SCIENCE CHINA
Information Sciences

• LETTER •

August 2026, Vol. 69, Iss. 8, 189403:1–189403:2
https://doi.org/10.1007/s11432-025-4697-y

Dynamic switching and oxygen ion transport in $(Hf+Zr)O_{2-x}$ ferroelectrics modulated by Al_2O_{3-x} interfaces

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Received 29 May 2025/Revised 27 August 2025/Accepted 21 November 2025/Published online 4 June 2026

Citation Feng Z, Liu H, Pan W W, et al. Dynamic switching and oxygen ion transport in $(Hf+Zr)O_{2-x}$ ferroelectrics modulated by Al_2O_{3-x} interfaces. Sci China Inf Sci, 2026, 69(8): 189403, https://doi.org/10.1007/s11432-025-4697-y

Hafnium oxide-based ferroelectrics have garnered broad interest for next-generation nanoscale devices owing to their compatibility with silicon electronics [1]. However, the dynamic switching mechanism of HfO_2-based ferroelectrics remains a subject of debate, primarily due to the complex roles played by oxygen vacancies within the material or at the interface. These vacancies not only help stabilize the ferroelectric phase but also migrate under electric fields, leading to reliability degradation such as wake-up, fatigue, and imprint [2]. Notably, oxygen vacancies/ions migration at interfaces is known to induce ferroelectric-like behavior in amorphous systems [3]. Although the migration of oxygen ion/vacancy has been incorporated into theoretical models for HfO_2-based ferroelectric devices [4], its dynamic participation mechanism remains poorly understood.

Herein, an ultrathin $Al_2^{18}O_{3-x}$ capping layer (CL) was employed to study the mechanisms of polarization switching in oxygen-deficient HfO_2-based ferroelectric capacitors and its effect on ferroelectric properties. P-V and frequency-dependent measurements were conducted. The crystalline phase and interface chemistry were investigated by grazing-incidence X-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS), respectively. The distribution of interface ^{18}O under different polarization states was characterized by time-of-flight secondary ion mass spectrometry (TOF-SIMS). A model of the switching mechanism in $CL/(Hf+Zr)O_{2-x}$ ferroelectrics has been proposed. Detailed deposition parameters and characterization conditions are provided in Supporting information.

Results and discussion. The GIXRD pattern of all samples (excluding the as-deposited sample) exhibits peaks at 28.2°, 30.4°, and 31.4° (2θ, Figure A1), corresponding to the ($\bar{1}$11) monoclinic phase (28.2°), a superposition of the (111) orthorhombic (o) and (101) tetragonal (t) phases (o+t), and the (111) monoclinic phase (31.4°), respectively. As shown in Figure 1(a), the GIXRD pattern of PMA (post-metallization annealing)-treated samples demonstrates a dominant o+t phase peak. Quantitative phase analysis reveals o+t phase fractions of (96.6 ± 0.1)% (no CL), (97.8 ± 0.1)% (3 cycles of Al_2O_{3-x} (H_2O: 50 ms)), and (98.8 ± 0.1)% (3 cycles of Al_2O_{3-x} (H_2O: 10 ms)), respectively. The insertion of the CL led to an increase in the concentration of the o+t phase and minimized the m-phase in the $(Hf+Zr)O_{2-x}$ film. For PDA (post-deposition annealing)-treated samples, the concentration of m-phase is higher than that of the corresponding PMA-treated sample. The reference sample without CL exhibits a high proportion of m-phase peaks, primarily attributed to the lack of strain during the annealing process. The o+t phase proportion increased significantly compared with the reference sample after the deposition of the CL, which is consistent with the trends observed from P-V measurements (Figure B1).

Figure 1(b) depicts the P-V hysteresis curves of capacitors at varying frequencies after the PMA/PDA treatment. The $2P_r$ value increases slightly as the test frequency increases for the reference sample. In contrast, the $2P_r$ value of capacitors with CL is notably higher at a frequency of 500 Hz compared to that observed at higher frequencies. This frequency response of the $2P_r$ value differs markedly from the reference sample and the previously reported $Hf_{0.5}Zr_{0.5}O_2$ results [5], suggesting that additional polarization mechanisms beyond ferroelectric dipoles may contribute to the observed behavior in this stack. For the PDA-treated samples, the $2P_r$ value of the sample with CL shows a slight decrease with frequency increases. Similar to the corresponding PMA-treatment sample, the sample with Al_2O_{3-x} CL exhibits a pronounced decrease in the $2P_r$ value as frequency increases. This indicates a

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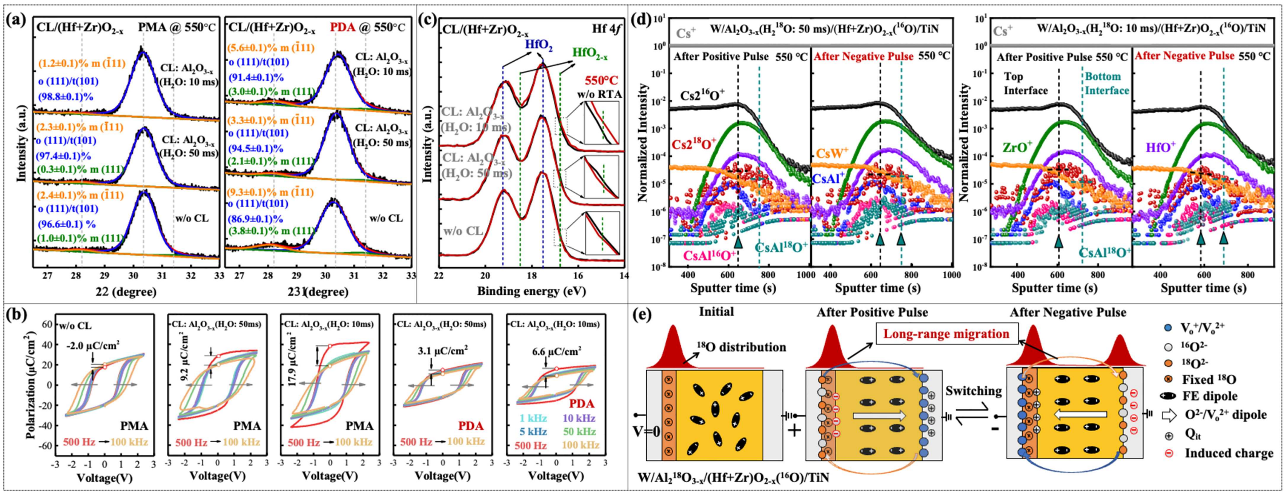

Figure 1 (Color online) (a) Phase deconvolution of the GIXRD spectra for W/CL/(Hf+Zr)O_{2-x}/TiN stacks (CL: w/o CL, Al_2O_{3-x} (H_2O: 50 ms), and Al_2O_{3-x} (H_2O: 10 ms)) after PMA and PDA treatment. (b) Measured the *P-V* curves of CL/(Hf+Zr)O_{2-x} capacitors after the PMA and PDA treatment at the different frequencies. (c) Hf 4*f* core level spectra for CL/(Hf+Zr)O_{2-x} stack before and after annealing at 550°C. Insert: enlarged portions of the Hf 4*f* XPS spectra at lower oxidation state. (d) TOF-SIMS depth profiles of oxygen isotopes ($Cs2^{16}O^+$, $Cs2^{18}O^+$), and metallic species (CsW^+, HfO^+, ZrO^+, $CsAl^+$, $CsAl^{16}O^+$, and $CsAl^{18}O^+$) in W/CL/(Hf+Zr)O_{2-x}/TiN capacitors after positive/negative pulse. (e) Schematic diagram of the (Hf+Zr)O_{2-x} polarization and interfacial ion migration model.

contribution from additional polarization mechanisms, likely involving oxygen vacancy/ion migration at the interface [3].

XPS analysis confirmed a significant oxygen deficiency at the surface of the (Hf+Zr)O_{2-x} films (Figure C2). As shown in Figure 1(c), the introduction of an Al_2O_{3-x} (H_2O: 10 ms) CL leads to a significant increase in HfO_{2-x} content after annealing. In contrast, for the samples without CL and Al_2O_{3-x} (H_2O: 50 ms) CL samples, the oxygen-deficient states (HfO_{2-x}) exhibit a slight reduction after annealing. Furthermore, the Al_2O_{3-x} (H_2O: 10 ms) capped sample developed substantially more intense suboxide features (HfO_{2-x}) than the Al_2O_{3-x} (H_2O: 50 ms) CL sample after annealing at 550°C (Figure C3). These results suggest that insertion of Al_2O_{3-x} thin films effectively modulates the oxygen vacancy concentration near the (Hf+Zr)O_{2-x} surface. Meanwhile, the combined strategy of employing a CL with PDA treatment also significantly improved the endurance performance and suppressed the wake-up effect of the devices (Figure B4).

Figure 1(d) illustrates the elemental distribution in capacitors after applying positive/negative pulse. After a positive pulse, $^{18}O^+$ accumulates predominantly at the CL/(Hf+Zr)O_{2-x} interface. Conversely, after a negative pulse, the $^{18}O^+$ concentration increases significantly at the (Hf+Zr)O_{2-x}/TiN interface compared to the top interface. Both additional post-bias characterization datasets show consistent results (Figures C4 and C5). This observation is further supported by the distribution of $CsAl^{18}O^+$ cluster ions, which exhibit accumulation at both interfaces under negative bias. These results demonstrate long-range migration of oxygen ions ($^{18}O^{2-}$) from the CL under an applied electric field.

Figure 1(e) illustrates a polarization switching model combining ferroelectric dipoles, charge trapping/detrapping, and interfacial oxygen ion/vacancy migration under low-frequency excitation. The movement of interfacial oxygen ion-vacancy pairs across the (Hf+Zr)O_{2-x} layer is primarily driven by the electric field, aligning the long-range dipoles formed by these movable ion-vacancy pairs with the polarization direction of the ferroelectric crystal dipoles. Additionally, charge trapping/detrapping at defect sites modulates the local electric field, further influencing the alignment dynamics of these dipoles. Thus, the $2P_r$ value is highest at low frequency. As the testing frequency increases, the migration process of O^{2-}/V_O^{2+} and charge trapping/detrapping process declines significantly, ultimately limiting their collective response to the field.

Conclusion. This work demonstrates that an ultrathin Al_2O_{3-x} CL effectively enhances the o+t phase content and electrical properties of (Hf+Zr)O_{2-x} capacitors by synergistically modulating interfacial oxygen vacancy concentration and interfacial stress. Notably, ^{18}O isotope tracing directly evidences the long-range migration of interfacial oxygen ions during field cycling, providing key experimental insight into the switching mechanism of HfO_2-based ferroelectrics. Based on this, a model for polarization dynamics was developed, which is applicable to oxygen-deficient HfO_2 ferroelectrics under low-frequency conditions. This study deepens the understanding of interface chemistry and switching dynamics, offering an effective strategy via interface engineering to address reliability issues in HfO_2-based ferroelectric devices.

Acknowledgements This work was supported by National Natural Science Foundation of China (Grant Nos. 22090010, 22090011), China Postdoctoral Science Foundation (Grant No. 2024M761518), China Postdoctoral Science Foundation—Tianjin Joint Support Program (Grant No. 2025T019TJ), and Postdoctoral Fellowship Program of China Postdoctoral Science Foundation (Grant No. GZC20250351).

Supporting information Appendixes A–C. The supporting information is available online at info.scichina.com and link.springer.com. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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