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Properties of multilayer composite thin films based on morphotropic phase boundary $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$

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ABSTRACT

It has been reported that ferroelectric and piezoelectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMNT) thin films, with compositions close to the morphotropic phase boundary (MPB), show lower values than those reported for bulk ceramics with the same composition, which has been attributed to a reduction of the remnant polarization caused by the small size of the grains in the films. An alternative has been proposed to take full advantage of the excellent piezoelectric properties of polycrystalline PMNT in thin film form: a multilayer configuration that uses ferroelectric layers with large remnant polarization, in this case $PbTiO_3$, to generate an internal electric bias within the PMNT layers and, thus, anchor an induced polarization on them, resulting in a consequent large piezoelectric behavior. The detailed study of the properties of these multilayer composite films reveals the complex correlations that arise in these heterostructures, which are key for the design of optimized piezoelectric films based on MPB PMNT.

1. Introduction

It is well known that the relaxor-ferroelectric $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PMNT) solid solution shows giant piezoelectric coefficients for compositions in the proximity of the morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases: single crystals of these compositions have d_{33} piezoelectric coefficients of ~2500 pm/V [1]. Therefore, they are excellent candidates for their use as piezoelectric transducers. The progressive miniaturization of the devices leads to the preparation of PMNT in thin film form for their integration in microelectronic devices [2–5]. However, in thin film form, it has been observed that the dielectric permittivity values (ε_{33}) and the functional properties of the PMNT system are lower than those reported for bulk materials [2]. The reported d_{33} coefficients of PMNT thick films (1500 nm) with compositions close to the MPB are of 197 pC/N, and decreasing quickly with the reduction of the film thickness down to values of d_{33} ~42 pC/N [2] or ~55 pC/N [3] for films between 200 and 400 nm thick, which has been attributed to grain size effects [4]. Nevertheless, in the ferroelectric response, the polarization saturation values remain close to those obtained in bulk ceramics [2,5], which implies that the problem relies on the decrease of the remnant polarization (P_r) values in the thin films.

Based on the principles traditionally used in bulk composites [6], the packing of layers of different ferroelectric compositions in a multilayer composite (MLC) configuration has proved to improve the dielectric and ferroelectric properties, when compared to those corresponding to single phase films [7,8]. Several multilayered ferroelectric films and superlattices have been designed searching stress or strain effects, not only due to epitaxial relations [9], but also in polycrystalline heterostructures [10]. Or a simply combination of the properties of the constituent phases is sought, which results in dielectric and ferroelectric properties different from the individual phases, like for example in the case of $Sr_{0.8}Bi_{2.2}Ta_2O_9$ and $SrBi_2Nb_2O_9$ [11] or relaxor phases, $Pb(Zn_{1/3}Nb_{2/3})O_3$-$BaTiO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ [12].

Couplings produce product properties that can be very attractive, like for example magnetoelectricity in ferroelectric/magnetostrictive composites. Regarding coupling of the polarization among two phases, it has been reported that a soft $(Pb,Zr)TiO_3$ (PZT) with large piezoelectric response is kept in a poled state by a hard PZT, in a 2-2 diphasic composite [13], whose properties as piezoelectric transducer are superior to those of a single-phase ferroelectric. This idea, transferred to piezoelectric films, was used by the authors of this work in a previous paper [14], who have proposed a multilayer composite thin film with

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alternating layers of PMNT (low P_r, but large P_s) and $PbTiO_3$ (PT) (large P_r, but not large piezoelectric coefficients). The induced polarization on the PMNT layers kept by the neighboring poled PT should result in an improved piezoelectric response of the PMNT based MLC films.

However, our previous work revealed the importance of factors that play an important role in the properties of the MLC films and must be considered in order to optimize their response. The small grain size obtained due to the low thickness of the individual layers deposited was a handicap due to size effects on the ferroelectric behavior of the layers. Besides, in order to establish the coupling among phases as the origin of the improved P_r values, the existence of a direct correlation between the relative amount of phases and net polarization of the composite film must be discarded. The comparison of MLC films with different amounts of the two phases allows also the discussion on the role of the dielectric permittivity of the phases, as we are studying effects related to the application of an electric field. This work explores these questions on MLC films where the thickness of the layers has been increased in order to avoid deleterious size effects, and different combinations of the layers are used. Not only ferroelectric response of the MLC films is studied, but also other functional properties are analyzed to obtain a complete picture of the behavior of these materials. From this study, the mechanisms leading to the enhancement of the functionality of these MLC films compared with the single phase films are discussed.

2. Experimental procedure

$PbTiO_3$ (PT) and $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.35PbTiO_3$ (PMNT) precursor sols were prepared, as reported elsewhere [15] and diluted in 1,3-propanediol ($OH-(CH_2)_3-OH$) in order to reach a 0.3 molar solution. Successive layers of the diluted PT sol were spin-coated onto (111)$Pt/TiO_2/SiO_2$/(100)Si substrates, dried at 350 °C for 60 s and crystallized by Rapid Thermal Processing (RTP) at 650 °C for 6 s, in oxygen and with a heating rate of 200 $°C \cdot s^{-1}$. The same deposition conditions and drying and crystallization processes were used for the preparation of PMNT thin films. The multilayer composite thin films (MLC) were fabricated by the deposition, drying and crystallization of seven alternating layers of PT and PMNT, starting and finishing either with a PMNT layer (MLC-PMNT) or with a PT layer (MLC-PT), in order to compare two configurations in which either every PMNT layer is sandwiched between two PT layers or, conversely, every PT layer is placed between two PMNT layers. Therefore, we got two multilayer composite films with different PT volume fractions (V_{PT}), 0.43 for MLC-PMNT and 0.57 for MLC-PT.

The crystalline phases developed in the films were monitored by X-ray diffraction (XRD) with Bragg–Brentano geometry. A Siemens D500 powder diffractometer equipped with a Cu anode was used to perform these measurements. Experimental diffraction patterns were compared with standard X-ray patterns of $PbTiO_3$ (JCPDSICDD 6-452) and $Pb(Mg_{0.33}Nb_{0.67})O_3$ (JCPDSICDD 27-1199) perovskite phases. Deconvolution and separation of reflections in the experimental patterns were carried out by using the profile program V1-40 and two pseudo-Voigt functions. Grain size and film thickness were estimated from the Scanning Electron Microscopy images, obtained by a ISI-DS-130 field emission gun microscope (FEG-SEM), working at 2 keV and 3 keV for the cross-section and plan-view images, respectively.

In order to carry out conductive, dielectric and ferroelectric measurements, Pt electrodes with different sizes were deposited at room temperature on the films surface by using shadow masks and a BAL-TEC SCD 050 RF sputtering equipment. Capacitors were subjected to a RTP post-annealing at 350 °C for 600 s in an oxygen atmosphere. The dielectric measurements were carried out at room temperature by a HP 4284A precision LCR meter using a 0.01 V at 1 kHz driving voltage. Ferroelectric hysteresis loops were measured with a home built system, consisting in a virtual ground circuit. In this system, a HP 8116A pulse generator was used to apply voltage sinusoidal waves at a frequency of 1 kHz and the loops were traced by a Tektronix TDS520 oscilloscope. All non-switching contributions were eliminated by a fitting procedure based on a model that simulates the linear part of these contributions by introducing the capacitance and resistance of the films [16]. Non-linear contributions, leakage currents, are fitted by a model that considers the electrical current proportional to V^2 [17]. Alternatively, a commercial RT66A standardized ferroelectric test system at a frequency of 1 kHz was also used for measuring hysteresis loops, where a delay time of 1 s between the voltage conditioning and the measuring triangular waves was applied. This allows us to observe the time relaxation of the polarization, by the comparison of the initial and final polarization values of the loops.

The macroscopic piezoelectric hysteresis loops were carried out by using a fiber optic, double-beam incidence Mach–Zehnder interferometer, as reported elsewhere [18]. The measurements were performed using an AC driving voltage of 5 V at 7.5 kHz, while the DC electric field was changed from 100 to 200 $kV \cdot cm^{-1}$. The local piezoelectric characterization was carried out with a commercial scanning force microscope (Nanotec® Electrónica, controlled by WSxM® software [19]), which piezoresponse force microscopy (PFM) has been implemented in. Conductive Pt/Ir coated tips (Nanosensors) on cantilevers with a force constant of 42 $N \cdot m^{-1}$ were used, with an applied AC voltage of 1 V at 50 kHz. In-field local piezoelectric hysteresis loops have been measured at different locations of the studied films.

The evolution of the pyroelectric coefficient (γ) with time, before and after poling, allowed us to evaluate the retention of the polarization of the PMNT and MLC films. The pyroelectric measurements were performed using a dynamic method [20,21]. Triangular thermal waves with 2 K of amplitude and frequency of $2 \cdot 10^{-3}$ Hz were used, around a temperature of 308 K. The thermo-stimulated current obtained was described by the equation:

$$I_{pyr} = A \cdot \gamma \cdot dT/dt \quad (1)$$

where A is the area of the capacitor and γ is the pyroelectric coefficient.

3. Experimental results

Fig. 1 shows the XRD patterns of the PT, PMNT and MLC thin films, where no secondary crystalline phases are detected in any of them. The PT and PMNT phases can be identified for the two MLC films, indicating that no significant interdiffusion between layers is produced. As the diffraction peaks of these two phases are usually too close, details of the patterns are shown in Fig. 1(a) to (d), where the solid lines correspond to the deconvolution of the experimental data into the 100 and 200 reflections of the PT and PMNT perovskite phases, providing additional evidence to the absence of other crystalline phases than those of the composite constituent layers.

The single phase PMNT film presents larger lateral grain size than the MLC films: 270 nm (Fig. 2(a)). By contrast, similar lateral grain size of the superficial PMNT and PT layers is observed in the FEG-SEM images of the MLC film surfaces, 130 and 100 nm, respectively (Fig. 2(b) and (c)). This can be attributed to the grain growth limitation imposed by the thickness of the alternating layers of both phases (around 35–40 nm) in the MLC films. Cross-section SEM images reveal that after seven deposited layers the total thickness of the MLC-PMNT and MLC-PT are 255 nm and 294 nm, respectively (see Fig. 2(b) and (c)). In single phase films, the grains can grow through the whole thickness of the film, leading to the columnar grain growth of the PMNT film, with thickness of 274 nm (see Fig. 2(a)). As a result, grains forming the MLC films show equivalent sizes in thickness and laterally. This is a condition that must be considered when the electrical behavior of the MLC films is compared to that observed in the PMNT single phase film.

The piezoresponse force microscopy images (Fig. 3) show that the films have strong self-polarization. The d_{33}^{eff} images do not show any trace of ferroelectric domains inside the grains of any of the studied