RRAM technology: From material physics to devices

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Outline

- Introduction: RRAM technology and applications
- Few examples:
 - Ferroelectric tunnel junction memory
 - Mott Insulator memory
 - Electro Chemical Memory (CB-RAM)
 - OxRAM
 - Valence Change Memory
 - Thermo Chemical Memory
- Conclusion: main challenges







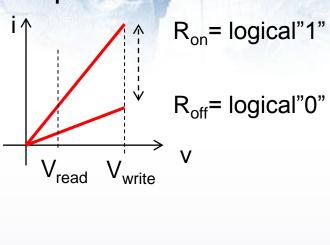






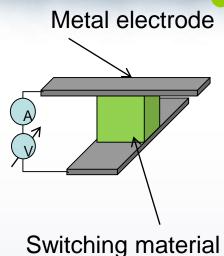
RRAM: big picture

Principle of RRAM



The time voltage dilemma

- Induce a change of resistivity to discriminate two (or more) resistance states by electrical stress (1 bit of information, or more)
- Evaluate this state by a "Read" voltage, i.e. probing current
 - Equivalent to a tunable resistor
- Non volatile



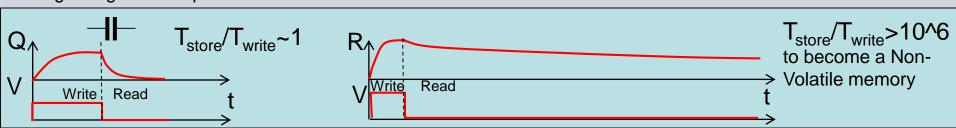
In other words: we want the write voltage V_{write} to be fast and to induce a large

change of resistance and we want to be able to read for a very long time at V_{read} w/o changing the state: not trivial.

Whatever is the physical mechanism originating the change of resistance, we need

NON LINEARITY

Ex: the worst non-volatile memory Storing charge on a capacitor



Some semantic...

There is today a debat around the proposition of memristance by HP in 2008.

If we follow precisely the definition of memristor, none of the RRAM belongs to this class, but if we extend memristor to memristive devices, all RRAM can fit into this class...

"More or less the same, but not exactly similar..."

Classification under construction









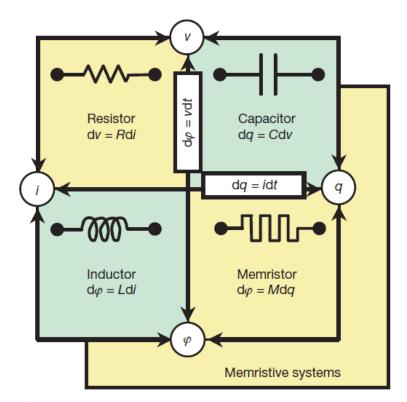


Figure 1 | The four fundamental two-terminal circuit elements: resistor, capacitor, inductor and memristor. Resistors and memristors are subsets of a more general class of dynamical devices, memristive systems. Note that R, C, L and M can be functions of the independent variable in their defining equations, yielding nonlinear elements. For example, a charge-controlled memristor is defined by a single-valued function M(q).

The Holy grale: a universal memory

For RRAM to become a success story, it needs to bring more to industry, not only equivalent

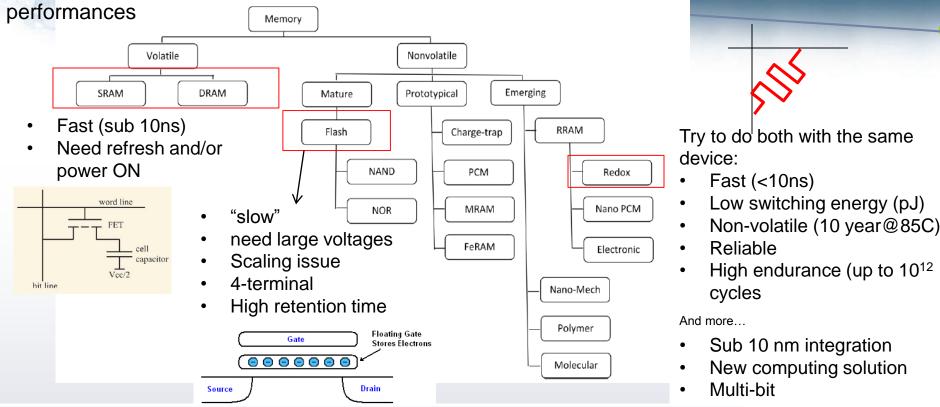


Table 1 | Comparison of memory and storage technologies¹¹⁹. Note that circuit-level overheads for the listed performance metrics are in general different among different device technologies and could often dominate individual device performance.

	Memristor	PCM	STTRAM	SRAM	DRAM	Flash (NAND)	HDD	
		P	rototypes		Commercialized technologies			
Reciprocal density (F ²)	<4	4-16	20-60	140	6-12	1-4 ⁺	2/3	
Energy per bit (pJ)	0.1-3	2-25	0.1-2.5	0.0005	0.005	0.00002	1-10×10 ⁹	
Read time (ns)	<10	10-50	10-35	0.1-0.3	10	100,000	5-8×10 ⁶	
Write time (ns)	~10	50-500	10-90	0.1-0.3	10	100,000	5-8×10 ⁶	
Retention	years	years	years	As long as voltage applied	< <second< td=""><td>years</td><td>years</td></second<>	years	years	
Endurance (cycles)	10 ¹²	10 ⁹	1015	>1016	>1016	104	10 ⁴	

^{*}The energy to operate NAND Flash is typically hundreds of picojoules per bit primarily because accessing the memory cells requires charging word and bit lines to high voltages. *Smaller number represents an effective area for multi-level cells. PCM, phase-change memory; STRAM, spin torque transfer random access memory; SRAM, static RAM; DRAM, dynamic RAM; HDD, hard disk drive.

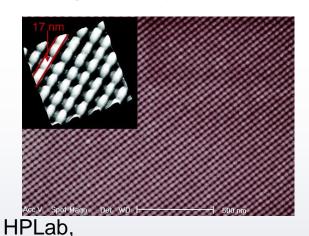




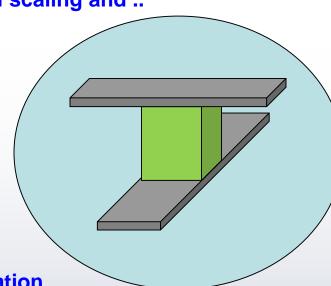
RRAM potential

PROS and **CONS**

- ☐ Wide range of material systems (many CMOS compatible) and physical phenomena
- High density due to lateral scaling and ...

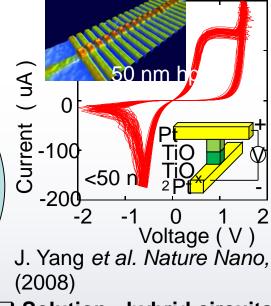


2005 ... monolithical 3D integration

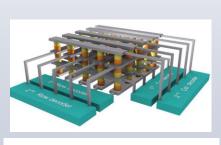


Kawahara et al. Samsung, 2012

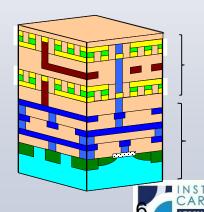
1 but simple functionality



☐ Solution: hybrid circuits



M.-J.Lee et al. *IEDM* 85 (2008)

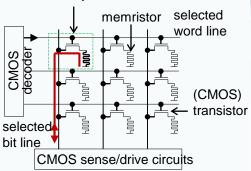


crossbar add-on with integrated memristive devices CMOS circuits



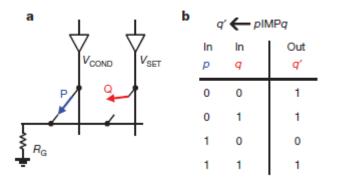
MEMORIES AND STORAGE

1transistor/1resistor(1T1R) memory cell



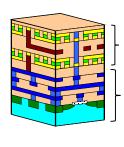
READ OPERATION leakage current VREAD OT1R memory cell

LOGIC (HPLab, Nature)

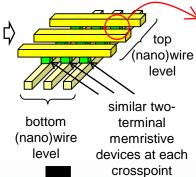


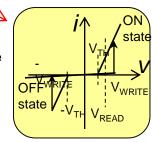
Killer Applications

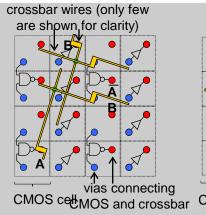
HYBRID CIRCUITS



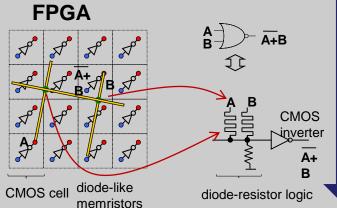
crossbar add-on with integrated memristive devices conventional complimentary metal oxide semiconductor (CMOS) circuits



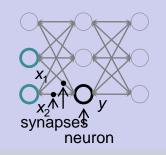


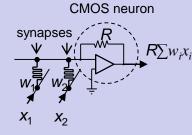


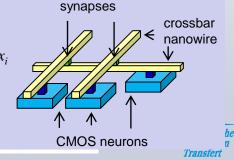
wires



BIO-INSPIRED AND MIXED-SIGNAL INFORMATION PROCESSING





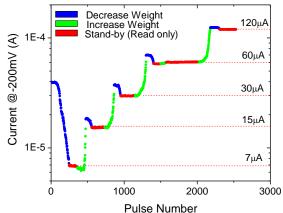


TIN Hf 9 HfO_{*} 8.5 10 TiN 32

RSE

Govoreanu, et all IEDM, 2012

Kawahara et al. Samsung, 2012



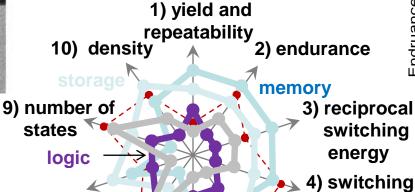
Alibart et al, Nanotechnology, 23, 074508, 2012

State-of-the-Art Performance

speed

demonstrated

retention



nonlinear

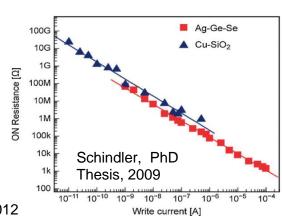
7) ON state

resistance 6) on/off

I-V

J. Yang and D. Strukov (Nature Nano 2013)

current ratio

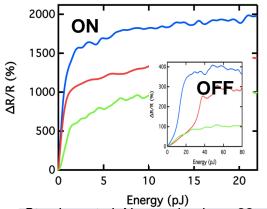


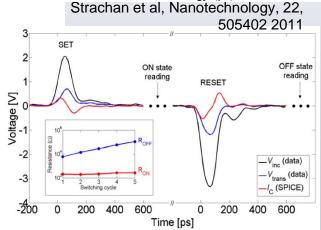
1E13
1E11
1E9
Panasonic Corp.

* Fujitsu Labs

* several groups

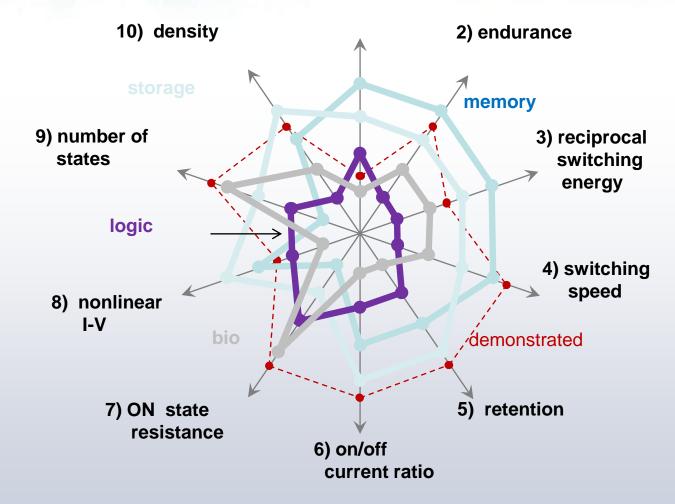
2006 2007 2008 2009 2010 2011
Year





Torrezan et al, Nanotechnology, 22, 485203 2011

1) yield and repeatability





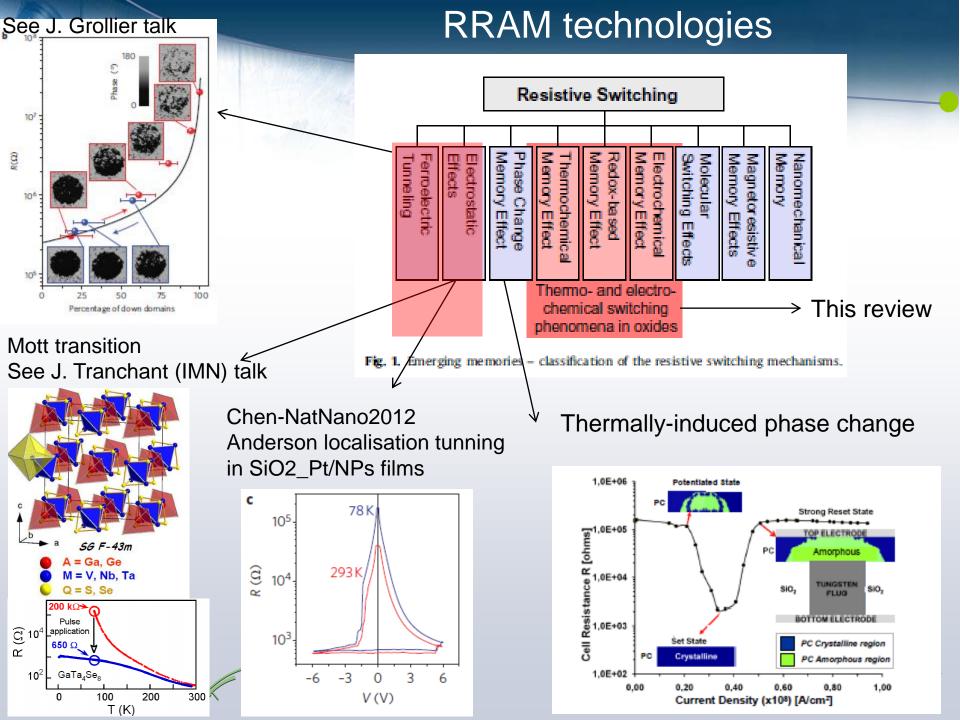








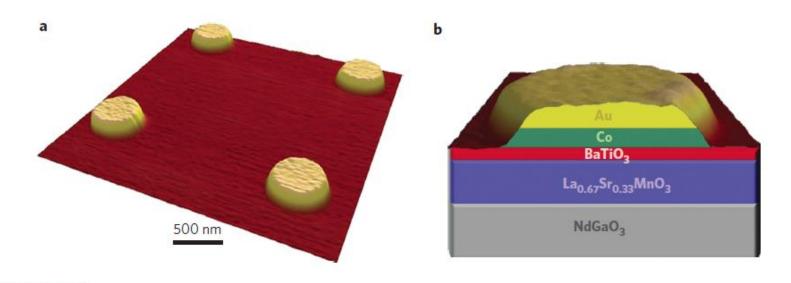


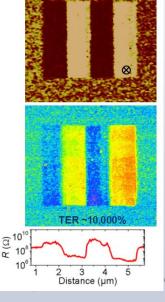


FeRAM

Work from UMPhys-Thales (Paris)

Change of resistivity is associated to the change of polarization of a ferroelectric thin film



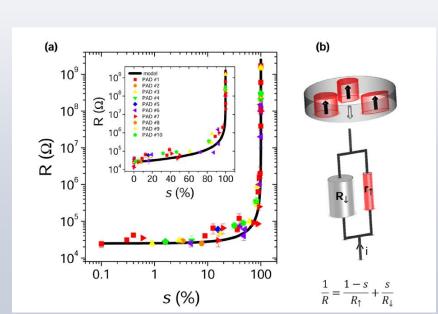


PFM analysis of domains reversal via electric field stress

Polarization -> change of band alignment -> change of resitivity



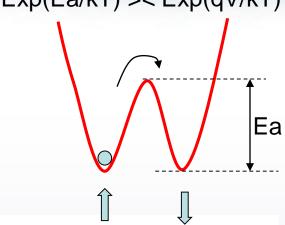


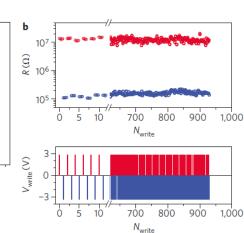


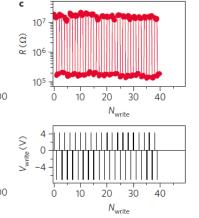
FeRAM

Non-linearity:







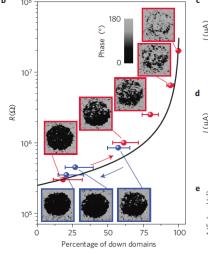


a	108	b	10
R(Ω)	10 ⁷ =	$R(\Omega)$	10
×	10°	R	10
	10 ^S = -4 -2 0 2 4		10

Sample no.

 R_{OFF}

(G) ≥ 10⁶



	Volatile		Non-volatile						
	DRAM	SRAM	NAND Flash	Trapping charge	FeRAM	MRAM	PCM	FTRAM	
Storage mechanism	Charge on capacitor	Interlocked state of logic gates	Charge on floating gate	Charge trapped in gate insulator	Ferroelectric polarization	Magne- tization	Amorphous/ cristalline phases	Ferroelectric polarization	
Cell elements	1T1C	6 T	1T	1T	1T1C	1(2)T1C	1T1R	1T1R	
Feature size (nm)	50	65	90	50	180	130	65	50	
Cell area	6F ²	140F²	5F²	6F²	22F ²	45F ²	16F²	4F ²	
W/E time	<10 ns	0.3 ns	0.1 ms	20 μs	10 ns	20 ns	50 ns	10 ns	
Retention time	64 ms	0	> 10 y	> 10 y	> 10 y	>10 y	>10 y	> 5 days	
Write cycles	>1E16	>1E16	>1E5	>1E5	1.00E+14	>1E16	1.00E+09	>900	
Write voltage	2.5	2.5	15	8	0.9-3.3	1.5	3	3	
Read voltage	1.8	1	2	1.6	0.9-3.3	1.5	3	0.1-1	
Write energy	5 fl	0.7 fl	10 fl	100 fl	30 fl	100 nJ	6 n l	<10f1	

Next big challenge:

Integration with CMOS friendly materials

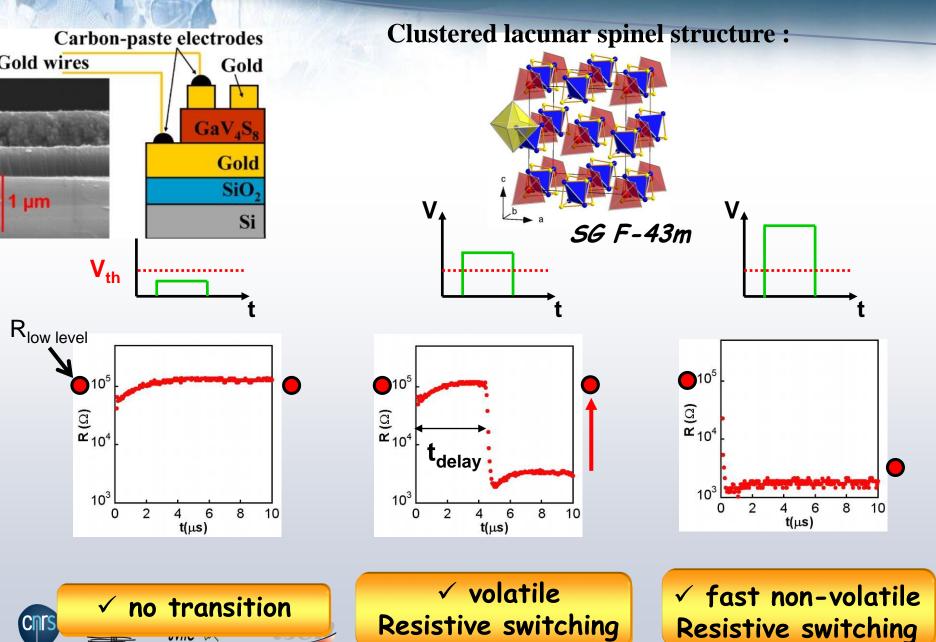




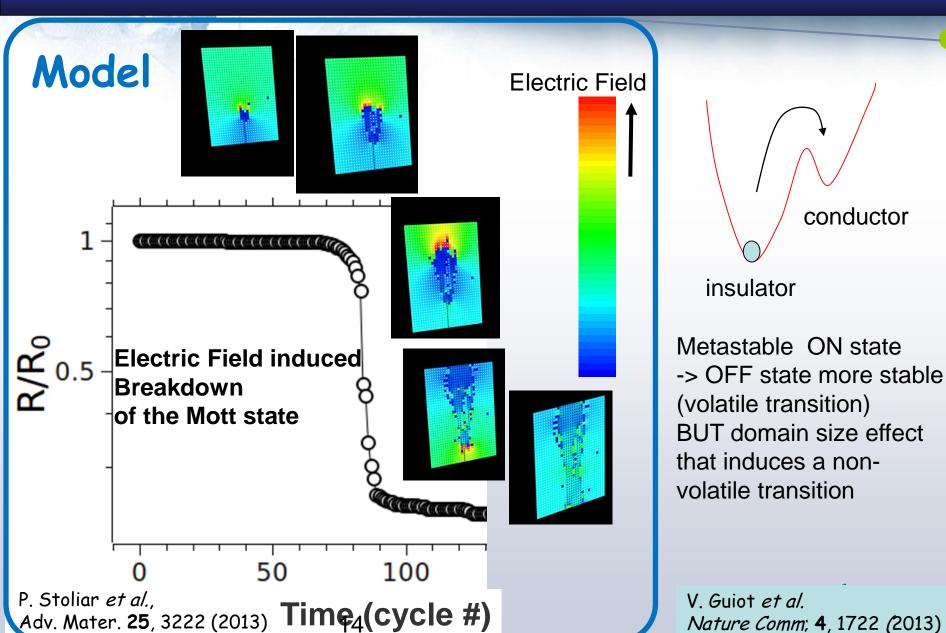


Work from IMN, Nantes

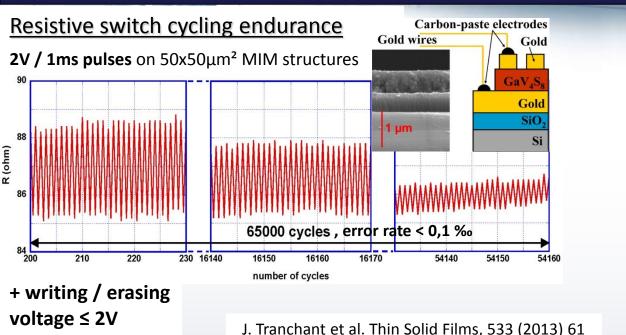
Mott Memory



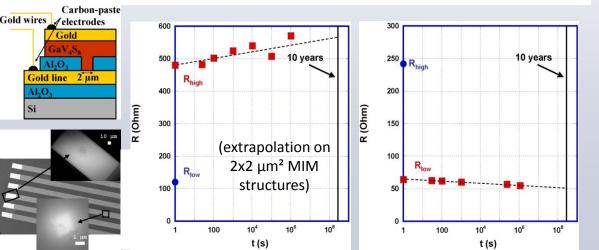
Modeling of the volatile resistive switching



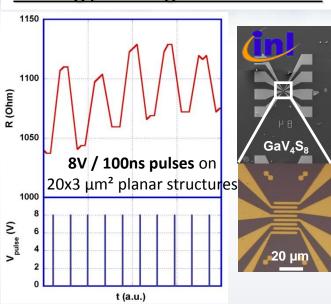
Electrical performances of GaV₄S₈ for Mott memories



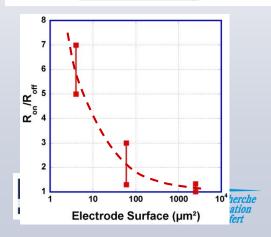




Writing / erasing times ≤ 100 ns



Increase of R_{on}/R_{off} with downscaling



Electrochemical Cell

Other names:

- Solid state electrolyte memory
- Conductive bridge memory
- Programmable metallization cell



Solid state electrolyte with host ions M^{Z+} ions
Active Electrode(e.g. Ag₂S, Cu₂S, RbAg₄I₅)
(e.g., Ag, Cu) or insulator doped with M^{Z+}
(e.g. SiO₂, WO₂, GeS,

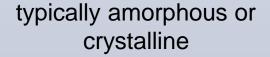
Counter Electrode (e.g., Pt, Ir, Au, W)











GeSe)





Electrolytes	Bottom Electrode	Top electrode	Switching mode	reference		
Sulfides:						
Ge_xS_x	W	Ag	Bipolar	55		
As_2S_3	Au	Ag	Bipolar	56		
Cu ₂ S	Cu	Pt	Bipolar	57, 58		
$Zn_xCd_{1-x}S$	Pt	Ag	Bipolar	59		
Iodides:						
AgI	Pt	Ag	Bipolar	60		
RbAg ₄ I ₅	Pt	Ag	Bipolar	61		
Selenides:						
Ge_xSe_y	W	Ag, Cu	Bipolar	62		
Tellurides:						
Ge_xTe_y	TiW	Ag	Bipolar	63		
Ternary chalcogenides:						
Ge-Sb-Te	Мо	Au, Ag	Bipolar	64		
oxides						
Ta ₂ O ₅	Pt	Cu	Bipolar	65		
SiO ₂	W	Cu	Uni/Bipolar	66		
HfO ₂	Pt	Cu	Bipolar	67		
WO_3	Pt	Cu	Bipolar	68		
ZrO_2	Ag	Au	Bipolar	69		
SrTiO₃	Pt	Ag	Bipolar	70		
TiO ₂	Pt	Ag	Bipolar	71		
CuO _x	Cu	Al	Unipolar	72		
ZnO	Pt, Al doped ZnO	Cu	Bipolar	73		
Al ₂ O ₃	Al	Cu	Bipolar	74		
MoOx	Cu	Pt	Bipolar	75		
$\mathrm{GdO}_{\mathrm{x}}$	Pt	Cu doped MoO _x		76		
Others:						
MSQ	Pt	Ag	Bipolar	77		
doped organic semiconductors	Pt	Cu	Bipolar	78		
nitrides	Pt	Cu	Bipolar	79		
amorphous Si	P ⁺ -Si	Ag	Bipolar	80		
Carbon	Pt	Cu	Bipolar	81		
vacuum gaps	RbAg ₄ I ₅ /Ag, Ag ₂ S/Ag	W, Pt	Bipolar	82, 83		







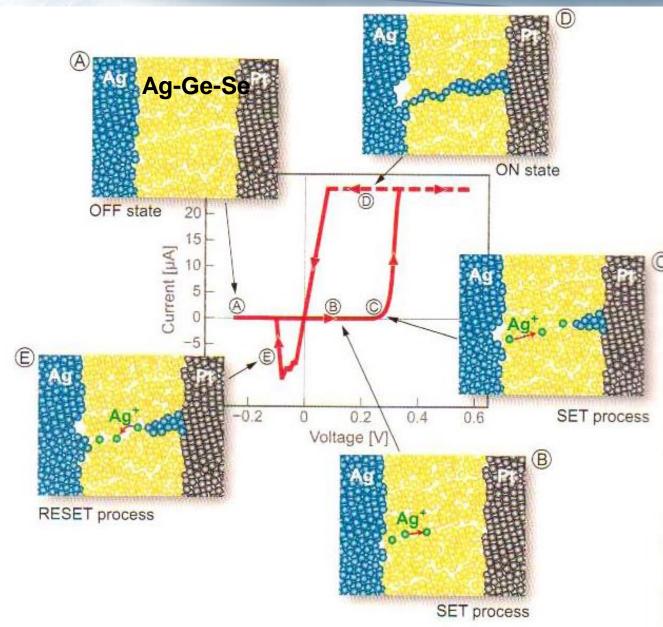
Typical I-V and Process Cartoon

- (A) OFF state
 (B, C) SET process:
 (i) Ag oxidized to
 Ag+; (ii) drift in
 electric field; (iii)
 reduced and
 electro-crystallized
- (D) SET process: complete bridging (compliance-related)
- (E) RESET process: opposite of SET (heat assisted?)







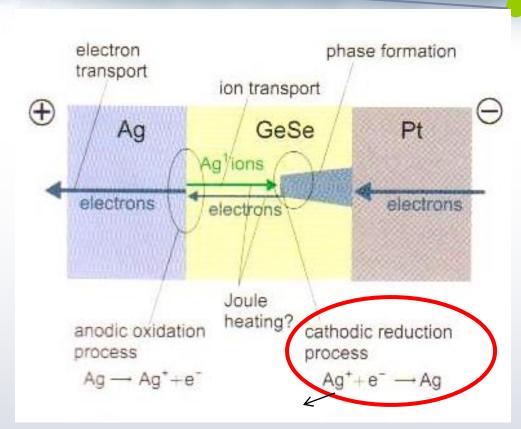


(a) Anodic oxidation and dissolution of M:

 $M \rightarrow M^{z+}+ze^{-}$

- (b) Migration of Mz+ across thin film (migrations is strongly enhanced by extended defects)
- (c) Reduction and electrocrystallization of M on the surface of CE:
 M^{z+}+ze⁻ → M
- → Formation of filament growing (typically) in the direction of the active electrode.
- → A forming step (first sweep) is required
- → The growth is limited by current compliance

SET Process



Origin of Non-linearity

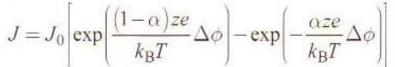
Butler-Volmer equation for oxidation reductions

Exponential for high overpotentials











Ox(ide)RAM (redox based)

OxRAM is typically a transition metal oxide sandwiched between inert electrodes

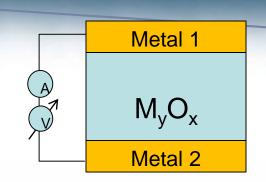
(no metal cations available as in ECM).

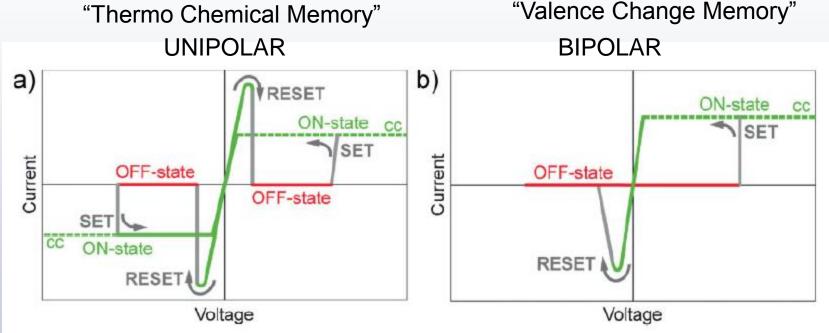
If a sufficient voltage (or current) stress is applied, the insulating material can become conductive

Two distinct I-V switching phenomena are reported

Unipolar: The same polarity can tune ON and OFF the cell

Bipolar: One polarity switch ON, the other switch OFF

















Valence Change Memory (redox-based)

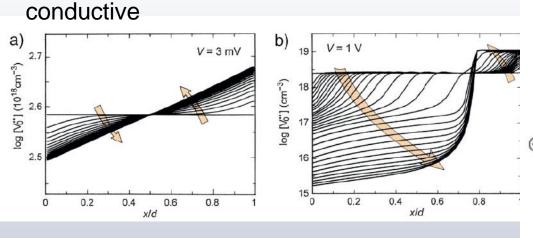
In TMO, oxygen vacancies (V_O²⁺)are much more mobile than cations.

This has been evidenced by coloration measurement in slightly doped oxide cristal

Metal 1 M_yO_x Metal 2

The doping vision (in cristal):

By changing the V_O²⁺ distribution, two doping region can be formed, n and p respectively. For highly doped TMO, the n-type can become highly



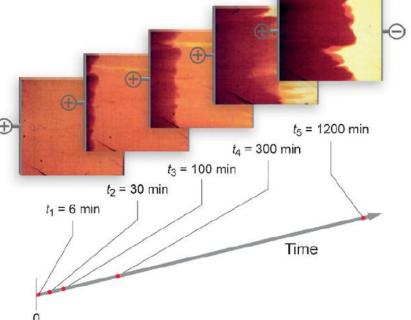
Slightly Fe doped STO

Red: Fe⁴⁺, p-type region

White: Fe^{<4+}, n-type region (Vo rich)







Valence Change Memory (redox-based)

In the case of thin films, the TMO are most of the time amorphous. But still, the V_0^{2+} are expected to be the mobile species (no direct evidence of V_0^{2+} migration in amorphous TMO)

The stochiometry vision:

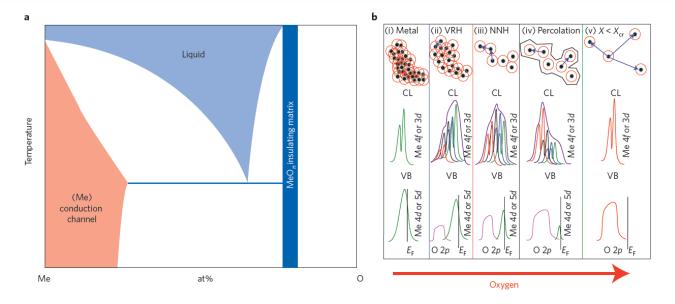
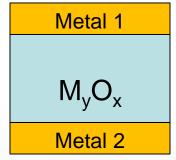


Figure 2 | Material selection criteria for high endurance and repeatability. a, Simplified schematic phase diagram of a metal-oxygen (Me-O) system with only two solid-state phases at low temperature. The MeO_n phase is an insulating stoichiometric phase, serving as the matrix material in the switching device illustrated schematically in Fig. 1. The (Me) phase is a metal-oxygen solid solution, serving as the conduction channel. These two phases are thermodynamically stable with each other and do not mix by reaction to form an intermediate phase even at high temperature, for example, locally induced by Joule heating. The metal (Me) has a large solubility of oxygen, readily accommodating mobile oxygen anions or vacancies during switching. b, With increasing oxygen content in the channel region, the electron transport mechanism changes, producing corresponding resistance changes. The schematic depicts a sequence of evolving conduction centre density and conduction mechanisms (top), and corresponding photoemission core-level (CL, middle) and valence-band (VB, bottom) measurements, from a disordered transition metal oxide in the course of oxidation. The red circles are the localization radii. Unoxidized metallic state (i), weakly localized variable range hopping (VRH) regime (ii), more strongly localized nearest-neighbour hopping (NNH, iii), strong localization regime on the verge of percolation breakdown (iv), and final highly insulating sub-percolation insulating state (v). X is the fraction of conduction centre sites and X_{cr} is the critical fraction at the percolation threshold. E_{Fr} Fermi energy. Panel b reproduced with permission from ref. 73, © 2012 Springer.





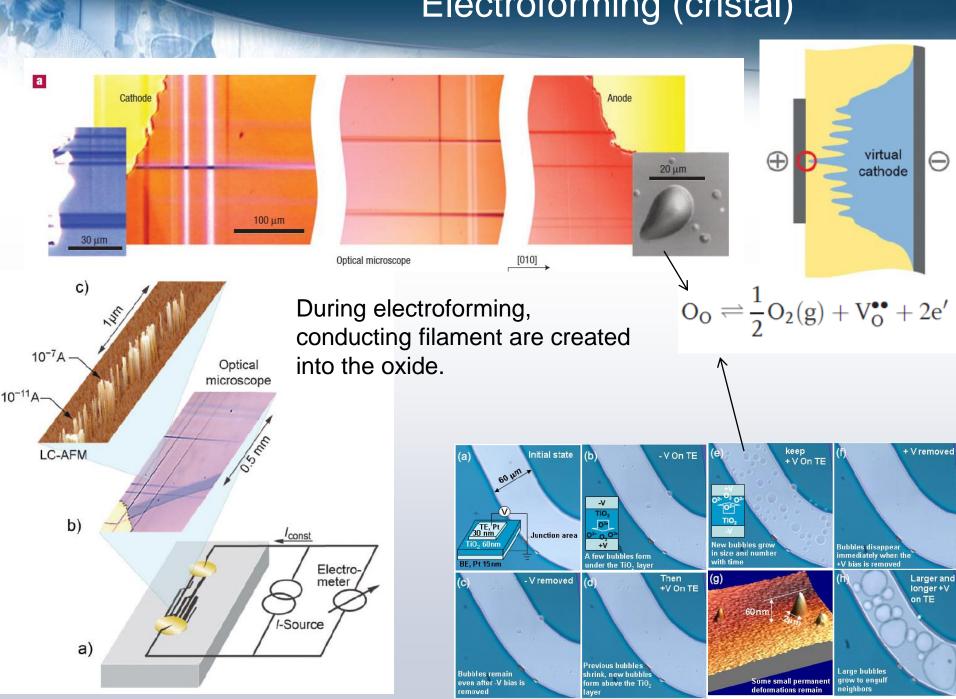


Insulators	Bottom Electrode	Top electrode	Switching mode	reference
MgO	Pt	Pt	Unipolar	1
TiOx	Ru, Pt	Al, Pt	Non/Uni/Bipolar	2, 3
ZrO_x	P ⁺ -Si , n ⁺ -Si	Pt, Cr	Uni/Bipolar	4-6
HfO_x	TiN	TiN	Bipolar	7
VO _x	N/A	N/A	Threshold	8, 9
NьO _х	P*-Si	Pt	Unipolar	10
${\sf TaO}_{\sf x}$	Pt, Ta	Pt, Ta	Bipolar	11, 12
CrO_x	TiN	Pt	Bipolar	13
MoO_x	Pt	Pt-Ir	Uni/Bipolar	14
WO_x	W, FTO	TiN, Au	Bipolar	15, 16
MnO_x	Pt	AI, TiN	Bipolar	17, 18
FeO_x	Pt	Pt	Non/Bipolar	19, 20
C ₀ O _x	Pt	Pt	Nonpolar	21
NiO _x	Pt	Pt	Nonpolar/Threshold	22, 23
CuO_x	TiN, TaN, SRO, Pt	Pt	Bipolar	24
ZnO_x	Pt, Au	TiN, Ag	Bipolar	25-27
AlO_x	Ru, Pt	Pt, Ti	Unipolar/Bipolar	28, 29
GaO _x	ITO	Pt, Ti	Bipolar	30
SiO _x	Poly-Si, TiW	Poly-Si, TiW	Unipolar	31
SiO_xN_y	W	Cu	Bipolar	32
GeO _x	ITO, TaN	Pt, Ni	Bipolar	33, 34
SnO ₂	Pt	Pt	Unipolar	35
BiO _x	Bi	W, Re, Ag, Cu	Bipolar	36
SbO _x	Pt	Sb	Unipolar/Bipolar	37
SmO_x	TiN	Pt	Bipolar	38
GdO_x	Pt	Pt	Unipolar	39
YO _x	Al	Al	Unipolar	40
CeO _x	Pt	Al	Bipolar	41
EuO _x	TaN	Ru	Uni/Bipolar	42, 43
PrO_x	TaN	Ru	Bipolar	42, 43
ErO _x	TaN	Ru	Unipolar	42, 43
DyO_x	TaN	Ru	Unipolar	42, 43
NdO_x	TaN	Ru	Unipolar	42, 43
Ba _{0.7} Sr _{0.3} TiO ₃	SrRuO₃	Pt, W	Bipolar	44
SrTiO₃	SrRuO ₃ , Au, Pt	Au, Pt	Bipolar	45
SrZrO₃	SrRuO₃	Au	Bipolar	46
BiFeO ₃	LaNiO ₃	Pt	Bipolar	47
$Pr_{0.7}Ca_{0.3}MnO_3$	YBCO, Pt, LaAIO ₃	Ag	Bipolar	48
$La_{0.33}Sr_{0.67}FeO_3$	Au	Al	Bipolar	49
Pr _y La _{0.625-y} Ca _{0.375} MnO ₃	Ag	Ag	Bipolar	50
Nitrides (AIN)	AI, TiN, Pt	AI, TiN, Pt	Bipolar	51
Telluride (ZnTe)	Si	Au	Bipolar	52
selenide (ZnSe)	P ⁺ -Ge	In, In-Zn	Bipolar	53
Polymers	Al, ITO, Cu	Al, ITO, Cu	Bipolar	54, 55



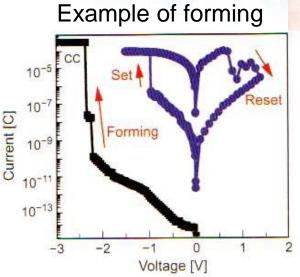


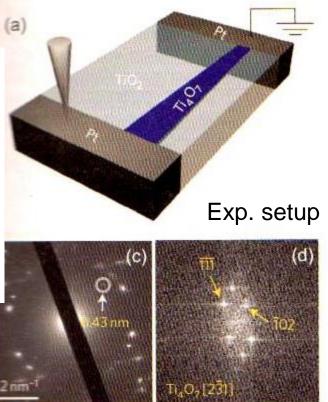
Electroforming (cristal)

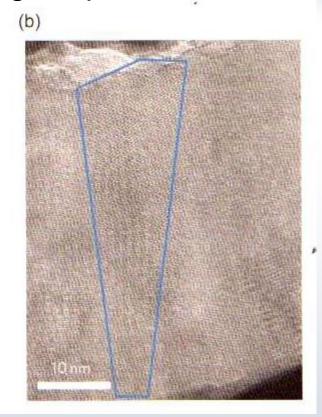


Electroforming (thin film)

Observation of Magneli phases in TiO2







X ray-diffraction

TEM image

- Forming is thermally assisted and two step process (reduction and migration)



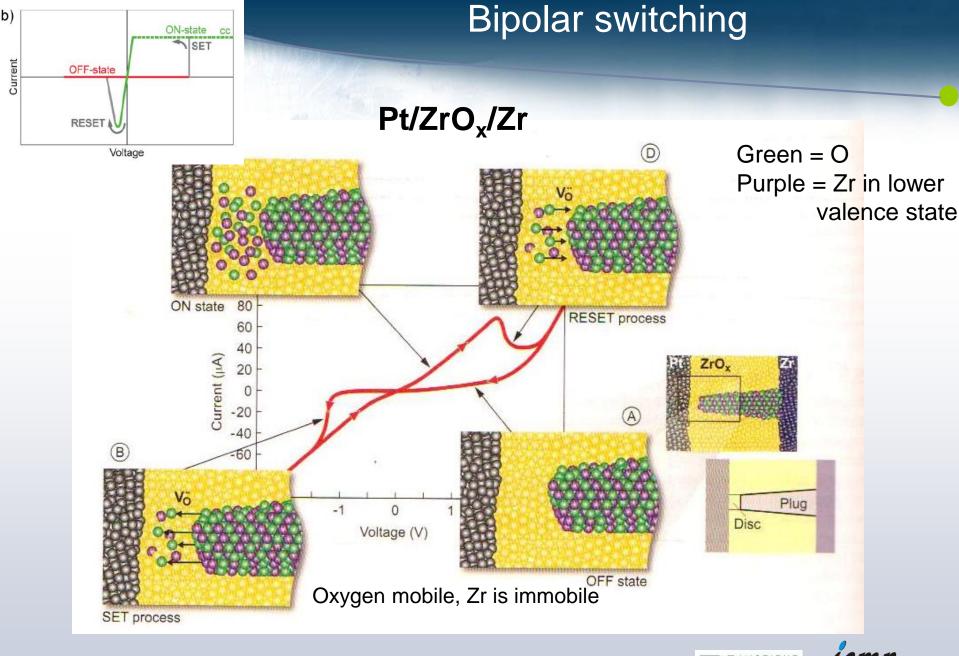
















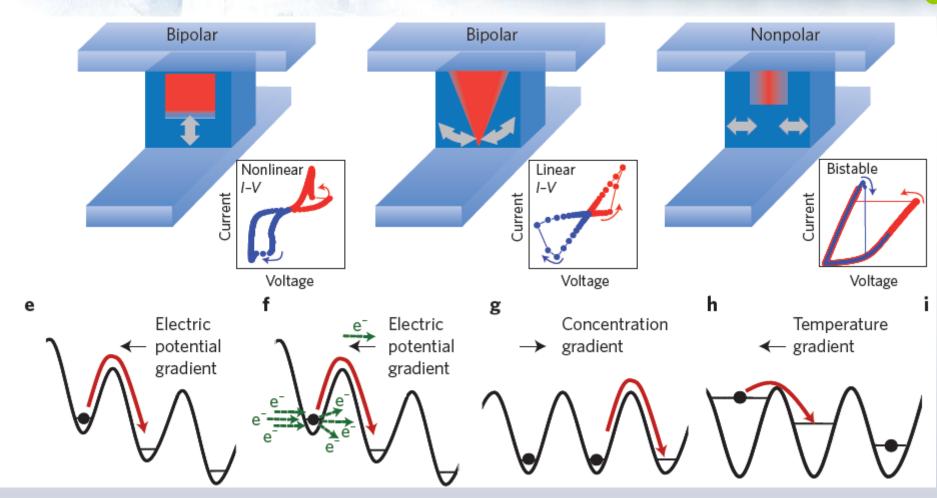








Mechanism for switching



Practically, even if one mechanism is more important, switching results from a combination





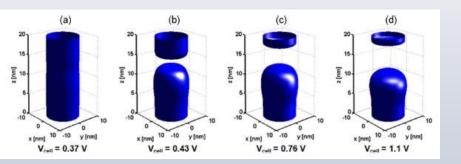






$\begin{bmatrix} \begin{bmatrix} E \\ 10 \\ 20 \end{bmatrix} & \begin{bmatrix} A \\ A \\ 0 \end{bmatrix} & \begin{bmatrix} A \\ A \end{bmatrix} & \begin{bmatrix} A \\ 10 \end{bmatrix} & \begin{bmatrix} A \\ 10 \end{bmatrix} & \begin{bmatrix} A \\ 10 \end{bmatrix} & \begin{bmatrix} A \\ 20 \end{bmatrix} & \begin{bmatrix} A \\ 2$

Fig. 5. Calculated map of (a) dopant density n_D , (b) T, and (c) potential ψ for bias points A, B, C, and D along the reset sweep in Fig. 4(a). Calculations are shown as a function of radial coordinate r and vertical coordinate z according to Fig. 1.











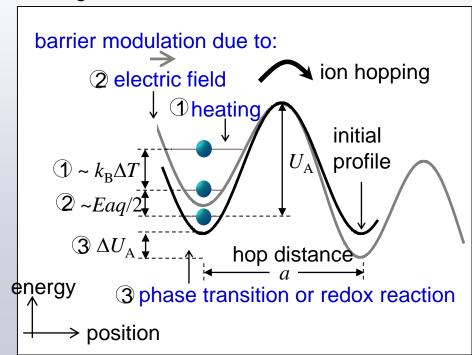
Non linearity

$$\mu_{Vo} = \frac{z_{Vo}e_0}{kT} D_0 \exp(-W_D/kT)$$

Vacancies mobility increase exponentially with temperature

Other factor:

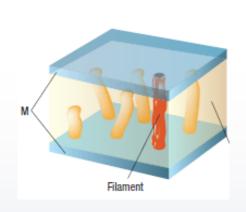
 Maybe the stability of the two phases (i.e. stochiometric vs high V_O²⁺ concentration)

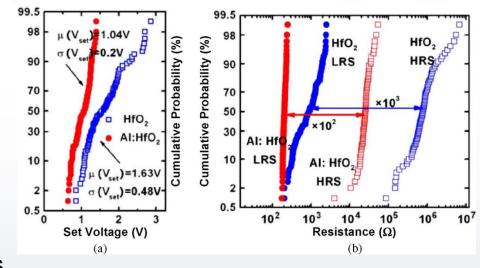


RRAM Challenges

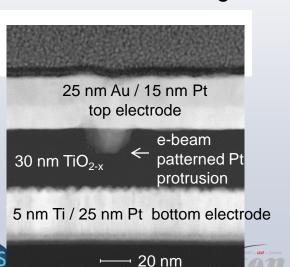
Main challenge: deal with dispersion

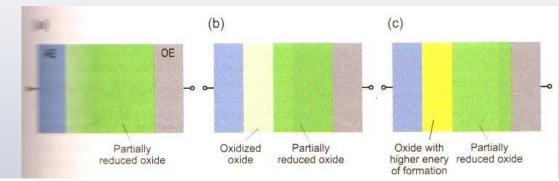
Because forming is stochastic, dispersion in switching properties are huge





Solution: towards forming free devices





AE = active electrode (low oxygen affinity, high work function, e.g Pt, Ir, TiN) OE = Ohmic electrode (opposite, e.g Ti, Ta)

- a) Homogeneous monolayer, e.g. TiO2-x forming is crucial
- (b) Homogeneous bi-layer, e.g. TiO2/TiO2-x or Ta2O5/TaOx
- (c) Hetergeneous bi-layer, e.g. Al2O3/TiO2-x or HfO2/TiO2-x

RRAM Challenges

Main challenge: energy consumption

Lowest E/Bit reported is few pJ. Ideally, we want to go to the sub pJ regime

Solution: filament engineering Trade off between filament resistance and ON/OFF ratio. (Need to increase the resistance of the filament)

High conductivity (metallic filament)



Moderate conductivity (Semi-metallic)



- Scaling of the filament
- Control of defects in the filament (i.e. control of conductivity)







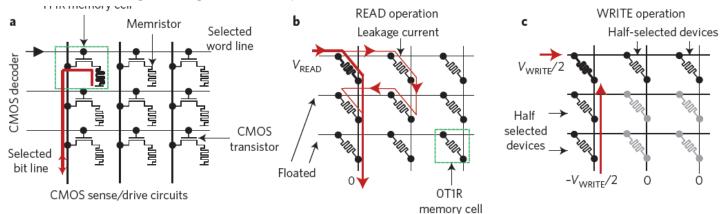






RRAM challenges

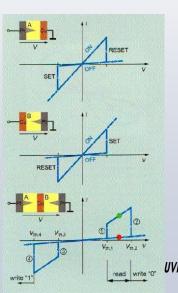
Main challenge: high density crossbar implementation

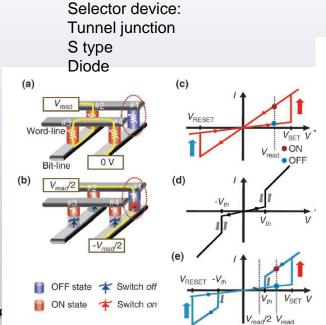


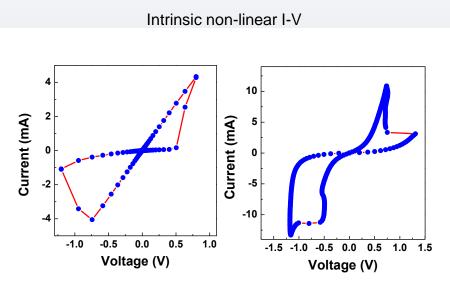
Additionnal challenges: Nanowire resistance contribution and high current effect on wire during operation

Solutions: Complementary

switching







Thanks for your attention











