Influence of the Strain on Dielectric and Ferroelectric Properties of 0.5BaZr0.2Ti0.8O3–0.5Ba0.7Ca0.3TiO3

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0.5BaZr0.2Ti0.8O3–0.5Ba0.7Ca0.3TiO3 ceramic and its epitaxial films on (0 0 1) SrTiO3 substrate were prepared to compare their dielectric and ferroelectric properties. The ceramic has a high dielectric permittivity, a weak dielectric relaxation, a low ferroelectric Curie temperature (Tc) of 60°C and a fast polarization relaxation. The films show much lower dielectric permittivities and mild dielectric relaxations. Furthermore, the Tc of film with 40, 100, and 200 nm thickness is 155°C, 110°C, and 60°C, respectively, because the epitaxial strain decreases with the film thickness increasing. The higher the Tc is, the more stable the room-temperature polarization is.

I. Introduction

LEAD-BASED piezoelectric materials, that is, lead zirconate titanate (PZT), contain excellent piezoelectric properties especially at the composition near their morphotropic phase boundaries (MPB), thus they are utilized in a wide variety of applications such as in nonvolatiles memories, actuators, sensors, and transducers.1,2 However, lead is volatile at conventional processing temperatures, leading to environmental and health concerns. There is an increasing demand for the lead-free materials with similar piezoelectric and ferroelectric properties to the lead-based ceramics. In consideration of the growing demand for green materials with minimized impacts on health and environment, researchers are making intensive efforts to replace lead-based ceramics with lead-free compositions.3–6 In particular, Liu and Ren reported a high piezoelectric coefficient up to 620 pC/N in a 0.5BaZr0.2Ti0.8O3–0.5Ba0.7Ca0.3TiO3 (BZT-BCT) ceramic with perovskite structure.7 BZT-BCT transforms from rhombohedral structure to tetragonal structure at ~14°C and then to cubic structure at ~60°C.7 It was thought that the high piezoelectric effect may originate from the MPB starting from a tetragonal-cubic-rhombohedral triple point, which has a very low energy barrier for polarization rotation and lattice distortion.7–10 Even so, the low Curie temperature (Tc) of ~60°C seriously limits the industrial application of BZT-BCT. The epitaxial strain from substrate is commonly used to manipulate the ferroelectric properties of and BaTiO3,11 and thus it may be effective to increase the Tc and optimize the dielectric and ferroelectric properties of BZT-BCT.

It is well-known that ferroelectric domains play an important role in the piezoelectric performance of materials. In fact, macroscopic piezoelectric coefficients are mainly determined by the domains and their dynamic response to applied electric fields. Therefore, intensive studies have been focused on domain structures and the corresponding crystallographic features of PZT and other piezoelectric systems.12–15 It is found that domain structures of these systems show a common feature: high piezoelectric-response MPB composition always coincides with nano-size domains. Such a microstructure feature indicates a low polarization anisotropy caused by phase instability, thus suggesting a good piezoelectric performance. Despite the extensive studies, the microstructure basis is still missing in the Pb-free BZT-BCT with PZT-comparable piezoelectric performance.

Here, we compare the dielectric and ferroelectric properties of BZT-BCT ceramic and its epitaxial films on (0 0 1) SrTiO3 substrate. The epitaxial strain plays an essential role in the phase transition, dielectric and ferroelectric properties of BZT-BCT films.

II. Experimental Details

The BZT-BCT ceramics were sintered with standard solid state sinter method. The raw chemicals are BaZrO3 (98%; Sinopharm Chem., Shanghai, China), CaCO3 (99.9%, Sinopharm Chem.), BaCO3 (99.95%; Sinopharm Chem.), and TiO2 (99.9%; Sinopharm Chem.). The calcining was performed at 1350°C and sintering was done at 1450°C in air. Details of their preparation, crystal structure, and electric properties were already described in a previous report.7–9 The ceramic surface was carefully polished by using polycrystalline diamond paste first and then by a colloidal silica polishing suspension to get nano-scale smooth surface. Furthermore, SrRuO3-buffered layer and then BZT-BCT ferroelectric films were grown on (0 0 1) SrTiO3 (STO) substrate at ~680°C and 13 Pa oxygen pressure by Pulsed laser deposition. The laser energy, the laser wavelength, and the pulse frequency were 150 mJ, 248 nm, and 2 Hz, respectively. After the film growth, the sample was postannealed in situ at ~680°C and 1000 Pa for half an hour to remove oxygen vacancies and then cooled down to room temperature with 5°C per minute. SrRuO3 layers are ~50 nm thicknesses while BZT-BCT films are ~40, ~100, ~200, and ~300 nm thicknesses in the 40-, 100-, 200-, and 300-BZT-BCT samples, respectively. To fabricate metal/insulator/metal capacitors, the Pt top electrodes with 100 μm diameter were grown on BZT-BCT films through a shadow mask.

The crystal structures of BZT-BCT ceramics and epitaxial films were characterized by X-ray diffraction (XRD; Brucker Advanced D8, Karlsruhe, Germany) at room temperature. The topography and ferroelectric properties of both ceramics and films were studied by an Atomic Force Microscope (AFM, Brucker Multimode 8, Camarillo, CA) with its piezoelectric force microscopy (PFM). The films’ thickness was estimated through scanning a designed gap by AFM. The A.C. probing voltage (f = 41 kHz, 2 V tip bias) was applied upon a conductive tip (MESP-RC, Co/Crcoating, USA) to observe PFM images. Samples were kept in a temperature-controlled chamber and then relative dielectric permittivity
versus temperature ($\varepsilon_r$-T) curve was measured with an impedance analyzer (Agilent 4294A, Santa Clara, CA). Ferroelectric polarizations versus electric field ($P$–$E$) loops were measured with a ferroelectric tester (Radiant multiferroic, Albuquerque, NM).

III. Results and Discussions

Although BZT-BCT ceramic has MPB near room temperature, the films with the compressive strain from (0 0 1) SrTiO$_3$ substrate have tetragonal structure. Figure 1(a) identifies the formation of a single perovskite structure of BZT-BCT ceramic, where each diffraction peak is marked according to pseudo-cubic structure. Ren et al. already proved that the BZT-BCT ceramic is composed of tetragonal phase and rhombohedral phase at room temperature.\textsuperscript{7,8,16} When the BZT-BCT film was grown on SrTiO$_3$ substrate ($a = b = c = 0.3901$ nm and $\alpha = \beta = \gamma = 90^\circ$), its in-plane lattices were compressed while its out-of-plane lattice elongated. BZT-BCT films are tetragonal phase within the limitation of our XRD system [Fig. 1(a)]. Only the diffraction peaks of (0 0 1), (0 0 2), and (0 0 3) planes of the BZT-BCT film, SrRuO$_3$-buffered layer and SrTiO$_3$ substrate were observed in the high-quality 40- and 100-BZT-BCT epitaxial films.\textsuperscript{17} The diffraction peak of (0 0 2) plane is at 44.85°, 45.06°, 45.13°, and 45.25° for 40-, 100-, 200-, and 300-BZT-BCT films and is at 45.42° for BZT-BCT ceramic [Fig. 1(b)], which correspond with the c-axis values of 0.4038, 0.4021, 0.4015, 0.4005, and 0.3990 nm, respectively. This suggests that the epitaxial strain relaxes with the film thickness increasing. The $\phi$ scans were measured on BZT-BCT (101), and SrTiO$_3$ (101) reflections as shown in Fig. 1(c). A set of four distinct peaks with 90° of separation indicates that a parallel epitaxial growth has been achieved. The high crystal-line quality of the films was further examined by the x-ray $\omega$-scan rocking curves on the BZT-BCT (001) reflections [Fig. 1(d)]. The full width at half maximum of the rocking curve, indicating the degree of dispersion of the film basal planes from the preferred $c$-axis orientation, was 0.6°–0.7°.

Dielectric permittivity is much smaller in the thin films than in the ceramics, and the thinner film shows the lower permittivity. The $\varepsilon_r$ of films is much lower than that of ceramics and strongly influenced by epitaxial strain and interface layer. The $\varepsilon_r$ of BZT-BCT ceramic has a broad shoulder at ~16$^\circ$C and an abrupt peak at ~65$^\circ$C in Fig. 2(a). The shoulder is due to the low-temperature rhombohedra ferroelectric to tetragonal ferroelectric phase transition (i.e., R–T phase transition) and the peak is as a result of the tetragonal ferroelectric to cubic paraelectric phase transition (T–C phase transition).\textsuperscript{7,8} The slight dielectric relaxation at
the broad shoulder [Inset of Fig. 2(a)] is consistent with the MPB of BZT-BCT ceramics near room temperature. The $\varepsilon_r$ of BZT-BCT films [Figs. 2(b)–(d)] is much smaller than that of BZT-BCT ceramics, partially because the $\varepsilon_r$ along $c$ axis is much smaller than that along another axis and/or high-density defects introduce low-$\varepsilon_r$ interface layers near...
The thinnest BZT-BCT film is well oriented, so it can have a lower permittivity along the c-axis than in the film plane (or than the effective permittivity in the ceramics). It is noted that grain boundaries usually have much lower permittivities than the grains, so the grain boundaries cannot enhance effective permittivity. Furthermore, the $\varepsilon_r$ shows an extremely broad maximum at a temperature ($T_m$) of ~155°C, ~110°C, and ~60°C for 40-, 100-, and 200-BZT-BCT, where $T_m$ is commonly close to the $T_C$ of the corresponding sample. The big increase in $T_C$ is reasonable since the epitaxial strain of BaTiO$_3$ film increases the $T_C$ by about 500°C than that of BaTiO$_3$ single crystals. The $T_m$ and $T_C$ decreases with the film getting thicker, because the strain decreases with the thickness increasing. Permittivity peak broadens probably due to strain gradient. The maximum value of $\varepsilon_r$ decreases with increasing frequency, and the $T_m$ shifts to a higher temperature with increasing frequency in Figs. 2(b)–(d). The relaxor behaviors in BZT-BCT thin films can be attributed to many reasons such as defect vacancies, strain gradient and so on.

Both BZT-BCT ceramic and films have large ferroelectric polarizations. The ceramic shows a saturated polarization ($P_S$) of 21 $\mu$C/cm$^2$ and a coercive field ($E_C$) of 3.4 kV/cm [Fig. 3(a)]. The $E_C$ is much smaller than most ferroelectrics (e.g., PbZr$_{0.52}$Ti$_{0.48}$O$_3$, 0.94Bi$_{0.5}$Na$_{0.5}$TiO$_3$–0.06BaTiO$_3$), because of the low Curie temperature (~60°C) and the MPB where one phase easily transforms to another under an external electric field. It is noted that the piezoelectric $d_{33}$ coefficient of the fully polarized ceramics is over 450 pC/N. The 100-BZT-BCT film with tetragonal phase has an increased $P_S$ of 38 $\mu$C/cm$^2$ and an enhanced $E_C$ of ~100 kV/cm [Fig. 3(b)], partially due to the tetragonal phase with a large compressive strain. The $P_S$ and $E_C$ of 200-BZT-BCT film decrease to 26 $\mu$C/cm$^2$ and ~50 kV/cm [Fig. 3(c)]. For 300-BZT-BCT, most of the epitaxial compressive strain relaxes, the $T_m$ decreases to ~60°C, and the $P_S$ and $E_C$ further
decrease to 19.7 μC/cm² and ~30 kV/cm [Fig. 3(d)]. Furthermore, the slim ferroelectric loops suggest the ferroelectric relaxor, too. 23

The domain structures suggest the existence of MPB in BZT-BCT ceramic; however, its ferroelectric polarization relaxes obviously due to the low $T_C$ of 60°C. Rhombohedral phase shows wedge-shaped domain with polarization ($P_S$) along [1 1 1] orientations and tetragonal phase shows parallel lamellar domains with $P_S$ along [0 0 1] orientations according to previous studies. 16,24,25 Both wedge-shaped and lamellar domains are observed in PFM images on a carefully polished ceramic surface [Figs. 4(a)–(c)]. Some wedge-shaped domains also consist of many lamellar domains inside, which is an important trait of the ferroelectric with MPB. 24 When the central 10 μm × 10 μm region was poled by a 27 V of PFM tip, the polarization orients inward in the vertical PFM phase images [Figs. 4(d)–(e)]. The color contrast of the poled and nonpoled regions becomes weak gradually when the poled ceramic relaxed under zero electric field for 10, 30, and 60 min, and finally the color contrast disappears when it relaxed for 120 min. The polarization relaxes obviously in the fully poled BZT-BCT ceramic as a result of the low $T_C$ and small $E_c$ of 3.4 kV/cm. 17

The ferroelectric polarization is stable at room temperature in 40-BZT-BCT film; however, it relaxes much faster with the thickness of the film increasing from 40 to 300 nm due to the decrease of $T_C$ from ~155°C to ~60°C. There is an atomic smooth surface of the 40-BZT-BCT film in Fig. 5(a), supporting the high-quality epitaxial films. 17 After the central 3 μm × 3 μm and 1 μm × 1 μm regions were polarized with +5 V and then −5 V applied from the SrRuO$_3$-buffered layer, the polarization orients outward and inward respectively [Fig. 5(b)]. These two regions partially depolarize after they relaxed under zero electric field for 60 min [Fig. 5(c)] and 180 min [Fig. 5(d)], which is slower than that of BZT-BCT ceramic. The 40-BZT-BCT epitaxial film is tetragonal phase with a $T_C$ of ~155°C, and thus the polarization of fully polarized film is stable. The 100-BZT-BCT film has an atomic smooth surface, too [Fig. 5(e)]. After its two regions were polarized, its vertical PFM images measured immediately...
With the film thickness increasing, the epitaxial strain 40 nm BZT-BCT film has a strain-introduced tetragonal taxial strain relaxes and the stable than that at room temperature [Figs. 5(m)] quently, the thick 300-BZT-BCT film shows a strong polari- zation relaxation again.

IV. Conclusion

The dielectric and ferroelectric properties of BZT-BCT cera- mic and its epitaxial films are compared. Being different from the BZT-BCT ceramic, the films show much lower dielectric permitivities and stronger dielectric relaxations mainly due to their defect, epitaxial strain, and dielectric permittivity anisotropy. The ceramic exhibits a strong ferroelectric polarization relaxation due to its low TC of ~60°C. The 40 nm BZT-BCT film has a strain-introduced tetragonal phase with a stable polarization and a high TC of ~155°C. With the film thickness increasing, the epitaxial strain releases and the TC decreases gradually to 60°C. Consequently, the thick 300-BZT-BCT film shows a strong polarization relaxation again.

Acknowledgments

The work is supported by the key project of the National Natural Science Foundation of China (11334004 and 51472118), the National Key Project for Basic Research of China (2012CB619406), and the normal project of National Natural Science Foundation of China (51472118).

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