A nonlinear thermodynamic theory is used to predict the equilibrium polarization states and dielectric properties of ferroelectric thin films grown on dissimilar substrates which induce anisotropic strains in the film plane. The “misfit strain-temperature” phase diagrams are constructed for single-domain PbTiO$_3$ and Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ films on orthorhombic substrates. It is shown that the in-plane strain anisotropy may lead to the appearance of new phases which do not form in films grown on cubic substrates. The strain-induced dielectric anisotropy in the film plane is also calculated and compared with the anisotropy observed in Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ films deposited on NdGaO$_3$. © 2005 American Institute of Physics. [DOI: 10.1063/1.1855389]
phases appear, which do not form at when the misfit strains are opposite in sign, new ferroelectric along one of the in-plane edges of the prototypic unit cell, shown in Fig. 2. It should be emphasized that anisotropic phase, where the spontaneous polarization $P_b$ of films grown on dissimilar orthorhombic substrates. The phase map is very different from the diagram of PT films grown on cubic substrates, 7 the triclinic $\gamma$ phase so that the dielectric response is isotropic to the plane $m_1=0, m_2=0).$ Variations of the film dielectric constants with the anisotropy factor $\beta=d$. The dielectric properties of ferroelectric films must depend on the strain anisotropy as well. To demonstrate this effect, we calculated small-signal dielectric constants $\varepsilon_{ij}$ of PT films with the out-of-plane polarization state ($P_1=P_2=0, P_3 \neq 0$). When $m_1=m_2$, this state corresponds to the tetragonal $c$ phase so that the dielectric response is isotropic in the film plane. At $m_1 \neq m_2$, the symmetry of the $c$ phase lowers to orthorhombic, which induces the in-plane dielectric anisotropy ($\varepsilon_{11} \neq \varepsilon_{22}$). Variations of the film dielectric constants with the anisotropy factor $\beta=(u_{m1}-u_{m2})/(u_{m1}+u_{m2})$. The dependencies are calculated at $u_{m1}+u_{m2}=10^{-4}$, they are valid only within the stability range of the $c$ phase.

Since the renormalized second-order coefficients $\alpha_{ij}^r$ of PT films are positive, 7 the paraelectric to ferroelectric phase transition is of the second order. The temperature $T_c$ of this transition can be calculated analytically as $T_c = \text{max}(T_1, T_2, T_3)$, where

$$T_1 = T_0 + \varepsilon_0 C \left( \frac{Q_{11} + \varepsilon_{12} (u_{m1} + u_{m2})}{s_{11} + s_{12}} + \frac{Q_{11} - \varepsilon_{12} (u_{m1} - u_{m2})}{s_{11} - s_{12}} \right)$$

$$T_2 = T_0 + \varepsilon_0 C \left( \frac{Q_{11} + \varepsilon_{12} (u_{m1} + u_{m2})}{s_{11} + s_{12}} - \frac{Q_{11} - \varepsilon_{12} (u_{m1} - u_{m2})}{s_{11} - s_{12}} \right)$$

$$T_3 = T_0 + 2 \varepsilon_0 C \frac{Q_{12} (u_{m1} + u_{m2})}{s_{11} + s_{12}},$$

(2)

$T_0$ and $C$ are the Curie–Weiss temperature and constant of a bulk crystal, and $\varepsilon_0$ is the permittivity of the vacuum. Equation (2) demonstrates that the anisotropy of positive misfit strains always raises $T_c$, whereas the anisotropy of negative misfit strains does not affect this temperature.

The dielectric properties of ferroelectric films must depend on the strain anisotropy as well. To demonstrate this effect, we calculated small-signal dielectric constants $\varepsilon_{ij}$ of PT films with the out-of-plane polarization state ($P_1=P_2=0, P_3 \neq 0$). When $u_{m1}=u_{m2}$, this state corresponds to the tetragonal $c$ phase so that the dielectric response is isotropic in the film plane. At $u_{m1} \neq u_{m2}$, the symmetry of the $c$ phase lowers to orthorhombic, which induces the in-plane dielectric anisotropy ($\varepsilon_{11} \neq \varepsilon_{22}$). Variations of the film dielectric constants with the anisotropy factor $\beta=(u_{m1}-u_{m2})/(u_{m1}+u_{m2})$ are shown in Fig. 3. It can be seen that the strain-induced anisotropy of the in-plane dielectric response may be significant.

In order to compare our theoretical predictions with available experimental data, 14 we also calculated the equilibrium phase states and dielectric properties of Pb$_{0.33}$Sr$_{0.67}$TiO$_3$ (PST) films grown on orthorhombic substrates. For PST of

FIG. 1. Vertical cross section of the 3D phase diagram of PbTiO$_3$ thin films grown on dissimilar orthorhombic substrates. The phase map corresponds to $T=25^\circ C$.

FIG. 2. Horizontal cross section of the 3D phase diagram of single-domain PbTiO$_3$ films grown on dissimilar orthorhombic substrates. The phase map corresponds to $T=25^\circ C$.

FIG. 3. Effect of the in-plane strain anisotropy on the dielectric constants of epitaxial PbTiO$_3$ films ($T=25^\circ C$). The anisotropy factor equals $\beta=(u_{m1}-u_{m2})/(u_{m1}+u_{m2})$. The dependencies are calculated at $u_{m1}+u_{m2}=10^{-4}$, they are valid only within the stability range of the $c$ phase.
this composition, we determined the dielectric stiffness \( \alpha_1 = (T - T_0)/(2\epsilon_0 C) \) from the experimental values of \( T_0 \) and \( C \). \( \alpha_1 \) Other material parameters of PST were calculated as weighted averages of those known for pure PbTiO\(_3\) and SrTiO\(_3\).\(^{7,21}\) The developed phase diagram of PST films at room temperature is shown in Fig. 4. Evidently, it differs from the diagram of PT films (see Fig. 2). In particular, at very small misfit strains, the 2D clamping stabilizes the \( r \) phase in PST films, but not the \( c \) phase as in PT films. Since all three polarization components differ from zero in the \( r \) phase, the physical properties of a clamped PST film are expected to deviate markedly from those of a mechanically free film, which stabilizes in the tetragonal ferroelectric phase.\(^{22}\)

The constructed diagram was used to evaluate the in-plane permittivities of the PST film grown on \( (110)\)-oriented NdGaO\(_3\) substrate. The misfit strains in this film/substrate system were estimated to be \( \epsilon_{11} = -5.4 \times 10^{-4} \) and \( \epsilon_{22} = -8 \times 10^{-5} \).\(^{23}\) Taking into account that these values fall into the stability range of the \( ca^* \) polarization state, we calculated the dielectric anisotropy of PST film to be \( \varepsilon_{22}/\varepsilon_{11} = 1.4 \). The predicted degree of anisotropy is in reasonable agreement with the measured value of \( \varepsilon_{22}/\varepsilon_{11} \approx 1.25 \).\(^{14}\)

Thus, the thermodynamic theory explains the influence of strain anisotropy on the dielectric properties of ferroelectric films. It may be further extended to describe the electric-field dependence of the dielectric response, which is important for the application of ferroelectric films in tunable microwave devices.

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17. Lattice parameters of a strained epitaxial film can be evaluated by the x-ray diffraction. If the epitaxial interface is commensurate, the crystallographic plane parallel to its surface. When dense arrays of misfit dislocations form at the interface, lattice parameters in the epitaxial layer tend to those of a free standing film.
19. Our results are also valid for epitaxial films grown on (110)-oriented cubic or orthorhombic substrates and other substrates that do not induce shear strains in the film plane.
23. The misfit strains were calculated from the measured lattice parameters of the PST film, which are given in Ref. 14. The lattice constant \( a_0 \approx 0.39 \) 197 nm of the prototypic cubic cell was found by fitting the theoretical out-of-plane lattice parameter to the measured value.