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Strain effect on coercive field of epitaxial barium titanate thin films

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Strain is generally known to increase the coercive field of a ferroelectric thin film as compared to a stress-free single crystal or a strain-relaxed film. We studied the coercive fields and remanent polarizations of (001)-oriented epitaxial barium titanate thin films using the phase-field approach. It is demonstrated, while the remanent polarization decreases as in-plane strain changes from being compressive to tensile, the variation of coercive field with strain is complicated. We noted more than two times drop in coercive field with a reduction of compressive strain of only ~0.05%, which we attribute to the existence of multiple ferroelectric phases. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2908210]

Ferroelectric materials form spontaneous polarization when it is cooled below a critical temperature also known as the Curie temperature. The polarization direction can be switched by externally applying a critical electric field. The behavior of the ferroelectric under an applied electric field is characterized by two important physical properties, namely, remanent polarization (polarization with applied electric field being reduced to zero) and coercive field (electric field required to reduce the net polarization to zero). From a scientific standpoint, the magnitude of these physical properties provide valuable information regarding polarization switching dynamics and physics of ferroelectricity in general.[1] In the form of thin films, while many factors are expected to determine the magnitude of these physical properties, the epitaxial strain arising primarily from the difference in lattice parameter and thermal expansion coefficient between the thin film and the substrate has been recognized as being of particular importance for ferroelectric materials.[2] Despite numerous studies, the exact nature on the effect of substrate strain on coercive field and remanent polarization is poorly understood. Generally, it has been both experimentally and theoretically observed that both coercive field[3–7] and remanent polarization[3,8–10] drastically increase with the increase of the substrate strain. For example, Pertsev *et al.* reported that coercive field in fully coherent $PbZr_{0.52}Ti_{0.48}O_3$ thin films on $SrTiO_3$ substrate under a biaxial strain of 2% can be about an order of magnitude higher compared to a thin film under zero substrate strain.[11] However, some reports show that these properties do not monotonically change with substrate strain.[1,12,13] Nonetheless, it is clear that understanding the effect of substrate strain on coercive field as well as remanent polarization, is critical for application of ferroelectric thin films.

Experimentally, it is often difficult to separate the intrinsic effect of substrate strain on ferroelectric properties from other factors such as defects and passive layers. In particular, passive layers are known to have significant effect on the measured coercive field[14] and remanent polarization.[15,16] In this paper, we employ the phase-field approach to study the effect of biaxial substrate strains on coercive fields and remanent polarization in ferroelectric thin films in an attempt to demonstrate that the coercive field and remanent polarization can be tuned by strain. We use (001)-oriented epitaxial barium titanate (BTO) thin films as a model system.

In the phase-field approach, a ferroelectric domain structure is described by the spatial distribution of polarization $\mathbf{P}=(P_1,P_2,P_3)$. Its temporal evolution is assumed to follow the time-dependent Ginzburg–Landau equation

$$\frac{\partial P_i(\mathbf{x},t)}{\partial t} = -L\frac{\delta F}{\delta P_i(\mathbf{x},t)}, \quad (i=1,2,3), \tag{1}$$

where L is a kinetic coefficient related to the domain wall mobility. F is the total free energy of the system, which includes the bulk free energy F_{bulk}, domain wall energy F_{wall}, elastic energy F_{elas}, and electrostatic energy F_{elec}, i.e.,

$$F = F_{\mathrm{bulk}} + F_{\mathrm{wall}} + F_{\mathrm{elas}} + F_{\mathrm{elec}}. \tag{2}$$

The mathematical expressions for the ferroelectric bulk free energy, ferroelectric domain wall energy, and elastic energy are exactly the same as those given in Ref. 17 so they are not listed here for the sake of brevity.

The electrostatic energy of a given polarization distribution is calculated by

$$F_{\mathrm{elec}} = -\frac{1}{2}\int E_i(\varepsilon_0\kappa_{ij}E_j + P_i)dV, \tag{3}$$

where E_i is the ith component of the electric field. It is related to the electric displacement D_i through the relation $D_i=\varepsilon_0\kappa_{ij}E_j+P_i$, in which, $\varepsilon_0=8.85\times10^{-12}\ \mathrm{F\,m^{-1}}$ is the dielectric permittivity of the vacuum and κ_{ij} is the relative dielectric permittivity of the ferroelectric film. The electric field is obtained by solving the electrostatic equilibrium equation $D_{i,i}=0$ with the boundary conditions,

$$\phi_{\text{substrate-film interface}} = 0, \quad \phi_{\text{film surface}} = \phi_1, \tag{4}$$

where ϕ is the electric potential, which is related to the electric field as $E_i=-\phi_{,i}$ and ϕ_1 is the uniform electric potential applied on the top surface of the thin film. The details on the calculation of electric fields are presented in Ref. 18.

Equation (1) is solved using the semi-implicit Fourier spectral method.[19] In the simulations, we discretized the simulation cell as $128\Delta x\times128\Delta x\times36\Delta x$, with periodic boundary conditions along x_1 and x_2 axes in the film plane,

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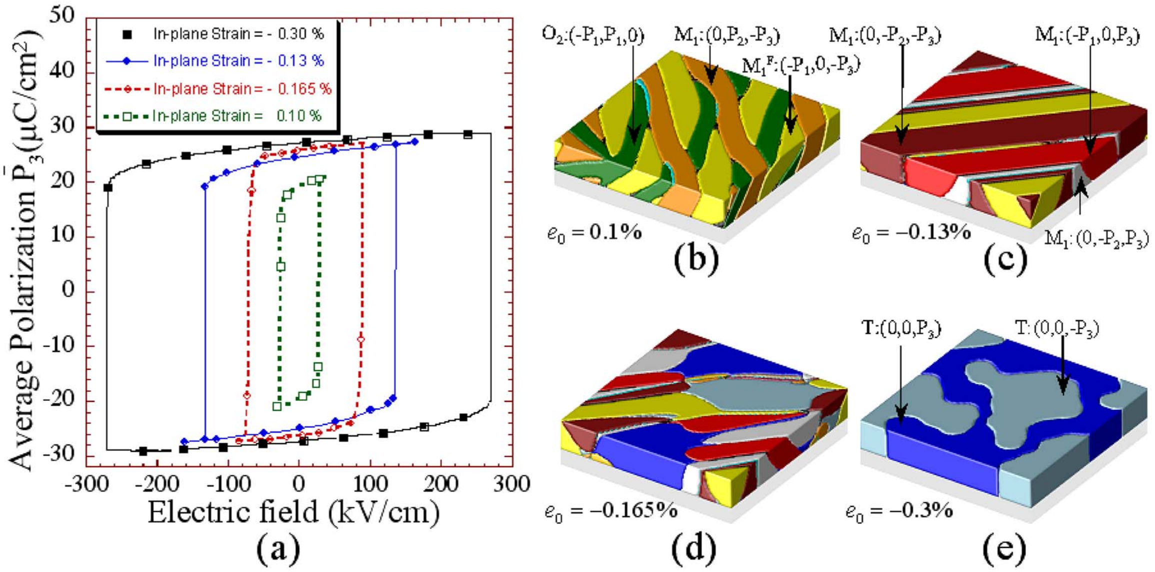

FIG. 1. (Color online) (a) Hysteresis loops for epitaxial BTO thin films at temperature $T=0$ °C with four representative in-plane strain $e_0=0.1\%$, -0.13%, -0.165%, and -0.3%; [(b)–(e)] simulated domain structures of BTO thin films under short-circuit electrostatic boundary conditions for the four given substrate strains. The domain structures are obtained from an initial paraelectric state with small random perturbations and used as the starting domain structure to construct the hysteresis loop. The polarization components of individual phases are indicated. The green and the blue color represent orthorhombic (O_2) and tetragonal (T) phases, respectively, while rest of the colors indicate M_1 ferroelectric phase.

where Δx is the simulation grid spacing. The thickness of the film is taken as $h_f=20\Delta x$. The bulk free energy coefficients, the elastic and the electrostrictive coefficients are given in Ref. 17 and references therein.[20–22] We used $\kappa_{11}=\kappa_{22}=\kappa_{33}=500$ for electrostatic energy calculations. The average strains induced by the substrate are assumed to be $\varepsilon_{11}=\varepsilon_{22}=e_0$. We assumed the domain wall energy to be isotropic for our simulations. A domain structure was first generated by performing the simulations under the short-circuit electrostatic boundary condition ($\varphi_1=0$), starting from an initial paraelectric state with small random perturbations. In order to compute the hysteresis loop, we gradually change the potential ϕ_1 in our simulations and the domain structure from a previous step was used as the input at each increment of the potential.

To study the effect of substrate strain on switching behavior, we choose a range of in-plane strains from $e_0=0.1\%$ to $e_0=-0.3\%$ while the temperature is maintained at $T=0$ °C. It has been reported by Li and Chen[17] that within this range of the strain different ferroelectric phases and their mixtures are observed. Further, each phase can have multiple ferroelectric variants. For example, under a compressive strain between $e_0=0.0\%$ and $e_0=-0.16\%$, a ferroelectric phase denoted as M_1 with polarization ($|P_1|>0$, $P_2=0$, $|P_3|>0$) or ($P_1=0$, $|P_2|>0$, $|P_3|>0$) is stabilized while for a larger compressive strain, tetragonal phase with polarization ($P_1=0$, $P_2=0$, $|P_3|>0$) is stable. For a tensile substrate strain between $e_0=0.0\%$ and $e_0=0.1\%$, a mixture of M_1 and O_2 phases is observed, where O_2 is a ferroelectric phase with polarization ($|P_1|>0$, $|P_2|=|P_1|$, $P_3=0$). Using the phase-field approach, the authors recently demonstrated that the coercive field in bulk lead zirconate titanate single crystals is closely related to the number of ferroelectric variants present in the system.[23] As the number of ferroelectric variants that are stabilized within the chosen range of substrate strain varies, we expect that coercive field will significantly change with the substrate strain.

Figure 1(a) presents the hysteresis loops for four representative strains within the range, namely, $e_0=0.1\%$, -0.13%, -0.165%, and -0.3%. It is seen that the remanent polarization monotonically increases as the substrate strain changes from tensile to compressive, and the highest remanent polarization is obtained at strain $e_0=-0.3\%$. This can be explained from the phase stability within the chosen range of the strain (Ref. 17). As the strain changes from tensile to compressive, phases with larger out of plane polarization component P_3 are stabilized. It is interesting to observe that unlike the remanent polarization, the coercive field does not monotonically change as the strain varies from tensile to compressive. Although the coercive field is the minimum at the tensile substrate strain of $e_0=0.1\%$, the coercive field at the compressive substrate strain of $e_0=-0.13\%$ is about 1.4 times higher than that at $e_0=-0.165\%$. The highest coercive field is observed for strain $e_0=-0.3\%$. To understand the change of the coercive field with the substrate strain, we analyzed the domain structures in Figs. 1(b)–1(e). They are obtained at the corresponding substrate strains under the short circuit boundary condition. In the figures, each color represents a ferroelectric variant. The colors green and blue represent orthorhombic (O_2) and tetragonal (T) phase while the rest of the colors indicate ferroelectric variants of M_1 phase. It is seen that the domain structures with $e_0=-0.3\%$ and $e_0=-0.13\%$ comprised of single phases of T and M_1, respectively, while the domain structures for $e_0=-0.165\%$ and $e_0=0.1\%$ are phase mixtures. It demonstrates once again that the coercive field can significantly change around phase boundaries.

To further analyze the effect of substrate strain on coercive field, we computed the hysteresis loops for epitaxial BTO thin films by changing the substrate strain within the range from $e_0=0.1\%$ to $e_0=-0.3\%$ and plotted the coercive field as well as the remanent polarization as a function of the in-plane substrate strain (Fig. 2). In the figure, the shaded areas represent the stability regions of a single ferroelectric phase and the nonshaded regions show a phase mixture. Error bars represent the range of the predicted coercive

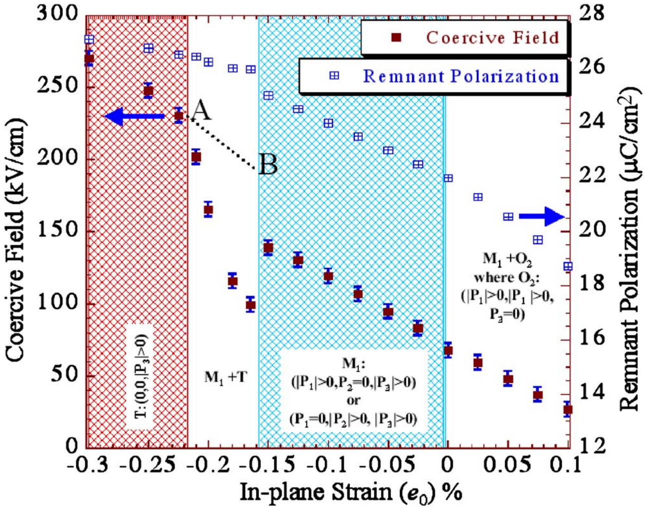

FIG. 2. (Color online) Plot for simulated coercive field and remanent polarization in an epitaxial BTO thin film as a function of in-plane biaxial substrate strain at temperature $T=0$ °C. The shaded areas indicate regions bounded by single ferroelectric phase while the nonshaded area represent regions where a phase mixture is stabilized under short-circuit electrostatic boundary conditions. The polarization components of individual phases are indicated.

fields obtained from the phase-field simulations starting with different sets of random numbers. The figure shows within the tetragonal phase stability region (from $e_0=-0.3\%$ to $e_0=-0.225\%$) that the coercive field linearly decreases with the substrate strain. The decrease in compressive strain reduces domain wall clamping by the substrate, resulting in an increase in domain wall mobility, thus, a smaller electric field is required for polarization switching.[24] As the compressive strain is reduced further (from $e_0=-0.225\%$ to $e_0=-0.16\%$) the coercive field significantly decreases. The decrease in coercive field with substrate strain in this range can be attributed to two factors. First, a decrease in compressive strain increases domain wall mobility, resulting in a decrease in predicted coercive field (schematically shown by the dotted line AB). Second, within this region, a phase mixture ($T+M_1$) is stabilized. Domain boundaries between these two phases provide additional sites for new domain nucleation during polarization switching. Similar to the area bounded by the tetragonal phase, coercive field linearly decreases with compressive substrate strain within the phase stability region bounded by the M_1 phase ($e_0=-0.16\%$ to $e_0=-0.0\%$). Within the tensile strain regime (from $e_0=-0.0\%$ to $e_0=0.1\%$), a phase mixture (M_1+O_2) is stabilized which causes a further decrease in coercive field with the increase in tensile strain. Unlike the coercive field, the remanent polarization continuously decreases within the chosen range of substrate strains. However, as the compressive substrate strain decreases from $e_0=-0.16\%$, a small jump in the value of remanent polarization is observed. This is because for strain below $e_0=-0.16\%$, phases with in-plane polarization components are stabilized.

In conclusion, we studied the effect of substrate strain on the coercive field in epitaxial thin films. It was found that coercive field is strongly dependent on the substrate strain especially if the strain can cause ferroelectric to ferroelectric or interferroelectric transitions. For such interferroelectric transitions in BTO thin films under biaxial substrate strain close to zero and temperature around 0 °C, it was observed that the coercive field can change more than a hundred percent just by changing the substrate strain by 0.05% without a significant drop in remanent polarization. Thus, choosing appropriate substrate strain, it is possible to control both polarization and coercive field in ferroelectric thin films.

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