Investigation of thickness dependence of electric properties of sol–gel BNT–BT thin films with stepwise crystallization

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6% BaTiO3-doped Na0.5Bi0.5TiO3 (BNT–BT) lead-free piezoelectric thin films with the composition around morphotropic phase boundary (MPB) were spin-coated via an economical water-based sol–gel method on Pt(111)/Ti/SiO2/Si substrates. High-quality BNT–BT thin films with the thickness ranging from 120 to 560 nm were synthesized by stepwise crystallization process, and the thickness effect on structures and electric properties were investigated. Two theoretical models are used to analyze the ferroelectric results. Intrinsic contribution and extrinsic contribution alternatively dominates under different conditions in the BNT–BT thin film. The piezoelectric properties of BNT–BT thin films were found to change monotonically with the increase of the thickness. The largest effective piezoelectric constant (d33) of the BNT–BT thin films can reach the value of 97.7 pm/V for the film with the thickness of 560 nm.

Key-words : Lead-free ceramics, Thin films, Piezoelectric materials/properties, Sol–gel, Electric properties

1. Introduction

In the recent decades, lead zirconate titanate (PZT) and its related solid solutions are still the most widely used piezoelectric materials in electronic devices (such as sensors, actuators and memories). However, the urgency of developing new, green piezoelectric materials grew rapidly because of the lead toxicity of the PZT materials. As one of the most promising candidates for the replacement of lead-based materials, Bi0.5Na0.5TiO3 and the tetragonal BaTiO3 perovskites have many deficiencies in the poling process. However, many methods were tried to mitigate these problems by forming solid solutions of BNT with a variety of other compounds including BaTiO3, K0.5Bi0.5TiO3, Na0.5K0.5NbO3 and BiFeO3.6) Due to the high conductivity and a large coercive field, BNT ceramics have many deficiencies in the poling process. However, many methods were tried to mitigate these problems by forming solid solutions of BNT with a variety of other compounds including BaTiO3, K0.5Bi0.5TiO3, Na0.5K0.5NbO3 and BiFeO3.6) Much more attention has been paid to the BNT–BT system owing to the MPB formed between the rhombohedral Bi0.5Na0.5TiO3 and the tetragonal BaTiO3 perovskites.7) BNT–BT bulk ceramics show good dielectric (relative dielectric constant at room temperature of 1200 and maximum values of 7000), ferroelectric (remanent polarization of 7000), and piezoelectric (relative dielectric constant at room temperature of 1200 and maximum values of 7000), and piezoelectric (d33 ~110 pC/N) properties in the MPB composition, which make BNT–BT lead-free material attractive for applications in electronics.10,16,17)

The thin film form of the piezoelectric materials exhibit lots of advantages for micro electromechanical systems (MEMS) owing to the large motions generated in films and high energy densities.15,19) However, further investigations into the optimization of the fabrication of the BNT–BT thin films are required to improve the electrical properties. As reported, chemical solution deposition16,19) pulse laser deposition,1,12,20) RF magnetron sputtering,22) metal organic decomposition26) and sol–gel deposition21) are among the most widely used methods to fabricate the BNT–BT thin films. The sol–gel method can offer good stoichiometry control of the film composition. We have focused on the fabricating process of the BNT–BT thin film and enhancing the piezoresponse of the thin films. Further investigations into the optimization of the various processing factors are required to improve the electrical properties of BNT–BT thin films. In this work, we found a novel crystallization process to fabricate the high-quality BNT–BT thin films with thickness over 300 nm. The thickness effect of BNT–BT films on structures and electric properties were also discussed.

2. Experimental

BNT–BT thin films were prepared by mixing BNT and BT precursor solutions which were first made separately. The BNT precursor solution was prepared by dissolving an appropriate amount of bismuth nitrate Bi(NO3)3·5H2O, sodium acetate trihydrate CH3COONa·3H2O in acetic acid at room temperature in air, followed by adding a 1:3:3 weight mixture of Ti(OCH(CH3)2)4, isopropyl alcohol (CH3)2CHOH and acetylacetone CH3COCH2COCH3. 10% excess of bismuth nitrate and 20% excess of sodium acetate were added to compensate Bi and Na losses during heat treatment. Then, acetic acid and distilled water was poured into the mixture (3:1:1 volume ratio). The BT solution was prepared with Ba(CH3COO)2 and Ti(OCH(CH3)2)4, in a manner similar to that described above. Finally, the BNT and BT precursor solutions were mixed together and stirred to a stable yellow solution. All the regents are from Sinopharm Chemical Reagent Co., Ltd. The BNT–BT thin films were deposited onto Pt(111)/Ti/SiO2/Si(111) substrates by spin coating at 5000 rpm for 30 s. And the wet layers were pyrolyzed and heat treated at 750°C for 30 min in ambient atmosphere, respectively. The samples prepared by single crystallization
Three different crystallization processes were used: single crystallization process (hereinafter named BT-a), multiple crystallization process (hereinafter named BT-b), and stepwise crystallization process (hereinafter named BT-c). BT-a films were coated, dried, pyrolyzed, and annealed. BT-b films were deposited, pyrolyzed, and annealed for each layer. BT-c films were deposited, pyrolyzed, and annealed for each layer, with additional annealing after every three layers. This process was repeated several times to obtain films with the desired thickness.

Figure 1 shows the difference between the three crystallization processes. The samples fabricated by stepwise crystallization were annealed once after being deposited and pyrolyzed for every three-layers, this process was conducted for several times to obtain the film with an appropriate thickness. In the stepwise crystallization process, the films were annealed for 3 or 4 times, between 1 time annealing by single crystallization process and 10 or more times annealing by multiple crystallization process. And the films with different thickness were prepared by stepwise crystallization process (hereinafter named BT-c-x nm).

The phase structures of the films were studied by X-ray diffraction (XRD, D/max-RB, Rigaku, Tokyo, Japan) with CuKα radiation. Auger electron spectroscopy (AES, PHI-700, ULVAC-PHI INC) is used with electron gun high voltage of 5 kV and 1‰ energy resolution. For electrical measurements, Pt top electrodes with a diameter of 0.4 mm were sputtered through a shadow mask onto the films. The ferroelectric hysteresis loops were evaluated using the FE module of the aixACCT thin-film TF2000 analyzer (Aachen, Germany). A precision impedance analyzer (4294A, Agilent, CA, USA) was used to evaluate the dielectric properties of the BT-c thin films. The microstructure and piezoelectric properties of thin films were characterized by an atomic force microscope (AFM, SPM4000&SPA3000HV, Seiko, Tokyo, Japan) under DFM (Dynamic Force Mode) for surface image observation and under contact mode for measuring field-induced displacement curve using Rh-coated cantilever (Si-DF3-R, Seiko) which had a spring constant of 1.9 N/m and a free resonance frequency of 28 kHz.

3. Results and discussion

The XRD patterns of the 360 nm-thick BT films prepared using three different crystallization processes and the films with different thickness prepared using stepwise crystallization are shown in Figs. 2(a) and 2(b), respectively. In Fig. 2(a), we find that all the films have been fully crystallized without any orientation, and the intensities of diffraction peaks of BT-b (except peak (110) of BT-b, which was influenced by substrate peak) and BT-c are higher than BT-a. The XRD pattern of BT-a indicates the coexistence of a perovskite phase and a secondary pyrochlore Bi$_2$Ti$_2$O$_7$ phase. The pyrochlore phase is formed because of the incomplete crystallization for too many layers in one-time crystallization process. The complete crystallization makes the pyrochlore phase transform into pure perovskite phase. However, there is obvious substrate peak between 33 and 36 degree in the pattern of BT-c. So many times of crystallization process for the sample make the diffusion of Pt atoms into BT-c layer. The XRD peak of BT-c is sharper and the value of the full width at half maximum of the peak is smaller with respect to BT-a and BT-b. So many times of crystallization process for the sample make the diffusion of Pt atoms into BT-c layer. The XRD peak of BT-c is sharper and the value of the full width at half maximum of the peak is smaller with respect to BT-a and BT-b, which indicates high quality thin film of BT-c by stepwise crystallization process.

In Fig. 2(b), we can find that the patterns of BT-c with different thickness show pure perovskite phases without any second phases or preferential orientation, and the intensities of the peaks increase with increas-
ing thickness of the films. The AES depth profiles for the samples prepared by three different crystallization processes are shown in Fig. 3. The component element atomic concentrations are found to vary as a function of the depth into films. Due to the easy volatility of Na when annealed, the atomic concentration of Na can reflect the influence on the quality of films from three crystallization processes. Figure 3(a) shows that atomic concentration of Na increases from a below-theoretical value as depth increases, which demonstrates that the final annealing makes Na near the surface volatilize more than that near the substrate. Compared to Fig. 3(b), the variance of Na atomic concentration in Fig. 3(c) is smaller, to blame too much times of annealing in multiple crystallization process at high temperature. As mentioned above on the diffusion of Pt atoms into BNT–BT layer, we can observe that the Pt atoms gradient of BNT–BT-b is smaller than that of BNT–BT-c, which means larger area with Pt diffusion in BNT–BT layer is found in BNT–BT-b.

Figures 4(a)–4(c) shows the surface morphologies of BNT–BT-a, BNT–BT-b and BNT–BT-c films measured by DFM, respectively, and Figs. 4(d)–4(g) shows the DFM surface morphologies of BNT–BT-c with different thickness. The DFM images show that there is no difference of grain size among the films derived by different crystallization processes and the films with different thickness, and the average grain size of the BNT–BT thin films is about 40–60 nm. All the BNT–BT films exhibit dense and smooth microstructures, with a RMS of roughness ranging from 3.24 to 5.10 nm.

Figure 5 shows the thickness dependence on ferroelectric properties of the BNT–BT-c films at room temperature. All films with different thickness show similar shapes of loops, meanwhile the maximum of polarization becomes larger as the thickness increases. The remnant polarizations $P_r$, coercive field $E_c$, extrapolated spontaneous polarization $P_s$ and the ratio of the $P_r/P_s$ as a function of the thin film thickness are shown in Fig. 6.
We can find that $E_c$ and $P_r$ of these films change monotonically with the film thickness, while $P_f$ first increases then decreases as the films become thicker. It is complicated to explain the $P_f$, as a non-monotonic function of film thickness, both passive interfacial layer model and charge injection model will be taken into account. $P_f$ of the ferroelectric films will monotonically increase as the thickness increases in the passive interfacial layer model, because the interfacial layer will act as a non-ferroelectric layer, which reduces the value of the saturation polarization of the film especially when the film is thin. However, in the charge injection model, when the field in the interfacial layer, $E_i$, is far higher than that in the bulk ferroelectric layer, it is reasonable for the free charge to be injected to the interface from the near-by electrode. The injected charge will reach its maximum value at the tip of the polarization loops, and charge will inject in opposite direction when the external field drops lower than a certain value, which contributes as a blocking effect on these domain reversal. The interfacial layer is affecting ferroelectric property not only as a non-ferroelectric layer, but also inhibit the back switching of the domain when the external electric field is fading out. Therefore, as the film thickness increases, the $P_f$ of the films will increase, but the ratio of $P_f/P_s$ will decrease. The two opposite effects on the $P_f$ by the interfacial layer result in a maximum value of $P_f$ observed in Fig. 6.

The DC bias dependence of the dielectric constant for the BNT–BT thin films with different thickness at room temperature is shown in Fig. 7. A little asymmetry behavior of the $C$–$V$ loop is due to the different deposition method used at top and bottom interfaces. It is well known that the influence of DC bias field on the dielectric properties is mainly due to the pinning effect of DC bias field on the domain wall mobility. We measured the dielectric constant under the DC bias field up to 300 kV/cm, as the motion of domain wall can be restricted by the DC bias field when the field is larger than the coercive field. As shown in Fig. 6, the difference of the dielectric constant between these BNT–BT thin films with different thickness is really small when the applied bias field reached over ±200 kV/cm. Generally speaking, there are both intrinsic and extrinsic contributions to the dielectric response at lower bias field. Under large DC bias field, dielectric response mainly comes from intrinsic contribution, and the extrinsic contribution is nearly the same to the film irrespective of the thickness. Around the zero DC bias field area, the dielectric constant becomes bigger with the increase of the thickness. We can conclude that there is more contribution from extrinsic effect to the dielectric response as the thickness of the film increases.

The effective piezoelectric coefficients $d_{33}$ calculated from the local displacement–voltage loops are plotted as a function of thickness for the BNT–BT thin film in Fig. 8, and these corresponding displacement–voltage loops are shown in the insets. All the samples exhibit typical “butterfly” shapes, and the calculated effective $d_{33}$ value increases from about 61.4 pm/V at the thickness of 120 nm to about 97.7 pm/V at 560 nm. From the
early researches,\textsuperscript{32} we can assume that there are more contributions from extrinsic effect to the piezoelectric response as the thickness of the film increases. Because the 180\degree domain walls have no contribution to the piezoelectric response, the smaller value of effective $d_{33}$ for the thinner films thus may be due to the reduced mobility of non-180\degree domain walls caused by the clamping of substrates or by the effect of pinning centers at the interface. For the thicker films, more domains located far from the interface, and the mobility of non-180\degree domain walls relatively increase, leading to more extrinsic contribution to the piezoelectric response.

4. Conclusions

Single phase crystalline thin films of BNT–BT have been fabricated on Pt(111)/Ti/SiO$_2$/Si substrates by a water-based sol–gel spin-coating method. The resulting films show random orientation and pure perovskite phase. The BNT–BT thin films prepared using stepwise crystallization process have higher quality, which could avoid the appearance of secondary pyrochlore and the influence from the substrates during the long time annealing. The thickness dependence on ferroelectric properties of BNT–BT thin films were investigated by passive interfacial layer model and charge injection model. A maximum value of $P_c$, $E_c$ and the monotonically changing of the $P_r$, $E_c$ and the $P_r/P_t$ with the increase of the thickness were observed. It is well explained by the combined effect of back switching of domain at the bulk ferroelectric layer and blocking effect on these domain reversal by the injected charge at the interface. The investigation of the dielectric properties shows that there is more contribution from extrinsic effect to the dielectric response as the thickness of the film increases. The effective piezoelectric coefficients $d_{33}$ grows larger with the increase of the thickness. The effect of clamping of the domain wall motions from the substrates has greater impact on the thinner films than the thicker ones. The largest effective piezoelectric constant $d_{33}$ can reach the value of 97.7 pm/N for the BNT–BT thin films with the thickness of 500 nm prepared using the stepwise crystallization process.

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