Effect of strain and deadlayer on the polarization switching of ferroelectric thin film

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The effect of misfit strain and deadlayer on the polarization switching of epitaxial ferroelectric thin film is investigated using a phase field model. Simulation results show that a compressive misfit strain increases the coercive field and remanent polarization of ferroelectric thin film with deadlayers, whereas a tensile misfit strain decreases these factors. The presence of a deadlayer between the ferroelectric thin film and the electrode prevents charge compensation on the ferroelectric surface and reduces the coercive field and remanent polarization of the film. A periodic a/c/a/c multiple domain structure is found in ferroelectric thin film with tensile misfit strain when there is no deadlayer. However, when a deadlayer is present in the film, the c domains vanish and the out-of-plane component of polarization degrades. The degradation of the out-of-plane polarization makes ferroelectric thin films with tensile misfit strain and deadlayers lose their ferroelectric property in the thickness direction, which can be attributed to the combined effects of the deadlayer and tensile strain. The coercive field and remanent polarization of ferroelectric thin film decrease with the thickness of the deadlayer. © 2011 American Institute of Physics. [doi:10.1063/1.3664913]

I. INTRODUCTION

Due to the strong coupling of polarization and strain, the application of misfit strain is becoming an important way of tuning many properties of epitaxial ferroelectric thin film.1,2 The lattice parameters and thermal expansion behavior of ferroelectric thin film and the underlying substrate are usually different. These differences can induce misfit, or mismatch, strain between the thin film and the substrate. Misfit strain can create large stresses in ferroelectric thin film, which are undesirable in many applications. However, misfit strain also provides an opportunity to tune the physical properties of ferroelectric thin film, a technique known as strain engineering. For example, misfit strain between ferroelectric thin film and the underlying substrate can be used to alter the equilibrium polarization state, shift the phase transition temperature, change the order of phase transition, and enhance spontaneous polarization.3,4 A full understanding of the relationship between misfit strain and material behavior will shed light on the engineering of the material properties of ferroelectric thin film with different misfit strains, which is crucial to the application of strain engineering in practice.

Remarkable progress has been achieved in the theoretical study, using the nonlinear thermodynamics theory, of the effect of strain on epitaxial ferroelectric thin film. For instance, “misfit strain-misfit strain” and “misfit strain-temperature” phase diagrams for single-domain ferroelectric thin film have been extensively constructed based on the Landau-Devonshire theory and Legendre transformation.5–9 However, the Landau-Devonshire model of a single domain cannot predict structures with multiple domains, which are very common in ferroelectric thin film. To model the multiple domain structure of ferroelectric thin film, the domain wall energy must be included in the thermodynamic framework. The phase field model, which incorporates both homogeneous bulk thermodynamics and inhomogeneous interface thermodynamics, is widely employed to study materials systems with multiply phases.10,11 Ferroelectric thin film with multiple domains can be regarded as a multiphase system, to which the phase field model is then applicable. Several phase field studies on the effect of strain in multi-domain ferroelectrics have been conducted,12–14 including research that examines the effect of strain on stable domain states and the polarization switching of epitaxial ferroelectric thin film.

In addition to misfit strain, another important factor that affects the properties of ferroelectric thin film is the presence of a deadlayer between the electrode and the film.15,16 Deadlayers are damaged ferroelectric material without ferroelectric properties that become dielectric at the ferroelectric-electrode interface.17,18 Deadlayers insulate the electrodes from the ferroelectric thin film and inhibit charge compensation, which generates a strong depolarization field in the ferroelectric thin film. The existence of a deadlayer is thought to be one of the reasons for Landauer’s paradox, which is the discrepancy between experimental observation and theoretical prediction of the coercive field for polarization switching in ferroelectric thin film.19,20 Considerable effort has been made over the past half century to resolve Landauer’s paradox, but it remains a mystery.20 In attempting to understand...
Recently, Artemev22 employed a phase field model to study a period
ic structure with an alternate ferroelectric and deadlayer arrangement and periodic boundary condition, in which the effect of misfit strain was excluded. However, ferroelec
tric thin film with deadlayers constrained by an elastic sub
strate with misfit strain behaves differently from that with a periodic ferroelectric and deadlayer structure without misfit strain. The elastic clamping of the substrate is expected to play a more significant role in polarization switching in ep
taxial ferroelectric thin film with both deadlayers and misfit strain. However, domain evolution or polarization switching in epitaxial ferroelectric thin film with misfit strain and dead
layers has seldom been studied in detail. In this work, a phase field model is employed to investigate the polarization switching of epitaxial ferroelectric thin film with upper and lower deadlayers constrained by a thick substrate, as shown in Fig. 1, in which the substrate accommodates a misfit strain of $\varepsilon$ in the ferroelectric thin film.

II. SIMULATION METHODOLOGY

A. General formulation of phase field model

The simulation methodology used in this study is based on the phase field model. In the phase field model, the total polarization $\mathbf{P}_{\text{tot}}$ is divided into two components, the sponta
neous polarization $\mathbf{P}$ and the induced polarization $\mathbf{P}_{\text{ind}}$. For simplicity, the induced polarization can be assumed to be linearly proportional to the electric field. In this case, the electric
displacement vector $\mathbf{D}$ can be given by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}_{\text{tot}} = \varepsilon_0 \mathbf{E} + \mathbf{P}_{\text{ind}} + \mathbf{P},$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$ Fm$^{-1}$ is the dielectric constant of the vacuum and $\kappa$ denotes the relative dielectric constant tensor of the background material. As the background material is the paraelectric phase, which has a cubic crystal structure, the relative dielectric constant matrix is diagonal and the relative dielectric constants in the three axis directions are the same, that is, $\kappa = \kappa_{11} = \kappa_{22} = \kappa_{33}$ and $\kappa_{ij} = 0$ ($i \neq j$).

In the phase field theory, the spontaneous polarization vector $\mathbf{P} = (P_1, P_2, P_3)$ is usually used as the order parameter to calculate the thermodynamic energies of the ferroelectric phase. The temporal polarization evolution can be calculated from the following time-dependent Ginzburg–Landau equation,

$$\frac{\partial \mathbf{P}_i(r, t)}{\partial t} = -L \frac{\delta F}{\delta \mathbf{P}_i(r, t)} \quad (i = 1, 2, 3),$$

where $L$ is the kinetic coefficient, $\delta F/\delta \mathbf{P}_i(r, t)$ represents the thermodynamic driving force for the spatial and temporal evolution of the simulated system, $\mathbf{r}$ denotes the spatial vector $\mathbf{r} = (x_1, x_2, x_3)$, and $t$ is time. The total free energy $F$ can be generally expressed as

$$F = \int \left[ \frac{1}{2} \sum_{ij} Q_{ijkl} \frac{\partial \mathbf{P}_i(r, t)}{\partial x_j} \frac{\partial \mathbf{P}_j(r, t)}{\partial x_i} + f_{\text{dep}}(\mathbf{P}_i, E^d_i) + f_{\text{elec}}(\mathbf{P}_i, E^d_i) \right] dV,$$

where $f_{\text{LD}}(\mathbf{P}_i, \sigma_{ij}) = x_i P_i^2 + x_{ij} P_i^2 P_j^2 + x_{ijk} P_i^2 P_j^2 P_k^2$ and $\sigma_{ij} - Q_{ijkl} \sigma_{kl} P_i P_j$ is the standard Landau–Devonshire energy density, $x_i$ is the dielectric stiffness, $x_{ij}$ and $x_{ijk}$ are the higher order dielectric stiffnesses, $\sigma_{ij}$ is the stress in the ferroelectric layer, $Q_{ijkl}$ are elastic constants, and $Q_{ijkl}$ are electro
crystalline coefficients. The second energy term of $f_{\text{G}}(\mathbf{P}_i) = \frac{1}{2} B_{ijkl} (\partial \mathbf{P}_i / \partial x_j) (\partial \mathbf{P}_j / \partial x_i)$ in Eq. (3) is the gradient energy density, which gives the energy penalty for spatially inhomogeneous polarization, where $B_{ijkl}$ are the gradient coefficients. The third energy term of $f_{\text{dep}} = -\frac{1}{2} E^d_i P_i$ in Eq. (3) represents the self-electrostatic energy density, where $E^d_i$ is the depolarization field induced by inhomogeneous polarization. The last energy term of $f_{\text{elec}} = -E^d_i P_i$ in Eq. (3) denotes an additional electrical energy density that is due to an external applied electric field $E^0_i$. A detailed description of the energy terms and related coefficients in Eq. (3) can be found in Ref. 23. In addition to Eq. (2), the mechanical equilibrium equation $\sigma_{ij} = 0$ and the electrostatic equilibrium equation $\varepsilon_0 \nabla^2 \phi / \partial x^2 + \kappa_{11} \nabla^2 \phi / \partial x^2 + \kappa_{22} \nabla^2 \phi / \partial x^2 + \kappa_{33} \nabla^2 \phi / \partial x^2 = \partial P_1 / \partial x_1 + \partial P_2 / \partial x_2 + \partial P_3 / \partial x_3$ must be satisfied for a given polarization distribution, where $\phi$ is the electrostatic potential. The depolarization field is the negative gradient of the electrostatic potential induced by spontaneous polarization, that is, $E^d_i = -\phi$. The mechanical equilibrium equation for a given polarization distribution is solved numerically by the finite element method. The electrostatic potential is obtained by using the finite difference method for a given polarization distribution and pre-defined boundary conditions. The finite difference method for spatial derivatives and the fourth order Runge-Kutta method for temporal derivatives is employed to solve Eq. (2) in real space.

B. Specific treatment for deadlayers and misfit strain

The present model is different from the previous model23 in two respects. The first is the existence of misfit strain in the ferroelectric thin film. The substrate is assumed to be infinitely thick so that the thin film assumption is valid for the film/substrate system. Under the thin film assumption, the
homogeneous misfit strain $\varepsilon$ can be applied to the film via the substrate. The stress related to the misfit strain is calculated from the given misfit strain through Hooke’s law, and is assumed to be constant during the polarization evolution. In addition to the homogeneous stress induced by the misfit strain, there are inhomogeneous stresses in the ferroelectric thin film and substrate due to the distribution of the inhomogeneous polarization. The stress induced by polarization is calculated by solving the mechanical equilibrium equation for a given polarization distribution at each time step. To solve the mechanical equilibrium equation, traction-free and coherent boundary conditions are applied along the free surface and the interfaces, respectively. The elastic deformation of the deadlayers and part of the substrate is included in the calculation. The elastic deformation of the substrate is considered only in the area surrounded by the dotted line in Fig. 1, and the deformation of the substrate outside the dotted lines can be ignored. The presence of deadlayers renders the mechanical constraint of ferroelectric thin film different from that of ferroelectric thin film without deadlayers.

The present model also differs from the previous model due to the presence of deadlayers, which changes the electrical boundary condition of the film. In ferroelectric thin film without deadlayers the electrodes contact the film directly, and the polarization induced surface charges are compensated by external charges through a short-circuit boundary condition. In ferroelectric thin film with deadlayers, the deadlayers insulate the film from the electrodes, which inhibits charge compensation. The uncompensated charges on the two interfaces between the ferroelectric layer and the two deadlayers result in a large depolarization field. To obtain this depolarization field, we set the electrostatic potential to $\varphi = 0$ at the electrodes, as shown in Fig. 1. When an external field $E_0^2$ is applied along the thickness direction of the film, the electrostatic potential is zero at the upper electrode and $-E_0^2 d$ at the lower electrode ($E_0^2 = -\varepsilon_2 - E_a^2$ in this case). Using the electric boundary condition, the depolarization field is then obtained by solving the electrostatic equilibrium equation.

C. Boundary conditions and material parameters

A Cartesian coordinator system is set up with the $x_2$ axis perpendicular to the film/substrate interface, as shown in Fig. 1. All of the interfaces are coherent, and the external electric field is applied in the thickness direction of the film. The periodic boundary condition is adopted for the simulated thin film in the $x_1$ direction. The material parameters PbTiO$_3$ are taken as an example in the simulation. For convenience, the same set of dimensionless variables as that used in Ref. 23 is employed. The size of the ferroelectric thin film is $d = 16$ nm, $w = 64$ nm, and $a/d = 0.6$. In the simulations, the discrete grids for the film are taken as 20 in the thickness direction and 80 along the film direction. The different thicknesses of the deadlayers are discretized with different grids. The size of each grid for both the ferroelectric layer and the deadlayers is 0.8 nm. Two-dimensional (2D) simulations are conducted, although the methodology described in Sec. II A can be applied to three-dimensional simulations. For simplicity, the dielectric and elastic constants of the deadlayers are assumed to be the same as those of the ferroelectric thin film. For the 2D ferroelectric thin film with deadlayers coherently constrained by an elastic substrate (see Fig. 1), the spontaneous polarization component $P_3$ and the electric field component $E_3$ are assumed to be zero. A Gaussian random fluctuation is introduced to initiate the spontaneous polarization evolution process.

III. SIMULATION RESULTS AND DISCUSSION

A. Ferroelectric thin film with compressive misfit strain

To investigate the polarization switching of epitaxial PbTiO$_3$ thin film with different misfit strains and deadlayers, the polarization responses to an external electric loading with a sine form are simulated at room temperature. An external electric field $E_0^2$ is applied along the thickness direction, or the $x_2$-axis, where a positive electric field denotes that the field is parallel or anti-parallel to the $x_2$-direction, and a negative electric field denotes that the field is anti-parallel to the $x_2$-direction. At each step $i$, the applied electric field, transformed into a sine function, is $E_0^2 = 1.2 \sin(2.5\pi i/10000)$. For each applied electric field, the simulated ferroelectric thin film is allowed to evolve one step with a step time of $\Delta t = 0.04$. The average polarization along the $x_2$-direction is taken as the macroscopic response of the simulated ferroelectric thin film. Fig. 2 shows the macroscopic polarization response to the external electric field with different thicknesses of deadlayer for a ferroelectric thin film subjected to a compressive misfit strain of $\varepsilon = -0.01$. The characteristic polarization and electric field are set to $P_0 = 0.757$ C m$^{-2}$ and $E_0 = 1.3 \times 10^8$ V m$^{-1}$, respectively. The simulation results show that the P-E hysteresis loop becomes smaller as the thickness of the deadlayer increases. The curve with solid triangles in Fig. 2 denotes the ferroelectric hysteresis loop without deadlayers, in which the normalized coercive field is 1.18. However, when there is a deadlayer of 1.6 nm between the ferroelectric thin film and the electrode, the coercive field

![Fig. 2](image-url)
reduces to 0.97, denoted by the curve with solid squares. When the thickness of the deadlayer further increases to 3.2 nm, the coercive field decreases to 0.64, as shown by the curve with solid circles. The phase field study shows that a deadlayer of 3.2 nm at the ferroelectric-electrode interface decreases the coercive field of the ferroelectric thin film nearly by 50% compared with the film without deadlayers. However, the decrease in remnant polarization that occurs with an increase in the deadlayer thickness is relatively small, from 0.89 to 0.76, which is an approximately 15% decrease.

Fig. 3 shows the polarization distribution of ferroelectric thin film with a deadlayer of 3.2 nm under an applied electric field $E_2/E_0$ of (a) 0.09, (b) –0.60, (c) –0.64, and (d) –0.68, which correspond to points A, B, C, and D in Fig. 2, respectively. In ferroelectric thin film with deadlayers, the ferroelectric layer and the electrode are separated by the deadlayers, and thus, charge compensation in the ferroelectric layer is inhibited due to the insulation effect of the deadlayers. The uncompensated charges due to the presence of deadlayers induce a stronger depolarization field compared with ferroelectric thin film without deadlayers. The stronger depolarization decreases the remnant polarization of the film, as shown in Fig. 2. Due to the compressive misfit strain in the ferroelectric thin film, the out-of-plane component of polarization still dominates, as shown in Fig. 3(a). The polarization distribution in Fig. 3(a) is a result of competition between the misfit strain and the depolarization field, with the compressive misfit strain preferring out-of-plane polarization and the depolarization field favoring in-plane polarization. When the misfit strain switches from compressive to tensile, the in-plane polarization dominates, as shown in Sec. III B. The depolarization field also has an influence on the polarization switching process. Figs. 3(a) and 3(b) show that most of the polarizations rotate from the vertical to a tilted orientation. This rotation decreases the vertical component of polarization, which reduces the depolarization field to some extent. However, there is still an inhomogeneous depolarization field in the thin film due to the inhomogeneous polarization distribution. Figs. 3(c) and 3(d) show that the polarization switching process is inhomogeneous. The inhomogeneous polarization switching is the reason for the decrease in the coercive field. As mentioned, in ferroelectric thin film without deadlayers the polarization induced surface charges are compensated by external charges through short-circuited boundaries. The switching process of the polarization is homogeneous, which makes the coercive field is much larger than the case with homogeneous switching. In very thin PbTiO$_3$ films, nucleation of new domain can be suppressed and the polarization switching occurs through the homogeneous mechanism, which was shown by in situ synchrotron x-ray scattering. The observed coercive electric field in the PbTiO$_3$ film during switching is very large and close to the theoretical intrinsic coercive field. The experiment observation supports the conclusion that homogeneous switching has larger coercive field in PbTiO$_3$ ferroelectric thin films.

### B. Ferroelectric thin film with a deadlayer of 3.2 nm

Fig. 4 shows the simulated hysteresis loops between the average polarization and applied electric field in the thickness direction for PbTiO$_3$ thin film with a deadlayer of 3.2 nm under misfit strains of $\varepsilon = -0.01$, 0, and 0.01, respectively. The coercive field of the ferroelectric thin film without misfit strain is 0.28, denoted by the curve with solid circles, which is about 56% smaller than that of thin film with a compressive misfit strain, denoted by the curve with downward-pointing triangles. The compressive misfit strain favors out-of-plane polarization due to the coupling between the polarization and the strain, which makes the polarization...
more difficult to switch compared with the case without misfit strain. This is why the coercive field under conditions of compressive strain is much larger than it is in the absence of strain. For the same reason, the remanent polarization is also larger than it is in the absence of misfit strain. Contrary to the situation with compressive misfit strain, tensile misfit strain in ferroelectric thin film prefers the in-plane component of polarization. An increase in in-plane polarization in the ferroelectric thin film makes the out-of-plane polarization decrease significantly, as shown by the remanent polarization in the curve with solid squares in Fig. 4. The curve with a tensile misfit strain of 0.01 in Fig. 4 shows that the normalized remanent polarization is 0.07, which is about one order smaller than that in the absence of misfit strain or under compressive strain. The ferroelectric hysteresis loop becomes a dumbbell shaped loop in Fig. 4, which implies that film with tensile misfit strain nearly loses its ferroelectric property in the thickness direction. This result is attributable to the disappearance of c domains or the degradation of the out-of-plane component of polarization in the ferroelectric thin film due to the presence of the deadlayers and tensile misfit strain.

To understand the degradation of the ferroelectric property in ferroelectric thin film with deadlayers and tensile misfit strain, the polarization evolution when an electric field is applied is examined in detail. Fig. 5 shows the specific polarization distribution of ferroelectric film under a different applied electric field \( E_{a} / E_0 \) of (a) 0.58, (b) 0.09, (c) −0.4, and (d) −0.68, which correspond to the points A, B, C, and D in Fig. 4. According to the polarization distribution in Fig. 5(a), the polarization has both in-plane and out-of-plane components. The out-of-plane component is mainly due to the external electric field and is thus parallel to the electric field. When the applied electric field decreases to 0.09, the out-of-plane component of polarization almost disappears and the in-plane component dominates, as shown in Fig. 5(b). When the applied electric field changes to a negative value of −0.4, the out-of-plane component of polarization also becomes negative, as shown in Fig. 5(c). When the negative electric field increases to 0.68, the out-of-plane component of polarization becomes larger, but is still much smaller than the in-plane component of polarization. Comparing Fig. 5 with that of Fig. 3 reveals that compressive misfit strain and tensile misfit strain have different influences on the polarization evolution with different electric fields in ferroelectric thin film with a deadlayer of 3.2 nm. The compressive misfit strain makes the polarization favor the out-of-plane component, whereas the tensile misfit strain induces more in-plane polarization.

C. Ferroelectric thin film without deadlayers

To further investigate the strain effect on ferroelectric thin film, the polarization evolution in ferroelectric thin film without deadlayers is also shown under different external electric fields. Fig. 6 shows the simulated hysteresis loops between the average polarization and applied electric field in the thickness direction for PbTiO₃ thin film under a misfit strain of \( \varepsilon = 0.01, 0, \) and 0.01, respectively. The simulation results show that a compressive strain of \( \varepsilon = −0.01 \) makes the coercive field about 27% larger than is the case without misfit strain. Under compressive strain, the remanent polarization is also larger than it is in the absence of misfit strain. The hysteresis loop with compressive misfit strain becomes more rectangular than is the case without misfit strain, which is desirable for the application of ferroelectric thin film in random access memory devices. However, the rectangularity of the hysteresis loop worsens when tensile misfit strain is applied, as shown by the curve with triangular dots in Fig. 6. The coercive field decreases from 0.91 to 0.46 and the remanent polarization decreases from 0.84 to 0.47 when the misfit strain \( \varepsilon \) changes from zero to 0.01. The curves in Fig. 6 show that the influence
of tensile misfit strain on the coercive field and remanent polarization is stronger than that of compressive misfit strain. These results can be attributed to the in-plane polarization induced by tensile misfit strain, which is similar to the results for the ferroelectric thin film with a deadlayer of 3.2 nm reported in Sec. III B. The in-plane polarization and out-of-plane polarization form an a/c/a/c multi-domain structure, as shown in Fig. 7(a). The a/c/a/c multi-domain state makes polarization switching much easier than is the case with a single domain state.

For ferroelectric thin film without deadlayers, the polarization induced surface charges are compensated by external charges due to the short-circuit boundary condition. The c domain can exist in ferroelectric thin film without a depolarization field or with a negligible depolarization field, which makes the polarization evolution differ from that of ferroelectric thin film with deadlayers. Figs. 7(a)–7(d) show the polarization distributions of ferroelectric thin film without a deadlayer under an applied electric field $E'/E_0$ of (a) 0.37, (b) 0.37, (c) 0.46, and (d) 0.54, which correspond to points A, B, C, and D in Fig. 6, respectively. From Figs. 7(a) and 7(b), the a/c/a/c multi-domain state does not change significantly, but the size of the c-domain is smaller and the size of the a-domain increases. When the electric field further increases to 0.46, the a-domain disappears gradually and the a/c/a/c multi-domain state becomes invisible, as shown in Fig. 7(c). The a/c/a/c multi-domain state appears again after polarization switching, as shown in Fig. 7(d). However, the a/c/a/c multi-domain state in Fig. 7(d) is somewhat different from the initial a/c/a/c multi-domain state in Fig. 7(a) for the domain walls. In Fig. 7(d) the polarizations have a head-to-head or tail-to-tail arrangement at the domain wall, whereas in Fig. 7(a) they have a head-to-tail arrangement. The switching process given in Figs. 7(a)–7(d) is totally different from the switching process of the single domain state in Ref. 23, in which polarization switching occurred at the surface or interface by anti-parallel polarization.

IV. CONCLUDING REMARKS

In this study, the polarization evolution of ferroelectric thin film with deadlayers and misfit strain under different external electric fields is investigated using a phase field model. The presence of deadlayers insulates the ferroelectric thin film from the electrodes, which prevents charge compensation and induces a depolarization field. The depolarization field decreases the out-of-plane polarization and the coercive field of the ferroelectric thin film. Simulation results indicate that compressive misfit strain increases the coercive field and remanent polarization of ferroelectric thin film, whereas tensile misfit strain decreases both the coercive field and remanent polarization. In particular, ferroelectric thin film with tensile misfit strain and deadlayers almost completely loses its ferroelectric property in the thickness direction. This result can be attributed to the disappearance of the c domains or the degradation of the out-of-plane component of polarization due to the combined effect of the deadlayers and tensile strain. The results suggest that the misfit strain imposed by the substrate has the power to tailor the material properties of lead titanate ultrathin film. The coercive field of ferroelectric thin film with deadlayers is also predicted to be much smaller than that without deadlayers, which is a possible reason for Landauer’s paradox of ferroelectrics.

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