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Aging behavior and recovery of polarization in $Sr_{0.8}Bi_{2.4}Ta_2O_9$ thin films

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Ferroelectric thin films of bismuth-containing layered perovskite $Sr_{0.8}Bi_{2.4}Ta_2O_9$ (SBT) have been prepared by both metalorganic decomposition (designated as MOD–SBT film) and magnetron sputtering (designated as sputtering-SBT film) processes. SBT thin films are well known to exhibit free-fatigue behavior with electrical field cycling. However, it was found that after the SBT films were applied with electrical field display, the polarization reduction with time was observed. The aging rate was related to microstructure, which in turn was dependent on the film processing. The sputtering-SBT films show a slower degradation rate than MOD–SBT films. The suppressed polarization can be near-completely recovered by applying either thermal treatment above 150 °C or electric-field cycling. There exists a minimum required thermal energy to restore the polarization. The easy recovery exhibited by SBT films in suppressed polarization reveals that a relatively weak domain pinning may exist between domain wall and electronic defects in SBT. The SBT shows little fatigue behavior during electric field cycling but exhibits an aging phenomenon after applied electric field. © *2000 American Institute of Physics.* [S0021-8979(00)04906-9]

INTRODUCTION

Ferroelectric memories offer several advantages over silicon-based memories such as faster write speeds and lower operating voltages.[1,2] In the past few years, $Pb(Zr, Ti)O_3$ (PZT) compositions have been widely studied and recognized to be highly promising for nonvolatile memory applications because of their excellent good ferroelectric properties and relatively low processing temperature. However, it was later found that PZT films for ferroelectric random access memory (FRAM) device applications still have several problems since it exhibits severe polarization fatigue during electric field cycling, particularly with a Pt electrode.[3,4]

Recently, alternative materials, belonging to the bismuth layered perovskite-like structure, show essentially no polarization fatigue with electric field cycling with a Pt electrode.[5] These materials have the general formula of $(Bi_2O_2)^{+2}(A_{m-}B_mO_{3m+1})^{2-}$, consisting of *m*-perovskite units sandwiched between bismuth oxide layers. (Here A and B are the two types of cations that enter the perovskite unit. A is Bi^{3+}, Ba^{2+}, Sr^{2+}, Pb^{2+}, or K^{1+}; B is Ti^{4+}, Nb^{5+}, Ta^{5+}, Mo^{6+}, or W^{6+}.)[6–8] Among these materials, ferroelectric thin films of $SrBi_2Nb_2O_9$, $SrBi_2Ta_2O_9$, and their solid solutions have been widely investigated for potential applications in high density nonvolatile FRAMS because of their excellent ferroelectric properties, characterized by free polarization fatigue and low coercive field.[5,9,10] According to Chen *et al.*'s report, the reason for good fatigue resistance of SBT or SBN films is due to higher ionic conductivity leading to easy recovery of defects.[11] However, in Dimos *et al.*'s investigation,[12] SBT thin films were revealed to exhibit significant polarization fatigue by electric-field cycling under broadband, optical illumination. Also the photoinduced fatigue was observed for $Pb(Zr, Ti)O_3$ thin-film capacitors with a $(La, Sr)CoO_3$ electrode.[13] Moreover, the fatigued sample under illumination can be fully rejuvenated by a dc saturating bias with light or electric-field cycling without light, which indicates an intrinsic, field-assisted recovery mechanism. Al-Shareef *et al.*[14] further suggests that the recovery of photoinduced fatigue of SBT films was due to a relatively weak domain pinning. These findings demonstrate that the relatively weak domain pinning plays a pretty important role in the fatigue behavior and recovery of SBT films.

Even though the fatigue phenomenon has received wide attention, aging behavior, i.e., polarization degradation with time is also a particular important reliability issue for FRAM devices. Furthermore, a similar effect was often observed in ferroelectric ceramics, especially for PZT[15,16] In this work, the polarization reduction of the ''free-fatigue'' SBT thin film with aging time at room temperature was observed. Moreover, we found that the polarization recovery of the aged sample was strongly related to both electric-field cycling and thermal treatment at a higher temperature. A detailed study and qualitative model was proposed to account for the unique aging behavior and subsequent polarization recovery in the free-fatigue SBT films.

II. EXPERIMENT

The $Sr_{0.8}Bi_{2.4}Ta_2O_9$ films were deposited on a $Pt(150\,nm)/Ti(20\,nm)/SiO_2(1\,\mu m)/Si(100)$ substrates by both metalorganic decomposition (designated as MOD–SBT film) and radio frequency magnetron sputtering (designated as sputtering-SBT film) techniques. The starting materials for the MOD process were bismuth 2-ethylhexanate $\{Bi[CH_3(CH_2)_3CH(C_2H_5)COO]_3\}$, strontium 2-ethylhexanate $\{Sr[CH_3(CH_2)_3CH(C_2H_5)COO]_2\}$, lead 2-ethylhexanate $\{Pb[CH_3(CH_2)_3CH(C_2H_5)COO]_2\}$, and tantalum ethoxide

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$[Ta(OC_2H_5)_5]$ with 2-ethylhexanoic acid as the solvent. The metalorganic precursors were mixed to form a solution with the compositions of $Sr_{0.8}Bi_{2.4}Ta_2O_9$. After the solutions were spin coated onto the substrate at a speed of 3000 rpm, the as-deposited film was dried on a hot plate at a temperature of about 150 °C to remove the solvent before the next coating was applied. A single coating generally gave a 0.14 μm crack-free film after firing. After the process was repeated three times, the films were pyrolyzed and crystallized at 800 °C temperatures for 30 min by directly placing the coated substrate into the tube furnace.

In the sputtering-SBT film, the SBT film was deposited on Pt by magnetron sputtering from the sintered $Sr_{0.8}Bi_{2.4}Ta_2O_9$ target. The films were prepared at a fixed power of 100 W. A constant chamber pressure of 20 mTorr was maintained by a mixture of argon and oxygen at a flow-rate ratio of 200/50. The details of the sputtering and annealing conditions of the SBT films were described in Ref. 17. The crystal structures of the films were analyzed using a Siemens D5000 x-ray diffraction (XRD) with Cu $K\alpha$ radiation and a Ni filter. The surface and cross-sectional morphologies of the films were investigated by a field-emission scanning electron microscope (FESEM, Hitachi S4000). The film thickness was measured by a Dektak surface profilometer. Patterned top Au electrodes through a shadow mask on an area of 8.0×10^{-4} cm^2 area were sputter deposited onto the SBT layers to define capacitors in order to perform electrical measurements. A ferroelectric testing system (RT-66A, Radiant Technologies Inc.) operating in the virtual-ground mode was used to obtain the remanent polarization (P_r)-coercive field (E_c) hysteresis characteristics and fatigue properties. After the films were applied at a voltage of 5 V for P_r-E_c measurement, the films were then aged at room temperature. The aging was interrupted by a certain time period to measure P_r-E_c on the same sample again. As the aged sample showed no apparent loss of remanent polarization with aging time, the thermal recovery was performed in a vacuum chamber at temperatures ranging from 75–450 °C for 2 min after the aged sample was loaded and the chamber was pumped down to ~20 mTorr. After the thermal treatment, the chamber was pumped down again while cooling down to room temperature. Fatigue tests for the aged films were also conducted with an applied voltage of 5 V at 1 MHz.

III. RESULTS

As the MOD–SBT films were annealed at 800 °C, the layered perovskite phase appears with a random orientation, as evidenced by the (115) and (200) reflections of the XRD pattern shown in Fig. 1(a). On the other hand, the XRD studies of sputtering-SBT films indicate that the films deposited at temperatures below 500 °C were amorphous and completely crystallized at 600 °C as shown in Fig. 1(b), in which a strong (115) reflection was observed. The polarization versus electrical field curves for both sputtering-SBT and MOD–SBT films were measured and shown in Fig. 2. The sputtering-SBT film has a higher remanent polarization than MOD–SBT film. The $2P_r$ values were 30.9 and 15.7 μC/cm^2 for the former and the latter under an applied voltage of 5 V, respectively. These excellent properties of sputtering-SBT films may be attributed to dense and larger-grain microstructure and unique crystal orientation as compared with those of MOD–SBT films. The SEM morphologies of sputtering-SBT films (Fig. 3) exhibit a dense structure and columnar microstructure. On the other hand, SEM observation in Fig. 4 shows the surface microstructure of MOD–SBT films composed of somewhat porous structure with rod-like grains. Furthermore, it was found that SEM cross-section morphology was composed of polycrystallites instead of columnar grains as in sputtering-SBT films.

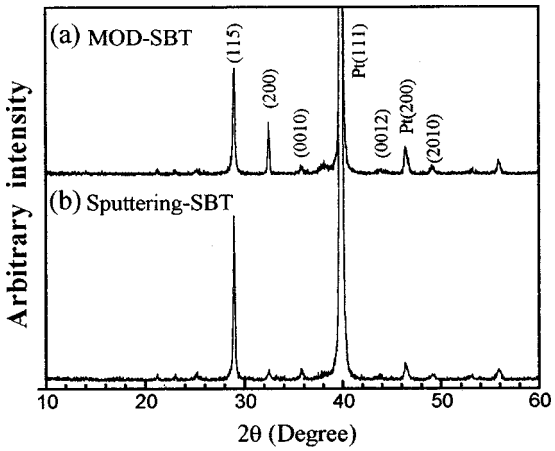

FIG. 1. XRD patterns of (a) sputtering-SBT and (b) MOD–SBT films.

The fatigue test was performed using a bipolar square wave of 5 V at 1 MHz. As shown in Fig. 5, no obvious fatigue was observed for sputtering-SBT films after the sample was switched up to 1×10^{10} cycles. However, for MOD–SBT films, a partial loss of $2P_r$ was observed after fatigue. The percentage of the remanent polarization after 10^{10} cycles lies around 86%. According to our previous report, it was found that the fatigue endurance of MOD–SBT films was somewhat influenced by the composition.[18] The Sr-stoichiometric $SrBi_{2.3}Ta_2O_9$ or $SrBi_2Ta_2O_9$ films show no any appreciable loss under the same applied voltage of 5 V after 10^9 cycles. However, a detectable degradation after fatigue was observed in the Sr-deficient $Sr_{0.8}Bi_{2.3}Ta_2O_9$ com-

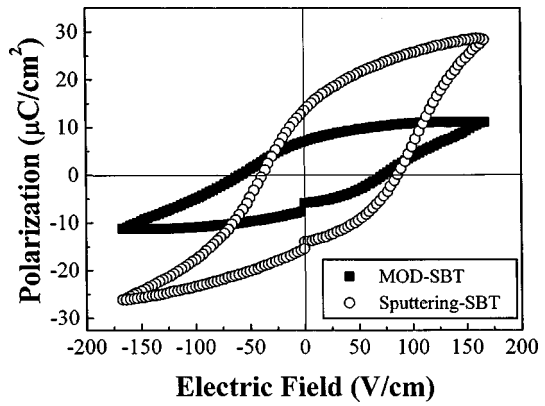

FIG. 2. SEM plan view and cross-section of sputtering-SBT films annealed at 600 °C.

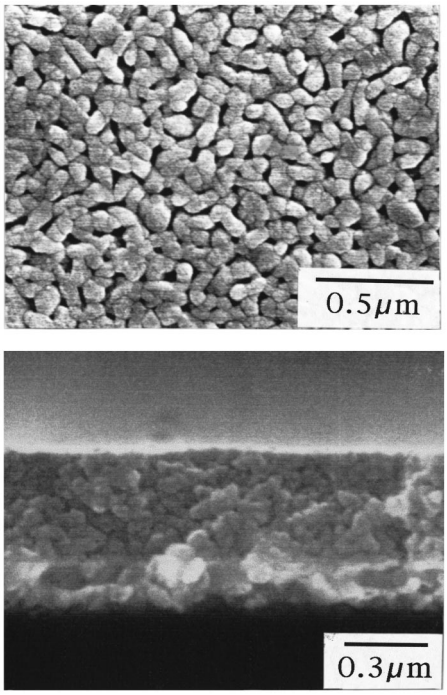

FIG. 3. SEM plan view and cross-section of MOD–SBT films annealed at 800 °C.

position. Similar phenomenon was also reported by Noguchi *et al.*[19] This observable fatigue behavior may be correlated with microstructure, crystal orientation and further, the substituting Bi for Sr vacancy.[18,20] The detailed discussion can be referred to Ref. 18.

As the SBT films were aged at 25 °C, Fig. 6 shows rapid polarization reduction with aging time after the films were

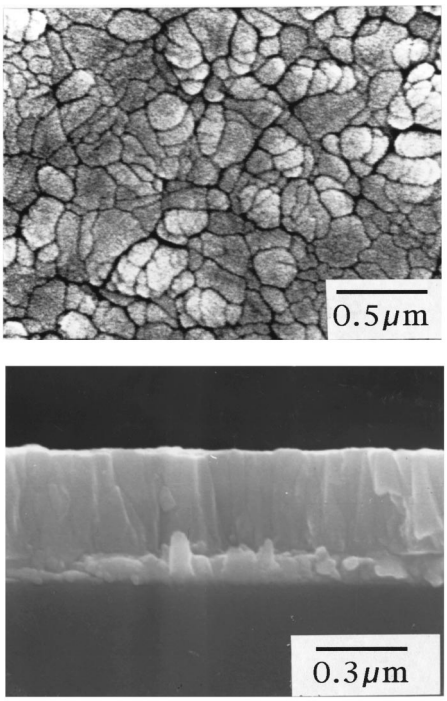

FIG. 4. $P-E$ hysteresis loops of both sputtering-SBT and MOD–SBT films under applied voltage of 5 V.

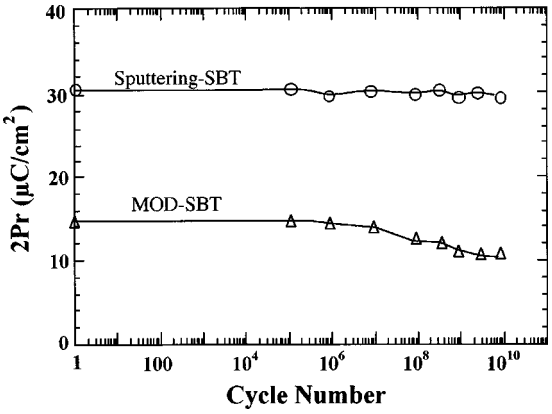

FIG. 5. Fatigue behavior of both sputtering-SBT and MOD–SBT films with an applied voltage of 5 V.

applied with a voltage of 5 V. The polarization reduction rate in MOD–SBT films was apparently faster than sputtering-SBT films. In the case of MOD films, the $2P_r$ value of MOD–SBT films rapidly degrades and decreases from 15.7 to 6.4 μC/cm^2 after 5 h aging. The average remanent polarization dropped by nearly 59%. A longer aging time period leads to substantially slight and additional continuous suppression of the switchable polarization, i.e., ~10% more loss of $2P_r$ for 25 h (67% loss of initial $2P_r$). In the other case of sputtering-SBT films, similar effects were also observed as the films were subjected to the same testing sequence. However, the degradation rate in sputtering-SBT films was much slower than MOD–SBT films. A slighter loss of $2P_r$ (~4%) was found in the sputtering-SBT film if the same aging time period of 2 h was evaluated. The $2P_r$ value gradually decreased from 30.9 to 6.9 μC/cm^2 after the sample was aged ~1440 h at room temperature. In this experiment, it was found that as the films were applied at a lower voltage such as 3 V, the reduction rate in remanent polarization during aging was somewhat slower than that at 5 V (not shown here).

However, interestingly, a rapid heating of the aged sputtering-SBT films in a vacuum at 450 °C for 2 min results in substantial recovery of the switchable polarization as shown in Fig. 7. In this case, a roughly of 90% of the initial

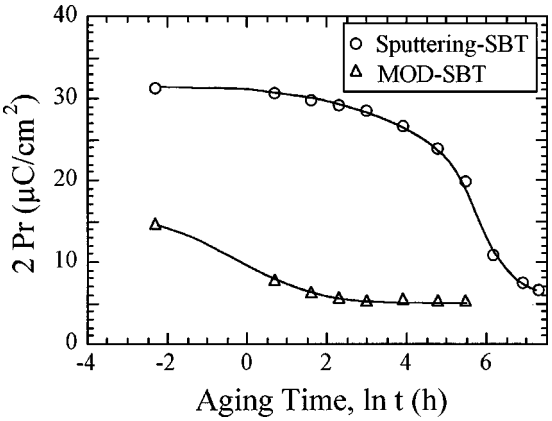

FIG. 6. Degradation of polarization with aging time for sputtering-SBT and MOD–SBT films after applied electric filed and then aged at 25 °C.

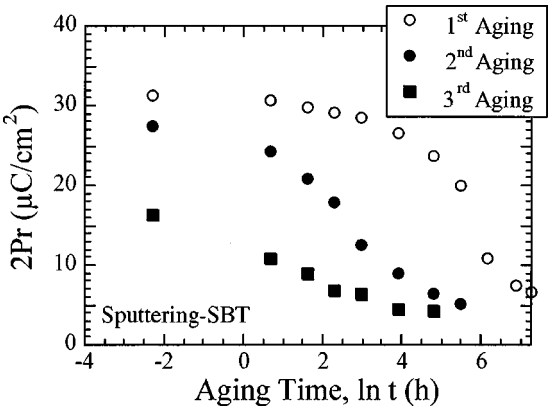

FIG. 7. Repeated aging and thermal treatment of sputtering-SBT films.

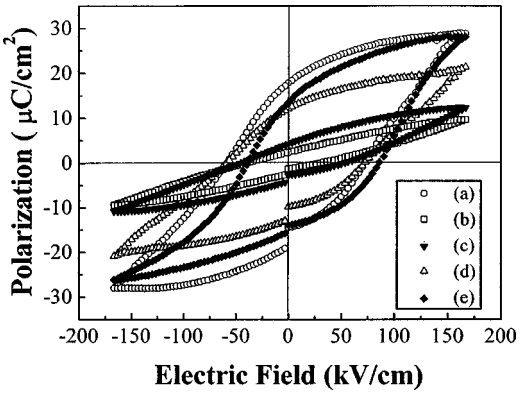

FIG. 9. Hysteresis loops of Au sputtering-SBT Pt films (a) before aging, (b) after aged for 2 months and (c) 75, (d) 150, and (e) 450 °C thermal treatment of aged samples.

switchable polarization is recovered. However, a second aging behavior of the recovered film was observed once again but the degradation rate of aged samples in the second run is faster than the first. It only took ~2 weeks to loss most of switchable polarization in the 2nd aging. If the aging cycling was repeated (3rd aging), the smaller the restored remanent polarization and the shorter the near-complete loss. Similar phenomena were also observed but the cycling process of aging to recovering only could be performed twice in MOD–SBT films (not shown here).

Moreover, as the aged sample was further applied with electric-field cycling, the $2P_r$ increases instead of decreases with cycling numbers. As shown in Fig. 8, the magnitude of $2P_r$ reaches 22.9 μC/cm^2 after 10^{10} cycles at an applied voltage of 5 V when the aged sputtering-SBT films were subjected to electric-field cycling. Similarly, for MOD–SBT films aged for 240 h, the $2P_r$ value increased from 4.7 to 9.1 μC/cm^2 after 10^{10} cycles (not shown here). The recovered percentage of the $2P_r$ value was around 63%–75% depending on the sample condition.

Alternatively, as observed in Fig. 9, a thermal rapid heat treatment at 150 °C was applied on the aged SBT films, roughly 74% of the initial switchable polarization of the aged SBT films was recovered after a thermal rapid heat treatment at 150 °C was applied. Furthermore, we found that the recovery was strongly correlated with temperatures used. A higher temperature such as 450 °C, which is higher the T_c (~320 °C) of SBT,[6,21] was employed to heat the aged films, a higher recovering percentage of the initial switchable polarization was detected as compared to that at 150 °C. Meanwhile, a comparable $2P_r$ recovery with the film at 450 °C was also obtained for the case of the film heated at 275 °C. However, at a slightly lower temperature, i.e., 75 °C, only a limited recovery was observed. The $2P_r$ value increases from 6.4 to 9.7 μC/cm^2.

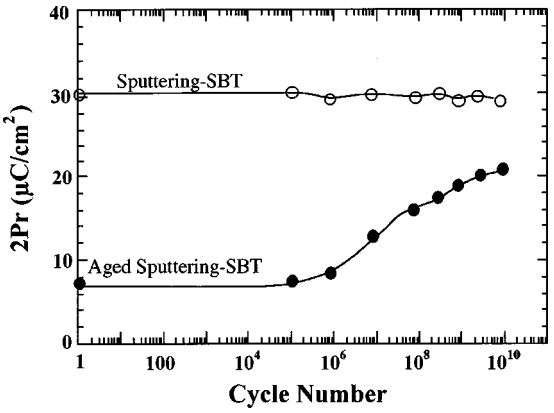

FIG. 8. The effect of electric-field cycling on the change of $2P_r$ for origin and aged sputtering-SBT films.

IV. DISCUSSION

The aging behavior was a common phenomenon and widely observed in ferroelectric ceramics.[15] Mason[22] suggested that the aging effect is a reduction of effective polarization produced by the domain-wall motion. The rearrangement of ferroelectric domains with time is considered to be the causes of aging phenomena.[23] As shown in Fig. 5, the polarization reduction with aging time occurs in SBT films after the films were applied with electric field. The occurrence of aging phenomenon was also dependent on the magnitude of applied field. While a larger electric field than the switching threshold was applied most of the domains will be switched and aligned in the same direction. An internal residual stress will be induced due to the electric field. However, as the applied electric field was removed, the polarization reduction with time was observed. Different mechanisms have been proposed for aging effects. Bradt and Ansell[24] assumed that the aging phenomenon results from the relief of the residual stress due to domain switching arising from electric and elastic fields. According to the report by Al-Shareef *et al.* SBT film exhibits a relatively weak domain wall pinning.[14] Consequently, as the applied electric field was removed, some of the domains tend to reorient in a variety of directions and attempt to move into lower energy configurations, which lead to the decrease of switchable or remanent polarization with time as one can see in Fig. 6. Therefore, it stands to reason that a larger external field or energy was required to switch these domains. The magnitude of induced strain due to electric field was dependent on the internal residual stress, which in turn was closely related to microstructure. As observed in Fig. 3, the sputtering-SBT

film, having columnar and dense structure, facilitates the domain switching. Therefore, the slower polarization degradation was observed as compared to that in MOD–SBT film, which is composed of loose and porous structure.

The aging recovery of SBT films can repeat many cycles by thermal treatment, as shown in Fig. 7, until the polarization switching completely diminishes at very short time which was probably correlated with the characterization of a relatively weak domain wall pinning in SBT film. It has been reported that the H^+ ions and electrons produced by the dissociative adsorption of the hydrogen molecules on the Pt surface play critical roles in degrading the ferroelectric properties of SBT and PZT thin films.[21,25–26] The P_r-induced internal electric field makes the H^+ ions and electrons form local space charges which pin the domains. There are two major factors, which in turn affect the aging behavior and recovery phenomenon of polarization in our case. One is the internal residual stress caused by either domain reorientation during applied electric field or space charge due to water molecules or H^+ ions from environment atmosphere. The other is the unique characteristic of relatively weak domain wall pinning. For the samples without applying thermal treatment or electric-field cycling, the release of internal residual stress plays the main role in aging behavior and the decrease of P_r.

When the heating temperatures are lower than T_c ($\sim$320 °C), the water molecules or hydrogen ions adsorpted on the electrode interfaces or domain boundaries are easily taken off in a vacuum chamber. Furthermore, the thermal treatment contributes domains more energy and therefore, the probability of overcoming the potential barrier to release the internal stress is increased. Consequently, the recovery is enhanced with increasing temperature and thus, almost 70%–90% recovery of initial polarization is obtained. When the heating temperature increases to over T_c, the uniform redistribution of electrons and effective removal of water molecules, as similar to those below T_c, continually occur, causing the relief of the internal electric field. Consequently, a little higher recovering percentage of the initial switchable polarization was obtained at 450 °C as compared to that at 275 °C. These results again demonstrate that the domain boundaries are weakly pinned in SBT and easily unpinned by thermal energy.

On the other hand, besides thermal treatment, the easy recovery of domain switching can be also further demonstrated from the electric cycling fatigue of the aged sample. As shown in Fig. 8, the magnitude of $2P_r$ increases when the aged SBT was subjected to electric field cycling at 5 V. A roughly 76% of the initial switchable polarization can be recovered after 10^{10} cycles. This behavior can be qualitatively explained based on model of self-recovery mechanism of SBT proposed by Al-Shareef *et al.* reporting that significant polarization suppression may be induced in SBT films using optical illumination but the optically fatigued SBT films can be rejuvenated using electric field cycling.[14]

Furthermore, in our case, either thermal treatment or electric-field cycling of the aged SBT films recovered a 76%–95% of the suppressed polarization. Also, in Fig. 9, we found the recovery percentage of the initial switchable polarization was related to the temperature used in the thermal treatment. The higher thermal treating temperature often results in higher recovery rate and recovery switchable polarization. However, when the temperature used was lower than 150 °C, the increment of recovery polarization is very small. This result may suggest that there exist a minimum threshold thermal energy for the unpinning of domain wall.

The weak domain wall pining in SBT films is postulated to result from smaller magnitude of ferroelectric polarization or relatively low oxygen vacancy concentration in the perovskite sublattice. However, we found a larger leakage current along with a larger loss tangent in the SBT films. That is pretty consistent with the investigation that the bulk ionic conductivities of SBT or SBN are much higher than those of the perovskite ferroelectric ceramics, e.g., PZT.[11] Warren *et al.*[27] reported that electrical fatigue is primarily due to electronic charge trapping by showing that application of a saturating bias with band gap light restored nearly 90% of the switchable polarization of electrically fatigued Pt/PZT/Pt capacitor. Therefore, the recovering behavior at either thermal treatment or electric-field cycling allow us to believe that the good fatigue resistance of SBT or SBN-based films is due to relative weak domain wall pinning which exists in between domain wall and electronic defects.

V. CONCLUSIONS

In this investigation, we observed that even the free-fatigue SBT films show aging phenomenon as similar to bulk ferroelectric materials, i.e., PZT. The aging raised from the relief of residual internal stress and domain wall reconfiguration caused by electric field when no thermal treatment is applied. The polarization degradation rate during aging was dependent on the microstructure and orientation of the films. A sputtering film with oriented and columnar structure shows a slower degradation rate. On the contrary, a MOD film with loose and small-grain structure presents a higher degradation rate. However, the electrically aged SBT films can be rejuvenated by either thermal treatment above 150 °C or electric-field cycling after 10^{10} cycles. A nearly 75%–90% of the initial switchable polarization can be restored during these processes. These might suggest that the domain wall energy to pin the electronic defects be easily balanced by the electric-field cycling or thermal treatment due to a weak domain wall pinning.

ACKNOWLEDGMENT

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