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Phase Transformation Characteristics of Barium Strontium Titanate Films on Anisotropic Substrates with (001)//(001) Epitaxy

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ABSTRACT

The role of anisotropic misfit strains on the spontaneous polarization of (100) oriented $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ thin films on (100) orthorhombic substrates is theoretically analyzed. A modified thermodynamic model is utilized to evaluate the equilibrium polarization values as a function of the anisotropic misfit strains. Results show that ferroelectric phases that cannot be observed in single-crystal $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ can be stabilized due to the reduction in the symmetry induced by the anisotropic strain state.

Keywords: Ferroelectric thin films, anisotropy, monoclinic phase, thermodynamics

INTRODUCTION

Thin films of barium strontium titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, BST) are of great technological interest due to their desirable ferroelectric and dielectric properties. Their high dielectric response offers the potential of replacing the current silicon oxide and nitride dielectrics in the next generation dynamic random access memories (DRAM) which require higher integration densities. The dielectric response of these materials is strongly dependent on the applied electric field. This is an attractive property for frequency-agile microwave electronic components (including phase shifters, varactors, tunable filters and antennas). Furthermore, BST compounds have high pyroelectric coefficients and thus can

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be used in infrared (IR) detection as active sensing elements of focal plane arrays in thermal imaging systems.

Much of the work concerning the high dielectric tunability and pyroelectric applications of BST films form consists of growing these on substrates with cubic (or pseudo-cubic) lattices such as Si, MgO, SrTiO₃, and LaAlO₃ [1–9]. Theoretical models have been devised to understand the relation between the internal stresses (or strains) and the electrical and electromechanical properties of BST films [10–12]. Cubic substrates generate internal stresses with equal orthogonal components along the in-plane directions and result in identical polarization components along the principal directions in a plane parallel to the film-substrate interface. Theoretically, the role of anisotropic in-plane misfit strains on the phase transformation characteristics and the dielectric response of (100) PbTiO₃ and (100) Pb_{0.35}Sr_{0.65}TiO₃ on (100) orthorhombic substrates has been addressed [13]. Moreover, recently, we have developed a model based on the Landau-Devonshire theory of phase transformations to describe the role of anisotropic misfit on the dielectric tunability of (110) BST 60/40 ferroelectric thin films on orthorhombic (100) NdGaO₃ (NGO) [14]. In this report, we utilize a thermodynamic approach developed in Ref. [13] to discuss the effect of anisotropy for (001) BST 60/40 films on any (001) orthorhombic substrate by treating the in-plane strains as variables. The three-dimensional plots of polarization as a function asymmetric in-plane misfit strains point to the existence of monoclinic and triclinic phases in BST 60/40 films on anisotropic substrates at certain misfit strain pairs. These phases are not observed in the bulk form of BST 60/40.

THEORY

Consider a (001) oriented BST 60/40 film on any thick (001) oriented orthorhombic substrate (Fig. 1). The total strain in the BST 60/40 film is the sum of the polarization-free misfit, u_{ij} , and self-strains, u_{ij}^0 expressed as:

$$u_{ij}^T = u_{ij} + u_{ij}^0, \quad i, j = 1, 2, 3 \quad (1)$$

The self-strain of the ferroelectric phase transformation can be expressed as a function of the electrostrictive coefficients Q_{ijkl} of bulk BST 60/40 and polarization P_i :

$$u_{ij}^0 = P_i \cdot Q_{ijkl} \cdot P_l \quad (2)$$

The total free energy density of the film is given by:

$$G_\Sigma = G_0 + G_L + G_{EL} + G_{ES}, \quad (3)$$

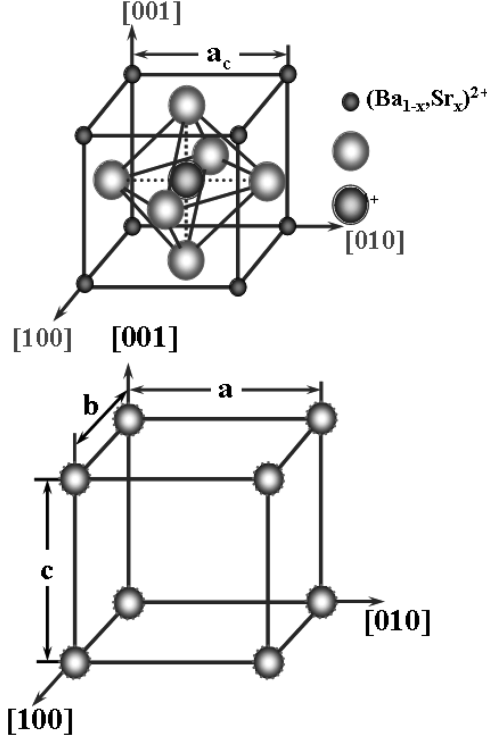


Figure 1. The crystal structure of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) and (001)//(001) epitaxy between the BST film and an orthorhombic substrate.

where G_0 is the energy of the paraelectric state. In Eq. (3), G_L , G_{EL} , and G_{ES} define the energy in the ferroelectric state, the elastic energy of the internal stresses, and the electrostatic energy due to an applied electric field E_i , respectively, such that:

$$G_L = \alpha_i P_i^2 + \alpha_{ij} P_i^2 P_j^2 + \alpha_{ijk} P_i^2 P_j^2 P_k^2, \quad (4)$$

$$G_{EL} = \frac{1}{2} u_{ij}^T \cdot C_{ijkl} \cdot u_{kl}^T, \quad (5)$$

$$G_{ES} = -E_i \cdot P_i \quad (6)$$

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 bulk film, defined in the pseudo-cubic coordinate system $(x_i // [100]_{\text{substrate}})$,

$x_2//[010]_{\text{substrate}}, x_3//[001]_{\text{substrate}}$). Thus, G_{Σ} is given by [13]:

$$\begin{aligned} G_{\Sigma} = & \bar{\alpha}_1 P_1^2 + \bar{\alpha}_2 P_2^2 + \bar{\alpha}_3 P_3^2 + \bar{\alpha}_{11} (P_1^4 + P_2^4) + \bar{\alpha}_{33} P_3^4 + \bar{\alpha}_{12} P_1^2 P_2^2 \\ & + \bar{\alpha}_{13} (P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{111} (P_1^6 + P_2^6 + P_3^6) \\ & + \alpha_{112} [P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2)] \\ & + \alpha_{123} P_1^2 P_2^2 P_3^2 + \bar{G}_{EL} - E_3 P_3 - E_2 P_2 - E_1 P_1 \end{aligned} \quad (7)$$

with $\bar{\alpha}_i$ and $\bar{\alpha}_{ij}$ being renormalized dielectric stiffness coefficients which are modified by $C_{ijkl}, Q_{ijkl}, u_{11}$, and u_{22} to reflect the presence of internal strain and its coupling to the polarization via electrostriction. These coefficients are given by:

$$\bar{\alpha}_1 = \alpha_1 + \frac{1}{C_{11}} [(C_{12}^2 - C_{11}C_{12}) Q_{12} + (C_{12}^2 - C_{11}^2) Q_{11}] (u_{11} + u_{22}) \quad (8a)$$

$$\bar{\alpha}_2 = \alpha_1 + \frac{1}{C_{11}} [(C_{12}^2 - C_{11}C_{12}) Q_{11} + (C_{12}^2 - C_{11}^2) Q_{12}] (u_{11} + u_{22}) \quad (8b)$$

$$\bar{\alpha}_3 = \alpha_1 + \frac{1}{C_{11}} (2C_{12}^2 + C_{11}C_{12} - C_{11}^2) Q_{12} (u_{11} + u_{22}) \quad (8c)$$

$$\bar{\alpha}_{11} = \alpha_{11} + \frac{1}{2C_{11}} [(C_{11}^2 - C_{12}^2) (Q_{11}^2 + Q_{12}^2) + (2C_{11}C_{12} - 2C_{12}^2) Q_{11}Q_{12}] \quad (8d)$$

$$\bar{\alpha}_{33} = \alpha_{11} + \frac{1}{C_{11}} (C_{11}^2 + 2C_{11}C_{12} - 2C_{12}^2) Q_{12}^2 \quad (8e)$$

$$\bar{\alpha}_{12} = \alpha_{12} + \frac{1}{C_{11}} [(C_{11}C_{12} - C_{12}^2) (Q_{11}^2 + Q_{12}^2) + 2(C_{11}^2 - C_{12}^2) Q_{11}Q_{12}] \quad (8f)$$

$$\bar{\alpha}_{13} = \alpha_{12} + \frac{1}{C_{11}} (C_{11}^2 + C_{11}C_{12} - 2C_{12}^2) (Q_{12}^2 + Q_{11}Q_{12}) \quad (8g)$$

In the above relations, $\alpha_1 = (T - T_C)/2\varepsilon_0 C$, T_C and C are the Curie-Weiss temperature and constant of BST 60/40, and ε_0 is the permittivity of free space. Furthermore, α_{ij} are the dielectric stiffness coefficients of bulk BST 60/40.

\bar{G}_{EL} in Eq. (7), is the polarization-free elastic energy of the BST in the paraelectric state:

$$\bar{G}_{EL} = \frac{1}{2C_{11}} [(2C_{11}C_{12} - 2C_{12}^2) u_{11}u_{22} + (C_{11}^2 - C_{12}^2) (u_{11}^2 + u_{22}^2)]. \quad (9)$$

For brevity, C_{ijkl} and Q_{ijkl} are expressed in the contracted (Voigt) notation in Eqs. (8) and (9).

The equilibrium values of the polarization are obtained by the optimization of the modified Landau potential with respect to the polarization vector resulting in:

$$\begin{aligned} \frac{\partial G_{\Sigma}}{\partial P_1} = & 2\bar{\alpha}_1 P_1 + 4\bar{\alpha}_{11} P_1^3 + 2\bar{\alpha}_{12} P_1 P_2^2 + 2\bar{\alpha}_{13} P_1 P_3^2 + 6\alpha_{111} P_1^5 \\ & + 4\alpha_{112} P_1^3 (P_2^2 + P_3^2) + 2\alpha_{112} P_1 (P_2^4 + P_3^4) + 2\alpha_{123} P_1 P_2^2 P_3^2 - E_1 = 0 \end{aligned} \quad (10a)$$

$$\begin{aligned} \frac{\partial G_{\Sigma}}{\partial P_2} = & 2\bar{\alpha}_2 P_2 + 4\bar{\alpha}_{11} P_2^3 + 2\bar{\alpha}_{12} P_2 P_1^2 + 2\bar{\alpha}_{13} P_2 P_3^2 + 6\alpha_{111} P_2^5 \\ & + 4\alpha_{112} P_2^3 (P_1^2 + P_3^2) + 2\alpha_{112} P_2 (P_1^4 + P_3^4) + 2\alpha_{123} P_1^2 P_2 P_3^2 - E_2 = 0 \end{aligned} \quad (10b)$$

$$\begin{aligned} \frac{\partial G_{\Sigma}}{\partial P_3} = & 2\bar{\alpha}_3 P_3 + 4\bar{\alpha}_{33} P_3^3 + 2\bar{\alpha}_{13} (P_3 P_1^2 + P_3 P_2^2) + 6\alpha_{111} P_3^5 \\ & + 4\alpha_{112} P_3^3 (P_1^2 + P_2^2) + 2\alpha_{112} P_3 (P_1^4 + P_2^4) + 2\alpha_{123} P_1^2 P_2^2 P_3 - E_3 = 0 \end{aligned} \quad (10c)$$

The simultaneous solution of these three equations with the modified coefficients will give us the spontaneous polarization of BST 60/40 films on orthorhombic substrates as a function of the in-plane misfit strains u_{11} and u_{22} (with $E_i = 0$).

RESULTS AND DISCUSSION

Figure 2 shows three-dimensional (3D) plots of the polarization vector components of BST 60/40 films on orthorhombic substrates with (001)//(001) epitaxy as functions of misfit strains. These plots can be used to predict the effects of anisotropic misfit strain on the polarization values, ferroelectric properties, and phase transformation characteristics. Hence, the ferroelectric behavior of BST 60/40 films can be forecast for a variety of anisotropic substrates with (001) epitaxy.

By looking at the intersections of 3D polarization surfaces [Fig. 2(d)], we define regions of misfit strains that correspond to possible ferroelectric phases (or microstructures) as seen in Fig. 3. The film would obviously be paraelectric for the points of all three zero polarization components ($P_1 = P_2 = P_3 = 0$). In Fig. 2(d), we observe this only at the origin of the 3D diagram where $u_{11} = 0$ and $u_{22} = 0$. This point defines a clamped BST 60/40 film with no misfit strain.

If only P_1 , P_2 or P_3 is present, the crystal structure would be tetragonal. In regions where the combinations of P_1 and P_2 ($P_3 = 0$), P_1 and P_3 ($P_2 = 0$), or P_3 and P_2 ($P_1 = 0$) coexist, the structure of the film would be orthorhombic. Furthermore, in the regions, where all three polarization components exist, the structure could be rhombohedral, monoclinic or triclinic. The set of $P_1 = P_2 = P_3 \neq 0$ (or variations of this condition) would give a rhombohedral phase while $P_1 = P_2 \neq P_3 \neq 0$ (or variations of this condition) would result in a

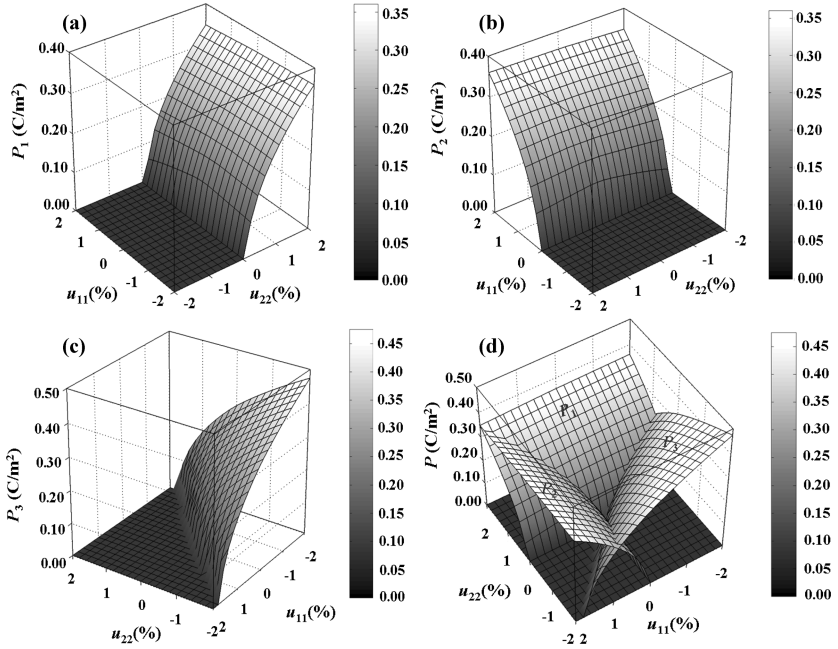


Figure 2. 3D diagrams of polarization components along three directions (P_1 , P_2 , P_3) of the BST 60/40 ferroelectric film as a function of the asymmetric in-plane misfit strains (u_{11} , u_{22}), corresponding to the strain states of different orthorhombic substrates.

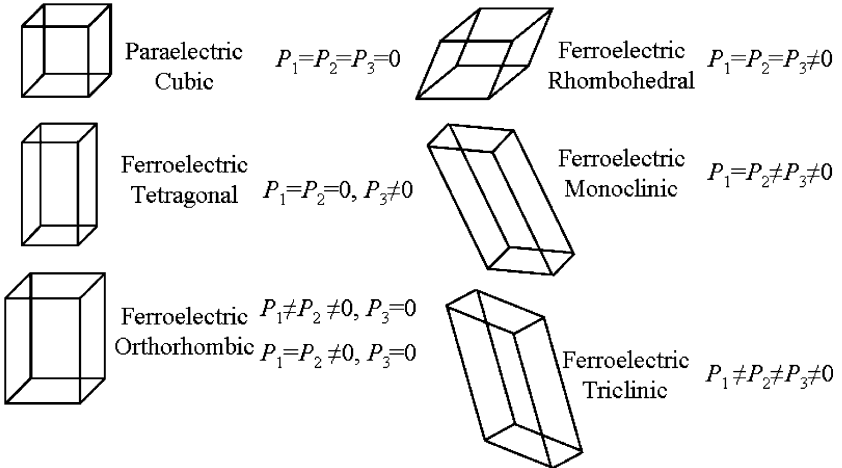


Figure 3. Possible ferroelectric microstructures (or phases) for a BST 60/40 on an orthorhombic substrate.

monoclinic phase. Moreover, the condition of $P_1 \neq P_2 \neq P_3 \neq 0$ would form a triclinic phase. In the case of BST 60/40 on any orthorhombic substrate with (001)//(001) epitaxy, there are no such regions where all the three polarization components co-exist. However, if the formation of the BST 60/40 film on the substrate occurs with a different epitaxy such as (110)//(100) [15, 16], it is possible to have all three polarization components, giving us three possible aforementioned sets of ferroelectric phases.

CONCLUSIONS

We analyzed theoretically the role of anisotropic in-plane strains on the polarization of barium strontium titanate films with (001) epitaxy on (001) orthorhombic substrates. The theoretical model was based on a non-linear thermodynamics approach that takes into account the asymmetric in-plane misfit strains. It was shown that the anisotropic strain would bring about a point group symmetry reduction in the ferroelectric film that is different than that of isotropic cubic substrates. This leads to the formation of unique crystal structures (or phases) that cannot be observed in bulk or in films on cubic substrates. These unusual crystal structures would promote highly directional ferroelectric properties, which can be used in practical applications where direction-dependent properties are desired.

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