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Influence of imperfect surface on properties of ferroelectric thin film

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Abstract

Using the Ginzburg–Landau–Devonshire theory and taking into account structural difference between imperfect surface layer and bulk ferroelectrics, the behavior of ferroelectric thin film coated with two metallic electrodes is studied. The effects of the imperfect surface layer are to reduce effective polarization, produce non-uniform polarization distribution and lower the phase transition temperature. We show that the non-screened depolarization field also makes the polarization distribution more uniform and shifts the hysteresis loop due to the asymmetric nature of thin film–substrate configuration.

Keywords: Phase transition; Ferroelectric film; Spontaneous polarization; Free energy.

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1. Introduction

With advancement of material processing techniques, the quality of ferroelectric thin films has improved greatly, which intrigued extensive research interest of many scientists and engineers for potential applications [1]. However, size effect is one of the important phenomena observed in ferroelectric thin films that needs further research [2]. It is recognized that the size effect is associated with the inhomogeneous distribution of spontaneous polarization [3]. Kretschmer and Binder [4] attributed the size effect to the surface degradation, and introduced the so-called extrapolation length and the surface free energy using the Ginzburg–Landau–Devonshire (GLD) free energy description. This concept has widely been used in many papers dealing with the influence of depolarization field

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on spontaneous polarization, transition temperature and critical thickness in the studies of ferroelectric films [5–10]. However, the physical meaning of this extrapolation length has not been given so far. Because there is a certain degree of arbitrariness for the choice of the extrapolation length, the physical basis of this description is in question. In reality, many surface factors, for example, interfacial stress, defects, impurities and the electrodes, can change the local structure and the spontaneous polarization near surfaces. The surface layer is often imperfect, at least showing some structural difference from that of the bulk. We believe that the inhomogeneous polarization distribution in the film originates from the imperfection of surface layers. Because of the Coulomb long-range interaction, the influence of imperfect surface layers on the polarization will be felt in certain depth of the film even if the thickness of imperfect surface layer itself could be very thin. The large ratio of surface layer to volume makes the surface effects more pronounced in thinner ferroelectric films. Therefore, better understanding of surface effect is very critical to study the properties of ferroelectric thin films.

In this paper, we have reformulated the GLD equation to study the influence of imperfect surface layers on the properties of ferroelectric thin films.

2. The model

The GLD thermodynamic theory for bulk ferroelectrics has been one of the most successful theoretical approaches treating ferroelectricity. It is necessary to generalize the GLD theory in order to treat thin polar films with imperfect surface layers. The fact that the structure of imperfect surface layers is different from that of bulk shows that the free energy density in imperfect surface layers must be different from that of the bulk, which has homogeneous polarization. We introduce the second power of polarization into the GLD free energy and assume its coefficient to be a function of position to reflect inhomogeneous nature.

The geometrical parameters of the thin film we are going to study are depicted in Fig. 1. We assume that the film has a single polar axis perpendicular to the film surface and along the positive direction of the z-axis. The film is in single domain state resulting from a second order ferroelectric phase transition. The metal electrodes can completely screen the depolarization effect produced by the

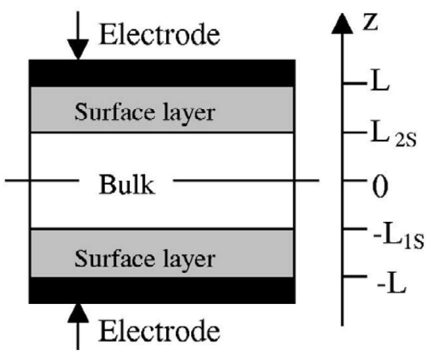

Fig. 1. Geometric structure of thin films under study.

surface polar charges and the film is homogeneous in planes parallel to the surface, i.e. variation is only along the film thickness direction.

The generalized GLD free energy for the second order transition ferroelectric film with unit area is as follows:

$$G_L = G_0 + \int_{-L}^{+L} \mathrm{d}z \left\{ \frac{1}{2}A[T - T_\mathrm{b}]P^2 + \frac{1}{2}B\psi(z)P^2 + \frac{1}{4}CP^4 + \frac{1}{2}K\left(\frac{\mathrm{d}P}{\mathrm{d}z}\right)^2 - \frac{1}{2}E_d P - EP \right\} \tag{1}$$

G_0 is the free energy of film in the paraelectric phase. The coefficients A, B, C, and K are independent of temperature T and position z; T_b is the transition temperature of the bulk ferroelectrics; E is an applied uniform external electric field. The depolarization field produced by bound polar charge in the film that is not being screened by the surface electrodes [4] is $E_d = -(P - \bar{P})/\epsilon_0$, where ϵ_0 is the vacuum dielectric permittivity. The average polarization is given by:

$$\bar{P} = \left(\frac{1}{2L}\right)\int_{-L}^{+L} P(z)\,\mathrm{d}z \tag{2}$$

The function $\psi(z)$ in (1) represents the imperfect surface effect. In order to ensure the continuity of $P(z)$ and its derivative, we require $\psi(-L_{1S}) = \psi(L_{2S}) = 0$ and $(\mathrm{d}\psi/\mathrm{d}z)_{z=-L_{1S}} = (\mathrm{d}\psi/\mathrm{d}z)_{z=L_{2S}} = 0$, where $-L_{1S}$ (L_{2S}) is the boundary position of lower (upper) surface layer in the film (see Fig. 1).

In our model, the polarization at the film surfaces is not fixed but determined by the natural boundary condition. For a film in equilibrium state, $\delta G_L = 0$, so that:

$$\begin{cases} K\dfrac{\mathrm{d}^2P}{\mathrm{d}z^2} = A[T - T_\mathrm{b}]P + B\psi(z)P + CP^3 - E_d - E \\ \dfrac{\mathrm{d}P}{\mathrm{d}z} = 0, \text{ when } z = \pm L \end{cases} \tag{3a,b}$$

The quantity $\bar{P}(E)$ can be measured experimentally from the hysteresis loop and also can be obtained theoretically by using Eq. (2). If there is only one easy polarization direction, this film loses the inversion symmetry. This can happen when there is interfacial stress between the film and the substrate. We can use different B value to reflect this situation. Therefore, $\bar{P}(+E) \neq -\bar{P}(-E)$, i.e. electric hysteresis loop will not have the center symmetry about the point ($E = 0, \bar{P} = 0$). The coercive field $|E_\mathrm{c}(+)|$ in the z-direction is different from the coercive field $|E_\mathrm{c}(-)|$ in the opposite direction. $\psi(z)$ in Eq. (1) can be determined based on the specific surface layer and analyzing the chemical composition of the film near the surface region.

3. Numerical results and discussions

It is convenient to rescale the variables into dimensionless forms. We set $t = T/T_\mathrm{b}$, $f = P/P_0$ with $P_0 = \sqrt{AT_\mathrm{b}/C}$, $e = E/E_0$ with $E_0 = P_0/\epsilon_0$, $\zeta = z/\xi_0$ with $\xi_0 = \sqrt{K/AT_\mathrm{b}}$, $\eta = B/B_0$ with $B_0 = AT_\mathrm{b}$. Finally, Eq. (3a,b) become:

$$\begin{cases} \dfrac{d^2 f}{d\zeta^2} = [t - 1.0]\, f + \eta\psi(\zeta)\, f + f^3 + \sigma(f - \bar{f}) - \sigma e \\ \dfrac{df}{d\zeta} = 0 \quad \text{when } \zeta = \pm l \end{cases} \tag{4a,b}$$

where $l = L/\xi_0$, $\bar{f} = \bar{P}/P_0$ and $\sigma = (\epsilon_0 A T_b)^{-1}$.

Because we do not have any real measured data available on the surface imperfection, a simple function is assumed for the distribution function $\psi(\zeta)$. This particular choice of the $\psi(\zeta)$ does not affect the generality of the results and conclusions:

$$\psi(\zeta) = \begin{cases} \dfrac{(\zeta + l_{1S})^2}{\lambda_1^2} & -l \le \zeta \le -l_{1S} \\ 0 & -l_{1S} \le \zeta \le l_{2S} \\ \dfrac{(\zeta - l_{2S})^2}{\lambda_2^2} & l_{2S} \le \zeta \le l \end{cases} \tag{5}$$

Parameter λ_1 (λ_2) reflects the variation intensity of the free energy density near lower (upper) surface. Define $\omega_1 = (l - l_{1S})/2l$ and $\omega_2 = (l - l_{2S})/2l$, which represent the relative thickness of the two surface layers in the film, respectively, where $l_{1S} = L_{1S}/\xi_0$, $l_{2S} = L_{2S}/\xi_0$.

The parameter σ is the ratio of the Curie constant to Curie temperature of bulk ferroelectrics. Based on the consideration of realistic second-order phase transition materials (the Curie constant ~10^3 K and the Curie temperature ~10^2 K) we take $\sigma = 6$ as a representative value in our calculations. The thickness of film is assumed as $4\xi_0$ in the calculations. The variation of the spontaneous polarization P along the film thickness as a function of position z is plotted in Fig. 2 for a film with two symmetric surface layers while different λ values are used. The dashed straight line is the polarization value of bulk material. The dotted line is the result corresponds to the case of neglecting depolarization field.

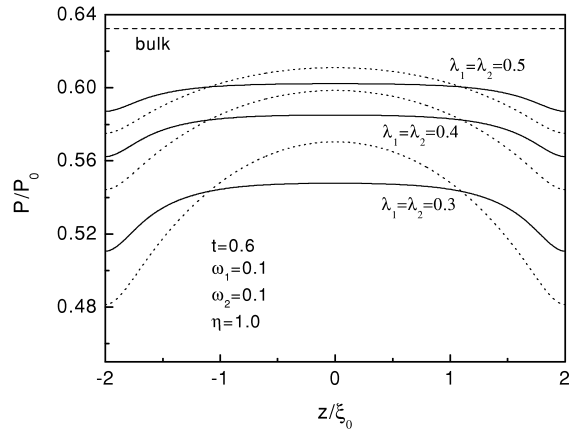

Fig. 2. Spontaneous polarization distribution profile along the thickness direction of the film with two symmetric surface layers but different λ values at the temperature $T = 0.6T_b$. The three dotted curves were obtained by neglecting the depolarization field. The dashed line corresponds to bulk material value.

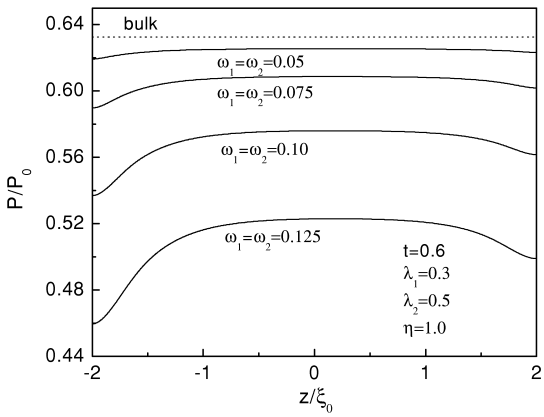

Fig. 3. Spontaneous polarization distribution profiles for films with two asymmetry surface layers and different relative thickness values at the temperature $T = 0.6T_b$.

We can see that the influence of the depolarization field is to flatten the spontaneous polarization profile. It effectively raises the spontaneous polarization near surface regions but reduces it in the interior region. The parameters λ_1 and λ_2 have strong influence on the polarization distribution. Larger λ_1 and λ_2 values will make the polarization distribution more uniform and the value of polarization closer to that of the bulk. In Fig. 3 we plot several curves of spontaneous polarization distribution for a film in which two surface layers have the same thickness but different λ values ($\lambda_1 = 0.3$ and $\lambda_2 = 0.5$). We can see that the distribution of the spontaneous polarization is asymmetric and the increase of relative thickness of surface layer causes the polarization to decrease. In Fig. 4, we have calculated the average spontaneous polarization as a function of temperature while keeping the parameters of imperfect surface layer constant. The imperfect surface layers lowered the phase transition temperature of the film. The influence of the relative thickness of the imperfect surface layers on the transition temperature is more obvious than that of the parameter λ. We also plot the spontaneous polarization versus temperature for film with perfect surfaces ($\omega_1 = \omega_2 = 0$) and the same

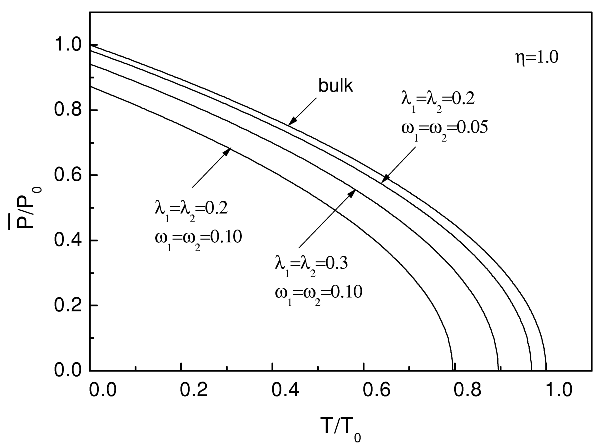

Fig. 4. Average spontaneous polarization $\bar{P}$ as a function of temperature T for a film with two symmetric surfaces.

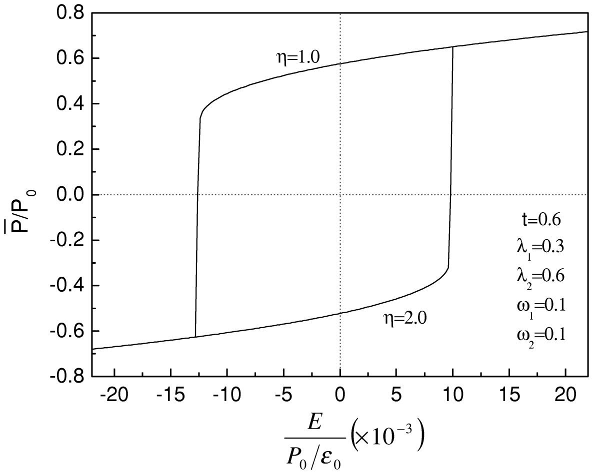

Fig. 5. The calculated electric hysteresis loop of film with two asymmetric surface layers at the temperature $T = 0.6T_b$.

relation as for bulk materials is obtained. This shows that the lowering of transition temperature of ferroelectric films comes from the relative thickness of imperfect surface layers not from the thickness of the film.

We have calculated the hysteresis loop of a ferroelectric film with two asymmetry surface layers, representing the case of one easy polarization direction, as shown in Fig. 5. One can see that the hysteresis loop is asymmetry about the point ($E = 0, \overline{P} = 0$). Coercive fields in the positive and negative directions are obviously different.

4. Conclusions

Using the generalized GLD free energy, the properties of the ferroelectric film with two imperfect surface layers are studied. A parameter λ is introduced to describe the degree of polarization variation near the surface region, which could be determined experimentally. Numerical examples are given for a second order ferroelectric phase transition. The following conclusions are obtained. (1) The relative thickness of imperfect surface layers and the λ parameters are the two main factors that influence the polarization profile. (2) The most obvious effects of imperfect surface layers are to lower the Curie temperature and reduce the amplitude of the spontaneous polarization. (3) The depolarization field produced by the non-screened bound charges has the effect of making the polarization distribution more uniform. (4) For the film with only one easy polarization direction, the hysteresis loop will be asymmetric.

Acknowledgements

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