Ceramics International 30 (2004) 1553–1556

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Ferroelectric properties of Au/$Bi_{3.25}La_{0.75}Ti_3O_{12}$/ITO thin film capacitors deposited under different partial oxygen pressures

Jaemoon Pak, Kuangwoo Nam, Jungsuk Lee, Gwangseo Park*

Department of Physics, Sogang University, Seoul 121-742, South Korea

Received 27 November 2003; received in revised form 13 December 2003; accepted 23 December 2003

Available online 6 May 2004

Abstract

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films were deposited onto indium-tin-oxide (ITO) coated glass substrates by the pulsed laser ablation method at a deposition temperature of 400 °C and an annealing temperature of 650 °C. An attempt to control the oxygen-induced defects in the ferroelectric material was conducted by varying the conditions of the deposition pressures. The fatigue properties resulted in a constant polarization switching due to charged oxygen vacancies for oxygen deficient 50 mTorr prepared films, and decreasing polarization with co-existing ferroelectric and pyrochlore phase for excessive oxygen 500 mTorr prepared films. However, for the film prepared at 200 mTorr, an unusual increase in the polarization value was observed. This might be attributed to the formation of a p–n junction with the n-type electrode and p-type ferroelectric material that creates a built-in bias inside the ferroelectric film or near the interface, concentrating the polarity to the direction of the electrode.

Keywords: C. Dielectric properties; C. Ferroelectric properties; C. Fatigue; $Bi_{3.25}La_{0.75}Ti_3O_{12}$

1. Introduction

Considerable attentions have been focused in developments of non-volatile ferroelectric random access memories (NVFRAM) [1] based on bismuth layered structured ferroelectric (BLSF) materials [2,3]. These BLSF materials are named Aurivillius phases after systematically synthesized by Aurivillius in the 1950s. Since then, results on the dielectric, ferroelectric, piezoelectric and electro-optic properties of the materials have been reported.

Aurivillius phase BLSF materials can be described as the intergrowth structure of fluoritelike $(Bi_2O_2)^{2+}$ units and perovskitelike $(A_{n-1}B_nO_{3n+1})^{2-}$ slabs, where $n = 2$–5. The 12-fold perovskite A-sites can be occupied by cations like Ba^{2+}, Ca^{2+}, Sr^{2+}, Bi^{3+}, and rare earth elements, and the six-fold B-sites are usually occupied by smaller cations like Ti^{4+}, Ta^{5+}, Nb^{5+}, and W^{6+}. Recently, the two-layer ($n = 2$) ferroelectric $SrBi_2Ta_2O_9$ (SBT) [2] and the three-layer ($n = 3$), $(Bi, Ln)_4Ti_3O_{12}$ [3–6], were found to possess excellent fatigue resistance (i.e. maintenance of remnant polarization (P_r) under repeated switching cycles) characteristics on using conventional Pt electrodes.

Up to this point, $(Pb, Zr)TiO_3$ (PZT) [7,8] and other related lead-based ferroelectric films have been most widely investigated. They usually have large (P_{sw}–P_{ns}) values of 20–70 $\mu C/cm^2$, depending on substituting elements and processing conditions. However, when a capacitor is fabricated with a PZT film on a conventional Pt electrode, its value of (P_{sw}–P_{ns}) usually becomes reduced after repetitive read/write cycles. It has been known that the oxygen vacancies play an important role in inducing the fatigue failures [2].

The fatigue problem in PZT films can be reduced significantly by using oxide or hybrid metallic-oxide electrodes instead of Pt electrodes.[9–12] In this configuration, the oxide electrode helps to control the amount of oxygen vacancies at the ferroelectric interface which is responsible for the fatigue phenomena. Requirements in considering the effects of defects in the perovskite units or at the film-electrode interface are important issues for determining the ferroelectric properties and electrical conduction of these films.

In this letter, considerable attention has been paid to understand the role of oxygen partial pressures during preparation of lanthanum-substituted bismuth titanate ($Bi_{3.25}La_{0.75}Ti_3O_{12}$, BLT) thin films on indium-tin-oxide (ITO) glass substrates. From the control of these deposition pressures, we were able to study the oxygen-induced

* Corresponding author. Tel.: +82-2-705-8430; fax: +82-2-705-8426.
E-mail address: gpark@ccs.sogang.ac.kr (G. Park).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.12.096

effects of the ferroelectric material. The measurements on the surface microstructures and electrical characterizations of these defect-driven films will be reported.

2. Experimental procedures

BLT films were prepared on conducting ITO coated glass substrates by the pulsed laser deposition (PLD) method with a KrF excimer laser source of $\lambda = 248$ nm, pulsed at a repetition rate of 3 Hz with a laser fluence of 2.5 J/cm^2. The target-to-substrate distance was stationed at 45 mm and pre-sputtering was carried out for 3 min. Deposition was carried out at a substrate temperature of 400 °C for 5 min, and post-annealing treatment was carried out in-situ for 1 h at 650 °C.

The description of the fabrication process at various deposition procedures and its electrical measurements has been given elsewhere [13]. On a well-matched substrate, the film grows in the plane that maintains structural coherency with the substrate. In this case, polycrystalline films are expected as the crystallizations of the ITO layer took place during the annealing process. Crystallizations of the ITO layer have been observed with polycrystalline films showing weak crystallizations to the *c*-axis [13].

The microstructures and electrical characterizations of the films deposited at the given partial oxygen pressures of 50, 200 and 500 mTorr have been taken into considerations. The surface micro-structural observations were carried out by JEOL JSM-6700F field effect scanning electron microscopy (SEM), and the *P–E* hysteresis and fatigue properties were measured by a computerized radiant technology RT66A system. The measurement of Au/BLT/ITO metal–ferroelectric–metallic oxide type capacitor configuration was carried out through a micro-meter manipulating probe method with gold (Au) dots of size 150 μm in diameter, thermally deposited for use as the top metal electrode.

3. Results and discussion

The use of an ambient gas during pulsed laser ablation method can be characterized as either passive or active. The passive use of an ambient gas is mainly to compensate for some loss of constituent elements, such as oxygen that is evaporative when the deposition process takes place. Problematic issues such as oxygen vacancies or deficiencies of the films [2] are bound to arise when a powerful physical energy, such as a laser beam, is supplied to the ceramic target. During the process where the particles are transported to the substrate via the plume, a passive method to regenerate the lost oxygen was applied with the presence of a nozzle right under the plume.

Deposition of the films was conducted at partial oxygen pressures of 50, 200, 500 mTorr, and 1 Torr. Fig. 1 shows,

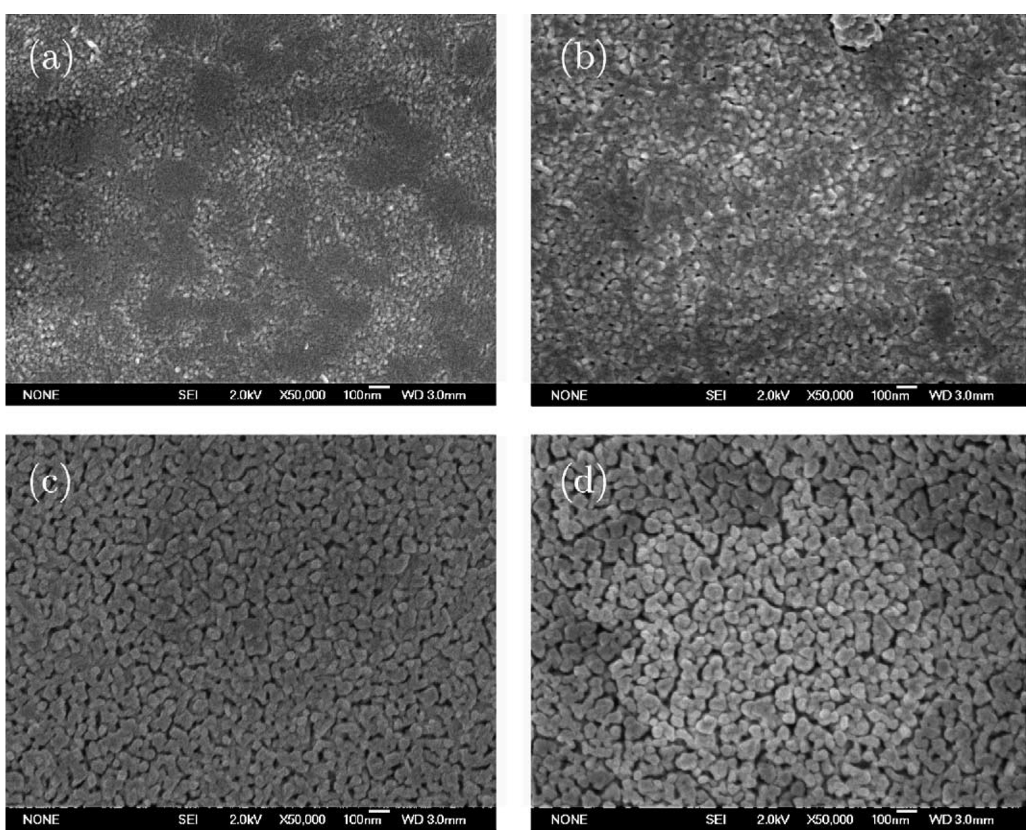

Fig. 1. Surface microstructures of films prepared at partial oxygen pressures of (a) 50 mTorr, (b) 200 mTorr, (c) 500 mTorr, and (d) 1 Torr.

in alphabetic order, the surface microstructures of the films with average grain sizes of 20, 50, 80 and 100 nm at the respective pressures. It can be seen that smooth columnar grains are obtained for the films deposited at 50 and 200 mTorr, while porous-like grain structures have been obtained at higher deposition pressures. In an overall observation, larger grain sizes are obtained at increasing pressures. The effects of oxygen induced defects in the perovskite units or at the film-electrode interface can be studied through this method.

The optimized conditions for PLD deposited BLT thin films with large polarization values and totally fatigue-free were reported to have a deposition pressure of 200 mTorr. In controlling the partial pressures, we were able to compare the electrical properties of defect driven films with deficiencies or excessive oxygen contents. The oxygen deficient film prepared at 50 mTorr will be denoted as “Film-A”, optimized film of 200 mTorr will be named “Film-B”, and the excessive oxygen film as “Film-C”. The BLT film prepared at 1 Torr was excluded, as it did not possess any ferroelectric property. It was assumed that this film was rather in the non-ferroelectric tetragonal phase or some other phase than BLT.

The measurements of the hysteresis loops for the films are shown in Fig. 2. The P_r and E_c (coercive field) values of Film-B were measured to be in the range of 14–16 μC/cm^2 and 90–100 kV/cm, respectively. This value was similar or even greater than those of other BLT films prepared by the same method [3,14]. However, for Films A and C, relatively poor ferroelectricity was obtained, giving clear insights that defects are present. In comparing the measurements made on both films, Film-A should have a higher magnitude as oxygen deficiencies result in the presence of charged oxygen vacancies. On the other hand, Film-C with excessive oxygen concentration should be in a co-existing phase with ferroelectric and pyrochlore properties.

Table 1
Measured dielectric and ferroelectric quantities of the thin film capacitors prepared at partial oxygen pressures of 50, 200, and 500 mTorr

	Film-A	Film-B	Film-C
Processing pressure (mTorr)	50	200	500
Grain size (nm)	20	50	80
Dielectric constant (ε)	250	365	70
Loss tangent ($\tan\delta$)	0.0011	0.0007	0.0122
Spontaneous polarization (μC/cm^2)	11.5	26.0	–
Remnant polarization (μC/cm^2)	5.8	15	–
Coercive field (kV/cm)	95	90	–

The measurements of electrical characterization for all films are sorted in Table 1. Dielectric properties were measured using a computerized HP4194A impedance/gain-phase analyzer at a given frequency of 1 MHz. The P_r and E_c values of Film-C were not noted as they were very low with a small dielectric constant (ε) value, implying the reduction of ferroelectricity. (Ferroelectric films are known to possess large ε values.) The measured value ε for Film-B was about 365, probably known to be the highest reported value from our survey.

The fatigue properties of all films are given at Fig. 3. Three different characteristics can be observed. Film-A maintained constant (P_{sw}–P_{ns}) values throughout the measurements as charged vacancies under cycling frequencies maintained their state that stabilized the fluoritelike and perovskitelike layers. Film-B had an unusual increase in the polarization value. This might be attributed to the formation of a p–n junction with ITO (n-type) and the ferroelectric material (p-type) creates a built-in bias inside the ferroelectric film or near the interface which concentrates the polarity in the direction of the ITO layer.[15] The decreasing switched polarization for Film-C is due to non-ferroelectric phase present in the film.

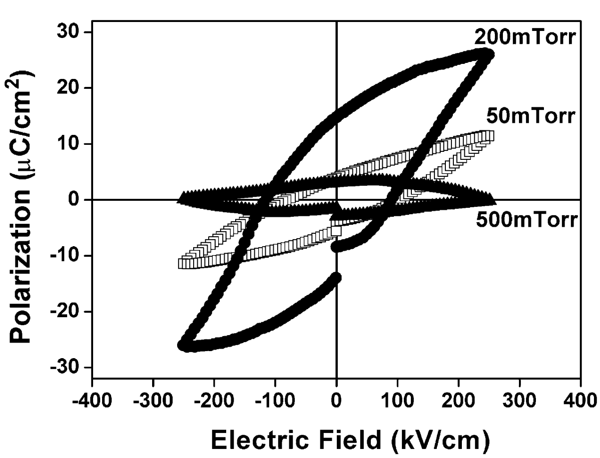

Fig. 2. Polarization–electric field hysteresis loop measurements of Au/BLT/ITO capacitors that were prepared at partial oxygen pressures of 50, 200, and 500 mTorr. The capacitor prepared at 1 Torr was excluded as it was in the non-ferroelectric phase. All measurements were taken with an applied field of 5 V.

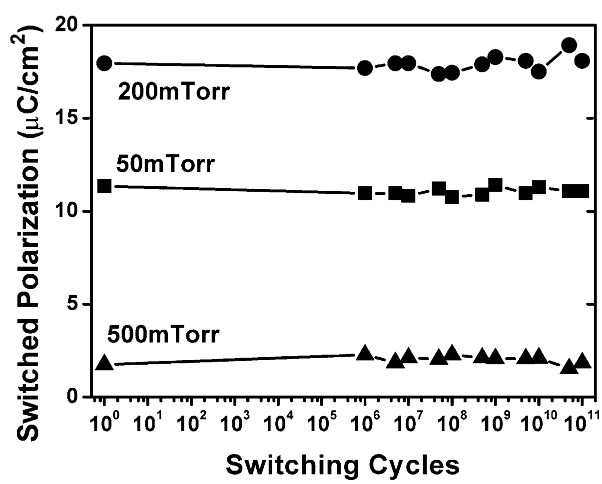

Fig. 3. Fatigue properties for the thin film capacitors prepared on partial pressures of 50 mTorr (■), 200 mTorr (●), and 500 mTorr (▲), measured with an applied voltage of 5 V and an external frequency of 500 kHz.

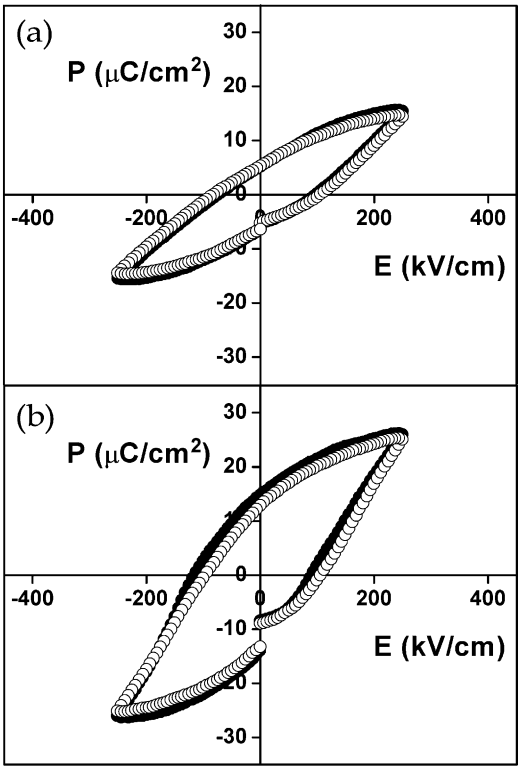

Fig. 4. Polarization–electric field hysteresis loop measurements before (●) and after (○) undergoing 1×10^{11} switching cycles for the thin film capacitors prepared on partial pressures of (a) 50 mTorr, and (b) 200 mTorr.

Fig. 4 shows the hysteresis loops before and after fatigue measurements for Films A and B. Differences are noted in that Film-A has constant P_r value and a slight decreased spontaneous polarization (P_s) value while Film-B shows a slight decrease in both polarizations and shifts to the direction of positive field. As mentioned, the built-in bias produced should be the main reason for such an asymmetric behavior.

4. Conclusion

Studies on the effects of defects on PLD deposited BLT thin film capacitors have been studied from alterations of the partial oxygen pressures during deposition. The surface microstructures for the films deposited at 50 and 200 mTorr showed smooth columnar grain structures while films deposited at 500 mTorr and 1 Torr had porous-like structures. Charged oxygen vacancies were found to be the main cause for the electrical properties of oxygen deficient ferroelectric films. The films prepared with excessive oxygen contents, however, had co-existing ferroelectric and pyrochlore phases. The optimal deposition pressure of 200 mTorr were fatigue resistive with an unusual increase in (P_{sw}–P_{ns}) values after a test of 1×10^{11} cycles. This abnormal switching behavior seems to be caused from the material character of the electrodes.

Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-2000-015-DP0135).

References

[1] J.F. Scott, C.A. Araujo, Ferroelectric memories, Science 246 (1989) 1400–1405.
[2] C.A. 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.
[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] U. Chon, G.C. Yi, H.M. Jang, Fatigue-free behavior of highly oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films grown on $Pt/Ti/SiO_2/Si(100)$ by metalorganic solution decomposition, Appl. Phys. Lett. 78 (5) (2001) 658–660.
[5] U. Chon, K.B. Kim, H.M. Jang, G.C. Yi, Fatigue-free samarium-modified bismuth titanate ($Bi_{4-x}Sm_xTi_3O_{12}$) film capacitors having large spontaneous polarizations, Appl. Phys. Lett. 79 (19) (2001) 3137–3139.
[6] U. Chon, H.M. Jang, M.G. Kim, C.H. Chang, Layered perovskites with giant spontaneous polarization for nonvolatile memories, Phys. Rev. Lett. 89 (8) (2002) 76011–76014.
[7] M. Keijser, G.J.M. Dormans, Chemical vapor deposition of electroceramic thin films, MRS Bull. 21 (1996) 37.
[8] H.D. Chen, K.R. Udayakumar, C.J. Gaskey, L.E. Cross, Electrical properties' maxima in thin films of the lead zirconate–lead titanate solid solution system, Appl. Phys. Lett. 67 (23) (1995) 3411–3413.
[9] R. Ramesh, J. Lee, T. Sands, V.G. Keramidas, O. Auciello, Oriented ferroelectric La–Sr–Co–O/Pb–La–Zr–Ti–O/La–Sr–Co–O heterostructures on [001] Pt/SiO_2 Si substrates using a bismuth titanate template layer, Appl. Phys. Lett. 64 (19) (1994) 2511–2513.
[10] T. Nakamura, Y. Nakao, A. Kamisawa, H. Takasu, Preparation of $Pb(Zr, Ti)O_3$ thin films on electrodes including IrO_2, Appl. Phys. Lett. 65 (12) (1994) 1522–1524.
[11] H.N. Al-Shareef, K.R. Bellur, A.I. Kingon, O. Auciello, Influence of platinum interlayers on the electrical properties of $RuO_2/Pb(Zr_{0.53}Ti_{0.47})O_3/RuO_2$ capacitor heterostructures, Appl. Phys. Lett. 66 (2) (1995) 239–241.
[12] B. Yang, S. Aggarwal, A.M. Dhote, T.K. Song, R. Ramesh, J.S. Lee, $La_{0.5}Sr_{0.5}CoO_3/Pb(Nb_{0.04}Zr_{0.28}Ti_{0.68})O_3/La_{0.5}Sr_{0.5}CoO_3$ thin film heterostructures on Si using TiN/Pt conducting barrier, Appl. Phys. Lett. 71 (3) (1995) 356–358.
[13] J. Pak, K. Nam, J. Lee, G. Park, Fabrications and electrical properties of ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films using indium-tin-oxide conductive layer as bottom electrode, J. Phys.—Condens. Mat., submitted for publication.
[14] C.H. Kim, J.K. Lee, H.S. Suh, J.Y. Yi, K.S. Hong, T.S. Hahn, Substrate temperature dependence of phase and orientation of pulsed laser deposited Bi–La–Ti–O thin films, Jpn. J. Appl. Phys. 41 (3A) (2002) 1495–1499.
[15] F. Wang, G.H. Haertling, Birefringent bistability in (Pb, La)(Zr, Ti)O_3 thin films with a ferroelectric–semiconductor interface, Appl. Phys. Lett. 63 (13) (1993) 1730–1732.