Effect of substrate-induced strains on the spontaneous polarization of epitaxial $BiFeO_3$ thin films

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A single-domain thermodynamic theory is employed to predict the spontaneous polarizations of $(001)_c$, $(101)_c$, and $(111)_c$ oriented epitaxial $BiFeO_3$ thin films grown on dissimilar substrates. The effects of various substrate-induced strains on the spontaneous polarization were studied. The dependences of the spontaneous polarization on film orientations and the types of substrate-induced strains were analyzed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2743733]

I. INTRODUCTION

There has been considerable interest in developing $BiFeO_3$ magnetoelectric materials, which are simultaneously antiferromagnetic and ferroelectric.[1–3] In its bulk form, the ferroelectric phase of $BiFeO_3$ has a rhombohedrally distorted perovskite structure with space group $R3c$. The spontaneous polarization of $BiFeO_3$ is along the pseudocubic $\langle 111\rangle_c$ crystallographic directions, and hence there are eight possible polarization variants: $r_1^+=[\bar{1}\bar{1}\bar{1}]_c$, $r_2^+=[\bar{1}\bar{1}1]_c$, $r_3^+=[\bar{1}1\bar{1}]_c$, $r_4^+=[\bar{1}11]_c$, $r_1^-=[\bar{1}11]_c$, $r_2^-=[\bar{1}1\bar{1}]_c$, $r_3^-=[\bar{1}\bar{1}1]_c$, and $r_4^-=[\bar{1}\bar{1}\bar{1}]_c$. However, for epitaxial $BiFeO_3$ thin films, the existence of a free surface and substrate constraint destroys the macroscopic symmetry of the system and may significantly affect the properties of $BiFeO_3$. Recently, large ferroelectric polarizations have been reported in heteroepitaxially constrained thin films of $BiFeO_3$.[1,4,5] Strong dependence of polarization on film thickness has also been observed in experiments, and a likely explanation is the change of strains with film thickness.[1] Previous studies have shown that substrate-induced strains can lead to a substantial increase in spontaneous polarization for conventional ferroelectric materials, e.g., $BaTiO_3$, $PbTiO_3$.[6,7] However, the substrate-induced strain effect for $BiFeO_3$ thin films is still unclear. For example, first-principles calculations showed[8,9] that the spontaneous polarization is rather insensitive to substrate-induced strains compared to conventional ferroelectric systems, while a recent thermodynamic calculation showed a strong dependence of spontaneous polarization on substrate-induced strains (film thickness) for $(001)_c$ oriented $BiFeO_3$ thin films.[10]

Landau-type phenomenological theory has been extensively used to study the physical properties of single-domain ferroelectric thin films.[11–15] In this article, we extend the thermodynamic theory of ferroelectric thin films to variously oriented [i.e., $(001)_c$, $(101)_c$, and $(111)_c$] epitaxial $BiFeO_3$ thin films with general substrate-induced strains. We focus on the spontaneous polarization of $BiFeO_3$ thin films and its dependence on substrate-induced strains at room temperature. Our results are compared to previous experimental and theoretical studies.

II. RESULTS AND DISCUSSION

We consider a single-domain $(001)_c$ oriented $BiFeO_3$ thin film grown on a dissimilar substrate. For a phenomenological description of $BiFeO_3$ with coexistence of ferroelectric and antiferromagnetic orders, in principle, both the spontaneous polarization $\mathbf{P}=(P_1,P_2,P_3)$ and spontaneous magnetization $\mathbf{M}=(M_1,M_2,M_3)$ should be chosen as the order parameters. If we set up a rectangular coordinate system $\mathbf{x}=(x_1,x_2,x_3)$ with the x_1, x_2, and x_3 axes along the $[100]_c$, $[010]_c$, and $[001]_c$ crystallographic directions of the $BiFeO_3$ film, respectively, the free energy of $BiFeO_3$ using a Landau type of expansion can be written as[16]

$$\begin{aligned} F(P,M,\varepsilon) = {} & \alpha_1\left(P_1^2+P_2^2+P_3^2\right)+\alpha_{11}\left(P_1^4+P_2^4+P_3^4\right)+\alpha_{12} \\ & \times\left(P_1^2P_2^2+P_1^2P_3^2+P_2^2P_3^2\right)+\beta_1\left(M_1^2+M_2^2+M_3^2\right) \\ & +\beta_{11}\left(M_1^4+M_2^4+M_3^4\right)+\beta_{12}\left(M_1^2M_2^2+M_1^2M_3^2\right. \\ & \left.+M_2^2M_3^2\right)+\gamma_{ijkl}P_iP_jM_kM_l+\frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} \\ & -\frac{1}{2}q_{ijkl}\varepsilon_{ij}P_kP_l-\frac{1}{2}\lambda_{ijkl}\varepsilon_{ij}M_kM_l+\cdots, \end{aligned} \tag{1}$$

where ε_{ij} are the strain components, α_1, α_{ij}, β_1, and β_{ij} are the phenomenological Landau expansion coefficients, γ_{ijkl} are the magnetoelectric coupling coefficients, c_{ijkl} and q_{ijkl} are the elastic constants and electrostrictive constants, respectively, and λ_{ijkl} are the magnetoelastic coupling coefficients. The summation convention for the repeated indices is

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employed and $i,j,k,l=1,2,3$. The electrostrictive coefficients, q_{ijkl}, defined here can be easily obtained from

$$q_{ijkl}=2c_{ijmn}Q_{mnkl}, \tag{2}$$

where Q_{mnkl} are the electrostrictive coefficients typically measured experimentally. Although sixth-order terms in polarization are required for a first-order ferroelectric transition in $BiFeO_3$,[17] we only considered terms up to fourth order due to the lack of sufficient experimental data to obtain the numerical values of all the coefficients. Since our focus is on the effect of substrate-induced strains on the spontaneous polarization of $BiFeO_3$ thin films at room temperature, such approximation will not impact the main results of this article. We also neglect the magnetoelectric coupling term in Eq. (1) due to fact that $BiFeO_3$ has a large polarization but a quite small saturated magnetization,[2] and the coupling term should have small effect on the spontaneous polarization. With these approximations, the free-energy expression of $BiFeO_3$ was reduced to

$$\begin{aligned}F(P,\varepsilon)=&\alpha_1(P_1^2+P_2^2+P_3^2)+\alpha_{11}(P_1^4+P_2^4+P_3^4)\\&+\alpha_{12}(P_1^2P_2^2+P_1^2P_3^2+P_2^2P_3^2)\\&+\frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl}-\frac{1}{2}q_{ijkl}\varepsilon_{ij}P_kP_l.\end{aligned} \tag{3}$$

The elastic constants of cubic phase $BiFeO_3$ are used, $c_{1111}=3.02\times10^{11}$ (N m^{-2}), $c_{1122}=1.62\times10^{11}$ (N m^{-2}), and $c_{1212}=0.68\times10^{11}$ (N m^{-2}), which were obtained from first-principles calculations. The Landau expansion coefficients and the electrostrictive coefficients were obtained by fitting them to experimental measurements,[18–21] i.e., $\alpha_1=4.9(T-1103)\times10^5$ (C^{-2} m^2 N), $\alpha_{11}=6.5\times10^8$ (C^{-4} m^6 N), $\alpha_{12}=1.0\times10^8$ (C^{-4} m^6 N), $Q_{1111}=0.032$ (C^{-2} m^4), $Q_{1122}=-0.016$ (C^{-2} m^4), and $Q_{1212}=0.01$ (C^{-2} m^4), where T is temperature in Kelvin. It should be noted that, due to the lack of reliable experimental data about the ferroelectric properties of bulk $BiFeO_3$, we calculated the ferroelectric properties of different oriented $BiFeO_3$ films grown on $SrTiO_3$ substrates, and fitted them with the corresponding experimental measurements of $BiFeO_3$ films[20,21] to obtain the needed coefficients. The calculated ferroelectric properties of $BiFeO_3$ films at room temperature are compared in Table I with the available experimentally measured values.

TABLE I. Properties of $BiFeO_3$ films at room temperature, $T=300$ K.

Properties of $BiFeO_3$ films (on $SrTiO_3$ substrates)	This work[a]	Experimental measurements
Polarization (P_3) of $(001)_c$ $BiFeO_3$ film (C/m^2)	0.63	0.55,[b] 0.64[c]
Polarization (P_3') of $(101)_c$ $BiFeO_3$ film (C/m^2)	0.80	0.80,[b] 0.81[c]
Polarization (P_3') of $(111)_c$ $BiFeO_3$ film (C/m^2)	0.96	1.00,[b] 0.96[c]
Dielectric constant of $(111)_c$ $BiFeO_3$ film	62	45,[b] 60[c]

[a]The substrate-induced strains were assumed to be $\varepsilon_{11}^0=\varepsilon_{22}^0=-0.015$, $\varepsilon_{12}^0=0$ in the calculations.
[b]Reference 20.
[c]Reference 21.

For a general case, strains are imposed along the x_1-x_2 directions, while all the stress components involving the x_3 direction are zero due to the existence of the free film surface, i.e.,

$$\begin{aligned}&\varepsilon_{11}=\varepsilon_{11}^0,\\&\varepsilon_{22}=\varepsilon_{22}^0,\\&\varepsilon_{12}=\varepsilon_{21}=\varepsilon_{12}^0,\\&\sigma_{13}=\sigma_{31}=\sigma_{23}=\sigma_{32}=\sigma_{33}=0,\end{aligned} \tag{4}$$

where the misfit strains ε_{ij}^0 depend on the lattice parameters of the film and substrate. With such specified boundary conditions, the free energy of $(001)_c$ oriented $BiFeO_3$ thin film is given by

$$\begin{aligned}F=&\left[\alpha_1-\frac{(c_{1111}q_{1111}-c_{1122}q_{1122})\varepsilon_{11}^0+(c_{1111}q_{1122}-c_{1122}q_{1122})\varepsilon_{22}^0}{2c_{1111}}\right]P_1^2\\&+\left[\alpha_1-\frac{(c_{1111}q_{1122}-c_{1122}q_{1122})\varepsilon_{11}^0+(c_{1111}q_{1111}-c_{1122}q_{1122})\varepsilon_{22}^0}{2c_{1111}}\right]P_2^2\\&+\left[\alpha_1-\frac{(c_{1111}q_{1122}-c_{1122}q_{1111})\varepsilon_{11}^0+(c_{1111}q_{1122}-c_{1122}q_{1111})\varepsilon_{22}^0}{2c_{1111}}\right]P_3^2\\&-2q_{1212}\varepsilon_{12}^0P_1P_2+\left(\alpha_{12}-\frac{q_{1122}^2}{4c_{1111}}\right)P_1^2P_2^2+\left(\alpha_{12}-\frac{q_{1111}q_{1122}}{4c_{1111}}-\frac{q_{1212}^2}{2c_{1212}}\right)(P_1^2P_3^2+P_2^2P_3^2)+\left(\alpha_{11}-\frac{q_{1122}^2}{8c_{1111}}\right)\\&\times(P_1^4+P_2^4)+\left(\alpha_{11}-\frac{q_{1111}^2}{8c_{1111}}\right)P_3^4-\frac{c_{1122}^2(\varepsilon_{11}^0+\varepsilon_{22}^0)^2}{2c_{1111}}+\frac{1}{2}c_{1111}[(\varepsilon_{11}^0)^2+(\varepsilon_{22}^0)^2]+c_{1122}\varepsilon_{11}^0\varepsilon_{22}^0+2c_{1212}(\varepsilon_{12}^0)^2.\end{aligned} \tag{5}$$

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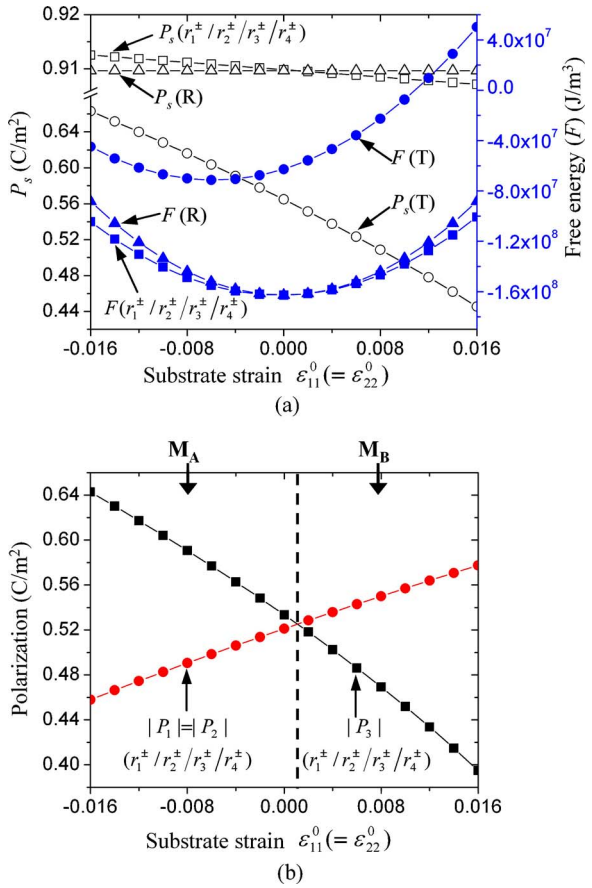

FIG. 1. (a) Free energy (F) and P_s; (b) polarization components of $(001)_c$ oriented $BiFeO_3$ thin films as a function of normal substrate-induced strains. [The free energy and P_s of rhombohedral phase (R) and tetragonal phase (T) were also given for comparison.]

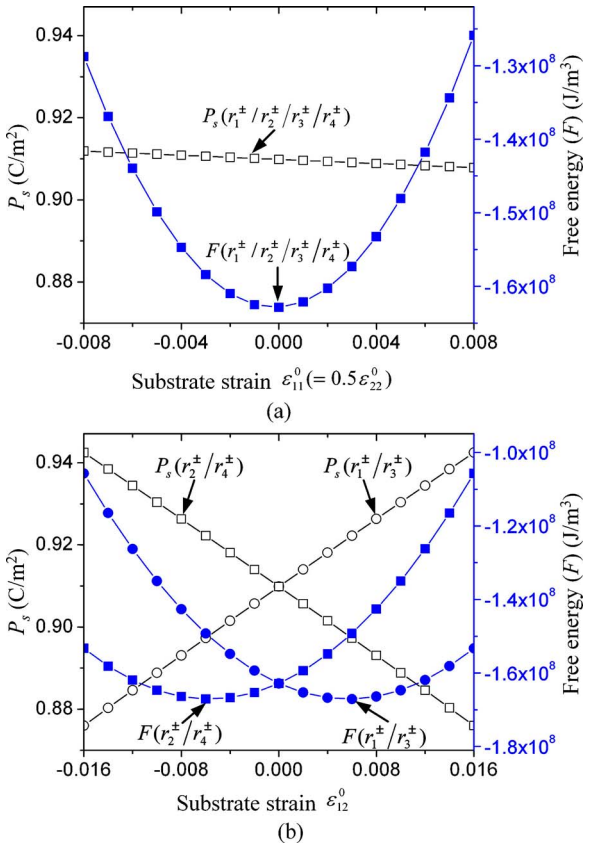

FIG. 2. Free energy (F) and P_s of various polarization variants for $(001)_c$ oriented $BiFeO_3$ thin films as a function of (a) anisotropic normal substrate-induced strains and (b) shear substrate-induced strains.

It should be noted that Eq. (5) is essentially the same as that reported in Ref. 14 except for the sixth-order terms and the different notation of coefficients. The spontaneous polarization can be derived from Eq. (5) by solving $\partial F/\partial P_i=0$ ($i=1,2,3$).

For the case of a $(001)_c$ oriented $BiFeO_3$ film epitaxially grown on a $(001)_c$ oriented cubic single-crystal substrate with an in-plane orientation relationship of $[100]_c^{BiFeO_3}\|[100]_c^s$, a constant dilatational plane strain, so-called biaxial strain, is imposed along the x_1-x_2 directions,

$$\varepsilon_{11}^0=\varepsilon_{22}^0, \quad \varepsilon_{12}^0=0, \tag{6}$$

where $\varepsilon_{11}^0=\varepsilon_{22}^0=(a_s-a_{BiFeO_3})/a_{BiFeO_3}$, a_s and a_{BiFeO_3} are the lattice parameters of the substrate and film, respectively. The dependence of the polarizations on the substrate-induced strains is shown as Fig. 1. We can see that the in-plane components of polarization ($|P_1|=|P_2|$) are not equal to the out-of-plane component $|P_3|$ due to the constraint of the substrate. As expected, compressive substrate-induced strains lead to an increase in $|P_3|$ and decrease in $|P_1|$ and $|P_2|$, while tensile substrate-induced strains have the opposite effect. Therefore, the direction of the polarization vector deviates from its equilibrium $\langle 111\rangle_c$ directions (toward $[001]_c/[00\bar{1}]_c$ directions for compressive strains and $[110]_c/[1\bar{1}0]_c/[\bar{1}\bar{1}0]_c/[\bar{1}10]_c$ directions for tensile strains). As shown in Fig. 1(b), $BiFeO_3$ becomes the monoclinic M_A phase and M_B phase,[22] respectively, which is consistent with prior experimental observations.[4,23] However, the change of the absolution value of the spontaneous polarization ($P_s=|\mathbf{P}|$) with the substrate-induced strains is rather small as shown in Fig. 1(a). For example, a rather large compressive strain of 1.6% leads to an increase of P_s only about 0.3%. It should be noted that all eight polarization variants are degenerate in energy and hence should exist with the same probability in the $(001)_c$ oriented $BiFeO_3$ thin film.

For the case of a $(001)_c$ oriented $BiFeO_3$ film epitaxially grown on a $(110)_o$ oriented orthorhombic substrate [for example $(110)_o$ oriented $DyScO_3$] with an in-plane orientation relationship of $[100]_c^{BiFeO_3}\|[\bar{1}10]_o^s$ and $[010]_c^{BiFeO_3}\|[001]_o^s$, an anisotropic in-plane strain is imposed along the x_1-x_2 directions, while there is no shear strain.

$$\varepsilon_{11}^0\neq\varepsilon_{22}^0, \quad \varepsilon_{12}^0=0, \tag{7}$$

where $\varepsilon_{11}^0=(\sqrt{a_s^2+b_s^2}-a_{BiFeO_3})/a_{BiFeO_3}$, $\varepsilon_{22}^0=(c_s-a_{BiFeO_3})/a_{BiFeO_3}$, and a_s, b_s, and c_s are the lattice parameters of the orthorhombic substrate. By fixing the ratio of $\varepsilon_{11}^0/\varepsilon_{22}^0$, we plot the dependence of free energy and P_s on the substrate-induced strains in Fig. 2(a). It was interesting to note that all eight polarization variants have equal energy even under the anisotropic substrate-induced strains. The absolution value of the spontaneous polarization P_s is insensitive to the normal substrate-induced strains.

Shear substrate strain may also exist for $(001)_c$ oriented $BiFeO_3$ films, i.e., $\varepsilon_{11}^0=\varepsilon_{22}^0\neq 0$, $\varepsilon_{12}^0\neq 0$. A potential example

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would be a $(001)_c$ oriented $BiFeO_3$ film constrained by a $(001)_o$ orthorhombic substrate with an in-plane orientation relationship of $[100]_c^{BiFeO_3} \| [110]_o^s$ and $[010]_c^{BiFeO_3} \| [\bar{1}10]_o^s$. The shear strain is $\varepsilon_{12}^0 = \frac{1}{2}\cos\gamma$, where γ is the angle between $[110]_o$ and $[\bar{1}10]_o$ crystallographic axes of the substrate. For simplicity, we assume $\varepsilon_{11}^0 = \varepsilon_{22}^0 = 0$ in this work. Unlike previously studied cases, the energies of the eight polarization variants are no longer degenerate under the shear substrate-induced strain as shown in Fig. 2(b). Under a negative shear substrate-induced strain, four variants (r_2^+, r_2^-, r_4^+, and r_4^-) have lower energy, while under a positive shear substrate-induced strain the energies of the other four variants (r_1^+, r_1^-, r_3^+, and r_3^-) are lower. From Fig. 2(b), one can see that P_s changes with the shear substrate-induced strain. For example, P_s (for r_1^+, r_1^-, r_3^+, and r_3^-) increases about 3.6% for a strain $\varepsilon_{12}^0 = 1.6\%$, which is significant compared to the effect of normal substrate-induced strains. However, the magnitude of change is still dramatically smaller than other traditional ferroelectric systems such as $BiFeO_3$.

For comparison, we also performed calculations by assuming that the symmetry of $BiFeO_3$ was fixed to be rhombohedral ($|P_1| = |P_2| = |P_3| = P_s/\sqrt{3}$) or tetragonal ($P_1 = P_2 = 0$, $|P_3| = P_s$). By reducing Eq. (5) with such symmetry relations, the corresponding spontaneous polarization can be obtained by solving $\partial F/\partial P_i = 0$. For rhombohedral symmetry,

$$P_s^2 = \frac{6c_{1212}\left[-6a_1c_{1111} + (c_{1111} - c_{1122})(q_{1111} + 2q_{1122})(\varepsilon_{11}^0 + \varepsilon_{22}^0) \pm 4c_{1111}q_{1212}\varepsilon_{12}^0\right]}{c_{1212}\left[24(a_{11} + a_{12})c_{1111} - (q_{1111} + 2q_{1122})^2\right] - 8c_{1111}q_{1212}^2}, \tag{8}$$

where "+" for the variants with $P_1 = P_2$ and "–" for the variants with $P_1 = -P_2$.

For tetragonal symmetry,

$$P_s^2 = \frac{-4a_1c_{1111} - 2(c_{1122}q_{1111} - c_{1111}q_{1122})(\varepsilon_{11}^0 + \varepsilon_{22}^0)}{8a_{11}c_{1111} - q_{1111}^2}. \tag{9}$$

From Eq. (8), one can see that, when $BiFeO_3$ has the rhombohedral symmetry, the effect of normal substrate-induced strains on P_s is highly related to the magnitude of $(q_{1111} + 2q_{1122})$, which is given by

$$q_{1111} + 2q_{1122} = 2(c_{1111} + 2c_{1122})(Q_{1111} + 2Q_{1122}). \tag{10}$$

For $BiFeO_3$ (also true for many ferroelectrics), the magnitude of $(Q_{1111} + 2Q_{1122})$ is quite small. Therefore, the dependence of P_s on normal substrate-induced strains is rather weak, and only a shear substrate-induced strain could affect the polarization effectively. However, P_s is only a function of normal substrate-induced strains when $BiFeO_3$ has a tetragonal symmetry [as shown in Eq. (9)]. It may explain the strong dependence of spontaneous polarizations on normal substrate-induced strains (film thickness) shown in Ref. 10, where the symmetry of $BiFeO_3$ was assumed to be tetragonal. It should be noted that the $BiFeO_3$ phases with tetragonal symmetry and rhombohedral symmetry have higher energy than the phase with monoclinic symmetry as shown in Fig. 1(a); therefore, they are unstable in the range of substrate-induced strains we studied.

We now discuss $(111)_c$ oriented $BiFeO_3$ thin films grown on a dissimilar substrate. Following Ref. 13, a new coordinate system, $\mathbf{x}' = (x_1', x_2', x_3')$, is set up with the x_1', x_2', and x_3' axes along the $[0\bar{1}1]_c$, $[\bar{2}11]_c$, and $[111]_c$ crystallographic directions of the $BiFeO_3$ film, respectively. The free energy of $BiFeO_3$ in the coordinate system $\mathbf{x}'$ is given by

$$\begin{aligned} F(P', \varepsilon') = {} & \alpha_1\left[(t_{i1}P_i')^2 + (t_{i2}P_i')^2 + (t_{i3}P_i')^2\right] + \alpha_{11}\left[(t_{i1}P_i')^4\right. \\ & \left. + (t_{i2}P_i')^4 + (t_{i3}P_i')^4\right] + \alpha_{12}\left[(t_{i1}P_i')^2(t_{i2}P_i')^2\right. \\ & \left. + (t_{i1}P_i')^2(t_{i3}P_i')^2 + (t_{i2}P_i')^2(t_{i3}P_i')^2\right] \\ & + \frac{1}{2}c_{ijkl}'\varepsilon_{ij}'\varepsilon_{kl}' - \frac{1}{2}q_{ijkl}'\varepsilon_{ij}'P_k'P_l', \end{aligned} \tag{11}$$

where t_{ij} is the transformation matrix from the coordinate system $\mathbf{x}$ to the coordinate system $\mathbf{x}'$. P_i', ε_{ij}', c_{ijkl}', and q_{ijkl}' are the polarizations, strains, elastic constants, and electrostrictive constants in the coordinate system $\mathbf{x}'$, which are given by

$$\begin{aligned} P_i' &= t_{ij}P_j, \\ \varepsilon_{ij}' &= t_{im}t_{jn}\varepsilon_{mn}, \\ c_{ijkl}' &= t_{im}t_{jn}t_{ko}t_{lp}c_{mnop}, \\ q_{ijkl}' &= t_{im}t_{jn}t_{ko}t_{lp}q_{mnop}, \end{aligned} \tag{12}$$

with the transformation matrix

$$t_{ij}^{(111)_c} = \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{2}} \\ \frac{-2}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \end{pmatrix}. \tag{13}$$

For a $(111)_c$ oriented film deposited on a $(111)_c$ oriented cubic crystal substrate with an in-plane orientation relationship of $[1\bar{1}0]_c^{BiFeO_3} \| [1\bar{1}0]_c^s$, the elastic boundary condition is given by

$$\varepsilon_{11}' = \varepsilon_{11}^0,$$

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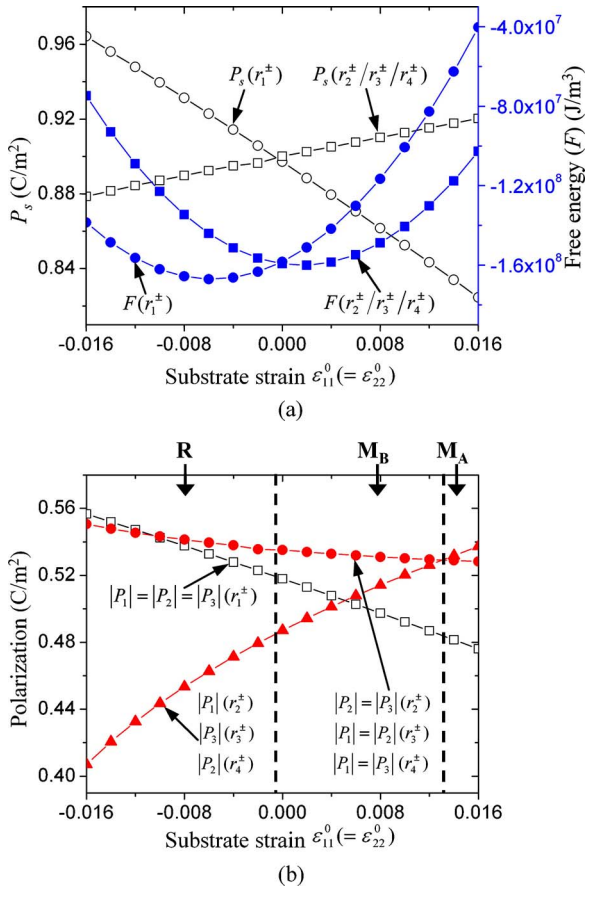

FIG. 3. (a) Free energy (F) and P_s; (b) polarization components of various polarization variants for $(111)_c$ oriented $BiFeO_3$ thin films as a function of normal substrate-induced strains.

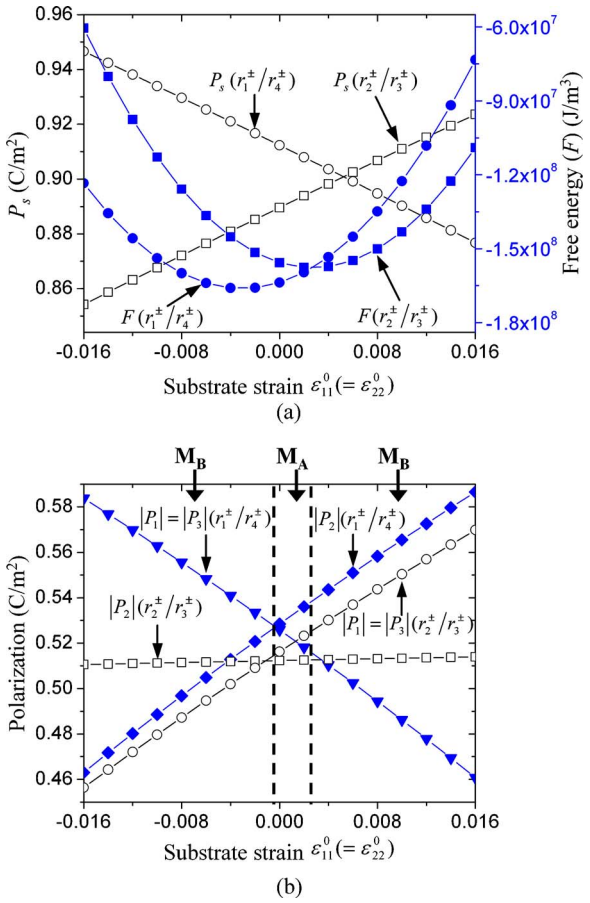

FIG. 4. (a) Free energy (F) and P_s; (b) polarization components of various polarization variants for $(101)_c$ oriented $BiFeO_3$ thin films as a function of normal substrate-induced strains.

$$\varepsilon'_{22}=\varepsilon^0_{22},$$

$$\varepsilon'_{12}=\varepsilon'_{21}=0,$$

$$\sigma'_{13}=\sigma'_{31}=\sigma'_{23}=\sigma'_{32}=\sigma'_{33}=0, \tag{14}$$

where $\varepsilon^0_{11}=\varepsilon^0_{22}=(a_s-a_{BiFeO_3})/a_{BiFeO_3}$, a_s and a_{BiFeO_3} are the lattice parameters of the substrate and film, respectively. Unlike the $(001)_c$ oriented film, under a biaxial substrate-induced strain the polarization variants do not have equal energy except for a critical point at $\varepsilon^0_{11}=\varepsilon^0_{22}\sim 0\%$ as shown in Fig. 3(a). For a large compressive strain, the two polarization variants perpendicular to the film surface (r_1^+ and r_1^-) have lower energy than the others, and the compressive substrate-induced strains increase the P_s of the variants, which is consistent with prior first-principles calculations.[8,9] It should be noted that in such a case, $BiFeO_3$ retains the rhombohedral (R) symmetry ($|P_1|=|P_2|=|P_3|$) [as shown in Fig. 3(b)], and indeed rhombohedral symmetry is found experimentally in $(111)_c$ epitaxial $BiFeO_3$ film deposited on a $(111)_c$ surface of $SrTiO_3$, which has smaller lattice parameters than $BiFeO_3$.[4,5,24] At the right side of the critical point in Fig. 3(a), the other six polarization variants become more stable energetically. One can see that the substrate-induced strains also increase the P_s of these polarization variants. However, the symmetry of $BiFeO_3$ is no longer rhombohedral, and the stable phases have been marked in Fig. 3(b).

We also study $(101)_c$ oriented $BiFeO_3$ thin films. The coordinate system $\mathbf{x}'$ was set up with the x'_1, x'_2, and x'_3 axes along the$[010]_c$, $[\bar{1}01]_c$, and $[101]_c$ crystallographic directions of the $BiFeO_3$ film, and the free energy of $(101)_c$ oriented $BiFeO_3$ thin films can be given by Eq. (11) with the transformation matrix from the coordinate system $\mathbf{x}$ to the coordinate system $\mathbf{x}'$,

$$t_{ij}^{(101)_c}=\begin{pmatrix} 0 & 1 & 0 \\ -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{pmatrix}. \tag{15}$$

For a $(101)_c$ oriented $BiFeO_3$ film deposited on a $(101)_c$ oriented cubic crystal substrate with an in-plane orientation relationship of $[010]_c^{BiFeO_3}\|[010]_c^s$, the elastic boundary condition is given by

$$\varepsilon'_{11}=\varepsilon^0_{11},$$

$$\varepsilon'_{22}=\varepsilon^0_{22},$$

$$\varepsilon'_{12}=\varepsilon'_{21}=0,$$

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$$\sigma'_{13} = \sigma'_{31} = \sigma'_{23} = \sigma'_{32} = \sigma'_{33} = 0, \tag{16}$$

where $\varepsilon^0_{11} = \varepsilon^0_{22} = (a_s - a_{BiFeO_3})/a_{BiFeO_3}$. At a critical point $\varepsilon^0_{11} = \varepsilon^0_{22} \sim 0.25\%$, the energies of eight polarization variants are the same; otherwise their energies are different. Polarization variants (r_1^+, r_1^-, r_4^+, and r_4^-) have lower energy on the left side of the critical point, while the other four polarization variants are more stable energetically on the right side of the critical point. Consistent with the experimental observation,[4,25] the crystal structure of $(101)_c$ $BiFeO_3$ film loses the rhombohedral symmetry as shown in Fig. 4(b). The substrate-induced strains also change the P_s of these variants as shown in Fig. 4(a).

III. SUMMARY

In summary, we have extended the thermodynamic theory of ferroelectric thin films to a number of different oriented [$(001)_c$, $(101)_c$, and $(111)_c$] epitaxial $BiFeO_3$ thin films with general substrate-induced strains. Our calculations show that the substrate effect on ferroelectric polarization of $BiFeO_3$ films depends on the film orientations and the types of substrate-induced strains. For $(001)_c$ oriented $BiFeO_3$ films, only shear substrate-induced strain will have a significant effect on the absolute value of the spontaneous polarization P_s, while the normal substrate-induced strains only rotate the polarization direction without changing its magnitude. However, for $(111)_c$ and $(101)_c$ oriented $BiFeO_3$ films, normal substrate-induced strains can significantly alter the magnitude of the spontaneous polarization.

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