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

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We 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)]. We 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 (2.5nm) is the same as given by ab-initio calculations, the actual critical thickness is set by the domains at 1.6nm. 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.

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Noh et al. have recently published a series of seminal experimental studies of very thin, down to 5nm, ferroelectric (FE) BaTiO$_3$ capacitors. They obtained hysteresis loops at frequencies up to 100kHz 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, from the Merz’s empirical formula for thickness and exposure time dependence of the activation field for polarization relaxation. Remarkably, the results show that the incomplete screening of the ferroelectric et al. may be different from that in thick films. Finally, we argue that the depolarization field due to incomplete screening by electrodes and limits the polarization retention. Kim speculated that the depolarizing film can be identified with an external field $E_0 = E_{0r}$ that stops the polarization relaxation. They claimed that it coincides with the one estimated from the monodomain ferroelectric is.

It is easy to find the external field $E_0 = E_{0d}$ 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. The homogeneous field in the monodomain ferroelectric is

$$E_f = (E_0 - 2P\lambda/\epsilon_0\epsilon l) / (1 + 2\lambda/\epsilon l).$$

where $E_0 = U/l$ is the external and

$$E_{0d} = -P L_0/\epsilon_0 l,$$  \hspace{1cm}  (2)

the depolarizing field, $L_0$ the characteristic length scale in electrodes, and we have used the fact that in a metal the screening length is small, $\lambda/\epsilon l \ll 1$. The relation between the polarization and the external field $E_0$ is then, using the equation of state renormalized by strain:

$$AhP + BP^3 + CP^5 + FP^7 = \frac{E_0}{1 + 2\lambda/\epsilon l},$$

$$Ah = \hat{A} + \frac{2\lambda}{\epsilon_0(\epsilon l + 2\lambda)} \simeq \hat{A} + \frac{2\lambda}{\epsilon_0\epsilon l}.$$  \hspace{1cm}  (4)

Here we have taken into account that the first coefficient may be renormalized by the additional boundary conditions (ABC), $\hat{A} = A + (2\alpha + \beta)/l$, but in the present case the ABC effect is not important, since the variation of the spontaneous polarization on thickness, where the $(2\alpha + \beta)/l$ term enters, is small, see Fig. 1a (inset). The equation of state for spontaneous polarization $P_s$ takes the form

$$\hat{A} + BP^3 + CP^5 + FP^7 = 0,$$  \hspace{1cm}  (5)

which is readily solved analytically. Since we know from the data the polarization at zero external field, $P_0 = P(E_0 = 0)$, we can indeed easily find $P_s$ from $\hat{A}$. We see from Eq. that $E_f = 0$ when
$E_{0b} = 2\lambda P_s/\left(\varepsilon_0\varepsilon\xi\right)$, the external field for multidomain-single domain boundary.

Finite depolarizing field does not imply that the domains will be detected after a certain observation time. Indeed, $E_{0b} = 1450\text{kV/cm}$ 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 $t_{relax} = 10^3\text{s}$, the domains begin to form only when there is a field $E_f = -1(490 \pm 70)\text{ kV/cm}$ opposite to the polarization (at $E_0 = E_{0b} = 910\text{kV/cm}$ for 5nm sample, raw data from Kim et al.[1]). The activation field strongly depends on FE film thickness for long application time ($\sim 10^3\text{s}$). Indeed, in the $l = 30$ nm FE film the activation field is practically zero, Fig.1a. 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.1b,2. Note that we used Eq. (2) to calculate $E_f$, which applies to homogeneous state. One, however, can apply it to an 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 5nm film the domain width $a = 2.2\text{nm}$ (see below), so this approximation should be semiquantitative. The use of Eq. (2) 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 for 5 nm sample as observed for much longer $10^3\text{s}$ 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 the Merz’s empirical formula in the form

$$E_a = \frac{\alpha\ln\tau}{l},$$

where $\tau$ is the switching time and $\alpha$ the coefficient. It describes a weak dependence of the activation field on the application time for $l = 5\text{nm}$ 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 (6).

We find using Eqs. (1)-(3) that the electric field in short-circuited 5nm sample is $E_f(E_0 = 0) = -1200\text{kV/cm}$, exceeding the magnitude of the estimated activation field. This means that in a short-circuited sample SD state relaxes quicker than in $10^3\text{s}$. 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 $10^3\text{s}$, retention of a SD state. We have found that for $d = 5\text{nm}$ such an electrode should have $\lambda/\varepsilon_e < 0.033\text{A}$. Since in [1] this value is about 0.1A, it does not seem impossible to find such an electrode. Alternatively, thinner films may show longer retention, as Eq. (6) suggests.

An unusual specific feature of replotted loops is that they all have a negative slope, most pronounced at $l = 5\text{nm}$. 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: it is a hallmark of domain structure governed mainly by electrostatics. There are no dead layers in the present films, but the voltage drop happens across a screening layer with the thickness $\lambda$ in an electrode, with an identical result and apparently beyond the precision of Ref. 5. Comparing theory with the data, the expression for the dielectric constant, given by Eq. (31) of Ref. 5, can be simplified to
\[ \epsilon_f \approx -\epsilon_c l / \lambda, \] (7)
where $\epsilon_f = 1 + \epsilon_0^{-1} dP/dE_f |_{E_f=0}$ Substituting the numbers, we find the theoretical value $\epsilon_f = -525$ for equilibrium conditions while the experimental one found from Fig.1b (raw data for 2kHz, Ref.[2]) is $\epsilon_f = -680$, i.e they are pretty close. According to Eq. (7), 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.1b,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 thickness. The loss of stability is signalled by appearance of a non-trivial solution of the equations of state which can be either homogeneous (SD) or inhomogeneous (MD). A homogeneous solution of (3) is possible at $l > l_h$, where $l_h = L_0/\epsilon_0 A$, at room temperature $l_{0RT} = 3.5$nm. The domain instability means the appearance of a solution in form of a “polarization wave” $P = P_k(z)e^{i k z}$ of the linearized equation of state with the gradient term included:
\[ AP - g \nabla_\perp^2 P = E, \] (8)
where $\nabla_\perp^2 = \partial^2_x + \partial^2_y$ is “in-plane” Laplacian. In the case of metallic screening, this gives the following condition 7:
\[ \chi \tan \frac{1}{2} \chi k d = \epsilon_\perp k / \epsilon_\perp \sqrt{k^2 + \lambda^2}, \] (9)
where $\chi^2 = -\epsilon_0 \epsilon_\perp (A + g k^2) > 0$, $\epsilon_\perp$ 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 $\epsilon_\perp \lambda k / \epsilon_\perp \chi \gg 1$. 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 $A_d = -2g_k^2$ at $k = k_c$ where this equality is first met and domains begin to form:
\[ -A_d = 2g_k^2 = \xi / \epsilon_0 l, \quad k_c = \left( \pi^2 / \epsilon_\perp \epsilon_0 g l^2 \right)^{1/4}, \] (10)
where $\xi = 2\pi \sqrt{\epsilon_0 / \epsilon_\perp}$ is the characteristic length scale. Now, checking the assumption that we used to solve the Eq. (7), we see that it boils down to $\lambda e^{1/2} / \epsilon_\perp \left( \epsilon_0 g l \right)^{1/2} \gg 1$. Using values of $\lambda, \epsilon_\perp$ from Ref. 1, the value of $g$ from Ref. 13, and calculating $\epsilon_\perp$ using the coefficients of Ref. 5, we find that this condition is satisfied. From Eq. (10), we obtain the following critical thickness for domains at room temperature:
\[ l_{dRT} = \xi / |A_d| \epsilon_0 \simeq 3.1 \text{ nm}. \] (11)
Since $l_{dRT} < l_{0RT}$, the phase transition is into a MD state. The spatial distribution of a spontaneous polarization is near sinusoidal at $l \gtrsim l_{dRT}$. 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 $a_{dRT} = \pi / k_c = 1.7$ nm at the transition and as $a_{dRT} = 2.2$nm for $l = 5$nm.

It is instructive to consider the phase transition with thickness at zero Kelvin, where we get $\epsilon_j = 408$, $\xi = 0.08$Å, $l_{dRT} = 1.6$nm, $l_{0RT} = 2.5$nm. The last result (homogeneous critical thickness of 2.5nm) is remarkable, since it practically coincides with the ab-initio calculation for the critical thickness of 2.4nm in Ref. 14. The ground state of the film is, however, not homogeneous but multidomain, and the domain ferroelectricity appears in films thicker than $l_{dRT} = 1.6$nm, which is the true “critical size” for ferroelectricity in FE films in the present study.

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