

# Atoms to go...

## Ionic memory and data storage

**Michael N. Kozicki**

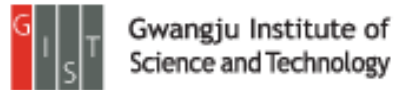
Professor of Electrical Engineering  
School of Electrical, Computer, and Energy Engineering, ASU

Adjunct Professor, GIST, Korea

Visiting Professor, University of Edinburgh, UK

Founder and CTO, Axon Technologies Corp.

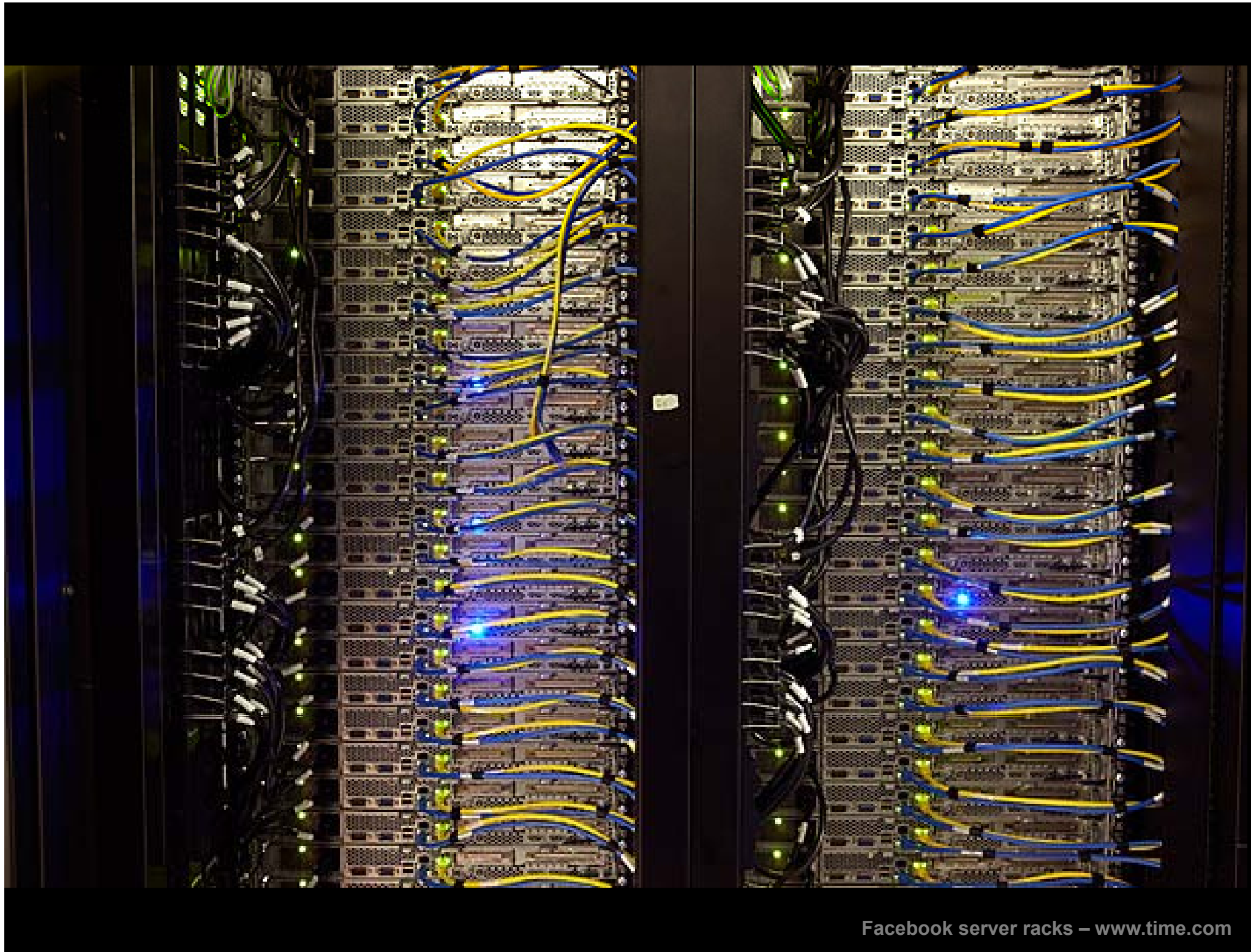
Chief Scientist, Adesto Technologies Corp.

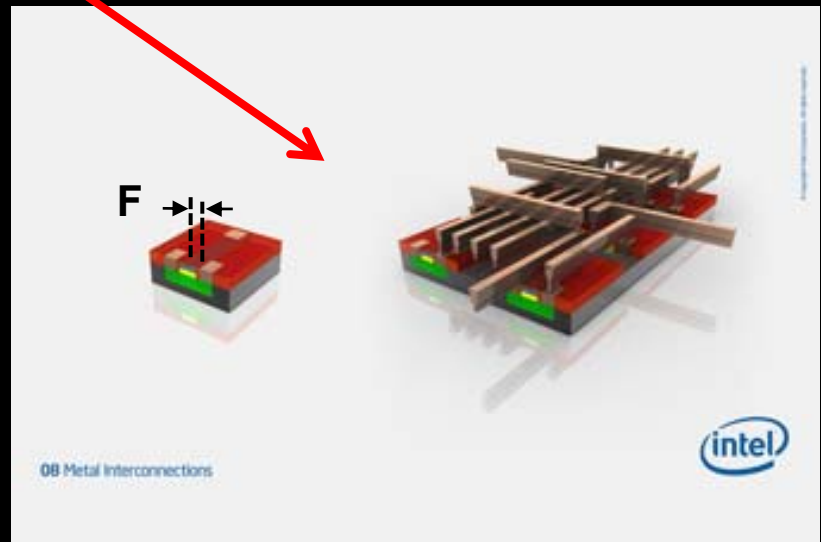
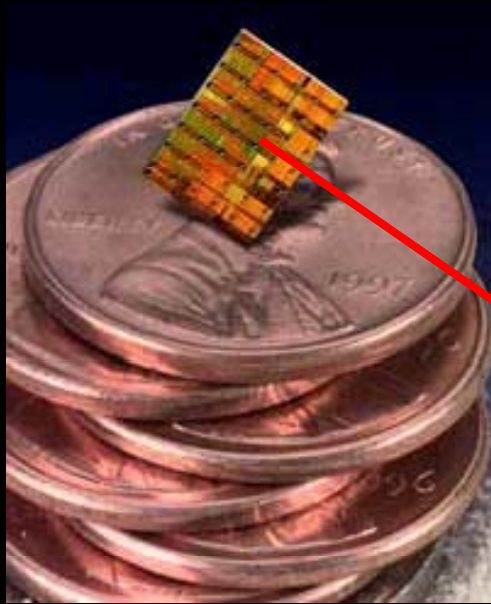


- **No exponential is forever...**
- **The need for new memory**
- **The contender - resistive memory**
- **Introduction to ionic memory**
- **Device characteristics and models**
- **Materials at the nanoscale**
- **Active and passive arrays**
- **Real stuff**
- **Questions and discussion**

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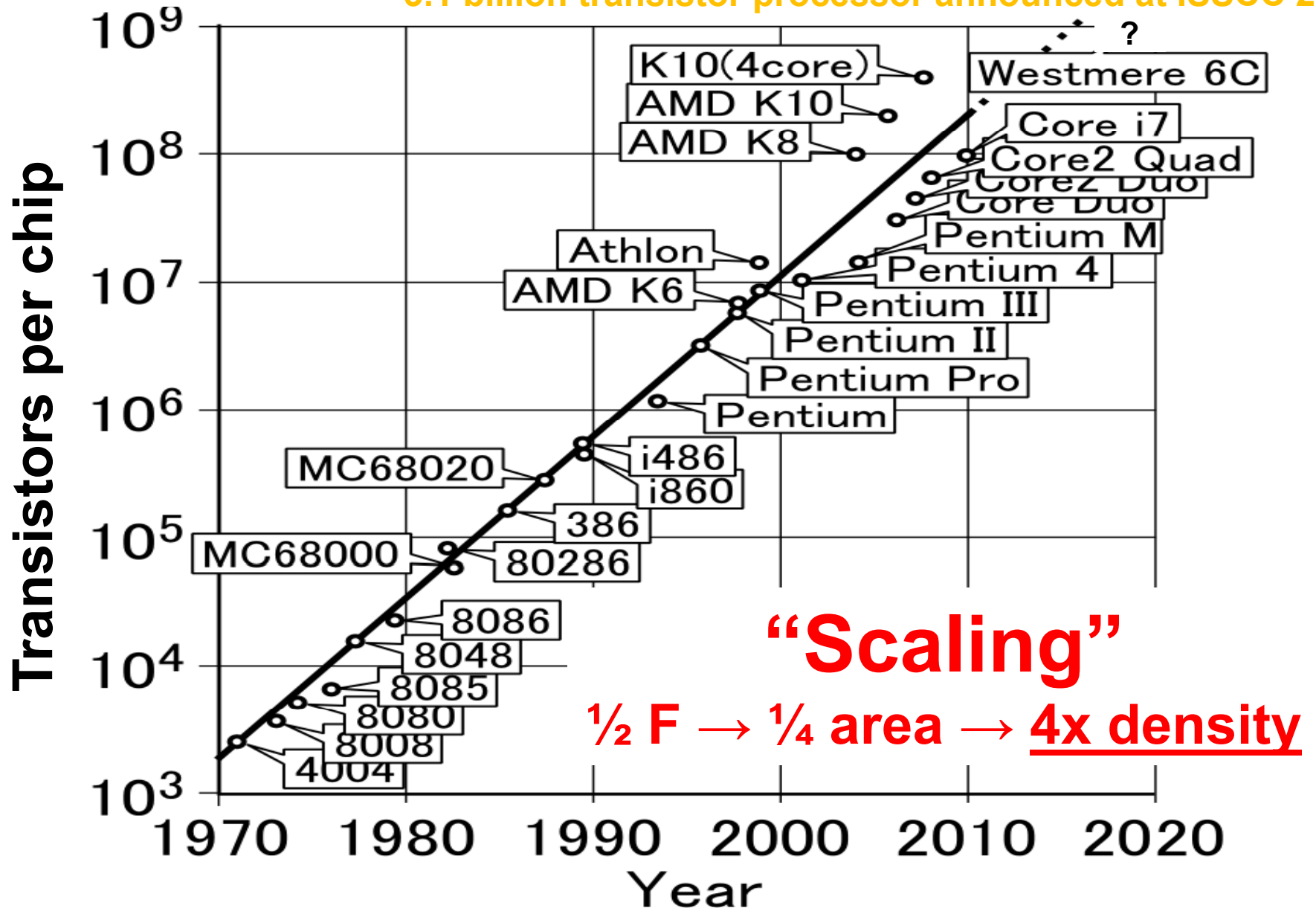
**“The future ain't what it  
used to be.” - Yogi Berra**



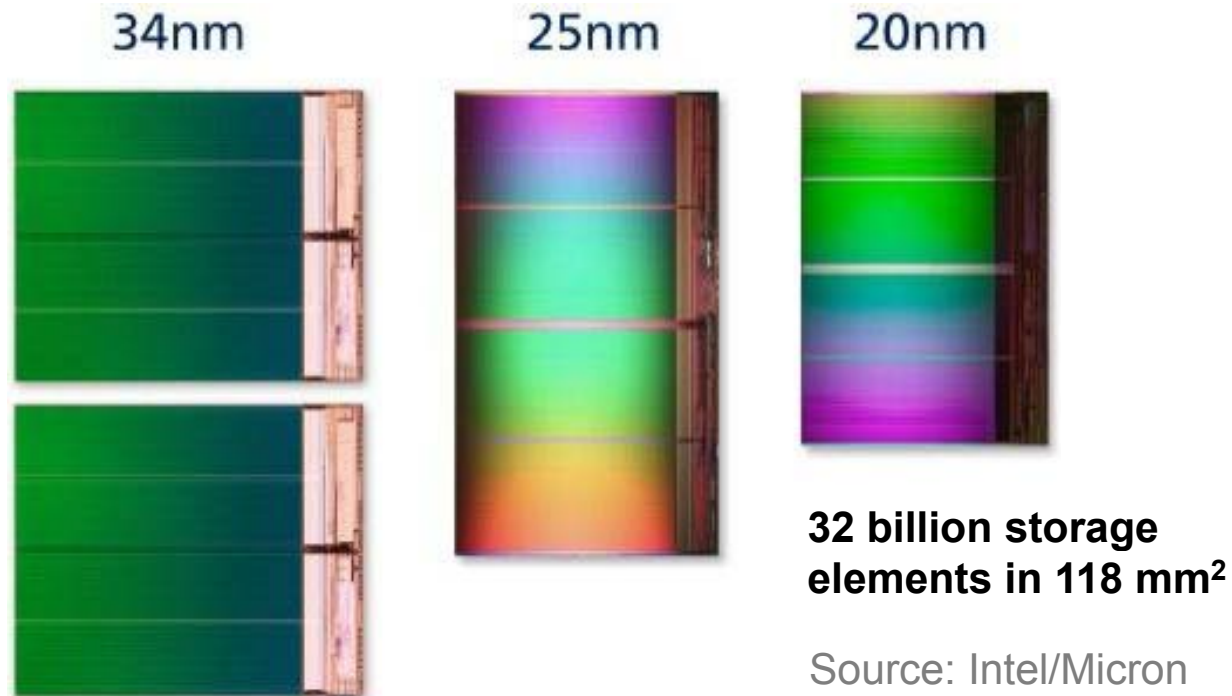


# Exponential growth - Moore's Law

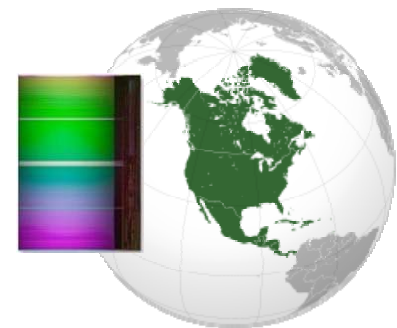
3.1 billion transistor processor announced at ISSCC 2011



# 64 Gb Flash memory shrink



**If a 20 nm feature in the chip was the size of a residential street, how big would the chip be?**



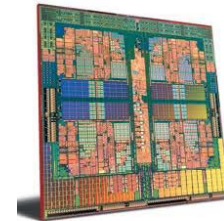


# Why the future ain't what it used to be

- **The fruits of Moore's "Law"**
  - Discrete electronics turned into microelectronics and Moore's *Observation* was born
  - More devices/cm<sup>2</sup> means more performance for less \$\$
    - » Higher speed, higher reliability, smaller systems also result
  - The best way to get more devices per cm<sup>2</sup> is to make them smaller – the cult of *scaling* was established
- **But scaling is breaking down at nano-dimensions**
  - Nano devices don't behave like wee versions of their bigger brothers
    - » Inhomogeneity and quantum mechanics make life interesting
  - Tightly packed structures, ultra-thin layers, small numbers of electrons all lead to big issues

# The end of scaling as we know it?

- **“...innovation has overtaken scaling as the driver of semiconductor technology performance...” - Bernard Meyerson, IBM**
- **Really smart design will keep logic on the Moore’s Law performance trajectory**
  - e.g., multi-core processors...



- **But what about memory?**

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# The memory market

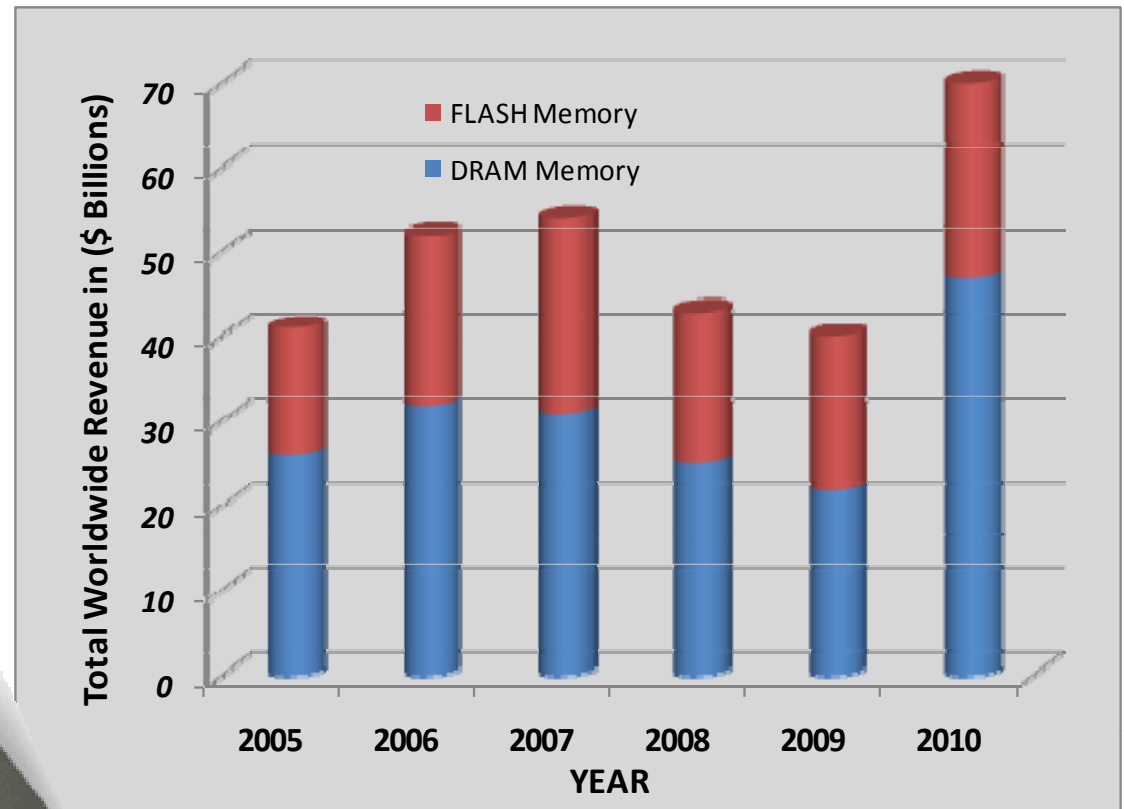
Markets and applications utilizing memory devices:

Computers  
Cell Phones  
Music Players  
Digital Cameras  
Appliances  
Cars/automotive  
Printers  
TVs  
Game consoles  
Video players  
Servers



**Solid state drives (SSDs)**

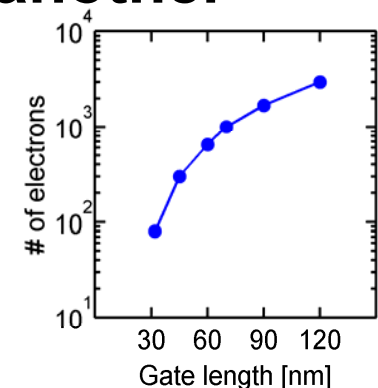
Total memory market size for two key types of memory:  
**Flash and DRAM**



Source: Denali, 2010

# The challenge we are facing...

- The **demand for memory capacity is growing**
  - » You can never have too much memory!
- **Memory scaling is stalling** as existing charge-storage devices will struggle to meet future industry requirements
  - » Smaller devices mean **fewer electrons** stored
    - small charge is **difficult to retain and detect**
  - » **Lower programming voltage** is required to prevent closely-spaced devices talking to one another
    - **programming time** rises greatly
    - compensate by **changing structure**
    - results in greatly **reduced retention**



# Requirements for next-generation memory



- **Physical scalability**

- Assume  **$10^{12}$  bits** in a “chip-like” form factor with extremely compact periphery/high array efficiency
- For a  $20 \times 20 \text{ mm}^2$  **terabit array** area and a  $4 - 6F^2$  cell,  $F$  must be **less than 10 nm**
- Not good news as nobody knows how to define/make reliable **sub-10 nm metallic interconnects** in a **manufacturing environment!**
- Implies  $F$  should be  $> 10 \text{ nm}$  but then **multi-level cell** and/or **multi-layer array** is absolutely necessary to achieve density

# More requirements...

- **Electrical scalability**
  - At the  $F = 22$  nm technology node, the supply voltage is **< 1V**
  - Critical current at 22 nm is no more than a **few tens of  $\mu\text{A}$**
  - Programming in the **pJ range** for energy conservation and heat dissipation
- **Manufacturability /economics**
  - Overall **cost** and *cost of first bit*
  - **Compatible** with existing processes
  - **Longevity** (multiple applications and technology generations)
  - **Reliability...** the killer of promising new technologies!

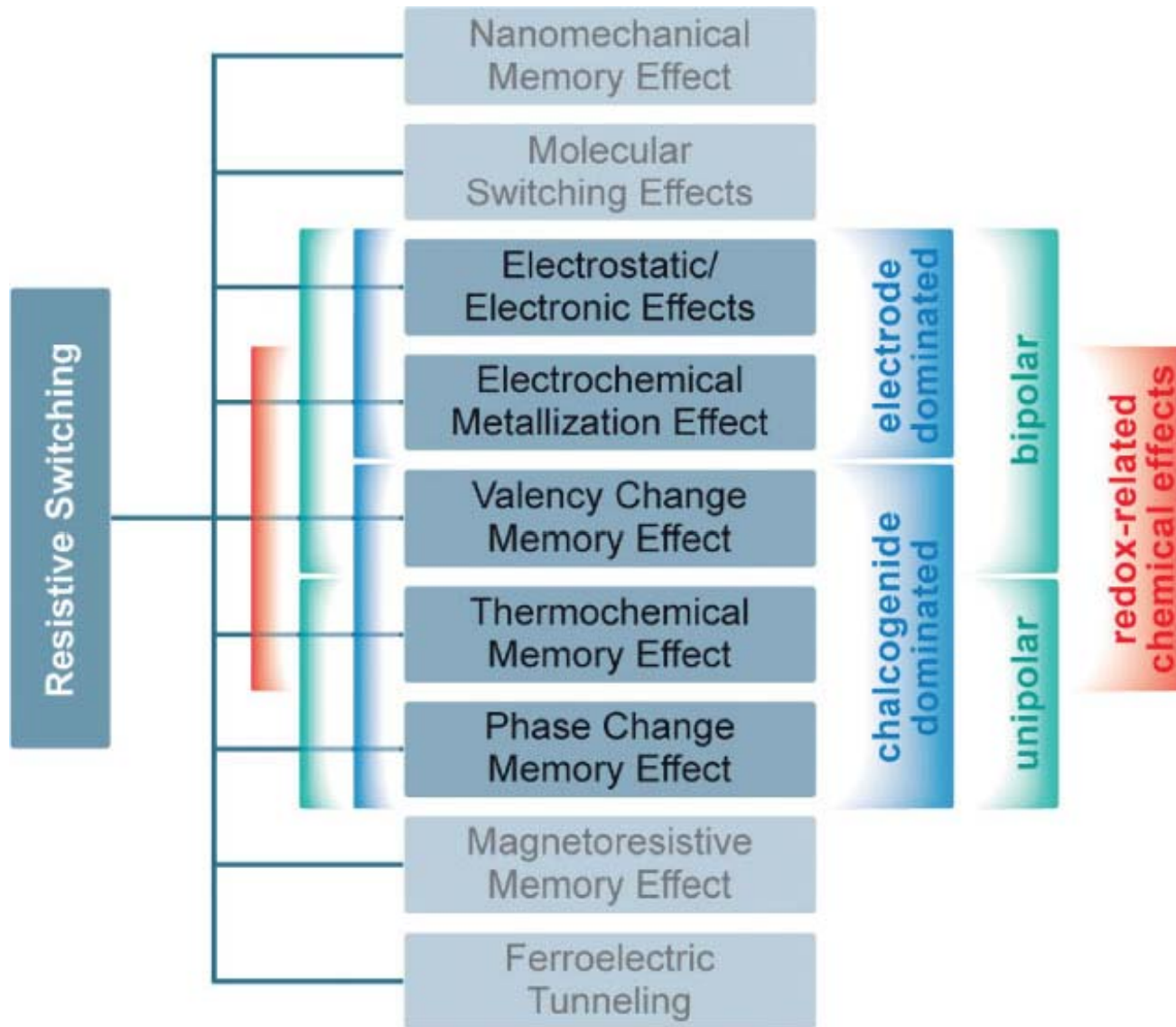
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# The basics of resistive memory

- **Change in resistance on the application of a voltage/current**
  - Devices have a high resistance state (*HRS, reset, off*) and one or more low resistance states (*LRS, set, on*)
  - Usually not a subtle effect
- **A variety of mechanisms are possible**
  - Field- or current-driven
  - Can involve a *change in material*
  - Bulk, interfacial, or *filamentary*
- **Can be *unipolar* or *bipolar***

# Resistive memory taxonomy



R. Waser et al., “Redox-Based Resistive Switching Memories – Nanoionic Mechanisms, Prospects, and Challenges”, Adv. Mater., vol. 21, 2632–2663 (2009).

# Physical changes in materials

- **“Heine Rohrer showed five examples of where, if the space becomes small, new phenomena happen... if the distance is very short, diffusion, atomic or ionic motion, is very fast.”**

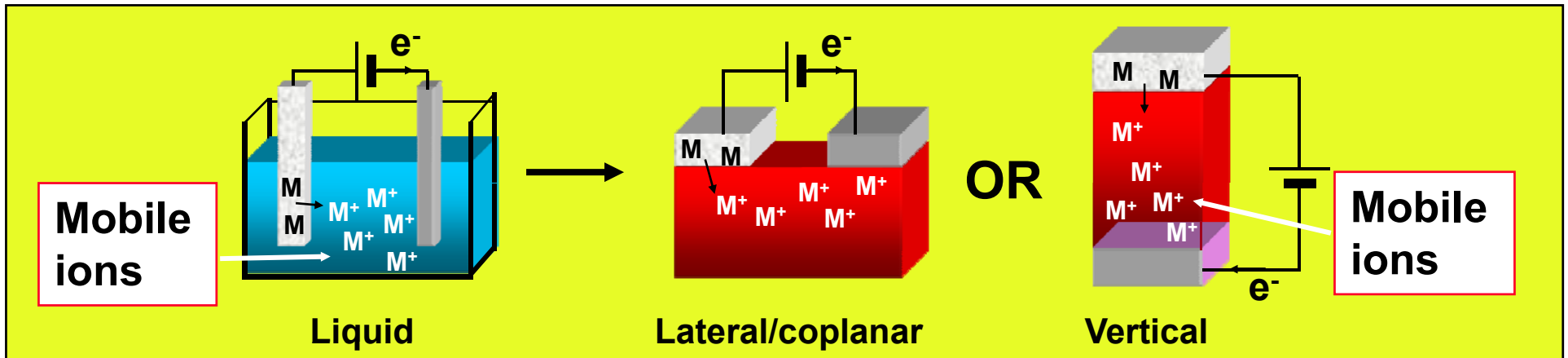
Interview with Masakazu Aono, ACS Nano, Vol. 1, No. 5, 379-383 (2007)

- **Physical changes can result in highly stable, widely spaced states**
  - inherently non-volatile resistance levels
  - small # of atoms can lead to large macroscopic effects
- **Filamentary processes are typically more scalable as on-state resistance is independent of device area**
  - filaments can be a few nm in radius

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# Solid electrolytes

- ***Solid electrolytes*** behave like liquid electrolytes...

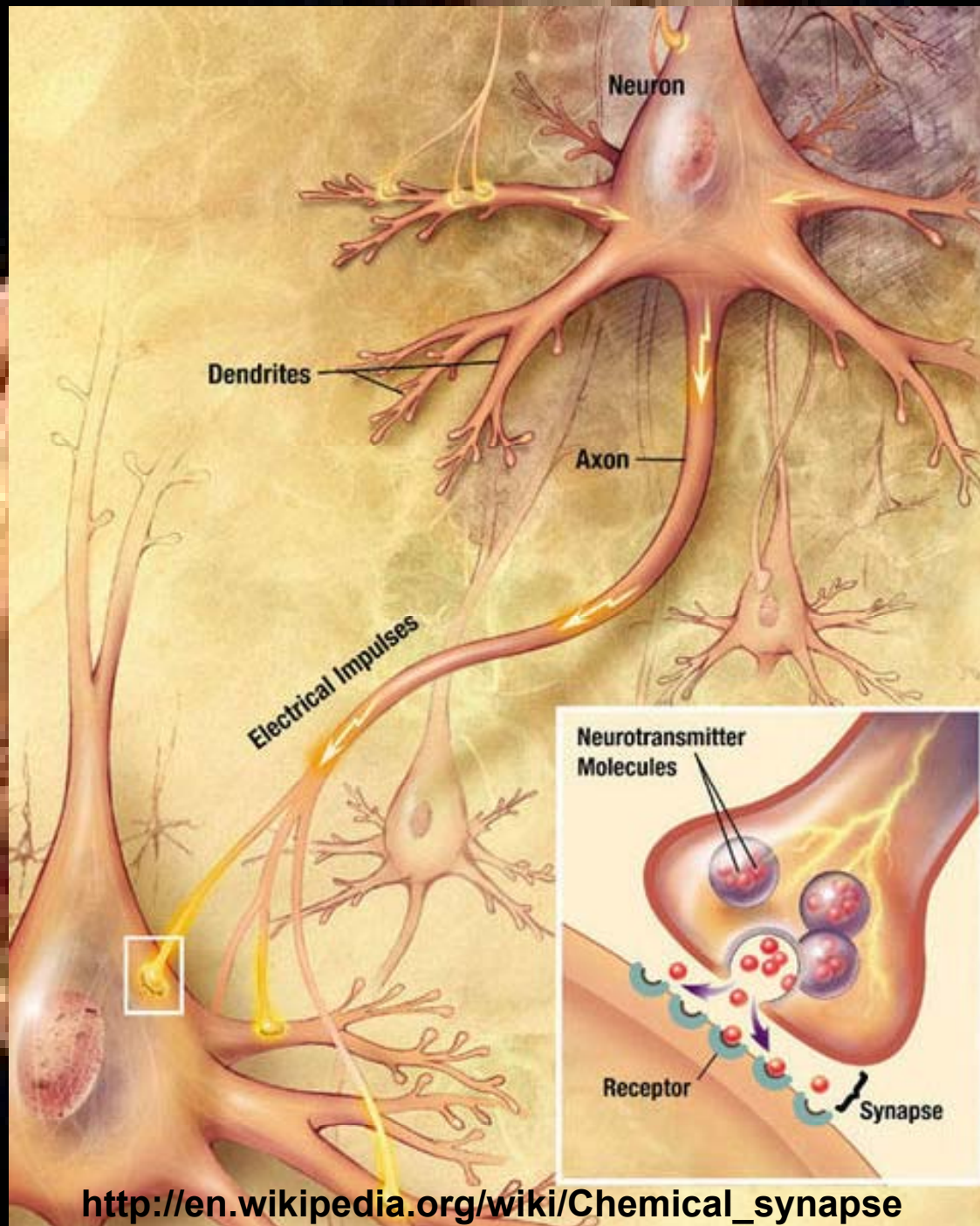


- Ions move under the influence of an electric field and *electrochemical reactions* are possible

cathode (conductor):  $M^+ + e^- \rightarrow M$  *reduction*

anode (with excess M):  $M \rightarrow M^+ + e^-$  *oxidation*

**Electrochemistry occurs at a few 100 mV**



[http://en.wikipedia.org/wiki/Chemical\\_synapse](http://en.wikipedia.org/wiki/Chemical_synapse)



# Nanoionics-based resistive switching memories

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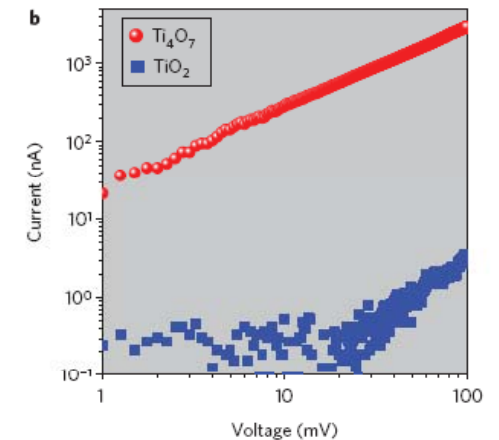
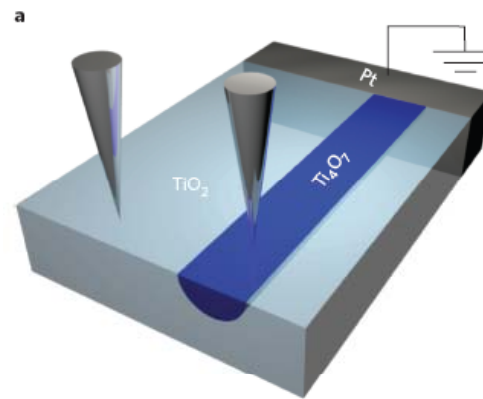
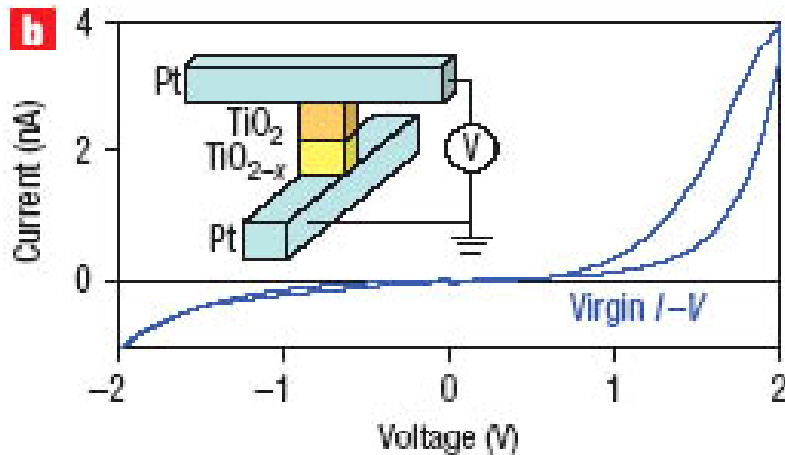
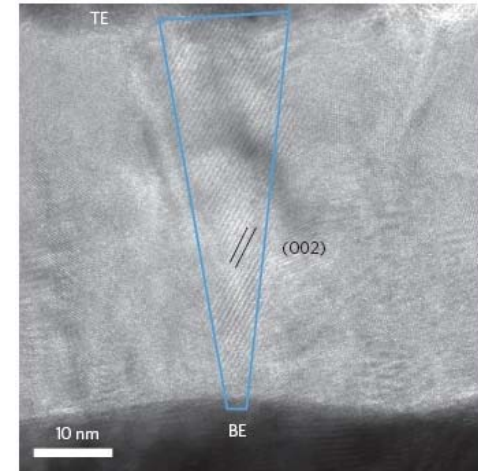
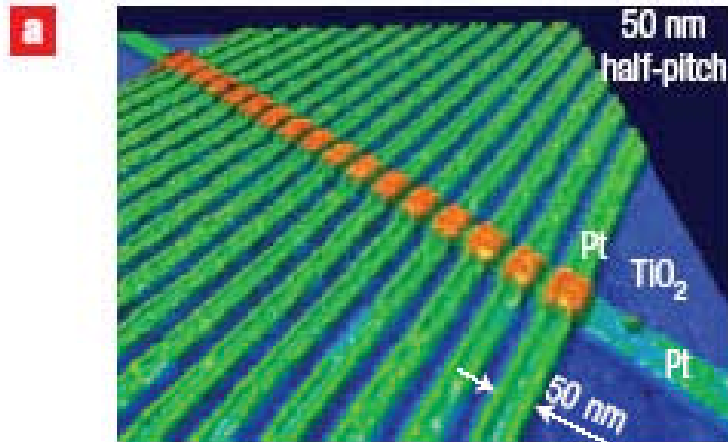
**Rainer Waser and Masakazu Aono**

nature **materials** | VOL 6 | NOVEMBER 2007 | [www.nature.com/naturematerials](http://www.nature.com/naturematerials)

...**ion-migration** effects are coupled to **redox processes** which cause the **change in resistance**. They are subdivided into **cation-migration** cells, based on the electrochemical **growth and dissolution of metallic filaments**, and **anion-migration** cells, typically realized with transition metal oxides as the insulator, in which **electronically conducting paths of sub-oxides** are formed and removed...



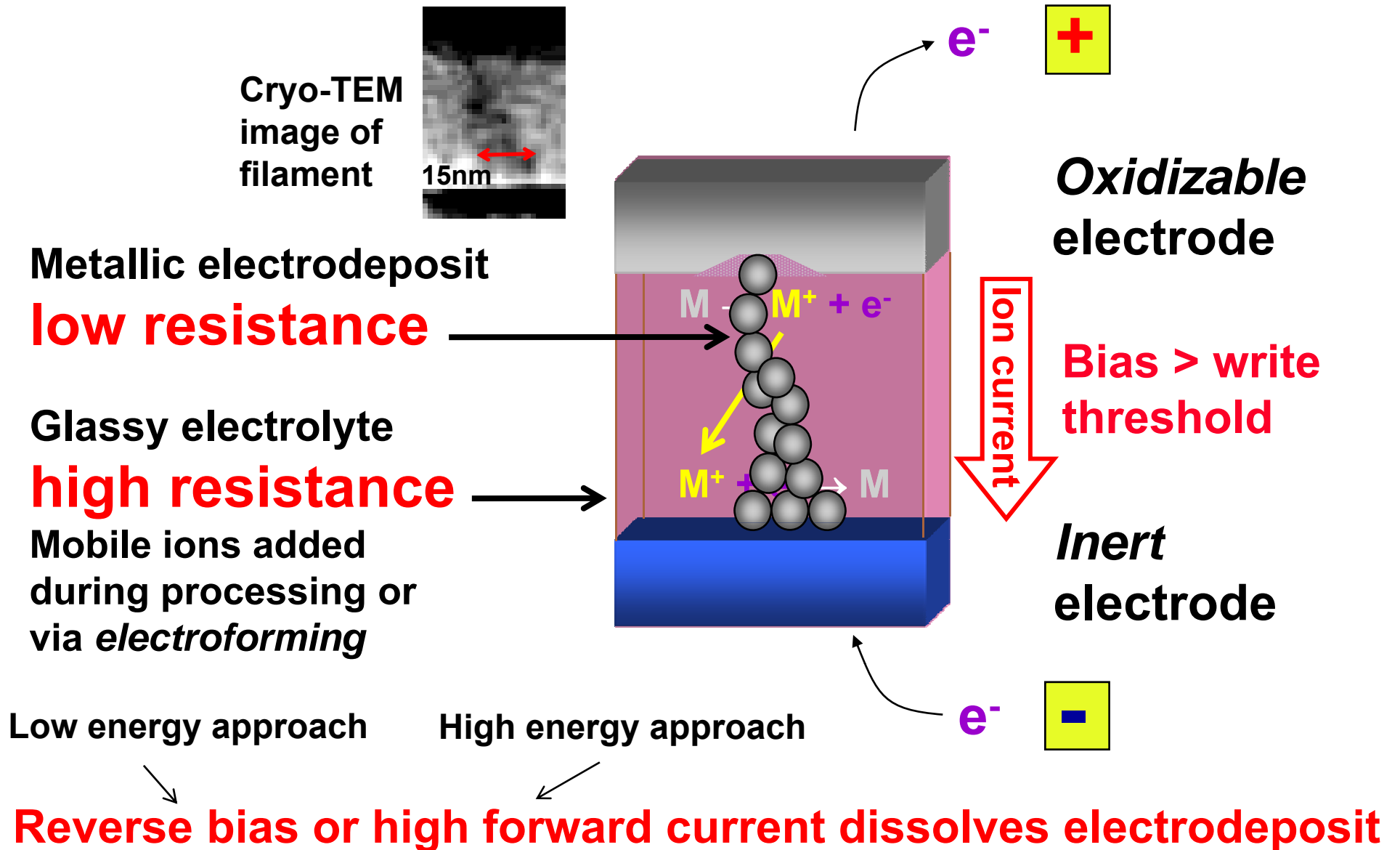
# The famous Memristor



J. J. Yang, M. D. Pickett, X. Li, D. A. A. Ohlberg, D. R. Stewart, R. S. Williams, "Memristive switching mechanism for metal/oxide/metal nanodevices," *Nature Nanotechnology*, Vol. 3, 429 (2008).

D.-H. Kwon *et al.*, "Atomic structure of conducting nanofilaments in TiO<sub>2</sub> resistive switching memory," *Nature Nanotechnology*, published online: 17 January 2010, DOI: 10.1038/NNANO.2009.456(2010).

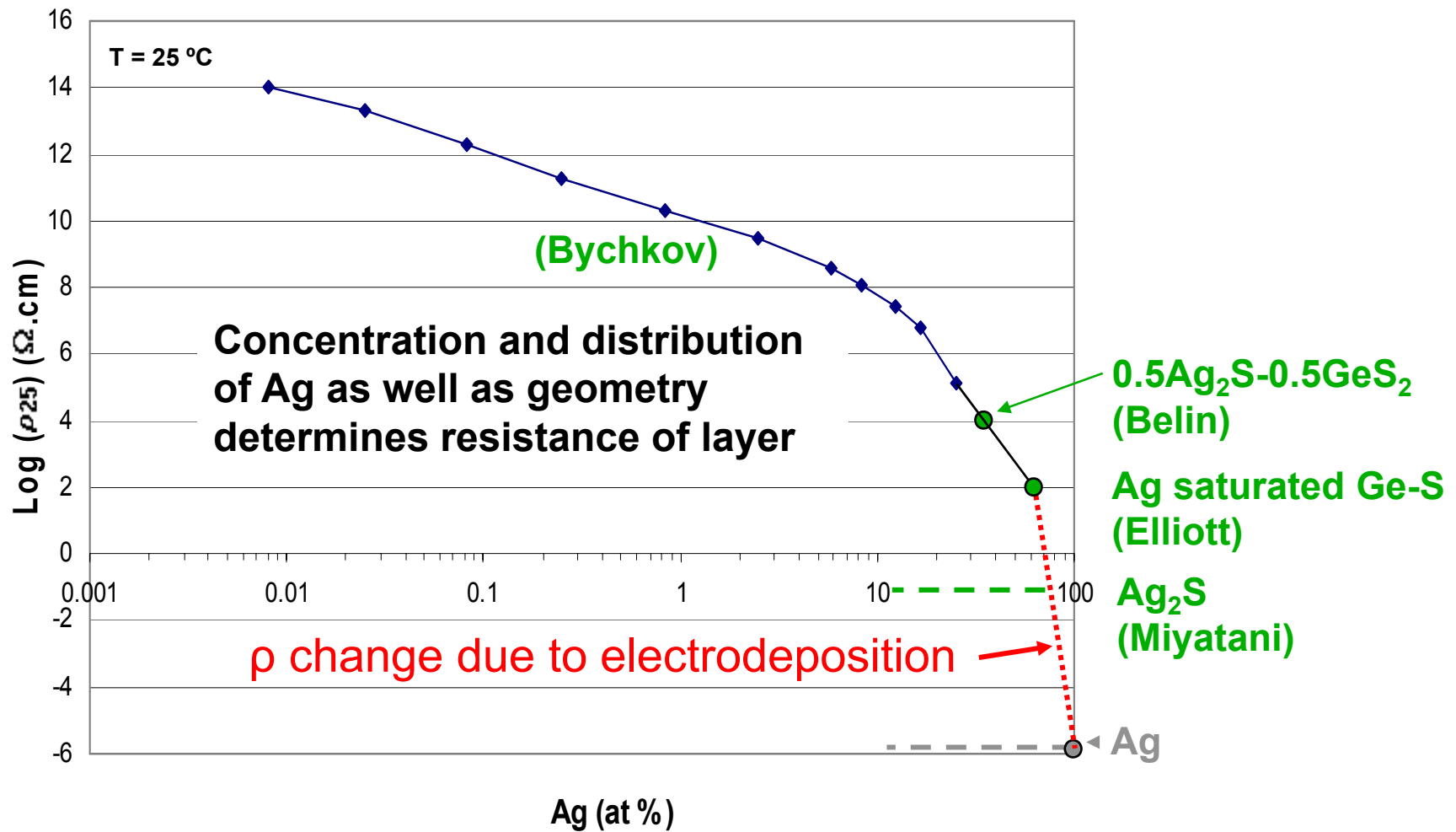
# Cation-based solid electrolyte device



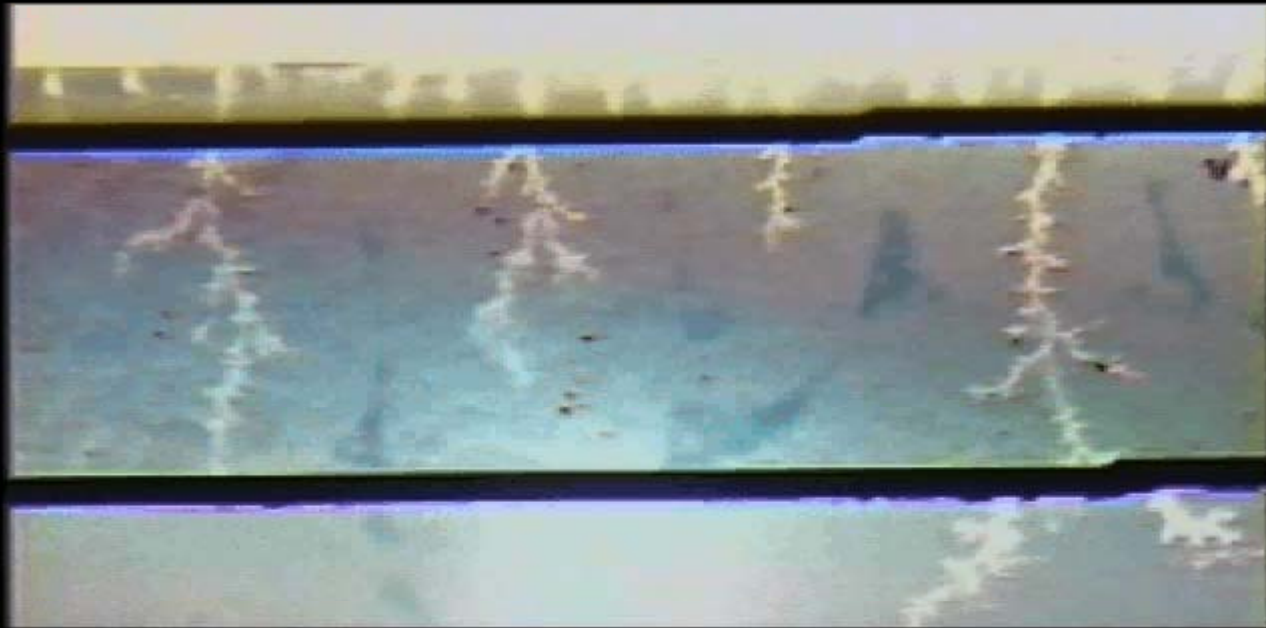
# Materials - electrolytes & electrodes

Electrolyte	Electrode metals	
	Ag	Cu
$\text{Ge}_x\text{S}_y$	<i>W</i>	<i>W</i>
$\text{Ge}_x\text{Se}_y$	<i>W, Pt, Ni</i>	<i>W</i>
Ge-Te	<i>TiW</i>	<i>TaN</i>
GST	<i>Mo</i>	
As-S	<i>Au</i>	
$\text{Zn}_x\text{Cd}_{1-x}\text{S}$	<i>Pt</i>	
$\text{Cu}_2\text{S}$		<i>Pt, Ti</i>
$\text{Ta}_2\text{O}_5$		<i>Pt, Ru</i>
$\text{SiO}_2$	<i>Co</i>	<i>W, Pt, Ir</i>
$\text{WO}_3$	<i>W</i>	<i>W</i>
$\text{TiO}_2$	<i>Pt</i>	
$\text{ZrO}_2$	<i>Au</i>	
MSQ ( $\text{SiO}_2$ )	<i>Pt</i>	
CuTe/GdOx		<i>W</i>
$\text{Ge}_x\text{Se}_y/\text{SiO}_x$		<i>Pt</i>
$\text{Ge}_x\text{Se}_y/\text{Ta}_2\text{O}_5$		<i>W</i>
$\text{Cu}_x\text{S}/\text{Cu}_x\text{O}$		<i>Pt</i>
$\text{Cu}_x\text{S}/\text{SiO}_2$		<i>Pt</i>

# Electrolyte example: Resistivity of Ge-S vs. Ag content

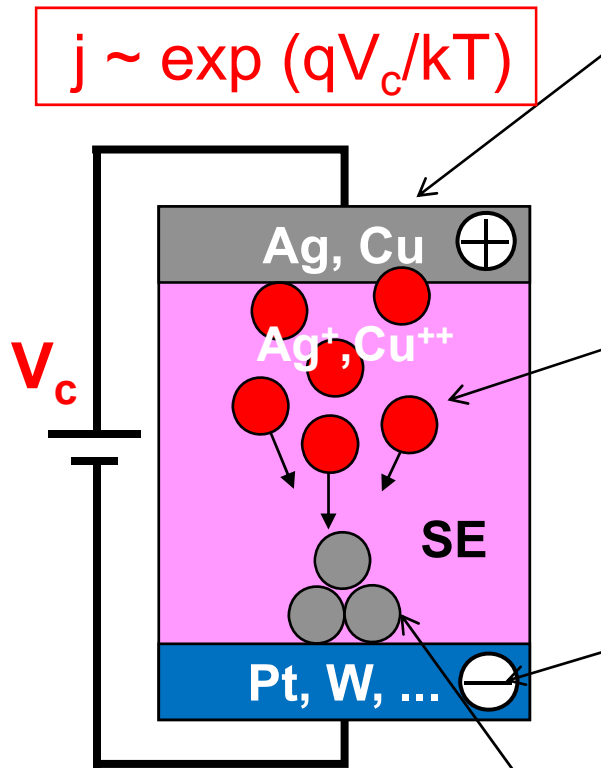


**Growth of electrodeposit**



**Reversal of electrodeposit growth**

# Reaction environment

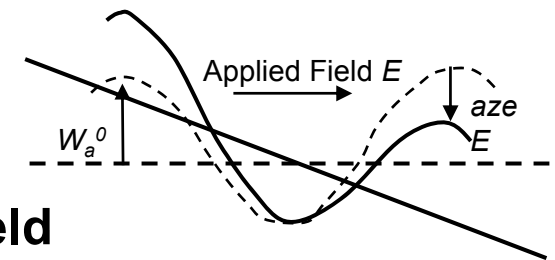


## Anodic dissolution

- equilibrium → oxidation for applied bias
- electrochemical electron transfer (Butler-Volmer)
- no overpotential, fast reaction

## Cation transport

- drift /diffusion transport
- high fields → drift dominant
- non-linear, very fast at high field

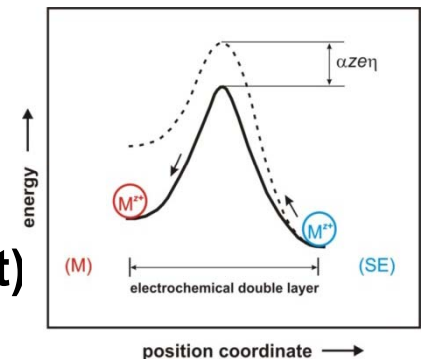


## Cathodic deposition

- electrochemical electron transfer (Butler-Volmer)
- crystallization overpotential

## Filament growth

- Even with multiple nucleation sites, “winner takes all” (field confinement)
- Filament forms within electrolyte

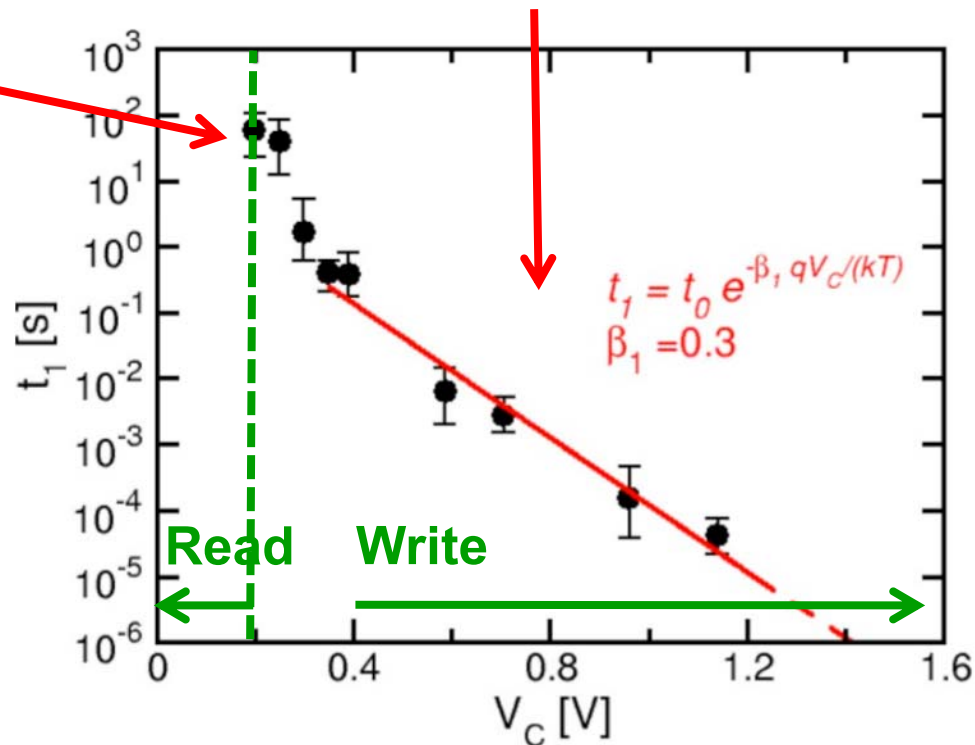


# Building a filament: voltage, time & charge

- Total charge transferred in time  $t$  is  $Q_0 = jtA_{\text{eff}}$ 
  - $A_{\text{eff}}$  is the effective area of the electrodeposit
  - $j = j_0 \exp(\alpha qV_c/kT)$

$$t_{\text{prog}} = Q_0 / [j_0 \exp(\alpha qV_c/kT) A_{\text{eff}}]$$

Saturation at low voltage (nucleation overpotential, work function difference, , etc.?)



$Q_0$  is in the fC range (from electrodeposit volume) - gives programming energy in the order of fJ...

$j_0$ =exchange current density,  $\alpha$ =transfer coefficient,  $q$ =cation charge,  $V_c$ = cell voltage

U. Russo, D. Kamalanathan, D. Ielmini, A.L. Lacaita, and M.N. Kozicki, "Study of Multilevel Programming in Programmable Metallization Cell (PMC) Memory," IEEE Transactions on Electron Devices, Vol. 56, 1040 – 1047 (2009).

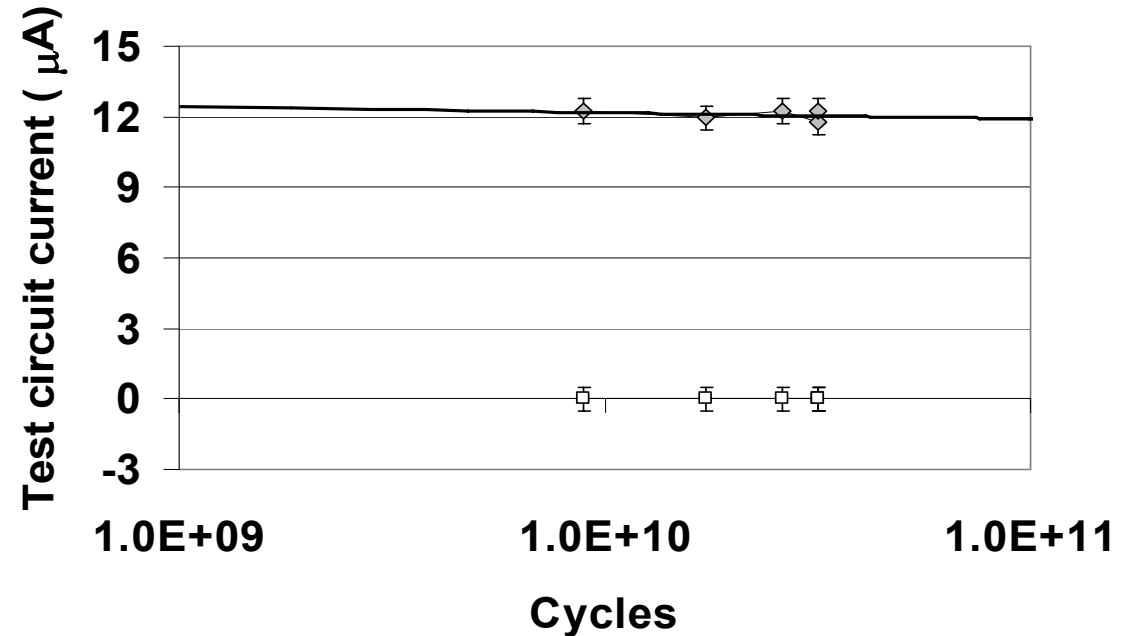


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# Endurance and retention

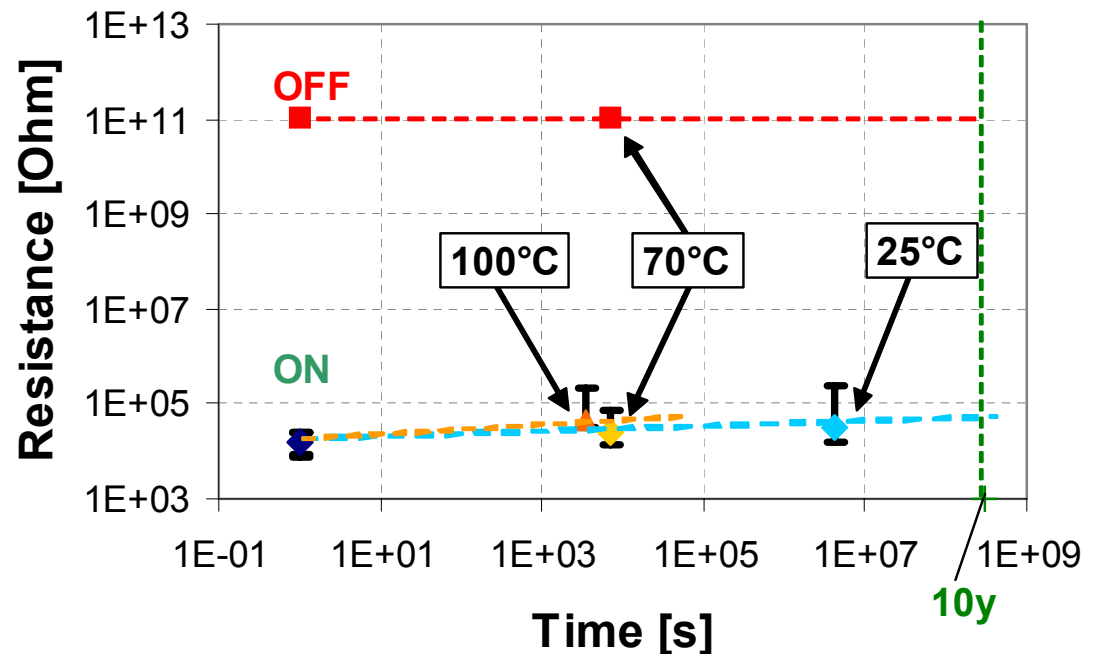
**Endurance  $>10^{10}$  cycles** with no degradation evident for 75 nm Ag-Ge-Se device ( $I_{\text{prog}} = 12 \mu\text{A}$ )

M.N. Kozicki, M. Park, and M. Mitkova, "Nanoscale Memory Elements Based on Solid-State Electrolytes," IEEE Trans. Nanotechnology, vol. 4, 331-338 (2005).

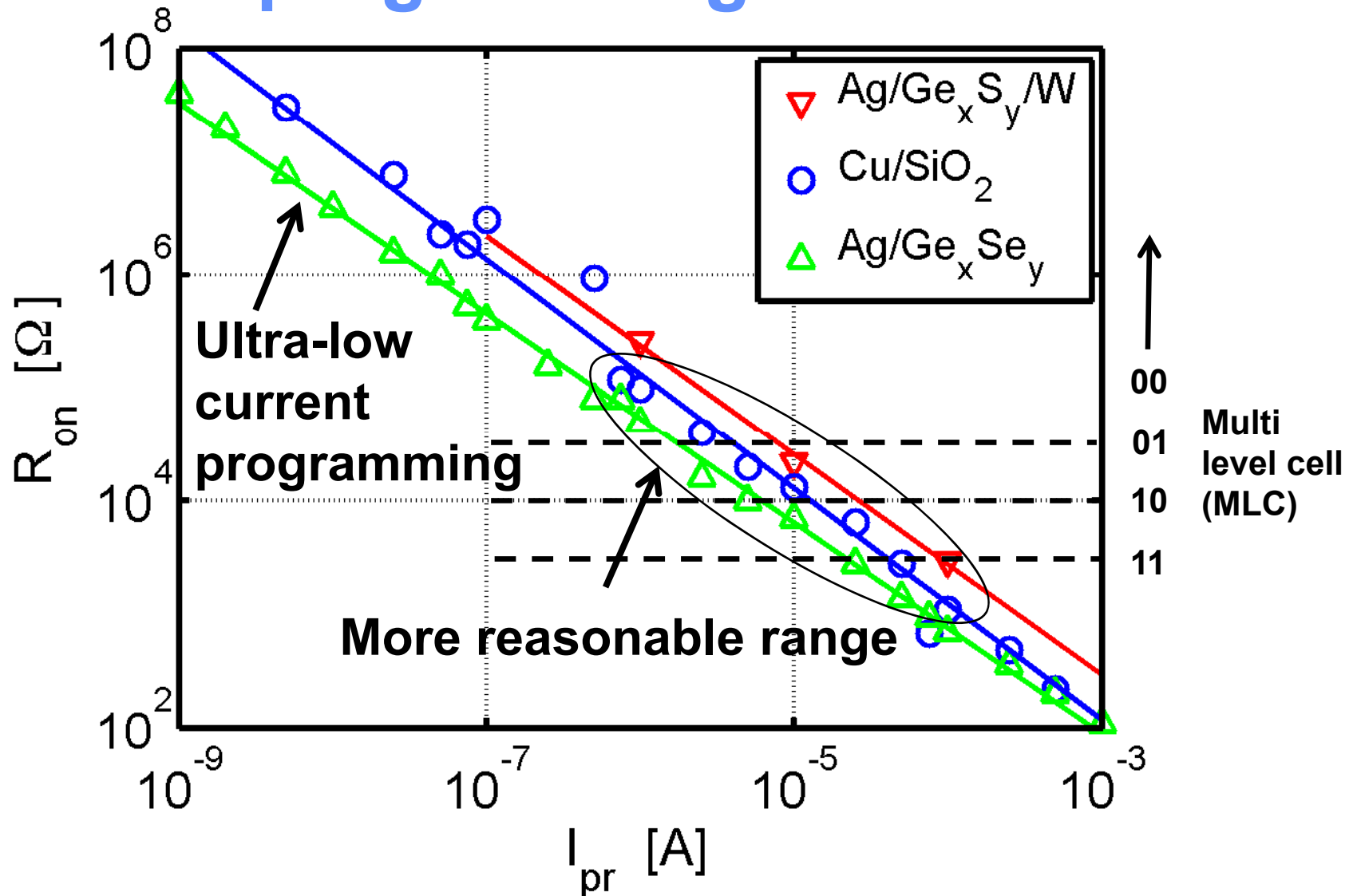


**Retention  $>10$  yrs** at 100°C for 90 nm Ag-Ge-S device (full wafer results)

R. Symanczyk, "Conductive Bridging Memory Development from Single Cells to 2Mbit Memory Arrays", 8th Non-Volatile Memory Technology Symposium, 2007.

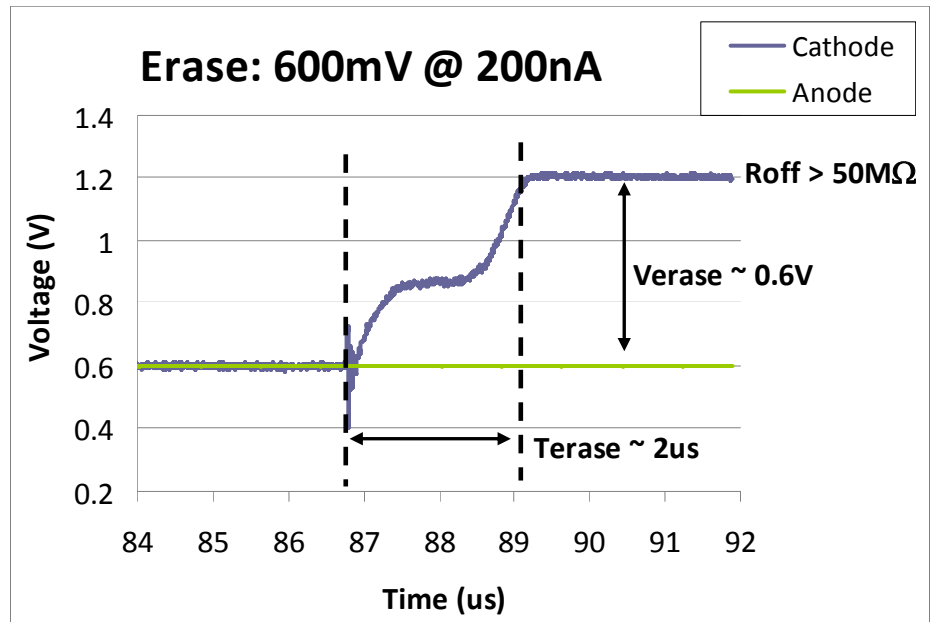
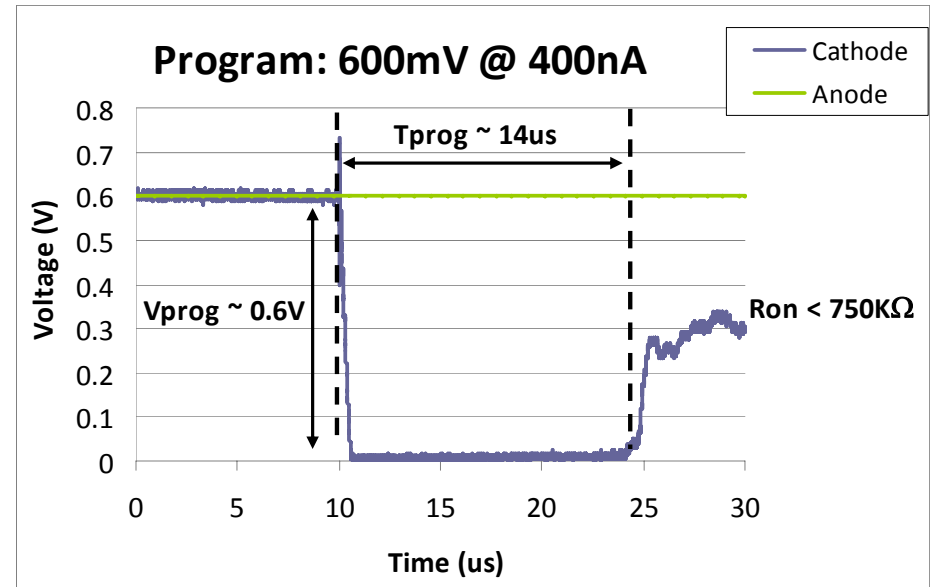
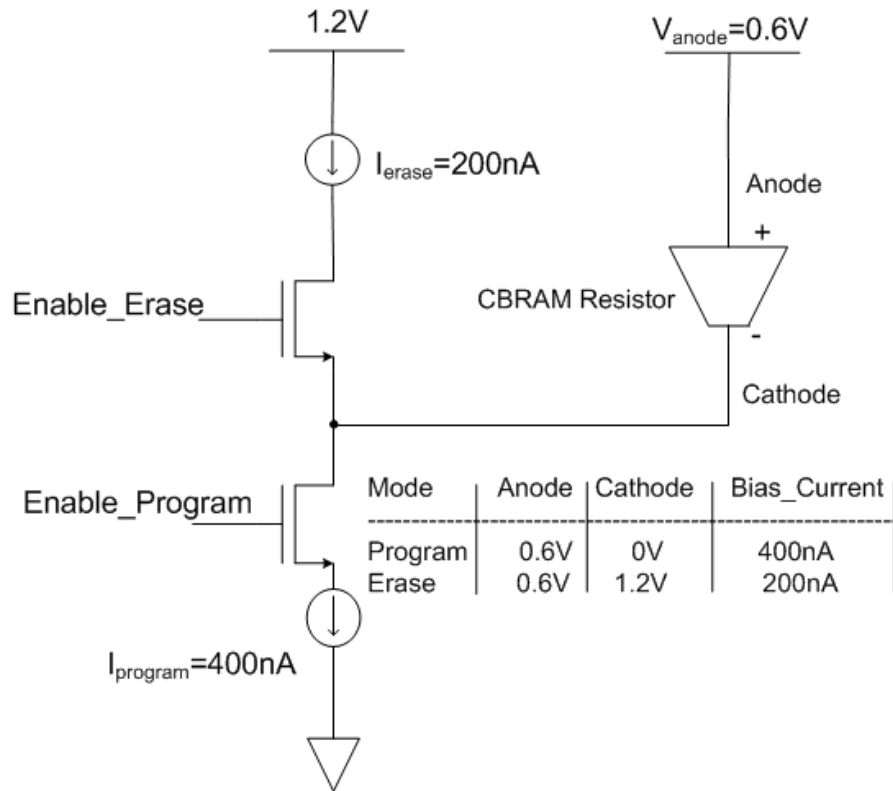


# On-state resistance vs. programming current



Data compiled by John Jameson, Adesto Technologies. Some data taken from R. Waser, R. Dittmann, G. Staikov, and K. Szot, "Redox-Based Resistive Switching Memories – Nanoionic Mechanisms, Prospects, and Challenges", *Adv. Mater.*, Vol. 21, 2632–2663 (2009).

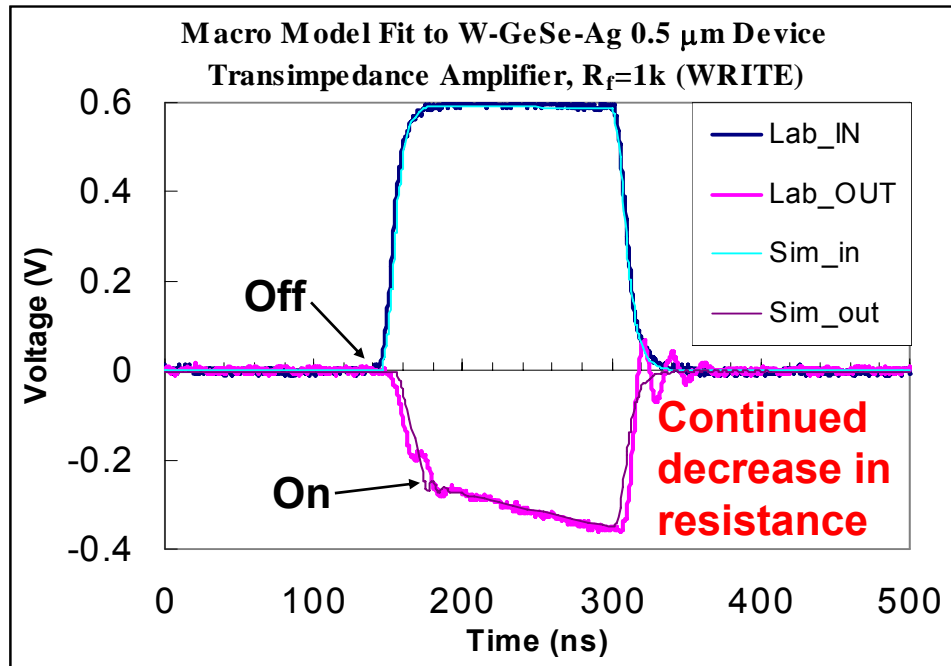
# Low voltage operation



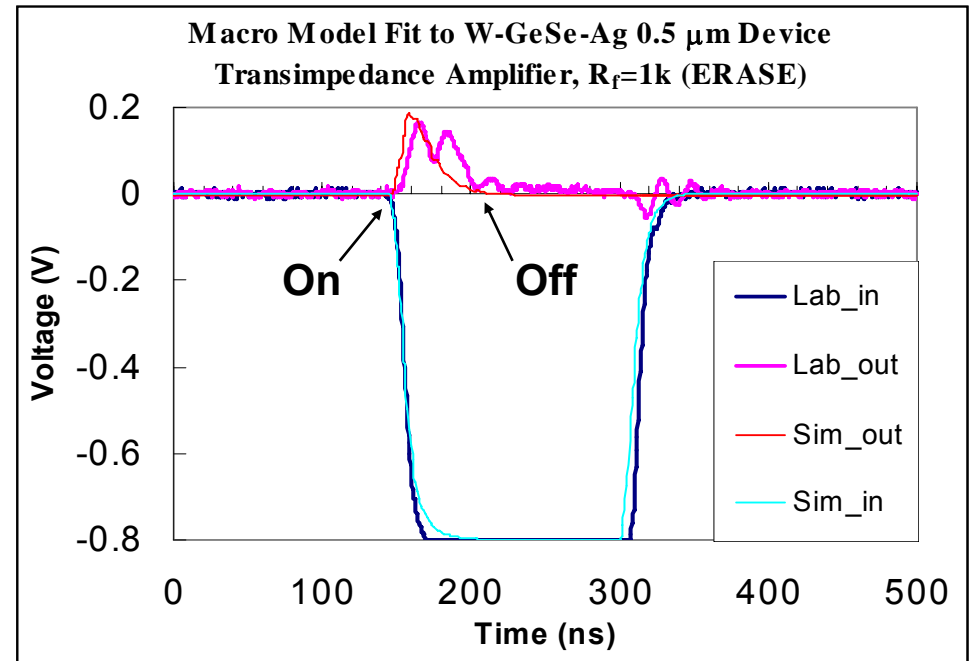
600 mV, 400/200 nA operation  
3.36 pJ write, 240 fJ erase

N. Derhacobian, S.C.Hollmer, N. Gilbert, M.N. Kozicki, "Power and Energy Perspectives of Nonvolatile Memory Technologies," Proc. IEEE, vol. 98, 283-298 (2010).

# Dynamic (pulse) programming of Ag-Ge-Se devices



**Write**

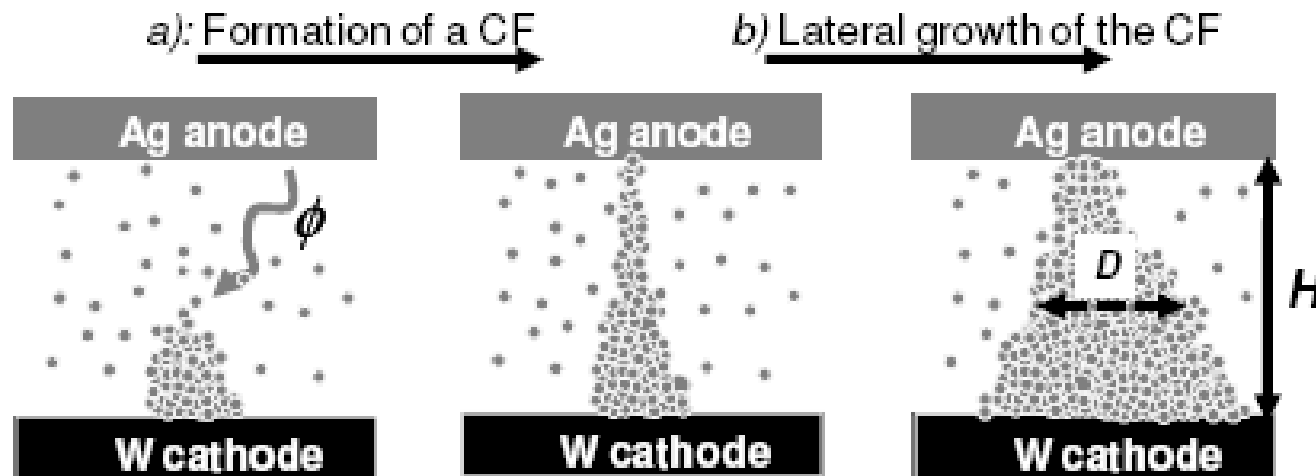


**Erase**

**Output signal is via a transimpedance amplifier so that increasing voltage magnitude means increasing current (or decreasing device resistance)**

N. Gilbert, C. Gopalan, and M. N. Kozicki, "A Macro model of Programmable Metallization Cell Devices," *Solid State Electronics*, vol. 49, 1813-1819 (2005).

# Schematic diagram of two-stage conducting filament formation process

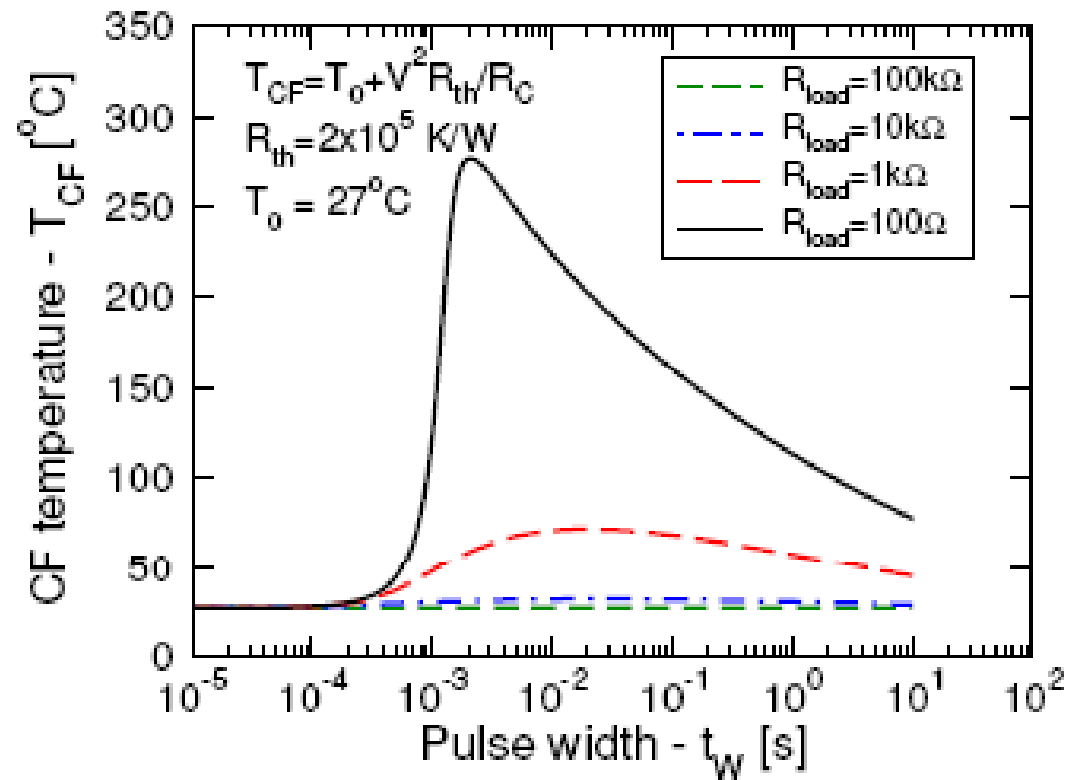
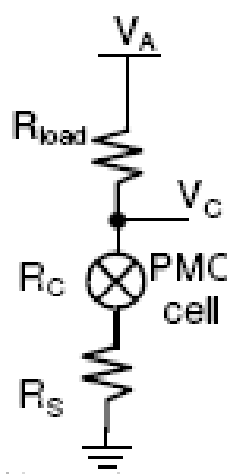


Both the *initial formation* and *radial growth* are driven by **ion migration**

But... is this everything?

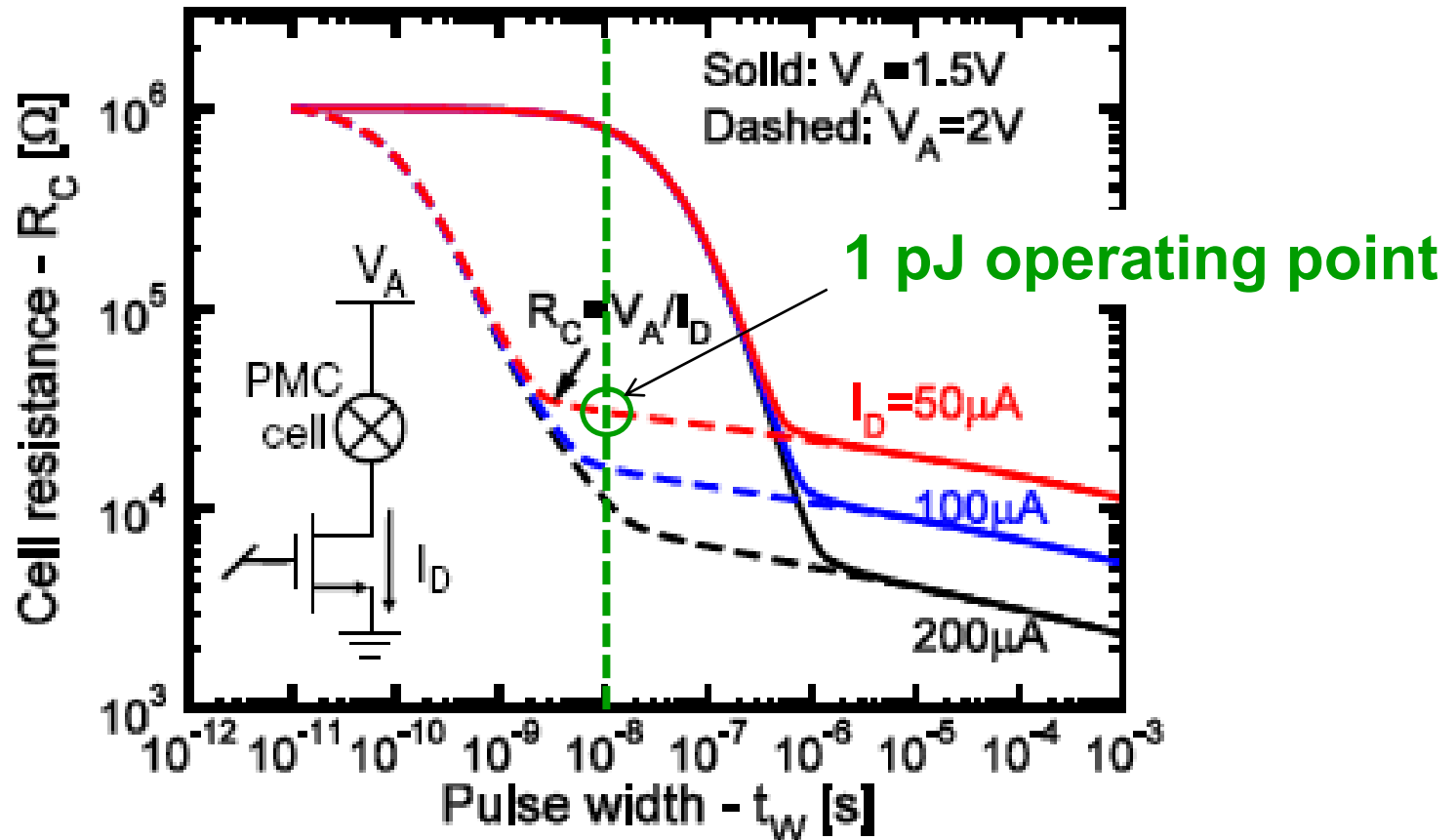
U. Russo, D. Kamalanathan, D. Ielmini, A.L. Lacaita, and M.N. Kozicki, "Study of Multilevel Programming in Programmable Metallization Cell (PMC) Memory," IEEE Transactions on Electron Devices, Vol. 56, 1040 – 1047 (2009).

# Joule heating during programming with high currents



- Joule heating is evident at low  $R_{load}$ /high current
- Maximum temperature rise for 1 k $\Omega$  load is 40°C

# Conservative programming model

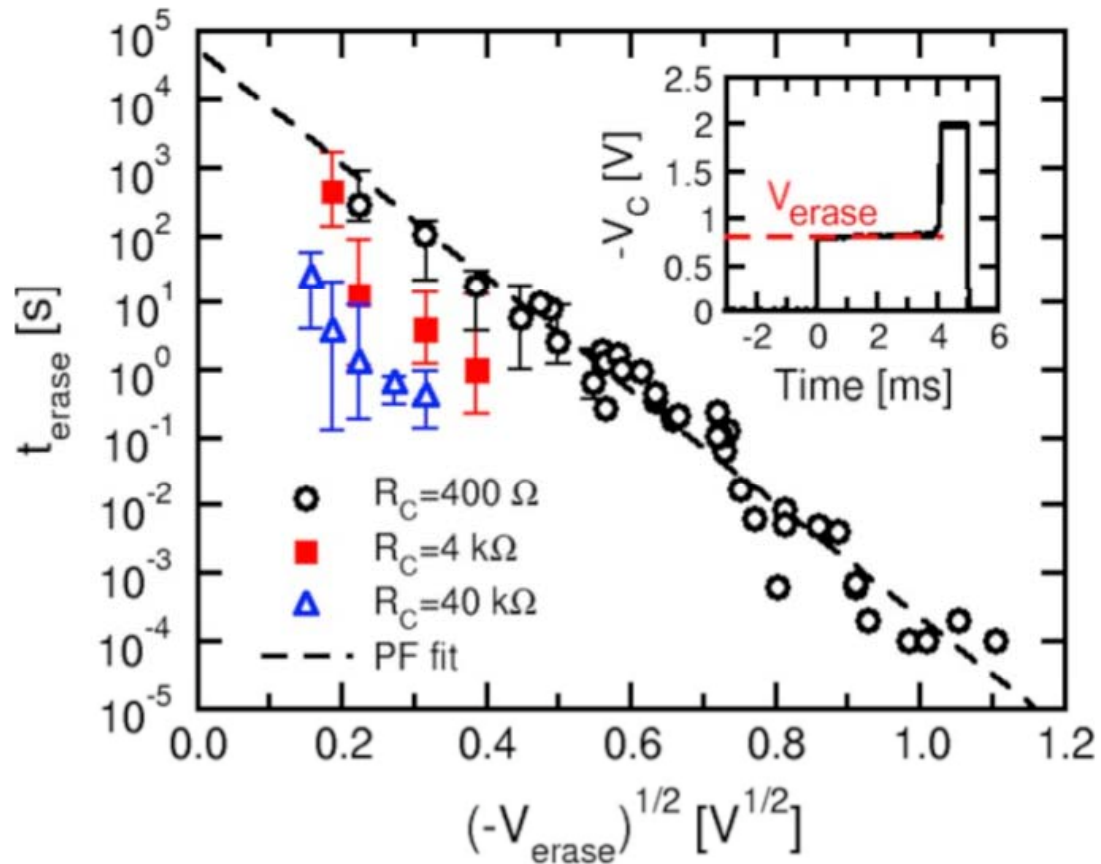


**Model is based on a Ag/Ag-Ge-S/W 1T-1R cell and includes transistor load and Joule heating effects**

U. Russo, D. Kamalanathan, D. Ielmini, A.L. Lacaita, and M.N. Kozicki, "Study of Multilevel Programming in Programmable Metallization Cell (PMC) Memory," IEEE Transactions on Electron Devices, Vol. 56, 1040 – 1047 (2009).



# Erase kinetics



**Erase time defined by 10x increase in resistance**

D. Kamalanathan, U. Russo, D. Ielmini, and M.N. Kozicki, "Voltage-Driven On–Off Transition and Tradeoff With Program and Erase Current in Programmable Metallization Cell (PMC) Memory," IEEE Electron Device Letters, Vol. 30, 553 – 555 (2009).

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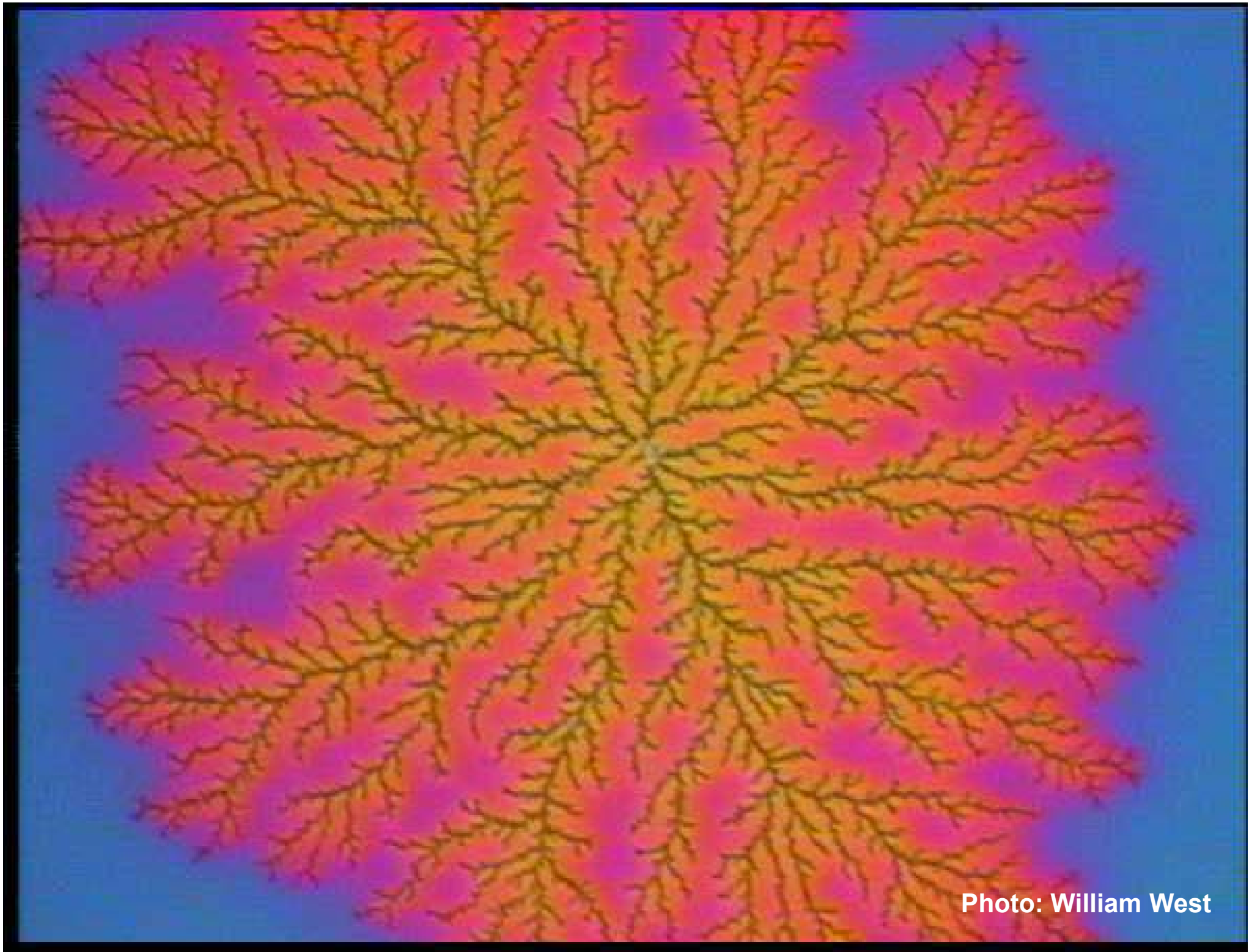
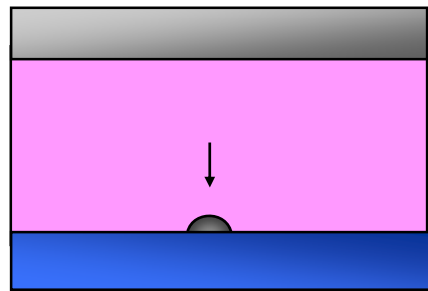


Photo: William West

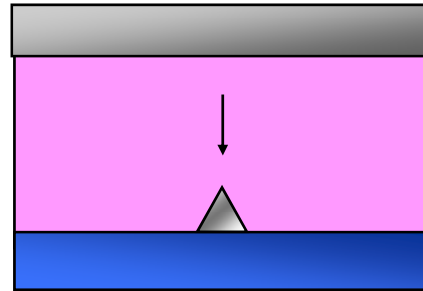


**Photo: Chakku Gopalan**

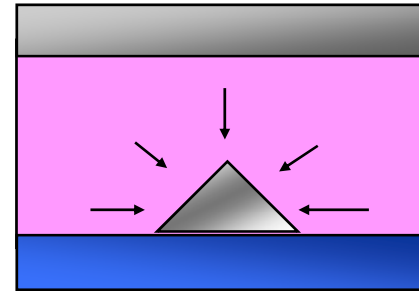
# Electrodeposit evolution in a homogeneous solid electrolyte



1,2D nucleation

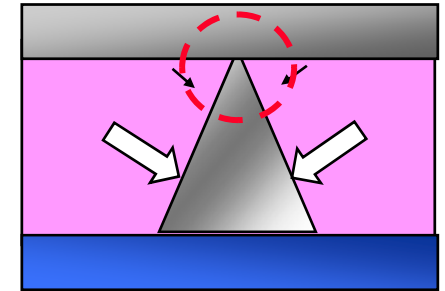


Outward growth



3D growth

Highest R region



Constrained 3D growth

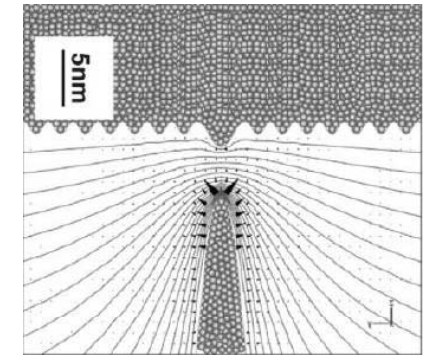
**Growth speed of a (cylindrical) nanofilament**

$$\dot{h}[\text{cm/s}] = \frac{M_A}{\pi r^2 z N_A e_0 \rho} I[\text{A}]$$

$M_A$ =atomic mass  
 $N_A$ =Avogadro's #  
 $Ze_0$ =charge on ion  
 $\rho$ =filament density  
 $r$ =filament radius

**Example: Ag filament of 10nm diameter at  $I = 1 \mu\text{A}$**

$$\rightarrow \dot{h} \sim 1.3 \text{m/s}$$



**Erase initiation via potential concentration at tip of electrodeposit**

X. Guo, C. Schindler, S. Menzel, and R. Waser, "Understanding the switching-off mechanism in Ag<sup>+</sup> migration based resistively switching model systems," Appl. Phys. Lett., Vol. 91, 133513 (2007).

# Where do the metallic filaments form?

**Jaakko Akola**

University of Jyväskylä and  
Tampere Technological University,  
Finland

**Bob Jones**

Jülich Research Center, Germany

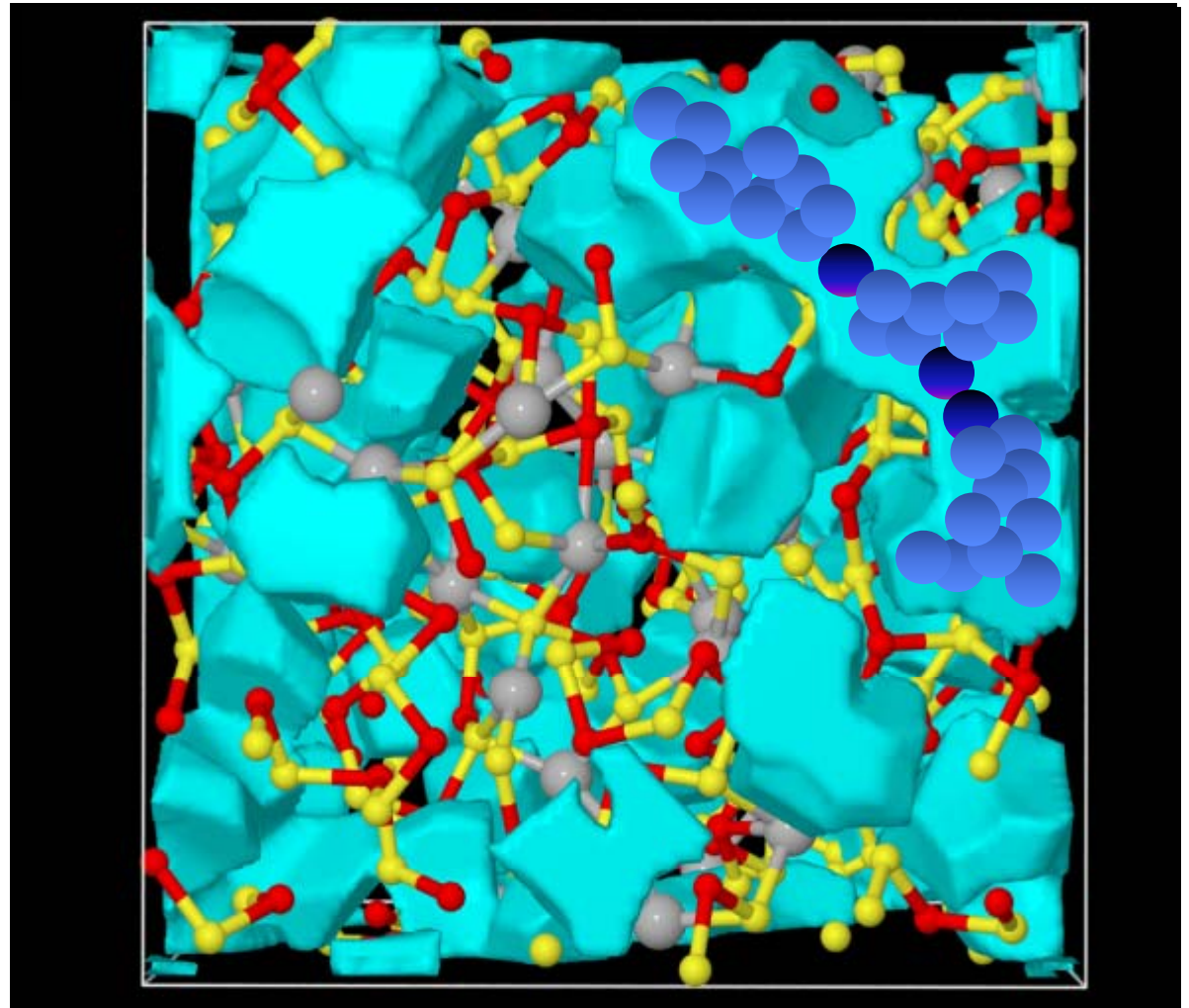
**Tomas Wagner**

University of Pardubice, Czech  
Republic

**Techniques:**

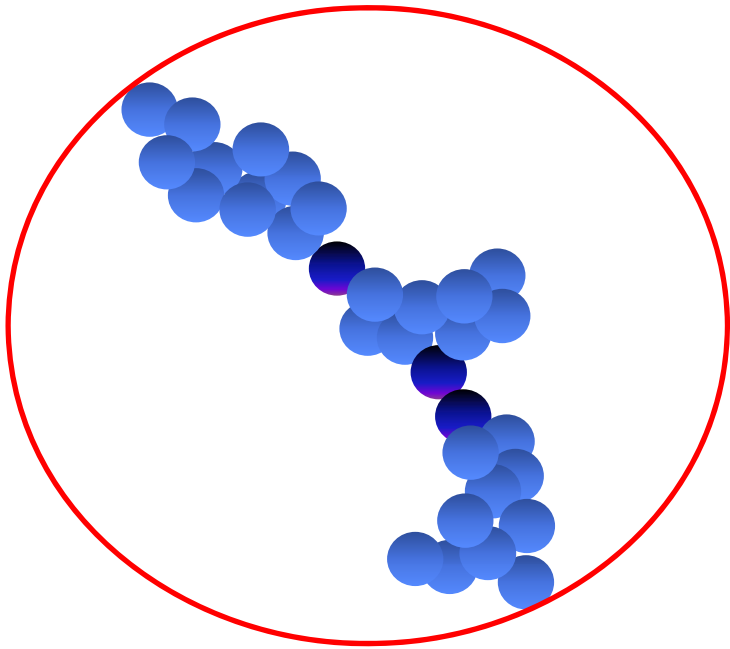
Full DFT, 500 atom system

X-ray diffraction, neutron  
scattering, EXAFS

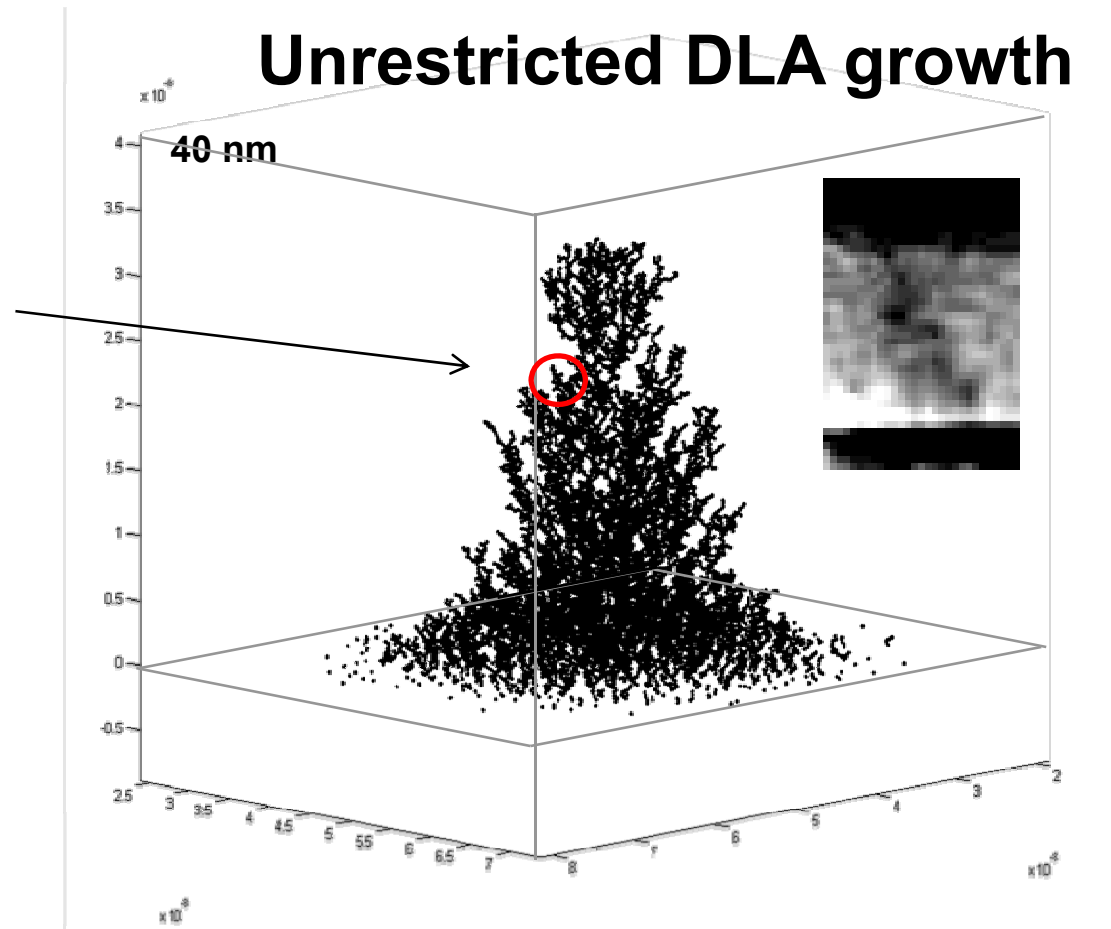


**Cavities** comprise 24% of the  
volume of  $\text{Ag}_{12}\text{As}_{35}\text{S}_{53}$ , ( $\text{SiO}_2$  is 32%  
but cavities are more dispersed?)

# Filament morphology



**Full filament may be composed of few to many nano-filaments in parallel.**



**Rainer Waser**  
RWTH Aachen and Jülich Research Center, Germany

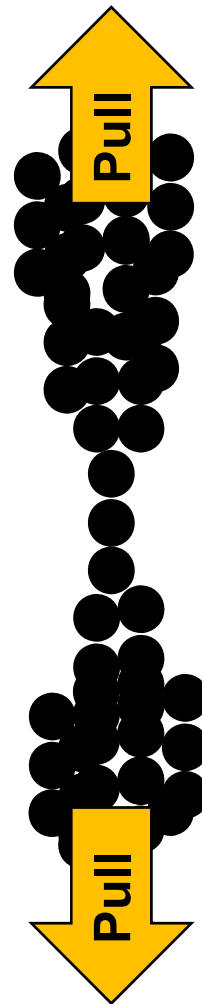
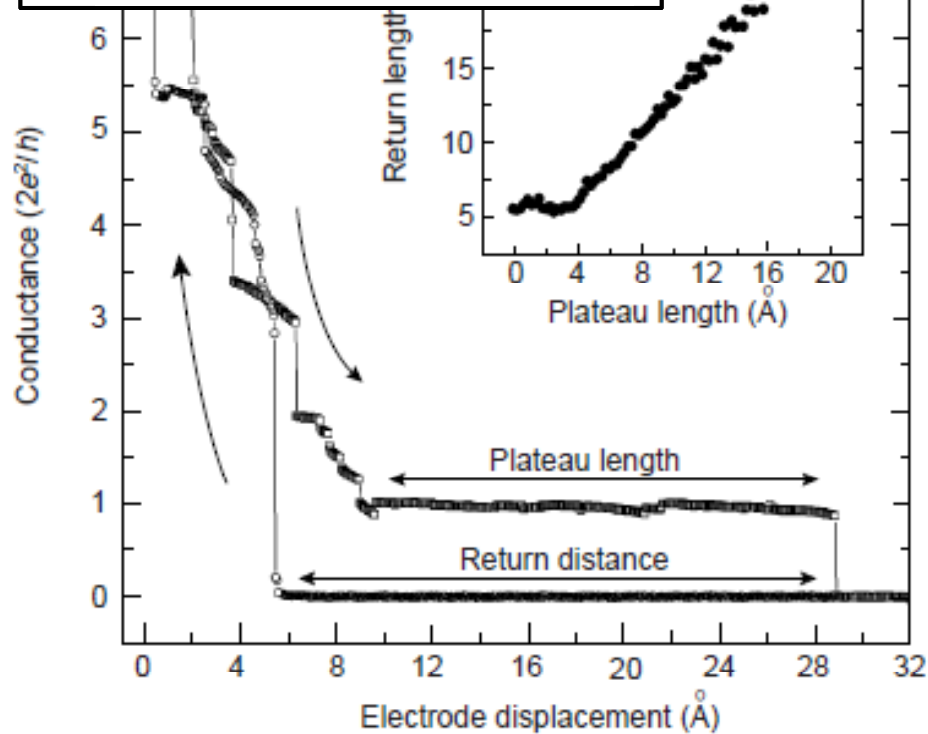
# Resistance in atomic-scale wires

Conductance quantized in units of  $2e^2/h$  ( $R = 12.9k\Omega$ )

## Formation and manipulation of a metallic wire of single gold atoms

A. I. Yanson<sup>+</sup>, G. Rubio Bollinger<sup>†</sup>, H. E. van den Brom<sup>+</sup>, N. Agrait<sup>†</sup> & J. M. van Ruitenbeek<sup>\*</sup>

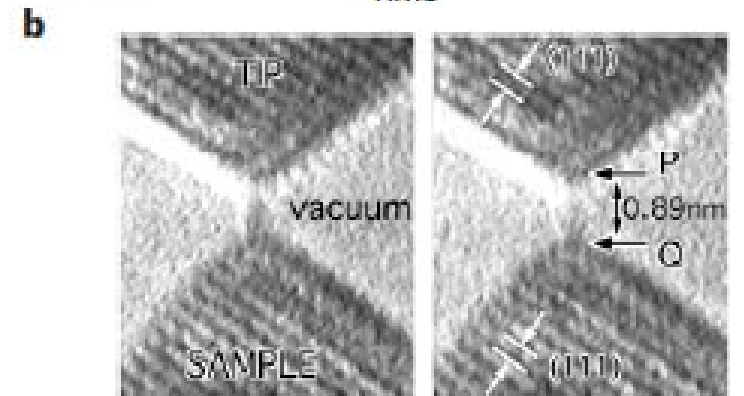
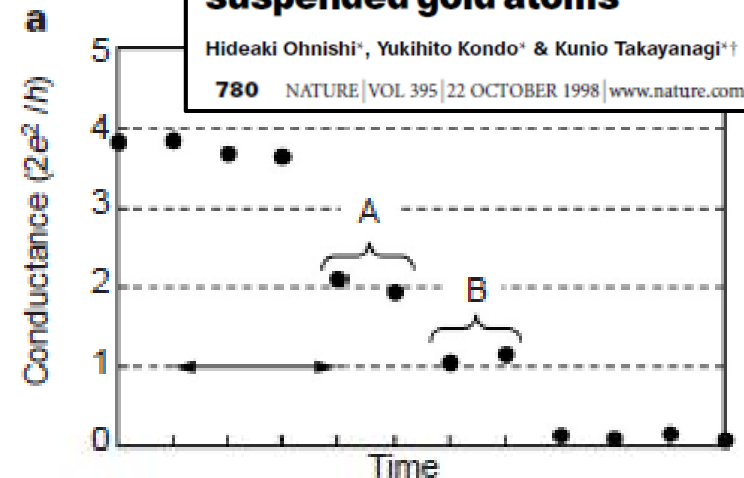
783 NATURE | VOL 395 | 22 OCTOBER 1998 | www.nature.com



## Quantized conductance through individual rows of suspended gold atoms

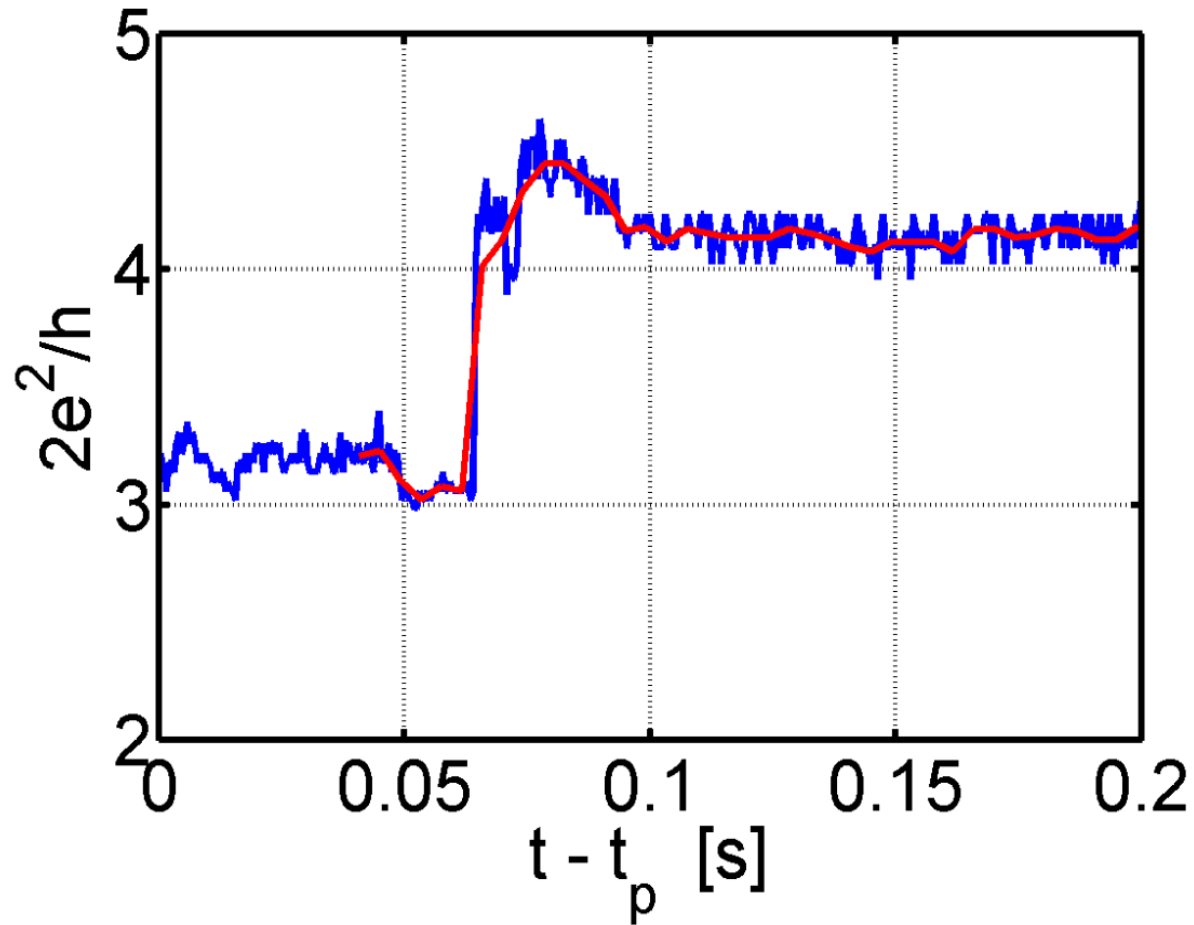
Hideaki Ohnishi<sup>+</sup>, Yukihiro Kondo<sup>+</sup> & Kunio Takayanagi<sup>††</sup>

780 NATURE | VOL 395 | 22 OCTOBER 1998 | www.nature.com





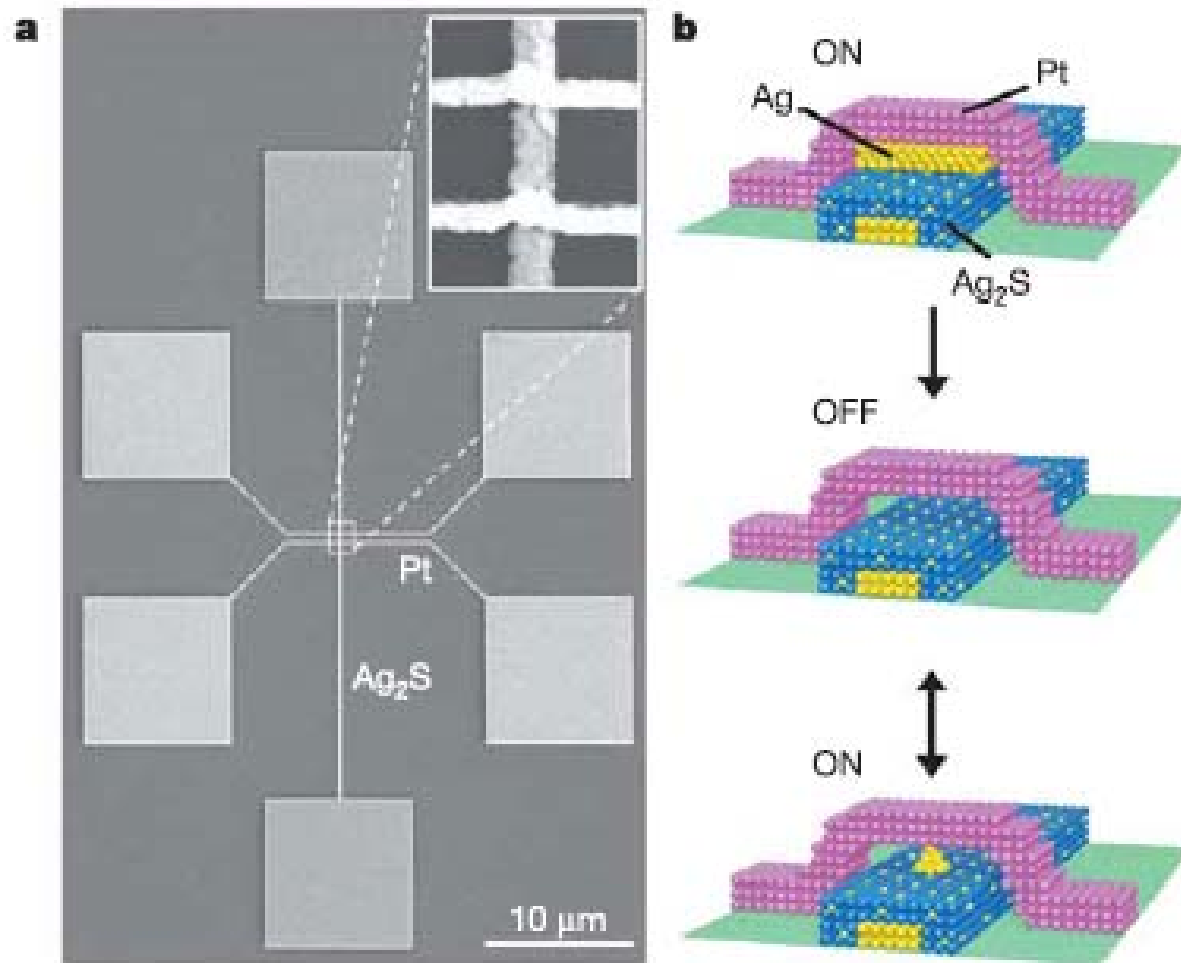
# Quantized conductance in CBRAM



John Jameson, Adesto Technologies

# Quantized conductance atomic switch

K. Terabe, *et al.*, NIMS, Nature, vol. 433, p. 47 (2005).

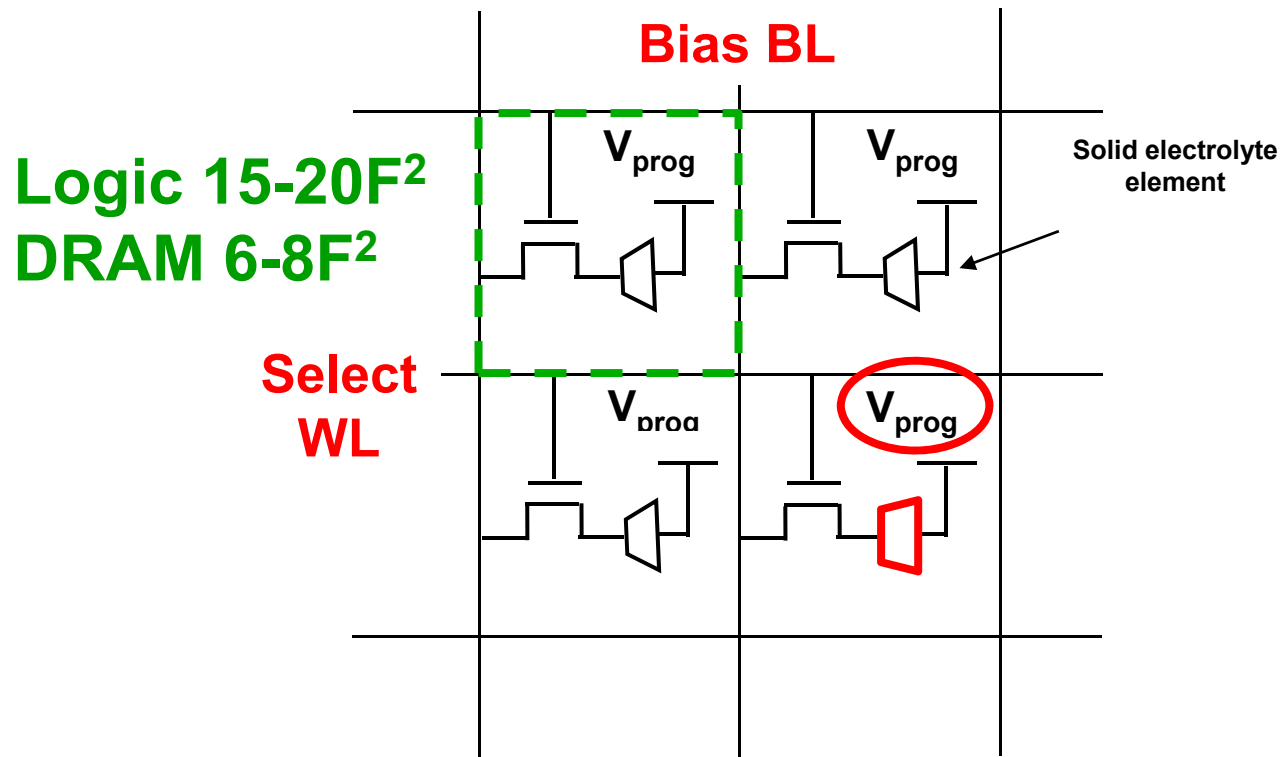


**Figure 1** Basics of the QCAS. **a**, SEM image of the QCAS. A QCAS is formed at each crossing point of the 150-nm-wide  $Ag_2S$  wire and the two Pt wires of 100 nm width. **b**, Schematic diagrams of the QCAS. As-formed switched-on state (top), switched-off state (middle) and switched-on state after the initial switching-off process (bottom).

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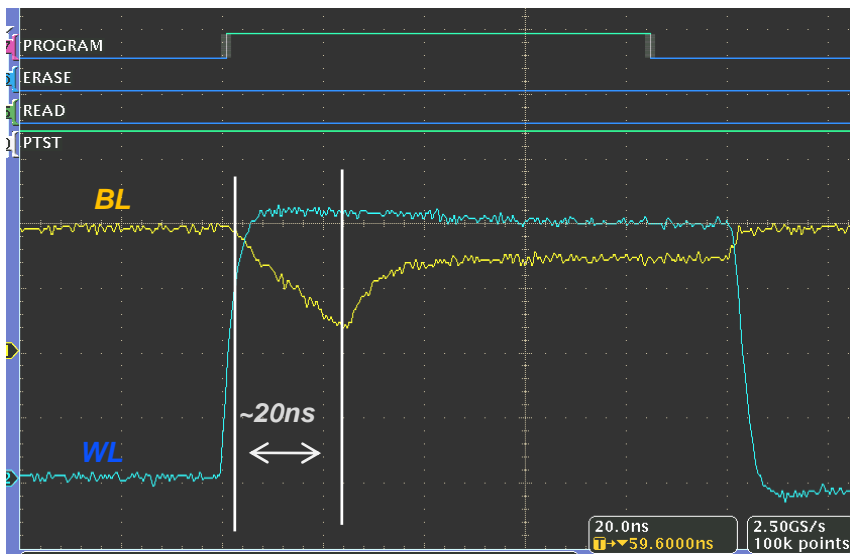
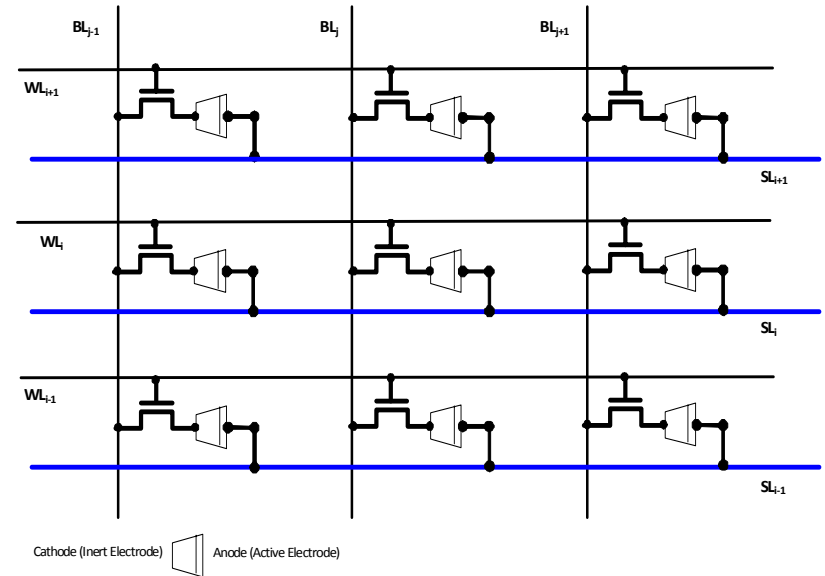
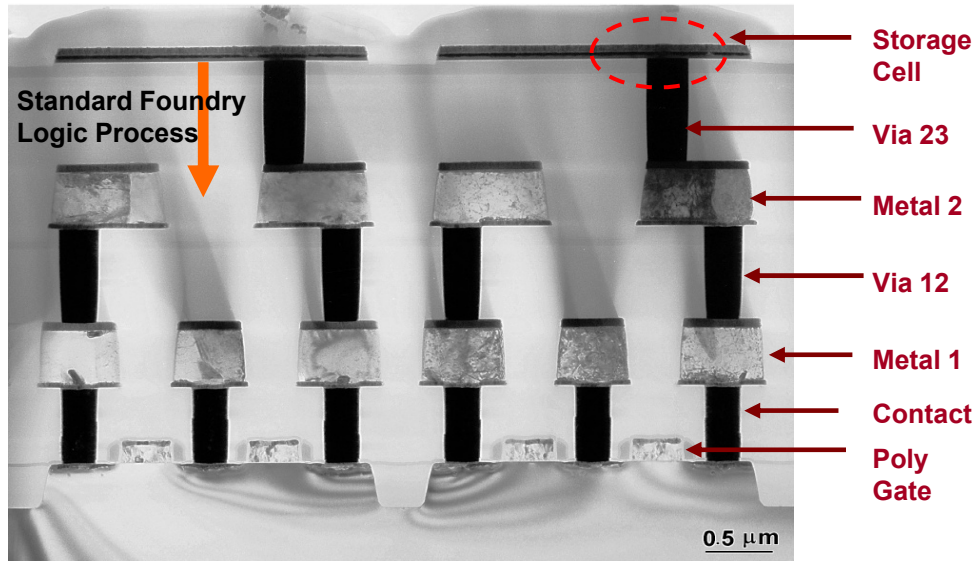
# Array options

## Active (1T-1R)

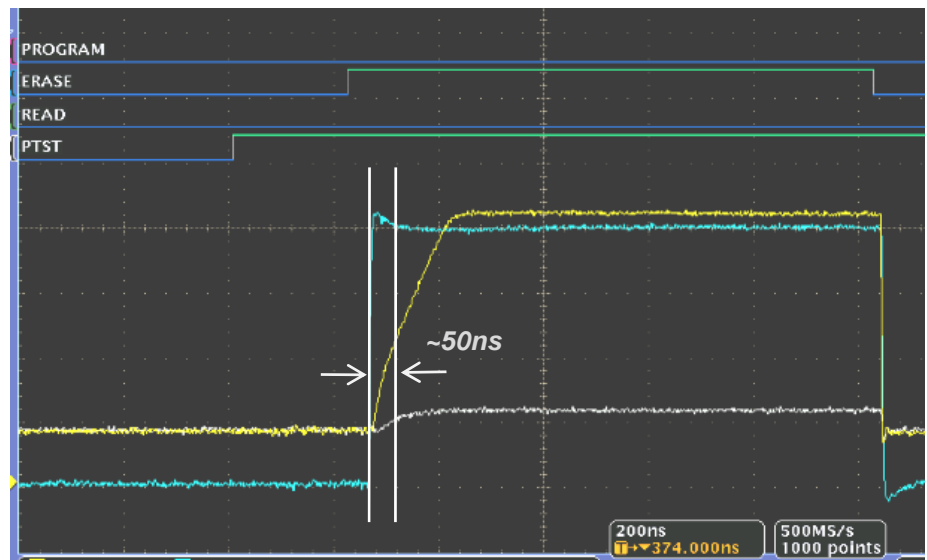


V<sub>prog</sub> is above or below transistor drain voltage to program or erase selected cell, programming current via bit line (BL)

# 1T-1R array fabrication and performance



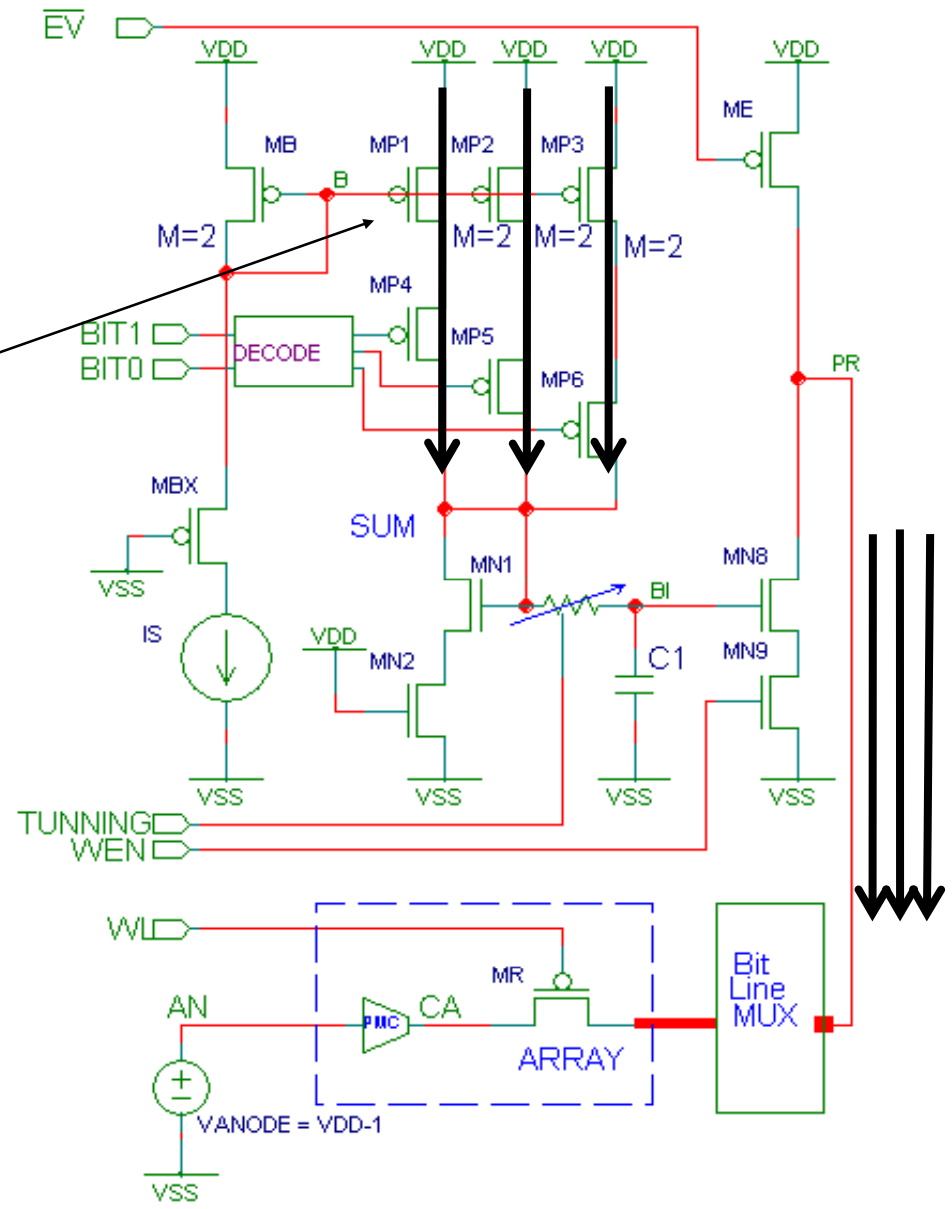
Program Operation (SET)  
20 ns



Erase Operation (RESET)  
50 ns

# Multi-level cell (MLC) write

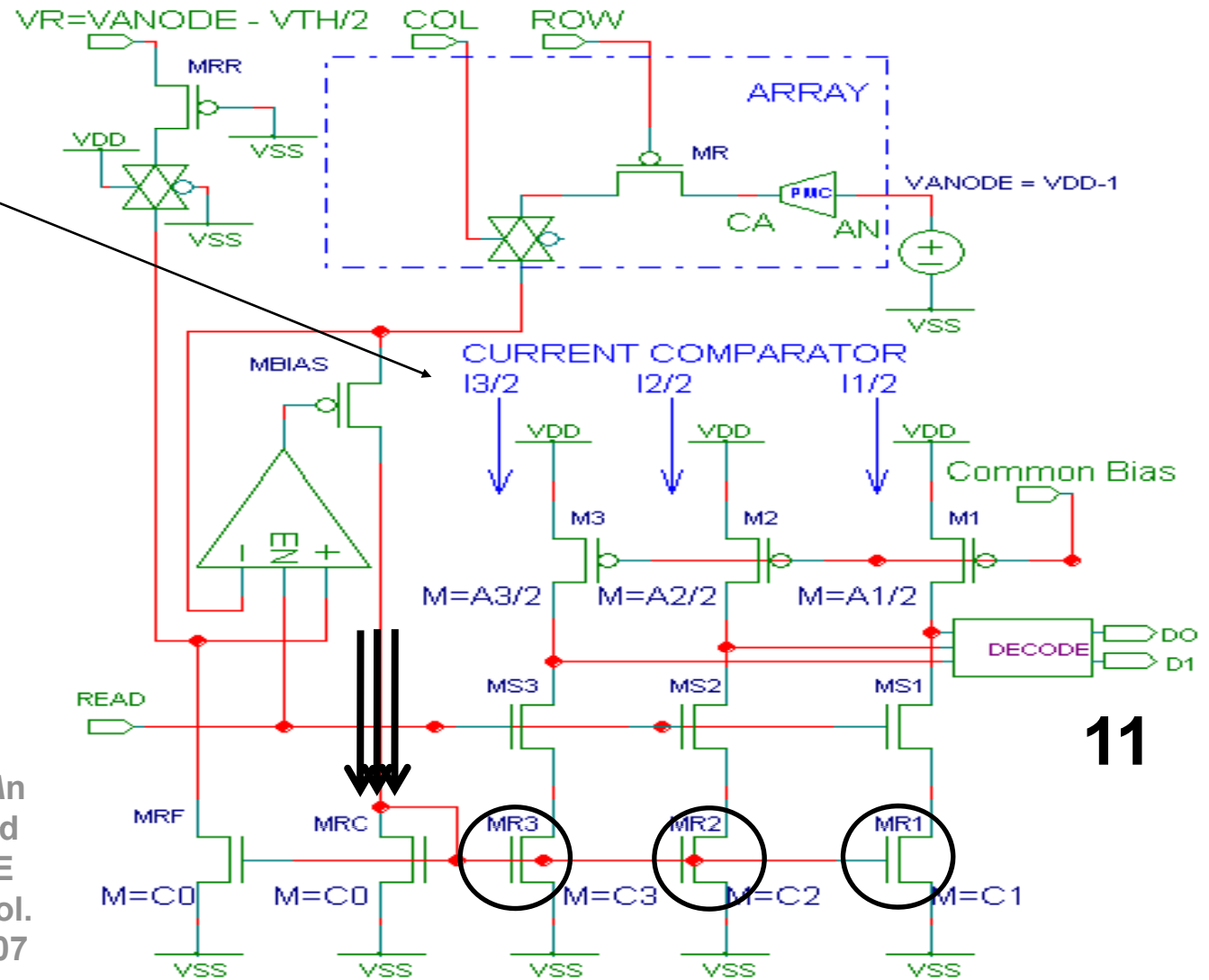
Three transistors are used to create **three discrete current levels** to set ON resistance (gives 4 resistance states = 2 bits).



N.E. Gilbert and M.N. Kozicki, "An Embeddable Multilevel-Cell Solid Electrolyte Memory Array," IEEE Journal of Solid-state Circuits, vol. 42, no. 6, pp 1383-1391, June 2007

# MLC read

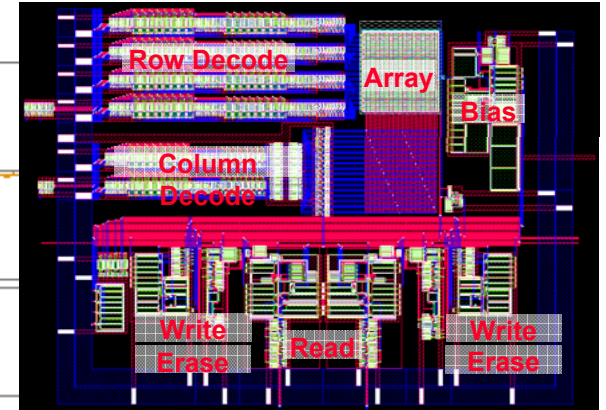
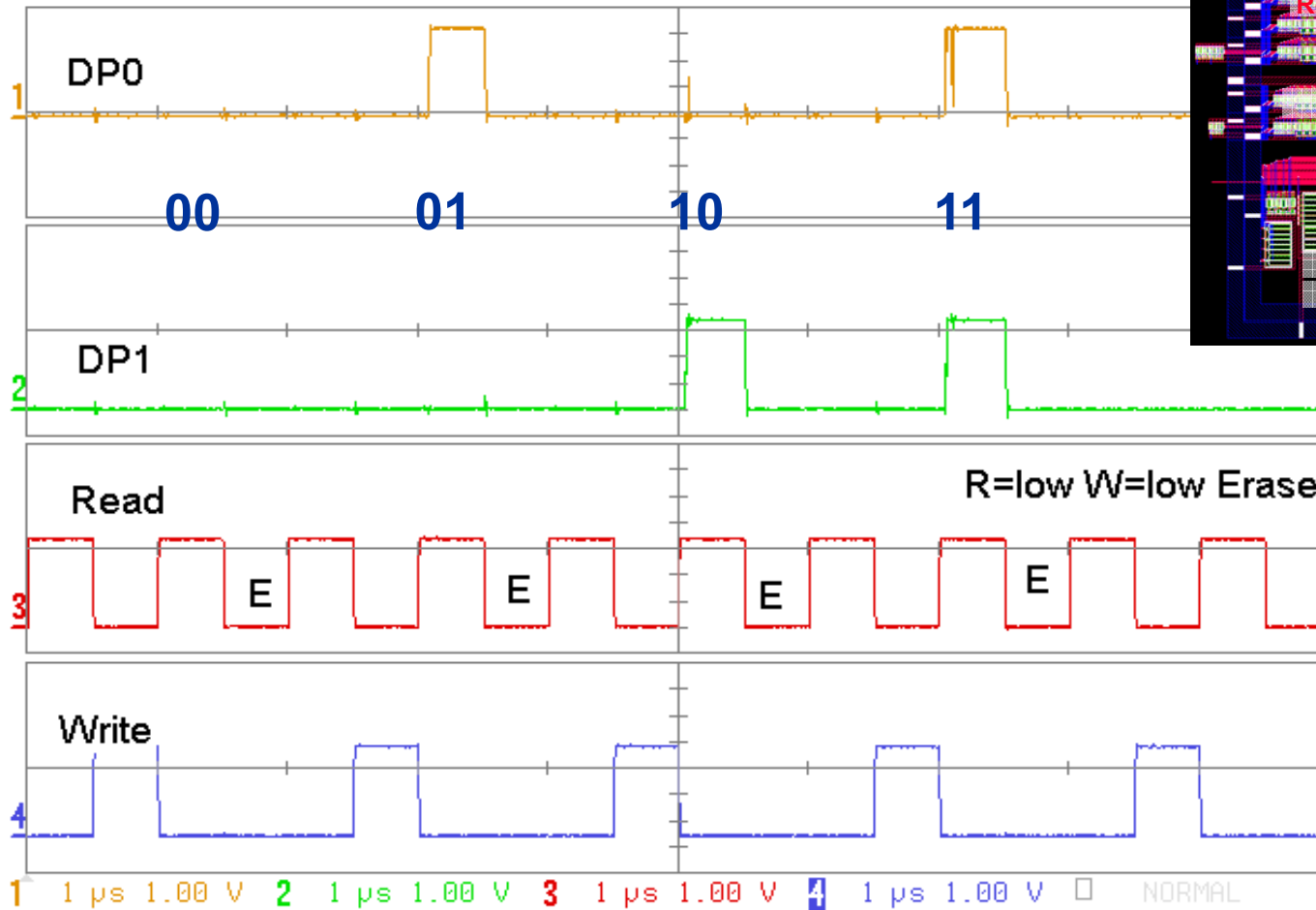
Current comparators used to sense device current



N.E. Gilbert and M.N. Kozicki, "An Embeddable Multilevel-Cell Solid Electrolyte Memory Array," IEEE Journal of Solid-state Circuits, vol. 42, no. 6, pp 1383-1391, June 2007

Fig. 3. Read circuit for multi-bit per cell implementations.

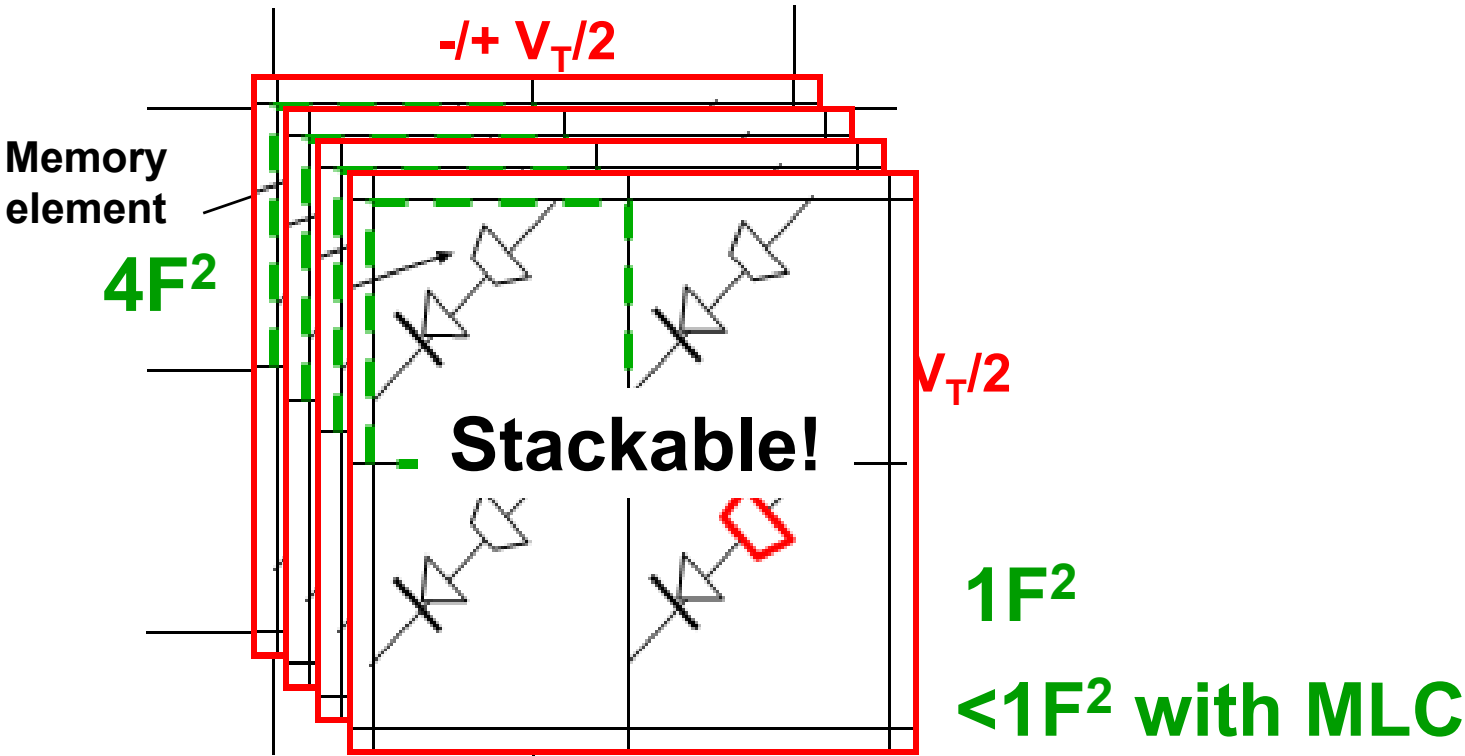
# MLC array operation



N.E. Gilbert and M.N. Kozicki, "An Embeddable Multilevel-Cell Solid Electrolyte Memory Array," IEEE Journal of Solid-state Circuits, vol. 42, no. 6, pp 1383-1391, June 2007

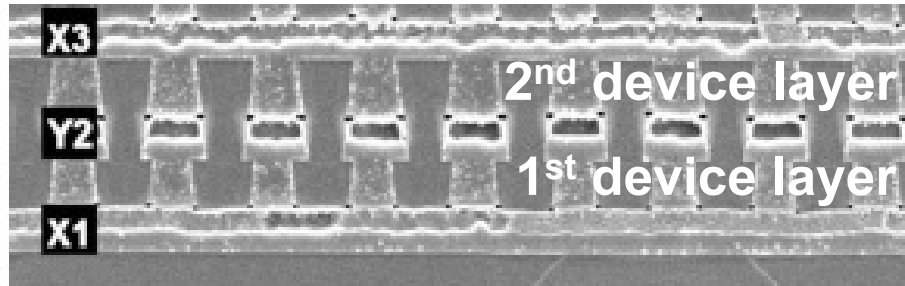


# Benefits of passive arrays

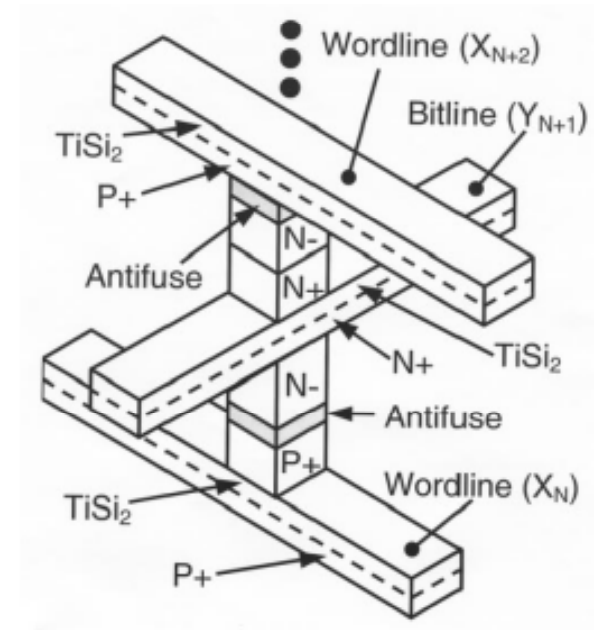


**Selected cell has +/-half threshold voltage on row and +/-half on column for write or erase**

# Example of multi-layer approach



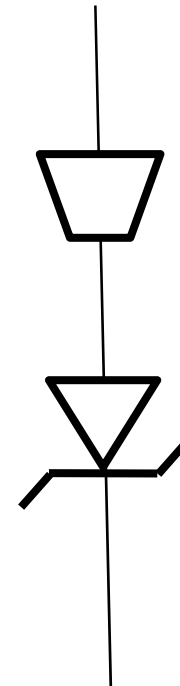
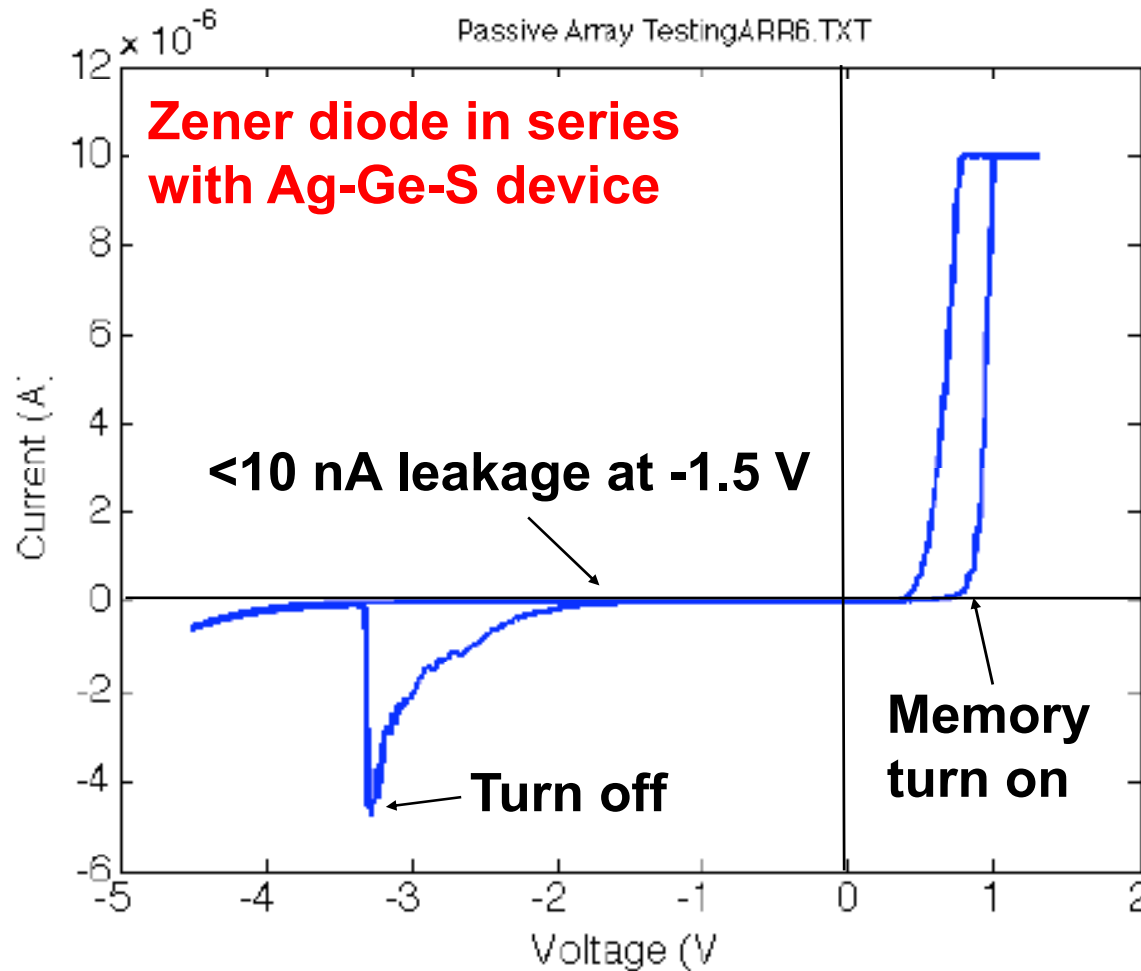
Example (from Matrix Semiconductor) showing diode isolation in a passive array of OTP structures



**Solid electrolyte devices are compatible with such 3-D approaches, although passive arrays require *unipolar* programming or *Zener diode* isolation**

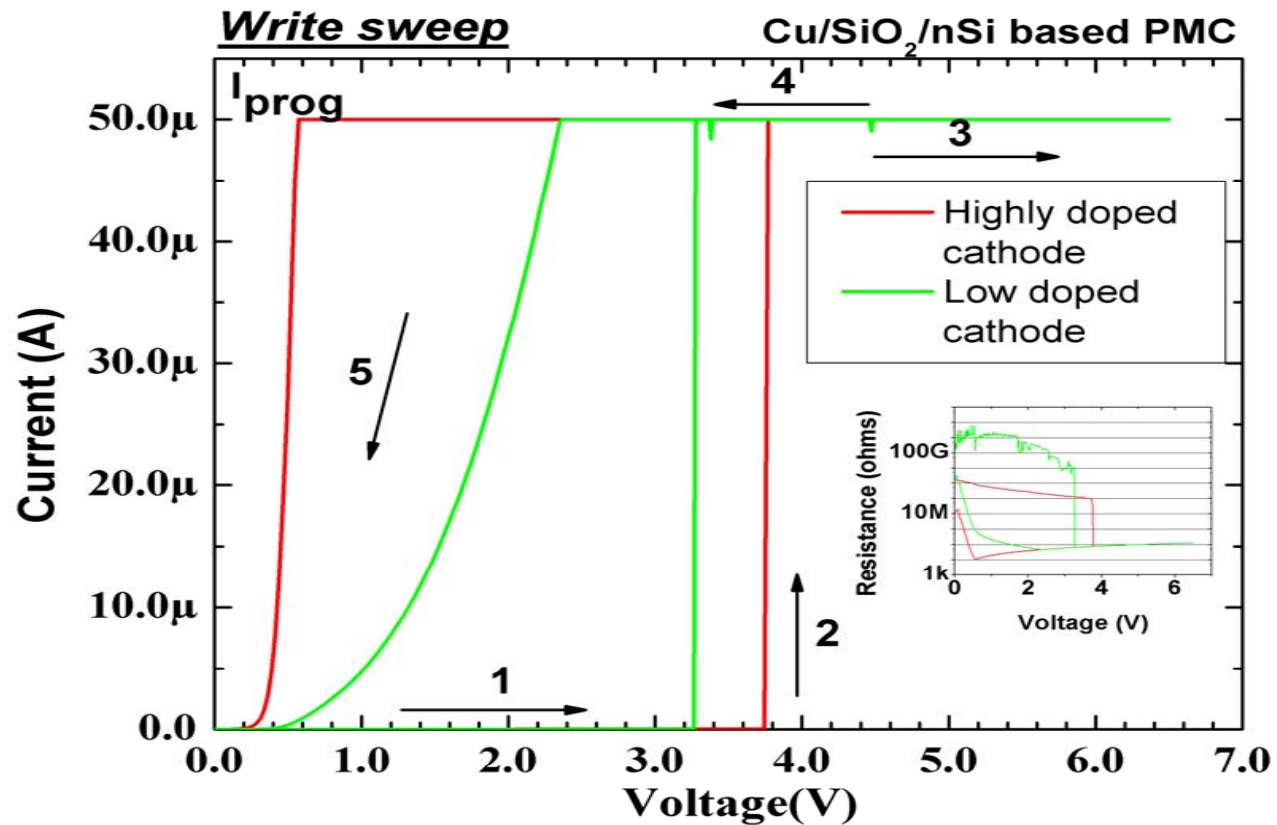
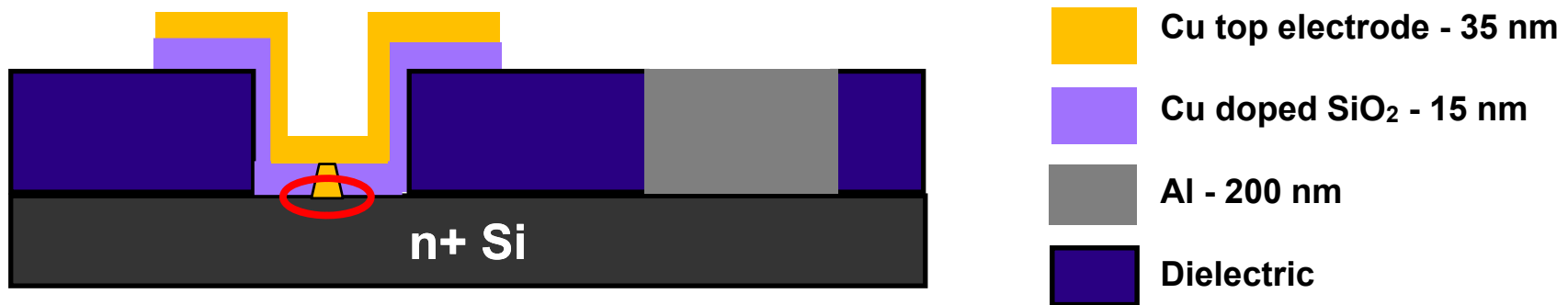
M. Johnson et al., "512-Mb PROM With a Three-Dimensional Array of Diode/Antifuse Memory Cells," IEEE Journal of Solid-state Circuits, vol. 11, no. 38, 1920-1928, 2003

# Discrete diode isolation



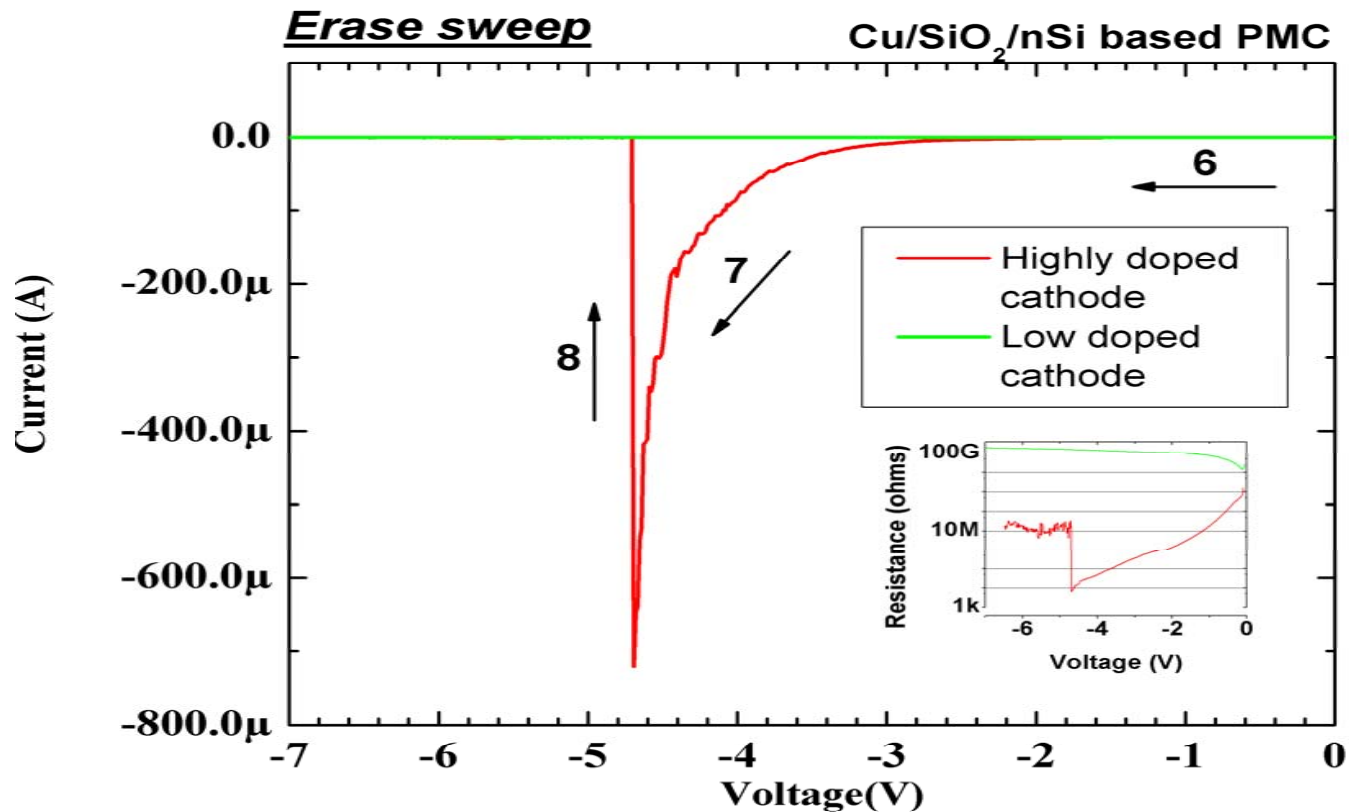
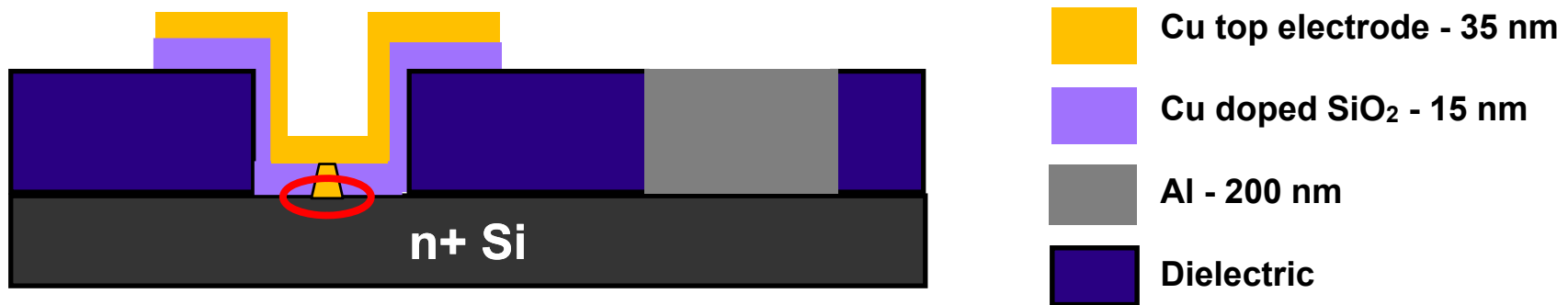
Data from Sarath C. Puthen Thermadam, ASU  
See also H. Toda (Toshiba), US Patent #7,606,059, October 20, 2009

# Integrated diode isolation - write



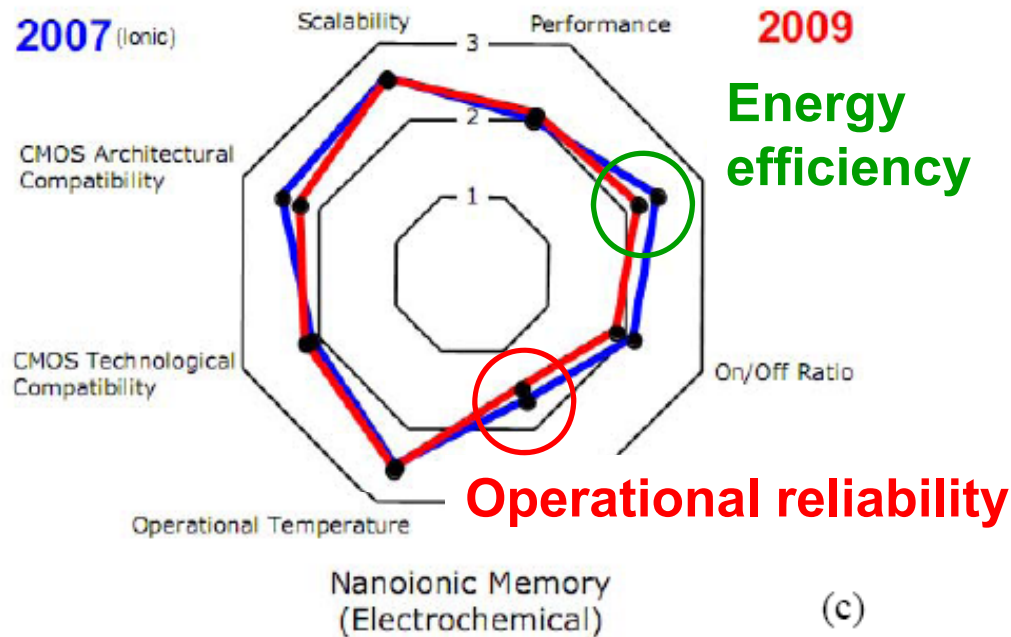
Data from Sarath C. Puthen Thermadam, ASU

# Integrated diode isolation - erase



Data from Sarath C. Puthen Thermadam, ASU

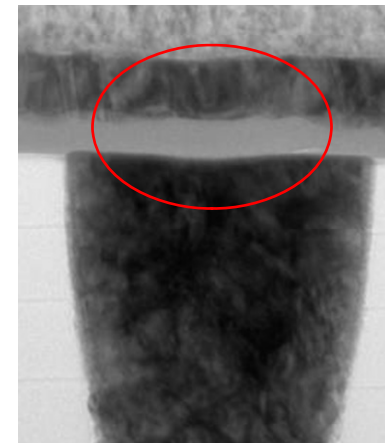
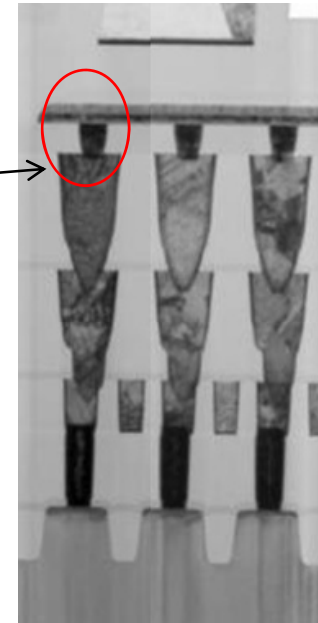
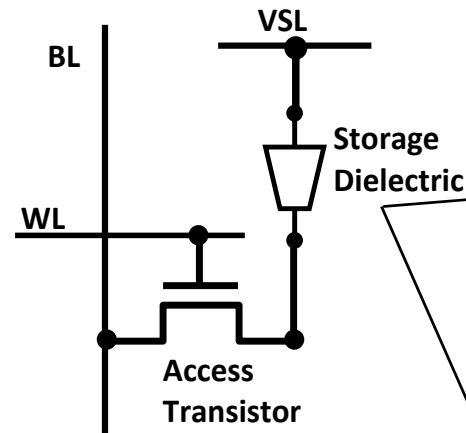
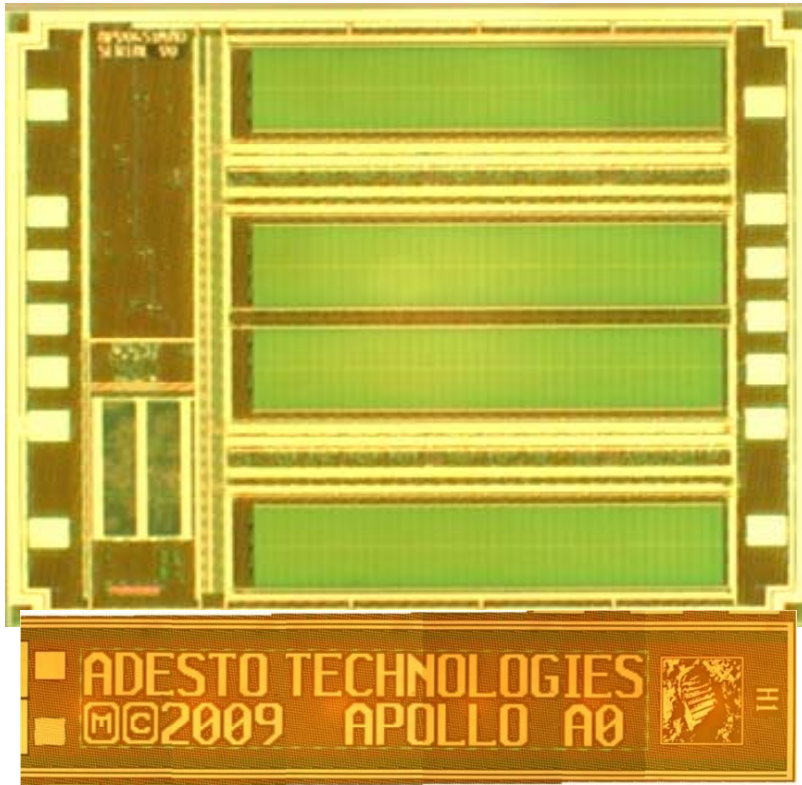
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Ionic memory gained a formal place in the ITRS in the 2007 Edition

**Operational reliability** is still a concern for most RRAM contenders but **energy efficiency** looks promising for ionic memory

# 130nm (Cu BEOL) integration



## Salient Features:

- 1Mb EEPROM/Flash Macro on Standard Foundry 130nm
- Programmable elements requires 2 non critical masks in BEOL flow
- Cell size determined by access device, core cell will scale with CMOS



# It's alive!



Image downloaded  
and stored on the  
hard drive

Image stored and  
read back on Adesto  
serial device

***Thank you for  
your attention!***

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