Strain Relaxation by Domain Formation in Epitaxial Ferroelectric Thin Films

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The origin of strain-induced, modulated domain structures observed in epitaxial ferroelectric lead titanate thin films is discussed using a phenomenological total-energy calculation. Linear elasticity is used to account for the substrate contribution while a free-energy functional of the Landau-Ginzburg-Devonshire type is used to calculate the domain-wall and the polarization contributions from the film. Good agreement between the predictions of this model and the experimental results is found for thickness-dependent properties such as the relative domain population and spontaneous strain.

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Equilibrium theories of epitaxy [1,2] predict that, below a certain critical thickness, lattice mismatch between a thick substrate and a thin film should be accommodated entirely by strain within the film. Above this critical thickness, the film's strain would be partially relieved by misfit dislocations. If the film undergoes a structural phase transition from a high-symmetry phase to a lower-symmetry phase during cooling from the growth temperature, however, the bulk epitaxial strain can be relieved by a domain formation suggested by Roitburd [3], and Bruinsma and Zangwill [4]. The phenomenon is reminiscent of the formation of coherent alternating twins in martensites [5,6]. It is particularly important to understand such domain formation in ferroelectrics and high-T_c superconductors since it can have a profound influence on the physical properties of these materials.

This Letter presents a new theoretical analysis for a specific epitaxial multidomain system, i.e., a $PbTiO_3$ thin film grown on $KTaO_3$, and compares the model predictions to the experimental measurements. A Landau-Ginzburg-Devonshire- (LGD-) type free energy is used to evaluate the thin-film energy including the domain walls. And, elasticity theory is employed to calculate the substrate-energy contribution close to the interface. Quantitative agreement between the theoretical predictions and experimental results is obtained for the relative domain abundances and spontaneous strains as a function of film thickness.

Epitaxial ferroelectric $PbTiO_3$ thin films were grown on [001]-oriented single-crystal $KTaO_3$ substrates using metalorganic chemical vapor deposition. The details of the deposition process have been reported previously [7]. X-ray diffraction studies showed that, for thicknesses greater than about 30 nm, the tetragonal films contained both domains with the *a* axis near the substrate surface normal (*a* domains) and domains with the *c* axis near the normal (*c* domains). X-ray studies further revealed that the films were three-dimensionally epitaxial. Rutherford backscattering analysis showed that the deposition stoichiometry is $PbTiO_3$ within an error of 5%. Ion channeling experiments along the [001] direction yielded a value of $\chi_{\min}=40\%$. This rather poor channeling is due to the existence of the periodic domain-wall structure treated here.

Cross-section transmission electron microscopy (TEM) reveals that the films consist of four different symmetry-equivalent twinned crystals, which result from the transition from a high-symmetry phase (cubic) to a low-symmetry phase (tetragonal). Each type of twinned crystals contains periodic *a* and *c* domains in an alternating sequence separated by 90° domain walls [8] that form an angle of about 45° with the surface of the substrate. The domain structure within one of the four variants of twinned crystals is shown schematically in Fig. 1(a). A high-resolution *Z*-contrast image of the crystal structure at the $PbTiO_3/KTaO_3$ interface provides evidence for the alignment of atomic rows with no misfit dislocations within the field of view.

Bulk $PbTiO_3$ has a cubic perovskite structure at high temperatures and, below about 763 K, transforms to a ferroelectric phase with a large tetragonal distortion [9]. $KTaO_3$ at zero stress, however, retains the prototype cubic perovskite structure down to the lowest temperatures [9]. At the growth temperature of 823 K, both $PbTiO_3$ and $KTaO_3$ are cubic. Below the Curie temperature, the thin film assumes a heterogeneous structure with periodic alternating domain walls so as to limit the extent of the strain field in the substrate to a distance comparable to the domain-wall periodicity, thereby reducing the strain energy. This is analogous to the formation of domain walls in ferromagnets under a magnetic field in order to minimize the magnetic energy in the vacuum near the free surface [10].

The present theoretical analysis of the substrate-film system is based on a consideration of the epitaxial strain

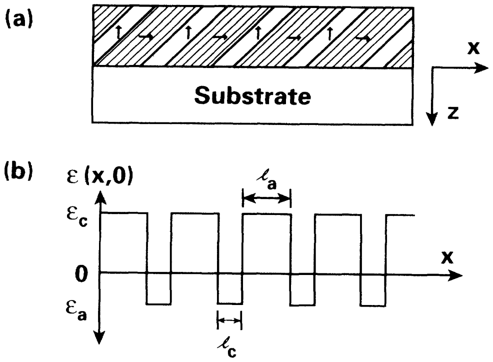

FIG. 1. (a) A schematic diagram of one of four variants of twinned crystals with its periodic *a* and *c* domains seen in PbTiO₃ film on KTaO₃. The arrows indicate the direction of spontaneous polarization. (b) The plot of the model strain field imposed on the substrate at interface.

constraint and the total energy of the structure. Three separate contributions to the total energy, E_t, are considered, i.e.,

$$E_t = E_s + E_d + E_f . \tag{1}$$

Here, E_s is the elastic energy stored in the substrate in the vicinity of the interface. E_d is the domain-wall creation energy obtained from the LGD free energy. E_f is the LGD free energy of the film which depends upon polarization and spontaneous strains [11]. These contributions are evaluated below. The spontaneous strains x_i are defined with respect to the extrapolated lattice parameter a_c of cubic lead titanate [i.e., $x_i = (a_i - a_c)/a_c$], while epitaxial misfits ε_i are defined with respect to the lattice parameter a_s of the substrate [i.e., $\varepsilon_i = (a_i - a_s)/a_s$]. Here, a_i stands for the thin-film lattice parameters *a*, *b*, or *c*.

Based on observations from the TEM micrographs, it is assumed that the *a* and *c* domains are coherent with the substrate in the model. For simplicity, we treat the problem as one of planar strain so that the *y* coordinate [see Fig. 1(a)] does not enter. Accordingly, the strain distribution function, $\varepsilon(x,0)$, imposed on the substrate at the interface is taken as shown in Fig. 1(b). Clearly, $\varepsilon(x,0) = \varepsilon(u + nl, 0)$ where $l = l_a + l_c$ (l is the domain period consisting of one *a* and an adjacent *c* domain), with $0 < u < l$, and n is an integer. An expansion into a Fourier series yields

$$\varepsilon(x,0) = \sum_n \left(A_n \cos\frac{2\pi n x}{l} + B_n \sin\frac{2\pi n x}{l} \right) , \tag{2}$$

where

$$A_n = \frac{1}{\pi n}(\varepsilon_a + \varepsilon_c)\sin 2\pi n w ,$$

$$B_n = \frac{1}{\pi n}(\varepsilon_a + \varepsilon_c)(1 - \cos 2\pi n w) .$$

In Eq. (2), w is defined to be the fraction of the *a* domains, and thus, $l_a = lw$ and $l_c = (1-w)l$. ε_a and ε_c are the misfits at the interfaces of *c* and *a* domains, respectively.

The strain energy per unit area in the substrate out to a distance t from the coherent interface is given by [12]

$$E(t) = \left(\frac{1}{l}\right) \int_0^t dz \int_0^l dx \left(\frac{1}{4\mu}\right) [(1-\nu)(\sigma_{xx}^2 + \sigma_{zz}^2) 2\nu\sigma_{xx}\sigma_{zz} + 2\sigma_{zx}^2] , \tag{3}$$

where σ_{ij} denote components of the stress tensor, and μ and ν are the shear modulus and Poisson's ratio of the substrate, respectively. Following van der Merwe and Ball [12] and Timoshenko [13], the stresses are computed as

$$\sigma_{xx} = \frac{\partial^2\phi}{\partial z^2},\quad \sigma_{zz} = \frac{\partial^2\phi}{\partial x^2},\quad \sigma_{zx} = -\frac{\partial^2\phi}{\partial x\,\partial z} \tag{4}$$

from the Airy stress function, ϕ, which satisfies $\nabla^4\phi = 0$.

The desired solution of the stress function should be such that (1) the strains have the boundary value $\varepsilon(x,0)$ of Eq. (2) at $z = 0$, (2) the stresses vanish at the free boundary, $z = +\infty$, and (3) the stresses have the periodicity l of the domain lattice.

The final result is

$$E_s = \frac{\mu(1+\nu)\alpha(w)}{8\pi^3(1-\nu)^2}[(\varepsilon_a + \varepsilon_c)^2 + (\varepsilon_b + \varepsilon_c)^2] l L_1 L_2 . \tag{5}$$

We assume that on the average over a large area, $\varepsilon_a = \varepsilon_b$. L_1 and L_2 are the dimensions of the film along x and y, respectively, and

$$\alpha(w) = \sum_{n=1}^{\infty} \frac{\sin^2 \pi n w}{n^3} .$$

This equation has the same form as that given by Khachaturyan [14], for twin bands in martensites.

The creation energy e_d per unit area of a 90° domain wall in PbTiO₃ is determined from the LGD theory of Bulaevskii [15] to be

$$e_d = \frac{\kappa P_0^2}{\delta}(1 + a^2) I(a) \tag{6}$$

so that $E_d = e_d(L_2 L_3)(L_1/l)$. Here, κ, P_0, a, and the function $I(a)$ are as defined by Bulaevskii [15]. We calculate E_d as 0.24 J/m² for PbTiO₃ at 23 °C using a value of $P_0 = 0.75$ C/m² for the polarization. The value of κ was determined by using the soft-ferroelectric-mode dispersion relation for PbTiO₃ [16].

To calculate the energy contribution from the film, we use the following elastic Gibb's free energy derived from the LGD theory, where the relationships, $X_{ik} = 0$ for $i \neq k$

and $X_{ii}=X_i$, have been applied [9,11]:

$$G_1(P,X)=\alpha_1P^2+\alpha_{11}P^4+\alpha_{111}P^6+\tfrac{1}{2}s_{11}(X_1^2+X_2^2+X_3^2)+s_{12}(X_1X_2+X_1X_3+X_2X_3)+Q_{11}X_3P^2+Q_{12}(X_1+X_2)P^2\,. \qquad (7)$$

Here, P and X_i are the spontaneous polarization and stresses, respectively. α_1, α_{11}, and α_{111} are dielectric stiffness and higher-order stiffness coefficients at constant stress. s_{ij} and Q_{ij} are elastic constants and cubic electrostrictive constants, respectively. We, then, perform a Legendre transform to the Helmholtz energy, $F(P,x_i)$, in terms of spontaneous strains, x_i. The total contribution from the film is thus $E_f=F(P,x_i)L_1L_2L_3$. All of the elastic constants for $KTaO_3$ and $PbTiO_3$ in the above equations are obtained from published results [11,17,18].

The total-energy function is now obtained by summing the contributions of Eqs. (5)-(7). Note that the resulting equation has a functional dependence on five parameters: spontaneous polarization, spontaneous strains (three parameters), and the domain period. By minimizing this total energy at a given film thickness, one can determine these five parameters which in turn can be used to determine other properties such as the relative c-domain population, N_c.

An expression for N_c can be derived from the coherency requirement that the lattice parameters of the film and the substrate are equal at the interface at each temperature. This condition results in the following equation when a fully relaxed heterostructure is assumed at the growth temperature:

$$\int_{T_s}^{T_0}\alpha_s(T)dT=\int_{T_s}^{T_c}\alpha_f(T)dT+N_c\varepsilon_a+N_a\varepsilon_c+N_b\varepsilon_b\,, \qquad (8)$$

where T_s is the growth temperature, T_c is the phase transition temperature, and T_0 is the measurement temperature. Here, N_a, N_b, and N_c are the normalized domain abundances. α_s and α_f are the thermal expansion coefficients for the substrate and the film, respectively. By assuming $N_a=N_b$ and $N_a+N_b+N_c=1$, one obtains a relation for N_c in terms of ε_i, which can be expressed in terms of the spontaneous strains, x_i. Thus, by using the x_i obtained through minimization of the total energy, we determine the relative population of the domains. w is related to N_c through the relation $w=(1-N_c)/(1+N_c)$.

Figure 2 shows the calculated and experimentally determined (measured using integrated x-ray intensities from θ-2θ scans) relative c-domain populations as a function of the film thickness, L_3. The dot-dashed line in the figure represents the values calculated using Eq. (8) if one assumes a totally relaxed film at the growth temperature. The dashed line is the calculated result assuming unrelaxed epitaxial strain at the growth temperature. For this calculation, an additional term, $\Delta\varepsilon_G=[a_c(T_s)-a_s(T_s)]/a_s(T_s)$, was added to the left-hand side of Eq. (8).

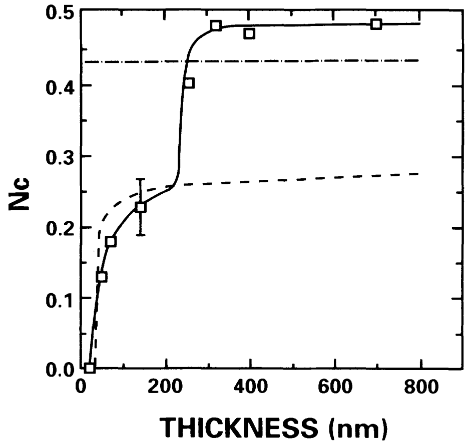

FIG. 2. Plot of the calculated and experimental normalized c-domain amount, N_c, as a function of film thickness. Dot-dashed and dashed lines are the calculations evaluated, respectively, with and without strain relaxation at the growth temperature in the film. Squares are the experimental data points. The solid line is a guide to the eye. The estimated error is also shown in the figure.

These results indicate that, depending on the film thickness, the film grows either in its coherent pseudomorphic cubic phase retaining its epitaxial strain or in a fully relaxed cubic phase with no epitaxial strain; both of which form a periodic domain pattern as they cool through the Curie temperature. Thus, for film thicknesses less than about 34 nm, the equilibrium structure consists only of a domains and equivalent b domains. From about 34 to 250 nm, the films appear to grow without relieving the interfacial strain that forms alternating a and c domains having the thickness dependence shown in Fig. 2. For film thicknesses greater than about 250 nm, the film appears to be almost fully relaxed at the growth temperature possibly as a result of misfit dislocation formation. A thickness of 250 nm can be considered as a critical thickness at the growth temperature.

In Fig. 3, a plot of the experimental and calculated spontaneous strains, x_3 and x_1, is shown. The spontaneous strains are determined using the 2θ positions from θ-2θ x-ray diffraction scans. As can be seen, there is reasonably good agreement for both x_3 and x_1 supporting the validity of the present model. It can be seen that the domains are not fully relaxed. However, the spontaneous strains approach the bulk values for thicker films. This implies that the domain formation treated above does not fully relax the film and that some strain is retained in each domain.

The present model should be universally applicable to all epitaxial ferroelectric and ferroelastic oxide thin films. A more detailed explanation of this model in conjunction with experimental results will be presented in a subsequent report.

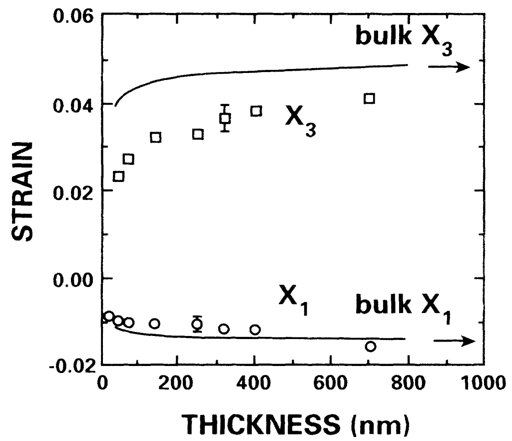

FIG. 3. Plot of the calculated and experimentally determined spontaneous strains, x_3 and x_1. The solid lines show the result of calculations for x_1 and x_3. Circles and squares show the experimental results for x_1 and x_3, respectively. The bulk strain values are also shown for comparison.

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