Effects of non-equally biaxial misfit strains on the phase diagram and dielectric properties of epitaxial ferroelectric thin films

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Abstract

The effects of non-equally biaxial in-plane misfit strains on the equilibrium polarization states and the dielectric properties of single-domain epitaxial ferroelectric thin films are investigated by a nonlinear thermodynamic theory. The “misfit strain-misfit strain” and “temperature-misfit strain” phase diagrams for single-domain BaTiO₃ (BT) and PbTiO₃ (PT) thin films grown on tetragonal substrates are developed by minimizing the Helmholtz free energy. The non-equally biaxial misfit strains cause the presence of two in-plane tetragonal ferroelectric phases, a_1 ($P_1 \neq 0, P_2 = P_3 = 0$) and a_2 ($P_2 \neq 0, P_1 = P_3 = 0$), in both BT and PT thin films, which do not exist if the misfit strains are equally biaxial.

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Ferroelectric thin films have been found wide applications in new generations of dynamic random access memories, nonvolatile memories, tunable microwave devices, and other microelectronic and electro-optic devices.¹⁻⁵ The misfit strains between a ferroelectric thin film and its substrate are able to change the Curie temperature, the order of the paraelectric/ferroelectric phase transition, the equilibrium polarization states, and the dielectric properties of the material.⁶ Certainly, a deep understanding of the relationship between the misfit strains and the material properties will provide guidelines on how to control the material properties by manipulating the misfit strains, which might be crucial for applications of ferroelectric thin films. Great progress has been achieved in the theoretical study of the misfit strains effect, especially, by using the powerful thermodynamics theories,⁶⁻¹⁶ and the “misfit strain-temperature” phase diagrams have been constructed.^{6,12-13} However, the previous work has investigated only equally biaxial misfit strains, called the isotropic misfit strains also in the literature, which are induced when ferroelectric thin films are grown on cubic substrates. If ferroelectric thin films are grown on tetragonal substrates, the misfit strain along a crystalline axis will differ from the misfit strain along the other crystalline axis, which are called non-equally biaxial (or anisotropic) misfit strains, as illustrated by recent experimental studies.¹⁷⁻¹⁹ The non-equally biaxial misfit strains may induce new material properties and thus open up other possibilities for the design of electronic devices.

In the present work, we study a single-domain ferroelectric thin film epitaxially grown on a thick tetragonal substrate and assume the film/substrate interface is coherent. Using the Voigt matrix notation of strains and the rectangular Cartesian coordinator system with the x_3 axis perpendicular to the film/substrate interface, we may define the non-equally biaxial in-plane

misfit strains as $e_1 = (b - a_0)/b$ and $e_2 = (c - a_0)/c$, where b and c are the substrate lattice parameters and a_0 is the lattice constant of the cubic paraelectric phase of the film at the stress-free state. The in-plane shear strain is approximately treated to be zero because of the tetragonal of the substrate and because the plane stress condition is held along the film thickness direction due to the thin thickness of the film.

Using the Gibbs free energy, G ,⁶ and the Legendre transformation of $F = G + e_1\sigma_1 + e_2\sigma_2$, the Helmholtz free energy, F , of a single domain ferroelectric film under non-equally biaxial in-plane misfit strains takes the form:

$$\begin{aligned}
F = & \alpha_1^* P_1^2 + \alpha_2^* P_2^2 + \alpha_3^* P_3^2 + \alpha_{11}^* (P_1^4 + P_2^4) + \alpha_{33}^* P_3^4 + \alpha_{12}^* P_1^2 P_2^2 + \alpha_{13}^* (P_2^2 P_3^2 + P_1^2 P_3^2) \\
& + \alpha_{111} (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} [(P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2))] \\
& + \alpha_{123} P_1^2 P_2^2 P_3^2 + \frac{s_{11}(e_1^2 + e_2^2) - 2s_{12}e_1e_2}{2(s_{11}^2 - s_{12}^2)},
\end{aligned} \quad (1)$$

where the renormalized coefficients α_{ij}^* can be found in Ref. 6 and α_i^* are given by

$$\begin{aligned}
\alpha_1^* &= \alpha_1 - \frac{Q_{12}(s_{11}e_2 - s_{12}e_1) + Q_{11}(s_{11}e_1 - s_{12}e_2)}{s_{11}^2 - s_{12}^2}, \\
\alpha_2^* &= \alpha_1 - \frac{Q_{12}(s_{11}e_1 - s_{12}e_2) + Q_{11}(s_{11}e_2 - s_{12}e_1)}{s_{11}^2 - s_{12}^2}, \\
\alpha_3^* &= \alpha_1 - \frac{Q_{12}(e_1 + e_2)}{s_{11} + s_{12}}.
\end{aligned} \quad (2)$$

In Eqs. (1) and (2), α_1 is the dielectric stiffness, α_{ij} and α_{ijk} are higher order stiffness coefficients at constant stress, Q_{ij} are the electrostrictive coefficients, and s_{ij} are the elastic compliances of the film. The same material parameters used in Ref. 6 are used in the present work.

The equilibrium phases under different misfit strains and temperatures are determined by minimization of the Helmholtz free energy. We introduce the following notation for the different equilibrium phases that may occur in the films: (i) the a_1 phase, where $P_1 \neq 0$ and $P_2 = P_3 = 0$; (ii) the a_2 phase, where $P_2 \neq 0$ and $P_1 = P_3 = 0$; (iii) the c phase, where $P_3 \neq 0$ and $P_1 = P_2 = 0$; (iv) the a_1c phase, where $P_3 \neq 0$, $P_1 \neq 0$ and $P_2 = 0$; (v) the a_2c phase, where $P_3 \neq 0$, $P_2 \neq 0$ and $P_1 = 0$; (vi) the a_1a_2 phase, where $P_2 \neq 0$, $P_1 \neq 0$ and $P_3 = 0$; (vii) the r phase, where $P_3 \neq 0$, $P_1 \neq 0$ and $P_2 \neq 0$. Figs. 1(a) and 1(b) show the misfit strain–misfit strain phase diagrams for epitaxial BT and PT films at room temperature, respectively. For the BT films, the r phase (monoclinic phase) does not exist in the entire region of misfit strains ranging from -0.004 to 0.008 . The other six phases, i.e., three orthorhombic phases (a_1a_2 , a_1c , a_2c) and three tetragonal phases (c , a_1 , a_2), show up in different regions of misfit strains, as shown in Fig. 1(a). The thermodynamics analysis exhibits that the transitions from the a_1a_2 phase to the ca_1 or ca_2 phase, and from the ca_1 phase to the ca_2 phase are of the first-order, whereas the transitions between two of other phases are of the second order. The a_1 and a_2 tetragonal phases appear only in the regions where the non-equal biaxial misfit strains are tensile in one direction and compressive in another direction. The tetragonal c phase exists when the misfit strains are compressive in both directions, whereas the a_1a_2 in-plane orthorhombic phase only exists when the misfit strains are tensile in both directions. For the PT films, a_1c and a_2c phases do not exist in the entire region of the misfit strains ranging from -0.02 to 0.02 . The other five phases, i.e., r , a_1a_2 , c , a_1 and a_2 , exist within different regions of misfit strains, as shown in Fig. 1(b). The in-plane a_1 or a_2 tetragonal phase appears in a region of the misfit strains, where one misfit strain

is compressive and the other is tensile or compressive. For both of the BT and PT films, the non-equally biaxial misfit strains with a compressive component are necessary for the formation of the a_1 and a_2 in-plane tetragonal phases, which are forbidden when the misfit strains are equally biaxial, thereby suggesting that the non-equally biaxial misfit strains must be imposed on the ferroelectric films by their substrates in order to obtain the stable and desired in-plane tetragonal phases.

Figs. 2(a) and 2(b) show two-dimensional “temperature-strain” phase diagrams for the BT and PT films, respectively, with $e_1 = 0.005$. The phase transition from the paraelectric state to a single-domain ferroelectric state occurs at a temperature, $T_c = \max[T_1, T_2, T_3]$, where T_1 , T_2 and T_3 denote the temperatures at which the paraelectric phase transfers into the a_1 , a_2 and c phases, respectively. Due to the non-equally biaxial misfit strains, the paraelectric-to-ferroelectric transition temperature $T_c(e_2, e_1 = 0.005)$ for both BT and PT films has a plateau above the a_1 phase, which is different from the “seagull” shape of the transition temperature versus the equal biaxial misfit strain.⁶ The significant feature induced by the non-equally biaxial misfit strains is the formation of the tetragonal ferroelectric phases, a_1 and a_2 , which do not exist in the BT and PT films under equally biaxial misfit strains.⁶

The misfit strain-induced phase transition may be accompanied by dielectric anomaly. The dielectric constants, ϵ_{ij} , at small-signals are identical to the reciprocal dielectric susceptibilities, χ_{ij} , which can be calculated from the second partial derivative of the free energy, i.e., $\chi_{ij} = \partial^2 F / \partial P_i \partial P_j$. Here, we plot in Fig. 3(b) the relative dielectric constants versus the misfit

strain, e_2 , with a constant value of the misfit strain of $e_1 = 0.005$ at temperature 300 °C for the PT films as an example to demonstrate the behavior of dielectric constants under non-equally biaxial misfit strains. To understand the behavior of the dielectric constants, the corresponding polarizations are plotted in Fig. 3(a). At the phase boundary between the c and a_1 phases, polarization components P_1 and P_3 are discontinuous, thereby indicating the phase transition is of the first order. The discontinuity of the P_1 and P_3 polarization components cross the boundary between the c and a_1 phases causes the anomalies in the ε_{11} and ε_{33} dielectric constants and the jump in the ε_{22} dielectric constant, as shown in Fig. 3(b), because the ε_{22} dielectric constant is related to the P_1 and P_3 polarization components.

In summary, the Helmholtz free energy, F , for ferroelectric thin films under non-equally biaxial misfit strains has been explicitly given, from which the relationships among the two misfit strains and temperature, i.e., the three-dimensional phase diagram can be constructed and the dielectric constant can be investigated as a function of temperature and the misfit strains. The present work is based on the single domain assumption, as many thermodynamic approaches do.⁶⁻¹⁰ Neither domain walls nor the long-range mechanical and electrical interactions are taken into account. The a_1a_2 , a_1c , a_2c and r -phases may represent the $a_1/a_2/a_1/a_2$, $a_1/c/a_1/c$, $a_2/c/a_2/c$ and $c/a_1/a_2$ multidomain structures, respectively. In this sense, the thermodynamics results based on the single domain assumption may be regarded as the macroscopic average of multidomain structures. Of course, the phase boundaries predicted by the thermodynamics approaches may be different from those in multidomain ferroelectric thin films.

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Figure captions

FIG.1. Misfit strain – misfit strain phase diagrams of single-domain BT (a) and PT (b) thin films at room temperature, where the thin and thick lines denote the second- and first-order phase transition boundaries, respectively

FIG.2. Temperature – misfit strain phase diagrams, at a constant misfit strain of $e_1 = 0.005$, of single-domain BT (a) and PT (b) thin films, where the thin and thick lines denote the second- and first-order phase transition boundaries, respectively.

FIG.3. Dependence of polarizations (a) and relative dielectric constants (b) on the misfit strain, e_2 , in single-domain PT films with a constant misfit strain of $e_1 = 0.005$ at 300 °C.

FIG.1.

FIG.2.

FIG.3.