

# Formation and characteristics of highly *c*-axis-oriented Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films on SiO<sub>2</sub>/Si(100) and Pt/Ti/SiO<sub>2</sub>/Si(100) substrates

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Highly *c*-axis-oriented Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> (BLT) films with a homogeneous in-plane orientation were successfully grown on SiO<sub>2</sub>/Si(100) and Pt/Ti/SiO<sub>2</sub>/Si(100) substrates by a sol-coating route. The substitution of lanthanum ions for bismuth ions in the layered perovskite suppressed the formation of pyrochlore phase and enhanced the *c*-axis-oriented growth. The *c*-axis-oriented BLT film fabricated on a Pt/Ti/SiO<sub>2</sub>/Si(100) substrate showed fatigue-free characteristics with a large remanent polarization of 26–28 μC/cm<sup>2</sup> and the coercive field of 50–75 kV/cm. These features significantly enhance the potential value of the BLT film for the applications to high-density ferroelectric random-access memories devices. In addition, the *c*-axis-oriented BLT film, with a homogeneous in-plane orientation on an amorphous surface, can be used as a suitable template material for applications to various electro-magneto-optic devices.

## I. INTRODUCTION

Thin-film Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> (BLT), prepared by pulsed laser deposition (PLD), was recently proposed as a promising alternative to ferroelectric thin films having polarization fatigue.<sup>1</sup> Thin-film BLT showed well-saturated polarization-electric field (P-E) switching curves and fatigue-free behavior after being subjected to  $3 \times 10^{10}$  read/write cycles at a frequency of 1 MHz. However, as Kingon pointed out, such films are characterized by a mixed orientation of grains with a possibility of increased bit-to-bit variability in a capacitor for high-density ferroelectric random-access memory (FRAM) devices.<sup>2</sup> In addition, PLD-grown films generally exhibit highly nonuniform film profiles. These are problematic for device applications because large-scale processing in the integrated circuit industry requires a uniform and homogeneous film over a large area of Si substrate for the reproducibility of devices. The sol-coating route employed in the present study is a useful method for the fabrication of various electronic and electro-optic thin films and has definite advantages over other commonly

used techniques. The advantages include (i) the ability to produce a uniform film over a large area, (ii) a relatively lower cost, (iii) easy control of composition and thickness, (iv) good chemical homogeneity, and (v) low processing temperature.

Park and co-workers<sup>1</sup> reported that lanthanum-modified Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BT) sustained the layered perovskite structure of BT phase. They proposed that lanthanum ions substituted for bismuth ions located near the Ti–O octahedron layer and thereby enhanced the stability of oxygen ions in the lattice. Accepting this proposition, one can expect that BLT also has a layered perovskite structure and thus possesses a high affinity for the *c*-axis-oriented preferential growth by virtue of its layered nature. Thus, the BLT film can potentially be used as a promising template layer for the growth of various functional thin films having a homogeneous orientation on a Si substrate.

The direction and the magnitude of spontaneous polarization in lanthanum-modified BT crystals have not been clearly understood, while those for the unmodified BT crystal are well known. Single-crystal BT has two distinct directions for its spontaneous polarization: one with a magnitude of  $50 \pm 5 \mu\text{C}/\text{cm}^2$  in the *b* direction, and the other with  $4.0 \pm 0.1 \mu\text{C}/\text{cm}^2$  along the *c* axis.<sup>3,4</sup> However, the direction and magnitude of spontaneous polarization of lanthanum-modified BT might be different from those of BT. This is because the lanthanum ion

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that substitutes for bismuth ion exerts a strong bonding influence on the Ti–O octahedron, stretching the octahedron unit. Provided that the lanthanum ion changes the direction and the magnitude of spontaneous polarization, these changes will be most readily reflected in the direction parallel to the *c* axis because the spontaneous polarization along the *c* direction is significantly smaller than the polarization perpendicular to the *c* axis. Thus, the spontaneous polarization along the *c* axis is expected to be highly susceptible to the lanthanum substitution.

In this study, highly *c*-axis-oriented Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> (BLT) films were successfully grown on both SiO<sub>2</sub>/Si(100) and Pt/Ti/SiO<sub>2</sub>/Si substrates using a sol-coating route. Contrary to the BLT film (*x* = 0.75) fabricated by PLD,<sup>1</sup> the present BLT films were characterized by a strong *c*-axis-oriented growth with a homogeneous in-plane orientation. A Pt/BLT/Pt/Ti/SiO<sub>2</sub>/Si(100) capacitor, fabricated in the present work, showed a well-saturated polarization–electric field (P-E) switching curve with its remanent polarization (*2P<sub>r</sub>*) of 26–28 μC/cm<sup>2</sup> and coercive field (*E<sub>c</sub>*) of 50–75 kV/cm at an applied voltage of 10 V.<sup>5</sup>

## II. EXPERIMENTAL

### A. Preparation of sol

The precursor solution for the BLT was prepared by first dissolving appropriate amounts of bismuth acetate [Bi(CH<sub>3</sub>COO)<sub>3</sub>] and lanthanum acetate hydrate [La(CH<sub>3</sub>COO)<sub>3</sub> · 2H<sub>2</sub>O] into an acetic acid solution at room temperature in a glove box flushed with nitrogen gas. Similarly, an acidic solution of bismuth acetate was prepared for the BT precursor. A stoichiometric amount of titanium isopropoxide solution {Ti[(CH<sub>3</sub>)<sub>2</sub>OCH]<sub>4</sub>} was slowly added to the mixed precursor solution in a glove box. Clear yellowish sols with a molar concentration of 0.3 M were obtained. These sols were stable over a period of several months. A 4 mol% excess amount of bismuth acetate was used to compensate the Bi loss that occurs during the thermal annealing of amorphous films.

### B. Fabrication and characterization films and capacitors

The BLT and BT films were fabricated onto both SiO<sub>2</sub>/Si(100) and Pt/Ti/SiO<sub>2</sub>/Si(100) substrates using a repeated coating/drying cycle. The drying was performed at room temperature. The dried films were amorphous as determined by x-ray diffraction (XRD). The amorphous films deposited on SiO<sub>2</sub>/Si(100) substrates were subsequently crystallized by thermal annealing at various temperatures between 300 and 800 °C for 15 min in an oxygen atmosphere. The films prepared on Pt/Ti/SiO<sub>2</sub>/Si(100) substrates were annealed in the temperature

range between 400 and 650 °C for 1 h in the same oxygen atmosphere. As-annealed films were crack free, uniform, and dense, and they adhered well on the substrates used.

Chemical compositions of the annealed films were examined using energy dispersive spectroscopy (EDS). For a reliable EDS analysis, the chemical compositions of the crystalline BLT and BT powders, as derived from the same precursor sols, were determined using an inductively coupled plasma emission spectrometer (ICPES) with a high-frequency argon plasma as an emission source. The stoichiometry of powders, as evaluated using an ICPES, was essentially the same as the intended one. The composition-identified BLT and BT powders were then used as standards for the quantitative EDS analysis. Both the stoichiometry of the BLT/SiO<sub>2</sub>/Si(100) annealed at 700 °C for 15 min and that of the BLT/Pt/Ti/SiO<sub>2</sub>/Si(100) annealed at 650 °C for 1 h were essentially the same as the desired composition.

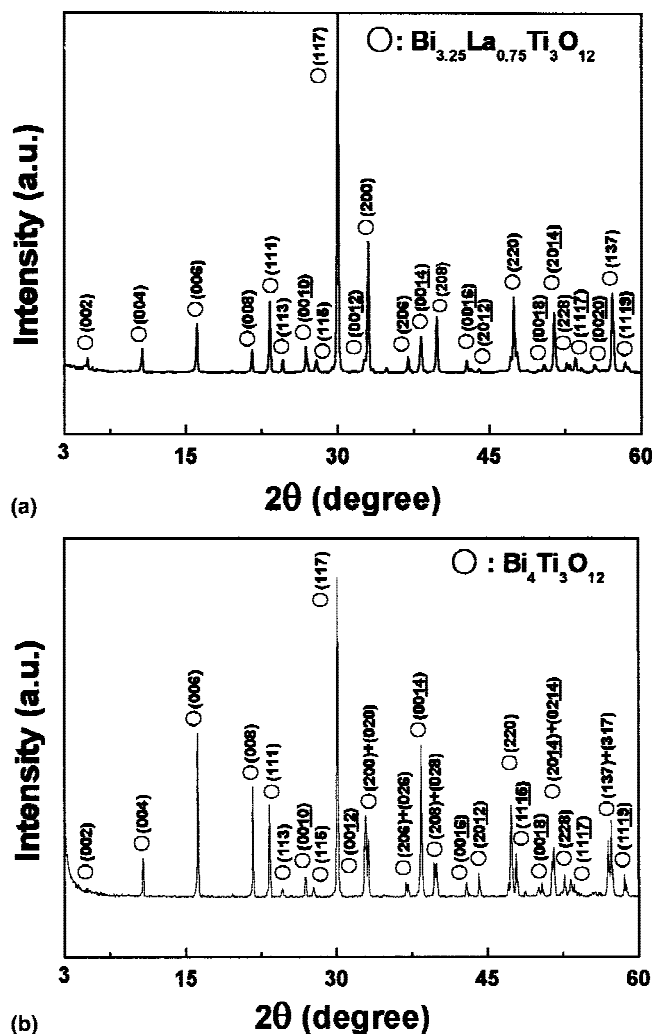


FIG. 1. XRD patterns of (a) BLT and (b) BT powders. The powders were derived from the same precursor sols used in the preparation of thin films.

It was Bi:La:Ti = 3.25:0.75:3. Similarly, the composition of the BT film annealed at the same temperature was Bi:Ti = 4.03:3. The thickness of the annealed films was estimated using a transmission electron microscope and a field-emission scanning electron microscope. The crystallinity of the annealed films was examined by XRD using  $\theta$ - $2\theta$  scans,  $\theta$ -rocking curve scans, and pole-figure analysis.

For the fabrication of BLT and BT capacitors, top Pt electrodes were deposited using an electron-beam evaporator. The typical area of a top electrode was  $10^{-4}$  cm<sup>2</sup>. The ferroelectric properties of the fabricated capacitors were measured using a RT6000S ferroelectric analyzer (Radiant Technology) equipped with a micrometer probe station.

### III. RESULTS AND DISCUSSION

#### A. Crystal structure of BLT

To identify the effect of lanthanum substitution on the phase stability, both BLT and BT powders were prepared, and their crystal structures were analyzed by XRD. All the XRD peaks of the BLT ( $x = 0.75$ ) were identified and indexed according to the XRD data of the perovskite BT phase compiled in the JCPDS (card no. 35-0795). There was an one-to-one correspondence between these two patterns despite some peak shifts and changes in the relative intensity. According to the XRD pattern presented in Fig. 1(a), the BLT ( $x = 0.75$ ) powder does not show any evidence of the formation of

lanthanum oxide or associated compounds that contain bismuth or titanium. This observation indicates that the lanthanum ions in the BLT do not form minority phases or segregate from the interior grain but dissolve into the perovskite lattice. It is known that the radius of a trivalent bismuth ion is very similar to that of a lanthanum ion:  $r(\text{Bi}^{3+}) = 1.02$  Å,  $r(\text{La}^{3+}) = 1.06$  Å.<sup>6</sup> This suggests that lanthanum ions can readily substitute for bismuth ions in the perovskite lattice. Therefore, one can conclude that the BLT maintains a layered structure similar to the perovskite BT even under extensive modifications by lanthanum. This conclusion agrees with the crystal structure of the BLT proposed by Park and his co-workers.<sup>1</sup>

However, small changes in the lattice parameters were observed with increasing concentration of lanthanum. It is known that the BT single crystal has a pseudo-orthorhombic structure with  $a = 5.411$  Å,  $b = 5.448$  Å, and  $c = 32.83$  Å at room temperature.<sup>7</sup> According to this, the peaks corresponding to (*h*0*l*)- and (*0**kl*)-type reflections should be distinguished from one another. As presented in Fig. 2, the XRD pattern of the BT ( $x = 0$ ) consistently shows the splitting of (*h*0*l*)- and (*0**kl*)-type reflections that are associated with orthorhombic structure. Contrary to this, the BLT does not show any peak splitting caused by the distinct (*h*0*l*) and (*0**kl*)-type reflections. This indicates that the BLT ( $x = 0.75$ ) has a tetragonal structure rather than a pseudo-orthorhombic structure. The computed lattice parameters of the BLT based upon the XRD patterns are  $a = b = 5.423$  Å, and  $c = 32.869$  Å at room temperature.

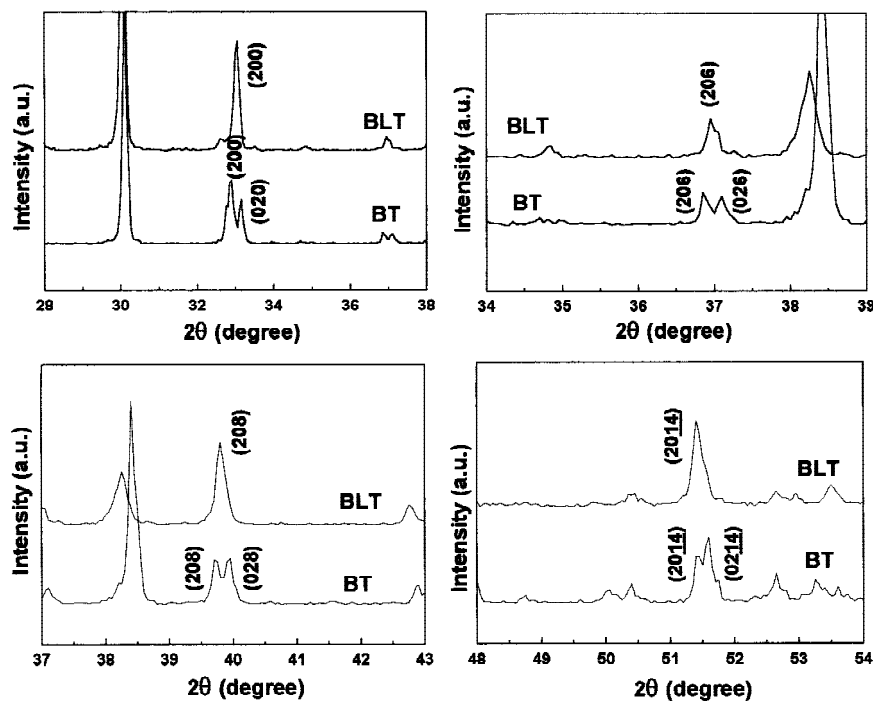


FIG. 2. XRD patterns of BLT and BT powders, showing the splitting of (*h*0*l*)- and (*0**kl*)-type reflections in the orthorhombic BT.

## B. Crystallization behavior and microstructure of BLT and BT films

To critically assess the effect of lanthanum substitution on the preferential growth without any disturbance by the texture of a bottom electrode, both BLT and BT films were first deposited on SiO<sub>2</sub>/Si(100) substrates and subsequently annealed at various temperatures for 15 min. Figure 3 compares the crystallization behavior of the BLT film on the SiO<sub>2</sub>/Si(100) substrate with that of the BT film. In case of the BLT film, as shown in Fig. 3(a), the XRD peak that corresponds to the (008) reflection appears at 400 °C, indicating that the onset of crystallization to a layered perovskite is close to 400 °C. The peaks corresponding to (00*l*)-type reflections grow continuously with the annealing temperature. The most prominent feature of the XRD patterns presented in Fig. 3(a) is that the BLT film shows a

highly *c*-axis-oriented preferential growth with the absence of the paraelectric pyrochlore phase of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> up to 800 °C.

In contrast, the BT film shows two broad peaks associated with (200) and (117) reflections at 400 °C, as evident in Fig. 3(b). The XRD pattern shows a mixed orientation while the formation of the pyrochlore Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is evident in the films annealed above 700 °C. According to previous investigations of BT film growth, the formation of the pyrochlore phase is quite common under thermal annealing above 750 °C<sup>8,9</sup> or under deposition conditions of a low oxygen pressure and a high fluence.<sup>10,11</sup> Investigators have avoided pyrochlore-phase formation by the addition of an excessive amount of bismuth<sup>8</sup> or by deposition under an oxygen-rich atmosphere and at a low fluence.<sup>11</sup>

In view of this, it can be inferred that the formation of the pyrochlore phase in the BT film results from a deficiency in bismuth, which, in turn, is caused by its high

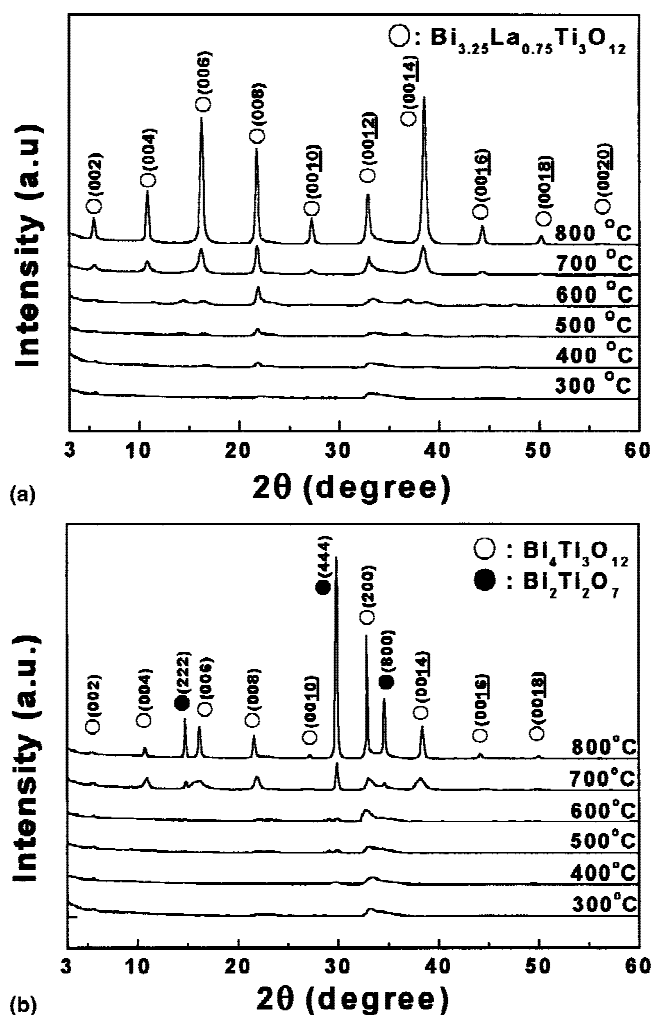


FIG. 3. XRD patterns of (a) BLT and (b) BT films prepared on SiO<sub>2</sub>/Si(100) substrates and thermally annealed at various indicated temperatures for 15 min.

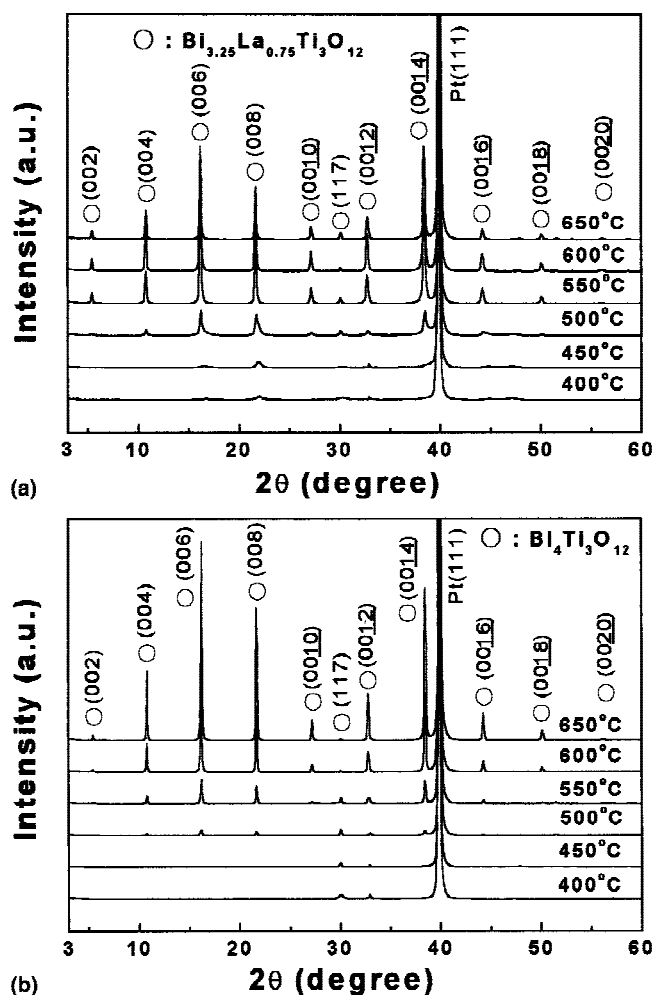


FIG. 4. XRD patterns of (a) BLT and (b) BT films prepared on Pt/Ti/SiO<sub>2</sub>/Si(100) substrates and thermally annealed at various indicated temperatures for 1 h.

volatility. Also, the deficiency in it may cause the nucleation of the layered perovskites of BT with a large amount of defects and subsequent crystallization of the perovskite with various amounts of defects, resulting in mixed orientation of the film. It is known that the vapor pressure of bismuth and that of lanthanum in the temperature range between 1150 and 1170 °C are 1 torr and 10<sup>-10</sup> torr, respectively.<sup>12</sup> Thus, the substitution of lanthanum for bismuth may suppress the formation of the pyrochlore phase and subsequently enhance the *c*-axis-oriented growth in the films annealed at high temperatures over 700 °C because the substitution tends not only to sustain the stoichiometry of cations in bismuth sites but also to retain oxygen ions in the layered perovskite structure. It seems that the stability of oxygen ions is closely related to the observed fatigue-free behavior of the BLT film, as inferred by Park and co-workers.<sup>1</sup>

So the effect of lanthanum substitution on ferroelectric properties could be analyzed, both BLT and BT films were deposited on Pt/Ti/SiO<sub>2</sub>/Si(100) substrates and subsequently annealed at various temperatures. In Fig. 4, we compare the crystallization behavior of the BLT film on

Pt/Ti/SiO<sub>2</sub>/Si(100) with that of the BT/Pt/Ti/SiO<sub>2</sub>/Si(100). The XRD diffraction peaks that correspond to (008), (0012), and (117) reflections appear at 400 °C in BLT film while the peaks corresponding to (117) and (0012) reflections are observed at the same temperature in BT film. For both films, compared with the (117) reflection, the intensity of (00*l*)-type reflections rapidly increases with annealing temperature. The BLT and BT films annealed above 550 °C then exhibit a highly *c*-axis-oriented preferential growth with a minor degree of (117) orientation. The degree of (00*l*)-type preferential growth, as estimated using Lotgering's orientation factor,<sup>13</sup> was over 99% for both BT and BLT films annealed at 650 °C. Crystallinity of BT films is higher than that of BLT films. This is caused by enhanced grain growth of BT films, as shown in Fig. 5. In contrast to BT/SiO<sub>2</sub>/Si(100) annealed at temperatures over 700 °C, the formation of the pyrochlore phase in BT/Pt/Ti/SiO<sub>2</sub>/Si(100), annealed below 650 °C, was completely suppressed. However, the pyrochlore phase was observed from BT/Pt/Ti/SiO<sub>2</sub>/Si(100) annealed at 700 °C. This is consistent with the phenomenon observed from BT/SiO<sub>2</sub>/Si(100). From these

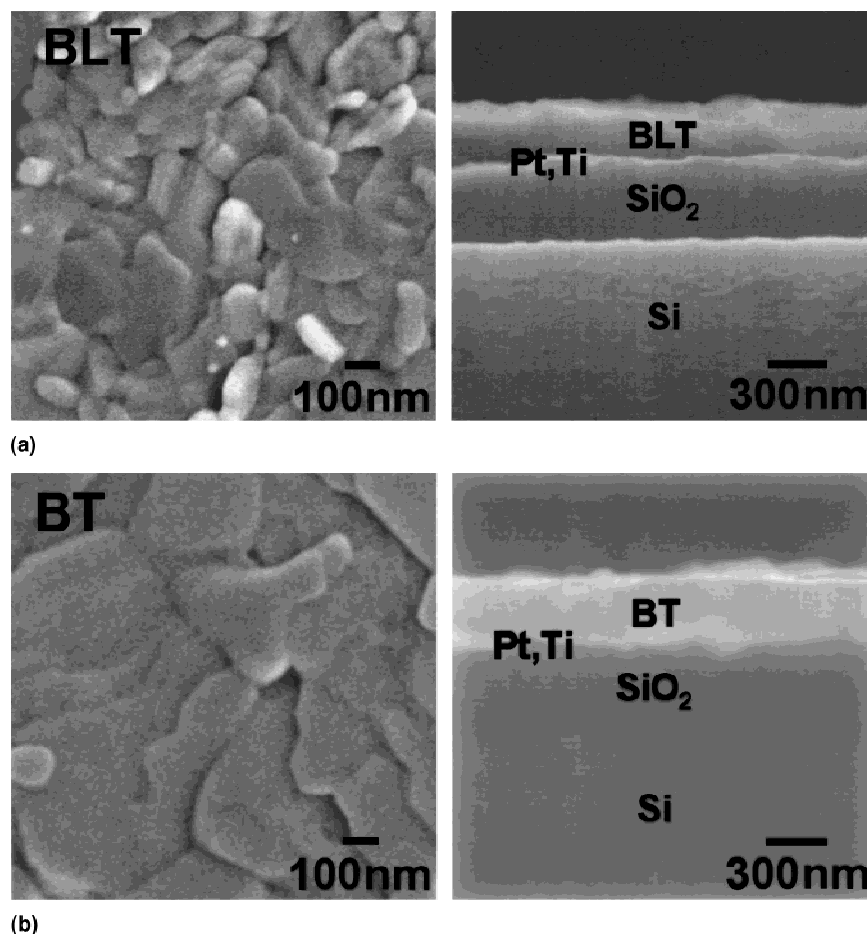


FIG. 5. Field emission scanning electron micrographs and cross-sectional images of (a) BLT film on Pt/Ti/SiO<sub>2</sub>/Si(100) and (b) BT film on Pt/Ti/SiO<sub>2</sub>/Si(100). The films were thermally annealed at 650 °C for 1 h. Pt and Ti layers were not clearly observed due to small thickness.



facts, it is clear that the pyrochlore-phase formation in BT/Pt/Ti/SiO<sub>2</sub>/Si(100) is avoided by lowering the annealing temperature below 700 °C (Fig. 4), below which the deficiency in bismuth, caused by evaporation, can be avoided. Thus the effect of lanthanum substitution on crystallization behavior is not critical in the films deposited on Pt/Ti/SiO<sub>2</sub>/Si(100) substrates and thermally annealed below 650 °C.

In addition crystallinity of BLT and BT films on Pt/Ti/SiO<sub>2</sub>/Si(100) substrate is higher than that of the films on SiO<sub>2</sub>/Si(100) substrate. This can be attributed to enhanced grain growth of the films on Pt(crystalline)/Ti/SiO<sub>2</sub>/Si(100) substrate, as shown in Figs. 5 and 6. It has been reported by other researchers that grain growth of BT film on crystalline layers, such as indium–tin oxide<sup>14</sup> or silver,<sup>15</sup> is largely enhanced, compared to that of those films on amorphous substrates of SiO<sub>2</sub>.

Microstructural features of the thermally annealed BT and BLT films are compared in Fig. 5. As shown in micrographs, the grain size of the BT film is substantially larger than that of the BLT film ( $x = 0.75$ ). Considering the well-known volatility of bismuth, one expects that the

diffusivity of bismuth will be significantly higher than that of lanthanum. In this case, because of lower diffusivity of lanthanum, the substitution of lanthanum for bismuth suppresses the grain growth of BLT, as observed in Fig. 5(a). For both films, the thickness of ferroelectric layers on Pt/Ti/SiO<sub>2</sub>/Si(100) are in the range between 2800 Å and 3100 Å. The lattice image and the selected-area electron diffraction (SAED) pattern of a cross-section of the BLT film on SiO<sub>2</sub>/Si(100) reveal the layered nature of the film and the *c*-axis-oriented preferential growth, as illustrated in Fig. 6.

### C. In-plane orientation of BLT and BT films on SiO<sub>2</sub>/Si(100) substrate

As mentioned previously, the BLT crystal has a layered perovskite structure with tetragonal symmetry at room temperature. Tetragonal BLT crystal with the *c*-axis orientation possesses fourfold symmetry. Thus, four poles separated from one another by 90° should appear in the pole figure if the film has a homogeneous in-plane orientation. As shown in Fig. 7 four poles, separated by 90°, are evident in the pole figure of the BLT film prepared on the SiO<sub>2</sub>/Si(100) substrate. This clearly

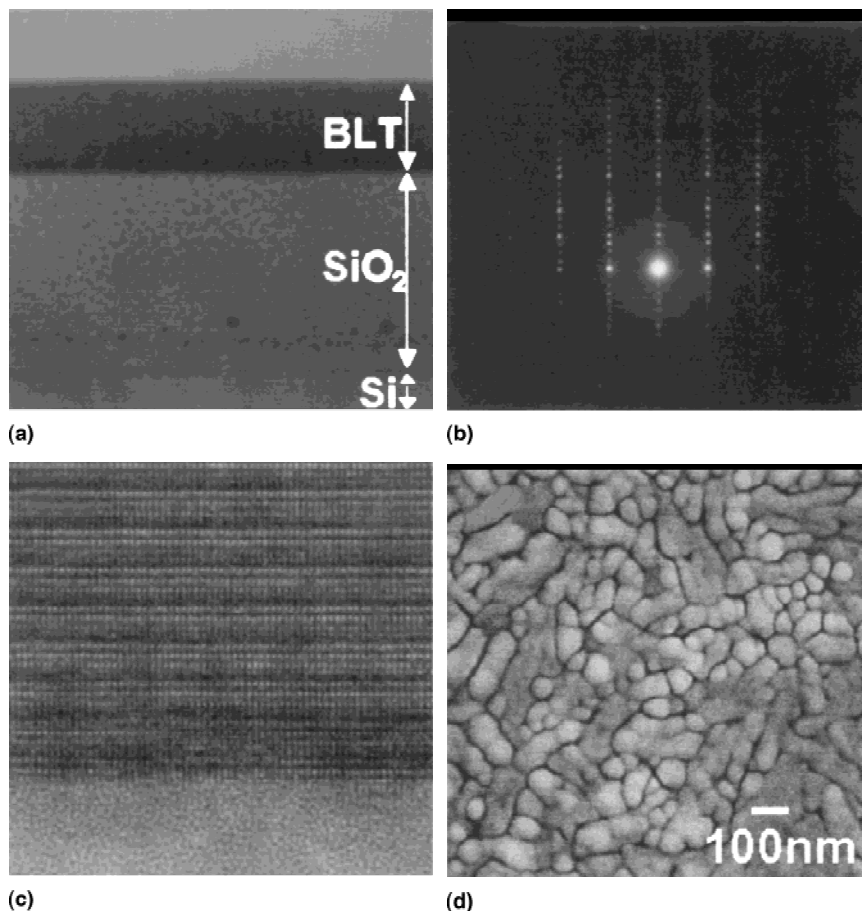


FIG. 6. (a) Cross-sectional view, (b) SAED pattern of a cross-section, (c) lattice image, and (d) microstructure of BLT film/SiO<sub>2</sub>/Si(100) thermally annealed at 700 °C for 15 min.

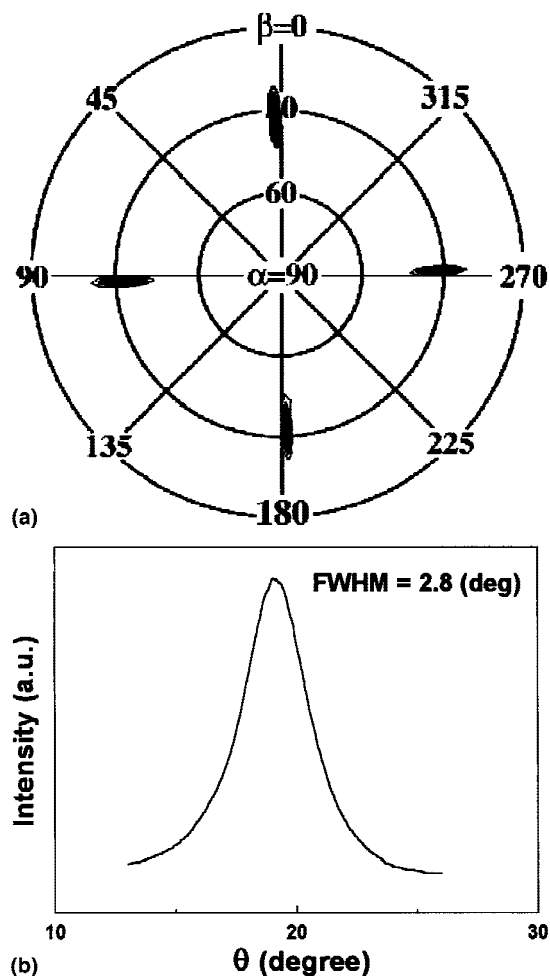


FIG. 7. Pole figure and rocking curve of BLT film/SiO<sub>2</sub>/Si(100) thermally annealed at 700 °C for 15 min: (a) pole figure for the (117) reflection, and (b)  $\theta$ -rocking curve of the (0014) plane.

indicates that the BLT film has a homogeneous in-plane orientation and is grown directly onto the SiO<sub>2</sub>/Si(100) substrate. Furthermore, the angle between the (00*l*)-type plane and the (117) plane, as estimated from the pole figure, is 54°. This value is very close to the reported value of 56° for the highly *c*-axis-oriented BT film grown on Al<sub>2</sub>O<sub>3</sub> (0001) substrate.<sup>16</sup> The rocking curve corresponding to (0014) plane indicates that the full-width at half-maximum is 2.8° [Fig. 7(b)].

To minimize the interfacial energy, a polycrystalline film on an amorphous heterogeneous surface, in general, should grow along the direction normal to its close-packed plane with the lowest surface energy. In addition to this, a homogeneous in-plane orientation is preferred because a low-angle grain boundary is energetically more favorable than a high-angle grain boundary, which leads to an inhomogeneous in-plane orientation. Since (00*l*)-type planes are the close-packed planes in the BLT film, the interfacial energy can be minimized by the formation of a highly *c*-axis-oriented film with

a homogeneous in-plane orientation. Thus, the observed homogeneous in-plane orientation of the BLT film is closely related to its thermodynamic stability on SiO<sub>2</sub>/Si(100) and Pt(111)/Ti/SiO<sub>2</sub>/Si(100) substrates. However, the BT film, fabricated using the PLD method, on a Si(100) substrate with a native oxide layer of SiO<sub>2</sub> showed a random in-plane orientation.<sup>17,18</sup> This suggests that the mechanism of nucleation and growth of a given BT-based film depends on the specific method used in film fabrication.

#### D. Ferroelectric properties of BLT and BT films

P-E hysteresis loops of Pt/BLT/Pt/Ti/SiO<sub>2</sub>/Si(100) and Pt/BT/Pt/Ti/SiO<sub>2</sub>/Si(100) capacitors were measured at 10 V. For both types of capacitors, well-saturated polarization–electric field switching curves (P-E curves) were obtained, as presented in Fig. 8. The remanent polarization ( $2P_r$ ) increases dramatically from 4 to 5  $\mu\text{C}/\text{cm}^2$  to

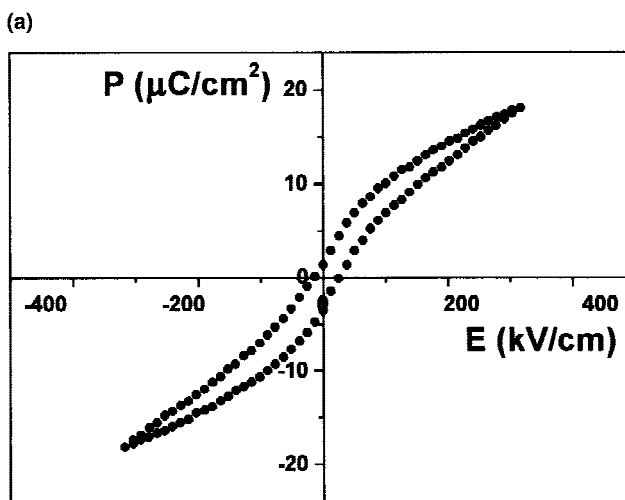
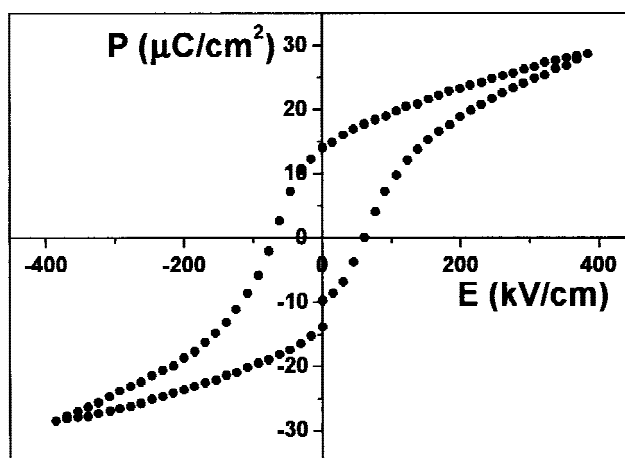


FIG. 8. P-E hysteresis loops for the highly *c*-axis-oriented (a) BLT and (b) BT films with a homogeneous in-plane orientation on Pt/Ti/SiO<sub>2</sub>/Si(100) substrates. Both BLT and BT films were thermally annealed at 650 °C for 1 h. The size of top Pt electrode was 10<sup>-4</sup> cm<sup>2</sup>.

26–28  $\mu\text{C}/\text{cm}^2$  by the lanthanum substitution. According to previous investigations,  $2P_r$  and  $E_c$  (coercive field) values of highly *c*-axis-oriented BT films are typically 5–8  $\mu\text{C}/\text{cm}^2$  and 2–5 kV/cm, respectively.<sup>19–21</sup> These values are similar to those of the present BT film.

The  $2P_r$  value of our BLT ( $x = 0.75$ ) capacitor is even higher than 24  $\mu\text{C}/\text{cm}^2$  obtained from the PLD-grown BLT film.<sup>1</sup> The coercive field of the present BLT capacitor is in the range of 50 to 75 kV/cm, which is somewhat higher than the previously reported value of 50 kV/cm for the PLD-grown capacitor.<sup>1</sup> In addition to these, the  $2P_r$  value of the present BLT capacitor is substantially higher than that of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>, another fatigue-free layered perovskite, which ranges between 6 and 20  $\mu\text{C}/\text{cm}^2$ .<sup>22–24</sup> More importantly, these values of  $P_r$  and  $E_c$  of the BLT capacitor are constant throughout the whole area of the film, which presumably results from the homogeneity of texture in the present BLT film. This homogeneity in the ferroelectric properties possibly removes the problems associated with the bit-to-bit variability in a film capacitor.<sup>2</sup>

The fatigue-resistance characteristics of the present Pt/BLT/Pt capacitor ( $x = 0.75$ ) are summarized in Fig. 9. The capacitor shows little change both in the switching polarization ( $P_{sw}$ ) and in the nonswitching polarization ( $P_{ns}$ ) up to  $3.5 \times 10^{10}$  switching cycles. The P-E curves were obtained at an applied voltage of 5 V before and after the electric fatigue test using a fatigue voltage of 3 V. The values of  $2P_r$  and  $E_c$  before the fatigue test were 14.3  $\mu\text{C}/\text{cm}^2$  and 50 kV/cm, respectively, at an applied voltage of 5 V. After the film was subjected to  $3.5 \times 10^{10}$  switching cycles, the values were still retained at 15.4  $\mu\text{C}/\text{cm}^2$  and 52 kV/cm at the same applied voltage. Furthermore, no significant change in the shape of hysteresis loops was observed even after the film was subjected to  $3.5 \times 10^{10}$  read/write cycles at a frequency of 1 MHz. These features of ferroelectric properties will significantly enhance the potential value of the BLT film capacitor for the applications to high-density FRAM devices.

In addition to this, the highly *c*-axis-oriented BLT film, with a homogeneous in-plane orientation even on an amorphous surface, can potentially be a suitable template material for the following applications: (i) magnetic-field sensors with a colossal magnetoresistance,<sup>25</sup> (ii) non-destructive read-out memories with metal/ferroelectrics/semiconductor structure,<sup>26</sup> and (iii) nonlinear optical waveguides.<sup>27,28</sup>

#### IV. SUMMARY

The results of the present investigation are summarized as follows: (1) Highly *c*-axis-oriented Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> (BLT) films with a homogeneous in-plane orientation were successfully grown on

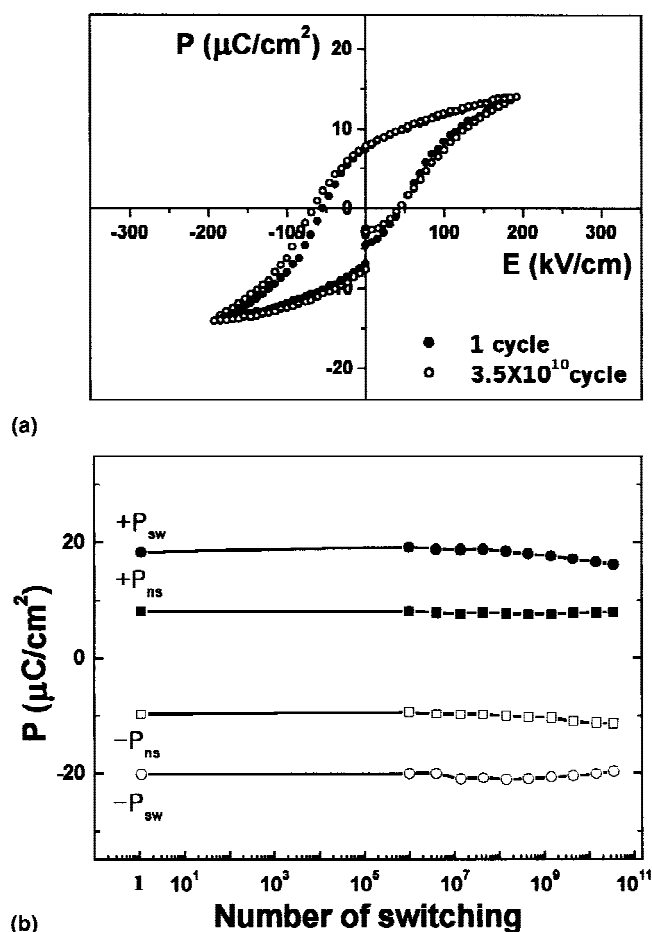


FIG. 9. Electrical fatigue characteristics of the Pt/BLT/Pt capacitor before and after being subjected to  $3.5 \times 10^{10}$  switching cycles at a frequency of 1 MHz: (a) P-E hysteresis loops measured at an applied voltage of 5 V before and after application of the switching cycles, and (b) results of the fatigue test, as determined with a fatigue voltage of 3 V and a measuring voltage of 5 V at a frequency of 1 MHz.

SiO<sub>2</sub>/Si(100) and Pt/Ti/SiO<sub>2</sub>/Si(100) substrates by a sol-coating route. (2) Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> (BLT) maintains the layered perovskite nature of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BT) but has a tetragonal structure rather than a pseudo-orthorhombic structure. The estimated lattice parameters are approximately  $a = b = 5.423 \text{ \AA}$  and  $c = 32.869 \text{ \AA}$ . (3) The substitution of lanthanum for bismuth suppresses the formation of the pyrochlore phase, Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, and subsequently enhances the *c*-axis-oriented growth with a homogeneous in-plane orientation. The stability of the perovskite phase was attributed to the lower volatility of lanthanum ions and the enhanced stability of oxygen in the lanthanum-modified BT. (4) The remanent polarization ( $2P_r$ ) increases dramatically from 4–5  $\mu\text{C}/\text{cm}^2$  to 26–28  $\mu\text{C}/\text{cm}^2$  by the substitution of lanthanum for bismuth in the layered perovskite. The highly *c*-axis-oriented Pt/BLT/Pt capacitor shows little change in both the switching polarization ( $P_{sw}$ ) or the nonswitching polarization ( $P_{ns}$ ) up to  $3.5 \times 10^{10}$  switching cycles.



These features of ferroelectric properties will significantly enhance the potential value of the BLT film capacitor for application in high-density FRAM devices.

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## REFERENCES

1. B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, and W. Jo, *Nature* **401**, 682 (1999).
2. A. Kingon, *Nature* **401**, 658 (1999).
3. S.E. Cummins and L.E. Cross, *J. Appl. Phys.* **39**, 2268 (1968).
4. E.C. Subbarao, *Phys. Rev.* **122**, 804 (1961).
5. U. Chon, G.C. Yi, and H.M. Jang, *Appl. Phys. Lett.* **78**, 658 (2001).
6. R.D. Shannon and C.T. Prewitt, *Acta Crystallogr.* **B25**, 925 (1969).
7. J.F. Dorrian, R.E. Newnham, and D.K. Smith, *Ferroelectrics* **3**, 17 (1971).
8. M. Sedlar and M. Sayer, *Ceram. Int.* **22**, 241 (1996).
9. K.S. Hwang, *Mater. Chem. Phys.* **56**, 222 (1998).
10. W. Wu, K. Fumoto, Y. Oishi, M. Okuyama, and Y. Hamakawa, *Jpn. J. Appl. Phys.* **34**, 5141 (1995).
11. S.B. Krupanidhi, D. Roy, N. Maffei, and C.J. Peng, *Integ. Ferroelectrics* **1**, 253 (1992).
12. R. Glang, in *Handbook of Thin Film Technology*, edited by L.I. Maissel and R. Glang (McGraw-Hill, New York, 1970), Part 1, Chap. 1.
13. F.K. Lotgering, *J. Inorg. Nucl. Chem.* **9**, 113 (1959).
14. J.M. Boulton, G. Teowee, W.M. Bommersbach, and D.R. Uhlman, in *Ferroelectric Thin Films II*, edited by A.I. Kingor, E.R. Myers, and B. Tuttle (Mater. Res. Soc. Symp. Proc. **243**, Pittsburgh, PA, 1992), p. 303.
15. Y. Lu, D.T. Hoelzer, W.A. Schulze, B. Tuttle, and B.G. Potter, *Mater. Sci. Eng.* **B39**, 41 (1996).
16. W. Jo and T.W. Noh, *Appl. Phys. Lett.* **65**, 2780 (1994).
17. N. Maffei and S.B. Krupanidhi, *J. Appl. Phys.* **72**, 3617 (1992).
18. H. Buhay, S. Sinharoy, W.H. Kasner, M.H. Francombe, D.R. Lampe, and E. Stepke, *Appl. Phys. Lett.* **58**, 1470 (1991).
19. K. Yoshimura, M. Ishinabe, S. Okamura, and T. Tsukamoto, *Jpn. J. Appl. Phys.* **34**, 2425 (1995).
20. M. Yamaguchi, T. Nagatomo, and O. Omoto, *Jpn. J. Appl. Phys.* **35**, 4984 (1996).
21. E. Kato, Y. Watanabe, T. Tsukamoto, and T. Tsuchiya, *J. Ceram. Soc. Jpn.* **104**, 1015 (1996).
22. R. Dat, J.K. Lee, O. Auciello, and A.I. Kingon, *Appl. Phys. Lett.* **67**, 572 (1995).
23. T. Li, Y. Zhu, S.B. Desu, C-H. Peng, and M. Nagata, *Appl. Phys. Lett.* **68**, 616 (1996).
24. K. Amanuma, T. Hase, and Y. Miyasaka, *Appl. Phys. Lett.* **66**, 221 (1995).
25. Z. Trajanovic, C. Kwon, M.C. Robson, K.C. Kim, M. Rajeswari, R. Ramesh, T. Venkatesan, W.E. Lofland, S.M. Bhagat, and D. Fork, *Appl. Phys. Lett.* **69**, 1005 (1996).
26. T.S. Kalkur, J. Kulkarni, Y.C. Lu, M. Rowe, W. Han, and L. Kamerdiner, *Ferroelectrics* **116**, 135 (1991).
27. T. Ueda, A. Noma, and D. Ueda, *Integ. Ferroelectrics* **7**, 45 (1995).
28. J.Y. Gu, C. Kwon, M.C. Robson, Z. Trajanovic, K. Fhosh, R.P. Sharma, R. Shreekala, M. Rajeswari, T. Venkatesan, R. Ramesh, and T.W. Noh, *Appl. Phys. Lett.* **70**, 1763 (1997).