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## Highly textured Sr, Nb co-doped BiFeO<sub>3</sub> thin films grown on SrRuO<sub>3</sub>/Si substrates by rf- sputtering

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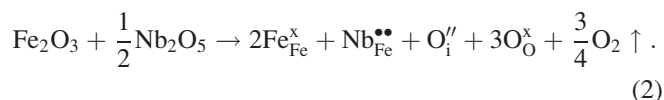
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In this study, (011)-highly oriented Sr, Nb co-doped BiFeO<sub>3</sub> (BFO) thin films were successfully grown on SrRuO<sub>3</sub>/Si substrates by rf-magnetron sputtering. The presence of parasite magnetic phases was ruled out based on the high resolution x-ray diffraction data. BFO films exhibited a columnar-like grain growth with rms surface roughness values of  $\approx 5.3$  nm and average grain sizes of  $\approx 65$ – $70$  nm for samples with different thicknesses. Remanent polarization values ( $2P_r$ ) of  $54 \mu\text{C cm}^{-2}$  at room temperature were found for the BFO films with a ferroelectric behavior characteristic of an asymmetric device structure. Analysis of the leakage mechanisms for this structure in negative bias suggests Schottky injection and a dominant Poole-Frenkel trap-limited conduction at room temperature. Oxygen vacancies and Fe<sup>3+</sup>/Fe<sup>2+</sup> trap centers are consistent with the surface chemical bonding states analysis from x-ray photoelectron spectroscopy data. The (011)-BFO/SrRuO<sub>3</sub>/Si film structure exhibits a strong magnetic interaction at the interface between the multiferroic film and the substrate layer where an enhanced ferromagnetic response at 5 K was observed. Zero-field cooled (ZFC) and field cooled (FC) magnetization curves of this film system revealed a possible spin glass behavior at spin freezing temperatures below 30 K depending on the BFO film thickness. © 2011 American Institute of Physics. [doi:10.1063/1.3610428]

### I. INTRODUCTION

Multiferroics comprise an exciting class of multifunctional materials because they simultaneously show some form of magnetic, elastic, and/or ferroelectric order.<sup>1</sup> The coexistence of these ferroic orderings contributes an additional degree of freedom which is very useful for memory and logic device applications.<sup>2</sup> Indeed, the magnetoelectric coupling in multiferroics allows an electric-field control of the magnetization, and vice versa.<sup>3,4</sup> BiFeO<sub>3</sub> (BFO), which belongs to the rhombohedral space group ( $R\bar{3}c$ ),<sup>5</sup> is perhaps, the most important multiferroic material because it exhibits both G-type antiferromagnetism ( $T_N \approx 640$  K) with a spatially modulated spin structure, and ferroelectric ( $T_C \approx 1100$  K) ordering at room temperature.<sup>6</sup> However, BFO has poor stability<sup>7</sup> and it is still a considerable challenge to obtain it as single-phase in both ceramic and in thin film form.<sup>8,9</sup> From an academic point of view, this situation is part of some interesting discrepancies grouped, essentially, according to two aspects, one related to the uncertainty that the high polarization response is only due to intrinsic phenomena,<sup>10</sup> and the other, to the statement that the reported magnetization values are due to the presence of traces of parasite magnetic phases and not to the suppression of the incommensurate spin structure.<sup>9,11,12</sup> After testing many different

approaches, one that is widely accepted for minimizing the presence of impurities produced during the BFO synthesis is through the use of suitable doping strategies. As a matter of fact, we have observed that the partial substitution of bismuth by strontium has great beneficial effects on the stability and purity of BFO ceramics.<sup>13</sup> In the case of thin films, a recent study showed that the effect of Sr<sup>2+</sup> ions doping on the magnetic and ferroelectric properties of BFO seems to be strongly related to the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> impurity phase and oxygen vacancies.<sup>14</sup> Following this line of thought, we proposed a Sr,Nb co-doping process for the synthesis of BFO due to the fact that some experimental reports suggest that niobium doping may improve both resistivity and fatigue in BFO films.<sup>15–17</sup> In the Kroger–Vink notation, this is written as follows:



Equation 1 implies that for every Sr<sup>2+</sup> ion positioned in the A-site, one oxygen vacancy is necessary to stabilize the charge; similarly, Eq. 2 implies that for every Nb<sup>5+</sup> ion positioned in the B-site, one interstitial oxygen site is also created. If we add Eqs. 1 and 2, a neutral perovskite with the general formula (Bi<sub>1-x</sub>Sr<sub>x</sub>)(Fe<sub>1-x/2</sub>Nb<sub>x/2</sub>)O<sub>3</sub> is obtained. One can observe that

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such a substitution combines the Schottky and Frenkel defect formation mechanisms to control the mobility of oxygen vacancies through the structure. The composition with an  $x$  value of 0.05 was selected to fabricate the sputtering ceramic target, which was later used to obtain the thin films, because it is the minimum value in the formula according to previous experiments where the synthesis of BFO was successful. This criterion helps us to avoid the weakening of the ferroelectric response due to the exaggerated dilution of the Bi ions, since the lone pair of bismuth seems to be greatly responsible for the ferroelectric nature of BFO.

Focusing our attention on thin film deposition now, it is evident from many reports in the literature that several deposition routes have been attempted to obtain BFO films. In particular, for the case of the rf-magnetron sputtering technique, reports are scarce, and in those reports, it is found that only polycrystalline BFO films have been obtained when they are deposited on silicon substrates (including platinized Si wafers with or without a buffer layer).<sup>18–20</sup> Thus, the only way to obtain highly textured or epitaxial films has been by using expensive substrates such as SrTiO<sub>3</sub> and LaAlO<sub>3</sub>.<sup>21–23</sup> Moreover, in most cases, parasitic phases were present.

In this work, single-phase and highly textured (011)-Sr, Nb co-doped BFO films were obtained by the rf-magnetron sputtering technique on a SrRuO<sub>3</sub> layer deposited on silicon substrates in our labs. The SrRuO<sub>3</sub> oxide simultaneously acts as the bottom electrode and a template layer. This proposal may have enormous benefits if we pretend to extend this knowledge to current technological demands, for instance, CMOS design for integrated circuits. Additionally, this alternative method may help avoid the formation of parasitic impurities and assure the growth of high quality BFO films once the deposition conditions are optimized. Besides the microstructural characterization of the films, the ferroelectric behavior and leakage current limiting mechanisms of doped films are discussed from data taken at room temperature. The magnetic response of the BFO/SrRuO<sub>3</sub>/Si system, including zero-field cooled (ZFC) and field cooled (FC) magnetization, is also evaluated.

## II. EXPERIMENTAL

In the experiments, the rf-magnetron sputtering technique was used for thin film deposition. First, a SrRuO<sub>3</sub> layer of  $\sim 450$  nm was deposited on a Si(001) commercial substrate from a SrRuO<sub>3</sub> polycrystalline ceramic target. Next, multiferroic thin films were grown on the (011)-oriented SrRuO<sub>3</sub>/Si substrates from a (Bi<sub>0.95</sub>Sr<sub>0.05</sub>)(Fe<sub>0.975</sub>Nb<sub>0.025</sub>)O<sub>3</sub> ceramic target. The target, 2 in in diameter, was synthesized by sintering the powder mixture of Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, and SrCO<sub>3</sub> at 850 °C; a 10 wt. % excess Bi<sub>2</sub>O<sub>3</sub> was added to compensate for the volatility of this component at high temperatures. The experimental conditions of thin film deposition are summarized in Table I. The substrate holder was in a fixed position 5 cm from the target. The BiFeO<sub>3</sub> films were annealed at 700 °C (15°/min<sup>-1</sup>) in a 0.67 Pa oxygen atmosphere for 20 min and rapidly cooled (30°/min<sup>-1</sup>) in the deposition chamber.

TABLE I. Experimental parameters used in rf-magnetron sputtering for depositing SrRuO<sub>3</sub> and BiFeO<sub>3</sub> thin films.

	SrRuO <sub>3</sub> films	BiFeO <sub>3</sub> films
Substrate temperature	700 °C	600 °C
Vacuum pressure	$1.3 \times 10^{-3}$ Pa	$1.3 \times 10^{-3}$ Pa
Work pressure	1.3 Pa	3.3 Pa
Gas atmosphere	Ar	Ar/O <sub>2</sub> (4:1)
RF power	150 W	200 W
Time of deposition	180 min	30 to 120 min

The phases present in the BFO thin films and their textures were analyzed by x-ray diffraction (XRD) using a Panalytical X-Pert PRO diffractometer with Cu  $K\alpha$  radiation. The film surfaces were studied with a Digital Instruments Nanoscope III atomic force microscope (AFM) operated in contact mode. Surface chemical analysis and bonding states were investigated by x-ray photoelectron spectroscopy (XPS) with an Al  $K\alpha$  (1,486.6 eV) x-ray source from Cameca. The photoelectric peak of C 1s located at 284.6 eV was used as a standard for XPS binding energies. The XPSPEAK Version 4.1 software was used to fit the narrow-scan spectra of Bi 4f, Fe 2p, and O 1s after Shirley-type background subtraction. To study the ferroelectric properties, 100 nm thick gold top electrodes with an area of  $100 \times 100 \mu\text{m}^2$  were evaporated onto the sample films through a metal shadow mask. Polarization-electric field (P-E) hysteresis loops were measured with a Precision LC analyzer from Radiant Technologies Inc. The P-E measurements were conducted with a standard triangular bipolar signal at 1 KHz and at room temperature. The leakage currents were measured using an electrometer (Keithley 6430) at room temperature. The magnetization loops (M-H) were measured at 5 K with the magnetic field oriented in-plane using a Quantum Design PPMS system. Zero-field cooled (ZFC) and field cooled (FC) magnetization measurements, were carried out by cooling the sample to the desired temperature in the absence or presence of applied magnetic field (in-plane) on a Quantum Design SQUID MPMS-XL susceptometer.

## III. RESULTS AND DISCUSSION

Figure 1(a) shows a representative XRD pattern of a Sr,Nb co-doped BiFeO<sub>3</sub> (BFO) film deposited on a SrRuO<sub>3</sub>/Si substrate. The peaks were indexed from a pseudocubic structure and they all correspond to a perovskite-type oxide. Note that the intensity counts of the deposited BFO film are greater than those of the SrRuO<sub>3</sub> layer used as a template, indicating the successful formation of the BFO phase. In the inset, diffraction counts of the fabricated BFO film were plotted in log scale to enhance contrast and draw attention to the high quality of the film. Indeed, the doped BFO films are single-phase and exhibit a strong preferred (011)-orientation following that of the SrRuO<sub>3</sub> layer. A thicker film of about 400 nm was selected to make the absence of parasitic phases more evident, given that impurities in thinner films could not be detected by standard XRD. Similarly, as we found in ceramics [Fig. 1(b)], the stability of the BiFeO<sub>3</sub> thin films seems to be enhanced by the A-site strontium and B-site

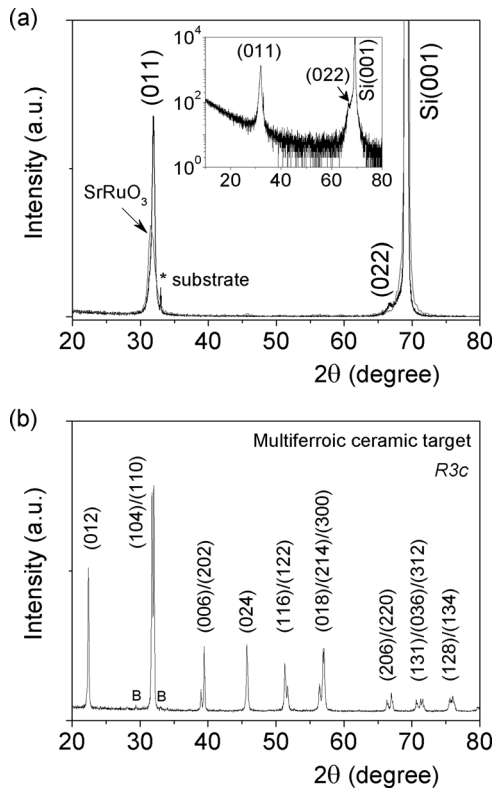


FIG. 1. (a) Indexed XRD profile for a 400 nm thick (011)-highly oriented Sr, Nb co-doped  $\text{BiFeO}_3$  film on (011)-oriented  $\text{SrRuO}_3/\text{Si}(001)$  substrate. The red line separately represents the XRD pattern of the  $\text{SrRuO}_3$  layer. The inset shows the intensity values of the fabricated BFO film in log scale. (b) XRD pattern of the multiferroic ceramic target employed for the thin film deposition (B for the  $\text{Bi}_2\text{O}_3$  phase). The Miller index is indicated by ticks.

niobium doping into the perovskite structure. Thus, thermodynamically favorable formation of parasite phases such as  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{Bi}_{25}\text{Fe}_{40}$  and  $\text{Bi}_2\text{Fe}_4\text{O}_9$  seemed to be avoided. The result is highly reproducible under the deposition conditions previously established.

Figure 2 shows the 3D AFM images of doped BFO films at two different times of deposition, hence the film thicknesses. Dark to bright contrast color in the figures is related to the height scale; 0 for the darkest, 50 nm for the brightest. The film surface shows columnar-like grain morphology; as the film thickness increases from 100 to 400 nm, the columns grow in height, but apparently not in width, and they are well-defined and sharply tipped. Since the columns grow close to each other dense materials are obtained. Figure 3 shows the root mean square (rms) surface roughness and average grain sizes for an area of analysis of  $6.25 \mu\text{m}^2$ . This growth behavior slightly affects the surface roughness of the films, and the grain sizes were fairly similar in a range of 60 to 70 nm for films of different thicknesses. The film formation seems to obey a general mechanism based on the adsorption of chemical species on the substrate surface, the diffusion and reaction onto highly reactive sites, the nucleation process, and the formation of nanoclusters with an oriented grain growth.

Figure 4 shows the fitted narrow-scan spectra of Bi 4f, Fe 2p, O 1s, and Sr 3d peaks for a 200 nm BFO film. Herein, Table II lists the peak positions and their corresponding

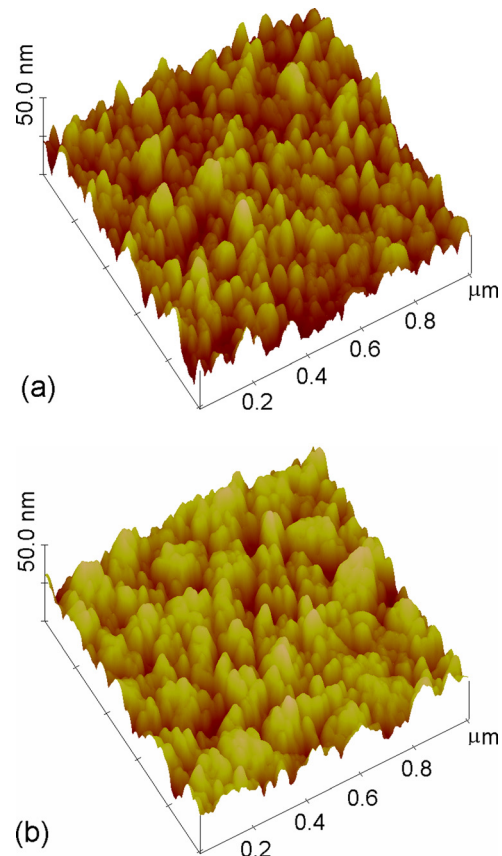


FIG. 2. (Color online) AFM images of doped  $\text{BiFeO}_3$  films with different thicknesses: (a) 100 nm and (d) 400 nm.

full-width at half-maximum (FWHM). The Bi 4f doublet [Fig. 4(a)] consists of two peaks mainly identified as a signal of Bi–O bonds. The spin-orbit splitting energy ( $\Delta E$ ) of the Bi 4f doublet is 5.31 eV, which is in good agreement with the theoretical value. This doublet is fitted with two pairs of subpeaks, B1 and B2. The first located at lower energies, B1, is mainly ascribed to Bi ( $4f_{7/2}$ )–O and Bi ( $4f_{5/2}$ )–O bonds, while the other subpeaks, B2, may be related to Bi–O–Fe bonds and Bi–O–Sr bonds in the oxygen octahedron and/or a relaxed Bi phase from defective octahedra.<sup>24</sup> Chemical shifts may be related to the fraction of ionicity and polarizing forces based on the Fajan's rules. Both of them help to predict whether a chemical bond will be more covalent or ionic,

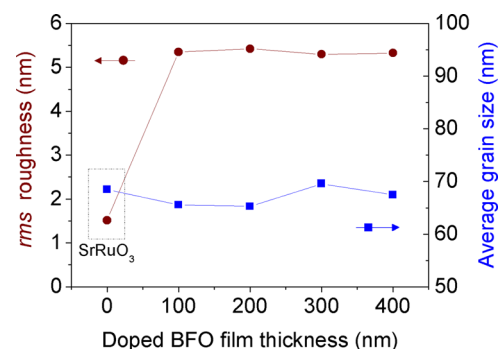


FIG. 3. (Color online) Average grain size and rms roughness variation of doped  $\text{BiFeO}_3$  films with different thicknesses. The data are obtained from AFM images. The lines are drawn only as a visual guide.

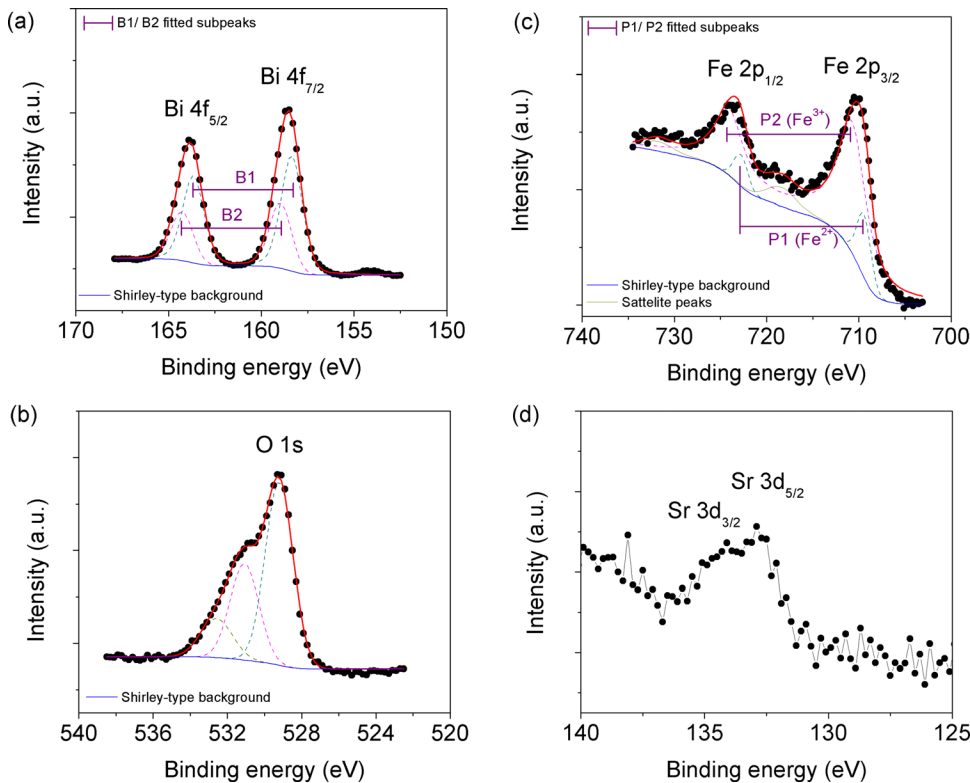


FIG. 4. (Color online) Fitted XPS narrow scan spectra of (a) Bi 4f, (b) Fe 2p, (c) O 1s, and (d) Sr 3d in a 200 nm doped BiFeO<sub>3</sub> film. Black dot points represent experimental results; the red solid line represents the fitting results after Shirley-type background subtraction, and dashed peaks with colors are fitted subpeaks.

and thereby, suggest if peaks shift to lower or higher energy values, respectively. Thus, the fraction of ionicity ( $F_i$ ) of Bi–O (0.40) and Sr–O (0.79) bonds given by,

$$F_i = 1 - e^{[-(\Delta EN)^2/4]}, \quad (3)$$

where  $\Delta EN$  is the difference of electronegativities, clearly show the higher ionic character of the Sr–O bond. This suggests that the bonding energy of the (Bi,Sr)–O bond in the oxygen octahedron may be larger than that of the single Bi–O bond. Indeed, the dependence of the cation charge ( $\sigma$ ) and its relative size ( $r_i$ ) confirms that the nature of the Sr–O bond is more ionic than that of Bi–O. Calculations of the polarizing force ( $\sigma/r_i$ ) were done from ionic radii of eight-fold coordination ( $r_{\text{Sr}^{2+}} = 1.26 \text{ \AA}$ ,  $r_{\text{Bi}^{3+}} = 1.17 \text{ \AA}$ ). As the polarizing force increases the covalent character increases. This behavior is clearly demonstrated in the O 1s signal because it is a well-defined single peak at about 531.0 eV and allows an accurate fitting process. The O 1s peak [Fig. 4(b)] consists of

three single subpeaks, which are mainly ascribed to Fe<sub>2</sub>–(O 1s)<sub>3</sub> and Fe–(O 1s) at lower energies, Bi<sub>2</sub>–(O 1s)<sub>3</sub> bonds (middle subpeak), and (Bi,Sr)–O and/or relaxed O phases at higher binding energies. The  $F_i$  value of the Fe–O (0.48) bond is closer to that of Bi–O, however, the  $\sigma/r_i$  ratio (4.65  $\text{\AA}^{-1}$ ) of Fe–O is greater in correspondence to its higher polarizing nature. This suggests that the O 1s subpeak of the Fe–O bonds may be located at lower energies. Apart from adsorbed chemical species from the environment as a consequence of this *ex situ* XPS analysis, the relaxed O phases may also be attributed to the absorbed oxygen associated with oxygen vacancies (some of them created by cation defects). Regarding the Fe 2p signal [Fig. 4(c)]: it consists of two wide peaks ascribed to Fe–O bonds with a  $\Delta E$  value of 13.6 eV obtained from Fe<sub>2</sub>O<sub>3</sub>. The Fe 2p doublet is fitted by two pairs of subpeaks with a comparable  $\Delta E$  value of 13.36 eV. The pair of subpeaks located at higher energies, P2, is ascribed to (Fe 2p<sub>3/2</sub>)<sub>2</sub>–O<sub>3</sub> and (Fe 2p<sub>1/2</sub>)<sub>2</sub>–O<sub>3</sub> bonds, which corresponds to a Fe<sup>3+</sup> ion. The second pair, located at low energies, P1, is mainly related to the Fe–O bonds for Fe<sup>2+</sup>. Similarly, other contributions from Fe–O–Bi bonds and Fe–O–Sr bonds may be pointed out. Otherwise, it is widely accepted that oxygen vacancies are formed during growth and, consequently, a portion of the Fe<sup>3+</sup> ions are reduced to Fe<sup>2+</sup> in the case of pure BiFeO<sub>3</sub> films. Finally, the Sr 3d wide peak [Fig. 4(d)] consists mainly of a doublet ascribed to Sr–O bonds ( $\Delta E = 1.79 \text{ eV}$ ). A good fitting of the Sr 3d<sub>5/2</sub> and Sr 3d<sub>3/2</sub> peaks was not possible due to the noisy signal resulting from the low molar quantity of strontium ( $\sim 5\%$ ) from the chemical composition of the target. Similarly, it was not possible to analyze the Nb 3d signal because it was within the noise level of the technique ( $\sim 1\%$  M).

TABLE II. Peak positions for the core levels Bi4f<sub>7/2</sub>, Fe2p<sub>3/2</sub>, and O1s relative to C1s (284.6 eV).  $\Delta E$  and FWHM are their corresponding spin-orbit splitting energy and full-width at half-maximum, respectively.

Core level	$\Delta E$ (eV)	Peak positions in eV (FWHM) <sup>a</sup>		
Fe 2p <sub>3/2</sub>	13.36	709.45 (1.80)	710.73 (3.76)	...
Bi 4f <sub>7/2</sub>	5.31	158.36 (1.35)	158.97 (1.39)	...
O 1s	...	529.21 (1.77)	531.08 (1.82)	532.59 (2.02)

<sup>a</sup>The uncertainty in the peak position is  $\pm 0.10 \text{ eV}$  and in FWHM it is  $\pm 0.20 \text{ eV}$ .

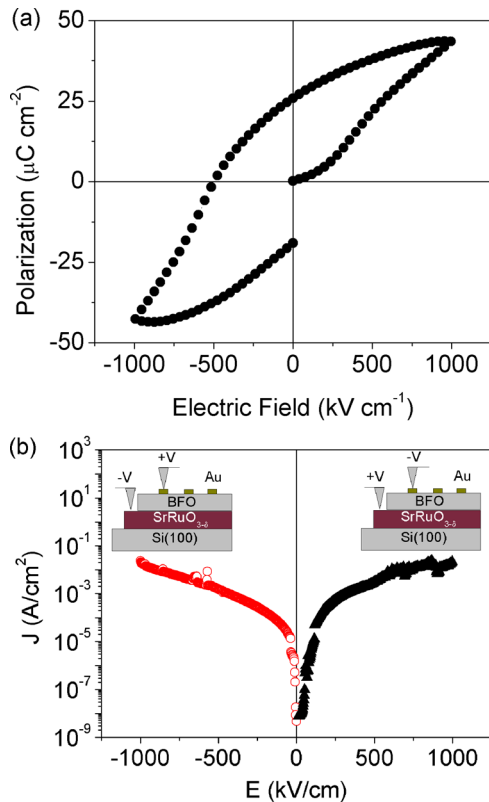


FIG. 5. (Color online) (a) Polarization-electric field (P-E) hysteresis loop conducted at 1 KHz, and (b) typical J-E characteristics of the Au/BFO/SrRuO<sub>3</sub>/Si thin film structure. Inset schematic diagram of bottom electrode, film, and top electrodes.

Figure 5(a) is a plot of the polarization-electric field (P-E) hysteresis loop for a 400 nm doped BFO film at room temperature. The P-E loop obtained is characteristic of a ferroelectric material with remanent polarization ( $2P_r$ ) of  $54 \mu\text{C cm}^{-2}$ . This  $2P_r$  value is lower than those reported for Sr-doped BiFeO<sub>3</sub> films ( $\sim 86 \mu\text{C cm}^{-2}$ )<sup>14</sup> and non-doped BiFeO<sub>3</sub> films ( $100\text{--}150 \mu\text{C cm}^{-2}$ )<sup>11,18,19</sup> deposited on SrRuO<sub>3</sub>-buffered substrates. The lower value obtained for our films is consistent with the fact that square saturated hysteresis loops were not achieved despite the large fields applied for switching the polarization. Indeed, the field was increased up to values of  $1 \text{ MV cm}^{-1}$  at 1 KHz; that is, an integration time for the current of 1ms. Also, the hysteresis loop is not closed mainly due to the difference between the electrode work functions (Au  $\sim 5.3 \text{ eV}$  and SrRuO<sub>3- $\delta$</sub>   $\sim 4.6 \text{ eV}$ ) and the electron affinity of the ferroelectric compound.<sup>10</sup> From the P-E loop a contribution of leakage currents is not evident; the curve is concave and well-defined. Figure 5(b) shows the leakage data as a function of the applied electric field (J-E). The asymmetry of the J-E curves is probably due to the different mechanisms operating at negative and positive bias. To investigate the possible leakage-current-limiting mechanisms of the doped BFO films, experimental data were plotted in four different ways as a function of voltage. Indeed, we fitted the leakage current curve by interface-limited conduction mechanisms: Schottky-injection (SI) and Fowler-Nordheim (FN) tunneling, and the bulk-limited conduction mechanisms: Poole-Frenkel (PF) trap-limited and

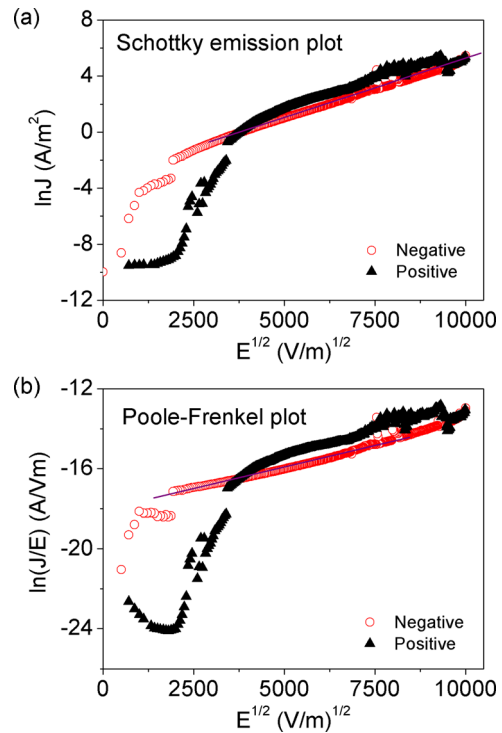


FIG. 6. (Color online) Fits of J-E data from an Au/BFO/SrRuO<sub>3</sub>/Si capacitor are shown to help determine the leakage mechanism: (a) SI, and (b) PF conduction.

space-charge-limited current (SCLC). The FN and SCLC can be ruled out as the leakage-current-limiting mechanisms because no linearity could be obtained in both  $\ln(J/E^2)$  versus  $1/E$  and double log plot  $J$  versus  $E$  (not shown here), in either negative and positive bias, similar to a previous report.<sup>25</sup> In fact, at positive bias any of these four leakage mechanisms fail to fit, suggesting that there is no clear dominant mechanism. At an applied field above  $100 \text{ kV/cm}$ , semilog plots of  $\ln(J)$  versus  $E^{1/2}$  [Fig. 6(a)] and  $\ln(J/E)$  vs  $E^{1/2}$  [Fig. 6(b)] show that a straight line fits the data. Both the SI and PF mechanisms, respectively, are dominant at negative bias. The Schottky barrier ( $\Phi_B$ ) and relative permittivity ( $\epsilon_r$ ) were estimated to be  $0.72$  and  $0.85 \text{ eV}$ , respectively. Here,  $\Phi_B$  is greater than that reported by Hartmann *et al.*<sup>26</sup> ( $\sim 0.3 \text{ eV}$ ). This result and a previous fitting process exclude an ohmic behavior. However, the magnitude of  $\epsilon_r$  seems to be too small, since a value of  $6.25$  was expected from the index of refraction for BFO ( $n = 2.5$ ). For the case of the PF mechanisms,  $\epsilon_r$  was estimated to be  $3.6$ , which is a closer value than that calculated from the SI equations. In this manner, the PF trap-limited conduction may be considered as the dominant leakage mechanism. Note that XPS analysis of the film surfaces had suggested the presence of oxygen relaxed phases probably attributed to oxygen vacancies and to the presence of mixed Fe<sup>3+</sup>/Fe<sup>2+</sup> ions, which is consequent with the previous leakage current analysis. From an intrinsic point of view, in the BiFeO<sub>3</sub> multiferroic, Fe ions are considered likely to be trap centers.<sup>25</sup> It is important to point out that leakage current densities of  $10^{-4} \text{ A/cm}^2$  are lower than those in other reports<sup>27,28</sup> for the range of values of the applied electric field ( $<200 \text{ kV/cm}$ ). At low electric fields ( $<100 \text{ kV/cm}$ ), a larger

electron injection from the SrRuO<sub>3</sub> electrode (negative field) than from the Au top electrode (positive field) into the film may be expected. This situation is usually found in film growth methods such as the rf-sputtering technique, where the bottom electrode is heated at higher temperatures (700 °C) with a low oxygen partial pressure ( $\leq 5$  mTorr). These conditions could lead to the formation of an oxygen deficiency and the presence of mixed ion valences in the electrode-ferroelectric interface.

Figure 7 shows the in-plane magnetization hysteresis (M-H) loops obtained at 5 K for the SrRuO<sub>3</sub>/Si substrate and two (011)-BFO/SrRuO<sub>3</sub>/Si film structures, denoted F1 and F2, with two different BFO film thicknesses of  $\sim 100$  and  $\sim 200$  nm, respectively. The film thickness of the SrRuO<sub>3</sub> layer plus that of the BFO film were considered to calculate the magnetization. It was observed that the SrRuO<sub>3</sub> perovskite layer exhibited ferromagnetism at cryogenic temperatures, which is in agreement with reports in the literature ( $T_C \sim 160$  K).<sup>29</sup> As an interesting effect, in Fig. 7 the two (011)-BFO/SrRuO<sub>3</sub>/Si film structures exhibit nonsaturated ferromagnetic loops with a noticeable difference between the maximum ( $M_m$ ) and remanent ( $M_r$ ) magnetization values in comparison with those of the SrRuO<sub>3</sub>/Si substrate. This enhanced ferromagnetic (FM) behavior of the F1 and F2 structures, characterized by the difference with the SrRuO<sub>3</sub>/Si substrate of  $\Delta M_m = 16.2$  and  $17.4$  emu cm<sup>-3</sup> and  $\Delta M_r = 4.0$  and  $4.6$  emu cm<sup>-3</sup>, respectively, can be explained by a strong magnetic exchange interaction at the interface, which is probably associated with a thin zone of transitional composition around the nominal BFO/SrRuO<sub>3</sub> junction. However, to estimate the value of magnetization for the multiferroic BFO film as a function of thickness, in Fig. 7 we plot the M-H loop obtained by the subtraction of the M-H loops of the F1 and F2 samples (F2-F1 curve), as Yan *et al.* suggest in a recent report.<sup>30</sup> A very low  $\Delta M_m$  value of about  $1$  emu cm<sup>-3</sup> ( $\sim 5 \times 10^{-4} \mu_B/\text{Fe}$ ) was obtained, suggesting that the interfacial interaction between the multiferroic film and the substrate layer is responsible for the enhanced FM response, since the magnetic contribution is slightly increased by a widening of the interface region when the

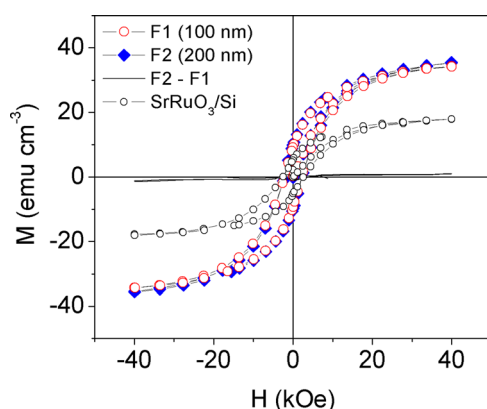


FIG. 7. (Color online) Magnetization-magnetic field (M-H) curves for doped BiFeO<sub>3</sub> films deposited on SrRuO<sub>3</sub>/Si substrates. F1 and F2 samples correspond to doped BFO film thicknesses of 100 and 200 nm, respectively. F2 - F1 represents the difference of the magnetization of the F2 and F1 samples.

doped BFO film thicknesses increase, but without changing the hysteresis features.

Figure 8 shows the field cooling (FC) and zero-field cooling (ZFC) magnetizations of the doped BFO/SrRuO<sub>3</sub>/Si structures with different values of the BFO film thickness as a function of temperature measured at a magnetic field of 100 Oe. The splitting of the FC and ZFC magnetizations at low temperatures exhibited in all cases [Figs. 8(a)–8(c)] correspond to the typical characteristics of a spin-glass-like behavior. As reported by Singh *et al.*,<sup>31</sup> this anomalous behavior of ZFC magnetization may be related to a typical blocking process of an assembly of superparamagnetic spins related to the presence of small particles, domains, or domain walls in the system. Moreover, it is observed that whereas the thickness of the BFO film increases, the spin freezing temperature ( $T_f$ ) and the Curie temperature ( $T_C$ ) shift toward lower temperatures. The experimental results suggest that changes in spin ordering

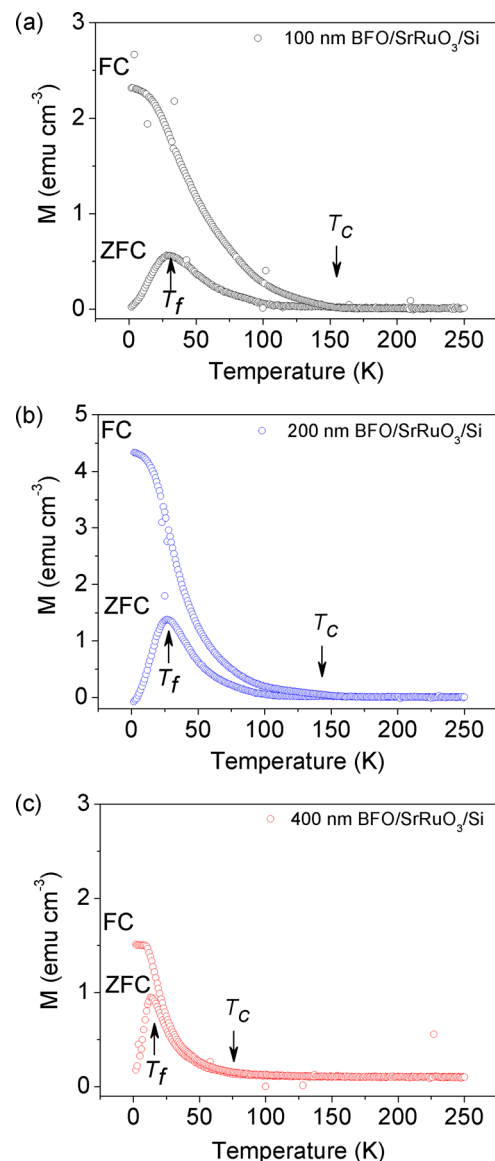


FIG. 8. (Color online) Temperature dependence of the dc magnetization ZFC and FC of doped BiFeO<sub>3</sub> thin films with different thicknesses deposited on a SrRuO<sub>3</sub> layer: (a) 100 nm, (b) 200 nm, and (c) 400 nm. The thickness values are approximated.

at low temperature in the BFO/SrRuO<sub>3</sub>/Si film structure may be due to induced spin reorientation in BiFeO<sub>3</sub> films by the SrRuO<sub>3</sub> layer, and/or interface phenomena originated by diffusion processes within the BFO/SrRuO<sub>3</sub> interface zone as mentioned in the preceding text. In fact, the observed  $T_C$  behavior is similar to that reported for the SrRu<sub>1-x</sub>Mn<sub>x</sub>O<sub>3</sub> system,<sup>32</sup> where  $T_C$  shifts toward lower temperatures as the value of  $x$  increases. Similarly, as the time of BFO deposition increases, for example, possible ion substitutions boosted by the high substrate temperatures employed during the sputtering process, may be leading to a SrRu<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> type-interface with the consequent modification of the  $T_C$  values. However, this hypothesis will be experimentally tested using the HRTEM technique. Moreover, to verify the existence and to understand the nature of the spin glass transition at low temperatures, a study of the frequency dependence of ac susceptibility for the film samples will be performed.

## CONCLUSIONS

In this study, (011)-highly oriented Sr, Nb co-doped BiFeO<sub>3</sub> (BFO) thin films were fabricated on Si substrates by using an intermediate SrRuO<sub>3</sub> template layer via rf-magnetron sputtering. The BFO films showed a columnar-type growth without detectable extra phases. The Au/BFO/SrRuO<sub>3</sub> film capacitor exhibited good ferroelectric behavior at room temperature; however, the migration of oxygen vacancies and trap centers of the Fe ions seem to be responsible for leakage currents in doped films. The Poole-Frenkel effect in negative bias was found to be the dominant leakage mechanism followed by Schottky injection. Interface phenomena between the multiferroic film and the SrRuO<sub>3</sub> layer in the (011)-BFO/SrRuO<sub>3</sub>/Si film structure may explain the enhanced ferromagnetic response at 5 K and the possible spin glass behavior observed at spin freezing temperatures below 30 K.

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