Asymmetry in mechanical polarization switching

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Recent demonstration of a mechanical 180° switching of ferroelectric polarization has enabled an alternative polarization control mechanism based on the flexoelectric coupling between polarization and strain gradient. Mechanical switching is a highly asymmetric phenomenon associated with the inhomogeneous strain induced by an atomic force microscope (AFM) tip pressed against the ferroelectric surface. Here, we demonstrate the asymmetric domain switching behavior in the vicinity of the 180° domain wall in $PbTiO_3$ thin films with respect to the AFM tip scanning direction. The writing-direction-dependent asymmetric domain response has been modeled by molecular dynamics simulation showing asymmetry in domain wall displacement due to the difference in the volume of mechanically switched domains. The obtained results show that the mechanically induced switching dynamics is very different from the conventional 180° switching realized by an external electric field and has to be exploited differently. In particular, nanoscale domain engineering via the tip-induced flexoelectric effect requires careful consideration of asymmetric interaction between the existing domain structures and the strain gradient. *Published by AIP Publishing.*
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Ferroelectric materials possess spontaneous polarization that can be switched by application of an external electric field. Ferroelectric polarization is also sensitive to other external stimuli, such as temperature change, mechanical stress, and magnetic field.[1,2] Recent studies demonstrated a possibility of mechanically induced polarization reversal through the flexoelectric effect—a coupling between polarization and strain gradient.[3–9] An inhomogeneous strain due to a probing tip of an atomic force microscope (AFM) pressed against an ultrathin ferroelectric film generates an electric field, which is sufficiently strong to induce polarization reversal. This finding opens a way for development of conceptually different ferroelectric devices based on domain topology, where domains and domain walls of any configuration can be controllably created by means of mechanical switching underneath a device top electrode.[10] Computer simulations showed that mechanical domain writing is more efficient in the sliding contact load regime than in the normal load experiments due to the presence of the tangential strain gradient. This result emphasizes a highly anisotropic nature of mechanical domain writing in contrast to the more isotropic domain growth during 180° switching induced by the electrically biased tip.[11] In this paper, we draw attention to another aspect of mechanical switching anisotropy, which is related to the tip sliding direction and its interaction with the existing domain structure. This result strongly suggests that anisotropy in flexoelectric polarization switching may be used as an additional degree of domain control that is not achievable with conventional electrical switching.

80-nm-thick *c*-oriented $PbTiO_3$ films epitaxially grown on the $SrRuO_3/SrTiO_3$ substrates have been used in this study. Details of sample growth information can be found elsewhere.[12] The ferroelectric domains were imaged by the piezoresponse force microscopy (PFM) technique[13,14] using a commercial AFM system (MFP3D, Asylum Research). Pt-coated conductive cantilevers (PPP-EFM, Nanosensors) were used for PFM imaging and electrical/mechanical writing.

The ferroelectric switching behavior of the $PbTiO_3$ films was first tested by means of PFM. Figures 1(a) and 1(b) show PFM images of the as-grown film with a downward polarization, while the film topographic image is in Fig. 1(c). A bipolar domain pattern resulting from electrical writing realized by scanning the sample surface with a DC-biased tip (±7 V) is shown in Figs. 1(d) and 1(e). Local PFM spectroscopy revealed typical hysteresis switching loops with coercive voltages of −3.5 V and +2.5 V [Fig. 1(f)].

Next, this electrically written domain pattern was used to study the domain switching behavior under a mechanical load. Mechanical writing was performed by scanning a $0.5 \times 1.0\ \mu m^2$ region (a dashed area in Fig. 2), while applying a high loading force of 1200 nN to the tip. The fast (2 μm/s) scan direction was perpendicular to the written 180° domain wall and the slow (4 nm/s) scan direction was parallel to it. The loading force magnitude was chosen such that the mechanical switching was induced only when the tip was in the immediate proximity to the domain wall (closer than several nanometers), while no switching occurred when the tip was farther away from the wall. This experimental tuning made use of a previously reported finding that the nucleation bias at the 180° domain wall is orders of magnitude lower in comparison with the bias required for domain nucleation in the bulk.[15] Note that the tip-induced pressure leads to the switching of the upward polarization (c^+ domain) to the downward polarization (c^- domain)[3] not to mention that the

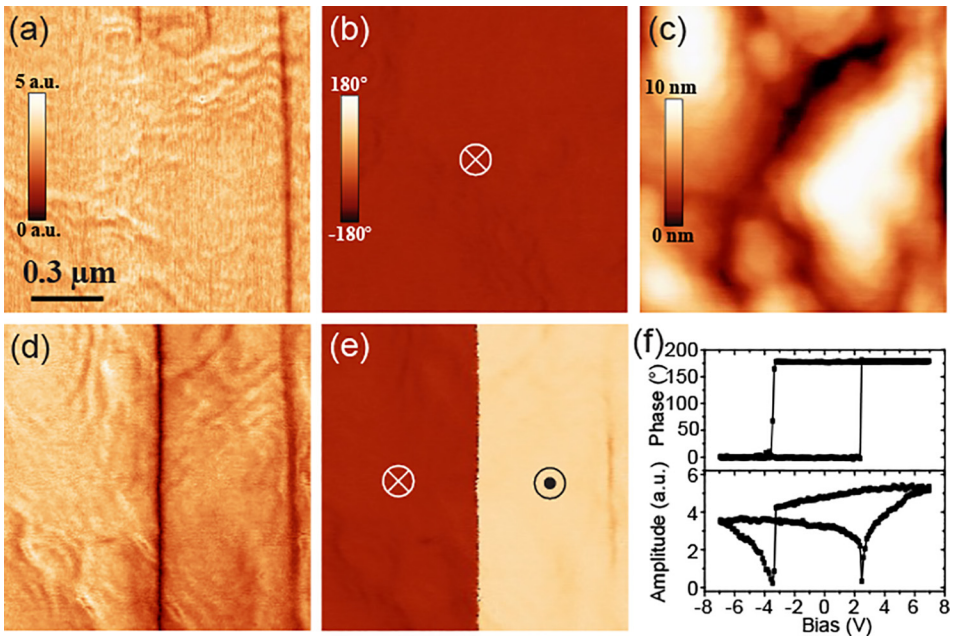

FIG. 1. PFM amplitude (a) and phase (b) images of the as-grown state in the $PbTiO_3$ film. (c) Topography image of the same area as in (a) and (b). PFM amplitude (d) and phase (e) images after electrical domain writing (+7 V was applied to the left half and −7 V to the right half of the image). (e) Local PFM hysteresis loops: phase (top) and amplitude (bottom) signals as a function of the poling voltage.

c^- domain does not show any response to the mechanical load applied via the AFM tip. Importantly, the high load was applied only during trace or retrace tip motion along the fast scan direction. For example, in Fig. 2(a), the high load was applied only when the tip was rastering from left to right. After reaching the turn-around point, the tip was lifted up and moved in the opposite direction [from right to left in Fig. 2(a)] under a 0 nN contact force. By this way, we could control the mechanical load while approaching the domain wall either from the downward or from the upward polarization side. Figures 2(a) and 2(b) show that this makes a strong difference in terms of the area of the mechanically switched region. Specifically, when the tip under a high load scanned in the direction normal to the domain boundary approaching it from the c^- domain side [from left to right in Fig. 2(a)], the overall shift of the domain wall to the right was rather limited. On the other hand, if the wall was approached by the pressing tip from the c^+ domain side [from right to left in Fig. 2(b)], the switched area was much larger: the domain wall shifted further and further to the right as the tip was slowly moving bottom-up line after line (in the slow scan direction). In other words, when mechanical writing was performed by the tip approaching the wall from the c^+ domain side, the wall moved farther than when it was approached from the c^- domain side. This domain wall motion asymmetry did not depend on the writing history or an angle between the fast scan direction and the wall but only from the approaching direction of the tip under mechanical load.

The effect of the scanning direction on evolution of domain configurations has been previously used to achieve deterministic control of ferroelastic switching by an electrically biased tip in $BiFeO_3$ films and nanoislands.[16–18] Specific polarization variants could be selected by inducing polarization rotation resulting from complex interplay between the elastic strain and the trailing electric field of the moving tip. Even in the case of conventional 180° tip-induced electrical switching, the shape of the written domains could change with the tip scanning direction due to the crystallographic direction dependence of the activation energy.[19] In our study, we confirmed that no asymmetry in the domain writing with respect to the scanning direction by the electrically biased tip was observed. In this case, while the tip was scanning across the domain wall, a 2.1 V dc bias (slightly below the coercive voltage) was turned on only during the trace or retrace tip motion, emulating the mechanical writing approach described

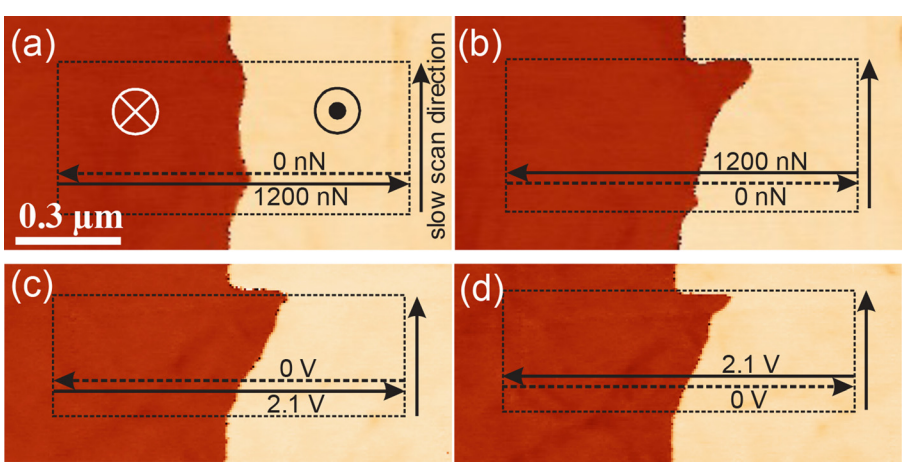

FIG. 2. PFM phase images of the $PbTiO_3$ film resulting from directional mechanical [(a) and (b)] and electrical [(c) and (d)] domain writing in the areas marked by a dashed frame starting from the original bi-domain structure shown in Figs. 1(a) and 1(b). (a) and (b) Mechanical load of 1200 nN was applied for the fast scan direction from left to right in (a) and from right to left in (b). A slow scan direction is bottom up. (c) and (d) Electrical bias of 2.1 V was applied for the fast scan direction from left to right in (c) and from right to left in (d).

above. PFM images resulting from such electrical switching [Figs. 2(c) and 2(d)] show that in both cases the domain wall shifted from its initial position by almost the same distance—an indication of the invariance of the electrical switching with respect to the tip approaching direction. The observed difference between mechanical and electrical writing under directional application of an external switching stimulus suggests that anisotropy in mechanical switching may play a significant role in tip-induced mechanical domain engineering by adding an additional aspect to the polarization reversal process due to interaction between the tip and the existing domain structure.

To get a better understanding of the asymmetric domain wall response to opposing mechanical writing directions, molecular dynamics (MD) simulations are performed on a $PbTiO_3$ thin film consisting of an 80-unit-cell-thick slab and 85 Å of vacuum along the surface normal, with the top surface terminated by a TiO_2 layer and the bottom surface terminated by a PbO layer. To stabilize the ferroelectric film under the open circuit condition, the bond-valence charges[20,21] of the surface TiO_2 and PbO layers are reduced by a factor of two, which results in a domain structure with unit cells close to the surface acquiring in-plane polarization (a-domain). The c^+-domain is obtained by adding 0.2 e/f.u. (electron/formula unit) to the top TiO_2 surface and removing 0.2 e/f.u. from the bottom PbO surface layer, while the c^- domain is obtained by reversing the process. A similar computational setup was recently applied to study the electron-beam-induced ferroelectric switching in $PbTiO_3$ thin films.[22] The slab model with 180° domain wall separating c^+ and c^-domains is shown in Fig. 3(a). The mechanical load of the tip is modeled by adding a constant force to the top atomic layer in a confined region. This mechanical load produces a curved/concave surface around the tip, as shown in Fig. 3(b). The profile of out-of-plane lattice constants obtained with MD simulations shows an inhomogeneous strain distribution and strain gradient below the tip [Fig. 3(c)].

It should be noted that the ferroelectric switching in thin films is intimately coupled with surface charge changes. We incorporate the effects of both mechanical load and dynamical surface charge compensation by updating them independently in sequential fashion. Computationally, we first apply the mechanical load. Whenever the majority of the unit cells in one plane are switched, the surface charge state is switched above and below that layer of unit cells while maintaining the mechanical load. The process is repeated for each mechanical switching step. In this way, the applied mechanical force determines the cells that switch, and the surface charges then stabilize them.[23,24]

We compare two cases of mechanically driven domain wall motions: the tip is placed entirely on the top of the (1) c^- domain and (2) c^+ domain, right next to the 180° domain wall. We find that in both cases the pressing tip moves the domain wall, but these two cases give significantly different responses. When the tip is initially on the top of the c^- domain, it makes the domain wall move away from the tip, but the domain wall stops moving when it is about two unit cells away from the boundary of the tip, regardless of the loading time of the tip [Fig. 4(a)]. This is due to the fact that the mechanical pressure from the tip only induces the strain gradient localized around the tip. The domain wall stops as it

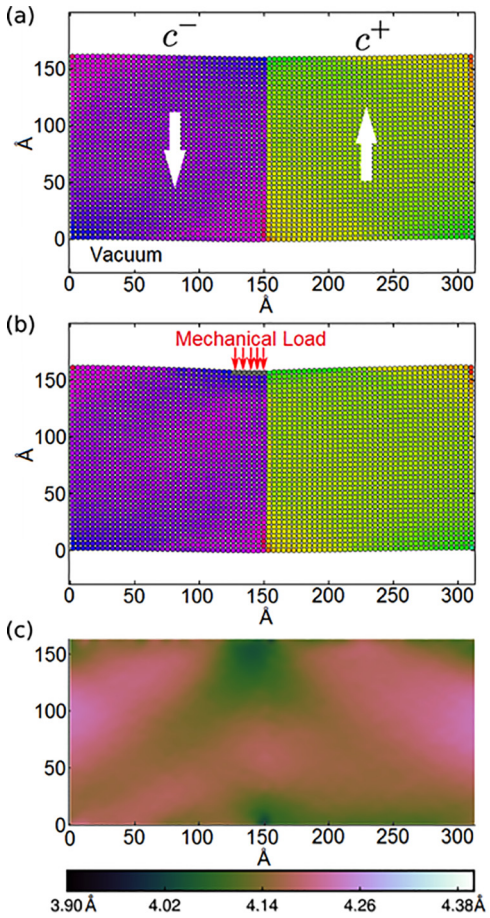

FIG. 3. Molecular dynamics simulation of the $PbTiO_3$ thin film. (a) Initial domain structure with the 180° domain wall separating c^+ and c^- domains in a slab model. Only Ti atoms are shown and plotted as filled circles, colored based on the directions of local dipoles. (b) Simulating mechanical load of the tip by adding a constant force to the top atomic layer in a confined region (colored in gray). The effect of mechanical load is evidenced by the curved/concave surface around the tip. (c) Out-of-plane lattice constant distribution in the presence of mechanical load.

moves to a region of a smaller strain gradient. On the contrary, placing the tip on the top of the c^+ domain drives the domain wall toward the tip, which effectively increases the interaction time between the tip and the domain wall. Simulations show that the tip pressure induced near the wall from the c^+ domain side generates domain switching in a larger volume [Fig. 4(b)].

Based on the results from MD simulations, we propose a model to explain the experimentally observed writing-direction-dependent asymmetric response. We keep in mind that the tip-induced mechanical load induces switching in a highly localized area of just several nanometers in diameter.[4] As illustrated in Fig. 5, at these conditions, when the tip approaches the domain wall from the c^- domain side, due to the induced switching ahead of the tip, the domain wall is pushed forward by a finite distant until it reaches a region where the low strain gradient is not strong enough to induce switching.[25,26] Assuming that the wall moves relatively slow, it cannot follow the tip once it passes over it into the c^+ domain side. As a result, the wall travels a relatively short distance. On the other hand, when the wall is approached from the c^+ domain side, the switching is induced both ahead and behind the tip so that in effect the domain wall will be

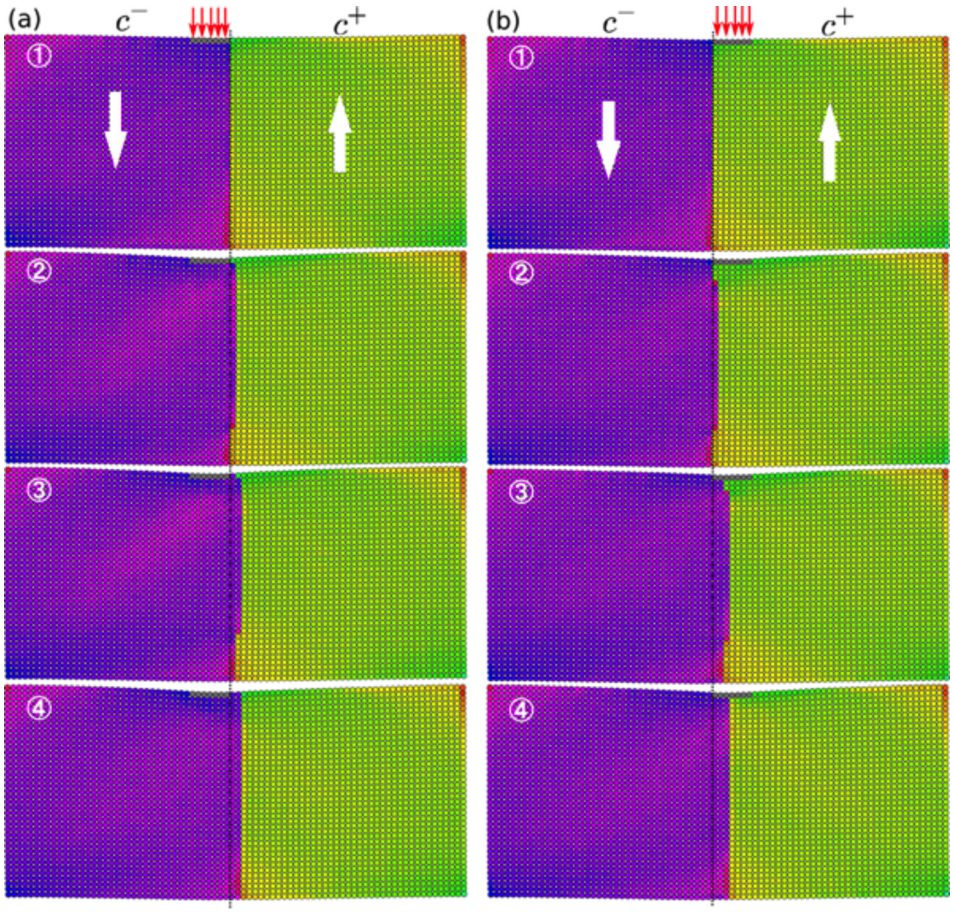

FIG. 4. Asymmetric response with respect to the mechanical writing direction. (a) Simulated evolution of the domain wall in response to the AFM tip pressing on the top of c^- domain near the 180° domain wall as a function of time from step 1 (initial state) to step 4 (final state). Steps 2–3 are the transient states between steps 1 and 4. The domain wall moves away from the tip and stops when it is two unit cells away from the tip. (b) Simulated evolution of the domain wall in response to the tip pressing on the top of c^+ domain near the domain wall. The domain wall moves toward the tip, and more layers of unit cells are switched compared to (a).

shifted by a larger distance. With each raster line when the tip approaches the wall from the c^+ domain side, the domain wall shifts further and further away from its initial position resulting at the end in a much larger displacement. Why then is there no writing-direction-dependent switching in the case of the electrically biased tip? This could be explained if we recall that the tip-generated electric field extends over the distance of up to several hundred nanometers from the tip-sample contact, which is comparable to the range of the 2D nucleation bias softening in the vicinity of the domain wall.[15] Thus, electrical switching will be initiated at large distances ahead of the tip (but not behind it) irrespective of which side it approaches the domain wall.

In conclusion, mechanically induced nanoscale domain writing via the flexoelectric effect presents an exciting approach for development of advanced ferroelectric devices based on domain topology. It has been found that the mechanically induced switching in the vicinity of the existing domain wall exhibits strong asymmetry with respect to the tip scanning direction. Specifically, the domain wall is moved farther from its initial position by the tip approaching the wall from the c^+ domain side than from the opposite direction. Molecular dynamics simulation illustrated the asymmetry by modeling the difference in the confined volume of the c^+ domain, over which mechanical stress is exerted for opposite tip scanning directions. The obtained results suggest that nanoscale domain engineering via the flexoelectric effect requires careful consideration of the asymmetric interaction between the existing domain structures and the strain gradient. It would be of interest to investigate the impact that the relationship between the domain wall velocity and the tip scanning speed might have on asymmetry of mechanical switching.

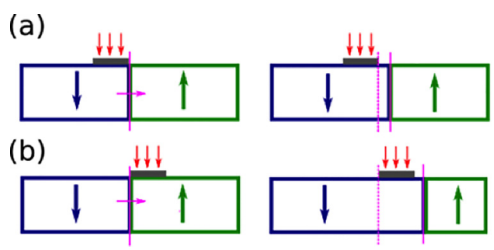

FIG. 5. A sketch illustrating a mechanism of asymmetric mechanical switching. (a) When the tip approaches the wall from the c^- domain side, the domain wall is pushed forward away from the tip eventually stopping at some distance from its initial position. (b) When the tip approaches the wall from the c^+ domain side, the switching is induced both ahead and behind the tip causing switching in a larger area.

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