Depolarizing field and "real" hysteresis loops in nanometer-scale ferroelectric films

A. M. Bratkovsky[a)]
Hewlett-Packard Laboratories, 1501 Page Mill Road, Palo Alto, California 94304

A. P. Levanyuk
Departamento de Física de la Materia Condensada, C-III, Universidad Autónoma de Madrid, 28049 Madrid, Spain and Hewlett-Packard Laboratories, 1501 Page Mill Road, Palo Alto, California 94304

The authors give detailed analysis of the effect of depolarizing field in nanometer-size ferroelectric capacitors studied by Kim *et al.* [Phys. Rev. Lett. **95**, 237602 (2005)]. They calculate a critical thickness of the homogeneous state and its stability with respect to domain formation for strained thin films of BaTiO$_3$ on SrRuO$_3$/SrTiO$_3$ substrate within the Landau theory. While the former (2.5 nm) is the same as given by *ab initio* calculations, the actual critical thickness is set by the domains at 0.8 nm. There is a large Merz's activation field for polarization relaxation. Remarkably, the results show a negative slope of the "actual" hysteresis loops, a hallmark of the domain structures in ideal thin films with imperfect screening. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2408650]

Kim *et al.*[1–3] have recently published a series of seminal experimental studies of very thin, down to 5 nm, ferroelectric (FE) BaTiO$_3$ capacitors with SrRuO$_3$/SrTiO$_3$ (SRO/STO) electrodes. They obtained hysteresis loops at frequencies up to 100 kHz and studied retention of a single domain (SD) state in various external fields. They have applied high external field to obtain polarization saturated state, perhaps a SD one, and observed its relaxation when the external field E_0 was reduced below a certain value $E_0 = E_{0r}$. They have approximately identified this field as a depolarizing field due to incomplete screening by electrodes and claimed that it coincides with the one estimated from electrostatics. We show below that such an interpretation does not apply and present a consistent interpretation, which reveals important features of multidomain (MD) structure in electroded thin FE films: (i) we find deviations from the Merz's empirical formula[4] for thickness and exposition time dependence of the activation field for domain wall movement and/or domain nucleation in very thin films, (ii) replotting the hysteresis loops as function of a field in the ferroelectric reveals a *negative* susceptibility of multidomain films governed by the electrostatics, predicted some time ago,[5] and (iii) finally, we argue that domain structure in the thinnest ferroelectric films with electrodes may be different from that in thick films.

In their study, Kim *et al.*[1] followed the idea by Mehta *et al.*[6] that the incomplete screening of the ferroelectric bound charge by electrodes leads to a depolarizing field inside the ferroelectric that promotes domain nucleation and movement and limits the polarization retention. Kim *et al.* speculated that the depolarizing film can be identified with an external field $E_0 = E_{0r}$ that stops the polarization relaxation. They claimed that the relaxation threshold field E_{0r} is very close to the depolarizing field E_d. This is incorrect, however, since E_d was estimated under *finite* external field E_0 from formula by Mehta *et al.* who did only the case of short-circuited capacitor ($E_0 = 0$). If they were right, the Merz

activation field for the domain motion and/or nucleation in their ultrathin samples would have been negligible, which is not the case.

It is easy to find the external field $E_0 = E_{0b}$ that *completely* compensates the depolarization field (i.e., corresponds to zero field in FE). This is the point where the field in FE changes sign from negative to positive with regards to the polarization, and the *monodomain-polydomain* transition should be taking place if the domain wall energy was zero. The homogeneous field in the monodomain ferroelectric is,[7] in notations of Ref. 1,

$$E_f = (E_0 - 2P\lambda/\epsilon_0\epsilon_e l)/(1 + 2\lambda/\epsilon_e l) \approx E_0 + E_d, \tag{1}$$

where E_0 is the external field, $E_d = -2P\lambda/\epsilon_0\epsilon_e l$ the depolarizing field, l the thickness of the film, λ (ϵ_e) the screening length (dielectric constant) in the electrode ($\lambda = 0.8$ Å, $\epsilon_e = 8.45$ in SRO, Ref. 1), and ϵ_0 the vacuum permittivity. We see from Eq. (1) that the field in FE film is zero, $E_f = 0$, which is the state with the spontaneous polarization $P = P_s$, when

$$E_0 = E_{0b} \equiv 2\lambda P_s/(\epsilon_0\epsilon_e l). \tag{2}$$

To find the spontaneous polarization from the experimental data we first obtain the relation between the polarization and the external field E_0. It can be found from the equation of state[8] for the component of polarization in c direction perpendicular to the film $P = P_3$ with Landau expansion coefficients renormalized by strain,[9] and the field in the film [Eq. (1)]. We write it in the form

$$\hat{A}P + BP^3 + CP^5 + FP^7 = E_f, \tag{3}$$

where have taken into account that the first coefficient may be affected by the additional boundary conditions (ABC), $\hat{A} = A + (2\alpha + \beta)/l$, where the material constants α and β characterize the interface.[10] Using Eq. (1), we obtain

$$A_h P + BP^3 + CP^5 + FP^7 = \frac{E_0}{1 + 2\lambda/\epsilon_e l} \simeq E_0, \tag{4}$$
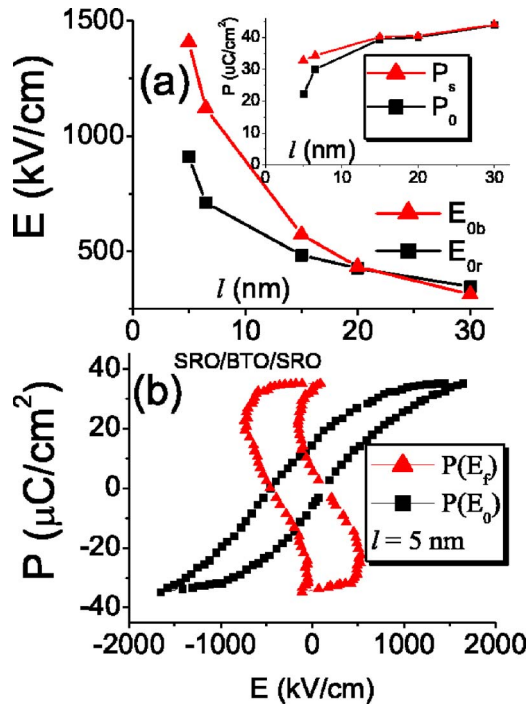
a)Electronic mail: alex.bratkovski@hp.com

FIG. 1. (Color online) (a) External field E_{0b} (where E_f=0) and E_{0r} where the relaxation of polarization starts in 5 nm thick film (Ref. 1). Inset: the spontaneous polarization P_s and the extrapolated P_0 (Ref. 1). (b) The measured $P(E_0)$ and the "actual" $P(E_f)$ hysteresis loops.

$$A_h = \hat{A} + \frac{2\lambda}{\epsilon_0(\epsilon_e l + 2\lambda)} \simeq \hat{A} + \frac{2\lambda}{\epsilon_0 \epsilon_e l}, \qquad (5)$$

where we have used the fact that in a metal the screening length is small, $\lambda/\epsilon_e l \ll 1$. The equation for spontaneous polarization P_s takes the form

$$\hat{A} + B P_s^2 + C P_s^4 + F P_s^6 = 0, \qquad (6)$$

which is readily solved analytically. Since we know from the data the polarization at zero external field, $P_0 = P(E_0=0)$,[1] we can easily obtain P_s from Eqs. (4) and (6). We find that in the present case the ABC effect is unimportant, since the variation of the spontaneous polarization P_s with thickness due to the $(2\alpha+\beta)/l$ term is small [see Fig. 1(a) (inset)].

With these results, we then find that E_{0b}=1450 kV/cm in 5 nm sample, which is about 60% *larger* than the relaxation field E_{0r} identified by Kim *et al.* This means that during the observation time t_{relax}=10³ s the domains begin to form only when there is a field E_f=−(490±70) kV/cm opposite to the polarization (at $E_0=E_{0r}$=910 kV/cm for 5 nm sample, raw data from Kim *et al.*[1]). The activation field strongly depends on FE film thickness for long application time (∼10³ s). Indeed, in the l=30 nm FE film the activation field is practically zero [Fig. 1(a)]. It is interesting to see how the activation field depends on the application time. To this end, we have replotted the hysteresis loops taken at 2 kHz as a function of a field in the ferroelectric E_f, $P=P(E_f)$ [Figs. 1(b) and 2]. Note that we used Eq. (1) to calculate E_f, which applies to homogeneous state. One, however, can apply it to a MD part of the loops around $P \approx 0$ too, since the domains are narrow and the field in the bulk is approximately homogeneous. Even in 5 nm film the domain width a=2.2 nm (see below), so this approximation should be semiquantitative. The use of Eq. (1) is justified for finding the activation field
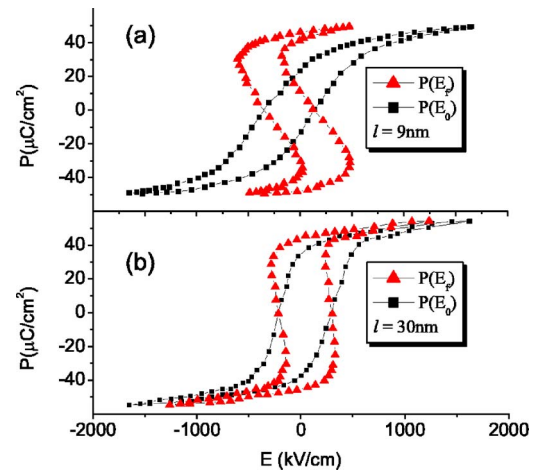
for domains (the ends of a horizontal parts of the loop). We see that the activation field of similar magnitude is observed at all thicknesses. This field is about the same as in 5 nm sample observed for much longer 10³ s of application time.

Comparing the data by Kim *et al.* with Merz,[4] one expects that the switching time is close to the application time mentioned above. We rewrite Merz's empirical formula in the form

$$E_a = (\alpha \ln \tau)/l, \qquad (7)$$

where τ is the switching time and α the numerical constant. It describes a weak dependence of the activation field on the application time for l=5 nm as well as strong reduction of the field with a sample thickness at a large application time rather well. However, weak dependence of E_a on the film thickness in the case of small application times is not captured by Eq. (7).

We find using Eqs. (1)–(4) that the electric field in short-circuited 5 nm sample is $E_f(E_0=0)$=−1200 kV/cm, exceeding the magnitude of the estimated activation field. This means that in a short-circuited sample SD state relaxes quicker than in 10³ s. If the value of the activation field is defined by the thickness only and not by properties of electrodes or an electrode-film interface, one can speculate about the properties of electrodes, which can facilitate a smaller field in a short-circuited sample and a longer, at least 10³ s, retention of a SD state. We have found that for d=5 nm such an electrode should have $\lambda/\epsilon_e \xi/2$=0.043 Å, c.f. Eq. (11). Since in Ref. 1 this value is about 0.1 Å, it does not seem impossible to find such an electrode. Alternatively, thinner films may show longer retention, as Eq. (7) suggests.

An unusual specific feature of replotted loops is that they all have a *negative slope*, most pronounced at l=5 nm. The exact value is affected by error bars, but there is a strong indication that it is characteristic of all samples. The negative slope has been predicted some time ago for an ideal ferroelectric plate between perfect metallic electrodes with a voltage drop across thin dead layers:[5] it is a hallmark of domain structure governed mainly by electrostatics. There are no dead layers in the present films,[3] but the voltage drop happens across a screening layer with the thickness λ in electrodes with an identical result and apparently beyond the precision of Ref. 3. Indeed, a net polarization of the domain structure is $\bar{P}$=0 in zero external field E_0. At small E_0 there

FIG. 2. (Color online) Measured $P(E_0)$ and the "actual" $P(E_f)$ hysteresis loops: (a) film thicknesses l=9 nm and (b) l=30 nm.

will be positive net polarization in external field because of growth of domains oriented along the external field, and the resulting *negative* field in the FE ($E_f > 0$ at $E_0 > E_{0b}$ and crosses zero at $E_0 = E_{0b}$) [Eqs. (1) and (2)]. Thus, the dielectric functions of the film is negative, $\epsilon_f = 1 + \epsilon_0^{-1} d\bar{P}/dE_f|_{E_f=0} < 0$.[5] Comparing theory with the data, the expression for the dielectric constant, given by Eq. (31) of Ref. 5, can be simplified to

$$\epsilon_f \approx -\epsilon_e l/\lambda. \qquad (8)$$

Substituting the numbers, we find the theoretical value $\epsilon_f = -525$ for equilibrium conditions while the experimental one found from Fig. 1(b) (raw data for 2 kHz, Ref. 2) is $\epsilon_f = -680$, i.e, they are pretty close. According to Eq. (8), the absolute value of the negative slope for $l=9$ nm should be about two times larger than for $l=5$ nm, and one sees from the Figs. 1(b) and 2 that this is indeed the case. If this agreement is not accidental, it indicates that in the films studied by Kim *et al.* the properties of the domain structure may be mainly defined by the electrostatics and not by some specific structural features of the samples, etc. The negative slope of the hysteresis loops is apparently observed for the first time.

To reveal specific features of domain structure in thinnest films, we take into account that at small enough thickness the system should be in the paraelectric phase (as shown explicitly below) and consider loss of stability of this phase when the film thickness increases, i.e., a paraelectric-FE phase transition *with film thickness*. The loss of stability is signalled by the appearance of a nontrivial solution of the equations of state which can be either homogeneous (SD) or inhomogeneous (MD). A homogeneous solution of Eq. (4) is possible at $A_h < 0$, i.e., $l > l_h$, where $l_h = 2\lambda/(\epsilon_0 \epsilon_e |A|)$, at room temperature $l_h^{RT} = 3.5$ nm. The domain instability means the appearance of a solution in form of a "polarization wave" $P = P_k(z)e^{ikx}$ (Refs. 11 and 12) of the (linearized) equation of state with the gradient term included,

$$AP - g\nabla_\perp^2 P = E \equiv -\partial_z \varphi, \qquad (9)$$

where $\nabla_\perp^2 = \partial_x^2 + \partial_y^2$ is the "in-plane" Laplacian. In the case of metallic screening, solving Eq. (9) together with the Poisson equation for the electrostatic potential φ readily gives the following condition:[7]

$$\chi \tan \frac{1}{2}\chi k d = \epsilon_\perp k/\epsilon_e \sqrt{k^2 + \lambda^{-2}}, \qquad (10)$$

where $\chi^2 = -\epsilon_0 \epsilon_\perp (A + gk^2) > 0$ and $\epsilon_\perp$ is the dielectric constant in the direction perpendicular to ferroelectric axis in the plane of the film. The case of interest to us is $k\lambda \ll 1$, easily met for metallic electrodes. We assume (and check validity later) that $\epsilon_\perp \lambda k/\epsilon_e \chi \gtrsim 1$. Then, the equation simplifies to $\chi k d = \pi$, the same as in FE film without electrodes or with a dead layer. We then find the maximal value (the highest temperature) of $A_d = -2gk_c^2$ at $k=k_c$ where this equality is first met and domains begin to form

$$-A_d = 2gk_c^2 = \xi/\epsilon_0 l, \quad k_c = (\pi^2/\epsilon_\perp \epsilon_0 gl^2)^{1/4}, \qquad (11)$$

where $\xi = 2\pi\sqrt{\epsilon_0 g/\epsilon_\perp}$ is the characteristic small length scale for this problem (see below). Now, checking the assumption

that we used to solve the Eq. (10), we see that it boils down to $\lambda \epsilon_\perp^{1/2}/\epsilon_e(\epsilon_0 g)^{1/2} \gtrsim 1$. Using values of λ and ϵ_e from Ref. 1, the value of $\sqrt{\epsilon_0 g} = 0.2$ Å from Ref. 13, and calculating $\epsilon_\perp$ using the coefficients of Ref. 8, we find that this condition is satisfied. From Eq. (11), we obtain the following critical thickness for domains at room temperature ($\epsilon_\perp = 218$):

$$l_d^{RT} = \xi/|A_d|\epsilon_0 \simeq 1.6 \text{ nm.} \qquad (12)$$

Since $l_d^{RT} < l_h^{RT}$, the phase transition is into a multidomain state. The spatial distribution of a spontaneous polarization is near sinusoidal at $l \gtrsim l_d^{RT}$. Higher harmonics develop with increasing thickness, and the polarization distribution tends to a conventional structure with narrow domain walls. But at small thicknesses it is nearly sinusoidal, and one can expect weaker pinning compared to thicker films. It is hardly surprising that the empirical Merz's formula obtained for conventional domain structure does not apply to a sinusoidal one. The half-period of the sinusoidal domain structure can be estimated as $a_c^{RT} = 1.2$ nm at the transition and as $a^{RT} = 2.2$ nm for $l=5$ nm from $a \approx \pi/k_c$ and Eq. (11).

It is instructive to consider the phase transition with thickness at 0 K, where we get $\epsilon_\perp = 409, \xi = 0.06$ Å, $l_d^{(0 \text{ K})} = 0.8$ nm, and $l_h^{(0 \text{ K})} = 2.5$ nm. The last result (homogeneous critical thickness of 2.5 nm) is remarkable, since it practically *coincides* with the *ab initio* calculation for the critical thickness of 2.4 nm in Ref. 14. The ground state of the film is, however, not homogeneous but multidomain, and the domain ferroelectricity appears in films thicker than $l_d^{(0 \text{ K})} = 0.8$ nm, which is the *true critical size* for ferroelectricity in FE films in the present study.

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