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Substrate effect on in-plane ferroelectric and dielectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films

D. Y. Wang · Y. Wang · J. Y. Dai · H. L. W. Chan · C. L. Choy

Abstract Heteroepitaxial $Ba_{0.7}Sr_{0.3}TiO_3$ thin films were grown on $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.35}$ (001) (LSAT) and $SrTiO_3$ (001) (STO) single crystal substrates using pulsed laser deposition (PLD). X-ray diffraction characterization revealed a good crystallinity and a pure perovskite structure for films grown on both LSAT and STO substrates. The in-plane ferroelectric and dielectric properties of the films were studied using interdigital electrodes (IDE). The film grown on LSAT substrate exhibited an enhanced in-plane ferroelectricity, including a well-defined P-E hysteresis loop with the remnant polarization $P_r = 10.5\,\mu C/cm^2$ and a butterfly-shaped *C-V* curve. Nevertheless, only a slim hysteresis loop was observed in the film grown on STO substrate. Curie temperature T_c of the film grown on LSAT substrate was found to be ~105°C, which is nearly 70°C higher than that of the bulk $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics. T_c of the film grown on STO substrate has almost no change compared to the bulk $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics. The dielectric tunabilities were found to be 64% and 52% at 1 MHz for the films grown on LSAT and STO substrates, respectively.

Keywords BST thin films · In-plane ferroelectric properties · IDE

Introduction

Thin films of barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$ or BST) have been very attractive to the microelectronic industry as good candidates for application in microwave devices, such as tunable oscillators, delay lines and phase shifters [1–5]. Thus, the fabrication of high-quality $Ba_{1-x}Sr_xTiO_3$ thin films possessing high dielectric tunability and low loss tangent (tanδ) values have become very important technical issues for developing these materials for practical applications. Generally, as for the thin films, the dielectric and ferroelectric behaviors are much more complicated in comparison with bulk ceramics because of the size effect. Many reasons for the size effect have been proposed, including local polar regions near the charged defects like oxygen vacancies, a dead layer near the interface and a residual stress from the lattice mismatch or different thermal expansion coefficients between the substrate and films [6].

Stress in the thin films has been suggested to be one of the key factors that induced the difference between the bulk and film behaviors [7–9]. Besides the thermal expansion mismatch, lattice mismatch between the substrate and the film is a main origin of the internal stress. Therefore, it is essential to understand the substrate effect on the ferroelectric and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ thin film. We have recently demonstrated that heteroepitaxy induced stress play a distinct role in the in-plane ferroelectric and dielectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films grown on MgO (001) single crystal substrates [10]. In this paper, we report the in-plane ferroelectric and dielectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films epitaxially grown on $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.35}$ (001) (LSAT) and $SrTiO_3$ (001) (STO) single crystal substrates. We chose to determine the in-plane ferroelectric and dielectric properties of the thin films not only because such properties have been less extensively studied compared with traditional parallel-plate capacitor structure, but also because the in-plane configuration is directly relevant to the actual coplanar devices.

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Experimental

Pulsed laser deposition (PLD) technique was employed in this study to produce epitaxial $Ba_{0.7}Sr_{0.3}TiO_3$ thin films since PLD provides unique advantages for multicomponent oxide films because it easily reproduces the stoichiometry of the target in the deposited films. $Ba_{0.7}Sr_{0.3}TiO_3$ films of approximately 300 nm thickness were grown on cubic LSAT (001) and STO (001) single crystal substrates by irradiating the stoichiometric target with a laser beam of 248 nm wavelength and 25 ns pulse duration from a KrF excimer laser (Lambda Physik COMPex 250). The pulse energy of the laser beam was 250 mJ and the repetition rate was 10 Hz. The distance between the target and the substrates was fixed at 5 cm. The substrate temperature was maintained at 750°C. The oxygen partial pressure was kept at 200 mTorr during the laser ablation process. After deposition, the films were post-annealed at 1000°C in a tube furnace for 3 h to reduce the oxygen vacancies. The crystal structure of the BST thin films was examined using an X-ray diffractometer (Bruker D8 Discover) equipped with Cu Kα radiation.

The dielectric permittivity and loss of the thin films were determined along an in-plane direction on an interdigital electrode capacitor (IDC) with a configuration of electrode/BST/LSAT or STO. The top Au interdigital electrodes (IDEs) were deposited by r.f. magnetron sputtering and patterned by 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 spacing is 3 μm. The IDE was wire-bonded to a piece of PCB for easy handling and better electrical contact in subsequent measurements. The ferroelectric hysteresis loop was measured using a TF Analyzer 2000 equipped with a FE-Module (HV) (aixACCT) along the in-plane direction. The dielectric properties were 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 developed based on Gevorgian's model [11–12], which has established the relationship between the capacitance and the electrode size and the material properties.

Results and discussions

Figure 1 shows the typical $\theta/2\theta$ X-ray diffraction (XRD) patterns of the $Ba_{0.7}Sr_{0.3}TiO_3$ thin films. Only strong $(00l)$ peaks appear in the XRD patterns, which implies that the BST thin film has a pure perovskite phase. The in-plane alignment of the BST thin film with respect to the major axes of the (001) substrate was also confirmed by the XRD off-axis Φ scan of the BST (202) and substrate (202) reflections, indicating an epitaxial growth of the BST thin film. The rocking curve measurements of the BST (002) reflections revealed that the full width at half maximum (FWHM) is about 0.14° and 0.12° for the films grown on LSAT and STO substrates, respectively, as shown in the insets of Fig. 1. 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 [13].

The in-plane and out-of-plane lattice parameters are shown in Table 1. It is seen that both of the films have

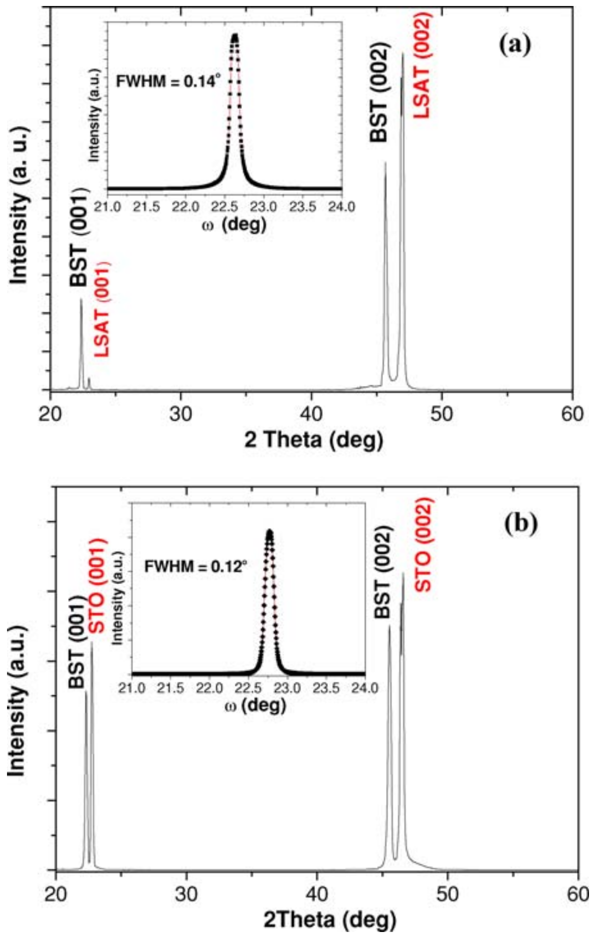

Fig. 1 XRD patterns of $\theta/2\theta$ scan from $Ba_{0.7}Sr_{0.3}TiO_3$ thin films deposited on (a) LSAT (001) and (b) STO (001) substrates. The insets are rocking curves of the $Ba_{0.7}Sr_{0.3}TiO_3$ thin films

Table 1 Lattice parameters of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films grown on LSAT (001) and STO (001) substrates

	Lattice parameters (Å)	
	Out-of-plane	In-plane
$Ba_{0.7}Sr_{0.3}TiO_3$/LSAT (001)	3.9706	3.9967
$Ba_{0.7}Sr_{0.3}TiO_3$/STO (001)	3.9796	3.9365
LSAT	3.868 (cubic)	
STO	3.901 (cubic)	
Bulk $Ba_{0.7}Sr_{0.3}TiO_3$	3.970 (cubic)	

a tetragonal structure, which is different from that of the bulk ceramics, indicating that structures of the films have been modified by the substrates. The film grown on STO (001) substrate has a shortened in-plane lattice parameter and an elongated out-of-plane lattice parameter. It is reasonable since the STO has a comparatively smaller lattice parameter which may cause a stress thus the in-plane lattice of BST thin film was compressed while the out-of-plane lattice was elongated as a result of an elastic deformation of the lattice. Nevertheless, situation for the film grown on LSAT is more complicated. The out-of-plane lattice has almost no change but the in-plane lattice parameter has been noticeable elongated. This seems somewhat different form the pure strain effect. Other factor, such as oxygen deficiency, may be responsible for the unusual lattice distortion [14]. The lattice mismatch will lead to the contraction of the lattice structure while the oxygen vacancies lead to the tensile stress due to the fact that oxygen vacancies affect the nearest neighbor distance by reducing the Coulombic attraction between cations and anions. Though the oxygen ambient is used to prevent the formation of oxygen vacancies in the deposited film, it has been shown that oxide films grown using PLD are still oxygen deficient [15]. In our case, oxygen deficiency is the dominant factor that affects the lattice distortion.

A well-defined hysteresis loop was clearly observed, as shown in Fig. 2(a) for thin film grown on LSAT (001) with the remnant polarization P_r of 10.5 μC/cm^2 and coercive field E_c of 1.9 V/μm. This remnant polarization value is much higher than that of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films grown on Pt/Ti/SiO_2/Si substrates [16]. But only a slim hysteresis loop was observed in the film grown on STO (001) as shown in Fig. 2(b). In comparison with bulk $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics, the P_r of the film grown on LSAT (001) along the in-plane direction has been significantly enhanced since the bulk $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics have a cubic structure and do not show obvious hysteresis loop at room temperature. It is believed that the increased tetragonality (a/c increased from 1 to 1.0066) contributed to the enhanced ferroelectricity. In contrast, it is easy to understand that the slim hysteresis loop of the film grown on STO (001) was attributed to the compressed in-plane lattice parameter. Normally, the substrate will affect the measurement results in the coplanar electrode configuration since the electric field may penetrate into the

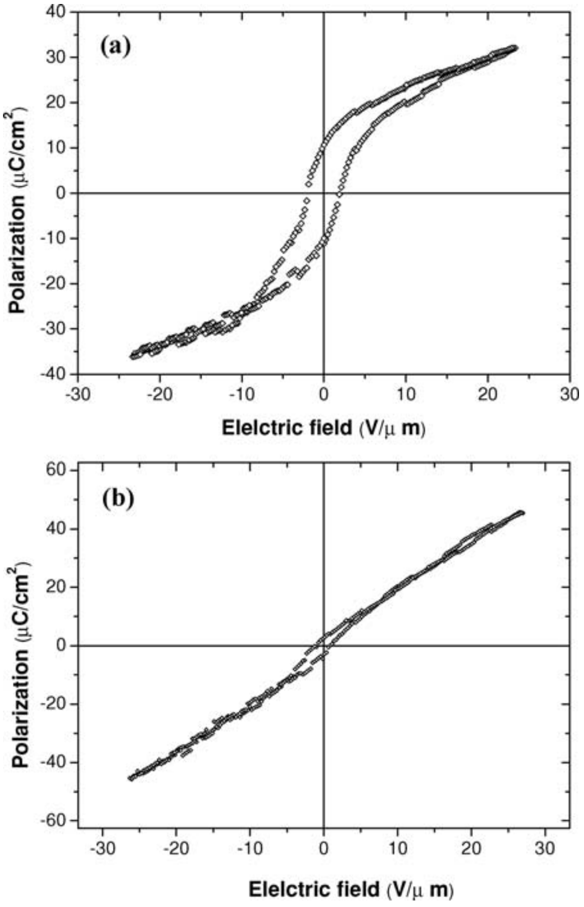

Fig. 2 In-plane ferroelectric hysteresis loops of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films grown on (a) LSAT (001) and (b) STO (001) substrates

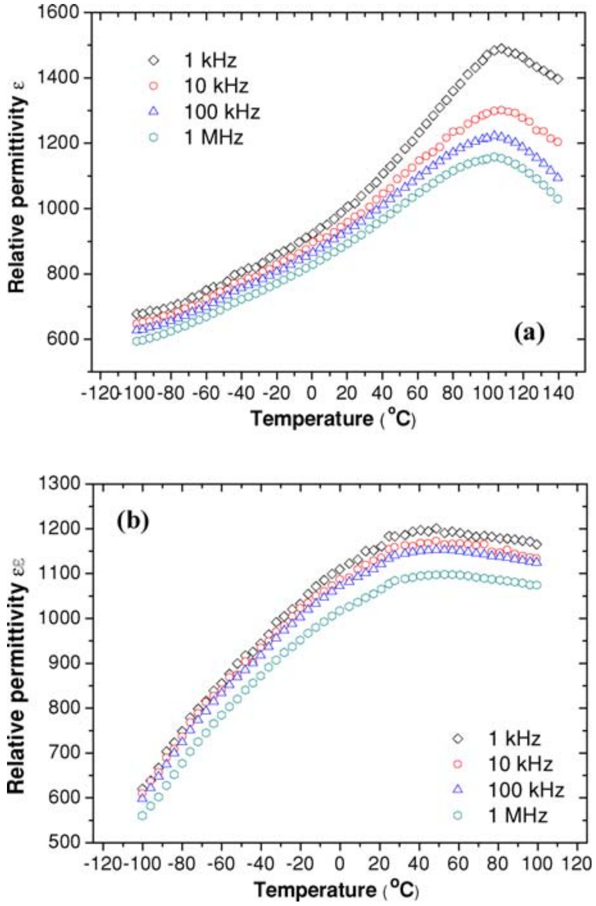

Fig. 3 In-plane relative permittivity ε of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films grown on (a) LSAT (001) and (b) STO (001) substrates as *s* function of temperature

substrate. The STO substrate has a high relative permittivity of ~300 at room temperature, which may cause part of the electric field penetrate into the STO substrate, thus the electric field may not be so effective as expected in exciting the in-plane ferroelectricity of the film grown on STO (001) when interdigital electrodes were used.

Figure 3 shows the temperature-dependent in-plane relative permittivity ε of the BST thin films. The curve for film grown on LSAT (001) exhibits a maximum in ε at $T_c = 105°C$, which is about ~70°C higher than that of bulk $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics ($T_c = 35°C$) [17]. The upward shift of T_c in the $Ba_{0.7}Sr_{0.3}TiO_3$ thin film along the in-plane direction is believed to be due to the elongation of the in-plane lattice parameter. In general, if there is a tensile stress along the in-plane direction inside the film, then the Curie temperature of the BST thin films is likely to shift towards the high temperature direction. Conversely, a compressive stress may lower the Curie temperature of the films. The film grown on STO (001) shows a broadened ε-T curve with the Curie temperature at 40°C, as shown in Fig. 3(b), which is almost the same as that of bulk $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics. Broadening of ε-T curve is presumably due to the diffusion of the STO substrate into BST near the film-substrate interface thus a layer of "gradient" BST thin film was formed near the interface.

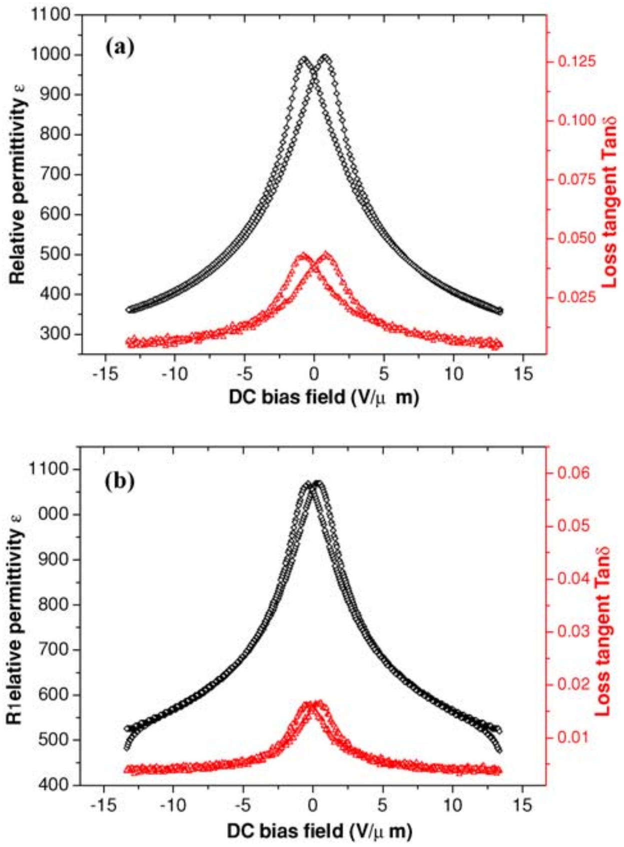

Fig. 4 In-plane C-V and tanδ-V curves of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films grown on (a) LSAT (001) and (b) STO (001) substrates at 1 MHz

The in-plane C-V characteristics of the BST films are shown in Fig. 4 and both the films exhibit strong dependence of ε on the applied dc bias field. The film grown on LSAT (001) shows a butterfly-shaped ε-E and tanδ-E dependence which is consistent with the enhanced in-plane ferroelectricity observed in the P-E loop and ε-T measurements. However, C-V characteristics of the film grown on STO (001) do not show obvious hysteresis behavior. The maximum in-plane dielectric tunabilities $[\Delta\varepsilon/\varepsilon = (\varepsilon_{\max} - \varepsilon_{\min})/\varepsilon_{\max}]$ are calculated to be 64% and 52% at 1 MHz under a moderated dc bias field of 13.3 V/μm for the films grown on LSAT and STO, respectively. Coplanar designs generally require higher driving voltage and offer lower tunability in comparison to the parallel-plate capacitors, but our results are comparable with some of the reported data of BST films based on parallel-plate capacitors [18–20]. It is noticed that the dielectric loss at zero field for film grown on LSAT is higher than that of the film grown on STO, which is probably due to the ferroelectric phase in the film grown on LSAT.

Conclusions

The substrate effect on in-plane ferroelectric and dielectric properties of the $Ba_{0.7}Sr_{0.3}TiO_3$ thin films was studied in this work. Heteroepitaxial $Ba_{0.7}Sr_{0.3}TiO_3$ thin films were grown on LSAT (001) and STO (001) single crystal substrates using pulsed laser deposition. Film grown on LSAT exhibits an enhanced in-plane ferroelectricity with $P_r = 10.5\ \mu C/cm^2$ and a butterfly-shaped C-V curve. Curie temperature of the film grown on LSAT shifts to ~105°C, which is nearly 70°C higher than that of the bulk $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics. The upward shift of the T_c can be explained in terms of the elongated in-plane lattice parameter induced mainly by the oxygen vacancies. However, the in-plane ferroelectric state of the film grown on STO is close to those of bulk $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics with a slim P-E hysteresis loop. Both of the films show strong dependence of ε subjected to dc bias field. The dielectric tunabilities were found to be 64% and 52% for films grown on LSAT and STO at 1 MHz, respectively. This work provides some useful information in substrate selection for developing BST- based microwave devices.

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References

1. F.W. Van Keuls, R.R. Romanofsky, N.D. Varaljay, F.A. Miranda, C.L. Canedy, S. Aggarwal, T. Venkatesan, and R. Ramesh, *Microwave Opt. Tech. Lett.*, **20**, 53 (1999).

2. C.M. Carlson, T.V. Rivkin, P.A. Parilla, J.D. Perkins, D.S. Ginley, A.B. Kozyrev, V.N. Oshadchy, and A.S. Pavlov, *Appl. Phys. Lett.*, **76**, 1920 (2000).
3. W. Chang, J.S. Horwitz, A.C. Carter, J.M. Pond, S.W. Kirchoefer, C.M. Gilmore, and D.B. Chrisey, *Appl. Phys. Lett.*, **74**, 1033 (1999).
4. 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, and R.R. Romanofsky, *Appl. Phys. Lett.*, **75**, 412 (1999).
5. C.L. Chen, J. Shen, S.Y. Chen, G.P. Luo, C.W. Chu, J.C. Jiang, E.I. Meletis, and H.Y. Chang, *Appl. Phys. Lett.*, **78**, 652 (2001).
6. W.Y. Park, K.H. Ahn, and C.S. Hwang, *Appl. Phys. Lett.*, **83**, 4387 (2003).
7. C.L. Canedy, H. Li, S.P. Alpay, L. Salamanca-Riba, A.L. Roytburd, and R. Ramesh, *Appl. Phys. Lett.*, **77**, 1695 (2000).
8. K.J. Choi, M. Biegalshi, 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).
9. 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).
10. D.Y. Wang, Y. Wang, X.Y. Zhou, H.L.W. Chan, and C.L. Choy, *Appl. Phys. Lett.*, **86**, 212904 (2005).
11. Y. Wang, Y.L. Cheng, K.C. Cheng, H.L.W. Chan, and C.L. Choy, *Appl. Phys. Lett.*, **85**, 1580 (2004).
12. S.S. Gevorgian, T. Matinsson, P.L.J. Linner, and E.L. Kollberg, *IEEE Trans. Microwave Theory Tech.*, **44**, 896 (1996).
13. E.D. Specht, H.-M. Christen, D.P. Norton, and L.A. Boatner, *Phys. Rev. Lett.*, **80**, 4317 (1998).
14. N. Navi, H. Kim, J.S. Horwitz, H.D. Wu, and S.B. Qadri, *Appl. Phys. A: Mate. Sci. Process*, **76**, 841 (2003).
15. 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).
16. P. Shi, X. Yao, and L. Zhang, *J. Crystal Growth*, **276**, 97 (2005)
17. *Ferroelectrics and Related Substances*, edited by H. Landolt, Landolt-Börnstein, New Series, Group III, (Springer-Verlag, Berlin, 2002), vol. 36, p. 416.
18. 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).
19. P. Padmini, T.R. Taylor, M.J. Lefevre, A.S. Nagra, R.A. York, and J.S. Speck, *Appl. Phys. Lett.,* **75**, 3186 (1999).
20. J. Im, O. Auciello, P.K. Baumann, S.K. Streiffer, D.Y. Kaufman, and A.R. Krauss, *Appl. Phys. Lett.*, **76**, 625 (2000).