UNIVERSITÉ DE NANTES

INSTITUT DES MATERIAUX JEAN ROUXEL

IMN UMR CNRS 6502 - Université de Nantes



Resistive switching in Mott insulators: from phenomenology to Mott memories

J. Tranchant, E. Janod, B. Corraze, M.P. Besland, P. Stoliar, L. Cario

Institut des Materiaux Jean Rouxel, Nantes (France)

December 3rd 2014

Nanotek 2014 conference
San Francisco, USA

IMN INSTITUT DES MATÉRIAUX JEAN ROUXEL

What after Flash Memories ?

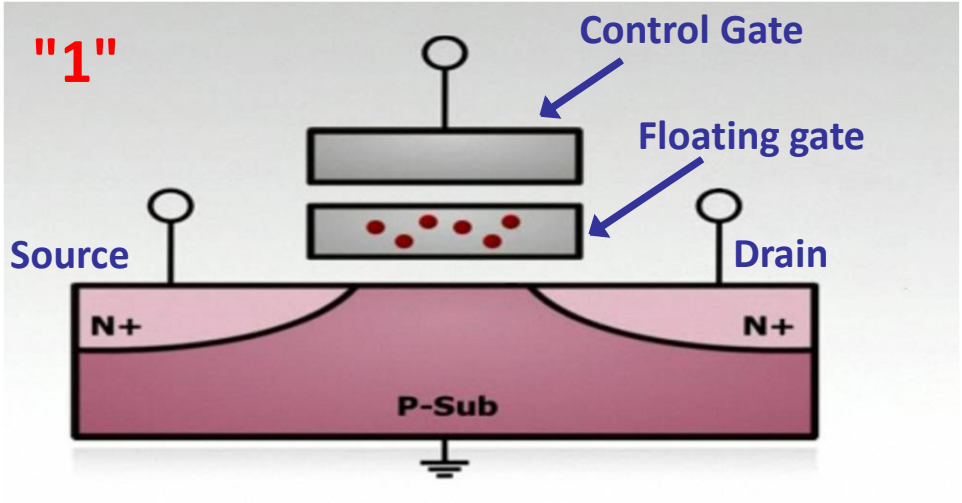








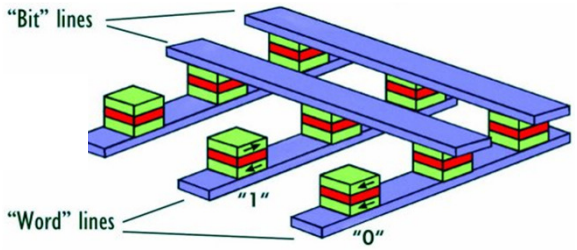
Flash memories : fantastic advances…

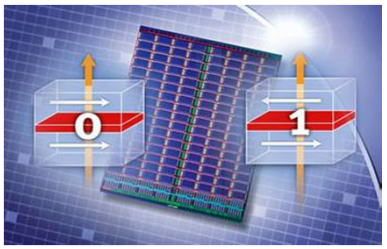


… but physical limits are close !

Some candidates to succeed Flash memories

➢ **Magnetic RAM (MRAM) ?**

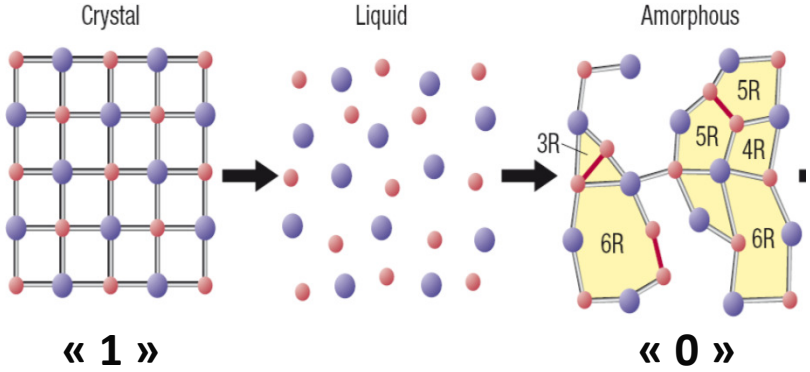




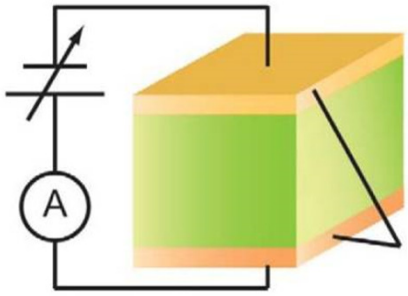
➢ **Phase-Change Memories (PCM) ?**

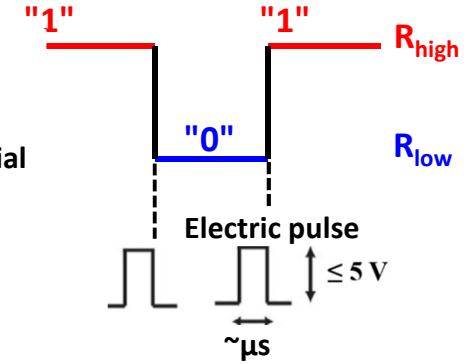
Phase transition between amorphous state(R_{high}) ⇔ crystalline (R_{low})

→ **Thermal mechanism**



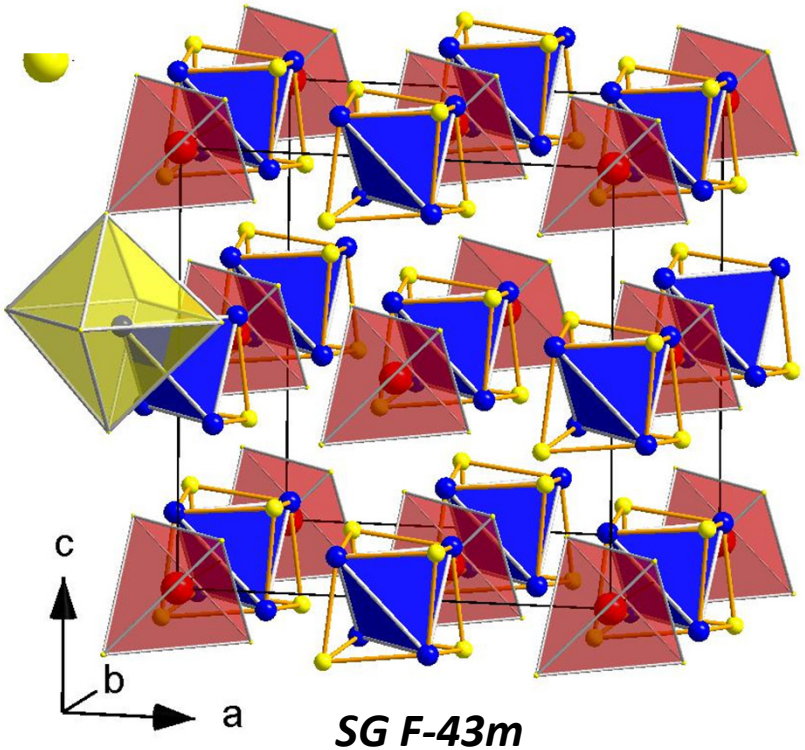
➢ **Resistive RAM (ReRAM) ?**



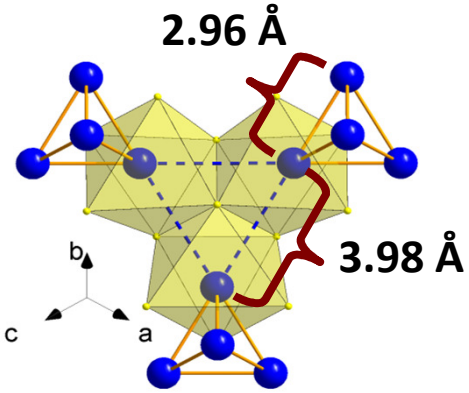


The Mott Insulator compounds AM_4Q_8

Clustered lacunar spinel structure :



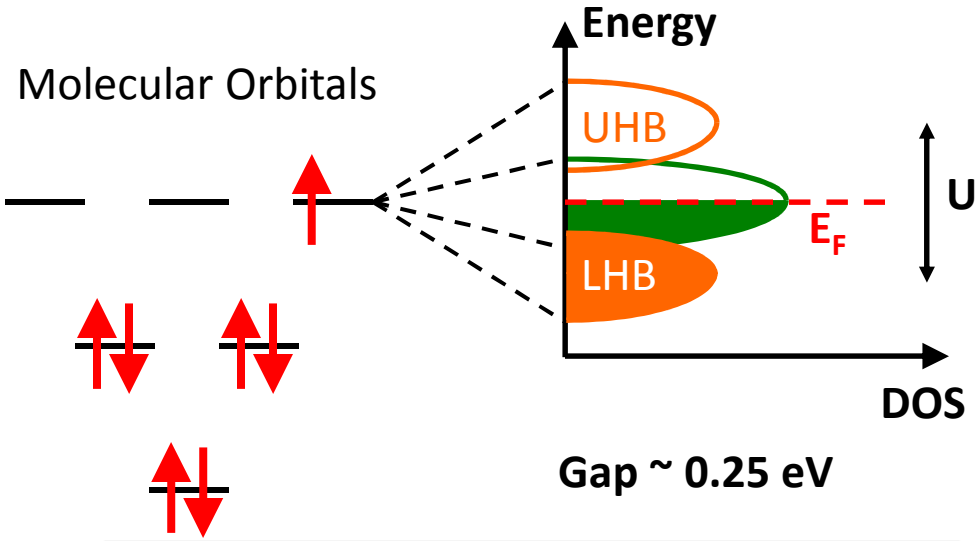
SG F-43m



Tetrahedral Clusters

(GaV_4S_8)

With coulombian repulsion U



Gap ~ 0.25 eV

A = Ga, Ge

M = V, Nb, Ta

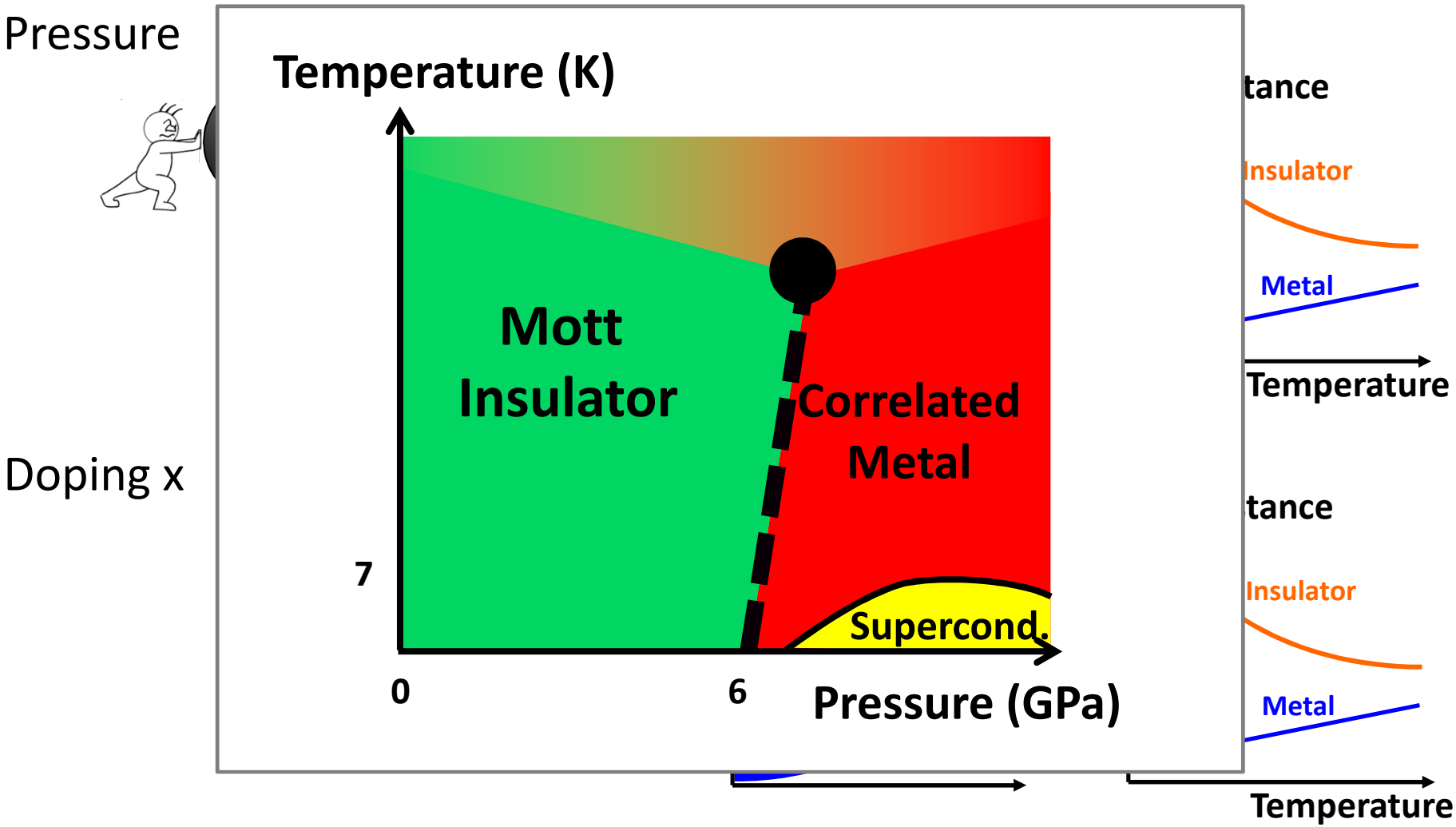
Q = S, Se

Ben Yaich, H.; Jegaden, J. C.; Potel, M.; Sergent, M.; Rastogi, A. K.;Tournier, R.
J. Less-Common Met. **1984**, *102*, 9.

AM_4Q_8 : Narrow Gap Mott Insulators

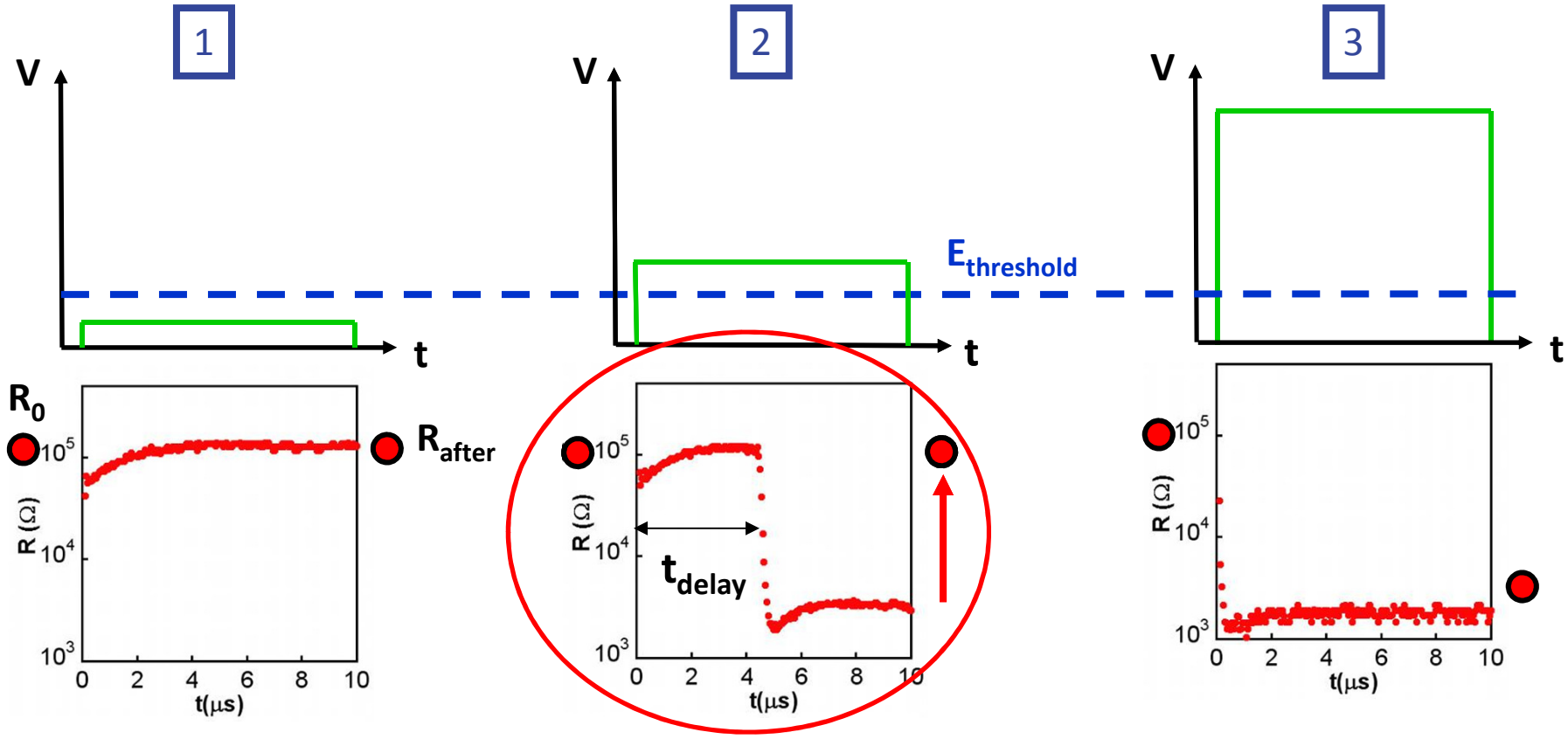
Pocha, R. et al., *J. Am. Chem. Soc.* **127**, *8732* (2005)

Bandwidth and filling control Insulator to Metal Transition



Exotic properties at the (Mott) insulator to metal transition

Resistive switching in AM_4Q_8



No transition

Volatile Resistive switching

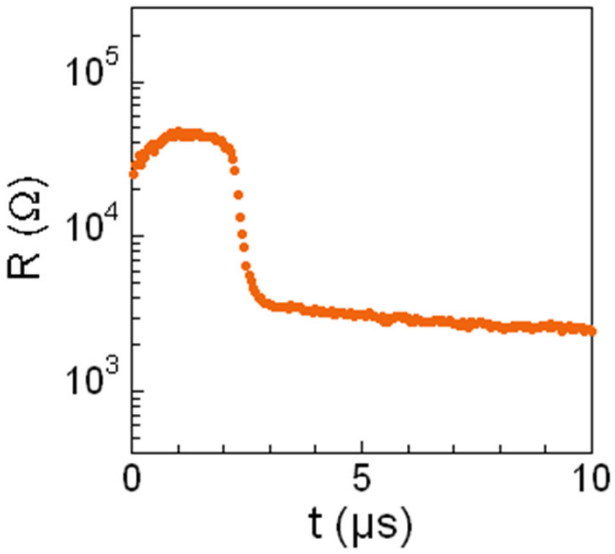
→ $E > E_{threshold} \cong 2.5$ kV/cm

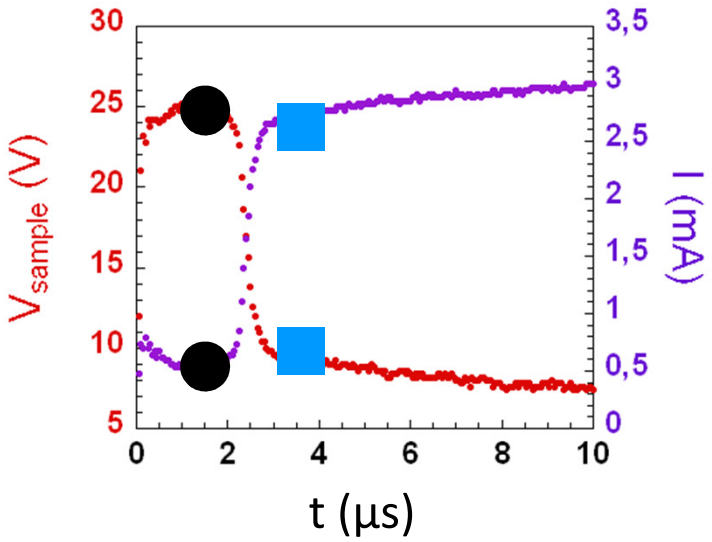
Non-volatile resistive switching

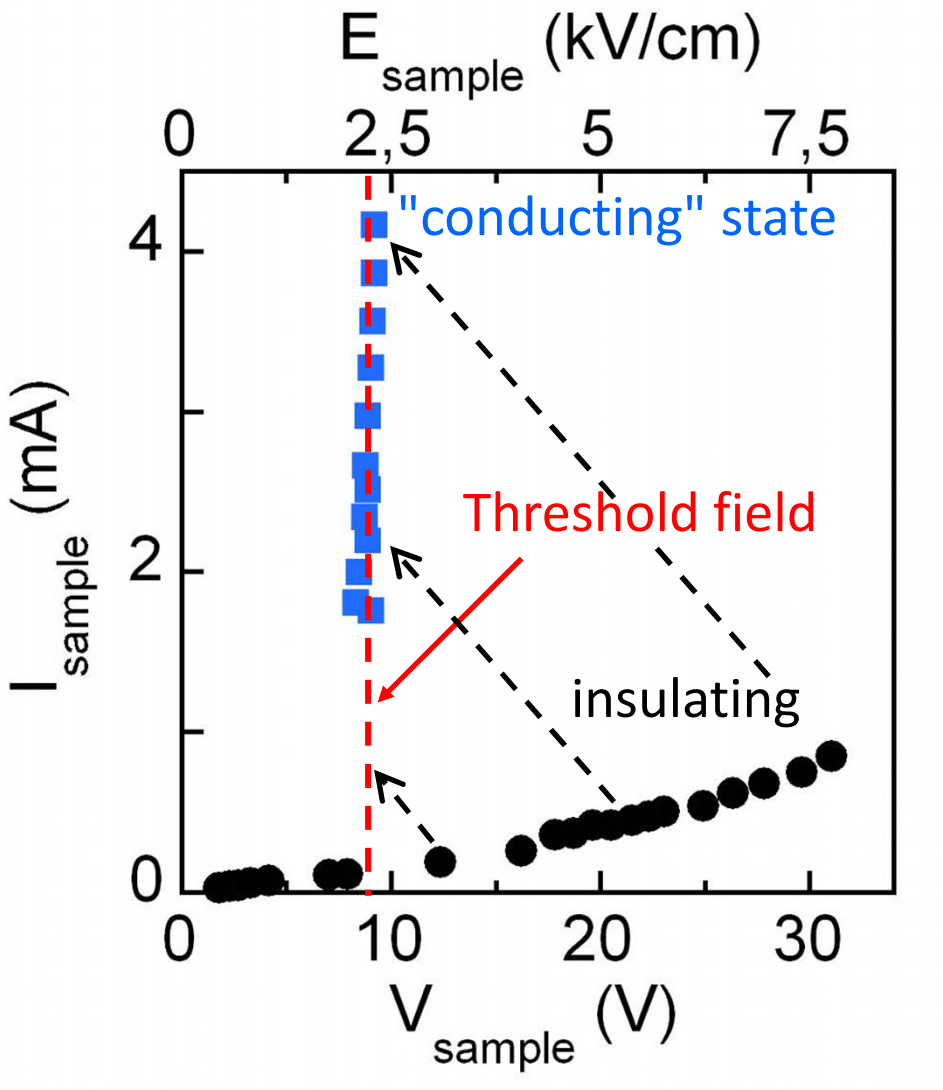
→ $E \cong 10$ kV/cm ($>> E_{threshold}$)

Evidence of a volatile resistive switching

Electric field triggered electronic transition



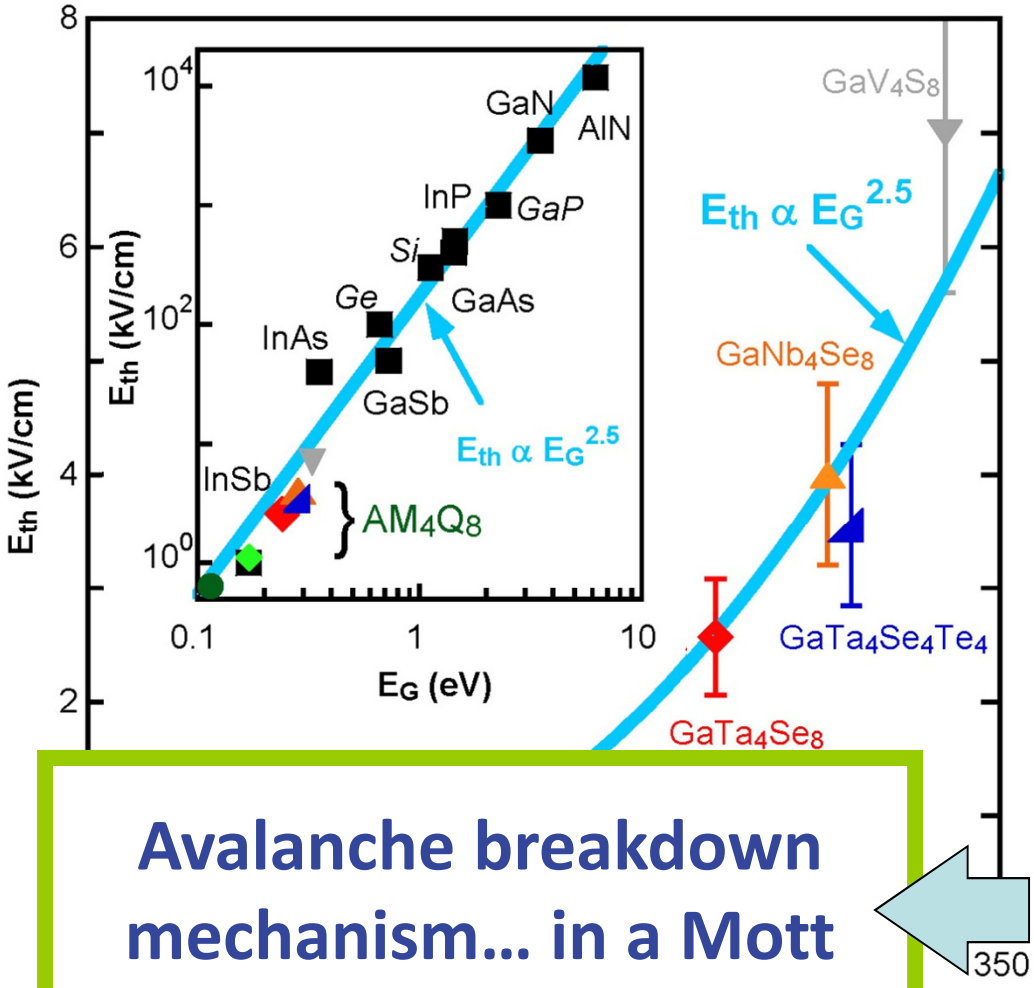


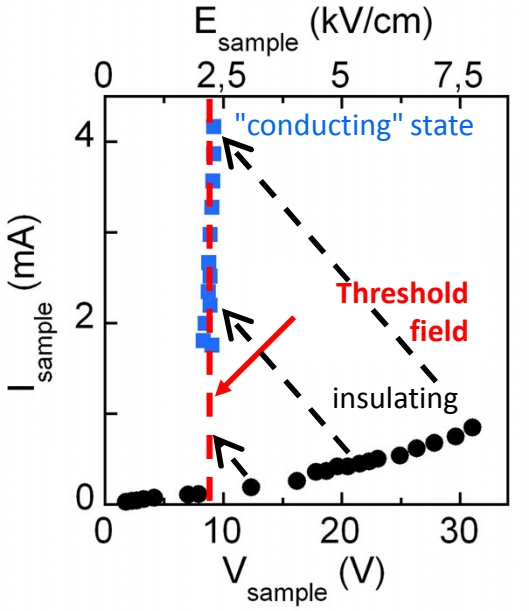


Electric field effect !

L. Cario *et al.,* Advanced Materials 22, 5193-5197 (2010)

Volatile resistive switching in AM_4Q_8





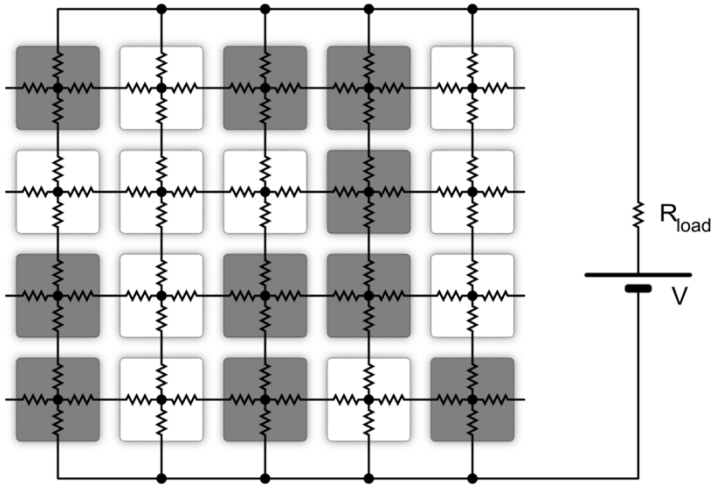
Avalanche breakdown mechanism… in a Mott insulator!

- **Resistive switching above** $E_{threshold}$ **(≈1-10 kV/cm)**
- $E_{threshold} \propto E_{gap}^{2.5}$
- **I(V) similar to InSb/Si/Ge…**

V. Guiot et al. Nature Communications (2013) DOI: 10.1038/ncomms2735

P. Stoliar *et al.* Adv. Mater. (2013) DOI: 10.1002/adma.201301113

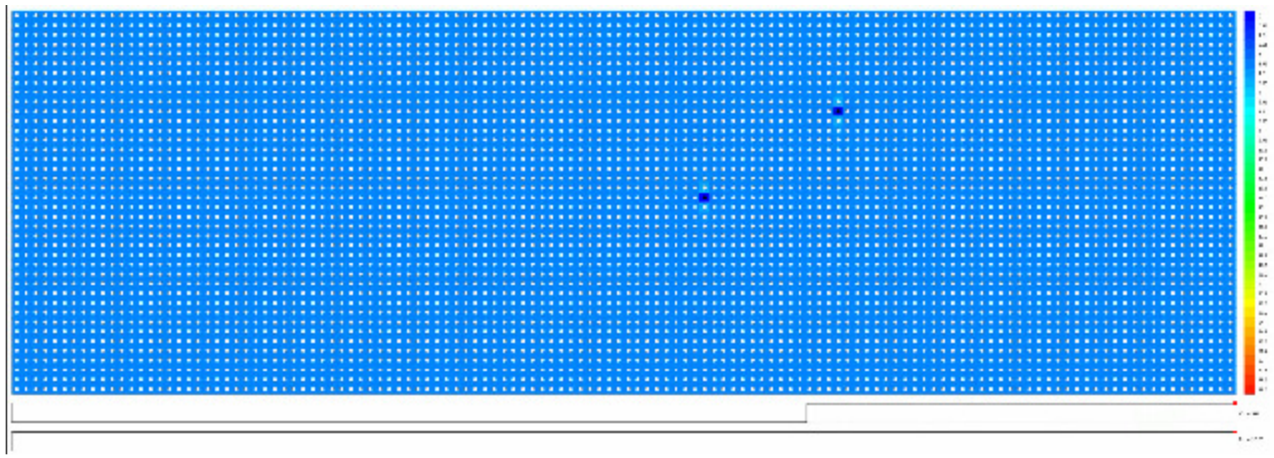
Modeling of the resistive switching: a simple assumption

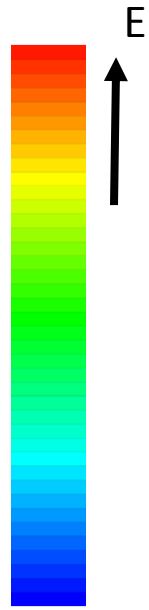


Local voltage drop destabilises the insulating cells

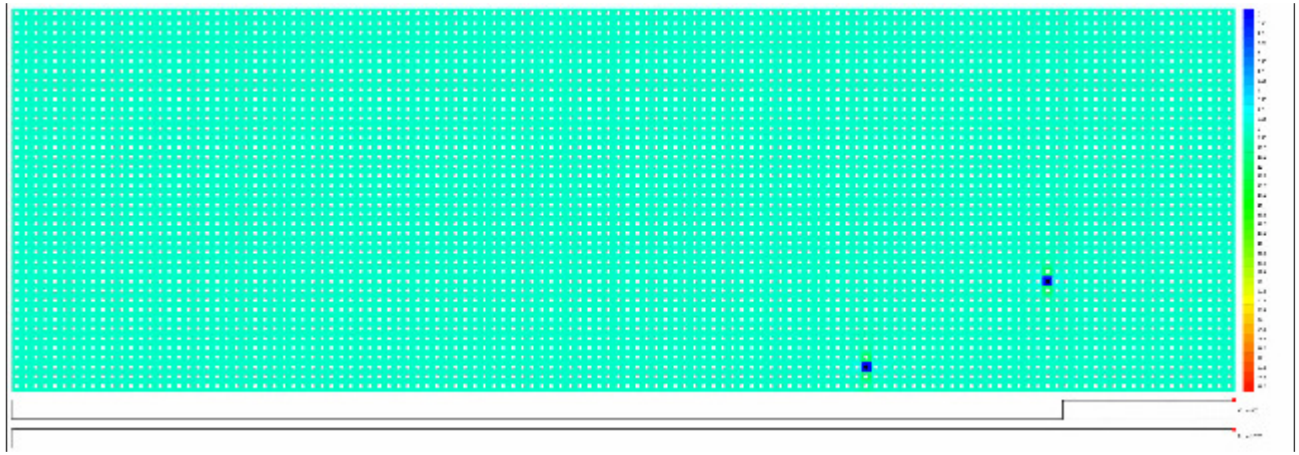
Time evolution of the resistor network

$V<V_{th}$



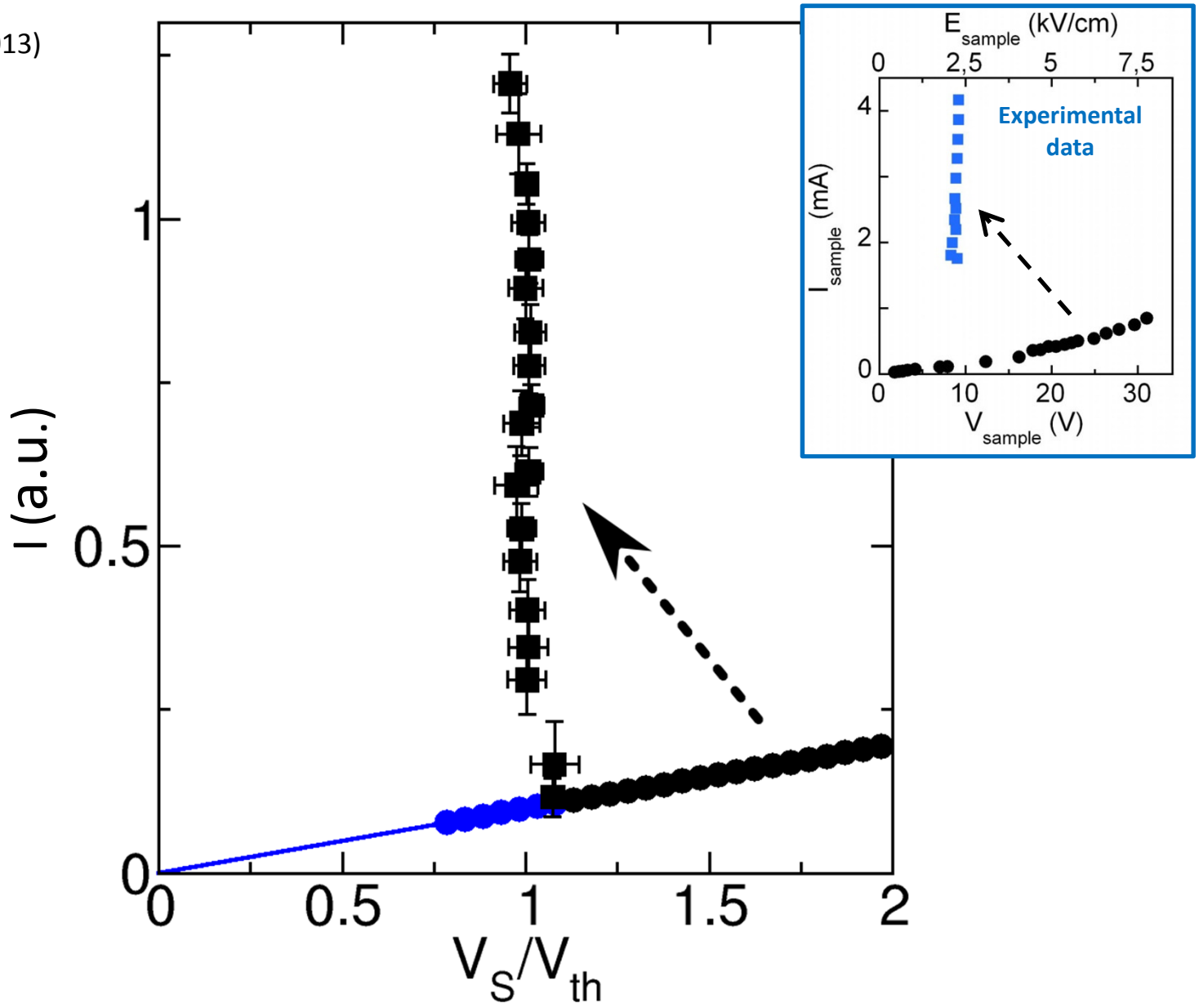


$V>V_{th}$



Modeling of the resistive switching

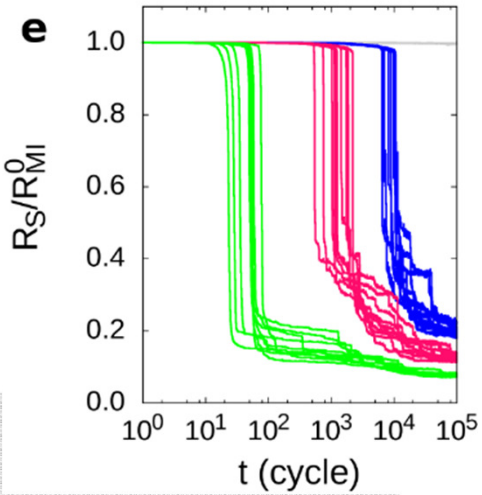
P. Stoliar *et al.*
Adv. Mater. 25, 3222 (2013)



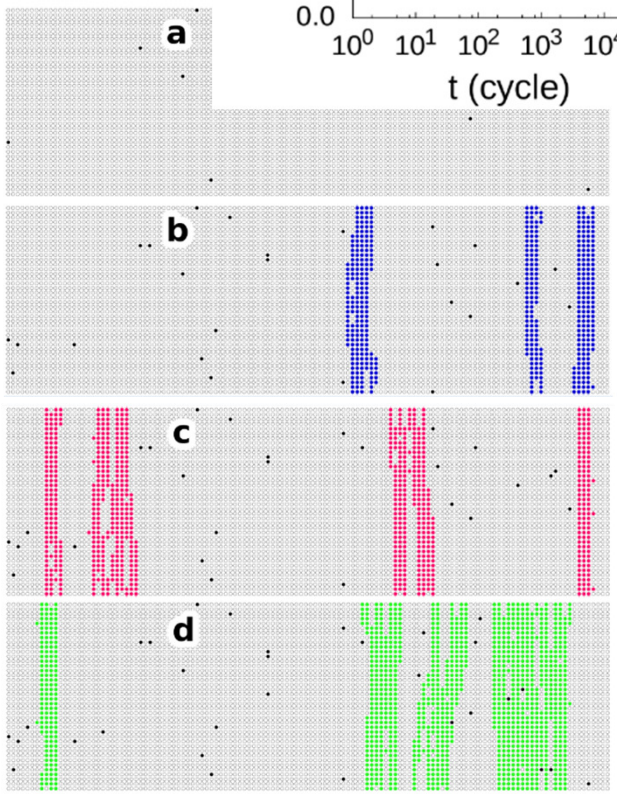
From volatile to non-volatile resistive switching

Model

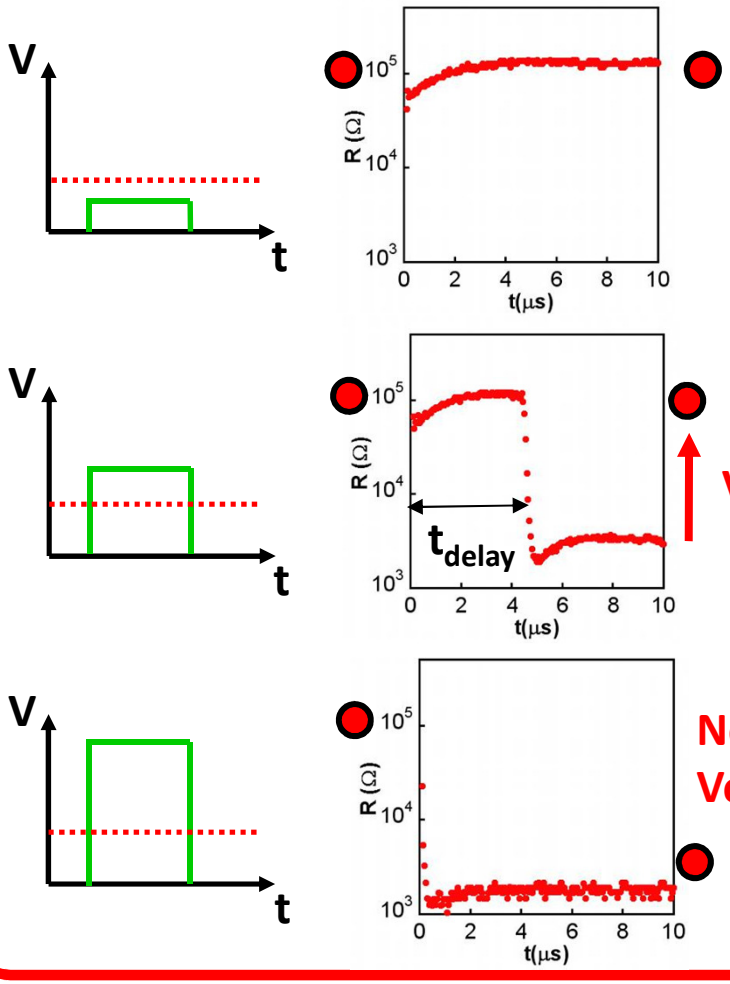
P. Stoliar *et al.*
Adv. Mater. **25**,
3222 (2013)



V_S / V_{th}=

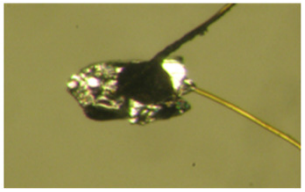


Experiments

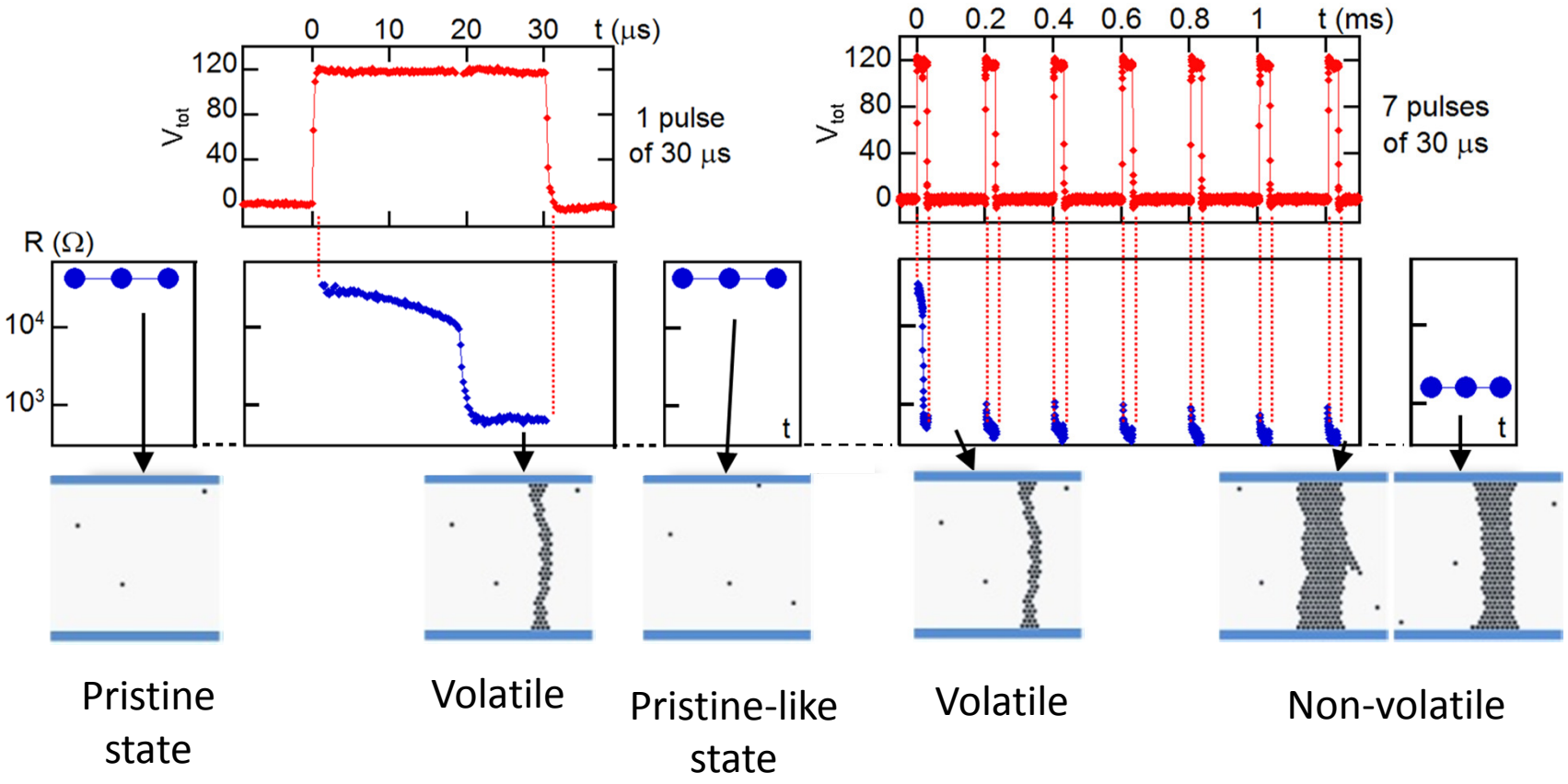


➔ Non Volatile for large metallic filaments ?

Control of SET and RESET transitions



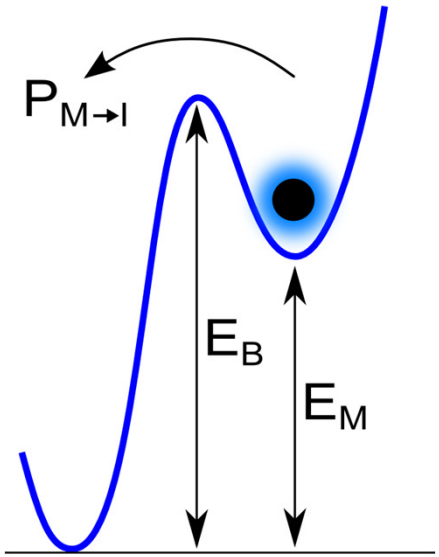
SET = Field assisted creation of large filaments

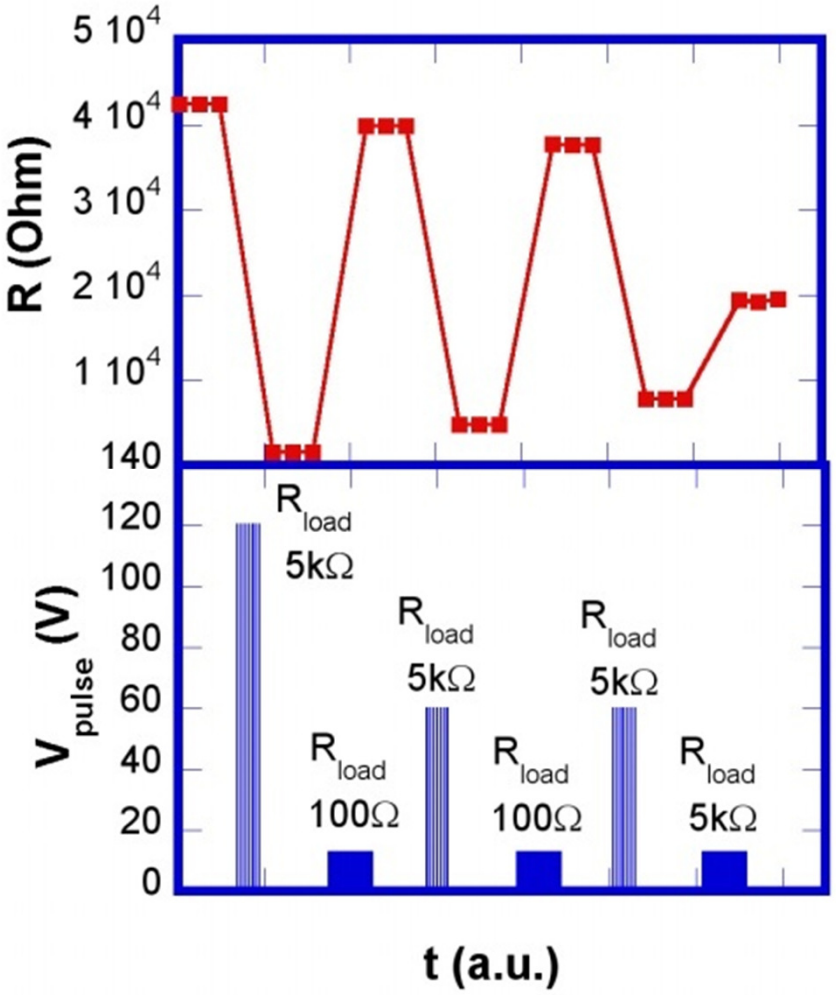


J. Tranchant *et al.,* Phys. Status Solidi A, DOI:10.1002/pssa.201400158 (2014)
E. Janod *et al.,* review to be published in Adv. Funct. Mater. (2015)

SET and RESET transitions

RESET = purely thermal effect



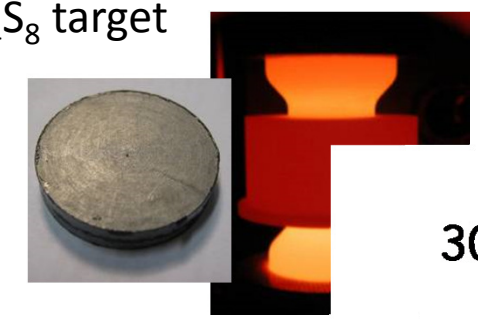


J. Tranchant *et al.,* Phys. Status Solidi A, DOI:10.1002/pssa.201400158 (2014)

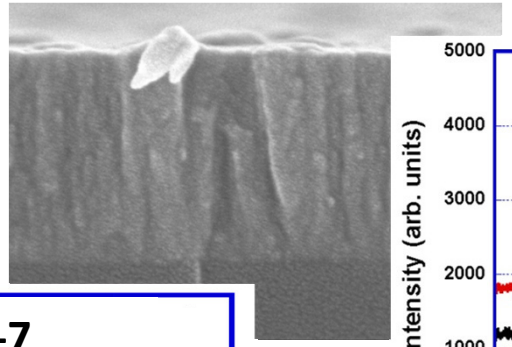
Towards multilevel switching and memristive behavior

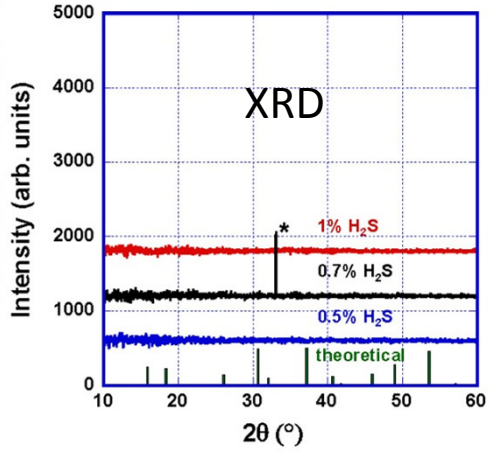
GaV_4S_8 thin films deposition

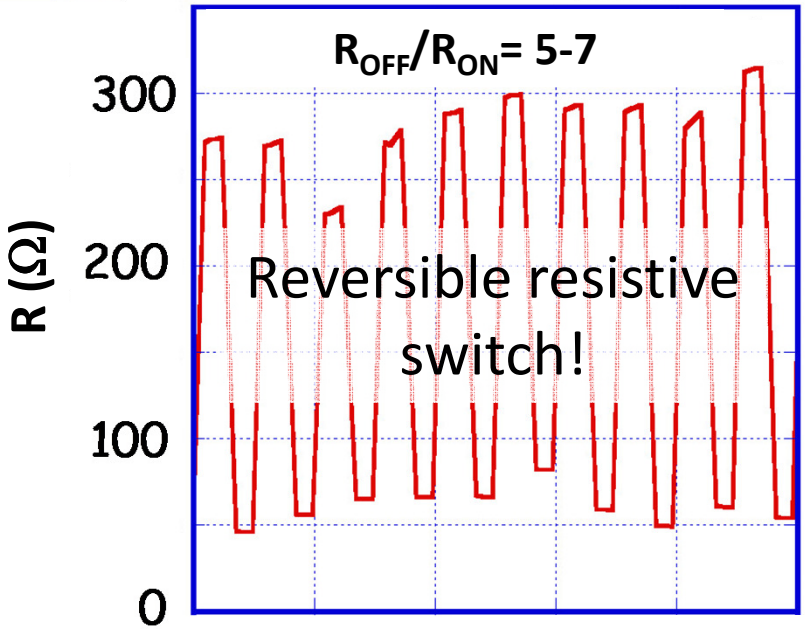
Spark Plasma Sintering of a home synthesized GaV_4S_8 target



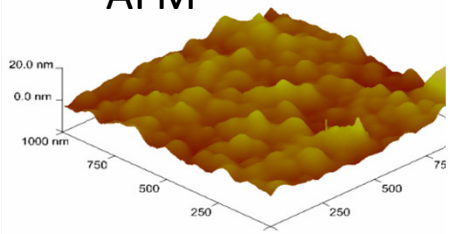
Ar/H_2S reactive sputtering







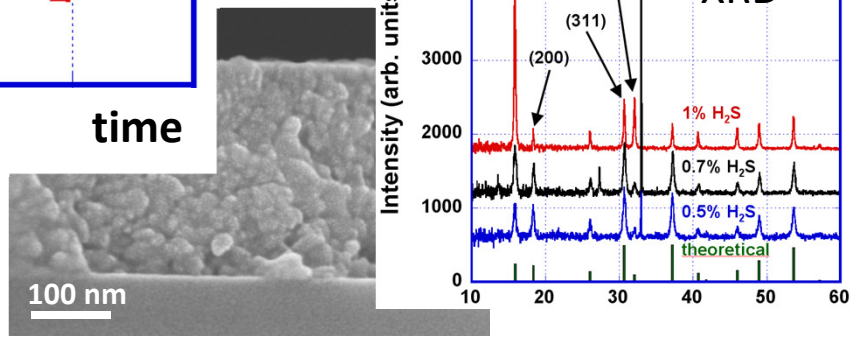
AFM



RMS roughness = 3 nm

Average grain size = 30 nm

annealing 450-600°C



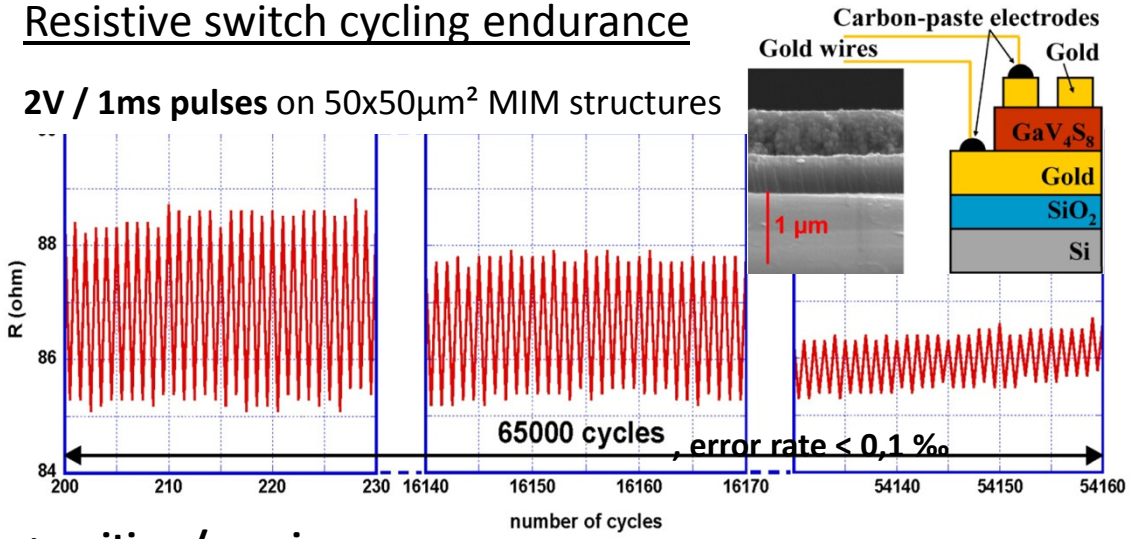
J. Tranchant *et al.*, J. Phys. D: Appl. Phys. **47,** 065309 (2014)

Polycrystalline GaV_4S_8 thin films

Electrical performances of GaV4S8 for Mott memories

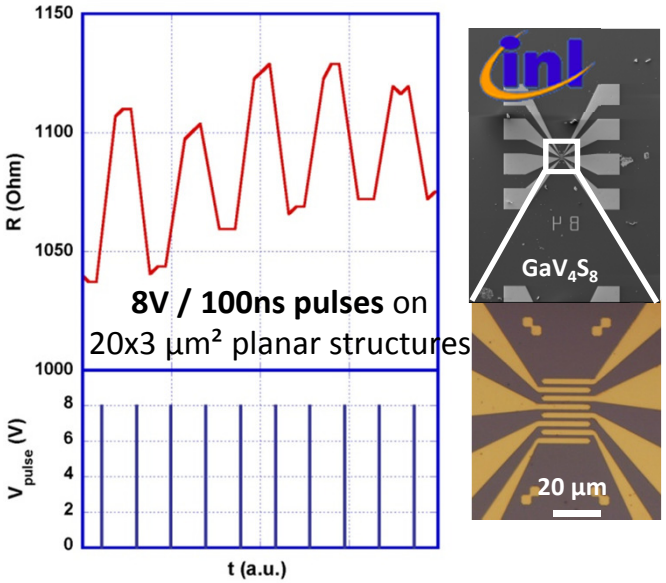
Resistive switch cycling endurance

2V / 1ms pulses on 50x50µm² MIM structures

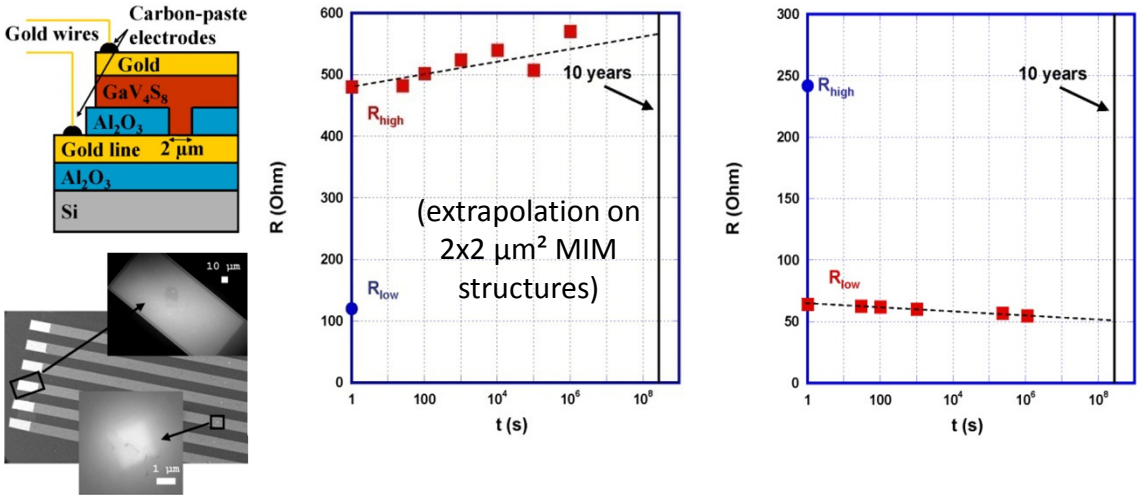


+ writing / erasing voltage ≤ 2V

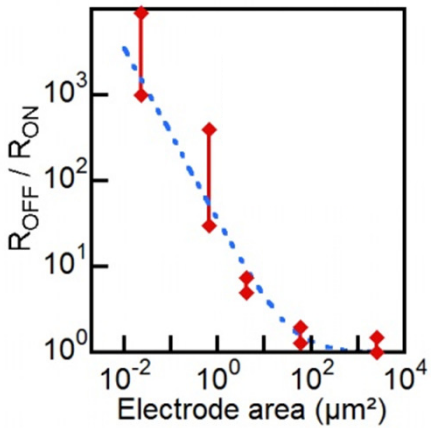
Writing / erasing times ≤ 100 ns



Data retention : high and low resistance states > 10 years



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

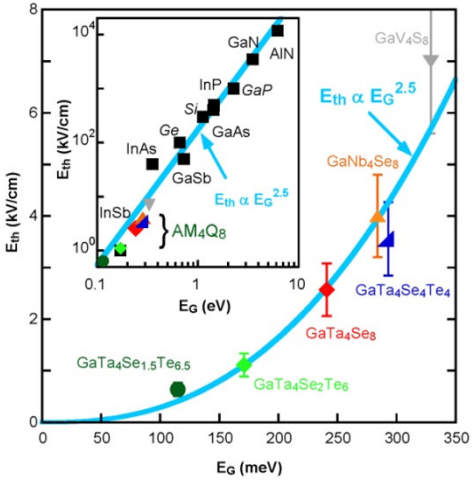


J. Tranchant et al. Thin Solid Films, 533 (2013) 61

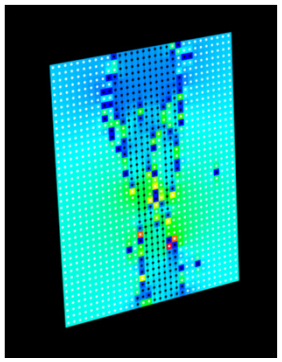
Conclusion

Resistive Switching in the AM_4Q_8 Mott Insulators

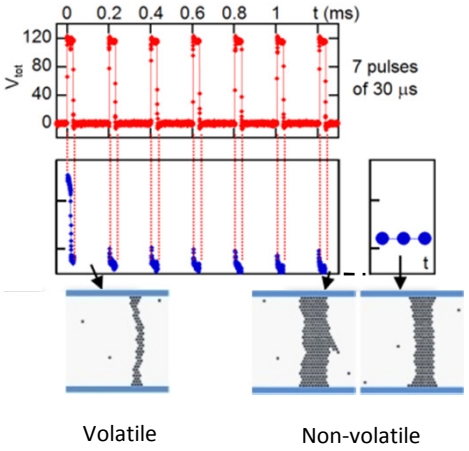
Electric field triggered avalanche phenomena



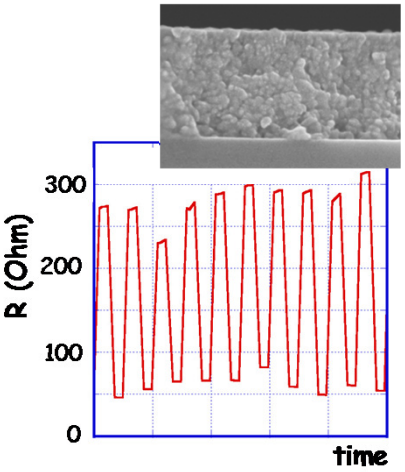
Filamentary paths



Non Volatile RS



Promising memory performances of thin films



ITRS

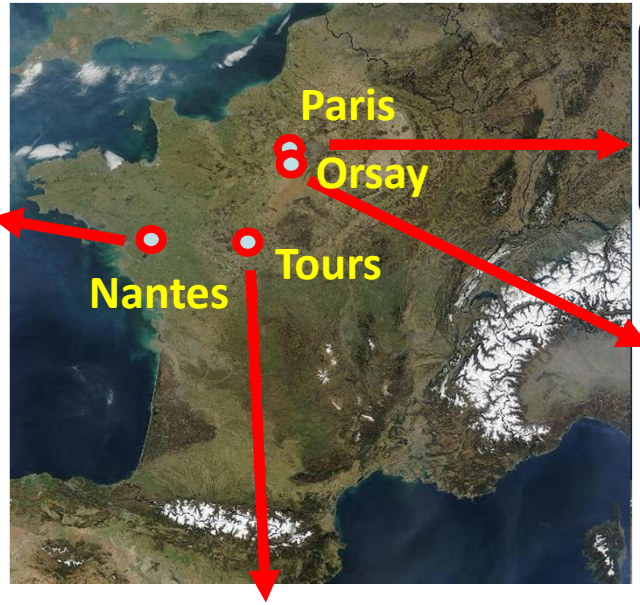
2011/13 Emerging Research Devices

A new type of Mott Memory !

Acknowledgments

INSTITUT des MATÉRIAUX JEAN ROUXEL
IMN
Physique Chimie et Génie des Matériaux

V. Guiot, C.Vaju,
E. Souchier, J. Martial
S. Salmon, J. Tranchant,
P. Moreau, L. Lajaunie,
M.P. Besland, B. Corraze,
E. Janod, L. Cario



IMPMC
Institut des NanoSciences de Paris
V. Dubost, F. Debontridder, T. Cren, D. Roditchev

LPS ORSAY
P. Stoliar, V. Bouet, M. Rozenberg

ICR Rennes
S. Cordier, M.G. Viry

UBA
C.Acha

GREMAN
matériaux microélectronique acoustique nanotechnologies
UMR 7347 - Université de Tours / CNRS
V. Ta Phuoc, M. Chligui

Cluj University
E. Dorolti, V. Pop

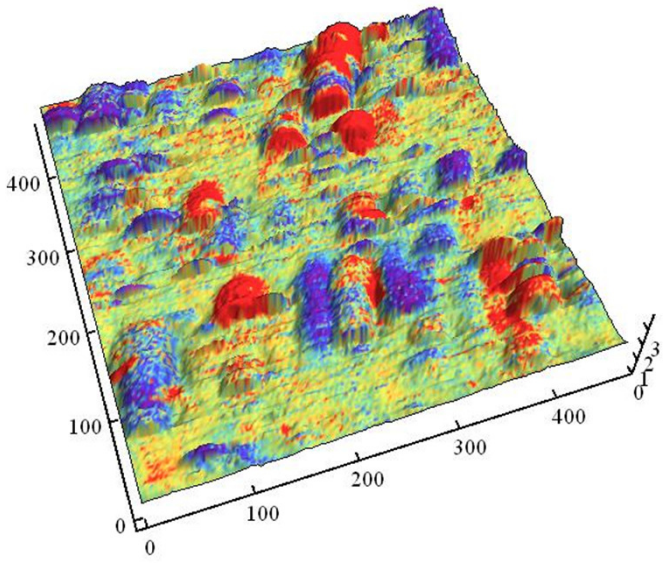
NC St. Univ.
H. Koo, E. Kan, M. Whangbo

Financial supports :

cnrs
UNIVERSITÉ DE NANTES
Agence Nationale de la Recherche ANR
Région PAYS DE LA LOIRE
NanoSciences NORD-OUEST
ST

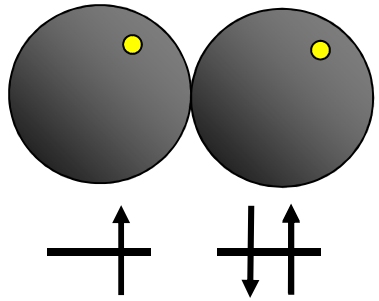
ANR NV-CER (2005-08)
ANR NanoMott (2009-13)
ANR Mott-RAM (2012-14)
ANR Gold-RAM (2013-2016)

Thank you for your attention



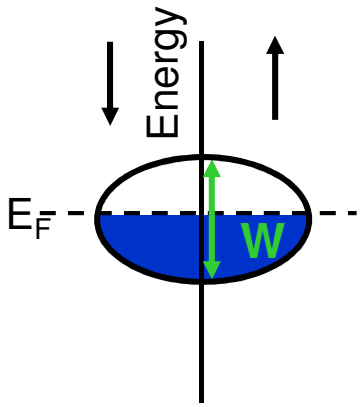
AM_4Q_8 Mott insulators

1 electron per site, band theory :



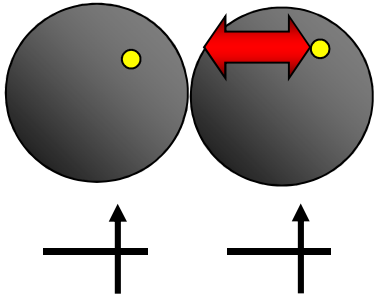
→ **metal!**

Solid :



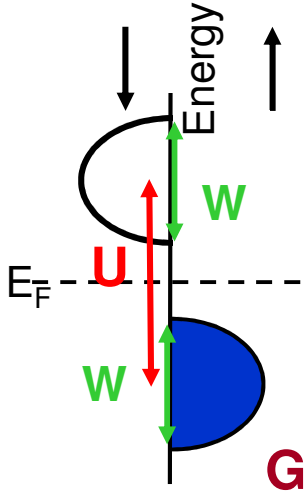
Electronic confinement → coulombian repulsion :

U = coulombian repulsion between electrons



→ **insulator**

Solid :



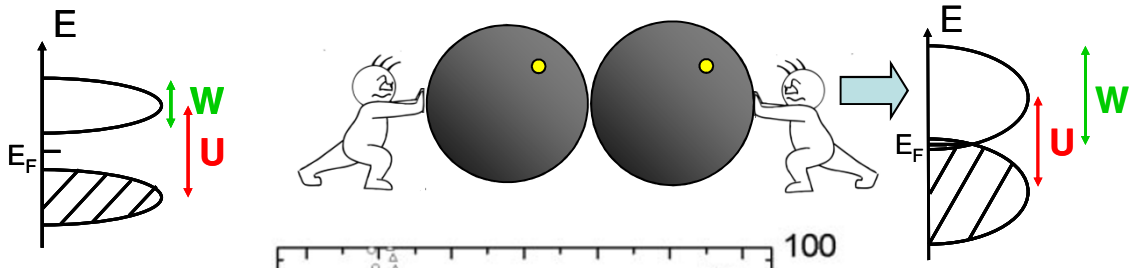
W < U

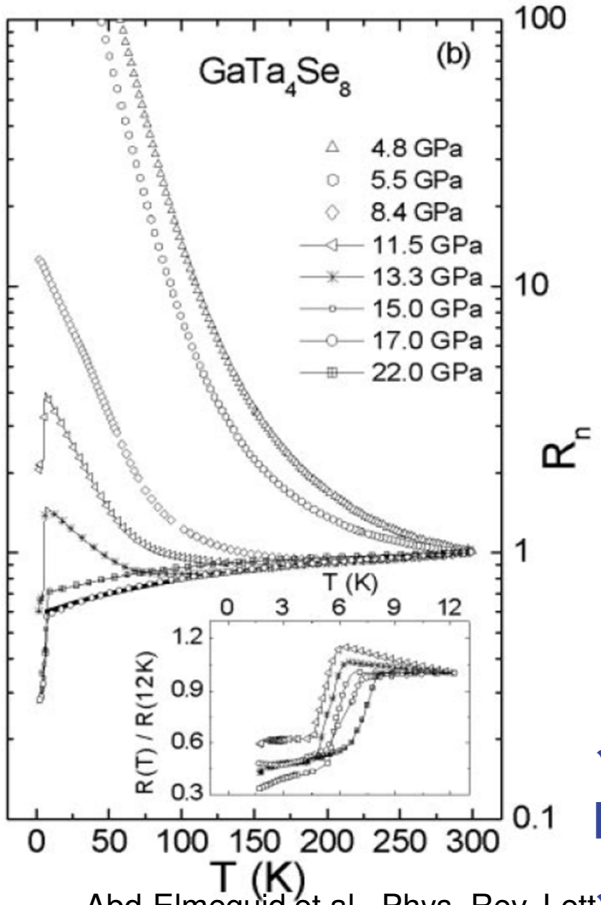
Gap ~ 0.20 eV for AM_4Q_8

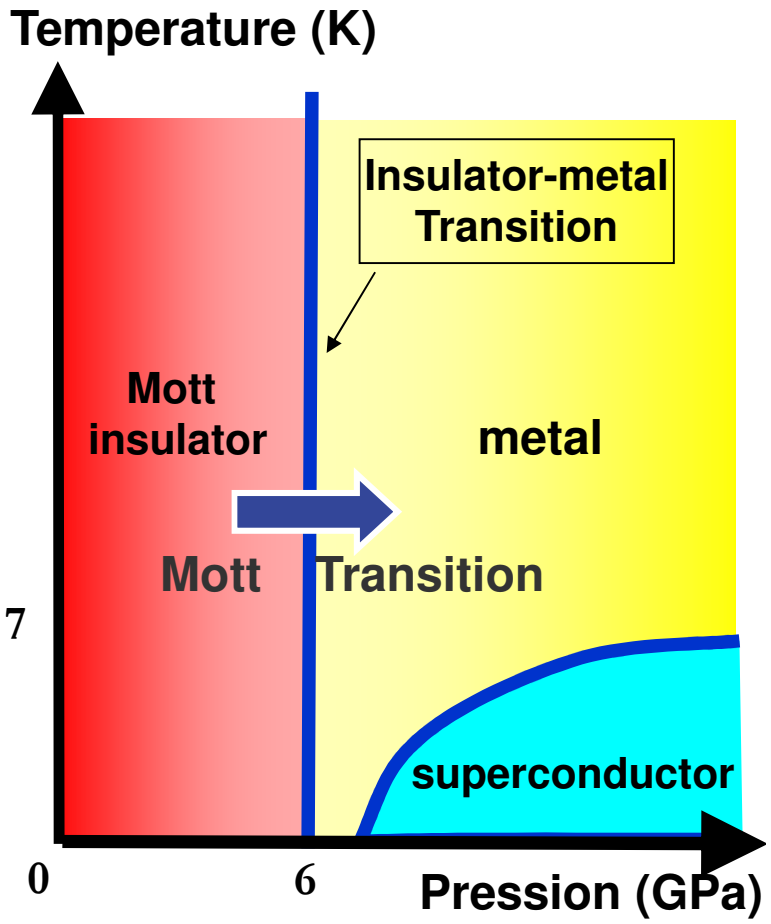
AM_4Q_8 = narrow gap Mott insulators

Pocha, R. et al., J. Am. Chem. Soc. 127, 8732 (2005)

AM_4Q_8 Mott insulators





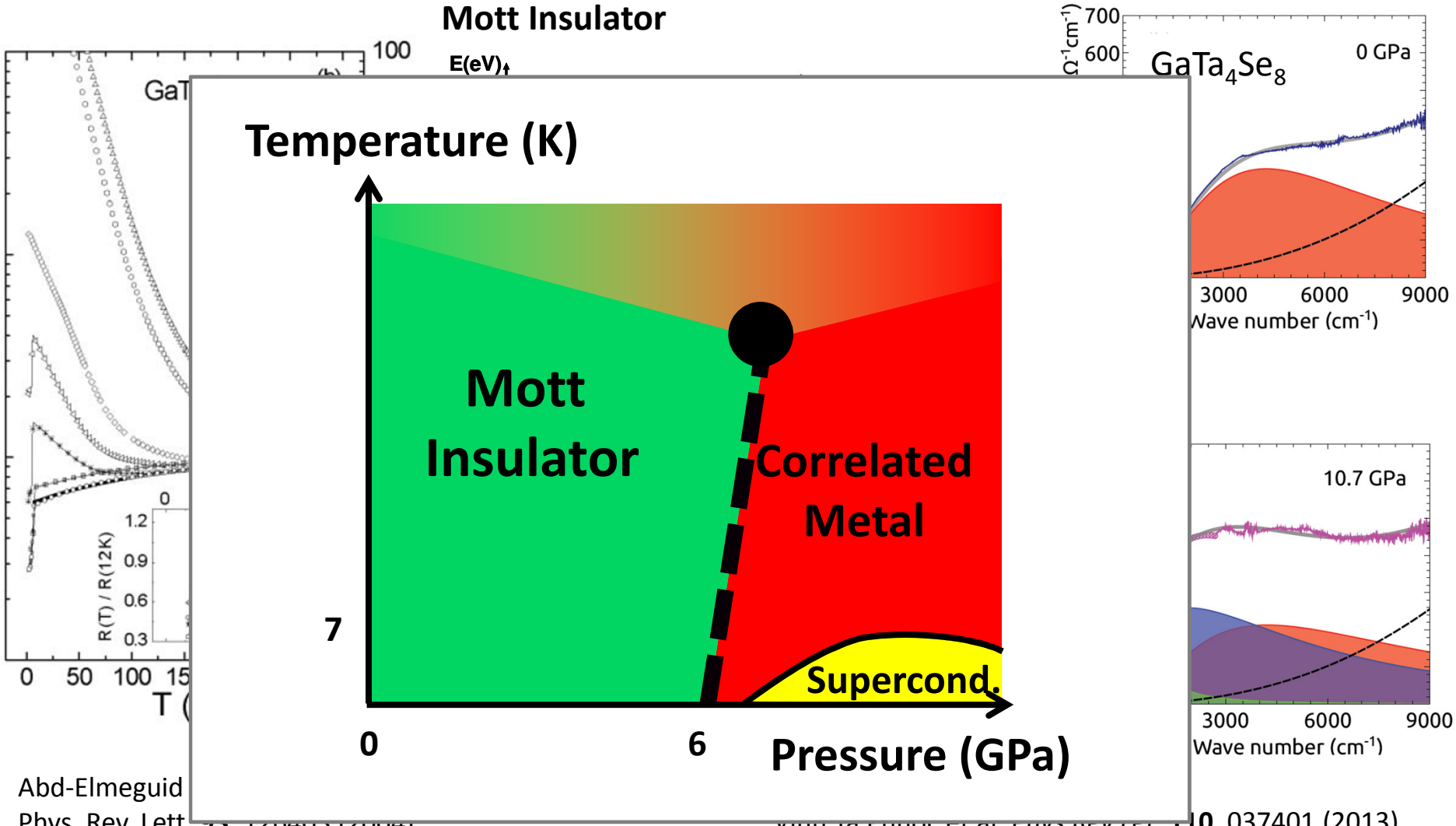


✓ **Transition Mott insulator – metal under pressure**

✓ **Superconductivity (T_c = 5.7K)**

Abd-Elmeguid et al., Phys. Rev. Lett. **93**, 126403 (2004); R. Pocha *et al.*, *J. Am. Chem. Soc.* **127**, *8732* (2005)

Bandwidth control MIT in the AM_4Q_8



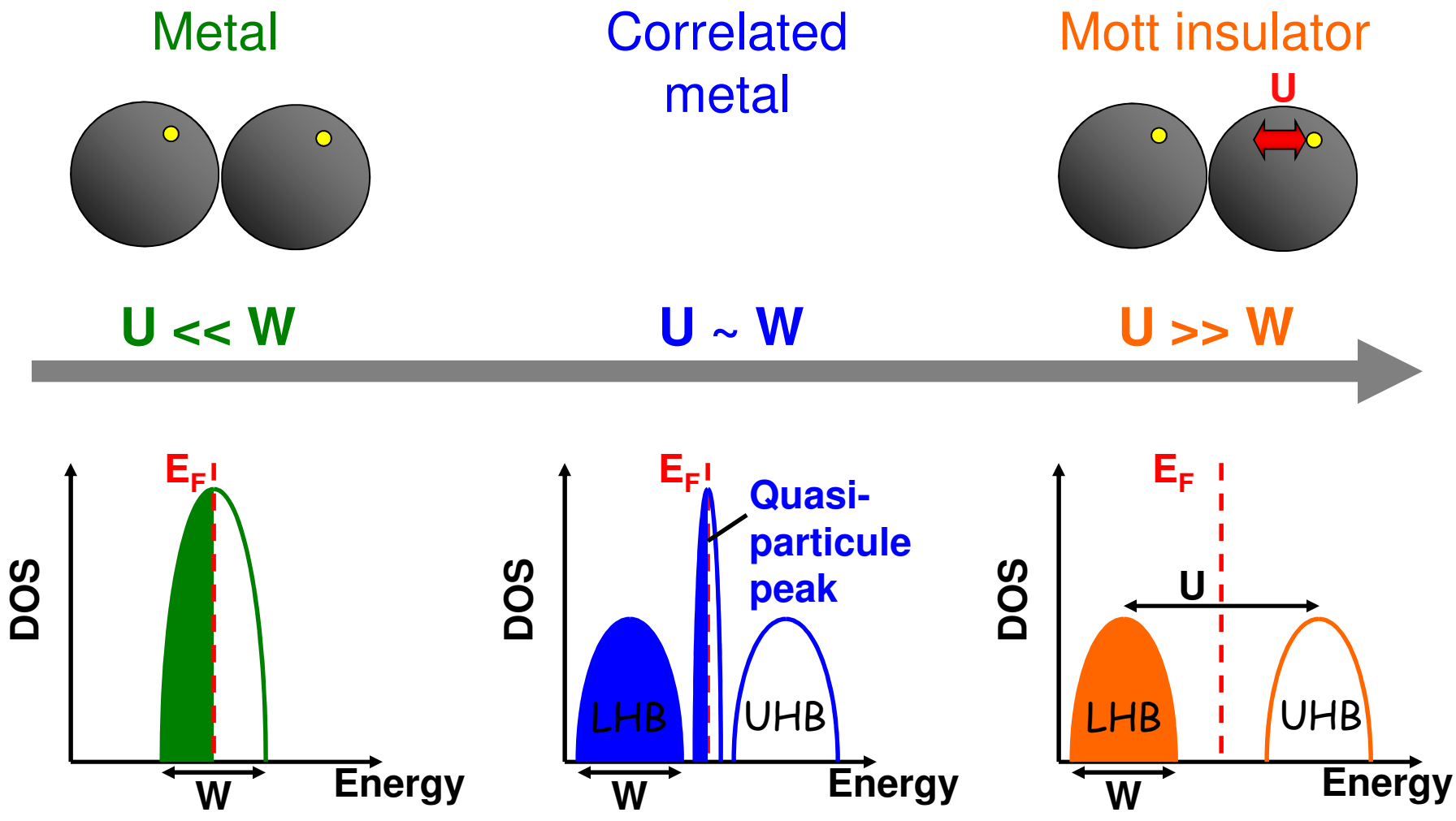
Abd-Elmeguid
Phys. Rev. Lett. **93**, 126403 (2004)

R. Pocha *et al.*,
J. Am. Chem. Soc. **127**, *8732* (2005)

Vinh Ta Phuoc et al. *Phys Rev Lett.* **110**, 037401 (2013)

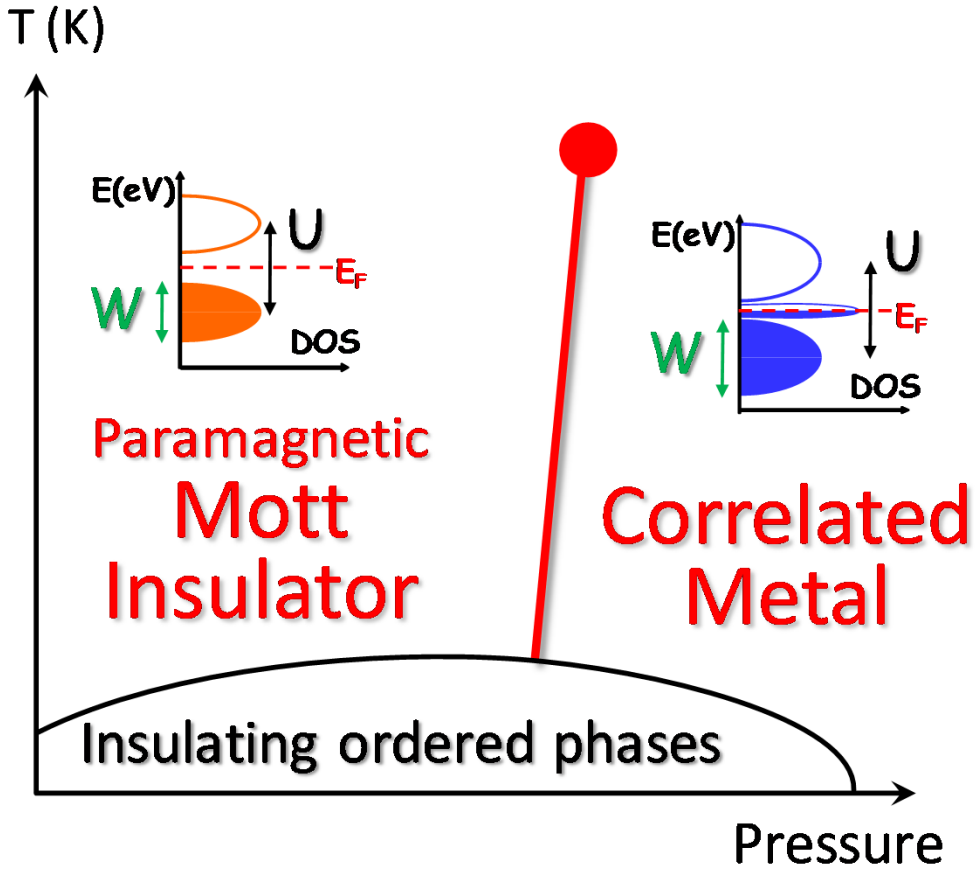
Mott insulator – metal transition under pressure

Context : Mott insulators and Insulator to Metal Transition



LHB (UHB) = Lower (Upper) Hubbard Band

Context : universal phase diagram of Mott insulators



Canonical Mott Insulators:

$(V_{1-x}Cr_x)_2O_3$

McWhan *et al.*, Phys. Rev. B 1970

$Ni(S_{1-x}Se_x)_2$

Miyasaka *et al.*, J. Phys. Soc. Jap. 2000

AM_4Q_8

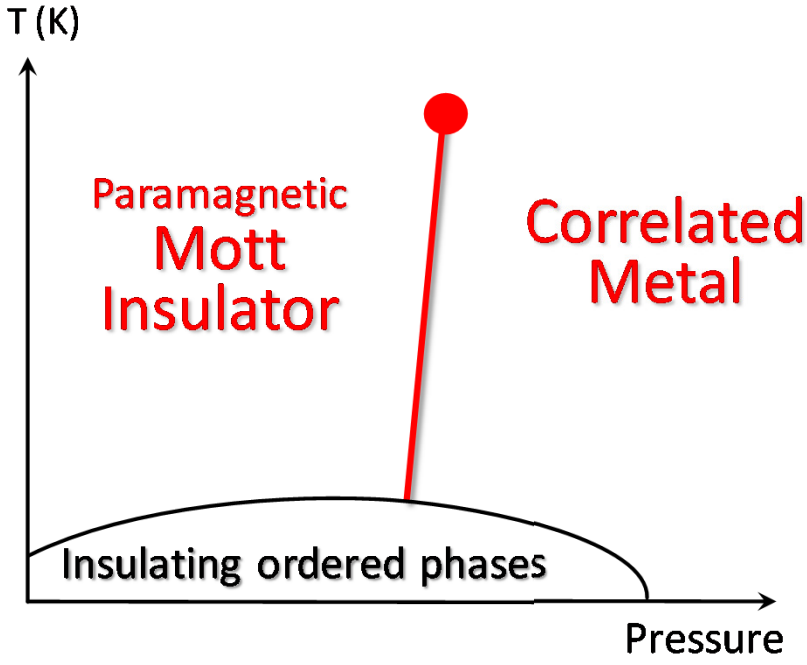
Corraze *et al.*, Eur. Phys. J. ST 2013

Mott insulator at equilibrium: well described by Dynamical Mean-Field Theory (DMFT).

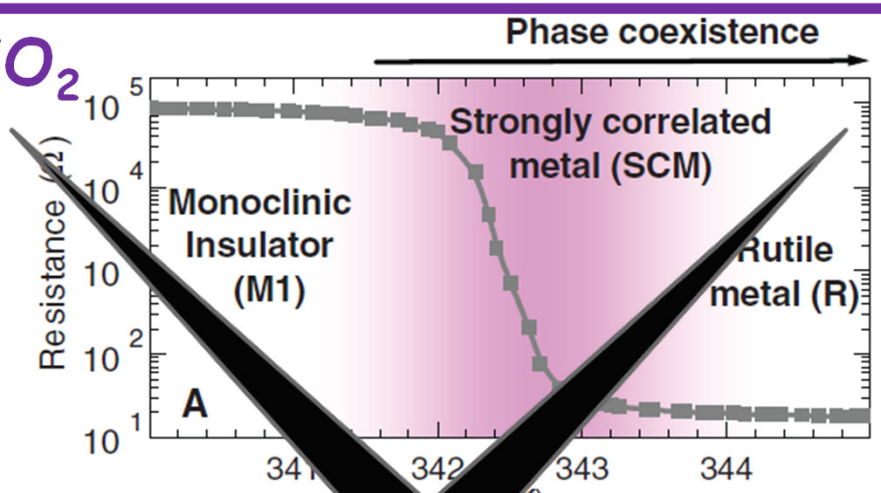
See e.g. Kotliar & Vollhardt, Physics Today 57, 53 (2004)

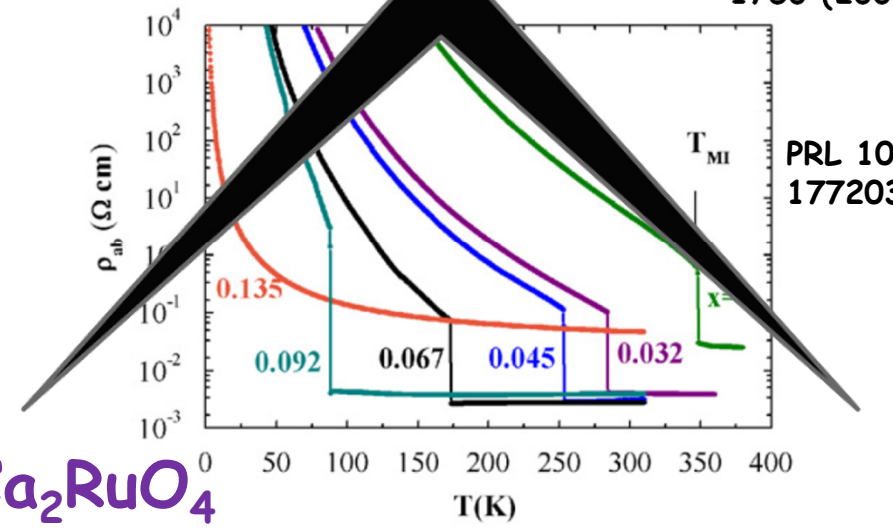
T-induced MIT (VO_2, NbO_2, Ca_2RuO_4,…): pure Mott physics ?

Universal Mott phase diagram



VO_2





Ca_2RuO_4

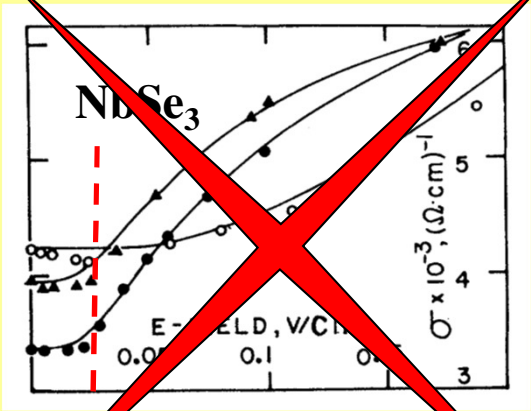
Temperature-induced Insulator to Metal Transition → non-universal Mott behavior

Non linear phenomena in the AM_4Q_8 : comparison with existing models

~~Effet Zener~~

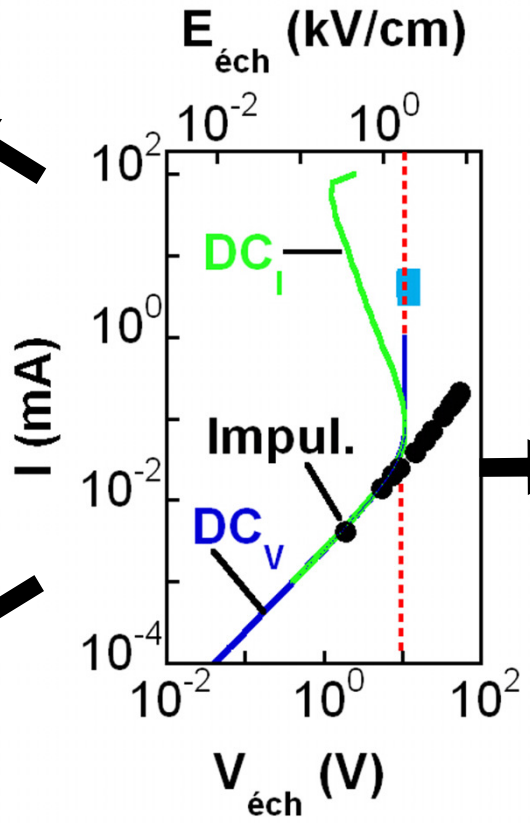
~~E_{th} ... V/cm~~

~~Charge density wave depinning (CDW)~~



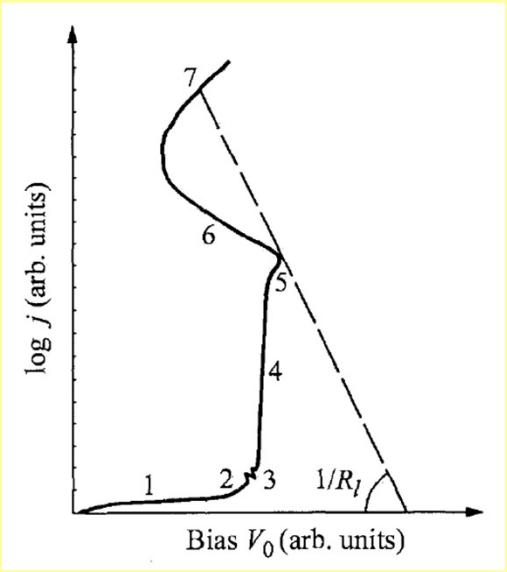
Monceau *et al.*,
PRL 37, 602 (1976)

~~E_{th} < 1 V/cm~~
~~I(V) different~~
~~No strutural transition~~



E_{th} ≈ 1-10 kV/cm
Gap ~ 0.2 eV
Electronic
Non homogeneous

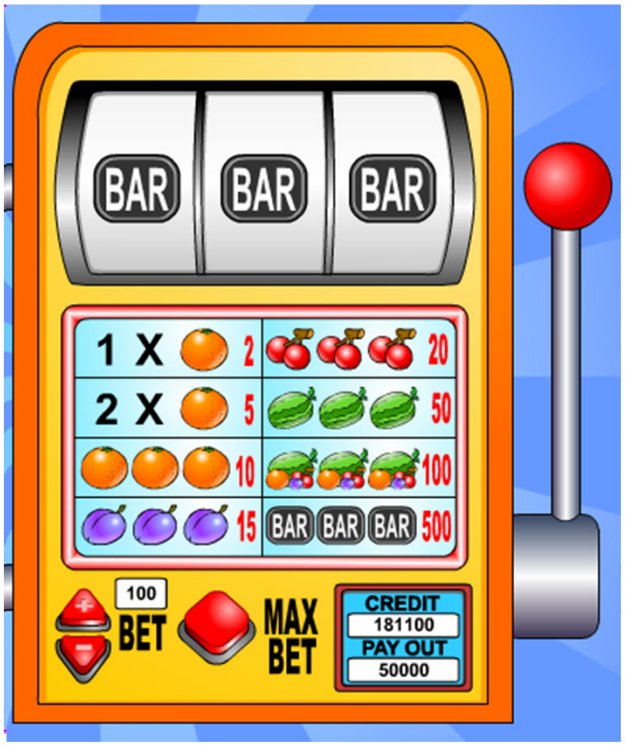
Avalanche



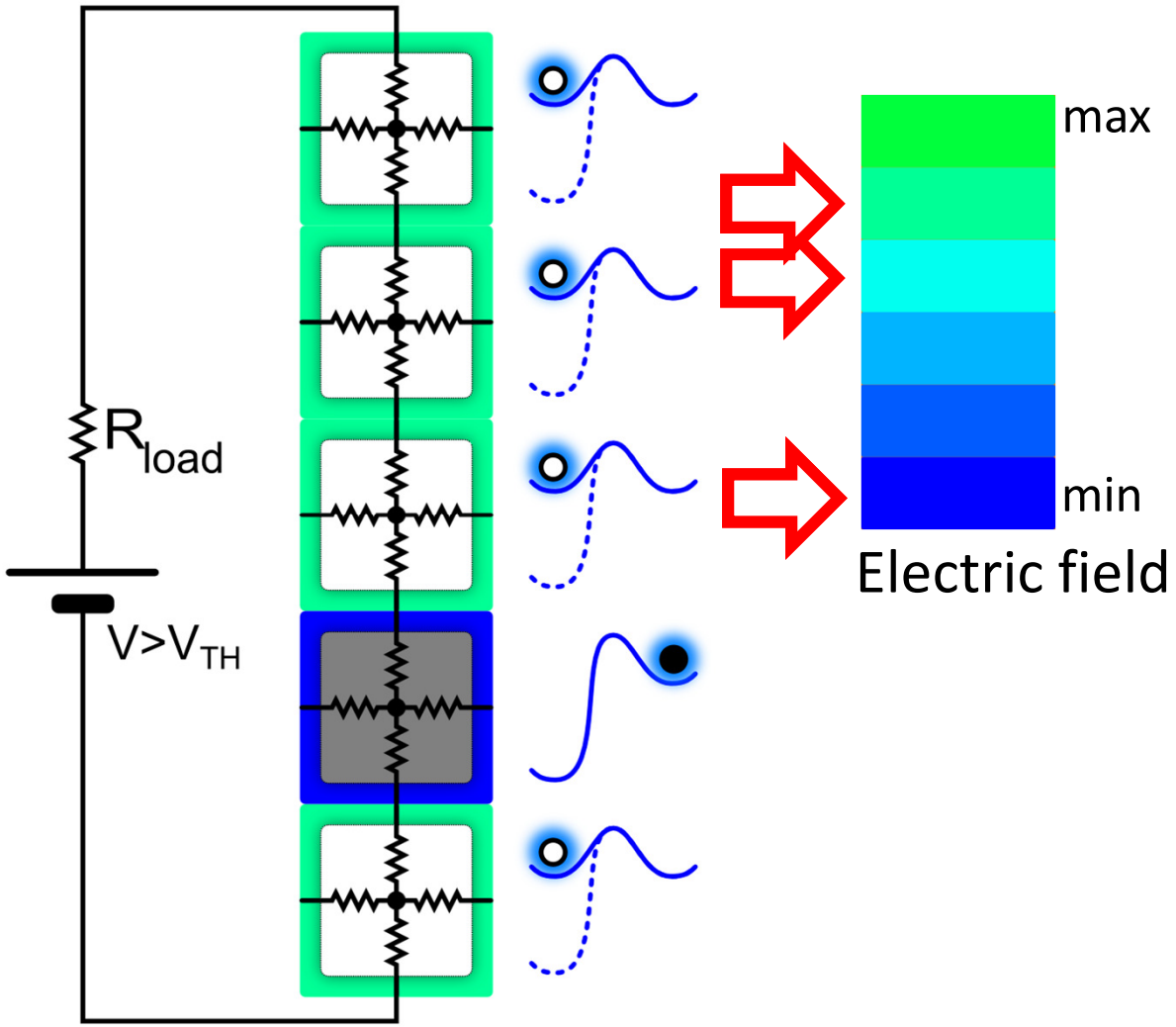
E_{th} comparable
E_{th} ≈ 1-100 kV/cm
I(V) similar

Possible Mechanism

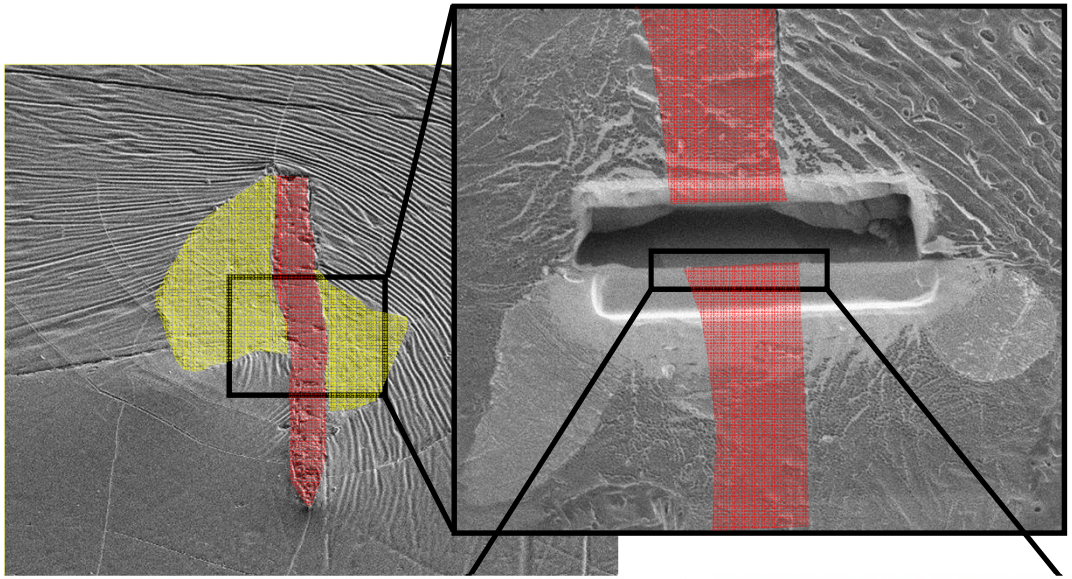
Modeling of the resistive switching : implementation of a resistor network



Trial number ≈ Time scale

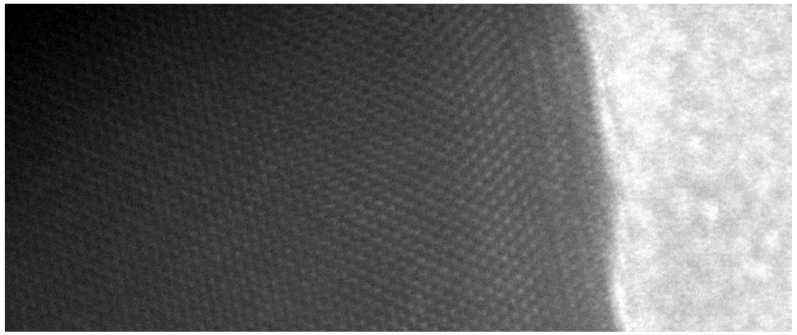


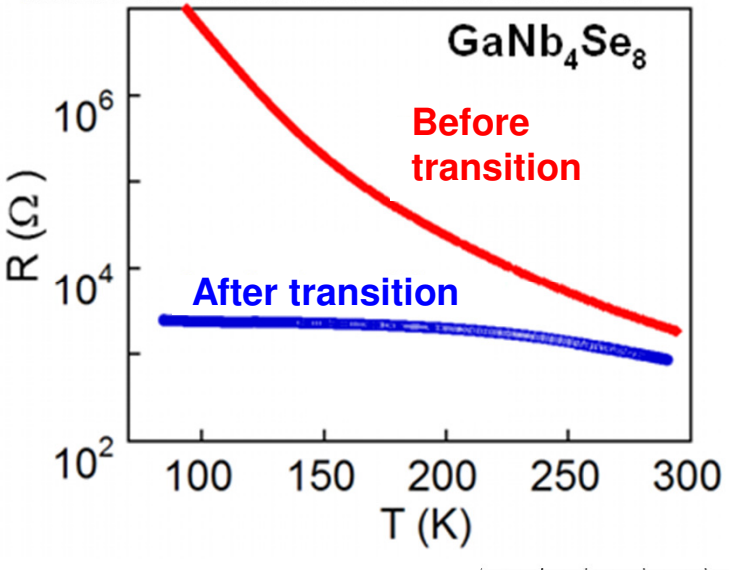
Non-volatile resistive switching : Chemical or structural changes ?

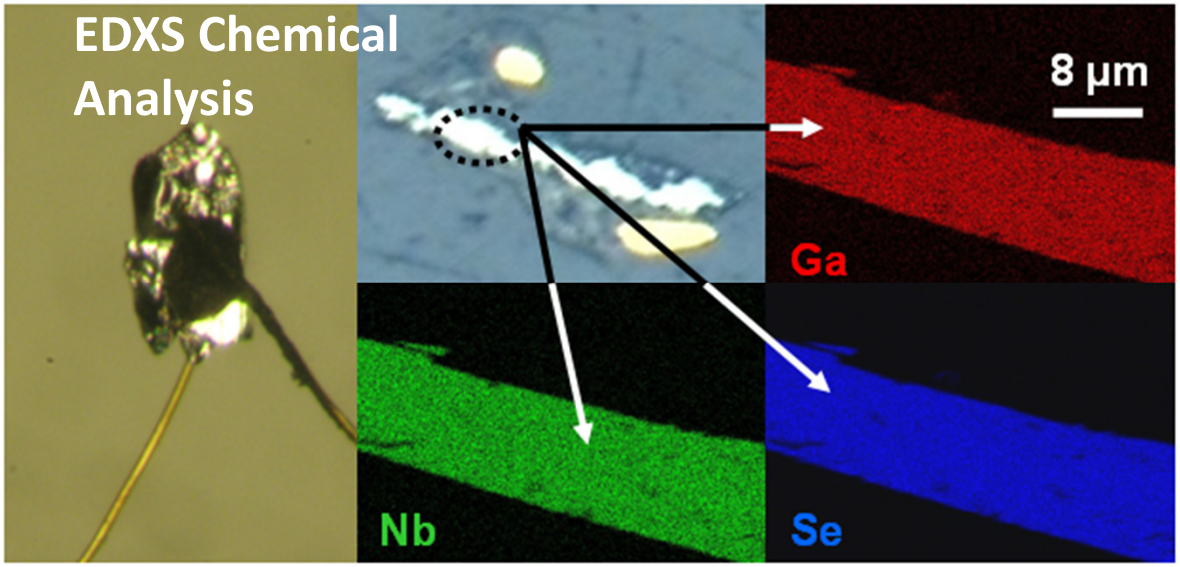


« Transited » crystal GaV_4S_8

TEM Images (IMN)

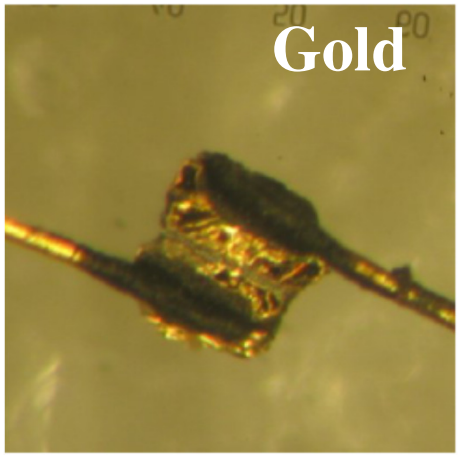




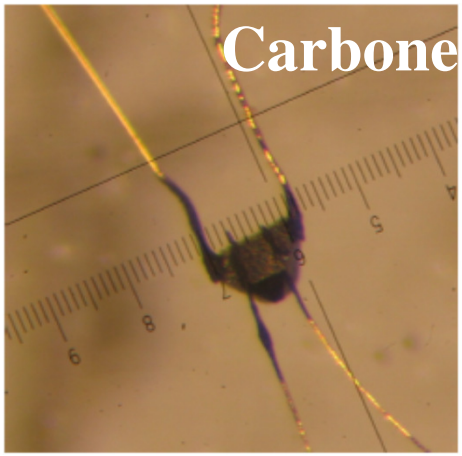


✓ no chemical or structural change (< 10-1000 nm)

AM_4X_8 : interfacial phenomena ?

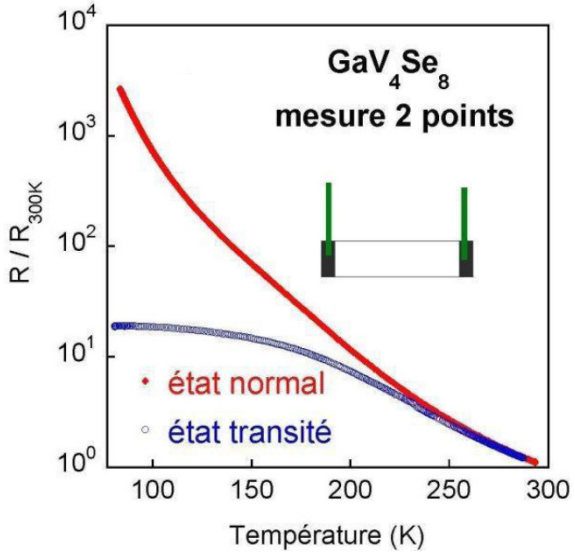


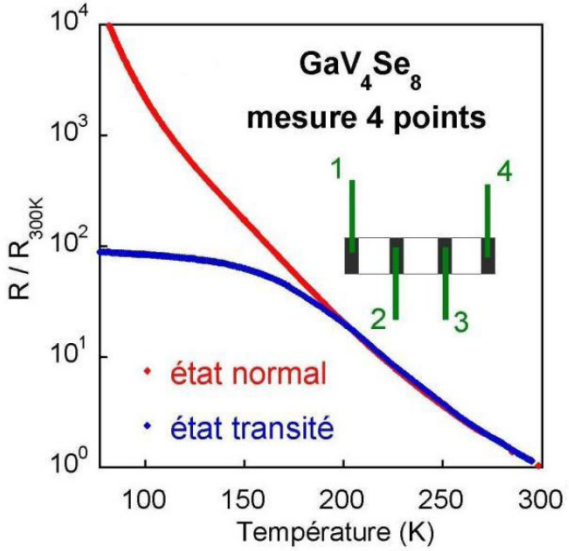




2 contacts measurements

4 contacts measurements





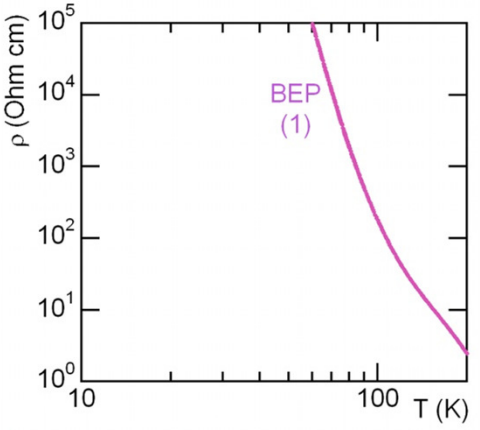
✓ "bulk" phenomena

Two resistances model

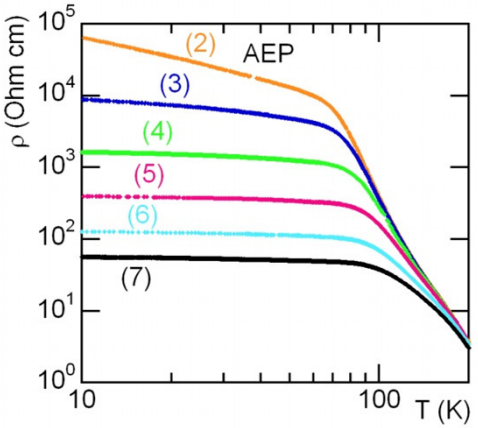
Before

Electric Pulse

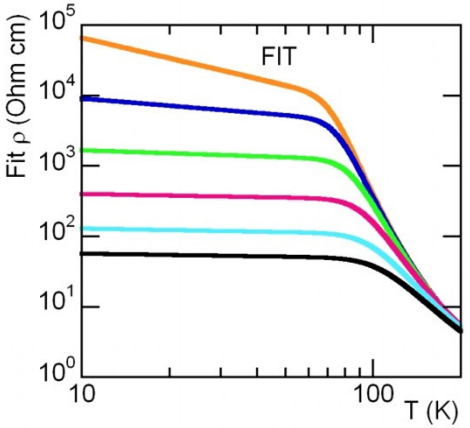
After

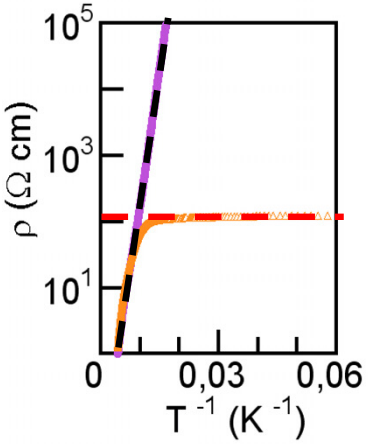


Experiments

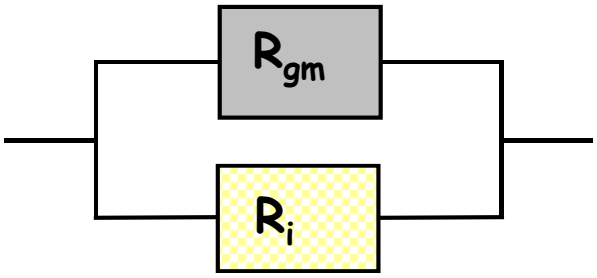


Simulation





$$\rho_{gm}=AT^{-\alpha}$$



$$\rho_i=\rho_{i0}\exp -E_a/k_BT$$

C. Vaju et al.,
Microelectronic Engineering, **85**, 2430 (2008)

Two resistances model : a filamentary conduction

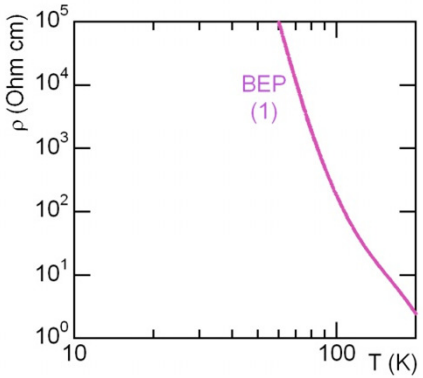
Before

Electric Pulse

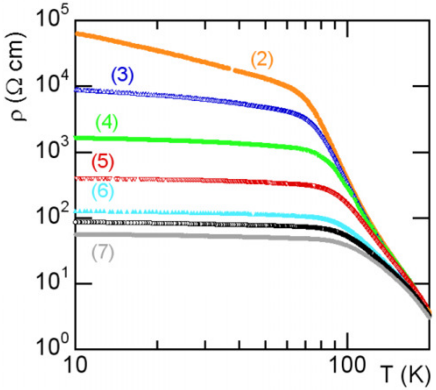
After

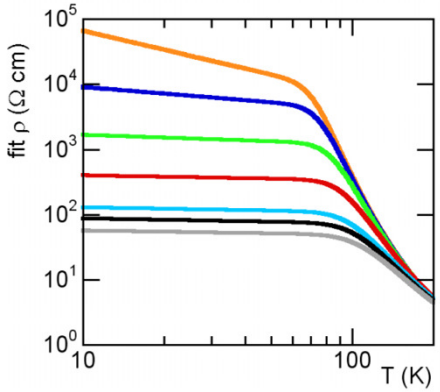
Experiments

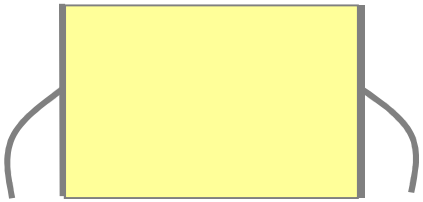
Simulation



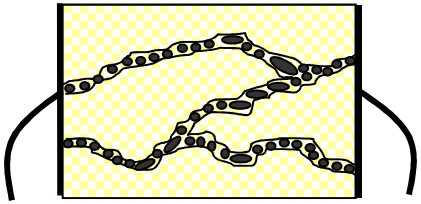




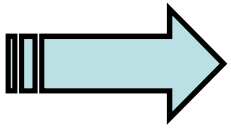








Electric pulses create and reorganize some filamentary paths



Electric pulse induced filamentary conduction

Electric pulse driven superconductivity ?

Current pulse applied at 70 K

100 mA

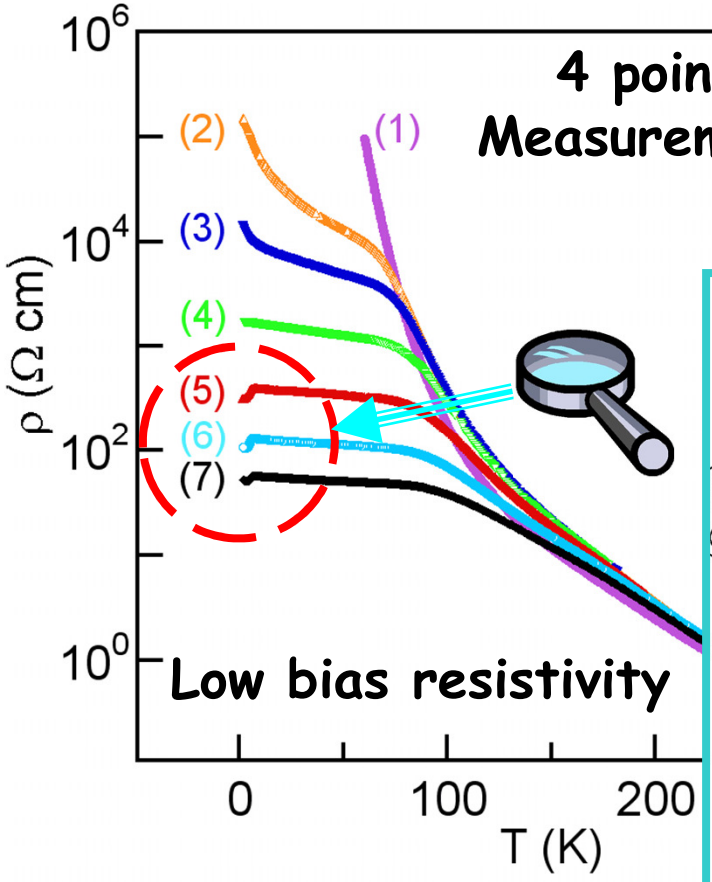
1.4 mA

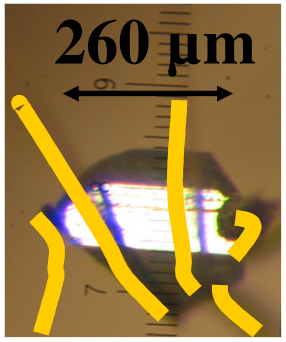
4.4 mA

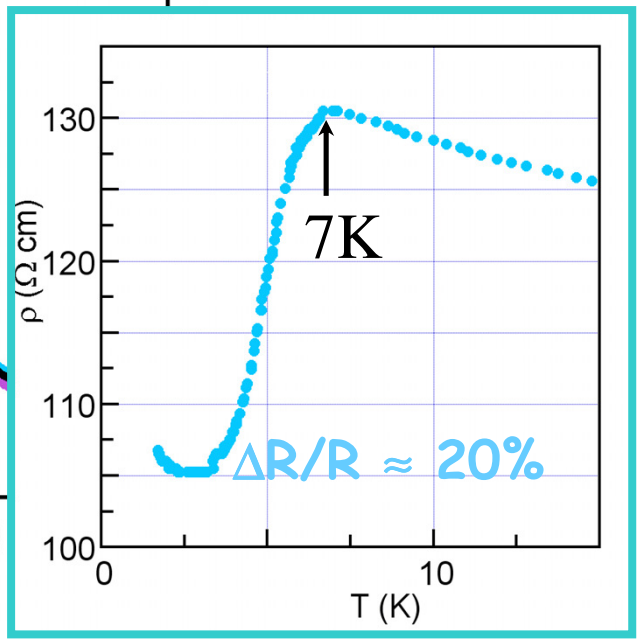
6.3 mA

25 mA

40 mA



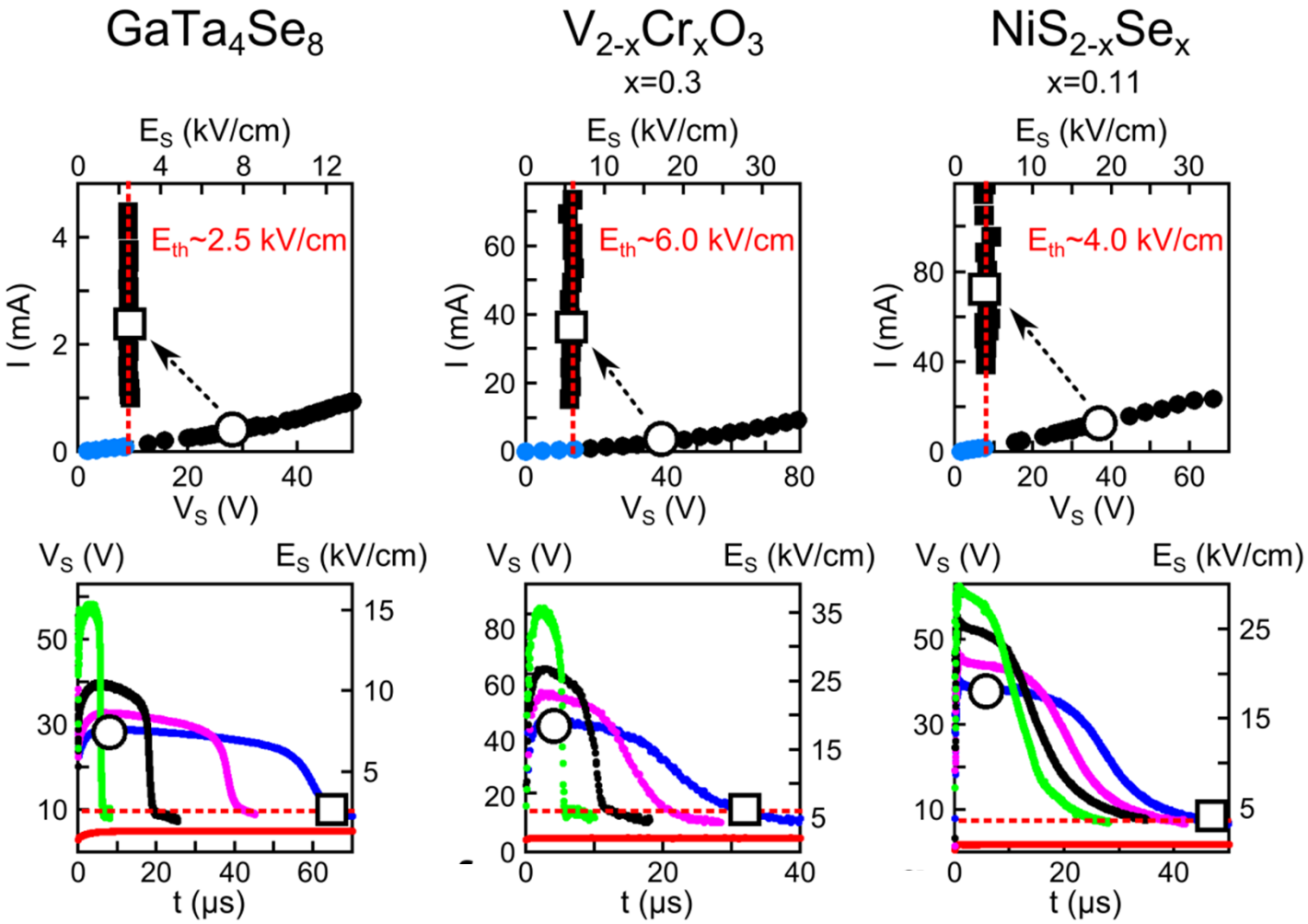




C. Vaju et al., Advanced Materials **20**, 2760 (2008); Microelectronic Engineering, **85**, 2430 (2008)

Volatile Resistive Switching = local Mott transition

✓ **The phenomenology is general to all Mott insulators !**



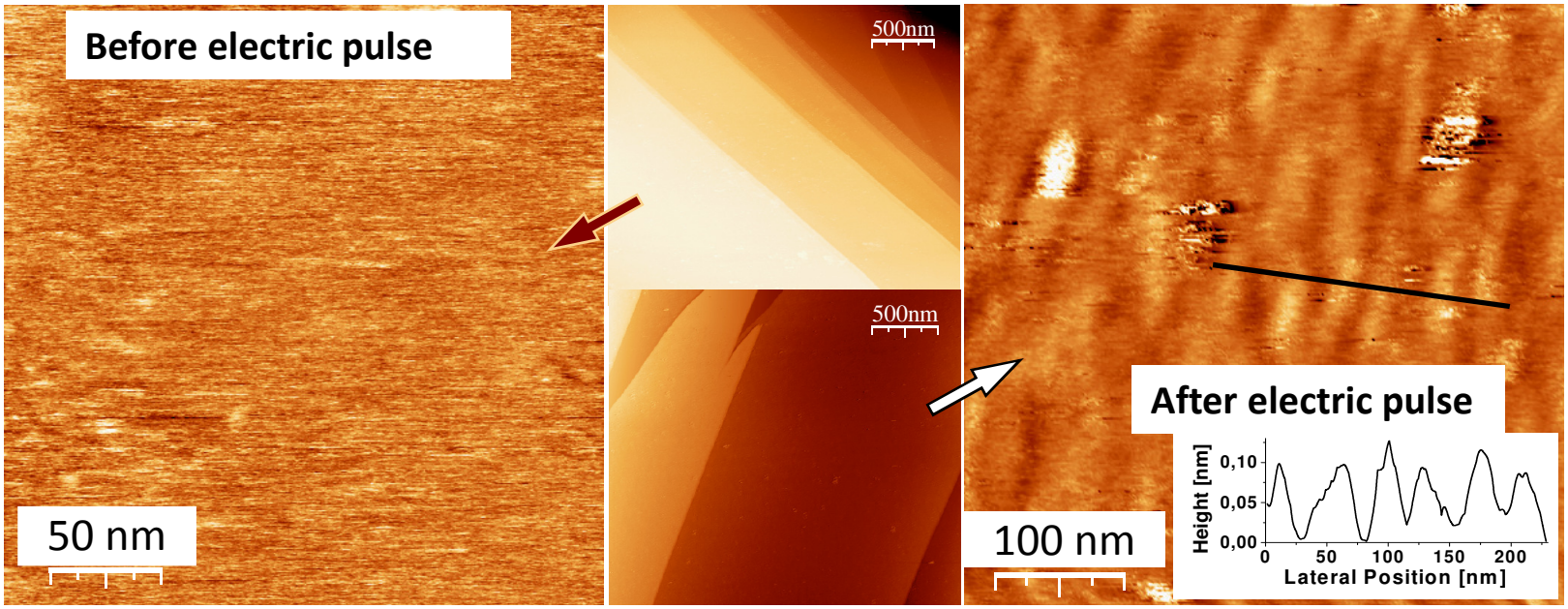
P. Stoliar *et al.* Adv. Mater. 25, 3222 (2013)
L. Cario *et al.* – Patent PCT/EP2013/057500. April 2012

Non-volatile resistive switching : electronic phase separation

STM study of $GaTa_4Se_8$

Institut des NanoSciences de Paris

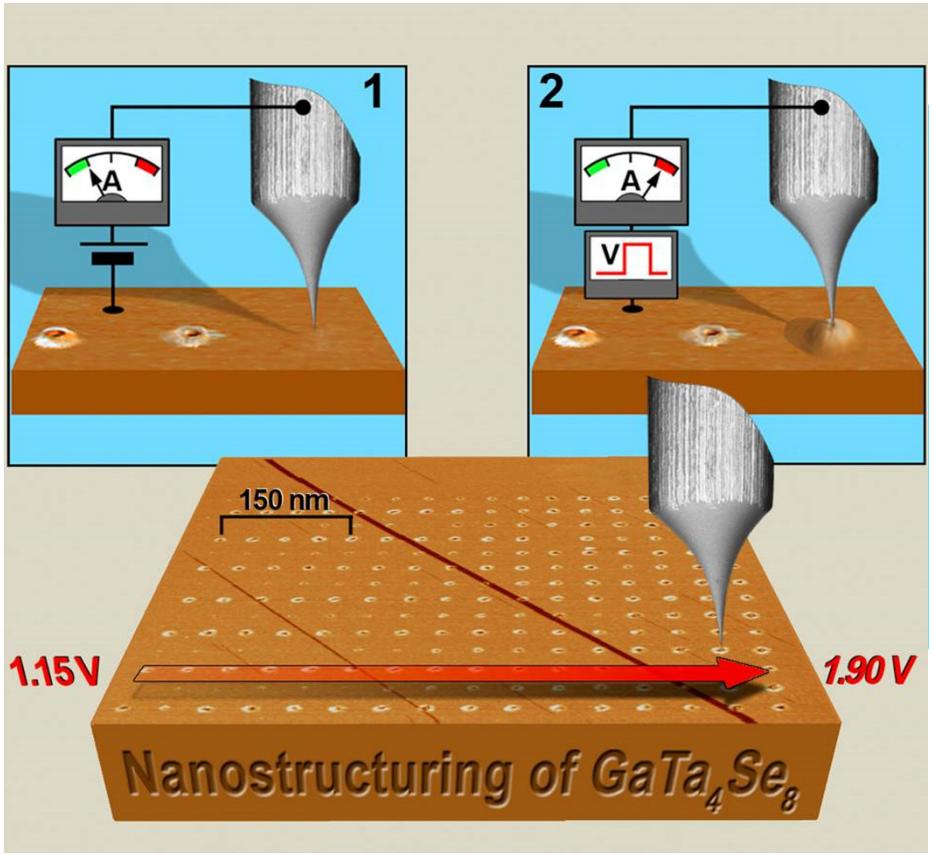
V. Dubost, F. Debrontrider,
T. Cren, D. Roditchev



Electronic phase separation

C. Vaju, *et al.* Advanced Materials 20, 2760 (2008)

Pulse application through the STM tip: large electro-mechanical coupling



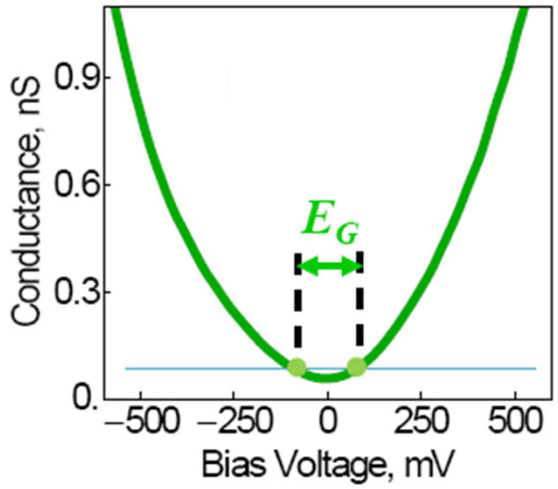
Nano-writing : 1 Tdots / cm² !

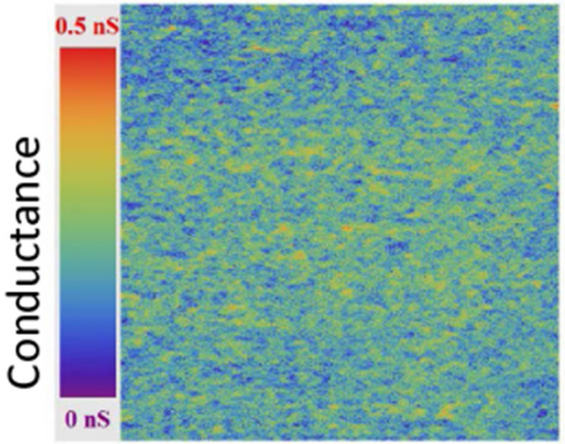


Gigantic electro-mechanical Effect

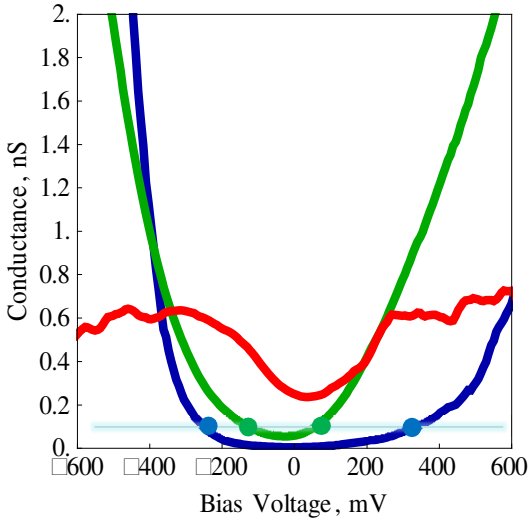
V. Dubost et al. *Adv. Funct. Mater.* 19, 2800-2804 (2009)

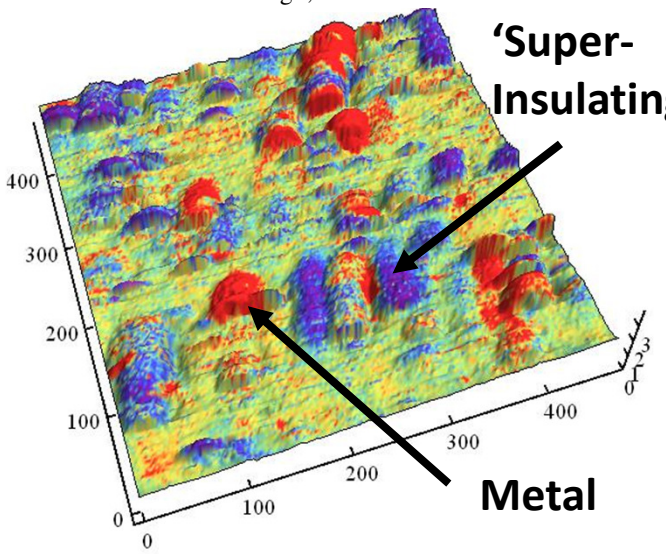
Electronic phase separation : an STS study





Electric pulse





'Super-Insulating'

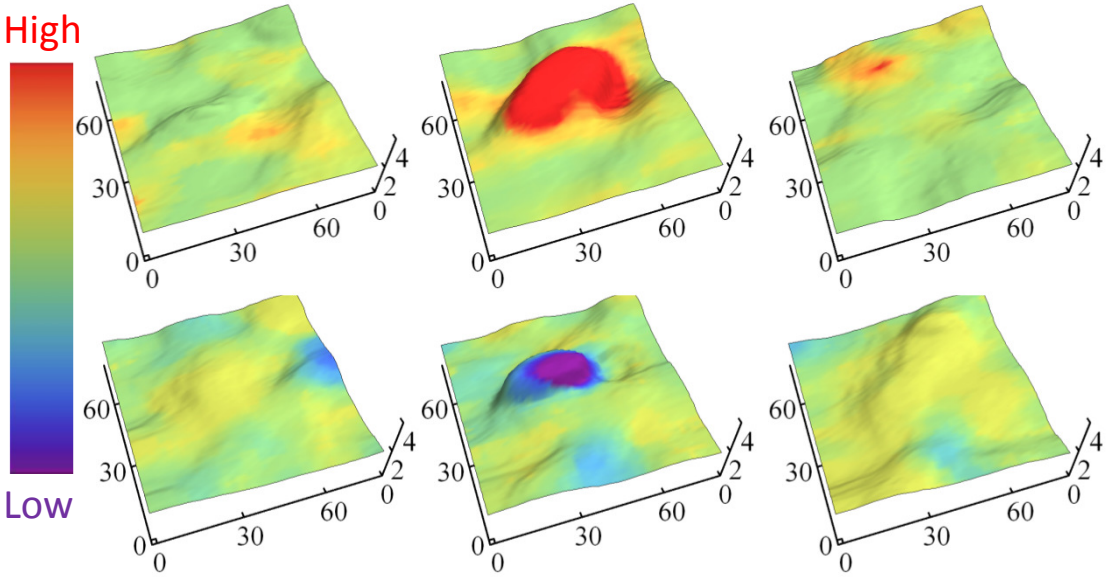
Metal

V. Dubost *et al.* Nanoletters **13**, 3648 (2013).

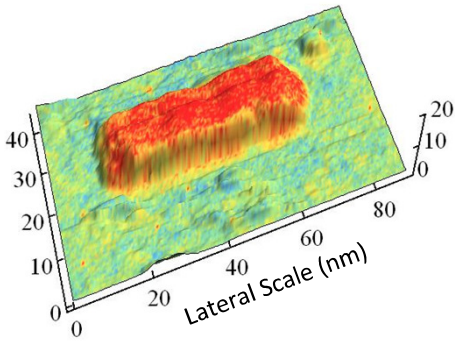
Insulator metal transition at the nanoscale !

Pulse application through the STM tip: writing and erasing at the nanoscale

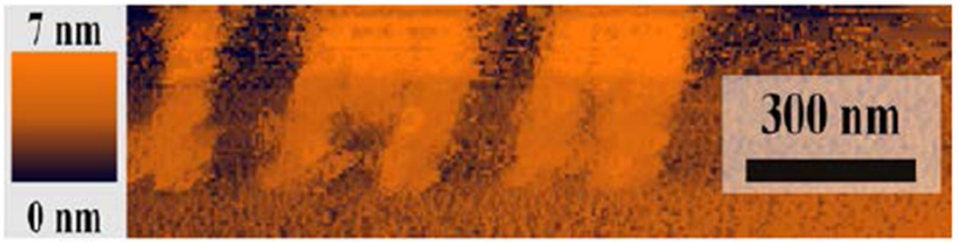
Successive spectroscopic Voltage ramps 600 mV



Electronic writing
with electric pulses

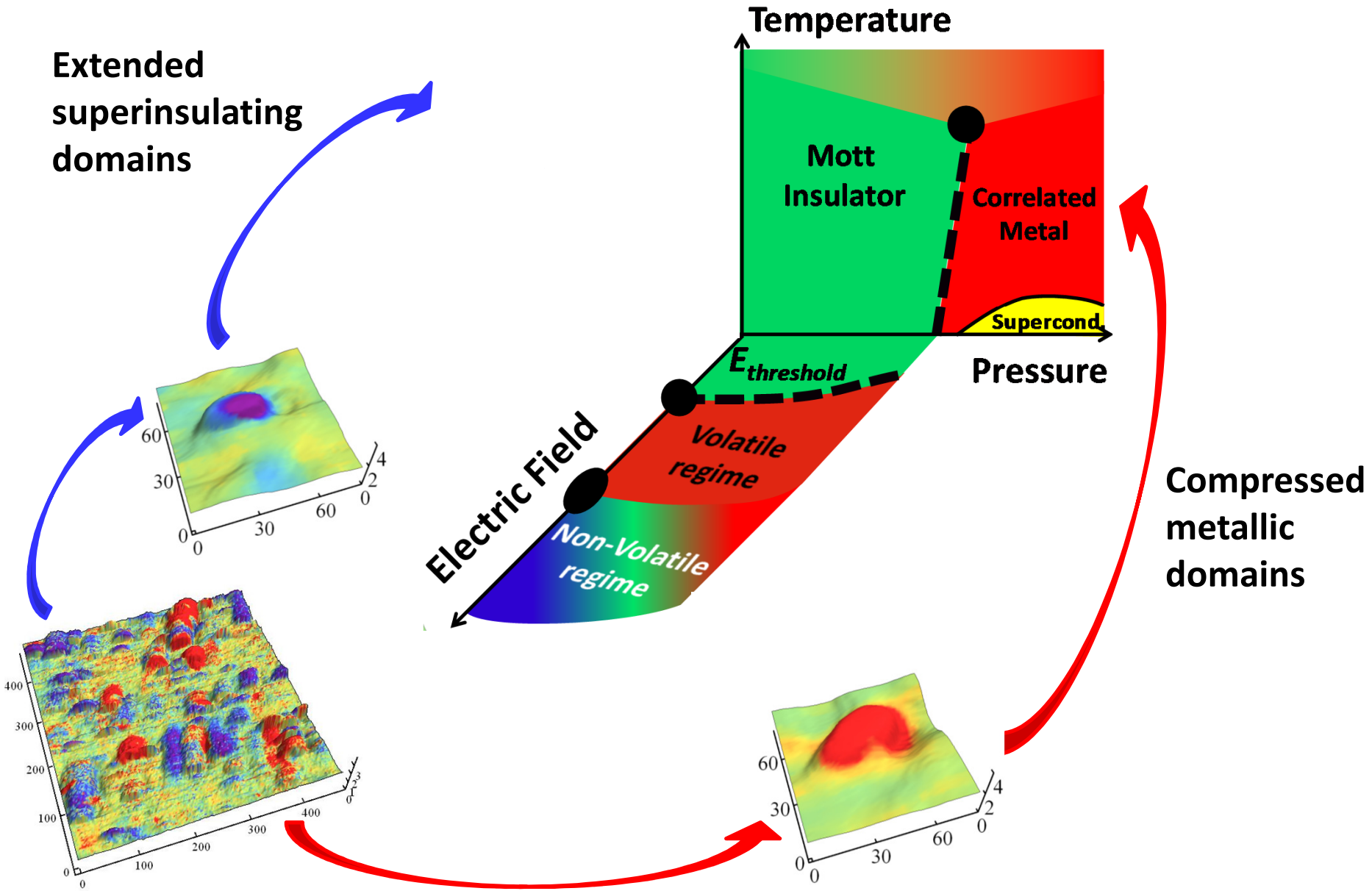


V. Dubost *et al.*
Nanoletters **13**, 3648 (2013).



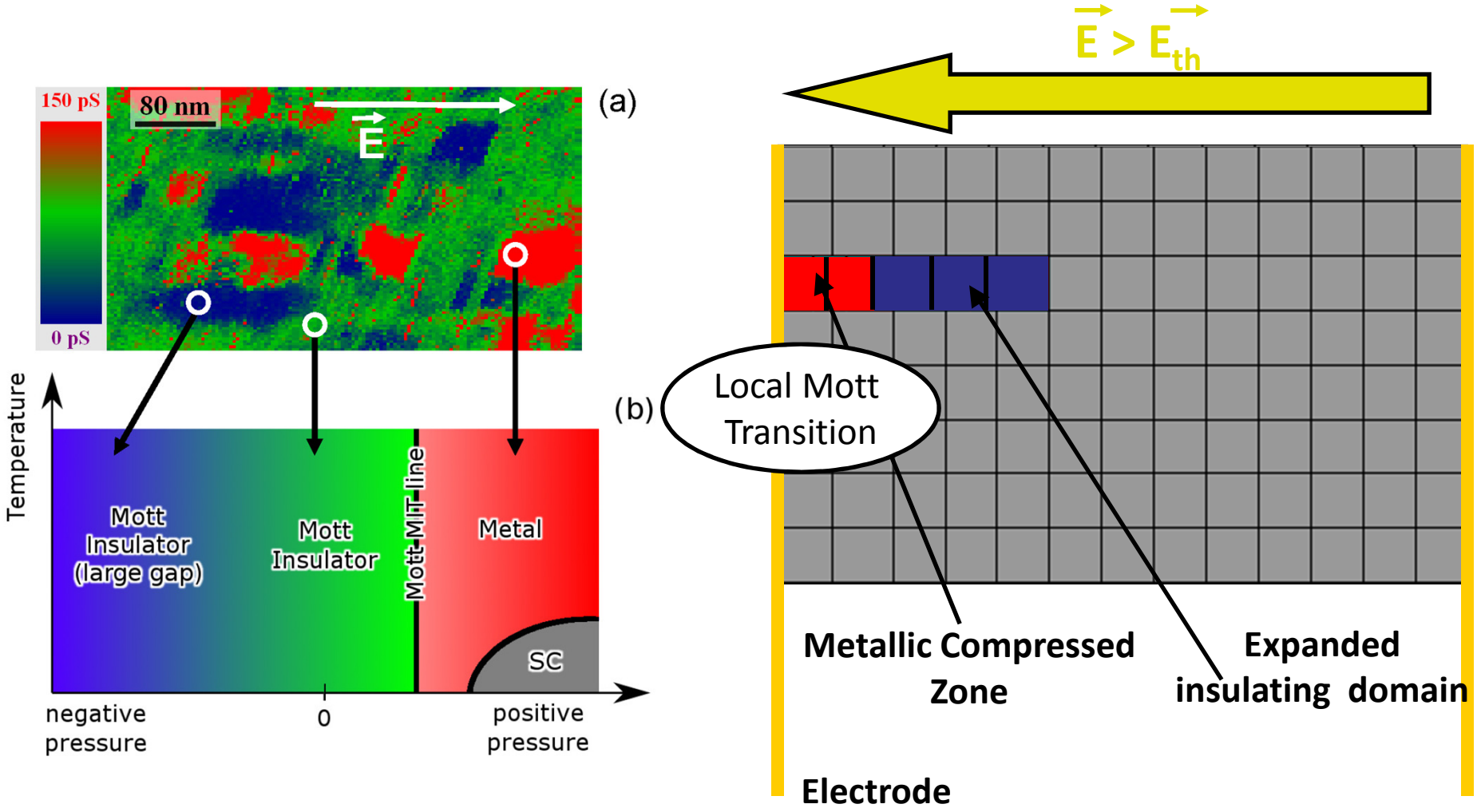
Reversible insulator metal transition at the nanoscale !

Compression or expansion of domains under electric field



Towards a model of the non-volatile resistive switching in the AM_4Q_8

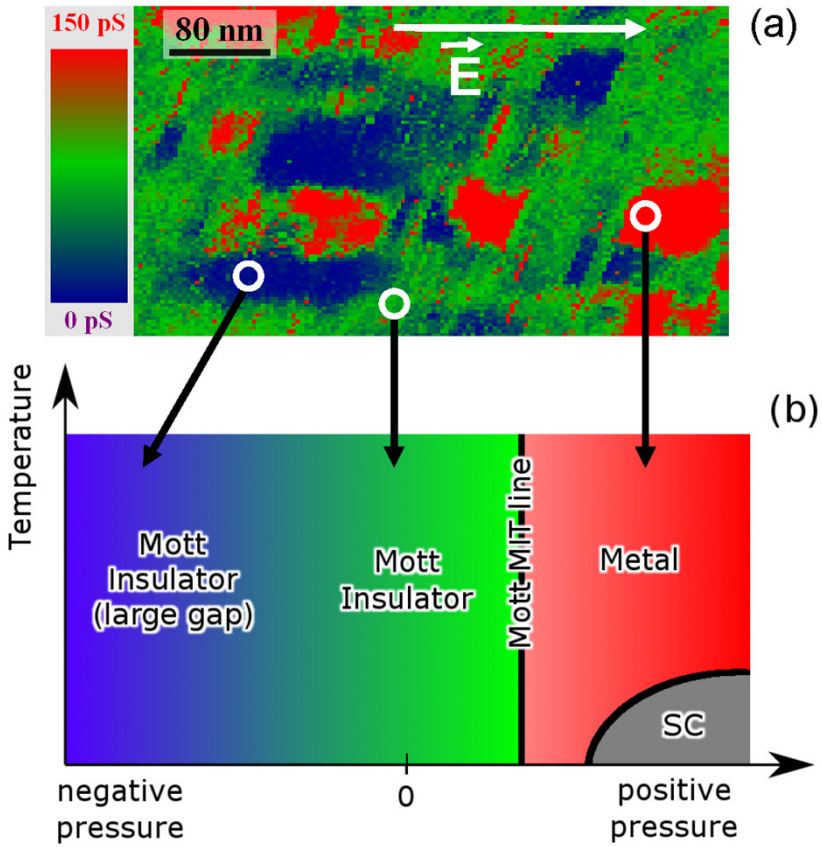
Corraze et al., Eur. Phys. J. Spec. Top. 222, 1046 (2013).



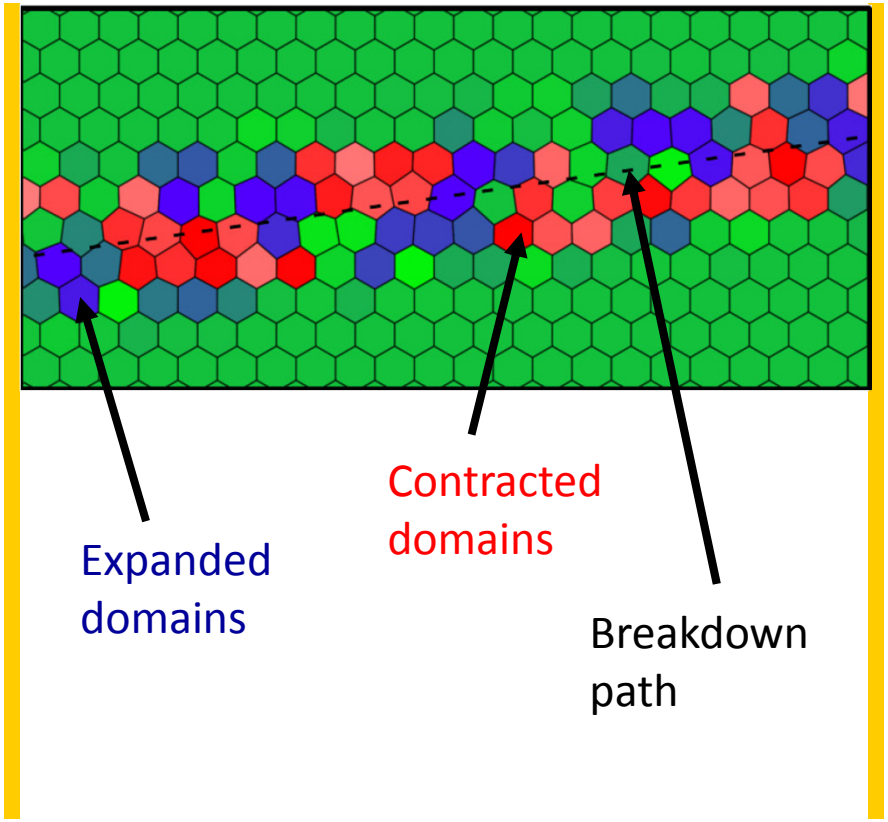
A local Mott transition with volume contraction creates both metallic and superinsulating domains

Towards a model of the non-volatile resistive switching in the AM_4Q_8

Corraze et al., Eur. Phys. J. Spec. Top. 222, 1046 (2013).

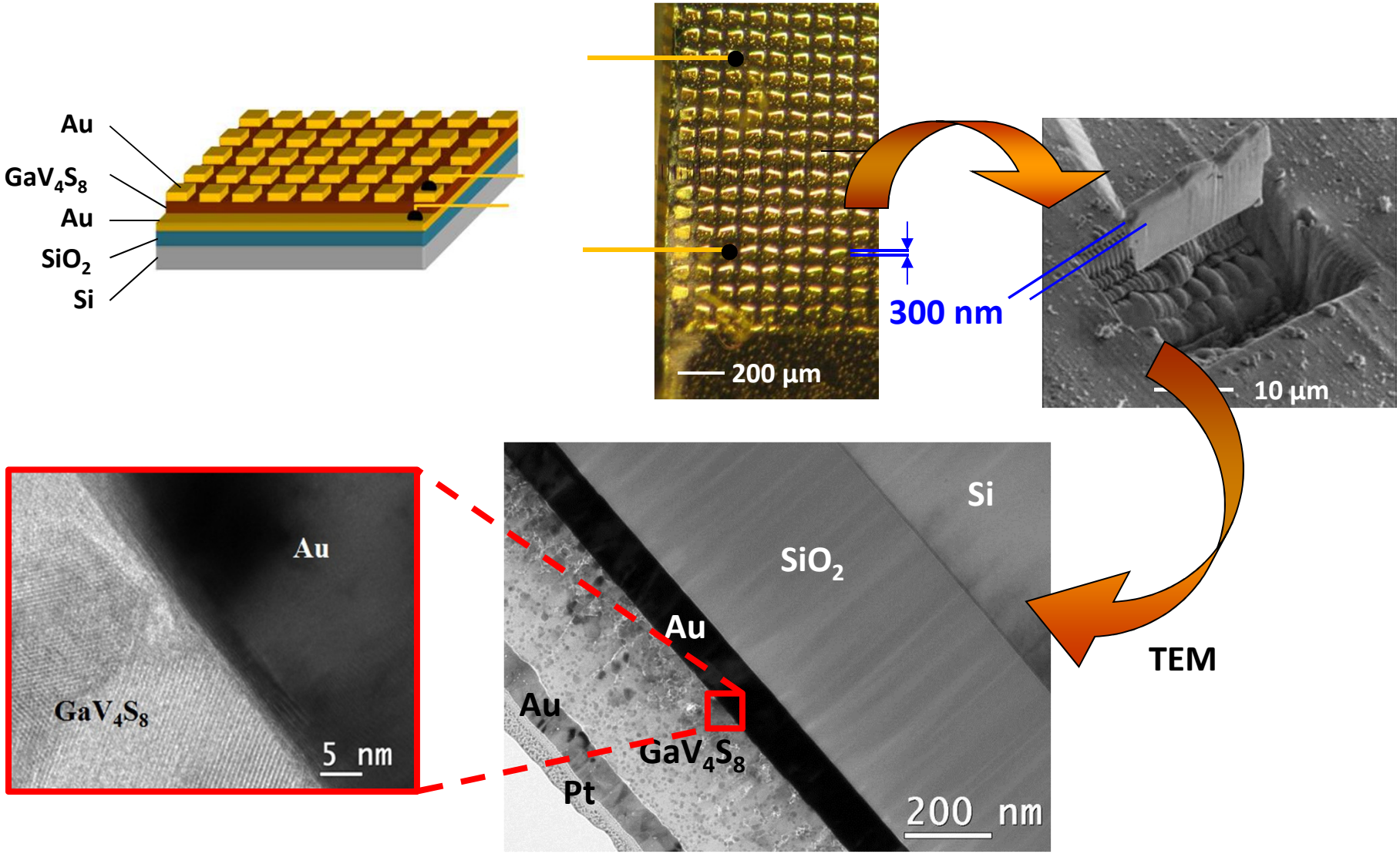


Voronoi diagram assuming total volume conservation



A local Mott transition with volume contraction creates both metallic and super-insulating domains

Metal/Insulator/Metal (MIM) Structure



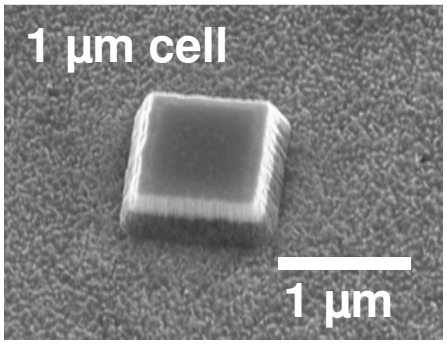
E. Souchier *et al.*, PSS-RRL 5, 53 (2011)

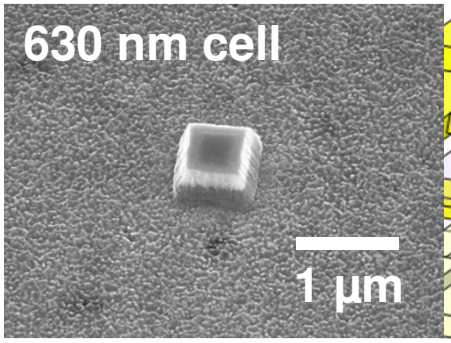
Fabrication of a Mott memory device

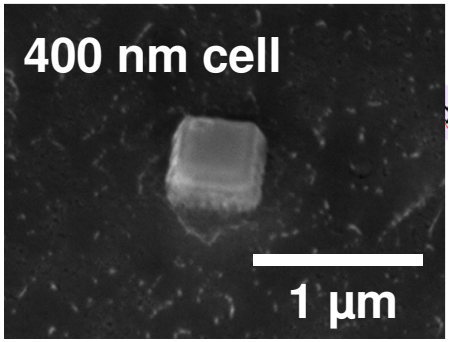
Plateforme Technologie Amont (CNRS/CEA,

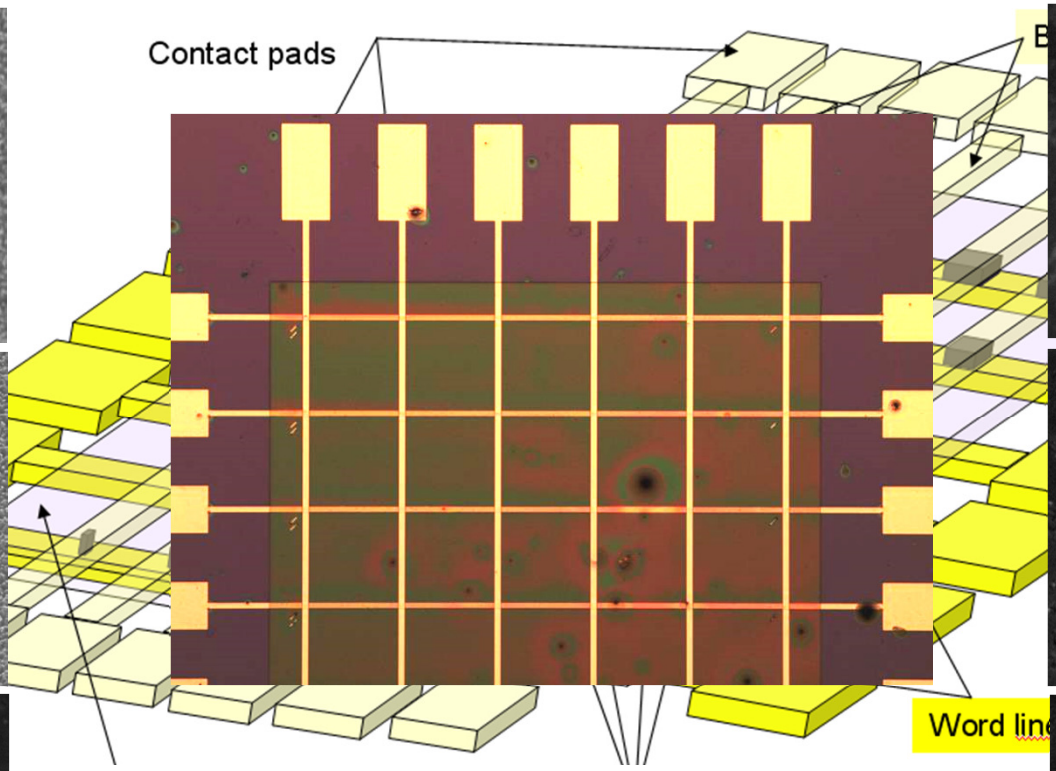
6x6 crossbar array GaV_4S_8 device

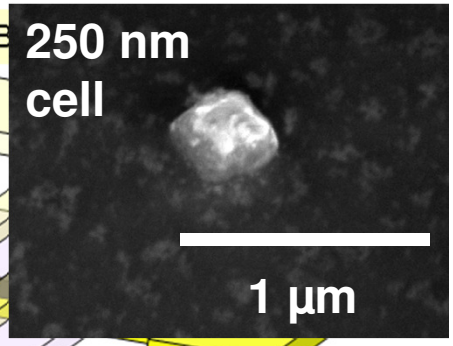
→ Cell sizes from 100 nm to 1 µm for scaling evaluation

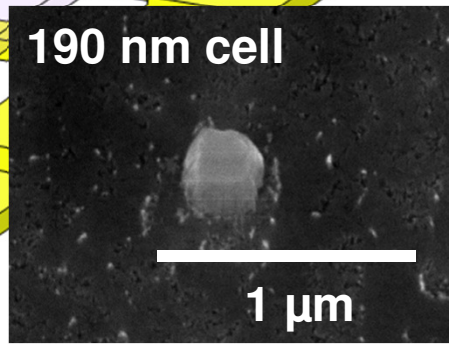


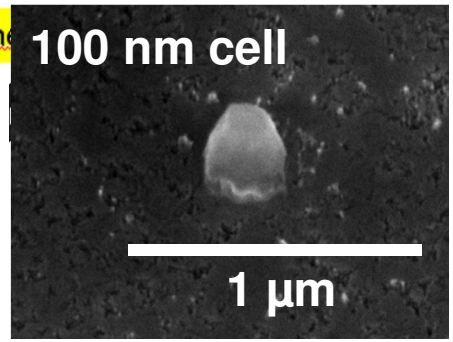












➔ First electrical characterizations currently running