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Microstructure and electrical properties of $Na_{0.5}Bi_{0.5}(Ti_{0.98}Zr_{0.02})O_3$ thin film deposited on indium tin oxide/glass substrate

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ABSTRACT

$Na_{0.5}Bi_{0.5}(Ti_{0.98}Zr_{0.02})O_3$ (NBTZr) thin film has been prepared by chemical solution deposition onto indium tin oxide (ITO)/glass under O_2 atmosphere. The microstructure and related electrical performance are investigated. The film exhibits a phase-pure polycrystalline perovskite structure, with evenly distributed grain size and full compactness. A well-defined polarization-electric field (P–E) loop can be observed with a remanent polarization (P_r) of 11.5 $\mu C/cm^2$ and small gap. At 14 V and 100 kHz, the dielectric tunability as high as 44.97% can be achieved and the dielectric constant of 205, dissipation factor of 0.092 as well as figure of merit of 3.58 are obtained.

1. Introduction

During the past decades, $Pb(Zr,Ti)O_3$ perovskite has been the most widely used ferroelectric material in electronic devices such as sensors, actuators and transducers [1]. Nevertheless, the toxicity of lead implies that the lead-based materials pose an inevitable environmental threat during the preparation and application. From this point of view, researchers are making intensive efforts to seek for lead-free alternatives. Among all, sodium bismuth titanate ($Na_{0.5}Bi_{0.5}TiO_3$, NBT) is considered to be a promising candidate due to its strong ferroelectricity with a large remanent polarization ($P_r = 38\ \mu C/cm^2$) and high Curie temperature ($T_c = 320\,^\circ C$) at room temperature [2].

However, the NBT film shows difficulty in poling due to its high conductivity, which is originated from the volatilization of A-site elements and partial valence transfer of B-site ions [3–5]. To improve the electrical properties of NBT thin film, site engineering has been demonstrated to be an effective approach, for example, doping low valence ions of $Mn^{2+,3+}$ or Fe^{3+} [6,7]. Nevertheless, isovalent-ion substitution has been rarely reported. As is known to us, Zr^{4+} is chemically more stable than Ti^{4+}. Also, the zirconium 4*d* states is hybridized with the oxygen 2*p* states, which is different from that (3*d*) of titanium. The introduction of Zr^{4+} into B-site in titanate with perovskite structure of ABO_3 type may bring in Zr–O valence band different from Ti–O [8]. Previous results have reported that zirconium substitution is known for the enhancement of high quality materials, such as $Pb(Zr,Ti)O_3$ and $Ba(Zr,Ti)O_3$ [9]. Therefore, NBT film with Zr^{4+} doping attracts our attention. In this paper, the $Na_{0.5}Bi_{0.5}(Ti_{0.98}Zr_{0.02})O_3$ (NBTZr) thin film is prepared on indium tin oxide (ITO)/glass substrate. The microstructure, ferroelectric, and dielectric properties are investigated.

2. Experimental

The NBTZr thin film was fabricated on ITO/glass substrate via a chemical solution deposition (CSD) process. The precursor solution was prepared by taking sodium acetate (CH_3COONa), bismuth nitrate [$Bi(NO_3)\cdot 5H_2O$], titanium isopropoxide {$Ti[OCH(CH_3)_2]_4$} and zirconium nitrate [$Zr(NO_3)_4\cdot 5H_2O$] as raw materials. CH_3COONa and $Bi(NO_3)\cdot 5H_2O$ were dissolved into acetic acid. $Zr(NO_3)_4\cdot 5H_2O$ was added into the mixture of acetylacetone and 2-methoxyethanol. Subsequently, appropriate amount of $Ti[OCH(CH_3)_2]_4$, acetylacetone and polyethylene glycol with molecular weights of 600 (PEG600) were mixed. Finally, a Na–Bi–Ti–Zr blended system was produced by mixing the three solutions above together and stirred constantly at room temperature. The precursor solution was deposited onto ITO/glass by spin coating and annealed at 500 °C under O_2 ambient. Both the deposition and annealing procedure were repeated several times until a certain thickness was obtained. The microstructure was measured by an X-ray diffraction (XRD, Bruker D8). The surface morphology and cross-sectional structure were examined by a field-emission

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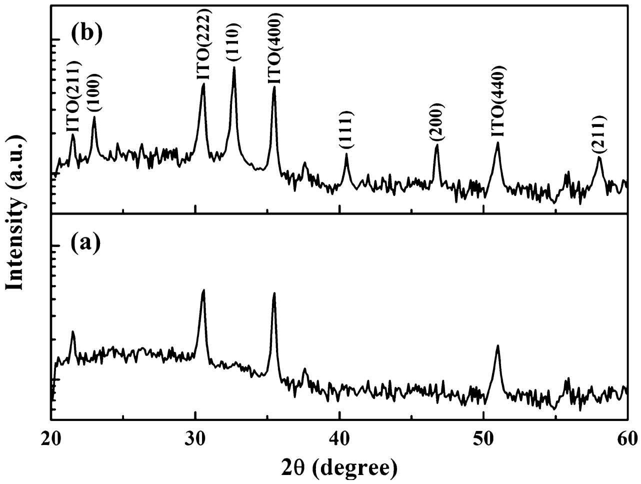

Fig. 1. XRD patterns of (a) ITO and (b) NBTZr thin films.

scanning electron microscope (FeSEM, Hitachi S-4200). The ferroelectric property was detected by a standard ferroelectric tester (Radiant Technologies). The dielectric properties were tested by an impedance analyzer (HP4294A).

3. Results and discussion

Fig. 1 displays the crystal structures of ITO and NBTZr films which are scanned at 2.4°/min in the scanning range of $2\theta = 20–60°$. The NBTZr film matches well with the rhombohedral perovskite structure and exhibits polycrystalline nature without preferential orientation. No detectable impurity phases can be observed although secondary phases can be formed sometimes along with the peroskite phase due to the volatilization of Na^+ or Bi^{3+} [10,11]. This is closely related to the addition of PEG600, which favors the formation of perovskite structure, as investigated in our previous work [7]. To be mentioned that, the phase-pure NBTZr film is obtained under the annealing temperature of 500 °C, which is lower than those of the similar preparing processes for the other NBT-based films ever reported [12,13]. This can be attributed to the favorable effects of oxide electrode on the nucleation and growth for the film, together with the high uniformity of the precursor solution.

The surface morphology and cross-sectional structure of the NBTZr film are shown in Fig. 2. From Fig. 2(a), one can note that the film exhibits homogeneous microstructure without evident cracks.

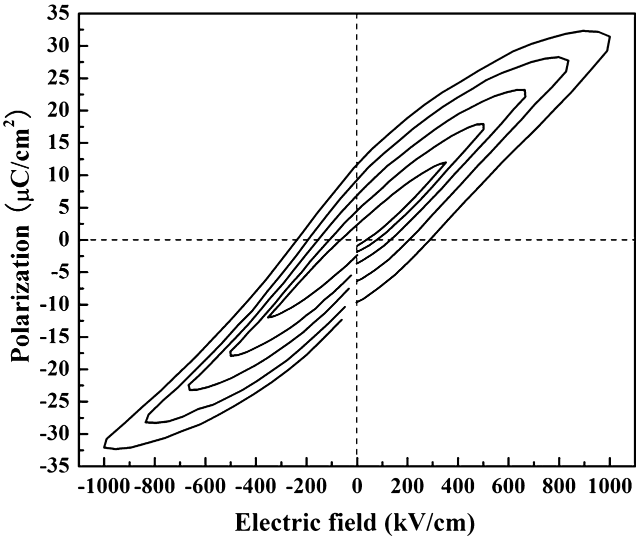

Fig. 3. *P–E* hysteresis loop for NBTZr thin film as a function of electric field at 10 kHz.

Meanwhile, some tiny pores are scattered randomly on the surface, which may be related to the inevitable volatilization of organic components during annealing process. The average grain size is estimated to be approximately only 40 nm. Usually, the content of $V_O^{\bullet\bullet}$ is important for the grain growth as it may have a direct effect on the transfer of energy and mass between reactants during heating [14]. Thus, the oxygen-rich condition may be significant for the fabrication of NBTZr film with smaller grain size. As can be seen from Fig. 2(b), the NBTZr film is about 300 nm in thickness. It exhibits a smooth surface and well-aligned texture. The interface between the film and electrode is clear, indicating relatively low ion diffusion.

Fig. 3 plots the typical polarization-electric field (*P–E*) hysteresis loops of the NBTZr film under various applied electric fields. Here, the maximum electric field value is the biggest that the film can withstand. Usually, a gap, which is reflected as the asymmetric polarization near zero voltage in *P–E* loop can be observed. Compared with the pure NBT film we have fabricated under air [15], this *P–E* loop exhibits a smaller gap and slim shape feature. Meanwhile, the P_r value of 11.5 μC/cm² can be obtained at 1000 kV/cm. This enhanced ferroelectricity can be due to the following aspects. (i) The oxygen atmosphere could lead to a decreasing $V_O^{\bullet\bullet}$ content. This can be attributed to the fact that under the oxygen-rich condition, the $V_O^{\bullet\bullet}$ generated from the following

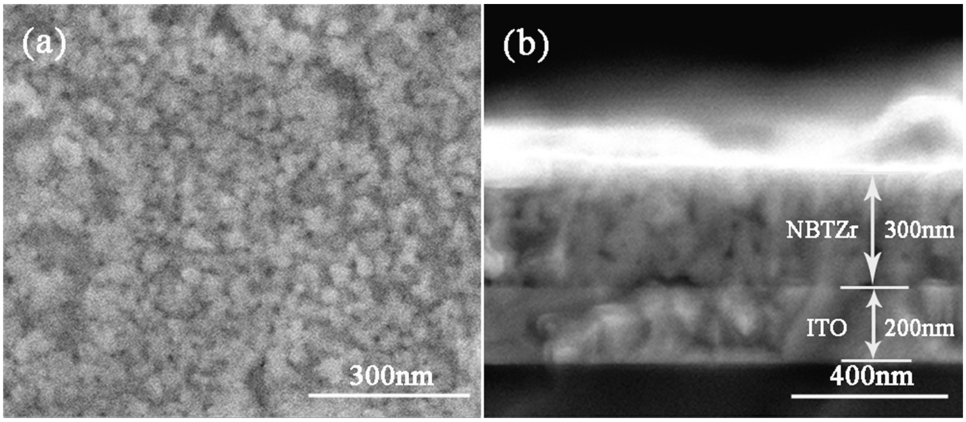

Fig. 2. FeSEM images of (a) surface and (b) cross-sectional structure of the NBTZr thin film deposited on ITO/glass substrate.