Rigidity of the elastic domain structure near the boundary of its existence in thin epitaxial films

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We consider an interesting and practically important case of elastic domain structure, which is the analogue of c/a domain pattern with 90° walls in perovskites, and is solvable analytically for arbitrary misfit strain. There is no critical thickness, below which the domain structure cannot exist, when the "extrinsic" misfit is zero and the domains are of equal width. At the boundary of polydomain-monodomain transition the period of the pattern diverges, as does the dynamic stiffness of the domain structure. It is unlikely, therefore, that one can achieve a softness of the dielectric response of the c/a elastic domains in ferroelectric-ferroelastic thin films.

Equilibrium domain structures in epitaxial ferroelectric films may appear even in the case of complete compensation of the depolarizing electric fields by the electrodes or finite conductivity of the film. This takes place if the film also behaves as a ferroelastic. Formation of a ferroelastic domain structure was first considered a while ago as a mechanism to relax the misfit imposed by a substrate \textsuperscript{1}. In widely studied perovskite ferroelectrics, which are improper ferroelastics, several elastic domain (and heterophase) structures were predicted \textsuperscript{2,3,4}. One of the typical structures, so-called c/a/c/a... domain pattern, is of a special fundamental and practical interest. Firstly, the ratio of the widths of the c- and a-domains changes with external conditions (film thickness and misfit strain). At some parameters the domain pattern does not exist, i.e. there is a phase transition between multi- and monodomain states. Although the corresponding phase diagrams have been discussed by several authors (see \textsuperscript{2,3} and references therein), the behavior close to the phase transition was not studied. The model calculations \textsuperscript{3} have predicted the response of the c/a domain structure to be large, even giant for some specific values of the ("extrinsic", see below) misfit $w$ and the film thickness $l$, and some data was even interpreted in this way \textsuperscript{4}. The enhancement of the response was expected near the border of existence of the c/a structure in the $w-l$ plane, i.e. near the phase transition. Previous analyses, mainly numerical, have not actually specified the system parameters needed to realize the giant susceptibility. We attempt, therefore, an exact solution of a simplest relevant model, analogous to the actual c/a structures. The present results put strict constraints on the system parameters where the softness of the dielectric response might be expected. It becomes clear that it would be very difficult to realize the domain structure with such a property. As a corollary, the existing data \textsuperscript{3} cannot be interpreted as being due to a large contribution of the elastic domain walls. We reveal in the present paper some unusual features of the polydomain-monodomain phase transition and show that the response of the system becomes more "rigid" in the vicinity of this transition.

We present here the first analytical calculations of the energy of a domain pattern analogous to the standard c/a structure. The structure can be viewed, without loss of generality, as a result of a ferroelastic transition in an epitaxial film, which breaks the symmetry of the parent phase and the substrate. All the strains are considered in the reference frame of the high symmetry phase, and the $z$-axis is selected to be perpendicular to the plane of the film. We consider the system far from the transition, where the pattern consists of the domains having the spontaneous strain, $u_{0}^{zz}, -u_{0}^{zz}$, of opposite signs, separated by the domain walls inclined at 45° with respect to the $z$-axis, as dictated by the elastic compatibility conditions and the lattice symmetry, Fig. 1. In ferroelectric perovskites this would correspond to the 90° walls separating the domains with the polarization parallel and perpendicular to the plane. The film consists of $a-$ and $c-$type domains with the widths $a_1$ and $a_2$, respectively. From the exact expressions for the free energy $F$ [see Eqs. (3),(4)], we calculate the period $2a = a_1 + a_2$ of the structure, the parameter of asymmetry $\delta = (a_1 - a_2)/2a$, and the corresponding stiffness $\kappa$. The stiffness $\kappa$ is closely related to the "mechanical force constant" discussed in Ref. \textsuperscript{3}. We shall consider two stiffnesses: the usually measured dynamic stiffness $\kappa_{\infty}$, calculated at fixed period of the structure, and the static stiffness $\kappa_0$, corresponding to the situation where the period of domain structure is allowed to relax via creation or annihilation of the domain walls. The latter corresponds to very slow processes, making its observation very challenging. One certainly deals with
the dynamic stiffness $\kappa_\infty$ in applications. We shall show that the two stiffnesses exhibit quite different behavior near the transition: the static one diminishes, while the dynamic one diverges. We also study the change of the stiffness with the film thickness and discuss the possibilities of obtaining films with small dynamic stiffness.

We consider first the case where the sole origin of the misfit is the spontaneous strain, $u^{0}_{xx} - u^{0}_{zz}$, appearing at the phase transition. We shall call this misfit “intrinsic”, to distinguish it from “extrinsic” misfit of any other origin. The latter includes e.g. the misfit of parent phase with the substrate, and other, “noncritical”, strain components, which might appear during the phase transition. The effect of extrinsic strain is a focus of the present paper. Similar to previous authors [5], we neglect the uncompensated electric fields, which would only increase the stiffness.

The method of calculating the energy of the domain structure is the same as in our previous paper [7] but with different equations of state for the stress tensor components $\sigma_{ik}$:

\[
\sigma_{zz} = (\lambda + 2\mu) e_{zz} + \lambda (e_{xx} + e_{yy}),
\]

\[
\sigma_{xx} = 2\mu e_{xx},
\]

with $\sigma_{xx}$ and $\sigma_{yy}$ components obtained from (1) by cyclic permutation of $x, y, z$. Here $\lambda, \mu$ are the Lamé coefficients, and $e_{ik} = u_{ik} - u^{0}_{ik}$ is the elastic strain, with $u^{0}_{ik}$ the components of the spontaneous strain. In contact with substrate, the film with symmetry-breaking misfit with the substrate must split into domains in such a way that the average in-plane strain will be zero, since the homogeneous strain in the substrate would cost an infinite energy. Without the “extrinsic” strain the spontaneous strain would alternate from domain to domain (which all would have the same width) as $u^{0}_{xx} = -u^{0}_{zz} \equiv \pm u_0$, $u^{0}_{yy} = 0$. On the other hand, with the “extrinsic” misfit strain $u$ the distribution of the spontaneous strain in the domains would be

\[
u^{0}_{xx}(u^{0}_{zz}) = \pm (\mp) u_0 + w, \quad u^{0}_{yy} = w.
\]

We assume for the substrate the same equations of state, as (1),(2), but with $u^{0}_{xx} = u^{0}_{yy} = u^{0}_{zz} = 0$.

To find the energy of the domain structure, we have to determine the energy of the homogeneous and inhomogeneous (stray) stresses. The energy of the homogeneous stresses $(F_h)$, which appears for domains with non-equal widths (i.e. for $\delta \neq 0$), can be easily found for an epitaxial film with any domain structure, provided that the elastic moduli in all domains are the same, and the non-linear effects can be neglected. We can readily find $F_h$ from the general expression for the elastic energy $F_{el} = -\frac{1}{2} \int dV \sigma_{ik} u^{0}_{ik}$ as

\[
F_{h} = -\frac{l}{2} (\sigma_{xx} u^{0}_{xx} + \sigma_{yy} u^{0}_{yy} + \sigma_{zz} u^{0}_{zz})
\]

\[
= MI \left[ (\bar{u}^{0}_{xx})^2 + (\bar{u}^{0}_{yy})^2 + 2\nu \bar{u}^{0}_{xx} \bar{u}^{0}_{yy} \right]
\]

\[
= M u^{0}_{0} l \left[ (\delta - \delta_0)^2 + w^2 (1 - \nu^2) / u^{0}_{0} \right]
\]

where $\delta_0 = -w(1+\nu)/u_0$ is the relative extrinsic misfit, $\nu = \lambda / 2 (\lambda + \mu)$ the Poisson’s ratio, and $M = 2 \mu (\lambda + \mu) / (\lambda + 2 \mu) = E/2 (1 - \nu^2)$, where $E$ is the Young’s modulus. The overbar here and below marks the averaging over the film (domain pattern). The condition $\bar{u}_{zz} = 0$ was used together with Eq.(4) to obtain for the planar stresses $\bar{\sigma}_{xx} = 2 M (e_{xx} + \nu e_{yy})$, $\bar{\sigma}_{yy} = \bar{\sigma}_{zz} (x \leftrightarrow y)$, where $\bar{e}_{xx} = \bar{u}_{xx} - \bar{u}^{0}_{xx} = -\bar{u}^{0}_{xx} = -u_0 \delta - w$, $\bar{e}_{yy} = -\bar{u}^{0}_{yy} = w$, Eq.(4). We have also used the absence of the in-plane strains, $\bar{u}_{xx} = \bar{u}_{yy} = 0$, imposed by the substrate, and an obvious relation $\bar{u}^{0}_{xx} = \frac{1}{2} (1 + \delta) (u_0 + w) + \frac{1}{2} (1 - \delta) (-u_0 + w) = u_0 \delta + w$. Note that Eq.(4) is rather general and can be applied to other kinds of domain patterns in the epitaxial films (cf. [3]).

The stray energy of inhomogeneous stresses in a stripe-like domain structure periodic in $x$–direction, Fig. 1, is to be found from exact solutions for the strain field produced by the domains. The pattern is defined by the distribution of spontaneous strains $u^{0}_{xx}(x)$ and $u^{0}_{zz}(x)$. The condition of the local equilibrium, $\partial \sigma_{ik} / \partial x_k = 0$, gives two sets of two equations for the displacement components $u_x, u_z$ in the film and the substrate with the use of a standard relation $2 u_{ik} = \partial u_{ik} / \partial x_k + \partial u_k / \partial x_i$. The boundary conditions are given by the absence of stresses,
\[\sigma_{zz} = \sigma_{xx} = 0\] at the free surface of the film \((z = l)\) and at \(z \to -\infty\). Both the strain tensor and the displacement vector are continuous at the film-substrate interface. The original system of partial differential equations is reduced to a system of the ordinary differential equations with the use of the Fourier transform and then solved, as described in detail in Refs. [3, 5], and we obtain the following simple expression for the stray energy per area \(A\):

\[
\frac{F_{\text{stray}}}{A} = \frac{2\pi^2 a}{\pi^3} \sum_{n=1}^{\infty} \left[1 - (-1)^n \cos \pi n \delta \right] \frac{1 - (1 + 2k^2) e^{-2k}}{n^3},
\]

where \(k = \pi n l / a\) [1]. The series is calculated with the result

\[
\frac{F_{\text{stray}}}{A} = \frac{2}{\pi^2} M u_0^2 a \left[ \zeta(3) - \frac{\pi l}{2} \ln 2 \delta^2 + \frac{\pi^4}{96} \delta^4 \right],
\]

where \(\zeta(n) = \sum_{n=1}^{\infty} z^n / s^n = \zeta(z, n, 1)\) [1], \(b = 2\pi l / a\). For \(\delta = 0\) this formula gives the total elastic energy of a symmetric domain structure (a pattern of opposite domains of equal widths). We have found earlier a somewhat similar formula for another symmetric domain structure of \(a_1/a_2\) type [2]. Let us consider the following general cases.

**Zero extrinsic misfit** \((w = 0)\). In this case the energy of the homogeneous elastic field is simply \(F_h / A = M u_0^2 \delta^2\). The stray energy has a simple form for the following two limiting cases. In the standard case of narrow domains \((a \ll l)\) and \(\delta \ll 1\)

\[
\frac{F_{\text{stray}}}{A} = \frac{2}{\pi^2} M u_0^2 a \left[ \zeta(3) - \frac{\pi^2 \ln 2}{2} \delta^2 + \frac{\pi^4}{96} \delta^4 \right].
\]

One has to add the surface energy of the domain walls to find the equilibrium domain width

\[
F_{dw} / A = \sqrt{2} \gamma l / a,
\]

where \(\gamma = M u_0^2 \Delta / \sqrt{2}\) is the energy of the unit surface of the domain walls, and \(\Delta\) is a characteristic microscopic length [13]. The total free energy, \(F = F_h + F_{\text{stray}} + F_{dw}\), is minimal for symmetric domain structure (\(\delta = 0\) and \(a_1 = a_2 = a\)), with the standard (Kittel) domain width (cf. [1])

\[
a = a_K = \left( \frac{2 \pi^2}{7 \zeta(3)} l \Delta \right)^{1/2} \sim \sqrt{\Delta} l \ll l.
\]

Using this result, we see immediately that the high-frequency response of the domain pattern (at a fixed domain width \(a\)) is

\[
\kappa_{\infty} = \frac{\partial^2}{\partial \delta^2} \left( \frac{F}{A} \right) = 2 M u_0^2 l \left(1 - \frac{\ln 2}{\pi} \frac{a}{l} + \frac{\pi a}{8 l \delta^2} \right) > 0,
\]

so the pattern is stable, although it softens because of the negative contribution to the stray energy from the terms \(\propto \delta^2\) in [8]. Note also that \(\kappa_{\infty}\) increases with \(\delta\), and this, as we shall see, is a general result.

If the elastic modulus \(\mu\) were soft, the domains could become wide, \(a \gg l (b \ll 1)\). There

\[
\frac{F_{\text{stray}}}{A} = M u_0^2 l \left[1 - \delta^2 \left(1 - \frac{\pi l}{a} - \frac{8 l}{\pi a} \ln \frac{e^{3/4} a}{4\pi l}\right)\right],
\]

and one finds a symmetric structure with the large domain width [11]

\[
a = 4\pi e^{1/4} l \exp \left(\pi \Delta / 8 l\right),
\]

which would be \(\gg l\) if we had a substrate with \(\Delta \gg d_{st}\) (cf. the answer for a ferroelectric capacitor [14]). This is contrary to a previously considered Kittel case with narrow domains \(a_K \ll l\). In the case of the wide domains the response softens considerably, but remains positive,

\[
\kappa_{\infty} = 2 \pi M u_0^2 l \frac{l}{a} > 0.
\]

It is unlikely, however, that the softness of the present domain structure is of any practical importance. The problem is that even a small extrinsic misfit in very thin films will push the domain structure to the boundary of its existence [3, 5], where it becomes rigid for experimentally accessible frequencies of external field, as discussed below.

**Non-zero extrinsic misfit** \((w \neq 0)\). The energy of homogeneous stresses is given by Eq. [5]. To find the domain structure close to the boundary of its stability we need all characteristics in the limit \(\delta \to 1\), and \(a \gg l (b \ll 1)\), i.e. close to a monodomain state. The stray energy in this limit is

\[
\frac{F_{\text{stray}}}{A} = \frac{1}{4} M u_0^2 \left(1 - \delta^2\right)^2 \left[\ln \frac{4 e l}{a \left(1 - \delta^2\right)} - \frac{\pi l}{a}\right].
\]

Note that Roylburd has approximated the numerically computed stray energy with the functional dependence \(1 - \delta^2)^2\), i.e. without the important log term [13]. Minimizing the total energy, \(F_{tot} = F_h + F_{\text{stray}} + F_{dw}\), with respect to the half-period of the structure \(a\), we obtain the equation

\[
\frac{(1 - \delta^2)^2}{4\pi} \ln \frac{4 l}{a (1 - \delta^2)} = \frac{l \Delta}{a^2},
\]

which has a solution

\[
a = \frac{1}{(1 - \delta^2) \ln^{1/2} (4 l / \pi \Delta)} \sqrt{\frac{8 \pi \Delta}{l}},
\]
where we have omitted the terms $\propto \ln \ln (4l/\pi \Delta) \ll \ln (4l/\pi \Delta)$. It shows that the domain period diverges as $1/(1 - \delta^2)$ close to the phase boundary with the monodomain state. The total energy then takes the form

$$\frac{F_{\text{tot}}}{Mu_{\alpha}^2 A} = (\delta - \delta_0)^2 + \phi (1 - \delta^2) - \frac{1}{4} (1 - \delta^2)^2,$$  \hspace{1cm} (18)

where from the equilibrium value of $\delta$ is to be found (subject to the constraint $\delta^2 \leq 1$), with the parameter $\phi \equiv (L\Delta/2\pi l)^{1/2} \ll 1$, and $L = \ln (4l/\pi \Delta)$ the logarithm of a large number $\sim l/\Delta \gg 1$.

The transition into a monodomain state ($\delta^2 = 1$) occurs as a function of the extrinsic relative misfit at $|\delta_0| = 1 - \phi$. This condition suggests a critical thickness of the film $l_c$, where the polydomain-monodomain transition takes place at a given misfit $\delta_0$ (i.e. the phase boundary in $\delta_0 - l$ plane),

$$\frac{l_c}{\Delta} = \frac{1}{\pi (1 - \delta_0)} \ln \frac{1}{1 - \delta_0}. \hspace{1cm} (19)$$

Thus, the domain structure may exist only at $l > l_c(\delta_0)$. This formula is obtained for $l_c/\Delta \gg 1$, but it also correctly gives an absence of the critical thickness of the film when the parameter $\delta_0$ is zero ($l_c = 0$ when $\delta_0 = 0$). The absence of the critical film thickness has been suggested earlier for another domain pattern, $a_1/a_2$, from numerical computations [3]. This is contrary to the speculations by Roytburd, who obtained $l_c \neq 0$ for $\delta_0 = 0$, apparently as an artifact of the employed approximations [12]. The critical point is approached linearly with $\delta_0$

$$\delta = 1 - (1 - \phi - \delta_0)/\phi. \hspace{1cm} (20)$$

We see that the slope is $d\delta/d\delta_0 = 1/\phi \gg 1$, so that the approach to the critical point is very steep, it looks almost discontinuous.

We readily obtain the high-frequency (measurable) dynamical stiffness close to the phase boundary,

$$\frac{\kappa_\infty}{Mu_{\alpha}^2 l} = \frac{1}{1 - \delta^2} \sqrt{\frac{8\Delta}{\pi \Delta}} \ln \frac{2\epsilon^2 L l}{\pi \Delta} \simeq \frac{1}{1 - \delta^2} \sqrt{\frac{8\Delta \delta}{\pi l}} \rightarrow \infty \hspace{1cm} (!) \hspace{1cm} (21)$$

which diverges when $\delta^2 \rightarrow 1$, i.e. close to the phase boundary. This is in striking disagreement with the results of Pertsev et al. [3] who claimed a softness of the $c/a$ domain structure close to the phase boundary, which actually does not materialize. The static stiffness, which has no practical significance since it requires very long time to relax the pattern in order to optimize the number of domain walls, sharply vanishes with increasing relative misfit $\delta_0$,

$$\frac{\kappa_0}{Mu_{\alpha}^2 l} \propto 1 - \delta^2 \propto 2(1 - \phi - \delta_0)/\phi \rightarrow 0, \hspace{1cm} (22)$$

see the exact result in Fig. 2. Interestingly, close to the transition into monodomain state the system splits into two groups of wide ($a_1$) and narrow ($a_2$) domains with

$$a_1 = \frac{1}{1 - \delta} \sqrt{\frac{8\pi l \Delta}{\pi l}} \sim \frac{a_K}{2(1 - \delta) \sqrt{l}} \rightarrow \infty, \hspace{1cm} (23)$$

$$a_2 = \sqrt{\frac{2\pi l \Delta}{\pi l}} \sim \frac{a_K}{\sqrt{l}} \leq a_K. \hspace{1cm} (24)$$

We see that the width of the wide domains diverges, the density of the domains walls decreases, but the width of the narrow domains, $a_2$, remains small. The narrow domains are somewhat compressed compared to the standard Kittel width $a_K$ [11].

It becomes obvious from the present analysis that it is unlikely that one can succeed in making a “soft” domain pattern with the small $\kappa_\infty$ in epitaxial thin ferroelectric films with elastic domains, suitable for the applications. In fact, the only way to do this would be to avoid any extrinsic misfit, i.e. to keep $\delta_0 = 0$, and to reduce the film thickness. However, in this case the interval of the extrinsic misfit strain, which allows the very existence of the domains, is very narrow. Then, the proximity to the phase boundary in systems with two kinds of inequivalent domains means that the stiffness rapidly increases, oppositely to what one actually desired. We have tacitly assumed above that the stiffness of the domain structure determines its dielectric response. Indeed, one can assume that there is a spontaneous polarization parallel to the film plane in one domain and perpendicular to it in
the other in the present $c/a$ domain structure (as in $c$-domains in perovskites). One can also assume, as in Ref. 3, that $\delta - \delta_{eq} = k P_s E_{ext}/\kappa_\infty$ in external field, where $P_s$ is the spontaneous polarization, $E_{ext}$ the external electric field, and $\delta_{eq}$ is the equilibrium value of $\delta$ in zero field.

We have shown earlier 6 that this relation may not hold, and in some cases it strongly overestimates the dielectric response. Additionally, the neglected contribution of uncompensated electric fields would only make the response stiffer. However, even this overestimate leads one to a conclusion that the dielectric response of the pattern with inequivalent elastic domains in the epitaxial thin films is actually suppressed.

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