



Nanometallic RRAM

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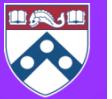
Size-dependent Metal-insulator Transition

Random Materials

Crystalline & Amorphous

Purely *Electronic* Switching

A Metal? An Insulator?



Periodic System



- With a **band gap**, or without
- **Insulator**: infinite resistivity at 0K
- **Metal**: finite resistivity at 0K



Random System

Aperiodic:

No sharp band edge

Mott :

Mobility edge (k space)

Anderson:

$\zeta = \text{diffusion distance @ 0K}$
(elastic tunneling)

$\zeta = \text{extent of wave function}$

Metal: $\zeta \rightarrow \infty$

Insulator: $\zeta < \infty$

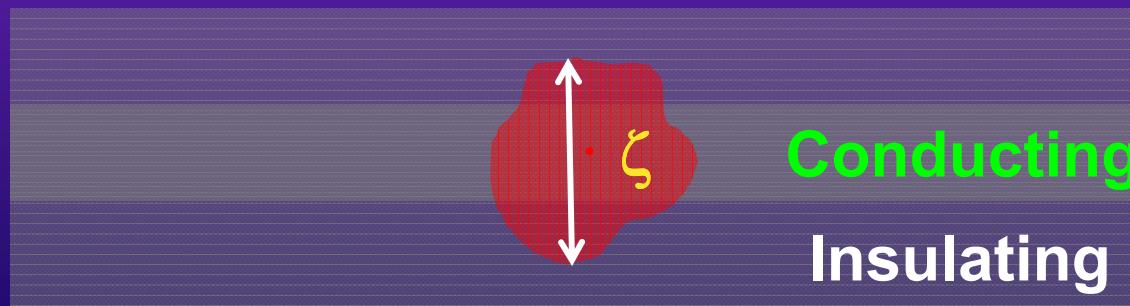
• *Metallic* if $\delta < \zeta$

• *Insulating* if $\delta > \zeta$

Sample size (thickness) = δ



*An insulator, small enough,
is a metal!*

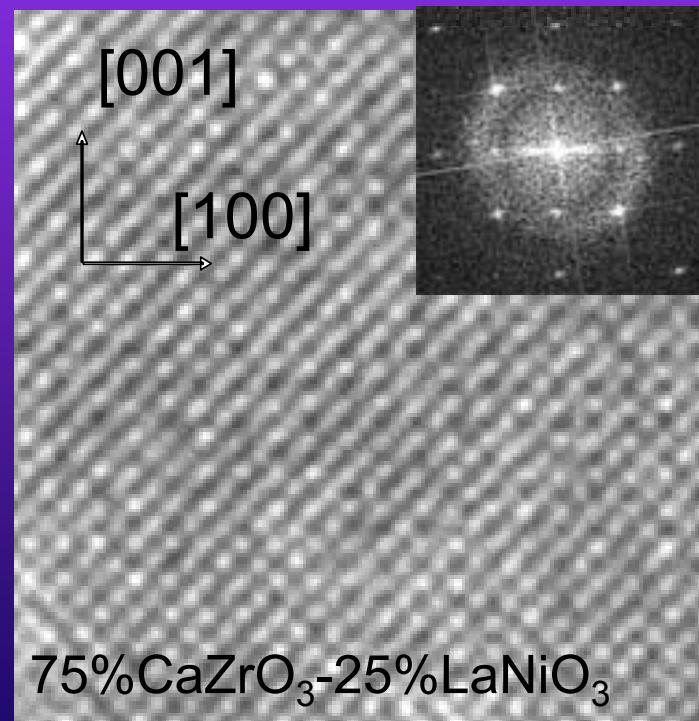
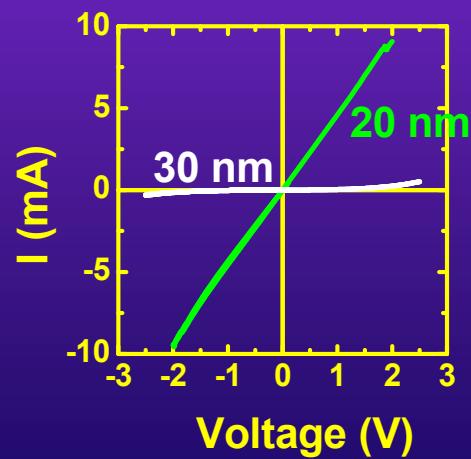
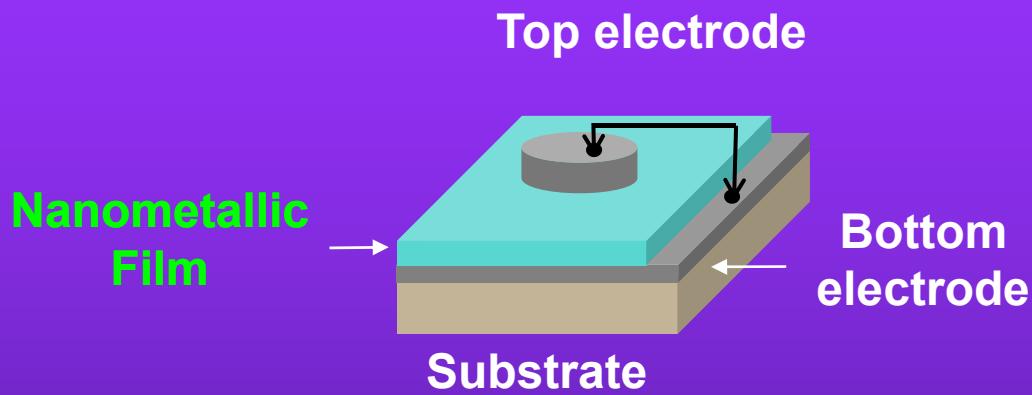


Long- ζ Random Insulator



- *Atomically mixing metal into insulator*

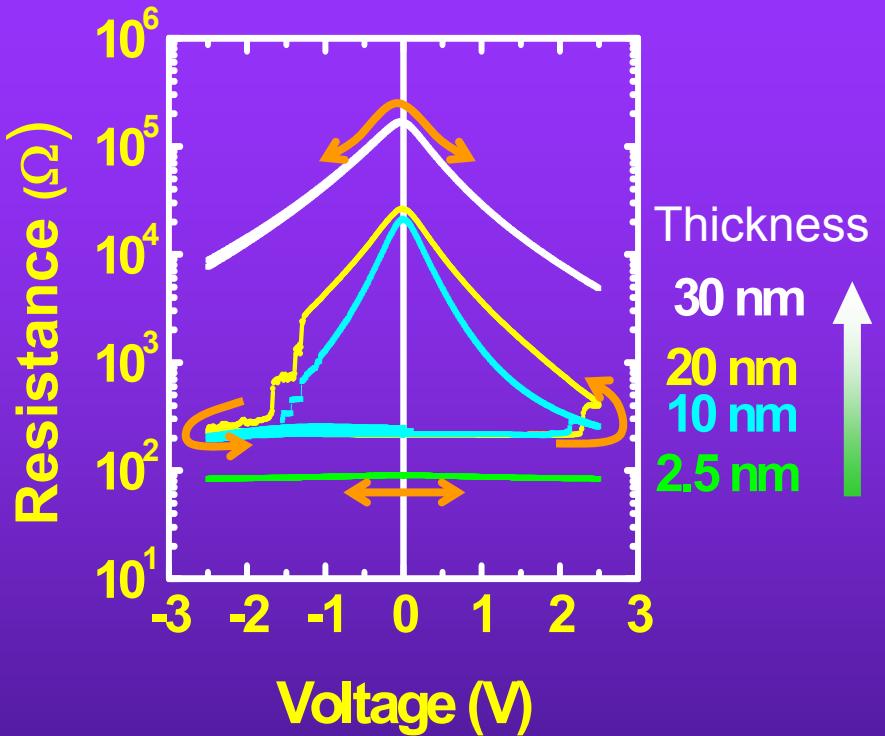
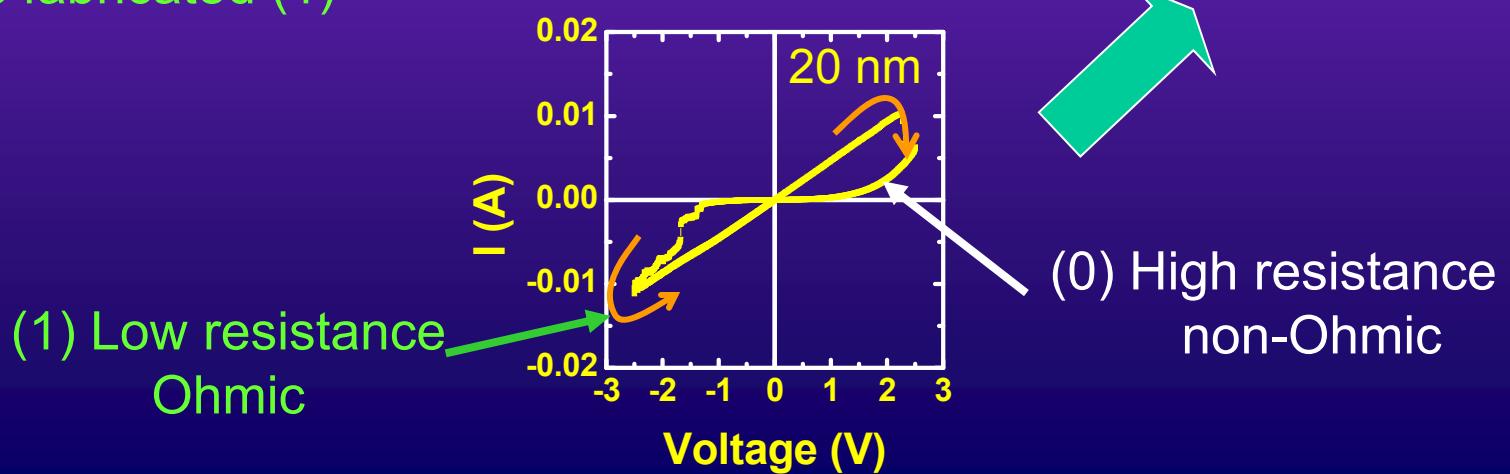
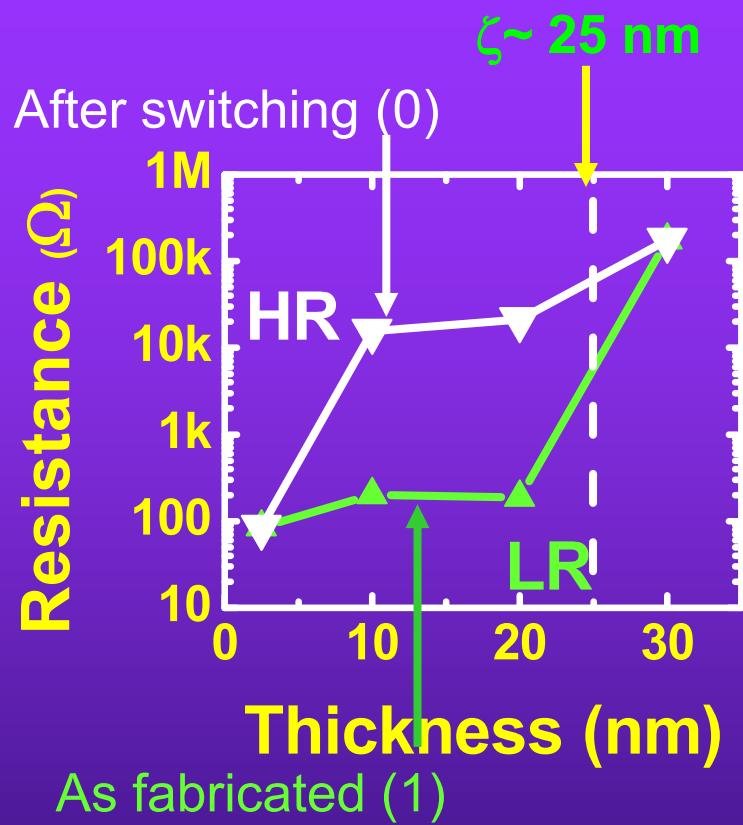
Nanometallic Thin Film: Crystalline



Insulator Metal



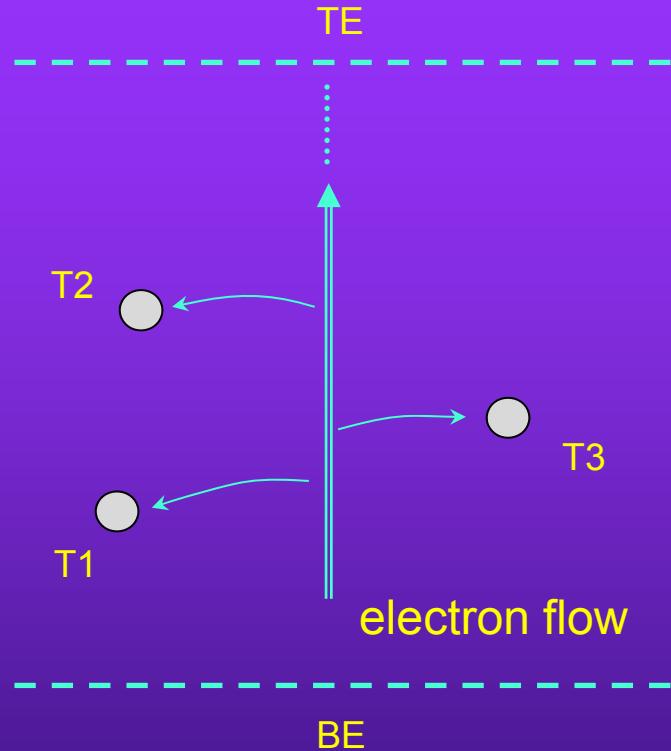
Voltage-controlled MIT



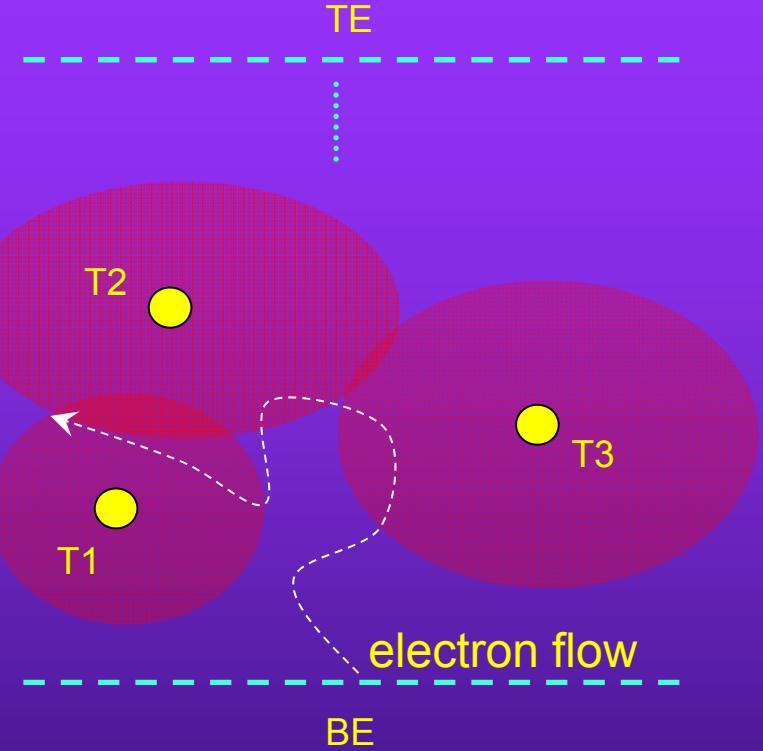
Mechanism for Switching (on/off)



LRS



HRS



Free electron path ($\zeta > \delta$)

● Isolated traps

● Filled traps ● Repulsion



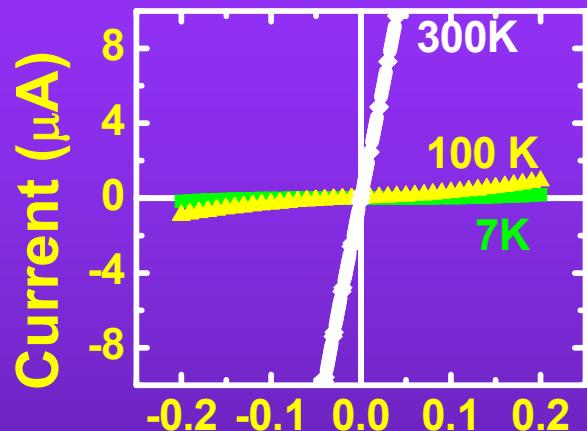
$\zeta < \delta$

Change Diffusion Length: on/off

Switching: A Metal-Insulator Transition

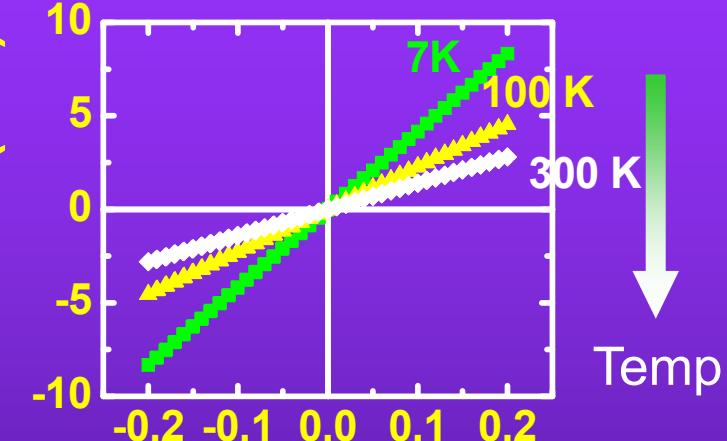


High resistance HR state
Insulating

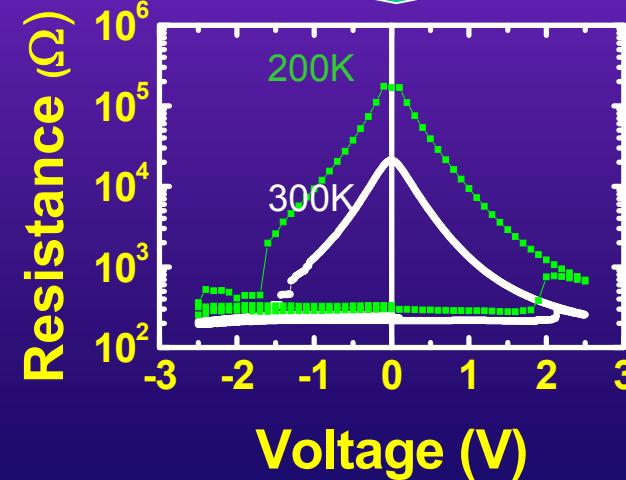


Voltage (V)

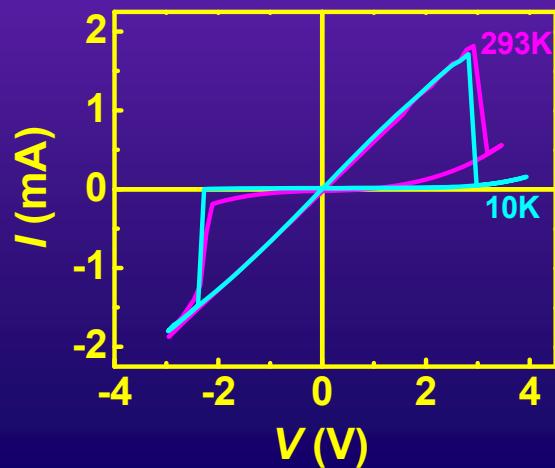
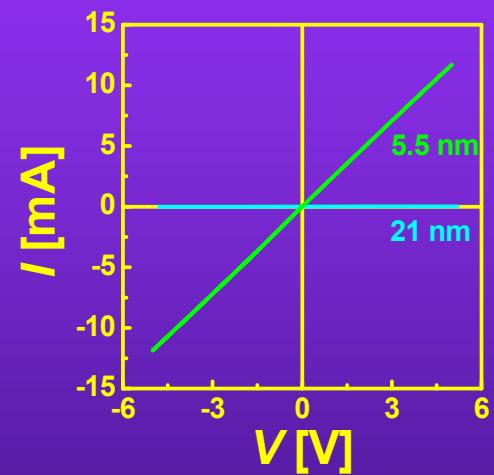
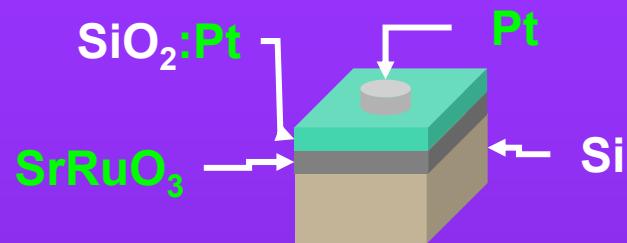
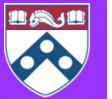
Low resistance LR state
Metallic



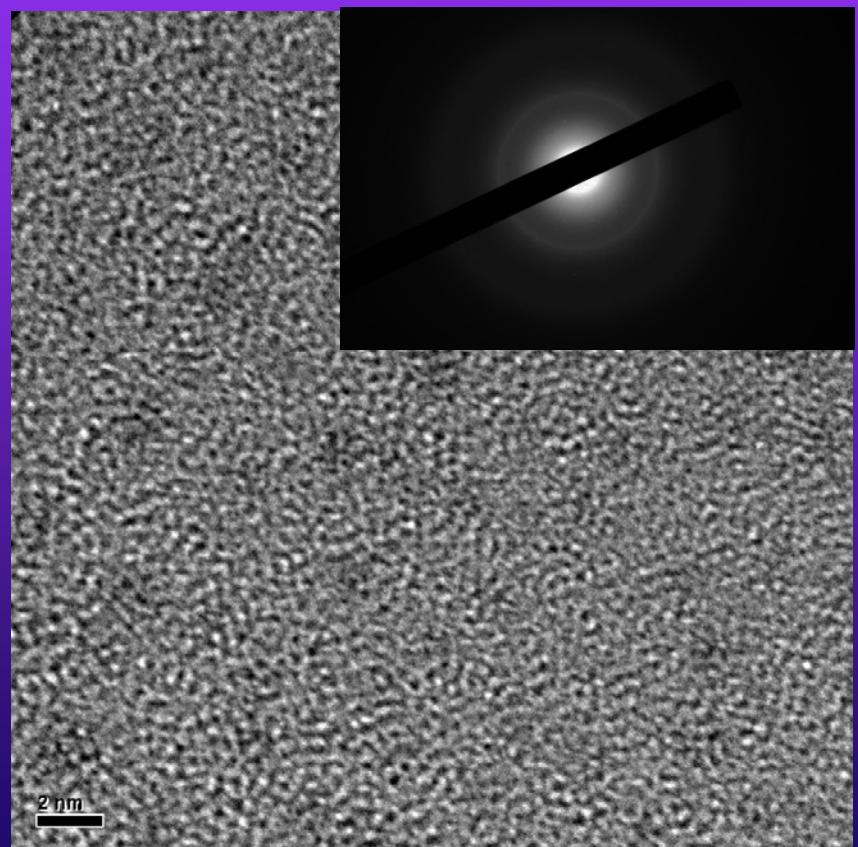
Voltage (V)



Nanometallic Glasses



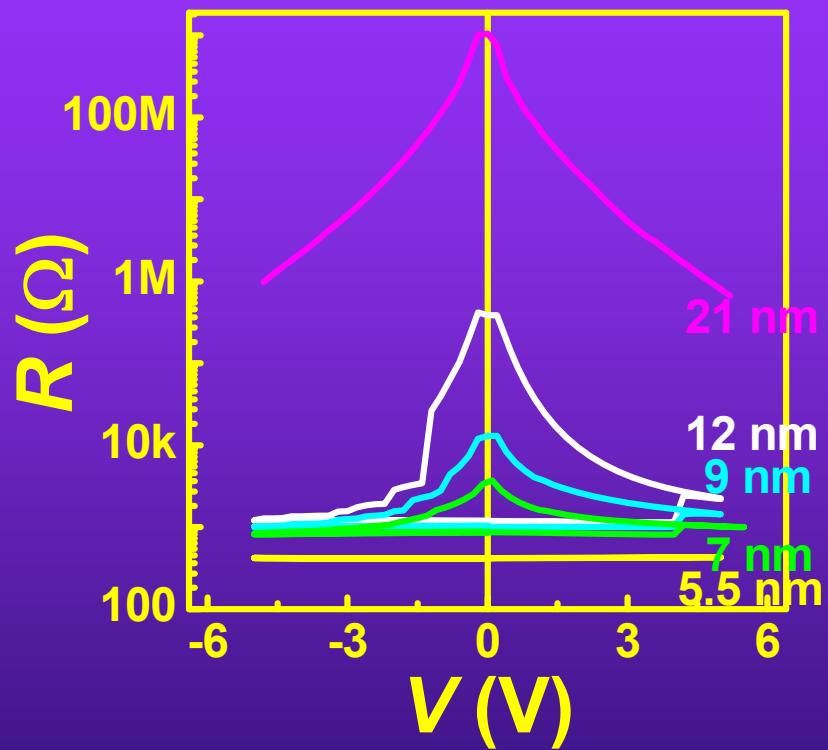
- Random $\text{SiO}_2:\text{Pt}$ alloy
Insulator Metal



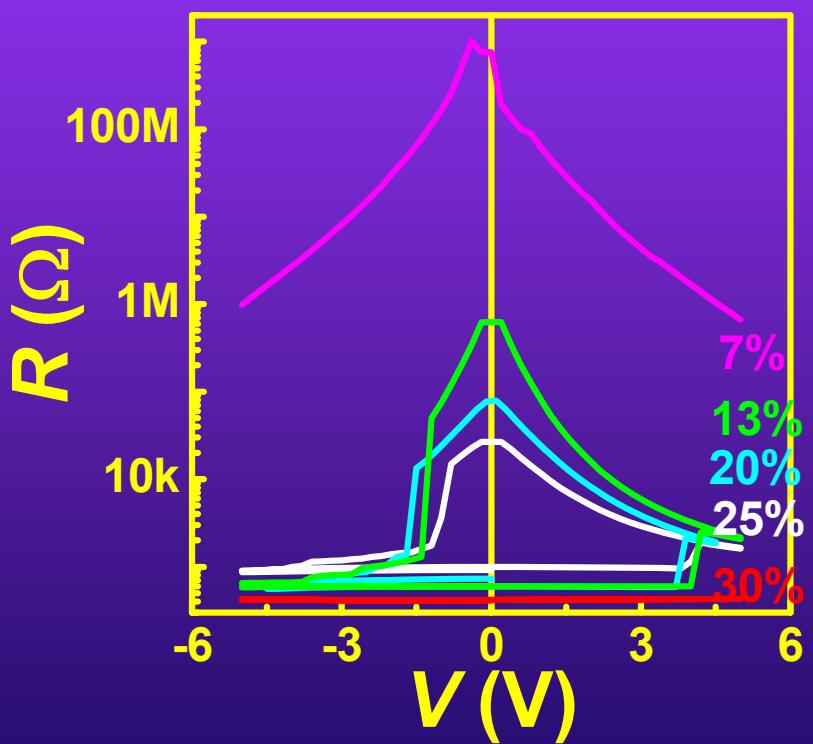


Nanoscale MIT

δ -triggered ($\text{SiO}_2:0.2 \text{ Pt}$)



f -triggered ($\delta \sim 20 \text{ nm}$)



Random Nanometallic Materials



Insulator : Metal

$\text{LaAlO}_3:\text{LaNiO}_3$

$\text{LaAlO}_3:\text{SrRuO}_3$

$\text{CaZrO}_3:\text{LaNiO}_3$

$\text{CaZrO}_3:\text{SrRuO}_3$

$\text{Si}_3\text{N}_4:\text{metal A}$

$\text{Si}_3\text{N}_4:\text{metal B}$

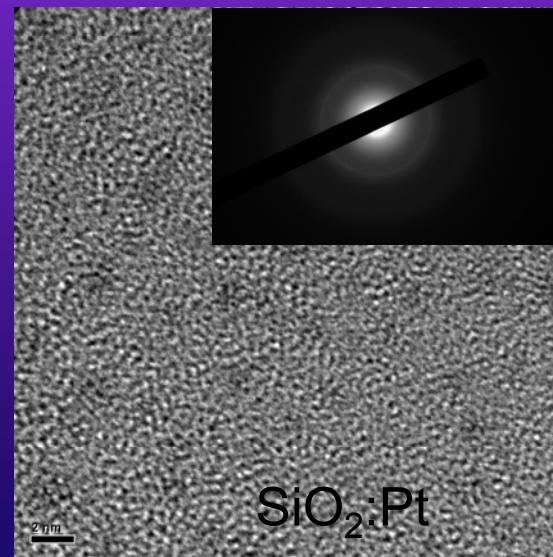
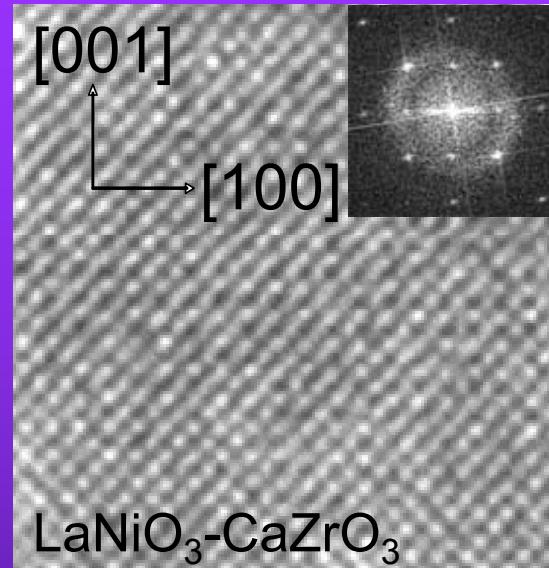
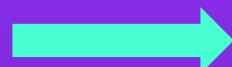
$\text{Si}_3\text{N}_4:\text{metal C}$

$\text{Si}_3\text{N}_4:\text{Pt}$

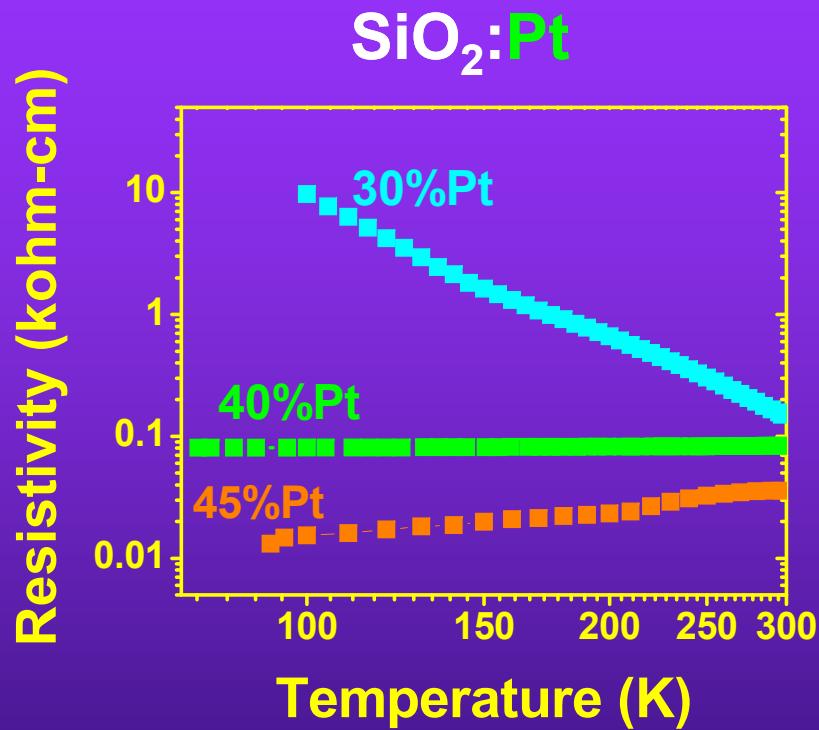
$\text{SiO}_2:\text{Pt}$

Oxide A:Pt

etc.



Nanometallicity \neq Percolation



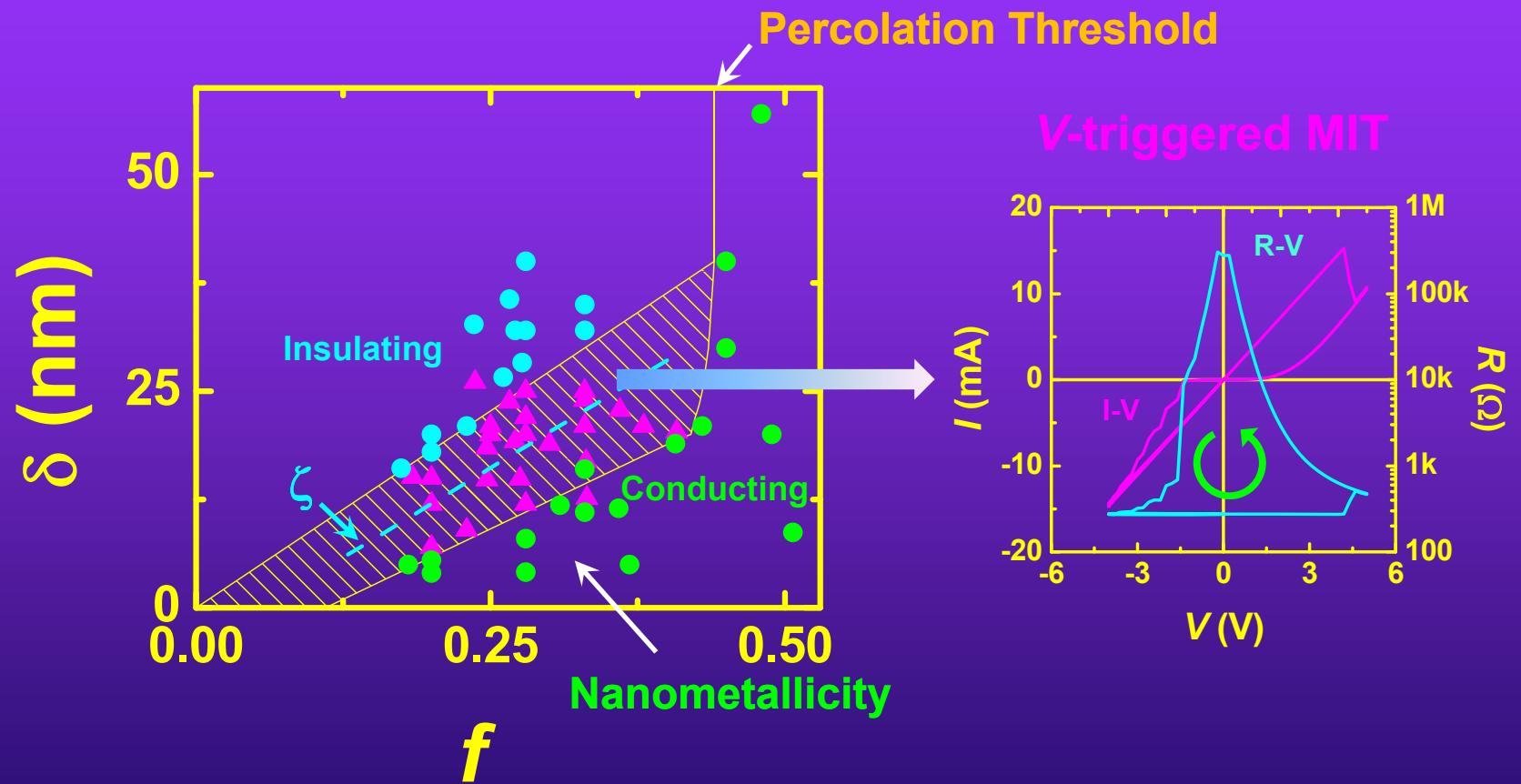
Bulk percolation: $f \sim 0.4$

	f_c (mol %)	$f_{\text{Percolation}}$ (mol%)
SiO ₂ :Pt	20	38
SiN _{3/4} :Pt	<<38	38
SiN _{3/4} :metal A	<<40	40
LaAlO ₃ :LaNiO ₃	12	-
LaAlO ₃ :SrRuO ₃	11	86
CaZrO ₃ :LaNiO ₃	25	-
CaZrO ₃ :SrRuO ₃	5.5	75

Not percolation-induced metallicity



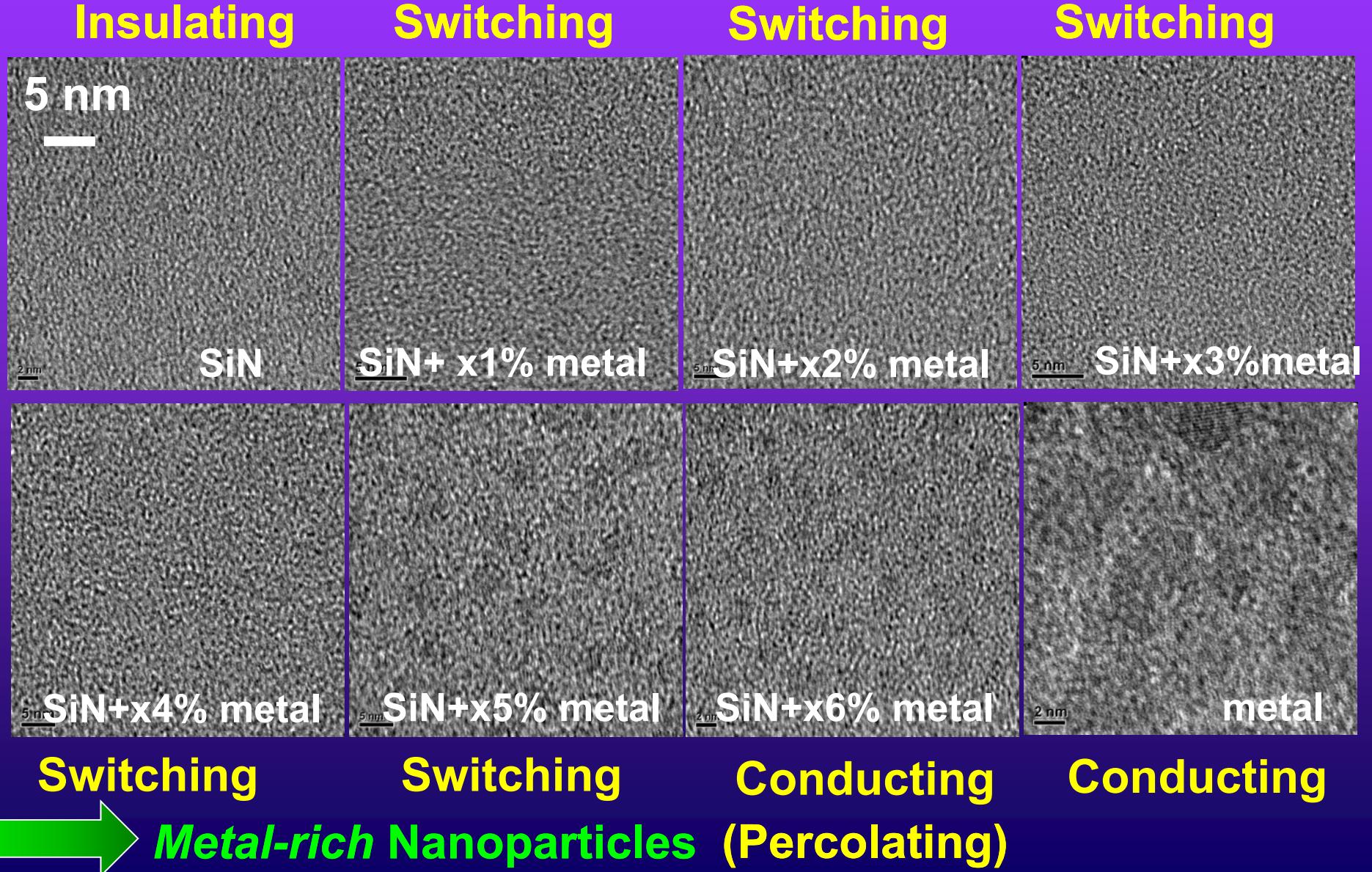
f - δ Map for MIT



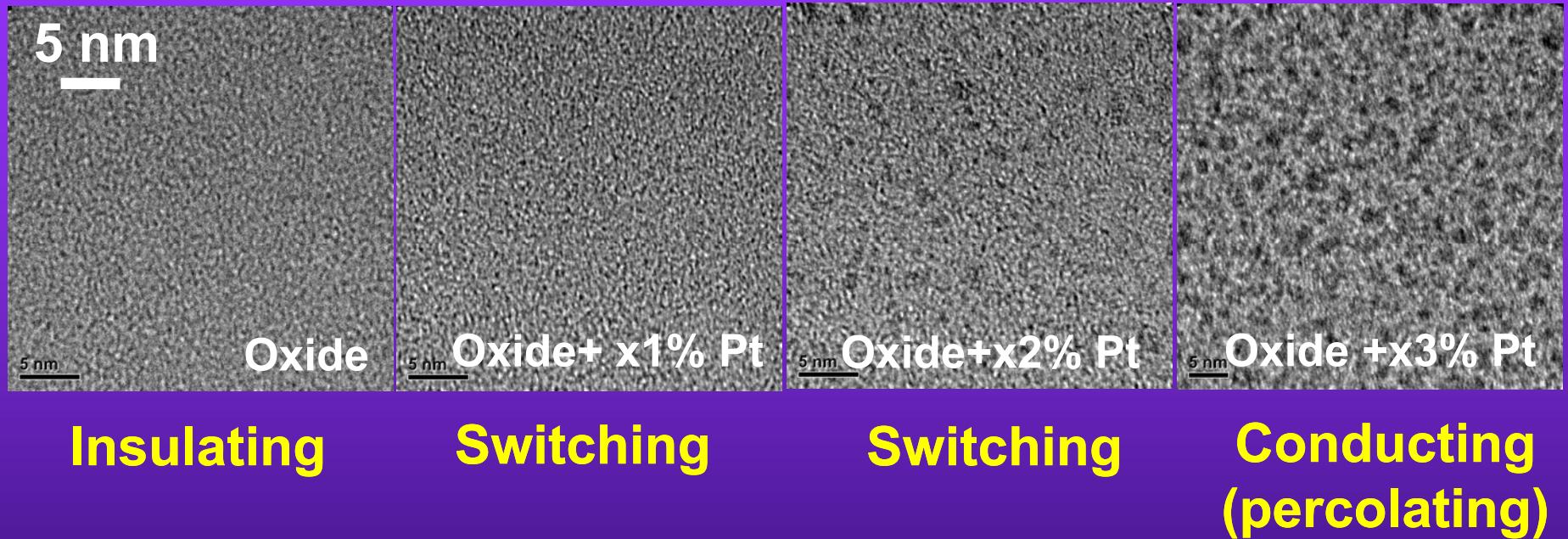


Nanostructure?

SiN:metal A System: 10 nm TEM Films

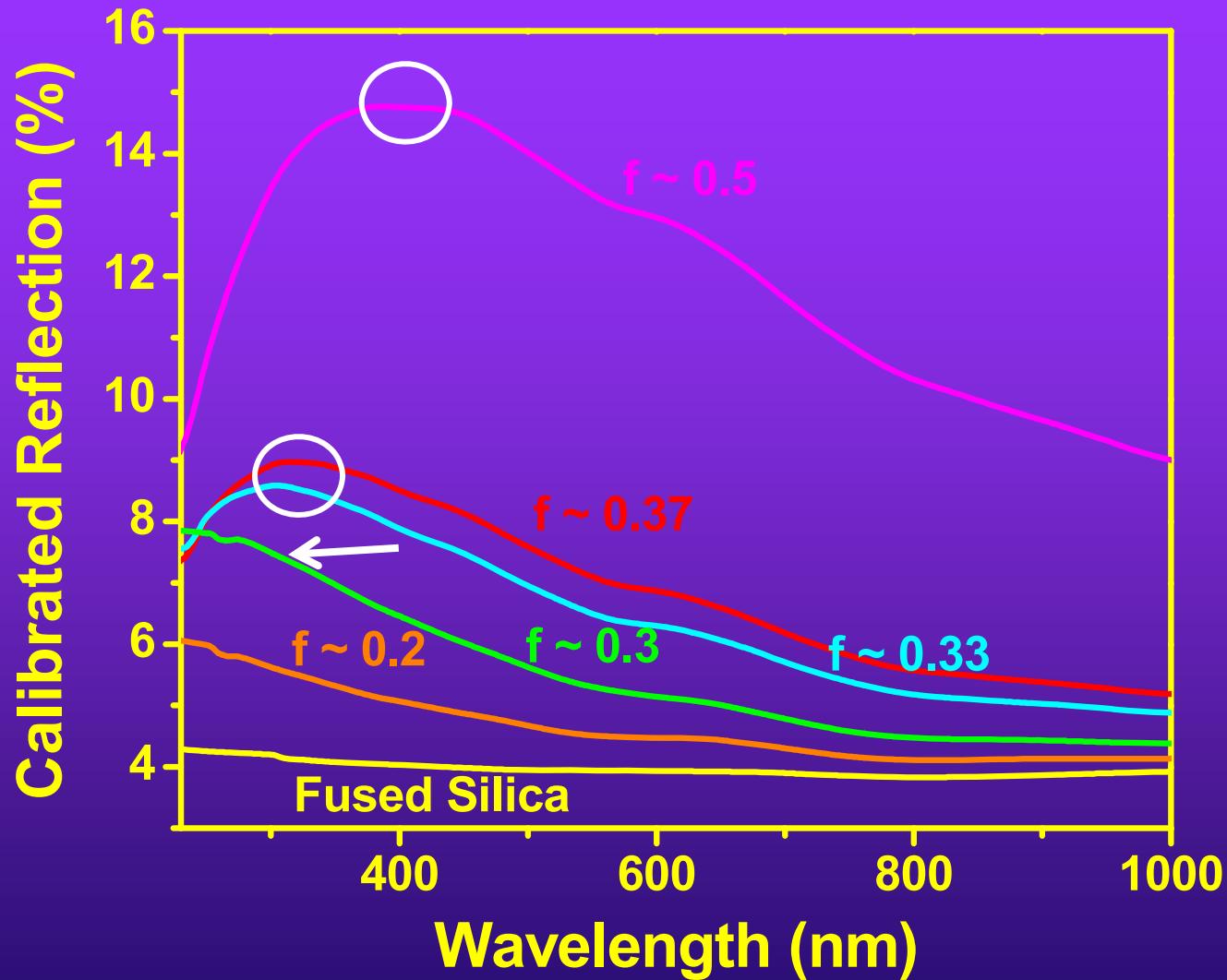


Oxide A:Pt System



**Metal-rich Nanoparticles
Irrelevant for Nanometallic Switching**

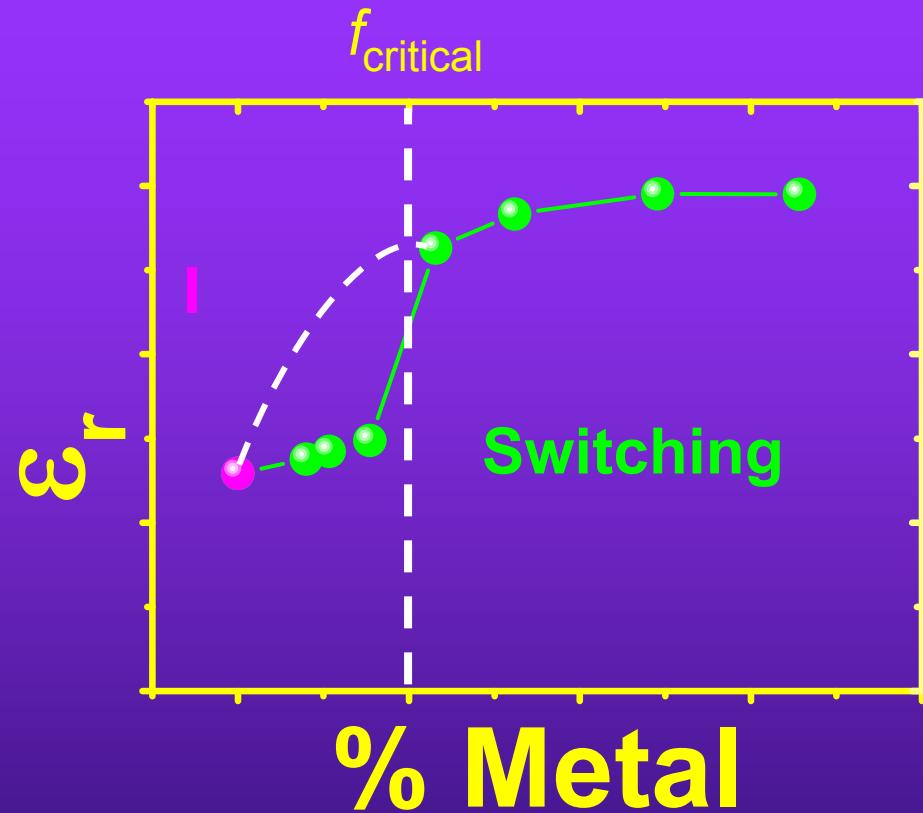
Metallic Nanoparticle? ($\text{SiO}_2:f\text{ Pt}$)



$f_{\text{Pt}} < 0.3$: No Metallic Nanoparticle

Plasmon Resonance: Signature of *Metallic* Nanoparticles

Capacitance (HR): SiN:Metal A



$$C = C_{\text{diel}} + C_{\text{met NP}}$$

$$C_{\text{met NP}} \sim n_{\text{met NP}} r_{\text{met NP}}^2$$

$$\% \sim n_{\text{met NP}} r_{\text{met NP}}^3$$

$$C_{\text{met NP}} \sim \% / r_{\text{met NP}}$$

$f_{\text{metal}} < f_{\text{critical}}$: No Metallic Nanoparticle

Reality Check



- Scaling: $x \text{ nm times } x \text{ nm}$
- Endurance: $>10^7$ cycles

Electronic Transition?



Fundamentally Different Features



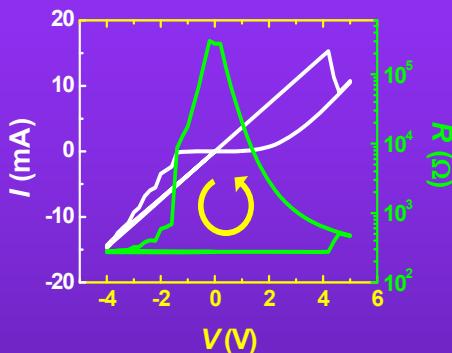
- T
- Initial State
- Electrode's Work Functions, ϕ_B
- UV
- R
- C
- Pulse Width, τ



Initial State

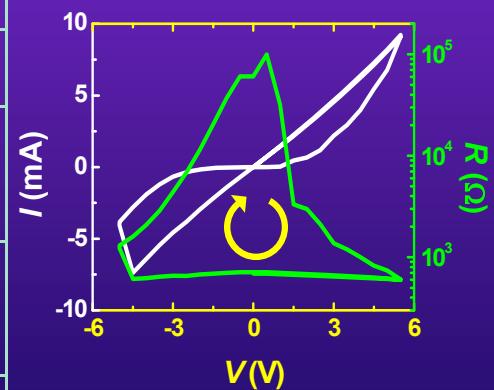
- No forming
- Initial state: metal
- High breakdown voltage >15 V

Top & Bottom Electrodes Must Be Different



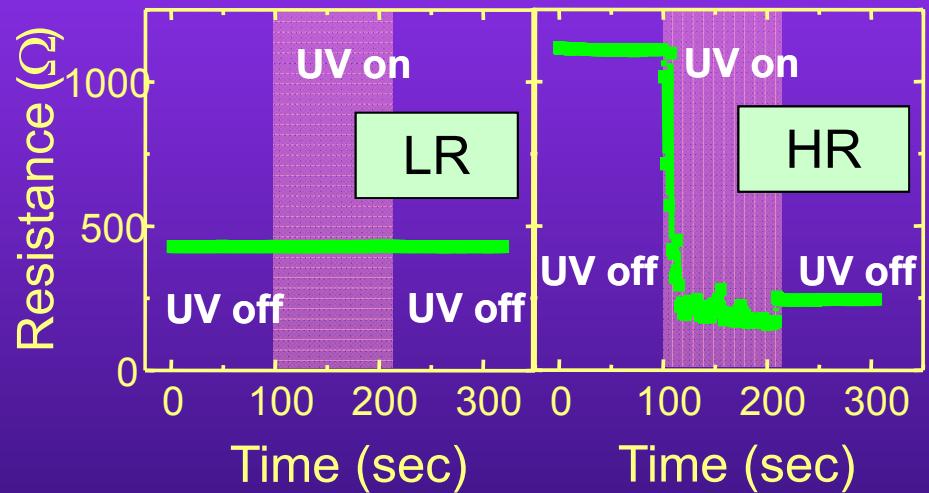
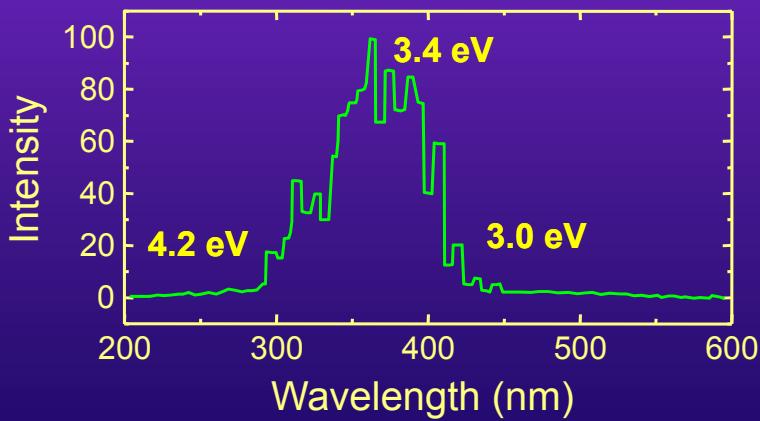
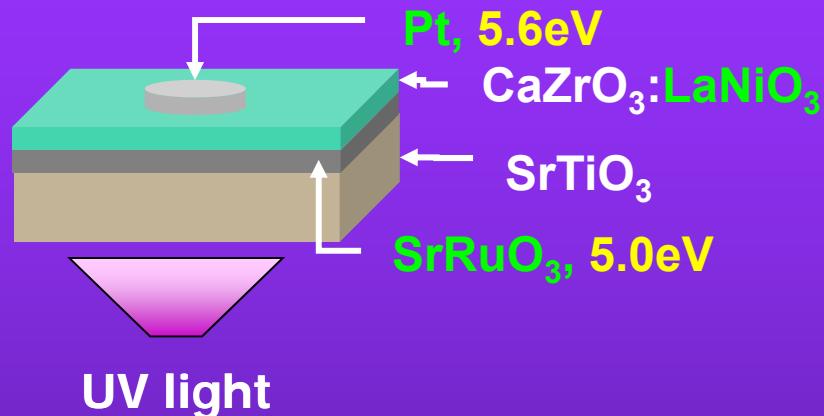
+ : Counter clockwise

	ϕ_{TE} (eV)	ϕ_{BE} (eV)	V_s Polarity
$\text{SiO}_2:\text{Pt}$	Pt 5.65	SRO 5.0	+
	Pt 5.65	Mo 4.6	+
	Mo 4.6	SRO 5.0	-
	Ag 4.26	Pt 5.65	-
	Pt 5.65	Ta 4.25	+
$\text{SiN}_{3/4}:\text{Pt}$	Pt 5.65	SRO 5.0	+
$\text{LaAlO}_3:$ LaNiO_3	Pt 5.65	SRO 5.0	+
	Au 5.10	SRO 5.0	+
	Ag 4.26	SRO 5.0	-
$\text{LaAlO}_3:$ SrRuO_3	Pt 5.65	SRO 5.0	+
	CaZrO ₃ :	SRO 5.0	+
LaNiO_3	Pt 5.65	SRO 5.0	+
CaZrO ₃ :	Pt 5.65	SRO 5.0	+
SrRuO_3			



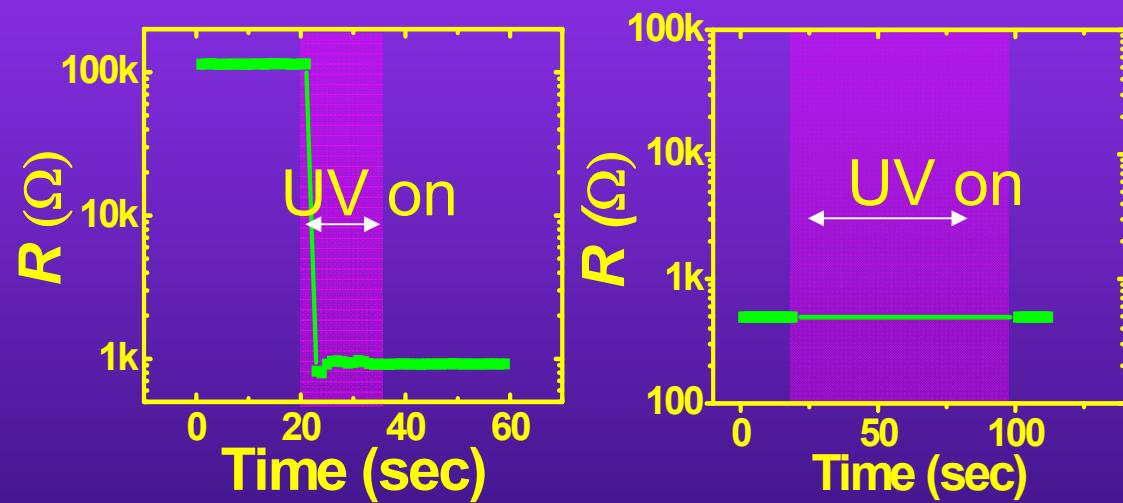
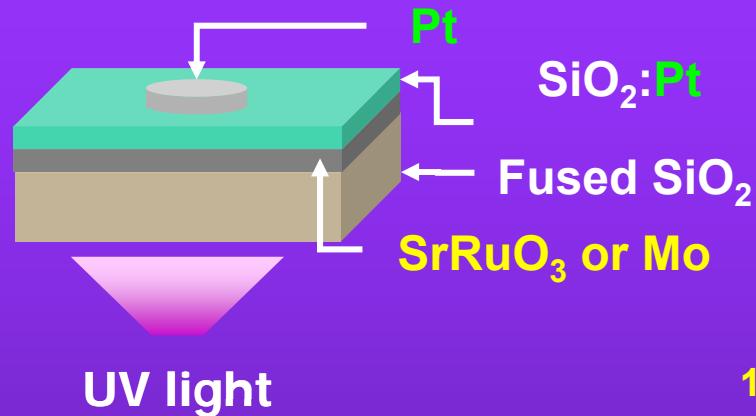
- : Clockwise

UV Resets Memory: Electronic



Not an ionic effect

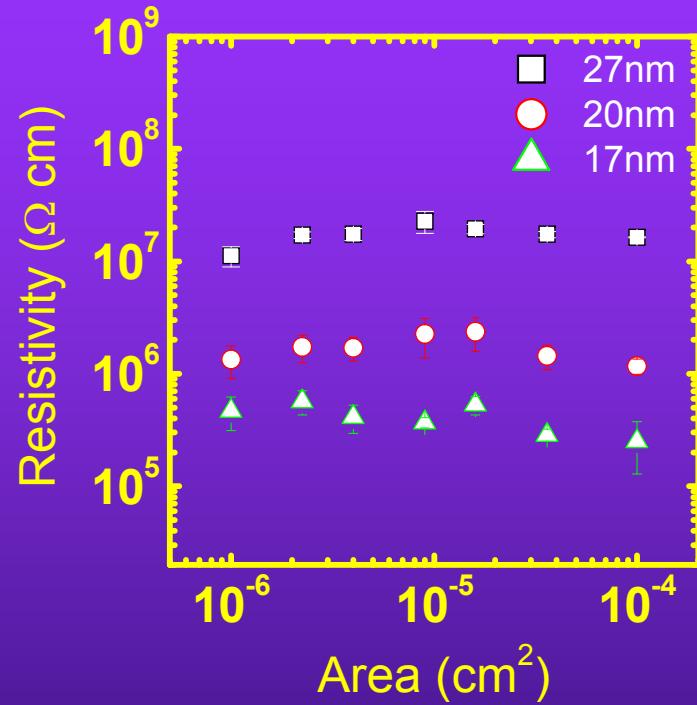
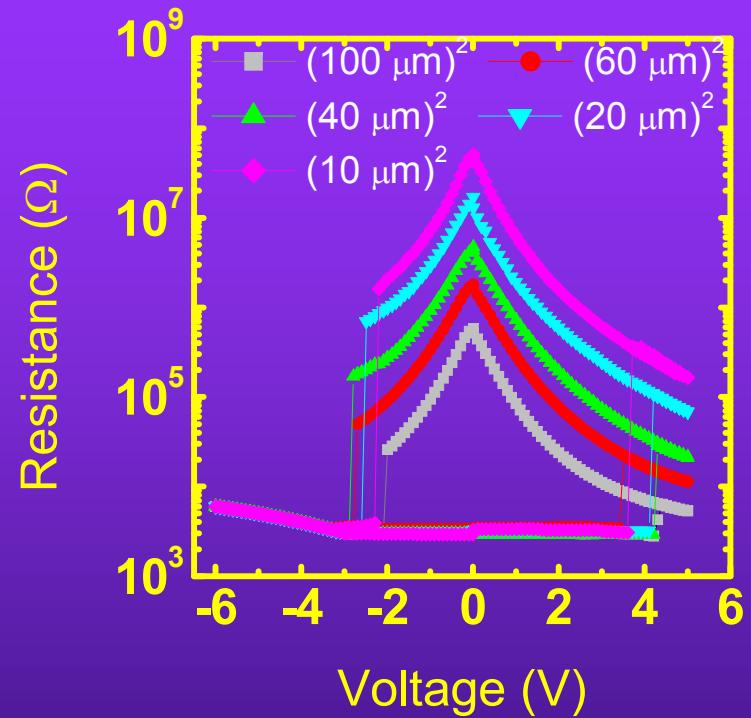
Electronic Transition: UV-triggered



Not an ionic effect



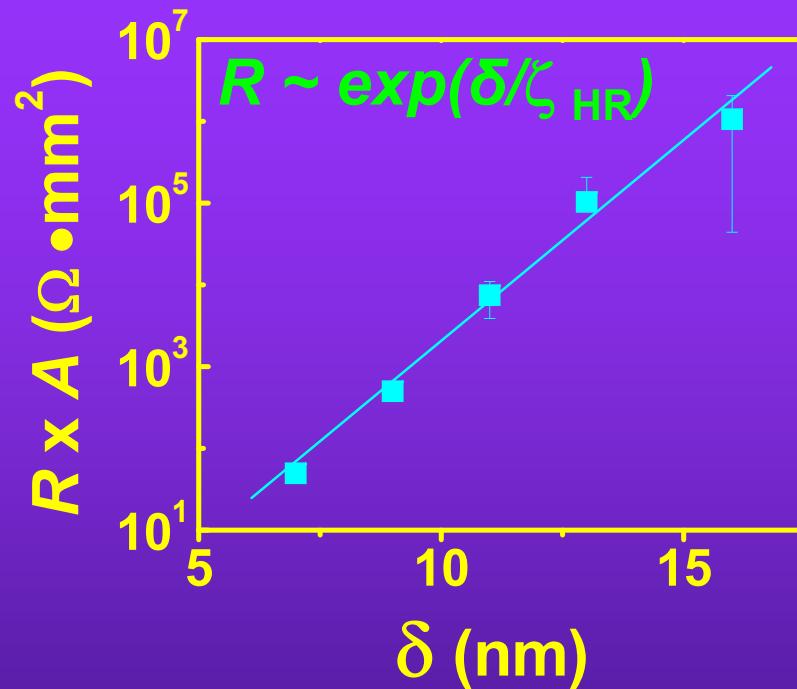
R_{HR} : A , δ Dependence



Obeys Ohm's law ($R_{HRS} \propto 1/A$)

Extreme thickness dependence!

Non-Ohmic Thickness Dependence



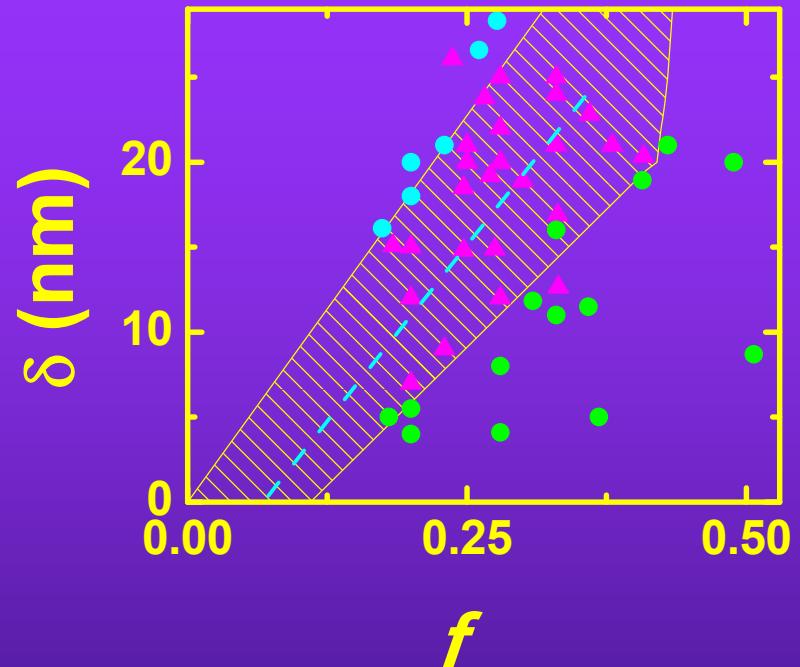
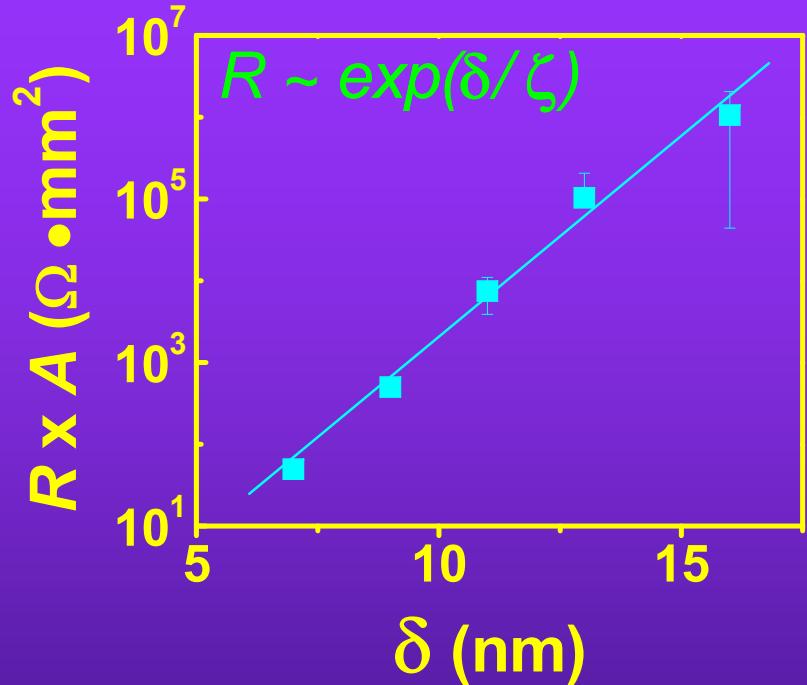
$\delta > \zeta$ (HR State)

Wave Function $\sim \exp(-\delta / \zeta_{\text{HR}})$

HR *Violates* Ohm's Law



ζ : Decreased by trapped charge



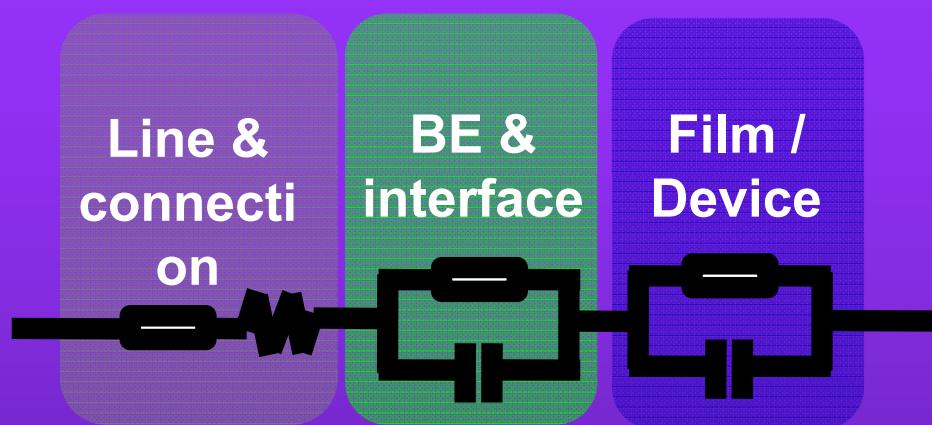
Diffusion length (ζ) : HR and LR

f	0.2	0.23	0.26	0.28	0.33
ζ_{HR} (nm)	1.1	1.7	2.1	2.5	2.8
ζ_{LR} (nm)	10.8	13.5	15.9	17.5	20.5

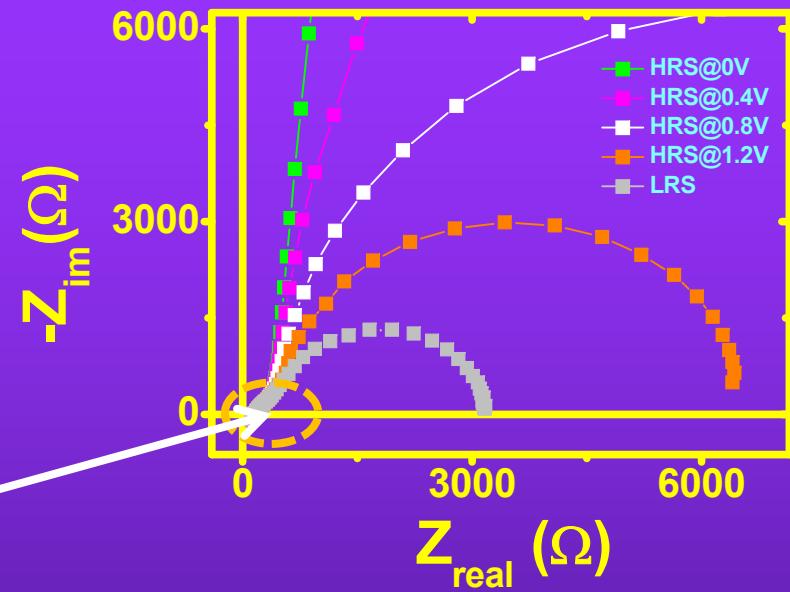
Symmetric Capacitance: Higher for HRS



Equivalent Circuit



Only at very
high ω



No Interface Barrier:
Symmetric $C(V)$

No Pulse Width τ Effect ($>RC$ time)



No Rate
Dependence:
Not A Memristor!

$\tau > RC$: Same switching voltage regardless of τ

$\tau < RC$: Increasing switching voltage at smaller τ

Same observations for HR-LR and LR-HR switching

$$RC \text{ Time} = R_{\text{Line}} C_{\text{Cell}} \sim \text{Cell Area}$$

Prediction: Same switching voltage
down to ps in sub- μm devices

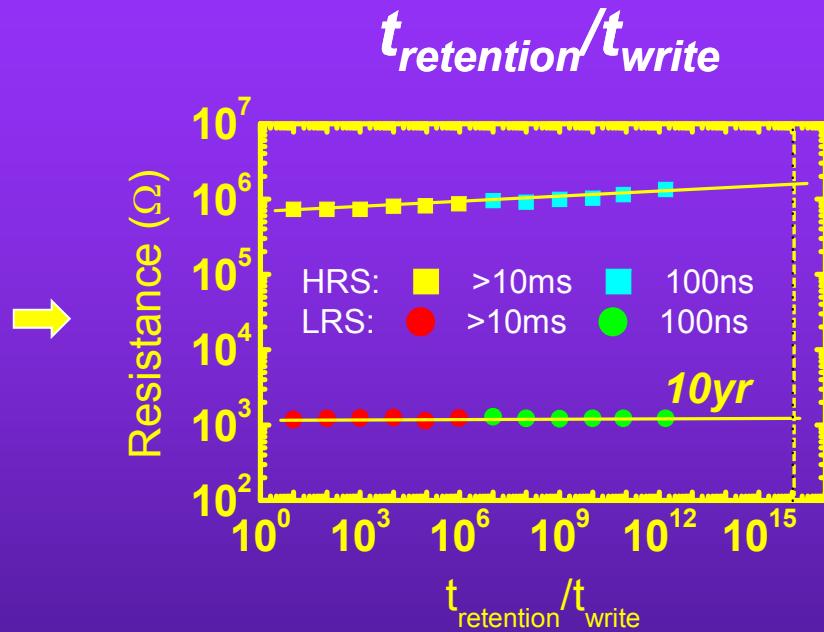
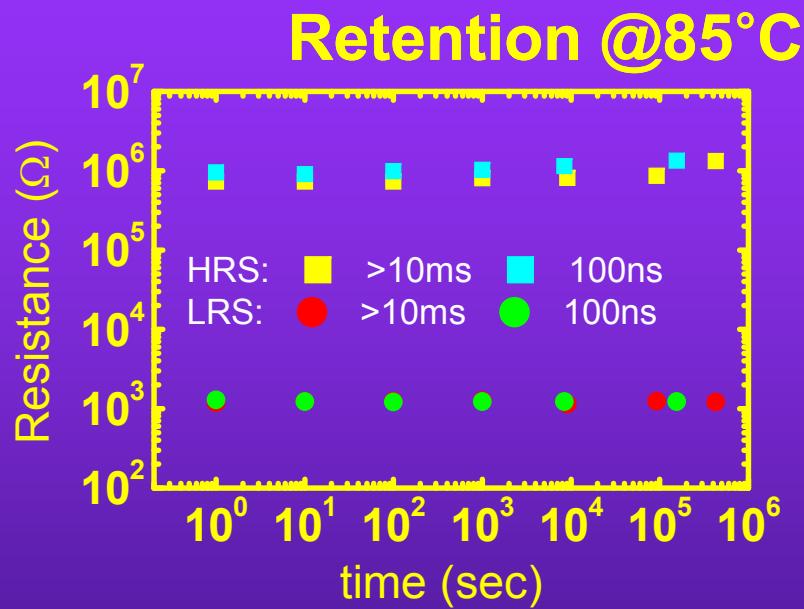
Device Performance



- Retention
- Variance



Memory Retention

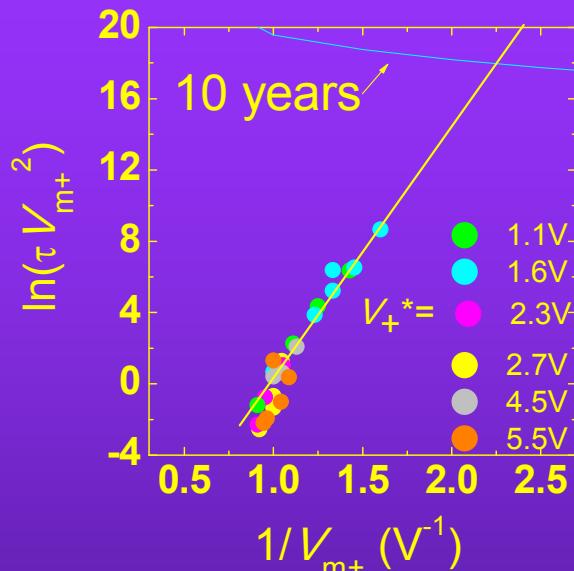
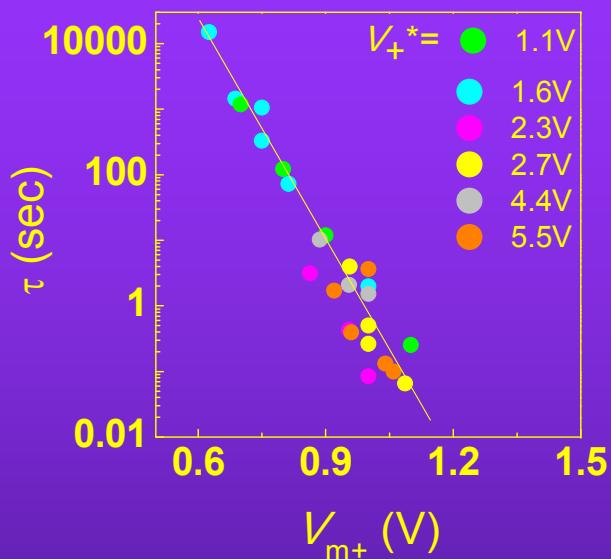


Good retention regardless of programming speed

Retention per Constant Voltage Stressing Test



LR to HR



Read @ < 0.4 V

>10 year data
retention

Fowler-Nordheim Tunneling over Barrier

$d: 1.5 \text{ nm} \sim 2.6 \text{ nm}$ thick

$$\frac{I}{V} = A V \exp(-\beta/V)$$

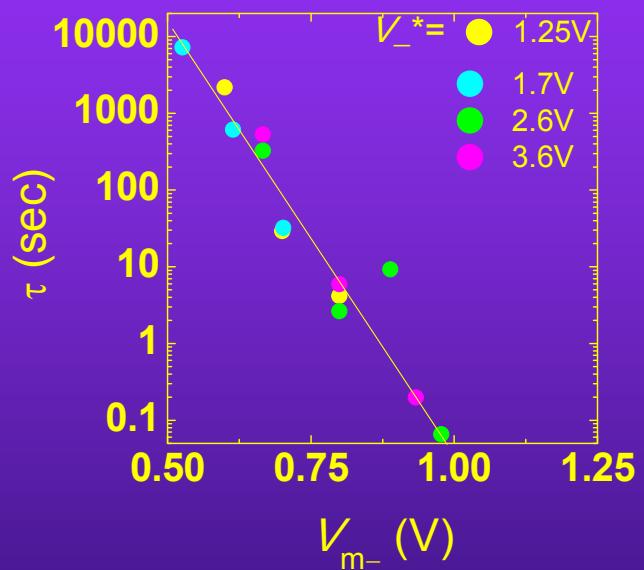
$$\ln(\tau V^2) = \ln \frac{Q}{A} + \frac{\beta}{V}$$

$$\beta = \frac{4(2m_{ox})^{1/2}d}{3e\hbar} \phi^{3/2}$$

Retention per Constant Voltage Stressing Test



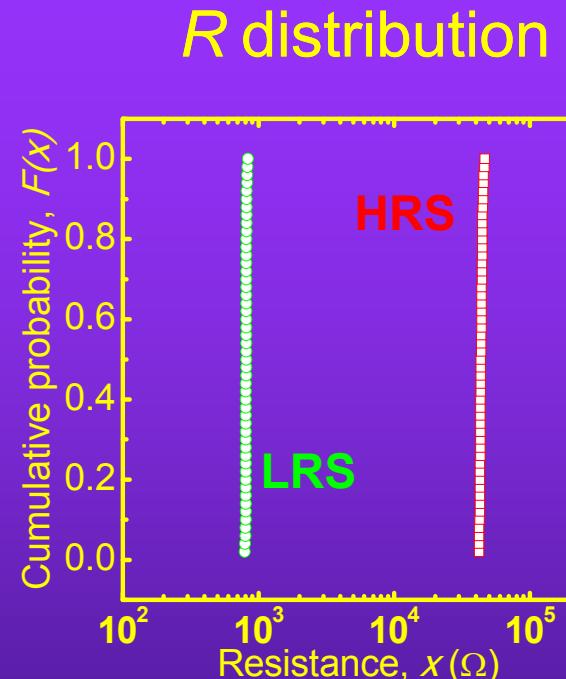
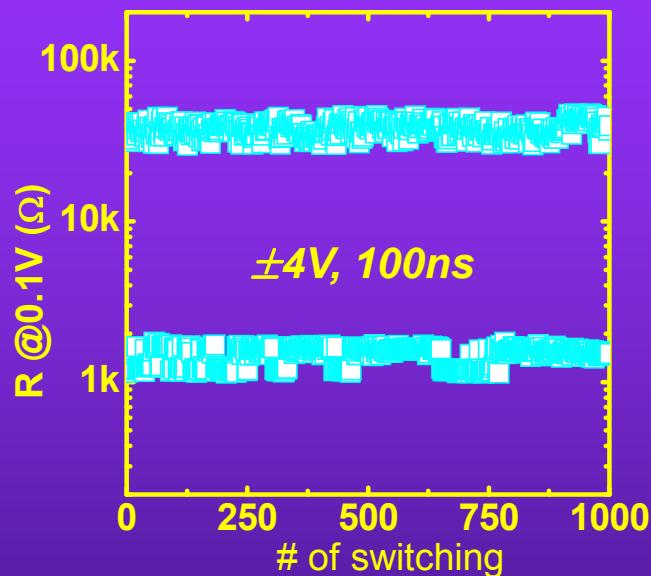
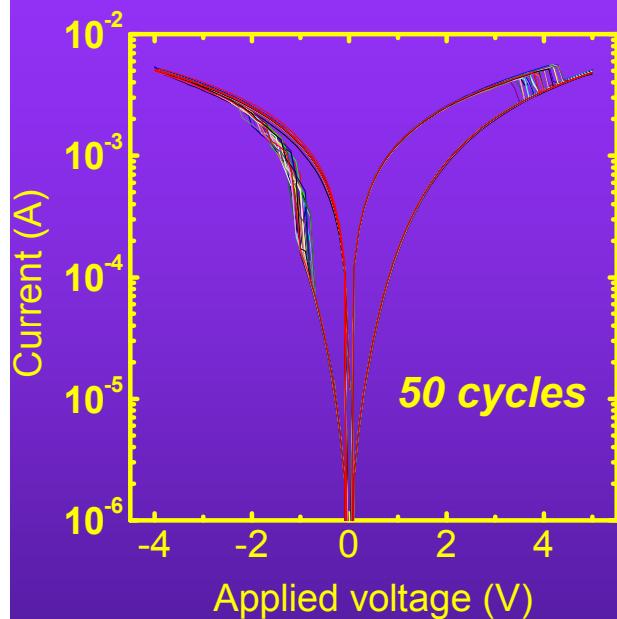
HR to LR



Read @ < 0.4 V
>10 year data
retention



Switching Uniformity



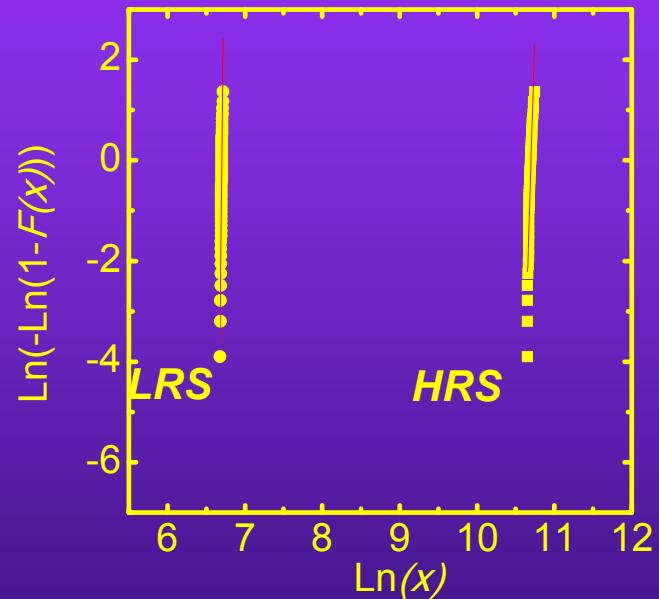
- Highly reproducible *on-off*
- Narrowly distributed resistance

Switching Uniformity: Weibull plot



Weibull plot (R) \rightarrow

$$F(x) = 1 - \exp(-(x/x_0)^k)$$



	k	Δ/μ
R_{HRS}	50	0.0233
R_{LRS}	145	0.0086
V_{off} (LRS \rightarrow HRS)	19.2	0.0602
$-V_{on}$ (HRS \rightarrow LRS)	9.8	0.1135

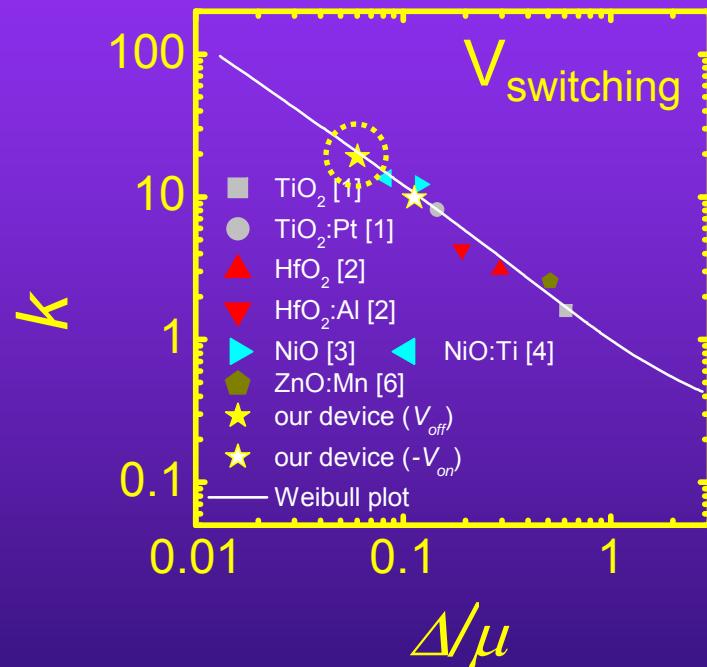
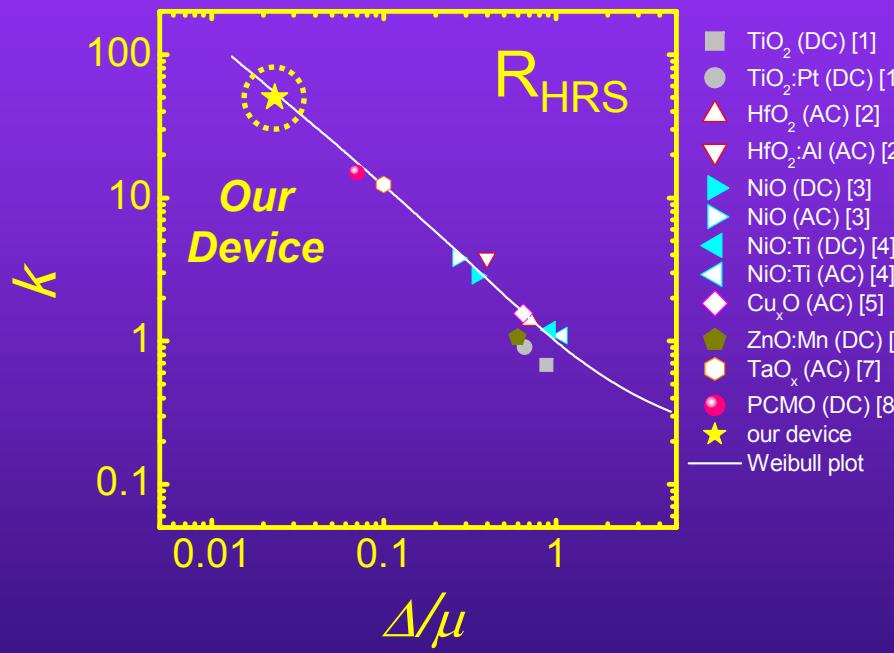
- Higher Weibull exponent k : more uniformity (lower Δ/μ)



Switching Uniformity: R_{HRS} & $V_{\text{switching}}$

Weibull distribution
(analytic relation)

$$\Delta / \mu = \frac{[\Gamma(1 + 2/k) - \Gamma^2(1 + 1/k)]^{1/2}}{\Gamma(1 + 1/k)}$$

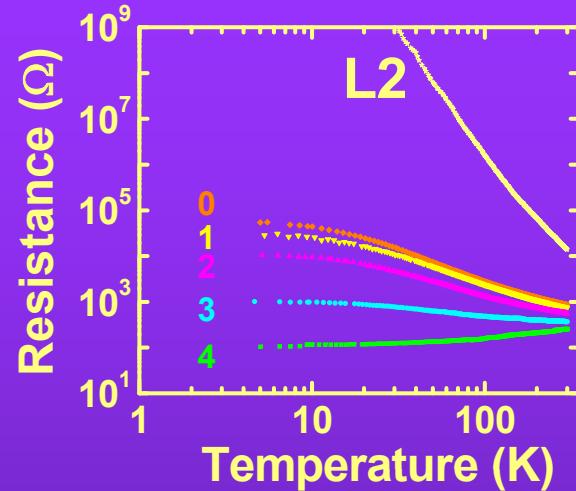
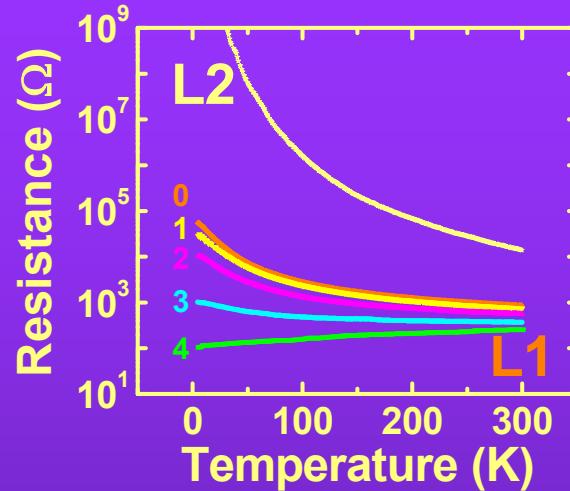
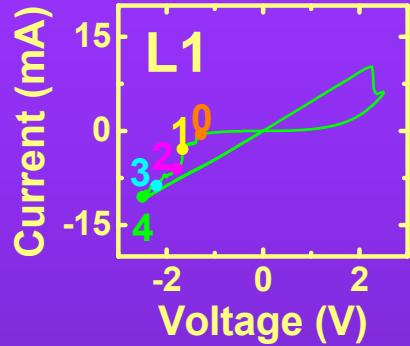


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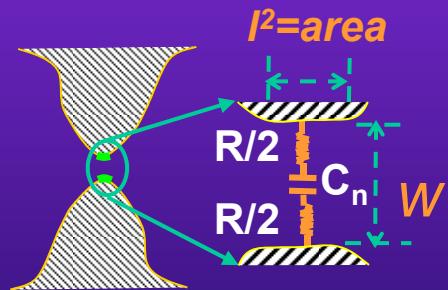
Intermediate States: Metals or Insulators?



Intermediate States – Insulator or Metal?

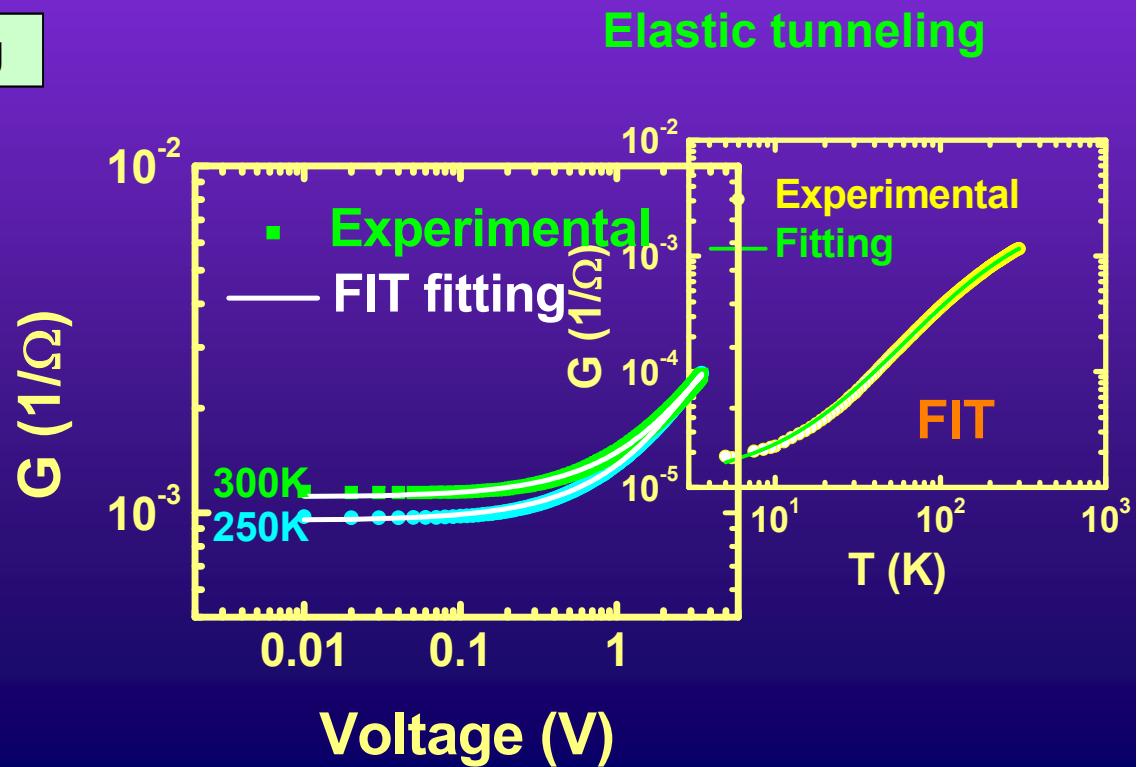


FIT: Fluctuation-induced Tunneling



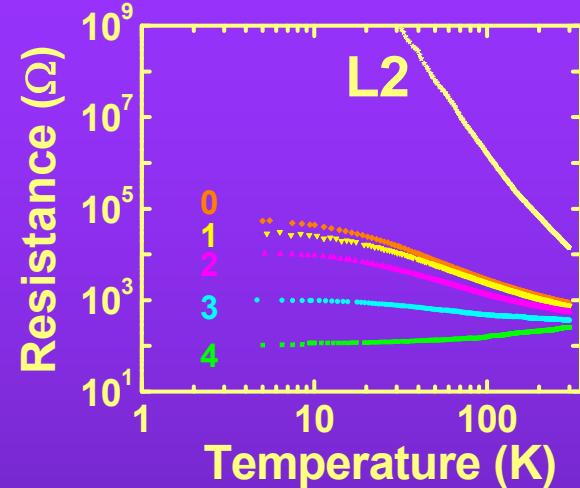
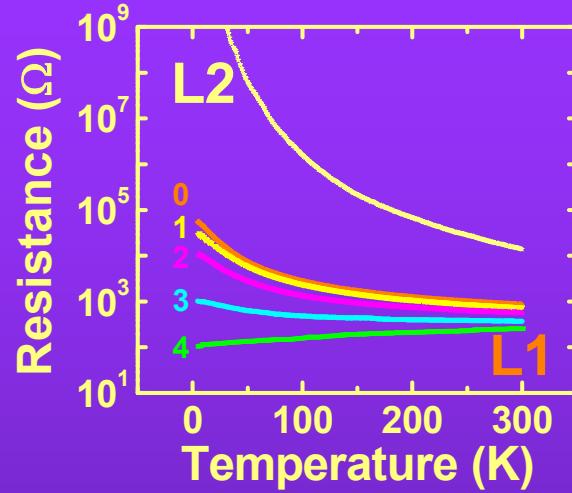
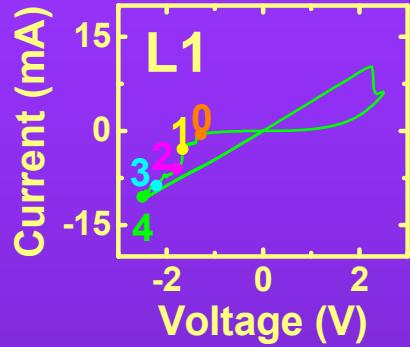
$$G_0(T) = G_0 \exp\left(-\frac{T_1}{T + T_0}\right)$$

$$G(V) = G_{0,T} \frac{\exp(V/V_0)}{1 + h_V [\exp(V/V_0) - 1]}$$



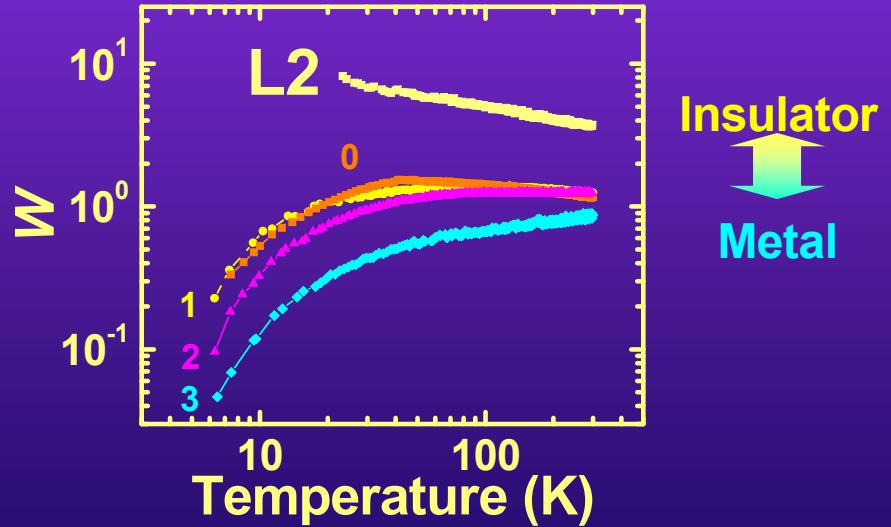
Elastic tunneling

Intermediate States – Insulator or Metal?



Reduced Activation Energy

$$W = -T \frac{d \ln \rho(T)}{dT}$$



- Multi-step on-switching: insulator->bad metal-metal transition
 - Multi-state ≠ Multi-filament



Nanometallic RRAM

*Size-dependent Nanometallicity
Metal Insulator Transition*

Random Materials

Purely *Electronic* Switching



Conclusions

- **Nanometallicty** : a size effect unique to random materials
- **MIT**: triggered via δ , f , V , & photon; switching due to changing localization length, direction controlled by electrode work function
- **Device properties**: highly reproducible switching parameters, short read/write time independent of voltage, long retention time, adjustable switching parameters
- **Nanostructure**: metallic nanoparticles irrelevant

Thank You