Size effect on permittivity in ferroelectric polydomain thin films

P. Mokrý,* A. K. Tagantsev, and N. Setter
Ceramics Laboratory, Materials Department, EPFL Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland
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The impact of electrode-adjacent passive layers on the small signal dielectric response of a ferroelectric film containing a 180°-domain pattern has been analyzed. It is shown that, for a realistic physical situation, the so-called "in-series capacitors formula" is still applicable for the description of the dielectric response of this system, however, with some apparent values of the passive-layer permittivity $\varepsilon_{\mathrm{mod}}$, which is a function of parameters of the ferroelectric and the layers. It is also shown that the suppressive effect of the passive layer on the permittivity of the ferroelectric film can be significantly reduced when the permittivity of the ferroelectric is mainly controlled by the extrinsic (domain) contribution.

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The large dielectric response of ferroelectrics is known to be easily affected by many factors such as the electric field, mechanical stress, or lattice imperfections. One comes across these phenomena in ferroelectric thin films and ceramics where the dielectric response in the regions close to the film surface or grain boundaries may be essentially reduced due to aforementioned factors. As a result the whole system feels these regions as low dielectric constant (passive) layers inserted in or attached to the high permittivity material. When oriented perpendicular to the applied field, these layers behave as capacitances connected in series to the remaining high permittivity parts of the material and may tremendously decrease the effective permittivity of the material. It is this effect that is presently pleaded guilty for the difference of dielectric constants in thin films.[1]

For the interpretation of suppression effect of the passive layer, one routinely uses the in-series capacitor formula. For the description of the out-of-plane capacitance C of a sandwich ferroelectric/dielectric structure of an area A, this formula reads

$$\varepsilon_0 A/C = (h/\varepsilon_f) + (d/\varepsilon_d), \tag{1}$$

where h and ε_f are the thickness and permittivity of the ferroelectric layer and d and ε_d are those of the dielectric layer, respectively, $\varepsilon_0 = 8.854\times10^{-12}$ F/m. The real experimental situation always corresponds to the passive layer, which is much thinner than the ferroelectric layer, $h \gg d$. Equation (1) describes the capacitance of a parallel plate capacitor containing the sandwich structure, in which electric field is homogeneous in the capacitor plane. Strictly speaking Eq. (1) may not work if the dielectric permittivity of the ferroelectric is controlled by the domain contribution. The reason for this is that, in the presence of the passive layer, the domain structure of the ferroelectric will lead to the appearance of inhomogeneous (stray) fields in the vicinity of the layer.[2] Thus, an important question arises: Can the in-series capacitor formula be applied for the description of the permittivity of ferroelectric/dielectric structures in the case where the permittivity of the ferroelectric is essentially controlled by the domain contribution?

Some theoretical studies that could answer this question were performed in terms of a model of ferroelectric capacitor with a domain pattern and two dielectric layers,[3,4] as shown in Fig. 1. However, a very important aspect of the problem was neglected in these papers. Namely, the lattice pinning of domain walls in the ferroelectric (due to their coupling with crystalline potentials and defects), which essentially controls the permittivity even in high quality crystals,[5] was ignored. For this reason, the prediction of these papers, an infinite dielectric permittivity in the limit of a vanishing passive layer, is inconsistent with a finite permittivity of any real ferroelectric material. Another simplification made in Refs. 3 and 4 is that only the case of the equilibrium 180° domain pattern was considered. This kind of pattern was never experimentally observed in the layered ferrolectric/dielectric structures. In real systems, the domain pattern is expected to be controlled by the prehistory of the sample so that the domain spacing may be essentially different from its equilibrium value. In view of the aforementioned simplifications, the discussion of the problem[2,4,6] based on results obtained in Refs. 3 and 4 cannot be considered as conclusive. Thus, the problem of applicability of in-series capacitor formula to the polydomain situation remained open.

In this Brief Report, we address this problem in terms of the same model as in the previous works (see Fig. 1), however, our analysis is free of the principle simplification adopted in the earlier works—we do not neglect the lattice pinning of the domain walls. We consider the permittivity of the ferroelectric itself as being controlled by the sum of intrinsic and finite domain (extrinsic) contributions. We mean that if the ferroelectric with the given domain pattern were

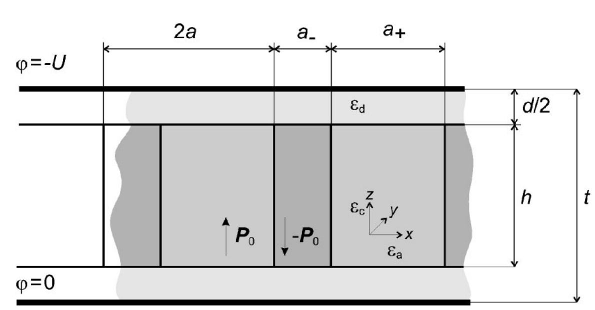

FIG. 1. Schema of the electroded ferroelectric film with passive layers. It is always considered that $h \gg d$.

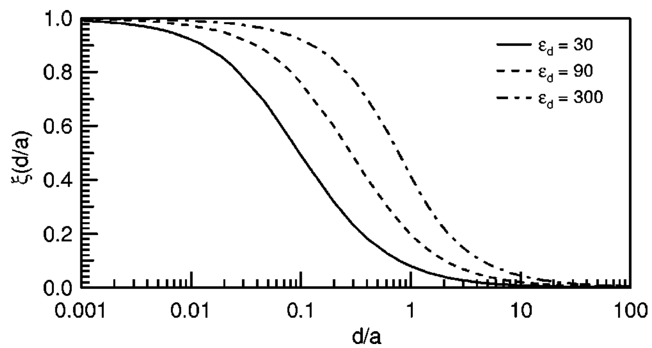

FIG. 2. Function $\xi(d/a)$ versus the fraction d/a for three values of the passive layer permittivity ε_d; ε_a, $\varepsilon_c=300$.

placed in a passive-layer-free capacitor, the permittivity $\varepsilon_f=\varepsilon_c+\varepsilon_m$ would be measured, where ε_c and ε_m are the crystal lattice and extrinsic contributions. In addition, we do not restrict our analysis to the case of the equilibrium domain pattern.

The principle result of the Brief Report is that in the case where the domain pattern in the ferroelectric is dense (i.e., the domain spacing is smaller than the thickness of the ferroelectric), Eq. (1) can be generalized to the form

$$\varepsilon_0 A/C=(h/\varepsilon_f)+(d/\varepsilon_{\mathrm{mod}}), \tag{2}$$

with $\varepsilon_{\mathrm{mod}}$ being the apparent permittivity of the passive layer

$$\varepsilon_{\mathrm{mod}}=\frac{\varepsilon_d}{1-(\varepsilon_m/\varepsilon_f)^2\xi(d/a)}, \tag{3}$$

where d and a stand for the thickness of the passive layer and the the domain spacing, respectively. The function $\xi(d/a)$ reaches values of 1 to 0 in the limits of $d/a\to 0$ and $d/a\to\infty$, respectively. For the periodic and symmetric domain pattern ($a_+=a_-$ in Fig. 1), the function $\xi(d/a)$ is given by Eq. (13) and shown in Fig. 2. Thus, the derived relation justifies the use of the in-series capacitors approach for the analysis of the dielectric response of polydomain ferroelectric films. At the same time, this analysis shows a way of getting additional information on the parameters of the studied system.

To obtain the above result, we follow Refs. 2 and 3. Using the "hard ferroelectric" approximation, we express the electric displacement of the ferroelectric layer as a sum of the constant spontaneous polarization P_0 (whose orientation alters from domain to domain) and the linear dielectric response of the crystal lattice:

$$D_x=\varepsilon_0\varepsilon_a E_x, \tag{4a}$$

$$D_z=\varepsilon_0\varepsilon_c E_z\pm P_0. \tag{4b}$$

We adopt the thermodynamic potential (per unit area of the sample) of the system with a given voltage U on the electrodes $G=G_{\mathrm{el}}+G_m$, which includes, first, the energy of the electric field with the subtracted work produced by the external voltage sources G_{el} and, second, the lattice pinning energy of the domain wall in the ferroelectric itself G_m. In order to calculate the small signal dielectric response, we use the lowest (linear and quadratic) terms of the expansion of G with respect to the average (net) spontaneous polarization of the ferroelectric layer $P_N=P_0(a_+-a_-)/(2a)$. Symbols a_+ and a_- stand for the width of domains where the vector of the spontaneous polarization is oriented along and against the direction of the applied electric field, respectively. We address in detail the case of the symmetric $(a_+=a_-)$ domain pattern, i.e., we set $P_N=0$ in the absence of the applied voltage U.

For the considered situation, the leading terms of G_{el} are readily available in the literature[2,3] in the form

$$G_{\mathrm{el}}=h\left[\frac{P_N^2}{2\varepsilon_0\varepsilon_{\mathrm{el}}}-\frac{P_N U/h}{1+\varepsilon_c d/(\varepsilon_d h)}\right], \tag{5}$$

where

$$\frac{1}{\varepsilon_{\mathrm{el}}}=\frac{d}{\varepsilon_d h+\varepsilon_c d}+\frac{4a}{\pi h}\sum_{n=1}^{\infty}\frac{(-1)^n}{nD_n}, \tag{6}$$

$$D_n=\varepsilon_d\coth\frac{n\pi d}{2a}+\sqrt{\varepsilon_a\varepsilon_c}\coth\left(\sqrt{\frac{\varepsilon_a}{\varepsilon_c}}\frac{n\pi h}{2a}\right).$$

Here the parameter $1/\varepsilon_{\mathrm{el}}$ has the meaning of the contribution to the inverse dielectric susceptibility of the system, which is controlled by the electrostatic energy of the domain pattern.

Function G_m can be expressed in terms of the extrinsic contribution ε_m to permittivity (in the sense as it was introduced above[7]):

$$G_m=\frac{hP_N^2}{2\varepsilon_0\varepsilon_m}. \tag{7}$$

Then, the function G has a compact form

$$G=h\left[\frac{P_N^2}{2\varepsilon_0\varepsilon_w}-\frac{P_N U/h}{1+\varepsilon_c d/(\varepsilon_d h)}\right], \tag{8}$$

where $1/\varepsilon_w=1/\varepsilon_m+1/\varepsilon_{\mathrm{el}}$.

The response of the net spontaneous polarization P_N to the voltage U applied to the capacitor can be found from the condition for the minimum of the thermodynamic potential G:

$$\partial G(P_N,U)/\partial P_N=0. \tag{9}$$

To calculate the effective capacitance per unit area of the system C/A, Eqs. (5)–(9) should be appended with the relation

$$C/A=\frac{P_N/U+\varepsilon_0\varepsilon_c/h}{1+\varepsilon_c d/(\varepsilon_d h)} \tag{10}$$

obtained in Refs. 2 and 3. Finally, Eqs. (5)–(10) yield

$$\frac{\varepsilon_0 A}{C}=\frac{h}{\varepsilon_c+\varepsilon_w}+\frac{d}{\varepsilon_d}\left[1-\left(\frac{\varepsilon_w}{\varepsilon_c+\varepsilon_w}\right)^2\frac{h}{h+h_c}\right], \tag{11}$$

where

$$h_c=\frac{d}{\varepsilon_w}\frac{\varepsilon_c^2}{\varepsilon_c+\varepsilon_w}.$$

Though formula (11) is similar to the in-series capacitors formula given by Eq. (1), the contribution of domain walls movements to the dielectric response of the system ε_w contains the function $\varepsilon_{\rm el}$, which depends, in general, on the film thickness h. Thus in general, Eq. (11) is not consistent with Eq. (1). However, in the addressed case of the dense domain pattern (i.e., for $h > a$), Eq. (11) can be simplified down to the form consistent with Eq. (1), which will be referred to below as the *dense pattern approximation*:

$$\frac{\varepsilon_0 A}{C} = \frac{h}{\varepsilon_c + \varepsilon_m} + \frac{d}{\varepsilon_d}\left[1 - \left(\frac{\varepsilon_m}{\varepsilon_c + \varepsilon_m}\right)^2 \xi(d/a)\right], \qquad (12)$$

where

$$\xi(\tau) = \frac{4\varepsilon_d}{\pi\tau}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{nD_n^{\infty}(\tau)}, \qquad (13)$$

$$D_n^{\infty}(\tau) = \varepsilon_d \coth(n\pi\tau/2) + \sqrt{\varepsilon_a\varepsilon_c}. \qquad (14)$$

Here $\xi(\tau)$ is a function decreasing from 1 to 0 with increasing τ. The plots of this function for three sets of the parameters of the studied system are shown in Fig. 2.[8] Taking into account that $\varepsilon_f = \varepsilon_c + \varepsilon_m$, we thus arrive at the result announced above, Eqs. (2) and (3). The physical reason for the simplification of the h dependence of the inverse capacitance of the system down to a linear one is as follows. In the case of the dense domain pattern the stray fields created by the periodic charge distribution at one electrode essentially decay within the distance of about a from this electrode. Thus, the effective capacitance of the passive layer becomes independent of the film thickness.

Comparing the obtained result to the simple "in-series" formula, (1), we see that though the slope of the h dependence is the same (permittivity of the ferroelectric itself), in the polydomain case, the offset of this dependence brings information not only on the d/ε_d parameter of the passive layer but also on the period of the domain pattern and the distribution of the dielectric response of the ferroelectric material itself between the intrinsic (ε_c) and extrinsic (ε_m) contributions.

The effect of the domain spacing on the offset of the h dependence of the inverse capacitance predicted by Eq. (12) is illustrated in Fig. 3. It is seen that, in the polydomain case, this offset can be essentially smaller than that predicted by the simple "in-series" formula shown with dashed line. In this figure, the predictions of the dense pattern approximations (12), are compared to those of the exact formula Eq. (11). It is seen that, for dense domain patterns, i.e., for $h > a$, the former provides a very good approximation. The sensitivity of the extrapolated offset of the h dependence of the inverse capacitance to the distribution of the dielectric response of the ferroelectric material between the extrinsic and intrinsic contributions is seen from Eq. (12). The greater the fraction $\varepsilon_m/\varepsilon_f$, the greater the difference between the apparent permittivity $\varepsilon_{\rm mod}$ and the passive layer permittivity ε_d.

Two qualitative predictions following from the results presented in this Brief Report are worth mentioning. First, in the limit of thick passive layer $d \gg a$, the dense pattern approximation (12), reduces down to Eq. (1) disregarding the other parameters of the system, since $\xi(d/a) \to 0$ at $d/a \to \infty$. The physical reason behind this effect is that, in this case, the stray fields occupy only a small ($\sim a/d$) fraction of the passive layer so that their contribution to the total energy and inverse permittivity [the sum in Eq. (6)] can be neglected. This readily leads to $\xi(d/a) \to 0$.

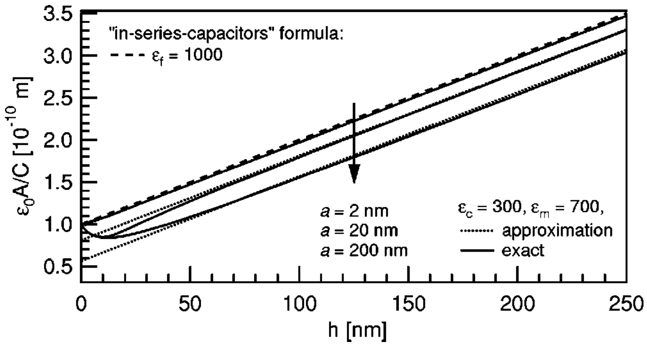

FIG. 3. Inverse capacitance per unit area of the ferroelectric capacitor $\varepsilon_0 A/C$ versus the thickness of the ferroelectric layer h for different values of the domain spacing a; $d=2$ nm and $\varepsilon_d=20$. The results of the exact theory are compared with their dense pattern approximation and "in-series" formula. Note that the offset of the approximation $d/\varepsilon_{\rm mod}$ decreases with an increase of the domain spacing a. For $a=2$ nm, all three curves concides.

The second prediction relates to the situation where the permittivity of the ferroelectric itself is dominated by the extrinsic contribution, i.e., $\varepsilon_m \gg \varepsilon_c$, and the domain spacing significantly exceeds the thickness of the passive layer, i.e., $a \gg d$. In this case $\varepsilon_m/(\varepsilon_c+\varepsilon_m) \to 1$ and $\xi(d/a) \approx 1 - \pi d/(4a)$, so that the two terms in the bracket in Eq. (12) start to cancel each other. Physical interpretation of this phenomenon is that, in this case, the energy densities of the depolarizing fields in opposite domains are equal to within $d/a \to 0$, disregarding the value of the ratio a_+/a_- of the domain pattern. This implies an essential reduction of the suppressive effect of the passive layers, which is driven by the difference in these energy densities. In terms of the effective capacitance density of the passive layer, this corresponds to its increase from $\varepsilon_0\varepsilon_d/d$ to $(\varepsilon_0\varepsilon_d/d)\ (4a/\pi d)$.

For the special case of infinite domain wall mobility, i.e., in the limit $\varepsilon_m \to \infty$ (so that $\varepsilon_f \to \infty$), our both aforementioned conclusions are consistent with the results by Kopal *et al.*[3] and Bratkovsky and Levanyuk.[2] The above analysis addresses the case of the dense, periodic, and symmetric domain pattern. However, some of the results obtained above can be readily extended to the more general case of a dense pattern, which can be characterized by a typical domain spacing a. Namely, the qualitative conclusions of the two preceding paragraphs hold for the more general case, since the physical argumentations summoned for these conclusions are equally applicable to this case. Formal estimates[9] performed for this case showed that, in the limits $d/a \to 0$ and $d/a \to \infty$, the main result of the Brief Report, Eqs. (2) and (3), holds (with $\xi=1$ and $\xi=0$), respectively.

The key element of our model, *taking into account the finite domain wall mobility in the ferroelectric itself*, makes the model quite realistic. However, we should recognize three factors limiting its applicability. First, we consider films with 180° domains crossing the film thickness from one electrode to another. Second, following the analysis in Refs. 2 and 3 we consider that domain walls are straight. Due to inhomogeneous fields, effects of domain wall bending can contribute to the dielectric response of a ferroelectric material. Straightforward electrostatic calculations show that the domain wall bending contribution to the free energy is $G \propto aP_N^2/\varepsilon_0$ with a proportionality factor of about 1.[9] When this term is much smaller than G_m [given by Eq. (7)] the effects of domain wall bending are negligible. The above condition leads to an estimate for the upper limit of the film thickness h below which our theory is applicable: $h \ll \varepsilon_m a$. Finally, the applicability of our macroscopic theory fails for ultrathin films (e.g., films of thicknesses of about a few unit cells).

We believe that the obtained results provide an efficient and simple tool for the interpretation of the dielectric data on ferroelectric thin films. As a prediction of the theory ready to be checked experimentally, we can indicate the temperature dependence of the extrapolated offset of the A/C vs h dependence. Namely, in the films where the dielectric data in the paraelectric phase suggests the presence of a passive layer [based on Eq. (1)], the aforementioned offset in the ferroelectric phase may be essentially temperature dependent due to expected temperature dependence of the ratio $\varepsilon_m/\varepsilon_c$. The only relevant experiment available to date is that on thin films of ferroelectric copolymer of vinidilene fluoride and tetrafluorethylene.[10] In this work, Takahashi *et al.* performed the analysis according to Eq. (1) in the temperature range covering the transition temperature of the ferroelectric. It was found that the estimated value of passive layer permittivity was temperature dependent in the ferroelectric phase. We suppose that it was the apparent value of this permittivity that was evaluated and our theory accounts for its temperature dependence.

To summarize, it is shown that the in-series capacitors formula for ferroelectric-dielectric sandwich structures can be applied to ferroelectric thin films with dense domain patterns, however, with an apparent value of the passive layer permittivity ε_{mod}, which is a function of the whole set of parameters of the system except the film thickness h. The use of Eq. (2) to the analysis of the experimental data can provide additional information on the ferroelectric, namely, on the distribution of the dielectric response of ferroelectric material between intrinsic (ε_c) and extrinsic (ε_m) contributions.

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*Electronic address: pavel.mokry@vslib.cz; On leave from Department of Electrical Engineering, Technical University of Liberec, CZ-46117 Liberec, Czech Republic.

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