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Ferroelectric Properties of (Bi, Sm)$_4$Ti$_3$O$_{12}$ (BST) Thin Films Fabricated by a Metalorganic Solution Deposition Method

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Abstract. Ferroelectric properties of samarium substituted $Bi_4Ti_3O_{12}$ films, $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ (BST), were evaluated for use as lead-free thin film ferroelectrics for FeRAM applications. The BST films were fabricated on the Pt/Ti/SiO$_2$/Si(100) substrates by a metalorganic solution deposition method. The measured XRD patterns revealed that the BST films showed only a $Bi_4Ti_3O_{12}$-type phase with a random orientation. The BST film capacitors showed excellent ferroelectric properties. For the film capacitor annealed at 700°C, $2P_r$ of 64.2 μC/cm^2 and $2E_c$ of 101.7 kV/cm at applied electric field of 150 kV/cm were observed. The capacitor did not show any significant fatigue up to 1.5×10^8 read/write switching cycles at a frequency of 1 MHz, which suggests that the samarium should be considered for a promising lanthanide elements to make a good thin ferroelectric film for memory applications.

Keywords: ferroelectric, $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$, $Bi_4Ti_3O_{12}$, thin film, remanent polarization

1. Introduction

The bismuth-layered ferroelectrics, such as SrBi$_2$Ta$_2$O$_9$ (SBT) and Bi$_4$Ti$_3$O$_{12}$(BIT), generally described as $(Bi_2O_2)^{2+}$ $(A_{m-1}B_mO_{3m+1})^{2-}$ where $m = 2, 3, 4$ and 5, have been extensively investigated for memory applications as a potential ferroelectric materials instead of lead based ferroelectrics, such as Pb(Zr, Ti)O$_3$ (PZT). SBT is used in nonvolatile ferroelectric random access memory (FeRAM) because of its very small polarization fatigue in comparison with PZT. However, SBT has a lower remanent polarization and a higher processing temperature than those of PZT [1, 2]. Bismuth titanate, Bi$_4$Ti$_3$O$_{12}$(BIT), thin films are considered to be candidate ferroelectrics for FeRAM applications, because its bulk value of remanent polarization value ($2P_r$) is about 60 μC/cm^2. However, BIT thin films have not been used in FeRAM applications due to its fatigue problem and relatively low remanent polarization value [1].

Recent studies revealed that Bi^{3+} ions in BIT structure could be substituted by trivalent lanthanide ions for the improvement of its ferroelectric properties [1, 2]. Park et al. showed that $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin film deposited on Pt/Ti/SiO$_2$/Si substrate by pulsed laser deposition has a relatively large remanent polarization value ($2P_r$) of 24 μC/cm^2 and good fatigue endurance [1]. Melgarejo et al. showed that the remanent polarization ($2P_r$) of $Bi_{3.54-}Nd_{0.46}Ti_3O_{12}$ (BNT) film fabricated on Pt/TiO$_2$/SiO$_2$/Si(100) substrates by chemical solution deposition was 50 μC/cm^2 [3]. Chon et al. reported that $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$(BST) films have large $2P_r$ value of 49 μC/cm^2 and fatigue-free characteristics [4]. However, the BST films were shown to have a strong c-axis orientation.

The present work is mainly concerned with the study of the ferroelectric properties of the randomly

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*To whom all correspondence should be addressed. E-mail: sskim@sarim.changwon.ac.kr oriented $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ (BST) films fabricated on the Pt/Ti/SiO_2/Si(100) substrates by a metalorganic solution deposition method.

2. Experiments

Metalorganic solution deposition method was used to prepare BST films. A transparent multi-component solution was prepared by mixing bismuth nitrate [$Bi(NO_3)_3{\cdot}5H_2O$], titanium isopropoxide [$Ti(OC_3H_2)_4$], and samarium nitrate [$Sm(NO_3)_3{\cdot}6H_2O$]. Bismuth nitrate (10 mol% excess) and samarium nitrate were dissolved at 40°C in 2-methoxyethanol. Separately, titanium isopropoxide was dissolved in 2-methoxyethanol, and acetylacetone was used as a chelating agent in a glove box. Each solution was stirred for 2 hours before the next step. The titanium solution was added in the bismuth-samarium solution with continuous stirring. The concentration of BST in the final solution was adjusted to about 0.1 M.

For preparing the films, the Pt/Ti/SiO_2/Si(100) substrates were spin-coated with the prepared solution at a speed of 3500 rpm for 20 s. The spin coated solution was preheated over a hot-plate at 150°C for 5 min and 350°C for 10 min, sequentially. The spin-coating and preheating process were repeated several times for each film to obtain a desired film thickness. The film was heated at 500°C for 10 min in the furnace to stabilize the coated films. Then the furnace temperature was increased to reach the desire annealing temperature of 500–700°C with a heating rate of 4 °C/min. The films were annealed for 30 min in oxygen for full crystallization.

The crystalline structures of the films were confirmed by X-ray diffraction (XRD) (Philips, APD system) analysis. The surface morphologies of the films were determined by scanning electron microscope (SEM) (Hitachi, S-2400) and microstructure of the films were examined by a high-resolution transmission electron microscope (HRTEM) (JEOL JEM3010). Electrical properties of the films were measured using a ferroelectric test system (RT66A) and an electrometer (Keithley 6517A).

3. Results and Discussion

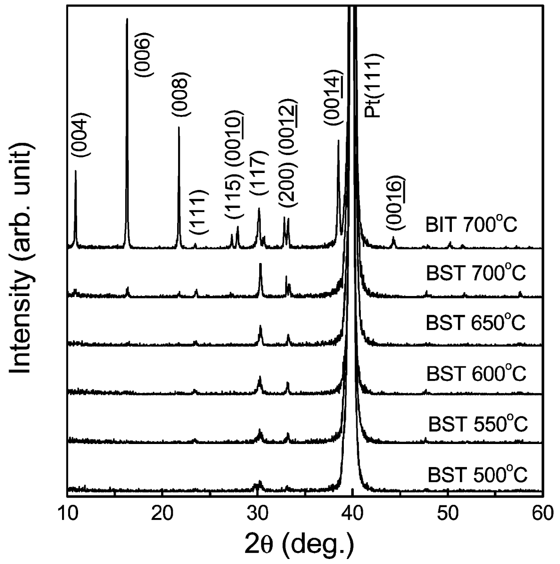

Fig. 1. XRD patterns of BIT film annealed at 700°C and BST films annealed at 500, 550, 600, 650, and 700°C for 30 min in oxygen atmosphere.

Figure 1 shows XRD patterns of BIT film annealed at 700°C and BST films annealed at 500–700°C for 30 min in an oxygen atmosphere, respectively. All of the films consist of single phase having ferroelectric bismuth-layered perovskite structure. As shown in the figure, BIT film prepared under the same conditions exhibits very strong (00*l*) peaks and a *c*-axis preferred orientation. However, BST films show relatively strong (117) peak suggesting that the films are randomly oriented. The degree of *c*-axis orientation calculated by the relation of I(006)/[I(006) + I(117)] [5] was 23.2% for the BST film annealed at 700°C, which indicates that the fully crystallized BST thin films show no preferred orientation. On the other hand, for the BIT film, the degree of *c*-axis orientation was 84.8%. BIT has a layered perovskite structure and exhibits very strong anisotropic properties. Along the *c*- and *a*-axis, BIT single crystals have a spontaneous polarization (P_s) of 4 and 50 μC/cm^2, and E_c of 3.5 and 50 kV/cm, respectively [6]. From this viewpoint, randomly oriented films are considered to be more favorable than *c*-axis oriented films for memory applications. It should be emphasized that the BST films obtained in this work have a suitable orientation compared to the *c*-axis oriented BIT film.

The surface morphologies of the BST films annealed at 550–700°C are shown in Fig. 2(a)–(d). For the BST film annealed at 550°C, the surface is composed of fine grains without cracks. With increased annealing temperature up to 700°C, it is observed

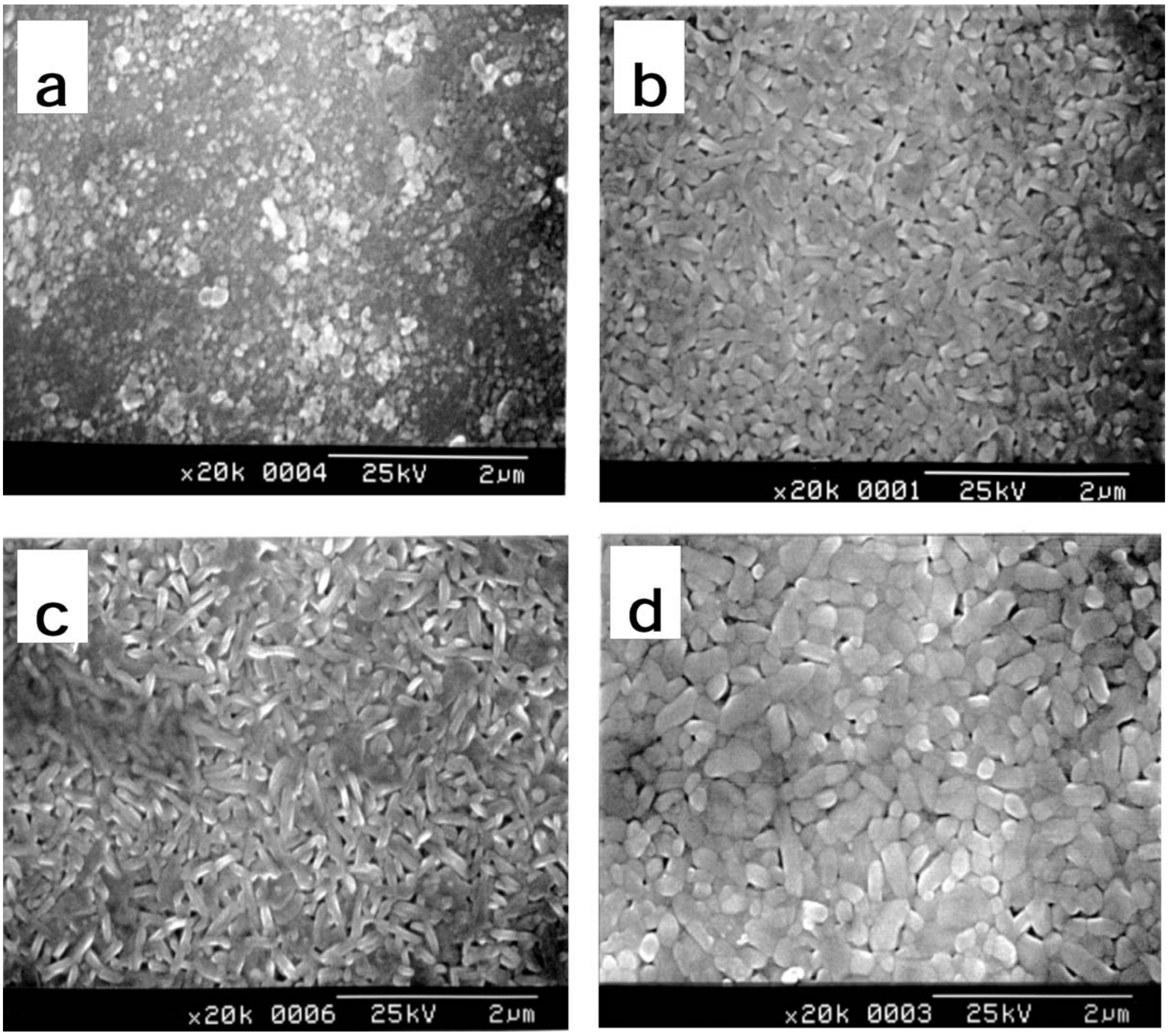

Fig. 2. Surface morphologies of BST films annealed at (a) 550°C, (b) 600°C, (c) 650°C and (d) 700°C.

that the grains are grow fast along a preferred orientation resulting elongated grain shape. The grain sizes of the films increase with increased annealing temperature, which is match well with the XRD results.

The BST film annealed at 700°C has been investigated by TEM to understand structural information of the film. The shape of the grains in the BST film observed by a cross sectional TEM image (Fig. 3(a)) is different from the columnar grains found in the BLT films on $Pt/TiO_2/SiO_2/Si$ substrates grown by PLD [7]. The measured film thickness of 350 nm match well with that observed by SEM. A bright field image of a BST grain is shown in Fig. 3(b), which exhibits lattice image of bismuth-layered perovskite structure. A large number of line defects, such as stacking faults, in HRTEM were observed. A selected area electron diffraction pattern of the same grain is shown in Fig. 3(c). Interestingly, forbidden electron diffraction spots, such as odd b-axis indices of $\{0\,l\,2n\}$, where $l = 1, 3, 5\ldots$, and $n =$ integer, are observed. In contrast, this type of electron diffraction spots are not observed in other bismuth-layered perovskite structures, such as BIT and BNT. These unexpected weak diffraction spots are unique in BST film, which may be caused by stacking faults along b-axis and/or irregular Sm^{3+}

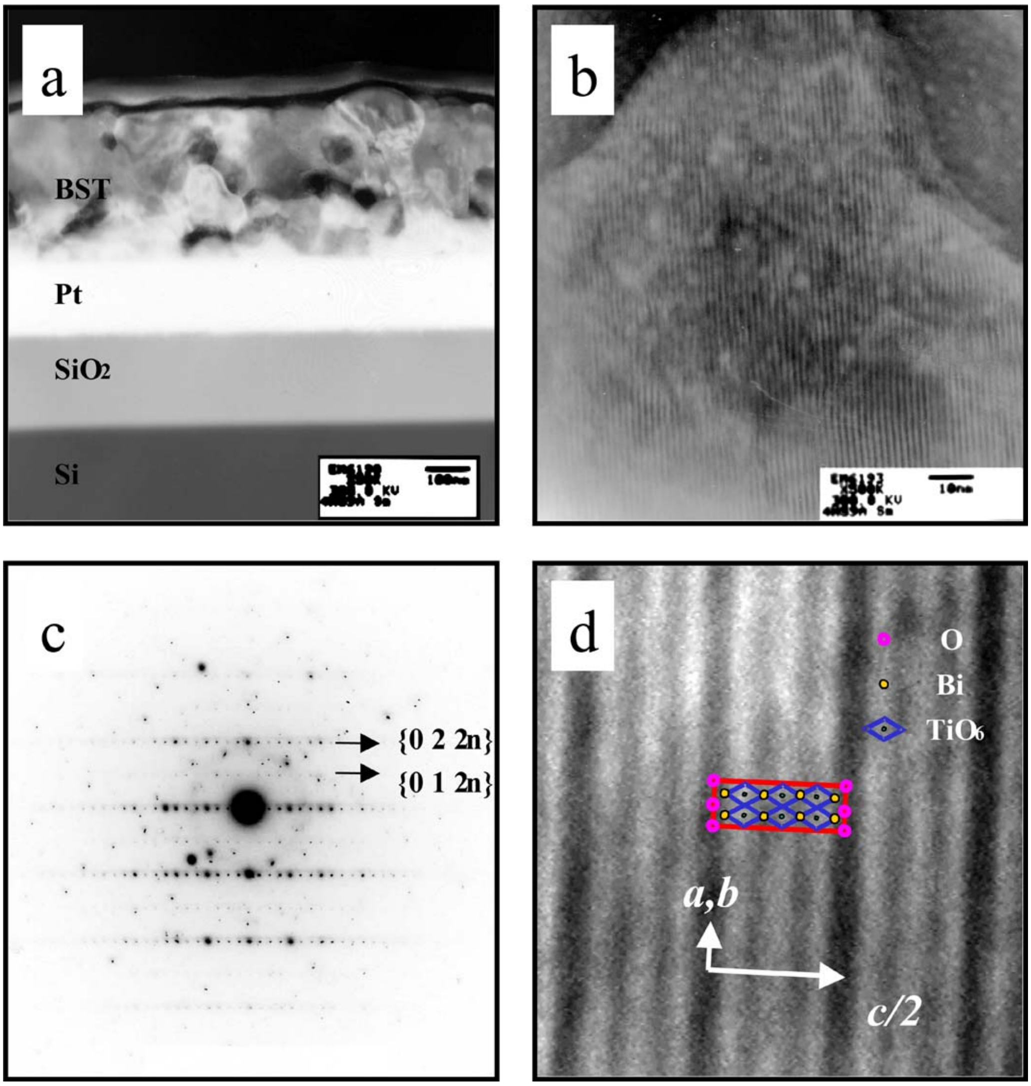

Fig. 3. (a) Cross sectional TEM image, (b) bright field TEM image, (c) selected area electron diffraction (SAD) patterns, and (d) corresponding enlarged HRTEM image of BST films annealed at 700°C.

occupancy in the structure. A half of BST unit cell was shown in the enlarged HRTEM image (Fig. 3(d)) as a reference.

For the electrical measurements, circular Au top electrodes of $7.85 \times 10^{-5}\text{cm}^2$ area were deposited by a thermal evaporation method. Ferroelectric hysterisis loops with $2P_r$, and $2E_c$ for the BST films annealed at 700° as a function of applied electric field are shown in Fig. 4. The characterized BST film capacitor exhibits well-saturated P-E switching curves at various applied electric fields. $2P_r$ of 64.2 μC/cm^2 and $2E_c$ of 101.7 kV/cm at applied electric field 150 kV/cm were observed. This $2P_r$ value is higher than those of the BLT films deposited by PLD and metalorganic solution decomposition, which were respectively 24 and 26–28 μC/cm^2 [1, 2]. This result for the BST films is comparable to the value reported on the randomly oriented BNT films fabricated by a chemical solution deposition [3]. The reason for a higher P_r value in BST film compared with BLT film can be explained by the chemical modification of the structure derived from the different ionic radius of Sm^{3+} and La^{3+} ions and/or by

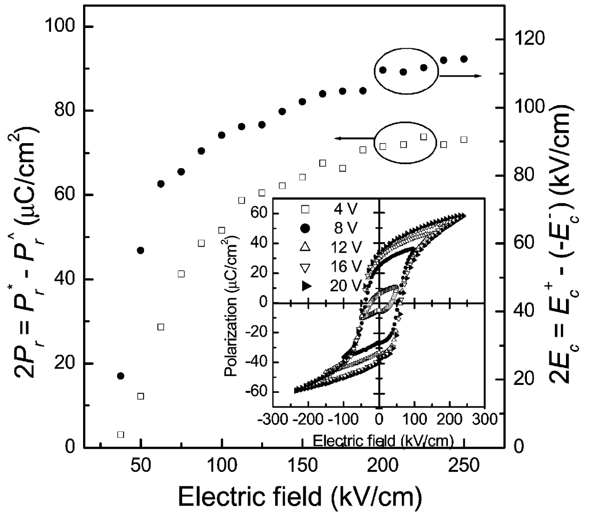

Fig. 4. Ferroelectric hysteresis loops and $2P_r$ and $2E_c$ values of BST film capacitors annealed at 700°C as functions of applied electric fields.

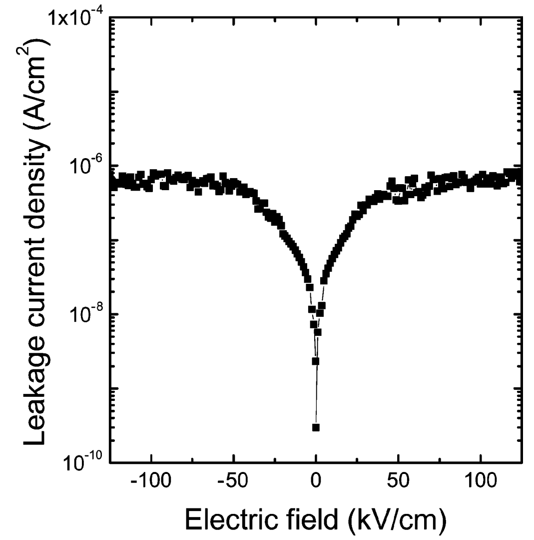

Fig. 5. *I*-*V* characteristics of BST film capacitor annealed at 700°C.

increased contribution of *a*-axis oriented polarization due to the random orientation in the films.

Figure 5 shows the leakage current density versus the applied electric field of the BST film capacitor annealed at 700°C. There is no significant difference in leakage when the voltage polarity is reversed. The leakage current density of 7.2×10^{-7} A/cm^2 for the BST film capacitor at 100 kV/cm was reduced about 1.5 orders of magnitude as compared with 3×10^{-5} A/cm^2 for the BIT film fabricated by CVD [8]. Improvement of leakage current with lanthanide ions-substitution is consistent with other results [9].

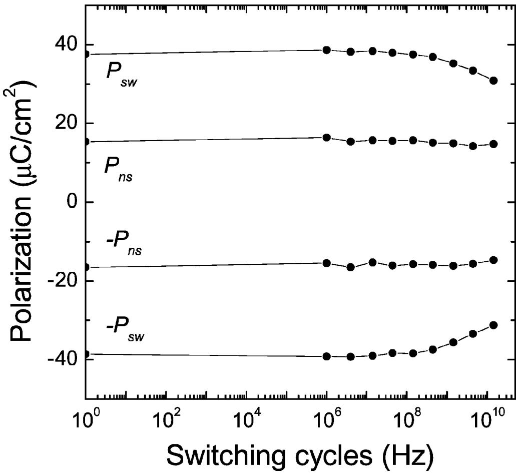

Fig. 6. Polarization fatigue characteristics of BST film capacitor annealed at 700°C as functions of applied electric fields.

Fatigue characteristics of the BST film capacitor are shown in Fig. 6. As shown in figure, the BST film capacitor did not show any significant changes in the switching polarization (P_{sw}) up to 1.5×10^8 read/write cycles at a frequency of 1 MHz, while P_{sw} of PZT is order of 10^5 [10, 11]. Interestingly, the values of the non-switching polarization (P_{ns}) did not show any significant change throughout the measured switching cycles up to 1.5×10^{11}. This P_{ns} property of the BST film is similar to that of the reported BLT and SBT films [12, 13].

Good ferroelectric properties, such as large remanent polarization and fatigue endurance, of the BST films may come from improved chemistry and structure of the films caused by substitution of samarium for Bi-site. In order to clarify the effect of substitution by other lanthanide elements on the ferroelectric properties, more studies are necessary in the future.

4. Conclusions

$Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ (BST) thin films were successfully fabricated on Pt/Ti/SiO$_2$/Si(100) substrates by a metalorganic solution deposition method. The BST films showed well-defined layered perovskite structures and random orientation, which were confirmed by XRD and TEM investigations. $2P_r$ of 64.2 μC/cm^2 and $2E_c$

of 101.7 kV/cm at applied electric field of 150 kV/cm were observed in the BST film annealed at 700°. This $2P_r$ value is larger than those of BLT and BIT films and comparable with that of BNT films. Moreover, BST thin films did not show any significant fatigue up to 1.5×10^8 read/write switching cycles at a frequency of 1 MHz. As a result, the lead free BST thin films having good ferroelectric properties are potentially important candidates for FeRAM applications.

Acknowledgment

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References

1. B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, L. Lee, and W. Joe, *Nature (London)*, **401**, 682 (1999).
2. U. Chon, G.C. Yi, and H.M. Jang, *Appl. Phys. Lett.*, **78**, 658 (2001).
3. R.E. Melgarejo, M.S. Tomar, S. Bhaskar, P.S. Dobal, and R.S. Katiyar, *Appl. Phys. Lett.*, **81**, 2611 (2002).
4. U. Chon, K.B. Kim, H.M. Jang, and G.C. Yi, *Appl. Phys. Lett.*, **79**, 3137 (2001).
5. M. Yamaguchi, K. Kawanabe, T. Nagatomo, and O. Omoto, *Mat. Sci. Eng.*, **B41**, 138 (1996).
6. S.E. Cummins and L.E. Cross, *Appl. Phys. Lett.*, **10**, 14 (1967).
7. C.-H. Kim, J.-K. Lee, H.-S. Suh, J.Y. Yi, K.-S. Hong, and T.-S. Hahn, *Jpn. J. Appl. Phys.*, **41**, 1495 (2002).
8. M. Schuisky, A. Harsta, S. Khartsev, and A. Grishin, *J. Appl. Phys.*, **88**, 2819 (2000).
9. W.S. Yang, N.K. Kim, S.J. Yeom, S.Y. Kweon, and J.S. Roh, *Jpn. J. Appl. Phys.*, **41**, 727 (2002).
10. R. Ramesh, W.K. Chan, B. Wilkens, H. Gilchrist, T. Sands, J.M. Tarascon, D.K. Fork, J. Lee, and A. Safari, *Appl. Phys. Lett.*, **61**, 1537 (1992).
11. O. Auciello, K.D. Gifford, and A.I. Kingon, *Appl. Phys. Lett.*, **64**, 2873 (1994).
12. D. Wu, A. Li, T. Zhu, Z. Liu, and N. Ming, *J. Appl. Phys.*, **88**, 5941 (2000).
13. D. Wu, A.D. Li, H.Q. Lin, T. Yu, Z.G. Liu, and N.B. Ming, *Appl. Phys. Lett.*, **76**, 2208 (2000).