Very large dielectric response of thin ferroelectric films with the dead layers

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(Received 31 October 2000; published 14 March 2001)

We study the dielectric response of ferroelectric (FE) thin films with the ''dead'' dielectric layer at the interface with electrodes. The domain structure inevitably forms in the FE film in the presence of the dead layer. As a result, the effective dielectric constant of the capacitor ϵ_{eff} increases abruptly when the dead layer is thin and, consequently, the pattern of 180° domains becomes ''soft.'' We compare the exact results for this problem with the description in terms of a popular ''capacitor'' model, which is shown to give qualitatively incorrect results. We relate the present results to fatigue observed in thin ferroelectric films.

DOI: 10.1103/PhysRevB.63.132103 PACS number(s): 77.80.Dj, 84.32.Tt, 85.50.−n

We have shown recently that the dead layer forming at the interface between ferroelectric (FE) thin films and electrodes has a drastic effect on the electric response of a capacitor.[1] It has direct bearing on fatigue observed in FE capacitors since in many cases the deterioration of the switching behavior, like the loss of the coercive force and of the squareness of the hysteresis loop, was attributed to the growth of a ''passive layer'' at the ferroelectric-electrode interface.[2–5] It is of principal importance that the presence of a dead layer, no matter how thin in comparison with thickness of the ferroelectric layer, triggers a formation of the domain structure in FE films.[1] We have shown that when the thickness of the dead layer d is not very small, the apparent (net) polarization P_a of the ferroelectric film with 180° domain walls follows an approximate relation $dP_a/dE \propto \epsilon_g/d$, which is in good correspondence with available experimental data (see e.g., Refs. 6 and 7, and references therein). Importantly, the response of this structure to an external bias voltage becomes more *rigid* when d increases, i.e., when the dead layer grows, even in the *absence* of pinning by defects.

The implication for real systems is that with the growth of the passive layer the hysteresis loop very quickly deteriorates and *loses its squareness*, as observed. The approximate $1/d$ dependence of the response suggests that the effective dielectric constant of the capacitor

$$\epsilon_{eff} = \frac{4\pi LC}{\mathcal{A}} \tag{1}$$

may become *very large* when the layer is thin. Here C is the capacitance of the electroded FE film of area $\mathcal{A}$, with L the separation between electrodes. Indeed, when the dead layer is thin, the domain width a becomes very large, and it grows exponentially with $1/d^2$.[1] The response of this domain structure is very soft, and this should translate into a very abrupt increase of the dielectric constant ϵ_{eff} of the capacitor. It is easy to show that in the present case (180° domains) the linear response is not changed by electromechanical effect, the change in ϵ_{eff} only appearing in quadratic terms in external field, but here we are interested in the zero-field value of ϵ_{eff} only. We have assumed a quadratic coupling between the elastic strains and the polarization (as in perovskites). In this case the linear response of the 180° domain structure without pinning is not affected by intimate contact between the ferroelectric and the dead layers (excluding mere renormalization of material constants by homogeneous stresses). Note that this is invalid in the case of 90° domains[8] or a linear coupling between the strain and the polarization.[9]

Here we address the anomalous behavior of the dielectric constant ϵ_{eff} in detail. We also discuss the important issue regarding the relation of the present results to the so-called ''capacitor'' model.[3,4,6] The ''capacitor'' model (incorrectly) presumes that the dielectric response of the dielectric layer is not affected by the presence of the dead layer, so the system looks like capacitances in series. We show that the effective ''dielectric constant'' of the FE layer ϵ_f, as found in the ''capacitor'' model,[3,4,6] is actually *negative*. In spite of this the system remains stable (the stiffness of the domain pattern is positive). The reason for this apparently unusual behavior is that the ''dielectric constant'' of the FE layer ϵ_f is the nonlocal quantity that characterizes the whole system. This nonlocal behavior is due to long-range Coulomb interaction, which makes the response rigid even when the FE film itself would have a negative ''dielectric constant'' (cf., Ref. 10, Fig. 1). The ''capacitor'' model neglects this essentially nonlocal behavior and, therefore, is hardly applicable to the problem of the dielectric response of thin ferroelectric films, and to the problem of fatigue for that matter. The present considerations remain valid until the period of the domain structure becomes much smaller than the *lateral size* of the film (or the grain size). Those will set some cutoffs for the effects considered below.

We shall find the response of a ferroelectric film under a bias voltage U with thickness l separated from the top and bottom electrodes by passive layers with thickness $d/2$ (Fig. 1, inset) with the use of the thermodynamic potential[1]

$$\tilde{F} = F_s + \tilde{F}_{es}, \tag{2}$$

$$\tilde{F}_{es} = \int dV E^2/(8\pi) - \sum_a^{\text{electrodes}} e_a \varphi_a . \tag{3}$$

Here F_s is the surface energy of the domain walls, $\tilde{F}_{es}$ is the electrostatic energy, $\vec{E}$ is the electric field, and e_a (φ_a) is the charge (potential) on the electrode a. The last term in Eq. (3)

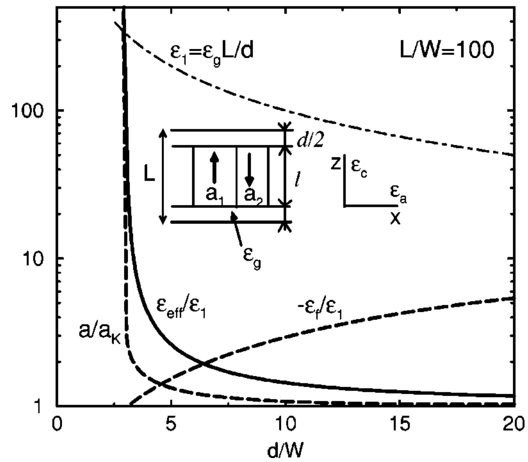

FIG. 1. The dielectric constants of the ferroelectric film with the dead layers of thickness $d/2$, as defined in the text. W is the domain-wall thickness. Note an abrupt increase of the effective dielectric constant of the capacitor ϵ_{eff} in comparison with $\epsilon_1=\epsilon_g L/d$, and that the ''dielectric constant'' of the FE layer is *negative*, $\epsilon_f<0$. The relation $\epsilon_{eff}\approx\epsilon_1$, which follows from the ''capacitor'' model, is clearly violated when the dead layer is thin and the domain width a is large ($\gg a_K$, the Kittel width). Inset shows schematics of the electroded ferroelectric film (capacitor) with the dead layers.

accounts for the work of the external voltage source(s). Note that the results would not change qualitatively if there were only one dead layer, since the accompanying depolarizing field would have the same effect.

We are interested in a case when the ferroelectric film has the spontaneous polarization $\vec{P}_s \| z$ (Fig. 1, inset), i.e., we are considering the case of 180° domain walls. The uniaxial ferroelectric film has the dielectric constant ϵ_c (ϵ_a) in the z direction (in the xy plane), and the dielectric constant of the passive layer is ϵ_g. We select the x axis perpendicular to the domain walls. The potential φ, which is related to the electric field in the usual way $\vec{E}=-\nabla\varphi$, satisfies the following equations of electrostatics in the ferroelectric and the passive layer,[1]

$$\epsilon_a \frac{\partial^2\varphi_f}{\partial x^2}+\epsilon_c\frac{\partial^2\varphi_f}{\partial z^2}=0, \quad \frac{\partial^2\varphi_g}{\partial x^2}+\frac{\partial^2\varphi_g}{\partial z^2}=0, \tag{4}$$

with the boundary conditions $\varphi=-(+)U/2$, $z=+(-)(l+d)/2$, and

$$\epsilon_c\frac{\partial\varphi_f}{\partial z}-\epsilon_g\frac{\partial\varphi_g}{\partial z}=4\pi\sigma(x), \quad \varphi_f=\varphi_g, \quad \text{at } z=l/2, \tag{5}$$

where the subscript f (g) denotes the ferroelectric (passive layer, or a vacuum gap). Here σ is the density of the bound charge due to spontaneous polarization at the ferroelectric-passive layer interface $\sigma=P_{ns}=\pm P_s$, depending on the normal direction of the polarization at the interface, alternating from domain to domain (see Fig. 1), inset. Thus, we assume that the absolute value of the *spontaneous* part of the polarization P_s is constant in all domains and only its direction is alternating from domain to domain. We have also assumed a usual separation of linear and spontaneous polarization, so that the displacement vector is $D_i=\epsilon_{ik}E_k+4\pi P_{si}$, where $i,k=x,y,z$, and the dielectric response ϵ_{ik} is uniaxial, (see Fig. 1 inset). Within this approximation we obtain

$$\tilde{F}_{es}=\frac{1}{2}\int_{\mathrm{FE}} d\mathcal{A}\sigma\varphi-\frac{1}{2}\sum_{a}^{\mathrm{electrodes}} e_a\varphi_a, \tag{6}$$

where $\sigma=\pm P_s$ is the density of the *bound charge* given by *only* the spontaneous polarization at the interface between the FE and the dead layers. The periodic pattern consists of c domains with widths a_1 and a_2, and the period $T=a_1+a_2$. The solution of Eq. (4) is then readily found by Fourier transformation,

$$\sigma(x)=\sum_k \sigma_k e^{ikx}, \quad \varphi_\alpha(x,z)=\sum_k \varphi_{k\alpha}(z)e^{ikx}, \tag{7}$$

$$\sigma_k=\frac{2iP_s}{kT}[1-\exp(ika_1)], \quad k\neq 0, \tag{8}$$

$$\sigma_{k=0}\equiv\sigma_0=P_s\frac{a_1-a_2}{a_1+a_2}\equiv P_s\delta, \tag{9}$$

where $k=2\pi n/T=\pi n/a$; $n=0,\pm1,\dots$; $a\equiv(a_1+a_2)/2$; and the index $\alpha=f,g$ marks the quantities for the FE layer and the dead layer. Note that by definition $P_a\equiv\sigma_0$ is the net spontaneous polarization of the FE layer. We obtain

$$\tilde{F}_{es}=\tilde{F}_h+\tilde{F}_{inh}, \tag{10}$$

$$\frac{\tilde{F}_h}{\mathcal{A}}=\frac{4\pi\sigma_0 d-\epsilon_g U}{\epsilon_g l+\epsilon_c d}\frac{l\sigma_0}{2}+\frac{1}{2}\sigma_0^{el}U, \tag{11}$$

$$\frac{\tilde{F}_{inh}}{\mathcal{A}}=\sum_{k\neq 0}\frac{4\pi|\sigma_k|^2}{kD_k}, \tag{12}$$

where

$$D_k=\sqrt{\epsilon_a\epsilon_c}\coth\left[\left(\frac{\epsilon_a}{\epsilon_c}\right)^{1/2}\frac{kl}{2}\right]+\epsilon_g\coth\left(\frac{kd}{2}\right), \tag{13}$$

and

$$\sigma_0^{el}=-\frac{\epsilon_g}{4\pi}\frac{4\pi l\sigma_0+\epsilon_c U}{\epsilon_g l+\epsilon_c d} \tag{14}$$

is the net charge density induced on the electrode at $z=L/2$. One can calculate the apparent dielectric constant of the whole capacitor from

$$\epsilon_{eff}=4\pi L\sigma_0^{el}/U. \tag{15}$$

The term $\tilde{F}_h$ in Eq. (10) is due to the net polarization of the FE film induced by the bias voltage U, with the first term in $\tilde{F}_h$ (11) corresponding to the term $k=0$, singled out in the stray field energy $\tilde{F}_{inh}$ (12). With the use of σ_k from Eq. (8) we obtain

$$\frac{\tilde{F}_{inh}}{P_s^2\mathcal{A}}=\frac{32a}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^3D_{2n+1}}+\frac{16a}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^3}\frac{1-\cos\pi n\delta}{D_n},\qquad(16)$$

where $D_n=D_{k_n}$, and $k_n=\pi n/a$.

The total free energy of the domain pattern per unit area is

$$\frac{\tilde{F}}{\mathcal{A}}=\frac{\gamma l}{a}+\frac{\tilde{F}_h+\tilde{F}_{inh}}{\mathcal{A}},\qquad(17)$$

where $\gamma=P_s^2\Delta$ is the surface energy of the domain wall, with Δ the characteristic microscopic length.[1] This free energy allows one to determine the equilibrium properties and response of the domain pattern to external field.

We can determine a linear response of the system to bias voltage from the total energy (17) that for small bias U can be expanded up to terms quadratic in U and σ_0,

$$\frac{\tilde{F}}{\mathcal{A}}=\frac{\tilde{F}_{stray}(a)}{\mathcal{A}}+\frac{1}{2}S\sigma_0^2-RU\sigma_0,\qquad(18)$$

where $\sigma_0\equiv P_s\delta$, and $\tilde{F}_{stray}$ is the usual stray energy $\tilde{F}_{stray}(a)=\tilde{F}_{inh}(a;\,\sigma_0=\delta=0)$, given by the first term in Eq. (16). This expression results from expanding Eqs. (12) and (16) in powers of U and δ (note that $\sigma_0\equiv P_s\delta$). Here S is the stiffness of the domain structure with respect to external bias voltage U [we have omitted the constant term $\propto U^2$ in Eq. (18)]. We have

$$R=\frac{\epsilon_g l}{\epsilon_g l+\epsilon_c d},\qquad(19)$$

$$S=S_h+S_{inh},\qquad(20)$$

$$S_h=\frac{4\pi dl}{\epsilon_g l+\epsilon_c d},\qquad(21)$$

where S_{inh} is the (negative) contribution of the inhomogeneous (stray) energy, corresponding to the second term in Eq. (16),

$$S_{inh}=16a\sum_{n=1}^{\infty}\frac{(-1)^n}{nD_n}.\qquad(22)$$

We can now consider the following limiting cases:

(i) Thick dead layer ($a\ll d$). There we can replace both coth's in Eq. (13) by unity, with the result

$$\frac{\tilde{F}(\delta=0)}{P_s^2\mathcal{A}}=\frac{\Delta l}{a}+\frac{28\zeta(3)a}{\pi^2\tilde{\epsilon}},\qquad(23)$$

with $\tilde{\epsilon}=\sqrt{\epsilon_a\epsilon_c}+\epsilon_g$. The domain structure has a minimum energy for the equilibrium (Kittel) domain width

$$a=a_K\equiv\left(\frac{\pi^2\tilde{\epsilon}}{28\zeta(3)}\Delta l\right)^{1/2}.\qquad(24)$$

Then the inhomogeneous contribution to stiffness $S_{inh}\approx-(16\ln 2/\tilde{\epsilon})a_K$, Eq. (22), and we obtain from Eqs. (20) and (21)

$$S=\frac{4\pi dl}{\epsilon_g l+\epsilon_c d}-\frac{16\ln 2}{\tilde{\epsilon}}a_K.\qquad(25)$$

When $d\gtrsim a_K$, one can neglect the second (stray) term in this expression for stiffness, thus recovering our approximate expression for the net spontaneous polarization $P_a\equiv\sigma_0$ of the ferroelectric film from Eq. (18),[1]

$$\frac{P_a}{U}=\frac{R}{S}\approx\frac{\epsilon_g}{4\pi d}.\qquad(26)$$

This approximation breaks down for thinner films but it is obvious that the response becomes *softer* for *thinner* dead layers. The breakdown of this approximate behavior has also been noticed by Kopal *et al.* for a similar model,[11] but they have not analyzed what actually happens to the response at very small thicknesses d of the dead layer. Note that $S_{inh}<0$, Eq. (22), and, consequently, the following inequality always holds: $P_a/U>\epsilon_g/4\pi d$.

(ii) Thin dead layer ($a\gg d$). In this case the replacement of coth by unity is not allowed. For $a\lesssim l$ and $\sqrt{\epsilon_a\epsilon_c}=\epsilon_g$ we have $D_n=\epsilon_g(1+\coth kd/2)$ and

$$\frac{\tilde{F}_{inh}}{P_s^2\mathcal{A}}=\frac{16a}{\pi^2\epsilon_g}\left[\frac{7}{8}\zeta(3)-Li_3(e^{-b})+\frac{1}{8}Li_3(e^{-2b})\right],\qquad(27)$$

$$S_{inh}=-\frac{8a}{\epsilon_g}\ln\frac{2}{1+e^{-b}},\qquad(28)$$

where $b=\pi d/a$, and $Li_n(z)=\Sigma_{k=1}^{\infty}z^k/k^n$.[12] By using the asymptotic expansion of $Li_n(z)$ we obtain for $d\ll a$ our earlier result[1]

$$a=\frac{\pi d}{2e^{1/2}}\exp\left(\frac{\epsilon_g\Delta l}{4d^2}\right),\qquad(29)$$

which corresponds to a very abrupt increase of the domain width to values $a\gg a_K$, with a_K the Kittel width (24) when the dead layer is very thin, Fig. 1. This approximation, however, is not sufficient to make an estimate of the stiffness for very thin dead layers. Indeed, formally the stiffness there becomes small and negative, $=4\pi d[1/(\epsilon_g+\epsilon_c d/l)-1/\epsilon_g]<0$. This fact simply indicates that for thin dead layers the stiffness diminishes $S\to 0$ and has to be calculated accurately. The exact results, illustrating the abrupt softening of the dielectric response for small d, are shown in Fig. 1.

One may wish to interpret the approximate result for slope of the net polarization $P_a\propto 1/d$, given by Eq. (26), in terms of the ''capacitors in series'' model.[4,6] Indeed, a similar result follows if one were to assume that the capacitance of the dead layer $\propto 1/d$ dominates at small thicknesses of the layer d.

An opinion has even been voiced that the effective dielectric constant of the FE layer ϵ_f is infinite since the domain walls in our model are not pinned.[13] However, such an interpretation would be incorrect since ϵ_f, as found in the ''capacitor'' model, is not infinite, but finite and actually *negative*. To establish this, one has to find the voltage drops across the dead layer and the FE film. The homogeneous part of the electric fields inside the FE (dead) layer E_f (E_d) and the corresponding voltage drops are found from the standard equations

$$E_d d + E_f l = U,$$

$$\epsilon_g E_d = \epsilon_c E_f + 4\pi P_a, \tag{30}$$

wherefrom one can, for instance, easily recover the expression (14) for the net charge density on electrodes. One obtains the ''capacitor'' model by assuming that the interface between the FE film and the dead layer is equipotential and can be viewed as the metallic film separating the two areas. Simple calculation gives

$$\epsilon_f \equiv \frac{4\pi l \sigma_0^{el}}{U_f} = \epsilon_c \frac{1 + 4\pi P_a l/(\epsilon_c U)}{1 - 4\pi P_a d/(\epsilon_g U)} < 0 \quad (!), \tag{31}$$

$$\epsilon_{eff} \equiv \frac{4\pi L \sigma_0^{el}}{U} = \frac{L \epsilon_g \epsilon_c}{\epsilon_c d + \epsilon_g l}[1 + 4\pi P_a l/(\epsilon_c U)], \tag{32}$$

where $U_f \equiv E_f l$. Since always $P_a/U > \epsilon_g/4\pi d$, Eq. (26), we obtain $\epsilon_f < 0$, Fig. 1. In spite of the formally negative ''dielectric constant'' of the ferroelectric layer ϵ_f, Eq. (31), which is an artifact of the ''capacitor'' model,[3,4,13] the system remains stable (the stiffness of the domain pattern is positive). Indeed, shifting the domain walls would create a net electric field, and its energy is the source of finite stiffness of the domain pattern, even when the walls are *not pinned*, as is well known since 1960.[14] The reason for this apparently unusual behavior is that the ''dielectric constant'' of the FE layer ϵ_f in Eq. (31) is the nonlocal quantity that characterizes the whole system: it depends on the properties of the dead layer. This nonlocal behavior is due to long-range Coulomb interaction, which makes the response rigid even when the FE film itself would have a negative ''dielectric constant'' (for an analogous situation in FE films with depletion charge see Ref. 10, Fig. 1). Thus, the ''capacitor'' model actually operates with obscure quantities without much physical meaning.

We illustrate the difference between the exact results for ϵ_{eff} and results from the ''capacitor'' model $\epsilon_{eff} \approx \epsilon_1 \equiv \epsilon_g L/d$ in the assumption $\epsilon_f = \infty$ (Ref. 13) in Fig. 1. The softness of the domain structure, characterized by P_a/U, increases very abruptly when the dead layer is thin and the width of the domains is $a \gg a_K$ (Kittel width). According to Eq. (32), ϵ_{eff} increases abruptly and becomes $\gg \epsilon_1$ in this region (Fig. 1), in stark deviation from the prediction of the ''capacitor'' model $\epsilon_{eff} \approx \epsilon_1$.[13] For thick ''dead layers'' the effective dielectric constant ϵ_{eff} becomes comparable to ϵ_1.[1]

We think that the above clearly demonstrates a danger of applying a naive electric circuit analysis to FE systems where the addition of one ''circuit element'' (dead layer) radically changes the electric response of the other (FE layer) by introducing a domain structure. It is not surprising, therefore, that such an approach cannot explain a fatigue observed in FE films (see, e.g., Refs. 6 and 7 and references therein). Certainly, there might be various reasons for the fatigue in FE capacitors. We simply observe that the growth of the dead layer at the interface with electrodes makes the dielectric response of the film *rigid* even when the domain walls are *not pinned*. The present mechanism gives a correct order of magnitude for the tilt of the hysteresis loops,[1] therefore the growth of the passive layer might be the main source of fatigue. In the limiting case of thin dead layers the period of the ferroelectric domains in the absence of pinning becomes much larger than the standard Kittel width. As a consequence, the domain pattern becomes very ''soft'' in the absence of the pinning of the domain walls, and its contribution to the dielectric response becomes very large, since the domains with polarization parallel to the external field can easily grow at the expense of the domains with the opposite polarization.

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[14] C. Kooy and U. Enz, Philips Res. Rep. **15**, 7 (1960). Those authors gave a transcendental equation for magnetization versus magnetic field $M = M(H)$ for a slab of ferromagnetic material in terms of some series that were evaluated numerically. Note that the effects of screening of electric field by electrodes, which are responsible for the present unusual behavior of the domain pattern in the ferroelectric capacitor, have no analogy in magnetic systems.