Ferroelectric and non-linear dielectric characteristics of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ thin films deposited via a metallorganic decomposition process

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Polycrystalline $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (NBT) thin films have been successfully fabricated via a metal organic decomposition process on Pt/Ti/SiO₂/Si substrates. The structural evolution of the as-prepared thin films annealed over the moderate temperature range 500–700 °C is studied. NBT thin films annealed at 700 °C are of single phase NBT perovskite type. They exhibit a well-defined *P-E* hysteresis loop at room temperature. The measured dielectric constant is 465–410 over the frequency range of 1 kHz to 1 MHz. The corresponding dielectric loss is $\sim 10^{-2}$. The measured capacitance-voltage curve shows strong non-linear dielectric behavior leading to a high tunability of the dielectric constant, up to 14% at 1 MHz. © 2008 American Institute of Physics.

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Lead-based ferroelectrics, such as lead zirconium titanate, $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, (PZT) and PbTiO_3 , are in widespread use as piezoelectric sensors, actuators, and transducers as a result of their excellent piezoelectric properties.¹ The use of lead-based ceramics, however, has caused serious lead pollution and resultant environmental problems as a result of the toxicity of lead oxide as well as its high vapor pressure during processing. It is therefore becoming increasingly necessary to develop high performance, lead-free, piezoelectric ceramics. The lone pair associated with the Pb^{2+} ion is known to play a very important role in the ferroelectric properties of Pb-based ferroelectric materials. Given that Bi^{3+} and Pb^{2+} are isoelectronic, the substitution of Bi^{3+} for Pb^{2+} in Pb-based perovskite materials has the potential to lead to high performance, Pb-free, ferroelectric and/or piezoelectric materials. In line with this approach, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (NBT) has already shown promise as a potential alternative to PbTiO_3 and PZT ceramics.^{2,3}

NBT, discovered by Kreisel and Glazer in 1960,⁴ shows strong ferroelectricity with a large remnant polarization $P_r = 38 \mu\text{C}/\text{cm}^2$ and a high Curie temperature T_C of 320 °C. Over recent years, considerable effort has been put into the fabrication and characterization of NBT ceramics as a potential replacement for the widely used Pb-based piezoelectric ceramics. The piezoelectric and ferroelectric properties,⁵ the thermal behavior,⁶ compressibility,⁴ and optical behavior³ of NBT have been reported. All of these studies, however, were performed on the bulk form of NBT. There is very little work reported to date on the fabrication of NBT thin films. In this work, we therefore present the results of a systematic investigation on the growth as well as the ferroelectric and non-linear dielectric characteristics of polycrystalline NBT thin films fabricated via a metallorganic decomposition method.

The starting materials used were bismuth nitrate (98%, Sigma), sodium nitrate (99 %, Fluka), and titanium (IV) iso-

propoxide (97%, Sigma). Glacial acetic acid (99%, Sigma) and acetylacetone (99%, Fluka) were used as the solvent and polymerizing agents, respectively. Bismuth nitrate and sodium nitrate were dissolved into heated glacial acetic acid. This was followed by the addition of titanium isopropoxide under constant stirring conditions. The acetylacetone was then added into this resultant mixture to form a stock solution. The spin-on solution was prepared by diluting the stock solution with equivolume amounts of glacial acetic acid to become 0.3M in concentration. After aging the hydrolyzed solution for 24 h, thin-film deposition was carried out on Pt(111)/Ti/SiO₂/Si substrates by spin coating each layer at 3000 rpm for 30 s. The resultant wet films were then dried and annealed on a hot plate for 5 min at 400 °C before a final annealing to crystallize the amorphous films at higher temperatures of 500, 600, and 700 °C for 30 min, respectively. The desired film thickness of 450 nm was achieved by repeating the above spin-coating–drying–annealing process.

The crystalline phase of the resultant thin films was identified by powder x-ray diffraction (XRD) (SIEMENS D-500) while the film surface and cross-sectional morphology was investigated using a field-emission scanning electron microscope (FESEM) (Hitachi 4300SE/N). The film thickness was also determined by FESEM. For the electrical measurements, a top gold electrode 400 μm^2 in size was deposited by dc sputtering. Hysteresis loop measurements were performed in dynamic mode using a TF2000 analyzer. Dielectric characteristics were measured using a high precision LCR meter (Agilent 4284A).

Figure 1 shows XRD patterns for the as-prepared NBT thin films annealed at 500, 600, and 700 °C, respectively. Below 400 °C, only an amorphous phase was present. With increasing annealing temperature, the crystallinity of the thin films improved significantly. By 500 °C, peaks corresponding to $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ appeared (see, e.g., the peak around 30.2° 2 θ). At an annealing temperature of 600 °C, the characteristic peaks of the NBT perovskite phase first appeared. The characteristic peaks of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase, however, still

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FIG. 1. XRD patterns of the NBT thin films annealed at different temperatures varying from 500 to 700 °C.

remained. After annealing at 700 °C, however, the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase had disappeared and the thin film had become single phase NBT.

Figure 2 shows the typical (a) surface and (b) cross-sectional morphology of the NBT thin film after annealing at 700 °C. The surface of the NBT film is rather smooth and crack-free. The multilayer trace of the deposited NBT layers is still apparent in the cross-sectional view. The total film thickness of the NBT was estimated to be about 450 nm, as shown in Fig. 2(b). The NBT/Pt interface is very clear without any diffuse layer between the NBT thin film and the bottom Pt electrode.

Figure 3 shows a typical polarization-electric field (P - E) hysteresis loop for the NBT films measured at a frequency of 300 Hz. A remnant polarization (P_r) of $\sim 10 \mu\text{C}/\text{cm}^2$ and a coercive electric field (E_c) of $\sim 130 \text{ kV}/\text{cm}$ were obtained at 550 kV/cm for the NBT film annealed at 700 °C. These values are comparable to those reported for other Bi-containing ferroelectric thin films, such as $\text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_3\text{O}_{12}$ ($P_r=10 \mu\text{C}/\text{cm}^2$ and $E_c=110 \text{ kV}/\text{cm}$),⁷ $\text{SrBi}_2(\text{V}_{0.1}\text{Nb}_{0.9})_2\text{O}_9$ ($P_r=12.5 \mu\text{C}/\text{cm}^2$ and $E_c=100 \text{ kV}/\text{cm}$),⁸ $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ($P_r=2 \mu\text{C}/\text{cm}^2$ and $E_c=150 \text{ kV}/\text{cm}$).⁹ Moreover, the remnant polarization of the obtained NBT films is lower and its coercive field higher than those obtained from sol-gel derived (111)-oriented NBT thin films ($20.9 \mu\text{C}/\text{cm}^2$, 112 kV/cm) (Ref. 10) indicating the high performance of the obtained NBT films. The difference of polarization behavior between polycrystalline and oriented thin films probably arises from the different amplitudes of the polarization, the growth mode of domains, and the concentration of domain walls and grain boundaries in the films.^{11,12} From Fig. 3, it is found that the obtained

FIG. 3. P - E hysteresis loops of the NBT thin films.

polarization-electric field hysteresis loop is not entirely symmetric, leading to slightly different $|E_{c+}|$ and $|E_{c-}|$ values. Such a difference is attributed to the imprint from the internal space charge field caused by trapped electronic charges near the ferroelectric-electrode interface.^{13,14}

The relation between the dielectric constant of the NBT film and applied electric field at 1 MHz frequency is shown in Fig. 4. Loops are observed in both the forward as well as the reverse directions of the applied field, indicating strong non-linear dielectric behavior. The observed “butterfly” hysteresis loop of Fig. 4 is typical for ferroelectrics and arises from domain wall motion during polarization switching, consistent with the P - E hysteresis loop character of Fig. 3. A slight asymmetry is observed in the ϵ - E curves, which suggests that either the films contain movable ions or charges accumulate at the interface between the film and the electrode. It is well known that boundary conditions, such as epitaxial, thermal, and/or phase transformation strains, can have a large influence on the kinds of domains formed in the thin film. The small difference between the maximum capacitance values of the two peaks in Fig. 4 suggests the presence of defect energy levels in the material. From the data shown in Fig. 4, the dielectric tunability (defined as $|\epsilon_r(T,0) - \epsilon_r(T,E)| / \epsilon_r(T,0)$, where $\epsilon_r(T,0)$ and $\epsilon_r(T,E)$ are the dielectric constant at zero electric field and applied electric field E , respectively) for dc bias electric fields up to an E_{max} of 250 kV/cm is $\sim 14\%$.

The dielectric constant and dielectric loss at a frequency of 1 kHz were ~ 464 and 0.04, respectively (see Fig. 5). The dielectric constant showed dispersion over the frequency range of 0.1–500 kHz. This dispersion is attributed to the existence of surface charge layers at the electrode-film interface and grain boundaries. It is well established that imperfections and space charge layers at electrode-ferroelectric interfaces generally dominate the dielectric behavior of small

FIG. 2. FESEM micrographs of the NBT films (a) surface view and (b) cross-sectional view.

FIG. 4. The room temperature dielectric constant as a function of applied dc voltage for NBT films.

FIG. 5. Dielectric constant and dielectric loss as a function of frequency for the NBT films.

grain ceramics where a significant fraction of the material volume may be influenced by grain boundaries.¹⁵

In conclusion, single phase NBT thin films have successfully been synthesized via a metallorganic decomposition technique and its ferroelectric and dielectric properties characterized. The thin films consisted of uniform grain size NBT crystals with an overall film thickness of ~ 450 nm, when thermally annealed at 700°C . The NBT thin films exhibit a well-defined P - E hysteresis loop with a promising remnant polarization and coercive field at room temperature. The typical dielectric constant and dielectric loss are 440 and 0.05 at 1 MHz, respectively. The tunability of the dielectric constant is $\sim 14\%$ at 250 kV/cm. The resultant dielectric and ferroelectric measurements indicate that such NBT thin films have potential for use in practical device applications such as in memory and switching devices.

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