The size effect on the switching properties of ferroelectric films: a one-dimensional lattice model

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Abstract. A one-dimensional lattice model with non-ferroelectric boundary sites has been used to study the effect of size on the polarization-reversal process in ferroelectric films. We assume non-ferroelectric imperfections at the boundary sites which act as nuclei for the polarization reversal, and include them explicitly in the free energy. The dependences of the switching time on film thickness and on electric field strength have been obtained, and fitted with empirical formulae. The time evolution of the polarization under a step field has also been simulated, from which we can clearly see domain wall formation and motion. The polarization and current under a bipolar pulse signal are also obtained to demonstrate the different memory state responses, in which a back-switching phenomena can be observed clearly.

1. Introduction

There has been renewed interest in the polarization-reversal phenomena in ferroelectric materials in association with the development of thin-film ferroelectric memories (Scott and Paz Araujo 1989). It is well known that the polarization reversal in ferroelectrics does not proceed homogeneously throughout a specimen, but inhomogeneously by a nucleation growth mechanism. The reversal process has often been analysed using a method based upon Kolmogorov–Avrami (KA) theory, which was originally a model of crystal growth (Kolmogorov 1937, Avrami 1939, 1940, 1941). Relying on several key assumptions, Ishibashi and co-workers have developed this theory to study how the switching property is influenced by size and surface effects in ferroelectric films (Ishibashi and Orihara 1992, Orihara and Ishibashi 1992, Ishibashi 1993). A detailed review of this work can be found in Nagaya *et al* (1993). This extended KA theory—Ishibashi theory as it was called (Dennis 1993)—has been compared with an earlier model of polarization reversal (Fatuzzo 1962), but no simple relationship between the two models has been found. It has recently been shown that after some mathematical manipulation the essential kinetics parameters in KA theory, which describe the domain structure evolution, can be obtained from the measurement of the transient current (Shur and Rumyantsev 1994, Shur *et al* 1994). This has been validated by computer simulation and measurements on model ferroelectric samples (Shur *et al* 1995).

On the other hand, simulation of the polarization-reversal process has also been performed based upon the Landau-type free energy for a homogeneous system (Ishibashi, 1992). Imperfections like impurities and defects play an important role in the switching process, but since it is difficult to include such imperfections within the continuum form

of the free energy, a lattice model—free energy in a discrete form—has been proposed (Ishibashi 1990a, b, Nagaya and Ishibashi 1991). The free energy was written as

$$F = \sum_{n-1}^{N} \left[\frac{1}{4}(1 - p_n^2)^2 + \frac{\kappa}{2}(p_n - p_{n-1})^2 - p_n e \right] \tag{1}$$

where all of the parameters and variables are dimensionless. p_n is the dipole moment at site n, e is the applied electric field and κ a positive constant representing the interaction between nearest neighbours. N is the total number of lattice sites. In the expression (1), the variables p_n have been scaled so that only one parameter κ is retained, the other parameters being scaled to be unity. A full unscaled expression in which all parameters are retained can be found in the paper by Omura *et al* (1991). The dynamics of the dipole moment at the site n is described by the Khalatnikov equation (Blinc and Zĕkš 1974)

$$\gamma \frac{\mathrm{d}p_n}{\mathrm{d}t} = -\frac{\partial F}{\partial p_n} \tag{2}$$

where γ is the viscosity coefficient. In this equation the effect of the kinetic energy is ignored, since it only contributes to phenomena for a range of much higher frequencies. By applying equation (2) to equation (1), one derives a set of differential equations which can be solved numerically.

In previous work (Ishibashi 1990b, Nagaya and Ishibashi 1991), the presence in the initial state of both positively and negatively polarized latent nuclei was assumed, and a periodic boundary condition was used, implying an infinite system. In spite of the simplicity of the lattice model, it reproduces many features of the polarization-reversal process. From the temporal evolution of the spatial dipole distribution in the polarization-reversal process, it is easy to see the motion of the domain walls under the switching field. The switching time is found to depend upon the applied field approximately as a power law, with the power index differing for different definitions of switching time. The polarization and switching current responses to a bipolar pulse field clearly discriminate between the '1' and '0' states. The dielectric hysteresis loop, the field dependence of the differential electric susceptibility, and the switching current have also been analysed.

Our approach to the switching problem is somewhat different. It has always been suspected that a thin passive layer (sometime it is called a non-ferroelectric layer, or dead layer) is formed between the ferroelectric and the electrode (Bell and Knight 1994, Tagantsev *et al* 1995). The thickness of this layer is supposed to be independent of the total film thickness. In one report (Benedetto *et al* 1994) this layer was estimated to be of the order of 10 nm for PZT film. In another report (Mukhopadhyay and Chen 1995) it was found that only a fraction of the first monolayer is non-ferroelectric. A method from a 'model-free' analysis has been proposed to identify this passive layer from measured switching parameters (Tagantsev *et al* 1995). A 'ferroelectric–dielectric' sandwich structure (Miller *et al* 1990, Mihara *et al* 1992, Brennan 1992) has also been used to model the switching behaviour in ferroelectric film with passive layers. In these works, the key point is to assume a particular form for the hysteresis loop describing the dependence of the polarization on the electric field.

The main purpose of this paper is to investigate the polarization reversal process qualitatively using a finite-lattice model in which non-ferroelectric boundary sites are taken to represent the passive layers. We believe that the lattice model has a more physical basis than both the KA theory and the modelling from an assumed hysteresis loop. In the next section, we obtain the relevant expressions from the free energy, present different definitions of switching time, and briefly describe several empirical formulae relating to the switching

time. The results, which include switching time for different numbers of sites and different electric field strengths, are given in section 3 and discussed. The last section presents some conclusions.
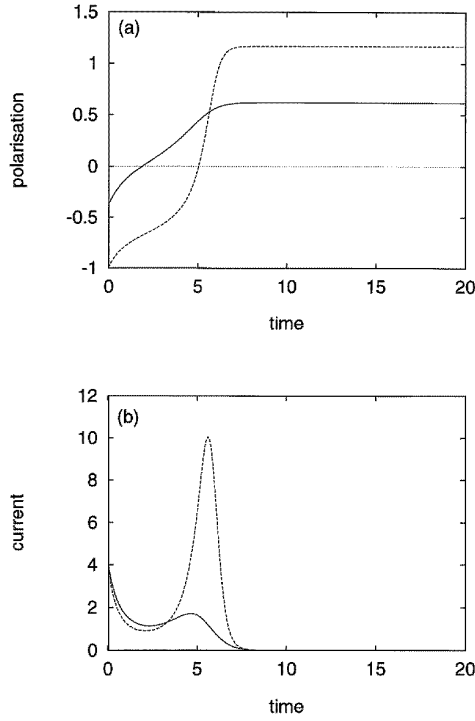
Figure 1. The time dependence of (a) the polarization and (b) the current response in a lattice with total site number $N = 10$ to an electric field $1.1e_c$ applied at $t = 0$. The dashed lines show the response of the central site.
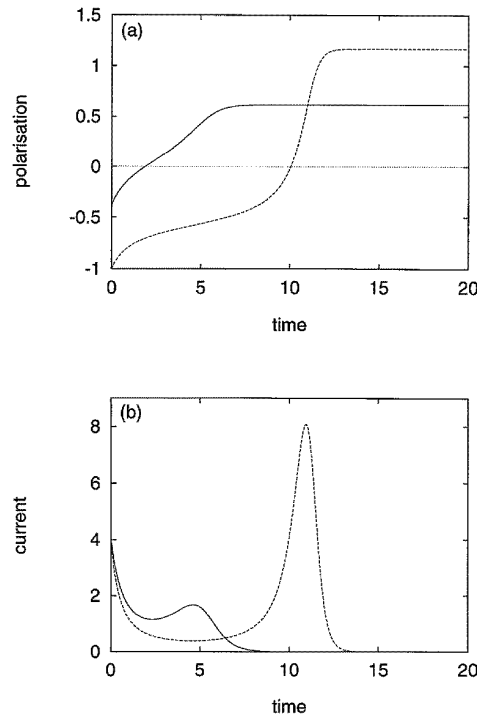
Figure 2. The time dependence of (a) the polarization and (b) the current response in a lattice with total site number $N = 100$ to an electric field $1.1e_c$ applied at $t = 0$. The dashed lines show the response of the central site.

2. Free energy and expressions

The free energy of a one-dimensional lattice model with non-ferroelectric boundary sites is written as

$$F = \frac{1}{4}(1 + p_1^2)^2 - ep_1 + \frac{1}{4}(1 + p_N^2)^2 - ep_N$$
$$+ \sum_{n=2}^{N-1}\left[\frac{1}{4}(1 - p_n^2)^2 - ep_n\right] + \frac{\kappa}{2}\sum_{n=2}^{N}(p_n - p_{n-1})^2 \tag{3}$$

of the same form as equation (1), except that we assume that the basic non-ferroelectric nature of the boundary sites ($n = 1$ and $n = N$) can be modelled by replacing the term $(1 - p_n^2)^2$ by $(1 + p_n^2)^2$. The basis of this assumption is the fact that the conventional Landau free energies in the ferroelectric and paraelectric phases differ only in the sign of the term that is quadratic in the polarization, so we can qualitatively model the non-ferroelectric surface sites by changing the sign of the term in p_n^2. The surface sites are still

coupled to the adjacent ferroelectric sites through the term in κ. Note that a 'site' in this context refers to a layer of thickness equivalent to the thickness of the passive surface layer, and so a film of N sites is of actual thickness N times the thickness of the surface layer.

The static properties can be obtained by minimizing the free energy (3). For the first site $n = 1$ we have

$$(1 + p_1^2)p_1 - e + \kappa(p_1 - p_2) = 0 \tag{4}$$

and a similar equation for the $n = N$ site. For the normal ferroelectric sites $2 \leqslant n \leqslant N - 1$, we have

$$-(1 - p_n^2)p_n - e + \kappa(2p_n - p_{n-1} - p_{n+1}) = 0. \tag{5}$$

Neglecting surface effects, the bulk polarization p satisfies the relation

$$(p^2 - 1)p = e$$

and the bulk coercive field (the field required for polarization reversal) has magnitude $e_c = 2/3\sqrt{3}$.

From (4) and (5) we can obtain the equilibrium polarization profile under electric field e and related properties such as susceptibility. The equations describing the relaxation behaviour can be obtained by combining equations (2) and (3), which yields

$$\gamma \, \frac{\mathrm{d}p_1}{\mathrm{d}t} = e - (1 + p_1^2)p_1 - \kappa(p_1 - p_2) \tag{6}$$

for the $n = 1$ boundary site and a similar expression for the $n = N$ site. For the ferroelectric sites, $2 \leqslant n \leqslant N - 1$, we have

$$\gamma \, \frac{\mathrm{d}p_n}{\mathrm{d}t} = e + (1 - p_n^2)p_n - \kappa(2p_n - p_{n-1} - p_{n+1}). \tag{7}$$

The above two equations are the basic expressions for simulating the switching process. The switching current (sometime called the polarization current or displacement current) is

$$i = \frac{\mathrm{d}p}{\mathrm{d}t}. \tag{8}$$

There are several definitions of switching time in the literature. At the early stage of studying domain wall motion in barium titanate single crystals, it was defined as the time t_s at which the current reaches zero. Other definitions used in the recent study of polarization reversal process are listed below.

(1) t_0 is the time at which the polarization crosses zero (Nagaya and Ishibashi 1991).
(2) t_{90} is the time when 90% of charge has been switched (Ishibashi 1992).
(3) t_m is the time at which the current reaches its maximum (Ishibashi 1992, Tura and Mitoseriu 1994).
(4) t_{50} is the time when half of the full polarization is attained (Ishibashi 1990a, b).

These four definitions are very practical. It is much easier to get t_0 from the numerical calculation, and it is not difficulty to measure t_m from experiment (Tura and Mitoseriu 1994). We will use these two definitions of switching time in the following calculations. However, we will not calculate t_s in this paper, since strictly speaking the current only reaches zero at infinite time.

Several empirical expressions have been obtained in the study of domain wall motion in bulk barium titanate single crystals. For example, Merz (1954) found that the reciprocal switching time has a linear dependence on the applied electric field:

$$t_s \cong \frac{\beta d}{E - E_0} \tag{9}$$
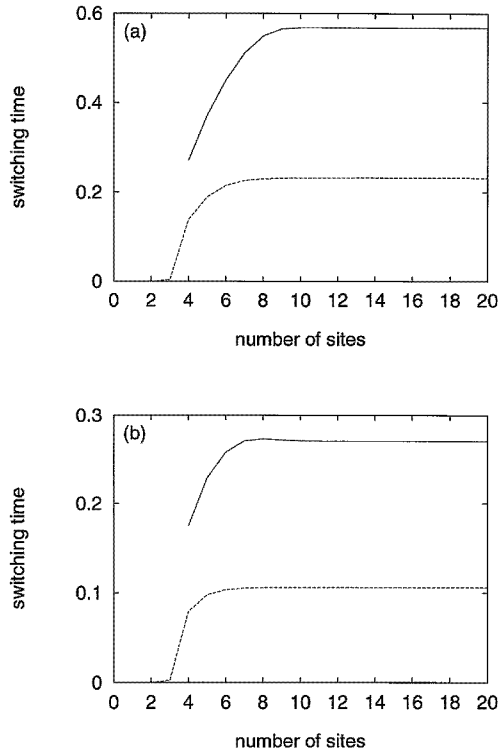
Figure 3. The dependence of the switching time t_m (solid lines) and t_0 (dashed lines) on the number of sites N under the electric fields (a) e_c and (b) $1.5e_c$.

where d is the thickness of the sample, E_0 is a kind of coercive field, and β is a constant. However, Miller and Weinreich (1960) found a power relation:

$$t_s = B\mathrm{e}^{b/E} \tag{10}$$

where B and b are constants, and Stadler (1958) found an exponential law

$$t_s = AE^{-n} \tag{11}$$

where A and n are constant. Fatuzzo (1962) combined the last two expressions together:

$$t_s \sim E^{-n}\mathrm{e}^{\alpha/E} \tag{12}$$

where n and α are the constants. The first three formulae will be used to fit our calculations of t_m and t_0.

3. Results and discussion

The differential equations (6) and (7) are solved by Runge–Kutta integration with the initial polarization profile in zero applied field obtained from (4) and (5) by a Newton–Raphson method. We set $\kappa = 1.0$ for convenience.

3.1. The step-field response

The time evolutions of the polarization and current following the application of an electric field $e = 1.1e_c$ are shown in figures 1 and 2, with total site number $N = 10$ and 100

respectively. The solid lines refer to the surface sites, and the dashed lines to the central site. The time-scale is in units of the arbitrary parameter γ. The polarization is dimensionless, and the current is defined in equation (8).
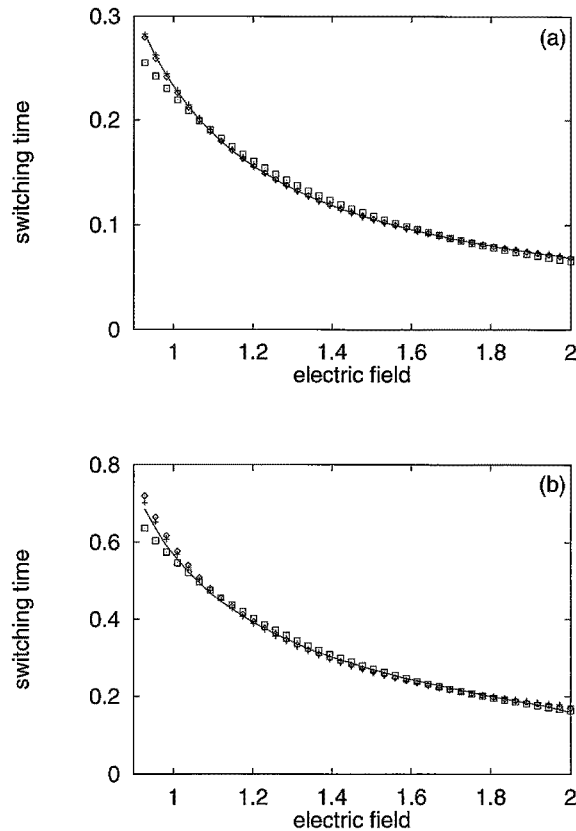
Figure 4. The electric field strength dependence of the switching times (a) t_0 and (b) t_m for a 100-site lattice fitted with empirical formula (9) (diamonds), equation (10) (plus signs) and equation (11) (squares). The electric field is in units of the bulk coercive field e_c.

From figure 1(a) we can see that the surface polarization is reversed earlier than that of the central site, and its magnitude is reduced. This is because the surface sites, which are non-ferroelectric as isolated sites, have weak ferroelectricity induced by the adjacent ferroelectricity sites. The weak surface ferroelectricity makes the surface sites easier to switch than the other sites. This leads to domain wall formation near the surface, followed by domain wall movement towards the centre. Hence there is delayed switching at the central sites. This kind of delay is much more obvious in figure 2(a), which is for a system with 100 sites. It obviously takes a longer time for a domain wall to move from the boundary to the central site in a long chain than in a short chain.

3.2. Switching time

As switching time is an important parameter describing the switching property, in this subsection we calculate the switching times t_0 and t_m, as defined in the last section.

Figure 3 shows the dependence of switching times on the number of sites N in the

film. Figure 3(a) shows, for under an electric field of $e = e_c$, the bulk coercive field, and figure 3(b) shows the switching under an electric field $1.5e_c$. Both switching times decrease as N decreases, and reach a saturated value at a number of sites N_s which decreases with increasing field. The value of t_m is around three times higher than that of t_0. This can be easily understood by reference to figures 1 and 2, where it is clear that the time t_m at which the current reaches its peak value is later than the time t_0 at which the polarization crosses zero. We do not find a maximum in the current (other than at $t = 0$) if the total number of sites N is less than four, though we can still find the switching time t_0 at $N = 3$ even though it is much reduced. t_0 in effect becomes zero when $N = 2$, because the sites are non-ferroelectric.
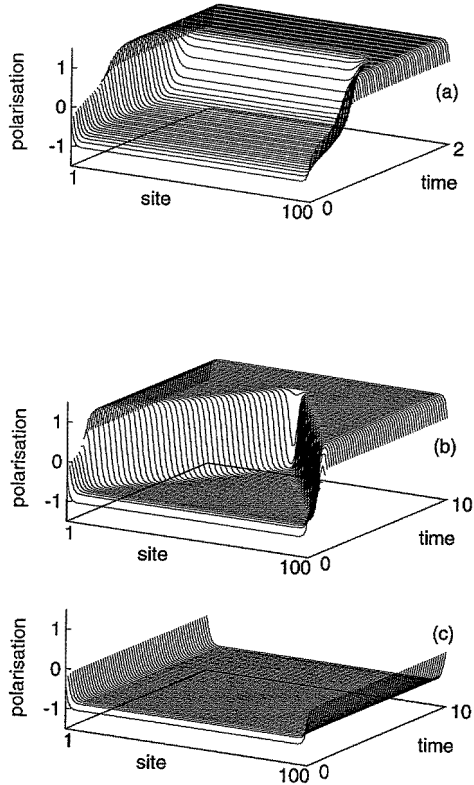
Figure 5. The polarization profile evolution for a 100-site lattice under the electric fields of (a) $1.1e_c$, (b) $0.8e_c$ and (c) $0.6e_c$.

The electric field strength dependence of the switching times is shown in figure 4(a) for t_0 and in figure 4(b) for t_m, both of which were fitted with the empirical formulae (9)–(11) using a least-squares method. The electric field is scaled by the bulk coercive field e_c. In both figures the switching times decrease as the field strength increases. By looking at the mean standard deviation obtained from the fitting, we find that t_m can be fitted with the empirical formulae a little better than can t_0, that both t_m and t_0 fit better for strong fields than for weak fields, and that equation (10) gives marginally the best fit. Another feature apparent in both figures is that the switching times are not infinite when e is equal to the bulk coercive field e_c, which implies that the polarization can be reversed by an electric field weaker than e_c. This indicates that the coercive field is weaker in films than in the
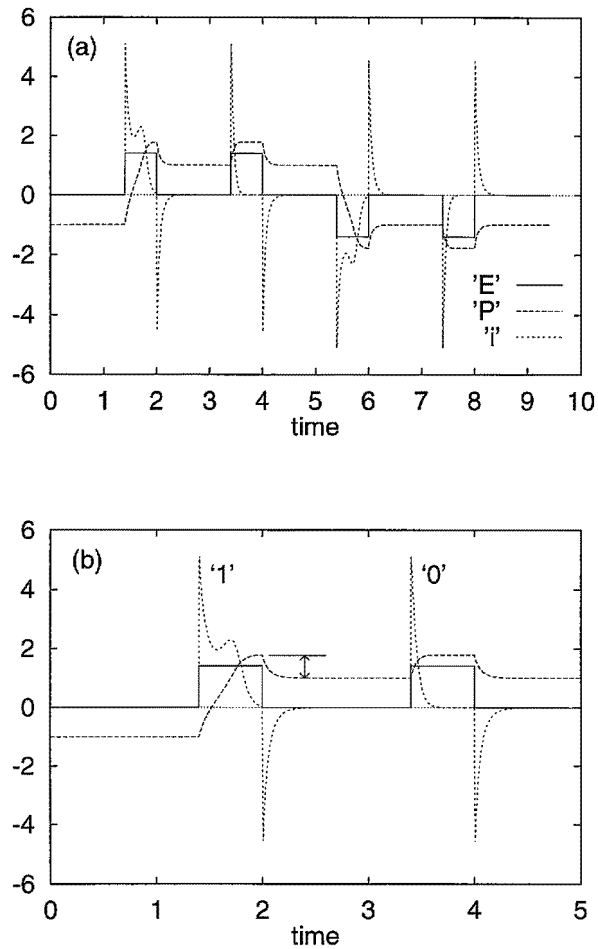
Figure 6. The polarization (P) and current (i) evolution under a pulsed electric field (E); $e = 1.4e_c$; total site number $N = 50$. (b) shows an enlargement of (a) for the first two pulses, showing the '1' and '0' responses. The magnitude of the back-switching polarization is indicated by the arrow.

bulk, in agreement with the latest analysis from a model-free calculation (Tagantsev *et al* 1995).

3.3. Profile evolution

Figure 5 shows the time evolution of the polarization profile under three different electric field strengths. The most striking feature is in figure 5(b). Immediately after the electric field is applied, the polarization at all sites increases, but the shape of the polarization profile does not change much apart from a small increase in magnitude. Thereafter, the polarization of the surface sites reverses, and domain walls are formed near the surfaces. These walls move inward until they coalesce and the reversal process finishes. When the applied field is stronger, as shown in figure 5(a), the above statements are still true but the domain wall movement is less obvious. The polarization at all sites increases while the domain walls

move inwards. Figure 5(c) shows the polarization profiles when a non-switching field is applied: the polarization reaches a saturated but non-switched value soon after the field is applied.

3.4. The pulsed-field response

In most devices, the polarization is reversed by a pulsed electric field. Figure 6(a) shows the time evolution of the polarization and the current under a bipolar pulse sequence. The polarization, initially negative, is reversed by the first positive pulse (pulse 1), then re-probed by a second positive pulse (pulse 2); the situation is then reversed by the negative pulses (3 and 4). Figure 6(b) shows an enlarged view of the first two pulses in figure 6(a). Two features are worth pointing out. First the figure shows clearly the difference in response when polarization reversal occurs (switching pulses 1 and 3) and when no reversal occurs (non-switching pulses 2 and 4). In the literature, the former is referred to as the '1' response, and the latter as the '0' response. The second feature is the back-switching phenomenon, defined as the decay of polarization after the removal of the applied field. The magnitude of the back-switching polarization change is indicated by the arrow in figure 6(b). There is also a large back-switching current associated with this polarization change. In some of the literature (Benedetto *et al* 1994, Mihara *et al* 1994, 1995) the back-switching phenomenon is called the depolarization effect.

4. Conclusions

From the calculations we can see that the lattice model with non-ferroelectric boundary sites predicts that the switching time decreases with the film thickness. The switching time obtained from this model decreases with increasing electric field strength, and can be fitted very well by the empirical formulae suggested in earlier work. The time evolution of the polarization profile shows clearly the formation of domain walls and their movement under the electric field. The back-switching phenomenon can be seen from the response of polarization and current under a pulse sequence. This model clearly can be used to simulate the behaviour of real ferroelectric thin-film structures. Our model gives a behaviour similar to that predicted in other work (e.g. Omura *et al* 1991), but without introducing latent nuclei that initiate the imperfections.

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