Theoretical study on the influence of surface imperfections on the properties of ferroelectric thin films in first-order ferroelectric systems

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A generalized Ginzburg–Landau–Devonshire (GLD) theory is used to study the properties of ferroelectric thin films sandwiched between two metal electrodes with a first-order phase transition. By taking into account the effect of the imperfect surface layer and a natural boundary condition, the temperature and film-thickness dependence of the spontaneous polarization and the dielectric susceptibility are calculated. The depolarization field makes the polarization distribution more uniform. In addition, an asymmetric hysteresis loop can be obtained due to the existence of asymmetrical imperfect surface layers.

1 Introduction

Size effects on ferroelectric thin films have intrigued extensive research interests since it is important both in terms of fundamental physics and practical application [1–10]. The effects of finite thickness on the phase transition temperature, the spontaneous polarization and the dielectric susceptibility were studied in both experimental and theoretical reports. Experimentally, Scott et al. [2] observed that the transition temperature of KNO$_3$ film increases with decreasing thickness. Hadni and Thomas [3] found that higher Curie temperatures and smaller dielectric constants existed than those of the bulk material with decreasing TGS film thickness. For BaTiO$_3$ film, it was reported that the dielectric constant and remanent polarization decrease with decreasing thickness [4]; while Yano et al. [5] found that a BaTiO$_3$ film on Pt/MgO electrodes with a thickness of 6.6 nm still sustains a ferroelectric phase and the c-axis lattice constant increases as the film thickness decreases; similar results are obtained in a BaTiO$_3$ film grown on SrTiO$_3$ [6]. Ferroelectric hysteresis loops can still be observed in the heteroepitaxial BaTiO$_3$ films prepared on SrRuO$_3$/SrTiO$_3$ substrates with a thickness of 12 nm at 200 °C [7]. The differences in these experimental results indicate that the existence of the polarization is strongly influenced by surface or interface effects due to the preparation methods, impurities, defects or stress induced by different substrates or electrodes, etc. Theoretically, the Ginzburg–Landau–Devonshire (GLD) thermodynamic theory has been widely used to describe the properties of ferroelectric thin films [8–16]. The extrapolation length $\delta$ is introduced to describe the variation of the polarization near the surfaces [8]. $\delta$ is positive when the polarization near the surface is smaller than that in the interior, whereas $\delta$ is negative when the surface polarization is larger than that inside. Zhong et al. [9, 10] investigated the size effects on phase transition and the dielectric properties in ferroelectric films.

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Tan studied the first-order transition in ferroelectric films [11]. In addition, they calculated the hysteresis loop in such a thin film and found that the coercive field varied with the value of $\delta$ [12]. Wang added a $P^4$ term to the surface term in the free-energy expression to explain the experimental observations in BaTiO$_3$ ceramics, namely, the polarization decreases while the Curie temperature increases with decreasing grain size [13]. But the physical meaning of $\delta$ and how to determine the amplitude of $\delta$ have not been reported. Using first principles calculations, BaTiO$_3$ thin films with SrRuO$_3$ electrodes have been predicted to lose their ferroelectric properties below 2.4 nm (six unit cells) [17]; Nakao et al. [18] reported that the critical thickness of BaTiO$_3$ is about 12 nm. Based on the Ising model, Wesselinowa [19–21] investigated the phase transition and the dielectric properties of ferroelectric thin films using a Green’s function technique.

In recent years, the effect of surface has motivated extensive research in the ferroelectric thin-film community [22–24]. It was reported that the existence of surfaces in a finite-size system has a strong influence on the physical properties of thin films [23]. Liu et al. [24] studied the PbTiO$_3$ ferroelectric thin films by glancing-angle XRD and found noticeable differences between the surface and bulk structures. In reality, many surface factors, such as interfacial stress, chemical composition, defects and impurities near the electrodes and the substrate employed, can make the local crystal structure of the surface different from that of the interior. By considering the existence of the imperfect surface layer, many properties of ferroelectric thin film with a second-order phase transition have been well explained [14–16].

In this paper, we use a generalized GLD free energy plus a natural boundary, instead of using the extrapolation length, to solve for the polarization profile and investigate the influence of imperfect surface layers on the properties of ferroelectric films with a first-order phase transition. The properties can be successfully described by the model, including the spontaneous polarization, the dielectric susceptibility, phase transition temperature and the critical thickness.

## 2 Model

The geometric structure of a ferroelectric thin-film system is shown in Fig. 1. The figure only illustrates the surface region, while the interior of the film, which can be much thicker than the surface layer, has been omitted. The total thickness of the film is $2L$ and the two film surfaces are coated with electrodes in the short-circuit condition. We assume that the film is homogeneous in planes parallel to the surface but varies toward the surfaces. We also assume that the film has a single polar axis perpendicular to the film surface along the positive direction of the $z$-axis. Because of the inhomogeneity in the surface regions, the free-energy density in the imperfect surface layers is different from that of the interior. This phenomenon...
can be described by introducing a second power term of the polarization in the free-energy expansion, moreover, the coefficient of this term should depend on the space variable \( z \).

Based on the above assumptions, the generalized GLD free energy per unit area of the film with two imperfect surface layers is given as follows:

\[
F_S = \frac{1}{2} \int_{-L}^{L} \left[ A(T - T_0) P^2 + B\psi(z) P^2 + \frac{1}{4} C P^4 + \frac{1}{6} D P^6 + \frac{1}{2} K \left( \frac{dP}{dz} \right)^2 - \frac{1}{2} E_a P - \overline{E}_a P - EP \right] dz .
\]  

(1)

Here, \( P \) is the spontaneous polarization and \( T_0 \) is the Curie–Weiss temperature; the parameters \( A, B, C, D \) and \( K \) are independent of temperature \( T \) and position \( z \). For a first-order phase transition \( A > 0, D > 0, K > 0, C < 0, E \) is an applied uniform external electric field, \( \overline{E}_a \) is the average effective internal bias field in an asymmetric ferroelectric thin film; if two imperfect surface layers are symmetric, \( \overline{E}_a = 0 \).

Although the metal electrodes can provide screening to the average depolarization field, there is still a residual depolarization field due to the inhomogeneity inside the film, which is given by [8]:

\[
E_a = -(P - \overline{P})/\varepsilon_0 ,
\]  

(2)

here \( \varepsilon_0 \) is the vacuum dielectric permittivity and \( \overline{P} \) is the average polarization.

The function \( \psi(z) \) represents the inhomogeneous nature of the surface layer and is determined based on the specific structure and chemical composition of the film near the surface region. In order to ensure the continuity of \( P(z) \) and its derivative in the whole film, we need:

\[
\psi(-L_1) = \psi(L_2) = 0 ,
\]  

(3)

\[
\frac{d\psi}{dz}\Big|_{z=-L_1} = \frac{d\psi}{dz}\Big|_{z=L_2} = 0 .
\]  

(4)

\( L_1, L_2 \) are the starting positions of the two imperfect surface regions as indicated in Fig. 1. The average polarization is given as follows:

\[
\overline{P} = \frac{1}{2L} \int_{-L}^{L} P(z) \, dz .
\]  

(5)

We can get the Euler–Lagrange equation from Eq. (1):

\[
K \frac{d^2 P}{dz^2} = A(T - T_0) P + B\psi(z) P + CP^3 + DP^5 - E_a - \overline{E}_a - E ,
\]  

(6)

\[
\frac{dP}{dz} = 0 \quad z = \pm L .
\]  

(7)

Equation (7) is the natural boundary condition. We could also derive the boundary condition based on the following consideration: when the film is coated with two electrodes, surface bound charges are completely neutralized by free charges of the electrode at the interface. Therefore, in the very thin region near the two electrode/film interfaces, the depolarization field does not change, that is, \( dE_a/dz = 0 \) [14]. Using Eq. (2), we can get Eq. (7).

Based on Eq. (6), when \( E_a \) and \( \overline{E}_a \) are omitted, we can obtain the reciprocal dielectric susceptibility \( \chi^{-1} \) and the mean dielectric susceptibility \( \bar{\chi} \):

\[
\chi^{-1} = \varepsilon_0 \frac{dE}{dP} = \varepsilon_0 \left[ A(T - T_0) + B\psi(z) + 3CP^2 + 5DP^4 \right] ,
\]  

(8)

\[
\bar{\chi} = 2L \int_{-L}^{L} \left[ 1 + \chi(z) \right]^{-1} dz .
\]  

(9)
Equations (8) and (9) describe the influences of imperfect surface layers on the dielectric susceptibility in a first-order ferroelectric thin film.

When the thin film has different conditions on the two surfaces, a bias field will effectively be produced, so the film will lose the inversion symmetry and the hysteresis loop will be asymmetric [25, 26]. Such asymmetrical hysteresis loops have been observed in many experiments [27]. It is also a known fact that acceptor impurities can cause internal bias in the ferroelectric thin film [28]. In this paper, \( E_{ic} \) is not zero when the surface layers are asymmetric. In reality, \( E_{ic} \) has a relaxation feature and may depend on temperature and time. For convenience of discussion, we use an average internal bias field \( \bar{E}_{ic} \) instead of \( E_{ic} \) in the analysis.

3 Numerical results and discussions

It is convenient to rescale the variables into dimensionless forms for computation. Setting \( p = P/P_0 \), \( P_0^2 = \xi|C|/D; \xi = z/\xi_0; \xi^2 = 4DK/C^2; e = E/E_0; \bar{E}_{ic} = E_{ic}/E_0; E_0 = P_0/\xi_0; f = F_0/F_0, F_0 = \xi_0(C)^2/(2D) \). Equations (1), (6) and (7) become:

\[
\psi = \frac{p^2}{4} + \frac{\eta\psi(\xi)p^2}{4} - \frac{p_4^2}{2} + \frac{p_6^2}{3} + \frac{1}{4}(\frac{dP}{d\xi})^2 - \frac{\sigma(p - \overline{P})}{4} - \frac{\sigma\overline{E}_{ic}p}{2} - \frac{\sigmaiep}{2},
\]

\[
\frac{d^2p}{d\xi^2} = tp + \eta\psi(\xi)p - 4p^3 + 4p^5 + \sigma(p - \overline{P}) - \sigma\overline{E}_{ic} - \sigmaie,
\]

\[
\frac{dp}{d\xi} = 0, \quad \xi = \pm l.
\]

Here, \( P_0 \) is the spontaneous polarization of the bulk at \( T = T_0, t = 4AD(T - T_0)/C^2, \eta = 4BD/C^2, \sigma = 4D(\xi_0C)^2, \overline{P} = P_0/P_0, \) and \( l = L/\xi_0 \). For simplicity, we set \( \eta = 1.0 \) or \( \eta = -1.0 \) in this paper. Positive \( \eta \) describes the case when the polarization near the surface is smaller than that in the interior, whereas negative \( \eta \) describes the case when the surface polarization is larger than that inside.

We assume \( \psi(\xi) \) to be a simple function that joins the surface region and the interior of the film with second-order continuity. It does not have to have inversion symmetry in general to reflect different boundary conditions of the two surfaces

\[
\psi(\xi) = \begin{cases} 
\frac{(\xi + l_1)^2/\lambda_1^2}{-l_1 \leq \xi \leq -l_2} \\
0 & \xi = -l_2 \\
\frac{(\xi - l_2)^2/\lambda_2^2}{0 \leq \xi \leq l_1} \\
\frac{(\xi - l_1)^2/\lambda_1^2}{l_1 \leq \xi \leq l_2} \\
\end{cases}
\]

Of course, the inversion symmetry is recovered if \( l_1 = l_2 \) and \( \lambda_1 = \lambda_2 \). It should be pointed out that there are some quantitative differences, but the qualitative results are the same, when a different functional form of \( \psi \) is assumed. Actually, the functional form can be obtained by measuring the compositional variation with chemical analysis layer by layer in the thin film. For convenience, we define relative variables \( \omega_1 = (l - l_2)/2l \) and \( \omega_2 = (l - l_1)/2l \), which represent the relative thickness of the two imperfect surface layers, and \( \lambda \) describes the degree of surface degradation, here \( l_{1s} = l_{1s}/\xi_0 \) and \( l_{2s} = l_{2s}/\xi_0 \). The thickness of the bulk material without imperfect surface layers is \( 2L \), which is described by \( \omega_1 = \omega_2 = 0 \).

For the ferroelectric bulk material having a first-order phase transition, there are three special temperatures: \( T_0, T_1, \) and \( T_1 \). The Curie–Weiss temperature \( T_0 \) is the lowest temperature for the metastable paraelectric phase to exist; \( T_1 \) is the Curie temperature at which a phase transition is supposed to occur and \( T_1 \) is the highest temperature at which the metastable ferroelectric phase can exist. From the above...
definitions, we can get the reduced temperatures \( t_{\text{SCB}} \), \( t_{\text{CB}} \) and \( t_{\text{SHB}} \), respectively. The subscript \( B \) represents that the quantities are for the bulk material:

\[
\begin{align*}
t_{\text{SCB}} &= 0 & T &= T_0 \\
t_{\text{CB}} &= 0.75 & T &= T_c \\
t_{\text{SHB}} &= 1.0 & T &= T_i
\end{align*}
\] (14)

Parameter \( \sigma \) can be represented as \( \sigma = \Delta / (T_1 - T_0) \), here \( \Delta \) is the Curie constant of the bulk material. For ferroelectric material with a first-order phase transition, the Curie constant is \( \sim 10^5 \) K, and \( T_1 - T_0 \sim 10^2 \) K, therefore we can take \( \sigma = 6000 \).

The spontaneous polarization versus space variable \( z \) is shown in Fig. 2. The solid lines and dashed lines correspond to the cases without and with the depolarization field \( E_d \), respectively. Curves (a)–(c) are plotted with \( \eta = 1.0 \), curve (d) is for the bulk material (namely, \( \omega_1 = \omega_2 = 0 \)) and curves (e)–(g) are plotted with \( \eta = -1.0 \). The thickness \( 2L \) is \( 0.4 \xi_0 \). With increasing \( \omega \) or decreasing \( \lambda \), that is, the strength of the imperfect surface layers becomes stronger, it is found that: for \( \eta > 0 \), the spontaneous polarization decreases, and its distribution becomes more inhomogeneous near the surface; the depolarization field makes \( P(\pm L) \) increase and \( P(0) \) decrease, and the corresponding distribution of the polarization becomes more uniform. On the contrary, for \( \eta < 0 \), the spontaneous polarization increases, and the depolarization field makes \( P(\pm L) \) decrease and \( P(0) \) increase. Although the above results look like those by using the extrapolation length \( \delta \), there are essential difference between the two methods. In our model \( dP/dz \) is always zero near the surface due to the existence of the metal electrodes, the inhomogeneous distribution of the spontaneous polarization and the overall shift of the polarization profiles origin from the influence of the imperfect surface layers, when the thickness of imperfect surface layer is zero, the calculated results are similar to those of the bulk material. In the extrapolation length model, the boundary conditions are \( dP/dz = \pm P/\delta \), the polarization profiles vary with \( \delta \), and \( \delta \to \pm \infty \) corresponds to the boundary condition \( dP/dz = 0 \), which describes the polarization distribution of the bulk material.

![Fig. 2](Image)

**Fig. 2** Spontaneous polarization profiles along the thickness direction of the film with two symmetric surface layers at the reduced temperature \( t = -2 \), \( 2L = 0.4 \xi_0 \). The solid and dashed lines are for the cases without and with the depolarization field. Curves (a)–(c) are for \( \eta = 1.0 \), curves (e)–(g) are for \( \eta = -1.0 \). Parameter values of curves: (a) \( \omega_1 = \omega_2 = 0.13 \), \( \lambda_1 = \lambda_2 = 0.01 \); (b) \( \omega_1 = \omega_2 = 0.1 \), \( \lambda_1 = \lambda_2 = 0.008 \); (c) \( \omega_1 = \omega_2 = 0.1 \), \( \lambda_1 = \lambda_2 = 0.01 \); (d) bulk; (e) \( \omega_1 = \omega_2 = 0.1 \), \( \lambda_1 = \lambda_2 = 0.01 \); (f) \( \omega_1 = \omega_2 = 0.13 \), \( \lambda_1 = \lambda_2 = 0.01 \); (g) \( \omega_1 = \omega_2 = 0.1 \), \( \lambda_1 = \lambda_2 = 0.005 \).
We also studied the effects of the asymmetric imperfect surface layers on the polarization profile, as shown in Fig. 3. The asymmetric imperfect surface layers can be described with different values of the $\lambda$ parameter, namely $\lambda_1 \neq \lambda_2$. The results show that the different strength of the imperfection of the two surface layers can cause the asymmetric distribution of the spontaneous polarization.

![Diagram](https://example.com/diagram.png)

**Fig. 3** Polarization profiles for films with two asymmetry surface layers at reduced temperature $t = -2.0$, $2L = 0.4\xi_0$. Here $\omega_3 = \omega_4$ and $\lambda_1 = 0.008$, $\lambda_2 = 0.01$. Curves (a)–(c) are for $\eta = 1.0$, curves (c)–(g) are for $\eta = -1.0$. Parameter values of curves: (a) $\omega_1 = \omega_2 = 0.12$; (b) $\omega_1 = \omega_2 = 0.11$; (c) $\omega_1 = \omega_2 = 0.1$; (d) bulk; (e) $\omega_1 = \omega_2 = 0.06$; (f) $\omega_1 = \omega_2 = 0.08$; (g) $\omega_1 = \omega_2 = 0.1$.

![Diagram](https://example.com/diagram2.png)

**Fig. 4** Average spontaneous polarization profiles and the free energy profiles versus the reduced temperature $t$, $2L = 0.4\xi_0$. Curves (a)–(c) correspond to $\eta = 1.0$, curves (e)–(g) correspond to $\eta = -1.0$. Parameter values of curves: (a) $\omega_3 = \omega_4 = 0.12$, $\lambda_1 = \lambda_2 = 0.01$; (b) $\omega_3 = \omega_4 = 0.12$, $\lambda_1 = \lambda_2 = 0.015$; (c) $\omega_3 = \omega_4 = 0.1$, $\lambda_1 = \lambda_2 = 0.015$; (d) bulk; namely, $\omega_3 = \omega_4 = 0$; (e) $\omega_3 = \omega_4 = 0.1$, $\lambda_1 = \lambda_2 = 0.015$; (f) $\omega_3 = \omega_4 = 0.12$, $\lambda_1 = \lambda_2 = 0.015$; (g) $\omega_3 = \omega_4 = 0.12$, $\lambda_1 = \lambda_2 = 0.01$. 

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The average spontaneous polarization and the free energy as a function of the reduced temperature $t$ are shown in Fig. 4. The thickness of the film is taken as $0.4 \xi_0$. Curves (a)–(c) are plotted with $\eta = 1.0$, curve (d) is for the bulk material and curves (e)–(g) are plotted with $\eta = -1.0$. The ordinate is reduced by $P_0$, that is the bulk’s polarization at $T = T_0$. With increasing temperature, the ferroelectric–paraelectric phase transition will occur, the spontaneous polarization jumps to zero at a phase transition temperature, and the corresponding free energy reaches zero. It should be noted that, in this paper we only discuss the case when the ferroelectric phase of the thin film is stable (not metastable), i.e. the corresponding free energy is always negative. So there is little difference between the polarization profiles in Fig. 4 and those in Ref. [11], in the latter one metastable ferroelectric state is discussed. When $\eta > 0$, with increasing $\omega$ or decreasing $\lambda$, polarization profiles shift to lower temperature, and the corresponding transition temperature is lower than that of the bulk. On the contrary, when $\eta < 0$, the polarization profiles shift to higher temperature and the corresponding transition temperature is higher than that of the bulk. This means that the stronger the influence of the imperfect surface, the more obvious the change of the transition temperature. In addition, the influence of parameter $\lambda$, which represents the degree of surface-layer degradation, on the transition temperature is more pronounced than that of the relative thickness of the imperfect surface layer. Similar results were obtained for ferroelectric films with a second-order phase transition [16].

The temperature dependence of the dielectric susceptibility for symmetric surface is shown in Fig. 5. The average dielectric susceptibility is not monotonic, and a finite dielectric peak appears near the phase transition temperature. When $\eta = 1.0$, the existence of imperfect surface layers makes the peak position shift to lower temperature, and the corresponding phase-transition temperature is lower than that of the bulk material. On the contrary, when $\eta = -1.0$, the peak position shifts to higher temperature and the phase-transition temperature is higher than that of the bulk material. These results are in agreement with those shown in Fig. 4.

The size effects can be studied by reducing the total film thickness but keeping the thickness of the imperfect surface layer constant. Figures 6a and b show the relationship between the polarization and the film thickness for $\eta = 1.0$ and $\eta = -1.0$, respectively. The two sets of curves are for different $\lambda$ values. $P(0), P(L)$ and $\overline{P}$ represent the polarization at the center of the film, at the surface and the mean polarization.

![Fig. 5](image-url) Mean susceptibility of a film with symmetry surface layers versus reduced temperature $t$, $2L = 0.4 \xi_0$. Curves (a)–(c) correspond to $\eta = 1.0$, curves (e)–(g) correspond to $\eta = -1.0$. Parameter values of curves: (a) $\omega_1 = \omega_2 = 0.12$, $\lambda_1 = \lambda_2 = 0.01$; (b) $\omega_1 = \omega_2 = 0.12$, $\lambda_1 = \lambda_2 = 0.015$; (c) $\omega_1 = \omega_2 = 0.1$, $\lambda_1 = \lambda_2 = 0.015$; (d) bulk; (e) $\omega_1 = \omega_2 = 0.1$, $\lambda_1 = \lambda_2 = 0.015$; (f) $\omega_1 = \omega_2 = 0.12$, $\lambda_1 = \lambda_2 = 0.015$; (g) $\omega_1 = \omega_2 = 0.12$, $\lambda_1 = \lambda_2 = 0.01$. 

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Fig. 6 Thickness dependence of the spontaneous polarization at the reduced temperature $t = -2$, $L - L_{1S} = L - L_{2S} = 0.04 \xi_0$. $P(0)$ and $P(L)$ are polarization values at the center and surface of the film, respectively, and $\bar{P}$ is the average effective polarization. The depolarization field has been neglected in the calculations. (a) $\eta = 1.0$; (b) $\eta = -1.0$.

Fig. 7 Thickness dependence of the mean susceptibility $\bar{\chi}$ for $\eta = 1.0$ and $\eta = -1.0$ are shown in Fig. 7a and b, respectively. Here $L - L_{1S} = L - L_{2S} = 0.04 \xi_0$. $P(0)$ is the spontaneous polarization at the center of the film $P(0)$ at the reduced temperature $t = -2.0$, $L - L_{1S} = L - L_{2S} = 0.04 \xi_0$. (a) $\eta = 1.0$; (b) $\eta = -1.0$. The depolarization field has been neglected here.
center of the ferroelectric thin film. For positive $\eta$, one can see that $P(0)$ decreases, while $\overline{F}$ increases with the reduction of the film thickness. When the "size-driven transition" occurs, the spontaneous polarization reaches zero while the mean susceptibility $\overline{F}$ goes up quickly. These phenomena are also found in a ferroelectric film with a second-order phase transition, and these can be ascribed to the fact that as the thickness of the film decreases down to a critical value, the polarization cannot line up under thermoequilibrium due to the weakened long-range interaction, but when a weak electric field is applied, they line up easily and show a large dielectric susceptibility [10].

For negative $\eta$, Fig. 7b shows that as the film thickness decreases, the mean susceptibility decreases, while the polarization increases. It can be explained that the polarization in the surface is greater than that of the interior for $\eta < 0$, the contribution of an imperfect surface layer becomes larger with decreasing film thickness, so the mean polarization and dielectric susceptibility will increase and decrease, respectively. These results are accord with those in Ref. [20], described based on the transverse Ising model.

We have also calculated the hysteresis loop of the ferroelectric thin film with asymmetric imperfect surface layers, as shown in Fig. 8. An average bias field $\overline{E}_a$ is introduced in the positive $z$-direction and different values of $\lambda$ are used to describe the asymmetric boundary conditions at the two surfaces. The following values are used in the calculations: $\lambda_1 = 0.01$, $\lambda_2 = 0.02$, and $\overline{E}_a = 5 \times 10^{-5}$. The dashed lines correspond to $\eta = -1.0$; the dotted lines are the bulk material and the solid lines correspond to $\eta = 1.0$. It is found that the remanent polarization and the coercive fields are smaller (larger) than those of the bulk material for $\eta > 0$ ($\eta < 0$). These results are also found in Ref. [12]. But in our model, $E_c(+) \neq E_c(-)$ and the hysteresis loops are asymmetric by introducing an internal bias; while in Ref. [12], $E_c(+) = E_c(-)$ and the hysteresis loops are symmetric.

4 Summary and conclusions

We use the generalized GLD free energy to study the properties of ferroelectric thin films in a first-order ferroelectric phase transition system. The films having imperfect surface layers are coated with metal electrodes. Parameters $\lambda$ and $\omega$ have been introduced to describe the degree of surface degradation and the relative thickness of the imperfect surface layer, respectively. We use a natural boundary condition instead of the extrapolation length concept to describe the spontaneous polarization distribution in the ferroelectric thin film. A simplified surface energy function is assumed in the paper. It is found that when
the spontaneous polarization is depressed near the surface layer, the corresponding transition temperature of the film is lower than that of the bulk, the mean susceptibility of the film increases with decreasing film thickness and a size-driven phase transition will take place at a critical thickness, furthermore, this critical size depends on the degree of degradation in surface layers. When the spontaneous polarization is enhanced near the surface layer, the corresponding transition temperature of the film is higher than that of the bulk, the mean susceptibility decreases with decreasing film thickness, and there is no size-driven phase transition. Our results also demonstrate that the depolarization field will make the polarization distribution more uniform. In addition, an asymmetric hysteresis loop was obtained by introducing an internal bias due to the existence of the two asymmetric imperfect surface layers.

References