

AVS Thin-films User Group meeting, October 15, 2008

Recent Progress in Resistance Change Memory



***Yoshio Nishi
Department of Electrical Engineering,
Stanford University, Stanford, California 94305-4070***

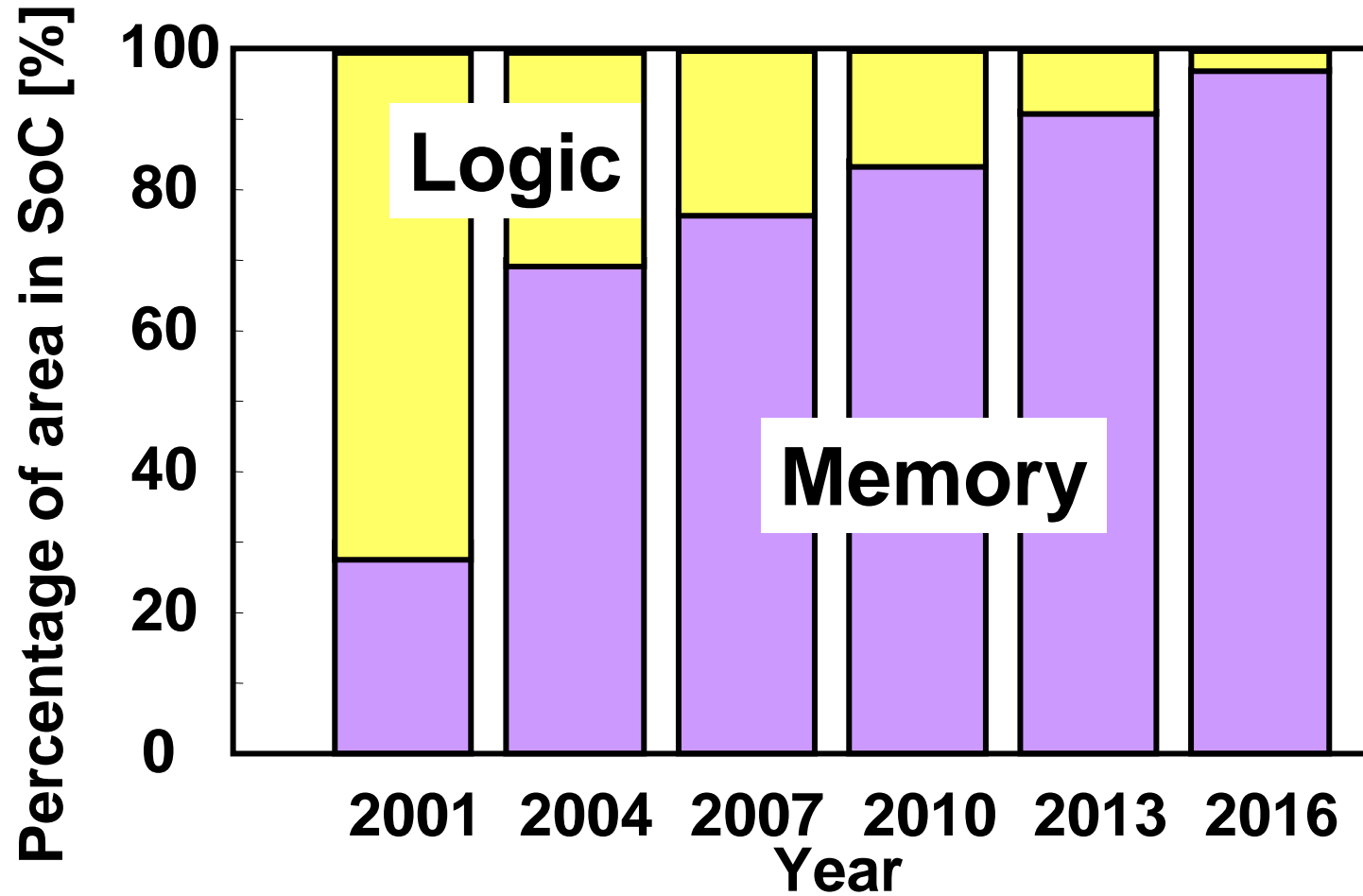
Outline

- ***Emerging nonvolatile memories***
- Switching behaviors
metal sulfides and metal oxides
- Device applications
nonvolatile memory and nonvolatile logic
- Phenomenological behaviors
- Physical mechanisms
- Scalability
- Summary

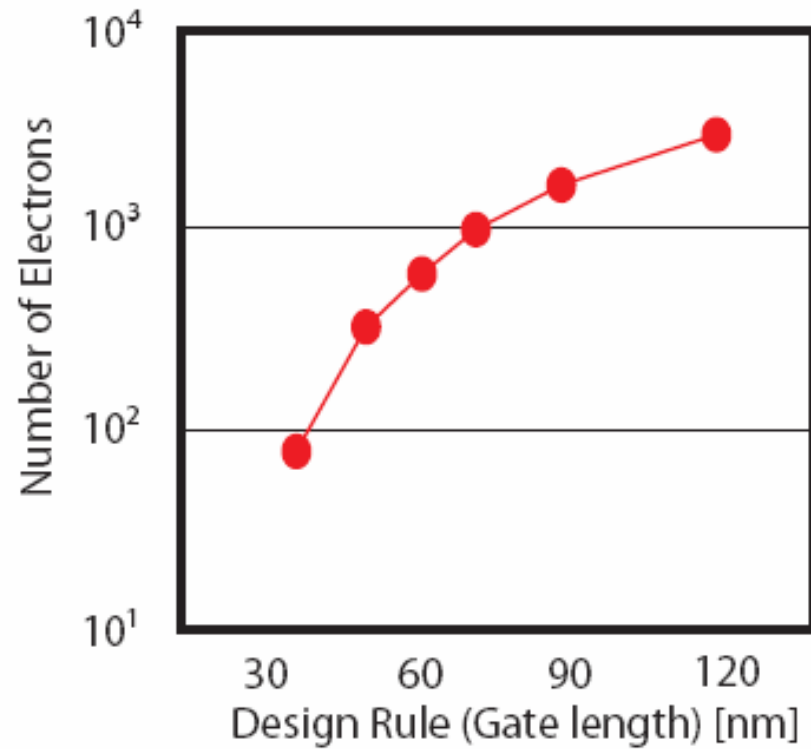
Motivations for new nonvolatile memory research

- Scalability limit beyond 32nm nodes of existing memory both volatile memory and nonvolatile memory
- Increasing needs for less power consumption on chip
- Increasing demands for on-chip memory size
- “Nano” materials evolution/revolutions have stimulated exploration of new memory opportunities
- Logic coupled with memory

Memory area on a chip will increase

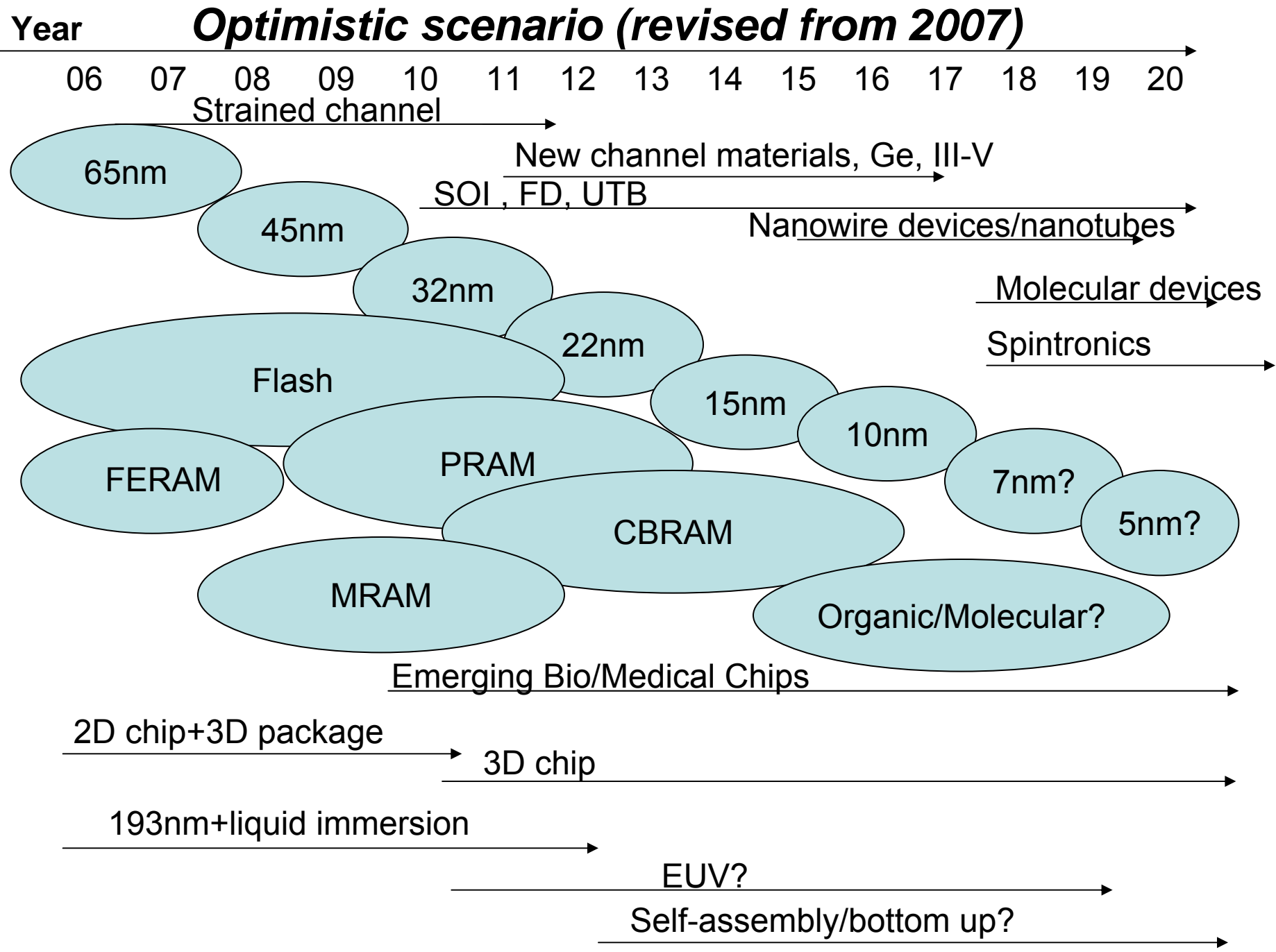


Due to design productivity, yield, and power

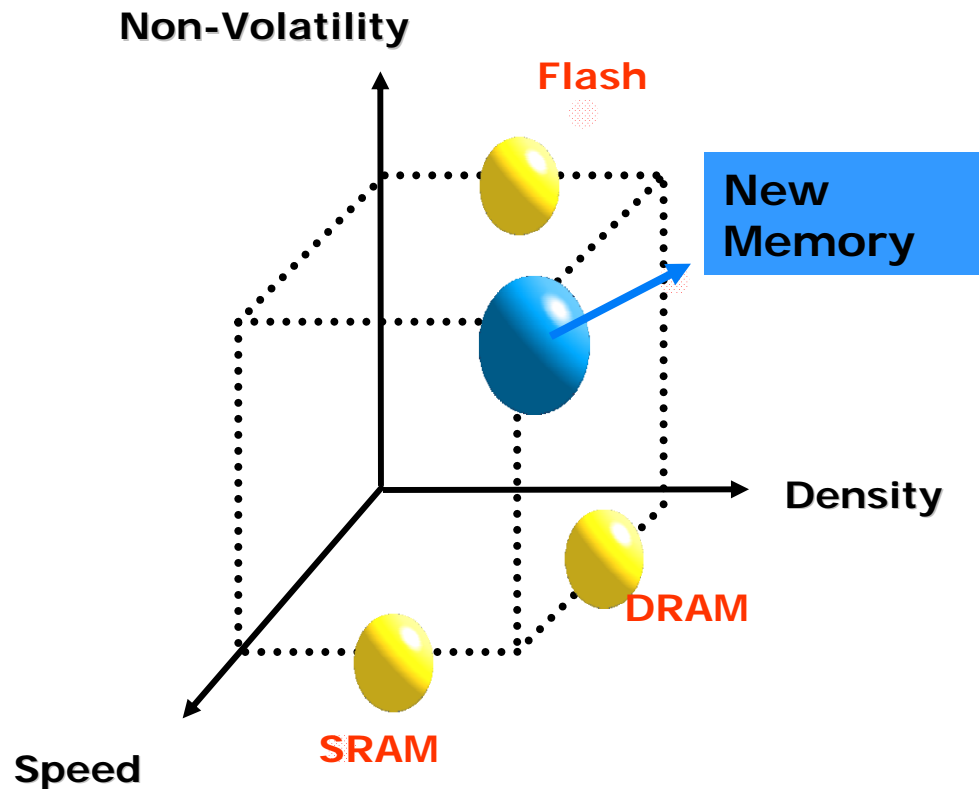


The number of electrons stored in the floating gate

A. Gibby, Stanford Univ Thesis, 2008



Requirements for next generation NVM



ITRSROADMAP 2005

- ✓ CMOS Compatibility
- ✓ Simple, Stable Process
- ✓ Low Cost Material
- ✓ Mass Productivity,
- ✓ Uniformity: 300mm and beyond
- ✓ R0~R1 Sensing Margin
- ✓ Non-Destructive Reading

New Functionalities

- Non-volatility
 - : > 10 years
- Fast random access
 - : $t_{\text{Read}} = 10\text{ns}$
 - : $t_{\text{Write}} = 5\text{ns} \sim 100\text{ns}$
- Virtually unlimited usage
 - : > 10^{12} cycles

ITRS 2007

2007 ITRS ERD Chapter Resistance-based memory technologies

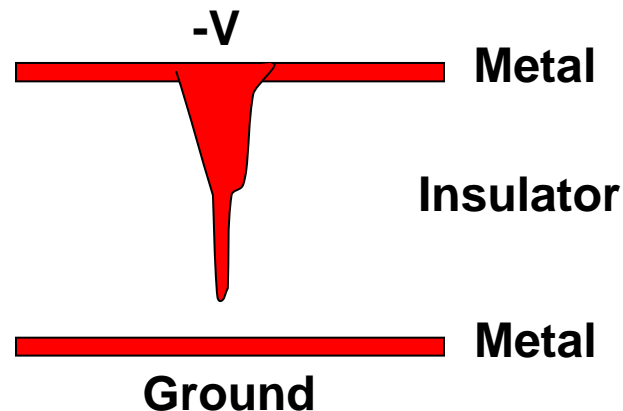
	Nanomechanical memory	Fuse/Anti fuse Memory	Ionic Memory	Electronic effects Memory	Polymer Memory	Molecular Memories
<i>Storage Mechanism</i>	Electrostatically-controlled bi-stable mechanical switch	Multiple mechanisms	Ion transport in solids	Multiple mechanisms	Not known	Not known
<i>Cell Elements</i>	1T1R or 1D1R	1T1R or 1D1R	1T1R or 1D1R	1T1R or 1D1R	1T1R or 1D1R	1T1R or 1D1R
<i>Device Types</i>	CNT bridge CNT cantilever Si cantilever Nanoparticle	M -I-M e.g. Pt/NiO/Pt	1) Solid Electrolyte 2) RedOx reaction	1) Charge trapping 2) Mott transition 3) FE Barrier effects	M-I-M (nc)-I-M	Bi-stable switch

Resistance changes

- Bulk material conduction changes depending upon whether the bulk is crystalline or amorphous----***phase change memory***
- Formation of nanoscale conductive pass in solid which creates “on” state---***nano-filament based resistance change memory***
- Lowering or thinning of the barrier between electrode and solid which defines “on” state conduction---***uniform switching resistance change memory***

Resistance Change Memory

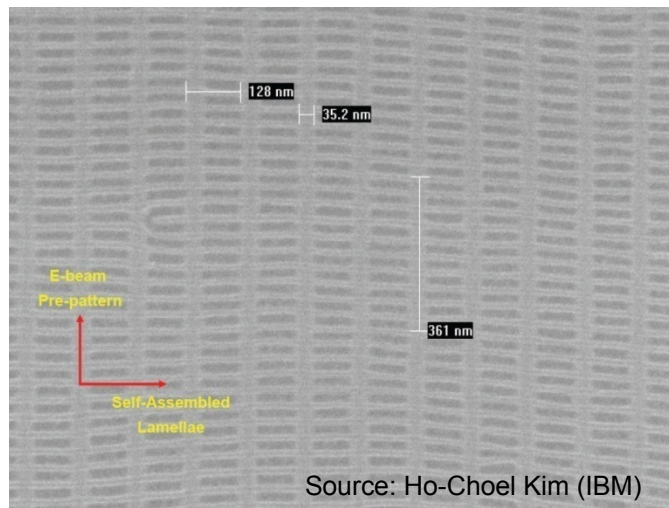
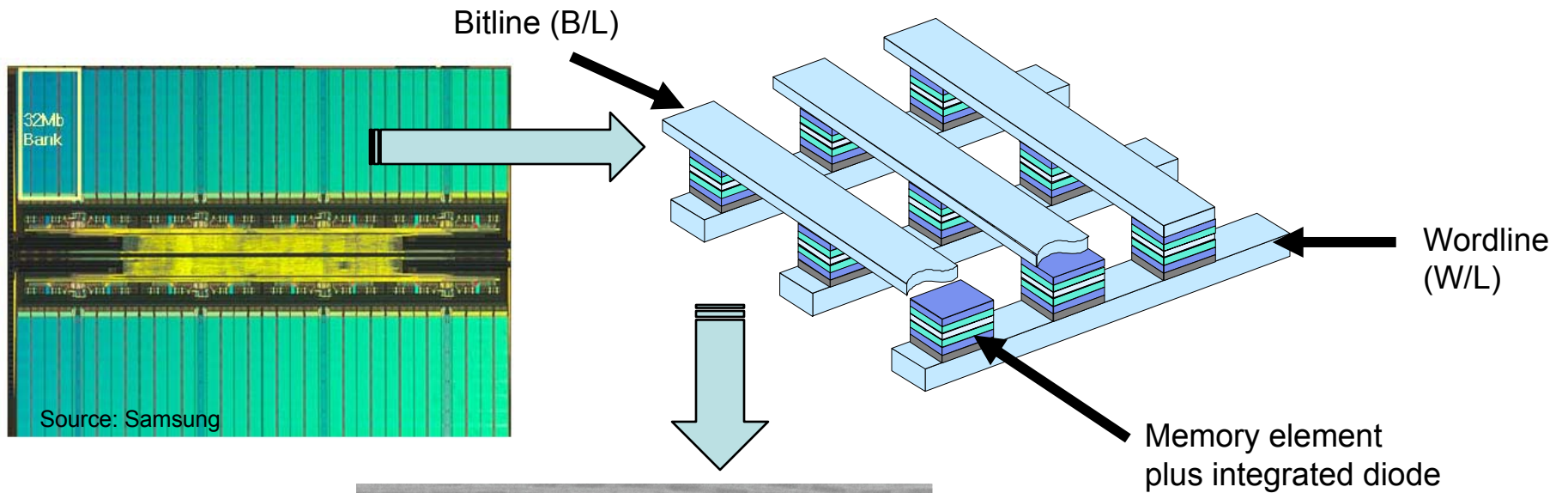
With Filament Formation



Conducting paths between the device's two terminals in a reversible process that changes electrical resistance by orders of magnitude

- Filament effect (contributed by metal ions, charged defects, soft breakdown, storage/release of charge carriers, etc)
- small applied voltage levels and energy
- large non-volatile resistance changes
- simple, highly scalable structure

3D, Stackable Cross-Point Memory



Self-assembled pattern (18 nm half-pitch)

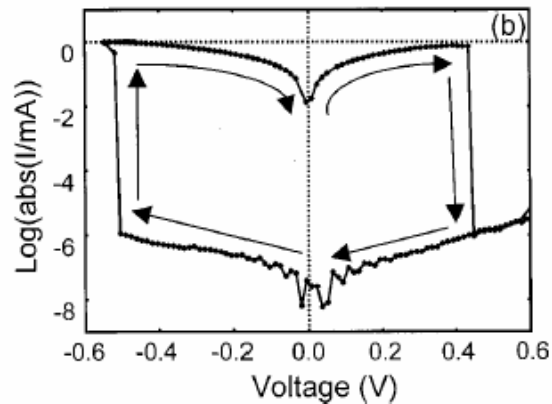
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Metal sulfide: Filament

Phillips Research Lab

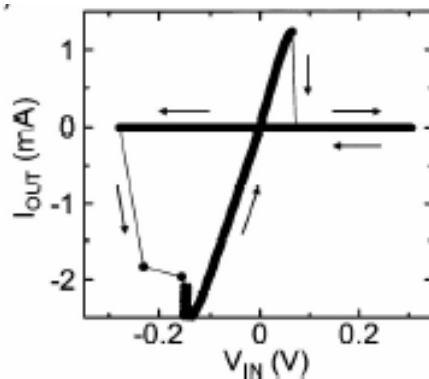
- P.W.M. Blom et al., *Ferroelectric Schottky Diode*, Phys. Rev. Lett. 73, 2107 (1994)
- P. van der Sluis, *Non-volatile Memory Cell in $Zn_xCd_{1-x}S$* , Appl. Phys. Lett. 82, 4089 (2003)



$Zn_xCd_{1-x}S$	
Read/Write Time	~ 50 ns
On/Off Ratio	10^6
On/Off Resistance	100 / 1M Ω

NEC Corp.

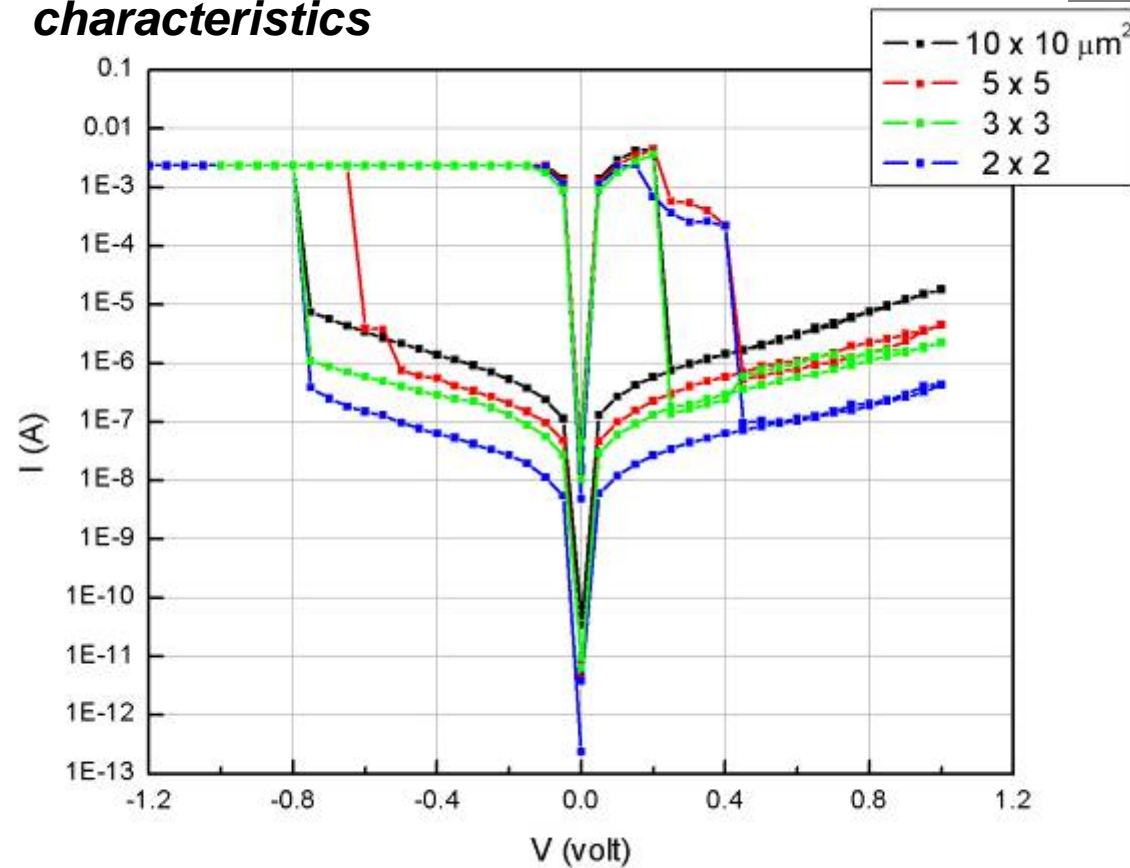
- T. Sakamoto et al., *Nanometer-scale Switches Using Copper Sulfide*, Appl. Phys. Lett. 82, 3032 (2003)



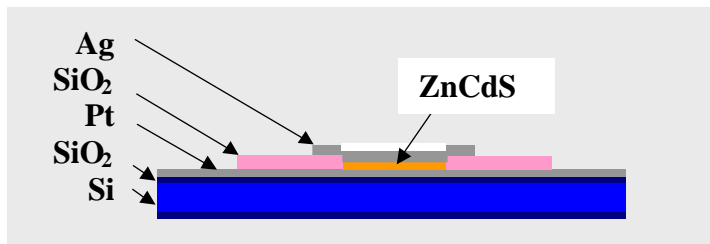
$Cu_{1-x}S$	
Read/Write Time	~ 100 us
On/Off Ratio	10^6
On/Off Resistance	50 / 100 M Ω

ZnCdS resistance change memory characteristics

Small-scale devices



On-resistance is independent of contact size → filament conduction
Off-resistance is proportional to contact size → bulk leakage
On/Off ratio improves with scaling

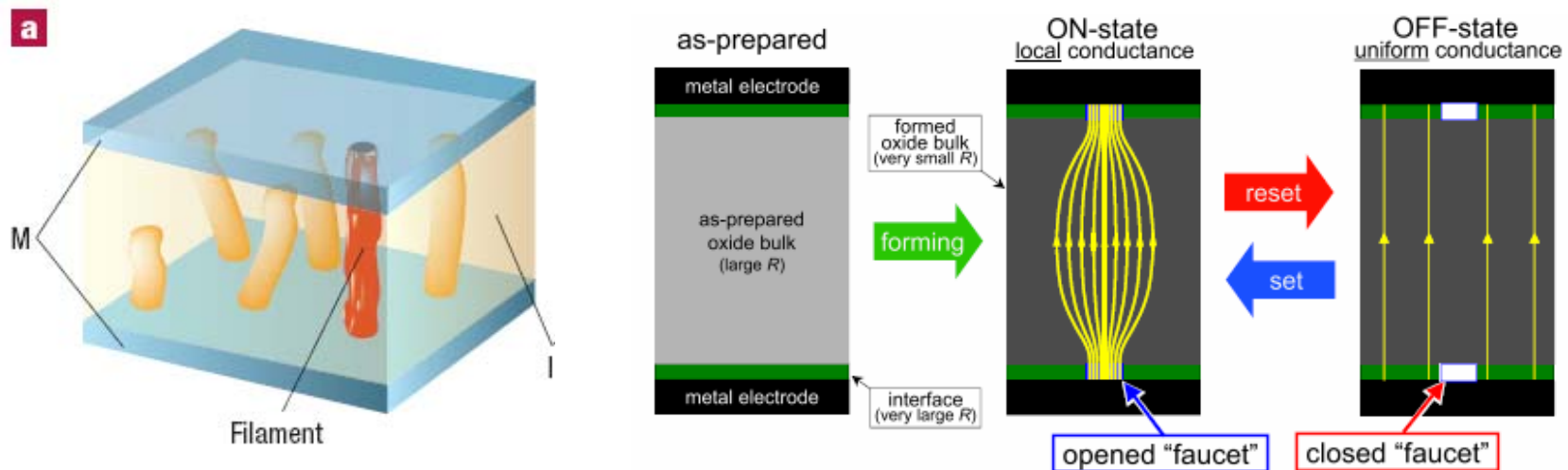


Z. Wang et al, *IEEE Electron Device Letters* Vol.28,(2007)
pp14-16

Metal Oxide: Filament

Fuse / Anti-fuse type (Conductive Filament)

- Set : voltage-induced partial dielectric breakdown
- Rest : disruption of conductive filament by high current density generated locally
 - ✧ e.g., TiO_2 , NiO , SrTiO_3

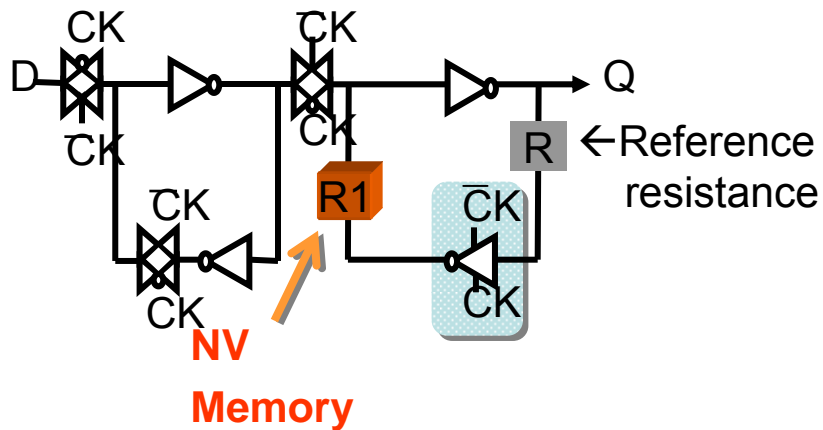


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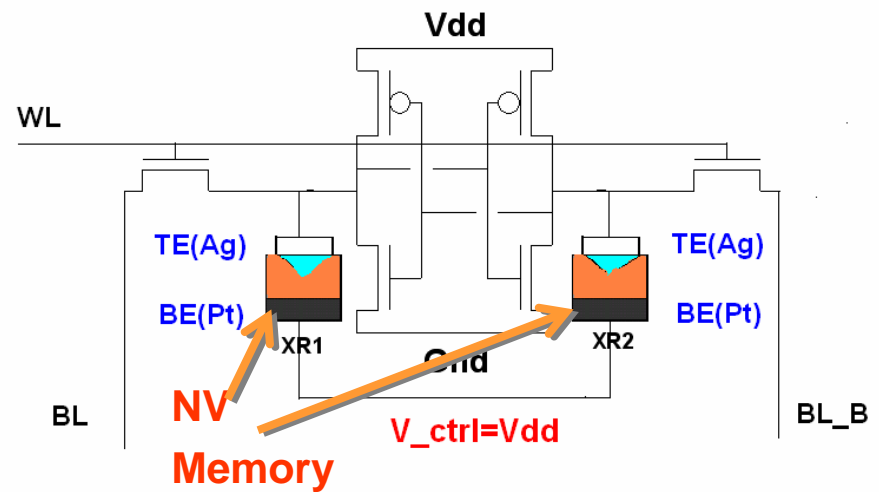
Compact "Non-volatile" Logic

Nonvolatile Flipflop

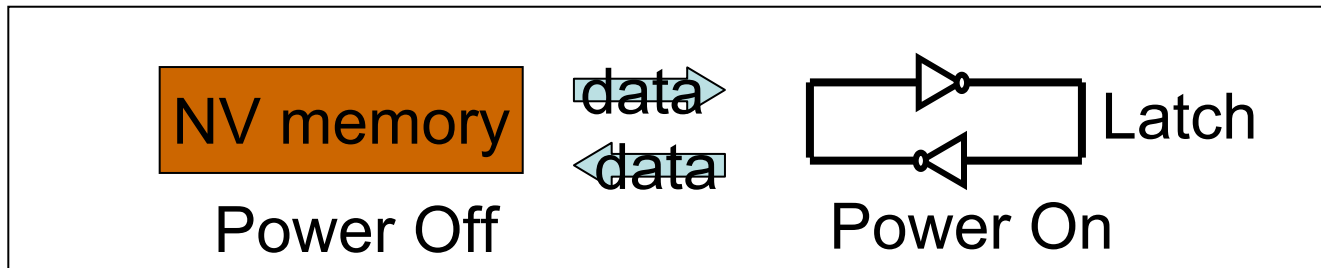


S. Fujita*, K. Abe, T. H. Lee
(3D conference 2004,
Nanotech conference 2005)

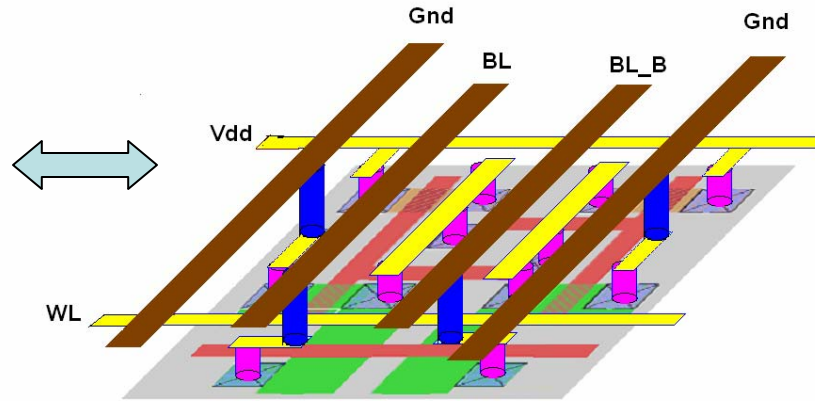
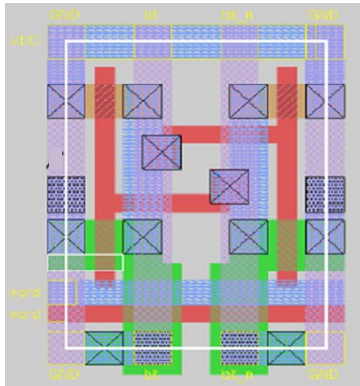
Nonvolatile SRAM (latch)



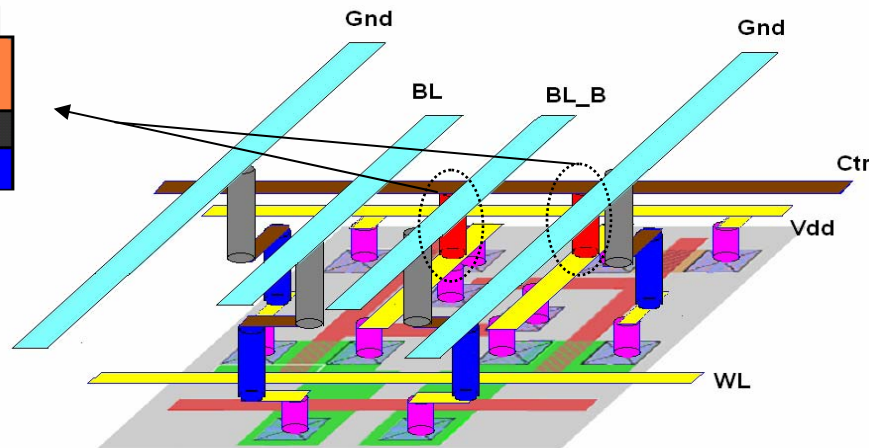
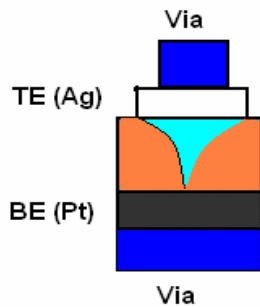
W. Wang, A. Gibby, Z. Wang, T. Chen,
S. Fujita*, P. Griffin, Y. Nishi, and S. Wong
(IEDM 2006), NMTRI review 2006.



NVSRAM: No Area Overhead



- N Diffusion
- P Diffusion
- Poly
- M1 Contact
- M1
- M1-M2 Via
- M2



- N Diffusion
- P Diffusion
- Poly
- M1 Contact
- M1
- M1-M2 Via
- M2
- Programmable Via
- M2-M3 Via
- M3

W. Wang et al, 2006 IEDM

2-terminal to 3 terminal devices

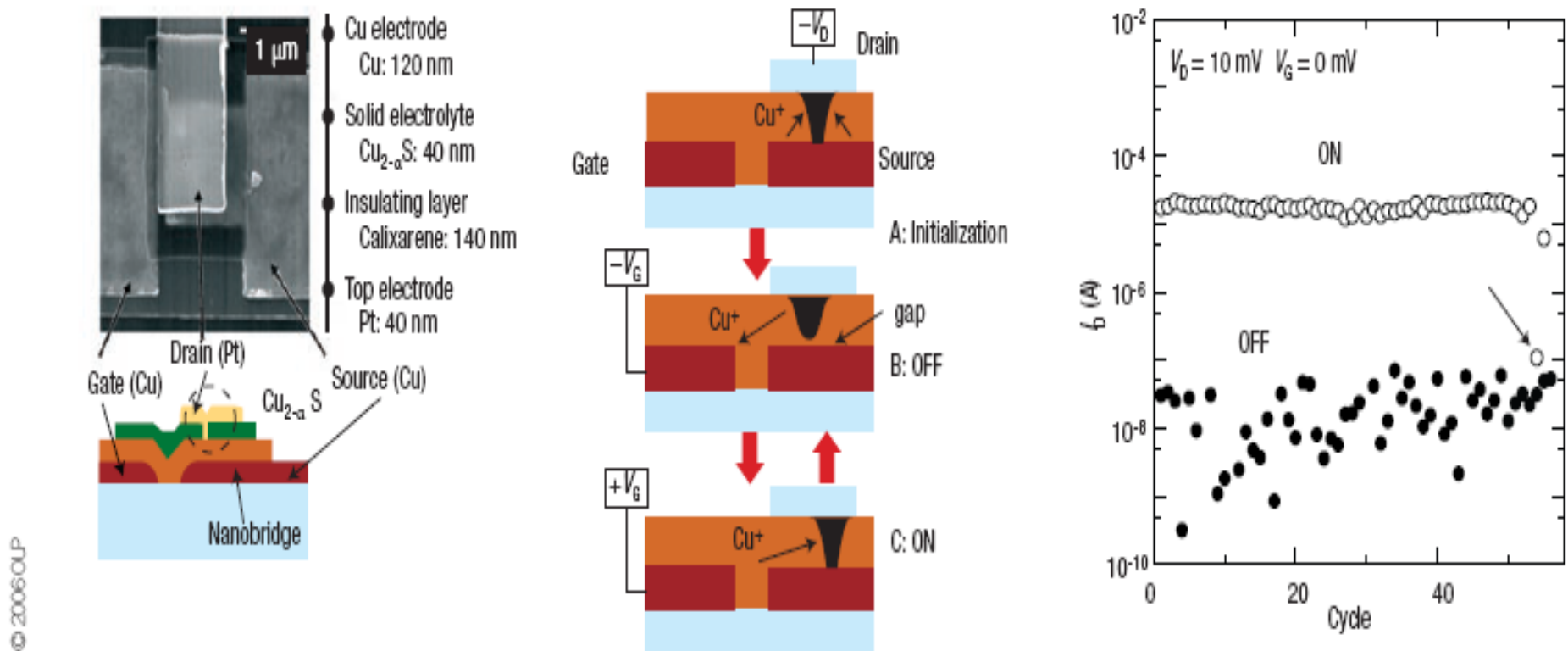


Figure 5 Three-terminal solid electrolyte switch. Electrochemical reaction for formation and annihilation of a metal filament between the source and the drain electrodes is controlled by the gate voltage. Reprinted with permission from ref. 47.

Banno, N., Sakamoto, T., Hasegawa, T., Terabe, K. & Aono, M. Effect of ion diffusion on switching voltage of solid-electrolyte nanometer switch. *Jpn. J. Appl. Phys.* 45, 3666–3668 (2006).

Outline

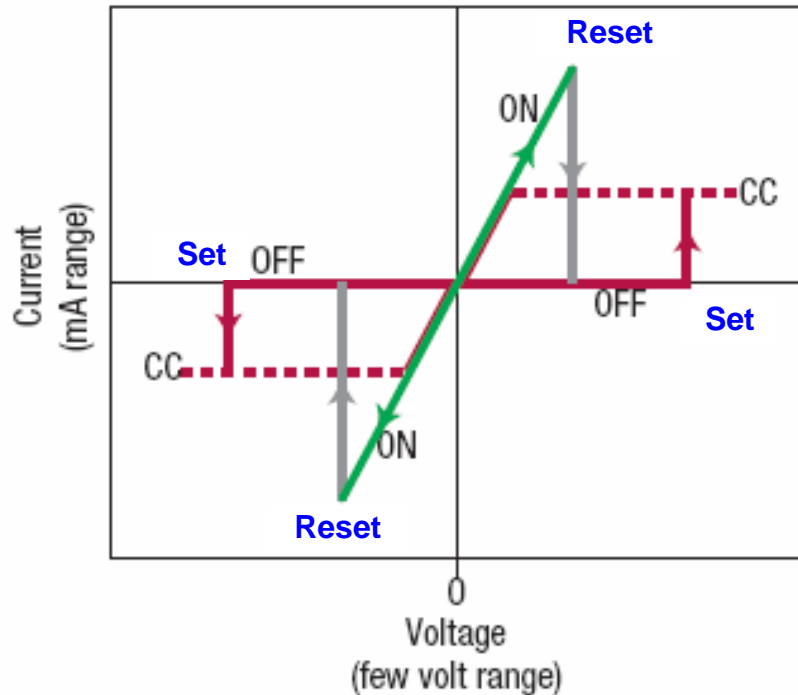
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Materials shown Resistance Switching

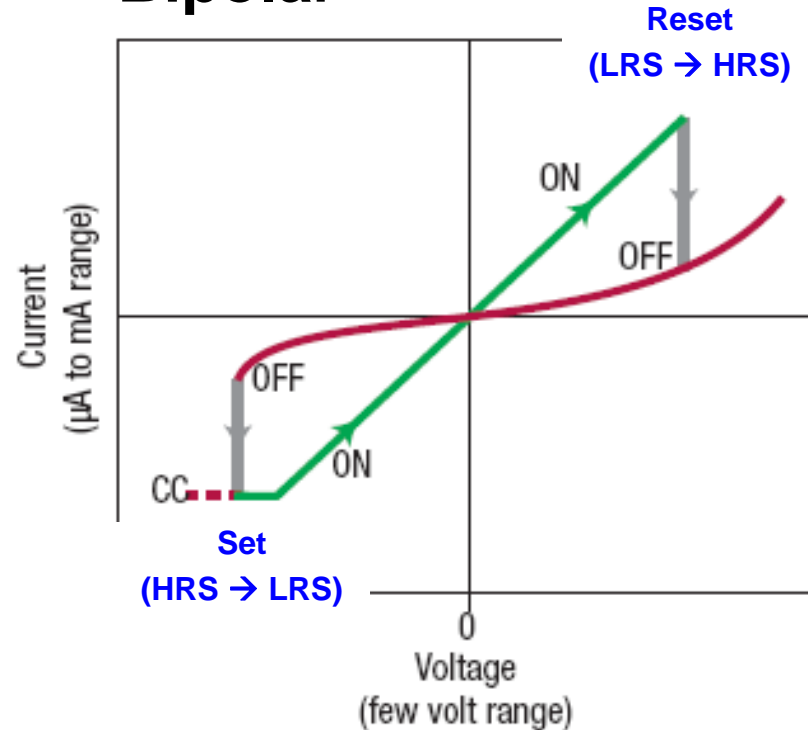
Binary Metal Oxide	TiO ₂ , NiO, Cu _x O, ZrO ₂ , MnO ₂ , HfO ₂ , WO ₃ , Ta ₂ O ₅ , Nb ₂ O ₅ , VO ₂ , Fe ₃ O ₄ ...
Perovskite	PCMO(Pr _{0.7} Ca _{0.3} MnO ₃), LCMO(La _{1-x} Ca _x MnO ₃) BSCFO(Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}), YBCO(YBa ₂ Cu ₃ O _{7-x}) (Ba,Sr)TiO ₃ (Cr, Nb-doped), SrZrO ₃ (Cr,V-doped), (La, Sr)MnO ₃ Sr _{1-x} La _x TiO ₃ , La _{1-x} Sr _x FeO ₃ , La _{1-x} Sr _x CoO ₃ , SrFeO _{2.7} , LaCoO ₃ , RuSr ₂ GdCu ₂ O ₃ , YBa ₂ Cu ₃ O ₇ ...
K ₂ NiF ₄	La _{2-x} Sr _x NiO ₄ , La ₂ CuO _{4+δ} ...
Others	Ge _x Se _{1-x} (Ag,Cu,Te-doped), Ag ₂ S, Cu ₂ S, CdS, ZnS, CeO ₂ ...

Switching Operation Polarity

Unipolar



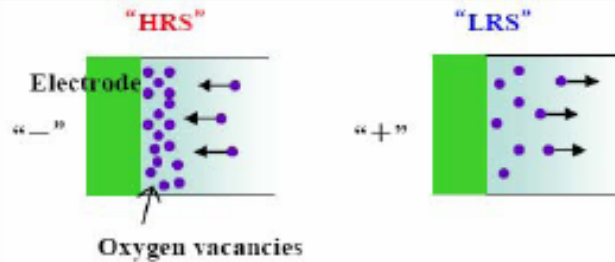
Bipolar



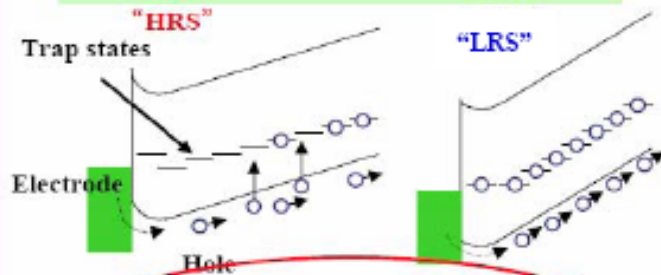
- Depending on the materials and measurement, the curves could vary considerably.

SUMMARY of switching models (A. Sawa, AIST, NVM, Japan)

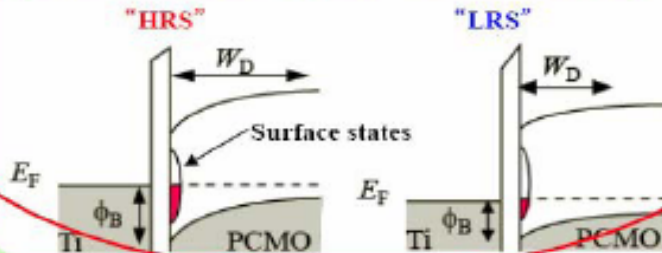
Electro-chemical migration of oxygen vacancies



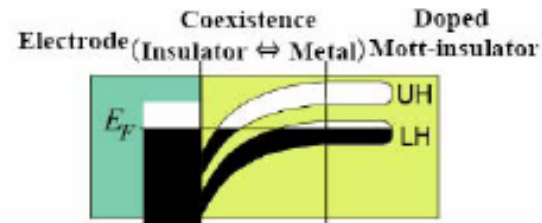
Space charge limited current with traps



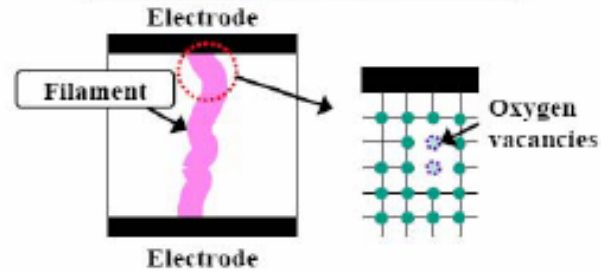
Charging effect at Schottky-like interface



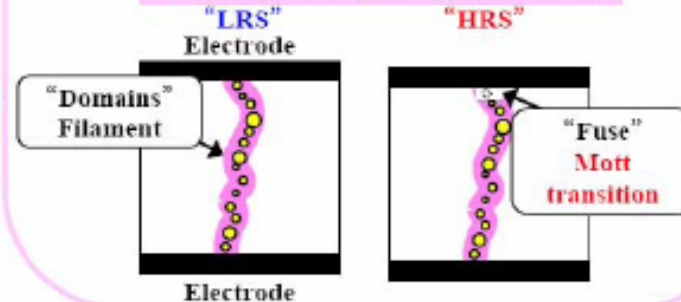
Interface Mott transition



Oxygen ion (vacancy) diffusion



Domain tunneling (Mott transition)



A. Sawa

T. Fujii, M. Kawasaki, and Y. Tokura

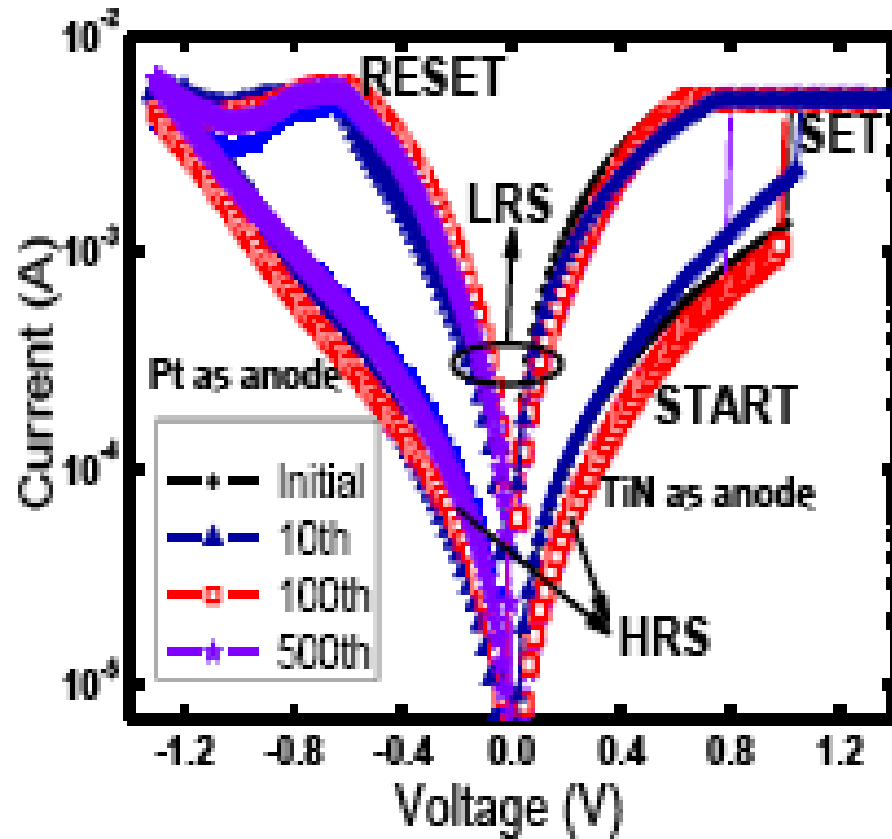


Fig.1 I - V curves of TiN/ZnO/Pt device for initial and 10th, 100th and 500th DC cycles using double voltage sweeping mode with $I_{\text{COMP}}=5\text{mA}$.

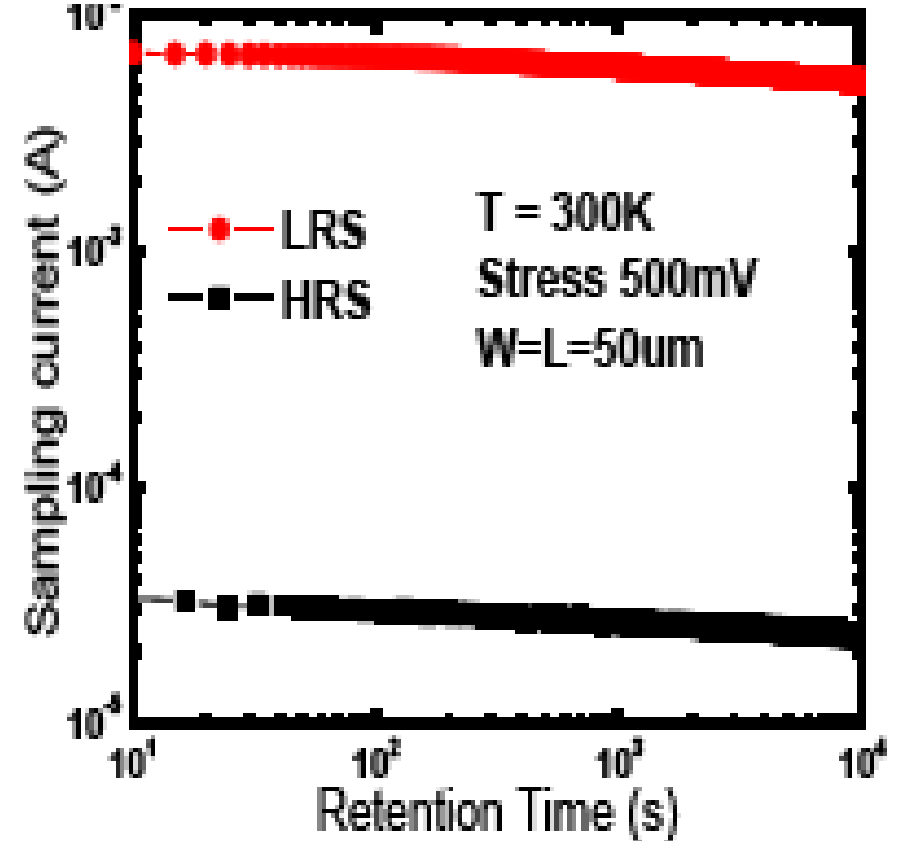


Fig. 2 Memory data retention in HRS and LRS, the current values were tested under a high durable stress (500mV) by using sampling mode

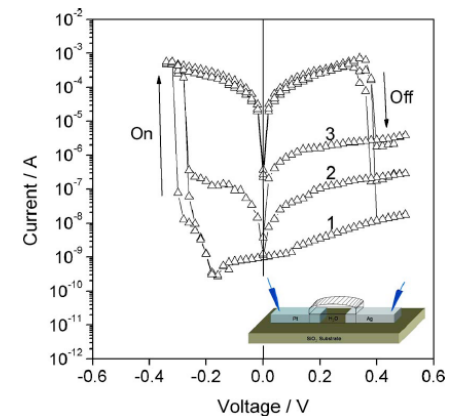
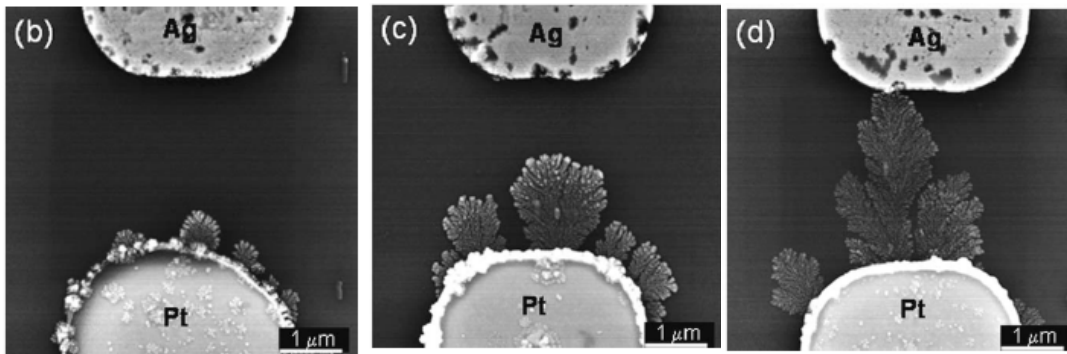
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Proposed Mechanism 1

Ionic Transport and electrochemical redox reaction type

- Set : - The oxidation of an electrochemically active electrode metal
 - The drift of the mobile cations toward counter electrode
 - Form a highly conductive filament
- Reset : An electrochemical dissolution of the conductive bridges
 - ※ e.g., Ag^+ in Ag_2S , Ag^+ in GeSe , Cu^{2+} in CuO_x



Xin Guo et al., Appl. Phys. Lett. 91, 133513 (2007)

Proposed mechanism 2

Electronic Effect type (Charge trap & Schottky Contact)

- Charge injection by tunneling at high electric field
- Trapped at interface states in insulator
- Modification of the electrostatic schottky barrier and its resistance
 - ✂ e.g., Ti/PCMO/SRO
- Electronic charge injection acts like doping to induce an insulator-metal transition
 - ✂ e.g., PCMO, Cr-doped SrTiO₃, Cu₂O

Sawa et al., Appl. Phys. Lett. 85, 4073 (2004)

T. Fuji et al., Apply. Phys. Lett. 86, 012107 (2005)

Chen et al., Appl. Phys. Lett. 91, 123517 (2007)

TiO₂ Switching

- V_O model of forming and switching in TiO_2
- Evidence supporting V_O model
- Critical look at data:
 - Are vacancies really the whole story?
- Evidence that H is origin of field-programmable rectification
- H + V_O model of forming in TiO_2 and related oxides

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Scalability questions

Can “on” resistance stays same or decrease?

Can “off” resistance stays same of decrease?

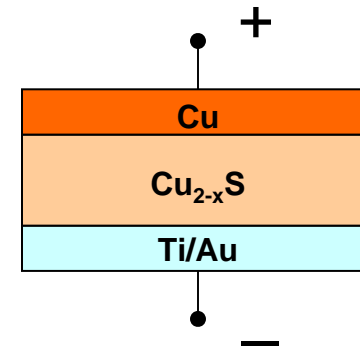
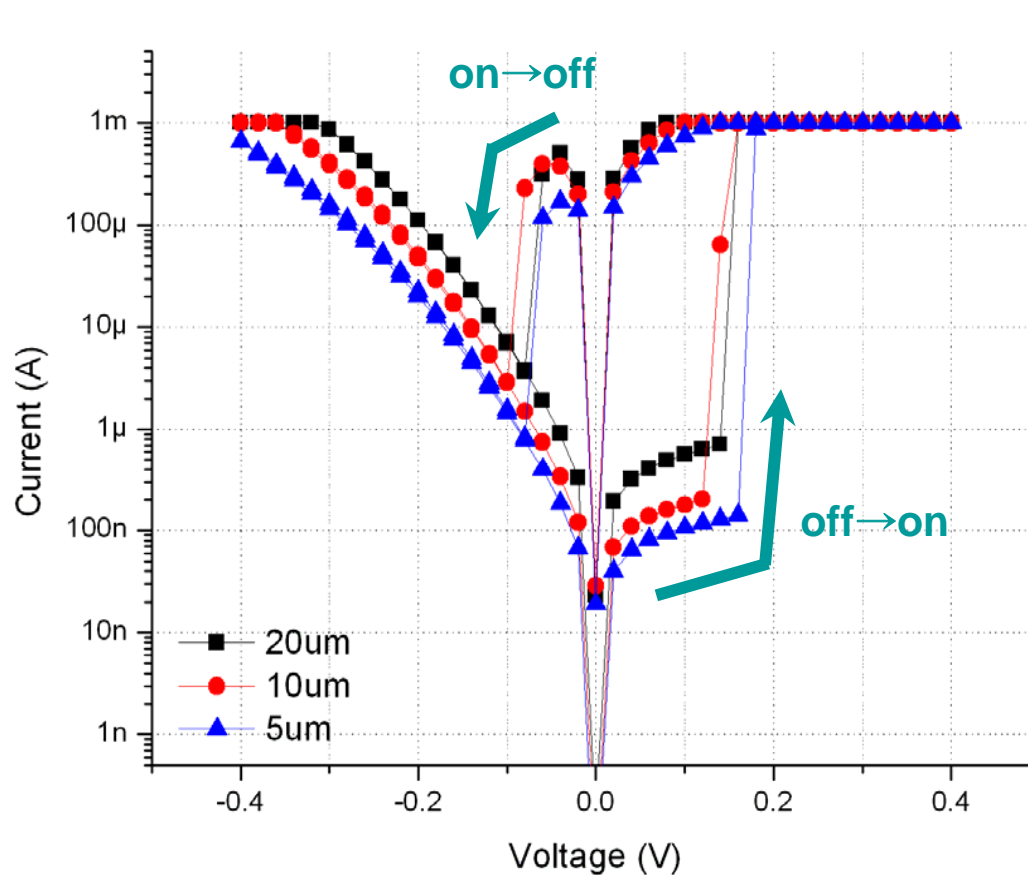
Retention characteristics

vs Programming speed ?

Endurance?

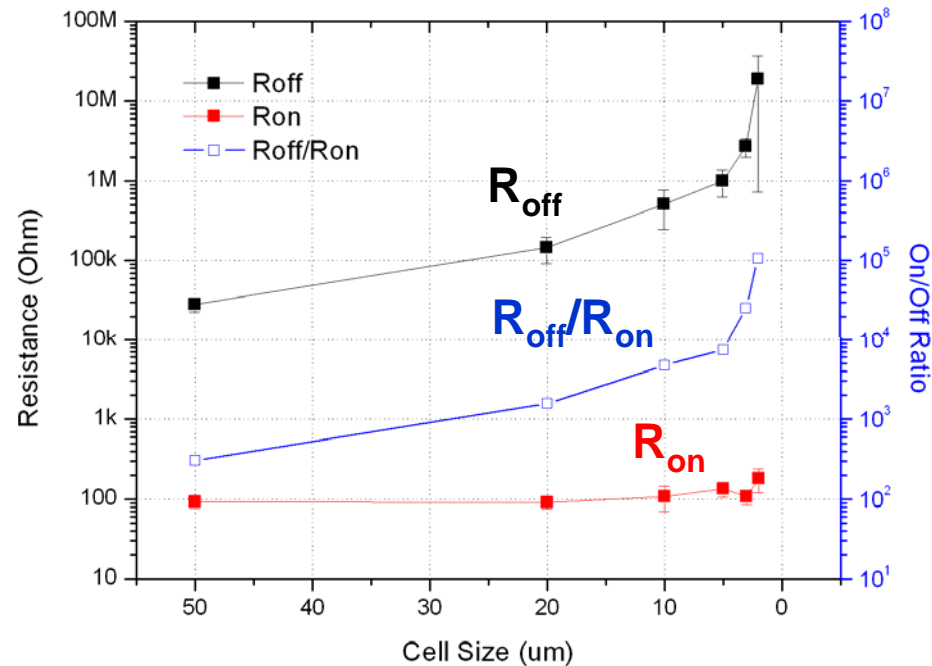
Programming voltage tunability?

I-V Characteristics



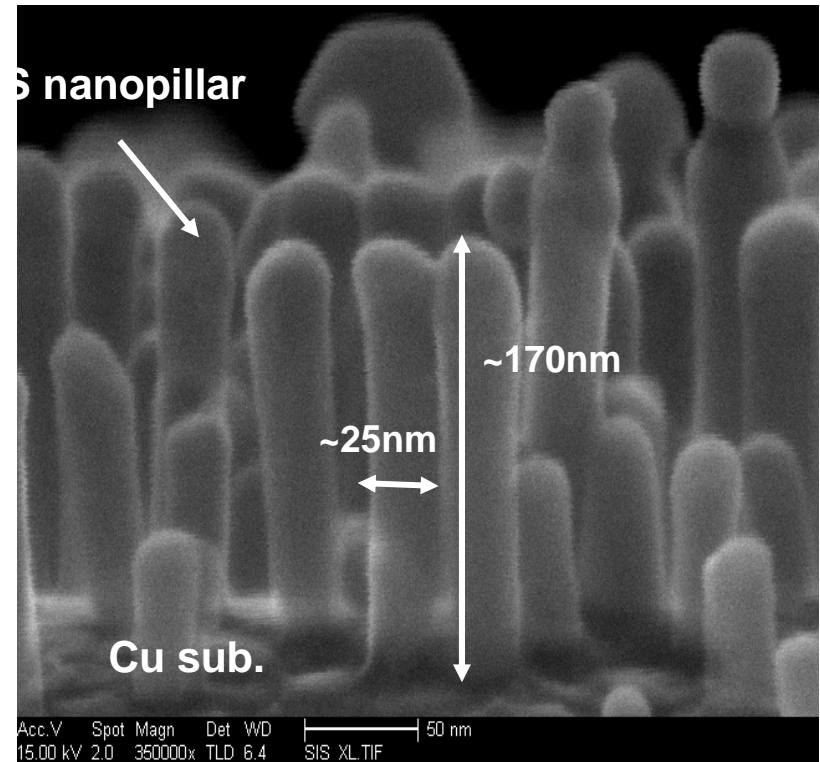
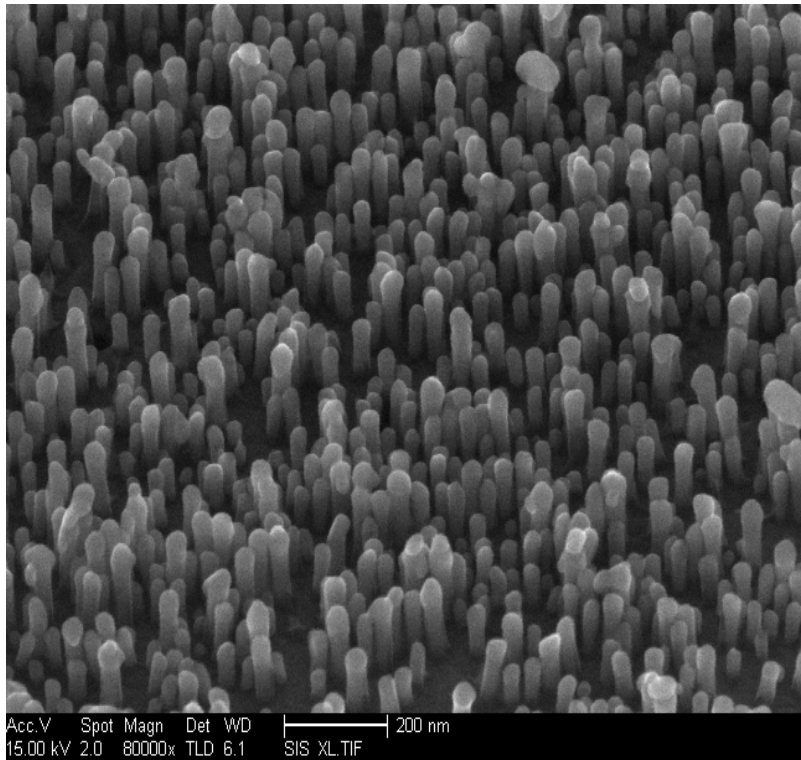
- $R_{\text{on}} : \sim 150\Omega$
- $I_{\text{comp.}} : 1\text{mA}$
- $V_{\text{on}} : \sim 0.15\text{V}$
- Consistent over 150 cycle sweeps

$R_{@0.1V}$ vs. Device Area ($I_{comp.} = 1mA$)







- R_{on} : $\sim 150\Omega$, almost **independent of device area**
 - Filament size ($\sim 5nm$) much smaller than device area
- R_{off} : increasing with scaling down of device area
 - Mainly determined by bulk properties
- R_{off}/R_{on} : **improving with scaling down of devices**

$Cu_{2-x}S$ Nanopillars



Manipulation of characteristics

- Simple structure : 2-terminal device
- Scalability : ~40nm  **25nm**
- Large on/off ratio : $> 10^5$ @ 3mA  **$> 10^7$** @ 2uA
- Compatibility to CMOS process

- Low V_{on} : $< 0.3V$  **~ 0.5V**
- High operating current : mA range  **2uA**

Summary

- **A variety of mechanisms for switching proposed**
 - **Interface switching, filament, SCLC, Electrochemical reaction**
 - **Role of oxygen ion (O^{2-}) or vacancy (V_o^{2+})**
 - **Substantial role of hydrogen in the vacancy model delineated**
- **Materials oriented issues and opportunities**
 - **Reproducibility and uniformity depends on defects/structure**
 - **Unipolar vs. Bipolar: depend on structure/process temp.**
 - **Single crystal, pure-amorphous, polycrystalline**
 - **Improved device performance vs. Process complexity**
 - **uniform (atomic scale) distribution of doping element**
- **Potential for exciting applications**
 - **Replacement of flash**
 - **New functionality such as non-volatile latch, programmable interconnect**
 - **Ultimate universal memory embedded in logic VLSIs**