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Surface and size effects on ferroelectric films with domain structures

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The spontaneous polarization and electrostatic potential in ferroelectric films with domain structures have been calculated based on phenomenological theory. The polarization is reduced at the film surface due to a depolarizing field. The domain width, free energy, and Curie temperature as functions of film thickness are obtained.

I. INTRODUCTION

In recent years, surface and size effects in ferroelectric films have been studied experimentally and theoretically due to the rapid progress in the manufacture and application of ferroelectric films.[1-8] Based on phenomenological theory, surface and size effects on the phase-transition properties of ferroelectric films have been studied by introducing a parameter called the extrapolation length. When the extrapolation length is positive, polarization is reduced at the film surface, and the Curie temperature is lower than its bulk value. If the extrapolation length is negative, polarization is enhanced at the film surface and can persist above the Curie temperature of the bulk material. So far, most theoretical work has treated films with single-domain structures,[1-5] and the depolarization effect has been omitted[2-5] because electrodes are deposited on film surfaces or the spontaneous polarization is parallel to the film surface. However, real ferroelectric films, which are of great practical importance for the fabrication of FRAM (ferroelectric random access memory), IR (infrared) detector, etc. are prepared to be *c* axis oriented (i.e., the polarization is perpendicular to the film surface). Furthermore, the surfaces of films are bare during preparation, and thus the depolarizing field can only partially be compensated for by the free carrier in the ferroelectrics. Most ferroelectrics are insulators; the free carrier concentration or its velocity is not high enough, and therefore multidomain structures will exist in the ferroelectric films. In addition, the upper surfaces of most ferroelectric films are dot electroded, hence even if the films have been electroded, the depolarizing field and the resultant domain structure will still have a great influence on the ferroelectric properties of the films.

The kinetics of ferroelectric domains has been a subject of both experimental and theoretical investigations.[9-15] Kittel[10] and Mitsui and Furuichi[9] have investigated 180° domains in crystals, and deduced the relation of domain width to crystal thickness based on a simplified model. Spontaneous polarization near the domain boundary has been shown to be a function of the distance from the domain boundary x, and the relation $P=P_0\tanh(x/\sqrt{2}\xi_{(T)})$ was obtained[9,14] when the depolarization effect was ignored, where $\xi_{(T)}=[D/A(T-T_{c\infty})]^{1/2}$ is the correlation length. The depolarizing field near the film surface can be deduced to be a function of the distance from the film surface[13] if the contribution of the domain boundary is neglected. Nevertheless, these investigations[9-15] have been restricted to bulk crystals, and spatial distributions of the polarization and electrostatic potential in domains for thin films have not been obtained. As far as the surface and size effects on ferroelectric films with domain structures are concerned, Wang[12] has studied films with 180° domain boundaries parallel to the film surface. In this work, a practical situation, i.e., ferroelectric films with 180° domain boundaries perpendicular to the film surface are studied using phenomenological theory. The polarization and electrostatic potential in the domains are calculated and the dependence of the domain width, free energy, and Curie temperature on film thickness are discussed.

II. METHODOLOGY

The free energy of a ferroelectric film with domain structure can be written as[1-5,16]

$$F=\int[\tfrac{1}{2}A(T-T_{c\infty})P^2+\tfrac{1}{4}BP^4+\tfrac{1}{2}D(\nabla P)^2-\tfrac{1}{2}E_dP+\tfrac{1}{2}s_{ij}X_iX_j+Q_{i3}X_iP^2]dv\ , \tag{1}$$

where the spontaneous polarization P is along the z axis. $T_{c\infty}$ is the bulk Curie temperature. A, B, and D are the phenomenological parameters of the ferroelectric. E_d is the depolarizing field, s_{ij} the elastic compliance, X_i the ith component of the stress, and Q_{i3} the electrostrictive coefficient. In ferroelectric ceramics, the depolarizing field can be compensated for by the surroundings, but the grains are clamped, so the stress induced by the phase transition plays the dominant role on the domain structure, and 90° domains are preferred.[17] Conversely, in *c*-axis-oriented or epitaxial films, there are only 180° domains, and the film properties are similar to those of single-crystalline films: the internal stress is expected to be smaller than that in ceramics. On the other hand, the depolarizing field is dominant since the polarization is perpendicular to the surface, and the free-carrier concentration is usually too low to compensate for it. Therefore, the effect of stress is ignored at this stage, and the free energy of the films is assumed to be

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

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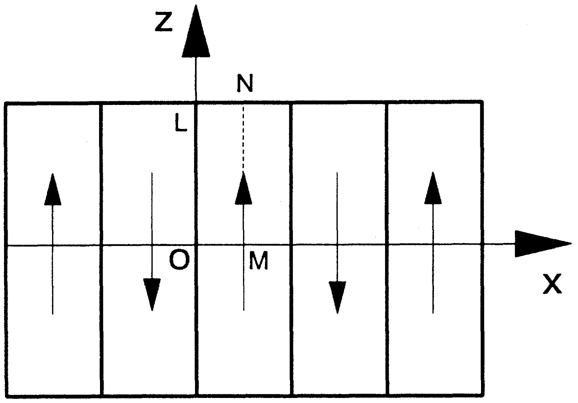

FIG. 1. The domain configuration of a ferroelectric film with a periodical 180° domain structure.

In this paper, the extrapolation length is assumed to be infinite, since we focus on the effect of domain on film properties, and only ferroelectrics with second-order phase transitions are discussed. Ferroelectrics with first-order phase transitions can be studied by changing the coefficient B into a negative, and adding a term of P^6 with a positive coefficient.

The domain configuration in ferroelectric films may be very complicated. However, in c-axis-oriented films, only 180° domain structures can exist. In this paper, the domain structure is assumed to be a simple periodical configuration (see Fig. 1), so that the surface and size effects in the films can be studied easily. The film normal is along the z axis, and the film thickness is d. The domain boundary is perpendicular to the x axis, and the domain width is w. The spontaneous polarization is in the z-axis direction, and its magnitude is assumed to be independent of y in the Cartesian coordinate. Taking the symmetry of the configuration into consideration, the ferroelectric properties of the film can be obtained if profiles of the polarization and electrostatic potential in the rectangle OMNL are calculated. For a ferroelectric film which is electroded on the lower surface and bare on the upper surface during the preparation process, its ferroelectric properties can also be obtained by studying the rectangle OMNL, since this can be considered as the upper half of the film in Fig. 1.

The free energy of the film is proportional to the free energy of the ferroelectric in the rectangle OMNL, therefore the minimum principle for free energy yields the differential equation[2–5]

$$D\nabla^2 P = A(T-T_{c\infty})P + BP^3 - \tfrac{1}{2}E_d \tag{3}$$

in the rectangle, as well as the following boundary conditions:

$$\begin{aligned} &\frac{\partial P}{\partial z}=0 \quad \text{when } z=0\,, \\ &\frac{\partial P}{\partial z}=0 \quad \text{when } z=\frac{d}{2}\,, \\ &P=0 \quad \text{when } x=0\,, \\ &\frac{\partial P}{\partial x}=0 \quad \text{when } x=\frac{w}{2}\,. \end{aligned} \tag{4}$$

To obtain the polarization profile in the domain, the spatial distribution of the electrostatic potential in the domain must be calculated, since $E_d=-\nabla\phi$. The electrostatic potential can be obtained by solving the differential equation

$$\nabla^2\phi=0 \tag{5}$$

in air, and the equation[9–11]

$$\varepsilon_1\frac{\partial^2\phi}{\partial z^2}+\varepsilon_3\frac{\partial^2\phi}{\partial z^2}-4\pi\frac{\partial P}{\partial z}=0 \tag{6}$$

in the rectangle subject to the boundary condition.[9–11]

$$\begin{aligned} &\phi=0 \quad \text{when } z=0\,, \\ &\phi=0 \quad \text{when } x=0\,, \\ &\frac{\partial\phi}{\partial x}=0 \quad \text{when } x=\frac{w}{2}\,, \\ &4\pi P-\varepsilon_3\frac{\partial\phi}{\partial z}\bigg|_{z=+0}=-\frac{\partial\phi}{\partial z}\bigg|_{z=+0} \quad \text{and} \quad \frac{\partial\phi}{\partial x}\bigg|_{z=-0}=\frac{\partial\phi}{\partial x}\bigg|_{x=+0} \quad \text{when } z=\frac{d}{2}\,. \end{aligned} \tag{7}$$

Here ϵ_1 and ϵ_3 are the dielectric constant along the x and z axes, respectively. At this stage, we study only the static behavior of the film; the effects of conductivity on the domain structure are ignored since most ferroelectrics are insulators. To examine the time dependence of the domain properties, this equation, including the conductivity,[9] should be used instead of Eqs. (6) and (7).

Equations (3)–(7) can be solved using the finite difference method by dividing the rectangle into 200×200 pieces. Once the profiles of the spontaneous polarization and electrostatic potential are obtained, the free energy as a function of domain width w, film thickness d, and temperature T can be calculated, and the dependence of domain width, free energy, and Curie temperature on film thickness obtained.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the spatial distributions of the polarization and electrostatic potential in the rectangle at temperature $T=0$ K, respectively. The polarization profile near the domain boundary is consistent with the theoretical formula[14] $P(x)=P_0\tanh(x/\sqrt{2}\xi_{(0)})$. Where $\xi_{(T)}$ is the correlation length at temperature T,

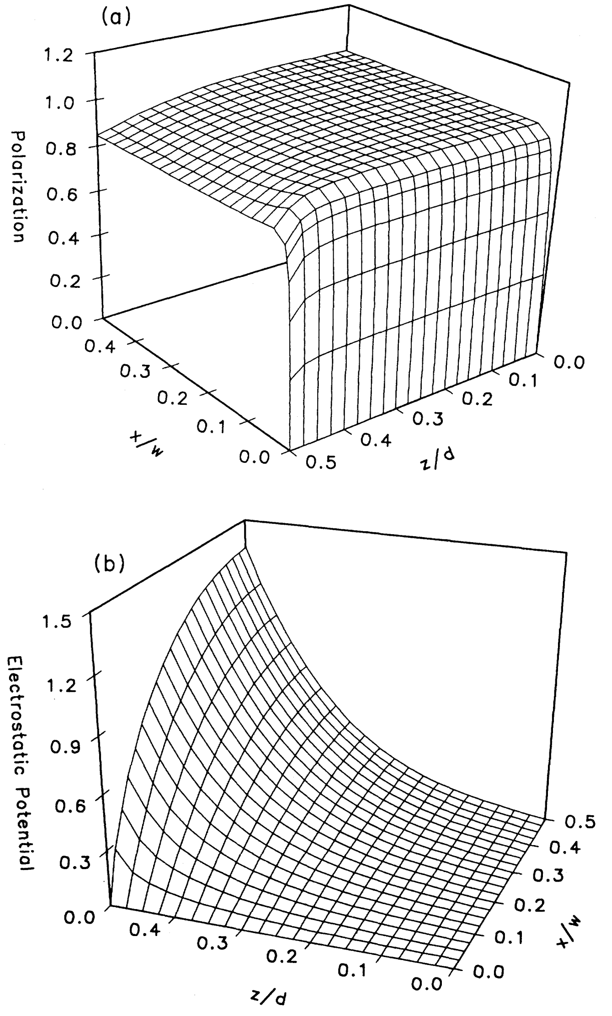

FIG. 2. The spatial distributions of the polarization (a) and electrostatic potential (b) in the rectangle OMNL of the film, where $d/\xi_{(0)}=100$, $w/\xi_{(0)}=23$, and $\xi_{(0)}$ is the correlation length at 0 K.

$\xi_{(T)}=|D/A(T-T_{c\infty})|^{1/2}$. It is interesting to note that the polarization near the film surface ($z=d/2$) is reduced. The thinner the film, the larger the relative area of reduced polarization. The polarization as a function of the coordinate z is similar to the single-domain film with a positive extrapolation length,[2] though the extrapolation length of the film is infinite. This result can be understood from the spatial distribution of the electrostatic potential. It has been shown theoretically[1] and experimentally[6] that the polarization in ferroelectric films will be reduced due to the depolarization effect. While the depolarizing field in the film, i.e., the negative gradient of the electrostatic potential, is stronger near the surface [see Fig. 2(b)], the polarization will therefore be reduced so as to minimize the free energy. When the thickness is large, the electrostatic potential near the film surface fits with the estimation by Kittel.[10]

At a given film thickness, the free energy at 0 K as a function of the domain width is calculated and shown in Fig. 3, where F_b is the free energy without depolarization and domain structure. With the increase of the domain width w, the free energy decreases when w is small and increases when w is larger. At a certain value of w, the free energy F is minimized. This corresponds to the stable configuration of the domain structure. The preferred domain width and the corresponding free energy (also reduced by F_b) at different film thickness d is shown in Fig. 4. It can be seen from the figure that the domain width as a function of the film thickness is in accordance with the relation[9,10] of $w=kd^{1/2}$ (k is a constant). The free energy increases with decreasing film thickness monotonically and becomes zero at a critical thickness. That means that a size-driven ferroelectric-paraelectric phase transition occurs at this critical size.

Figure 5 shows the Curie temperature T_c of the films at different film thicknesses. With a decrease of film thickness, the Curie temperature T_c decreases slowly when d is large, and decreases quickly when d is small. The size dependence of the Curie temperature and free energy is similar to that of single-domain ferroelectric films with

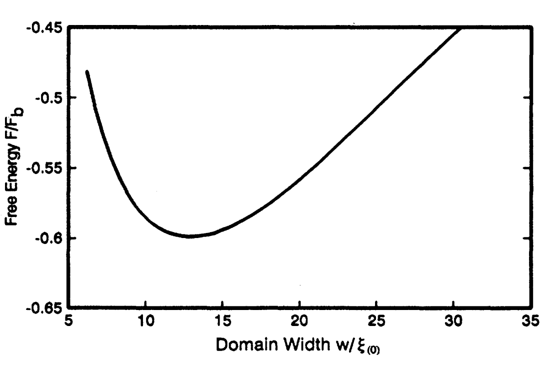

FIG. 3. The free energy at 0 K as a function of the domain width for a film with thickness $d/\xi_{(0)}=30$, where F_b is the free energy without depolarization effect and domain structure.

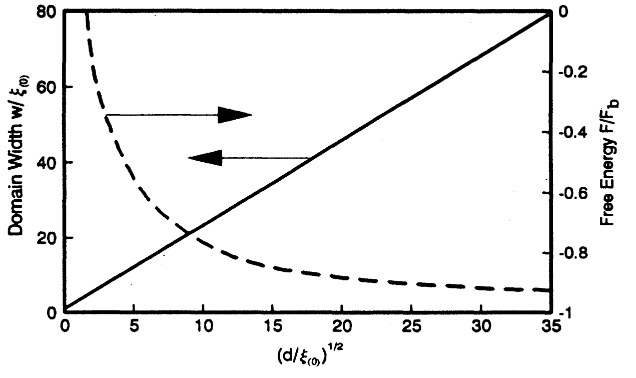

FIG. 4. The thickness dependence of the domain width and the corresponding free energy when $T=0$ K, where $T_{c\infty}$ is the bulk Curie temperature, and F_b is the same as in Fig. 3.

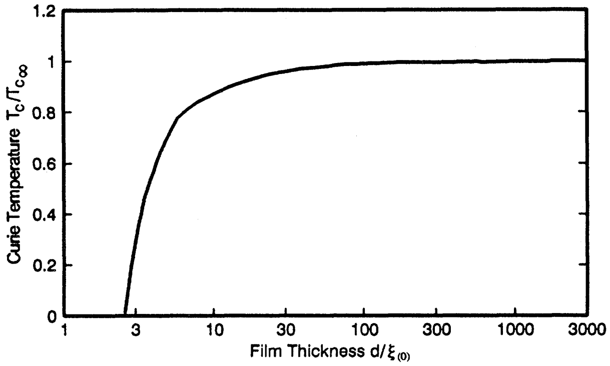

FIG. 5. The Curie temperature as a function of the film thickness. $T_{c\infty}$ is the bulk Curie temperature.

positive extrapolation lengths.[2,4] The thickness dependence of T_c implies that the thinner the film, the weaker its ferroelectricity. Thus the ferroelectricity of very thin films with domain structure may be unstable. The average value of the polarization is also calculated to decrease with decreasing film thickness. These results agree with the work of Batra, Wurfel, and Silverman[1] and Wurfel, Batra, and Jacobs.[6] They have shown that the depolarizing field in ferroelectric films with semiconducting electrodes is enhanced with the decrease of film thickness. The polarization and Curie temperature are consequently reduced, and the ferroelectricity becomes unstable for very thin films. In our work, the depolarizing field is not uniform, but its average value increases with decreasing film thickness since $w = kd^{1/2}$ (see Fig. 4). Therefore, similar results (that is, the Curie temperature and the average polarization is reduced with the decrease of film thickness, and the ferroelectricity of very thin films becomes unstable) are obtained.

IV. CONCLUSION

Ferroelectric films with periodical 180° domain structure have been studied. The polarization and electrostatic potential in a domain have been illustrated to be a function not only of the distance from the domain boundary, but also of the distance from the film surface. The free energy of the films at 0 K is shown to increase with decreasing film thickness, and reach to zero at a critical thickness. The thickness dependence of the Curie temperature and polarization is similar to that of a single-domain film with a positive extrapolation length, and to one with semiconducting electrodes.

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