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Electrical properties of lanthanum doped $Bi_4Ti_3O_{12}$ thin films annealed in different atmospheres

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Abstract

Pure and lanthanum doped $Bi_4Ti_3O_{12}$ thin films were deposited on $Pt/Ti/SiO_2/Si$ substrate using a polymeric precursor solution. Annealing in static air and oxygen atmosphere was performed at 700 °C for 2 h. The obtained films were characterized by X-ray diffraction and atomic force microscopy. The dielectric constant and dissipation factor were measured in the frequency region from 1 kHz to 1 MHz. Electrical characterization of the films pointed to ferroelectricity via hysteresis loop. Films annealed in static air possess a dielectric constant higher than films annealed in oxygen atmosphere due to differences in the grain size, crystallinity and structural defects. A regularly shaped hystereses loop is observed after annealing in static air. The obtained results suggest that the annealing in oxygen atmosphere can increase the trapped charge and the relaxation phenomenon.

Keywords: Bismuth compounds; Crystal structure; Ferroelectric materials

1. Introduction

In recent years, several studies have been reported on thin films for memory applications. The most popular ferroelectric material for nonvolatile memories is lead zirconate titanate (PZT). However, the PZT thin films on platinum electrode present serious problems of degradation due to oxygen vacancies created at the interface [1]. As alternative a new class of ferroelectric based on Bi-layered perovskites has been attempted. The bismuth layer structure was originally described by Aurivillius to have the formula $(Bi_2O_2)^{2+}$–$(A_{m-1}B_mO_{3m+1})^{2-}$, where A is Bi, Ba, Sr, Ca, Pb, K or Na; B is Ti, Nb, Ta, Mo, W or Fe. Recently, Bi-layered perovskite thin films such as $Bi_4Ti_3O_{12}$, $SrBi_2Ta_2O_9$ (SBT) or $SrBi_2Nb_2O_9$ (SBN) have been developed. Because of the fatigue-free behavior of lanthanum-substituted bismuth titanate [Bi_x-$La_{1-x}Ti_3O_{12}$ (BLT)], a Bi-layered perovskite oxide with a platinum electrode has received increasing attention on ferroelectric applications, such as nonvolatile memory [2,3]. Compared with $SrBi_2Ta_2O_9$ (SBT), another well-known fatigue-free ferroelectric material which is also a Bi-layered perovskite oxide, BLT has many attractive properties, such as low processing temperature and large values of remnant polarization. Two reasons for the fatigue-free behavior of BLT have been found. One is the charge-compensating role of the (Bi_2O_2) layers. Another is the chemical stability of the perovskite layers against oxygen vacancies after substituting some La atoms for Bi atoms, since the oxygen ions near Bi ions in BIT are likely to be less stable than those near Sr ions in SBT due to the high volatility of Bi ions [3–5].

Obviously, the substitution of bismuth by lanthanum influences the ferroelectric properties of this material dramatically. Bu et al. [6] prepared thin films of BIT doped with lanthanum by pulsed laser deposition. The authors found that these films were appropriate for nonvolatile random access memory devices. It is known that BIT compounds have a high leakage current and domain pinning due to defects such as Bi vacancies (V'''_{Bi}) accompanied by oxygen vacancies ($V_0^{\bullet\bullet}$). In order to minimize these defects the substitution of Bi by La ion on A-site is required [3]. It is known that the role of A-site substitution is to displace the volatile Bi with La to suppress the A-site vacancies which are accompanied by oxygen vacancies that act as space charges. It has been reported that ferroelectric properties were improved by ion doping on A- or B-site [7]. Recently, effects of ion doping on ferroelectric properties and

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electrical conduction have been widely studied [8]. For practical FRAM application, it is necessary to obtain BLT thin film with high remnant polarization and low leakage current.

In recent years sol–gel processing and the co-precipitation method have become popular for producing ceramic materials with improved compositional homogeneity and with lower sintering temperature. Although the sol–gel process utilizes expensive precursors and depends of a critical drying process, the co-precipitation process is limited by cation solutions with similar solubility constants. On the other hand, polymeric precursor process which employs complexing of cations in an organic media, makes use of low cost precursors and results in a homogeneous ion distribution at molecular level [9]. Due to the formation of a polyester resin during the synthesis, no segregation of cations was observed during the thermal decomposition of organic material. The polymeric precursor method presents many advantages, such as the possibility to work in aqueous solutions with the high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method (inexpensive precursors and equipments).

It has been reported that the crystallization process is affected by variables such as substrate, annealing temperature, atmosphere, drying condition [10]. It was noticed that the oxygen atmosphere has a prominent influence on crystallization process of ferroelectric materials avoiding the loss of volatile species and controlling the stoichiometry of the film. Besides that, the use of higher atmosphere flows was found to affect the microstructure of the films decreasing the grain size and increasing the content of perovskite phase [11].

Considering that the literature reports no data about the effect of oxygen atmosphere on crystallization, morphology and properties of lanthanum doped $Bi_4Ti_3O_{12}$ thin films deposited by a spin-coating process using a polymeric solution, in this work, we describe our results on the deposition of thin films and their electrical properties relating to random access memory applications.

2. Experimental procedure

Titanium isopropoxide (Hulls AG), hydrated lanthanum carbonate (Aldrich) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth, titanium and lanthanum were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Ti, Bi and La were mixed and homogeneized by stirring at 90 °C. The molar ratio of metal:citric acid:ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. Films were spin-coated from $Bi_{4-x}La_xTi_3O_{12}$ ($x = 0$, 0.25, 0.50 and 0.75) deposition solution onto $Pt/Ti/SiO_2/Si$ substrate. From a previous paper, BLT films were completely crystallized at 700 °C for 2 h, so this was the temperature at which films were heat-treated [12]. Multilayered films were obtained by spinning 10 times the deposition solution on the surface of the substrate at 5000 rpm. Films were heat-treated by the ''amorphous intermediate layer'' route at 400 °C for 2 h and spinned again, until the desired number of layers was reached. All layers were crystallized at the same time at 700 °C for 2 h in static air and oxygen dynamic atmosphere (100 mL/min).

In this work, an excess of 5 wt.% of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Phase analysis of the films was performed at room temperature by X-ray powder diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 20-2000) and Cu Kα radiation. The thickness of the annealed films was studied using scanning electron microscopy (Topcon SM-300) by looking at the transversal section. In this case back scattering electrons were utilized. The thickness results obtained from SEM represent an average value of three measurements. Surface roughness (RMS) was examined by AFM, using tapping mode technique. Next, a 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace, at 300 °C, in oxygen atmosphere for 1 h. Here, the desired effect is to decrease eventually present oxygen vacancies.

The dielectric constant ε_r and dissipation factor tan δ were measured versus frequency using an impedance analyser (model 4192 A, Hewlett Packard). 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). The leakage current–voltage (*I–V*) characteristic was determined with a voltage source measuring unit (Radiant Technology 6000 A). The *I–V* measurements were recorded on the Radiant technology tester in the current-voltage mode, with a voltage changing from 0 to +10 V, from +10 to −10 V and back to 0 V. All measurements were performed at room temperature. For the fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristics of the films was measured over a range of frequencies.

3. Results and discussion

It is known that the films properties are significantly affected by the crystallographic orientation of thin film which is controlled by the orientation of the underlying layer, film thickness and atmosphere flow. It is important to control the thickness of the layer which strongly influences the grain size, dielectric and ferroelectric properties. For thinner films interfacial ''dead layers'' could appear at the film-substrate interface influencing the performance of the device. These dead layers are originated from oxygen interdiffusion, chemical reaction, or structural defects at the interfaces and could be suppressed with films thickness higher than 300 nm. This

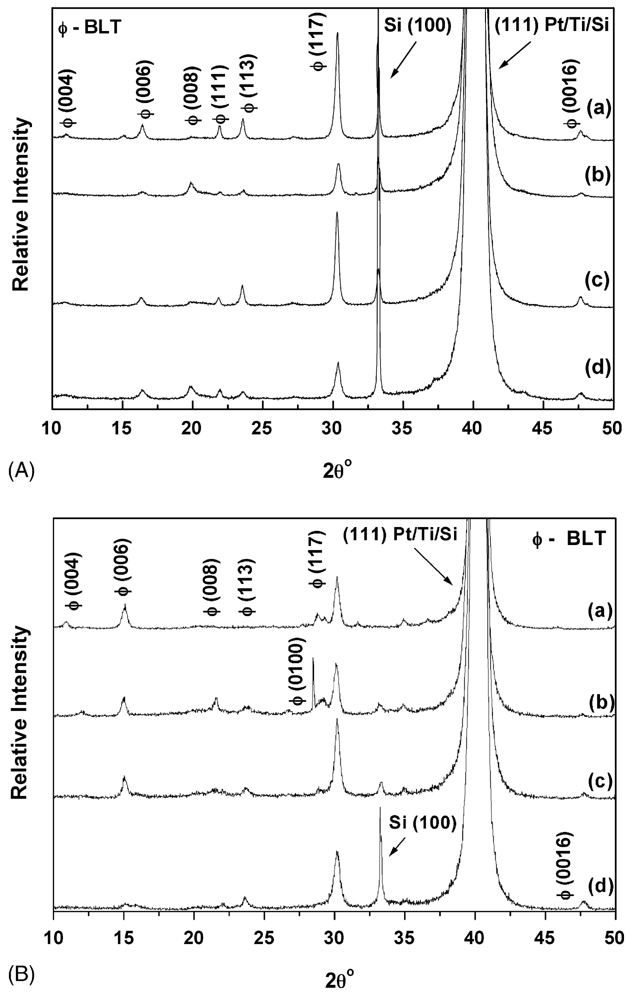

Fig. 1. X ray diffraction for $Bi_{4-x}La_xTi_3O_{12}$ films annealed at static air (A) and oxygen atmosphere (B), respectively: (a) $x = 0$; (b) $x = 0.25$; (c) $x = 0.5$; (d) $x = 0.75$.

critical thickness could be obtained by multi layer depositions. To obtain films with thickness higher than 300 nm it was necessary to deposit ten layers on the substrate.

The X-ray diffraction data obtained of pure and lanthanum doped $Bi_4Ti_3O_{12}$ thin films deposited with 10 layers on platinum coated silicon (1 1 1) substrates and annealed at 700 °C for 2 h in static air and oxygen atmosphere are shown in Fig. 1A and B. The peaks located at $2\theta = 11°$, 16.4°, 19.9°, 21.9°, 23.6°, 28.5°, 30.3° and 47.2° correspond to the polycrystalline $Bi_4Ti_3O_{12}$ phase for films annealed in static air and oxygen atmosphere (Fig. 1A and B). The characteristic peak for platinum coated silicon (1 1 1) substrates was observed in the range of $38° < 2\theta < 41°$. In the investigated case, no preferential orientation was observed for pure and lanthanum doped $Bi_4Ti_3O_{12}$ films. It was also noted a decrease of peak intensities for films annealed in oxygen atmosphere pointing to worst crystallinity. The obtained results suggest that the oxygen atmosphere influences the amount of $Bi_4Ti_3O_{12}$ crystalline phase.

Fig. 2 shows a typical surface morphology of films annealed in static air and oxygen atmosphere. The nucleation rate of the films annealed in oxygen atmosphere is higher compared with the films annealed in static air leading to a decrease in the grain size. The average surface roughness value for the film annealed in static air is 14 nm while the average grain size is 100 nm. Meanwhile, in the case of the film annealed in oxygen atmosphere the average grain size is 70 nm and the surface roughness is 8.0 nm. Defects as bismuth and oxygen vacancies located in the grains can interact with domain boundaries influencing the switching characteristics of the system [13]. This behavior is more expressed for smaller grains and when the film grows in *c*-axis direction showing p-type conductivity such as in the investigated case.

It is known that the dielectric constant and dissipation factor depend on several factors such as annealing temperature, type of electrodes, defects, domain walls and phase composition. The data of electric characterizations present the average

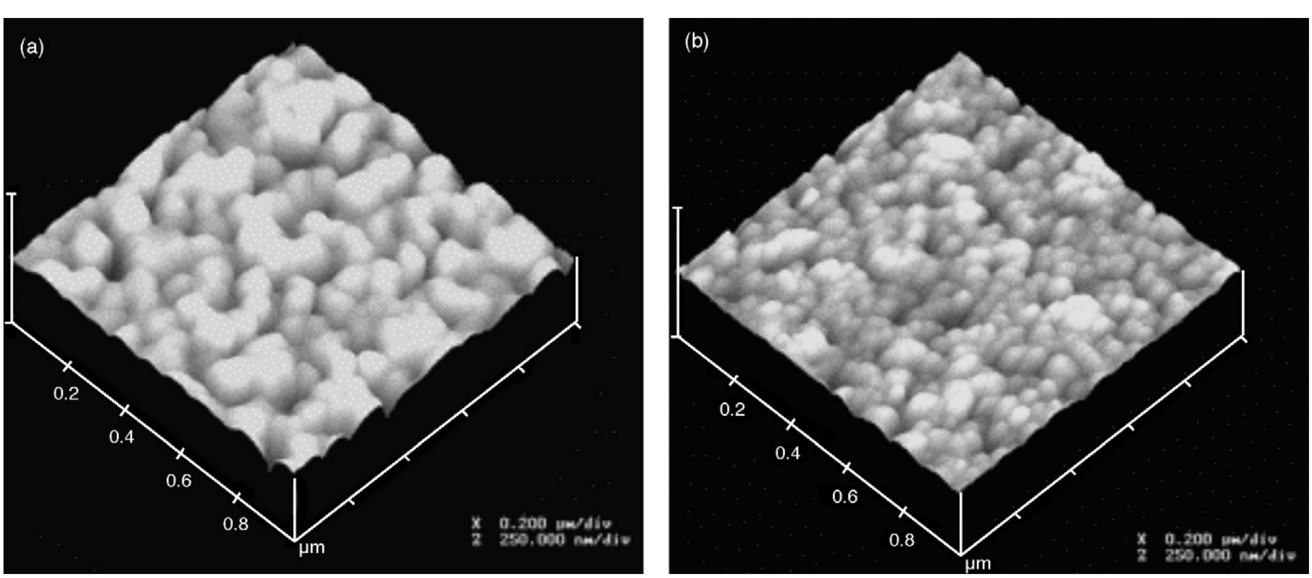

Fig. 2. AFM images for BLT films ($x = 0.5$) annealed at: (a) static air and (b) oxygen atmosphere.

measurement values of three samples. The dielectric constant and dissipation factor of the films are presented in Fig. 3. As it can be seen, in Fig. 3b, the sample annealed in oxygen atmosphere presents an intense drop in dielectric constant in the range of frequency from 10 to 100 kHz. It is possible that this decrease in the dielectric constant in this frequency range is caused by space charge polarization or Maxwell Wagner type interfacial polarization. The space charge polarization is inherently related to the nonuniform charge accumulation. These charges can be originated during the annealing in oxygen atmosphere. When the films are annealed in static air a reduction of the dispersion of dielectric constant was observed in this range of frequency. This result indicates that there is a reduced charge space effect in the dielectric properties strongly confirming that the dielectric relaxation observed is not a bulk-related phenomenon, but an oxygen related interface phenomenon. The obtained results pointed that the films annealed in static air possess a dielectric constant higher than films annealed in oxygen atmosphere due to differences in grain size, crystallinity and structural defects. As a consequence of these results one can say that the atmosphere of annealing deeply influences on the dielectric properties of bismuth titanate thin films.

Fig. 4 shows the relationship between the d.c. bias and capacitance (*C–V* curve) for BLT films annealed in static air and oxygen atmosphere at 100 kHz and d.c. sweep voltage from +10 to −10 V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domain switching. The *C–V* curve for the film annealed in static air indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. This indicates that there is a low concentration of movable ions or charge accumulation at the interface between the dielectric and the electrode. On the other hand, when the capacitor was treated in an oxygen atmosphere, deviations from this symmetry occur which suggests that an additional capacitance at the interface arises from space charges [14].

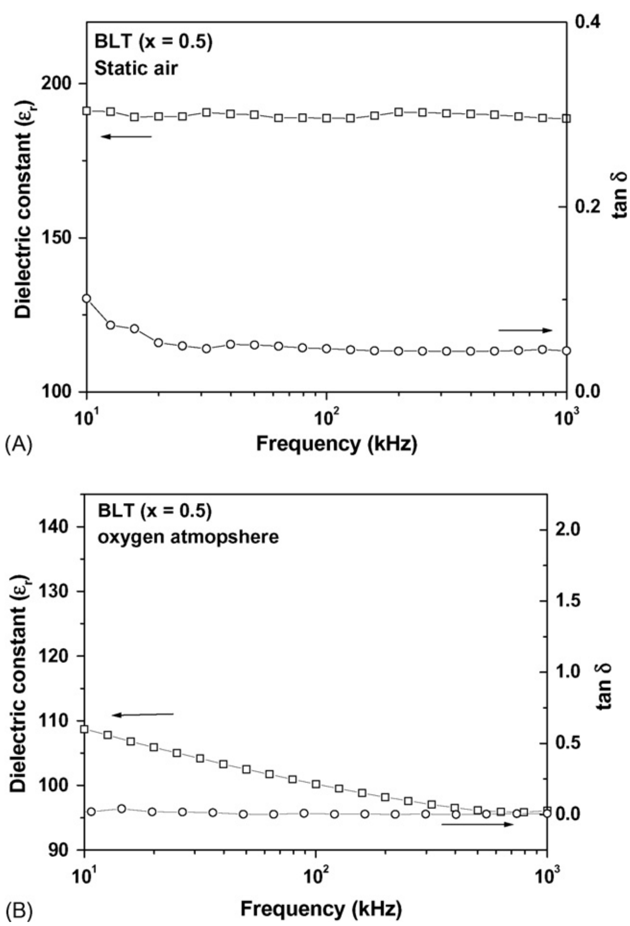

Fig. 3. Dielectric constant and loss tangent in dependence of frequency for BLT films ($x = 0.5$) annealed at: (a) static air and (b) oxygen atmosphere.

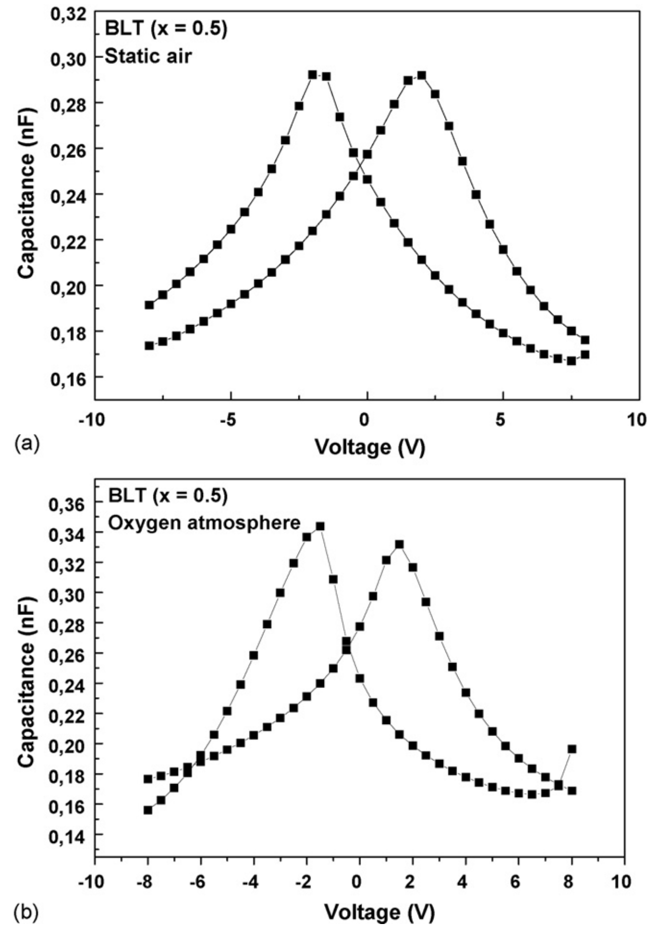

Fig. 4. *C–V* curves for BLT films ($x = 0.5$) annealed at: (a) static air and (b) oxygen atmosphere.

The insulating properties of the films were found to be dependent on the atmosphere present during thermal treatment. As shown in Fig. 5, the leakage current density was greatly changed by the atmosphere of thermal treatment. The leakage current density decreased for the films annealed in static air. Such a reduction in leakage current density may be attributed to improved crystallinity and complete perovskite phase formation. The mechanisms of carriers transport through thin insulator films have been the subject of extensive theoretical and experimental investigations. The steady-state field dependent d.c. conductivity was examined through the measurement

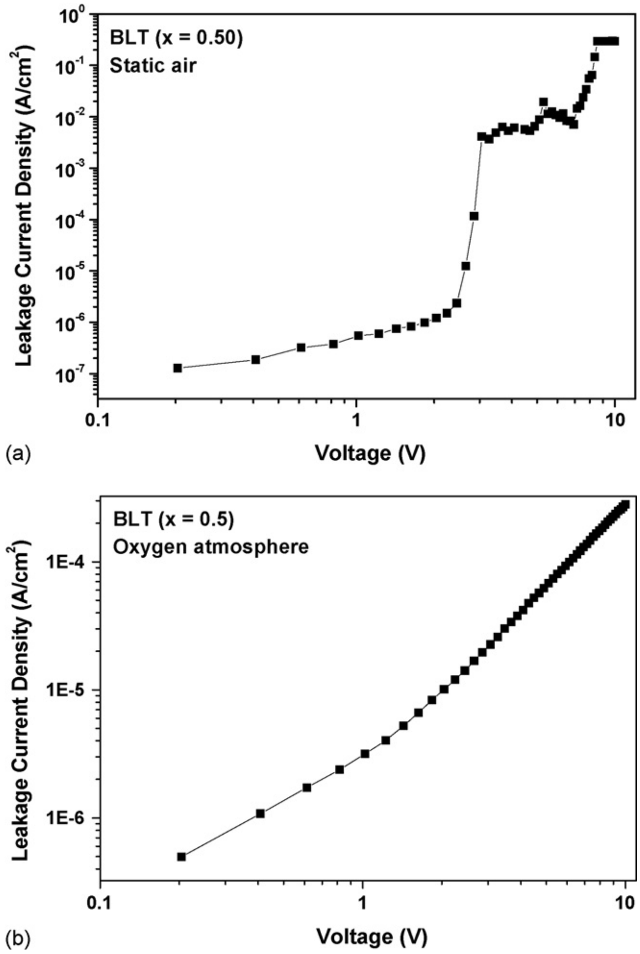

Fig. 5. Leakage current density in dependence of voltage for BLT films ($x = 0.5$) annealed at: (a) static air and (b) oxygen atmosphere.

of the *I–V* characteristics in MFM capacitors. Several processes allow a charge movement in insulators, leading to sizable current densities. The low field electrical properties are usually of ohmic nature which means the current *I* is a linear function of voltage *V*. At high fields, these films exhibit nonlinear *I–V* relationships. Their non-ohmic behavior can be expressed by the empirical power law $I = KV^{\alpha}$ [15]. Generally, the high field electrical characteristics cannot be adequately described by a single conduction process; usually different field strength ranges manifest different electrical phenomena. Fig. 5 shows the *I–V* curves for the BLT films annealed in different atmospheres. 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 the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanisms. The leakage current density at 1.0 V decreases from 3.2×10^{-6} to 5.49×10^{-7} A/cm^2 when the films are annealed in static air. The lower leakage current observed for the film annealed in static air may be attributed to probable differences in grain size, density, and surface structure due to differences in crystallization. As the applied field increased, defects such as oxygen vacancies interacted strongly with domains boundaries and had significant influences on the conducting process. It seems that mobile vacancies such as Bi and O vacancies can assemble in polarization extended structures near the domain boundaries and may contribute to an increase in the leakage current. An increase in conductivity with increasing oxygen content indicates that the mobile carriers are positively charged and that the possibility of hopping through the Bi ion can be considered.

The characteristics of the film-electrode interface and the surface morphology of BLT thin films are the major factors determining the leakage current of capacitors in MFM configuration. Giridharan and coworkers [16] observed similar behaviour to BIT films prepared by sol–gel method with leakage current density of 10^{-7} A/cm^2 at an applied voltage of 1.0 V. In addition, Sedlar and Sayer [17] reported leakage current density of 10 nA/cm^2 at an electric field of 60 kV/cm for BIT thin films prepared by the sol–gel method.

Ferroelectricity in the lanthanum doped bismuth titanate thin films was performed in a standardized ferroelectric tester and the results were presented in Fig. 6. The hysteresis loop for film annealed in static air pointed that the polarization process could be easier accomplished in comparing with films annealed in oxygen atmosphere leading to a more regularly shaped hysteresis loop. However, for the film annealed in oxygen

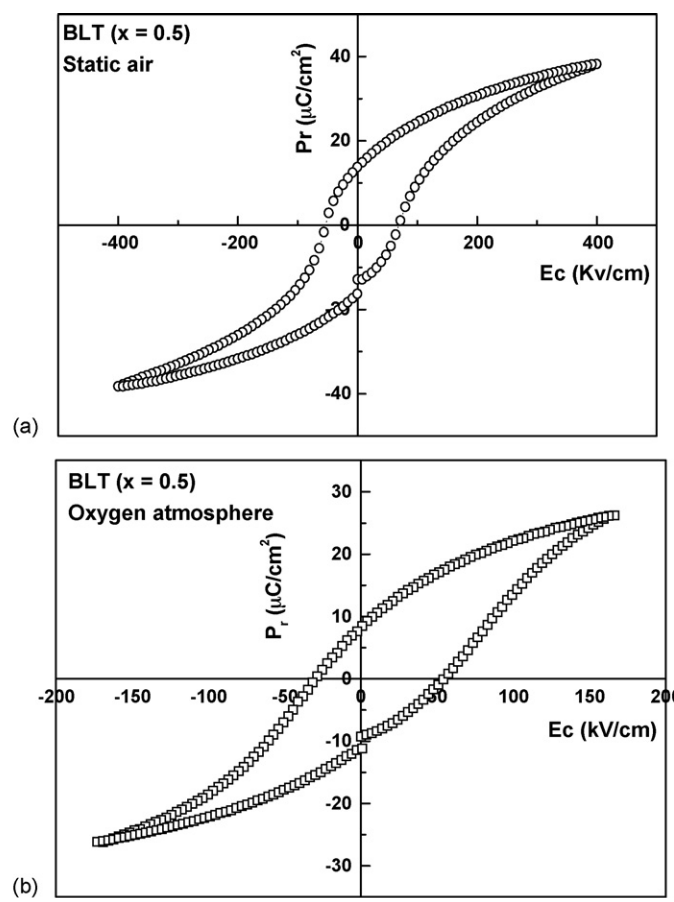

Fig. 6. *P–E* hysteresis loop for BLT films ($x = 0.5$) annealed at: (a) static air and (b) oxygen atmosphere.

atmosphere the trapped charge (O_2'') associated with other defects ($V_0^{\bullet\bullet}$) or even defect dipole complexes such as oxygen vacancies associated to bismuth vacancies ($V'''_{Bi} - V_0^{\bullet\bullet}$) located in the grain boundary and in film-electrode interface can promote a local stoichiometry deviation influencing the shape of the hysteresis loops. Ferroelectricity in the films was observed with remnant polarization of 15 $\mu C/cm^2$ and coercive field of 60 kV/cm for films annealed in static air and 9 $\mu C/cm^2$ and 40 kV/cm for films annealed in oxygen atmosphere. The spontaneous polarization value in bulk single crystal of bismuth titanate is 50 $\mu C/cm^2$ which is much higher than the corresponding value in our films [18]. This could be due to fact that the loop presented in Fig. 6 was obtained from the major polarization component vectors lying in the c plane which present low values of remnant polarization. The hysteresis loop of the film annealed in oxygen atmosphere shows a significant shift along the electric field axis towards the positive side, which is defined as imprint. The voltage shifts may lead to a failure of the capacitor due to the apparent loss of polarization in one of the remnant states. Consequently, an increase in the coercive voltage in one direction occurs. These two effects may cause a memory failure. These results are consistent with the *C–V* measurements and are caused by the high concentration of bismuth and oxygen vacancies trapped in the interface film/electrode.

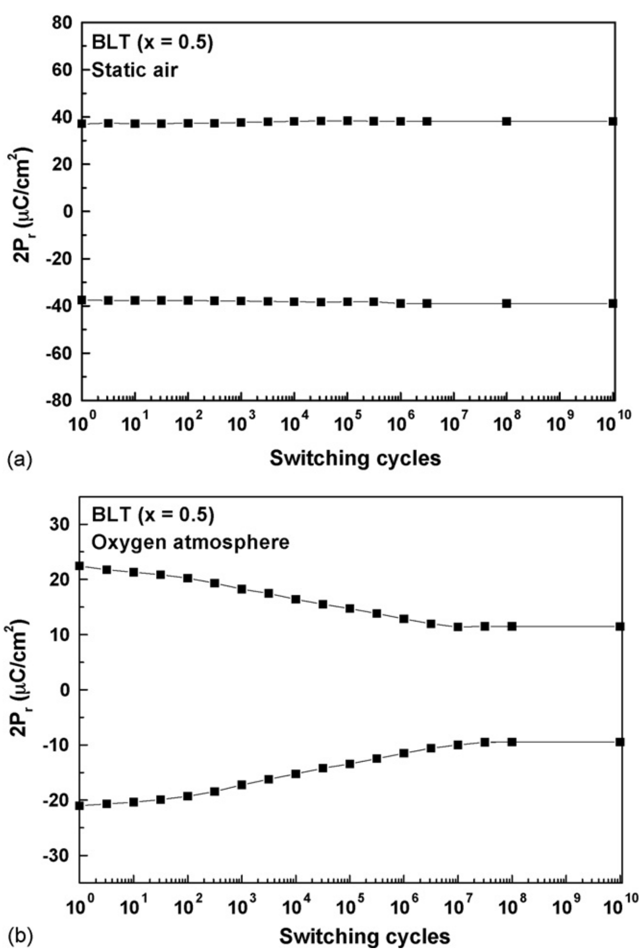

Fig. 7. Fatigue as a function of polarization cycles for BLT films ($x = 0.5$) annealed at: (a) static air and (b) oxygen atmosphere.

The fatigue endurance of BLT thin films as a function of switching cycles was examined by applying 8.6μs wide bipolar pulses with a 10 V amplitude (Fig. 7). Fatigue resistance was observed up to 10^{10} cycles for the films annealed in static air. The substitution of La for Bi can change the chemical environment of the perovskite layers and solve the fatigue problem of pure BIT thin films. However, it is not yet clear whether La changes the chemical environment of the perovskite layers. It is quite possible that the La substitution will enter the $(Bi_2O_2)^{2+}$ layers since the sizes of Bi^{3+} and La^{3+} ions are quite similar. No fatigue resistance was observed for films annealed in oxygen atmosphere due to the increase of local current which eventually destroy the film-electrode interface leading to decrease of remnant polarization [19].

4. Conclusions

Dense lanthanum doped bismuth titanate films on (1 1 1) platinum coated silicon substrate were obtained through polymeric solution by spin coating technique. Films annealed in static air possess a dielectric constant higher than films annealed in oxygen atmosphere due to differences in the grain size, crystallinity and structural defects. A regularly shaped hysteresis loop is observed after annealing in static air. The obtained results suggest that the annealing in oxygen atmosphere can increase the trapped charge and the relaxation phenomenon. High fatigue resistance was observed for films annealed in static air, whereas films annealed in oxygen atmosphere showed no fatigue resistance.

Acknowledgments

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References

[1] H.N. Al-Shareef, K.R. Bellur, A.I. Kingon, O. Auciello, Phase evolution and annealing effects on the electrical properties of $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin-films with RuO_2 electrodes, Appl. Phys. Lett. 66 (1995) 239–241.

[2] J.F. Scott, C.A. Paz de Araujo, Ferroelectric memories, Science 246 (1989) 1400–1405.

[3] B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, W. Jo, Lanthanum-substituted bismuth titanate for use in non-volatile memories, Nature 401 (1999) 682–684.

[4] B.H. Park, S.J. Hyun, S.D. Bu, T.W. Noh, J. Lee, H.-D. Kim, T.H. Kim, W. Jo, Differences in nature of defects between $SrBi_2Ta_2O_9$ and $Bi_4Ti_3O_{12}$, Appl. Phys. Lett. 74 (1999) 1907–1909.

[5] C.A. Paz de Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott, J.F. Scott, Fatigue-free ferroelectric capacitors with platinum electrodes, Nature 374 (1995) 627–629.

[6] S.D. Bu, B.S. Kang, B.H. Park, T.W. Noh, Composition dependence of the ferroelectric properties of lanthanum-modified bismuth titanate thin films grown by using pulsed-laser deposition, J. Kor. Phys. Soc. 36 (2000) L9–L12.

[7] A.Q. Jiang, Z.X. Hu, L.D. Zhang, The induced phase transformation and oxygen vacancy relaxation in La-modified bismuth titanate ceramics, Appl. Phys. Lett. 74 (1999) 114–116.

[8] Y.P. Wang, W.I. Lee, T.Y. Tseng, Degradation phenomena of multilayer ZnO-glass varistors studied by deep level transient spectroscopy, Appl. Phys. Lett. 69 (1996) 1807–1809.

[9] M.P. Pechini, US Patent 3,330,697 (1967).

[10] S.K. Park, M.S. Baek, S.C. Bae, S.Y. Kwun, K.T. Tim, K.W. Kim, Properties of $LiNbO_3$ thin film prepared from ceramic Li–Nb–K–O target, Solid State Commun. 111 (1999) 347–352.

[11] A.H. Carim, B.A. Tuttle, D.H. Doughty, S.L. Martinz, Microstructure of solution-processed lead zirconate titanate (PZT) thin-films, J. Am. Ceram. Soc. 74 (1991) 1455–1458.

[12] A.Z. Simões, B.D. Stojanovic, M.A. Zaghete, C.S. Riccardi, A. Ries, F. Moura, E. Longo, J.A. Varela, Electrical characterization of lanthanum-modified bismuth titanate thin films obtained by the polymeric precursor method, Integr. Ferroelectrics 60 (2004) 21–31.

[13] H.S. Shulman, M. Testorf, D. Damjanovic, N. Setter, Microstructure, electrical conductivity, and piezoelectric properties of bismuth titanate, J. Am. Ceram. Soc. 79 (1996) 3124–3128.

[14] F.M. Pontes, E.R. Leite, E. Longo, J.A. Varela, E.B. Araújo, J.A. Eiras, Effects of the postannealing atmosphere on the dielectric properties of (Ba, Sr)TiO_3 capacitors: evidence of an interfacial space charge layer, Appl. Phys. Lett. 76 (2000) 2433–2435.

[15] P.C. Joshi, S.B. Desu, Structural and electrical characteristics of rapid thermally processed ferroelectric $Bi_4Ti_3O_{12}$ thin films prepared by metalorganic solution deposition technique, J. Appl. Phys. 80 (1996) 2349–2357.

[16] S. Madeswaran, N.V. Giridharan, R. Jayavel, Sol–gel synthesis and property studies of layered perovskite bismuth titanate thin films, Mater. Chem. Phys. 80 (2003) 23–28.

[17] M. Sedlar, M. Sayer, Structural and electrical properties of ferroelectric bismuth titanate thin films prepared by the sol–gel method, Ceram. Int. 22 (1996) 241–247.

[18] S.Y. Wu, W.J. Takei, M.H. Francombe, S.E. Cummins, Domain-structure and polarization reversal in films of ferroelectric bismuth titanate, Ferroelectrics 3 (1972) 217–219.

[19] D. Damjanovic, Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics, Rep. Prog. Phys. 61 (1998) 1267–1324.