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Synthesis and electrical properties of lead-free piezoelectric $Bi_{0.5}Na_{0.5}TiO_3$ thin films prepared by Sol-Gel method

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ABSTRACT

Lead-free $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) piezoelectric thin films were deposited on $Pt/TiO_x/SiO_2/Si$ substrates by Sol-Gel method. A dense and well crystallized thin film with a perovskite phase was obtained by annealing the film at 700 °C in a rapid thermal processing system. The relative dielectric constant and loss tangent at 12 kHz, of BNT thin film with 350 nm thickness, were 425 and 0.07, respectively. Ferroelectric hysteresis measurements indicated a remnant polarization value of 9 μC/cm^2 and a coercive field of 90 kV/cm. Piezoelectric measurements at the macroscopic level were also performed: a piezoelectric coefficient ($d_{33effmax}$) of 47 pm/V at E = 190 kV/cm was obtained. The piezoresponse force microscopy data confirmed that BNT thin films present ferroelectric and piezoelectric behavior at the nanoscale level.

1. Introduction

Piezoelectric materials play an important role in electronic and microelectronic systems (actuators, sensors, transducers, etc.) [1]. Lead-based compounds (such as PZT) are the most used materials due to their excellent piezoelectric properties. However, due to the effects of lead toxicity, it has recently desired to reduce lead-based materials usage in electronic devices [2]. Therefore, lead-free materials have a high interest recently in the microelectronic industry.

Bismuth sodium titanate $Bi_{0.5}Na_{0.5}TiO_3$, discovered by Smolenskii et al. in 1961 [3], is considered a good alternative lead-free material to PZT systems. BNT ceramics showed good ferroelectric properties: a strong remanent polarization P_r = 30–38 μC/cm^2, and a high Curie temperature Tc ~320 °C [4,5]. Relatively high piezoelectric coefficients (d_{33} = 60–90 pC/N) were reported for BNT ceramics [5,6].

However pure BNT, especially in the form of thin film, suffers from large coercive field and high leakage current which make difficult to achieve successful poling. These disadvantages limit BNT system applications. Thus, to overcome these problems and to improve electrical properties, several approaches were adopted, such as composition modification of BNT [7,8], multilayer structure [9] and orientation control [10]. In particular, the solid solution systems of BNT and $BaTiO_3$ (BT) show remarkable piezoelectric performance for composition close to the Morphotropic Phase Boundary (MPB) [4].

For BNT-BT thin films deposited on Pt/TiO_2/SiO2/Si by chemical solution deposition (CSD), Alonso-Sanjose et al. demonstrated that an excess on the A-site (Na + Bi) improves electrical properties [11]. Furthermore, Pérez-Mezcua et al. investigated the crystallographic nature and the structural properties of BNT-BT thin films prepared by CSD with and without excesses of (Bi + Na) [12,13]. They have also studied the electrical properties of these BNT-BT thin films [14], and obtained, for films without excesses, the best piezoelectric properties in the region of MPB, while the films prepared with excess of Na or Bi presented a deformed piezoelectric response which could be related with the large conductivity and leakage currents.

However, up to now, few studies have focused on BNT thin films. Films were prepared by different methods: RF sputtering [15,16], sol-gel [17–21], laser ablation [22–24]. Although growth parameters, dielectric and ferroelectric properties for BNT thin films were

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discussed, piezoelectric properties at the macroscopic scale were rarely investigated [16,25].

In this paper, we present structural results obtained for BNT thin films prepared by Sol-Gel method on $Pt/TiO_x/SiO_2/Si$ substrate. Then, dielectric, ferroelectric and piezoelectric properties of these films were also investigated. Electrical characterizations of the films were carried at the local scale as well as at the macroscopic level.

2. Experimental procedure

BNT precursor was prepared by a modified nitrate–alkoxide sol–gel technique [20]. Bismuth III nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), sodium nitrate ($NaNO_3$) and titanium isopropoxide ($Ti(OC_3H_7)_4$) were used as starting materials, while acetic acid, distilled water, and acetylacetone were used as solvents. In order to prepare BNT solution, Bi:Na:Ti ratio of 1:1:2 was used with a 20 mol% excess of sodium nitrate (to compensate the loss of sodium during heat treatments). First, sodium nitrate and bismuth nitrate were dissolved in distilled water and acetic acid, respectively. The solution of nitrates was then mixed at 70 °C under magnetic stirring. Acetylacetone was added to titanium (IV) isopropoxide in order to prevent hydrolysis. Finally the solution of nitrates was mixed with stabilized titanium isopropoxide under magnetic stirring until a transparent and stable yellow precursor is obtained.

The films were deposited on $Pt/TiO_x/SiO_2/Si$ substrate by spin coating, at 3000 rpm for 20 s. Each layer was dried at 100 °C on a hot-plate, pyrolyzed at 200 °C to remove residual organic compounds and annealed by Rapid Thermal Processing (RTP), ramping at 25 °C/s, at various temperatures in ambient air. 350 nm-thick BNT films were obtained after repeating the process for 6 times.

The crystalline structure of the prepared BNT film was examined using X-ray diffraction (XRD, Siemens D5000, Germany). The surface and cross-sectional morphologies were observed by scanning electronic microscope (SEM, Zeiss Ultra 55). LNO top electrodes (circular shape, diameter = 150 μm) were deposited on the films by magnetron sputtering and patterned by a photolithography liftoff process for the subsequent electrical measurements. Dielectric constant and loss tangent were measured at 10 kHz frequency, at room temperature, using a HP 4192A LCR – meter under ac voltage of 0.1 V. Ferroelectric properties at the macroscopic scale of BNT films were studied using an aixACCT TF 2000 analyzer (Germany). P-E loops were measured at a frequency of 1 kHz at room temperature. An atomic force microscope (AFM, Multimode, Nanoscope IIIa; Digital Instruments, Digital Instrument) was used to observe the surface topography and the local piezoelectric response of the BNT film.

In addition, piezoresponse force microscopy (PFM) was utilized to investigate local electromechanical activity by the measurement of the small displacement of the film induced by the converse piezoelectric. The measurement was achieved by applying a sequence of DC bias up to 10 V superimposed on an AC signal V_{ac} (1.5 V, 2 kHz) via the PFM tip directly on the film surface without the top electrodes. Platinum/iridium coated silicon tips-cantilevers (k ≈ 45 N/m) were used to reduce the electrostatic force effects. “In-field” loops were recorded after each step of DC bias applied to film surface (V_{DC} max) while “remnant” loops were recorded when DC bias was stepped back to zero (V_{DC} = 0). To minimize the electrostatic interaction between the tip and the surface, remnant loops for BNT films were recorded [26]. PFM loops were obtained by plotting the phase and the displacement as a function of the DC voltage.

Piezoelectric properties at the macroscopic level were studied using a system based on a laser Doppler vibrometer [27]. A home-made system was developed in our laboratory to measure the d_{33} piezoelectric coefficient by the single beam method. A detailed description of the measurement method was reported by Herdier et al. [27]. This method used in our laboratory means to minimize the substrate contribution using small top electrodes (maximum diameter of 150 μm) and fixing the sample on a glass slide (with glue). The sample is clamped on a support (in our case, glass substrate) using a thin film of adhesive (glue) with good mechanical coupling. To carry out the piezoelectric hysteresis loop measurements, a V_{ac} voltage of 1 Vmrs at the frequency of 12 kHz was applied to the film with a variable V_{DC} bias voltage.

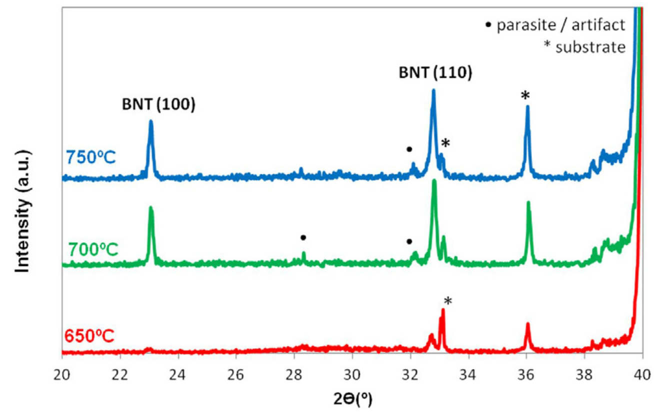

Fig. 1. XRD patterns of BNT thin films prepared by the rapid thermal process at different temperature in air.

3. Results and discussions

The XRD patterns of BNT thin films prepared at different temperature by RTP are shown in Fig. 1. Films annealed at 650 °C showed a low crystallization of BNT while films annealed at 700 °C were completely crystallized with a polycrystalline structure without any preferred orientation or secondary phase.

Fig. 2 shows SEM micrographs of BNT thin films (plan-view and cross-section images). BNT films annealed at 650 °C (Fig. 2a – top) present few small intergrain pores on the surface, while films annealed at 700 °C possess dense, uniform and crack-free micro-structure (Fig. 2b – top). Increasing the annealing temperature (Fig. 2c – top) cracks and pores were produced. The grains of BNT films are evenly distributed, and the grain size is about 100 nm. Thicknesses of these films were obtained from cross-sectional micrographs (Fig. 2 – bottom). BNT films show a uniform thickness of about 350 nm. The films annealed at 700 °C (Fig. 2b – bottom) exhibit a relatively dense and uniform grained structure, while the films annealed at 650 °C (Fig. 2b – bottom) present a heterogeneous structure with pores along the entire film thickness. However, for the films annealed at 750 °C (Fig. 2c – bottom), the lower layers (first layers) seem to be denser than the surface.

Raman spectroscopy of BNT thin film annealed at 700 °C with the RTP was recorded at room temperature (Fig. 3). The deconvolution of the Raman spectrum shows six vibration modes for BNT situated at 109, 250, 502, 542, 778 and 861 cm^{-1}. Our results are close to the values reported in the literature for BNT thin films and ceramics [28–31].

Fig. 4 shows the voltage dependence of the dielectric properties for BNT thin films, calculated from the capacitance measured at room temperature and 12 kHz. Dielectric constant and loss tangent exhibit a significant change with the applied voltage with a hysteresis behavior typical for ferroelectric capacitors.

Dielectric loops for BNT films annealed at different temperature are not centered at 0 V; this shift could be attributed to different electrodes work function [32]. The maximum dielectric constant