Strain induced internal potentials of compositionally graded epitaxial ferroelectric thin films

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Compositionally graded ferroelectrics produce internal potentials that manifest themselves as asymmetric hysteresis in polarization versus applied field plots. The direction and magnitude of the built-in fields depend on the sense of the chemical gradient in unclamped graded ferroelectrics. A thermodynamic model was employed to understand how these potentials would be affected by an inhomogeneous internal strain in epitaxial compositionally graded ferroelectric structures. The analysis indicates that the strain field can be employed to control both the magnitude and direction of the internal potentials. Indeed, the sense of the polarization gradient may be completely reversed with the appropriate strain gradient. © *2007 American Institute of Physics*.
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Polarization graded ferroelectrics have captured a great deal of interest in recent years as they display strikingly new behavior uncommon to homogeneous materials, the most notable being a translation of the ferroelectric hysteresis loop along the polarization axis in an otherwise conventional hysteresis graph when driven by a symmetric period potential.[1–4] It was shown both experimentally and theoretically that spatial variations in the polarization produce this asymmetry, the former of which can be achieved through composition, temperature, and/or strain gradients. The resulting internal electrical and stress fields are much akin to the internal potentials developed in the space charge regions of semiconductor diode junctions. Polarization graded structures have thus given rise to a new class of transcapacitive ferroelectric devices.[3,5] More recent work has extended the ferroelectric results to ferromagnetics and to the general class of ferroics, coining the terminology *transponent devices*.[6,7]

In compositionally graded ferroelectrics, the sense of the internal potential is determined from the direction of the compositional gradient and results in a characteristic displacement offset in an otherwise typical hysteresis curve obtained from placing the devices in a Sawyer-Tower circuit.[1–3,8–11] We define an "up graded" structure as a material with larger polarization at the ferroelectric/substrate interface and a smaller polarization at the free surface. Conversely, in a "down graded" ferroelectric, the polarization gradient is reverse. The terminology arises in an "up" ("down") device produces a positive (negative) offset along the polarization axis in a hysteresis plot.

A number of applications for transcapacitive devices have been identified, the most notable being active pyroelectric devices and large strain piezoelectrics.[6,12] One of the more deleterious effects of such structures, however, is the internal potentials created by compositional variations and nonuniform stress states in ferroelectric random access devices, yielding "imprint effects," thus making them unsuitable for data storage.[13] In this study, we analyze the polarization distribution and the charge offset of compositionally graded epitaxial thin films as a function of the inhomogeneous internal strain state that arises from lattice misfit and the self-strain of the ferroelectric transformation. The results show not only that strain fields can be employed to control the magnitude of the charge offset through the average misfit, but also the sense of the polarization gradient and hence the internal potential may actually be reversed under extreme conditions.

Consider an epitaxial compositionally graded ferroelectric structure of total thickness h and lateral dimensions L such that $L \gg h$ (Fig. 1). We will assume that the easy axis of polarization is along the film thickness such that $P_1 = P_2 = 0$ and $P_3 = P(z)$, where P_i are the components of the polarization vector. Each "layer" of the heterostructure is homogeneous in the lateral directions (x and y). The free energy density of the film can be written as

$$F = F_P + \int_0^h \left[\alpha P(z)^2 + \beta P(z)^4 + \gamma P(z)^6 + \frac{1}{2} A \left(\frac{dP(z)}{dz} \right)^2 - \frac{1}{2} E_d(z) P(z) + F_{\mathrm{EL}}(z) \right] dz, \qquad (1)$$

where F_P is the sum of energies of the layers that make up the graded heterostructure in their paraelectric state, α, β, and γ are dielectric stiffness coefficients, and $A(z)$ is the gradient (Ginzburg) coefficient. The quadratic stiffness coef-

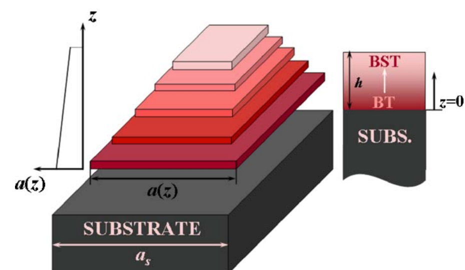

FIG. 1. (Color online) Schematic illustration of an epitaxial compositionally graded $Ba_xSr_{1-x}TiO_3$ (BST) thin film ($x = 1 \rightarrow 0.7$) on a cubic substrate.

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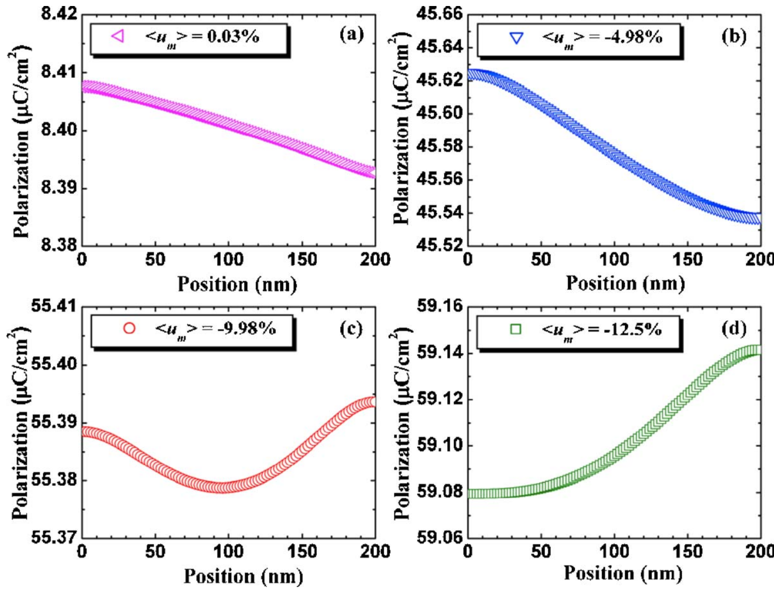

FIG. 2. (Color online) Polarization profiles of compositionally graded $Ba_xSr_{1-x}TiO_3$ (BST) thin film ($x=1 \rightarrow 0.7$) at different misfit strains.

ficient α follows the Curie-Weiss law, such that $\alpha=(T-T_C)/(2C\varepsilon_0)$, where T_C and C are the Curie-Weiss temperature and constant of a bulk ferroelectric, respectively, and ε_0 is the permittivity of free space. E_d is the depolarization field due to polarization gradient that can be expressed as[14]

$$E_d = -\frac{1}{\varepsilon_0}\left[P(z) - \frac{1}{h}\int_0^h P(z)dz\right] = -\frac{1}{\varepsilon_0}[P(z) - \langle P(z)\rangle]. \tag{2}$$

The last term of the integral in Eq. (1) is the elastic energy due to lattice misfit and self-strain of the phase transformation given by

$$F_{\mathrm{EL}} = \frac{1}{\tilde{S}(z)}[u_m(z) - Q_{12}(z)P(z)^2]^2, \tag{3}$$

where $\tilde{S}(z)=S_{11}(z)+S_{12}(z)$, and S_{ij} and Q_{ij} are the elastic compliances at constant polarization and electrostrictive coefficients, respectively, given in Voigt notation. $u_m(z)$ is the polarization-free misfit strain,

$$u_m(z) = \frac{a_S - a(z)}{a_S}, \tag{4}$$

where a_S is the lattice parameter of the substrate and $a(z)$ is the lattice parameter of the graded film as a function of the position z. In Eq. (3), the elastic energy due to bending is neglected since the substrate thickness is much larger than h.[15]

Thermodynamic equilibrium is dictated by the equation of state $\partial F/\partial P=0$, which yields an Euler-Lagrange relation,

$$A\frac{d^2P}{dz^2} = 2\tilde{\alpha}P + 4\tilde{\beta}P^3 + 6\gamma P^5 - \frac{1}{2h\varepsilon_0}\int_0^h P dz, \tag{5}$$

where $\tilde{\alpha}=\alpha+1/2\varepsilon_0-2Q_{12}u_m/\tilde{S}$ and $\tilde{\beta}=\beta+Q_{12}^2/\tilde{S}$. The solution to Eq. (5) results in a polarization profile that can be used to compute the charge offset ΔQ from[3]

$$\Delta Q = \frac{k}{h}\int_0^h z\left(\frac{dP(z)}{dz}\right)dz, \tag{6}$$

where k is the ratio of the capacitance of a load capacitor in Sawyer-Tower circuit to the capacitance of the graded ferroelectric thin film. In order to clearly illustrate the intrinsic role of the internal strains, k was taken as 1. We note that the charge offset can always be amplified externally via a device configuration with $k>1$.

In our analysis, we have taken compositionally graded $BaTiO_3$ (BT)–$Ba_xSr_{1-x}TiO_3$ (BST) thin films ($x=1\rightarrow 0.7$) as an example since BST is a potential material system for many applications including infrared detectors and tunable microwave devices.[16] The thermodynamic coefficients and elastic constants $Ba_{0.7}Sr_{0.3}TiO_3$ (BST 70/30) were obtained by averaging the corresponding parameters of BT and $SrTiO_3$ (ST), which were taken from Ref. 14. For electrostrictive coefficients, we assume a defect-free pseudomorphic BT–BST 70/30 down graded film on a cubic substrate with lattice parameter of a_S. By varying the value of the substrate lattice parameter, we evaluate the effect of the epitaxial strains on the polarization profile and the charge offset. The lattice parameter of the graded thin film $a(z)$ can be calculated by using a linear regression,

$$a(z) = \frac{z}{h}(a_{\mathrm{BT}} - a_{\mathrm{BST\ 70/30}}), \tag{7}$$

where $\alpha_{\mathrm{BT}}=0.4005$ nm and $\alpha_{\mathrm{BST\ 70/30}}=0.3993$ nm are the lattice parameters of BT and BST 70/30, respectively. In this way, the position dependent internal strain can be calculated from Eq. (4). The polarization profiles of the graded film as a function of the average strain,

$$\langle u_m\rangle = \frac{1}{h}\int_0^h u_m(z)dz, \tag{8}$$

were calculated at room temperature and are shown in Fig. 2.

Intuitively, since BT is a "harder" ferroelectric in bulk than BST, the BT end should have a larger polarization than the BST end, which is true for cases with tensile strain and moderate compressive strains, as shown in Figs. 2(a) and 2(b). However, for larger compressive strains, the polariza-

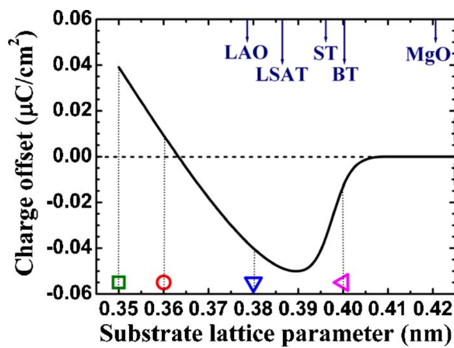

FIG. 3. (Color online) Charge offset of compositionally graded $Ba_xSr_{1-x}TiO_3$ (BST) thin film ($x=1\rightarrow0.7$) as a function of the average misfit strain. Also marked as a reference are lattice parameters of commonly used materials as substrates and/or films, such as $LaAlO_3$ (LAO), $(LaAlO_3)_x(SrAl_{0.5}Ta_{0.5}O_3)_{1-x}$ (LSAT), MgO, ST, and BT.

tion of the BST end increases more than the BT end, which results in a polarization profile that is completely reversed under extremely large compressive strains ($\langle u_m\rangle=-12.5\%$). Thus, a down graded heterostructure in bulk may become up graded in thin film form due to internal strains. This can be related to the difference between elastic compliances and lattice parameters of BT and BST. BST has smaller elastic compliance than BT, which results in larger elastic displacements in the BST compared to BT (we ignore anomalies in the elastic behavior near BST 70/30). This immediately translates to larger polarization in the BST. Furthermore, we also note that BST has a smaller lattice parameter than BT. Therefore, on the same substrate, lattice mismatch induces less compressive strain at the BST end than the BT end. We note that the interplay of these two effects results in the polarization profile shown in Fig. 2(c) which resembles a down graded and an up graded ferroelectric back to back. When the graded thin film is under a large compressive strain, the direction of polarization gradient is completely reversed [Fig. 2(d)].

We plot the charge offset from Eq. (6) as a function of the average misfit in Fig. 3. Also marked on this graph are the lattice parameters of common substrates and the strains corresponding to polarization profiles of Fig. 2. The charge offset varies from positive to negative when the polarization profile changes directions and vanishes for sufficiently high in-plane tensile strains (1.3%). This critical strain corresponds to a graded structure wherein all layers become paraelectric; in each layer, in-plane tensile stresses suppress ferroelectricity.

The presented analysis is applicable to very thin graded epitaxial structures where each layer is pseudomorphic with respect to the underlying substrate. For relatively thicker graded films, relaxation by the formation of interfacial dislocations has to be considered in establishing the strain state. While the role of misfit dislocations in graded semiconductors has been studied experimentally and theoretically,[17,18] there are only a few studies on the relaxation mechanisms and dislocation substructures in films of multilayer ferroelectric oxides.[11] If the grading starts from a layer with a high misfit and proceeds to layers with lower misfit, relaxation can be assumed to occur primarily near the film-substrate interface. In this case, the nonlinear misfit strain can be approximated using, for example, a Heaviside function H of the form $u_m(z)=\langle u_m\rangle[H(-z+h_c)+\xi H(z-h_c)e^{-z/h_c}]$, where ξ is a constant and h_c is a characteristic dimension that describes the length scale of the strain relaxation (typically ~10 nm in homogeneous epitaxial ferroelectrics[19]). Otherwise, the strain as a function of the position within the film has to be determined experimentally, which is a challenging task.

The model developed for epitaxially graded ferroelectrics has significant implications besides the strain-induced reversal of the polarization direction. It shows qualitatively that imprint in ferroelectric films can be related to compositional and strain variations. Any slight variation in the strain state or composition may result in the shift of the symmetric polarization hysteresis loops in homogeneous films. As an immediate consequence of these findings, we note from Fig. 2 that by suitably adjusting the internal stresses of ferroelectric devices, imprint effects may be suppressed [see, e.g., Ref. 20]. Moreover, Fig. 2(c) clearly shows that back-to-back graded devices and more complicated transponent devices (such as push-pull amplifiers[5]) may readily be constructed by careful consideration of the stress state of the structures, thus opening the way for the fabrication of heterostructures akin to semiconductor multilayer devices [see, e.g., Ref. 21].

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[1] J. V. Mantese, N. W. Schubring, A. L. Micheli, M. S. Mohammed, R. Naik, and G. W. Auner, Appl. Phys. Lett. **71**, 2047 (1997).
[2] M. Brazier, M. McElfresh, and S. Mansour, Appl. Phys. Lett. **72**, 1121 (1998).
[3] Z. Chen, K. Arita, M. Lim, and C. A. P. Araujo, Integr. Ferroelectr. **24**, 181 (1999).
[4] D. Bao, N. Mizutani, X. Yao, and L. Zhang, Appl. Phys. Lett. **77**, 1041 (2000).
[5] J. V. Mantese, N. W. Schubring, and A. L. Micheli, Appl. Phys. Lett. **80**, 1430 (2002).
[6] S. Zhong, Z. G. Ban, S. P. Alpay, and J. V. Mantese, Appl. Phys. Lett. **89**, 142913 (2006).
[7] C. Sudakar, R. Naik, G. Lawes, J. V. Mantese, A. L. Micheli, G. Srinivasan, and S. P. Alpay, Appl. Phys. Lett. **90**, 062502 (2007).
[8] T. Tsurumi, T. Miyasou, Y. Ishibashi, and N. Ohashi, Jpn. J. Appl. Phys., Part 1 **37**, 5104 (1998).
[9] D. Bao, N. Mizutani, X. Yao, and L. Zhang, Appl. Phys. Lett. **77**, 1203 (2000).
[10] I. Boerasu, L. Pintilie, and M. Kosec, Appl. Phys. Lett. **77**, 2231 (2000).
[11] X. H. Zhu, H. L. W. Chan, C.-L. Choy, K.-H. Wong, and D. Hesse, Appl. Phys. A: Mater. Sci. Process. **82**, 709 (2006).
[12] G. Akcay, S. Zhong, and S. P. Alpay, Solid State Commun. **137**, 589 (2006).
[13] Y. Zhou, H. K. Chan, C. H. Lam, and F. G. Shin, J. Appl. Phys. **98**, 024111 (2005).
[14] Z.-G. Ban, S. P. Alpay, and J. V. Mantese, Phys. Rev. B **67**, 184104 (2003).
[15] L. B. Freund, J. Mech. Phys. Solids **44**, 723 (1996).
[16] N. W. Schubring, J. V. Mantese, A. L. Micheli, A. B. Catalan, M. S. Mohammed, R. Naik, and G. W. Auner, Integr. Ferroelectr. **24**, 155 (1999).
[17] T. G. Andersson, Z. G. Chen, V. D. Kulakovskii, A. Uddin, and J. T. Vallin, Appl. Phys. Lett. **51**, 752 (1987).
[18] E. A. Fitzgerald, A. Y. Kim, M. T. Currie, T. A. Langdo, G. Taraschi, and M. T. Bulsara, Mater. Sci. Eng., B **67**, 53 (1999).
[19] S. P. Alpay, I. B. Misirlioglu, V. Nagarajan, and R. Ramesh, Appl. Phys. Lett. **85**, 2044 (2004).
[20] P. J. Schorn, P. Gerber, U. Boettger, R. Waser, G. Beitel, N. Nagel, and R. Bruchhaus, Integr. Ferroelectr. **73**, 83 (2005).
[21] G. K. Celler and S. Cristoloveanu, J. Appl. Phys. **93**, 4955 (2003).