AIP Applied Physics Letters

Tuning the remanent polarization of epitaxial ferroelectric thin films with strain

J. X. Zhang, D. G. Schlom, L. Q. Chen, and C. B. Eom

Citation: Appl. Phys. Lett. **95**, 122904 (2009); doi: 10.1063/1.3231444

View online: http://dx.doi.org/10.1063/1.3231444

View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v95/i12

Published by the American Institute of Physics.

Related Articles

Additional information on Appl. Phys. Lett.

APPLIED PHYSICS LETTERS 95, 122904 (2009)

Tuning the remanent polarization of epitaxial ferroelectric thin films with strain

J. X. Zhang,[1,a)] D. G. Schlom,[1] L. Q. Chen,[1] and C. B. Eom[2]
[1]*Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[2]*Department of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin 53706, USA*

(Received 1 July 2009; accepted 26 August 2009; published online 25 September 2009)

The effect of biaxial strain on the remanent polarization of epitaxial thin films of various ferroelectric materials is studied using phenomenological Landau–Devonshire theory. It is shown that the strain dependences of the remanent polarizations are strongly dependent on crystal symmetries and film orientations. For $(001)_p$-oriented ferroelectric films with (distorted) rhombohedral symmetry, strain-induced polarization rotation leads to stronger strain dependences than in ferroelectric films with tetragonal or orthorhombic symmetries. For $(111)_p$-oriented ferroelectric films with rhombohedral symmetry, however, the remanent polarization is less sensitive to the biaxial strain. © *2009 American Institute of Physics*. [doi:10.1063/1.3231444]

Biaxial strain, induced in epitaxial ferroelectric thin films due to differences in lattice parameters or thermal expansion behavior between the films and the underlying substrates, can result in enhanced properties compared to their bulk counterparts.[1,2] For example, enhancements of the paraelectric to ferroelectric transition temperature (T_c) hundreds degrees have been observed in strained $BaTiO_3$ thin films.[1] Biaxial strain is thus recognized as a useful tool to modify the properties of ferroelectric materials. It is still unclear, however, whether the strong coupling between strain and polarization is a common feature of all ferroelectric materials. Recent first-principles studies[3] and phase-field simulations[4] suggest that it is not universally true, and the sensitivity to biaxial strain depends on the piezoelectric and elastic properties of materials. Especially, $(111)_p$-oriented $BiFeO_3$ films, where the subscript p denotes pseudocubic indices, showed very little strain dependence of remanent polarization, much smaller than the conventional ferroelectrics such as $PbTiO_3$ and $BaTiO_3$.[3] On the other hand, thermodynamic calculations reveal the remanent polarization to be very sensitive to biaxial strain for $(001)_p$-oriented $BiFeO_3$ thin films.[5]

In this study, we examine the effect of biaxial strain on the remanent polarization, which is the out-of-plane component of the polarization vector $\mathbf{P}$, of several ferroelectric materials using phenomenological Landau–Devonshire theory.[6,7] In particular, we determine the strain dependence of the remanent polarization for $(001)_p$-oriented $BaTiO_3$, $PbTiO_3$, $PbZr_{0.6}Ti_{0.4}O_3$, and $BiFeO_3$ thin films at room temperature. For comparison, we also calculate the strain dependence of the remanent polarization for $(111)_p$-oriented $BiFeO_3$ and $PbZr_{0.6}Ti_{0.4}O_3$ thin films and discuss the differences in strain tunability between $(001)_p$ and $(111)_p$-oriented ferroelectric thin films.

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 $[100]_p$, $[010]_p$, and $[001]_p$ crystallographic directions of a ferroelectric crystal, the free energy of the ferroelectric crystal as a function of strain (ε_{ij}) and polarization $\mathbf{P}(P_1, P_2, P_3)$ can be written as

$$\begin{aligned} F = F_{\text{bulk}} + F_{\text{elastic}} &= \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) \\ &+ \alpha_{12}(P_1^2P_2^2 + P_1^2P_3^2 + P_2^2P_3^2) + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) \\ &+ \alpha_{112}[P_1^2(P_2^4 + P_3^4) + P_2^2(P_1^4 + P_3^4) + P_3^2(P_1^4 + P_2^4)] \\ &+ \alpha_{123}P_1^2P_2^2P_3^2 + \alpha_{1111}(P_1^8 + P_2^8 + P_3^8) + \alpha_{1112}[P_1^6(P_2^2 \\ &+ P_3^2) + P_2^6(P_1^2 + P_3^2) + P_3^6(P_1^2 + P_2^2)] + \alpha_{1122}(P_1^4P_2^4 \\ &+ P_1^4P_3^4 + P_2^4P_3^4) + \alpha_{1123}(P_1^4P_2^2P_3^2 + P_1^2P_2^4P_3^2 + P_1^2P_2^2P_3^4) \\ &+ \tfrac{1}{2}c_{ijkl}(\varepsilon_{ij} - \varepsilon_{ij}^0)(\varepsilon_{kl} - \varepsilon_{kl}^0), \end{aligned} \tag{1}$$

where α_1, α_{ij}, α_{ijk}, and α_{ijkl} are the phenomenological Landau–Devonshire coefficients under stress-free boundary conditions, c_{ijkl} are the elastic constants, and ε_{ij}^0 is the stress-free strain caused by the polarization field, i.e.,

$$\varepsilon_{ij}^0(i = j) = (Q_{11} - Q_{12})P_i^2 + \beta,$$

$$\varepsilon_{ij}^0(i \neq j) = Q_{44}P_iP_j, \quad \beta = Q_{12}(P_1^2 + P_2^2 + P_3^2) \tag{2}$$

where Q_{ij} are electrostrictive coefficients in Voigt notation. It should be noted that $BiFeO_3$ is simultaneously antiferromagnetic and ferroelectric at room temperature. However, experimental measurements showed that $BiFeO_3$ has a large spontaneous polarization but a quite weak saturated magnetization.[8] Therefore, the spontaneous magnetization is expected to have an insignificant effect on the spontaneous polarization through magnetoelectric coupling, and it is ignored in this work as an approximation. For a $(001)_p$-oriented ferroelectric thin film grown epitaxially on a cubic substrate, biaxial strain is imposed along film/substrate interface ($x_1 - x_2$); while all the stress components involving the out-of-plane direction (x_3) are zero due to the existence of free film surface, i.e.,

$$\varepsilon_{11} = \varepsilon_{22} = e^0, \quad \varepsilon_{12} = \varepsilon_{21} = 0,$$

$$\sigma_{13} = \sigma_{31} = \sigma_{23} = \sigma_{32} = \sigma_{33} = 0, \tag{3}$$

where the biaxial strain e^0 depends on the lattice parameters and/or thermal expansion coefficients of the film and the

---

[a)] Electronic mail: jxianzhang@hotmail.com.

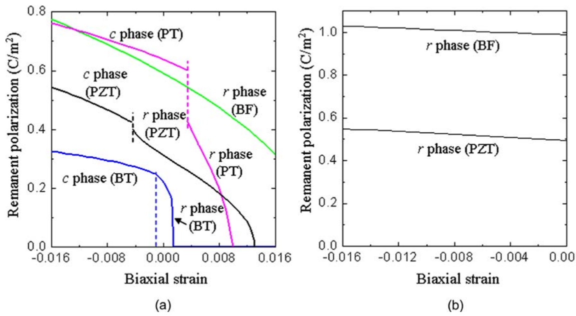


FIG. 1. (Color online) Remanent polarization of (a) $(001)_p$-oriented ferroelectric thin films and (b) $(111)_p$-oriented ferroelectric thin films as a function of biaxial strain at room temperature.

substrate. It should be noted that for thick ferroelectric films, biaxial strain will also depend on the formation of dislocations near film/substrate interface,[7,9] which could be calculated following the approach, e.g., of Ban and Alpay.[7] By taking into account the above boundary conditions, Eq. (1) reduces to

$$F = F_{\text{bulk}} + \frac{c_{11}-c_{12}}{c_{11}}(c_{11}+2c_{12})(e^0-\varepsilon_{11}^0)^2 + 2c_{44}(\varepsilon_{12}^0)^2. \qquad (4)$$

We can see that the elastic energy will be minimized when the in-plane stress-free strains $\varepsilon_{11}^0(=\varepsilon_{22}^0)$ equal to the biaxial strain e^0 and $\varepsilon_{12}^0=0$. Any change to the polarization value, however, would result in an energy penalty to the bulk Landau free energy. Therefore, the polarization of an epitaxial ferroelectric thin film is determined by the minimization of the total free energy, i.e., $\partial F/\partial P_i=0$ $(i=1,2,3)$. The Landau–Devonshire coefficients, elastic constants, and electrostrictive coefficients employed in the calculations are listed in Ref. 10.[11,12]

The effect of the biaxial strain on the remanent polarizations of $(001)_p$-oriented ferroelectric films is shown in Fig. 1(a). For BiFeO_3 films, the remanent polarization P_3 increases and the in-plane polarization (P_1 and P_2) decreases under a compressive biaxial strain to decrease the elastic energy (misfit). This follows route A on the free energy contour map shown in Fig. 3(a). In contrast, a tensile biaxial strain decreases the remanent polarization and increases the in-plane polarization. The spontaneous polarization, which is the absolute value of the polarization vector ($|\mathbf{P}|$), does not change much with the biaxial strain, as shown in Fig. 2.

To understand the relationship between spontaneous polarization and biaxial strain, we will first ignore the elastic energy term $2c_{44}(\varepsilon_{12}^0)^2$ in Eq. (4), which originated from the shear deformation of ferroelectric materials. In this case the spontaneous polarization is

$$P_s = \frac{\sqrt{2}}{2}\sqrt{\frac{\gamma}{\lambda}},$$

$$\gamma = -a_1[6a_{11}c_{11} - 3a_{12}c_{11} + (c_{11}-c_{12})(c_{11}+2c_{12})(Q_{11} - Q_{12})^2] + 2(2a_{11}-a_{12})(c_{11}-c_{12})(c_{11}+2c_{12})(Q_{11} + 2Q_{12})e_0, \qquad (5)$$

$$\lambda = 2a_{11}^2c_{11} - a_{12}[a_{12}c_{11} + (c_{11}-c_{12})(c_{11}+2c_{12})Q_{12}(2Q_{11} + Q_{12})] + a_{11}[a_{12}c_{11} + (c_{11}-c_{12})(c_{11}+2c_{12})(Q_{11}^2 + 2Q_{11}Q_{12} + 3Q_{12}^2)].$$

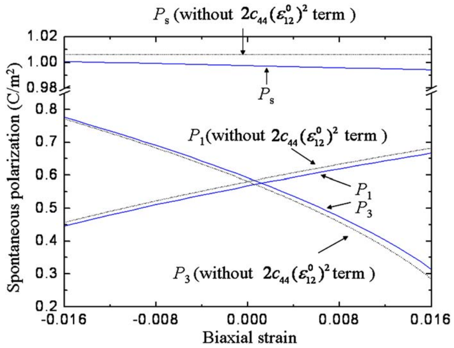
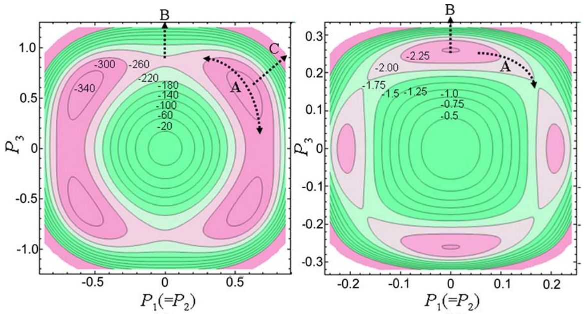


FIG. 2. (Color online) Spontaneous polarization of $(001)_p$-oriented BiFeO_3 thin films as a function of biaxial strains at room temperature. The dashed lines show the calculated spontaneous polarization when the contribution of the $2c_{44}(\varepsilon_{12}^0)^2$ term to the total free energy is ignored.

We can see that the strain dependence of the spontaneous polarization is proportional to $Q_{11}+2Q_{12}$. The value of $Q_{11}+2Q_{12}$ is very small for BiFeO_3; therefore, the spontaneous polarization does not change much with strain, as shown by the dashed line in Fig. 2.

We now discuss the effect of the $2c_{44}(\varepsilon_{12}^0)^2$ term on polarization. As $\varepsilon_{12}^0=Q_{44}P_1P_2$, including the $2c_{44}(\varepsilon_{12}^0)^2$ term in the minimization of the free energy results in a decrease in P_1 (P_2), and thus a smaller spontaneous polarization P_s (solid line in Fig. 2). We also note that under a compressive biaxial strain, the effect of $2c_{44}(\varepsilon_{12}^0)^2$ term is less significant than under a tensile biaxial strain, i.e., the difference between the solid line [with $2c_{44}(\varepsilon_{12}^0)^2$ term] and the dashed line (without this term) decreases from the tensile strain end to the compressive strain end of Fig. 2. As a result, the spontaneous polarization increases slightly as this difference decreases. The net result is that for the BiFeO_3 films with (distorted) rhombohedral symmetry, the biaxial strain just rotates the polarization direction without significantly changing its magnitude.

When the compressive biaxial strain is larger than −0.042, a phase transition from the (distorted) rhombohedral phase to a tetragonal c phase $(P_1=P_2=0, P_3\neq 0)$ occurs. This is similar to the electric-field-induced rhombohedral to tetragonal phase transitions in relaxor ferroelectric single crystals. For the tetragonal phase, the change in polarization will follow route B as the biaxial compressive strain is increased, as shown in Fig. 3(a). Note that the isoenergy contours along route B are much more dense than those along route A because there is a much larger energy penalty of the bulk Landau free energy. Therefore, it is expected that BiFeO_3 films show weak strain dependence for the tetragonal phase. On the other hand, when the tensile biaxial strain is large enough, the (distorted) rhombohedral phase will transform to an orthorhombic phase $(P_1=P_2\neq 0, P_3=0)$, for which the remanent polarization will reduce to zero. Therefore, the largest strain dependence of the remanent polarization will be in films with (distorted) rhombohedral symmetry. These findings also hold for other ferroelectric materials for which the rhombohedral phase is stable under stress-free



(a) (b)

FIG. 3. (Color online) Free energy (unit: 10^6 $\mathrm{Jm^{-3}}$) of bulk stress-free (a) $BiFeO_3$ [route A describes the polarization changing under biaxial strain for $(001)_p$-oriented films with (distorted) rhombohedral symmetry; route B describes the polarization changing under compressive biaxial strain for $(001)_p$-oriented films with tetragonal symmetry; and route C describes the polarization changing under compressive biaxial strain for $(111)_p$-oriented films with rhombohedral symmetry] and (b) $BaTiO_3$ [route A describes the polarization changing under tensile biaxial strain for $(001)_p$-oriented films with (distorted) rhomobhedral symmetry; route B describes the polarization changing under compressive biaxial strain for $(001)_p$-oriented films with tetragonal symmetry] crystal at room temperature.

conditions at room temperature, e.g., $PbZr_{0.6}Ti_{0.4}O_3$, as shown in Fig. 1(a).

For ferroelectric materials, such as $PbTiO_3$ and $BaTiO_3$, that have tetragonal symmetry under stress-free conditions at room temperature, the remanent polarization will change along route B under compressive biaxial strains, as shown in Fig. 3(b). Under tensile biaxial strains, these tetragonal phases will first transform to a (distorted) rhombohedral phase and then to an orthorhombic phase along route A. Note that there is a smaller increase in the bulk Landau free energy along route A than along route B. Therefore, a stronger strain dependence is also obtained in the (distorted) rhombohedral phase region, as shown in Fig. 1(a). For such materials, however, the (distorted) rhombohedral phase region is small as the tetragonal phase is more stable in terms of bulk Landau free energy.

We also calculated the effect of biaxial strain on the remanent polarization of a $(111)_p$-oriented $BiFeO_3$ thin film using thermodynamic analysis, as previous first-principles calculations showed very little strain dependence of the remanent polarization,[3] which is quite different from what we observed for $(001)_p$-oriented $BiFeO_3$ films. In this paper, we only study the effect of compressive biaxial strain, for which the remanent polarization is essentially the spontaneous polarization.[5] Details of the thermodynamic calculations for $(111)_p$-oriented thin films can be found in Ref. 5. A very small strain tunability of $(111)_p$-oriented $BiFeO_3$ thin films is observed [shown in Fig. 1(b)], in agreement with previous first-principles calculations.[3] From previous studies,[5] we know that the film maintains its rhombohedral symmetry ($P_1=P_2=P_3$) under a compressive biaxial strain. Therefore the change in polarization follows route C shown in Fig. 3(a). The much larger energy penalty along route C, compared to route A [that is for $(001)_p$-oriented $BiFeO_3$ films], is responsible for the smaller strain tunablility of $(111)_p$-oriented $BiFeO_3$ films. We note that the results on $BiFeO_3$ thin films in this work are slightly different from those reported in our previous work.[5] This is because the coefficients used in Ref. 5 are based on earlier measured values of spontaneous polarization. The good strain stability of $(111)_p$–oriented films is not particular to $BiFeO_3$ but hold for other ferroelectric materials, such as $PbZr_{0.6}Ti_{0.4}O_3$, as shown in Fig. 1(b).

In summary, we have studied the effect of biaxial strain on the remanent polarization of epitaxial ferroelectric thin films using phenomenological Landau–Devonshire theory. Our calculations reveal that the remanent polarization is quite sensitive to biaxial strain for $(001)_p$-oriented thin films with (distorted) rhombohedral symmetry. In contrast, the remanent polarization of $(111)_p$-oriented rhombohedral thin films is much more stable and only weakly affected by strain due to the significant Landau free energy costs associated with changing the remanent polarization for this orientation. It should be noted that the present work is focused on the strain effect of spontaneous polarization and assumes single domain with short-circuited boundary condition. For open-circuited boundary condition, the charges at surfaces will have significant effect on ferroelectric properties. Phase-field method needs to be employed to take into account the open-circuited boundary condition and domain formation.

The authors are grateful for the financial support from the Department of Energy under Grant No. DOE DE-FG02-07ER46417 (L.Q.C.) and from the National Science Foundation under Grant Nos. DMR-0820404 (D.G.S.) and ECCS-0708759 (C.B.E.).

[1] K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L. Q. Chen, D. G. Schlom, and C. B. Eom, Science **306**, 1005 (2004).

[2] J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, Nature (London) **430**, 758 (2004).

[3] C. Ederer and N. A. Spaldin, Phys. Rev. Lett. **95**, 257601 (2005).

[4] Y. L. Li, L. Q. Chen, G. Asayama, D. G. Schlom, M. A. Zurbuchen, and S. K. Streiffer, J. Appl. Phys. **95**, 6332 (2004).

[5] J. X. Zhang, Y. L. Li, Y. Wang, Z. K. Liu, L. Q. Chen, Y. H. Chu, F. Zavaliche, and R. Ramesh, J. Appl. Phys. **101**, 114105 (2007).

[6] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998); N. A. Pertsev, A. K. Tagantsev, and N. Setter, Phys. Rev. B **61**, R825 (2000); A. G. Zembilgotov, N. A. Persev, U. Böttger, and R. Waser, Appl. Phys. Lett. **86**, 052903 (2005).

[7] Z. G. Ban and S. P. Alpay, J. Appl. Phys. **91**, 9288 (2002).

[8] T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M. P. Cruz, Y. H. Chu, C. Ederer, N. A. Spaldin, R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, and R. Ramesh, Nature Mater. **5**, 823 (2006).

[9] D. Balzar, P. Ramakrishnan, P. Spagnol, S. Mani, A. Hermann, and M. Matin, Jpn. J. Appl. Phys., Part 1 **41**, 6628 (2002); V. Nagarajan, I. G. Jenkins, S. P. Alpay, H. Li, S. Aggarwal, L. Salamanca-Riba, A. L. Roytburd, and R. Ramesh, J. Appl. Phys. **86**, 595 (1999).

[10] The parameters (in SI units, where the temperature T in °C) of free energy used in the calculations are as follows: for $BaTiO_3$, $\alpha_1=4.124(T-115)\times10^5$, $\alpha_{11}=-2.097\times10^8$, $\alpha_{12}=7.974\times10^8$, $\alpha_{111}=1.294\times10^9$, $\alpha_{112}=-1.950\times10^9$, $\alpha_{123}=-2.500\times10^9$, $\alpha_{1111}=3.863\times10^{10}$, $\alpha_{1112}=2.529\times10^{10}$, $\alpha_{1122}=1.637\times10^{10}$, $\alpha_{1123}=1.367\times10^{10}$, $Q_{11}=0.10$, $Q_{12}=-0.034$, $Q_{44}=0.058$, $c_{11}=1.78\times10^{11}$, $c_{12}=0.96\times10^{11}$, and $c_{44}=1.22\times10^{11}$; for $PbTiO_3$, $\alpha_1=3.8(T-479)\times10^5$, $\alpha_{11}=-7.3\times10^7$, $\alpha_{12}=7.5\times10^8$, $\alpha_{111}=2.6\times10^8$, $\alpha_{112}=6.1\times10^8$, $\alpha_{123}=-3.7\times10^9$, $Q_{11}=0.089$, $Q_{12}=-0.026$, $Q_{44}=0.0675$, $c_{11}=1.75\times10^{11}$, $c_{12}=0.794\times10^{11}$, and $c_{44}=1.11\times10^{11}$; for $PbZr_{0.6}Ti_{0.4}O_3$, $\alpha_1=2.33(T-364.3)\times10^5$, $\alpha_{11}=1.362\times10^8$, $\alpha_{12}=2.391\times10^8$, $\alpha_{111}=2.712\times10^8$, $\alpha_{112}=1.213\times10^9$, $\alpha_{123}=-5.690\times10^9$, $Q_{11}=0.073$, $Q_{12}=-0.027$, $Q_{44}=0.063$, $c_{11}=1.681\times10^{11}$, $c_{12}=0.826\times10^{11}$, and $c_{44}=0.407\times10^{11}$; for $BiFeO_3$, $\alpha_1=8.78(T-830)\times10^5$, $\alpha_{11}=4.71\times10^8$, $\alpha_{12}=5.74\times10^8$, $Q_{11}=0.035$, $Q_{12}=-0.0175$, $Q_{44}=0.0403$, $c_{11}=3.02\times10^{11}$, $c_{12}=1.62\times10^{11}$, and $c_{44}=0.68\times10^{11}$.

[11] K. M. Rabe, C. H. Ahn, and J. M. Triscone, *Physics of Ferroelectrics: A Modern Perspective* (Springer, Berlin, 2007), pp. 363–371.

[12] Y. L. Li, L. E. Cross, and L. Q. Chen, J. Appl. Phys. **98**, 064101 (2005); M. J. Haun, E. Furman, S. J. Jand, H. A. McKinstry, and L. E. Cross, J. Appl. Phys. **62**, 3331 (1987); N. A. Pertsev, V. G. Kukhar, H. Kohlstedt, and R. Waser, Phys. Rev. B **67**, 054107 (2003).