THE ROLE OF BOTTOM ELECTRODE ON THE ELECTRICAL PROPERTIES OF $Bi_{3.75}La_{0.75}Ti_3O_{12}$ THIN FILMS.

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Abstract

$Bi_{3.25}La_{0.75}Ti_4O_{12}$ thin films were deposited on $LaNiO_3$, RuO_2 and $LaSr_{0.5}Co_{0.5}O_3$ electrodes by spin coating and annealed at 700°C for 10 minutes in a microwave furnace. From XRD analyses it was observed that the bottom electrode has no strong influence on the phase formation of BLT thin films. The shape and size of the grains change with the bottom electrode used. From the electrical characterization it was noticed an increase in the remnant polarization and a decrease in the drive voltage for the films deposited on LSCO/SiO_2/Si due to the significant reduction in oxygen vacancies caused by the high oxygen affinity of the LSCO electrode.

Keywords: A. Films, C. Dielectric properties, C. Fatigue, C. Ferroelectric properties, D. Perovskites.

I - INTRODUCTION

Many thin films with perovksite-type structure have been extensively investigated for a variety of integrated device applications. However, it is a generally acknowledged fact that ferroelectric oxide thin films with perovskite-type structure, deposited on $Pt/Ti/SiO_2/Si$ substrates, present serious fatigue problems after a great number of polarization switching cycles[1]. Therefore, much research has been extensively undertaken in order to obtain fatigue-free ferroelectric thin films. In order to achieve these characteristics, electrodes based on metallic oxides such as $LaNiO_3$, $SrRuO_3$, LSCO, RuO_2 and $YBa_2Cu_3O_{7-x}$, replacing the electrodes based on noble metals like platinum, and the growth of epitaxial or highly oriented thin films, are an alternative approach to reach better properties[2].

Some attempts have been made to enhance the crystallization ability of ferroelectric thin films and metallic oxide electrodes. This has stimulated a search for other techniques for the annealing process, in which conventional annealing furnace and rapid thermal annealing processes are utilized nowadays. Another approach utilizes the microwave frequency source of energy that is being developed as a way to process materials and has opened an opportunity to enhance crystallization with a lower annealing processing time since it decreases the interfacial reactions between ferroelectric thin films and electrodes and also improves the control over the crystallographic orientation of the thin films[3-4].

Recently, polycrystalline La-substituted $Bi_4Ti_3O_{12}$ (BLT) films have attracted attention because of their possible application to ferroelectric random access memories due to their high fatigue endurance as well as low deposition temperature[5]. Pure bismuth titanate [$Bi_4Ti_3O_{12}$ (BIT)] is prone to fatigue. Two reasons for the fatigue-free behavior of BLT have been found. One is the charge-compensating role of the $(Bi_2O_2)^{2+}$ 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 bismuth oxide volatility[6].

Within several preparation methods, the polymeric precursor method has a high potential for technological applications, because of their precise control of composition and homogeneity and good conformality[7]. 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).

In the present work, we report the preparation of BLT films on the metallic oxides with excellent structural, microstructural, dielectric, and ferroelectric properties by the polymeric precursor method, and a domestic microwave oven was used to crystallize these thin films.

II. EXPERIMENTAL PROCEDURE

Titanium isopropoxide (Hulls AG), bismuth nitrate (Aldrich) and lanthanum carbonate (Merck) were used as raw materials. 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 BLT deposition solution onto $LaNiO_3$, RuO_2 and LSCO electrodes previously prepared on SiO_2/Si substrates from the microwave furnace at 700°C for 10 minutes. Multilayered films were obtained by spinning 10 times the deposition solution on the surface of the substrate at 5000 rpm and completely crystallized at 700°C for 10 minutes.

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. Phase analysis of the films was performed at room temperature by X-ray diffraction (XRD) using a Bragg- Brentano diffractometer (Rigaku 2000) and CuKα radiation**.** The thickness of the annealed films was studied using scanning electron microscopy (Topcon SM-300) by looking at the transversal section. 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 under oxygen atmosphere at 300°C for 1 hour. Here, the desired effect is to decrease eventually present oxygen vacancies.

The relative dielectric constant ε_r were measured versus frequency using an impedance analyser (model 4192 A, Hewlett Packard). The leakage current-voltage (I-V) characteristic and ferroelectric properties were investigated using a Sawyer-Tower circuit attached to a computer controlled standardized test system (Radiant Technology 6000 A). For the fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses with a 10 mV amplitude were used. After the end of each fatigue period, the polarization characteristics of the films was measured over a range of frequencies.

III. RESULTS AND DISCUSSION

The X-ray diffraction data obtained for lanthanum doped $Bi_4Ti_3O_{12}$ thin films deposited with 10 layers on $LaNiO_3$, LSCO and RuO_2 electrodes and annealed at 700°C for 10 minutes in static air are shown in Fig. 1. The peaks located at 2θ = 16.4°, 21.9°, 23.6°, 30.3^0 , 33.1^0, 39.9^0 and 47.2° correspond to the polycrystalline BLT phase. Considering that the main peaks of $LaNiO_3$ and LSCO electrodes overlap with the BLT phase the only

characteristic peak of electrode which appears in the X ray data belongs to the RuO_2 at $2\theta = 28°$. In the investigated case, no preferential orientation was observed for lanthanum doped $Bi_4Ti_3O_{12}$ films deposited on different electrodes indicating that a large difference in the lattice parameters between eletrode and film inhibits preferred orientation.

Fig. 2 shows a typical surface morphology of films deposited on different electrodes. Independently of the used electrode a homogeneous surface was observed indicating that the microwave furnace allows the preparation of films with controlled morphology. As can be clearly seen, films deposited on LSCO electrodes possess a plate-like morphology of the grains when compared to the films deposited on $LaNiO_3$ e RuO_2 electrodes (rounded grains) due to the difference in the thermal expansion coefficient which changes the nucleation rate of the films.

It is well 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[8]. The dielectric constant and dissipation factor of the films present the average measurement values of three samples (Table I). It was also observed that the films deposited on different electrodes lead to the identical dielectric properties. This result is not surprising because although the film deposited in the LSCO electrode present a plate like morphology the magnitude of the grain is comparable with the films deposited on $LaNiO_3$ and RuO_2 electrodes leading to identical dieletric constants.

The insulating properties of the films were found to be dependent on the bottom electrode. As shown in Table I, the leakage current density decreased for the films deposited on LSCO electrode. Such a reduction in leakage current density may be attributed to high oxygen affinity of the LSCO electrode avoiding that oxygen in the electrode material will be depleted by the ferroelectric material, thus leaving an oxygen deficient layer of the electrode material at the interface and increasing the contact resistance.

Ferroelectricity in the lanthanum doped bismuth titanate thin films was performed in a standardized ferroelectric tester and the results were presented in Fig. 3. It can be observed that films deposited on $LaNiO_3$ and RuO_2 electrodes present trapped charge ($O_2^{"}$) associated with other defects ($V_0^{\circ\circ}$ or even defect dipole complexes such as oxygen vacancies associated to bismuth vacancies ($V^{'''}_{Bi}$ - $V_0^{\circ\circ}$) located in the grain boundary and in film-electrode interface can promote a local stoichiometry deviation influencing the shape of the hysteresis loops. These charges may be originated during the heat treatment process due to the decomposition of the polymeric precursor[9].

It can be assumed that if oxygen vacancy accumulation near the film-electrode interface occurs during heat treatment, mainly the LSCO conductive oxide can consume the oxygen vacancies by changing their oxygen nonstoichiometry and thus, the accumulation of oxygen vacancies near the interface is prevented or reduced leading to a more symetric hysteresis loop. Ferroelectricity in the films was observed with remnant polarization ranging from 11 to 23 $\mu C/cm^2$ and drive voltages from 0.85 to 1.56 V. It should also be noted that the hystereses loops of the films deposited on $LaNiO_3$ and RuO_2 electrodes show 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.

The fatigue behavior of ferroelectric thin films has been studied for several years and have been attributed to defect entrapment at film-electrode interfaces and/or at the grain and domain boundary[10]. Since all oxide electrodes such as RuO_2, LSCO, $LaNiO_3$ result in fatigue-free films, it is consequently, to believe that if oxygen vacancy accumulation near the film-electrode interface occurs during fatigue, the conductive oxide can consume the oxygen vacancies by changing their oxygen nonstoichiometry and thus, the accumulation of oxygen

vacancies near the interface is prevented or reduced. For this purpose, the LSCO electrode is the most effective to reduce the oxygen vacancies accumulated in the film-electrode interface probably due to it´s high oxygen affinity which is an important criterion for selecting electrode materials. The fatigue endurance of BLT thin films was observed up to 10^{10} cycles for all electrode oxides utilized in this study (Fig. 4). Since a La^{3+} ion has no outer electron, in contrast to a Bi^{3+} ion, which has a lone pair of 6*s* electrons, less hybridization with O 2*p* should lead to less structural distortion favouring the improvement of its ferroelectric properties.

IV. CONCLUSIONS

Polycrystalline BLT thin films were obtained on $LaNiO_3$, RuO_2 and LSCO electrodes by using the polymeric solution and spin coating technique. A plate-like morphology of the grains was observed for the films deposited on LSCO electrodes whereas rounded grains were observed for the films deposited on $LaNiO_3$ and RuO_2 electrodes. A regularly shaped hystereses loop is observed for the films deposited on the LSCO electrode due to the high oxygen affinity which avoids the migration of charge species to the electrode-film interface. High fatigue resistance was observed for films deposited on $LaNiO_3$, RuO_2 and LSCO electrodes. However, due to the imprint phenomenon the films deposited on $LaNiO_3$ and RuO_2 electrodes are unsuitable for memory applications.

ACKNOWLEDGMENTS

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FIGURE AND TABLE CAPTIONS

Fig 1. X ray diffraction for $Bi_{4-x}La_xTi_3O_{12}$ films (x = 0.75) deposited on different bottom electrodes at700°C for 10 minutes (a) $LaNiO_3$, (b) RuO_2 and (c) LSCO.

Fig 2. AFM images for for $Bi_{4-x}La_xTi_3O_{12}$ films (x = 0.75) deposited on different bottom electrodes at700°C for 10 minutes (a) $LaNiO_3$, (b) RuO_2 and (c) LSCO.

Fig 3. P-E hysteresis loop for $Bi_{4-x}La_xTi_3O_{12}$ films (x = 0.75) deposited on different bottom electrodes at700°C for 10 minutes (a) $LaNiO_3$, (b) RuO_2 and (c) LSCO.

Fig. 4. Fatigue as a function of polarization cycles for $Bi_{4-x}La_xTi_3O_{12}$ films (x = 0.75) deposited on different bottom electrodes at700°C for 10 minutes (a) $LaNiO_3$, (b) RuO_2 and (c) LSCO.

Table 1. Data obtained for $Bi_{4-x}La_xTi_3O_{12}$ films (x = 0.75) deposited on different bottom electrodes at700°C for 10 minutes (a) $LaNiO_3$, (b) RuO_2 and (c) LSCO.

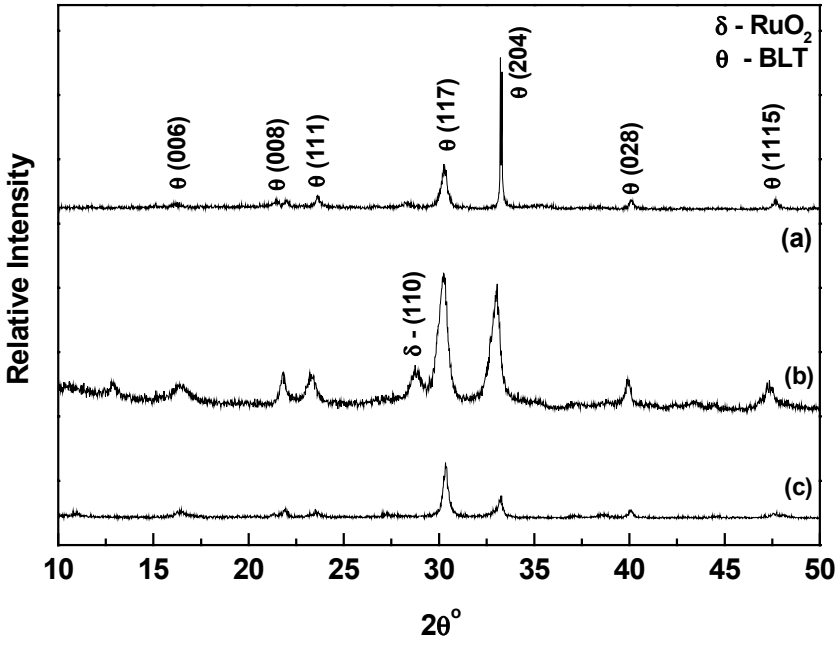
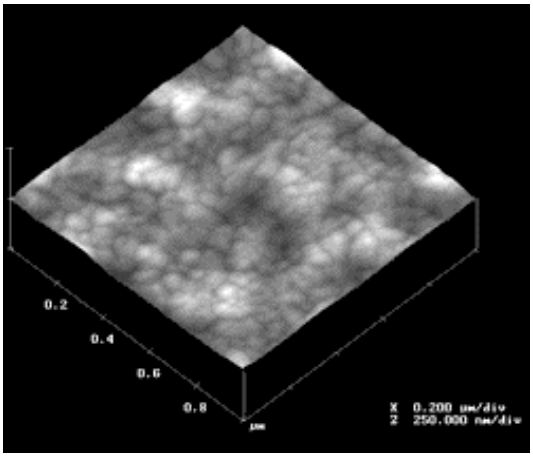
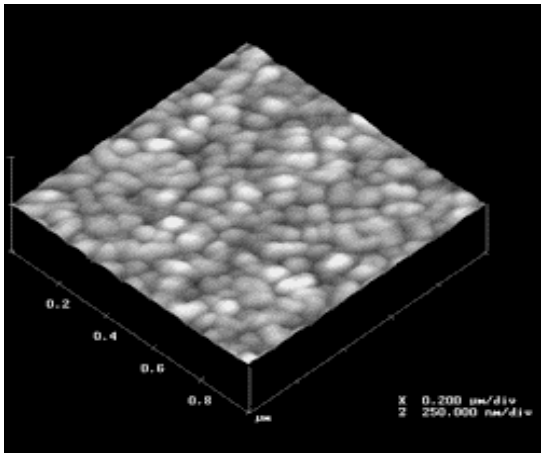


Fig 1. A. Z. Simões, M. A. Ramirez, A. Ries , E. Longo and J. A. Varela.



(a)



(b)

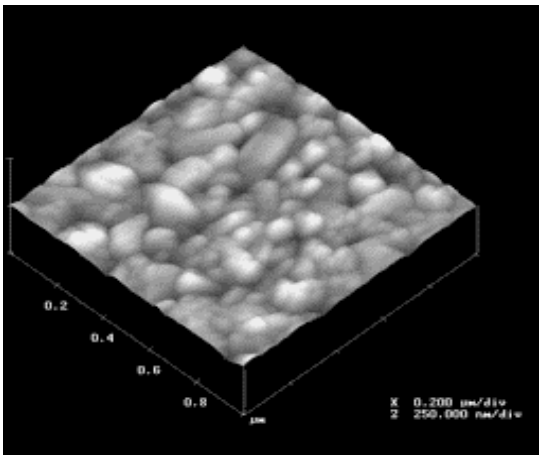


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Fig 2. A. Z. Simões, M. A. Ramirez, A. Ries , E. Longo and J. A. Varela.

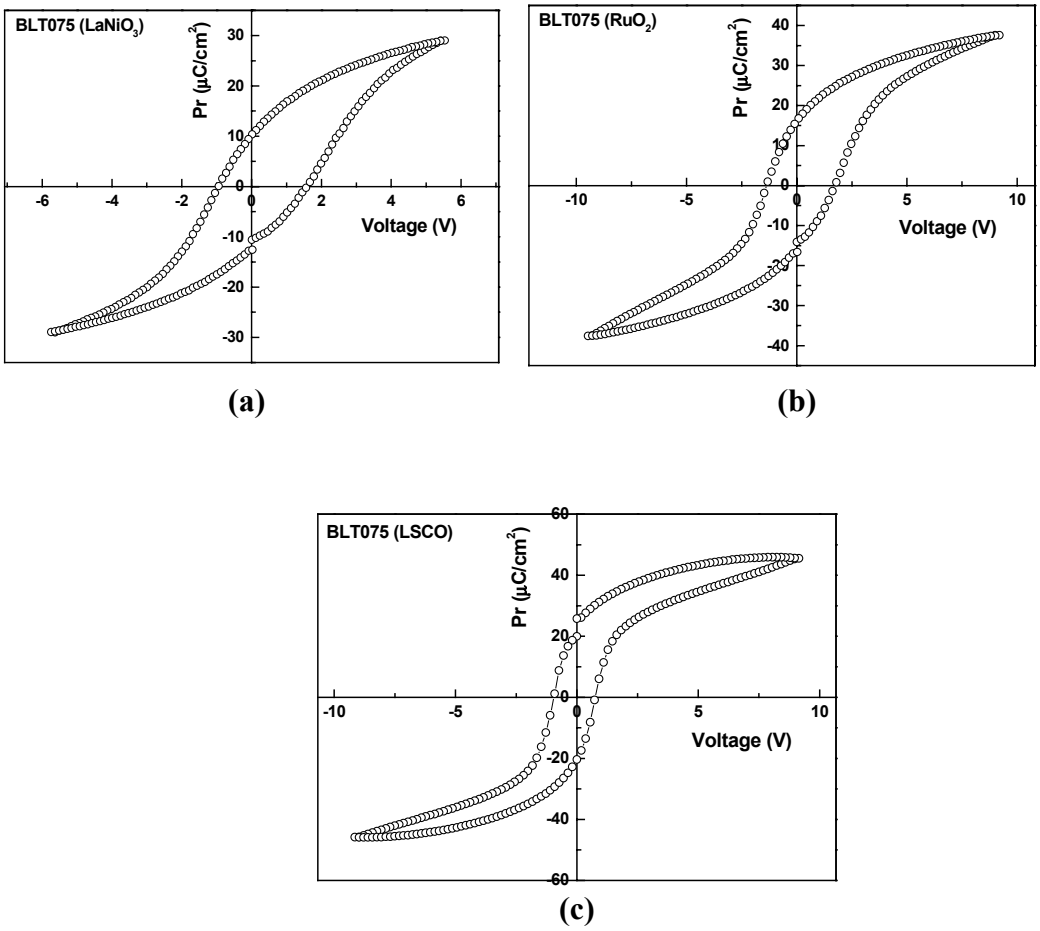
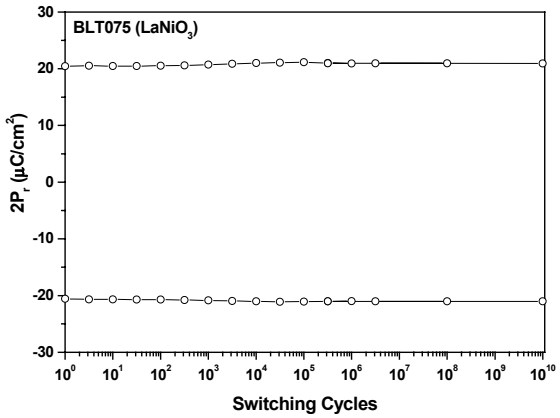
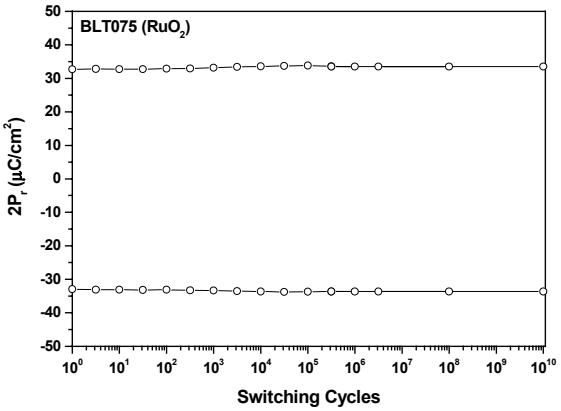


Fig 3. A. Z. Simões, M. A. Ramirez, A. Ries , E. Longo and J. A. Varela.



(a)



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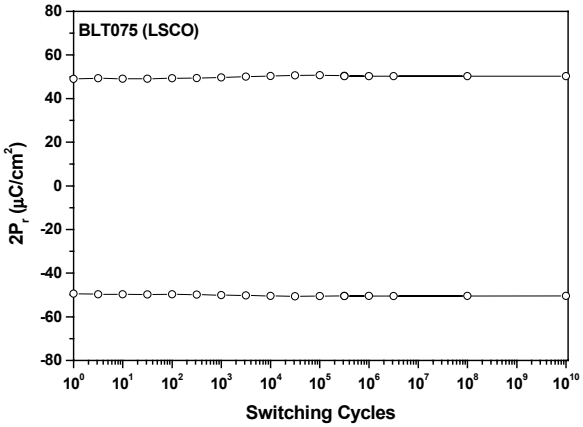

(c)

Fig 4. A. Z. Simões, M. A. Ramirez, A. Ries , E. Longo and J. A. Varela.

Table I - A. Z. Simões, M. A. Ramirez, A. Ries , E. Longo and J. A. Varela.

BLT	**P_r ($\mu C/cm^2$)**	**V_c (V)**	**J ($\mu A/cm^2$)**	**ε (1 MHz)**	**tan δ (1 MHz)**	**Roughness (nm)**	**Thickness (nm)**	**Average Grain Size (nm) ± 1%**
($LaNiO_3$)	11.4	1.26	4.3	176	0.047	4.4	283	81
(RuO_2)	16.7	1.56	2.2	160	0.019	4.3	270	58
(LSCO)	23.1	0.84	0.4	182	0.012	7.5	305	65