# Pressure-induced switching in ferroelectrics: Phase-field modeling, electrochemistry, flexoelectric effect, and bulk vacancy dynamics

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Pressure-induced polarization switching in ferroelectric thin films has emerged as a powerful method for domain patterning, allowing us to create predefined domain patterns on free surfaces and under thin conductive top electrodes. However, the mechanisms for pressure-induced polarization switching in ferroelectrics remain highly controversial, with flexoelectricity, polarization rotation and suppression, and bulk and surface electrochemical processes all being potentially relevant. Here we classify possible pressure-induced switching mechanisms, perform elementary estimates, and study in depth using phase-field modeling. We show that magnitudes of these effects are remarkably close and give rise to complex switching diagrams as a function of pressure and film thickness with nontrivial topology or switchable and nonswitchable regions.

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#### I. INTRODUCTION

Nanoscale ferroelectrics have attracted broad attention as potential materials for domain wall electronics [1–3], tunneling barriers, [4–6], and data storage [7]. Many of these applications are based on thin film, nanowire, or nanoparticulate materials at the device stage or intermediate synthesis steps, giving rise to significant interest in the physical functionalities and microstructure evolution in these materials. This in turn necessitates spatially resolved studies of these materials systems, readily enabled via Piezoresponse force microscopy (PFM) [8,9] and associated spectroscopies [10–13]. Multiple observations of domain nucleation and dynamics [14–16], domain wall pinning and geometry [17–20], and local switching behaviors [21–23] have been reported, providing new insight into physics of these materials and stimulating new directions of scientific enquiry.

The associated theory of signal formation mechanism in PFM originating from the bias induced piezoelectric deformation of the solid has been developed [8] and further extended to describe spectroscopic signals reflecting the formation and evolution of the domain or displacement of domain wall. This simple interpretation was supported by the exact [24,25]and decoupled theories [26,27] that related the measured signal, piezoelectric, dielectric, and elastic properties of materials, and domain/wall geometries [28-30], often with the analyses available in the form of simple linear relationships. Jointly, these theoretical developments provide well developed numerical foundation of PFM and establish the veracity of physical interpretations. This has further stimulated studies of ferroelectric switching behaviors using rigid polarization (P =const) models [13,31-35] and Landau-Ginzburg-Devonshire (LGD) theory based models in which polarization is defined from the minimum of corresponding free energy functional [20,23,36–41]. However, in all these analyses, the driving force for the ferroelectric switching is the modification of

While electric field-induced ferroelectric switching has been well understood, there have been recent reports on mechanical pressure-induced switching in ferroelectric thin film via a scanning probe. The latter becomes important as it potentially allows to create domain structures in the systems with conductive top electrode [42]. To date, pressure switching is preponderantly attributed to the flexoelectric effect, i.e., polarization and associated electric fields induced due to the large strain gradient near the tip on top of the film [42–46]. However, a broader context for tip bias and pressure -induced phenomena is given by multiple recent studies that emphasize the role of surface and electrochemical phenomena in ferroelectrics and other oxides [47,48], ranging from vacancy dynamics at surfaces and interfaces [49] to oxygen exchange to more complex electrochemical phenomena [50,51]. The possibility of tip induced electrochemical phenomena is vastly amplified under the SPM tip, with high localization of mechanical strains and electric fields. In fact, several studies exploring irreversible tip-induced electrochemistry of ferroelectrics have been reported [50,52,53]. On the other hand, arising attention has been paid to the importance of strain gradient and surface/bulk electrochemical phenomena in ferroelectric thin film. For example, stress and its gradient effect has been used to explain the graded ferroelectric thin film in both experiments [54,55] and theories [56,57]. And the importance of surface charge screening, surface-adsorbed polar molecules in ferroelectric oxide thin film has been studied by DFT calculations [58,59] and synchrotron x-ray scattering [60]. Surface modification has recently been realized to control the electrical properties of the two-dimensional electron gas (2DEG) at LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interfaces [61,62]. These results ignited our investigation into the electromechanical and electrochemical interactions with ferroelectric polarization in the scanning probe scenario. Furthermore, chemical changes and ionic dynamics under tip underpin the electrochemical strain microscopy, demonstrated

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electrostatic energy by applied electric field, i.e.,  $f_{elec} \sim -\mathbf{PE}$ , where **P** is the polarization vector and **E** is the electric field, and mechanical response stems purely from piezoelectricity and electrostriction.

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to provide readily discernible contrast to a large gamut of nonpolar materials [63,64].

These considerations necessitate the detailed analysis of the comparative role of ferroelectric, surface, and bulk electrochemical phenomena in the mechanisms of PFM switching in ferroelectric films. Here, we focus on the switching under the mechanical [43] stimuli, to follow a set of work where mechanism of bias-induced strain formation in the ferroelectrics with ionic and flexoelectric couplings have been explored [65–69]. Here, we utilize both the simple analytical estimates and the phase-field modeling with chemical boundary conditions to quantify these contributions, and analyze their observability. Surprisingly, the magnitudes of these effects (given the uncertainty in experimentally known constants) are remarkably similar, suggesting the importance of multiple coupled mechanisms of pressure-induced switching.

## II. ELEMENTARY PHENOMENOLOGY OF TIP-INDUCED POLARIZATION SWITCHING

The ferroelectric materials are characterized by strong coupling between the polarization, mechanical, and chemical phenomena. Here, we classify basic mechanisms and derive simple numerical estimates for possible pressure-induced switching. Here, the analysis is based on the LGD thermodynamic potential, including bulk and surface contributions from ferroelectric, ferroelastic, ionic and electronic subsystems, as given in Refs. [65,70,71] as well as in Supplemental Material [72] along with the chosen boundary conditions and numerical values of parameters collected from Refs. [73-75]. In this, Euler-Lagrange equations for ferroelectric polarization components  $P_i$  obtained from the LGD-potential variation are coupled with electrostatic equations for electric field, material equations relating the field and displacement, generalized Hooke's relations, and mechanical equilibrium equations for elastic stresses  $\sigma_{ij}$  and strains  $u_{ij}$ . Elastic boundary conditions are  $\sigma_{ij}n_j|_{S_j} = -p_i^{\text{ext}}$  at the free surfaces of the system, where  $n_j$  is the component of the outer normal to the surface, and  $p_i^{\text{ext}}$  is the external pressure (e.g., imposed by the tip) [76]. The boundary conditions for  $P_i$ , which in general case should be of the third kind [77], become inhomogeneous via joint action of external pressure and the flexoelectric coupling [71], namely,  $\left(\frac{F_{kl33}}{g_{33}^{eff}}\sigma_{kl}\mp\frac{P_3}{\lambda}-\frac{\partial P_3}{\partial x_3}\right)|_{x_3=0,h}=0.$   $F_{kl33}$  is the component of the flexoelectric effect tensor. The extrapolation length  $\lambda$ is equal to the ratio of surface energy coefficient  $A_{33}^S$  and the nonzero effective polarization gradient coefficient  $g_{33}^{\text{eff}}$ ,  $\lambda = g_{33}^{\text{eff}}/A_{33}^{S}$ . Realistic range for  $\lambda$  is 0.5–50 nm [71,78], but the phenomenological parameters is usually unknown (as defined by the surface energy and short-range interactions [79]). Generally, it is beneficial to consider the two limiting cases of very small and big  $\lambda$ , with the latter corresponding to the minimal contribution from the flexoeffect near the surface. However, such an analysis necessarily lacks transparency and calls for numerical estimates.

Here, we enumerate main mechanisms that can be derived from LGD functional or derived based on elementary physical considerations.



FIG. 1. Schematic illustration of polarization suppressions and rotations from (001) to (100) orientations under applied pressure for unclamped crystal and clamped crystals (a), and some possible domain configurations of different in-plane polarization components creating positively (+) charged, negatively (-) charged, and neutral (O) domain walls under the tip (b).

#### A. Ferroelastic mechanism

The application of the mechanical pressure to the SPM tip creates the driving force for the ferroelastic switching between mechanically nonequivalent structural variants. In comparison, it does not induce switching between antiparallel domains, i.e., classical ferroelectric switching. Notably, for unclamped crystal the switching will be thermodynamically favorable for arbitrarily small pressure. For clamped crystal the normal/lateral polarization is enhanced/inhibited, and a larger pressure is required for the in-plane switching. Based on LGD theory normal polarization suppression could even occur in clamped crystal before the in-plane switching [Fig. 1(a)]. Hence establishing the critical pressure for switching from out-of-plane to in-plane domain configuration for material with rigid polarization (i.e.,  $\mathbf{P} = \text{const}$ ) necessitates analysis of nucleation and clamping effects to derive switching fields, etc.

#### **B.** Polarization suppression

The application of the pressure can suppress polarization in a nonrigid multiaxial ferroelectric with coordinate-dependent polarization vector  $\mathbf{P}(\mathbf{r},t)$ . To derive the estimates of corresponding critical pressure, we note that the internal stresses  $\sigma_{ij}$  couple to the polarization direction via piezoelectric and electrostriction couplings [74,80]. Within LGD theory, the piezoelectricity is described as linearized electrostriction, and corresponding effective piezoelectric coefficient is  $d_{ijk} =$  $2\varepsilon_0(\varepsilon_{km}^f - \delta_{km})Q_{ijml}P_l^S$ , where  $Q_{ijkl}$  is electrostriction tensor,  $P_k^S$  is a spontaneous polarization component,  $\varepsilon_0$  is the dielectric permittivity of vacuum,  $\delta_{km}$  is a Kroneker symbol, and  $\varepsilon_{ij}^f$  is the relative dielectric permittivity of ferroelectric that includes a soft-mode-related electric field-dependent contribution  $\varepsilon_{ij}^{sm}$ . The electrostrictive coupling renormalizes the coefficients in LGD-thermodynamic potential (see Supplemental Material [72]). Namely, the coefficient  $a_{33}$ , that determines the FE transition temperature of the out-of-plane polarization component, becomes  $a_{33}^{\text{eff}} = \alpha_T (T - T_c) + 2Q_{33}^{\text{eff}} p_{\text{ext}}$ , where  $Q_{33}^{\text{eff}} = Q_{33} - 2s_{12}Q_{12}/(s_{11} + s_{12})$ , and so the last term increases or decreases  $a_{33}^{\text{eff}}$  depending on the  $p_{\text{ext}}$  sign. The coefficient  $a_{11}$ , that determines the ferroelectric transition temperature of the inplane polarization component, becomes  $a_{11}^{\text{eff}} = \alpha_T (T - T_c) + Q_{11}^{\text{eff}} p_{\text{ext}}$ , where  $Q_{11}^{\text{eff}} = (Q_{12}s_{11} - Q_{11}s_{12})/(s_{11} + s_{12})$  and  $s_{ijkl}$  is elastic stiffness coefficient.

Here, we perform the estimates for PbZr<sub>0.2</sub>Ti<sub>0.8</sub>O<sub>3</sub>, PZT(20/80), for which  $Q_{33}^{\text{eff}} \cong 0.4307 \text{ C}^{-2} \text{ m}$  [4] and  $Q_{11}^{\text{eff}} \cong$ +0.0036 C<sup>-2</sup>m [4]. Since  $Q_{33}^{\text{eff}} \gg Q_{11}^{\text{eff}} > 0$ , the negative pressures (compression) more strongly favors out-of-plane polarization component with the spontaneous value  $P_3[p_{\text{ext}}] \cong$  $\sqrt{-a_{33}^{\text{eff}}[p_{\text{ext}}]/a_{111}}$ . At that a renormalized temperature of PE phase instability is  $T_3^c[p_{\text{ext}}] = T_c - 2Q_{33}^{\text{eff}}p_{\text{ext}}/\alpha_T$ . Compression slightly increases the in-plane component so that  $P_1[p_{\text{ext}}] \cong \sqrt{-a_{11}^{\text{eff}}[p_{\text{ext}}]/a_{111}}$  and corresponding transition temperature  $T_1^c[p_{\text{ext}}] = T_c - Q_{11}^{\text{eff}}p_{\text{ext}}/\alpha_T$ , where  $\alpha_T =$  $3.12 \times 10^5 \text{ C}^{-2} \text{ Jm/K}$  and  $T_c = 768 \text{ K}$ . At the same time, positive pressures (tension) strongly suppress the out-of-plane component appearance, and slightly suppress the in-plane one. The estimates are in qualitative agreement with the results [74,81]. However, in the case of ferroelectric thin film subjected to a local scanning probe tip pressure, the local strains/stresses under the tip are highly anisotropic, thus the trend of out-of-plane polarization in response to tip pressure can be different from the results above.

The 1D estimate of the maximal normal pressure corresponding to the tip-surface mechanical contact radius  $R = 50 \,\mathrm{nm}$  and indentation force  $N = 1 \,\mu\mathrm{N}$ , gives the pressure under the tip as  $|p_i^{\text{ext}}| \cong N/(\pi R^2) \approx$  $10^{-6}/(25\pi \times 10^{-16}) = 1.27 \times 10^8$  Pa. The pressure favors the out-of-plane polarization, since  $T_3^c[p_{ext}] \approx 1110 \text{ K}$  is about increased by 342 K in comparison with  $T_c = 768$  K. Hence, within the 1D estimate  $P_3[p_{ext}]$  becomes 1.45 times more at room temperature. At the same time in-plane component changes relatively insufficiently and  $T_1^c[p_{ext}]$  shift at about 1K, because  $Q_{11}^{\text{eff}}$  is about 100 times smaller than  $Q_{11}^{\text{eff}}$ . To resume, the effect of pressure (compression  $p_{\text{ext}} < 0$  or tension  $p_{\text{ext}} >$ 0) on  $T_3^c[p_{\text{ext}}]$  depends on the signs and relative magnitude of  $Q_{11}^{\text{eff}}$  and  $Q_{33}^{\text{eff}}$ . The pressure increases the out-of-plane  $T_3^c[p_{\text{ext}}]$  if  $-Q_{33}^{\text{eff}}p_{\text{ext}} > 0$  and decreases it in the materials with  $-Q_{33}^{\text{eff}} p_{\text{ext}} < 0.$ 

The situation becomes more complex for the SPM geometry. In this case, the tip-induced pressure is concentrated directly below the tip and is sensitive to the exact tip geometry. For rigid piezoelectric materials, the corresponding field distributions have been calculated [24,25,82-85]. Similar to classical Hertzian indentation, the pressure (and electric field) is maximal at the periphery of the contact area and decreases away from it, and both in-plane and out-of-plane components are present. Under the conditions inducing switching, the concentration of field below tip serve as potential nucleation centers, with the type of switching process being determined by the interplay between materials and tip field symmetry. For example, for the *c* domain in tetragonal material, some of the possible domain configurations are shown in Fig. 1(b). Note that some of these will be associated with the charged domain walls under the tip; others will be charge neutral under the tip and generate charges at the boundary forming dipolar field. The direction of symmetry breaking will be affected by local defects, tip motion [39], etc. However, it is important to note that we can expect significant changes in induced ferroelastic domain structures under pressure and when pressure is reduced, and strong dependence on defects and trajectory of tip motion. While ferroelectric domain switching is possible in this case, it will be the result of interplay of multiple secondary mechanisms and cannot be predicted without phase-field modeling with defined surface conditions.

#### C. Flexoelectric mechanisms

The next broadly considered mechanism is flexoelectric switching, suggested by Gruverman et al. [43]. By definition, stress gradient in the tip-surface junction generates builtin field in the material that can result in switching. As it was shown in Ref. [71], the main contribution of the flexoelectric effect is the appearance of the out-of-plane surface polarization  $P_3^{\text{FL}}$  and built-in normal flexoelectric field  $E_3^{\text{FL}}$ , which are proportional to the product  $F_{33}p_i^{\text{ext}}$ . For nonzero extrapolation length  $\boldsymbol{\lambda}$  it can be estimated as  $P_3^{\text{FL}} \sim \frac{h\lambda F_{33}^{\text{eff}} \sigma_{33}}{g_{33}^{\text{eff}}(h+\lambda)} \cong \frac{I_{33}^{\text{eff}} p_i^{\text{ext}} h\lambda}{g_{33}^{\text{eff}}(h+\lambda)}$ , where effective flexocoefficient is  $F_{33}^{\text{eff}} = F_{33} - 2s_{13}F_{13}/(s_{11} + s_{12})$ , and h is a slab thickness that can be substituted by the characteristic depth of the indentation (for the latter case  $h \sim R$ ). The estimates of the maximal normal pressure corresponding to the tip-surface contact radius R = 50 nm and indentation force  $N = 1 \mu \text{N}$ , gives the high enough pressure  $p_i^{\text{ext}} \cong 1.27 \times 10^8 \,\text{Pa}$ . The surface polarization  $P_{31}^{\text{FL}}$  estimated for typical flexocoefficient range  $F_{33}^{\text{eff}} = (0.5-5) \times 10^{-11} \text{C}^{-1} \text{m}$  [3], gradient coefficient  $g_{33}^{\text{eff}} = (0.5-2) \times 10^{-10} \text{C}^{-2} \text{m}^4 \text{N}$  [86], h = 10 nm and  $\lambda \gg$ h gives  $P_3^{\text{FL}} = (0.015 - 1.2) \text{ C/m}^2$ ; so that it can be small enough but also can be comparable with the spontaneous polarization value, or even several times higher. The values in the middle of this range are sufficient to stimulate polarization switching of in the bulk. Corresponding flexoelectric field is inversely proportional to the thickness h,  $E_i^{\rm FL} \sim F_{ijkl} \partial \sigma_{jk} / \partial x_l \sim F_{33} p_i^{\rm ext} / h$ . Thus, for the case  $h \sim R$ it gives  $E_3^{\rm FL} \sim 0.5 \, {\rm V/nm}$  or even higher. Note that the latter interval contains coercive field, and so can indeed reverse the polarization. However, being rather important qualitatively, the above 1D estimations of  $P_3^{\text{FL}}$  and  $E_3^{\text{FL}}$  can be of small significance quantitatively to the great discrepancy (several orders of magnitude) in the numbers steaming from the scattering for the flexoelectric tensor  $F_{ijkl}$  and gradient tensor  $g_{ii}^{\text{eff}}$  values (several orders of magnitude) in the literature even for well-known ferroelectrics [87,88]. A possible escape from the situation is to decouple the problem, i.e., to consider all contributions separately in a rigorous phase-field modeling suggesting coupled 3D problem. To realize the idea, one can consider zero or negligibly small convolution  $F_{ijkl}^{\text{eff}}\sigma_{kl}$  at the surface as well as  $\frac{\partial P_3}{\partial x_3}|_{x_3=0,h} = 0$  that will be done in the next section.

However, this simple estimate has to be complemented by several important considerations. First, the flexoelectric field is active only in the pressure on state and disappears instantly when the pressure is removed. Correspondingly, it can



FIG. 2. Schematic 1D profiles of elastic strain (b), electric potential (c), and propensity for switching (d) along (001) direction in ferroelectric thin film subjected to tip pressure in SPM geometry (a).

facilitate polarization switching via complementary fields (e.g., pressure assisted bias-induced switching detectable as lateral shift of hysteresis loops) and result in metastable domain configurations, but is not equivalent to uniform electric field effect. Second, the flexoelectric induced strain gradient and resultant electric field are subject to the boundary conditions at the tip and in the bulk [Fig. 2(b)], and can have complex dipolar structure for the grounded tip [Fig. 2(c)]. Thus, the polarization switching could be strongly size-dependent [Fig. 2(d)]. Finally, similar to ferroelastic effects, flexoelectric field has both in-plane and out of plane components, potentially leading to complex metastable domain structures sensitive to load history and tip motion.

## D. Surface electrochemistry

Pressure will strongly affect the electrostatics of screening charges on ferroelectric surfaces, hence affecting the stability of associated polarization state. For example, the positive polarization state screened by OH- and negative polarization charge screened by H+ will respond differently to external pressure, with the chemical shift defined by the difference of molar volume between the two. The normal component of the effective electric field induced by the surface ions with a Langmuir-type charge density  $\sigma$  is given by expression [89],  $E_3^{\text{SEC}}(U,\sigma) = \frac{\varepsilon_0 \varepsilon_d U + \Lambda \sigma}{\varepsilon_0 (\varepsilon_d h + \Lambda \varepsilon_{33}^b)}$ , where  $\Lambda$  is the effective separation between the ferroelectric polarization and the ion layer,  $\varepsilon_d$  is the relative dielectric permittivity of the separated region (i.e., it is a background permittivity in the considered case,  $\varepsilon_d = \varepsilon_{33}^b \sim 5$ ). Since  $\lambda$  is about or smaller than the lattice constant (0.4 nm), and *h* has an order of the contact radius *R*, the inequality  $h \gg \Lambda$  is valid, and so  $E_3^{\text{SEC}}(U,\sigma) \approx \frac{\varepsilon_0 \varepsilon_{33}^b U + \Lambda \sigma}{\varepsilon_0 \varepsilon_{33}^b h}$ . Estimates at zero applied bias (U = 0) gives  $E_3^{\text{SEC}}(\sigma) \approx \Lambda \sigma / (\varepsilon_0 \varepsilon_{33}^b h) \sim \Lambda P_S / (\varepsilon_0 \varepsilon_{33}^b h) \sim \frac{0.5 \text{ nm}}{5 \text{ nm}} \frac{0.5 \text{ C/m}^2}{5 \cdot 8.85 \times 10^{-12} \text{ F/m}} \sim 10^9 \text{ V/m} \sim 1 \text{ V/nm}$ . As one can see, the surface electrochemical contribution in number can be comparable with the flexoelectric one, but it tends to zero at  $\Lambda \rightarrow 0$ . Note that both contributions are proportional to 1/h.

Unlike other coupling mechanisms, the relationships between applied pressure and electrochemical potential shift can be highly nonmonotonic. For example, for water the difference in molar volume for  $H_3O_+$ , OH-, and  $H_+$  can give rise to oscillatory dependence of chemical potential on pressure, similar to phenomena observed in ionic liquids [90–92]. Finally, relevant consideration here is that of triboelectric charging, known to produce very high (tens and hundreds of V) potentials (but quantitative mechanisms of which are not well-known).

#### E. Bulk electrochemistry

Finally, applied pressure can shift electrochemical potential of vacancies, resulting in local charging and resultant polarization switching. In this case, the relationship between applied pressure and induced potential potentials is most complex, since the coupling proceeds through multiple steps affected by relevant boundary conditions, etc. Notably, for surface and bulk electrochemical mechanisms time becomes a significant component. For example, the development of potential distributions in electrochemical systems in response to step wise change in external stimulus (e.g., pressure or bias at the electrode) is determined by a set of relaxation times, i.e., the Debye time  $(\tau_D)$ , the bulk diffusion time  $(\tau_L)$ and the diffuse charge relaxation time  $(\tau_C)$  from the physics of diffuse-charge dynamics [93,94]. The ionic migration and accumulation/depletion in electrochemical system under applied field forms electrical double layers that can screen the electrode. The Debye time describes the characteristic time for ion to diffuse across electric double layer while the bulk diffusion time is for ion diffusion from neutral bulk towards the electrodes. They are determined by  $\tau_D = \lambda_D^2 / D$  and  $\tau_L =$  $L^2/D$ , respectively, where  $\lambda_D$  and L are the Debye screening length and the separation distance between electrodes, and D is the ionic diffusivity. The Debye screening length is determined from  $\lambda_D = \sqrt{(\varepsilon k_B T)/(2z^2 e_0^2 C)}$ , where C is the ionic concentration,  $e_0$  is the electronic charge, z is the charge number,  $k_B$  is the Boltzmann constant, T is the temperature, and  $\varepsilon$  is the permittivity of the host material. For oxygen vacancies at a concentration of  $10^{18}$  cm<sup>-3</sup> with a diffusivity of  $\sim 10^{-16} \,\mathrm{cm^2/s}$  at room temperature [95] in 10-nm-thick PZT thin film, the Debye length Debye time and bulk diffusion time are estimated to be 0.422 nm, 6.37 s, and 3580 s.  $\tau_D$ is deterministic for surface electrochemical behavior and  $\tau_L$ for bulk diffusion mechanism. For diffuse charge relaxation dynamics, a third primary time scale is for  $(\tau_C)$  is introduced as the harmonic mean of Debye and bulk diffusion time  $\tau_C = \sqrt{\tau_D \tau_C} = \lambda_D L/D$ , which is estimated to be 151.1 s.



FIG. 3. Schematic illustration and equations of multieffect coupling, including (1) pure piezoelectricity, (2) surface chemistry, (3) flexoelectricity, and (4) bulk Vegard strain effect, and their effects on ferroelectric polarization and ionic defects (5).

## **III. PHASE-FIELD MODELING**

The analysis above provides simple estimates of the pressure induced phenomena in the ferroelectrics. However, these mechanisms are intrinsically coupled, and in many cases the indirect couplings (e.g., pressure  $\rightarrow$  vacancy concentration  $\rightarrow$  electric field  $\rightarrow$  polarization dynamics) can exceed direct coupling. Hence, we analyze the phenomena using coupled phase-field model by considering the surface chemical effect, flexoelectric effect, and bulk Vegard strain effect, as schematically illustrated in Fig. 3.

#### A. Description of phase-field model

In the phase-field simulations of ferroelectric phenomena, we choose ferroelectric polarization ( $P_i$ ,  $i = 1 \sim 3$ ) as the order parameter, and the total free energy of the system is written as a function of  $P_i$ , elastic strain ( $\varepsilon_{kl}$ ), electric field ( $E_i$ ), and the polarization gradient ( $\nabla P_i$ ):

$$f = f_{\text{land}}(P_i) + f_{\text{elas}}(P_i, \varepsilon_{kl}) + f_{\text{elec}}(P_i, E_i) + f_{\text{grad}}(\nabla P_i),$$
(1)

in which  $f_{\text{land}}$ ,  $f_{\text{elas}}$ ,  $f_{\text{elec}}$ , and  $f_{\text{grad}}$  represent the Landau bulk free energy density, the elastic energy density, the electrostatic energy density, and gradient energy density, respectively.  $f_{\text{land}}$  is written as a sixth order polynomial expansion of  $P_i$ :

$$f_{\text{land}}(P_i) = \alpha_i P_i^2 + \alpha_{ij} P_i^2 P_j^2 + \alpha_{ijk} P_i^2 P_j^2 P_k^2$$
  

$$= \alpha_1(T) (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4)$$
  

$$+ \alpha_{12} (P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2)$$
  

$$+ \alpha_{111} (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} [P_1^2 (P_2^4 + P_3^4)]$$
  

$$+ P_2^2 (P_1^4 + P_3^4) + P_3^2 (P_1^4 + P_2^4)] + \alpha_{123} P_1^2 P_2^2 P_3^2$$
(2)

where  $\alpha_i$ ,  $\alpha_{ij}$ , and  $\alpha_{ijk}$  are the second-, fourth-, and sixthorder Landau coefficients. Only  $\alpha_1$  is linearly dependent on temperature (*T*) as  $\alpha_1 = \frac{1}{2\varepsilon_0 C}(T - T_0)$ . Here  $\varepsilon_0$  is the vacuum permittivity, C is the Curie constant, and  $T_0$  is the transition temperature.

The elastic energy density is written as

$$f_{\text{elas}} = \frac{1}{2} c_{ijkl} \left( \varepsilon_{ij} - \varepsilon_{ij}^0 \right) \left( \varepsilon_{kl} - \varepsilon_{kl}^0 \right), \tag{3}$$

in which  $c_{ijkl}$  is the elastic stiffness coefficient tensor,  $\varepsilon_{ij}$  is the total strain, and  $\varepsilon_{ij}^0$  is the eigenstrain. In the absence of ionic defects such as oxygen vacancies,  $\varepsilon_{ij}^0$  is induced by the spontaneous polarization as

$$\varepsilon_{ij}^0 = \varepsilon_{ij}^{0P} = Q_{ijkl} P_k P_l, \tag{4}$$

in which  $Q_{ijkl}$  is the electrostrictive coefficient tensor. The electrostatic energy of a domain structure is introduced through

$$f_{\text{elec}}(P_i, E_i) = -P_i E_i - \frac{1}{2} \varepsilon_0 \varepsilon_r E_i E_j, \qquad (5)$$

where  $E_i$  is the total electric field.  $\varepsilon_0$  and  $\varepsilon_r$  are the vacuum permittivity and relative permittivity, respectively.  $E_i$  is related to the electric potential ( $\phi$ ) distribution through

$$E_i = -\nabla_i \phi(i = 1 \sim 3), \tag{6}$$

where  $\nabla$  is the gradient operator. The gradient energy density is introduced through the polarization gradient,

$$f_{\text{grad}}(\nabla P_i) = \frac{1}{2} g_{ijkl} \left( \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l} \right)$$
  
$$= \frac{1}{2} g_{11} \left[ \left( \frac{\partial P_1}{\partial x_1} \right)^2 + \left( \frac{\partial P_2}{\partial x_2} \right)^2 + \left( \frac{\partial P_3}{\partial x_3} \right)^2 \right]$$
  
$$+ g_{12} \left( \frac{\partial P_1}{\partial x_2} \frac{\partial P_2}{\partial x_1} + \frac{\partial P_2}{\partial x_3} \frac{\partial P_3}{\partial x_2} + \frac{\partial P_3}{\partial x_1} \frac{\partial P_1}{\partial x_3} \right)$$
  
$$+ \frac{1}{2} g_{44} \left[ \left( \frac{\partial P_1}{\partial x_2} + \frac{\partial P_2}{\partial x_1} \right)^2 + \left( \frac{\partial P_2}{\partial x_3} + \frac{\partial P_3}{\partial x_2} \right)^2 \right]$$
  
$$+ \left( \frac{\partial P_3}{\partial x_1} + \frac{\partial P_1}{\partial x_3} \right)^2 \right], \qquad (7)$$

in which  $g_{ijkl}$ 's are the gradient energy coefficient tensor.

The temporal evolution of ferroelectric polarization is governed by the time-dependent Landau-Ginzburg-Devonshire (LGD) equations,

$$\frac{\partial P_i(\mathbf{x},t)}{\partial t} = -L \frac{\delta F_{\text{total}}}{\delta P_i(\mathbf{x},t)}, \quad i = 1,2,3,$$
(8)

in which x is the position, t is the time, L is the kinetic coefficient related to the domain movement,  $\delta$  is the variational derivative operator, and  $F_{\text{total}} = \int_V f dV$  is the total free energy written as the volume integral of f.

To model the effect of mechanical pressure on the ferroelectric thin film induced from a scanning probe, we define the stress distribution as that created by a spherical indenter on top of the film. Using Hertzian model for isotropic solid,

$$\sigma_{33}^{\text{tip}}(r) = \begin{cases} -\frac{3p}{2\pi a^2} \sqrt{1 - \frac{r^2}{a^2}} (r \leqslant a), \\ 0.0(r \geqslant a) \end{cases}$$
(9)

where *p* is the mechanical load, *a* is the radius of the tip-surface contact area, and  $r = \sqrt{(x - x_0)^2 + (y - y_0)^2}$  is the distance from any points (x, y) inside the contact area to the tip center  $(x_0, y_0)$ .

The local mechanical tip pressure would create inhomogeneous strain, and consequently a large strain gradient near the tip in nanoscale thin film. While homogeneous strains ( $\varepsilon_{kl}$ ) would induce polarizations in ferroelectric oxides through the piezoelectric effect, the inhomogeneous strain or strain gradient ( $\partial \varepsilon_{kl} / \partial x_j$ ) would additionally contribute to the ferroelectric polarization through the flexoelectric effect, i.e.,

$$P_i = d_{ijk}\varepsilon_{jk} + \mu_{ijkl}\frac{\partial\varepsilon_{kl}}{\partial x_j}(i, j, k, l = 1 \sim 3), \qquad (10)$$

where  $d_{ijk}$  and  $\mu_{ijkl}$  are the piezoelectric and flexoelectric polarization tensors respectively. The coupling between  $P_i$ and  $\partial \varepsilon_{kl} / \partial x_j$  give rises to an additional flexoelectric energy density ( $f_{\text{flexo}}$ ) to be added to the total free energy density defined in Eq. (1),

$$f_{\text{flexo}}(P_i, \varepsilon_{kl}, \nabla P_i, \nabla \varepsilon_{kl}) = \frac{1}{2} f_{ijkl} \left( \frac{\partial P_k}{\partial x_l} \varepsilon_{ij} - \frac{\partial \varepsilon_{ij}}{\partial x_l} P_k \right) \\ = \frac{1}{2} F_{ijkl} \left( \frac{\partial P_k}{\partial x_l} \sigma_{ij} - \frac{\partial \sigma_{ij}}{\partial x_l} P_k \right),$$
(11)

in which  $f_{ijkl}$  (unit: V) and  $F_{ijkl}$  (unit: Vm<sup>2</sup>N<sup>-1</sup>) are the flexocoupling coefficient tensors. The relations between  $f_{ijkl}$ ,  $F_{ijkl}$ , and  $\mu_{ijkl}$  are  $f_{ijkl} = c_{ijmn}F_{mnkl}$ ,  $\mu_{ijkl} = \varepsilon_0\chi_{mn}f_{mnkl}$ , where  $\chi_{mn}$  is the dielectric susceptibility. The driving force of  $P_i$  from the flexoelectric energy density yields the so-called flexoelectric field  $(E_k^f)$ ,

$$\frac{\delta f_{\text{flexo}}}{\delta P_k} = \frac{\partial f_{\text{flexo}}}{\partial P_k} - \frac{\partial}{\partial x_l} \frac{\partial f_{\text{flexo}}}{(\partial P_k / \partial x_l)} = -F_{ijkl} \frac{\partial \sigma_{ij}}{\partial x_l} = -E_k^f.$$
(12)

 $E_k^f$  is defined in a similar way to the electric field  $(E_k)$ , which is actually the driving force of electrostatic energy to  $P_i$ , i.e.,  $\delta f_{\text{elec}}/\delta P_k = -E_k$ . Expanding Eq. (12) based on the Voigt notation for cubic symmetry,  $F_{ijkl} = F_{mn}(i, j, k, l = 1 \sim 3; m, n = 1 \sim 6)$ , yields

$$E_1^f = F_{11}\frac{\partial\sigma_1}{\partial x_1} + F_{12}\left(\frac{\partial\sigma_2}{\partial x_1} + \frac{\partial\sigma_3}{\partial x_1}\right) + F_{44}\left(\frac{\partial\sigma_5}{\partial x_3} + \frac{\partial\sigma_6}{\partial x_2}\right),$$
(12a)

$$E_2^f = F_{11}\frac{\partial\sigma_2}{\partial x_2} + F_{12}\left(\frac{\partial\sigma_3}{\partial x_2} + \frac{\partial\sigma_1}{\partial x_2}\right) + F_{44}\left(\frac{\partial\sigma_6}{\partial x_1} + \frac{\partial\sigma_4}{\partial x_3}\right),$$
(12b)

$$E_3^f = F_{11}\frac{\partial\sigma_3}{\partial x_3} + F_{12}\left(\frac{\partial\sigma_1}{\partial x_3} + \frac{\partial\sigma_2}{\partial x_3}\right) + F_{44}\left(\frac{\partial\sigma_4}{\partial x_2} + \frac{\partial\sigma_5}{\partial x_1}\right).$$
(12c)

Defects, such as oxygen vacancies are ubiquitous in ferroelectric oxide thin film and are important to ferroelectric properties. For example, oxygen vacancies create additional charge compensation and strain relaxation in ferroelectric thin film, both of which influence the ferroelectric switching behavior. On the other hand, the polarization distribution induces local bound charges and spontaneous strains that will affect the oxygen vacancy transport under mechanical tip pressure. To consider this coupled effect, we solve the electrostatic equilibrium (Poisson) equation for the electric potential ( $\phi$ ) distribution,

$$-\nabla^2 \phi = \frac{z_i e_0 c_i - \nabla \bullet P_i}{\varepsilon_0 \varepsilon_r},\tag{13}$$

in which  $z_i$  is the charge number for species i,  $e_0$  is the unit charge, and  $c_i$  is the concentration of charge species i. The local eigenstrain  $(\varepsilon_{ij}^{0d})$  induced from the oxygen vacancy is described by the converse Vegard effect,

$$\varepsilon_{ij}^{0d} = V_{ij}^d \Delta X_V \delta_{ij}, \qquad (14)$$

where  $\delta_{ij}$  is the Kronecker operator,  $V_{ij}^d$  is the Vegard coefficient, which measures the change of lattice parameter (*a*) with respect to oxygen vacancy composition  $(X_V)$ ; i.e.,  $V_{ij}^d = (1/a)(da/dX_V)$ .  $\Delta X_V = X_V - X_{V0}$  is the variation of ionized oxygen vacancy composition where constant value of  $X_{V0}$  corresponds to a stress-free reference state at zero electric field. The unitless oxygen vacancy composition is related to its concentration ( $[V_O^{\circ\circ}]$ , in the unit of cm<sup>-3</sup>) through

$$X_V = \left( [V_O^{\bullet \bullet}] \bullet \mathrm{AW} \right) / (\rho \bullet N_A), \tag{15}$$

where  $N_A = 6.022 \times 10^{23} (\text{mol}^{-1})$  is the Avogadro constant. AW and  $\rho$  represent the atomic weight and density of the matrix material. For PZT we choose AW = 303.09 (g/mol) and  $\rho = 7.52 (\text{g/cm}^3)$ . Thus, Eq. (3) should be modified as

$$f_{\text{elas}} = \frac{1}{2} C_{ijkl} e_{ij} e_{kl}$$

$$= \frac{1}{2} C_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^{0P} - \varepsilon_{ij}^{0d}) (\varepsilon_{kl} - \varepsilon_{kl}^{0P} - \varepsilon_{kl}^{0d})$$

$$= \frac{C_{ijkl}}{2} (\varepsilon_{ij} \varepsilon_{kl} - \varepsilon_{ij}^{0d} \varepsilon_{kl} - \varepsilon_{ij}^{0P} \varepsilon_{kl} - \varepsilon_{ij} \varepsilon_{kl}^{0d} + \varepsilon_{ij}^{0P} \varepsilon_{kl}^{0Q} + \varepsilon_{ij}^{0P} \varepsilon_{kl}^{0P} + \varepsilon_{ij}^{0P} \varepsilon_{kl}^{0P} + \varepsilon_{ij}^{0P} \varepsilon_{kl}^{0P}).$$
(16)

The derivative of  $f_{\text{elas}}$  with respect to vacancy composition is

$$\frac{\partial f_{\text{elas}}}{\partial X_{V}} = \frac{C_{ijkl}}{2} \Big( -V_{ij}^{d} \delta_{ij} \varepsilon_{kl} - \varepsilon_{ij} V_{kl}^{d} \delta_{kl} + 2V_{ij}^{d} \delta_{ij} V_{kl}^{d} \delta_{kl} X_{V} \\ + \varepsilon_{ij}^{0P} V_{kl}^{d} \delta_{kl} + V_{ij}^{d} \delta_{ij} \varepsilon_{kl}^{0P} \Big) \\ = V_{ij}^{d} \delta_{ij} C_{ijkl} \Big( -\varepsilon_{kl} + V_{kl}^{d} \delta_{kl} X_{V} + \varepsilon_{kl}^{0P} \Big) \\ = -V_{ii}^{d} C_{iikl} \Big( \varepsilon_{kl} - \varepsilon_{kl}^{0Q} - \varepsilon_{kl}^{0P} \Big).$$
(17)

Note that the unit of  $f_{elas}$  is J/m<sup>3</sup>, and  $X_V$  is unitless. The elastic potential ( $\mu_{el}$ ) of species  $X_V$  is given by (unit: J/mol):

$$\mu_{\rm el} = \frac{1}{\Omega} \frac{\partial f_{\rm elas}}{\partial X_V} = -\frac{V_{ii}^d C_{iikl}}{\Omega} \left( \varepsilon_{kl} - \varepsilon_{kl}^{0d} - \varepsilon_{kl}^{0P} \right) = -\frac{V_{ii}^d \sigma_{ii}}{\Omega},$$
(18)

where  $\Omega$  is molar density of matrix material (unit: mol/m<sup>3</sup>) and is calculated to be  $\Omega = \rho/AW$ .

Thus, the chemical potential of  $X_V$  including the bulk, the electric, and elastic potential is written as

$$\mu = RT \ln X_V + z_V F \phi + \mu_{\rm el}, \tag{19}$$

in which R is the gas constant and F is the Faraday constant. The flux of oxygen vacancy is proportional to the gradient of the chemical potential, which yields

$$J = -MX_V \nabla \mu$$
  
=  $-\left(\frac{D_V}{RT}\right) X_V \left[ RT \frac{\nabla X_V}{X_V} + \nabla(z_V F \phi) + \nabla \mu_{\text{el}} \right], \quad (20)$ 

in which M and  $D_V$  are the mobility and diffusivity of oxygen vacancy. Thus, the oxygen vacancy transport under diffusional, electrical, and mechanical driving force can be described by the continuum equation,

$$\frac{\partial X_V}{\partial t} = -\nabla \bullet J = D_V \nabla^2 X_V + \frac{D_V z_V e}{k_B T} \nabla \bullet [X_V \nabla \phi] + \frac{D_V}{RT} \nabla \bullet [X_V \nabla \mu_{el}], \qquad (21)$$

where t is the time step and  $k_B$  is the Boltzmann constant.

To study surface electrochemical effect on the mechanical switching dynamics, we applied phase-field model with chemical boundary condition [96]. In classic phase-field model, the electrostatic equilibrium equation [Eq. (13)] and LGD equations [Eq. (8)] are typically solved with boundary conditions,

$$\phi|_{Z=0} = 0$$
, and  $\phi|_{Z=L} = V_{app}$ , (22)

$$\left. \frac{\partial P_z}{\partial z} \right|_{Z=0,L} = 0, \tag{23}$$

in which *L* is the film thickness and  $V_{app}$  denotes the applied electric bias. These represent the situation when the polarization bound charges at the top/bottom surface are fully screened by the metal electrode at fixed bias ( $V_{app}$ ). While these boundary conditions match well with the bulk ferroelectrics, they are not applicable to free ferroelectric surfaces. Here we used chemical boundary condition based on S&H model [97], which maintains electrochemical equilibria between

surface compensating charges and electrochemical potentials and environment. For simplicity, we consider that surface charges include only excessive oxygen ions (such as negatively charged adsorbed oxygen,  $O_{ad}^{2-}$ ) and deficient oxygen ions (such as positively charged oxygen vacancy,  $V_{O}^{2+}$ ), although other electrochemical reactions are treated similarly without the loss of generality. Thus, the surface reaction involving oxygen ions yields

$$\text{IonSite} + \frac{1}{n_i} O_2 = z_i e^- + \text{Ion}^{z_i}, \qquad (24)$$

where  $n_i$  is the number of surface ions per  $O_2$ ,  $e^-$  is the electronic free charge, and  $z_i$  is the charge number of surface ions. When the polarization is positive that attract negative surface oxygen ions ( $O_{ad}^{2-}$ ) for charge compensation, the ion site and ion in Eq. (24) refer to vacant oxygen ion adsorption site ( $V_{ad}$ ), and  $n_i = 2$  and  $z_i = -2$  in Eq. (24). When the polarization is negative so that positive surface ions (such as  $V_0^{2+}$ ) are created for charge compensation, the ion site in Eq. (24) refer to occupied oxygen site ( $O_0$ ) and that are able to create  $V_0^{2+}$ , and correspondingly  $n_i = -2$  and  $z_i = +2$  in Eq. (24). The surface ion concentration is defined so that  $\theta_i = 1$  when all the oxygen ion sites are occupied. When  $\theta_i < 1$ , the concentration of ion sites is  $1 - \theta_i$ . Therefore, the equilibrium reaction constant (K) for Eq. (24) can be expressed as

$$K = \frac{\theta_i}{(1 - \theta_i) P_{O_2}^{1/n_i}},\tag{25}$$

where  $P_{O_2}$  is the oxygen partial pressure. In a general electrochemical reaction the driving force  $(\Delta G)$  can be written as

$$\Delta G = \Delta G^{\circ} + RT \ln K, \qquad (26)$$

where *R* is gas constant, *T* is the temperature, and  $\Delta G^{\circ}$  is the standard energy formation. In Eq. (26) where charge transfer between ions and electrons are involved,  $\Delta G$  is equal to the work done by transferring *Q* amount of charge under external bias  $V_{\text{ex}}$ , i.e.,

$$\Delta G = W = -V_{\text{ex}}Q = -V_{\text{ex}}z_i N_A e_0 = -V_{\text{ex}}z_i F, \quad (27)$$

in which  $V_{\text{ex}}$  is the electrochemical potential,  $N_A$  is the Avogadro's number,  $e_0$  is the unit charge, and F is the Faraday constant. Combing Eqs. (25)  $\sim$  (27) yields the Langmuir adsorption isotherm [98],

$$\frac{\theta_i}{1-\theta_i} = P_{O_2}^{1/n_i} \exp\left(\frac{-\Delta G^\circ - z_i e_0 V_{\text{ex}}}{k_B T}\right).$$
(28)

We assumed that the surface charges are limited on top of the dielectric layer of thickness  $\lambda$  atop the ferroelectric thin film of thickness *L*, and are homogeneous in the *x*-*y* plane. To avoid singularity problem in the simulation caused from the sudden jump of surface ion concentration, we convert the surface localized ion concentration  $\theta_i(x, y)$  into a 3D distribution of  $\theta(x, y, z)$  by using a 1D Gaussian function,

$$\theta(x, y, z) = \theta_i(x, y) \exp\left(-\frac{(z - (L + \lambda))^2}{2t^2}\right),$$
  
(0 \le z \le L + \lambda), (29)

Landau coefficients		Elastic coefficients		Parameters in the simulation	
$\overline{\alpha_1(10^8 C^{-2} m^2 N)}$	- 1.485	<i>c</i> <sub>11</sub> (GPa)	173	T (°C)	25
$\alpha_{11}(10^8 \mathrm{C}^{-4} \mathrm{m}^6 \mathrm{N})$	-0.305	$c_{12}$ (GPa)	80.2	System size	$128 \times 128 \times 20$
$\alpha_{12}(10^8 \text{C}^{-4} \text{m}^6 \text{N})$	6.320	$c_{44}$ (GPa)	69.4	Film (nm)	$5.0 \sim 30$
$\alpha_{111}(10^8 \text{C}^{-6} \text{m}^{10} \text{N})$	2.475	$s_{11}(10^{-12} \text{m}^2 \text{N}^{-1})$	8.2	Tip load $(\mu N)$	$0.5 \sim 4.0$
$\alpha_{112}(10^8 \text{C}^{-6} \text{m}^{10} \text{N})$	0.968	$s_{12}(10^{-12} \text{m}^2 \text{N}^{-1})$	-2.6	$F_{\rm ii}$ (10 <sup>-11</sup> C <sup>-1</sup> m <sup>3</sup> )	$F_{11} = 0 \sim 10, F_{12} = F_{44} = 0$
$\alpha_{123}(10^9 \text{C}^{-6} \text{m}^{10} \text{N})$	-4.901	$s_{44}(10^{-12} \text{m}^2 \text{N}^{-1})$	14.4	$\Delta G^{\circ}$ (eV)	0.0
$\alpha_{1111}(10^8 C^{-8} m^{14} N)$	0.0	Electrostrictive coefficients		$n_i, z_i$	+2.0, -2.0
$\alpha_{1112}(10^8 C^{-8} m^{14} N)$	0.0	$Q_{11}(10^{-2}\mathrm{C}^{-2}\mathrm{m}^4)$	8.1	$V_{ii}^d$	0.02
$\alpha_{1122}(10^8 C^{-8} m^{14} N)$	0.0	$Q_{12}(10^{-2}\mathrm{C}^{-2}\mathrm{m}^4)$	-2.4	$\varepsilon_{\rm r}$	50
$\alpha_{1123}(10^8 \mathrm{C}^{-8} \mathrm{m}^{14} \mathrm{N})$	0.0	$Q_{44}(10^{-2}\mathrm{C}^{-2}\mathrm{m}^4)$	3.2	$\Omega \ (mol \ \times \ m^{-3})$	24811

TABLE I. Energy coefficients and parameters used in the simulation.

in which t controls the width of the Gaussian function and is chosen to be 0.05 to ensure that the majorities of the ions are localized at  $z = L + \lambda$ . The surface ions are assumed not evolving in the current simulation.

We also assumed the ferroelectric polarization remain constant in the ferroelectric thin film (0 < z < L) and vanishes in the dielectric layer  $(L < z < L + \lambda)$ . The electric potential is assumed to be zero at the bottom surface (z = 0) of the film, and equal to the electrochemical potential  $(V_{ex})$  on the top surface  $(z = L + \lambda)$ . Based on these we modified the boundary conditions of ferroelectric polarization [Eq. (22)] and electric potential [Eq. (23)] into

$$P_{Z}|_{Z=L+\lambda} = 0, \quad \frac{\partial P_{z}}{\partial z}\Big|_{Z=0} = 0, \tag{30}$$

$$\phi|_{Z=0} = 0, \quad \phi|_{Z=L+\lambda} = V_{\text{ex}}.$$
 (31)

It should also be noted that the electrochemical potential  $(V_{ex})$  is also subjected to the mechanical pressure at the tipsurface junction. The shift of formation energy  $(\Delta G^{\circ})$  by the tip pressure is estimated to be  $P\Delta V$ , where P is the applied pressure and  $\Delta V$  is the difference in ionic volume. Therefore, at fixed  $\theta_i$  and  $P_{O_2}$ ,  $V_{ex}$  varies at different tip pressures. More detailed formulation of introducing surface chemical effect in the framework of phase-field simulation can be found in literature [96,97].

So far we have established a comprehensive phase-field model that takes into account the surface chemical effect, flexoelectric effect, and bulk electrochemical effect. In the next sections, we will systematically analyze these effects on the mechanical switching in ferroelectric thin film at different thickness under different tip pressures. Based on this we will elucidate their relative contributions and couplings in the switching dynamics.

As a model system, we chose Pb(Zr<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub> (PZT) thin film consisting of a (001) oriented single domain under room temperature. The simulation is run on a 3D coordinate system with period boundary conditions along x and y directions, and general boundary condition along z direction. The system is discretized into a 3D mesh of  $128\Delta x \times 128\Delta y \times 20\Delta z$ in which  $\Delta x = \Delta y = 1.0$  nm and  $\Delta z$  is nonuniform. The thickness of the film varies from 5, 10, 15, 20, and 30 nm. The film is constrained by -1.0% in-plane compressive strain. The tip-surface contact areas of is set to be a = 10 nm and is assumed to be independent on the tip pressure. The gradient energy coefficients are set to be  $G_{11}/G_{110} = 0.6$ , while  $G_{110} = 1.73 \times 10^{-10} \text{C}^{-2} \text{m}^4 \text{N}$ . The background dielectric permittivity of PZT is reported to be 5–7 [99,100]. However, to compare with experimental results, we used background dielectric constant ( $\varepsilon_r$ ) of 50 as suggested from literature [101]. The Landau coefficients, electrostrictive coefficients, and elastic compliance constants of Pb(Zr<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub> are collected from literature [73,102,103] and listed in Table I. The flexoelectric coefficients, the Vegard coefficients, and other parameters used in the simulation are also listed in Table I.

#### B. Ferroelastic phenomena

We started with the polarization state under pure mechanical pressure from the probing tip without considering the surface charge effect, the flexoelectric effect, and the bulk vacancy transport effect. One of the advantages in phase-field method is that one can easily separate contributions from different effects and understand their relative roles in the mechanical switching. To do this we chose conventional boundary conditions for polarization and electric potential [see Eqs. (18) and (19)], set the flexoelectric coefficients to be 0, assumed charge neutral in the bulk, and froze the oxygen vacancy migration. We applied tip load from 0.5  $\mu$ N to 4.0  $\mu$ N on PZT thin film consisting of a (001) oriented single domain, with thickness from 5 to 20 nm. Figures 4(a)-4(d) illustrate the final polarization states under lower (0.5  $\mu$ N) and higher (4.0  $\mu$ N) mechanical loads in thinner (5.0 nm) and thicker (20 nm) films. For all thickness, the magnitude of  $P_z$  component near the tip was slightly suppressed from  $0.8 \,\text{C/m}^2$  under 0.5  $\mu\text{N}$ , and eventually became  $0.0 \text{ C/m}^2$  under 1.0  $\mu$ N (Fig. S1 in the Supplemental Material [72]), indicating that the polarization switched to in-plane orientation beneath the tip. The in-plane switching regions eventually penetrate through the entire film depending on the film thickness. Notably no 180° switching occurred even when tip load increased to 4.0  $\mu$ N, implying that the pure ferroelastic effect is symmetric. This is further evidenced by the almost symmetric distribution of out-of-plane electric field  $(E_z)$  under the tip region, [Fig. 4(e)], where the upward  $E_{z}$  near the bottom layer prevented the in-plane polarization from further switching into [001] orientation.

## C. Surface electrochemistry

To study the surface charge effect on the switching dynamics, we applied chemical boundary conditions



FIG. 4. Vertical polarization  $(P_z)$  profiles in 5-nm-thick (a, b) and 20-nm-thick (c, d) PZT thin film with pure piezoelectric effect. The applied tip load is 0.5  $\mu$ N (a, c) and 4  $\mu$ N (b, d), respectively. (e) The out-of-plane electric field distribution  $(E_z)$  in 5-nm-thin film under 4  $\mu$ N.

[Eqs. (20)  $\sim$  (22)] taking into account the interaction between surface charge concentration, electrochemical potential and oxygen partial pressure. The flexoelectric effect and bulk vacancy effect were turned off. Figures 5(a)-5(d) show the final polarization states under different tip loads in PZT thin films of different thickness. Clearly, 180° switching were seen in ultrathin film (5.0 nm) under 0.5  $\mu$ N. This is due to the shift of electrochemical potential on top of the film. The electrochemical potential shift scales with tip pressure, creating an additional downward electric field under the tip [Fig. 5(e)]. When the tip load increased to 4.0  $\mu$ N, the 180° switching region was mainly seen at the edges. Inside the tip region the polarization became in-plane [Fig. 5(b)]. This implies that there is a competition between the electrochemical shift that favors the 180° switching, and the pure ferroelastic effect that favors in-plane switching (as studied in Sec. III B), and both effects increase with tip pressure. This is clearly illustrated in 10-nm-thin film (see Fig. S2 in the Supplemental Material [72]), where polarization experienced three distinctive states (suppression, 180° switching, and in-plane switching) with increasing tip pressures. Below 10 nm surface electrochemical effect is dominant, while above 10 nm ferroelastic effect takes over. Therefore, 180° switching only occurred in ultrathin film below 10nm when surface effect is on.

## **D.** Flexoelectric effect

The high localization of mechanical strains from the tip load couples with ferroelectric polarization through flexoelectric



FIG. 5.  $P_z$  profiles in 5-nm-thick (a, b) and 20-nm-thick (c, d) PZT thin film with surface electrochemical effect. The applied tip load is 0.5  $\mu$ N (a, c) and 4  $\mu$ N (b, d), respectively. (e) The out-of-plane electric field distribution ( $E_z$ ) in 5-nm-thin film under 0.5  $\mu$ N.

effect. The strain/stress gradient over nanoscale thin film induces a giant flexoelectric field which act as an additional electric field besides the electrostatic field and applied field. Figure 6(a) illustrates the 180° switched polarization state under 2.0  $\mu$ N tip load in 15 nm PZT thin film, which is otherwise not found in cases considering pure piezoelectric effect (see Sec. III B) and surface chemical effect (Sec. III C). Figures 6(b) and 6(c) illustrate the local distributions of out-of-plane electric field and flexoelectric field respectively. It is seen that the strain gradient induced flexoelectric field was along [001] direction and reached  $\sim -2.0 \,\text{MV/cm}$ , which is comparable to the electric field. Therefore, the 180° switching can be attributed to this additional flexoelectric field. It should be noted this flexoelectric field increases linearly with stress gradient based on Eq. (11), thus under large tip pressure the flexoelectric effect is expected to increase. However, large tip pressure will inhibit 180° switching through ferroelastic effect as illustrated in Sec. III B. Therefore, there also exists a competing mechanism between flexoelectric and ferroelastic effect, similar to that between surface chemical and ferroelastic effect as mentioned in Sec. III C. Supplemental Material Fig. S3 illustrates the final polarization states for film thickness/tip load combinations [72]. Only three distinct 180° switching cases  $(10 \text{ nm}/1 \mu \text{N}, 15 \text{ nm}/2 \mu \text{N}, \text{and } 20 \text{ nm}/4 \mu \text{N})$ were seen and highlighted by the blue ellipse (Fig. S3 in the Supplemental Material [72]). In the lower-left region of the ellipse, the tip pressure and thus the flexoelectric field is too small to induce 180° switching. In the upper-right region of



FIG. 6.  $P_z$  profiles (a), vertical electrostatic field ( $E_z$ ) (b), and vertical flexoelectric field ( $E_z^f$ ) (c) in 15-nm-thick PZT thin film under 2  $\mu$ N tip load with flexoelectric effect. One-dimensional profiles of  $P_z$  along z direction beneath the tip in 10-nm-thick (d), 15-nm-thick (e), and 20-nm-thick (f) PZT thin film under different tip loads.

the circle, the ferroelastic effect that favors in-plane switching overwhelms the flexoelectric effect.

Importantly, the flexoelectric effect has nontrivial dependence on the film thickness. In ultrathin PZT film (5.0 nm), the stress under the tip is almost homogeneous ( $d\sigma \sim 0$ ) so that the stress gradient is limited, while in thicker film the stress gradient is also inhibited due to larger thickness. Therefore 180° switching is never seen in PZT thin film below 5 nm or above 20 nm. Consequently, there is only a narrow window of thickness/pressure combination for flexoelectricity facilitated 180° switching, due to the complexity of aforementioned competing mechanism and its sensitivity on film thickness. This is best illustrated by the 1D plot of the  $P_z$  along z direction beneath the tip in 10-, 15-, and 20-nm-thick films under different tip loads [Figs. 6(d)–6(f)], where  $P_z$  near the bottom of the film (z = 0) decreased initially and then increased again with increasing tip loads.

### E. Bulk electrochemistry

Oxygen vacancies are one of the most important charged defects that are ubiquitous in many ferroelectric oxide thin films. Compared to surface charges that reside on the film surface, oxygen vacancies can diffuse into the film bulk. The redistribution of positively charged oxygen vacancies inside the film create local charges and elastic strain, which couple to the ferroelectric polarization through the electrostatic effect and Vegard strain effect. Therefore, it is important to understand the effect of oxygen vacancies on the mechanical switching behavior.

We assumed the oxygen vacancy concentration is high,  $10^{21}$  cm<sup>-3</sup>, in PZT thin film. They were homogeneously distributed inside the film in the absence of mechanical tip load and initially balanced by monovalent acceptors introduced from the substitution of +3 elements such as Fe on the Ti sites (Fe<sub>Ti</sub>' = A'). The acceptors were considered fully ionized and immobile, while oxygen vacancies are mobile [104] under external electrical/mechanical stimuli, as described from Eq. (16). For simplicity, we do not consider electronic charge effect in the current study. Figure 7 illustrates the equilibrium  $P_z$  profiles in PZT thin film of different thickness

subjected to different mechanical loads. In 5-nm-thick film, the polarization was slightly suppressed under 0.5  $\mu$ N mechanical load [Fig. 7(a)] and switched to in-plane direction ( $P_z \approx 0$ ) under 4  $\mu$ N load [Fig. 7(b)]. No 180° switching was seen [similar to Figs. 4(a) and 4(b)], indicating that the piezoelectric effect is dominant. In 30-nm-thick film under 4  $\mu$ N tip load, 180° switching occurred at both the tip edges on top of the film and at the bottom surface beneath the tip [Fig. 7(c)]. A close examination of the oxygen vacancy profile in 30 nm [Fig. 7(d)] indicated that oxygen vacancies migrate in both lateral direction (near the film surface) and vertical direction (toward the film bottom) away from the tip, resulting in a vacancy depleted region under the tip due to the tip induced compressive strains that disfavor the vacancies. By comparing Figs. 7(c) and 7(d), it is implied that the vacancy induced



FIG. 7.  $P_z$  profiles in 5-nm-thick PZT film under 0.5  $\mu$ N (a) and 4  $\mu$ N (b) tip loads, and  $P_z$  profile (c) and oxygen vacancy concentration (d) in 30-nm-thick PZT film under 4  $\mu$ N tip load. One-dimensional profiles of (e) oxygen vacancy concentration and (f)  $P_z$  along z direction beneath the tip in PZT thin films of different thickness (5, 10, 20, and 30 nm) under 4  $\mu$ N tip load (initial homogeneous oxygen vacancy concentration is  $10^{21}$  cm<sup>-3</sup>).



FIG. 8. Switchable and nonswitchable diagrams for various film thicknesses and tip loads under separate effects (a) pure ferroelastic effect, (b) ferroelastic and surface charge effect, (c) ferroelastic and flexoelectric effect, and (d) ferroelastic and bulk chemical effect.

strain effect could potentially facilitate the switching process. Figures 7(e) and 7(f) illustrate the 1D profile of oxygen vacancies and  $P_z$  along z direction under the tip center in 5-, 10-, 20-, and 30-nm-thick film. It is seen that the degree of oxygen vacancy accumulation/depletion at the bottom/top surfaces increases with film thickness. This further validates why 180° switching is only seen in thicker films (>20 nm), as vacancy transport and the Vegard strain effect is too small to facilitate the switching in films less than 10 nm thick.

## F. Pressure-thickness phase diagram of mechanical switching

We thus calculated the final polarization state under different film thickness and tip load conditions, by turning on only one effect (surface charge, flexoelectricity, or bulk oxygen vacancy) at a time while freezing the others (Figs. S1–S4 in Supplemental Material [72]). Based on this, we constructed four separate pressure-thickness phase diagrams for each effect, as illustrated in Figs. 8(a)-8(d). Pure piezoelectric effect is insufficient for 180° switching under any tip loads in PZT thin film of any thickness [Fig. 8(a)], while the presence of surface charges and oxygen vacancies could enable 180° switching in ultrathin film [<10 nm, Fig. 8(b)] and thicker film [>20 nm, Fig. 8(d)], respectively. The flexoelectric effect could potentially result in 180° switching in intermediate range of film thickness ( $10 \sim 20$  nm) depending on certain tip pressures [Fig. 8(c)]. We thus combined Figs. 8(a)-8(d) into a general phase diagram of 180° switchable/nonswitchable PZT thin film of different thickness under different tip loads, as illustrated in Fig. 9. In ultrathin film (<5 nm), the 180° switching is driven by the surface chemical effect (circles



FIG. 9. Switchable and nonswitchable diagrams for various film thicknesses and tip loads under multiple effects. The red region with circles indicates that the switching is facilitated by surface charge effect. The green region with triangles indicates that the switching is facilitated by flexoelectric effect. And the blue region with squares indicates that the switching is facilitated by bulk Vegard strain effect. The yellow region with cross is nonswitchable region.

in red region in Fig. 9), while in thicker film (>20 nm)the bulk oxygen vacancy induced Vegard strain effect is dominant (squares in blue region in Fig. 9). The surface charge facilitated switching occurred at any tip loads in 5-nm-thick film; however, it only occurred under 1  $\mu$ N load in 10-nm-thick film. This is due to the competition between the electrochemical potential that promotes the 180° switching and piezoelectric effect that favors the in-plane orientation, both of which scale with the tip pressure. On the other hand, the bulk vacancy facilitated switching occurred in thicker film under large tip pressure. This is because significant oxygen vacancy migration and local segregation requires large tip pressure and enough diffusion length. Finally, the flexoelectric effect becomes dominant in thin films from  $10 \sim 20$  nm thick under certain tip loads in a narrow "channel" (triangles in green region in Fig. 9). The critical switching pressure increases with film thickness. This is due to the fact that the flexoelectric field depends on strain gradient which scales with both tip load and film thickness. In ultrathin film (<5 nm), the stress across the film becomes homogeneous that lacks stress gradient, while in thicker film (>20 nm) the strain gradient is localized only near the film surface under the tip and is insufficient to switch the entire film.

## **IV. COUPLED MODELING**

One of the advantages of phase-field simulation is that we can not only study the response of certain properties (such as mechanical switching) to one particular effect independently by freezing other effects, but also tune the strength of this effect to study the linearity of its response, and turn on more effects to understand their coupling behaviors. As an example, we turned on all the aforementioned effects (surface charge, flexoelectricity, and bulk vacancy dynamics) to study



FIG. 10. Dependence of  $P_z$  on top surface under the tip on the oxygen vacancy concentration (a) and longitudinal flexoelectric strength (b), and  $P_z$  on bottom surface below the tip on the oxygen vacancy concentration (c) and longitudinal flexoelectric strength (d).

the mechanical switching behavior in a 20-nm PZT thin film subjected to 4  $\mu$ N tip load. Figure 10 illustrates the magnitude of  $P_z$  on top surface under the tip  $(P_{z_{top}})$  and on bottom surface beneath the tip  $(P_{z.bottom})$ , at different oxygen vacancy concentration  $V_{O}^{\bullet\bullet}$  and longitudinal flexoelectric strength  $(F_{11})$ . It is seen that  $P_{z_{top}}$  decreases substantially at larger oxygen vacancy concentration (>10<sup>20</sup> cm<sup>-3</sup>) under given  $F_{11}$ [Fig. 10(a)], while it decreases almost linearly with increasing  $F_{11}$  at fixed vacancy concentration [Fig. 10(b)]. This indicated that the flexoelectric field effect on  $P_{z_{-top}}$  is instantaneous and linear, while the Vegard strain effect on  $P_{z_{-top}}$  only becomes significant when vacancy concentration is above a threshold. On the other hand, sudden jumps of  $P_{z\_bottom}$  from positive to negative polarity were seen at critical vacancy concentrations [Fig. 10(c)]. This critical concentration is independent of  $F_{11}$ when  $F_{11}$  is smaller than 2.0 ( $10^{-11}$  Vm<sup>3</sup>N<sup>-1</sup>), indicating that flexoelectric effect is negligible in this region. The critical concentration becomes smaller ( $\sim 10^{20} \,\mathrm{cm}^{-3}$ ) when  $F_{11}$  reaches 5.0 ( $10^{-11}$  Vm<sup>3</sup>N<sup>-1</sup>) and eventually disappear when  $F_{11}$  is 10 ( $10^{-11}$  Vm<sup>3</sup>N<sup>-1</sup>), implying that flexoelectric field becomes dominant. Similarly, the critical flexoelectric strength for  $P_{z\_bottom}$  switching becomes smaller with increasing oxygen vacancy concentration and finally  $P_{z_{\text{bottom}}}$  becomes switchable at any  $F_{11}$  [Fig. 10(d)]. Analysis on the coupled flexoelectric and Vegard strain effect allows us to understand which effect is dominant under what condition.

It should be noted that in this study we do not consider the kinetic process of each effect, i.e., all the effects are assumed to reach steady state with final ferroelectric polarization state. In fact, ferroelectric switching under mechanical pressure can be very fast and the flexoelectric effect occurs instantaneously in the presence of strain gradient. On the other hand, surface electrochemistry is limited by the transport rate of ionic species along the surfaces (available from time resolved PFM data [105,106]) and by transport from gas phase to the film surface. And the Vegard strain effect is limited by the oxygen vacancy diffusivity, which is normally very slow in solids under room temperature, but becomes much faster once the local electric bias and mechanical load overcome the activation energy barrier of vacancies. These makes the mechanical switching dynamics more complicated and is not taken into account in the current model. Nevertheless, our model still clarifies some important issues about the recently reported pressure-induced writing, and it provides a clear picture about the possibility of multieffect in pressure switching and in which realm (spatial and pressure combination) they become dominant.

## V. SUMMARY

We developed a phase-field model to explore the surface electrochemical phenomena, bulk flexoelectric effect, and bulk vacancy dynamics as thermodynamic driving force to the pressure-induced mechanical switching in Pb(Zr<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub> ferroelectric thin film. Our model confirms that pure mechanical pressure only rotate the out-of-plane polarization to the in-plane orientation and is not allowed to switch the initial polarization by 180°. We found that surface charges shift the electrochemical potential that is responsible for the 180° switching in ultrathin film, while bulk Vegard strain effect is dominant and accounts for the 180° switching in thicker film under large tip pressure. The flexoelectricity-induced switching becomes more important in thin film at intermediate thickness ( $10 \sim 20$  nm). A linearity analysis on polarization field dependence on vacancy concentration and flexoelectric strength indicate that all three effects couple and interact with each other. In this study, we only focus on the final steady state of polarization, surface charge, and bulk vacancy and do not consider the kinetics process of each of them. Our work successfully differentiates the surface phenomena, long-range strain gradient, and bulk vacancy transport dynamics in the mechanical switching behavior, providing a clear picture of thickness- and pressure-dependence of mechanical switching behavior in ferroelectric thin film.

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- P. Maksymovych, J. Seidel, Y. H. Chu, P. P. Wu, A. P. Baddorf, L. Q. Chen, S. V. Kalinin, and R. Ramesh, Nano. Lett. 11, 1906 (2011).
- [2] J. Seidel et al., Phys. Rev. Lett. 105, 197603 (2010).
- [3] J. Seidel *et al.*, Nat. Mater. **8**, 229 (2009).
- [4] A. Gruverman et al., Nano. Lett. 9, 3539 (2009).
- [5] E. Y. Tsymbal and H. Kohlstedt, Science 313, 181 (2006).
- [6] L. Bocher et al., Nano. Lett. 12, 376 (2012).
- [7] J. F. Scott, Science 315, 954 (2007).
- [8] A. Gruverman, O. Auciello, R. Ramesh, and H. Tokumoto, Nanotechnology 8, A38 (1997).
- [9] A. L. Gruverman, J. Hatano, and H. Tokumoto, Japan. J. Appl. Phys. Part 1: Reg. Papers Short Notes Rev. Papers 36, 2207 (1997).
- [10] N. Balke, I. Bdikin, S. V. Kalinin, and A. L. Kholkin, J. Am. Ceram. Soc. 92, 1629 (2009).
- [11] D. A. Bonnell, S. V. Kalinin, A. L. Kholkin, and A. Gruverman, Mrs. Bull. 34, 648 (2009).
- [12] S. V. Kalinin, N. Setter, and A. L. Kholkin, Mrs. Bull. 34, 634 (2009).
- [13] A. Gruverman and S. V. Kalinin, J. Mater. Sci. 41, 107 (2006).
- [14] L. Chen, J. Ouyang, C. S. Ganpule, V. Nagarajan, R. Ramesh, and A. L. Roytburd, Appl. Phys. Lett. 84, 254 (2004).
- [15] C. S. Ganpule, A. L. Roytburd, V. Nagarajan, B. K. Hill, S. B. Ogale, E. D. Williams, R. Ramesh, and J. F. Scott, Phys. Rev. B 65, 014101 (2001).
- [16] A. Roelofs, N. A. Pertsev, R. Waser, F. Schlaphof, L. M. Eng, C. Ganpule, V. Nagarajan, and R. Ramesh, Appl. Phys. Lett. 80, 1424 (2002).
- [17] P. Paruch, T. Giamarchi, and J. M. Triscone, in *Physics of Ferroelectrics: A Modern Perspective*, edited by K. M. Rabe, C. H. Ahn, and J. M. Triscone (Springer-Verlag, Berlin, 2007), Vol. 105, p. 339.
- [18] P. Paruch, T. Giamarchi, and J. M. Triscone, Phys. Rev. Lett. 94, 197601 (2005).
- [19] T. Tybell, P. Paruch, T. Giamarchi, and J. M. Triscone, Phys. Rev. Lett. 89, 097601 (2002).
- [20] V. R. Aravind et al., Phys. Rev. B 82, 024111 (2010).

- [21] S. V. Kalinin, B. J. Rodriguez, S. Jesse, A. N. Morozovska, A. A. Bokov, and Z. G. Ye, Appl. Phys. Lett. 95, 142902 (2009).
- [22] S. V. Kalinin, B. J. Rodriguez, S. H. Kim, S. K. Hong, A. Gruverman, and E. A. Eliseev, Appl. Phys. Lett. 92, 152906 (2008).
- [23] S. Jesse et al., Nat. Mater. 7, 209 (2008).
- [24] S. V. Kalinin, E. Karapetian, and M. Kachanov, Phys. Rev. B. 70, 184101 (2004).
- [25] S. V. Kalinin, J. Shin, M. Kachanov, E. Karapetian, and A. P. Baddorf, in *Ferroelectric Thin Films Xii*, edited by S. HoffmannEifert, H. Funakubo, V. Joshi, A. I. Kingon, and I. P. Koutsaroff (Cambridge University Press, Cambridge, 2004), Vol. 784, p. 43.
- [26] S. V. Kalinin, E. A. Eliseev, and A. N. Morozovska, Appl. Phys. Lett. 88, 232904 (2006).
- [27] A. N. Morozovska, E. A. Eliseev, and S. V. Kalinin, Appl. Phys. Lett. 89, 192901 (2006).
- [28] A. N. Morozovska, E. A. Eliseev, S. L. Bravina, and S. V. Kalinin, Phys. Rev. B 75, 174109 (2007).
- [29] A. N. Morozovska, E. A. Eliseev, and S. V. Kalinin, J. Appl. Phys. **102**, 074105 (2007).
- [30] A. N. Morozovska, S. V. Svechnikov, E. A. Eliseev, B. J. Rodriguez, S. Jesse, and S. V. Kalinin, Phys. Rev. B 78, 054101 (2008).
- [31] S. V. Kalinin, A. Gruverman, B. J. Rodriguez, J. Shin, A. P. Baddorf, E. Karapetian, and M. Kachanov, J. Appl. Phys. 97, 074305 (2005).
- [32] M. I. Molotskii and M. M. Shvebelman, Philos. Mag. 85, 1637 (2005).
- [33] M. Molotskii and E. Winebrand, Phys. Rev. B **71**, 132103 (2005).
- [34] G. Rosenman, D. Shur, K. Garb, R. Cohen, and Y. E. Krasik, J. Appl. Phys. 82, 772 (1997).
- [35] A. N. Morozovska, E. A. Eliseev, S. L. Bravina, and S. V. Kalinin, J. Appl. Phys. **110**, 052011 (2011).
- [36] A. N. Morozovska, E. A. Eliseev, Y. L. Li, S. V. Svechnikov, P. Maksymovych, V. Y. Shur, V. Gopalan, L. Q. Chen, and S. V. Kalinin, Phys. Rev. B 80, 214110 (2009).

- [37] S. V. Kalinin *et al.*, Proc. Natl. Acda. Sci. USA **104**, 20204 (2007).
- [38] S. V. Kalinin, A. N. Morozovska, L. Q. Chen, and B. J. Rodriguez, Rep. Prog. Phys. 73, 056502 (2010).
- [39] N. Balke, S. Choudhury, S. Jesse, M. Huijben, Y. H. Chu, A. P. Baddorf, L. Q. Chen, R. Ramesh, and S. V. Kalinin, Nat. Nanotechnol. 4, 868 (2009).
- [40] Y. Xiao, V. B. Shenoy, and K. Bhattacharya, Phys. Rev. Lett. 95, 247603 (2005).
- [41] Y. Xiao and K. Bhattacharya, Arch. Ration. Mech. Anal. 189, 59 (2008).
- [42] H. D. Lu et al., Nano. Lett. 16, 6460 (2016).
- [43] H. Lu, C. W. Bark, D. E. de los Ojos, J. Alcala, C. B. Eom, G. Catalan, and A. Gruverman, Science 336, 59 (2012).
- [44] P. Sharma et al., Nano. Lett. 15, 3547 (2015).
- [45] J. Ocenasek, H. Lu, C. W. Bark, C. B. Eom, J. Alcala, G. Catalan, and A. Gruverman, Phys. Rev. B 92, 035417 (2015).
- [46] Y. J. Gu, Z. J. Hong, J. Britson, and L. Q. Chen, Appl. Phys. Lett. 106, 022904 (2015).
- [47] M. J. Highland, T. T. Fister, D. D. Fong, P. H. Fuoss, C. Thompson, J. A. Eastman, S. K. Streiffer, and G. B. Stephenson, Phys. Rev. Lett. 107, 187602 (2011).
- [48] S. M. Yang et al., Nat. Phys. 13, 812 (2017).
- [49] A. Y. Borisevich et al., Phys. Rev. B 86, 140102 (2012).
- [50] S. V. Kalinin, A. Borisevich, and D. Fong, Acs Nano 6, 10423 (2012).
- [51] S. V. Kalinin and N. A. Spaldin, Science 341, 858 (2013).
- [52] S. V. Kalinin, S. Jesse, A. Tselev, A. P. Baddorf, and N. Balke, Acs Nano 5, 5683 (2011).
- [53] A. V. Ievlev, P. Maksymovych, M. Trassin, J. Seidel, R. Ramesh, S. V. Kalinin, and O. S. Ovchinnikova, Acs Appl. Mater. Interf. 8, 29588 (2016).
- [54] J. V. Mantese, N. W. Schubring, A. L. Micheli, M. P. Thompson, R. Naik, G. W. Auner, I. B. Misirlioglu, and S. P. Alpay, Appl. Phys. Lett. 81, 1068 (2002).
- [55] J. C. Agar et al., Nat. Mater. 15, 549 (2016).
- [56] Z. G. Ban, S. P. Alpay, and J. V. Mantese, Phys. Rev. B 67, 184104 (2003).
- [57] J. Zhang, R. Xu, A. R. Damodaran, Z. H. Chen, and L. W. Martin, Phys. Rev. B 89, 224101 (2014).
- [58] S. Prosandeev and L. Bellaiche, Phys. Rev. B 75, 172109 (2007).
- [59] S. Hong, S. M. Nakhmanson, and D. D. Fong, Rep. Prog. Phys. 79, 076501 (2016).
- [60] H. Lee et al., Nano. Lett. 16, 2400 (2016).
- [61] W. T. Dai, M. Yang, H. Lee, J. W. Lee, C. B. Eom, and C. Cen, Nano. Lett. 17, 5620 (2017).
- [62] H. Lee, N. Campbell, S. Ryu, W. Chang, J. Irwin, S. Lindemann, M. K. Mahanthappa, M. S. Rzchowski, and C. B. Eom, Appl. Phys. Lett. 109, 191604 (2016).
- [63] S. Jesse, N. Balke, E. Eliseev, A. Tselev, N. J. Dudney, A. N. Morozovska, and S. V. Kalinin, Acs Nano 5, 9682 (2011).
- [64] A. Kumar, F. Ciucci, A. N. Morozovska, S. V. Kalinin, and S. Jesse, Nature Chemistry 3, 707 (2011).
- [65] A. N. Morozovska, E. A. Eliseev, G. S. Svechnikov, and S. V. Kalinin, Phys. Rev. B 84, 045402 (2011).
- [66] A. N. Morozovska, E. A. Eliseev, A. K. Tagantsev, S. L. Bravina, L. Q. Chen, and S. V. Kalinin, Phys. Rev. B 83, 195313 (2011).

- [67] A. N. Morozovska, E. A. Eliseev, N. Balke, and S. V. Kalinin, J. Appl. Phys. **108**, 053712 (2010).
- [68] A. N. Morozovska, E. A. Eliseev, and S. V. Kalinin, Appl. Phys. Lett. 96, 222906 (2010).
- [69] N. Balke et al., Nat. Nanotechnol. 5, 749 (2010).
- [70] M. Y. Gureev, A. K. Tagantsev, and N. Setter, Phys. Rev. B 83, 184104 (2011).
- [71] A. N. Morozovska, E. A. Eliseev, Y. A. Genenko, I. S. Vorotiahin, M. V. Silibin, Y. Cao, Y. Kim, M. D. Glinchuk, and S. V. Kalinin, Phys. Rev. B 94, 174101 (2016).
- [72] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.96.184109 for detailed formulation and all cases of pressure induced mechanical switching.
- [73] M. J. Haun, Z. Q. Zhuang, E. Furman, S. J. Jang, and L. E. Cross, Ferroelectrics 99, 45 (1989).
- [74] N. A. Pertsev, V. G. Kukhar, H. Kohlstedt, and R. Waser, Phys. Rev. B 67, 054107 (2003).
- [75] D. A. Freedman, D. Roundy, and T. A. Arias, Phys. Rev. B 80, 064108 (2009).
- [76] A. I. Lurie, Spatial Problems of the Elasticity Theory (Gos. Izd. Teor. Tekh. Lit., Moscow, 1955).
- [77] R. Kretschmer and K. Binder, Phys. Rev. B **20**, 1065 (1979).
- [78] C. L. Jia, V. Nagarajan, J. Q. He, L. Houben, T. Zhao, R. Ramesh, K. Urban, and R. Waser, Nat. Mater. 6, 64 (2007).
- [79] J. Wang, A. K. Tagantsev, and N. Setter, Phys. Rev. B 83, 014104 (2011).
- [80] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. 80, 1988 (1998).
- [81] V. G. Kukhar, N. A. Pertsev, H. Kohlstedt, and R. Waser, Phys. Rev. B 73, 214103 (2006).
- [82] E. Karapetian, M. Kachanov, and S. V. Kalinin, Philos. Mag. 85, 1017 (2005).
- [83] K. Pan, Y. Y. Liu, S. H. Xie, Y. M. Liu, and J. Y. Li, Acta Mater. 61, 7020 (2013).
- [84] W. Q. Chen, E. N. Pan, H. M. Wang, and C. Z. Zhang, J. Mech. Phys. Solids 58, 1524 (2010).
- [85] W. Q. Chen and H. J. Ding, Acta Mech. Solida Sinica 12, 114 (1999).
- [86] E. A. Eliseev, A. N. Morozovska, G. S. Svechnikov, P. Maksymovych, and S. V. Kalinin, Phys. Rev. B 85, 045312 (2012).
- [87] P. Zubko, G. Catalan, P. R. L. Welche, A. Buckley, and J. F. Scott, Phys. Rev. Lett. 99, 167601 (2007).
- [88] A. Biancoli, C. M. Fancher, J. L. Jones, and D. Damjanovic, Nat. Mater. 14, 224 (2015).
- [89] A. N. Morozovska, E. A. Eliseev, N. V. Morozovsky, and S. V. Kalinin, Phys. Rev. B 95, 195413 (2017).
- [90] J. S. Huang, B. G. Sumpter, and V. Meunier, Chem-Eur J. 14, 6614 (2008).
- [91] P. Wu, J. S. Huang, V. Meunier, B. G. Sumpter, and R. Qiao, Acs Nano 5, 9044 (2011).
- [92] P. Wu, J. S. Huang, V. Meunier, B. G. Sumpter, and R. Qiao, J. Phys. Chem. Lett. 3, 1732 (2012).
- [93] M. Z. Bazant, K. Thornton, and A. Ajdari, Phys. Rev. E 70, 021506 (2004).
- [94] L. Collins et al., Nat. Commun. 5, 3871 (2014).
- [95] H. I. Yoo, M. W. Chang, T. S. Oh, C. E. Lee, and K. D. Becker, J. Appl. Phys. **102**, 093701 (2007).
- [96] Y. Cao and S. V. Kalinin, Phys. Rev. B 94, 235444 (2016).

- [97] G. B. Stephenson and M. J. Highland, Phys. Rev. B 84, 064107 (2011).
- [98] K. Y. Foo and B. H. Hameed, Chem. Eng. J. 156, 2 (2010).
- [99] A. K. Tagantsev, G. Gerra, and N. Setter, Phys. Rev. B 77, 174111 (2008).
- [100] A. N. Morozovska, E. A. Eliseev, S. V. Svechnikov, A. D. Krutov, V. Y. Shur, A. Y. Borisevich, P. Maksymovych, and S. V. Kalinin, Phys. Rev. B 81, 205308 (2010).
- [101] G. Rupprecht and R. O. Bell, Phys. Rev. 135, A748 (1964).

- [102] M. J. Haun, E. Furman, S. J. Jang, and L. E. Cross, Ferroelectrics 99, 13 (1989).
- [103] M. J. Haun, E. Furman, S. J. Jang, H. A. Mckinstry, and L. E. Cross, J. Appl. Phys. 62, 3331 (1987).
- [104] Y. Gil, O. M. Umurhan, and I. Riess, J. Appl. Phys. 104, 084504 (2008).
- [105] E. Strelcov, S. Jesse, Y. L. Huang, Y. C. Teng, Kravchenko, II, Y. H. Chu, and S. V. Kalinin, Acs Nano. 7, 6806 (2013).
- [106] J. L. Ding, E. Strelcov, S. V. Kalinin, and N. Bassiri-Gharb, Nano. Lett. 15, 3669 (2015).