Curie-Weiss law in thin-film ferroelectrics

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The stationary self-polarization field of a thin film in an open circuit is analytically solved for temperatures near the para-/ferroelectric transformation within the Ginzburg-Landau theory. For second-order ferroelectrics, or first-order ferroelectrics with a sufficiently large elastic self-energy of the transformation strain, the solution is real and stable, from which the corresponding electric susceptibility of the film can be derived. A Curie-Weiss-type relation of the permittivity is obtained for both the supercritical and subcritical temperature regimes near the transition. In the paraelectric state, the Curie parameter of the thin film is found to be independent of its thickness, whereas in the ferroelectric state, its magnitude decreases rapidly with decreasing film thickness. © 2006 American Institute of Physics. [DOI: 10.1063/1.2336979]

I. INTRODUCTION

The large surface to bulk ratio causes ferroelectric thin films to exhibit phase-transition characteristics that are generally different from their bulk counterparts. Indeed, in extreme cases, such as in $PbTiO_3$, $BaTiO_3$, and lead zirconic titanate (PZT) thin films, the ferroelectric transition can even be totally suppressed, when the film thickness is below certain critical values. This dependence of the phase-transition characteristics on the sample size has been investigated using both first-principles calculations[1,2] and thermodynamic models.[3–5] Experiments have also confirmed that the Curie temperatures of epitaxial films of $PbTiO_3$ grown on $SrTiO_3$ (001) substrate decrease rapidly with the film thickness below 50 nm, as predicted theoretically.[5,6]

Due to the ever-increasing size and complexity of electronic circuitry that has to be packed into the limited space of modern integrated circuit (ICs), the influence of sample size on material properties is a subject of general interest to both scientific and technological investigations.[10–12] For the general phase-transition problem of finite size systems, some scaling laws have been established,[7–9] and it is not unusual that controlling parameters for phase transitions such as the Curie temperature may differ substantially from those in the bulk materials. In addition, important physical properties may also become sensitive to sample dimensions through the stability of the prevailing phase.

In a previous paper,[5] we studied the relationship between the film thickness and the Curie temperature of the para-/ferroelectric transition in a thin film on a rigid substrate. By considering the dynamic stability of the stationary solution of the Ginsberg-Landau equation, simple expressions of the Curie temperature as a function of film thickness were derived without having to go through the complexities of an explicit solution. The order of the transition and the difference between the heat-up and cool-down transition tempera-

tures, on the other hand, were found to be independent of the film thickness, but might depend on the constraint of the substrate. This conclusion was further investigated in another work,[13] in which the Ginzburg-Landau equation for a thin film on a substrate with varying compliance was solved in the neighborhood of the transition temperature. Although the conclusion of Ref. 5 was confirmed, yet for the case of a compliant substrate, Ref. 13 found that the order of transition of a thin film of first-order ferroelectric material did not remain constant, but may indeed change according to the film thickness relative to that of the substrate.

In the present paper, we are interested in the effect of the film thickness on the Curie-Weiss law of electric susceptibility. In this calculation, the explicit solution of the Ginzburg-Landau equation is required, which we obtained via a perturbation series expansion method.[13] In Sec. II, the evolution of the ferroelectric thin films is formulated following Wang and Woo[5] within the dynamic Ginzburg-Landau theory using the corresponding free energies, in which the local self-polarization near a free surface is subsumed in the boundary conditions through the "extrapolation length" parameter. The constraint of a rigid substrate is assumed, and we consider electric boundary conditions under which the film is between electrodes from which it is insulated. In Sec. III, the stationary solutions of the Ginzburg-Landau equation are obtained in the neighborhood of the transition temperature, by means of a perturbation series expansion method. The solutions are then used in our investigation in Sec. IV. The paper is summarized and concluded in Sec. V.

II. FORMULATION

We consider a ferroelectric thin film of dimensions $\infty \times \infty \times h$ (i.e., h=film thickness) on a rigid substrate, i.e., one with a thickness much larger than h. The origin of the coordinate system is at the center of the cell. We base our formulation on the classical description of electrical susceptibility of a collection of polar molecules, the local polarization $\mathbf{P}_{\text{total}}$

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at any point consists of a permanent molecular component $\mathbf{P}$ and an induced component $\mathbf{P_E}$. $\mathbf{P}$ arises from the permanent electric moment due to the polar nature of the molecular structure/configuration of the material, e.g., its crystallography, in its prevailing para-/ferroelectric phase. $\mathbf{P}$ is thus a function of the temperature, the electric field and the mechanical stresses in the sample through its Curie temperature. We call $\mathbf{P}$ the self-polarization, instead of "spontaneous polarization" like what we used to Ref. 5, to distinguish it from the more commonly used meaning of the total (i.e., observed) polarization in the absence of an external field. We note that $\mathbf{P}_{\text{total}}$ and $\mathbf{P}$ are equal only when the depolarization field vanishes, such as in the bulk material between short-circuited electrodes.

The induced component $\mathbf{P_E}$ is the polarizations (ionic +electronic) induced by the total electric field $\mathbf{E}$ in the material according to $\mathbf{P_E}=\chi_d\mathbf{E}$, where χ_d is the temperature-independent component of the susceptibility corresponding to the field-induced part of the polarization. We may identify $\mathbf{E}$, which has its origin from the combined effects of $\mathbf{P}$ and $\mathbf{E}_x$, as the sum of the external field $\mathbf{E}_x$ and the depolarization field $\mathbf{E}_d$. In this regard, the displacement field in the ferroelectric can be written either in terms of $\mathbf{P}_{\text{total}}$ or $\mathbf{P}$:

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P}_{\text{total}} = \varepsilon_0\mathbf{E} + \mathbf{P} + \chi_d\mathbf{E} = \varepsilon_d\mathbf{E} + \mathbf{P},$$

where ε_0 is the background permittivity, and ε_d is that part of the permittivity of the ferroelectric corresponding to χ_d.

For simplicity the nonzero component of the self-polarization P of the ferroelectric thin film is assumed to be orthogonal to the surface of the film. The eigenstrain $\varepsilon_{xx}^T = \varepsilon_{yy}^T = QP^2$ due to the para-/ferroelectric transition is constrained by the rigid substrate, causing an elastic self-energy $F_e = GQ^2\iiint_V P^4 d\nu$, where $G = (C_{11}+C_{12}-2C_{12}^2/C_{11})$, C_{11} and C_{12} being components of the elastic modulus, and V the volume, of the film. We neglect the effects of the epitaxial stresses to simplify the discussion in the present work. It is clear from Ref. 5 that its inclusion only has the equivalent effect of shifting the bulk transition temperature. Following Ref. 5, with the help of the Ginzburg-Landau functional, the dynamic equation of the self-polarization in the thin film can be written as

$$M\frac{\partial P}{\partial t} = -\frac{\delta F}{\delta P} = -A(T-T_{C0})P - (B+4GQ^2)P^3 - CP^5$$

$$+ E_d + D\frac{d^2P}{dz^2}, \tag{1}$$

with the boundary conditions,

$$\frac{dP}{dz} = \mp\frac{P}{\delta}, \quad z = \pm\frac{h}{2}, \tag{2}$$

where M is the kinetic coefficient related to the domain wall mobility; A, B, C, and D, are expansion coefficients of the Ginzburg-Landau functional of the homogeneous self-polarization in the bulk ferroelectric; T_{C0} is the corresponding Curie temperature; E_d is the depolarizing field, and δ is the extrapolation length that describes the near-surface relaxation effect of the local self-polarization.[14,15] The meaning of the other symbols are as given in Ref. 5.

The electric and polarization fields in the ferroelectric are related through conditions on the boundaries via the laws of electrostatics. In this paper, a ferroelectric thin film in an open circuit is considered, i.e., the film is insulated from the electrodes. In this case, the depolarization field E_d has been derived[5]

$$E_d = -\frac{P}{\varepsilon_d}. \tag{3}$$

Note that the E_d here is different from and generally much larger than that in Ref. 15.

Most of bulk ferroelectrics exhibit a first-order phase transition. In such cases, the parameter B is negative, and the parameter C is positive. For bulk materials in which the ferroelectric transition is second order, the parameter B is positive and the higher order terms can be neglected.

III. STEADY-STATE SOLUTION NEAR THE BIFURCATION POINT

The condition of dynamic stability of the paraelectric state of the evolution equation Eq. (1) has been established,[5] from which the critical temperature T_c at which the state becomes unstable can be obtained as a function of the film thickness h:

$$T_c = T_{C0} - \frac{1}{A\varepsilon_d} - \frac{D}{A}k_{z\,\text{min}}^2, \tag{4}$$

where $k_{z\,\text{min}}$ is the minimum solution of the following transcendental equation:

$$\cot\left(\frac{k_z h}{2}\right) = k_s\delta. \tag{5}$$

As explained in Ref. 5, T_c is the para-/ferroelectric transition temperature for the thin film. Putting $\partial P/\partial t = 0$ in Eq. (1), the corresponding stationary equation of the order parameter P can be written as

$$L_c P \equiv -A(T_c-T_{C0})P - \frac{1}{\varepsilon_d}P + D\frac{d^2P}{dz^2}, \tag{6}$$

where L_c is the parabolic operator evaluated at the bifurcation point $T=T_c$, in the neighborhood of which the solution P is small, if assumed continuous. Following Nicholis and Prigogine,[16] both P and $\gamma \equiv T-T_c$ can be expanded in a power series in terms of a small perturbation λ from the critical point:

$$P = \lambda P_1 + \lambda^2 P_2 + \cdots,$$

$$\gamma = T - T_c = \lambda\gamma_1 + \lambda^2\gamma_2 + \cdots. \tag{7}$$

This expansion is more flexible than the seemingly more natural one in which P is expanded in a power series of $(T-T_c)$.[16] More importantly, it allows fractional power dependence of P on $(T-T_c)$. By substituting the expansion (7) into Eq. (6), and equating coefficients of equal powers of λ, a set of relations of the following form can be obtained:

$$L_c P_k = a_k, \quad k = 1, 2, \cdots, \tag{8}$$

which have to be satisfied together with the boundary and the initial conditions:

$$\frac{dP_k}{dz} = \mp \frac{P_k}{\delta}, \quad z = \pm \frac{h}{2}. \tag{9}$$

The first several coefficients a_k are

$$a_1 = 0,$$

$$a_2 = A\gamma_1 P_1, \tag{10}$$

$$a_3 = A\gamma_1 P_2 + A\gamma_2 P_1 + (B + 4GQ^2)P_1^3.$$

It is easy to check that under the boundary condition (9), the operator L_c is self-adjoint, and

$$
\begin{aligned}
(L_c P^*, P_k) &= \int_{-h/2}^{h/2} P_k L_c P^* dz \\
&= (P^*, L_c P_k) \\
&= (P^*, a_k) \\
&= \int_{-h/2}^{h/2} P^* a_k dz = 0,
\end{aligned}
\tag{11}
$$

where P^* is the solution of the following homogeneous equation:

$$L_c P^* = 0, \quad \frac{dP^*}{dz} = \mp \frac{P^*}{\delta}, \quad z = \pm \frac{h}{2}, \tag{12}$$

Eq. (11) can be used to determine the coefficients γ_i. Then from the second relation of Eq. (7), one can determine λ as a function of $(T - T_c)$. Substituting the resulting λ into the first relation of Eq. (7) and solving the inhomogeneous equations (9) results in an explicit expression for the solution P.

Let us consider the $\delta > 0$ case, which is satisfied by most ferroelectrics. Equation (4) dictates that the transition temperature of the thin film is lower than that of the bulk material. The solution of Eq. (12) can be written as

$$P^* = M\cos(\beta z) + N\sin(\beta z), \tag{13}$$

where

$$\beta = \sqrt{A(T_{C0} - T_c)/D - 1/\varepsilon_d D}. \tag{14}$$

Suppose the P is distributed symmetrically along the thickness direction, i.e., $dP^*/dz = 0$ at $z = 0$, then $N = 0$, and the solution (13) becomes

$$P^* = M\cos(\beta z). \tag{15}$$

Similarly, the solution of the first equation in Eq. (8) can be obtained in the same form as P^*. Thus,

$$P_1 = M\cos(\beta z). \tag{16}$$

By using the orthogonal condition in Eq. (11), γ_1 and γ_2 can be determined,

$$\gamma_1 = 0 \quad \text{since} \int_{-h/2}^{h/2} P_1 P^* dz = \int_{-h/2}^{h/2} P_1^2 dz \neq 0. \tag{17}$$
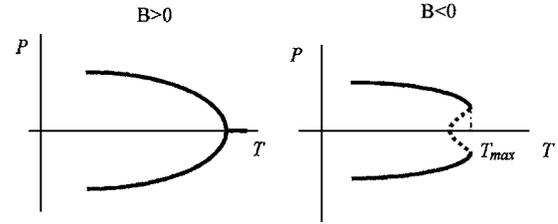
FIG. 1. Schematic of bifurcation diagram for ferroelectric thin film.

$$\gamma_2 = -\frac{B + 4GQ^2}{A} \frac{\displaystyle\int_{-h/2}^{h/2} P_1^4 dz}{\displaystyle\int_{-h/2}^{h/2} P_1^2 dz}. \tag{18}$$

If the corresponding bulk ferroelectrics transition is of second order, i.e., $B > 0$, $B + 4GQ^2$ is also positive, and substitution of Eq. (18) into (7) gives

$$\lambda = \pm \left(\frac{T_c - T}{-\gamma_2}\right)^{1/2} \quad \text{for } T < T_c, \tag{19}$$

i.e., the solution is defined in the supercritical (ferroelectric) regime. According to Theorem 3.1 for the bifurcation of a simple eigenvalue,[17] the bifurcating solutions are both asymptotically stable in the supercritical regime. The phase diagram for this case is shown in Fig. 1(a). Thus, if the bulk ferroelectrics exhibits second-order phase transition, their thin-film counterparts will also exhibit the same order of phase transition, and the universal critical exponents remain unchanged.

On the other hand, if the corresponding transition in the bulk material is first order, i.e., $B < 0$, then depending on the magnitude of the elastic self-energy of the transformation volume $4GQ^2$, which is positive definite and has a magnitude of the same order as B, $B + 4GQ^2$ can be either positive or negative. When $4GQ^2$ is sufficiently large, $B + 4GQ^2$ is positive definite, as in BaTiO$_3$ and PbTiO$_3$, then a first-order bulk ferroelectrics becomes second-order one in a rigidly constrained thin film. This is consistent with the results of Pertsev et al.[18] For the two classical perovskite ferroelectrics, BaTiO$_3$ and PbTiO$_3$, these authors also found that the two-dimensional clamping of the film could result in a change of transition order. Nevertheless, the results of Ref. 18 should be interpreted noting the assumption that the gradient terms in the free energy were negligible.

If the transformation volume satisfies $B + 4GQ^2 = 0$, the solution will include higher order terms of expansions, and thus the critical exponents will differ from their bulk counterpart. If $B + 4GQ^2$ is negative, substitution of Eq. (18) into Eq. (7) gives

$$\lambda \simeq \pm \left(\frac{T - T_c}{\gamma_2}\right)^{1/2} \quad \text{for } T > T_c, \tag{20}$$

i.e., the solution is defined only in the subcritical (paraelectric) regime, and both branches are unstable. Physically, there is a maximum value of $T_{\max}$ above which only one solution is admissible. Therefore, the subcritical branches have to turn, at some value $T_{\max}$, in the direction of decreas-

HHHHH

HHHH

FIG. 3. The normalized Curie-Weiss parameter $-[\Theta(h)]^{-1}$ vs the film thickness h for PbTiO$_3$.

TABLE I. Phenomenological parameters of PbTiO$_3$ (in cgs unit).

Material	T_{o0} (K)	A 10^{-5}	D 10^{-15}	δ nm	α
PbTiO$_3$	763	8.37	3	5	210

transition temperature was derived using a perturbation approach. It was found that the order of the transition and the critical exponents can be changed by the constraint of the substrate. A Curie-Weiss-type relation of dielectric permittivity was obtained in both the supercritical and subcritical regions. It was found that in paraelectric state, the Curie parameter is independent of the film thickness, and remains the same as their bulk counterpart. In the ferroelectric state, on the other hand, the magnitude of the Curie parameter of the film decreases rapidly as its thickness decreases.

Accordingly, for a film thickness of $h=8\delta$, the Curie parameter $\kappa_d^{-1}\Theta^{-1}$ of the ferroelectric phase would have dropped 33%. These characteristics are shown in Fig. 2, where the normalized susceptibility, i.e., $\Theta^{-1}/(T-T_c)$ as a function of temperature, is compared between thick films $(h\rightarrow\infty)$ and thin films $(h\rightarrow 0)$. We note that $\langle\chi_{\text{total}}\rangle$ also has a similar relation to $T-T_c$, as discussed in the foregoing.

From the free energy expression in Ref. 5, the contribution from the upper and lower surfaces of the ferroelectric thin film increases the susceptibility according to

$$\Delta\chi = \frac{2\delta}{D}, \quad (29)$$

which is negligible near the transition temperature.

In the following, we consider the example of a well known ferroelectric PbTiO$_3$, the material constants of which are shown in Table I.[5] The normalized Curie parameter $-[\Theta(h)]^{-1}$ is plotted against the film thickness h in Fig. 3, in which the Curie temperature was obtained as a function of h by using Eqs. (4) and (5). It can be seen that the magnitude of the normalized Curie parameter does decrease rapidly from 1 to 0.5 with decreasing thickness. Indeed, for films of PbTiO$_3$ about 40 nm ($=8\delta$), the ferroelectric transition is accompanied with a decrease of the Curie parameter of about 33%. Similar behavior is also found experimentally for BST films.[19] A review on the properties of ferroelectric materials was given in references.[20–22]

V. SUMMARY AND CONCLUSIONS

In this paper, the explicit solution of the steady-state Ginzburg-Landau equation for a ferroelectric film near the

[1] J. Junquera and Ph. Ghosez, Nature (London) **422**, 506 (2003).
[2] Ph. Ghosez and K. M. Rabe, Appl. Phys. Lett. **76**, 2767 (2000).
[3] Y. G. Wang, W. L. Zhong, and P. L. Zhang, Phys. Rev. B **51**, 17235 (1995).
[4] D. R. Tilley, in *Ferroelectric Thin Films: Synthesis and Basic Properties*, edited by C. Paz de Araujo, J. F. Scott, and G. W. Taylor (Taylor and Francis, Oxford, 1996), p. 11.
[5] B. Wang and C. H. Woo, J. Appl. Phys. **97**, 084109 (2005).
[6] S. K. Streiffer *et al.*, Phys. Rev. Lett. **89**, 067601 (2002).
[7] M. E. Fisher and M. Barber, Phys. Rev. Lett. **28**, 1516 (1972).
[8] D. P. Landau, Phys. Rev. B **14**, 255 (1976).
[9] D. P. Landau and K. Binder, J. Appl. Phys. **63**, 3077 (1988).
[10] S. Li, J. A. Eastman, J. M. Vetrone, C. H. Foster, R. E. Newnham, and L. E. Cross, Jpn. J. Appl. Phys., Part 1 **36**, 5169 (1997).
[11] W. L. Zhong, Y. G. Wang, P. L. Zhang, and B. D. Qu, Phys. Rev. B **50**, 698 (1994).
[12] I. P. Batra, P. Wurfel, and B. D. Silverman, Phys. Rev. Lett. **30**, 384 (1973).
[13] B. Wang and C. H. Woo, Acta Mater. **52**, 5639 (2004).
[14] P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966), p. 227.
[15] R. Kretschmer and K. Binder, Phys. Rev. B **20**, 1065 (1979).
[16] G. Nicolis and I. Prigogine, *Self-organization in Nonequilibrium Systems* (Wiley, New York, 1977), p. 85.
[17] D. H. Sattinger, *Group Theoretic Methods in Bifurcation Theory* (Springer-Verlag, Berlin, 1979).
[18] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).
[19] S. K. Streiffer, C. Basceri, C. B. Parker, S. E. Lash, and A. I. Kingon, J. Appl. Phys. **20**, 4565 (1999).
[20] A. K. Tagantsev, V. O. Sherman, K. F. Astafiev, J. Venkatesh, and N. Setter, J. Electroceram. **11**, 5 (2003).
[21] A. K. Tagantsev, V. O. Sherman, K. F. Astafiev, J. Venkatesh, and N. Setter, J. Electroceram. **14**, 199 (2005).
[22] B. Wang and C. H. Woo, J. Appl. Phys. **94**, 4053 (2003).