A possible mechanism of anomalous shift and asymmetric hysteresis behavior of ferroelectric thin films

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We studied theoretically the hysteresis behavior of ferroelectric thin films. The anomalous ferroelectric response is discussed by use of a bilayer model. Electrical conductivities of the films have been taken into account. To model the effects of the inhomogeneity of polarization and permittivity across the interface, the film is assumed to possess a secondary dielectric/ferroelectric phase (a dead or passive layer) with asymmetric conductivity. This configuration is found to produce large shifting (along the field axis) and deformation of the measured hysteresis loop. This is a manifestation of the asymmetric conductivity of the material. Theoretical calculation based on this model shows that the observed phenomena of shifted and skewed hysteresis loop in ferroelectric thin films can be explained in this way. © *2005 American Institute of Physics*.
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The hysteresis behaviors of ferroelectric thin films have attracted great research interest for many years. Their bistable polarization as well as small size are promising characters for developing compact nonvolatile memories. Research studies of the anomalous effects and degradation mechanisms in the hysteresis behavior of ferroelectric thin films are essential for device applications. A most notable phenomenon is the large voltage offset along the horizontal (electric field) axis found in the hysteresis loop measurements.[1–11] The result is a deformed hysteresis loop with asymmetric switching.[6] Many researchers attributed the shift effect to the internal field caused by trapped charge carriers.[1–4] Other explanations included domain pinning,[5,6] rectifying effects formed at the ferroelectric–electrode interface[7–9] and the effect of passive layers.[10–12] It seems that the definitive mechanism is still not fully understood and the voltage shift may arise from multiple sources. Theoretical models to gain deeper insight using different approaches have been proposed.[11–15] In the absence of a unifying theory to account for all possible origins, we believe that the current theoretical understanding of the shift phenomenon can benefit from further input in terms of ideas and models. This work attempts to model this offset phenomenon by introducing a passive dielectric/ferroelectric layer at the film–electrode interface. In the framework of the Landau–Ginzburg theory, the variation of polarization, which is usually more pronounced in thinner films, is modeled by a gradient term and extrapolation lengths in the free energy expression. This approach is suggested to be effectively the same as the existence of a passive layer (or dead layer).[16]

It has been demonstrated that polarization gradient across a ferroelectric film can lead to asymmetric conduction.[17] The spatially varied polarization near the thin film surfaces is then thought to possess asymmetric electrical conductivity, while asymmetric conductivity may not emerge from the "normal" region of the film since the polarization should be quite uniform there. We therefore assume the passive layer possesses asymmetric conductivity but not the bulk layer in our model. This configuration will allow the buildup of a large internal field within the passive layer. We will demonstrate that the horizontal (electric field) offset is strongly dependent on the asymmetry in electrical conductivity and the thickness of the passive layer.

A dead layer is a region adjacent to an electrode, characterized by a much reduced ferroelectricity and dielectricity than in the rest of the film.[15,18,19] Although the nature and origin of the dead layer may still be under debate, it has been pointed out that its formation is an intrinsic effect for ferroelectric thin films.[18] Note that dead layer effect may take place at the two sample–electrode interfaces, but we include the overall effect in a single passive layer (layer 2) to account for all relaxation in polarization and permittivity for convenience. Such is already sufficient to demonstrate the shift phenomenon. The constitutive equation is

$$D_i = \varepsilon_i E_i + P_i, \tag{1}$$

where D is electric displacement, ε is permittivity, E is electric field, and P is polarization. Subscript i may take "1" or "2" to denote the normal region and the passive layer of the sample, respectively.

When an external electric field E is applied in the thickness direction across the film:

$$E = (1-\nu)E_1 + \nu E_2, \tag{2}$$

where ν represents the thickness ratio of the dead layer in the ferroelectric film. The boundary conditions for continuity of current density J require

$$J = \sigma_1 E_1 + \dot{D}_1 = \sigma_2^{\pm} E_2 + \dot{D}_2, \tag{3}$$

where $\dot{D}$ represents $\partial D/\partial t$ and σ is electrical conductivity. The superscript "$\pm$" denotes σ_2 may take on different values for $E_2 > 0$ (represented by "+") and $E_2 < 0$ (represented by "−"). This usage is consistent with the notation adopted by Zheng *et al.*[20] and Bouregba *et al.*[21] Using Eqs. (1)–(3) and the relation $\dot{P}_i = \chi_i \dot{E}_i$ where $\chi_i \equiv \partial P_i/\partial E_i$ with $i=1$ or 2, we obtain, after some manipulation,

$$[\nu(\varepsilon_1+\chi_1)+(1-\nu)(\varepsilon_2+\chi_2)]\dot{E}_2 + [\nu\sigma_1 + (1-\nu)\sigma_2]E_2 = \sigma_1 E + (\varepsilon_1+\chi_1)\dot{E}. \tag{4}$$

Equation (4) is a first order differential equation. For a given

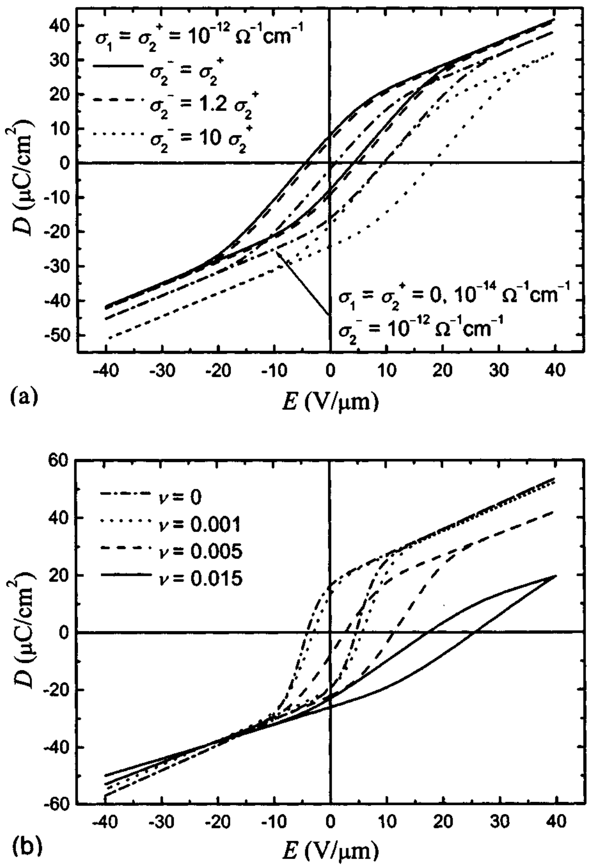

FIG. 1. Variations of the D–E hysteresis loop with (a) the asymmetry of conductivity in passive layer, and (b) the thickness ratio of passive layer.

external sinusoidal field E, we may obtain E_1 and E_2 as a function of time t when the P–E relations for layers 1 and 2 are known. Then the electric displacement of the sample at a certain time t_0 is normally obtained from the current integration technique: $D(t_0)=\int_0^{t_0} J\, dt$. In this work, the model of Miller *et al.*[19] is used to describe ferroelectric P–E relations:

$$\frac{\partial P_i}{\partial E_i} = \left[1 - \tanh \sqrt{\frac{P_i - P_{\mathrm{sat},i}}{\xi_i P_{s,i} - P_i}}\right] \frac{\partial P_{\mathrm{sat},i}}{\partial E_i}, \tag{5}$$

where $P_{\mathrm{sat},i}=\xi_i P_{s,i} \tanh\{(\xi_i E_i/E_{c,i}-1)\ln[(1+P_{r,i}/P_{s,i})/(1-P_{r,i}/P_{s,i})]/2\}$. In this model, ξ_i takes +1 and −1 for increasing E_i and decreasing E_i, respectively. P_{sat} is the polarization on the saturated hysteresis loop. P_r, P_s, and E_c denote the remanent polarization, saturation polarization, and coercive field, respectively.

Assuming the measuring frequency is 10 kHz, $\nu=0.01$, $P_{s,1}=20\ \mu\mathrm{C/cm}^2$, $P_{r,1}=0.9\ P_{s,1}$, $E_{c,1}=5\ \mathrm{V}/\mu\mathrm{m}$, $\varepsilon_1=1000\ \varepsilon_0$, and $\varepsilon_2=30\ \varepsilon_0$ where ε_0 is the permittivity of vacuum, simulated results of the D–E hysteresis loop for ferroelectric thin films with a nonferroelectric passive layer are shown in Fig. 1(a). Different pairs of asymmetric σ_2 values have been adopted to demonstrate the horizontal shift phenomenon with σ_1 identical to σ_2^+. In the figure, all the modeled results correspond to 3 s after the application of the external ac field. According to our simulations, the horizontal shift of the loops with $\sigma_1=\sigma_2^+=10^{-12}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at this time should be quite close to their steady state. When the passive layer has symmetric conductivity ($\sigma_2^+=\sigma_2^-$), the hysteresis loop centers at the origin and no horizontal and vertical shifts are observed. Suppose asymmetry of conductivity is introduced into the passive layer, significant horizontal shift is observed. As more asymmetry in σ_2 is introduced, the magnitude of horizontal shift increases. Note that very large horizontal shift (about three times of $E_{c,1}$) is achieved when σ_2^- is only larger than σ_2^+ by an order. Actually, we find that the shift behavior is mainly determined by the asymmetry ratio $\sigma_2^+:\sigma_2^-$ rather than their absolute magnitudes but using smaller σ_2 values would slow the development of the shift behavior and require more time to reach the steady state. Hence, large shift may rarely be observed for low conductivity films unless the measurement time is sufficiently long, while for high conductivity films this may be observed within a few seconds. This is demonstrated by two larger asymmetry ratios with smaller σ values in Fig. 1(a), but shown to be overlapping with each other (dash–dotted line). The shift magnitude at $t=3$ s is not comparable with the dotted line which has adopted a smaller asymmetry ratio of higher σ. We also found (not shown) that for $\sigma_1=\sigma_2^+=10^{-13}$ and $\sigma_2^-=10^{-12}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, the shift magnitude at $t=3$ s will be very close to the dash–dotted loop, but the steady state loop will be almost identical to the dotted line. On the other hand, notable vertical shift is also observed in Fig. 1(a). Some previous works which demonstrated the horizontal shift also revealed some vertical shift.[22,23] However, if one allows the normal layer (layer 1) to possess asymmetric conductivity, a phenomenon of large vertical shift similar to that found in compositionally graded ferroelectrics will be observed.[21]

Figure 1(b) shows the effect of thickness ratio of the passive layer on the hysteresis loop. All σ values adopted are identical to that for the dotted line in Fig. 1(a). When a thick ferroelectric film is used, in which the effect of surface and film–electrode interaction is limited (this corresponds to a thin passive layer, i.e., $\nu\approx 0$), the hysteresis loop centers at the origin and no horizontal and vertical shifts are observed. Suppose a nonferroelectric passive layer with asymmetric conductivity is introduced, the simulated hysteresis loop starts to twist to one side, resulting in a skewed loop with unequal positive and negative switching fields which is commonly described as a horizontal shift. A comparison of Fig. 1(b) with some previous experimental results shows a fairly good agreement in the shift magnitude and loop shape (see Refs. 1–6). For a larger fraction ν of the passive layer, the magnitude of the horizontal shift increases. With only $\nu\approx 0.5\%$, both switching fields of the hysteresis loop have been shifted totally to one side of the field axis [see Fig. 1(b)].

The phenomenon of shifted and skewed hysteresis loop demonstrated in Fig. 1 is the result of a dynamic accumulation of an internal dc electric field in the passive layer. Figure 2 shows the time development of the accumulated dc electric fields in the normal ferroelectric layer (E_1^{dc}) and the nonferroelectric passive layer (E_2^{dc}). For each period of the external ac field, $1/T\int_T E_i dt$ are calculated where T represents period and the calculation is based on the same set of materials parameters as in Fig. 1(a) with $\sigma_2^+/\sigma_2^-=0.1$. In Fig. 2, the development of E_1^{dc} is negligible. However, a large dc bias develops in the passive layer continuously until saturation. This is the effect of asymmetric conductivity, which produces asymmetric interfacial trapped charge. Hence the asymmetric internal field displaces the hysteresis loop from the origin.[15]

In Fig. 1 the passive layer is assumed to be nonferroelectric. Thus, the magnitude of E_2 is much larger than E_1. Now

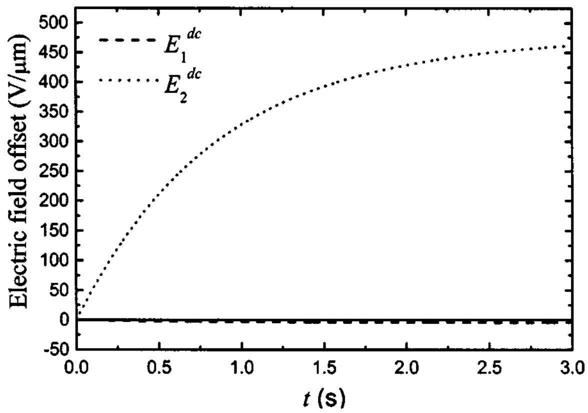

FIG. 2. Theoretical results of the electric field offset in the normal (E_1^{dc}) and passive (E_2^{dc}) layers vs time for $\nu=0.01$.

suppose the passive layer is ferroelectric with lower value of saturation polarization than the normal layer. The comparison of the simulated hysteresis loops between systems with $P_{s,2}=0$ (nonferroelectric passive layer), $P_{s,2}=2$ and $P_{s,2}=10\ \mu\mathrm{C/cm}^2$ is shown in Fig. 3. When the passive layer has weak ferroelectricity ($P_{s,2}=2\ \mu\mathrm{C/cm}^2$), the magnitude of the horizontal shift is slightly smaller than for the case of nonferroelectric passive layer. As $P_{s,2}$ increases, the magnitude of horizontal shift reduces. It is interesting to note that the curve for $P_{s,2}=10\ \mu\mathrm{C/cm}^2$ at $D\approx-20\ \mu\mathrm{C/cm}^2$ shows a "kink" (arrow in Fig. 3) due to the two sharply distinct ferroelectric layers. In reality, the effect may not be so pronounced because structural variations adjacent to the interface between the normal and passive layers are expected to have gradual changes.

All in all, the presence of a dielectric/weak ferroelectric passive layer with asymmetric conductivity is capable of deforming and shifting the hysteresis loop of a ferroelectric film. The asymmetric conduction in the passive layer (symmetric conduction in the normal layer) generates an internal field progressively until saturation. At the same time, its dielectric/weak ferroelectric nature tends to enhance the electric field in the layer, thus leading to a strong effect. This phenomenon cannot be accounted for by a model which solely considers the presence of a nonferroelectric second phase in the ferroelectric film or an average asymmetric conductivity across a "homogeneous" film sample (which is what is measured experimentally).

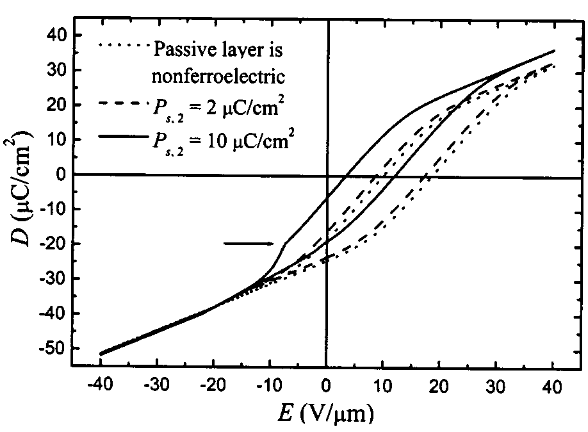

FIG. 3. Variation of the $D-E$ hysteresis loop corresponding to different strengths of ferroelectricity in the passive layer. For the weakly ferroelectric cases, $E_c=5\ \mathrm{V}/\mu\mathrm{m}$ and $P_r=0.9P_s$.

In conclusion, based on a multilayer model that simulates the ferroelectric thin film with a passive (dead) layer, the anomalous shift and deformation observed in the hysteresis measurement of such films can be simulated. The main features of the experimental observations have been reproduced by our simulation. These suggest that the ferroelectric–electrode interaction which forms a nonferroelectric/weak ferroelectric region with asymmetric conductivity due probably to polarization and permittivity inhomogeneity is quite likely to be responsible for the horizontal shift observed in some experiments. Both a thicker passive layer and larger asymmetry of conductivity in the layer will enhance the effect of horizontal offset, as have been illustrated from our simulation results. The present model also gives the dynamic behavior. However, so far only very few experimental investigations have been performed to study the dynamics of the offset along the field axis.

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