Supplementary Information

The Transport Mechanism in $Hf_{0.5}Zr_{0.5}O_2$ based Ferroelectric Diode

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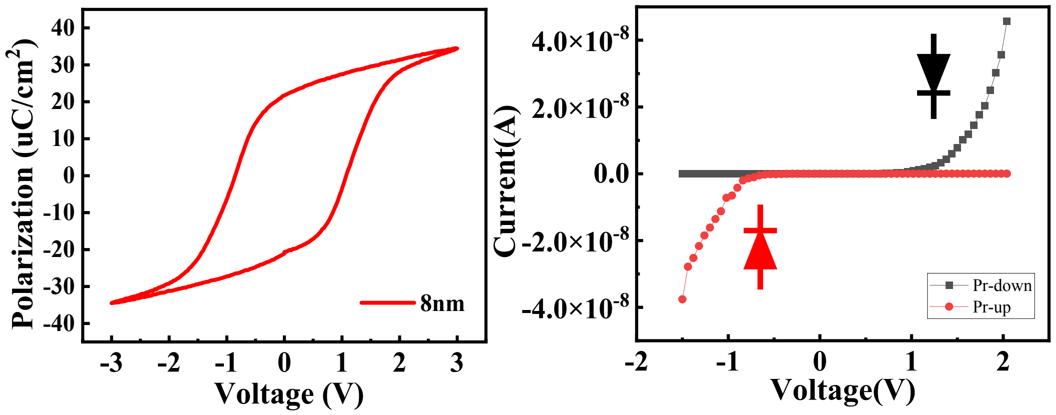
Supplementary Figures S1, Tables SI-SIV, Note.



(a) (b)

Fig. S1 (a) the P-V loop of 8nm MFM structure. (b): Switchable FE-diode. The on and off state were tested in the small voltage range. Diode characteristic could be clearly obtained. It is noted that the FE-diode conduction direction is controlled by the polarization. When the polarization direction is consistent with the applied voltage direction, the Fe-diode can realize a large conduction current, which is on-direction; while the polarization direction is opposite to the applied Voltage, the Fe-diode exhibits a small current, which means off-direction

Table SI. R^2 with different temperature and different model at on-state

Method	**T (K)**	**303K**	**313K**	**323K**	**333K**	**343K**	**363K**
Schottky model	R2-7nm	NA	0.99937	0.9978	0.97773	0.98378	0.98749
Poole-Frankel model	R2-7nm	NA	0.99896	0.99629	0.96659	0.97695	0.98289

R^2 with different temperature in Schottky model and Poole-Frankel model, Schottky model was fitted with a high R^2 (correlation coefficient, a statistic representing how closely two variables co-vary)

Table SII. $\varphi_0$with different temperature (eV)

Method	**Thickness**	**303K**	**313K**	**323K**	**333K**	**343K**	**363K**
Schottky model	R^2-7nm	NA	0.5785	0.5761	0.5552	0.5816	0.5941

Based on Schottky model, barrier heights and permittivity were calculated in Table SII and SIII. Our result is approximately 0.6 eV. Different thickness might cause difference.

Table SIV. ε r with different temperature

Method	**Thickness**	**303K**	**313K**	**323K**	**333K**	**343K**	**363K**
Schottky Model d=thickness	R^2-7nm	NA	5.52280	4.3831	4.5489	3.34110	2.4855
Schottky Model d=2.5nm	R^2-7nm	15.4638	12.2732	12.7369	9.35522	6.9596	15.4638

the calculation ε_r must be smaller than the real. If we consider d=constant=2.5nm, we can get a nearly estimate ε_r. Seungyeol work could give some evidence to explain that circumstance [1] HZO thin films exhibit typical C-E butterfly shape loops with two peaks, which characterize spontaneous polarization switching. The strong polarization means the ε_r is at the bottom [2]

The calculation and description are shown below:
According to the R-S equation:

$$J = AT^2 \exp \frac{e\beta_{RS}E^{\frac{1}{2}} - \varphi_0}{kT}$$

β_{RS} is the Richardson-Schottky constant:

$$\beta_{RS} = (e/4\pi\varepsilon_r\varepsilon_0)^{1/2}$$

And:

$$I = J * S$$
$$E = V/d$$

d is the film thicknesses that actually involved in conducting, same to a junction.
We can obtain:

$$\ln(I) = (\ln(SAT^2) - \frac{\varphi_0}{kT}) + \frac{\left(\frac{e^3}{4\pi\varepsilon_r\varepsilon_0}\right)^{\frac{1}{2}}}{kT} E^{\frac{1}{2}} = (\ln(SAT^2) - \frac{\varphi_0}{kT}) + \frac{\left(\frac{e^3}{4\pi\varepsilon_r\varepsilon_0 d}\right)^{\frac{1}{2}}}{kT} (V)^{\frac{1}{2}}$$

Slope can be obtained from the fitting, so we can calculate the ε_∞:

$$\varepsilon_r = \frac{e^3}{4\pi\varepsilon_0 d * (slope * kT)^2}$$

Since we do not know the d of the actually conductive junction, this calculation is only a rough estimate.

Intercept can be obtained from the fitting, so φ_0:

$$\varphi_0 = \left(In(SAT^2) - intercept\right) * kT$$

Which, A≈120 A*cm^{-2}*K^{-2}., S= 19 nm × 1.31um

Table SIIII. R^2 with different thickness, different temperature and different model at off-state

Method	**T (K)**	**303K**	**313K**	**323K**	**343K**
Hopping Model	R2-7nm	0.99649	0.97957	0.92979	0.98914
Schottky Model	R2-7nm	0.99106	0.96214	0.87041	0.97869
Poole-Frankel Model	R2-7nm	0.95590	0.64893	0.02054	0.13974

R^2 with different temperature in Hopping, Schottky model and Poole-Frankel model, the Hopping model fits better.

The experimental 3D integration of Fe-diode:

Firstly, multiple TiN (20 nm)/SiO_2 (30-nm) layers were deposited by physical vapor deposition (PVD) and Plasma Enhanced Chemical Vapor Deposition (PECVD), respectively. Patterning and only one-step etching were applied to form stacked wordlines (WL) with a smooth sidewall profile. After SiO_2 filling in the trench, a 500nm hole is etched down to the bottom SiO_2. HZO bilayers was deposited on the sidewall sequentially by ALD (260 °C, $Hf[N(C2H_5)CH_3]_4$ and $Zr[N(C_2H_5)CH_3]_4$, 1:1 ratio), followed by depositing of TiN/W by the sputtering to fill the hole as the pillar electrode (BL). Then, successively using selective etching to open the horizontal WL. The area of the memory cell was defined by the thickness of the bottom electrode TiN (20 nm) and the perimeter of the hole (500 nm). Finally, after crystallizing by rapid thermal annealing in an N_2 ambient at 400 °C for 30 s, 8-layer 3D vertical memory with Fe-diode cells were prepared well. The DC I-V pulse of a self-selective cell were tested by an Agilent B1500A semiconductor parameter analyzer connected to the experimental device. The pulse measurements were performed using the HVSPGU module of Agilent B1500A, where W top electrode was biased, while the TiN bottom electrode was grounded.

Reference:

[1] Oh S., Kim H., Kashir A., et al. Effect of dead layers on the ferroelectric property of ultrathin HfZrOx film. Applied Physics Letters, 117(25): 252906 (2020).

[2] Muller J., Boscke T. S., Schroder U., et al. Ferroelectricity in simple binary ZrO2 and HfO2. Nano letters, 12(8): 4318-4323 (2012).