Simulation of thickness effect in thin ferroelectric films using Landau–Khalatnikov theory

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The thickness effect in ferroelectric thin films has been theoretically investigated using the Landau–Khalatnikov theory. Ferroelectric properties such as the hysteresis loop, and its associated coercive field and the remanent polarization of various film thicknesses have been numerically simulated. In this simulation, the thin film was modeled by the stacking of layers, each of which has unique parameters for the Landau free energy. Due to the interfacial effects near the electrodes, the parameters for the surface layers are different from those for the bulk. The simulated result shows that the coercive field decreases while the remanent polarization increases with thickness. Both of these trends qualitatively agree with experiments. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Due to the recent development in thin-film fabrication techniques, there is an increasing number of applications of ferroelectric materials in microelectronics, such as nonvolatile memory, random access memory, microwave devices, and microelectromechanical systems. A number of advantages are expected from thin-film based devices: Light weight, small volume, high density, high switching speed, and low-power consumption. However, these applications are possible only when the quality of the thin films is good enough. On the other hand, distinct physical properties have been observed in thin films from experiments, which are completely different from their counterparts in bulk form. Consequently, thickness dependences of various physical properties in ferroelectric films have been extensively studied. Moreover, the thickness effect can be visualized as the influence due to the presence of boundaries in a finite system. Thus, the former can be generalized into a finite-size effect to include the grain-size effects which have been investigated in many polycrystalline materials.

The thickness effect in ferroelectric thin films includes its influence on the coercive field, remanent polarization, phase transition temperature, and dielectric permittivity. All of these dependences might be caused by the same origin. In this article, only the effects on the first two properties are presented. They are important for nonvolatile memory application because the former determines the minimal switchable voltage across film and the latter the amount of charge stored in the medium. From the experimental investigations on both lead–zirconate–titanate and strontium–bismuth–tantalate films,[1–5] it reveals that the coercive field decreases as the film thickness increases. In particular, similar to the ferromagnetism,[6] the relation $E_C \sim d^n$ has been proposed for ferroelectric thin films;[7] where E_C is the coercive field, d is the film thickness, and n is a positive integer. A consistent

conclusion on the remanent polarization can also be drawn from experiments that it increases with film thickness. Moreover, Tagantsev and Stoilichnov[8] claimed that samples which are comparatively fatigue free exhibit less thickness dependence. Larsen *et al.*[9] attributed the polarization fatigue to the presence of "blocking layer." The latter is also responsible for the thickness dependence of the coercive field. They suggested that the origin of the "blocking layers" is the damage created during the electrode deposition where a lot of oxygen vacancies are generated. These remarks also imply that the thickness effects depend on the combination of electrode/ film system, as well as the conditions that they are formed. It also reflects that the presence of the surface layer, right beneath the electrode, is one of the important factors to induce thickness effects.

Ferroelectricity is a result of the collective behavior of many interacting dipoles. For a bulk sample, this collective behavior is so strong that the surface effects can be ignored. The thickness effect becomes significant only when the sample size is small enough. Approaches to tackle the thickness effects include: (i) The introduction of inhomogeneous polarization profile across the film and the incorporation of the extrapolation length δ such that: $dp/dz = -P_0/\delta$,[10] and (ii) the presence of surface layer with completely different properties from those in the interior layers of the film. This layer has been attributed to one of the following mechanisms: (i) The presence of a dielectric layer,[9,11,12] (ii) nucleation of domains with opposite polarity,[13] (iii) pinning of domain-wall motions,[14] and (iv) the presence of depletion layer where the internal field is screened.[15] Comments on these models have been made elsewhere. In a summary, all of these models only provide qualitative arguments on how the coercive field varies with thickness, without simulating the corresponding hysteresis loops.

In this article, the thickness dependence of the coercive field E_c and remanent polarization P_r are presented. Their values are determined from the simulation of polarization–electric ($P-E$) hysteresis loops using Landau–Khalatnikov theory. The justification of using this theory and the

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simulation results are presented in the following sections.

II. THEORY AND MODELING

The ferroelectric film is considered as the stacking of thin layers. Each of these layers is infinite along the XY plane and with a finite thickness Δz along the z direction. When the value Δz is much larger than lattice constant of the sample, the thermodynamic description is valid. The physical properties are uniform within each layer. The number of this layer stack is N. Thus, the film thickness is $d = N\Delta z$. If the origin is located at the top surface, such that $z = 0$ then an arbitrary layer located at a position z can be identified by the index i, such that $z = i\Delta z$ (where $1 \leq i \leq N$). The polarization and electric field within this layer are denoted by P_i and E_i, respectively. Both of them are along the z direction. The free energy of the film can be expressed by the Landau-type free energy expression:[16]

$$F = \sum_{i=1}^{N} \left[\frac{\alpha_i}{2} P_i^2 + \frac{\beta_i}{4} P_i^4 - E_i P_i + \kappa (P_i - P_{i-1})^2 \right], \quad (1)$$

where α_i, β_i, and κ_I are parameters. The last term in Eq. (1) represents the coupling effect between neighboring layers. The polarization gradient $(dP/dz)^2$ might also contribute to the free energy, as has been explicitly expressed in many articles.[17] If each layer is thin enough that the polarization is uniform inside it, then, polarization gradient within each film can be ignored. Moreover, the finite difference expansion of the last term can include the effect of polarization gradient between layers. The justification for absorbing the polarization gradient term is shown in the Appendix. The dynamics of the free energy in response to a time-dependent driving field can be obtained by the Landau–Khalatnikov equation as follows:

$$\gamma \frac{\partial P_i}{\partial t} = -\frac{\partial F}{\partial P_i} = -\alpha_i P_i - \beta_i P_i^3 + E_i$$
$$+ \kappa_i (P_{i+1} + P_{i-1} - 2P_i) \quad (2)$$

The variables in Eq. (2) are then normalized into dimensionless variables by the following relations:

$$p_i = \frac{P_i}{P_S} \quad \eta = \frac{t}{\tau} \quad a_i = \frac{\alpha_i \tau}{\gamma}$$
$$b_i = \frac{\beta_i P_S^2 \tau}{\gamma} \quad k_i = \frac{\kappa_i \tau}{\gamma} \quad e_i = \frac{E_i \tau}{P_S \gamma}, \quad (3)$$

where P_S is the remanent polarization for a bulk sample, τ is a characteristic relaxation time for the system. By relating Eqs. (1) and (2), the following constraint for the parameters can be obtained

$$F_0 = \frac{\gamma P_S^2}{\tau}, \quad (4)$$

where F_0 is a characteristic free energy for the system. Adopting these normalized variables, Eq. (3) becomes

$$\frac{dp_i}{d\eta} = -a_i p_i - b_i p_i^3 + e_i + k_i (p_{i+1} + p_{i-1} - 2p_i). \quad (5)$$

Another index j is introduced to represent the discretized time $\eta = j\Delta\eta$. The time-dependent polarization at each layer is now denoted by $p_{i,j}$. By taking the forward difference in time for the left-hand side of Eq. (5), the difference equation for $p_{i,j}$ can then be obtained as follows:

$$p_{i,j+1} = p_{i,j} + \Delta\eta[-a_i p_{i,j} - b_i p_{i,j}^3 + e_{i,j}$$
$$+ k_i(p_{i+1,j} + p_{i-1,j} - 2p_{i,j})] \quad (6)$$

The overall polarization of the whole film can then be evaluated by the following summation:

$$p_j^T = \frac{\sum_{i=1}^{N} p_{i,j}}{N}. \quad (7)$$

This initial condition for the film can be set by assigning a random number $p_{i,0}$ such that $-1 < p_{i,0} < +1$ for each layer. Thus, the initial overall polarization of the whole film is nearly zero.

It has been observed from experiments that both the remanent polarization and coercive field increase with the amplitude and frequency of the driving field. In order to investigate the thickness dependence, it is necessary to keep both of these two quantities constant while varying the film thickness. Experimentally, the electric field is determined by the potential difference across the film divided by the thickness. This relation only gives rise to an averaged electric field across the film. Moreover, keeping the potential difference constant while varying the thickness results in fault thickness dependence, because the amplitude of the driving field will then be increased upon the reduction in thickness. In this work, the normalized external electric field is given by

$$e_{\text{ext},j} = e_m \sin\left(\frac{2\pi\eta}{T}\right) = e_m \sin(2\pi f\eta) = e_m \sin(2\pi f_n j), \quad (8)$$

where e_m, T, and $f = 1/T$ ($f_n = f\Delta\eta$) are the normalized amplitude, period, and frequency, respectively. The electric field at every point in the film is obtained by the addition of local field $e_{i,j}^{\text{local}}$ and the external field $e_{\text{ext},j}$ such that

$$e_{i,j} = e_{i,j}^{\text{local}} + e_{\text{ext},j}. \quad (9)$$

In the absence of the depolarizing field or space charge at the surface layer, the first term is zero. We will also discuss the cases where the depolarizing field or space charge is present.

The polarization distribution is, in general, inhomogeneous. The boundary conditions are characterized by the extrapolation length δ,[10] such that

$$\left(\frac{dP}{dz}\right)_{z=0} = \frac{P_{z=0}}{\delta} \quad \text{and} \quad \left(\frac{dP}{dz}\right)_{z=d} = -\frac{P_{z=d}}{\delta}. \quad (10)$$

In terms of normalized variables and with finite difference for the derivative (dP/dz) in second-order smallness, they become

$$p_{0,j} = \frac{4p_{1,j} - p_{2,j}}{3+\lambda} \quad \text{and} \quad p_{N,j} = \frac{4p_{N-1,j} - p_{N-2,j}}{3+\lambda} \quad (11)$$

where $\lambda = 2\Delta z / \delta$. A positive δ implies that the surface polarization is smaller than the value in the interior of the film. If δ is negative the surface polarization is larger than that within the film.

It has been mentioned that the parameters a_i, b_i, and k_i might be distinct for each layer. This distinction is due to the difference in material properties as well as the presence of external influences such as electric field and/or space charge. In the present work, a surface layer of normalized thickness u is presented at each electrode. Two sets of parameters, one for the surface layers and the other for the film interior, are introduced as follows:

$$a_i = a_1 \quad b_i = b_1 \quad k_i = k_1$$

(for the surface layers: $1 \leqslant i \leqslant u$ or $N - u \leqslant i \leqslant N$)

and

$$a_i = a_2 \quad b_i = b_2 \quad k_i = k_2$$

(for the interior layers: $u \leqslant i \leqslant N - u$).

The surface layers might still be ferroelectric as they are parts of the film, where a lot of damage are present. Larsen et al.[9] have called it the blocking layer, where the damage is created by the bombardments of the sputtering ions on film surface during the deposition of the top electrode. Another source of damage is by the loss of volatile elements, such as oxygen in PZT. The presence of oxygen vacancies at the surface layers has been suggested as the cause of the polarization fatigue.[18-21] Stoilichnov and Tagantsev[22] have mentioned the direct relation between the fatigue and the thickness dependence. It is natural to consider the role of oxygen vacancies on the polarization switching, especially at the surface layers. Experiments have shown that the coercive field is larger while the remanent polarization is lower in the presence of defects or damage vacancies are present.[22-27] On the other hand, due to the interaction between the electrode and the film, interfacial stress is always present at the surface. This stress might be induced by thermal-mismatch or lattice mismatch. Li et al.[28] have performed depth profile studies of the structure of $PbZr_{0.2}Ti_{0.8}O_3$ film pulsed laser deposited on $SrTiO_3$ substrate, using grazing incident x-ray scattering. Both the distributions of lattice parameters and tetragonality as functions of depth were observed. The difference in lattice parameters between the surface layers and those in the interior region is another reason to adopt a different set of coefficients for the surface layers. Algeró et al.[29] have also suggested that the presence of a layer with different stoichiometry, dielectric permittivity, and switchable polarization next to the bottom electrode is responsible for the thickness dependence of various ferroelectric parameters. In summary, the difference in lattice parameters and structural properties for the surface layers leads to the selection of a different set of coefficients for the Landau's free energy expression on one hand. On the other, how these parameters are related to the coefficients requires further investigation.
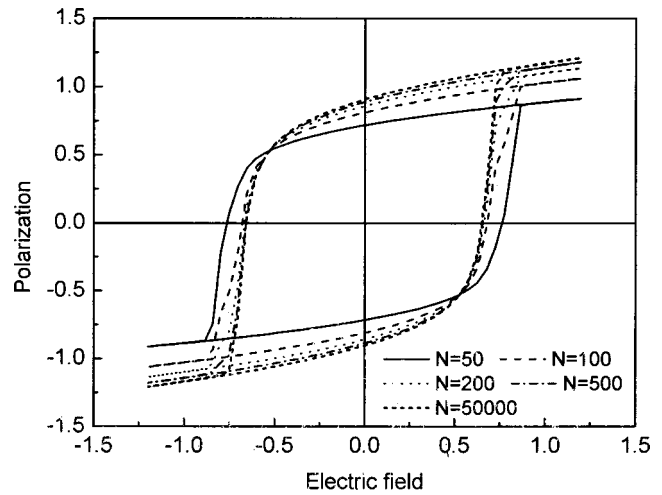

FIG. 1. Hysteresis loops for different thicknesses: $N = 50$ (solid), 100 (dash), 200 (dot), 500 (dash–dot), and 50 000 (short dash), respectively. The parameters are: $a_1 = -2.5$, $b_1 = 5.5$, $k_1 = 3.5$, $a_2 = -1.2$, $b_2 = 1.5$, $k_2 = 1.2$, $e_m = 1.2$, $f = 0.01$, $\Delta\eta = 0.02$, $\Delta z = 0.2$, $\delta = 0.8$, $\lambda = 0.5$, and $u = 20$.

III. RESULTS AND DISCUSSION

The purpose of this article is to investigate the mechanism responsible for the thickness dependence which is common to all ferroelectric materials. As mentioned before, the thickness effects of ferroelectric properties in thin film not only depend on the material of the film itself, but also the combination of electrode/film interface. The way to deposit this electrode is also an important factor. The selection of parameters in fitting a particular experiment is based on the relations in Eq. (3). In order to maintain the generality for all ferroelectric materials, the present simulation only provides a qualitative trend. These parameters are chosen in order that the hysteresis loops in the typical shape observed in ferroelectrics can be simulated. From these loops, the resultant coercive field and remanent polarization can be determined, and their thickness dependence is consistent with experiments. The parameters are listed as follows: $e_m = 1.2$, $f = 0.01$, $\Delta\eta = 0.02$, $\Delta z = 0.2$, $\delta = 0.8$, $\lambda = 0.5$, and $u = 20$. The parameters for the surface layers are: $a_1 = -2.5$, $b_1 = 5.5$, $k_1 = 3.5$; and those for the interior layers are: $a_2 = -1.2$, $b_2 = 1.5$, and $k_2 = 1.2$. The resultant $P-E$ loops for different thickness are shown in Fig. 1. The plots of coercive field and remanent polarization against thickness for different δ values are shown in Fig. 2. From Figs. 1 and 2, the coercive field is decreasing but the remanent polarization is increasing as the film thickness increases. Both of these trends qualitatively agree with experiments. It also reveals that the thickness dependences are pronounced when the thickness is small (for $N < 100$). Both the coercive field and remanent polarization approach their asymptotic values when N is large, corresponding to their respective bulk values. In Fig. 2, the effect of the extrapolation length δ is demonstrated. It slightly affects the values of E_C and P_r for small N values, but makes no appreciable difference for large N. Nevertheless, the general trends of the coercive field and the remanent polarization are not affected by the selection of δ. The decreasing trend of coercive field against thickness can be
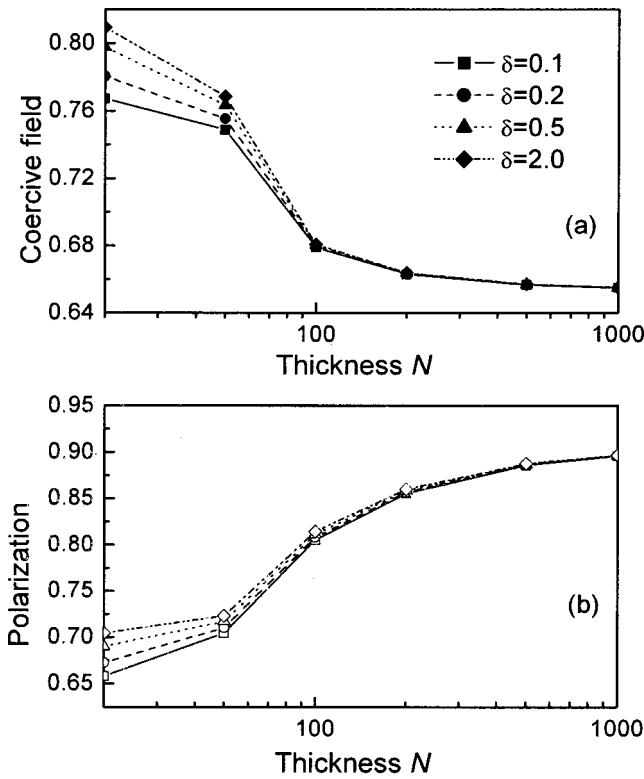
FIG. 2. Thickness dependences of (a) coercive field E_c (lines and solid symbols) and (b) remanent polarization P_r (lines and open symbols) for different δ values, all other parameters except δ are the same as in Fig. 1.
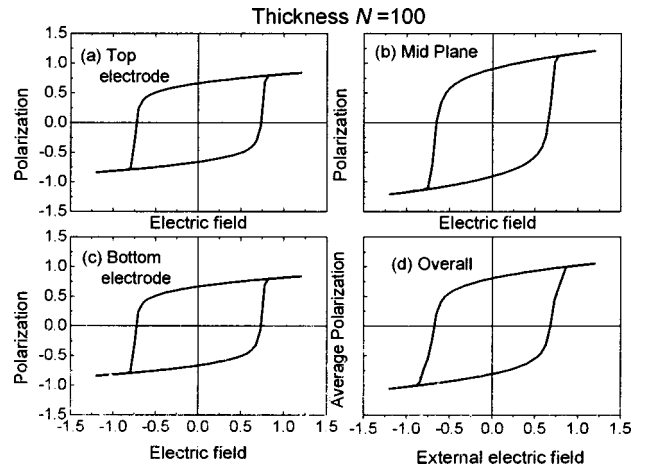

FIG. 3. Hysteresis loops for the layers at (a) the top surface (upper left-hand side), (b) central region (upper right-hand side), (c) bottom surface (lower left-hand side), respectively, and (d) the overall hysteresis loop of the whole film (lower right-hand side).

obtained by adopting one set of parameters over the entire film if $\delta < 0$, where the surface polarization is higher than the values in the interior region. However, it also results in a decreasing trend for the remanent polarization which is contradictory with experiment. The value u represents the thickness of the surface layer. The general trends are not affected by the selection of u, except being shifted horizontally toward the right- (or left-hand side) by increasing (or decreasing) the value u.

The hysteresis loops of different layers of the film: At the top surface, central plane, and the bottom surface, are shown in Fig. 3. The overall hysteresis loop is also shown in Fig. 3. The polarization profiles at different times within a period: $T/4$, $T/2$, $3T/4$, and T, are shown in Fig. 4. From both of these graphs, it is revealed that the surface layers are ferroelectric with a switchable, but depressed, polarization value. The central region of the film has identical properties as in a bulk sample, with a larger remanent polarization and a smaller coercive field.

The presence of space charge and/or depolarizing field at the surface layers[30,31] have been suggested as the cause of the thickness effects. Both of them are attributed to the presence of charge. The first one is induced by point defects or band bending at the electrode/film interface. The second one is the result of incomplete compensation of polarization charge by the electrode. In the following discussion, it can be shown that neither of these factors induces the expected thickness effects.

Assuming that a uniform space-charge layer of density ρ_0 and thickness ℓ is present, the space-charge-induced local field E_{in} can be obtained by solving Poisson equation:

$$\frac{dE_{\text{in}}}{dz} = \frac{\rho_0}{\varepsilon_r \varepsilon_0} \tag{12}$$

where ε_r is the relative dielectric permittivity and ε_0 is the dielectric permittivity in a vacuum. Superimposing the external driving field across the film, the total electric field at each point is given by

$$E(z,t) = E_{\text{ext}}(t) + E_{\text{in}}(z)$$

$$= \begin{cases} E_{\text{ext}}(t) + \dfrac{(z-\ell)\rho_0}{\varepsilon_r \varepsilon_0} & 0 \leq z \leq \ell \\[2mm] E_{\text{ext}}(t) & \ell \leq z \leq (d-\ell) \\[2mm] E_{\text{ext}}(t) + \dfrac{(z-d+\ell)\rho_0}{\varepsilon_r \varepsilon_0} & (d-\ell) \leq z \leq d. \end{cases}$$
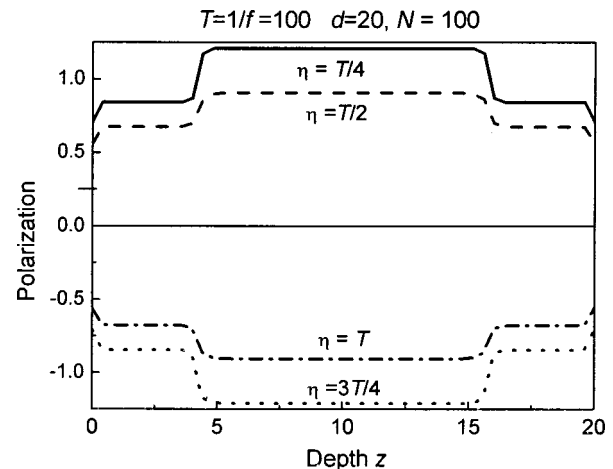
$$\tag{13}$$

FIG. 4. Polarization profiles across the film of thickness $N = 100$ ($d = 20$) at different times: One-quarter (solid line), one-half (dashed line), three-quarter (dotted-line) and one full cycle (dashed–dotted line), respectively, across the film. The parameters are the same as in Fig. 1.
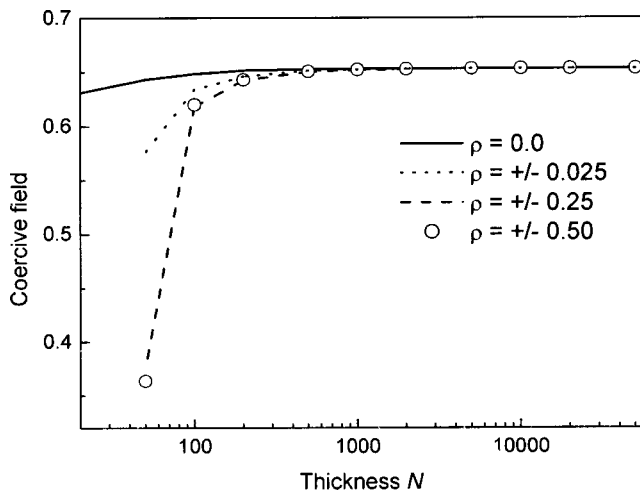
FIG. 5. Effect of various space-charge conditions on the thickness dependence of coercive field: $\rho = \pm 0.025$ (dotted line), $\rho = \pm 0.25$ (dashed line), $\rho = \pm 0.50$ (open circles), and no space charge (solid line). The coefficients for the Landau's free energy expression are the same throughout the film: $a_1 = a_2 = -1.2$, $b_1 = b_2 = 1.5$, and $k_1 = k_2 = 1.2$. All other parameters are the same as in Fig. 1.
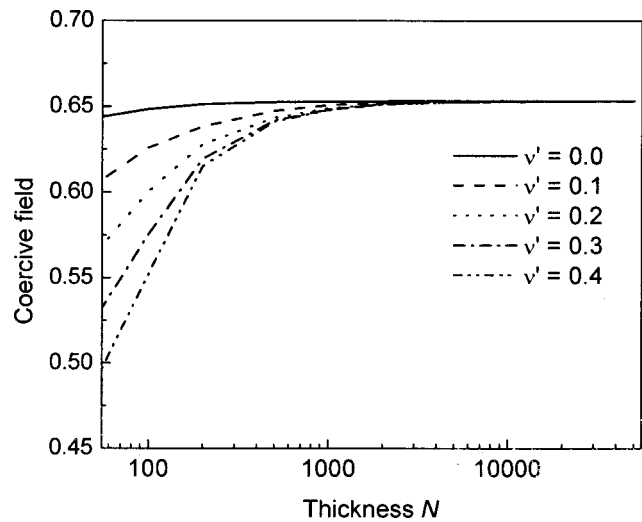

FIG. 6. Effect of depolarization field on the thickness dependence of coercive field: $v' = 0.0$ (solid line), $v' = 0.1$ (dashed line), $v' = 0.2$ (dotted line), $v' = 0.3$ (dashed–dotted line) and $v' = 0.4$ (dash–dot–dot line). The coefficients for the Landau's free energy expression are the same throughout the film: $a_1 = a_2 = -1.2$, $b_1 = b_2 = 1.5$, and $k_1 = k_2 = 1.2$. All other parameters are the same as in Fig. 1.

The second term in Eq. (13) is independent of time if the space charge is static. In terms of dimensionless variables, Eq. (13) is converted into

$$e_{i,j} = \begin{cases} e_{ext,j} + \rho(i-u) & 0 \le i \le u \\ e_{ext,j} & u \le i \le (N-u) \\ e_{ext,j} + \rho(i-N+u) & (N-u) \le i \le N \end{cases} \quad (14)$$

where $\rho = \rho_0 \Delta z \tau / (\varepsilon_r \varepsilon_0 P_s \gamma)$, $\ell = u \Delta z$ and $d = N \Delta z$; $e_{ext,j}$ is the normalized electric field expressed in Eq. (8). The effect of space charge on the thickness dependence of coercive field is shown in Fig. 5. To demonstrate the effect induced by the space charge, the coefficients $a_i = -1.2$, $b_i = 1.5$, and $k_i = 1.2$ are uniform throughout the film. From Fig. 5, it is obvious that the coercive field monotonically increases with thickness in the presence of space charge. Moreover, the sign of the space-charge density does not make any difference in the thickness dependence. When the space charge density is large enough, the polarization at the surface layers is not switchable because of the high space-charge-induced local field.[9] In this case, the thickness dependence is independent of the space-charge density.

On the other hand, the depolarization field might be present at the surface layers, because of the inhomogeneity in polarization and incomplete compensation of polarization charge. This depolarization field is related to the polarization[32] by $E_{dep} = -vP$, where v is called depolarizing factor. The value v depends both on geometry and the charge compensation at the electrode. Assuming that the polarization profile is homogeneous throughout the film except at the thin surface layers because of the electrode/film interaction, this field only exists at the surface layers. The electric-field distribution can then be represented by

$$E(z,t) = \begin{cases} E_{ext}(t) - vP(z,t) & 0 \le z \le \ell \\ E_{ext} & \ell \le z \le d - \ell \\ E_{ext}(t) - vP(z,t) & d - \ell \le z \le d. \end{cases} \quad (15)$$

After normalizing all variables into dimensionless ones, Eq. (15) is converted into the following form:

$$e_{i,j} = \begin{cases} e_{ext,j} - v'p_{i,j} & 0 \le i < u \\ e_{ext,j} & u \le i \le N-u \\ e_{ext,j} - v'p_{i,j} & N-u < i \le N \end{cases} \quad (16)$$

where $v' = v \tau / \gamma$. The difference between the local field induced by the depolarization effect and the space-charge effect is that the former changes with the external driving field while the latter does not. Applying the field distribution described in Eq. (16) into Eq. (6), with the coefficients a_i, b_i, and c_i uniform throughout the film, the thickness dependence of coercive field for various v' can be obtained, as shown in Fig. 6. From Fig. 6, it is obvious that the coercive field is reduced in the presence of depolarization. The extent of reduction increases with v'. Again, the depolarization field can only induce a monotonically increasing trend of the coercive field. Some authors have considered the depolarization effect to account for the thickness dependence of the coercive field.[8,33] What they did was to evaluate the effective field in the film from subtracting the external field by the thickness-dependent depolarization field. The thickness dependence of coercive field was then obtained from this qualitative argument. In the present calculation, on the other hand, the coercive field is determined from the P–E loop.

The possibilities for the existence of the depolarizing field and space charge are not ruled out, nor they are related to any thickness-dependent ferroelectric properties. For example, the presence of depolarization is closely related to the shift in phase transition temperature in thin films.[34] Likewise, the size dependence of fatigue behavior,[35] dielectric response,[36] and breakdown voltage[37] have been attributed to the presence of a space-charge layer. However, our present

calculation demonstrates that both the space charge and depolarization field are not the primary causes for the thickness dependence of coercive field.

In Sec. II, the justification of adopting a different set of coefficients for the surface layers was presented: The presence of defects/damage and the different lattice parameters at the surface layers. Furthermore, there are a lot of experimental investigations on the thickness dependence of the lattice constants: Both c and a. Fujisawa et al.[38] observed that c increased with thickness while a remained constant in metalorganic chemical vapor deposition (MOCVD)-grownlead zirconate titanate (PZT) film on MgO/Pt substrate. For the MOCVD-grown PZT film on $SrRuO_3/SrTiO_3/SiO_2/Si$ system,[1] however, it was found that c gradually decreased while a increased with thickness. They attributed their difference to the different directions of stresses for these two systems.[38] Horii et al.[39] found that c gradually increased while a decreased with film thickness in rf sputtered PZT film on an $Ir/(ZrO_2)_{1-x}(Y_2O_3)_x/Si$ system. They also suggested that the presence of strain, especially for small thickness, is responsible for this phenomenon.[39] Even though the ways these lattice constants vary with thickness are still unequivocal, the strain/stress induced by the electrode/film interface by lattice mismatch and thermal mismatch seems to be the explanation. Moreover, a distribution of tetragonality, i.e., the ratio of c/a, over the film has been observed.[28] The corresponding distributions of the lattice constants also exist. They must be closely related to the coefficients in Eq. (1). The determination of the explicit relation between the lattice constants and the coefficients used in the Landau's free energy expression demands further investigation. The distribution of tetragonality may also imply a smoothly varying distribution of these coefficients across the film. In the present case, a step function is adopted for each of these coefficients for simplicity reason. In summary, the thickness dependence of ferroelectric properties is actually determined by the presence of the surface layers, even though other causes might also have an influence on it. The physical properties of these surface layers are strongly influenced by the combination of the electrode/film interfaces, and how these interfaces are formed.

There has been discussion on the existence of critical thickness below which the ferroelectricity disappears,[40,41] even though some suggested that this critical thickness does not exist[42] so that the ferroelectric phase still persists even down to one monolayer thick. One indication for the existence of the critical thickness is the drop in paraelectric–ferroelectric phase transition temperature to zero or a very small value at some finite thickness. An implication for the existence of this thickness limit is that the coercive field must also be very small for small film thickness, because in this case, the polarization state can be easily reverted or even randomized by a very small field. Consequently, this might lead to an alternative trend that the coercive field increases with the film thickness. In fact, Bune et al.[43] have investigated the ferroelectric properties of crystalline Langmuir–Blodgett-deposited polymer films, of P(VDF–TrFE 70:30). The coercive field decreases when the number of monolayers is reduced. To observe a similar effect in perovskite films, it is necessary to improve thin-film deposition techniques to obtain quality films in such a small thickness. On the other hand, Chandra et al.[44] have made numerical simulation on the thickness dependence of coercive field of PVDF film based on the modified Kolmogorov–Avrami model, in which the electric field penetrates into the oxide electrode over a finite length. Their result shows two different thickness regimes for different trends.[44] For small thickness, the coercive field increases with thickness until a maximum coercive field is attained. Upon further increasing the film thickness, the coercive field decreases again. The second trend is consistent with the traditional thought that the coercive field decreases with the film thickness. Moreover, the existence of these two different trends for two different thickness regimes can also be observed in ferromagnetism.[45,46]

The present simulation only presents the decreasing trend for large thickness regime. It can be attributed to the dominance of the influence induced by the surface layers in this regime. For smaller thickness, another influence might take over. One argument for the existence of critical thickness is the influence of electrode/film interface. The latter always induces a depolarizing field.[40] Electrical, mechanical, and chemical boundary conditions at this interface should also be considered. Even in the absence of the electrode, the surface of the film creates a discontinuity of ferroelectricity in space. It, in turn, causes the inhomogeneity of the polarization distribution at the surface. The inhomogeneous polarization creates a depolarization field near the surface.[47] In other words, the depolarization effect is also present and might be the dominant influence for small thickness. In the present calculation, the reduction of the coercive field in the presence of a depolarization effect was demonstrated (Fig. 6), even though the latter is not responsible for the decreasing trend for large thickness regime. The present work can be further extended in this direction to investigate the thickness dependence of a coercive field in the small thickness regime incorporating the depolarization effect.

IV. CONCLUSION

Thickness dependence for both the remanent polarization and coercive field has been numerically simulated using the Landau–Khalatnikov theory with two sets of parameters: One for the surface layers and the other for the interior layers. These trends cannot be produced by other models such as: Depolarizing field or space-charge models by adopting only one set of parameters. The impetus for using different sets of parameters for different regions in the film is the presence of defects at the surface layers and also the existence of the tetragonality distribution over the film.

ACKNOWLEDGMENT

APPENDIX

If the contribution of the polarization gradient is included in the Landau's free energy expression, such that

$$F = \sum_{i=1}^{N} \left[\frac{\alpha_i}{2} P_i^2 + \frac{\beta_i}{4} P_i^4 - E_i P_i + \kappa_i (P_i - P_{i-1})^2 \right.$$
$$\left. + \varepsilon_i \left(\frac{dP}{dz} \right)_i^2 \right], \tag{A1}$$

then the Landau–Khalatnikov equation becomes

$$\frac{\partial P_i}{\partial t} = -\frac{\partial F}{\partial P_i} = -\alpha_i P_i - \beta_i P_i^3 + E_i$$
$$+ \kappa_i (P_{i+1} + P_{i-1} - 2P_i) - \varepsilon_i \left(\frac{d^2 P}{dz^2} \right)_i. \tag{A2}$$

The last term in Eq. (A2) can be approximated by the finite difference method as follows:

$$\frac{d^2 P}{dz^2} = \frac{P_{i+1} - 2P_i + P_{i-1}}{\Delta z^2}. \tag{A3}$$

Thus, Eq. (A2) can be modified into

$$\frac{\partial P_i}{\partial t} = -\frac{\partial F}{\partial P_i}$$
$$= -\alpha_i P_i - \beta_i P_i^3 + E_i + \kappa_i' (P_{i+1} + P_{i-1} - 2P_i), \tag{A4}$$

where $\kappa_i' = \kappa_i - \varepsilon_i / \Delta z^2$. The polarization effect can be absorbed by the coupling term.

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