IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Fabrications and electrical properties of ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films using a indium–tin-oxide conductive layer as the bottom electrode

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 4983

(http://iopscience.iop.org/0953-8984/16/28/018)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 27/05/2010 at 15:59

Please note that terms and conditions apply.

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 4983–4990 PII: S0953-8984(04)72770-8

Fabrications and electrical properties of ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films using a indium–tin-oxide conductive layer as the bottom electrode

Jaemoon Pak, Kuangwoo Nam, Jungsuk Lee and Gwangseo Park[1]

Department of Physics, Sogang University, CPO Box 1142, Seoul 121-742, Korea

E-mail: gpark@sogang.ac.kr

Received 28 November 2003
Published 2 July 2004
Online at stacks.iop.org/JPhysCM/16/4983
doi:10.1088/0953-8984/16/28/018

Abstract
Systematic effort was made to optimize the quality of ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films, that were pulsed laser deposited onto indium–tin-oxide coated glass plates, by varying the conditions of laser fluence density, partial oxygen pressure and post-annealing temperature. Characterizations from the dielectric and ferroelectric measurements concluded that the films deposited with a laser power of 2.5 J cm^{-2}, a deposition pressure of 200 mTorr and an annealing temperature of 650 °C showed the finest electrical properties, consisting of remnant polarization ($2P_r$) and coercive field (E_c) values of 28–32 μC cm^{-2} and 90–100 kV cm^{-1}, respectively. No significant reduction in switching polarization magnitudes were observed until 1×10^{11} switching cycles, indicating that these electrical properties and the relevancy of the film with metallic-oxide ITO electrodes have satisfied the necessary requirements for applications in nonvolatile ferroelectric memory devices.

1. Introduction

Since ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) was reported as being used in nonvolatile memories [1], extensive research has been carried out in observing its ferroelectric properties when fabricated in a thin film capacitor module. There are two distinctive structures in ferroelectric random access memory (FeRAM) applications. The first and most widely investigated FeRAM device is a single transistor and single capacitor (1T–1C) structured memory device [2] that uses a ferroelectric material enclosed between metal electrodes in a parallel plate capacitor, and the other is a single transistor type memory device [3]. The issues of 1T–1C type FeRAM integration are directly related to the properties of the ferroelectric

---

[1] Author to whom any correspondence should be addressed.

© 2004 IOP Publishing Ltd Printed in the UK

film capacitor, i.e. the magnitude of polarization, processing temperature, and high fatigue resistance. Ferroelectric BLT is known to fulfil these requirements and has thus attracted tremendous attention to FeRAM research faculties worldwide.

Various approaches have been carried out to maximize the polarization magnitude by using different deposition techniques [4–6] or substituting other rare earth elements [7, 8]. Other than the above attempts, enhanced ferroelectricity has been observed through the use of conducting oxide electrodes [9, 10]. These oxide electrodes are favourable for use in FeRAM research, but problems such as difficult fabrication, high cost and complicated etching processes have proven that numerous unsolved technical issues still remain. We therefore propose the use of transparent and electrically conducting films of indium tin oxide (ITO, 1:1 ratio In_2O_2:SnO_2), a widely used electrode material in display technologies, as the conductive metal oxide bottom layers in ferroelectric nonvolatile memories.

ITO finds many applications in contemporary and emerging technologies, including applications in displays of various kinds, solar cells and electrochromic devices [11]. Other than the above applications, it can be a transparent electrode that acts as a conduction layer in floating gate memories [12]. The advantages of using ITO films with excellent conductivity include low thermal emittance and prevention of radiative cooling, which are favourable for applications in display technology. Likewise, since commercialization and long term usage of the material, technological issues such as etching and integrated circuit interconnect technologies are widely known. The above-mentioned success of the material makes it an attractive candidate for numerous application fields. This paper will report on the fabrication and electrical properties of BLT thin films on ITO layers and discuss its appropriateness as an electrode material for FeRAM applications.

2. Experimental procedures

Ferroelectric BLT films were successfully deposited on ITO coated glass substrates by the pulsed laser deposition (PLD) method. Detailed descriptions of the deposition procedure have been given elsewhere [13], where the results of its electrical properties were shown in contrast to films deposited on platinized silicon substrates. This paper is focused on the survey done on the deposition parameters and its relation to the dielectric and ferroelectric properties of the thin film capacitor.

Parameters such as laser fluence density, partial oxygen pressures and annealing temperatures are decisive factors regarding the generation of the material particulates and crystallization of the deposited film. The nature of the particulates, including the generation rate, the energy or velocity, the size, the chemistry, and the microstructure depends upon the mentioned processing conditions and the type of material used [14]. We will concentrate on these primary parameters being interpreted from the electrical measurements made after fabricating the film into a metal–ferroelectric–metallic oxide configured capacitor structure. Circular gold (Au) dots with an area of 1.44×10^{-4} cm^2 were thermally evaporated as the top metal electrodes. As the deposition rate of the material differs with respect to the laser fluence or oxygen pressure, the deposition time for every film was controlled to reveal a film thickness of 200 nm.

The films were shown to be polycrystalline from studies carried out using Rigaku Model D/Max-3C x-ray diffraction (XRD) θ–2θ measurements. The surface morphologies at different oxygen pressures were investigated by JEOL JSM-840A scanning electron microscopy (SEM) and the obtained grain size was averaged to be 20, 50 and 80 nm at the given oxygen pressures of 50, 200 and 500 mTorr, respectively. The chemical compositions of the film deposited at 400 °C in an oxygen ambient of 200 mTorr and annealed at 650 °C were measured using

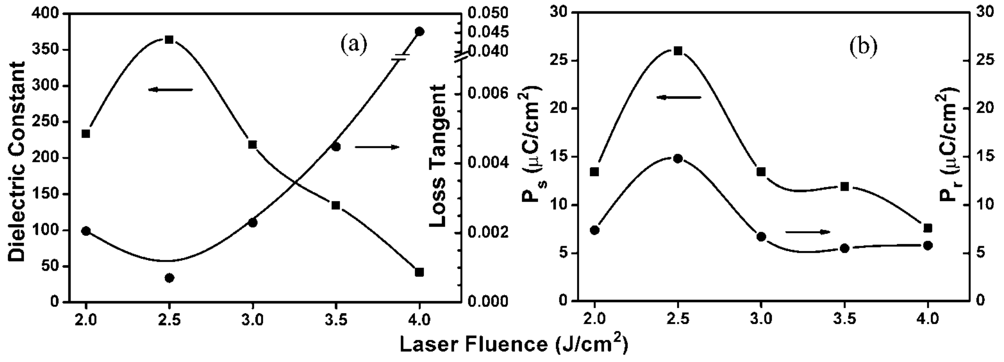

Figure 1. Variations of (a) relative dielectric constant and loss tangent values, and (b) spontaneous and remnant polarization values at various laser fluence density. Deposition was carried out at 400 °C in an oxygen ambient of 200 mTorr and annealed at 650 °C for 1 h. In order to prevent complications, the ticks and titles for the right-axis were placed into the graph itself.

a JEOL JXA-8900R electron probe microanalyser (EPMA) and it was found that the molar ratio of Bi:La:Ti was 3.66:0.59:2.81, showing the most similar values in relation to the target composition. The electrical properties of the films were characterized using a computerized impedance gain/phase analyser HP4194A and ferroelectric test system RT66A. The measured results of the dielectric properties at various conditions were plotted with a given frequency of 1 MHz, and polarization-field hysteresis loops were measured with 5 V applied voltage.

3. Results

3.1. Laser fluence

The generation of the laser plume in a pulsed laser deposition technique can be varied by applying different laser power or by alteration of the laser spot size. The incident laser beam in this report was rectangular in shape with a size of 7 mm × 3 mm, not increasing by more than 10% when the power was doubled. It was focused to scan an area having a width of 2 cm at the lower quarter of a 1 inch ceramic target with an incident angle of 45° and a target-to-substrate distance of 45 mm. For a chosen material and a fixed laser wavelength, which is 248 nm in our case, the laser fluence on the ceramic target has the most significant effect on the particulate size and density [14].

Figures 1(a) and (b) show the respective dielectric and ferroelectric properties of the fabricated films at different laser fluence densities ranging at 0.5 J $\mathrm{cm^{-2}}$ in an interval from 2.0 to 4.0 J $\mathrm{cm^{-2}}$. Other parameters during the deposition were a deposition pressure of 200 mTorr, an annealing temperature of 650 °C, and deposition times varying for each fluence step to make the film thickness roughly the same. The relations of the measured values on fluence variations showed a Gaussian-like distribution with a maxima at 2.5 J $\mathrm{cm^{-2}}$ and a minima at 4.0 J $\mathrm{cm^{-2}}$. Films deposited at 2.5 J $\mathrm{cm^{-2}}$ showed the largest dielectric constant (ε_r) of 375, remnant and spontaneous polarization (P_r, P_s) of 14 and 36 μC $\mathrm{cm^{-2}}$, respectively, and the lowest loss tangent (tan δ) value of about 0.001. On the other hand, films deposited at 4.0 J $\mathrm{cm^{-2}}$ had the highest loss tangent value of 0.046, resulting in the immense decrease of polarization values.

Bu *et al* [15] asserted that the electrical properties of the bismuth layer structured ferroelectric films were strongly dependent on the laser fluence. Therefore, optimized fluence density is required to achieve high-quality BLT films with good electrical properties, and the poor ferroelectricity observed from films deposited at higher fluence densities should be attributed to the nonstoichiometric Bi ratio in the films [16, 17]. Studies are still ongoing to find the correlations of the laser fluence density with the Bi concentration and electrical properties of these films.

3.2. Annealing temperature

Post-annealing treatments are strongly related to the physical properties of the films. Several parameters, such as the rate of temperature increase, annealing atmosphere, pressure and temperature during post-annealing treatment, are known to effectively influence film crystallizations. Orientation of thin films can be discussed from two points of view; lattice mismatch and surface energy. On a well-matched substrate, the film grows in the plane that maintains structural coherency with the substrate [18]. In our case, polycrystalline films are expected as crystallizations of the ITO layer occurring during the annealing process.

Figure 2(a) shows the XRD θ–2θ measurements for films deposited at a laser fluence density of 2.5 J cm^{-2} and treated at various annealing temperatures. Peaks at 38.1° and 44.4° are those of the XRD sample holder during measurements. The polycrystalline state in the films showed clear (117) and (200) peaks at low annealing temperatures, while weak *c*-axis crystallizations were observed for films annealed above 600 °C. Similar results were observed elsewhere for other perovskite-type ferroelectric materials [19]. It can be noticed that only the formation of perovskite phases were present, no sign of any pyrochlore phases were obtained. ITO(400) and (440) peaks were also observed at 35.7° and 51°, indicating the crystallizations of the bottom ITO layers which were previously observed in rapid thermal annealed $Bi_4Ti_3O_{12}$ films fabricated on identical substrates [20].

The chemical composition of the post-annealed films at different temperatures is given in figure 2(b). The amount of bismuth, titanium and lanthanum atoms at various temperatures are plotted with solidified squares (■), circles (●) and triangles (▲), respectively. Note that the volatility of bismuth atoms increases severely with the post-annealing temperature, which results in the relative increment of titanium and lanthanum contents. As the annealing temperature was increased to 650 °C, the concentration ratio of Bi:La:Ti was found to approach the value of 3.66:0.59:2.81, which is the closest to the concentration of the target. Further increasing the temperature resulted in a higher Bi concentration that is due to increased volatility of both Bi and Ti atoms [21].

The electrical properties of ferroelectric thin films can be characterized by their structures and compositions. Previous reports have shown that BLSF thin films strongly depend on the degree of *a*–*b* plane orientation, the grain size, and the chemical composition [22, 23]. Our results have clearly verified these assumptions. Figure 2(c) shows the ferroelectric measurements of the deposited films at different annealing conditions. As easily seen from the graph, the ferroelectric properties of low post-annealing treated samples were measured to be very weak. Recalling from XRD results, we have observed polycrystalline films, indicating that low post-annealing treatment leads to poor crystallinity of the films. This, however, is not the sole reason for the low measured results. The chemical compositions also give rise to the poor ferroelectricity.

Relative increase of titanium and lanthanum atoms arises from the volatility of bismuth, and it is known that ferroelectricity of BLSF thin films is favourable when the amount of bismuth is 15% in excess of than the amount it should be [24]. An excessive bismuth concentration also shows poor ferroelectricity, as seen for the films annealed at 500 and 550 °C. A gradually enhanced ferroelectric magnitude was obtained with increasing temperatures, but later showed a sudden declined value when the annealing treatment was carried out at 700 °C. The influence

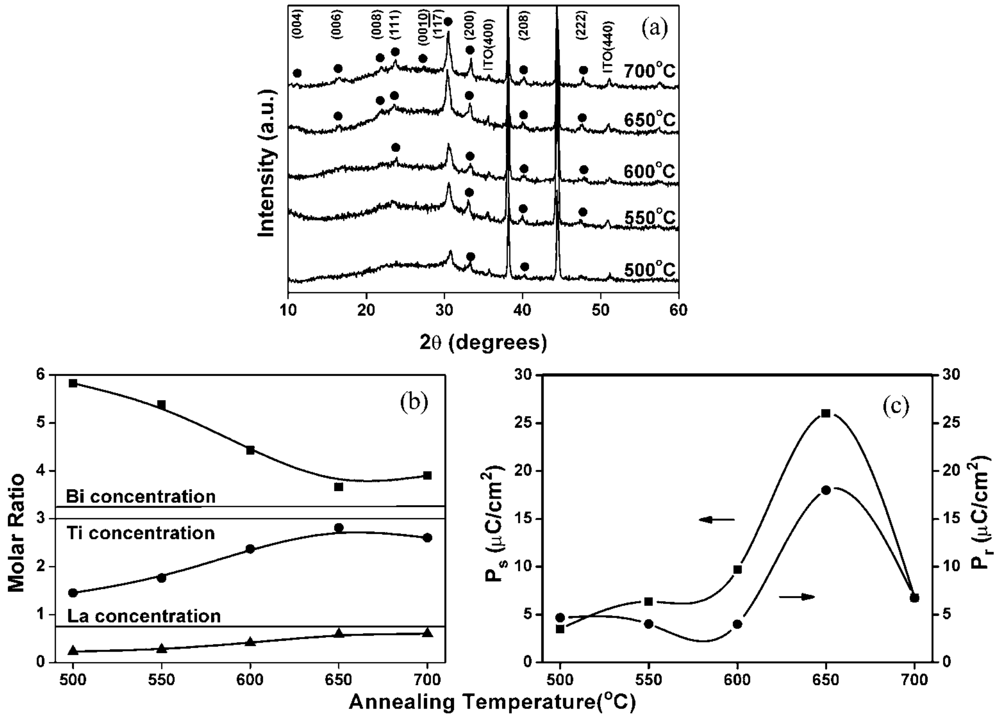

Figure 2. (a) X-ray diffraction θ–2θ scan, (b) chemical composition analysis extracted by electron probe microanalyser where the straight lines are ideal values for Bi, Ti and La, and (c) variations of spontaneous and remnant polarization values of films annealed at different annealing temperatures. Films are deposited at a given fluence density of 2.5 J cm^{-2}, a deposition temperature of 400 °C and an oxygen ambient of 200 mTorr.

of the laser fluence density on bismuth concentration is a well known occurrence in pulsed laser deposition [16, 17], but we find that the correlations of post-annealing temperatures with Bi ratio should also be considered. It has been mentioned that the volatility of both Bi and Ti atoms resulted for the films annealed at 700 °C [21], and such a decrease in electrical properties should be induced from factors regarding atomic concentrations. Besides atomic concentrations, we also notice that the ferroelectric properties of BLT films may be reduced significantly when crystallization is enhanced in the (00*l*) direction, as seen for the films treated at 700 °C, which agrees with the previously reported results [25].

This relative comparison of the electrical properties with crystallizations and atomic concentration can help conclude the resulting properties of films annealed above 600 °C. Weak ferroelectric properties observed in 600 °C annealed films were attributed to excessive Bi concentrations while influence from both crystallizations and atomic concentrations were affected in films treated at 700 °C. Films annealed at 650 °C showed relatively large electrical properties that are contributed to both factors. It is still unclear why a large difference resulted in polarization magnitudes between the films treated at temperatures of 650 and 700 °C, and thus more studies may have to be done around these temperatures.

3.3. Partial oxygen pressure

Problematic issues such as oxygen vacancies or deficiencies of the films [26] are bound to arise when a powerful physical energy, such as a laser beam, is supplied to the ceramic target.

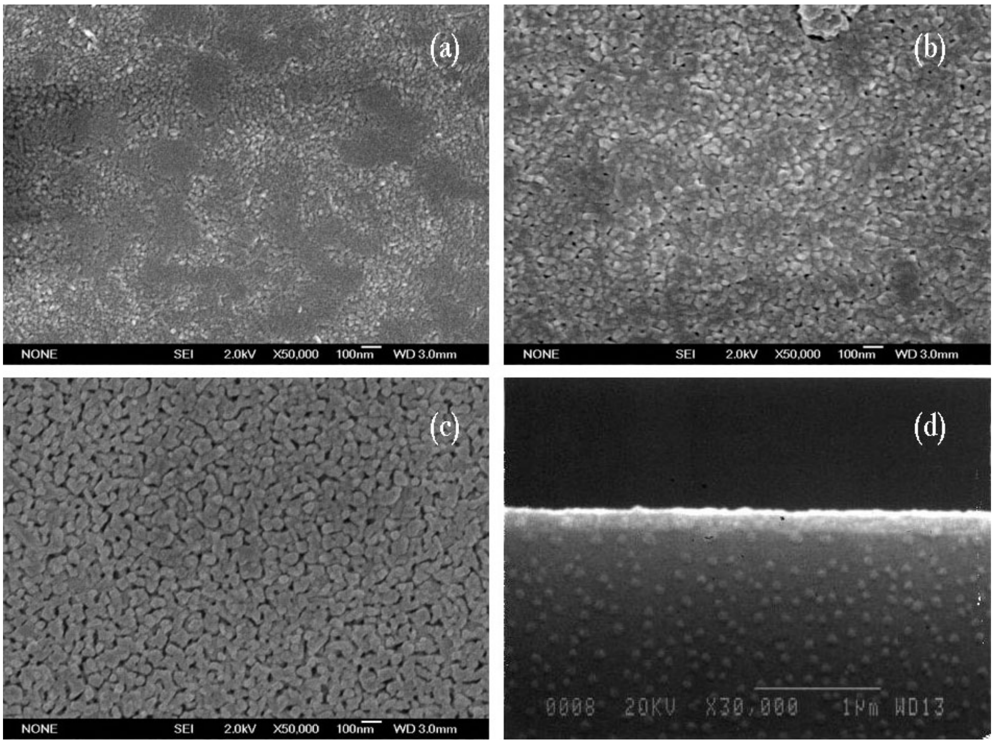

Figure 3. Surface SEM images of the films deposited at a partial oxygen pressure of (a) 50 mTorr, (b) 200 mTorr, (c) 500 mTorr and (d) cross-sectional image for the film deposited at 200 mTorr. Averaged grain sizes are 20, 50 and 80 nm at the respective pressures. The bubble-like structures seen in (d) are structural features of the glass substrates.

During the deposition process where the particles are transported to the substrate via a plume, a passive method to compensate for the lost oxygen has been applied with the presence of a nozzle right under the plume.

A direct effect on the grain growth of the material relies on the partial oxygen pressures. Other deposition parameters were a deposition temperature of 400 °C, a fluence density of 2.5 J cm^{-2}, and an annealing temperature of 650 °C. The oxygen pressures during deposition were varied at 50, 200 and 500 mTorr, and the surface morphology and electrical properties of the films were observed. Figure 3 shows the surface images of the films having columnar grains with sizes of 20 and 50 nm at deposition pressures of (a) 50 mTorr and (b) 200 mTorr, respectively. The surface of the films deposited at 500 mTorr resulted in nucleation of grain boundaries as shown in figure 3(c). The cross-sectional SEM image for the film deposited at 200 mTorr is shown in figure 3(d). The thicknesses of all films were constantly fixed to be about 2000 Å by varying the deposition time.

The electrical properties for these films were summarized in table 1. These properties at different partial pressures reveal that the films prepared at 50 mTorr are oxygen deficient while those prepared at 500 mTorr have excessive oxygen resulting in a co-existing ferroelectric and pyrochlore phase [27]. As for the film prepared at 200 mTorr, the dense surface with an average grain size of 50 nm revealed good ferroelectric properties, similar to previous results reported by other workers [5, 6, 8–10].

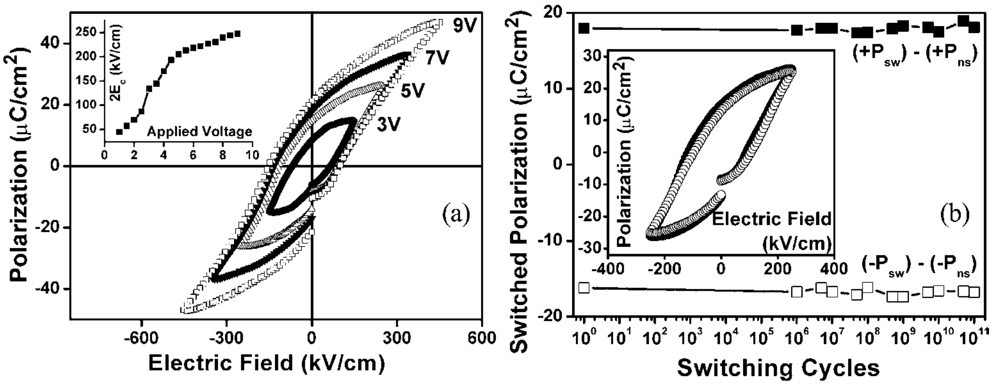

Figure 4. Optimized film deposited at 400 °C in an oxygen pressure of 200 mTorr and annealed at 650 °C, showing (a) polarization-electric field hysteresis loops with different applied voltages. The inset graph shows the plot of a doubled coercive field as a function of applied voltage, where a saturation point is observed around an applied voltage of 5 V. (b) Fatigue properties of BLT thin films under cycling frequency of 500 kHz without any significant reduction of polarization magnitude. The inset graph shows the hysteresis loops before (●) and after (○) undergoing 1×10^{11} switching cycles.

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

	50 mTorr	200 mTorr	500 mTorr
Grain size (nm)	20	50	80
Dielectric constant, ε	250	365	70
Spontaneous polarization (μC cm^{-2})	11.5	26.0	—
Remnant polarization (μC cm^{-2})	5.8	15	—
Coercive field (kV cm^{-1})	95	90	—

3.4. Ferroelectric properties

Hysteresis measurements for films deposited at 200 mTorr and post annealed at 650 °C were carried out at different applied voltages of which the results are plotted in figure 4(a). P_s and P_r values of the films at an applied voltage of 5 V were found to be approximately 25 and 15 μC cm^{-2}, respectively, which is comparable with those of the films deposited on conventional platinum electrodes [1, 4–6]. On the other hand, relatively large coercive field values in the range of 90–100 kV cm^{-1} were measured. These phenomena can be normally observed for ferroelectrics deposited on conductive oxide electrodes [28]. The leaky characteristics of the electrode material would be the main reason for such large coercive fields of the Au/BLT/ITO capacitor [18]. The inset graph shows the saturation plot of the film. As the hysteresis loops did not seem to be fully saturated, the doubled coercive field was plotted as a function of applied voltage, which resulted in a saturation point around an applied voltage of 5 V.

The fatigue properties measured at an applied field of 5 V and an external frequency of 500 kHz are shown in figure 4(b) where no significant degradation in polarization magnitudes can be observed. The inset graph shows the hysteresis loops before (●) and after (○) 1×10^{11} switching cycles, showing almost no change in polarization values. It is an interesting fact that the fatigue properties of BLT thin films are not dependent on the types of electrode used, whether they are based on pure metals or on metallic compounds [1, 4–10]. Progress is still ongoing to understand the role of metallic oxide electrodes on bismuth layered structure ferroelectric BLT thin film capacitors fabricated on other types of conductive oxide electrode.

4. Conclusions

Electrical characterizations of pulsed laser deposited $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films were performed through systematically varying the deposition conditions. In this search for an optimized film, it has been found that the electrical properties were highly dependent on crystallizations and Bi ratios at various post-annealing temperatures. On changing the partial oxygen pressures, oxygen deficient and excessive films were producible, but relatively good properties were achieved from 200 mTorr deposited films with a dense surface having columnar grains of size 50 nm. The films deposited at a given fluence of 2.5 J cm^{-2}, a deposition temperature of 400 °C and post-annealed at 650 °C showed relatively large hysteretic properties consisting of remnant polarization ($2P_r$) and coercive field (E_c) values of about 28–32 μC cm^{-2} and 90–100 kV cm^{-1}, respectively. No significant reduction in switching polarizations have been observed in the fatigue test, implying that ITO electrodes can be used as a bottom electrode layer in applications of FeRAMs or floating gate memories.

Acknowledgment

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

References

[1] Park B H, Kang B S, Bu S D, Noh T W and Jo W 1999 *Nature* **401** 682

[2] Yang B, Lee S S, Kang Y M, Noh K H, Lee S W, Kim N K, Kweon S Y, Yeom S J and Park Y J 2003 *Japan. J. Appl. Phys.* **42** 1327

[3] Yu J, Hang Z, Zhou W, Cao G, Zie J, Li X, Li S and Li Z 1997 *Appl. Phys. Lett.* **70** 490

[4] Chon U, Yi G C and Jang H M 2001 *Appl. Phys. Lett.* **78** 658

[5] Wu D, Li A, Zhu T, Liu Z and Ming N 2000 *J. Appl. Phys.* **88** 5941

[6] Hou Y, Xu X H, Wang H, Wang M and Shang S X 2001 *Appl. Phys. Lett.* **78** 1733

[7] Chon U, Kim K B, Jang H M and Yi G C 2001 *Appl. Phys. Lett.* **79** 3137

[8] Kojima T, Sakai T, Watanabe T, Funakubo H, Saito K and Osada M 2002 *Appl. Phys. Lett.* **80** 2746

[9] Yang W S, Kim N K, Yeom S J, Kweon S Y, Choi E S and Roh J S 2001 *Japan. J. Appl. Phys.* **40** 6008

[10] Saito T, Kuroiwa T, Sugahara K and Ishiwara H 2002 *Japan. J. Appl. Phys.* **41** 2105

[11] Suzuki A, Matsushita T, Aoki T, Mori A and Okuda M 2002 *Thin Solid Films* **411** 23

[12] Moise T S and Summerfelt S R 2001 *US Patent Specification* 6225655

[13] Pak J, Chang J, Nam K, Lee J, Kim J and Park G 2003 *J. Korean Phys. Soc.* **42** S1330

[14] Chrisey D B and Hubler G K 1994 *Pulsed Laser Deposition of Thin Films* (New York: Wiley–Interscience)

[15] Bu S D, Park B H, Kang B S, Kang S H, Noh T W and Jo W 1999 *Appl. Phys. Lett.* **75** 1156

[16] Bu S D, Kang B S, Park B H and Noh T W 2000 *J. Korean Phys. Soc.* **36** L9

[17] Ahn C W, Lee H J, Kang S H, Kim I W, Bae J S, Jeong J H, Yi S S and Lee J S 2003 *J. Korean Phys. Soc.* **42** s1334

[18] Eom C B, Marshall A F, Laderman S S, Jacowitz R D and Geballe T H 1990 *Science* **249** 1549

[19] Ramesh R, Luther K, Wilkens B, Hart D L, Wang E, Tarascon J M, Inam A, Wu X D and Venkatesan T 1990 *Appl. Phys. Lett.* **57** 1505

[20] Cho H-J, Jo W and Noh T W 1994 *Appl. Phys. Lett.* **65** 1525

[21] Kim C H, Lee J K, Suh H S, Yi J Y, Hong K S and Hahn T S 2002 *Japan. J. Appl. Phys.* **41** 1495

[22] Chen T-C, Li T, Zhang X and Desu S B 1997 *J. Mater. Res.* **12** 1569

[23] Noguchi T, Hase T and Miyasaka Y 1996 *Japan. J. Appl. Phys.* **35** 4900

[24] Dat R, Lee J K, Auciello O and Kingon A I 1995 *Appl. Phys. Lett.* **67** 572

[25] Sun Y M, Chen Y C, Gan J Y and Hwang J C 2002 *Appl. Phys. Lett.* **81** 3221

[26] Araujo C A, Cuchiaro J D, Mcmilan L D, Scott M C and Scott J F 1995 *Nature* **373** 627

[27] Pak J, Nam K, Lee J and Park G 2004 *Ceram. Int.* at press

[28] Al-Shareef H N, Bellur K R, Kingon A I and Auciello O 1995 *Appl. Phys. Lett.* **66** 239