

## Enhanced in-plane ferroelectricity in $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films grown on MgO (001) single-crystal substrate

D. Y. Wang,<sup>a)</sup> Y. Wang, X. Y. Zhou, H. L. W. Chan, and C. L. Choy

Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Hong Kong, China

(Received 31 January 2005; accepted 15 April 2005; published online 17 May 2005)

Highly oriented  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin films were grown on MgO (001) single-crystal substrate using pulsed-laser deposition and the in-plane ferroelectric properties of the film were evaluated. X-ray diffraction characterization revealed a good crystallinity and tensile in-plane stress in the film. A well-defined ferroelectric hysteresis loop with  $P_r=9.5 \mu\text{C}/\text{cm}^2$  was observed along the (100) direction, which implied an enhanced in-plane ferroelectricity in the  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin film in comparison with the  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  ceramics. Curie temperature of the film was found to be  $\sim 88^\circ\text{C}$ , which is nearly  $50^\circ\text{C}$  higher than that of the  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  ceramics. The butterfly-shaped  $C$ - $V$  characteristic curve also evidenced the enhanced in-plane ferroelectric property in the film, and a large dielectric tunability of 69% was found at 1 MHz under a moderate dc bias field. The observation of enhanced ferroelectricity along the in-plane direction in the highly oriented  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin film was explained in terms of the increased tetragonality ( $a/c = 1.016$ ) induced by the lattice misfit strain. © 2005 American Institute of Physics.

[DOI: 10.1063/1.1938247]

Tetragonality ( $c/a$ ) is strongly correlated with ferroelectric properties in perovskite oxides; for example,  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ceramics with  $x \geq 0.30$  are paraelectric with cubic structure ( $c/a=1$ ), but when  $x < 0.30$ , it shows a ferroelectric phase with tetragonal structure ( $c/a > 1$ ).<sup>1</sup> Therefore, the ferroelectric properties can be modified by changing the tetragonality. In ceramics, the lattice structure modification is usually realized by doping or by changing the composition. The tetragonality of perovskite oxide thin films can be also effectively modified by choosing appropriate substrates.<sup>2,3</sup> For instance, when the lattice parameter of the substrate is smaller than the lattice parameter of the film, the thin film will have an elongated lattice along the out-of-plane direction, leading to an improved out-of-plane ferroelectric properties and usually associated with an enhanced piezoelectric performance. Because the modification via the film-substrate interface can effectively improve the ferroelectric properties, in recent years, the substrate effect on thin-film properties have attracted increasing attentions.<sup>4-8</sup>

Modification of the structure and property in ferroelectric thin films is a very active area. However, research in the literatures has mostly been focusing on the out-of-plane characterization, the in-plane investigation is limited. Barium strontium titanate ( $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ) thin films have been extensively studied for their excellent dielectric nonlinearity.<sup>9-11</sup> In this letter, the in-plane ferroelectric properties of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  (BST) thin films were investigated. The nominal composition of the thin films was  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ , a composition with Curie point near room temperature, where the giant room-temperature dielectric tunability was observed.<sup>12</sup> The ferroelectric characterization was conducted along the in-plane direction rather than a conventional out-of-plane direction, not only because the in-plane ferroelectric properties of BST thin films had been seldom studied, but also because

the in-plane configuration is more directly relevant to the actual coplanar devices.

The  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin films were deposited on MgO (001) single-crystal substrates by pulsed-laser deposition (PLD) using a krypton fluoride (KrF) excimer laser (Lambda Physik COMPex 205) with a wavelength of 248 nm. A laser energy of 250 mJ and a repetition rate of 10 Hz were adopted. The distance between the target and the substrate was fixed at 5 cm. The substrate temperature was maintained at  $750^\circ\text{C}$ . The oxygen partial pressure was kept at 27 Pa during the laser ablation process. The  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin films of approximately 300 nm thickness were grown on MgO (001) substrates by irradiating the stoichiometric target for 15 min. After deposition, the film was postannealed in a tube furnace at  $1000^\circ\text{C}$  for 3 h to reduce the oxygen vacancies.

The crystallographic characterization was performed on a Bruker AXS D8 Discover x-ray diffractometer (XRD). Only strong (00 $l$ ) peaks appear in the  $\theta/2\theta$  scan pattern, which implied that the BST thin film has a pure perovskite phase, as shown in Fig. 1. The in-plane alignment of the BST thin film with respect to the major axes of the (001) MgO substrate was also confirmed by the XRD off-axis  $\phi$  scan of the BST (202) and MgO (202) reflections, indicating a highly oriented growth of the BST thin film. The rocking curve measurements of the BST (002) reflections revealed that the full width at half-maximum is about  $0.48^\circ$ . 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  $c (=2d_{002})$  and the in-plane lattice parameter  $a=(2/\sqrt{d_{202}^2-d_{002}^2})$  were derived.<sup>13</sup> The in-plane and out-of-plane lattice parameters were found to be 4.0344 and 3.9718 Å, respectively, indicating that the BST film has a tetragonal structure with  $a/c$  of 1.016, which is different from the cubic structure of the  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  ceramics. It is noticed that the in-plane lattice parameter is much larger than that in bulk BST (3.9650 Å). The lattice deformation in our

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: 02901276r@polyu.edu.hk

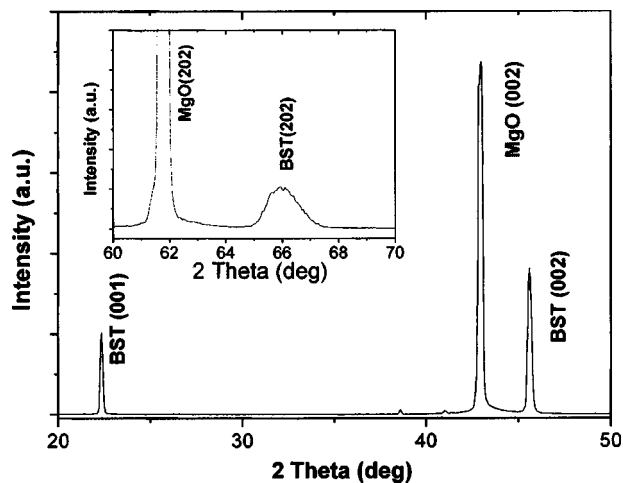


FIG. 1. XRD patterns of  $\theta/2\theta$  scan from a  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin film deposited on MgO (001) substrate. The inset is the  $\theta/2\theta$  scan of a  $45^\circ$  tilted  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin film.

BST thin film is presumably due to a result of the lattice misfit between the BST and the MgO substrate (cubic structure with lattice parameter of  $4.215 \text{ \AA}$ ). This result also implies that the BST film is stressed in tension along the in-plane direction. Meanwhile, it is found that not only the in-plane but also the out-of-plane lattice parameter is larger than the bulk value. This seems somewhat different from the pure strain effect. Other factors, such as anisotropic thermal contraction<sup>4</sup> and oxygen deficiency,<sup>14</sup> may also be responsible for the unusual lattice distortion. The surface morphology of the BST thin films was checked on an atomic force microscope (Digital Instrument Nanoscope IV) working in a tapping mode (images not shown here). The average grain size was estimated to be about 40–50 nm in diameter. The rms roughness is about 2 nm over a  $1 \times 1 \mu\text{m}^2$  area, which implies a relatively smooth film surface.

The in-plane ferroelectric 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  $925 \mu\text{m}$  and finger width of  $5 \mu\text{m}$ . The finger gap spacing is  $3 \mu\text{m}$ . The IDE was wire-bonded to a piece of PCB for easy handling and better electrical contact during the subsequent measurement process. The ferroelectric hysteresis loop was measured using TF Analyzer 2000 equipped with a FE-Module (HV) (aixACCT) along the in-plane direction.

A well-defined hysteresis loop was clearly observed, as shown in Fig. 2. The remnant polarization  $P_r$  and coercive field  $E_c$  were found to be  $9.5 \mu\text{C}/\text{cm}^2$  and  $2.1 \text{ V}/\mu\text{m}$ , respectively. A bulk  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  ceramics have a cubic structure and do not show obvious hysteresis loop,<sup>15</sup> as shown in the inset of Fig. 2. In comparison with  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  ceramics, the  $P_r$  of the film along the in-plane direction has been noticeable enhanced. It is believed that the increased tetragonality ( $a/c$  increased from 1 to 1.016) contributed to the enhanced ferroelectricity. Normally, the substrates will affect the measurement results in the coplanar electrode configuration since the electric field may penetrate into the substrate. The low dielectric constant of MgO substrate ( $\epsilon=9.8$ ) can reduce the field penetration in the sub-

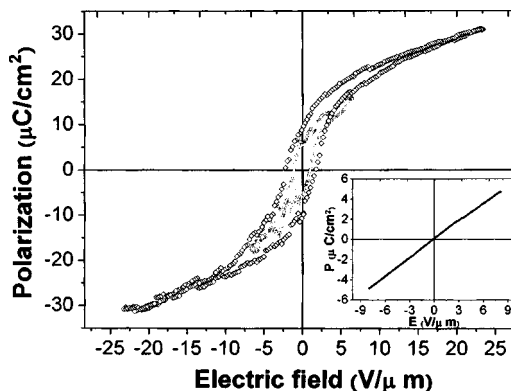


FIG. 2. In-plane ferroelectric hysteresis loop of  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin film grown on MgO (001) substrate. Inset is the  $P$ - $E$  hysteresis loop of  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  bulk ceramics.

strate and the applied field can be more effective in exciting the in-plane ferroelectricity of the BST films when interdigital electrodes were used. However, due to the IDE configuration, the distribution of the electric field inside the film is not uniform as that in a parallel plate capacitor so that the effective field applied to the film may not be as high as expected. Therefore, the actual in-plane ferroelectric properties of the BST films should be even better than that shown in Fig. 2.

Figure 3 shows the temperature-dependent in-plane relative permittivity  $\epsilon$  of the BST thin film measured using an HP 4294A impedance analyzer connected to a temperature-controlled chamber (Oxford). The calculation from the capacitance of the film to obtain the dielectric constant was conducted by using a MATHEMATICA program that we developed based on Gevorgian's model,<sup>16,17</sup> which has established the relationships among the capacitance, the electrode size, and the material properties. The curves exhibit a maximum in  $\epsilon$  at  $T_c \approx 88^\circ\text{C}$ , which is about  $50^\circ\text{C}$  higher than that of bulk  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  ceramics as shown in the inset of Fig. 3. The shift of  $T_c$  in the  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin film along the in-plane direction is believed to be the contribution of in-plane tensile strain induced by the lattice misfit. It has been reported that a biaxial tensile strain of order 1% in ferroelectric thin films is enough to push the Curie temperature  $T_c$  to several hundred degrees higher than its inherent value.<sup>7,8</sup> The

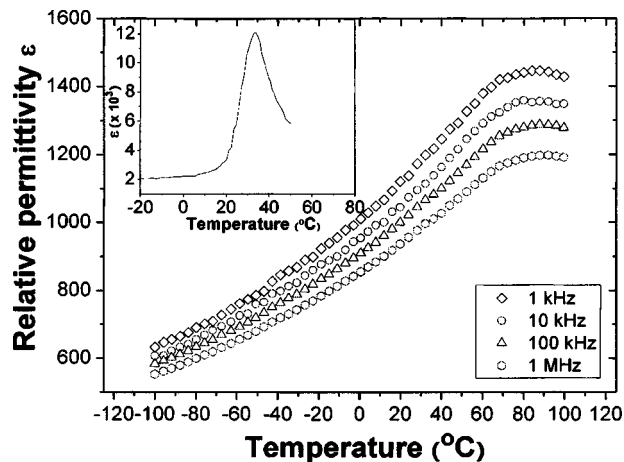


FIG. 3. In-plane relative permittivity  $\epsilon$  in a  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin film deposited on MgO (001) as a function of temperature. The inset is the  $\epsilon$  vs  $T$  of  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  bulk ceramics.

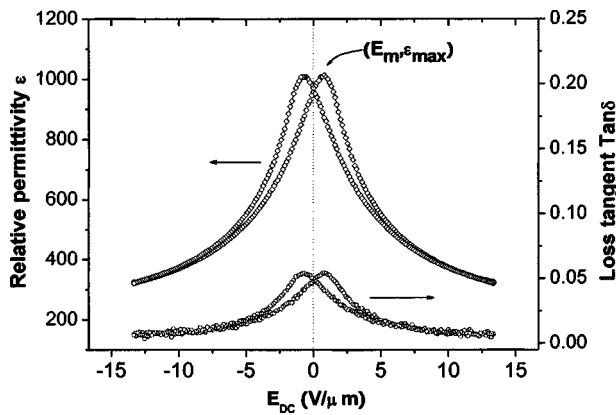


FIG. 4. In-plane  $C$ - $V$  and  $\tan \delta$ - $V$  curve of  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin film grown on  $\text{MgO}$  (001) substrate at 1 MHz.

in-plane strain  $s$  in our BST thin film was calculated to be 1.65% by using  $s = (a_{\parallel} - a_0) / a_0$ , where  $a_{\parallel}$  is the in-plane lattice parameter and  $a_0$  is the lattice parameter of freestanding BST ceramics. The shift of  $T_c$  in our tensile stressed BST film is not so significant as expected because the film thickness has greatly exceeded its critical values, resulting in a relaxation towards a zero-strain state by the introduction of dislocations. The large lattice misfit energy induced by the lattice misfit at the interface can only be released by creating lots of edge dislocations at the interface between the BST film and  $\text{MgO}$  substrate.<sup>18,19</sup> The high dislocation densities in epitaxial BST thin films (typical  $\sim 10^{11} \text{ cm}^{-2}$ ) may cause the inhomogeneous strain which will further smear the phase transition. Nevertheless, the shift of  $T_c$  in BST thin films to higher temperature has strongly supported the enhanced in-plane ferroelectric properties.

The in-plane  $C$ - $V$  characteristics of the BST film were investigated using an HP 4292A impedance analyzer and a strong dependence of  $\epsilon$  on the dc bias field was observed. As shown in Fig. 4, the film exhibits a butterfly-shaped  $\epsilon$ - $E$  and  $\tan \delta$ - $E$  dependence which further evidenced the enhancement in the in-plane ferroelectric property of the BST film. The electric field  $E_m$  at which  $\epsilon$  is a maximum, which corresponds to the coercive field, is found to be 2.2  $\text{V}/\mu\text{m}$ . This value is consistent with that observed from the ferroelectric hysteresis loop. The maximum in-plane dielectric tunability [ $\Delta\epsilon/\epsilon = (\epsilon_{\text{max}} - \epsilon_{\text{min}}) / \epsilon_{\text{max}}$ ] is calculated to be 69% at 1 MHz under a moderate dc bias field of 13.3  $\text{V}/\mu\text{m}$ . In comparison to the parallel-plate capacitors, coplanar designs generally require higher driving voltage and offer lower tunability, but our results are comparable with some of the reported data on BST films based on parallel plate capacitors.<sup>20-22</sup> It is noticed that the dielectric loss at zero field is relatively high, which is probably due to the ferroelectric phase induced by the strain.

In summary, this study investigated the ferroelectric properties of highly oriented  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin film along the in-plane direction. The films show an increased tetragonality with  $a/c = 1.016$  compared with the  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  ceramics. Owing to the increased tetragonality, enhanced in-plane ferroelectricity was found in the film. A well-defined ferroelectric hysteresis loop was observed along the in-plane

direction with an enhanced  $P_r$  of 9.5  $\mu\text{C}/\text{cm}^2$  compared with the  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  ceramics. The  $T_c$  of BST film shifts to  $\sim 88^\circ\text{C}$ , which is nearly  $50^\circ\text{C}$  higher than that of the  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  ceramics. Butterfly-shaped  $C$ - $V$  characteristic curves gave further evidence of the enhancement in-plane ferroelectricity; meanwhile, a large dielectric tunability of 69% was found at 1 MHz. This work demonstrates a possible way to enhance the ferroelectricity in thin-film form by using conventional materials and substrates.

The authors would like to thank Dr. S. G. Lu for his help in the PLD target preparation. Financial support from the Centre for Smart Materials of the Hong Kong Polytechnic University is acknowledged.

- <sup>1</sup>*Ferroelectrics and Related Substances*, edited by H. Landolt, Landolt-Börnstein, New Series, Group III, Vol. 36 (Springer-Verlag, Berlin, 2002), p. 416.
- <sup>2</sup>V. Nagarajan, S. P. Alpay, C. S. Ganpule, B. K. Nagaraj, S. Aggarwal, E. D. Williams, A. L. Roytburd, and R. Ramesh, *Appl. Phys. Lett.* **77**, 438 (2000).
- <sup>3</sup>W. J. Kim, W. Chang, S. B. Qadri, J. M. Pond, S. W. Kirchoefer, D. B. Chrisey, and J. S. Horwitz, *Appl. Phys. Lett.* **76**, 1185 (2000).
- <sup>4</sup>J. H. Chen, C. L. Lia, K. Urban, and C. L. Chen, *Appl. Phys. Lett.* **81**, 1291 (2002).
- <sup>5</sup>W. Y. Park, K. H. Ahn, and C. S. Hwang, *Appl. Phys. Lett.* **83**, 4387 (2003).
- <sup>6</sup>N. Yanase, K. Abe, N. Fukushima, and T. Kawakubo, *Jpn. J. Appl. Phys., Part 1* **38**, 5305 (1999).
- <sup>7</sup>J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, *Nature (London)* **430**, 758 (2004).
- <sup>8</sup>K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L. Q. Chen, D. G. Schlom, and C. B. Eom, *Science* **306**, 1005 (2004).
- <sup>9</sup>C. L. Chen, H. H. Feng, Z. Zhang, A. Brazdeikis, Z. J. Huang, W. K. Chu, C. W. Chu, F. A. Miranda, F. W. Van Keuls, R. R. Romanofsky, and Y. Liou, *Appl. Phys. Lett.* **75**, 412 (1999).
- <sup>10</sup>C. L. Chen, J. Chen, S. Y. Chen, G. P. Luo, C. W. Chu, F. A. Miranda, F. W. Van Keuls, J. C. Jiang, E. I. Meletis, and H. Y. Chang, *Appl. Phys. Lett.* **78**, 652 (2001).
- <sup>11</sup>B. H. Park, Y. Gim, Y. Fan, Q. X. Jia, and P. Lu, *Appl. Phys. Lett.* **77**, 2587 (2000).
- <sup>12</sup>Y. Lin, J.-S. Lee, H. Wang, Y. Li, S. R. Foltyn, Q. X. Jia, G. E. Collis, A. K. Burrell, and T. M. McCleskey, *Appl. Phys. Lett.* **85**, 5007 (2004).
- <sup>13</sup>E. D. Specht, H.-M. Christen, D. P. Norton, and L. A. Boatner, *Phys. Rev. Lett.* **80**, 4317 (1998).
- <sup>14</sup>N. Navi, H. Kim, J. S. Horwitz, H. D. Wu, and S. B. Qadri, *Appl. Phys. A: Mater. Sci. Process.* **76**, 841 (2003).
- <sup>15</sup>S. Min Rhim, S. Hong, H. Bak, and O. K. Kim, *J. Am. Ceram. Soc.* **83**, 1145 (2000).
- <sup>16</sup>Y. Wang, Y. L. Cheng, K. C. Cheng, H. L. W. Chan, and C. L. Choy, *Appl. Phys. Lett.* **85**, 1580 (2004).
- <sup>17</sup>S. S. Gevorgian, T. Matinsson, P. L. J. Linner, and E. L. Kollberg, *IEEE Trans. Microwave Theory Tech.* **44**, 896 (1996).
- <sup>18</sup>C. L. Chen, T. Garret, Y. Lin, J. C. Jiang, E. I. Meletis, F. A. Miranda, Z. Zhang, and W. K. Chu, *Integr. Ferroelectr.* **42**, 165 (2002).
- <sup>19</sup>C. L. Canedy, Hao Li, S. P. Alpay, L. Salamanca-Riba, A. L. Roytburd, and R. Ramesh, *Appl. Phys. Lett.* **77**, 1695 (2000).
- <sup>20</sup>S. G. Lu, X. H. Zhu, C. L. Mak, K. H. Wong, H. L. W. Chan, and C. L. Choy, *Appl. Phys. Lett.* **82**, 2877 (2003).
- <sup>21</sup>P. Padmini, T. R. Taylor, M. J. Lefevre, A. S. Nagra, R. A. York, and J. S. Speck, *Appl. Phys. Lett.* **75**, 3186 (1999).
- <sup>22</sup>Jaemo Im, O. Auciello, P. K. Baumann, S. K. Streiffer, D. Y. Kaufman, and A. R. Krauss, *Appl. Phys. Lett.* **76**, 625 (2000).

Applied Physics Letters is copyrighted by the American Institute of Physics (AIP).  
Redistribution of journal material is subject to the AIP online journal license and/or AIP  
copyright. For more information, see <http://ojps.aip.org/aplo/aplcr.jsp>