Very high frequency (~100 MHz) Plasma Enhanced Atomic Layer Deposition High-κ Hafnium Zirconium Oxide Capacitors near Morphotropic Phase Boundary with Low current density@0.8V of 2×10^{-8} A/cm^2 & high-κ of 70 for DRAM Technology

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Supporting information

This file includes:

Figure S1. MPB phase formation in RF-deposited and VHF-deposited HZO films.

Figure S1 illustrates the formation of the MPB phase in HZO films treated with conventional RF and VHF methods. In VHF-processed HZO films, the MPB phase forms at lower Zr doping ratios and manifests across a wider range of thickness conditions compared to RF-processed films.
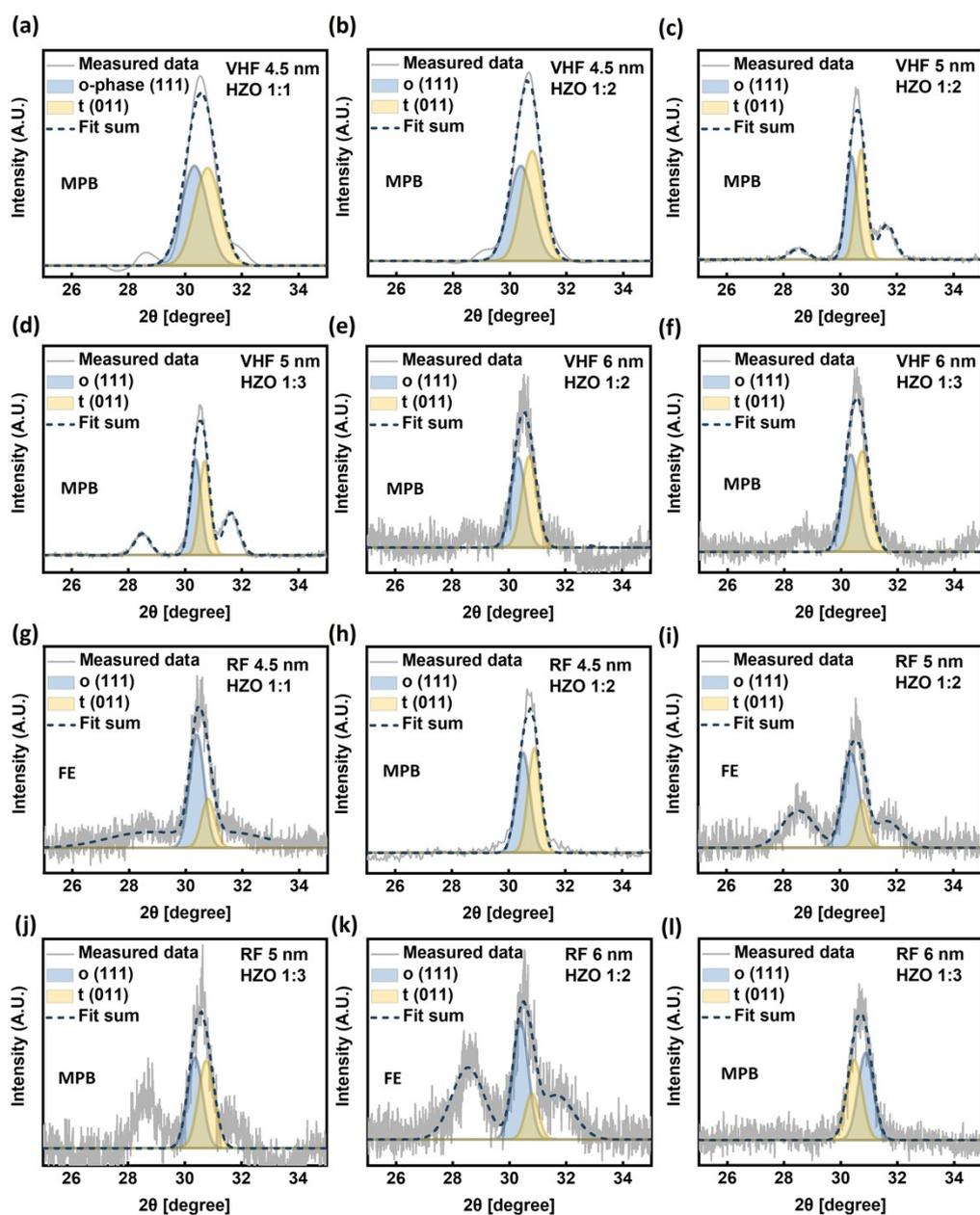
Figure S2. GIXRD of RF-deposited and VHF-deposited HZO films. VHF HZO shows MPB characteristics at 4.5 nm 1:1 (a), 4.5 nm 1:2 (b), 5 nm 1:2 (c), 5 nm 1:3 (d), 6 nm 1:2 (e), 6 nm 1:3 (f). RF HZO only shows MPB characteristics at 4.5 nm 1:2 (h), 5 nm 1:3 (j), 6 nm 1:3 (l). It shows ferroelectricity at 4.5 nm 1:1 (g), 5 nm 1:2 (i), 6 nm 1:2 (k).

The properties of HZO—ferroelectricity (FE), morphotropic phase boundary (MPB), and antiferroelectricity (AFE)—are primarily determined by the o-phase (111) and t-

S4

phase (111), observed at 30.4° and 30.8°, respectively. When the o-phase is dominant, the sample exhibits ferroelectricity, whereas a dominant t-phase results in antiferroelectricity. At an o-phase to t-phase ratio of 1:1, the sample displays MPB characteristics. Other peaks have minimal impact on the properties of HZO and are therefore omitted from the figure for clarity.
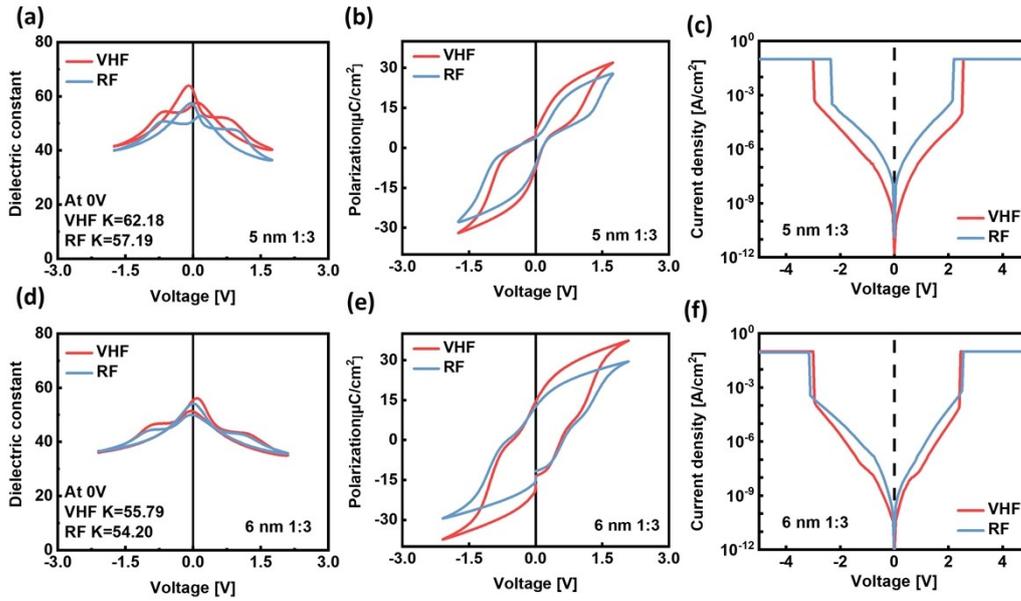
Figure S3. Basic characteristics of the 5 nm and 6 nm MPB HZO (1:3). The basic characteristics of the 5 nm MPB HZO (1:3) at room temperature are shown in (a) the Dielectric Constant-Voltage (D-V) curve, (b) the Polarization-Voltage (P-V) curve, and (c) the Current-Voltage (I-V) curve. Similarly, the basic characteristics of the 6 nm MPB HZO (1:3) at room temperature are presented in (d) D-V, (e) P-V, and (f) I-V.
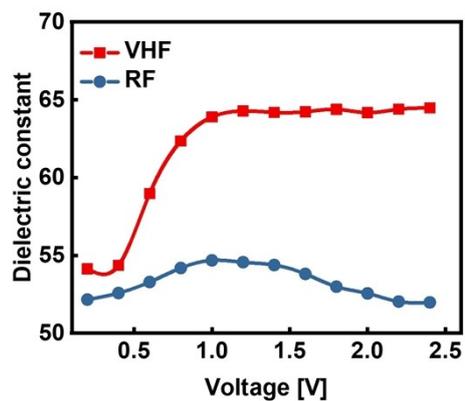
Figure S4. Dielectric constant of RF-deposited and VHF-deposited HZO films with voltage.

The VHF HZO film exhibits a non-flat curve, while the RF HZO film, which displays ferroelectric characteristics, shows a nearly flat curve resembling that of a dielectric capacitor. Moreover, the k value of the VHF HZO film increases in the low-field region, achieving an impressive k value of 63.89 even at 1 V.

PEALD Single Cycle Sequence

Precursor time 0.5 S

⬇

Purge time 5 S

⬇

O_2 exposure time 0.5 S

⬇

Plasma time 1 S

⬇

Purge time 5 S
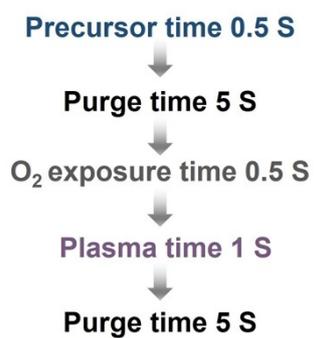
Figure S5. The steps involved in a single deposition.
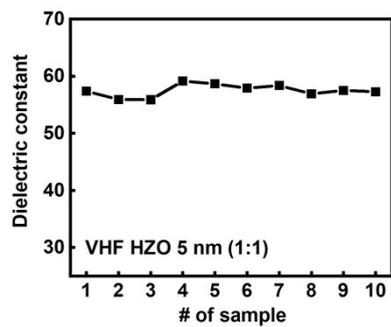
Figure S6. 10 different VHF HZO 5 nm (1:1) samples K value.

Dielectric Constant					
Thickness (nm)	VHF PE-ALD			RF PR-ALD		
	Hf:Zr ratio			Hf:Zr ratio		
	1:1	1:2	1:3	1:1	1:2	1:3
3	29.93	31.11	32.62	34.59	34.37	36.97
4.5	64.47	63.90	63.85	59.08	62.28	43.54
5	57.89	61.30	62.18	53.42	54.68	57.19
6	46.89	55.38	55.79	43.93	50.96	54.20
8	40.33	41.36	42.35	40.55	40.19	41.39

Table S1. Dielectric Constant of RF-deposited and VHF-deposited HZO films.

Table 1 compares the dielectric constants of HZO films deposited using VHF PE-ALD and RF PE-ALD, across film thicknesses ranging from 3 to 8 nm and Hf: Zr ratios of 1:1 to 1:3. The HZO films deposited with VHF PE-ALD exhibit higher dielectric constants.

Trap states (eV)	Thickness (nm)	Doping atom	Deposition method	Structure	Explanation	Ref.
1.36	16		ALD	$TiN/HfO_2/TiN$	Nitrogen containing defects	1
0.6 and 1.0	10		ALD	$Pt/Ta_2O_5/HfO_{2-x}/TiN$	Nanocrystalline grain boundaries	2
0.35-0.4	50		ALD	$TiN/HfO_2/TiN$	Oxygen vacancies	3
0.2	15		Sputtering	$Al/ZrO_2/SiO_2/Si$	Interstitial hydrogen atoms	4
0.3	4-6		Calculations	$TiN/HfO_2/TiN$	Interstitial hydrogen atoms	5
0.1	4-6		Calculations	$TiN/ZrO_2/TiN$	Interstitial hydrogen atoms	5
0.15–0.19	10	Zr	ALD	TiN/HZO/TiN	Interstitial hydrogen atoms	6
0.48–0.58	10	Zr	PLD	$Pt/HZO/La_{0.7}Sr_{0.3}MnO_3$	Oxygen vacancies	7
0.6	10	Zr	PE-ALD	$W/Hf_{0.5}Zr_{0.5}O_2/W$	Oxygen vacancies	8
0.65	10	Zr	ALD	TaN/HZO/TaN	Oxygen vacancies	9
0.56	8.5	Al	ALD	TiN/HAO/Si	Oxygen vacancies	10
0.58	4.5	Zr	VHF PE-ALD	TiN/HZO/TiN	Oxygen vacancies	**This work**
0.42	4.5	Zr	RF PE-ALD	TiN/HZO/TiN	Oxygen vacancies	**This work**

Table S2. Trap states energy level of our sample and other reported hafnia films.

By comparing trap states with the references, we can determine that the main defects in VHF and RF HZO are oxygen vacancies [1-10].

Material	Ratio	Plasma frequency	Thickness (nm)	Growth Rate (Å/Cycle)
HZO	1:1	Very high frequency 100 MHz	3	1.57
			4.5	1.48
			5	1.35
			6	1.53
			8	1.55
		Radio frequency 13.56 MHZ	3	1.35
			4.5	1.27
			5	1.20
			6	1.22
			8	1.31

Table S3. Deposition rate of the HZO (1:1) films.

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