Oxygen vacancy concentration as a function of field cycling and polarization in TiN/$Hf_{0.5}Zr_{0.5}O_2$/TiN ferroelectric capacitors

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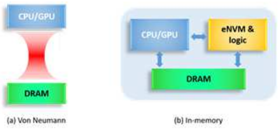
- ☐ Ferroelectric hafnia-based thin films are one of the most promising candidates for emerging high-density embedded non-volatile memory technologies thanks to their compatibility with silicon technology and the possibility of 3D integration.
- ☐ Typical oxide thickness in capacitive memory cells is 10 nm, hence the electrode-ferroelectric interface and the annealing temperature may play an important role in electrical performance.
- ☐ We have studied the field cycling behavior of microscopic TiN/$Hf_{0.5}Zr_{0.5}O_2$/TiN ferroelectric capacitors using synchrotron-based soft x-ray photoemission electron microscopy
- ☐ Specific interface chemistry and oxygen vacancy concentration are observed and believed to be linked to wake-up, imprint and endurance.

Motivation Optimization of ferroelectric $HfZrO_2$ capacitors

What is at stake: Edge processing vs. Cloud for artificial intelligence

- ➢ Memory wall
- ➢ Data transfer cost
- ➢ Latency
- ➢ TOPS/W
- ➢ Non-volatility & leakage
- ➢ Data retention
- ➢ **Endurance**

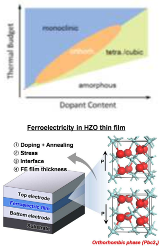


(a) Von Neumann (b) In-memory

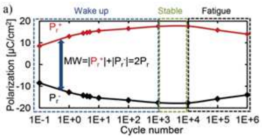
Solution: embedded non-volatile memories & logic

1. N-off computing (10% ON (active) and 90% OFF (idle)): eNVMs
2. In-memory computing (overcome van Neumann bottleneck): eNVMs

Hafnia: CMOS compatible material



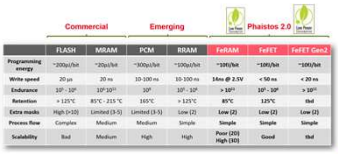
T. Boscke *et al*, *Appl. Phys. Lett.* **99**, 102903 (**2011**)



Endurance issues

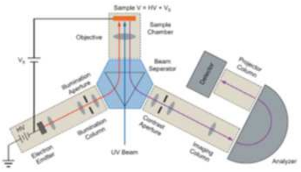
Pešic´*et al*, ***Adv. Funct. Mater.*** **26**, 4601 (2016)

Emerging NVM technologies:



	Commercial		Emerging		Phaistos 2.0		
	FLASH	MRAM	PCM	RRAM	FeRAM	FeFET	FeFET Gen2
Programming energy	~200pJ/bit	~20pJ/bit	~300pJ/bit	~100pJ/bit	~10fJ/bit	~10fJ/bit	~10fJ/bit
Write speed	20 µs	20 ns	10-100 ns	10-100 ns	14ns @ 2.5V	< 50 ns	< 20 ns
Endurance	10^5 - 10^6	10^6-10^{15}	10^9	10^5 - 10^6	> 10^{11}	10^5 - 10^9	> 10^{11}
Retention	> 125°C	85°C - 215 °C	165°C	> 125°C	85°C	125°C	tbd
Extra masks	High (>10)	Limited (3-5)	Limited (3-5)	Low (2)	Low (2)	Low (2)	Low (2)
Process flow	Complex	Medium	Medium	Simple	Simple	Simple	Simple
Scalability	Bad	Medium	High	High	Poor (2D) High (3D)	Good	tbd

Experiment



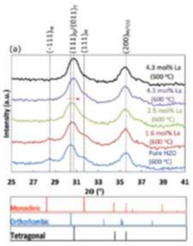
- ☐ Nanospectroscopy beamline, Elettra
- ☐ hν = 670 eV
- ☐ Top electrode TiN 2 nm
- ☐ Hf 4f core levels
- ☐ Ex-situ cycling, electrodes grounded in-situ

TiN (2nm)
$Hf_{0.5}Zr_{0.5}O_2$ (10nm)
TiN (9nm)
Si/SiO_2

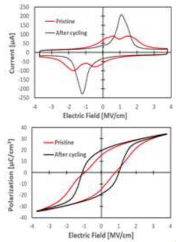
- ➢ TiN bottom and top electrodes are sputtered @ RT
- ➢ ALD (Oxford Instruments OpAL) @ 300°C TEMAHf, ZyALD and O_3 precursors, HfO_2:ZrO_2 ratio 1:1
- ➢ RTA : N_2 atmosphere 600°C for 20s

Structural & Electrical characterization

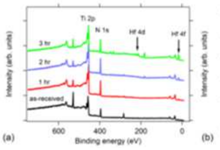
X-ray diffraction



Ferroelectric properties

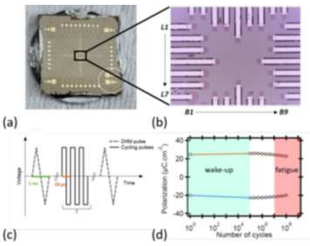


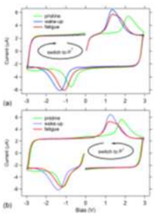
Top electrode thinning

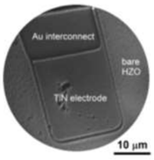


- ☐ Ar ion sputtering @ 500 eV
- ☐ Full stack before patterning
- ☐ TiN top electrode → 2 nm
- ☐ IMFP Hf 4f1.4 nm (TPP-2M)

Field cycling of microscopic capacitors



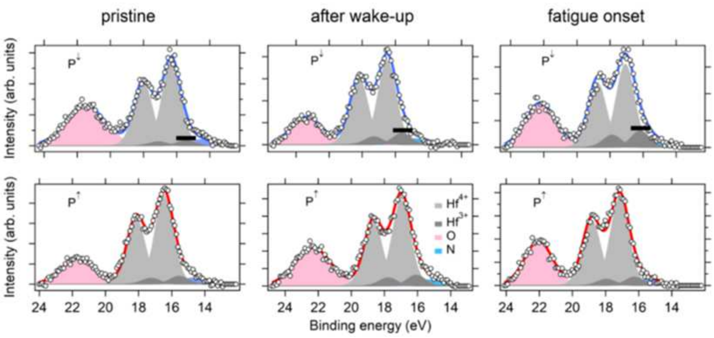




- ☐ LEEM image of microscopic capacitor
- ☐ Au interconnect provides Fermi level reference
- ☐ Bare HZO is reference for Schottky barrier

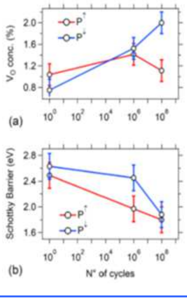
- ☐ Au vias placing 24 microscopic capacitors at the centre of sample
- ☐ 100 kHz field cycling for three data points: pristine; woken up; fatigued
- ☐ Capacitors left in P↑ and P↓ polarization states one week before beamtime
- ☐ T = 300 K

Microspectroscopy as a function of field cycling



- ☐ Each oxygen vacancy V_O frees two electrons which reduce neighbouring Hf^{4+} to Hf^{3+}
- ☐ V_O near top interface increases with cycling
- ☐ Polarization state modulates VY concentration

Oxygen vacancies and Schottky barrier height evolution as a function of field cycling and polarization state



- ☐ The oxygen vacancy (V_O) concentration near the top TiN/$Hf_{0.5}Zr_{0.5}O_2$ interface is estimated from the reduction of Hf^{4+} to Hf^{3+} as measured in the Hf 4f core level spectra
- ☐ The V_O concentration increases with field cycling and redistributes under the effect of the internal field due to the polarization
- ☐ Upward pointing polarization slightly depletes the concentration near the top interface, whereas downward polarization causes V_O drift toward the top interface
- ☐ The V_O redistribution after wake-up is consistent with shifts in the I–V switching peak
- ☐ The Schottky barrier height for electrons decreases systematically with cycling in polarization states, reflecting the overall increase in V_O.

Hamouda *et al. Appl. Phys. Lett.* **120**, 202902 (2022)

Funding

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 780302