A new type of first-order phase transition in ferroelectric thin films

A new type of first-order phase transition in ferroelectric thin films

Bao-Dong Qu, Wei-Lie Zhong and Pei-Lin Zhang

Physics Department, Shandong University, Jinan 250100, People's Republic of China

Abstract. Phase transition behaviour in ferroelectric thin films is studied via the calculation of free energy for the case when the bulk phase transition is second order. If the spontaneous polarization is reduced near the surface, the phase transition in ferroelectric thin films will become of first order. As well as shifts in the Curie point to a lower temperature, the peak height of susceptibility at the critical point decreases with decrease in the film thickness. When the spontaneous polarization is enhanced near the surface, the phase transition behaviour of spontaneous polarization shows a tail-like structure.

1. Introduction

In recent years, there has been considerable interest in the surface effects on the phase transition properties of ferroelectric thin films. In the framework of the Landau theory, a form of free energy based on the earlier work by Lubensky [1] and Mills [2] for ferromagnetic films has been used to describe the phase transition in ferroelectric thin films. A number of papers were devoted to the surface and size effects on the ferroelectric properties [3–6]. Among these studies Kretschmer and Binder [3] studied extensively the surface, especially the depolarizing field effects on the order parameter profile and various critical exponents at the surface. Tilley and Zeks [5] derived explicit mean field expressions for critical temperatures and equilibrium forms of the order parameter, but all these researchers studied the phase transition, assuming implicitly that it is second order. However, this is not necessarily the case, because the added surface free energy might influence the stability of ferroelectric phase in the films. Therefore, it is expected that more details of phase transition behaviour in ferroelectric thin films might be revealed via the calculation of the film free energy. In this context, results for the case when the bulk phase transition is second order have not been found. For the case when the bulk phase transition is first order, a foot-like curve of spontaneous polarization P_s versus temperature can be obtained from the phenomenological theory [7], and the results were compared with the experimental measurement on KNO_3 thin films. When the bulk phase transition is second order, experiments on TGS thin crystal plates showed a tail-like P_s–T curve [8], but explicit calculated curves have not been given except for the transverse Ising model of a semi-infinite ferroelectric [4]. Therefore, in the present work, we study the phase transition properties via the calculation of the film free energy and discuss the transition behaviour of spontaneous polarization in ferroelectric thin films.

2. General theory

Considering a monodomain ferroelectric film with thickness L, we suppose that the polarization lies in the plane of the film surface and that the depolarization effects are negligible. The free energy expansion has the form

$$\frac{F}{S} = \int_{-L/2}^{L/2} \left[\frac{1}{2} A P^2 + \frac{1}{4} B P^4 + \frac{1}{2} C \left(\frac{dP}{dz} \right)^2 \right] dz + \frac{1}{2} C \delta^{-1} (P_-^2 + P_+^2) \qquad (1)$$

where S is the surface area of the film with plane surface at $z = \pm \frac{1}{2} L$, P_+ and P_- the spontaneous polarization at $z = \pm \frac{1}{2} L$, and δ the extrapolation length measuring the strength of coupling in the surface layer. It is assumed that $B > 0$, $C > 0$ and $A = A_0 (T/T_{0c} - 1)$. T_{0c} is the bulk Curie temperature. The equilibrium form of $P(z)$ is determined by minimizing the free energy with respect to $P(Z)$, which yields

$$C \, d^2 P/dz^2 - AP - BP^3 = 0 \qquad (2)$$

with boundary conditions

$$dP/dz \pm \delta^{-1} P(z) = 0 \qquad z = \pm \frac{1}{2} L. \qquad (3)$$

Suppose that the configuration is symmetric, i.e. $P_+ = P_- = P_1$; the polarization reaches its extreme value $P(0)$ at the centre of the film, and $dP/dz = 0$ at $z = 0$. The first integration of equation (2) is

$$\frac{1}{2} C \left(\frac{dP}{dz} \right)^2 = \frac{1}{2} A \left[P^2 - P^2(0) \right] + \frac{1}{4} B \left[P^4 - P^4(0) \right]. \qquad (4)$$

Inserting equation (3) into equation (4), we have the relation between $P(0)$ and P_1:

$$B \delta^2 P_1^4 + \left(2\delta^2 A - 2C \right) P_1^2 - \delta^2 P^2(0) \left[B P^2(0) + 2A \right] = 0. \qquad (5)$$

The polarization profiles are given by

$$z = \pm \int_{P(0)}^{P(z)} \left(\frac{2C}{2A[P^2 - P^2(0)] + B[P^4 - P^4(0)]} \right)^{1/2} dP. \qquad (6)$$

The signs before the integration depend on the signs of δ. Then the film thickness

$$L = \pm 2 \int_{P(0)}^{P_1} \left(\frac{2C}{2A[P^2 - P^2(0)] + B[P^4 - P^4(0)]} \right)^{1/2} dP. \qquad (7)$$

The phase transition behaviour of spontaneous polarization is calculated by keeping the film thickness constant; and the film free energy is obtained by inserting the polarization back into equation (1).

3. Transition behaviour for $\delta > 0$

From equations (2) and (3), Tilley and Zeks [5] had found the solution of $P(z)$ explicitly using the standard properties of elliptic functions. The spontaneous polarizations at different depths z have similar temperature dependences and reach zero at a critical temperature T_0 simultaneously. On the assumption implicitly that the transition is second order, the stability of the ferroelectric phase in the film is not involved in their work and the critical temperature T_0 was considered to be the Curie temperature which is determined by $\tan(L/2\xi) = \xi/\delta$ for $\delta > 0$, where $\xi^2 = C/|A|$ is the bulk coherent length, but the added surface free energy might influence the stability of the ferroelectric phase in the films. If the ferroelectric phase in the film is stable, its free energy must be negative. Figure 1 shows the dependence of spontaneous polarization at the centre of the film as well as the film free energy on the temperature. It can be seen that the spontaneous polarization decreases with increase in the temperature and reaches zero continuously at the critical temperature T_0. The free energy, however, does not reach zero monotonically. It increases with increasing temperature and reaches zero firstly at T_c, then goes through a positive maximum and finally comes back to zero at T_0. Obviously, that stable ferroelectric phase can only be maintained up to T_c, although $P(z)$ has an explicit solution below T_0. For $T_c < T < T_0$, the ferroelectric phase is metastable. The spontaneous polarization in the film might vanish abruptly at a temperature higher than T_c. The behaviour shows that the phase transition in the film is rather first order and the Curie temperature should be T_c. We noticed that a change in phase transition order from second to first also occurs when the free energy associated with the semiconducting electrodes and the influence of depolarization field are taken into consideration [9–11], but the first-order phase transition in our calculation results from the intrinsic changes in polarization near the surface; no electrode is involved in the model.
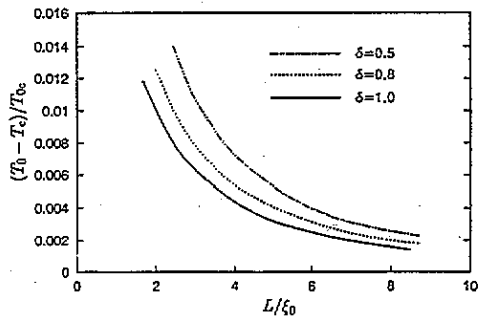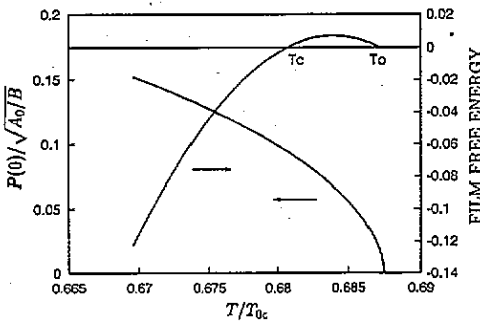

Figure 1. Temperature dependence of the spontaneous polarization and the film free energy ($A_0 = 10$; $B = 0.1$; $C = 5$; $\delta = 0.5$; $L/\xi_0 = 4.2$; $\xi_0^2 = C/A$).

Figure 2. Thickness dependence of the difference between T_0 and T_c.

It is difficult to determine T_c generally. The thickness dependence of $(T_0/T_c)/T_{0c}$ is shown in figure 2. The results show that the difference between T_0 and T_c increases with decrease in the film thickness. Let us see the extreme case when the surface effects are sufficiently weak; the differences between T_0, T_c and T_{0c} are small. At the temperature just below T_0, the polarization in the films can be expressed approximately by [5]

$$P = P_0 \cos(z/\xi) \tag{8}$$

where P_0 is the spontaneous polarization at the centre of the film, which is determined by the thermodynamic parameters and the film thickness. For a definite film thickness, the temperature dependence of P_0 is shown in figure 1. It is expected that P_0 would have a non-zero value P_c corresponding to the Curie temperature T_c, at which the film free energy is zero. Inserting equation (8) into equation (1), we have the film free energy

$$F/S = \tfrac{3}{32}BLP_0^4 + \tfrac{1}{2}\xi AP_0^2 \ \sin(L/\xi) + \tfrac{1}{2}\xi BP_0^4\big[\sin(L/\xi) + \tfrac{1}{8} \ \sin(2L/\xi)\big]$$
$$+ \left(CP_0^2/\delta\right) \ \cos^2(L/2\xi). \tag{9}$$

Let $F = 0$, $P_0 = 0$, be an explicit solution of zero free energy but, when $P_0 \neq 0$ and $L \ll \xi$, we have another solution which gives

$$- A(T_c) = 2C/L\delta + \tfrac{1}{2}BP_c^2 \tag{10}$$

where P_c is the polarization at the centre of the film when $T = T_c$. Another characteristic temperature T_0 is determined by $\tan(L/2\xi) = \xi/\delta$. When $L \ll \xi$, it gives $-A(T_0) = 2C/L\delta$. Therefore, the difference between $A(T_0)$ and $A(T_c)$ is $\tfrac{1}{2}BP_c^2$.

In the following we shall show that the dielectric susceptibility is divergent at T_0. Adding an weak external electric field E_{ext}, equation (2) will become

$$- C \ d^2P/dz^2 + AP + BP^3 = E_{ext}. \tag{11}$$

We now consider the weak-field dielectric susceptibility for $T > T_0$. The cubic term in equation (11) can be neglected. $\chi = \partial P/\partial E_{ext}$; then we obtain

$$C \ d^2\chi/dz^2 - A\chi + 1 = 0. \tag{12}$$

It can be shown from equation (3) that the boundary condition of $\chi(z)$ is

$$d\chi/dz \pm \delta^{-1}\chi = 0 \qquad z = \pm\tfrac{1}{2}L. \tag{13}$$

Solving equation (12) with the boundary conditions of (13), we obtain

$$\chi = (1/|A|)\Big(\big[\{1/[1 - (\delta/\xi) \ \tan(L/2\xi)]\}[\cos(z/\xi)/\cos(L/2\xi)] - 1\big]\Big). \tag{14}$$

Equation (14) shows explicitly that $\chi(z)$ is divergent at T_0 which is determined by $\tan(L/2\xi) = \xi/\delta$. At the extreme case $\xi \gg L$,

$$\chi \sim 1/(A + 2C/L\delta) = 1/[A(T) - A(T_0)] = 1/a(T - T_0). \tag{15}$$

The phenomenon is similar to that in the bulk material, but the divergent point here is T_0 rather than T_{0c}. For $T < T_0$, it is difficult to derive $\chi(z)$ explicitly. At the extreme case when the surface effect is weak, suppose that the behaviour of film susceptibility still obeys the regulation as it does in the bulk materials, but the divergent point is moved to T_0; then

$$\chi \sim 1/ = 2a(T - T_0) = 1/\big[-2(T - T_c) + BP_c^2\big]. \tag{16}$$

Then it is seen that the peak of susceptibility is limited at the Curie temperature T_c. In addition, since P_c increases with decrease in the film thickness as is shown in figure 3, the peak of susceptibility will decrease with decrease in the film thickness. A sketch map of the transition properties of the film susceptibility is shown in figure 4. Note that the film susceptibility in ferroelectric phase increases with decrease in the film thickness [12].
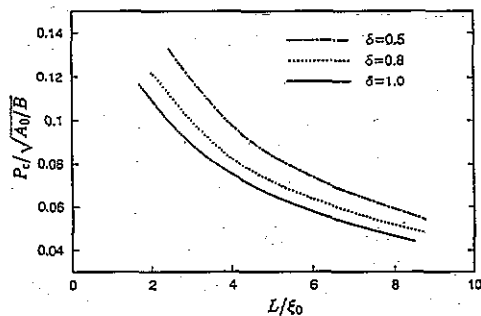
Figure 3. Thickness dependence of the spontaneous polarization at the Curie temperature.
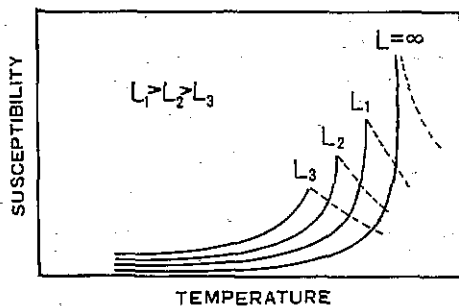

Figure 4. A sketch of the transition property susceptibility versus temperature for different film thicknesses.
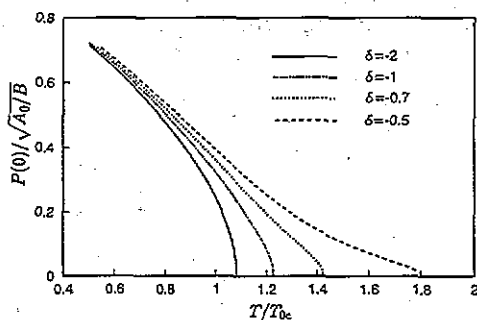

Figure 5. Phase transition behaviour of spontaneous polarization for $\delta < 0$.

4. Phase transition behaviour for $\delta < 0$

When $\delta < 0$, that is the spontaneous polarization is enhanced in the surface layer, no first-order phase transition is found in the film. Figure 5 shows the temperature dependence of spontaneous polarization near the critical points. When δ is small, the transition behaviour of spontaneous polarization shown a tail-like structure. Experiments on TGS thin crystal plates really give a tail-like structure of the polarization versus temperature curve [8] but to compare with the experiments quantitatively, the depolarization effects should be taken

into consideration in the model, for the results in [8] also show a decrease in spontaneous polarization with decrease in the thickness of crystal plate at a temperature lower than the critical point.

5. Conclusion

In the present paper, we discussed the phase transition behaviour in ferroelectric thin films for the case when the bulk phase transition is second order. When the polarization is reduced in the surface layer, a new type of first-order phase transition was predicted. Corresponding to the two zero points of free energy, there are two characteristic temperatures in the film. Because the film susceptibility is singular at T_0, the phase transition peak of susceptibility will be limited at the Curie temperature T_c. As well as shifts in the Curie point to a lower temperature, the peak height of the susceptibility decreases with decrease in the film thickness. When the polarization is enhanced in the surface layer, the transition behaviour of spontaneous polarization shows a tail-like structure as was measured in the TGS thin crystal plate.

References

[1]   Lubensky T C and Rubin M H 1975 *Phys. Rev.* B **11** 4533
[2]   Mills D L 1971 *Phys. Rev.* B **3** 3887
[3]   Kretschmer R and Binder K 1979 *Phys. Rev.* B **20** 1065
[4]   Cottam M G, Tilley D R and Zeks B 1984 *J. Phys. C: Solid State Phys.* **17** 1793
[5]   Tilley D R and Zeks B 1988 *Solid State Commun.* 49 3413
[6]   Wang C L, Zhong W L and Zhang P L 1992 *J. Phys.: Condens. Matter* 3 4743
[7]   Scott J F, Duiker H M, Beale P D, Pouligny B, Dimmler K, Parris M, Butler D and Eaton S 1988 *Physica*
         B **150** 160
[8]   Hadni A and Thomas R 1984 *Ferroelectrics* **59** 221
[9]   Batra I P, Wuefel P and Silverman B D 1973 *Phys. Rev. Lett.* **30** 384
[10] Mehta R R, Silverman B D and Jacobs J D 1973 *J. Appl. Phys.* **44** 3379
[11] Wurfel P and Batra I P 1973 *Phys. Rev.* B **8** 5126
[12] Qu B D, Zhong W L, Wang K M and Wang Z L 1993 *Integrated Ferroelect.* **3** 7