Deterministic Creation and Manipulation of Isolated Three-fold Polar Vertices

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Recently various topological polar structures have been discovered in oxide thin films. Despite the increasing evidence of their switchability under electrical or mechanical fields, the ability to control an isolated one, which is usually required for applications such as data storage, is still challenging as they strongly interact with their neighbors. Here, we demonstrate deterministic control of nucleation and long-range motion of isolated three-fold vertices by an applied electric field. In PbTiO\textsubscript{3} thin film on DyScO\textsubscript{3} substrate with SrRuO\textsubscript{3} bottom electrode, nano-sized three-fold vertices can be created at heterointerface during the generation of 180° domain walls. A two-unit-cell thick SrTiO\textsubscript{3} layer formed at the interface due to the elemental diffusion between PbTiO\textsubscript{3} and SrRuO\textsubscript{3}, provides critical electrical boundary conditions for stabilization of three-fold vertices. These isolated three-fold vertices could move a long distance along the interface under electric fields in a controllable and reversible manner, accompanied by 180° domain wall motion. This work provides a simple pathway to fabricate three-fold polar vertices, and the deterministic control of individual ones enables novel ferroelectric devices.
A variety of topological polar configurations have been created in complex oxides by precisely mediating the electrical and mechanical boundary conditions.\textsuperscript{1, 2, 3, 4, 5, 6} For example, vertices (meeting points of two or more domain walls),\textsuperscript{7, 8, 9} vortices (require a non-zero polarization curl),\textsuperscript{1, 10} polar skyrmions\textsuperscript{11} and polar merons\textsuperscript{12} have been synthesized in (PbTiO\textsubscript{3})\textsubscript{n}/(SrTiO\textsubscript{3})\textsubscript{n} superlattices or directly written in ferroelectrics by scanning probe techniques.\textsuperscript{8, 13, 14, 15} These topological structures host unique properties, such as local negative capacitance in vortex and polar skyrmions,\textsuperscript{16, 17} enhanced conductivity at vortex cores\textsuperscript{18} and chirality in vortices.\textsuperscript{19} These emergent phenomena allow the development of novel electronics including negative capacitance field-effect transistors\textsuperscript{20} and high-density non-volatile memories.\textsuperscript{21} Practical applications of these topological structures require the ability to manipulate them by using external stimuli.\textsuperscript{22, 23, 24, 25} To date, extensive theoretical and experimental studies have been carried out to explore the evolution of topological structures under electric and mechanical fields.\textsuperscript{8, 14, 26, 27, 28, 29} Particularly, in PbTiO\textsubscript{3}/SrTiO\textsubscript{3} superlattices, reversible phase transition between flux-closure and trivial ferroelectric phase driven by either electrical or mechanical fields have been observed.\textsuperscript{30} In such a similar system, vortex arrays can switch to out-of-plane and in-plane polarization by electric fields and mechanical loading, respectively.\textsuperscript{31, 32} In these studies, the emergent of topological structures are collective behavior due to the strong interaction between their neighbors. For instance, one clockwise vortex is always sandwiched between two anticlockwised ones in a PbTiO\textsubscript{3} layer,\textsuperscript{10} and similar for flux-closure domains.\textsuperscript{4} However, some applications demand the ability to control individual ones independently, e.g., data storage, for which one-by-one writing and erasing is required. Therefore, a critical problem...
that has been raised for these applications is how to deterministically manipulate individual topological polar structures independently.

Here, we deterministically create isolated three-fold vertices at the interface of PbTiO$_3$ thin film on DyScO$_3$ substrate with SrRuO$_3$ bottom electrode by generating 180° domain walls. The atomic resolution characterization suggests elemental diffusion induces the formation of a two-unit-cell SrTiO$_3$ layer at interfaces, which is the key to stabilize three-fold vertices. By manipulating 180° domain wall motion under electric fields, we further demonstrate a long-range motion of these isolated three-fold vertices along the interface in a controllable and reversible manner. This simple and feasible strategy to deterministically create, and manipulate individual three-fold polar vertices independently may enable some new functions for topological polar structures.

Fig. 1a shows a schematic of an isolated three-fold vertex. The three-fold vertex is the intersection of a 180° domain wall and two 90° domain walls in ferroelectrics.$^5$ $^7$ It can be simply taken as one-half of closure domains (Fig. S1, Supporting information).$^4$ $^8$ With a triangular 90° domain at the interfaces, the polarization flux transits from downward to upward with no poles are formed. Because the component of polarization normal to 90° domain walls is continuous.$^{33}$ Such an arrangement was firstly proposed by Landau and Lifshitz in 1935 in their study of ferromagnetic domains by minimized the energy of crystals.$^{34}$ To demonstrate the static and dynamic features of three-fold vertices, we performed experiments on PbTiO$_3$ films.

For this work, 100-nm-thick PbTiO$_3$ thin films were deposited on single-crystal (110)$_o$ DyScO$_3$ substrates (the subscript O indicates orthorhombic) with 50-nm-thick SrRuO$_3$ as the bottom electrode. A cross-sectional view of the PbTiO$_3$/SrRuO$_3$ interface is shown in Fig. 1b by a dark-field TEM image. The typical $a/c$ domain patterns and two vertical 180° domain walls are
observed by diffraction contrast imaging.\textsuperscript{24,35} In the enlarged images in Fig. 1b, small triangular prisms with \(\sim 45^\circ\) tilted domain walls indicate the existence of nanometer-scale three-fold vertices at interface. The atomic-resolution high-angle annular dark-field (HAADF) image in Fig. 1c further prove the formation of isolated three-fold vertices. One 180\(^\circ\) domain wall and two 90\(^\circ\) domain walls were denoted by yellow dashed lines. Analogous arrangements of magnetic flux have been reported in ferromagnetic films.\textsuperscript{36}

The atomic structure was analyzed in details by performing quantitative analysis with a home-developed code.\textsuperscript{37,38} Since the inevitable drift of samples and other factors can cause deviation in measurements,\textsuperscript{37} a careful calibration has been performed with DyScO\textsubscript{3} substrates as the reference. The out-of-plane and in-plane lattice parameters were measured at the unit-cell scale as mapped in Fig. 1d and e respectively. The spatial variation of in-plane and out-of-plane lattice parameters across the three-fold vertex are shown in Fig. S2 (Supporting information) with the corresponding \(c/a\) ratio. The in-plane lattice parameters of triangular 90\(^\circ\) domain are suppressed to 405 pm compared with 415.8 pm in typical 90\(^\circ\) domains.\textsuperscript{39} Besides the suppression of in-plane lattice parameters, the lattice rotation in triangular 90\(^\circ\) domain is also revealed by measuring the angle of the Pb sublattice. Fig. 1f shows the mapping of lattice rotation angles with the definition of lattice rotation angle \(\theta\). The contrast in triangular 90\(^\circ\) domain indicates a sinusoidal lattice rotation. The range of rotation angle of the marked region is about \(\pm 1^\circ\) as shown in Fig. S2 (Supporting information). How to understand the lattice suppression and rotation? Because of the elongated lattice parameter along the polarization direction in PbTiO\textsubscript{3}, the triangular 90\(^\circ\) domain with in-plane polarization possesses larger in-plane lattice parameters (415.8 pm) compared with neighbor domains (390.4 pm) and DyScO\textsubscript{3} substrates (395.6 pm).\textsuperscript{40} By sinusoidal lattice rotation and the suppression of in-plane lattice parameters,
the triangular prism smoothly fit into basic domains at atomic scale.

**Fig. 1. Three-fold vertices at PbTiO$_3$/SrRuO$_3$ interfaces.** (a) Schematic diagram of a single three-fold vertex. (b) A cross-sectional dark-field TEM image with $g = (101)$ showing the domain structure in PbTiO$_3$ films. (c) A atomic-resolution HAADF image of an isolated three-fold vertex at PbTiO$_3$/SrTiO$_3$ interfaces. Yellow dashed lines indicate 180° and 90° domain walls. (d-f) Quantitatively atomic structure analysis showing the distribution of out-of-plane lattice parameters (d), in-plane lattice parameters (e) and lattice rotation (f). The inset schematic shows the definition of lattice rotation angle $\theta$.

To figure out why three-fold vertices are formed at ferroelectric/electrode interfaces, we analyzed the atomic structure and elemental distribution of the interfaces. Fig. 2a shows the atomic structure of PbTiO$_3$/SrRuO$_3$ interfaces. The interfacial region presents a different contrast with PbTiO$_3$ and SrRuO$_3$ layers, indicating the elemental diffusion across the interface. The corresponding atomic-resolution energy-dispersive X-ray spectroscopy (EDS) mapping in Fig. 2b further prove the diffusion of Ti into SrRuO$_3$. The substitution of Ru by Ti generates a
two-unit-cell thick SrTiO$_3$ layer at interfaces which is marked by dashed white lines. Since SrTiO$_3$ is insulating, it can impair the perfect screening of polarization charges at interfaces. The residual depolarizing field provide proper electrical conditions for the formation of three-fold vertices.$^{2,41,42,43}$ Polar displacements of Ti cations were measured relative to the center of surrounding Pb cations by a home-developed code.$^{37,38}$ Fig. 2c shows a map of relative displacement vectors of Ti cations around the interface which reflects the polarization distribution. The schematic in Fig. 2c suggests the location of the SrTiO$_3$ spacer. A profile of polar displacements across the interface is shown in Fig. 2d. The suppression of polarization is apparent within about 6 unit cells from the interface. However, the transition layer is just 1.5 unit cells in PbZrTiO$_3$/SrRuO$_3$ interfaces according to the previous study.$^{44}$ In addition, the displacement between cations even exists in SrTiO$_3$ and SrRuO$_3$. These displacements near ferroelectric films can act as alternative screening mechanism of polarization charges which has been proposed in theoretical and experimental reports.$^{45,46}$ Therefore, the wider transition layer and displacements in SrTiO$_3$ and SrRuO$_3$ suggest the imperfect screening of depolarizing field induced by the diffused SrTiO$_3$ layer. The residual depolarizing field can provide ideal electrical boundary conditions for the formation of three-fold vertices when electric-field-induced 180° domain walls intersect interfaces.
Fig. 2. Atomic structure and elemental diffusion at PbTiO$_3$/SrRuO$_3$ interfaces. (a) A high-resolution HAADF image of PbTiO$_3$/SrRuO$_3$ interface. (b) Corresponding atomic-resolution EDS elemental mappings for Pb, Ti, Sr and Ru. White dashed lines indicate a two-unit-cell SrTiO$_3$ layer induced by Ti diffusion into SrRuO$_3$. (c) A mapping of polar displacements with a schematic diagram of the atomic structure of the interface. (d) The quantitative measurement of polar displacements as a function of the distance away from the PbTiO$_3$/SrRuO$_3$ interface. The colored region denoting the location of diffused SrTiO$_3$ layer.

In order to directly demonstrate how three-fold vertices evolves under an electric field, we employed in situ TEM electrical testing system to recorded the switching process. The in situ TEM tests allow us to directly observe the domain structure at interfaces and track their evolution in ferroelectric films.$^{25,47,48}$ A 3D sketch in Fig. 3a depicts the probe-based electrical testing system. A tungsten tip acts as the top electrode to apply a bias on PbTiO$_3$ films while the SrRuO$_3$ electrode is grounded. The distribution of electric fields in ferroelectric films has been simulated in similar systems in our previous work.$^{49}$ A chronological diffraction contrast
TEM image series in Fig. 3b-g shows the domain structure evolution under varying electric fields. Fig. 3b presents the initial state of PbTiO₃ films with typical a/c domain patterns. The polarization in PbTiO₃ films is downward as illustrated in Fig. 2d. When a negative voltage is applied, a 180° domain with upward polarization appears (Movie S1, Supporting information). Nanoscale isolated three-fold vertices formed at interfaces where 180° domain walls meet interfaces as shown in Fig. 3c. The three-fold vertices are distinguished by small triangular domains with ~45° tilted domain walls as shown in enlarged images. We measured the distance d between two isolated three-fold vertices to characterize their motion behavior. When the voltage increases from negative 6 volts to zero, the isolated three-fold vertices remain at interfaces in Fig. 3d, indicating their non-volatile property.

In addition, when the opposite electric field is applied, 180° domain walls move in the opposite directions (from Fig. 3d to 3f) accompanied by the approaching of isolated three-fold vertices. The movement of 180° domain walls caused an increasing in the volume of 180° domain at the expense of unfavorably oriented domains with respect to the applied electric field. Note that these isolated three-fold vertices move along the interfaces following 180° domain walls from Fig. 3d to 3f. The nearly synchronous motion of 180° domain walls and three-fold vertices along the interfaces can avoid the large derivation of 180° domain walls from the symmetric permitted axis. Because tilted 180° domain walls are charged and thus energetically unfavorable. Finally, two three-fold vertices coalesce and 180° domain walls leave the interface in Fig. 3g. In Fig. 3h, we plot d and applied voltage U as functions of time to quantitatively analyze the switching process. The distance between two isolated three-fold vertices is up to ~134 nm. Therefore, the generation and motion of three-fold vertices is controlled by an applied voltage in a reversible manner. The creation and motion of isolated
three-fold vertices are repeatable (Fig. S3 and Movie S2, Supporting information).

**Fig. 3. Electric-field control of isolated three-fold vertices at PbTiO$_3$/SrRuO$_3$ interfaces.**

(a) Schematic diagram of the probe based *in situ* TEM experimental set-up. Two isolated three-fold vertices are formed at PbTiO$_3$/SrRuO$_3$ interfaces. (b-g) Chronological TEM dark-field image series illustrate nucleation and lateral motion of two three-fold vertices along PbTiO$_3$/SrRuO$_3$ interfaces under applied electric fields. (h) Plots of applied voltage (orange line) and distance between two isolated three-fold vertices (blue diamond) as functions of time.

For the formation of three-fold vertices at interfaces, both electrical and mechanical boundary conditions are important. In electrical, the appearance of a SrTiO$_3$ layer impairs perfect screening of metallic SrRuO$_3$ electrode. When 180° domain walls end at interfaces, the formation of three-fold vertices with triangular 90° domains can reduce polarization charges since no polarization charges accumulate at interfaces under the triangular 90° domains. In other words, the formation of three-fold vertices at interfaces also acts as a screening mechanism besides suppressed polarization and displacements in SrTiO$_3$ and SrRuO$_3$ layers. Formation of three-fold vertices in PbZrTiO$_3$ films has been predicted theoretically by adjusting the screening of depolarizing field.$^{41}$ In mechanical, a tensile strain from DyScO$_3$ substrates provides proper
mechanical boundary conditions for the formation of three-fold vertices. The in-plane lattice mismatch between DyScO$_3$ and PbTiO$_3$ is 1.3%, calculated by the following formula:\(^{51}\)

\[
f = \frac{a_2 - a_1}{(a_2 + a_1)/2} \times 100\% = 1.3\%
\]  

(1)

where $a_1$ is the in-plane lattice parameter of PbTiO$_3$ films, 390.4 pm, and $a_2$ is the in-plane lattice parameter of DyScO$_3$, 395.6 pm.\(^{40}\) Since three-fold vertices are induced by electrical and mechanical conditions at interfaces, it is not surprising that dramatic changes of domain structure will happen when interface conditions changed. We characterized the atomic structure of 180° domain walls at PbZrTiO$_3$/SrTiO$_3$ interfaces for comparison. A single-layer PbZrTiO$_3$ films was directly grown on insulating SrTiO$_3$ substrates with 180° domain walls. However, no three-fold vertices are formed where 180° domain walls and interfaces intersect. The in-plane lattice mismatch between PbTiO$_3$ and SrTiO$_3$ is negligible, i.e. 390.4 pm in PbTiO$_3$ vs 390.5 pm in SrTiO$_3$.\(^{52}\) Without the tensile stress, a sharp 180° domain wall appears at PbZrTiO$_3$/SrTiO$_3$ interfaces (Fig. S4, Supporting information. Therefore, the two-unit-cell thick SrTiO$_3$ layer not only mediate the screening of depolarizing field, but also maintain the strain field from substrates. These results demonstrate the possibility of employing interface engineering to fabricate topological polar structures in ferroelectric films.

To build a bridge between topological polar structures and practical applications, the dynamics of isolated structures are critical as they may be regarded as single functional elements. Many impressive progress has been made in exploring dynamic behavior of topological structures by state-of-art electron microscopy and other techniques.\(^{19,29,30,53}\) During the collective switching process, these topological structures are almost fixed at their locations in superlattices. In contrast, our results demonstrate the highly mobile feature of isolated three-fold vertices. With
the driving force from electric fields, three-fold vertices are capable to move over 100 nm along the interface which enables the design of novel devices like electric racetrack memory. The unusual mobility of isolated three-fold vertices indicates the dynamic property of individual topological polar structures may be extraordinary. Since the similarity of topological structures between ferroelectrics and ferromagnetic, it is possible to explore the dynamics and related physical properties of isolated topological structures in ferroelectrics just as their counterparts in magnetics. In magnetics, many topological structures have been proven to be highly mobile and controllable under external stimuli. For example, isolated magnetic skyrmions can be generated and driven by current. The skyrmion Hall effect has also been discovered by driving the motion of isolated magnetic skyrmions. What’s more, the interaction between topological structures are excepted to happen like these in magnetics. However, this field is still poorly understood. In situ TEM combined with interface engineering offers an effective tool to determine the dynamic properties and interactions of isolated topological polar structures.

In summary, our work has demonstrated the formation and dynamic behavior of isolated three-fold vertices under electric fields at interfaces. The nucleation and long-range motion of isolated three-fold vertices were directly observed under electric-fields. According to the atomically resolved elemental mapping, a two-unit-cell SrTiO$_3$ layer is identified to exist at interfaces and assists the formation and stabilization of nanoscale three-fold vertices. This result suggests the possibility of employing interface engineering to fabricate isolated topological structures. These isolated three-fold vertices are mobile under electric fields in a controllable and reversible manner. The highly mobile nanoscale three-fold vertices provide additional dimensions for the design of novel ferroelectric devices. The interface engineering and in situ electrical testing might also be applicable to investigate physical properties and dynamic behavior of other
isolated topological structures.

**Experimental Section**

*Film Growth:* The 100-nm-thick PbTiO$_3$ thin films were grown on single crystal (110)$_c$ DyScO$_3$ substrates buffered with ~50-nm-thick SrRuO$_3$ electrodes using pulsed laser deposition method, as well as the Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ films on (001) SrTiO$_3$ substrates. A KrF excimer laser ($\lambda = 248$ nm) was focused on the targets with an energy density of ~2.5 mJ cm$^{-2}$ and repetition rate of 10 Hz. During the growth of the SrRuO$_3$, the temperature and the oxygen pressure were kept at 700 °C and 100 mTorr, respectively. To avoid the easy evaporation of the lead in PbTiO$_3$ thin film at high temperature, the target with 5% excess lead was used and the temperature for the subsequent growth of PbTiO$_3$ thin film was decreased to 650 °C at the same oxygen atmosphere. After the deposition process, an *in situ* post annealing process with the same temperature and high oxygen pressure environment of ~300 Torr for 30 min was adopted to effectively eliminate the oxygen vacancies of the sample. Finally, the sample was slowly cooled down to room temperature with a ramp rate of 5 °C min$^{-1}$.

*Sample preparation and Characterization:* TEM samples were prepared by conventional mechanical polishing and subsequent argon ion milling in a Precision Ion Polishing System 691 (Gatan). The procedure for ion milling consisted of two steps. During the first stage, the guns were operated at 4 keV and at angles of 6° and -6°. During the second stage, the guns were operated at 1 keV for 5 min and at angles of 3° and -3°, and lowered further to 0.1 keV for 2 min for final surface cleaning. Diffraction contrast TEM experiments were carried out using a FEI Tecnai F20 microscope. Samples were tilted off the zone axis and imaged in the bright field or dark field with two-beam alignment condition using a $\mathbf{g} = (101)$ vector. High-angle annular
dark-field (HAADF) images and energy-dispersive X-ray spectroscopy (EDS) images in this work were obtained using probe aberration-corrected FEI Titan Cubed Themis G2 operated at 300 kV in Electron Microscopy Laboratory of Peking University. Atom positions were determined by simultaneously fitting two dimensional Gaussian peaks to a perovskite unit cell using a home-developed code. Polar displacements of the Ti cations were measured relative to the center of the surrounding Pb cations in HAADF images. Annular bright field (ABF) images were recorded at 300 kV in JEM ARM300CF (JEOL Ltd.). The convergence semi-angle for imaging is 24 mrad, collection semi-angles snap is 12 to 24 mrad for ABF.

In situ study: In situ TEM experiments were carried out on a FEI Tecnai F20 microscope operated at 200 kV with a PicoFemto double-tilt TEM-STM holder provided by ZEPTools Technology Company. A tungsten tip acted as the top electrode which was precisely controlled by a piezoelectric system. The switching processes were recorded with a OneView camera (Gatan). The imaging rate was set at 10 frames per second in order to get a better contrast.

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**Acknowledgements**

We acknowledge the supported by the National Natural Science Foundation of China (52125307, 52021006), the Key R&D Program of Guangdong Province (2018B030327001, 2018B010109009).
Supporting Information

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Fig. S1. A pair of three-fold vertices. Arrows suggest the formation of a closure of polarization flux.

Fig. S2. Atomic structure of three-fold vertices. (a) Out-of-plane and in-plane lattice parameters across three-fold vertex corresponding to the marked regions in Fig. 1d and e,
respectively. (b) Distribution of $c/a$ ratio corresponding to the image in Fig. 1c. (c) Line profile of $c/a$ ratio corresponding to the marked area in (b). (d) Line profile of lattice rotation across the three-fold vertex corresponding to the marked area in Fig. 1f.

Fig. S3. Electric-field control of isolated three-fold vertices at PbTiO$_3$/SrRuO$_3$ interfaces. (a-g) Chronological TEM dark-field image series illustrates nucleation and lateral motion of two three-fold vertices under applied electric fields. (h) Plots of applied voltage (orange line) and distance between two isolated three-fold vertices (blue diamond) as functions of time. (i) Schematic diagrams of the electric-field-driven motion of three-fold vertices. White arrows indicate the direction of motion.
**Fig. S4. Atomic structure of 180° domain wall at PbZrTiO$_3$/SrTiO$_3$ interfaces.** (a) An annular bright field (ABF) image of PbZrTiO$_3$/SrTiO$_3$ interface with a 180° domain walls. Open arrows show the direction of polarization. The inset intensity profile indicated the location of PbZrTiO$_3$/SrTiO$_3$ interfaces. Quantitatively atomic structure analysis showing the distribution of out-of-plane lattice parameters (b), in-plane lattice parameters (c) and corresponding $c/a$ ratio (d). Dashed lines indicate the location of PbZrTiO$_3$/SrTiO$_3$ interfaces.