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The enhanced piezoelectricity in compositionally graded ferroelectric thin films under electric field: A role of flexoelectric effect

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Compositionally graded ferroelectric thin films are found to produce large strain gradients, which can be used to tune the physical properties of materials through the flexoelectric effect, i.e., the coupling of polarization and the strain gradient. The influences of the flexoelectric effect on the polarization distribution and the piezoelectric properties in compositionally graded $Ba_{1-x}Sr_xTiO_3$ ferroelectric thin films are investigated by using an extended thermodynamic theory. The calculation results show that the presence of the flexoelectric effect tends to enhance and stabilize polarization components. The polarization rotation induced by the flexoelectric field has been predicted, which is accompanied by more uniform and orderly polarization components. A remarkable enhancement of piezoelectricity is obtained when the flexoelectric field is considered, suggesting that compositionally graded $Ba_{1-x}Sr_xTiO_3$ ferroelectric thin films with a large strain gradient are promising candidates for piezoelectric devices. *Published by AIP Publishing.*
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I. INTRODUCTION

Compositionally graded ferroelectric thin films possess a smoothly spatial variation in the chemical composition throughout the thickness, which demonstrates a macroscopic asymmetry in comparison to their homogeneous counterparts.[1–3] Such a unique characteristic has been shown to result in self-poling,[4] shifted hysteresis loops,[5–7] enhanced susceptibilities,[8–10] and signatures of geometric frustration.[11] Furthermore, they have attracted significant attention for their potential applications in microelectronic devices such as high-density dynamic random access memories, pyroelectric infrared detectors, and microwave devices because of their high relative dielectric constant, low dielectric loss, high pyroelectric coefficient, and good dielectric tenability.[12–14]

Theoretical work has shown that a large strain gradient can be more easily sustained in thin films ($>10^5\,m^{-1}$)[15] than in bulk crystals ($<1\,m^{-1}$).[16] In particular, a much larger strain gradient induced by the difference of lattice constant between material compositions may exist in compositionally graded ferroelectric thin films. A detailed investigation on the compositionally graded $PbZr_{1-x}Ti_xO_3$ thin films with a strain gradient of $5\times10^5 m^{-1}$ has been performed by using Ginzburg-Landau-Devonshire theory.[17] A recent experiment also has confirmed the presence of a large out-of-plane strain gradient of $4.3\times10^5 m^{-1}$ along the compositionally graded ferroelectric thin film thickness.[18] Therefore, the flexoelectric effect, i.e., the coupling of polarization and the strain gradient,[19–22] may significantly affect the properties of materials.[23–29] In contrast to ferroelectricity that exists only in materials with non-centrosymmetric crystal structures, the flexoelectric effect can exist in all dielectric materials regardless of symmetry, which can be used to realize the conversion of mechanical energy and electrical energy.[30–33] Furthermore, the flexoelectric effect has drawn more and more attention in recent years due to its wide variety of potential applications in nanoscale electromechanical devices, including actuators, nanogenerators, energy harvesters, and sensors.[34–36]

To fully understand how the flexoelectric effect will change the physical properties of compositionally graded ferroelectric thin films, some theoretical and experimental works have been done to explore internal mechanisms. For instance, theoretically, Martin *et al.* found that the large built-in electric field caused by the flexoelectric effect is directly responsible for the observed voltage offsets in the hysteresis loops.[17] Meanwhile, this result was observed by experiments.[37,38] What's more, large built-in fields produced by flexoelectric effects can diminish the temperature dependence of the polarization and susceptibilities.[39] Therefore, the flexoelectric effect plays a key role in dramatically influencing the properties of compositionally graded ferroelectric thin films.

More recently, many articles have focused on the influences of the flexoelectric effect on the dielectric and

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electrocaloric properties of compositionally graded ferroelectric thin films.[14,40,41] However, the contribution of the flexoelectric effect to the piezoelectric properties of compositionally graded ferroelectrics is less investigated although electromechanical behaviors of ferroelectrics become more and more important in recent works.[42–44] Previous studies demonstrated that the electrical signals can be readily written on ultrathin ferroelectric polymer films by mechanical force-induced polarization switching via the flexoelectric effect.[45–48] In addition, Catalan *et al*. investigated the electromechanical response of ferroelectrics and found that the inhomogeneous deformation induces a flexoelectric polarization, which either adds to or subtracts from the piezoelectricity of the domains depending on their ferroelectric sign.[49] Additionally, in some potential applications of electromechanical properties in ferroelectric films, especially the flexoelectric effect on the piezoelectricity of materials has stimulated a surge of interest.[50–52] Furthermore, in the context of considering the importance of the flexoelectric effect for compositionally graded ferroelectric thin films, the question of how the electromechanical responses should evolve remains unanswered, which motivates us to further explore.

In this work, we construct the effective energy expression of compositionally graded ferroelectric thin films, in which the energies related to the flexoelectric effect are included. The polarization distribution and piezoelectric properties of the film are successfully analyzed and predicted by using the nonlinear Landau Devonshire theory. By carefully taking into account the influence of the flexoelectric effect, our studies reveal that polarization components and polarization rotation are changed dramatically, which results in the complex evolution of piezoelectric properties. We further introduce a flexoelectric field and an external electric field to control physical performances of films together. Interestingly, we find that the flexoelectric effect is beneficial to the piezoelectric properties of compositionally graded ferroelectric thin films under the influence of the external electric field.

II. THERMODYNAMIC MODEL

Here, we perform a comprehensive study of the flexoelectric effect on the polarization distribution and piezoelectric properties in (001)-oriented, single-domain, compositionally graded $Ba_{1-x}Sr_xTiO_3$ ferroelectric films using a nonlinear Landau Devonshire theory.[53–57] For a compositionally graded film epitaxially grown on a substrate, the in-plane strain within the film is a function of the distance x_3 away from the misfit strain with the substrate due to the composition dependence of the lattice constants in $Ba_{1-x}Sr_xTiO_3$. Meanwhile, the out-plane strain is only produced by the Poisson effect, which can be ignored. Therefore, the flexoelectric coupling between the polarization components and the in-plane strain gradient along the thickness is considered in this work. The total effective energy expression takes the form of

$$G = \int (G_h + G_{elec})dv + \int G_{surf} ds, \quad (1)$$

where G_h, G_{elec}, and G_{surf} are the Helmholtz energy, electric field energy, and surface energy, respectively.

A complete free energy expression for the consideration of the flexoelectric effect of the epitaxial film has been given in our previous work. In the previous study, we assumed that the polarization component of a 5 nm-thick $BaTiO_3$ ultrathin film is homogenous along the film thickness. Therefore, the effect of the polarization gradient on the energy expression can be neglected.[58] However, the magnitude of the polarization component P_3 of compositionally graded ferroelectric films varies along the compositionally graded direction in this work. To describe an inhomogeneous polarization field, the polarization gradient energy should be included in the total free energy of a thin film.[59] Thus, the complete Helmholtz free energy can be further expressed as[58,60,61]

$$\begin{aligned} G_h = {} & a_1^*(P_1^2+P_2^2) + a_3^* P_3^2 + a_{11}^*(P_1^4+P_2^4) + a_{33}^* P_3^4 \\ & + a_{13}^*(P_1^2P_3^2+P_2^2P_3^2) + a_{12}^* P_1^2P_2^2 + a_{111}(P_1^6+P_2^6+P_3^6) \\ & + a_{112}\left[P_1^4(P_2^2+P_3^2)+P_2^4(P_1^2+P_3^2)+P_3^4(P_1^2+P_2^2)\right] \\ & + a_{123}P_1^2P_2^2P_3^2 + a_{1111}(P_1^8+P_2^8+P_3^8) \\ & + a_{1112}\left[P_1^6(P_2^2+P_3^2)+P_2^6(P_1^2+P_3^2)+P_3^6(P_1^2+P_2^2)\right] \\ & + a_{1122}(P_1^4P_3^4+P_2^4P_3^4+P_2^4P_1^4) \\ & + a_{1123}(P_1^4P_2^2P_3^2+P_1^2P_2^4P_3^2+P_1^2P_2^2P_3^4) + \frac{u^2}{s_{11}+s_{12}} \\ & + \frac{Q_{12}\mu_{12}}{s_{11}+s_{12}}P_3^2\frac{dP_3}{dz} - \frac{\mu_{12}^2}{s_{11}+s_{12}}P_3\frac{d^2P_3}{dz^2} - \frac{\mu_{12}}{s_{11}+s_{12}}\frac{du}{dz}P_3 \\ & + \frac{\mu_{12}u}{s_{11}+s_{12}}\frac{dP_3}{dz} + \frac{1}{2}g_{11}\left(\frac{dP_3}{dz}\right)^2, \end{aligned} \quad (2)$$

where

$$a_1^* = a_1 - u\frac{Q_{11}+Q_{12}}{s_{11}+s_{12}}, \quad (3a)$$

$$a_3^* = a_1 - u\frac{2Q_{12}}{s_{11}+s_{12}}, \quad (3b)$$

$$a_{11}^* = a_{11} + \frac{1}{2}\frac{1}{s_{11}^2 - s_{12}^2}\left[(Q_{11}^2+Q_{12}^2)s_{11} - 2Q_{11}Q_{12}s_{12}\right], \quad (3c)$$

$$a_{33}^* = a_{11} + \frac{Q_{12}^2}{s_{11}+s_{12}}, \quad (3d)$$

$$a_{12}^* = a_{12} - \frac{1}{s_{11}^2 - s_{12}^2}\left[(Q_{11}^2+Q_{12}^2)s_{12} - 2Q_{11}Q_{12}s_{11}\right] + \frac{Q_{44}^2}{2s_{44}}, \quad (3e)$$

$$a_{13}^* = a_{12} + \frac{Q_{12}(Q_{11}+Q_{12})}{s_{11}+s_{12}}, \quad (3f)$$

$$a_1 = \frac{T-T_0}{2\varepsilon_0 C}, \quad (3g)$$

where a_1, a_{ij}, a_{ijk}, and a_{ijkl} are the dielectric stiffness coefficients, P_i is the polarization component, s_{ij} and Q_{ij} are the elastic compliances and electrostrictive coefficients, and g_{11} and μ_{12} are the gradient coefficient and the flexoelectric coefficient, respectively. Note that we focus on the piezoelectric effect in the thickness direction of the thin films, in which the flexoelectric field and the external electric field are along the thickness direction. The out-of-plane polarization component, P_3, is dominated in the thin films. Therefore, the flexoelectric coefficient μ_{12} is considered in this work. T_0 and C are the Curie-Weiss temperature and constant, respectively, ε_0 is the permittivity of free space, and u is the lattice mismatch strain.

When the compositionally graded ferroelectric film is sandwiched between top and bottom electrodes, the electric field energy can be written as

$$G_{elec} = -P_i E_i - \frac{1}{2} E_{dep} P_3 - E_{bi} P_3, \tag{4}$$

where E_i is the applied electric field, E_{dep} is the depolarizing field, and E_{bi} is the work function field due to the difference between work function steps of ferroelectric-electrode 1 and ferroelectric-electrode 2 interfaces. E_{dep} and E_{bi} can be expressed as follows:[62,63]

$$E_{dep} = -\frac{\lambda_1 + \lambda_2}{h\varepsilon_0 + (\lambda_1 + \lambda_2)\varepsilon_b} P_3, \tag{5}$$

$$E_{bi} = -\frac{\Delta\varphi_2 - \Delta\varphi_1}{h} = -\frac{\varphi}{h}, \tag{6}$$

where h is the thickness of the film, λ_i is the effective screening length of the interface, ε_b is the background dielectric constant, $\Delta\varphi_i$ is the work function step for the ferroelectric electrode i interface, and φ is the difference between work function steps. For a ferroelectric thin film at nanoscale, it is necessary to consider the surface energy which contains contributions of the near interface variation of polarization and the direct coupling between polarizations and interfaces. Note that the surface energy is given by[62,63]

$$G_{surf} = (\zeta_1 - \zeta_2) P_i + \frac{1}{2}(\eta_1 + \eta_2) P_i^2, \tag{7}$$

where ζ_i and η_i are the first order and second order coefficients of the surface energy G_{surf} expansion for the two ferroelectric electrode interfaces.

Minimization of the total free energy of Eq. (1) yields the Euler-Lagrange relations as

$$\frac{\partial G}{\partial P_i} - \frac{d}{dz}\left(\frac{\partial G}{\partial P_i'}\right) = 0. \tag{8}$$

From Eqs. (1) and (8), the equations of state for the ferroelectric films can be obtained.

It should be noted that our previous work has proved the phase diagram of $BaTiO_3$ consists of four equilibrium phases: (1) paraelectric p-phase: $P_1 = P_2 = P_3 = 0$, (2) c-phase: $P_1 = P_2 = 0, P_3 \neq 0$, (3) aa-phase: $P_1 = P_2 \neq 0, P_3 = 0$, and (4) r-phase: $P_1 = P_2 \neq 0, P_3 \neq 0$. Therefore, the equilibrium polarization P_i in the above phases can be given as follows:

For instance, (1) c-phase: $P_1 = P_2 = 0, P_3 \neq 0$, the Euler-Lagrange equation is derived from the minimization of the total free energy

$$\frac{\partial G}{\partial P_3} - \frac{d}{dz}\left(\frac{\partial G}{\partial P_3'}\right) = 0. \tag{8a}$$

Thus, the equations of state for the ferroelectric films can be written as

$$(\eta_1+\eta_2)P_3/h + \Big[8a_{1111}P_3^7 + 6a_{111}P_3^5 + 4a_{33}^*P_3^3 + 2a_3^*P_3 - \left(g_{11} + \frac{2\mu_{12}^2}{s_{11}+s_{12}}\right)\frac{d^2P_3}{dz^2} - \frac{2\mu_{12}}{s_{11}+s_{12}}\frac{du}{dz} - E_3 - E_{dep} - E_{bi}\Big] = 0. \tag{8b}$$

The governing equations of other phases can also be obtained in the same way.

(2) For aa-phase: $P_1 = P_2 \neq 0, P_3 = 0$, the equations of state for the ferroelectric films can be written as follows:

$$2(\eta_1+\eta_2)P_1/h + (16a_{1111}P_1^7 + 16a_{1112}P_1^7 + 8a_{1122}P_1^7 + 12a_{111}P_1^5 + 12a_{112}P_1^5 + 8a_{11}^*P_1^3 + 4a_{12}^*P_1^3 + 4a_1^*P_1) = 0\,. \tag{8c}$$

(3) For r-phase: $P_1 = P_2 \neq 0, P_3 \neq 0$, the equations of state for the ferroelectric films can be written as follows:

$$2(\eta_1+\eta_2)P_1/h + (16a_{1111}P_1^7 + 4a_{1112}(P_1^7 + P_1P_3^6 + 3P_1^5(P_1^2+P_3^2)) + 8a_{1122}(P_1^7 + P_1^3P_3^4) + 4a_{1123}(3P_1^5P_3^2 + P_1^3P_3^4) + 12a_{111}P_1^5 + 4a_{112}\Big(P_1^5 + P_1P_3^4 + 2P_1^3(P_1^2+P_3^2) + 4a_{123}P_1^3P_3^2 + 8a_{11}^*P_1^3 + 4a_{12}^*P_1^3 + 4a_{13}^*P_1P_3^3 + 4a_1^*P_1 - 2\frac{\mu_{12}(Q_{12}+Q_{11})}{(s_{11}+s_{12})}P_1\frac{\partial P_3}{\partial z}\Big) = 0, \tag{8d}$$

$$(\eta_1+\eta_2)P_3/h + \Big(8a_{1111}P_3^7 + 4a_{1112}(P_1^6P_3 + 3P_1^2P_3^5) + 8a_{1122}P_1^4P_3^3 + 4a_{1123}(P_1^6P_3 + P_1^4P_3^2) + 6a_{111}P_3^5 + 4a_{112}(P_1^4P_3 + 2P_1^2P_3^2) + 2a_{123}P_1^4P_3 + 4a_{13}^*P_1^2P_3 + 4a_{33}^*P_3^3 + 2a_3^*P_3 - \left(g_{11} + \frac{2\mu_{12}^2}{s_{11}+s_{12}}\right)\frac{\partial^2P_3}{\partial z^2} - \frac{2\mu_{12}}{s_{11}+s_{12}}\frac{\partial u}{\partial z} - E_3 - E_{dep} - E_{bi}\Big) = 0. \tag{8e}$$

Since the flexoelectric effect is taken into account, the phase can be redefined as follows:[58] (1) ferroelectric c_1-phase (metastable phase): $P_1 = P_2 = 0, |P_{3+}| > |P_{3-}| \neq 0$; (2) dielectric c_2-phase: $P_1 = P_2 = P_{3-} = 0, |P_{3+}| \neq 0$ (Note that there is a nonswitchable polarization in the dielectric phase); (3) dielectric c_3-phase: $P_1 = P_2 = P_{3+} = 0, |P_{3-}| \neq 0$; (4) ferroelectric r_1-phase (metastable phase): $P_1 = P_2 \neq 0, |P_{3+}| > |P_{3-}| \neq 0$; (5) ferroelectric r_2-phase: $P_1 = P_2 \neq 0, |P_{3+}| \neq 0$; and (6) ferroelectric r_3-phase: $P_1 = P_2 \neq 0, |P_{3-}| \neq 0$. Meanwhile, the above equations of state for the ferroelectric films remain unchanged.

The boundary conditions at the interfaces between the film and the bottom or top electrodes are[64,65]

$$\left[P + \lambda\frac{dP}{dZ}\right]_{Z=0,h} = 0, \tag{9}$$

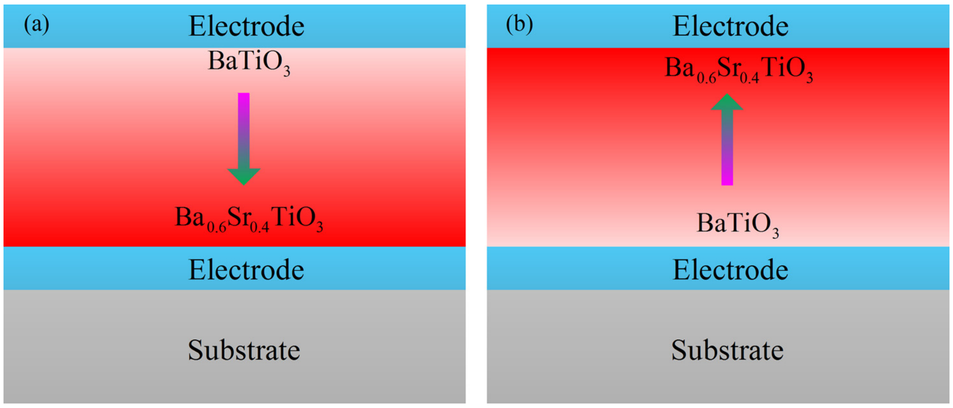

FIG. 1. Schematic configurations of compositionally (a) down-graded and (b) up-graded ferroelectric thin films.

where λ is the extrapolation length, which is taken as infinite here. The equilibrium polarization P_i is determined by solving Eq. (8) numerically.

Once the polarization components of the equilibrium phase are determined, its electromechanical properties can also be derived, such as the relative dielectric constants,[53]

$$\varepsilon_{ij} = 1 + \frac{\eta_{ij}}{\varepsilon_0}, \tag{10}$$

with dielectric susceptibilities

$$\eta = \chi^{-1} = \begin{pmatrix} \frac{\partial^2 G}{\partial P_1 \partial P_1} & \frac{\partial^2 G}{\partial P_1 \partial P_2} & \frac{\partial^2 G}{\partial P_1 \partial P_3} \\ \frac{\partial^2 G}{\partial P_2 \partial P_1} & \frac{\partial^2 G}{\partial P_2 \partial P_2} & \frac{\partial^2 G}{\partial P_2 \partial P_3} \\ \frac{\partial^2 G}{\partial P_3 \partial P_1} & \frac{\partial^2 G}{\partial P_3 \partial P_2} & \frac{\partial^2 G}{\partial P_3 \partial P_3} \end{pmatrix}^{-1} \tag{11}$$

and piezoelectric coefficients $d_{in} = (n = 1, 2 \ldots, 6)$

$$d_{in} = \frac{\partial u_n}{\partial E_i} = \frac{\partial u_n}{\partial P_1}\eta_{i1} + \frac{\partial u_n}{\partial P_2}\eta_{i2} + \frac{\partial u_n}{\partial P_3}\eta_{i3}. \tag{12}$$

III. RESULTS AND DISCUSSION

We explore two model heterostructures: (a) compositionally down-graded ferroelectric thin films (which smoothly transition from $Ba_{0.6}Sr_{0.4}TiO_3$ to $BaTiO_3$ from the substrate to the film surface) and (b) compositionally up-graded ferroelectric thin films (which smoothly transition from $BaTiO_3$ to $Ba_{0.6}Sr_{0.4}TiO_3$ from the substrate to the film surface). The configurations the 100 nm-thick $Ba_{1-x}Sr_xTiO_3$ thin films are schematically shown in Fig. 1. In calculations, we select a moderate flexoelectric coefficient $\mu_{12} = 1.6 \times 10^{-9}\,m^3/C$ which has been theoretically studied by first-principle calculations.[66–69] Meanwhile, the thermodynamic, elastic, and electromechanical coefficients for $BaTiO_3$ are obtained from Ref. 70 and those of $Ba_{0.6}Sr_{0.4}TiO_3$ are assumed to be a linear function of the composition determined by averaging the corresponding values of $BaTiO_3$ and $SrTiO_3$ listed in Ref. 70.

We first investigate the influence of the flexoelectric effect on the ferroelectric properties of compositionally graded ferroelectric thin films. The curves of average polarization components with the lattice mismatch strain of compositionally graded ferroelectric thin films are plotted in Fig. 2. It is necessary to point out that the in-plane lattice mismatch strain is defined as $u_m = (a_{substrate} - a_{BST60/40})/a_{BST60/40}$ for compositionally down-graded ferroelectric thin films, where a is the lattice constant. Meanwhile, for compositionally up-graded ferroelectric thin films, the in-plane lattice mismatch strain can be written as $u_m = (a_{substrate} - a_{BTO})/a_{BTO}$. As shown in Fig. 2, the flexoelectric effect is beneficial to the enhancement of average polarization components.

In the case of compositionally down-graded ferroelectric thin films from Fig. 2(a), the values of strain gradients are negative $[(a_{substrate} - a_{BTO})/a_{BTO} - (a_{substrate} - a_{BST60/40})/a_{BST60/40}]$. It should be noted that the numerical value of the flexoelectric field is proportional to the flexoelectric coefficient and the strain gradient of films, and the direction is determined by two factors together. Moreover, the flexoelectric coefficient is positive in the calculations. Thus, the negative flexoelectric field leads to an increase in the polarization

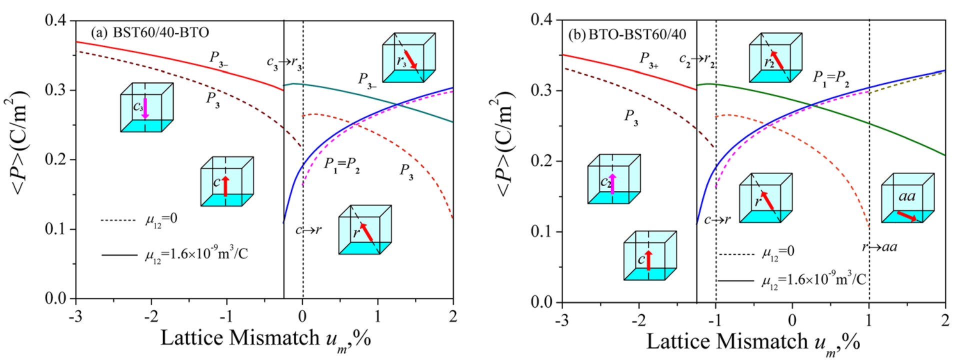

FIG. 2. Average polarization component P as a function of the lattice mismatch strain of compositionally (a) down-graded and (b) up-graded ferroelectric thin films.

component P_{3-}. At the same time, the polarization components $P_1 = P_2$ are found to be increased. This is caused by the item of $2\frac{\mu_{12}(Q_{12}+Q_{11})}{(s_{11}+s_{12})}P_1\frac{\partial P_3}{\partial z}$ in Eq. (8d). Furthermore, Fig. 2(b) displays the effect of the positive flexoelectric field on compositionally up-graded ferroelectric thin films, which causes polarization component P_{3+} to increase. Additionally, the presence of P_{3+} induced by the flexoelectric effect produces a new r_2 phase, which takes the place of the original *aa* phase.

To further explore the influence of the flexoelectric effect on the polarization components of compositionally graded ferroelectric thin films, the evolution of polarization components across the thickness is presented in Fig. 3. As shown in Figs. 3(a) and 3(b), it is found that for compositionally down-graded ferroelectric thin films, decreasing tensile strain in the film causes the out-of-plane polarization P_3 to increase and the in-plane polarization $P_1 = P_2$ to reduce. This result is in line with a previous study.[17] Note that for the compositionally down-graded ferroelectric thin films, the strain gradient is $-9.89 \times 10^4 \mathrm{m}^{-1}$ across the 100 nm thick film, which results in a flexoelectric field of −599 kV/cm. Therefore, the polarization state is actually shown as P_{3-}. For compositionally up-graded ferroelectric thin films, on the contrary, increasing tensile strain in the film causes the out-of-plane polarization P_3 to reduce and the in-plane polarization $P_1 = P_2$ to increase. At the same time, the strain gradient is $9.99 \times 10^4 \mathrm{m}^{-1}$ across the 100 nm thick compositionally up-graded ferroelectric thin films, which results in a flexoelectric field of 605 kV/cm. In a word, the flexoelectric effect is beneficial in the enhancement of polarization components. Furthermore, it also makes the distribution of the polarization components more stable along the thickness direction. This result is consistent with the work of Zhang *et al.*[39]

Polarization rotation has been shown to be the key in the driving mechanism for the ultrahigh piezoelectric response.[71] Hence, we discuss how the direction of polarization components will evolve along the thickness, as depicted in Fig. 4. It should be noted that P_r is defined as the magnitude of the polarization vector $(P_r = \sqrt{(P_1^2 + P_2^2 + P_3^2)}$, and θ is expressed as the rotation angle between P_r and the positive direction of the Z axis. In the case of $\mu_{12} = 0$ from Fig. 4(a), the change in polarization components $\Delta P_r \approx 0.14\,\mathrm{C/m^2}$ and the rotation angle $\Delta\theta \approx 37°$ in compositionally down-graded ferroelectric thin films. However, once the flexoelectric effect is taken into account, the result of the calculations changes dramatically. We observe that $\Delta P_r \approx 0.02\,\mathrm{C/m^2}$ and $\Delta\theta \approx 3°$ throughout the thickness of films. In order to directly reflect the evolution of polarization rotation, schematic diagrams of polarization rotation are given in Fig. 4(b). As is shown in the picture, 100 nm-thick compositionally graded ferroelectric thin films are sandwiched between symmetric electrodes. In the meantime, the dark blue arrows denote directions of polarization P_r along the thickness of films. It can be clearly seen that the rotation angle of the polarization component becomes smaller after considering the flexoelectric effect. This distinctive result can be understood by consideration of the flexoelectric field. For the case of compositionally down-graded ferroelectric thin films, there is a negative strain gradient. This strain gradient will generate a negative flexoelectric field along the thickness of films, causing polarization components to rotate towards the negative direction of the Z axis.

Meanwhile, the same change trend of polarization rotation occurs in compositionally up-graded ferroelectric thin films, as shown in Figs. 4(c) and 4(d). In this case, the positive flexoelectric field results in the rotation of polarization components towards the positive direction of the Z axis. The result suggests that the flexoelectric effect plays an important role in making polarization components more uniform and orderly. Generally speaking, polarization rotation appears only in the morphotropic phase boundary of ferroelectric

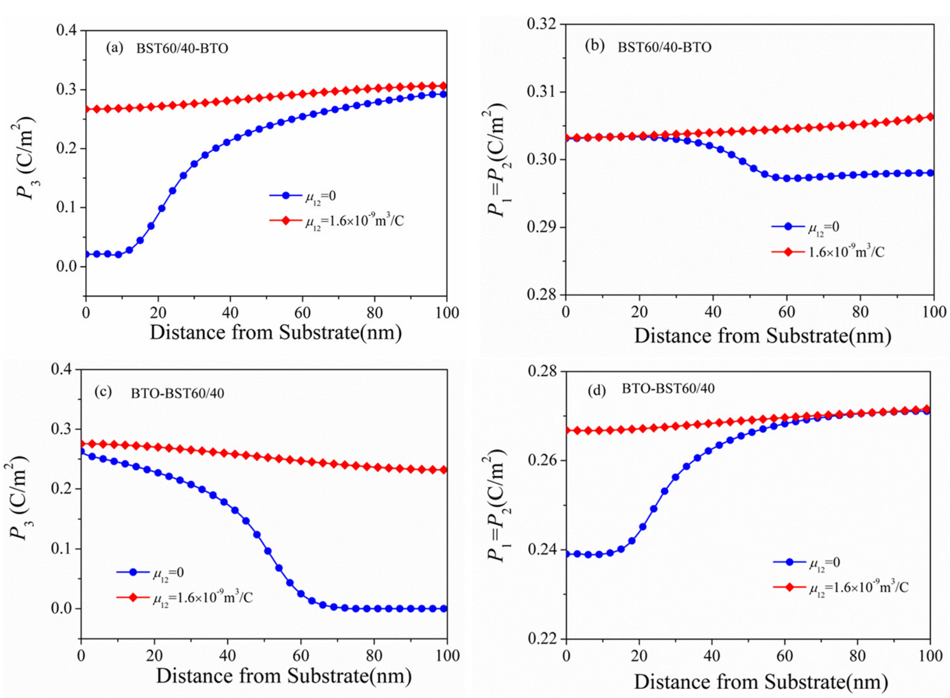

FIG. 3. Polarization component P as a function of the distance from the substrate of compositionally (a) and (b) down-graded and (c) and (d) up-graded ferroelectric thin films.

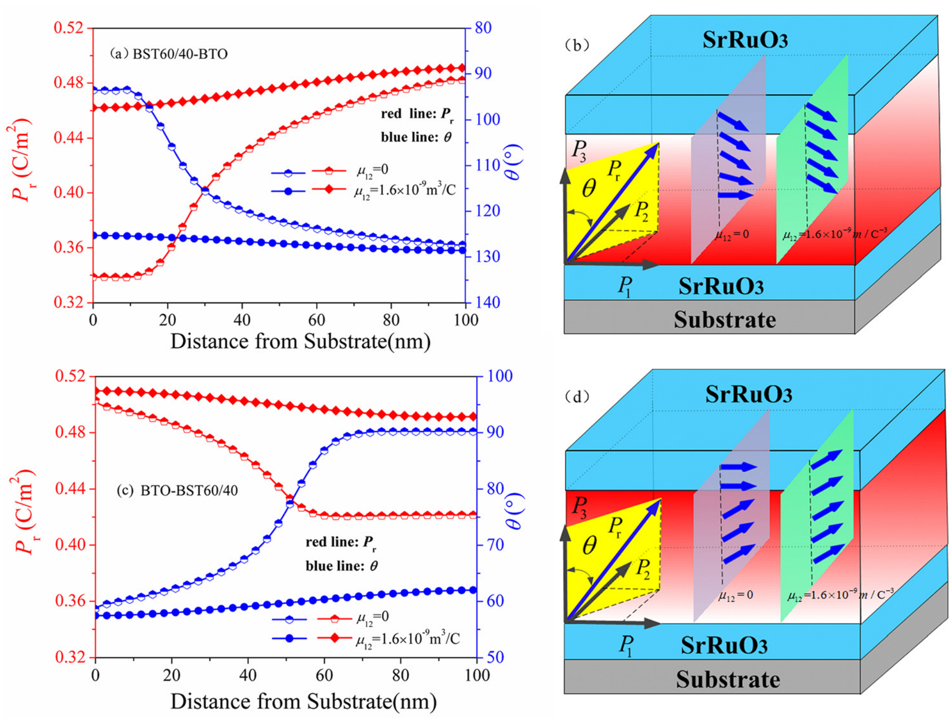

FIG. 4. Polarization component P_r and polarization rotation as a function of the distance from the substrate of compositionally (a) and (b) down-graded and (c) and (d) up-graded ferroelectric thin films.

materials with high piezoelectric properties.[72,73] Nevertheless, the flexoelectric effect provides a new method for obtaining polarization rotation in ordinary ferroelectric materials. Moreover, the flexoelectric effect provides an alternative route to the generation of ferroelectrics with rotated polarization, a feature thought to enhance piezoelectricity.

To check how the polarization rotation affects the piezoelectricity of compositionally graded $Ba_{1-x}Sr_xTiO_3$ ferroelectric films, the piezoelectric coefficient d_{33} as a function of the lattice mismatch strain is calculated and shown in Fig. 5. In the case of $\mu_{12} = 1.6 \times 10^{-9}\ \mathrm{m}^3/\mathrm{C}$ from Figs. 5(a) and 5(b), it is clearly seen that the compositionally graded ferroelectric films exhibit a relatively low piezoelectric coefficient, which can potentially be explained by the function of the flexoelectric field. More concretely, the built-in field caused by the flexoelectric effect can effectively lead to a reduction of the relative dielectric permittivity. Meanwhile, a previous experiment has reported that the built-in potential is observed to act to suppress the dielectric permittivity in compositionally graded heterostructures. According to our theory [Eqs. (10), (11), and (12)], the piezoelectric coefficient is known as to be dependent on the relative dielectric permittivity. Thus, a reduction of piezoelectricity is observed when the flexoelectric effect is taken into account.[18,37,38] Meanwhile, due to the flexoelectric field, such a small polarization rotation mentioned above generates a small piezoelectric response. Furthermore, the piezoelectric coefficients d_{33} exhibit huge responses at the phase transition boundaries, indicating the importance of structural discontinuity at the phase boundary in realizing enhanced functional properties. Interestingly, for the case of compositionally up-graded ferroelectric thin films in Fig. 5(b), polarization component P_{3+} induced by the flexoelectric field begins to emerge when the tensile strain $u_m \geq 1\%$, which results in the formation of a new r_2 phase. Meanwhile, the new region shows the piezoelectricity, which shows a potential significance of the flexoelectric effect in the future piezoelectric applications.

As can be seen from the above analyses, the flexoelectric effect is unfavorable to the electromechanical coupling behavior of compositionally graded ferroelectric thin films. Nevertheless, for the case of epitaxial constrained thin films that have large strain gradients, the flexoelectric effect

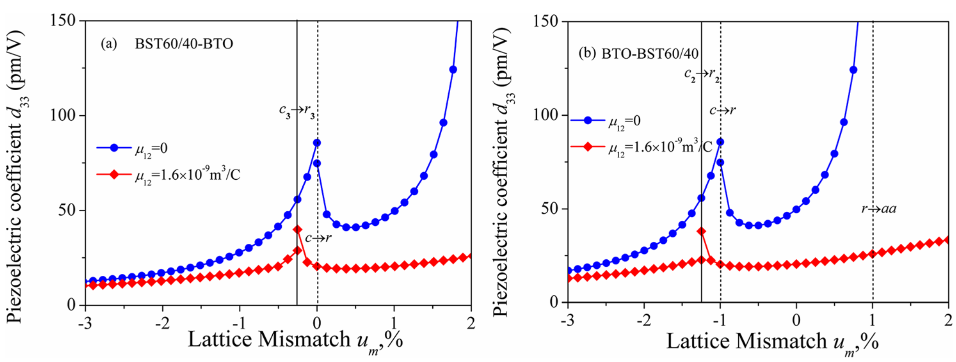

FIG. 5. Piezoelectric coefficient d_{33} as a function of the lattice mismatch strain of compositionally (a) down-graded (b) up-graded ferroelectric thin films.

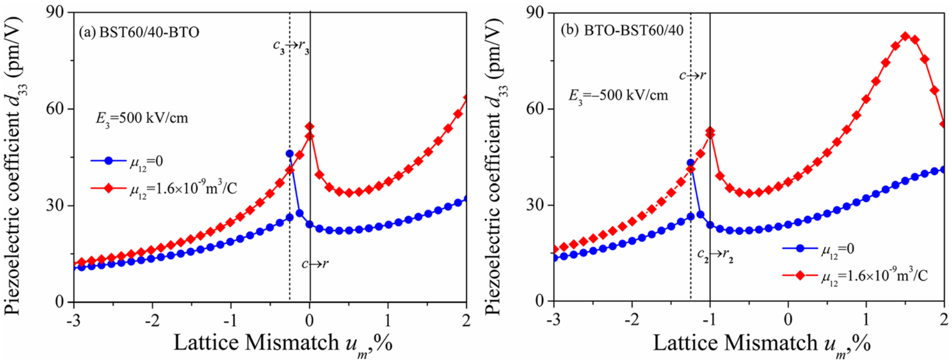

FIG. 6. Piezoelectric coefficient d_{33} as a function of the lattice mismatch strain of compositionally (a) down-graded (b) up-graded ferroelectric thin films under the external electric field.

cannot be neglected. Thus, when the flexoelectric effect is taken into account, how to improve the electromechanical performance of materials becomes critical. Considering that the flexoelectric effect would cause a built-in flexoelectric field to act on the material properties, we introduce an external electric field to tune performances of films together. As shown in Fig. 6, the flexoelectric effect is beneficial to the piezoelectric properties of compositionally graded ferroelectric thin films under the influence of the external electric field. This can be explained by the decrease in the total electric field. Here, it becomes imperative to mention that the direction of the external electric field we applied is in the reverse direction with a flexoelectric field. Compared with Figs. 6(a) and 6(b), the respective flexoelectric fields are opposite, which is caused by the strain gradient. Specifically, the flexoelectric field is negative in compositionally down-graded ferroelectric thin films. In order to decrease the total electric field, the applied electric field is positive ($E_3 = 500\,\mathrm{kV}/cm$), as shown in Fig. 6(a). In contrast, for the case of compositionally up-graded ferroelectric thin films, the flexoelectric field is positive. Then, Fig. 6(b) demonstrates that the applied electric field is negative ($E_3 = -500\ \mathrm{kV}/cm$). Thus, the decrease in the total electric field induces an enhancement of the piezoelectric properties. The present findings imply that it is possible to consider the mutual effect of the flexoelectric effect and external electric field, thereby leading to a new strategy to improve the piezoelectric properties.

In order to further explain the favourable influence of the flexoelectric effect on the piezoelectric properties of compositionally graded ferroelectric thin films, we plot the curves of piezoelectric coefficient d_{33} with a distance from the substrate in Fig. 7. In order to better explain the effect of thickness on the piezoelectric properties, the interface in-plane lattice mismatch strain is assumed to be -2% in Fig. 7. It can be clearly seen that when the film thickness is larger than 63 nm, the piezoelectric coefficient with the consideration of the flexoelectric effect is larger than that in the absence of the flexoelectric effect in compositionally down-graded ferroelectric thin films, as depicted in Fig. 7(a). Meanwhile, for compositionally up-graded ferroelectric thin films, the influence of the flexoelectric effect on electromechanical coupling behaviors becomes a favorable factor when the film thickness is larger than 65 nm. Therefore, this result clearly demonstrates the importance of selecting the suitable thickness of the film. In addition, the result indicates that the flexoelectric effect can be an effective tool to induce a large piezoelectric coefficient.

IV. CONCLUSIONS

In conclusion, we have studied the influence of the flexoelectric effect on the polarization distribution and piezoelectric properties in compositionally graded ferroelectric thin films using an extended thermodynamic model. Our results reveal that the polarization components can be significantly increased by the flexoelectric field. Meanwhile, it is found that the polarization components are stabilized throughout the thickness of the film. Moreover, the flexoelectric effect plays an important role in polarization rotations, which makes polarization components more uniform and orderly. The results demonstrate that an enhancement of piezoelectric properties can be achieved by taking into account the flexoelectric field and external electric field. Thus, our preliminary findings suggest a potential route to design piezoelectric devices controlled by a flexoelectric field and combine a modest external electric field based on compositionally graded ferroelectric thin films. We hope that the present study will encourage further theoretical works

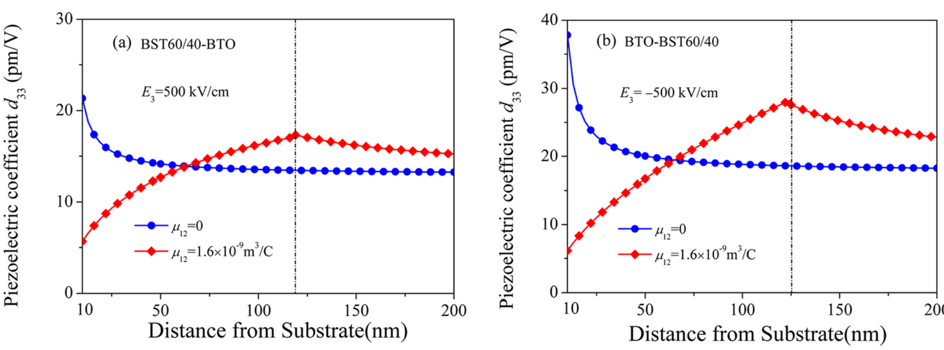

FIG. 7. Piezoelectric coefficient d_{33} as a function of the distance from the substrate of compositionally (a) down-graded and (b) up-graded ferroelectric thin films under the external electric field.

and experimental investigations to measure the electromechanical response of compositionally graded ferroelectric thin films.

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