



**UNIVERSITÀ  
DEGLI STUDI  
DI MILANO**

 **CNR - IMM**  
Laboratorio MDM

# Nanoscale resistive switching devices based on metal oxides

**Jacopo Frascaroli**

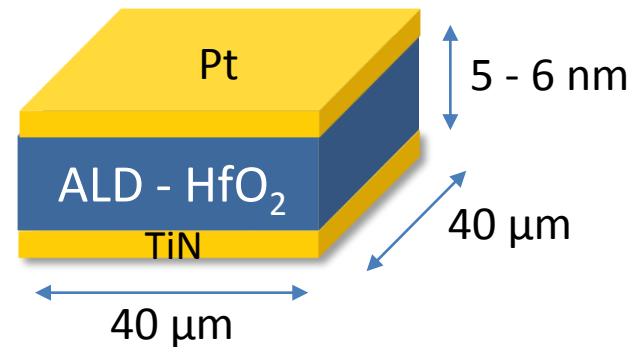
**Supervisor Prof. Alberto Pullia**

**Co-Supervisor Dr. Sabina Spiga**

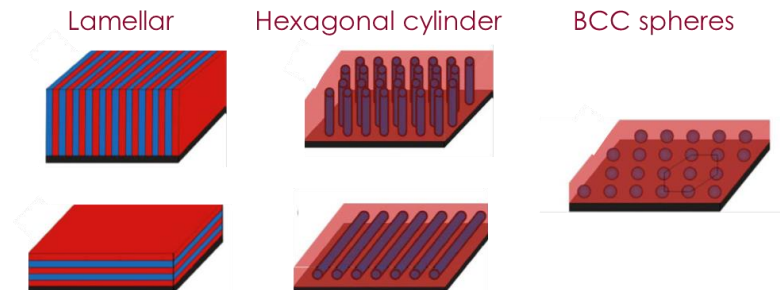
# Outline

- ▶ Resistive switching:  
phenomenology and applications

- ▶ Device characterization

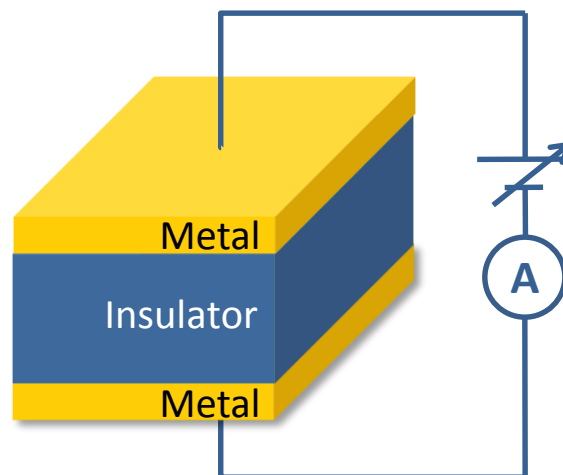


- ▶ Nano devices using block copolymers



# Resistive switching in MIM structures

Capacitor-like structure with electrically alterable resistivity

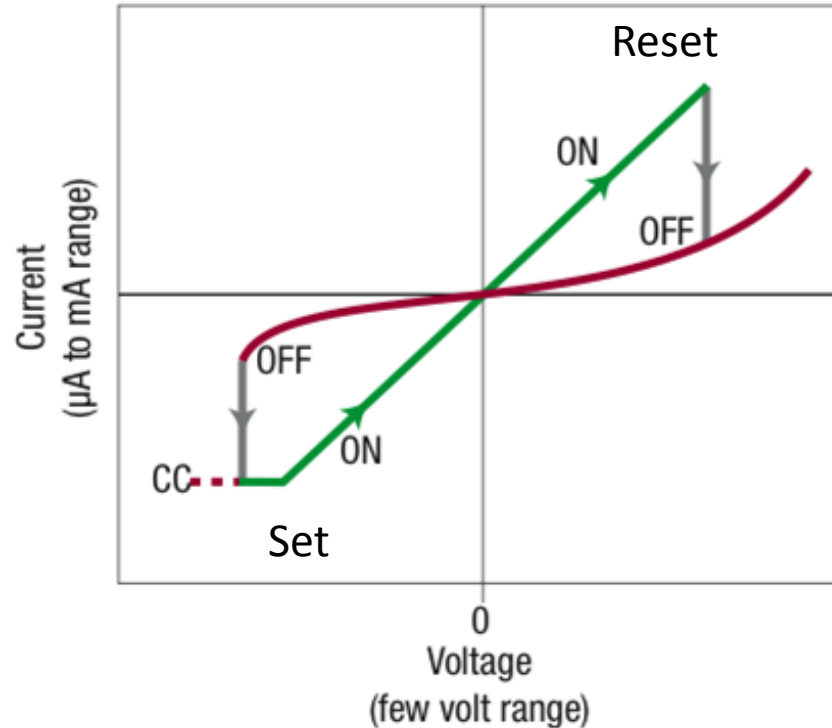


A large variety of insulating materials shows resistive switching properties:

- ▶ Transition metal oxides (TMO)
- ▶ metal doped perovskites
- ▶ Polymers
- ▶ ...

# Switching behavior

Applying a proper potential difference at the two electrodes, the device resistance changes

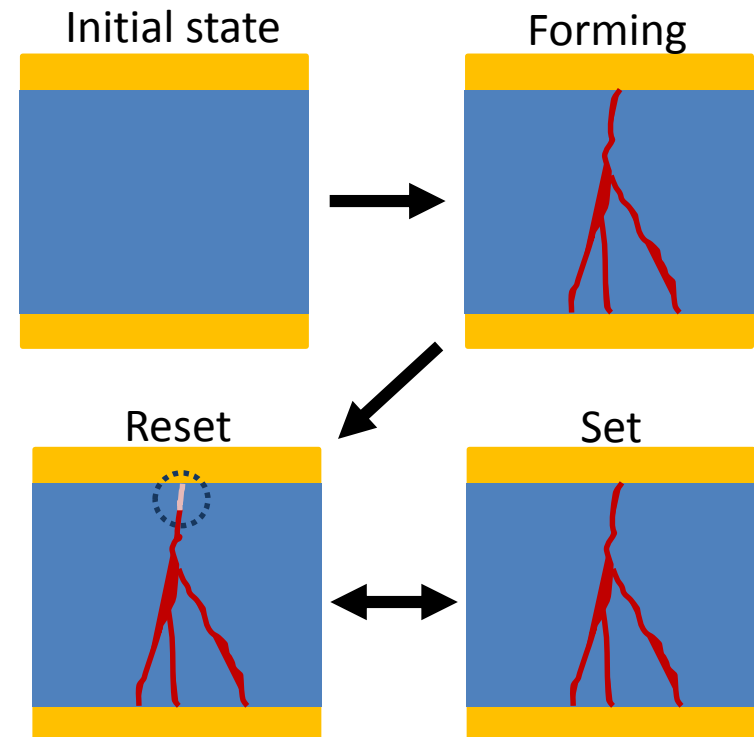
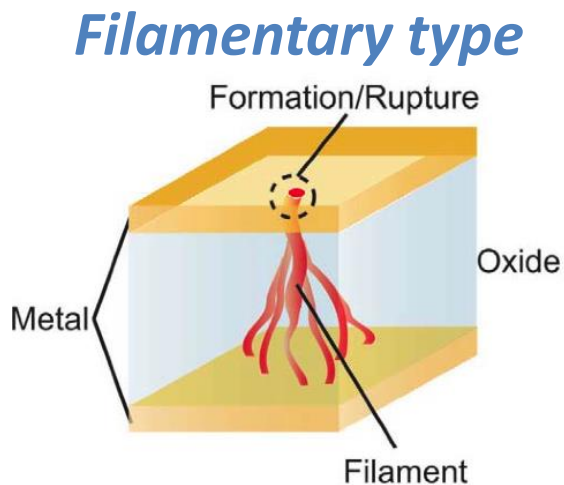


# Resistive switching mechanism in TMO

*R. Waser, Adv. Mater. 2009 and ref. therein;*  
*A. Sawa, Materials Today 2008*

The anion motion leads to a **valence change** of the metal sublattice (cations)  $\rightarrow$  R change

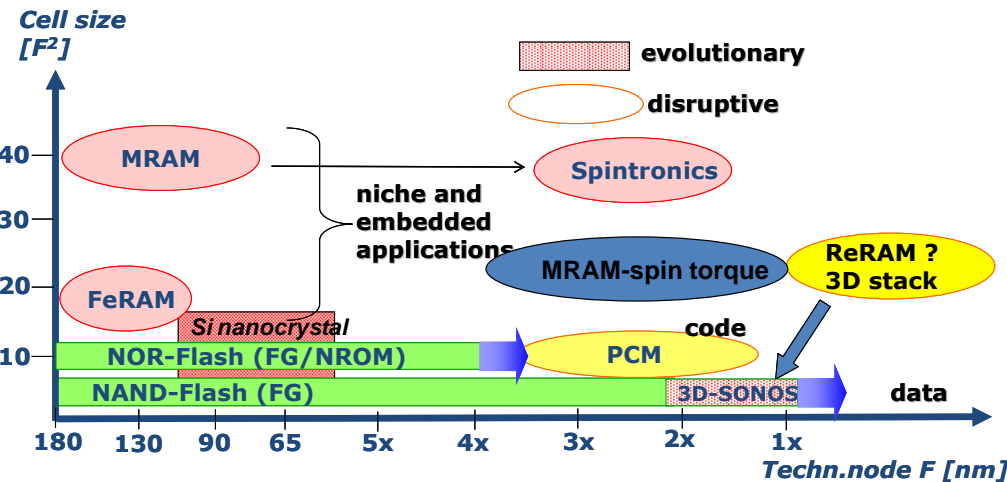
Mobile species:  
Oxygen ions – oxygen vacancies



# Resistive switching applications

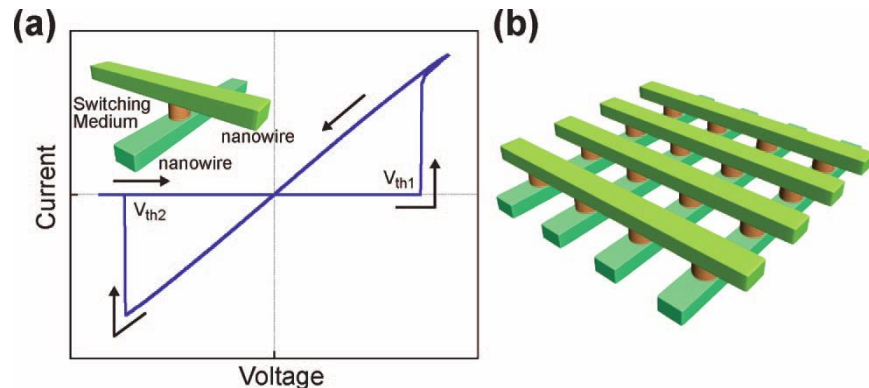
## Memory

- ▶ Very simple structure
- ▶ Highly **scalable**
- ▶ CMOS process compatibility
- ▶ Low switching time
- ▶ Low power consumption



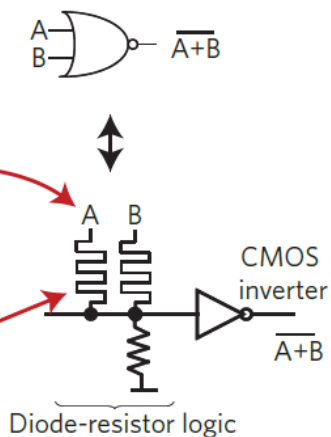
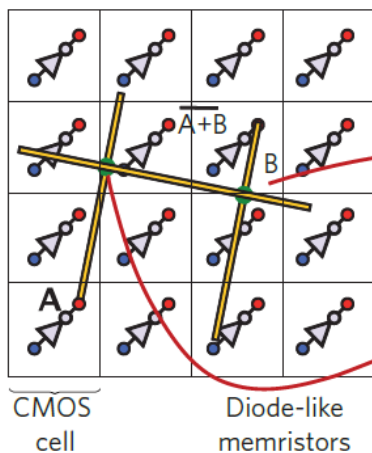
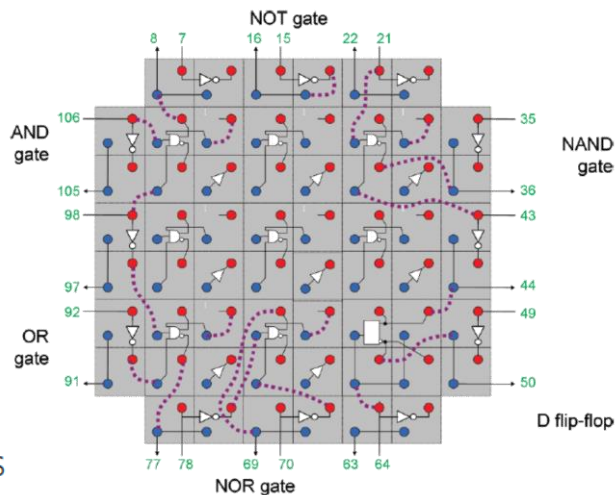
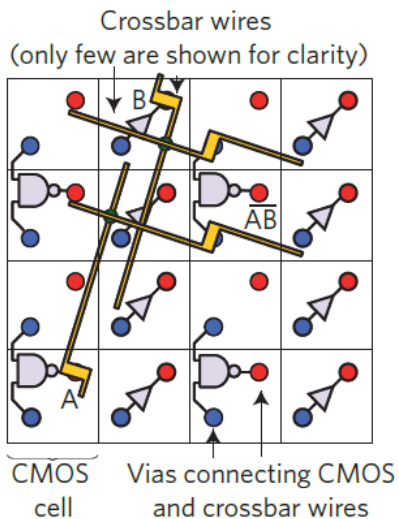
Need for a lithographic technology to enable cell scaling

## Crossbar array

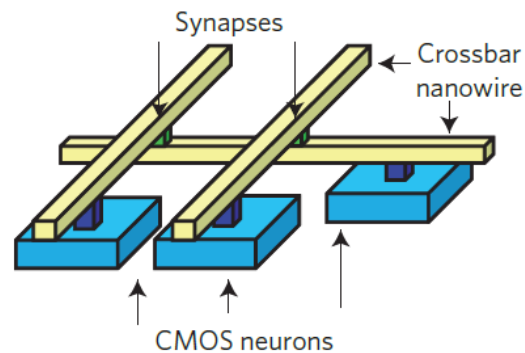
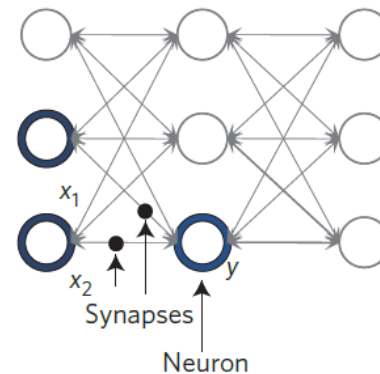


# Resistive switching applications

## Logic

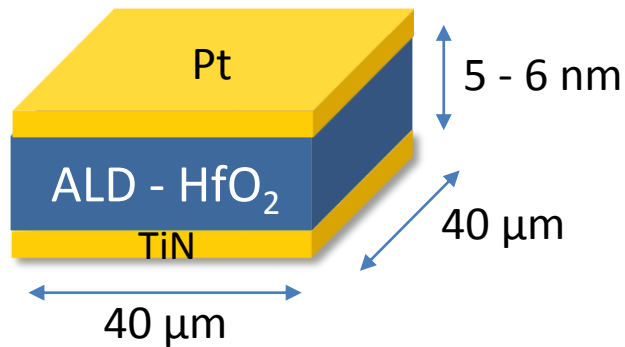


## Artificial neural networks

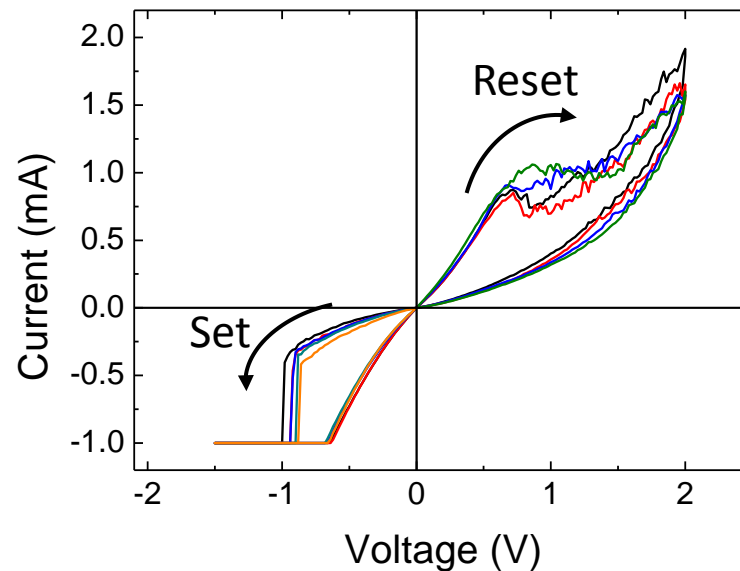


Yang, J. Joshua, Dmitri B. Strukov, and Duncan R. Stewart. "Memristive devices for computing" *Nature nanotechnology* 8.1 (2012)

# Experimental results



*Microscopic device  
characterization*



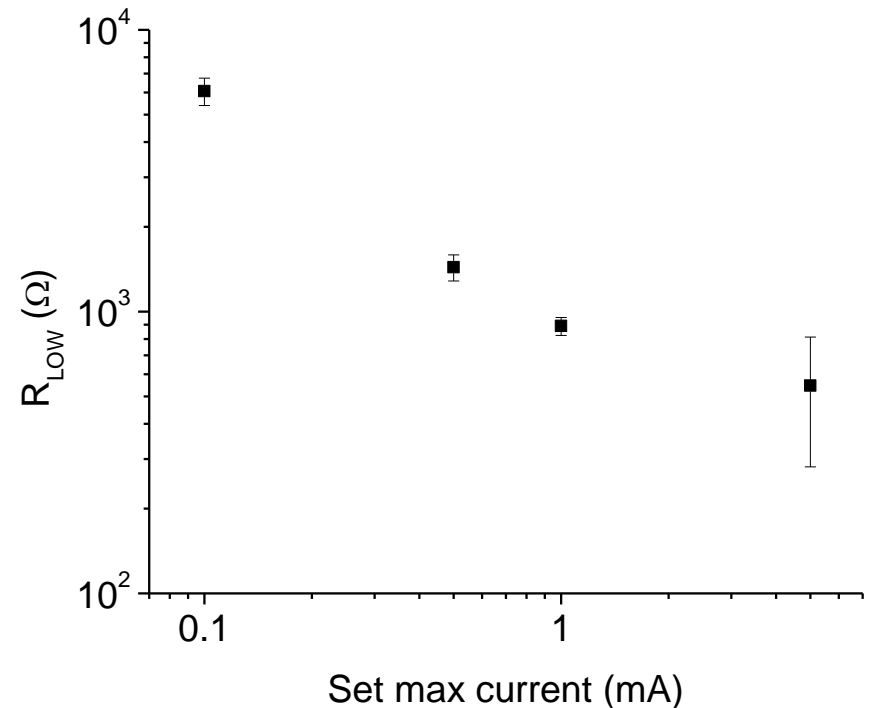
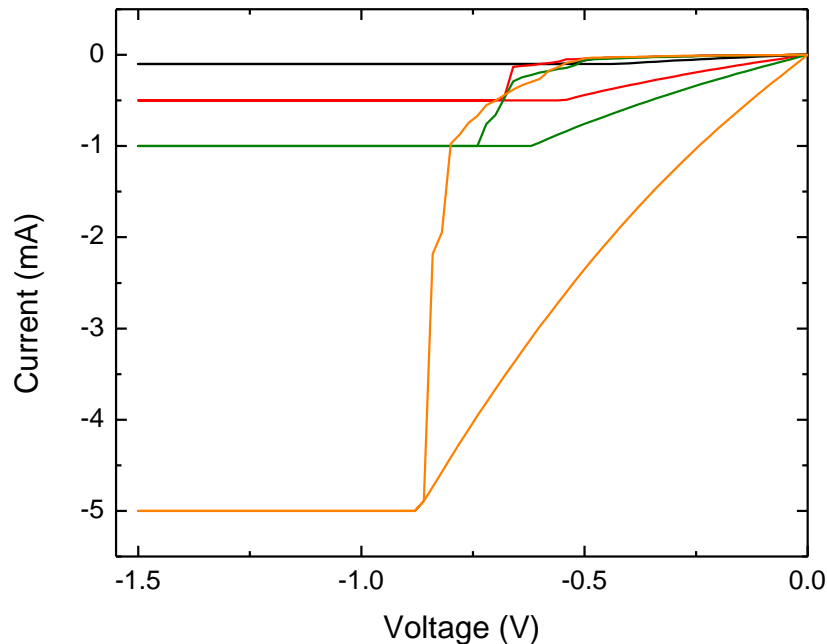
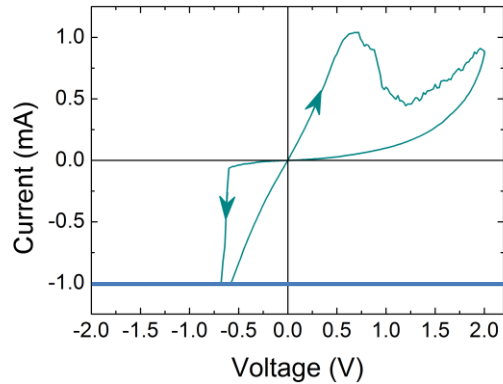
Up to 2000 reproducible  
switching cycles demonstrated



# Experimental results

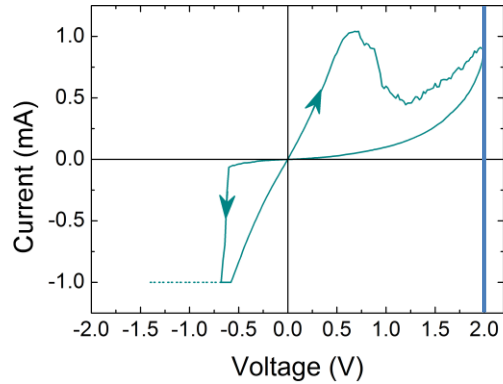
## *Electrical characterization*

Possible to tune the low resistance  
varying the maximum allowed current  
during set (current compliance)

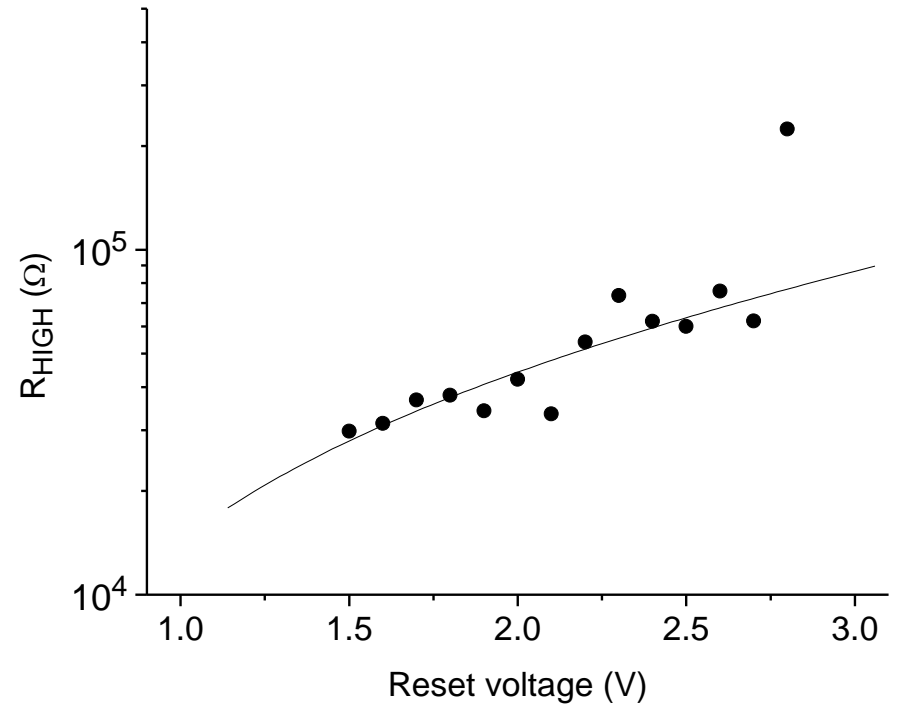
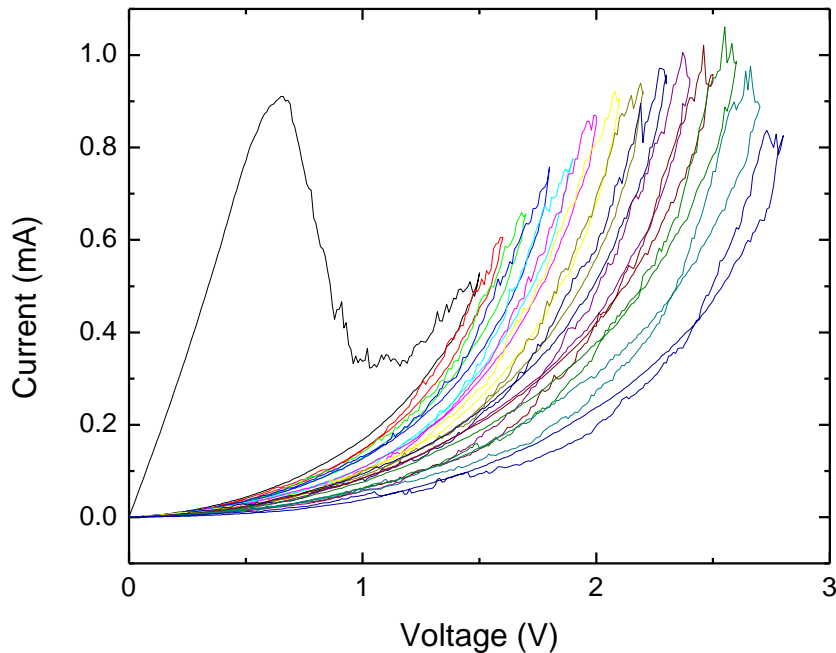


# Experimental results

## *Electrical characterization*



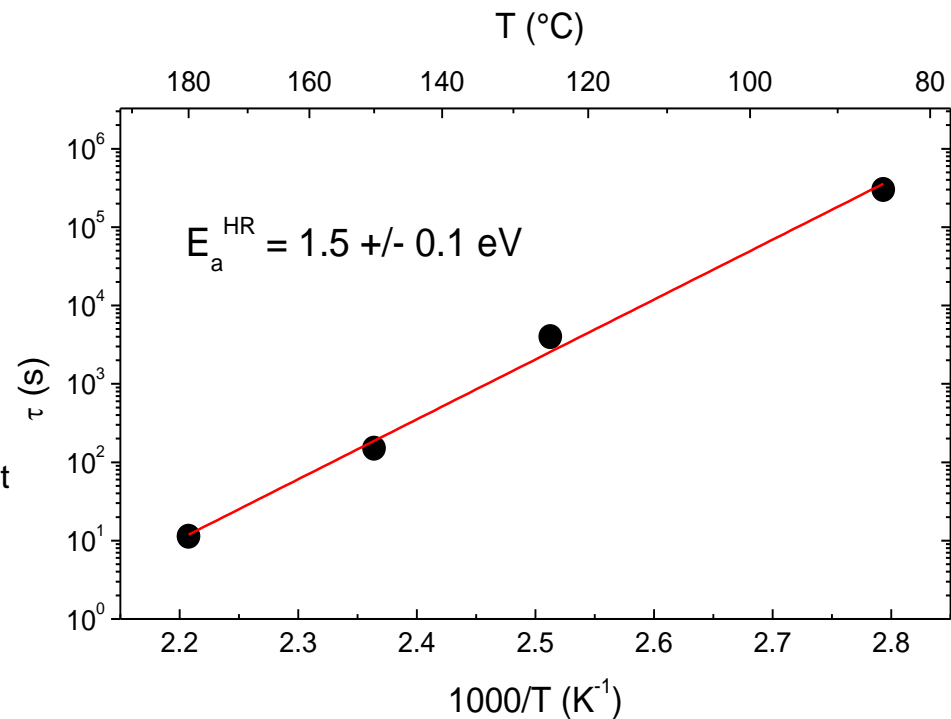
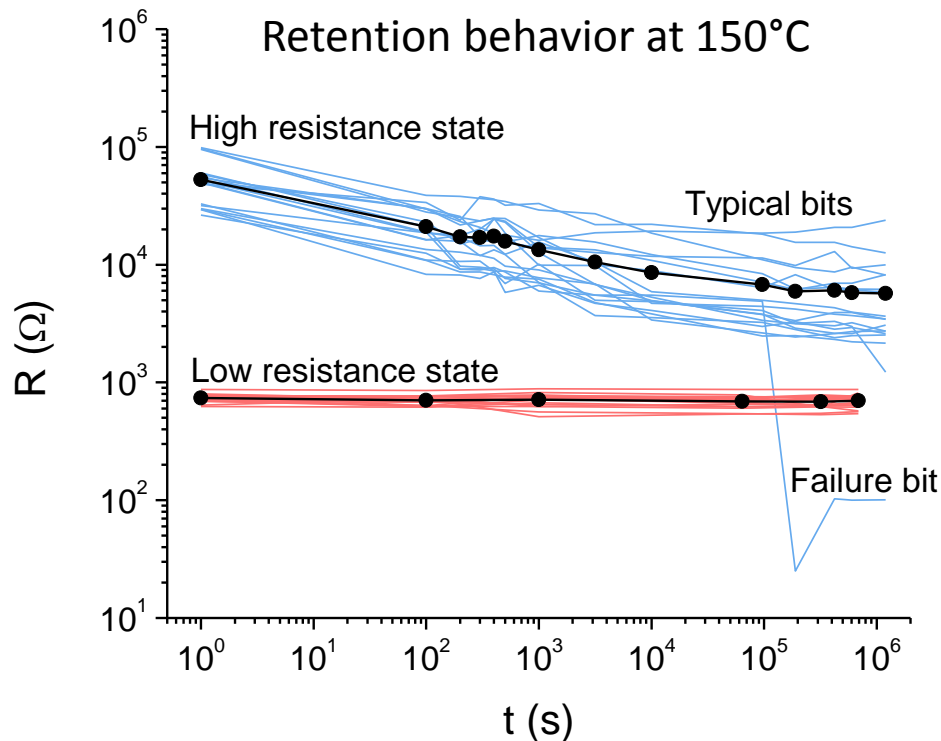
Possible to tune the high resistance varying the maximum reset voltage



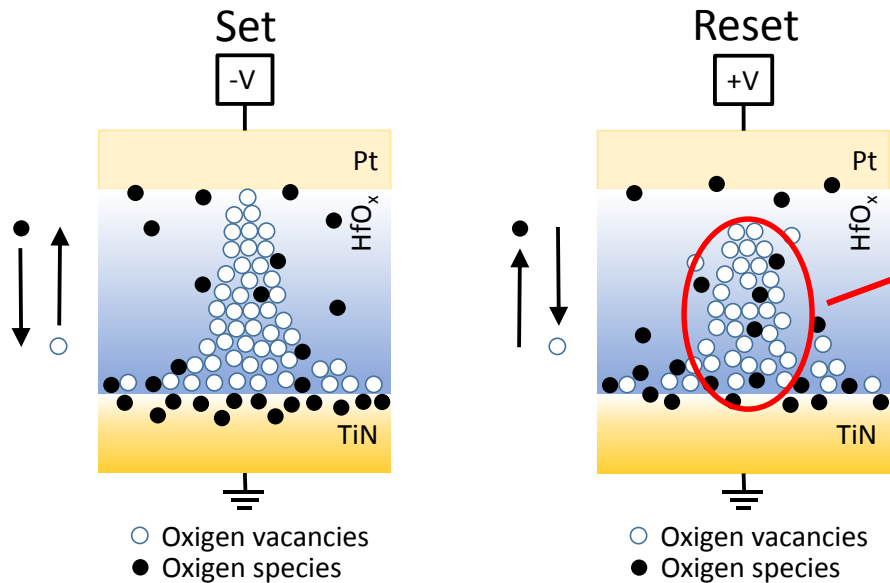
# Experimental results

## Retention behavior

- Two different retention behaviors
- Arrhenius dependence of the retention time on temperature



# Experimental results



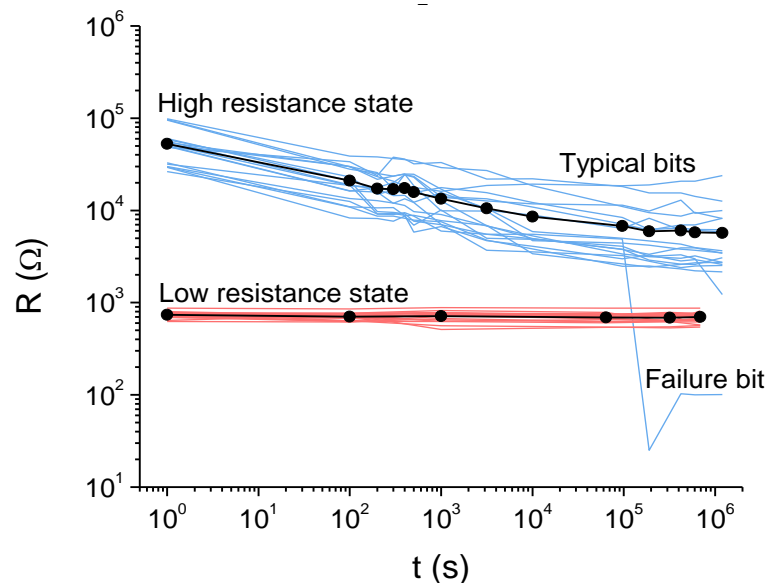
## Retention modeling

### Slow retention loss

- Modification of the residual filament
- The TiO<sub>x</sub>N<sub>y</sub>/HfO<sub>2</sub> interface may play a role

### Fast retention loss

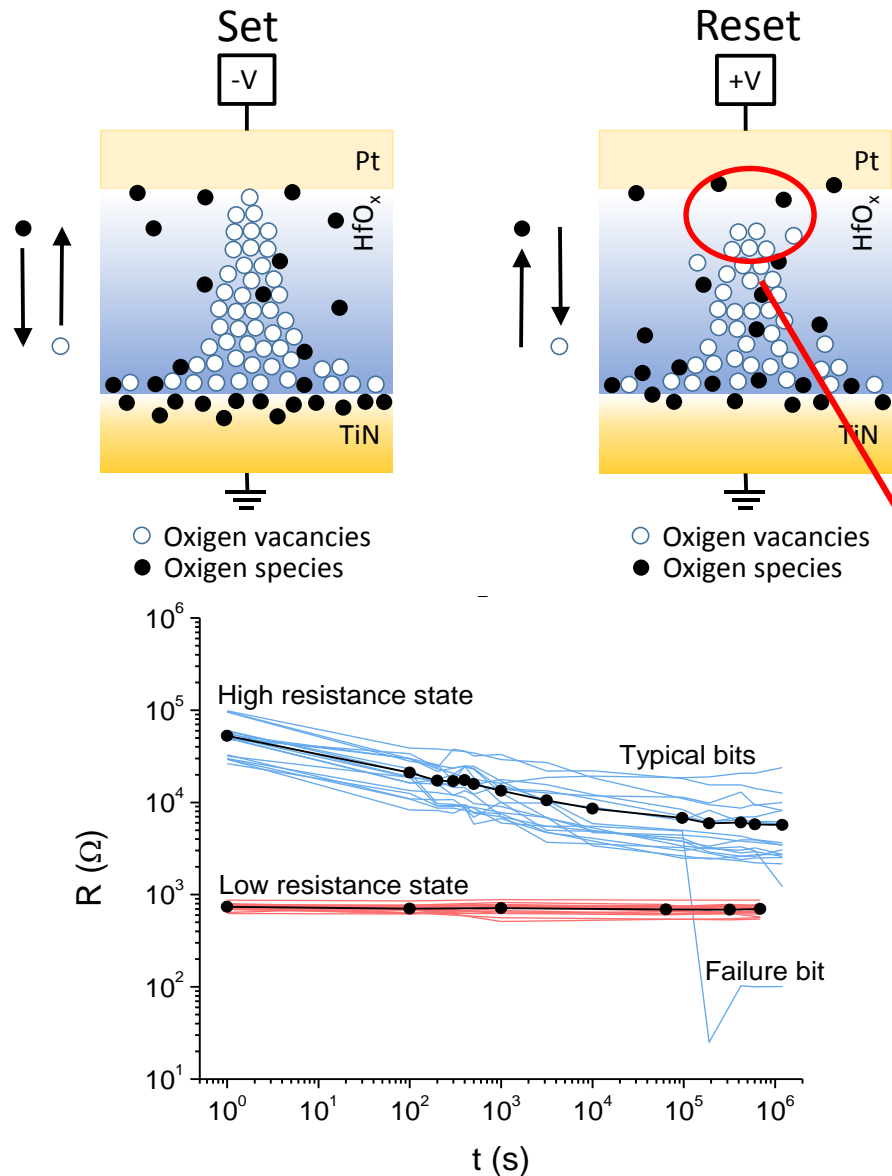
- Very narrow gap. Diffusion of a few vacancies can reconstruct the conductive channel



J. Frascaroli et al., in preparation



# Experimental results



## Retention modeling

### Slow retention loss

- Modification of the residual filament
- The TiO<sub>x</sub>N<sub>y</sub>/HfO<sub>2</sub> interface may play a role

### Fast retention loss

- Very narrow gap. Diffusion of a few vacancies can reconstruct the conductive channel

J. Frascaroli et al., in preparation

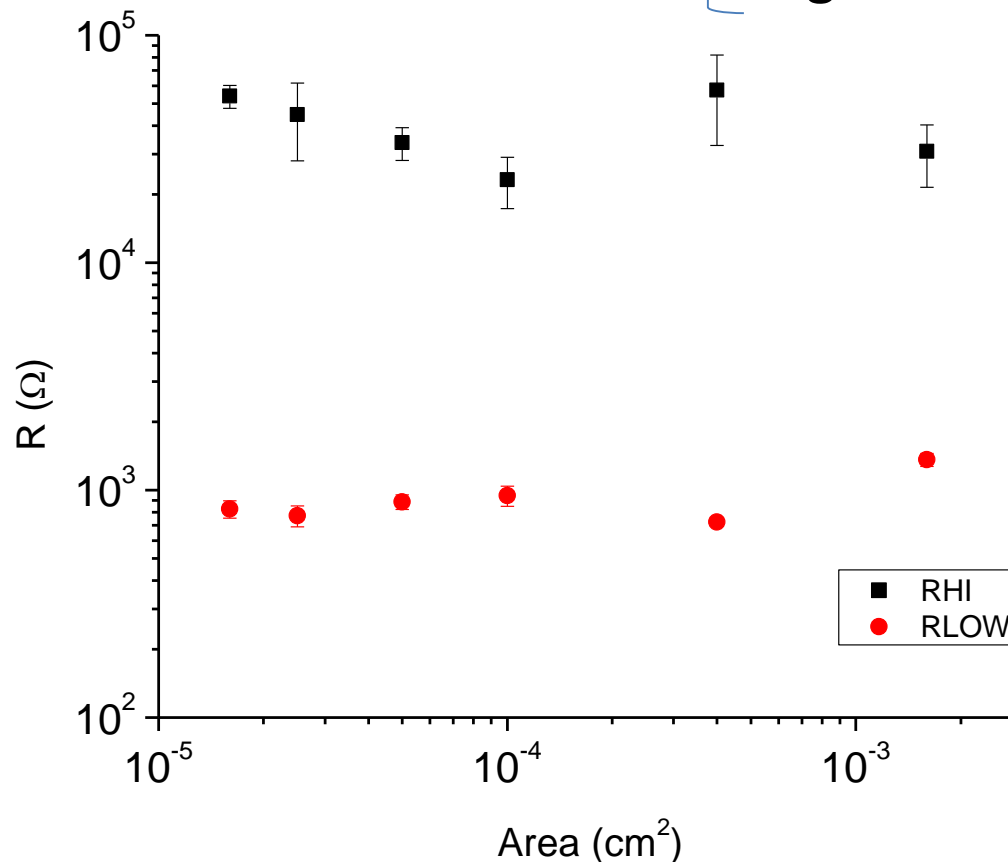


# Experimental results

## *Device area dependence*

No area dependence of the resistance

Filamentary conduction  
High scalability potential



# Previous works

B. Govoreanu et al.  
IEEE *Electron Devices Meeting* (2011)

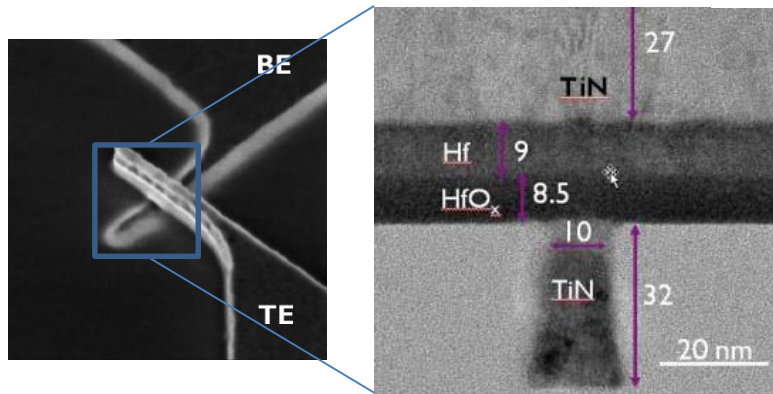
ReRAM nanoscaling

D. Perego et al.  
*Nanotechnology* 24 (2013)

Top-down

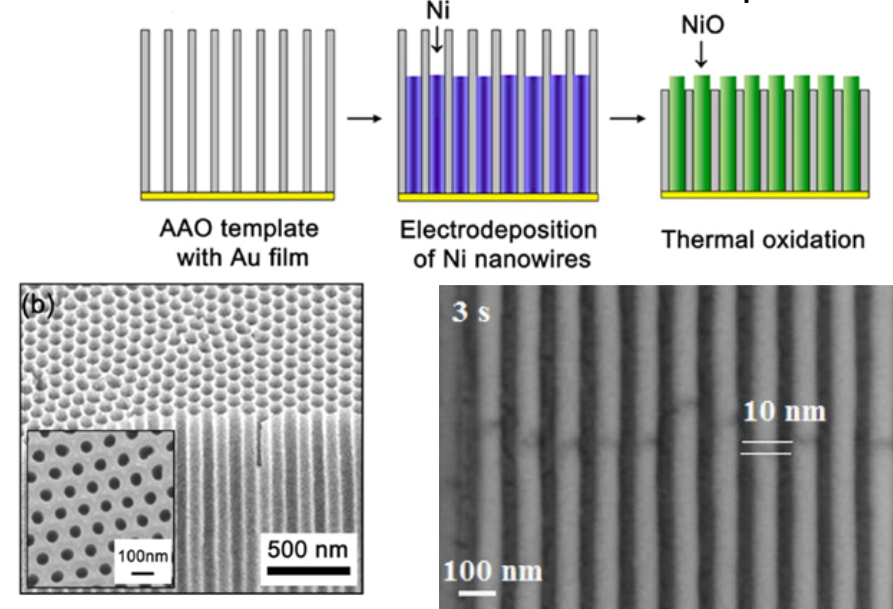
Bottom-up

Electron beam lithography



- Slow and serial lithographic technique
- Limited number of devices

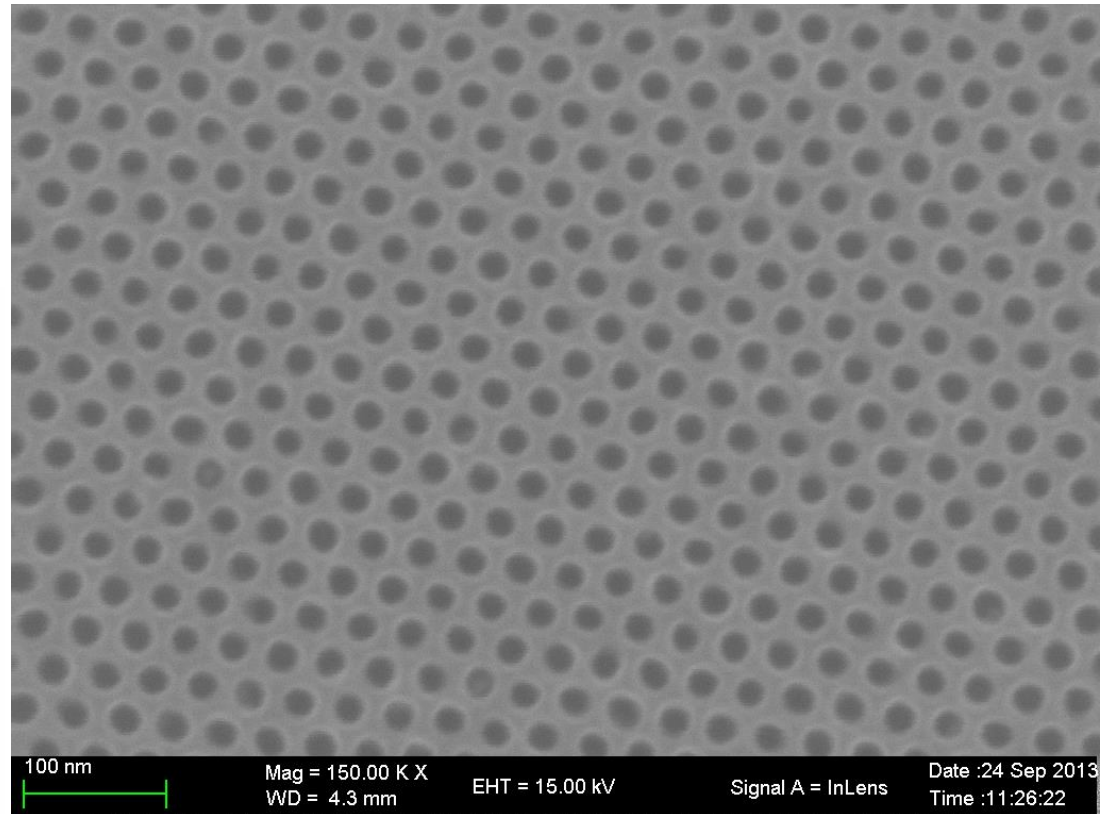
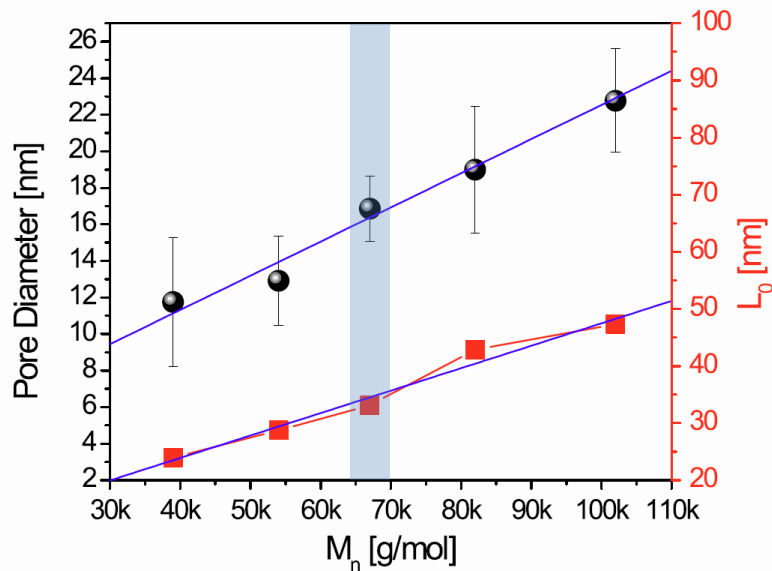
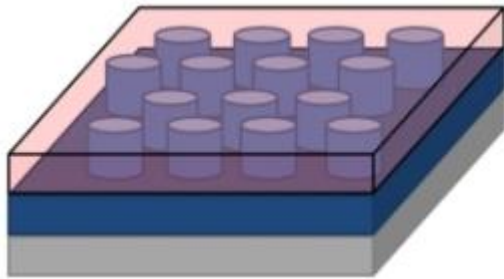
Anodized-Aluminium Oxide templates



- Not compatible with actual technology

# Block Copolymers

## Hexagonal cylinders template

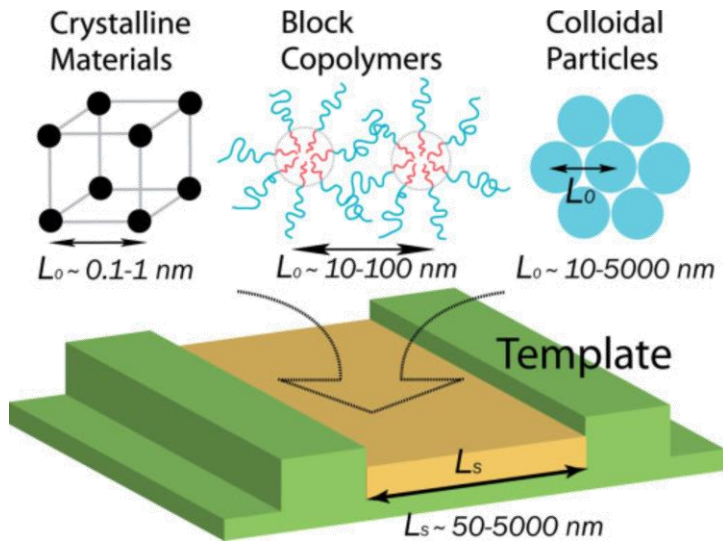


Experimental result: block copolymers self assembling of hafnium dioxide

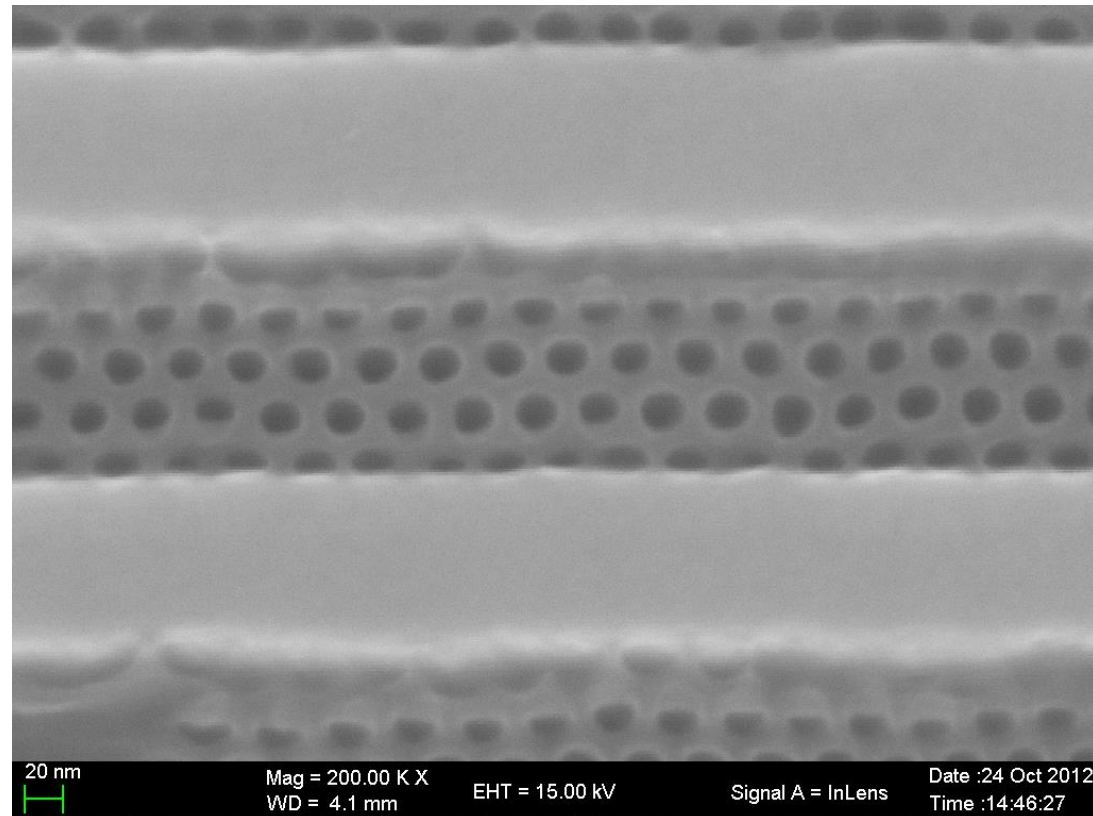


# Graphoepitaxy

M. Perego et al. Nanotechnology 24, 8 (2013)



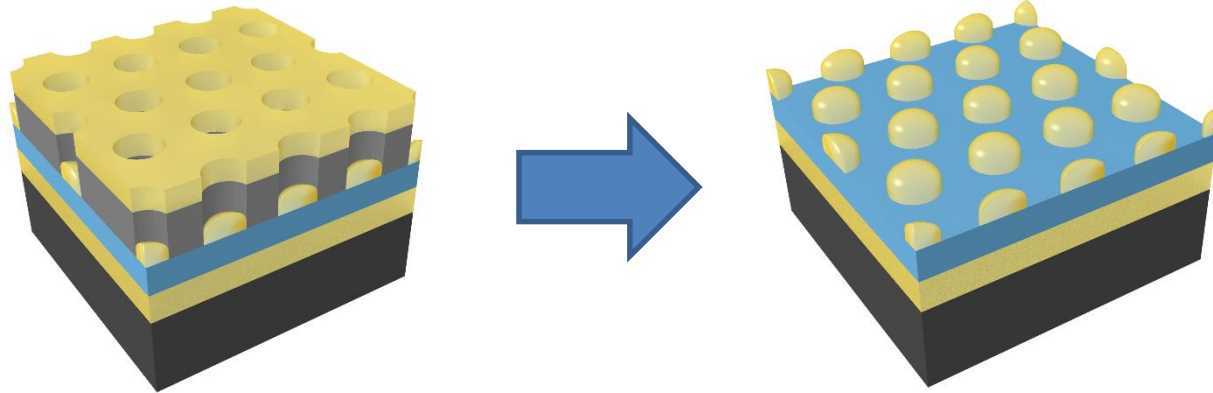
Pre-patterned structures can be used to drive the self assembly of block copolymers



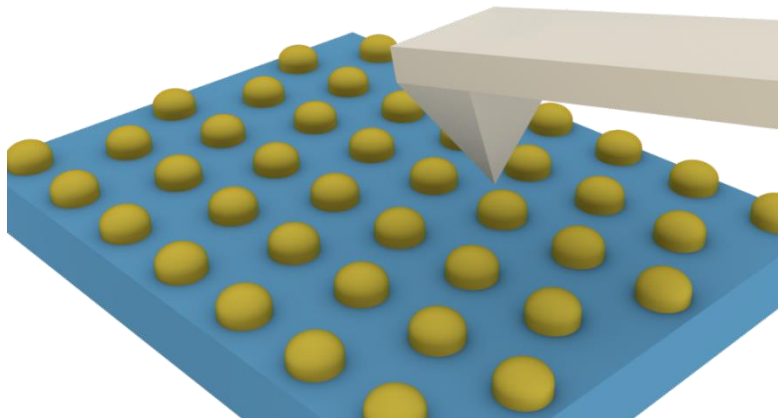
Courtesy of F. Ferrarese Lupi, MDM IMM-CNR

# Top electrode nano patterning

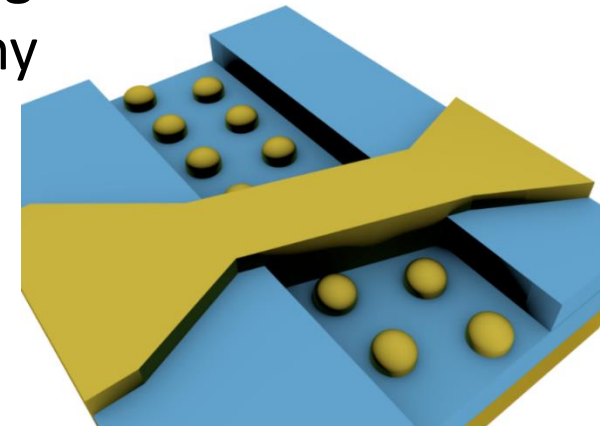
## *Lift-off process*



Electrical measurements  
with c-AFM



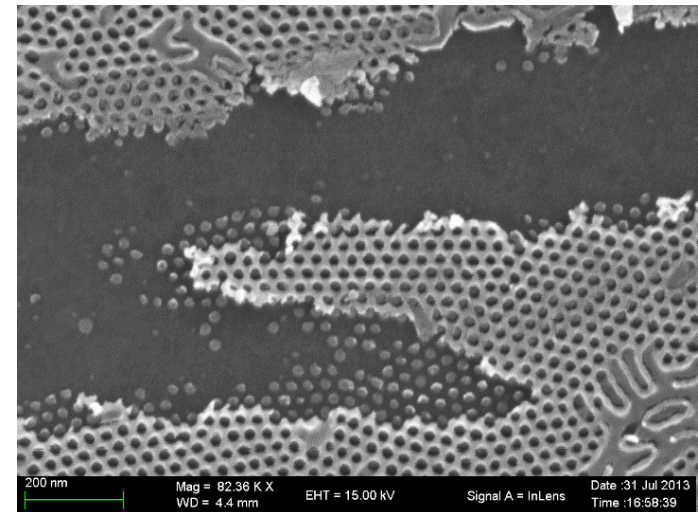
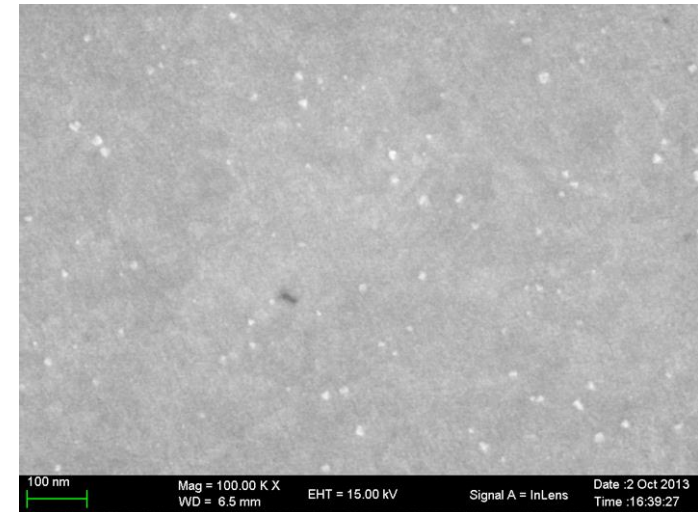
Combining directed self-  
assembling with electron beam  
lithography



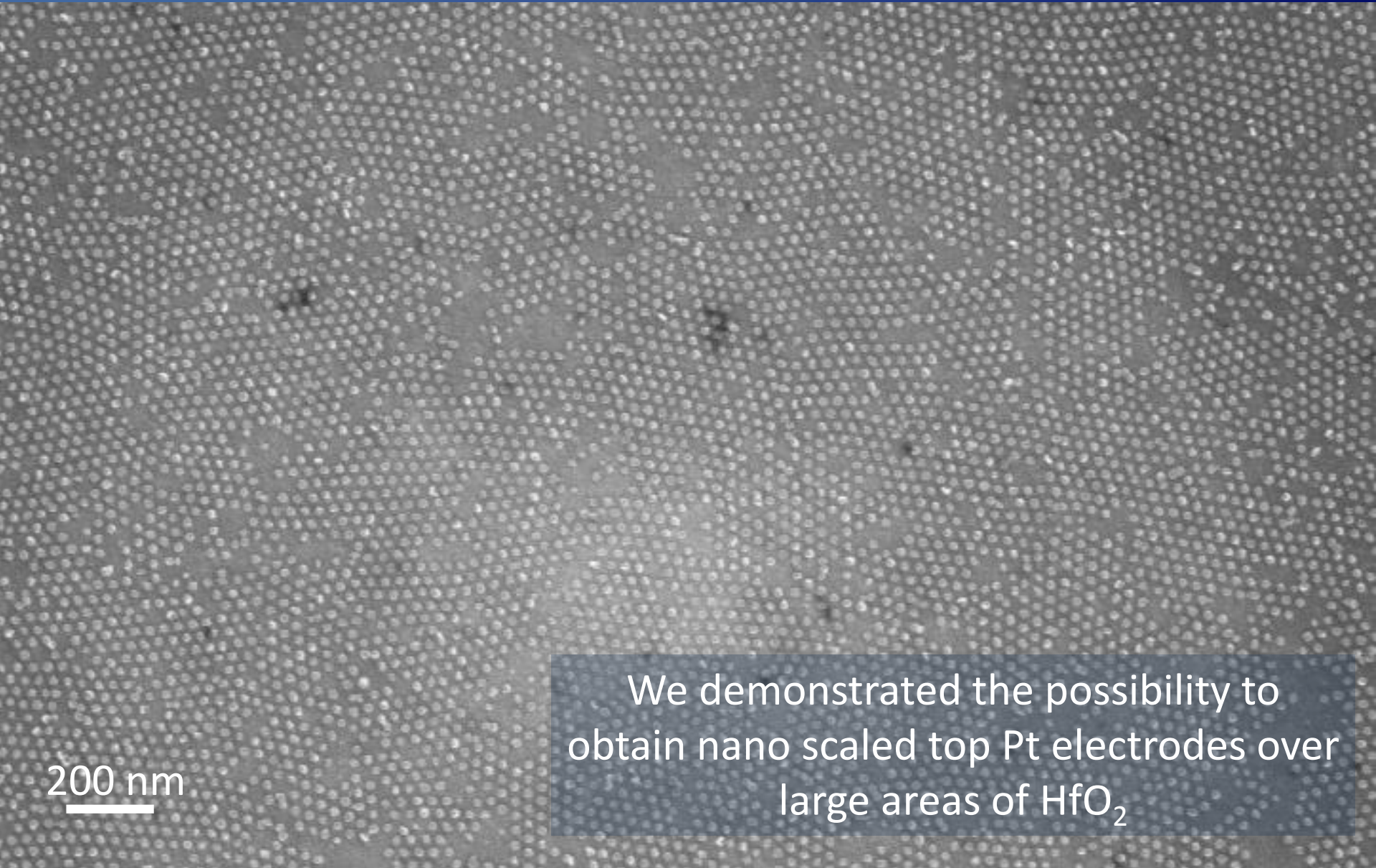
# Experimental result

## *Lift-off process study*

Substrate: ALD – HfO <sub>2</sub>		
Metal	Physical deposition	Thickness
Tungsten (W)	sputtering	5 nm
Platinum (Pt)	sputtering	5 nm
	ebeam	5 nm



# Experimental result




200 nm


We demonstrated the possibility to obtain nano scaled top Pt electrodes over large areas of  $\text{HfO}_2$




# Current activity



CNR - IMM  
Laboratorio MDM



UNIVERSITÀ  
DEGLI STUDI  
DI MILANO



INRiM  
ISTITUTO  
NAZIONALE  
DI RICERCA  
MICROLOGICA

## Hafnium oxide-based resistive switching devices

J. Frascaroli <sup>a,b,c</sup>, F. Volpe <sup>a</sup>, F. F. Lupi <sup>a</sup>, M. Perego <sup>a</sup>, L. Boarino <sup>b</sup>, and S. Spiga <sup>a</sup>

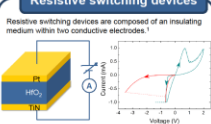
<sup>a</sup> Laboratorio MDM, IMM-CNR, Via C. Olivetti 2, 20041 Agrate Brianza (MB), Italy  
<sup>b</sup> INRiM, NanoFacility, Division Electromagnetism, Strada delle Cacce 91, 10135 Torino, Italy  
<sup>c</sup> Università degli studi di Milano, Via Celoria 16, 20133 Milano, Italy

Resistive switching devices are capacitor-like structures that exhibit a reversible resistance change on applying a potential difference at the two electrodes. The resistance switching effect is at the basis of the ReRAM memory design, one of the main candidates for future memory technology applications given its simple structure and scalability potential. Among the wide variety of materials showing resistive switching behavior, transition metal oxides proved their advantageous properties in terms of low power, fast switching mechanism and CMOS process compatibility.

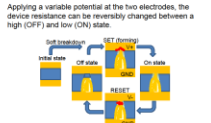
We tested the electrical switching properties of atomic layer deposited (ALD) Hafnium oxide cells employing a TiN bottom electrode and Pt top electrodes defined using optical lithography. We also examined the cells resistance retention behavior at various temperatures finding two different types of high resistance loss processes. Our work on HfO<sub>2</sub>-based resistive switching devices will continue testing the possibility of exploiting polymeric self-assembled templates and electron beam lithography for the fabrication of nanostructured devices with a lateral dimension down to 20 nm.

### Resistive switching devices

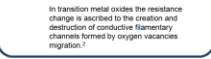
Resistive switching devices are composed of an insulating medium within two conductive electrodes.<sup>1</sup>



Applying a variable potential at the two electrodes, the device resistance can be reversibly changed between a high (OFF) and low (ON) resistance.



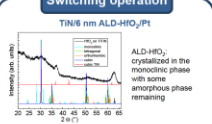
In transition metal oxides the resistance change is ascribed to the creation and destruction of conductive filamentary channels formed by oxygen vacancies migration.<sup>2</sup>



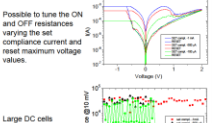
### Switching operation

TiN/nm ALD-HfO<sub>2</sub>/Pt

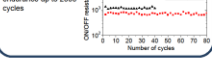
ALD-HfO<sub>2</sub> crystallized in the monoclinic phase with some amorphous phase remaining.



Possible to tune the ON and OFF resistance varying the set compliance current and reset maximum voltage values.




Large DC cells endurance up to 2000 cycles.

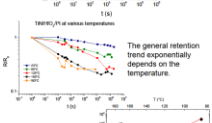


### Cells retention behavior

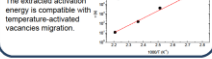
Two different types of retention behavior were detected as a function of time for the high resistance state.



The general retention trend exponentially depends on the temperature.




The extracted activation energy is compatible with temperature-activated vacancies migration.



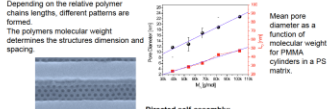
### Nano scaling

### Block copolymers self assembling


Block copolymers consist of two or more chemically different polymer chains joined covalently at their ends. Upon annealing, block copolymers can self-assemble in regular patterns. Vertically aligned PMMA cylinders inside a PS matrix can be selectively removed, forming a self-assembled tetragonally-packed template.<sup>1</sup>



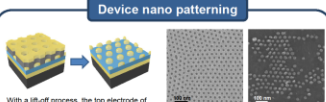
Depending on the relative polymer chains lengths, different patterns are formed. The polymers molecular weight determines the structures dimension and spacing.



Directed self-assembly: With a pre-patterned surface, the self-assembling process can be externally directed.<sup>2</sup>



### Device nano patterning

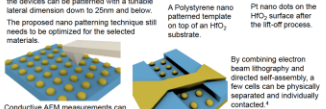


With a lift-off process, the top electrode of the devices can be patterned with a tunable lateral dimension down to 20nm and below. The proposed nano patterning technique still needs to be optimized for the selected materials.

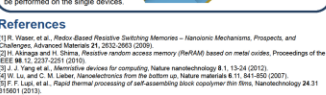
A Polystyrene nano patterned template on top of an HfO<sub>2</sub> substrate.

Pt nano dots on the HfO<sub>2</sub> surface after the lift-off process.

By combining electron beam lithography and directed self-assembly, a few cells can be physically separated and individually contacted.<sup>3</sup>



Conductive AFM measurements can be performed on the single devices.



### Acknowledgment

C. Traversi (IMM) is gratefully acknowledged for XPS data, while S. Binello (INRiM) is acknowledged for sputtering deposition and ITRM discussions. Part of this work was supported by the MOORE Project (Fondazione Cariplo): "Advanced Metal-Oxide heterostructures for nanoscale ReRAM" (01/14/2010 - 31/01/2013). For additional information: [www.imm.cnr.it](http://www.imm.cnr.it) [www.inrim.it](http://www.inrim.it) [www.unimi.it](http://www.unimi.it) [www.fondazione-cariplo.it](http://www.fondazione-cariplo.it) [www.moores-project.com](http://www.moores-project.com) [www.safira-segna.com](http://www.safira-segna.com)

### References

[1] H. Yoon, et al., *Hydroxide-Based Resistive Switching Memories - Nanoscale Mechanisms, Prospects, and Challenges*, *Advanced Materials* 21, 2632-2663 (2009).  
 [2] H. Adachi and H. Shima, *Resistive random-access memory (ReRAM) based on metal oxides*, *Proceedings of the IEEE* 98, 2257-2281 (2010).  
 [3] L. A. Vlasov, et al., *Nanoscale devices for computing*, *Nature nanotechnology* 6, 1, 13-24 (2012).  
 [4] W. Lu, and C. N. Laiser, *Nanoelectronics from the bottom up*, *Nature materials* 6, 1, 84-89 (2007).  
 [5] T. L. Liu, et al., *Periodic thermal processing of self-assembling block copolymer thin films*, *Nanotechnology* 24, 315601 (2013).  
 [6] M. Perego, et al., *Collective behavior of block copolymer thin films with periodic topographical structures*, *Nanotechnology* 24, 245201 (2013).

ESONN 2013 – 25 August – 14 September 2013 – Grenoble, France

- ▶ Device characterization and study of the retention behavior
- ▶ Implementing the block copolymer self-assembling on HfO<sub>2</sub>
- ▶ Study of the lift-off process for top electrodes nano patterning



# Future outlook

- ▶ Electrical characterization of the nano devices using C-AFM to inspect the physical properties at the nano scale
- ▶ Find alternative strategies for the fabrication of resistive switching devices using block copolymers self-assembly



# The end



# Resistive switching mechanism

H. Akinaga and H. Shima, *Proceedings of the IEEE* 2010

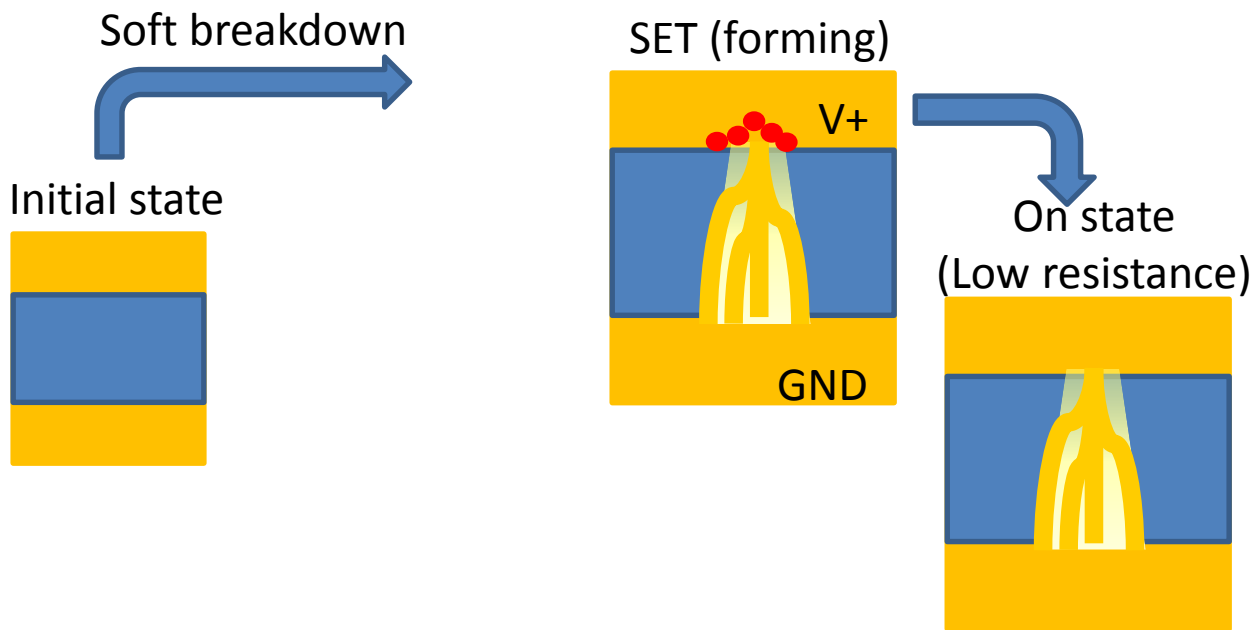
► Fresh cell

Initial state

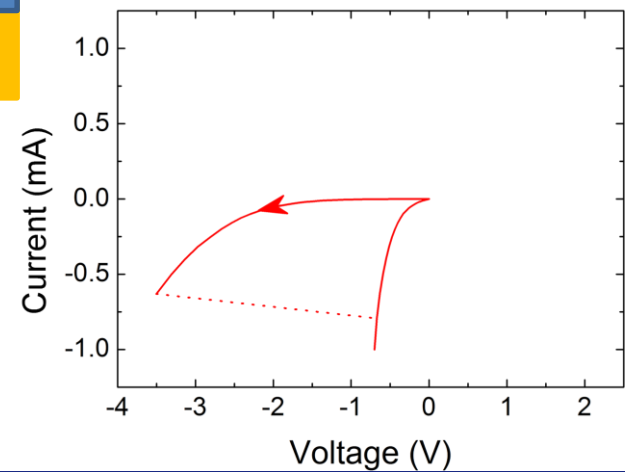




# Resistive switching mechanism

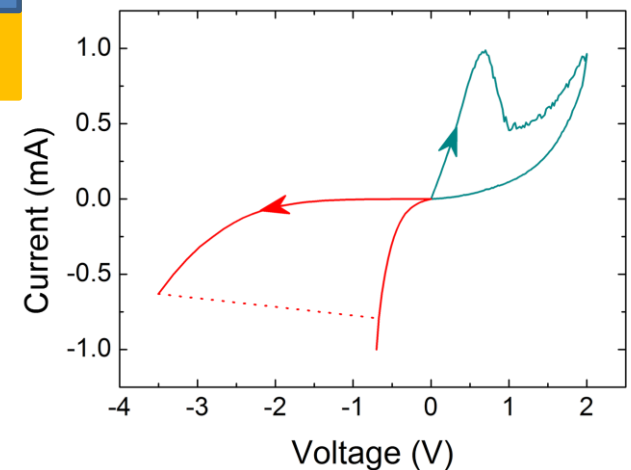
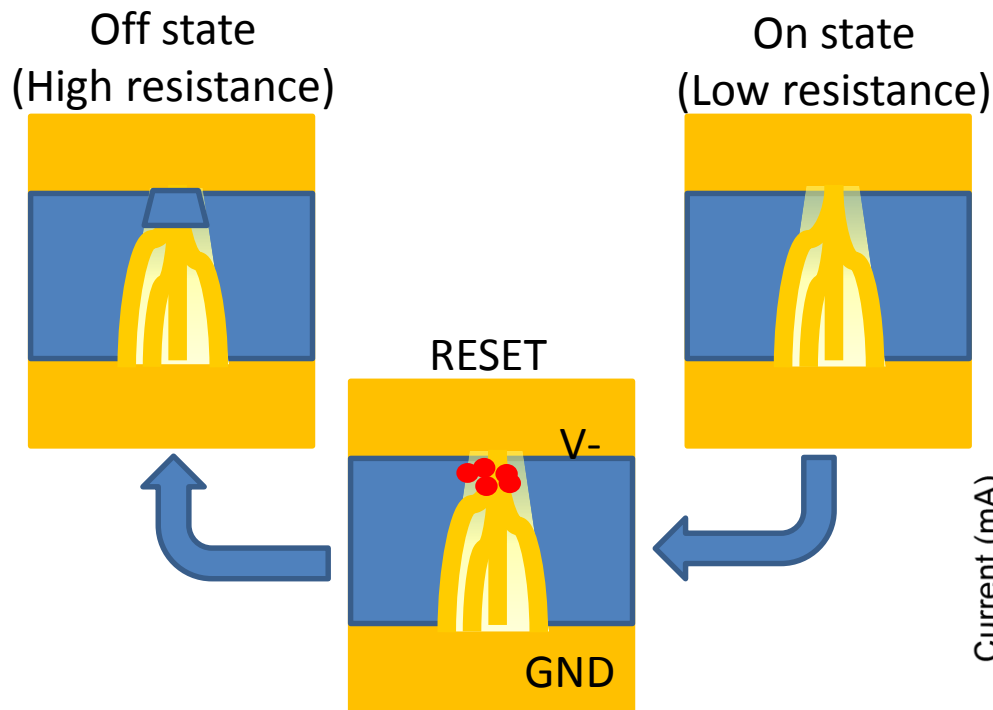


- ▶ Fresh cell
- ▶ Forming

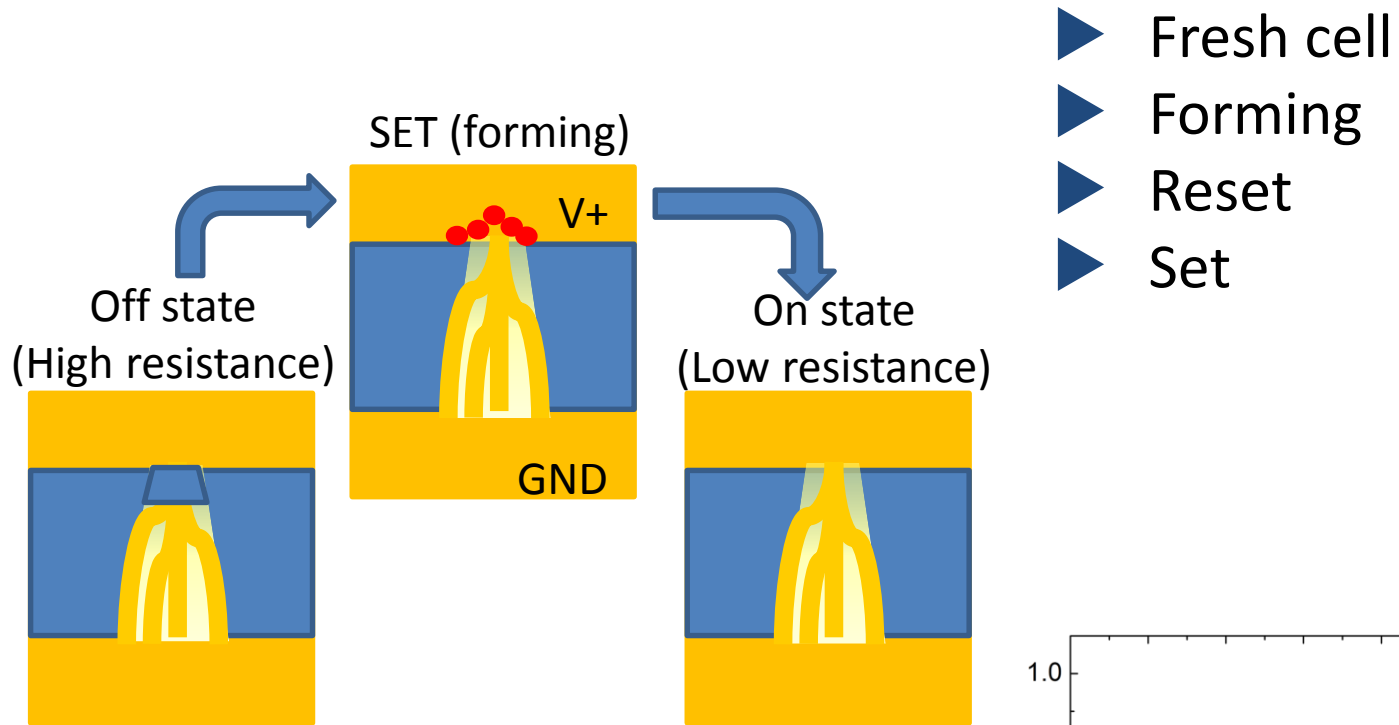


# Resistive switching mechanism

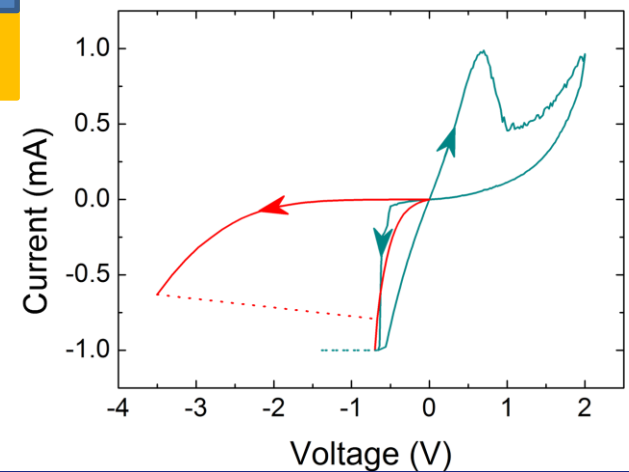
- ▶ Fresh cell
- ▶ Forming
- ▶ Reset



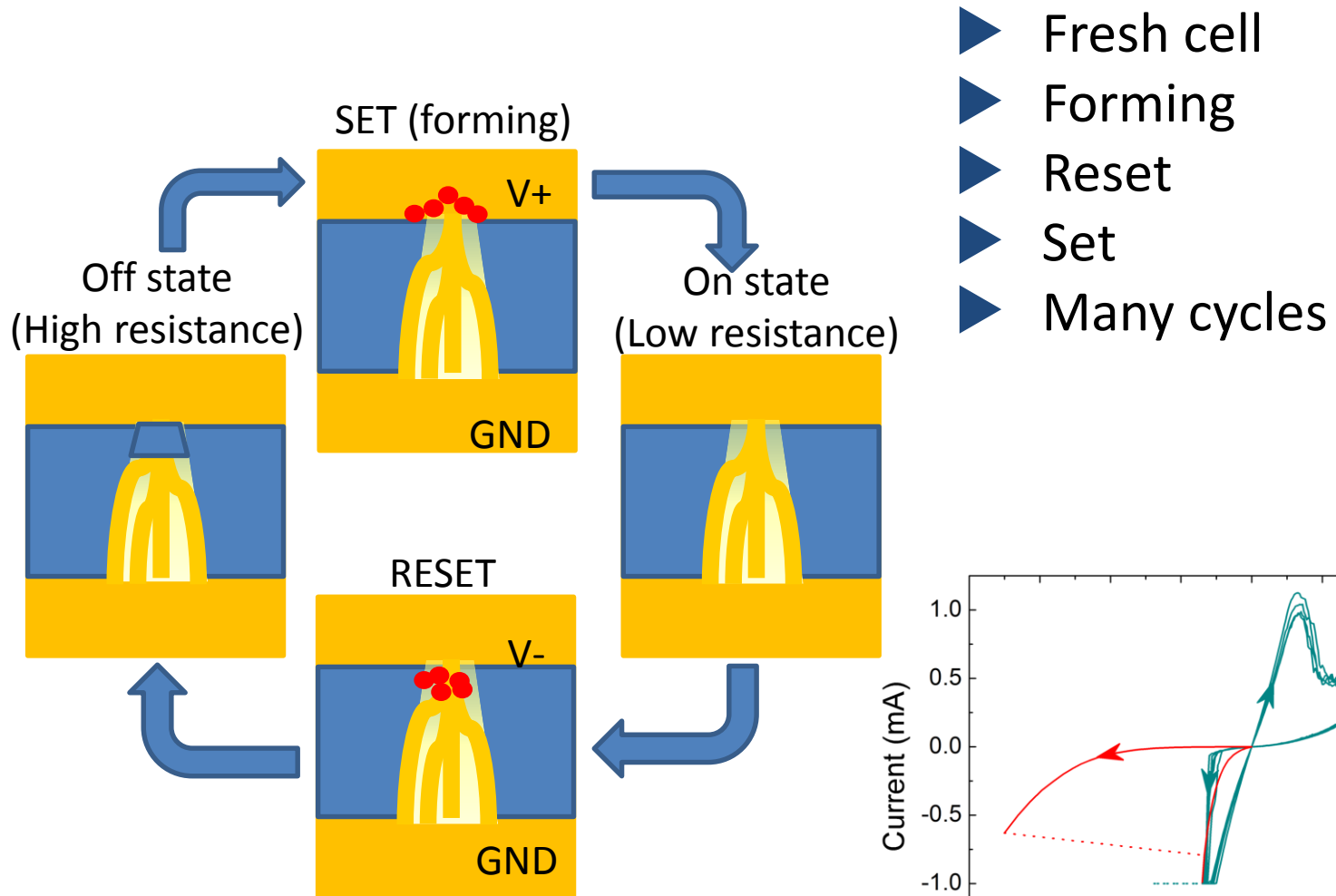
# Resistive switching mechanism



- ▶ Fresh cell
- ▶ Forming
- ▶ Reset
- ▶ Set



# Resistive switching mechanism



# Experimental results

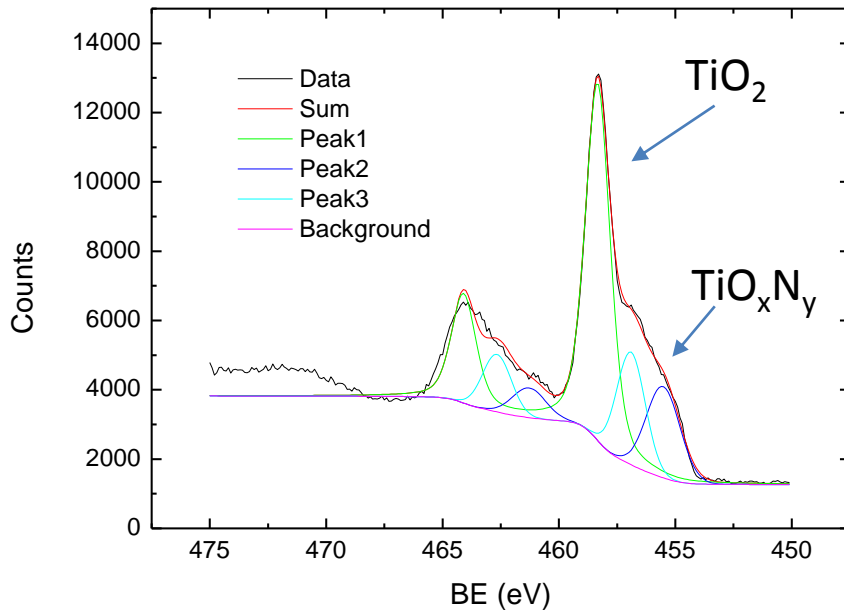
## Metal/Oxide interface

### X-ray photoemission spectroscopy

- $\text{TiO}_2/\text{TiO}_x\text{N}_y$  in serie with the  $\text{HfO}_2$  film
- Significant percentage of non-lattice oxide

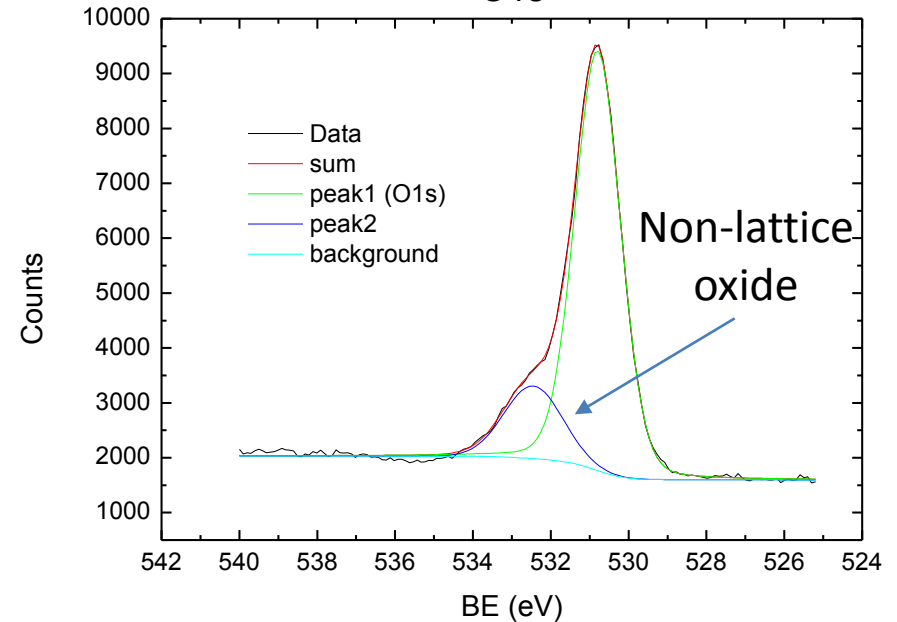
#### *TiN film*

Ti2p



#### *HfO<sub>2</sub> film*

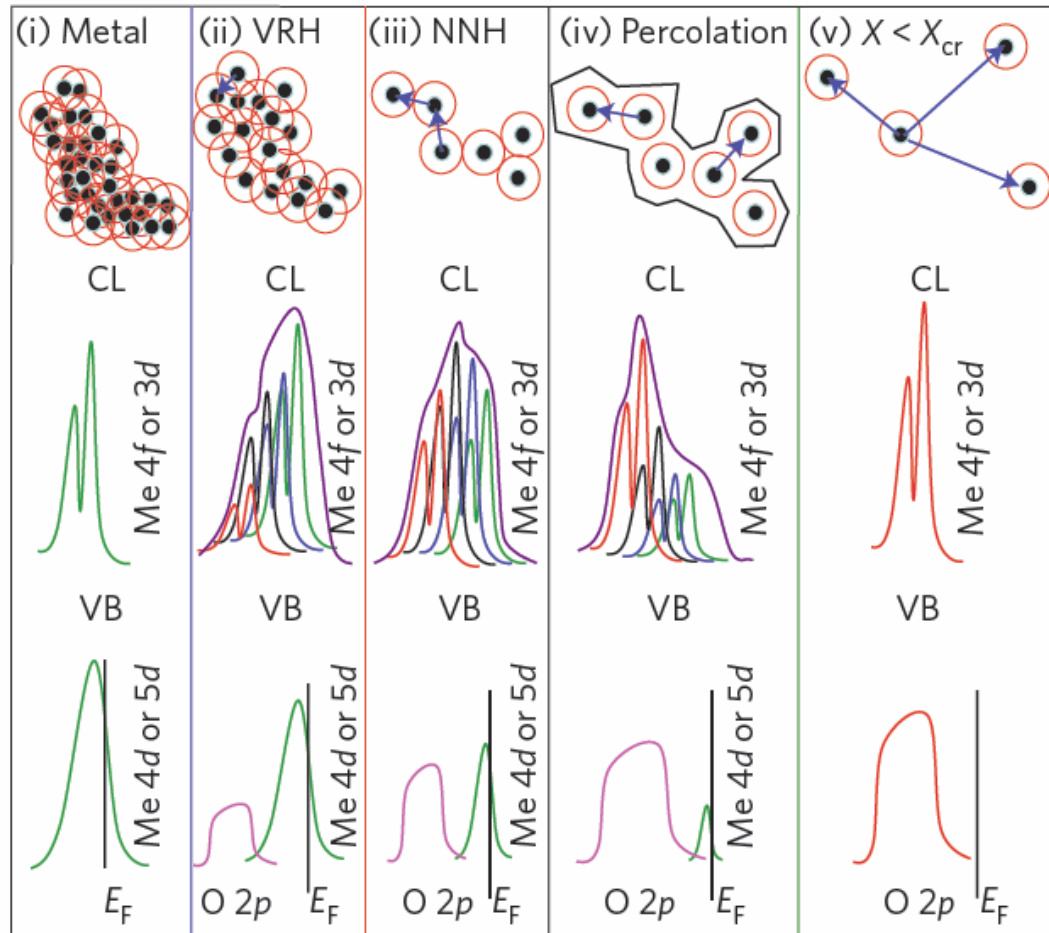
O1s



# ITRS 2012 UPDATE - Winter Presentations

	<i>Prototypical (Table ERD3)</i>			<i>Emerging (Table ERD5)</i>					
<b>Parameter</b>	<b>FeRAM</b>	<b>STT-MRAM</b>	<b>PCRAM</b>	<b>Emerging ferroelectric memory</b>	<b>Nanomechanical memory</b>	<b>Redox memory</b>	<b>Mott Memory</b>	<b>Macromolecular memory</b>	<b>Molecular Memory</b>
<i>Scalability</i>									
<i>MLC</i>									
<i>3D integration</i>									
<i>Fabrication cost</i>									
<i>Endurance</i>									

# Conduction in metal oxides



  
 Oxygen

**J. Joshua Yang et al., "Memristive devices for computing" Nature nanotechnology 8.1 (2012)**

