

February 2001

# Polarization retention in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films investigated at nanoscale

Alexei Gruverman

University of Nebraska-Lincoln, agruverman2@unl.edu

M. Tanaka

Core Technology Development Center, Sony Corporation, 4-14-1 Asahi-cho, Atsugi, Kanagawa 243-0014, Japan

Follow this and additional works at: <http://digitalcommons.unl.edu/physicsgruverman>



Part of the [Physics Commons](#)

---

Gruverman, Alexei and Tanaka, M., "Polarization retention in  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  thin films investigated at nanoscale" (2001). *Alexei Gruverman Publications*. 25.

<http://digitalcommons.unl.edu/physicsgruverman/25>

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Alexei Gruverman Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

# Polarization retention in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films investigated at nanoscale

A. Gruverman<sup>a)</sup>

*Environment and Analysis Technology Department, Sony Corporation, 134 Godo-cho, Hodogaya-ku, Yokohama 240-0005, Japan*

M. Tanaka

*Core Technology Development Center, Sony Corporation, 4-14-1 Asahi-cho, Atsugi, Kanagawa 243-0014, Japan*

(Received 5 May 2000; accepted for publication 29 October 2000)

The nanoscale mechanism of retention behavior in  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) thin films has been investigated by means of piezoresponse scanning force microscopy. It has been found that SBT films with Pt electrodes (SBT/Pt) exhibit a strong dependence of retention characteristics upon domain polarity: positive domains with the polarization vector pointing to the bottom electrode exhibit excellent stability in sharp contrast to the negative domains which show poor retention. The backswitching of the negative domains proceeds via sidewise motion of the domain walls and shows a log-time dependence. The strong effect of the poling voltage parameters (duration and amplitude) and the previous switching pattern on domain retention behavior is reported. On the other hand, in SBT films with  $\text{IrO}_2$  electrodes (SBT/ $\text{IrO}_2$ ), the written domains of both polarities show no sign of relaxation to the original state irrespective of the parameters of the poling voltage. The difference in retention behavior of opposite domains in SBT/Pt films is explained by the presence of the polarization-independent built-in bias at the SBT/Pt interface pointing to the bottom electrode. This built-in bias triggers the backswitching of a negative domain by generating positive nuclei at the interface. The forward growth of the nuclei is further governed by the field of the space charge which screens the original polarization state. The symmetric retention behavior and the stability of domain in SBT films with  $\text{IrO}_2$  electrodes are attributed to the inhibition of the nucleation process at the SBT/ $\text{IrO}_2$  interface. © 2001 American Institute of Physics. [DOI: 10.1063/1.1334938]

## I. INTRODUCTION

Ferroelectric switching and readout of the resulting polarization state are basic operations in ferroelectric memory devices.<sup>1</sup> The ability of ferroelectric films to maintain their polarization in the absence of external voltage provides the unique nonvolatility of ferroelectric memories. However, retention in ferroelectric capacitors is affected by a degradation effect which manifests itself in the spontaneous reversal of polarization, leading to a progressive loss of stored data. It has been proposed that retention failure in thin ferroelectric films, which has been the subject of extensive research, is largely determined by the depolarizing fields resulting from incomplete compensation of the polarization charges at the film–electrode interface.<sup>2–6</sup> Recently, significant progress made in the application of scanning force microscopy (SFM) to the characterization of ferroelectric materials has provided a unique opportunity to obtain microscopic information on degradation processes in ferroelectric thin films by direct observation of their domain structures.<sup>7–17</sup> However, reports on the retention properties observed using SFM-based methods have been inconsistent. For example, Hidaka *et al.*<sup>9</sup> reported a retention time of about 70 years for 90–110 nm domains formed in  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) thin films. On the other hand, Gruverman *et al.*<sup>7,8</sup> observed retention loss in 200 nm size

grains of PZT films within the time range of several days. There is also no consensus on the time dependence of retention loss. While some groups have reported a log linear time dependent decay of polarization, suggesting a broad distribution of relaxation times,<sup>6,14</sup> other groups have deduced stretched exponential retention behavior, suggesting a random walk type mechanism of retention loss in PZT films.<sup>8</sup> Other studies indicate that retention characteristics vary widely depending on various parameters such as film thickness, domain size, poling time, and voltage. Application of ferroelectric films to memory devices would seem to require a better understanding of the mechanism of retention loss and a detailed investigation of this effect at the nanoscale level.

The aim of this article is to investigate the nanoscale retention behavior of ferroelectric  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) thin films. One of the advantages of these films compared to films of the PZT family is their fatigue-free behavior.<sup>18</sup> However, their retention properties, which are closely related to the performance of memory devices, have been studied less.<sup>19–24</sup> In this article, we focus on investigation of polarization decay dynamics by means of SFM and on the effect of the switching pulse parameters, switching prehistory, and domain polarity on polarization retention. It will be shown how a particular bottom electrode material affects film retentivity. A model will be proposed to account for the observed retention behavior of SBT films.

<sup>a)</sup>Present address: Department of Materials Science and Engineering, North Carolina State University, Box 7920, Raleigh, NC 27695; electronic mail: alexei\_gruverman@ncsu.edu

## II. EXPERIMENT

In a typical retention experiment, a test capacitor is written in a polarization state and left in that state for a fixed period of time, after which the polarization remaining in the capacitor is measured. From a practical point of view, the degree of retention of the switched polarization should be known for up to 10 years. Obviously, experiments of such duration are not practical to implement. Retention properties are normally measured in the range of up to  $10^6$  s with subsequent extrapolation of the obtained data. Most SFM retention studies, except recent work by Ganpule *et al.*,<sup>12</sup> Hong *et al.*,<sup>16</sup> and Alexe *et al.*<sup>17</sup> were carried out using films without top electrodes. Retention measurements using SFM involve nanoscale polarization reversal (poling) by applying dc voltage pulses through the conductive probing tip and subsequent observation of the domain structure and examination of its evolution using the same tip. This approach allows not only direct study of the retention loss mechanism at the nanoscale level but also accelerated retention measurements. Retention loss is usually attributed to the presence of an internal electric bias which supports a given polarization state opposing the antiparallel one. The tip/film/electrode heterostructure gives rise to exaggerated asymmetry of the boundary conditions at the top and bottom interfaces and, therefore, by producing a stronger internal bias, leads to poor retention. Thus, the decay of a certain polarization direction in the film without a top electrode is significantly accelerated and SFM retention measurements can be made within a reasonable time frame. Also, this approach allows better understanding of the film/electrode interface effect on domain retention behavior.

Domain imaging was carried out using the SFM piezoresponse mode which is described in detail elsewhere.<sup>7</sup> Briefly, this imaging method is based on the detection of the piezoelectric vibration of the ferroelectric film excited by an external ac voltage  $V$  applied through the SFM tip. The deflection signal from the cantilever is detected by a lock-in amplifier. The amplitude of the first harmonic signal  $I_{pr}$  (piezoresponse) is coupled to the normal component of the polarization, expressed by

$$I_{pr} = k d_{33} V \cos \theta, \quad (1)$$

$$d_{33} = 2 Q_{11} \epsilon \epsilon_0 P, \quad (2)$$

where  $k$  is a calibration constant determined by the sensitivity of the optical detector of the microscope,  $d_{33}$  is the piezoelectric coefficient,  $Q_{11}$  is the electrostriction coefficient which only weakly depends on external parameters,<sup>25</sup> and  $\epsilon$  is the dielectric constant. The polarization direction can be determined from the phase difference  $\cos \phi$  between the piezoresponse signal and the modulation (imaging) voltage. In a piezoresponse image, domains of opposite polarity will be distinguished by different contrast.

In this study, a commercial force microscope Autoprobe CP (Park Scientific Instruments) was used. The external dc or ac voltage was applied to a standard gold coated  $\text{Si}_3\text{N}_4$  cantilever with a spring constant of 0.1 N/m and a resonant frequency of 34 kHz. The probing tip with an apex curvature radius of about 20 nm was in mechanical contact with the

film surface during the measurements (the repulsive force regime). The domains were imaged by scanning the film surface while applying a 3.5 V, 10 kHz ac voltage to the tip. We confirmed that the imaging process had a minimal effect on the domain structure; this was documented in our earlier publication.<sup>26</sup> Repeated imaging of as-grown domains showed that there was no change in the domain patterns due to the imaging process. Also, we did not observe any strong effect of a number of images taken during the retention loss process on the domain retention time.

A topographic image of the film surface was taken simultaneously with the domain image. At a scan rate of 1 Hz, it took about 4 min to acquire one pair of images. However in some cases, this time could be reduced to 2 or 1 min by obtaining only part of the image containing the area of interest. The time required for image acquisition determined the time resolution for retention measurements. For retention studies, local polarization reversal was induced by applying a voltage pulse of certain polarity through the probing tip positioned at the center of a single-domain region. Subsequently, the evolution of the domain structure was monitored by acquiring piezoresponse images of the poled area at different time intervals.<sup>8,27</sup> The retention behavior was determined by measuring the time dependence of the fraction of the area retaining the switched polarization, taking into account the magnitude of the piezoresponse signal within the written domain. For this, the recorded patterns were analyzed using the ULTIMAGE 2.5.1 image processing program.<sup>28</sup> This program allowed quantitative evaluation of the area of domains of any shape, taking into account variations in the domain contrast from dark to white on a 256 level gray scale. This approach allowed us to obtain quantitative information on the dynamics of polarization decay at the nanoscale level.

The SBT samples used in this study were 140-nm-thick chemical vapor deposition (CVD) grown films which were deposited at 250–350 °C followed by postannealing for 1 h at 700 °C in oxygen atmosphere. Two types of bottom electrodes were used in our measurements, Ir (120 nm) and Pt (180 nm) electrodes sputtered on silicon wafers with  $\text{TiO}_2$  (25 nm)/ $\text{SiO}_2$  (300 nm) layers. Auger electron spectroscopy of the SBT films on the Ir electrode showed the presence of a 25-nm-thick  $\text{IrO}_2$  layer at the SBT/Ir interface after annealing. Details of the film preparation are given elsewhere.<sup>29</sup> Ferroelectric testing of the samples gave the following values of remanent polarization  $P_r$  and coercive voltage  $V_c$  for an applied voltage of 5 V:  $P_r = 10.2 \mu\text{C}/\text{cm}^2$  and  $V_c = 0.68$  V for the SBT/Pt film;  $P_r = 6.6 \mu\text{C}/\text{cm}^2$  and  $V_c = 0.85$  V for the SBT/ $\text{IrO}_2$  film. It has been reported that SBT capacitors with Pt electrodes exhibit good retention when switched by a voltage higher than 4.5 V.<sup>23,24</sup> On the other hand, Amanuma and Kunio<sup>19</sup> observed poor retention in similar capacitors at a writing voltage of 1 V.

## III. RESULTS

Figure 1 shows the simultaneously acquired topographic and piezoresponse images of the SBT/Pt sample. The bright and dark areas seen in the piezoresponse image represent regions with opposite  $d_{33}$  piezoelectric constants and antipar-

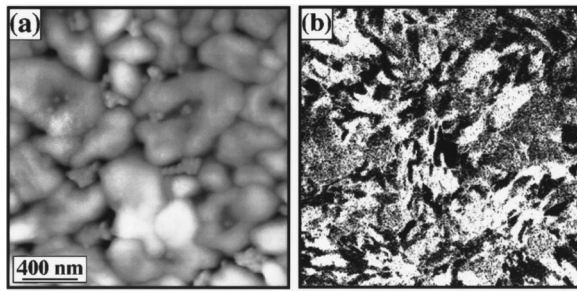


FIG. 1. Simultaneously obtained (a) topographic and (b) piezoresponse images of the  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  film on the Pt electrode. White and black regions in the piezoresponse image correspond to negative and positive domains, respectively.

allel polarization vectors. Cross-sectional analysis revealed that the width of the boundary between the dark and bright areas, which can be interpreted as a  $180^\circ$  domain wall, was in the range of 8–14 nm. It should be emphasized that these numbers reflect only the thickness of the “visible” domain wall, which is determined by the experimental conditions, not the real physical thickness of the  $180^\circ$  domain wall which could be much smaller (of the order of several unit cells). The measured thickness value, which is close to the resolution limit of our SFM piezoresponse system, led us to conclude that these boundaries are perpendicular to the film surface and separate the antiparallel domains with polarization vectors normal to the film surface. This conclusion is supported by quantitative SFM characterization of single grains in Bi-layered perovskite films.<sup>26,30</sup> By monitoring the phase of the piezoresponse signal it was determined that the dark regions in Fig. 1(b) represent domains with the polarization vector oriented toward the bottom electrode (hereafter designated “positive” domains), while the bright regions correspond to domains oriented upward (“negative” domains). According to our earlier SFM data, the gray tone in the piezoresponse can be attributed to the crystallographic orientation of the grains.<sup>26,31</sup> Note that the secondary nonferroelectric phases of SBT which usually exhibit very different morphology could also cause a gray tone in the piezoresponse image [for example, the small inclusions in the center part in Fig. 1(a) exhibit a gray tone in Fig. 1(b)].

### A. Retention loss dynamics

For retention measurements, single grains about 200–400 nm in size which exhibit a sharp as-grown domain contrast were chosen. A topographic image of the SBT/Pt sample in Fig. 2(a) shows two grains, mostly in a positive polarization state (oriented downward) which was deduced from the piezoresponse image in Fig. 2(b). Application of a switching (poling) voltage pulse of  $-6$  V, 5 s to the left grain resulted in the formation of a negative domain about 180 nm in size, seen as a bright spot in the center of the grain [Fig. 2(c)]. Figures 2(d)–2(f) illustrate the process of retention loss which appears as a gradual decrease in the size of the written domain due to spontaneous backswitching. As no significant change in the magnitude of the piezoresponse signal within the domain was detected, it can be stated that the backswitching process proceeds mainly through the sidewise

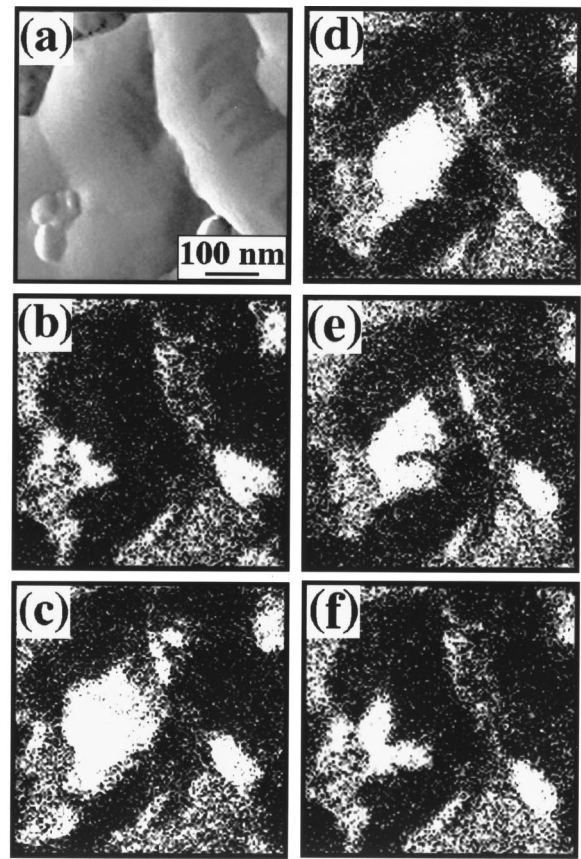


FIG. 2. Retention loss observed in the SBT/Pt film: (a) topographic image; (b) as-grown domain structure; (c) domain structure approximately 1 min after dc poling ( $-6$  V; 5 s); (d)–(f) domain structures appearing after the removal of the dc bias and acquired at different time intervals: 5 min after poling; 20 min after poling; 40 min after poling, respectively.

motion of the domain walls. It should be noted that the thickness of the domain walls of the shrinking domain ranges from 19 to 36 nm, which is larger than the value measured for the walls of stable domains [Fig. 1(b)]. This effect, which reflects the basic mechanism of polarization decay, is caused by the disparity between the scanning rate during image acquisition and the velocity of the moving domain wall. From a quantitative analysis of the domain images it can be inferred that during the backswitching process the wall speed changes. Very approximate estimations give values from 1.5 nm/s at the initial stage of decay to 0.06 nm/s at the end of this process.

Figure 3 shows the time dependence of the normalized retained polarization  $P(t)$  with respect to the initial polarization  $P_0$  for different poling times. The retained polarization  $P(t)$  shows a log-time dependence:

$$P(t) = P_0 - m \log(t/t_0), \quad (3)$$

where  $m$  can be interpreted as a decay rate.<sup>6</sup> The log-time dependence suggests a broad distribution of relaxation times in SBT films even at the nanoscale level. Note that the shape of the shrinking domain becomes irregular due to the spatial variation in the wall velocity. It should be stressed, however, that the accuracy of SFM measurements for fast polarization decay (e.g., less than 15 min) is not sufficient to determine a true fitting.

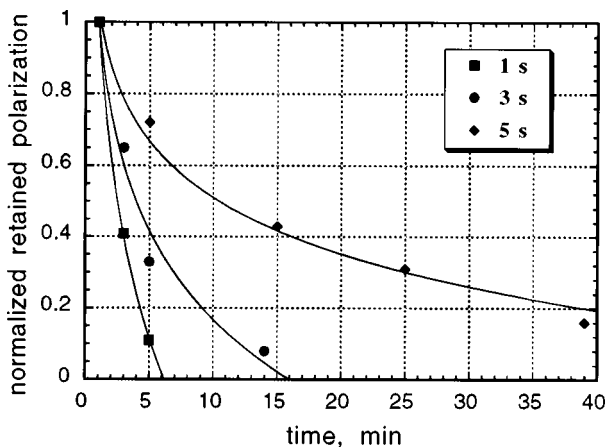


FIG. 3. Dynamics of retention loss in the SBT/Pt film for different poling times. The poling voltage is  $-6$  V.

**B. Effect of switching pulse parameters**

As can be seen in Fig. 3, there is a clear effect of the switching pulse width (poling time) on polarization decay which manifests itself in the better retention with an increase in the poling time. Domains written with  $-6$  V voltage pulses shorter than 10 s in width disappeared with time, while domains written with voltage pulses of the same amplitude as their width ranging from 10 to 30 s exhibited only partial decay before reaching equilibrium. Application of switching pulses longer than 30 s resulted in stable domains which showed no or very slight decay when imaged 6 days after poling. Correspondingly, the size of the written domain depends essentially on the width of the switching pulse, an effect reported previously for PZT films and barium titanate crystals.<sup>7,32</sup> Figure 4 shows the size of written domains and their retention time plotted as functions of the poling time. It can be seen that, while the domain size approaches the saturation value, the retention time increases exponentially. This retention behavior, which cannot be explained simply in terms of domain size dependence, can be attributed to the charge redistribution during poling and will be discussed later.

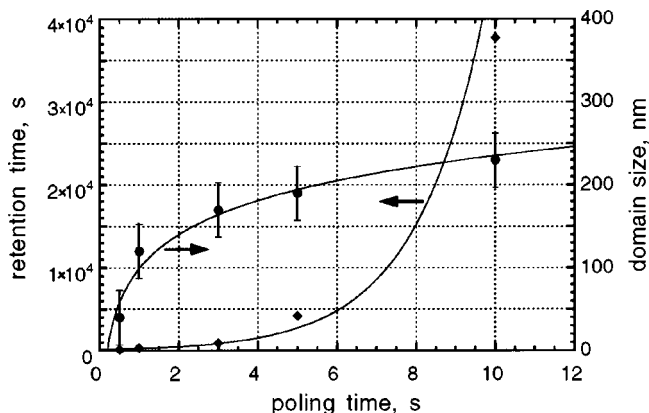


FIG. 4. Size of written domains in the SBT/Pt film and corresponding retention times plotted as functions of the poling time. The poling voltage is  $-6$  V.

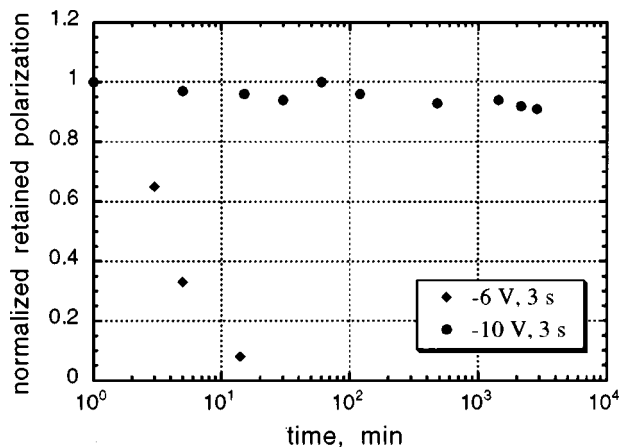


FIG. 5. Effect of the poling voltage on domain stability in the SBT/Pt film. The poling time is 3 s.

There are indications that in SBT/Pt films small grains ( $<200$  nm) tend to retain polarization better than large grains, although no systematic measurements have been performed. This effect could be similar to that observed previously in PZT thin films where it was found that grain boundaries stabilize the switched polarization state.<sup>7,33</sup> However, further studies are necessary to distinguish the effect of the grain boundaries from the effect of domain boundaries. In this sense, measurements of retention behavior of SBT films as a function of the average grain size would be very important.

An increase in the switching pulse amplitude also leads to the enhanced stability of negative domains as can be seen in Fig. 5. A domain produced by a  $(-6$  V; 3 s) voltage pulse disappeared within 15 min. At the same time, switching by a  $(-10$  V; 3 s) voltage pulse produced a fairly stable domain up to 48 h of retention. These results are consistent with the data on the macroscopic retention properties of Pt/SBT/Pt capacitors which exhibited excellent retention when switched by high voltage pulses and poor retention in the low-voltage regime.<sup>19,23,24</sup>

**C. Effect of switching prehistory**

If the space charges, which screen the polarization field, plays an important role in retention behavior, then their redistribution during repeated switching should lead to a change in the polarization decay dynamics. We have carried out experiments to determine the effects of the previous switching on domain retention. Experiments were performed by applying several switching pulses to the same site on the film surface, with subsequent examination of domain decay after each pulse. Generally, the effect of switching prehistory can be summarized as follows: the size of the written domain and its retention increase with each switching pulse. Figure 6 illustrates this trend. It can be seen in Fig. 6 that a domain formed by the initial switching pulse ( $-6$  V; 1 s) is much smaller and less stable than the domain formed at the same site by the second but identical pulse: the former domain of 60 nm disappeared within 6 min, while the latter domain of

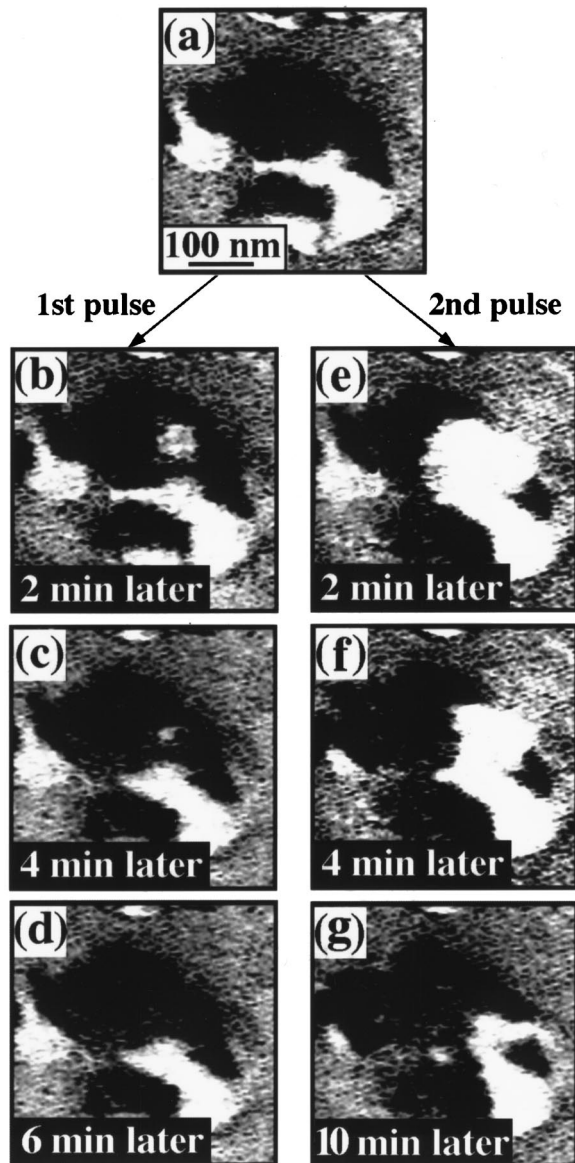


FIG. 6. Piezoresponse images of the SBT/Pt film illustrating the effect of switching prehistory on retention behavior: (a) as-grown domain structure; (b)–(d) retention loss after application of the first switching pulse of  $-6$  V, 1 s; (e)–(g) retention loss after application of the second but identical switching pulse.

150 nm lasted for more than 10 min. After several pulses, the domain size reaches a saturation value of 190 nm and the domain retention time surpasses 144 h.

#### D. Effect of domain polarity

The heretofore presented results concerned domains in a negative polarization state, i.e., oriented toward the film surface. However, as mentioned earlier, the exaggerated asymmetry of boundary conditions in the tip/film/electrode heterostructure should lead to a significant difference in the stability of domains of opposite polarities due to the presence of a strong internal bias. To verify this assumption we carried out retention measurements of positive domains, i.e., oriented toward the bottom electrode, using the same experimental approach: an as-grown negative domain detected on

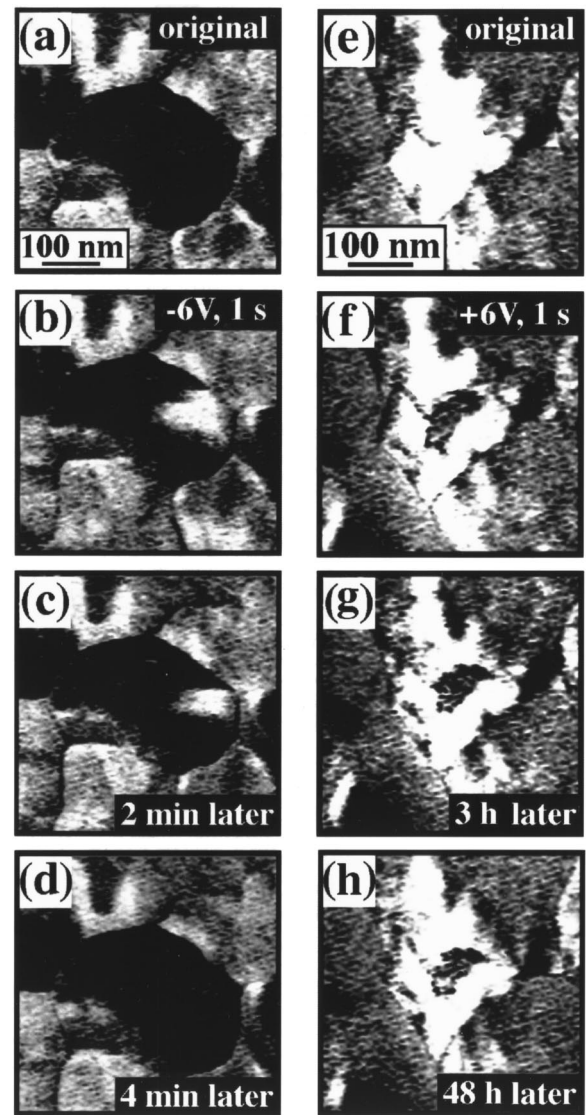


FIG. 7. Piezoresponse images of the SBT/Pt film illustrating a difference in stability of negative (a)–(d) and positive (e)–(h) domains. The poling time in both cases is 1 s and the switching pulse amplitude is 6 V.

the film surface was switched by applying a positive voltage pulse, after which the evolution of the written positive domain was examined by acquiring piezoresponse images at different times. Indeed, it was found that positive domains exhibited quite different retention behavior compared to negative domains, namely, they were found to be fairly stable and did not show any significant dependence on switching parameters up to 96 h of retention. This behavior is illustrated in Fig. 7. While the negative domain produced by a ( $-6$  V; 1 s) voltage pulse disappeared in 6 min [Figs. 7(a)–7(d)], the positive domain written by a (6 V; 1 s) voltage pulse showed almost no decay 48 h after poling [Figs. 7(e)–7(h)].

#### E. Effect of the bottom electrode

An important finding of the present study is that SBT films deposited on an  $\text{IrO}_2$  electrode retained its polarization much better than SBT films on a Pt electrode. In the SBT/ $\text{IrO}_2$  film, domains of both polarities written by (8 V; 1

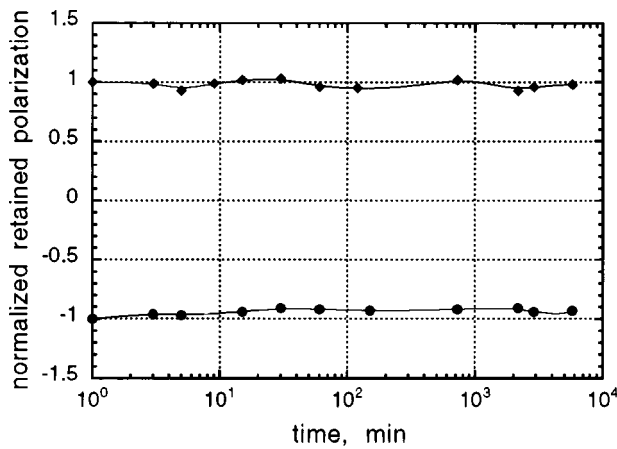


FIG. 8. Retained polarization as a function of time for positive and negative domains in the SBT/IrO<sub>2</sub> film.

s) switching pulses showed almost no sign of relaxation to the original state for 96 h, in striking contrast to the retention behavior of the SBT films on Pt electrode. Figure 8 illustrates the stability of both negative and positive domains in the SBT/IrO<sub>2</sub> film. It should be noted that the threshold switching voltage in the SBT/IrO<sub>2</sub> sample was higher than in the SBT/Pt film and that reliable switching of the same scale in the SBT/IrO<sub>2</sub> sample was achieved at a higher switching amplitude.

#### IV. DISCUSSION

Retention loss in ferroelectric capacitors is generally attributed to the presence of the internal electric field due to two basic effects: incomplete screening of the depolarizing field and formation of a depletion layer at the film/electrode interface.<sup>2-6,34-37</sup> However, the observed difference between the retention properties of SBT/Pt and SBT/IrO<sub>2</sub> films suggests a strong effect of the film/electrode interface on their retention behavior.

It was pointed out by Mehta *et al.*<sup>3</sup> that the polarization charges are not completely compensated for by the electrode charges seen in a short-circuit ferroelectric capacitor due to the fact that the distribution centers of polarization charges and electrode charges are separate from each other. The reasons for the charge separation may be the existence of a low dielectric constant surface layer<sup>6,38,39</sup> or spatial variation of polarization near the electrode<sup>40</sup> in addition to the finite thickness of the compensation charge layers in the electrodes mentioned by Mehta *et al.*<sup>3</sup> This effect suggests the existence of a residual depolarizing field,  $E_{rd}$ , which is compensated for via redistribution of electronic charges in the interior of the film and subsequent formation of the space (screening) charge trapped near the film/electrode interface. The residual depolarizing field is polarization dependent and quickly changes its sign upon polarization reversal. At the same time, the field produced by the space charge, the screening field  $E_s$ , retains its sign long after switching, since its decay rate is determined not by the RC time constant of the electric circuit but rather by the Maxwell relaxation time, which is a function of the bulk conductivity of the film (Fig. 9).<sup>39</sup>

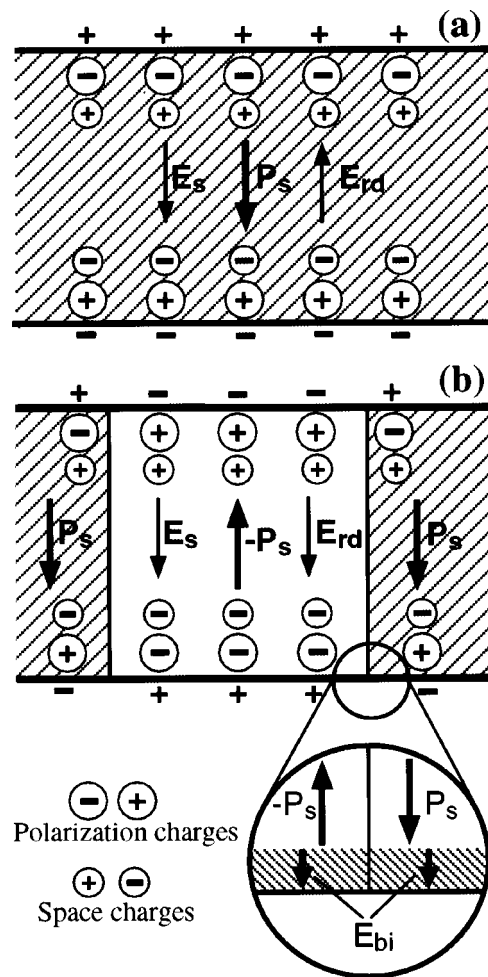


FIG. 9. Charge and field distribution for (a) a single-domain ferroelectric capacitor under stable conditions and (b) after a new domain was written down by an applied bias. Note the (b) shows a situation in which the external screening is finished and the internal screening is not. The inset in (b) shows the orientation of the polarization-independent built-in bias in the depletion layer.

Another cause of the internal field could be the depletion layer which appears at the film/electrode interface as a result of the semiconductor properties of perovskite ferroelectric films. The potential barrier region and the internal built-in bias arise due to the difference between the work functions of the metal electrode and the film. The built-in bias, which is localized in the depletion layer, is not polarization dependent and is always pointing in one direction. Formation of the built-in bias in the SBT/Pt sample can be understood in terms of Scott's analysis of the band structure of the SBT/Pt interface.<sup>41,42</sup> Scott showed that, in SBT films, which behave like a *p*-type semiconductor, an inversion *n*-type layer exists near the SBT/Pt interface. Electrons trapped at positively charged oxygen vacancies produce an internal bias in the depletion layer, which was estimated to be about 2 nm thick. From that analysis it could be inferred that the internal bias  $E_{bi}$  should point to the electrode (Fig. 9).

Under stable conditions, for as-grown domains of both polarities the residual depolarizing field is fully compensated for by the screening field of the space charge. After an external bias is applied to the film to produce the opposite

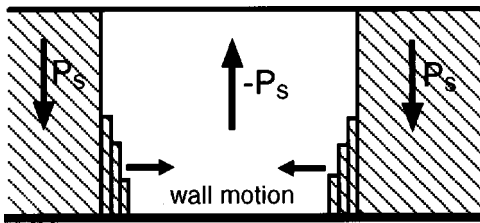


FIG. 10. Backswitching of a negative domain as a result of nucleation at the existing domain wall and at the facets of growing steps.

domain, the screening field which stabilized the original domain tends to switch the new domain back. However, as we saw in Sec. III, in SBT/Pt films only negative domains follow this pattern while positive domains exhibit strong retention. The reason for this different retention behavior of opposite domains can be attributed to the presence of the built-in electric bias  $E_{bi}$  in the depletion layer. This field, which is oriented downward (Fig. 9), generates nuclei of positive domains near the film/electrode interface triggering the backswitching process. Forward growth of these nuclei towards the film surface is driven by the screening field  $E_s$  which extends through the film thickness. As a result, the decay of the written negative domain is observed. In contrast, when a positive domain is written by the external voltage, its polarization points in the same direction as  $E_{bi}$  and, hence, the nucleation of negative domains at the interface is hampered and backswitching of the positive domain does not occur. The sidewise wall motion mechanism of polarization decay can be explained by the higher nucleation probability at the existing domain wall since such nuclei have lower energy.<sup>43</sup> The nuclei grow through the film, forming steps on the existing domain wall (Fig. 10). It is possible that nucleation occurs at the facets of these growing steps as well. However, the apparent broadening of the domain walls of the shrinking domains due to the disparity between the scanning rate and the wall velocity makes it difficult to directly observe this nucleation process. It should be noted that the presence of  $E_{bi}$  could also lead to noncomplete switching in the depletion layer in the low-voltage regime.<sup>6</sup> In this case, the latent positive domains retained at the bottom interface would enhance backswitching of the negative written domain even more. (This possibility, as well as the role of the depletion layer in polarization reversal, was considered in detail by Tagantsev *et al.*<sup>34,35</sup>). However, in this case it is possible that the backswitching could proceed not only via the sidewise motion of the domain walls but also via the forward growth of the latent nuclei and the formation of through domains within the written domain, i.e., the mechanism of polarization decay would be different from that observed. Nevertheless, given that the size of the latent domains in the direction of the film thickness is likely to be of the order of the depletion layer, it would be difficult to detect these domains in the 140-nm-thick film by SFM and to verify or refute this hypothesis.

The above consideration implies that the depletion layer plays an important role in the retention behavior of SBT films by triggering the backswitching process. Hence, the retention behavior would be significantly improved in the

absence of a built-in electric bias at the interface. This situation could be realized by using metal oxide electrodes, such as  $\text{IrO}_2$ , which forms an ohmic contact with SBT.<sup>44</sup> The oxide electrode provides a source of oxygen ions which should result in a reduced built-in field at the interface and enhanced retention. The excellent retention behavior observed in the SBT/ $\text{IrO}_2$  films supports this model and the role of the depletion layers. It is interesting to note that the improved retention of PZT films on oxide electrodes was earlier observed by Hong *et al.*<sup>13</sup>

The enhancement of retention behavior with an increase in the poling time can be explained as follows. We noted above that compensation of the polarization charges involves the accumulation of charges on electrodes (external screening) and formation of space charges in the film/electrode interfaces (internal screening). The rate of these screening processes depends on the time constant of the external circuit and the Maxwell relaxation time, respectively. Obviously, the relation between the switching pulse width and the characteristic time constants of the screening processes has a significant effect on the growth and stability of new domains. There are a number of indications that, in SFM measurements of ferroelectric films without a top electrode, the electric contact between the SFM tip and the film surface is poor, therefore the time constant of the external screening in the SFM switching experiments is rather large. (This also could help explain why the domain wall velocity measured in SFM is several orders lower than that estimated from the transient current measurements<sup>7</sup>). The Maxwell relaxation time at room temperature could be in the range of several seconds to minutes.<sup>40</sup> In this situation, application of a wider switching pulse provides more time for compensating the polarization charges of a new domain by redistributing the screening charges. While the voltage is applied, screening charges accumulate on the surface and the bottom electrode. Grossmann *et al.*,<sup>21</sup> who observed the enhancement of imprint with increasing bias, suggested that the origin of imprint in SBT films is due to electronic charge transport from the electrode into the film. However, thin depletion layers should be transparent to electrons in both directions, so during positive bias application to the bottom electrode, electrons can be transported into the electrode and a new space charge stabilizing a new polarization state may start forming at the film/electrode interface with time. We assume that similar effects occur during switching with a larger pulse amplitude. Repetitive unipolar switching also leads to relaxation of the screening field  $E_s$  due to redistribution of the space charge. As a result, domain stability is enhanced with each consecutive switching.

As can be seen from the above discussion, the concept of an internal electric field provides a consistent explanation for all features of domain retention behavior observed in our study. It is important to emphasize again that the roles of the space charge (screening) field and the built-in bias at the interface are different: the latter initiates the process of retention loss while the former carries on this process. Further experiments are necessary to provide direct proof of the existence of the internal electric field.



Let us make a final remark. Obviously, retention behavior of SBT capacitors should be more symmetric and independent of domain polarity.<sup>19</sup> However, even when the same material is used for the top and bottom electrodes, their work functions could be different due to the different thermal conditions during processing which could cause a difference in their structures.<sup>45,46</sup> In PT/SBT/Pt capacitors, this could lead to retention loss under low operating voltage and development of imprint under high operating voltage. Therefore, considering that SBT/IrO<sub>2</sub> films exhibit excellent retention properties even in the case of the exaggerated asymmetry of the tip/film/electrode heterostructure, it seems that in the SBT capacitors with IrO<sub>2</sub> electrodes the switched polarization will be retained much better, i.e., long enough for use in nonvolatile memories.

## V. CONCLUSION

In this study, we investigated the nanoscale mechanism of retention loss in SBT films. It was found that the retention behavior of SBT films on Pt electrodes is polarization dependent: positive domains with the polarization vector pointing to the bottom electrode exhibit excellent stability in contrast to negative domains oriented upward which show poor retention. This effect is attributed to the presence of the polarization-independent built-in bias at the SBT/Pt interface which triggers the backswitching process by nucleating positive domains. Once started, this process is further governed by the polarization-dependent space charge field which screens the original polarization state. The backswitching of negative domains, which proceeds via the sidewise motion of domain walls, shows a log-time dependence, suggesting a broad distribution of relaxation times even at the nanoscale level. The effect of the poling voltage parameters and switching prehistory on the retention behavior of negative domains is explained by redistribution of the space charge. This model is supported by the observed stability of both the positive and negative domains in the SBT films with IrO<sub>2</sub> electrodes due to inhibited nucleation at the SBT/IrO<sub>2</sub> interface.

## ACKNOWLEDGMENTS

The authors would like to thank K. Hironaka and C. Isobe of the FeRAM Research group, Core Technology and Network Company, Sony Corporation, for providing SBT samples for this study.

<sup>1</sup>O. Auciello, J. F. Scott, and R. Ramesh, *Phys. Today* **51**, 22 (1998).

<sup>2</sup>I. P. Batra and B. D. Silverman, *Solid State Commun.* **11**, 291 (1972).

<sup>3</sup>R. R. Mehta, B. D. Silverman, and J. T. Jacobs, *J. Appl. Phys.* **44**, 3379 (1973).

<sup>4</sup>G. Arlt and H. Neumann, *Ferroelectrics* **87**, 109 (1988).

<sup>5</sup>S. Sum and P. A. Fuierer, *Integr. Ferroelectr.* **23**, 45 (1999).

<sup>6</sup>J. M. Benedetto, R. A. Moore, and F. B. McLean, *J. Appl. Phys.* **75**, 460 (1994).

<sup>7</sup>A. Gruverman, O. Auciello, and H. Tokumoto, *Integr. Ferroelectr.* **19**, 49 (1998).

<sup>8</sup>A. Gruverman, H. Tokumoto, S. A. Prakash, S. Aggarwal, B. Yang, M. Wuttig, R. Ramesh, O. Auciello, and V. Venkatesan, *Appl. Phys. Lett.* **71**, 3492 (1997).

- <sup>9</sup>T. Hidaka, T. Maruyama, I. Sakai, M. Saitoh, L. A. Wills, R. Hiskes, S. A. Dicarolis, and J. Amano, *Integr. Ferroelectr.* **17**, 319 (1997).
- <sup>10</sup>I. K. Yoo, B. M. Kim, D. S. Kim, and S. J. Park, *Mater. Res. Soc. Symp. Proc.* **493**, 299 (1998).
- <sup>11</sup>H. Shin, K. Lee, W.-K. Moon, J. U. Jeon, G. Lim, Y. E. Pak, J. H. Park, and K. H. Yoon, *Proceedings of the 11th International Symposium on Applications of Ferroelectrics, Montreux, Switzerland, 24–27 August 1998*, edited by E. Colla, D. Damjanovic, and N. Setter (IEEE, Piscataway, NJ, 1998), p. 407.
- <sup>12</sup>C. S. Ganpule, A. Stanishevsky, Q. Su, S. Aggarwal, J. Melngailis, E. Williams, and R. Ramesh, *Appl. Phys. Lett.* **75**, 409 (1999).
- <sup>13</sup>J. W. Hong, W. Jo, D. C. Kim, S. M. Cho, H. J. Nam, H. M. Lee, and J. U. Bu, *Appl. Phys. Lett.* **75**, 3183 (1999).
- <sup>14</sup>W. Jo, D. C. Kim, and J. W. Hong, *Appl. Phys. Lett.* **76**, 390 (2000).
- <sup>15</sup>E. L. Colla, S. Hong, D. V. Taylor, A. K. Tagantsev, and N. Setter, *Appl. Phys. Lett.* **72**, 2763 (1998).
- <sup>16</sup>S. Hong, E. L. Colla, E. Kim, D. V. Taylor, A. K. Tagantsev, P. Murali, K. No, and N. Setter, *J. Appl. Phys.* **86**, 607 (1999).
- <sup>17</sup>M. Alexe, C. Harnagea, D. Hesse, and U. Gösele, *Appl. Phys. Lett.* **75**, 1793 (1999).
- <sup>18</sup>C. A. Paz de Araujo, J. D. Cuchiaro, L. D. Macmillan, M. C. Scott, and J. F. Scott, *Nature (London)* **374**, 627 (1995).
- <sup>19</sup>K. Amanuma and T. Kunio, *Jpn. J. Appl. Phys., Part 1* **35**, 5229 (1996).
- <sup>20</sup>Y. Shimada, K. Nakao, A. Inoue, M. Azuma, Y. Uemoto, E. Fujii, and T. Otsuki, *Appl. Phys. Lett.* **71**, 2538 (1997).
- <sup>21</sup>M. Grossmann, O. Lohse, D. Bolten, U. Boettger, R. Waser, W. Hartner, M. Kastner, and G. Schindler, *Appl. Phys. Lett.* **76**, 363 (2000).
- <sup>22</sup>K. Ashikaga and T. Ito, *J. Appl. Phys.* **85**, 7471 (1999).
- <sup>23</sup>Z. G. Zhang, J. S. Liu, Y. N. Wang, J. S. Zhu, J. L. Liu, D. Su, and H. M. Shen, *J. Appl. Phys.* **85**, 1746 (1999).
- <sup>24</sup>B. S. Kang, B. H. Park, S. D. Bu, S. H. Kang, and T. W. Noh, *Appl. Phys. Lett.* **75**, 2644 (1999).
- <sup>25</sup>A. L. Kholkin, K. G. Brooks, and N. Setter, *Appl. Phys. Lett.* **71**, 2044 (1997).
- <sup>26</sup>A. Gruverman, K. Hironaka, Y. Ikeda, K. M. Satyalakshmi, A. Pignolet, M. Alexe, N. D. Zakharov, and D. Hesse, *Integr. Ferroelectr.* **27**, 159 (1999).
- <sup>27</sup>A. Gruverman, O. Auciello, and H. Tokumoto, *Annu. Rev. Mater. Sci.* **28**, 101 (1998).
- <sup>28</sup>A. Gruverman, *Appl. Phys. Lett.* **75**, 1452 (1999).
- <sup>29</sup>C. Isobe *et al.*, *Integr. Ferroelectr.* **14**, 95 (1997).
- <sup>30</sup>C. Harnagea, A. Pignolet, M. Alexe, D. Hesse, and U. Gösele, *Appl. Phys. A: Mater. Sci. Process.* (in press).
- <sup>31</sup>A. Gruverman and Y. Ikeda, *Jpn. J. Appl. Phys. Part 2* **37**, L939 (1998).
- <sup>32</sup>A. Gruverman, J. Hatano, and H. Tokumoto, *Jpn. J. Appl. Phys., Part 1* **36**, 2207 (1997).
- <sup>33</sup>A. Gruverman, S. A. Prakash, S. Aggarwal, R. Ramesh, O. Auciello, and H. Tokumoto, *Mater. Res. Soc. Symp. Proc.* **493**, 53 (1998).
- <sup>34</sup>A. Tagantsev, Cz. Pawlaczyk, K. Brooks, and N. Setter, *Integr. Ferroelectr.* **4**, 1 (1994).
- <sup>35</sup>A. Tagantsev, Cz. Pawlaczyk, K. Brooks, M. Landivar, E. Colla, and N. Setter, *Integr. Ferroelectr.* **6**, 309 (1995).
- <sup>36</sup>H. N. Al-Shareef, D. Dimos, W. L. Warren, and B. A. Tuttle, *J. Appl. Phys.* **80**, 4573 (1996).
- <sup>37</sup>I. G. Jenkins, T. K. Song, S. Madhukar, A. S. Prakash, S. Aggarwal, and R. Ramesh, *Appl. Phys. Lett.* **72**, 3300 (1998).
- <sup>38</sup>M. Drougard and R. Landauer, *J. Appl. Phys.* **30**, 1663 (1959).
- <sup>39</sup>V. Shur, A. Gruverman, and E. Romyantsev, *Ferroelectrics* **111**, 123 (1990).
- <sup>40</sup>M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977).
- <sup>41</sup>J. F. Scott, *Integr. Ferroelectr.* **9**, 1 (1995).
- <sup>42</sup>J. F. Scott, K. Watanabe, A. J. Hartmann, and R. N. Lamb, *Ferroelectrics* **225**, 83 (1999).
- <sup>43</sup>R. C. Miller and G. Weinreich, *Phys. Rev.* **117**, 1460 (1960).
- <sup>44</sup>J. F. Scott, *Annu. Rev. Mater. Sci.* **28**, 79 (1998).
- <sup>45</sup>X. Chen, A. I. Kingon, H. Al-Shareef, and K. R. Bellur, *Ferroelectrics* **151**, 133 (1994).
- <sup>46</sup>B. G. Chae, C. H. Park, Y. S. Yang, and M. S. Jang, *Appl. Phys. Lett.* **75**, 2135 (1999).