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Non-Kolmogorov–Avrami–Ishibashi Switching Dynamics in Nanoscale Ferroelectric Capacitors

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ABSTRACT Switching dynamics of nanoscale ferroelectric capacitors with a radius of 35 nm were investigated using piezoresponse force microscopy. Polarization switching starts with only one nucleation event occurring only at the predetermined places. The switching dynamics of nanoscale capacitors did not follow the classical Kolmogorov–Avrami–Ishibashi model. On the basis of the consideration of two separate (nucleation and growth) steps within a nonstatistical finite system, we have proposed a model which is in good agreement with the experimental results.

KEYWORDS Ferroelectrics, PFM, switching dynamics, nanoscale capacitor

Ferroelectric devices are still in the race for nonvolatile memories due to a number of obvious advantages such as high density and fast read/write speed.[1] As there are increasing demands for a very high memory density, ferroelectric capacitors need to be downsized into the nanoscale range. A physical operation of the ferroelectric devices is based on the polarization switching by external electric field, and there has been much effort to understand switching dynamics inside micrometer-scale capacitors.[2−7] Nevertheless, there is still lack of information, i.e., on the detailed switching behavior including nucleation and growth process and switching dynamics of nanoscale capacitors. The switching dynamics of nanoscale ferroelectric capacitors might be very different from their macroscopic counterparts as a single defect might have a tremendous influence on them. However, there are no reports and theories for the switching dynamics of nanoscale ferroelectric capacitors.

In order to understand polarization switching mechanisms, electrical measurements are usually performed on micrometer-scale ferroelectric capacitors and further on analyzed within the frame of nucleation and growth theory, i.e., the Kolmogorov–Avrami–Ishibashi (KAI) model.[2−6] The KAI model is based on the statistical theory of nucleation and unrestricted domain growth by considering the phase transformation with a random distribution of nucleation sites.[2,3] It has been successfully applied to describe ferroelectric switching in epitaxial thin films and single crystals.[3,8,9] However, it has been shown that the KAI model does not provide a proper description of switching dynamics for systems that are far from ideal such as polycrystalline thin films. To explain the behavior in polycrystalline thin films, the nucleation-limited switching (NLS) model was developed.[4,5,8] The NLS model assumes that the ferroelectric capacitors consist of several regions that have independent switching dynamics with distribution functions for the nucleation time. In addition, there has been some attempts based on the Kolmogorov–Avrami model to describe switching in a finite system.[10,11]

Experimentally, the switching mechanism in macroscopic ferroelectric capacitors is evaluated by measuring the switching current during the application of external bias pulses. However, as the capacitor size decreases, it is difficult to analyze the switching mechanism using the switching current, because the current also becomes small. To analyze nanoscale capacitors using the classical electrical macroscopic measurements is virtually impossible. Fortunately, methods based on piezoresponse force microscopy (PFM) involving ferroelectric domain imaging through the top electrodes have been developed. These methods allow the direct observation of the nanoscale domain evolution and implicitly the switching dynamics.[8,12−17] Recent studies on micrometer-scale ferroelectric capacitors showed that the PFM-based study of the switching dynamics is a powerful method, which allows the direct visualization of domain nucleation and growth and implicitly a better understanding of the mechanisms that govern these processes.[15,16,18] Gruverman et al. showed, for instance, that small polycrystalline capacitors of $1 \times 1.5\,\mu m^2$ are dominated by domain wall motion and switch faster at high fields but slowly at low fields, while capacitors larger than $3 \times 3\,\mu m^2$ have opposite features.[16] It has been directly shown that the KAI model cannot be applied due to the presence of grain boundaries, but instead the NLS model seems to be valid for the large capacitors.

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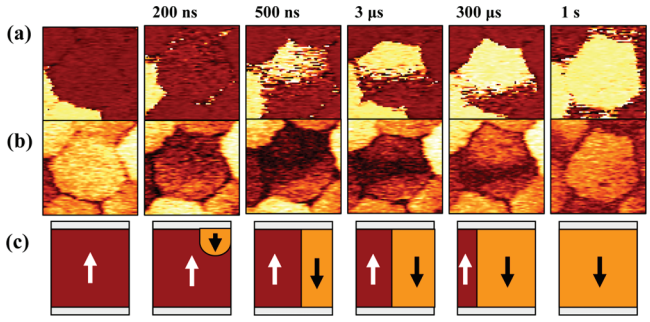

FIGURE 1. (a) PFM phase, (b) PFM amplitude images, and (c) schematic cross-sectional domain structures of instantaneous domain configurations developing at different pulse widths under an applied voltage of +2 V.

In contrast, the KAI model can be well applied to describe the switching dynamics in epitaxial ferroelectric capacitors, due to the absence of grain boundaries.[8] However, there are no direct studies on switching dynamics in ferroelectric capacitors with the characteristic size in the deep submicrometer range, i.e., nanoscale capacitors, as well as no theories capable of predicting the switching dynamics in these nanoscale capacitors. Here we present switching dynamics of nanoscale (ca. 35 nm radius) epitaxial capacitors. Due to the finite lateral size, switching in these nanoscale capacitors does not obey the KAI model, as for the micrometer large counterparts. Thus, we propose a non-KAI model to explain the switching dynamics of these nanoscale ferroelectric capacitors.

An epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PZT) thin film with a thickness of about 35 nm was deposited by pulsed laser deposition on an epitaxially grown Pt(001) bottom electrode on a MgO(001) single-crystal substrate. In order to fabricate the nanoscale capacitors on this PZT thin film, we deposited Pt top electrodes by electron beam evaporation at room temperature through an ultrathin anodic alumina membrane used as a stencil mask.[19,20] The pore size and interpore distance of the anodic alumina mask were about 70 and 100 nm, respectively, and defined the final diameter and pitch of the ferroelectric capacitors. In order to observe switching dynamics, we have used the method described by Gruverman et al. (ref 16) where voltage pulse trains of different pulse widths are applied and the switching is evaluated by subsequent direct domain imaging using PFM. The PFM measurements were preformed under ambient conditions using a commercial atomic force microscope (AFM, XE-100, Park Systems) combined with a lock-in amplifier (SR830, Stanford Research Systems). The piezoresponse images were acquired using an ac modulation voltage of 0.2−0.3 V_{rms} at 6.5 kHz applied to a conductive probe with a spring constant of 2.8 N/m. The low excitation ac voltage (0.2−0.3 V_{rms}) was especially chosen not to affect the domain configuration. Switching was evaluated by analyzing the contrast in the PFM phase images.

Figure 1 shows PFM images of the domain configuration developed at different pulse widths. Polarization switching for most of the nanoscale capacitors typically proceeds as expected via nucleation and following lateral domain growth, but unlike the case of micrometer-size capacitors, in which many nuclei occur at different places,[16,17] here only one nucleus occurs. As observed for macroscopic capacitors, nucleation occurs only in predetermined sites, corresponding most probably to local defects at the ferroelectric/electrode interface.[16,17] This is also happening in the present case of nanoscale capacitors, but there is always only one nucleus, which is always generated at the edge of the nanoscale capacitor and always in the same place. There are several reasons why this is happening. It is known and widely accepted that the nucleation occurs at the ferroelectric/electrode interface rather than inside of ferroelectric thin films. First, it is known and widely accepted that the ferroelectric/electrode interfaces and/or defects near the sample surface are preferred sites for the nucleation phenomena.[21−23] Second, the interface with the free surface at the edge of the capacitor is more prone to defects than the bulk, the surface itself being for the ferroelectric a "defect" layer where the polarization has to decay from its bulk value to zero. Moreover the edge of the capacitor forms an interface of three different phases, ferroelectric, metal electrode, and air. Finally, it is well-known that the local electrical fields are higher at the edges of the electrodes.[19] The alternative skyrmion model, which describes nonfixed nucleation, might not be applied to the present case due to predetermined nucleation sites.[24]

Although defining a nucleation density for the present nanoscale capacitors, where only one nucleation event occurs, is not really meaningful, we can nevertheless estimate the equivalent nucleation density to about 2.6×10^{14} m^{-2}. Obviously, due to the fixed size of capacitor as well as the number of nuclei, the nucleation density is always constant. This equivalent nucleation density is much larger than that of micrometer-scale epitaxial capacitors (7.1×10^8 m^{-2}).[8]

Finally, the switching then proceeds after nucleation as a one-dimensional (1D) lateral domain wall movement toward the inside of the capacitor. As shown in Figure S1 in Supporting Information, the switching of nanoscale capacitors does not follow the classical KAI switching model. There are features of the present system that are not in agreement with the KAI model. First, in general, the size of the nuclei must be negligible compared to the characteristic size of the investigated system, i.e., in the present case the capacitor radius, ensuing in this way that the nucleation process alone should not significantly affect the switched polarization. However, our experimental results show that the area of the nucleus is about 30−50% compared to the entire area of the capacitors, unlike in macroscopic cases.[8,16,17] We are aware that the present stroboscopic PFM investigation method might actually imagine minimal domains rather than nuclei, but intensive investigation showed that even the smallest nuclei have a significant volume compared to the

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entire volume of the capacitor. Due to this fact, the nucleation and growth processes need to be separately considered. Second, the KAI model is only applicable to infinite media, whereas our capacitors obviously have a finite dimension. Third, the KAI model—and the NLS model as well—are based on a statistical approach where nucleation occurs randomly in many different locations.[11,16,17] This is not the case for our nanoscale capacitors where only one nucleation event occurs always at the same position. Therefore, in order to explain switching in nanoscale capacitors, a rather deterministic approach, in which the nucleation and growth steps are separately addressed, needs to be considered.

On the basis of the present experimental results on nanoscale capacitors, we developed a simple switching model based on the following assumptions:

(i) The system is finite and has a defined shape.

(ii) There is only one nucleation event that occurs at the edge of the system (capacitor).

(iii) The characteristic dimension of a nucleus is significantly large.

(iv) The nucleation is not instantaneous. We define the nucleation time t_n as the time required for a nucleus of length l_n to occur. The nucleation time is dependent on the applied field.

(v) After nucleation, the polarization switching proceeds only by domain wall motion along one direction.

(vi) The domain wall movement can be either linear, i.e., with a constant domain wall velocity, or a logarithmic relationship with time t.

According to (vi), the distance l of the domain wall propagation at time t after nucleation has either a linear or a logarithmic relationship with time t[25−27]

$$l = v(t - t_n) \tag{1}$$

$$l = c \ln\left(\frac{v_0(t - t_n)}{c} + 1\right) \tag{2}$$

where t, t_n, v, v_0, and c are the elapsed time, the nucleation time, the domain wall velocity, and the constants related to the domain wall motion, respectively.

Figure 2a shows schematically nucleation and growth inside a capacitor of square shape. The polarization switching proceeds from the nucleus by domain wall moving across the capacitor according to either eq 1 or 2. The fraction $Q(t)$ of the total switched area to the total capacitor area can be obtained by dividing the switched area, which is directly determined from the PFM images, by the total area A of the capacitor.

For a square shape capacitor, the length of the nucleus, the distance from the nucleus to the actual position of the domain wall at the time t, the total capacitor area, and the lateral size of the capacitor are l_n, l, A, and $A^{1/2}$, respectively. The newly switched area $lA^{1/2}$ (yellow region) is given by the domain wall propagation at the time t from the nucleus (orange region). The total switched area $(l_n + l)A^{1/2}$, which is determined by the PFM imaging, is assumed to be proportional to the switched polarization. Considering the above discussion, the fraction $Q(t)$ of the switched area for a linear and a logarithmic relationship with time t of the domain wall movement can be written using eqs 1 and 2 as

$$\begin{aligned} Q(t) &= \frac{v}{\sqrt{A}}(t - t_n) + \frac{l_n}{\sqrt{A}} \quad (t_n < t) \\ Q(t) &= 0 \qquad\qquad\qquad\quad (0 < t < t_n) \end{aligned} \tag{3}$$

for the linear relationship, and

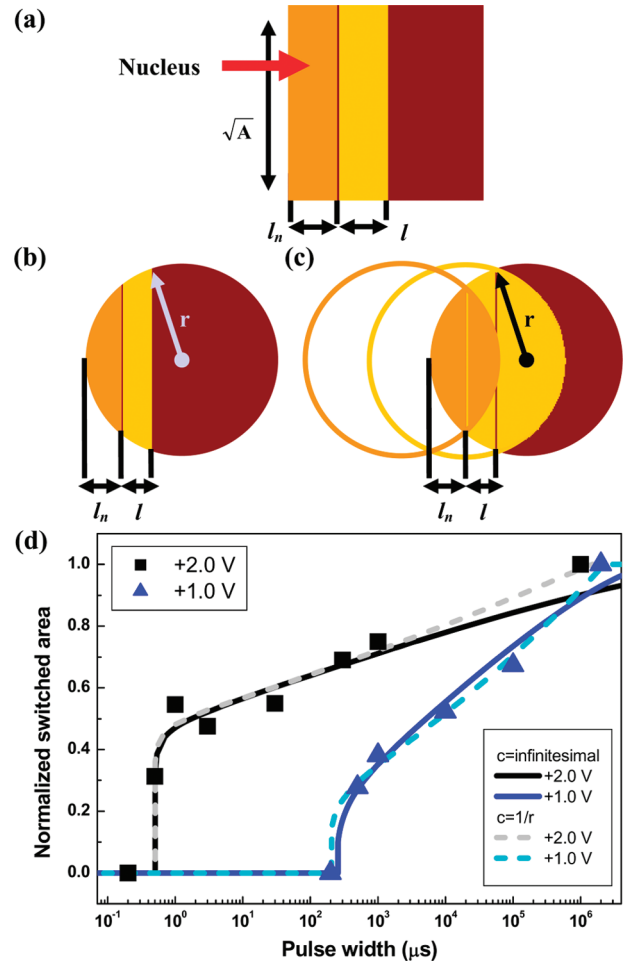

FIGURE 2. Schematics of nucleation and growth inside a capacitor of (a) square and (b, c) circular shapes. The circular capacitor has two different domain wall curvatures: (b) infinitesimal and (c) finite (1/*r*). The orange (yellow) region presents the area of nucleus (newly switched region). (d) Fitting of the pulse width dependence of the normalized switched area for +1 V (blue triangle) and +2 V (black square) by the proposed model of circular shape. The solid (dashed) line represents the fit with the curvature of infinitesimal (1/*r*) value by eq 5 [(6)].

$$Q(t) = \frac{c}{\sqrt{A}} \ln\left(\frac{v_0(t - t_n)}{c} + 1\right) + \frac{l_n}{\sqrt{A}} \quad (t_n < t)$$
$$Q(t) = 0 \quad (0 < t < t_n) \tag{4}$$

for the logarithmic relationship.

However, the time dependence of the switched area in eq 3 does not fit properly the experimental data, which indicates that the domain wall motion does not have a linear relationship with time t, i.e., domain wall velocity is not constant. Instead the relationship in eq 4 fits well the experimental data as shown in Figure S2 in Supporting Information, revealing that the domain wall velocity in nanoscale capacitors is not constant just like in macroscopic capacitors.

Moreover, the model can be refined assuming the real shape of the capacitor, i.e., a circular shape. In this case, an additional supposition needs to be postulated to the above assumptions (i) to (vi) of the model, respectively that the curvature of a domain wall remains constant during the domain wall motion. The polarization switching proceeds also from the nucleus by domain wall moving across the capacitor according to eq 2. The actual curvature of the domain wall seems to be (or close to) infinitesimal, as shown in Figure 1. However, in order to have clear information on the wall geometry, the curvatures of the domain wall are considered as either infinitesimal, i.e,. straight domain wall, or as a (maximum) value $1/r$ correlated to the initial curvature of the nucleus, where r is the radius of the capacitor, as shown in parts b and c of Figure 2. Accordingly, for both cases, the length of nucleus can be written as l_n and $2l_n$, respectively. The newly switched area (yellow region) that propagated from the area of the nucleus (orange region) is also assumed to be proportional to the switched polarization. The ratio of the total switched area to the total area at the time t, $Q(t)$, for both infinitesimal and $1/r$ curvature can be rewritten as

$$Q(t) = \frac{1}{\pi} \cos^{-1}\left(\frac{r - l_n - c \ln\left(\frac{v_0(t - t_n)}{c} + 1\right)}{r}\right) - \frac{1}{\pi r^2}\left\{r - l_n - c \ln\left(\frac{v_0(t - t_n)}{c} + 1\right)\right\} \sqrt{\left(2r - l_n - c \ln\left(\frac{v_0(t - t_n)}{c} + 1\right)\right)\left(l_n + c \ln\left(\frac{v_0(t - t_n)}{c} + 1\right)\right)} \tag{5}$$

$$(t_n < t)$$
$$Q(t) = 0 \quad (0 < t < t_n)$$

for the straight domain wall, and

$$Q(t) = \frac{2}{\pi} \cos^{-1}\left(\frac{r - l_n - \frac{c}{2} \ln\left(\frac{v_0(t - t_n)}{c} + 1\right)}{r}\right) - \frac{2}{\pi r^2}\left\{r - l_n - \frac{c}{2} \ln\left(\frac{v_0(t - t_n)}{c} + 1\right)\right\} \sqrt{\left(2r - l_n - \frac{c}{2} \ln\left(\frac{v_0(t - t_n)}{c} + 1\right)\right)\left(l_n + \frac{c}{2} \ln\left(\frac{v_0(t - t_n)}{c} + 1\right)\right)} \tag{6}$$

$$(t_n < t)$$
$$Q(t) = 0 \quad (0 < t < t_n)$$

for the $1/r$ curvature.

Figure 2d shows the fits of the experimental data by eqs 5 and 6 of the above proposed model. For both cases, with respect to domain curvatures, there is a good agreement between the experimental and calculated data on the whole time range, with only a small difference in the long pulse width region, where the real curvature ($1/r$) fits better. This shows that the domain wall moves laterally with a certain curvature which is smaller than an infinitesimal curvature (straight domain wall). The increase of the effective switching field shortens the nucleation time and increases the initial size of the nucleus. For instance, the nucleation time is 207 and 0.5 μs, and the nucleus size is about 18 and 33 nm, for switching voltages of +1 and +2 V, respectively.

Both processes, nucleation and domain wall movement, are field activated, and the activation energy of both processes needs to be estimated. We have assumed that the domain wall velocity is not constant; it has a maximum value after the nucleation, then decreases gradually during the switching process.[26] Nevertheless we have estimated an average domain wall velocity v as well as the nucleation rate R as a function of the electric field E. Figure 3 shows the values and a fitting using an exponential dependence on the electric field according to the following relationships[16,28]

$$R = R_\infty \exp\left(-\frac{\alpha_n}{E}\right) \tag{7}$$

$$v = v_\infty \exp\left(-\frac{\alpha_w}{E}\right) \tag{8}$$

where α_n and α_w are the activation fields of nucleation and wall motion, respectively. The activation fields were estimated from the slope of the linear fit in Figure 3. The values of the activation fields of nucleation and wall motion are about 1.73×10^8 and 1.87×10^8 V/m, respectively. As it can be seen, the activation field of nucleation is almost the same with that of the domain wall motion. This suggests that, as separately operated by nucleation and domain wall

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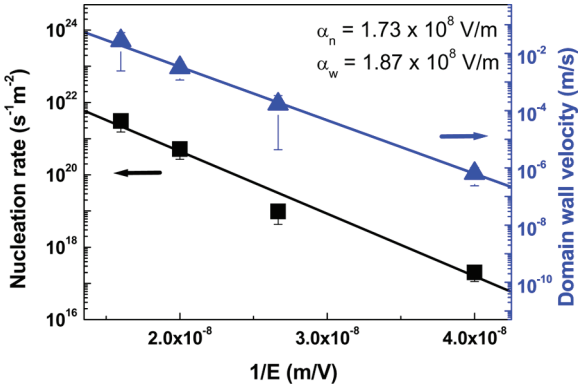

FIGURE 3. Electric field dependence of nucleation rate (black square) and domain wall velocity (blue triangle). The solid lines are approximated by eqs 7 and 8.

motion, both nucleation and domain wall motion equivalently contribute to the overall switching behavior. The obtained activation field of is of the same order of magnitude as for the micrometer-scale PZT capacitors (8.3×10^7 V/m),[16] but much larger than that of single crystal $BaTiO_3$ (4.0×10^5 V/m).[28] The domain wall motion inside the nanoscale capacitors may need more energy than for the micrometer-scale one because it occurs along the capacitor boundary.

In summary, we have investigated switching dynamics of nanoscale ferroelectric capacitors with a radius of 35 nm by direct observation of domain switching at the nanoscale using PFM. The switching dynamics of nanoscale capacitors do not follow the classical KAI model, similar to their micrometer-size counterpart. This is due to their finite size and nonstatistical time and space distribution of the nucleation processes; i.e., there is only one nucleation event occurring at the same spot. The nucleus has a significantly large size compared to the entire size of the capacitors. A simple model based on nucleation-subsequent domain growth within a finite system, a logarithmic domain wall movement, and different curvatures of domain wall was proposed for the switching dynamics of nanoscale capacitors. The results will be helpful to understand further investigations on the nanoscale switching dynamics as well as general phase transformations in small volumes of nanoscale range beyond ferroelectric materials.

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Supporting Information Available. KAI model (Figure S1), proposed model with square capacitor (Figure S2), and mathematical derivations of the proposed model with circular capacitor. This material is available free of charge via the Internet at http://pubs.acs.org.

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