Transactions of the Materials Research Society of Japan 31[1] 35-39 (2006)

Simulation of Field-Dependent Switching Kinetics and its Influence on Ferroelectric Hysteresis Loops

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We have employed a Landau theory based lattice model for the simulation of switching curves and hysteresis loops in the total and partial switching regime. The polarization reversal is triggered by defect sites interacting with neighboring ferroelectric units via gradient-type terms in the total energy, at fields lower than the coercive field of Landau theory. Domain maps reveal the nucleation-growth characteristics of the switching process. Model parameters have been varied in order to account for the hysteresis loops of various PZT samples. The results suggest that the negative susceptibility region on minor loops of PZT ceramics and epitaxial PZT films, associated to domains that continue their growth after the electric field on the loop starts to decrease after passing its peak level, is due to domain "inertia" in a sample with a lower defect density. By increasing the nuclei density, the minor hysteresis loops have a normal appearance, as found in polycrystalline PZT films with lower quality. The linear dielectric constant calculated from this model exhibits a typical butterfly-shaped hysteresis loop, with peaks in the zero-polarization state due to enhanced domain activity.

Key words: ferroelectric, switching, hysteresis, Landau theory

1. INTRODUCTION

With the advances of nonvolatile memory applications of ferroelectric thin films, clarifying the switching mechanisms and simulating the electric response of nonvolatile memory cells becomes imperative. Recent observations of domain dynamics and measurements of switched polarization [1-2] suggested physical mechanisms departing from traditional Kolmogorov-Avrami interpretations. Further, although some models for the major hysteresis loop do exist [3-6], there has been only limited success in calculating minor loops in the sub-switching field range, by using models based on Preisach-type distributions [7-8]. In this paper we have employed a lattice model based on a discretization of Landau-Devonshire free energy, that is able to reflect the nucleation-growth character of switching and reproduce the trends of experimental curves of bulk and thin film ferroelectrics.

2. SWITCHING ON THE BASIS OF LANDAU-KHALATNIKOV KINETICS

In this model, the polarization reversal proceeds on the basis of Landau-Khalatnikov (LK) equation [6]:

$$\gamma\frac{dP}{dt} = -\alpha P - \beta P^3 + E\,, \qquad ()$$

with Landau coefficients α, β and viscosity γ.

One readily notices that, starting from one of the two possible remanent polarization states, switching to the opposite polarization state can be induced only if the external electric field E is larger than the coercive field:

$$E_c = \frac{-2\alpha}{3}\sqrt{\frac{-\alpha}{3\beta}} \qquad (2)$$

An important feature of switching described by the LK equation is that the polarization range between $-P_r$/sqrt(3) and P_r/sqrt(3), where P_r=sqrt($-\alpha/\beta$) is the remanent polarization, is inaccessible in an equilibrium state. As explained in Ref. [6], this polarization range is associated to a instability region intrinsic to the Landau-type free energy. This is the origin of unphysical negative susceptibility regions on dynamical hysteresis loops calculated from Eq. (1) [6,9].

In this paper we have included defects in the switching scenario, for two reasons. First, one should obtain lower coercive fields than the nominal one of Landau theory, in accord with numerous experimental observations. And secondly, it would be desirable to avoid the above-mentioned negative susceptibility regions by tuning the model parameters governing the switching process.

3. INHOMOGENEOUS SWITCHING IN A TWO-DIMENSIONAL LATTICE WITH DEFECTS

In this model, switching is described by the a system of discrete LK differential equations. Polarization at each lattice site switches under the influence of the external field E and an internal one given by the coupling between polar units.

$$\gamma\frac{dP_{ij}}{dt} = -\alpha P_{ij} - \beta P_{ij}^3 - k(2\cdot P_{ij} - P_{i-1j} - P_{i+1j}) - k(2\cdot P_{ij} - P_{ij-1} - P_{ij+1}) + E \qquad (3)$$

where k is a coupling coefficient increasing the total energy of the system whenever polarization inhomogeneities are present. Average polarization over the lattice is considered as global order parameter. Assumed values of model coefficients α=-1.0, β=1.0, k=2.0, γ=0.01 are unchanged throughout the paper. As we only consider the switching of the z-axis component of polarization, we have selected equal coupling coefficients along x and y-axes of the lattice. The differential equations have been solved numerically, with periodical boundary conditions.

In a lattice with no defects, the polar units switch homogeneously, as in this case there would be no internal electric field. In presence of defects, a nonzero internal electric field will affect the polar units neighboring the defect sites, triggering an inhomogeneous switching process even when the external electric field is lower than the nominal coercive field of the lattice. Actually by selecting a certain density of sites as occupied by polar units with the polarization fixed with equal probability at its positive and negative remanent values, we obtain a nucleation-growth switching process triggered by latent (preexistent) nuclei. This mechanism rather than the homogeneous polarization reversal reflects the experimentally-proven nucleation-growth nature of ferroelectric switching. In the case of thin films, the latent nuclei may be located at the film-electrode interfaces and therefore one should consider interface nucleation in a three dimensional lattice. However, as our immediate purpose is to obtain a qualitative agreement between the model predictions and typical measurements, the calculations have been performed using a more computationally-efficient two-dimensional lattice, in which one does not explicitly differentiate between interface and bulk nucleation. Our previous experience with this type of model has shown that calculations in a three-dimensional lattice do not exhibit significant changes as far as macroscopic switching responses are concerned.

As a first step we study the effect of a variable nuclei density (2% and 4%, respectively, with polarization fixed with equal probability at its positive and negative remanent values) on switching in constant electric field. The time dependence of the average polarization is depicted in Fig. 1.

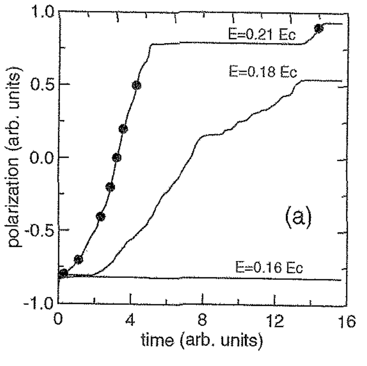

Fig. 1(a) Polarization reversal in a 2% nuclei lattice, for the indicated electric field range.

We note that an electric field of $0.21E_c$ ($0.36E_c$) for the case of 2% (4%) nuclei density is needed for complete switching, in a longer (shorter) reversal time, respectively. Fig. 2 depicts the domain evolution for the case of single-pulse complete switching in a lattice with 2% nuclei density. Switching proceeds by growth of few nucleated domains (due to the lower defect density there are few regions with defect agglomerations where domains can be easily formed) that end up impinging onto each other in final stages. The domain growth is enhanced in regions neighboring nucleation sites with favorable polarization orientation and where few oppositely polarized latent nuclei exist. On the other hand, due to the negatively polarized latent nuclei, a few polar units around them will maintain their original polarization state.

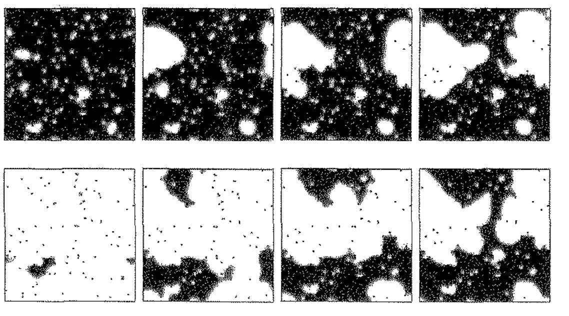

Fig. 2 Domain evolution (clockwise) for stages indicated by symbols in Fig. 1(a).

In order to test whether it is possible to obtain equilibrium intermediate switching stages, we also studied the switching behavior for weaker electric fields. Fig. 1 reveals that intermediate switching states can indeed be stabilized, which is an essential difference from the case of polarization dynamics of a single LK unit. In case of 2% nuclei density, a state with P=0.5P_r is stabilized upon applying E=0.18E_c. In this equilibrium state, a ferroelectric domain extending over approximately 25% of area preserves its original polarization orientation. The 180^0 domain walls are clamped due to the balance between the external electric field energy and the energy of coupling to the defects.

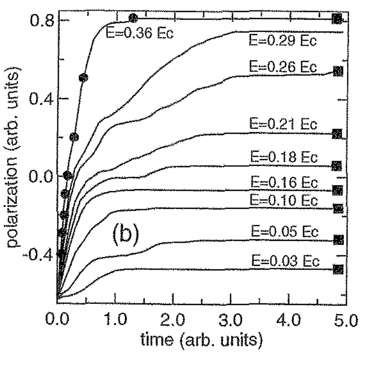

Fig. 1(b) Polarization reversal in a 4% nuclei lattice, for the indicated electric field range.

More precisely, the gradient terms in the total free energy allow the stabilization of partially switched states, effectively breaking the Landau-type potential. However, only in the case of a larger nucleation density it is possible to map with sufficient resolution the partially switched states, as there is still a considerable polarization range inaccessible as an equilibrium state in the case of a low latent nuclei density [see Fig. 1(a)].

The domain evolution snapshots along the total switching curve for the case of larger nuclei density is shown in Fig. 3. The main difference from the patterns displayed in Fig. 2 is that in this case the polarization reversal proceeds with growth of several nucleated domains, as there are now more regions with defect agglomerations where domains can form. We have compared these patterns with those in Fig. 4, stabilized during a step-by-step switching procedure, by application of electric fields with increasing intensity (the square symbols in Fig. 1b). We note that the snapshots corresponding to any given value of average polarization are similar, i. e. domain nucleation-growth appears to be triggered from same sites in the lattice, irrespective on the switching procedure.

However, a careful comparative observation of patterns in Figs. 3-4 also reveals some differences between them. It appears that, for a given polarization state, more domains are nucleated in case of switching induced by a strong electric field than during a step-by step switching sequence under fields with increasing intensity. For example, the upper-left quadrant of snapshots in Fig. 4 preserves its dark contrast up to the last stages of the reversal process, whereas a domain with bright contrast is nucleated and grows from the initial switching stages of patterns in Fig. 3. This peculiarity discloses that there is a large density of latent nuclei with polarization oriented oppositely with respect to the applied electric field in that respective region of the lattice, so that a large field and a long time to reverse its polarization is effectively needed. If the existence of such regions can be proven experimentally, it may provide physical support for hysteresis loop models based on Preisach-type distributions of ferroelectric properties [7].

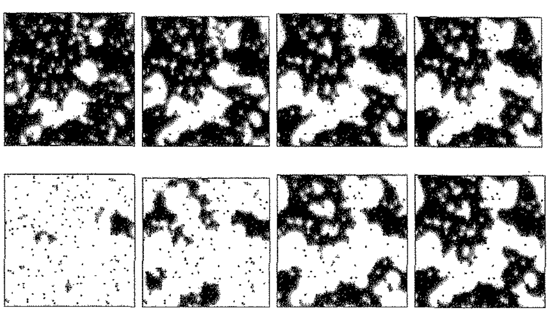

Fig. 3 Evolution (clockwise) of non-equilibrium domain patterns during switching under a high intensity electric field, in a 4% nuclei lattice [corresponding to round symbols in Fig. 1(b)].

4. DOMAIN KINETICS ON HYSTERESIS LOOPS

After the characterization of switching induced by a constant electric field, we are concentrating next on studying the hysteresis loops. In literature there are two categories of papers dealing with modeling of hysteresis loops on the basis of such implementations of Landau theory. One category only considers defect-free switching, when the electric field needed for inducing the polarization reversal exceeds the nominal coercive field of the Landau theory [5-6,9]. Other papers include defects in the switching scenario, so that the polarization reversal may be triggered at lower fields [3-4]. This latter approach seems more justified given the well-known fact that the experimental coercive fields are some orders of magnitude lower than those predicted by Landau theory. However, using both approaches it was possible to obtain reasonable shapes of theoretical hysteresis loops only for the case of a high enough electric field, when the entire polarization of the sample is switched. For so-called partial switching this type of modeling approaches typically yield hysteresis loops with unphysical negative susceptibility regions (NSR), rarely found in experiments.

In the case of our model, the occurrence of NSR is caused by domains that continue their growth after the electric field starts its decrease in intensity on a minor loop. Therefore, as a preliminary step before actual calculations of hysteresis loops in time-dependent electric field, we investigated the switching behavior of the ferroelectric lattice upon a sudden decrease in field intensity during polarization reversal. As an example, Fig. 5 depicts similar polarization reversal curves as in Fig. 1 up to t=5.0, when the electric field intensity decreases to 75% of its initial value. We note that in the case of a lattice with larger nuclei density, the average polarization instantly 'feels' the decrease in electric field intensity and back-switches to a certain extent, whereas domain switching triggered by a smaller nuclei density progresses even with a weaker electric field.

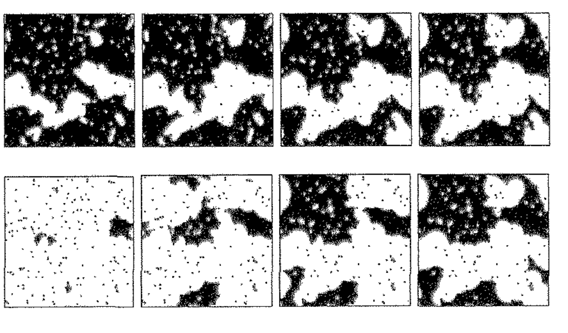

Fig. 4 Evolution (clockwise) of equilibrium domain patterns switched by an electric field with increasing intensity, in a 4% nuclei lattice [corresponding to square symbols in Fig. 1(b)].

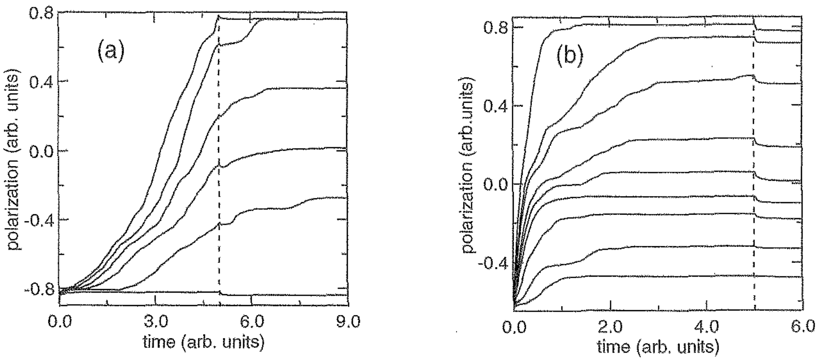

Fig. 5 Polarization reversal in a 2% (a) and 4% (b) nuclei lattice; electric field increases from bottom to top. At the moment indicated by a vertical broken line, the electric field drops to 75% of its initial value.

In other words, the ferroelectric domains have a larger "inertia" in responding to variations of the external electric field if there are few defects in the lattice. Consequently, one expects that minor hysteresis loops in case of switching triggered by a low nucleation seed density should exhibit NSR, whereas they should maintain a normal appearance in presence of a larger latent nuclei density.

Fig. 6(a-b), contains hysteresis loops with total and partial switching calculated with same model parameters as in Figs. 1-5 (averaging over 10 runs with different seeds for the random number generator has been performed in order to smoothen the noise-like features of switching curves visible in Figs. 1 and 5). NSR are revealed for the case of small latent nuclei density, while an instant decrease of average polarization when the electric field starts to decrease its intensity occurs for a lattice with a larger nuclei density.

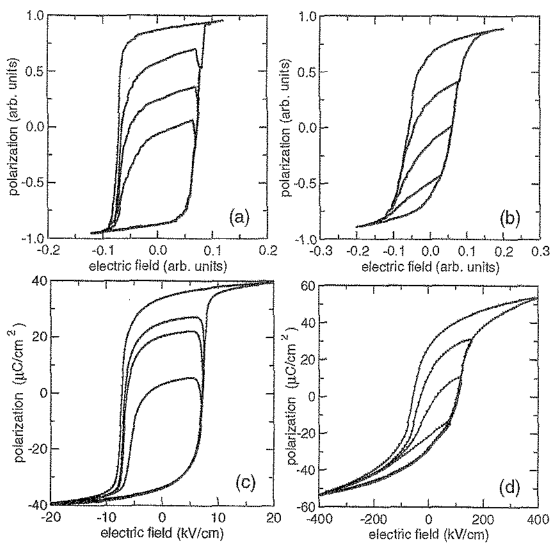

Fig. 6 Hysteresis loops with total and partial switching calculated for a 2% (a) and 4% (b) nuclei density and measured on PZT ceramics (c) and polycrystalline PZT thin films (d).

Other features are a more rectangular hysteresis loop shape in the former case and a slanted one in the latter. The calculated hysteresis loops have similar shapes with measured ones on PZT ceramics and polycristalline thin films shown in Fig. 6(c-d). The NSR is only visible on the hysteresis loops of ceramic samples (and also epitaxial PZT films [10]), due to their smaller defect density. As the number of defect sites that effectively clamp neighboring polar units is small, domains are allowed to have an enhanced "inertial" growth after the electric field starts to decrease, compared with the thin film case. This agreement between experimental and theoretically predicted behavior attests the appropriateness of the proposed model for the study of ferroelectric switching and hysteresis loops.

Further, we have used the lattice model for probing the various domain states (intermediate stages of switching) shown in Figs. 2-4 using a low-signal applied external field.

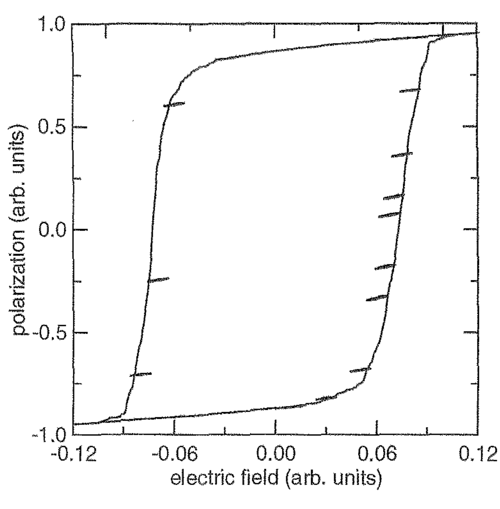

Fig. 7 Simulation of a sequence for measuring the hysteresis loop of the dielectric constant. The low signal minor loops have been calculated by applying a weak electric field in states with various average polarization.

Specifically we have simulated a measurement sequence for acquiring the hysteresis loop of the dielectric constant by superposing a small ac test signal on the poling bias field that establishes the (unswitched, partially switched or completely switched) domain state of the sample. Fig. 7 shows a few of the calculated low-signal hysteresis loops, superposed on the major hysteresis loop of the lattice with low nuclei density.

Subsequently we have estimated the linear dielectric constant from the calculated low-signal hysteresis loops for all domain states, in case of both small and large latent nuclei density. The results shown in Fig. 8 display typical butterfly-like hysteresis loops for the dielectric constant, reaching their peaks close to the coercive field, as expected. This illustrates the enhanced domain activity (domain wall vibrations under the low-signal applied electric field) in the zero-polarization state, with a subsequent drop in dielectric response once the switching becomes complete.

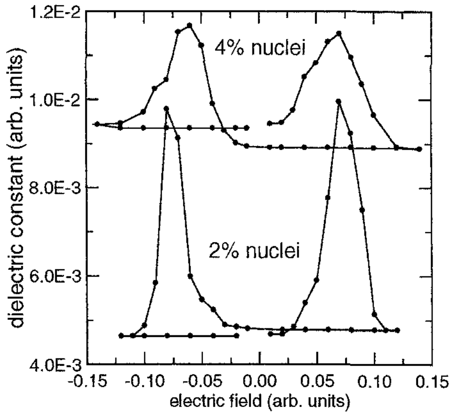

Fig. 8 Hysteresis loops of linear dielectric constant calculated in various states obtained during polarization reversal in a lattice with small and large nuclei density.

Fig. 8 also reveals that in case of a larger nuclei density the dielectric response is stronger in all polarization states. This behavior is attributed to a larger density of domain walls in Figs. 3-4 compared to Fig. 2, contributing to more significant variations of the average polarization in the applied low-signal electric field. Also, in case of a larger latent nuclei density, considerable domain wall vibrations persist in regions neighboring the nucleation sites even when the polarization reversal process has been completed. These findings in agreement with known experimental facts prove again the validity of the present modeling approach and its usefulness for simulating various ferroelectric responses as well as to a better understanding of ferroelectricity physics.

Further work on the basis of this model should be concerned with the frequency dependence of hysteresis loops, where some difficulties concerning the agreement with experimental data still persist. In this respect, there are also drawbacks relating to the time scales of ferroelectric switching when the applied electric field intensity is varied; recent experiments have shown that switching time can extend over several decades, whereas it does not vary so drastically in this model. However, although it also lacks the simplicity of analytical expressions in the Kolmogorov-Avrami-Ishibashi theory of switching, the present model has definitely enough versatility to make it applicable to a wide scope of real-life situations involving ferroelectrics' behavior.

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(Received December 10, 2005; Accepted January 31, 2006)