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Competing polarization reversal mechanisms in ferroelectric nanowires

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Polarization reversal in ferroelectrics has been a subject of intense interest for many years owing to both its scientific appeal and practical utility. In the recent years the interest has increased even further thanks to the expectations of achieving ultrafast polarization reversal at the nanoscale. While most of the studies up to now are focused on the polarization reversal in ferroelectric thin films, we report the intrinsic dynamics of ultrafast polarization reversal in ferroelectric nanowires. Using atomistic first-principles-based simulations, we trace the time evolution of polarization under applied electric field to reveal the existence of two competing polarization reversal mechanisms: (i) domain-driven and (ii) homogeneous. The analysis of their microscopic origin allows us to postulate the associated laws and leads to a deeper understanding of polarization reversal dynamics in general. In addition, we find that in defect-free nanowires the polarization reversal can occur within picoseconds which potentially is very promising for ultrafast memory and other applications.

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I. INTRODUCTION

Ferroelectrics are materials that exhibit spontaneous polarization in the absence of electric field. Similar to magnetization in ferromagnets, spontaneous polarization in ferroelectrics can be reversed by the application of an external field. In addition, the polarization in ferroelectrics is strongly coupled to strain and temperature. Thanks to such unique properties, ferroelectrics are widely used in a variety of practical applications that include non-volatile memories, acoustic, electronic and optical devices¹. The recent discoveries of ferroelectricity at the nanoscale have brought ferroelectrics under the glare of scientific attention owing to the scientific appeal and practical utility of ferroelectric nanostructures²⁻⁶. One of the most promising practical application of such nanostructures is in ultra high-density memories where a single nanostructure is used as a logical bit which is operated through the control of polarization direction. Technically, an electric field is applied to reverse polarization direction in order to read/write or erase a bit of information. The polarization reversal (PR) dynamics becomes a critical factor in such applications since it imposes a fundamental limit on the performance of the memory elements and any other application that require PR.

The PR dynamics in bulk samples has been a subject of active studies for many years⁷⁻¹⁵. It is generally established that PR occurs via a three step process: (i) nucleation at defect site, (ii) forward growth of needle-like domain and, (iii) side-way spreading of these needles¹⁶. It is also believed that under very high fields, the mechanism of PR maybe different¹⁶. Such mechanism does not involve the formation of domains but rather consists of nearly homogeneous nucleation (homogeneous PR). Such homogeneous PR was observed in experiments conducted on thin films¹¹⁻¹⁴. In addition, PR mechanisms and dynamics are strongly influenced by the presence of defects which can be both PR nucleation sites and pinning centers for the domain walls propagation. Recently the PR in ferroelectric thin and ultra thin films has attracted a lot of attention owing to the revolutionary advances in film growth and characterization techniques, the possibility to apply much larger electric fields, and the films' practical utility for nanoscale applications. A recent study of domain wall dynamics in thin $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ films has revealed that their motion is a disorder-controlled creep process¹⁷. It was reported in Ref.10, that in thin PZT epitaxial films, the domain wall velocity is a non-linear function of an electric field with different regions corresponding to creep, depinning and flow regimes. Very recently, aberration-corrected transmission electron microscopy was used to directly observe domain nucleation sites and domain wall pinning on point defects¹⁵. Interestingly, while the PR dynamics in thin films are under the focus of current attention, we are not aware of many studies of PR dynamics in ferroelectric nanowires. Such nanowires are quasi-one dimensional objects^{2,5,18-20} in which the polarization can be confined along the axial direction^{5,21,22} and, therefore, are very attractive for many practical applications including memory units and nanosensors.

In this Article we use atomistic first-principles-based simulations to study PR in defect-free ferroelectric nanowires with a view to; (1) reveal the intrinsic dynamics of PR at nanoscale, (2) derive the fundamental laws that govern such dynamics and, (3) identify the unique features of PR in quasi-one dimensional objects. Our findings also allow us to expand the knowledge on the dynamics of domain-driven and homogeneous PR mechanisms in general.

II. COMPUTATIONAL METHOD

We used classical molecular dynamics (MD) with the force-field derived from a first-principles-based effective Hamiltonian²³⁻²⁵ to investigate seven ferroelectric ultrathin nanowires made of $\text{PbTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$ ferroelectric alloy. The nanowires have square cross sections with lateral size ranging from 3.2 to 8 nm. The degrees of freedom for the Hamiltonian include a local soft mode which is proportional to the dipole moment of a unit cell $p = Z^*\tau$, where Z^* is the Born effective charge and τ is the atomic displacements, homogeneous and inhomogeneous strain variables. The Newton's equations of motion are solved numerically for each local dipole and local strain vector. The ionic masses in the unit cell and the eigenvectors of the soft mode are used for calculating the mass of the local dipole. This approach has been successfully applied to study static and dynamical properties of $\text{PbTi}_x\text{Zr}_{1-x}\text{O}_3$ alloys^{2,4,6,26-28} and other perovskites²⁹⁻³². We simulate nanowires grown along the [001] direction and subject to partial screening of the surface charge to model open circuit boundary conditions. Specifically, the total surface charge is screened by 10% using the computational approach of Ref.25. In our setup x , y and z -directions are chosen along [100], [010], and [001] crystallographic directions, respectively, with the z -direction being along the nanowire's axial direction. Periodic boundary conditions are applied along the z -direction to simulate infinitely long nanowires. The nanowires were first annealed from $T=2000$ K down to $T=10$ K in steps of $\Delta T=100$ K. For each temperature, we equilibrate the dipoles by simulating NPT ensemble using MD with the Evans-Hoover thermostat and a barostat mimicked via a PV term in the effective Hamiltonian^{29,33}. Technically, we used 40,000 MD steps with each step being 0.5 fs. We found that under such conditions the nanowires are polarized along the axial direction as consistent with some previous theoretical^{5,21,22} and experimental reports³⁴⁻³⁷. The polarization distribution inside the nanowires is slightly inhomogeneous with smaller polarization values close to the surface.

III. DYNAMICS OF POLARIZATION REVERSAL AND ITS DEPENDENCE ON THE ELECTRIC FIELD

To study the dynamics of PR in such nanowires we subject them to *dc* electric field E applied in the direction opposite to the direction of polarization. The possibility to manipulate axial polarization in individual ferroelectric nanowires by application of *dc* bias was demonstrated in the recent experiments²⁰. Our simulation setup mimics nanowires placed between relatively large electrodes which would be analogous to experiments conducted recently on array of nanowires³⁸. The simulations typically run for 15 ps. The electric fields applied were in the range of 0.5-8 MV/cm and are similar to the electric fields attainable in thin films samples^{10,11,39}.

We begin by studying PR in a 7.2×7.2 nm² cross section nanowire. We first notice that, in agreement with previous studies⁴⁰, the PR is associated with a continuous rotation of individual dipoles towards the electric field. The PR typically originates at the surface of the nanowire where the local environment reduces the barrier for the dipoles' flips²⁸. For lower fields this leads to formation of a coaxial nucleus which then expands inside the nanowire. To trace the time evolution of the coaxial nucleus we decompose the nanowire into 9 coaxial shells. Each shell is one unit cell thick and contains a single layer of dipoles. For convenience, we will call the dipoles pointing along (opposite to) the direction of applied electric field "up" ("down") dipoles.

Fig.1(a) shows the normalized count of the "up" dipoles N_{up} in individual shells as a function of time obtained from simulations with the electric field of $E = 2.8$ MV/cm. The onset of PR occurs at $t = 0.13$ ps and is associated with the dipoles' flips in the outermost shell. Fig.1(a) indicates that, for this particular field, the PR propagates by sweeping one coaxial shell at a time. This allows us to define a domain wall which is the area that separates the volumes of opposite polarization. The domain wall is atomically thin and nearly cylindrical in shape. The snapshots of the dipole patterns in the nanowire's cross section are shown in Fig.1(e). Note, that similar core-shell structures were reported in BaTiO₃ nanowires⁴¹ and observed experimentally^{36,42}. Our data, therefore, suggest that under given conditions, PR occurs through formation and propagation of cylindrical coaxial domain.

Next we focus on the dynamics of PR in the same nanowire but under much higher electric field of 4.5 MV/cm (Fig.1(b)). We notice that while PR still originates at the surface, most of the shells switch almost simultaneously which suggests that the applied field is sufficiently strong to induce nearly homogeneous PR in the cross section of the nanowire. Such homogeneous PR does not involve domain formation and propagation and was observed in ultra thin films¹¹⁻¹⁴. Our calculations, thus, indicate that, depending on the strength of the electric field applied to the nanowire, there exists two PR mechanisms. Domain-driven PR occurs at lower electric fields and is associated with the formation and propagation of coaxial domain. Under higher electric fields polarization reverses its direction homogeneously and without the formation of domains.

To identify the range of the electric fields associated with different PR mechanisms we compute the speeds of PR along the radial and axial direction of the nanowire. The radial PR speed characterizes the speed of propagation of the PR along the nanowires's radius and is computed as $v_r = r/t_r$, where r is the distance between the outermost and innermost shells, and t_r is the time required for the domain wall to travel that distance. The axial PR speed characterizes how fast the PR occurs within one coaxial shell and is computed as $v_a = L/t_a$, where L is the nanowire length taken to be equal to the supercell period along the axial direction and t_a is the average time of PR in the shell. Fig.2(a) shows the field dependencies for both v_r and v_a . For the field 3.1 MV/cm and lower $v_a > v_r$, which indicates that the PR occurs via relatively slow PR propagation between nanowires's shells followed by very rapid PR within a shell. This is a characteristic feature of domain-driven PR. For the field of 3.9 MV/cm and higher, v_r overtakes v_a indicating that switching follows the trends shown in Fig.1(b). This is a signature of homogeneous PR. It is convenient to introduce the effective PR speed as $v_e = R_{NW}/t_p$, where R_{NW} is the average nanowire radius calculated as $R = \sqrt{S/\pi}$ with S being the nanowire's cross section. t_p is the PR propagation time calculated as the time from the beginning of PR to the moment when 90% of the nanowires's volume is reversed. Our choice of 90% is based on the fact that this corresponds to the situation when most of the nanowire volume has reversed its polarization. The field dependence of v_e is shown in solid line in Fig.2(a). In the low field range v_e is dominated by the radial speed v_r , while in the high field range it is dominated by the axial speed v_a . In our calculations the domain wall speed is about 2.5 km/s which is comparable with the speed of domain walls at nanoscale⁴³. The observed dependence $v_e(E)$ resembles closely experimental data for triglycine sulphate⁸ as well as the dependence predicted in the framework of nonlinear response¹⁰.

IV. HOMOGENEOUS POLARIZATION REVERSAL FROM A MICROSCOPIC APPROACH

To understand the observed field dependence we will focus on the atomistic picture behind homogeneous PR. In the absence of electric field all the dipoles p occupy the states near one of the minima in the Gibbs free energy, for example, $-p_0$. The free energy profile at 0 Kelvin denoted as G_0 can be obtained directly from the effective Hamiltonian and is

given in Fig.3(a). The zero field density of states $\rho(p) = A \exp^{-\mathcal{E}(p)/k_B T}$ computed at $T = 100$ K is given in Fig.3(b). Here A is the normalization constant, $\mathcal{E}$ is the potential energy as given by the effective Hamiltonian. As we apply electric field in the positive direction, the minima in the free energy evolve (see dashed curves in Fig.3(a)) and at a certain value of the electric field the $G_0(-p_0)$ minimum aligns with the barrier near $p = 0$ point. This is the coercive field, E_c , for homogeneous PR at zero Kelvin. In our calculations, $E_c = 4.5$ MV/cm. Our calculations are likely to overestimate the coercive field since the barrier for the dipoles that rotate from negative to positive states is lower than for the dipoles that displace their charges to transition into new states. For fields below E_c , there exists a barrier ΔG_0 between the two minima in the free energy. The height of the barrier depends quadratically on the electric field (Fig.3(c)). At finite temperatures a dipole can cross the barrier if it has sufficient kinetic energy $\mathcal{E}_{kin} = \Delta G_0$. By approximating $\mathcal{E}_{kin}$ with its equilibrium value per degree of freedom, $k_B T/2$, we can predict the qualitative dependence of the coercive field on the temperature (see Fig.3(d)). We find that, in agreement with experimental findings of Ref.10, the coercive field will decrease with the temperature indicating that at elevated temperatures the homogeneous PR will occur under lower fields. Furthermore, our coercive fields are in quantitative agreement with the coercive fields for homogeneous PR in BaTiO₃ ultra thin films^{39,44}.

Once the electric field applied is larger than the coercive field at a given temperature, the dipoles will be reversing their direction. In the phase space the dipoles will move from the negative $-p$ states towards the positive p states (see Fig.3(b)). The transition time, defined as the time it takes for a dipole to reverse its direction, is $t = p/u$, where u is the average speed at which charges are displacing in a dipole (see schematization in Fig.3(b)). The speed u can also be defined as the average speed of the dipole states propagation in the phase space under the driving force of the electric field. We can now derive the transition rate for the dipoles $n(t)$ using the following identity: $\int_{-\infty}^0 \rho(p) dp = \int_{-\infty}^0 u \rho(ut) dt = \int_{-\infty}^0 n(t) dt = 1$. Note, that the integration limits reflect the fact that initially the nanowire is polarized along the negative z -axis and the dipoles occupy $-p$ states. From these the transition rate is

$$n(t) = A v \exp^{-\mathcal{E}(ut)/k_B T}. \quad (1)$$

The transition rates can be obtained from our simulations by computing $dN_{up}(t)/dt$ and are given in Fig.1(c) and (d). Indeed in the homogeneous PR region the flipping rates follow very precisely the proposed transition rate $n(t)$ which is quite remarkable given that only one adjustable parameter u is used. Moreover, both the computational and modeling data of Fig.1(d) closely resembles experimental measurements of Ref.45. We, therefore, conclude that our model that approximates homogeneous PR by the propagation of dipole states p in the phase space with the average speed u correctly captures the physics behind such phenomenon. Within this approximation, the average speed of the states propagation u is proportional to the observed inverse switching time t_{sw}^{-1} since $2p = ut_{sw}$.

At an atomistic level the speed u is due to the driving force of the electric field. When no electric field is applied, the dipoles are confined to one of the minima by the local field, $E_l = -d\mathcal{E}/dp$. Under applied electric field, E , the total field felt by a dipole is $E - E_l$. If $E < E_l$ the local field is strong enough to confine the dipoles to their original states and no PR occurs. For $E > E_l$, the applied field will drive the dipoles towards the reversed states. The local field is, of course, the atomistic counterpart of the coercive field. In the presence of the driving field, the dipoles acquire an additional kinetic energy $\mathcal{E}_E = mu^2/2$ which can be used to predict the dependence of u on the E from classical relation $mu^2/2 = (E - E_l)p$. This equation does not have a real solution for $E < E_l$, or equivalently for $E < E_c$. For $E > E_c$ we expect the quadratic dependence $E = E_c + ku^2$, where constant k gathers all the coefficients. Since u is proportional to t_{sw}^{-1} we propose the following field dependence for the inverse switching time

$$t_{sw}^{-1}(E) = t_0^{-1} \sqrt{E - E_c}, \quad (2)$$

where t_0^{-1} is a constant. As an estimate for the t_{sw} we will use the time elapsed from the moment the field was applied to the moment when 90% of the sample underwent switching.

Fig.2(b) shows our computational $t_{sw}^{-1}(E)$ along with the fitting curve given by Eq.(2). For the fitting we used $E_c = 3.0$ MV/cm obtained from our computational data for $T = 100$ K, while allowing t_0^{-1} to vary. Indeed $t_{sw}^{-1}(E)$ follows the predicted dependence for the homogeneous PR given in Eq.(2). The same conclusion holds for all studied nanowires and different temperatures (see Fig.2(b) for our data obtained at $T = 600$ K). For comparison, we also fitted our computational data with Merz's law $t_{sw}^{-1}(E) = t_1^{-1} e^{-E_A/E}$, where t_1^{-1} is a constant and E_A is the activation field. As evident from Fig.2(b) the Merz's law does not correctly capture the observed trends, which is not surprising since this law is expected to describe the field dependence of the switching rates under lower electric fields where the PR occurs via creep or domain driven mechanisms^{7,10}. The power law field dependence for the inverse switching time $t_{sw}^{-1} = KE^{\frac{3}{2}}$ was first observed in the high-field region of BaTiO₃⁹. The linear dependence, $t_{sw}^{-1} \approx E$, was observed in the high-field region of triglycine sulphate⁸ and proposed in the framework of nonlinear response¹⁰. The square root dependence similar to our Eq.(2) was proposed in the framework of phenomenological approach¹¹ and observed experimentally in ultrathin ferroelectric copolymer films^{11,13,14}.

Next we turn to domain-driven PR. During this process only the dipoles in the vicinity of the domain wall flip. These dipoles have a lower energy barrier to overcome since they are surrounded by both "up" and "down" neighbors.

We calculated the free energy profile for an idealized PR that occurs via an instantaneous sweeping of one coaxial shell at a time (see data indicated in circles in Fig.3(a)). The barrier height in this case is about half the height of the barrier for the homogeneous PR. Our simulations further suggest that the domain-driven PR may be considered as homogeneous PR within a shell or volume adjacent to the domain wall and might follow the same square root field dependence as for homogeneous PR. In that case the coercive field for the domain-driven PR is associated with the barrier for the dipoles flipping near the domain wall and is lower than E_c for homogeneous PR. We note that the data that we have for the domain-driven PR at $T = 100$ K can indeed be fitted with the square root field dependence of Eq.(2).

V. EFFECT OF NANOWIRE SIZE AND TEMPERATURE ON THE POLARIZATION REVERSAL

We find that for all nanowires considered our conclusions remain valid. Moreover, the inverse switching time given in Fig.4 shows very little dependence on the nanowire lateral size. We find that for the lower temperature ($T = 100$ K) the coercive field for the homogeneous PR decreases very slightly with the nanowire lateral size. This is a consequence of the fact that the axial polarization of a nanowire decreases slightly as the diameter of the nanowire decreases.

At elevated temperature of 600 K we observe the decrease in the coercive field for homogeneous PR (see Fig.4) as consistent with the predictions of our microscopic model given in Fig.3(d). At this temperature the inverse switching time is nearly independent of the nanowire lateral size.

VI. CONCLUSIONS

In summary we have studied ultra fast PR in ferroelectric nanowires at an atomistic level to reveal the existence of two competing PR mechanisms. Domain-driven PR activates at lower fields but is inefficient due to limited number of dipoles that can participate. Homogeneous PR activates at higher fields, but completely overpowers domain-driven mechanism since all the dipoles can engage at the same time. Since both mechanisms compete for the same dipoles, there exists only a very narrow region of electric fields where they overlap. In our computations conducted on free-standing nanowires at $T=100$ K this region is between 3.1-3.9 MV/cm and is associated with the domain driven PR in the outer part of the nanowire and homogeneous PR in the inner part.

VII. ACKNOWLEDGMENTS

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FIG. 1. Dynamics of polarization reversal. (a), (b) Fraction of the dipoles flipped during PR as a function of time for different electric fields. The dashed lines indicate the data for individual shells, while solid line corresponds to the data for the whole nanowire. The leftmost (rightmost) dashed line correspond to the outermost (innermost) shell. (c), (d) fractional flipping rates $n(t) = dN_{up}/dt$ as a function of time for two different fields. In (c) the rates are reported for three shells. In (d) the rate for the whole nanowire is given. Solid line indicates the fitting with Eq.(1). (e) Snapshots for the dipole patterns in the nanowire cross section obtained for $E = 2.8$ MV/cm. The red and blue colors indicate the areas with dipoles pointing “up” and “down”, respectively.

FIG. 2. (a) Dependencies of radial, axial and effective speeds on the applied electric field. The vertical lines separate the regions of domain-driven (DD) and homogeneous (H) polarization reversal. In the middle region C the two mechanisms coexist. (b) The field dependence of inverse switching time. The solid and dashed lines indicate the fitting using Eq.(2) and Merz's law, respectively.

FIG. 3. (a) 0 Kelvin free energy profiles for a nanowire with cross section 4.8×4.8 nm² under different electric fields. Lines (dots) indicate the free energy profile associated with homogeneous (domain-driven) PR. (b) Zero field density of states computed at $T = 100$ K. Pink (blue) shading indicates equilibrium states occupied by the dipoles p before (after) PR. Dipoles are schematically shown on top. (c) The energy barrier between the p_0 and $-p_0$ states as a function of the electric field. The intersection of the dashed lines gives the estimate of the coercive field at T . (d) Dependence of the coercive field for homogeneous PR on the temperature assuming $\mathcal{E}_{kin} = k_B T/2$ (solid line) and $\mathcal{E}_{kin} = 3k_B T/2$ (dashed line). Circles indicate the coercive fields obtained from MD simulations.

FIG. 4. The field dependence of inverse switching time for nanowires with different lateral size. Computational data are given for two different temperatures.