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Kinetics of polarization reversal in ferroelectric films: role of domain nucleation and domain wall motion

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Abstract

Understanding of polarization reversal mechanisms in ferroelectric films is essential for evaluation and prediction of the properties of ferroelectric devices including nonvolatile memories. The widely accepted approach based on the domain wall motion kinetics describes correctly switching in single crystals but does not work properly for thin ferroelectric films used for memory applications. Recently an alternative approach based the on statistics of nucleation of the reversed polarization domain has been proposed. The switching model based on this approach provides an adequate description of the polarization reversal in thin films as a function of time and voltage at room temperature. The present paper examines the validity of this concept at different voltages and temperatures and discusses the competing switching mechanisms. In particular, it is shown that at very low temperatures a crossover between nucleation-limited switching kinetics and switching kinetics of domain wall motion typical for single crystal occurs in PZT ferroelectric films. The practical application of the polarization reversal models for evaluation of the switching behavior of ferroelectric capacitors is discussed.

Keywords: D. PZT; Polar materials; Thin films

1. Nucleation-Limited Switching model: key results and predictions

Kinetics of polarization domain reversal in ferroelectric materials has been studied since 1950s [1] because of its importance for the analysis of ferroelectric device operation and because of fundamental interest in this problem. The widely accepted approach for the description of switching behavior of ferroelectric single crystals has been developed by Ishibashi and coworkers [2] who considered the switching process as a growth of domains nucleated at different sites of the crystal under influence of the applied electric field. Due to the overlapping volumes of different growing domains the total switched polarization increases with time according to the formula:

$$P(t) = 1 - \mathrm{e}^{-(t/t_0)n} \quad (1)$$

where, $P(t)$ is the fraction of the volume of the ferroelectric switched by time t and the parameters t_0 and n depend on the mobility of domain walls, dimension of the domain growth and other parameters. This theory enables a correct description of switching kinetics in ferroelectric bulk materials, however, encounters difficulties when applied to the thin films [3,4]. For description of the switching kinetics in thin films the authors recently proposed an alternative concept [4] called hereafter the Nucleation-Limited Switching (NLS) model, which describes adequately the polarization reversal in thin films for a wide range of switching times and applied voltages. The most important results of this model are summarized below.

The NLS model describes the fraction of reversed polarization as a function of time and switching voltage under the following key assumptions: (i) the film is presented as an ensemble of elementary regions switched independently; (ii) the switching of an elementary region occurs once a domain of reversed polarization is nucleated in the region; (iii) time needed for complete switching of the region is equal to the waiting time for the first nucleation, that is, the time of domain wall movement is neglected compared to the nucleation time; (iv) the distribution of the waiting times for the ensemble of the regions is smooth and exponentially broad, that is, covers many decades.

In Ref. [4] for the waiting times, τ the following distribution function $g(z)$ where $z = \log \tau$ has been used: between the two edges of the spectrum of waiting times $\tau_{\min}$

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($z_1 = \log \tau_{min}$) and τ_{max} ($z_2 = \log \tau_{max}$) $g(z)$ was flat and out of these regions $g(z)$ decays as z^{-2}, the rate of the decay being controlled by the parameter Γ. Specifically, $g(z)$ was defined as

$$\begin{aligned} g(z) &= \frac{\Gamma^2 h}{(z - z_1)^2 + \Gamma^2}, \quad \text{for} \quad z < z_1 \\ g(z) &= h, \quad \text{for} \quad z_1 < z < z_2 \\ g(z) &= \frac{\Gamma^2 h}{(z - z_2)^2 + \Gamma^2}, \quad \text{for} \quad z_2 < z \end{aligned} \tag{2}$$

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

This distribution function leads to the following expression for the normalized polarization $P(t)$ where, $z_0 = \log t$:

$$\begin{aligned} P(t) &= \Gamma h \left(\frac{\pi}{2} - \arctan \frac{z_1 - z_0}{\Gamma} \right), \quad \text{for } z_0 < z_1 \\ P(t) &= \Gamma h \left(\frac{\pi}{2} + \frac{z_0 - z_1}{\Gamma} \right), \\ &\text{for } z_1 < z_0 < z_2 \\ P(t) &= \Gamma h \left(\frac{\pi}{2} + \frac{z_2 - z_1}{\Gamma} + \arctan \frac{z_0 - z_2}{\Gamma} \right), \quad \text{for } z_2 < z_0 \end{aligned} \tag{3}$$

These formulas allow for the calculation of the switching curve $P(t)$ for given parameters of the spectrum of switching times τ_{min}, τ_{max}, and Γ. Alternatively, once the switching curve is measured these parameters can be found through the fitting procedure. It was demonstrated in Ref. [4] that the dependence of edges of the spectrum of switching times of the switching voltage can be approximated with the following formula:

$$\tau = \tau_0 \exp \left(\frac{V_0}{V} \right)^p \tag{4}$$

where, τ is τ_{min} or τ_{max}; τ_0 is close to the reverse soft mode frequency that is put 10^{-13} s; V_0 is comparable with the thermodynamic coercive field and p is within the range from 1 to 2.5.

In order to verify the concept of nucleation-limited switching the polarization reversal in La-doped PZT 135 nm films has been studied. The films for this experiment were grown by chemical solution deposition on Pt bottom electrodes. The IrOx top electrodes with size of 15 μm × 15 μm were patterned by dry etching. The switching curves were measured using pulse technique described in detail in Ref. [4]. The rise time for all the pulses was 10 ns and the polarization was switched using the pulses of 0.5, 0.6, 0.7, 0.8, 1, and 3 V, the pulse width ranging from 30 ns to 0.1 s for each voltage. The switching polarization was measured with the pulses of 5 V, the polarity with respect to the bottom electrode was positive. The switching curves measured in this way, where the normalized reversed polarization is plotted as a function of time for different voltages are represented in Fig. 1 together with the fit generated using Eqs. (2) and (3) where, $\Gamma = 0.8$. The parameters τ_{min} and τ_{max} used for the fit for different voltages are represented in Table 1.

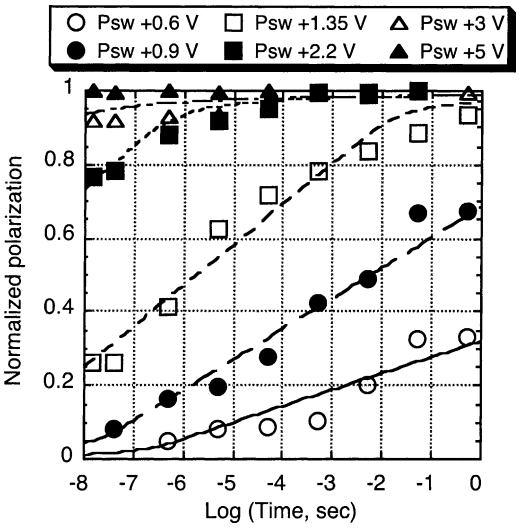

Fig. 1. Switching data representing normalized reversed polarization vs. time for different voltages for the 135 nm PZT capacitor and fitting curves generated by NLS model using the parameters from Table 1.

The data in Fig. 1 show that the NLS model is able to reproduce the main features of the switching curves observed for the PZT thin films and provides reasonable quantitative description of the reversed polarization versus time. The model can be extended for description of the switching polarization as a function of temperature. The assumption (iii) suggests that the switching time for each region is essentially the waiting time of nucleation, hence, the switching in an elementary region can be described as an activation process characterized by an activation energy U_{act}:

$$\tau = \tau_0 \exp \left(\frac{U_{act}}{kT} \right) \tag{5}$$

For the case of low activation energy the waiting time asymptotically approaches τ_0, which is close to the reverse soft mode frequency.

Using Eqs. (2) and (3) one can calculate the switching curves at different temperatures based on the parameters of the spectrum of switching times extracted from the fit of room temperature data using the following procedure. First, one measures the curves of switching polarization versus

Table 1
Parameters of the spectra of switching times τ_{min} and τ_{max} used for the fitting curves in Fig. 1

Voltage (V)	Log(τ_{min}, s)	Log(τ_{max}, s)
0.6	−6	14
0.9	−7	2.5
1.35	−9	−2.5
2.2	−12.5	−7

time for different voltages at room temperature. Then, fitting the normalized switching curves to the Eq. (3) one finds the parameters of the spectrum of switching times τ_{min}, τ_{max}, and Γ, for each voltage. In the next step one finds activation energies U_{act} corresponding to τ_{min}, τ_{max}, for each voltage using Eq. (5). Based on the obtained values of U_{act} one can calculate $\tau_{min}(T_1)$, $\tau_{max}(T_1)$ for the same switching voltage at a different temperature T_1. Finally, using these new parameters of the spectrum of switching times the switching curve at the temperature T_1 can be calculated.

2. Limits of validity of the NLS model and switching at low temperatures

The limits of validity of the assumptions (i–iii) specified in the previous section represent the basic restrictions for use of the NLS switching model. In particular, the assumption (iii) suggests that the switching time is virtually the same as the nucleation time. Analysis of the NLS concept shows that there is a high voltage limit as well as low temperature limit of validity of this assumption. Indeed, at high voltages the energy barrier for the domain nucleation becomes negligible so that the switching speed is not longer limited by the nucleation rate but by other internal factors such as soft mode frequency or external factors like RC constant of the circuit. Additionally, the rate of domain wall motion decreases exponentially with the temperature decrease so that at low temperatures the contribution of the domain growth to the switching speed cannot be neglected. Hence, at very low temperatures one should expect the switching curves similar to single crystals because the low temperature switching kinetics must be determined by domain wall motion. In this section we explore the limits of applicability of the NLS model by comparing the switching properties of PLZT films at room temperature and at low temperature of −233 °C. For this study the (1 1 1) oriented PLZT films with Zr/Ti ratio of 40/60 and the thickness of 180 nm were deposited on Pt (1 1 1) bottom electrodes by sputtering. Two types of differently processed IrO_x where $1 < x < 2$ and IrO_2 top electrodes with different sizes have been patterned by dry etching.

The difficulty of using NLS model for the switching kinetics description at very low temperatures can be illustrated by analysis of the shape of the hysteresis loops. Fig. 2 shows the loops measured at four different temperatures from −233 °C to room temperature. As Fig. 2 shows the loops become more vertical with the temperature decrease. On the other hand, the NLS model implies that the switching times change with the temperature according to the activation law (Eq. (5)) suggesting that at lower temperatures the spectrum of switching times is broader and the loops are more tilted.

For more comprehensive analysis of the kinetics of polarization reversal the switching curves have been measured using the pulse switching technique as described in previous section. At room temperature, the switching time ranged

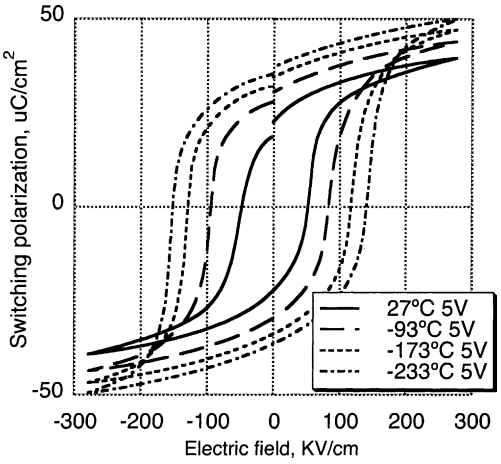

Fig. 2. Hysteresis loops measured on the 180 nm PZT capacitor at different temperatures.

from 30 ns (with 5 ns risetime) to 0.5 s for the capacitors with size 15 $\mu m^2 \times 15\ \mu m^2$, whereas, at −233 °C the shortest pulse duration is 1 μs with risetime of 100 ns (capacitors 50 $\mu m^2 \times 50\ \mu m^2$) because of limitations imposed by the cryostat setup.

The room temperature switching curves for the capacitors with IrO_2 top electrodes (type I) and IrO_x top electrodes (type II) are shown in Fig. 3. It is clear from comparison betweenFig. 3a and b that the capacitor of type II is switched at lower voltage and has different shape of switching curves compared to the capacitor of type I. This shows that the modification of only one top interface may change considerably the capacitor switching performance in agreement with the concept of nucleation-limited switching. Fig. 4 represents switching curves measured at −233 °C on the same samples as in Fig. 3 with the same voltage polarity. As expected, at lower temperature the capacitors have higher coercive field and switched at higher voltage. Additionally, the shape of switching curves at −233 °C change considerably compared to the room temperature results so that the curves measured at −233 °C cannot be modeled by voltage scaling of the room temperature data. The difference is particularly pronounced for capacitors of type I. These capacitors are characterized at room temperature by relatively smooth switching curves compared to FeCAPs of type II. At room temperature the switching curves taken at different voltages look like a fan, whereas, at −233 °C the change of switching voltage results in a shift of switching curves along the log(time) axis the same way as observed in single crystals. However, the essential difference between the observed curves and the single crystal case is the saturation behavior. In single crystals the switching curves taken at different voltages typically saturate at the same value corresponding to the complete polarization reversal. On the other hand, Fig. 4 shows that in studied PLZT film capacitors the saturation value of the switching polarization increases with the switching voltage increase, for both types of capacitors.Another remarkable feature in the results in Fig. 4

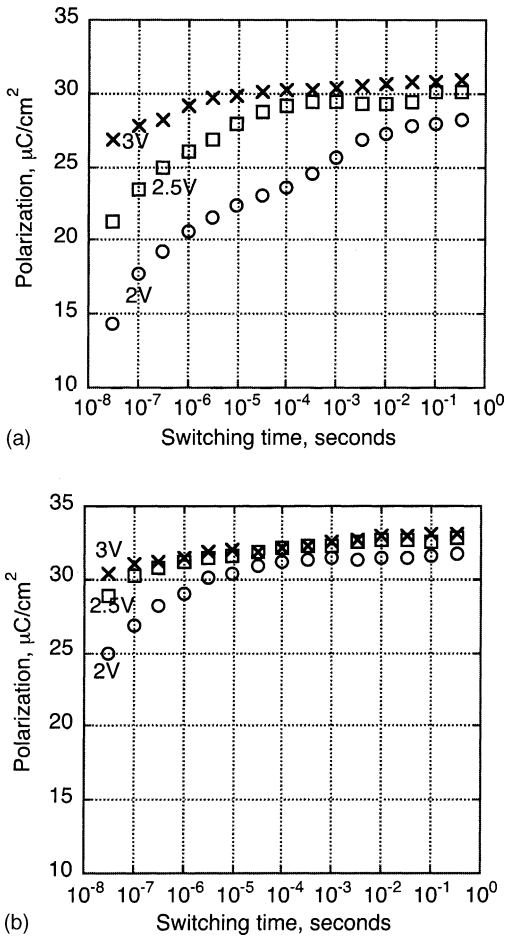

Fig. 3. Reversed polarization vs. time, for different voltages, measured at room temperature on 180 nm PZT capacitors of type I (a) and type II (b).

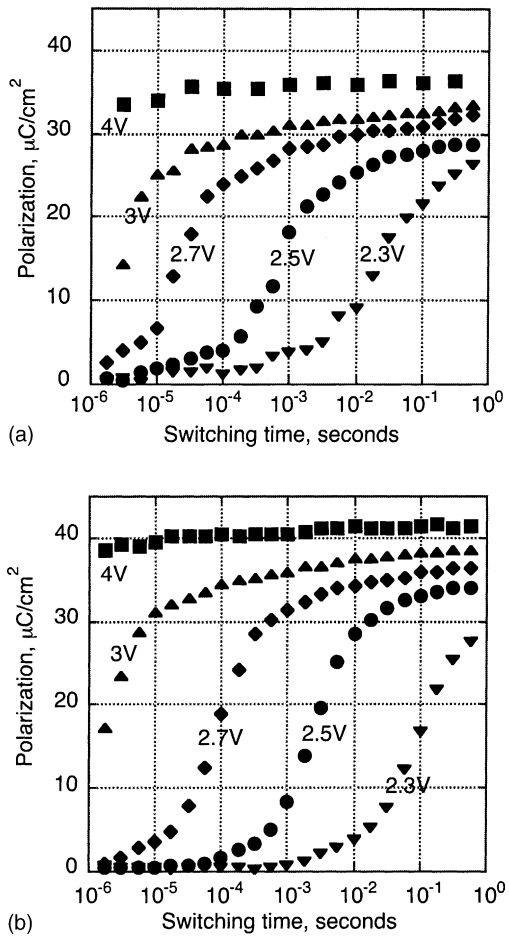

Fig. 4. Reversed polarization vs. time, for different voltages, measured at −233 °C on 180 nm PZT capacitors of type I (a) and type II (b).

is the similarity of switching curves measured on capacitors of type I and II at the same voltages. Hence, the substantial difference between the switching properties of the two types of capacitors seen at room temperature tends to disappear at low temperatures. The similarity of low temperature switching curves for the two types of capacitors presents a reasonable starting point for the data analysis. It is natural to suggest that the difference of the top interfaces between the capacitors of type I and II gives rise to the different distribution of domain nucleation energies resulting in different switching properties observed at room temperature. The fact that this difference virtually disappears at −233 °C suggests that the polarization reversal is not longer limited by its initial stage of domain nucleation but by domain wall motion. In this case one should expect the normalized switched polarization P_{sw} to change with time according to Eq. (1).

In this context, the low temperature switching scenario can be described as follows. At very low temperatures like −233 °C, the thermoactivation mechanism of domain nucleation results in extremely long switching times making domain reversal within the time range below 1 s virtually impossible. In each independently switched region the domain nucleation can be triggered only if the driving voltage reaches a critical level V_{cr} high enough to suppress nearly completely the potential barrier of the nucleation. In this case the nucleation occurs at a very high rate and does not limit the switching speed. Similar to single crystals, the switching kinetics in this case is determined by domain growth, which is relatively slow at −233 °C even within the switching voltage range of 2–3 V corresponding to electric field about 100–150 kV/cm.

The concept of independently switched regions explains the dependence of the saturation points of the switching curves in Fig. 4 of the driving voltage. Each region contributes to the measured switched polarization only if some nuclei within this region can be activated at given voltage amplitude. Because of the variation of the parameter V_{cr} from one region to another the number of regions contributing to the polarization reversal increases with the voltage and the measured switching charge increases accordingly. Hence, for fitting each switching curve to Eq. (1) one needs first to renormalize the curve to its saturation value. Fig. 5 represents the normalized switching curve measured on the

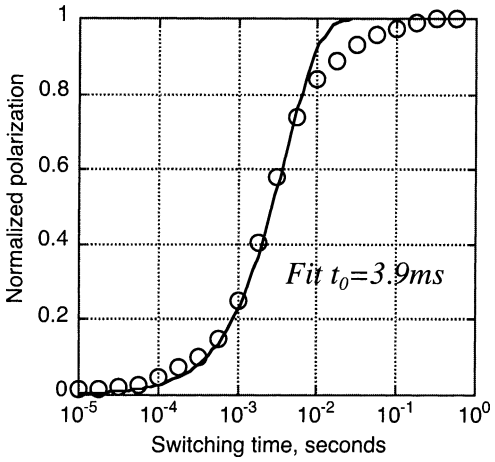

Fig. 5. Switching data measured on PZT capacitor of type II at 2.5 V at −233 °C and the fit (solid line) generated using Eq. (1) for $n = 1$ and $t_0 = 3.9$ ms.

capacitor of type II at 2.5 V together with the fitting curve produced by formula (1), with $n = 1$ and $t_0 = 3.9$ ms. The satisfactory fit in Fig. 5 suggests that in studied thin films the polarization reversal is limited by domain wall movement.

The case of room temperature switching at high voltage is more complicated for analysis of switching kinetics. Indeed, NLS model applies to the case where the domain nucleation rates are controlled by thermoactivation mechanism. However, for the regions characterized by V_{cr} lower than the applied voltage the switching kinetics is different. The low temperature measurements provide a tool for direct evaluation of the total area of these regions. For example, Fig. 4b shows that at 2.5 V the switching curve saturates at switching polarization value of 34 μC/cm^2, whereas, the maximal switching polarization (measured at 5 V) is as high as 41 μC/cm^2. Hence, only 83% of the film is switched at 2.5 V. Assuming the same distribution of parameters V_{cr} at room temperature we conclude that at 2.5 V the NLS model describes polarization reversal only in 17% of the film, whereas, the rest of the film switches at room temperature as fast as the RC constant of the external circuit allows.

3. Summary

In conclusion, the Nucleation-Limited Switching model provides an adequate quantitative description of the polarization reversal in PZT ferroelectric films at room temperature. The fitting procedure based on this model delivers the essential parameters of the switching process that can be used for prediction of the switching properties at different temperatures. The calculation of switching curves at different temperatures and their experimental verification as well as the exact temperature limits of validity of the procedure will be addressed in the upcoming papers.

The role of nucleation-limited switching and the competing mechanisms is studied by comparing switching kinetics at room temperature and at −233 °C. It is demonstrated that at low temperature such as −233 °C the switching kinetics is controlled by domain wall movement like in single crystals. Apart from the fundamental scientific interest in observing the crossover between the thin-film-like switching kinetics and single-crystal-type kinetics the low temperature switching results are found to be useful for modeling of the room temperature switching behavior of ferroelectric capacitors.

Acknowledgements

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