

Influence of Surface Transition Layers on Phase Transformation and Pyroelectric Properties of Ferroelectric Thin Film *

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Taking into account surface transition layers (STLs), we study the phase transformation and pyroelectric properties of ferroelectric thin films by employing the transverse Ising model (TIM) in the framework of the mean field approximation. The distribution functions representing the intra-layer and inter-layer couplings between the two nearest neighbour pseudo-spins are introduced to characterize STLs. Compared with the results obtained by the traditional treatments for the thin films using only the single surface transition layer (SSL), it is shown that the STL model reflects a more realistic and comprehensive situation of films. The effects of various parameters on the phase transformation properties have shown that STL can make the Curie temperature of the film higher or lower than that of the corresponding bulk material, and the thickness of STL is a key factor influencing the film properties. For a film with definite thickness, there exists a critical STL thickness at which ferroelectricity will disappear when the intra-layer and inter-layer interactions are weak.

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Although the influence of surface and size effects on ferroelectric phase transformation has been known since the 1950s,^[1,2] in recent years it has aroused renewed interest due to the fast development of fabrication techniques of ferroelectric thin films and composites.^[3–16] It has been recognized that a structure transition layer may exist near the film surface, which has different properties compared with the interior of the film due to the limitations of processing techniques and the interaction between the film and substrate.

In the theoretical treatment, Ginzburg–Landau–Devonshire (GLD) thermodynamic theory is frequently used to study the properties of ferroelectric thin films.^[17–20] On the microscopic level, Wu *et al.*^[21] have investigated the surface effect on the dielectric properties of relaxor ferroelectric films using the Monte Carlo simulation.

The TIM with the mean field approximation has been applied to study properties of ferroelectric thin films containing surface transition layers. When surface exchange interaction between two pseudo-spins and surface transverse field is different from that of the bulk material, many novel characteristics have been found recently in terms of phase diagrams and physical properties.^[22–37]

The traditional TIM method used to describe the property difference of the surface transition layers from the interior of a film is to modify Ω_i and J_{ij} (the transverse field and the two pseudo-spin exchange interaction) from bulk values. The Ω_i and J_{ij} values

are treated to be uniform in surface transition layers and the structural difference between surface transition layer and the interior of film is a ‘single-step’ model. Considering the multilayer structure of surface transition layers, it is more realistic to investigate the role of the intra-layer (within a pseudo-spin layer) and inter-layer (cross pseudo-spin layers) interactions [$J_a(m)$ and $J_e(m)$ shown in Fig. 1] between two pseudo-spins in the surface transition layer. We introduce distribution functions of the intra-layer and inter-layer interactions $J_a(m)$ and $J_e(m)$ to describe the structure change from the surface transition layer to the perfect interior of the film. From such more realistic model, one may find the way to better control the properties of artificially fabricated films by controlling STL. Such a model can reflect a more realistic situation of the film than the SSL model. We assume that the film properties only change along the film thickness direction are uniform in the same pseudo-spin layer parallel to the surface. For simplicity, the transverse field is taken to be the same value as that of bulk in our calculations.

The Hamiltonian of the TIM is^[6–11]

$$H = -\Omega_i \sum_i s_i^x - \frac{1}{2} \sum_{ij} J_{ij} s_i^z s_j^z, \quad (1)$$

where Ω_i is the transverse field, s_i^x and s_i^z are the x and z components of a $1/2$ -spin operator at site i , J_{ij} is the two-spin exchange interaction constant between site i and site j , and the sum \sum_{ij} runs over all pseudo-spin pairs. We assume that $J_{ij} = J_a(m)$ if sides i and

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j are within one pseudo-spin layer; $J_{ij} = J_e(m)$ if two sites are across two different pseudo-spin layers. However, when both the two sites are inside perfect interior of the film, the exchange interaction J_{ij} is taken to be the same value as the bulk constant J , i.e. $J_{ij} = J_a(m) = J_e(m) = J$ (see Eqs. (2) and (3)).

The structure model used to describe the ferroelectric properties of the thin film is illustrated in Fig. 1. For simplicity but without loss of generality, we assume that the z -direction is perpendicular to the surface and parallel the spontaneous polarization. In this Letter, we are interested in the influence of the STL on the properties of film. Hence, for simplicity, an N -layer film with symmetrical surface structure is studied as a model system. The number of pseudo-spin layers included in the STL is n_s . We take J_{ij} to be non-zero only for the nearest-neighbour sites i and j , and let $J_{ij} = J$ if both sites (i, j) are inside the film (see Fig. 1).

Because there are no experimentally measured data available to accurately describe the surface imperfection, two simple functions are assumed to describe the inhomogeneous distribution of the intra-layer and inter-layer exchange interactions.

$$J_a(m) = \alpha \left(\frac{m}{n_s + 1} \right)^\sigma J, \quad m = 1 \sim n_s, \\ m = N - (n_s - 1) \sim N, \quad n_s \leq N/2, \quad (2a)$$

$$J_a(m) = J, \quad n_s < m < N - (n_s - 1), \quad n_s \leq N/2, \quad (2b)$$

$$J_e(m) = \beta \left(\frac{m}{n_s + 1} \right)^\sigma J, \quad m = 1 \sim n_s, \\ m = N - (n_s - 1) \sim N, \quad n_s \leq N/2, \quad (3a)$$

$$J_e(m) = J, \quad n_s < m < N - (n_s - 1), \quad n_s \leq N/2, \quad (3b)$$

where m is the sequence number of the pseudo-spin layer, N is the total layer number across the film, the parameter σ reflects the variable intensity of the intra-layer and inter-layer interactions near the lower (upper) surface. The parameters α and β are adjustable parameters representing the strength of intra-layer and inter-layer interactions. This particular choice of $J_a(m)$ and $J_e(m)$ does not affect the generality of the results and conclusions.

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

$$\langle s_i^z \rangle = \left(\langle H_i^z \rangle / 2|\mathbf{H}_i| \right) \tanh \left(|\mathbf{H}_i| / 2K_B T \right), \quad (4)$$

where $\mathbf{H}_i = (\Omega_i, 0, \sum_j J_{ij} \langle s_j^z \rangle)$ is the mean field acting on the i th spin, $\langle H_i^z \rangle = \sum_j J_{ij} \langle s_j^z \rangle$, H_i^z is the z -component of \mathbf{H}_i . K_B is the Boltzmann constant. The spontaneous polarization P_s is proportional to $\langle s_i^z \rangle$. Let R_i denote the value of $\langle s_i^z \rangle$ in the i th layer

from the uppermost layer into the film, then

$$R_i = \frac{\langle H_i^z \rangle}{2|\mathbf{H}_i|} \tanh(|\mathbf{H}_i|/2K_B T), \quad i = 1, 2, \dots, N, \quad (5)$$

where

$$\langle H_i^z \rangle = 4J_i R_i + J_{i+1} R_{i+1} + J_{i-1} R_{i-1}, \quad (6)$$

$$|\mathbf{H}_i| = \sqrt{\Omega_i^2 + (\langle H_i^z \rangle)^2}. \quad (7)$$

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

$$P_i = 2n\mu R_i, \quad (8)$$

where n is the number of pseudo-spins per volume, and μ is the dipole moment.

Considering that R_i will be small when the temperature is near the Curie temperature, we have the following linear equations:

$$\Gamma_i R_i = 4J_a(m) R_i + J_e(m) R_{i+1} + J_e(m-1) R_{m-1}, \\ m = 1 \sim n_s, \quad m = N - (n_s - 1) \sim N, \quad (9a)$$

$$\Gamma_i R_i = 4J R_i + J R_{i+1} + J R_{i-1}, \\ n_s < m < N - (n_s - 1), \quad (9b)$$

where $\Gamma_i = 2\Omega_i \coth(\Omega_i/2K_B T)$.

From Eq. (9a) and (9b) the Curie temperature can be determined by taking the coefficient determinant to be zero. For bulk material with a second-order phase transition, the Curie temperature T_b can be determined from the transcendental equation:^[25]

$$\tanh(\Omega/2K_b T_b) = 2\Omega/n_0 J, \quad (10)$$

where J is the nearest neighbour interaction and $n_0 = 6$ is the coordinate number.

The pyroelectric coefficient reflects the ability to generate charge through temperature variation, which is defined as

$$\alpha = \left. \frac{\partial \bar{P}}{\partial T} \right|_T = 2nu \left. \frac{\partial \bar{R}}{\partial T} \right|_T. \quad (11)$$

Generally speaking, the spontaneous polarization of the ferroelectrics decreases with the increasing temperature, hence the pyroelectric coefficient is usually negative. In our calculation, we take the opposite value to make the pyroelectric coefficient to be positive,

$$\rho = - \left. \frac{\partial \bar{R}}{\partial T} \right|_T, \quad (12)$$

where $\bar{R} = \frac{1}{N} \sum_{i=1}^N R_i$.

The phase transformation temperature T_c as a

function of σ is shown in Fig. 2 for a ten-layer film with the number n_s taking a value from 1 to 5. One can see from Fig. 2 that with the increasing σ , the transformation temperature decreases and there is a critical dot σ_b ($\sigma = \sigma_b$, when $T_c/T_b = 1$. T_b is the bulk transformation temperature) in every curve. Films with different thicknesses of STLs have different critical intra-layer and inter-layer interactions strength (J_{ab} and J_{eb}). When $\sigma < \sigma_b$, the film Curie temperature T_c is higher than the bulk transformation

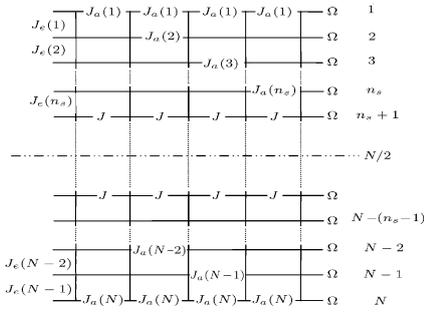


Fig. 1. Geometric structure of the thin film, $J_a(m)$ the intra-layer interaction, $J_e(m)$ the inter-layer interaction, and J the bulk interaction.

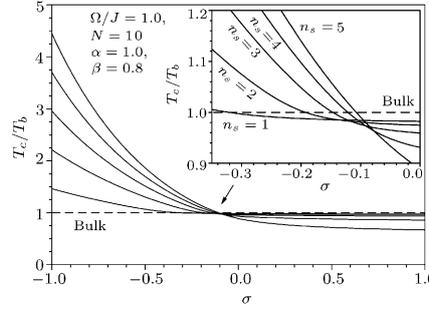


Fig. 2. Curie temperature vs σ for ten-layer films with n_s from 1 to 5.

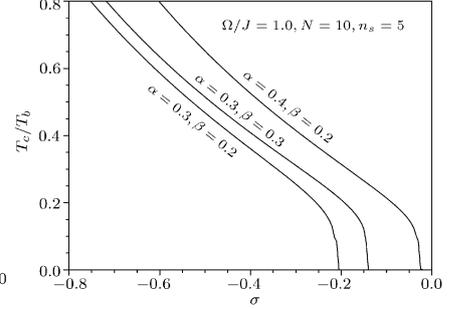


Fig. 3. Curie temperature vs σ for ten-layer films with $n_s = 5$.

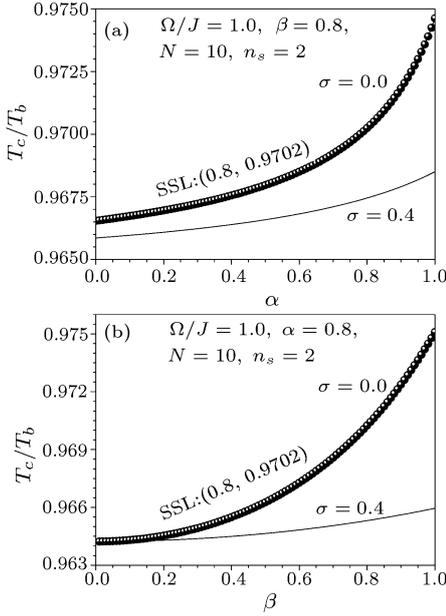


Fig. 4. (a) Curie temperature vs α for ten-layer films with $n_s = 2$. (b) Curie temperature vs β for ten-layer films with $n_s = 2$.

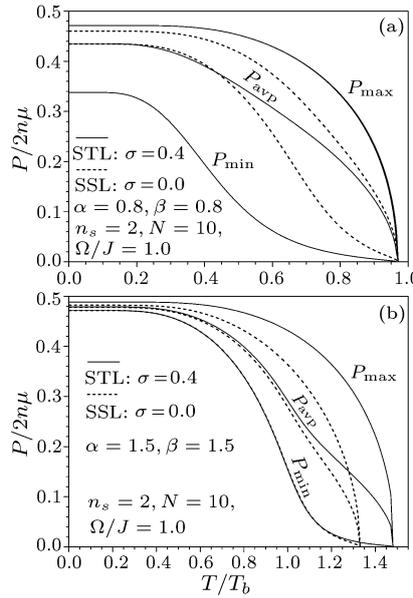


Fig. 5. Temperature dependences of the middle, average and first-layer spontaneous polarization (P_{\max} , P_{avp} and P_{\min}) with different n_s values: (a) the surface polarization is lower than the bulk value, (b) the surface polarization is larger than the bulk value.

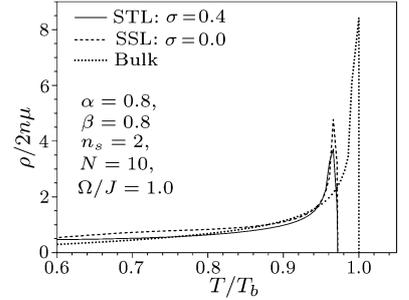


Fig. 6. Comparison of the temperature dependence of the pyroelectric coefficient calculated by the SSL and STL model, respectively.

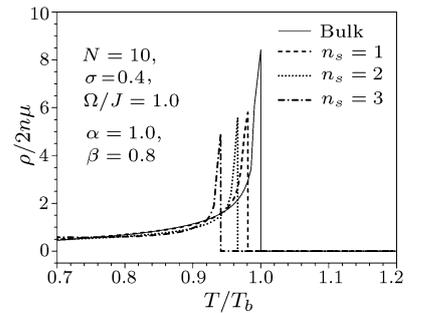


Fig. 7. Temperature dependence of the pyroelectric coefficient with different n_s values when the surface polarization is lower than the bulk value.

The σ dependence of the phase transformation temperature T_c for a ten-layer film with $n_s = 5$ is shown in Fig. 3. For certain α and β values, there exists a critical σ_c . When $\sigma > \sigma_c$ there will be no ferroelectric phase. Based on the above analysis, we can draw the conclusion that a critical STL thickness or critical film thickness exists at which ferroelectricity will disappear if the intra-layer and inter-layer interactions are weak. From Fig. 3, we can also see that both parameters α and β have influence on the transition temperature as well as the critical σ_c value, but α has stronger influence than β .

The influence of parameters α and β on the phase transformation behaviour of a ten-layer film with $n_s = 2$ is demonstrated in Figs. 4(a) and 4(b). The phase transformation temperature increases monotonously with the increasing α and β . When $\sigma = 0$, $\alpha = \beta = 0.8$, the structure is simplified to the SSL model and the phase transformation temperature $T_c/T_b = 0.9702$, which only corresponds to a point in Fig. 4(a) or Fig. 4(b). Hence, our model provides a more complete picture on the behaviour of intra-layer and inter-layer interactions and reflects a more comprehensive and realistic situation of ferroelectric thin films.

Figures 5(a) and 5(b) show the temperature dependence of the middle, average and first-layer spontaneous polarizations (P_{\max} , P_{avp} and P_{\min}) for a ten-layer film with $n_s = 2$. For comparison, the corresponding results of the 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. One can see from Fig. 5(a) that P_{\max} , P_{avp} and P_{\min} in the STL model are lower than the corresponding polarizations in the SSL model, and the difference reflecting on P_{\min} is most obvious, that is to say, the SSL model may magnify the polarization and transition temperature. In Fig. 5(b), the difference reflecting on P_{\max} is most obvious. That is to say, in this case the SSL model may reduce the polarization and transition temperature. The interaction gradient variation in surface transition layer should be responsible for these results, which has not been considered in the SSL model.

In Fig. 6, the corresponding results calculated from the SSL model have also been given for comparison. It is shown that the pyroelectric peak of the SSL model is higher than that of the STL model, which can easily be explained from Fig. 5(a) due to the magnified phase transformation temperature and polarization in the SSL model. When the surface polarization is larger, the contrary conclusions can be easily drawn from Fig. 5(b).

Figure 7 shows the temperature dependence of the pyroelectric coefficient for a ten-layer film with different n_s . We can see that n_s is an important factor

influencing on the film properties. With the increasing n_s , the pyroelectric peak shifts to lower temperature and the peak value decreases.

The phase transformation and pyroelectric properties of a ten-layer ferroelectric thin film have been studied by a modified transverse Ising model. Inhomogeneous intra-layer and inter-layer interactions $J_a(ij)$ and $J_e(ij)$ are introduced to characterize the surface transition layers (STL). Our results can be summarized as follows: (1) The STL model can reflect a more realistic and comprehensive situation of films than the SSL model. (2) STL may make the film Curie temperature higher or lower than the corresponding value of bulk material. (3) Thickness of the STL is an important factor influencing the film properties. (4) There exists a critical STL thickness or critical film thickness, i.e., the ferroelectricity of a film with the critical thickness will disappear if the intra-layer and inter-layer interactions are weak. (5) The phase transformation properties depend more strongly on intra-layer interaction than inter-layer interaction.

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