Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ films on La$_2$Ti$_2$O$_7$ thin films prepared by Chemical Solution Deposition.

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Abstract. We report the synthetic and physical procedures for obtaining the Lanthanum-substituted Bi$_4$Ti$_3$O$_{12}$ (BLT) ferroelectric films, Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$, with its polarisation axis (a) oriented perpendicular to the surface of the electrode by employing partially oriented (001) polycrystalline thin films of La$_2$Ti$_2$O$_7$ (LTO) as a buffer onto Si-wafers. The LTO thin film was achieved by dip coating and annealing at high temperatures while the BLT film was deposited using RF magnetron sputtering and annealing at a temperature as low as 650°C. Furthermore, the dependence of the thickness, grain size and orientation of the LTO films on the withdrawal speed of the dip-coating and annealing temperature is reported.

1. Introduction

Among the ferroelectric materials, perovskite type structures and their layered derivatives are of much interest due to their particular characteristics: high remanent polarization, high coercivity and low applied voltage during reading-writing cycles in non-volatile ferroelectric memories (NVFRAM). Initially, PbZr$_x$Ti$_{1-x}$O$_3$ (PZT) was found to have all these characteristics but suffers from fatigue, especially when Pt electrodes are deposited to switch the applied voltage. Recently, other layered perovskites were suggested as candidates to overcome this drawback. Among them, the Aurivillius’s phases, SrBi$_2$(Nb or Ta)$_2$O$_6$ (SBN or SBT) or Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ (BLTx) [1] were investigated. These materials are built up of MO$_6$ (M=Nb, Ta, Ti) octahedra sharing corners forming bilayered SBT or SBN or trilayered BLT. The so-obtained perovskite sheets are separated, along the c axis, by Bi$_2$O$_2^{2+}$ layers adopting a fluorite arrangement. The particularity of the BLTx is the anisotropy of the polarization which lies along [1 0 0]. An interesting way to optimize the remanent polarization in the ferroelectric response of BLTx films is to deposit the structure with the layers perpendicular to the bottom electrode and therefore to the substrate. Such an orientation has been successfully induced when BLT films were deposited on (110) planes of the conductive SrRuO$_3$ perovskite [2],[3] or on (110) Pt faces since the misfit with (110) planes of perovskite is quite low [4]. Among the layered perovskites, Nanot-Queyroux’s phases [5] A$_a$B$_b$X$_{3a+2}$, A=Ln, Sr, Ba or Na, B=Ti, Nb, Ta, X=O, F, 2≤n≤6, are formed by stacking layers which are cut along the (110) plane of the perovskite instead of (100) as for SBT or BLT. Due to the preferential [001] orientation of these layered structures, the thin
films exhibit naturally at the very surface a (110) plane of perovskite. Our aim is to use such a buffer layer to induce the growth of Pt (as bottom electrode) along (110) or to favor the (011)-oriented BLT film. In order to minimize the misfit between both titanates, we chose La$_2$Ti$_2$O$_7$ (LTO) as a buffer layer, since the lattice mismatch between LTO and BLT is lower than 3%. In addition, LTO presents a high Curie temperature of 1500°C and hence exhibits piezoelectric and electro-optic effects [6],[7]. The layers are formed by four TiO$_6$ octahedra sharing corners, in which the La cations occupy the center of the perovskite cages [8]. Since LTO melts congruently at 1790°C [9], obtaining a pure phase generally requires annealing at high temperatures, especially when using a classical solid state reaction involving lanthanum and titanium oxides as precursors. Alternative low temperature routes were developed involving co-precipitation [10], [11] or urea precipitation [12], hydrothermal treatments [13], self combustion methods with citric acid and ethylene glycol[14]-[17 and more widely sol-gel techniques [18],[19]. However organo-metallic reactants are expensive, moisture sensitive and highly toxic (especially acetylacetonate salts). Such criteria lead us to develop a method starting from inorganic reactants such as a Ti oxychloride solution to synthesize La$_2$Ti$_2$O$_7$, as detailed below in the experimental section.

Among deposition techniques, sputtering or PVD (Physical Vapour deposition technique) enables one to deposit at low temperature well-crystallized films with a good uniformity over large areas. During the past decade, PVD has been successfully used to deposit perovskite thin-films, using a multi-component oxide target [20]. Recently, researchers suggested that the use of a buffer layer may be an interesting solution to obtain bilayered perovskite films with enhanced dielectric constant [21]-[23]. Therefore, on the basis of our first results on BLT thin films deposition by RF magnetron sputtering [24], we present here first investigations on the effect of a La$_2$Ti$_2$O$_7$ buffer layer, previously deposited by dip coating, on the structure and orientation of the BLT films deposited subsequently by RF magnetron sputtering.

2. Experimental

Commercially available TiOCl$_2$ solution in HCl, (Millenium TiOCl$_2$,1.4HCl,7H$_2$O, 4.85 mol.L$^{-1}$ in HCl) was used as starting material. The solution is neutralized and the TiO$_2$ nH$_2$O gel is precipitated by an excess of ammonium hydroxide (typically 1 mL TiOCl$_2$ is precipitated with 10mL NH$_4$OH, 6.5 mol.L$^{-1}$). Cl$^-$ anions are to be removed since their incorporation in the oxide framework would alter the crystallization. After filtering and careful washing with water, in order to avoid Cl$^-$ ions, the TiO$_2$.nH$_2$O gel was dissolved in nitric acid (5 mL HNO$_3$, 5 mol.L$^{-1}$ is then necessary to obtain a clear solution). The absence of chlorine is checked on the dried gel by EDX. Such procedure allows us to prepare a stable solution with a [Ti$^{IV}$] concentration up to 1 mol.L$^{-1}$. The lanthanum nitrate is then introduced in stoichiometric molar ratio La/Ti =1. The required amount is added to the Ti$^{IV}$ solution in order to vary the La$_2$Ti$_2$O$_7$ concentration in the 0.075 to 0.45 mol.L$^{-1}$ range, and thus investigate the effect of Ti$^{IV}$ concentration.

Silicon wafers (100), used as substrates for dip coating, were pretreated in HCl and then rinsed in boiling acetone or ethanol. Dip coatings were performed using a DC-multi/4 Nima Dip Coater, allowing control of the dipping rate. Four dipping rates were investigated: 15, 40, 80 and 120 mm.min$^{-1}$, and before pulling, the substrate was maintained in immersion for 2 minutes. After deposition, each layer was allowed to dry at room temperature in a 50% RH atmosphere for 1 h. 6 deposition-drying cycles were performed before the final annealing at high temperature ranging from 600 to 1000 °C. The X ray diffraction (XRD) patterns were recorded in the 2θ region of 5-55° and a 0.03° scan step at a 1° grazing angle, for films deposited on Si substrate (1x1 cm$^2$). Each diagram was accumulated for 3h in order to enhance the signal to noise ratio.

Scanning Electron Microscopy images were recorded using a JEOL JSM-6400F microscope, (Akishima, Japon) with a field emission gun. The chemical composition of the films was checked by Energy dispersive spectrometry (EDX) at a voltage of 10 kV. Analyzing SEM images provided us information related to grain size.
RF magnetron sputtering of BLT films were performed in a customized reactor equipped with a 25 mm diameter planar magnetron cathode (with a balanced magnetic field) [24]. A target was prepared by Spark Plasma Sintering at 750°C for 5 minutes. The powder was obtained by precipitation with ammonium hydroxide and a thermal treatment at 600°C was performed in order to decompose the hydroxides before sintering. Depositions were performed at 60W RF power and a total pressure of 47 mTorr, in an argon/10% oxygen gas mixture. Substrates were located downstream at 7.5 cm from the target. A two step deposition process, duration of 70 min, was involved with an intermediate (1 hour) and final (4 hours) ex-situ annealing at 650°C under flowing oxygen.

3. Results and discussion

Our aim is to develop in the LTO layer a grain growth with the c axis perpendicular to the substrate and to further induce the BLT deposition along a-axis, as illustrated in figure 1.

3.1.1. La$_2$Ti$_2$O$_7$ as a buffer layer. The optimisation of LTO thin layer deposition by dip coating will be described in detail elsewhere. The best results regarding the crystalline quality of the films were obtained for [Ti$^{4+}$]=0.30 mol.L$^{-1}$ and six deposition-drying cycles performed at RT. The surface of LTO layers, as checked by AFM before thermal treatment, exhibits a granular morphology with an average and homogeneous grain size of 30 nm and a roughness of 1 nm (estimated for 5x5 µm$^2$ area). The La/Ti ratio determined by EDX analysis is, as expected, equal to 1. Finally, the crystallisation of the titanate is performed at 1000°C for 12h in air.

![Figure 1: representations of the epitaxial relationship between LTO and BLT.](image1)

![Figure 2: X-ray diffraction patterns of films, prepared at different withdrawal speeds, (a) 15 mm.min$^{-1}$, (b) 40 mm.min$^{-1}$, (c) 80 mm.min$^{-1}$ and (d) 120 mm.min$^{-1}$, annealed at 1000°C for 12h.](image2)

Figure 2 presents the XRD diagrams of LTO layers obtained at different pulling rates and shows variation of the LTO orientation after crystallization. La$_2$Ti$_2$O$_7$ films with enhanced (00$l$) reflections can be deposited for a pulling rate of 80 mm.min$^{-1}$ or 120 mm.min$^{-1}$ and a further annealing at 1000°C for 12h, as evidenced by the XRD patterns. Sample thickness was determined by SEM imaging (figure 3). A 75 nm thick LTO film was obtained for a dipping rate of 80 mm.min$^{-1}$, whereas smaller thicknesses were obtained for the other pulling rates: around 50 nm for 15 and 40 mm.min$^{-1}$ (figure 3, (a)) and less than 20 nm for 120 mm.min$^{-1}$ (figure 3, (d)). On the basis of the Landau-Levich equation [25], the amount of reactant on the substrate is expected to increase as the withdrawal speed increases. Therefore, assuming a homogeneous density of the film, a thickness increase would have been expected with increasing pulling rate. In our case, this evolution is
verified only for pulling rates in the 15 to 80 nm.min\(^{-1}\) range. We assume this could be related to the grain size evolution as the speed rate increases. In all conditions, the grain size distribution is roughly bimodal. The first population of particles exhibits size ranging from 80 (15 mm.min\(^{-1}\)) to 100 nm for speed rate higher than 40 mm.min\(^{-1}\).

**Figure 3**: SEM images of two LTO films obtained by dip-coating in a [Ti\(^{4+}\)] = 0.30 mol.L\(^{-1}\) solution for two withdrawal speed after annealing at 1000°C for 12h in air: 40 mm.min\(^{-1}\) (a) cross section by backscattered imaging, (b) secondary image of the film surface and 120 mm.min\(^{-1}\) (c) cross section by backscattered imaging, (d) secondary image.

In addition, for a deposition performed at 15 mm.min\(^{-1}\), the grain size of the second population is centered on 130 nm, whereas when the pulling rate increases from 40 to 80 mm.min\(^{-1}\), the grain size of the particles increase to 200-220 nm and even up to 270 nm for 120 mm.min\(^{-1}\). When the speed rate is increased, the amount of reactant on the substrate is larger. Therefore, the growth is favored with respect to nucleation and Ostwald ripening upon annealing leads to bigger grains for higher speed rates. Based on previous results [26], we assume that these larger particles are oriented along [001] as required.

3.1.2. **RF magnetron sputtering of BLT on LTO buffer layer.** BLT films were deposited by RF magnetron, for sputtering conditions described in the experimental section, on La\(_2\)Ti\(_2\)O\(_7\) buffer layer oriented along c-axis (obtained for a withdrawal rate of 120 mm.min\(^{-1}\)). As shown on figure 4, a preferential orientation of the BLT layer along the a-axis was obtained after the final annealing for a 500 nm thick BLT layer (inset (a)). When comparing powder diffraction intensities (blue bars) a sharp and intense (200) peak is evidenced in the XRD diagram. The particle size ranges between 30 and 80 nm as measured on SEM image (cross view) whereas the surface of the film (inset (b) in figure 4) exhibits a melted aspect.

This preliminary study validates our two-step process, including two thermal treatments, i.e. an intermediate between the two deposition steps (1 hour) and a final one (4 hours), both at 650°C under oxygen. Such procedure leads to the better results, since a single deposition followed by an ex-situ annealing at 650°C appears not suitable to favor any orientation of the BLT film.

**Figure 4**: X-ray diffraction pattern of a BLT film sputtered on an oriented LTO buffer layer on Si substrate, bars: diffraction peaks of (Bi(La))\(_3\)Ti\(_3\)O\(_{12}\), insets SEM a) cross and b) plane views.

4. **Conclusion**
A two step RF magnetron process performed at low O\(_2\) content, high pressure and low RF power allowed us to partly control the crystalline orientation of sputtered BLT layers. We succeed to induce such preferential growth of Bi\(_{3.25}\)La\(_{0.75}\)Ti\(_3\)O\(_{12}\) thanks to a first La\(_2\)Ti\(_2\)O\(_7\) buffer layer oriented along the...
c axis exhibiting crystallographic features equivalent to a (110) perovskite plane. Our two-step process includes two thermal treatments, i.e. an intermediate (1 hour) one between the two deposition steps and a final one (4 hours), performed at 650°C under oxygen. These preliminary results obtained on Si (100) substrates are very promising for the enhancement of the ferroelectric response of perovskite layers. Further studies on multi-layer structures including bottom and top Pt electrodes are needed to control fully the effect of such crystalline orientation on the polarization of BLT films and their ferroelectric response. Such results could be of great interest for future development of ferroelectric-based NVFRAM in general and BLT-one in particular.

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