Non-Kolmogorov-Avrami switching kinetics in ferroelectric thin films

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The switching kinetics in ferroelectric thin films has been intensively studied during the past decade. It is widely accepted that this kinetics is basically governed by the dynamics of domain coalescence (the Kolmogorov-Avrami-Ishibashi model). This conclusion is mainly supported by fitting the time dependence of the switching currents to that predicted by this model, the fit being typically performed in a 1–2 decade interval of time. The present paper reports on a study of the switching kinetics in modified $Pt/Pb(Zr,Ti)O_3/Pt$ thin films as a function of time and applied voltage, performed in time intervals from 10 ns to 1s. Our experimental data show that both the time and applied field dependences of the switching polarization (when monitored over a wide enough time interval) are in a strong qualitative disagreement with the predictions of the Kolmogorov-Avrami-Ishibashi approach. For the interpretation of our result, an alternative approach is forwarded. In contrast to Kolmogorov-Avrami-Ishibashi approach, we assume that the film consists of many areas, which have independent switching dynamics. The switching in an area is considered to be triggered by an act of the reverse domain nucleation. The switching kinetics is described in terms of the distribution function of the nucleation probabilities in these areas. The developed approach enables a good description of the polarization dynamics in typical ferroelectric thin films for memory applications.

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I. INTRODUCTION

Switching of polarization domains in ferroelectric materials has been intensively studied since the 1950's both theoretically and experimentally, in view of numerous applications. In particular, considerable progress has been achieved in understanding the polarization reversal kinetics in ferroelectric crystals. The commonly accepted approach to modeling the switching kinetics in ferroelectrics employs the model developed by the group of Ishibashi[1] based on the classical results by Kolmogorov[2] and Avrami.[3] A substantial contribution to the development of this approach was made by the group of Shur.[4–6] This approach, which enables a correct description of switching kinetics in ferroelectric bulk materials, has been also applied to a description of switching in ferroelectric thin films.[6,7] However, as was recently shown by the group of Waser, in the case of ferroelectric thin films, the application of this approach is limited especially in the case where the switching kinetics is monitored over a wide interval of switching times.[8] Based on the observation of the Curie–von Schweidler behavior of the switching current response, the authors in Ref. 8 concluded that the switching kinetics in thin films could not be explained by the classical theory of nucleation and growth of reversed domains. They suggested by that it is not the domain walls and their motion that are decisive for the polarization switching but rather other polarization processes with a broad distribution of relaxation times.

In the present paper we show that an adequate explanation of the polarization reversal in thin films can be obtained within the traditional approach involving an analysis of the domain nucleation and growth. We will demonstrate that within this approach an alternative switching kinetics, which is qualitatively different from that stemming from the Kolmogorov-Avrami-Ishibashi model, is possible. The principle difference between our model and that by Kolmogorov-Avrami-Ishibashi is that the former is focused on the statistics of nucleation whereas the latter focuses on the statistics of domain coalescence. We test our model by using it for a description of switching dynamics in an 8-decade interval of switching times in $Pt/Pb(Zr,Ti)O_3/Pt$ thin films.

II. EXPERIMENTAL

For this study we used PZT films of (111)-orientation grown on Pt (111) bottom electrode by chemical solution deposition. The films with Zr/Ti ratio of 40/60 contained dopants including Ca, Sr, and La as described in Ref. 9. The thickness of PZT films was 135 nm. 15 by 15 μm IrO_x top electrodes were patterned by photoreactive ion etching. For measurements of the switched polarization as a function of the applied voltage and time of exposure we employed a pulse switching method using an electrical circuit similar to that described in Ref. 10. The pulses with rise times of 10 ns and widths ranging from 10 ns to 0.5 s we produced using an HP33250A function generator. The voltage drop across the ferroelectric capacitor and the current associated with the switched polarization was detected using a 1GHz LC 564A oscilloscope equipped with an active probe with 1 GHz bandwidth. The 15 by 15 μm capacitors were found to be small enough to allow for accurate square pulses with 10 ns rise time. The shape of switching current response was virtually unchanged as we tested capacitors with size ranging from 5 by 5 to 15 by 15 μm, showing that our results are not affected by RC parameters of the measuring circuit. The charge associated with the switched polarization in a ferro-

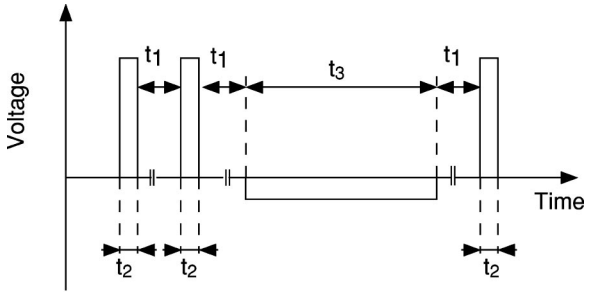

FIG. 1. Sequence of voltage pulses used for measurements of the switching polarization.

electric capacitor can be studied as a function of switching voltage and time in several different ways. One possibility is to apply to the capacitor the pulses of different amplitudes and to measure directly the corresponding switching current.[11] The drawback of this method is that in the case of very long switching times, e.g., within ms range the switching current amplitude at the tail of switching curve is far too low to be measured. An alternative method involves a two-step procedure including a polarization reversal by a pulse of given amplitude and width followed by a subsequent measurement of the switched polarization using a short pulse of high amplitude.[12] We used the latter method since, in our opinion, it provides much better accuracy than the former. The pulse sequence used for our measurements (similar to that presented in Ref. 12) consisted of four voltage pulses separated by equal time intervals $t_1=1$ s (Fig. 1). Pulse numbers 1, 2, and 4 had a fixed amplitude of 5V and a duration of $t_2=50$ ns. Duration of pulse 3, t_3, ranged from 10 ns to 0.5 s, for voltage amplitudes of 0.6, 0.9, 1.35, 2.2, 3, and 5 V. The role of pulse 1 was to define the polarization state of the film. Since pulse 2 had the same polarity as pulse 1, the current response corresponding to pulse 2 determined the nonswitching polarization. Pulse 3 switched polarization partially or completely depending on its amplitude and width; pulse 4 measured the polarization switched by pulse 3. Figure 2 shows ''switching curves'' measured this way. In this figure, values of the switched polarization have been plotted as a function of the switching time (duration of pulse 3) for amplitudes of pulse 3 ranging from 0.6 V to 5 V. Overall, Fig. 2 shows a switching behavior characterized by a broad variation of switching times, similar to the results reported in Ref. 8. Specifically, at 5 V our ferroelectric capacitor switched completely during a time interval shorter than 10 ns (this is comparable to the switching data from Ref. 7), whereas for an applied voltage of 1.5 V, the complete switching of the capacitor took as long as 0.5 s.

III. MODEL FOR SWITCHING KINETICS

The traditional approach to the interpretation of the switching kinetics in ferroelectrics[1,4–6] based on the classical result by Kolmogorov[2] and Avrami[3] is often called the Kolmogorov-Avrami-Ishibashi (KAI) model. The basic idea of this model is that ferroelectric domains, which have been initiated from independent nucleation centers, unrestrictedly grow under the action of the applied electric field. At the

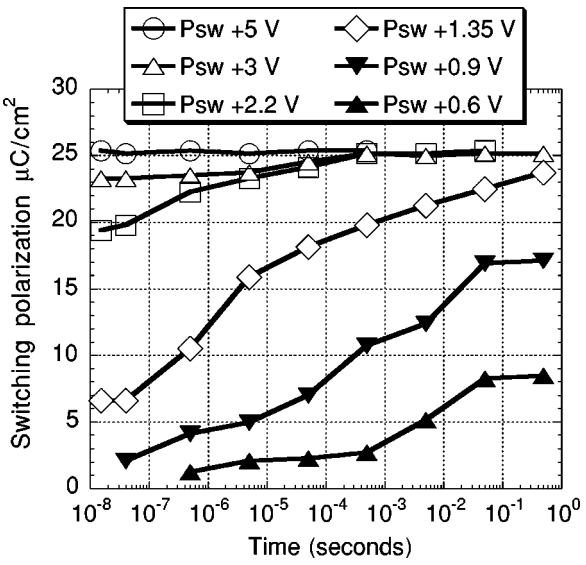

FIG. 2. Switching polarization as a function of switching time, for different voltages, measured on a capacitor containing 135 nm thick PZT film.

early stages of switching, the appeared domains grow without overlapping, so that the volume where the polarization is reversed can be found as the sum of those of the individual domains. However, when domain overlapping occurs, this sum ceases to yield the switched volume and the problem requires an additional mathematical treatment. A general mathematical treatment of this problem was offered by Kolmogorov[2] and Avrami.[3] For the case of ferroelectric switching the obtained result can be presented in the form[1]

$$p(t)=1-e^{-(t/t_0)^n}, \tag{1}$$

where $p(t)$ is the fraction of the volume of the ferroelectric switched by time t, the parameters t_0 and n depend on the density of the nucleus of reversed domains, mobility of the domain walls, the electric field acting on the moving domain walls E, and the dimension of the domain growth. In the simplest version of the theory n is just the dimension of the domain growth, which for thin films can be taken as about 2 and t_0 is a decreasing function of E. This approach [Eq. (1) or results of a modified version of the model[6]], when applied to the case of ferroelectric thin films, was found to provide a good description for the time dependence of the switching currents typically in a 1–2 decade interval of time.[6] However, this approach fails when one addresses the switching kinetics of ferroelectric thin films monitored in a broad time interval (as we report and was reported in Ref. 8). This is clear from the comparison of Fig. 2 with Fig. 3 where we plot Eq. (1) for $n=2$ and two different values of t_0 corresponding to two different values of the applied voltage. Indeed, the result of modeling contradicts the main features of the experimental result. First, the theory does not reproduce the logarithmically slow increase of $p(t)$. Second, in theory, a variation of the field leading to a change of t_0 does not change the semilogarithmic slope of the curve; contrary to the experimental observations, it just shifts the curve along the log-time axes. The drastic difference between the predic-

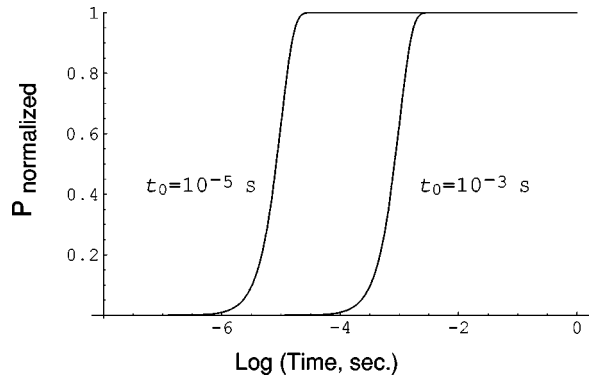

FIG. 3. Prediction by the Komlogorov-Avraami-Ishbashi model: fraction of switched polarization normalized to its maximal value as a function of time, for different values of parameter t_0 according to Eq. (1) with $n=2$.

tions of the KAI model and our experimental data suggests that the polarization switching when treated in an exponentially wide time interval is inconsistent with the domain-overlapping KAI model. In this paper we propose an alternative model that enables a consistent description of the reported switching kinetics.

In our model we do not use the basic assumption of the KAI model that once nucleated, a new domain can unrestrictedly expand until it encounters another expanding domain. Actually, in terms of the KAI model one nucleus, in principle, can provide switching of the whole sample. We know from the direct observations of switching in thin films[13,14] that the switching occurs region-by-region, and the switching in a region does not necessarily lead to the subsequent switching of the neighboring ones as is expected according to the KAI model. This means that the film can be represented as an ensemble of regions, we call these elementary regions, where the switching is provided by the domains nucleated at centers belonging to this region (these domains not participating in switching of the rest of the film). Actually this switching scenario has been already successfully applied to the interpretation of polarization fatigue in thin ferroelectric films.[15–17] For the moment, the information on the size distribution of the elementary regions is very limited. Among these, there may be regions that behave differently with respect to the switching kinetics. We mean that in large enough elementary regions, which contain a large number of nucleation centers, the switching kinetics should obey the KAI model whereas in regions containing only a few nucleation centers a very different type of the switching kinetics takes place. The total contribution of the second type of regions is controlled by the statistics of virtually independent switching of these regions, which is very different from the statistics of coalescence of growing domains in the KAI model. Since our experimental data are inconsistent with the KAI kinetics, we conclude that the elementary regions of the first type do not essentially contribute to the switching response of the films. For this reason, we will model the switching as determined by the contribution by regions of the second type. We will consider the simplest model of this kind which we call nucleation-limited-switching (NLS) model. We define it by the following assumptions.

(i) The film is presented as an ensemble of elementary region.

(ii) The switching of an elementary region occurs once a domain of reversed polarization is nucleated in the region.

(iii) Time needed for switching of an elementary region is equal to the waiting time for the first nucleation, i.e., the time needed for filling the region with the expanding domain is neglected compared to the waiting time.

(iv) The distribution of the waiting times for the ensemble of the elementary regions is smooth and exponentially broad, i.e., covering many decades.

To describe the switching kinetics yielded by the NLS model we introduce τ_i as the typical waiting time of the elementary region (i), $1/\tau_i$ being the nucleation rate in the region and $\gamma_i = S_i/\langle S_i \rangle$ for the ratio of the area of region (i) S_i to the average area $\langle S_i \rangle$ of elementary regions in the film. The fraction of the volume of the ferroelectric switched by time t, $p(t)$ is given by the obvious relation

$$p(t) = 1 - \frac{\sum_{\mathrm{NS}} S_i}{\sum_{\mathrm{all}} S_i}, \tag{2}$$

where NS means nonswitched by time "t."

The special case of this problem where the elementary regions are identical, i.e., all τ_i and all S_i are equal, is readily described in term of the classical decay equation for the number of nonswitched areas N_{NS}

$$dN_{\mathrm{NS}} = -N_{\mathrm{NS}} \frac{dt}{\tau}, \tag{3}$$

where τ is the unique waiting time of the elementary regions. The solution of Eq. (3) satisfying the boundary condition $N_{\mathrm{NS}} = N_0$ at $t=0$, where N_0 is the total number of the elementary regions in the film, obviously reads $N_{\mathrm{NS}} = N_0 e^{-t/\tau}$. This solution leads, via Eq. (2), to the expression for $p(t)$ identical to the prediction of KAI model for the case of one-dimensional domain growth

$$p(t) = 1 - e^{-t/\tau}. \tag{4}$$

The real situation addressed by the NLS model comprises a distribution of τ_i and γ_i so that Eq. (4) should be applied to groups of elementary regions with close values of τ_i. It is straightforward to show that once the averaging over τ_i and γ_i is taken into account, the expression for the switched fraction of the film reads

$$p(t) = 1 - \langle \gamma_i e^{-t/\tau_i} \rangle \simeq 1 - \langle e^{-t/\tau_i} \rangle. \tag{5}$$

In this expression, one should perform the averaging $\langle \cdots \rangle$ over the distributions of the waiting times and areas of the elementary regions. Since the waiting time enters the exponent of this expression, averaging over its broad distribution is decisive for our problem. For this reason, addressing in this paper the main trends of the phenomenon, we neglect

with the logarithmic accuracy the correlation between the distributions of τ_i and γ_i and replace $\langle \gamma_i e^{-t/\tau_i} \rangle$ by $\langle \gamma_i \rangle \langle e^{-t/\tau_i} \rangle = \langle e^{-t/\tau_i} \rangle$ in the right-hand side of Eq. (5). The final averaging over an exponentially broad spectrum of the waiting times will be performed in the continuous approximation widely used in the theory of disordered systems (see, e.g., Ref. 18), i.e., we set

$$\langle e^{-t/\tau_i} \rangle = \int_{-\infty}^{\infty} e^{-t/\tau} g(\ln \tau) d(\ln \tau), \tag{6}$$

where the distribution function $g(z)$ meets the normalizing condition

$$\int_{-\infty}^{\infty} g(z) dz = 1. \tag{7}$$

The broadness of the spectrum of τ makes also possible (on the lines of Ref. 18) a further simplification of the expression for the switched fraction of the film. Namely, passing in Eq. (6) to the logarithmic variables, $z = \ln \tau$ and $z_0 = \ln t$, we find $\langle e^{-t/\tau_i} \rangle = \int_{-\infty}^{\infty} \exp(10^{z_0 - z}) g(z) dz$. The double exponential function, which enters this integral, exhibits a very fast growth compared to the distribution function $g(z)$. This justifies the replacement of the former by the step function centered at $z = z_0$ to get $\langle e^{-t/\tau_i} \rangle = \int_{z_0}^{\infty} g(z) dz$. Finally, making use of Eqs. (5)–(7) we arrive at a simple relation between the fraction of switched volume and the distribution function of the waiting times

$$p(t) = \int_{-\infty}^{\ln t} g(z) dz. \tag{8}$$

IV. APPLICATION OF THE NLS MODEL

We have found that the main features of our experimental results on the switching kinetics in ferroelectric thin films can be reasonably modeled by using Eq. (8) with a distribution function of the waiting times, which is flat for z lying between z_1 and z_2 ($\tau_{\min} = 10^{z_1}$ and $\tau_{\max} = 10^{z_2}$ stands for the lower and upper limits of the spectrum of the waiting times) and which, out of this region, decays as $1/z^2$, the rate of the decay being controlled by parameter Γ. Specifically, we set

$$g(z) = \frac{\Gamma^2 h}{(z - z_1)^2 + \Gamma^2} \quad \text{for } z_0 < z_1,$$

$$g(z) = h \quad \text{for } z_1 < z_0 < z_2,$$

$$g(z) = \frac{\Gamma^2 h}{(z - z_2)^2 + \Gamma^2} \quad \text{for } z_2 < z_0,$$

$$h = (z_2 - z_1 + \Gamma \pi)^{-1}. \tag{9}$$

This distribution function leads to the following expression for $p(t)$:

$$p(t) = \Gamma h \left(\frac{\pi}{2} - \arctan \frac{z_1 - z_0}{\Gamma} \right) \quad \text{for } z_0 < z_1,$$

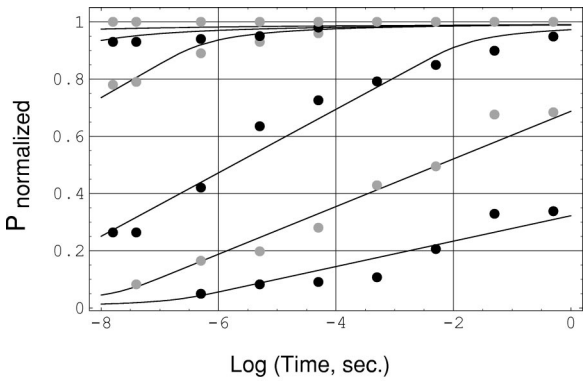

FIG. 4. Fit of the switching curves from Fig. 2 using the prediction of the NLS model, Eq. (10). Experimental data from Fig. 2 for voltages of 0.6, 1.35, and 3 V are marked with black dots, the data for 0.9, 2.2, and 5 V are marked with gray dots.

$$p(t) = \Gamma h \left(\frac{\pi}{2} + \frac{z_0 - z_1}{\Gamma} \right) \quad \text{for } z_1 < z_0 < z_2,$$

$$p(t) = \Gamma h \left(\frac{\pi}{2} + \frac{z_2 - z_1}{\Gamma} + \arctan \frac{z_0 - z_2}{\Gamma} \right) \quad \text{for } z_2 < z_0,$$

$$z_0 = \log t. \tag{10}$$

This relation can reproduce the main features of the experimental data for $p(t)$ once we use z_1 and z_2 as voltage dependent fitting parameters. The result of the fit of our data to Eq. (10) where we fix $\Gamma = 0.8$ is shown in Fig. 4. The values of z_1 and z_2 corresponding to this fit are plotted as functions of voltage V are shown in Fig. 5. This analysis reveals that the observed switching kinetics can be described in terms of the NLS model where the spectrum of the waiting times of the elementary regions rapidly shrinks with increasing applied voltage. As seen from Fig. 5 a pronounce exponential voltage dependence is exhibited by the typical maximal waiting time $\tau_{\max}$. This dependence can be approximated as

$$\tau_{\max} = \tau_0 10^{(V_0/V)^n}, \tag{11}$$

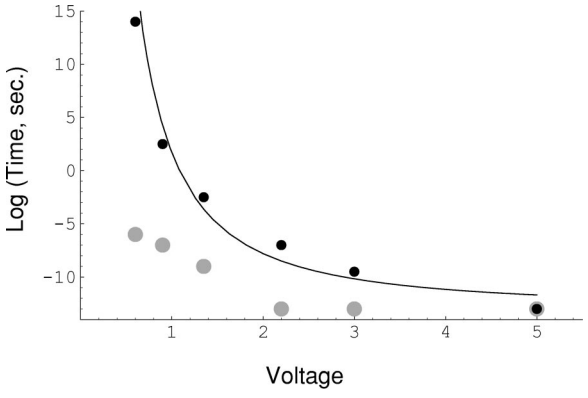

FIG. 5. Upper (black dots) and lower (gray dots) limits for the spectrum of waiting times for domain nucleation used for fitting curves in Fig. 4 as functions of the applied voltage. The solid line shows a fit of the experimental data for voltage dependence of the maximal waiting time to the function given by Eq. (11).

where $\tau_0 = 10^{-13}$ s, $n = 1.5$, and $V_0 = 6$ V. For a 135 nm thick film, this equation can be rewritten in terms of the applied field E as

$$\tau_{\max} = \tau_0 e^{(E_0/E)^{1.5}}, \tag{12}$$

where $E_0 = 770$ kV/cm. The presented fit is not unique, however, physically, the ambiguity is not so large since the preexponential factor is expected to be of the order of the inverse of the soft-mode frequency ω_{Sm} whereas the activation field E_0 should not be greater than the thermodynamic coercive field E_{th}. For PZT at room temperature, these parameters are expected to be $\omega_{\mathrm{Sm}} \simeq 10^{13}\ \mathrm{s}^{-1}$ (Ref. 19) and $E_{\mathrm{th}} = 0.5-1$ MV/cm.[20] It is seen that the used fitting parameters meet these requirements.

For the moment, despite extensive efforts (see for the discussion Refs. 21,22), there is no self-consistent theory of domain nucleation in ferroelectrics. For this reason, comparison of Eq. (12) with the results of existing theories is not instructive. However, the following remarks may be of interest. First of all, the clearly exponential field dependence of the upper edge of the spectrum of the waiting times, which we have obtained, is consistent with the expected activation nature of the phenomenon. On the other hand the obtained exponent $n = 1.5$ is also comparable with those derived in early theories of the activated polarization reversal, namely, $n = 1$ and $n = 2$ in Ref. 23, and $n = 1.5$ in Ref. 24.

To conclude this section we would like to address the origin of the exponentially broad spectrum of waiting times. It has been clearly established[24,21,22] that, using the Landau theory for an ideal crystal, the energy barriers for the nucleation of reversed domains $\Delta\varepsilon_0$ are very large, making at least thousands of thermal energies kT for typical experimental situations. This implies that, in the ideal situation, the waiting times for the nucleation, which are inverse proportional to the Gibbs factor $\exp(-\Delta\varepsilon_0/kT)$, are infinitely long. In the real situation, the nucleation barriers are believed to be reduced by the external factors (such as defects or free carriers) by orders of magnitude from some thousands of thermal energies kT down to a few tens of kT. Thus, the resulting activation energy for the nucleation $\Delta\varepsilon_r$ actually represents the difference between two energies that are orders of magnitude larger than this energy itself. This implies that small fluctuations of these two energies can lead to an essential spread of $\Delta\varepsilon_r$. Since the waiting time is an exponential function of the activation energy, this spread should lead to an exponentially broad spectrum of waiting times our approach is based upon.

To summarize, we see that the model we have forwarded above gives a good description of the switching kinetics in ferroelectric thin films employing a rather limited set of assumptions which look reasonable in the context of physics of the problem. At the same time we recognize the weak points relating to the phenomenological nature of this model. In particular, no direct evidence on the microscopic origin of the elementary regions of independent switching is available, for the moment. Here, the issue of primarily importance is the typical size of these regions, i.e., the typical displacement of the domain walls during switching. To identify possible obstacles for the domain wall movement we examined the transmission electron microscopy images of the PZT/electrode interface. These images revealed a high-quality epitaxial PZT/SRO interface where the only observable defects were stacking faults observed with the intervals of 10–20 nm. We believe that this scale may correspond to the minimal size of the elementary regions. However, this issue requires special experimental investigations.

V. DISCUSSION AND CONCLUSIONS

The analysis of the experimental data performed in the paper as well as the consistency of the basic assumptions of the NLS model with the physical situation in the ferroelectric thin films suggests that the kinetics of polarization switching in these systems is governed by the statistics of the nucleation rather than that of the domain coalescence inherent to KAI model.

However, because of the phenomenological nature of our model, the above conclusion might be questioned. An objection is that a description similar to that presented above can be formally obtained by averaging the result of the KAI model, Eq. (1), over an exponentially broad distribution of parameter t_0. We admit that it is formally possible, however, this kind of description is not supported by the microscopical aspect of the problem. It is seen from the following arguments. The exponentially broad distribution of parameter t_0, which would be required for a successful application of the KAI model to our system, implies this kind of distribution for the domain wall mobilities. In any real sample, a certain spread of the wall mobilities, e.g., due to fluctuations of the defect concentration, is expected. However, being a macro(meso)scopic characteristic of the wall, its mobility feels the defect concentration averaged over the wall area. This averaging suppresses the fluctuations of the wall mobility so that it can hardly exhibit an exponentially broad distribution. This feature actually makes the principal difference between the NLS and KAI models. In the former, the switching kinetics via nucleation is sensitive to the local fluctuations of the parameters of the system whereas the latter deals with the macroscopic wall motion that averages these fluctuations. As a result, in the NLS model the polarization response is controlled by a distribution of relaxation (waiting) times whereas a unique-relaxation-time kinetics is inherent to the KAI model.

In conclusion, the KAI model which is commonly used for the description of switching kinetics in ferroelectric materials is found to be inapplicable to the case of PZT thin films. Recent experimental data including original results presented in this paper show a strong qualitative disagreement with the switching kinetics predicted by KAI model. An alternative model, which provides an adequate description of the switching kinetics for PZT thin films has been proposed. The model suggests that the switching in thin films is limited by the nucleation of reversed domains rather than by the sideway motion of domain walls. According to this concept the switching kinetics is determined by the statistics of domain nucleation instead of that of domain coalescence as implied by the KAI model. The proposed model enables a description of the polarization reversal in PZT thin films for

a wide range of the switching times and applied voltages. It is shown that the electric field impacts the switching kinetics via influencing the spectrum of the local waiting times for the nucleation of reversed domains: an increase of the field results in a shrinkage of the spectrum.

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