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Local polarization switching in the presence of surface-charged defects: Microscopic mechanisms and piezoresponse force spectroscopy observations

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The thermodynamic description of probe-induced polarization switching in ferroelectrics is reversible and is not associated with diffusion, significant heat exchange, and strain effects. Combined with the atomic-scale width of the ferroelectric domain wall, this enables applications such as nonvolatile random access memories, ferroelectric tunnel junctions, and high-density data storage. Furthermore, electric-field induced polarization switching in ferroelectrics provides a convenient model system for more complex electrochemical processes. These considerations necessitate quantitative understanding of polarization switching in nanoscale volumes, and the role of local defects (or their absence) on the thermodynamics and kinetics of the switching process.

Ferroelectric and multiferroic films and crystals contain a range of point and extended defects in the bulk, at surfaces and interfaces. The role of defects on kinetics and thermodynamics of polarization switching is threefold. Defects can determine local phase stability (e.g., shift the Curie temperature), act as nucleation centers in-phase transitions, and act as pinning centers for moving transformation fronts. The collective role of defects on these processes has been extensively studied for the last 50 yrs. The defect contribution to the thermodynamic properties can be analyzed on a statistically averaged level. On the macroscopic level, the spatial and energy distributions of nucleation sites are a central element of Kolmogorov-Avrami type theories of phase transitions. Finally, the role of defects on domain-wall dynamics was addressed in a number of recent studies, uncovering the plethora of emergent behaviors such as dynamic phase and depinning transitions.

As a complementary approach to capacitor-based studies, switching in a nonuniform field of a scanning probe microscope has been studied by several groups. Landauer model of the prolate semiellipsoidal domain formation in an ideal ferroelectric material was adapted for tip-induced switching by Molotskii and co-workers. Recently this approach was significantly extended by taking into account a finite tip size and different surface screening conditions to determine the critical parameters of nucleation process. Overall, despite the significant effort on studies of domain switching mechanisms in ferroelectrics, the key element required for linking macroscopic statistical theories and probe
microscopy experimental studies—the influence of a single-defect center on thermodynamics of the nanoscale polarization reversal in the highly localized electric field produced by the tip—is missing.

Here we develop the thermodynamical description of the probe-induced nucleation process in the vicinity of well-separated surface field defects, relating the probe-induced phase transition to defect properties. Furthermore, we calculate the signature of local defect on piezoresponse force spectroscopy (PFS) measurements. This paper is organized as follows. Section II provides a brief overview of piezoresponse force microscopy and spectroscopy. The thermodynamics of defect-mediated phase transition, and relationship between nascent domain size and PFM signal is developed in Sec. III for arbitrary defect and domain geometry. Section IV summarizes the analytical results developed for the case of surface field defect, as suggested by Guerra and Tagantsev. Finally, Sec. V illustrates representative experimental studies of point-defect spectroscopy. This analysis lays the foundation for local studies of defect effects on phase transitions at a single-defect level.

II. PIEZORESPONSE FORCE MICROSCOPY STUDIES OF DOMAIN-DEFECT LOCAL INTERACTIONS

A significant insight into local switching processes in ferroelectrics was achieved with the invention of PFM imaging, domain patterning, and spectroscopy. In PFM, the probe concentrates an electric field to a nanoscale volume of material (∼10–50 nm), and induces local domain nucleation and growth (bias-induced local phase transition). The size of the created domain as a function of length and duration of the switching pulse is imaged, providing information of switching process. Recent studies by Ramesh and co-workers, Agronin et al., Kholkin et al., and Woo et al. demonstrate the scaling laws for bias-induced domain growth. These studies allow direct imaging of domain growth but are extremely time consuming (∼10 s/hour/location). Complementary to these are the studies by Shvartsman and Kholkin, and Likodimos and co-workers based on the statistical analysis of the domain patterns and domain-wall roughness, which provide the information on the collective effect of defect centers on the switching process.

In contrast to the direct imaging studies, switching dc bias and probing ac bias are applied to the tip simultaneously in PFM spectroscopy, offering the advantage of larger bandwidth (∼1 s/spectrum). Resulting local electromechanical hysteresis loop contains information on local switching, specifically domain size-voltage dependence. In particular, recent studies illustrate that PFS hysteresis loops often possess the fine structure that can be interpreted as the interaction between growing domain and adjacent defect. Such “non-ideal” loop shape can be noticed on many published examples of PFM spectroscopy. The work of Applanalp et al. and Harnagea et al. attribute anomalous loop shapes to high-order switching and spatial confinement effects, respectively. An extensive number of anomalous loops were collected in work by Buhlmann. The first interpretation of anomalous loop shape as due to domain-ferroelastic wall interaction was published by Le Rhun and co-workers, and Jesse and co-workers.

The significant advantage of the spectroscopic studies is that hysteresis loops can be measured at a finely spaced grid of locations on sample surface (since process is reversible, unlike, e.g., nanoindentation). In this manner, the switching can be probed at different separation from known or unknown defect, allowing to study defect role on switching systematically (e.g., by varying tip-defect separation). Correspondingly, imaging and spectroscopic studies of domain-defect interactions require both the signatures of the defect on local spectroscopic data to be established, and quantitative relationship between the defect parameters and the measured signal to be developed.

III. GENERAL APPROACH AND PROBLEM STATEMENT

Defects in ferroelectric materials are associated with the disruption in lattice periodicity and associated changes in electronic structure. Local charge redistribution in the defect core is compensated by local band bending and Debye screening, leading to the exponential vanishing of Coulomb electric fields away from the localized defect. Far from structurally distorted defect core, the electric field couples linearly to the polarization order parameter, stabilizing preferential polarization states. Therefore, the natural choice for defect model in ferroelectric material is the random-field defect, as analyzed by Gerra et al. The choice of electric field, rather than charge or elastic stress distribution, as a defect model is motivated by (a) the fact that field, rather than charge, linearly couples to the polarization, (b) the field-distribution models are less sensitive to the exact atomic and electronic structures of the defect, and (c) evident analytical expressions for free energy cannot be obtained for localized elastic defects.

A. Problem statement

We assume that the defect causes the built-in electric field that directly couples to polarization (random field). The analysis of the switching process thermodynamics is simplified for a rigid piezoelectric, for which effective material constants are independent of the electric field. The surface and electrostatic energies of the semiellipsoidal domain in semi-infinite ferroelectric material is

\[ \Phi(r, U) = \Phi_s(r) + \Phi_d(r) + \Phi_p(r, U) + \Phi_p^s(r), \]

where the surface, depolarization, tip-induced, and defect contributions to free energy are

\[ \Phi_s(r) = \psi_2 S, \]

\[ \Phi_d(r) = \frac{\mu_D}{\epsilon_D} P_{d1}^2 V, \]

\[ \Phi_p(r, U) = -2P_S \int_V d^3x \cdot E^s(x), \]
\[
\Phi_d(r) = -2P_S \int d^3x \cdot E_d^3(x). \tag{2d}
\]

S and V are the domain surface and volume, \(\psi_S\) is the domain-wall energy density, and \(P_S\) is the magnitude of material spontaneous polarization \(P = (0, 0, P_S)\). Depolarization field energy is calculated under the condition of perfect tip-surface electric contact and/or surface screening by free charges. Rigorous expression for the depolarization factor \(n_D\) is given in Ref. 45. Electric field established by the probe is \(E^d(x) = -\nabla \psi_D(x)\), and electric field created by the defects is \(E^d(x) = -\nabla \psi_d(x)\). \(U\) is the electric bias applied to the PFM probe; vector \(r\) describes the domain geometry (e.g., sizes and position).

Typical energy barriers for the polarization switching in perfect ferroelectric materials well below Curie temperature are much higher than thermal fluctuations (e.g., barrier is much greater than \(\sim 10^{-1}k_BT\) for the plain electrode geometry). Hence, the thermal disorder is anticipated to be negligibly small and the equilibrium domain growth will proceed along the lowest free-energy path on the free-energy surface given by Eq. (1). This is in agreement with high reproducibility of fine structure between the loops.37 The switching process can then be analyzed from the bias-dependent geometry of \(\Phi(r, U)\) surface.

Stable domain configurations correspond to local minima on the \(\Phi(r, U)\) surface. In the case of first-order phase transitions, the minima and coordinate origin are separated by saddle points. The saddle-point-metastable minimum pair appears at voltage, \(U_s\). The minimum becomes stable (i.e., \(\Phi(r, U) < 0\)) at the critical voltage, \(U_{cr}\). Numerically, for most ferroelectric materials for typical tip parameters, \(U_s\) is close to \(U_{cr}\). The free-energy value in the saddle point determines the activation energy, \(E_{act}\), of domain nucleation. The relaxation time necessary for the stable domain formation at \(U_{cr}\) is maximal and the critical slowing down appears in accordance with general theory of phase transitions. Within the framework of activation rate theory, the domain nucleation takes place at higher activation voltage \(U_a\) determined from the condition \(\Phi(U_a) = E_{act}\), corresponding to the activation time \(\tau_a = \tau_0 \exp(E_a/k_BT)\). For instance, the activation energy \(E_a = 20k_BT\) corresponds to a relatively fast nucleation time \(\tau_a \sim 10^{-3}\) s for phonon relaxation time \(\tau_0 = 10^{-12}\) s while the condition \(E_a = 2k_BT\) corresponds to “instant” or thermal nucleation.

The difference between the voltages corresponding to the formation of a saddle point and a stable domain, \(U_a - U_{cr}\), determines the width of the (rather thin) thermodynamic hysteresis loop. More realistic models of piezoresponse hysteresis loop formation consider domain-wall pinning effects. In the weak pinning limit, the domain growth in the forward direction is assumed to follow the thermodynamic energy minimum while on decreasing bias, the domain remains stationary due to domain-wall pinning by the lattice and atomic defects.

Further analysis is performed, assuming that the domain possesses well-defined semiellipsoidal geometry, i.e., it has radius \(r\) and length \(l\), but allowing for defect influence, its center is shifted on value \(y_0\) compared to the tip location.

![FIG. 1. (Color online) Schematics of domain nucleation in the vicinity of surface Gaussian field defect of radius \(r_D=5\) nm and maximal field strength \(E_S\) located at distance \(x_0=5\) nm from the biased at voltage \(U\) probe apex of characteristic size \(d=8\) nm, \(\gamma = 1\). (a) \(U=10\) V and \(E_S=-1\) V/nm, (b) \(U=3\) V and \(E_S = 1\) V/nm, (c) \(U=10\) V and \(E_S=1\) V/nm, and (d) \(U=30\) V and \(E_S=1\) V/nm. Contour lines correspond to the constant electric field. Domain nucleation appears inside the filled area with the highest field strength.](image)

The domain center shift, \(y_0\), is thus the parameter defining defect effect on tip-induced switching. The center of the nearest surface field defect is assumed to be located at position \(x_0=\{x_{10}, 0, 0\}\), whereas the tip is located at the coordinate origin (see Fig. 1). Hereinafter, we consider the domain center displacement as a variational parameter.

Rigorously speaking, the domain shape will deviate from semiellipsoidal when \(x_{10} \neq 0\) (the system radial symmetry is broken). However, analytical treatment of the problem necessitates a limit on the number of free parameters describing geometry and development of analytical theory requires no more than three independent parameters (e.g., domain center shift or general ellipsoid shape of the domain). Additional numerical calculations proved that the choice of domain shift, as an optimal variation parameter, works surprisingly well for domain nucleation in the presence of well-localized rotationally symmetric field defect. For instance, domain nucleation appears inside the filled area shown in Fig. 1 since the field strength is highest here. Because isopotential line shape is almost axisymmetric inside the filled area, the nucleus shape can be expected to be close to axisymmetric as well. This reflects the well-known behavior of the isopotential lines in the system of two point charges. Moreover, experimental data21 proved that deviations of equilibrium domain shape from the radial symmetry are small even in nanograin ceramics, which contained numerous surface defects.

**B. Domain-probe and domain-defect interaction energies**

For transversally isotropic material and a rotationally symmetric probe, corresponding to the prototype case of
switching in tetragonal and hexagonal ferroelectrics, the probe electric potential, \( \varphi_p(x) \), is an axially symmetric even function. Hence, \( \varphi_p(x) = \varphi_p(\rho, x_z) \), where \( x_z \) and \( x_z = \rho \) and \( x_z \) are the radial and vertical coordinates, respectively. In this case, the domain-tip interaction energy \( \Phi_{\rho}(r, l, y_0) \) can be rewritten as

\[
\Phi_{\rho}(r, l, y_0) = 2P_S \int_0^l dx_3 \int_0^{2\pi} d\varphi \int_{r_1 - \sqrt{x_3^2}}^{r_1 + \sqrt{x_3^2}} \rho d\rho E_3^p \\
\times (\sqrt{\rho^2 + x_3^2} + 2\rho y_0 \cos \varphi, x_3). \tag{3}
\]

The flattened or spherical probe potential \( \varphi_p \) can be modeled using an effective point-charge approximation. The probe is represented by a single charge \( Q \) located at distance \( d \) from a sample surface (see details in Ref. 46). The potential \( \varphi_p \) at \( x_z = 0 \) has the form

\[
\varphi_p(\rho, x_z) = \frac{Ud}{\sqrt{\rho^2 + (x_z + d)^2}}. \tag{4}
\]

Here \( \gamma = \sqrt{x_3^2 + e_1^2} \) is the dielectric anisotropy factor. In the case of local point-charge model, the probe is represented by a single charge \( Q = 2\pi e_0 e_p R_0 (\kappa + 2e_\gamma)/\kappa \) located at \( d = e_0 R_0/\kappa \) for a spherical tip or \( d = 2R_0/\pi \) for a flattened tip represented by a disk in contact, where \( \kappa = \sqrt{x_3^2 + e_1^2} \) is the effective dielectric constant.

Substituting potential Eq. (4) into Eq. (3) and performing the integration, we derive the Padé approximation for the tip-induced interaction energy for a shifted domain as

\[
\Phi_{\rho}(r, l, y_0) = \frac{-4\pi U_\rho d r^2 l / \gamma}{(\sqrt{\rho^2 + d^2 + y_0^2} + d)(\sqrt{\rho^2 + d^2 + y_0^2} + d + l / \gamma)}. \tag{5}
\]

Assuming that the defect-induced built-in electric field can be represented as \( E_3^p(x) = E_3^p(\sqrt{(x_1 - x_0)^2 + x_3^2}) \), i.e., it is rotationally symmetric with respect to the defect center, the domain-defect interaction energy can be rewritten via the overlap integral:

\[
\Phi_{d}(r, l, x_0 - y_0) = -2P_S \int_0^l dx_3 \int_0^{2\pi} d\varphi \int_{r_1 - \sqrt{x_3^2}}^{r_1 + \sqrt{x_3^2}} \rho d\rho E_3^d \\
\times \left[ (\sqrt{\rho^2 + (x_0 - y_0)^2} - 2\rho \cos \varphi(x_0 - y_0), x_3) \right]. \tag{6}
\]

Equation (6) thus describes the defect contribution into the free energy of domain.

### C. Effective piezoresponse calculations

Measured in a PFS experiment is the electromechanical response related to the size of ferroelectric domain formed below the tip. Hence, to calculate the shape of the PFM hysteresis loop, the electromechanical response change induced by the domain is required. A number of approximate solutions for PFM responses have been recently derived using decoupling approximations.47–49 Here, we employ the same approach for calculation of PFM response from the domain of arbitrary geometry. Within the framework of linearized theory by Felten et al.,50 the surface displacement vector \( u_i(x) \) at position \( x \) is

\[
u_i(x) = \int_0^\infty d\xi_3 \int_{-\infty}^{\infty} d\xi_2 \int_{-\infty}^{\infty} d\xi_1 \frac{\partial G_{ij}(x, \xi)}{\partial \xi_l} E^p_{ij}(\xi) d_k(m)(\xi, r, l, y_0) \times c_{nmij}, \tag{7}
\]

where \( \xi \) is the coordinate system related to the material, \( d_{nmij} \) are strain piezoelectric coefficients distribution, \( c_{nmij} \) are elastic stiffness and the Einstein summation convention is used, and \( E^p_{ij} \) is the electric field created by the biased probe. For typical ferroelectric perovskites, the symmetry of the elastic properties can be approximated as cubic (anisotropy of elastic properties is much smaller than that of dielectric and piezoelectric properties) and therefore an isotropic approximation can be used for Green’s function, \( G_{ij}(x, \xi). \48,51 \)

Integration of Eq. (7) for \( x_z = 0, \rho = 0 \) yields the expression for effective vertical piezoresponse, \( d_{33}^{eff} = u_3 / U \), as

\[
d_{33}^{eff}(r, l, y_0) = d_{31}g_1(r, l, y_0) + d_{35}g_2(r, l, y_0) + d_{333}g_3(r, l, y_0). \tag{8}
\]

Functions \( g_i(r, l, y_0) \) for effective vertical piezoresponse changes negligibly when the domain is far from the tip, i.e., \( |y_0| \ll |r| \) under the condition \( |y_0| \gg r \). For the opposite case \( |y_0| < r \), functions \( g_i \) have integral representations:

\[
w_1(r, l, y_0) = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \int_0^{\pi/2} d\theta \frac{3 \cos^2 \theta - 2}{3 \cos^2 \theta - 2} \times (1 + n) \cos \theta \sin \theta R_{w}(\theta, \varphi, r, l, y_0) \\
R_{C}(\theta, \varphi, r, l, y_0), \tag{9}
\]

\[
w_2(r, l, y_0) = \frac{3}{2\pi} \int_0^{2\pi} d\varphi \int_0^{\pi/2} d\theta \left[ \gamma d + \cos \theta R_{w}(\theta, \varphi, r, l, y_0) \right] \\
- \gamma \cos^2 \theta \sin \theta, \tag{10}
\]

\[
w_3(r, l, y_0) = \frac{3}{2\pi} \int_0^{2\pi} d\varphi \int_0^{\pi/2} d\theta \times d\theta \cos^3 \theta \sin \theta R_{w}(\theta, \varphi, r, l, y_0) \\
R_{C}(\theta, \varphi, r, l, y_0). \tag{11}
\]

Here, the radius \( R_{w}(\theta, \varphi, r, l, y_0) \) determines the domain-wall shape and its center position. In the typical case of prolate semiellipsoid \((r \ll l) \) or cylinder, we derive
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\[ R_n(\theta, \varphi, r, y_0) = \frac{|y_0| \cos \varphi + \sqrt{r^2 - y_0^2} \sin \varphi}{\sin \theta}. \]  

(12a)

The function \(1/R_0(\theta, \varphi, r, y_0)\) is related to the probe electrostatic potential in the domain-wall point determined by \(R_n(\theta, \varphi, r, y_0)\), namely

\[ R_n(\theta, \varphi, r, y_0) = \sqrt{|y_0| + \theta R_n(\theta, \varphi, r, y_0)^2 + \gamma^2 \sin^2 \theta R_n^2(\theta, \varphi, r, y_0) \sin \theta}. \]  

(12b)

At \(y_0=0\) (no lateral shift), expressions (9)–(11) coincide with the ones derived for domain nucleating on the tip axis in Ref. 27, as expected.

Using the approach proposed in Ref. 49 for \(y_0=0\) and superposition principle of PFM signal calculations at \(y_0=0\) [see Fig. 1(c)], we obtained Padé approximations for effective electromechanical response, \(d_{33}^{H}(r, y_0)\), as

\[ d_{33}^{H}(r, y_0) = \left[ \frac{3}{4} d_{33}^T \left[ 1 - \frac{16r}{\pi d + 8r} + \frac{8 \pi d (\pi d + 24r)}{r (\pi d + 8r)^3} \frac{y_0}{y_0} \right] \right] + \frac{d_{33}}{4} \left[ 1 - \frac{16r}{3 \pi d + 8r} + \frac{24 \pi d (3 \pi d + 24r)}{r (3 \pi d + 8r)^3} \frac{y_0}{y_0} \right]. \]  

(13)

Here, the material is regarded dielectrically isotropic, \(r=1\), \(r=r(U)\) is the voltage dependent domain radius, and \(d_{33}^{H}=d_{33}+(1+4\nu)d_{33}/3\).

**IV. SURFACE FIELD DEFECTS**

**A. Domain free energy affected by a surface field defect**

Here we adopt a model of a laterally localized surface field defect with characteristic radius, \(r_d\), and penetration depth, \(h_d\), located at the point \(\{x_0, 0, 0\}\), for which the longitudinal component of electric field is

\[ E_3^l(x) = E_S \exp \left[ -\frac{(x-x_0)^2}{r_d^2} - \frac{x_3^2}{h_d^2} \right]. \]  

(14)

Corresponding charge distribution could be related with charge accommodation at the vertical dislocation line and dislocation-surface junction (see Appendix A), as is expected for domain nucleation in polar materials. In the limit \(|x_0|<r_d\gg d\), the tip is well-separated from the defect, and hence, the defect role on tip-induced switching is minimal. Therefore, here we analyze the switching behavior for \(|x_0|<r_d\sim d\). Based on comparison with the critical nucleation domain size and switching fields, the relevant values of the penetration depth are \(h_d \sim 1\sim 2\) nm, maximal field strength \(E_S=10^8\sim 10^{10}\) V/m, and defect radius is \(r_d \sim 1\sim 50\) nm. For larger radius, the defect becomes significantly larger than PFM tip size, and hence, can be approximated by the homogeneous surface field considered in Ref. 21. Similarly, field strength below \(-10^8\) V/m is much smaller than the fields at tip-surface junction during the PFM experiment, and hence, the defect is unlikely to affect the nucleation process. Finally, the condition on penetration depth is chosen to correspond to surface field defect associated with surface structural defects.

Substituting defect-induced electric field from Eq. (14) into the domain free energy given by Eq. (2), we obtain

\[ \Phi_d(r, l) = \pi \psi_d l \left[ \frac{r}{t} + \frac{\arcsin \sqrt{1-r^2/t^2}}{\sqrt{1-r^2/t^2}} \right]. \]  

(15a)

\[ \Phi_d(r, l, y_0) = \frac{P_0^2}{\epsilon_0 \epsilon_{33}} 4 \pi r^2 l \left[ \frac{1}{3} - (r/l)^2 \right] \left[ \frac{\arctanh \sqrt{1-(r/l)^2}}{\sqrt{1-(r/l)^2}} - 1 \right], \]  

(15b)

\[ \Phi_p(r, l, x_0, y_0) = -\frac{4 \pi U P_d d^2 l / \gamma}{(\sqrt{r^2 + d^2} + y_0^2 + d)(\sqrt{r^2 + d^2} + y_0^2 + d + l / \gamma)}, \]  

(15c)

\[ \Phi_d(r, l, x_0, y_0) = -2 \pi r^2 h_d P_d E_S(d, r_0, x_0 - y_0). \]  

(15d)

The dimensionless overlap integral \(I_d(r, l, x)\) has the form

\[ I_d(r, l, x) = \left[ 1 - \exp \left( -\frac{r^2}{r_d^2} \right) \right] \left[ 1 - \exp \left( -\frac{r^2}{r_d^2} \right) \right] \left[ 1 - \exp \left( -\frac{x^2}{h_d^2} \right) \right]. \]  

(16)

After minimization of Eq. (15) with respect to the domain center shift toward the defect, \(y_0\), the domain free energy can be represented as a two-dimensional (2D) surface in coordinates \(r, l\). The nucleus size \(\{r_d, l_d\}\), minimal critical domain size \(\{r_{cr}, l_{cr}\}\), and equilibrium size-voltage dependences \(\{r(U), l(U)\}\) are found from the free-energy saddle point and minima, correspondingly.

To illustrate this behavior, below we consider the free-energy contour maps, activation barrier, critical voltage, and domain size that correspond to the states with different \(x_0\) i.e., tip positioned at different separations from the defect.

**I. Defect center below the probe apex**

Even in the simplest case when the surface field defect is located just below the tip apex (i.e., \(x_0=0\)), the spatial distribution of the driving electric field is rather complex depending on the surface field amplitude, \(E_d\), its sign, and half-width, \(r_d\). On the sample surface, the total electric field can be written as \(E_d(p, 0) = U(r^2 + d^2)^{1/2} d / \gamma + E_S \exp(-r^2 / r_d^2)\) and illustrated in Fig. 2(a).

A number of universal interesting behaviors can be predicted depending on the relative magnitude of tip-induced and defect-induced electric fields. For a positive surface field \((E_d>0)\) and a positive tip bias \((U>0)\), the field \(E_d(p, 0)\) is maximal just below the tip \((p=0)\) and so the domain forms exactly at \(y_0=x_0=0\) [see curves 1–3 in Fig. 2(a)]. For positive bias and negative surface defect of sufficient field strength, \(E_d<-U/ \gamma d\), the driving electric field \(E_d(p, 0)\) could be maximal on the ring \(r=p=0\) at \(x_3=0\) [see Fig. 2(a), curves 5 and 6]. Thus every point of the ring is an equal-probable candidate for domain nucleation. For instance, the domain-tip-defect negative interaction energy \(\Phi_d(r, l, y_0) + \Phi_p(r, l, y_0)\) depicted in Fig. 2(b) is minimal at
more than several $r_f$ should be located below the tip. Thus, the lowest thermodynamic path of domain formation effected
by the strong negative surface field defect located at $x_{01}=0$ is expected to start on the ring $\rho=y, \neq 0$ (nucleation stage) and then transforming into the stable domain with center at $y_0=0$.

Voltage-dependent free-energy surfaces defined by Eq. (15) in the presence of a surface field defect located directly
below the tip apex ($x_{01}=0$) are shown in Fig. 3. The maps are calculated for PZT-6B ceramics [modified Pb(Zr,Ti)O$_3$ solid solution].

Shown in Fig. 3 are the cross section of $\Phi(r,l,y_0)$ in coordinates of domain radius, $r$, and length, $l$, at $y_0=0$. As shown above, the case $y_0=0$ is the nucleation site for voltages $U>\gamma \delta E_S$ that corresponds to $U>8$ V for $E_S=10^9$ V/m, and $U>-8$ V at $E_S=+10^9$ V/m for chosen materials and tip parameters. Thus the saddle points in parts (b)–(f) correspond to the lowest activation barrier, whereas the saddle shown in part (a) for $U=2.5$ V corresponds to the highest barrier. Shown in Fig. 3(a) is the saddle at $y_0=0$ corresponding to the barrier of $2400 k_BT$. The lowest saddle (with activation energy $2600 k_BT$) appeared at $y_0=8$ nm (not shown since it corresponds to the ringlike nucleus).

Similar to switching on a defect-free surface, the activation barrier rapidly decreases with applied voltage. A favorable (positive) surface field defect decreases the activation barrier and thus stimulates domain nucleation at lower applied voltages [Figs. 3(d)–3(f)] in comparison with an unfavorable (negative) field defect [Figs. 3(a)–3(c)].

$y_0=6$ and maximal at $y_0=0$ for nucleus radius and typical material parameters similar to those above [note that this behavior is a result of the different distance behavior of the field components, and hence, is nonuniversal]. However, for large enough biases (2–3 V for chosen material parameters), the interaction energy becomes minimal at $y_0=0$ with domain radius increasing up to 10–20 nm, indicating that the center of the stable semiellipsoidal domain with a radius of

\begin{figure}[h]
\centering
\includegraphics[width=\linewidth]{fig2.png}
\caption{(Color online) (a) Driving electric-field $E_S(\rho,0)$ distribution on the surface at applied voltage $U=2.5$ V. Surface field defect of radius $r_f=4$ nm, penetration depth $h_f=0.8$ nm, and amplitude $E_S=0;10^9;5 \times 10^9;10^8;10^7;5 \times 10^7;10^6$ V/m (curves 0–6) is located below the tip apex ($x_{01}=0$). (b) Corresponding interaction energy via the shift $y_0$ for $E_S=-10^9$ V/m, $l=10$ nm, and different domain radius $r_f=0.4, 0.8, 1.2$ nm (figures near the curves). Material parameters $\varepsilon_3=0.5$ C/m$^2$ and $\gamma=1$; point-charge-surface separation $d=8$ nm.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\linewidth]{fig3.png}
\caption{(Color online) Voltage dependence of free-energy surfaces in the presence of surface field defect located below the tip apex ($x_{01}=0$) with radius $r_f=4$ nm, penetration depth $h_f=0.8$ nm, amplitude $E_S=-10^9$ V/m (parts a–c), and $E_S=+10^9$ V/m (parts d–f). Labels correspond to the domain shift $y_0$ in nanometer and activation energy values in $k_BT$ units. Dashed contour corresponds to zero energy. Small circle and arrow with label denote absolute minimum (equilibrium domain sizes) and activation barrier $E_a$ (saddle point and contour), correspondingly. Material parameters correspond to PZT-6B: $\varepsilon_3=0.5$ C/m$^2$, $E_S=500$, $\gamma=1$, and $\psi_s=150$ mJ/m$^2$; point-charge-surface separation $d=8$ nm corresponds to the local charge approximation for sphere-plane model of tip-surface contact.}
\end{figure}
Activation voltages (corresponding to the case when thermal nucleation is possible) are typically much greater than the critical ones (corresponding to the thermodynamic stability of the domains). For the chosen material parameters and a negative surface field \( E_S < 0 \), the critical voltage \( U_{cr} \), determined from the condition \( \Phi(U_{cr}) = 0 \) at minimum, is about 2 V, whereas the activation voltage \( U_a \), determined from the condition \( \Phi(U_a) = 20k_BT \) in a saddle point, is about 20 V [compare parts (a) and (c) of Fig. 4].

The favorable field defect \( (E_S > 0) \) acts as a nucleation center at zero or even negative voltages [see, e.g., Figs. (d) and (e)]. The surface state (i.e., stable domain with length \( l = h_d \), radius \( r \leq r_d \), and center at \( y_0 = x_0 \)) appears when the defect field strength exceeds the critical value, \( E_S^{cr} \), determined as (see Appendix B for details)

\[
E_S^{cr} = \frac{2e}{3(\varepsilon-1)} \left( \frac{\psi_S}{h_d P_S} + \frac{P_S}{e_0 e_1} \right). 
\]

The surface state becomes unstable for a negative external field \( E_0 < -E_S^{cr} \). Experimentally, the surface state will correspond to a "frozen" polarization level for low enough fields.

2. Defect at the intermediate separation from the tip apex

The effect of domain attraction or repulsion by the surface field defect with center located at different distances \( x_0 \) from the probe apex is illustrated in Fig. 4. Numerical calculations show that positive field defects with sufficient electric-field strength, \( E_S > E_S^{cr} \), located at distances \( |x_0| \leq r_d \) always act as nucleation centers at voltages \( U \geq 0 \). During this process, \( y_0 = x_0 \) in the saddle point and the positive difference \( x_0 - y_0 \) slightly increases with applied voltage increase (see insets indicating defect-induced nucleation). Even at high voltage the domain position is centered at the defect. However, the equilibrium domain position is below the tip, i.e., \( y_0 \neq 0 \) under the same conditions (see main plots indicating tip-induced growth). This analysis implies that the domain nucleates at the defect site \( y_0 \approx x_0 \) in the saddle point and then evolves to its equilibrium location below the tip \( (y_0 \approx 0) \) when the probe electric field substantially exceeds the defect field.

Negative defects with sufficient field strength located at distances \( |x_0| \geq r_d \) always delay the nucleation [Figs. 4(c)], i.e., the domain nucleus repulses from the defect, \( y_0 \approx 0 \) (see corresponding saddle points). Similarly to the case of positive field defect, the equilibrium thermodynamic domain position is below the tip (see main plots in Fig. 4).

The effect of domain attraction or repulsion by the surface field defect with center located at different distances \( x_0 \) from the probe apex is numerically analyzed in Fig. 5. Corresponding defect-mediated domain nucleation and growth in thermodynamic and weak pinning limits are shown in Fig. 6. In thermodynamic limit, critical nucleus typically appears at the nearest favorable defect site, and rapidly grows and moves as a whole toward the probe apex [see Fig. 6(a)]. In the presence of the wall pinning by the lattice or point defect that prevents domain movement as a whole, domain can only grow and thus may acquire the bulb-like shape as shown in Figs. 6(b) and 6(d). Such morphology was observed by Kholkin et al. Such morphology was observed by Kholkin et al.31
To describe the nucleus position analytically, we performed minimization on $y_0$ of the free energy Eq. (15) under the conditions $r < 2d$ and $l \leq 2y_d$, typically valid in a saddle point, and derived in Appendix B the set of approximate expressions for the shift $y_0$ at $x_{01} \neq 0$:

$$y_0(U) = \begin{cases} 
-x_d r_0 \left( d + h_d \right) E_s \exp \left( -\frac{x_0}{l} \right) & U_{E>S} > 0 \\
\frac{2y_d h_d x_{01}}{r_d^2 (d + h_d)} U & U_{E<S} < 0
\end{cases} \quad (18)$$

Equation (18) qualitatively describes the behavior depicted in Fig. 5 including the cases of nucleus repulsion ($y_0 < 0$) at $E_S < 0$ and attraction ($y_0 > 0$) at $E_S > 0$, as well as $y_0 = 0$ at $x_{01} = r_d$. As anticipated, $y_0 = 0$ at high voltages. For the stable domains with sizes $l \gg r$ and $l \gg h_d$, we obtained that $y_0 \approx 0$ for all voltages $U > \gamma [E_S d^2 h_d / r_d^2]$. At $x_{01} = 0$ and biases $0 < U < -2\gamma [E_S d^2 h_d / r_d^2 (d + h_d)]$, the (nonuniversal) ring-structure of radius $r_d [\ln \left( 2 \gamma E_S d^2 h_d / U r_d^2 (d + h_d) \right)]$ is most probable.

**B. Activation barrier, critical voltage, and domain sizes**

For a favorable field defect ($E_S < 0$), domain nucleation can be either activationless at high enough built-in field or the activation barrier is lowered compared to ideal material, rendering the process feasible at lower biases. For an unfavorable field defect ($E_S > 0$) or its absence ($E_S = 0$), the domain formation process is always characterized by the activation energy, $E_a$, determined as the free-energy value in the saddle point. Minimization of the free energy [Eq. (15)] on the nucleus sizes $r$ and $l$ leads to the estimation of the activation barrier $E_a(U)$:

$$E_a(U) = \frac{2\pi \rho \gamma / 3 \left( 3P_d d \cdot U \gamma [d^2 + y_0^2 + d^2] - \frac{P_S^2}{3\varepsilon_0 \varepsilon_{11}} \right)}{\gamma \gamma_{\cap} d^2 + y_0^2 + d^2}$$

Here the function $F(h_d) = \exp (-9\varepsilon_0 \rho \gamma / 8 h_d P_S^2)$. Corresponding nucleus sizes are $l_1(U) = r_1(U) \equiv \sqrt{3E_a(U)} / 2y_0 \gamma$, at that typically $r < 2d$ and $l < 2d$.

Activation voltages $U_{a}^{0}(E_S = 0)$ and $U_{a}^{*}(E_S \neq 0)$, corresponding to different polarization sign $\pm P_S$ (or, equivalently, forward and reverse switchings), can be determined numerically from the free energy [Eq. (15)] using the conditions $\Phi(U_a^{0}, E_S = 0, \pm P_S, l_1, r_0) = E_a$ and $\Phi(U_r^{*}, E_S, \pm P_S, l_1, r_0) = E_r$ or estimated analytically from Eq. (19). The following expressions were derived for the defect-free case:

$$U_{a}^{0} = \frac{4}{3} \gamma d \sqrt{\frac{2 \gamma \rho \gamma / 3 \gamma_{\cap} E_a P_S^2}{3\varepsilon_0 \varepsilon_{11}}}$$

and for defect-mediated switching:

$$U_{a}^{*} = \frac{\gamma}{3d} \sqrt{\left( d^2 + y_0^2 + d^2 \right) \frac{2 \gamma \rho \gamma / 3 \gamma_{\cap} E_a P_S^2 + P_S^2}{3\varepsilon_0 \varepsilon_{11}}} - \Delta U(E_S),$$

FIG. 6. (Color online) Sketch of domain nucleation, and growth in (a) thermodynamic limit and (b) weak pinning limit. [(c)-(f)] Calculated domain nucleation and growth in weak pinning limit at different $x_{01}$. Nucleus sizes are enlarged; $r(U)$ is equilibrium domain size at voltage $U$. Material parameters and tip characteristics are the same as in Fig. 5.
FIG. 7. (Color online) (a) Dependence of the energy barrier (in $k_BT$ units) on the applied voltage $U$ for surface field defect of $r_d$ $=4$ and $h_d=0.8$ nm, and field strength $E_d$ located at position $x_{01}$. Curve 0 corresponds to $E_d=0$. Curve 1 corresponds to the saddle $y_0=0$ [corresponding to the highest barrier, see schematics (b) for $E_d(y_0)$] at $E_d=-10^9$ V/m and $x_{01}=0$. Curve 2 corresponds to the saddle $y_0=0$ [corresponding to the lowest barrier, see schematics (c) for $E_d(y_0)$] at $E_d=-10^9$ V/m and $x_{01}=0$. Curve 3 is calculated at $E_d=-10^9$ V/m and $x_{01}=3r_d$. Curve 4 is calculated at $E_d=-10^9$ V/m and $x_{01}=3r_d$. Curve 5 is calculated at $E_d=-10^9$ V/m and $x_{01}=0$. Intermediate thin curves are calculated at $x_{01}=2r_d$, $1.5r_d$, $r_d$, and $0.5r_d$, nm, correspondingly. (c) Dependence of the activation voltage $U_a$ at level 2 and $20k_BT$ on the distance to defect center, $x_{01}$. PZT-6B material parameters and tip characteristics are the same as in Fig. 3.

$$\Delta U(E_d) = \frac{\gamma}{2d}(\sqrt{d^2+y_0^2}+d)E_d \exp\left[-\frac{(x_{01}-y_0)^2}{r_d^2}\right]F(h_d).$$  

Here $E_d$ is the potential barrier height chosen as a condition for thermally induced nucleation, e.g., $2k_BT-20k_BT$. The lateral domain nucleus shift $y_0$ could be estimated from Eq. (18) self-consistently.

From the analysis above, the effect of defect on the hysteresis loop shape can be predicted as follows. In the presence of a defect, the hysteresis loop is broadened by the factor $(\sqrt{1+y_0^2/d^2}+1)^2-4$ compared to the defect-free case [see Eq. (20b)] due to the change in nucleation biases. Furthermore, the loop is shifted along the voltage axis by the value $\Delta U$ due to domain-defect interactions. The value $\Delta U$ exponentially decreases with the distance $|x_{01}-y_0|$ from the defect center.

For a favorable field defect ($E_d>0$), the domain nucleation with $P_S>0$ is characterized by the smaller activation voltages, $U_a^*$, or can even be spontaneous [i.e., $U_a^*=0$ because $E_d(0)<2k_BT$] at some values of $x_{01}$ and $E_d$. This corresponds to the case when the surface state already exists at zero voltage and a certain negative voltage $U_a^*$ is required to destroy it. Voltage dependence of the domain activation energy $E_a$ is shown in Fig. 7(a). Dependences of activation voltages $U_a^*_{01}$ (at levels $2k_BT$ and $20k_BT$) on the distance $x_{01}$ from the defect center are depicted in Fig. 7(c).

For a material with PZT-6B parameters, the activation barrier may be extremely low in the vicinity of the positive surface field defect with field strength $E_d>10^9$ V/m. Curves 4 and 5 demonstrate that the surface state disappears at $U_a^*=5$ V. For a negative surface field defect, no surface state exists and the activation barrier drastically increases, as follows from curves 1 and 2. For defects with equal absolute field strength, the role of positive defect in facilitating nucleation is much more long-range than a negative one. This reflects the fact that domain has much more preferential directions away from the defect than toward the defect.

Similar analysis for the reversed domain nucleation with $P_S<0$ affected by a negative surface field $E_d<0$ requires the introduction of voltage $U_a^*$, corresponding to the surface-state disappearance ($U_a^*=0$ is possible).

We compare the influence of the defect field and location on the voltage dependence of equilibrium domain and nucleus sizes in Fig. 8.

From Fig. 7(a), the equilibrium domain sizes are insensitive to the defect position and the field strength at the chosen material parameters. Only the positions of the origins of the curves (corresponding to activation voltage $U_a^*_{01}$ or $U_a^*$) are sensitive to the defect characteristics. The reason for this behavior is the condition $U_a^*_{01} \gg U_a^*$, ($U_a^* \approx 20$ V and $U_a^* \approx 3$ V). The critical voltage $U_a^*$ depends on the defect characteristics but it governs the thermodynamic domain formation only at a close activation barrier $U_a^* \sim U_a^*$. At voltages $U \gg U_a^*$, domain growth becomes almost independent of the initial critical point. In contrast, the bias dependence of nucleus sizes is sensitive to the surface field defect, as demonstrated in Figs. 8(b) and 8(c). This analysis suggests that...
FIG. 9. (Color online) (a) Dependence of normalized PFM response on the applied voltage affected by the surface field defect. (b) and (c) PFM response loops in the weak pinning limit at surface field amplitudes 0, +10^6 V/m and 0, −10^6 V/m. Dotted (Es=0), dashed (x01=r_d and Es ≠0), and solid (x01=0, Es ≠0) curves are calculated for coercive biases \(U_a^d\), \(U_a^b\), and \(U_a^c\), estimated for nucleation onset \(E_a=20k_BT\). Piezoelectric coefficients \(d_{31} = 135.6 \text{ pm/V}, \ d_{33} = -28.7 \text{ pm/V}, \) and \(d_{31} = 74.9 \text{ pm/V}\) are used. (d) Typical experimental PFM response loop with fine structure (filled regions) (Ref. 37).

the primary influence of the surface field effect on the domain switching is the shift of activation energy (saddle point on free-energy surface) while equilibrium domain size is almost unaffected.

C. Effective piezoresponse and hysteresis loop fine structure

The effect of a surface field defect on the voltage dependence of the effective piezoresponse \(d_{33}^{eff}(V)\) calculated from Eqs. (9)–(11), (12a), and (12b) is shown in Fig. 9(a). Similarly to the behavior in Fig. 8(a), only the starting points of the piezoresponse curves (voltages \(U_{a^d}, U_{a^b}, \) or \(U_{a^c}\)) are sensitive to the defect characteristics. However, the change in the nucleation voltage defines piezoresponse loop fine structure and horizontal asymmetry, as shown in Figs. 9(b) and 9(c).

For the above scenario, the positive (PNB) and negative nucleation biases (NNB) can be written as \(U_{a^d}^{+} = \Delta U_{a^d}^{+} \) and \(U_{a^d}^{-} = -\Delta U_{a^d}^{-} \), correspondingly, where \(\Delta U_{a^d}\) is the activation voltage that corresponds to defect-free nucleation [see symmetric dotted loops in Figs. 9(b) and 9(c)] and \(\Delta U\) is described by Eq. (20c). The shift along the voltage axis is a direct effect of a defect influence. For \(E_s > 0\), the nucleation bias can be zero, \(U_{a^d}^{+} = 0\), as shown in Fig. 9(b). In this case, the piezoresponse loop exhibits fine structure at voltage \(U_{a^d}^{0}\), i.e., a bumplike feature corresponding to a delayed nucleation [the filled region in Fig. 9(b)]. For a negative surface field, \(E_s < 0\), the piezoresponse loop fine structure appeared at voltage \(U_{a^d}^{-}\) and represents a bumplike feature corresponding to rapid switching within the defect [the filled region in Fig. 9(c)]. Such loop fine structure is often observed on experimental data,\(^3^7\) as shown in Fig. 9(d).

Performing analysis proved that the presence of the localized surface field defects can strongly affect the structure of the hysteresis loop in PFM, inducing significant asymmetry and introducing reproducible fine-structure features. Thus, the analysis of the fine structure and its variation from point to point on the surface can potentially provide information on the density and strength of the defect, i.e., allowing the disorder potential to be reconstructed.

V. SURFACE STATE MAPS AND FINE-STRUCTURE LOOP DECONVOLUTION

The analysis of switching spectroscopy PFM (SS-PFM) three-dimensional (3D) data sets allows the characteristic parameters describing polarization switching such as work of switching (area within the loop), positive and negative nucleation biases, positive and remnant coercive biases, etc. to be plotted as 2D maps, correlating switching behavior with local topography. Characteristic feature of the field defect on the surface is the asymmetry of local nucleation bias. Illustrated in Fig. 10 are dependences of activation voltage on the distance from the defect, defect maximum field, and defect radius in PZT-6B.

The quantitative description of the piezoresponse loop \(d_{33}^{eff}(U)\) fine structure requires several steps to be followed, including (i) tip shape calibration, (ii) deconvolution of the domain radius-voltage dependence \(r(U)\), and (iii) analysis of
FIG. 11. (Color online) (a)–(c) Normalized PFM response loops in 200-nm-thick BiFeO₃ film with growth defects. (d) Tip calibration. Effective charge-surface separation \(d = \varepsilon_R R/\kappa\) at BiFeO₃ polarization \(P_s = 0.5 \ \text{C/m}^2\) with permittivity \(\varepsilon_{13,33} = 80\). Ambient permittivity value \(\varepsilon_1 = 11\) was obtained from the fitting of domain-wall profile (d) within the nominated tip curvature \(R_t = 50 \ \text{nm}\). (e)–(g) Voltage dependence of domain radius deconvoluted from (a)–(c).

For deconvolution, the following parameters have been used: \(d_{13} = 26 \ \text{pm/V}, d_{15} = 3.5 \ \text{pm/V}, d_{31} = -12 \ \text{pm/V},\) and \(\gamma = 1\) (Ref. 55).

Deconvolution of the 3D data set of ferroelectric hysteresis loops acquired at each point of the image represents a complex problem, generally amenable only to numerical algorithms. However, well-separated multiple field defects can be considered as a linear superposition of individual defects. Then generalizing analytical expressions [Eqs. (20)] for a distribution of Gaussian defects, deconvolution of the defect parameters from hysteresis loop nucleation bias and fine structure is possible as summarized below.

Typical deconvolution examples of BiFeO₃ hysteresis loops affected by growth defects are shown in Fig. 11. It is clear that \(U^c\) values could be (a) negative, (b) approximately zero, or (c) positive. Description of experimental details can be found in Ref. 37.

Deconvolution of the 3D data set of ferroelectric hysteresis loops acquired at each point of the image represents a complex problem, generally amenable only to numerical algorithms. Using Eqs. (20), we derive a simplified analytical model for the deconvolution of the nucleation bias and fine-structure maps. For positive and negative nucleation bias maps for the case of nucleation below the tip, the nucleation biases are

\[
U^c_{an} = \pm U^0_a - 2 \gamma d \sum E_{di}(x_{1a}, x_{01a} - x_{2a}, x_{02a}),
\]

where \(n = 1 \ldots N\) is the number of scanning points, \(\{x_{1a}, x_{2a}\}\) and \(\{x_{01a}, x_{02a}\}\) are the center position of \(i\)th surface field defect, and \(E_{di}(x_{1a}, x_{2a})\) is the domain center position that coincides with the tip apex location.

From Eq. (21) the defect-free nucleation bias

\[
U^0_a = \frac{N}{N} \sum \frac{U_a^n - U_a^m}{2N} - 2 \gamma d \sum E_{di}(x_{1a} - x_{01a}, x_{2a} - x_{02a}),
\]

and the bias difference (horizontal imprint bias)

\[
\Delta U_{an} = U_{an} + U_{am} = - 2 \gamma d \sum E_{di}(x_{1a} - x_{01a}, x_{2a} - x_{02a}).
\]

For purely surface field defects, Eq. (23) allows the reconstruction of the electric fields of the defect directly from the SS-PFM imprint map where separation \(d\) is determined from the probe calibration and the relevant basis for the resulting field \(\Sigma E_{di}(x_{1a}, x_{2a})\) expansion is chosen. For the Gaussian basis considered, the \(i\)th defect surface field is \(\tilde{E}_{di}(x_{1a}, x_{2a})\) and is given by

\[
\tilde{E}_{Si} = E_{Si}(h_{di}) = \tilde{E}_{Si} \exp \left[\frac{-\gamma d^2}{(x_{1a}^2 + x_{2a}^2) / d_{di}}\right],
\]

where \(\tilde{E}_{Si} = E_{Si}(h_{di})\) is the field amplitude.

The voltages corresponding to the fine-structure features are

\[
U^c_{Sn} = \left(\gamma d + y_{0m}^2 / 3d^2\right)^2 \left[ U^0_a - 2 \gamma d \sum E_{di}(y_{01a}^i - x_{01a}, y_{02a}^i - x_{02a}) \right],
\]

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Gaussian fits from the imprint biases

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The amount of defects

zoomed imprint

maps

Deconvolution of experimental data, nucleation and

free-field defects in accordance with Eq.

\( U_{an} \) in the scanning

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in the points

The set of parameters

the defect can impede or facilitate the nucleation, resulting in

switching is controlled by the defect, giving rise to univer-
sality of switching behavior.

The thermodynamics of bias-induced phase transition in

ferroelectric material in the presence of well-localized sur-

face field defects is analyzed, providing the extension of

Landauer-Molotskii phenomenology. We demonstrate that

well-localized field defect significantly affects the activation

energy and nucleation bias of domain formation, and derived

corresponding closed-form analytical expressions. Depend-

ing on the relative sign of the defect field and tip potential,

the defect can impede or facilitate the nucleation, resulting in

significant asymmetry of the hysteresis loop in piezoresponse

force microscopy. For the case of well-localized defects, the

equilibrium domain size is not affected by the defect strength

at high voltages while the nucleation voltage required for

switching is controlled by the defect, giving rise to univer-

sality of switching behavior.

The domain-defect interaction results in the reproducible

fine structure of the hysteresis loops, somewhat similar to the

force-distance curves in force-based atomic force micros-

copy. The presence of a reproducible fine feature is indica-

tive of the finite defect size since extended defects (much

larger than tip size) will result in uniform shift of hysteresis

loop along the voltage axis. Correspondingly, fine feature

variations in SS-PFM maps are predicted to be strongly cor-

related with nucleation bias distributions. This behavior is

found to be in good agreement with experimental data on

model Pb(Zr, Ti)O3 and BiFeO3 materials. The approach for

the deconvolution of the hysteresis loop fine structure and

analysis of the defect parameters has been demonstrated.

Presented analysis performed for local polarization

switching can be similarly extended to other voltage induced

phase transitions, including amorphization-crystallization in

phase change memories, bias-induced metal-insulator transi-

tions, and electrochemical reactions. For electromechanically

active materials such as ferroelectrics and multiferroics,

biopolymers, and biological systems, the detection method

can be based on local electromechanical response. The com-

bination of scanning probe microscopy with in situ electron

microscopy will allow correlation of defect-mediated ther-

modynamics and kinetics of phase transitions with atomic

structure, paving the pathway for understanding the atomistic

mechanisms of switching.

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APPENDIX A: FIELD DEFECT CHARGE-DENSITY DETERMINATION

We define the coordinate system with the origin at the defect center \( \{x_0, y_0, z_0\} \) and use the cylindrical coordinate system \( \{r, \phi, z\} \). The bulk charge density \( \sigma_d(\rho, z) \) induced by the axisymmetric field defect with a given \( z \) component of the electric field, \( E_z^d(\rho, z) \), can be found from the system of electrostatic Maxwell equations \( \nabla \mathbf{E} = 0 \) and \( \varepsilon_0 \ \text{div}(\varepsilon \mathbf{E}) = -\sigma_d \). In cylindrical coordinates \( \{\rho, \phi, z\} \), we obtain

\[
\frac{\partial}{\partial z} E^d_z(\rho, z) = \frac{\partial}{\partial \rho} E^d_\rho(\rho, z), \quad E^d_\rho(\rho, z) = \int_z^{\infty} \frac{\partial}{\partial \rho} E^d_\rho(\rho, z') dz'.
\]

(A1)

The charge density is maximal near the surface and rapidly decreases with depth, \( z \). However it tends to constant value at \( z \to \infty \), namely

\[
\sigma_s(x, y, \infty) = -4 \varepsilon_0 \varepsilon_{11} E_s \exp \left[ -\frac{(x-x_0)^2 + y^2}{r_d^2} \right] \left( \frac{r_d^2}{r_d^2} - \frac{(x-x_0)^2 - y^2}{r_d^2} \right).
\]

(A5)

Thus Eq. (A4) describes a continuous distribution resembling that of a charged dislocation line, in agreement with analysis in Ref. 53.

The dimensionless overlap integral \( I_d(r,l,x) \) in Eq. (16) has the form

\[
I_d(r,l,x) = 2 \int_0^{h_d} dz f(z) \exp(-z) \int_0^{r_d} \rho d\rho \\
\times I_0 \left( \frac{x}{2 \rho r_d} \right) \exp \left( -\rho^2 - \frac{x^2}{r_d^2} \right) \\
= \left[ 1 - \exp \left( -\frac{l}{h_d} \right) \right] \\
\times \left[ 1 - \exp \left( -\frac{l^2}{h_d} \right) \right] \exp \left( -\frac{x^2}{r_d^2} \right).
\]

(A6)

APPENDIX B: APPROXIMATE ANALYTICAL ANALYSES

1. Saddle point

To obtain approximate analytical results, we simplify the free energy [Eq. (15)] under the conditions \( r < 2d \) and \( l \) and

\[
\sigma_d(\rho, z) = \varepsilon_0 \left\{ \frac{\varepsilon_{11}}{\rho} \left[ \delta_{\rho} E^d_\rho(\rho, z) \right] + \frac{\varepsilon_{33}}{\partial z} E^d_z(\rho, z) \right\}. \quad \text{(A2)}
\]

Equation (A1) should be supplemented with relevant boundary conditions. For the perfect electric contact between the conductive tip and surface, \( E_z^d(\rho, z=0)=0 \) and \( -\varepsilon_3 \varepsilon_0 E^d_z(\rho, z=0)=\sigma_s(\rho) \). The same model was used for depolarization and interaction energy calculations [e.g., Eq. (15)]. The free charge density \( \sigma_d(\rho) \) is located inside the screening layer, or flattened tip apex or top electrode. Further derivation depends on the expression for \( E_z^d(\rho, z) \). Z component of the electric field is

\[
E_z^d(x, y, z) = E_s \exp \left[ -\frac{(x-x_0)^2 + y^2}{r_d^2} - \frac{z}{h_d} \right]. \quad \text{(A3)}
\]

Corresponding defect charge density is

\[
\sigma_d(x, y, z) = -\varepsilon_0 E_s^2 \frac{3 \varepsilon_{11}^2 [\exp(z/h_d) - 1]}{h_d r_d} \left( \frac{l^2}{h_d} \right)^2 \left( \frac{r_d^2}{r_d^2} - \frac{(x-x_0)^2 - y^2}{r_d^2} \right). \quad \text{(A4)}
\]

\[<2 \gamma d, \text{ typically valid at nucleation stage (i.e., in a saddle point).} \]

For \( l < h_d \) and \( r < r_d \), the free-energy [Eqs. (15) and (16)] Padé approximation becomes

\[
\Phi = f_s r^2 S_d(\xi) + f_d r^2 N_d(\xi) + (f_U + f_d) r^3 / \xi. \quad \text{(B1a)}
\]

Note that Eq. (B1a) is valid at \( d < h_d \) (since \( r_d > h_d \)).

For \( r > r_d \) and \( I \gg h_d \), it acquires the form

\[
\Phi = f_s r^2 S_d(\xi) + f_d r^2 N_d(\xi) + f_d^2 / \xi + f_d h_d^2 / \xi. \quad \text{(B1b)}
\]

In Eqs. (B1) the domain aspect ratio \( \xi = r/l \) determines the shape-function \( S_d(\xi) \) and depolarization factor \( N_d(\xi) \). The characteristic energies are \( f_s = \pi \eta \), \( f_d = 4 \pi P_s^2 / 3 \varepsilon_0 \varepsilon_{11} \), \( f_d(U) = -\pi P_s d U / \sqrt{(d^2 + \eta^2 + d^2)^2} \), and \( f_d = -2 \pi P_s E_s \times \exp \left[ -(x_0 - y_0)^2 / r_d^2 \right] \). The nucleus center shift \( y_0 \) should satisfy transcendental equation \( f_d(U + f_d) / \eta d y_0 = 0 \).

Minimization of Eq. (B1a) on the variables \( r \) and \( \xi \) leads to the parametric dependences on \( \xi \) of domain radius \( r \), length \( l \), and activation energy \( E_a \):

\[
r(U) = \frac{-2 \xi \delta S_d(\xi)}{3 \left[ f_U + f_d + f_d \delta N_d(\xi) \right]}, \quad \text{(B2a)}
\]

\[
l(U) = \frac{-2 \xi S_d(\xi)}{3 \left[ f_U + f_d + f_d \xi N_d(\xi) \right]} \quad \text{(B2b)}
\]
Transcendental equation for the parameter $\xi$ has the form:

$$
\xi^2 \frac{2S_D(\xi)[dN_D(\xi)/d\xi] - 3N_D(\xi)[dS_D(\xi)/d\xi]}{2S_D(\xi) + 3\xi[dS_D(\xi)/d\xi]} = \frac{f_U + f_d}{f_D}.
$$

At $\xi \to 1$ denominator $2S_D(\xi) + 3\xi[dS_D(\xi)/d\xi]$ tends to zero so that for the case of high biases $-(f_U + f_d) \gg f_D$, one can obtain approximate expressions for $\xi$. For the corresponding $S_D(\xi)$ and $N_D(\xi)$, the asymptotic representation is $\xi \approx 1 + f_d/2(f_U + f_d)$ (see Fig. 13).

The expression along Eq. (B2) leads to:

$$
r(U) \approx \frac{-4f_S}{3(f_U + f_d) + f_D},
$$

$$
l(U) \approx \frac{-4f_S}{3(f_U + f_d) + f_D} \left[ 1 - \frac{f_D}{2(f_U + f_d)} \right],
$$

and

$$
E_a(U) \approx \frac{32(f_d)^3}{3[3(f_U + f_d) + f_D]^{5/2}}.
$$

The Eqs. (B2)–(B4) are valid for $l \ll h_d$ and $r \ll r_d$ (by definition $r_d \gg h_d$).

Consideration of the free energy [Eq. (B2)–(B4)] valid in the opposite case, $l \gg h_d$ and $r \gg r_d$, leads to the same functional dependencies [Eqs. (B3)], where $f_U + f_d \to f_U$. Taking into account that the overlap integral [Eq. (16)] derivatives on $l$ exponentially vanish as $\exp(-l/h_d)$ with domain length increase and the critical nucleus length, estimated under the condition $f_U + f_d \to f_D$, is about $1.5(f_U/f_D)$, expressions, particularly cases $l \ll h_d$ and $r \gg r_d$, can be joined by substitution $f_U \to f_D \exp(-3f_U/2f_Dh_d)$. Thus, substituting the characteristic energies in Eq. (B4) yields

$$
E_a(U) = -\frac{4f_S^2S_D(\xi)^3}{27(f_U + f_d + f_D\xi N_D(\xi))^2}.
$$

FIG. 13. (Color online) Parameter $\xi$ via the ratio $-(f_U + f_d)/f_D$. Solid curve is exact solution and dashed curve is approximation $\xi = 1 + f_d/2(f_U + f_d)$.

FIG. 14. (Color online) Dependence of activation voltage $U_a$ on (a) the distance $x_{01}$ from the positive field defect (field strength $E_{x}=10^9$ V/m, $r_d=10$ nm, and $h_d=0.8$ nm) and (b) maximum defect field strength $E_s$ for $x_{01}=0$ in BiFeO$_3$ for different values of activation energy $E_a$ (figures near curves are $E_a$ values in $k_BT$ units). (c) and (d) Contour maps of $U_a$ via the distance $x_{01}$ and defect radius $r_d$ at $E_s=20k_BT$ (figures near the curves are $U_a$ values in V) for field strength (c) $E_s=10^9$ V/m and (d) $E_s=-10^9$ V/m. Material parameters correspond to a tetragonal BiFeO$_3$: $P_S =0.5$ C/m$^2$, $\varepsilon_{11}=\varepsilon_{33}=80$, $\gamma=1$, and $\phi_S=100$ mJ/m$^2$. Point-charge-surface separation $d=7$ nm.

Here the function $F(h_d)=\exp(-9\varepsilon_0\phi_S/8h_dP_S^2)$, where the thickness $\varepsilon_0\phi_S/P_S^2$ is proportional to the intrinsic domain-wall width, of the order of several lattice constants. It reflects...
the fact that the critical domain sizes cannot be smaller than the width.

2. Domain center shift

Minimization of the free energy [Eq. (B1a)] on \( y_0 \) leads to the transcendental equations:

\[
y_0(U) = \frac{x_0 E_S \exp\left[-\frac{(x_0 - y_0)^2}{r_d^2}\right]}{E_S \exp\left[-\frac{(x_0 - y_0)^2}{r_d^2}\right] + 4U r_d^2 d \gamma (d^2 + y_0^2 + d)^3 (d^2 + y_0^2)}.
\]

(B6a)

Equation (B6a) can be rewritten as

\[
y_0 - \frac{x_0}{r_d} \exp\left[-\frac{(y_0 - x_0)^2}{r_d^2}\right] = \frac{-4U y_0 d}{E_S \gamma (d^2 + y_0^2 + d)^3 (d^2 + y_0^2)}.
\]

(B6b)

In special case \( x_0 = 0 \), Eqs. (B6) give two possibilities: \( y_0 = 0 \) for \( E_S U > 0 \) and the special point \( y_0 = y_r \neq 0 \), corresponding to the divergence of domainenergizer and existing at \( E_S U < 0 \), namely:

\[
y_r = \pm r_d \sqrt{\ln\left(-\frac{\gamma E_S \gamma d^2 + y_r^2}{4r_d^2}\right)} = \pm r_d \sqrt{-2 \frac{\gamma E_S d^2}{r_d^2}}.
\]

(B7)

When the denominator in Eq. (B6a) is finite, it includes the cases \( y_0 < 0 \) at \( U E_S < 0 \) and \( y_0 > 0 \) at \( U E_S > 0 \). So, under the condition \( x_0 \neq 0 \), approximate expression for the shift \( y_0(U, r_d, l_d) \) is

\[
y_0 \approx \begin{cases} 
\frac{x_0 E_S \exp\left[-\frac{x_0^2}{r_d^2}\right]}{E_S \exp\left[-\frac{x_0^2}{r_d^2}\right] + U r_d^2 2d \gamma}, & E_S U > 0 \\
\frac{2 \gamma^2 \frac{x_0^2}{r_d^2} \exp\left[-\frac{x_0^2}{r_d^2}\right]}{\left(2 \gamma^2 \frac{E_S}{r_d^2} - 1\right) \left(2 \gamma^2 \frac{x_0^2}{r_d^2}\right)}, & E_S U < 0
\end{cases}
\]

(B8)

Note that Eqs. (B7) and (B8) are derived for the case \( l < h_d \) and \( l < y_d \). Also we consider the case \( l > h_d \), \( l > y_d \), and obtained after elementary transformations:

\[
y_r = \pm r_d \sqrt{\ln\left(-\frac{2 \sqrt{2} \gamma E_S d^2 h_d}{U r_d^2}\right)}.
\]

(B9)

Under the condition \( x_0 \neq 0 \) and \( E_S > 0 \),


The kinetic instability corresponding to the switching between these two saddles \((y_0 = 0 \) and \( y_0 = y_r \)) is possible while in thermodynamic limit, the one corresponding to the lowest activation energy is realized.

3. Surface state critical field

From symmetry considerations, \( x_0 = y_0 \) under the absence of external voltage \( U \). For the case, numerical simulations proved that spontaneous (i.e., activationless) domain appearance is possible at \( P_3 E_S > 0 \). At \( U E_S > 0 \), the free energy is

\[
f_S = -\frac{\gamma E_S}{2r_d^2} \left(1 - \exp\left(-\frac{r_d^2}{r_d^2}\right)\right) \left[1 - \exp\left(-\frac{r_d^2}{r_d^2}\right)\right].
\]

Typically, the spontaneous domain appears with sizes \( l < r_d \), \( h_d < r_d \), and \( l < r \) (since \( h_d < r_d \)) if the built-in field is more than the critical value: \( E_{cS} = \left(2/3\right)\left(\psi_d / h_d P_S + P_0^b / \epsilon_{0} \epsilon_{11}\right) \). More rigorous estimation of the critical built-in field of surface-state appearance leads to

\[
E_{cS} = \frac{2e}{3(e - 1)} \left(\frac{\psi_d}{h_d P_S + \epsilon_{0} \epsilon_{11}}\right).
\]

(B11)

The voltage of the saddle-point appearance (preceding to the critical point or surface-state origin) could be estimated from Eq. (B5c) as \( E_a \approx 2 \sim 20 k_B T \), allowing for the condition \( y_0 \sim x_0 \) at \( U_{cS}^* E_S \leq 0 \). Note, that the voltage could be negative, indicating the possibility of surface-state (meta)stability.

Under the condition \( E_S > 0 \), the jump appeared at voltage \( U_a^* < 0 \) \((U_a^* = 0)\) of surface domain state origin,

\[
U_a^* = \frac{\gamma}{3d} \left(\frac{2\pi \psi_d}{3E_S P_S} + \frac{|P_3|}{3\epsilon_{0} \epsilon_{11}}\right)
\]

(B12a)

Under the condition \( E_S < 0 \), the jump appeared at voltage \( U_a^* > 0 \) \((U_a^* = 0)\) of surface domain state appearance,

\[
U_a^* = -\frac{\gamma}{3d} \left(\frac{2\pi \psi_d}{3E_S P_S} + \frac{|P_3|}{3\epsilon_{0} \epsilon_{11}}\right)
\]

(B12b)

Here \( E_a \) is the activation energy chosen as condition for thermally induced nucleation, e.g., \( 2k_B T \sim 20 k_B T \).

Illustrated in Fig. 14 are dependences of activation voltage on the distance from the defect, defect maximum field, and defect radius in BiFeO3 of tetragonal symmetry.
