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Effects of interface dislocations on properties of ferroelectric thin films

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Abstract

Effects of interfacial dislocations on properties of thin-film ferroelectric materials, such as the self-polarization distribution, Curie temperature, dielectric constant and the switching behaviors, are investigated via the system dynamics based on the Landau–Devonshire functional. Dislocation generation in the film is found to reduce the overall self-polarization and the Curie temperature. The spatial variations are both very strong, particularly in the immediate neighborhood of the dislocation cores. In agreement with previous results based on a stationary model, a dead layer exists near the film/substrate interface, in which the average self-polarization is much reduced. Moreover, it is evident from our results that interface dislocations play an important role in suppressing the remnant polarization and the coercive field of the polarization.

Keywords: Interface dislocations; Self polarization; Ferroelectric thin film; Remnant polarization; Coercive field

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1. Introduction

Much work has been done recently on nano-scale ferroelectric thin films because of their remarkable properties that make them very useful in electro-optic, pyroelectric, and piezoelectric devices, as well as ultra-high-density nonvolatile memories (Haeni et al., 2004; Fong et al., 2004; Streiffer et al., 2002; Balzar et al., 2004). It is well known that properties of ferroelectrics in the bulk and thin-film forms may be significantly different, depending on the combined effects of film surfaces, depolarization field, film/substrate interfaces, epitaxial stress and the external electric field, etc (Catalan et al., 2005; Sinnamon et al., 2002; Wesselinawa et al., 2005; Scott et al., 2005; Wang et al., 2003). In this regard, misfit dislocations introduces a large stress field superimposing on the epitaxial stresses to significantly affect the physical properties of the film. Related investigations constitute an active area of thin-film research.

Dislocation structure formed in $BaTiO_3$ grown on $SrTiO_3$ substrate has been analyzed by using X-ray and transmission electron microscopy, and determined the critical thickness of the misfit dislocation generation (Suzuki et al., 1999). They also confirmed that the misfit relaxation depended on the presence of dislocations. Similar investigations have been carried out and result showed that misfit dislocations were very important on the stability of the polarization field (Sun et al., 2004; Chu et al., 2004). The dielectric properties of ferroelectric thin film also depended on internal stresses and dislocation-type defects (Li et al., 2001; Canedy et al., 2000). Using the phase-field model, effects of interfacial dislocations on the polarization distribution and domain structure of ferroelectric thin film have been investigated (Hu et al., 2003). They also developed a method to predict the evolution of a domain structure in a ferroelectric thin film with an arbitrary spatial distribution of dislocations. However, the effects of the depolarization field and the near-surface eigenstrain relaxation could not be readily taken into account within this approach. Another concern also arose from the non-linear nature of the model, which did not always admit a unique solution.

In our previous work (Wang and Woo, 2005; Zheng et al., 2006a), we adopted the time-dependent Ginzburg–Landau equation approach to investigate the self polarization distribution near misfit dislocations, successfully including the effects of relaxation of the surface effect and the depolarization. The existence of a dead layer near the film/substrate interface was confirmed (Haun et al., 1987). However, the dielectric constant was assumed to be spatially uniform. This assumption is inconsistent with the spatially varying polarization field, on which the dielectric constant is functionally dependent. Besides, among many of the most important properties of a ferroelectric thin film, only the spontaneous polarization distribution was discussed.

In this paper, effects of interfacial dislocations on the self-polarization, Curie temperature and dielectric constant are considered as functions of temperature and film thickness. The spatial variations of the self-polarization, the depolarization, and the extrapolation length are specifically taken into account. This is done via the finite-difference solution of the evolution equation derived from a thermodynamic model in which the free energy is constructed with the help of the Landau–Devonshire functional. The interface dislocations effects on the remnant polarization and the coercive field of ferroelectric thin film also is investigated. The results are discussed and the observations concluded.

2. Theory

2.1. The free energy equation

We consider a single-domain ferroelectric thin film on a compliant substrate, which undergoes a cubic to tetragonal (tetragonal to cubic) phase transformation on cool-down (heat-up). We use a coordinate system in which the x-axis is parallel to [1 0 0], the y-axis to [0 1 0], and the z-axis to [0 0 1], where the film in the x- and y-directions extend to infinity, the film surface and the film/substrate interface are on the $z=h$ and $z=0$ planes, respectively, h being the film thickness (Fig. 1). A straight edge dislocation is placed at the origin, with Burgers vector in the x-direction and dislocation line in the y-direction.

As in the classical description of electrical susceptibility of polar molecules, we may identify E, which has its origin from the combined effects of P and E_{ext}, as the sum of the external field E_{ext} and the depolarization field E_{d}. We call P the self-polarization instead of the spontaneous polarization in our previous work (Wang and Woo, 2005; Zheng et al., 2006a). The evolution of the system is then driven by the chemical potential derived from a total free energy that can be written as the sum of self-energies due to the self-polarization P, the induced polarization P_{E} and the stress field. The total polarization P_{total} at any point is considered to be the sum of a permanent molecular component P characteristic of the specific para/ferroelectric phase it is in, and an induced component P_{E}. The induced component P_{E} is the polarizations (ionic + electronic) induced by the total electric field E in the dielectric according to the law of electrostatics in the absence of free charges, $\nabla \cdot D = 0 = \nabla \cdot (\varepsilon_0 E + P_{\text{total}}) = \nabla \cdot (\varepsilon_0 E + \chi E + P) = \nabla \cdot (\boldsymbol{\varepsilon} E + P)$ subject to the appropriate boundary conditions on the dielectric surfaces. Without external electric field ($E_{\text{ext}}=0$), we have $E = E_{\text{d}}$. The total polarization is sum of the self-polarization and induced polarization by the depolarization filed E_{d}, and which can be obtained by $P_{\text{total}} = P + \chi E_{\text{d}}$. Here χ and ε are the temperature-independent components of the susceptibility and permittivity, which corresponds to the induced polarization. The same relation has also been discussed for investigating size effects in expitaxial islands and films (Wang and Woo, 2006; Wang and Zhang, 2006). In this work, we only establish a simple model trying to represent the complex influence of misfit dislocations on the properties of ferroelectric thin films. P in ferroelectric thin film is only assumed to have a non-zero Cartesian component only along the z-direction, i.e., $P_z = P$ and $P_x = P_y = 0$.

Considering the effects of the depolarization and applied electric fields, the total free energy of a ferroelectric thin film with the interface dislocations, including Landau–Devonshire energy, the gradient energy, the depolarization energy, the electrical energy induced by external electric field. When an interface dislocation is generated in film/

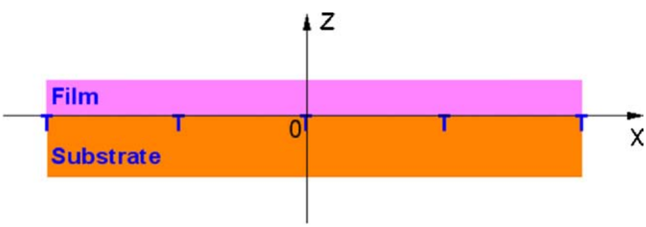

Fig. 1. Schematic of the interfacial dislocation between the ferroelectric thin film and the substrate.

substrate system, the total Helmholtz free energy $\tilde{G}$ is obtained from a Legendre transformation from a Gibbs free energy G (Pertsev et al., 1998)

$$\tilde{G} = G + \mu_{11}\sigma_{11} + \mu_{22}\sigma_{22} + \mu_{33}\sigma_{33} + \mu_{13}\sigma_{13}. \tag{2.1}$$

Then $\tilde{G}$ can be written as (Wesselinawa et al., 2005; Sun et al., 2004; Li et al., 2001; Zheng et al., 2006a; Wang and Zhang, 2006),

$$\begin{aligned}\tilde{G} = \iint_{\Sigma} \Bigg\{ & G_0 + \frac{A}{2}(T - T_{c0})P^2 + \frac{B}{4}P^4 + \frac{C}{6}P^6 + \frac{1}{2}S_{11}(\sigma_{11}^2 + \sigma_{22}^2 + \sigma_{33}^2) \\ & + S_{12}(\sigma_{11}\sigma_{22} + \sigma_{11}\sigma_{33} + \sigma_{22}\sigma_{33}) + \frac{1}{2}S_{44}(\sigma_{12}^2 + \sigma_{13}^2 + \sigma_{23}^2) - Q_{11}\sigma_{33}P^2 \\ & - Q_{12}(\sigma_{11}P^2 + \sigma_{22}P^2) + \frac{D_{44}}{2}\left(\frac{\partial P}{\partial x}\right)^2 + \frac{D_{11}}{2}\left(\frac{\partial P}{\partial z}\right)^2 - \frac{1}{2}E_{\mathrm{d}}P - E_{\mathrm{ext}}P \Bigg\} \,\mathrm{d}x\,\mathrm{d}z \\ & + \int_{\Sigma_x} \frac{D_{11}P^2}{\delta_1}\,\mathrm{d}x + \int_{\Sigma_z} \frac{D_{44}P^2}{\delta_2}\,\mathrm{d}z, \end{aligned} \tag{2.2}$$

where A, B, C, D_{11} and D_{44} are expansion coefficients of the Landau–Devonshire functional at constant stress. T_{c0} is the Curie temperature of the bulk crystal. σ_{ij} is the total stress field in the film, in the presence of the interfacial dislocations, Q_{ij} is the electrostrictive tensor (Tilley, 1996; Pertsev et al., 1998). Σ_z and Σ_x represent the upper–lower and left–right surface planes that cover the entire surface Σ of the film. δ_1 and δ_2 are the extrapolation lengths, which measure the surface effects on the film surface and the film/substrate interface, respectively, including near-surface eigenstrain relaxations (Zhong et al., 1994).

2.2. *The stress field induced by the interface dislocations*

We use periodic boundary conditions along the x-direction to reflect a configuration in which the interfacial dislocations form an array lying on the $z = 0$ plane, with C_{II} interface dislocation (Hu et al., 2003) and line directions parallel to the y-direction, through the centers of identical simulation cells repeated *ad infinitum* along the x-direction. The surface effects on Σ_x and Σ_y as well as the depolarization field along the x and y directions are neglected.

The resultant stress field of the dislocation array, within isotropic linear elasticity theory, is given by (Hirth and Lothe, 1982; Hull and Bacon, 2001)

$$\begin{aligned} \sigma_{11}(x,z) &= -\frac{b}{2\pi S_{44}\left(1 + \frac{S_{12}}{S_{11}}\right)} \sum_m z \frac{(3x_m^2 + z^2)}{(x_m^2 + z^2)^2}, \\ \sigma_{22}(x,z) &= -\frac{b}{\pi S_{44}\left(1 + \frac{S_{12}}{S_{11}}\right)} \frac{S_{12}}{S_{11}} \sum_m \frac{z}{x_m^2 + z^2}, \\ \sigma_{33}(x,z) &= \frac{b}{2\pi S_{44}\left(1 + \frac{S_{12}}{S_{11}}\right)} \sum_m z \frac{(x_m^2 - z^2)}{(x_m^2 + z^2)^2}, \\ \sigma_{13}(x,z) &= \sigma_{31}(x,z) \end{aligned}$$

$$= \frac{b}{2\pi S_{44}\left(1+\frac{S_{12}}{S_{11}}\right)} \sum_m \frac{x_m(x_m^2 - z^2)}{(x_m^2+z^2)^2},$$

$$\sigma_{12}(x,z) = \sigma_{21}(x,z) = \sigma_{32}(x,z) = \sigma_{23}(x,z) = 0, \tag{2.3}$$

where S_{ij} is the elastic compliance tensor at constant polarization. L_x is the average separation between dislocations. $b = |\mathbf{b}|$ is the magnitude of the Burgers vector of the dislocations, and $x_m = x + mL_x$, where $m = \ldots -2,\ -1,\ 0,\ 1,\ 2,\ldots,$ denotes the mth simulation cell. We note that the singularity of the strain field of a dislocation in the dislocation core is caused by the break down of the linear elasticity theory in that region. Nevertheless, it is well known, through computer simulation studies that the linear elasticity strain field is a good approximation except in a small region within a few burgers vectors (~1 nm) from the dislocation center, where it is almost constant. In our calculation, we simply kept away from this small region.

2.3. The electric field in thin film

We assume that the self-polarization in the film is along the z-direction in the absence of external free charge carriers. The depolarization field can be obtained by solving the electrostatic equilibrium, $\nabla \cdot D = 0$ with special boundary conditions, such as short-circuit and open-circuit boundary conditions (Li et al., 2002a; Wang and Woo, 2005; Wang and Woo, 2006). In writing E_d in terms of ε, where ε is the dielectric constant of the ferroelectric material, we note that P is not the total polarization (Kretchmer and Binder, 1979), but the self-polarization. Nevertheless, the equivalence of the two different forms can be easily deduced (Wang and Woo, 2005). When the ferroelectric film is sandwiched between two short-circuited metallic electrodes, the depolarization field E_d has been approximately obtained (Wang and Woo, 2005; Wang and Zhang, 2006; Lupascu, 2004; Mehta et al., 1973).

With the external field switched off, ε is a function of P given by

$$\varepsilon(P) = \left(\frac{\partial^2 f}{\partial P^2}\right)^{-1}, \tag{2.4}$$

where f is the local energy density (Li et al., 2001). Through this relation, it can be seen that (P) and the self-polarization P at each location has to be solved self-consistently (see Section 3).

2.4. The time-dependent Ginzburg–Landau equation

From Eqs. (2.1)–(2.4), the time evolution of the self polarization in ferroelectric thin film is governed by the time-dependent Ginzburg–Landau equation (Zheng et al., 2006a–c and Li et al., 2001),

$$\begin{aligned}\frac{\partial P(x,z,T,t)}{\partial t} &= -M\frac{\delta \tilde{G}}{\delta P} \\ &= M\left[-A^*(x,z,T,t)P - BP^3 - CP^5 \right. \\ &\quad \left. + D_{44}\frac{\partial^2 P}{\partial x^2} + D_{11}\frac{\partial^2 P}{\partial z^2} - E_\mathrm{d}(x,z,T,t)\right],\end{aligned} \tag{2.5}$$

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

$$A^*(x,z,T,t) = A(T - T_{c0}) - 2Q_{11}\sigma_{33}(x,z,t) - 2Q_{12}(\sigma_{11}(x,z,t) + \sigma_{22}(x,z,t)). \tag{2.6}$$

The electrical and mechanical boundary conditions have a significant effect on properties of ferroelectric thin films. In this work, the electric boundary condition is (Zhong et al., 1994; Zheng et al., 2006b),

$$\frac{\partial P}{\partial z} = \mp\frac{P}{\delta}, \quad \text{for } z = 0, h \tag{2.7}$$

from the surface term in Eq. (2.2).

When surface effects are negligible, $\partial P/\partial z = 0$ at $z = 0$ and h, corresponding to extrapolation lengths of $\delta_0 = \delta_L \to \infty$ (Zheng et al., 2006c). The mechanical boundary conditions for the ferroelectric thin film are taken as: the "upper" surface is traction-free and the interface is determined by the interface dislocation.

3. Numerical method

3.1. The finite difference method and the Runge–Kutta method

The evolution of the self-polarization field P is obtained by numerically solving the time-dependent Ginzburg–Landau Eq. (2.5) subject to the electric and mechanical boundary conditions. We adopt the second-order finite difference method for spatial integration and the fourth-order Runge–Kutta method for time integration to solve Eq. (2.5) in this work (Wang and Zhang, 2006). The ferroelectric thin film is considered as a stack of layers, each of which has a finite thickness Δz with physical properties that are assumed to be uniform. To ensure the validity of the thermodynamic description, Δz is chosen to be sufficiently large compared with the lattice constant. N is the total number of the layers, satisfying $h = N\Delta z$. A layer located at a position between z and $z+\Delta z$ is identified by the index j, so that $z_j = j\Delta z$. We also use a finite thickness Δx in the x-direction, so that any location along the x direction can be expressed in the form $x_i = i\Delta x$. The ferroelectric thin film is represented by repeated simulation cells in the x-direction, each with width $L = W\Delta x$, where W is the total number of layers along the x direction. The depolarization field equation and the boundary conditions equation can be given by the difference equations for computing effects of the depolarization field and the near-surface eigenstrain relaxation.

3.2. The dielectric constant at each location

The local polarization P from Eq. (2.5) with the boundary conditions and the corresponding dielectric constant ε can be solved self-consistently with an iterative scheme using a spatially homogeneous value from the experiments (Zhong et al., 1994) to calculate P as an initial estimate. Corrected values of ε and P at each location in subsequent iterations then follow from $\varepsilon = (\partial^2 f/\partial P^2)^{-1}$, the form of which is given by

$$\varepsilon^{-1}(x_i, z_j, T) = A^*(x_i, z_j, T) + 3BP^2(x_i, z_j, T) + 5CP^4(x_i, z_j, T). \tag{3.1}$$

4. Simulation results and discussions

To be specific, we consider a $PbTiO_3$ thin film on a rigid $LaAlO_3$ substrate. We use as an approximation material constants for the Landau free energy, the electrostrictive coefficients and the elastic properties for bulk materials from the literatures (Lakovlev et al., 2002; Pertsev et al., 1998; Streiffer et al., 2002; Li et al., 2002b). We consider that this approximation should be sufficient for our discussion.

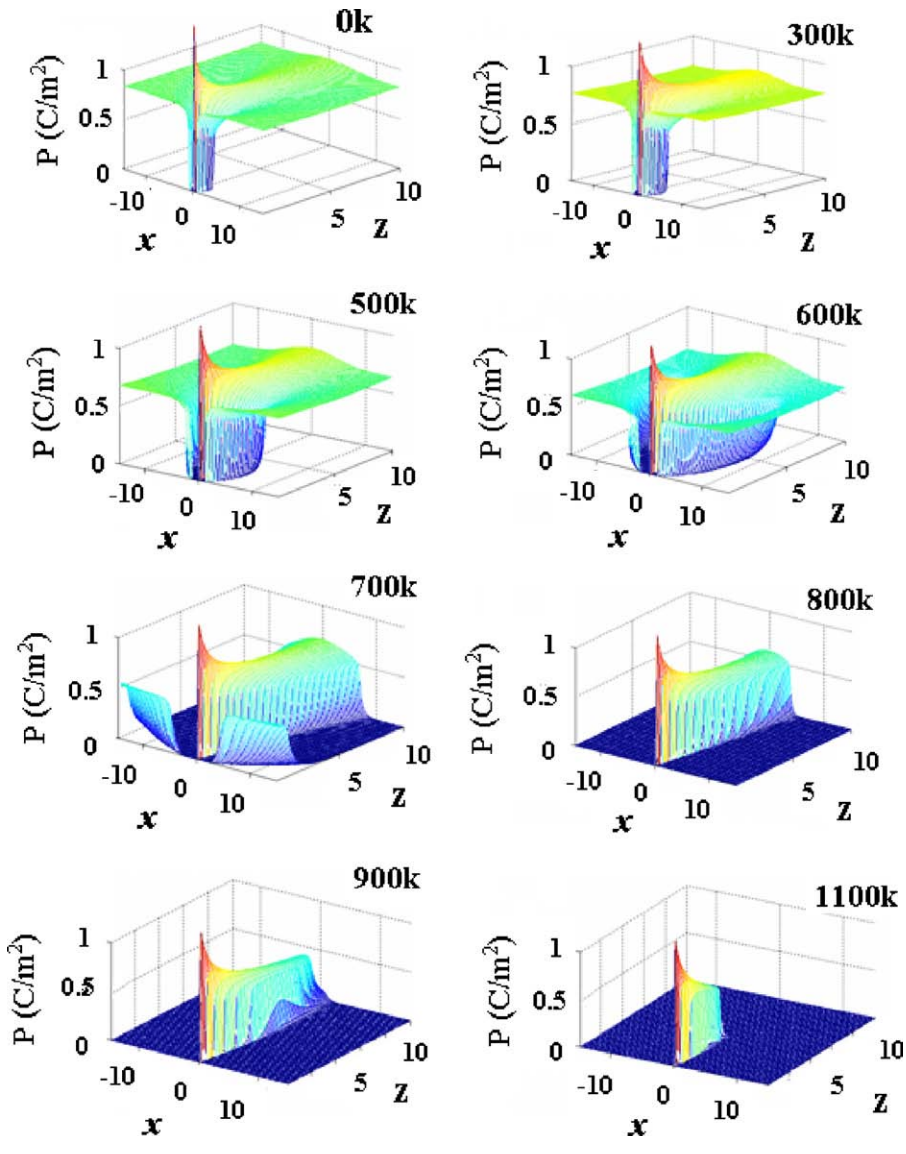

Fig. 2. The stable polarization field in a $PbTiO_3$ film in the presence of an interfacial edge dislocation at (0 0 0) at different temperature of $T = 0$–1100 K.

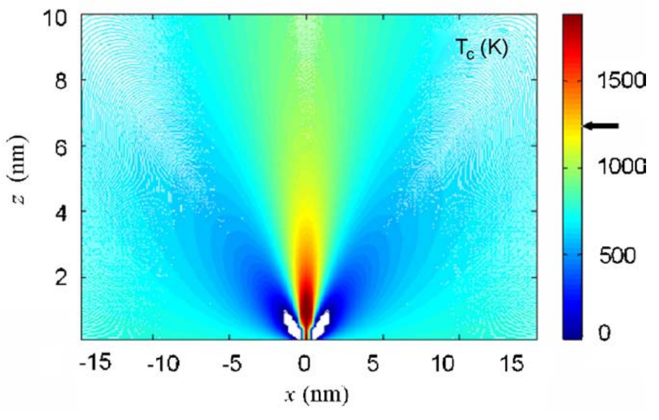

Fig. 3. Curie temperature around a $\mathbf{b} = a[\bar{1}\,0\,0]$ interfacial edge dislocation at (0 0 0). Arrow indicates Curie temperature of $PbTiO_3$ film grown on $LaAlO_3$ substrate without the interface dislocations.

We first consider the polarization field near a $\mathbf{b} = a[\bar{1}\,0\,0]$ single edge dislocation, neglecting the external electric field, depolarization field and near-surface eigenstrain relaxation. The calculated self-polarization field P with an interfacial edge dislocation at (0,0,0) for a $PbTiO_3$ film at different temperature between 0 and 1100 K are shown in Fig. 2. The dead zone near the dislocations in the ferroelectric state below 600 K, in which the polarization diminishes, and the residual polarization zone near the dislocation in the paraelectric state above 900 K are clearly shown. The sizes of both zones can be seen to depend on temperature. The local Curie temperature around the dislocation can be obtained by noting the locations at which the polarization vanishes. In Fig. 3, the variation of the Curie temperature near a single dislocation is shown. Although most regions experience a drop of the Curie temperature by several hundred degrees due to the presence of the dislocation, it can also rise by as much as 800° in the compressive regions and lower by over 1000° in the tensile regions, within $\sim$2 nm from the dislocation core, giving a variation over a range of nearly 2000° in the Curie temperatures in this small region. As a result, while the self-polarization may still persists in the compressive regions at temperatures much higher than the Curie temperature of the bulk crystal ($T_{C0} = 763$ K), polarization already begins to disappear in the tensile regions at temperatures much below the bulk T_{C0}. Nevertheless, these results must be interpreted with caution because the linear elastic stress field near the dislocation core in Eq. (2.3) may be much overestimated (Woo and Puls., 1977).

The equilibrium thermodynamic theory of the misfit dislocations was developed by Matthews and Blakeslee and well established by Nix (Matthews and Blakeslee, 1974; Nix, 1989). The theory can only approximately predict the critical thickness of the dislocation generation and the dislocation density can be obtained. In this work, the critical thickness of the interface dislocation generation is about 4 nm when ferroelectric is in paraelectric state, the calculated dislocation separations for the 10, 20 and 50 nm-thick films are, respectively, $\sim$18, $\sim$15 and $\sim$13 nm. We must note that the interface dislocation density and critical thickness of the interface dislocations generation should also be determined by the polarization in ferroelectric thin film (Wang et al., 2003; Zheng et al., 2006c). In this work, we only assume that no additional dislocations form during ferroelectric phase

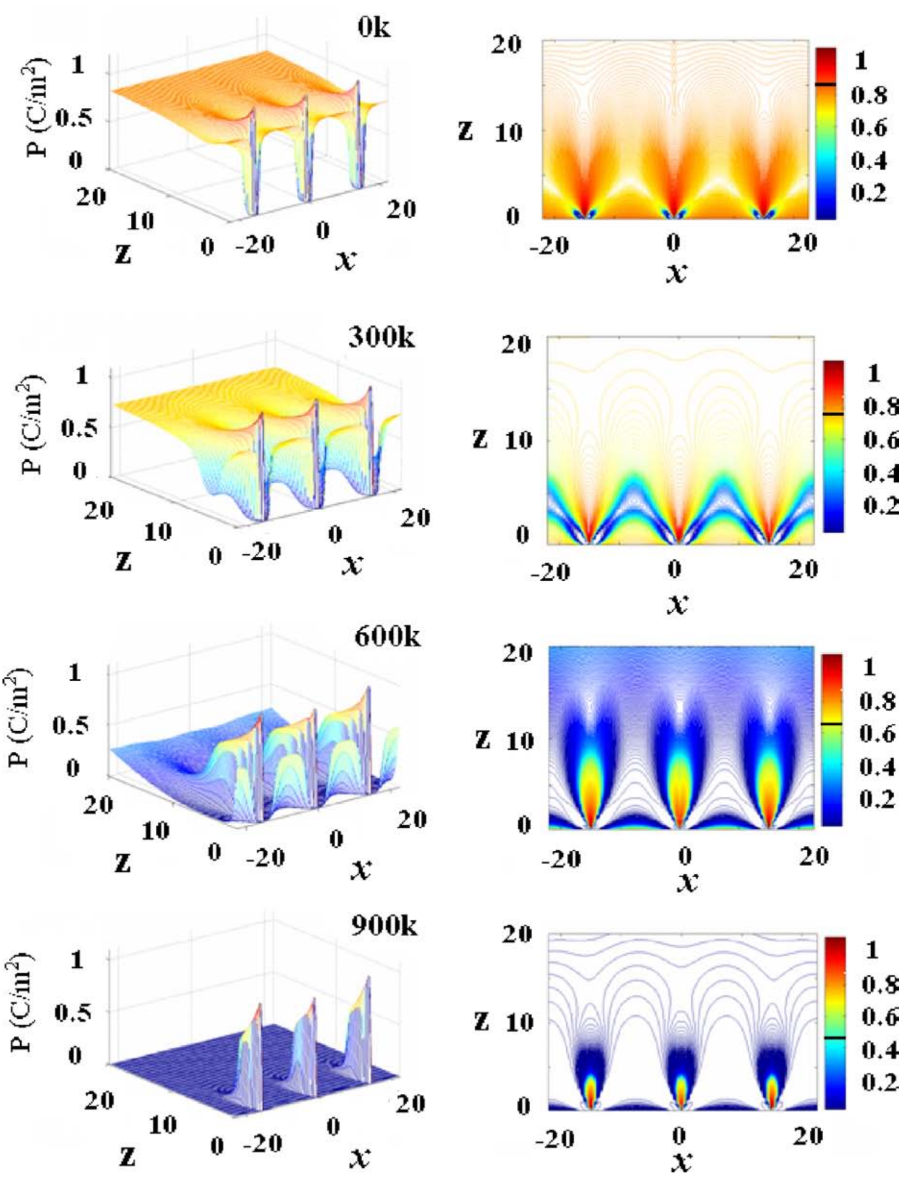

Fig. 4. The stable polarization distribution around periodic interface at different temperature of (a)–(d) $T = 0$, 300, 600, 900 K without considering effects of the depolarization field and the surface energy. Arrows indicate the spontaneous polarization in $PbTiO_3$ film grown on $LaAlO_3$ substrate without the interface dislocations.

transition. The polarization field for different temperatures in a film with a dislocation separation of 15 nm is calculated. Fig. 4 shows the case with the depolarization field and the surface effect neglected (i.e., putting $\varepsilon = \infty = \delta$). Compared to Fig. 2, a similar dead zone in the ferroelectric state and residual polarization near the dislocation in the paraelectric state can be seen.

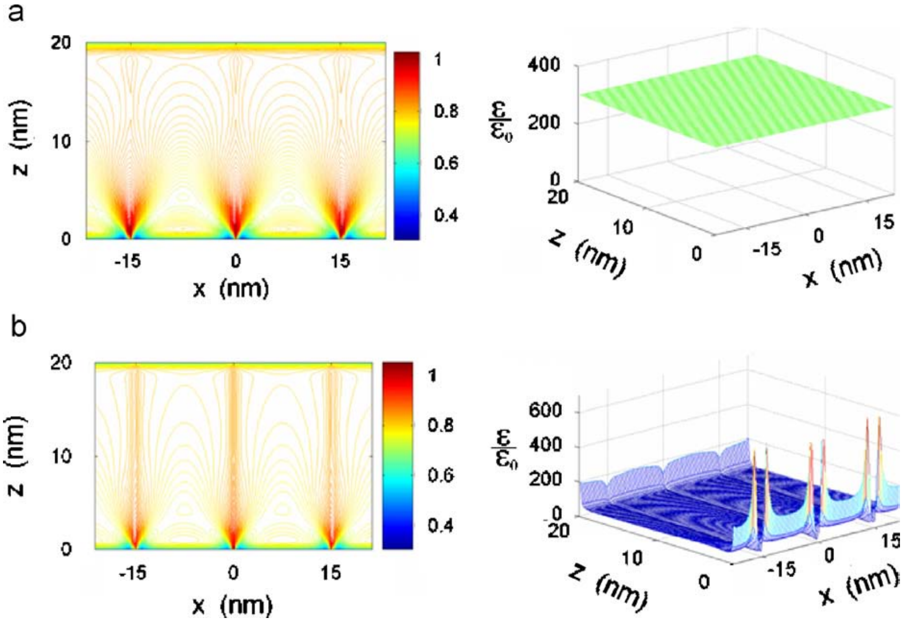

Fig. 5. The stable polarization distribution around periodic interface dislocation, with effects of the depolarization field and the surface energy taken into account, (a) $\delta = 3\,\text{nm}$ and $\varepsilon = \text{constant}$ at $T = 0\,\text{K}$, (b) $\delta = 3\,\text{nm}$ and $\varepsilon(P, T)$ at $T = 0\,\text{K}$.

In Figs. (5)–(6), we show the case when effects of the depolarization field and the surface effect are taken into account. Figs. (5)–(6) show the corresponding spatial distribution of P at 0 and 300 K, with these effects taken into account under various assumptions. In Figs. 5a and 6a, the calculation is performed assuming a spatially homogeneous dielectric constant (Lakovlev et al., 2002; Zhong et al., 1994, Wang and Zhang., 2006). In Figs. 5(b) and 6(b), P and ε are solved self-consistently as functions of x and z from Eqs. (2.6) and (3.1). The difference in the spatial variations of ε and P, when Figs. 5(a)–(b) is compared with Fig. 4 at 300 K, shows that both effects are to reduce the self-polarization field in the film. Taking into account the dependence of ε on the polarization reduces its overall magnitude at temperatures far from the Curie temperature, thus increasing the overall depolarization field. Near the Curie temperature, the opposite happens. The presence of the dead layer and its location seems to be little affected by these effects.

From above method, then we can obtain relation between the self-polarization and temperature with temperature heating-up when effects of the depolarization field and the extrapolation length are taken into account. Fig. 7 shows the effect of the dislocation on the average polarization of the film as a function of temperature under considering effects of the depolarization. In Fig. 7(a), we compare the average self polarization at various temperatures with and without interface dislocations, in a $PbTiO_3$ film epitaxially grown on a rigid $LaAlO_3$ substrate. The presence of the dislocation can be seen to substantially weaken the overall polarizability of the film, particularly at higher temperatures ($800\,\text{K} < T < 1265\,\text{K}$), where the averaged polarization drops to less than 10% of the dislocation-free case. This weakening is due to the development of the dean zone in areas where the Curie temperature is reduced below the ambient temperature by the dislocation

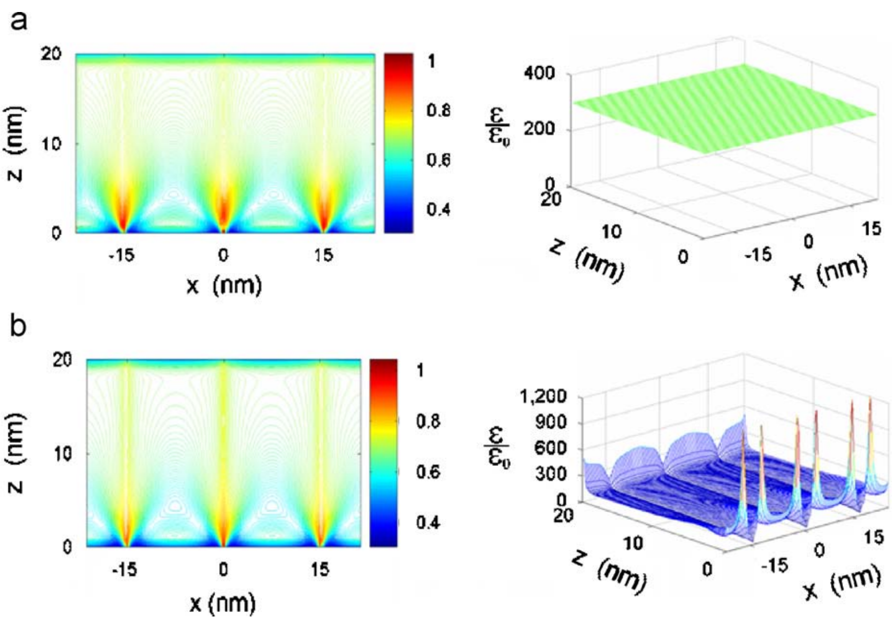

Fig. 6. The stable polarization distribution around periodic interface dislocation, with effects of the depolarization field and the surface energy taken into account, (a) $\delta = 3\,\text{nm}$ and $\varepsilon = \text{constant}$ at $T = 300\,\text{K}$, (b) $\delta = 3\,\text{nm}$ and $\varepsilon(P, T)$ at $T = 300\,\text{K}$.

strain field. Thus, approximately half of the thin film is occupied by dead zones at ~550 K. The temperature at which the average polarization drops by half of its peak value also reduces by 500°, from 1000 to 500 K, in the presence of dislocations. In the highly strained core region of the dislocations, the ferroelectric phase persists at temperatures much higher than the Curie temperature of the bulk material. Thus, when dislocations are present, the spatial distribution of the polarization is inhomogeneous and a sharp cutoff of the polarization at the Curie temperature does not exist, unlike the case without dislocations (Fig. 7(b)). Nevertheless, since the dislocation cores only occupy a small fractional volume, the associated effects are practically negligible when averaged over the entire film. In the forgoing calculations, we note that the dislocation spacing depends on the film thickness, and the relation between the dislocation spacing and the film thickness has been summarized (Matthews and Blakeslee, 1974; Nix, 1989). Such a comparison is also made to consider the effect of dislocations as a function of film thickness. For the same interfacial dislocation line density there is a tendency that the effect is enhanced with the film thickness increasing due to effect of the surface effect and the depolarization field of ferroelectric film (Wang and Woo, 2003; Zheng et al., 2006a, Jo et al., 2006). Nevertheless, the effect has to be considered together with the influence of film thickness and the polarization on the interfacial dislocation density, these results have been discussed in many works (Sharma et al., 2004; Ban and Alpay, 2003; Zheng et al., 2006b).

With short-circuit electrical boundary condition, the total polarization in ferroelectric thin film is sum of the self-polarization and induced polarization by the depolarization filed E_{d}. The total polarization can be easily obtained by $P_{\mathrm{total}} = P + \chi E_{\mathrm{d}}$, where P and χ can be calculated by solving Eqs. (2.7–3.1) (Wang and Woo, 2005). Due to effect of the

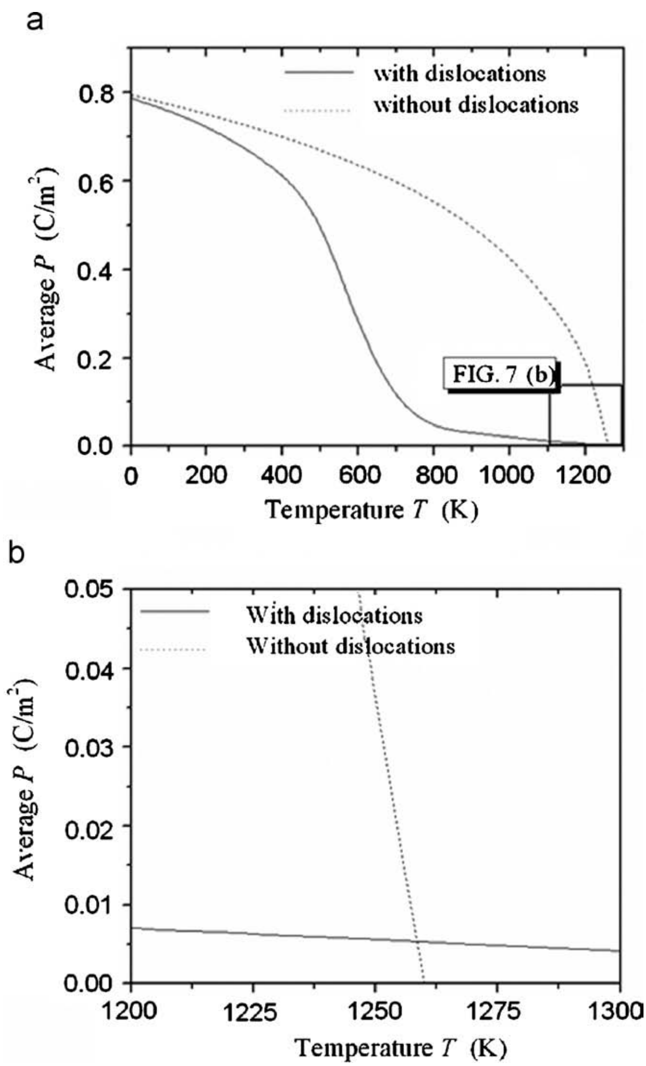

Fig. 7. Under considering effects of the depolarization field and the surface energy, (solid line) also considering effect of the periodic dislocations, and (dot line) assuming film is commensurate, (a) the relation between the average polarization and temperature. (b) The relation between the average polarization and temperature near the phase transition of Fig. 6(a).

depolarization field, the inhomogeneous distribution $P(x,z)$ and average polarization $\langle P \rangle$ of self polarization induced by the stress field of the interface dislocations should be much weakened, which also indicate that effect of the depolarization field can much plane variation of the polarization for ferroelectric thin film with this electrical boundary condition. This behavior of the depolarization field has been discussed by theoretical and experimental methods (Bratkovksy and Levanyuk, 2002; Chu et al., 2003). Moreover, with other electrical boundary condition, such as open-circuit (Wang and Woo, 2006) and short-circuit with incomplete compensation of the ferroelectric

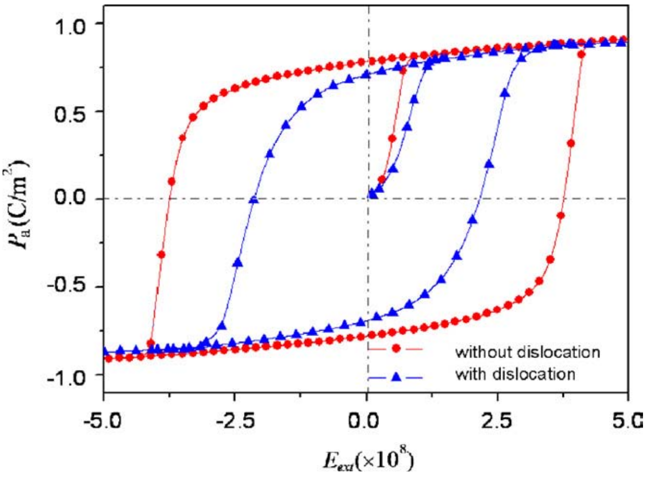

Fig. 8. Hysteresis loops of ferroelectric thin films ($h = 20\,\mathrm{nm}$) without interface dislocations (red) and with interface dislocations (blue).

polarization charge (Mehta et al., 1973), the distributions of the total polarization are different completely due to difference of the depolarization field with these different boundary conditions.

We compare two cases: (i) a thin film on a coherent substrate (i.e., no interface dislocations), and (ii) a thin film with interface dislocations. With applying external electric field, the average polarization is $P_a = \langle P_{\text{total}}(T, E_{\text{ext}})\rangle$, which is determined by the self-polarization, the depolarization and applied electric field by solving Eq. (1). Where the external electric field changes as sine function, and can be written as $E_{\text{ext}} = E_0 \sin(2\pi t/T') = E_0 \sin(2\pi t f')$, where E_0, T' and f' are the amplitude, period and frequency, respectively. Where $E_0 = 5 \times 10^8\,\mathrm{V/m}$ and the step time $\Delta t = 50 \times 10^{-10}\,\mathrm{s}$. Fig. 8 shows the corresponding hysteresis loops of $PbTiO_3$ thin films ($h = 20\,\mathrm{nm}$) at 300 K (ferroelectric). The remnant polarization P_r and coercive field E_c all see reductions, as expected, in the presence of dislocations because of the resulting stress relaxation and polarization drop.

5. Summery and conclusions

The time-dependent Ginzburg–Landau equation of a ferroelectric thin film with interfacial dislocations is solved numerically using a finite-difference scheme. Taking into account the inter-dependence of the polarization and depolarization fields, as well as the surface effect, effects of interfacial dislocations on ferroelectric thin films are investigated. We obtain the self-polarization field around a single edge misfit dislocation at different temperatures, and determine the dead region (i.e. where $P = 0$) for various temperatures. The results allow us to map out the Curie temperature at every location in the film around the dislocation as a function of x and z. In this calculation, the dielectric constant ε is calculated self-consistently with the self-polarization P as a function of T, x and z, via the free energy of the system. The value of the dielectric constant is obtained numerically via an iterative procedure.

Our results show that misfit dislocations have very important effects on the self-polarization field and the local dielectric properties in thin-film ferroelectrics, particularly near the dislocations. The existence of a dead layer near the film/substrate interface is confirmed, where self-polarization is much reduced. The extent of the dead layer is found to be temperature dependent. As a result, the presence of interfacial dislocations significantly reduces the average polarization of ferroelectric thin film at high temperatures, which causes the lowering of the effective Curie temperature by hundreds of degrees. This significant reduction of self-polarization by the presence of misfit dislocations at higher temperatures is seen in all film thicknesses up to 100 nm. Beyond the Curie temperature, however, self-polarization does not vanish completely in the presence of misfit dislocations. In the present calculation, the effects of the depolarization fields as well as the near-surface eigenstrain relaxation are both found to be relatively unimportant. Our results also show that the presence of interfacial dislocations significantly affects the spatial distribution of the polarization and reduces remnant polarization and the coercive field because of stress relaxation. Even at zero average polarization, the spatial heterogeneity of the polarization can be very large. In future works, we will consider that the presence of inhomogeneous elastic fields created by the misfit dislocations, the self-polarization and total polarization distribution in the film inevitably becomes non-uniform too. In this situation, the in-plane polarization component P_1 and P_2 may appear in the film (owing to the depolarization field and electrostriction) even when the homogeneously strained film has only the out-of-plane component P_3. At the same time, the dislocation density and the Burgers vector will change (increase and turn or move) due to coupling relation between the polarization and the stress field induced by the interface dislocation. Properties, such as phase diagram, domain patterns and tenability etc., will be investigated under consider general these cases.

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