (Nova 200, FEI Co.). All the specimens were first coated with gold (Au) at room temperature using sputter coating. This was carried out to protect the film surface from gallium (Ga) ion damage during TEM specimen preparation. The LS50BF35FC cross-sectional TEM specimen was prepared using the conventional tripod method followed by conventional ion beam thinning.²⁵ Bright field TEM images were obtained using a Philips CM 200 (FEG) microscope operated at 200 kV. Atomic resolution Z-contrast STEM images were obtained using the TEAM 0.5 instrument, an improved double-corrected FEI Titan³ 80–300 microscope²⁶ equipped with a special high-brightness Schottky-field emission electron source and a gun monochromator.

The local chemistry at the interfaces was investigated using STEM-EDS and EFTEM. STEM-EDS was performed in a Philips CM 200 (FEG) operated at 200 kV with a probe size of ~ 1.5 nm. The principal advantage of using STEM-EDS to analyze the interface is mainly due to the nanosized probe, which has the potential to yield more accurate spatial information regarding the chemical nature at the interface.²⁷ The possible overlap of elemental signals in the STEM EDS spectra was considered, and thus care was taken to avoid mapping the elements [Ti- $K\alpha$ (4.51 keV) and La- $L\alpha$ (4.65 keV)] which have close peak energy windows. In the present analysis, chemical mapping of Sr- $K\alpha$, Mn- $K\alpha$, Bi- $L\alpha$, and Fe- $K\alpha$ was carried out using windows located at peak energies of 14.16 keV, 5.89 keV, 10.83 keV, and 6.40 keV, respectively, with an energy window width of 0.2 keV at these energies. EFTEM was performed, in tandem with STEM-EDS, in order to improve the understanding of the interface structure.

A JEOL 3000F TEM operated at 300 kV and fitted with a Gatan Imaging Filter was used to perform EFTEM (Ref. 28) elemental mapping. The spatial resolution of EFTEM is expected to be of the order of 1 nm.²⁹ The EFTEM analysis for Ti, O, Mn, Fe, and La was carried out by mapping the Ti- $L_{2,3}$, O- K , Mn- $L_{2,3}$, Fe- $L_{2,3}$, and La- $M_{4,5}$ edges across the heterostructure interfaces following the conventional three-window method. The pre-edge and postedge energies at which the elemental mapping was acquired are given in Table II, and an acquisition time of 45 s was used for each of the pre-edge and postedge images. Atomic resolution STEM-EELS studies were carried out by acquiring line scans across the BFO-LSMO interface over ten equivalent regions in a

FIG. 1. (Color online) (a) XRD data for LS50BF20SC. (b) XRD data for LS50BF12FC. (c) AFM image of LS50BF12FC.

dedicated STEM (Nion-corrected VG HB 501) operated at 100 kV and equipped with an Enfina parallel EELS detector. The O- K , Fe- $L_{2,3}$, and Mn- $L_{2,3}$ edges were simultaneously acquired, using a dispersion of 0.3 eV per channel. The convergence and collection semi-angles were 21 mrad and 19 mrad, respectively.

III. RESULTS

The XRD data for the LS50BF20SC and LS50BF12FC specimens is shown in Figs. 1(a) and 1(b), respectively. The XRD data not only confirms the epitaxial growth of LSMO and BFO films but also the absence of any parasitic phases. (The peak at $\sim 15^\circ$ belongs to the aluminum specimen holder). The 5 mm scan AFM image of the LS50BF12FC specimen is shown in Fig. 1(c). The AFM image shows that the film has a very smooth surface. The AFM data for LS50BF20SC was not obtained due to the protective SRO coating.

A bright field TEM image of LS50BF20SC is shown in Fig. 2(a). The thickness of the LSMO film is ~ 50 nm. The thickness of the BFO layer is ~ 20 nm. These values are in agreement with those expected from the PLD deposition rates.

The STEM-EDS element maps for this specimen for Bi- $L\alpha$ and Fe- $K\alpha$ are shown in Figs. 2(b) and 2(c). The analysis of the Bi- $K\alpha$ and Fe- $K\alpha$ maps clearly shows that while Bi- $K\alpha$ has a very sharp map, the Fe- $K\alpha$ map suggests a diffuse level of contrast from Fe extending into the LSMO region. This leads to the possibility that there is diffusion of Fe into the LSMO layer. The spatial resolution of the STEM-EDS mapping is expected to be of the order of 2–4 nm based on the conditions of chemical mapping (probe size ~ 1.5 nm, electron energy 200 KeV, without any aberration correction).^{30,31} The EFTEM elemental maps for Ti, La, Mn, and Fe are shown in Figs. 2(d)–2(g), respectively. The normalized profile analysis of the EFTEM data [Figs. 3(a)–3(d)] for Ti, La, Mn, and Fe in the LS50BF20SC specimen reveals

FIG. 2. (Color online) (a) Bright field TEM image of LS50BF20SC. [(b) and (c)] STEM-EDS chemical mapping of Bi- $L\alpha$ and Fe- $K\alpha$, respectively, for LS50BF20SC. [(d)–(g)] EFTEM images of Ti- $L_{2,3}$, La- $M_{4,5}$, Mn- $L_{2,3}$, Fe- $L_{2,3}$ edges respectively for LS50BF20SC.

FIG. 3. [(a)–(d)] Normalized profile analyses of EFTEM images [Figs. 2(d)–2(g)] showing intermixing (regions below $\sim 5\%$) at all the interfaces of the order of 4–7 nm.

that there is some diffusion/intermixing of Ti, La, Mn, and Fe at the STO-LSMO and LSMO-BFO interfaces over a length scale of 4–7 nm, defined here by the distance away from the interface at which the extended tail of the normalized intensity profile drop below 5%.

In order to investigate if the observed diffusion of Fe into the LSMO film is due to the PLD growth conditions, a much thinner BFO (~ 10 nm) film specimen (LS50BF12FC) with rapid cooling ($20^\circ\text{C}/\text{min}$) was prepared. As explained earlier, the smaller thickness and faster cooling rates will reduce the exposure time of volatile BFO to high temperatures and thereby reduce the possibility of Fe diffusion. The STEM-EDS chemical mapping of the LS50BF12FC specimen is shown in Fig. 4. When analyzing the Bi- $L\alpha$ [Fig. 4(a)] and Fe- $K\alpha$ [Fig. 4(b)] maps, it is clear that despite

FIG. 5. [(a)–(d)] Normalized profile analysis of EFTEM images [Figs. 4(d)–4(g)] showing intermixing (regions below $\sim 5\%$) of interfaces of the order of 4–7 nm.

modified heterostructure growth conditions there is still observable Fe diffusion into the LSMO layer. It can be argued that even though high-resolution imaging [Fig. 4(c)] does not reveal the presence of any physical defects (e.g., dislocations), the LSMO-BFO interface clearly exhibits chemical diffusion.

The EFTEM elemental maps for Ti, La, Mn, and Fe, for LS50BF12FC specimen are shown in Figs. 4(d)–4(g) respectively. The chemical nature of the STO-LSMO-BFO interface can be studied by performing normalized line profile analysis of the Ti, La, Mn, and Fe elemental maps, shown in Figs. 5(a)–5(d). The La and Mn profiles indicate 5 to 6 nm of diffusion into the BFO layer. Further, analysis of the Fe profile shows 5 to 7 nm of Fe diffusion into the LSMO layer. In addition to this, there is also a diffusion of La and Mn into

FIG. 4. (Color online) [(a) and (b)] STEM-EDS chemical mapping for Bi- $L\alpha$, Fe- $K\alpha$, respectively, for LS50BF12FC. (c) High resolution bright field image of LS50BF12FC. [(d)–(g)] EFTEM images of Ti- $L_{2,3}$, La- $M_{4,5}$, Mn- $L_{2,3}$, Fe- $L_{2,3}$ edges respectively for LS50BF12FC.

FIG. 6. (Color online) Aberration corrected (atomic resolution) Z-contrast image of LS50BF32FC obtained at 300 kV acceleration voltage on the TEAM 0.5 instrument. The inset and line is a visual guide to indicate where the interface appears to be located.

the STO, of the order of 6–7 nm. The Ti profile also reveals diffusion of Ti into the LSMO. Overall, these studies show diffusion/intermixing across all the interfaces at a length scale of 4–7 nm, as defined by the distance away from the interface at which the extended tail of the normalized intensity profile drop below 5%.

It is possible that such effects are intrinsically due to chemical intermixing across the interfaces but consideration needs to be given as to whether such effects are due to factors associated with the data collection parameters such as electron beam broadening, data acquisition method, etc. First, EFTEM data is not acquired with a small focused probe and therefore the electron beam does not experience the same sort of beam broadening effects that STEM-EDS data might show. Thus, concerns regarding the effects of beam broadening applicable to STEM-EDS are less applicable to EFTEM data.

The EFTEM data was acquired with a broad parallel beam covering the entire specimen. For EFTEM, the spatial resolution of the images is a combination of factors such as the amount of energy lost by the electrons passing through the specimen, the spectrometer slit width, and the objective aperture size. In this case, the resolution of images based on the conditions under which they were collected was expected to be of the order of ~ 1 nm (or perhaps better).³² This would probably lead to some slight blurring at the interface. In addition to this, the resolution limit of the images is not expected to blur the interface by distances of ~ 5 nm. This is why the observed interfacial diffusion is likely to be a real effect from the specimen rather than an artifact of the EFTEM image resolution.

Additional EFTEM experiments were carried out for two supplementary specimens with ultrathin BFO (~ 7 nm) films fabricated under two different cooling (fast and slow cooling) conditions. AFM images of these samples (not reported) showed a very smooth atomic surface with terracing evident. For these specimens the LSMO thickness was decreased to ~ 25 nm to understand the effect of its thickness on the quality of the interface. The profile analysis of Ti, La, Mn, and Fe in both of the specimens shows a similar trend to previous

specimens. In both cases there is diffusion across the interfaces (the extended tail of the normalized intensity below $\sim 5\%$) at the length scale of 5–7 nm. This result confirms that, irrespective of the surface structure the interfaces exhibited inter diffusion.

To further strengthen the observation of interdiffusion across the LSMO-BFO interface, an additional STO-LSMO-BFO (LS50BF35FC) specimen was investigated using atomic resolution STEM-EELS. The PLD growth conditions (substrate temperature, deposition pressure, cooling pressure laser energy, and laser frequency) for this specimen were the same as the previous specimens but the thickness of the BFO was deliberately increased to ~ 35 nm to study the effect of extended high temperature exposure of BFO on the quality of interface. A high angle annular dark field (HAADF) image of the specimen is shown in Fig. 6. In this imaging mode, the intensity of each atomic column can be directly related to the n th power ($n=1.5-2$) of its average atomic number Z and can therefore be used as a guide for chemical identification.³³ In Fig. 6(b) it can be seen that although the LSMO-BFO interface is free from any defects (some defects can be seen further inside the BFO layer but not at the interface itself) it appears diffuse over a distance of several atomic planes. One should note that a small number of defects were observed at the STO/LSMO interface, as evidenced by the occasional discontinuity in the Moiré pattern seen across Fig. 6(a). The concentration of such defects was in effect very small [see the scale bar on Fig. 6(a): Moiré pattern discontinuities are seen at most every 50 nm]. Interfacial steps, which are a characteristic of atomically sharp interfaces, were however not observed in any section of the LSMO/BFO interface investigated with ultrahigh resolution imaging.

The results of atomic resolution STEM-EELS analysis are given in Fig. 7. This shows a series of EEL spectra for the O-K, Fe- $L_{2,3}$, and Mn- $L_{2,3}$ edges collected serially across the LSMO-BFO interface [along the line shown in Fig. 7(a)]. Spectra at the top of the figure are from BFO and those at the bottom of the image from LSMO. On analysis, as we move from the BFO toward the LSMO, the Fe- $L_{2,3}$ peak gradually decreases, but does not sharply disappear at the LSMO-BFO

FIG. 7. (Color online) (a) HAADF survey image of LS50BF35FC for the EELS line scan recorded across the indicated beam path. The arrows show where visually one would place the LSMO-BFO interface. (b) Individual spectra from the STEM-EELS line scan across the BFO-LSMO interface of the LS50BF35FC along the beam path indicated in (a), starting from spectrum 1 in the BFO to spectrum 15 in the LSMO.

interface. Rather, it shows a measurable intensity even in spectra where there is a clear observation of the Mn- $L_{2,3}$ edge. One should note that the spatial resolution of EELS maps or line scans in STEM-EELS is still the subject of on-going investigations.³⁴ EELS signal delocalization can play a major role and very careful simulations are often necessary to interpret atomically resolved EELS data.³⁵ Nevertheless, the scale of the measurable diffusion through the present analysis is of the order of 4–5 nm, far larger than the spatial resolution that can be achieved with similar instruments³⁶ in similar systems, as previously reported in a case where the deposition was carried out using the molecular beam epitaxy technique and any interdiffusion was measured to be negligible.³⁷ These observations therefore clearly point to the migration of Fe from the BFO film into the LSMO, and vice versa, thereby confirming our previous EFTEM measurements.

IV. DISCUSSION

The above analytical characterization of all specimens, irrespective of PLD growth conditions and layer thickness, confirm intermixing of the interfaces over a length scale of the order of 4–7 nm. The diffusion at the STO-LSMO interface can be understood because Sr is a common element in both the layers and can always induce movement of atoms across the interface. The XRD data confirms the epitaxial nature of the LSMO-BFO film and also confirms the absence of any impurity phases such as Bi_2O_3 , $\gamma\text{-Fe}_2\text{O}_3$, and $\alpha\text{-Fe}_2\text{O}_3$. In addition, since diffusion is a high temperature-assisted process then the specimen with highest thickness (LS50BF35FC) should exhibit the highest degree of diffusion. However, it is not so and the diffusion profile (4–7 nm) is consistent in the entire set of samples irrespective of high temperature exposure and cooling conditions. Therefore, the observed intermixing at the LSMO-BFO interface should primarily arise from high temperature instability of the BFO. The observed diffusion is more to do with the high temperature reaction kinetics associated with formation of the BFO film on LSMO rather than any high temperature assisted intermixing. At the initial stage of the BFO growth, due to the combined effect of lattice mismatch, temperature, and the relative instability of BFO, dissociation of BFO into $\gamma\text{-Fe}_2\text{O}_3$ or $\alpha\text{-Fe}_2\text{O}_3$ takes place possibly for one or two atomic layers.

On obtaining subsequent equilibrium, BFO becomes phase-stabilized and starts to grow in an epitaxial and phase pure manner. Meanwhile, the continued exposure of the film to higher temperatures (until completion of BFO deposition and subsequent cooling to room temperature) will result in kinetic energy capable of dissociating $\gamma\text{-Fe}_2\text{O}_3$ or $\alpha\text{-Fe}_2\text{O}_3$ into iron and oxygen and thereby resulting in subsequent diffusion of Fe into the LSMO layer. Possibly due to initial dissociation of the BFO which takes place only for one or two atomic layers, the interface is able to retain its physical integrity without any defects irrespective of these chemical reactions. In addition to this, in the BFO perovskite structure Fe occupies the B site in the ABO_3 while Mn occupies a similar B-site in the LSMO structure. The ionic radii of Fe^{3+} (0.063 nm) and Mn^{4+} (0.053 nm) (Ref. 38) are very closely matched and it is therefore highly probable that they can diffuse across the LSMO-BFO interface and replace each other at their respective B-site positions. Since the atomic radii are very similar this does not create any dislocations during diffusion thereby keeping the interface dislocation-free. To what extent the dissociation and migration of Fe can alter the functional nature³⁹ of the LSMO-BFO interface is the subject of our ongoing studies. Finally, these outcomes suggest that variables in PLD conditions such as faster deposition and cooling rates are not the governing factors in controlling the chemical inhomogeneity across the LSMO-BFO interface, and that it is high temperature dissociation kinetics that limits the quality of the interface. This puts significant onus on the development of thin film epitaxy approaches at lower growth temperatures being required to test this hypothesis.

V. SUMMARY AND CONCLUSION

Epitaxial and phase pure ferromagnetic-multiferroic heterostructures were fabricated and the interfaces were investigated using bright field TEM imaging, STEM-EDS, EFTEM, and STEM-EELS. HRTEM images confirm that there are no physical dislocations present across the interface but the interface itself is not sharp. The STEM-EDS, EFTEM, and STEM-EELS studies of the heterostructure show a clear trend of interfacial diffusion on the order of a 4 to 7 nm length scale. Interfacial diffusion takes place irrespective of thickness of the layers or cooling conditions of

the specimen. The possible cause of the intermixing across the interface explaining the present results would be a dissociation and subsequent stabilization of BFO at the heterostructure fabricating temperature. The possible effects of diffusion on multiferroic properties of BFO film will be reported subsequently.

ACKNOWLEDGMENTS

This work at The University of New South Wales was supported by an ARC Discovery project. The authors acknowledge access to the UNSW node of the Australian Microscopy & Microanalysis Research Facility (AMMRF). UNSW authors wish to thank AMMRF TAP Grant No. TAP 8034. We also acknowledge the facilities, scientific, and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy, Characterization & Analysis, The University of Western Australia, a facility funded by The University, State and Commonwealth Government. This work was carried out in part at the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, which is supported by the Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH1123.

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