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Electronic Supporting Information

Improving the memory window of ferroelectric thin film transistor using atomic layer deposited HfN_x interfacial layer

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I. Supplementary figures

A. Experimental

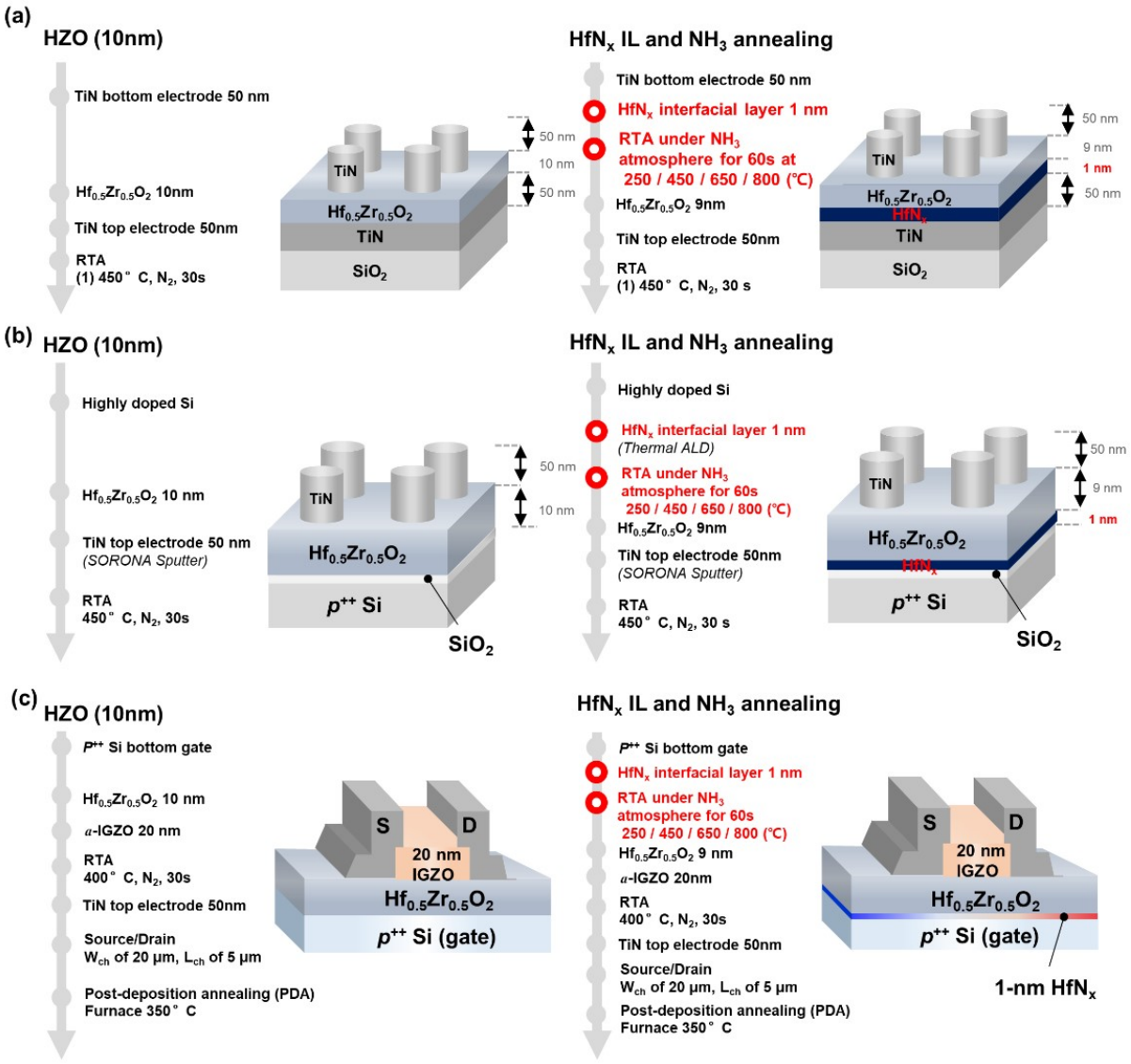

Figure S1. Schematic diagram showing the (a) key fabrication steps of the HZO-based MFM capacitors, showing the processes for 10-nm thick HZO film and with the NH_3 annealed HfN_x IL, b) the main fabrication steps for MFIS capacitors, detailing the procedures both 10-nm thick HZO film and with the NH_3-annealed HfN_x IL, and (c) the fabricated ferroelectric HZO-based *a*-IGZO TFTs, including configurations both 10-nm thick HZO film and with the NH_3-annealed HfN_x IL.

B. Structural properties

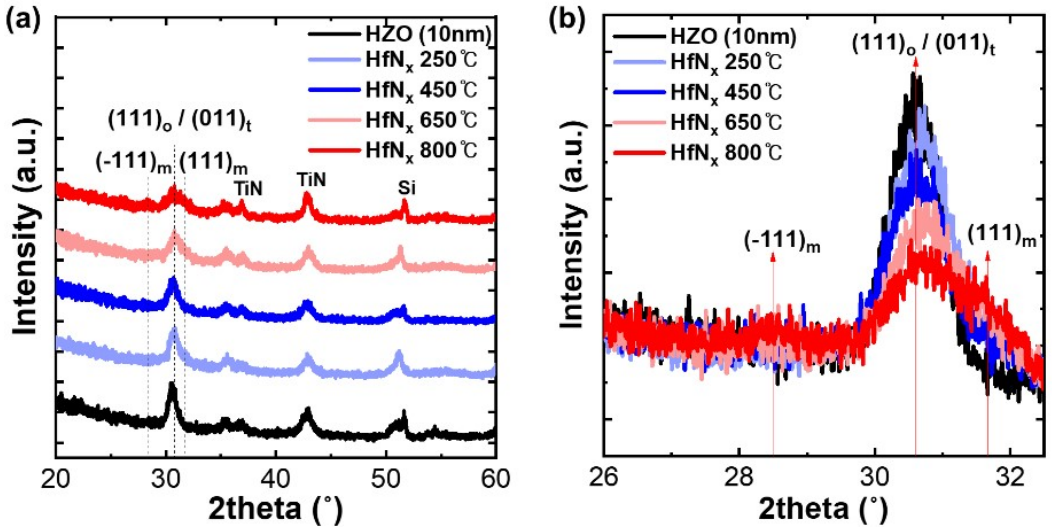

Figure S2. GIXRD patterns of 10-nm-thick HZO and HfN_x IL samples annealed in NH_3 at various temperatures: (a) GIXRD patterns of the 10-nm-thick HZO and 1-nm-thick HfN_x IL annealed at 250 °C to 800 °C, and (b) enlarged GIXRD patterns in the 26°-32.5° range.

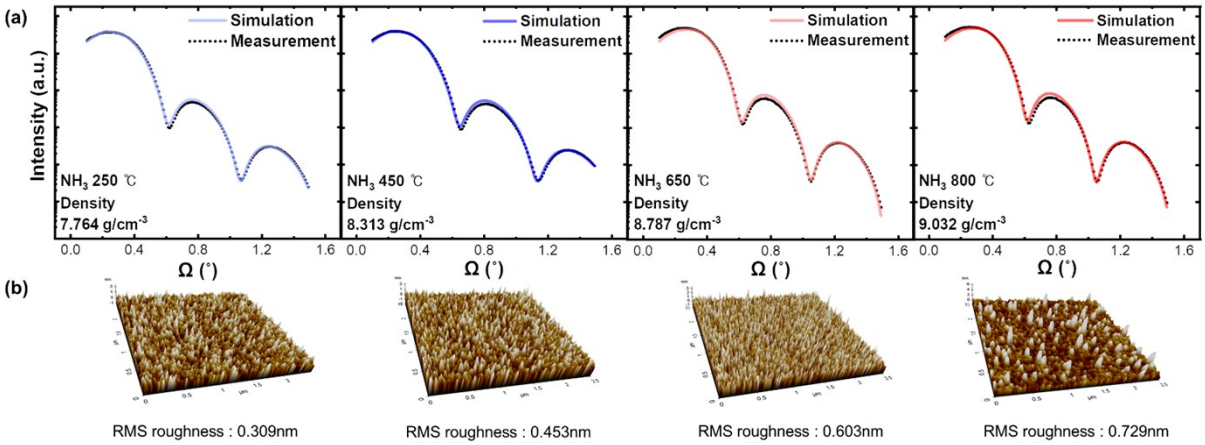

Figure S3. (a) XRR results and (b) AFM results of 10-nm-thick HfN_x films annealed in NH_3 at 250 °C, 450 °C, 650 °C, and 800 °C, showing the measured film density and surface roughness.

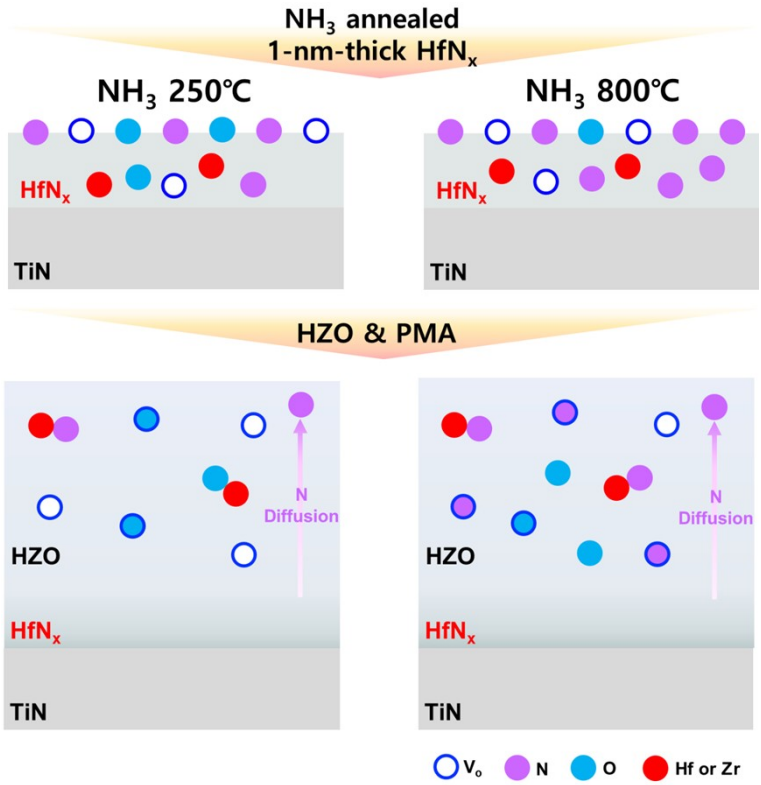

Figure S4. Schematic diagram depicting a proposed model for the role of nitrogen (N) and oxygen (O) in influencing the ferroelectric properties of 1-nm-thick HfN_x films subjected to NH_3 annealing at 250 °C and 800 °C.

C. Electrical properties

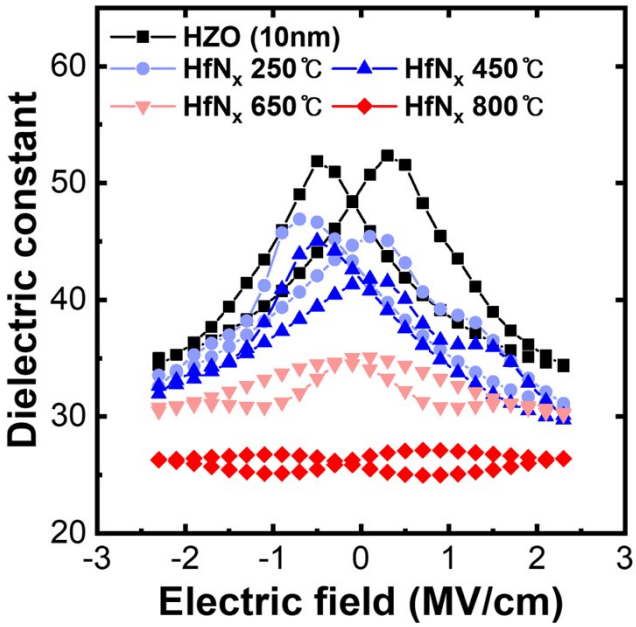

Figure S5. ε_r–E curves of TiN/10-nm-thick HZO/TiN and TiN/HZO/HfN$_x$/TiN capacitors annealed in NH_3 from 250 °C to 800 °C.

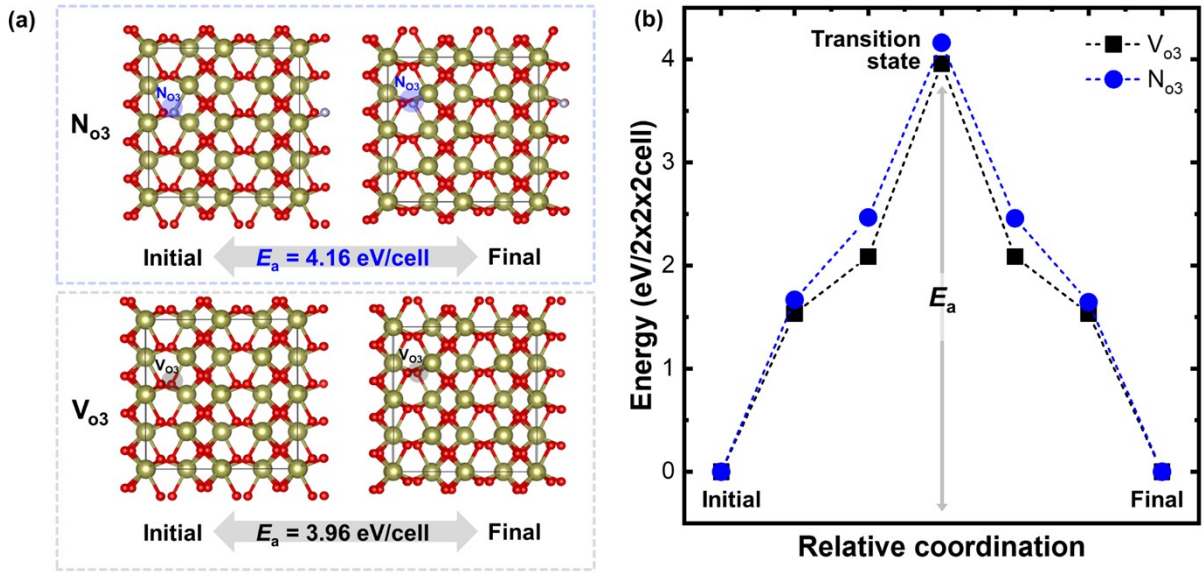

Figure S6. Calculated switching barrier for 2×2×2 *Pca2₁* HfO_2 cells, including (a) N_{o3} and V_{o3}. Transition state calculations show (b) diffusion barriers of N_{o3} and V_{o3}.

Note

Figure S6(a) shows the impact of N-doping on the switching barrier within the HZO matrix based on DFT calculations. To confirm this effect, the E_a of the switching barrier was calculated for a 2×2×2 cell structure. Atomic displacements along the x- and y-directions were included in the model to realistically simulate switching behavior. According to the equation, E_a was defined as the energy difference between the transition state (F) and the initial energy (I):

$$E_a = E(F)\text{-}E(I)$$

E_a for N_{o3} was calculated to be 4.16 eV/cell, which was relatively higher than the 3.96 eV/cell obtained for V_{o3}.

Figure S6(b) shows the energy curve for the transition states between N_{o3} and V_{o3}, with N_{o3} consistently exhibiting higher activation energy. This increase in E_a was caused by nitrogen incorporation, which influenced the lattice configuration and restricted ion mobility during polarization switching. This effect increased the electric field required to overcome the switching barrier and corresponded to higher E_c values. These results were consistent with the XPS results in Figure 4, which demonstrated the effect of nitrogen introduced through NH_3 annealing of HfN_x IL on the binding energy. XPS analysis further supported the conclusions derived from DFT calculations.