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Preparation of La-doped BiFeO₃ thin films with Fe²⁺ ions on Si substrates

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La-doped BiFeO₃ thin films with Fe²⁺ ions have been prepared on Pt/TiO₂/SiO₂/Si substrates by pulsed laser deposition in order to enhance the ferroelectric and magnetic properties. The targets for the film deposition were synthesized using a rapid liquid phase sintering technique to ensure the low leakage. The dielectric properties at room temperature and above were investigated. It was observed that the La doping greatly enhances the ferroelectric polarization at room temperature by modifying the film structure from rhombohedral to monoclinic. The saturation magnetization was enhanced about two times due to the Fe²⁺ ions in the thin films. © 2006 American Institute of Physics. [DOI: 10.1063/1.2195368]

I. INTRODUCTION

Ferroelectromagnets are the class of materials exhibiting coexistence of magnetic and ferroelectric orderings in a certain range of temperature.¹ These materials, therefore, not only can be used in magnetic and ferroelectric devices but also have the potential ability to couple the electric and magnetic polarizations, providing an additional degree of freedom in device design and applications. Consequently, ferroelectromagnetism becomes the subject of intensive investigations because ferroelectromagnetic materials potentially offer a whole range of applications, including the emerging field of spintronics, data-storage media,² and multiple-state memories.³

However, there are very few materials exhibiting both ferromagnetic and ferroelectric properties at room temperature (RT). Among the materials studied so far, BiFeO₃ (BFO) is known to be one of several compounds that exhibit ferroelectromagnetism at RT. BFO was reported to show *G*-type antiferromagnetic ordering with relatively high Néel temperature^{4,5} T_N (~ 310 °C)^{4,5} and ferroelectric ordering with high Curie temperature T_C (~ 850 °C).^{6,7} Powder x-ray diffraction (XRD) and neutron diffraction studies revealed that BFO has a rhombohedrally distorted perovskite structure.^{8,9} However, several serious drawbacks of BFO associated with its electrical properties, such as high leakage current,¹⁰ small ferroelectric spontaneous polarization,¹¹ and weak magnetization,¹² hinder its potential applications in the near future.

In recent years, many attempts have been made to overcome the above drawbacks. In addition to intensive efforts in terms of improving the materials preparation and property optimization, a rapid liquid phase sintering technique was developed in our laboratory to enhance the electric resistivity.¹⁰ The saturated ferroelectric hysteresis loop of te-

tragonal BFO thin films with desirable polarization value was reported by controlling the oxygen pressure in the deposition process of BFO thin films.¹³ Lee *et al.* improved the magnetic properties of BFO-based films on SrTiO₃ substrates by partial substitution of Bi by La, on the basis that La doping brings the spatial homogenization of spin arrangement.¹⁴ Wang *et al.* reported the enhanced ferroelectric polarization and magnetization in heteroepitaxially constrained BFO thin films with tetragonal-like structure on SrTiO₃ substrates.¹⁵ And in a succeeding report, Wang *et al.* ascribed the great enhancement of polarization to the epitaxially induced change in structure and the magnetization to the presence of Fe²⁺ ions in the films, both of which were thickness dependent.¹⁶ However, a recent report¹⁷ showed that the increase in the ferromagnetism as a result of Fe²⁺ in BFO is not as significant as that claimed by Wang *et al.*

In the present work, we report our experimental effort of preparation of BFO-based thin films with enhanced ferroelectric polarization and magnetization on Pt/TiO₂/SiO₂/Si substrates, which is essential to semiconductor industry applications. In order to improve the ferroelectric properties we partially substitute Bi by La to change the structure of BFO thin films, and we also introduce Fe²⁺ ions into the films to enhance the magnetization,¹⁵⁻¹⁷ which is different from the motivation of Lee *et al.*¹⁴ However, unlike the thin films prepared by Wang *et al.*, our samples on Si substrates are essentially free of compressive epitaxial strain because the as-prepared thin films are polycrystalline. In addition, we study the dielectric properties of BFO and La-modified BFO thin films.

II. EXPERIMENTS

The Bi-rich targets of Bi_{1.1}FeO₃ and Bi_{0.88}La_{0.2}FeO₃ were synthesized by the rapid liquid phase sintering technique.¹⁰ The films with a thickness of about 250 nm on commercial Pt/TiO₂/SiO₂/Si substrates were deposited by pulsed laser deposition (PLD) with a KrF excimer laser

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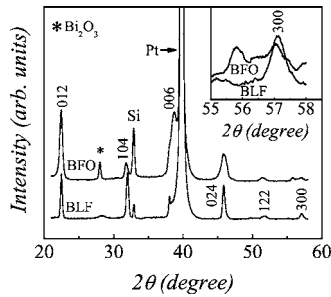


FIG. 1. XRD patterns of BiFeO_3 and $\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3$ thin films prepared on Pt/TiO₂/SiO₂/Si substrates. The inset magnifies the difference between the two sets of patterns, indicating that BLF is monoclinic while BFO is rhombohedral.

(248 nm, $\sim 3\text{J}/\text{cm}^2$, 6 Hz). The deposition was carried out in oxygen atmosphere of 10 Pa for 20 min while the deposition temperature was fixed at 550 °C. After the deposition, the as-deposited thin films were cooled normally to 400 °C in 40 kPa oxygen, annealed for 10 min, and then cooled to RT normally. These deposition parameters represent the optimized values in our experiments.

The crystalline phases of BiFeO_3 (BFO) and $\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3$ (BLF) thin films were checked using x-ray diffraction (XRD) technique. Taking into account the significant effect of the oxidation state on the magnetic ordering behavior of the films, we employed x-ray photoelectron spectroscopy (XPS) to identify the valences of Fe ions in our film samples. It is noted that XPS is a surface sensitive technique with the penetration depth of only a few nanometers. Therefore, in order to exclude the possible difference between the topmost surface and inside bulk of the film, the XPS probing was performed after an ~ 20 nm thick top layer of the film was removed away by Ar⁺ ion beam, so that the result was representative of the bulk film. Furthermore, the binding energy (BE) data in the XPS spectrum were carefully calibrated referring to the C 1s peak after setting its BE to 284.6 eV. In order to identify precisely the locations of Fe²⁺ and Fe³⁺ ions in the XPS data, we measured the XPS spectrum of commercial Fe₃O₄ powders as reference to our data analysis.

For characterization of the electrical and magnetic properties, circular Pt electrodes were formed on the film surface by sputtering through a shadow mask with diameter of 0.2 mm. The dielectric and ferroelectric properties were measured in the Pt/film/Pt/Si structure. The leakage current was examined by an HP 4140B, while the dielectric constant and loss as a function of temperature were evaluated using an HP 4294A impedance/phase analyzer with an effective test signal voltage of 50 mV. The RT ferroelectric hysteresis and magnetic hysteresis of the films were measured by the RT66 tester (in a virtual ground mode) and the superconducting quantum interference device (SQUID) magnetometer, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for the prepared BFO and BLF thin films, and the inserted is the locally amplified patterns over $2\theta=55^\circ-58^\circ$. It is revealed that both films

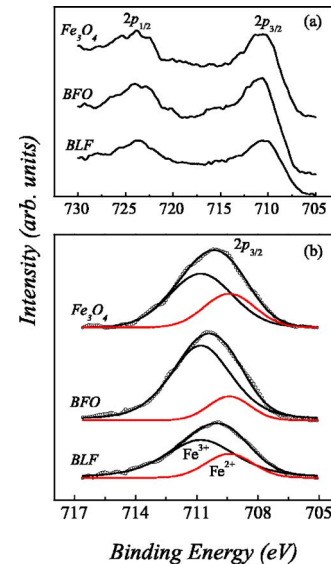


FIG. 2. (Color online) (a) XPS results of the Fe 2p lines for BFO and BLF thin films and together with Fe₃O₄ for comparison. (b) The Gaussian dividing of the Fe 2p_{3/2} core levels for all the samples, indicating that our films consist of both Fe²⁺ and Fe³⁺.

exhibit single-phase perovskite structure, while no nonperovskite phase such as Bi₂Fe₄O₉ is observed. However, an additional phase appearing at $2\theta\sim 28^\circ$ could be assigned to the diffraction peak of Bi₂O₃, probably formed due to the Bi excess in the targets. The effect of La doping on the structure variation of BFO-based thin films can be assessed by examining (*h*00)-type diffraction peaks. As shown in the inset of Fig. 1, the weak peak at $2\theta=55.8^\circ$ identified in BFO does not appear in BLF. This difference implies a structural transition from rhombohedral for BFO to monoclinic for BLF and this structure transition was demonstrated to be essential for the ferroelectric polarization enhancement.¹⁸

We check carefully the cationic state of Fe ions in the as-prepared BFO and BLF films using XPS technique. As well known, due to the spin-orbit coupling, the Fe 2p core level is split into the 2p_{1/2} and 2p_{3/2} components. For Fe²⁺ iron, the 2p_{3/2} core level appears at 709.4 eV while for Fe³⁺ ion it appears at 710.8 eV.^{19,20} Therefore, we give our attention to the Fe 2p_{3/2} core levels in the films.²¹ Figure 2(a) shows the probed XPS spectra covering 705–730 eV of the two films as well as Fe₃O₄ powders for comparison. Referring to the spectrum of Fe₃O₄, an asymmetric broad band at ~ 710.0 eV was identified for both BFO and BLF films, which represents that both films contain Fe²⁺ and Fe³⁺ ions.²² A more detailed analysis of the data can be performed following the Shirley background subtraction.²³ For each of the three spectra (Fe₃O₄, BFO, and BLF), we partition the Fe 2p_{3/2} band into two subbands centered at 709.4 and 710.8 eV, respectively, using the standard Gaussian fitting method. The decoupled two subbands for all the three samples are shown in Fig. 2(b), corresponding to the 2p_{3/2} core levels of Fe²⁺ ion and Fe³⁺ ion, respectively. The fitting seems to be satisfying within the measurement uncertainties. According to the fitting results, the atomic ratio of Fe²⁺ ions and Fe³⁺ ions in Fe₃O₄ is $\sim 36/64$, matching well with the fact.

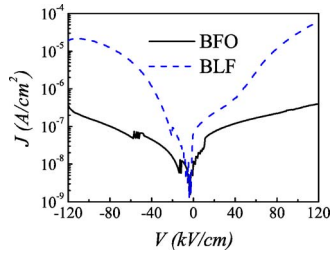


FIG. 3. (Color online) Leakage current J -applied electric field V characteristics of BFO and BLF thin films about 250 nm thick.

The present XPS analysis indeed demonstrates the existence of Fe^{2+} ions in addition to Fe^{3+} ions, in both BFO and BLF films. The most likely origin of Fe^{2+} ions in the films is the presence of oxygen vacancies, which are common in perovskite oxides.¹⁶ In addition, we can find that for BFO the Fe^{2+} ions are about 15% of the entire Fe component while for BLF the Fe^{2+} ions occupy about 27%, according to an evaluation of the peak area. This indicates more Fe^{2+} ions involved in BLF, which may be one of the reasons for enhanced ferroelectric property in BLF than in BFO, to be shown below.

The measured leakage current J against applied voltage V for BFO and BLF thin films, respectively, is shown in Fig. 3. Compared to the BFO films, the leakage of BLF films is relatively larger. In particular, under high applied field, the leakage of BLF thin films is almost two orders of magnitude higher than that of BFO. This difference is considered to originate from more Fe^{2+} ions in BLF than in BFO, as revealed in the previous XPS results. However, even so the leakage of BLF thin films with more Fe^{2+} ions is still one order of magnitude smaller than the data for BFO thin films as prepared by Yun *et al.*²⁴ We attribute this result to the technique we used for preparing our targets, which excludes formation of nonperovskite phase.

Figure 4(a) shows the dielectric constant ϵ and loss $\tan \delta$ of both BFO and BLF thin films as a function of measuring frequency ($f=10^4$ – 10^6 Hz) at RT. It is clear that La doping

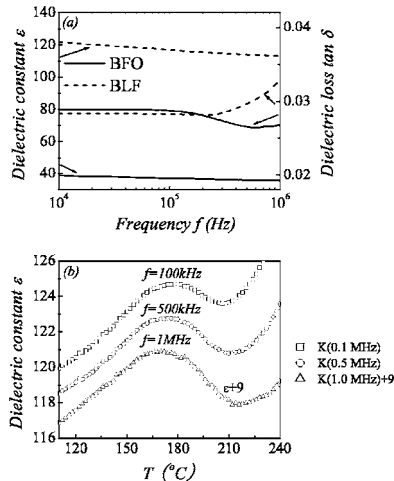


FIG. 4. (a) Frequency dependence of dielectric constant and dielectric loss for the BFO and BLF thin films. (b) The dielectric response with temperature measured for the BLF thin film at 0.1, 0.5, and 1 MHz.

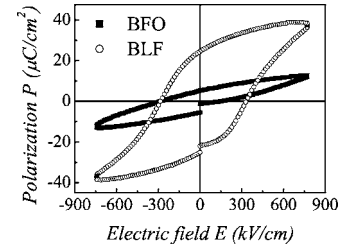


FIG. 5. Ferroelectric hysteresis loops for BFO and BLF thin films at room temperature. The film thickness is 250 nm.

enhances significantly the value of ϵ of BFO thin films as much as about three times but has little influence on loss $\tan \delta$. It is also observed that the temperature dependence of the dielectric properties over the entire frequency range remains similar for both films. Since the films have low loss $\tan \delta$ ($\tan \delta$ in the range of 0.026–0.033), it is possible to conduct the dielectric response study with varying temperature, and the results are shown in Fig. 4(b). A dielectric anomaly has been observed in BLF thin films at the three frequencies ($f=0.1, 0.5,$ and 1.0 MHz). This type of dielectric anomaly in simultaneous ferroelectrically and ferromagnetically ordered systems was predicted by the Landau-Devonshire theory of phase transition as an influence of varying magnetic order on the electric order²⁵ and a similar result was reported by Palkar *et al.* in their $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$ ceramic system.²⁶ We can also see that the anomalous temperature decreases with increasing frequency. In addition, such an anomaly of this kind was not found in BFO thin films for the reason that for BFO the anomalous temperature was reported above 300°C ,²⁷ at which the dielectric loss was high for our films.

The ferroelectric hysteresis for both BFO and BLF thin films at RT was measured and the data are shown in Fig. 5. Under the same applied electric field, the remnant polarization for pure BFO is small ($2P_r=10.7 \mu\text{C}/\text{cm}^2$) while that for La-doped BFO thin films is more than four times larger ($2P_r=49.6 \mu\text{C}/\text{cm}^2$). Such a result is due to the structure modification from rhombohedral to monoclinic induced by La doping, as analyzed from XRD patterns. Besides, both the coercive fields ($2E_c=440$ kV/cm for BFO and 610 kV/cm for BLF) and the applied electric fields that our films can endure (900 kV/cm) are high, which is consistent with the high resistivity.

The magnetization versus applied magnetic field at RT for both BFO and BLF films is shown in Fig. 6. Our BFO thin film with Fe^{2+} shows a saturated weak ferromagnetic

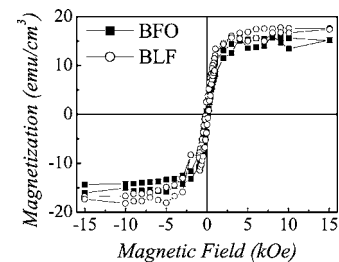


FIG. 6. Magnetic hysteresis loops obtained at RT on BFO and BLF thin films grown on Pt/TiO₂/SiO₂/Si substrates by PLD.

response and the saturation magnetization is about 15 emu/cm^3 , about twice of that without Fe^{2+} ,²⁸ consistent with the report of Li and MacManus-Driscoll.¹⁷ With the presence of Fe^{2+} in the thin films, the extra observed moment may originate from either Fe^{2+} or oxygen vacancies. One possibility is a ferromagnetic arrangement in which the moments of the Fe^{2+} ions are aligned oppositely to those of the Fe^{3+} ions, leading to a net magnetic moment. However, Wang *et al.* argued that such an arrangement was unlikely.¹⁶ On the other hand, Ederer and Spaldin calculated the influence of oxygen vacancies on the magnetic properties using the LSDA+U method²⁹ and their result is consistent with our experimental observation. From this figure, we can also see that the saturation magnetization of the BLF thin film is a little larger than that of BFO. We suggest that such difference comes not only from the spatial homogenization of spin arrangement induced by La doping^{14,30} but also from the different oxygen vacancy contents caused by different Fe^{2+} contents.

IV. CONCLUSION

In conclusion, BFO and La-doped BFO (BLF) thin films with Fe^{2+} ions have been prepared on Pt/ TiO_2 / SiO_2 /Si substrates by PLD technique. It has been revealed that the as-prepared thin films are highly resistive electrically due to the rapid liquid phase sintering technique used for preparing the targets. The BLF films show an enhancement of the dielectric constant at RT and a dielectric anomaly with varying temperature. The La doping has helped to improve the ferroelectric properties by the structure transition and the Fe^{2+} ions have helped to increase the magnetic properties because of the oxygen vacancies related to Fe^{2+} .

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