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Influence of seed layer on crystal orientation and electrical properties of $(Na_{0.85}K_{0.15})_{0.5}Bi_{0.5}TiO_3$ thin films prepared by a sol–gel process

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Abstract

Sol–gel derived lead-free $(Na_{0.85}K_{0.15})_{0.5}Bi_{0.5}TiO_3$ (NKBT) thin films, with and without a $Pb_{0.8}La_{0.1}Ca_{0.1}Ti_{0.975}O_3$ (PLCT) seed layer, were fabricated on (111)Pt/Ti/SiO_2/Si substrates. The influences of the seed layer on crystal orientation and electrical properties were investigated in detail. XRD indicated that the NKBT thin films fabricated with a seed layer were fully crystallized into a single perovskite structure, while the films fabricated under the same conditions, but without a seed layer, possessed a certain amount of pyrochlore phase. The NKBT film with a 14 nm-thick seed layer showed high (100) orientation, and exhibited enhanced electrical properties, such as a higher remanent polarization (Pr~18 μC/cm^2), a lower dielectric loss tangent (tan δ ~0.023) and smaller transient current density ($J < 10^{-5}$ A/cm^2).

Keywords: A. Films; A. Sol–gel process; B. Interfaces; C. Electrical properties

1. Introduction

Nowadays, lead-based ferroelectrics, such as $PbTiO_3$ and Pb(Zr, Ti)O_3, are indispensible functional materials which are widely used in various electronic devices, because of their superior dielectric, piezoelectric, ferroelectric and pyroelectric properties [1–3]. However, the toxicity of lead-based materials means that they pose a significant environmental threat both during their preparation and application. Inevitably, considerable attention has been directed towards lead-free ferroelectric materials with electrical properties comparable to those of lead-based ones. $Bi_{0.5}Na_{0.5}TiO_3$ (NBT) is regarded as one of the key lead-free ferroelectric materials, because of its excellent performance at room temperature: a relatively high Curie temperature, Tc=320 °C; and a large remanent polarization, Pr=38 μC/cm^2 [4,5]. However, its larger coercive field value makes it difficult to pole pure NBT [6]. Compared with pure NBT, the NBT-based solid solution modified with $K_{0.5}Bi_{0.5}TiO_3$, $(Na_{0.85}K_{0.15})_{0.5}Bi_{0.5}TiO_3$ (NKBT), shows enhanced electrical properties owing to a morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases [7,8].

For ferroelectric materials, the electrical properties are strongly dependent on crystal orientation, as a result of the close relationship between polar axes and crystallographic directions [9,10]. Recently, many researchers found that highly (100)-oriented ferroelectric thin films show improved properties. For example, Fu et al. [11] obtained highly (100)-oriented $(Pb_{0.8}Ca_{0.2})TiO_3$ films with reduced leakage current and enhanced pyroelectric properties. Zhu et al. [12] also reported excellent piezoelectric and ferroelectric properties in highly (100)-oriented Nb-doped $Pb(Zr_{0.3}Ti_{0.7})O_3$ film, where the orientation resulted from the formation of a PbO seed layer. However, for lead-free NKBT films deposited on Pt/Ti/SiO_2/Si substrates, there are few reports on whether orientation of the crystals produces excellent properties.

The aim of this paper is to investigate the influence of a seed layer on crystal orientation and electrical properties of NKBT

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thin films. To optimize properties of NKBT thin films, a $Pb_{0.8}La_{0.1}Ca_{0.1}Ti_{0.975}O_3$ (PLCT) seed layer was introduced at the interface between the film and the electrode. The possible mechanisms for the effects of the seed layer on crystal orientation, ferroelectric, dielectric and leakage current characteristics are also discussed.

2. Experimental

NKBT thin films were prepared by a sol–gel spin-on technique. The precursor sol of NKBT was synthesized using bismuth nitrate, sodium acetate, potassium acetate, and titanium isopropoxide as the raw materials and 2-methoxyethanol as the solvent. 5 mol% excess of bismuth, sodium and potassium were introduced to compensate for evaporation during high-temperature treatment, and the concentration of the final sol was adjusted to 0.25 M. The preparation method for the PLCT seed layer was reported in our previous study [13]; the concentration of the PLCT sol was adjusted to either 0.1 or 0.15 M, and the corresponding thicknesses of the seed layer were about 9 and 14 nm, respectively [13]. First, a thin PLCT layer was deposited on a $Pt/Ti/SiO_2/Si$ substrate and pyrolyzed on a hot-plate at 450 °C for 2 min. Next, the NKBT layers were deposited repeatedly on the PLCT coating and also pyrolyzed at 450 °C for 2 min, until the desired film thickness was achieved. Finally, the films were annealed at 700 °C for 3 min by rapid thermal annealing (RTA, the heating rate is 60 °C/s) in an oxygen atmosphere. The phase composition and orientation were investigated by X-ray diffraction (XRD, Philips, CuKα radiation). To measure the electrical properties of the films, dot-type gold electrodes with an area of 3.14×10^{-4} cm^2 were deposited on each NKBT film by magnetron sputtering. Ferroelectric properties and leakage current characteristics were evaluated using a Radiant Precision workstation ferroelectric measurement system, and the dielectric properties were tested with an Agilent 4294A tester.

3. Results and discussion

The inset shows the expanded XRD patterns of (200) peaks of corresponding thin films. Fig. 1 shows the XRD patterns of NKBT thin films formed without and with different thicknesses of PLCT seed layer. All the NKBT films have been fully crystallized. The NKBT film without seed layer exhibits random orientation, and a weak peak corresponding to pyrochlore phase is clearly displayed at 2θ–30°. With increasing thickness of seed layer, the (110) peak intensity of the NKBT film weakens gradually, while the intensities of (100) and (200) peaks increase significantly; when the seed layer thickness is 14 nm, the NKBT film shows high (100) orientation. According to our previous report [13], the high (100) orientation of the NKBT/14 nm PLCT film can be attributed to a strong orientation-inducing effect of the highly (100)-oriented PLCT seed layer. As shown in the inset, it is interesting that the (200) peak of the NKBT/14 nm PLCT film has obviously broadened; there may be a variety of ferroelectric phases, indicating that this film may be close to the morphotropic phase boundary (MPB).

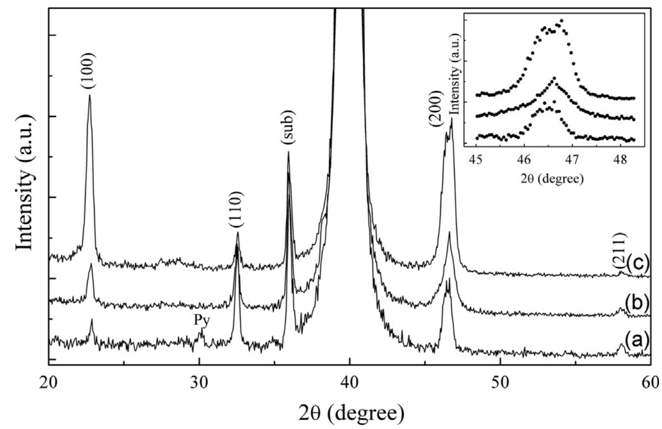

Fig. 1. XRD patterns of (a) NKBT film, (b) NKBT/9 nm PLCT film and (c) NKBT/14 nm PLCT film.

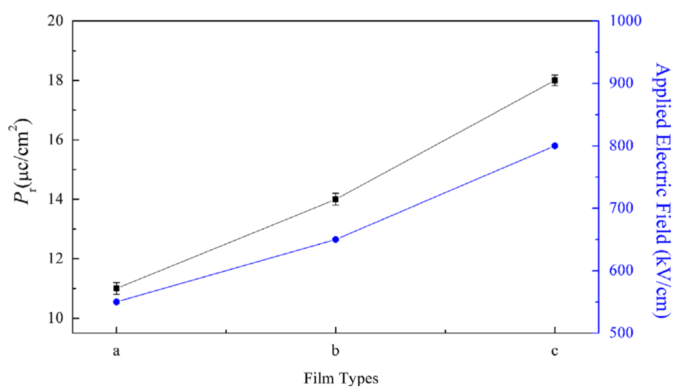

Fig. 2. Pr and applied electric field values of (a) NKBT, (b) NKBT/9 nm PLCT and (c) NKBT/14 nm PLCT film.

The Pr and applied electric field values of all the NKBT films, measured at room temperature, are given in Fig. 2. The ferroelectric properties of NKBT formed with a seed layer are obviously superior to the properties of the film without a seed layer, and the remanent polarization (*Pr*) of the NKBT film becomes larger when the thickness of the seed layer is increased. The *Pr* values of NKBT film, NKBT/9 nm PLCT film and NKBT/14 nm PLCT film are 11, 14 and 18 μC/cm^2, respectively. The NKBT/14 nm PLCT thin film shows enhanced ferroelectric properties; its value of *Pr* is larger than that of lithium doped NKBT thin film ($Pr = 13.9$ μC/cm^2) [14]. It is very interesting that the NKBT films with seed layers can withstand much higher applied electric fields than the NKBT film without a seed layer; the maximum applied field for the NKBT/14 nm PLCT film is 800 kV/cm.

The dielectric constant (ε_r) and loss tangent ($\tan\delta$) as functions of frequency for three types of NKBT films are presented in Fig. 3. The NKBT thin films with seed layers possessed larger dielectric constants and lower loss tangents compared with those of the film without a seed layer. As the thickness of the seed layer increased, there was an increase in the dielectric constant, and a decrease in the loss tangent. For the NKBT film, NKBT/9 nm PLCT film, and NKBT/14 nm

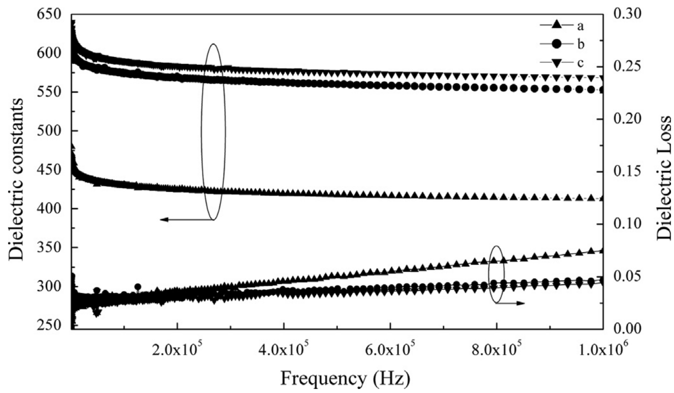

Fig.3. Dielectric constant (ε_r) and loss tangent ($\tan\delta$) as the function of frequency for three kinds of NKBT films. (a) NKBT film, (b) NKBT/9nm PLCT film and (c) NKBT/14 nm PLCT film.

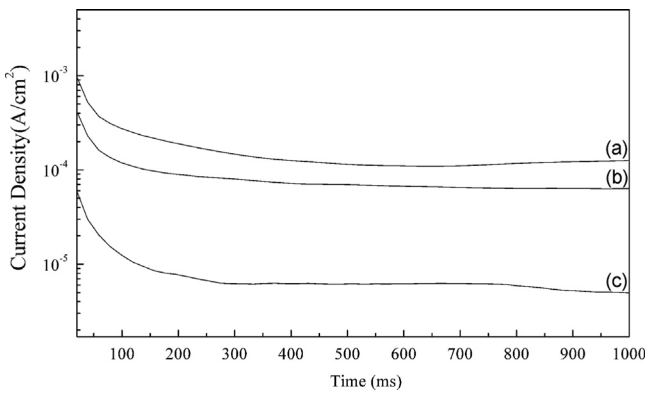

Fig. 4. Typical *J–t* transient characteristics measured at a constant voltage of 200 kV/cm for (a) NKBT film, (b) NKBT/9 nm PLCT film and (c) NKBT/14 nm PLCT film.

PLCT film, the values of dielectric constant measured at a frequency of 10 kHz were 447, 590 and 610, and the values of dielectric loss were 0.032, 0.025 and 0.023, respectively.

Typical *J–t* transient characteristics measured at a constant voltage of 200 kV/cm for the three different NKBT thin films are shown in Fig. 4. The transient current of all thin films decreases exponentially with time, and finally reaches a saturated steady state value; this is consistent with previous reports [15]. The leakage current density decreases sharply as the thickness of the seed layer increases. The NKBT/14 nm PLCT film possesses the lowest saturated steady state current density value of approximately 10^{-5} A/cm^2; in contrast, the saturated steady state current density value for the NKBT film is higher than 10^{-4} A/cm^2. These results demonstrate that introducing a seed layer is a very effective means of reducing leakage current and improving the insulating properties of films.

Because of severe interfacial diffusion and volatilization of Bi, Na and K during high-temperature treatment of NKBT films, a large number of vacancies or point defects will be produced within the film and at the film/electrode interface [16]. Interfacial diffusion can be greatly inhibited by introducing a seed layer; furthermore, La^{3+} from the PLCT seed layer can also act as a donor to reduce or compensate for vacancy-type defects [17]. This reduction in defects means that the numbers of both pinning centers of domains and charge carriers in the films will decrease significantly, making reorientation of domains easier and reducing the leakage current, leading to improved electrical properties for the NKBT film with a seed layer. As the thickness of the seed layer increases, the enhancement in the electrical properties of the NKBT films is more pronounced, which means that the NKBT films with thicker seed layers can withstand higher applied electric fields. This is part of the reason for the NKBT/14 nm PLCT film showing the best electrical properties amongst the films studied. The enhanced ferroelectric properties of NKBT/14 nm PLCT film may also be partly ascribed to the high (100) orientation of this film [12] and the existence of multiple ferroelectric phases at the MPB composition [7], which is consistent with the results reported by others [18].

4. Conclusions

In summary, lead-free NKBT films with and without a PLCT seed layer were deposited on $Pt/Ti/SiO_2/Si$ substrates via the sol–gel method. XRD showed that the NKBT films with seed layers were fully crystallized after annealing at 700 °C, while the film without a seed layer possessed a certain amount of pyrochlore phase under the same conditions. The NKBT/14 nm PLCT film exhibited good (100) orientation; however, the NKBT film and the NKBT/9 nm PLCT film showed random orientation. The electrical properties of NKBT films were greatly enhanced with increasing seed layer thickness. The NKBT/14 nm PLCT film possessed the best electrical properties of the films studied here. It showed a high remanent polarization ($Pr\sim18$ μC/cm^2) and dielectric constant (610), and a lower dielectric loss ($\tan\delta\sim0.023$) and transient current density ($J<10^{-5}$ A/cm^2). Therefore the NKBT film with a seed layer is a promising candidate for lead-free memory device applications.

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