La-doped effect on the ferroelectric properties of $Bi_4Ti_3O_{12}-SrBi_4Ti_4O_{15}$ thin film fabricated by pulsed laser deposition

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$Bi_4Ti_3O_{12}-SrBi_4Ti_4O_{15}$ (BT–SBTi) thin film was fabricated successfully on $Pt/TiO_2/SiO_2/Si(110)$ substrates by the pulsed laser deposition technique. Films annealed at 650 °C by the rapid temperature process (RTP) have $P_r = 12\ \mu C/cm^2$. But, the fatigue behavior has been observed although no obvious decrease in P_r up to 10^5 s retained time in the BT–SBTi capacitor. After being La doped, the $Bi_{3.25}La_{0.75}Ti_3O_{12}-SrBi_4Ti_4O_{15}$ (BLT–SBTi) has fatigue free properties. $P_r = 13.5\ \mu C/cm^2$ was measured in a BLT–SBTi film of 300 nm thickness. It did not show any significant fatigue up to 10^{10} switching cycles above the applied field of 250 kV/cm. It also has good retention properties. The field dependence of fatigue behavior and La-doped effect are discussed.
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INTRODUCTION

Ferroelectric thin films have attracted much attention due to the potential application in nonvolatile ferroelectric random access memories (NvFeRAMs).[1,2] Many materials have been proposed as candidates for NvFeRAM applications. Among them, $Pb(Zr_xTi_{1-x})O_3$ (PZT) and $SrBi_2Ta_2O_9$ (SBT) thin films have been extensively studied for their good ferroelectric properties. ABO_3 type ferroelectric PZT thin films have large P_r and lower fabricating temperatures and Bi layer-structured ferroelectric (BLSF) SBT thin films have an excellent fatigue endurance against repeated switching of polarization even using Pt electrodes. Both the PZT and the SBT thin films are leading candidates for FeRAM applications.[3] However, the degradation of the polarization state of the capacitor with Pt electrode and Pb toxicity for PZT thin films and the relatively lower remanent polarization, higher fabricating temperature, and low Curie temperature for SBT thin films indicate that there is a space to improve or to search for materials for the application of NvFeRAM.

Solid solution,[4,5] substitution,[6,7] doping,[8,9] intergrowth,[10] and composition variations have been used to improve, to modify, and even to find the FeRAM materials with better ferroelectric properties. Desu *et al.*[4] reported that the solid solution thin film $(1-x)\ SrBi_2Ta_2O_9-xBiTaTiO_3$ fabricated by the modified metalorganic solution deposition technique showed highly improved properties. In particular, $0.7SrBi_2Ta_2O_9-0.3BiTiTaO_3$ thin film has $P_r = 6.2-13.9\ \mu C/cm^2$ and $E_c = 68-80$ kV/cm. Park *et al.*[6] made the $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin film by substituting La for Bi in $Bi_4Ti_3O_{12}$ and BLT thin film shows larger P_r ($P_r = 12\ \mu C/cm^2$) even after annealing at 650 °C and it is fatigue free. Also, works on substitution of some kinds of atoms such as Ca for Sr in $SrBi_2Ta_2O_9$ or Ca for Bi in $Bi_4Ti_3O_{12}$ have been reported. As Kato[7] pointed out that precise substitution of bismuth ions by other cations would be one of the effective approaches for improving the microstructure and electrical properties in BLSFs. In addition, Noguchi[8] doped a small amount of vanadium into $Bi_4Ti_3O_{12}$ ceramics to obtain $Bi_{4-x/3}Ti_{3-x}V_xO_{12}$ ceramics with $P_r = 20\ \mu C/cm^2$ without sacrificing other physical properties. The polarization characteristics of this ceramic were superior to that of $SrBi_2Ta_2O_9$ and $SrBi_{0.8}Ta_{2.2}O_9$. Noguchi[10] also reported that regular intergrowth BLSF $Bi_4Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$ (BT–SBTi) ceramics have a large remanent polarization P_r of 15 $\mu C/cm^2$ and high Curie temperature of 610 °C. However, both the materials reported by Noguchi are ceramics, so no thin films are fabricated and no endurance properties for these materials were reported. The endurance is very important for the memory application. Recently, Watanabe *et al.*[11] reported the effect of consubstitution of La and V in $Bi_4Ti_3O_{12}$ thin film fabricated by metalorganic chemical vapor deposition at 600 °C, where they got $(Bi_{3.2}La_{0.8})\times(Ti_{2.97}V_{0.03})O_{12}$ (BLTV) films with $P_r = 8.5\ \mu C/cm^2$ and good fatigue endurance up to 10^9 switching cycles. In this article, we report the fabrication for the BT–SBTi and the BLT–SBTi thin films by the pulsed laser deposition (PLD) technique and the measurement of ferroelectric properties. A possible origin for the improvement of endurance in BLT–SBTi thin film is discussed. The results indicate that this kind of intergrowth thin film may be a promising candidate for application of FeRAM.

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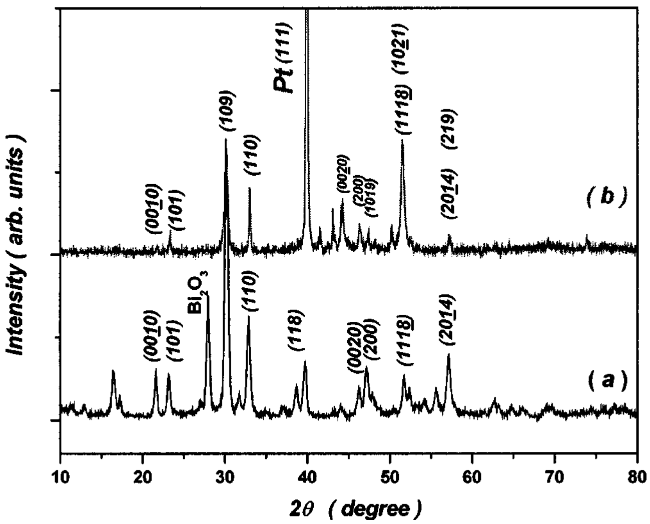

FIG. 1. The XRD pattern with Cu $K\alpha$ radiation for BT–SBTi (a) ceramics and (b) thin film annealed at 650 °C.

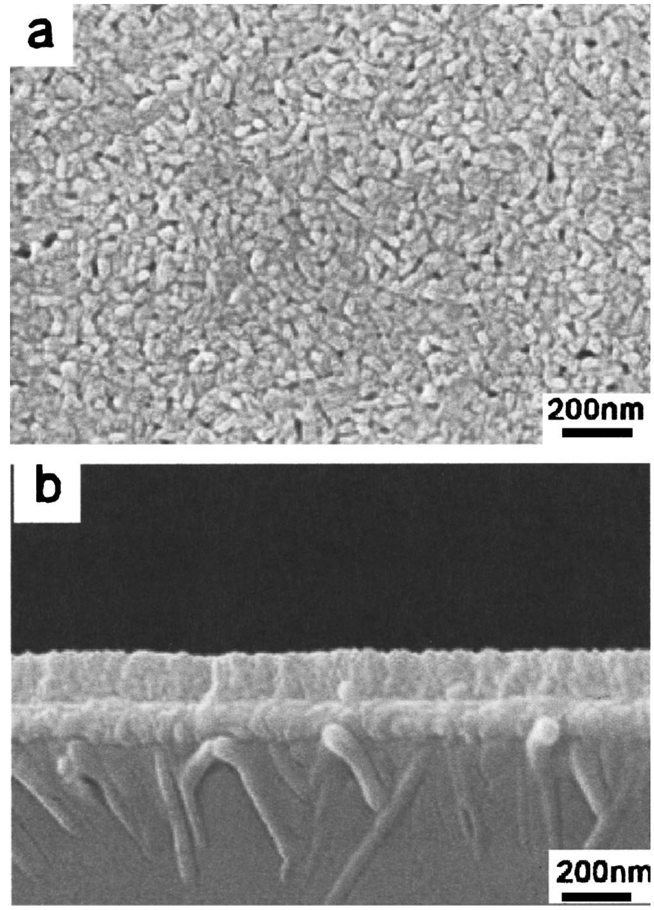

FIG. 2. The SEM images for BT–SBTi thin film annealed at 650 °C: (a) surface morphology and (b) cross section of SEM micrograph.

EXPERIMENT

BT–SBTi and BLT–SBTi pellets used as PLD targets were prepared by solid state reactions with the starting materials Bi_2O_3 (in excess by 30% due to its volatile property), $SrCO_3$, TiO_2, and La_2O_3. The mixture of Bi_2O_3, $SrCO_3$, and TiO_2 with the ratio of 10.4:1:7 for BT–SBTi and Bi_2O_3, $SrCO_3$, TiO_2, and La_2O_3 with the ratio 18.85:1:7:1.5 for BLT–SBTi were ball milled for 6 h, presintered at 800 °C for 2 h, and then pressed into pellets. Finally the pellets were sintered at 1200 °C for 2 h. The BT–SBTi and BLT–SBTi thin films were deposited on the Pt $(111)/TiO_2/SiO_2/Si$ (100) substrates at 400 °C for 15 min using a krypton fluoride (KrF) excimer laser (Lambda Physik COMPex 205) of 248 nm wavelength and 25 ns pulse duration. In this experiment, the average laser energy and frequency were 132 mJ/shot and 10 Hz, respectively. The oxygen pressure in the chamber was kept at about 200 mTorr during the laser ablation process. The thin films with thicknesses around 250–350 nm were obtained. After deposition, the films were post-annealed in a rapid thermal processor (RTP) at 650 or 700 °C for 5 min in an oxygen flow. The crystal phase of the thin films was identified by x-ray diffractometer (XRD) using Cu $K\alpha$ radiation. The microstructure and surface morphology of the thin films were observed using a scanning electron microscope (SEM) (Leica stereoscan 440). Prior to electrical measurement, circular Pt electrodes 200 μm in diameter were deposited by rf sputtering, which was followed by annealing at 600 °C as crystallization for 5 min in oxygen flow. Ferroelectric hysteresis loops as well as retention characteristics were measured using a Radiant Technology RT66A instrument. Fatigue property was also performed by RT66A.

RESULTS AND DISCUSSION

Figure 1 shows the XRD results for BT–SBTi materials measured with Cu $K\alpha$ radiation. The diffraction pattern of ceramics for the PLD target is shown in Fig. 1(a). It is similar to that reported by Noguchi[10] besides the line due to excessive Bi_2O_3. Figure 1(b) is the one for BT–SBTi thin film. It is almost the same as Noguchi's result and indicates that the film has regular intergrowth structure and a single phase of BT–SBTi was obtained. Figure 2 shows the surface morphology (a) and the cross sectional view (b) of the BT–SBTi thin film annealed at 650 °C. The film is 250 nm thick and the surfaces are uniform without any cracks. Large grains about 100 nm were found and a clear and sharp boundary between the film and Pt electrode was revealed by SEM. Figure 3 shows the hysteresis loop of BT–SBTi thin film at various applied voltages. It can be seen that the BT–SBTi thin films have a larger remenant polarization $P_r = 12\ \mu C/cm^2$, $E_c = 114$ kV/cm, and the hysteresis loops show saturation with increasing applied voltage. The P–E hysteresis property of BT–SBTi thin films was comparable to that of $Bi_4Ti_3O_{12}$ thin film[12] or La substitution $Bi_4Ti_3O_{12}$ (BLT),[6] and was better than $SrBi_4Ti_4O_{15}$ thin film[13]

The retention characteristics of BT–SBTi thin film annealed at 650 °C for 5 min by RTP over a range of $1-10^5$ s at 5 V are shown in Fig. 4. The polarization decay showed good linearity when plotted against logarithmic retention time and almost no obvious decay was found for retained time up to 10^5 s. However, the fatigue measurement of BT–SBTi film showed serious degradation of Pr after 10^6 switching cycling, as shown in Fig. 5, and therefore it is not suitable for the application of FeRAM for its fatigue behavior although it has large Pr and good retention property.

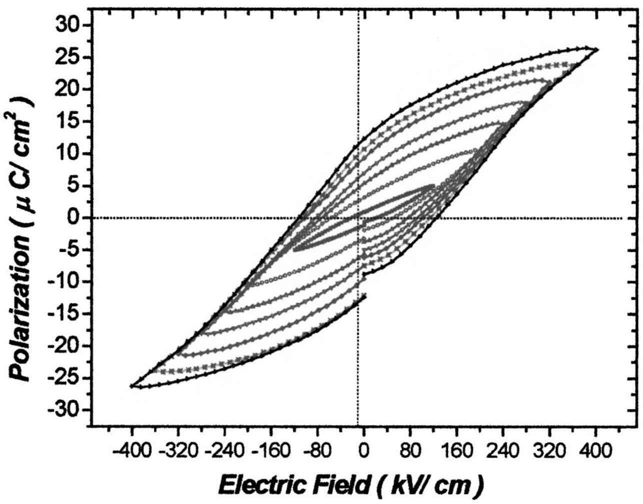

FIG. 3. The hysteresis loops for BT–SBTi thin film with different applied voltages.

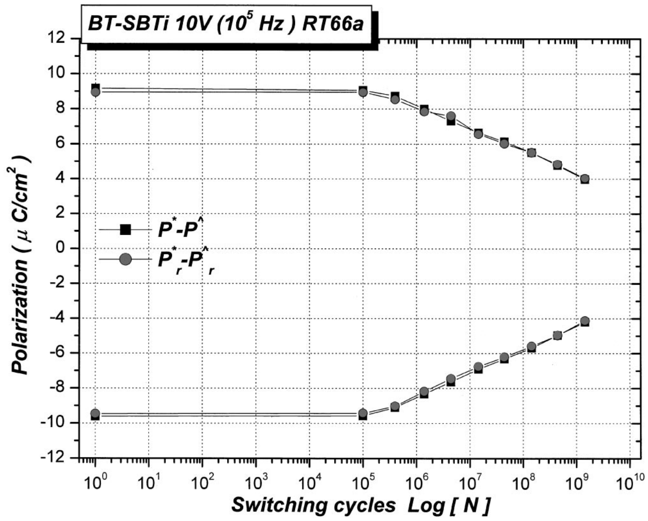

FIG. 5. The fatigue behavior with 10 V applied voltage 100 kHz for 350 nm BT–SBTi thin film annealed at 650 °C.

It is well known that La doped in BT has improved the fatigue properties of BT.[6] For improving the fatigue properties of BT–SBTi, the partial Bi element was substituted by the La element. The BLT–SBTi ceramic target and thin film were obtained by a method similar to the BT–SBTi. The XRD patterns indicate that the regular intergrowth structure spreads throughout the crystal and single phase BLT–SBTi was obtained. The crystal structure of intergrowth BLT–SBTi is made up of one half of the unit cell of both BLT ($m=3$) and SBTi ($m=4$). The perovskite blocks of BLT and SBTi are in turn sandwiched between $(Bi_2O_2)^{2+}$ layers, and the BO_6 octahedra in BLT–SBTi are all TiO_6. 1.25Bi and 0.75La ions occupy the A site of the BLT block, while two Bi ions and one Sr ion occupy the A site of the SBTi block. The surface morphology and the cross-sectional view of the BLT–SBTi thin film annealed at 700 °C showed no cracks on the surface and elliptical grains of length 100–150 nm, as shown in Fig. 6(a). A sharp boundary between the film and Pt electrode was also clearly seen in Fig. 6(b). Figure 7 shows a well defined hysteresis loops of 300 nm BLT–

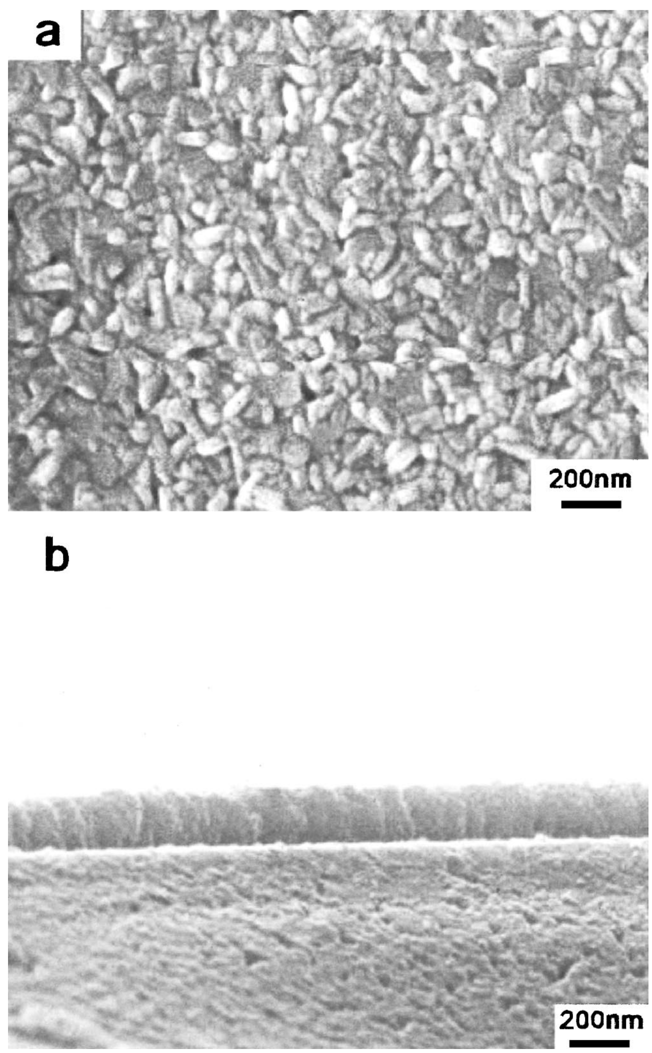

FIG. 6. The SEM images for BLT–SBTi thin film annealed at 700 °C: (a) surface morphology and (b) cross section of SEM micrograph.

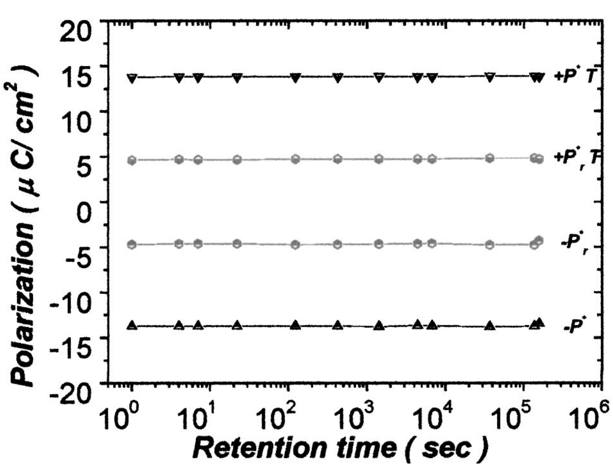

FIG. 4. The time dependence of retention properties over the range $1-10^5$ s for BT–SBTi thin film annealed at 650 °C.

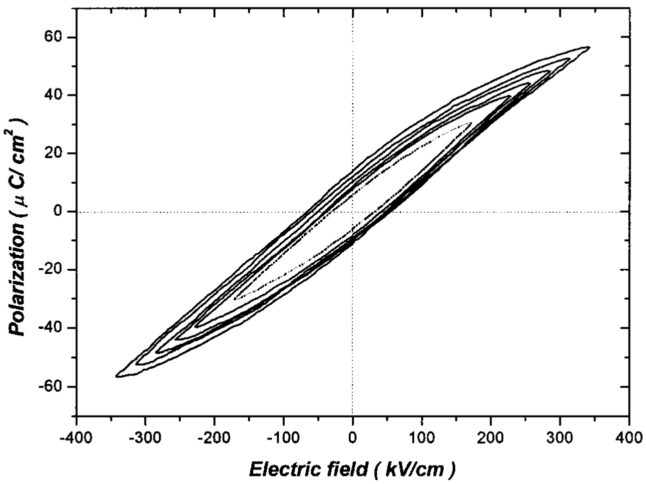

FIG. 7. The hysteresis loops for BLT–SBTi thin film with different applied voltages.

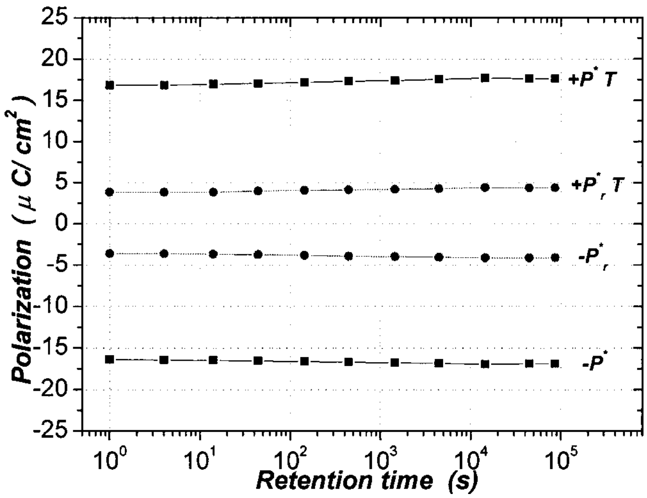

FIG. 9. The time dependence of retention properties over the range $1-10^5$ s for BLT–SBTi thin film annealed at 700 °C.

SBTi thin film with $Pr=13.5\ \mu C/cm^2$ at an applied field of 300 kV/cm.

The fatigue properties of BLT–SBTi films are shown in Fig. 8. The test pulses are 100 kHz bipolar square pulses with voltage amplitudes ranging from 5 V (170 kV/cm) to 9 V (300 kV/cm). The polarization values were normalized to their respective initial values. The polarization exhibits almost no change up to 10^{10} switching cycles at applied fields above 250 kV/cm (8 and 9 V), indicating that the BLT–SBTi thin films have good fatigue resistance. However, as the applied field decreases below 250 kV/cm, a 25% decrease in P_r was observed after 10^{10} switching cycles. The number of switching cycles at which the onset of fatigue or polarization decrease occurs depends on the applied voltage. The onset occurs at about 10^7 switching cycles at an applied voltage of 7 V (230 kV/cm), 10^6 switching cycles at 6 V (200 kV/cm), and 10^5 switching cycles at 5 V (170 kV/cm).

The dependence of the onset of polarization degradation on the applied field is quite similar to those of SBT thin film[14,15] and BLT thin film.[16] Shareef *et al.*[17] and Dimos *et al.*[18] have shown that the fatigue-free behavior in SBT thin film arises from the fact that field assisted domain unpinning occurs at least as rapidly as domain pinning. The fatigue properties in BLT–SBTi, SBT[14,15] and BLT[16] films exhibit a stronger field dependence than other ferroelectric films, which implies a deeper trap and more effective domain pinning. Wu *et al.*[16] pointed out that because of the volatility of Bi and the possible reduction of Ti^{4+} to Ti^{3+}, oxygen vacancies may be present in films. These oxygen vacancies may be driven to domain walls by the switching pulses; they are trapped there and serve to pin the domains. The strong interaction of the oxygen vacancies with the domain walls leads to effective domain pinning and relatively difficult unpinning, which leads to the strong field dependence of fatigue resistance. This is also the case for BLT–SBTi films.

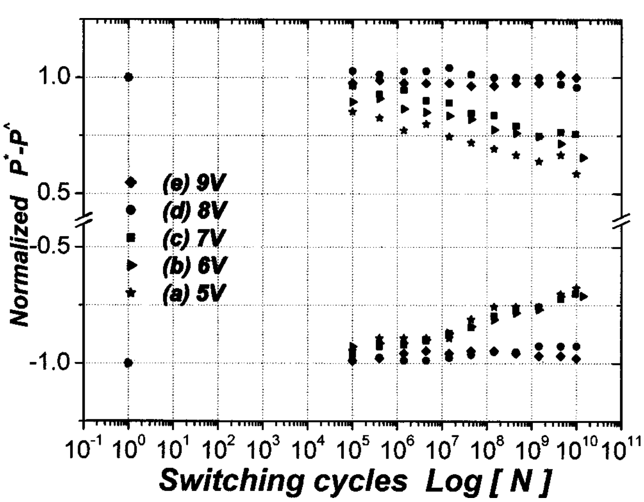

FIG. 8. Polarization degradation of 300 nm thick BLT–SBTi film at 10^5 Hz and 5 V (170 kV/cm); 6 V (200 kV/cm); 7 V (230 kV/cm); 8 V (270 kV/cm); and 9 V (300 kV/cm).

The retention characteristics of BLT–SBTi thin film annealed at 700 °C for 5 min over the range of $1-10^5$ s at 6 V indicated that the polarization decay showed good linearity when plotted against logarithmic retention time, as shown in Fig. 9. Compared to $SrBi_2Ta_2O_9$ thin film, the BLT–SBTi thin film has a larger P_r and lower annealing temperature; compared to PZT thin film, BLT–SBTi thin film on the Pt electrode is fatigue free up to 10^{10} switching cycles and there is no Pb toxicity problem. Therefore, BLT–SBTi film is a promising candidate for FeRAM applications.

There are several reports on the La-doped effect on ferroelectricity.[19–21] Park[6] reported that La-substituted bismuth titanate $Bi_{3.25}La_{0.75}Ti_3O_{12}$ is fatigue free with $P_r=12\ \mu C/cm^2$. Recently, Watanabe[11] reported the effect of con-substitution of La and V in $Bi_4Ti_3O_{12}$ thin films. They got fatigue-free $(Bi_{3.2}La_{0.8})(Ti_{2.97}V_{0.03})O_{12}$ thin film. As noted above La substitution (doped) has a large effect on the ferroelectric properties. However, the reason why the La doped can improve the fatigue properties of thin film is being researched. Chu *et al.*[22] used x-ray photoelectron spectroscopy and high resolution electron microscopy (HREM) to study the polycrystalline powder of $Bi_{4-x}La_xTi_3O_{12}$ (with $x=0$, 0.5, 0.75, 1, and 2). They found that there is an outermost Bi-rich region followed by a La-rich region. A HREM

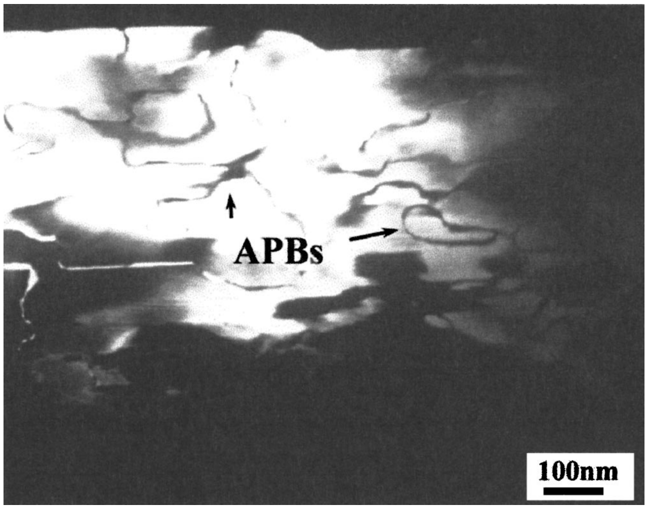

FIG. 10. Dark-field image obtained by using a superlattice diffraction spot of BLT–SBTi.

study on the La-0.75 sample confirms that there is some intergrowth defects with thickness of 5 nm appearing on the crystal edge, which is also observed in compounds with $x = 1.0$ and 2.0, but not in $x = 0$. They pointed out that the surface configurations of La-containing $Bi_4Ti_3O_{12}$ (BT) compounds should be considered as one of the fatigue-free factors. Park *et al.*[6] considered that the chemical stability of the perovskite layers against oxygen vacancies and self regulation to compensate for space charge of the $(Bi_2O_2)^{2+}$ layers are the causes of the fatigue-free factor in La-doped $Bi_4Ti_3O_{12}$. Recently, Ding *et al.* observed the domain structure in BLT[23] and SBT[24] by transmission electron microscope (TEM) and found that in the polarization reversals, polarization domains nucleate not only at the interface between electrode and ferroelectric capacitors but also at antiphase boundaries (APBs).[24] As we know, usually the fatigue occurs in PZT thin film with a metal electrode as the nucleation at the electrode interface is suppressed. The fatigue property of SBT will not depend solely on the electrode interface for the existence of the high density of APBs. They observed the existence of APBs in BLT[23] and SBT[24] but not in BT and proposed that it may be the reason for the fatigue-free factor in SBT and BLT, but not in BT. We have observed the domain structure by TEM and found the APBs in BLT–SBTi. Figure 10 is a dark-field image obtained using a superlattice diffraction spot of BLT–SBTi and shows the APBs clearly as noted by the arrow. The APBs could provide plenty of nucleation sites of polarization domains in the switching process, and even the nucleation of the polarization domains at the electrode interface is seriously suppressed. That may be one of the reasons for fatigue-free BLT–SBTi. For the origin of the fatigue-free factor in some Bi layered perovskites, it is a challenging topic for us. Why does the fatigue-free factor appear in SBT, BLT-0.75, BLTV, BLT-SBTi, etc. thin films, not in BT, BLT-0.75, BTV, BT-SBTi, etc. thin films.

CONCLUSION

The BT–SBTi and BLT–SBTi ferroelectric thin films have been fabricated by the PLD technique. They have intergrowth structure. The P_r is 12 and 13.5 $\mu C/cm^2$ in BT–SBTi and BLT–SBTi thin films respectively. Both of them show a defined hysteresis loop and good retention properties up to 10^5 s retained time. The BT–SBTi shows fatigue behavior, where more than 40% of P_r decrease was observed after switching cycles of 10^{10}, but no obvious degradation of P_r was observed up to 10^{10} switching cycles at an applied field above 250 kV/cm in BLT–SBTi film. The pinning of oxygen vacancies and field assisted domain unpinning lead to the strong field dependence of fatigue resistance. The chemical stability of perovskite layer again oxygen vacancies and APBs existence may be the main reason for fatigue-free BLT-SBTi thin film. Larger P_r, good retention, and fatigue-free properties demonstrate that BLT-SBTi thin film is a promising candidate for FeRAM applications.

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