Effect of substrate-induced strains on the spontaneous polarization of epitaxial BiFeO₃ thin films

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A single-domain thermodynamic theory is employed to predict the spontaneous polarizations of (001)ₐ, (101)ₐ, and (111)ₐ oriented epitaxial BiFeO₃ 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 BiFeO₃ magnetoelectric materials, which are simultaneously antiferromagnetic and ferroelectric. In its bulk form, the ferroelectric phase of BiFeO₃ has a rhombohedral distorted perovskite structure with space group R3c. The spontaneous polarization of BiFeO₃ is along the pseudocubic (111)ₐ crystallographic directions, and hence there are eight possible spontaneous polarizations. However, for epitaxial BiFeO₃ thin films, the existence of spontaneous polarization on substrate-induced strains compared to conventional ferroelectric systems, while spontaneous polarization is rather insensitive to substrate-induced strain effect for BiFeO₃ thin films is still unclear. For example, first-principles calculations showed that 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)ₐ oriented BiFeO₃ thin films.

Landau-type phenomenological theory has been extensively used to study the physical properties of single-domain ferroelectric thin films. In this article, we extend the thermodynamic theory of ferroelectric thin films to variously oriented [i.e., (001)ₐ, (101)ₐ, and (111)ₐ] epitaxial BiFeO₃ thin films with general substrate-induced strains. We focus on the spontaneous polarization of BiFeO₃ 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)ₐ oriented BiFeO₃ thin film grown on a dissimilar substrate. For a phenomenological description of BiFeO₃ with coexistence of ferroelectric and antiferromagnetic orders, in principle, both the spontaneous polarization \( \mathbf{P} = (P_x, P_y, P_z) \) 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]ₐ, [010]ₐ, and [001]ₐ crystallographic directions of the BiFeO₃ film, respectively, the free energy of BiFeO₃ using a Landau type of expansion can be written as

\[
F(P, M, \mathbf{e}) = \alpha_1 \left( P_1^2 + P_2^2 + P_3^2 \right) + \alpha_11 \left( P_1^4 + P_2^4 + P_3^4 \right) + \alpha_12 \times \left( P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2 \right) + \beta_1 \left( M_1^2 + M_2^2 + M_3^2 \right) + \beta_13 \left( M_1^2 M_2^2 + M_2^2 M_3^2 + M_3^2 M_1^2 \right) + M_2^2 M_3^2 + \gamma_{ijkl} P_i P_j M_k M_l + \frac{1}{2} \sum_{ijkl} c_{ijkl} \epsilon_{ij} \epsilon_{kl}
\]

\[
- \frac{1}{2} q_{ijkl} \epsilon_{ij} P_k P_l - \frac{1}{2} \lambda_{ijkl} \epsilon_{ij} M_k M_l + \cdots, \tag{1}
\]

where \( \epsilon_{ij} \) are the strain components, \( \alpha_1 \), \( \alpha_{ij} \), \( \beta_1 \), and \( \beta_{ij} \) are the phenomenological Landau expansion coefficients, \( \gamma_{ijkl} \) are the magnetoelastic coupling coefficients, \( c_{ijkl} \) and \( q_{ijkl} \) are the elastic constants and electrostrictive constants, respectively, and \( \lambda_{ijkl} \) are the magnetoelastic coupling coefficients. The summation convention for the repeated indices is
employed and $i,j,k,l=1,2,3$. The electrostrictive coefficients, $q_{ijkl}$, defined here can be easily obtained from

$$q_{ijkl} = 2c_{ijkl}Q_{mnkl},$$

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 magnetoelastic 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

$$F(P,e) = \alpha_1(p_{11}^2 + p_{22}^2 + p_{33}^2) + \alpha_1(p_{11}^3 + p_{22}^3 + p_{33}^3) + \left\{\begin{array}{l}
\frac{1}{2}c_{ijkl}e_{ij}e_{kl} - \frac{1}{2}q_{ijkl}e_{ij}P_kP_l.
\end{array}\right.$$ (3)

The elastic constants of cubic phase BiFeO$_3$ are used, $c_{1111} = 3.02 \times 10^{11}$ (N m$^{-2}$), $c_{1122} = 1.62 \times 10^{11}$ (N m$^{-2}$), and $c_{1212} = 0.68 \times 10^{11}$ (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., $\alpha_1 = 4.90(T - 1103) \times 10^5$ (C$^{-2}$ m$^2$ N), $\alpha_2 = 6.5 \times 10^{8}$ (C$^{-2}$ m$^6$ N), $\alpha_3 = 1.0 \times 10^8$ (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.

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.,

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

$$\varepsilon_{22} = \varepsilon_{22}^0,$$

$$\varepsilon_{12} = \varepsilon_{21} = \varepsilon_{12}^0,$$

$$\sigma_{13} = \sigma_{31} = \sigma_{23} = \sigma_{32} = \sigma_{33} = 0,$$

where the misfit strains $\varepsilon_{ij}^0$ depend on the lattice parameters of the film and substrate. With such specified boundary conditions, the free energy of (001), oriented BiFeO$_3$ thin film is given by

$$F = \left[\begin{array}{l}
\alpha_1 - \frac{(c_{1111}q_{1111} - c_{1122}q_{1122})e_{11}^0 + (c_{1111}q_{1111} - c_{1122}q_{1122})e_{22}^0}{2c_{1111}}
\end{array}\right]p_{11}^2 + \left[\begin{array}{l}
\alpha_1 - \frac{(c_{1111}q_{1111} - c_{1122}q_{1122})e_{11}^0 + (c_{1111}q_{1111} - c_{1122}q_{1122})e_{22}^0}{2c_{1111}}
\end{array}\right]p_{22}^2 + \left[\begin{array}{l}
\alpha_1 - \frac{(c_{1111}q_{1111} - c_{1122}q_{1122})e_{11}^0 + (c_{1111}q_{1111} - c_{1122}q_{1122})e_{22}^0}{2c_{1111}}
\end{array}\right]p_{33}^2 - 2q_{1122}e_{12}^0p_1p_2 + \left[\begin{array}{l}
\alpha_1 - \frac{q_{1122}^2}{4c_{1111}}
\end{array}\right]p_{11}^2p_{22} + \left[\begin{array}{l}
\alpha_1 - \frac{q_{1122}^2}{4c_{1111}}
\end{array}\right]p_{11}^2p_{33} + \left[\begin{array}{l}
\alpha_1 - \frac{q_{1122}^2}{4c_{1111}}
\end{array}\right]p_{22}^2p_{33} + \left[\begin{array}{l}
\alpha_1 - \frac{q_{1122}^2}{4c_{1111}}
\end{array}\right]p_{11}^2p_{33} + \left[\begin{array}{l}
\alpha_1 - \frac{q_{1122}^2}{4c_{1111}}
\end{array}\right]p_{22}^2p_{33} + \left[\begin{array}{l}
\alpha_1 - \frac{q_{1122}^2}{4c_{1111}}
\end{array}\right]p_{33}^2 + \left[\begin{array}{l}
\alpha_1 - \frac{q_{1122}^2}{4c_{1111}}
\end{array}\right]p_{33}^2.
\right.$$ (5)
The components of polarization strains is shown as Fig. 1. We can see that the in-plane independence of the polarizations on the substrate-induced lattice parameters of the substrate and film, respectively. The direction of the polarization vector deviates from its equilibrium directions for compressive strains and orientations for tensile strains. As shown in Fig. 1(b), BiFeO₃ becomes the monoclinic phase and $M_B$ phase, respectively, which is consistent with prior experimental observations. However, the change of the absolute value of the spontaneous polarization ($P_s$) 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)-oriented BiFeO₃ thin film.

For the case of a (001)-oriented BiFeO₃ film epitaxially grown on a (001)-oriented cubic single-crystal substrate with an in-plane orientation relationship of [100]$_c$BiFeO₃/[100]$_p$, a constant dilatational plane strain, so-called biaxial strain, is imposed along the $x_1$-$x_2$ directions, 

\[ \varepsilon_{11}^0 = \varepsilon_{22}^0, \quad \varepsilon_{12}^0 = 0, \]

where $\varepsilon_{ii}^0 = \varepsilon_{kk}^0 = (a_i - a_{BiFeO_3})/a_{BiFeO_3}$, 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 ($|P_i| = |P_k|$) 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 $|P_i|$ and $|P_k|$, while tensile substrate-induced strains have the opposite effect. Therefore, the direction of the polarization vector deviates from its equilibrium (111)ₐ directions (toward [001], [001]ₐ directions for compressive strains and [110], [110], [110], [110] directions for tensile strains). As shown in Fig. 1(b), BiFeO₃ becomes the monoclinic $M_A$ phase and $M_B$ phase, respectively, which is consistent with prior experimental observations. However, the change of the absolute value of the spontaneous polarization ($P_s$) 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)-oriented BiFeO₃ thin film.

For the case of a (001)-oriented BiFeO₃ film epitaxially grown on a (110)ₐ oriented orthorhombic substrate [for example (110)ₐ oriented DyScO₃] with an in-plane orientation relationship of [100]$_c$BiFeO₃/[110]₀ and [010]$_c$BiFeO₃/[001]₀, an anisotropic in-plane strain is imposed along the $x_1$-$x_2$ directions, while there is no shear strain.

\[ \varepsilon_{11}^0 \neq \varepsilon_{22}^0, \quad \varepsilon_{12}^0 = 0, \]

where $\varepsilon_{ii}^0 = (a_i^0 - a_{BiFeO_3})/a_{BiFeO_3}$, and $a_{BiFeO_3}$, $b_{BiFeO_3}$, and $c_{BiFeO_3}$ 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 absolute value of the spontaneous polarization $P_s$ is insensitive to the normal substrate-induced strains.

Shear substrate strain may also exist for (001)-oriented BiFeO₃ films, i.e., $\varepsilon_{11}^0 = \varepsilon_{22}^0 \neq 0$, $\varepsilon_{12}^0 \neq 0$. A potential example...
would be a (001) \text{c} oriented BiFeO\text{3} film constrained by a (001) \text{c} orthorhombic substrate with an in-plane orientation relationship of \text{[100]}_\text{BiFeO\text{3}} || \text{[110]}_\text{c} and \text{[010]}_\text{BiFeO\text{3}} || \text{[\overline{1}0\overline{0}]}_\text{c}. The shear strain is \( \varepsilon_{12} = \frac{1}{2} \cos \gamma \), where \( \gamma \) is the angle between \text{[110]}_\text{c} and \text{[\overline{1}0\overline{0}]}_\text{c}, crystallographic axes of the substrate. For simplicity, we assume \( \varepsilon_{12}^0 = \varepsilon_{23}^0 = 0 \) 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 \( (r^+_1, r^-_1, r^+_2, \text{ and } r^-_2) \) have lower energy, while under a positive shear substrate-induced strain the energies of the other four variants \( (r^+_1, r^-_1, r^+_2, \text{ and } r^-_2) \) are lower. From Fig. 2(b), one can see that \( P_s \) changes with the shear substrate-induced strain. For example, \( P_s \) for \( r^+_1, r^-_1, r^+_2, \text{ and } r^-_2 \) 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\text{3}.

For comparison, we also performed calculations by assuming that the symmetry of BiFeO\text{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,

\[
P_s^2 = \frac{6c_{1211}[-6a_1c_{1111} + (c_{1111} - c_{1122})(q_{1111} + 2q_{1122})](\varepsilon_{11}^0 + \varepsilon_{22}^0) + 4c_{1111}q_{1122}\varepsilon_{12}^0]}{c_{1111}[24(a_1 + a_2)c_{1111} - (q_{1111} + 2q_{1122})^2] - 8c_{1111}q_{1122}^2},
\]

where "+" for the variants with \( P_1=P_2 \) and "-" for the variants with \( P_1=-P_2 \).

For tetragonal symmetry,

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

From Eq. (8), one can see that, when BiFeO\text{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

\[
q_{1111} + 2q_{1122} = 2(c_{1111} + 2c_{1122})(Q_{1111} + 2Q_{1122}).
\]

For BiFeO\text{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\text{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\text{3} was assumed to be tetragonal. It should be noted that the BiFeO\text{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) \text{c} oriented BiFeO\text{3} thin films grown on a dissimilar substrate. Following Ref. 13, a new coordinate system, \( \text{x'}=(x'_1,x'_2,x'_3) \), is set up with the \( x'_1, x'_2, \text{ and } x'_3 \) axes along the \text{[0\overline{1}\overline{1}]}_\text{c}, \text{[\overline{1}1\overline{1}]}_\text{c}, \text{ and } \text{[111]}_\text{c} \) crystallographic directions of the BiFeO\text{3} film, respectively. The free energy of BiFeO\text{3} in the coordinate system \( \text{x'} \) is given by

\[
F(P'_s,e'_s) = \alpha_1[(t_{11}P'_1)^2 + (t_{22}P'_2)^2 + (t_{33}P'_3)^2] + \alpha_2[(t_{11}P'_1)^4 + (t_{22}P'_2)^4 + (t_{33}P'_3)^4] + \alpha_3[(t_{11}P'_1)^2(t_{22}P'_2)^2 + (t_{11}P'_1)^2(t_{33}P'_3)^2 + (t_{22}P'_2)^2(t_{33}P'_3)^2]
\]

where \( t_{ij} \) is the transformation matrix from the coordinate system \( \text{x} \) to the coordinate system \( \text{x'} \). \( e'_s, e'_i, c'_{ijkl}, \text{ and } q'_{ijkl} \) are the polarizations, strains, elastic constants, and electrostrictive constants in the coordinate system \( \text{x'} \), which are given by

\[
P'_i = t_{ij}P_j,
\]

\[
e'_s = t_{ims}f_{ms},
\]

\[
c'_{ijkl} = t_{ims}t_{i'k's'}f_{m's'},
\]

\[
q'_{ijkl} = t_{ims}t_{i'k's'}q_{m's'},
\]

with the transformation matrix

\[
t_{ij}^{(11\overline{1})} = \begin{pmatrix}
0 & 1 & -1 \\
1 & \sqrt{2} & \sqrt{2} \\
-2 & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\
\frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}}
\end{pmatrix}.
\]

For a (111) \text{c} oriented film deposited on a (111) \text{c} oriented cubic crystal substrate with an in-plane orientation relationship of \text{[\overline{1}0\overline{1}]}_\text{c} BiFeO\text{3} || \text{[1\overline{1}\overline{0}]}_\text{c}, \text{ the elastic boundary condition is given by}

\[
\varepsilon'_{11} = \varepsilon_{11}.
\]
substrate-induced strains increase the energy than the others, and the compressive strain the polarization variants do not have equal energy except for a critical point at $\varepsilon_{11}^0 \approx 0\%$ as shown in Fig. 3(a). For a large compressive strain, the two polarization variants perpendicular to the film surface ($r_1^*$ and $r_2^*$) have lower energy than the others, and the compressive substrate-induced strains increase the $P_y$ of the variants, which is consistent with prior first-principles calculations. 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), epitaxial BiFeO$_3$ film deposited on a (111), surface of SrTiO$_3$, which has smaller lattice parameters than BiFeO$_3$. 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 $P_y$ 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 $x'$ was set up with the $x'_1$, $x'_2$, and $x'_3$ axes along the[010]$_c$, [101]$_c$, 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 $x$ to the coordinate system $x'$,

$$t_{ij}^{(110)} = \begin{pmatrix} 0 & 1 & 0 \\ -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & 1 & 0 \end{pmatrix}.$$  (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]$_c$SrTiO$_3$, the elastic boundary condition is given by

$$\varepsilon_{11}^{'(101)} = \varepsilon_{11}^0,$$
$$\varepsilon_{22}^{'(101)} = \varepsilon_{22}^0,$$
$$\varepsilon_{12}^{'(101)} = \varepsilon_{12}^0,$$

where $\varepsilon_{ij}^{(101)} = (a_s - a_{BiFeO_3})/a_{BiFeO_3}$, $a_s$ 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 $\varepsilon_{11}^0 \approx 0\%$ as shown in Fig. 3(a). For a large compressive strain, the two polarization variants perpendicular to the film surface ($r_1^*$ and $r_2^*$) have lower energy than the others, and the compressive substrate-induced strains increase the $P_y$ of the variants, which is consistent with prior first-principles calculations. 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), epitaxial BiFeO$_3$ film deposited on a (111), surface of SrTiO$_3$, which has smaller lattice parameters than BiFeO$_3$. 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 $P_y$ 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).
normal substrate-induced strains can significantly alter the variants the same; otherwise their energies are different. Polarization dnal symmetry as shown in Fig. 4. Consistent with the experimental observation, the are more stable energetically on the right side of the critical point, while the other four polarization variants are more stable energetically on the right side of the critical point.  

III. SUMMARY

In summary, we have extended the thermodynamic theory of ferroelectric thin films to a number of different oriented BiFeO3 films with general substrate-induced strains. Our calculations show that the substrate effect on ferroelectric polarization of BiFeO3 films depends on the film orientations and the types of substrate-induced strains. For (001), oriented BiFeO3 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), and (101), oriented BiFeO3 films, normal substrate-induced strains can significantly alter the magnitude of the spontaneous polarization.

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\[ \sigma'_{11} = \sigma'_{22} = \sigma'_{33} = 0, \]

where \( \sigma'_{ij} = \sigma_{ij} - \alpha_{BIEO3} \). At a critical point \( e_{11}^0 = 0.25\% \), the energies of eight polarization variants are the same; otherwise their energies are different. Polarization variants \( (r^1_1, r^1_2, r^2_1, r^2_2) \) 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, the crystal structure of (101) BiFeO3 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).