

# Domain structures in continuously graded ferroelectric films

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Thermodynamic analysis of a graded ferroelectric epitaxial film demonstrates that in the equilibrium state the films subdivide into an alternation of polydomain bands consisting of wedge- or lens-shape domains and single-domain bands. Polarization under an external electrical field proceeds through an interband boundary movement due to the growth/shrinkage of the wedge domains. The domain structure and its evolution are determined by the distribution of the spontaneous polarization and dielectric constant. Through film grading, it is possible to design a controlled domain structure with desirable tunability. Graded films exhibit a sharp increase of the dielectric constant as electrical field approaches zero. © 2009 American Institute of Physics. [DOI: 10.1063/1.3120555]

Graded ferroelectric films and multilayers are promising materials for microelectronic applications.<sup>1</sup> However, after many years of experimental and theoretical studies of special dielectric and piezoelectric responses of graded ferroelectrics, their domain structure remains unknown. It was suggested in Ref. 2 that the principal cause for functional properties of graded ferroelectrics lies in the formation of special wedge-domain structures that minimize the electrostatic energy of the nonuniform polarization distribution. The thermodynamic theory based on this idea provided a principal explanation of the dielectric properties of graded multilayer films, in particular of the strong dependence of the dielectric constant on the field.

In this paper we develop the concept of wedge domains to continuously graded ferroelectric films. We will consider the equilibrium state of a ferroelectric film, with its parameters (spontaneous polarization, dielectric constant, etc.) changing continuously throughout the film thickness. For simplicity we consider uniaxial ferroelectrics.

We will show that in the equilibrium state, a graded ferroelectric film adopts the structure of alternating bands of single-domain and polydomain layers. The band structure is completely determined by the applied electric fields  $E$  and by the microscopic Landau–Devonshire potential  $f(P(X), X)$ , where  $P(X)$  is the polarization in the layer with coordinate  $X$  (see Fig. 1). The change in the field induces the change in the domain structure due to the motion of the interband boundaries caused by the single domain  $\rightleftharpoons$  polydomain transformations in the layers. The average polarization and film displacement change correspondingly to the changing domain structure.

First we consider the simplest two-band architecture that arises when the spontaneous polarization  $P_0(X)$  increases monotonically from  $P_0(0)=P_0$  on one surface of the film to  $P_0(L)$  on the other. We will prove that in this case the film will subdivide into two bands: a single-domain band at  $0 < X < \mathcal{L}$  and a polydomain one at  $\mathcal{L} < X < L$  (Fig. 1). In the dimensionless form the Gibbs free energy for the two-band film is as follows:

$$\begin{aligned} \mathcal{F}(p, \mathcal{E}) = F/(L\mathcal{P}_0^2/\epsilon_0) = \mathcal{F}_1 + \mathcal{F}_2 = & \int_0^\xi \{ \phi(p, x) - \mathcal{E}p(x) \\ & + [p(x) - \bar{p}]^2/2 \} dx + \int_\xi^1 \{ \phi[\bar{p}(x)] - \mathcal{E}\bar{p}(x) \\ & + [\bar{p}(x) - \bar{p}]^2/2 \} dx, \end{aligned} \quad (1)$$

where  $x=X/L$ ,  $\xi=\mathcal{L}/L$ ,  $\phi=f/(\mathcal{P}_0^2/\epsilon_0)$ ,  $\mathcal{E}=E/(\mathcal{P}_0/\epsilon_0)$ ,  $p(x)=P(xL)/\mathcal{P}_0$ ,  $\bar{p}(x)=(1-2\beta(x))p(x)$ , and  $\bar{p}=\int_0^\xi p(x)dx + \int_\xi^1 \bar{p}(x)dx$ . To avoid complications due to the elastic interaction between the layers we consider an epitaxial film clamped by the substrate; thus we use the Landau–Devonshire potential that is normalized to include the elastic effect of the substrate. The other terms in Eq. (1) represent the macroscopic contribution of the electrostatic field to the Gibbs free energy: the electrostatic energy of the interaction between the layers, and the work of the electric field.

To realize the minimum of the Gibbs free energy, the polarization fields  $p(x)$ ,  $\bar{p}(x)$ , as well as the domain fraction  $\beta(x)$  have to satisfy the variational equations  $\delta\mathcal{F}_1/\delta p=0$  and  $\delta\mathcal{F}_2/\delta\bar{p}=\delta\mathcal{F}_2/\delta\beta=0$ . Then

$$\partial\phi/\partial p - \mathcal{E} + p(x) - \bar{p} = 0, \quad (2)$$

in the single-domain band ( $x < \xi$ ).

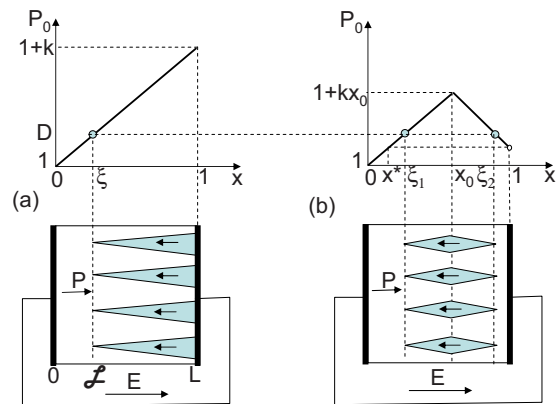


FIG. 1. (Color online) Spontaneous polarization profiles and domain structures at the same displacement  $\mathcal{D}$ : (a) a monotonic  $p_0(x)$  with the minimum at  $x=0$ ; (b) a nonmonotonic  $p_0(x)$  with the minima at  $x=0$  and  $x=1$ .

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In the polydomain band ( $\xi < x < 1$ )

$$\mathcal{E} - \bar{p}(x) + \bar{p} = 0. \quad (3)$$

Then  $\partial\phi/\partial p=0$  and therefore  $p(x)=p_0(x)$  and  $\bar{p}(x)=[1-2\beta(x)]p_0(x)$  is a constant equal to  $p_0(\xi)$ . The domain fraction is given by  $\beta=1/2[1-p_0(\xi)/p_0(x)]$ . It also yields a simple relation between the interband boundary position  $\xi$  and the electrostatic displacement  $\mathcal{D}$ ,

$$\mathcal{D}(\mathcal{E}) = \mathcal{E} + \bar{p} = p_0(\xi). \quad (4)$$

On the other hand, the equation of state for the single-domain phase (2) allows us to express the external field through  $\xi$

$$\mathcal{E}(\xi) = \mathcal{D} - \bar{p} = \xi p_0(\xi) - \int_0^\xi p(x; \xi) dx, \quad (5)$$

where  $p(x; \xi)$  is a solution of Eq. (2) that takes into account (4). Thus Eqs. (4) and (5) define  $\mathcal{D}$  versus  $\mathcal{E}$  as a parametric curve for the field  $\mathcal{E} < \mathcal{E}_{cr} = p_0(1) - \int_0^1 p(x; \xi) dx$ . For  $\mathcal{E} \geq \mathcal{E}_{cr}$  the film is in the single-domain state and its displacement is determined by the equations

$$\partial\phi/\partial p - \mathcal{D} + p(x) = 0, \quad \mathcal{D} = \mathcal{E} - \int_0^1 p(x; \mathcal{D}) dx. \quad (6)$$

The  $\mathcal{D}(\mathcal{E})$  dependence for a general potential  $f$  can be obtained by numerical solution of Eq. (6) and Eq. (4) and (5). If  $f$  is a  $P^4$  Landau–Devonshire potential these equations have an explicit solution via Cardano's formulas.<sup>3</sup>

In practically important cases of moderate gradients of spontaneous polarization, the Landau–Devonshire potential is well-approximated by a quadratic function

$$\phi = [p(x) - p_0(x)]^2 / \{2[\varepsilon(x) - 1]\}, \quad (7)$$

where  $\varepsilon(x)$  is a relative dielectric constant. Then the expression in Eq. (5) is transformed into the equation

$$\mathcal{E} = \int_0^\xi \left[ \frac{dp_0(x)}{dx} \int_0^x \frac{1}{\varepsilon(s)} ds \right] dx, \quad (8)$$

which relates  $\xi$  and  $\mathcal{E}$  through the basic characteristics of the graded film: the gradient of spontaneous polarization and dielectric constant distribution. The film displacement equals to

$$\mathcal{D} = p_0(\xi) = \left[ \mathcal{E} + \int_0^\xi \frac{p_0(x)}{\varepsilon(x)} dx \right] / \int_0^\xi \frac{dx}{\varepsilon(x)}. \quad (9)$$

For example, if the polarization and susceptibility are given by  $p_0(x) = 1 + kx^n$ ,  $n > 0$ , and  $1/\varepsilon(x) = (1/\varepsilon_{\max})(1 + \chi x^m)$  then  $\xi(\mathcal{E})$  is determined from the following equation:

$$\frac{1}{n+1} \xi^{n+1} + \frac{\chi}{(m+1)(n+m+1)} \xi^{n+m+1} = \frac{\varepsilon_{\max}}{kn} \mathcal{E}. \quad (10)$$

It clearly shows that for relatively weak fields ( $\xi < 1/2$ ) the first term in Eq. (10) dominates and  $\xi$  as well as  $\mathcal{D}$  are determined by the polarization gradient  $dp_0/dx$ . On the other hand, the field  $\mathcal{E}_c$  (at  $\xi=1$ ) corresponding to the complete transformation to the single-domain state depends also on the distribution of the dielectric constant. However, the influence of the nonuniformity in the dielectric constant on the  $\mathcal{D}(\mathcal{E})$  dependence is much smaller than the effect of the polariza-

tion gradient; the former can be neglected even for  $x$  close to one.

For example, assuming the approximation  $\varepsilon(x) = \varepsilon_m$  we compute the  $\mathcal{D}(\mathcal{E})$  curves and domain fractions  $\beta(x, \mathcal{E})$  for the two polarization profiles in Fig. 1:

(i)

$$p_0(x) = 1 + kx, \quad 0 \leq x \leq 1,$$

(ii)

$$p_0(x) = \begin{cases} 1 + kx, & 0 \leq x \leq x_0, \quad (x_0 \geq \frac{1}{2}) \\ 1 + 2kx_0 - kx, & x_0 \leq x \leq 1 \end{cases},$$

[if  $k=0.1$  and  $\varepsilon_m=140$  (i) corresponds to the lead zirconate titanate film with the compositional gradient from 70%  $\text{PbTiO}_3 + 30\% \text{ZrTiO}_3$  to 100%  $\text{PbTiO}_3$ ].

For film (i) with the monotonic  $p_0(x)$ , according to Eq. (10) with  $n=1$  we get

$$\mathcal{D} = \begin{cases} 1 + \sqrt{2k\varepsilon_m \mathcal{E}}, & 0 \leq \varepsilon_m \mathcal{E} \leq k/2 \\ 1 + k/2 + \varepsilon_m \mathcal{E}, & k/2 \leq \varepsilon_m \mathcal{E} \end{cases}.$$

For film (ii) with the nonmonotonic  $p_0(x)$ , in the one single-domain band regime we again obtain

$$\mathcal{D} = 1 + \sqrt{2k\varepsilon_m \mathcal{E}}, \quad \text{for } \mathcal{D} \leq p_0(1) = 1 - k + 2kx_0.$$

For  $\mathcal{D} > p_0(1)$  the integrals in Eqs. (5) and (9) split into two parts corresponding to the appearance of the second single-domain band. The band interface locations  $\xi_1$  and  $\xi_2$  are determined from the equations

$$\frac{k\xi_1^2}{2} + \frac{k(1-\xi_2)^2}{2} = \varepsilon_m \mathcal{E}; \quad 1 + k\xi_1 = 1 - k\xi_2 + 2kx_0 = \mathcal{D}(\mathcal{E}).$$

Then

$$\mathcal{D} = \begin{cases} 1 + \frac{k}{2} x^* + \sqrt{k\varepsilon_m \mathcal{E} - k^2 x^{*2}/4}, & k_1 \leq \varepsilon_m \mathcal{E} \leq k_2 \\ 1 + \frac{k}{2} (x^* + 1) - \frac{k}{4} (x^{*2} + 1) + \varepsilon_m \mathcal{E}, & k_2 \leq \varepsilon_m \mathcal{E} \end{cases},$$

where  $x^* = 2x_0 - 1$ ,

$$k_1 = \frac{k}{2} x^{*2},$$

and

$$k_2 = \frac{k}{4} (x^{*2} + 1).$$

In Fig. 2 we present graphs of  $\mathcal{D}(\mathcal{E})$  together with  $\varepsilon(\mathcal{E}) = d\mathcal{D}/d\mathcal{E}$ . It is clear that the introduction of the second single-domain band results in the deviation of the  $\mathcal{D}(\mathcal{E})$  curve from the initial  $\mathcal{D} = 1 + \sqrt{2k\varepsilon_m \mathcal{E}}$  curve, which is accompanied by the kink in the  $\varepsilon(\mathcal{E})$  curve. In the general case the number of single-domain bands corresponds to the number of minima of the spontaneous polarization  $P_0(x)$ . Then the  $\mathcal{D}(\mathcal{E})$  and  $\varepsilon(\mathcal{E})$  curves are determined from Eqs. (5) and (9) with the integrals consisting of a number of subintegrals corresponding to the single-domain bands.

The thermodynamic approach presented above does not take into account hysteresis effects due to the domain wall movement and to the generation/annihilation of bands during

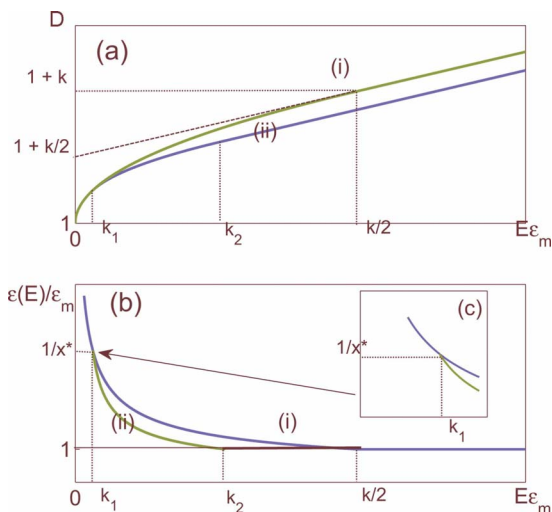


FIG. 2. (Color online) Displacement  $\mathcal{D}$  [Fig. 2(a)] and the dielectric constant  $\epsilon(E)$  [Fig. 2(b)] of graded films with the monotonic and nonmonotonic spontaneous polarization profiles from Fig. 1. (c) A blow-up of the kink in Fig. 2(b).

the domain evolution. However, the wedge domain walls are expected to be highly mobile because they deviate from the close-packed plane orientation.<sup>4</sup> If the complete transformation of the film to the single-domain state is not attained (in particular, for films with strong polarization gradients) the domain evolution can be highly reversible. On the other hand, the depolarizing field induces the domain nucleation even in slightly homogeneous ferroelectrics.<sup>5</sup>

Our thermodynamic approach relies on the homogenization approximation, which is valid if the domain structure period is much smaller than the domain length, and the domain walls contribution to the energy of the film is relatively small comparing to the energy of the long-range electrostatic interaction. Our theoretical results support this approximation for films with thickness exceeding hundreds nanometers.<sup>6,7</sup> Although to clarify this issue a further experimental and theoretical investigation is necessary, the thermodynamic approach of this paper provides useful insights into understanding of domain structure and properties of graded ferroelectrics. The theory presented shows how optimal domain structures in the epitaxial film could be designed through the film grading. A practical realization of this idea by fabrication of high quality epitaxial films with controlled grading may enable engineering of ferroelectric films with desired response to external stimuli (such as electrical field, temperature, or stress).

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