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Processing and structural properties of random oriented lead lanthanum zirconate titanate thin films

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ABSTRACT

Polycrystalline lead lanthanum zirconate titanate (PLZT) thin films have been prepared by a polymeric chemical route to understand the mechanisms of phase transformations and map the microstructure and elastic properties at the nanoscale in these films. X-ray diffraction, atomic force microscopy (AFM) and ultrasonic force microscopy (UFM) have been used as investigative tools. On one side, PLZT films with mixed-phase show that the pyrochlore phase crystallizes predominantly in the bottom film-electrode interface while a pure perovskite phase crystallizes in top film surface. On the contrary, pyrochlore-free PLZT films show a non-uniform microstrain and crystallite size along the film thickness with a heterogeneous complex grainy structure leading to different elastic properties at nanoscale.

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1. Introduction

The lead lanthanum zirconate titanate, (Pb,La)(Zr,Ti)O_3 (referred as PLZT), is known to exhibit remarkable dielectric, piezoelectric and electro-optic properties [1,2]. Depending on the Zr/Ti ratio and La amount in the PLZT system, the material reveals a relaxor behavior giving rise to very large dielectric constants, electro-mechanical and electro-optical coefficients [3]. The composition La/Zr/Ti = 9/65/35 mol% is particularly important because most of the properties of technological interest show their maximum values at this ratio [4]. In the thin film form, the great potential of the PLZT system has been demonstrated in the past years for applications in capacitors [5], nonvolatile ferroelectric random memories [6], waveguide [7], and others.

PLZT thin films can be deposited by various methods, such as pulsed laser deposition PLD [8], sol–gel [9], rf-sputtering [10], and others. Sol–gel technique is the most convenient method due to low cost, high control of the composition and high degree of homogeneity of the films. The kinetic of the perovskite phase transformation in PLZT thin films has been studied in details for films deposited by the different methods. In general, the crystallization of PLZT films using chemical routes is similar to the Pb(Zr,Ti)O_3 (PZT) system [11] and, starting from the amorphous structure, it first transforms into an intermediate non-ferroelectric phase and then into the perovskite phase after an adequate pyrolysis and thermal annealing [12]. Often described as pyrochlore, sometimes also referred as Pb-deficient fluorite phase [12], the non-ferroelectric phase forms during the film crystallization due to slight deviations from the nominal stoichiometry as a consequence of the PbO volatilization. The pyrochlore phase is usually described as cation-ordered structure while the absence of ionic ordering is related to the fluorite structure [13]. In the present work, we will use the term pyrochlore for the secondary non-ferroelectric phase.

The presence of the pyrochlore phase degrades the most important physical properties of Pb-based ferroelectric thin films. Then, to fabricate high-quality thin films for an eventual use in integrated devices, the control and suppression of the pyrochlore phase during the preparation are essentials. Reducing the processing temperatures or adding excess of PbO to compensate the Pb-loss are the traditional alternatives to suppress the pyrochlore phase in ferroelectric films. In addition, the pyrolysis temperature and post-pyrolysis treatments are fundamental parameters to control the nucleation and perovskite growth in thin films produced by chemical routes. Recent studies on the transformation of pyrochlore phase in PLZT thin films show that the subject remains open to discussions [12].

Herein, we present PLZT thin films prepared by an alternative technique to the conventional ones. Main goals of the present paper are to study the perovskite phase transformation and the

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suppression of the pyrochlore phase which can be successfully achieved in the films and have not been so far the subject of systematic investigations for films prepared by the mentioned technique.

2. Experimental

PLZT thin films with $(Pb_{0.91}La_{0.09})(Zr_{0.65}Ti_{0.35})O_3$ nominal composition have been prepared using a chemical route. The general idea is the modification of the Pechini [14] method to prepare a polymeric resin, to deposit it onto a substrate and then crystallize the perovskite phase under adequate heat annealing. The modification introduced in Pechini method is based on the fact that not all used precursor oxides (PbO, La_2O_3, ZrO_2 or TiO_2) are soluble in acid media, but only the reacted complex PLZT oxide is soluble. Then, it is possible to use the PLZT powder to prepare the precursor polymeric solution instead of metalorganic alkoxide or carboxylate as usual starting reagents. Then, the PLZT powder with 10 mol% of lead in excess can be prepared by the conventional solid-state reaction using commercial reagents PbO (Synth, 98%), La_2O_3 (Aldrich, 99.99%), TiO_2 (Aldrich, 99%) and ZrO_2 (Aldrich, 99%). The mixed oxides are calcined in two steps, at 850 °C for 3.5 h and then at 1100 °C for 3.5 h. At room temperature, a high quality PLZT powder (stoichiometric and free of secondary phases) is obtained and ready to be used as starting precursor to prepare the polymeric resin.

To prepare the stoichiometric polymeric resin, PLZT powder (100 mg) is dissolved in 50 mL of nitric acid solution (10% of HNO_3 and 90% of H_2O) at 80 °C during 1 h. After the complete dissolution and adding distilled water, ~30 mL of a clean and transparent stock solution is obtained at room temperature. Next, citric acid (CA) is added to the stock solution (CA/metal molar ratio equal to 15) to form a metallic ions citrate heating and stirring this mixture at 90 °C for 50 min. When the volume of this solution reaches ~5 mL, ethylene glycol (EG) is added to the solution (CA/EG mass ratio equal to 60/40) maintaining the mixture under heating and stirring at 90 °C for 20 min to complete the polymerization of the stoichiometric resin. To compensate the loss of lead during the film preparation and to stabilize the growth of the perovskite phase, a second resin is prepared dissolving 0.0126 g of PbO in 10 mL of nitric acid solution at 80 °C during 10 min. The amount of PbO in the second resin represents 20 mol% in excess of the nominal composition of PLZT in the first resin. The second resin is prepared following the same procedures of the first one. Finally, the two resins are mixed at room temperature and stirred during 1 h for homogenization. After the complete homogenization, the final transparent resin (~15 mL) is ready to start the film depositions. This procedure is necessary, since introducing the PbO excess directly in the PLZT powder leads to unstable resins that precipitates within some days after the preparation.

Films of polymeric resins are initially deposited by spin coating on Pt/Ti/SiO_2/Si(100) substrates at 6000 rpm for 20 sec. The pyrolysis is performed in air putting the deposited films directly on a hot plate at ~200 °C for 5 min and then in an electric furnace at 300 °C for 1 h. The film thickness increases with depositing a new layer on the previous pyrolyzed film and repeating the same heat annealing procedure to remove the organics. After obtaining the required film thickness, a final heat annealing in conventional electric furnace at 700 °C for 1 h promotes the film crystallization. The final films are uniform and crack-free with thicknesses between 240 and 540 nm. The thicknesses were examined using scanning electron microscopy (SEM) images of transverse sections of the films.

X-ray diffraction (XRD) technique has been used to study the structural properties of the PLZT films using a Rigaku Ultima IV diffractometer with CuK_α (λ = 1.5406 Å) radiation. Additionally, the films structure in depth profile has been studied by using XRD measurements at room temperature in step scan mode at the grazing incidence θ angle configuration ($2° \leq \theta \leq 6°$) scanning the 2θ angle from 20° to 60°. The Williamson–Hall [15] analysis has been applied to evaluate the microstrain ($\Delta d/d$) and crystallite size (D) of the PLZT films according to $\Gamma \cos\theta = \lambda/D + (\Delta d/d)4\sin\theta$, where d is the lattice spacing, Γ is the full width at half maximum (FWHM) value due to peak broadening, λ is the wavelength and θ is the Bragg angle.

The atomic force microscope (AFM) used in the present work is a setup made of a commercial head (NT-MDT, Smena), with electronics and software for control and acquisition developed in our laboratories. The cantilevers used for this work are rectangular silicon ones with stiffness constant between 0.1 and 1 N/m (CSCS12, NT-MDT). Ultrasonic force microscopy (UFM) is operated at 4 MHz, while the amplitude is modulated at 4 kHz, by means of a piezo-plate located directly under the sample [16] and driven by a function generator (Agilent 33,220 A). The maximum displacement amplitude is less than 1 nm [17]. Additionally, to collect the UFM data a digital lock-in amplifier (Zurich, HF2LI) is employed. The color codes of the images are the following: topography, brighter for higher regions; UFM, brighter for higher elastic modulus.

3. Results and discussion

Fig. 1 summarizes the grazing incidence XRD patterns of the PLZT thin films prepared from the Pb-stoichiometric resin. Recorded at a fix glancing angle θ = 13° and between $27.5° \leq 2\theta \leq 46.5°$, the XRD patterns for the films prepared under pyrolysis at 300 °C, 350 °C and 400 °C for 30 min and crystallized at 700 °C for 1 h are shown in Fig. 1a–c, respectively. In these figures, the (110) reflection refers to the orthorhombic perovskite PLZT phase (Pmmm space group) while the peak observed at around 2θ = 29.5° is attributed to the pyrochlore phase. This result suggests

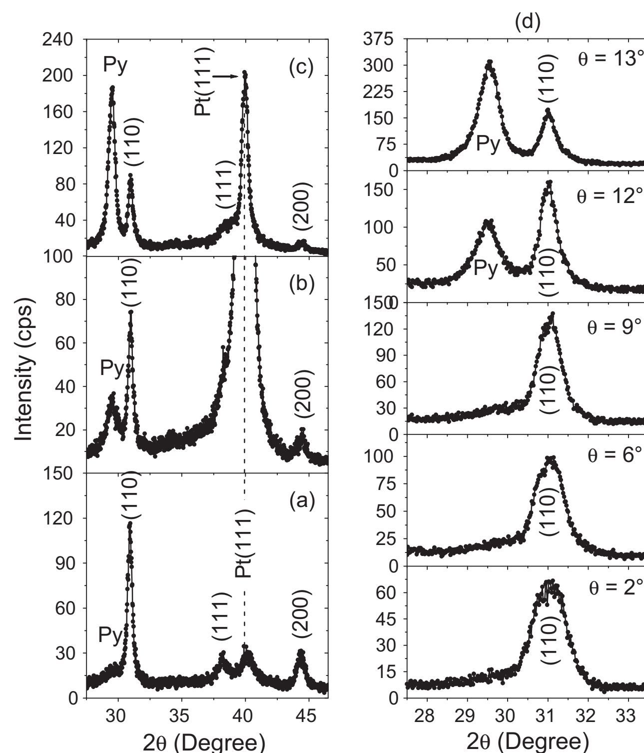

Fig. 1. Grazing incidence XRD patterns (at a fix θ = 13°) of PLZT thin films with 600 nm in thickness (prepared from Pb-stoichiometric solution) pyrolyzed at 300 °C (a), 350 °C (b) and 400 °C (c) for 30 min and crystallized at 700 °C for 1 h. (d) XRD patterns at different glancing angle θ for PLZT film pyrolyzed at 400 °C for 30 min and crystallized at 700 °C for 1 h.

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