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Generalized continuum theory for ferroelectric thin films

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A generalized Ginzburg-Landau-Devonshire free energy has been used to describe the influence of imperfect surface layers or interface layers in ferroelectric thin films. The natural boundary condition has been employed in solving the polarization profile, which can reflect a more realistic situation compared to the previous treatments of the same problem using the so-called extrapolation length. We show that the unscreened portion of the depolarization field makes the polarization distribution more uniform while reducing the amplitude of the effective polarization. The less perfect layer can lower the effective phase-transition temperature. We also used the model to study the effect of asymmetric boundary conditions, which will cause a shift of the hysteresis loop from the center point, similar to the effect of a bias field.

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I. INTRODUCTION

Ferroelectric thin films are of great importance for various technological applications. One of the important phenomena observed in ferroelectric films is the size effect.[1,2] It was shown that phase-transition temperature changes noticeably with decreasing film thickness. In addition, effective polarization and coercive field were also affected by the film thickness. Many experimental and theoretical studies have been devoted to this effect and it has been recognized that a surface layer may exist in the film, which is different from the interior due to the limitations of processing techniques and the interaction with substrate.

Ginzburg-Landau-Devonshire (GLD) thermodynamic theory is frequently used to study ferroelectric thin films.[3–8] Kretschmer[3] introduced the so-called extrapolation length in order to include the variation of the polarization in the vicinity of free surfaces. This concept has widely been used in many papers dealing with the effect of surface and/or interface in ferroelectric thin films.[5–8] The mathematical treatment using this procedure is similar to that for domain walls in bulk, in which a gradient term of polarization was introduced in the GLD free energy while the whole film was treated as made of the same material. A boundary condition (the extrapolation length) is imposed in order to include the variation of polarization in the vicinity of surfaces or interfaces. Using the extrapolation length scheme the influence of depolarization field in film on spontaneous polarization, transition temperature, and critical thickness has been studied.[8] The uncertainty in this scheme is that the extrapolation length has to be predefined and there is a certain degree of arbitrariness for the choice of this extrapolation length. The physical meaning of this extrapolation length is also not well understood. So far as we know, there are no experiments, directly or indirectly, that can validate this extrapolation length concept or determine this parameter.

In reality, many surface factors, for example, interfacial stress, defects, impurities, and the electrodes, are some obvious causes of the variation of polarization near the surface. The larger surface layer to volume ratio in thinner films makes the surface effects more pronounced in very thin films, therefore, size effect is naturally unavoidable.

In this paper we have reformulated the continuum theory by including imperfect surface layer and also used a more realistic natural boundary condition to model the influence of surfaces in ferroelectric thin films. The less perfect surface layer is introduced through a position-dependent Curie temperature. The natural boundary conditions applied here can closely mimic the real experimental situations.

II. THE MODEL

The GLD thermodynamic theory has been one of the most successful theoretical approaches treating ferroelectric materials. Because surfaces, usually less perfect than the interior, contribute significantly to the effective properties of thin films, it is necessary to generalize the GLD theory of homogeneous ferroelectrics to include a surface layer. According to the microscopic explanation of ferroelectricity, the ionic long-range force drives the formation of the spontaneous polarization. The surface factors will influence the long-range forces as well as local short-range forces and hence will change the spontaneous polarization distribution. Above the transition temperature, polarization does not exist but surfaces are still present. For the ferroelectric phase, the GLD free energy should include the surface effects that depend on the polarization. This means that in addition to the polarization gradient energy, the inhomogeneous nature of the film near the surface region may be described by the variation of the "Curie temperature" with a space variable. In other words, T_C is replaced by a position-dependent function along the film thickness. This idea is similar to the method used to reflect the stress influence, which causes the change of effective Curie temperature.[4]

The advancement of thin-film processing technologies has already helped to eliminate many extraneous surface effects, particularly in epitaxial films, which can be made almost like single crystals. However, surfaces still present as a type of defects that affect the material properties. The two electrodes coated at the top and bottom of the film will produce some degree of diffusion near the surface region. The interfacial stress caused by lattice mismatch between the film and the substrate will also influence the polarization distribution near the surface of the film. Therefore, dealing with the surface layer of ferroelectric film has practical importance in addition to its fundamental interest.

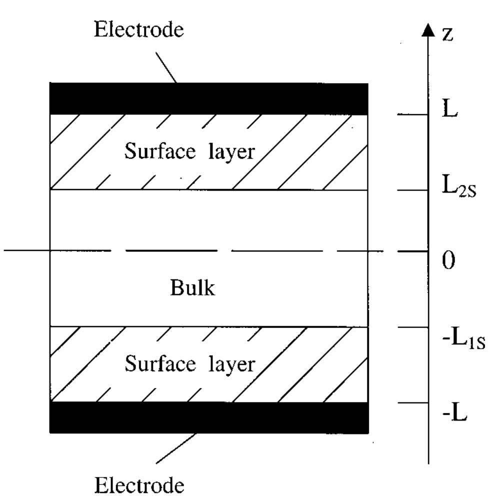

FIG. 1. Geometric structure of the thin film under study.

The geometrical parameters of the thin film we are going to study are indicated in Fig. 1. The easy polar axis of the film is normal to its surface and the film is in single domain state. We assume that the metal electrodes (in the short circuit state) can completely screen the depolarization effect produced by the surface bound charges and the film is homogeneous in planes parallel to the surface. With such assumptions, the problem becomes one-dimensional since the variation is only along the *z* direction, i.e., along the surface-normal direction.

The generalized GLD free energy for unit area is given as follows:

$$G_L=G_0+\int_{-L}^{+L}dz\left\{\frac{1}{2}A[T-T_b\psi(z)]P^2+\frac{1}{4}CP^4+\frac{1}{6}DP^6+\frac{1}{2}K\left(\frac{dP}{dz}\right)^2-\frac{1}{2}E_dP-\overline{E}_{ie}P-EP\right\}. \tag{1}$$

The parameters *A*, *C*, *D*, and *K* are independent of temperature *T* and position *z*. For a first-order transition *A*, *D*, and $K>0$, $C<0$. For a second-order transition, *A*, *C*, $K>0$, and $D=0$. T_b is the transition temperature of bulk material; *E* is an applied uniform external field along the *z* direction. The direction of average effective internal bias field $\overline{E}_{ie}$ is parallel to the direction of the easy polarization of an asymmetry ferroelectric film, $\overline{E}_{ie}=0$ if there is inversion symmetry; E_d is the depolarization field[3]

$$E_d=-\frac{1}{\varepsilon_0}(P-\overline{P}), \tag{2}$$

where ε_0 is the vacuum dielectric permittivity. The average polarization is given by

$$\overline{P}=\frac{1}{2L}\int_{-L}^{+L}P(z)dz. \tag{3}$$

The depolarization field does not exist if the system is perfect up to the surface and the surfaces are coated with metal electrodes. The depolarization field will also vanish if there are injected charges that totally neutralized the bound charges near the surface region.[9] The function $\psi(z)$ in Eq. (1) represents the inhomogeneous nature of the surface layer. In order to ensure the continuity of $P(z)$ and its derivative in the whole region of interest, we require

$$\psi(-L_{1S})=\psi(L_{2S})=1 \quad \text{and} \quad \left.\frac{d\psi}{dz}\right|_{z=-L_{1S}}=\left.\frac{d\psi}{dz}\right|_{z=L_{2S}}=0,$$

where L_{1S} (L_{2S}) is boundary position of the lower (upper) surface layer in the film (see Fig. 1).

The Euler's equation for such a systems is given by

$$K\frac{d^2P}{dz^2}=A[T-T_b\psi(z)]P+CP^3+DP^5-E_d-\overline{E}_{ie}-E, \tag{4}$$

$$\text{with } \frac{dP}{dz}=0 \quad \text{when } z=\pm L.$$

The quantity $\overline{P}(E)$ can be measured experimentally from the hysteresis loop and can also be calculated theoretically by using Eqs. (1)–(4). Since there is an effective bias reflecting the asymmetry of the two surfaces, $\overline{P}(+E)\neq-\overline{P}(-E)$, i.e., electric hysteresis loop will not have the center symmetry about the point $E=0$ and $P=0$. The coercive field $|E_c(+)|$ in the *z*-axis direction and $|E_c(-)|$ in opposite direction are obviously different for such a case. This phenomenon, i.e., the electric hysteresis loop deviates from central symmetry, was often observed experimentally.[10,11] It is known that acceptor impurities can also cause an electric hysteresis loop to deviate from central symmetry. This impurity effect has been explained microscopically using an internal bias field E_i.[12] This bias field E_i, however, has relaxation feature, while the electric hysteresis loop deviation caused by $\overline{E}_{ie}$ in the free energy Eq. (1) is an asymmetry effect that does not relax with time. Therefore, $\overline{E}_{ie}$ in Eq. (1) can be obtained from the experimental measurement of the hysteresis loop. The inhomogeneous distribution $\psi(z)$ in Eq. (1) will be determined on the basis of the specific surface layer state by analyzing the chemical composition of the film near the surface region. In other words, all parameters in our model may be obtained experimentally.

On the surfaces of ferroelectric films coated with metal electrodes

$$\left.\frac{dP}{dz}\right|_{z=\pm L}=0.$$

This boundary condition comes from the following physical consideration: Owing to surface electrodes, bound charges are completely neutralized by free charges on the surface, therefore, in the infinitesimal region immediately beneath the surface, the depolarization field does not change, i.e.,

$$\left.\frac{dE_d}{dz}\right|_{z=\pm L}=0.$$

From Eq. (2) this leads to the boundary condition

$$\left.\frac{dP}{dz}\right|_{z=\pm L}=0.$$

Of course, the depolarization field will change going further into the film. While in all previous extrapolation length treatments, the polarization gradient is required to be proportional to the amplitude of the polarization on the surface, which is difficult to be interpreted using simple physical arguments.

III. NUMERICAL RESULTS AND DISCUSSIONS

For demonstration purpose, we take a ferroelectric film with a second-order ferroelectric phase transition to perform the numerical calculations. Since there are no real measured data on the imperfect surface layer available, we have chosen a simple function for the distribution function $\psi(z)$. This particular choice of the $\psi(z)$ does not affect the generality of the results so long as the function has at least continuous first derivative at the interfaces,

$$\psi(z)=\begin{cases} 1.0-\left(\dfrac{z+L_{1S}}{\lambda_1}\right)^2, & -L\leqslant z\leqslant -L_{1S}\\ 1.0, & -L_{1S}\leqslant z\leqslant L_{2S}\\ 1.0-\left(\dfrac{z-L_{2S}}{\lambda_2}\right)^2, & L_{2S}\leqslant z\leqslant L. \end{cases} \tag{5}$$

In Eq. (5), λ_1 (λ_2) represents the degree of imperfection of the lower (upper) surface layer. For convenience, we use $\omega_1=(L-L_{1S})/2L$ and $\omega_2=(L-L_{2S})/2L$, as normalized variables representing the relative thickness of the two surface layers of the film, respectively.

It is convenient to rescale the variables into dimensionless forms. We set $t=T/T_b$, $f=P/P_0$ with $P_0=\sqrt{AT_b/C}$, $\overline{e_{ie}}=\overline{E_{ie}}/E_0$ and $e=E/E_0$ with $E_0=P_0/\varepsilon_0$, $\zeta=z/\xi_0$ with $\xi_0=\sqrt{K/AT_b}$. Finally, the rescaled Eq. (4) becomes

$$\frac{d^2f}{d\zeta^2}=[t-\psi(\zeta)]f+f^3+\sigma(f-\overline{f})-\sigma\overline{e_{ie}}-\sigma e \tag{6}$$

$$\text{with }\frac{df}{d\zeta}=0\quad\text{when }\zeta=\pm l,$$

where $l=L/\xi_0$, $\overline{f}=\overline{P}/P_0$, and $\sigma=(\varepsilon_0AT_b)^{-1}$.

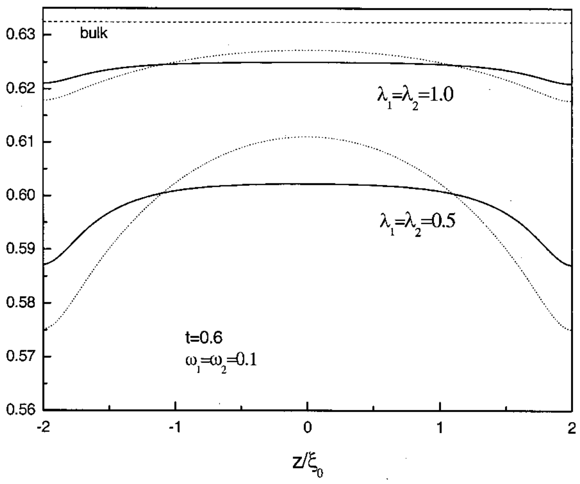

FIG. 2. Polarization profile along the thickness direction film with two symmetric surface layers but different λ values at the temperature $T=0.6T_b$. The two dashed lines were obtained by neglecting the depolarization field.

Using Eqs. (6) we can calculate the polarization profile $P(z)$ [or $f(\zeta)$], the average polarization $\overline{P}$ (or $\overline{f}$) as a function of the applied external E (or e) and as a function of temperature T (or t). We take the thickness of film to be $2L=4\xi_0$ in our numerical calculations. The quantity σ is the ratio of the Curie constant to Curie temperature of the bulk material. In reference to some realistic second-order materials (Curie constant $\sim 10^3$ K and the Curie temperature $\sim 10^2$ K) we take $\sigma=6$ as a representative value in our calculations. The polarization profile $P(z)$ is plotted in Fig. 2 for a film with two symmetric surface layers. The results for two different λ values are given in the figure. The dashed straight line near the top of the figure is the polarization value of bulk material. As we can see that the film polarization is always smaller than the bulk due to surface effects. The dotted line is the result obtained by neglecting the depolarization field. This could happen only when the bound charges are neutralized by charged defects. From Fig. 2 we can see that the influence of the depolarization field is to flatten the polarization profile inside the film. In a sense, it reduces the amplitude inside the film but raises the polarization value in the boundary layers. The parameters λ_1 and λ_2 have strong influence on polarization value and its profile as well. The larger are the λ's, the more uniform is the polar-

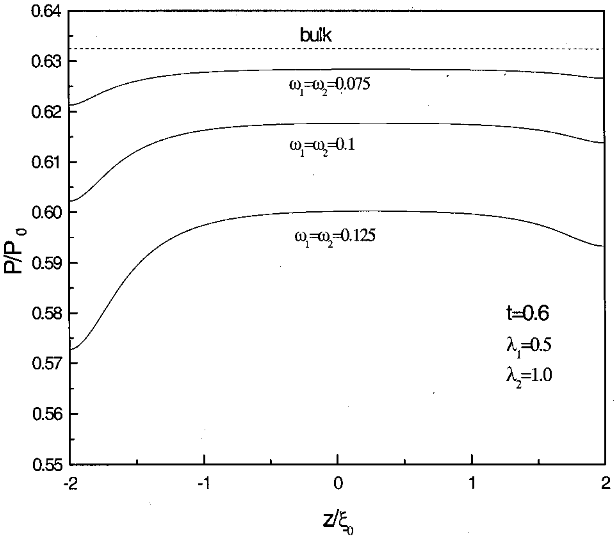

FIG. 3. Polarization profiles for films with two asymmetry surface layers and different relative thickness values at temperature $T=0.6T_b$.

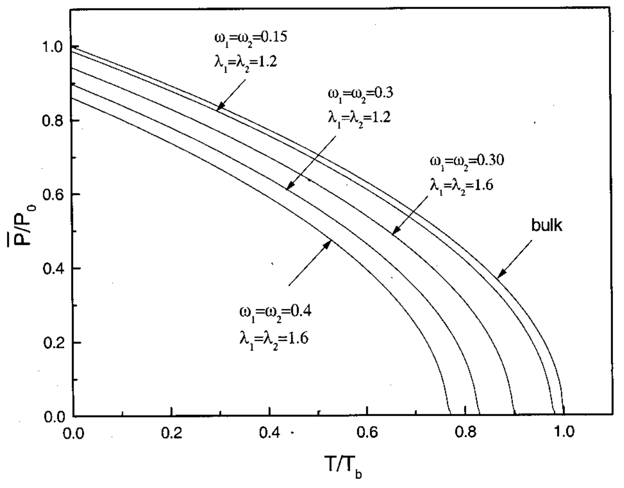

FIG. 4. Average spontaneous polarization $\overline{P}$ as a function of temperature T for a film with two symmetric surfaces. The relative thickness of surface layers has been taken different values.

ization distribution. The physics of larger λ corresponds to less surface influence and hence the value of polarization will be closer to that of bulk material.

In Fig. 3 we plot several curves of polarization profile for films with two surface layers of the same thickness but different λ parameters ($\lambda_1=0.5$ and $\lambda_2=1.0$). The temperature and relative surface thickness values are set at $t=0.6$ and $\omega_1=\omega_2=0.075$, 0.1, 0.125, respectively. For showing the asymmetry boundary effect in above situations we set $\overline{e_{ie}}=0.0005$. We can see that the distribution of polarization is asymmetric in this case and the increase of the relative thickness of surface layer causes the polarization to decrease. If a film has no imperfect surfaces, i.e., $\omega_1=\omega_2=0$, Eq. (6) returns to the Euler's equation of bulk ferroelectrics. Therefore, the relative thickness of surface layers and the parameter λ are two key parameters that determine the polarization profile of the ferroelectric film. In Fig. 4 we have calculated the average spontaneous polarization as a function of temperature for different parameters. If a film has two perfect surfaces $(\omega_1=\omega_2=0.0)$, the spontaneous polarization with temperature T curve will be the same as that of the bulk material. With the increase of the relative thickness of surface layers, the effective Curie temperature becomes lower. On the other hand, the increase of parameter λ will reduce the surface effects. For a film with two different surface layers, the effect is similar to adding a bias field, which makes the polarization hysteresis loop shift from the center point $E=0$. The positive and negative coercive fields become different. Figure 5 shows a shifted hysteresis loop calculated for a film with surface layers of the same thickness but different λ, the effective bias was set to $\overline{e_{ie}}=0.002$.

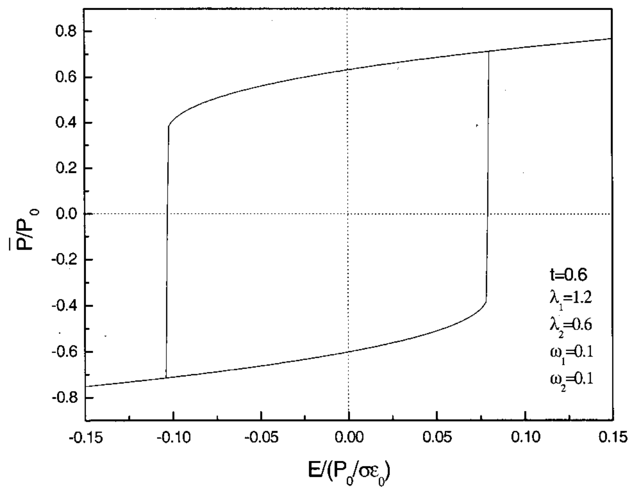

FIG. 5. The calculated electric hysteresis loop of film with two asymmetry surface layers at temperature $T=0.6T_b$. The effective bias field has been set at $\overline{e_{ie}}=0.002$.

IV. SUMMARY AND CONCLUSIONS

We have generalized the GLD free energy by including surface layers with reduced polarization to describe ferroelectric thin films. From our numerical calculations, the relative thickness of imperfect surface layers in ferroelectric film and the λ parameter, which reflects the degree of imperfection of the surface, are the two main factors that influence the polarization profile of the film. The most obvious effects of imperfect surface layers are to decrease the effective Curie temperature and force the magnitude of the effective polarization to become smaller than that of the bulk value. The depolarization field produced by the nonscreened bound charges has the effect of making the polarization distribution more uniform. Because most films have two asymmetric boundary conditions, for example, one side is attached to the substrate and the other side free, the hysteresis loop will be generally asymmetric, which was experimentally observed but often artificially corrected. We have used a small effective bias field to reflect such asymmetric boundary condition. Based on our scheme, by measuring the asymmetry of the hysteresis loop, one could quantitatively assess the degree of asymmetry boundary condition of the thin film. The only parameter introduced in our model is the λ parameter, which could be determined based on layer-by-layer chemical analysis of the thin film, or by comparing the effective polarization with that of the bulk material.

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