PHYSICAL REVIEW B VOLUME 51, NUMBER 23 15 JUNE 1995-I

Lateral size effects on cells in ferroelectric films

Y. G. Wang, W. L. Zhong, and P. L. Zhang
Physics Department, Shandong University, Jinan 250100, China

(Received 28 November 1994)

On the basis of phenomenological theory, ferroelectric films with cells finite in three dimensions are studied by considering their practical applications in ferroelectric random-access memory. The lateral size dependence of the Curie temperature and the polarization is obtained and the stability of the ferroelectricity of the cells is discussed.

I. INTRODUCTION

In recent years, surface and size effects in ferroelectric films have aroused great interest with the rapid progress in the manufacture and applications of ferroelectric films. Various approaches, including phenomenological theory[1-6] and the transverse Ising model,[6,7] have been exploited to study the polarization and Curie temperature anomaly due to the existence of the surface. In phenomenological theory, a parameter called the extrapolation length δ is introduced to describe the difference between the surface and the interior. The polarization is reduced at the surface, and the Curie temperature decreases with decreasing film thickness when $\delta > 0$, while the polarization is enhanced at the surface and the Curie temperature increases with decreasing film thickness when $\delta < 0$.[1,3-6] Phenomenological theory has been successful in explaining many experimental results,[5,8] such as the increase of the Curie temperature and the polarization of KNO_3 with decreasing film thickness.[5] So far, however, this theory has only treated films with single-domain structure, i.e., only the size effect in one dimension (the thickness direction) has been considered. Hence it is worthwhile to extend the theory to ferroelectrics which are finite in three dimensions. Furthermore, recent developments[9-12] in ferroelectric films have enabled the fabrication of nonvolatile memory cells with lateral sizes (dimensions in film plane) of micrometers. The available area per memory cell will decrease significantly with the increase in the number of memory cells for the fabrication of next-generation ferroelectric random-access memories (FRAM's).[11] Therefore, it is of great practical importance to investigate not only the thickness effect but also the lateral size effect on the ferroelectric properties of memory cells. In this paper, we will study the effect of lateral size on the polarization and Curie temperature of the ferroelectric films with cell structures, and discuss the ferroelectricity stability of the cells at different sizes and temperatures.

II. METHODOLOGY

Consider a ferroelectric film composed of cells of the same size $a_0 \times b_0 \times c_0$ which form a rectangular periodical structure in the film plane. a_0 and b_0 are periods in the x and y directions, respectively, and c_0 is the film thickness. The channels between the cells are negligibly small. The polarization direction of each cell is opposite to that of its four nearest neighbors. For ferroelectric films applied to fabricate FRAM's, each cell is a memory cell, and the above polarization configuration corresponds to a status of the FRAM's. Locating the coordinate origin at the center of the cell, the polarization will then be zero at the four cross sections $x = \pm a_0/2$ and $y = \pm b_0/2$. Based on phenomenological theory,[1-6] the free energy in one cell of the ferroelectric with the second-order phase transition can be written

$$F = \int \left[\tfrac{1}{2}A(T - T_{c\infty})P^2 + \tfrac{1}{4}BP^4 + \tfrac{1}{2}D(\nabla P)^2\right]dv + \int \tfrac{1}{2}D\delta^{-1}P^2 dS \ , \tag{1}$$

where A, B, and D are phenomenological parameters, $T_{c\infty}$ is the Curie temperature of the bulk material, and δ the extrapolation length. The depolarizing field has been neglected, since electrodes have been deposited on the surface.

Considering the polarization configuration of the cells in the film, the minimum principle for the free energy yields the following Euler-Lagrange equation:

$$D\left[\frac{\partial^2 P}{\partial x^2} + \frac{\partial^2 P}{\partial y^2} + \frac{\partial^2 P}{\partial z^2}\right] = A(T - T_{c\infty})P + BP^3 \ , \tag{2}$$

and the corresponding boundary conditions

$$\begin{aligned} &P|_{x=\pm(a_0/2)} = 0 \ , \\ &P|_{y=\pm(b_0/2)} = 0 \ , \\ &\left[\frac{dP}{dz} \pm \frac{P}{\delta}\right]\Bigg|_{z=\pm(c_0/2)} = 0 \ , \end{aligned} \tag{3}$$

where the third equation in Eq. (3) is the same as the boundary condition for ferroelectric films without cell structures.[1-6] When $\delta > 0$, $T_c < T_{c\infty}$. At a temperature near the Curie temperature T_c, the polarization is very small, thus Eq. (2) can be linearized as

$$\frac{\partial^2 P}{\partial x^2} + \frac{\partial^2 P}{\partial y^2} + \frac{\partial^2 P}{\partial z^2} = -\frac{P}{\xi_{(T)}^2} \ , \tag{4}$$

where $\xi_{(T)} = |D/A(T - T_{c\infty})|^{1/2}$ is the correlation length at temperature T. The solution of Eq. (4) gives the spatial distribution of the polarization in the cell near T_c:

$$P=P_0\cos k_1x\cos k_2y\cos k_3z\ . \tag{5}$$

Substituting the expression into the boundary conditions [Eq. (3)] and Eq. (4), we can obtain the value of k_1, k_2, and k_3:

$$\begin{aligned} k_1&=\frac{n\pi}{a_0}\ ,\\ k_2&=\frac{n\pi}{b_0}\ ,\\ k_3\tan\frac{k_3c_0}{2}&=\frac{1}{\delta}\ , \end{aligned} \tag{6}$$

and the relation

$$k_1^2+k_2^2+k_3^2=\frac{1}{\xi_{(T)}^2}\ , \tag{7}$$

where $n=1,3,5,\ldots$. Since the situation of $n>1$ corresponds to multidomain structures, which is practically impossible in FRAM's, we take $n=1$ in the paper. From Eqs. (6) and (7), the Curie temperature of the film can be expressed as a function of the cell dimensions a_0, b_0, and c_0 and the extrapolation length δ at the cell surface. In the case of $\delta<0$, such as in KNO_3 films, the polarization is enhanced at the film surface and the Curie temperature is higher than that of the bulk.[1,5] Near the Curie temperature, a procedure similar to that of $\delta>0$ can be carried out, which gives the expression of the polarization,

$$P=P_0\cos k_1x\cos k_2y\cosh k_3z\ , \tag{8}$$

and the equation relating the Curie temperature with the cell dimensions and the extrapolation length δ,

$$k_1^2+k_2^2-k_3^2=\frac{1}{\xi_{(t)}^2}\ , \tag{9}$$

where k_1 and k_2 are the same as in Eq. (6), while k_3 satisfies the relation

$$k_3\tanh\frac{k_3c_0}{2}=\frac{1}{|\delta|}\ . \tag{10}$$

It can be seen from the above formulas that the size effect in ferroelectric films is the effect of both the thickness and lateral size. Since the effect of thickness on the properties of ferroelectric films without cell structures has been studied in detail in the cases of both $\delta>0$ and $\delta<0$,[1–6] hereafter we discuss only the lateral size effect. That is, the extrapolation length is assumed to be infinite, and thus the surface or thickness effect is not included in the following.

When $\delta=\infty$ and $dp/dz=0$, Eq. (7) or (9) can be simplified since $k_3=0$ [see Eqs. (6) and (10)]. Considering the relation between the correlation length and the Curie temperature, we have the expression for T_c:

$$T_c=T_{c\infty}-\frac{D}{A}\left[\frac{\pi^2}{a_0^2}+\frac{\pi^2}{b_0^2}\right]\ . \tag{11}$$

At a temperature well below T_c, the polarization cannot be expressed as in Eq. (5), because Eq. (2) cannot be linearized in this case. Equation (2) is then solved numerically using the finite difference method. The polarization profile in the cell is calculated, and the average value of the polarization as well as the polarization in the cell center as a function of the cell lateral size are obtained.

For ferroelectrics with a first-order phase transition, Eq. (2) should be written

$$D\left[\frac{\partial^2P}{\partial x^2}+\frac{\partial^2P}{\partial y^2}+\frac{\partial^2P}{\partial z^2}\right]=A(T-T_{0\infty})P+BP^3+CP^5\ , \tag{12}$$

which cannot be linearized even at temperature near T_c, where B is negative and $T_{0\infty}$ is the Curie-Weiss temperature of the bulk material. In this case, we solve numerically using the finite difference method. First, the spatial distribution of the polarization in a cell is calculated, then the free energy at different temperatures is calculated. Thus the Curie temperature at which the free energy equals zero can be determined. By the calculation at different cell sizes, we obtain the size dependence of the Curie temperature and polarization.

III. RESULTS AND DISCUSSION

Figure 1 shows the Curie temperature of a ferroelectric film as a function of its cell lateral sizes a_0 and b_0. It can be seen from the figure that the Curie temperature decreases monotonically with the decrease of a_0 or b_0. The numerical calculation and Eq. (11) give the same result. A calculation on ferroelectrics with a first-order phase transition yields the same dependence of the Curie temperature on the cell lateral size.

Figure 2 shows the spatial distribution of the polarization in a ferroelectric cell at 0 K. Near the cell boundary, the polarization decreases quickly. The profile is similar to the spatial distribution of the polarization near a domain boundary. The relative area with reduced polar-

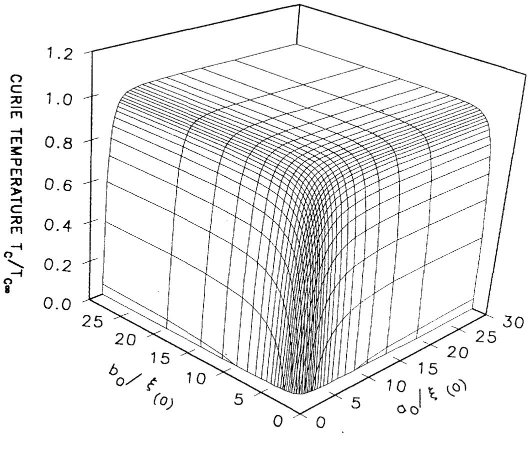

FIG. 1. The Curie temperature of a ferroelectric cell as a function of the lateral sizes a_0 and b_0. $\xi_{(0)}$ is the correlation length at 0 K.

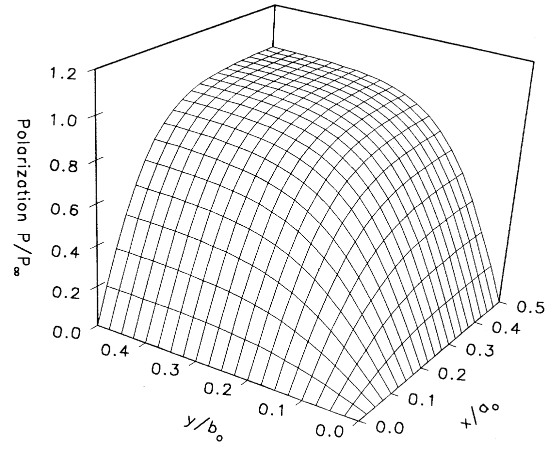

FIG. 2. The spatial distribution of the polarization in a cell in ferroelectric films. P_∞ is the polarization of the bulk material. $a_0=b_0=5\xi_{(0)}$.

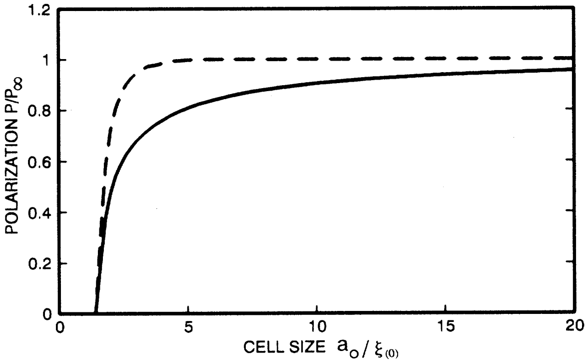

FIG. 3. The lateral size dependence of the average polarization (solid line) and the polarization in the cell center (dashed line) of a ferroelectric film with a second-order phase transition at 0 K.

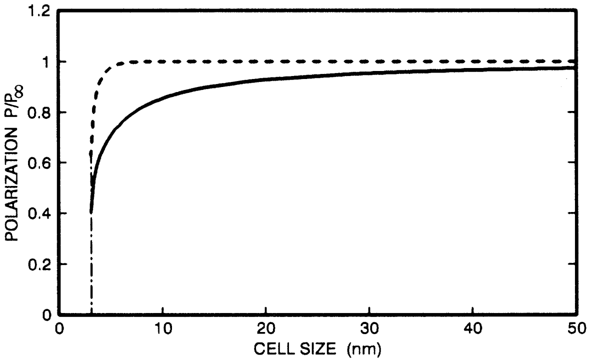

FIG. 4. The lateral size dependence of the average polarization (solid line) and the polarization in the cell center (dashed line) for a ferroelectric film with a first-order phase transition at 0 K. The phenomenological parameters are those of $BaTiO_3$ (see Table I).

TABLE I. Phenomenological parameters of $PbTiO_3$ and $BaTiO_3$ (in cgs units).

	$T_{0\infty}$ (K)	$T_{0\infty}$ (K)	Curie constant (10^5 K)	A 10^{-5}	B 10^{-12}	C 10^{-21}	D 10^{-16}
$PbTiO_3$	765[a]	722[a]	4.1[a]	3.1[a]	−2.0[a]	5.8[a]	5[b]
$BaTiO_3$	403[c]	391[c]	1.7[c]	7.4[c]	−4.4[c]	3.7[c]	5[b]

[a] Reference 14.
[b] Reference 13.
[c] Reference 15.

ization increases with decreasing lateral size.

When $a_0=b_0$, the average polarization (the solid line) and the polarization in the cell center (the dashed line) at 0 K as a function of cell lateral size are shown in Figs. 3 and 4. Figure 3 is for a ferroelectric with a second-order phase transition, where a_0 is reduced with $\xi_{(0)}$, the correlation length at 0 K. Figure 4 is for a ferroelectric with a first-order phase transition; the phenomenological parameters of $BaTiO_3$ were used. It is seen that the average polarization and the polarization in the cell center decrease with decreasing cell size. They reach zero continuously for a second-order phase transition ferroelectric, but jump down to zero for a ferroelectric with a first-order phase transition. The results are similar to the temperature dependence of the polarization of ferroelectrics with a second-order phase transition and a first-order phase transition, respectively.

The size at which ferroelectricity becomes unstable is the ferroelectric critical size. Obviously, this critical size is temperature dependent. It can be seen from Figs. 1, 3, and 4 that ferroelectricity becomes unstable when the lateral size of cells becomes very small. This gives the lower limit to the lateral size of a nonvolatile memory cell in ferroelectric films. Using the available parameters (see Table I) in the literature,[13–15] the critical sizes ($a_0=b_0$) of the memory cell of $BaTiO_3$ and $PbTiO_3$ at 300 K are calculated to be 9.1 and 7.4 nm, respectively. Since the polarization is greatly reduced if the cell dimensions are near the critical size (see Fig. 4), the memory cells in practical FRAM's should be much larger than the theoretical critical size. When the surface effect is included, the critical size is expected to be larger because the extrapolation length of $PbTiO_3$ and $BaTiO_3$ are positive based on experimental results.[16]

When one (or some) of the nearest neighbors of the cell has (have) polarization directed parallel to that of the cell, the boundary condition [Eq. (3)] should be rewritten to be $\partial p/\partial n=0$ at the cross section between two cells of parallel polarization, where n is the unit normal to the cross section, while the boundary conditions between cells with opposite polarizations remain the same as that in Eq. (3). Under these boundary conditions, parallel calculations can also be carried out, and the dependence of the Curie temperature and polarization on lateral size can be obtained. The critical size is expected to increase with the number of neighbors with parallel polarizations. When all neighbors have polarizations in the same direction, the film becomes the same as that without cell structures, which has been well studied.[1–6]

[1] D. R. Tilley, in *Ferroelectric Ceramics,* edited by N. Setter and E. L. Colla (Birkhaus, Basel, 1993), p. 163.

[2] D. L. Mills, Phys. Rev. B **3**, 3887 (1971).

[3] R. Krestschmer and K. Binder, Phys. Rev. B **20**, 1065 (1979).

[4] T. C. Lubensky and M. H. Rubin, Phys. Rev. B **12**, 3885 (1975).

[5] J. F. Scott, H. M. Duiker, P. D. Beale, B. Pouligny, K. Dimmler, M. Parris, D. Butler, and S. Eaton, Physica B **150**, 160 (1988).

[6] M. G. Cottam, D. R. Tilley, and B. Zeks, J. Phys. C **17**, 1793 (1984).

[7] C. L.Wang, W. L. Zhong, and P. L. Zhang, J. Phys. Condens. Matter **3**, 4743 (1992).

[8] J. F. Scott, Phase Transitions **30**, 107 (1991).

[9] *Proceedings of the 1st and 2nd International Symposia on Integrated Ferroelectrics,* edited by C. A. Araujo and G. W. Taylor [Ferroelectrics **112**, 1 (1990); **116**, 1 (1991)].

[10] J. F. Scott and C. A. Paz de Araujo, Science **246**, 1400 (1989).

[11] S. K. Dey, Ferroelectrics **135**, 117 (1992).

[12] B. M. Melnick, J. F. Scott, C. A. Paz De Araujo, and L. D. Mcmillan, Ferroelectrics **135**, 163 (1992).

[13] V. A. Zhirnov, Zh. Eksp. Teor. Fiz. **35**, 1175 (1958) [Sov. Phys. JETP **8**, 822 (1959)].

[14] J. P. Remeika and A. M. Glass, Mater. Res. Bull. **5**, 37 (1970).

[15] T. Mitsui, I. Tatsuzaki, and E. Nakamira, *An Introduction to the Physics of Ferroelectrics* (Gordon and Breach, New York, 1974), p. 151.

[16] R. Vest, Ferroelectrics **102**, 53 (1990).