



RRAM-An Emerging Non-Volatile Memory Technology

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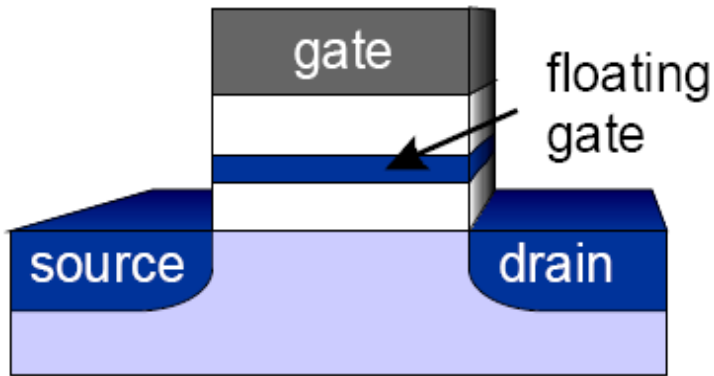
Feb.10th, 2012



Outline

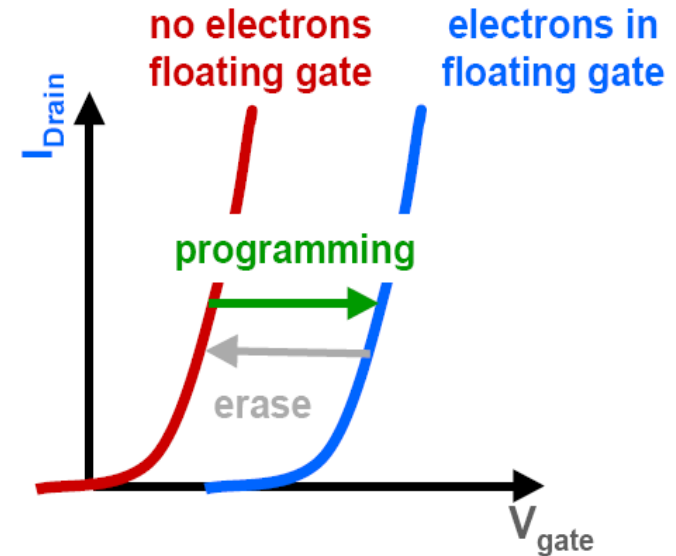
- **An overview of Non-volatile memory**
- **RRAM technology: Opportunities and Challenges**
- **RRAM research in IMECAS**
- **Summary**

Flash Memory



Concepts proposed by D. Kahng and S. M. Sze, Bell Lab, 1967

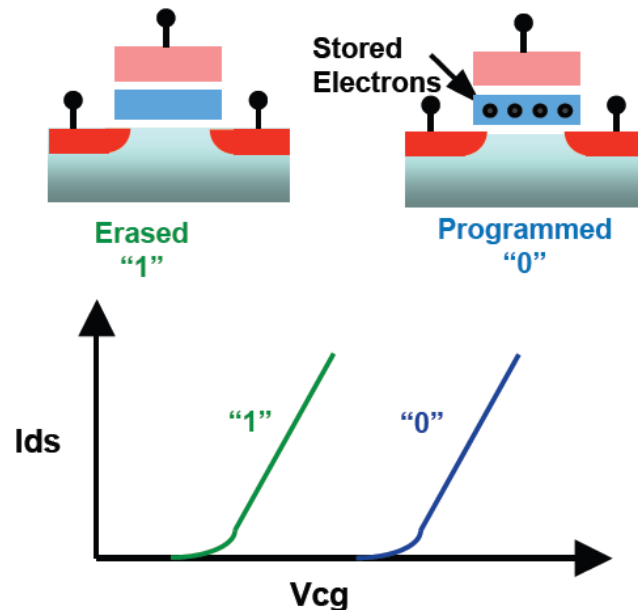
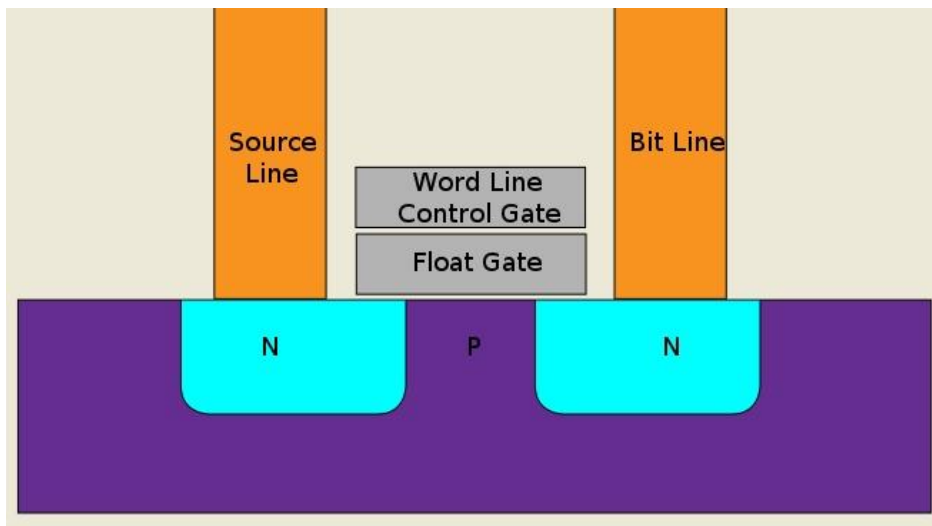
Kahng and S. M. Sze, *Bell Systems Technical Journal* **46** (1967) 1288.



- Uses Fowler-Nordheim tunneling to erase the memory
- Uses CHE or FN to program the memory
- The NVM bit information is represented by the change in I_d - V_g curve of the read-transistor connected to the floating gate

Dominated the NVM in the last two decades

Flash Scaling Challenges



Physical limitations exist!

- leakage current
- High voltage operations
- Charge storage requirements of the dielectrics and reliability issues
- Slow writing speed

Year	1999	2001	2003	2007	2009	2012	2015
Node	180 nm	130 nm	90 nm	65 nm	45 nm	25 nm	16 nm?

It is very hard for conventional Flash memory to go through 16 nm node!

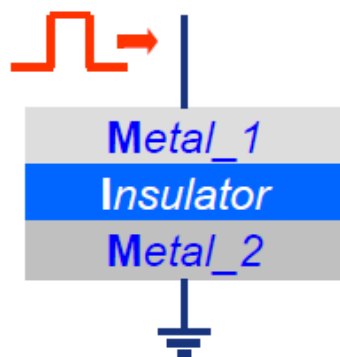


Outline

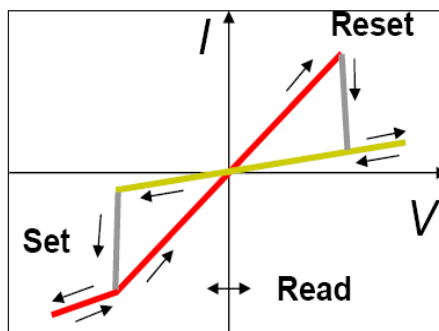
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What is RRAM?

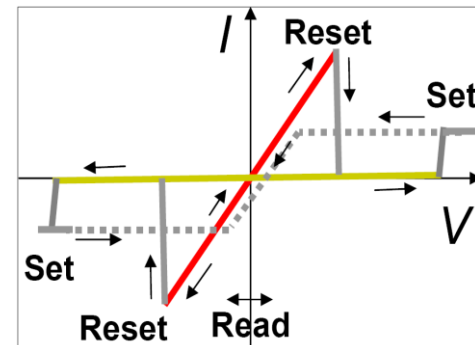
electric pulse



MIM structure



Bipolar switching



Unipolar switching

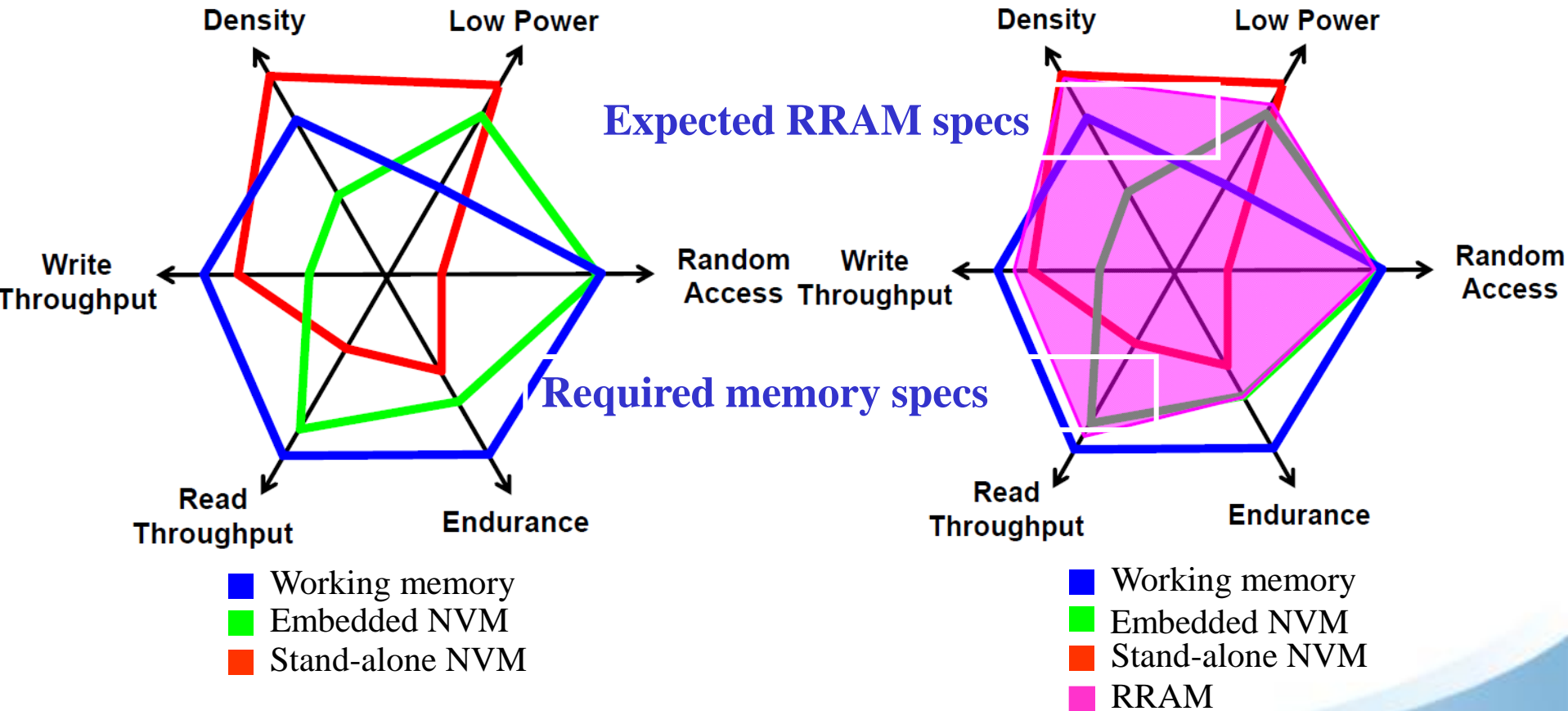
Advantages of RRAM:

- ✓ Simple device structure (Metal/Insulator/Metal)
- ✓ Good compatibility with CMOS process
- ✓ Easy scaling down to 8 nm
- ✓ Large on/off ratio ($10^3 \sim 10^6$)
- ✓ Fast operating speed ($\sim ns$)
- ✓ Good endurance ($> 10^6$)
- ✓ Good retention (> 10 years)

Materials for RRAM

Class	Typical Materials
TMO (Transition Metal Oxide) = binary oxide	Cu_xO , TiO_x , ZrO_x , NiO_x , VO_x , CeO_x , AlO_x , HfO_x , MnO_x ,.....
Metal doped perovskite	PCMO, Cr-SrTiO ₃ , Cr - SrZrO ₃ ,.....
Chalcogenide	GeSbTe.....
PMC (programmable metallization cell)	$Cu-SiO_2$, $Cu-WO_x$, TaO_x , Cu_2S , $GeTe_3$,.....

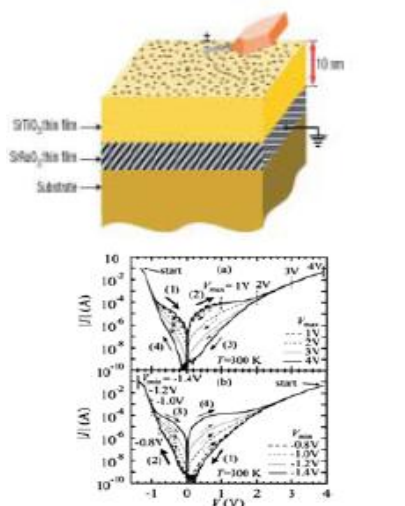
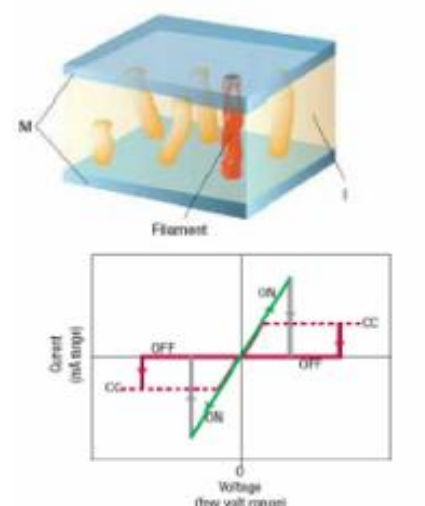
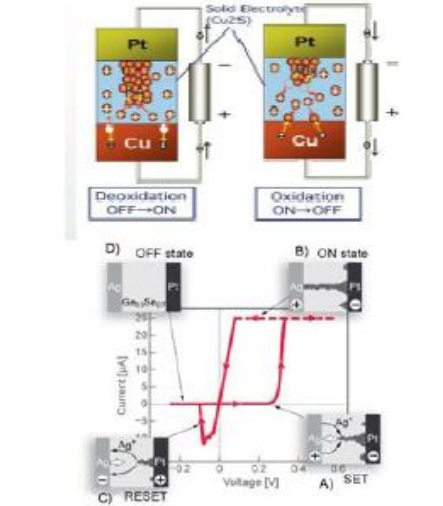
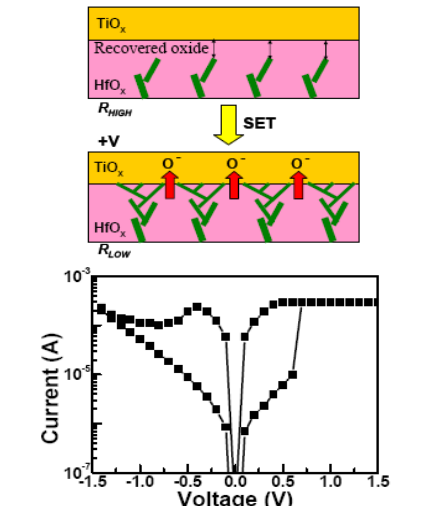
Opportunities for RRAM



RRAM is not suitable for working memory, but quite competitive for embedded and stand-alone NVM application.

Challenges for RRAM

1. Switching mechanism:

Electronics effect based memory	Fuse/anti-fuse memory	Cation redox based memory	Anion redox based memory
			
<p>Excellent uniformity Multilevel</p>	<p>Unipolar switching Easy to 1D1R Good retention</p>	<p>High speed Lower Power Excellent scalability Multi level</p>	<p>High speed Lower Power Excellent scalability Multi level</p>
<p>Poor scalability Poor retention</p>	<p>High power Electroforming</p>	<p>Poor retention Poor uniformity</p>	<p>Poor retention Poor uniformity</p>

Challenges for RRAM

2. Which RRAM materials are worthy manufacturing? Contamination free, low thermal budget, acceptable performance,.....

X = Materials in RRAM literature report
X = Materials in fabs today

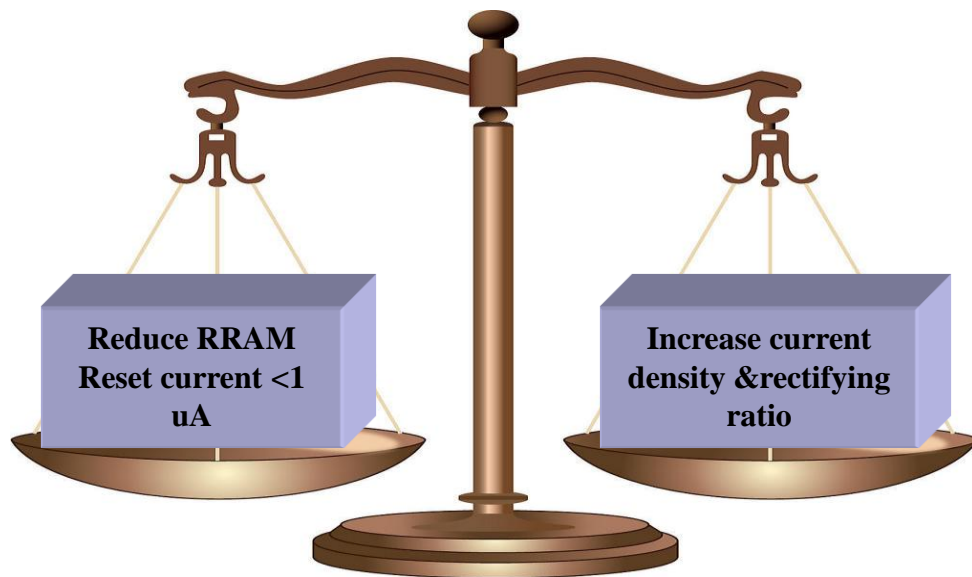
H																		He
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg								

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Challenges for RRAM

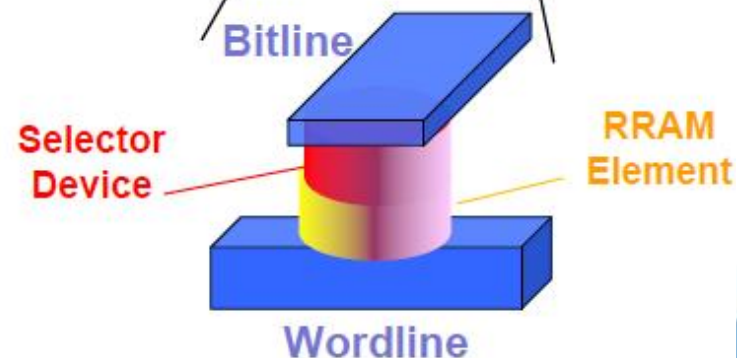
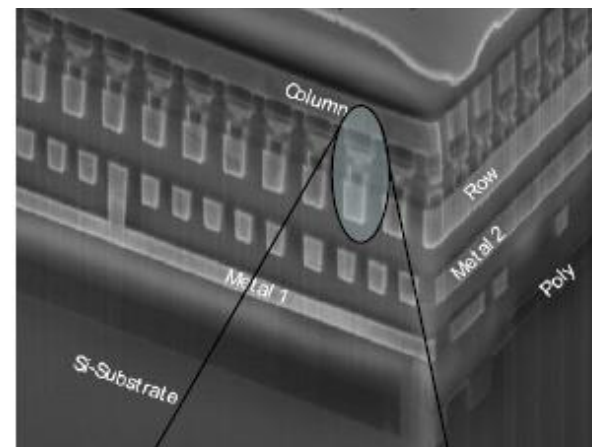
3. Selector challenge for 3D integration:

- Reduce I_{reset} —less diode current required
- Increase current density of Diode, rectifying ratio of Diode and decrease fabrication temperature.



Trade off

D. Kau, IEDM, 2009



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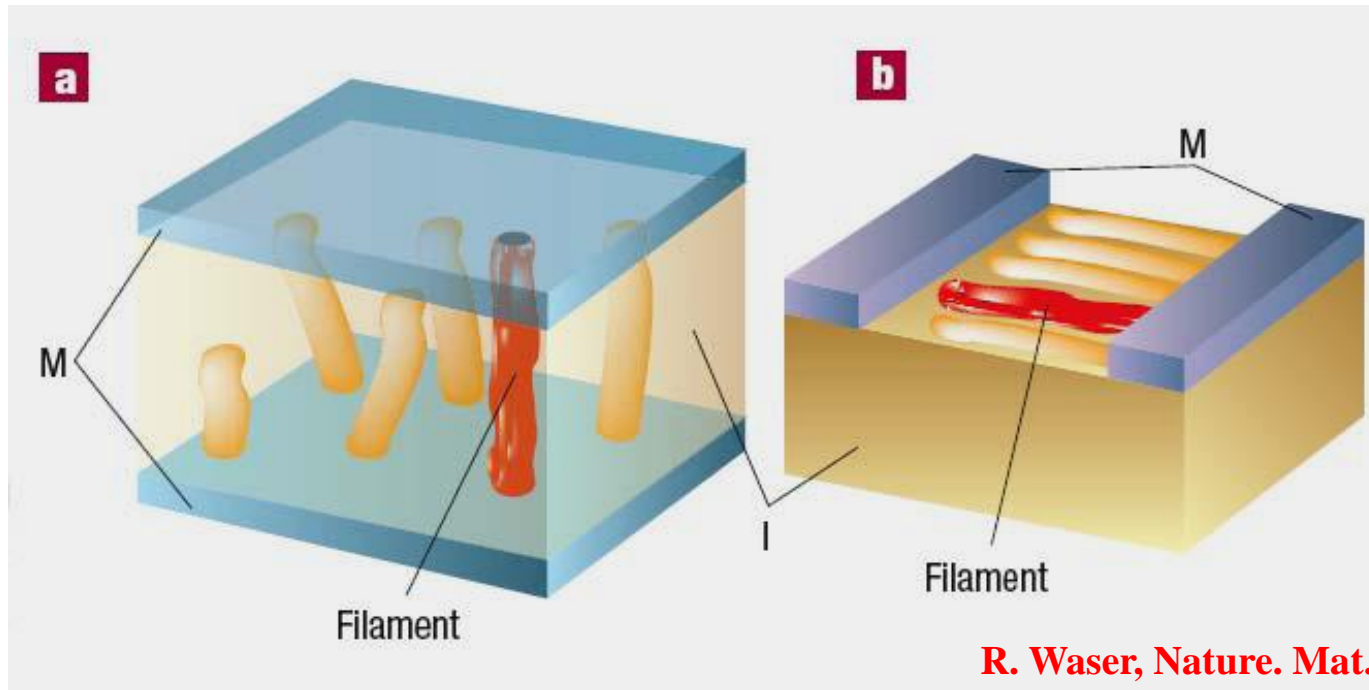


RRAM research in IMECAS

- **Switching Mechanism Study**
- **Device performance improvement**
- **Solution for 3D Integration**
- **Statistics Modeling Work**
- **Integration**

Mechanism of Resistive Switching

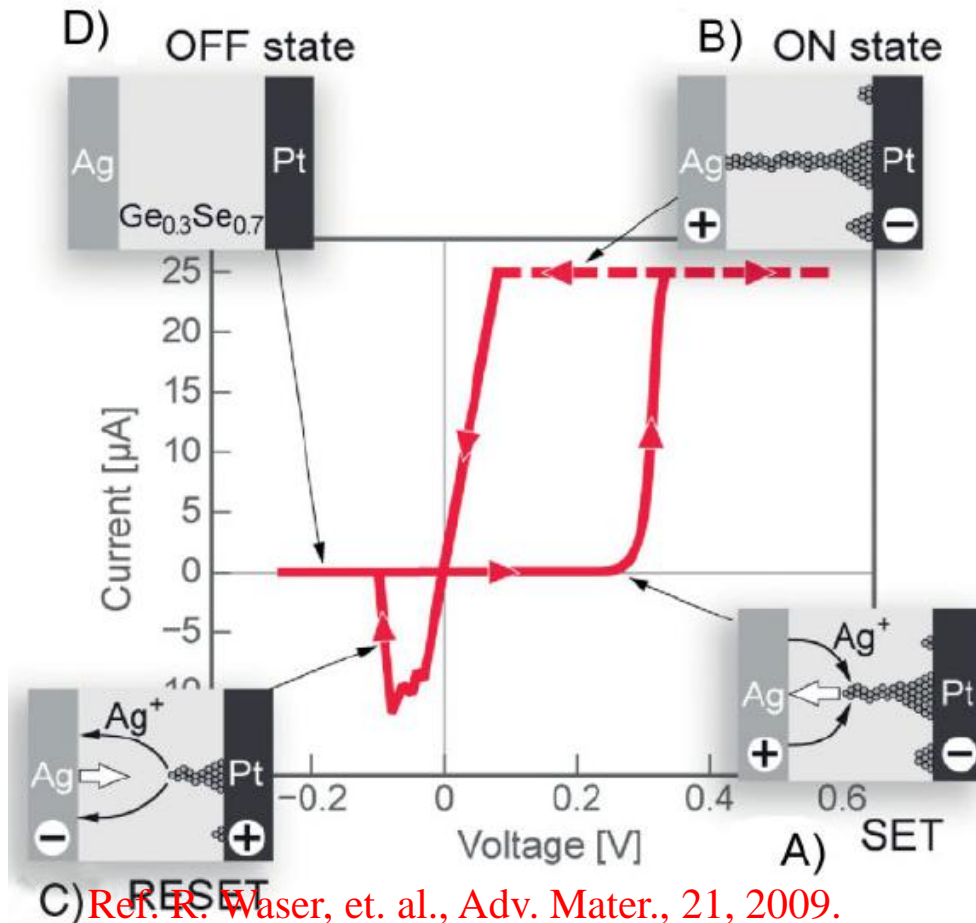
The unclear switching mechanism hinders rapid development for RRAM



The general accepted mechanism of RRAM:

Formation and rupture of localized conductive filaments (CF).

Solid-electrolyte-based RRAM



CF formation process:

- i) anodic metal atoms (M) oxidize metal ions (M^{z-}) according to the reaction ($\text{M} \rightarrow \text{M}^{z-} + z\text{e}^-$)
- ii) the M^{z-} cations migrate toward the cathode under the high electric field;
- iii) M^{z-} deoxidize back to M and electrodeposits on the surface of the inert electrode according to the reversed reaction ($\text{M}^{z-} + z\text{e}^- \rightarrow \text{M}$)

Solid electrolyte materials: AgS, CuS, AgGeSe, SiO_2 , Ta_2O_5 , ZrO_2 , HfO_2 , ZnO, a-Si, ...

Formation and Rupture Conductive Filament

- **What's the evident for this mechanism?**
- **Composition of CF?**
- **How many CF?**
- **Dynamic process of CF formation and rupture?**
- **Do CF growth and dissolution be controlled?**

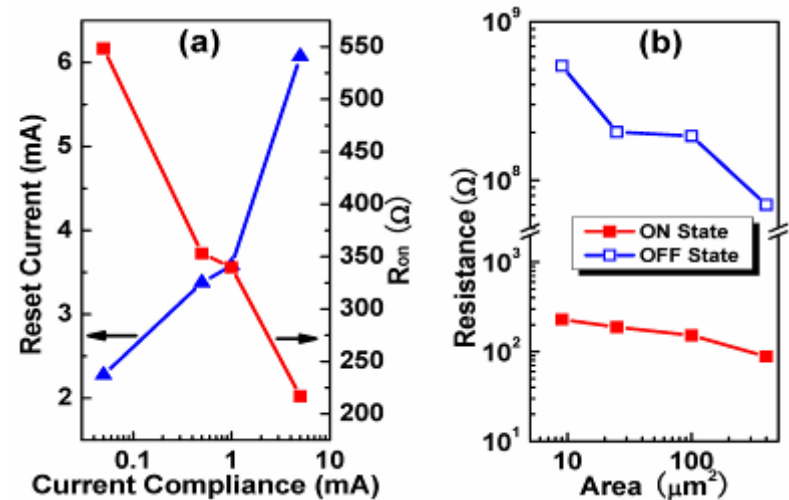
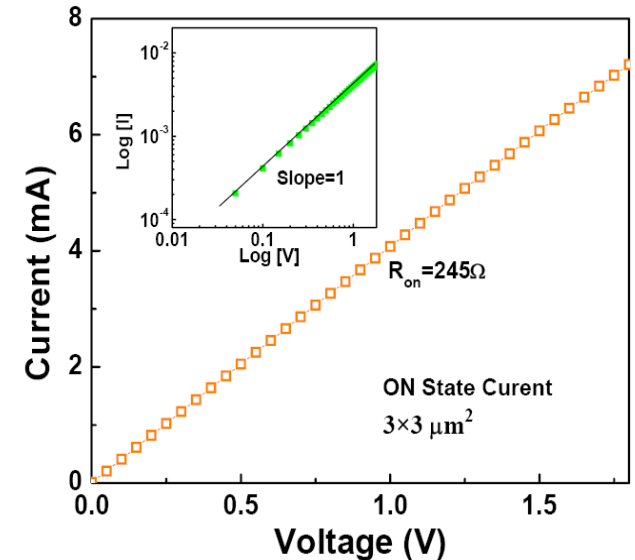
How to capture the dynamic process of CF formation and rupture is a very tough topic to study because of the difficulties in sample preparing.

Conductive Filaments Mechanism

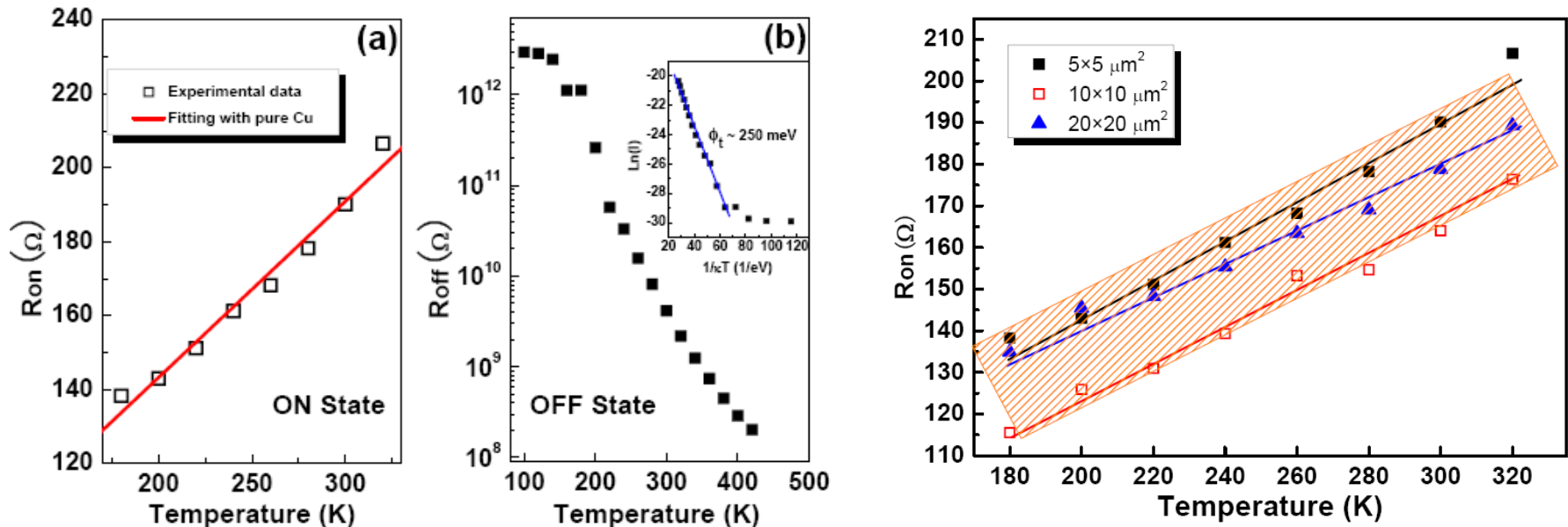
✚ The resistive switching phenomena are dominated by conductive filaments mechanism

- *The current slope is close to 1 in ON state.*
- *I_{Reset} increases with increasing I_{Comp} in Set process.*
- *The resistance of ON state is insensitive to the cell sizes.*

How to confirm the nature of filaments is a trouble to RRAM researcher.



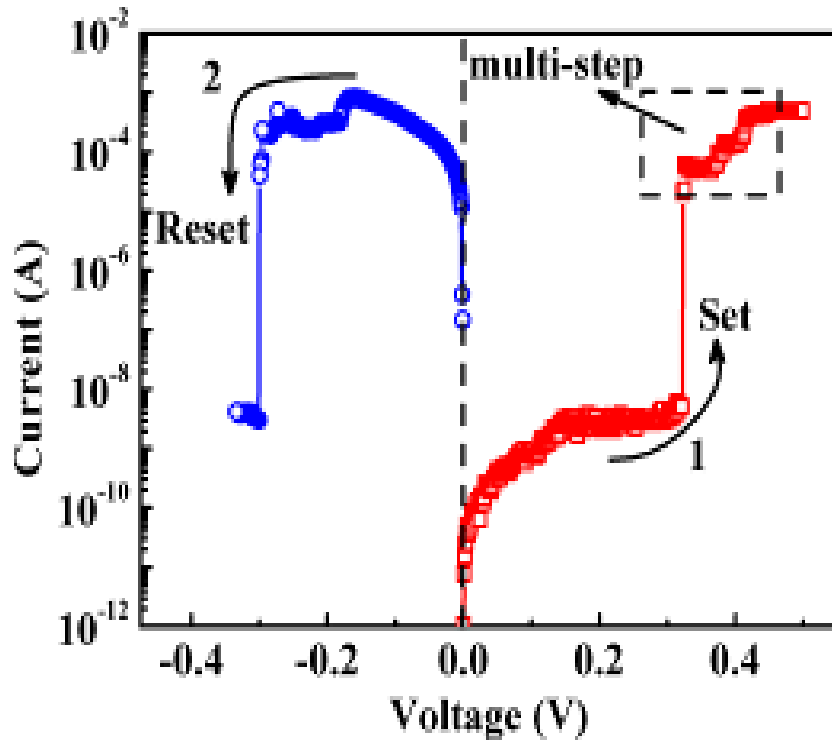
Dependence on Temperature



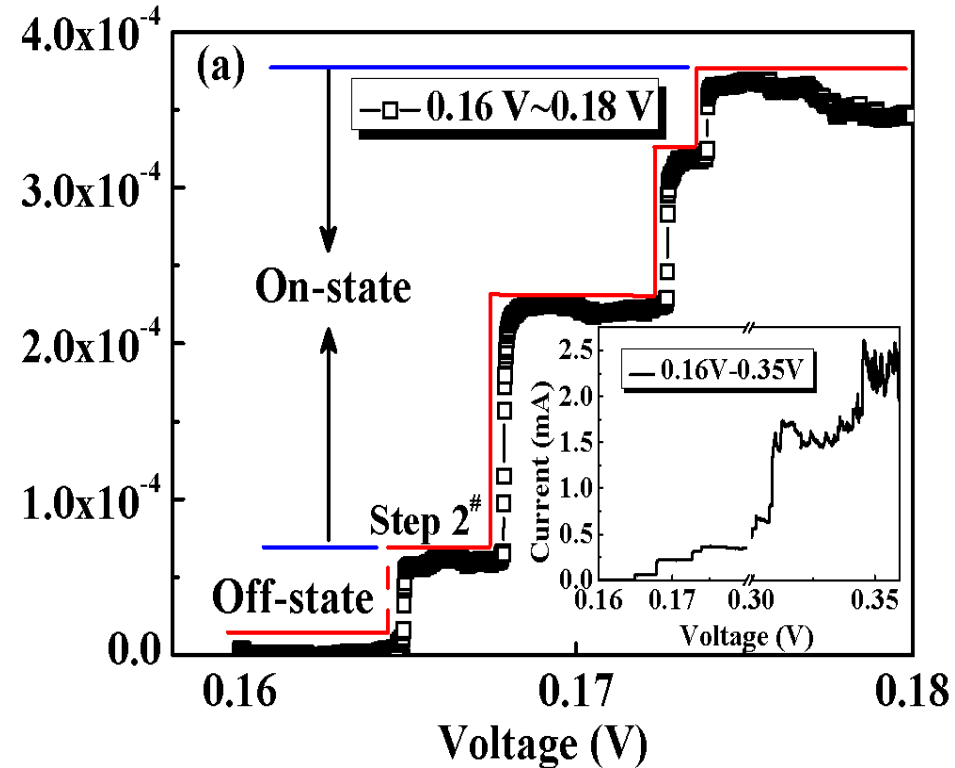
- In the LRS, thermal coefficient is 0.00298/K @ 293K ($5 \times 5 \mu\text{m}$), 0.00249/K @ 293K ($10 \times 10 \mu\text{m}$) and 0.00239/K @ 293 ($20 \times 20 \mu\text{m}$)
- Thermal coefficient of Cu nanowire ($>15\text{nm}$) is 0.0025/K @ 293K

Conduction in LRS arises from copper metal!

How many of CF?



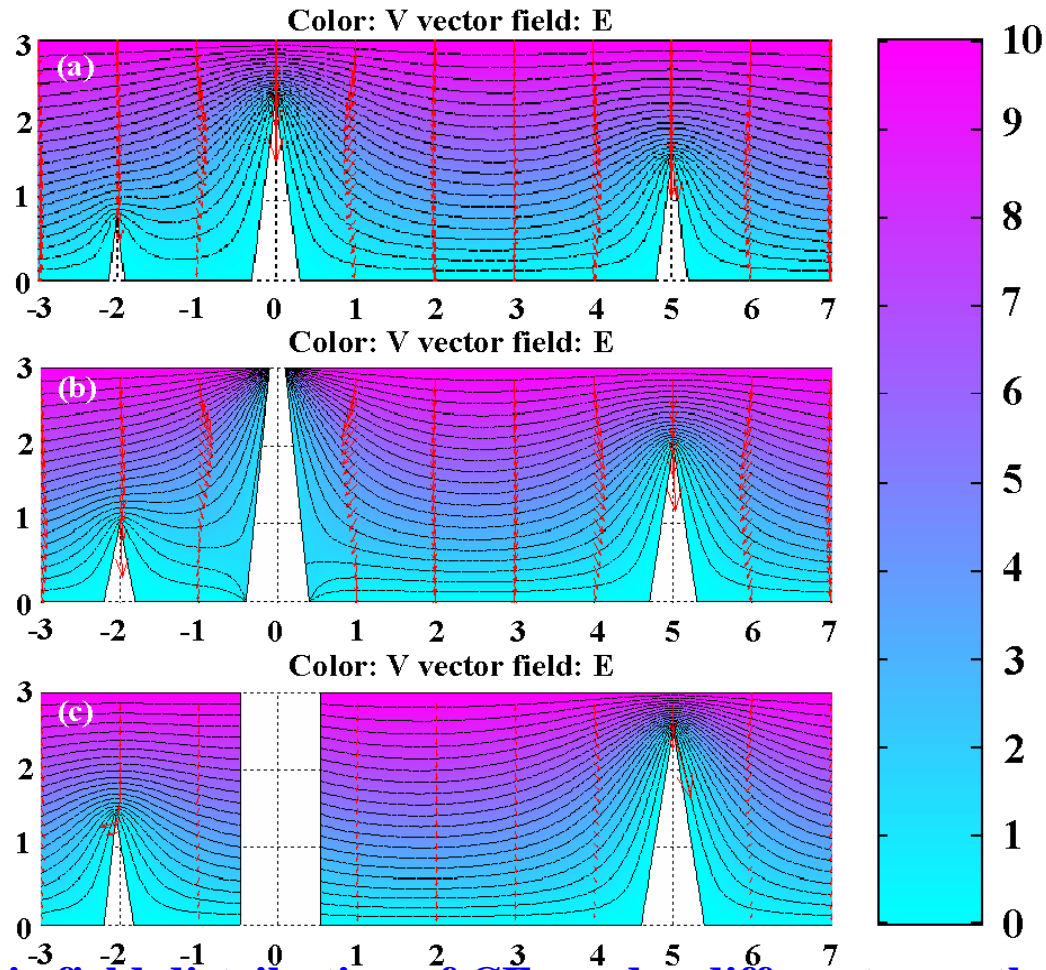
Step: 1mV/step



Step: 10uV/step

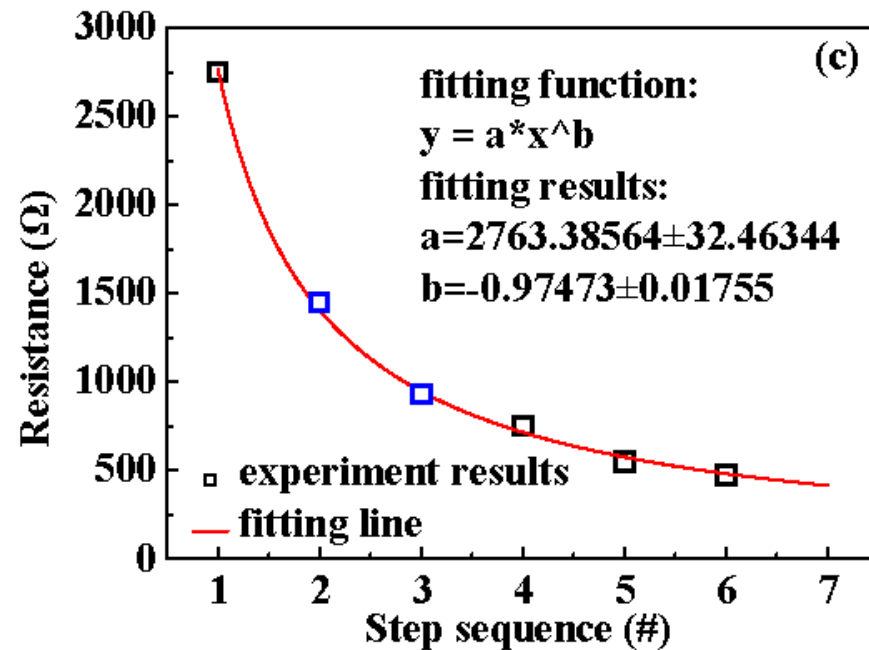
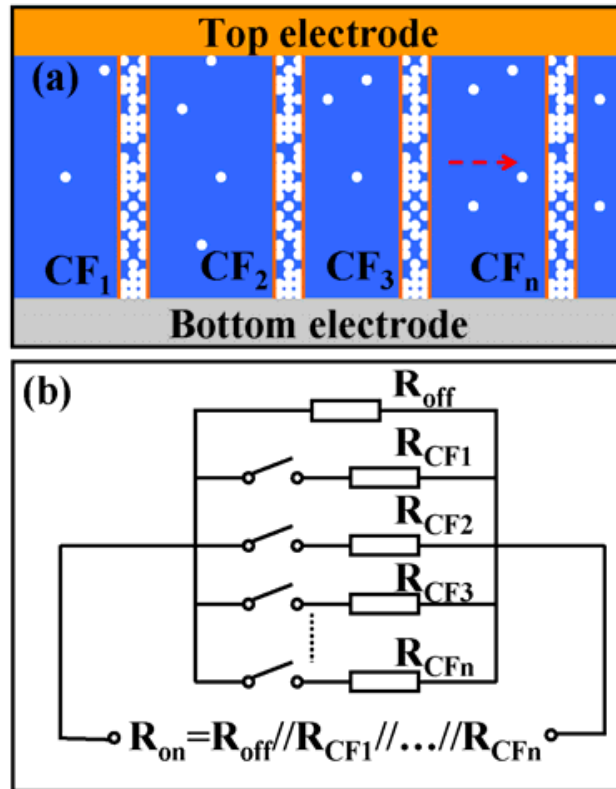
Observed a stair-like I-V by ultra low sweeping speed, demonstrated the existence of multi filaments.

Electronic field simulation



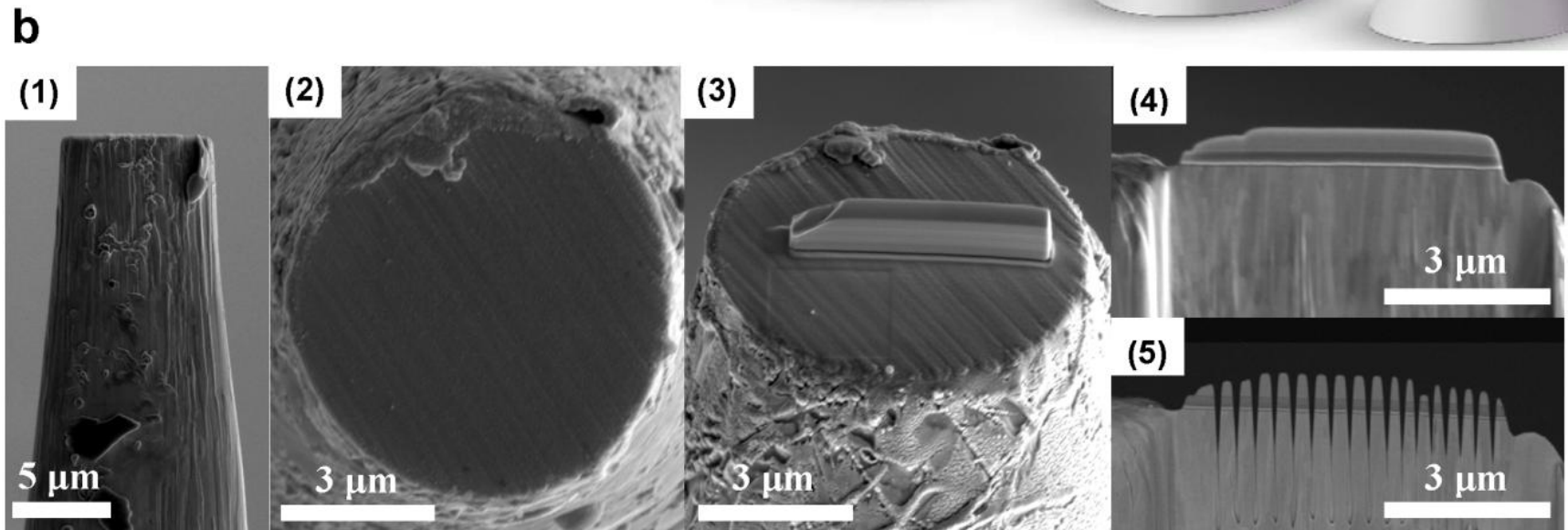
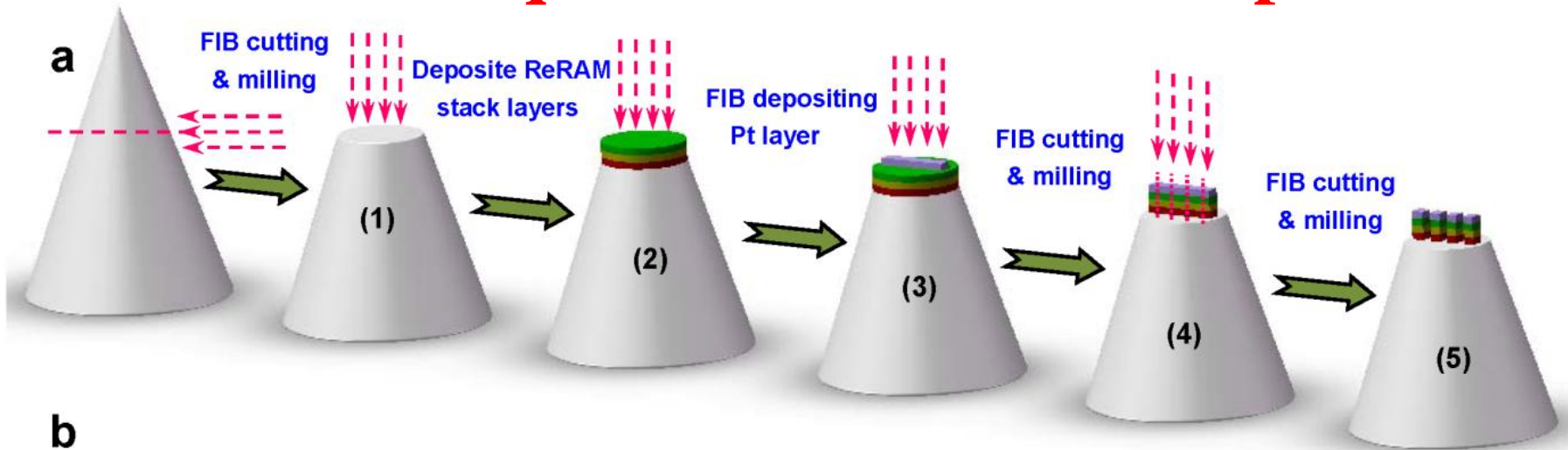
The simulation of electric field distribution of CFs under different growth stages uses the MATLAB PDE-tool, (a) pre-connection (b) connect establishment and (c) post-connection. Simulating result indicate that multiple cylinder-like CFs will be formed in the Cu-doped ZrO_2 film.

Multiple Filaments Mechanism

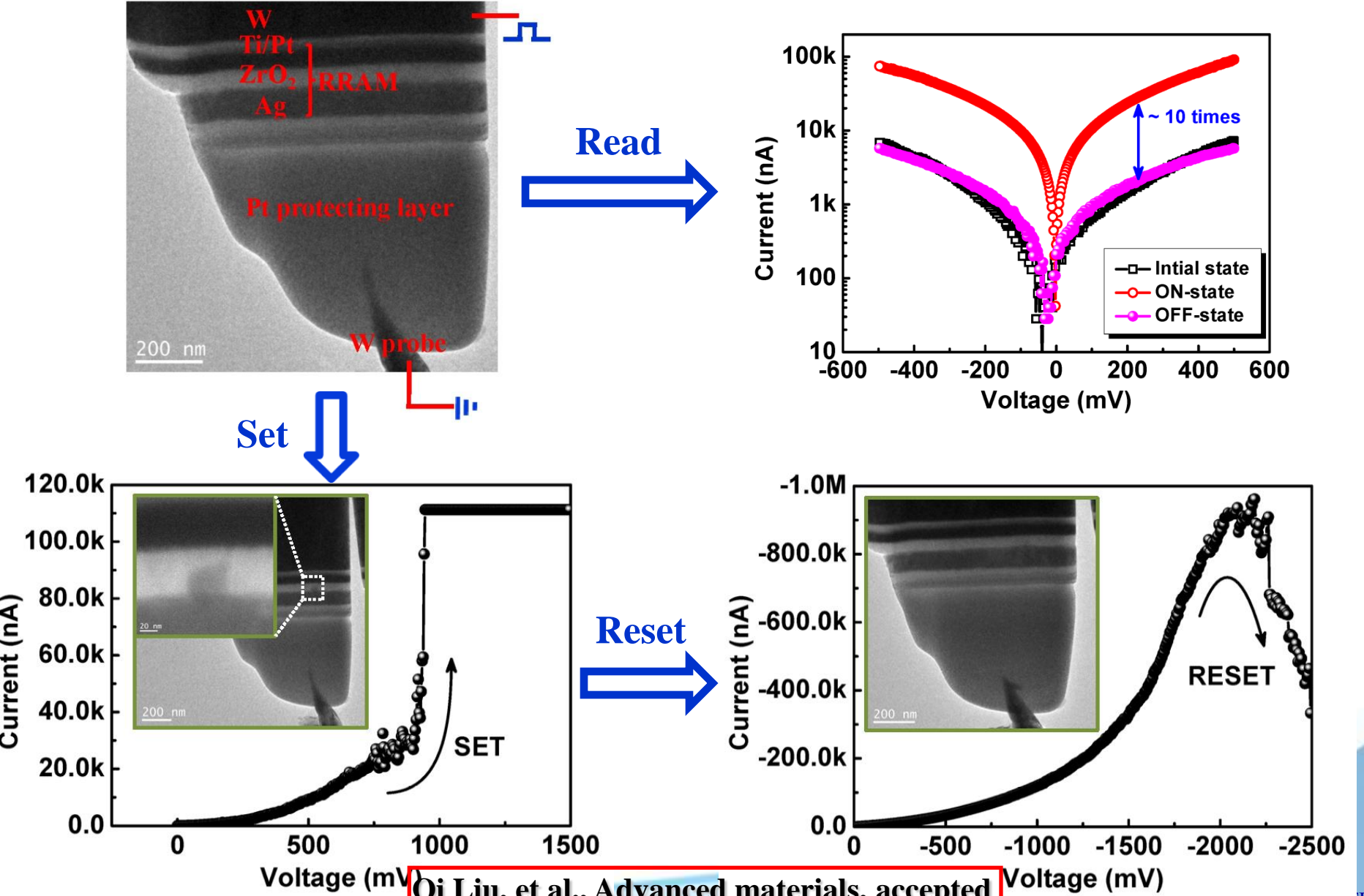


The stepwise switching behavior can be explained by multiple parallel filaments are successively connected between the bottom and top electrodes during set process. The resistance steps in on-state follow the inverse relationship of forming sequence of these filaments, further verifying the multiple filaments mechanisms.

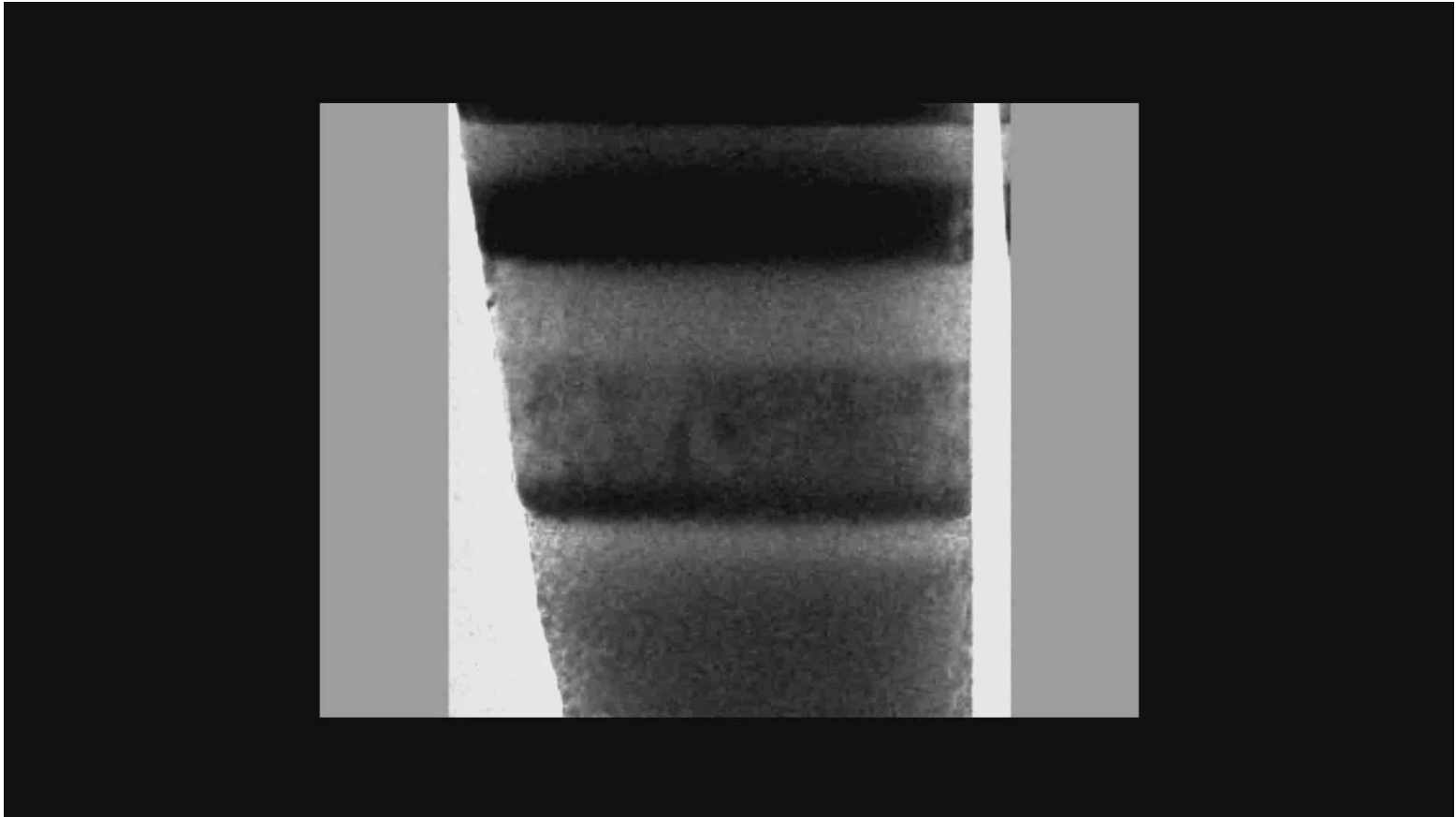
Fabrication technique for ReRAM TEM specimen



Dynamic process of CF formation and rupture

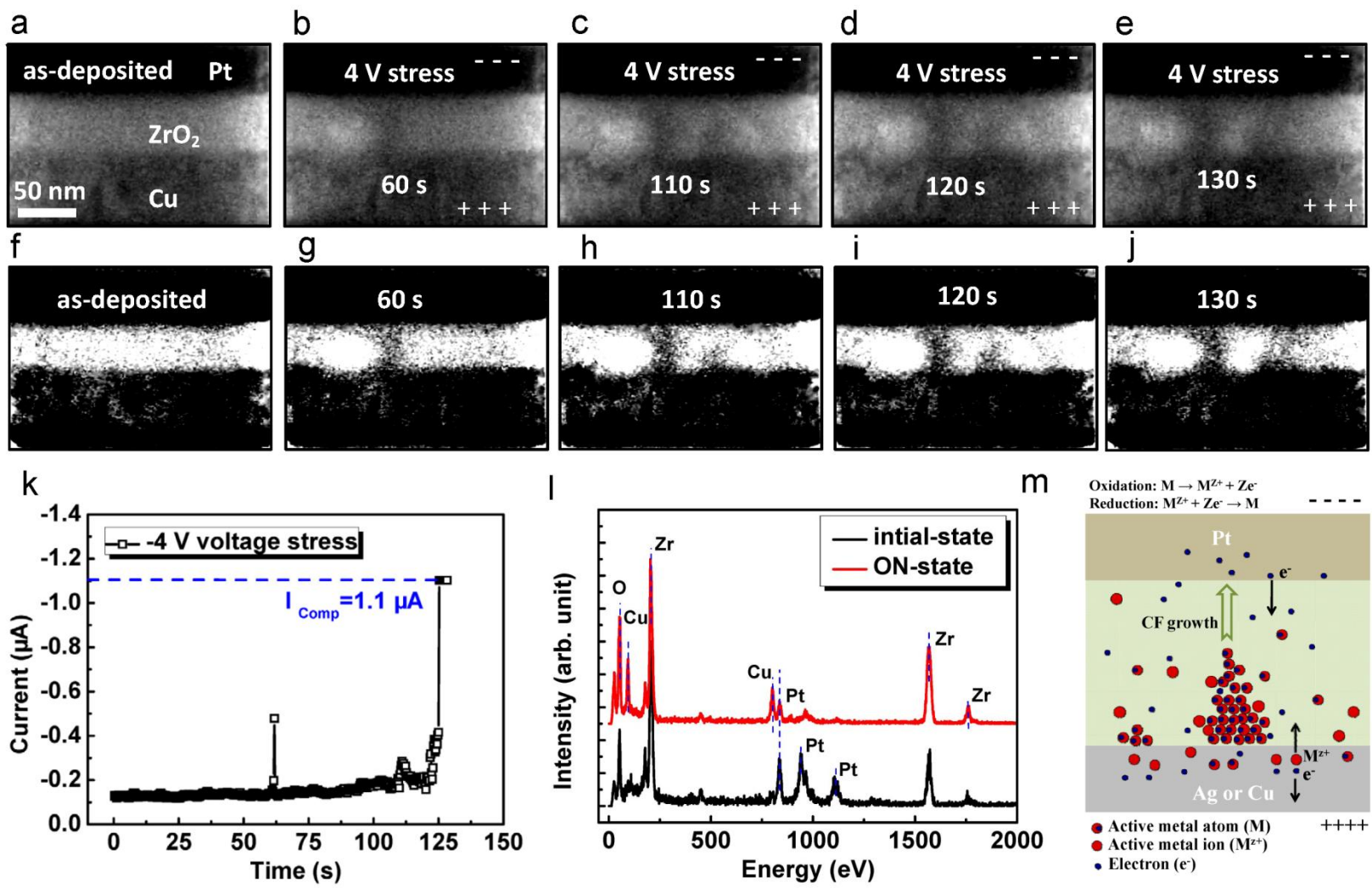


Growth of the multiple conductive filament



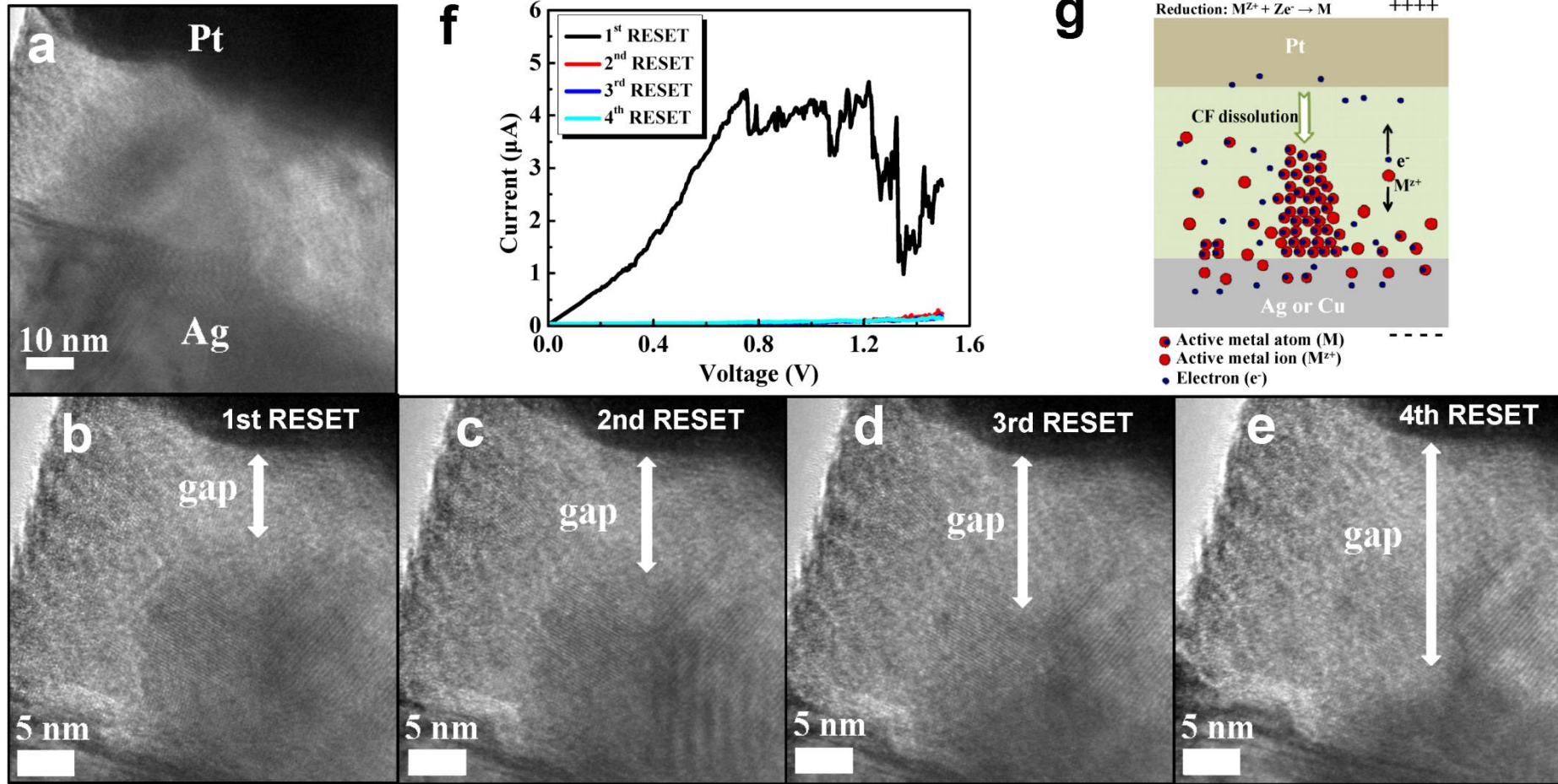
Under voltage stress, the dynamic growth of the conductive filament were observed in the above movie. As can be seen from the video, there are two conductive filaments were formed from the Cu to the Pt electrodes through the ZrO_2 layer.

Dynamic process of CF formation



In oxide based electrolyte material, the metal bridge is found grown from the anode, rather than the cathode, which is opposite to the conventional PMC theory.

Dynamic process of CF Rupture

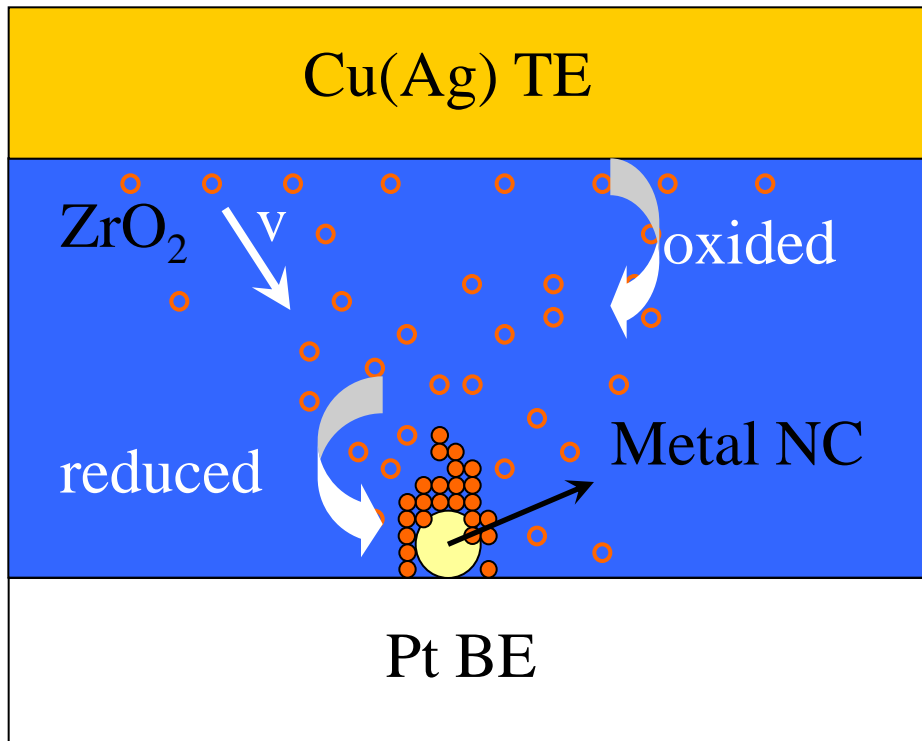


The rupture process, from the cathode, also opposite to the conventional theory.

(Qi Liu, et al., Advanced Materials accepted)

CF growth by inserting nano-crystal

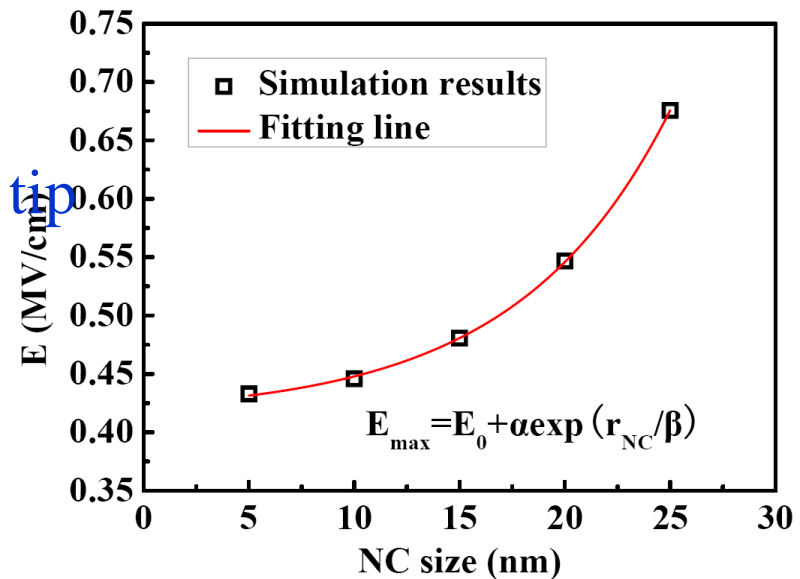
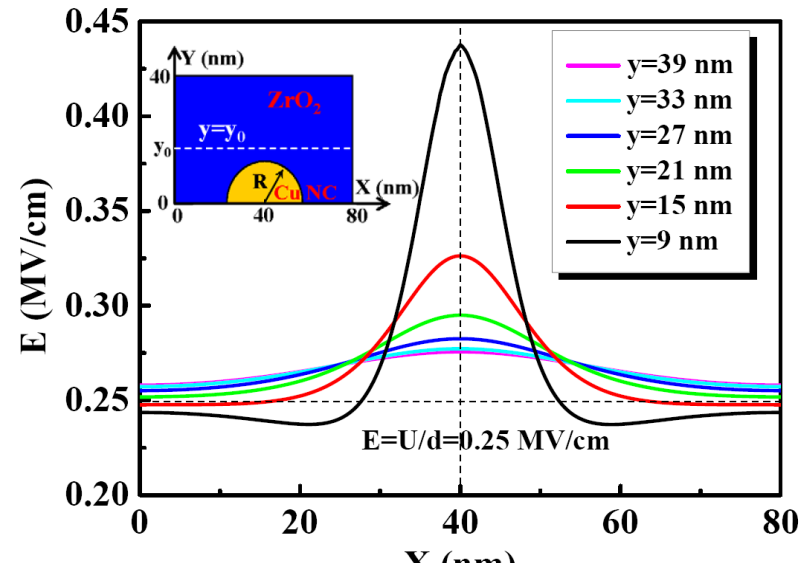
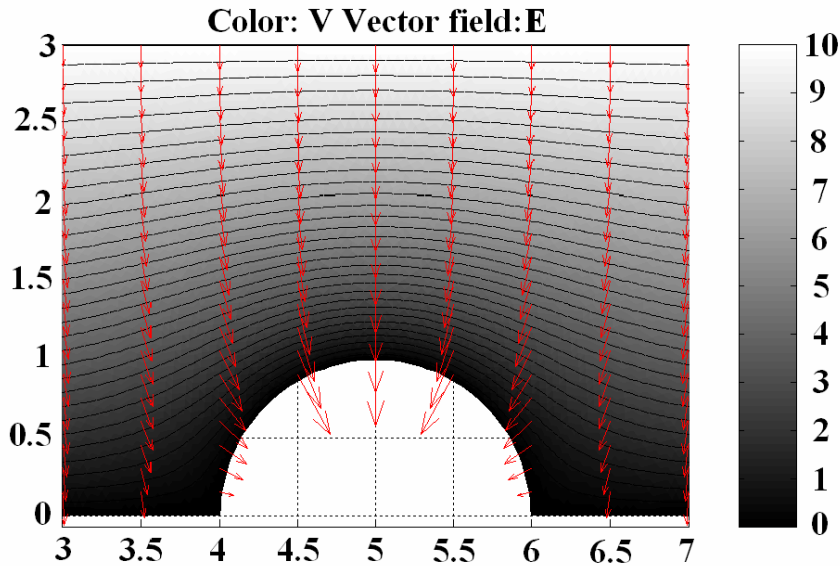
○ ion ○ atom + + +



- i) anodic metal atoms (M) oxidize metal ions (M^{z-}) according to the reaction ($M \rightarrow M^{z-} + ze^{-}$)
- ii) the M^{z-} cations migrate toward the cathode under the high electric field, more M^{z-} gathered around NC;
- iii) M^{z-} deoxidize back to M and electrodeposits on the surface of the inert electrode according to the reversed reaction ($M^{z-} + ze^{-} \rightarrow M$)

- Enhancing and converging the electrical field by metal NC
- Accelerating metal ions velocity
- Controlling filament growth location by metal NC

Electric field simulation



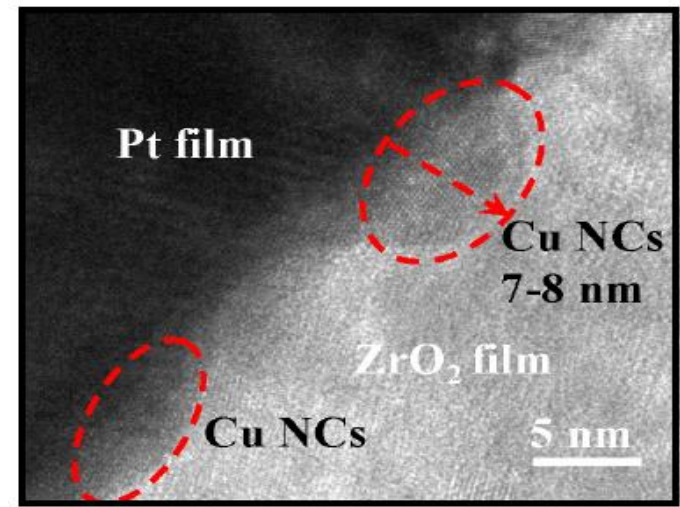
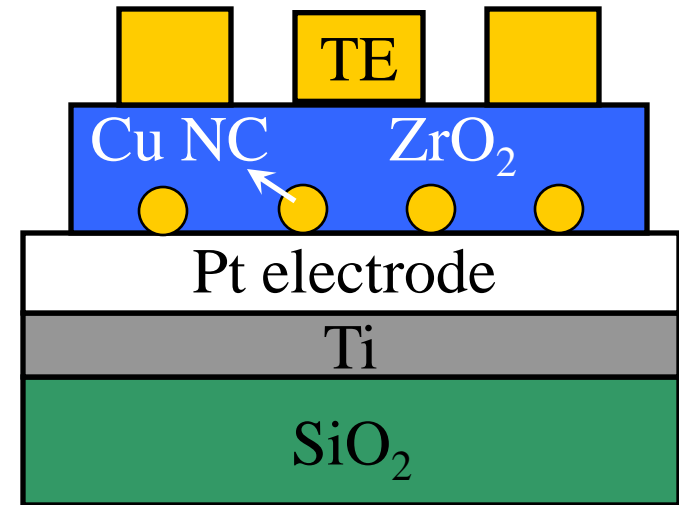
➤ The maximum intensity of E at the NC tip

➤ The intensity of E rapidly decays outside the column region above the NC location

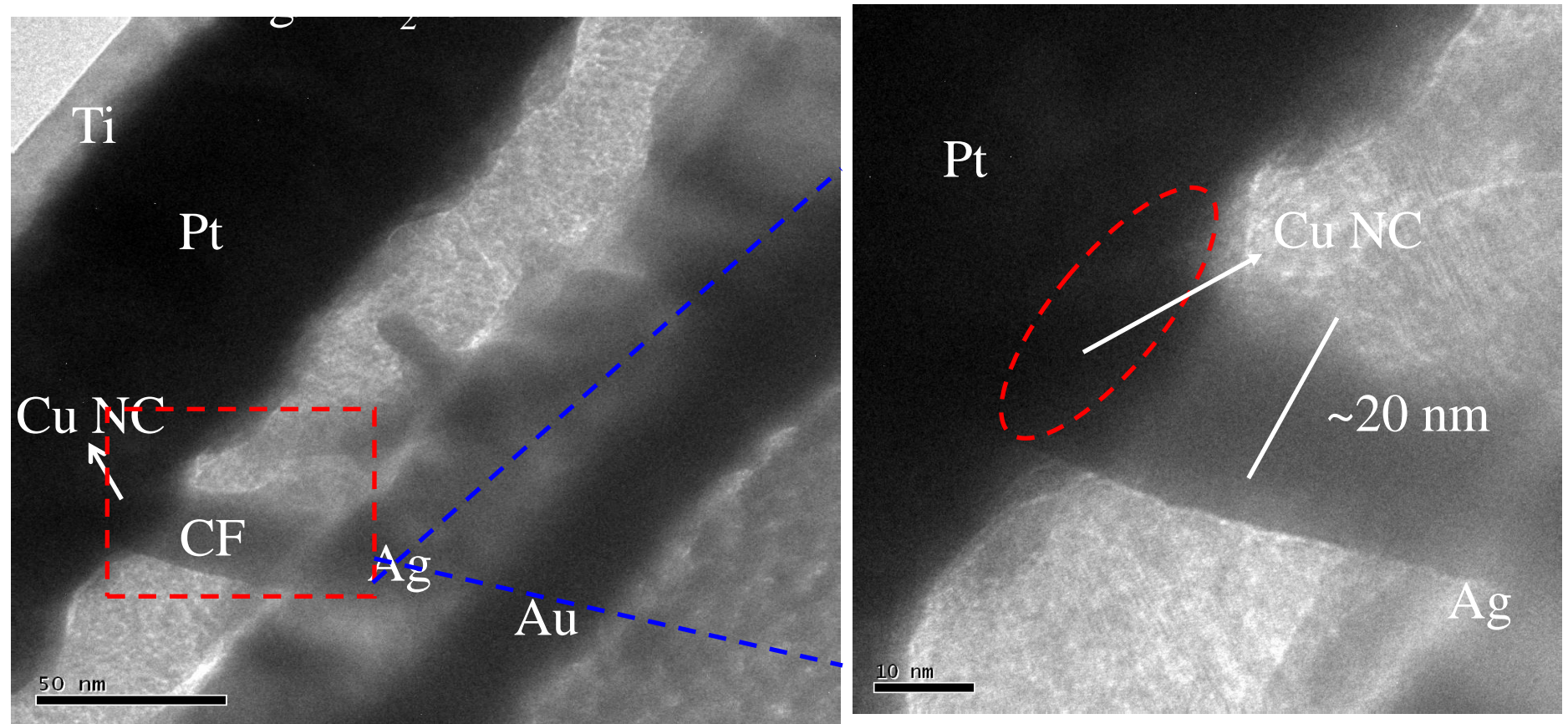
➤ The maximum intensity of E exponentially increase with the NC size

TE/ZrO₂/Cu NC/Pt

- clear Si wafer
- thermal SiO₂ layer
- deposit BE electrode materials
- deposit Cu thin film (3nm)
- deposit ZrO₂ film (40 nm)
- rapid thermal annealing (600°C, 5s, N₂)
- defining TE electrode shape
- deposit TE electrode materials
- lift-off to forming TE electrode
- electrical test

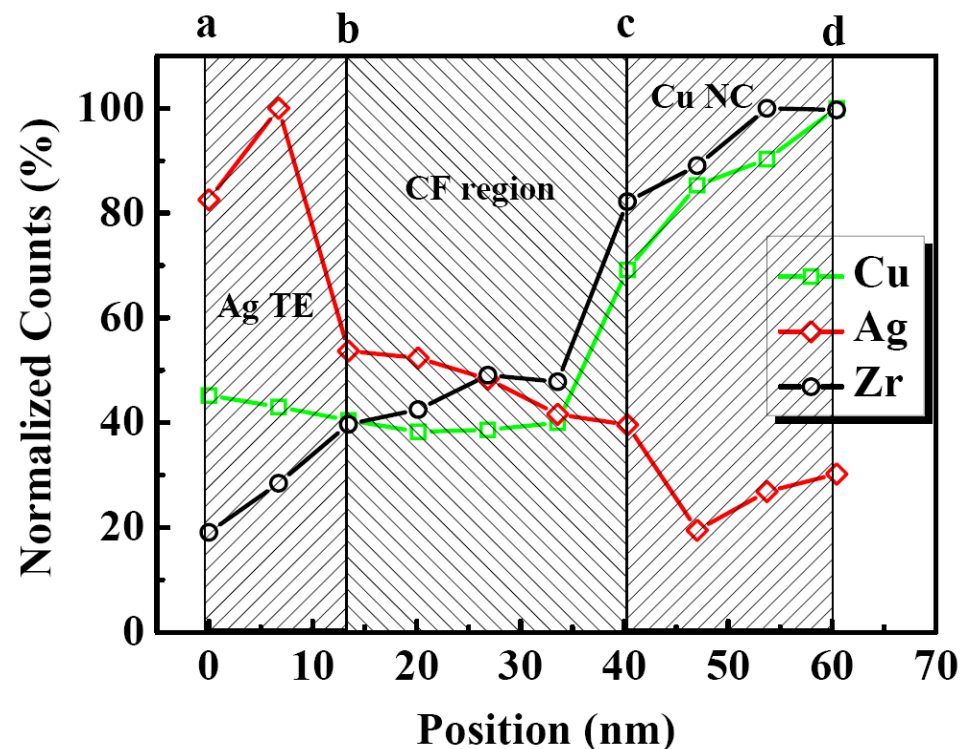
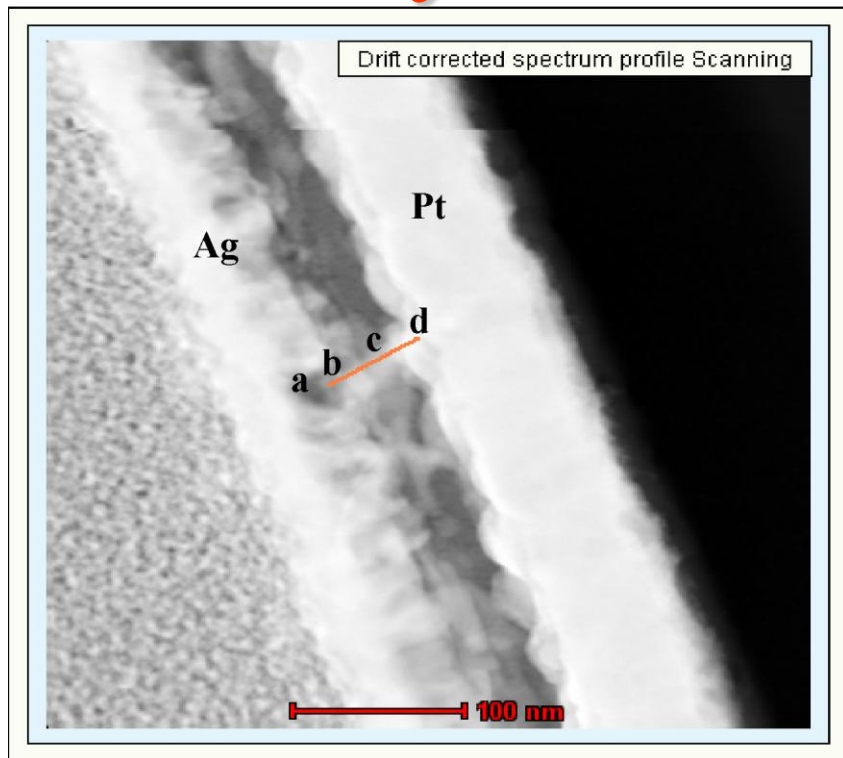


TEM images CF



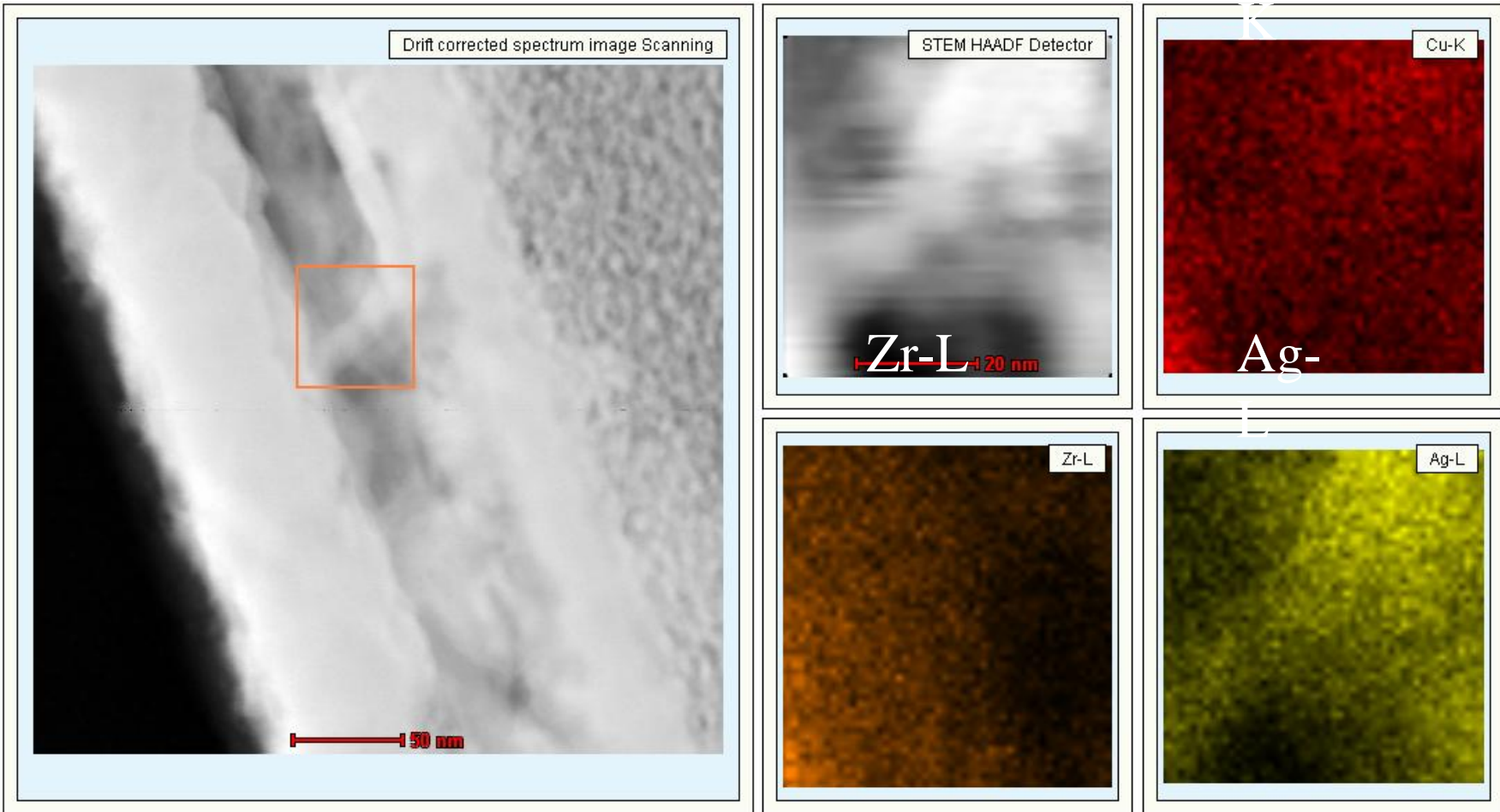
The nano-bridge region is directly connected to a protrusion of the Pt BE, and the protrusion is a Cu NC based on elements analysis by EDS !

EDS analysis



- i) a→b corresponds to the Ag electrode region;
- ii) b→c corresponds to the CF electrode region;
- iii) c→d corresponds to the Cu NC region.

Element mapping



The component of nano-bridge in the Ag/ZrO₂/Cu NC/Pt device is mainly Ag elements !

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Summary

- ◆ **Temperature-dependent switching characteristics reveals that microscopic nature of the metallic conductive is Cu element in Cu/BTMO:Cu/Pt based RRAM.**
- ◆ **Multiple resistance steps in Cu/BTMO:Cu/Pt device was observed, it is due to successively established parallel filaments between the bottom and top electrodes during Set process.**
- ◆ **We have indentified the metallic nature of CF in Cu/ZrO_x/Pt device and observed the existence of multi-CFs Oxide-Electrolyte-based ReRAM.**
- ◆ **Adding a metal NC layer, CFs grow easily along the direction of metal NC, which reduces the randomness of the CF formation and rupture processes.**



**Thanks for your
attention!**

