

**Fine-grained BaZr<sub>0.2</sub>Ti<sub>0.8</sub>O<sub>3</sub> thin films for tunable device applications**

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A study of the structure and in-plane dielectric properties of BaZr<sub>0.2</sub>Ti<sub>0.8</sub>O<sub>3</sub> thin film epitaxially grown on (LaAlO<sub>3</sub>)<sub>0.3</sub>(Sr<sub>2</sub>AlTaO<sub>6</sub>)<sub>0.35</sub> (001) single-crystal substrates through pulsed-laser deposition has been carried out. X-ray diffraction measurements revealed a good crystallinity and tensile in-plane stress in the film. Fine grains with an average size of ~20 nm were observed using atomic force microscopy. Curie temperature of the film was found to be ~120 °C, which is 100 °C higher than that of the ceramic. Butterfly-shaped C-V curve confirmed the in-plane ferroelectric state in the film. A large dielectric tunability of ~50% was found in the film. © 2007 American Institute of Physics. [DOI: [10.1063/1.2721968](https://doi.org/10.1063/1.2721968)]

In the last decade there has been an extensive effort to develop ferroelectric thin films for frequency-agile microwave components (antenna, phase shifter, filters, etc). Barium strontium titanate (Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>, abbreviated as BST) as a promising candidate for these applications has been widely investigated; in recent years barium zirconate titanate (Ba<sub>x</sub>Zr<sub>1-x</sub>TiO<sub>3</sub>, abbreviated as BZT) has also attracted interest.<sup>1-8</sup> Both BST and BZT share some common features (e.g., good dielectric tunability), but they have different atom arrangements in their lattices. In BST, barium atoms are partially replaced by strontium; while in BZT the titanium atoms are partially substituted by zirconium. Because of this difference, BZT is expected to have a better insulation property since Zr<sup>4+</sup> is chemically more stable than Ti<sup>4+</sup>, giving rise to suppression to the conduction induced by the electron hopping between Ti<sup>4+</sup> and Ti<sup>3+</sup>. On the other hand, BZT thin films usually possess a smaller grain size than BST prepared under same conditions, as we have noticed. This is possibly another desirable feature of BZT for microwave devices—as observed in BST, the reduction in grain size could lead to the decrease of the dielectric loss and an increase in the figure of merit (FOM).<sup>9,10</sup> Despite the attractiveness of BZT thin films, however, the study of these materials in literature is rather limited as compared with the work on BST.

In this study, the structure and properties of the BaZr<sub>0.2</sub>Ti<sub>0.8</sub>O<sub>3</sub> thin film grown on the (LaAlO<sub>3</sub>)<sub>0.3</sub>

(Sr<sub>2</sub>AlTaO<sub>6</sub>)<sub>0.35</sub> (001) single-crystal substrate have been investigated. We chose to work on BZT with a Zr/Ti ratio of 20/80 mainly because the Curie temperature of the ceramic of this composition is around room temperature, making it convenient to compare the dielectric and ferroelectric properties of the thin films and ceramics.<sup>11</sup> The films were deposited by pulsed laser deposition (PLD) using a krypton fluoride (KrF) excimer laser (Lambda Physik COMPex 205) with a wavelength of 248 nm, energy of 220 mJ, and repetition rate of 10 Hz. The distance between the target and the substrate was fixed at 5 cm. The substrate temperature was 700 °C. The oxygen partial pressure was kept at 27 Pa during the laser ablation process. After a 40 min deposition, thin film with a thickness of ~300 nm was obtained. Postannealing was conducted in air at 1000 °C for 3 h to improve the crystallinity and reduce the oxygen vacancy concentration. The crystal and microstructure of the film were characterized by x-ray diffraction (XRD) and atomic force microscope (AFM, Digital Instrument Nanoscope IV). The in-plane dielectric characterization was carried out using coplanar interdigital electrodes (IDE). The top electrode was prepared by the deposition of a 200 nm thick Au layer on the film surface, followed by patterning using standard photolithography and wet chemical etching techniques. The IDE has a total of 21 fingers with the finger length of 925 μm and finger width of 5 μm. The finger gap spacing is 3 μm. The IDE was wire-bonded to a piece of PCB for easy handling and better electrical contact during the subsequent measurement process. The dielectric properties were measured using a HP 4294A impedance analyzer (for low frequency) connected to a

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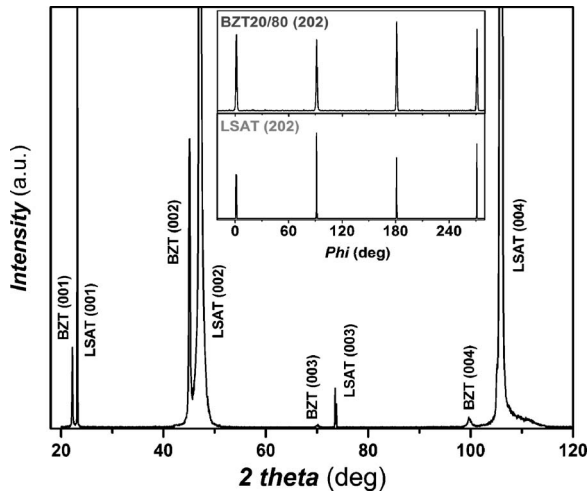


FIG. 1. XRD patterns of  $\theta/2\theta$  scan from  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin film deposited on LSAT (001) substrate. The inset is the  $\phi$ -scan of  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  (202) and LSAT (202) reflections.

temperature-controlled chamber (Oxford) or a network analyzer Agilent 8740S (for frequencies up to 10 GHz).

Figure 1 shows the x-ray diffraction patterns of the heterostructure of BZT on  $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.35}$  (LSAT). Only strong (00 $l$ ) peaks appear in the  $\theta/2\theta$  scan pattern, indicating that the  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin film has a pure perovskite phase and is highly oriented. The in-plane alignment of the  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin film with respect to the major axes of the (001) LSAT substrate was also confirmed by the XRD off-axis  $\Phi$ -scan of the  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  (202) and LSAT (202) reflections, as shown in the inset of Fig. 1, which indicates a heteroepitaxial growth of the thin film. The rocking curve measurements of the BST (002) reflections revealed that the full width at half maximum (FWHM) is about  $0.60^\circ$ . Lattice parameters were determined from the XRD results. The lattice spacing  $d_{002}$  and  $d_{202}$  were calculated, and then the out-of-plane lattice parameter  $c (=2 d_{002})$  and the in-plane lattice parameter  $a = (2/\sqrt{d_{202}^{-2} - d_{002}^{-2}})$  were derived.<sup>12</sup> The in-plane and out-of-plane lattice parameters were calculated to be 4.0588 and 4.0138 Å, respectively. It is found that the film has a tetragonal structure with  $a/c$  of 1.011, which is different from the rhombohedral structure of bulk  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  ceramics ( $a=c=4.043$  Å), suggesting that structure of the film has been modified by the substrate. Lattice distortion in perovskite oxide thin films grown on cubic-structured single-crystal substrates, especially in the  $\text{BaSrTiO}_3$ -related heterostructures, has been extensively studied in the literature. The possible reasons for the distortion, as generally believed, should include the stress induced by the lattice mismatch between the film and the substrate, the difference in thermal expansion coefficient between the thin film and the substrate and defects (oxygen vacancies) in thin films.<sup>13–17</sup> For our BZT on LSAT, the elongation of the lattice along the in-plane direction cannot be explained as a result of the stress caused by the lattice mismatch because the lattice constant of bulk BZT (4.043 Å) is about 3% larger than that of LSAT (cubic structure with lattice parameter of 3.868 Å). So, very likely the thermal expansion and oxygen deficiency (caused by the

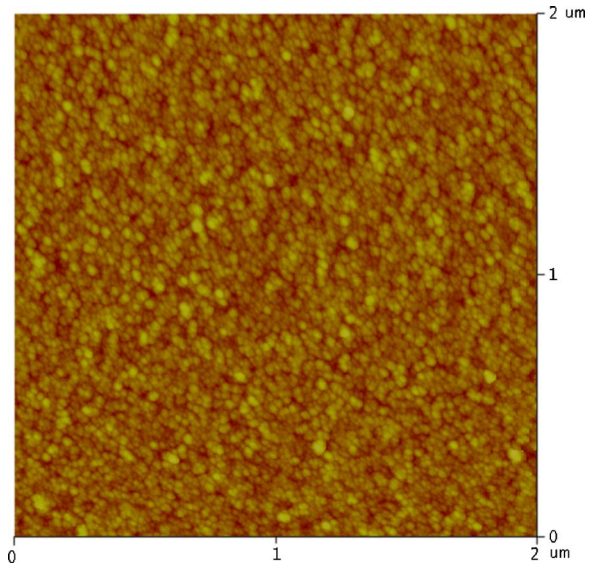


FIG. 2. (Color online) AFM image of  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin film grown on the LSAT (001) substrate.

high vacuum deposition process) are the dominant factors that have caused the lattice distortion.

The surface morphology of the  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin film was checked on AFM working in a tapping mode. Figure 2 shows the AFM image. Fine grains were observed and the average grain size of the BZT film was estimated to be  $\sim 20$  nm in diameter, which is much smaller than the average grain size of BST prepared under the same conditions ( $\sim 40$ – $50$  nm, according to our experience).

Figure 3 shows the in-plane relative permittivity  $\epsilon$  of the  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin film over a temperature range from  $-75$  to  $140^\circ\text{C}$ . The curve exhibits a maximum in  $\epsilon$  at  $T_c \approx 120^\circ\text{C}$ , which is about  $100^\circ\text{C}$  higher than that of bulk  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  ceramics as shown in Fig. 3. The upward shift of  $T_c$  in the  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin film is believed to be the contribution of in-plane lattice elongation confirmed by the XRD measurements, which is analog to what we have previously observed in the  $\text{BaSrTiO}_3$  thin films.<sup>13,17</sup> In general,

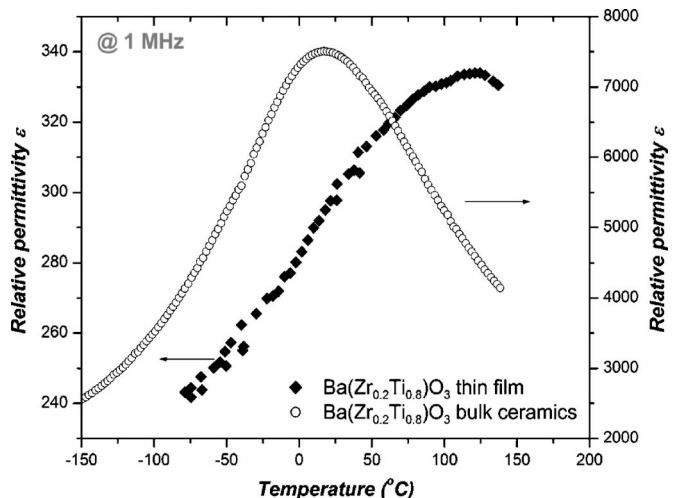


FIG. 3. In-plane  $\epsilon$  in  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin film deposited on LSAT (001) as a function of temperature. The  $\epsilon$ - $T$  curve of  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  bulk ceramics was also shown for comparison.

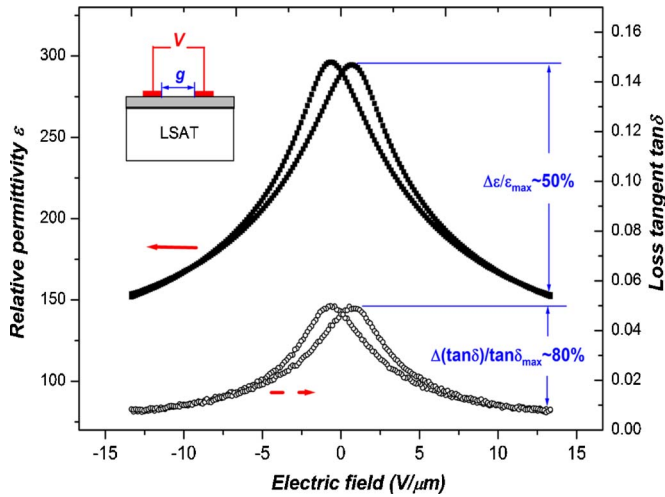


FIG. 4. (Color online) In-plane  $\epsilon$ - $E$  and  $\tan \delta$ - $E$  curves of  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin film grown on LSAT (001) substrate.

if there is a tensile stress along the in-plane direction inside the film, then the Curie temperature of the thin films is likely to shift toward the high temperature direction. Conversely, a compressive stress may lower the Curie temperature of the films. As a matter of fact, we have also observed upward shift of  $T_c$  in our  $\text{BaZrTiO}_3$  thin films with other Zr/Ti ratios (25/75, 30/70, and 35/65, respectively). This shift of  $T_c$  makes the BZT film possess a good dielectric tunability over a wide frequency range, which is desirable for applications. The negative side of the  $T_c$  shift is that it causes BZT to be in the ferroelectric state and thus have a relatively large dielectric loss when working at room temperature.

The in-plane  $C$ - $V$  characteristics of the  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  film were determined over a wide frequency and temperature range. A strong dependence of  $\epsilon$  on the applied dc bias is found. Figure 4 shows the  $\epsilon$ - $E$  and  $\tan \delta$ - $E$  dependence measured at 1 MHz, where the electrical field strength  $E$  is defined as the ratio of the dc voltage ( $V$ ) over the gap ( $g$ ) between the top electrodes. The curves are in the shape of a butterfly, which is consistent with the room-temperature ferroelectric state observed in the  $\epsilon$ - $T$  measurement. At room temperature, the dielectric tunability, defined as  $\Delta\epsilon/\epsilon = (\epsilon_{\text{max}} - \epsilon_{\text{min}})/\epsilon_{\text{max}}$ , is  $\sim 50\%$  at 1 MHz under a moderated dc bias field of  $13.3 \text{ V}/\mu\text{m}$  and it remains  $>30\%$  in the gigahertz range. It is known that, due to the nonuniform distribution of electrical fields, coplanar designs generally require a higher driving voltage and offer lower apparent tunability in comparison to the parallel-plate capacitors. This means that, if our  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  film were characterized in a parallel-plate capacitor, a larger value of the tunability could be obtained. Some other important characteristics have also been found in the BZT film. First, the tunability did not show strong temperature dependence in the test range of 25–150 °C (data not shown). Second, while the  $\epsilon$ - $E$  dependence in a ferroelectric material is often described by an equation  $\epsilon_r(T, E) = \epsilon_r(T, 0) / \{1 + [\epsilon_0 \epsilon_r(T, 0)]^3 B(T) E^2\}^{1/3}$  [where  $B(T)$  is a phenomenological constant,  $\epsilon_r$  and  $\epsilon_0$  are the relative permittivity and vacuum permittivity, respectively],<sup>18</sup> the experimental data for our BZT film could not be well fitted into

the equation, probably because of the different definitions of the electrical field. Third, the dielectric constant drops faster than the loss tangent when tested under a same dc bias. For example, the tunability of the dielectric constant under a bias field of  $13.3 \text{ V}/\mu\text{m}$  is  $\sim 50\%$ , whereas the tunability of the loss tangent is  $\sim 80\%$ . The mechanism is not yet clear, but we believe it should be very much similar to the dielectric aging of ferroelectric materials (a theoretical model was proposed in an earlier paper by us).<sup>19</sup>

In summary, this study has presented the fabrication and in-plane dielectric characterization of heteroepitaxial  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin film. The film shows a distorted lattice structure with the in-plane and out-of-plane lattice parameters of 4.0588 and 4.0138 Å, respectively. Owing to the in-plane lattice elongation, the  $T_c$  of the  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  film shifted upwards to  $\sim 120$  °C, which is nearly 100 °C higher than that of the  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  ceramics. Butterfly-shaped  $C$ - $V$  characteristic curve confirmed the in-plane ferroelectricity; meanwhile, a high dielectric tunability of  $\sim 50\%$  was found, in addition to many other important features. This work demonstrates the potential in  $\text{BaSrTiO}_3$  thin films as a candidate for microwave device applications.

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