Influence of the solution pH on the morphological, structural and electrical properties of Bi$_{3.50}$La$_{0.50}$Ti$_3$O$_{12}$ thin films obtained by the polymeric precursor method

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Abstract

Lanthanum-doped Bi$_4$Ti$_3$O$_{12}$ thin films (BLT) were deposited on Pt/Ti/SiO$_2$/Si substrates using a polymeric precursor solution. The spin-coated films were specular, crack-free and crystalline after annealing at 700 °C for 2 h. Crystallinity and morphological evaluation were examined by X ray diffraction (XRD) and atomic force microscopy (AFM). The stability of the formed complex is of extreme importance for the formation of the perovskite phase. Films obtained from acid pH solution present elongated grains around 200 nm in size, whereas films obtained from basic solution present a dense microstructure with spherical grains (100 nm). The dielectric and ferroelectric properties of the BLT films are strongly affected by the solution pH. The hysteresis loops are fully saturated with a remnant polarization and coercive voltage of $P_r = 20.2$ µC/cm$^2$ and $V_c = 1.35$ V and $P_r = 15$ µC/cm$^2$ and $V_c = 1.69$ V for the films obtained from basic and acid solutions, respectively.

Keywords: Crystal structure; Dielectrics; Ferroelectrics; Thin films

1. Introduction

Ferroelectric thin films have received considerable attention in recent decades for the potential applications in nonvolatile random access memories [1]. Among related materials of interest, lead zirconate titanate (PbZr$_x$Ti$_{1-x}$O$_3$, PZT) is probably the most extensively studied. PZT films have favourable characteristics, including high polarization, a low processing temperature, and remaining apparently fatigue-free when used as conducting oxide electrodes [2,3]. Nevertheless, environmental safety issues concerning the Pb-containing formula may ultimately prevent it from being used in many applications. Layer-structured perovskite like strontium bismuth tantalate (SrBi$_2$Ta$_2$O$_9$, SBT) has also been studied [4]. Although SBT is a fatigue-free material, the practical application of SBT is limited, primarily due to its small polarization ($2P_r = 4–16$ µC/cm$^2$) and high processing temperature of over 750 °C.

Recently, polycrystalline La-substituted bismuth titanate (Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$, 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]. Compared with another well-known fatigue-free ferroelectric material SrBi$_2$Ta$_2$O$_9$ (SBT) which is also a Bi-layered perovskite oxide, BLT has many attractive properties, such as low processing temperature and large values of remnant polarization. However, pure bismuth titanate (Bi$_4$Ti$_3$O$_{12}$, BIT) is prone to fatigue. Two reasons for the fatigue-free behaviour of BLT have been found. One is the charge-compensating role of the (Bi$_2$O$_2$) layers. Another is the suppression of oxygen vacancies after substituting some La atoms for Bi atoms, since the oxygen ions near Bi ions in BIT are likely to be

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less stable than those near Sr ions in SBT due to the high volatility of bismuth oxide [6–8].

It is well known that the phase formation is directly related with the purity of the precursor, processing method, as well as of the time and temperature of the reaction. Any change in these parameters can induce the formation of the undesired phases [9], as it was already observed in the process of preparation of PZT [10] by the polymeric precursor method. This chemical method involves the formation of a chelate through the reaction of the citric acid with the metallic cation, followed by polyesterification with ethylene glycol. Even so, this reaction presents a chemical memory, in which the metallic cations responsible to form the net can be separated. The key for the obtaining of perovskite phase is intimately related with the structure originating from the chemical memory.

Ferroelectric films have been fabricated by rf sputtering [11], pulsed laser deposition [12], electron cyclotron resonance plasma sputtering [13] and metalorganic chemical vapor deposition [14]. In this work, we report the preparation of BLT thin films on platinum-coated silicon substrates by the polymeric precursor method. Compared with other techniques, the polymeric precursor method has the advantages of easier composition control, better homogeneity, low processing temperature (compatible with Si processing), easier fabrication of large areas and low cost [15]. In this work, BLT thin films were prepared by the polymeric precursor method. The effects of solution pH on the structural, morphological and electrical properties of BLT thin films were investigated.

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 concentrated aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Ti, Bi and La were mixed and homogenized by stirring at 90 °C. The solution pHs were adjusted at values of 3 and 9. To obtain the basic pH, ethylenediamine was added to the solution until a complete complexation of the cations was present in the system. 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$_{x-1}$La$_x$Ti$_3$O$_{12}$ ($x = 0.50$) deposition solution onto Pt/Ti/SiO$_2$/Si substrate. It was observed from a previous work that BLT films were completely crystallized at 700 °C for 2 h; so this was the temperature at which films were heat-treated [16]. Multilayered films were obtained by spinning 5 times (pH = 3, [M] = 0.1 mol L$^{-1}$) and 10 times (pH = 9, [M] = 0.05 mol L$^{-1}$) the deposition solution on the surface of the platinum-coated silicon substrate previously cleaned with Extran solution and ethanol. The films were heat-treated at 400 °C for 2 h with a heating rate of 3 °C/min in a conventional furnace and immediately crystallized at 700 °C for 2 h, before the next deposition. All films were heat-treated in static air. In this work, an excess of 5.0 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 as it has been reported in the literature [17]. 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 morphology of the annealed films was studied using scanning electron microscopy. The thicknesses were measured from the transversal section by using back-scattering electrons (Topcom SM-300). 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 with a constant heating rate of 1 °C/min, in oxygen atmosphere for 1 h. Here, the desired effect is to decrease eventually present oxygen vacancies.

The relative dielectric constant $\varepsilon_r$ and dissipation factor (tan δ) were measured versus frequency using an impedance analyser (model 4192 A, Hewlett Packard). The capacitance–voltage characteristic was recorded 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 characteristic was recorded with a voltage source measuring unit (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

It is well known that the thickness of the layer is a function of viscosity, ionic concentration of the solution and spinning speed. It is important to control the thickness of the layer due to its strong influence on the grain size, dielectric and ferroelectric properties. It was observed that for thinner films interfacial “dead layers” could appear at the interface between films and substrate. These layers possess poor dielectric properties influencing the performance of the device [18]. These dead layers are originated from oxygen interdiffusion, chemical reaction, or structural defects at the
interfaces and could be suppressed with thickness of films higher than 200 nm. Considering that the ionic concentration differs greatly from one solution to another it was necessary to increase the number of layers for the basic solution in order to reach the minimum thickness value to get desired electrical properties.

Fig. 1 shows the collected XRD data of the BLT films deposited from solution with different pHs. Independent of the solution pH only peaks of the BLT phase were detected suggesting that substitution of Bi by La does not lead to formation of secondary phases. Besides the BLT peaks, the characteristic peak for (111) platinum-coated silicon substrates at $2\theta=40^\circ$ was identified. It is confirmed from XRD results that the BLT films are polycrystalline in nature with a single perovskite phase independent from the pH of the solution.

Fig. 2 shows a typical surface morphology of the film obtained from different pHs solution. The roughness measured is about 11 nm. These results are better compared to polycrystalline films obtained by chemical methods (about 17 nm) and similar to that obtained by physical method (nearly 9 nm) [19,20]. Table 1 presents the average grain size and roughness values for films obtained at different pHs. The average grain sizes obtained from AFM represent an average value of several measurements performed in the length and width of each single grain. An increase in the grain size was observed for acid solution and can be caused by the higher ionic concentration of this solution which retains more material deposited on the surface of the substrate leading to bigger grains. A strongly marked difference in the film microstructure can be observed for the different solution pHs used to obtain the films. The films obtained from solution with pH=3 present a typical bismuth layer perovskite structure. As reported for films with good ferroelectric properties the grain size was around 200 nm with an elongated shape [21]. On the other hand, the films obtained from solution with pH=9 presented spherical grains around 100 nm in size. The difference in the shape of the grains could be of the fact that the complexation of the metals by the carboxyl groups is dependent of the solution pH. The complexation of bismuth by citric acid leads to a linear polymer and a typical plate-like morphology. Meanwhile, the addition of ethylenediamine competes with the citric acid for the complexation of the bismuth site making the volumetric effect more pronounced and leading to a rounded grain morphology. Another reason is that in acid pH the molecule is more symmetrical because of the largest number of tied up hydrogen, which increases the possibility of a homogeneous interaction between any of the carboxyl groups. However, in the basic pH citric acid is partly deprotonated, decreasing the symmetry of the molecule and the possibilities of a homogeneous interaction. A similar behaviour was observed for (PMN) thin films obtained by the polymeric precursor method where it was noticed that basic pH of niobium solution lead to pyrochlore phase and neutral pH to the perovskite [22].

The dielectric constant and dissipation factor of the films are presented in Table 1. The obtained results indicate that the films obtained from acid solution possess a dielectric constant higher than films obtained from basic solution. Considering that the dielectric constant depends on several factors such as annealing temperature, grain size, type of electrodes and phase composition it

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**Fig. 1.** X-ray diffraction data for Bi$_{x}$La$_{x}$Ti$_3$O$_{12}$ ($x=0.5$) thin films deposited from (a) acid solution and (b) basic solution.

**Fig. 2.** AFM images for BLT films ($x=0.5$) deposited from (a) acid solution and (b) basic solution.
could be observed that the dielectric constant increases with the increase in grain size. Taking into account that the magnitude of the grain size is mainly dependent on the ionic concentration and solution pH one can say that both parameters deeply influence the dielectric properties of lanthanum-doped bismuth titanate thin films. The increase in losses for the basic solution can also be attributed to the small grain size present in these films favouring the pinning of domain walls by defects segregated in the wall regions. Our dielectric properties are consistent with the crystallographic and microstructural data.

The $I-V$ measurements were taken using the radiant technology tester in the current–voltage mode, with the voltage changing from 0 to $+10$ V, from $+10$ to $-10$ V and back to 0 V. Table 1 shows the leakage data for the BLT films obtained from different pH solutions. The leakage current density at 1.0 V increases from 0.55 to 4.29 $\mu$A/cm$^2$ when the pH is increased from 3 to 9. The lower leakage current observed for the film obtained from the acid solution may be attributed to probable differences in grain size, density, and surface structure. The characteristics of the film–

<table>
<thead>
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<th>pH</th>
<th>$P_r$ ($\mu$C/cm$^2$)</th>
<th>$J$ (1 V) ($\mu$A/cm$^2$)</th>
<th>$V_c$ (V)</th>
<th>$\varepsilon$ (1 MHz)</th>
<th>$\tan \delta$ (1 MHz)</th>
<th>Roughness (nm)</th>
<th>Thickness (nm)</th>
<th>Average grain size (nm)</th>
</tr>
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<td>1.35</td>
<td>112</td>
<td>0.024</td>
<td>11.4</td>
<td>418</td>
<td>208</td>
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<td>9</td>
<td>15.1</td>
<td>4.29</td>
<td>1.69</td>
<td>80</td>
<td>0.048</td>
<td>13.9</td>
<td>275</td>
<td>103</td>
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The ferroelectricity in the BLT thin films was performed with a standardized ferroelectric tester and the results are presented in Fig. 3. The hysteresis loops were measured at a frequency of 100 Hz and an applied voltage in the order of 10 V. The loops are fully saturated with a remnant polarization of the films ranging from 15 to 20 $\mu$C/cm$^2$ and coercive voltages from 1.35 to 1.7 V. The saturation of the loops at these low frequencies indicates that the losses are minimal, suggesting the films are highly resistive. A more regularly shaped hysteresis loop is observed for films obtained from solution with acid pH. It may also be seen in Fig. 3 that the remnant polarization was much higher than normally expected for a perfect $c$-axis-oriented single crystal and may be

![Fig. 3. $P-E$ hysteresis loop for BLT films ($x=0.5$) deposited from (a) acid solution and (b) basic solution.](image)

![Fig. 4. $C-V$ curves for BLT films ($x=0.5$) deposited from (a) acid solution and (b) basic solution.](image)
The fatigue characteristics of BLT films deposited on silicon substrates have been studied extensively. Fatigue is saturated at accumulation at the film–electrode interface. Although the films contain few movable ions or charge deposited from (a) acid solution and (b) basic solution. Compared to literature data, our results are similar to those published by Lee et al.\[24\]. The authors showed the fabrication of BLT films. Fatigue resistance was observed up to $10^{10}$ cycles independently of the pH solution used. B. H. Park et al. also verified the fatigue characteristics of BLT films deposited on platinum-coated silicon substrates. They observed that the values of $(P_{sw}/P_{m})$ do not change significantly during the fatigue test indicating that the BLT films have good fatigue resistance [6]. 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 2p should lead to less structural distortion favouring the improvement of its properties [25]. 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.

### 4. Conclusions

Independently of the solution pH used to obtain the films, dense lanthanum-doped bismuth titanate films on (111) platinum-coated silicon substrate were obtained through polymeric precursors solution by a spin-coating technique. An evident difference in the shape of the grains was noted when the films were obtained from different solution pHs. The $C−V$ measurements of the BLT films in metal–ferroelectric–metal configuration presented two peaks ascribed to ferroelectric domain switching. Because of their high remnant polarization and low coercive voltage, Bi$_{4−x}$La$_x$Ti$_3$O$_{12}$ ($x=0.50$) films are good candidates for FeRAM applications. No fatigue behaviour was verified in both cases which proves that these films possess enough quality to be used in non-volatile random access memories.

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### References