Simulation of interface dislocations effect on polarization distribution of ferroelectric thin films

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Effects of interfacial dislocations on the properties of ferroelectric thin films are investigated, using the dynamic Ginzburg–Landau equation. Our results confirm the existence of a dead layer near the film/substrate interface. Due to the combined effects of the dislocations and the near-surface eigenstrain relaxation, the ferroelectric properties of about one-third of the film volume suffers. *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2177365]

To fully realize their potential in applications to electro-optic devices, ultrahigh-density memory devices and nonvolatile memories, etc.[1–6] In the case of ultrathin films, the influence of film surfaces and interfaces and associated effects, such as that due to interfacial dislocations, constitutes an area of serious concern.

Experimentally, misfit dislocations have been shown to have important effects on the stability of the polarization field of nanostructured ferroelectric perovskites.[6] It is also well known that dielectric properties of ferroelectric thin film depend on internal stresses and dislocation-type defects.[2,7] Theoretically, the effects of interfacial dislocations on ferroelectric phase stability have been studied by Hu *et al.*,[3] using a phase-field model, developed to predict the evolution of a domain structure in a ferroelectric thin film with an arbitrary spatial distribution of dislocations. In this calculation, a Fourier-spectral method is adopted, which makes it difficult to include the effects of the depolarization field. Alternately, Alpay *et al.*[5] developed a thermodynamic model based on the stationary Landau–Devonshire equation, taking into account the effects of the dislocation field, the depolarizing field, and the spatial variation of the polarization field. Unfortunately, the nonlinear nature of the problem does not always allow a convergent numerical solution due to the instability of the stationary solution near phase boundaries. In both calculations, furthermore, contributions due to the presence of the film surface, such as the relaxation of the near-surface eigenstrain, are neglected, thus limiting their general applicability to ultrathin films.

In this work, we adopt a dynamical approach using the dynamic Ginzburg-Landau (DGL) equation to describe the evolution of the spontaneous polarization field in a ferroelectric thin film. Using this approach, we investigate the effects of interfacial dislocations, taking into account surface effects, such as polarization gradient, near-surface eigenstrain relaxation, and depolarization.

We consider a monodomain perovskite ferroelectric $PbTiO_3$(PTO) that undergoes a cubic-tetragonal phase transformation upon cooling. We consider a coordinate system in which the x axis is parallel to [100], the y axis to [010], and the z axis/ to [001]. The film surface and the film/substrate interface are, respectively, the planes $z=h$ and $z=0$, i.e., h is the film thickness. Straight edge dislocations lie on the interface with the dislocation line in the y direction, and the Burger's vector in the x direction. We suppose the spontaneous polarization P is along the z direction.

The total free energy of a ferroelectric thin film with interfacial dislocations on a rigid substrate is the sum of contributions from the Landau free energy, the polarization field gradient, the depolarization field, the elastic energies, and the electrostriction due to the epitaxial and other internal and external stresses, and the near-surface eigenstrain relaxation, given by[8–13]

$$G=\int\int_{\Sigma}\Bigg\{G_0+\frac{A}{2}(T-T_{c0})P^2+\frac{B}{4}P^4+\frac{C}{6}P^6+\frac{D_{44}}{2}\left(\frac{\partial P}{\partial x}\right)^2+\frac{D_{11}}{2}\left(\frac{\partial P}{\partial z}\right)^2-\frac{1}{2}E_dP-\frac{1}{2}S_{11}(\bar{\sigma}_{11}^2+\bar{\sigma}_{12}^2+\bar{\sigma}_{33}^2)-S_{12}(\bar{\sigma}_{11}\bar{\sigma}_{22}+\bar{\sigma}_{11}\bar{\sigma}_{33}+\bar{\sigma}_{22}\bar{\sigma}_{33})-\frac{1}{2}S_{44}(\bar{\sigma}_{12}^2+\bar{\sigma}_{13}^2+\bar{\sigma}_{23}^2)-Q_{11}\bar{\sigma}_{33}P^2-Q_{12}(\bar{\sigma}_{11}P^2+\bar{\sigma}_{22}P^2)+u_{11}\sigma_{11}+u_{22}\sigma_{22}+u_{33}\sigma_{33}+u_{13}\sigma_{13}\Bigg\}dxdz+\int_{\Sigma_x}\frac{D_{11}P^2}{\delta_1}dx+\int_{\Sigma_z}\frac{D_{44}P^2}{\delta_2}dz, \quad (1)$$

where A, B, C, D_{11}, and D_{44} are expansion coefficients of the corresponding bulk material, T_{c0} is the Curie temperature of the bulk crystal, $\bar{\sigma}_{ij}$ is the external (including epitaxial) stress tensor, σ_{ij} and u_{ij} are, respectively, the components of the stress and strain (transformed) fields due to the interfacial dislocations, Q_{ij} are the components of the electrostrictive tensor, and S_{ij} are components of the elastic compliance tensor at constant polarization. We use the extrapolation lengths $\delta_1=\delta_2=\delta$ to measure the effect of near-surface eigenstrain relaxation. Σ_z and Σ_x represent the upper-lower and left-right surface planes that cover the entire surface Σ of the film. In this work, we use periodic boundary conditions along the x direction to reflect a configuration in which all the interfacial dislocations lie parallel along the y direction, through the

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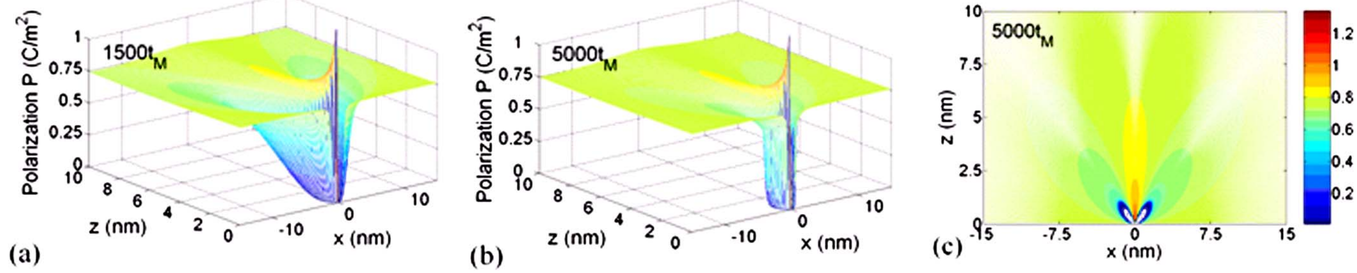

FIG. 1. (Color online) Evolution of the polarization field from the paraelectric to ferroelectric state in a PTO thin film in the presence of an interfacial edge dislocation at (0,0,0) at a temperature of $T=300$ K.

centers of identical simulation cells repeated *ad infinitum* along the x direction. The dimension of the simulation cells along the x direction L_x is defined according to the density of the interfacial dislocations. Therefore, the surface effect on Σ_x is ignored in Eq. (1) and the depolarization field along x direction is absent.

The depolarization field comes from the polarization-induced surface charges, which also depends on the electric boundary conditions. In the case we consider in this letter, the ferroelectric film is sandwiched between two short-circuited metallic electrodes. Although perfect screening is not achieved in this case due to the variation of the spontaneous polarization in the z direction, partial compensation due to the electrodes does reduce the depolarization field. Indeed, if P is uniform, complete screening occurs, and the depolarization field vanishes. This is clear from the relation between the depolarization field E_d and the spontaneous polarization P:[8,12]

$$E_d = -\frac{1}{\epsilon}\left(P - \frac{1}{h}\int_0^h P dz\right), \tag{2}$$

where ϵ is the dielectric constant of ferroelectric thin film, and the value of the dielectric constant of PTO used is from Ref. 14. The interested readers are referred to the Appendix of Ref. 8 for the detailed derivation of Eq. (2).

In this letter, we only consider the case where the ferroelectric thin film is under short-circuit boundary conditions, and the depolarization field is give by Eq. (2). Moreover, ϵ is supposed to be a constant, and its dependence on the film thickness is neglected. It should be noted that both the depolarization energy and the polarization field depend on the film thickness.

If an array of edge dislocations with Burger's vector, $\mathbf{b}=a[100]$, lying parallel to the y direction on the $z=0$ plane. The stress field $\sigma_{ij}(x,z)$ of the dislocation array, with the mth dislocation in the mth cell, can be written as[11,14]

$$\sigma_{11} = -B\sum_m z\frac{(3x_m^2+z^2)}{(x_m^2+z^2)^2}, \quad \sigma_{22} = -B\nu\sum_m \frac{z^2}{x_m^2-z^2},$$

$$\sigma_{33} = B\sum_m z\frac{(x_m^2-z^2)}{(x_m^2+z^2)^2}, \quad \sigma_{13} = \sigma_{31} = B\sum_m \frac{x_m(x_m^2-z^2)}{(x_m^2+z^2)^2},$$

$$\sigma_{12} = \sigma_{21} = \sigma_{32} = \sigma_{23} = 0, \tag{3}$$

where $B=\mu b/[2\pi(1-\nu)]$ μ is the shear modulus, ν is Poisson's ratio, $b=|b|$ is the magnitude of the Burger's vector of the dislocation, and $x_m=x+mL_x$; where $m=\ldots-2, -1,0,1,2,\ldots$. Using Eq. (3), the time evolution of the system is governed by the DGL equation

$$\frac{\partial P(x,z,t)}{\partial t} = -M\frac{\delta F}{\delta P} = M\left\{-A^*(x,z,t)P - BP^3 - CP^5 + D_{44}\frac{\partial^2 P}{\partial x^2} + D_{11}\frac{\partial^2 P}{\partial z^2} - \frac{P}{\epsilon} + \frac{1}{\epsilon h}\int_0^h P dz\right\} \tag{4}$$

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

$$A^*(x,z,t) = A(T-T_{c0}) - 2Q_{11}\sigma_{33}(x,z,t) - 2Q_{12}[\sigma_{11}(x,z,t) + \sigma_{22}(x,z,t)] \tag{5}$$

accounts for the interaction between the dislocation array and the eigenstrain. The surface term in Eq. (1) yields the boundary conditions,[13]

$$\frac{\partial P}{\partial z} = \mp\frac{P}{\delta}, \quad \text{for } z=0,h. \tag{6}$$

To take into account the film surface effect explicitly, the ferroelectric thin film is considered as a stack of layers of finite thickness Δz along the z direction, which is sufficiently large compared with the lattice constant for the thermodynamic description to be applicable. In this study, the physical properties are assumed to be uniform within each layer. 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 an arbitrary position along the x direction can be expressed as $x_i=i\Delta x$. 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.

Where the time step for integration is $t_M=\Delta tM=0.01$ ns, the lattice spacing in real space is chosen to be $\Delta x=L_x/100$ and $\Delta z=h/100$. Taking the forward difference in time and based on the finite-difference solution of DGL, we solve Eq. (4) numerically.

To verify the applicability of the present approach, we first consider for comparison with Alpay[5] the case of a PTO thin film on a rigid $SrTiO_3$ substrate using material constants from Refs. 2 and 10. We neglect the sample-size dependence of the dielectric constant and use an approximate value of $\epsilon=2.8\times10^{-9}$ F/m.[14] Using Eqs. (4)–(6), but neglecting the depolarization and the near-surface eigenstrain relaxation, the evolution of the spontaneous polarization for the case of a $\mathbf{b}=a[\bar{1}00]$ single edge dislocation is determined. Since the initial paraelectric state is metastable in general, the evolution of the system has to be initialized by applying a small push in the form of a perturbation of $\Delta P=0.001$ C/m^2 to Eq. (4). In Figs. 1(a) and 1(b), we show the evolution of the

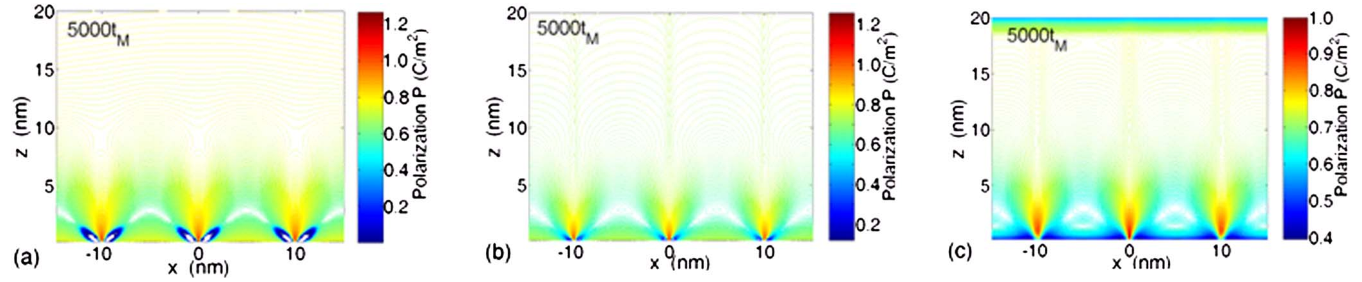

FIG. 2. (Color online) The stationary polarization field in the thin film with periodic interfacial dislocations. For three cases: (a) Only consider the effect of the interfacial dislocation, (b) item (a) + the effect of the depolarization field, (c) item (b) + the effect of the near-surface eigenstrain relaxation.

polarization field as time increases. The solution achieves asymptotic stability at $t=5000t_M$, i.e., in 50 ns, and may be interpreted as the stationary solution. The agreement between the color-coded stationary polarization field presented in Fig. 1(c), with corresponding results in Fig. 1(a) of Ref. 5, verifies the present dynamic approach.

Using the dynamic approach, the stationary spontaneous polarization field in a thin film with periodic misfit dislocations with $\mathbf{b}=a[\bar{1}00]$ in a 30×20 nm^2 is also obtained. We first consider for comparison the case in which effects of the depolarization field and the near-surface eigenstrain relaxation are both neglected in Eqs. (4)–(6). Figure 2(a) shows the calculated stationary state at $5000t_M$, from which the dead layer of reduced ferroelectricity near the interface due to the misfit dislocations can be seen clearly from the color-coded version. Adding the depolarization field in the calculation, its effect on the polarization field can be seen by comparing Figs. 2(a) and 2(b). There is a general reduction in the heights of the peaks and depths of the valleys of the polarization field, consistent with our expectation. However, the presence of the dead layer and its location seems to be largely unaffected. Taking into account the combined effects of the depolarization field and the near-surface eigenstrain relaxation in Eqs. (4)–(6), a comparison between Figs. 2(b) and 2(c) shows the important role played by this effect on the polarization field, which seems to negate the modulating effects of the depolarization field, with a general reduction of the polarization. The presence of the dead layer and its location again does not seem to be much affected. In this case, the relaxation of the near-surface eigenstrain also results in a reduction of ferroelectricity the region near the film surface. In about one-third of the total volume of the film material, ferroelectricity is substantially reduced in this example.

In summary, a comprehensive model for the study of ferroelectric thin films is formulated in this study based on a real-space finite-difference solution of the DGL equation. In this model, we may take into account the effects due to the spatial variation of the polarization, the coupling between the internal and external stress fields and the eigenstrain, the depolarization, and the near-surface eigenstrain relaxation. We use this model to study the effect of misfit dislocations on the ferroelectric properties of a thin film. The present dynamic model arrives at the stationary solution readily, unlike methods involving the direct numerical solution of the stationary equation, which sometimes encounter convergence problems when the nonlinearity of the equation becomes too high, such as when the depolarization field is included. Fourier-spectral methods in a dynamical approach, on the other hand, make it difficult to include the effects of the depolarization field.

Our results confirm the existence of a dead layer near the film/substrate interface where the average spontaneous polarization is much reduced, in agreement with previous results based on the stationary equation. The depolarization field produces a general modulation of the peaks and valleys of the polarization field, consistent with our expectation of the effects of depolarization. The near-surface eigenstrain relaxation appears to negate the modulating effects of the depolarization field, with a general minor reduction of the spontaneous polarization. This term also produces a reduction of ferroelectricity in the region near the film surface. The corresponding changes in the locality of the dead layer, on the other hand, are less significant. In the present case under investigation, due to the combined effects of the dislocations and the near-surface eigenstrain relaxation, the ferroelectric properties are degraded in about one-third of the film volume.

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