Ferroelectric properties and leakage current characteristics of Bi 3.25 La 0.75 Ti 3 O 12 thin films prepared by the polymeric precursor method

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Ferroelectric properties and leakage current characteristics of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films prepared by the polymeric precursor method

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The ferroelectric properties and leakage current mechanisms of preferred oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films deposited on $La_{0.5}Sr_{0.5}CoO_3$ by the polymeric precursor method were investigated. These films showed excellent ferroelectric properties in terms of large remnant polarization $(2P_r)$ of 47.6 $\mu C/cm^2$ and $(2E_c)$ of 55 kV/cm, fatigue-free characteristics up to 10^{10} switching cycles, and a current density of 0.7 $\mu A/cm^2$ at 10 kV/cm. X-ray diffraction and scanning electron microscope investigations indicate that the deposited films exhibit a dense, well-crystallized microstructure having random orientations and with a rather smooth surface morphology. The improved ferroelectric and leakage current characteristics can be ascribed to the platelike grains of the BLT films, which make the domain walls easier to be switched under external field. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2133902]

I. INTRODUCTION

Ferroelectric thin films have attracted much attention due to potential applications in nonvolatile ferroelectric random access memories (FeRAMs).[1,2] In the FeRAM cells, the two remanent polarization P_r states of ferroelectric thin film capacitors can be used to store binary "0" and "1." The stored information can be maintained without any external energy supply, making these memories nonvolatile. When a read pulse is applied, the sense amplifier compares the switched charges with a reference to determine the stored polarization state and to distinguish 0 or 1. With their nonvolatile nature, FeRAMs also have the advantages of lower power consumption, radiation hardness, overall robustness, and high access speed.[3] Many materials have been studied as candidates for FeRAMs applications. Among them, $PbZr_xTi_{1-x}O_3$ (PZT) thin films with various compositions are the most promising and the most intensively investigated. Although PZT has advantages of large P_r values (typically 20–70 $\mu C/cm^2$), depending on compositions and low processing temperature, PZT thin films suffer severe fatigue after repetitive read/write cycles when sandwiched between Pt metal electrodes. Additionally, Pb evaporation leads to environmental safety issues and health concerns. Recently, $Bi_4Ti_3O_{12}$ (BIT) is an Aurivillius-phase Bi-layered oxide, and can be denoted by the formula $(Bi_2O_2)^{2+}(Bi_2Ti_3O_{10})^{2+}$, in which perovskite units of Ti-O octahedra are sandwiched between Bi_2O_2 layers. Bulk undoped BTO shows a very high $2P_r$ (about 100 $\mu C/cm^2$),[4] but thin films have much lower values of switching polarization and suffer from fatigue upon bipolar switching.[5] It was proposed that doping with La led to improved oxygen ion stability in the lattice, and hence improved fatigue resistance because some of the Bi ions in the pseudoperovskite layers containing Ti-O octahedra were substituted by La ions. Substitution of the nonspherical Bi^{3+} cation with La^{3+}, however, reduces the structural distortion of the perovskite block, thereby reducing P_r.

Among several methods used to deposit thin films, solution deposition is a process that improves the stoichiometric control of complex mixed oxides and is compatible with many semiconductor manufacturing technologies. In previous works, our group has reported the preparation of thin films by the polymeric precursor method.[6] The overall process consists of preparing a coating solution based on metallic citrate polymerization. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase. The polymeric precursor method presents many advantages, such as the possibility to work in aqueous solutions with high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method (inexpensive precursors and equipment). To obtain good crystallized films, heat treatment at high temperatures for a long time is necessary, normally 2 h. These long heat treatments can cause multiple damage to the stack, leading to interdiffusion between the film and the substrate, and sometimes loss of stoichiometry (due to volatile element). So, it is important to decrease the temperature and time of the thermal treatment. Microwave energy is being developed as a new tool for high-temperature processing of materials. This technology has received great attention due to the advantages observed with microwave processing, which include: reduced processing costs, better production quality, new materials and product, among others. With proper understanding and control, many technically important materials can be heated rapidly, uniformly, selectively, less expansively, and with greater control than is possible with conventional methods.[7] In this work, microwave energy to promote a rapid thermal way for the crystallization of the film was investigated with the advantage of reducing the time and, in some cases, the temperature of the thermal treatment. The purpose of this study is to use LSCO as the oxide bottom electrode, and at the same time to provide a template to grow better quality BLT films with preferred orientation. Our results demonstrate promising properties better than reported data films. We have also examined the ferroelectic, dielectric, and leakage current characteristics of BLT films with definite conclusion and quality for the application in FeRAMS.

II. EXPERIMENTAL PROCEDURE

The LSCO and BLT thin films were prepared via the polymeric precursor method, as described elsewhere.[6] The bottom electrode thin films were spin coated on (100) Si/SiO_2 substrates by a commercial spinner operating at 5000 revolutions/min for 30 s (spin coater KW-4B, Chemat Technology). Each annealing layer was prefired at 400 °C for 2 h in a conventional oven. After the prefiring, each layer was crystallized in a microwave oven at 700 °C for 10 min. Using the same procedure, the BLT thin films were deposited by spinning the precursor solution on the desired substrates. Through this process, we have obtained thickness values of about 150 nm for the bottom electrodes and around 300 nm for BLT, reached by repeating the spin-coating and heating treatment cycles. The microwave oven used was a simple domestic model similar to that described in the literature.[7] The crystallization was performed placing the SiC susceptor below the substrate. After crystallization, the films were characterized by x-ray diffraction (Rigaku, 20-2000), 40 kV and 150 mA from 2θ (10°–50°) following the phase evolution. The thickness of the annealed films was determined by using scanning electron microscopy (Topcom SM-300) at the transversal section. In this case backscattering electrons were used. Atomic force microscopy (AFM, Digital, Nanoscope 3A) was used to analyze the surface topography and roughness. A 0.5 mm diameter top Au electrode for the electrical measurements was prepared by evaporation through a shadow mask at room temperature. The electric properties were measured by a $Au/BLT/LSCO/SiO_2/Si$ (100) capacitor structure. The relative dielectric constant ε_r was measured versus frequency using an impedance analyzer (model 4192 A, Hewlett-Packard). The leakage current-voltage (I-V) characteristic was determined with a voltage source measuring unit (Radiant Technology 6000 A). The capacitance-voltage characteristic was measured in the MFM configuration using a small ac signal of 10 mV at 100 kHz. The ac signal was applied across the sample, while the dc was swept from positive to negative bias. Ferroelectricity was investigated using a Sawyer-Tower circuit attached to a computer-controlled standardized ferroelectric test system (Radiant Technology 6000 A). For the fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses were used with a 10 V amplitude.

III. RESULTS AND DISCUSSION

The x-ray diffraction (XRD) pattern of BLT thin films annealed at 700 °C for 10 min is shown in Fig. 1. It was observed that the film was fully crystallized and exhibited polycrystalline nature with the growth of (117) predominant. XRD analyses indicated no evidence of secondary phase formation. This demonstrates that, with the substitution of Bi ions by La ions up to 0.75, the single-phase layered perovskite was preserved.

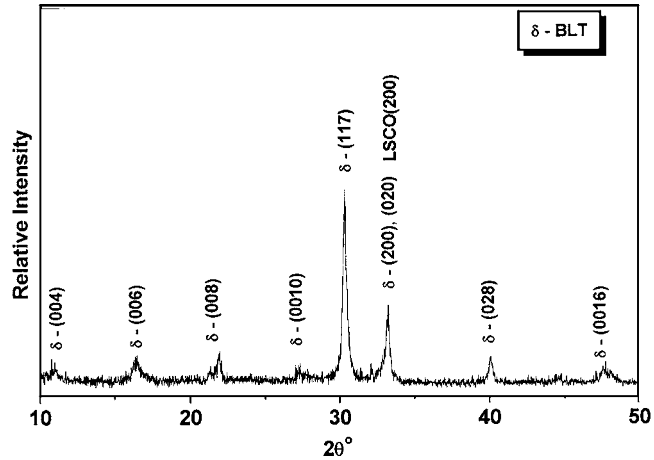

FIG. 1. X-ray diffraction for BLT film deposited on LSCO bottom electrode and annealed in microwave oven.

Figure 2 shows a typical surface morphology of BLT films deposited on LSCO electrodes. It can be observed that the grown film was dense and homogeneous, indicating that the microwave furnace allows the preparation of films with controlled morphology. BLT consisted of well-developed platelike grains with considerable volume fractions of micrograins; the grain size is close to 65 nm. The root-mean-square (rms) roughness of the film annealed at 700 °C for 10 min is about 7.5 nm. The observed platelike morphology of the grains may be related to the stress created due to the film annealing and the difference in the thermal expansion coefficient which changes the growth of the films.

The ferroelectric nature of the BLT thin film was confirmed by the polarization hysteresis loop, which is displayed in Fig. 3. The ferroelectric hysteresis loops of typical BLT films were measured at an applied electric field of 300 kV/cm, exhibited a remnant polarization ($2P_r$) of 47.6 $\mu C/cm^2$, and a coercive field ($2E_c$) of about 55 kV/cm. The improved polarization in BLT film is attributed to the platelike grains of the BLT films. The domain walls in plate-

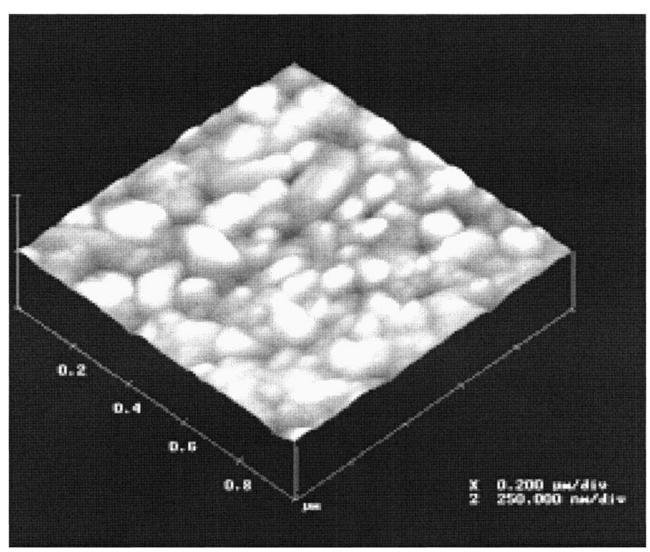

FIG. 2. AFM images for BLT film deposited on LSCO bottom electrode and annealed in microwave oven.

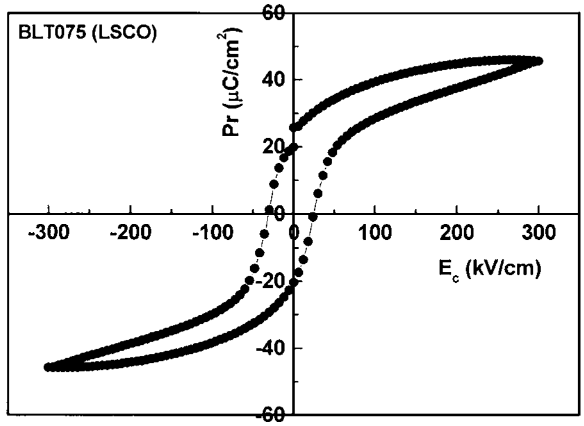

FIG. 3. *P-E* hysteresis loops for BLT film deposited on LSCO bottom electrode and annealed in microwave oven.

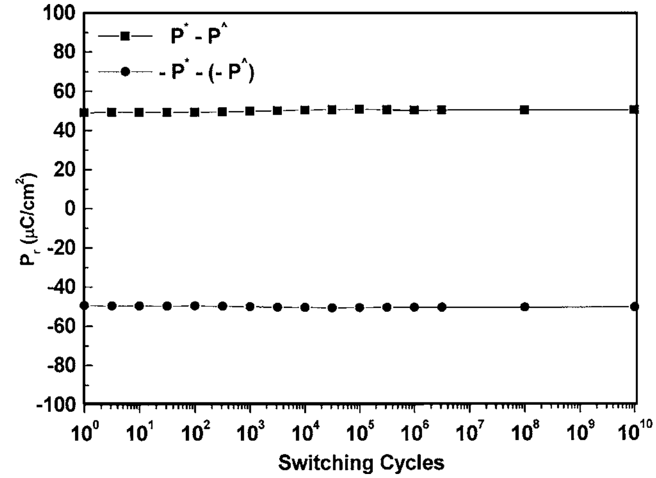

FIG. 5. Fatigue as a function of polarization cycles for BLT film deposited on LSCO bottom electrode and annealed in microwave oven.

like grains are easier to be switched under external field. Similar phenomena have been found in SBT and PT thin films.[8,9] Therefore, the growth of the film in one direction not coincident to *c*-axis preferred orientation will favor the plate-like morphology, such as that grown on LSCO oxide electrode leading to a lower E_c and a higher remnant polarization. The contribution of the La substitution to the large remanent polarization of the polycrystalline BLT films is not to enhance the intrinsic polarization but to bring out the polarization easily. It is considered that the pinned domain motion of the BIT is relaxed by La substitution and a saturated hysteresis is observed.[10]

The hysteresis behavior was also reflected in the*C-V* characteristics of the BLT films, which are shown in Fig. 4. At 100 kHz, the applied voltage was swept from a positive bias to a negative bias and back again. Two peaks are clearly seen in this figure. The BLT film capacitance changes from to with applied voltage bias. The presence of two peaks is attributed to the ferroelectric domains switching. The curve for the film deposited on LSCO electrode is symmetric around the zero bias axis, indicating that the films contain few movable ions or charge accumulation at the film-electrode interface. The narrowing of the *C-V* curves indicates that the process to switch the domains is faster in these electrodes, and the saturation occurs with low energy for the ferroelectric domain alignment.

Figure 5 shows the fatigue behavior of BLT films annealed at 700 °C for 10 min. The fatigue endurance was tested with 1 MHz bipolar pulses at 10 V. The BLT film demonstrated no fall of remnant polarization and exhibited no fatigue after 10^{10} switching cycles, respectively. The fatigue behavior in perovskite thin films is generally explained on the basis of oxygen vacancy and electron/hole injection mechanisms.[11] Oxygen vacancies can be generated during annealing of BLT films, which can be charge compensated by the higher oxygen affinity of the bottom electrode. It can be assumed that if oxygen vacancy accumulation near the film-electrode interface occurs during heat treatment, the conductive oxide LSCO can consume the oxygen vacancies by changing their oxygen nonstoichiometry; thus, the accumulation of oxygen vacancies near the interface is prevented or reduced. Therefore, the fatigue behavior can be minimized.

Figure 6 shows the dielectric constant and dissipation factor as a function of frequency ranging from 10 kHz to 1 MHz at room temperature for the BLT film annealed at

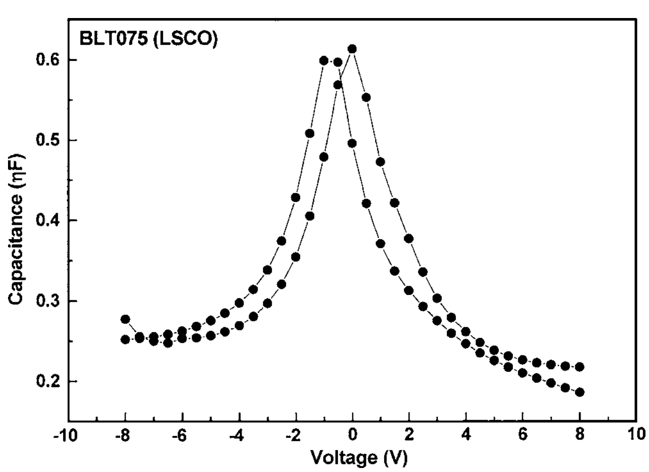

FIG. 4. *C-V* curves for BLT film deposited on LSCO bottom electrode and annealed in microwave oven.

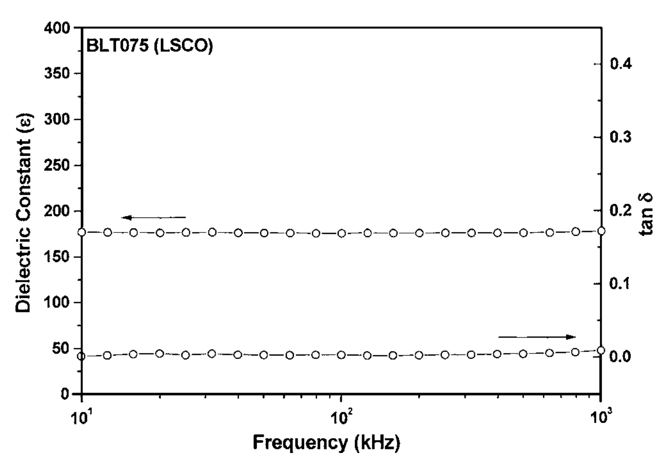

FIG. 6. Dielectric properties in dependence of frequency for BLT film deposited on LSCO bottom electrode and annealed in microwave oven.

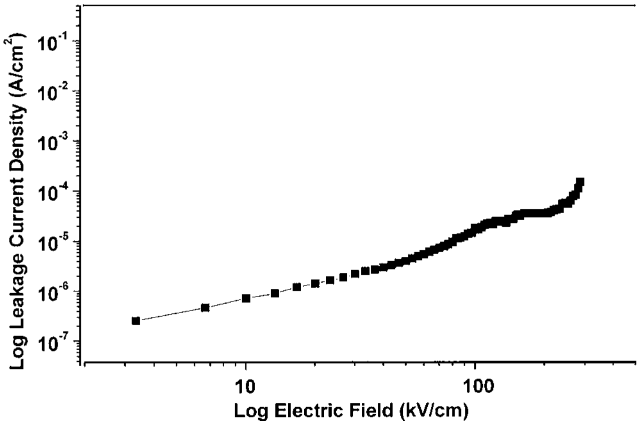

FIG. 7. Log J vs log E characteristics for BLT film deposited on LSCO bottom electrode and annealed in microwave oven.

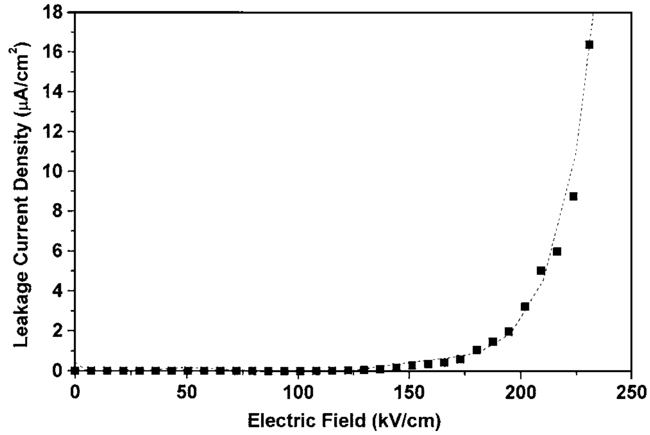

FIG. 8. log J vs E plot for BLT film deposited on LSCO bottom electrode and annealed in microwave oven showing a space-charge-limited mechanism.

700 °C for 10 min. The dielectric constant and loss tangent shows no dispersion with frequency, indicating that our films possess low defect concentration at the interface film-substrate. The low dispersion of the dielectric constant and the absence of any relaxation peak in tan δ indicate that interfacial polarization of the Maxwell-Wagner type and that produced by the electrode barrier is negligible in the film. The annealed films exhibited good dielectric properties, a dielectric constant, ε, of 177 and loss tangent, tan δ, of 0.012, at 1 MHz.

One of the most important features for a material to be used as an alternative FeRAMS is the low leakage current density. Figure 7 shows the *I-V* characteristics of the BLT film annealed at 700 °C for 10 min. It is well known that BIT thin films prepared from stoichiometry composition suffer from high leakage current due to defects such as Bi vacancies accompanied by oxygen vacancies. To improve the leakage current properties in this experiment, the addition of lanthanum was verified. The low leakage current density observed for the films deposited on LSCO may be attributed to high oxygen affinity of this material, avoiding the fact that oxygen in the electrode material will be depleted by the ferroelectric material, thus leaving an oxygen-deficient layer of the electrode at the interface and increasing the contact resistance. Another reason is that the La substitution reduces the number of defect complexes that act as space charge in the pseudoperovskite layer. From this study, it can be demonstrated that the microstructures of ferroelectric films play an important role in their conductivity properties.[12]

Further, different regimes can be distinguished in the *I-V* characteristics (Fig 7). At very low electric fields, the films display nearly ohmic conduction. This current would be due to the hopping conduction mechanism in a low electric field, because thermal excitation of trapped electrons from one trap site to another dominates transport in the films. At higher fields, the current densities are limited by a different conduction mechanism from that in the low-field region. The J vs E plot in Fig. 7 for the films deposited on LSCO clearly shows a nonlinear behavior in high-E field. A conduction mechanism based on space-charge-limited (SCL) emission predicts that *J-E* characteristics for the film deposited on LSCO can be well fitted with polynomials.[13]

The data for the LCSO deposited film can be fitted reasonably well with the modified Langmuir-Child law;[14] that is, $J(E)=aE+bE^2$. The solid line in Fig. 8 is the best-fitted curve where the coefficients a and b are $2.320\,57 \times 10^{-8}$ A/cm V and $1.565\,34 \times 10^{-9}$ A/V^2, respectively. The fact that *J-E* characteristics of the LSCO annealed film can be fitted well with polynomials suggests that the role of traps is not significant for this film.[12] As a consequence, a model based on SCL emission provides the most consistent explanation of the *J-E* characteristics of the BLT film on LSCO bottom electrode. The formation of space charge can be attributed to the platelike nature of the film, as shown in Fig. 2. The current from the SCL with traps can be expressed as[15]

$$J = (9/8)\varepsilon_r \varepsilon_0 \theta \mu V^2/d^3, \qquad (1)$$

where θ is the ratio of free-to-trapped electrons, μ is the electron mobility, ε_r is the optical dielectric constant, ε_0 is the permittivity of free space, and d is the film thickness. From the obtained results, the platelike morphology seems to be fundamental in the explanation of the mechanism of SCL predominant in the LSCO deposited film resulting in a good fit with the Langmuir-Child law. In this kind of structure, carrier injection into the insulator appears very important, so space charge can distribute along the platelike grain boundaries.

IV. CONCLUSION

BLT thin films were successfully obtained on LSCO electrode from a polymeric solution and annealed by a microwave oven through the spin-coating technique. A remarkable improvement in the remnant polarization and coercive field suggests that BLT thin films deposited on a LSCO oxide electrode are suitable for integrated device applications. The *C-V* characteristics of the metal-ferroelectric-metal structure showed a typical butterfly loop that confirms the ferroelectric properties of the film, which is related to ferroelectric domain switching. High fatigue resistance was observed, which proves that our films are of high enough quality to be used in nonvolatile random access memories. The *J-E* characteristics showed ohmic conductivity in the low voltage and space-charge-limited conductivity in high voltage due to the plate-like morphology of the grains.

ACKNOWLEDGMENTS

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