Carton House - Summer NT 2011

Redox-Based Resistive Switching
- from Semiconductors to Chemiconductors?

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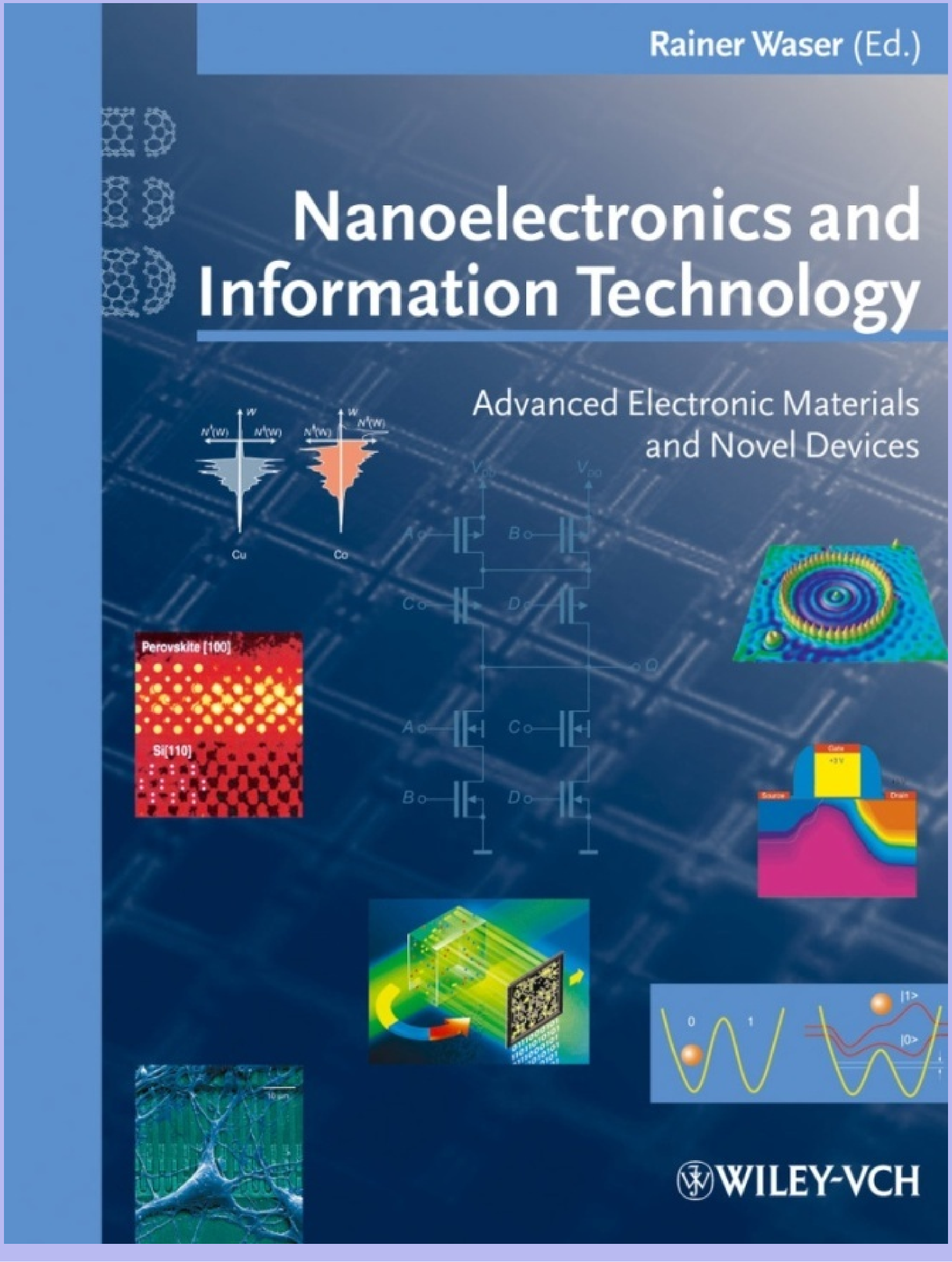
**Semiconductor Research Corporation,
Raleigh, USA



Rainer Waser (Ed.)

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and Novel Devices

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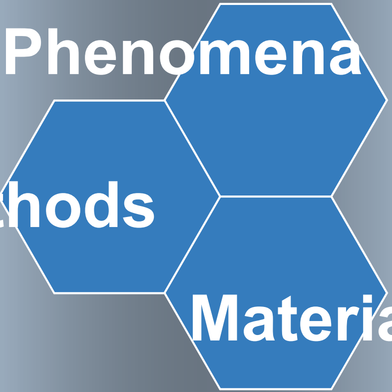
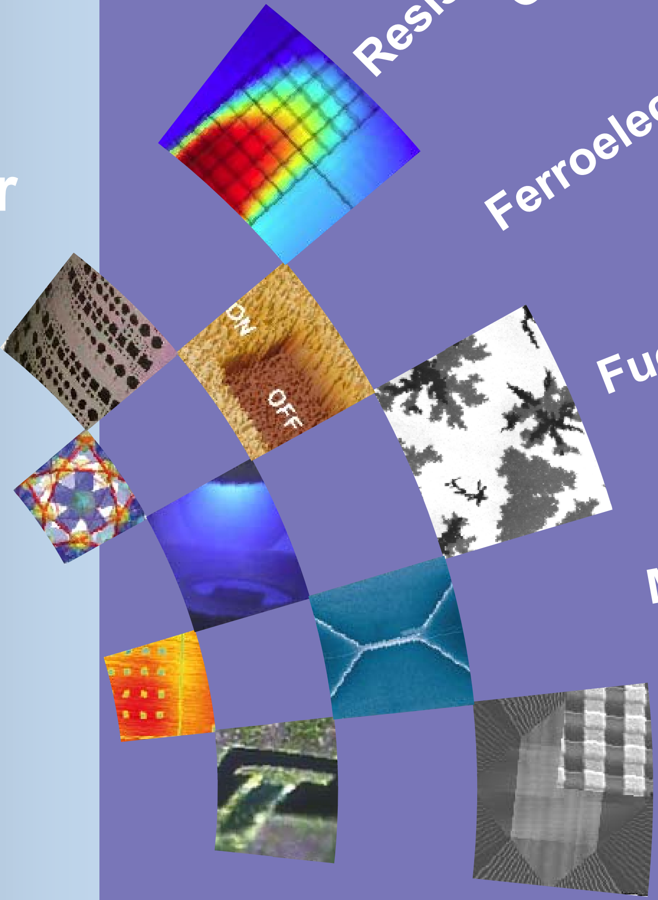


Phenomena

Methods

Materials



Resistive Switching Group

Ferroelectrics Group

Fuel cells & sensors Group

MEMS Group

Nanoarchitecture Group

Outline

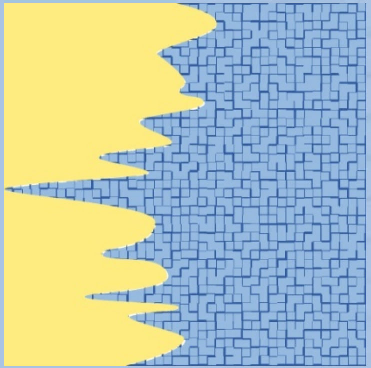
1 Introduction
2 Electrochemical metallization (ECM)
3 Valence change mechanism (VCM)
  – fundamentals, formation, switching, kinetics
4 Thermochemical mechamism (TCM)
5 Ultradense and 3-D stackable Architecture Concepts
6 Scaling Rules
7 Conclusions

1

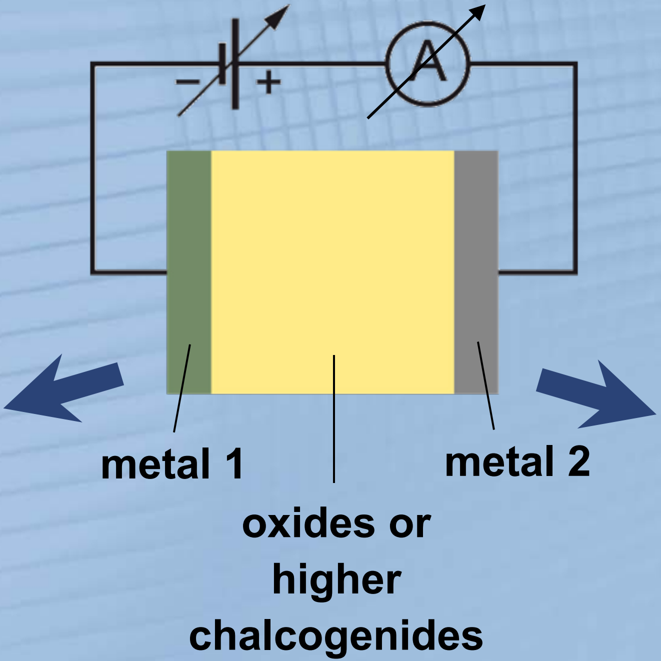
Introduction

Basic Definition of Resistive Random Access Memory

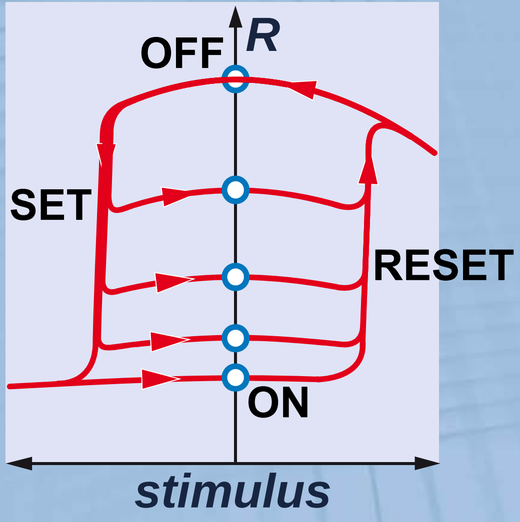
Structure



electronically
active
defects



Characteristics



memristive behaviour

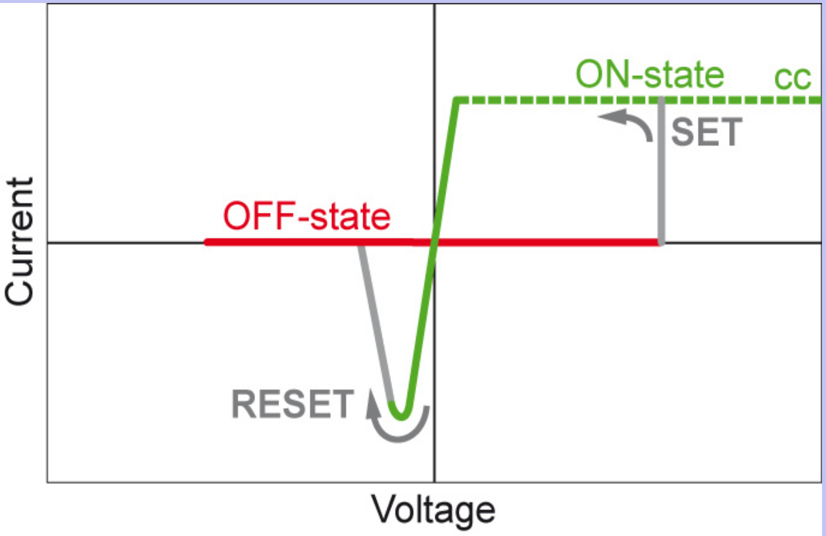
❍ Leon Chua (1971, 1976)

❍ R. S. Williams et al. (2008)

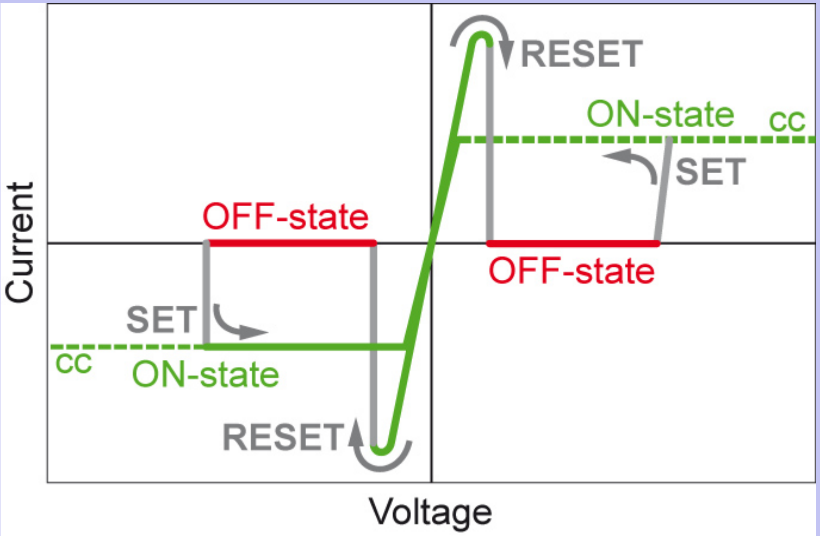
Basic Definition

Polarity modes

Bipolar (antisymmetrical)



Unipolar (symmetrical)



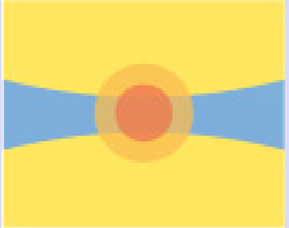
Classification of the working principle

Resistive Switching
by Thermal / Chemical / Electronic Mechanisms

Phase Change Mechanism

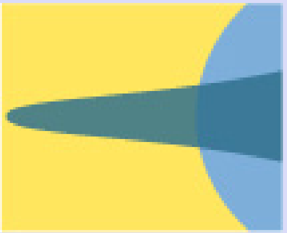
PCM

Thermo-chemical Mechanism



TCM

Valency Change Mechanism



VCM

Electro-chemical Metallization

ECM

Electrostatic/ Electronic Mechanism

EEM

Material Impact

Chalcogenide Dominated | Electrode Dominated

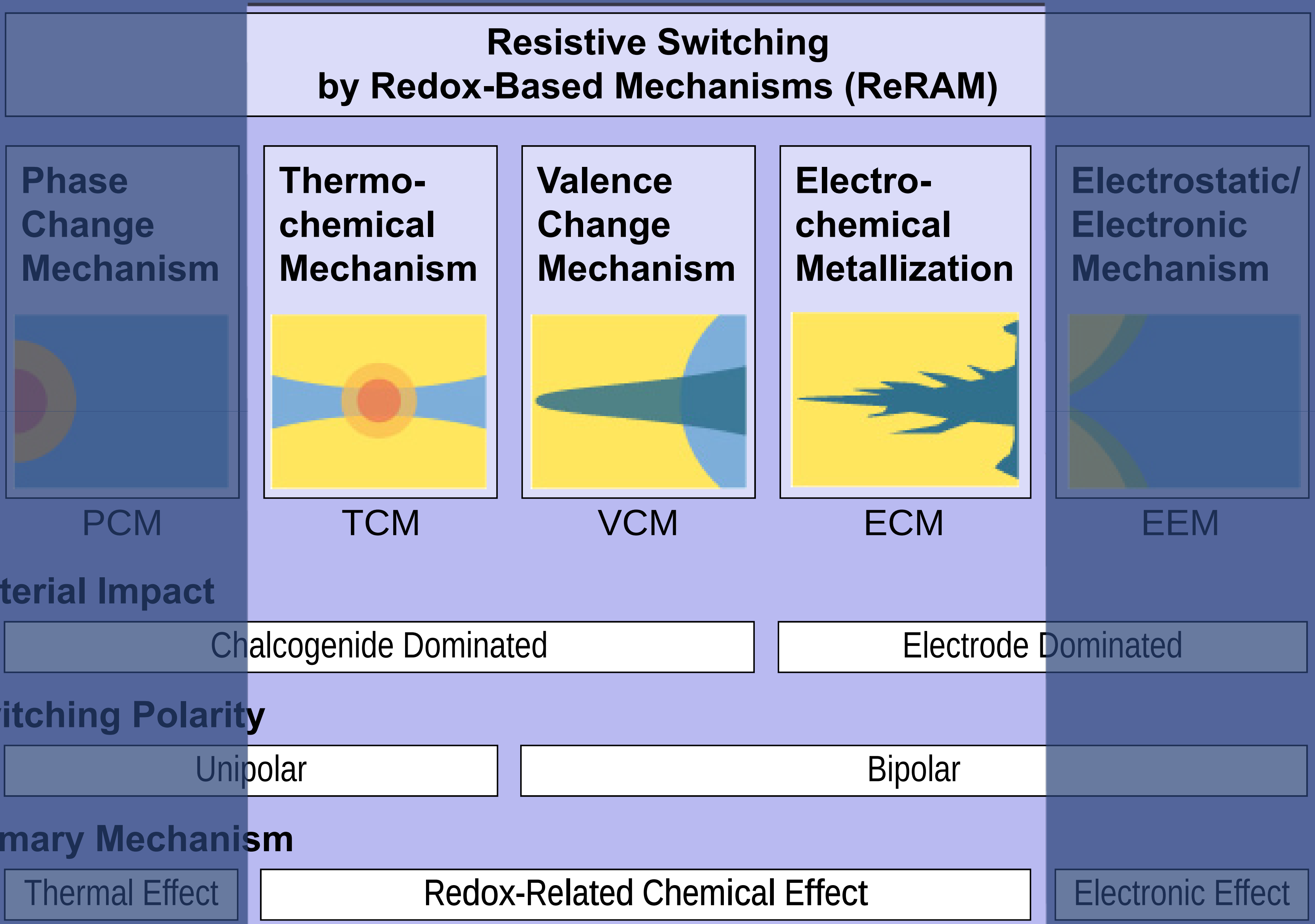
Switching Polarity

Unipolar | Bipolar

Primary Mechanism

Thermal Effect | Redox-Related Chemical Effect | Electronic Effect

Classification of the working principle



Resistive Switching by Redox-Based Mechanisms (ReRAM)

Phase Change Mechanism	Thermo-chemical Mechanism	Valence Change Mechanism	Electro-chemical Metallization	Electrostatic/ Electronic Mechanism
PCM	TCM	VCM	ECM	EEM

Material Impact

Chalcogenide Dominated | Electrode Dominated

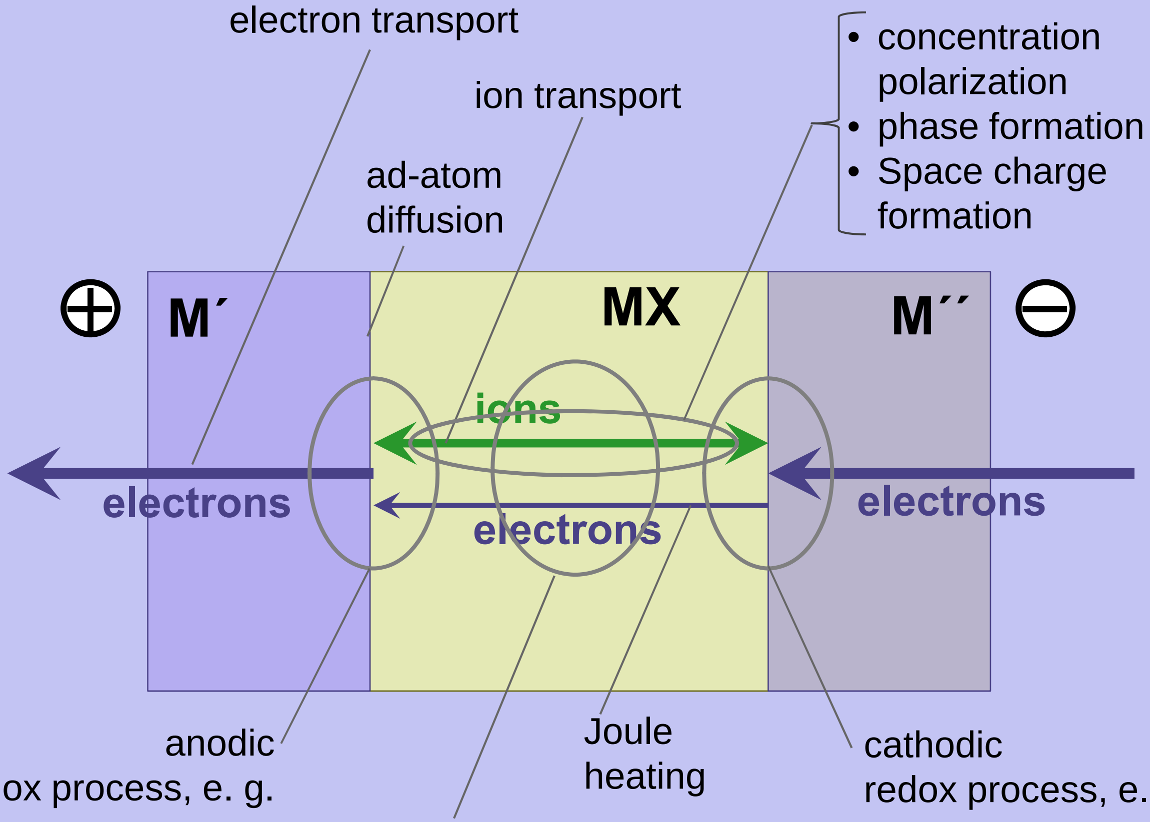
Switching Polarity

Unipolar | Bipolar

Primary Mechanism

Thermal Effect | Redox-Related Chemical Effect | Electronic Effect

Processes during redox-based switching



electron transport

ion transport

ad-atom diffusion

- concentration polarization
- phase formation
- Space charge formation

anodic redox process, e. g.

$$MX + \delta e^- \xleftarrow[\text{oxidation}]{} MX_{1-\delta} + \delta X^-$$

Joule heating

thermodiffusion -> thermochemical redox process

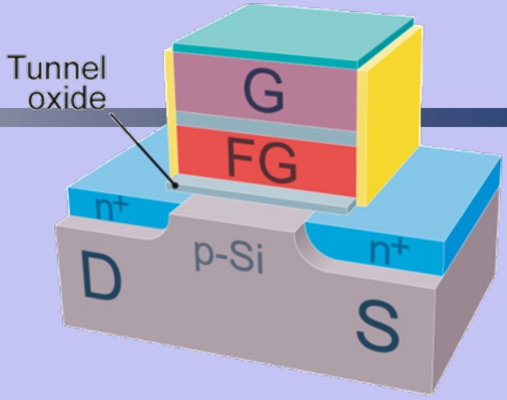
$$2MX \rightleftharpoons MX_{1-\delta} + MX_{1+\delta}$$

cathodic redox process, e. g.

$$MX + \delta e^- \xrightarrow{\text{reduction}} MX_{1-\delta} + \delta X^-$$

Note: these are <u>all</u> conceivable (relevant) processes during forming and switching.
The actual processes depend on the type of ReRAM

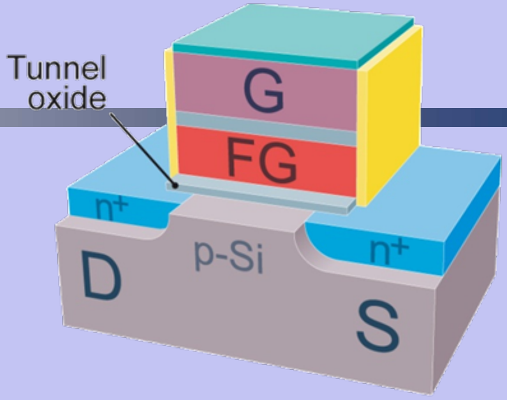
Requirements



... to compete with Flash

Endurance:	**$> 10^7$ cylces**	(Flash $10^3 \ldots 10^7$)
Resistance ratio:	**$R_{OFF} / R_{ON} > 10$**	
Scalability:	**F < 22 nm and/or 3-D stacking**	
Write voltage:	**approx. 1 ... 5 V**	(Flash > 5 V)
Read voltage:	**0.1 ... 0.5 V**	
Write speed:	**< 100 ns**	(Flash > 10 μs)
Retention:	**> 10 yrs**	

Requirements



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Retention:	**> 10 yrs**

Voltage – time dilemma

Kinetics of switching process requires non-linearity of > 15 orders of magnitude

Link between devices and physics

Criteria of ReRAM

1. Existence of a (compositional) state variable x, such that

$$I = G(x,V)\cdot V$$

2. Kinetics of change of *x* controlled by V

$$\dot{x} = f(x,V)$$

3. Ultrahigh non-linearity of the kinetics

$$\dot{x} = x_0[(V - V_{\mathrm{th}})/V_0]^n \quad \text{with } n >> 1$$

4. Limits to the range of *x*

$$x_{\min} \le x \le x_{\max}$$

Memristors
as defined
by Leon Chua
[1971, 1976, 2011]

2

Electrochemical metallization (ECM) - Cation-migration redox systems

- basic process
- non-linear switching kinetics

Electrochemical Metallization (ECM)

Operation

ON-switching:
Reduction @ cathode
→ Ag filament formation

$Ag^+ + e‘ \rightarrow Ag$
M. Faraday (1834)

OFF-switching:
Oxidation @ anode

$Ag \rightarrow Ag^+ + e‘$

Electrolyte

* amorphous $GeSe_{2+x}$
and GeS_{2+x}
* Disordered and amorphous
sulfides and oxides

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Electrolyte

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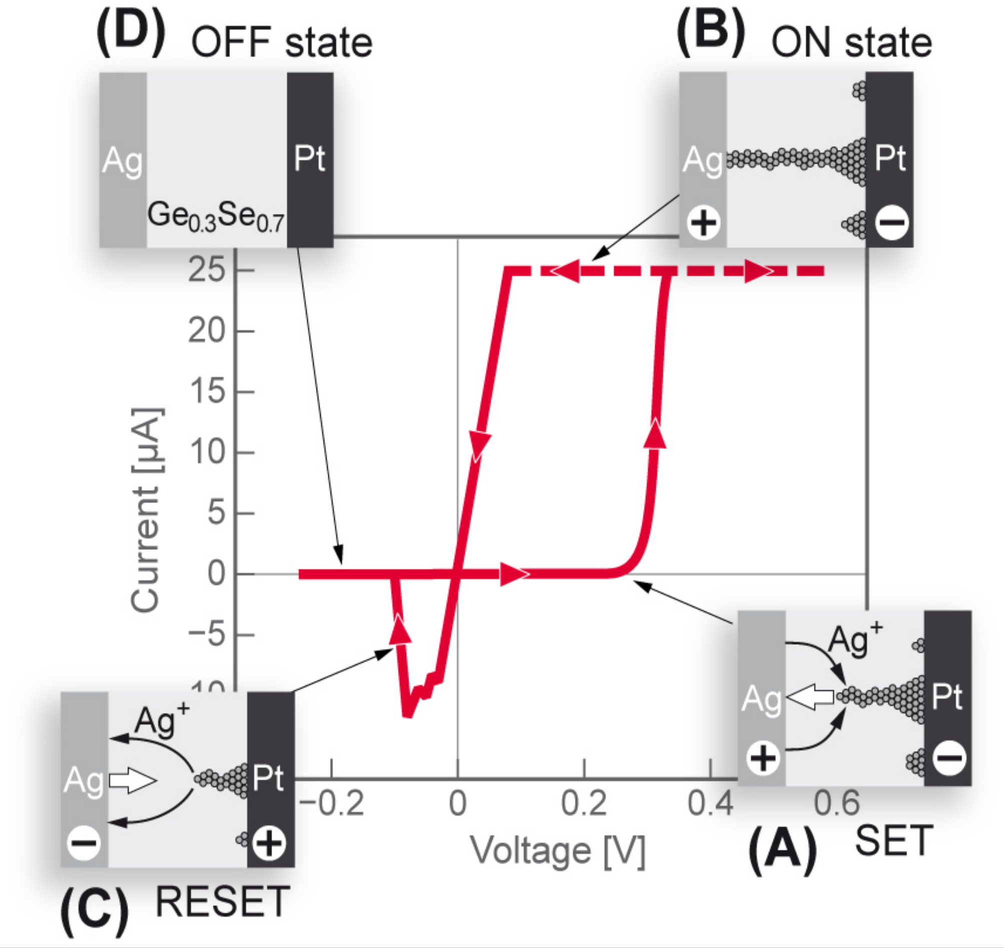
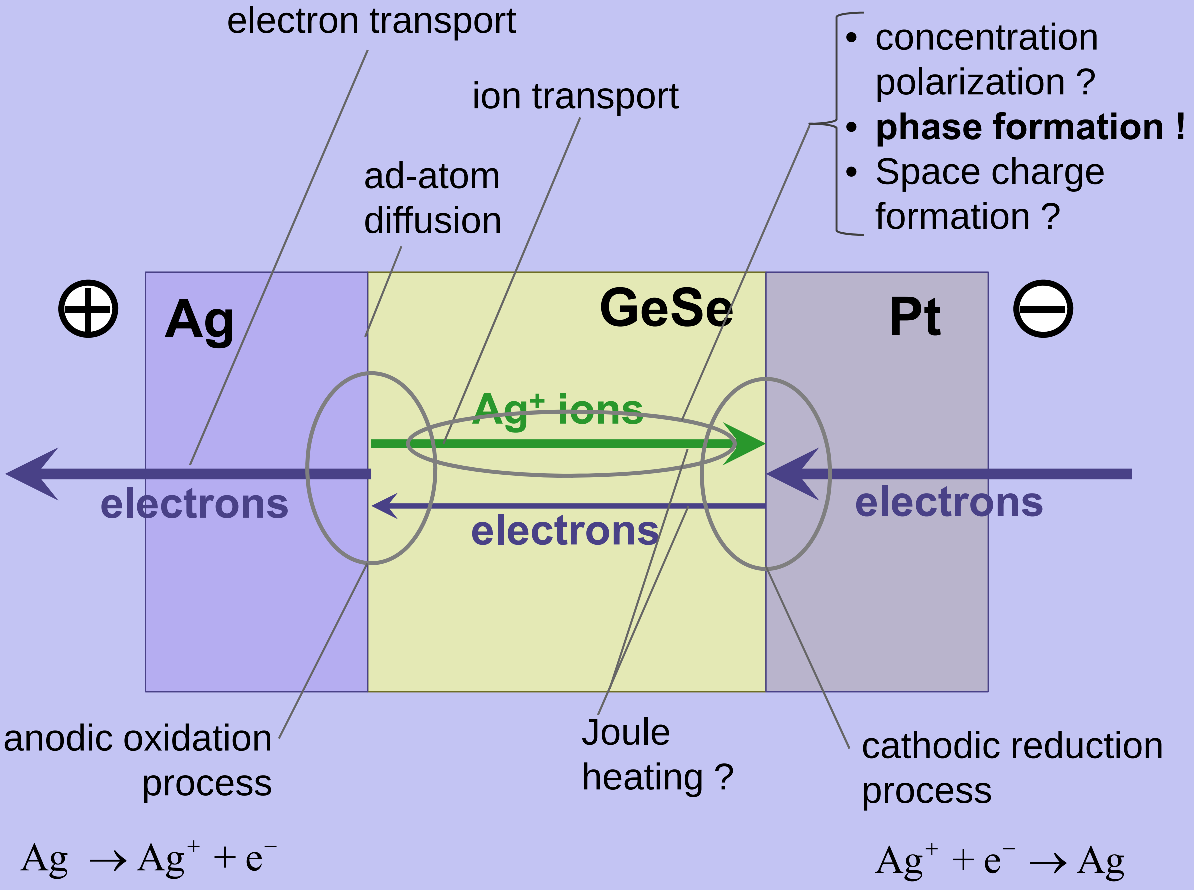
* Disordered and amorphous sulfides and oxides



C. Schindler et al., IEEE T-ED, 54 (2007) 2762

Processes during ECM switching



$Ag \rightarrow Ag^+ + e^-$

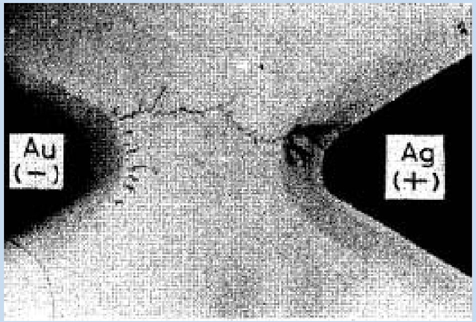
$Ag^+ + e^- \rightarrow Ag$

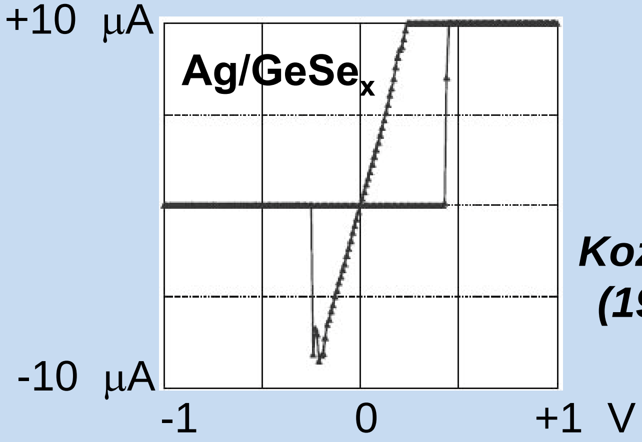
Sketch shows initial stages of the SET process

Electrochemical Metallization (ECM) Memory

Historical aspects

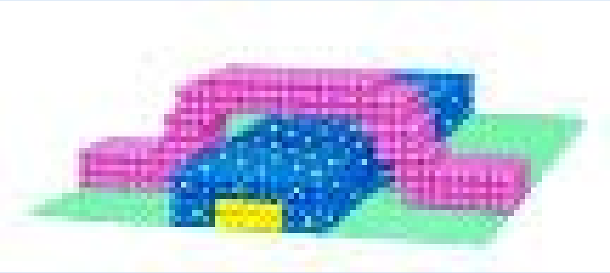
Hirose & Hirose (1976)

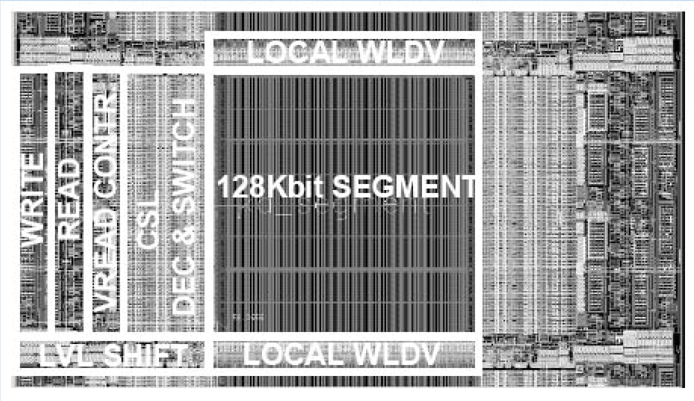




Kozicki (1997)

Aono et al (2005)



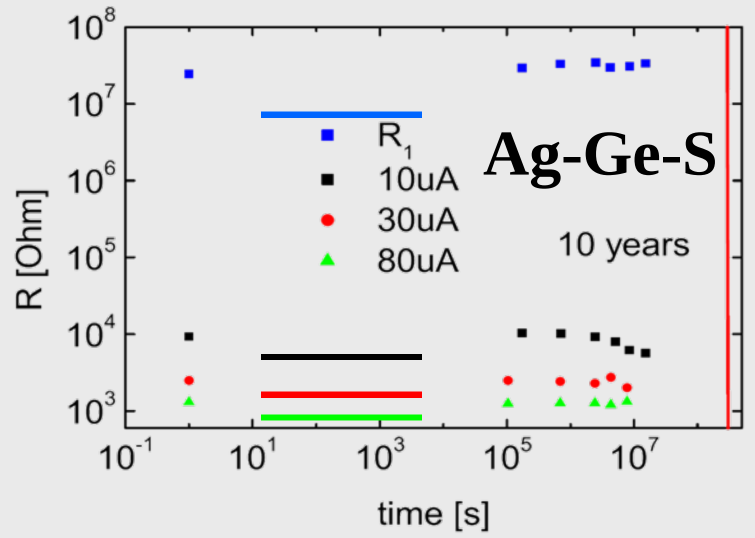


Qimonda group (2006)

Scaling potential: multibit storage

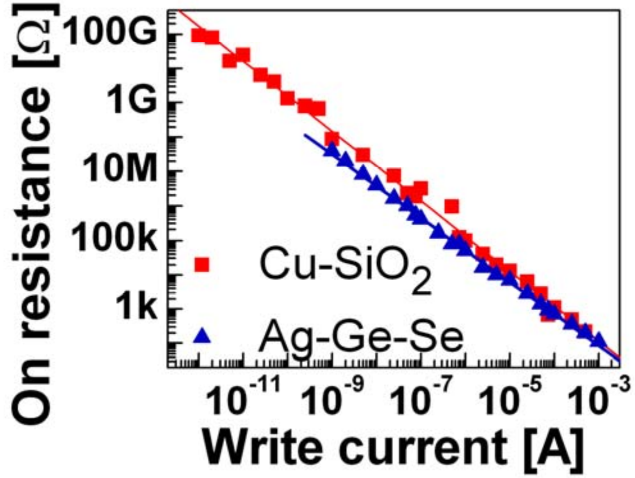
… true memristive behaviour

Drive towards an ever increasing memory density:
- storage of multiple states per cell
- shrinking the cell size



C. Liaw (2007)

Experimental results



C. Schindler (2008)

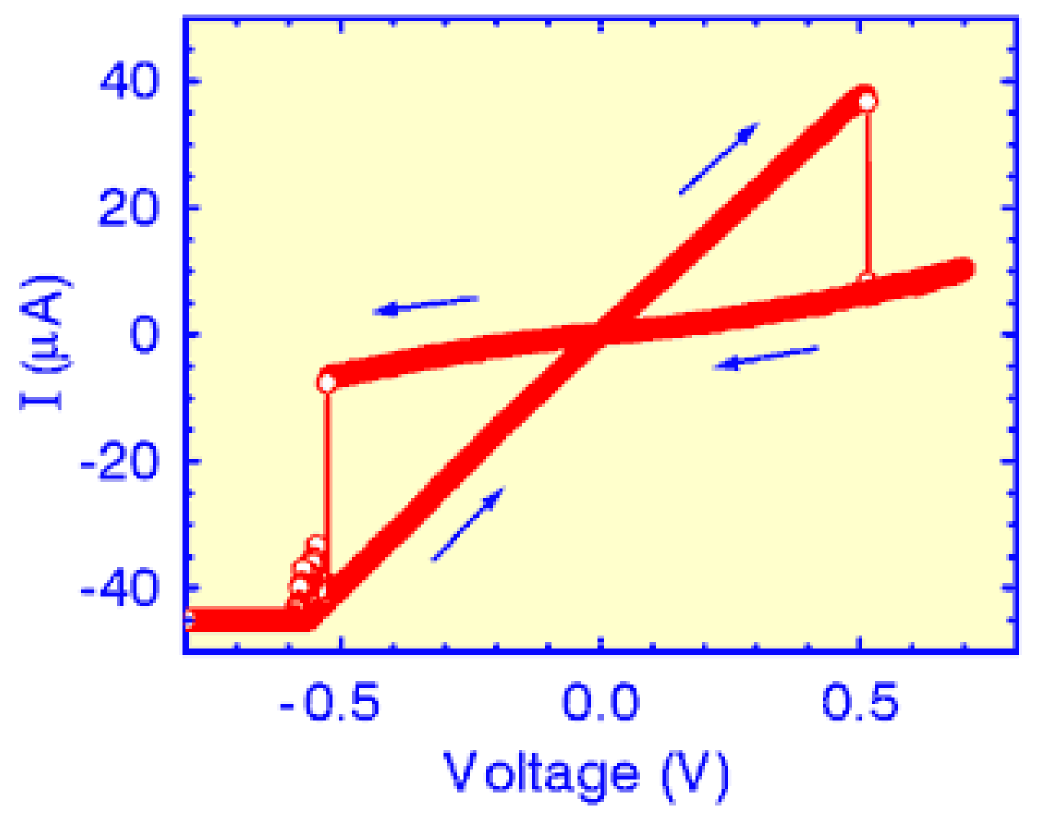
3

Valence change mechanism (VCM) - anion-migration redox systems

- TiO_2 and $SrTiO_3$ as model systems
  - – defect related electronic structure
- forming process
- filamentary switching

Bipolar resistive switching in transition metal oxides

Example **$SrZrO_3$ (0.2 at% Cr)**



A. Beck, J. G. Bednorz, Ch. Gerber, C. Rossel and D. Widmer, Appl. Phys. Lett. 77, 139 (2000).

Thin film systems

- $SrZrO_3$, $SrTiO_3$
- $(Pr,Ca)MnO_3$
- TiO_2
- etc.

Single crystals

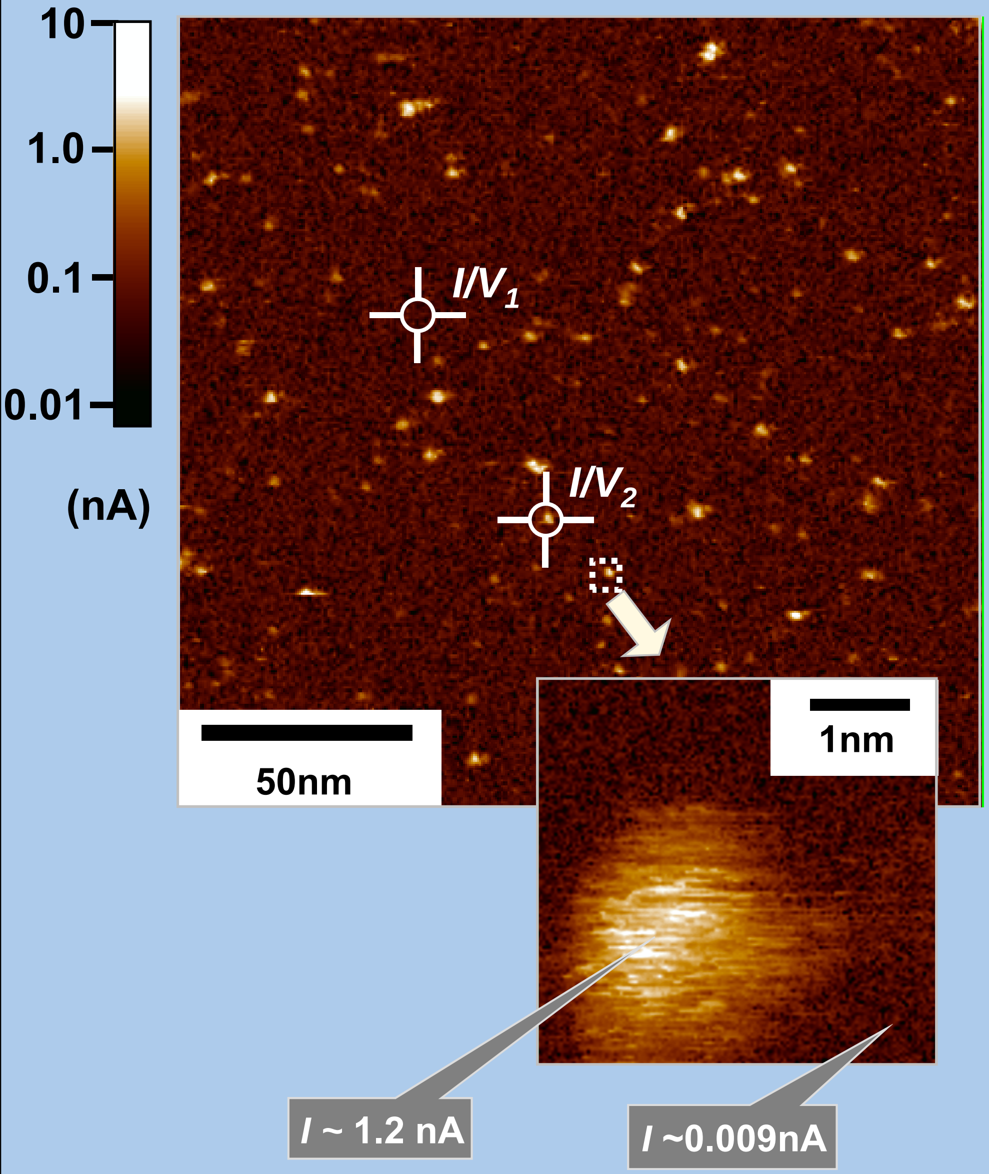
- $SrTiO_3$
- TiO_2

Characteristics

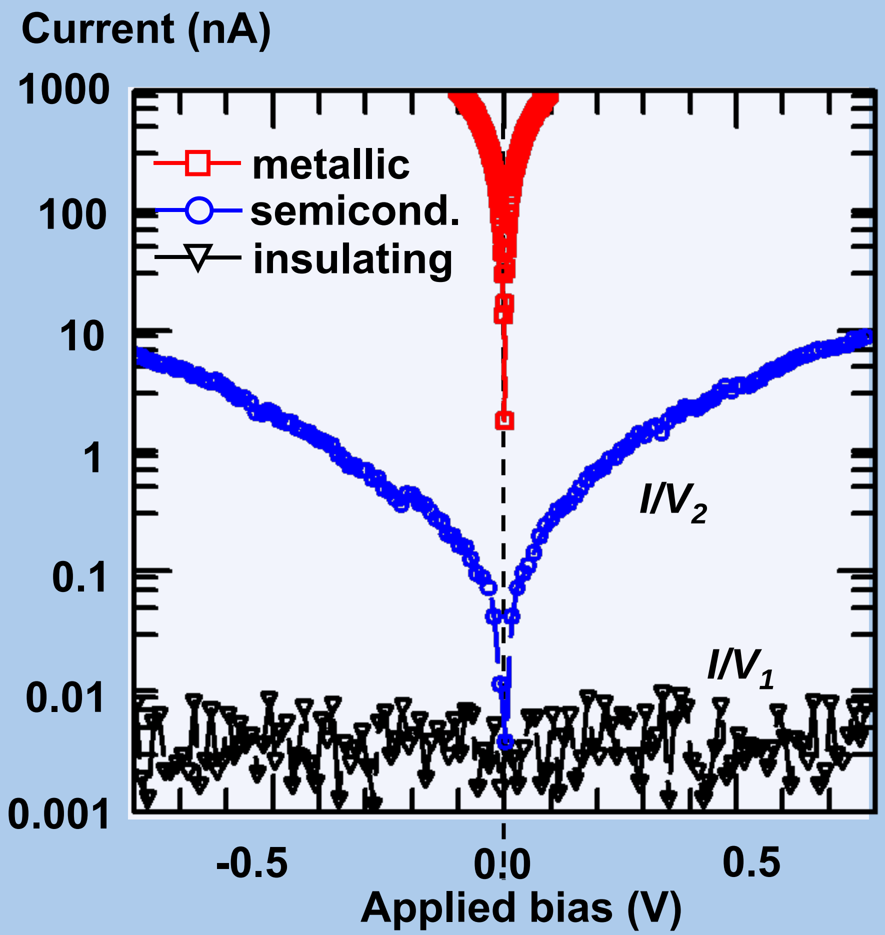
⇨ **Typically forming required**

⇨ **Bipolar resistive switching by asymmetric cell**

Thermal preformation by reduction annealing: conductive Tip AFM Mapping – types of I-V Characteristics



SrTiO$_3$ s.c. thermally reduced at 850 C, pO2 ~ 10^{-20} bar

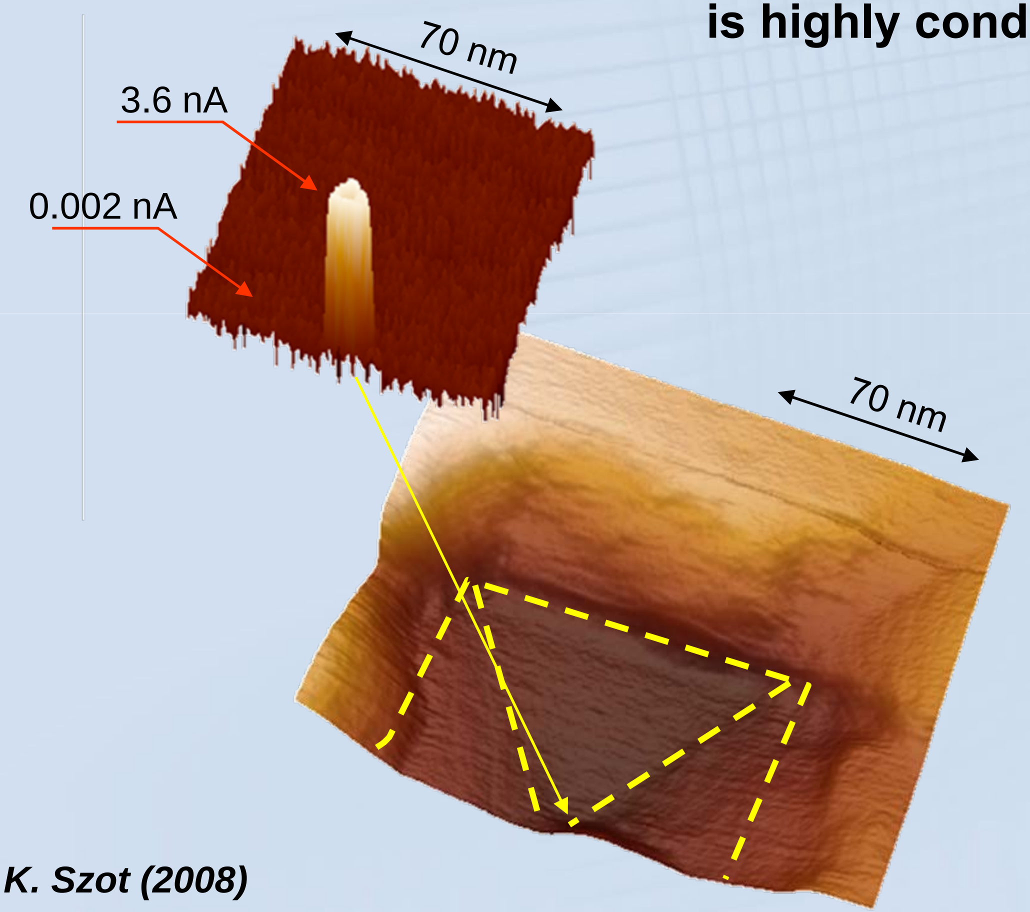


K.Szot et al., Nature Mat. (2006)

Extended defects in $SrTiO_3$ & their electronic structure

Dislocation exit ...

... at a center of an etch pit is highly conducting (!)



Procedure

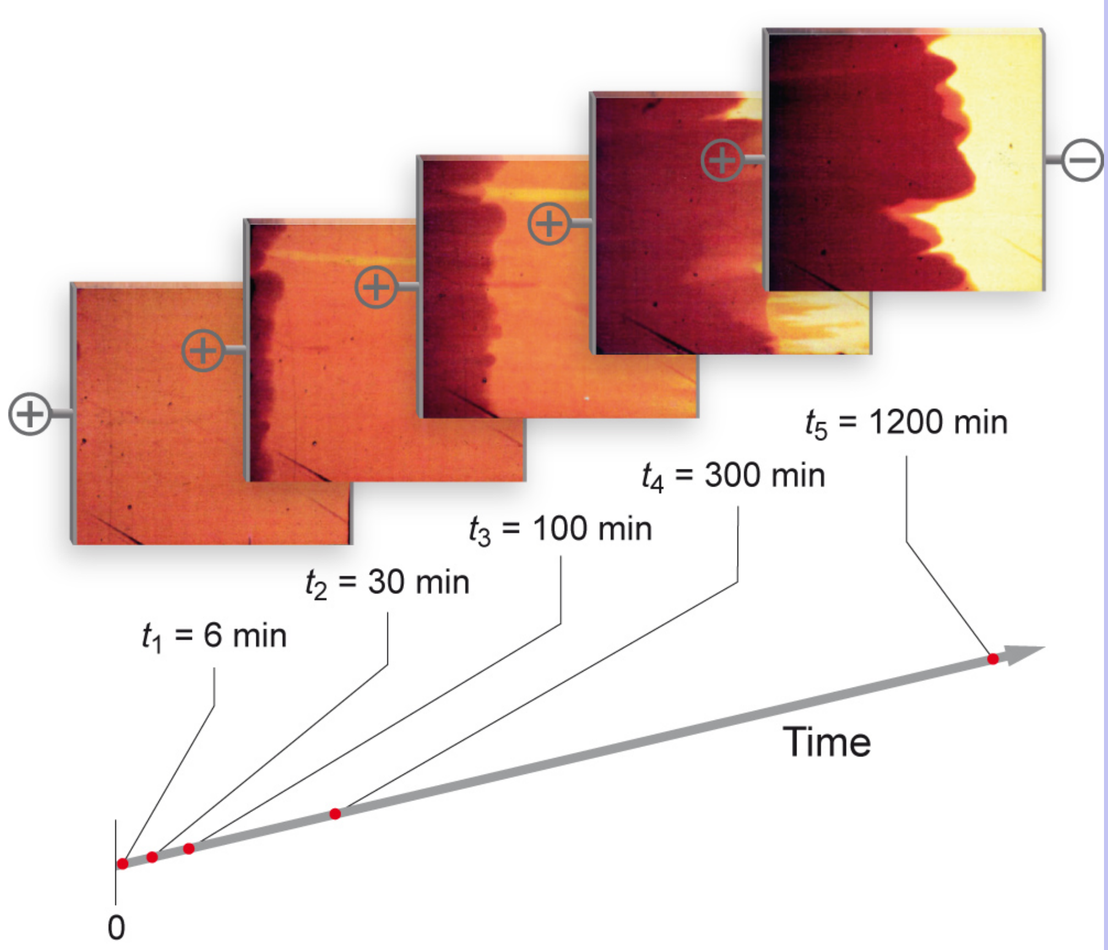
- Surface chemically etched
- reduction anneal at 1000 K
- simultaneous AFM topography and LC-AFM current scan

K. Szot (2008)

Formation process - $SrTiO_3$ crystal as a model system

Electrochemical concentration polarization

... based on oxygen vacancy drift-diffusion in STO:Fe as a mixed ionic-electronic solid electrolyte Pt/STO:Fe/Pt cell



5x5 mm^2 / 0.5 mm

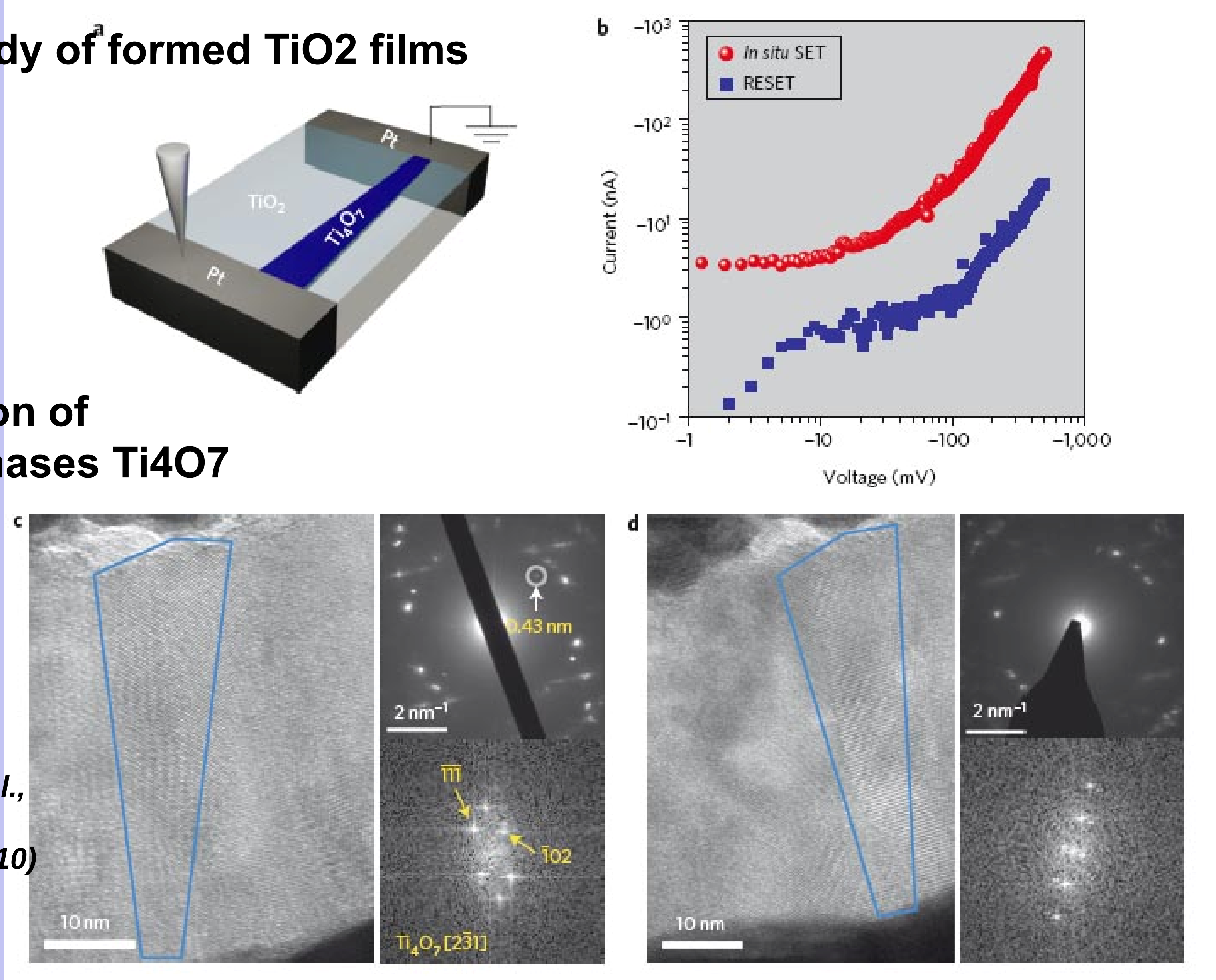
T = 453 K

E = 1 kV/cm

R. Waser, in: Ferroelectric Ceramics, Birkhäuser (1991)

Forming – Phase formation

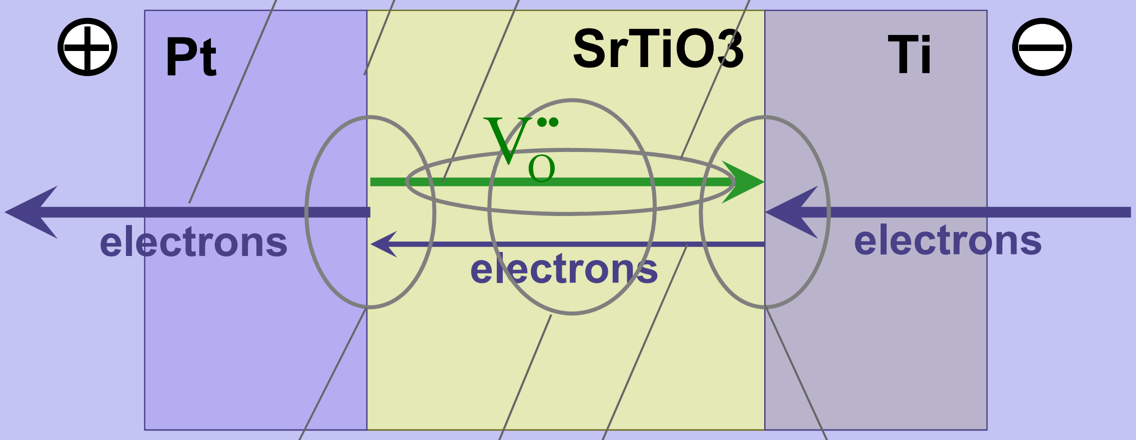
HRTEM study of formed TiO2 films



Identification of
Magnelli phases Ti4O7

D. H. Kwon et al.,
Nature Nano-
technology (2010)

Processes during formation into the OFF state



electron transport

ion transport

ad-atom diffusion

- **concentration polarization !**
- **phase formation !**
- Space charge formation ?

Pt

SrTiO3

Ti

⊕

⊖

$V_O^{\bullet\bullet}$

electrons

electrons

electrons

anodic redox process, e. g.

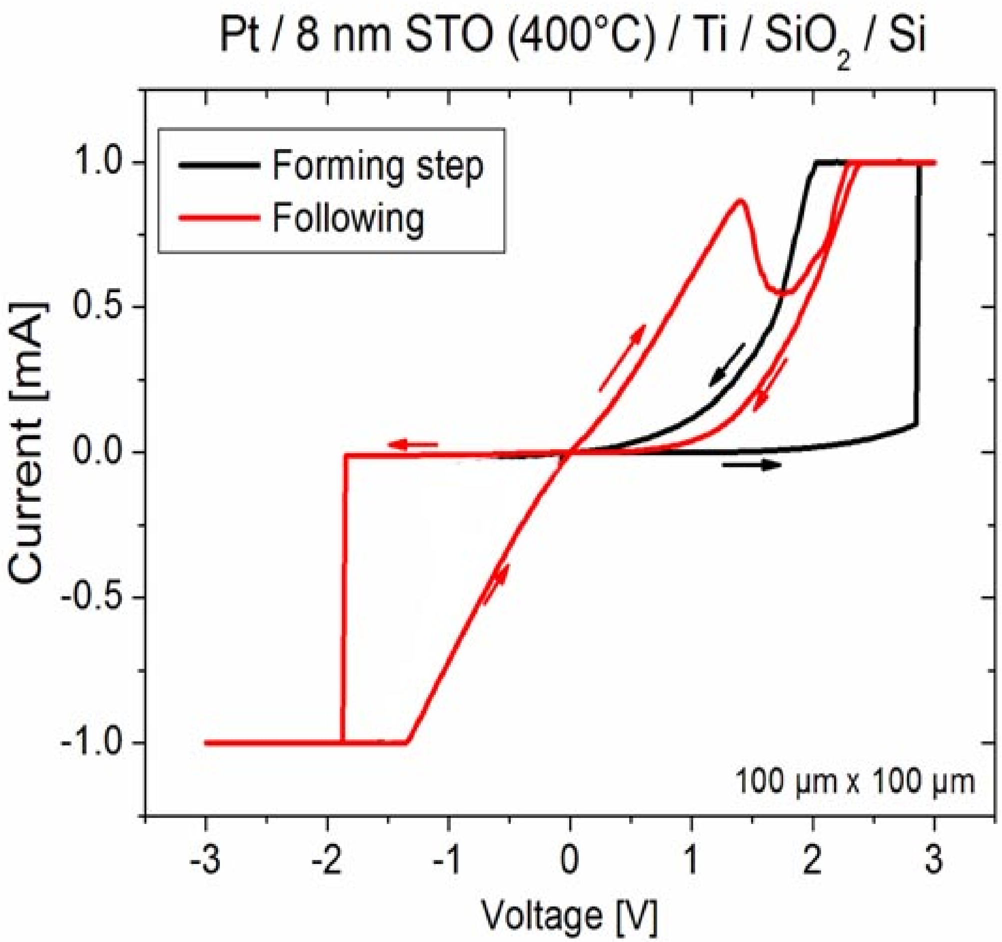
$$\frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e^- \xleftarrow[\text{oxidation}]{} O_O$$

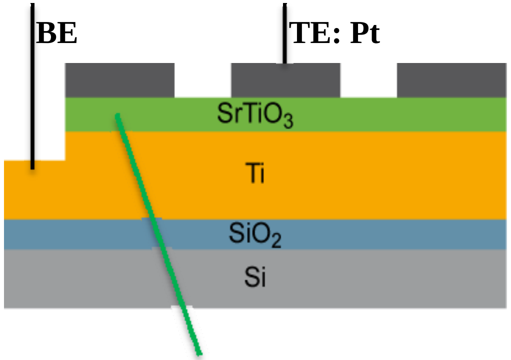
Joule heating

thermochemical redox process ?

no cathodic redox process, i. e. ion blocking

Forming into the OFF state – an example

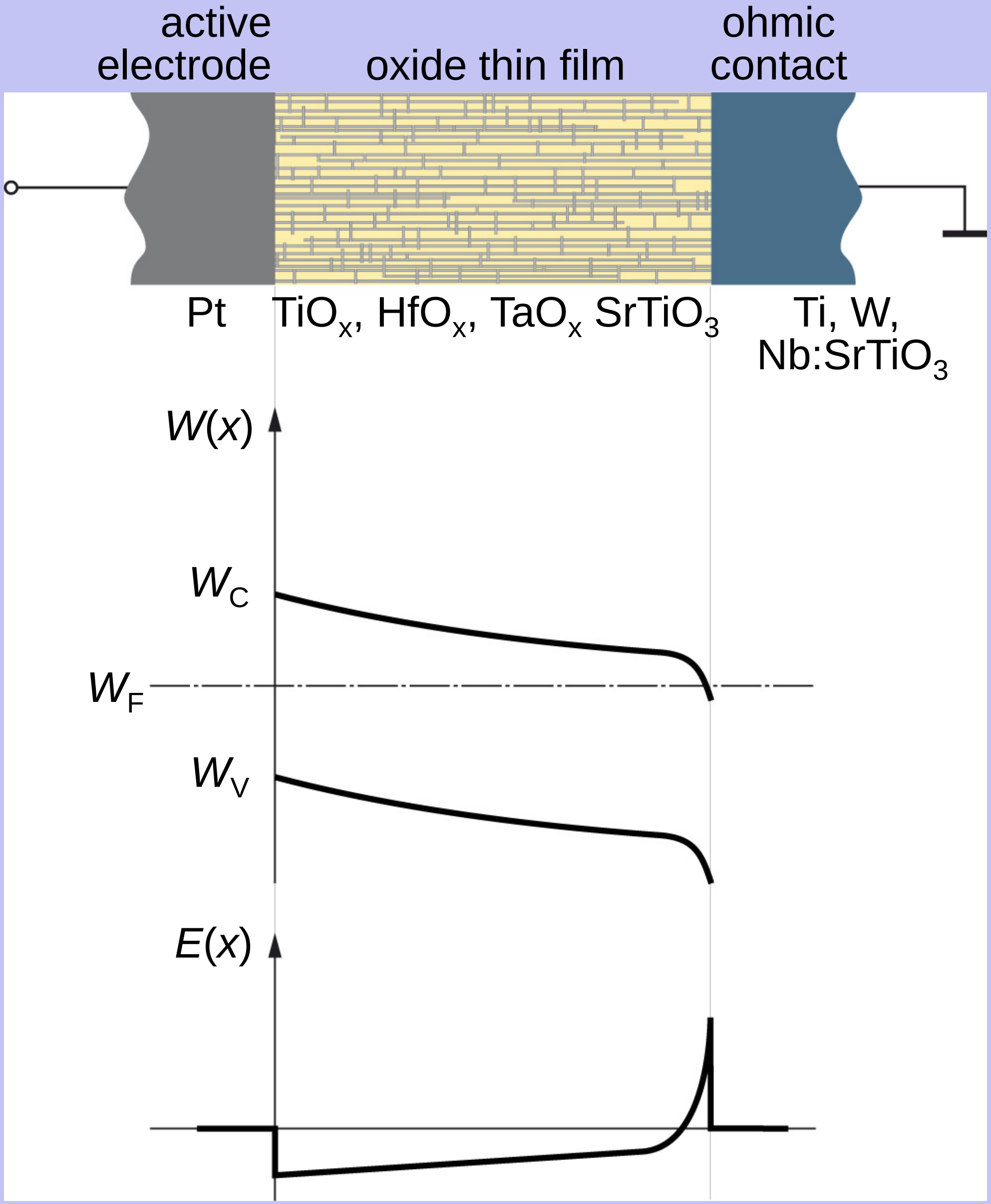




SrTiO$_3$: nanocrystalline thin film by sputter deposition

S. Schmelzer et al.
(to be published)

Details of the forming process: Initial situation

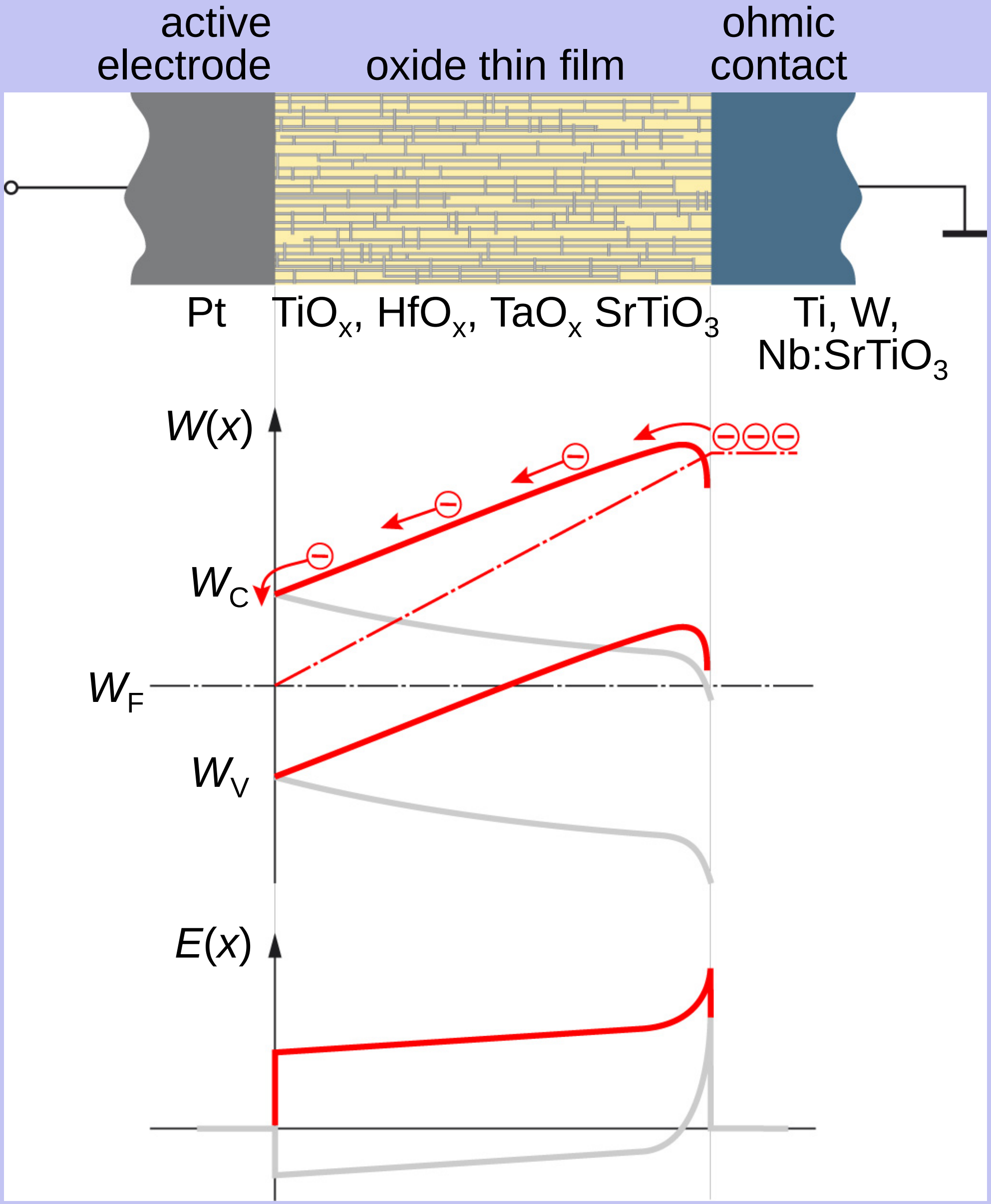


Metal / n-semiconductor Schottky diode

Band diagram of the fully depleted oxide thin film

Profile of the electrical field

Details of the forming process: electronic process



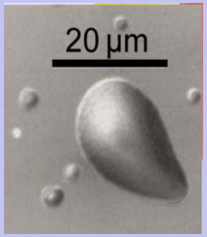
Metal / n-semiconductor
Schottky diode
- under forward bias

Band diagram for
forward biased cell
- electron flow

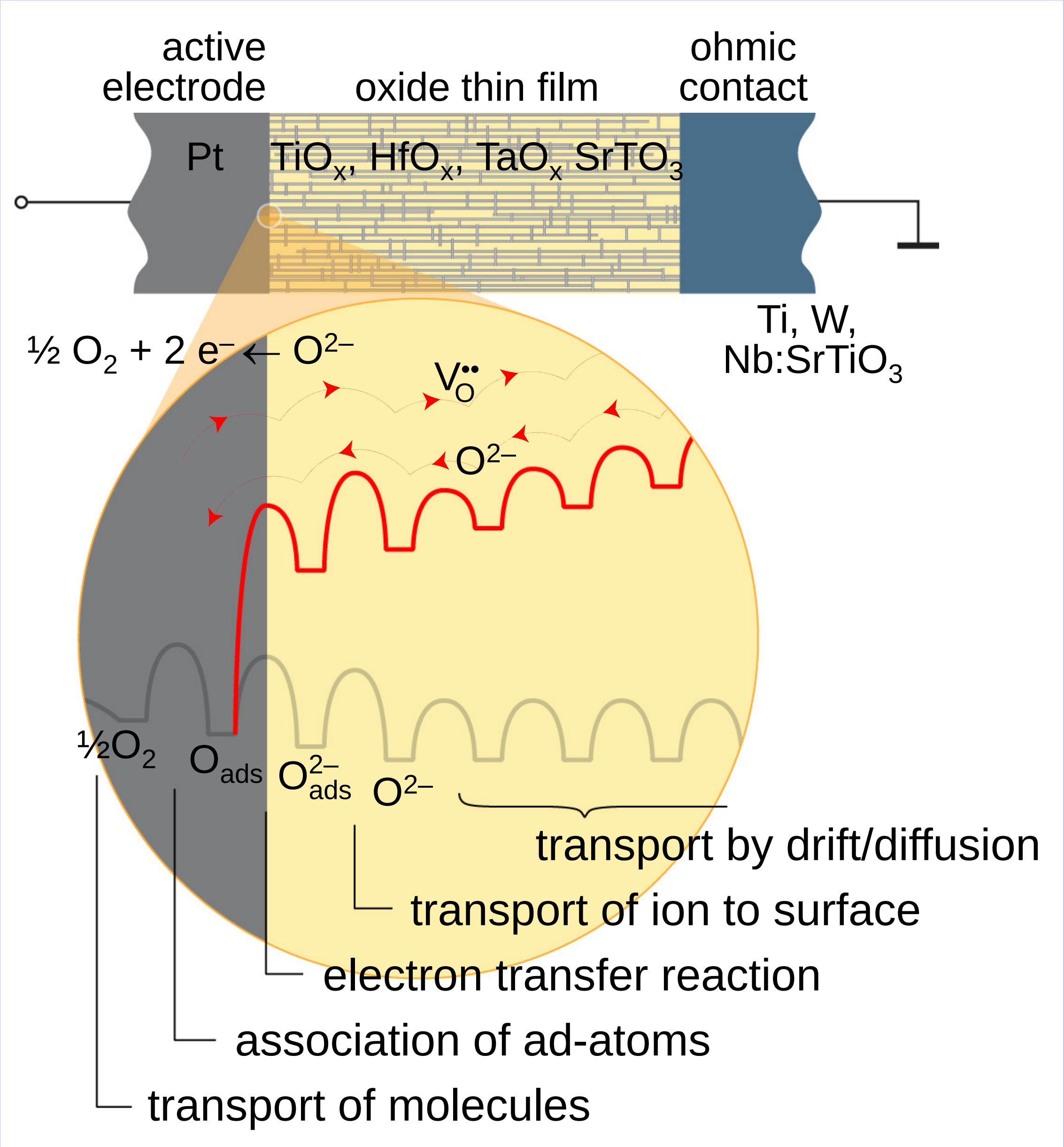
Profile of the
electrical field

Details of the forming process: ionic process

Processes involving ions:
1. anodic oxidation of O^{2-}
2. generation of oxygen vacancies and their drift towards the cathode

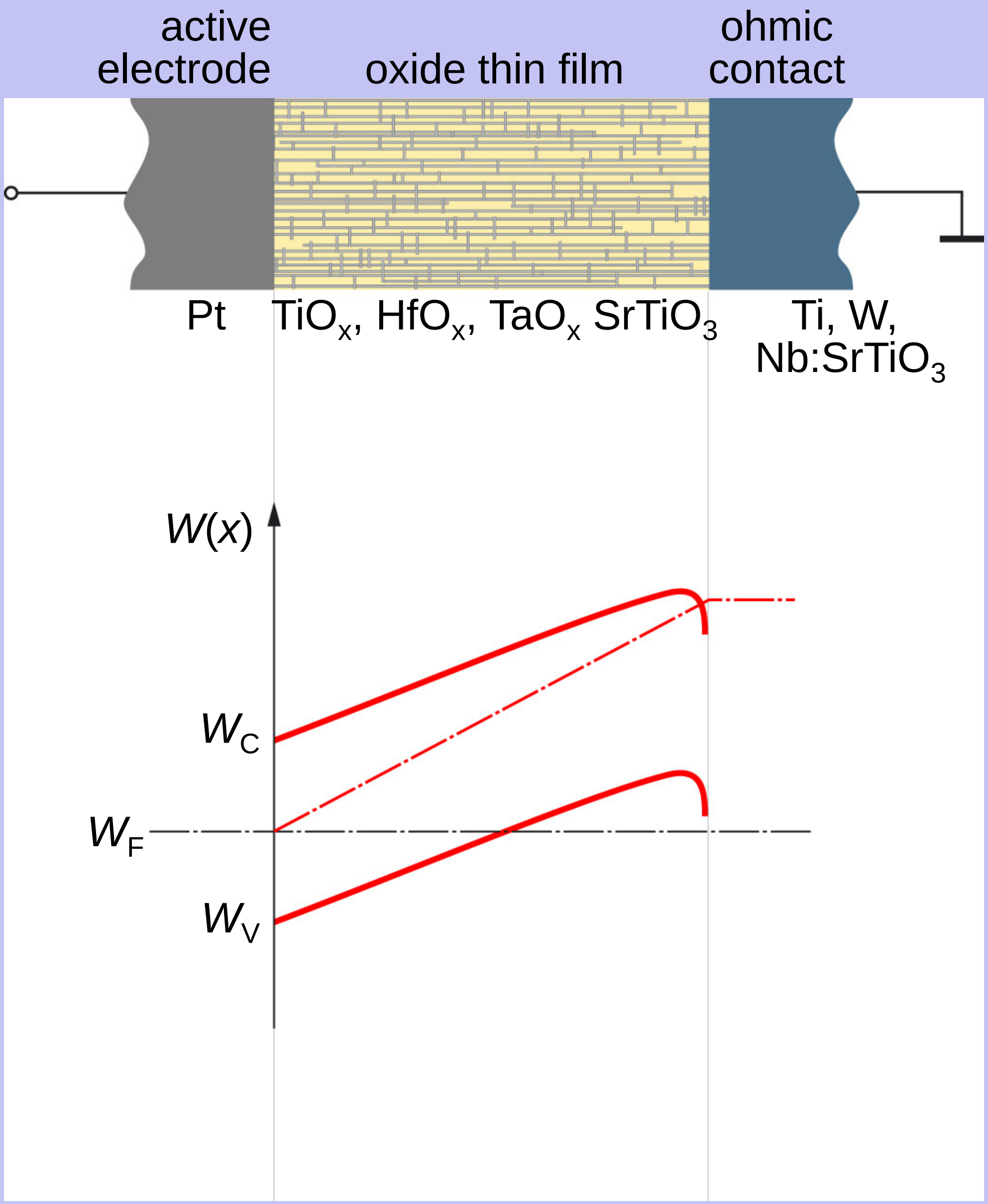


O_2 are released to the gas phase or adsorbed by the grain boundaries of the Pt electrode



Details of the forming process: overall process

- generation of oxygen vacancies at the anode
- drift towards the cathode
- formation of a virtual cathode which approaches the anode



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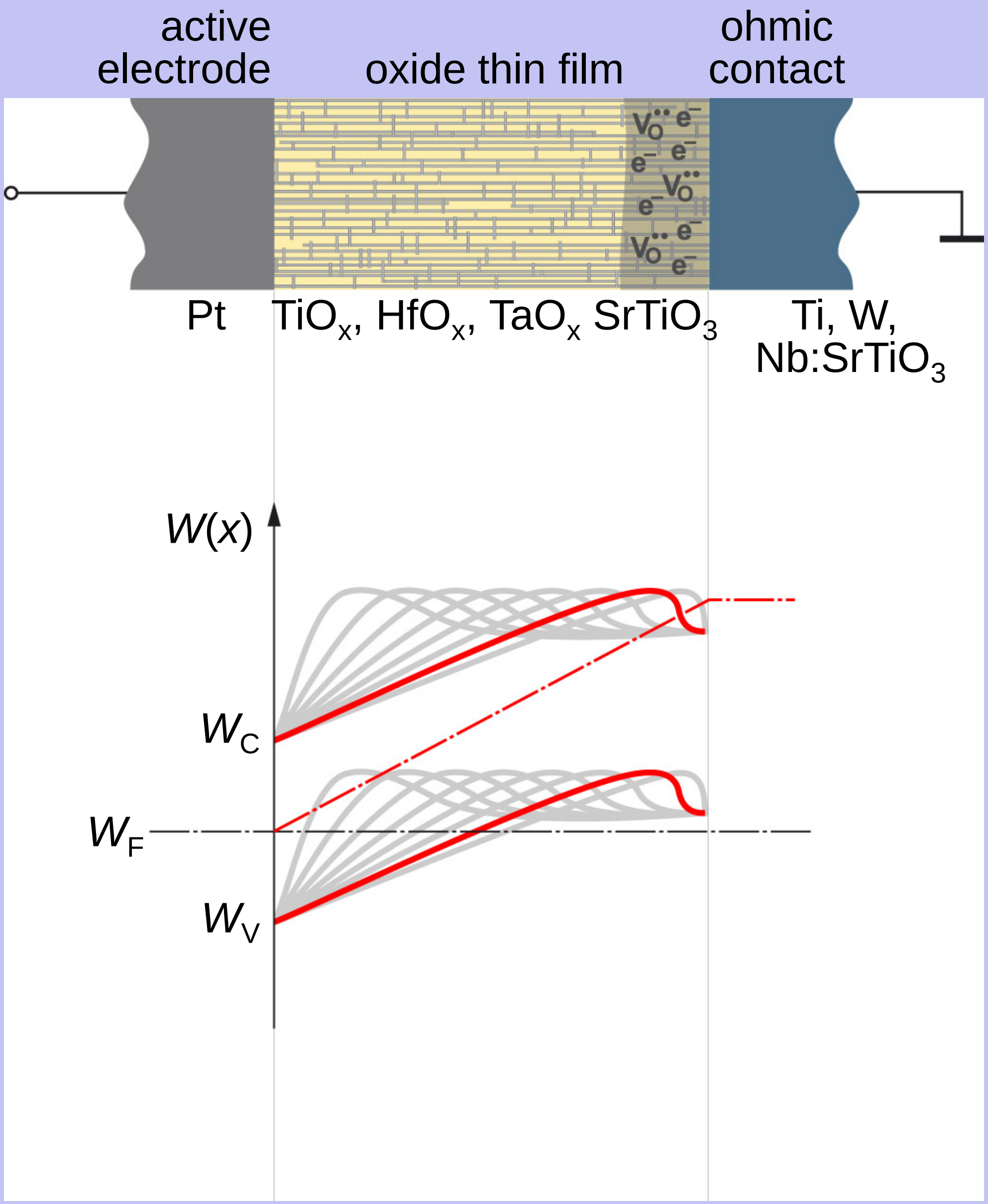

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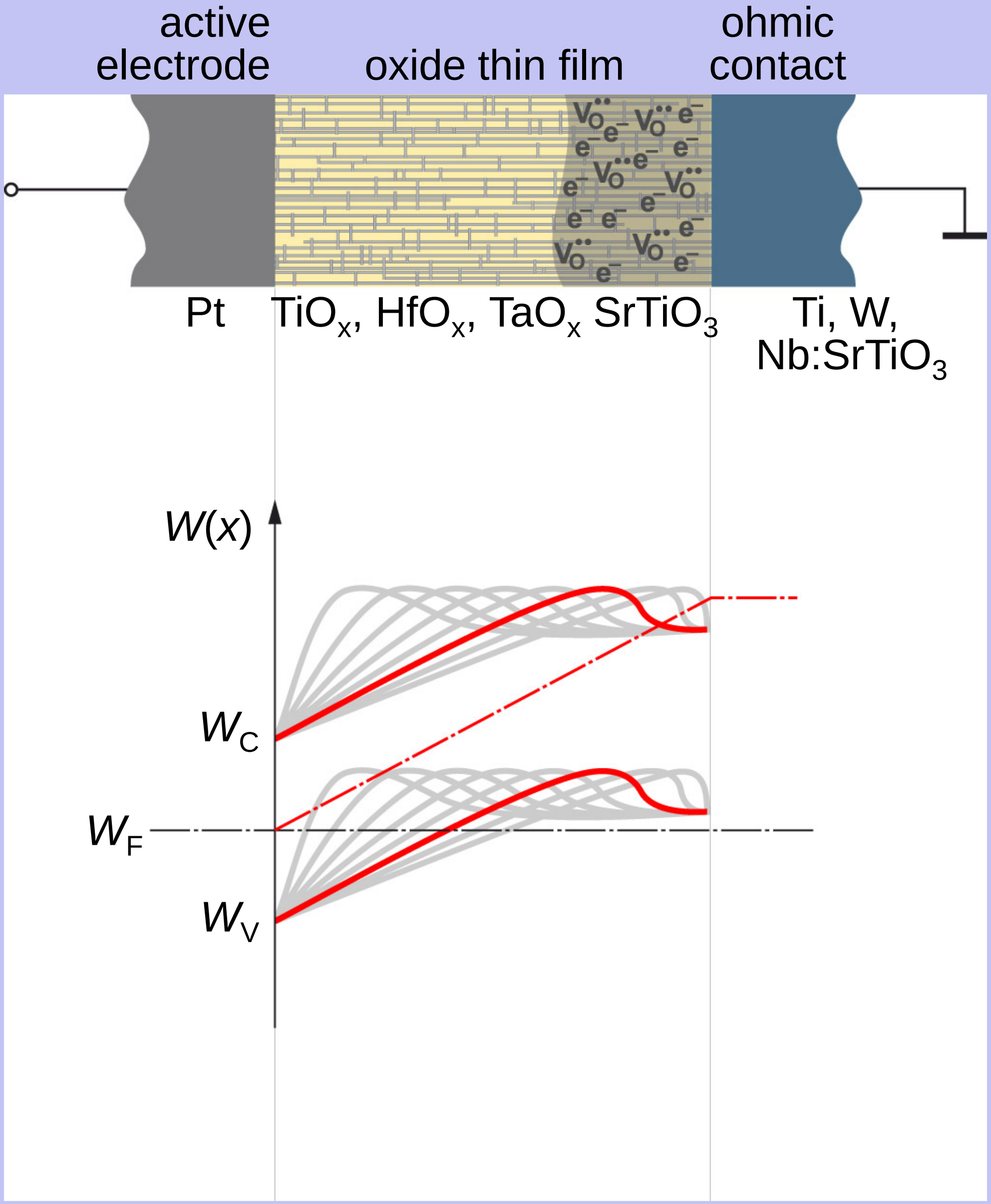

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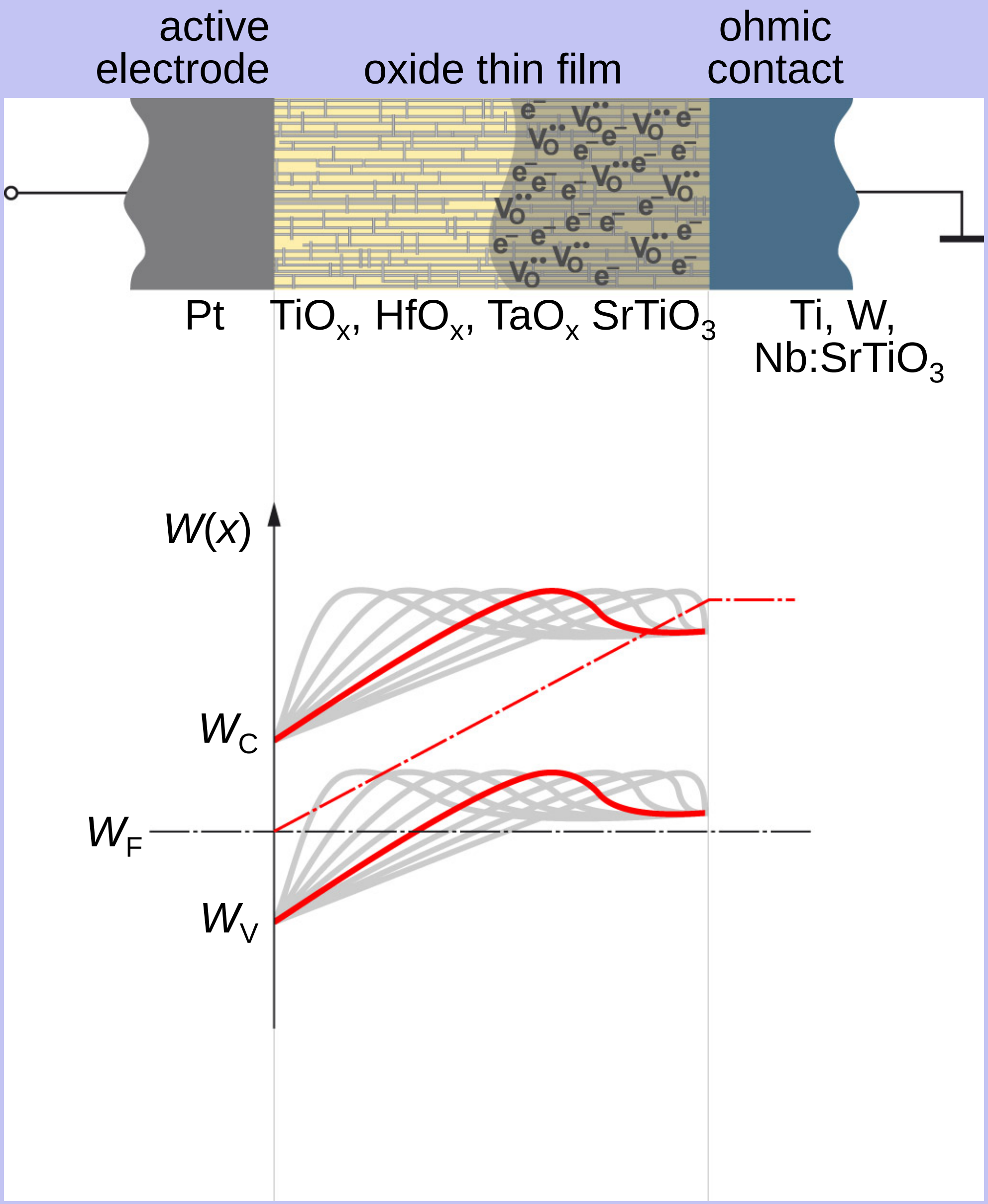

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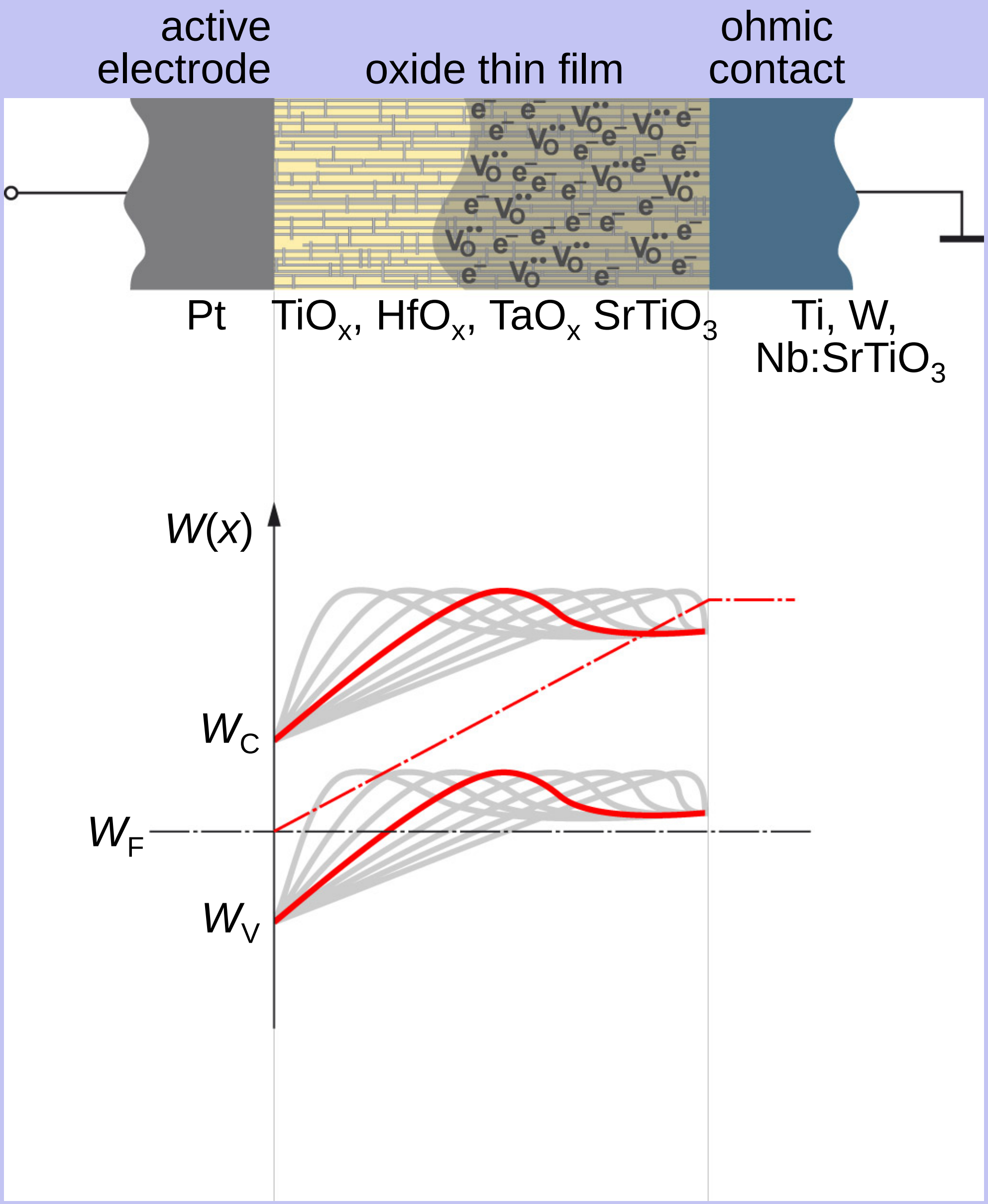

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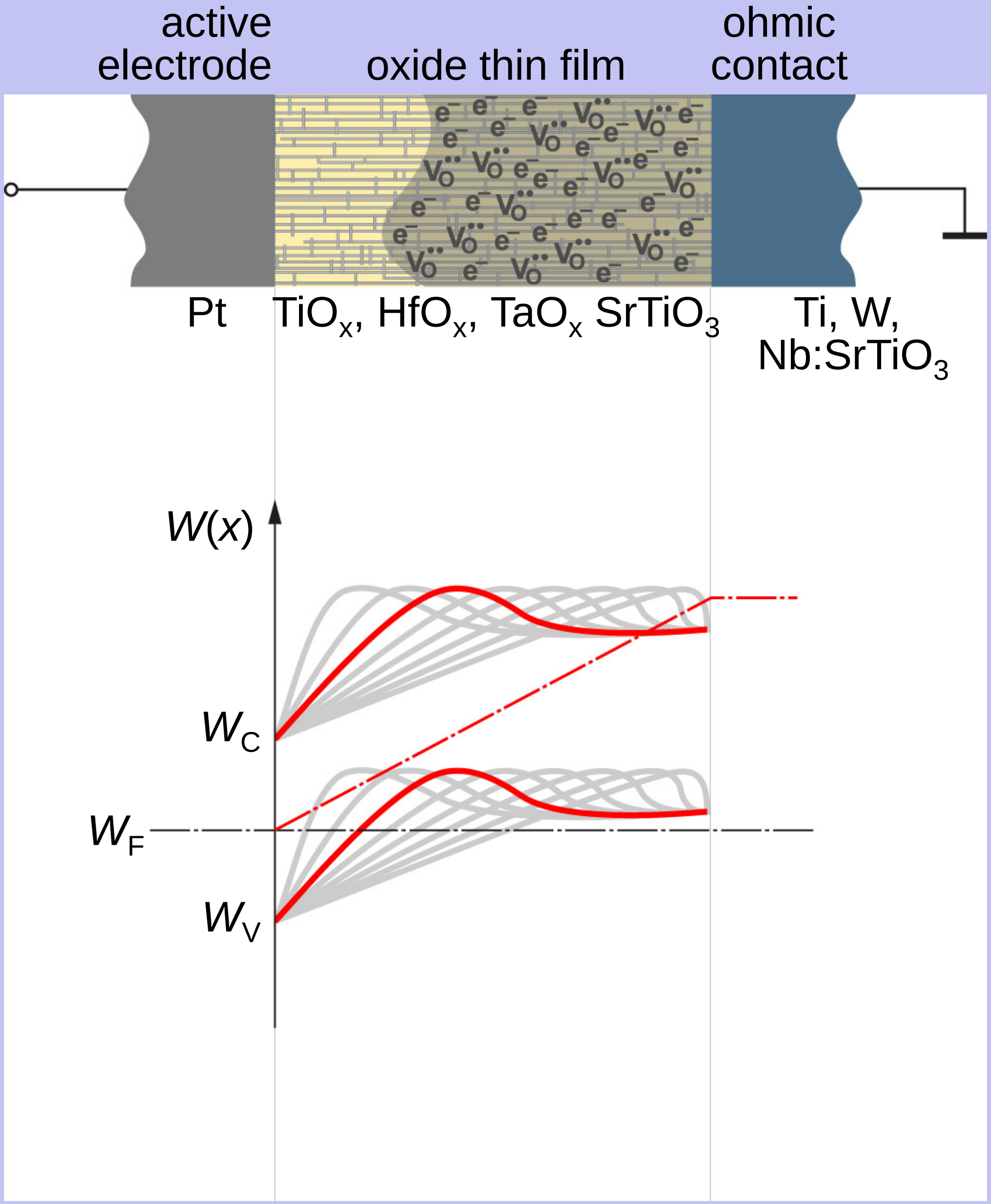

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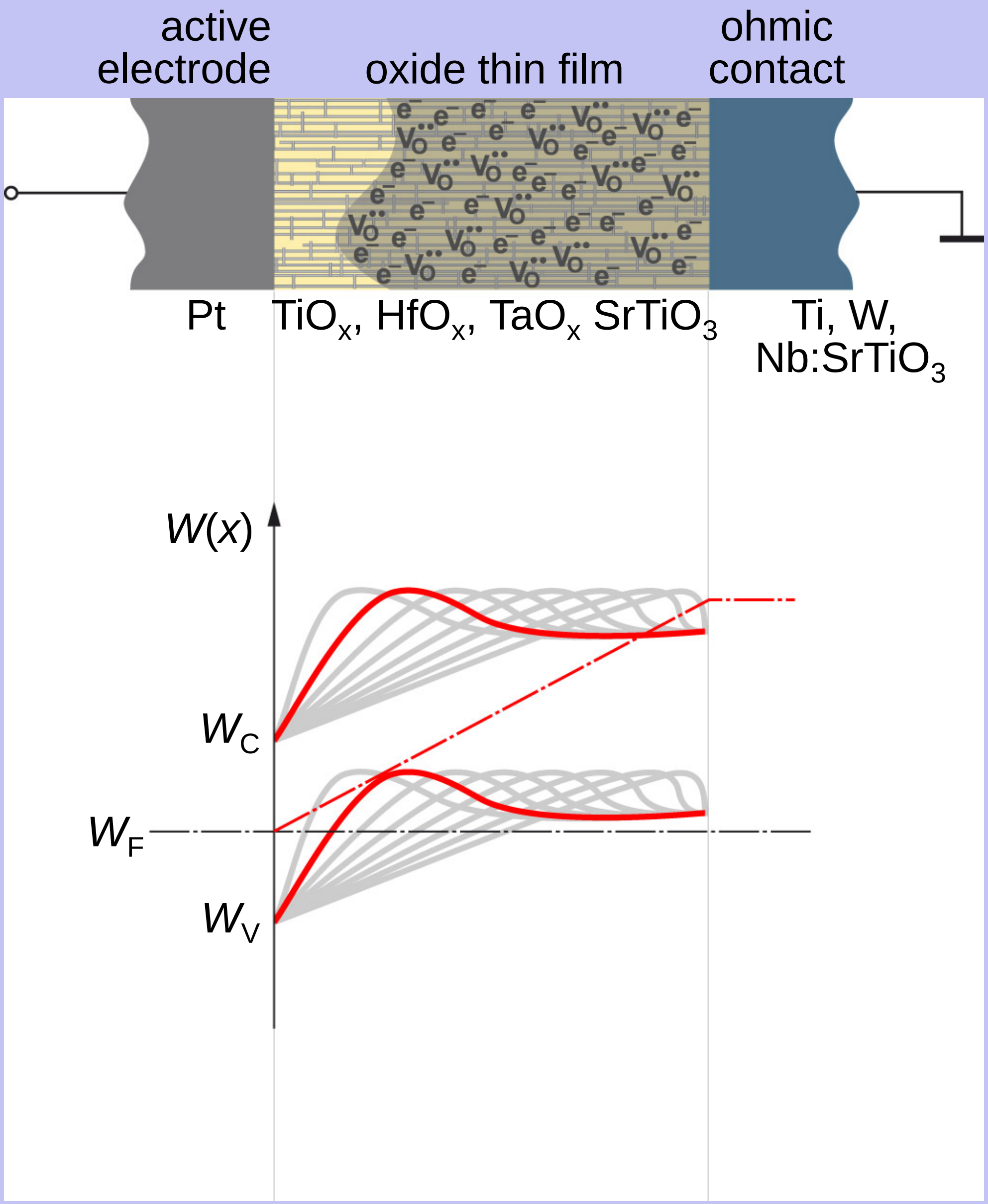
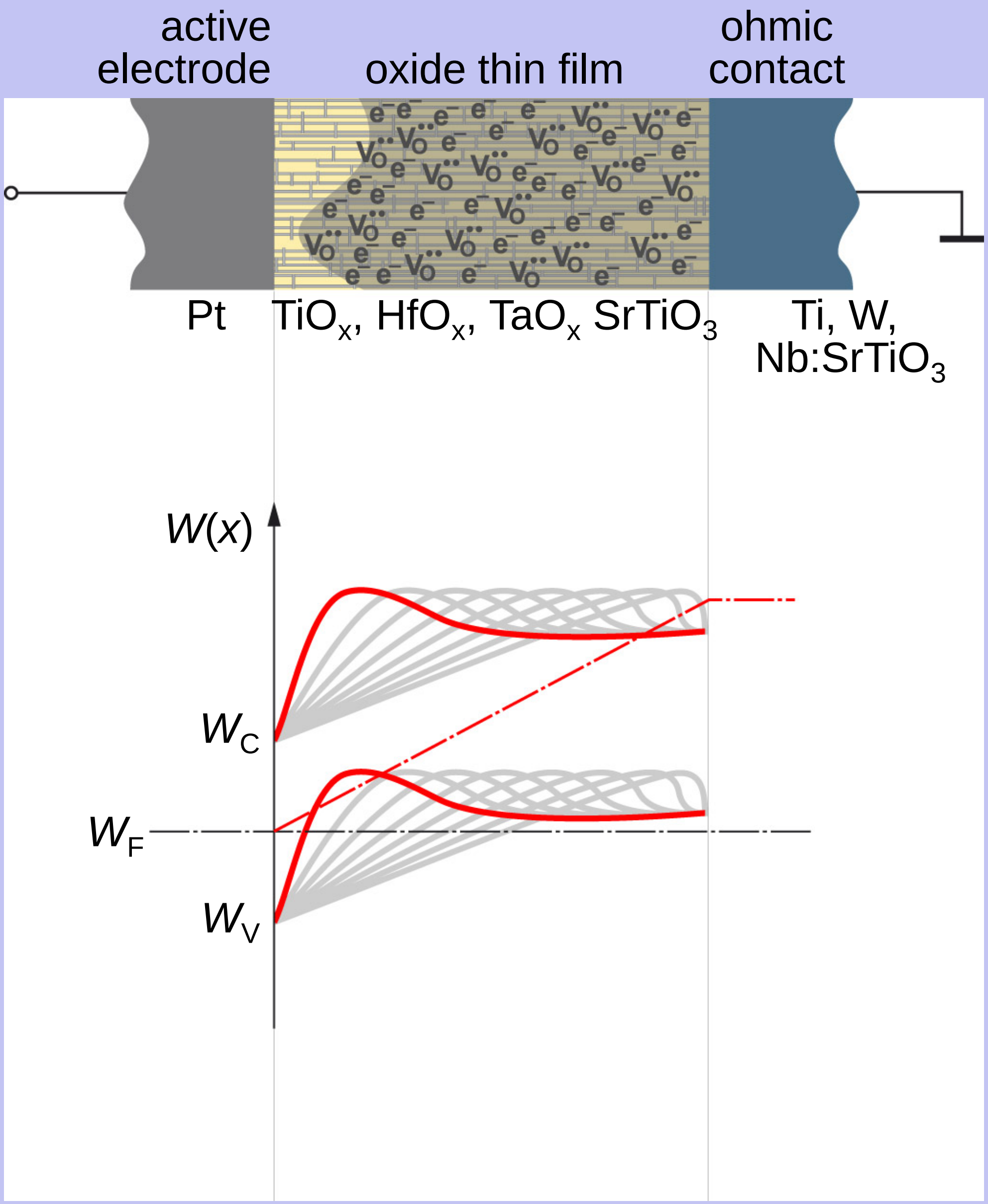


Details of the forming process: overall process

- generation of oxygen vacancies at the anode
- drift towards the cathode
- formation of a virtual cathode which approaches the anode

=> termination of the formating process by current compliance (or else)



Details of the forming process: overall process

- generation of oxygen vacancies at the anode
- drift towards the cathode
- formation of a virtual cathode which approaches the anode

=> final situation: OFF state

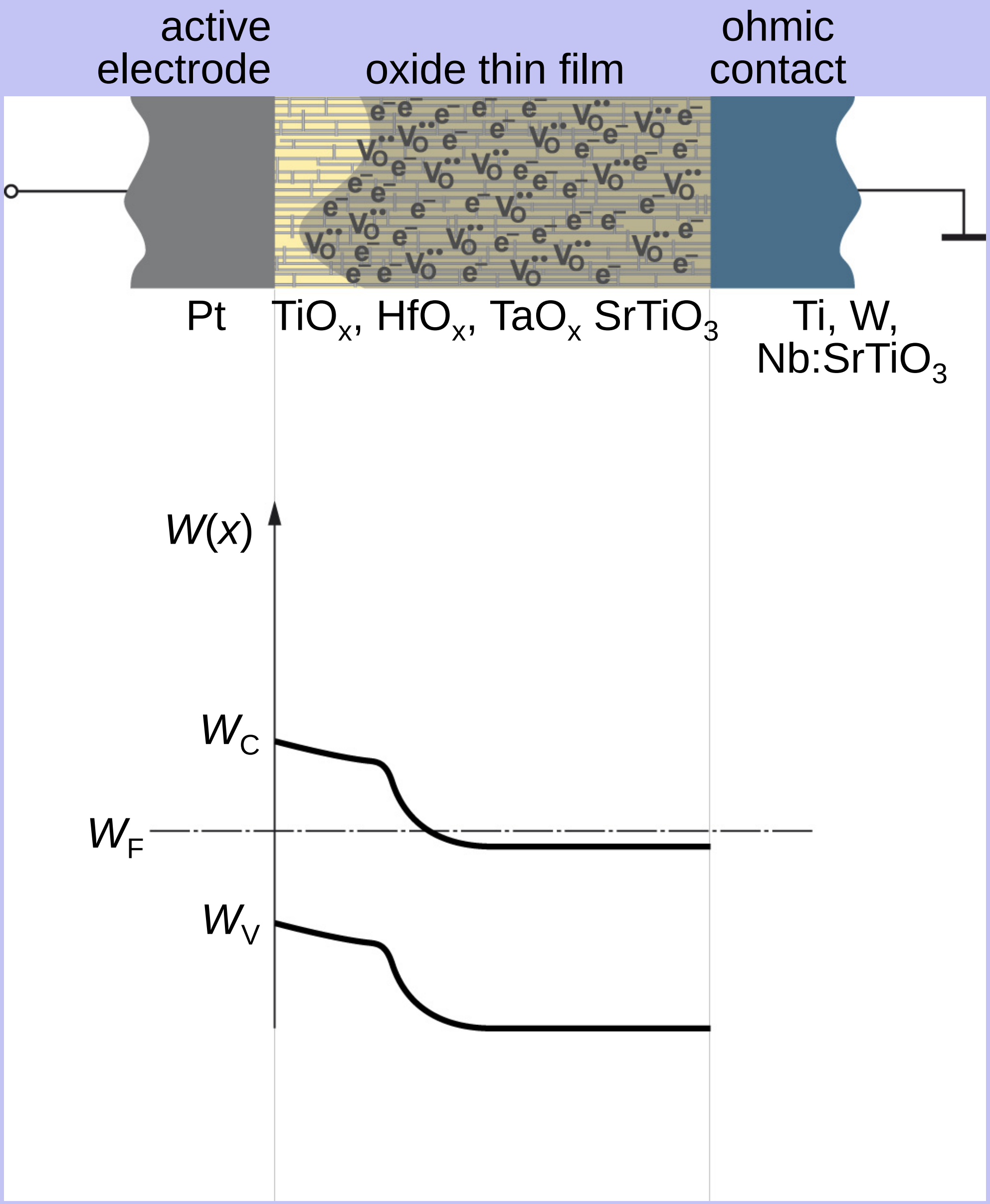
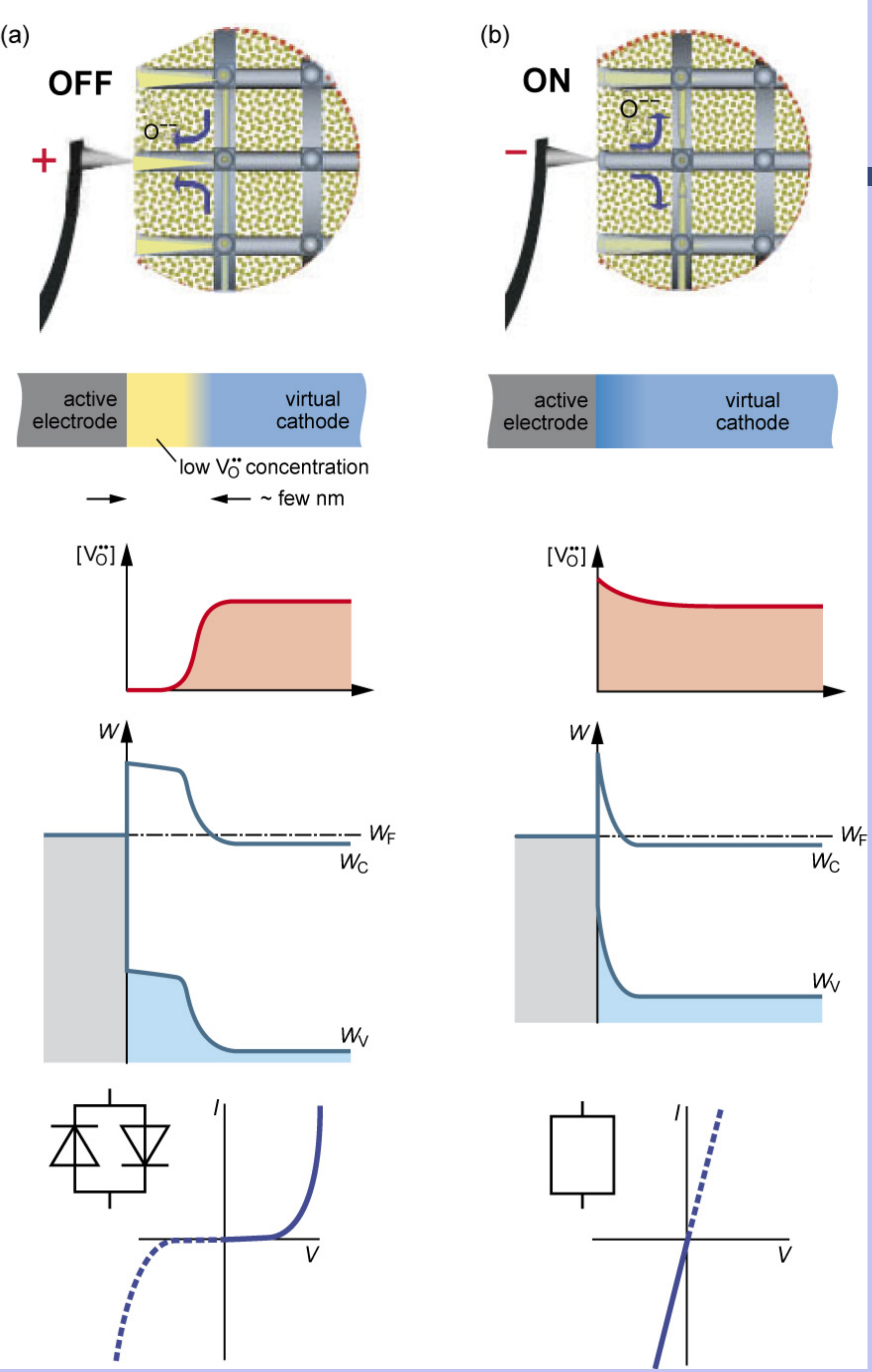


Illustration of the resistive switching

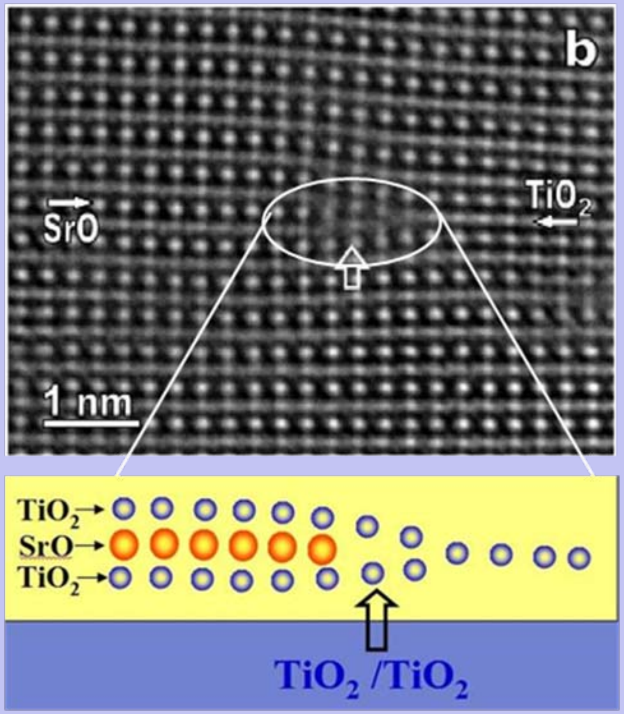
Modification of the barrier by push/pull of oxygen vacancies

... using extended filaments as „heating rods“

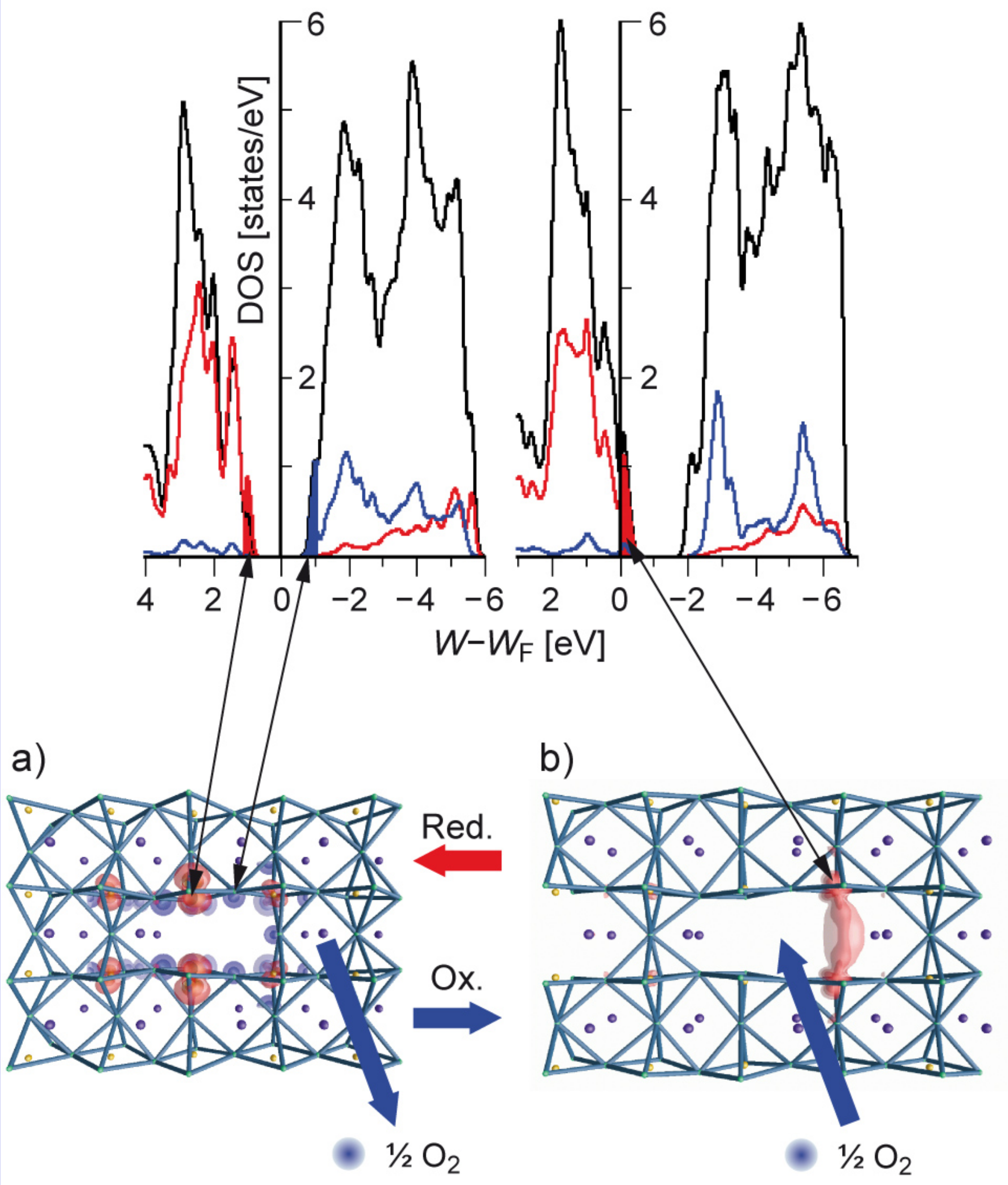
K. Szot et al.
Nature Mat. (2006)
& R. Waser, et al.
Adv. Mat. (2009)



Redox-process at dislocations

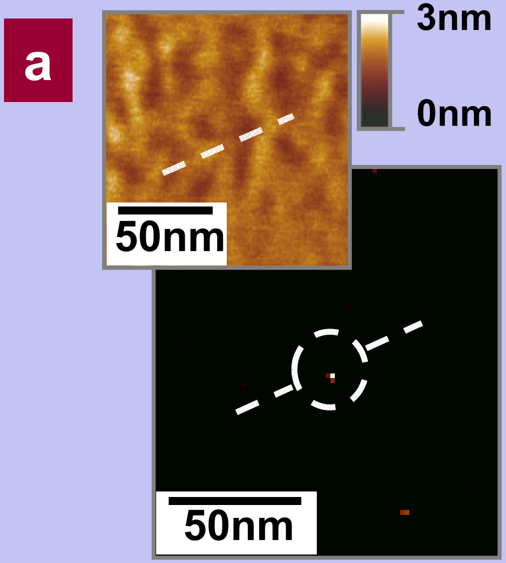


J. L. Jia, et al. PRL (2005)

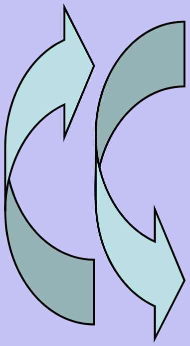


G. Bihlmayer in:
K. Szot, et al.
Nature Mat. (2006)

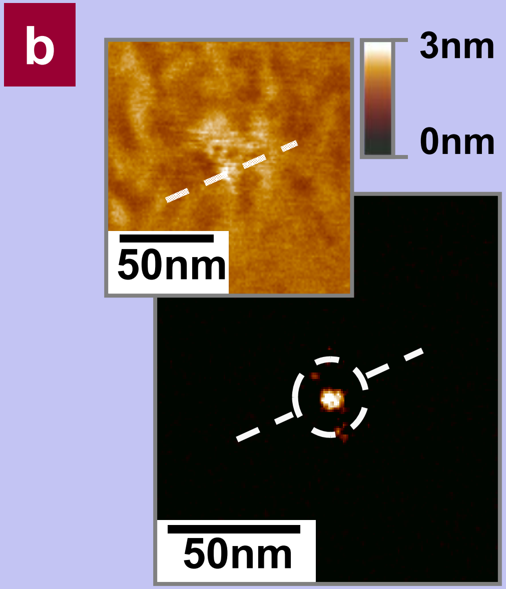
Tip-induced switching of dislocations in $SrTiO_3$

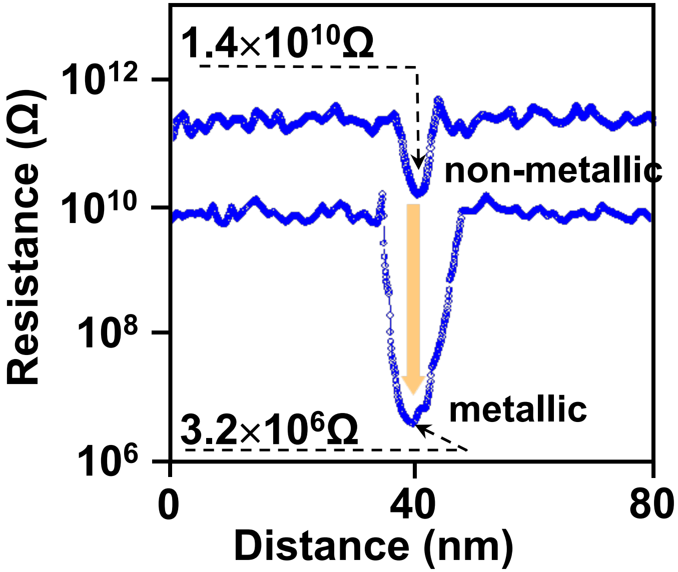


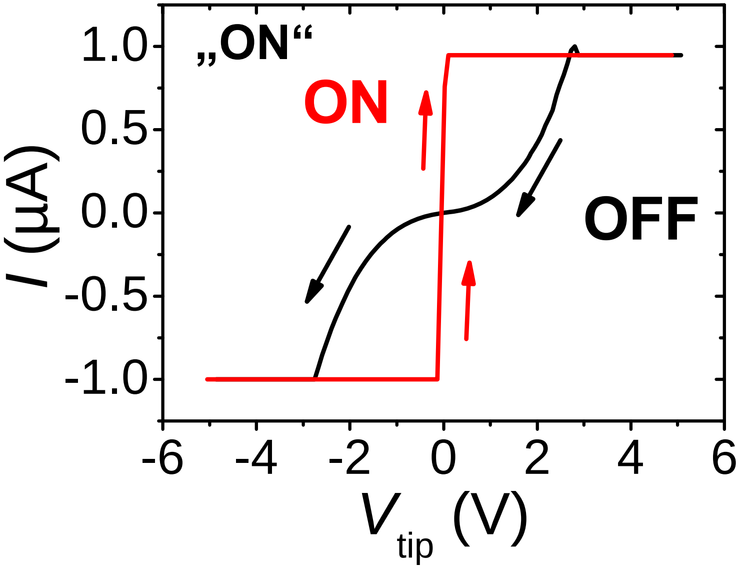
„OFF“



„ON“

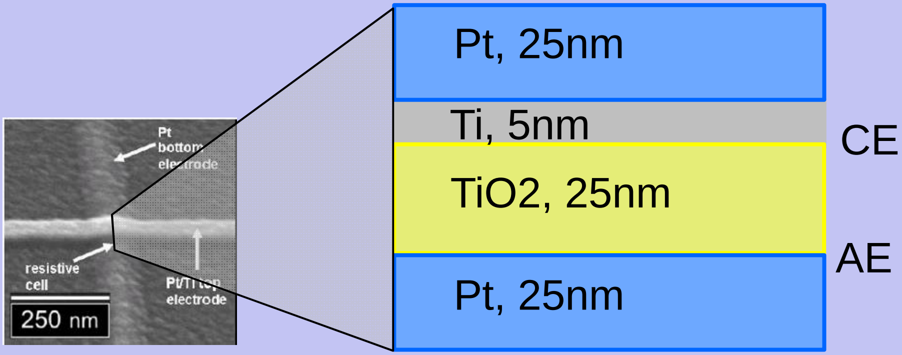






K. Szot et al., Nature Materials, 2006

Switching kinetics of TiO_2 cells



Pt, 25nm

Ti, 5nm

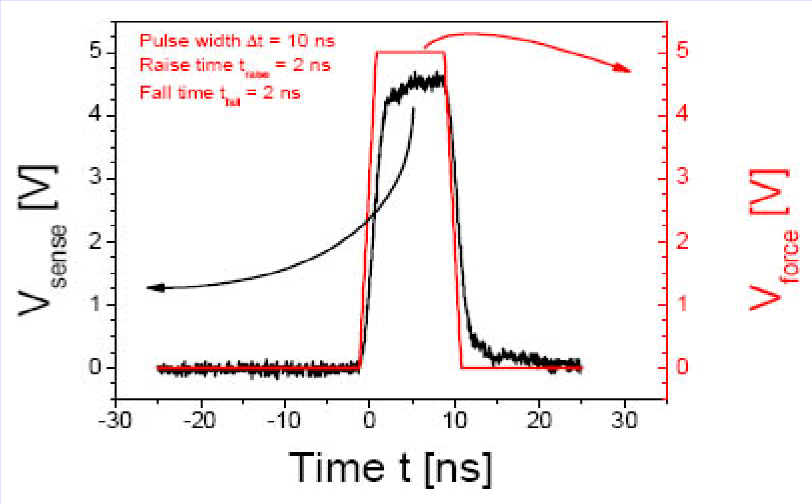
TiO2, 25nm

Pt, 25nm

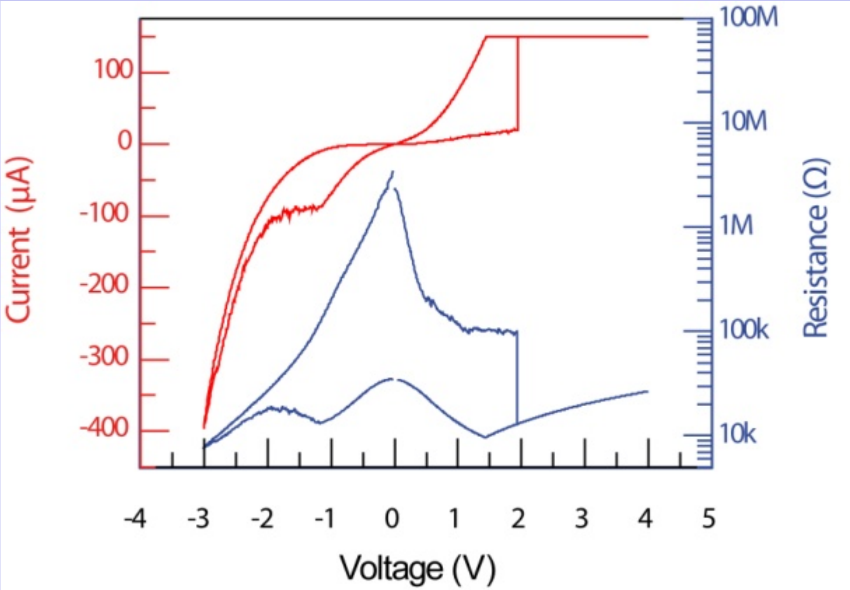
CE

AE

Pulse testing



C. Nauenheim, et al., Microel. Eng. (2009)



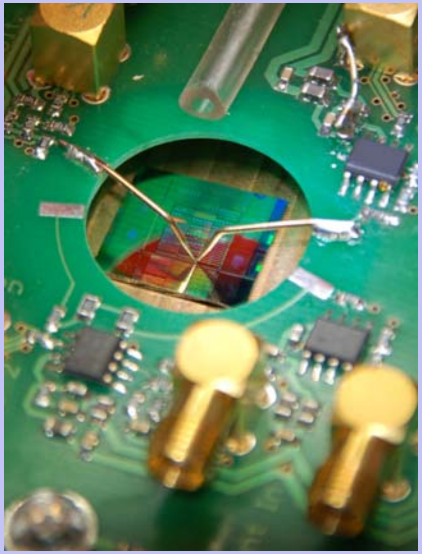
C. Hermes et al., EDL (2011)

- SET-time < 10 ns
- Limitation: R only before and after
- When does the cell actually switch?

Ultrafast switching kinetics of TiO_2 cells

Initial system developed for ultrafast pulse testing of unipolar PCM cells

G. Bruns et al., APL 2009

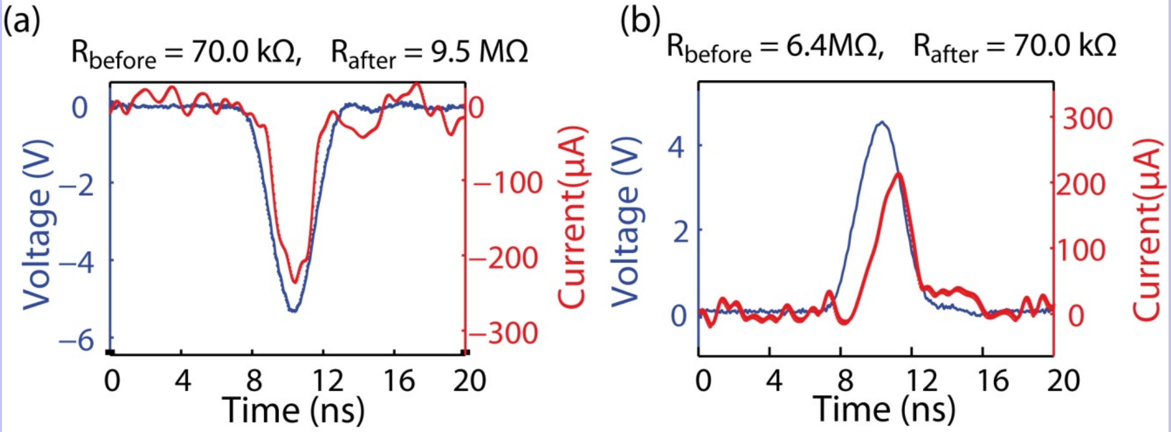


aixACT

extended into bipolar operation

- **2 ns rise time**
- **200 ps resolution**
- **optimized to suppress reflections**

RESET **SET**

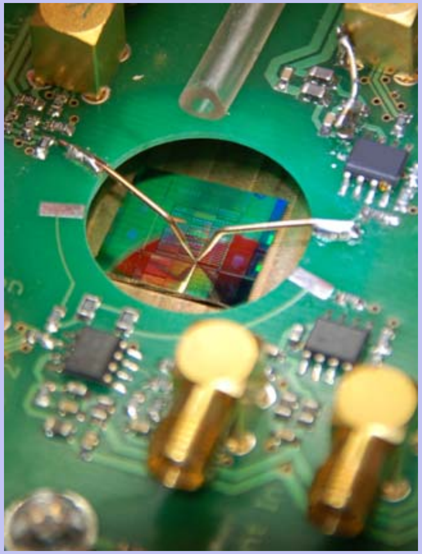


C. Hermes et al., EDL 2011

Ultrafast switching kinetics of TiO_2 cells

Initial system developed for ultrafast pulse testing of unipolar PCM cells

G. Bruns et al., APL 2009

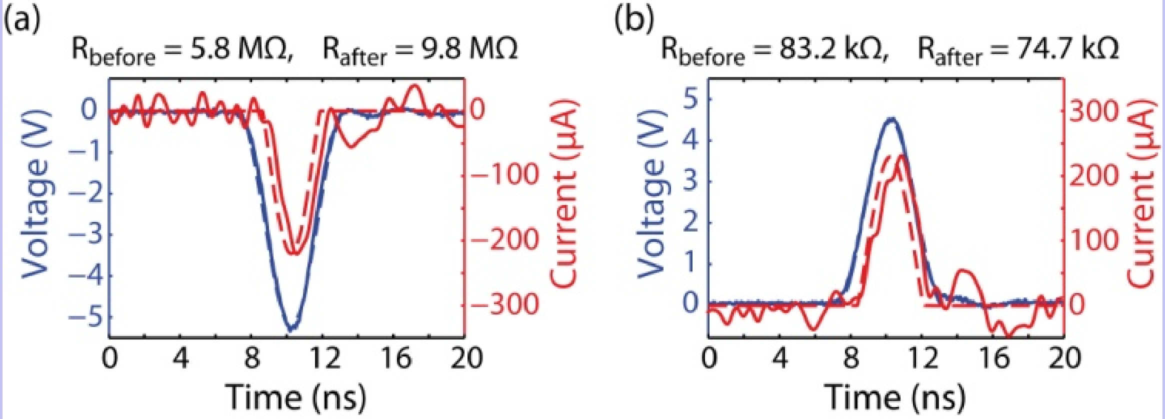


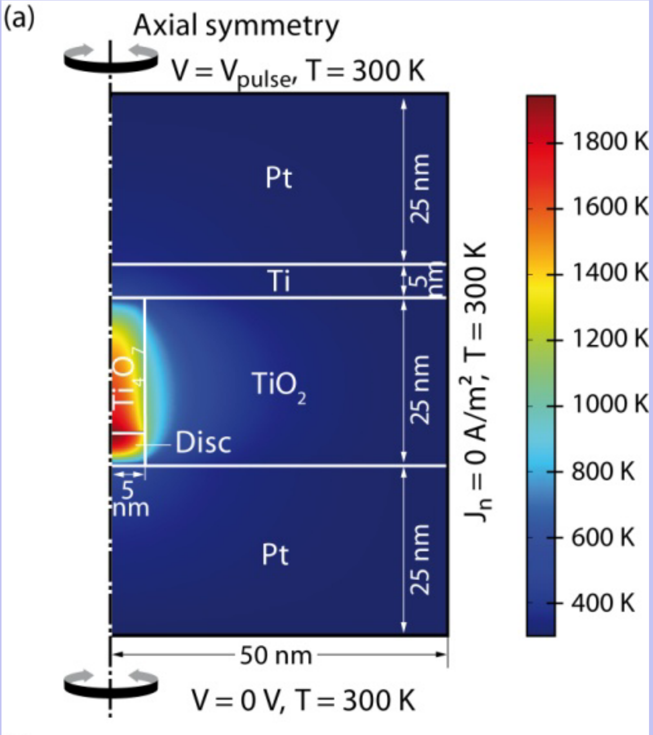
aixACT

extended into bipolar operation

- **2 ns rise time**
- **200 ps resolution**
- **optimized to suppress reflections**

OFF state **ON state**





C. Hermes et al., EDL 2011

4

Thermochemical mechanism (TCM) - bulk redox systems

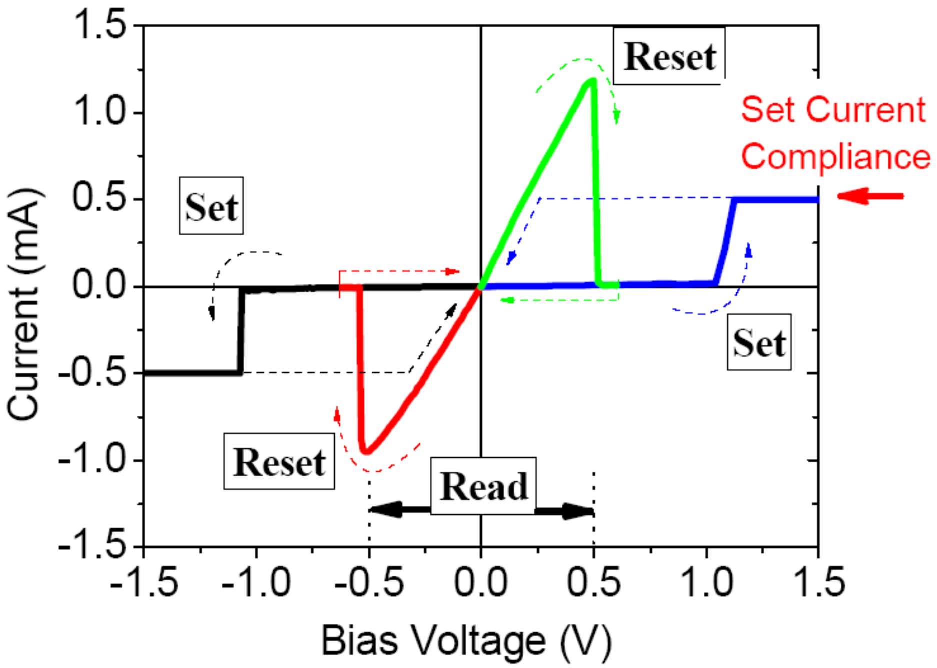
- unipolar switching
- internal redox-process

Thermochemical Memory (TCM) Effect

System

MIM thin film stack with
I = **transition metal oxide**
showing a slight
conductivity

e. g. Pt/NiO/Pt



I. G. Baek et al.
Samsung Electronics,
IEDM 2004

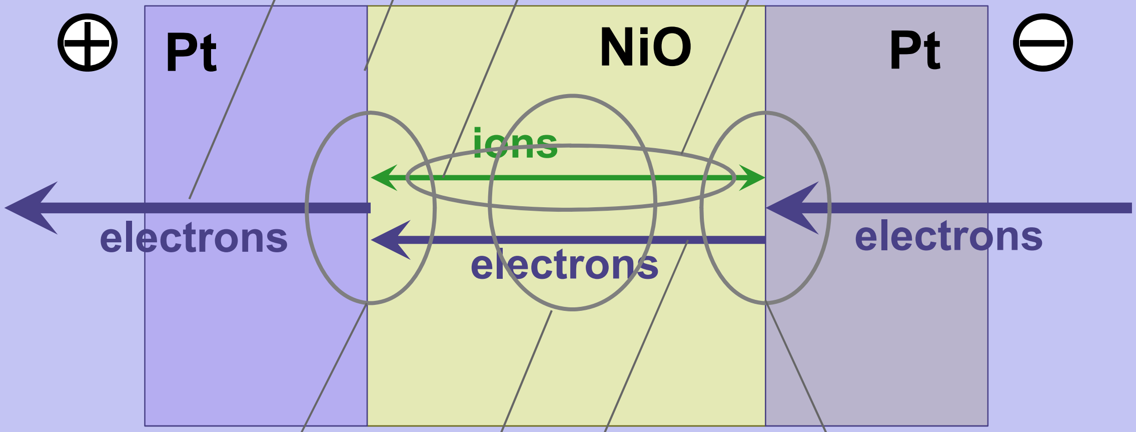
Processes during TCM formation (and SET)

electron transport

ion transport

ad-atom
diffusion

- concentration polarization ?
- **phase formation !**
- Space charge formation ?



no anodic
redox process

Joule
heating

no cathodic
redox process

thermodiffusion ->
thermochemical
redox process !

$$2\mathrm{NiO} \rightleftharpoons \mathrm{NiO}_{1-\delta} + \mathrm{NiO}_{1+\delta}$$

Thermochemical (Fuse-Antifuse) Switching Mechanism

Example: lateral Pt/CuO/Pt cell

SET process

Controlled dielectric breakdown by thermal runaway

⇨ formation of a conducting filament (fuse formed)

$$2\,\mathrm{CuO} \longrightarrow \mathrm{Cu_2O} + \mathrm{O(s)}$$

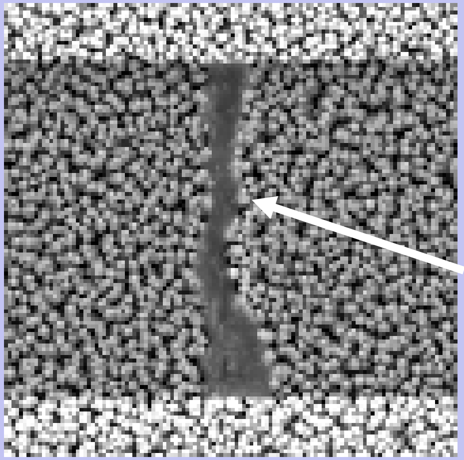
$$\mathrm{Cu_2O} \longrightarrow 2\,\mathrm{Cu} + \mathrm{O(s)}$$

RESET process

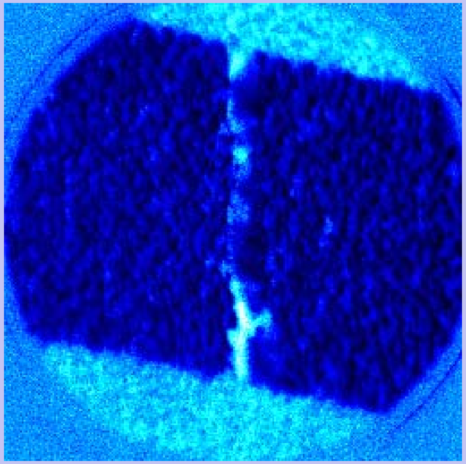
Thermal dissolution of the filament (fuse blow)

⇨ disconnected filament

SEM image



PEEM image



R. Yasuhara, H. Kumigashira, Tagaki, et al., WOE 2008

Processes during TCM formation (and SET)

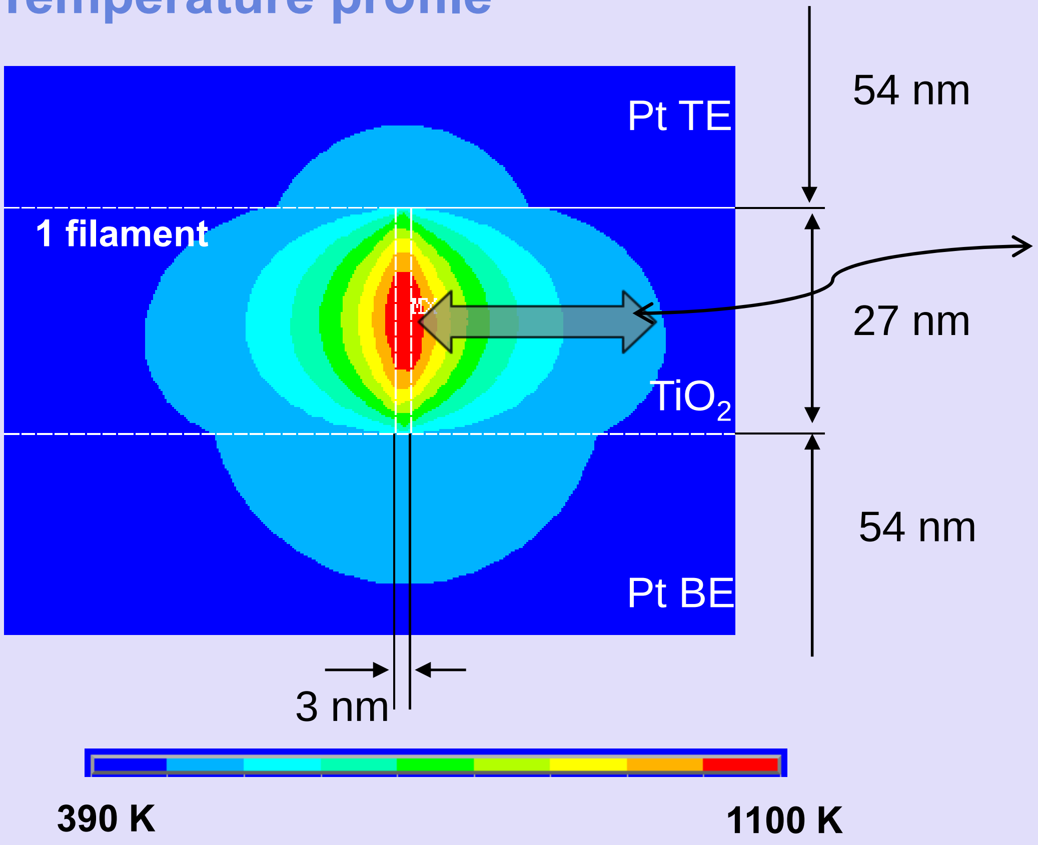
Toggle between bipolar and unipolar switching

⇨ demonstrated for TiO2 thin films (Jeong et al. 2006)

High current compliance ⇨ unipolar fuse/antifuse switching

Temperature profile

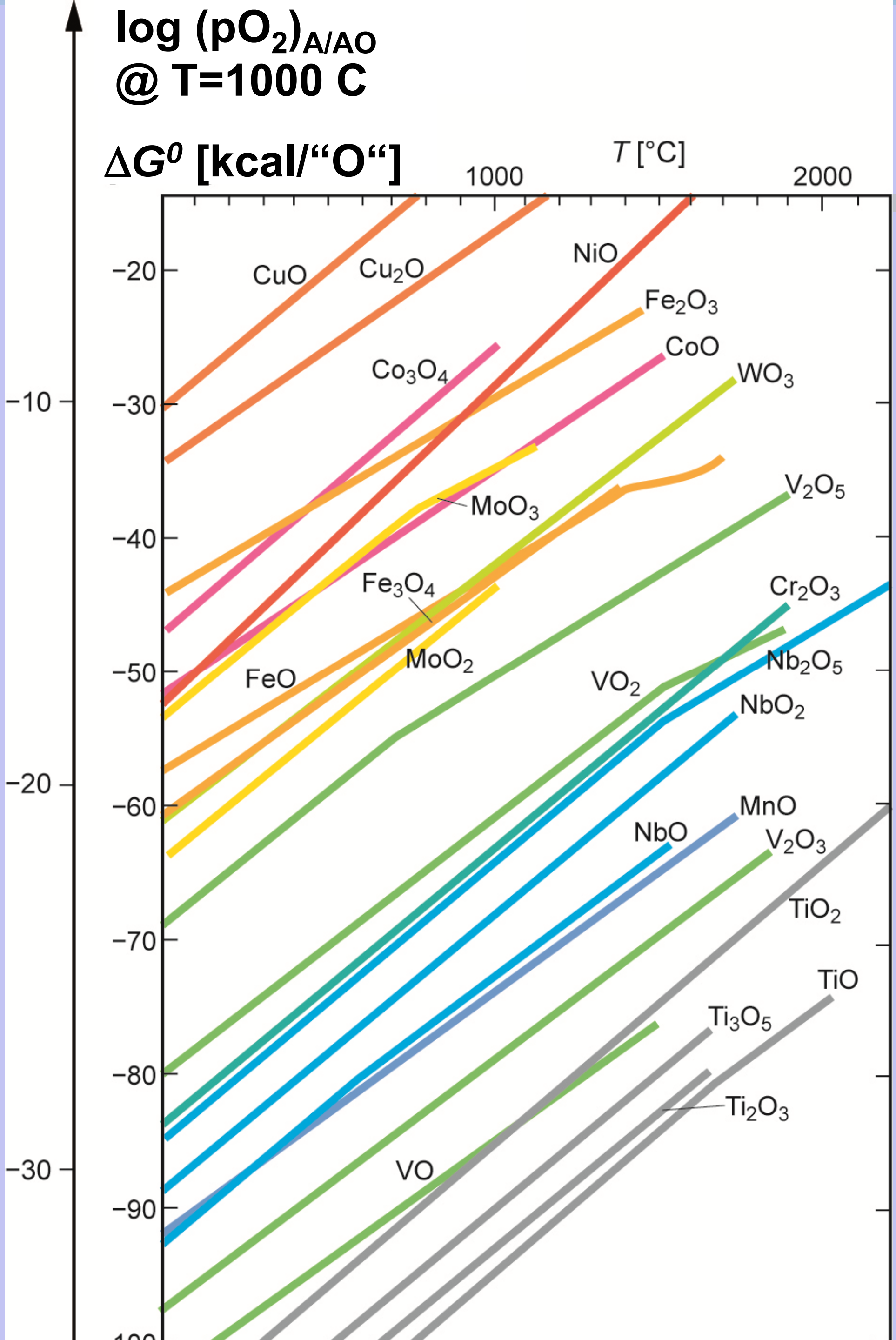
FEM simulation (Ansys ®) of a metallic TiO filament in TiO2 matrix



Thermodiffusion in an extremely high T-gradient

D.S.Jeong et al., 2007

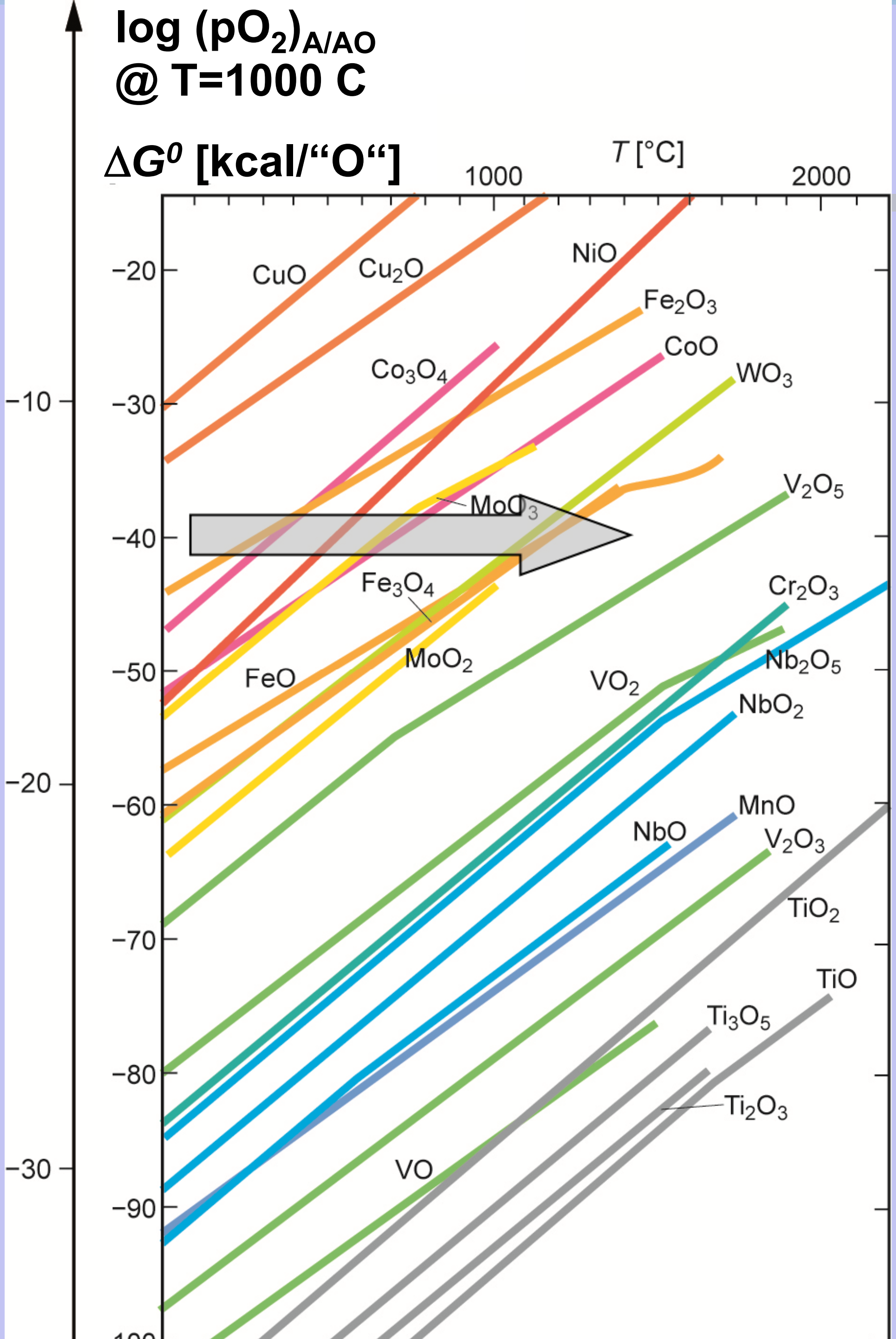
Thermochemical behaviour of transition metal oxides



Temperature dependence of the free formation energy ΔG^0

⇨ redox characteristics:
lower valent states more stable at higher T

Thermochemical behaviour of transition metal oxides



Temperature dependence of the free formation energy ΔG^0

⇨ redox characteristics: lower valent states more stable at higher T

Comprehensive Review on TCM:

D. Ielmini, R. Bruchhaus, R. Waser, Phase Transitions 84 (2011)

5

Scaling rules

Semiconductor

- the ions forming donor and acceptor levels are due impurities ('foreign bodies') introduced into the host matrix
  - e.g. P, B atoms in Si
- The *dopants* (i.e. donors and acceptors) don't change their positions
  - Invreasingly difficult to put them in precise location

- Electrons are the only movable particles
  - Used to represent and sense state
  - Difficult at <10nm

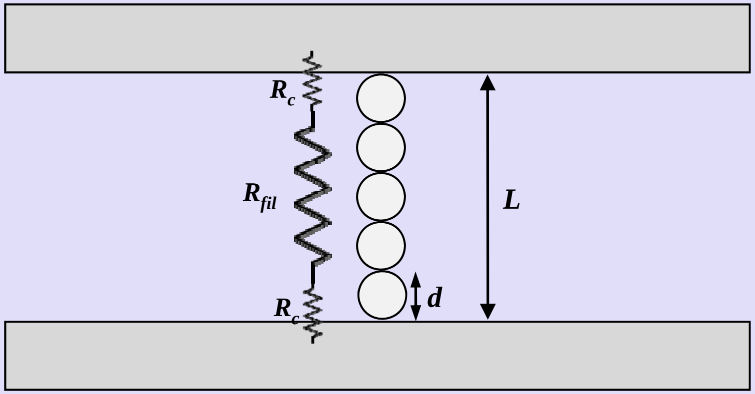
- Rigid interfaces
  - EITHER Ohmic OR Blocking

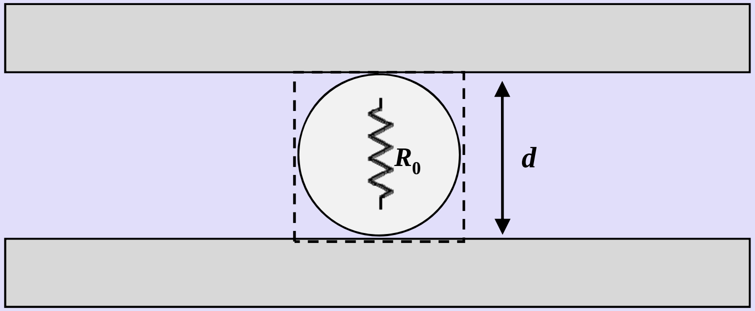
Chemiconductor

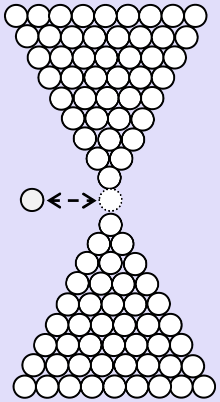
- the ions forming donor and acceptor levels are due to composition variation in the host matrix
  - lattice point defects (e.g. vacancies or interstitial atoms) can electrically act as donors or acceptors
  - e.g. ionized oxygen vacancy VO^{+2} in TiO_2
  - the ions can move in electrical fields
    - e.g. under external bias
- Atoms and electrons are movable
  - e.g. Atoms – change state; electrons – sense state
  - Operate at <10nm

- Adaptive interfaces
  - Can switch from Ohmic to Blocking

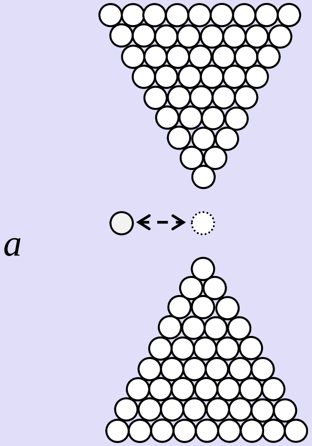
Ultimate case:
Minimal Conductive Bridge

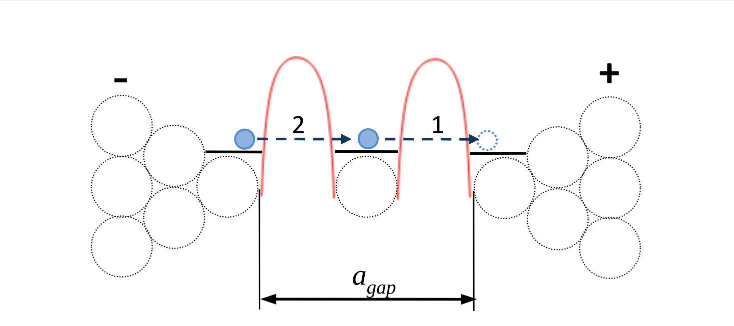






Discontinuous atomic bridge





g	I_{on}, A	I_{off}, A	ON/OFF	a_{gap}, nm
2	7.80E-06	3.37E-07	23	0.77 (3δ)
3	3.39E-06	4.28E-09	792	1.29 (5δ)
4	2.46E-06	1.86E-11	132258	1.81 (7δ)

$$I(g) = \frac{1}{g^2} I_1$$

The minimal 2-gap structure (1 atom in the inter-electrode space) is in principle sufficient to obtain both a sufficiently large ON current and a reasonably large resistance ON/OFF ratio to satisfactorily differentiate the state of the ReRAM cell.

6

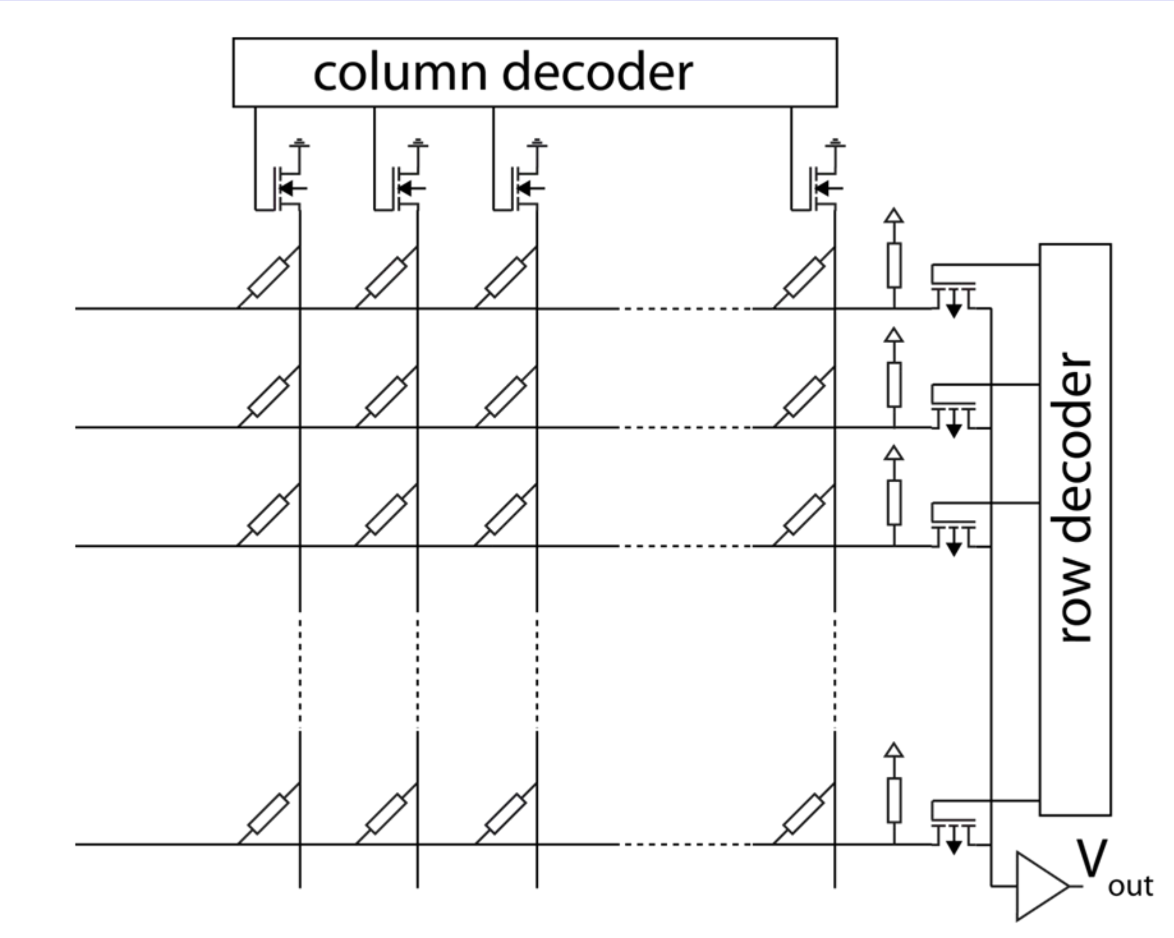
Ultradense and 3-D stackable Architecture Concepts

Memory Architecture – Passive Arrays

Advantages

- simple structure
- small area (4 F^2)
- easy to manufacture

- high scalability
- suited for two terminal devices



Passive Arrays – Sneak Path Problem

- $\Delta I = I_{\text{sense},2} - I_{\text{sense},1} \rightarrow \Delta V$
- several elements in LRS

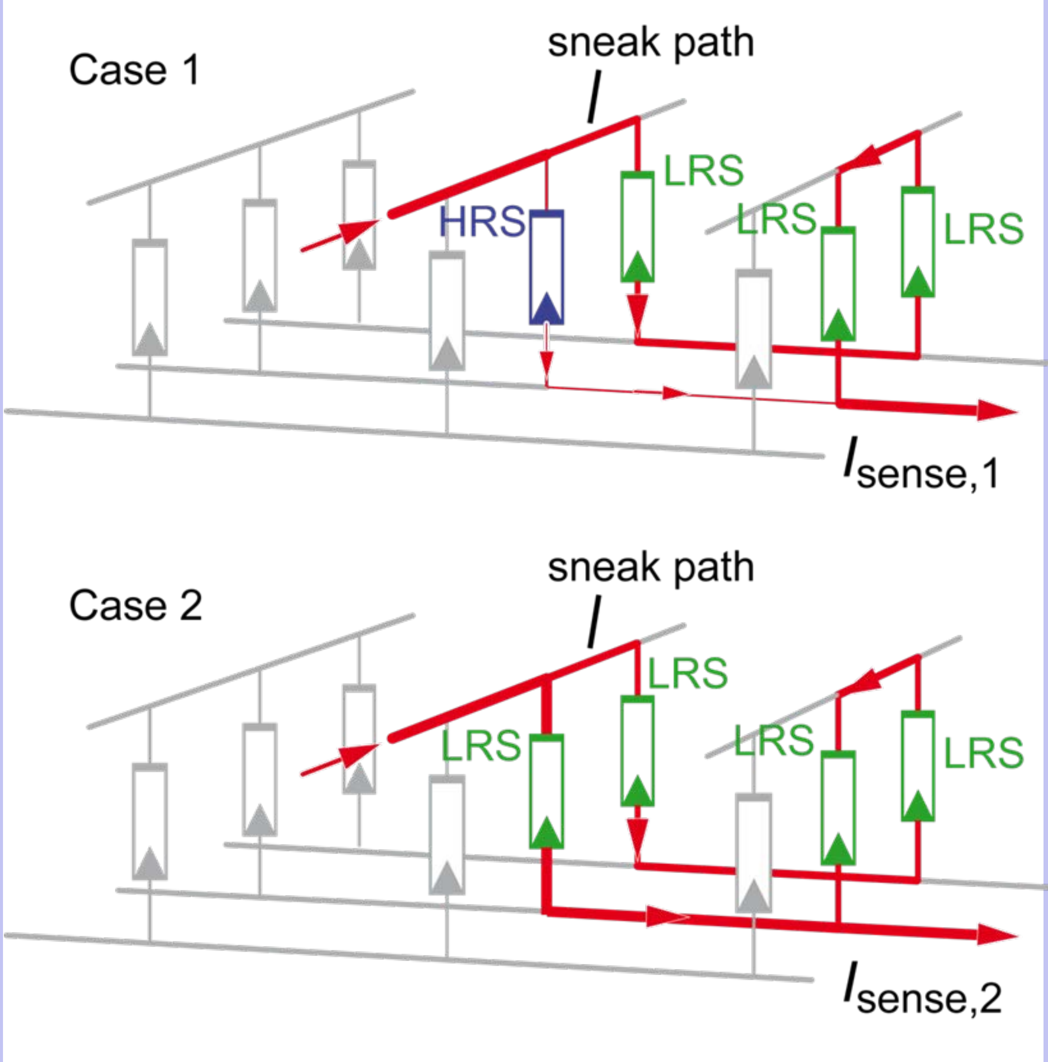
→ Reading is disturbed

- ΔV small even for small arrays
- pattern dependencies
  - circuitry difficult to design
  - static power consumption high

→ Only small arrays can be built

Alternative:

→**Sneak paths must be avoided**



Passive Arrays – Sneak Path Problem

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→ Reading is disturbed

- ΔV small even for small arrays
- pattern dependencies
  - circuitry difficult to design
  - static power consumption high

→ Only small arrays can be built

Alternative:

→**Sneak paths must be avoided**

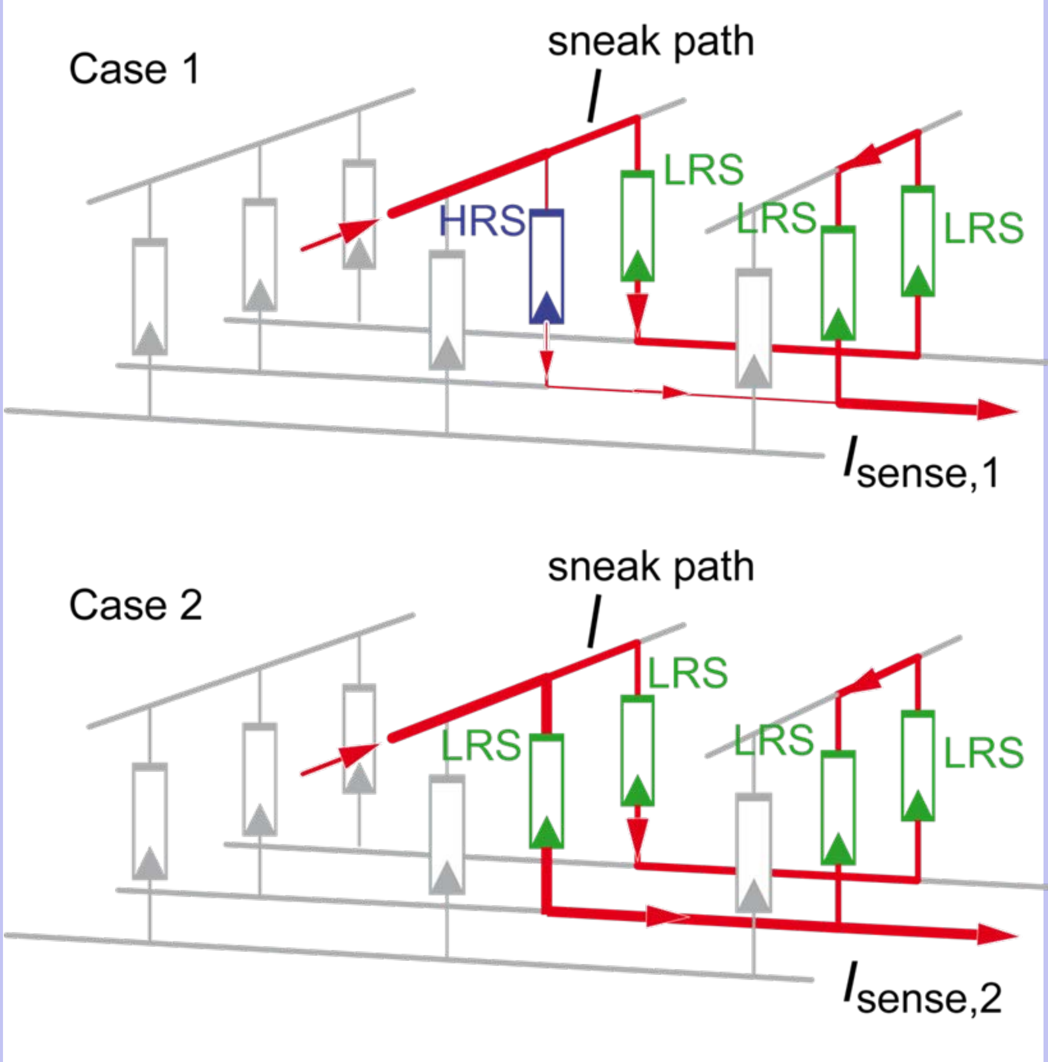
Conventional attempts:

Non-linear (Z-diode type) elements in series

Problems:

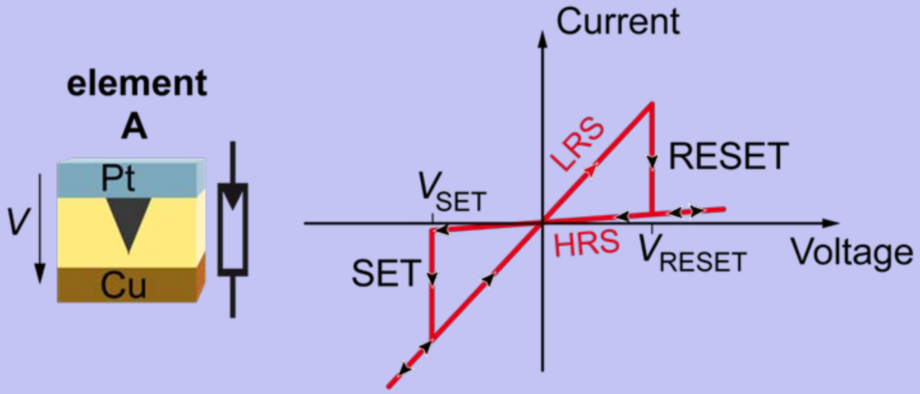
→ Read dynamics reduced

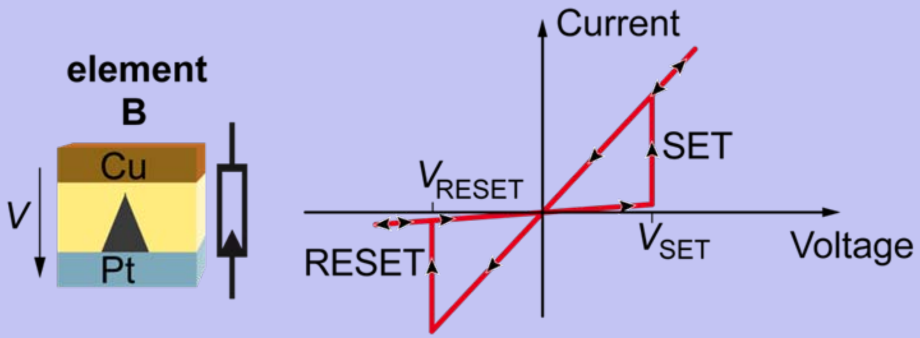
→ High current density



Solution – Complementary Resisitve Switch (CRS)

Complementary resistive switch (CRS)
- two antiserial memristive elements





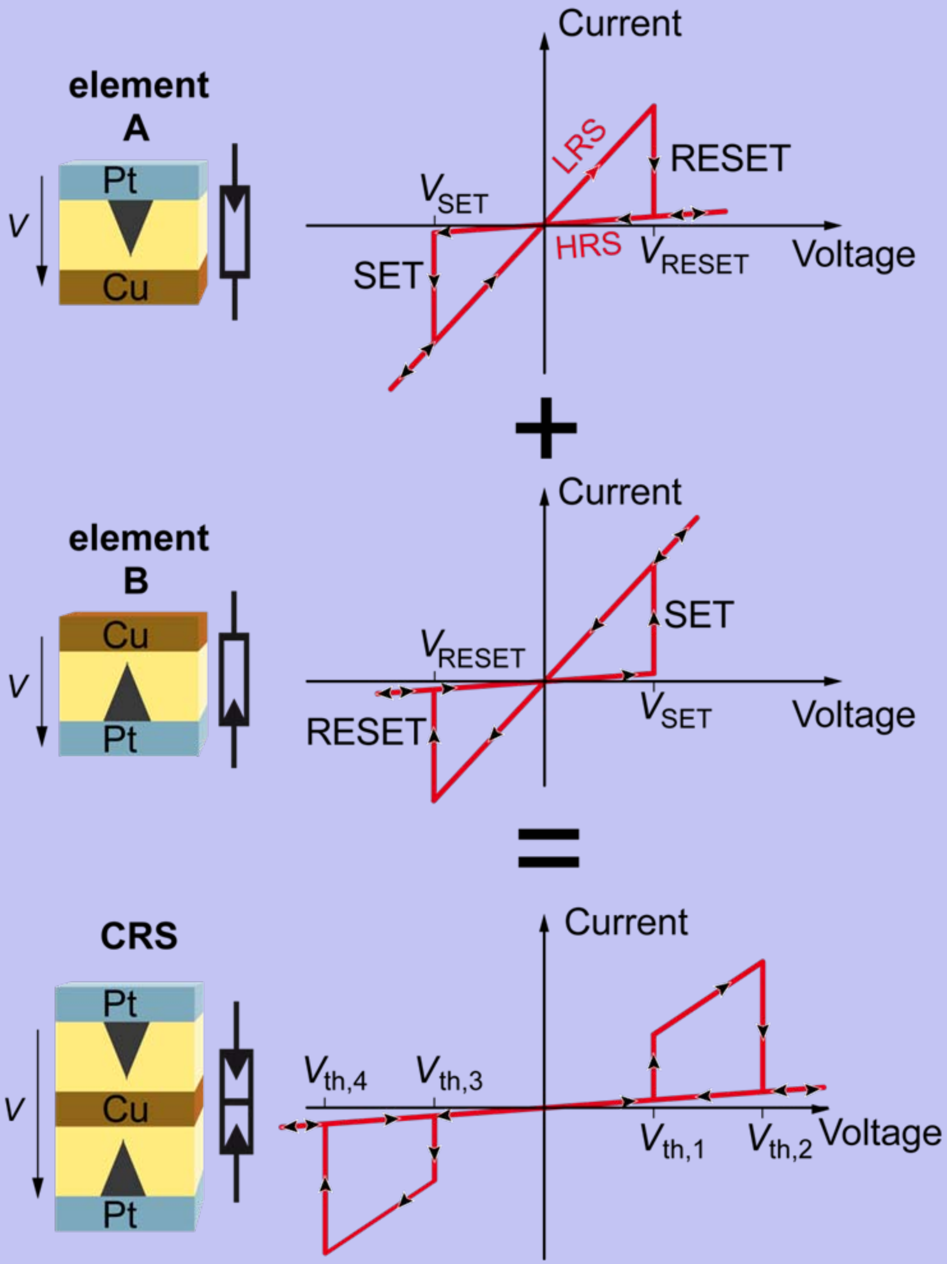
Solution – Complementary Resisitve Switch (CRS)

Complementary resistive switch (CRS)
- two antiserial memristive elements

CRS in a Passive Array

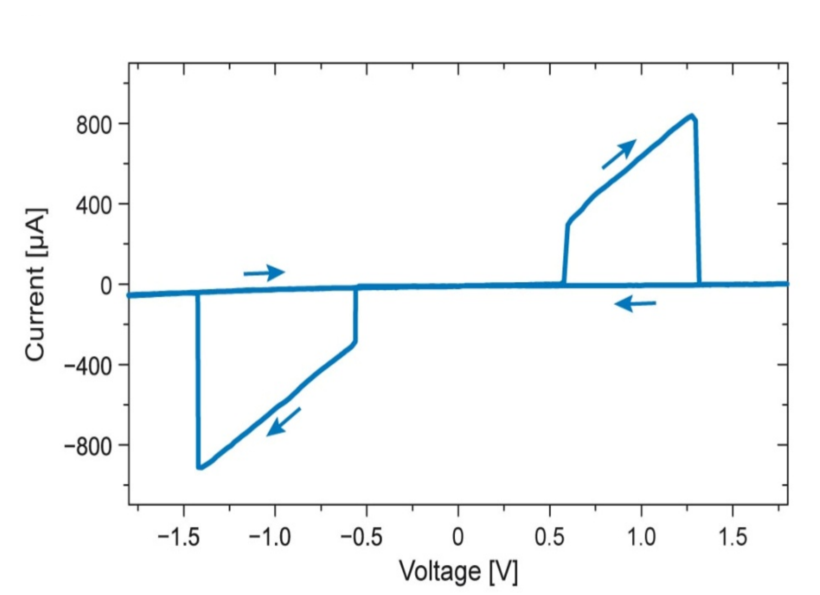
- **high cell resistance**
- **not pattern dependent**
- **low static power losses**

E. Linn, R. Rosezin, C. Kuegeler, and
R. Waser, *Nature Mater.* 9, 403-406 (2010)

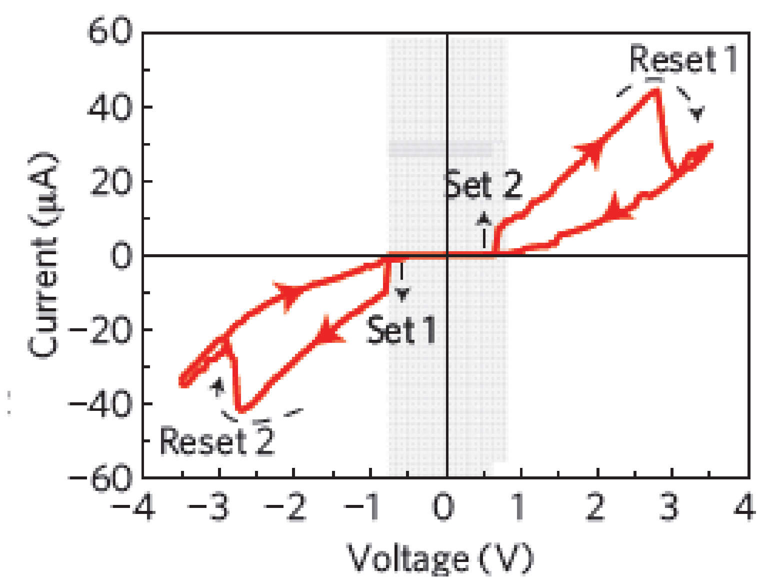


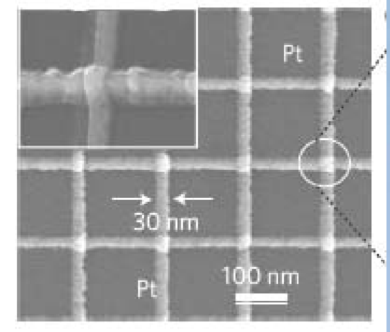
Complementary Resistive Switching (CRS) cells

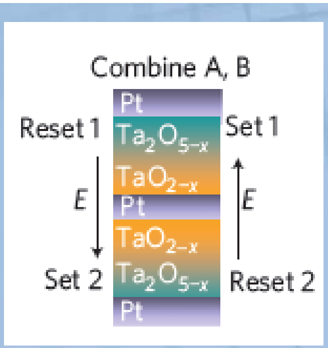
Experimental proof … by ECM cells … by VCM cells



30nm Pt/ 3nm SiO2 / 20nm GeSe / 70nm Cu cells







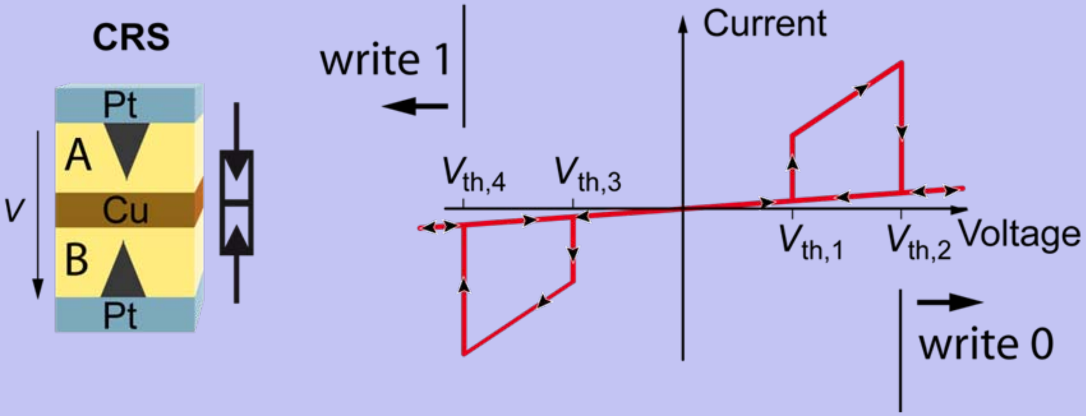
E. Linn, et al. *Nature Mat.* 9 (2010)

M.-J. Lee, et al. *Nature Mat.* 10 (2011)

Complementary Resisitve Switch (CRS)

Write operation:

- – write 1: $V < V_{th,4}$
- – write 0: $V > V_{th,2}$



- 1 and 0: high resistive

storage states {

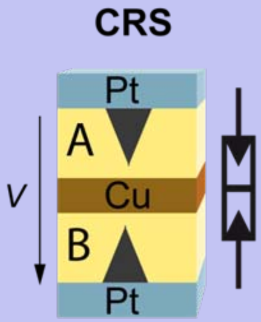
CRS state	element A	element B	resistance CRS
0	HRS	LRS	≈ HRS
1	LRS	HRS	≈ HRS
ON	LRS	LRS	LRS+LRS
OFF	HRS	HRS	>> HRS

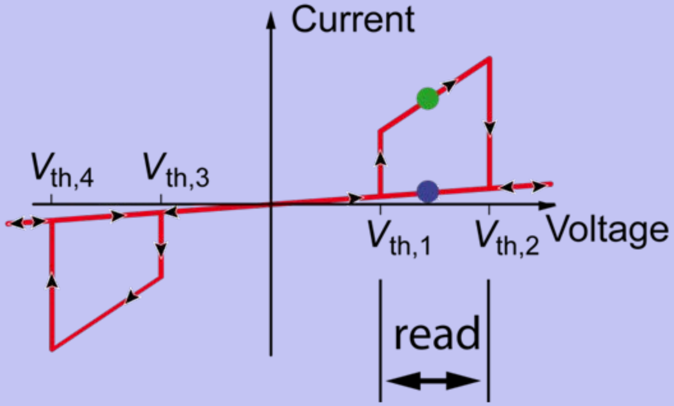
E. Linn, et al.
***Nature Mater.* 9, 403-406 (2010)**

Complementary Resisitve Switch (CRS)

Read operation:

$V_{th,1} < V < V_{th,2}$





- high current: read 1
- low current: read 0

→ Easy to distinguish
(but: destructive Read-out
like in FeRAM !)

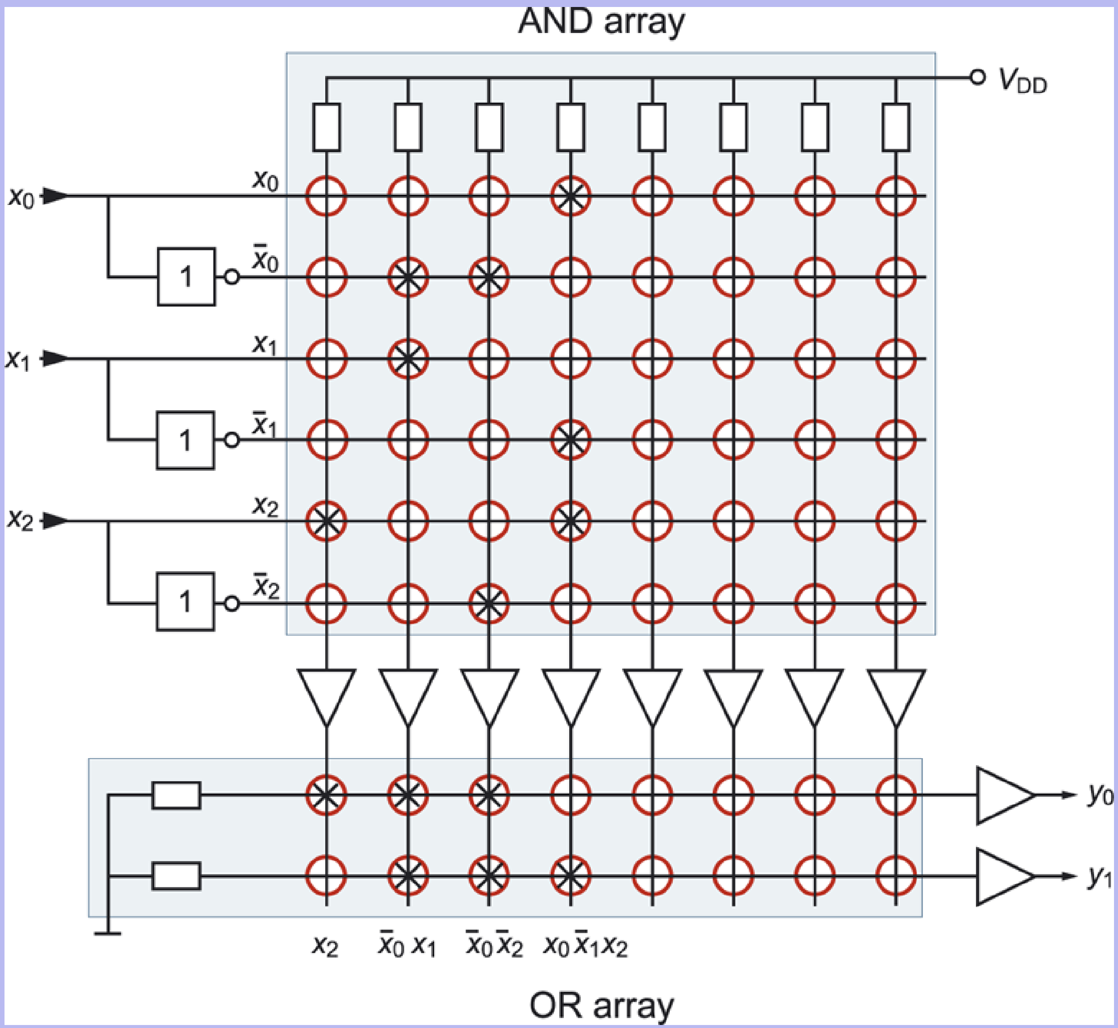
	CRS state	element A	element B	resistance CRS
read 0	0	HRS	LRS	≈ HRS
	1	LRS	HRS	≈ HRS
read 1	ON	LRS	LRS	LRS+LRS
	OFF	HRS	HRS	>> HRS

E. Linn, et al.
***Nature Mater.* 9, 403-406 (2010)**

Complementary Resisitve Switch (CRS)

http://www.emrl.de/pu_crs.html#crs-model

Towards Logic: Free Programmable Gate Array (FPGA)

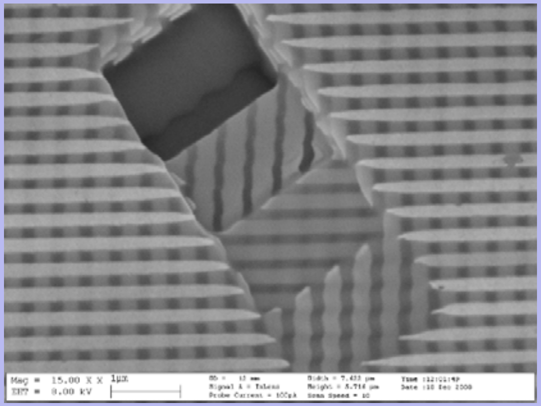


R. Waser (ed.), “Nanoelectronics and Information Technology”, Wiley 2005

Floor plan advantage:
RRAM-Xbar vs CMOS
> 1:30

Additonal aspects:

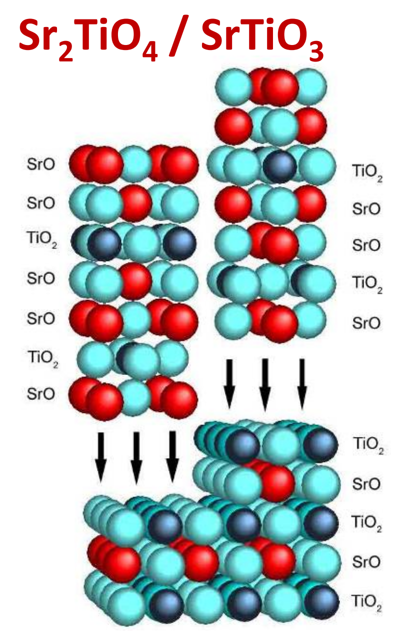
- **fusion of memory and logic**
- **defect tolerance**
- **energy efficiency**
- **3-D stacking**



C. Kügeler et al. (2008)

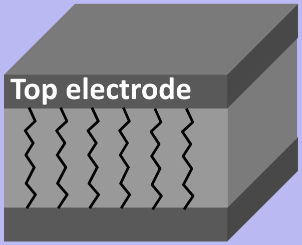
Defect engineering – towards crossbar architectures

- ... by anti-phase boundaries

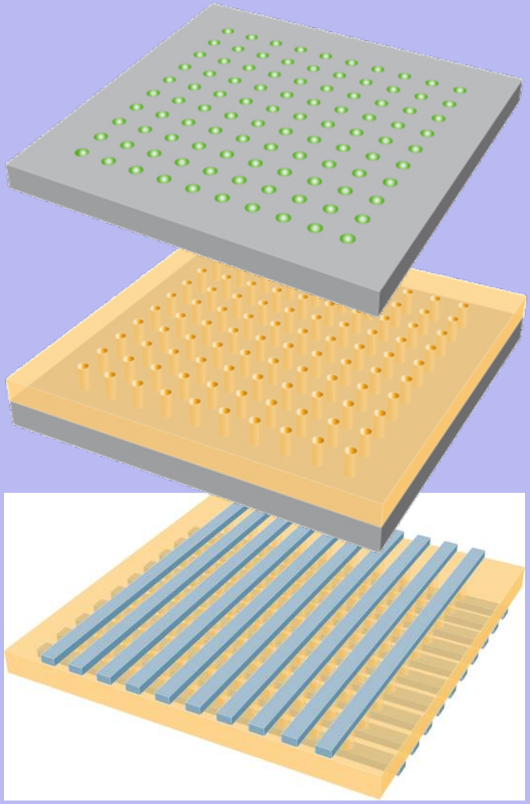


Sr_2TiO_4 / $SrTiO_3$

Vicinal surfaces

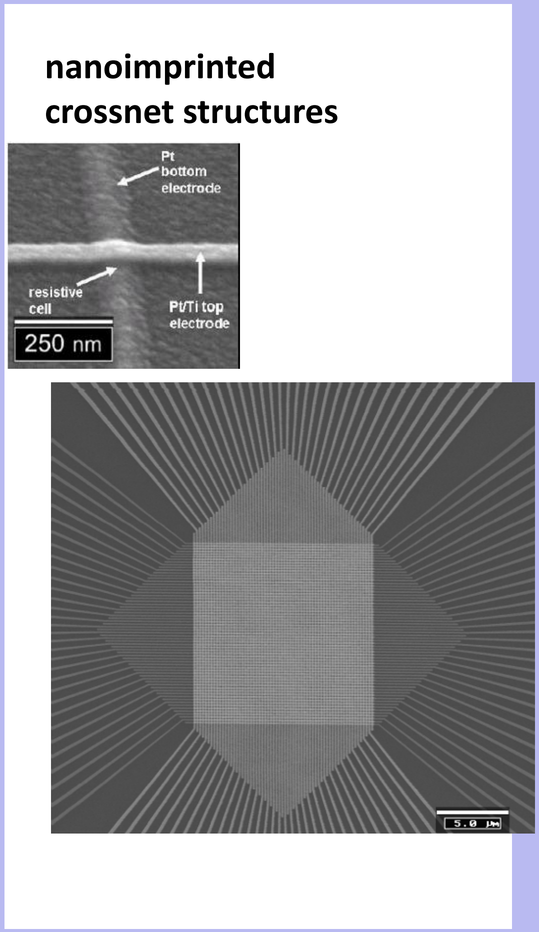


- ... or templated growth



concept - R. Dittmann (2008)

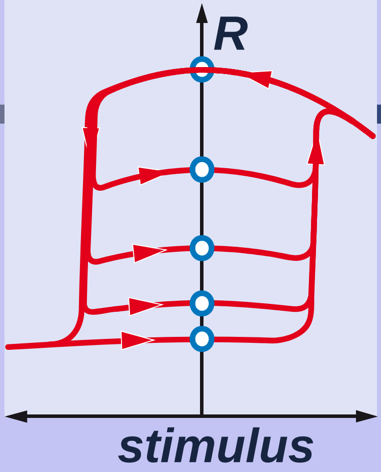
- ultrathin nano-crystalline films

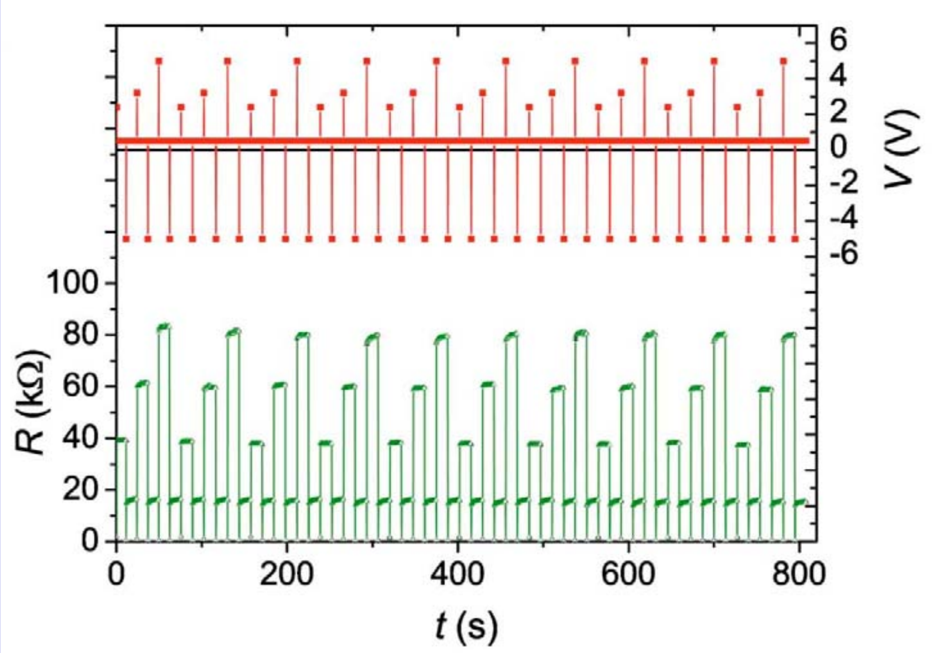


nanoimprinted crossnet structures

C. Kügeler et al. (2008)

From Multibit memory to artificial neurons

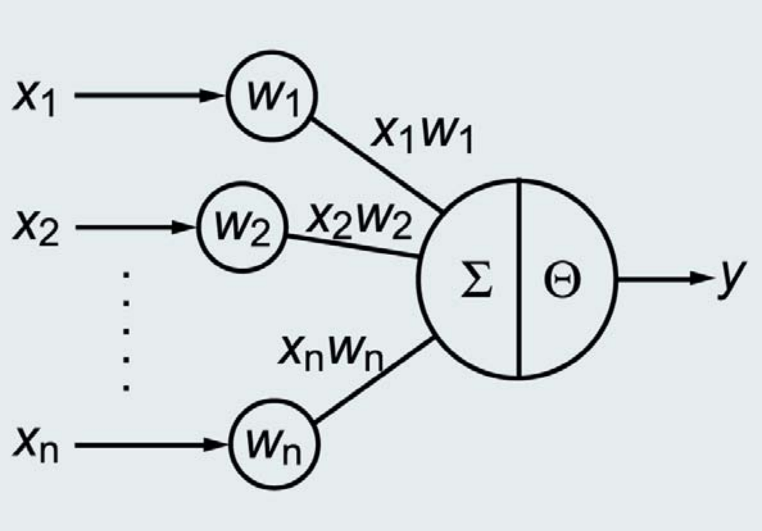


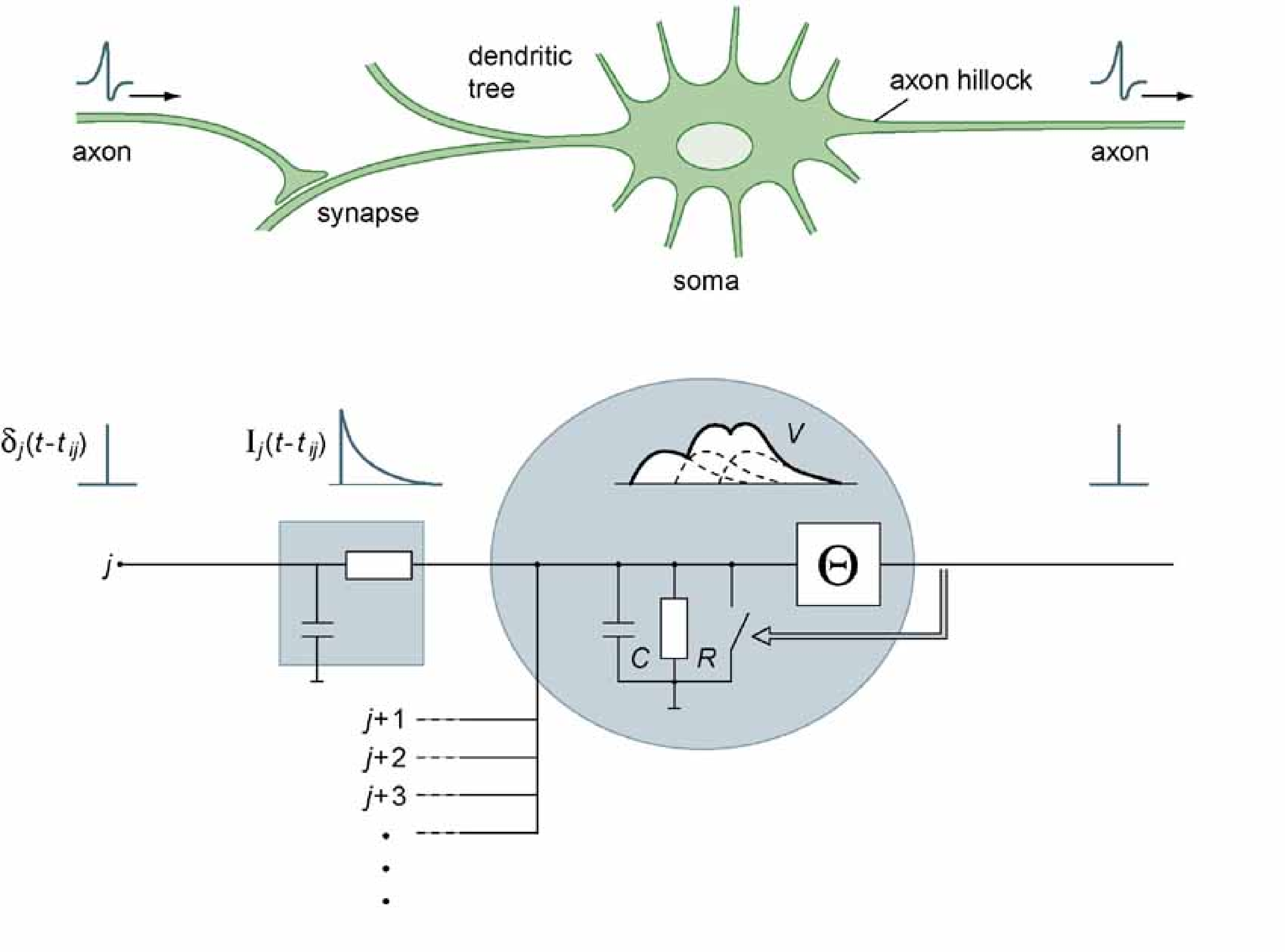


R. Oligschläger,
et al., APL (2006)

Resistive switch (memristive element),
= multilevel non-volatile memory

.... synapses in a
threshold gate (neuron model)





R. Waser (ed.), “Nanoelectronics and Information Technology”, Wiley 2005

Mouse Cortex Simulation on an IBM Blue Gene

IBM BlueGene/L (4 racks)

4096 CPUs

1000 Terabytes RAM

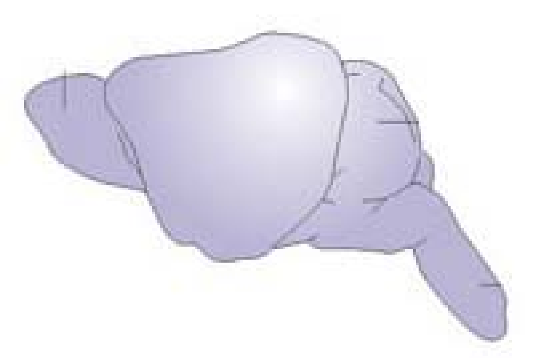
10^9 Hz clock freq.

40 kW power dissipation

Mouse brain

10^6 neurons

10^{10} synapses



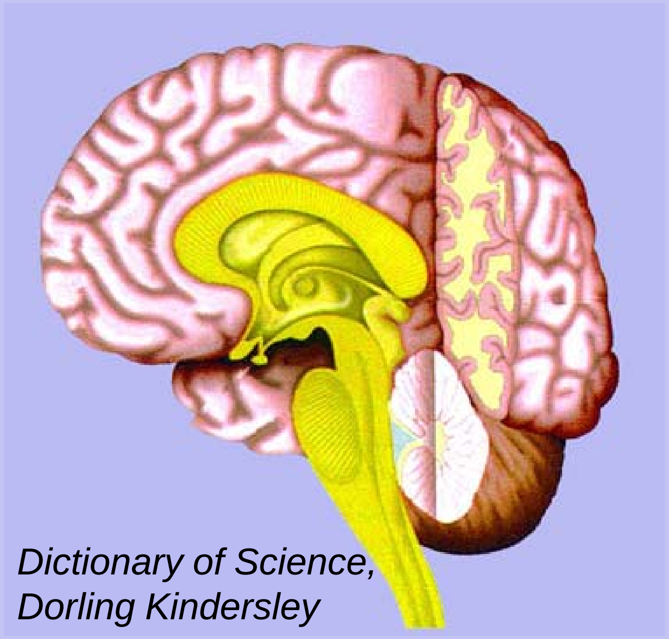
10^2 Hz "clock" freq.

0.5 W power dissipation

Frye, et al, IBM Almaden Research Center, 2007

Human Brain .... on a chip ??

10^{10} neurons
10^{14} synapses

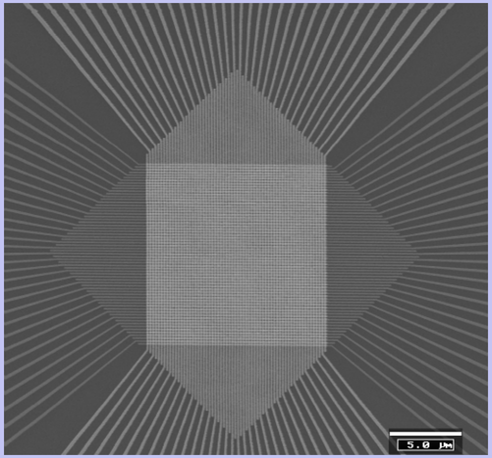


Dictionary of Science, Dorling Kindersley

10^3 cm^2 projected area

→ 10^{11} cm^{-2} synpases density

Nano-crossbar



expected 10^{11} cm^{-2} density of resistive elements

Projects on artificial brain

- **IBM Almaden, Stanford, et al.**
- **HP Research Palo Alto**

7

Conclusions

Challenges

- Design rules not yet fully known
  ... to guide search in the material´s „treasure map“
- Long-term reliability
  ... and overcoming the voltage-time dilemma
- Defect engineering
  ... just at it´s very beginning
- Highly scaled interconnect lines
  ... and reliable electrode contacts

Prospects

- Technologically compatible to CMOS interface
- Ultimately high scaling potential
  .... of redox-based resistive switching concepts
- Functions beyond pure memory
  ... from FPGA type logic to neural functions to cognitive computing

nature conference

Frontiers in Electronic Materials:
Correlation Effects and Memristive Phenomena

Aachen, Germany

Eurogress Conference Centre

June 17th to 20th, 2012

Scientific Organization Committee

Jörg Heber, *Nature Publishing Group*
Rainer Waser and Matthias Wuttig,
RWTH Aachen & FZ Jülich, JARA -FIT
Yoshi Tokura, *Tokyo University*
Darrell Schlom, *Cornell University*

Thank You!

JÜLICH
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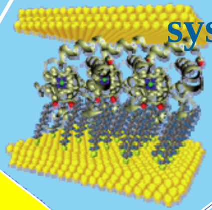
Research Topics

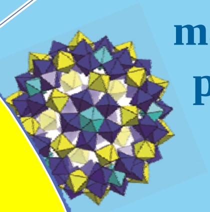
Topic 1
Frontiers of charge based electronics

Topic 2
Spin-based and quantum information

Topic 3
Sensorics and bioinspired systems



Topic 4
Exploratory materials and phenomena



Peter Grünberg Institut

JARA|FIT
Fundamentals of Future Information Technology

Peter Grünberg Institut in JARA|FIT

Fundamentals of Future Information Technology

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S. Blügel

Scattering Methods
Th. Brückel

Semiconductor Nanoelectronics
D. Grützmacher

Theoretical Nanoelectronics
D. DiVincenzo

Bioelectronics
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Electronic Properties
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