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A nucleation-growth model for ferroelectric hysteresis loops with complete and partial switching

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Abstract

This work proposes a two-dimensional lattice model based on a discrete Landau–Devonshire-type potential for calculating hysteresis loops of ferroelectric thin films in switching and sub-switching regimes, yielding good agreement with experimental data. Such a model is valuable for simulating the electric response of nonvolatile memory cells based on ferroelectric film capacitors. Setting the electric field below the nominal coercive field of Landau theory and placing nucleation seeds randomly in the lattice, switching proceeds with a nucleation-growth mechanism. Interactions with neighbors have also been taken into account. We have been able to qualitatively reproduce the shapes of experimental hysteresis loops measured on two types of PZT films in both switching and sub-switching regimes, as the negative susceptibility regions of minor loops are eliminated in our model. Snapshots of domain patterns associated to various points of hysteresis loops help understanding the nature of switching in time dependent electric field and may establish a link to modeling approaches based on ferroelectric property distributions.

Keywords: Ferroelectric properties; Dielectric properties; Films; Hysteresis

With the advent of nonvolatile memory applications of ferroelectric thin films, clarifying and simulating the electric response of nonvolatile memory cells based on ferroelectric film capacitors becomes imperative. Although some models for the major hysteresis loop do exist,[1–4] there has been only limited success when calculating minor loops in the sub-switching field range. Several hysteresis models assume Preisach-type distributions of ferroelectric properties in the material.[5,6] While such distributions may indeed exist in real materials, it is more valuable to develop a physical model based on theories of ferroelectricity for calculating minor hysteresis loops. As hysteresis loops can be regarded as a polarization reversal process in time-dependent electric field, we have employed a nucleation-growth model of ferroelectric switching based on the Gibbs–Landau–Devonshire theory of phase transitions in ferroelectrics.[4]

The model is based on a simple discretization of Gibbs–Landau–Devonshire free energy. We have included the on-site anharmonic potential responsible for the occurrence of a ferroelectric phase, the first-neighbors coupling energy and the electric field energy.

$$F = \sum_{i,j=1}^{N} \left[\frac{\alpha}{2} p_{ij}^2 + \frac{\beta}{4} p_{ij}^4 + \frac{k}{2}(p_{ij} - p_{i-1j})^2 + \frac{k}{2}(p_{ij} - p_{ij-1})^2 - p_{ij} E_{\text{ext}} \right] \quad (1)$$

Regarding other physical contributions to the ferroelectric thin film behavior, it is known that elastic effects can be included by a renormalization of the coefficients in the Landau power expansion of the free energy. Also, finite size effects can be also taken into account by a renormalization of the same coefficients.[4]

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 should exceed the nominal

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coercive field predicted by the Landau theory.[3,4,7] Other papers include defects in the switching scenario, so that the polarization reversal may be triggered at lower fields.[1,2] This latter approach seems more justified given the well-known fact that the experimental coercive fields are order of magnitude lower than those predicted by Landau theory. However, using both approaches it is possible to obtain reasonable shapes of theoretical hysteresis loops only for the case when a high enough electric field is applied, so that the entire polarization is switched. For so-called partial switching this type of modeling approaches typically predicts hysteresis loops with unnatural negative susceptibility regions (NSR),[4,7] rarely found in experiments. As thoroughly explained by us in Ref. [4], the NSR is an intrinsic feature of the Landau-type on-site anharmonic potential, containing nonequilibrium states normally replaced by vertical lines in textbook descriptions.

In this paper we have chosen to include defects in the switching scenario, for two reasons. One is to remain within the experimentally proven facts relating to coercive fields much lower than the nominal one of Landau theory. The other was to examine whether it would be possible to get rid of the negative susceptibility regions by tuning the model parameters governing the switching process.

Switching in our model is governed by the kinetic Landau–Khalatnikov equation. The polarization at each site in the lattice will switch under the influence of the external field E and the internal one given by the first neighbor coupling between polar units in the lattice.

$$\begin{aligned}\gamma \frac{\mathrm{d}P_{ij}}{\mathrm{d}t} &= -\frac{\partial F}{\partial P_{ij}} \\ &= -\alpha P_{ij} - \beta P_{ij}^3 - k(2P_{ij} - P_{i-1j} - P_{i+1j}) \\ &\quad -k(2P_{ij} - P_{ij-1} - P_{ij+1}) + E_0 \sin(\omega t)\end{aligned} \tag{2}$$

Assuming an infinite lattice with no defects present, polarization homogeneously switches through the lattice, as the internal electric field is zero. In presence of defects, a nonzero internal electric field will decisively influence 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 polar units. Actually by selecting a certain density of sites as occupied by polar units with the polarization set not less than its positive and negative remnant values, with equal probability we are in the situation of a nucleation-growth switching process triggered by latent (preexistent) nuclei. This mechanism rather than the homogeneous polarization reversal is in agreement with the experimentally-proved nucleation-growth character of ferroelectric switching. In case of thin films, it appears that the latent nuclei are located mainly at the film-electrode interfaces and therefore an attempt to fit such experimental data should consider interface nucleation in a three dimensional lattice. However, as our immediate purpose is to obtain only a qualitative agreement between the model predictions and typical hysteresis measurements, we will perform our calculations on a more computationally-efficient two-dimensional lattice, in which one does not explicitly differentiate between interface and bulk nucleation. Our previous experience with this model has shown that the results of calculations in a three-dimensional lattice do not exhibit significant changes as far as hysteresis loops are concerned.

We have set the model parameters in order to attempt to qualitatively reproduce the results measured for two types of PZT films, one polycrystalline, (1 1 1)-oriented and the other epitaxial, (0 0 1)-oriented, presented further on. As we only consider the switching of the z-axis component of polarization, we have selected equal coupling coefficients along x- and y-axis of the lattice. A higher latent nuclei density (6%) has been set for the case of the polycrystalline films. Also, we have accounted for imprint phenomena in these films by selecting asymmetrical densities for the latent nuclei of opposite polarization. As the epitaxial films are thought to be of a better quality, we have reduced the latent nuclei density to 3% and assumed perfect symmetry of the latent nuclei with upward and downward polarization.

Figs. 1 and 2 show major hysteresis loops corresponding to full polarization reversal for the two types of model systems used in calculations. We have also portrayed theoretical domain maps showing with black/white contrast the fraction of switched domains associated to the important points of these loops ($-P_r$, $+E_c$, $+P_s$, $+P_r$, $-E_c$, $-P_s$), where P_r is the remanent polarization, P_s is the saturation polarization and E_c is the coercive field. Such a representation enables us to identify a nucleation-growth switching process, triggered by the latent nuclei and propagating through first-neighbor interactions. We note that in the case of high latent nuclei density, the sizes of transient domains active during switching tend to be smaller than in case of low nuclei density. As expected, the coercive field in the former case is lower than in the latter due to the additional contribution of the higher internal field

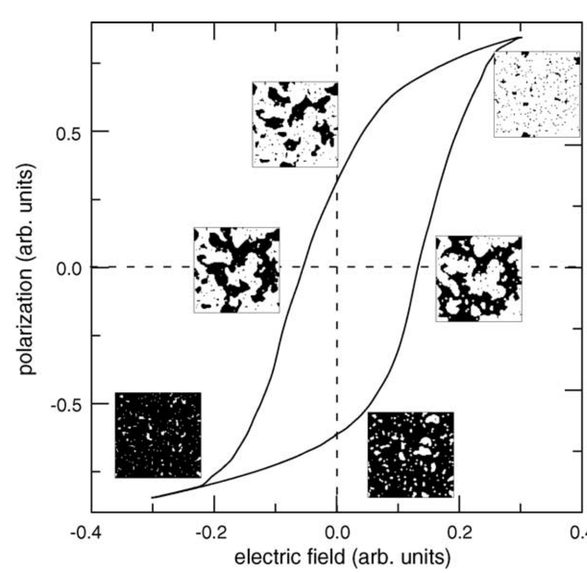

Fig. 1. Theoretical major hysteresis loops and domain evolution snapshots associated to important points (remanent polarization and coercive field) on hysteresis loops, for the case of 6% latent nuclei density.

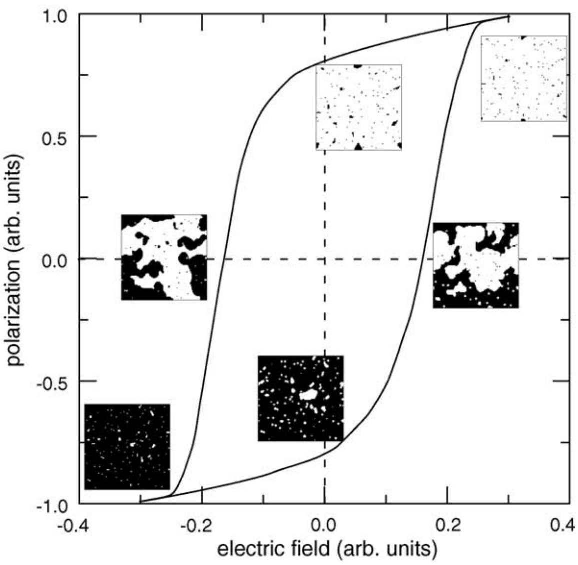

Fig. 2. Theoretical major hysteresis loops and domain evolution snapshots associated to important points on hysteresis loops (remanent polarization and coercive field), for the case of 3% latent nuclei density.

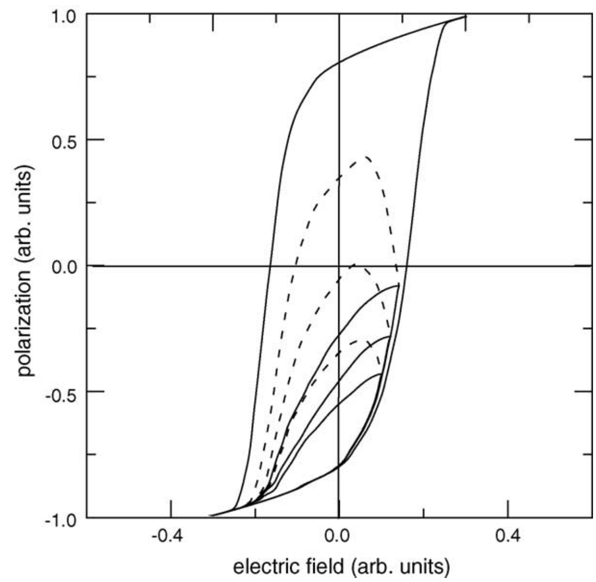

Fig. 4. Correction of minor hysteresis loops for eliminating the NSR, for the case of switching with 3% latent nuclei density. Original (corrected) loops are shown with broken (solid) lines.

given by the larger latent nuclei density. Another peculiarity is that the domain patterns on ascending and descending hysteresis loop branches seem to be rather similar in case of high latent nuclei density, whereas for small latent density the domain evolution from negative to positive polarization passes through different states than on the backward evolution. In this latter case the domains originating from latent nuclei of both polarities are freer to grow up to larger sizes, so that the domain evolution is less influenced by the nuclei of opposite polarity.

After clarifying the above characteristics of complete polarization reversal, we now turn our attention to switching on minor loops. Fig. 3 shows typical minor loops at various field amplitudes. We note immediately that all loops except the one with complete polarization switching exhibit negative susceptibility regions, that is, regions where upon decreasing the electric field (after reaching its maximum value), the polarization continues to increase. Their occurrence is due to the fact that the internal field still allows switching to proceed even though the external electric field has started its decrease. However, by decreasing the electric field strength and increasing the latent nuclei density in the model, we have successfully avoided the intrinsic NSR associated to the nonequi-

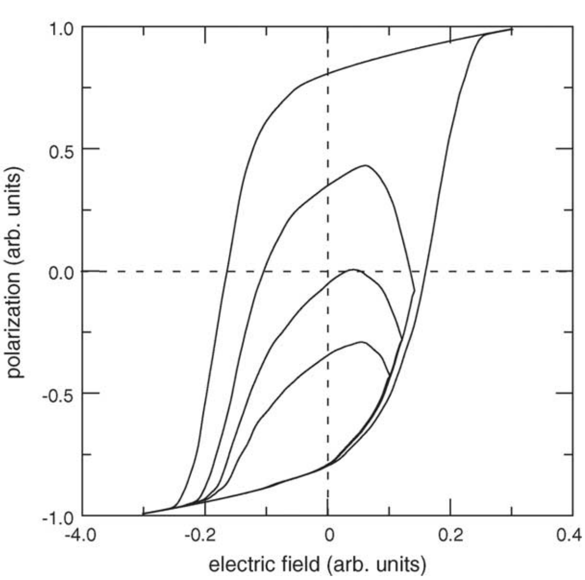

Fig. 3. Typical minor loops exhibiting negative susceptibility regions in model for switching with 3% latent nuclei density.

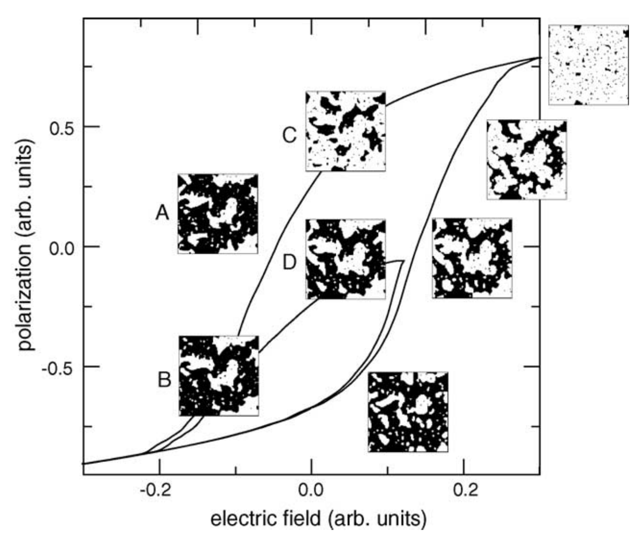

Fig. 5. Domain evolution snapshots along the major and a minor hysteresis loop for the switching model with 6% latent nuclei density. Vertically aligned snapshots (A, B) and (C, D), respectively, correspond to a field on the descending branch illustrated by the snapshots' position along the abscissa.

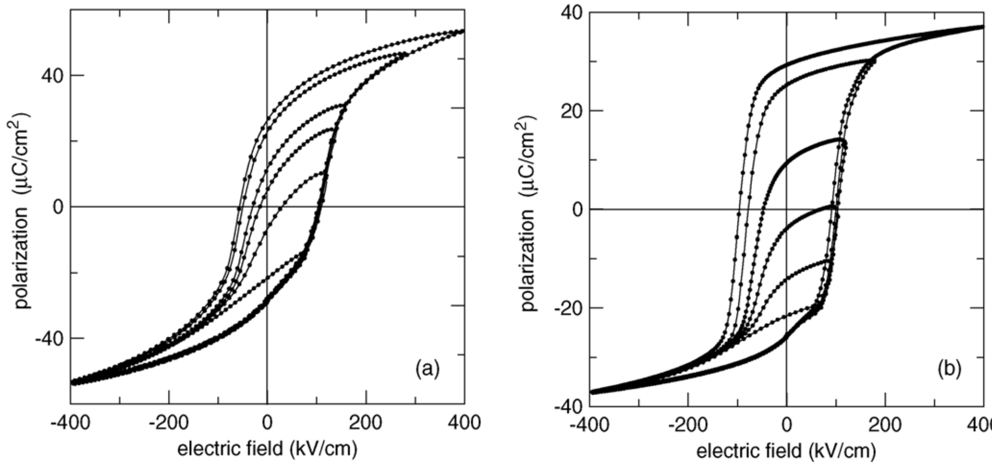

Fig. 6. Experimental hysteresis loops at various field levels for polycrystalline PZT film (a) and epitaxial PZT film (b).

librium nature of switching in such systems.[4] The NSR in Fig. 3 are less anticlockwise slanted than the intrinsic ones and of a different nature, being associated to the peculiarities of domain kinetics.

Specifically studying the domain dynamics on NSR by drawing snapshots such as in Figs. 1 and 2 (not shown here), it appears that smaller reversed domains tend to shrink when the electric field decreases, whereas the larger reversed domains tend to continue their expansion and coalescence for a considerable time after the external field starts to decrease. Such a switching scenario is unrealistic, as all domains should exhibit a similar evolution. A simple way to alleviate this unnatural switching behavior and simultaneously get rid of the unwanted NSR is to inhibit the growth of the large domains after the external field starts to decrease. In this way the minor hysteresis loops exhibiting NSR are expected to be transformed to hysteresis loops with normal behavior.

Fig. 4 shows how this correction works for the case of small latent nuclei density. It is seen that indeed by eliminating the unnatural domain growth of large domains after the external electric field starts its decrease, the minor loops have normal shapes and may be compared with real experimental data. Before so doing, let us examine comparatively the domain evolution on ascending and descending branches of a minor loop with that of a hysteresis loop with total switching (see Fig. 5). First we note that the ascending branches of all loops (further referred to as activation process in what follows) are very similar irrespective of the maximum field on the loop (see the unlabeled snapshots). On descending branches, the domain pattern evolution strongly depends on the maximum electric field previously applied on the loop. For weak activation fields, only the domains around the positively polarized latent nuclei will be switched. On the descending branch of such minor loops, the previously activated domains will need stronger opposite fields to be switched back, because they are far from the negatively polarized latent nuclei. So there are hardly any changes in the evolution from snapshot D to B. On the other hand, the domains activated by a strong field tend to cover all sample area. Among them, the domains close to the negatively polarized

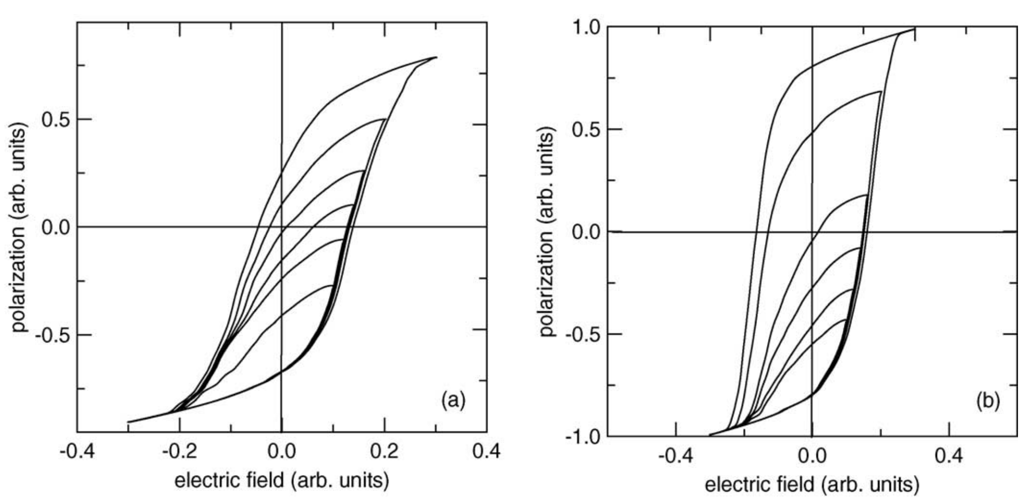

Fig. 7. Theoretical hysteresis loops after NSR elimination at various field levels, for model of polycrystalline PZT film (a) and epitaxial PZT film (b).

domains will be able to switch back at weaker electric fields than the corresponding activation field. Therefore, at same weak (strong) fields on the descending branches, we find different (similar) domain patterns C and D (A and B), respectively, on the major hysteresis loop and minor loop. Such an analysis of domain switching characteristics is very helpful for the interpretation of first-order reversal curve diagrams[8] that are used for the characterization of ferroelectric samples from viewpoints of local property distributions.

Finally we turn our attention to comparing the model predictions with actually measured hysteresis loops. As mentioned, we have measured both a polycrystalline PZT film and an epitaxial PZT film. Various amplitudes have been employed for the hysteresis measurements in 1 kHz triangular signal. The experimental results are shown in Fig. 6. We note that the ascending branches of all minor loops are close to that of the major hysteresis loop, as expected. The descending branches are free of NSR at all field levels and may reflect domain kinetics on the type presented above. The corresponding theoretical hysteresis loops being shown in Fig. 7, we note a good qualitative agreement with the experimental results in Fig. 6.

In conclusion, we have proposed a lattice model based on a discrete Landau–Devonshire-type potential for hysteresis loops with complete and partial switching. Setting the electric field below the nominal coercive field of Landau theory and placing nucleation seeds randomly in the lattice, switching proceeds with a nucleation-growth mechanism. The negative susceptibility regions have been eliminated by proper selection of model parameters so that we have been able to reproduce the shapes of experimental hysteresis loops measured on two types of PZT films. Snapshots of domain patterns associated to various points of hysteresis loops helps understanding the nature of switching in time dependent electric field that may be related to ferroelectric property distributions.

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