Dielectric tunability of (110) oriented barium strontium titanate epitaxial films on (100) orthorhombic substrates

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We develop a thermodynamic model to determine the polarization, dielectric permittivity, and tunability of epitaxial ferroelectric films on orthorhombic substrates. In particular, we study the film thickness dependence of the tunability in epitaxial (110) $Ba_{0.6}Sr_{0.4}TiO_3$ films on (001) $NdGaO_3$ substrates. The analysis takes into account the thickness dependence of the internal stress state due to the anisotropic relaxation of epitaxial stresses through the formation of misfit dislocations along the two in-plane directions. We predict significant improvement in the tunability along both in-plane and out-of-plane directions of $Ba_{0.6}Sr_{0.4}TiO_3$ films with increasing film thickness compared to the similar films on cubic substrates. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2234839]

In recent years, much attention has been devoted to the development of tunable dielectric materials for voltage-controlled, frequency-agile phase shifters and filters operating in the microwave regime. Ferroelectric (FE) materials such as barium strontium titanate $[Ba_{1-x}Sr_xTiO_3$ (BST)] have emerged as leading candidates for such applications due to their highly nonlinear dielectric response to an applied electric field, especially in the vicinity of the paraelectric-to-ferroelectric phase transformation temperature T_C. Ideally, a tunable device would operate in the paraelectric (PE) state not too far from T_C where the dielectric tunability is the greatest to eliminate losses due to nucleation-and-growth controlled polarization switching leading to a hysteretic behavior in the FE state. It is, therefore, not surprising that $Ba_{0.6}Sr_{0.4}TiO_3$ (BST 60/40) has attracted significant interest as the material of choice, since bulk T_C of BST 60/40 is just below room temperature (5 °C). The dielectric tunability of FEs in thin film form displays a significant dependence on the internal stress state and the clamping of the substrate. This has been well documented both experimentally[1–4] and theoretically[4,5] for FE films on cubic substrates for which the in-plane internal stresses are isotropic.

Very recently, it was shown that by depositing FE films on orthorhombic substrates such as $NdGaO_3$ (NGO), it is possible to induce directionally dependent dielectric and tunable properties due to the anisotropic in-plane internal stresses.[6–11] In a series of studies, Simon *et al.* have systematically analyzed the structure, strain state, dielectric response, and tunability of (110) BST 60/40 on (001) NGO.[6–8] Electrical measurements reveal that higher tunabilities can be obtained by adjusting anisotropic in-plane stresses through the film thickness (>50% at 50 kV/cm) (Ref. 6) compared to similar films on cubic substrates.[4,11] Theoretically, the effect of anisotropic in-plane strains on phase transformation characteristics and dielectric response for epitaxial (001) FE films on (001) orthorhombic substrates was investigated.[12] This epitaxial relation, however, is not observed in experimental reports of FE films on orthorhombic substrates. For example, epitaxial BST 60/40 grows preferentially on NGO with the orientational relation $(110)_{BST}\|(001)_{NGO}$ to minimize in-plane strains.[6–8] Such an epitaxial relation obviously generates a different reduction in the point group symmetry of the FE compared to $(001)_{BST}\|(001)_{NGO}$. In this study we analyze theoretically the dielectric tunability of such films as a function of film thickness as to provide quantitative tools to guide experimental studies that aim to develop highly tunable devices.

Consider an epitaxial (110) FE film on a thick (001) orthorhombic substrate (Fig. 1). The total strain in the film is the sum of the polarization-free effective misfit u_{ij} and self-strains u_{ij}^0 expressed as

$$u_{ij}^T = u_{ij} - u_{ij}^0, \quad i,j = 1,2,3. \tag{1}$$

Given the mechanical boundary conditions for the film, u_{12}, u_{13}, u_{23}, and u_{33} are stress-free strains due to the traction-free surfaces and do not contribute to the elastic energy of the film. u_{11} and u_{22} are the in-plane misfits along $[001]_{FE}$ and $[\bar{1}10]_{FE}$ given by $u_{11}=[a_{[100]}-d_{[001]}]/a_{[100]}$ and $u_{22}=[a_{[010]}-d_{[\bar{1}10]}]/a_{[010]}$, respectively, where $a_{[100]}$ and $a_{[010]}$ are the lattice parameters of the substrate in the given directions and $d_{[001]}$ and $d_{[\bar{1}10]}$ are the lattice parameters along [001] and $[\bar{1}10]$ of unconstrained (bulk) FE in the PE state at room temperature (RT). The self-strain of the FE phase transformation can be expressed as a function of the electrostrictive coefficients Q_{ijkl} and polarization P_i:

$$u_{ij}^0 = P_i \cdot Q_{ijkl} \cdot P_l. \tag{2}$$

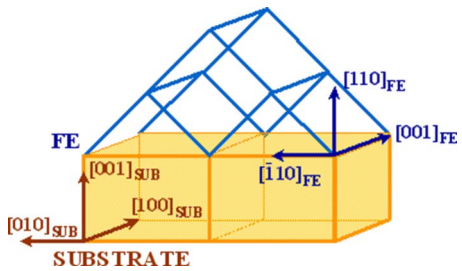

FIG. 1. (Color online) Crystallographic relation of the (110) BST 60/40 film with respect to the (001) NGO substrate and the coordinate systems used in the calculations.

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The total free energy density of the film is given by $G_\Sigma = G_0 + G_L + G_{EL} + G_{ES}$, where G_0 is the energy of the PE state. In this relation, G_L, G_{EL}, and G_{ES} define the energy in the FE state, the elastic energy of the internal stresses, and the electrostatic energy due to an applied electric field E_i, respectively, and are given by

$$G_L = \alpha_i P_i^2 + \alpha_{ij} P_i^2 P_j^2 + \alpha_{ijk} P_i^2 P_j^2 P_k^2, \tag{3a}$$

$$G_{EL} = \frac{1}{2} u_{ij}^T \cdot C_{ijkl} \cdot u_{kl}^T, \quad G_{ES} = -E_i \cdot P_i, \tag{3b}$$

where α_i, α_{ij}, and α_{ijk} are the dielectric stiffness coefficients, P_i is the polarization vector, and C_{ijkl} are the elastic coefficients at constant polarization of the film. After some rearrangement, we obtain

$$\begin{aligned} G_\Sigma = {} & \bar{\alpha}_1 P_1^2 + \bar{\alpha}_2 P_2^2 + \bar{\alpha}_3 P_3^2 + \bar{\alpha}_{11} P_1^4 + \bar{\alpha}_{22} P_2^4 + \bar{\alpha}_{33} P_3^4 \\ & + \bar{\alpha}_{12} P_1^2 P_2^2 + \bar{\alpha}_{13} P_1^2 P_3^2 + \bar{\alpha}_{23} P_2^2 P_3^2 + \alpha_{111}(P_1^6 + P_2^6 \\ & + P_3^6) + \alpha_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_1^2 + P_3^2) + P_3^4(P_1^2 \\ & + P_2^2)] + \alpha_{123} P_1^2 P_2^2 P_3^2 + \bar{G}_{EL} - E_3 P_3 - E_2 P_2 - E_1 P_1, \end{aligned} \tag{4}$$

with $\bar{\alpha}_i$ and $\bar{\alpha}_{ij}$ being renormalized dielectric stiffness coefficients. These are a function of C_{ijkl}, Q_{ijkl}, u_{11} and u_{22}. The first-order renormalized coefficients are given by

$$\begin{aligned} \bar{\alpha}_1 &= \alpha_1 + Q_{11} A + Q_{12} B, \quad \bar{\alpha}_2 = \alpha_1 + Q_{12} A + Q_{22} B, \quad \bar{\alpha}_3 \\ &= \alpha_1 + Q_{13} A + Q_{23} B, \end{aligned} \tag{5}$$

where $\alpha_1 = (T - T_C)/2\varepsilon_0 C$, T_C and C are the Curie-Weiss temperature and constant of the FE, ε_0 is the permittivity of free space, and

$$A = -\frac{4C_{13}^2 + 2C_{11}C_{33}}{2C_{33}} u_{11} - \frac{4C_{13}C_{23} + 2C_{12}C_{33}}{2C_{33}} u_{22},$$

$$B = -\frac{4C_{13}C_{23} + 2C_{12}C_{33}}{2C_{33}} u_{11} - \frac{2C_{22}C_{33} + 4C_{23}^2}{2C_{33}} u_{22}. \tag{6}$$

$\bar{G}_{EL}$ in Eq. (4) is the polarization-free elastic energy of the PE state:

$$\begin{aligned} \bar{G}_{EL} = {} & \left(\frac{C_{11}}{2} + \frac{C_{13}^2}{C_{33}} \right) u_{11}^2 + \left(C_{12} + \frac{2C_{23}C_{13}}{C_{33}} \right) u_{11} u_{22} \\ & + \left(\frac{C_{22}}{2} + \frac{C_{23}^2}{C_{33}} \right) u_{22}^2. \end{aligned} \tag{7}$$

For brevity, in Eqs. (5)–(7), C_{ijkl} and Q_{ijkl} are expressed in the Voigt convention.

The elastic and electrostrictive coefficients of the film with $(110)_{FE} \| (001)_{sub}$ epitaxy can be determined from the single-crystal values of the (001) FE through a tensor transformation:

$$C_{mnop} = a_{mi} a_{nj} a_{ok} a_{pl} c_{ijkl}, \tag{8}$$

$$Q_{mnop} = a_{mi} a_{nj} a_{ok} a_{pl} q_{ijkl}, \tag{9}$$

where c_{ijkl} and q_{ijkl} are the elastic and the electrostrictive constants of a (001) oriented single-crystal FE of the same composition, respectively, and a_{ij} is the transformation matrix consisting of the direction cosines:

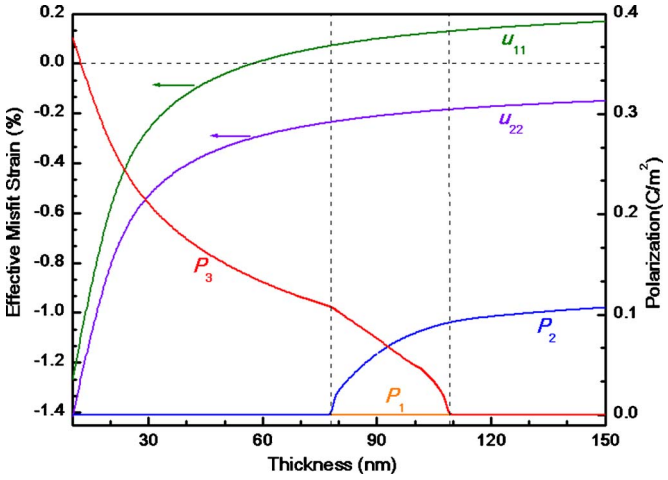

FIG. 2. (Color online) Effective in-plane misfit strains (u_{11} and u_{22}) and the polarization components (P_i) as functions of film thickness in an epitaxial (110) BST 60/40 film on (001) NGO substrate.

$$a_{ij} = \begin{bmatrix} 0 & 0 & -1 \\ -\sqrt{2}/2 & \sqrt{2}/2 & 0 \\ \sqrt{2}/2 & \sqrt{2}/2 & 0 \end{bmatrix}. \tag{10}$$

In this study, we numerically analyzed (110) BST 60/40 films on (001) NGO substrates. Thermodynamic, electrostrictive, and elastic constants of BST 60/40 were compiled from Ref. 13. The lattice parameters of BST 60/40 are 0.3965 and 0.5607 nm along $[001]_{BST}$ and $[\bar{1}10]_{BST}$, respectively, at RT. The interplanar spacing along $[100]_{NGO}$ and $[010]_{NGO}$ are 0.7715 and 0.5501 nm, respectively, at RT.[7] Thus, the misfit strains for pseudomorphic BST 60/40 films are $u_{11} = -2.79\%$ and $u_{22} = -1.93\%$ considering that NGO has two Bravais lattices per unit cell. Assuming a typical growth temperature of $T_G = 600\ ^\circ\text{C}$, relaxation by misfit dislocations is expected to occur at two different critical thicknesses that can be estimated as 5 and 7 nm along $[001]_{BST}$ and $[\bar{1}10]_{BST}$, respectively.[7] Using these values, the thickness dependent in-plane "effective" misfit strains[14] u_{11} and u_{22} are calculated as shown in Fig. 2. Both strains are compressive at first and gradually relax with increasing thickness. u_{22} reaches small tensile values above 60 nm and levels off. This is due to the difference between the misfit at T_G and RT that results in thermal stresses.

Spontaneous polarization in the BST 60/40 can be determined through the simultaneous solution of the equations of state $dG_\Sigma/dP_i = 0$ for u_{11}-u_{22} pairs at a given thickness. In our calculations, we do not assume *a priori* phase(s) resulting from the loss of symmetry due to the anisotropic internal stress state but seek solutions corresponding to global minimum of the free energy functional from real, positive values of the components of the spontaneous polarization vector as a function of u_{11} and u_{22}. The thickness dependences of spontaneous polarizations P_1, P_2, and P_3 are plotted in Fig. 2. The different misfit values in the plane of the film at compressive values favor polarization along $[110]_{BST}$ (P_3) that gradually disappears with increasing thickness. Polarization along $[\bar{1}10]_{BST}$ (P_2) emerges after u_{22} becomes tensile, at ~80 nm. For thicknesses between 80 and 110 nm, P_2 and P_3 coexist. There is no spontaneous polarization along $[001]_{BST}$ (P_1) in the entire thickness range due to the compressive

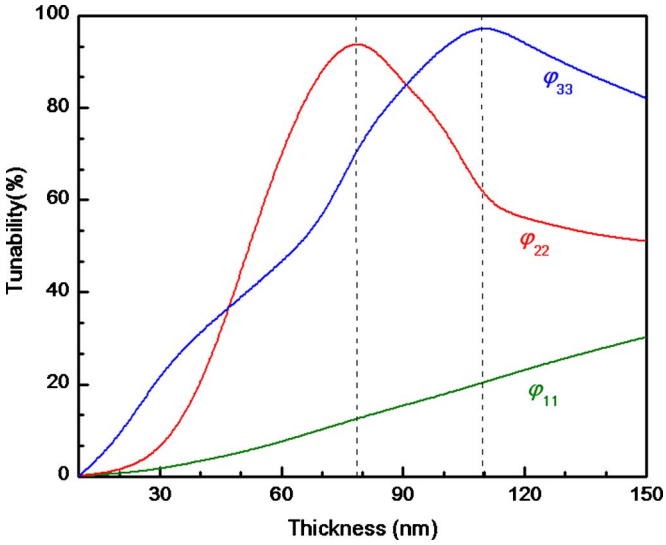

FIG. 3. (Color online) Tunabilities along in-plane ($\varphi_{11}, \varphi_{22}$) and out-of-plane ($\varphi_{33}$) directions as a function of film thickness in an epitaxial (110) BST 60/40 film on (001) NGO substrate.

strain along this direction. The coexistence of P_2 and P_3 results in an asymmetrical case in contrast to films under tensile strains on cubic substrates, where two polarization components of *equal magnitude* along orthogonal axes are favored.[13] Furthermore, different misfit dislocation densities along $[\bar{1}10]_{\mathrm{BST}}$ and $[001]_{\mathrm{BST}}$ produce a more pronounced anisotropic in-plane polarization behavior along various film directions.

The dielectric permittivity is given by

$$\varepsilon_{ij} = \frac{1}{\varepsilon_0}\left(\frac{\partial^2 G_\Sigma}{\partial P_i \cdot \partial P_j}\right)^{-1}, \tag{11}$$

and the dielectric tunability can be defined as $\varphi_{ij}=[\varepsilon_{ij}(E_i=0)-\varepsilon_{ij}(E_i>0)]/\varepsilon_{ij}(E_i=0)$. The dielectric permittivities along $[\bar{1}10]_{\mathrm{BST}}$ (ε_{22}) and $[110]_{\mathrm{BST}}$ (ε_{33}) display the characteristics of a phase transition at two critical thicknesses of ~80 and 110 nm (not shown) which coincide with the emergence of P_2 and the disappearance of P_3, respectively (see Fig. 2). Tunabilities along in-plane and out-of-plane directions as a function of film thickness for an applied field of 50 kV/cm are plotted in Fig. 3. The maximum tunable response along $[\bar{1}10]_{\mathrm{BST}}$ (φ_{22}) and $[110]_{\mathrm{BST}}$ (φ_{33}) are at ~80 and 110 nm, which correspond to the λ-type response in the permittivity at these critical thicknesses. φ_{11} is smaller than both φ_{22} and φ_{33} and increases almost linearly with film thickness. This is due to the absence of a spontaneous polarization along $[001]_{\mathrm{BST}}$. The tunability is in this case a result of the variation in the induced polarization with the applied electric field. The theoretically calculated values of φ_{33} of BST 60/40 on NGO are relatively higher even at low film thicknesses compared to the predicted values for BST on isotropic cubic substrates.[5] The findings of this study are also in excellent qualitative agreement with the experimental observations where a similar trend in the out-of-plane tunability was measured as a function of film thickness.[6] Experimentally, a maximum in the tunability was found to occur at a film thickness ⩾600 nm. This can be attributed to a number of dynamic factors including the kinetics of formation of misfit dislocations which usually start at thicknesses significantly larger than the calculated critical thickness[15] and the high frequency of the measurement (in the gigahertz regime).

In summary, we have analyzed theoretically the dielectric tunability of FE films on substrates that induce anisotropic in-plane stresses. Results for (110) BST 60/40 films on (001) NGO as a function of film thickness show that very high tunabilities can be realized along *two* directions ($[110]_{\mathrm{BST}}$ and $[\bar{1}10]_{\mathrm{BST}}$) at two critical thicknesses. This behavior is due to strain-induced phase transitions along these directions that arise from the reduction in the point group symmetry brought about by the anisotropic stress state.

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