

Revealing wake-up mechanism in antiferroelectric $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ capacitors through spatially selective wake-up

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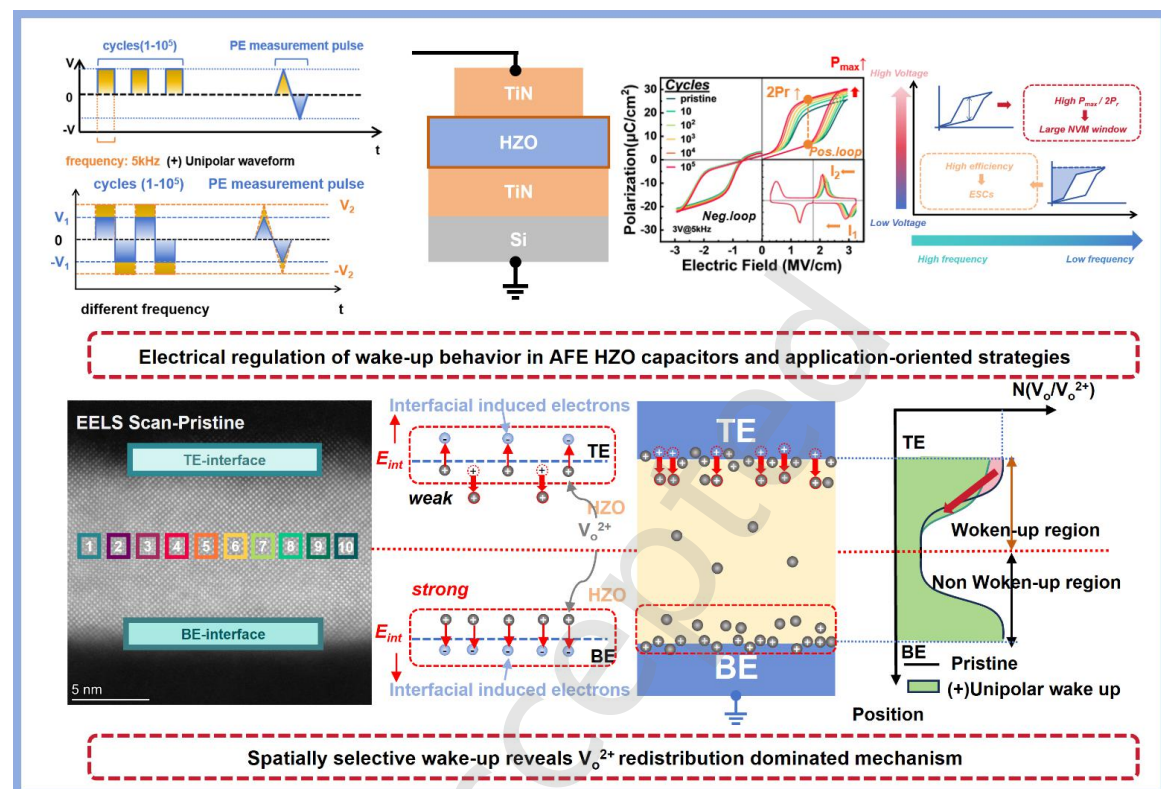
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ABSTRACT: Antiferroelectric (AFE) devices are promising for nonvolatile memory applications due to their high endurance and low operating voltage, while their double hysteresis loops and high breakdown fields enable static energy-storage applications. However, their reliability evolution under electric-field cycling and the underlying physical mechanism remain insufficiently understood. In this work, we systematically investigate the wake-up behavior of AFE $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (HZO) capacitors and quantitatively evaluate its dependence on cycling frequency and voltage amplitude. By designing a unipolar electrical excitation, spatially selective unipolar wake-up is realized within a single device, creating coexisting woken and non-woken-up regions. Combined energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) analyses reveal that the wake-up effect is primarily governed by the field-driven directional migration and redistribution of charged oxygen vacancies near the electrode/HZO interfaces. Furthermore, we uncover the application-dependent impact of wake-up behavior. Tailored electrical excitation with enhanced wake-up effectively enlarges the memory window for nonvolatile memory operation, whereas suppressing excessive wake-up preserves the energy storage performance of AFE capacitors. These findings reveal an oxygen-vacancy-redistribution-dominated wake-up mechanism in AFE HZO capacitors and provide an application-oriented electrical regulation strategy for optimizing their performance in both memory and energy-storage technologies.

KEYWORDS: antiferroelectric, $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$, wake-up, oxygen-vacancy

1. Introduction

Owing to their nanoscale scalability, environmental friendliness, and excellent compatibility with complementary metal oxide semiconductor (CMOS) technology, functional HfO_2 -based thin films have emerged as promising candidates for advanced energy storage systems and next-generation nonvolatile memory (NVM) devices [1-9]. Among HfO_2 -based AFE systems, $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (HZO) films with characteristic double hysteresis loops are particularly attractive because they are expected to offer superior endurance and reduced operating voltages, which has also been considered a promising DRAM dielectric beyond the 20 nm technology node [10-11]. Besides, their reversible field-induced polarization response also makes them highly promising for energy storage [12-13], thermoelectric energy harvesting [14], and solid-state cooling technologies [15]. Despite these advantages, reliability issues in fluorite-structured HfO_2 -based systems, especially electric field cycling induced wake-up and fatigue

effects, remain critical challenges that hinder their practical implementation [16-20]. In FE HfO_2 -based thin films, wake-up and fatigue are generally manifested as an initial enhancement followed by a subsequent degradation of the remanent polarization (P_r) during electric-field cycling [21-22]. These behaviors have been widely associated with the redistribution of charged oxygen vacancies (V_o^{2+}) under repeated electrical excitation [16, 23-28]. Asymmetric defect migration has also been reported in FE HfO_2 -based systems, where it is primarily associated with the evolution of built-in fields, imprint, and conventional single-loop wake-up behavior [29-32]. However, these studies mainly concern FE systems characterized by a single polarization-switching loop. In contrast, AFE HZO exhibits characteristic double hysteresis loops, in which positive and negative electric fields access distinct antipolar-polar transition pathways. Whether asymmetric defect redistribution can selectively affect these individual transition pathways during electrical cycling remains insufficiently understood. More broadly, compared with FE systems, the cycling-induced evolution of

AFE hysteresis loops and the associated reliability mechanisms remain much less understood. In particular, how defect redistribution is coupled to the pathway-dependent wake-up behavior of AFE HfO₂-based capacitors remains unclear.

As illustrated in Fig. 1(a), AFE thin films exhibit typical double P-E hysteresis loops (positive loop and negative loop). For NVM applications, an internal bias field can be introduced during device fabrication to directionally shift the AFE hysteresis loop, thereby enabling FE-like memory functionality through the one-sided loop opening while retaining the high endurance advantage of AFE devices. In this case, the memory window is characterized by the 2Pr value after loop shifting. For AFE devices with double P-E hysteresis loops, 2Pr is defined as the polarization window width at the single-side polarization switching field (E_F), corresponding to the separation indicated by the red double-headed arrow in Fig. 1(a) [33-34]. Meanwhile, AFE devices are also promising candidates for energy-storage capacitors (ESCs), where the energy storage efficiency (η) is evaluated by the ratio of the energy-storage density (W_{ESD}) (orange area) to W_{Total} (sum of the orange and blue areas) [34-35]. Therefore, systematically elucidating the reliability evolution of AFE devices during electric-field cycling, uncovering the underlying physical mechanisms, and further assessing their implications for diverse application scenarios are of great significance for improving device reliability, optimizing performance engineering strategies, and advancing the practical implementation of AFE-HfO₂-based devices.

In this work, we fabricated AFE-Hf_xZr_{1-x}O₂ (HZO) capacitor and systematically tracked the complete evolution of its AFE hysteresis loops during electric-field cycling. A pronounced wake-up behavior was observed, characterized by simultaneous increases in the maximum polarization (P_{max}) and 2Pr. The wake-up degree was further quantitatively evaluated under different cycling frequencies and voltage amplitudes. To further elucidate the evolution of V_o^{2+} behavior within the film during the wake-up process in AFE devices, we designed a unique unipolar cycling waveform that enables the construction of coexisting “woken” and “non-woken” regions within the same device, thereby allowing selective one-sided wake-up. In parallel, energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) were used to spatially resolve elemental distributions and to compare the evolution of V_o^{2+} in HZO films across three representative wake-up states: pristine state, after bipolar wake-up cycles, and after positive (+) unipolar wake-up cycles. These results suggest that the wake-up behavior of AFE devices is primarily associated with the field-cycling-driven localized redistribution of interfacial V_o^{2+} , which mitigates the defect-induced internal bias field. Further analysis reveals that the wake-up process enlarges the memory window for NVM applications, but simultaneously reduces the η and W_{ESD} of ESCs. Based on different application scenarios, application-specific electrical excitation and wake-up schemes can be designed to achieve targeted regulation of the memory and energy-storage performance of AFE devices.

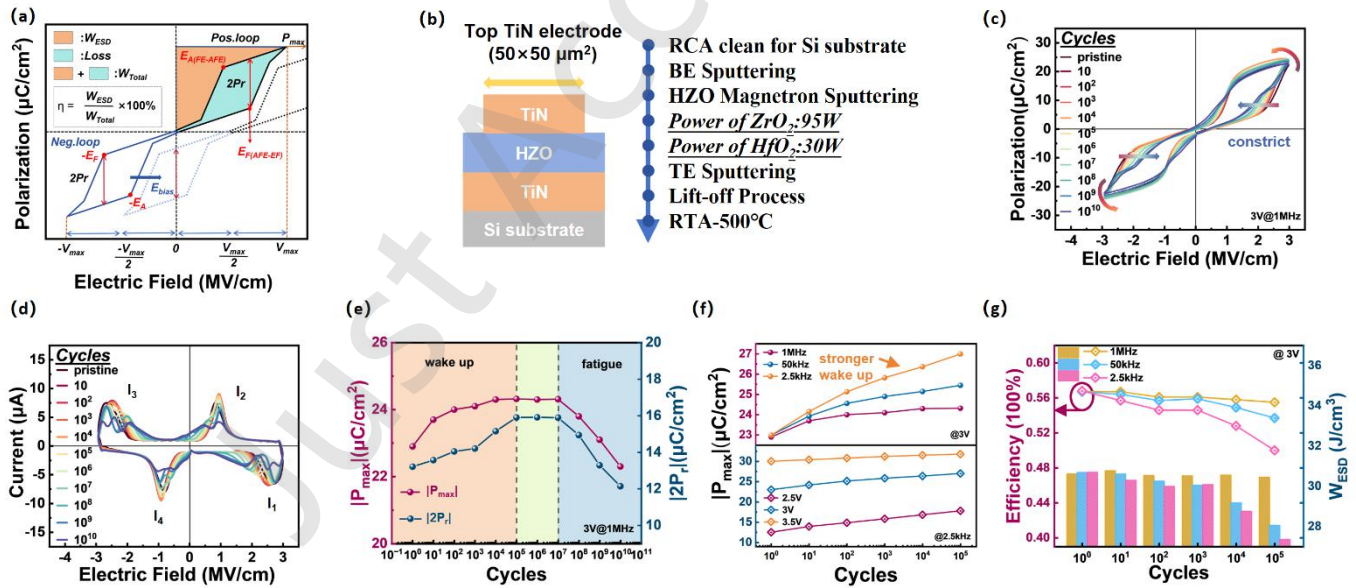


Fig.1. (a) Schematic illustration of AFE hysteresis-loop analysis. (b) Fabrication process flow of the device. Evolution of the (c) P-E hysteresis loops and (d) I-E characteristics of the AFE capacitor during electric-field cycling at 3V and 1MHz frequency. (e) Statistical evolution of $|P_{max}|$ and $|2P_r|$ during cycling. (f) Evolution of $|P_{max}|$ during 10^5 bipolar wake-up cycles under different frequencies (1MHz, 50kHz, and 2.5kHz at 3V) and different voltage amplitudes (2.5V, 3V, and 3.5V at 2.5 kHz). (g) Evolution of the η (left axis) and W_{ESD} (right axis) of the AFE capacitor during 10^5 bipolar wake-up cycles.

2. Experimental

The detailed fabrication process of typical AFE-TiN/HZO/TiN capacitor is illustrated in Fig. 1(b). First, highly doped p-Si wafers were cleaned by the RCA process, followed by 40nm TiN bottom electrode (BE) films and

10nm HZO films. Then, 40nm TiN top electrode (TE) was sputtered and patterned by photo-lithography and lift-off process. The TiN films were deposited by ion beam sputtering (IBS) and HZO films were deposited by magnetron sputtering. During HZO deposition, the

sputtering powers of ZrO_2 and HfO_2 were set to 95W and 30W, respectively. The size of the TE was $50 \times 50 \mu\text{m}^2$. Finally, the capacitor was subjected to rapid thermal annealing (RTA) at 500°C for 30s in flowing N_2 ambient. The AFE characteristics under different wake-up states were measured using an Agilent B1500 semiconductor parameter analyzer. During electrical testing, positive pulse excitation was applied to the TE, while the BE was grounded. During the EELS mapping scan, the pixel array size was 40×70 pixels, an energy dispersion of 0.15eV for the spectrometer and an instrument resolution of 0.4eV.

3. Results and discussion

3.1 Wake-Up Behavior of AFE HZO Capacitors under Electric-Field Cycling

To systematically elucidate the evolution of AFE devices during electric-field cycling, bipolar rectangular cycling measurements were performed at 3V and 1MHz frequency. As shown in Fig. 1(c), the AFE capacitor maintains a pronounced polarization response after more than 10^{10} cycles, demonstrating excellent cycling endurance. With increasing cycle number, the polarization-electric (P-E) hysteresis loops exhibit a clear stage-dependent evolution: the loops first rotate counterclockwise accompanied by a gradual opening, and then begin to contract upon further cycling, indicating a transition from wake-up to fatigue behavior. Fig. 1(d) presents the corresponding current-electric field (I-E) characteristics during electric-field cycling. The AFE device exhibits four characteristic switching-current peaks, denoted as I_1 - I_4 . During the initial cycling stage, the peak intensity gradually increases, suggesting that more polarization regions participate in the electrical response. Upon further cycling, the current peaks show splitting and a gradual decrease in magnitude, corresponding to the onset of fatigue. This evolution is similar to the switching-current behavior commonly observed during the wake-up to fatigue process in FE devices [36-38]. To further quantify this evolution, Fig. 1(e) summarizes the $|P_{\text{max}}|$ and $|2P_r|$ values extracted from the P-E loops at different cycling stages. Each value was calculated as the average of the absolute values obtained from the positive and negative branches of the hysteresis loop. Both $|P_{\text{max}}|$ and $|2P_r|$ initially increase and subsequently decrease with increasing cycle number, corresponding to the wake-up and fatigue processes of the AFE capacitor, respectively. To more clearly elucidate the wake-up behavior of AFE capacitor and its performance evolution under different application scenarios, we performed systematic electric-field cycling measurements under different conditions. As shown in Fig. 1(f), at a fixed voltage amplitude of 3V, the cycling frequency was varied among 1MHz, 50kHz and 2.5kHz, and the evolution of $|P_{\text{max}}|$ during wake-up was quantitatively evaluated. The results reveal a pronounced wake-up effect with the strongest enhancement observed at 2.5kHz. This behavior suggests that a larger pulse width allows more polarization regions to participate in field-induced switching. Meanwhile, under a fixed condition (2.5kHz frequency), we further investigated the voltage dependence (2.5V, 3V, 3.5V) of the wake-up behavior. $|P_{\text{max}}|$ is positively correlated with the voltage amplitude, in the pristine state, the device

exhibits the maximum $|P_{\text{max}}|$ at a relatively high voltage of 3.5V. The corresponding P-E characteristics under various testing conditions (3V at 50kHz frequency, 3.5V at 2.5kHz frequency, 2.5V at 50kHz frequency and 2.5V at 2.5kHz frequency) are shown in Figs. S1(a), (c) and (e-f) in the Electronic Supplementary Material (ESM), and the evolution of $|2P_r|$ follows the same trend as that of $|P_{\text{max}}|$ as shown in Figs. S1(g-h) in the ESM. Among the different frequency conditions, the most pronounced increase in $|2P_r|$ is observed at 2.5kHz. Further comparisons under different voltage amplitudes show that $|2P_r|$ increases remarkably after bipolar wake-up at 2.5V compared with the pristine state, whereas a slight increase in $|2P_r|$ observed after wake-up at 3.5V as shown in Fig. S1(h) in the ESM. Combined with the above statistical analysis, in the pristine state, $|P_{\text{max}}|$ and $|2P_r|$ exhibit pronounced differences under different testing voltages. At a testing voltage of 3.5V, the device shows larger $|P_{\text{max}}|$ and $|2P_r|$, whereas both values remain relatively low at 2.5V. Furthermore, the P-E curves shown in Figs. S1(c) and (f) reveal that the hysteresis branches gradually shift toward 0 voltage during the wake-up process, with a more pronounced shift observed under the 3.5V wake-up condition. The evolution of the P-E hysteresis loops indicate that, compared with the 2.5V cycling condition, the application of a 3.5V electric field can more rapidly activate the polarization response and induce earlier polarization switching. The comparison of the different wake-up behaviors indicates that a certain internal bias field (E_{int}) exists within the capacitor in the pristine state, which suppresses both the positive and negative polarization responses of the AFE device. Therefore, the device exhibits different polarization performance metrics under different applied voltage amplitudes. A higher applied voltage can more effectively overcome the suppression of polarization response induced by the E_{int} , thereby providing a larger effective electric field (E_{eff}) inside the capacitor. During the wake-up process, the evolution of the P-E hysteresis loops and the earlier occurrence of the polarization response with field cycling further suggest that the E_{int} within the capacitor is also modified during cycling. As wake-up proceeds, the blocking effect of the E_{int} on the polarization response is gradually weakened, resulting in a progressively enhanced E_{eff} inside the capacitor under the same applied voltage.

Subsequently, as shown in Fig. 1(g), we further calculated the η (left axis) and W_{ESD} (right axis) of the AFE capacitor during wake-up cycling at 3V under different frequencies to evaluate the impact of the wake-up effect on ESCs. In contrast to the enlarged memory window induced by a stronger wake-up effect, the energy storage performance exhibits an opposite trend: both the η and W_{ESD} degrade markedly under conditions with more pronounced wake-up behavior. Therefore, understanding the physical mechanism underlying the wake-up effect in AFE devices and strategically suppressing this effect are crucial for their further application, as they enable the devices to maintain a large memory window in the pristine state as well as stable η and W_{ESD} . Considering that the absolute values of $|P_{\text{max}}|$ and $|2P_r|$ remain relatively small at the lower voltage amplitude of 2.5V, while the wake-up degree is not obvious at the higher voltage amplitude of 3.5V, the condition of 3V

and 2.5kHz frequency was selected as a representative case for the following discussion of the AFE HZO wake-up behavior.

To reveal the physical mechanism underlying the wake-up process of AFE devices during electric-field cycling and reveal the origin of the enhanced E_{eff} during field-cycling-induced wake-up, we designed specific electrical pulse excitation schemes. As shown in Fig. 2(a), a positive excitation was applied to the TE during the measurements. The device was then subjected to the bipolar electric-field cycling pulses shown in Fig. 2(b) and the (+) unipolar electric-field cycling pulses shown in Fig. 2(c), respectively. It should be noted that the two pulse waveforms have the same pulse width during the positive-field stage (200 μ s),

ensuring a direct comparison of the positive wake-up process. Fig. 2(d) shows the evolution of the P-E hysteresis loops of the AFE capacitor during bipolar wake-up cycling. A pronounced wake-up behavior is observed, with both the positive and negative branches exhibiting gradually enlarged loop openings, corresponding to a significant increase in $|P_{max}|$ and $|2P_r|$. The corresponding I-E characteristics are shown in Fig. 2(e). As wake-up proceeds, all four polarization-switching current peaks of the AFE device increase in intensity and gradually shift toward zero electric field. Previous studies have suggested that such peak-position shifts may be associated with changes in the E_{int} within the device during field cycling [18,30,39].

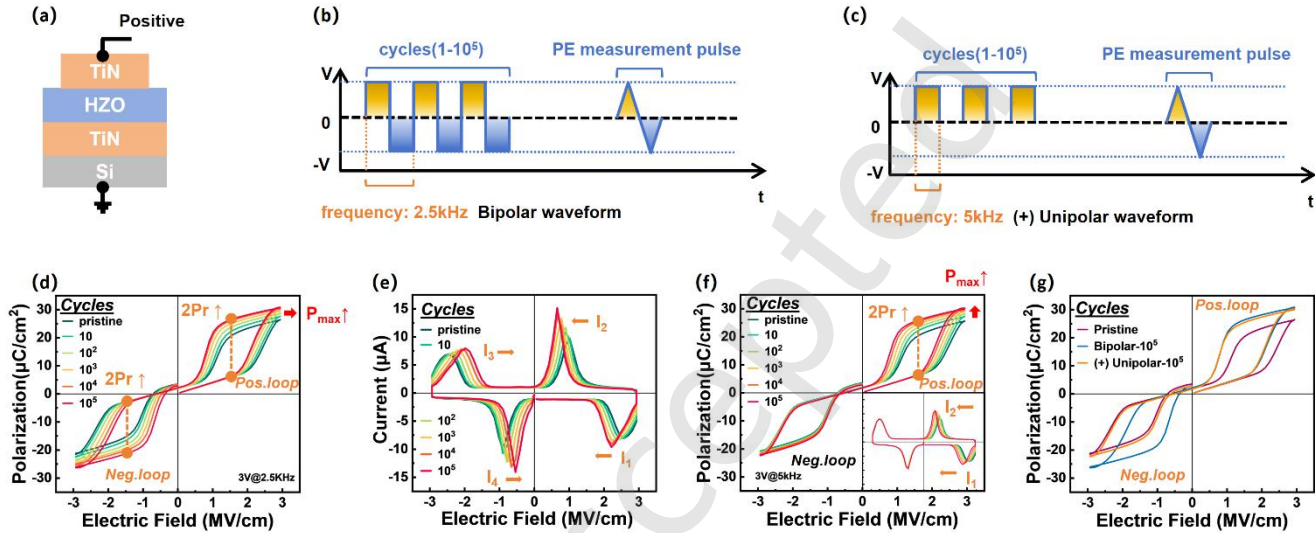


Fig.2. (a) Schematic illustration of the electrical bias configuration applied to the device. Schematic illustrations of the wake-up waveform and the P-E loop measurement waveform during (b) Bipolar wake up and (c) (+) Unipolar wake up. Evolution of the (d) P-E hysteresis loops and (e) I-E characteristics during bipolar wake-up cycling at 3V and 2.5kHz frequency. (f) Evolution of the P-E hysteresis loops during (+) unipolar wake-up, with the corresponding I-E characteristics shown in the inset. (g) Comparison of the P-E hysteresis loops in different device states: pristine state (red), after 10^5 bipolar wake-up cycles (blue), and after 10^5 (+) unipolar wake-up cycles (yellow).

Fig. 2(f) shows the P-E hysteresis loops of the device after (+) unipolar wake-up, only the positive P-E branch exhibits a pronounced wake-up response, whereas the negative branch remains essentially unchanged from its pristine state. Consistently, the inset I-E curves show that only the positive polarization-current peaks (I_1 and I_2) become enhanced and shift in position, while the negative current peaks remain nearly unaffected, this indicates that the positive E_{eff} within the device is enhanced after positive field cycling, whereas the negative E_{eff} remains nearly unchanged compared with the pristine state. A mirrored selective wake-up behavior was also observed under negative unipolar cycling (Fig. S2 in the ESM), only the negative P-E branch exhibits a pronounced wake-up response, whereas the positive branch remains essentially unchanged from its pristine state. Fig. 2(g) further compares the P-E loops obtained under different wake-up states. The positive branch after (+) unipolar wake-up (yellow lines), closely overlaps with the positive branch after bipolar wake-up (blue lines). By contrast, the negative branch of the (+) unipolar wake-up device (yellow lines) remains nearly identical to that of the pristine device (red lines), the slight difference between the two cases may originate from the

influence of repeated P-E readout operations on the BE, resulting in minor variations in the hysteresis loops. These results indicate that wake-up in AFE capacitors can proceed relatively independently along the two polarization directions associated with the TE and BE interfaces. Accordingly, the one-sided wake-up process provides an effective strategy for constructing coexisting “woken” and “non-woken-up” states within the same device, thereby offering an experimental platform for probing the microscopic mechanism underlying AFE wake-up behavior.

3.2 Field-Cycling-Induced V_o^{2+} Migration and Redistribution in AFE HZO Capacitors

As indicated by the statistical $|P_{max}|$ results under different voltages in Fig. 1(f), the presence of an E_{int} in the device may influence the wake-up behavior of AFE capacitors, which closely associated with defect-related behavior [30]. Oxygen vacancies (V_o) are one of the most prevalent defect types in HfO_2 -based devices and can be ionized under electric-field cycling, giving rise to V_o^{2+} . To further clarify the evolution of V_o^{2+} during electric-field cycling, we systematically analyzed the spatial distribution of oxygen and tracked its migration behavior. Fig. 3(a) shows the cross-sectional TEM image and corresponding EDS maps

of various elements (N, O, Ti, Zr, and Hf) for the TiN/AFE-HZO (10.71nm)/TiN capacitor, demonstrating a uniform dielectric thickness and clear interfaces of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2/\text{TiN}$. In addition, the elemental profiles along the cross-section of the capacitor are drawn in Fig. 3(b) with a scanning depth of approximately 40nm. EDS analysis shows that the O-signal intensity near the electrode/HZO interfaces is markedly lower than that in the HZO interior. During the fabrication of MFM capacitors, redox reactions between the HZO layer and TiN electrodes can readily occur, leading to the formation of an interfacial oxide layer, as illustrated in Fig. 3(c). To further verify the existence of the interfacial layer, EELS analysis was first performed at different depths of the pristine device, as shown in Fig. 3(d). By extracting the Ti and O elemental signals from different regions, first, the O-signal intensity near the electrode interfaces is significantly reduced, which is consistent with the EDS analysis results. This further confirms the oxygen-deficient environment at the

electrode/HZO interfaces, where a higher concentration of $\text{V}_0/\text{V}_0^{2+}$ -related defects is more likely to form. Therefore, in the pristine state, $\text{V}_0/\text{V}_0^{2+}$ -related defects are nonuniformly distributed within the film, with a higher concentration near the electrode/HZO interfaces than in the interior of the HZO film. Furthermore, distinct EELS spectral features are observed in different regions, indicating different local chemical environments and electronic structures. Only a pronounced Ti signal was observed in the top and bottom TiN electrode regions, whereas both Ti- $\text{L}_{2,3}$ and O-K signals were simultaneously detected at the TiN/HZO interfaces, indicating the formation of an interfacial oxide layer. In contrast, only the O signal was detected in the interior region of the HZO film, furthermore, the O-K edge in this region exhibits a more pronounced peak feature with a sharper edge, demonstrating the distinct chemical environments between the electrode interfaces and the HZO bulk region.

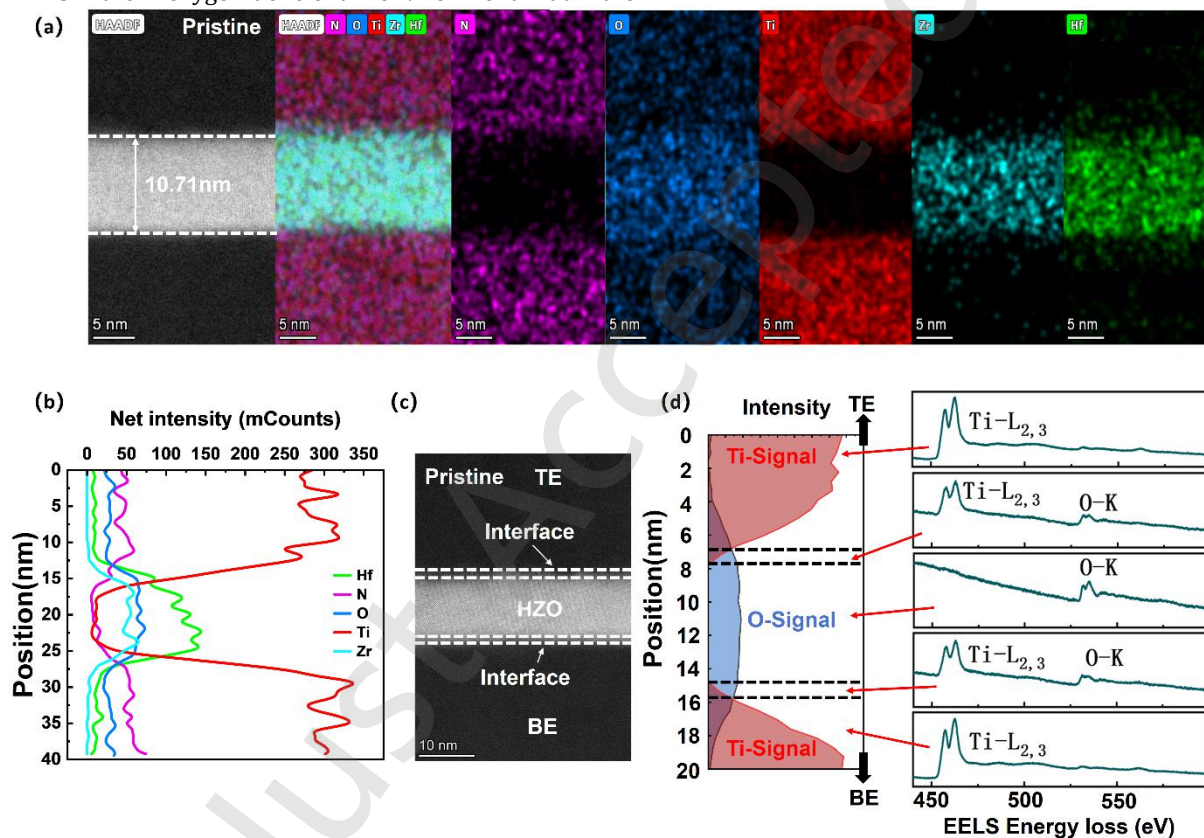


Fig. 3 (a) EDS elemental maps of N, O, Ti, Zr, and Hf in the pristine AFE HZO film. (b) The EDS elemental mapping intensity distribution over a 40 nm depth range (c) TEM image of the AFE HZO film in the pristine state (d) The averaged Ti and O signal intensities were extracted from the depth-dependent EELS data of the film in the pristine state, and different regions were distinguished based on their EELS spectral features.

To further clarify its specific migration and redistribution behavior, we statistically analyzed the A/B ratios of the EELS O-K edge extracted from different regions of the HZO film. Electron energy-loss near-edge structures (ELNES) of O-K edges provide useful information on the electronic structures of the excited atoms in the presence of $\text{V}_0/\text{V}_0^{2+}$. Two peaks with intensities A and B can be observed at each position from the hybridization of O 2p orbitals with Hf (or Zr) d_{eg} orbitals [39-40]. The spectral feature of the EELS O-K edge is sensitive to the $\text{V}_0/\text{V}_0^{2+}$ concentration, because the presence of $\text{V}_0/\text{V}_0^{2+}$ can significantly suppress the intensity of peak A [39, 41]. Therefore, within the same

local region, an increase in the O-K-edge A/B ratio may indicate a reduction trend in the local $\text{V}_0/\text{V}_0^{2+}$ concentration. As shown in Fig. 3(d), due to variations in the local chemical environments among different regions, the A/B ratio of the O-K edge extracted from EELS data can only be used to evaluate the relative variation trend of $\text{V}_0/\text{V}_0^{2+}$ concentration within the same local region of the film, rather than to directly quantify or compare the absolute $\text{V}_0/\text{V}_0^{2+}$ concentration among regions with different chemical environments. In addition, previous studies have revealed a pronounced difference in the migration barriers of V_0 and V_0^{2+} under an electric field. V_0 exhibits a relatively high

migration barrier and is therefore largely immobile, whereas the migration barrier of V_o^{2+} is below 1eV, making it considerably more susceptible to field-driven migration. Therefore, we attribute the variations in the V_o/V_o^{2+} distribution revealed by the EELS measurements primarily to the field-driven migration and redistribution of V_o^{2+} [31, 42]. Therefore, in this work, we compare the evolution of the EELS O-K-edge features within the same local region under three different states, which provides a local indicator of V_o^{2+} evolution during the wake-up process. As shown in Fig. 4(a), we analyzed three representative regions along the thickness direction of the film, namely the region near the TE interface, the interior of the HZO film, and the region near the BE interface. In each region, a rectangular sampling area containing 20 points along the lateral direction and 4 points along the vertical direction was defined for EELS analysis. The A/B ratio for each region was calculated by averaging all EELS spectra acquired from the corresponding region indicated in Fig. 4(a). Prior to spectral averaging, background subtraction was conducted using *DigitalMicrograph* to remove noise and contributions from other elements, while preserving the O K-edge signals in the energy range of 520–550 eV. The O-K-edge spectra and corresponding A/B ratios in the pristine state, after bipolar wake-up, and after (+) unipolar wake-up are shown in Figs. 4(b–d), respectively, while the statistical summary of the A/B ratios in different depth regions under the three states is presented in Fig. 4(e). In the region near the TE interface, the A/B ratios after both bipolar wake-up and (+) unipolar wake-up are significantly higher than that in the pristine state, indicating a gradual decrease trend in the local V_o^{2+} concentration during the wake-up process. Meanwhile, the A/B ratio in the central region of the HZO film shows a slight decrease after both wake-up processes, indicating a tendency toward increased V_o^{2+} concentration in the HZO center region. However, this variation is weaker compared with the pronounced change observed at the interface. Notably, after bipolar wake-up, the A/B ratio in the region near the BE interface also exhibits a pronounced increase, similar to that observed near the TE interface. In contrast, after (+) unipolar wake-up, no obvious change in the A/B ratio is observed near the BE interface, which is consistent with the fact that, during (+) unipolar wake-up, the wake-up process mainly occurs near the TE interface connected to the positive electrode. Considering that the O-K-edge signal in EELS measurements can be influenced by multiple factors, additional analyses were performed on two other grains from different locations to ensure the statistical reliability of the results, as shown in Fig. S3(a–d) and Fig. S4(a–d) in the ESM. Although the absolute A/B ratios vary among different grains due to local structural variations, the overall evolution trends of the A/B ratios before and after wake-up remain consistent. Fig. S5 in the ESM shows the leakage current characteristics of the capacitors under different states. It can be observed that, after both 10^5 bipolar wake-up cycles and 10^5 (+) unipolar wake-up cycles, the leakage

current level remains nearly unchanged compared with that of the pristine state. This suggests that the wake-up process does not induce the generation of additional defects in the HZO bulk region, and that the dynamic redistribution of V_o^{2+} during wake-up does not result in excessive defect accumulation leading to device breakdown. Therefore, the wake-up effect mainly originates from the field-cycling-induced localized migration and redistribution of pre-existing V_o^{2+} [16]. Furthermore, the breakdown characteristics of the devices are presented in Fig. S5(b) in the ESM, multiple breakdown measurements were performed on different devices, and the average breakdown electric field was determined to be 4.06 MV/cm. To further elucidate the V_o^{2+} localized redistribution behavior during the wake-up process, the grain was divided into ten positions along the vertical direction from the TE/HZO interface to the BE/HZO interface, as illustrated in Fig. S6(a) in the ESM. The EELS spectra collected from each position were averaged using the same processing method described above are shown in Fig. S6(b–c) in the ESM. Figure S6(d) compares the A/B ratios at different positions before and after (+) unipolar wake-up. It is observed that the A/B ratios at the TE interface regions exhibit a pronounced increase after (+) unipolar wake-up (positions 1–2), whereas the central HZO region shows a slight decrease in the A/B ratio with a much weaker variation (positions 4–6). Meanwhile, the regions near the BE interface exhibit nearly unchanged A/B ratios after (+) unipolar wake-up. Based on these detailed spatial analyses, we suggest that the field-cycling-induced redistribution of V_o^{2+} during the wake-up process exhibits a migration tendency from the electrode toward the HZO bulk region, while remaining primarily confined near the electrode/HZO interfaces. In addition to the vertical redistribution of V_o^{2+} , we further investigated the lateral distribution of V_o^{2+} in the middle region of the film during electrical cycling. As shown in Fig. 4(f), ten different lateral regions inside the HZO film were selected for EELS analysis under the three different states. Figs. 4(g–i) show the O-K-edge spectra and corresponding A/B ratios extracted from the ten regions in the pristine state, after bipolar wake-up, and after (+) unipolar wake-up, respectively. Fig. 4(j) summarizes the distribution of the extracted A/B ratios. The A/B ratios of the ten regions are scattered in the pristine state, whereas their dispersion is significantly reduced after wake-up, especially after bipolar wake-up. The corresponding analyses of the other two grains are presented in Fig. S3(e–h) and Fig. S4(e–h) in the ESM, respectively, and exhibit consistent variation trends. These results further indicate that the wake-up process promotes the redistribution of V_o^{2+} , leading to a more homogeneous distribution rather than localized accumulation. Such redistribution therefore does not result in a noticeable increase in leakage current or induce premature device breakdown. Meanwhile, the more homogeneous distribution of V_o^{2+} gives rise to slight variations in the EELS line-scan profiles within the central region of the HZO layer.

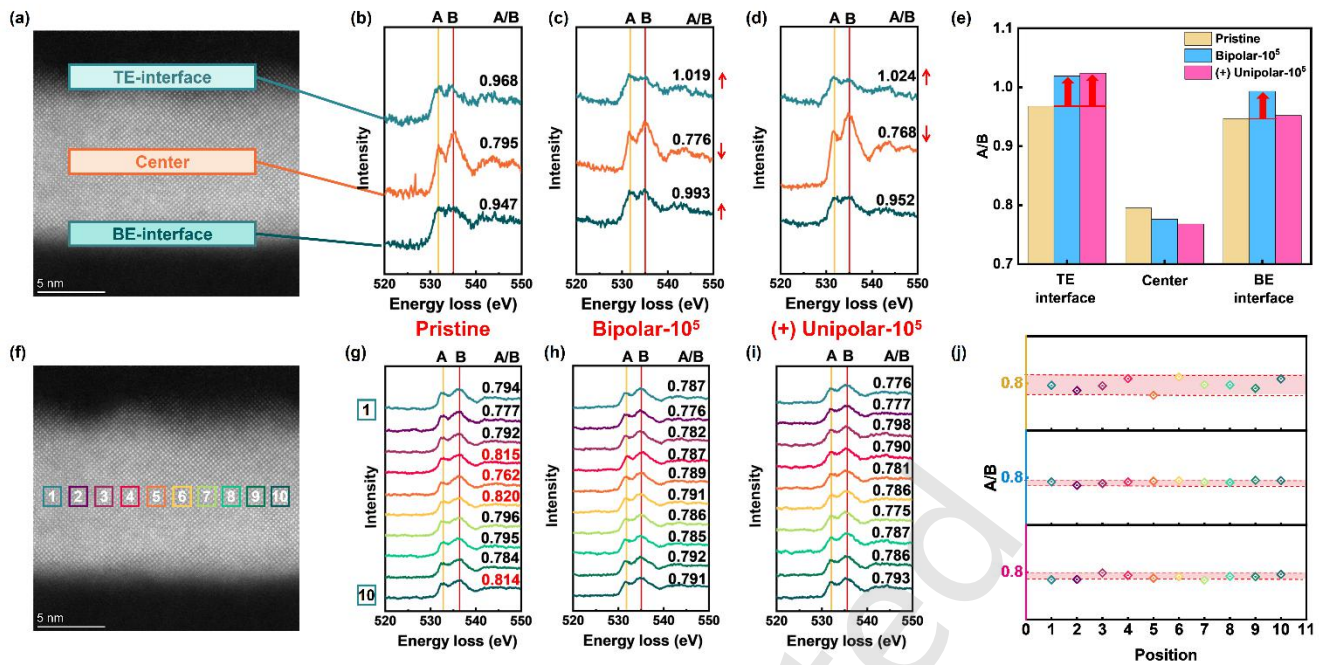


Fig.4 (a) Schematic illustration of the EELS line-scan region along the thickness direction of the HZO film. EELS O-K-edge spectra and the corresponding A/B ratios extracted from the regions near the TE interface, inside the HZO film, and near the BE interface under (b) the pristine state, (c) after bipolar wake-up, and (d) after (+) unipolar wake-up. (e) Statistical summary of the A/B ratios extracted from different depth regions of the HZO film under the three states. (f) Schematic illustration of the lateral EELS scan region in the HZO film. EELS O-K-edge spectra and the corresponding A/B ratios extracted from ten different lateral regions inside the HZO film under (g) the pristine state, (h) after bipolar wake-up, and (i) after (+) unipolar wake-up. (j) Schematic distribution of the A/B ratios from the ten lateral scan regions inside the HZO film under the three states.

3.3 V_o^{2+} Related Wake-Up Mechanism in AFE HZO Capacitors

Based on the above analysis, Fig. 5 schematically illustrates the evolution of the internal structural and defect-related behaviors of the film during the wake-up process of AFE capacitors. As shown in Fig. 5(a), compared with the pristine state, both $|P_{\max}|$ and $|2P_r|$ in the P-E hysteresis loops of the AFE capacitor increase simultaneously after wake-up. As illustrated in Fig. 5(a), the characteristic double hysteresis loop of the AFE HZO film originates from its antipolar ground state in the absence of an external electric field (E_{ext}). When a positive applied field exceeds the forward transition field ($+E_F$), the antipolar dipoles undergo a field-induced transition toward a polar state, and the $P_{\max}$ is reached at the maximum applied voltage. As the voltage subsequently decreases toward zero, the backward transition field ($+E_A$) drives the field-induced polar state back to the initial antipolar state. A similar transition process occurs under negative bias. Based on the (+) unipolar wake-up

measurements combined with EDS and EELS characterization, the wake-up mechanism is schematically illustrated in Figs. 5(b-d). In the pristine state, V_o are enriched near both the TE and BE interfaces (The black curve represents the V_o/V_o^{2+} concentration distribution in the pristine state). During P-E hysteresis loop measurement and field cycling, V_o accumulated near the electrode/HZO interfaces can be electrically activated under the local interfacial environment and applied electric field, thereby establishing the E_{int} distribution in the pristine state together with the interfacial induced electrons at the electrode interfaces, as illustrated in Fig. S7 in the ESM. During P-E measurements, for both positive and negative polarization responses, the E_{ext} must overcome the local E_{int} near the two electrode interfaces. Therefore, the polarization transition in the device is governed by the E_{eff} determined by the combined effects of the E_{ext} and the local E_{int} . Accordingly, the E_F of the pristine capacitor is denoted as V_1 and the $P_{\max}$ is $P_{\max 1}$.

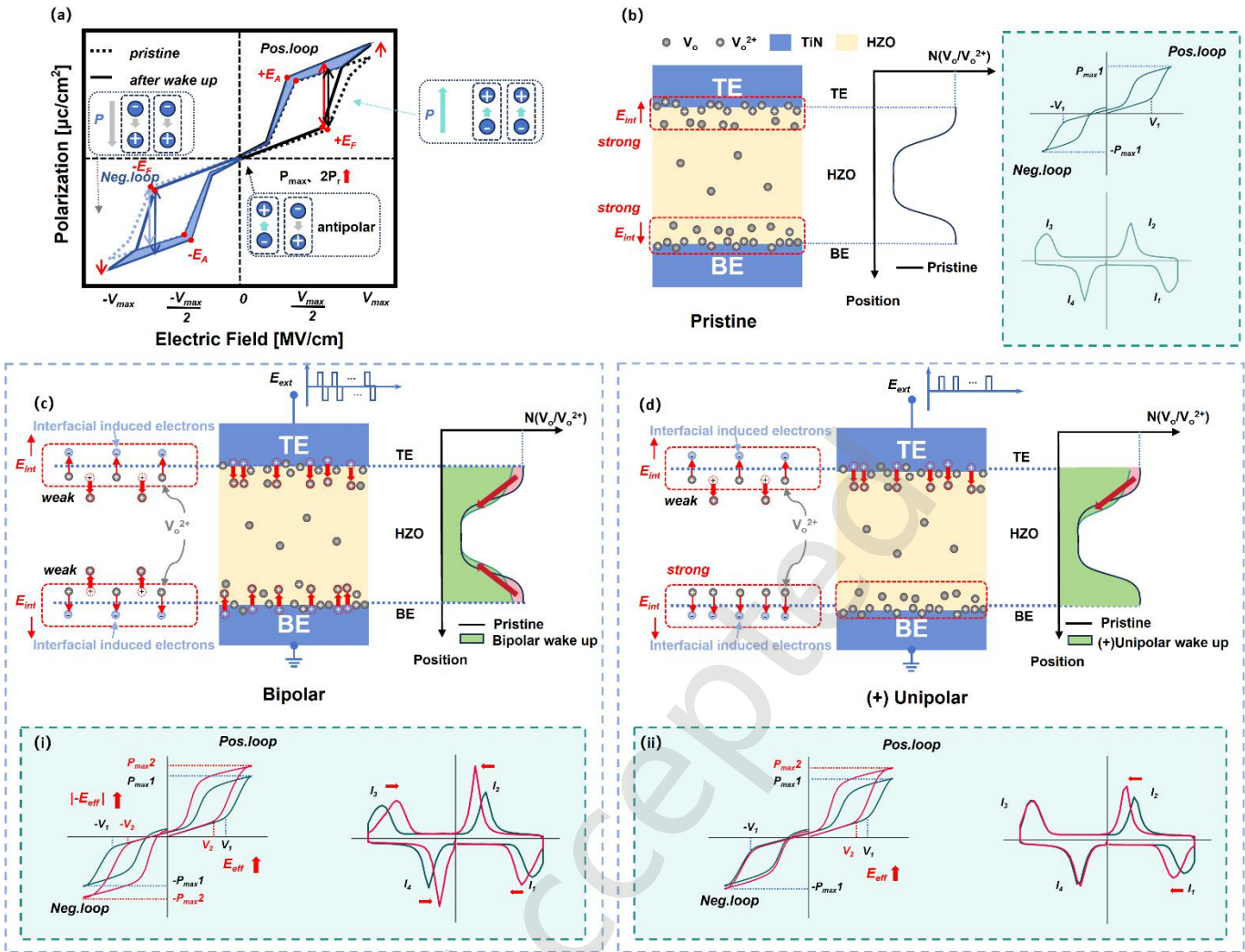


Fig. 5 (a) Schematic illustration of the internal evolution of the AFE film under different wake-up processes. (b) V_o/V_o^{2+} distribution in the pristine AFE-HZO device and the corresponding P-E and I-E characteristics. (c) V_o/V_o^{2+} distribution in the AFE-HZO device after bipolar wake-up, together with the corresponding P-E and I-E evolution shown in panel (i). (d) V_o/V_o^{2+} distribution in the AFE-HZO device after (+) unipolar wake-up, together with the corresponding P-E and I-E evolution shown in panel (ii).

During electric-field cycling, V_o^{2+} at both electrode interfaces exhibit a redistribution tendency from the electrodes toward the HZO bulk region. However, as evidenced by the nearly unchanged leakage current in Fig. S5(a) and the limited variation observed in the HZO bulk region from the EELS analysis, the wake-up-induced V_o^{2+} redistribution does not result in defect accumulation within the HZO layer, preventing the formation of leakage paths and subsequent breakdown. Therefore, this redistribution remains primarily confined near the electrode interfaces, as indicated by the red arrows in Fig. 5(c). Consequently, the redistributed V_o^{2+} contribute less significantly to the local E_{int} . As a result, the local E_{int} and polarization-suppression effects originally induced by defect accumulation near the two electrode interfaces are substantially reduced. Under the same E_{ext} , the polarization transition during P-E measurement experiences a weaker influence from the local E_{int} , leading to an enhanced E_{eff} inside the capacitor, enabling the field-induced polarization transition to occur at a lower voltage (V_2), where $V_2 < V_1$. Meanwhile, the maximum polarization values in both polarities increase from $|P_{max1}|$ to $|P_{max2}|$ during the wake-up process. Correspondingly, the four switching-current peaks in the I-V characteristics shift noticeably toward 0V, indicating that the polarization transition can be activated at a lower applied voltage as

shown in Fig. 5(i).

However, as illustrated in Fig. 5(d) and Fig. S7, after (+) unipolar wake-up, a fraction of V_o^{2+} near the TE interface undergoes localized redistribution. Their contribution to the local E_{int} at the TE side is significantly reduced, thereby alleviating the suppression of the positive polarization response. In contrast, the V_o^{2+} near the BE/HZO interface remain mainly accumulated at the interface, without obvious field-induced migration or redistribution. Therefore, the corresponding local E_{int} remain close to those in the pristine state, and the suppression of the negative polarization response is largely preserved. Based on the above analysis, as shown in Fig. 5(ii), the E_{eff} in the positive polarization switching direction is enhanced, while the E_{eff} in the negative direction remains nearly unchanged compared with the pristine state, as a result, during the positive-voltage branch of the P-E measurement, the polarization transition can occur at the reduced transition voltage $V_2 < V_1$. Consequently, only the positive branch is activated, giving rise to the observed one-sided wake-up behavior, the positive P_{max} increases from $+P_{max1}$ to $+P_{max2}$, whereas the negative P_{max} remains nearly unchanged. Consistently, the positive switching-current peaks in the I-V characteristics shift toward 0V, whereas the negative-side peaks remain nearly identical to those in the pristine state.

In conclusion, the wake-up process of AFE HZO capacitors under electric-field cycling is primarily governed by the field-driven directional redistribution of V_o^{2+} near the electrode interfaces. This redistribution remains largely confined to the interfacial regions, which effectively mitigates the E_{int} present in the pristine state.

3.4 Application-Specific Regulation of Wake-Up Effects in AFE HZO Capacitors

According to the above investigation of the wake-up mechanism, V_o^{2+} accumulated near the electrode interfaces undergoes directional migration and redistribution during electric-field cycling, leading to a more uniform distribution within the HZO film. This process effectively weakens the defect-induced E_{int} in the HZO film, thereby allowing more regions to participate in the polarization response. This mechanism is consistent with the electrical results observed in the pristine state, where a large pulse width and a relatively high voltage amplitude (2.5kHz and 3.5V) produce a larger memory window. Meanwhile, as shown in Figs. 1(f-g), different wake-up degrees can affect the performance of AFE capacitors in different application scenarios. The memory window and η are critical figures of merit for these two functionalities, respectively. Therefore, application-specific wake-up waveforms can be designed according to specific application requirements to enable efficient regulation of AFE capacitors for memory and energy-storage applications. To this end, we modulated the voltage-amplitude relationship between the cycling waveform and the P-E readout waveform to achieve deliberate control over the wake-up response. As shown in Fig. 6(a), the initial investigation of wake-up behavior employed a testing scheme in which the bipolar rectangular cycling waveform and the P-E readout waveform shared the same voltage amplitude, denoted as V_1 . Building on this configuration, we introduced a higher cycling voltage V_2 to establish a “high-voltage wake-up–low-voltage readout” strategy. According

to the results in Fig. 1(f) and Fig. S1(h), a larger cycling voltage favors the generation of a larger effective memory window, whereas a lower readout voltage provides higher sensitivity to wake-up-induced loop opening. Accordingly, under a fixed low frequency of 2.5 kHz, the P-E readout voltage was set to $V_1=2.5V$, while the cycling voltage was increased to $V_2=3V$, and compared with the case using 2.5 V for both cycling and readout. As shown in Fig. 6(b), relative to the pristine state (red curve), the P-E loop after 3V cycling wake-up (yellow lines) exhibits a substantially enlarged memory window, with a much greater enhancement than that obtained under the “2.5V cycling–2.5V readout” condition (blue lines). The complete evolution of the P-E hysteresis loops during 3V field cycling with a subsequent 2.5V readout is presented in Fig. S1(b) in the ESM. As shown in Fig. 6(c), the device performances after two different wake-up conditions were statistically compared. After wake-up at 3V, the $|P_{max}|$ value was enhanced by 39% compared with that obtained after 2.5V wake-up, while $|2P_r|$ value increased by 70%. To evaluate whether the higher wake-up voltage would degrade device endurance, endurance tests were performed under field cycling at 2.5V at 2.5kHz (purple curve) and 3V at 2.5kHz (blue curve), as shown in Fig. S8(a) in the ESM. Both conditions achieved an endurance of 10^7 cycles. Furthermore, Fig. S8(b) compares the charging and discharging behaviors of the pristine device and devices subjected to different wake-up voltages. The device after 3V wake-up exhibits a significantly enhanced current response. These results demonstrate that applying a higher voltage during the cycling stage while maintaining a lower readout amplitude provides an effective electrical strategy to enhance the wake-up response and significantly enlarge the storage window of AFE capacitors without sacrificing device endurance. This approach offers a practical design methodology for optimizing AFE-based nonvolatile memory (NVM) applications.

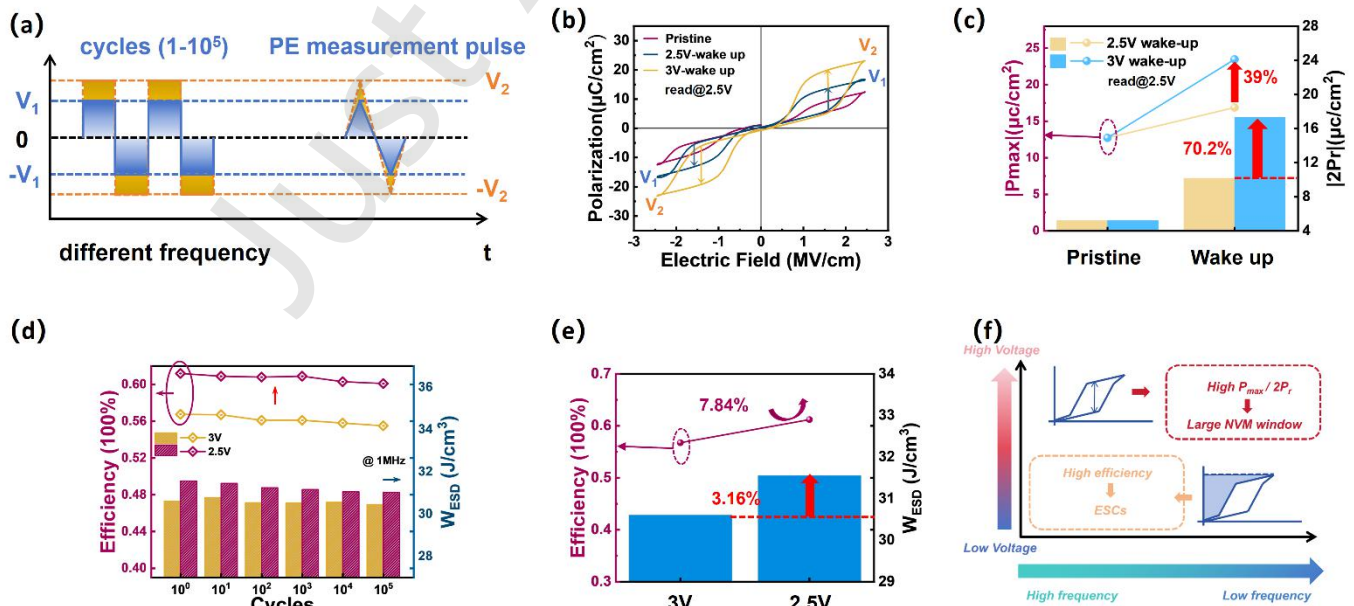


Fig. 6 (a) Schematic illustrations of the bipolar wake-up waveform and the P-E loop measurement waveform. (b) P-E hysteresis loops of the AFE capacitor in the pristine state (red), after 10^5 bipolar wake-up cycles at 2.5V (blue) and after 10^5 bipolar wake-up cycles at 3V (yellow), measured at a fixed P-E readout voltage of 2.5V. (c) Comparison of the enhanced $|P_{max}|$ and $|2P_r|$ values of AFE HZO capacitors after wake-up under different cycling conditions. (d) Evolution of the η (left axis) and W_{ESD} (right axis) of the AFE device after bipolar cycling under 2.5V–1MHz (red) and 3V–1MHz (yellow), with the P-E readout

voltage fixed at 3V. (e) Comparison of the enhanced η (left axis) and W_{ESD} (right axis) of AFE HZO capacitors after wake-up under different voltage conditions. (f) Schematic illustration of the applicable application scenarios for AFE capacitors under different wake-up conditions.

Beyond memory applications, the influence of wake-up on the energy-storage performance of AFE capacitors is equally important. Further guided by the trend shown in Fig. 1(g), at a frequency of 1MHz, we compare the η and W_{ESD} of the capacitors after wake-up cycling at 3V and 2.5V as shown in Fig. 6(d). The complete evolution of the P-E hysteresis loops measured under 2.5V at 1MHz field cycling is presented in Fig. S1(d), and the corresponding endurance performance is shown in Fig. S8(a) in the ESM (yellow curve). As shown by the red curve and corresponding shaded area, compared with the 3V wake-up condition, reducing the wake-up voltage significantly improves the η to above 60% and maintains an almost constant η during cycling. The W_{ESD} is likewise enhanced and remains stable. As shown in Fig. 6(e), the device subjected to 2.5V field cycling exhibits a 7.84% improvement in η and a 3.16% increase in W_{ESD} compared with the device cycled at 3V. These results suggest that a strong wake-up effect is not required for ESCs applications. Instead, low-voltage cycling enables efficient and stable energy storage while avoiding excessive wake-up-induced degradation. Collectively, these results demonstrate that rationally engineering the relationship between cycling and readout voltages—through targeted switching between a lower voltage V_1 and a higher voltage V_2 —enables application-adaptive regulation of AFE capacitor performance. This strategy provides an effective means to enhance the memory window for NVM applications while preserving high energy-storage efficiency and suppressing cycling-induced degradation for capacitor applications. In summary, as shown in Fig. 6(f), different electrical excitation conditions induce distinct wake-up degrees and thereby influence the application-oriented performance of AFE capacitors. Under high-voltage and low-frequency cycling, the capacitors exhibit a pronounced wake-up response, leading to a substantial enlargement of the memory window represented by $2P_r$, which is highly beneficial for NVM applications. In contrast, low-voltage and high-frequency cycling can suppress significant wake-up of the device, thereby mitigating loop expansion and energy dissipation, which helps preserve a high η and W_{ESD} . These results demonstrate that rational control of cycling voltage and frequency provides an effective pathway for application-specific optimization of AFE capacitors toward both NVM and energy-storage technologies.

4. Conclusions

In conclusion, this study systematically evaluates the wake-up degree of AFE-HZO capacitors under electric-field cycling with different frequencies and voltage amplitudes, the results show that low-frequency cycling and a relatively large voltage amplitude are favorable for achieving higher $|P_{\text{max}}|$ and $|2P_r|$, thereby enabling a larger memory window. By designing a unique unipolar wake-up pulse, coexisting “woken” and “non-woken” regions were constructed within the same device, enabling a targeted investigation of the wake-up mechanism in AFE capacitors. Electrical measurements show that even in the pristine state, the

voltage amplitude significantly affects $|P_{\text{max}}|$ and $|2P_r|$, indicating that different applied voltages produce different effective electric fields within the capacitor. Meanwhile, the gradual enhancement of the effective electric field during field-cycling-induced wake-up further indicates that an additional internal bias field may exist within the capacitor and evolves during the wake-up process. Combined EDS and EELS analyses were employed to systematically track the evolution of V_o^{2+} inside the AFE film during electric-field-cycling-induced wake-up. As a result, in the pristine state, a large amount of V_o/V_o^{2+} accumulated near the two electrode/HZO interfaces can generate local internal bias fields, which suppress the positive and negative polarization responses of the AFE device, respectively. During electric-field cycling, V_o^{2+} undergo directional redistribution from the electrode interfaces toward the HZO bulk region. However, this redistribution remains primarily confined near the electrode interfaces, effectively reducing the local internal bias field near the interfaces and alleviating its suppression of the polarization response. Therefore, under the same externally applied electric field, the effective electric field acting inside the capacitor is increased, thereby facilitating the polarization transition and wake-up behavior. Therefore, the wake-up effect in AFE capacitors is primarily governed by the dynamic migration and redistribution of V_o^{2+} under electric-field cycling. In addition, by investigating the impact of wake-up on device performance, we find that the wake-up process gradually enlarges the memory window for NVM applications, but significantly reduces the energy-storage density and energy-storage efficiency for capacitor applications. Based on this mechanistic understanding, application-specific electric-field cycling waveforms were strategically designed to achieve either an enlarged memory window or stable and efficient energy-storage performance.

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

X.Y. Wang: Conceptualization, methodology, investigation, data curation, formal analysis, writing — original draft. Z.Q. He: Methodology, investigation, data curation, validation, writing — original draft. Y. Yang: Methodology, validation, investigation. G.L. Li: Investigation, formal analysis. X.X. Liu: Investigation, data curation. S.B. Wang: Investigation. X.L. Zhou: Validation, formal analysis. B.P. Wang: Methodology, resources. T.C. Gong: Resources, investigation. P.F. Jiang: Resources. W. Wei: Supervision, review & editing. X. Long: Supervision, methodology, review & editing. Y. Wang: Conceptualization, supervision, project administration, funding acquisition, review & editing. Q. Luo: Conceptualization, supervision, project administration, funding acquisition, review & editing. All authors have approved the final manuscript.

Use of AI statement

None

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Electronic Supplementary Material

Revealing wake-up mechanism in antiferroelectric $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ capacitors through spatially selective wake-up

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1. P-E loops and statistical variations of $|2P_r|$ under different wake-up conditions.

Figs. S1(g-h) summarize the evolution of $|2P_r|$ in AFE devices under different wake-up conditions. As shown in Fig. S1(g), when the cycling voltage is fixed at 3V, pulse excitations with different frequencies, including 1MHz, 50kHz, and 2.5kHz, induce distinct wake-up responses. Among them, the 2.5kHz condition produces the most pronounced increase in $|2P_r|$, indicating that a longer pulse duration is favorable for enhancing the wake-up effect in AFE devices. Fig. S1(h) further compares the wake-up degree under different cycling voltages. At a cycling voltage of 2.5V, $|2P_r|$ increases by approximately 140%, corresponding to the strongest wake-up response. As the cycling voltage further increases, the relative enhancement in $|2P_r|$ gradually decreases, revealing a clear voltage dependence of the wake-up behavior.

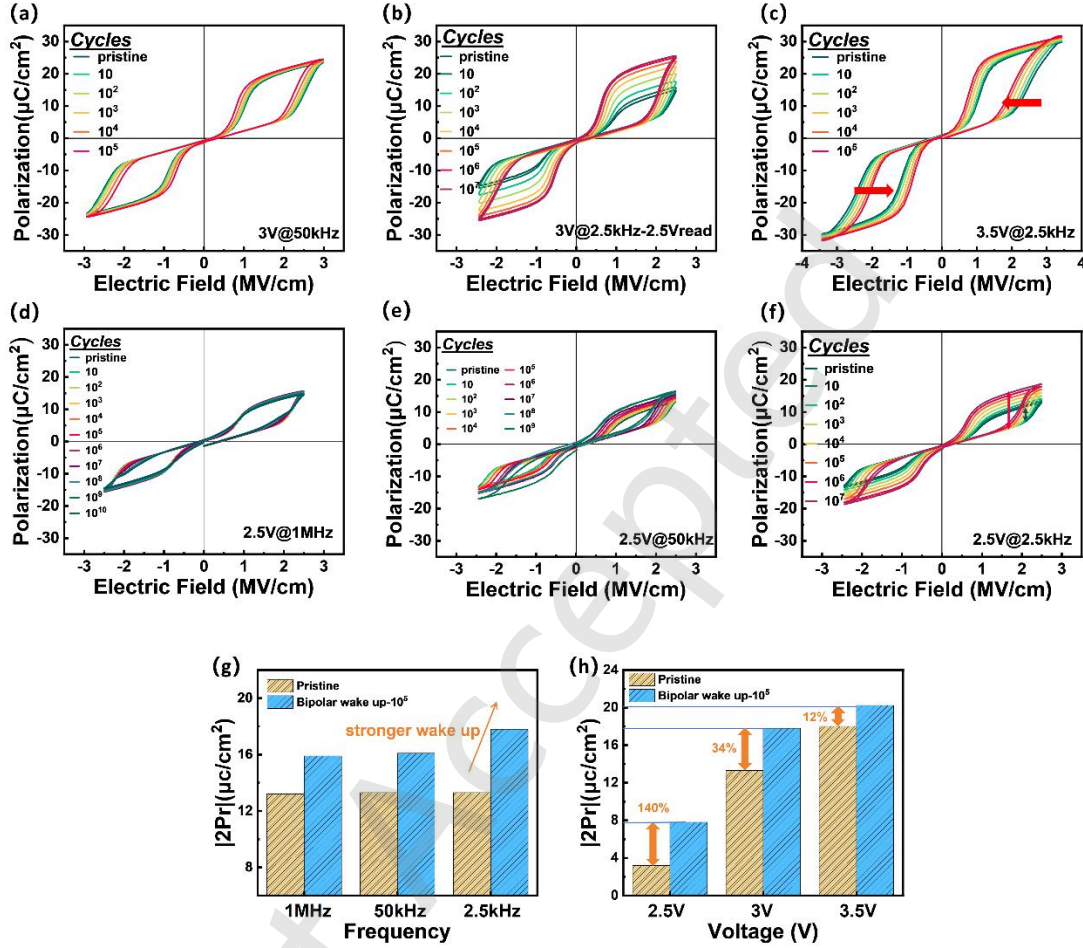


Fig. S1. (a) The P-E loops under cycling at 3V and 50kHz. (b) The P-E loops after wake-up cycling at 3V and 2.5kHz with a subsequent 2.5V P-E readout. (c) The P-E loops under cycling at 3.5V and 2.5kHz. (d) The P-E loops under cycling at 2.5V and 1MHz. (e) The P-E loops under cycling at 2.5V and 50kHz. (f) The P-E loops under cycling at 2.5V and 2.5kHz. Changes in $|2P_r|$ before and after wake-up in AFE devices under (g) different frequencies at a voltage amplitude of 3V and (h) different voltage amplitudes at a frequency of 2.5 kHz.

2. P-E hysteresis loops of the AFE device under negative unipolar wake-up.

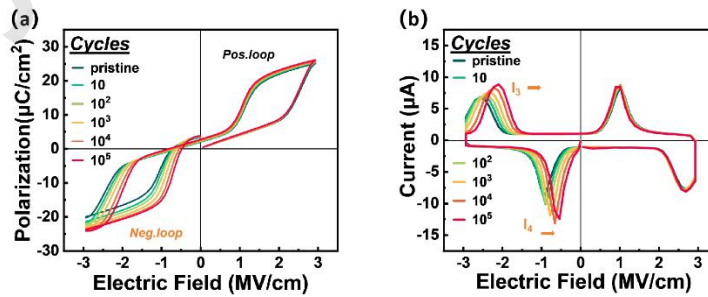


Fig. S2 (a) Evolution of the P-E hysteresis loops during negative unipolar wake-up. (b) Evolution of the I-E hysteresis loops during negative unipolar wake-up.

3. EELS analysis results from different grains

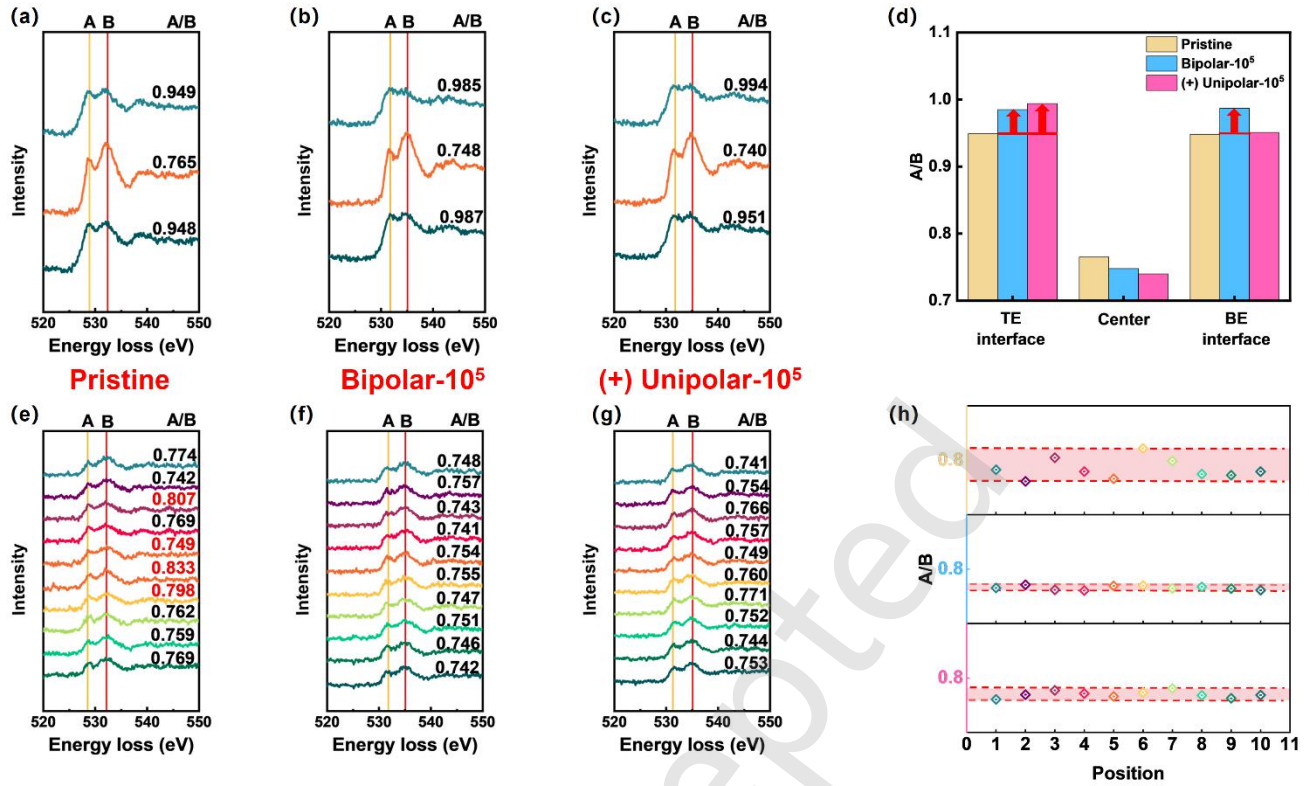


Fig.S3 EELS O-K-edge spectra and the corresponding A/B ratios extracted from the regions near the TE interface, inside the HZO film, and near the BE interface under (a) the pristine state, (b) after bipolar wake-up, and (c) after (+) unipolar wake-up. (d) Statistical summary of the A/B ratios extracted from different depth regions of the HZO film under the three states. EELS O-K-edge spectra and the corresponding A/B ratios extracted from ten different lateral regions inside the HZO film under (e) the pristine state, (f) after bipolar wake-up, and (g) after (+) unipolar wake-up. (h) Schematic distribution of the A/B ratios from the ten lateral scan regions inside the HZO film under the three states.

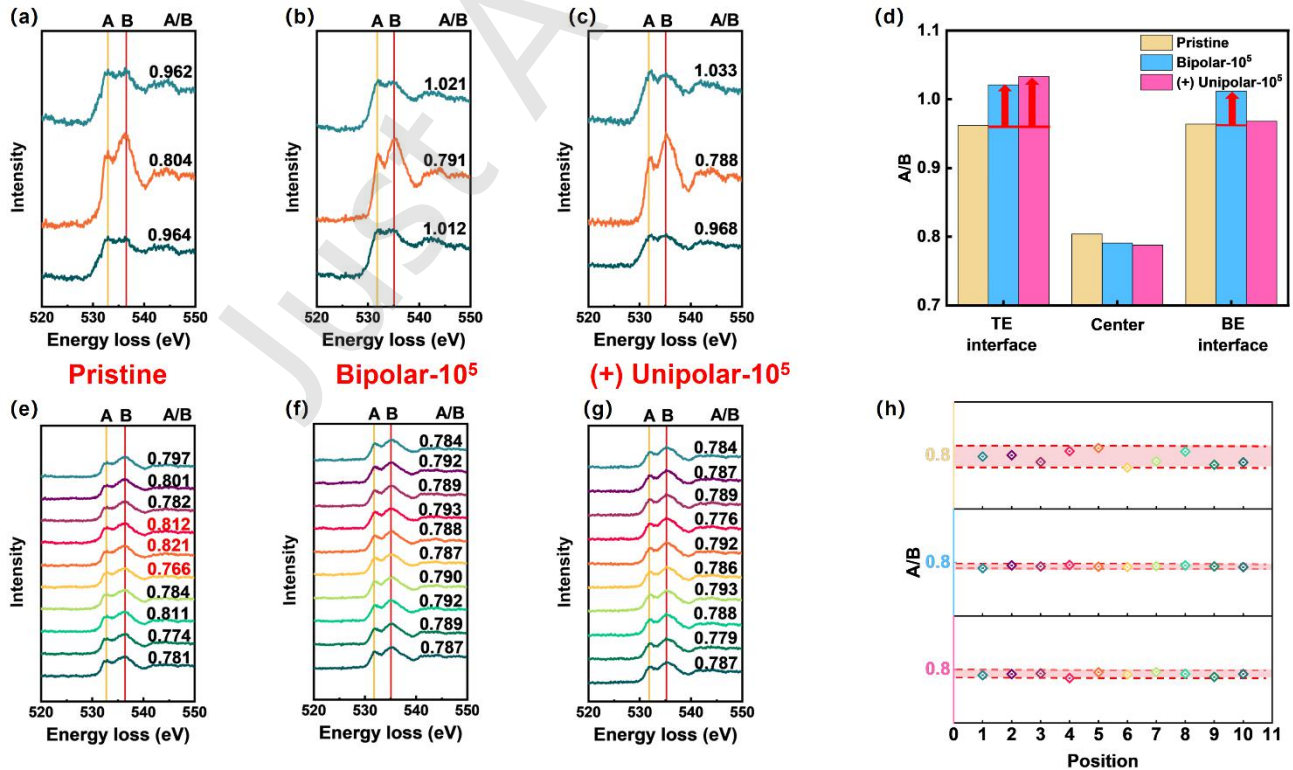


Fig.S4 EELS O-K-edge spectra and the corresponding A/B ratios extracted from the regions near the TE interface, inside the HZO film, and near the BE interface under (a) the pristine state, (b) after bipolar wake-up, and (c) after (+) unipolar wake-up. (d) Statistical summary of the A/B ratios extracted from different depth regions of the HZO film under the three states. EELS O-

K-edge spectra and the corresponding A/B ratios extracted from ten different lateral regions inside the HZO film under (e) the pristine state, (f) after bipolar wake-up, and (g) after (+) unipolar wake-up. (h) Schematic distribution of the A/B ratios from the ten lateral scan regions inside the HZO film under the three states.

4. Statistical analysis of leakage current and breakdown characteristics of AFE devices.

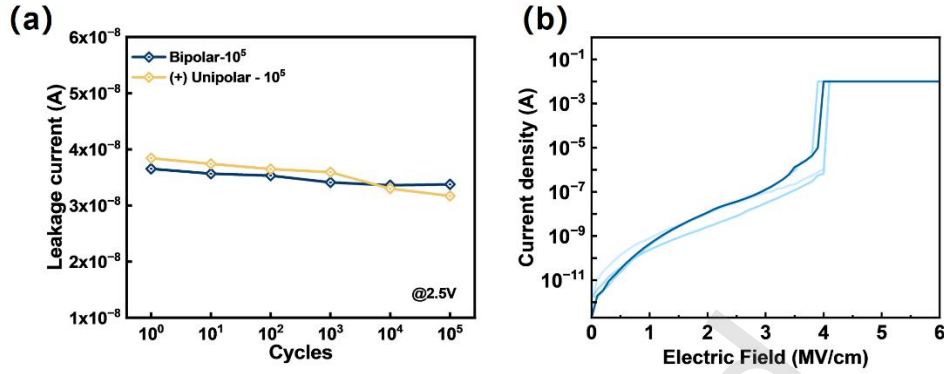


Fig. S5 (a) Leakage-Current Evolution of AFE Devices during Electric-Field Cycling. (b) Breakdown electric-field statistics of five AFE devices.

5. EELS analysis at ten different positions along the depth direction from the top electrode/HZO interface to the bottom electrode/HZO interface

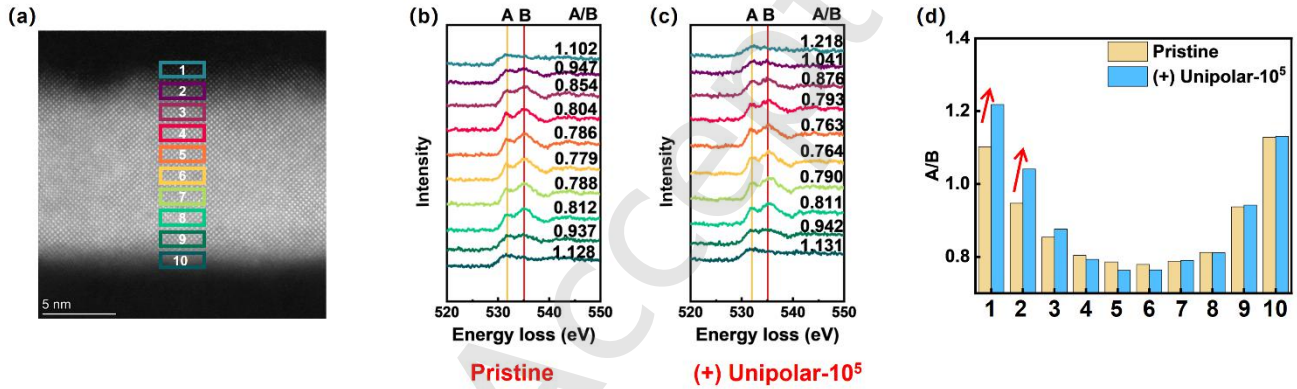


Fig.S6 (a) Schematic illustration of the 10 EELS line-scan regions along the thickness direction of the HZO film. EELS O-K-edge spectra and the corresponding A/B ratios extracted from 1 to 10 positions under (b) the pristine state, (c) after (+) unipolar wake-up. (d) Statistical summary of the A/B ratios extracted from 1 to 10 positions of the HZO film under the two states.

6. Schematic illustration of the formation of the interfacial internal bias field at the electrode interfaces and its evolution after positive unipolar wake-up.

Following positive unipolar wake-up, the Vo^{2+} accumulated near the top electrode/HZO interface undergo localized redistribution, together with charge injection, which reduces the interfacial defect-induced internal bias.

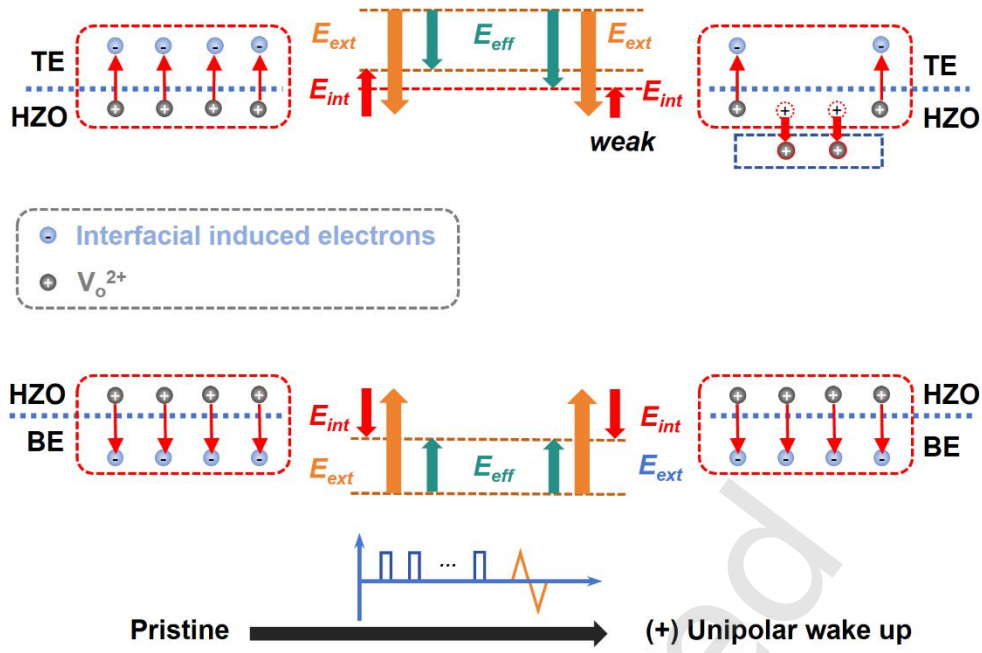


Fig. S7 Schematic illustration of the presence of the internal bias field and its evolution after positive unipolar wake-up.

7 Endurance performance and charge–discharge current transient of AFE devices under different testing conditions

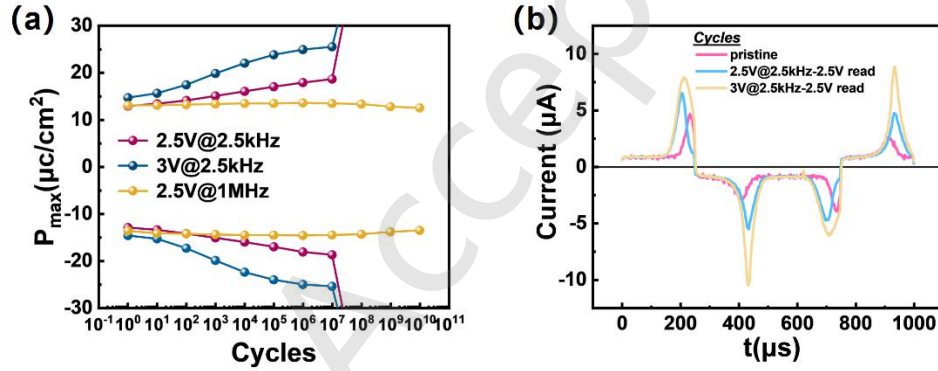


Fig. S8 (a) Endurance characteristics of AFE HZO capacitors during electric-field cycling under different conditions, including 2.5V at 2.5kHz (pink), 3V at 2.5kHz (blue), and 2.5V at 1MHz (yellow). (b) I–t characteristics of AFE HZO capacitors after different wake-up conditions: pristine state (pink), 2.5 V at 2.5 kHz wake-up with 2.5V P–E readout (blue), and 3 V at 2.5 kHz wake-up with 2.5V P–E readout (yellow).