Supporting Information

Damage Mitigation as a Strategy to Achieve High Ferroelectricity and Reliability in Hafnia for Random-Access-Memory

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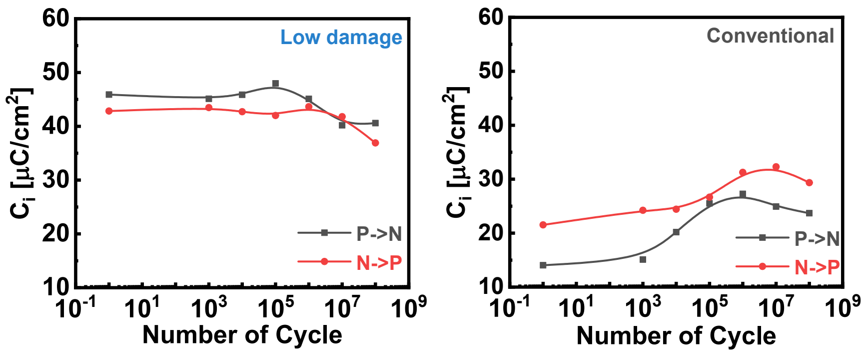
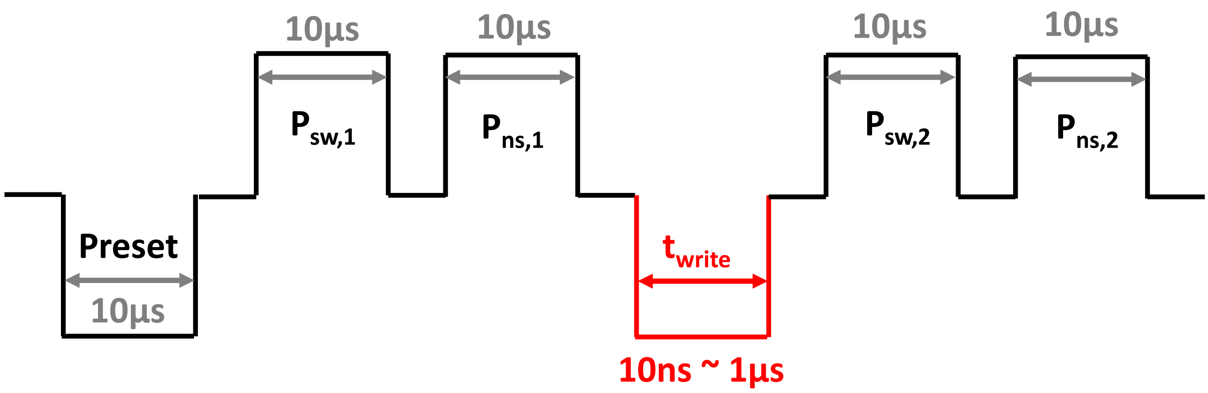
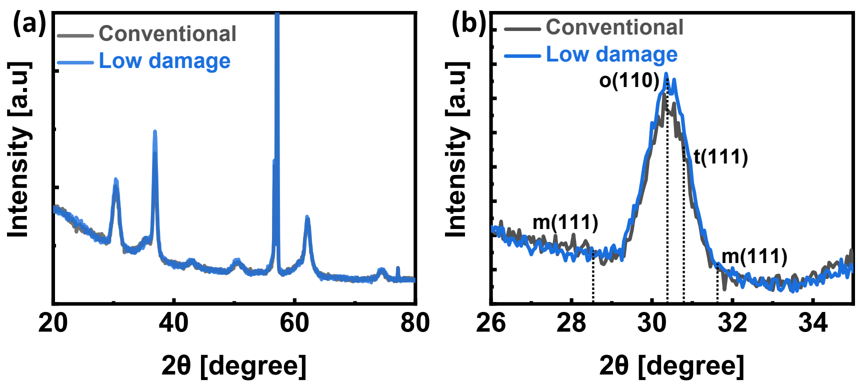


Supplementary Figure 1. Comparison of interfacial capacitance (C_i) values over wake-up cycles. The low-damage process shows stable C_i values, while the conventional process exhibits significant wake-up behavior and a subsequent decline in C_i values after 10^7 cycles, highlighting the impact of oxygen vacancy migration and defect generation within the interfacial layer.

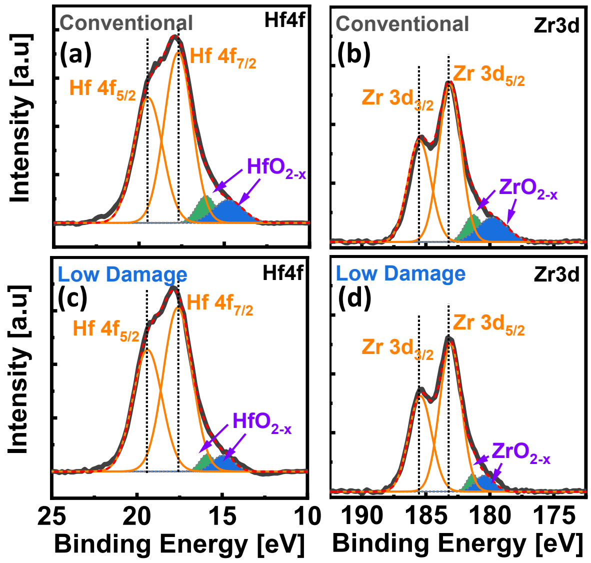


Supplementary Figure 2. Schematic diagrams of pulse profiles used to measure switching speed

A pre-set pulse with a magnitude of -1.75V and a width of 10 μs was applied to induce unidirectional switching of the ferroelectric polarization. Subsequently, pulses with a magnitude of 1.75V, termed P_{sw1} (switching) and P_{ns1} (non-switching), and the same pulse width of 10 μs were applied. This was followed by the application of write pulses at -1.75V across varying durations from 10 μs down to 1 μs. Finally, pulses P_{sw2} and P_{ns2}, each with a magnitude of 1.75V and a pulse width of 10 μs, were applied. In this pulse sequence, P_{sw1} and P_{sw2} include currents resulting from the switching of ferroelectric domains, which encompass both ferroelectric and non-ferroelectric components such as dielectric polarization and leakage currents. Conversely, P_{ns1} and P_{ns2} solely contain contributions from dielectric polarization and leakage currents. By subtracting the non-switching pulses (P_{ns}) from the switching pulses (P_{sw}), the pure ferroelectric component can be isolated. The relative ratio of the switching polarization ($P/2P_s$) was obtained using the formula: $(P_{sw2}–P_{ns2})/(P_{sw1}–P_{ns1})$.



Supplementary Figure 3. Grazing incidence X-ray diffraction (GIXRD) spectra with 2θ range of (a) 20º-80º and (b) 26º-35º of conventional process and low damage process $HfZrO_2$ thin film.



(e)

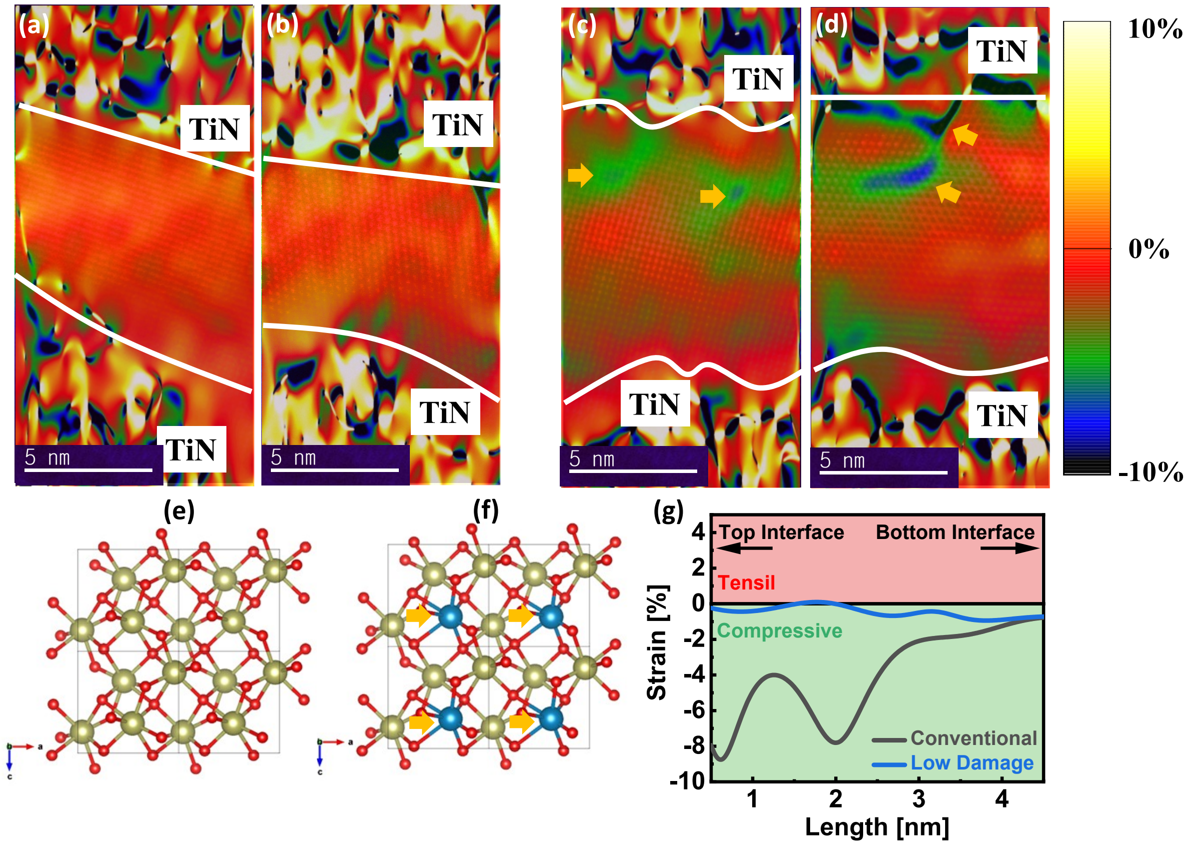
% of suboxide	Conventional	Low Damage
Zr5d	17.02%	8.51%
Hf4f	12.53%	6.74%

Supporting Fig. 4 XPS depths spectra of Zr 3d for MFM capacitor with **(a)** conventional process and **(b)** low damage process. XPS depths spectra of Hf 4f in for MFM capacitor with **(c)** conventional process and **(d)** low damage process. **(e)** Summary table for the relative ratio of sub-oxide in HfO_2 and ZrO_2

We analyzed the X-ray photoelectron spectroscopy (XPS) characteristics to discern the chemical property transitions between devices processed using conventional methods and those subjected to a low-damage process. **Supporting figures 4(a)-(b)** depict the Zr 3d spectra of $HfZrO_2$ (HZO) thin films in metal-ferroelectric-metal (MFM) capacitors fabricated via traditional and low-damage processes, respectively. The presence of ZrO_2 is indicated by the Zr 3d 3/2 peak at 182.7 eV and the Zr 3d 5/2 peak at 185.2 eV. Peaks located at 179.5 and 181.5 eV correspond to sub-stoichiometric ZrO_2-x, signifying oxygen deficiency within the film that leads to oxygen vacancy defects.

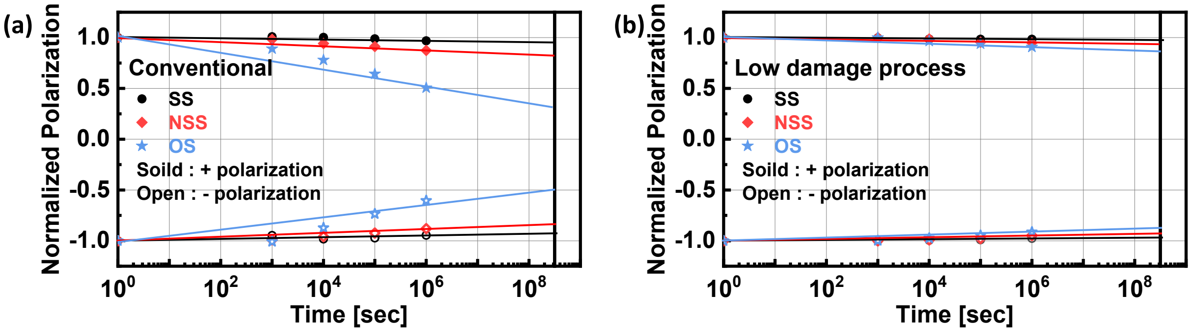
Similarly, the Hf 4f spectra of HZO thin films in MFM capacitors, shown in **Supporting figures 4 (c)-(d)**, are composed of peaks assigned to HfO_2 at 14.77 and 16.07 eV, and sub-stoichiometric HfO_{2-x} at 17.57 and 19.23 eV for devices processed by conventional and low-damage methods, respectively. We observed a substantial reduction in the quantity of sub-stoichiometric oxides in the Hf 4f and Zr 3d spectra for the devices processed with the low-damage method. (Figure 5(e)) This indicates that the low-damage metallization process decreases oxygen vacancies across the thin film. Notably, the reduction of oxygen vacancies was more pronounced in ZrO_2 than in HfO_2. This disparity is attributed to the higher formation energy of oxygen vacancies (V_O) in HfO_2 compared to ZrO_2, making HfO_2 more resistant to the formation of V_O.

The presence of oxygen vacancies, which possess a positive charge, has a direct implication on the pinning of polarization, effectively diminishing the residual polarization within the ferroelectric material. The reduction of oxygen vacancy-induced defects at the interface, achieved through the adoption of a low-damage process, not only enhances the residual polarization but also serves to reduce the leakage currents that are typically associated with such defects.



Supporting Fig. 5 Merged HADDF STEM images and GPA result for MFM capacitor with **(a)-(b)** low damage process and **(c)-(d)** conventional process. **(e)** crystal structure of standard t-phase HfO_2. **(f)** Schematic of distorted t-phase HfO_2 crystal structure. Dislocated atoms are highlighted in blue color **(g)** The strain distribution for MFM capacitor with low damage process and conventional process.

We used scanning transmission electron microscope (STEM) to observe defects in the film, such as strain, cracks, or non-uniform areas, at the microstructural level to verify the quality of the top interface between the metal and ferroelectric layer. **Supporting Figure 5 (a)-(d)** compares geometric phase analysis (GPA) results merged with high-angle annular dark-field STEK (HADDF-STEM) images for the MFM capacitor produced using two different processes: a low-damage process (**Supporting Figure 5 (a)-(b)**) and a conventional process (**Supporting Figure 5 (c)-(d)**). GPA analysis is a useful method for identifying strain and dislocation at the atomic level [S1-S3]. If a dislocation occurs, causing the atomic spacing to be longer than the reference atomic spacing, it indicates the presence of positive strain in the film, whereas if it is shorter, it indicates the presence of negative strain in the film. **Supporting Figure 5 (e)-(f)** shows schematics of the atomic structure of a crystal with and without dislocation. **Supporting Figure 5 (e)** shows the crystal structure of a standard t-phase HfO_2. This crystal structure has a symmetrical tetragonal shape, with atoms arranged in a regular pattern. **Supporting Figure 5 (f)** shows a schematic of a distorted t-phase HfO_2 crystal structure under compressive stress, in which some of the atoms have been dislocated from their regular positions. These dislocated atoms are highlighted in blue in the schematic. Dislocation acts as a defect in ferroelectric thin films, creating trap sites and increasing leakage current. The film produced using the low-damage process has less strain, while the film produced using the conventional process has an area of negative strain (compressive strain) at the top interface, as indicated by the blue color in **Supporting Figure 5(c)-(d)**. To show the strain distribution quantitatively, **Supporting Figure 5 (g)** presents the strain distribution for the MFM capacitor produced using the low-damage process and the conventional process. The results indicate that the low damage process leads to a more uniform strain distribution compared to the conventional process, which suggests that it may result in improved performance of the MFM capacitor. We have confirmed that one of the reasons for improved leakage current is that the low-damage metallization process effectively suppresses dislocation in the film.



Supplementary Figure 6. Long-term retention properties of the **(a)** conventional process and **(b)** low damage process MFM capacitor.

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