

Oxygen vacancy migration engineering for CMOS-compatible hafnium-based ferroelectric synaptic devices

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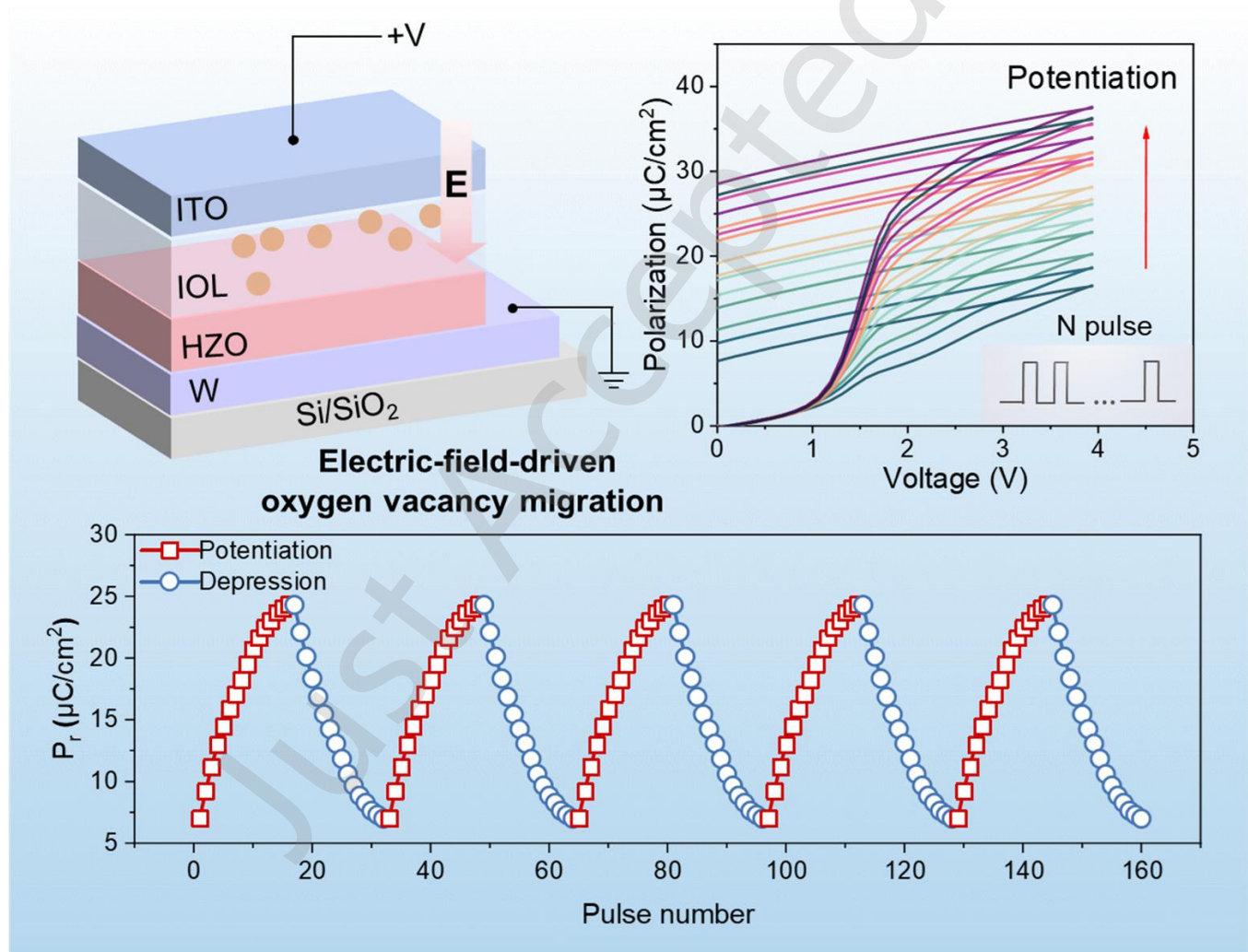
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Electric-field-driven oxygen vacancy migration at the ITO/HZO interface stabilizes ferroelectric ordering, enabling reliable and repeatedly readable multilevel polarization and linear synaptic behavior in CMOS-compatible FeRAM devices.

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ABSTRACT: Hafnium oxide (HfO₂)-based ferroelectric memory devices have emerged as promising CMOS-compatible nonvolatile memories, yet ferroelectric synaptic devices still suffer from polarization-state read-disturb issues and abrupt polarization variations in neuromorphic computing applications. Here, we demonstrate a ferroelectric synaptic device with highly linear and continuously tunable multilevel polarization states as well as improved resistance to read-disturb issues through electrically driven oxygen-vacancy migration in Hf_{0.5}Zr_{0.5}O₂ (HZO) devices. Using an oxygen-active indium tin oxide (ITO) electrode, electric-field cycling induces interfacial oxygen-vacancy redistribution, leading to vacancy compensation and interface stabilization. Spectroscopic and nanoscale analyses reveal field-driven redox processes, including Ti³⁺ to Ti⁴⁺ transformation and three-dimensional oxygen-vacancy migration across the interface. This dynamic defect regulation enhances remanent polarization (P_r), increases breakdown strength, and enables robust endurance. Importantly, controlled vacancy migration allows continuous P_r modulation, supporting multilevel analog synaptic behavior with high uniformity and reversibility. Implemented in a 1T1C architecture, the device exhibits a large and linear memory window with excellent retention. These results establish electrically driven oxygen vacancy engineering as an effective post-fabrication strategy for high-reliability ferroelectric synaptic devices.

KEYWORDS: Zirconium-doped hafnium oxide, interface oxygen vacancy engineering, multi-polarization state regulation, ferroelectric synaptic device.

1 Instructions

Neuromorphic computing aims to overcome the energy-efficiency and scalability limitations of conventional von Neumann architectures by emulating the adaptive signal processing of biological neural systems [1, 2]. Artificial synaptic devices have played a crucial role in advancing neuromorphic computing owing to their capability for continuously tunable, non-volatile, and energy-efficient weight modulation. Among various emerging synaptic device candidates, ferroelectric-based devices have attracted increasing attention due to their intrinsic non-volatility, fast switching speed, low power consumption, and excellent scalability, making them highly compatible with large-scale

integrated neuromorphic systems [3-5].

Ferroelectric materials exhibit spontaneous polarization that can be reversibly switched by an external electric field, a property that has been widely exploited in non-volatile memory technologies. More recently, this polarization-switching behavior has been leveraged to emulate synaptic plasticity, where gradual polarization modulation enables analog weight update, potentiation–depression symmetry, and multilevel conductance states [6-8]. Among many ferroelectric candidates, hafnium oxide (HfO₂) and its doped variants have emerged as particularly attractive material for ferroelectric synaptic and memory devices owing to their

intrinsic compatibility with CMOS processing, high switching speed, and low power operation [9-11]. The ability to grow $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) films with precise control over stoichiometry and thickness through atomic layer deposition (ALD) has further enhanced their appeal for device applications [12, 13].

Despite these advantages, the reliable implementation of HZO-based ferroelectric synaptic devices remains challenging. Due to the ultrafast switching speed of ferroelectric materials and their coercive-field-controlled polarization reversal behavior, it is difficult to achieve analog multilevel polarization states with high linearity through voltage operation alone [14]. Moreover, the nearly identical voltages required for read and write operations in ferroelectric devices lead to polarization-state read-disturb issues, necessitating additional rewrite operations [15]. Previous studies have shown that the distribution and mobility of oxygen vacancies can be partially manipulated through approaches such as post-deposition annealing and surface electrochemical treatments [16-18]. In practical devices, ferroelectric performance, endurance, and retention are strongly influenced by oxygen vacancies, which act as mobile charge defects and can dynamically redistribute under electrical operation [19-23]. Therefore, optimizing the device structure to enable controllable modulation of interfacial oxygen vacancies under electrical operation is expected to be an effective approach for achieving multilevel remanent polarization states. This is essential for realizing CMOS-compatible ferroelectric synaptic devices with stability, linearity, and reversibility of synaptic weight modulation in ferroelectric devices. Previous oxygen-vacancy engineering approaches in HfO_2 -based ferroelectrics mainly rely on thermal treatments, interface modification, or process optimization during fabrication. In contrast, the present work introduces an electrically driven regulation strategy that enables post-fabrication tuning of oxygen-vacancy distribution during device operation. This dynamic and reversible defect-engineering approach provides additional flexibility for both memory and neuromorphic applications while maintaining full CMOS compatibility.

In this work, we investigate the electrically driven redistribution of oxygen vacancies at ALD-grown HZO interfaces under electric-field cycling, combining advanced spectroscopic and nanoscale structural characterization techniques. X-ray photoelectron spectroscopy (XPS) [24, 25], scanning transmission electron microscopy (STEM) [26], electron energy loss spectroscopy (EELS) [19, 27, 28], and atom probe tomography (APT) [29] collectively reveal field-induced oxygen-vacancy migration accompanied by interfacial redox reactions, manifested as a transformation from Ti^{3+} to Ti^{4+} and a reconfiguration of interfacial charge states. In particular, APT uncovers a spatially non-uniform vacancy distribution across oxide interfaces, with vacancy accumulation at the electrode interface and depletion within the HZO layer, leading to stabilized interfacial ordering [30]. This controlled oxygen-vacancy redistribution enables continuous and reversible modulation of remanent polarization, allowing analog-like multilevel polarization states. Such defect-mediated polarization control directly supports linear, energy-efficient synaptic weight updates

with improved uniformity and reliability. Beyond elucidating the fundamental role of oxygen vacancies in ferroelectric HZO, this work establishes electrically driven vacancy engineering as an effective route toward stable, CMOS-compatible ferroelectric synaptic devices for large-scale neuromorphic computing systems.

2 Experimental

Device Fabrication. Firstly, the Si/SiO₂ (300 nm) substrate was first ultrasonically cleaned using acetone, ethanol, and deionized water in sequence for 5 mins, and then an 80 nm W layer was sputtered on the cleaned substrate as the bottom electrode. Then HZO film (10 nm) was deposited on the metal layer by atomic layer deposition (ALD) using $\text{Hf}[\text{N}(\text{C}_2\text{H}_5)\text{CH}_3]_4$ and $\text{Zr}[\text{N}(\text{CH}_3)_2]_4$ as the metal precursors, and the ALD cycle ratio of $\text{HfO}_2/\text{ZrO}_2$ was fixed at 1:1. Subsequently, TiN (50 nm) cap layers were grown by sputtering and under a nitrogen atmosphere at 500°C. Rapid annealing was performed for 60 s as a way to stabilize the ferroelectric orthorhombic phase of HZO; then the TiN was wet etched by modulating the etching solution with the ratio of $\text{NH}_3\text{-H}_2\text{O:H}_2\text{O}_2\text{:H}_2\text{O}=1:1:5$. Finally, the pattern is fabricated through typical photolithography technology, and ITO (100 nm) or TiN (70 nm) is deposited by PVD as the top electrode.

Characterization. The TEM sample were prepared by using standard focus ion beam (FIB) system (Thermo Fisher Scientific Helios G4). The atomic structure analysis was performed using STEM (JEOL ARM300F) equipped with Cs-corrector at 300 kV. The probe-forming aperture semiangle was set to be 24 mrad. The collection semi-angle of >64 mrad and 12-24 mrad were set to obtain High-angle annular dark-field (HAADF) and annular ABF images, respectively. The EELS spectrums (Gatan GIF) were acquired from Ti $L_{2,3}$ and O K edges using an energy dispersion of 0.1 eV/channel. Dual-EELS mode was used to simultaneously acquire the zero-loss and core-loss spectra, enabling accurate energy calibration and comparison of chemical shifts.

Needle-shaped ITO/TiO_{2-x}/HZO/W capacitors were prepared using a standard FIB lift-out process, yielding apex diameters below 50 nm. The samples were analyzed in an ultrahigh vacuum ($\sim 3 \times 10^{-11}$ mbar) using a local electrode atom probe (LEAP 5000 XR, Cameca Instruments). A DC voltage of 2-6.5 kV was applied, and the tips were illuminated with 10 ps laser pulses to trigger field evaporation. Ionized surface atoms were projected onto a position-sensitive detector. The x- and y-coordinates from the detector, combined with time-of-flight-derived z-coordinates, enabled 3D reconstruction of the specimen. Chemical identification of ions was achieved via time-of-flight mass spectrometry. Data reconstruction and analysis were performed using IVAS software (version 3.6.14).

3 Results and discussion

In order to explore the effect of oxygen vacancy modulation on the performance of hafnium-based ferroelectric devices [31-33], we used plasma-enhanced atomic layer deposition (PEALD) to grow 10 nm thin films of HZO (Hf:Zr = 1:1) on the bottom electrode tungsten (W). The fabricated devices adopt an ITO/TiO_{2-x}/HZO/W stack structure, as shown in Figure. 1a,

where the TiO_{2-x} interfacial layer is formed due to partial oxidation of the TiN cap during processing. The detailed fabrication process is illustrated in Figure S1, confirming the sequential deposition and annealing steps that ensure reproducibility of the device structure. The surface morphology of the HZO film was characterized by atomic force microscopy. As shown in Figure S2, the film exhibits a low root-mean-square roughness of ~ 0.95 nm, indicating a smooth surface with minimal topographic defects. Such a uniform surface is beneficial for achieving homogeneous electric field distribution and reducing extrinsic variability in ferroelectric switching [34–36]. Grazing-incidence X-ray diffraction measurements (Figure 1c and Figure S3) reveal the coexistence of orthorhombic and monoclinic phases in the HZO film [37].

Figure 1d shows an atomic-resolution microscope photograph of the HZO film using aberration-corrected High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), where the individual grains that

make up the film can be observed. This is consistent with the atomic model of HZO (Figure 1b). From the fast Fourier transform (FFT) image, a clear distribution of diffraction spots can be seen, which correspond to different grain surfaces on [100], such as (002) and (020). The corresponding inverse FFT shows that the crystallographic spacing of (002) and (020) crystal planes are 2.53 Å and 2.52 Å, respectively. The orthorhombic (O) phase in hafnium oxide thin films corresponds to the $Pca2_1$ space group, as determined by Fourier transform analysis of transmission electron microscopy data. This is consistent with the polar orthorhombic phase commonly observed in hafnium oxide-based ferroelectrics [38, 39]. Piezoelectric force microscopy (PFM) [40] measurements (Figure 1e–g) demonstrate clear 180° phase switching and butterfly-shaped amplitude loops, confirming robust ferroelectricity. These results indicate that the as-fabricated films possess intrinsic ferroelectric properties.

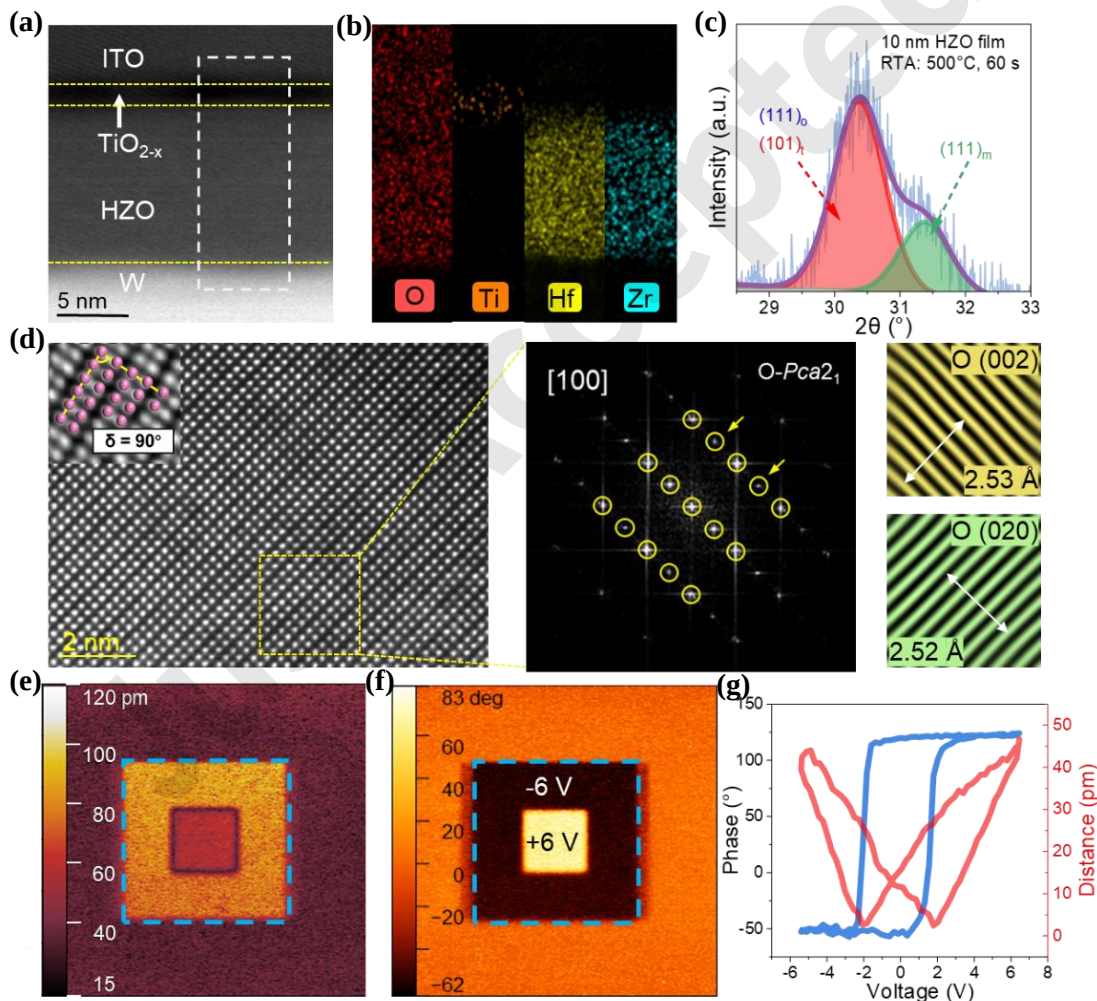


Figure 1 Device structure and ferroelectric characteristics of HZO films. (a) Cross-sectional HAADF-STEM image of the device. (b) TEM-EDS mapping showing the elemental distribution. (c) Grazing-incidence XRD pattern of the HZO film. (d) Atomic-resolution STEM image and FFT pattern of a representative grain. (e–g) PFM phase and amplitude responses and corresponding switching loops.

To verify the device's ferroelectric properties and reliability, we conducted a series of electrical characterization tests on the device. As shown in Figure 2a, the device exhibits an unsaturated hysteresis loop with low P_r , indicating the

presence of fixed oxygen vacancies at the top-electrode interface in the initial crystalline HZO film. After undergoing a high-voltage cycle of 6 V (Figure 2b), the ferroelectric hysteresis loop becomes saturated, and the P_r increased. This

behavior indicates that an increasing fraction of ferroelectric domains participates in polarization switching. Since oxygen vacancies can act as charge-trapping centers and domain-wall pinning sites in HZO ferroelectrics, the progressive improvement in switching characteristics suggests that defect-induced pinning is gradually alleviated during electrical conditioning. Consequently, more complete polarization reversal is achieved, resulting in enhanced remanent polarization. Based on this electrical behavior, oxygen-vacancy redistribution is proposed as the primary origin of the observed activation process, which is further corroborated by the subsequent material characterizations [41, 42].

The reliability of the devices is further evaluated through breakdown and endurance measurements. Time-zero dielectric breakdown (TZDB) (Figure 2c) [43] shows that the breakdown voltage increases by 2.7 V after electrical activation. This improvement is attributed to the initially non-uniform electric field distribution and weak breakdown spots caused by the accumulation of oxygen vacancies at the ITO/HZO interface. After electrical activation, oxygen-vacancies migrate from the ITO electrode to the HZO interface and recombine with vacancies, thereby alleviating domain wall pinning and improving interfacial quality. These

processes facilitate ferroelectric domain alignment, leading to a more uniform electric field distribution. Time-dependent dielectric breakdown (TDDB) [44] measurements at different voltages (Figure 2d, e) show a prolonged breakdown time after electrical activation. The Weibull distribution (see Figure 8a,b) corresponding to the TDDB measurements shows an increase in the slope parameter (β) after electric field cycling, indicating reduced oxygen vacancy clustering at the interface and improved defect ordering [45].

Endurance tests (Figure 2f, g) show that under an electric field of 4.4 MV/cm, these devices exhibit no breakdown after 10^{11} cycles while retaining 96% of their initial P_r , indicating excellent operational stability under high-voltage. Furthermore, the rate of P_r decay was observed to slow as the electric field strength increased (see Figure S10), and endurance tests at different frequencies (Figure 2g) also follow this trend. The above improvements can be attributed to the electric-field-induced imigration and redistribution of oxygen-vacancies, as schematically illustrated in Figure 2h and 2i. Notably, this vacancy redistribution is closely related to the interfacial oxygen-vacancies modulation induced during device fabrication, highlighting the critical role of interface engineering in achieving both high ferroelectric performance and reliability.

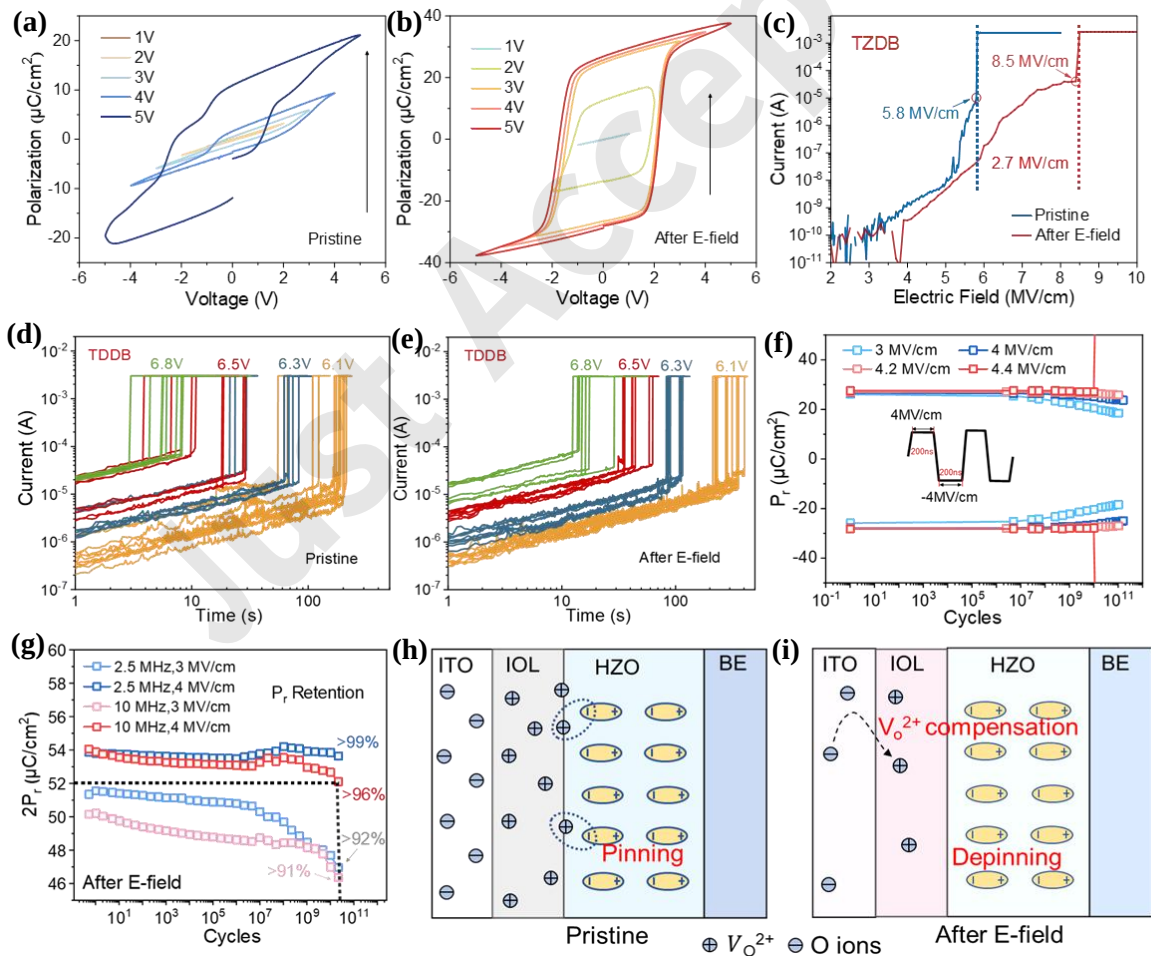


Figure 2 Ferroelectric performance and reliability improvement in HZO devices. (a,b) Polarization-electric field (P-V) loops before and after high voltage cycling. (c) Time-zero dielectric breakdown (TZDB) characteristics. (d,e) Time-dependent dielectric breakdown (TDDB) characteristics. (f,g) Endurance performance of the device under various electric field. (h,i) Schematic illustration of interfacial oxygen-vacancy migration and redistribution under electric field.

To verify the interfacial oxygen-vacancy migration under an electric field, comparative characterization measurements

were performed before and after electrical stressing. The evolution of the oxidation state and local coordination environment induced by oxygen vacancy regulation before and after electric-field cycling were investigated using STEM-EELS. Figure 3a and 3b show the annular dark-field (ADF) images and line-scan EELS spectrum images across the ITO/TiO_{2-x}/HZO/W structure, recorded before and after electrical biasing, respectively. Figure 3c and 3d show the EELS spectrum of the Ti L_{2,3}-edge and the O K-edge, integrated and extracted from spot1 to spot 6 in Figure 3a and Figure 3b.

The Ti L_{2,3}-edge spectra (Figure 3e) exhibit pronounced evolution after electric-field cycling. In the pristine state, the spectra are dominated by Ti³⁺-related features, indicating

oxygen-deficient TiO_{2-x}. After cycling, distinct peak splitting and energy shifts emerge, indicating a transition toward Ti⁴⁺. This valence transition is further confirmed by XPS analysis (Figure S4), where quantitative fitting reveals an increased fraction of Ti⁴⁺ and a corresponding reduction in non-lattice oxygen. These results consistently indicate that oxygen incorporation occurs at the interface under electric-field stimulation. The O K-edge spectra (Figure 3f) also exhibit a systematic shift toward higher energy, reflecting enhanced metal-oxygen covalency and increased lattice oxygen ordering. This behavior suggests that oxygen ions are injected from the ITO electrode into the interfacial region, driven by the applied electric field.

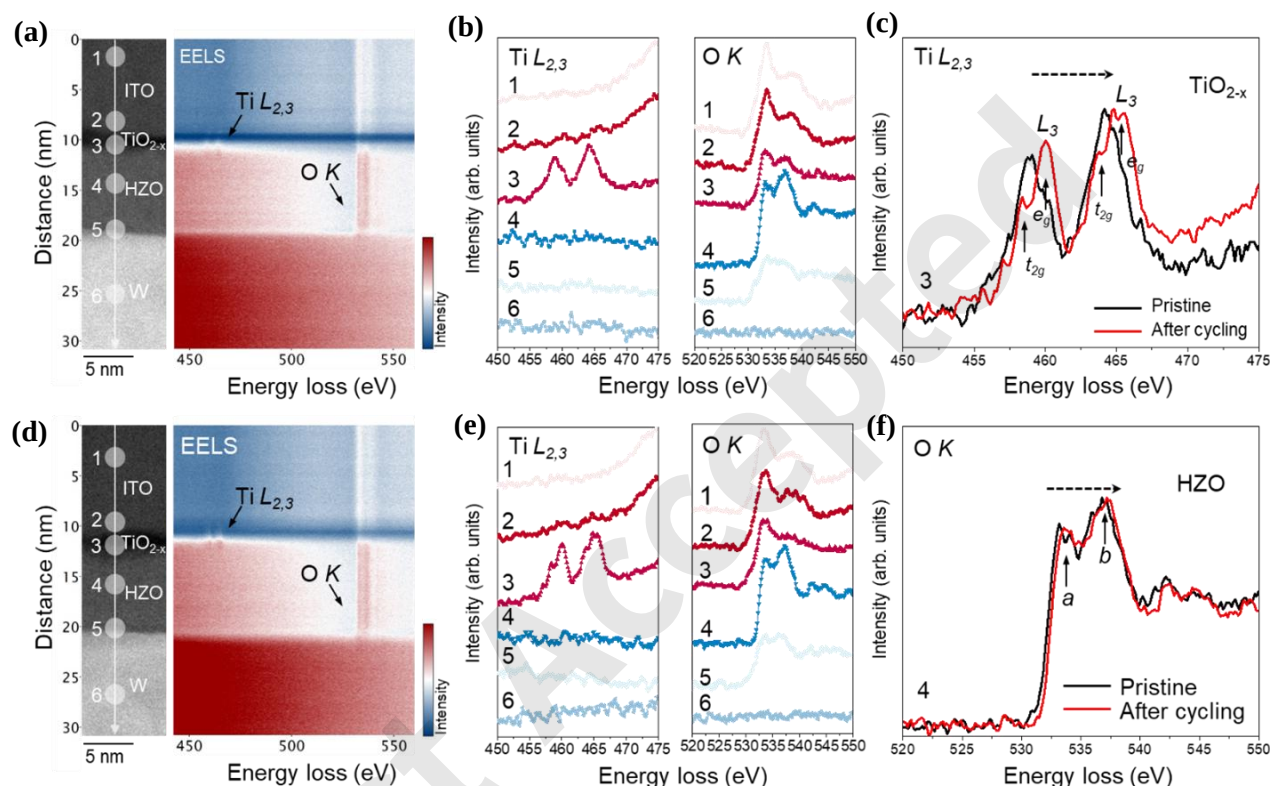


Figure 3 Interfacial chemical states and valence evolution under electrical cycling. (a,b) STEM and EELS spectrum images of the ITO/TiO_{2-x}/HZO/W before and after electric field cycling. (c,d) Corresponding Ti L_{2,3}-edge and O K-edge EELS spectra. (e) Overlay of Ti L_{2,3}-edge EELS spectrum at spot 3 before and after cycling. (f) Overlay of O K-edge EELS spectrum at spot 4.

To further confirm the evolution of oxygen vacancies in the interfacial layer before and after electrical biasing, in situ APT characterization was performed to elucidate the three-dimensional nanoscale redistribution of oxygen vacancies under electrical cycling. APT was employed to map the elemental distribution across the ITO/TiO_{2-x}/HZO/W stack with atomic-scale resolution. The APT sample preparation and reconstruction process are shown in Figure S11-S13, confirming the reliability of nanoscale compositional mapping. As shown in Figure 4a and 4b, prior to electrical cycling, a pronounced oxygen-deficient region is observed at the ITO/TiO_{2-x} interface (region ②), while a slight oxygen enrichment relative to the stoichiometric expectation is present at the TiO_{2-x}/HZO interface (region ③). These features are visualized in the three-dimensional stoichiometry map (Figure 4c) as a “puddle-like” oxygen-deficient region (blue) and a “flame-like” oxygen-rich region

(red), revealing the intrinsic interfacial chemical asymmetry before electrical activation.

Following electric field cycling, a marked redistribution of oxygen is observed (Figure 4d-f). The oxygen concentration in region ② increases significantly, approaching the stoichiometric level, while region ③ exhibits further oxygen enrichment beyond the initial state. The three-dimensional stoichiometric ratio map (Figure 4f) indicates that excess oxygen ions accumulate at the HZO side boundary, confirming the migration of oxygen ions from the ITO electrode to the HZO layer under the driving force of the electric field.

These APT results provide direct evidence that electric field cycling promotes oxygen ion injection from the ITO reservoir into the interfacial TiO_{2-x} layer, leading to the compensation of oxygen vacancies at the ITO/TiO_{2-x} interface and simultaneous oxygen accumulation at the HZO boundary. This spatially resolved oxygen-vacancies redistribution

corroborates the EELS and XPS findings of Ti^{3+} to Ti^{4+} oxidation and underscores the critical role of interfacial oxygen engineering in modulating ferroelectric wake-up and reliability enhancement. Notably, this redistribution of oxygen vacancies not only facilitates polarization switching, but also improves device endurance and dielectric breakdown characteristics by reducing the accumulation of localized defects and charge trapping at the interface, and by suppressing defect generation during repeated operation. This also highlights the critical role of interface engineering in achieving both strong ferroelectric properties and high reliability.

It is worth noting that the electrical activation observed in this work is distinct from the conventional wake-up effect

commonly reported in metal/ HfO_2 /metal ferroelectric capacitors. In conventional HfO_2 -based ferroelectrics, the wake-up effect is generally associated with the redistribution of oxygen-vacancy-related defects within the ferroelectric layer during repeated electrical cycling under moderate electric fields. In contrast, the oxygen-active ITO electrode employed in this work enables electrically driven oxygen exchange across the ITO/ HfO_2 interface under a sufficiently high electric field, introducing an additional interfacial oxygen-vacancy regulation mechanism. Therefore, the electrical activation proposed in this work should be regarded as an interfacial oxygen-exchange-assisted activation process rather than a conventional wake-up effect observed in metal/ HfO_2 /metal ferroelectric structures.

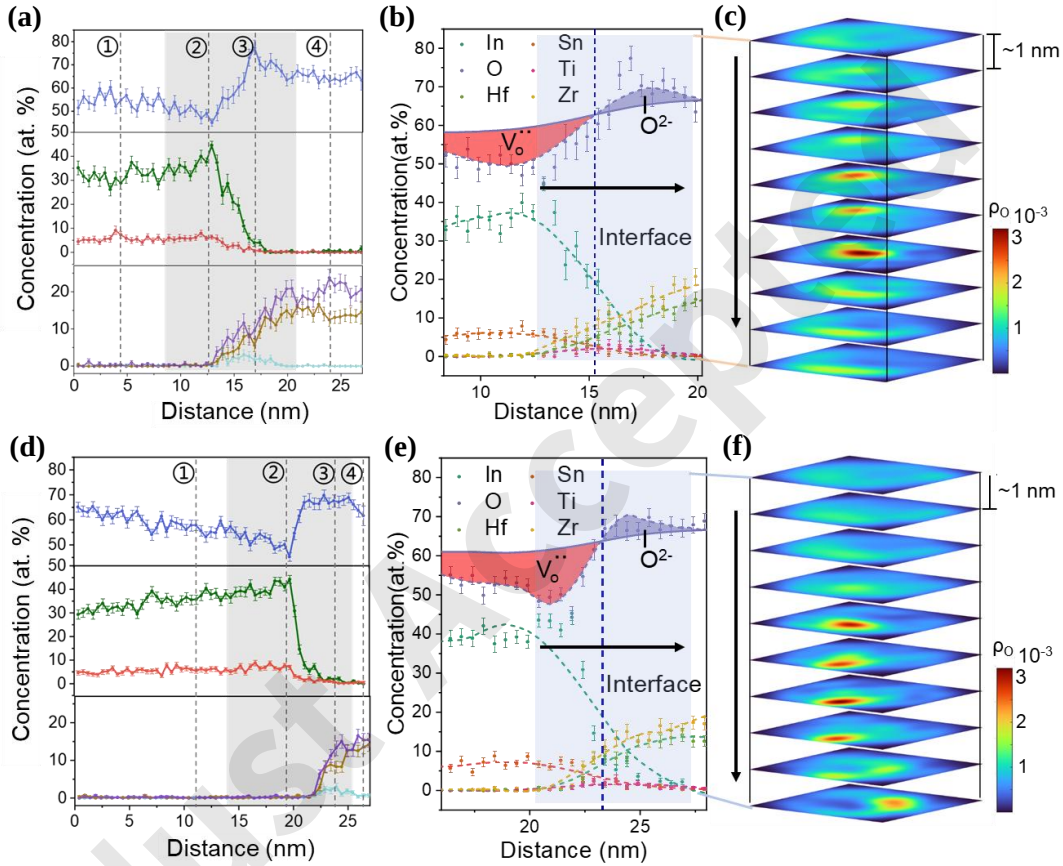


Figure 4 Three-dimensional oxygen distribution revealed by APT. (a,b) Relative chemical composition profiles are plotted as cross-sectional distributions. Error bars indicate standard deviations. (c,d) Measured (data points) and theoretically expected (solid lines) chemical concentration profiles at regions ② and ③. (e,f) Three-dimensional visualization of oxygen stoichiometry based on the APT dataset. Among these, a–c represent the device characteristics in the initial state, while d–f represent the device characteristics after the electric field cycle.

The dynamic control of oxygen vacancies enables continuous modulation of ferroelectric polarization under pulsed operation, which is essential for synaptic applications. As shown in Figure. 5a,b and FigureS14, the P_r gradually evolves with variations in pulse width and polarity. The interplay between these two processes enables bidirectional and reversible polarization modulation, effectively mimicking synaptic potentiation and depression. Importantly, the gradual evolution of polarization indicates that oxygen-vacancy migration occurs on a timescale comparable to that of domain switching, enabling fine control over intermediate states. In addition, Figure 5c-e demonstrate excellent cycle-

to-cycle reproducibility, endurance, and retention characteristics, indicating that the oxygen-vacancy distribution remains stable during repeated operation. These properties are critical for practical neuromorphic applications, where reliable and repeatable analog weight updates are required.

To evaluate the applicability of the proposed mechanism at the circuit level, the device was integrated into a 1T1C FeRAM architecture, as shown in Figure. S15. In this configuration, the polarization states of the ferroelectric capacitor are converted into electrical signals through charge sharing with the bit-line capacitance. Changes in P_r are not directly

intuitive for neuromorphic applications. Therefore, a 1T1C FeRAM architecture is adopted, as shown in Figure S15(a). Conventional FeRAM exhibits binary polarization states ("0"/"1"), whereas neuromorphic operation enables multi-level states via different stored charges, allowing synaptic weight representation and pulse-modulated learning/forgetting. Figure S15(b) illustrates the read/write scheme. Word line (WL) controls the access transistor. During the write operation, a voltage pulse is applied to the bit line (BL) while the plate line (PL) is grounded; during the

read operation, a voltage is applied to the PL with the BL left floating. Charge sharing between ferroelectric capacitor (C_{fe}) and parasitic capacitance on the BL (C_{BL}) produces the output V_{out} and distinct memory windows.

As shown in Figure 5f, memory window evolution (5 V, 100 ns write; 6 V, 200 ns read) strongly depends on parasitic capacitance due to charge sharing. Figure 5g shows that small capacitance yields good linearity but poor distinguishability (<10 mV), while large capacitance improves separation but degrades linearity and reduces the memory window. An

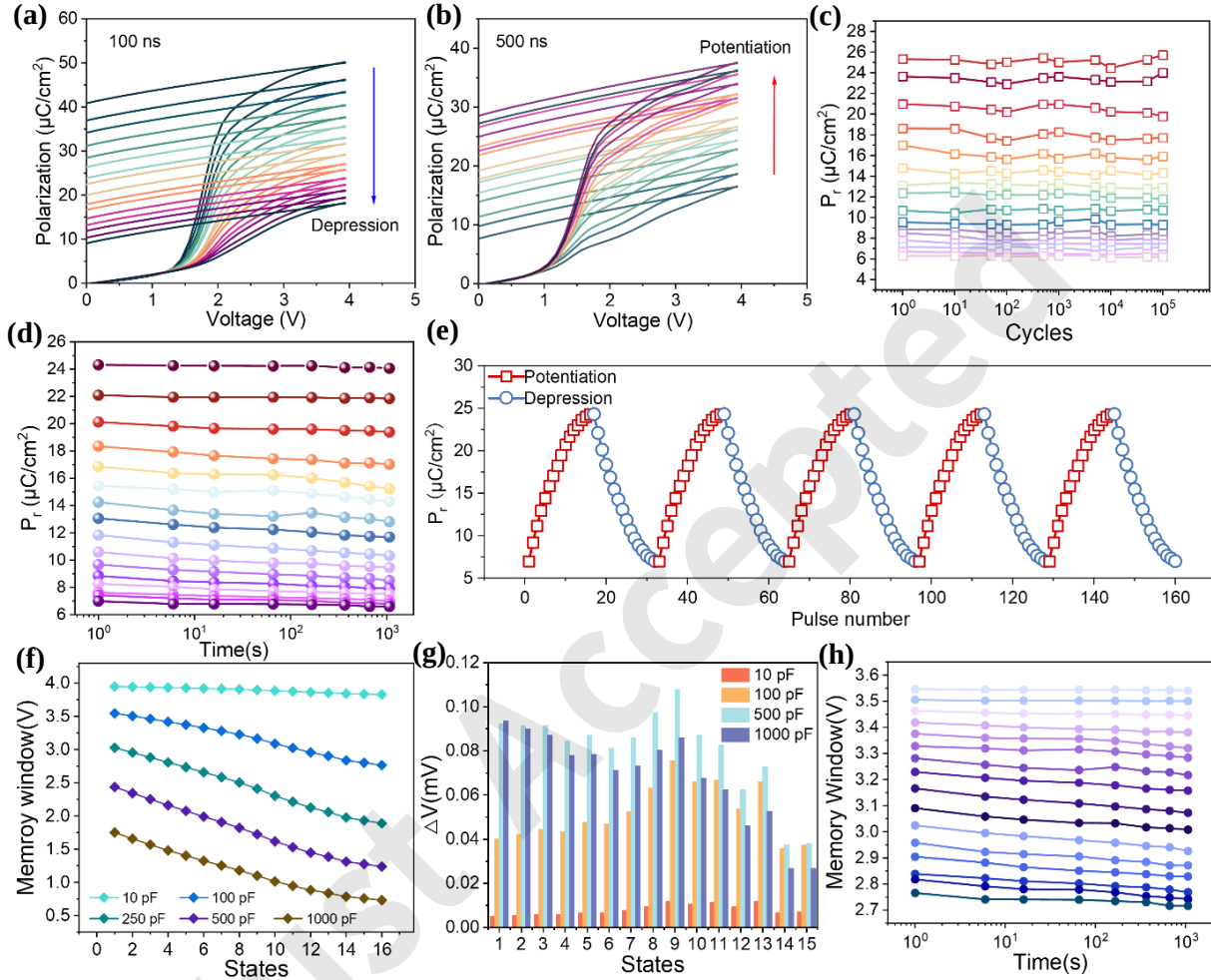


Figure 5 Analog polarization modulation and synaptic characteristics. (a,b) Polarization evolution under pulsed operation. (c,d) Endurance characteristics and retention characteristics of the device under different polarization states. (e) Statistical graph of the device's P_r regulation (potentiation and depression) over ten consecutive cycles. (f) Memory window of the device under different modulation states with varying parasitic capacitance (C_{BL}) conditions. (g) Distribution of the memory window differences between adjacent states under different C_{BL} . (h) Retention characteristics of the memory window after 1000 s under a read voltage of 6 V.

optimal value (~ 100 pF) balances both, giving ~ 40 mV margin. Figure 5h shows stable retention at 100 pF, with no obvious degradation after 1000 s. The memory-window-based metric also shows better linearity than P_r -based evaluation, confirming good device reliability.

Beyond the demonstrated synaptic characteristics, the proposed strategy also exhibits significant potential for practical neuromorphic hardware implementation. Since the oxygen-vacancy regulation is realized entirely through electrical operation without introducing additional fabrication complexity, the proposed approach is inherently compatible with CMOS fabrication processes and existing hafnium-based ferroelectric technologies. Consequently, it is

expected to be integrated into large-scale ferroelectric memory and neuromorphic array architectures, further highlighting its potential for future scalable neuromorphic computing systems.

To facilitate comparison with representative HZO-based ferroelectric synaptic devices, a benchmark summary is presented in Table 1. As shown, previous studies have successfully demonstrated analog synaptic functionality based on HZO ferroelectrics using different device architectures and operation mechanisms [46-48]. In comparison, the present work introduces an electrically driven oxygen-vacancy engineering strategy through an oxygen-active electrode, which enables effective regulation of

ferroelectric polarization while simultaneously improving device reliability. This defect-engineering approach provides an additional degree of freedom for optimizing HZO-based

ferroelectric synaptic devices without compromising CMOS compatibility.

Table 1. Comparison of representative HZO-based ferroelectric synaptic devices.

	[1]	[2]	[3]	This work
Type	FeCAP	FeCAP	FeFET	FeCAP
Analog weight modulation	>64	5(demonstrated)	Multi-level (via conductance)	Multi-level (continuous P_r modulation)
Endurance	N/A	N/A	>10 ⁴ cycle	>10¹¹ cycle
CMOS-compatible	Yes	No	Yes	Yes
Destructive readout	Yes	Yes	No	No

4 Conclusions

In summary, by introducing an ITO top electrode after TiN annealing and applying high-voltage cycling activation, we demonstrate that electrically driven oxygen-vacancy redistribution provides a dynamic and effective approach for interfacial defect regulation in hafnia-based ferroelectric devices. Through combined spectroscopic and nanoscale analyses, we reveal that electric-field-induced oxygen-vacancy redistribution leads to vacancy compensation, interfacial stabilization, and consequently improved ferroelectric switching. Furthermore, by precisely controlling the distribution of interfacial oxygen vacancies, continuous P_r modulation is achieved, enabling robust analog synaptic functionality. Moreover, the demonstrated CMOS compatibility effectively mitigates the read-induced weight degradation issue in two-terminal ferroelectric devices.

Notably, the proposed strategy is based on the concept of an oxygen-active interface rather than the specific ITO/HZO material combination. Therefore, it could potentially be extended to other ferroelectric systems incorporating oxygen-active electrodes or oxygen-exchange interfaces, offering a scalable and CMOS-compatible strategy for the development of reliable hafnium-based ferroelectric neuromorphic systems. By establishing a direct correlation between nanoscale defect dynamics and macroscopic device behavior, this work provides valuable insights for the design of high-performance ferroelectric synaptic devices.

Electronic Supplementary Material: Supplementary material (Detailed device fabrication procedures, supplementary electrical and neuromorphic characterization, reliability analysis, and supporting XPS, STEM-EELS, and APT results related to oxygen-vacancy regulation) is available in the online version of this article at <https://doi.org/10.26599/NR.xxxx.949xxxxx>

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

J.Z.: Conceptualization, formal analysis, investigation, methodology, validation, writing manuscript. Y.Z.: methodology, writing manuscript. J.Y.: Formal analysis, investigation, writing manuscript. J.M.: project administration, resources, supervision. H.Z.: project administration, resources. T.W.: resources. Q.S.: project administration, resources. X.Z.: project administration, resources. Y.C.: project administration, resources. D.Z.: project administration, resources. All the authors have approved the final manuscript.

Use of AI statement

None.

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Electronic Supplementary Material

Oxygen vacancy migration engineering for CMOS-compatible hafnium-based ferroelectric synaptic devices

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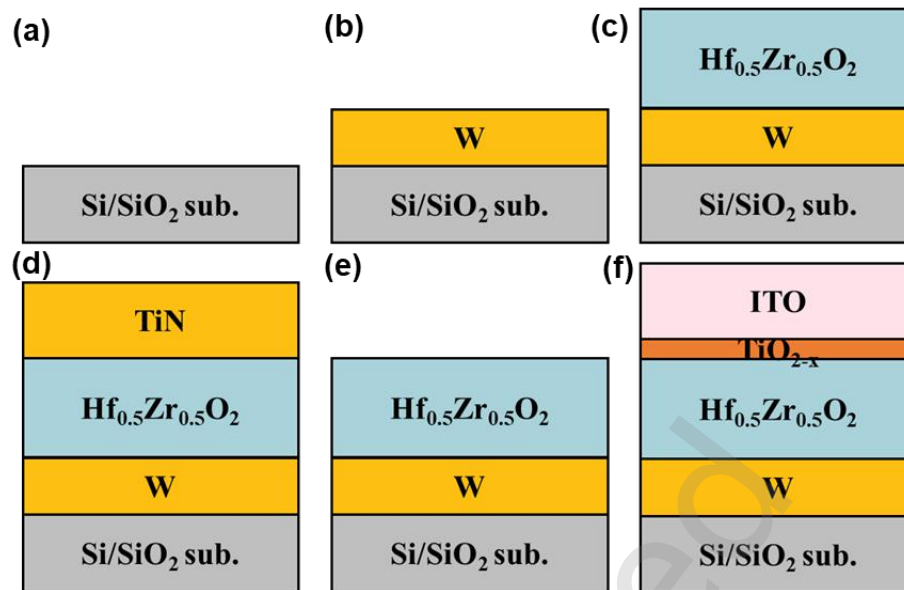


Figure S1. Device fabrication process. (a) The silicon wafer was sequentially cleaned with acetone, isopropanol, and deionized water, each for 10 minutes. (b) A 50 nm W bottom electrode was deposited on the cleaned silicon wafer by physical vapor deposition (PVD). (c) A 10 nm HZO ferroelectric thin film was grown using atomic layer deposition (ALD). (d) A 170 nm TiN capping layer was deposited by PVD, followed by rapid thermal annealing at 500 °C for 60 seconds. (e) A solution was prepared by mixing $\text{NH}_3 \cdot \text{H}_2\text{O}$, H_2O_2 , and H_2O in a 1:1:5 ratio for the wet etching of TiN. After rapid thermal annealing, the wafer was immersed in the solution for 5 minutes, followed by rinsing with deionized water and drying with nitrogen gas. (f) A 100 nm ITO top electrode was deposited by PVD.

The device fabrication schematic (a-f) provides a clear view of the sequential deposition and fabrication processes, ensuring reproducibility in the preparation of the ITO/HZO/W stack.

Structural characteristics of the device and HZO film

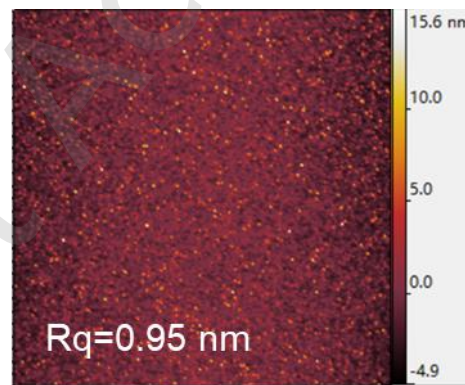
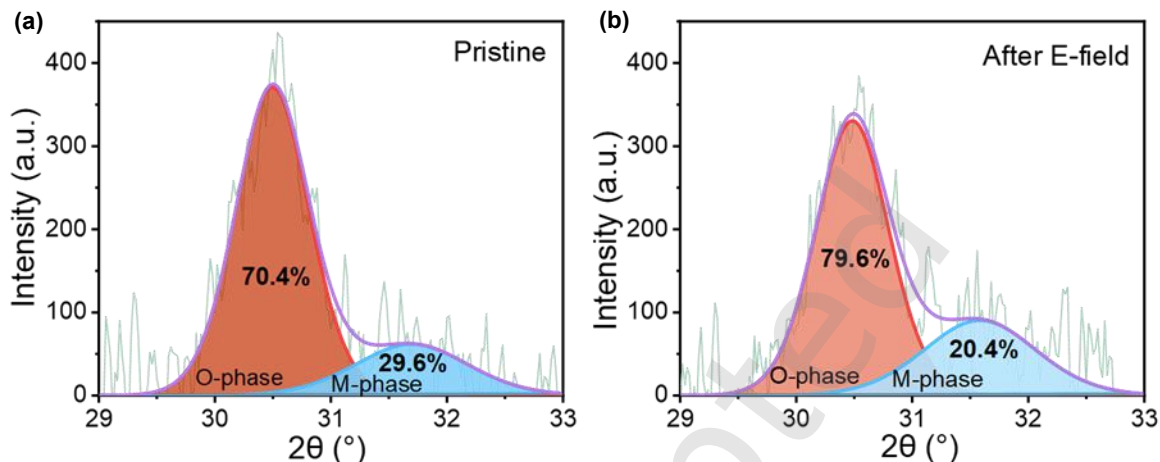


Figure S2. AFM Topography: Atomic Force Microscopy (AFM) topographic image of the HZO surface, showing a root-mean-square (RMS) roughness of 0.95 nm.

The AFM data (Figure S2, Supporting Information) shows a surface roughness of 0.95 nm, indicating a smooth film surface [1, 2], which is favorable for reliable device performance and reduces the likelihood of defects affecting polarization behavior.

XPS analysis of the ITO/HZO interface

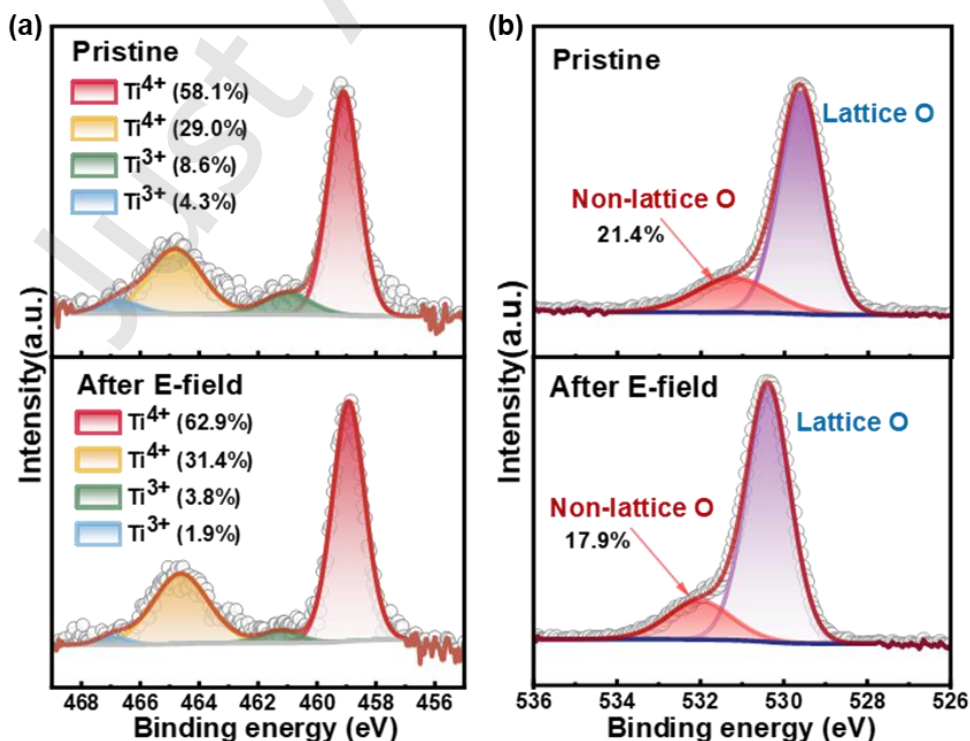
X-ray Photoelectron Spectroscopy (XPS) is commonly used to characterize the photoelectron peaks of different elements or chemical states and their variations under different sample conditions or treatments, which helps analyze the chemical composition and states of materials' surfaces [3]. Below are the XPS spectra of O and Ti before and after electric field application. Understanding the chemical states and distribution of elements is crucial for comprehending the ferroelectric mechanisms and optimizing the material's



performance.

Figure S3. Grazing incident X-ray diffraction (GIXRD) patterns of the HZO film in the initial state (a) and after the electrical cycle (b) (with the M/T phase peaks separated).

For the pristine film, the fitting reveals an O-phase fraction of 70.4 % and a M-phase fraction of 29.6 %. After electrical cycling, the O-phase fraction increases to 79.6 %, while the M-phase fraction decreases to 20.4 %, as shown in Figure S3. This quantitative result clearly confirms that the applied electric field slightly enhances the population of the polar orthorhombic phase at the expense of the



nonpolar component.

Figure S4. XPS of different elements. (a) XPS of Ti before and after electric field application. (b) XPS of O before and after electric field application.

The Ti 2p peak was analyzed using XPS, where the binding energy, peak shape, and intensity were used to distinguish between Ti^{3+} and Ti^{4+} . The binding energy of Ti^{3+} is typically higher than that of Ti^{4+} , and the peak may appear broader or asymmetric. Peak fitting and area calculation were performed to quantitatively analyze the Ti content in different oxidation states before and after electric field application. The electric field application facilitated the oxidation reaction, resulting in the conversion of Ti^{3+} to Ti^{4+} . The XPS spectra of O reveal two main components in the oxygen peak: lattice oxygen (Lattice O) and non-lattice oxygen (Non-lattice O). Lattice oxygen corresponds to the oxygen atoms directly involved in the crystal structure, while non-lattice oxygen is indicative of defects such as oxygen vacancies or adsorbed oxygen species on the surface.

Electrical Performance and Endurance Test

The polarization–voltage (P–V) hysteresis loops of the devices in this study were measured using the following triangular pulse. The ferroelectric polarization–voltage hysteresis loops and P_r statistics of the control TiN/HZO/W devices are presented. Furthermore, the endurance and breakdown characteristics of the devices were thoroughly investigated. Understanding the fundamental properties of the devices is crucial for optimizing their performance.

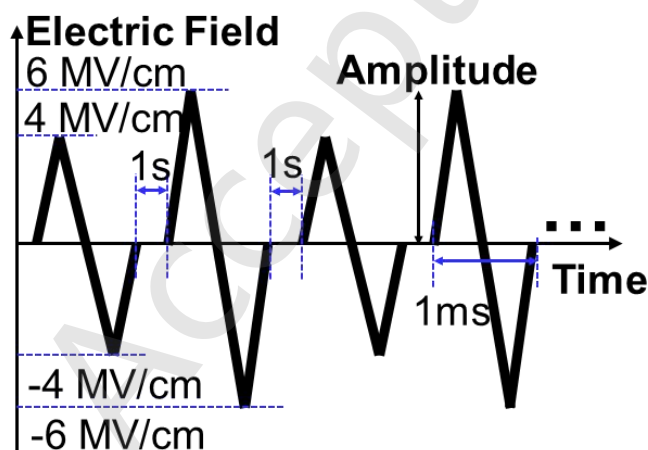


Figure S5. Pulse waveforms used for high electric field operation and P-V testing.

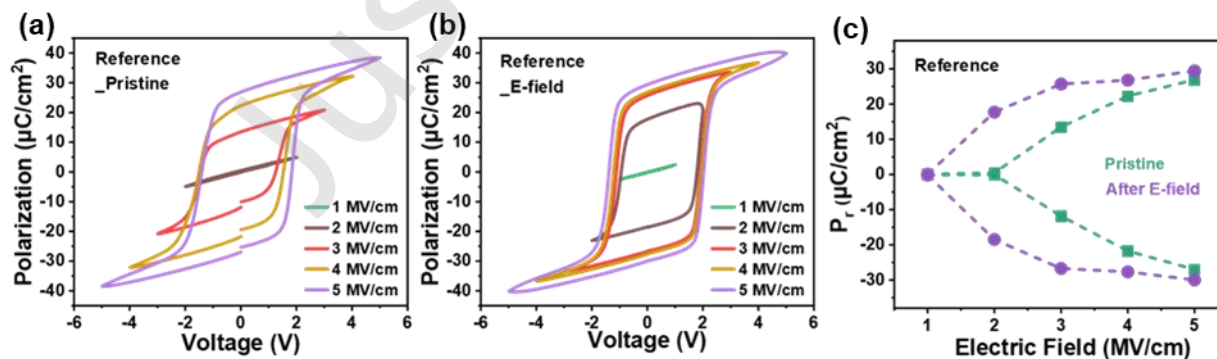
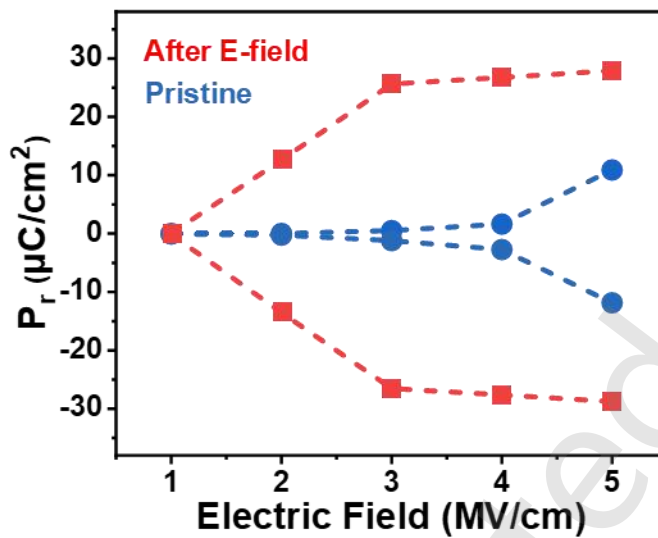


Figure S6. Polarization–voltage (P–V) hysteresis loops of TiN/HZO/W devices pristine (a) and after electric field cycling (b), showing increased remanent polarization (P_r) and saturation polarization. (c) Statistical analysis of remanent polarization (P_r) in TiN/HZO/W devices before and after electric field cycling. P–V hysteresis loops of TiN/HZO/W capacitors in the initial state and after electric field application, with minimal change in P_r compared to the initial state. The P_r value of the ITO electrode devices is nearly identical to that of devices fabricated with traditional TiN electrodes, indicating that the devices with ITO electrodes retain similar excellent ferroelectric properties after surface vacancy control, comparable to those fabricated with TiN electrodes.

From the P-V curve of the TiN electrode device (see Figure S6a, b), it is evident that the changes in P_r and E_c before and after wake-up are minimal, and the curve is saturated, indicating that the O-phase proportion is already high in the initial state, and the electric field



cycling has a limited impact on the phase structure, as further confirmed by Figure S6c.

Figure S7. Statistical plot of remanent polarization (P_r) for ITO/HZO/W devices in the initial state and after electric field cycling, indicating that the device is awakened under high voltage and maintains a high level of remanent polarization after surface vacancy control.

Figure S7 provides a more intuitive representation of the change in P_r values of the ITO device before and after wake-up, where the ITO electrode plays a crucial role in this process. Prior to wake-up, the high oxygen vacancy concentration leads to carrier injection. When the electric field is applied, the ITO electrode regulates the oxygen vacancy concentration in the HZO layer through oxygen exchange, redistributing the oxygen vacancies and enhancing the ferroelectricity. This behavior can be understood by considering the initial defect distribution. In the pristine state, high concentrations of oxygen vacancies near the interface lead to strong internal field screening and domain wall pinning, preventing complete polarization switching. During electric-field cycling, vacancy redistribution reduces these effects, allowing more domains to switch coherently, resulting in enhanced polarization.

It should be noted that the device activation process was performed by gradually increasing the cycling voltage from 1 V to 6 V with a step size of 1 V. Specifically, the device was first subjected to repeated bipolar P-V measurements at ± 1 V. Upon completion of the measurements at this voltage, the cycling voltage was successively increased to ± 2 V, ± 3 V, ± 4 V, ± 5 V, and finally ± 6 V, while the same measurement protocol was employed at each voltage level. This stepwise conditioning procedure allowed the ferroelectric switching characteristics to evolve progressively under increasingly stronger electric fields. It should be noted that repeated electrical cycling at relatively low voltages (≤ 5 V) did not produce a pronounced activation effect, even after multiple cycles, indicating that the applied electric field was insufficient to induce complete oxygen-vacancy redistribution and full activation of the ferroelectric layer. A significant enhancement in remanent polarization was observed only after the conditioning voltage reached 6 V, suggesting that a sufficiently high electric field is required to fully activate the device.

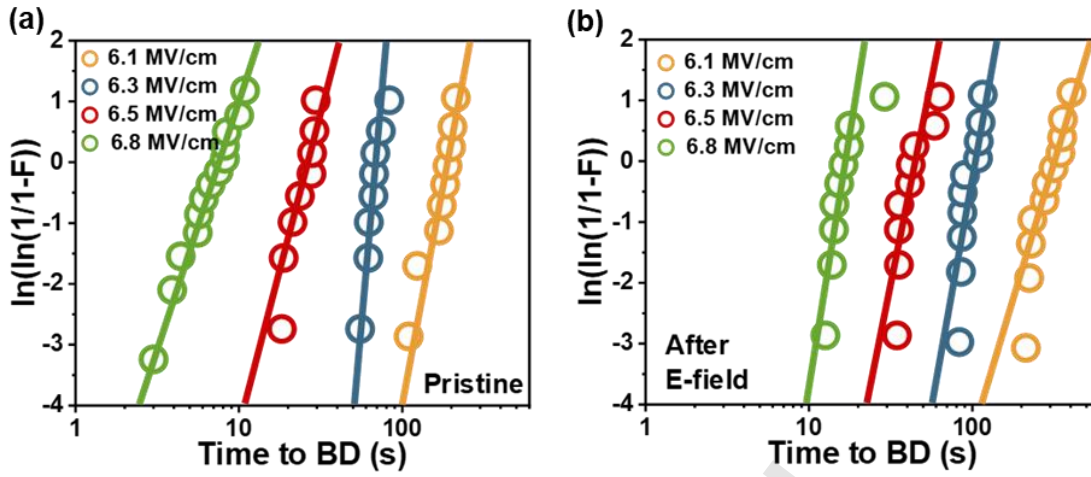
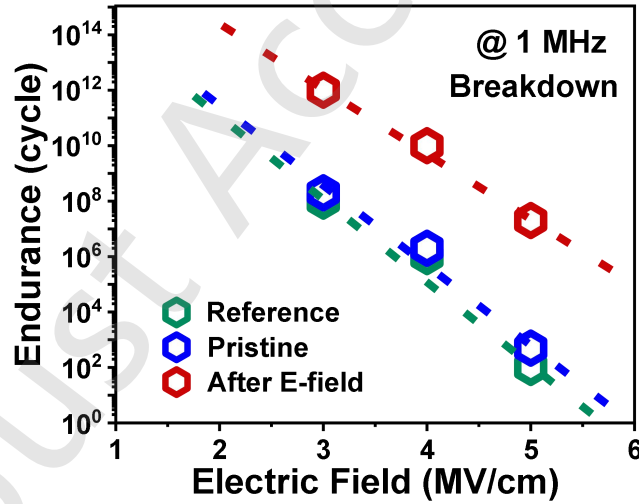


Figure S8. Time-dependent dielectric breakdown (TDDDB) characteristics of ITO/HZO/W devices before (a) and after (b) electric field application. Weibull distributions corresponding to TDDDB measurements (c, d) indicate improved reliability and more uniform defect distribution following electric field cycling.

TDDDB testing is a crucial method for evaluating the reliability of ferroelectric capacitors[4], such as ITO/HZO/W structures. By applying long-term stress under constant voltage until dielectric breakdown occurs, the capacitor's lifetime under various voltages can be determined, providing insights into its reliability under practical operating conditions. The Weibull distribution is a commonly used statistical method for analyzing TDDDB data. By fitting breakdown time data, it offers reliability and consistency information about the capacitor's lifetime. The Weibull distribution (see Figure S8a, b) corresponding to the TDDDB measurements shows an increase in the slope parameter (β) after electric field cycling, indicating reduced oxygen vacancy clustering at the interface and improved defect ordering. This improvement is reflected in the device performance, where a longer time-to-breakdown is observed, contributing to



enhanced breakdown characteristics and overall device reliability.

Figure S9. Breakdown distribution statistics of the devices under different cycling voltages.

By statistically analyzing the relationship between endurance and electric field strength for the three types of devices, it can be observed that the distribution of the ITO devices in the initial state is similar to that of the reference devices. However, after electric field application, the endurance of the ITO devices is significantly superior to the other two types. This indicates that the ITO-based device exhibits excellent reliability and uniformity.

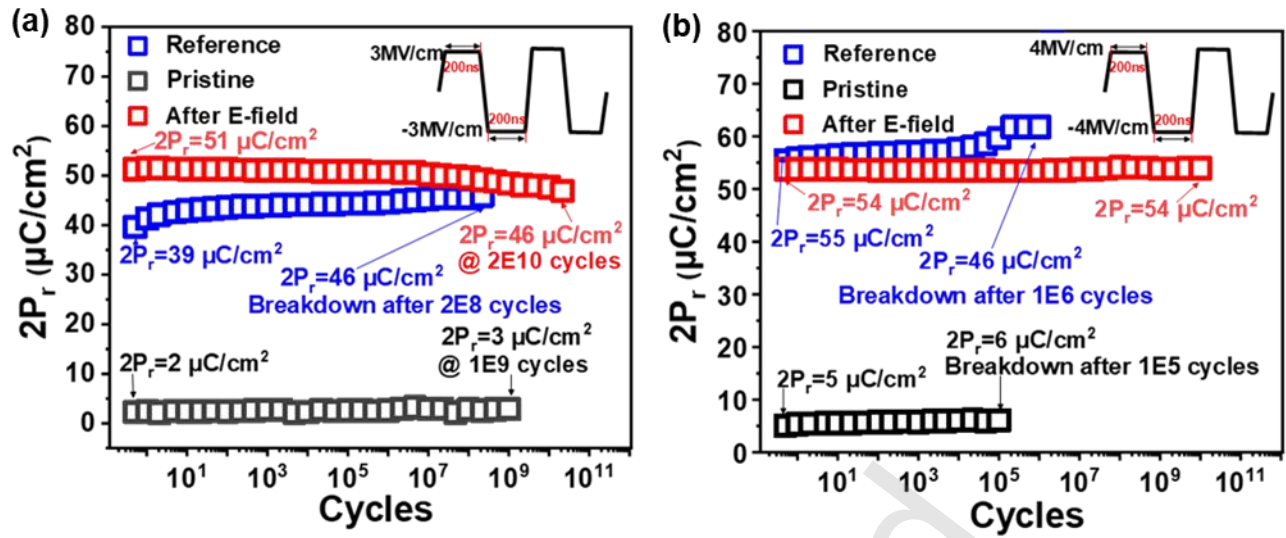


Figure S10. Endurance performance of the devices. Endurance performance of different devices measured at electric field strengths of 3 MV/cm (a) and 4 MV/cm (b).

Regardless of the electric field strength (3 MV/cm or 4 MV/cm), the devices after electric field application exhibit the best cycling endurance. Additionally, after the same number of cycles, the P_r decay is faster for devices subjected to lower electric field strengths.

By measuring the P-V hysteresis loops of the devices before and after the same number of cycling operations under different electric field strengths, it can be clearly observed that the decay rate of remanent polarization (P_r) gradually decreases with increasing electric field strength. Furthermore, endurance tests conducted at different frequencies (Figure 2g) follow the same trend, which is consistent with previously reported studies [4].

Atom probe tomography (APT).

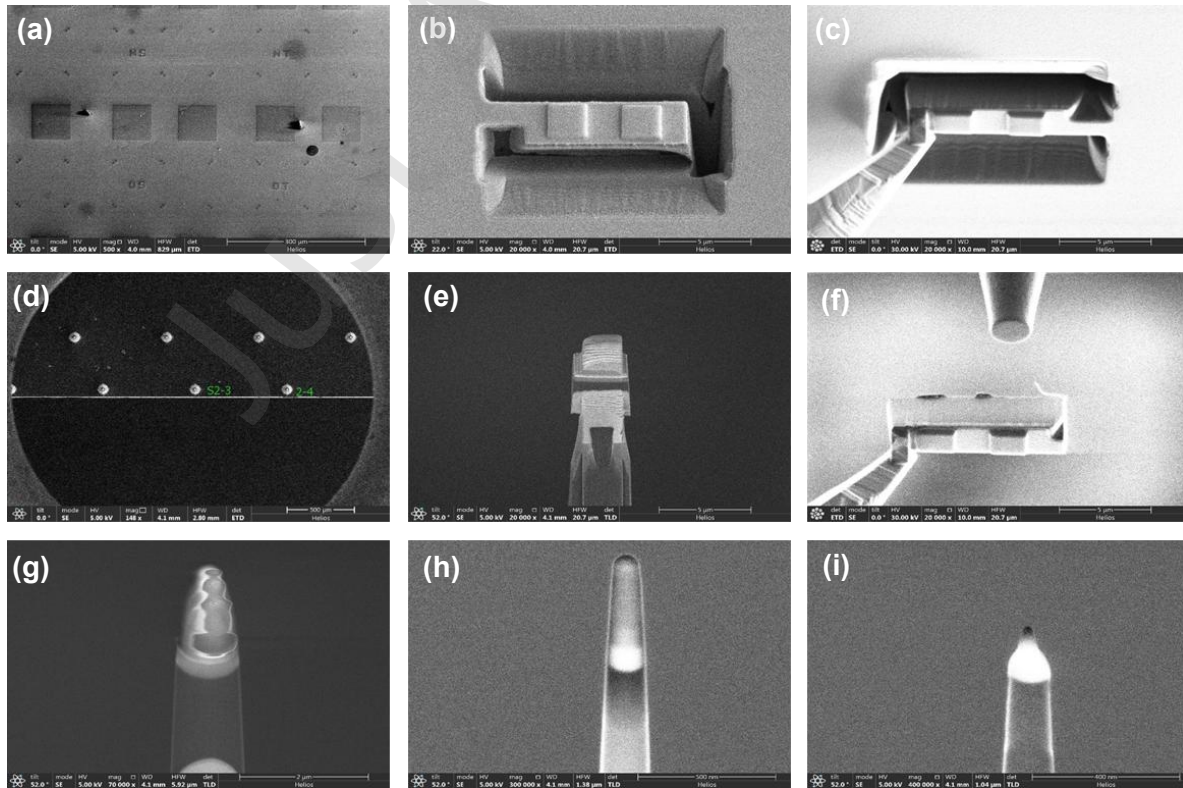


Figure S11. APT sample preparation steps. (a) Selection of the sampling site. (b) Trenching at the target location to isolate the region of interest. (c) Deposition of a Pt protective layer above the selected region. (d) Preparation of the sample stage for needle mounting. (e) Transfer of the extracted pillar to the center of a pre-fabricated post on the sample stage. (f) Side-view image of the mounted specimen. (g, h) Progressive thinning of the pillar to form a sharp needle.

(i) Final atom probe tip prepared for analysis.

Atom probe tomography (APT) is a powerful high-resolution characterization technique that enables three-dimensional reconstruction of materials with near-atomic spatial precision and sub-parts-per-million chemical sensitivity[5, 6]. By sequentially field-evaporating atoms from a needle-shaped specimen and identifying their mass-to-charge ratios, APT provides detailed spatial and chemical information at the single-atom level. This capability is particularly critical for probing nanoscale compositional gradients, elemental clustering, and interfacial diffusion phenomena that are often inaccessible by conventional microscopy or spectroscopy techniques. In the context of functional materials and device, APT offers unique insights into the interplay between local chemistry and emergent physical properties, such as interfacial redox reactions, oxygen vacancy migration, and compositional asymmetry across oxide layers.

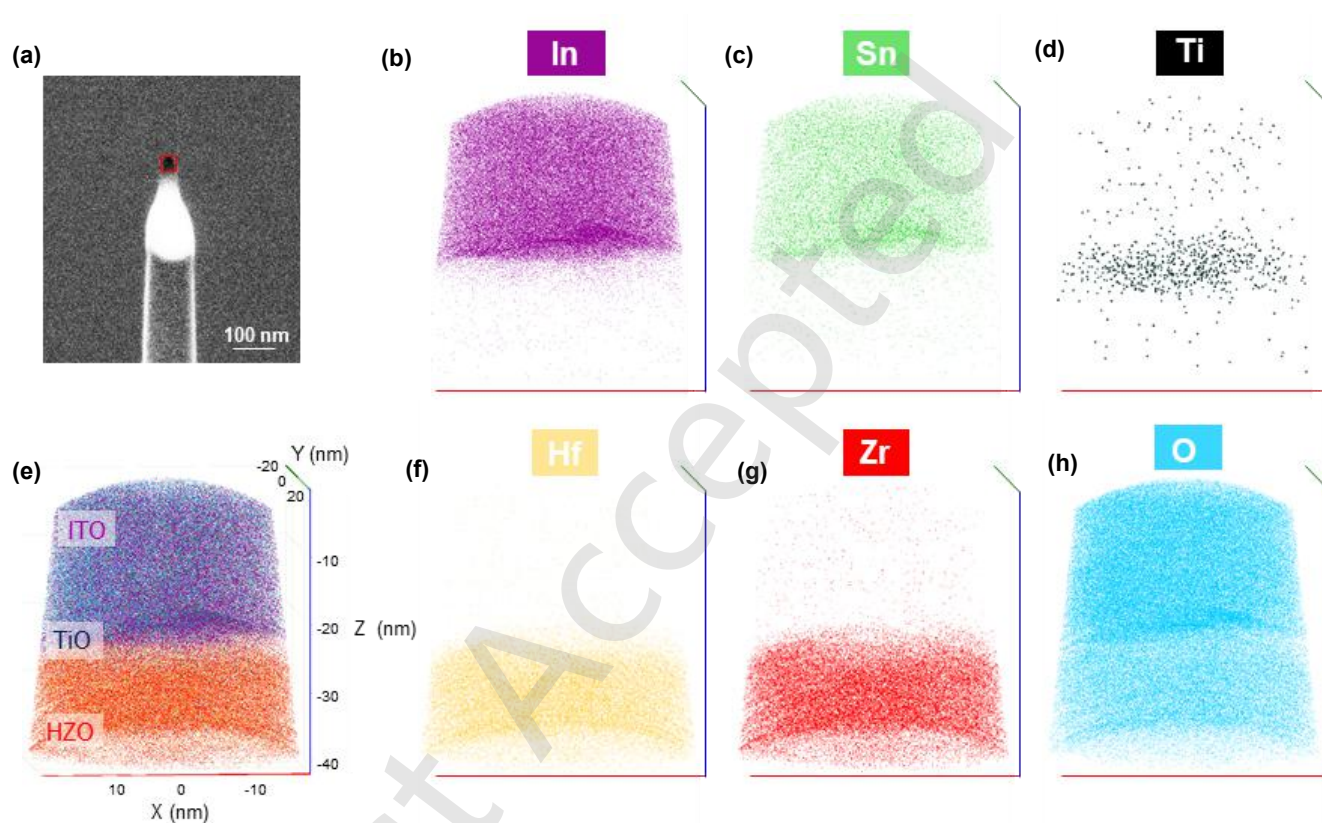


Figure S12. (a) Scanning electron microscopy (SEM) image of the APT tip, illustrating the geometry and dimensions of the specimen prepared for atom probe tomography (scale bar: 100 nm). (b) Cross-sectional APT reconstruction of the sample, revealing the distribution of layered structures such as ITO, TiO, and HZO. (c-h) Three-dimensional elemental maps showing the spatial distribution of selected elements within the sample, providing insights into its chemical composition.

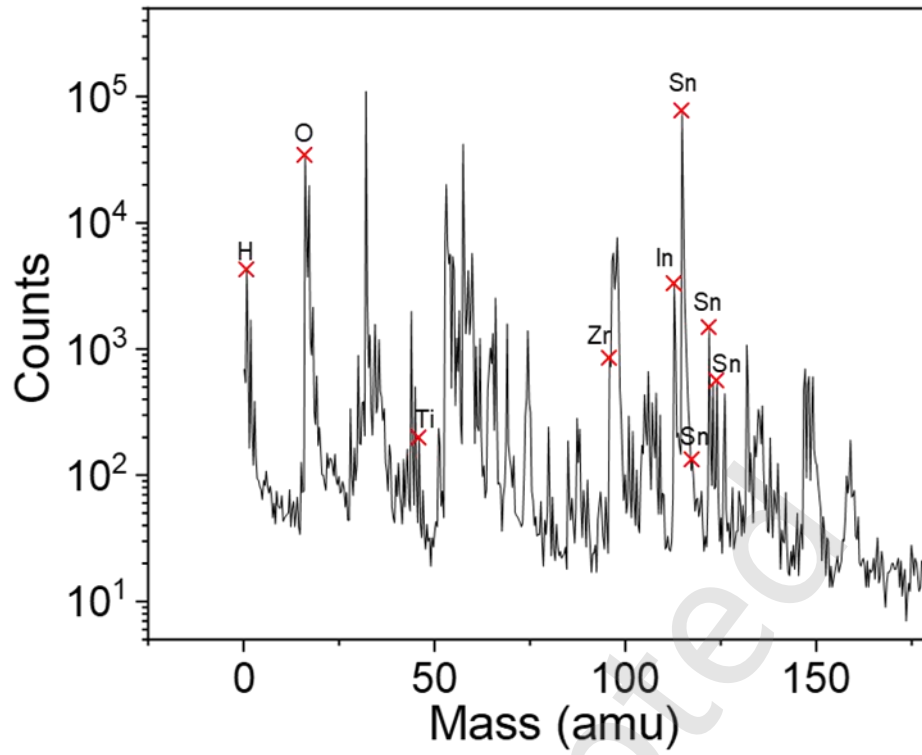


Figure S13. Mass spectrum obtained by atom probe tomography (APT), revealing the mass-to-charge ratios and corresponding atomic counts of different elements present in the sample.

Vacancy Redistribution and Synaptic Behavior

In the HZO ferroelectric layer, oxygen vacancies (V_o) are common defects. The presence of oxygen vacancies affects the polarization state and electrical properties of the ferroelectric layer [7]. The redistribution of oxygen vacancies can influence remanent polarization (P_r) by altering the electric field distribution and local charge states [8]. When positive/negative pulsed voltages are applied to the ITO top electrode, the corresponding electric field direction drives the migration of oxygen vacancies, thereby affecting the polarization state of HZO. The phenomenon of controlling P_r through positive and negative pulses can be analogized to synaptic plasticity in biological systems. In biological synapses, signal transmission between neurons involves the release of neurotransmitters from the presynaptic membrane, leading to changes in the postsynaptic membrane potential. These potential changes can strengthen or weaken the synaptic connection, thereby enabling information storage and processing.

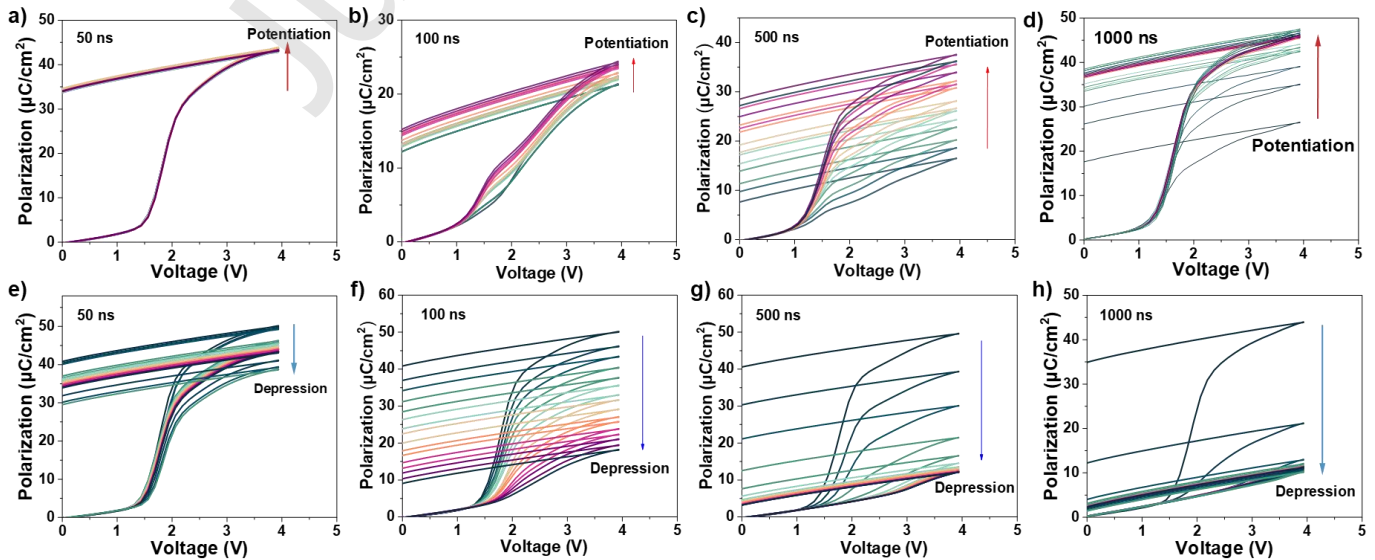


Figure S14. (a-d) First quadrant P–V hysteresis loops obtained by applying different numbers of negative pulses to the device, showing a gradual increase in P_r . (e-h) First quadrant P–V hysteresis loops obtained by applying different numbers of positive pulses, showing a gradual decrease in P_r . Both measurements were conducted under an electric field strength of 4 MV/cm.

When a forward pulse voltage is applied to the ITO top electrode, the electric field direction is from the ITO to the W bottom electrode. This electric field direction drives oxygen vacancies in the ITO toward the HZO side. The migration of oxygen vacancies causes them to accumulate near the ITO/HZO interface, forming a positive charge layer. This positive charge layer partially shields the applied electric field, thereby reducing the effective electric field within the ferroelectric layer. Due to the weakened effective electric field, the polarization state of the ferroelectric layer is suppressed, leading to a decrease in the residual polarization (P_r). When a negative pulse voltage is applied to the ITO top electrode, the electric field direction is from the W bottom electrode to the ITO electrode. This electric field direction drives oxygen ions to migrate toward the HZO side, neutralizing a portion of the oxygen vacancies at the HZO interface. The positive charge layer at the ITO/HZO interface decreases, while the effective electric field within the ferroelectric layer increases. The enhanced effective electric field strengthens the polarization state of the ferroelectric layer, leading to an increase in the residual polarization (P_r).

System-level implementation and multilevel memory operation

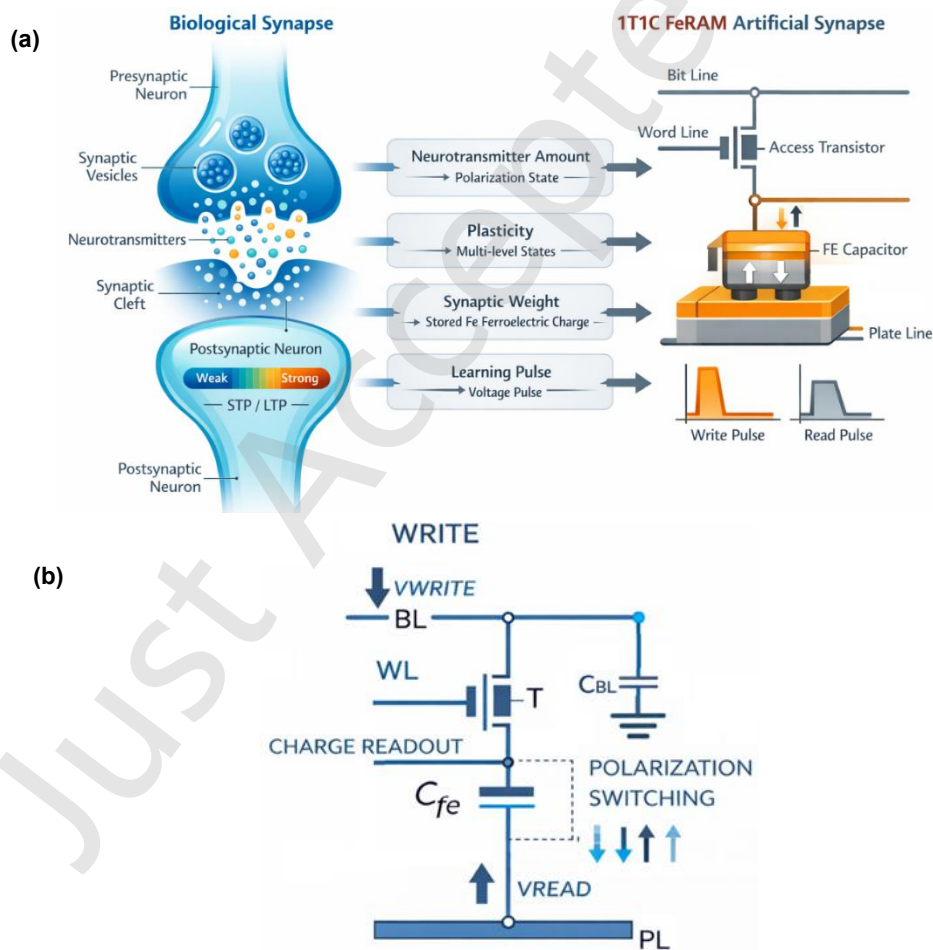


Figure S15. (a) Schematic illustration of the synaptic device based on a 1T1C FeRAM architecture. (b) Read and write operations and the corresponding circuit schematics of the 1T1C device.

Under different storage states, the C–V curves of the device still exhibit a typical butterfly-shaped hysteresis, with slight variations in the maximum capacitance. However, the overall capacitance values remain distributed within the range of 100 pF to 180 pF.

Supplementary Methods

Device fabrication

ITO//HZO/W ferroelectric capacitors were fabricated on thermally oxidized silicon substrates (300 nm SiO_2). A 10 nm thick tungsten

(W) bottom electrode was deposited by magnetron sputtering in an argon atmosphere. Subsequently, a 10 nm HZO film was grown using plasma-enhanced atomic layer deposition (PEALD) at 250°C, with Tetrakis(dimethylamino)hafnium (TDMA-Hf) and TDMA-Zr as metal precursors. The Zr:Hf ratio was maintained at 1:1. After HZO deposition, a TiN capping layer was fabricated by magnetron sputtering, followed by rapid thermal annealing (RTA) at 500 °C for 60 seconds in an N₂ environment, which crystallized the HZO film and stabilized the orthorhombic (o-phase). After cooling, the sample was immersed in an etching solution (NH₃ · H₂ O:H₂ O₂ :H₂ O = 1:1:5) for 10 minutes to remove the TiN layer, followed by nitrogen blow-drying. Finally, a 100 nm thick ITO top electrode was deposited by magnetron sputtering in an Ar/O₂ (5% O₂) environment, completing the device stack. The TiO_{2-x} interfacial oxide layer (IOL) formed during the annealing and ITO growth process.

Electrical measurements

Polarization-voltage (P–V) hysteresis loops were measured using a Precision Premier II ferroelectric tester (Radiant Technologies) with bipolar triangular waveforms at 1kHz, unless otherwise specified. Endurance measurements were performed under unipolar square pulse cycling using a custom pulse generator. Time-zero dielectric breakdown (TZDB) and time-dependent dielectric breakdown (TDDb) were evaluated using a Keysight B1500A semiconductor parameter analyzer by applying constant voltage stress. Oxygen vacancy migration tests was performed using sequentially increasing triangular pulses ranging from 1 V to 6 V. Pulse-width-dependent P_r modulation experiments were conducted using single-polarity square pulses with varying widths (50-1000 ns), applied through a waveform generator synchronized with an oscilloscope for real-time monitoring.

STEM and EELS characterization

Cross-sectional transmission electron microscopy (TEM) samples were prepared using focused ion beam (FIB) milling (FEI Helios NanoLab). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and annular bright-field (ABF) imaging were conducted on a JEOL ARM200F microscope operated at 200 kV, equipped with a probe spherical aberration corrector. Electron energy loss spectroscopy (EELS) was performed using a Gatan Quantum ER energy filter. The Ti L_{2,3} and O K edges were acquired in dual EELS mode with an energy resolution of ~0.7 eV and spatial resolution of <1 nm. EELS spectra were recorded across multiple positions spanning the ITO, TiO_{2-x}, HZO, and W layers, before and after electric field cycling. Spectral alignment and background subtraction were performed using Digital Micrograph software.

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