Supporting Information

Superior and Stable Ferroelectric Properties of Hafnium-Zirconium-Oxide Thin Films Deposited via Atomic Layer Deposition using Cyclopentadienyl-Based Precursors without Annealing

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A. Ferroelectric properties of HZO thin films deposited using TEMAHf and TEMAZr

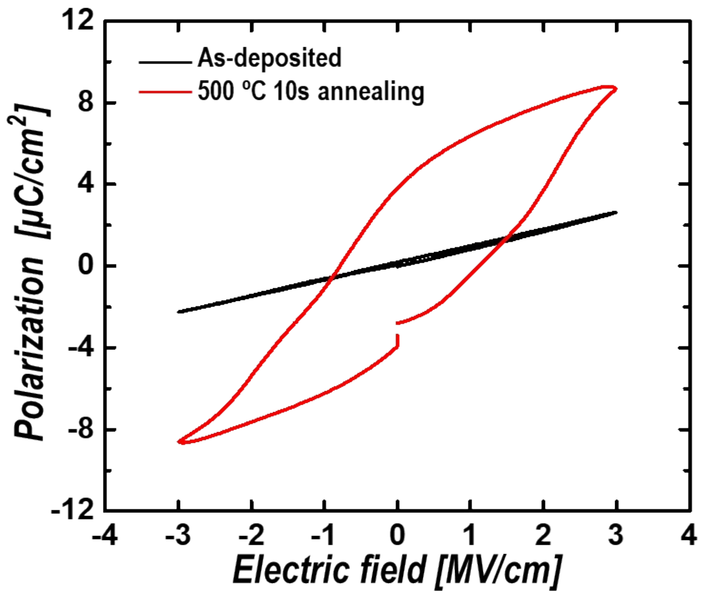


Fig. S1 Polarization-electric field (*P-E*) curves of HZO thin films deposited at 250 °C using TEMAHf and TEMAZr as precursors.

We investigated the polarization characteristics of HZO thin films deposited using tetrakis(ethylmethylamido)Zr [TEMAZr] and tetrakis(ethylmethylamido)Hf [TEMAHf] in the same ALD chamber at 250 °C prior to and after rapid thermal annealing. As shown in Figure S1, the as-deposited HZO thin film did not exhibit ferroelectricity, and a hysteresis loop was observed after post-thermal annealing at 500 °C for 10 s.

B. Ferroelectric properties of HZO thin films deposited using a Cp-based cocktail precursor with a molar ratio of Hf[Cp(NMe_2)$_3$]:Zr[Cp(NMe_2)$_3$] = 50:50.

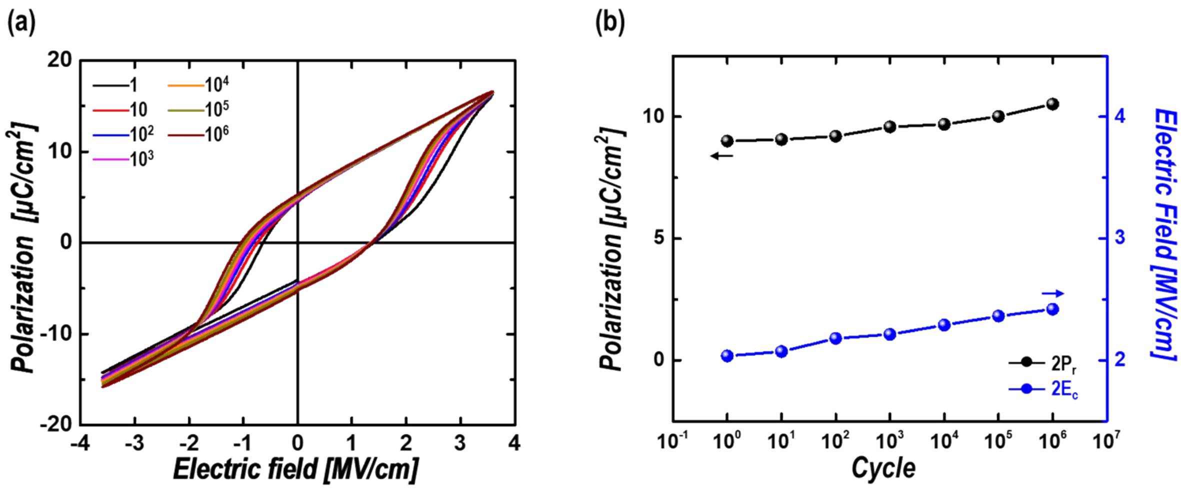


Fig. S2 Ferroelectric properties of as-deposited HZO thin films deposited using a Cp-based cocktail precursor with a molar ratio **Hf[Cp(NMe_2)$_3$]:Zr[Cp(NMe_2)$_3$] = 50:50**: (a) *P-E* loops of the HZO thin film for the pristine state and the subsequently measured cycles. (b) Variation of the remanent polarization and coercive field as a function of number of cycles measured at an applied electric field of 3.5 MV/cm.

To compare the cocktail precursor composed of a molar ratio of Hf[Cp(NMe_2)$_3$]:Zr[Cp(NMe_2)$_3$] = 35:65, we additionally investigated the ferroelectric properties of a HZO thin film deposited at 320 °C using a cocktail precursor with a molar ratio of 1:1 without post-annealing. Even in this case, ferroelectric loops were observed without annealing; however, the 2Pr value (~10 μC/cm^2) was relatively small.

C. Electrical properties of HZO thin films deposited using a Cp-based cocktail precursor with a molar ratio of $Hf[Cp(NMe_2)_3]$:$Zr[Cp(NMe_2)_3]$ = 35:65.

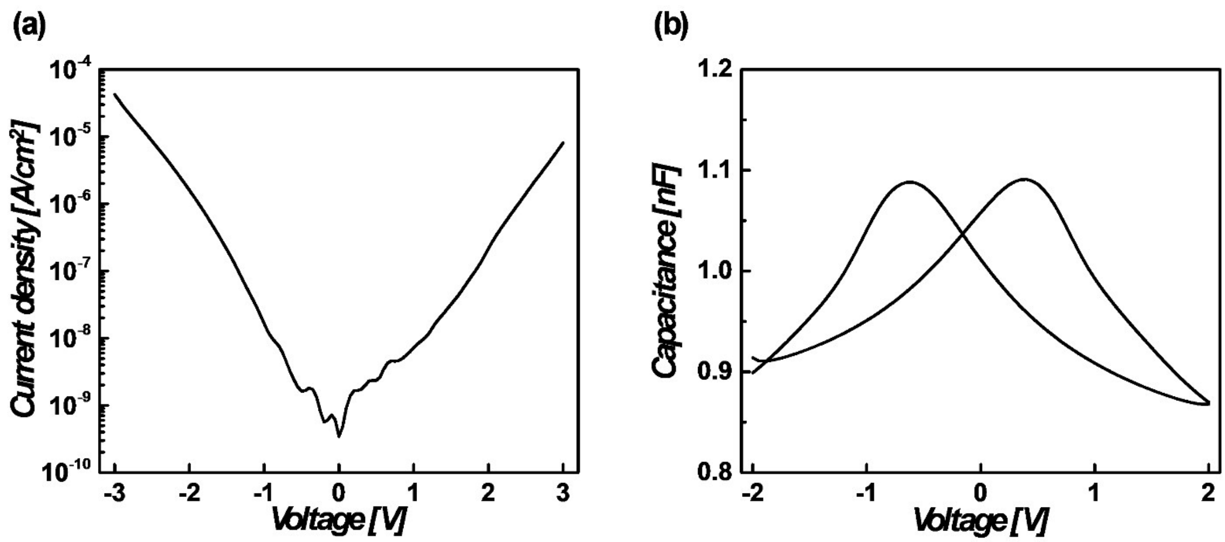
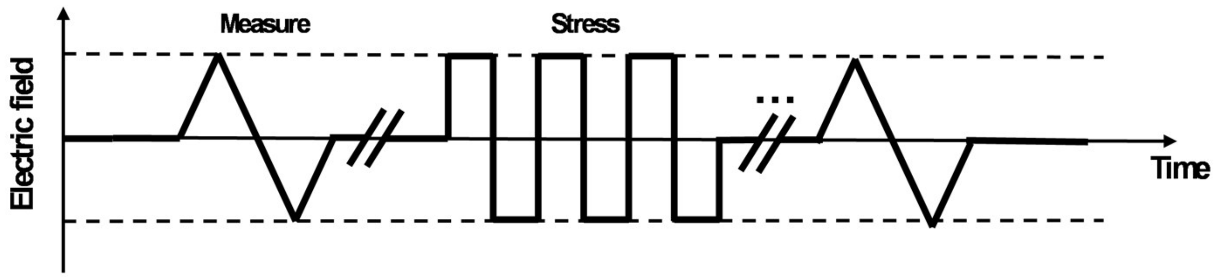


Fig. S3 Electrical properties of HZO thin films deposited using a Cp-based cocktail precursor with a molar ratio of $Hf[Cp(NMe_2)_3]$:$Zr[Cp(NMe_2)_3]$ = 35:65: (a) current density-voltage(J-V) curve of the 10-nm-thick HZO thin film. (b) capacitance-voltage(C-V) curve of the 10-nm-thick HZO thin film measured at 100kHz.

We investigated the electrical characteristics of HZO thin films deposited using a Cp-based cocktail precursor with a molar ratio of $Hf[Cp(NMe_2)_3]$:$Zr[Cp(NMe_2)_3]$ = 35:65. As shown in Figure S3(a) and (b), the as-deposited HZO based MFM capacitors exhibited good leakage current properties, and a typical C-V butterfly-like curve, characteristics of ferroelectric capacitors, also observed.

D. Schematic diagram for applied pulse for endurance switching cycle test.



	Voltage	Rising time	Pulse width	Termination
P-E	3.5V	1kHz frequency	Sine wave	50Ω
Endurance		20ns	5µs	

Fig. S4 Schematic diagram for applied pulse used to measure P-E endurance switching cycle.

Referring to the previous paper,[S1, S2] we conducted the P-E endurance switching cycle measurement with the following waveforms. In the measure section, a 1 kHz triangle wave field was used as in general P-E measurement. In stress section, rectangular wave field with a pulse width of 5 µs and rising/falling time of 2 ns were utilized to switching cycle.

E. Schematics of the transient measurement circuit diagram and HZO-based FeFET.

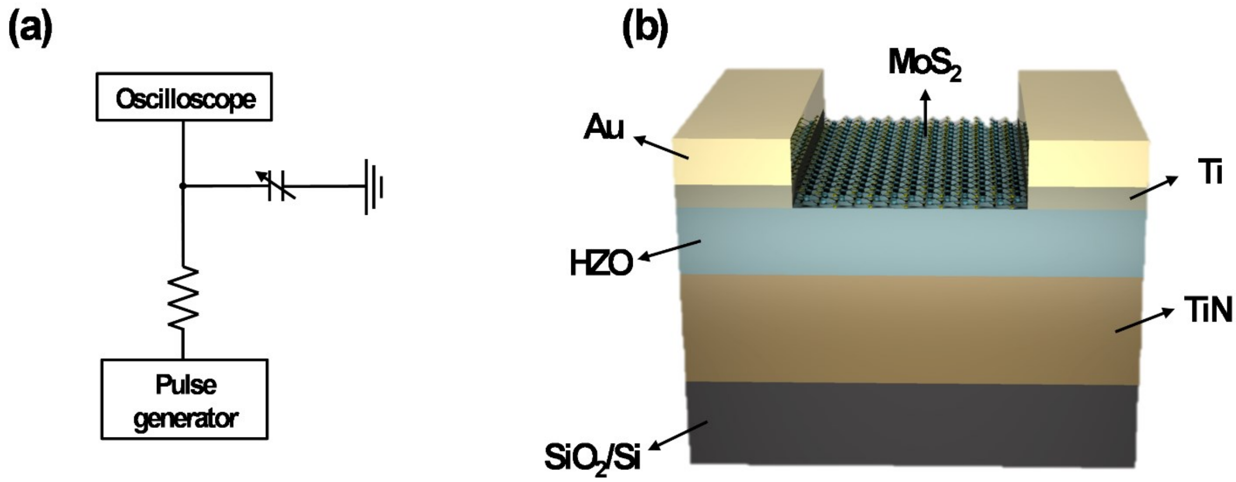


Fig. S5 Schematics of (a) transient measurement circuit diagram, (b) the HZO-based FeFET.

References

S1. S. Starschich, S. Menzel and U. Böttger, Appl. Phys. Lett., 2016, 108, 032903.

S2. T. Schenk, U. Schroeder, M. Pešić, M. Popovici, Y. V. Pershin and T. Mikolajick, ACS Appl. Mater. Interfaces, 2014, 6, 19744-19751.