Dislocation mechanism of ferroelectric fatigue during multiple switching

A. S. Sidorkin

*Experimental Physics Department, Voronezh State University
University sq., 1 Voronezh, 394006 Russia
sidorkin@phys.vsu.ru*

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The paper is concerned with the characteristic features of the dislocation mechanism related to fatigue in ferroelectrics in the process of their repeated switching. In a polarized crystal, dislocations possess a charge the sign of which depends on the orientation of the spontaneous polarization vector relative to the dislocation line. In the process of hysteresis switching, the average force from the applied field acting on a charged dislocation for one period of the hysteresis loop is not equal to zero. Such long-acting force leads to the accumulation of defects near the surface, which can fix a polarization and so partially remove it from the switching process. The proposed mechanism explains the key dependences of the critical number of switching cycles on the field amplitude, frequency and temperature of the sample.

Keywords: Fatigue; charge dislocations; drift; gradient of deformation; internal field.

1. Introduction

The numerous advantages of ferroelectric films, in particular, lead titanate and lead zirconate–titanate films, characterized by large values of switchable polarization make them promising materials for the creation of nonvolatile memory devices with large storage capacity.^{1–3} However, there are a number of problems, limiting the wide commercial deployment of such devices. These include, in particular, the process of fatigue in ferroelectric materials, meaning a reduce of the switching charge (polarization) with an increase in the number of switching cycles of polarization by an external electric field.

A few basic types of the fatigue models were proposed to explain this phenomenon. One of the earliest is the model that associates the reduction of the switchable polarization with the decreasing area of electrodes due to their burning or peeling and with the development of mechanical stresses and formation of cracks near the area of contact between the ferroelectric and surface of nonferroelectric layer under repeated cycling.^{4–6}

There are some other reasons for decreasing of switchable polarization: formation of nonferroelectric boundary layer between the metal electrode and ferroelectric sample^{7,8}; suppression of the domain growth at the film — electrode boundary by trapping the charge injected into a film from the electrode at high values of applied electric fields.^{9–13} Moreover, the defects already existing in the crystal can cause the blocking effect in the switching processes.^{14,15}

2. Dislocation Motion in Ferroelectrics caused by an Alternating Electric Field

Formally, charged point defects and dislocations compensating a bound charge at the domain boundary and therefore

providing its fixing may be active in the given phenomenon of fatigue. However, at least for the antisymmetric harmonic signal usually used in the experiment, point defects must be excluded from consideration as the possible causes of fatigue effects accumulation. The reason for this phenomenon is that the force, averaged over the period, acting on these defects due to the applied electric field is equal to zero. The impact of the harmonic signal on the specified defects causes their oscillations, but not a directional motion required for the accumulation of defects fixing the polarization near the ends of reverse domains.

An alternative situation is realized with regard to the dislocations. It is obvious that in the spontaneously polarized crystal the edge dislocations representing are inserted into the crystal half-planes are charged due to the breaking on them of the polarized structure. The sign of charge at the dislocations is not constant unlike of the point defects, but depends on orientation of the spontaneous polarization vector relative to the dislocation line.

Charged dislocations in polarized crystal undergo the action of the biasing force from the applied electric field. Herewith, the sign of the driving force depends on the sign of charge at the dislocations and thus varies with the orientation of the spontaneous polarization vector. As a result, the same dislocations undergo the impact of forces of the opposite sign in different domains. When the domain structure of the ferroelectric changes in the switching process, the direction of the force acting on dislocation by the external field also changes, respectively.

At any moment on the impact of the switching field, the sign of force acting on the dislocation is determined by multiplication of signs of the charge at the dislocation and the applied field. As a result, for rather perfect rectangular hysteresis loop the above impacts of the field on the charged

dislocations on an opposite loop “whiskers” do not compensate each other, as for the point charges, but are rather summarized. Directly in the hysteresis part of the loop, the above — mentioned impact compensates each other in the different branches of the loop. So, the total effect of the applied field on the charged dislocations here proves to be zero. As a result, in the absence of an internal bias field for the samples with rectangular hysteresis loop the total effect of the field on the dislocation in the framework of this model is defined by proportion of the hysteresis loop “whiskers” and actually hysteresis part. It is equal to zero only for the idealized case of a complete absence of “whiskers” and vice versa, it is maximal for the other idealized case of zero coercive field, when the dependence of polarization on the field represents a step.

As a result, during the periodic switching of the domain structure in ferroelectric a constant force component appears, which moves dislocations of the same sign in one and the same direction (Fig. 1). Long-term effects of such a force lead to a spatial separation of the dislocations of the opposite sign. So, it ensures an accumulation of the necessary compensating fields near charged boundaries of the reverse domains or near the outlet of the spontaneous polarization on the surface.

The peculiarity of thin film ferroelectric materials is their actual synthesis on a substrate. It has a significant impact on the static domain structure and the processes of its switching observed as a formation of the biased loop of dielectric hysteresis, is formally ascribed to the so-called internal field.

The dislocation mechanism of the fatigue process in materials without internal field was considered previously in Ref. 16. In this paper, we consider a more general situation

Fig. 1. The appearance of nonzero average force acting on the charged dislocations during cyclic switching of ferroelectric with internal bias field: 1 — the applied sinusoidal field, 2 — change of polarization and 3 — a sign of the force acting on a charged dislocation as a function of switching time.

connected with the presence of a nonzero internal bias field in the studied materials, including analysis of the possible reasons for its appearance and changes in the fatigue process.

The critical value of the number of switching cycles in the case of polarization fixing on the surface of the ferroelectric layer can be estimated from the condition of equality of the switching polarization (i.e., the surface charge density on the ferroelectric surface) to the charge density carried here by a stream of charged dislocations for a time equal to the total duration of the critical number of switching cycles:

$$P = \Delta P \cdot N = N \int j dt. \quad (1)$$

In (1) P — switching polarization, ΔP — change in polarization in a single cycle, N — critical number of the switching cycles; an integration is over one switching cycle.

The surface current density j , associated with the motion of charged dislocations, may be written as:

$$j = \tau n_s \mu E, \quad (2)$$

where $\tau = Pb$ — linear charge density at the dislocation, b — Burgers vector of dislocation, n_s — the surface density of dislocations, μ — the mobility of dislocations and E — the electrical field acting over a unit of dislocation length.

To limit the rectangular hysteresis loop (Fig. 2), the influence on the charged dislocations at lines BC and FD are canceling each other out. Uncompensated influence is realized only on the “whiskers” of the hysteresis loop — lines AB and DE .

We assume that switching of the ferroelectric film is implemented by a harmonic signal

$$E = E_0 \sin 2\pi ft, \quad (3)$$

with E_0 as amplitude and f as switching frequency in the presence of internal bias field E_b .

For the displaced hysteresis loop (segments AB and DE are not equal) the charge transferred by the current with density j through a unit surface area is

$$\Delta P = 2 \int_{t_1}^{t_2} j dt + 2 \int_{t_3}^{t_4} j dt, \quad (4)$$

Fig. 2. A rectangular dielectric hysteresis loop of the sample with internal field.

where time moments t_1, t_2, t_3, t_4 are determined by the conditions $E = E_c + E_b, E = E_0, E = -(E_c - E_b), E = -E_0$ (coercive field E_c is defined as half the width of the hysteresis loop) and are equal, respectively, to:

$$\begin{aligned} t_1 &= \frac{1}{2\pi f} \arcsin\left(\frac{E_c + E_b}{E_0}\right), & t_2 &= \frac{1}{4f}, \\ t_3 &= \frac{1}{2\pi f} \arcsin\left(-\frac{E_c - E_b}{E_0}\right), & t_4 &= -\frac{1}{4f}. \end{aligned} \quad (5)$$

Calculating ΔP (4) with account of (5), on the basis of ratio (1) we obtain

$$N = \frac{\pi f}{n_s \mu b \left(\sqrt{E_0^2 - (E_c + E_b)^2} + \sqrt{E_0^2 - (E_c - E_b)^2} \right)}. \quad (6)$$

As it was noted in Ref. 16 according to (6), all of the experimentally observed principal dependencies of fatigue on the characteristic parameters of the switching process (field amplitude, frequency, temperature) are explained in the proposed model.

In particular, the critical number of switching cycles decreases with increasing the length of the “whiskers”, i.e., the difference between E_0 and $E_c \pm E_b$, decreases with the raise of temperature and with a decrease of frequency as well. Decrease of N with increasing temperature in this model is explained by increased mobility μ of the dislocations; their directed motion to the surface during the fatigue process occurs as a “climb”, i.e., growth or “dissolution” of inserted plane through the accession of additional atoms or vacancies. Obviously, this motion has an activation nature and is significantly (exponentially) accelerated with an increase of temperature. This behavior of the fatigue (i.e., reduction of the number of the critical switching cycles with the temperature increase) is observed in all the cases when the effect of fatigue is determined by mobility the pinning centers fixing polarization. At the same time, the increase of temperature can result in the annealing of the pinning points that was not accounted in this paper. This would obviously result in a decrease of the fatigue effect (see, for example, Refs. 17 and 18).

The reason for reducing the “fatigue” processes with the increase of frequency f is connected with the decrease of the total time when the applied field is effected on the charged dislocations.

3. Internal Bias Field in Materials with Substrate

The role of the common factor causing the shift of hysteresis loop named as internal bias field can create, as is known, the system of ordered polar defects facilitating the appearance of a preferred direction of polarization in the sample. Also, there may be any asymmetry in position of the opposite ends of spontaneous polarization vector or switching conditions, for example, due to different electrodes on the opposite surfaces

Fig. 3. Appearance of misfit dislocations in the contact area of the ferroelectric film with the substrate.

of the polar plate or availability of a substrate on one of its side and some other.¹⁹

Here we consider the role of the latter factor, namely, the influence of the substrate, creating the specified asymmetry for the opposite surfaces of the polar plate, in case of so-called epitaxial films. The physical reason for this asymmetry is an emergence of misfit dislocations in the subsurface layer of the ferroelectric plate is due to different values of the lattice constant of the ferroelectric film and the substrate material (Fig. 3).¹⁸

Deformations caused by these dislocations decrease with the distance from the plane of a ferroelectric — substrate contact and thus create a gradient of deformation. The gradient, in its turn, induces linear polarization due to the flexoelectric effect, that can be generally interpreted as created by an effective internal field.

Let us denote by a the size of the unit cell of the non-deformed ferroelectric in the plane parallel to the film surface and by a_s similar size of the cell of the substrate. Appearance of misfit dislocations with a density ρ will result in a partial uprise of stresses and change the size of the cell with increasing the distance from the contact plane up to the value of

$$a_s^* = a_s(1 - a\rho), \quad (7)$$

in a layer with a thickness approximately equal to $1/\rho$. Accordingly, the gradient of deformation perpendicular to the contact plane can be estimated as

$$\text{grad } \varepsilon = \Delta \varepsilon \rho = a_s \rho^2, \quad (8)$$

where $\Delta \varepsilon = (a_s - a_s^*)/a$.

Effective electric field produced by the strain gradient due to flexoelectric effect can be estimated taking into account the approximate value of the flexoelectric constant $\gamma = e/a$ (here e — electron charge) and relations $\rho = \varepsilon/a, \varepsilon = (a_s - a)/a$:

$$E_b = 2\gamma \cdot \text{grad } \varepsilon = 2 \frac{e}{a} a_s \rho^2 \approx 2ea^2 \varepsilon^2. \quad (9)$$

If the value of the lattice constant $a = 3.8 \cdot 10^{-8} \text{ cm}$ and a misfit deformation is about $1 - 5\%$, we obtain the value of the electric field of about $20 - 500 \text{ kV/cm}$.²⁰

Within this mechanism of formation of the internal field it is possible, in principal, to explain the experimentally

Fig. 4. Dependencies of the internal bias field E_b on the number of switching cycles N for $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ films with a thickness of 200 nm. The amplitude of the switching field $E_0 = 800 \text{ kV/cm}$.

observed growth of its magnitude in the process of fatigue (Fig. 4).

This can be due to an increase in the concentration of dislocations in the subsurface layer as a result of the field stimulated motion of the part of misfit dislocations from the contact plane in the subsurface layer.

4. Conclusions

For the explanation and description of the experimentally observed features of fatigue in ferroelectric materials the dislocation mechanism with a drift of the charged dislocation in the applied alternative electric field as an active reason of this phenomenon was proposed and considered. An alternating sign of the dislocation charge in the polar phase of ferroelectrics is the source of a constant force component acting on these dislocations by the alternating electric field. Long-term effect of the applied field separates dislocation of the opposite sign and provides conditions for the accumulation of the compensating fields near the ferroelectric surface, thus fixing switchable polarization. This mechanism makes it possible to explain principal dependencies of the fatigue process on the amplitude of electric field, its frequency and the temperature.

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