The influence of crystallization route on the properties of lanthanum-doped Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} thin films prepared from polymeric precursors

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Abstract

Pure and lanthanum-doped Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} thin films were deposited on Pt/Ti/SiO\textsubscript{2}/Si substrate using a polymeric precursor solution. The spin-coated films were specular and crack-free and crystalline after annealing at 700 °C for 2 h. Crystallinity and morphological evaluation were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Multilayered films obtained using the intermediate-crystalline layer route present a dense microstructure with spherical grains. Films obtained using the intermediate-amorphous layer, present elongated grains around 250 nm in size. The dielectric and ferroelectric properties of the lanthanum-doped Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} films are strongly affected by the crystallization route. The hysteresis loops are fully saturated with a remnant polarization and drive voltage of the films, heat-treated by the intermediate-crystalline (P\textsubscript{r} = 20.2 μC/cm\textsuperscript{2} and V\textsubscript{d} = 1.35 V) and for the film heat-treated by amorphous route (P\textsubscript{r} = 22.4 μC/cm\textsuperscript{2} and V\textsubscript{d} = 2.99 V).

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1. Introduction

Ferroelectric switching fatigue, which is the loss of switchable polarization by repeated polarization reversals, is one of the most common and important degradation processes in ferroelectric materials [1]. Because of the fatigue-free behavior of lanthanum-substituted bismuth titanate [Bi\textsubscript{4-x}La\textsubscript{x}Ti\textsubscript{3}O\textsubscript{12} (BLT)], a bi-layered perovskite oxide with a platinum electrode has received increasing attention in ferroelectric applications, such as in nonvolatile memory [2,3]. Compared with another well known fatigue-free ferroelectric material SrBi\textsubscript{2}Ta\textsubscript{2}O\textsubscript{6} (SBT) which is also a bi-layered perovskite oxide, BLT has many attractive properties: low processing temperature and large values of remnant polarization. But pure bismuth titanate [Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{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\textsubscript{2}O\textsubscript{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 [3–5].

Obviously, the substitution of bismuth by lanthanum influences the ferroelectric properties of this material dramatically. Bu et al. [6] prepared thin films of BIT doped with lanthanum by pulsed laser deposition. The authors found that these films were appropriate for non-volatile random access memory devices. It is known that BIT compounds have a high leakage current and domain pinning due to defects such as Bi vacancies (V\textsubscript{Bi}) accompanied by oxygen vacancies (V\textsubscript{O}). In order to minimize these defects, the substitution of Bi by La ion on A-site is required [7]. It is known that the role of A-site substitution is to displace the volatile Bi with La to suppress the A-site vacancies which are accompanied by oxygen

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vacancies that act as space charges. It has been reported that ferroelectric properties were improved by ion doping on A- or B-site [8]. Recently, effects of ion doping on ferroelectric properties and electrical conduction have been widely studied [9]. For practical FRAM application, it is necessary to obtain BLT thin film with high remnant polarization and low leakage current.

Several thermal treatments can be used to crystallize thin films obtained by chemical methods such as: rapid thermal annealing, microwave furnace and conventional furnace. In a conventional furnace, two types of thermal treatment can be performed. The first one consists of decomposing the organic material at low temperatures (usually 400 °C) and crystallizing the film at high temperatures. Those steps are repeated until the desired thickness is obtained (this route is called “intermediate-crystalline layer”). In the second route, all organic materials are decomposed (usually 400 °C) until the desired thickness is obtained and then all layers are crystallized in a single high-temperature process (called “intermediate-amorphous layer”).

The crystallization route was found to affect the microstructure of the films [10]. It is well known that films treated by the intermediate-crystalline layer route consists of relatively small number of grains and a microstructure with isolated perovskite grains of uniform size [11,12]. This route favours a higher nucleation rate leading to a higher number of crystalline nuclei. As a consequence, the grain growth decreases leading to a fine grain microstructure. In the case of the film heat-treated by intermediate-amorphous layer route, the nucleation rate may be lower, promoting a lower number of crystallization sites (nuclei) leading to increased grain growth. One possible explanation for the increase in the grain size for the different crystallization routes can be the thermal history of the first layer. A nucleus formed on the thermal treatment of the first layer can grow during the treatment of the next layers. So, the crystallization of the film changes, leading to an increase in the grain size. Basically in this case, the nucleation starts from the film surface [13].

Several attempts to prepare BIT thin films are reported in the literature. Due to the high temperatures required for the formation of the ferroelectric perovskite phase, the production of BIT thin film has not proved easy and, at present, a wide range of thin film synthesis techniques, such as MOCVD, sol-gel, rf magnetron, ion beam sputtering, and laser ablation are subjected to intensive research [14–18]. Nakamura [19] deposited highly c-axis oriented BTO thin films with a Bi$_2$Ti$_2$O$_7$ buffer layer on Pt/SiO$_2$/Si by MOCVD technique. This film had a coercive field of 133 kV/cm and also very low remnant polarization (0.6 μC/cm$^2$). Wang [20] developed an atmospheric pressure MOCVD technique to prepare BTO thin films. These films exhibited high (1 0 0) orientation with high remnant polarization (38 μC/cm$^2$) and high coercive field (45 kV/cm). Si and Desu [21] fabricated randomly oriented BIT thin films at low temperature (550 °C) by hot-wall MOCVD. A remnant polarization of 19 μC/cm$^2$ and a high coercive field of 244 kV/cm were obtained. In previous works, our group had reported the preparation of thin films by the polymeric precursor method [22]. The overall process consists of preparing a coating solution based on metal citrate polymerization. The precursor film is deposited by dip or spin coating and then thermally treated to eliminate the organic material and synthesise the desired phase.

In this work, pure and La-doped BIT thin films were prepared by the polymeric precursor method. The effects of crystallization route on the ferroelectric and dielectric properties of BIT thin films were investigated.

2. Experimental procedure

2.1. BIT and BLT deposition solutions

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 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.

2.2. Preparation of BIT and BLT films

Films were spin-coated from Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ (x = 0—BIT) and Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ (x = 0.25, 0.50 and 0.75 —BLT) deposition solution onto Pt/Ti/SiO$_2$/Si substrate. From a previous paper, BLT films were completely crystallized at 700 °C for 2 h, so this was the temperature at which films were heat-treated [23]. Multilayered films were obtained by spinning five times the deposition solution on the surface of the platinum-coated silicon substrate previously cleaned in Ethanol solution and ethanol. Two sets of multilayered films were heat-treated by two different routes. Route A, films were heat-treated at 400 °C for 2 h with heating rate of 3 °C/min in a conventional furnace and spun again, until the desired number of layers was reached. Each layer was amorphous and all layers were crystallized at 700 °C for 2 h at the same time. Route B, each layer was heat-treated at 400 °C for 2 h with heating rate of 3 °C/min in a conventional furnace and immediately crystallized at 700 °C for 2 h, before the next one. Hereafter, this procedure will be called the intermediate-crystalline layer route. All films were heat-treated in static air. Fig. 1 illustrates the procedure. In this work, an excess of 5 wt.% 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
reported in literature [24]. Phase analysis of the films was performed at room temperature by X-ray diffraction, using a Bragg-Brentano diffractometer (Rigaku, 2000) and Cu Kα radiation. The morphology of the annealed films was studied using scanning electron microscopy (Topcon SM-300). The BLT film surfaces were analyzed without any cover or special preparation and with incidence of secondary electrons detection while the thickness were measured from the transversal section. In this case back-scattering electrons were utilized. 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 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 measured 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). All measurements were performed at room temperature. For the fatigue measurements, internally generated 8.6-s-wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristcs of the films were measured over a range of frequencies.

3. Results and discussion

Fig. 2a and b show the collected XRD data of the BLT films heat-treated for both routes. Independent of the used route, 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 (1 1 1) platinum-coated silicon substrates at \( 2\theta = 40^\circ \) was identified. Independently of lanthanum content, films obtained by the route A (Fig. 2a) are polycrystalline. In contrast, for the route B, the increase in lanthanum content leads to preferential orientation in the (001) direction (Fig. 2b–d). Considering that the thickness of the film obtained by the intermediate-crystalline layer route is lower when compared with the film obtained by the intermediate-amorphous layer, the appearance of preferential orientation due to interface nucleation was observed [12]. In the interface nucleation the crystallization process starts from the surface of substrate which possess oriented planes with lower energy for the crystallization of BLT phase. In contrast, for route A, the higher thickness may give rise to other phenomena, like surface nucleation originating a polycrystalline film.

![Flow chart of the thin film preparation process by the polymeric precursor method](image)

![X-ray diffraction for Bi\(_{4-x}\)La\(_{x}\)Ti\(_3\)O\(_{12}\) films heat-treated by route A (a) and route B (b), respectively: (a) x = 0; (b) x = 0.25; (c) x = 0.5; and (d) x = 0.75.](image)
Fig. 3 presents the SEM micrographs of the Bi$_{4-x}$La$_x$Ti$_3$O$_12$ films ($x = 0.50$) heat-treated by different routes. Here, the lanthanum content ($x = 0.50$) was randomly chosen in order to verify the effect of the crystalline route on the structural, morphological and electrical properties of the BLT thin films. The average grain sizes obtained from SEM represent an average value of several measurements performed in the length and width of each single grain. A strongly marked difference in the film microstructure can be observed for the different crystallization routes used for heat-treating the films. The film heat-treated by route B presents a dense and granular microstructure, with spherical grains around 200 nm in size. The absence of cracks and fissures indicates that the film presents a uniform microstructure. For the route A (Fig. 3a) a dense and granular microstructure is maintained, although the grains become elongated (250 nm in size). The difference in the shape of the grains is related to the amount of material deposited on the substrate surface to crystallize the films. Considering that the films treated by the intermediate-crystalline layer route, possess less material to be crystallized layer by layer, the grains tend to assume the more energetic favourable form (rounded). Meanwhile, the films treated by the intermediate-amorphous layer route possess a large amount of material to be crystallized in a single-step process leading to a less energetic favourable form (elongated grains).

Fig. 4 shows a typical surface morphology of the film heat-treated by both routes. 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) [25,26]. Table 1 presents the average grain size and roughness values for films heat-treated by both routes. The results presented show that different crystallization routes lead to films with different microstructures. The films crystallized using the route A presents a typical bismuth layer perovskite structure. As reported, for films with good ferroelectric properties...
Table 1
Data obtained for BLT films ($x = 0.5$) heat-treated by: (a) intermediate-amorphous layer and (b) intermediate-crystalline layer

<table>
<thead>
<tr>
<th></th>
<th>$P_s$ (µC/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) ± 1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>22.4</td>
<td>2.99</td>
<td>112</td>
<td>0.024</td>
<td>11.6</td>
<td>453</td>
<td>250</td>
</tr>
<tr>
<td>Crystalline</td>
<td>20.2</td>
<td>1.35</td>
<td>112</td>
<td>0.024</td>
<td>11.4</td>
<td>418</td>
<td>208</td>
</tr>
</tbody>
</table>

the grain size was around 250 nm with elongated shape [27]. On the other hand, the films crystallized using the route B presented spherical grains around 200 nm in size. Considering both crystallization routes, the route B seems to favour a higher nucleation rate, leading to a higher number of crystalline nuclei. Each intermediate-crystalline BIT layer acts like a nucleation seed to the next layer to be crystallized. In the case of route A, the nucleation rate may be lower, promoting a lower number of crystallization nuclei, leading to an increase in the grain growth and resulting in a bigger grain microstructure. Basically, the nucleation occurs in the film surface and in the film–substrate interface.

The dielectric constant and dissipation factor of the films are presented in Fig. 5. The dielectric measurements were carried out at room temperature as a function of frequency in the range of 10 kHz–1 MHz. As shown in Fig. 5, the dielectric constant shows very little dispersion with frequency indicating that our films possess low defect concentrations at the film–substrate interface. The low dispersion of the dielectric constant and the absence of any relaxation peak in $\tan \delta$ indicate that both, interfacial polarization of the Maxwell–Wagner type and a polarization produced by the electrode barrier can be neglected in the film. It was also observed that the films treated by different routes lead to the identical dielectric properties. This result is not surprising because although the film heat-treated by the intermediate-crystalline layer route present a rounded grains morphology, the magnitude of the grain is comparable with the films heat-treated by the intermediate-amorphous layer route leading to identical dielectric constants. Therefore, to obtain higher dielectric properties a-oriented films are desired. Our results of $\varepsilon$ 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. Fig. 6 shows the $I$–$V$ curves for the BIT films heat-treated by different routes. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an ohmic conduction. At higher field the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanisms. The leakage current density at 1.0 V decreases from $5.6 \times 10^{-7}$ to $2.7 \times 10^{-7}$ A/cm$^2$ when the intermediate-amorphous layer route is used to heat-treat the films. The lower leakage current observed for the film heat-treated by intermediate-amorphous layer might be attributed to probable differences in grain size, density, and surface structure due to differences in crystallization procedures. The characteristics of the film–electrode interface and the surface morphology of BLT thin films are the major factors determining the leakage current of capacitors in metal–ferroelectric–metal configuration. Giridharan et al. [28] observed similar behaviour to BIT films prepared by sol–gel method with leakage current density of $10^{-7}$ A/cm$^2$ at an electric field of 60 kV/cm. M. Sedlar [29] reported leakage current density of $10^{-9}$ A/cm$^2$ at an applied voltage of 1.0 V. In addition, M. Sedlar [29] reported leakage current density of $10^{-9}$ A/cm$^2$ at an electric field of 60 kV/cm for BIT thin films prepared by sol–gel method.

Fig. 7 illustrates the $C$–$V$ curves for BLT films obtained at 100 kHz and dc sweep voltage from $+10$ to $-10$ V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting...
from the domain switching. The $C-V$ curve for the film heat-treated by the intermediate-crystalline layer also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization 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. For the film heat-treated by the intermediate-amorphous layer a slight change in capacitance values is observed indicating that charge carriers exist, trapped near the electrode–film interface.

Ferroelectricity in the BLT thin films was performed with a standardized ferroelectric tester and the results are presented in Fig. 8. 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 20 to 22 $\mu$C/cm$^2$ and drive voltages from 1.35 to 3.0 V. The saturation of the loops at these low frequencies indicates that the losses are minimal, suggesting that the films are highly resistive. A more regularly shaped hysteresis loop is observed for films heat-treated by the intermediate-crystalline layer. It is observed that the intermediate-crystalline layer leads to films with preferred orientation which results in lower drive voltages to attain saturation in polarization hysteresis. It may also be seen from Fig. 7a, that the remnant polarization was much higher than 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. Compared to literature data, our results are similar to those published by Lee et al. [30]. The authors showed the fabrication of high-quality films of bismuth lanthanum titanate prepared by chemical synthesis method and their applications in handsets, smart phones and smart cards. It should also be noted that the hysteresis loop of the film heat-treated by amorphous route shows an appreciable 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. These two effects may cause a memory failure. These results are consistent with the $C-V$ measurements.
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. 9). Fatigue resistance was observed up to $10^{10}$ cycles, independent of the route 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 $(P_{\text{sw}} - P_{\text{ns}})$ do not change significantly during the fatigue test indicating that the BLT films have good fatigue resistance [7]. Since a La$^{3+}$ ion has no outer electron, in contrast to a Bi$^{3+}$ ion, which has a lone pair of 6s electrons, less hybridization with O 2p should lead to less structural distortion favouring the improvement in its properties [31]. 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. 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$_2$O$_2$)$_2^{2+}$ 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. Conclusion

Independent of the route used to obtain the films, dense lanthanum-doped bismuth titanate films on (1 1 1) 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 prepared by the intermediate-amorphous layer route. The dielectric properties of the films were independent of the crystallization route. The C–V measurements of the BLT films in metal–ferroelectric–metal configuration presented two peaks ascribed to ferroelectric domain switching. From the electric field dependence of the leakage current, space charge limited currents can be dominant on BLT/Pt junction. Because of their high remnant polarization and low drive voltage, Bi$_{3-x}$La$_x$Ti$_3$O$_{12}$ (x = 0.50) are good candidates for FeRAMs applications. No fatigue behaviour was verified in both cases, which proves that our films possess enough quality to be used in non-volatile random access memories. However, due to the imprint phenomenon, the films obtained by the intermediate-amorphous layer are unsuitable for memory
applications as a consequence of the substantial difference between $+\nu_c$ and $-\nu_c$.

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