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Strain behavior of lanthanum modified $BiFeO_3$ thin films prepared via soft chemical method

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Pure and lanthanum modified BFO ($La_xBi_{1-x}FeO_3$, $x=0.0$, 0.08, 0.15, 0.30) thin films were fabricated on Pt(111)/Ti/SiO_2/Si substrates by the soft chemical method. The effect of La substitution on the structural and electrical properties was studied. Scanning electron microscopy, x-ray diffraction, and Raman spectroscopy have been employed to characterize the thin films while the piezoelectric measurements were carried out using a setup based on an atomic force microscope. It was found that La-doped BFO thin films exhibited good ferroelectric properties, such as improved leakage current density and retention-free characteristics. The unipolar strain is strongly reduced by the amount of lanthanum added to the system. © *2008 American Institute of Physics*.
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I. INTRODUCTION

Multiferroic materials have attracted renewed interest in recent years[1–5] due to both its potential applications for electronic device and its fascinating fundamental physics.[6–8] In particular, special attention has been designed for multiferroic oxides such as $BiFeO_3$ (BFO),[9] $BiMnO_3$,[10] $TbMnO_3$,[11] and $TbMn_2O_5$ (Ref. 12) due the potential to provide a wide range of applications, including the emerging field of spintronics,[13] data-storage media,[14] and multiple-state memories.[8] These multiferroic materials have simultaneous ferromagnetic, ferroelectric, and/or ferroelastic ordering.[15]

The well-known single phase multiferroics are mainly Mn- or Fe-based oxides.[16–19] Among them, BFO is the only known material that is both ferroelectric ($T_C \sim 1083$ K) and antiferromagnetic ($T_N \sim 625$ K).[20,21] It has a rhombohedrally distorted ferroelectric perovskite structure ($T_C = 123$ K) with the space group $R3c$.[22,23] Recent reports of a large spontaneous polarization ($\sim 100\ \mu C/cm^2$) in thin films,[24] bulk ceramic,[25] and single crystals[26] of BFO have led to an explosion of interest in its growth and properties.

The ferroelectric mechanism in BFO is controlled by the stereochemical activity of the Bi^{3+} $6s^2$ lone pair, responsible of a charge transfer process from $6s^2$ to formally empty $6p$ orbitals,[27,28] while the weak ferromagnetic property can be associated with the residual moment from the canted Fe^{3+} spin structure.[29] The coupling effect between both magnetic and electric behaviors occurs through lattice distortion of BFO (Ref. 30) and Khomskii[31] has been emphasized the different ways to combine magnetism and ferroelectricity in mutiferroics materials.

The structure and properties of thin films are well known to exhibit a number of deviations from those of bulk ceramics and single crystals. The origin of the size-dependent ferroelectric properties remains a challenging problem, and a better understanding as to which extent the bulk physical properties can be used for design of thin-layer devices, is actually required. Retention, which is the time-dependent change in the polarization state of the ferroelectric film, is another factor which limits the life of a ferroelectric memory device. In bismuth-based ferroelectrics, such as $Bi_4Ti_3O_{12}$ (Ref. 32) and $SrBi_4Ti_4O_{15}$,[33] the doping of lanthanum (La) was effective to enhance the insulating and ferroelectric properties because of the reduced oxygen vacancy by the stabilized oxygen octahedron.[34] Some studies reported in literature[35–37] suggest that the inhomogeneous magnetic spin structure can be effectively suppressed by La doping. Therefore, the influence of La doping on polarization switching, ferroelectric reliability, and multiferroic properties of BFO films deserves more attention.[38] In this respect, strain engineering and functional tuning of thin films are the leading activities for the development of the next generation of electronic devices. Recently, several research groups have substituted Bi by La and Tb in order to study the effect of doping on electric and magnetic behavior of pure BFO and lanthanum doped (BLFO) thin films.[39–42] Recently, Zheng *et al.*[43] presented synthesis and ferroelectric properties of $BiFeO_3$ thin films grown by sputtering, while Li *et al.*[44] employed a cosputtering method to obtain $BiFeO_3$ thin films on Pt/Ti/SiO_2/Si substrates.

Our group has expanded significant effort in developing synthetic routes of $BiFeO_3$ thin films[45,46] and we have previously reported the preparation of BLFO thin films grown on Pt(111)/Ti/SiO_2/Si substrates with good structural, microstructural, and electrical properties by the soft chemical method.[9,32,47,48] In the present investigation and as a natural extension of previous work, pure and lanthanum modified $Bi_{1-x}La_xFeO_3$ ($x=0.0, 0.08, 0.15, 0.30$) thin films were prepared on Pt(111)/Ti/SiO_2/Si substrates by the soft chemical

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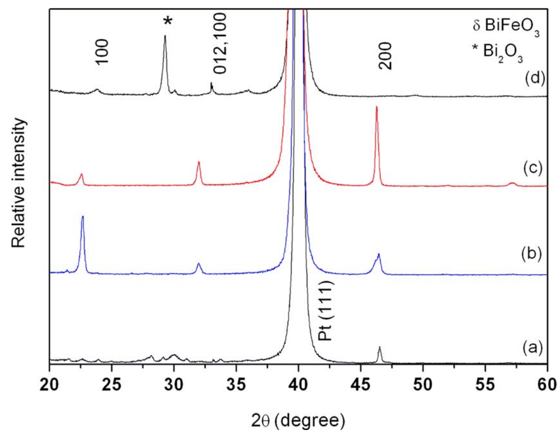

FIG. 1. (Color online) XRD data for BFO films deposited by the polymeric precursor method with different La contents: (a) $x=0.0$, (b) $x=0.08$, (c) $x=0.15$, and (d) $x=0.30$.

method. Structural and electrical properties of the films, mainly related to strain behavior, were investigated by using various techniques with a view to explore their technological applications.

II. EXPERIMENTAL PROCEDURE

Lanthanum modified bismuth ferrite thin films were prepared by the soft chemical method, as described elsewhere.[46] The films were spin coated on $Pt/Ti/SiO_2/Si$ substrates by a commercial spinner operating at 5000 rpm for 30 s (spin coater KW-4B, Chemat Technology). An excess of 5 wt % of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. The thin films were annealed at 500 °C for 2 h in the conventional furnace under static air atmosphere. The film thickness was reached by repeating ten times the spin coating and heating treatment cycles. The thickness of the annealed films was measured using scanning electron microscopy (Topcom SM-300) at the transversal section. We have obtained films with thickness in the range of 340–360 nm. In this case backscattering electrons were used. Phase analysis of the films was performed at room temperature by x-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and Cu $K\alpha$ radiation. Raman measurements were performed using an ISA T 64000 triple monochromator. An optical microscope with 80× objective was used to focus the 514.5 nm radiation from a Coherent Innova 99 Ar^+ laser on the sample. The same microscope was used to collect the backscattered radiation. The

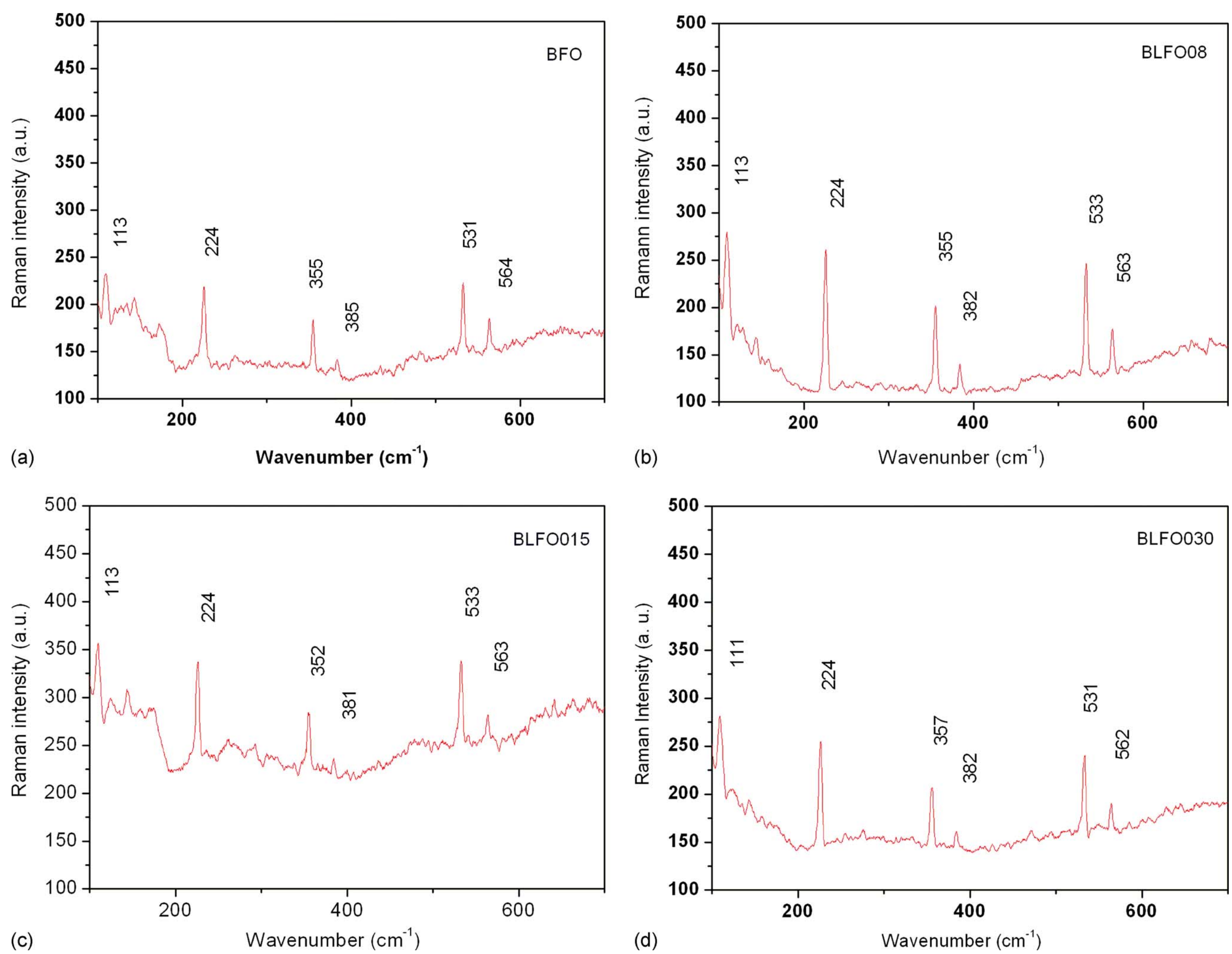

FIG. 2. (Color online) Micro-Raman spectra for BFO film deposited by the polymeric precursor method and annealed at 500 °C for 2 h, with different La contents: (a) $x=0.0$, (b) $x=0.08$, (c) $x=0.15$, and (d) $x=0.30$.

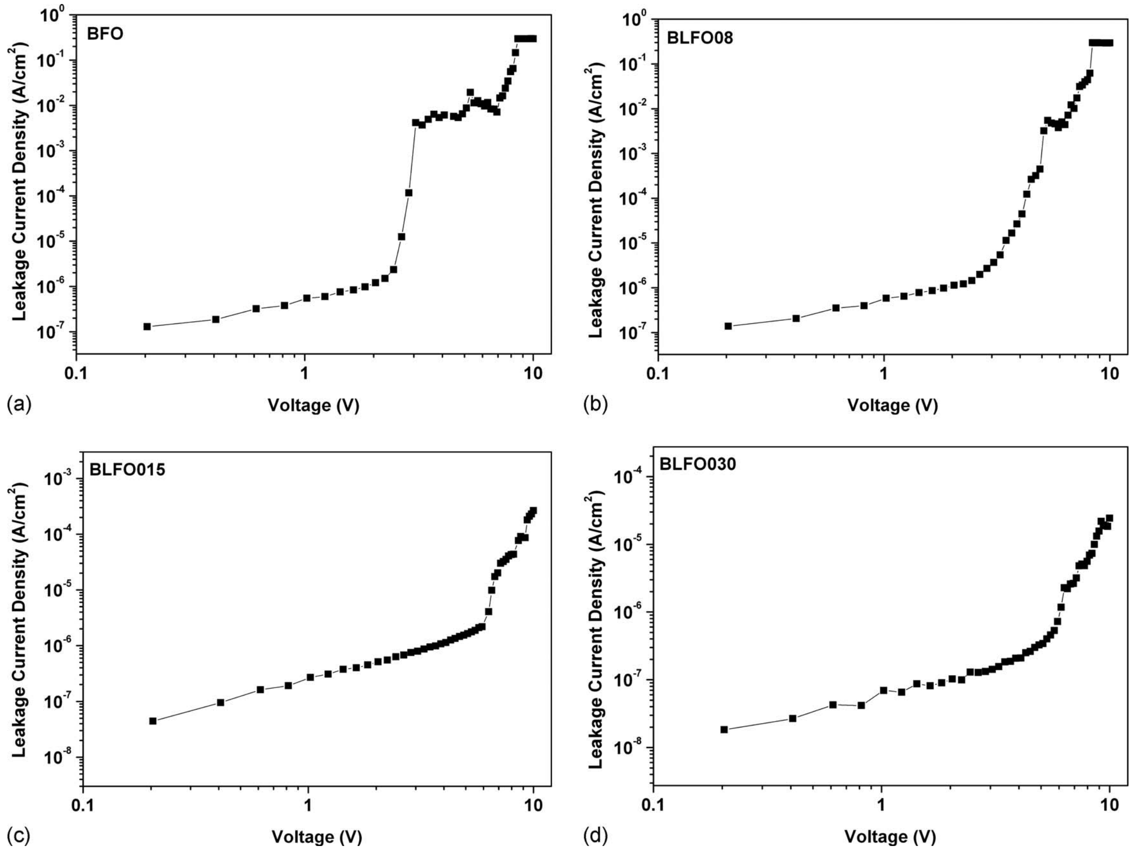

FIG. 3. Leakage current density vs applied electric field for BFO films deposited by the soft chemical method with different La contents: (a) $x=0.0$, (b) $x=0.08$, (c) $x=0.15$, and (d) $x=0.30$.

scattering light dispersed was detected by a charge-coupled device detection system =0.3 mm. The leakage current-voltage (I-V) characteristic was determined with a voltage source measuring unit (Radiant Technology 6000 A). Piezoelectric measurements were carried out using a setup based on an atomic force microscope in a multimode scanning probe microscope with Nanoscope IV controller (Veeco FPP-100). In our experiments, piezoresponse images of the films were acquired in ambient air by applying a small ac voltage with an amplitude of 2.5 V (peak to peak) and a frequency of 10 kHz while scanning the film surface. To apply the external voltage we used a standard gold coated Si_3N_4 cantilever with a spring constant of 0.09 N/m. The probing tip, with an apex radius of about 20 nm, was in mechanical contact with the uncoated film surface during the measurements. Cantilever vibration was detected using a conventional lock-in technique. Top Au electrodes (0.5 mm diameter) were prepared for the electrical measurements by evaporation through a shadow mask at room temperature. Retention characteristics of the films were measured by independently observing the time-dependent changes in P^* (switched polarization), and P^ (nonswitched polarization). For P^*, the capacitor was switched with a negative write pulse and read by a positive read pulse after retention time t. For P^, positive pulses were used for both writing and reading. The pulse width for all triangular pulses was 1.0 ms. The time delay between the right pulse and the first read pulse is referred to as retention time.

III. RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns of BFO and BLFO films deposited on platinum coated silicon substrates. The films were well crystallized at a processing temperature of 500 °C. The BFO film self-organized to produce (200)-preferred orientation, while the BLFO film crystallized with random orientation and better crystallinity. With partial substitution of isovalent La ions for A-site bismuth ions, the (100) diffraction peak of the BLFO film shifted toward a higher angle. Increasing lanthanum content leads to an additional peak at $2\theta=28°$ that could be assigned to the diffraction peak of Bi_2O_3, probably formed due to the substitution of lanthanum by bismuth in the crystal lattice.

An analysis of the evolution of Raman spectra in the lanthanum modified bismuth ferrite shows the order-disorder degree of the atomic structure at short range (Fig. 2). The modes further split into longitudinal and transverse components due the long electrostatic forces associated with lattice ionicity. Substitution of lanthanum in the A-site of the lattice reduces the distortion of octahedral clusters having little influence in the relative intensity of the bands. The vibrational modes located at 224, 355, 385, 531, and 564 cm^{-1} result from the FeO_6 octahedral (Fe=5 or Fe=6). The band located below 200 cm^{-1} is due to the different sites occupied by bismuth within the perovskite layer. Raman frequencies are not strongly affected by lanthanum substitution. Slight changes which occur above 200 cm^{-1} in the BFO can be associated with structural distortion and reduction in vibra-

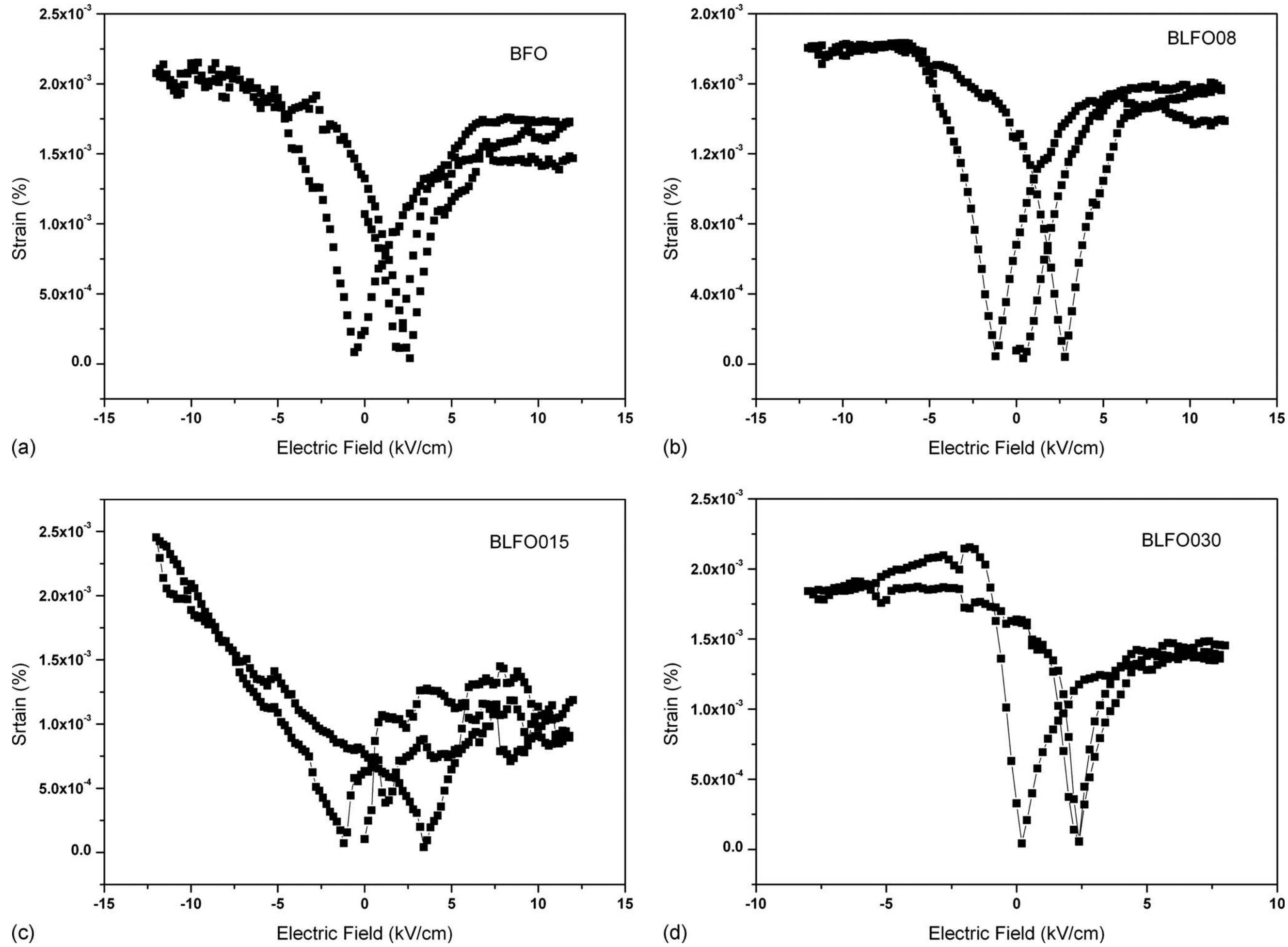

FIG. 4. Strain response for BFO films deposited by the soft chemical method with different La contents: (a) $x=0.0$, (b) $x=0.08$, (c) $x=0.15$, and (d) $x=0.30$.

tions in the FeO_5 octahedra. Lanthanum atoms substitute bismuth within the perovskite structure having marginal influence in the interactions between the $(Bi_2O_2)^{2+}$ layers and perovskite.

A typical leakage current characteristic for the films is given in Fig. 3. The curves were recorded with a voltage step width of 0.1 V and elapsed time of 1.0 s for each voltage, here the measured logorithmic current density $(\log J)$ versus the logorithmic electric field (E) is shown. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an Ohmic conduction. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanism. The leakage current density at 1.0 V decreases after substitution for lanthanum. The main reasons for such behavior can be attributed to changes in the surface roughness and reduction in microcracks due the modification in the lattice volume after lanthanum addition. In this way, lanthanum acts reducing the oxygen vacancies and as consequence improves the switching process of electrical dipoles. On the other hand, undoped BFO present defects as Bi or Ti vacancies resulting in an increase in conductivity. Therefore, this fact indicates the presence of mobile carriers which are positively charged and that the possibility of hopping through the Bi ion can be considered. The unipolar strain behavior at room temperature is shown in Fig. 4. The unipolar strain presents a maximum at 5 kV/cm while the saturation regime is reached at 10 kV/cm. Lanthanum decreases the strain behavior, in part, due to domain reorientation. Beyond that point, it is possible that a modest bias field results in the transition from asymmetric to symmetric phase. This field-induced phase transition may be ascribed to the pinching effect, that is, the consequent decrease in free energy difference among polymorphic phases. A careful inspection of the $S-E$ plots reveals that there are two apparent linear regions at low fields ($E<5$ kV/cm) and high fields ($E>10$ kV/cm) and one transition region, which corresponds to domain reorientation induced by external electric fields. The hysteretic strain could be associated with domain reorientation. The strain is hysteresis-free at electric fields higher than 5 kV/cm, indicating a stable single domain/poling state induced by the high external electric fields. In addition, from the S versus E profiles, no noticeable induced phase transition is observed at such high electric fields. It is shown that lanthanum reduces the unipolar strain when compared to BFO films, i.e., the strain was ($S=0.16\%$, 0.12%, and 0.11%) and ($S=0.17\%$) for lanthanum doped films and BFO, respectively. The decreasing of both strain response and strain en-

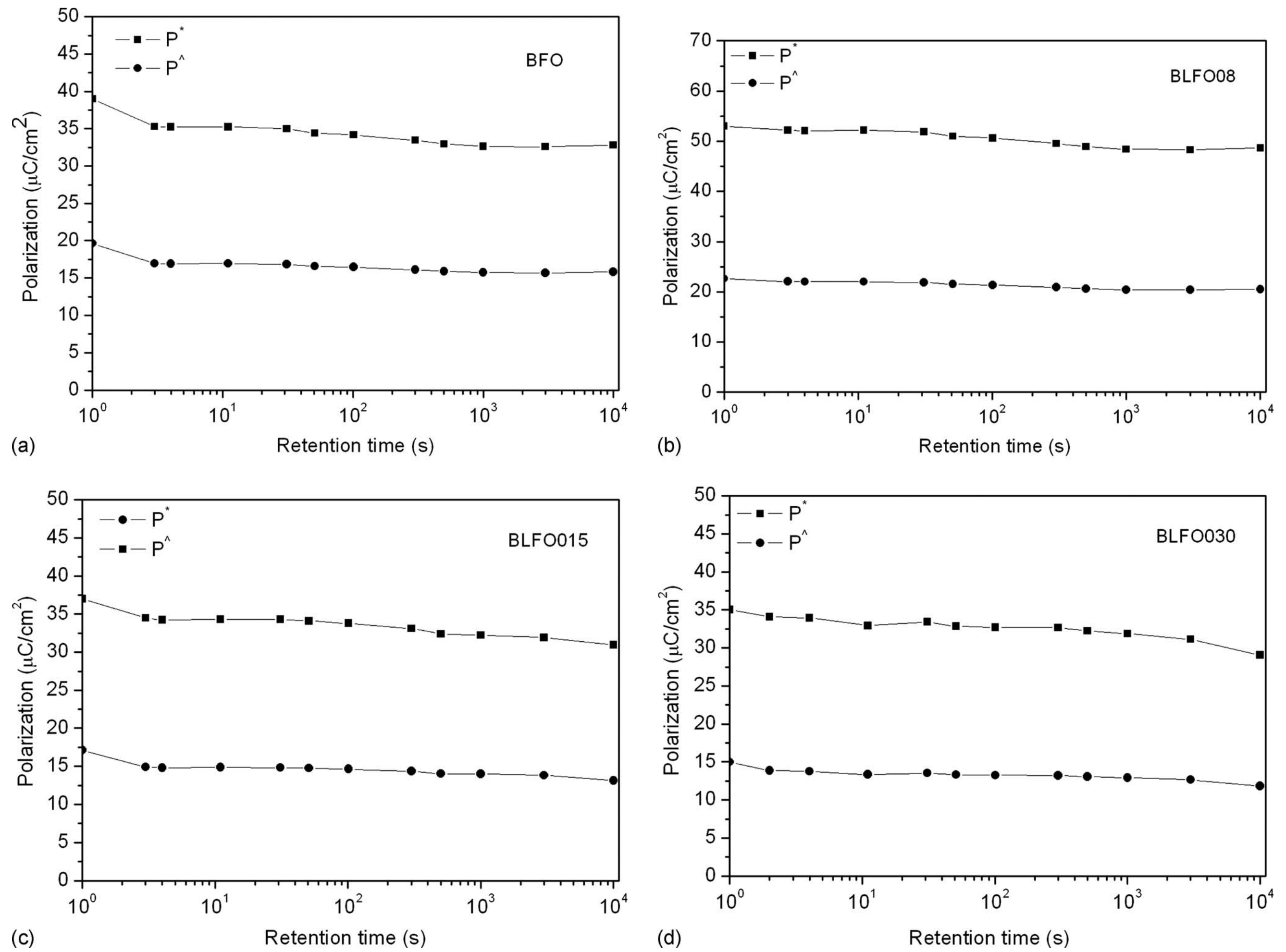

FIG. 5. Retention curve characteristics of BFO film deposited by the soft chemical method with different La contents: (a) $x=0.0$, (b) $x=0.08$, (c) $x=0.15$, and (d) $x=0.30$.

ergy after doping process can be associated with the reduced polarizability and the pinning effect. As can be seen, the small strain variations one each curve with electric field can be probably caused by clamping effect due to the stress created in the film-substrate interface and the existence of an ultrathin air gap between the tip and the sample which might lower the actual voltage drop in the film.

Figures 5(a)–5(d) show the retention characteristics of the films as a function of retention time from 1 to 1×10^4 s. The value of initial polarization decayed and approached a nearly steady-state value after a retention time of 10 s. The small decay of the retained charge in the films is a favorable indication for memory applications. After a retention time of 1×10^4 s, the polarization loss was only about 6% of the value measured at $t=1$ s for an applied electric field of 150 kV/cm. Depolarization fields generated by the redistribution of space charge, defects, and dipole charges could be the origin of the polarization decay after writing. For the infant period (within 10 s), depolarization fields could be the main contribution to polarization loss. The depolarization field increases with increasing the retained polarization and is time dependent. The long-time retention loss is attributed to the effect of redistribution of defect charges. This effect leads to a small decrease in the polarization by compensating the polarization charges when the redistribution of defect charges is driven by polarization.[36] The retention failure tests showed that the BLFO films have quite good long-time retention characteristics, retaining 94% of the values measured at $t=1\times10^4$ s for an applied electric field of 150 kV/cm. Polarization charge compensation by the redistribution of defect charges should be considered to explain this small retention loss in lanthanum doped bismuth ferrite thin films. The results of these studies are very promising and suggest that BLFO thin films are attractive for use as storage element in nonvolatile ferroelectric random access memories.

IV. CONCLUSIONS

Pure and lanthanum doped bismuth titanate thin films were fabricated on Pt substrate using the soft chemical method through annealing at 500 °C for 2 h. Raman modes are not strongly affected by lanthanum substitution. It was found that lanthanum reduces the strain behavior of BFO films. From leakage current density values we noted that La^{+3} substitution for Bi^{+3} is an effective way to reduce bismuth vacancies that are accompanied by oxygen vacancies decreasing the film conductivity. The results of these studies are very promising and suggest that BLFO thin films can be used as storage element in nonvolatile ferroelectric random access memories.

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[1]N. A. Spaldin and M. Fiebig, Science **309**, 391 (2005).
[2]W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London) **442**, 759 (2006).
[3]S. W. Cheong and N. Mostovoy, Nature Mater. **6**, 13 (2007).
[4]R. Ramesh and N. A. Spaldin, Nature Mater. **6**, 21 (2007).
[5]W. Eerenstein, M. Wiora, J. L. Prieto, J. F. Scott, and N. D. Mathur, Nature Mater. **6**, 348 (2007).
[6]M. Fiebig, J. Phys. D **38**, R123 (2005).
[7]G. Catalan, Appl. Phys. Lett. **88**, 102902 (2006).
[8]N. A. Hill, J. Phys. Chem. B **104**, 6694 (2000).
[9]A. H. M. Gonzalez, A. Z. Simões, L. S. Cavalcante, E. Longo, J. A. Varela, and C. S. Riccardi, Appl. Phys. Lett. **90**, 052906 (2007).
[10]A. M. dos Santos, S. Parashar, A. R. Raju, Y. S. Zhao, A. K. Cheetham, and C. N. R. Rao, Solid State Commun. **122**, 49 (2002).
[11]T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature (London) **426**, 55 (2003).
[12]N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S. W. Cheong, Nature (London) **429**, 392 (2004).
[13]H. Béa, M. Bibes, M. Sirena, G. Herranz, K. Bouzehouane, E. Jacquet, S. Fusil, P. Paruch, M. Dawber, J. P. Contour, and A. Barthelemy, Appl. Phys. Lett. **88**, 062502 (2006).
[14]M. Fiebig, Th. Lottermoser, D. Frhlich, A. V. Golsev, and R. V. Pisarev, Nature (London) **419**, 818 (2002).
[15]H. Schmid, Ferroelectrics **62**, 317 (1994).
[16]O. P. Vajk, M. Kenzelmann, J. W. Lynn, S. B. Kim, and S.-W. Cheong, Phys. Rev. Lett. **94**, 087601 (2005).
[17]B. B. Van Aken, T. T. M. Plastra, A. Filippetti, and N. A. Spaldin, Nature Mater. **3**, 164 (2004).
[18]J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Vieland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science **299**, 1719 (2003).
[19]M. Fiebig, M. T. Lottermoser, D. Fröhlich, A. V. Goltsev, and R. V. Pisarev, Nature (London) **419**, 818 (2002).
[20]J. R. Teague, R. Gerson, and W. J. James, Solid State Commun. **8**, 1073 (1970).
[21]G. A. Smolenskii and I. E. Chupis, Sov. Phys. Usp. **25**, 475 (1982).
[22]F. Kubel and H. Schmid, Acta Crystallogr. B **46**, 698 (1990).
[23]C. Michel, J. M. Moreau, G. D. Achenbach, R. Gerson, and W. J. James, Solid State Commun. **7**, 701 (1969).
[24]J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science **299**, 1719 (2003).
[25]V. V. Shvartsman, W. Kleemann, R. Haumont, and J. Kreisel, Appl. Phys. Lett. **90**, 172115 (2007).
[26]D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J. F. Marucco, and S. Fusil, Phys. Rev. B **76**, 024116 (2007).
[27]R. Seshadri and N. A. Hill, Chem. Mater. **13**, 2892 (2001).
[28]T. Shishidou, N. Mikamo, Y. Uratani, F. Ishii, and T. Oguchi, J. Phys.: Condens. Matter **16**, S5677 (2004).
[29]P. Fischer, M. Polomska, I. Sosnowska, and M. Szymanski, J. Phys. C **13**, 1931 (1980).
[30]S.-W. Cheong and M. Mostovoy, Nature Mater. **6**, 13 (2007).
[31]D. I. Khomskii, J. Magn. Magn. Mater. **306**, 1 (2006).
[32]A. Z. Simões, C. S. Riccardi, L. S. Cavalcante, E. Longo, J. A. Varela, B. Mizaikoff, and D. Hess, J. Appl. Phys. **101**, 084112 (2007).
[33]Y. P. Chen, Y. Y. Yao, Z. H. Bao, J. S. Zhu, and Y. N. Wang, Mater. Lett. **57**, 3623 (2003).
[34]Y. Kan, X. Jin, G. Zhang, P. Wang, Y.-B. Cheng, and D. Yan, J. Mater. Chem. **14**, 3566 (2004).
[35]D. Lee, M. G. Kim, S. Ryu, H. M. Jang, and S. G. Lee, Appl. Phys. Lett. **86**, 222903 (2005).
[36]C. Ederer and N. A. Spaldin, Phys. Rev. B **71**, 224103 (2005).
[37]Y. Zhong, G. Hu, and T. A. Tang, Jpn. J. Appl. Phys., Part 1 **42**, 7424 (2003).
[38]Y.-H. Lee, J.-M. Wu, and C.-H. Lai, Appl. Phys. Lett. **88**, 042903 (2006).
[39]Y. Wang and C.-W. Nan, J. Appl. Phys. **103**, 024103 (2008).
[40]D. Lee, M. G. Kim, S. R. Ryu, and H. M. Jang, Appl. Phys. Lett. **86**, 222903 (2005).
[41]V. R. Palkar, K. G. Kumara, and S. K. Malik, Appl. Phys. Lett. **84**, 2856 (2004).
[42]C. Wang, M. Takahashi, H. Fujino, X. Zhao, E. Kume, T. Horiuchi, and S. Sakai, J. Appl. Phys. **99**, 054104 (2006).
[43]Z. Chaodan, Z. Duanming, Y. Jun, Y. Bin, W. Yunyi, W. Longhai, W. Yunbo, and Z. Wenli, Integr. Ferroelectr. **94**, 23 (2007).
[44]Y. Li, T. Sritharan, S. Zhang, X. He, Y. Liu, and T. Chen, Appl. Phys. Lett. **92**, 132908 (2008).
[45]A. Z. Simoes, A. H. M. Gonzalez, C. S. Riccardi, E. C. Souza, F. Moura, M. A. Zaghete, E. Longo, and J. A. Verela, J. Electroceram. **13**, 65 (2004).
[46]A. Z. Simões, B. D. Stojanovic, M. A. Zaghete, C. S. Riccardi, A. Ries, F. Moura, E. Longo, and J. A. Varela, Integr. Ferroelectr. **60**, 21 (2004).
[47]A. Z. Simoes, C. S. Riccardi, L. S. Cavalcante, J. A. Varela, and E. Longo, Mater. Res. Bull. **43**, 158 (2008).
[48]A. Z. Simões, L. S. Cavalcante, C. S. Riccardi, J. A. Varela, and E. Longo, J. Sol-Gel Sci. Technol. **44**, 269 (2007).