Reversible transition between the polar and antipolar phases and its implications for wake-up and fatigue in HfO$_2$-based ferroelectric thin film

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Atomic-resolution Cs-corrected scanning transmission electron microscopy revealed local shifting of two oxygen positions (O$_I$ and O$_{II}$) within the unit cells of a ferroelectric (Hf$_{0.5}$Zr$_{0.5}$)O$_2$ thin film. A reversible transition between the polar Pbc$_{21}$ and antipolar Pbc$_a$ phases, where the crystal structures of the 180° domain wall of the Pbc$_{21}$ phase and the unit cell structure of the Pbc$_a$ phase were identical, was induced by applying appropriate cycling voltages. The critical field strength that determined whether the film would be woken up or fatigued was -0.8 MV/cm, above or below which wake-up or fatigue was observed, respectively. Repeated cycling with sufficiently high voltages led to development of the interfacial nonpolar P4$_2$/nmc phase, which induced fatigue through the depolarizing field effect. The fatigued film could be rejuvenated by applying a slightly higher voltage, indicating that these transitions were reversible. These mechanisms are radically different from those of conventional ferroelectrics.
Ensuring reliable and repeatable electrical performance from ferroelectric (FE) thin films and devices present a significant challenge for conventional FE materials such as perovskite-structured Pb(Zr,Ti)O₃ (PZT) to enable their use in FE memory devices. Among the potential problems, fatigue, which is induced by defect (mainly oxygen vacancy (V̅O)) generation and the accompanying FE domain pinning, which occurs during repeated electrical stimulation, is one of the most critical concerns. While the discovery of ferroelectricity in doped HfO₂ thin films by Böské et al. in 2011 has again triggered enormous interest in FE memories and several other novel applications, these films are not exempt from serious fatigue concerns. However, the much higher binding energy of the Hf–O bond when compared with the Ti–O bond in PZT makes serious V̅O involvement in the fatigue in this material unlikely.

Another interesting but also undesirable effect in this new FE material is wake-up (a temporal increase in the switchable polarization during the first 10⁴–10⁵ switching cycles). This has been ascribed to the decrease in the non-ferroelectric tetragonal interfacial layer (T-phase, P4_2/mmc) caused by the reduced V̅O concentration in the layer. However, a reactive TiN electrode would be likely to increase the V̅O concentration during repeated cycling. Therefore, these two issues, i.e., severe fatigue and wake-up, as direct consequences of the V̅O effect are hardly understood.

In fluorite-structured FE materials, four of the eight oxygen ions within each unit cell were shifted along the c axis direction (O̅II ions), while the other four oxygen ions (O̅I ions) remained in centrosymmetric positions. The energy of the polar phase (FE Pbca, where all O̅II ions shift in the same direction) is only slightly higher than that of the antipolar phase (antiferroelectric (AFE) Pbcn, where O̅II ions shift into antiparallel directions) by ~10 meV/f.u. These specific crystallographic features of HfO₂-based FE materials may render the transition between the FE Pca₂₁ and AFE Pbcn phases to be both fluent and reversible, depending on the bias voltage conditions, and maybe the origin of the fatigue and wake-up phenomena. However, this probability has scarcely been examined to date.

This work used an advanced imaging technique, Cs-corrected scanning transmission electron microscopy in annular bright-field mode (STEM-ABF), which enables reliable imaging of light atomic columns (oxygen) in the presence of much heavier atomic columns (Hf and Zr) in fluorite-structured (Hf₀.₅Zr₀.₅)O₂ (HZO) films. The pristine, woken-up, fatigued, and rejuvenated 10- to 15-nm-thick HZO films were prepared by electrical cycling of TiN/HZO/TiN FE capacitors. The atomistic structural evolutions occurring in each state were examined using the STEM-ABF technique. The involvement of V̅O effect was observed during fatigue cycling, which increased the interfacial T-phase, but the direct cause of the fatigue differed fundamentally from that in conventional FE materials. The wake-up, fatigue, and rejuvenation were mediated by the (reversible) transition between the FE Pca₂₁ and AFE Pbcn phases. This conclusion was further supported by theoretical calculations based on density functional theory (DFT). The theoretical findings on the switching path and the bias voltage dependence matched the experimental results very well.

Results

A TiN/HZO/TiN capacitor with HZO thickness of 15 nm was fabricated using the atomic layer deposition (ALD) process at a substrate temperature of 280 °C (see “Methods” section). Because the FE orthorhombic phase (O̅I, phase, Pca₂₁) is not the thermodynamically stable bulk phase, it could be achieved by kinetic means, supplemented by the surface energy/stress effects in the fine-grained (~10 nm) polycrystalline thin films. This phase formation could be enabled by a specific kinetic phase transition from the amorphous-as-deposited ALD material during post-deposition annealing (PDA). The typical thickness of the HZO film with the highest remanent polarization (P̅rm) was ~10 nm, but a slightly greater thickness (15 nm) was used in this work to ease the STEM characterization.

Figure 1a shows the cross-section of the pristine (before electrical cycling) TiN/HZO/TiN structure, which was observed by STEM in the high-angle annular dark-field (HAADF) mode. In the figure, one of the grains in the HZO film that penetrates through the entire film thickness was identified. The bright contrast region corresponds to the Hf and Zr ionic columns, which confirmed that the grain’s crystal structure is O-phase. However, the different space groups (SGs) among the various O phases cannot be identified by recognition of heavy Hf/Zr ions alone. In particular, identification of the O̅I₂₁ phase Pca₂₁ (SG: 29) and the antipolar O̅II₄₋₁ phase Pbcn (SG: 61) is an advantage of the STEM-ABF technique, which has a high sensitivity to light elements, i.e., oxygen ions. Zooming in to the dashed green square area in Fig. 1a in STEM-ABF mode allowed the oxygen ion positions to be determined clearly, as shown in Fig. 1b. Using the shifts in the oxygen ion positions from the centers of the four nearest Hf/Zr ion positions, the oxygen ions can be divided into O̅I₁₁-type (navy blue, at the centrosymmetric position) and O̅I₀₁ type (cyan, at the off-center position). Here, for ease of comparison of the two crystal structures, the polar O̅I₂₁ phase was identified as

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**Fig. 1 The observation of oxygen atoms of single orthorhombic (O̅) phase grain in pristine TiN/Hf₀.₅Zr₀.₅O₂ (HZO, 15 nm)/TiN device.**

a) Scanning transmission electron microscopy (STEM) high-angle annular dark-field (HAADF) image of the TiN/HZO/TiN cross-section. b) Annular bright-field (ABF) image extracted from the green square area in a, in which the position of the O atomic columns can be clearly detected with different offset and direction. According to the O atomic columns deviated from the center of the four nearest Hf/Zr columns, it can be divided into O̅I₁₁ type (center) and O̅I₀₁ type (off-center). Some of the O̅I₁₁-site columns shift along the [001], while others shift to the opposite direction. c) The atomic models of the Pca₂₁ and Pbcn phases along [010] direction. The purple, navy blue, and cyan-colored solid balls correspond to the Hf/Zr, O̅I (center), and O̅I₀₁ (off-center) ions, respectively.
the Pbc21 phase rather than the standard Pca21, which causes the α-, β-, and γ axis directions of the two O-phases to coincide. There are two shift directions for the OII-type ions: along the [001] direction (green arrows; majority of OII ions) and along the [001] direction (purple arrow; minority of OII ions). Note that atomic-resolution TEM images show the projected positions of atoms along the beam direction (in this case, the [010] O-phase direction). If mixtures of OI and OII positions were present along this direction, there could hardly be a clear distinction between the OI and OII positions in the STEM-ABF image, but this was not the case (see the enlarged images in the insets). Therefore, there are two types of crystal region: one with all OII ions shifting along the [001] direction (green arrows) and another with OII ions shifting alternatingly along the [001] and [001] directions (purple and green arrows, respectively), which can be identified more clearly in the enlarged insert images from Fig. 1b. The larger proportion with green arrows corresponds to the Pbc21 Ope domain with uniform polarization (P). The regions with alternating green- and purple-colored arrows might be regarded as the Pbc21 Ope-phase with a one-unit-cell-thick FE domain width, but an even more appropriate interpretation would be that it is the OAFE Pbca phase. Figure 1c exhibits the two kinds of atomic models of the Pbc21 and Pbca phases along [010] direction, in which the purple, navy blue, and cyan-colored solid balls correspond to the Hf/Zr, Oi (center), and OII (off-center) ions, respectively. A detailed atomic structure comparison of the Ope Pbc21 and OAFE Pbca phases is shown in Supplementary Fig. S1, which contains self-consistent experimental and theoretical ABF images. These results indicate that many of the O-phase single grains in the pristine state are composed of a mixture of the Ope Pbc21 and OAFE Pbca phases. This is expected because the free energies of these two phases are quite similar, and the crystallization stage during PDA processing thus involved a high probability of formation of these structures.

It is commonly believed that the hafnia-based ferroelectric capacitors undergo a wake-up-fatigue-breakdown trend under continuous switching cycles. Figure 2a shows the variations in 2Pr and the leakage currents of a TiN/Hf0.5Zr0.5O2 (15 nm)/TiN capacitor with increasing numbers of switching cycles (bipolar voltage pulses of ±5 V at f = 500 kHz). The 2Pr was measured by ±3 V P–V loop, and the leakage current was measured at 2 V. During the first 104 cycles, wake-up occurs, and the leakage current remains almost constant. During subsequent cycling up to ~107 cycles, the samples showed gradual fatigue (with 2Pd decreasing from ~20.7 to 13.7 μC/cm2) and a simultaneous increase in the leakage current by more than 50 times. The sample broke down completely after 108 cycles. The field-dependent wake-up process was shown in Supplementary Fig. S2 (for the 15 nm Hf0.5Zr0.5O2 film), where all 2Pr values were measured using a ±3 V P–V loop after each decade of cycles. At low voltages (<3.2 V), no obvious wake-up was observed, but the 2Pr value decreased monotonically with increasing numbers of switching cycles. However, at Vd > 3.6 V, wake-up was clearly observed. Figure 2b shows the 2Pr evolution of samples with 15-nm-thick Hf0.5Zr0.5O2, 10-nm-thick Hf0.6Zr0.4O2, 10-nm-thick Hf0.7Zr0.3O2, 10-nm-thick Hf0.4Zr0.6O2, and the nanolaminated 10-nm-thick Hf0.5Zr0.5O2 films, under bipolar Vd pulses of ±1.8 MV/cm, which are lower than the critical wake-up field (Supplementary Fig. S3). The 2Pr values remained relatively constant up to ~104 cycles and decreased rapidly toward much smaller values at 107 cycles. The capacitor leakage currents were also measured at each decade of low-field cycling pulses, but no obvious increase in leakage current was observed, as shown in Fig. 2c. These findings indicated that the fatigue caused by low Vd values is irrelevant to the generation of new defects. Figure 2d shows the low-Vd fatigue and subsequent rejuvenation process. After the devices were fatigued using bipolar ±1.8 MV/cm, 107 pulse cycles, and then rejuvenated by subsequent application of ±3 MV/cm, 104 recovery pulse cycles. The rejuvenated capacitor could be fatigued and rejuvenated again, with ten cycles of repetitive fatigue/recovery process, as shown in Fig. 2e. This “temporary” low-Vd fatigue and rejuvenation phenomenon is
quite different from the conventional perception of fatigue, which is generally regarded as an irreversible process that causes permanent $P_r$ degradation and device failure. These findings indicate that the changes in the internal (defect) structure of the HZO film during field cycling are different for the low and high $V_a$ values. In the low-$V_a$ cycling case, the main fatigue mechanism is probably the phase transition from the O$_{FE}$ Pb$_{2}$C$_{2}$$_1$ to the O$_{AFE}$ Pb$_{2}$o phase, while the rejuvenation can be ascribed to the reverse phase transition without involving permanent structural change or $V_G$ generation. In contrast, the changes shown during high-$V_a$ cycling may involve a specific permanent structural change, e.g., $V_G$ generation and an accompanying phase transition. The subsequent STEM-ABF observations of the woken-up, fatigued, and rejuvenated samples confirmed the above hypotheses.

Figure 3a shows a STEM-HAADF image of the woken-up sample, which was cycled $10^4$ times at $V_a = \pm 4$ V and $f = 500$ kHz to wake-up the sample effectively but minimize the damaging effects of defect generation. The image shows an O$_{FE}$- or O$_{AFE}$-phase grain projected along the [010] zone axes. The corresponding STEM-ABF image is shown in Fig. 3b, in which the oxygen ion locations can be observed clearly. The image shows that most of the O$_{II}$ atomic columns shift along the [001] direction (green), with only two vertical O$_{II}$ columns with the opposite shift (purple) remaining; this indicates that almost the entire film becomes the O$_{FE}$ Pb$_{2}$C$_{2}$$_1$ phase. The inset image in Fig. 3b shows a close-up that clearly reveals that all the O$_{II}$ ions shifted in the same direction. Therefore, the wake-up effect could be correlated positively with the structural transition from the O$_{AFE}$-phase in the pristine state to the O$_{FE}$-phase after cycling. This is a distinctive interpretation of the wake-up effect in this material when compared with the previous interpretation, which described it as the result of $V_G$ redistribution from the interfacial nonpolar T-phase into the interior part of the O$_{FE}$-phase film. However, STEM observation of the interfacial region near the top electrode across the broad areas of both the pristine and woken-up samples (Supplementary Fig. S4a, b) showed that the interfacial T-phase thickness actually increased slightly, from 0.75–1.0 nm (pristine state) to 0.94–2.11 nm (woken-up state). This indicates that the interfacial nonpolar T-phase to O$_{FE}$-phase transition may not be the major mechanism of the wake-up process. In contrast, the interpretation of the wake-up effect based on the O$_{AFE}$-phase to O$_{FE}$-phase transition in the bulk thin-film region does not involve such a difficulty. Additionally, it is consistent with the non-varying leakage current observed during the wake-up process (Supplementary Fig. S2).

The same reasoning implies that fatigue could also be induced by the reverse transition, i.e., from the O$_{FE}$ Pb$_{2}$C$_{2}$$_1$ phase in the pristine state to the O$_{AFE}$ Pb$_{2}$o phase after the fatigue. To confirm this hypothesis, a pristine 15-nm-thick Hf$_{0.3}$Zr$_{0.2}$O$_{2}$ film was cycled $10^6$ times at $V_r = \pm 2.5$ V and $f = 500$ kHz, which corresponds to low-$V_a$ fatigue without involving an intermediate wake-up. This cycling operation reduced the 2$P_r$ value from $\sim$9.4 to $\sim$2.0 $\mu$C/cm$^2$ (read at $\pm 2.5$ V, data not shown here). Figure 4a, b shows STEM-HAADF and STEM-ABF images of such a low-$V_a$ fatigued sample, respectively. The images demonstrate that almost the entire area of the film was now in the O$_{AFE}$-phase, which was further confirmed by the magnified view shown in Fig. 4c. To further verify the validity of the antipolar-phase transition model, the crystalline structure of other devices were examined at the low field fatigued and woken-up states, respectively. Supplementary Figs. S5–6 show the STEM-HAADF and STEM-ABF cross-sectional images of the 10-nm-thick nanolaminated Hf$_{0.3}$Zr$_{0.7}$O$_{2}$ film. They also show a clear Pb$_{2}$o phase structure after the low-field fatigue and Pb$_{2}$C$_{2}$$_1$ phase-dominated structure after the wake-up. Similarly, Supplementary Figs. S7 and 8 show the reversible transition between the antipolar Pb$_{2}$o and polar Pb$_{2}$C$_{2}$$_1$ phases as the origin of the low-field fatigue and rejuvenation in the 10-nm-thick Hf$_{0.3}$Zr$_{0.7}$O$_{2}$ film. As discussed below, the O$_{AFE}$-phase free energy is lower than that of the O$_{FE}$-phase by $\sim$10 meV/$\mu$m, thus indicating that this transition is energetically favorably driven. It was noted that the low-$V_a$ fatigue only occurred with bipolar switching pulses. Stressing the device using unipolar voltages of the same amplitude did not cause fatigue (see Supplementary Fig. S9 and related discussion).

The question then becomes this: what is the critical field strength that determines whether fatigue or wake-up (and also rejuvenation) will occur? To answer this question, DFT was used to simulate the switching path from the Pb$_{2}$o global minimum energy phase to the Pb$_{2}$C$_{2}$$_1$ local minimum energy phase. Details of the calculations are included in SM (Supplementary Fig. S10). The effective electric field ($E_{eff}$) distribution across the O$_{FE}$ region of the film, which must be smaller than the applied field ($E_{app}$) because of the presence of the non-FE layer, was also calculated by assuming the presence of the interfacial T-phase based on the STEM results (Supplementary Fig. S11). The presence of nonpolar layers in series with the FE film induces the depolarization field, which reduces the effective field greatly during the switching cycles. The goal of these calculations is to estimate the critical field ($E_{C}$) that can make the polar O$_{FE}$ phase more stable than the O$_{AFE}$ phase by its electrostatic energy contribution.
Figure 4 shows the schematic diagrams of the energy landscape for Pbc2 (center global minimum) and Pbc21 (two local minima at finite P). Under the application of a negative $E_{app}$ (more precisely, $E_{eff}$), the $-P_s$ and $+P_s$ (saturation polarization) states of the Pbc21 phase become more unstable and stable, respectively, while the nonpolar phase energy remained unchanged. When $E_{eff} > E_0$, the Pbc21 phase becomes energetically more favorable than the Pbca phase; this is summarized in Fig. 5b. The calculations showed that $E_0$ is ~0.8 MV/cm, i.e., when $E_{eff}$ is lower or higher than 0.8 MV/cm, the OAFE Pbca phase or the O$_{FE}$ Pbc21 phase becomes stable, respectively. The activation barrier ($E_a$) of the direct transition between Pbc21 and Pbca in HfO$_2$ was also calculated, which is directly related to the wake-up, fatigue, and rejuvenation. They are summarized with the calculated relative energy of Pbc21 to Pbca ($\Delta E$), by ~10 meV/f.u., which is consistent with previous reports$^{17,19}$ in Supplementary Table S1. Although the $E_a$ depends on the transient path, i.e., the movement of O$_{II}$ (off-center) atoms, these calculation results are comparable with previous studies, including the recent report by Xu et al.$^{29}$.

Table 1 shows $E_{eff}$ across the O$_{FE}$ layer when the interfacial T-phase layer is present at $V_a$ of 3, 4, and 5.5 V. $E_{eff}$ became smaller because of the involvement of the higher depolarizing effect. Therefore, a $V_a$ of at least ~4 V was necessary to keep the Pbc21 phase more stable than the Pbca phase during cycling. These calculation results strongly support the hypothesis for the wake-up and fatigue processes discussed in Figs. 1–4.

Finally, the structural variations and accompanying electrical performances after fatigue cycling with a $V_a$ of ±4 V are discussed. Supplementary Fig. S12a shows a STEM-HAADF image of the TiN/HZO/TiN capacitor after high-$V_a$ fatigue testing (±4 V, $10^9$ cycles).
cycles), which reduced the $2P_f$ value from 18.9 to 9.8 μC/cm² (Supplementary Fig. S13a). The corresponding STEM-HAADF image along the [010] direction in Supplementary Fig. S12b clearly shows the alternating distributions of the O$_2^-$ ion positions being shifted along the [001] (green) and [001] (purple) directions. This finding demonstrates that high-$V_f$ fatigue was also induced by the transition from the OFE Pb$c_{21}$ phase to the OAFE Pbca phase. Another notable finding from this sample is the development of a fairly thick interfacial T-phase, which can be seen in Supplementary Fig. S12a. The STEM-HAADF images of this high-field fatigued sample confirmed that the thickness of this layer was $\sim$3.25–4.25 nm. The last row of Table 1 indicates that $E_{\text{eff}}$ across the remaining $\sim$11.75–10.75 nm-thick OFE-$P_{bc21}$-phase is as low as 0.29–0.55 MV/cm for $V_f = 4$ V under these circumstances because of the severe depolarizing field effect. These calculation results thus corroborated the finding that high-$V_f$ fatigue is induced by the transition from the Pb$c_{21}$ phase to the Pbca phase and not by defect generation and the accompanying domain pinning.

Following the same line of reasoning used for rejuvenation of the low-$V_f$ fatigued sample shown in Fig. 2f, a similar rejuvenation was attempted using $V_c = 5.5$ V that increased $E_{\text{eff}}$ to $\sim$0.84–1.09 MV/cm, as also shown in Table 1. Supplementary Fig. S13b shows the evolution of the $P$–$V$ curve with increasing rejuvenation cycling numbers up to $10^4$. As expected, the fatigued sample is partly recovered. This is further strong evidence that the high-$V_f$ fatigue was also induced by the phase transition mentioned above.

Similar electrical and structural characterizations were performed for the 5.6-nm-thick HZO film to prove the general applicability of the reversible phase transition model for the thinner films. The results are summarized in Supplementary Figs. S14–S21. Although the thinner film contained a higher portion of T-phase grains in the pristine state, in addition to the O-phase grains, it showed similar wake-up, fatigue, and rejuvenation processes. Therefore, it can be inferred that the reversible transition between the nonpolar Pbca phase and polar Pb$c_{21}$ phase also occurs in the 5.6-nm-thick HZO film. The only difference is that the wake-up process in this thinner film is also contributed by the structural transition from the $P_{42/nmc}$ T-phase to $Pca_{21}$ O-phase.

The knowledge acquired based on the effects of the $V_O$ concentration on the phase stability indicates that the increase in the interfacial T-phase thickness is reasonable; it has been reported previously that the highest $V_O$ concentration stabilizes the T-phase over the O- and monoclinic (M)-phases. It must then be reasonable to believe that the repeated electrical stimuli enhanced the chemical interactions between the HZO film and the reactive TiN electrode, which would also increase the $V_O$ concentration. It was also noted that these interfacial T-phases were mostly found around the top electrode interface. The bottom electrode interface was formed by depositing an HZO film on the TiN layer, which may produce a stable interface structure. However, the top electrode interface was formed by depositing the TiN layer on the HZO film using a reactive sputtering process. Rapid thermal oxidation or deposition of one cycle of HfO₂ and one cycle of ZrO₂. Also, 10-nm-thick nanolaminated HfO₂/ZrO₂ film, where each layer’s thickness was 1 nm, was prepared. Subsequently, the top electrode (TiN) layer was deposited and patterned into different sizes. Finally, the as-fabricated TiN/HZO/ TiN ferroelectric capacitors were annealed for 30 s at 500 °C in a nitrogen atmosphere to crystallize the HZO.

**Methods**

**Device fabrication.** The TiN/HZO/TiN capacitor fabrication processes were as follows. First, the TiN bottom electrodes were deposited on the SiO₂/Si substrate by ion beam sputtering. Then, 10–15-nm-thick HZO thin films were deposited by ALD at 280 °C. h-[C₆H₄CH₂]₃, Zr[N(C₂H₅)CH₃]₄, and H₂O were used as the HF precursor, the Zr precursor, and the oxygen source, respectively. The HF/Zr ratio was controlled by alternating deposition of one cycle of HZO, and one cycle of ZrO₂. Also, 10-nm-thick nanolaminated HfO₂/ZrO₂ film, where each layer’s thickness was 1 nm, was prepared. Subsequently, the top electrode (TiN) layer was deposited and patterned into different sizes. Finally, the as-fabricated TiN/HZO/ TiN ferroelectric capacitors were annealed for 30 s at 500 °C in a nitrogen atmosphere to crystallize the HZO.

**Electrical measurements.** The polarization–voltage ($P$–$V$) and leakage current characteristics of the metal-Fe-metal devices were measured using a Radiant Technologies ferroelectric tester with an Agilent B1500 semiconductor parameter analyzer. During all electrical measurements, a bias voltage was applied to the bottom electrode, and the top electrode was grounded. The capacitor size was 100 μm x 100 μm.

**Cs-STEM experiment.** After the different electrical operations, the TiN/HZO/TiN capacitors were processed into cross-sectional samples using the focused ion beam (FIB) technique in the FEI Helios G4 system, including low-pressure polishing processes at 5 and 2 keV. The sample was treated in a Gatan 691 precision ion polishing system at 0.5–0.15 keV to remove any residual contamination and damage from the sample surface. The STEM experiments were then conducted on a JEM Grand ARM 300F microscope operating at 300 kV in the STEM mode with a probe aberration corrector. The HAADF and ABF images were acquired at a probe convergence semi-angle of 18 μrad. The STEM-HAADF images were acquired using an annular dark-field image detector with an inner semi-angle of more than 64 μrad. The STEM-ABF images were acquired using a bright-field image detector.
with its central section blocked using a beam stopper; the collection semi-angle was in the 12–24 mrad range.

**DFT calculations.** Ab initio calculations were performed using the Vienna Ab initio Simulation Package (VASP)\(^{32,33}\). The generalized gradient approximation of the Perdew–Burke–Ernzerhof (GGA-PBE) exchange-correlation functional\(^{34}\) and Blöchl’s projector augmented wave (PAW) approach\(^{35,36}\) were used with an energy cut-off of 600 eV. The k-points were sampled and found to be 8 × 8 × 8 for the PbO\(_2\) unit cell and 8 × 4 × 8 for the PbO unit cell. The dielectric constant was obtained via density functional perturbation theory (DFPT)\(^{37,38}\), and the spontaneous polarization was calculated using the Berry phase method\(^{39}\). The activation barrier \(E_a\) for switching was estimated using the solid-state nudged elastic band (SS-NEB) method\(^{40}\).

**Reporting summary.** Further information on research design is available in the Nature Research Reporting Summary linked to this article.

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**Author contributions**

Y.C., Z.G., C.S.H. and H.L. designed the experiments. Z.G. and J.G. carried out sample fabrication. Z.G. and H.L. carried out electrical experiments. Y.C., Y.H.Z., and Y.Z.Z. carried out the STEM measurement and result analysis. H.W.P., M.H.P., K.H.Y., and J.H.C. proposed the model and did the theoretical calculation. J.G. and K.-H.X. provided help on data analysis and discussion. H.L., Y.C., J.-H.C., and C.S.H. wrote the paper. C.S.H. and H.L. supervised the research.

**Competing interests**

The authors declare no competing interests.
