Fatigue-free samarium-modified bismuth titanate ($Bi_{4-x}Sm_xTi_3O_{12}$) film capacitors having large spontaneous polarizations

Uong Chon,[a)] Ki-Bum Kim, Hyun M. Jang,[b)] and Gyu-Chul Yi
Department of Materials Science and Engineering, and National Research Laboratory (NRL) for Ferroelectric Phase Transitions, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea

(Received 23 April 2001; accepted for publication 22 August 2001)

Fatigue-free and highly c-axis oriented $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ (BSmT) thin films were grown on $Pt/TiO_2/SiO_2/Si(100)$ substrates using the method of metalorganic sol decomposition. The BSmT film capacitor with a top Pt electrode showed significantly improved values of the remanent polarization ($2P_r$) and the nonvolatile charge as compared to those of the $Bi_{4-x}La_xTi_3O_{12}$ ($x=0.75$) film capacitor, recently known as the most promising candidate for nonvolatile memories. The $2P_r$ value of the BSmT capacitor was 49 $\mu C/cm^2$ at an applied voltage of 10 V while the net nonvolatile switching charge was as high as 20 $\mu C/cm^2$ and remained essentially constant up to 4.5×10^{10} read/write switching cycles at a frequency of 1 MHz. In addition to these, the capacitor demonstrated excellent charge–retention characteristics with its sensing margin of 17 $\mu C/cm^2$ and a strong resistance against the imprinting failure.
[DOI: 10.1063/1.1415353]

There have been extensive research efforts to enhance the reliability of perovskite-based ferroelectric thin films for use in nonvolatile ferroelectric random access memory (NvFRAM) devices. Among these ferroelectrics, lead zirconate titanate (PZT) is known to be the most important candidate for NvFRAM applications. However, it shows a serious degradation of ferroelectric properties after being subjected to $\sim10^7$ read/write switching cycles. Although the fatigue problem of PZT-based capacitors can be solved by using metal oxide electrodes,[1,2] these electrodes are difficult to be prepared and tend to increase leakage current, in general. Some layered perovskites such as strontium bismuth tantalate [$SrBi_2Ta_2O_9$, (SBT)][3,4] and lanthanum-modified bismuth titanate [$Bi_{3.25}La_{0.75}Ti_3O_{12}$, (BLT)][5] showed superior fatigue resistances as compared to Pt/PZT/Pt capacitors.

As one of the fatigue-free ferroelectrics, the BLT film is of particular interest. This is not only because it can be crystallized at low processing temperatures possibly below 650 °C, which is compatible with Si-based integrated circuit technology, but also because it shows larger spontaneous polarizations than those of SBT-based films. However, the BLT film prepared by the pulsed laser deposition method was characterized by a mixed orientation of grains.[5,6] The mixed orientation tends to increase bit-to-bit variability in a capacitor for high-density ferroelectric memory devices.[6] More recently, highly c-axis oriented BLT films having fatigue-free characteristics were grown on $Pt/Ti/SiO_2/Si(100)$ substrates using metalorganic sol decomposition (MOSD).[7] The highly c-axis oriented capacitor showed a well-saturated polarization–electric field ($P-E$) switching curve with its remanent polarization ($2P_r$) of 27 $\mu C/cm^2$ at an applied voltage of 10 V.[7] Notwithstanding the fatigue-free characteristics, the $2P_r$ value or, more relevantly, the nonvolatile switching charge of the highly oriented BLT film needs to be substantially improved to ensure the reliability of devices (i.e., sufficient sensing margin) and to apply the capacitor to high-density NvFRAM.

Our preliminary study indicated that the direction and the magnitude of $2P_r$ of highly c-axis oriented bismuth titanate (BT)-based films were very susceptible to the substitution of trivalent rare-earth lanthanides (e.g., La) for bismuth. X-ray diffraction (XRD) analysis of highly oriented BT-based films, in conjunction with ferroelectric measurements, indicated that the observed large increase in $2P_r$ values parallel to the c-axis with increasing content of lanthanides was closely related to the change in the major direction of the spontaneous polarization from the b-axis direction to the direction parallel to the c axis.[8] Thus, one would expect to obtain BT-based thin films having both fatigue-resistance characteristics and large $2P_r$ values by suitably substituting stable trivalent ions for volatile bismuth ions.

In selecting appropriate trivalent cationic species for this purpose, one has to consider various physicochemical factors. Among these, the following three factors seem to be most appropriate: (i) the stability of perovskite phase, (ii) the ionic radius, and (iii) the Curie–Weiss temperature. Among rare-earth lanthanides having electrons in the $4f$ orbitals, Sm, Nd, and Pr basically meet the requirement of the phase stability of $(BiO)_2R_2Ti_3O_{10}$-type layered perovskites.[9] Of these three lanthanides, samarium (Sm) seems to satisfy all of the three criteria. Its ionic radius of 1.00 Å in the Ahren's scale is compatible with that of Bi (0.93 Å).[9] The Curie–Weiss temperature of $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ is estimated to be 470 °C,[9] which is high enough to be used in ferroelectric memory devices that require a stability of polarization switching against thermal agitation. In view of these, the

a)Permanent address: Research Institute of Industrial Science and Technology (RIST), P.O. Box 135, Pohang 790-330, Republic of Korea.
b)Author to whom all correspondence should be addressed; electronic mail: hmjang@postech.ac.kr

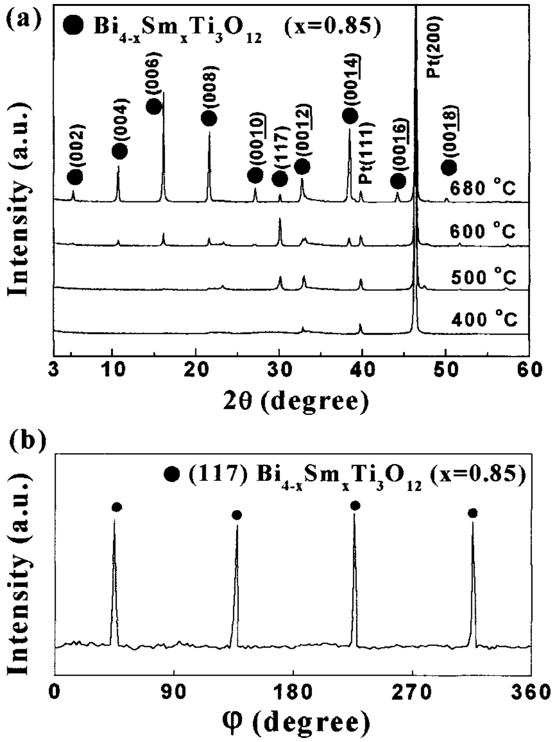

FIG. 1. XRD θ–2θ patterns and φ-scan spectrum of BSmT films grown on Pt/TiO_2/SiO_2/Si(100) substrates (a) XRD θ–2θ scan results of BSmT films annealed at various indicated temperatures for 1 h, and (b) φ-scan spectrum for the (117) reflection of the c-axis oriented BSmT film annealed at 680 °C for 1 h.

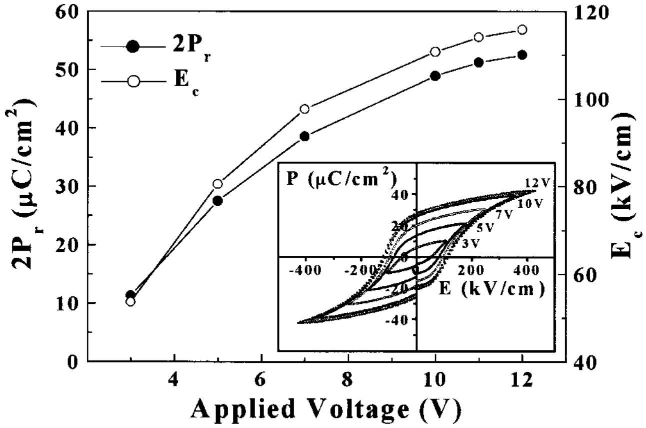

FIG. 2. Variations of $2P_r$ and E_c values of the Pt/BSmT/Pt capacitor are plotted as a function of the applied voltage. The inset shows hysteresis loops measured at various applied voltages ranging between 3 and 12 V. The corresponding film was thermally annealed at 680 °C for 1h.

main purpose of the present study is to develop highly c-axis oriented Sm-modified bismuth titanate (BSmT) films having fatigue-free characteristics as well as improved remananent polarizations along the unique c direction.

The BSmT ($Bi_{4-x}Sm_xTi_3O_{12}$ with $x=0.85$) films were fabricated on Pt/TiO_2/SiO_2/Si(100) substrates using the method of MOSD. The precursor sol for the coating was prepared by dissolving appropriate amounts of bismuth acetate [$Bi(CH_3COO)_3$], samarium acetate hydrate [$Sm(CH_3COO)_3\cdot 2H_2O$], and titanium isopropoxide {$Ti[(CH_3)_2CHO]_4$} in an acetic acid solution at room temperature in a glove box being flushed with nitrogen gas. The dried amorphous films were crystallized by thermal annealing in an oxygen-rich atmosphere at various temperatures ranging between 400 °C and 680 °C for 1 h.

As-annealed films were specular, crack-free, dense, and adhered well on the substrates used. Microstructural examination using a field-emission scanning electron microscope (FE-SEM) showed only fine-sized, uniform grains in the films. The chemical composition of the BSmT film, as determined using energy dispersive x-ray and electron microprobe techniques, was Bi:Sm:Ti=3.15:0.85:3. In order to fabricate capacitors, top Pt electrodes were deposited using a rf magnetron sputter. A typical area of the top electrode was 10^{-4} cm^2. The ferroelectric and dielectric measurements were performed on the BSmT capacitors using a RT6000S ferroelectric tester and a HP4194A impedance analyzer equipped with a micrometer probe station.

Figure 1 shows the XRD θ–2θ scan results of the BSmT films annealed at various indicated temperatures for 1 h. All the XRD patterns can be readily identified and indexed using the standard XRD data for the perovskite BT ($Bi_4Ti_3O_{12}$) compiled in the Joint Committee on Powder Diffraction Standards card. This indicates that the BSmT film maintains a pseudotetragonal-layered structure similar to the perovskite BT even under extensive modifications by Sm. The most prominent feature of the XRD patterns in Fig. 1(a) is that the film annealed at 680 °C shows a highly c-axis oriented preferential growth with a minor fraction of (117) orientation. The degree of the $(00l)$-type preferential growth, as estimated using Lotgering's orientation factor,[10] is 96% for the BSmT film annealed at 680 °C. The x-ray φ-scan spectrum for the (117) reflection shows four peaks separated one from another by 90°, as presented in Fig. 1(b). This indicates that the c-axis oriented tetragonal BSmT film ($x=0.85$) has a homogeneous in-plane orientation.

Figure 2 summarizes the variations of $2P_r$ and E_c (coercive field) of the BSmT capacitor with the applied voltage. The film was annealed at 680 °C for 1 h, and its thickness, as estimated using cross sectional FE-SEM, was 280 nm. The inset presents hysteresis loops measured at various applied voltages ranging between 3 and 12 V. The capacitor is characterized by well-saturated $P-E$ switching curves. As shown in Fig. 2, both $2P_r$ and E_c values increase rather steeply at a low applied voltage but do not change much beyond 10 V. The capacitor is nearly saturated at an applied voltage of 12 V (i.e., ~430 kV/cm). $2P_r$ value of the capacitor is 49 $\mu C/cm^2$ at an applied voltage of 10 V. This value is remarkably higher than $2P_r$ of 27 $\mu C/cm^2$ for the highly c-axis oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ capacitor, recently reported as a fatigue-free ferroelectric capacitor.[7]

The relative dielectric permittivity [$\varepsilon'(\omega)$] and the dissipation factor [$\varepsilon''(\omega)/\varepsilon'(\omega)=\tan\delta$] of the capacitor were measured at 25 °C as a function of frequency. $\varepsilon'(\omega)$ and $\tan\delta$ were 387 and 0.054 at a frequency of 1 MHz, respectively. These values are comparable to those of PZT, SBT, and BLT capacitors.[3,5,11] Although both $\varepsilon'(\omega)$ and $\tan\delta$ decreased slightly with increasing frequency, there was no sudden change in their values up to 1 MHz. All these indicate that the observed $P-E$ hysteresis behavior of the BSmT capacitor originates from the ferroelectric polarization switching of bound charges, not from the response of freely moving charges.

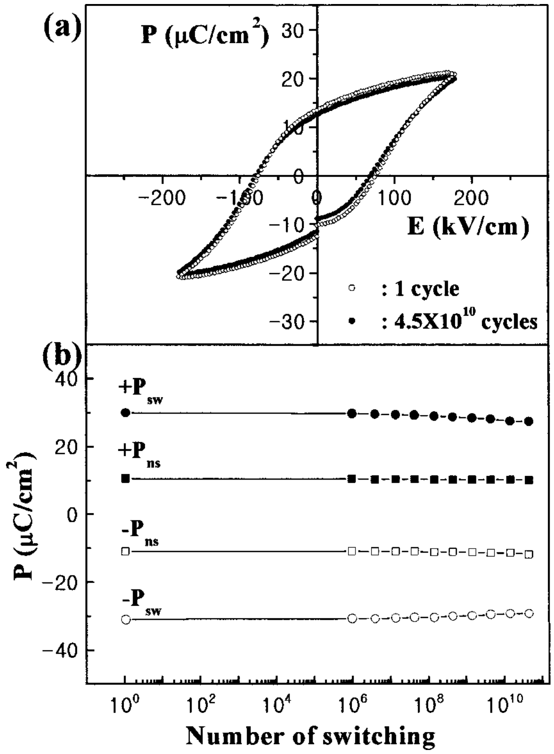

FIG. 3. Electrical fatigue characteristics of the Pt/BSmT/Pt capacitor are shown before and after being subjected to 4.5×10^{10} read/write cycles at a frequency of 1 MHz. (a) $P-E$ hysteresis loops measured at an applied voltage of 5 V before and after the switching cycle, and (b) the fatigue test results determined using a switching (fatigue) voltage of ±3 V, and a measuring voltage of 5 V at a frequency of 1 MHz.

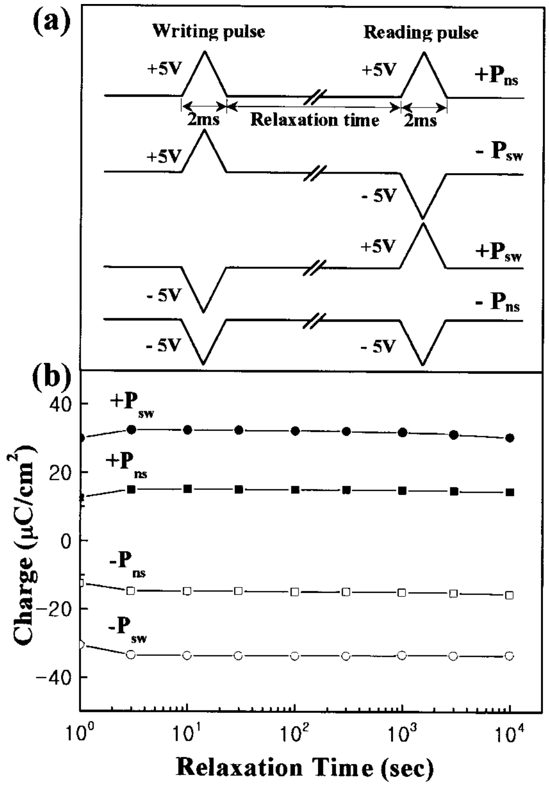

FIG. 4. Charge–retention characteristics of the Pt/BSmT/Pt capacitor at 85 °C are plotted as a function of time after the application of a writing pulse.

The fatigue-free characteristics of the BSmT capacitor are summarized in Fig. 3. The capacitor shows little change both in the switching polarization (P_{sw}) and in the nonswitching polarization (P_{ns}) up to 4.5×10^{10} read/write cycles at a switching voltage of ±3 V (i.e., 107 kV/cm). The values of the nonvolatile charge [i.e., $(+P_{sw})-(+P_{ns})$ or $(-P_{sw})-(-P_{ns})$] are approximately 20 μC/cm^2, and remain essentially constant throughout the switching cycles. The fatigue-free behavior was also observed at a higher switching voltage of ±5 V (i.e., 180 kV/cm). The $P-E$ curves of Fig. 3(a) were obtained at an applied voltage of 5 V before and after the electrical fatigue test. The values of $2P_r$ and E_c before the fatigue test were 27 μC/cm^2 and 79 kV/cm, respectively. After being subjected to 4.5×10^{10} cycles, these were still retained at 25 μC/cm^2 and 76 kV/cm. Besides, the $P-E$ curves do not show any noticeable asymmetric behavior resulting in imprint failures, even after being subjected to 4.5×10^{10} switching cycles.

The charge–retention characteristics of the BSmT capacitor are summarized in Fig. 4 by plotting the switching polarization ($\pm P_{sw}$) and the nonswitching polarization ($\pm P_{ns}$) as a function of time. Figure 4(a) represents four distinctive test-pulse sequences employed for measuring the charge retention of $+P_{sw}$, $+P_{ns}$, $-P_{sw}$, and $-P_{ns}$. The sensing margin, as defined by $P_{nv}=(\pm P_{sw})-(\pm P_{ns})$, of the capacitor was 17 μC/cm^2 at 85 °C and remained essentially constant up to 10^4 s after applying a writing pulse, demonstrating an excellent charge-retaining ability of the BSmT capacitor. Compared with the reported sensing margin of a highly c-axis oriented SBT capacitor[12] (6 μC/cm^2) and that of a $SrBi_2(Ta,Nb)_2O_9$ capacitor[13] (11 μC/cm^2), this is a substantial improvement. In addition to this, $|-P_{sw}|$ was essentially the same as $+P_{sw}$ throughout the relaxation (retaining) time, and the same trend was also observed for $|-P_{ns}|$ and $+P_{ns}$. This indicates that the BSmT capacitor has a strong resistance against the imprinting failure.

This study was financially supported by the KISTEP of Korea through the NRL Program.

[1] R. Ramesh, J. Lee, T. Sands, V. G. Keramidas, and O. Auciello, Appl. Phys. Lett. **64**, 2511 (1994).
[2] H. N. Al-Shareef, K. R. Bellur, A. I. Kingon, and O. Auciello, Appl. Phys. Lett. **66**, 239 (1995).
[3] R. Dat, J. K. Lee, O. Auciello, and A. I. Kingon, Appl. Phys. Lett. **67**, 572 (1995).
[4] C. A. Paz de Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott, and J. F. Scott, Nature (London) **374**, 627 (1995).
[5] B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, Nature (London) **401**, 682 (1999).
[6] A. Kingon, Nature (London) **401**, 658 (1999).
[7] U. Chon, G. C. Yi, and H. M. Jang, Appl. Phys. Lett. **78**, 658 (2001).
[8] U. Chon, H. M. Jang, S.-H. Lee, and G.-C. Yi, J. Mater. Res. (in press).
[9] R. W. Wolfe and R. E. Newnham, J. Electrochem. Soc. **116**, 832 (1969).
[10] F. K. Lotgering, J. Inorg. Nucl. Chem. **9**, 113 (1959).
[11] H. D. Chen, K. R. Udayakumar, C. J. Gaskey, and L. E. Cross, Appl. Phys. Lett. **67**, 3411 (1995).
[12] J. J. Lee, C. L. Thio, and S. B. Desu, Phys. Status Solidi A **151**, 171 (1995).
[13] Y. Shimada, K. Nakao, A. Inoue, M. Azuma, Y. Uemoto, E. Fujii, and T. Otsuki, Appl. Phys. Lett. **71**, 2538 (1997).