Effect of thickness on the magnitude of spontaneous polarization in thin ferroelectric films

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Abstract. The influence of the thickness of a ferroelectric film and the depolarizing field on its spontaneous polarization and the order parameter has been investigated by means of the Monte-Carlo method. Dependences of the polarization of the thin ferroelectric film on temperature at different values of its thickness and the potential well depth of the Lennard-Jones potential are calculated. The thickness of the "dead" layer is analyzed depending on the temperature and of the potential well depth.

1. Introduction
The introduction of ferroelectric films in modern microelectronic devices, related with limitations on the reduction in the size of the element base, has revived interest in the question of the possible existence of a critical thickness of the films necessary for the appearance of ferroelectricity[1].

The critical size of the ferroelectric film is usually understood to mean the minimal thickness of the sample, at which its ferroelectric properties disappear, and it becomes a usual dielectric material [2]. To describe the properties of the film vs. its thickness, different models are used, taking into account: a) correlation effects [3,4], b) the presence of a transient dielectric layer ("dead" layer)[5], c) the bulk charge density and the surface charge density near boundaries of ferroelectric [6], d) thermoelastic properties [7,8].

However, these effects cannot be considered isolated, because they all are related each with other. We used the Ising model for computer simulation of ferroelectric systems. This model has a discrete symmetry group. Onsager has been strictly proved that there is a spontaneous polarization in this model of monolayer [9]. However, it has been experimentally established that there are sufficient ferroelectric thin films, in which the spontaneous polarization may be absent [2]. In this paper, the Ising model was modified to take into account thermoelastic properties and a depolarizing field.

2. Model
To describe properties of the ferroelectric films and to study of ordering effects we use a three-dimensional lattice model (Fig.1), consisting of \( N_1, N_2 \) and \( N_3 \) nodes along the respective axes of the Cartesian coordinate system. The position of the lattice node is characterized by the set of three numbers \( \vec{n} = (n_1, n_2, n_3) \).

In this paper, the interaction energy of dipoles is described by a potential that takes into account orientational interactions of particles (as in the classical Ising model) and the additional term representing the Lennard-Jones potential:
where $\mathcal{E}$ is the well depth of the Lennard-Jones potential, $r_{i,j}$ is the distance between the dipoles, $R_0$ is average distance between the dipoles (in the absence of orientational interactions). The second term of equation (1) does not depend on temperature and polarization, in contrast to the first term.

When the polarization reduced transverse film dimensions in the directions $N_2$ and $N_3$, the distances between the dipoles change in these directions. Therefore, the potential of orientational interactions $H_{or}$ may be represented by the formula:

$$
H_{or} = -\sum_n K_1 S_{n_1,n_2,n_3} S_{n_1,n_2,n_3} - \sum_n K_20 \frac{r_0^3}{\pi} S_{n_1,n_2,n_3} S_{n_1,n_2,n_3} - \sum_n K_20 \frac{r_0^3}{\pi} S_{n_1,n_2,n_3} S_{n_1,n_2,n_3} + p \sum_n S_n E_d
$$

where the quantity $S_n$ takes two values: +1 and -1, $K_1$ is coefficient of exchange interactions in the longitudinal direction $N_1$, $p$ is the module of dipole moment, $K_20$ is the constant of exchange interactions between the dipoles in the transverse directions $N_2$ and $N_3$. The quantity $E_d$ is the projection of the vector of strength of the depolarizing field on the direction $N_1$.

The short-range orientational order parameters in the longitudinal and transverse directions $\mu$ and $\mu'\perp$ are determined correspondingly by the following formulas:

$$
\mu = \frac{1}{N_1 N_2 N_3} \left( \sum_n S_{n_1,n_2,n_3} S_{n_1,n_2,n_3} \right)
$$

$$
\mu'\perp = \frac{1}{N_1 N_2 N_3} \left( \sum_n S_{n_1,n_2,n_3} S_{n_1,n_2,n_3} \right)
$$
\[ \mu_\perp = \frac{1}{2N_1N_2N_3} \left( \sum_n S_{n_1,n_2,n_3} S_{n_1,n_2,n_3-1} + \sum_n S_{n_1,n_2,n_3} S_{n_1,n_2,n_3-1} \right) \]  

(3b)

To simplify the calculations the variable \( x^3 = \frac{r_0}{r} \) was introduced. The values \( \mu_\parallel \) and \( \mu_\perp \) depend on the variable \( x \). As an example, figure 2 shows the dependence of the short-range orientational order parameter \( \mu_\parallel \) on the variable \( x \) at different reduced temperatures.

![Figure 2. The short-range orientational order parameter \( \mu_\parallel \) vs. the variable \( x \) at different reduced temperatures \( k_B T / K_1 = 15(1), 20(2), 25(3) \), \( \epsilon / K_1 = 0.01, K_20 / K_1 = 1 \).](image)

In contrast to the classical Ising model, the interactions between dipoles in the model considered depend on the distance between them. Therefore, it was necessary to calculate the average value of the distance between dipoles at which the potential energy has a minimum. This problem is reduced to finding the minimum of the function:

\[ h = 4\epsilon \left( \frac{r_0^{12}}{r^{12}} - 2 \frac{r_0^6}{r^6} \right) - 2K_1\mu_\parallel - 4K_{20}\mu_\perp \frac{r_0^3}{r^3} \]  

(4)

The differentiation of equation (4) with respect to \( r \) leads to the equation:

\[ \epsilon(4x^3 - 4x) - \frac{1}{2}K_1 \frac{\partial \mu_\parallel (x)}{\partial x} - K_{20} \frac{\partial \mu_\perp (x)}{\partial x} x - K_{20} x \mu_\perp (x) = 0 \]  

(5)

To solve equation (5) the functions \( \mu(x) \) and \( \mu_\perp (x) \) were calculated by the Monte Carlo method, and they were approximated by the function \( \text{erf} \left( \frac{x - m}{\sigma} \right) \), where \( m \) and \( \sigma \) are fitting coefficients.

3. Results of simulation

Usually, the change of properties of the system under an external action is described as its response to this action. For example, the dielectric susceptibility reflects a change in the polarization upon an electric field:

\[ \chi = \frac{1}{k_B T} \left[ \langle S_n^2 \rangle - \langle S_n \rangle^2 \right] \]  

(6)
Figure 3 shows the dependence of the average distance between the dipoles (a) and the susceptibility of the ferroelectric system (b) on the reduced temperature for different values of the potential well depth in the absence of the depolarizing field.

As is seen from Fig.3, if the temperature is increased, the average distance between dipoles near the phase transition point increases abruptly. At high temperatures, the distance \( r \rightarrow r_0 \). With a decrease in the of the potential well depth of the Lennard-Jones potential, the average distance between the dipoles decreases, that leads to a shift of the phase transition point to higher temperatures.

4. Influence of depolarizing field

Under the action of internal electric field caused by spontaneous polarization, free particles move to the outer surfaces of the film and create an additional depolarizing field which depends on the value of the long-range orientational order parameter:

\[
E_d(n_i) = E_0 \mu \left( e^{-\lambda(n_i-n_0)}S_{n_i,n_0,n_0} + e^{-\lambda(n_i-n_1)}S_{n_i,n_0,n_1} \right)
\]

where \( E_0 \) and \( \lambda \) are constants determined by the number of free carriers in the film, the quantity \( \mu \) is the long-range order parameter in the ferroelectric film, which value is determined by the following formula:

\[
\mu = \frac{1}{N_1N_2N_3} \sum_n S_n
\]

Figure 4 shows the dependence of the long-range orientational order parameter \( \mu \) on the reduced temperature \( k_B T / K_1 \) for different values of the depolarizing field. It is shown that the inclusion of the depolarizing field leads to following effects: 1) a decrease in the order parameter and 2) a shift of the phase transition point to the region of lower temperatures.
Figure 4. The long-range orientational order parameter $\mu$ vs. the reduced temperature $k_B T / K_1$ without the depolarizing field (1) and in the presence of the field at the value $pE_d / K_1 = 5(2), 10(3)$ at the potential well depth $\varepsilon / K_1 = 0.01$.

Figures 5-6 show the dependence of the long-range order parameter on the thickness of the ferroelectric film $N_l$ at different reduced temperatures and the potential well depth. As the thickness of the film decreases, the polarization decreases, and decreases sharply to zero at a certain thickness.

Figure 5. The long-range order parameter $\mu$ vs. the thickness of the ferroelectric film $N_l$ at different reduced temperatures $k_B T / K_1 = 2(1), 7(2), 10(3)$ and the potential well depth $\varepsilon / K_1 = 0.01$.

Figure 6. The long-range order parameter $\mu$ vs. the thickness of the ferroelectric film $N_l$ at different potential well depths $\varepsilon / K_1 = 0.01(1), 1(2)$ at the reduced temperature $k_B T / K_1 = 5$. 
5. Conclusion

Therefore, correlation effects related with the ordering in thin ferroelectric films lead to the appearance of a surface charge density, the depolarizing field, and also to the presence of the "dead" layer. It is shown that the depolarizing field decreases the polarization of the film and shifts the phase transition point to the region of lower temperatures. In sufficiently thin films, the polarization is not observed even at low temperatures. This result can be explained by the fact that its size is less than double thickness of the "dead" layer that is considered as the critical size of the film, at which its ferroelectric properties disappear, and the film becomes a usual dielectric material. As shown in figures 5-6, the thickness of the "dead" layer is 2-10 unit cells. The value of the critical thickness \( N_c \) increases with decrease in the well depth of the potential of Lennard-Jones (Fig.5) and increasing temperature (Fig.6). Experimental techniques allowed to obtain perovskite ferroelectric films with a thickness of 40 Å (ten unit cells) [10]. The authors [11] identified a critical thickness of about three unit cells, below which there was no ordering at low temperatures. In the frame of approach proposed in this paper, such difference in the experimental results can be explained by the difference in the potential well depths and the concentrations of free carriers in the materials considered.

6. References

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