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Ferroelectric and Dielectric Properties of Lanthanum-Modified Bismuth Titanate Thin Films Obtained by the Polymeric Precursor Method

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Abstract. Lanthanum-modified bismuth titanate, $Bi_{4-x}La_xTi_3O_{12}$ (BLT), thin films with a La concentration of 0.75 was grown on Pt/Ti/SiO_2/Si substrates by using the polymeric precursor solution and spin-coating method. The scanning electron microscopy (SEM) showed rounded grains, which is not typical for these system. The BLT films showed well-saturated polarization-electric field curve which $2P_r = 41.4$ $\mu C/cm^2$ and $V_c = 0.99$ V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domains switching. These properties make BLT a promising material for FERAM applications.

Keywords: bismuth lanthanum titanate, FERAM, thin film

1. Introduction

$Bi_4Ti_3O_{12}$ (BTO) is a member of the ferroelectric, bismuth-layered perovskite structure family with a general formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m-1})^{2-}$ where m takes on integer values, A is a relatively large divalent or trivalent cation, and B a small, highly charged cation such as Ti^{+4}, Nb^{+5}, or Ta^{+5}. For BTO, the following values apply: A = Bi, B = Ti, and $m = 3$ [1]. This structure is composed of alternating stacked layers of bismuth oxide and bismuth titanate. The structure of bismuth titanate, first described by Aurivillius some 40 years ago and later by others [1], has the layered perovskite structure with lattice constants $a = 5.4489$ Å, $b = 5.4100$ Å and $c = 32.815$ Å ,when indexed to orthorhombic symmetry. Below the ferroelectric Curie temperature (675°C), there exists a spontaneous polarization vector which lies in the b-c plane at an angle of 4.53° to the b-axis. As a result, strong anisotropic properties are observed. In bulk, BTO shows coercive field values of 3.5 and 50 kV/cm, spontaneous polarization values of 4 and 50 $\mu C/cm^2$, and dielectric constant of 130 and 160, along the c- and b-axis, respectively [2]. For nonvolatile memories, ferroelectric thin films with low coercive field are required. Low coercive field translates to lower operating voltage, faster switching speed, and better fatigue resistance. Since the c-component of polarization involves only 180° switching, there is no associated transverse strain. The small coercive field and 180° switching of the c-component make the c-axis-oriented BIT thin films an attractive capacitor material in destructive readout (DRO) ferroelectric random access memory (FERAM) or a gate dielectric in nondestructive readout (NDRO) ferroelectric memory or field-effect transistor (FEMFET) designs [3]. To optimize the properties of BTO thin films, it is obvious that c-axis [001]-oriented films are preferred. Another advantage of BTO is its high Curie temperature. This should minimize thermal depolarization problems.

Several attempts to prepare BTO thin films are reported in the literature. Due to the high temperatures required for the formation of the ferroelectric perovskite

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phase, the production of BTO thin film has not proved easy and, at present, a wide range of thin films synthesis techniques, such as MOCVD, sol-gel, RF magnetron, ion beam sputtering, and laser ablation are subject to intensive research [4]. Nakamura [5] deposited by MOCVD technique highly *c*-axis-oriented BTO thin films with a $Bi_2Ti_2O_7$ buffer layer on Pt/SiO_2/Si (100). The film had a relatively low coercive field (13 kV/cm), but the remanent polarization was very low (0.6 $\mu C/cm^2$). Wang [6] developed an atmospheric pressure MOCVD technique to prepare BTO thin films. These films exhibited high (100) orientation with high remanent polarization (38 $\mu C/cm^2$) and high coercive field (45 kV/cm). Si and Desu [7] fabricated randomly oriented BIT thin films at low temperature (550°C) by hot-wall MOCVD. A remanent polarization of 19 $\mu C/cm^2$ and a high coercive field of 244 kV/cm was obtained.

Obviously, the substitution of bismuth for lanthanum influences the ferroelectric properties of this material dramatically. Bu et al. [8] prepared thin films of BTO doped with lanthanum by pulsed laser deposition. The authors found that these films were appropriate for non-volatile random access memory devices.

In previous works, our group have reported the preparation of thin films by the polymeric precursor method [9]. The overall process consists of preparing a coating solution by the type process, based on metallic citrate polymerization [10]. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase.

Considering that the literature reports no data about the preparation of lanthanum doped BTO films through a polymeric precursor method, in this work, we describe our preliminary 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. From this solution the films were deposited by the spin-coating technique on (111) Si/Ti/Pt substrates. A platinum layer (140 nm) was used as bottom electrode. The BLT films were then calcinated at 700°C for 2 h in air resulting in a film thickness of approximately 220 nm. Next, a 0.3 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 hour. Here, the desired effect is to decrease eventually present oxygen vacancies.

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 were performed at room temperature by X-ray powder diffraction (XRD) using a Bragg-Brentano diffractometer (Rigaku 20-2000) and Cu K_α radiation.

Microstructural characterization of the films was carried out using scanning electron microscopy SEM (Topcon SM-300). The thickness of the annealed films was studied using scanning electron microscopy (Topcon SM-300) by looking the transversal section. The thickness results obtained from SEM represent an average value of three measurements. The relative 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 by the MFM configuration using a small AC signal of 10 mV at 100 kHz. The signal was measured 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). 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 were measured over a range of frequencies.

3. Results and Discussion

Figure 1 shows the collected XRD data of the BLT film. Only peaks of the BTO phase were detected suggesting that substitution of Bi by La does not lead to formation of secondary phases. The split of the (0100) and (200) peaks into two duplets indicates the change of crystal structure from the orthorrombic to the tetragonal system. Besides the BLT peaks, the characteristic peak for (111) platinum coated silicon substrates at $2\theta = 40^\circ$ was identified. Comparing the peak intensities of the BLT pattern to some BTO literature [8], the addition of 0.75 La results in a preferred orientation at $2\theta = 16^\circ$. This fact could be probably due to the change of the crystal system orthorrombic to tetragonal.

SEM photograph of the surface of BLT film is shown in Fig. 2. For pure BTO obtained by several methods a plate-like morphology of the grains was observed [11]. Our results show that lanthanum changes this typical morphology because the grains are rounded. The image also reveals that the surface appears to be dense, smooth and cracks free. The grains are evenly distributed with an average grain size of 140 nm.

The dielectric constant and dissipation factor of the films are presented in the Fig. 3. The dielectric measurements were carried out at room temperature as a function of frequency in the range of 10 kHz – 1 MHz. The annealed films exhibited good dielectric properties, a dielectric constant, ε, of 158 and loss tangent, $\tan\delta$, of 3.6×10^{-3}, at 1 MHz. As shown in Fig. 3, the dielectric constant shows very little dispersion with frequency indicating that our films possess low defects concentration at the interface film-substrate. Otherwise, with an increase of frequency, the dissipation factor rises, indicating that the conductivity of the films increases with the measuring frequency. The low dispersion of the dielectric constant and the absence of any relaxation peak in $\tan\delta$ indicate that interfacial polarization of the Maxwell Wagner type and that produced by the electrode barrier is negligible in the film. It was also observed that La doped films comparing with pure BTO possess higher dielectric constant and lower loss tangent indicating that the lanthanum plays an important role on the electrical properties of the thin BTO layers [11].

Figure 4 illustrates the C-V curve for BLT film obtained at 100 kHz by imposing a dc voltage of +10 to −10 V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domains switching. The C-V curve also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization

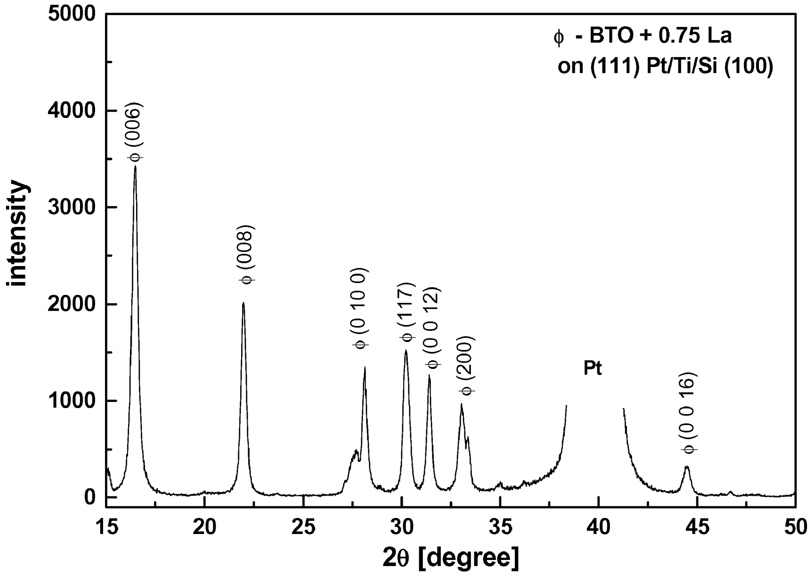

Fig. 1. X-ray diffraction for BLT film deposited by the polymeric precursor method and annealed at 700°C for 2 hours.

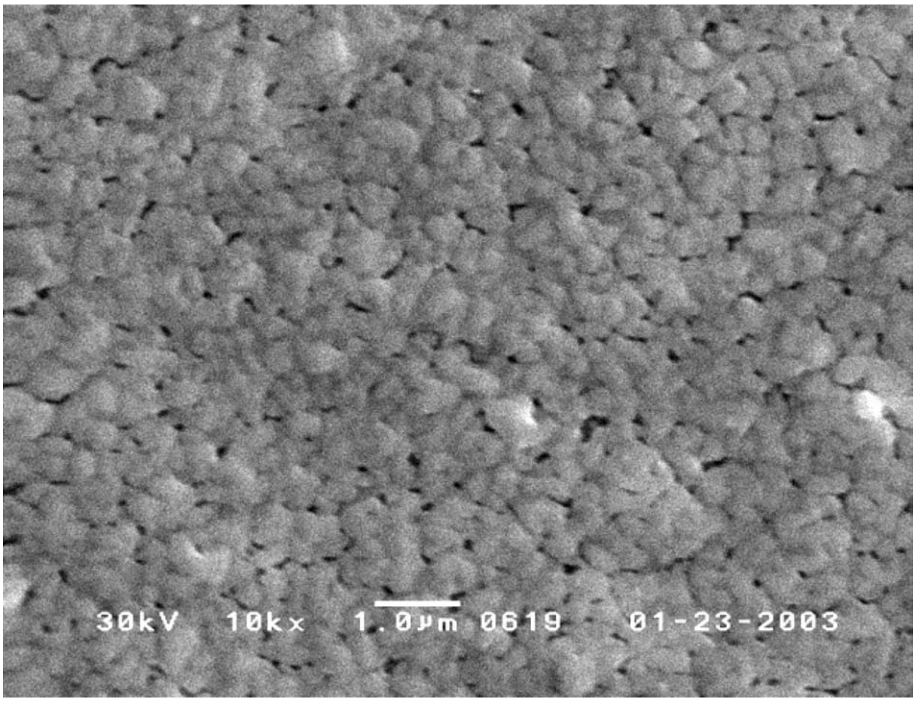

Fig. 2. SEM photograph for BLT film deposited by the polymeric precursor method and annealed at 700°C for 2 hours.

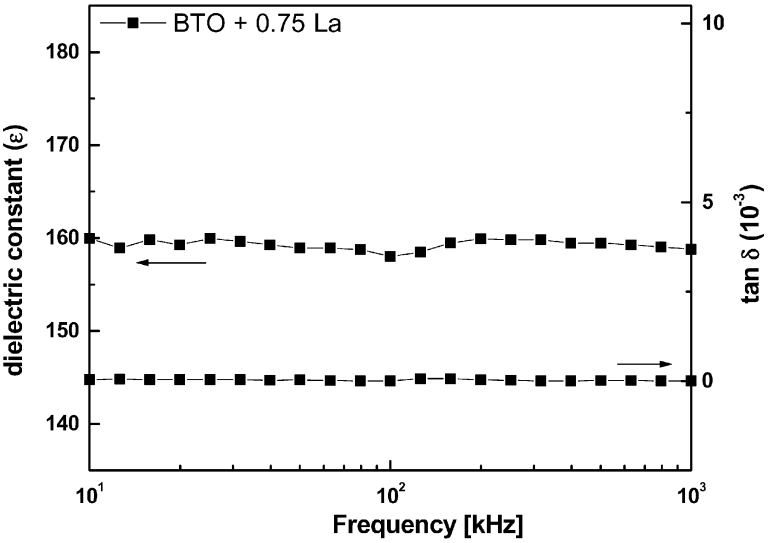

Fig. 3. Dielectric constant and loss tangent in dependence of frequency for BLT films obtained by the polymeric precursor method and annealed at 700°C for 2 hours.

switching. The C-V curve is symmetric around the zero bias axis, indicating that the films contain few movable ions or charge accumulation at the film-electrode interface.

Ferroelectricity in the BLT thin films was performed in a standardized ferroelectric tester and the resulting hysteresis curve is presented in Fig. 5. The hysteresis loop was measured at a frequency of 100 Hz and an

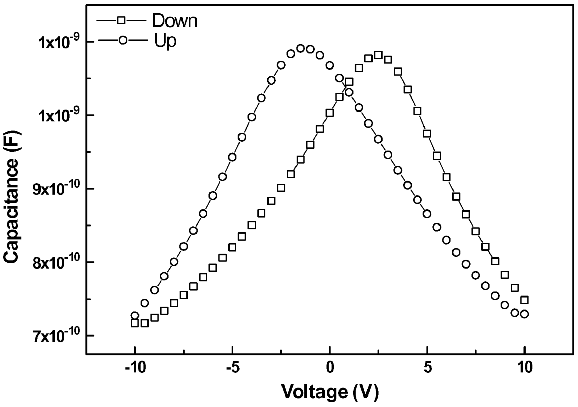

Fig. 4. C-V curve for BLT film deposited by the polymeric precursor method and annealed at 700°C for 2 hours.

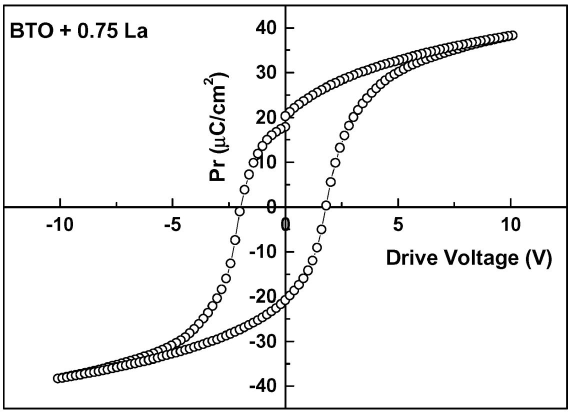

Fig. 5. P-E hysteresis loop for BLT film deposited by the polymeric precursor method and annealed at 700°C for 2 hours.

applied voltage in the order of 10 V. The loop is fully saturated with a remanent polarization $2P_r$ of 41.4 μC/cm^2 and drive voltage of 1.0 V. The saturation of the loop at this low frequency indicates that the losses are minimal, suggesting the films are highly resistive. It may also be seen from Fig. 4 that the remanent polarization was much higher than that normally expected for a perfect c-axis oriented single crystal and may be ascribed to the presence of a-axis polarization components, as also seen from the XRD data. However, to the best of our knowledge, such highly saturated loops are being reported for the first time from the polymeric precursors method of bismuth titanate thin films.

The fatigue endurance of BLT thin films as a function of switching cycles was examined by applying 8.6 μs wide bipolar pulses with a 10 mV amplitude (Fig. 6).

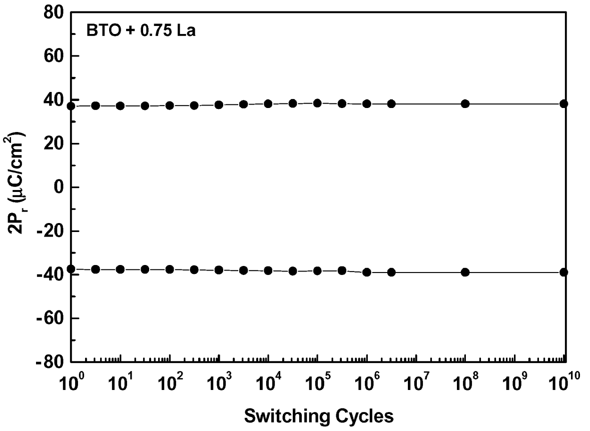

Fig. 6. Fatigue as a function of polarization cycles for BLT film deposited by the polymeric precursor method and annealed at 700°C for 2 hours.

Fatigue resistance was observed up to 10^{10} cycles indicating that the substitution of La for Bi can change the chemical environment of the perovskite layers and solve the fatigue problem of pure BTO 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. In order to understand all the phenomena involved on the fatigue behaviour of BLT thin films new tests should be accomplished in future.

4. Conclusions

Dense lanthanum doped bismuth titanate films on (111) platinum coated silicon substrate were obtained through polymeric precursors solution by a spin-coating technique. The films show a homogeneous structure with low porosity combined with good ferroelectric properties, e.g. a regularly shaped hysteresis loop and low conductivity ($2P_r = 41.4$ μC/cm^2 and low drive voltage $V_c = 1.0$V). Because of their high remanent polarization and fatigue free behaviour, the 0.75 lanthanum doped BTO films are good candidate for FeRAMS applications.

Acknowledgments

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