Can interface dislocations degrade ferroelectric properties?

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A thermodynamic analysis has been carried out to investigate the role of dislocations in ferroelectric materials. Due to the coupling of the stress field of the dislocation and the polarization, there is a drastic variation in the polarization near the dislocation. These polarization gradients result in strong depolarizing fields that suppress the polarization in a region that extends over several nanometrers. In epitaxial ferroelectric films, these polarization gradients should result in the formation of dead layers that severely degrade ferroelectric properties. The detrimental effect of such regions will be enhanced in ultrathin ferroelectric thin films, and hence play a critical extrinsic role in size effect studies of ferroelectrics. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1788894]

Ferroelectric thin films have gained considerable importance in recent years because of their numerous potential device applications as they possess many unique dielectric, piezoelectric, and pyroelectric properties.[1] There has been a significant push in the downscaling of the lateral and vertical dimensions of ferroelectric thin films. However, ferroelectric ultrathin films and nanostructures exhibit a considerable degradation in these properties that can be more than an order of magnitude when compared to bulk. While this reduction is pursued in terms of an intrinsic size effect, often it stems from compositional and microstructural inhomogeneities, defects, and internal stresses. [2,3] Over the past years, a significant amount of research has been devoted to understand the effects of various microstructural features such as point defects, grain boundaries and texture, and formation of structural (90°) domains on the physical properties of ferroelectric films. Surprisingly, studies on the role of the most common defects, dislocations, on the physical properties have been limited both experimentally and theoretically.

Experimentally, a significant improvement in the dielectric response was observed in epitaxial $Ba_{0.6}Sr_{0.4}TiO_3$ thin films upon annealing.[4] This change was attributed to the drastic decrease in the threading dislocation density. The suppression of ferroelectricity in 9 nm $PbZr_{0.52}Ti_{0.48}O_3$ nano-islands was ascribed to the strain fields of misfit dislocations.[5] Theoretically, it was shown that dislocations in ferroelectric crystals could result in a reduction in the dielectric response accompanied with a broadening in the dielectric constant versus temperature behavior[6] and could induce the formation of structural domains.[7]

In this letter, a preliminary thermodynamic model based on the Landau–Devonshire formalism is developed incorporating the coupling between the stress field of dislocation and the polarization and the consequence depolarizing field. We find that the magnitude of this depolarizing field is sufficiently large to suppress ferroelectricity in a region extending over several nanometers in diameter around the dislocation core.

Consider a monodomain perovskite ferroelectric that undergoes a cubic $[Pm\bar{3}m]$ to tetragonal $[P4mm]$ phase transformation upon cooling. We define a Cartesian coordinate system with the principal axes $x//[100]$, $y//[010]$, and $z//[001]$. The spontaneous polarization of the ferroelectric is parallel to the z-axis such that $P=P_3$ and $P_1=P_2=0$, or $\boldsymbol{P}=P[001]$. The Landau–Devonshire (LD) free energy of the phase transformation is given by[8]

$$\begin{aligned} G_{\mathrm{LD}}(T,P,\sigma_{ij}) = G_0 + a_1P^2 + a_{11}P^4 + a_{111}P^6 - \tfrac{1}{2}S_{11}(\bar{\sigma}_{11}^2 \\ + \bar{\sigma}_{22}^2 + \bar{\sigma}_{33}^2) - S_{12}(\bar{\sigma}_{11}\bar{\sigma}_{22} + \bar{\sigma}_{11}\bar{\sigma}_{33} \\ + \bar{\sigma}_{22}\bar{\sigma}_{33}) - \tfrac{1}{2}S_{44}(\bar{\sigma}_{12}^2 + \bar{\sigma}_{13}^2 + \bar{\sigma}_{23}^2) \\ - Q_{11}\bar{\sigma}_{33}P^2 - Q_{12}(\bar{\sigma}_{11}P^2 + \bar{\sigma}_{22}P^2), \end{aligned} \quad (1)$$

where G_0 is the energy in the paraelectric state, a_1, a_{11}, and a_{111} are the dielectric stiffness coefficients at constant stress, $\bar{\sigma}_{ij}$ the (external) stress, and Q_{ij} and s_{ij} the elastic compliances at constant polarization, respectively, in the contracted notation. The dielectric stiffness a_1 is given by the Curie–Weiss law, $a_1=(T-T_C)/2\varepsilon_0 C$, where T_C and C are the Curie-Weiss temperature and constant of bulk ferroelectric, respectively, and ε_0 is the permittivity of free space.

If there is an edge dislocation in the xz plane with a Burgers vector $\mathbf{b}=a[001]$, its stress field as a function of the distance from the core can be described in the continuum limit by[9]

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$$\sigma_{11} = -Bx\frac{(3z^2+x^2)}{(z^2+x^2)^2}, \quad \sigma_{22} = 2B\frac{S_{12}}{S_{11}}x\frac{x}{z^2+x^2},$$

$$\sigma_{33} = Bx\frac{(z^2-x^2)}{(z^2+x^2)^2},$$

$$\sigma_{12} = \sigma_{21} = 0, \quad \sigma_{13} = \sigma_{31} = Bx\frac{z^2-x^2}{(z^2+x^2)^2}, \tag{2}$$

$$\sigma_{23} = \sigma_{32} = 0,$$

where $B = b/[2\pi S_{44}(1+S_{12}/S_{11})]$, and $b = |\mathbf{b}|$ is the magnitude of the Burgers vector of the dislocation.

The free energy functional given in Eq. (1) has to be modified since it describes the effect of external stresses and not the effect of the internal stress field due to the presence of the dislocation. This can be done via

$$\tilde{G}_{\mathrm{LD}}[P,T,\sigma_{ij}(x,z),u_{ij}(x,z)] = G_{\mathrm{LD}} + u_{11}\sigma_{11} + u_{22}\sigma_{22} + u_{33}\sigma_{33} + u_{13}\sigma_{13}, \tag{3}$$

where $u_{ij}(x,z)$ are the strains associated with the stress field of the dislocation. Taking into account that $u_{22}=0$, and expressing strains in terms of stresses (with some rearrangement), we obtain

$$\tilde{G}_{\mathrm{LD}}[P,T,\sigma_{ij}(x,z)] = G_0 + a_1^* P^2 + a_{11}P^4 + a_{111}P^6 + \tfrac{1}{2}S_{11}(\sigma_{11}^2+\sigma_{22}^2+\sigma_{33}^2) + S_{12}(\sigma_{11}\sigma_{22} + \sigma_{11}\sigma_{33} + \sigma_{22}\sigma_{33}) + \tfrac{1}{2}S_{44}\sigma_{13}^2, \tag{4}$$

where

$$a_1^*[T,\sigma_{ij}(x,z)] = a_1 - [Q_{11}\sigma_{33} + Q_{12}(\sigma_{11}+\sigma_{22})]. \tag{5}$$

Minimization of Eq. (4) with respect to polarization $(\partial\tilde{G}_{\mathrm{LD}}/\partial P = 0)$ gives

$$P^2[T,\sigma_{ij}(x,z)] = \frac{-a_{11} \pm \{a_{11}^2 - 3a_1^*[T,\sigma_{ij}(x,z)]a_{111}\}^{1/2}}{3a_{111}}. \tag{6}$$

Using Eq. (5) with $a_1^*=0$ and Eq. (6), the distribution of the spontaneous polarization and the Curie temperature around the dislocation can be determined as shown in Figs. 1(a) and 1(b), respectively, for a $\mathbf{b}=a[100]$ edge dislocation in $PbTiO_3$.[10] The dislocation cut-off parameter was taken to be one lattice parameter.[9] Figures 1(a) and 1(b) clearly show the large deviation of the spontaneous polarization and Curie temperature from the bulk values due to coupling with the stresses induced by the extra half plane. The compressive regions enchance the polarization and increase Curie temperature whereas tensile stresses decrease polarization with a commensurate drop in the Curie temperature.

Obviously, Eq. (4) is not the total energy of the system. There exists a depolarizing field $E_D(x,z)$ due to the polarization variation induced by the stress field of the dislocation and gradient terms describing equilibrium polarization fluctuations that have to be included. The total energy G_Σ is given by

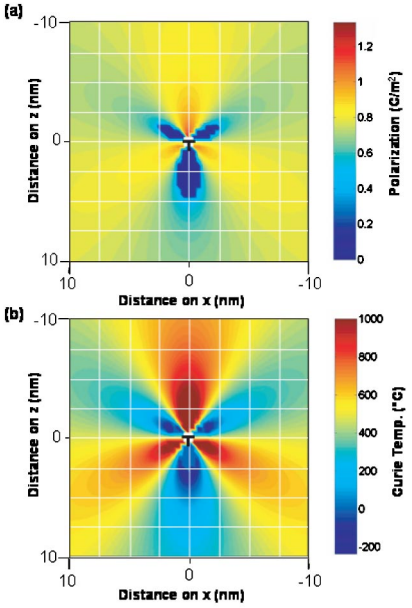

FIG. 1. (Color online) The (a) polarization distribution and (b) variation of the Curie temperature around a $\mathbf{b}=a[100]$ edge dislocation at (0,0,0) in single-crystal $PbTiO_3$ on an xz plane. Area shown represents 40×40 nm cross section along the y direction (dislocation line). Individual elements were taken ~0.4 nm.

$$G_\Sigma = \int_A \int \left[\tilde{G}_{\mathrm{LD}} + \frac{1}{2}D_1\left(\frac{\partial P(x,z)}{\partial x}\right)^2 + \frac{1}{2}D_2\left(\frac{\partial P(x,z)}{\partial z}\right)^2 - \frac{1}{2}E_D(x,z)P(x,z)\right] dz dx, \tag{7}$$

where D_1 and D_2 are Ginzburg coefficients. The depolarizing field is determined by the Maxwell relations $\nabla\times\boldsymbol{E_D}=0$, and $\nabla\cdot\boldsymbol{E_D}=(1/\varepsilon_0)(\rho-\nabla\cdot\boldsymbol{P})$ where ρ is the density of free charges. The minimization of Eq. (7) should give the polarization distribution in the xz plane. This, however, is difficult to accomplish mainly because of the complexities in establishing electro-mechanical boundary conditions for the depolarizing field around the dislocation core.

As a first-order approximation, let us consider a ferroelectric that is an insulator with no free charges to compensate for the depolarizing field such that at a given x:

$$\frac{dE_D}{dz} = -\frac{1}{\varepsilon_0}\cdot\frac{dP}{dz}. \tag{8}$$

For a parallel-plate ferroelectric with a thickness $2L$ along which there are polarization fluctuations, the solution for the above-given relation employing proper boundary conditions is given by[11]

$$E_D(z) = -\frac{1}{\varepsilon_0}\left[P(z) - \frac{1}{2L}\int_L^L P(z)dz\right]. \tag{9}$$

Assuming that the depolarizing field can be realized as the integral of noninteracting strips in the z direction, Eq. (9) can be employed to estimate the depolarizing energy for a given x using the (initial) polarization distribution shown in Fig. 1(a). This energy is approximately 100–1000 times larger than the other terms of Eq. (7). As a result of this, minimization of Eq. (7) with respect to the polarization does not converge to a solution in a region ~10 nm in radius except

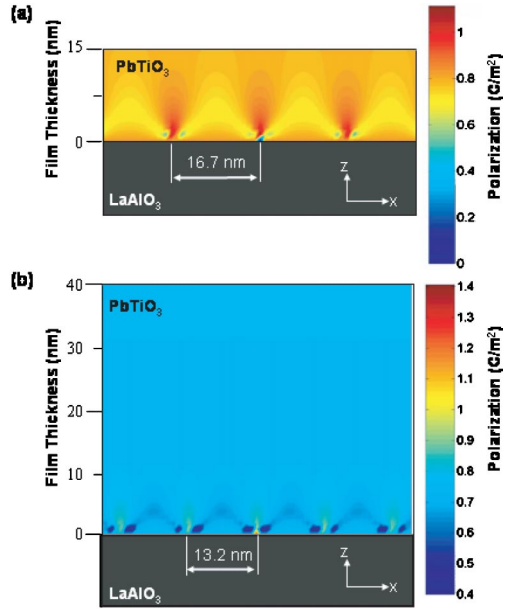

FIG. 2. (Color online) The polarization distribution around periodic misifit dislocatios with $\mathbf{b}=a[\bar{1}00]$ in a (a) 15-nm- and (b) 40-nm-thick (001) $PbTiO_3$ films on (001) $LaAlO_3$ substrate, assuming a deposition temperature of 600 °C. Areas shown in (a) and (b) represent 15×50 and 40×50 nm^2 cross section across the film thickness in the *xz* plane, respectively. Individual elements were taken ~0.4 nm.

$P(x,z)=0$, indicating instability of the ferroelectric state. This outcome is in complete agreement with theoritical results that predict total suppression of ferroelectricity in the presence of even the slightest variation in the polarization[12] and experimental observations.[5]

In epitaxial films, one of the strain relaxation mechnaisms is the formation of interfacial, or misfit, dislocations.[13] To simulate the role of such dislocations, we analyze the polarization distribution around misfit dislocations with $\mathbf{b}=a[\bar{1}00]$ in (001) $PbTiO_3$ films with 15 and 40 nm thickness on thick (001) $LaAlO_3$ substrate. The internal stress due to lattice mismatch is coupled with the stress field of dislocations in the linear limit. Assuming a deposition temperature of 600 °C where the nominal misfit strain is −4%, and that no additional dislocations form during cooling down, we calculate the average dislocation spacing to be ~17 nm and ~13 nm for the 15 and 40-nm-thick films, respectively, using the Matthews–Blakeslee analysis.[13] The critical thickness of misfit dislocation is calculated to be ~4 nm. As shown in Figs. 2(a) and 2(b), there is a drastic variation in the polarization near the film–substrate interface that should result in the formation of ~10- and 11-nm-thick ferroelectrically dead layers on 15 and 40 nm films, respectively.[14] These plots display the thickness dependence of the dead layer-to-film thickness ratio. As films get thicker, the equilibrium dislocation density increases and hence the dislocation periodicity decreases resulting in better relaxation of epitaxial stresses. The thickness of the dead layer depends on the dislocation density, which theoretically levels off above 100 nm in $PbTiO_3$ films on $LaAlO_3$. It is thus clear that there will be a significant improvement of the electrical properties in the films with increasing film thickness as the dead layer-to-film thickness ratio becomes smaller. The extent of the relief by interface dislocations influences the average polarization throughout the film since the polarization is also coupled with epitaxial stresses. In-plane compressive stresses increase the overall polarization and as these stresses are relaxed by the generation of misfit dislocations the average polarization approaches its bulk value (Fig. 2).

These results have significant implications in terms of properties of ultrathin ferroelectric films and nanostructures. First, there exists a significant volume that will not contribute to the polarization, dielectric, piezoelectric, and pyroelectric response. Second, because of this dead layer, the applied electrical field that is necessary to activate the unique properties of ferroelectrics will essentially be screened. And last, these regions may serve as pinning centers for reversible 180° and non-180° domain wall motion in the presence of an applied field.

There remains much to be done in the future that starts with accurate calculations of the depolarizing field. Furthermore, ferroelectrics, although considered to be perfect insulators, have small but a finite conductivity resulting in charge compensation and reduction in the depolarizing field that should slightly reduce the size of the dead layer. In addition, the dislocation line in ferroelectrics may be charged depending on the type of termination at the dislocation core. The size of the dead layer in ferroelectric films should strongly depend on the film composition, the substrate material, and the deposition conditions.

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