Polarization Relaxation Induced by a Depolarization Field in Ultrathin Ferroelectric $BaTiO_3$ Capacitors

D. J. Kim,[1] J. Y. Jo,[1] Y. S. Kim,[1] Y. J. Chang,[1] J. S. Lee,[1] Jong-Gul Yoon,[2] T. K. Song,[3,*] and T. W. Noh[1]

[1]*ReCOE and School of Physics, Seoul National University, Seoul 151-747, Korea*

[2]*Department of Physics, University of Suwon, Kyunggi-do 445-743, Korea*

[3]*Department of Ceramic Science and Engineering, Changwon National University, Changwon, Kyungnam 641-773, Korea*

(Received 21 June 2005; published 1 December 2005)

Time-dependent polarization relaxation behavior induced by a depolarization field E_d was investigated on high-quality ultrathin $SrRuO_3/BaTiO_3/SrRuO_3$ capacitors. The E_d values were determined experimentally from an applied external field to stop the net polarization relaxation. These values agree with those from the electrostatic calculations, demonstrating that a large E_d inside the ultrathin ferroelectric layer could cause severe polarization relaxation. For numerous ferroelectric devices of capacitor configuration, this effect will set a stricter size limit than the critical thickness issue.

DOI: 10.1103/PhysRevLett.95.237602 PACS numbers: 77.22.Ej, 77.22.Gm, 77.55.+f, 77.80.Dj

With recent breakthroughs in fabricating high-quality oxide films [1–3], ultrathin ferroelectric (FE) films have attracted much attention from the scientific as well as application points of view. As the FE film thickness d approaches tens of unit cell length, the FE films often show significantly different physical properties from those of bulk FE materials. Some extrinsic effects, especially coming from FE film surfaces and/or interfaces with other materials, could be very important [4]. For some other cases, intrinsic physical quantities could play vital roles in determining the unique properties of ultrathin films.

Many FE-based electronic devices have the capacitor configuration, where a FE layer is inserted between two conducting electrodes. Then, polarization bound charges will be induced at the surfaces of the FE layer, but compensated by free charge carriers in the conducting electrodes. In real conducting electrodes, however, the compensating charges will be induced with a finite extent, called the screening length λ. This will result in an incomplete compensation of the polarization charges. Such an incomplete charge compensation should induce a depolarization field E_d inside the FE layer, with a direction opposite to that of the FE polarization P [5]. Therefore, E_d will appear in every FE capacitor, and its effects will become larger with the decrease of d [5]. E_d has been known to be important in determining the critical thickness [6] and domain structure of ultrathin FE films [7–9] and reliability problems of numerous FE devices [10,11].

Recently, using a first principles calculation, Junquera and Ghosez investigated the critical thickness of $BaTiO_3$(BTO) layers in $SrRuO_3$(SRO)/BTO/SRO capacitor [6]. They assumed that all of the BTO and SRO layers were fully strained with the $SrTiO_3$ substrate. By taking the real SRO/BTO interfaces into account properly, they showed that E_d could make the ferroelectricity vanish for the BTO films thinner than 6 unit cells, i.e., 2.4 nm [6]. More recently, using pulsed laser deposition with a reflection high energy electron diffraction monitoring system, we fabricated high-quality fully strained SRO/BTO/SRO capacitors on $SrTiO_3$ substrates with d between 5 and 30 nm [2,12]. With a very low leakage current, we could directly measure their P-E hysteresis loops [2]. In this Letter, we report the time-dependent polarization changes of the ultrathin BTO films. We find that the net P of the ultrathin BTO films decreases quite rapidly in time. We will show that the P relaxation should originate from E_d. By compensating for E_d with an external voltage, we can determine the E_d values of the SRO/BTO/SRO capacitors experimentally. These measured E_d values agree with the values from the electrostatic calculations. Finally, we will discuss the effect of the P relaxation on a practical size limitation imposed on actual FE devices.

In our earlier report [2], we obtained the thickness-dependent remnant polarization P_r values from the P-E hysteresis loops, measured at 2 kHz in ultrathin FE films as thin as 5–30 nm. With further studies on the frequency dependence of the P_r values in P-E hysteresis loops, as shown in Fig. 1(a) for a 15 nm thick BTO capacitor, we found differences in the P_r values when the measuring frequency is varied. These results suggest that the FE domain dynamics should play an important role for ultrathin FE films, where the FE domain wall motion is known to be strongly suppressed [13]. Note that the first principles calculation (FPC) and the Landau-Devonshire calculation (LDC) do not consider the domain dynamics, so their predicted polarization values should be called as spontaneous polarization P_s.

Since the P value significantly affects the subsequent analysis of P relaxation, precise determination of P_s values is necessary. To determine the precise values of P_s, we applied pulse trains, which are schematically shown in the inset of Fig. 1(a) [14]. The interval between write and read pulses was set to 1 μs to minimize the effects of the P relaxation, and the current responses under the read pulse were measured. The total amount of charge is obtained by integrating the current responses in time. The read pulses

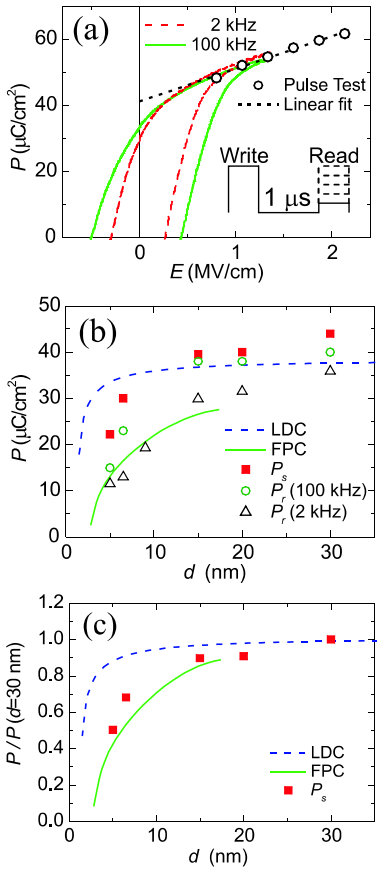

FIG. 1 (color online). (a) Upper halves of hysteresis loops for 15 nm thick BTO capacitor at the measurement frequencies 2 and 100 kHz. The values of spontaneous polarization P_s were obtained from linear extrapolation of pulse measurements. (b) The polarization values obtained from pulse measurements, first principles calculation (FPC), and Landau-Devonshire calculation (LDC). (c) Normalized behaviors of LDC, FPC, and P_s to the values of BTO capacitors with 30 nm thickness.

with different heights were used to obtain the linear part of the polarization under an external electric field. The P_s values can be obtained by extrapolating the linear part of the polarization to zero electric field. The triangles (black) and circles (green) in Fig. 1(b) show the P_r values measured at 2 and 100 kHz, respectively. Also, the squares (red) show the P_s values from the pulse test. The solid (green) and dashed (blue) curves show the theoretical predictions from the FPC [6] and the LDC [15], respectively, which take account of E_d. Note that neither of these theories can explain the thickness dependence of P_s quantitatively. However, it is known that the FPC predicts systematically somewhat lower bulk lattice constants compared to real values, so the compressive stress predicted by the FPC could be smaller than that in the fully strained sample, resulting in a smaller P_s. To avoid this systematic error, we normalized the polarization values to those of a 30 nm thick BTO capacitor. We found that the thickness-dependent scaling of P_s also follows the FPC predictions quite well, as shown in Fig. 1(c).

The large difference in P values between the 2 and the 100 kHz tests indicates that there should be a strong change in the net P between 10 and 500 μs. Time-dependent P changes were investigated by applying two kinds of pulse trains, as shown in the inset of Fig. 2(a). For the write and the read pulses with the same (opposite) polarities, the amount of nonswitching (switching) P can be determined [10]. The difference ΔP, between the switching and the nonswitching P should be twice as large as the net P. As shown in Fig. 2(a), ΔP decreases quite rapidly for the film with $d = 15$ nm; ΔP falls to less than 10% of the P_s value within a relaxation time t_{relax} of 1000 s. As shown with the solid squares (black) in Fig. 2(b), ΔP decay follows a power-law dependence on t_{relax}. Similar power-law decays of ΔP were observed for all the BTO films in the thickness range of 5–30 nm. Note that such a strong polarization relaxation could pose a serious problem in capacitor-type ultrathin FE devices.

What is the origin of such strong polarization relaxations? We thought that they could be closely related to large E_d induced inside the BTO films. To verify this idea, we slowed down the relaxation phenomena by applying an external voltage, as shown in the inset of Fig. 2(a). The values of the applied external electric field E_{ext} were obtained by dividing the applied external voltage by the corresponding film thickness. When E_{ext} is applied in the opposite direction of E_d, the potential gradient inside the FE layer will decrease. Figure 2(b) shows that the slope of the power-law decay becomes smaller, as E_{ext} increases. Assuming that the depth of the double-well potential for BTO ferroelectricity can be considered negligible compared to the effect of E_d, we approximately determined experimental E_d values from the applied E_{ext} under which the slope becomes zero. Since E_d is proportional to P, the E_d value should increase slightly on application of E_{ext}. After correcting this minor contribution, we could determine the E_d values, which are plotted as solid (red) circles in Fig. 2(c).

From electrostatic calculations on the capacitor geometry, Mehta *et al.* showed that

$$E_d = -\frac{P}{\epsilon_0 \epsilon_F}\left(\frac{2\epsilon_F/d}{2\epsilon_F/d + \epsilon_e/\lambda}\right), \qquad (1)$$

where ϵ_F and ϵ_e are the relative dielectric constants of the FE layer and the electrode, respectively [5]. To obtain theoretical E_d values for our SRO/BTO/SRO capacitors, we have to know accurate values of ϵ_e, λ, and ϵ_F. Unfortunately, the reported physical parameter values in the literature vary [5,6,16,17]. Also, we could not find any definite experimental study on ϵ_e of SRO.

To obtain the value of ϵ_e for an SRO electrode, we used optical spectroscopy. We measured the optical reflectivity spectra of epitaxial SRO films (thickness: about 0.5 μm) in a wide frequency region between 5 meV and 30 eV and

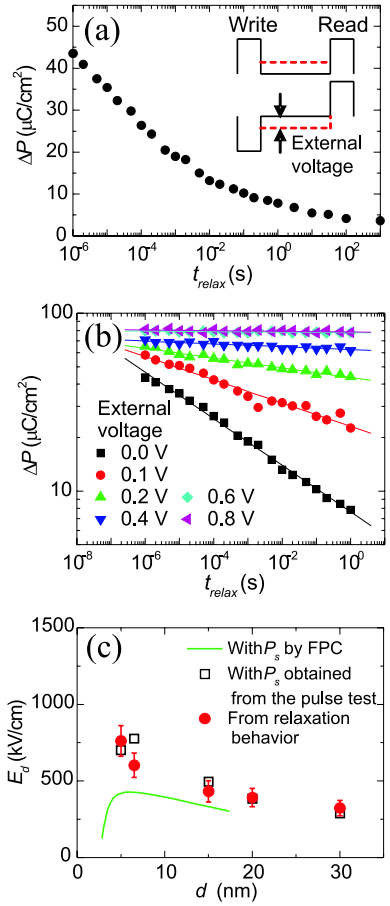

FIG. 2 (color online). (a) Polarization relaxation in the 15 nm thick BTO capacitor. The inset shows the schematics of measuring relaxation behaviors under an external voltage. (b) Slowing down of the relaxation behavior under external voltages in the 15 nm thickness BTO capacitor. (c) Thickness-dependent E_d in the ultrathin BTO capacitors. The E_d values obtained from relaxation behaviors experimentally (red solid circles) and those from electrostatic calculations with the parameters determined and measured P_s in this work (open squares). The (green) line indicates the E_d from electrostatic calculations with the polarization values obtained from first principles calculation.

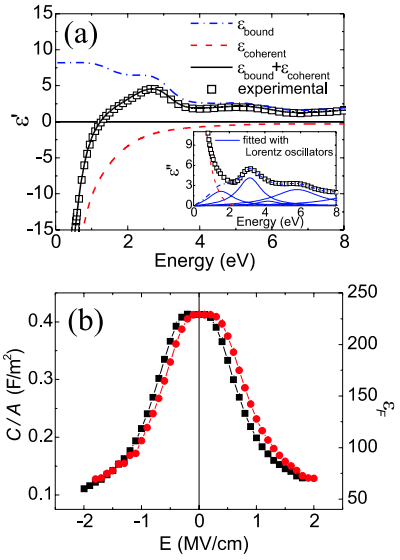

FIG. 3 (color online). (a) Frequency-dependent dielectric functions of SRO. (b) Capacitance-electric field curve of the SRO/BTO/SRO capacitor with 5 nm thick BTO.

performed a Kramers-Kronig analysis to obtain the frequency-dependent dielectric function, $\epsilon(\omega)[= \epsilon'(\omega) + i\epsilon''(\omega)]$. The details of these measurements and analysis were published elsewhere [18,19]. The open squares in Fig. 3(a) and the inset show experimental values of $\epsilon'(\omega)$ and $\epsilon''(\omega)$, respectively. Note that ϵ_e in Eq. (1) represents the dielectric response from the bound charges, namely, bound electrons and phonons. Since SRO is metallic, there should be a large contribution from the free Drude carriers, which masks the dielectric response from the bound charges. To obtain ϵ_e, we decompose $\epsilon(\omega)$ into a free carrier contribution $\epsilon_{\text{coherent}}(\omega)$ and a bound electron contribution $\epsilon_{\text{bound}}(\omega)$ by fitting the experimental $\epsilon(\omega)$ with a series of Lorentz oscillators, which are displayed as the dotted (blue) lines in the inset of Fig. 3(a). The dash-dotted (blue) lines indicate the bound electron contribution. From the dc limit of $\epsilon_{\text{bound}}(\omega)$, we could estimate that the bound electron contribution to ϵ_e is about 8.17. The phonon contribution to ϵ_e was evaluated in a similar way by analyzing the phonon spectra and found to be about 0.28 [18]. Consequently, ϵ_e is determined to be about 8.45.

Using the carrier density $n_0 \cong 1.2 \times 10^{22}/\text{cm}^3$ of SRO [20], the experimental value of ϵ_e, and the effective mass of an electron $m_{\text{eff}} \cong 7m_e$, where m_e is the mass of a free electron [21,22], we applied the free electron model and obtained $\lambda = 0.8 \pm 0.1$ Å [5,23]. We also measured ϵ_F from the capacitance-electric field C-E curves of BTO capacitors. Figure 3(b) shows the C-E curve for the 5 nm BTO capacitor. The C-E curve has the hysteretic behavior typical for a FE capacitor. The BTO capacitors with 5–30 nm thickness show almost the same $\epsilon_F - E$ curves. The ϵ_F values can vary from 70 to 230 depending on the applied E. Since most of our experiments were performed under a finite applied field, which corresponds to a value between 1 and 2 MV/cm, the ϵ_F were estimated to be about 80 [24].

With the measured values of ϵ_e, λ, and ϵ_F, we could estimate the theoretical E_d values from Eq. (1) with the P_s values obtained from the pulse test. The open squares in Fig. 2(c) are the theoretical E_d values. The solid (green) line shows the theoretical E_d values with the P_s values, obtained from the FPC. These theoretical E_d values from the electrostatic model agree quite well with the experimental E_d values from the polarization relaxation, indicated with solid (red) circles in Fig. 2(c). It should be noted that the E_d values are comparable with or even larger than the measured coercive fields (in our samples, 300–400 kV/cm). These large E_d values can cause P reversal and FE domain formation, which will result in a

reduction of the net P value as time elapses. The fact that two independent determinations provided nearly the same E_d values demonstrates that the polarization relaxation behavior should be dominated by E_d inside the FE layer.

Note that the E_d-induced ΔP decay comes intrinsically from the incomplete compensation of the P charges (due to the finite screening length of the electrodes) in real conducting electrode, so that it will inevitably pose a fundamental limit for most FE device applications using the capacitor configuration. This limitation should be much more severe than that due to the critical thickness of the FE ultrathin films [6]. Even if the FE film is thicker than the critical thickness, it is feasible that the E_d-induced ΔP decay is large enough to make the net P decrease significantly, resulting in retention failures for numerous FE devices. As d decreases, E_d increases significantly. With the current miniaturization trends in some FE devices, the large value of E_d should play a very important role in determining the ultimate size limits of FE devices.

In order to reduce device failure due to the polarization relaxation, we can try to select better electrode and FE materials. Noble metals, such as Pt, have been considered better electrodes because they have high carrier density (resulting in λ values smaller than that of SRO). However, the ϵ_e values of typical noble metals are much smaller than that of SRO, i.e., 8.45 [25], so E_d in capacitors with noble metal electrodes can be large. For example, E_d in the range of 500–900 kV/cm is expected for a 15 nm thick BTO film with noble metal electrodes (typically, $\lambda = 0.4$–0.5 Å, $\epsilon_e = 2$–4). Thus, the E_d-induced P relaxation for the ultrathin BTO capacitors with the noble metal electrodes could be at least equal to or worse than that with SRO electrodes. Proper FE material selection can be another option. Since $PbTiO_3$ is known to have a much deeper double-well potential than that of BTO [15,26], the P relaxation should occur at a much lower rate even with the same value of E_d. Optimization of FE materials should be of great importance for the improvement of ultrathin film nanoscale FE device performances.

In summary, we demonstrated that the depolarization field inside the ferroelectric film could cause a severe polarization relaxation. By slowing down the relaxation under an external field, we could determine the depolarization field in a real capacitor of ultrathin $SrRuO_3$/$BaTiO_3$/$SrRuO_3$ experimentally, which result is in good agreement with electrostatic calculations. Our investigation demonstrates that the depolarization field originates from intrinsic properties of electrode material such as the finite screening length and that the depolarization field should play an important role in domain dynamics in ultrathin FE films. The polarization relaxation due to the depolarization field could pose a serious size limitation for ultrathin ferroelectric devices.

The authors thank Professor Sug-Bong Choe in Seoul National University for valuable discussions. This work was financially supported by the Korean Ministry of Science and Technology through the Creative Research Initiative program and by KOSEF through CSCMR.

*Electronic mail: tksong@changwon.ac.kr

[1] C. H. Ahn, K. M. Rabe, and J.-M. Triscone, Science **303**, 488 (2004).
[2] Y. S. Kim *et al.*, Appl. Phys. Lett. **86**, 102907 (2005).
[3] H. N. Lee, H. M. Christen, M. F. Chisholm, C. M. Rouleau, and D. H. Lowndes, Nature (London) **433**, 395 (2005).
[4] T. W. Shaw, S. Trolier-McKinstry, and P. C. McIntyre, Annu. Rev. Mater. Sci. **30**, 263 (2000).
[5] B. B. Mehta, B. D. Silverman, and J. T. Jacobs, J. Appl. Phys. **44**, 3379 (1973).
[6] J. Junquera and P. Ghosez, Nature (London) **422**, 506 (2003).
[7] I. Kornev, H. Fu, and L. Bellaiche, Phys. Rev. Lett. **93**, 196104 (2004).
[8] Z. Wu, N. Huang, Z. Liu, J. Wu, W. Duan, B.-L. Gu, and X.-W. Zhang, Phys. Rev. B **70**, 104108 (2004).
[9] D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thompson, Science **304**, 1650 (2004).
[10] B. S. Kang *et al.*, Appl. Phys. Lett. **82**, 248 (2003).
[11] B. S. Kang *et al.*, Appl. Phys. Lett. **82**, 2124 (2003).
[12] Y. S. Kim *et al.*, cond-mat/0506495.
[13] T. Tybell, P. Paruch, T. Giamarchi, and J.-M. Triscone, Phys. Rev. Lett. **89**, 097601 (2002).
[14] G. A. Smolenskii, V. A. Bokov, V. A. Isupov, N. N. Krainik, R. E. Pasynkov, and A. I. Sokolov, *Ferroelectrics and Related Materials* (Gordon and Breach, New York, 1984), pp. 4–5.
[15] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).
[16] C. T. Black and J. J. Welser, IEEE Trans. Electron Devices **46**, 776 (1999).
[17] M. Dawber, P. Chandra, P. B. Littlewood, and J. F. Scott, J. Phys. Condens. Matter **15**, L393 (2003).
[18] J. S. Lee *et al.*, Phys. Rev. B **70**, 085103 (2004).
[19] J. S. Lee *et al.*, Phys. Rev. B **64**, 245107 (2001).
[20] M. Shepard, S. McCall, G. Cao, and J. E. Crow, J. Appl. Phys. **81**, 4978 (1997).
[21] G. Cao, S. McCall, M. Shepard, J. E. Crow, and R. P. Guertin, Phys. Rev. B **56**, 321 (1997).
[22] J. Okamoto, T. Mizokawa, A. Fujimori, I. Hase, M. Nohara, H. Takagi, Y. Takeda, and M. Takano, Phys. Rev. B **60**, 2281 (1999).
[23] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1996), 6th ed. pp. 280–282.
[24] Note that the charge compensation in the finite screening length in electrodes might result in space charge capacitance in series with ferroelectric capacitance. For the case of the 5 nm thick film, ϵ_F should be increased to 112 from 80 with the correction. However, this increase of ϵ_F does not change E_d so much; from 708 to 650 kV/cm (about 8%). Because this is the most serious case, corrections are not necessary for thicker films.
[25] H. Ehrenreich and H. R. Phillipp, Phys. Rev. **128**, 1622 (1962).
[26] R. E. Cohen, Nature (London) **358**, 136 (1992).