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Polarization properties of ferroelectric thin films on transverse Ising model

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By taking into account surface transition layers (STL), an improved transverse Ising model (TIM) with a depolarization field effect also considered is used to describe the polarization properties of ferroelectric thin films in the framework of the mean-field approximation. Functions representing the intralayer and interlayer couplings are introduced to characterize STL, which makes the model more realistic compared to previous treatment of surface layers using uniform surface exchange interactions and a transverse field. By comparison with the results obtained from the traditional treatments for the thin films using only the single surface layer (SSL), some new results are derived by adding the STL in the model. The results also show that the effect of the transverse field is notable when tunneling is essential. The influence of the depolarization field is to flatten the spontaneous polarization profile and make the polarization distribution of films more homogeneous, which is consistent with the results obtained from the Ginzburg–Landau–Devonshire (GLD) theory.

1 Introduction The character of ferroelectric thin films has been of growing interest because of their significance in the field of microelectronics [1] and optoelectronics [2], such as random access memory [3]. However, the surface effect is one of the important phenomena observed in ferroelectric thin films that needs further research [4]. Many researchers have focused their attention on ferroelectric thin films for their surface effects, it is recognized that the surface effect is associated with many surface factors, for example, interfacial stress, defects, impurities and electrodes. Kretschmer and Binder [5] attributed the size effect in the films to surface degradation, and introduced the extrapolation length and surface free-energy term using the GLD free-energy description. The concept has been widely used in many papers dealing with the effect of surface and/or interfaces in ferroelectric thin films [6–9]. Also from the GLD theory, Lü et al. [10–13] have studied the influence of imperfect surfaces on polarization distribution, phase-transition temperature, dielectric susceptibility of ferroelectric thin films using a different formulation. They introduced an imperfect surface layer concept without using the extrapolation length concept, which reflected a more realistic situation. Taking into account that a surface of a ferroelectric is a defect of a field type, Bratkovsky and Levanyuk have used a modified boundary condition to study the surface effect of ferroelectric nanostructures by GLD theory. They coupled the surface (interface) field to a normal component of polarization and found that the second-order phase transitions are generally suppressed [14]. Stephanovich et al. [15] have investigated the ferroelectric phase transition in a periodic superlattice consisting of alternate ferroelectric and paraelectric layers of nanometric thickness. By coupling the electrostatic equations with those obtained by minimizing the Ginzburg–Landau functional, they calculated the transition temperature as a function of superlattice wavelength and quantitatively explain the experimental data of $KTaO_3/KNbO_3$ strained-layer superlattices.

The transverse field Ising-type model has been widely applied to study the properties of ferroelectric thin films with surface layers. Recently, when including the modification of both surface exchange interaction and surface transverse field from the bulk values, many characteristic features have been found both experimentally [16–19] and theoretically [20–36].

In theoretical works within TIM mentioned above, the method to describe the lowering of symmetry at the surface is to make a modification of Ω_i and J_{ij} (the transverse field and the two-spin exchange interaction) compared with their bulk values, and the traditional treatments for the thin films using only SSL, that is, the modified Ω_i and J_{ij} are treated as uniform in the surface transition layer and the structure difference between the surface and the interior of film is a "step" model. Considering the multilayer structures of surface layers, it is more realistic to investigate the role of the intralayer (within layer) and interlayer (across layers) interactions ($J_a(m)$ and $J_e(m)$ shown in Fig. 1) between two pseudospins in the formation of properties of ferroelectric thin films. So, in this paper, functions representing the intralayer and interlayer couplings, $J_a(m)$ and $J_e(m)$ are introduced to describe the structure change from the imperfect surface to perfect interior of the film. Such a model reflects a more realistic situation of the film than the step-function type model, and one may find the way to better control the properties of artificially fabricated films by controlling STL, such as its thickness, the intensity of exchange interactions near the surface, etc.

The aim of this work is to investigate the surface effects on polarization properties of ferroelectric thin films from the microscopic level. We assume that the film properties change along the film thickness direction but are uniform in the same pseudospin layer parallel to the surface. The effects of the transverse field Ω_i on the phase transition properties of ultrathin ferroelectric films have been studied in Ref. [36]. When the exchange interaction parameter J_s is fixed, to characterize the film surface layer, the deviation of Ω_i from the corresponding bulk value Ω can only lead to numerically different results, which will not influence the changing tendency of the Curie temperature (see group Fig. 3(I), 3(II) and group Fig. 3(III), 3(IV) in Ref. [34]). So, for simplicity, the transverse field is taken as a constant across the whole film to be $\Omega/J = 1.0$, which is held fixed in all calculations.

2 The model

The Hamiltonian of the TIM [20–36] is

$$H = -\Omega_i \sum_i s_i^x - \tfrac{1}{2} \sum_{ij} J_{ij} s_i^z s_j^z - 2\mu \sum_i E_i^{\mathrm{d}} s_i^z \,, \tag{1}$$

where the last term of the equation represents the depolarization energy, and E_i^{d} is the depolarization field on the i-th layer. Ω_i is the transverse field, s_i^x and s_i^z are the x and z components of pseudospin at site i (the thermal average of s_i^z is related to the polarization), J_{ij} is the two-spin exchange interaction constant between site i and site j, and the sum $\sum_{ij}$ runs over all sites.

The model used to describe the ferroelectric properties of the thin film with second-order phase transition is illustrated in Fig. 1. For simplicity and without loss of generality, we assume that the z-direction is perpendicular to the surface and the polarization is along the z-direction. An N-layer film with symmetrical surface structure is studied as a model system. The number of pseudospin layers included in the STL is n_s. The parameter Ω on the right side of Fig. 1 is the transverse field. For H-bond ferroelectrics the theory of spontaneous polarization focuses on the ordering of protons. $\Omega \approx E_- - E_+$ is the difference between the energy level of the antisymmetrical state and the energy level of the symmetrical state, so Ω is called the tunneling frequency representing the proton tunneling between the two equilibrium positions on the H-bonds, whose direction is along the x-axis. When $\Omega = 0$, the proton doesn't tunnel between the two equilibrium positions, and the ferroelec-

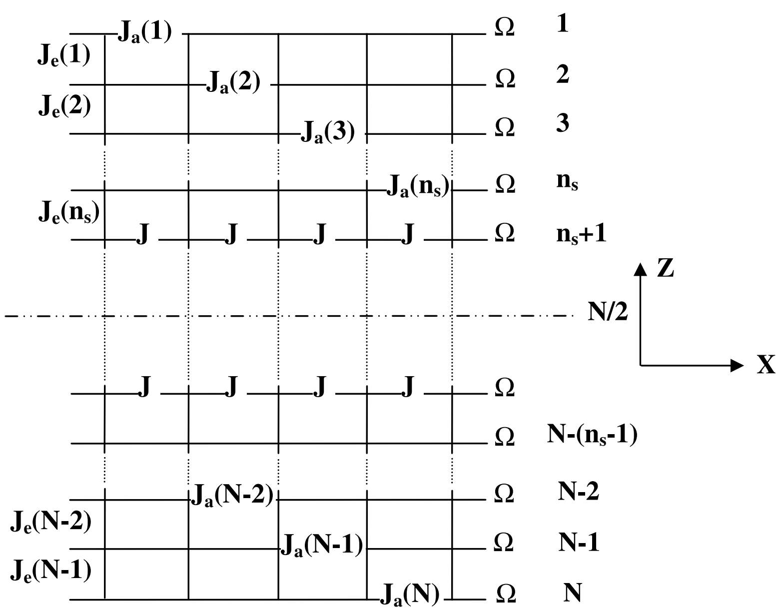

Figure 1 Geometric structure of the thin film under study, where $J_a(m)$ is the intralayer interaction, $J_e(m)$ is the interlayer interaction and J is the bulk interaction strength.

tric thin films do not pass through the ferroelectric–paraelectric phase transition. The film will keep only one state, ferroelectric state or paraelectric state throughout. If Ω is taken as a transverse field, the Hamiltonian of the pseudospin model is the same as the Hamiltonian of the Ising model under transverse field. So this model is called TIM. In TIM the interactions between any two pseudospins exist across the whole film, so the TIM can be applied to the multilayer. We take J_{ij} to be nonzero only for the nearest-neighbor sites i and j, and let $J_{ij} = J$ if both sites (i, j) are inside the film (see Fig. 1).

The pseudospin interactions in ferroelectrics are very complicated and there are no experimentally measured data available to accurately describe the surface imperfection so that an analytical expression is the only theoretically possible one conceived within the framework of the transverse Ising model. Two simple functions are assumed for the distribution functions of the intralayer and interlayer exchange interactions. The forms of two interaction functions are based on physical considerations. Because the structure of the STL is to match the structure of an imperfect surface at one end and the structure of a perfect interior at the other end, as the main factors to characterize the STL, the intralayer and interlayer exchange interaction are position dependent. Then, we chose a simple function (exponential function, trigonometric function, or any proper function) to describe the variation rules of interactions. Since the film is of a symmetrical surface, only the function for the upper film with $N/2$ layers is given:

$$J_{\mathrm{a}}(m) = \alpha\left(\frac{2m}{N}\right)^{\sigma} J, \qquad m = 1 \sim n_{\mathrm{s}}$$

and

$$m = N - (n_{\mathrm{s}} - 1) \sim N\left(n_{\mathrm{s}} \le \frac{N}{2}\right), \tag{2a}$$

$$J_{\mathrm{a}}(m) = J, \qquad n_{\mathrm{s}} < m < N - (n_{\mathrm{s}} - 1) \left(n_{\mathrm{s}} \le \frac{N}{2}\right), \tag{2b}$$

$$J_{\mathrm{e}}(m) = \beta\left(\frac{2m}{N}\right)^{\sigma} J, \qquad m = 1 \sim n_{\mathrm{s}}$$

and

$$m = N - (n_{\mathrm{s}} - 1) \sim N\left(n_{\mathrm{s}} \le \frac{N}{2}\right), \tag{3a}$$

$$J_{\mathrm{e}}(m) = J, \qquad n_{\mathrm{s}} < m < N - (n_{\mathrm{s}} - 1) \left(n_{\mathrm{s}} \le \frac{N}{2}\right), \tag{3b}$$

where m is the sequence number of the pseudospin layer, N is the film total layer number across the film, n_{s} is the number of pseudospin layers included in the STL, the parameter σ reflects the variable states of the intralayer and interlayer interactions near the lower(upper) surface. The parameters α and β are adjustable parameters representing the strength difference between the intralayer and interlayer interactions. This particular choice of $J_{\mathrm{a}}(m)$ and $J_{\mathrm{e}}(m)$ does not affect the generality of the results and conclusions.

Using the mean-field approximation the spin average along the z direction in the i-th layer can be expressed by:

$$\langle s_i^z \rangle = (\langle H_i^z \rangle / 2|H_i|) \tanh (|H_i|/2k_{\mathrm{B}}T) , \tag{4}$$

where $H_i = \left(\Omega_i, 0, \sum_j J_{ij}\langle s_j^z\rangle + 2\mu E_i^{\mathrm{d}}\right)$ is the mean field acting on the i-th spin, $\langle H_i^z\rangle = \sum_j J_{ij}\langle s_j^z\rangle + 2\mu E_i^{\mathrm{d}}$, k_{B} is the Boltzmann constant. The spontaneous polarization P_{s} is in proportion to $\langle s_i^z\rangle$. Let R_m denote the value of $\langle s_i^z\rangle$ in the m-th layer from the uppermost layer into the film, then

$$R_m = \frac{\langle H_m^z\rangle}{2|H_m|} \tanh (|H_m|/2k_{\mathrm{B}}T) \quad (m = 1, 2 \ldots N) , \tag{5}$$

where

$$\langle H_m^z\rangle = 4J_m R_m + J_{m+1}R_{m+1} + J_{m-1}R_{m-1} , \tag{6}$$

$$|H_m| = \sqrt{\Omega_m^2 + (\langle H_m^z\rangle)^2} . \tag{7}$$

Equation (5) represents a set of equations, from which R_m can be calculated iteratively using Eq. (6). When $m = 1$ or N, R_0 and R_{N+1} appeared in Eqs. (6) and (9) are taken to be zero in the calculations. The polarization of the m-th layer is proportional to the thermal average of R_m, i.e.

$$P_m = 2n\mu R_m , \tag{8}$$

where n is the number of pseudospins per volume, and μ is the dipole moment. And the mean polarization $\bar{P}$ is determined by

$$\bar{P} = \frac{1}{N}\sum_{m=1}^{N} P_m = 2n\mu \frac{1}{N}\sum_{m=1}^{N} R_m . \tag{9}$$

The depolarization field is expressed as [21]

$$E_i^{\mathrm{d}} = -\frac{P_i - \bar{P}}{\varepsilon_0} , \tag{10}$$

where ε_0 is the vacuum dielectric permittivity.

3 Numerical results and discussions Considering the depolarization effect, the phase-transition temperature T_{c} as a function of σ for a ten-layer film with several n_s values is shown in Fig. 2. The number n_s has been taken to be 1 to 5 as shown in the right part of Fig. 2. We can see that with the increase of σ, the transition temperature decreases, and every curve has a crossing point with the bulk line. At the crossing point $T_{\mathrm{c}} = T_{\mathrm{b}}$, every σ has its critical value σ_{c}. When $\sigma < \sigma_{\mathrm{c}}$, the film Curie temperature T_{c} is higher than the bulk transition temperature T_{b}. When $\sigma > \sigma_{\mathrm{c}}$, $T_{\mathrm{c}} < T_{\mathrm{b}}$. From Fig. 2, we can see that films with different thickness of STL have different critical intralayer

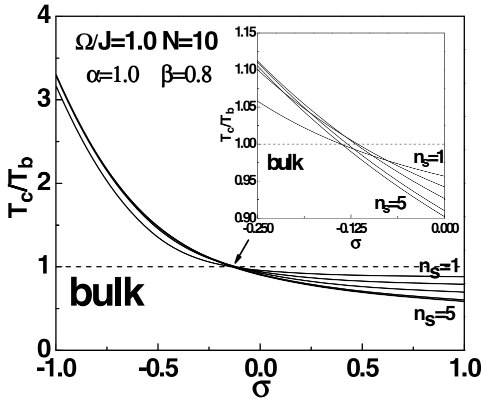

Figure 2 Curie temperature versus σ for ten-layer films with n_s from 1 to 5.

and interlayer interactions strength (J_{ac} and J_{ec}), and for films with definite thickness, increasing of the thickness of STL makes the film Curie temperature deviate further from the bulk value. In Ref. [37], the SSL model was introduced and the critical surface interaction strength is given. For a single-surface-layer film that has the critical surface interaction strength given by $J_{sc}/J = 1.25$, while for multisurface-layer films they have the same critical surface interaction strength $J_{sc}/J = 1.078$. So, by adding the STL in our model a new result have been obtained as described above.

To investigate the Ω effect in TIM, the phase-transition temperature as a function of parameter σ for a ten-layer film with $n_s = 5$ is shown in Fig. 3. Ω is the tunneling frequency between two equilibrium positions, which measures the quantum effect. When $\Omega = J$, as the dashed line shows, for certain α and β values, there exists a critical σ_c' (different from the σ_c mentioned in Fig. 2). When $\sigma > \sigma_c'$ there will be no ferroelectric phase, only a higher interaction strength can lead to the ferroelectric to paraelectric phase transition. It should be mentioned that for ten-layer films when n_s is less than five, no matter how low the strength of the intralayer and interlayer interactions, the ferroelectric phase can always exist. Based on the above analysis, we can draw the conclusion that there exists a critical STL thickness or critical film thickness at which ferroelectricity will disappear if the intralayer and interlayer interactions are weak enough. In the Ising limit $\Omega = 0$, i.e. there is no tunneling effect. As the solid line shows, if the temperature is low enough and the surface interaction strength is nonzero, a ferroelectric phase always exists.

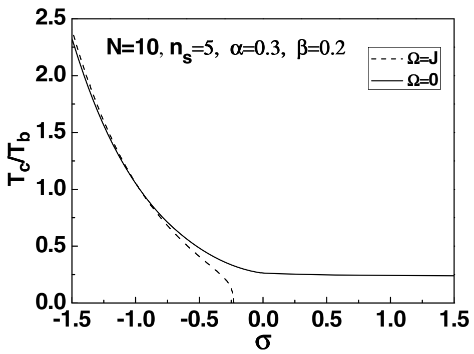

Figure 3 Curie temperature versus σ for ten-layer films with $n_s = 5$.

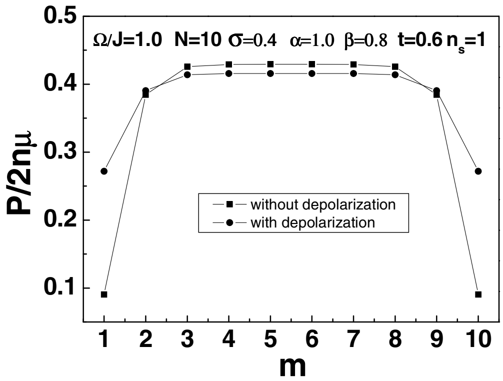

Figure 4 Polarization distribution along the thickness direction of the film with $n_s = 1$.

The geometry in most film applications is that polarization is normal to the surfaces. In this case, the effects of the depolarization field associated with the inhomogeneous polarization are important and must be included. In Fig. 4 we calculate the spontaneous polarization for a thin film of ten layers in the presence of the depolarization field, and compare the results with those in the absence of a depolarization field. The surface spontaneous polarizations are weaker than the interior polarizations in the film. We can see that the depolarization effect is to reduce the polarizations at the center, and to enhance those on the surface. This means that the influence of the depolarization field is to flatten the spontaneous polarization profile, which is in accord with results obtained by Ginzburg–Landau theory [10]. For simplicity, and focusing our attention to investigate the STL effects, the depolarization field is neglected in the following calculations.

For films with different thickness of STL, the variation of the spontaneous polarization along the film thickness as a function of sequence number m is plotted in Fig. 5. The

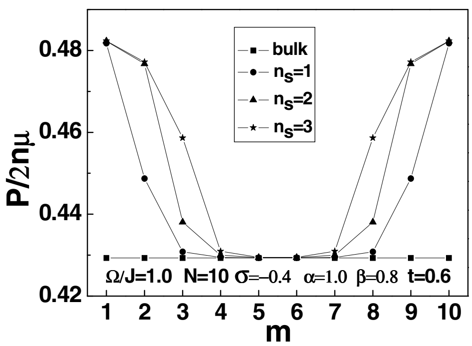

Figure 5 Polarization distribution along the thickness direction of the film with different n_s.

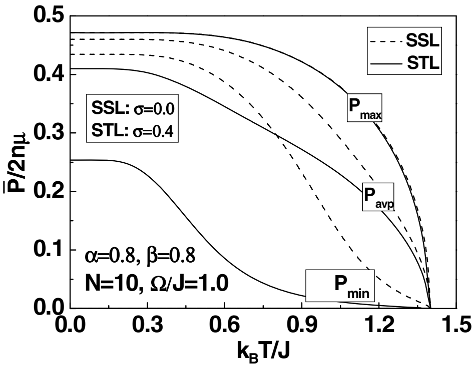

Figure 6 Average spontaneous polarization as a function of temperature.

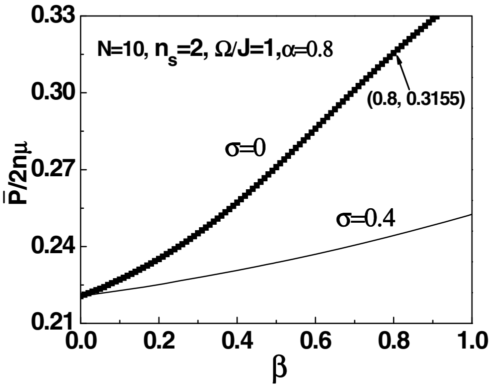

Figure 8 Average spontaneous polarization versus β for ten-layer films with different σ.

parameters α and β are taken as 1.0 and 0.8 for these calculations. The straight line represents the bulk polarization distribution. Only the case when the surface ferroelectricity is higher than the interior ferroelectricity is considered. We can see that the STL has a strong influence on the polarization. It makes the polarization distribution in the film inhomogeneous, and makes the polarization higher compared with the bulk value. The inhomogeneous polarization distribution in the film originates from the uppermost layer, changes gradually in the transition layers, and ends in the film. Because of the Coulomb long-range interaction, the influence of the STL on the polarization will be felt at a certain depth of the film even if the thickness of STL could be very thin. The large ratio of STL to volume makes the surface effects more pronounced in thinner ferroelectric films. We can see that the thicker the STL, the larger the polarization, and whatever the value of n_s, the uppermost layer has the largest polarization. In Ref. [20], a SSL model was introduced, and it is reported that when the film polarization is larger than the corresponding bulk value, the uppermost layer had the largest polarization in the case of one-surface-layer films, while for multisurface-layer films the second layer has the largest polarization. In the SSL model the interaction strength remained uniform at the surface, and the pseudospin in the second surface layer has a larger coordinate number (six in our case, the coordinate number in the first layer is five) and a larger indirection, which means the second layer has the largest polarization. In reality, the surface is a transition layer and the interaction strength is of gradient variation, hence, in the STL model the first layer has the largest polarization, which is in better agreement with the results obtained from GLD theory [10].

We have also studied ferroelectric thin films with smaller polarization near the surface than that of the bulk. Figure 6 shows the temperature dependence of the middle, average and first-layer spontaneous polarization ($P_{\max}$, P_{avp} and $P_{\min}$) for a ten-layer film with different n_s. For comparison, the corresponding results of SSL system are also calculated. Parameters α and β taken as the same value 0.8, in this case when $\sigma = 0$ the film has SSL. In STL model, σ is taken as 0.4. One can see from the results in Fig. 6 that $P_{\max}$, P_{avp} and $P_{\min}$ in the STL model are lower than the corresponding polarizations in SSL model, and the difference reflecting on $P_{\min}$ is most obvious, that is to say, the SSL model can magnify the polarization and transition temperature. The interaction gradient variation in the surface layer is responsible for these results, and the film polarization properties are greatly influenced by surface situations.

The influence of parameters α and β on the mean polarization of a ten-layer film with $n_s = 2$ is demonstrated in Figs. 7 and 8. The mean polarization increases monotonously with the increase of α and β. When $\sigma = 0$, $\alpha = \beta = 0.8$, the structure is simplified to the SSL model and the mean polarization $\bar{P}/2n\mu = 0.3155$, which only corresponds to a point in Figs. 7 or in 8. Hence, our model provides a more complete picture on the effects of intralayer and interlayer interactions and reflects a more comprehensive and realistic situation of ferroelectric films.

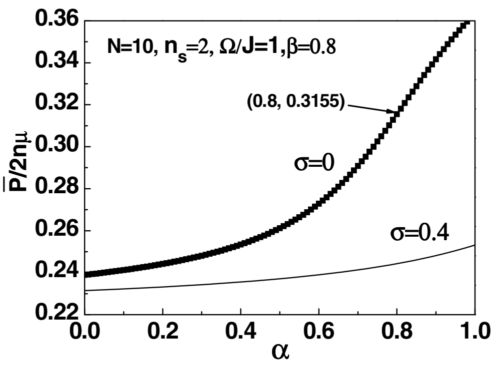

Figure 7 Average spontaneous polarization versus α for ten-layer films with different σ.

4 Conclusion Ferroelectric thin films described by an Ising model in a transverse field have been studied under the mean-field approximation. The influence of STL on the polarization properties are investigated. Numerical examples are given for a second-order ferroelectric phase transition, and the following conclusions are obtained: (1) σ is an important parameter to characterize the STL. There exists a critical σ_c to make the Curie temperature of the film higher or lower than the corresponding bulk material value. (2) The effect of Ω in TIM has an important influence on ferroelectric thin films. (3) The depolarization field flattens the spontaneous polarization distribution in ferroelectric thin films. (4) The traditional SSL model magnifies the polarization and transition temperature, the STL model reflects a more realistic situation of applied films.

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