LETTER TO THE EDITOR

Depolarization Corrections to the Coercive Field in Thin-Film Ferroelectrics

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Abstract. Empirically the coercive field needed to reverse the polarization in a ferroelectric increases with decreasing film thickness. For ferroelectric films of 100 microns to 100 nanometers in thickness the coercive field has been successfully described by a semi-empirical scaling law. Accounting for depolarization corrections, we show that this scaling behavior is consistent with field measurements of ultrathin ferroelectric capacitors down to one nanometer in film thickness. Our results also indicate that the minimum film thickness, determined by a polarization instability, can be tuned by the choice of electrodes, and recommendations for next-generation ferroelectric devices are discussed.

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Thin-film ferroelectrics offer tremendous possibilities as key components of data storage devices.[1] Demand for microelectronics with increased densities requires size-dependent characterization of ferroelectric-electrode structures. Empirically the coercive field (E_c) needed to reverse the polarization increases with decreasing film thickness (d).[2] Knowledge of the length-dependence of E_c is crucial for the optimal design of ferroelectric devices with specified voltage levels. $E_c(d)$ for ferroelectric films of 100 microns to 100 nanometers in thickness has been successfully described by a semi-empirical scaling law.[3, 4] Accounting for depolarization corrections, we show that this scaling behavior is consistent with field measurements of ultrathin ferroelectric capacitors down to one nanometer in film thickness. Our results also indicate that the minimum film thickness, determined by a polarization instability,[5, 6] can be tuned by the choice of electrodes, and recommendations for next-generation ferroelectric devices are discussed.

For the last forty years the semi-empirical scaling law, [3, 4] $E_c(d) \propto d^{-2/3}$, has been used successfully to describe the thickness-dependence of the coercive field in ferroelectric films ranging from 100 microns to 200 nanometers. [1] In the derivation of this Janovec-Kay-Dunn (JKD) scaling, [3, 4] it is implicitly assumed that there are no internal electric fields in the ferroelectric sample so that the coercive fields measured in the external circuit and that in the film itself are identical. This is true in an idealized ferroelectric capacitor where the plates are perfect conductors (see Fig. 1 a,b). Then charge resides on a plane of negligible thickness at the electrode-ferroelectric interface, compensating for the spontaneous polarization, P_s , in the ferroelectric film. However



Figure 1. A schematic of (a) a short-circuited electrode-ferroelectric structure with the spontaneous polarization displayed; (b) its charge distribution in the presence of perfect electrodes; its (c) charge distribution, (d) voltage and (e) field profiles in the presence of realistic electrodes. Please note that here the film is taken to be a perfect insulator.

realistically the charge is distributed over a small but finite region in the metal (cf. Fig. 1 c). The crucial physics associated with realistic electrodes is incomplete charge compensation: screening charge in the metal plates is displaced from the ferroelectricelectrode interface. For a short-circuited ferroelectric capacitor, this spatial charge distribution leads to an associated voltage drop in the metal electrodes (cf. Fig. 1 d), and a compensating depolarization potential across the film is necessary to ensure that the whole structure is an equipotential.[7] There is therefore an associated finite depolarization field in the film (cf. Fig. 1 e), which must play a role in the switching process. Since the potential in the realistic electrodes results from the induced charge density, it will be proportional to the spontaneous polarization. In many systems P_s is weakly dependent on film thickness; in this case the depolarization field will scale simply as 1/d and will assume increasing importance in films with decreasing thickness.

Based on these arguments, we expect deviations between the measured and the JKD values of the coercive fields for ultrathin ferroelectric films. We assume that the charge density at the ferroelectric-electrode interface takes the simple form $\rho(x) = \frac{Q}{\lambda}e^{\left(-\frac{x}{\lambda}\right)}$ where λ is a screening length (Fig. 1 (c)). The voltage drop across the total capacitor system is then $V = E_f d + E_e(2\lambda)$ where E_f and E_e refer to the fields in the film and the electrodes at the interface (see (Fig. 1 (e)) respectively. Using the continuity of the displacement fields at the interface, $E_e = \frac{e_f}{\epsilon_e} E_f - \frac{4\pi}{\epsilon_e} P_s$, we obtain

$$E_f = \frac{V + 8\pi P_s a}{d + \epsilon_f(2a)} \tag{1}$$

for the field in the film where ϵ_f is the dielectric constant in the film; here $a = \frac{\lambda}{\epsilon_e}$ where ϵ_e refers to the dielectric constant of the metal electrodes. This result is consistent with expectations for image charges in dielectrics.[8] We note that for a = 0, namely perfect electrodes, we recover the result, $E_f = E_{meas} = \frac{V}{d}$, where the measured and



Figure 2. Measured coercive field data (Ref. 24) for PVDF, the Kay-Dunn scaling and the present current theory vs. thickness; as explained in the text, the latter incorporates field-penetration effects via a depolarization contribution to the field as a function of thickness.

the film fields coincide.

The expression for the field in the film, (1), has two limits of practical interest. The first is when the spontaneous polarization is large compared to the dielectric constant of the film, $4\pi P_s \gg \epsilon_f E$. In this case, we have

$$E_f = \frac{V + 8\pi P_s \frac{\lambda}{\epsilon_e}}{d} \qquad \qquad E_{meas} < E_f \qquad (2)$$

where the measured field will be less than that in the film, due to the presence of the finite depolarization field that assists the switching process. By contrast, for large dielectric constant, $\epsilon_f E \gg 4\pi P_s$, the expression (1) becomes

$$E_f = \frac{V}{d + (2\lambda)\frac{\epsilon_f}{\epsilon_e}} \qquad \qquad E_{meas} > E_f \qquad (3)$$

so that now the measured field exceeds that in the film; physically this is due to the additional voltage drop in the electrodes.[9]

We have treated the ferroelectric as a perfect insulator rather than as a semiconductor. There is circumstantial evidence that the depolarization field in PZT, a ferroelectric with a large dielectric constant, decays with time, [10] and this effect would require an expanded version of our current approach. Indeed there are some hints of "non-scaling" behavior of $E_c(d)$ in films of PZT between 100 and 200 nanometers, [11] but detailed comparison between theory and experiments has to wait for modelling of intrinsic dynamic screening effects and for the determination of $E_c(d)$ on thinner high-dielectric ferroelectric films.

Recently coercive field measurements of ferroelectric PVDF films with thicknesses down to one nanometer have been reported; on these length-scales significant deviation from the scaling (cf. Figure 2) described above is observed.[12, 13] PVDF is a highly resistive ferroelectric, where our insulating assumptions should be valid; furthermore its spontaneous polarization is large (e.g. $4\pi P_s \gg \epsilon_f E$), making (2) the relevant expression for the field in the film. Here we show quantitatively that the incomplete charge compensation effect described above accounts for the observed deviation from



Figure 3. The corrected log coercive field vs. log thickness where the depolarization contribution has been subtracted from the measured data (Inset) Normalized corrected log coercive field vs. thickness for all materials which indicates Kay-Dunn scaling over five decades of lengths. The slope is -0.66 ± 0.02 , in agreement with the theoretical value of $-\frac{2}{3}$.

the expected scaling behavior at small film thicknesses (cf. Figure 2); furthermore we demonstrate that, using these ideas, we can include a correction to the measured coercive fields and recover the scaling result for films ranging from 100 microns down to 1 nanometer (cf. Figure 3).

Let us now turn to a more quantitative analysis. In Figure 2, we display the measured coercive field data[12, 13] for PVDF and the Janovec-Kay-Dunn scaling prediction. We note that there is deviation from the scaling behavior at approximately 100 nanometers. Experimentally P_s is observed to be independent of film thickness in the nanometer PVDF samples studied;[12, 13] thus the depolarization field scales inversely with d and assumes increasing importance with decreasing film thickness. Next, using (2), we plot the measured coercive field of the system, $E_{meas} = E_c - E_{dp}$ where $E_{dp} = \frac{8\pi P_s \lambda}{\epsilon_c d}$. We have taken the values of $P_s = 0.2C/m^2$ for PVDF from experiment, $\epsilon_e = 1$ and $\lambda_{TF} = 0.45$ angstroms for the aluminum electrodes ($\epsilon_e = 1$ is required for self consistency with the use of the Thomas-Fermi screening length in this free-electron approach); we have estimated λ using the assumption of a slow-varying potential,[14] leading to $\lambda^2 = \epsilon_e \lambda_{TF}^2$ where λ_{TF} is the Thomas-Fermi screening length. We note the the resulting value for $a = \frac{\lambda}{\epsilon_c} = 0.45$ angstroms in (1) is consistent with the reported inverse-capacitance vs. thickness data of PVDF films,[12, 15] where our fit yields $a = 0.34 \pm 0.15$ angstroms. Here we argue that the presence of a screening length-scale in the electrodes contributes crucially to the behavior of the thin films; good fit to experiment (cf. Figure 2) is achieved without invoking an analogous layer in the ferroelectric itself considered by other authors.[16]

Letter to the Editor

For thicknesses greater than 100 nm, the modified and the scaling curves in Figure 2 are identical, indicating that the depolarization contribution is not important in this regime. However the modified E_c continues to display a good fit to the data for nanometer thicknesses, particularly as it deviates from the scaling curve. We note that the observed rollover in $E_c(d)$ will correspond to the thickness where the depolarization and the scaling coercive fields are comparable; here we expect a polarization instability^[5] that will determine the minimum allowed film thickness, d_{min} . Our approach suggests that this instability can be tuned by varying the spontaneous polarization of the ferroelectric and the screening length of the electrodes. This is consistent with the results of Ghosez and Rabe[6] who found that d_{min} for a ferroelectric film with perfect electrodes was less than that found with semiconducting ones.[5] Recent ab initio results on a series of ferroelectric capacitors support our ideas that screening in the electrodes plays an importance role in the switching parameters of ultrathin films. [17, 18] Indeed a key test of our ideas would be to remeasure $E_c(d)$ for PVDF with semiconducting electrodes; we predict that the deviation from scaling would occur at larger thicknesses than those currently reported [12, 13] where specific numbers could be determined.

Alternatively we can use (1) to add depolarization corrections to the measured coercive field; the resulting film E_c displays JKD scaling for five decades in thicknesses ranging from 100 microns to 1 nanometers (cf. Figure 3). We present the modified data for three different materials in the main part of the figure; since $E_c = C \times d^{2/3}$ where C is material-specific, we expect universal behavior for $\log E_c - \log C$. Indeed this is the case, as indicated in the inset of Figure 3; we emphasize that the slope here is -0.66 ± 0.02 , in agreement with the scaling value of $-\frac{2}{3}$. It is unusual to see universal scaling over such a large number of decades. The agreement between theory and experiment is particularly satisfying for the case of PVDF, since it demonstrates that the switching kinetics of films on nanometer scales are domain-wall limited and are qualitatively similar to those of their 100 micron counterparts.[19]

Our results have several implications for the design and fabrication of ferroelectric devices. Ideally FeRAMS should be designed at film thicknesses where the measured coercive field is less than the scaling value, but before it is equal to the depolarization field; this gives a processing window for PVDF, the polymeric ferroelectric used for this study, for 10 - 100 nm. Furthermore the minimum film thickness, associated with a polarization instability, can be tuned by varying P_s and λ . Oxide electrodes, known for reducing ferroelectric fatigue, [1] would not be optimal for very thin (< 10 nm) devices due to large field-penetration in the capacitor plates. Indeed the optimization of very thin devices should emphasize the screening properties of the electrodes, favoring Pt or Au over SrRuO₃. For the DRAM market, the primary objective is maximizing total capacitance; our results indicate that it is limited by the electrodes. Thus use of larger dielectric materials and thinner films will not improve it significantly. Instead one should optimize the electrical resistivity of the ferroelectric film and the screening properties of the electrodes. Though we have emphasized the latter effects in parallel-plate ferroelectric capacitors, they will also play a significant role in most scanning probe measurements, including atomic force microscopy. More specifically tips of different materials, including various metals, silicon and diamond, should lead to different results; therefore quantitative measurements, using for example Kelvin probe techniques, of work functions, contact potentials, coercive fields and especially surface dielectric constants should yield distinct numerical values that depend on the screening properties of the tips used.

Letter to the Editor

In summary, in this paper we have brought together the ideas of Janovec, [3] Kay and Dunn, [4] Batra and Silverman, [5] and Ghosez and Rabe[6] to develop a model for the coercive field as a function of thickness. For thin films, we have shown the importance of incomplete charge compensation at the ferroelectric-electrode interface; the resulting depolarization field leads to the distinction between the measured and the true coercive fields. In Figure 2, with no adjustable parameters, we display good agreement between our modified coercive field and that measured in PVDF, particularly for thicknesses < 100 nm where there is deviation from scaling behavior. In Figure 3 the measured data are corrected to include the depolarization field; the result obeys Kay-Dunn scaling for five decades in length-scale. Our results indicate that the choice of electrode is very important for optimizing performance for very thin film devices. Given increasing clock speeds, an improved understanding of the coercive fields at finite frequencies would also be of great interest for the development of future ferroelectric devices.

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