Domain Switching Kinetics in Disordered Ferroelectric Thin Films

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We investigated domain kinetics by measuring the polarization switching behaviors of (111)-preferred polycrystalline Pb(Zr, Ti)O_3 films, which are widely used in ferroelectric memories. Their switching behaviors at various electric fields and temperatures could be explained by assuming the Lorentzian distribution of logarithmic domain-switching times. We suggested that the local field variation due to dipole defects at domain pinning sites could explain the Lorentzian distribution.

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Domain-switching kinetics in ferroelectrics (FEs) under an external electric field $E_{\rm ext}$ have been extensively investigated for several decades [1–7]. The traditional approach to explain the FE switching kinetics, often called the Kolmogorov-Avrami-Ishibashi (KAI) model, is based on the classical statistical theory of nucleation and unrestricted domain growth [1,2]. For a uniformly polarized FE sample under $E_{\rm ext}$, the KAI model gives the time (t)-dependent change in polarization $\Delta P(t)$ as

$$\Delta P(t) = 2P_s[1 - \exp\{-(t/t_0)^n\}], \tag{1}$$

where n and t_0 are the effective dimension and characteristic switching time for the domain growth, respectively, and P_s is spontaneous polarization. When the nuclei arise instantaneously at the very beginning of the process, $n = 3$ for bulk samples and $n = 2$ for thin films [8]. In addition, t_0 is proportional to average distance between the nuclei, divided by domain wall speed. Using the KAI model, several studies have succeeded to explain the $\Delta P(t)$ behaviors of FE single crystals and epitaxial thin films [6].

Recently, FE thin films have been intensively investigated for FE random access memory (FeRAM) [9,10]. Most FeRAM use polycrystalline Pb(Zr, Ti)O_3 (poly-PZT) films, and their $\Delta P(t)$ behaviors determine reading or writing speeds of the FeRAM. In such nonepitaxial FE films, a domain cannot propagate indefinitely due to pinning caused by numerous defects, so the KAI model cannot be applied. Therefore, it is important both scientifically and technologically to clarify the domain-switching kinetics of poly-PZT films.

Numerous studies have examined the $\Delta P(t)$ behaviors of polycrystalline FE films, and reported results varying markedly [3–5,7]. Lohse *et al.* measured the polarization switching currents of poly-PZT films, and showed that $\Delta P(t)$ slowed significantly compared to Eq. (1) [3]. Tagantsev *et al.* observed similar phenomena for poly-PZT films. To explain these behaviors, they developed the nucleation-limited-switching (NLS) model. They assumed that films consist of several areas that have independent switching kinetics:

$$\Delta P(t) = 2P_s \int_{-\infty}^{\infty} [1 - \exp\{-(t/t_0)^n\}]F(\log t_0)d(\log t_0), \tag{2}$$

where $F(\log t_0)$ is the distribution function for log t_0 [4]. They assumed a very broad mesalike function for $F(\log t_0)$, and could explain their $\Delta P(t)$ data. The same authors also

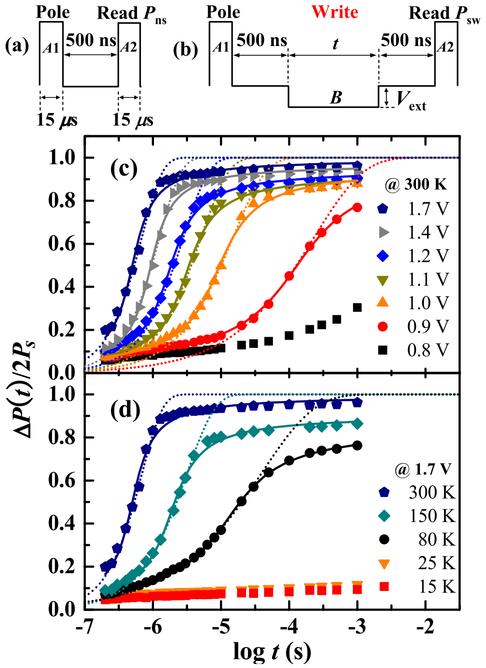

FIG. 1 (color online). Schematic diagrams of the pulse trains used to measure (a) nonswitching polarization ($P_{\rm ns}$) and (b) switching polarization ($P_{\rm sw}$). Time (t)-dependent switched polarization $\Delta P(t)$ (c) under various external voltages ($V_{\rm ext}$) at room temperature and (d) under 1.7 V at various temperatures. The dotted and solid lines correspond to fitted results using the KAI model and the Lorentzian distribution function in log t_0, respectively.

studied La-doped poly-PZT films and found that $\Delta P(t)$ at room temperature is limited mainly by nucleation, while at a low temperature (T), the switching kinetics are governed by domain wall motion, implying the validity of the KAI model [5].

In this Letter, we investigate the polarization switching behaviors of (111)-preferred poly-PZT films. We can explain the measured $\Delta P(t)$ in terms of the Lorentzian distribution for $F(\log t_0)$, in wide range of E_{ext} and T. We suggest that such distribution arises from local field variation in a disordered system with dipole-dipole interactions.

Note that (111)-preferred poly-PZT films with a Ti concentration near 0.7 are the most widely used material in FeRAM applications. We prepared our polycrystalline $\mathrm{PbZr_{0.3}Ti_{0.7}O_3}$ thin film on $\mathrm{Pt/Ti/SiO_2/Si}$ substrates using sol-gel method. The poly-PZT film had a thickness of 150 nm. X-ray diffraction studies showed that it has the (111)-preferred orientation, and scanning electron microscopy studies indicated that our poly-PZT film consists of grains with a size of about 200 nm. We deposited Pt top electrodes using sputtering with a shadow mask. The areas of the top electrodes were about $7.9 \times 10^{-9}\ \mathrm{m}^2$.

We obtain the $\Delta P(t)$ values of our Pt/PZT/Pt capacitors using pulse measurements [6,11]. Figure 1(a) shows the pulse trains used to measure the nonswitching polarization change (P_{ns}). Using pulse $A1$, we poled all the FE domains in one direction. Then, we applied pulse $A2$ with the same polarity, and measured the current passing a sensing resistor. By integrating the current, we could obtain the P_{ns} values. Figure 1(b) shows the pulse trains used to measure the switching polarization (P_{sw}). Inserting pulse B with the opposite polarity between pulses $A1$ and $A2$, we could reverse some portion of the FE domains, so the difference between the values of P_{sw} and P_{ns} represents the polarization change due to domain switching, namely $\Delta P(t)$. We varied t from 200 ns to 1 ms, and V_{ext} from 0.8 to 4 V. The value of E_{ext} can be estimated easily by dividing V_{ext} by the film thickness. At T of 80–300 K, we used pulses $A1$ and $A2$ with a height of 4 V, which was larger than the coercive voltage. Below 80 K, the coercive voltage increases, so we increased the pulse height to 6 V [12].

Figure 1(c) shows the values of $\Delta P(t)/2P_s$ at room T with numerous values of V_{ext}. Figure 1(d) shows the values of $\Delta P(t)/2P_s$ at various T with $V_{\mathrm{ext}} = 1.7$ V. The dotted lines in both figures are the curves best fitting from Eq. (1). The KAI model predictions deviated markedly from the experimental $\Delta P(t)$ values in the late switching stage, in agreement with Gruverman *et al.* [7]. In addition, the best fitting results with the KAI model gave unreasonable values of n. As shown in Fig. 2(a), the values of n varied markedly with T and E_{ext}. In addition, in the low E_{ext} region, we obtained n values much smaller than 1, which are not proper as an effective dimension of domain growth. Therefore, Eq. (1) fails to describe the $\Delta P(t)$ behaviors of our PZT films.

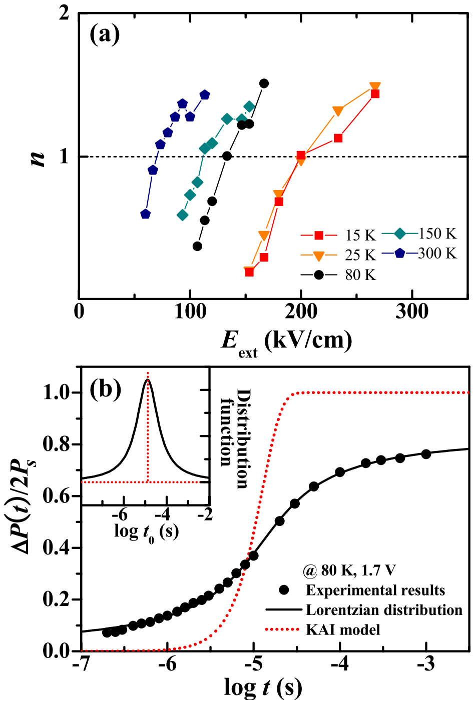

FIG. 2 (color online). (a) Values of n for various T and E_{ext}. (b) $\Delta P(t)$ results for (solid symbols) experimental data and fitted results using the Lorentzian (solid line) and delta (dotted line) distributions for $\log t_0$. The inset shows the distribution functions corresponding to the fitted results.

We found that Lorentzian functions for $F(\log t_0)$ in Eq. (2) could explain $\Delta P(t)$ behaviors. The opposite domain, once nucleated, will propagate inside the film, so we fixed $n = 2$. The solid circles in Fig. 2(b) show the experimental $\Delta P(t)$ at 80 K with $V_{\mathrm{ext}} = 1.7$ V. For $F(\log t_0)$, we tried the delta and Lorentzian distribution functions, as shown in the inset. The dotted line indicates the fitting results using Eq. (2) with a delta function. Note that this curve corresponds to a fit with the KAI model, and thus the classical theory cannot explain our experimental data. Although this fitting seems reasonable, some discrepancies occur. The solid line shows the fitting results with the Lorentzian distribution

$$F(\log t_0) = \frac{A}{\pi}\left[\frac{w}{(\log t_0 - \log t_1)^2 + w^2}\right], \qquad (3)$$

where A is a normalization constant, and w ($\log t_1$) is the half-width at half-maximum (a central value) [13]. The Lorentzian fit can account for our observed $\Delta P(t)$ behaviors quite well.

We applied the Lorentzian fit to all of the other experimental $\Delta P(t)$ data. As shown by the solid lines in Figs. 1(c) and 1(d), the Lorentzian fit provides excellent explanations. Figure 3(a) presents the Lorentzian distribution functions used for the 300 K data. As V_{ext} increases, $\log t_1$ and w decrease. We rescaled the experimental $\Delta P(t)/2P_s$ data using $(\log t - \log t_1)/w$. All the data merge into a single

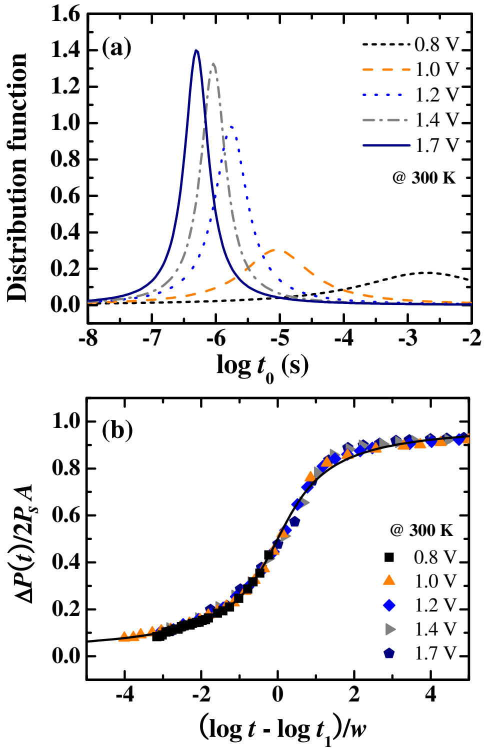

FIG. 3 (color online). (a) The E_{ext}-dependent Lorentzian distribution functions at room T. (b) Rescaled $\Delta P(t)$ using fitting parameters for the Lorentzian distribution function.

line, an arctangent function [13], as shown in Fig. 3(b). Although not indicated in this figure, the experimental data for all other T also merged with this line. This scaling behavior suggests that the Lorentzian distribution function for $\log t_0$ is intrinsic.

Our $F(\log t_0)$ results with Lorentzian distribution might be different with a basic statistical belief, in which the resulting distribution should be Gaussian, regardless of the process details [14]. For example, impurities (or crystal defects) inside a crystal result in inhomogeneous broadening of the light absorption line, which has a Gaussian line shape. However, some studies have observed that magnetic resonance line broadening of randomly distributed dipole impurities follows the Lorentzian distribution [15]. The first rigorous theoretical result is that of Anderson, who showed that the distribution of any interaction field component in the system of dilute aligned dipoles should be Lorentzian [16].

Characteristic distribution functions of local fields, generated by randomly distributed point sources, have been investigated theoretically for the long-range interactions by many workers [14]. The force f can be written as $f \sim r^{-S}$, where r and S are a distance between two point sources and a characteristic exponent, respectively. Then the random field distribution will have a functional form of $F(f) \sim 1/f^{1+\mu}$ with $\mu = D/S$, where D is dimensionality of the force [14]. For the problem of dipole defects, $S = 3$ and $D = 3$. Therefore, $\mu = 1$, which corresponds to the Lorentzian function. Using electron paramagnetic resonance, many workers experimentally found that PZT materials contain lots of dipole defects [17]. Such dipole defects will act as pinning sites for domain wall motion inside the PZT films. Therefore, we assume that a local field $\overline{E}$ with Lorentzian distribution exists at the FE domain pinning sites

$$F(\overline{E}) = \frac{A}{\pi}\left[\frac{\Gamma}{\overline{E}^2 + \Gamma^2}\right], \tag{4}$$

where Γ is the half-width at half-maximum, related to the concentration of pinning sites.

In the low E_{ext} region, the domain wall motion should be governed by thermal activation process at the pinning sites. Without $\overline{E}$ effects, thermal activation results in a domain wall speed in the form $v \propto 1/t_0 \propto \exp[-(U/k_BT) \times (E_0/E_{ext})]$, where U is the energy barrier and E_0 is the threshold electric field for pinned domains [18]. Since $\overline{E}$ results in a change in the effective electric field at pinning sites, the associated t_0 can be expressed as

$$t_0 \sim \exp\left[\left(\frac{U}{k_BT}\right)\left(\frac{E_0}{E_{ext} + \overline{E}}\right)\right]. \tag{5}$$

Then, the distribution of $\overline{E}$ results in a distribution in $\log t_0$, using the relation $F(\log t_0) = F(\bar{E})|d\bar{E}(\log t_0)/d(\log t_0)|$. With

$$\log t_1 \approx \frac{UE_0}{k_BT}\left(\frac{1}{E_{ext}}\right) \tag{6}$$

and

$$w \approx \frac{UE_0\Gamma}{k_BT}\left(\frac{1}{E_{ext}^2}\right), \tag{7}$$

we can obtain the desired Lorentzian distribution for $F(\log t_0)$, i.e., Eq. (3), from Eqs. (4) and (5).

Our experimental values for $\log t_1$ and w agree with the analytical forms. Figures 4(a) and 4(b) plot $\log t_1$ *vs.* $1/E_{ext}$ and w vs $1/E_{ext}^2$ at various T, respectively. Both $\log t_1$ and w follow the expected E_{ext} dependence in the low E_{ext} region. Note that Eq. (6) is consistent with Merz's law [19], which states that the current coming from FE polarization switching should have a characteristic time of $\exp(\alpha/E_{ext})$, where α is the activation field. Using this empirical law, several studies have measured α values, e.g., 1700 kV/cm for 100-nm-thick epitaxial PZT films [6] and 270 kV/cm for 350-nm-thick poly-PZT films [9]. These values are consistent with our room T value of UE_0/k_BT, i.e., 1400 kV/cm.

Our model viewed the FE domain-switching kinetics as domain wall motion driven by E_{ext} with a random pinning potential. In the low E_{ext} region, thermal activation at the pinning sites can be important, resulting in the so-called domain wall creep motion. Using atomic force microscopy, Tybell *et al.* demonstrated that the domain-switching kinetics in epitaxial PZT films is governed by the domain

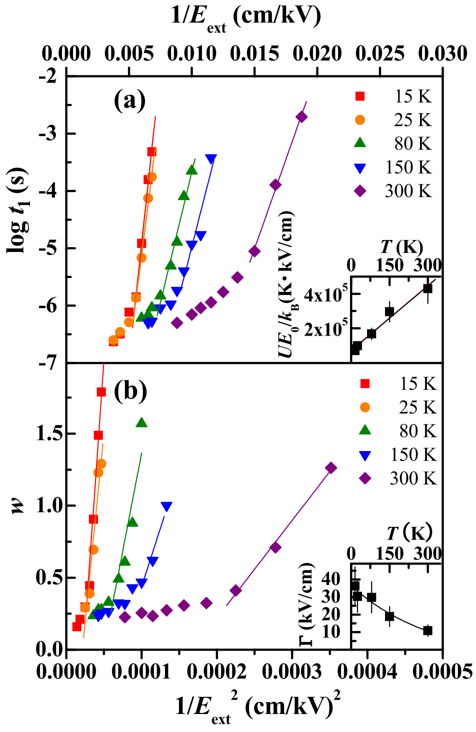

FIG. 4 (color online). E_{ext}-dependent (a) $\log t_1$ and (b) w at various T. Note that $\log t_1$ and w are proportional to $1/E_{\text{ext}}$ and to $1/E^2_{\text{ext}}$ in the low E_{ext} region, respectively. The insets show UE_0/k_B and Γ. The solid lines are guidelines for eyes.

wall creep motion [18]. Some theoreticians studied the domain wall creep motion of an elastic string in a random potential and found a linear increase in U with an increase in T [20]. The inset in Fig. 4(a) shows that the value of UE_0/k_B obtained from the linear fits in Fig. 4(a) increase linearly with T, consistent with the theoretical prediction for U [20]. The inset in Fig. 4(b) shows Γ obtained from the fits to Fig. 4(b). Similar exponential decay behavior was predicted in a magnetic resonance study of randomly distributed dipoles [21].

Using the Lorentzian distribution for $F(\log t_0)$, our model can be used for both epitaxial and polycrystalline FE films [6]. Using Eqs. (2) and (3) with small w values, we could successfully explain the $\Delta P(t)$ for FE single crystals or epitaxial thin films [6]. We also performed similar domain-switching experiments on (111)-preferred poly-PZT films with Ti concentrations of 0.48, 0.60, and 0.65 [22]. We found that the Lorentzian distribution can explain the $\Delta P(t)$ data for all the other poly-PZT films [22]. Therefore, our model can be applied to domain-switching kinetics of many FE films.

Thermally activated domain-switching kinetics can be viewed as the famous problem that treats the propagation of elastic objects driven by an external force in presence of a pinning potential [18,20]. Note that the domain wall motion should be related to $\Delta P(t)$ for FE system. Therefore, the $\Delta P(t)$ studies can be used to investigate numerous issues concerning nonlinear systems, such as creep motion, avalanche phenomenon, and pinning/depinning transition.

In summary, we investigated the polarization switching behaviors of (111)-preferred poly-PZT films and found that the logarithmic characteristic switching time obeyed the Lorentzian distribution. We explained this intriguing phenomenon by introducing the local electric field due to the defect dipole.

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