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Simulation of characteristics of phase transitions in ferroelectric thin films

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Abstract

Characteristics of phase transition in ferroelectric thin films are studied using the time dependent Ginzburg–Landau equation. Properties such as the spontaneous polarization, Curie temperature, critical thickness and susceptibility are investigated as a function of the extrapolation length, film size and the misfit strain. For free-standing $PbTiO_3$ thin film, the supercooling and superheating temperatures can be separately determined from the spontaneous polarization changes, under temperature heating-up and cooling-down conditions, respectively. When the film grown on compressive substrate, clamped effect on film may cause film made of first-order ferroelectric material to undergo a second-order transition. In addition, we have also comprehensively analyzed the effects of film size, the extrapolation length and substrate on characteristics of phase transitions. For free standing $PbTiO_3$ film, the different of superheating and supercooling temperature is insensitive to the film thickness and extrapolation length. The decrease of extrapolation length would not decrease the Curie temperature, but also decrease the critical thickness of the ferroelectricity. When film is thinner, the effect of the extrapolation length is larger on the change of the Curie temperature.

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Keywords: Ferroelectric thin films; Critical thickness; Curie temperature

1. Introduction

Characteristics of phase transitions in ferroelectric materials have attracted much attention because of the surge of recent technological interests in modern nonvolatile random access memories (FeMRAMs), ultra-miniaturized electronics and nanotechnologies in general. Physical properties of ferroelectric thin films, such as their phase transitions characteristics, are significantly different from those of bulk ferroelectrics. Ferroelectric materials are being dependent on the combined effects of many factors, including boundary conditions, misfit epitaxial stresses and applied electric field. Ferroelectric thin films are also controlled via such factors [1–18].

The thermodynamic approach has been successfully applied to many studies of ferroelectric thin films. Since the early 1980's, Tilley and Zeks [1] investigated surface effect on the phase transitions of free-standing ferroelectric films. Taking into account the effect of the substrate, and using Landau-type theory, Zembigotov et al. [2] analyzed the properties of epitaxial ferroelectric thin films on dissimilar cubic substrate. Zhong et al. [3] studied the first-order phase transitions properties of ferroelectric thin films using the thermodynamic approach. Tan et al. [4] considered a Landau–Devonshire model for ferroelectric thin films undergoing a first-order phase transitions, and their results showed that the spontaneous polarization is depending on the film thickness, temperature and boundary-conditions. Moreover, they identified the supercooling and superheating transition temperatures. Properties of second-

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order transitions in ferroelectric thin films were studied by Ong et al. [5] within the thermodynamic approach. They established an analytic model to describe the second-order phase transitions, and obtained numerical results which indicated the importance of the size and surface effects on phase transition. The characteristics of phase transitions in ferroelectric thin film can be obviously affected by clamped behavior from mismatch between film and substrate. This result was experimentally observed by Streiffer et al. [6] and theoretically justified by Pertsev et al. [7] and Catalan et al. [8]. Moreover, the fact that free-standing films remain first-order has recently been experimentally verified for the first time by M. Saad et al. [9].

Using the time dependent Ginzburg–Landau theory, Wang and Woo [10] obtained analytic expressions for the critical conditions that control the transition between the paraelectric and ferroelectric states. They found that the supercooling and superheating transition temperatures are insensitive to the film thickness and surface boundary conditions for first-order phase transitions. They also discovered that the restraint of the misfit strain due to the rigidity of the substrate may enhance the polarization of ferroelectric state, increase the Curie temperature, and even cause a thin film of first-order ferroelectric material to undergo a second-order transitions. But we must note that there are many assumptions in their calculations for solving differential equations. Otherwise, the differential equations in Ref. [10] cannot be solved without these assumptions. But results of Ref. [10] are not comprehensively general and effective for investigating ferroelectric thin film. At the same time, their results cannot show relationships, such the extrapolation length/Curie temperature, the extrapolation length/the critical thickness etc. In recent years, there were many other researchers working on phase transitions of ferroelectric thin film in recent years [11–14]. The scope of which were limited by the difficulties on solving the complex and nonlinear thermodynamic equation which is formulated together with the effect of film surface effect, epitaxial stresses, depolarization field etc. In this regard, it is well known that the characteristics of phase transitions, such as the spontaneous polarization, Curie temperature, critical thickness and susceptibility, are different under temperature heating-up and cooling-down. Unfortunately, solution of the static equation is insensitive to the conditions of the initial state and is thus inadequate to distinguish these two conditions. Effects of the extrapolation length, the misfit strain, the depolarization field and the film size etc. in these two conditions, are still remained to be completely clarified.

In this Letter, using the time dependent Ginzburg–Landau equation, we established an approach to describe the evolution of the spontaneous polarization field in ferroelectric materials. Since the equation depends sensitively on the initial state, a distinction between the behavior of the spontaneous polarization during heat-up and cool-down is then possible. Ferroelectricity is a collective phenomenon, the change of which depends on the combined effects of many other factors. Therefore, a comprehensive analysis of the effects of film size, the extrapolation length and misfit strains on the characteristics of phase transitions is needed. We also investigated the change of supercooling/superheating transition temperature under different film thickness, and extrapolation length. The behavior of the susceptibility for different cases, such as ferroelectric bulk, free-standing film and film grown on compressive substrate is also explored. When the thin films grown on compressive substrate, clamped effect induced by compressive substrate on ferroelectric thin film may even cause a thin film made of first-order ferroelectric material to undergo a second-order transition.

2. Theoretical development

We consider a thin film of ferroelectric material of dimensions $\infty \times \infty \times h$, h being the film thickness. The origin of the coordinate system is at the interface of film and substrate. We suppose the polarization P is orthogonal to the surface of the film. For a free-standing film, the electrical component of the free energy per unit area can be expressed in terms of the order parameter P and the temperature using the Ginzburg–Landau functional. Including the surface effect, depolarization field and external field, the generalized free energy is given as [1,4,15–17],

$$G = G_0 + \int_0^h \left\{ \frac{1}{2}A(T - T_{C0})P^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + \frac{1}{2}D\left(\frac{dP}{dz}\right)^2 - \frac{1}{2}E_d P - E_{\text{ext}}P \right\} dz + \frac{1}{2}\left(\frac{DP_0^2}{\delta} + \frac{DP_h^2}{\delta}\right). \tag{1}$$

When ferroelectric thin film is grown on a substrate, the contribution of the elastic energy determined by the misfit strain and self-strain on the total free energy should be considered. Under the Legendre transformation of the Gibbs free energy [2], we can establish the Helmholtz free energy for ferroelectric thin film grown on a substrate. The total free energy is the sum of electrical and the mechanical components. Compared to free-standing films, both the lattice mismatch and the polarization give rise to equal biaxial stresses and strains in films on substrates, and the total free energy can be written as [2,7,10,18,19],

$$\begin{aligned} F = G_0 + \int_0^h \Bigg\{ & \left[\frac{1}{2}A(T - T_{C0}) - u_m \frac{2Q_{12}}{s_{11} + s_{12}}\right]P^2 + \left(\frac{1}{4}B + \frac{Q_{12}^2}{s_{11} + s_{12}}\right)P^4 + \frac{1}{6}CP^6 + \frac{1}{2}D\left(\frac{dP}{dz}\right)^2 \\ & - \frac{1}{2}E_d P - E_{\text{ext}}P + \frac{u_m^2}{s_{11} + s_{12}} \Bigg\} dz + \frac{1}{2}\left(\frac{DP_-^2}{\delta} + \frac{DP_+^2}{\delta}\right), \end{aligned} \tag{2}$$

where A, B, C, and D are the expansion coefficients. T_{C0} is Curie temperature of the bulk crystal [10]. $u_1 = u_2 = u_m$ are the in-plane misfit strains between the thin film and substrate. We assume that the misfit strain in ferroelectric thin film is homogeneous through out the film in this work. P_- and P_+ are the polarization at the surface and the interface of thin films, respectively. δ is the extrapolation length that measures the effect of lattice relaxation on the surface. Two separate cases may be considered: the more common case $\delta > 0$, which is corresponding to a reduction of self-polarization on the surface; and the rarer case $\delta < 0$, which is corresponding to an enhancement. We note that in general δ is not an absolute constant, which should be confirmed by experimental methods for different ferroelectric materials and boundary conditions. Furthermore, the epitaxial stress and the surface lattice relaxation may act for or against the transformation. In this study, we focus on the effects of the extrapolation length, film size and compressive substrate on the phase transitions of ferroelectric thin films. E_d is the depolarization field. E_{ext} is the external electric field.

Using Eqs. (1) and (2), the time evolution of the system is governed by the dynamic Ginzburg–Landau (DGL) equation [10],

$$\frac{\partial P(z,T,t)}{\partial t} = -M\frac{\delta F}{\delta P} = -M\left\{A^*P + B^*P^3 + CP^5 - D\frac{\partial^2 P}{\partial z^2} - E_d - E_{\text{ext}}\right\}, \tag{3}$$

where M is the kinetic coefficient related to the domain wall mobility, and the renormalized coefficients,

$$A^* = A(T - T_{C0}) - \lambda\frac{4Q_{12}}{s_{11}+s_{12}}u_m,$$
$$B^* = B + \lambda\frac{4Q_{12}^2}{s_{11}+s_{12}}, \tag{4}$$

where λ equals 0 if the film is free-standing, and 1 if grown on a substrate.

The surface term in Eqs. (1) and (2) yields the boundary conditions [16],

$$\frac{\partial P}{\partial z} = -\frac{P_-}{\delta} \quad \text{for } z = 0 \quad \text{and} \quad \frac{\partial P}{\partial z} = \frac{P_+}{\delta} \quad \text{for } z = h. \tag{5}$$

Surface depolarization and extrapolation length effects were first calculated under considering the short-circuit boundary conditions by Kretschmer and Binder [20]. In their work it appears that big extrapolation lengths are detrimental, rather than the other way round. Other relative work by Glinchuk et al. [21] on Landau theory of surface effects also have been investigated. However, we should note that the size and depolarization effects are different with the different boundary conditions, such as short-circuit and open-circuit conditions etc. Relative works refer to Ref. [22–24], which have given detail derivation of the depolarization field under different boundary conditions. In this work, we do not discuss the depolarization field effect on properties of the ferroelectric film. However, our theory provides the basis for the analysis of its effects. For example, it is straightforward to show that the depolarizing-field-induced shift of the transition temperature can be easily incorporated into it [23,25].

3. Numerical method

In the following calculations, we employed a finite element scheme. The ferroelectric thin film is considered as a stack of N uniform layers with finite thickness Δz in the z direction, i.e., $h = N\Delta z$. Δz is sufficiently large comparing with the lattice constant, so that the thermodynamic description is applicable. A layer located at a position between z and $z + \Delta z$ is identified by the index i, i.e. $z_i = i\Delta z$. By taking the forward difference $M\Delta t$ in time, the corresponding evolution of $P(z_i, T, t)$ according to the time dependent Ginzburg–Landau equation is given by

$$\begin{aligned}P(z_i,T,t+M\Delta t) = P(z_i,T,t_M) = P(z_i,T,t) + M\Delta t\big\{&-A^*(T)P(z_i,T,t) - B^*P(z_i,T,t)^3 - CP(z_i,T,t)^5 \\ &+ D\big(P(z_{i-1},T,t) - 2P(z_i,T,t) + P(z_{i+1},T,t)\big)/\Delta z^2\big\},\end{aligned} \tag{6}$$

where the initial values of the spontaneous polarization at a temperature T is set at

$$P(z_i,T,t_M=0)\begin{cases} P(z_i,T-\Delta T,t_M>t_s), & \text{for temperature heating-up,} \\ P(z_i,T+\Delta T,t_M>t_s), & \text{for temperature cooling-down.}\end{cases} \tag{7}$$

Here temperature step is ΔT. Eq. (7) calculates the polarization as a function of t for various depths z during heat-up or cool-down for every time step. $P(z_i, T, t = 0)$ is the initial value in the solution of Eq. (6) at a specified temperature. $P(z_i, T - \Delta T, t_M > t_s)$ and $P(z_i, T + \Delta T, t_M > t_s)$ represent the asymptotic stationary values of polarization for Eq. (6) near a certain temperature for the heating-up and cooling-down, respectively. And t_s is time for getting stable of $P(z_i, T - \Delta T)$ or $P(z_i, T + \Delta T)$ from $P(z_i, T)$. The difference equations for the boundary conditions can be obtained as follows:

$$\begin{aligned}&\frac{-3P(z_N,T,t_M) + 4P(z_{N-1},T,t_M) - P(z_{N-2},T,t_M)}{2\Delta z} + \frac{P(z_N,T,t_M)}{\delta} = 0, \quad \text{for } z = h, \\ &\frac{3P(z_0,T,t_M) - 4P(z_1,T,t_M) + P(z_2,T,t_M)}{2\Delta z} - \frac{P(z_0,T,t_M)}{\delta} = 0, \quad \text{for } z = 0,\end{aligned} \tag{8}$$

where the total time for integration $t_M = \Delta t M$. The temperature step is $\Delta T = 1$ K.

The inverse susceptibility is given by [8,13,14]

$$\chi = \left(\frac{d^2 f}{dP^2}\right)^{-1} = \left[A^* + 3B^* P^2 + 5CP^4 - D\frac{d}{dP}\left(\frac{d^2 P}{dz^2}\right)\right]^{-1}, \tag{9}$$

where f is the total free energy density in Eqs. (1) and (2).

According to Eqs. (6)–(8), we can simulate the evolution of the inverse susceptibility for ferroelectric thin film undergoing cubic/tetragonal phase transformation upon cooling and heating. The simulation equation of the susceptibility can be written as follows [8,23,26,27],

$$\chi(z_i, T, t) = \left[A(T - T_C) + 3B^* P(z_i, T, t)^2 + 5CP(z_i, T, t)^4\right]^{-1}, \tag{10}$$

where T_C is the Curie temperature. It can be redefined conventionally as: $T_C = T_{C0}$ for ferroelectric bulk, $T_C = T_C(h, \delta)$ for free-standing ferroelectric thin film and $T_C = T_C(h, \delta, u_m)$ for a ferroelectric thin film grown on a substrate. For the first-order phase transition, the Curie temperature is $T_C = T_{SC}$ for temperature cooling-down and $T_C = T_{SH}$ for temperature heating-up. For the second-order phase transition, the Curie temperature is $T_C = T_{SC} = T_{SH}$. These values can be obtained by solving the dynamic Eqs. (6)–(8).

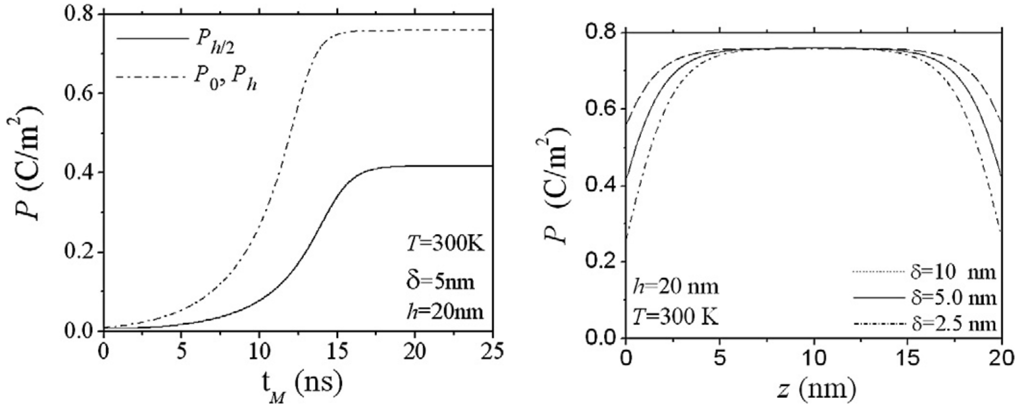
The average value of $\chi_a(T, t)$ is defined as

$$\chi_a(T, t) = \frac{1}{h}\int_0^h \chi(z, T, t)\,\mathrm{d}z = \frac{1}{h}\sum_{n=0}^{n=N} \chi(z_n, T, t)\Delta z. \tag{11}$$

4. Results and discussion

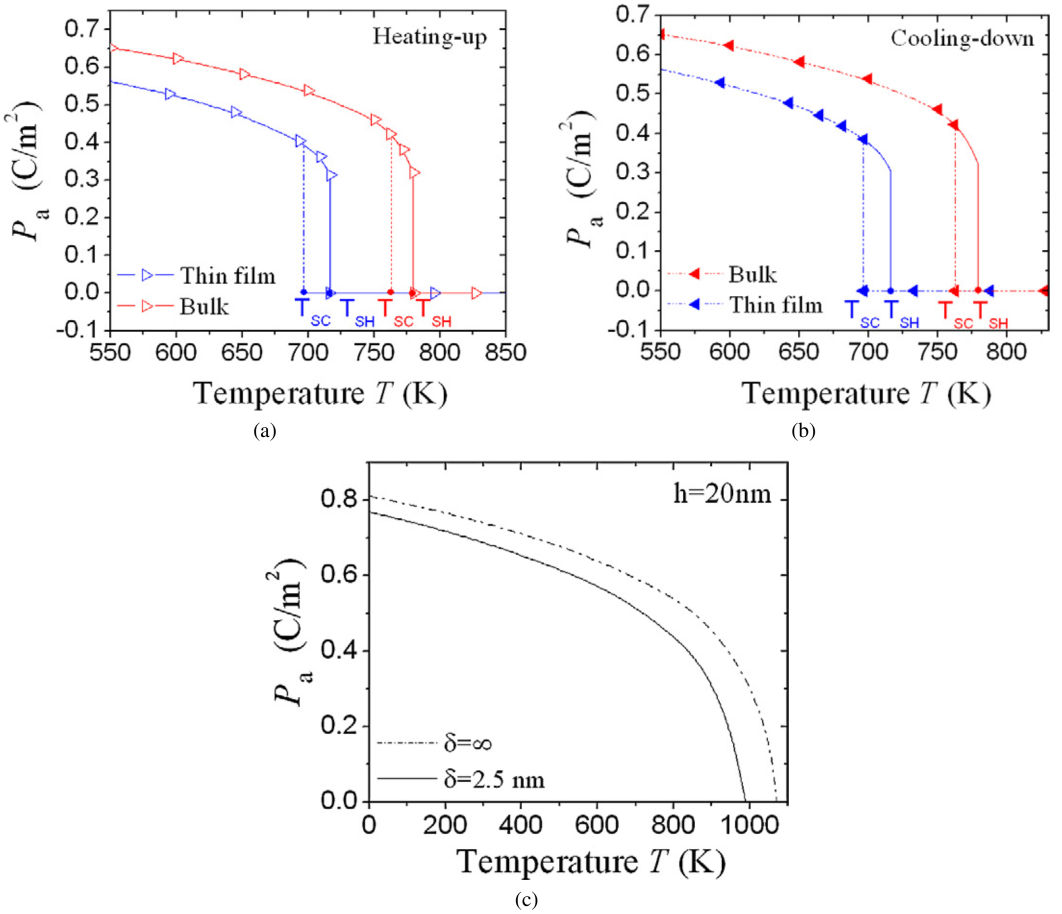
In the following, we consider the numerical simulations of free-standing $\mathrm{PbTiO_3}$ thin film and film growth on $\mathrm{SrTiO_3}$ substrate. The corresponding material constants for the Landau free energy, the electrostrictive coefficients and the elastic properties are from Refs. [3,7,10]. According to former workers [1–4], the characteristics of phase transitions in $\mathrm{PbTiO_3}$ bulk and free-standing thin films are first-order. In heat-up and cool-down conditions, the initial value of the spontaneous polarization at a special temperature can be solved using Eqs. (6)–(8). We assume the initial value of the polarization at a special temperature is a very small Gaussian random distribution. The polarization will get stable when time increases. The polarization distribution is inhomogeneous and its values at the surface and at the center of film are different. It is because of the surface relaxation on the polarization distribution in ferroelectric thin film. We note that the extrapolation length δ should be confirmed by experimental methods for different ferroelectric materials and boundary conditions [3]. Some workers reported that the extrapolation length is actually the same as the domain wall half-width. This domain wall half-width/extrapolation length has been recently discussed in Refs. [28,29].

Firstly, we discuss the evolution process of the polarization from an initial very small Gaussian random distribution ($t_M = 0$) to a stable distribution ($t_M > t_s$). In Fig. 1(a), it shows the evolution process of the polarization of a free-standing film with film thickness $h = 20$ nm, extrapolation length $\delta = 5$ nm and temperature $T = 300$ K. When the number of time step increases, both the polarization at the center of film $z = h/2$ and surface of film $z = 0$ or h are attaining an asymptotically stable values. The polarization grew from a very small random distribution and reached certain finite stable value. In Fig. 1(b), it shows the distribution of the stable



(a) (b)

Fig. 1. (a) Evolution of the spontaneous polarization at center $z = h/2$ and surface $z = 0, h$ of $\mathrm{PbTiO_3}$ ferroelectric free-standing thin films at $T = 300$ K and $\delta = 5$ nm. (b) Distribution of the stable polarization along z direction in ferroelectric thin film at $T = 300$ K and $\delta = 2.5, 5, 10$ nm.



(a) (b)

(c)

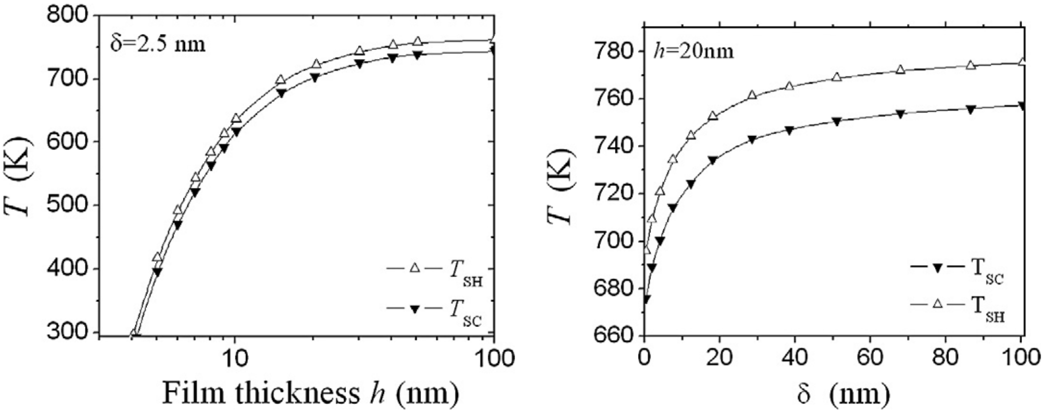
Fig. 2. (Color online.) Dynamic process of the average polarization changing with (a) temperature heating-up, and (b) temperature cooling-down for bulk and free-standing thin film, (c) temperature heating-up and cooling-down for ferroelectric thin film grown on compressive substrate, where the film thickness is $h = 20$ nm and the extrapolation length is $\delta = 2.5$ nm.

polarization along z direction in ferroelectric thin film with different extrapolation lengths $\delta = 2.5, 5, 10$ nm. Due to the surface effect, the polarization at the surface is lower than that at the center, which explains the different values showing in Fig. 1(a). At the same time, the polarization distributions are also determined by the extrapolation length as shown in Fig. 2(b).

Based on methods of Fig. 1, we consider that the stable value of the polarization in $\mathrm{PbTiO_3}$ at a low or high temperature is initial value for process of temperature heating-up or cooling-down, and using Eqs. (6)–(8), we can simulate the whole process of the polarization changing with temperature heating-up or cooling-down. In Fig. 2(a), we find that the polarization will rapidly disappear when temperature is above certain value for bulk and free-standing thin film, which we define them as super-heating temperature for bulk T_{SH}^{B} and free-standing thin film T_{SH}^{F}. Using foregoing approach, we also compute changes of the polarization during cooling-down. In Fig. 2(b), it shows the supercooling temperature for bulk T_{SC}^{B} and free-standing thin film T_{SC}^{F}. The polarization will get a stable value when temperature is below T_{SC}. It confirmed that the Curie temperatures are different for heat-up and cool-down in $\mathrm{PbTiO_3}$ bulk and free-standing thin films. These results also indicate that the surface effect reduces the Curie temperature of the ferroelectric phase transition in thin film.

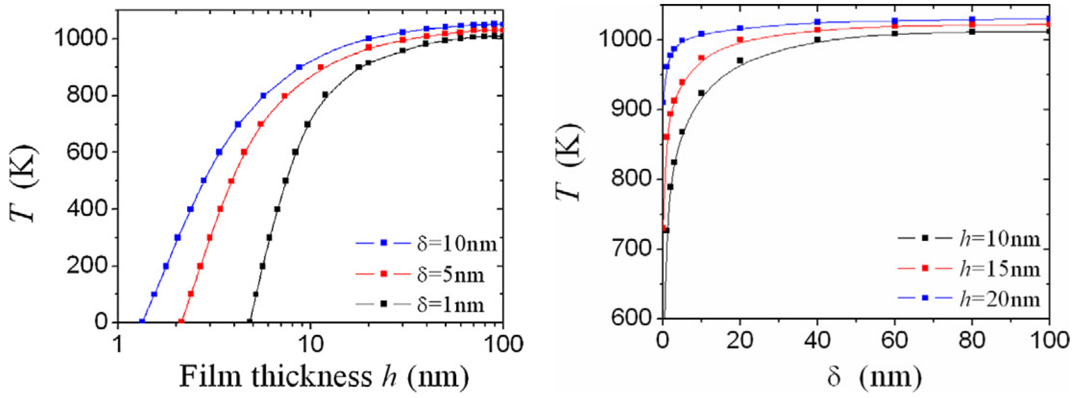
Other works have discuss some properties of ferroelectric thin films grown on compressive substrate, their results show that clamped effect induced by a compressive substrate can cause a thin film made of first-order ferroelectric material to undergo a second-order transitions, and change the Curie temperature and the spontaneous polarization etc. [2,4,5,10]. In this Letter, we also investigate behavior of second-order phase transitions in ferroelectric thin films grown on compressive substrate. We are focus on investigate general relationships between size/surface/strain and polarization/Curie temperature/susceptibility. In Fig. 2(c), we investigated the different between the polarization change of $\delta = 2.5$ nm and $\delta = \infty$, where $\delta = \infty$ means the effect of film surface is neglected. We find that the transform from the first-order transition to second-order when $\mathrm{PbTiO_3}$ is grown on compressive $\mathrm{SrTiO_3}$ substrate. Which results are similar to previous work [10]. These correct results confirm our approach is right for studying phase transition of ferroelectric materials.

In our numerical calculations, there are not any assumptions, which is important difference compared to Wang and Woo's work of Ref. [10]. In Fig. 3, it shows an interesting result that, for $\mathrm{PbTiO_3}$ free-standing thin film, the difference between the superheating T_{SH} and supercooling T_{SC} transition temperatures is insensitive to the film thickness h and the extrapolation length δ. Even when the



(a) (b)

Fig. 3. (a) Superheating temperature T_{SH}^F and supercooling temperature T_{SC}^F vs the film thickness, where the extrapolation length is $\delta = 2.5$ nm. (b) Superheating temperature T_{SH}^F and supercooling temperature T_{SC}^F vs the extrapolation length for free-standing ferroelectric thin film, where the film thickness is $h = 20$ nm.



(a) (b)

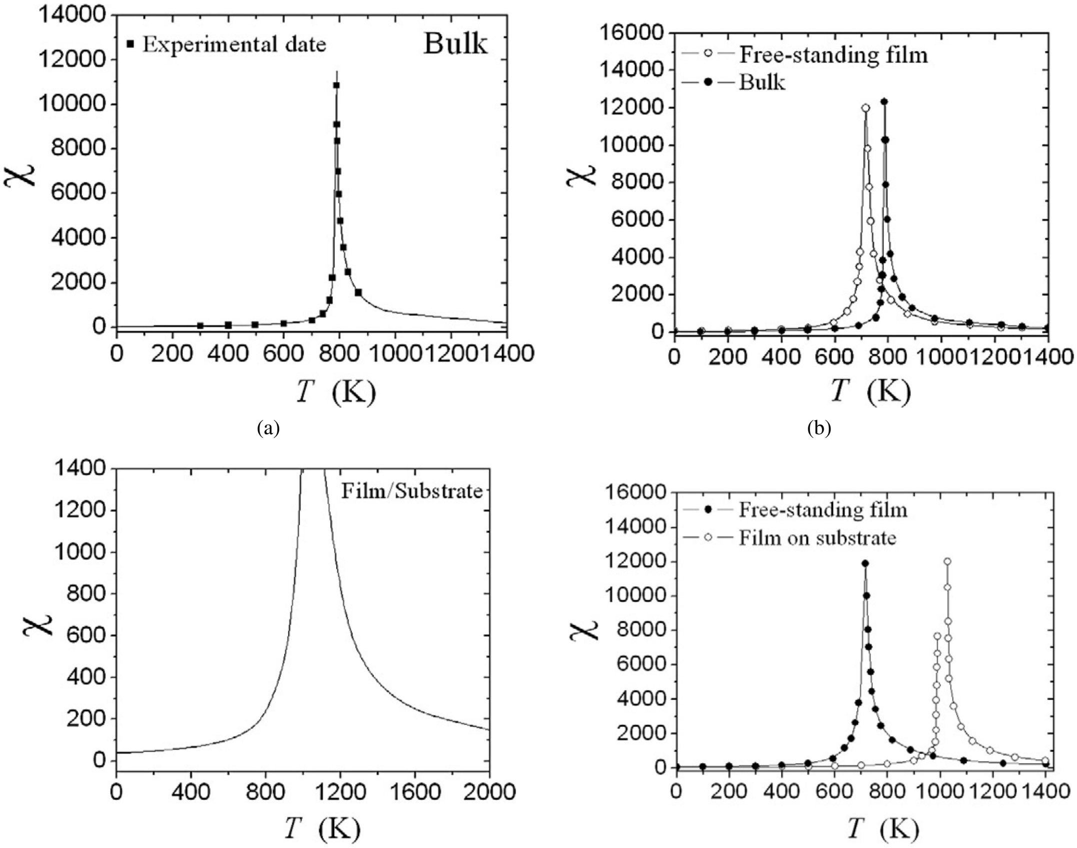
Fig. 4. (Color online.) For $PbTiO_3$ ferroelectric thin film grown on $SrTiO_3$ compressive substrate. (a) Curie temperature vs the film thickness, where the extrapolation lengths are $\delta = 1$ nm, 5 nm and 10 nm, respectively. (b) Curie temperature vs the extrapolation length, where the film thickness are $h = 10$ nm, 15 nm and 20 nm.

film thickness is of few nanometers, the difference of them still keeps almost constant. Similarly, even the decrease of extrapolation length causes a decrease of Curie temperature, the difference of them still keeps almost constant too.

Then, we investigated the effects of the film size and the surface on the characteristics of phase transitions in $PbTiO_3$ thin film grown on compressive substrate. In this condition, the superheating and supercooling temperatures are the same. In Fig. 4(a), the relation between the phase transition temperature and the film thickness are shown with different extrapolation length. The phase transition temperature increases with the extrapolation length increasing. Moreover, the critical thickness is greatly affected by the dimension of the extrapolation length. For the same thin film thickness, the critical thickness can be altered from about 1.4 nm to 4.8 nm when the extrapolation length is change from 1 nm to 10 nm. Note that, the extrapolation length can be tuned by supplementary changes with different boundary conditions. This leads to a consequence that the critical thickness of ferroelectricity is tunable. In Fig. 4(b), it shows the relationship between the phase transition temperature and the extrapolation length with different the film thickness as shown in. For all film thickness, the Curie temperatures show drastic decreases when extrapolation length decrease. However, for thinner film, this effect occurs earlier.

Based on our evolution model, we can easily find the relationship between superheating/supercooling temperature and the film thickness; superheating/supercooling temperature and the extrapolation length, for both free-standing ferroelectric thin film and ferroelectric thin film grown on compressive substrate. The Curie temperature T_C for $PbTiO_3$ bulk, free-standing thin film and film grown on compressive substrate can be obtain by solving Eqs. (6)–(8) without any assumptions, respectively..

Using Eqs. (9)–(11), we computed the average susceptibility for the case of cooling down. Similar behavior can be obtained by the analytic solution of the thermodynamic theory [27,30] and experimental data [31] for first-order and second-order phase transition. In this study, differences of susceptibility can be computed under considering effects of surface relaxation, film size and compressive substrate. Fig. 5(a) shows results of susceptibility versus temperature by our dynamic evolution model, which agrees well with experimental data [31]. We find both surface effect and compressive substrate can shift value of the susceptibility. At the same time we also give values of the relationship between the average susceptibility and temperature for free-standing thin film and film grown on compressive substrate, which are shown in Fig. 5(b)–(d).



(a) (b)

(c) (d)

Fig. 5. Susceptibility versus temperature for ferroelectric. (a) Bulk (squares determined from experimental date in Ref. [19]). (b) Bulk and free-standing film ($h = 20$ nm and $\delta = 2.5$ nm). (c) Thin film grown on substrate ($h = 20$ nm and $\delta = 2.5$ nm). (d) Free-standing film and thin film grown on substrate ($h = 20$ nm and $\delta = 2.5$ nm).

5. Conclusions

In summary, we investigate the supercooling and superheating temperature of first-order phase transitions for free-standing ferroelectric thin by using time dependent Ginzburg–Landau approach. We observed the effects of film surface, polarization gradient, and surface effect on the behaviors of phase transitions of ferroelectric thin films. Our results show characteristics of ferroelectric thin films are depend on effects of film surface and thickness. Moreover, if ferroelectric thin film grow on compressive substrate, its characteristics of phase transitions change due to the clamped effects induced by a compressive substrate, and this effect may even cause a thin film made of first-order ferroelectric material to undergo a second-order transition, then characteristics of ferroelectric thin film will change accordingly. Furthermore, the different between the superheating and supercooling temperature for free standing film is insensitive to the change of film thickness and extrapolation length. Even though the decreases of film thickness or extrapolation length can drastically decrease the Curie temperature, it would not affect the relative difference of superheating/supercooling temperature. In addition, the decrease of extrapolation length not only causes the decrease of Curie temperature, but also decreases the critical thickness of ferroelectivity. If we can control the complementary charges, we can tune this critical thickness. If the film is thin, the effect of extrapolation length on the Curie temperature is larger.

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