Subcritical growth of repolarization nuclei in polycrystalline ferroelectric films

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ABSTRACT

The problem of subcritical growth of repolarization nuclei in ferroelectric crystals is considered. Following the approach of Barenblatt to the theory of equilibrium brittle cracks, a concept of cohesive forces, acting on adjacent domain walls in a region near the domain tip, is introduced. These cohesive forces are intimately related to the gradient term in the Ginzburg-Landau energy and become substantial as the separation between the domain walls compares with their thickness δ . The condition of equilibrium for a ferroelectric domain is formulated by taking into account the internal field associated with the cohesive forces. Criteria for stable subcritical growth of nuclei in non-uniform electric fields are presented in terms of a gradient modulus, which is an extension of the cohesion modulus concept of Barenblatt. **KEYWORDS**

subcritical growth • ferroelectrics • ferroelectric domains • polycrystalline thin films

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Introduction

One of the main factors that determines the efficacy of application of functional materials in various devices is the high sensitivity of their physical properties to the features of the real structure. In the case of ferroics (ferroelectrics, ferroelastics, ferromagnets), it is the behavior of the real (domain) structure that is the cause of physical nonlinearities observed in the form of hysteresis phenomena, the mechanism of which is often the subject of debate. Elucidation of the mechanism of the subcritical growth of ferroelectric domains in polycrystalline films is one of the current controversial issues in the physics of ferroelectrics.

The lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) solid solution near the morphotropic phase boundary x = 0.47, separating two ferroelectric phases — rhombohedral and tetragonal, is one of the most widely used smart materials due to unique combination of its piezoelectric and dielectric properties. In such applications as nonvolatile random access memories also the nonlinear properties of PZT become important, especially its resistance to dynamic fatigue resulting from the polarization switching and reducing life time of the memory cells. The experimental studies of the influence of dynamic fatigue on ferroelectric

hysteresis revealed a considerable difference in physical mechanisms, underlying the polarization reversal in polycrystalline PZT films of different microstructure. In particular, for (Pb_{1-y}La_y)(Zr_{1-x}Ti_x)O₃ (PLZT) polycrystalline films, including tetragonal Pb(Zr₅₀Ti₅₀)O₃, deposited on Pt/Ti-coated Si substrates [1] the grain size D of ~0.3 μ m was comparable with the film thickness $H = 0.55 \,\mu\text{m}$. These films show a frequency dependence of a coercive field $E_c(v)$ in the Merz form, $\ln(v/v_0) = -\alpha/E_c$, for a wide range of frequencies $v = 10^1 - 10^5$ Hz. An important observation made in [1] is that the dynamic fatigue does not affect the characteristic frequency v_0 , which lies around 10⁹ Hz for different PLZT compositions and can be considered as a signature of the physical mechanism of polarization switching. Unlike v_0 , the activation field α increases with the number of cycles used in fatigue tests and is the only parameter in the Merz equation that characterizes the degree of fatigue [1]. Surprisingly, it was found that in polycrystalline Pb(Zr_{0.53}Ti_{0.47})O₃ films deposited on Pt/Ti/SiO₂/Si substrates the frequency dependence of the coercive field $E_{c}(v)$ differs significantly from the Merz equation and follows the unusual law: $\ln(v/v_0) = -(\beta/E_c)^2$ [2], which was never observed before and can be referred to as $1/E^2$ -law. This result not only means the change in the physical mechanism governing the polarization switching rate in these films, but also implies the existence of a low limiting frequency v_0 , approaching which the coercive field diverges. The value of v_0 obtained by the extrapolation of the experimental dependence of $\ln v$ on $1/E_c^2$ to the point $1/E_c^2 = 0$ was about 10⁵ Hz [2]. This value is much less both the Debye frequency in ferroelectric crystals with perovskite structure (~10¹³ Hz for PZT [1]) and also the aforementioned limiting frequency for PZT films, in which the polarization switching rate is given by the Mertz equation. Fatigue tests [2] showed that the limiting frequency v_0 for the new mechanism is also independent of the number of cycles, whereas the activation field β increases with cycling, as shown in Fig. 1. Despite their importance, the results obtained in [2] remained unnoticed until they were reproduced in [3,4] for tetragonal Pb(Zr_{0.40}Ti_{0.60})O₃ films grown on Ir/SiO₂/Si substrates using the sol-gel process. Here, it is worth to mention that the $1/E^2$ -law was also reported for some other ferroelectric materials [5,6].

The existence of two principally different mechanisms of polarization switching in polycrystalline PZT films raises the question of what structural features of the films are responsible for realization of a particular mechanism. However, there is no information on the film thickness in [2]. The films grown in [3,4] had the thickness of 240 nm, but the grain size values were reported neither in [2] nor in [3,4]. Some insight into the microstructure can be gained from [7], where tetragonal $Pb(Zr_{0.20}Ti_{0.80})O_3$ films with thickness of 260 nm were composed of elongated single-domain grains with the mean size of ~ 50 nm. The switching of polarization by an electric field is a multistage process. It includes the stage of formation of repolarization nuclei; the stage of their forward growth into the crystal, which results in the formation of planar domain walls; and subsequent sideways motion of the domain walls. According to [8], it is the nucleation stage of the repolarization nuclei that is responsible for $1/E^2$ -law. Furthermore, as was shown in [8], thin repolarization nuclei arise as the result of thermal fluctuations. Taking into account the experimental value of $v_0 = 10^6$ Hz from [3], the activation energy was estimated as $\Delta G(E_c) \sim 10 kT$, where the coercive field $E_c = 62.5$ kV/cm corresponds to the hysteresis loop at a frequency v = 9.3 Hz [3] and kT – to room temperature. Thus the nucleation due to thermal fluctuations is not so prohibitive as is sometimes accepted. Among additional factors, which could contribute to the dependence of E_c on v, one should mention the thermally activated

sideways motion of domain walls in the field of short-range obstacles. For instance, such interactions become important in bulk PZT-based ceramics and lead to a logarithmic dependence of the coercive field on frequency [9–12].



Fig. 1. Semi-log plots $\ln v$ vs $1/E_c^2$ illustrating schematically shift of the limiting frequency $v_0(D)$ with a change in the electrode diameter D ($D_2 < D_1$) in fresh PZT films (squares correspond to *RT* data and $D_1 = 320 \ \mu m$ [3]). An expected transformation of the plot in fatigued films is sketched

The original model [8] of the polarization reversal was not flexible enough to explain some features of the $1/E^2$ -law, namely some size (or geometric) effects. According to [3,4], the observable limiting frequency v_0 is not a fundamental characteristic of the film material or structure. It depends on the size of the upper electrode R as well: $v_0 = v_0(R)$. A qualitative phenomenological model [13], explaining the origin of such effects, assumes the existence of an additional mechanism for the growth of nuclei, which must be much faster than the usual nucleation due to thermal fluctuations. Further development [14] led to the conclusion that such mechanism is subcritical growth of repolarization nuclei in a nonuniform electric field at the edges of the electrode. In this work, following the approach of Barenblatt [15] to equilibrium brittle cracks, a concept of cohesive forces, acting on adjacent domain walls in a region near the domain tip, is introduced. These cohesive forces stem from the gradient term in the Ginzburg-Landau energy. The condition of equilibrium for a ferroelectric domain is formulated by explicit incorporation of the internal field associated with the cohesive forces. Criteria for stable subcritical growth of nuclei in nonuniform electric fields are presented in terms of a gradient modulus, which is an extension of the cohesion modulus of Barenblatt.

Thin domain approximation

In the theory of brittle cracks proposed by Barenblatt the concept of atomic cohesive forces is introduced to describe interaction of the crack surfaces in the cohesion zones near its tips. The cohesive forces are assumed to be local. Like surface forces in the continuum elasticity theory they are applied directly to the crack surfaces. Therefore, they differ from the real interatomic forces acting on atoms situated in a surface layer, which

thickness depends on the range of interatomic interaction. The idea of cohesive forces turns out to be also useful for ferroelectric domains, where they act locally on the adjacent domain walls. These forces are related to the gradient term in the Ginzburg-Landau energy and become substantial in the region near the domain tips, where the separation between the domain walls compares with their thickness δ . This region can be referred to as the gradient zone. To illustrate incorporation of the cohesive forces into equations of equilibrium of ferroelectric domains, we consider a two-dimensional

problem of a thin 180° domain of length $l = a_2 - a_1 = 2a$ in an infinite uniaxial crystal. The domain is infinitely long in the *z*-direction and polarized in the *x*-direction. Its tips are situated at points $x = a_1$ and $x = a_2$, respectively, as shown in Fig. 2. From the microscopic viewpoint, the shape h(x) of the domain profile in *xy*-plane depends on distribution of atomic steps at the curved domain walls bounding the domain. Since each step increases the domain thickness by one interplanar distance *c*, the thickness h(x) at a point *x* is determined by the total number of steps situated between this point and the domain tip $x = a_2$. By introducing the step density function n(x), h(x) can be represented as:

$$h(x) = \begin{cases} c \int_{x}^{a_2} n(u) du, \ (a_1 \le x \le a_2) \\ 0, \qquad (x < a_1 \text{ or } x > a_2) \end{cases}.$$
(1)



Fig. 2. A 180° domain of length $2a = a_2 - a_1$. Atomic steps on the domain wall *W* are schematically shown. The thickness of the domain cross section in the *xy*-plane is described by the function h(x). The gradient zone *G* is shown for the tip a_2

Further analysis throughout the paper is based on the thin domain approximation [8]. It means that all steps are situated in one plane y = 0 and we deal with a plane step distribution. Within the framework of this approximation the spontaneous polarization, which in our case has only one component, is localized in the plane y = 0 and can be expressed as:

 $P_x^0(x,y) = -P^s + \Delta P^s h(x)\delta(y), \tag{2}$

where P^s denotes the value of spontaneous polarization and $\Delta P^s c = 2P^s c$ is the bound charge (per unit length along the *z*-axis) associated with a step on the domain wall. The shape of an equilibrium domain is to be found from the condition of vanishing the configuration force $f_x(x)$ acting on each step. Provided that the potentials of remote electrodes are fixed, it is to be derived from the electric free energy [8]. In general, the condition of step equilibrium contains three terms of different nature:

$$f_x(x) = f_x^E(x) + f_x^{GL}(x) + f_x^{lat}(x) = 0.$$
(3)

However, the main contribution to the configuration force in Eq. (3) is due to the cohesive (or gradient) force:

$$f_x^{GL}(x) = -(\Delta P^s c) E_x^*(x),$$
(4)
where $E_x^*(x) = E_x^*[h(x)]$ is the internal field associated with the Ginzburg-Landau energy,

and the electric force: $f_x^E(x) = \Delta P^s c(E^U(x) + E_x^d(x, y = 0)).$ (5)

Here, $E^{U}(x) = E_{x}^{U}(x, y = 0)$ is the electric field of remote electrodes with an account of the depolarization field of the homogeneously poled ferroelectric crystal and $E_{x}^{d}(x, y = 0) = \frac{\Delta P^{s}c}{2\pi\varepsilon} \int_{a_{1}}^{a_{2}} \frac{n(u)}{x-u} du$ (6)

is the depolarization field due to bound charges of the steps. Correspondingly, $\varepsilon = (\varepsilon_{11}\varepsilon_{22})^{1/2}$ stands for the effective dielectric constant. As concerns the force $f_x^{lat}(x)$ in Eq. (3), it has the lattice periodicity and plays the same role as Peierls force on a crystal dislocation. Its mean value over the lattice period vanishes and we neglect it in the step equilibrium condition given in Eq. (3). Finally, taking into account Eq. (6), we obtain the equation of domain equilibrium:

$$\frac{1}{2\pi\varepsilon} \int_{a_1}^{a_2} \frac{n(u)}{x-u} \, du = E_x^U(x) - E_x^*(x), \ (a_1 < x < a_2), \tag{7}$$

which is a singular integral equation for the step density function n(x). The self-force on a step, resulting from Eq. (6) for the depolarization field, has a singularity at x = u, but it can be excluded, using the principal value of the integral in Eq. (7). Unlike the previous analysis [8,14], here we include explicitly the internal field $E_x^*(x)$ acting only on few steps in the neighbourhood of the domain tips. It is the field, which work gives rise to an increase in the domain wall surface energy as the domain grows. It cannot be derived within the framework of the semi-continuum approach used here. More details on properties of $E_x^*(x)$ following from the Ginzburg-Landau theory will be published elsewhere. Moreover, one can consider the internal field phenomenologically, like it was done for elastic twins [16-18] and brittle cracks [15]. In fact, the internal field is not a usual function of the step position x, namely, it is a functional of the domain thickness h(x) at this point and thereby is a functional of the step density n(x). Therefore, strictly speaking, Eq. (7) is nonlinear. However, this difficulty can be overcome in the same way as in Barenblatt's theory [15].

The concept of gradient modulus

Eq. (7) can be solved analytically, see [14] for details. Let's consider the solution for the depolarization field defined in Eq. (6). Ahead the right domain tip $x = a_2$ it has the form:

$$E_x^d(x > a_2, y = 0) = \frac{1}{\pi\sqrt{(x - a_1)(x - a_2)}} \int_{a_1}^{a_2} \frac{\sqrt{(a_2 - u)(u - a_1)}}{x - u} \left[E_x^U(u) - E_x^*(x) \right] du, \tag{8}$$

$$E_x^d(x \to a_2, y = 0) = \frac{1}{\sqrt{2\pi} (x - a_2)} \left\{ K(a_2) - \frac{1}{\sqrt{\pi} a} \int_{a_1}^{a_2} \sqrt{\frac{u - a_1}{a_2 - u}} E_x^*(u) \ du \right\},\tag{9}$$

where the quantity

$$K(a_2) = \frac{1}{\sqrt{\pi a}} \int_{a_1}^{a_2} \sqrt{\frac{u - a_1}{a_2 - u}} E_x^U(u) \, du \tag{10}$$

is a weighted average (or intensity factor) of the external field. Since for the equilibrium domain the depolarization field has to be non-singular, the singularity in Eq. (9) is to be eliminated. This requirement leads to the condition:

$$K(a_2) = \frac{1}{\sqrt{\pi a}} \int_{a_1}^{a_2} \sqrt{\frac{u - a_1}{a_2 - u}} E_{\chi}^*(u) \ du.$$
(11)

Since the internal field rapidly vanishes outside the gradient zone, Eq. (11) takes the form: $K(a_2) = K^*$, (12)

where the quantity K^* characterizes the behaviour of the cohesive forces in the gradient zone and can be referred to as *gradient modulus*. It is a material constant and can be represented as:

$$K^* = \sqrt{\frac{2}{\pi}} \int_0^d \frac{E^*(u)}{\sqrt{u}} \, du = \sqrt{\frac{2}{\pi}} \int_0^\infty \frac{E^*(u)}{\sqrt{u}} \, du, \tag{13}$$

where *d* is the gradient zone size and $E^*(u) = |E_x^*(x)|$. In practice, one can use $d = \infty$, since beyond the gradient zone the internal field is vanishing. Eq. (12) is the first equation for the unknown positions a_1 and a_2 of the equilibrium domain tips. The second equation for a_1 and a_2 can be obtained similarly, eliminating the singularity at the left tip a_1 .

Subcritical growth of a repolarization nucleus

If the external field is uniform, the intensity factors for both domain tips coincide,

 $K(-a) = K(a) = E^U \sqrt{\pi a}$, (14) where the domain tip positions are chosen at $a_1 = -a$ and $a_2 = a$. The size of the equilibrium domain in terms of the gradient modulus is given as:

$$l_c = \frac{2}{\pi} \left(\frac{K^*}{E^U}\right)^2. \tag{15}$$

Such domain is unstable [14]. If the size of a repolarization nucleus exceeds the critical value given in Eq. (15), the nucleus can grow, thus reducing the thermodynamic potential, otherwise it shrinks. Comparing Eq. (15) with the results of [14], one can obtain the important relation between the gradient modulus and the domain wall surface energy γ_{w} ,

$$K^* = 2\sqrt{\gamma_w/\varepsilon}.$$
(16)

In the case of non-uniform electric fields, the thermodynamics of the growth process can be analyzed by means of the known in fracture mechanics Irwin formula for a crack in an elastic solid. Its extension to the case of a ferroelectric domain was made in [14] and represents the variation in the electric free energy when the domain size changes by the value of δl ,

$$\frac{\delta \tilde{F}}{D} = -\frac{1}{2} \int_{a_2}^{a_2 + \delta l} [E_x^U(x) + E_x^d(x, y = 0)] \left(\int_{-\infty}^{\infty} \delta P_x^0(x - \delta l, y) dy \right) dx.$$
(17)
According to [14] calculation of the integral in Eq. (17) gives rise to a simple result

$$\frac{\delta \tilde{F}}{R} = -\frac{\varepsilon K^2(a_2)}{2} \,\delta l, \tag{18}$$

for the electric free energy release, and the domain growth in a non-uniform electric field becomes thermodynamically favourable if

$$\frac{\delta G}{D} = \frac{\delta \tilde{F}}{D} + 2\gamma_{w}\delta l = \left(-\frac{\varepsilon K^{2}(a_{2})}{2} + \frac{\varepsilon K^{*2}}{2}\right)\delta l \le 0.$$
(19)

For the tip $x = a_1$ a similar condition takes place.

The mechanism of subcritical growth can be demonstrated within the framework of a simple model presented in Fig. 3, where it is assumed that a repolarization nucleus of size l = 2a arose at the edge of the electrode x = -b as a result of thermal fluctuation. This model is directly relevant to the forward growth of nuclei near the electrode edges in PZT films. Analysis of the results of numerical calculations of the coefficients K(-a) and K(a) depending on the value of the geometric parameter b/a, where b is the distance from the edge of the electrode to the centre of the nucleus, shows that if the right tip of the nucleus is in equilibrium, its left tip cannot be in equilibrium and always shifts towards the edge of the electrode. However, the main conclusion is that at b = a the value of the intensity factor $K(a) = 2K^{\epsilon}/\pi$ for the right edge of the nucleus turns out to be independent of its size. Here, $K^{\epsilon} = Q/(2\epsilon(\pi R)^{1/2})$, Q is the linear charge of the electrode, and 2R is its width. Consequently, if condition (19) is met, nuclei of arbitrarily small size resulting from thermal fluctuations do not annihilate, but can grow, lowering the thermodynamic potential G of the system. This means the fundamental possibility of stable subcritical growth of repolarization nuclei in the vicinity of the electrode edges.



Fig. 3. A sketch of a 180° repolarization nucleus of length 2a near the edge x = -b of a thin planar electrode occupying the region $-2R - b \le x \le -b$

Conclusions

Stable subcritical growth of repolarization nuclei, which doesn't require thermal activation, becomes possible due to the lack of dependence of electric energy release on the nucleus size. This growth regime is provided by specific behaviour of the non-uniform electric field near electrode edges. Since the electric field decreases with the distance r from the electrode edge as $1/\sqrt{r}$, the electric free energy released by the domain expansion is fully consumed by the newly formed domain wall surfaces whatever nucleus size is. This effect is very similar to the microcrack formation mechanism by arrested dislocation pile-ups (Zener-Mott-Stroh model), where elastic energy release turns out to be independent of crack size [19–21].

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