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Thermally activated switching kinetics in second-order phase transition ferroelectrics

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The understanding of electric polarization dynamics is a complex problem of critical importance for both fundamental studies of ferroelectric materials and their applications to nonvolatile memories. In this paper we focus on second-order phase transition ferroelectrics, as defined in Landau—Devonshire framework, which display a particular free-energy profile as a function of the ordering parameter, that has two energy minima separated by an energy barrier. Assuming a domain nucleation polarization reversal mechanism, this particular energy dependence allowed us to introduce an electric polarization reversal model based on the nonequilibrium statistics of the domain nucleation process. Using the Pauli master equation we have determined the time-dependent occupation probabilities of the polarization states of the nucleation sites, which can be used to generate analytical expressions for the temporal dependence of the reversed polarization, transient switching current, and the switching time. In addition, we have derived an analytic expression for the time and thermal dependence of the coercive field and we discuss the depolarization field effects on the polarization reversal dynamics in thin-film ferroelectric structures.

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I. INTRODUCTION

Polarization dynamics have been extensively investigated experimentally and theoretically in normal ferroelectric materials due to the recent interest in ferroelectrics for applications in memory devices such as ferroelectric random access memory (FRAM).[1–4] FRAM is a nonvolatile memory device, which contains a ferroelectric thin film[5] as a memory cell and uses the remanent directions of the polarization to store the data as logical "0" and "1." The FRAM technology is very important as it brings some considerable advantages over existing floating-gate memories. For example, FRAM cells can be easily embedded as part of a larger integrated circuit to provide system-on-chip solutions. Another advantage of FRAM is the low-energy consumption, the possibility of achieving record storage densities,[6] and short write-access times.[7,8] The short write time of FRAM is closely related to the dynamics of polarization switching.

It is well known that a ferroelectric material in a relaxed state forms domains with polarization aligned accordingly to minimize the electrostatic energy. The experimental evidence suggests that when an electric field is applied to a ferroelectric material, the reversal does not occur via a spontaneous reorientation of the polarization in a domain at once, but rather through nucleation of domains and the movement of domain walls, which subsequently expand and grow at the expense of the existing domains.[9–14]

One of the pioneering theoretical models of the polarization switching is the Kolmogorov-Avrami-Ishibashi (KAI) domain nucleation-switching model (and variants of it), which treats polarization reversal as a nucleation process and it has been derived from the original Avrami nucleation model of crystal growth.[15–20] According to the KAI model, upon the application of the electric field, nuclei of reversed polarization are generated and the polarization switching takes place in a few steps: (i) nucleation of domains; (ii) rapid growth of nuclei along polarization direction; (iii) sidewise growth of the domains; and (iv) coalescence of the domains until the reversal of the entire polarization direction. The KAI model predicts the following temporal dependence of polarization/electric displacement during the switching process:

$$\Delta D(t) = 2p_s \cdot (1 - e^{-(t/t_{sw})^n}), \tag{1}$$

where t is the experimental time; t_{sw} is the switching time; $2p_s$ is the amount of reversed polarization with p_s the spontaneous polarization at zero applied field E; and n is the Avrami exponent. The switching current per unit area associated with the polarization reversal is given in the KAI model by

$$I_{sw}(t) = \frac{d\Delta D(t)}{dt} = \frac{2p_s n}{t_{sw}}(t/t_{sw})^{n-1}e^{-(t/t_{sw})^n}. \tag{2}$$

The KAI model assumes two main physical mechanisms: "one-step nucleation" and "continuous nucleation." One-step nucleation takes place when all nuclei of the new phase are created at the beginning of the process, followed by the domain growth without any further nucleation. The continuous nucleation mechanism is the process in which the nuclei continue to appear during the whole transformation with a constant rate. The Avrami exponent can take only integer values and depending on the nucleation process taking place, $n=d$ for the one-step process and $n=d+1$ for the continuous process, where d is the dimensionality of the domain growth ($d=1,2$). When $d=1$ we have stripe domains [one-dimensional (1D)] formation, $d=2$ corresponds to circular (or two-dimensional) domain formation. Although we have no knowledge of studies reporting three-dimensional domain formation, theoretically $d=3$ is possible, leading to the formation or spherical domains. The KAI model of polarization switching has successfully given a good description of polarization kinetics of ferroelectric single crystals[15] and some epitaxial thin films.[21] However, the KAI model is not fully applicable to the reversal behavior over larger time periods or the reversal behavior in polycrystalline thin films.[22,23] Attempts to refine the KAI model in order to increase its applicability have been made by assuming a distribution of relaxation times,[24] a nucleation limited switching model,[23] and a statistical time-dependent depolarization field.[25] However, one of the main limitations of the KAI model, or modified versions of it, is the failure to predict the relationship between the switching time to the applied electric field and temperature. Several empirical expressions, linking the switching time to the applied electric field, have been obtained in the study of domain-wall motion. Miller and Weinreich[26] found that switching time has an exponential relation with the electric applied field in $BaTiO_3$ single crystals,

$$t_{sw} = Be^{b/E}, \tag{3}$$

where B and b are constants.

Stadler[27] found empirically for $BaTiO_3$ crystals at high voltages an inverse power law,

$$t_{sw} = AE^{-n}, \tag{4}$$

where A and n are constants.

Fatuzzo[28] combined the two models and derived the switching time as

$$t_{sw} = CE^{-n}e^{\alpha/E}, \tag{5}$$

where C, n, and α are constants.

In 1954, Merz[9] found that the reciprocal switching time has a linear dependence on the applied electric field for $BaTiO_3$ single crystals

$$t_{sw} \cong \frac{\beta d}{E - E_c}, \tag{6}$$

where d is the thickness of the sample, E_c is the coercive field, and β is a constant. Other important studies of polarization dynamics involved the size effects[29–32] and the thermal effects[33,34] on the polarization switching. Chong *et al.*[34] have used a model of thermal activation of the nuclei, which predicts activation energy of around 0.15 eV and the nucleation activation volume of around 10^{-25} m^3 in soft lead zirconic titanate (PZT)-5H samples. However, all models involving thermal activation of the nuclei assume that they are generated thermally with a certain probability followed by the fast reversal of polarization, without giving a relationship between the probability of nuclei formation and the driving forces (electric field, temperature, etc.). Hence the statistical treatments are usually applied to the nucleation sites rather than to the microscopic mechanisms responsible for nucleation inside a nucleus. In this paper, although we assume a nucleation mechanism of polarization switching, we take a rather different approach to derive the kinetic equations of the polarization switching. We assume that all nucleation sites are already present at any time in the sample. They can be activated (i.e., nucleation process of the nuclei) when the polarization of the critical volume nucleation site is reversed. Therefore, the switching rate is controlled by the switching rate of the nucleation site with a critical volume V^*, rather than the rate of expansion of the nuclei or the rate of formation of critical nuclei. Within this framework, we apply a nonequilibrium statistical model to describe the time-dependent reversal probability of the polarization of a nucleation site. In this way we directly account for both: applied electric field and thermal energy as contributing to the reversal process of the nuclei, followed by polarization reversal. Our model predicts relations for the time-dependent reversed polarization and transient switching current similar to those obtained in the KAI model for the particular case of $n=1$.[35] Moreover, our model yields an analytical expression of the polarization switching time, which is a function of both the applied electric field and temperature. Even at zero applied electric field, the model predicts a nonzero probability of polarization reversal of small polar sites at a temperature $T \neq 0$. Finally we have analytically derived the time- and temperature-dependent coercive fields of ferroelectrics. Therefore, this work is very relevant at explaining aging effects in ferroelectrics or other time/temperature-dependent effects.

II. THEORETICAL MODEL

We assume that the switching is provided by the nucleation of a domain per an elementary polar site, where the ferroelectric material is represented as an assembly of N elementary polar sites. Although for simplicity we consider the nucleation to occur at a random location within the elementary polar site, it is widely accepted that the preferred sites for nucleation are the domain walls, crystal imperfections or the electrodes.[26–28,33–36] The switching of the elementary polar site occurs once a critical domain (volume V^*) has reversed polarization and can expand unrestrictedly under the applied electric field E. Therefore, the time taken to reverse the polarization is called the switching time (t_{sw}) and is assumed to be equal to the time required for the nucleation site to reverse while the time for the expansion of the domain until it reverses the entire polarization of the elementary polar site is negligible in comparison with the nucleation time (Tagantsev *et al.* have also used this assumption in their nucleation limited switching model—see Ref. 23). We introduce the Landau-Devonshire free energy of the elementary ferroelectric polar site "i" under applied electric field E_{app} as[37]

$$\frac{F_i}{V^*} = \frac{\alpha}{2}D_i^2 + \frac{\beta}{4}D_i^4 - D_iE_{dep} - D_iE_{app}\cos(\theta), \tag{7}$$

where $i=1,2,\ldots,N$ and higher order energy terms have been ignored. α and β are the Landau coefficients and they are assumed equal for all N elementary polar sites; D is the electric displacement; θ is the angle between E_{app} and D, which is either 0 or π corresponding to elementary polar sites textured in one preferred orientation; E_{dep} is the depolarization electric field, which can appear at the interface between a ferroelectric thin film and the electrodes, due to poor screening of the charge at the interface and the existence of a polarization gradient. Assuming a potential ϕ due to the uncompensated charge at the interface, the depolarization field is then given by $E_{dep}=-\nabla\phi$. The Maxwell equation $\nabla D=0$ (with $D=\varepsilon_0E_{dep}+P$) gives rise to the constraint: $-\varepsilon_0\nabla^2\phi+\nabla P=0$. It is clear that a nonzero polarization gradient ∇P will result in the occurrence of a depolarization field in the ferroelectric. It is widely accepted that the depolarization field depends on the interface layer thickness (d_{int}), ferroelectric material/film thickness (d_{FE}) and is linear with the internal polarization of the ferroelectric,[25,38]

$$E_{dep} = -\frac{d_{int}D}{d_{FE}\varepsilon_0\varepsilon_{int}} = -\gamma D, \tag{8}$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$ C/V m; ε_{int} is the dielectric constant of the interface layer and the minus sign indicates that the depolarization field is opposed to the internal polarization of the ferroelectric; $\gamma = d_{int}/d_{FE}\varepsilon_0\varepsilon_{int}$ is a geometric depolarization factor expressed in units of volt meter per coulomb and can be significant for thin-film ferroelectrics where the thickness $d_{FE} < 1$ μm while for large thickness/bulk ferroelectrics the depolarizing field can be negligible; Using Eq. (8) we can rewrite relation (7) as

$$\frac{F_i}{V^*} = \frac{\alpha}{2}D_i^2 + \frac{\beta}{4}D_i^4 + \gamma D_i^2 - D_i E_{app}\cos(\theta). \tag{9}$$

The second-order coefficient in Eq. (9) is usually temperature dependent with a relationship of the form: $\alpha = \eta(T - T_c)$, where η is a positive constant, T is the temperature, and T_c is the Curie temperature. It results immediately that for ferroelectric phase ($T < T_c$), then $\alpha < 0$ and for paraelectric phase ($T > T_c$), then $\alpha > 0$. Depending on the discontinuity in the partial derivative of the free energy at the transition temperature, the phase transition from paraelectric to ferroelectric can be of first or second order. In this model we consider only second-order phase transition ferroelectrics, which implies that $\beta > 0$.[39] Assuming the system is in a ferroelectric state (i.e., $T < T_c$ and $\alpha < 0$), we now examine the free energy at zero applied electric field, which implies that $D_i = p_s$, where p_s is the spontaneous polarization.

Figure 1(A) shows the energy dependence on the polarization of a nucleation site at zero external applied electric field. This indicates only two possible stable energy states: 1 and 2 corresponding to polarization "up" and "down," respectively. Assuming the nucleation polar site has been poled in one of the two directions initially, before the E field has been removed, then in order to reverse the polarization from state 1 to state 2 the system must overcome a positive-energy barrier equal to the absolute value of the energy of the state 1, W_1. Similarly the reversal from state 2 to state 1 requires a minimum-energy barrier equal to the absolute value of the energy of state 2, W_2. From relation (9), imposing $E = 0$ and differentiating the free energy F in respect to p_s, we find that the minimum energy corresponds to a spontaneous polarization,

$$p_s^2 = -\frac{(\alpha + 2\gamma)}{\beta} \tag{10}$$

and the energy minima is derived as

$$F_{\min} = -\frac{(\alpha + 2\gamma)^2}{4\beta}V^*. \tag{11}$$

For the case $E = 0$, the two minima states have equal energies: $W_1 = W_2 = -(\alpha + 2\gamma)^2/4\beta$ and the energy barrier to overcome them is $W_B = (\alpha + 2\gamma)^2/4\beta$. The energy barrier is usually much larger than the thermal energy k_bT so that only over very long periods of time some reversal can occur thermally. However, we observe that the existence of a depolarizing field has the effect to lower the energy barrier ($\alpha < 0$ and $\gamma > 0$) as well as the spontaneous polarization p_s. Although not accounted for in this study, in real systems the energy barrier can also be lowered by other effects including crystal defects,[22,23] charge tunneling,[13] etc., and can also display a distribution of energies. However, when an electric field is applied, the energies of states 1 and 2 are substantially modified facilitating the reversal from one state to another. Figures 1(B) and 1(C) show the change in the energy states when an electric field is applied parallel or antiparallel to the polarization [i.e., $\theta = \pi$, $\cos(\theta) = -1$ or $\theta = 0$, $\cos(\theta) = 1$]. The resulting energy shift of states 1 and 2 due to the applied field is given to a good approximation by

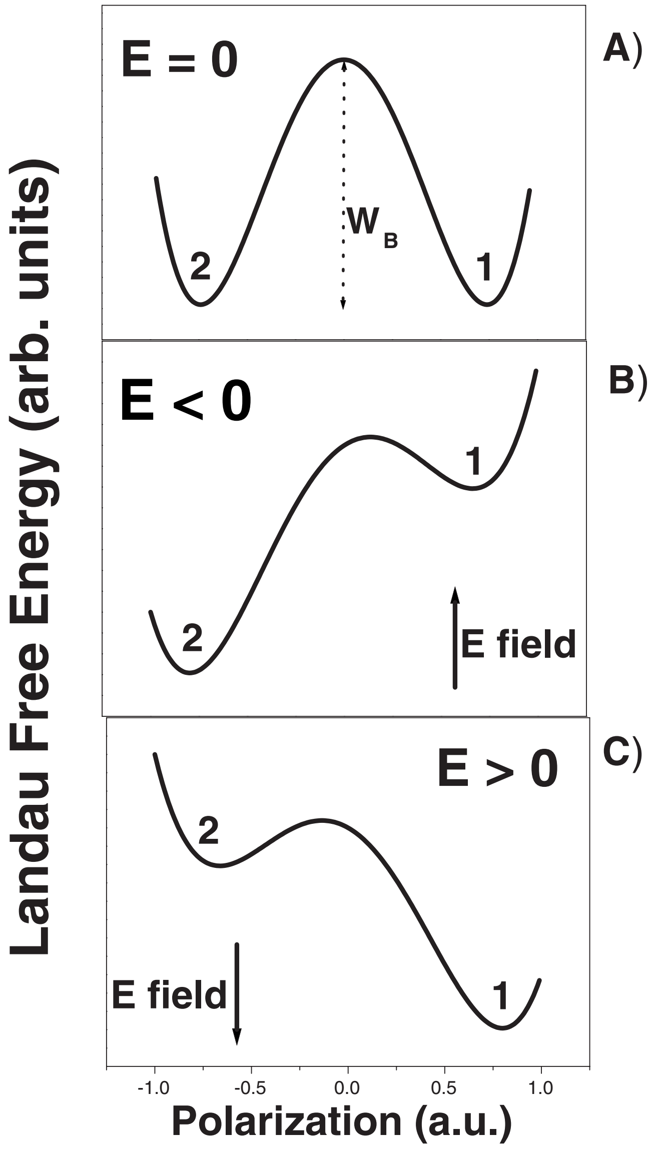

FIG. 1. Energy profile of a second-order transition ferroelectric as a function of the polarization at different applied electric fields: (A) $E = 0$; (B) E negative; and (C) E positive.

$$W_{1,2} = (-W_B \mp p_s E_{app}) \cdot V^*. \tag{12}$$

Since transitions between the two states are physically permitted on a continuous basis, the nucleation site is fundamentally a nonequilibrium two state system so that the occupation probabilities P_1 and P_2 of states 1 and 2 are also time dependent (throughout the paper capital "P" refers to occupation probability and lower case "p" refers to electric polarization). The time evolution of the probabilities when a nonequilibrium system goes through different possible states are described by the general Pauli master equation[40]

$$\frac{dP_l}{dt} = \sum_{m \neq l} [a_{l,m} P_m(t) - a_{m,l} P_l(t)], \tag{13}$$

where $1 \leq l, m \leq \Omega$ with l and m taking integer values and Ω is the number of possible states of the system (or the number of microstates compatible with the macrostate); $P_l(t)$ and $P_m(t)$ are the probabilities that the system is in the state l or m at the time t, respectively; $a_{l,m}$ and $a_{m,l}$ are the transition rates per unit time from the state m to state l and vice versa, respectively; the transition probability from state l to state m during the time interval $t \rightarrow t+dt$ is then for $m \neq l$,

$$P_{m,l}(t) = a_{m,l} \cdot dt \tag{14}$$

and the probability that the system is in state l during the time interval $t \rightarrow t+dt$ is

$$P_{l,l}(t) = 1 + a_{l,l} \cdot dt. \tag{15}$$

Applying the normalization condition,

$$\sum_m P_{m,l}(t) = 1, \tag{16}$$

which using relations (14) and (15) can also be expressed as

$$\sum_m P_{m,l}(t) = P_{l,l} + \sum_{m \neq l} P_{m,l} = 1 + a_{l,l}dt + \sum_{m \neq l} a_{m,l}dt = 1. \tag{17}$$

From Eq. (17) a relationship between the transition rates per unit time results

$$a_{l,l} = -\sum_{m \neq l} a_{m,l}. \tag{18}$$

Furthermore, for a system in contact with a temperature reservoir (i.e., canonical ensemble), the pseudosymmetry relation between the transition rates at equilibrium states is derived as

$$a_{l,m} e^{-(W_m/k_bT)} = a_{m,l} e^{-(W_l/k_bT)} = \upsilon_0, \tag{19}$$

where W_m and W_l are the energies in the state m and l, respectively, k_bT is the thermal energy, and ν_0 is a constant equal to the total number of trials per second to overcome the energy barrier. In our case this is taken as 10^{13} Hz, which is the frequency of the optical phonons in the crystal.[25] We now particularize the master equation for $\Omega=2$ (i.e., a two-state system as described in Fig. 1). For $l, m=1,2$ and using relations (18) and (19), the master Eq. (13) becomes a system of two differential equations,

$$\begin{cases} \dfrac{dP_1}{dt} = a_{1,1}P_1 + a_{1,2}P_2 = \upsilon_0(-P_1 e^{(W_1/k_bT)} + P_2 e^{(W_2/k_bT)}) \\ \dfrac{dP_2}{dt} = a_{2,1}P_1 + a_{2,2}P_2 = \upsilon_0(P_1 e^{(W_1/k_bT)} - P_2 e^{(W_2/k_bT)}). \end{cases} \tag{20}$$

Solving Eq. (20) for constant E we obtain the following time-dependent probabilities:

$$P_1(t) = C_1 + C_2 \cdot e^{-(t/t_{sw})} \tag{21}$$

$$P_2(t) = C_1 \cdot e^{(W_1 - W_2)/k_bT} - C_2 e^{-(t/t_{sw})}, \tag{22}$$

where C_1 and C_2 are constants to be determined, $W_1 - W_2 = -2p_sE_{app}V^*$, and t_{sw} is the relaxation time of the system,

$$t_{sw}^{-1} = \upsilon_0 \cdot (e^{(W_1/k_bT)} + e^{(W_2/k_bT)}) = \upsilon_0 \cdot (e^{-[(W_B - p_sE_{app})/k_bT] \cdot V^*} + e^{-[(W_B + p_sE_{app})/k_bT] \cdot V^*}). \tag{23}$$

This represents the characteristic response time of the system to an external perturbation (i.e., applied field, temperature change, etc.) or, in our case, the polarization switching time. More details and discussion on the switching time are given in Sec. IV.

Constants C_1 and C_2 can be determined from the initial and final conditions in conjunction with the normalization condition. Hence, imposing $t=0$ (initial condition), then relation (21) becomes

$$P_1(0) = C_1 + C_2. \tag{24}$$

Imposing $t \rightarrow \infty$ where the system tends to equilibrium, relations (21) and (22) become

$$P_1(\infty) = P_{eq}^1 = C_1, \tag{25}$$

$$P_2(\infty) = P_{eq}^2 = C_1 \cdot e^{(W_1 - W_2)/k_bT}. \tag{26}$$

However, from the normalization condition we have: $P_1(\infty) + P_2(\infty) = 1$, which combined with relations (24)–(26) results

$$C_1 = P_{eq}^1 = (1 + e^{(W_1 - W_2)/k_bT})^{-1}, \tag{27}$$

$$C_2 = P_1(0) - C_1 = P_1(0) - P_{eq}^1. \tag{28}$$

Having the two constants determined, the occupation probabilities [Eqs. (21) and (22)] can be written as

$$P_1(t) = P_1(0) \cdot e^{-(t/t_{sw})} + P_{eq}^1 \cdot (1 - e^{-(t/t_{sw})}), \tag{29}$$

$$P_2(t) = (1 - P_{eq}^1) + [P_{eq}^1 - P_1(0)] \cdot e^{-(t/t_{sw})}. \tag{30}$$

As seen from relations (29) and (30), in order to determine the occupation probabilities for the states 1 and 2, one needs to have a precise knowledge of the initial occupation probability of the state 1 at $t=0$, $P_1(0)$. The initial conditions of the system depend in turn on the history of the experiment (hysteretic character of ferroelectrics). Therefore, a comparison between the polarization dynamics of the same system during different experiments is relevant only if the system has been reset back to the same initial conditions before each experiment. In this work we assume, for example, that the sample has been initially poled fully into state 1 by the application of a large electric field so that $P_1(0)=1$. Using the imposed initial state $P_1(0)=1$, relations (29) and (30) become

$$P_1(t) = e^{-(t/t_{sw})} + P^1_{eq} \cdot (1 - e^{-(t/t_{sw})}), \tag{31}$$

$$P_2(t) = (1 - P^1_{eq}) \cdot (1 - e^{-(t/t_{sw})}) \tag{32}$$

and they give a full temporal description of the occupation probability of the two possible states of a nucleation site. For N elementary polar sites, we define $N_1(t)=P_1(t)\times N$ as the number of sites in state 1 at time t and $N_2(t)=P_2(t)\cdot N$ the number of sites in state 2 at time t, with $N=N_1+N_2$.

III. POLARIZATION SWITCHING

We examine the case when the applied field is $E_{app}=0$. From Sec. II, this results in $W_1-W_2=0$. From Eq. (27) we notice that the equilibrium probability at $t\rightarrow\infty$ is $P^1_{eq}=0.5$. Applying the normalization condition we obtain $P^2_{eq}=P^1_{eq}=0.5$. This implies that at equilibrium, the two energy states are equally probable. This is equivalent to saying that a ferroelectric system at a sufficiently large temperature in zero applied field under the action of depolarizing field and over a very long period of time will depolarize spontaneously.

The nucleation process is assumed to occur fast and simultaneously in all the elementary polar sites. Also relations (31) and (32) describe the state of each polar nucleation site at time t. We also assume that the sample has been initially poled so that all polar sites are reversed into state 1, $P_1(0)=1$, which results in $N=N_1(0)$ and $N_2(0)=0$. In order to reverse the polarization into state 2, we now apply instantaneously a constant electric field E_{app}. Over a period of time t, the total amount of polarization (electric displacement) switched from state 1 into state 2 is equal to

$$\Delta D(t) = 2p_s \cdot N_2(t)/N = 2p_s \cdot P_2(t) = 2p_s \cdot [1 - P_1(t)], \tag{33}$$

where p_s the spontaneous polarization. Using relation (31), the time-dependent expression for the switched polarization/electric displacement is obtained,

$$\Delta D(t) = 2p_s \cdot (1 - e^{-(t/t_{sw})}) \cdot (1 - P^1_{eq}). \tag{34}$$

Consequently, the associated transient switching current is derived as

$$I_{sw}(t) = \frac{d\Delta D(t)}{dt} = \frac{2p_s}{t_{sw}} \cdot (1 - P^1_{eq}) \cdot e^{-(t/t_{sw})}, \tag{35}$$

where P^1_{eq} is given in relation (27) and depends only on the strength of the applied E_{app} field, its orientation [i.e., $\cos(\theta)$], temperature, and depolarization field via p_s.

Relations (34) and (35) are in good agreement with those derived in the KAI model [see relations (1) and (2)] when the Avrami exponent is $n=1$. This corresponds to one-step nucleation and the formation of 1D stripe domains in the KAI model. However, the expressions derived in our model contain explicit dependence of the applied electric field and temperature via the P^1_{eq} and the switching time t_{sw}. Moreover, our relations, in comparison to those derived in the KAI model, contain the factor $(1-P^1_{eq})$, which can take positive real values from 0 to 1. This accounts for the amount of reversed polarization, which can be 0 if $P^1_{eq}=1$ and $2p_s$ if $P^1_{eq}=0$. Fractional values $2p_s(1-P^1_{eq})$, are obtain for $P^1_{eq}\neq 0$ or 1, which accounts for the fact that at equilibrium not all the polar sites are necessarily reversed. For comparison, a zero and nonzero depolarizing field has been assumed in numerical simulations. Without depolarization field, an energy barrier of 0.99 eV (1.58×10^{-19} J) for zero applied field results at room temperature and a spontaneous polarization of 0.74 C/m^2. In order to estimate a typical depolarizing field the following parameters have been used: interface layer thickness $d_{int}=1$ nm, ferroelectric thickness $d_{FE}=250$ nm and the dielectric constant of the interface layer $\varepsilon_{int}=100$, resulting in a depolarizing factor $\gamma=4.5\times10^6$ Vm/C, an energy barrier of 0.84 eV (1.34×10^{-19} J) and a spontaneous polarization $p_s=0.71$ C/m^2. This in turn results in a maximum depolarizing field of $E_{dep}=32$ kV/cm, which is indeed rather significant. For all calculations the energy barrier has been kept constant with the shifts in the energy resulting only from the applied electric field, as schematically represented in Fig. 1.

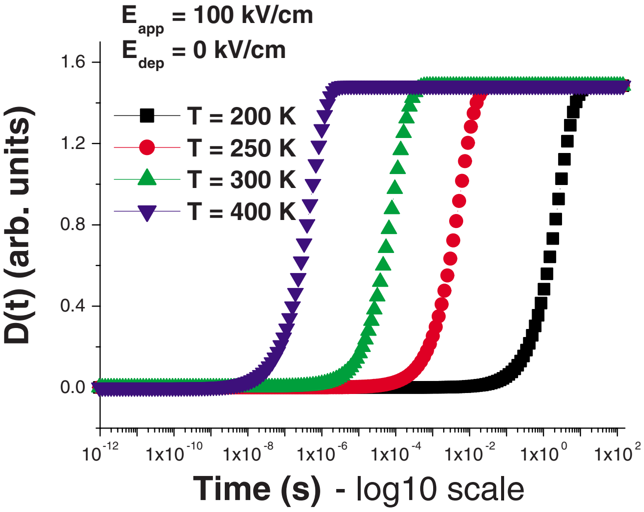

FIG. 2. (Color online) Time dependence of the reversed polarization at $E=100$ kV/cm for different temperatures with zero depolarizing field. We performed the numerical simulations using the following set of parameters: $\alpha=-11.57\times10^7$ Vm/C; $\beta=2.1\times10^8$ Vm^5/C^3; $k_b=8.61\times10^{-5}$ eV/K (or 1.38×10^{-23} J/K); and $V^*=10^{-26}$ m^3.

Figure 2 shows the time dependence of the switched polarization for four different temperatures for an applied electric field of 100 kV/cm and no depolarizing field ($\gamma\cdot p_s \ll E_{app}$). The data indicate a faster polarization reversal at higher temperatures. Figure 3 shows the same parameter plotted as a function of time for four different applied electric fields at a constant temperature of 300 K and no depolarizing field. All numerical results were obtained from Eq. (34) and they indicate that the dominant parameter in the polarization switching is the strength of the applied electric field with an additional large contribution to the switching

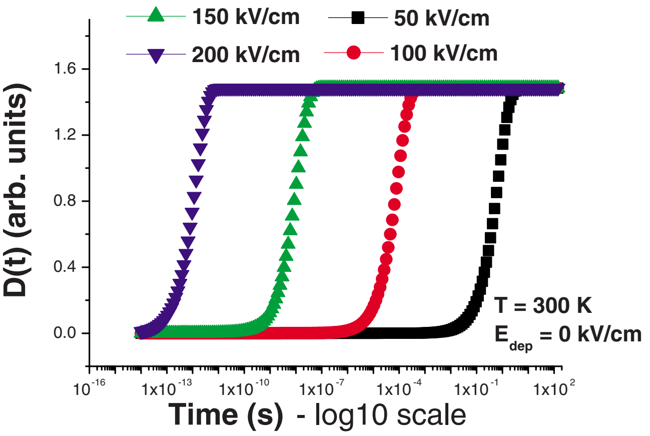

FIG. 3. (Color online) Time dependence of the reversed polarization at room temperature for different applied E fields and zero depolarization field.

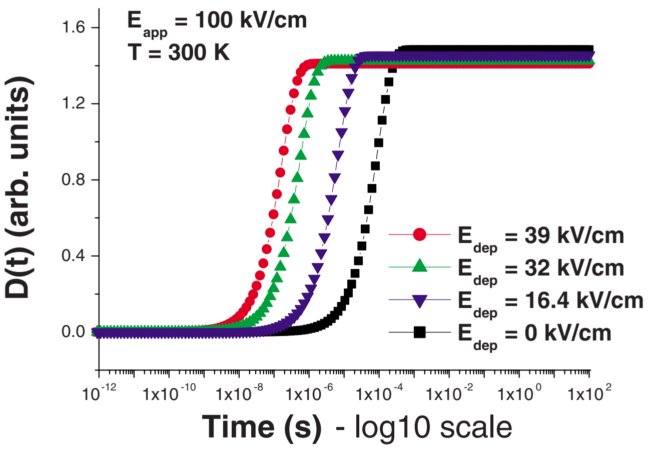

FIG. 4. (Color online) Time dependence of the reversed polarization at room temperature and 100 kV/cm applied field at different depolarizing E_{dep} fields.

dynamics from the thermal energy. Although in this study the numerical results are not absolute and they are intended only for guidance, these finding are very important as they suggest a substantial thermal dependence of the switching time, which should be carefully considered in the design, operation, and stability considerations of memory devices based on ferroelectrics. The depolarization field effect on the switching behavior has also been considered. Table I shows the values of the depolarization field, energy barrier and spontaneous polarization for bulk, and three different ferroelectric films, assuming each film has the same interface layer thickness.

As expected, the depolarization field lowers the energy barrier, which helps in turn the reversal process. However, the depolarization field also lowers the spontaneous polarization, which is not desirable. This is very well depicted in Fig. 4, which shows the time-dependent polarization reversal calculated at room temperature under an applied field of 100 kV/cm with and without depolarization fields. It is clear that bulk ferroelectric reverses at much longer switching time than the thin films. Larger depolarization field promotes faster reversal.

Our model is capable of reproducing with reasonable accuracy shapes of the polarization switching curves reported experimentally. In terms of the transient switching current, at the initial stage of reversal the current is a maximum and decays exponentially with time.

This resembles the KAI model for the particular case $n=1$. It is well known that values $n>1$ (including fractional values) have been reported when fitting experimental data using the KAI model or variants of it. For values of $n>1$ the transient switching current takes on a Gaussian (bell shaped) profile. In the KAI model n represents a dimensionality of reversed domains and nucleation mechanism.

The present model has nothing to do with such matters and too much emphasis should be put on the value of n. The reason why our model resembles the $n=1$ case is that we assume the pre-existence of the elementary nucleation polar sites in the ferroelectric system at any time t. Therefore, when an external electric field is applied instantaneously, the rate of change in the polarization is a maximum at the initial stage, resulting in a maximum switching current that decays exponentially with time. In order to get the Gaussian bell shape of the switching current, there must be a temporal evolution of the nucleation sites, which provides a delayed response in the switching. This could be built into the model presented here as a further development of it, which is beyond the scope of this paper. Within the limits of the system described in this paper, we were able to demonstrate the temperature, time, E_{app} field, and E_{dep} field dependence of the polarization switching process. This is based on quantified and documented physical quantities rather than fit to the experimental data.

IV. SWITCHING TIME, t_{sw}

The switching time is directly provided by relation (23) and includes explicit dependence on the temperature and ap-

TABLE I. Maximum depolarization fields, energy barriers, and spontaneous polarization for bulk ferroelectric and there different thin-film ferroelectrics calculated using $d_{int}=1$ nm, $\varepsilon_{int}=100$, and $\varepsilon_0=8.85\times10^{-12}$ C/V m.

Ferroelectric thickness d_{FE} (nm)	Depolarization field E_{dep} (kV/cm)	Energy barrier W_B (eV)	Spontaneous polarization p_s (C/m^2)
>500 (bulk)	0	0.99	0.74
500	16.4	0.91	0.72
250	32	0.84	0.71
200	39	0.81	0.7

plied electric field. This relation can be used to fit experimental data in future studies or to directly calculate the switching time for a given temperature, applied electric field, energy barrier, and critical volume. Another option to determine the switching time, mostly implemented in the experimental studies, is to determine the switching time from the transient switching current [Eq. (35)], as the time taken for the current to decrease to 5% of its maximum value. Numerical results indicate that the second exponential term of relation (23) is much smaller than the first term and can be ignored (for example, $e^{-35} \approx 10^{-15}$), especially for larger energy barriers. Hence, for $E_{app} \neq 0$, the general expression of the switching time can then be written as

$$t_{sw} \cong \frac{1}{\upsilon_0} \cdot e^{[(W_B - p_s E_{app})/k_b T] \cdot V^*}, \tag{36}$$

which is function of the energy barrier, applied electric field, and temperature. According to this model, theoretically switching can occur even for zero applied field under the action of the thermal energy and depolarization fields. For the case $E_{app}=0$, the switching time is only function of the energy barrier and the temperature,

$$t_{sw} \cong \frac{1}{2\upsilon_0} \cdot e^{(W_B/k_b T) \cdot V^*}. \tag{37}$$

Although in this study a simple expression of the energy barrier is derived from a Landau-type free energy and the addition of the depolarization field, relations derived for polarization switching, switching time, and transient switching current have a general validity for any type of energy barrier. Therefore, a more detailed analysis can be easily implemented using our formalism by including in the energy expression the effect of crystal defects, domain-wall energy, etc. Since there are numerous types of defects, for example, a more realistic representation of the system could be obtained by considering a distribution of the energy barrier for nucleation.

According to relations (23), (36), and (37), such a distribution would be translated into a distribution of the switching times for different elementary regions due to the effect of the local variations in the crystal.[41] A similar effect would be the result of a distribution of the size/volume of the elementary polar sites. Tagantsev *et al.*[23] have successfully introduced these ideas in their nucleation limited switching model and later used by Jo *et al.*[22] to explain the experimental switching behavior of PZT thin films at various temperatures and applied fields.

Similarly to Tagantsev's work, they found that a Lorentzian distribution of the logarithmic domain switching times could successfully explain a broad range of experimental polarization switching data. A possible explanation of the Lorentzian distribution of the logarithmic switching times was the local-field variations due to the dipole defects at domain pinning sites.[22]

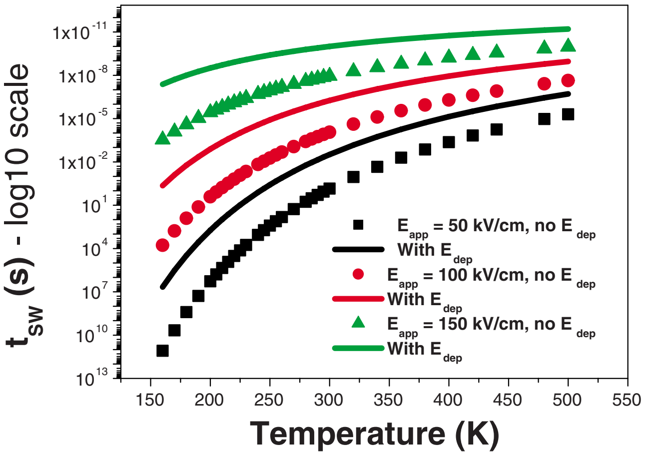

FIG. 5. (Color online) Switching time dependence on the temperature at different applied fields. Dotted line represents switching time with no depolarizing field and the continue line shows the effect of the depolarizing field at p_s.

Figure 5 shows the switching time dependence on the temperature for three different applied electric fields with and without depolarization fields, as given by relation (23). Although this has an exponential variation, we have represented the data using logarithmic scales for better illustration. The data show that at the same arbitrary temperature (i.e., 300 K), the polarization can reverse in 10 ns for 150 kV/cm or 1 ms for 100 kV/cm applied electric field (10^6 times slower reversal from a 30% reduction in the applied electric field). For fields of around 50 kV/cm the switching time is extremely long suggesting that the applied field is probably below the coercive field, $E_{app} < E_c$. The dotted curves represent the switching time with no depolarization and the continue lines represent the switching time when a depolarization field is included in the calculation. Once again, just as indicated in Fig. 4, a depolarization field has the effect of lowering the polarization switching time. Although not explicitly introduced in the equations, it is important to mention that all calculations are performed assuming temperatures below the Curie temperature. Figure 6 shows the switching time variation with the applied electric field for three different temperatures without depolarizing field. It can be seen again that, for example, at a fixed applied electric field of 100 kV/cm, the effect of the temperature is rather

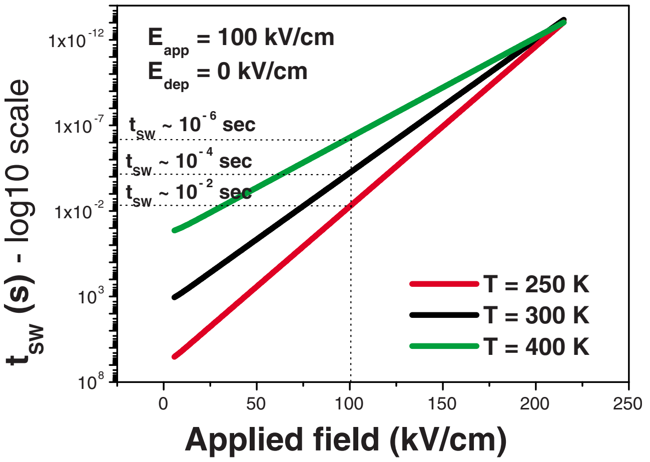

FIG. 6. (Color online) Switching time dependence on the applied field at different temperatures without depolarization field.

substantial. At higher temperatures the reversal time is much faster, as the increased thermal energy makes the exponential term $(W_{1,2}/k_bT)$ lower (the transition rates over the barrier are more probable). For example, the switching at 400 K occurs in 1 μs while at room temperature it occurs in 100 μs (10^2 times slower reversal for a 25% reduction in temperature). On lowering further the temperature, for the same applied field, the switching time increases substantially.

V. COERCIVE FIELD, E_c

One important experimental observation is the variation in the coercive force with the measurement time and temperature. For example, the thermal *P*-*E* loop measurements showed an increase in the coercive field when the measurement temperature decreases.[13,34] Similar coercive field variations have been reported for different measurement frequencies, most notable Merz has determined experimentally that the coercive field increases with the measurement frequency[9] and Viehland and Chen[42] reported more recently similar results.

Our polarization switching model can be used to derive an analytical description of the coercive field of ferroelectrics and its simultaneously dependence on the measurement temperature and time. We start by assuming that the sample has been poled at time $t=0$ into state 1 (positive polarization), as described in Sec. II. An arbitrary constant negative *E* field is applied to the sample, opposite to the polarization direction. The field will induce the nucleation and switching of elementary sites into state 2 (negative polarization). Under the action of the negative field, in time, enough sites will switch into state 2 so that the total net polarization of the sample is zero. This implies that the depolarization field is also zero, as the internal polarization is zero. Zero polarization is achieved at the coercive field (E_c). Within the framework of our model, at the coercive field the occupation probabilities of the two possible states are equal: $P_1(t)=P_2(t)$ at E_c. Since $P_1(t)+P_2(t)=1$, it results that $P_1(t)=0.5$. Using expression (31) and the condition $P_1(t)=0.5$, we determine that

$$\frac{t}{t_{sw}} = \ln\left[\frac{2(1-P_{eq}^1)}{(1-2P_{eq}^1)}\right]. \tag{38}$$

Using the expression of the switching time [Eq. (36)] in logarithmic form we obtain

$$\ln(t_{sw}\upsilon_0) = \frac{(W_B - p_s E_{app})\cdot V^*}{k_b T}. \tag{39}$$

Combining Eq. (38) with Eq. (39) and accounting for the fact that Eq. (38) is valid at the coercive field, after some algebraic rearranging the following expression for the coercive field is obtained:

$$E_c(t,T) = \frac{W_B}{p_s} - \frac{k_b T}{V^* p_s}\cdot \ln\left\{\upsilon_o t \cdot \ln\left[\frac{2(1-P_{eq}^1)}{(1-2P_{eq}^1)}\right]^{-1}\right\}. \tag{40}$$

For large enough applied fields we numerically determined that $P_{eq}^1 \ll 1$, so it can be approximated to zero. Equation (38) becomes

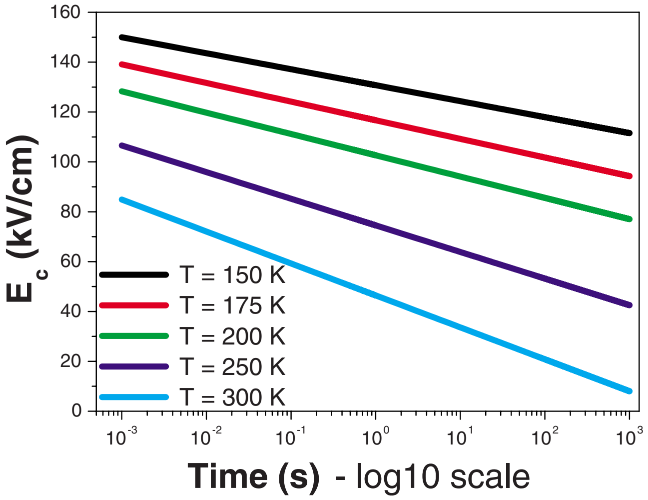

FIG. 7. (Color online) Time-dependent coercive field for different temperatures.

$$\frac{t}{t_{sw}} \cong \ln(2) \tag{41}$$

and the coercive field [Eq. (40)] can be written in a simplified form

$$E_c(t,T) \cong \frac{W_B}{p_s} - \frac{k_b T}{V^* p_s}\cdot \ln\left(\frac{\upsilon_o t}{\ln(2)}\right). \tag{42}$$

V^* is the volume of the elementary nucleation site, which is taken as 10^{-26} m^3 in this calculation example. Equation (42) can be used to study time and thermal dependence of the coercive field in ferroelectric materials. This is applicable only for temperatures below the Curie's temperature ($T < T_c$). In terms of the time/frequency range applicability, Eq. (42) has no lower time limit but the maximum measurement time (frequency) is given by the condition that E_c does not change sign. From Eq. (42) the upper time limit is determined as

$$t \le \frac{\ln(2)}{\upsilon_o} e^{(W_B V^*/k_b T)}. \tag{43}$$

Figure 7 shows the time dependence of the coercive field at different temperatures, when the time varied from 10^{-3} to 10^3 s (frequency of 1 kHz to 1 mHz). The data show a consistent decrease in the E_c when the measurement time increases (i.e., faster measurement results in larger E_c) and a reduction in the E_c at higher temperatures. For example, at room temperature the coercive field calculated at 1 kHz is 71.5 kV/cm. When calculated at the same temperature but for a measurement time of 5 s the coercive field becomes 37.5 kV/cm. This is a 48% reduction in the coercive field when the measurement time changes from 1 ms to 5 s. The numerical result is in good agreement with experimental studies published by Viehland and Chen.[42] They showed experimentally that the *P*-*E* loops of $0.7\text{Pb}(\text{Mb}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.3\text{PbTiO}_3$ ceramics display at room temperature no frequency relaxation in the remanent polarization but a strong relaxation in the coercive field.

A reduction of 33% in the coercive field was experimentally observed when the measurement time was increased from 100 ms to 100 s. In a different experimental study, Jian *et al.*[13] have published the coercive voltage of PZT thin films from *P*-*E* loops measurements at various temperatures and 1 kHz frequency. For example, their *P*-*E* measurement of 300-nm-thick PZT film deposited on a 6-nm-thick Al_2O_3 buffer layer indicates that the coercive field measured at 200 K is reduced by about 32% when the temperature increases to 320 K. Our theoretical prediction estimates at 1 kHz a reduction in the coercive field by 33% when the temperature increases from 200 to 300 K, which again shows a reasonable good agreement to experimental data. However, the comparison between our theoretical estimations and the experimental data is intended for guidance only, as the main objective is to support some of the trends and theoretical predictions with published experimental data. The real importance of our findings is the fact that these time/thermal effects can be modeled using our formulas when designing real systems and devices. In particular, this study can support the design of FRAM devices[43] as the temperature and the frequency of the "write" operation has a substantial effect on the coercive field and therefore on the voltage required to produce switching.

VI. CONCLUSIONS

Despite intensive studies of ferroelectrics, the theoretical models of polarization switching are not fully complete or generally applicable. The main limitation of the KAI domain nucleation switching model is the fact that it does not yield a thermal dependence of the switching time. Moreover, the switching time has no direct dependence of the applied electric field. The experimental evidence shows that both of these external parameters are strongly influencing the reversal mechanism. However, most of the relations linking the total switching time to the electric field are based on empirical/phenomenological studies. In this paper we introduced an electric polarization reversal model for second-order phase transition ferroelectrics, which is based on the nonequilibrium statistics of the domain nucleation process. This approach makes similar assumptions to the "nucleation limited switching" model introduced by Tagantsev *et al.*[23] and the "random-field model" published by Viehland and Chen[42] in which "clusters" with reversed polarization within ferroelectric domains are nucleated under the action of applied electric field and random fields around defects. In order to assess the predictions of our model we have numerically calculated the thermal effect, the electrical applied field effect, and the depolarization field effect on the reversal dynamics. As expected, this study shows that the switching process is dominated by the externally applied electric field but it is also very susceptible to thermal effects. Depolarization field can also play an important role in the reversal process, especially in the case of thin-film ferroelectrics. The depolarization field has the effect of lowering the switching time as well as the spontaneous polarization. An analytical relation for the switching time that explains both the thermal and electric field dependence of the polarization switching has been derived. We also derived the analytical relations for the time dependence of the total switched polarization and the associated transient current. Finally an analytical expression showing the relationship between the measurement time and temperature to the coercive field of ferroelectrics has been derived. As expected in the case of ferroic materials, our relation is similar to Sharrock's formula[44,45] that describes the time-dependent coercive field of ferromagnetic materials. In good agreement with the previously published experimental data, we showed that the coercive field decreases at longer experimental times and higher temperatures. Equations derived in this work can be further developed or used in studies of polarization dynamics, time, and temperature-dependent *P*-*E* loops or fatigue[46] and aging effects of ferroelectrics.

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