



innovations
for high
performance
microelectronics

In-operando HAXPES as a non-destructive technique for investigating the resistive switching phenomenon

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1. Motivation

- Embedded Non-Volatile Memory
- Material Research for RRAM at IHP

2. „*In-operando*“ measurements

- HAXPES, a non-destructive study
- *in-operando* experiment

3. $V_{O''}$ -based RS mechanism

- Study of the electroforming
- *in-operando* study of the OFF- and ON-states

4. Conclusion & Outlook

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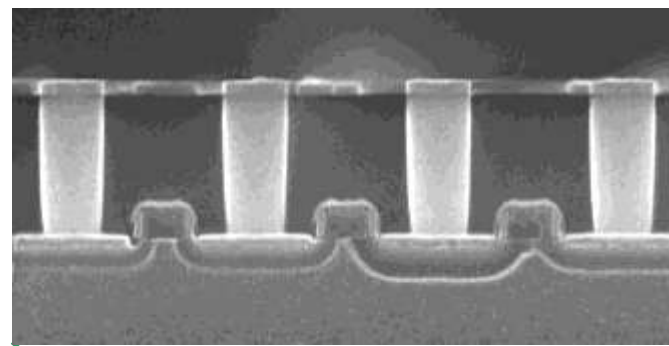
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3. V_O -based RS mechanism

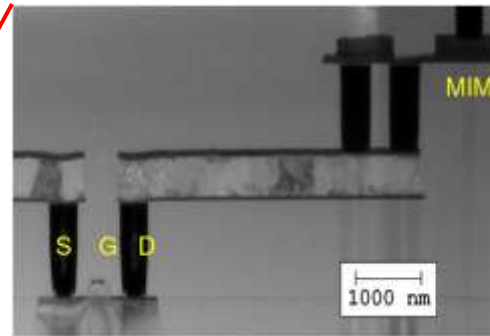
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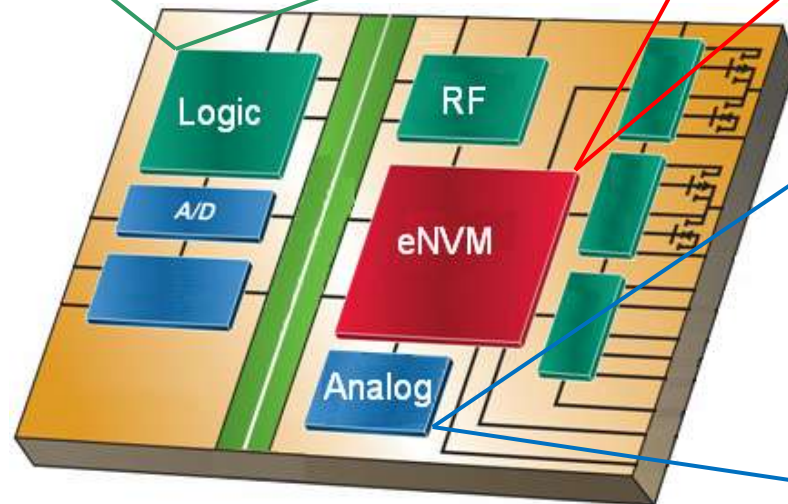
1.1. Embedded Non-Volatile Memory (eNVM)



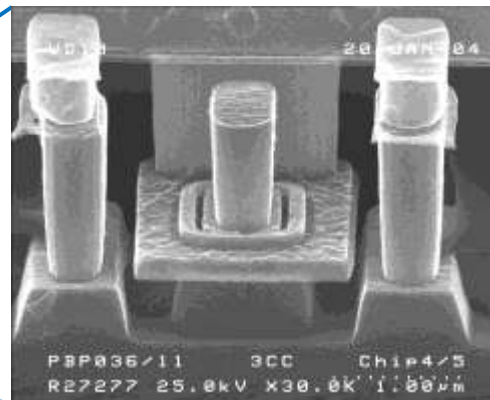
CMOS



1T1R Embedded
Non-Volatile Memory (eNVM)



System-on-Chip (SoC)


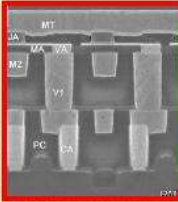
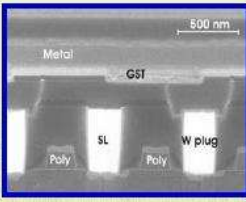
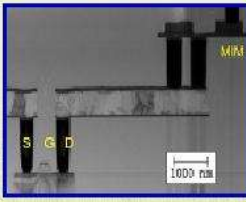


HBT

- Advantages of eNVM:
 - Low-power dissipation
 - I/O pins reduced
 - Reduced system cost
 - Reduced PCB area
 - Improved data security

- eNVM developed for IHP's Si CMOS technology platform for SoC solutions.
- Improvement of performance specifications compared to established eNVM modules.

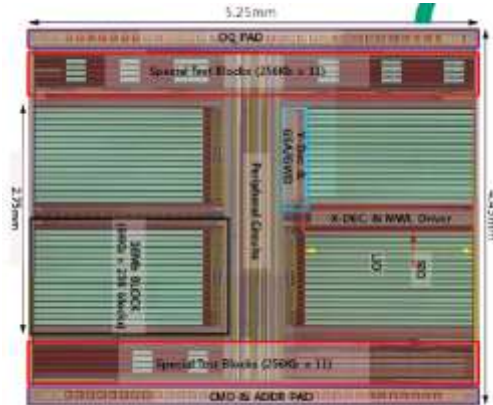
1.1. Why RRAM?

	FRAM (ferroelectric)	MRAM (magnetic)	PCM (phase change)	RRAM (resistance change)
Storage Mechanism	Permanent polarization of a ferroelectric material (PZT or SBT)	Permanent magnetization of a ferromagnetic material in a MTJ	Amorphous/poly-crystal phases of chalcogenide alloy	Resistance states in oxides
Cell Size F ²	Large ~40 → 20	Large ~25	Small ~8	Small ~ 4
Scalability	Poor	Poor	Good	Good
Endurance	10 ¹⁰ (destructive read)	>10 ¹⁴	10 ¹²	10 ¹²
Write	Low power capacitive Theoretically good speed	Power constrained, Scales poorly	Power constrained, Improves with scaling	Low power
Application	Embedded, Low Density	Embedded, Low Density	Stand Alone or Embedded High Density, Low Cost	Embedded, Low Density
Maturity	Limited prod.	Test chips	Test chips	Test chips
Cell Cross-Section	 Samsung, IEDM 04	 IFX-IBM, VLSI-TSA 05	 STM, LESSDERC 04	

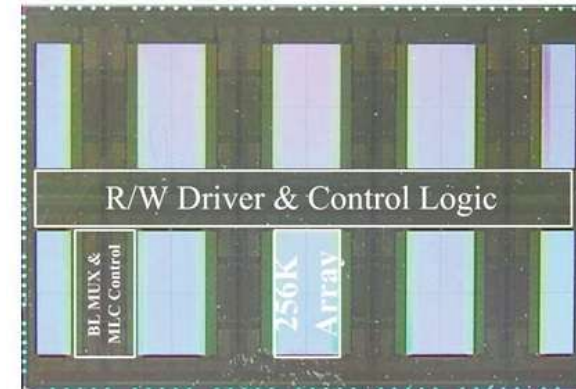
- Advantages of Resistive RAM as eNVM
 - High academic research relevance.
 - Cost-effective back-end-of-line (BEOL) process integration.
 - Improved performance specifications compared to established eNVM (low-power).

1.2. Benchmark

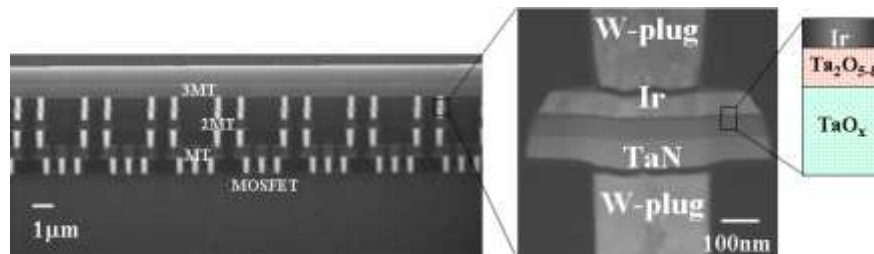
Hynix: 256-kbit array with TiO_2/Al_2O_3
(Memory Workshop, Grenoble, June 2011)



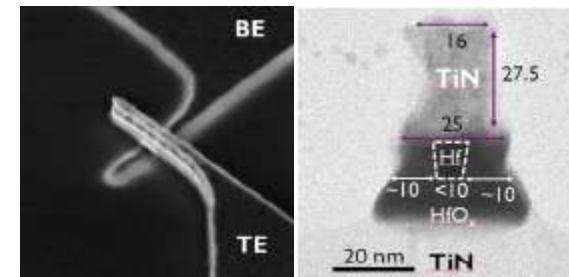
ITRI: 4-Mbit array with $TiN/Ti/HfO_2/TiN$
(IEEE ISSCC, 2011)



Panasonic: 256-kbit array with $Ir/Ta_2O_5/TaO_x$
(IEDM 2011)



IMEC: $10 \times 10 \text{ nm}^2$ record RRAM with Hf/HfO_2
(IEDM 2011)



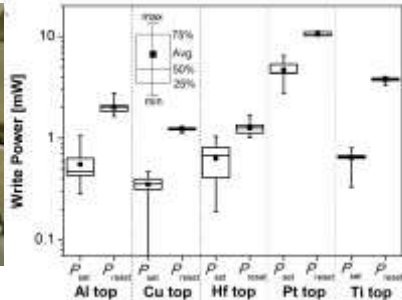
And also Hewlett Packard, Samsung...



**Increasing interest and focus on HfO_2 and Ta_2O_5 -based systems.
Towards memory array demonstrators realization!**

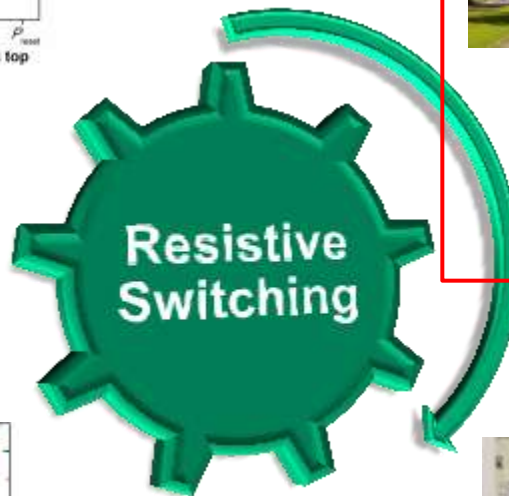
1.3. Material Research for RRAM

Selection of CMOS compatible materials

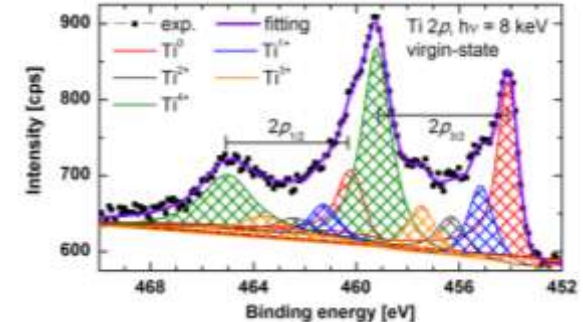


TiN + HfO₂ + Ti/TiN

Ch. Walczyk et al., *JAP* **105**, 114103 (2009).
 T. Bertaud et al., *Thin Solid Films* **520**, 4551 (2011).



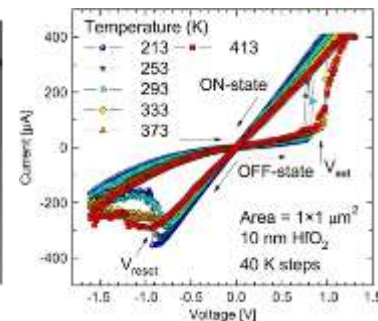
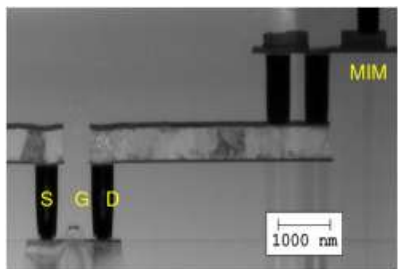
Innovative HAXPES studies



„In-operando“ HAXPES

M. Sowinska et al., *APL* **100**, 233509 (2012).
 T. Bertaud et al., submitted to *APL* (2012).

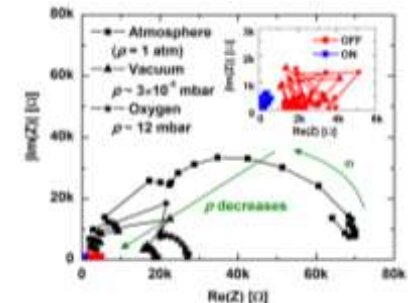
Characterization of 1T1R



4-kbit array integration

Ch. Walczyk et al., *IEEE T. Electron Dev.* **58**, 3124 (2011).
 D. Walczyk et al., *Microelectron. Eng.* **88**, 1133 (2011).

Impact of the oxygen partial pressure



Role of oxygen / oxygen vacancies

T. Bertaud et al., *EMRS* (2012).

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2. **„In-operando“ measurements**

- **HAXPES, a non-destructive study**
- ***in-operando* experiment**

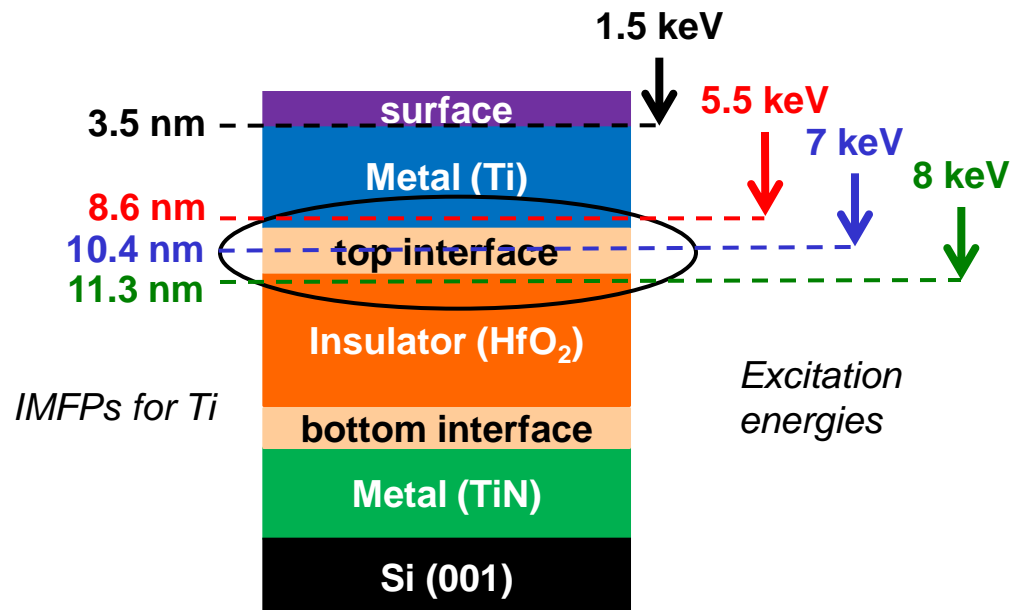
3. *V_O^{••}-based RS mechanism*

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2.1. Hard X-ray Photoelectron Spectroscopy (HAXPES)

- Correlation of the material properties with the electrical state of the Ti/HfO₂/TiN RRAM cell thanks to *in-operando* HAXPES
- Understand the modifications occurring at the Ti/HfO₂ interface during the RS process.



- Standard XPS techniques are surface sensitive
- Hard X-ray PhotoElectron Spectroscopy (HAXPES) allows non-destructive depth profile characterization of the buried Ti/HfO₂ interface.
 - High flux and brilliance of photon beam
 - High energy resolution

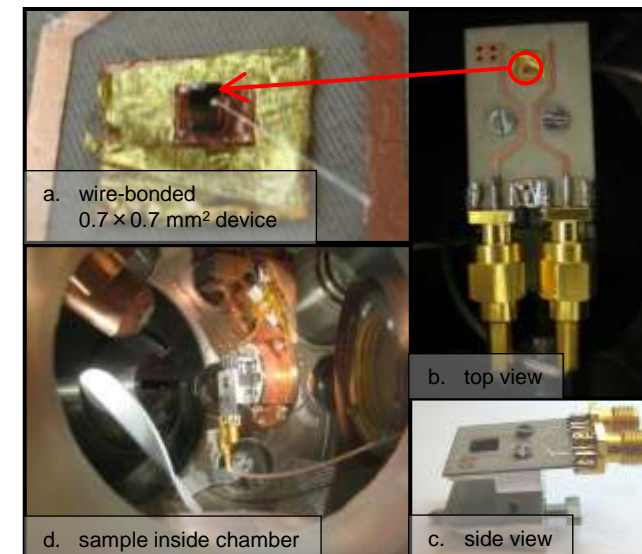
2.2. “*in-situ*“ HAXPES: sample preparation

- Special setup developed at IHP in order to:
 - Dynamically monitor the RS inside the HAXPES chamber for one and the same sample.
 - Investigate the differences between the ON- and OFF-states of the RS.

10 nm Ti
interface
14 nm HfO ₂
interface
112 nm TiN

- MIM stack (thicknesses obtained via X-Ray Reflectometry):
 - 112 nm TiN bottom electrode,
 - 14 nm HfO₂ deposited by AVD,
 - 10 nm of Ti deposited by PVD.

- *in-situ* setup realization:
 - 700 × 700 μm² device divided,
 - Bottom electrode contact (200 × 200 μm²) opened via ToF-SIMS,
 - Sample mounted on a printed circuit board (PCB) and wire-bonded.
 - Device connected to the semiconductor analyser inside the HAXPES vacuum chamber.



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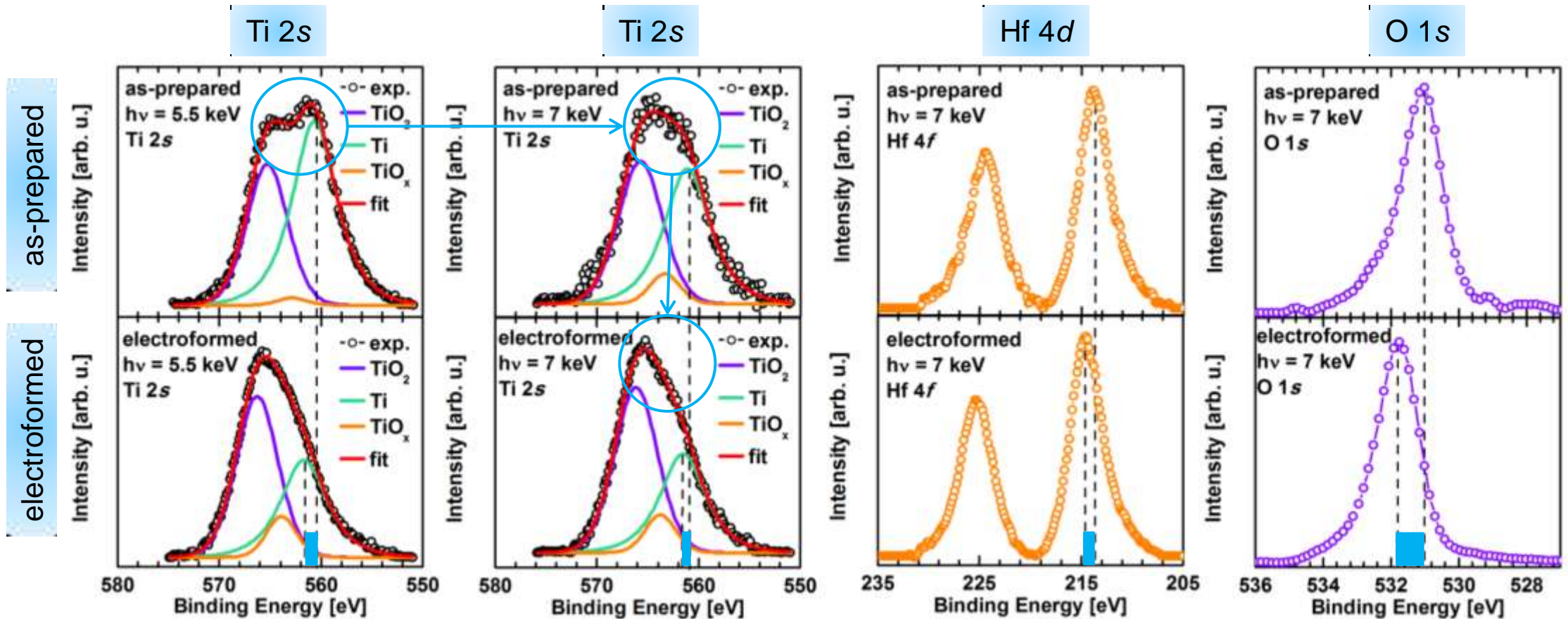
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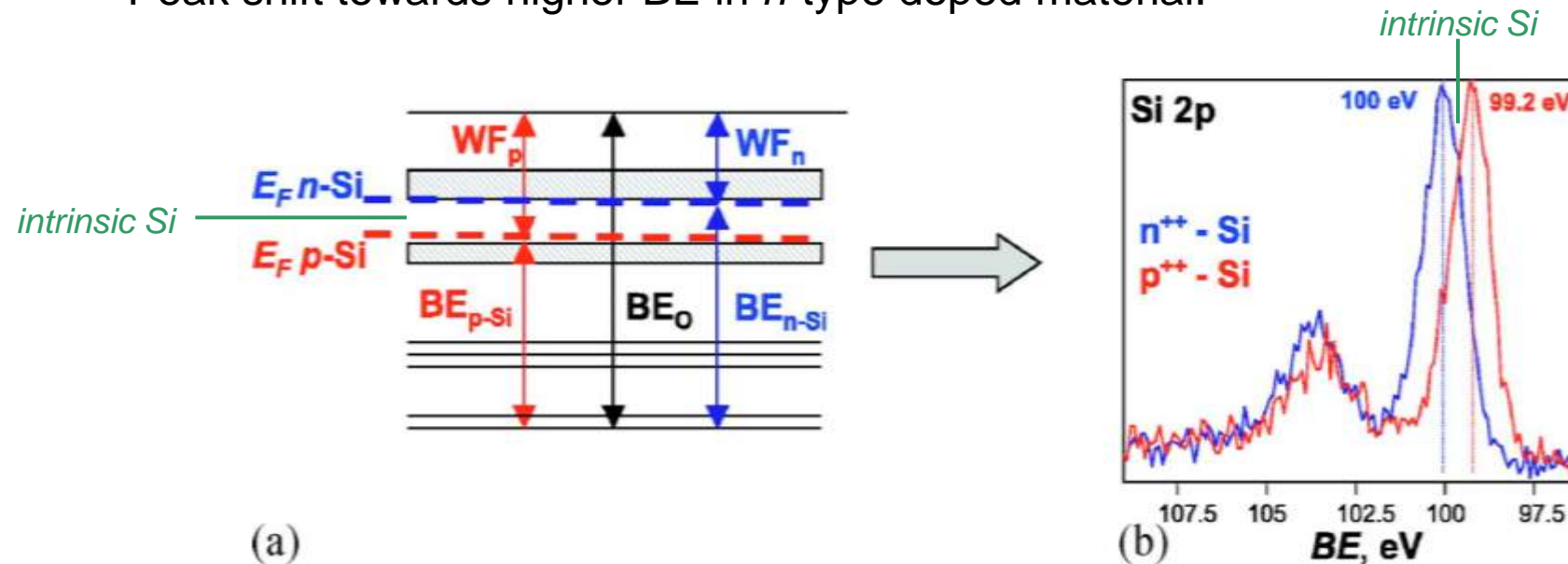
3.1. Characterization of the electroforming



- Presence of a TiO_x interfacial layer between the metallic Ti top electrode and the HfO₂:
 - Decrease of the metallic Ti peak,
 - increase of the TiO_x sub-peak → oxygen-gettering activity of the Ti.
- As-prepared → electroformed:
 - Increase of Ti oxidation at the Ti/HfO₂ interface,
 - shift toward higher BE of all Ti, Hf and O peaks.

3.1. Origin of the peak shift

- Peak shift towards higher BE in *n*-type doped material.

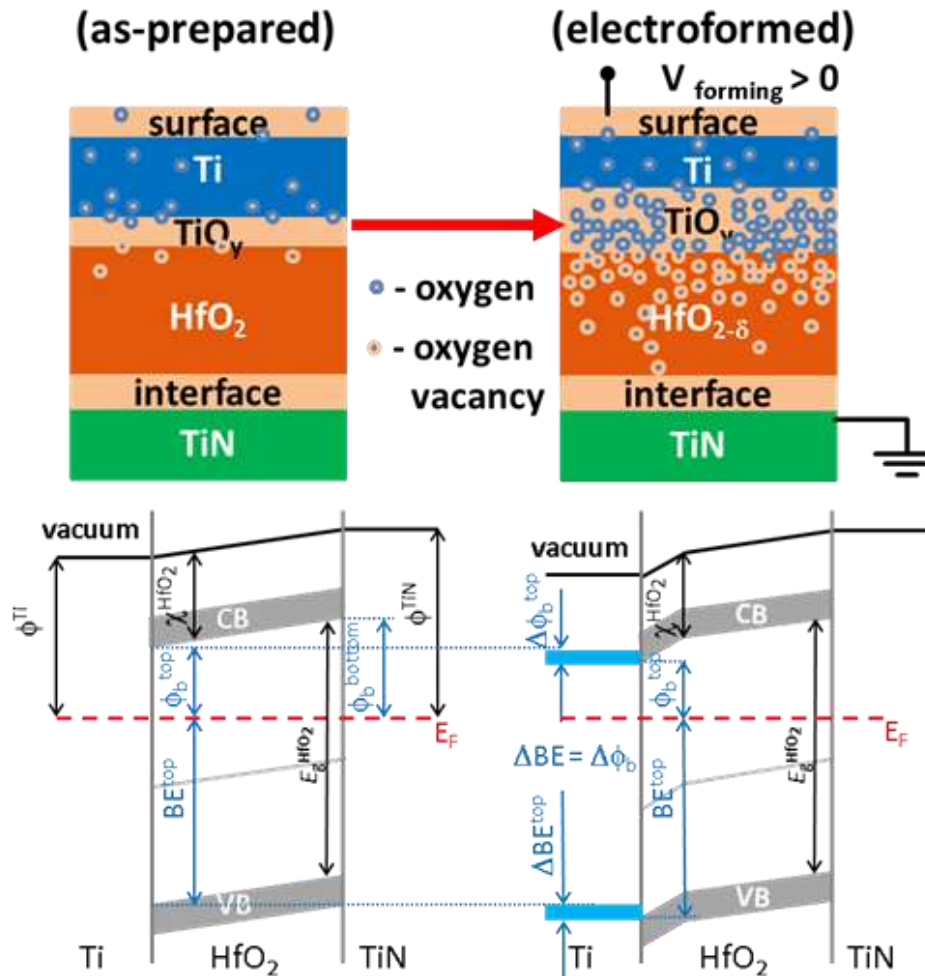


- $V_{O^{\bullet\bullet}}$ as a stable n-type defects in HfO_2 .
- We link the observed peak shift to an increase of the band bending at the interface because of higher space charge potential created by the higher concentration of $V_{O^{\bullet\bullet}}$ at the Ti/ HfO_2 interface.

Y. Lebedinskii et al., JAP 101, 074504 (2007).

J. Robertson, et al., Appl. Phys. Lett. 91, 132912 (2007).

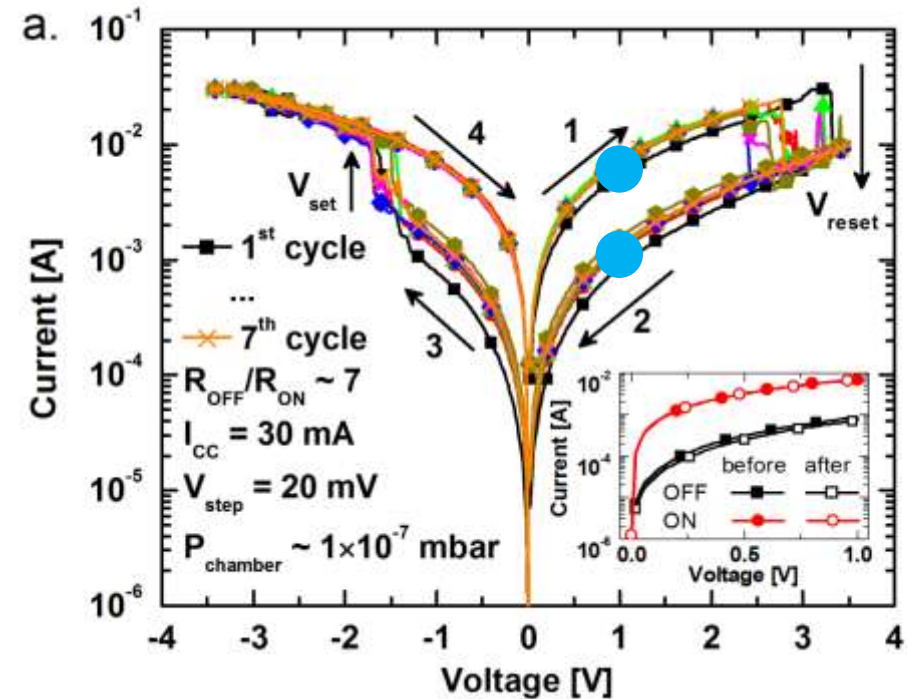
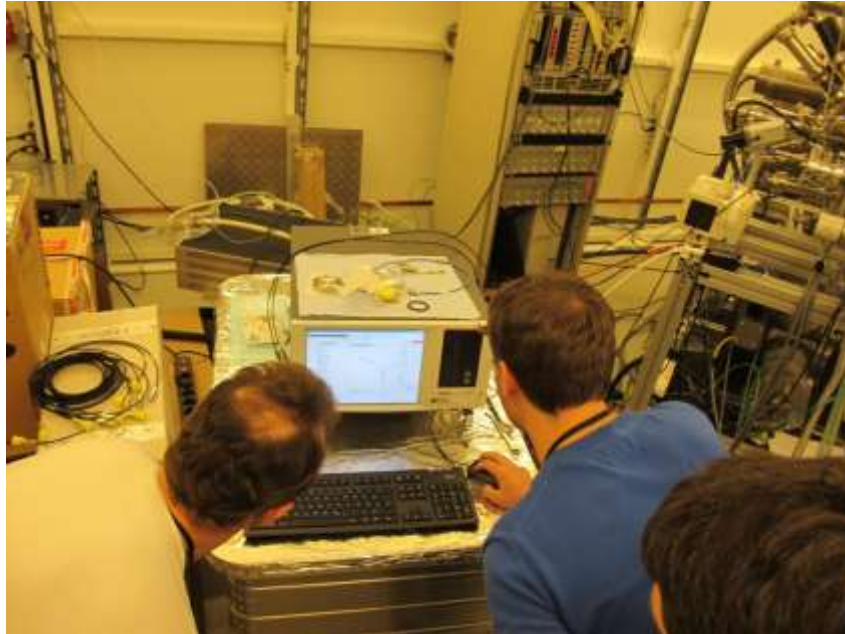
2.1. Proposed modifications caused by the electroforming



- Chemical modifications at the Ti/HfO₂ interface:
 - Increase of the Ti oxidation at the interface by oxygen-gettering activity of the Ti.
 - Creation of a Ti/TiO_x/HfO_{2-δ} structure.
- Electronic modifications at the Ti/HfO₂ interface:
 - Increase of the downward band bending due to higher concentration of *n*-type dopants (V_O^{••}).
 - Decrease of $\phi_b \rightarrow$ increase of the conduction

M. Sowinska et al., APL 100, 233509 (2012).

2.2. *in-operando* HAXPES: electrical results



- Successful *in-operando* resistive switching during HAXPES measurements:
 - 7 cycles with a $R_{\text{OFF}}/R_{\text{ON}}$ ratio of ~ 7 and at a pressure of 1×10^{-7} mbar,
 - HAXPES spectra recorded for the virgin-, OFF- and ON-states:
 - Ti 2p line,
 - Hf 4f,
 - O 1s.

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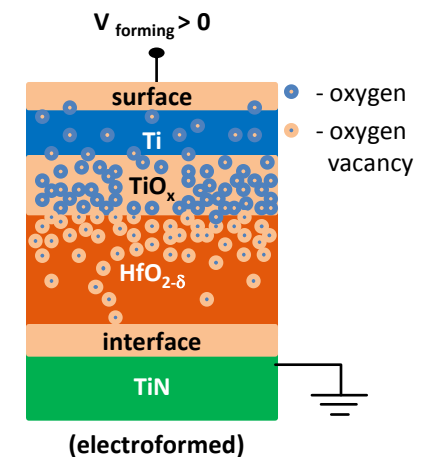
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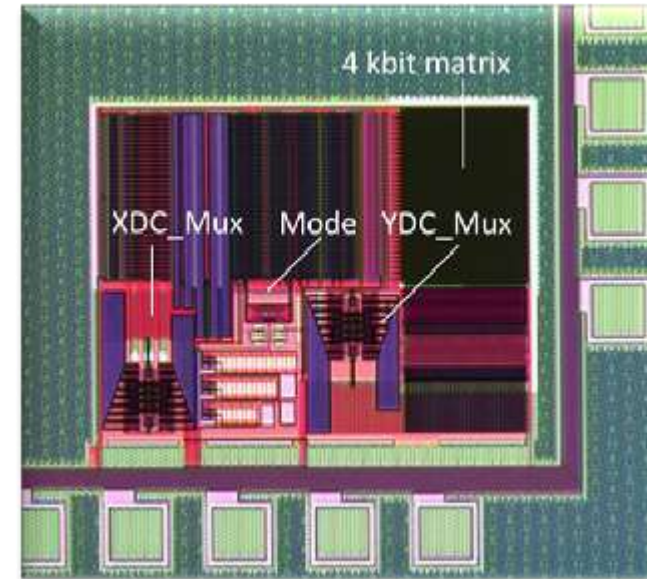
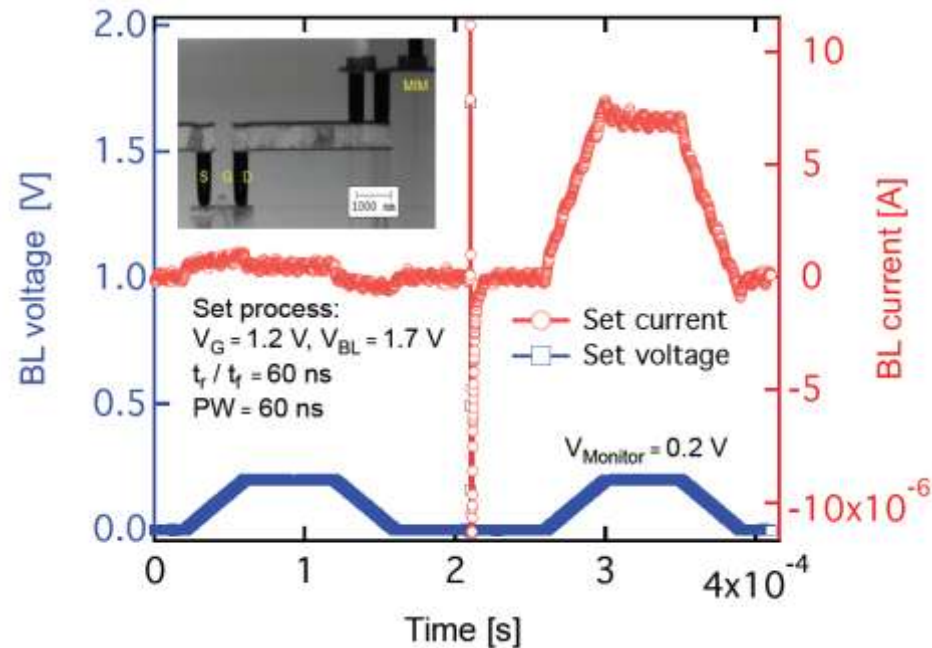
- HAXPES as a powerful technique for RRAM investigations:
 - non destructive analysis of buried interfaces,
 - *in-operando* experiment performed.
- Proposed modifications induced by the electroforming:
 - $V_{\text{forming}} > 0 \rightarrow$ oxygen migration towards TE \rightarrow Ti/HfO₂ interface oxidation,
 - removed oxygen atoms leave $V_{\text{O}}^{\cdot\cdot}$ in the HfO₂ \rightarrow *n*-type doping of the HfO_{2- δ} .
- Proposed RS mechanism in the Ti/HfO₂/TiN:
 - push-pull model of $V_{\text{O}}^{\cdot\cdot}$ migration as a function of voltage polarity,
 - TiO_x interface layer acts as an oxygen reservoir.



M. Sowinska et al., APL 100, 233509 (2012).

T. Bertaud et al., submitted to APL.

4. Outlook



- Pulse-induced *in-operando* HAXPES measurements:
 - To perform electrical measurements in adequation with future integrated devices,
 - To understand the physics of the RS degradation,
- A 4 kbit array based on Ti/HfO₂/TiN 1T1R cells was recently processed in IHP's Si CMOS technology and is currently under characterization.

D. Walczyk et al., to be presented at ISCDG, Grenoble (2012).

Thank you for your attention!

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