Functional thin films oxide: science and application

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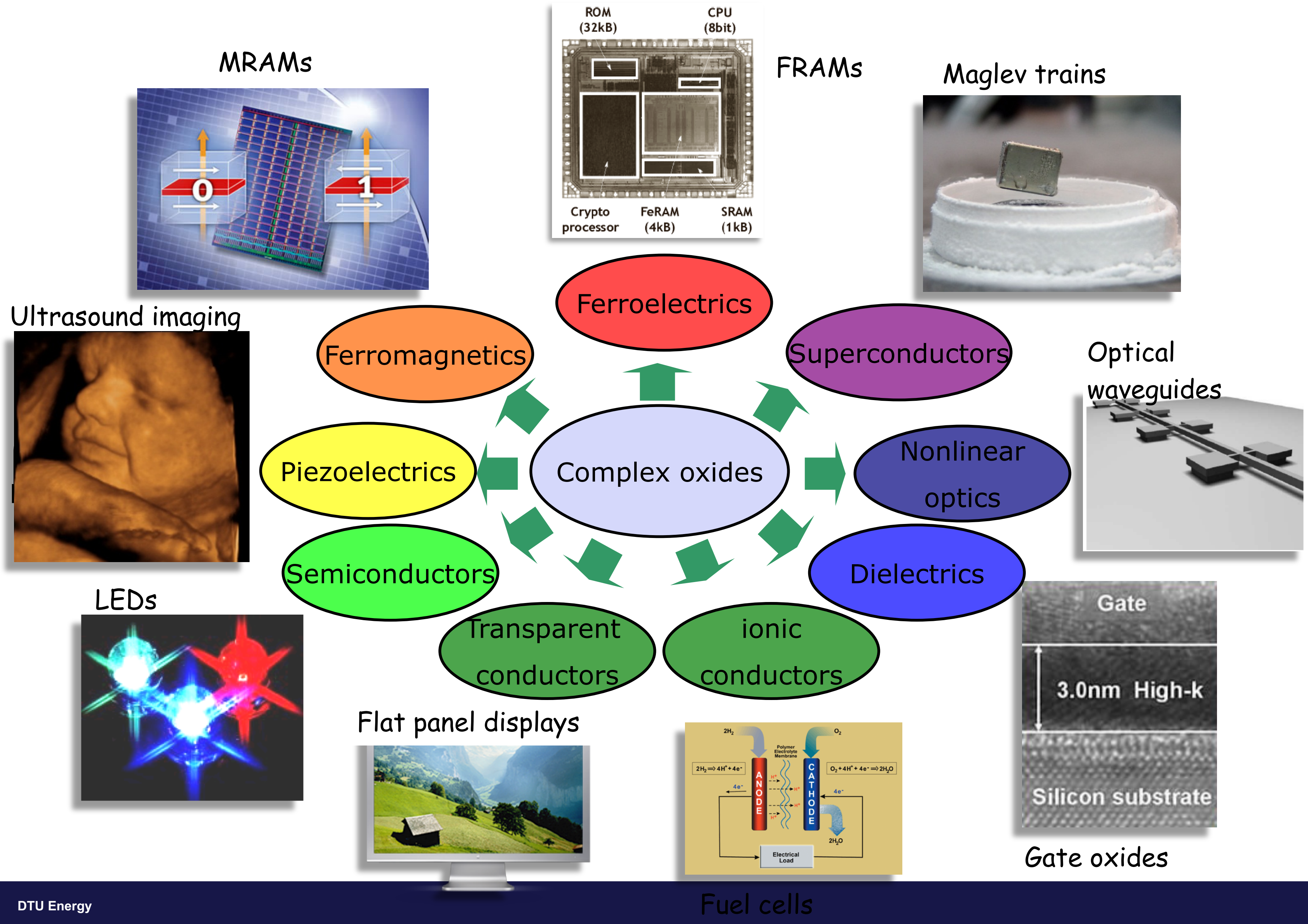
Department of Energy Conversion and Storage (**DTU Energy**)
Technical University of Denmark

Why the interest in Complex Oxides?



The richness of properties arises from strongly correlation between…..

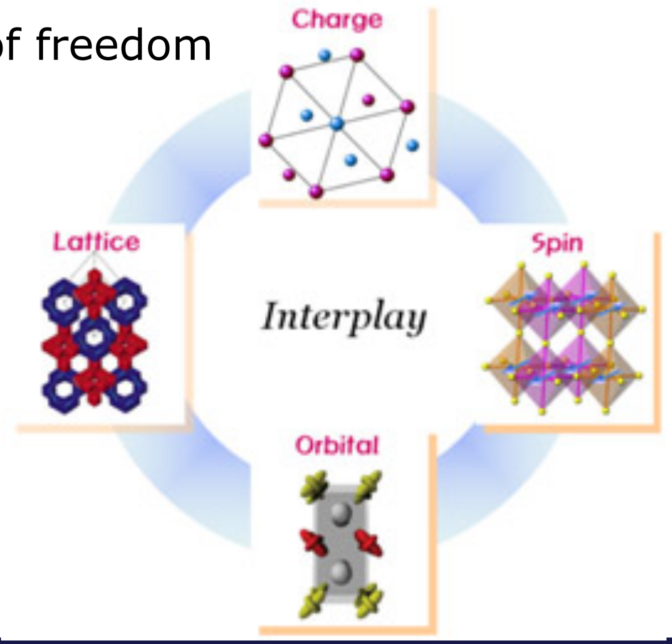
e-e interaction

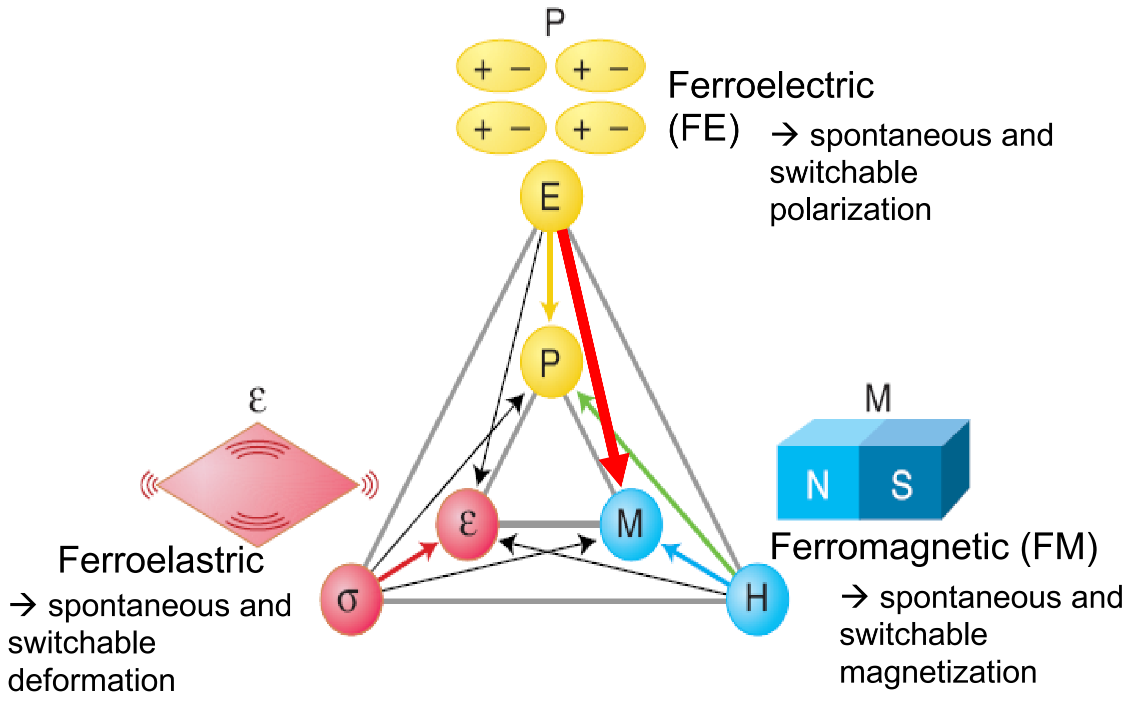
e-l interaction

Defect chemistry

Interplay between:

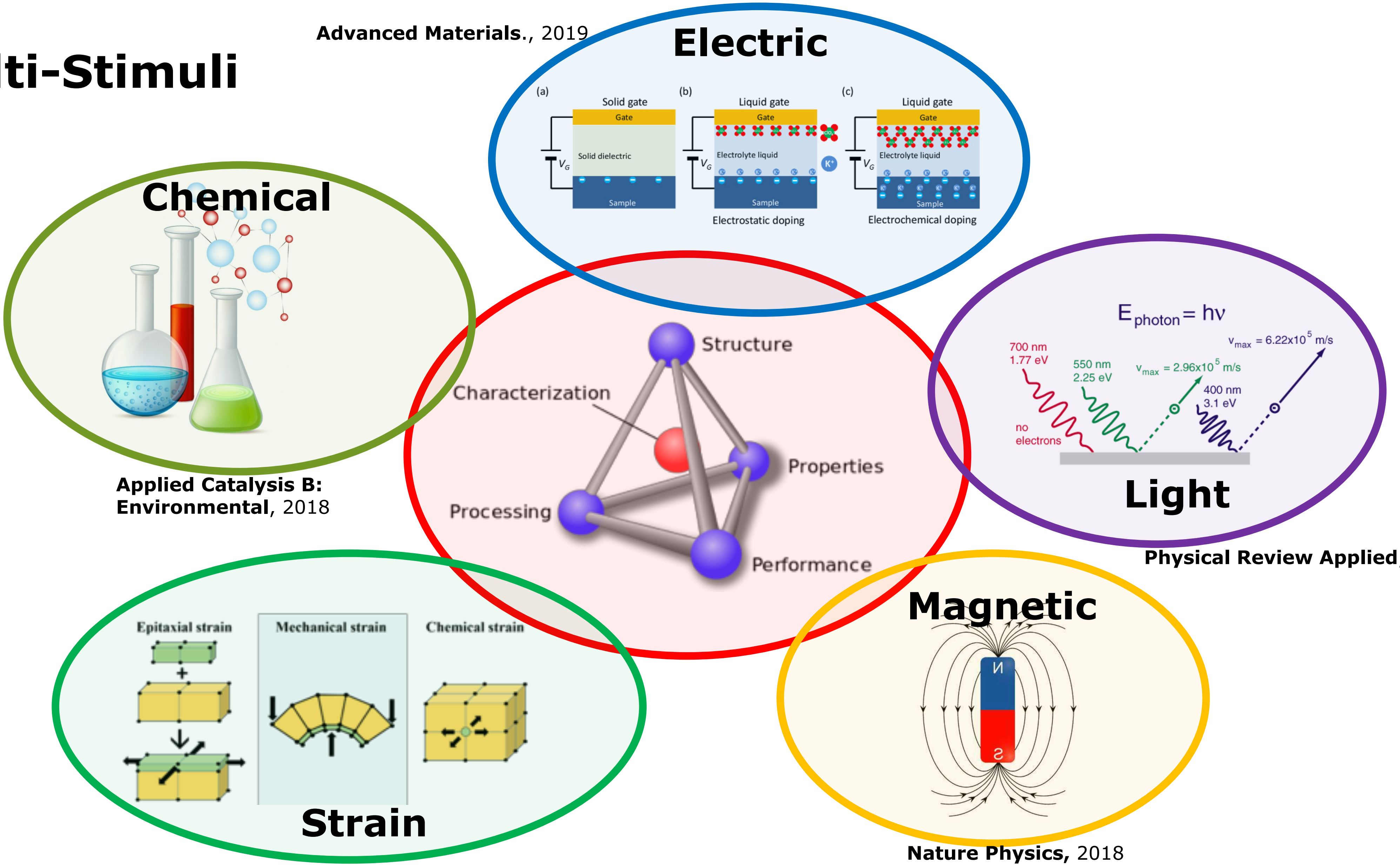
- Charge
- Spin and
- Orbital degree of freedom





Nature Reviews Materials **1**, 16046 (2016)

Multi-Stimuli



Advanced Materials., 2019

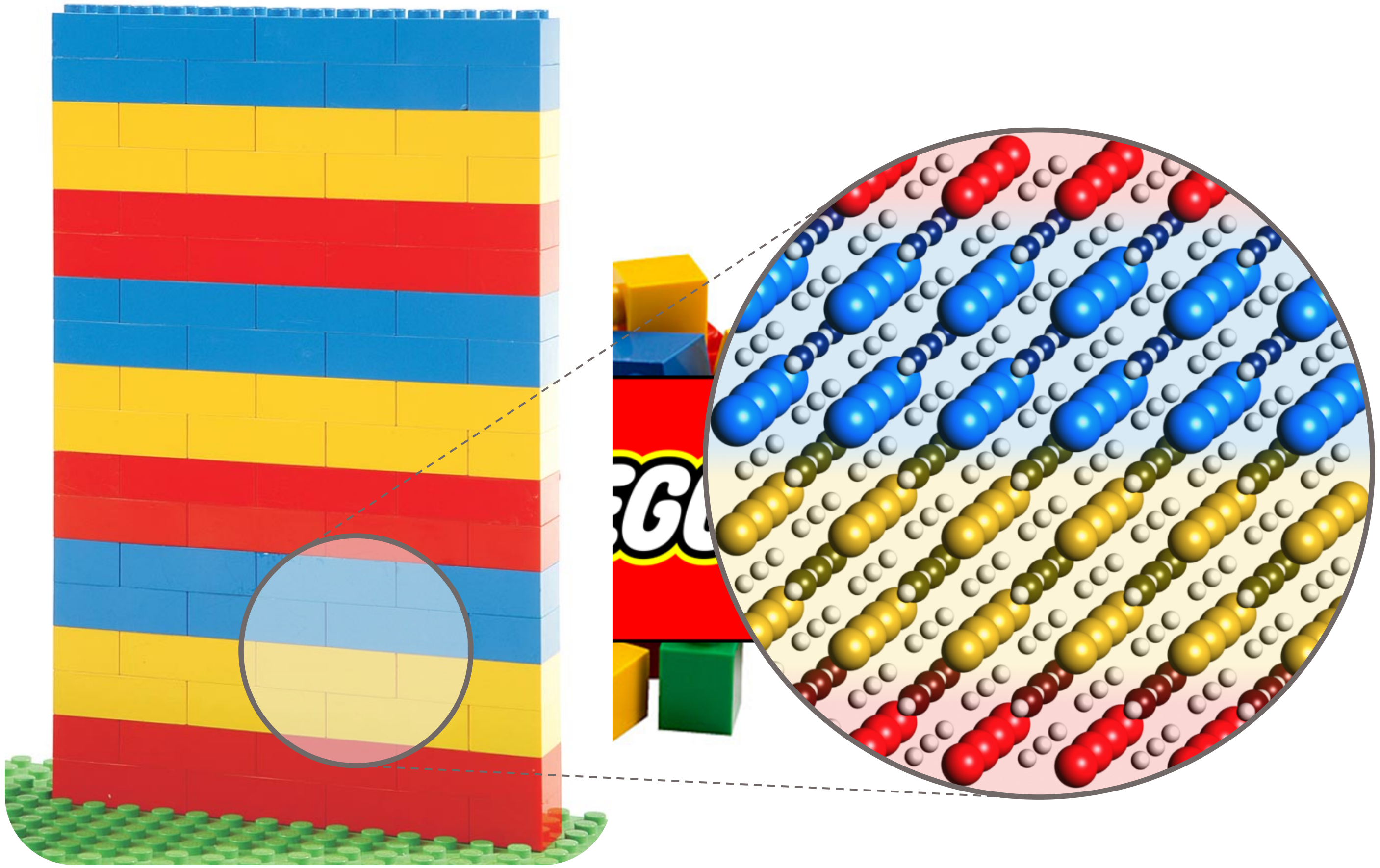
Applied Catalysis B: Environmental, 2018

Physical Review Applied, 2018

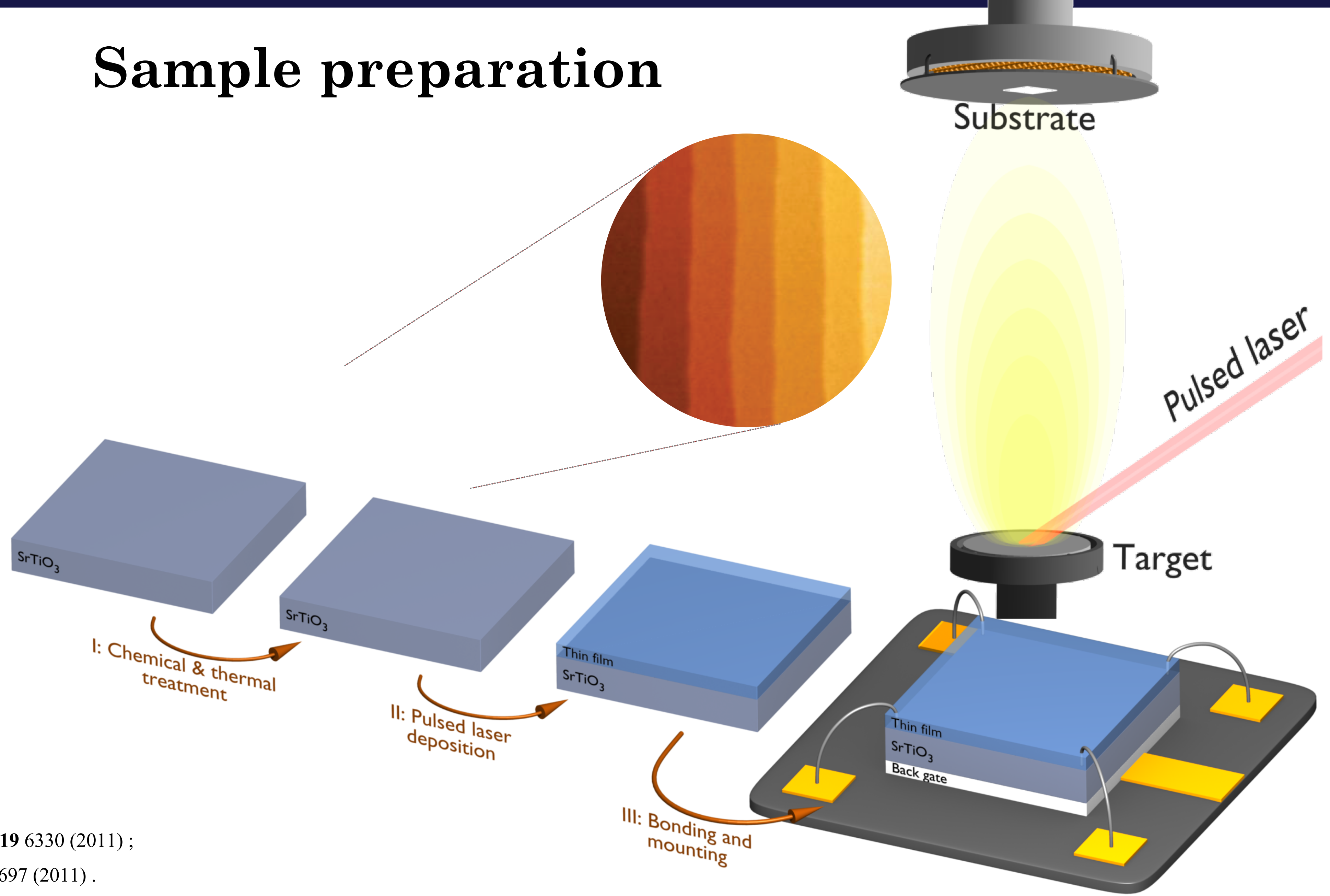
Nature Physics, 2018

Advanced Materials, 2018

Interfaces or confined systems?



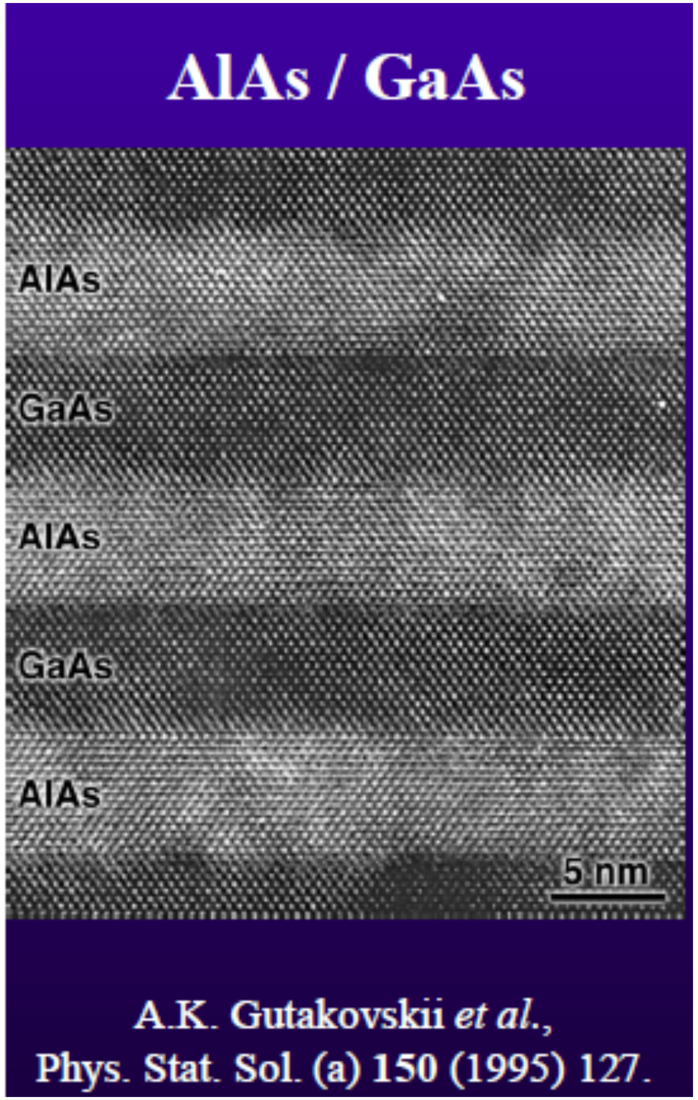
Sample preparation

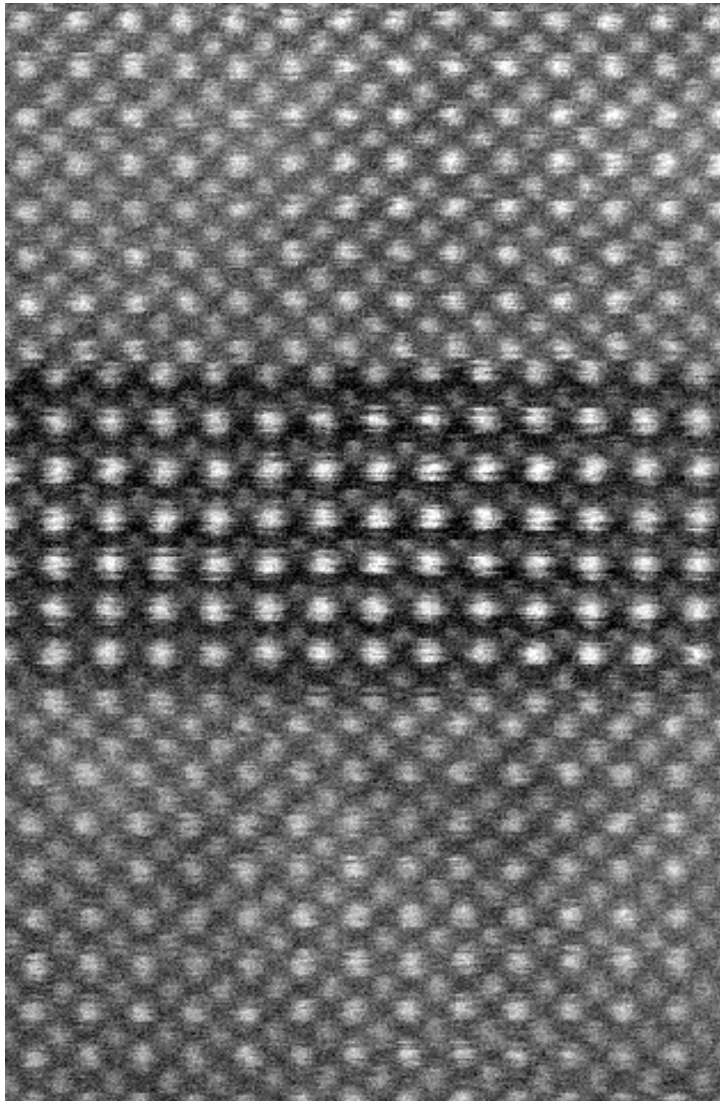


Thin Solid Films **519** 6330 (2011) ;

Appl Phys A **105**, 697 (2011) .

Control and identification of point defects are challenges.



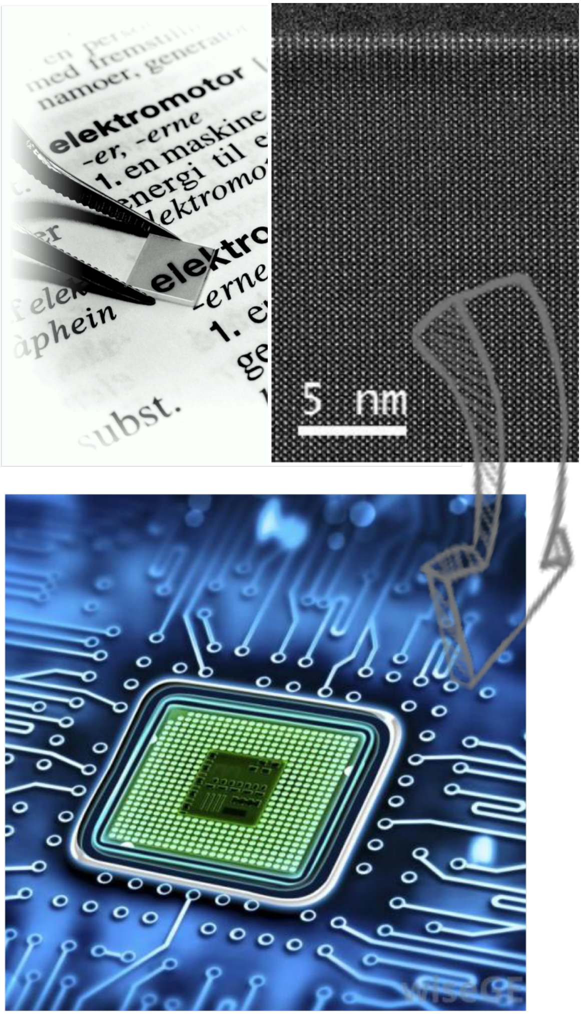


$SrRuO_3$

$BaTiO_3$

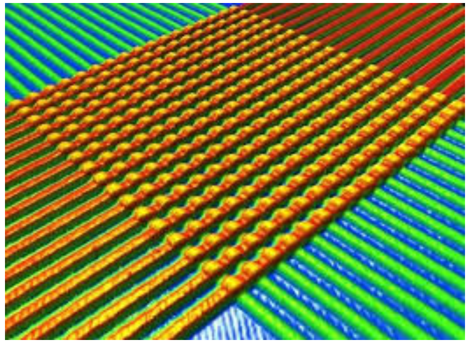
$SrRuO_3$

Oxide electronic



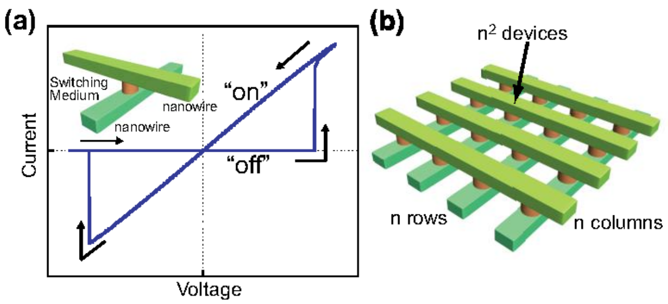
- **New functionality**
- **Completely new parameters**

Memory devices

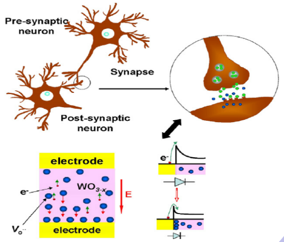


ReRAM devices: memristors

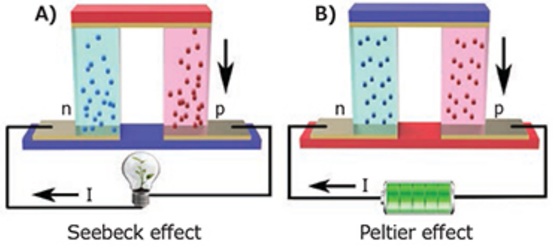
Non-Volotiel

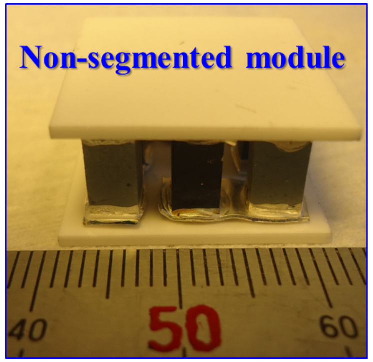


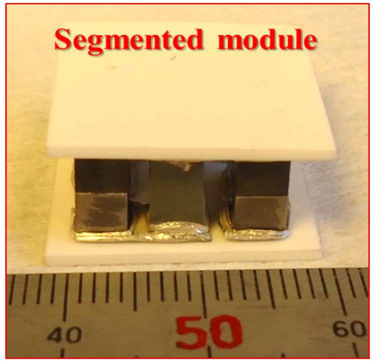
Neuromorphic computing



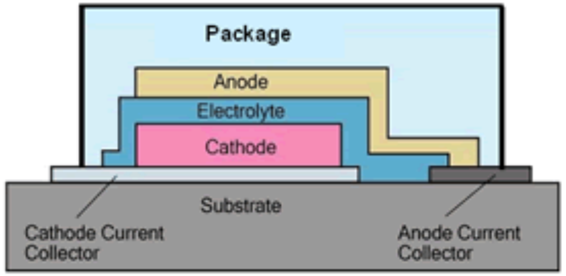
Thermoelectricity

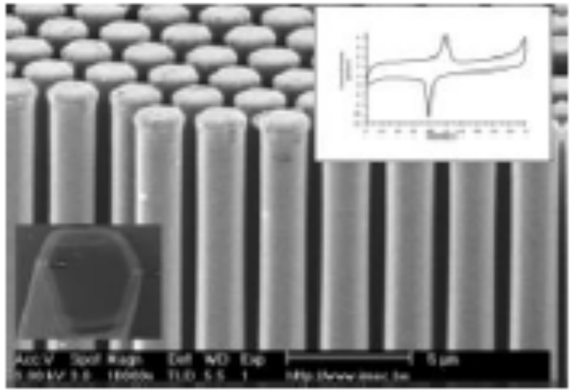




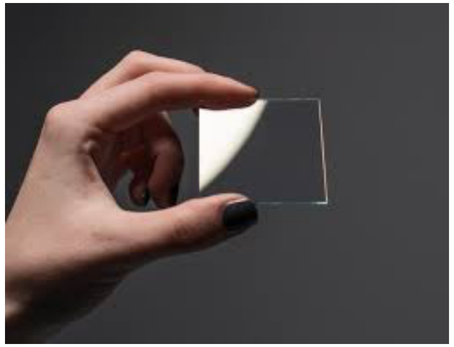


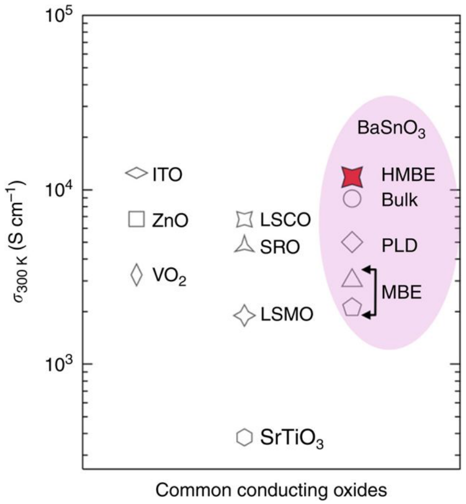
Solid-state Batteries



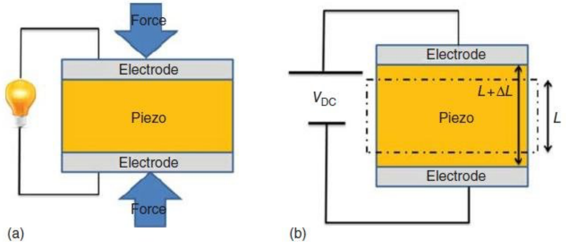


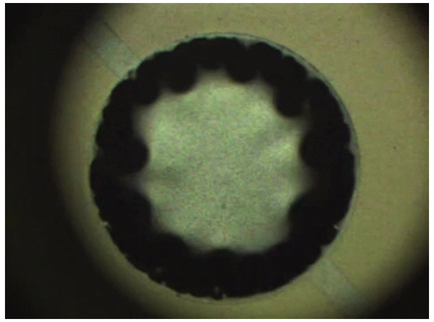
Conductive transparent oxide

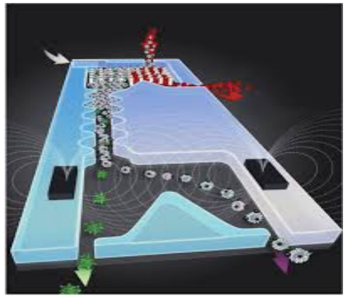




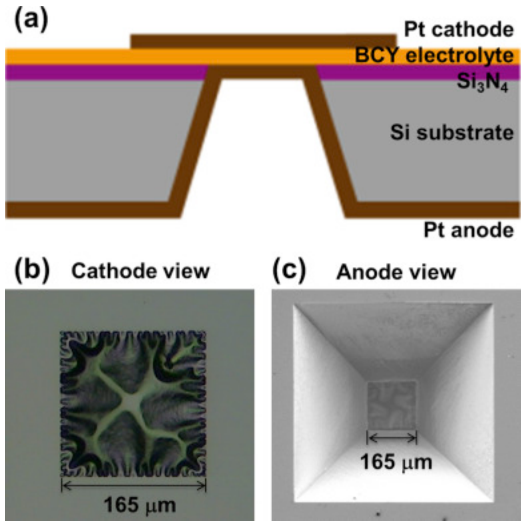
Piezoelectricity And electrostriction oxide

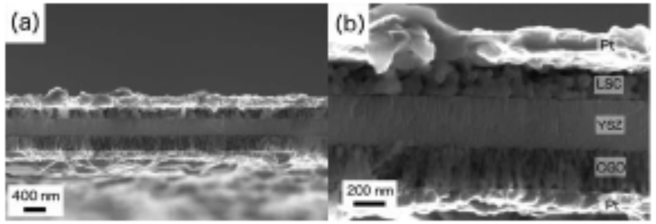




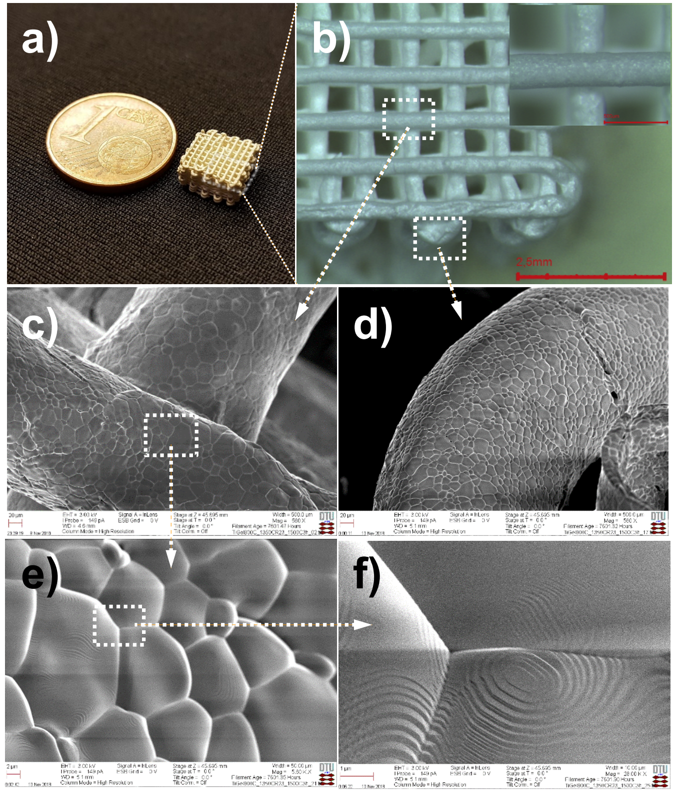


µ-SOFC

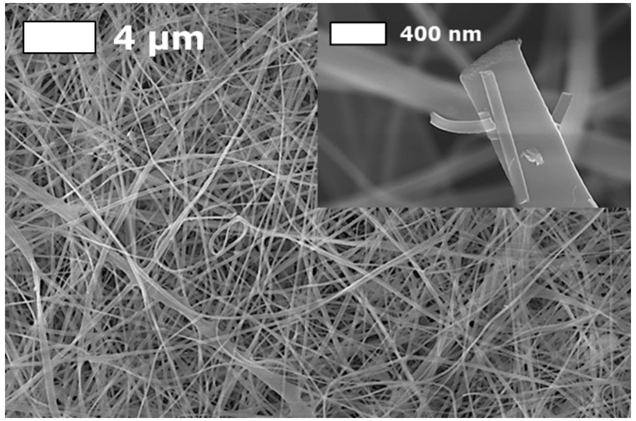


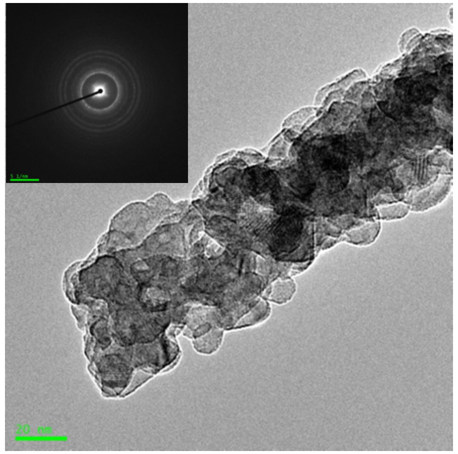


3D Printing



Catalyst





Oxide electronic

Often, it may be said that the interface is the device.

Kroemer H (Nobel Lecture) *Review of Modern Physics* **73**, 783-793 (2001).

editorial

The interface is still the device

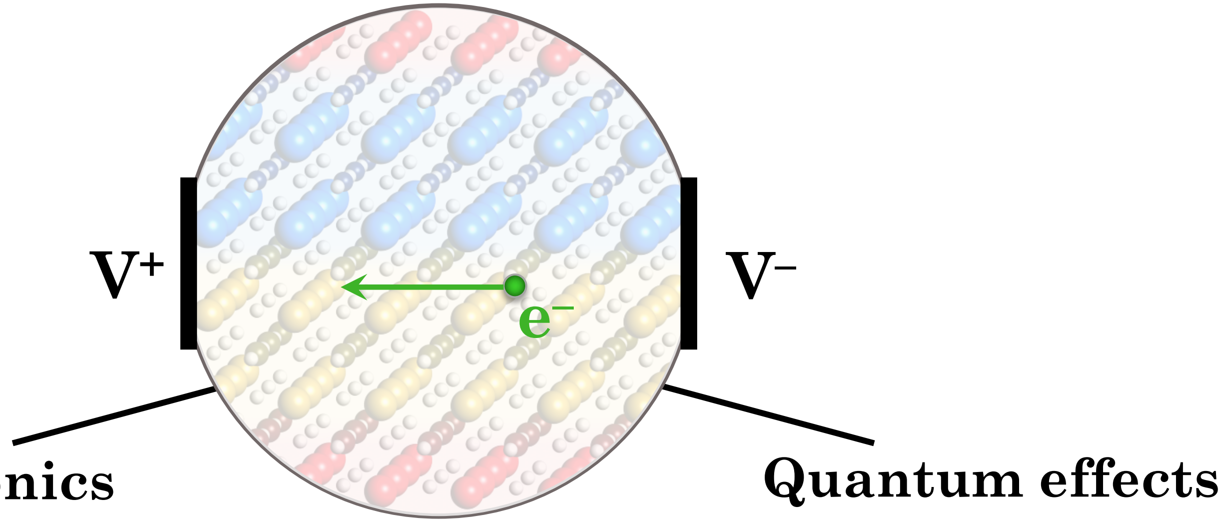
Oxide materials show an amazing variety of electronic and ionic phenomena. However, despite considerable advances in understanding and utilizing these effects, experimental and theoretical challenges still need to be addressed before the promised applications can be realized.

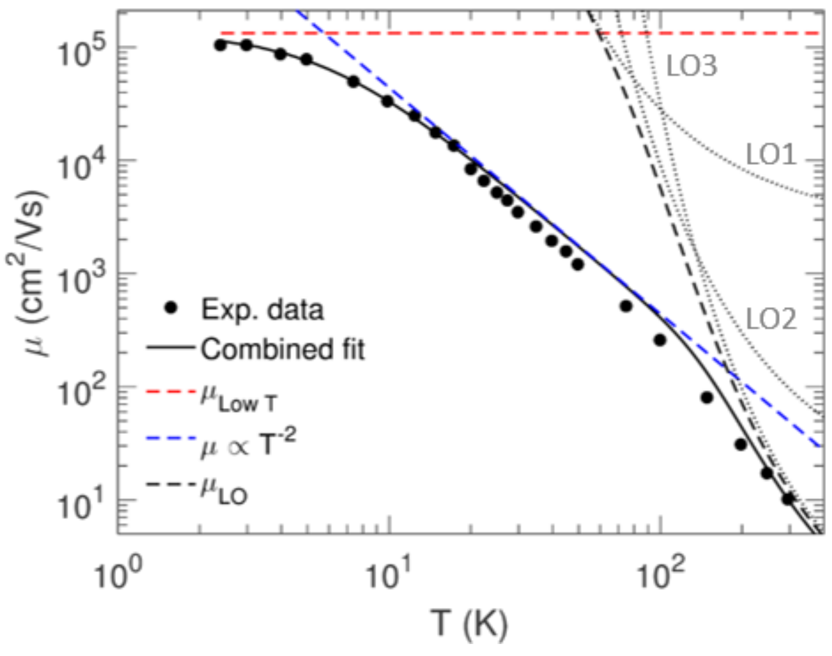
Editorial *Nature Materials* **11**, 91 (2012)

The $LaAlO_3/SrTiO_3$ heterostructure

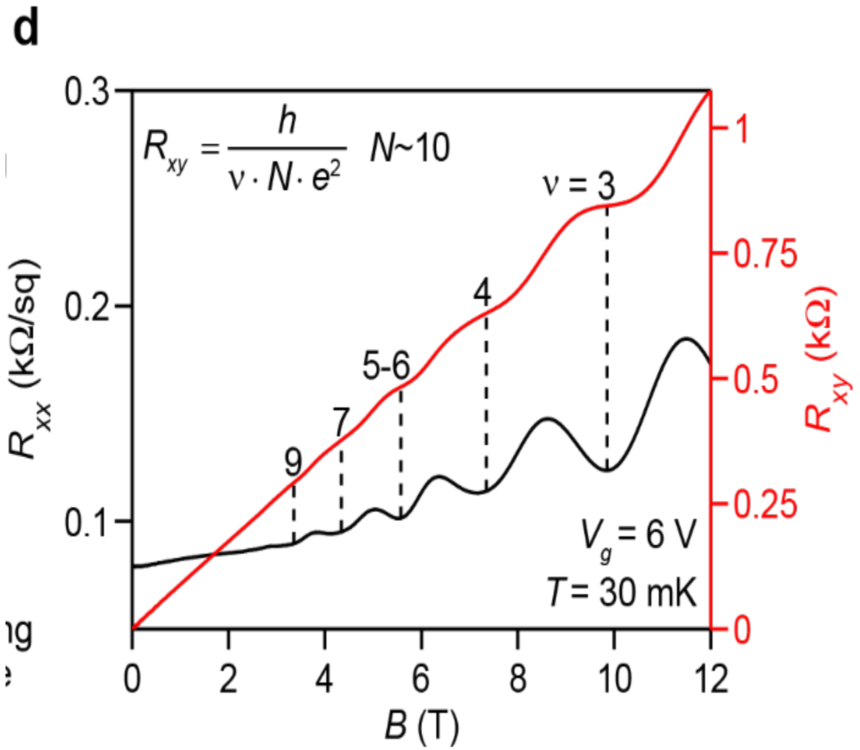
- Electron gas
  Ohtomo A et al. *Nature* **427**, 423 (2004)
- Superconductivity
  Reyren N et al. *Science* **317**, 1196 (2007)
- Electron pairing without superconductivity
  G. Cheng et al. *Nature* **521**, 196 (2015)
- Two-dimensional hole gas at oxide interfaces
  CB Eom et al. *Nature Materials*17, 231–236 (2018)
- Resistance switching
  Thiel S et al. *Science* **313**, 1942 (2006)
- Magnetism
  Brinkman A et al. *Nature Materials* **6** 493 (2007)

High mobility



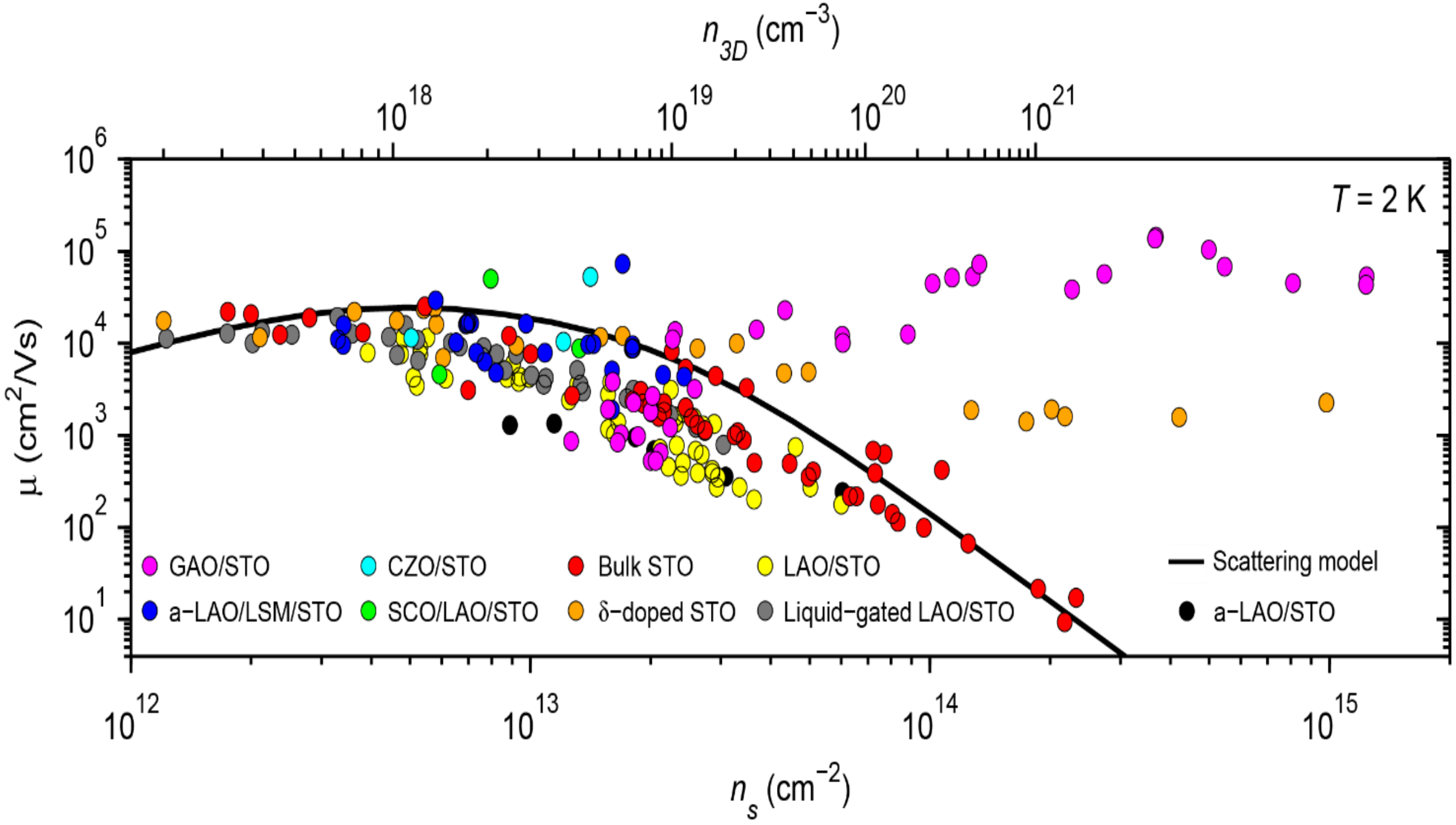


Electron mobility in γ-Al_2O_3/$SrTiO_3$, Phys. Rev. Applied 9, 054004 (2018)



Physical Review letter, 117 (2016)

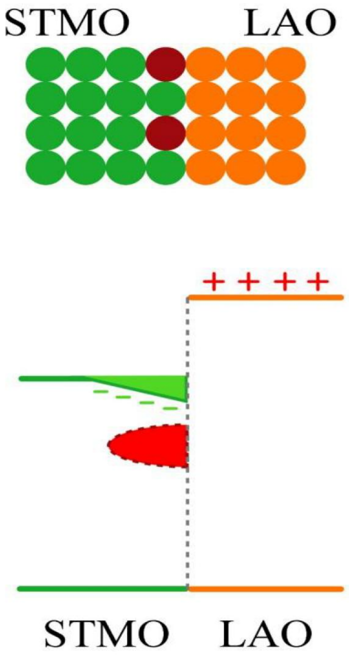
Confined systems and bulk STO

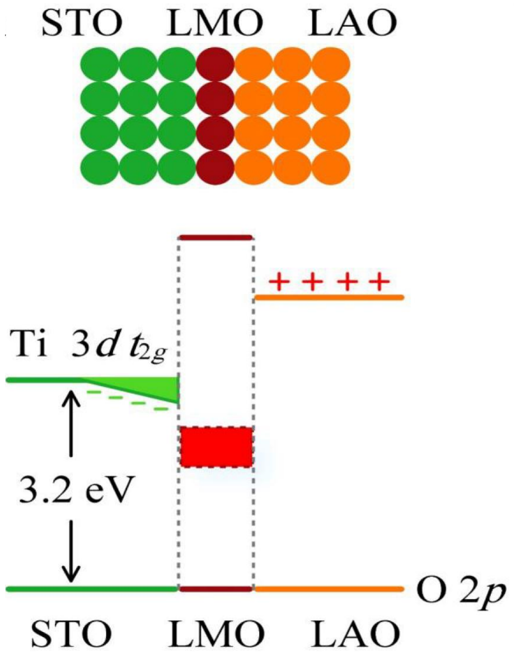


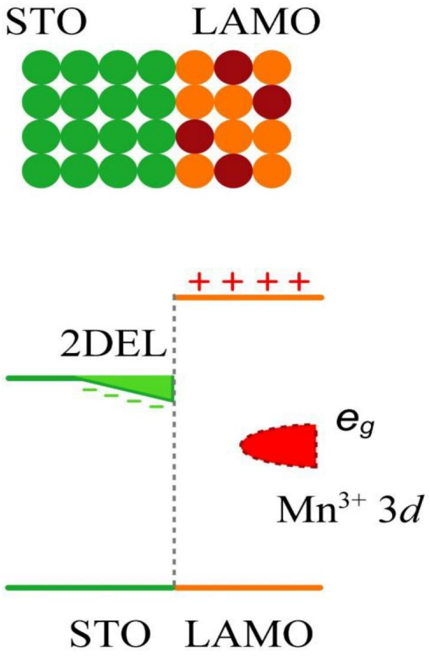
Electron mobility in oxide heterostructures, Journal of Physics D: Applied Physics, Topical Review (2018)

Universality of electron mobility in LaAlO3/SrTiO3 and bulk SrTiO3, Appl. Phys. Lett. 111, 092106 (2017)

Different strategies to control the mobility







PRL 103, 166802 (2009) PHYSICAL REVIEW LETTERS week ending 16 OCTOBER 2009

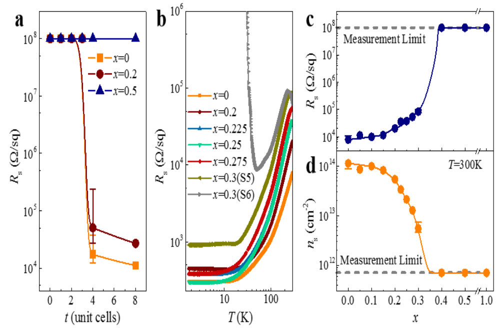
Charge Confinement and Doping at $LaAlO_3/SrTiO_3$ Interfaces

T. Fix, F. Schoofs, J. L. MacManus-Driscoll, and M. G. Blamire

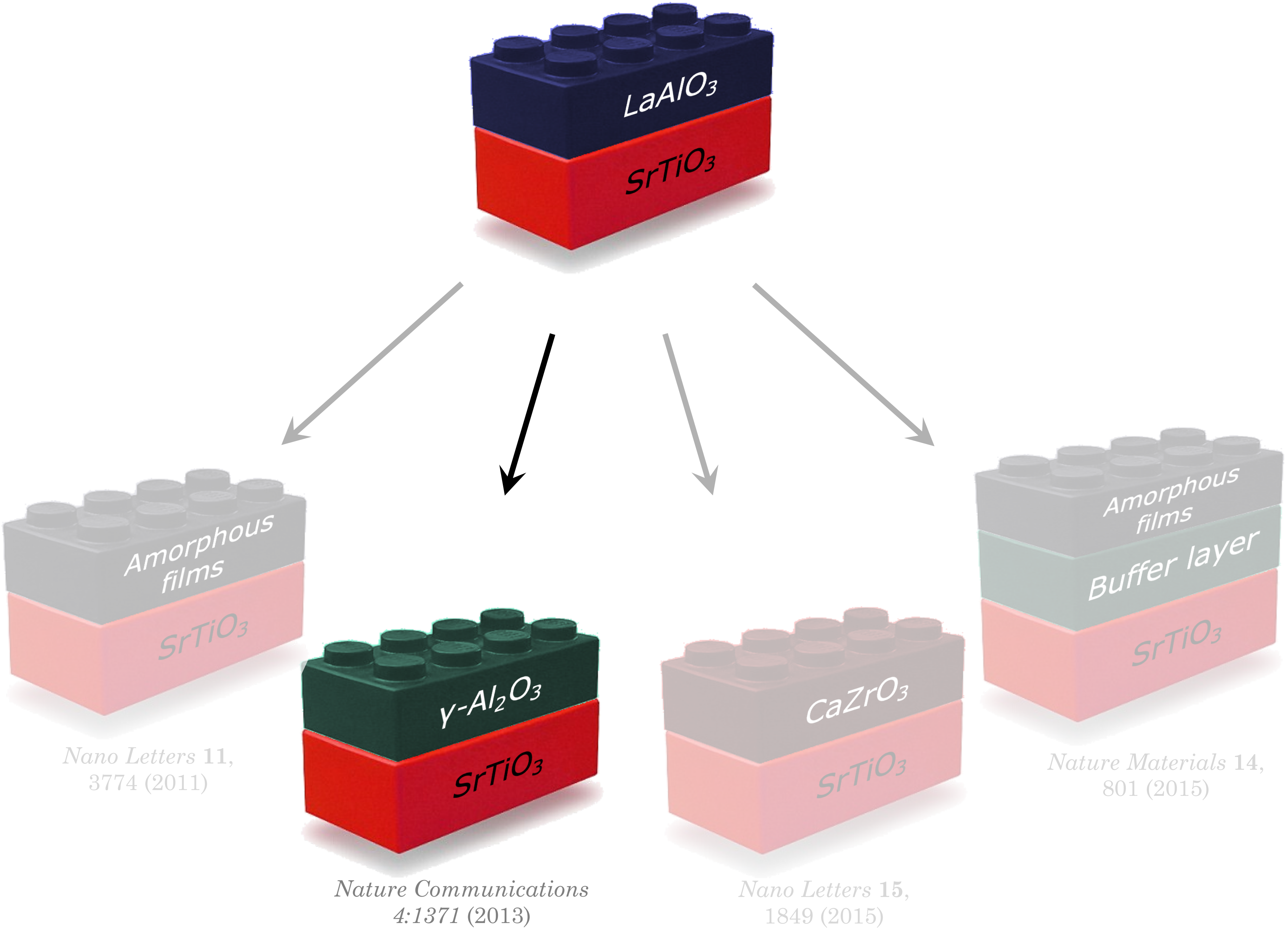
nature materials ARTICLES
PUBLISHED ONLINE: 1 JUNE 2015 | DOI: 10.1038/NMAT4303

Extreme mobility enhancement of two-dimensional electron gases at oxide interfaces by charge-transfer-induced modulation doping

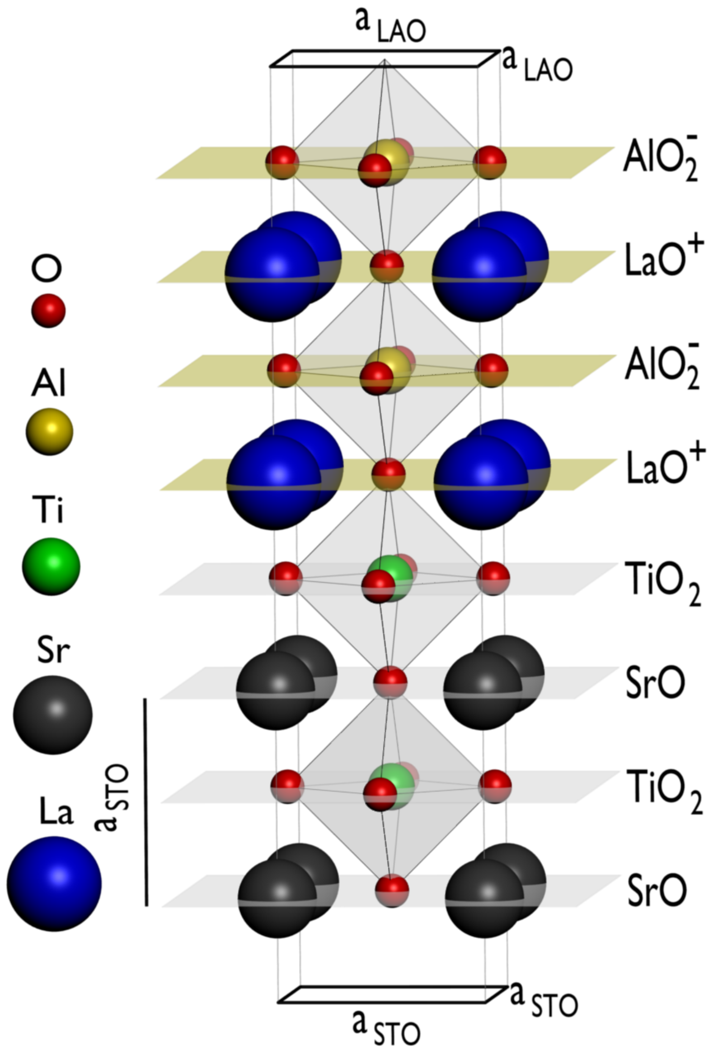
Y. Z. Chen[1]*, F. Trier[1], T. Wijnands[2], R. J. Green[3,4], N. Gauquelin[5], R. Egoavil[5], D. V. Christensen[1], G. Koster[2], M. Huijben[2], N. Bovet[6], S. Macke[3,7], F. He[8], R. Sutarto[8], N. H. Andersen[9], J. A. Sulpizio[10], M. Honig[10], G. E. D. K. Prawiroatmodjo[11], T. S. Jespersen[11], S. Linderoth[1], S. Ilani[10], J. Verbeeck[5], G. Van Tendeloo[5], G. Rijnders[2], G. A. Sawatzky[3] and N. Pryds[1]



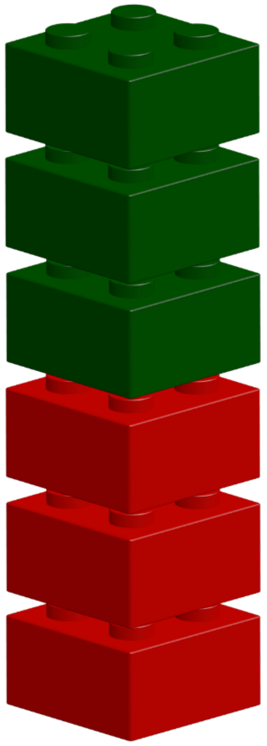
Submitted under review


LaAlO3
SrTiO3
Amorphous films
SrTiO3
Nano Letters 11, 3774 (2011)
γ-Al2O3
SrTiO3
Nature Communications 4:1371 (2013)
CaZrO3
SrTiO3
Nano Letters 15, 1849 (2015)
Amorphous films
Buffer layer
SrTiO3
Nature Materials 14, 801 (2015)

How to make interfaces

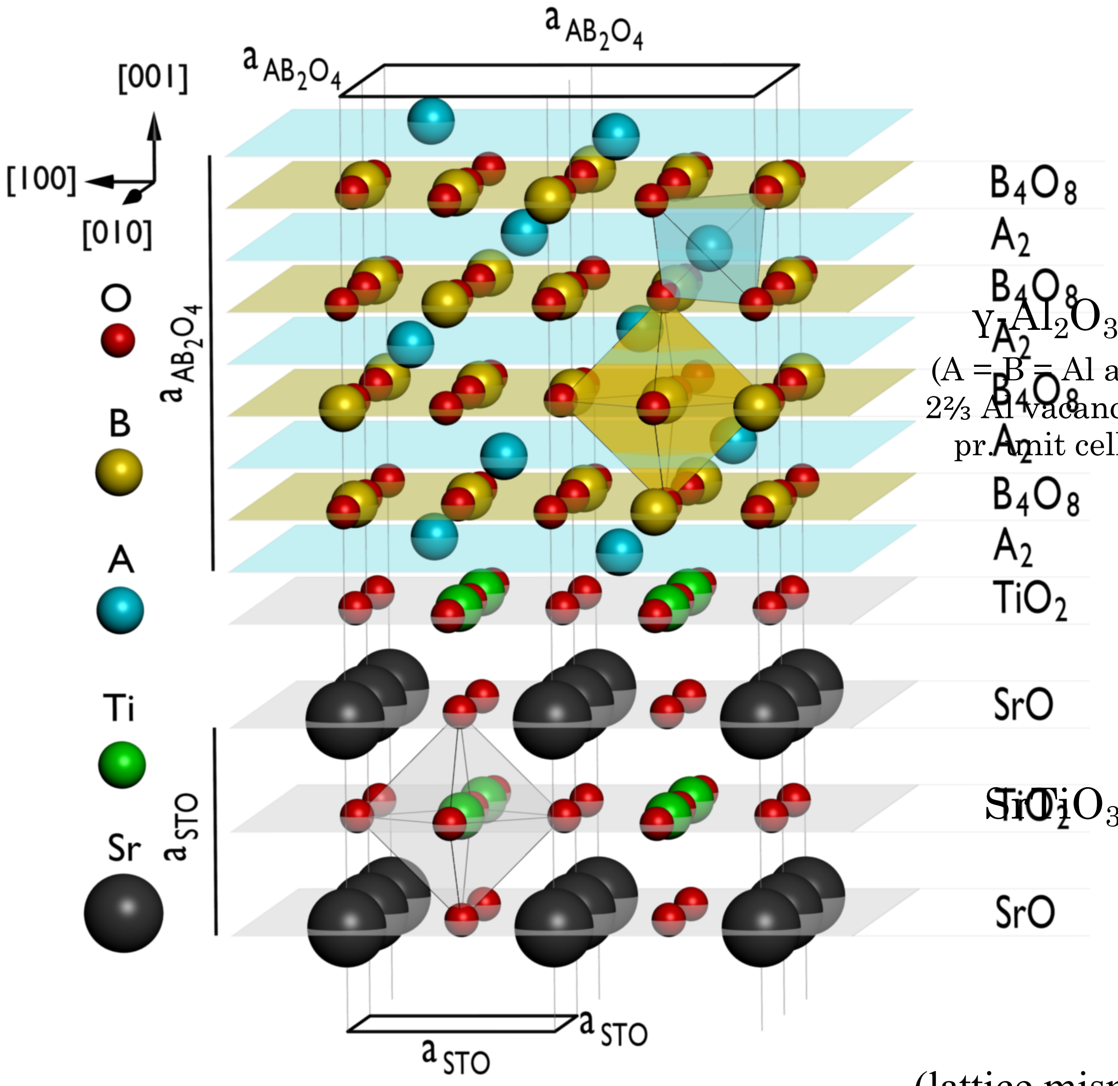


$LaAlO_3$



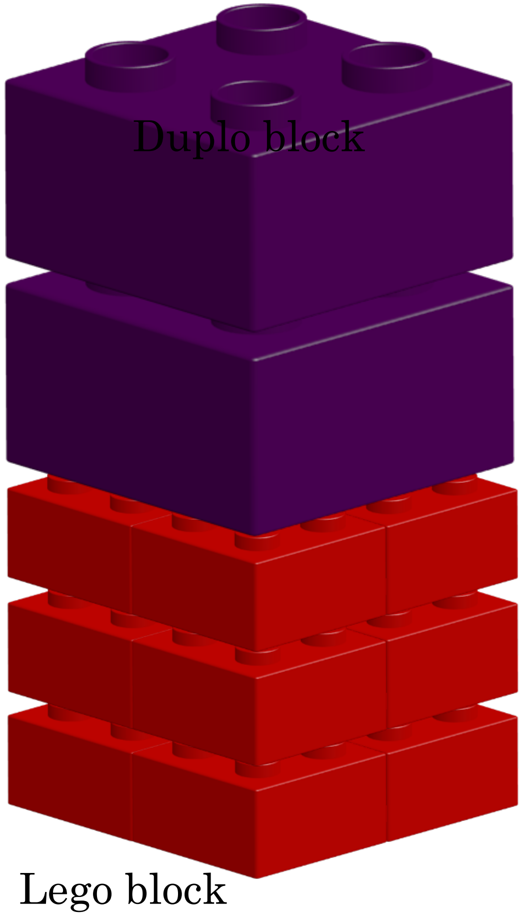
$SrTiO_3$

How to make interfaces



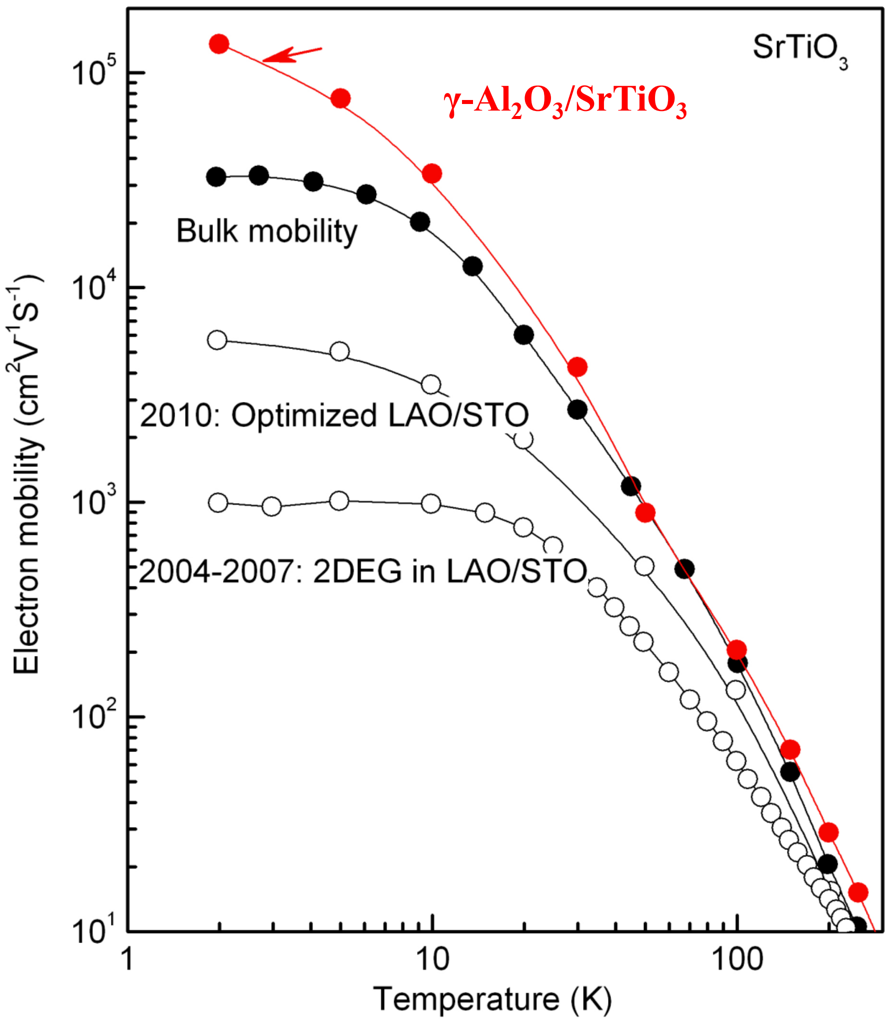
γ-Al_2O_3
(A = B = Al and 2⅔ Al vacancies pr. unit cell)

$SrTiO_3$



(lattice mismatch 1.2% for GAO/STO).

Highest electron mobility at oxide interfaces 2DEGs !



For GAO/STO :

μ_{Hall} =140,000 cm²/Vs
μ_{SDH} =7200 cm²/Vs

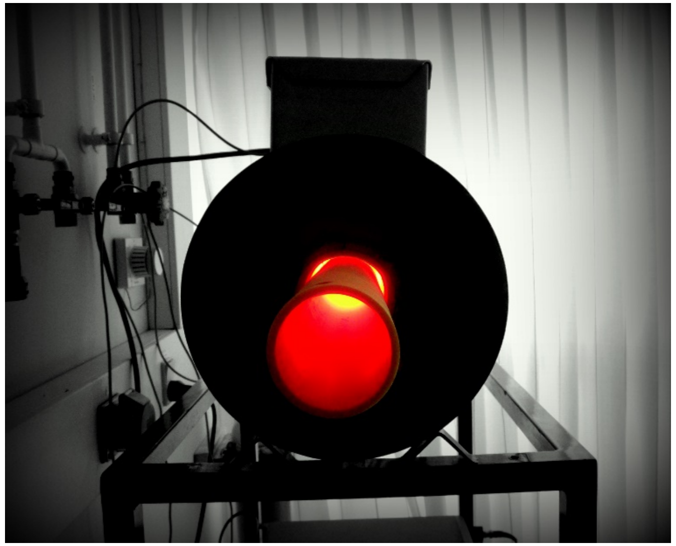
For LAO/STO

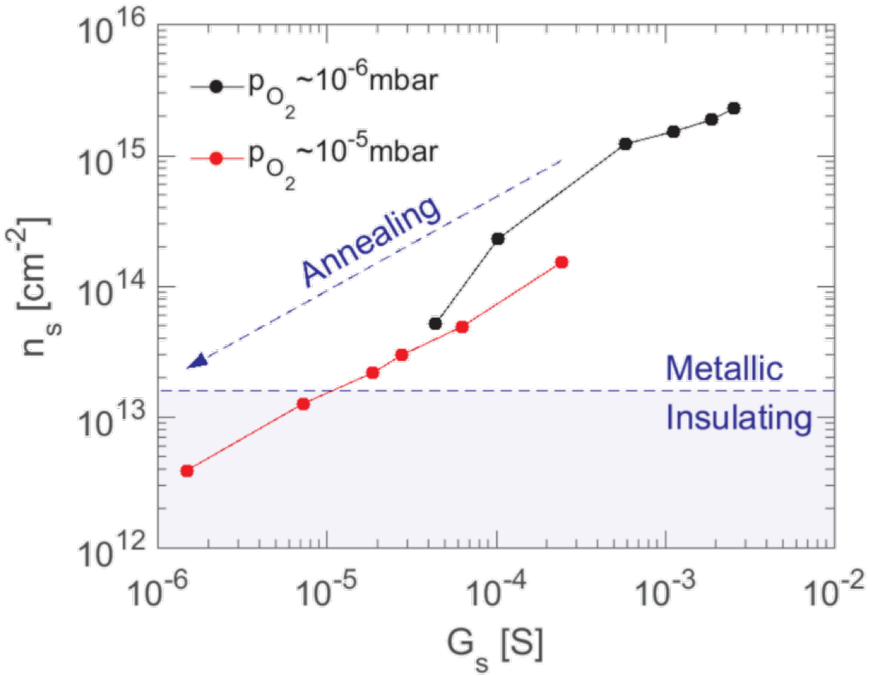
μ_{Hall} =7000 cm²/Vs ,

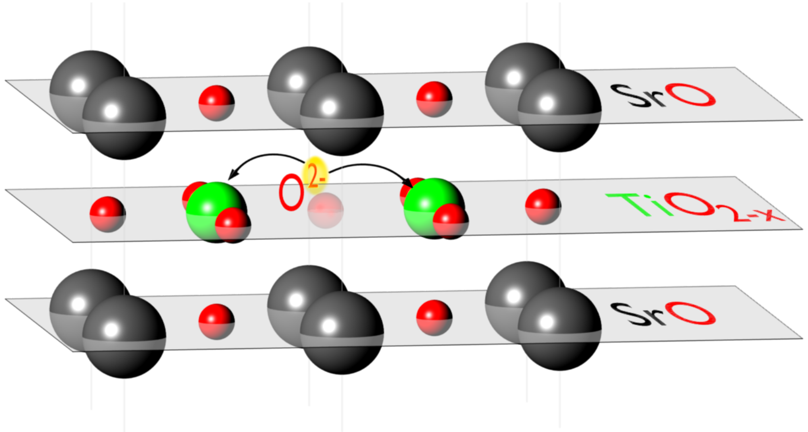
μ_{SDH} <300 cm²/Vs

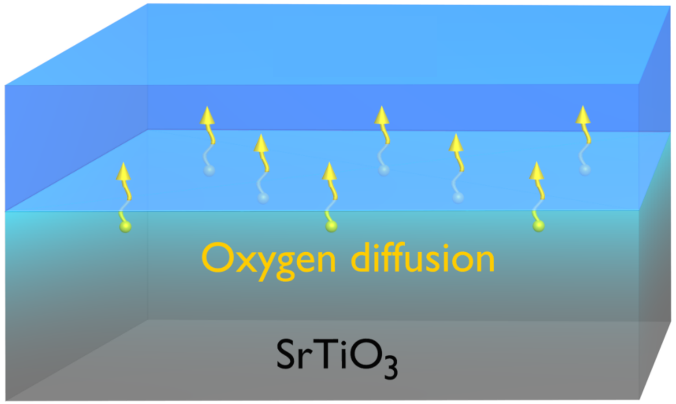
Nature Communications, 4:1371, (2013)

Understanding the conductivity







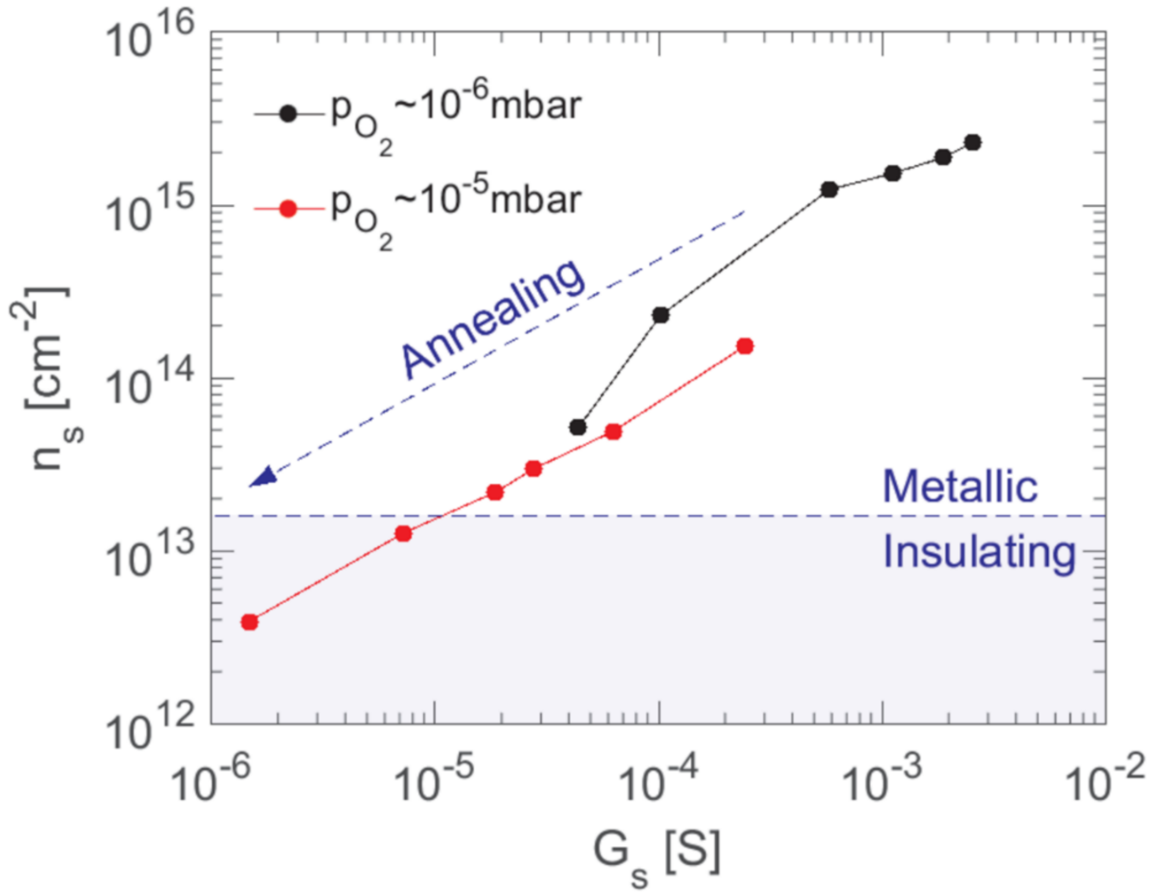


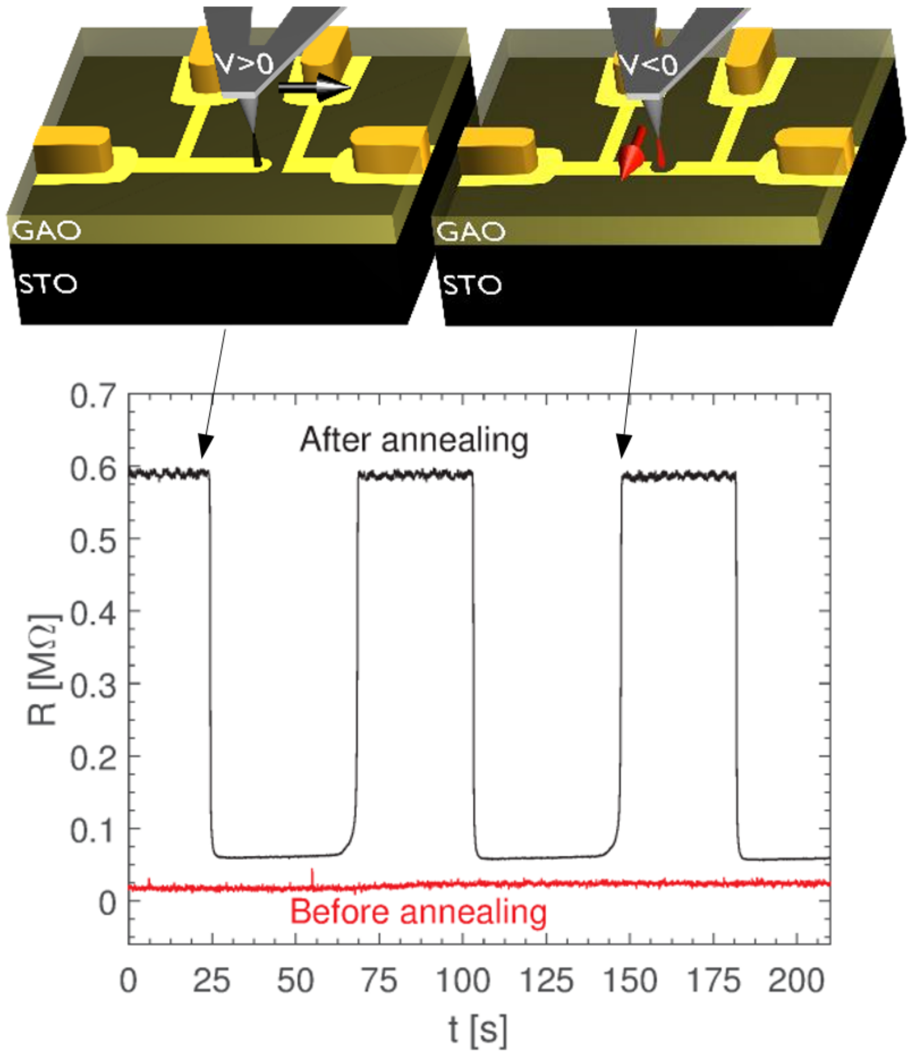
Nano Letters **11**, 3774 (2011)

- *Advanced Electronic Materials, 1700026 (2017).*
- *ACS Appl. Mat. Interfaces 9, 1086-1092 (2017).*

When 'nothing' is tuned

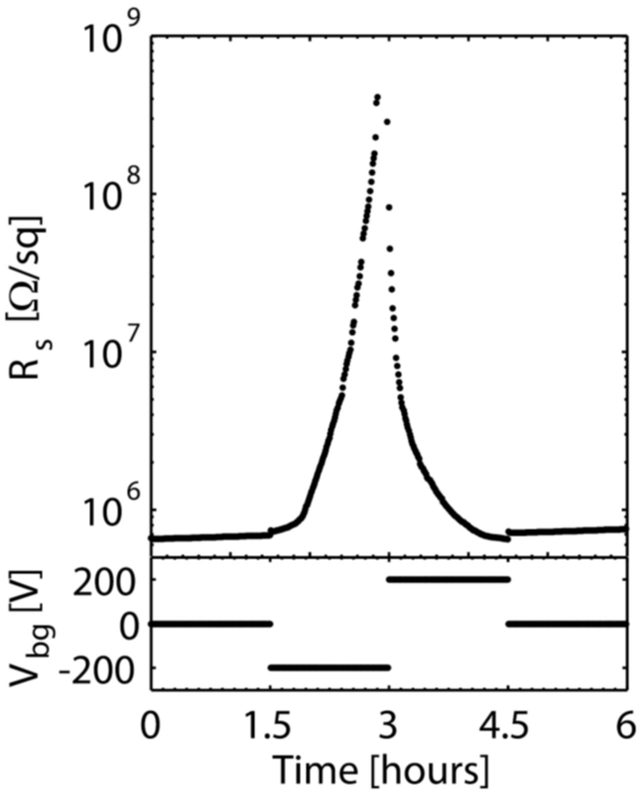
Carrier density control by annealing

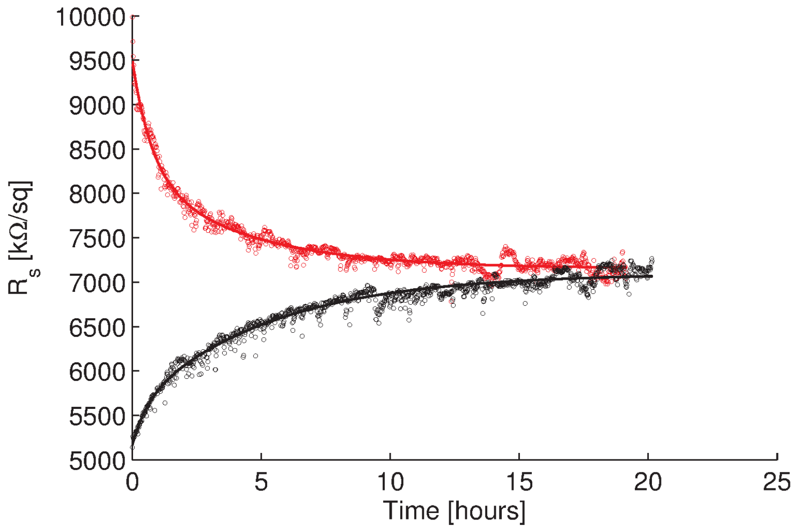




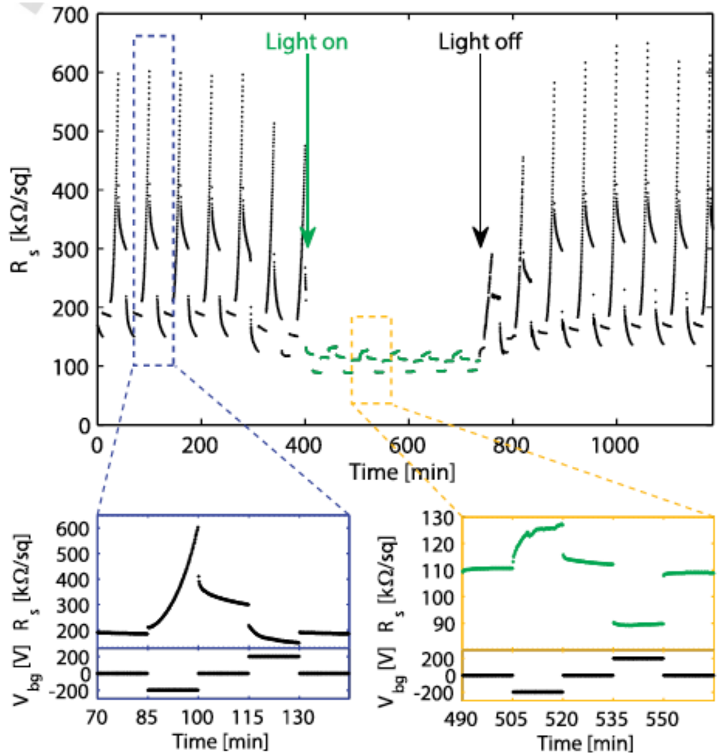
Advanced Electronic Materials, 1700026 (2017).

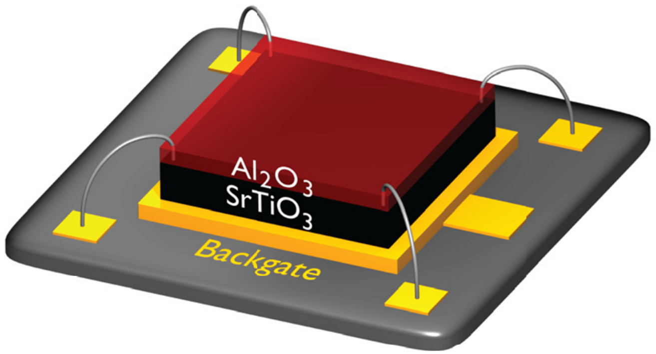
When ‘nothing’ is tuned: Resistive switching





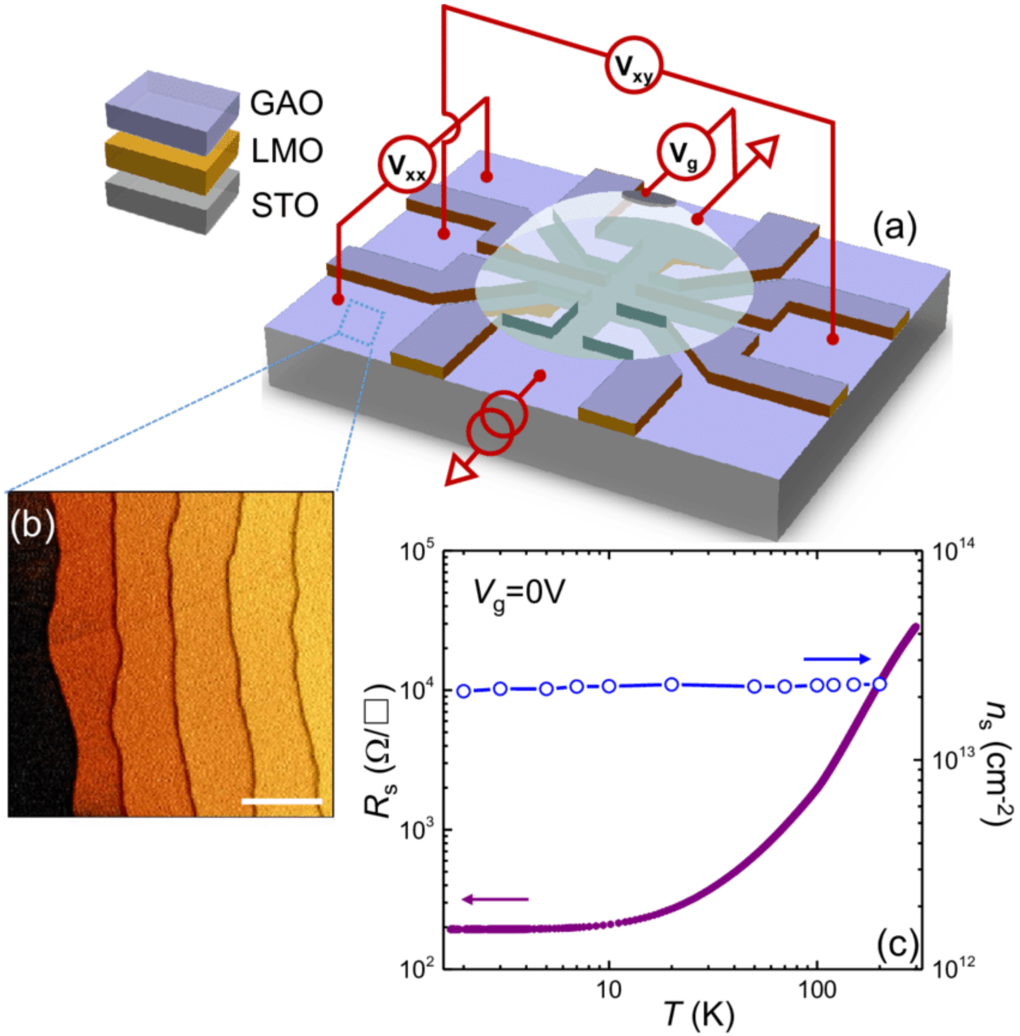
- V_g=0 Photocurrent
- Light -> RS ability
- Dark -> Non-volatile
- Light -> Volatile

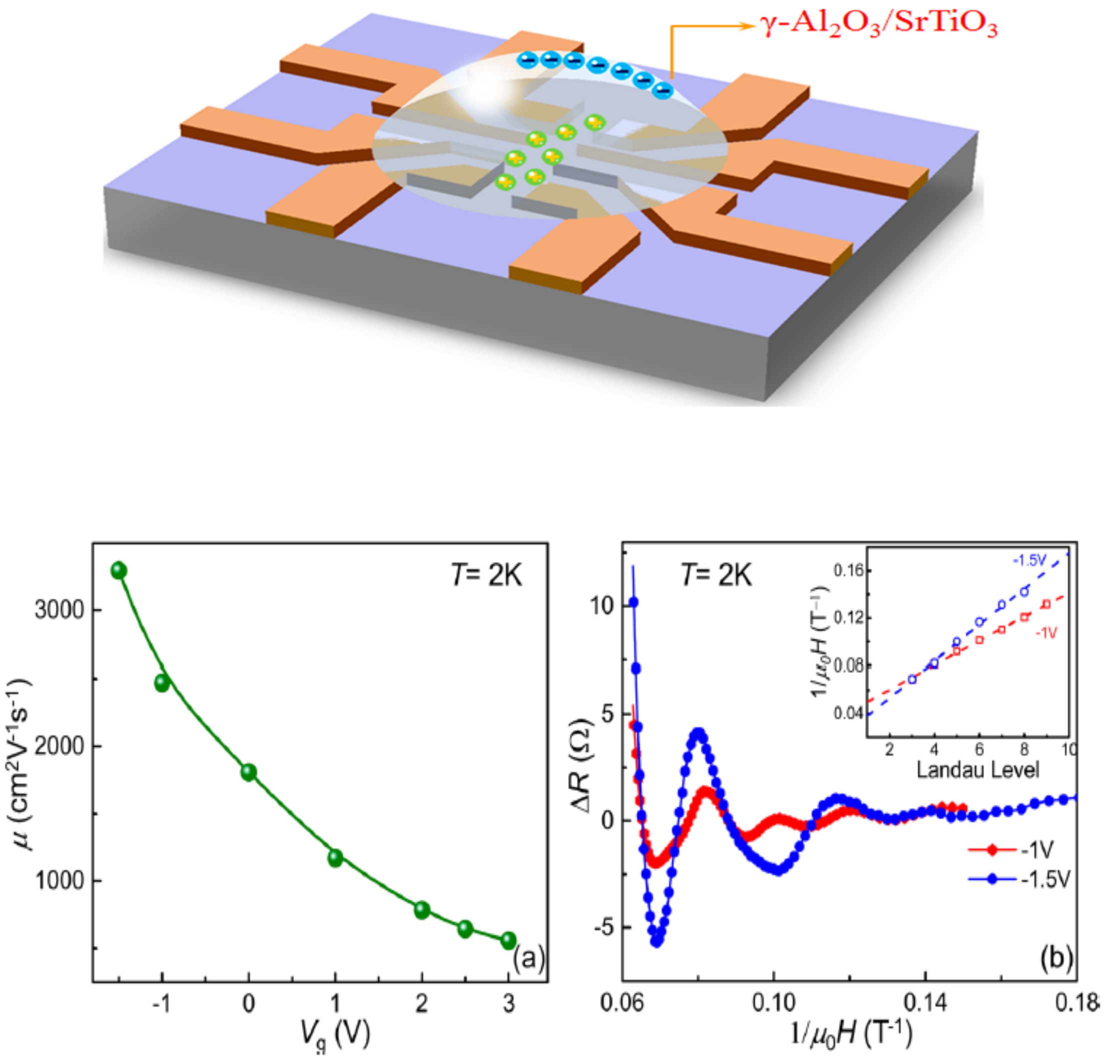




Appl. Phys. Lett. 106, 021602 (2016)
Nature Communications **5**, 5554 (2014)
Scientific Reports, 6, 22418 (2016)

Ionic Liquid Gatting

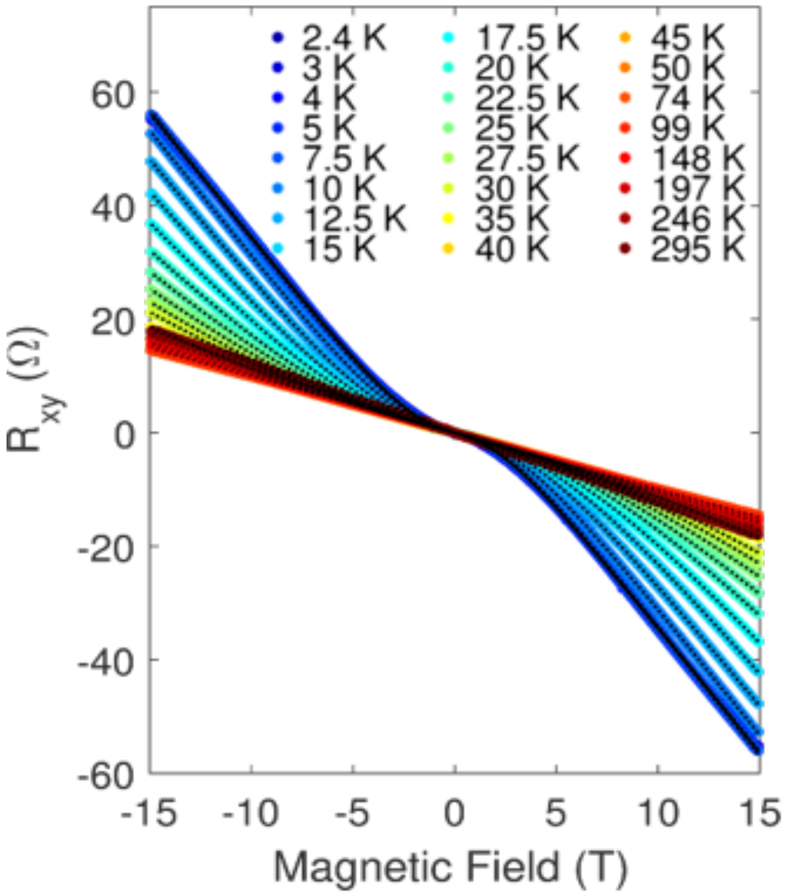


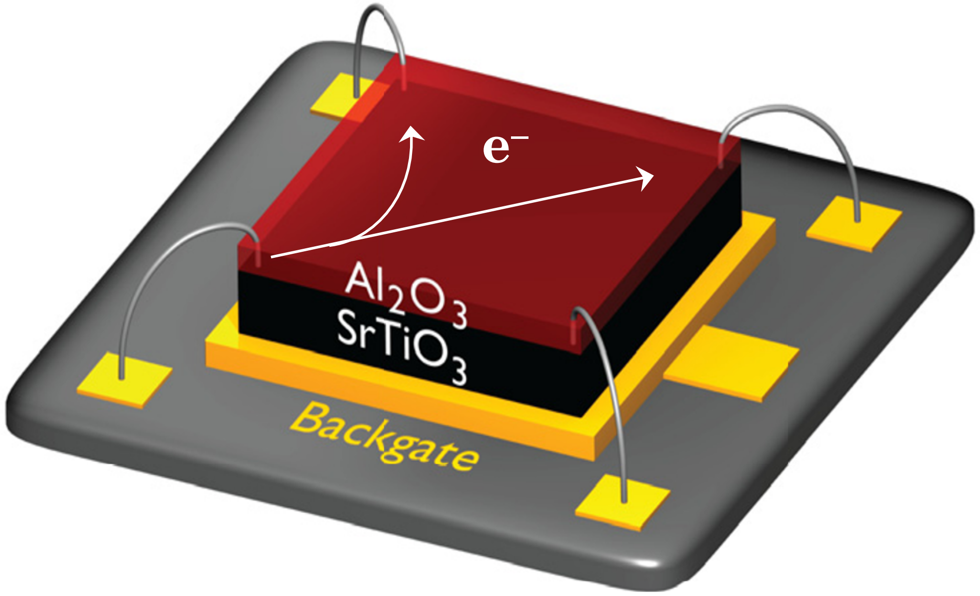


Giant Tunability of the Two-Dimensional Electron Gas at the Interface of -Al2O3/SrTiO3, Nano Letter (2017)

Emergence of magnetism

$$R_{xy} = R_{xy}^{OHE} + R_{xy}^{AHE}$$

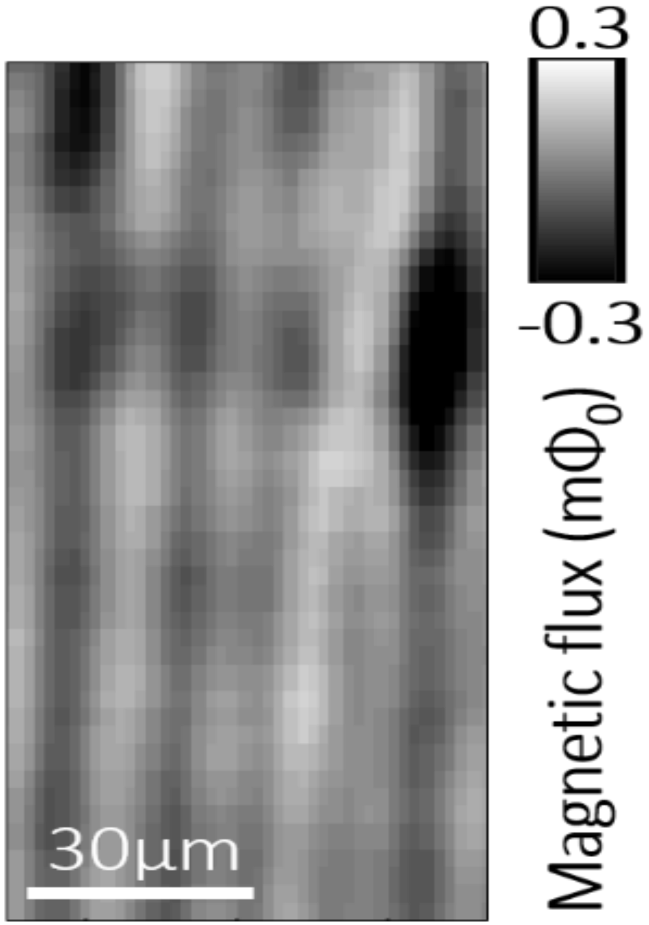


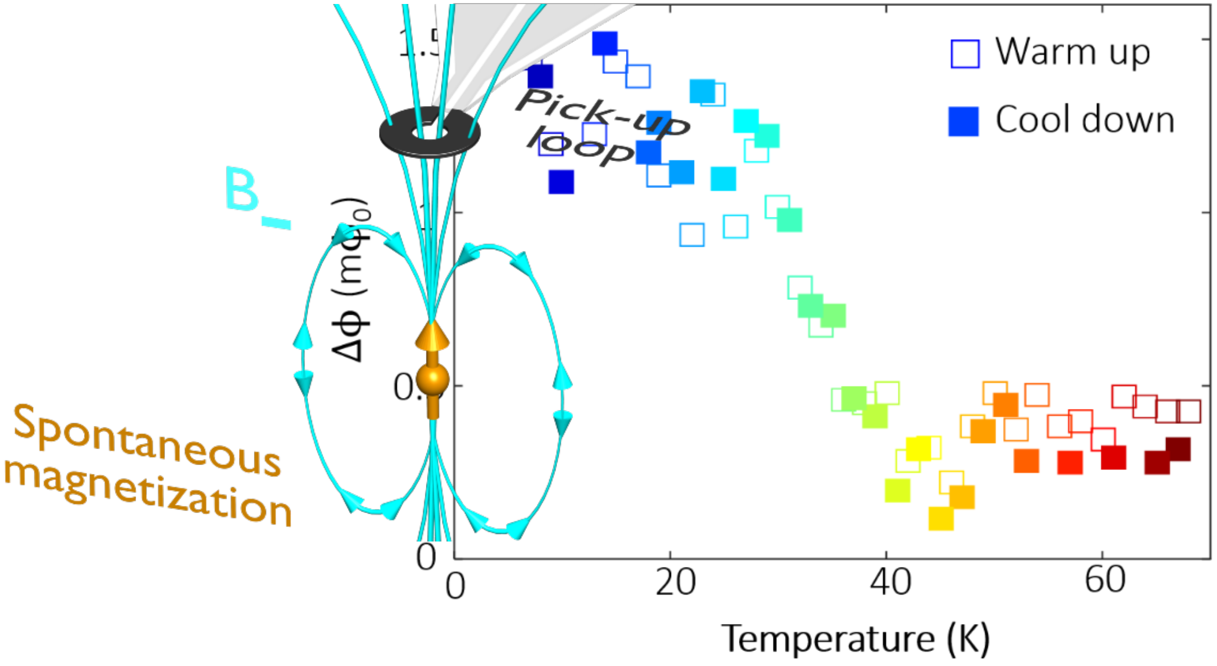


Strain-tunable magnetism γ-Al_2O_3/$SrTiO_3$, Nature Physics 2018

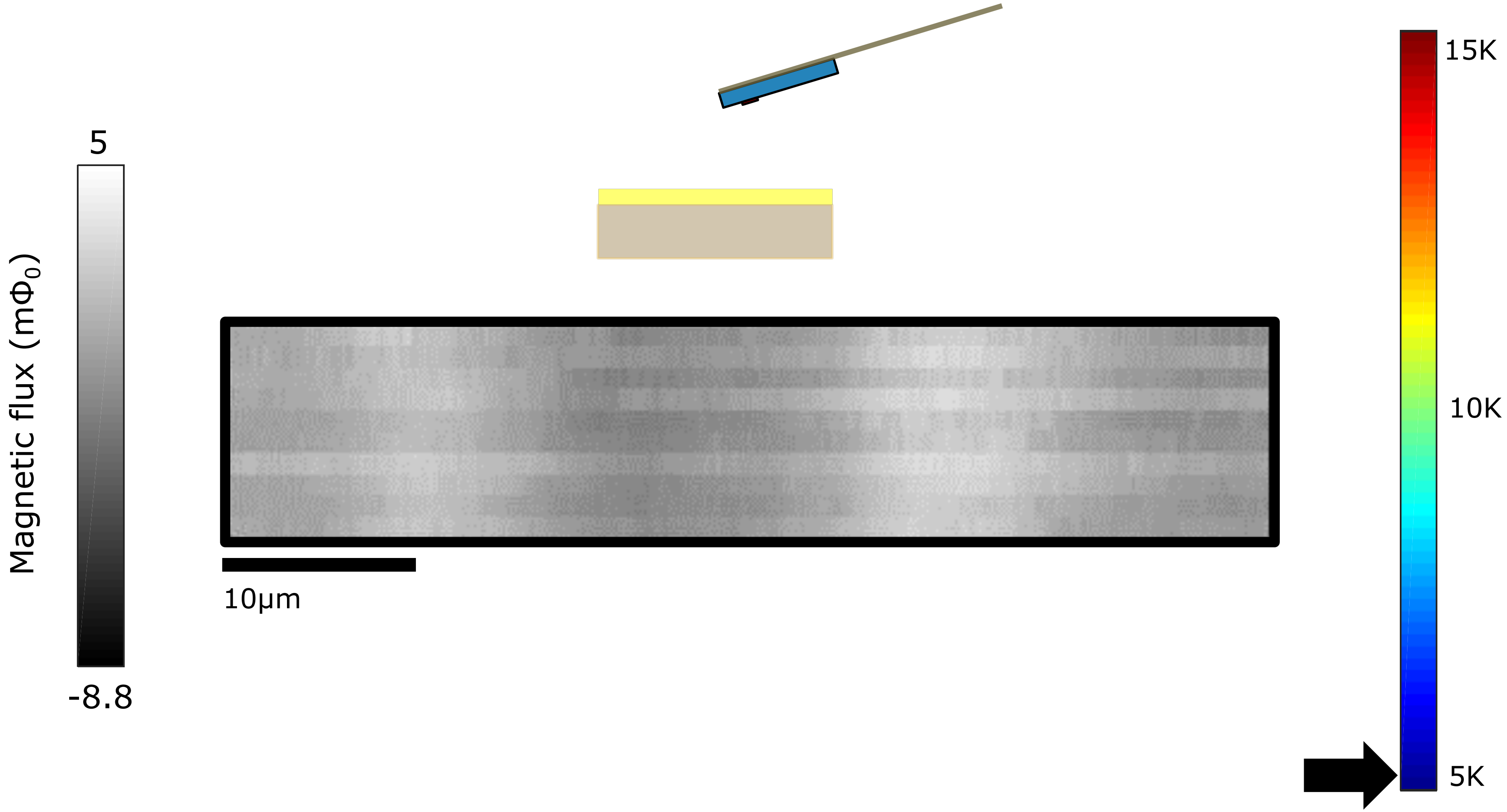
Emergence of magnetism

Scanning Superconducting Quantum Interference Device (Scanning-SQUID)



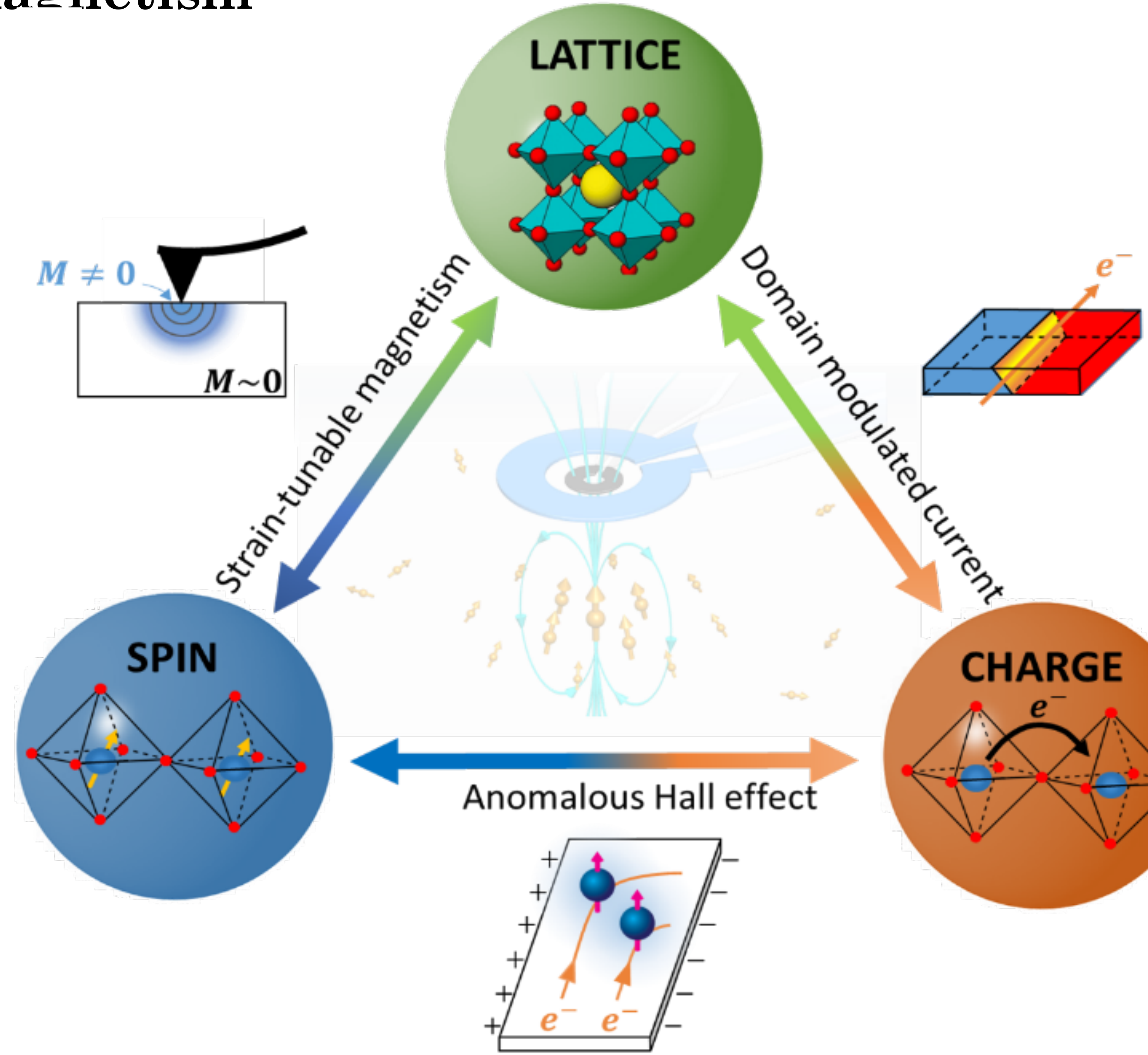


Emergence of magnetism

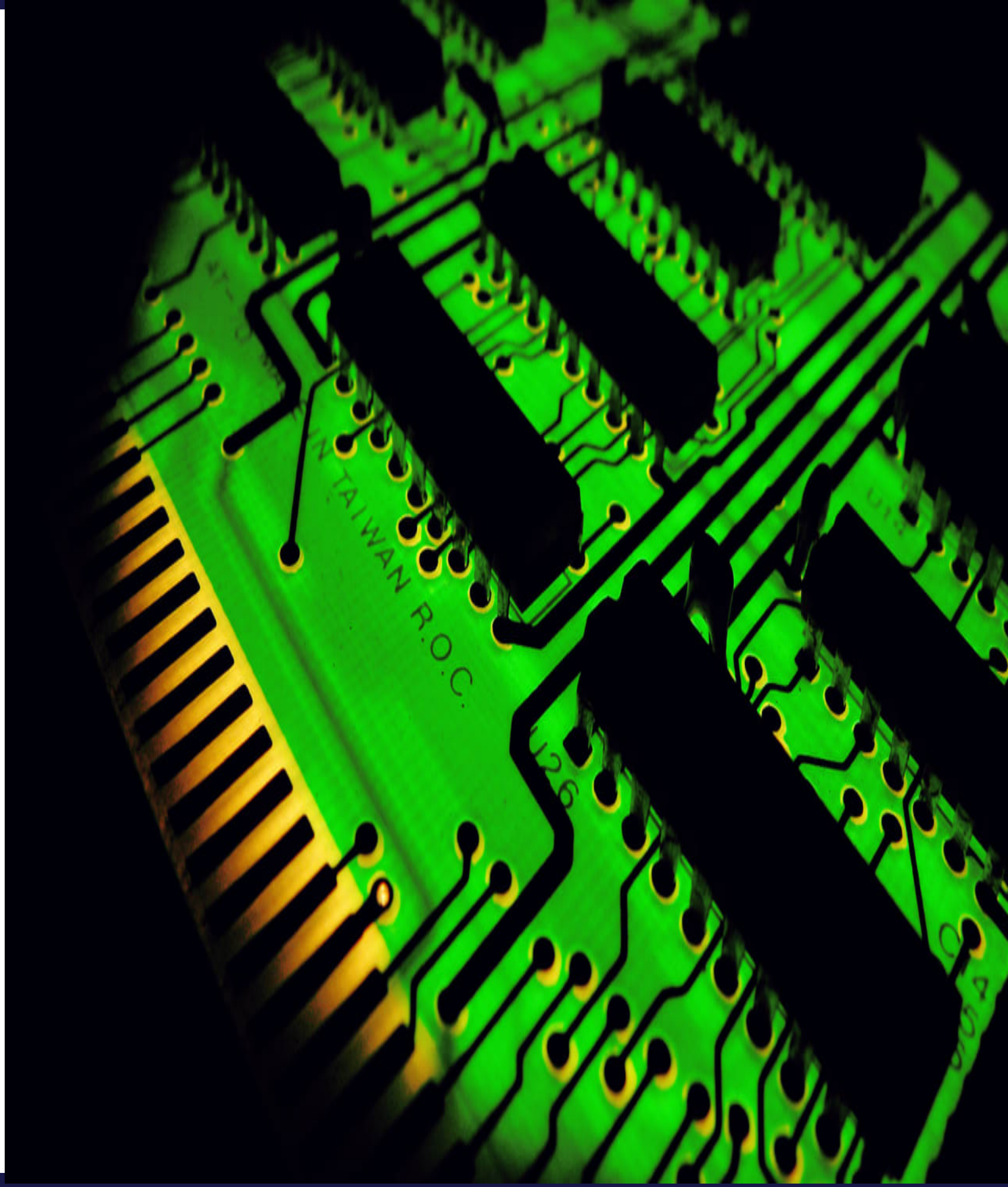


Strain-tunable magnetism γ-Al_2O_3/$SrTiO_3$, Nature Physics 2018

Emergence of magnetism



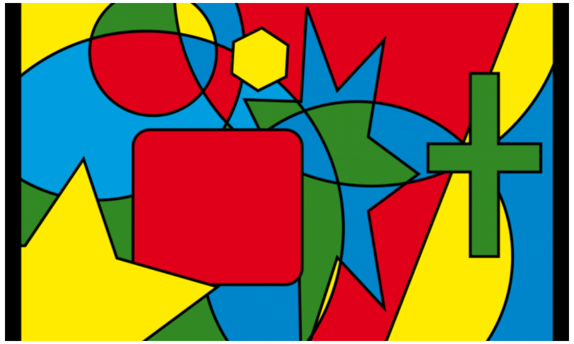
Memristors



Motivation: The computer challenges

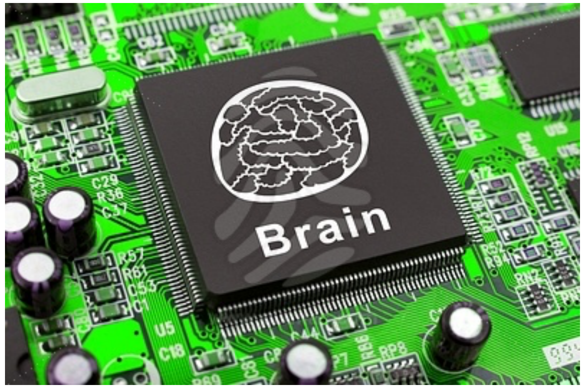
- ✓ **Computer wins the chess world championship**
- ✓ **Computer generate new Jokes which people find really funny**
- ✓ **Computer invented new proof of mathematical theorems**
- ✓ **Computer wins final of US Quiz show Jeopardy**

1997



2011

The main difference is the energy efficiency!



Watson:

2880 processors

~ 100.000 kg.

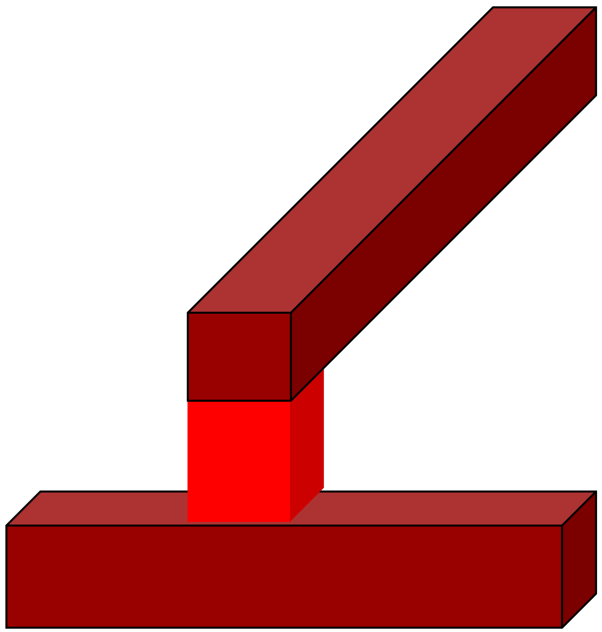
2.300.000 Watt

Human Brain:

100 bill Neurons

~ 5 kg

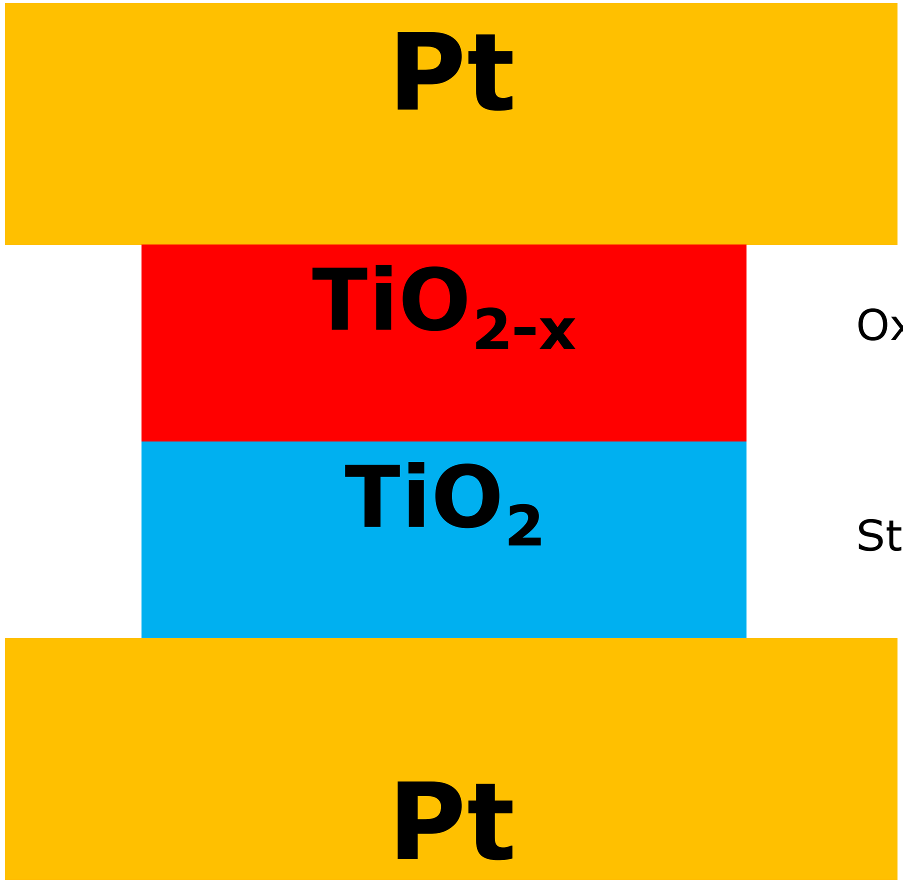
~ 25 Watt



Switching a few nm (thickness) but still going to change
Its resistance by at least factor of 1000!

How can we make such a switching unit?

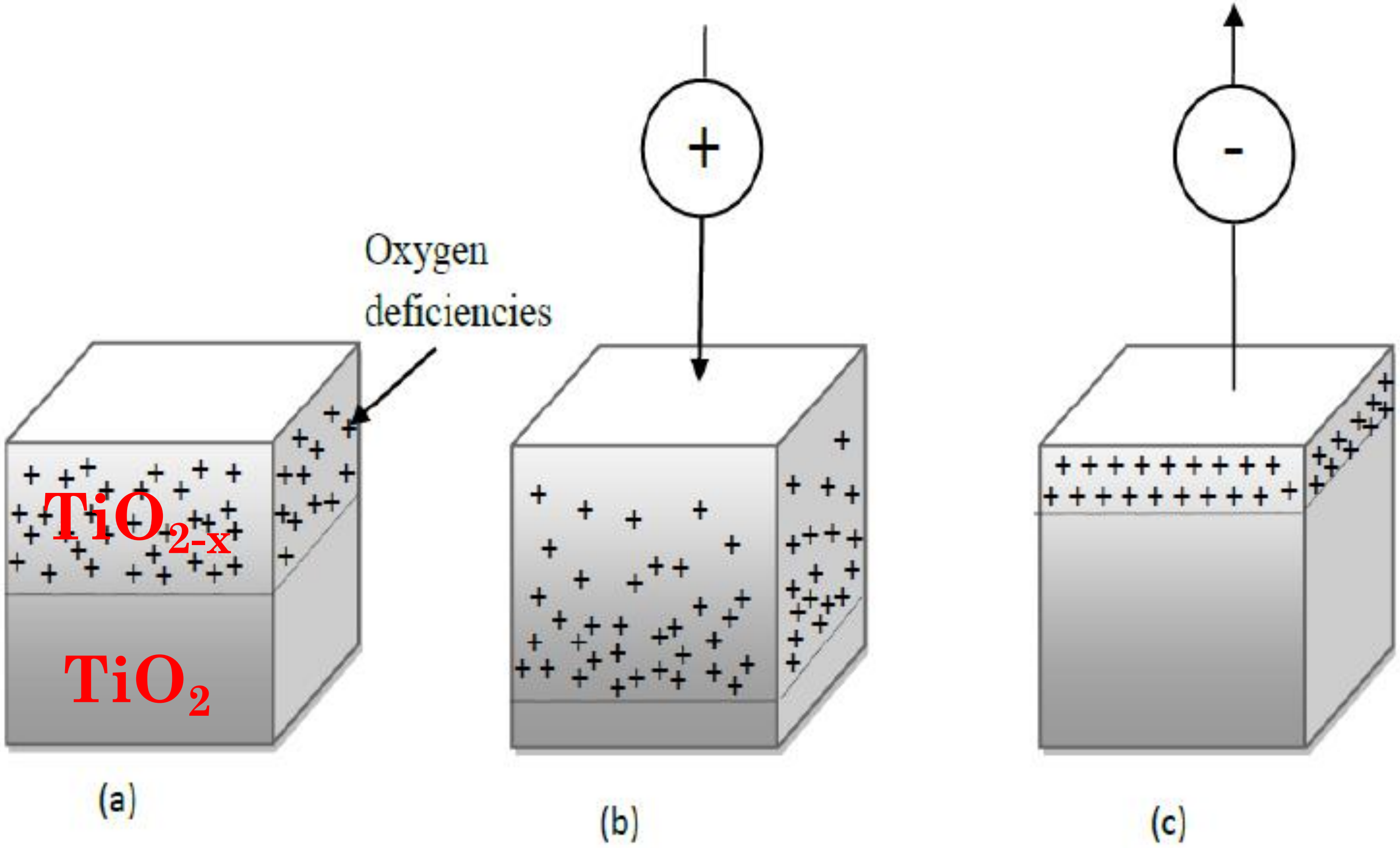
So here is the idea!



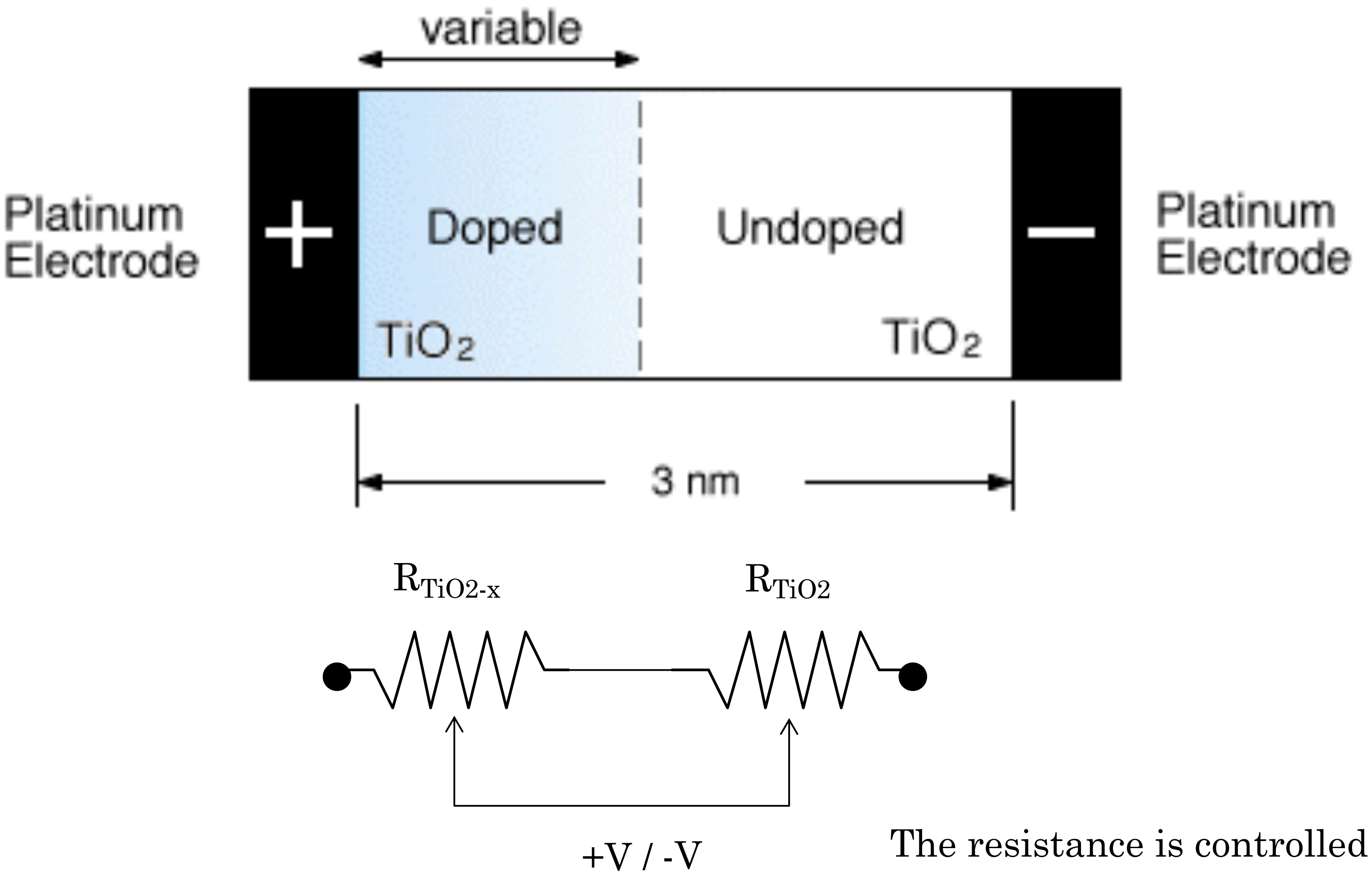
Oxygen deficient, Conductor

Stoichiometric, Insulating

How does it work?



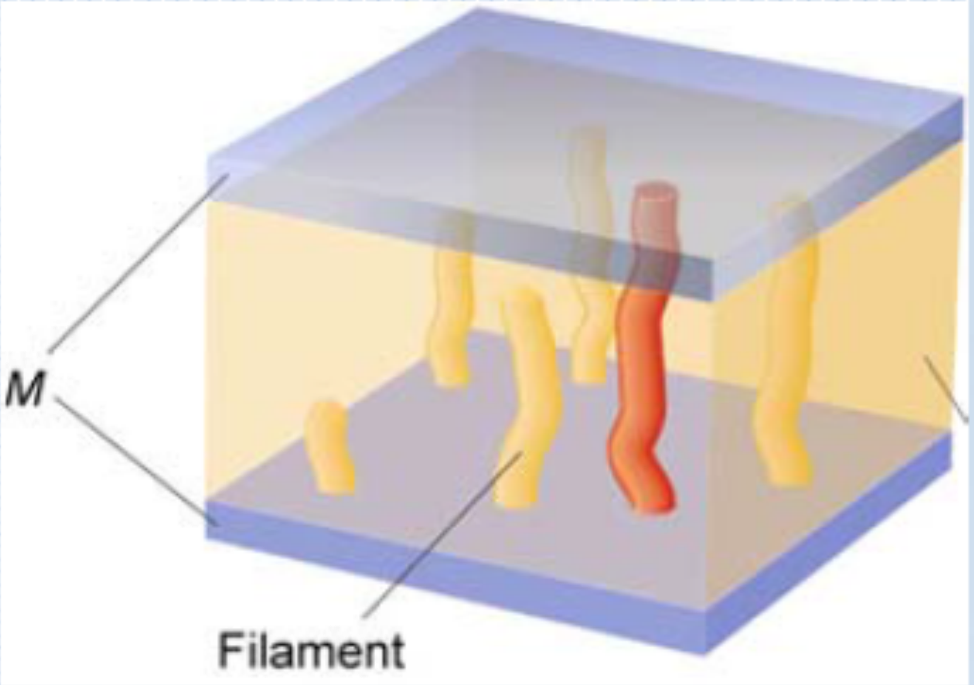
How does it work?



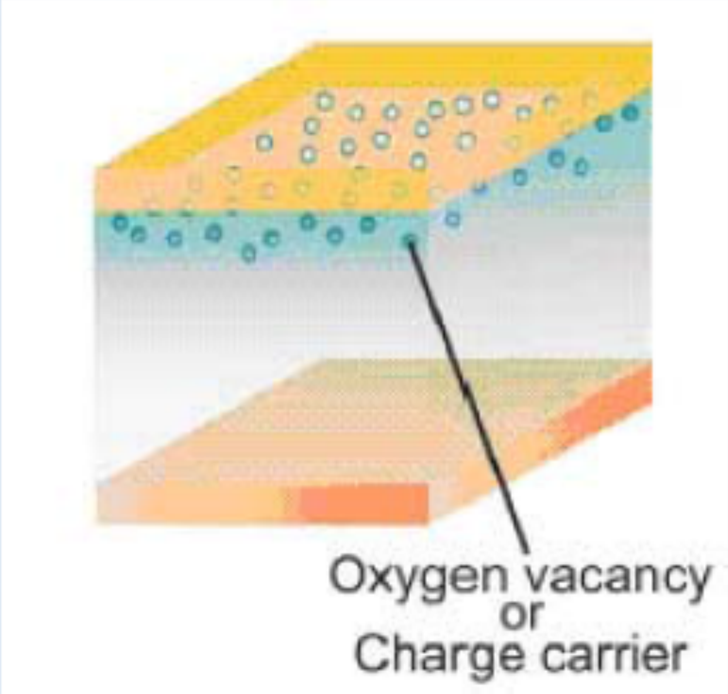
The resistance is controlled by how much TiO_2 is left

• homogeneously distributed effect?

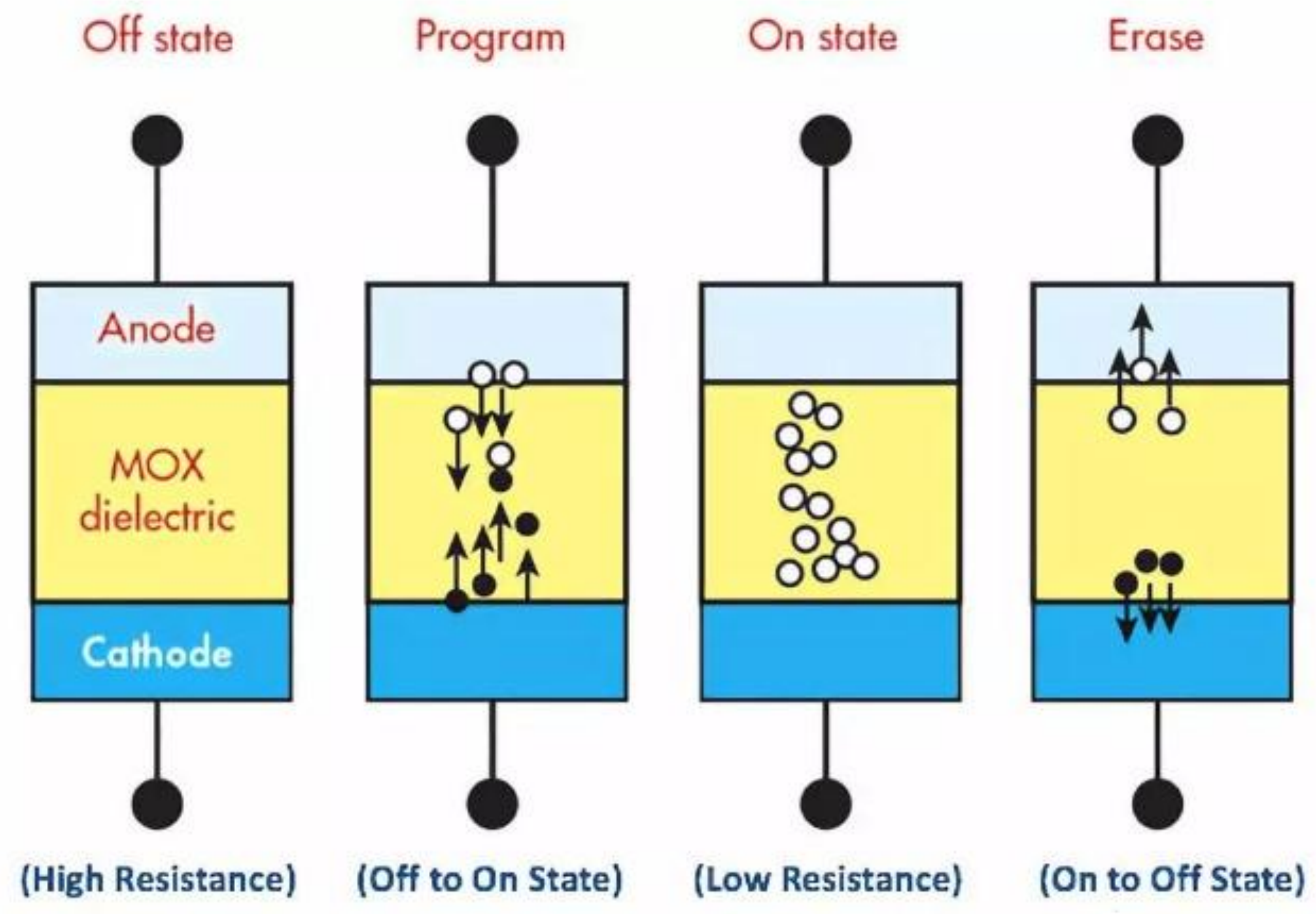
• effect confined to filaments?

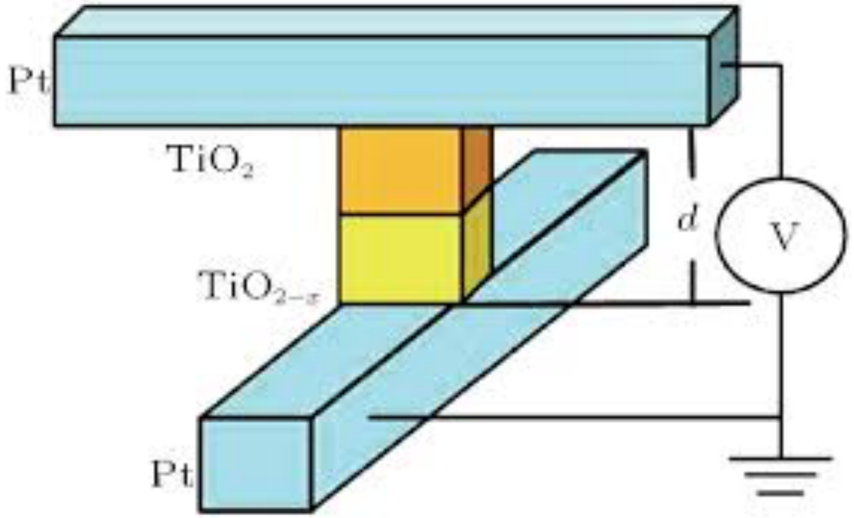


Waser & Aono, Nat.Mat. (2007)



A. Sawa, Mat.Today (2008)


Off state
Program
On state
Erase
Anode
MOX
dielectric
Cathode
(High Resistance)
(Off to On State)
(Low Resistance)
(On to Off State)

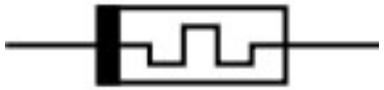


This is the physical picture of the memristors!

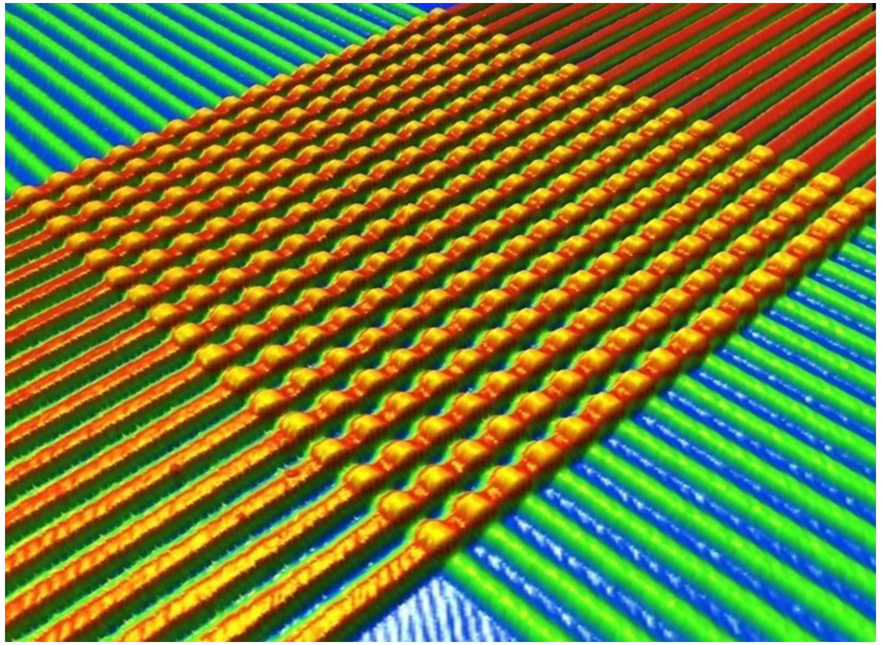
Memristor

memory + Resistor

Symbol:

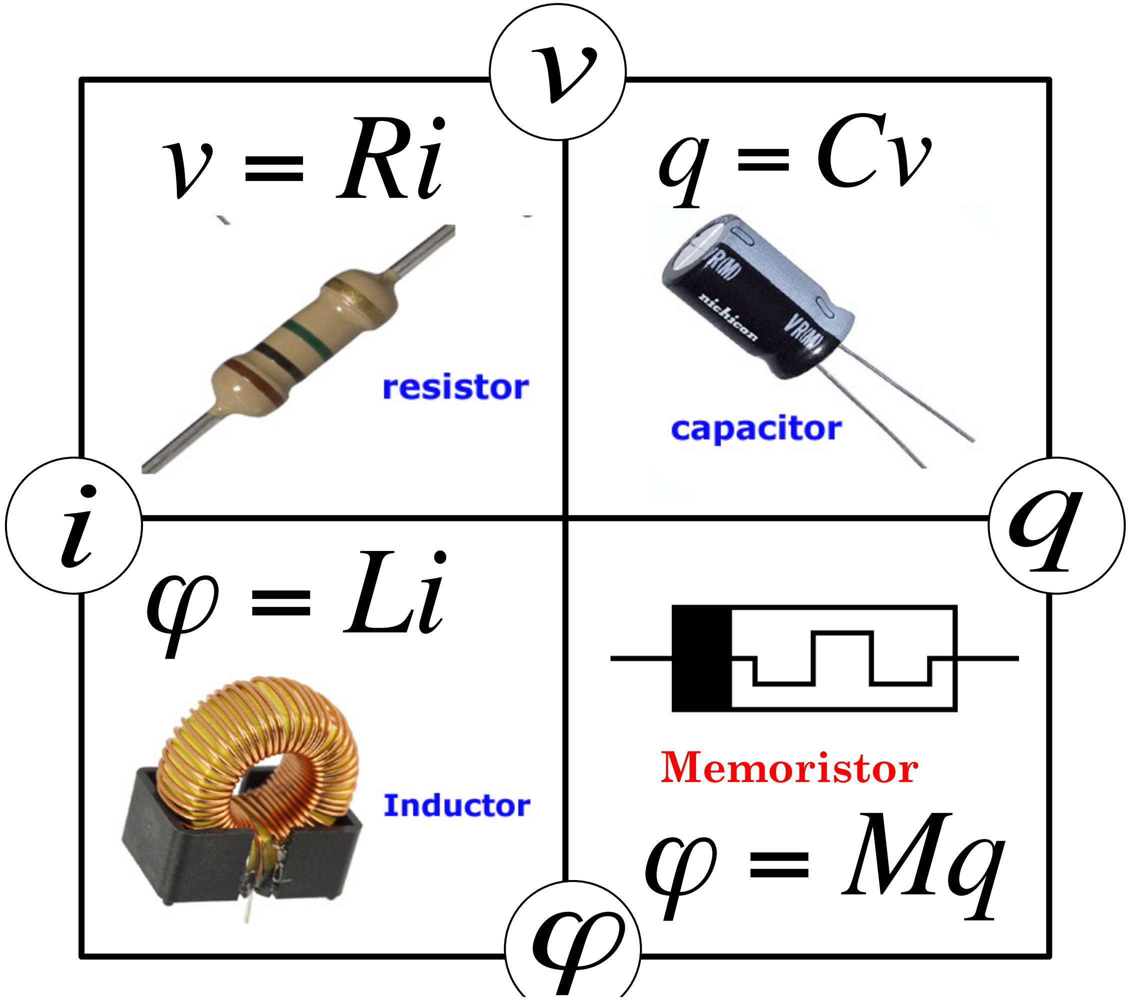


Unit: Ohm (Ω)



Memristor from HP lab

Memoristor 1971



Leon Chua 1971

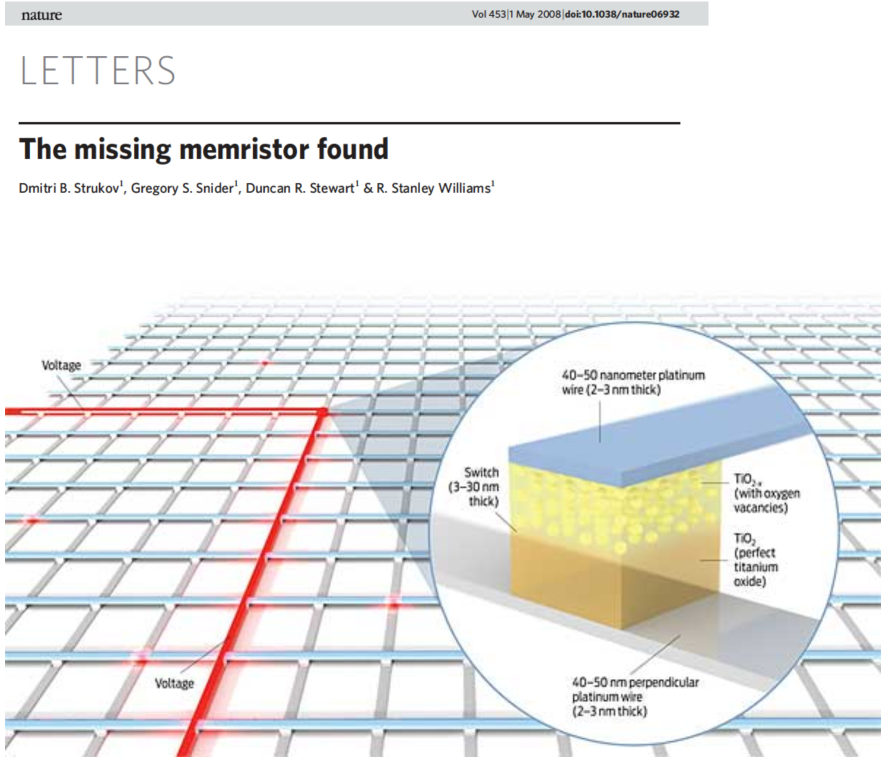
IEEE TRANSACTIONS ON CIRCUIT THEORY, VOL. CT-18, NO. 5, SEPTEMBER 1971

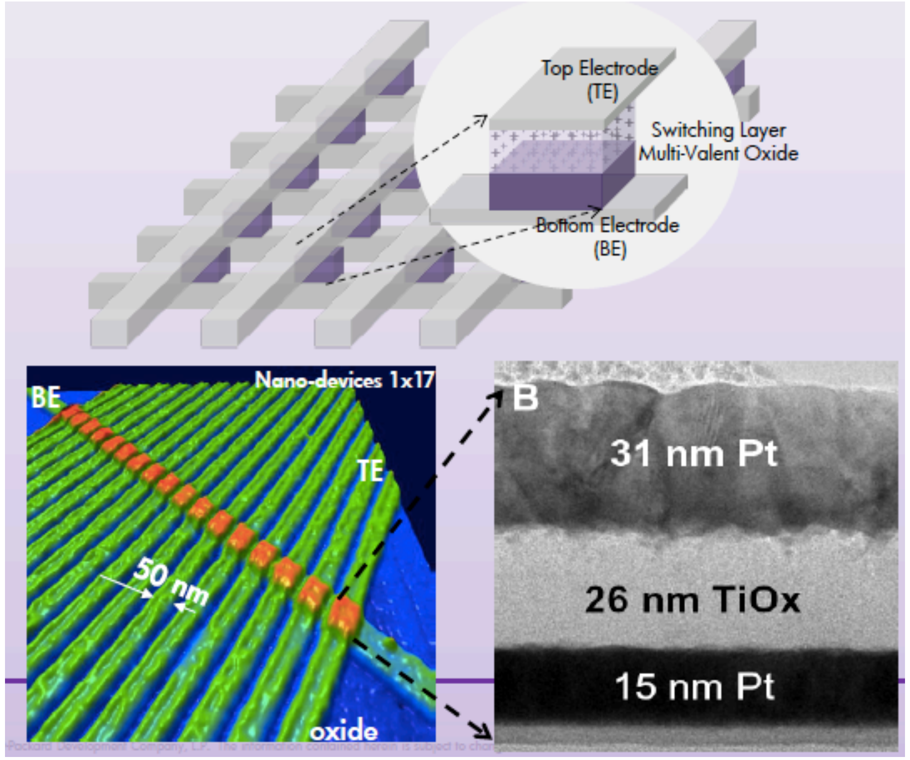
Memristor: Information storage device.

ReRAM (Resistive Random Access Memory)

Non-volatile memory technology, based on the metal-oxide–metal structure

A passive two-terminal circuit elements that maintains a functional relationship between the time integrals of current and voltage.

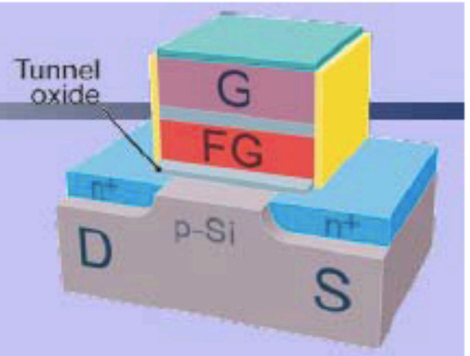




Advantages

- Low Energy consumption
- Great Resilience and Reliability
- Scalability
- Multiple states
- Logic

Requirements



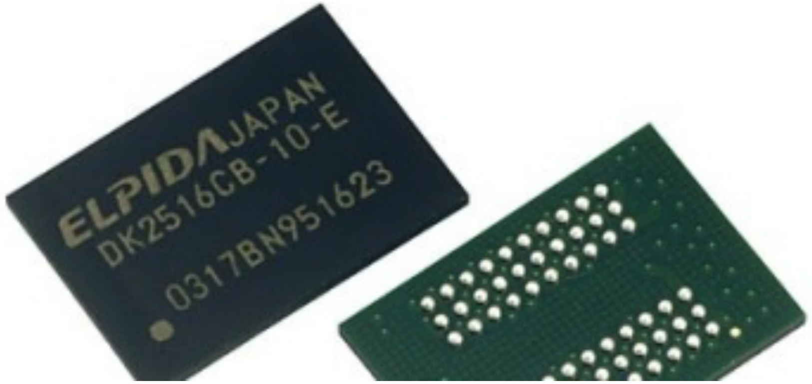
... to compete with Flash

Endurance:	> 10^7 cylces (Flash 10^3 ... 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

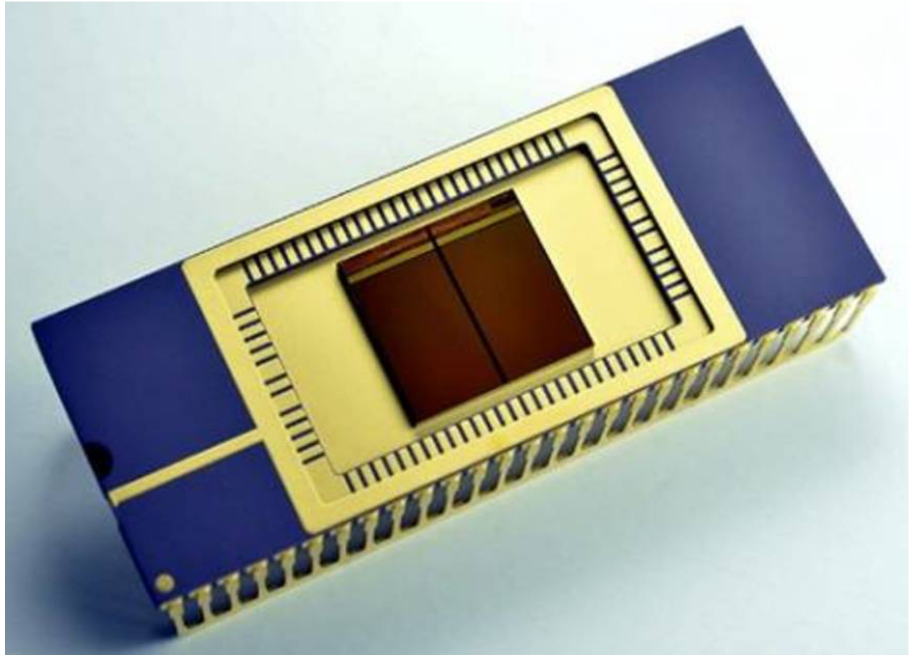
R. Waser, ISIF 2011

Elpida Memory Inc.

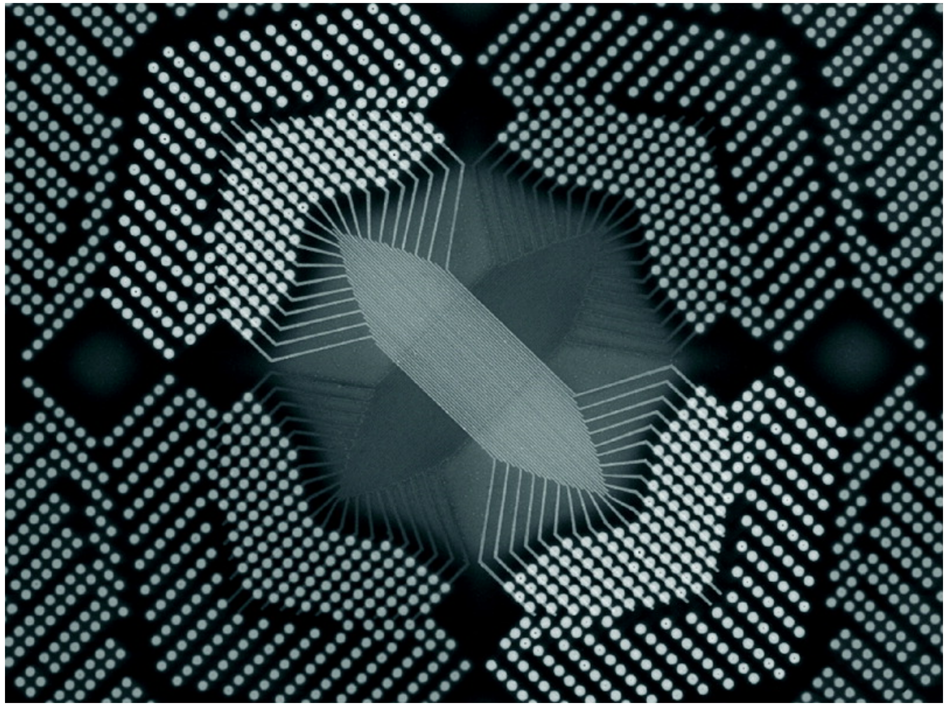
ReRam [nonvolatile resistance memory, a DRAM/flash memory]



HP - Hynix

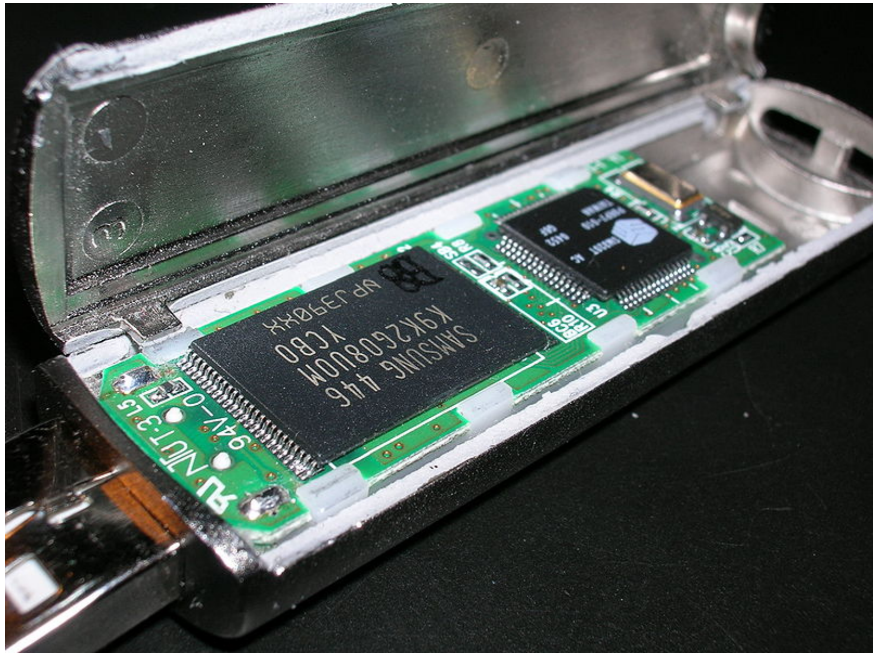


IBM - SyNAPSE

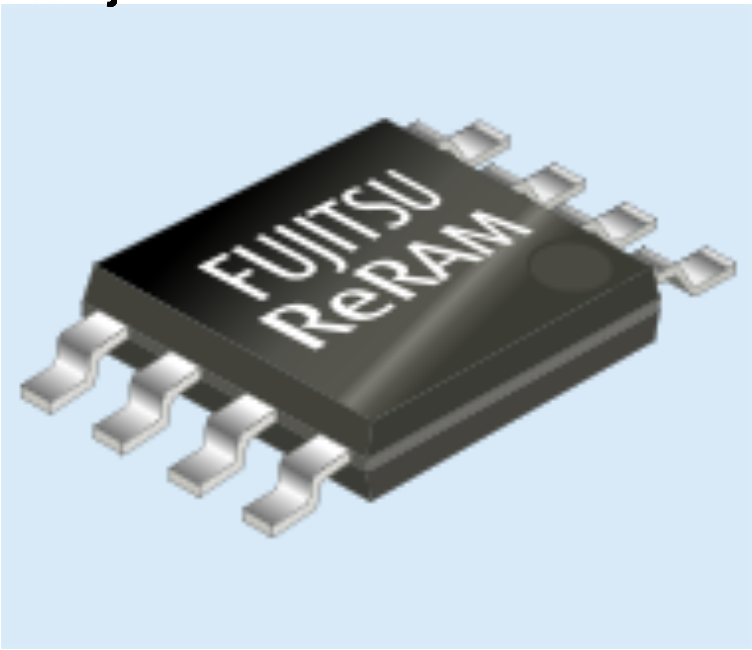


Panasonic

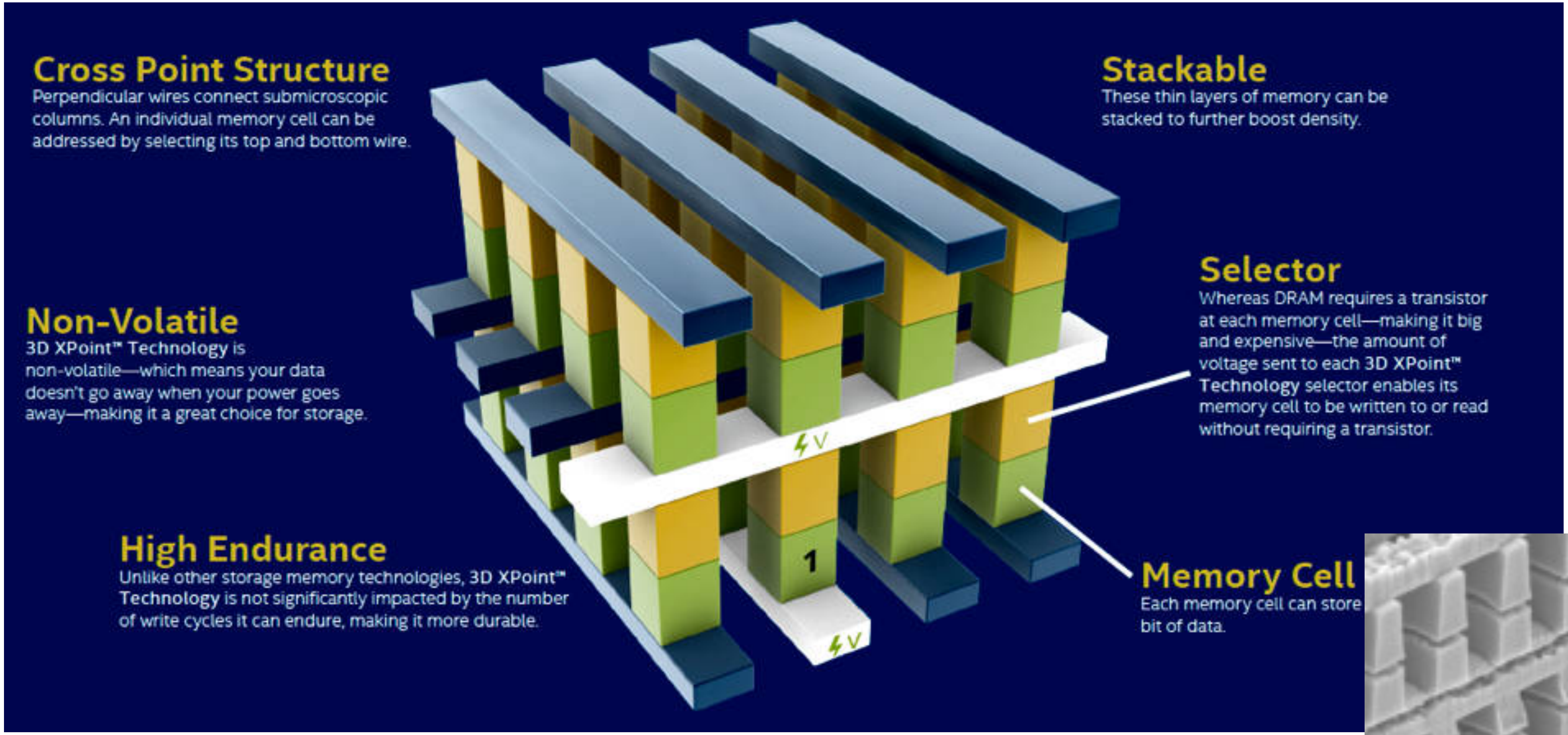
Sumsung



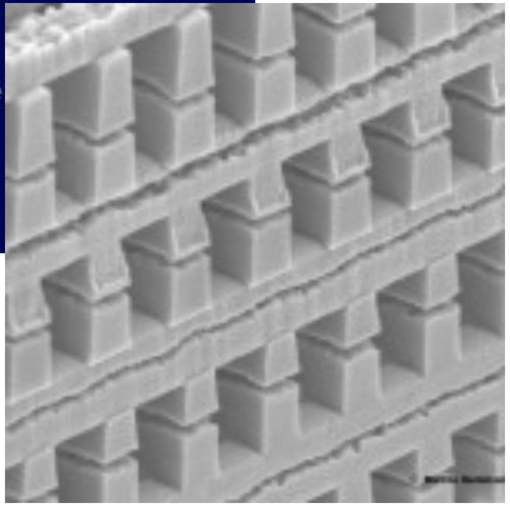
Fujitsu Semiconductor



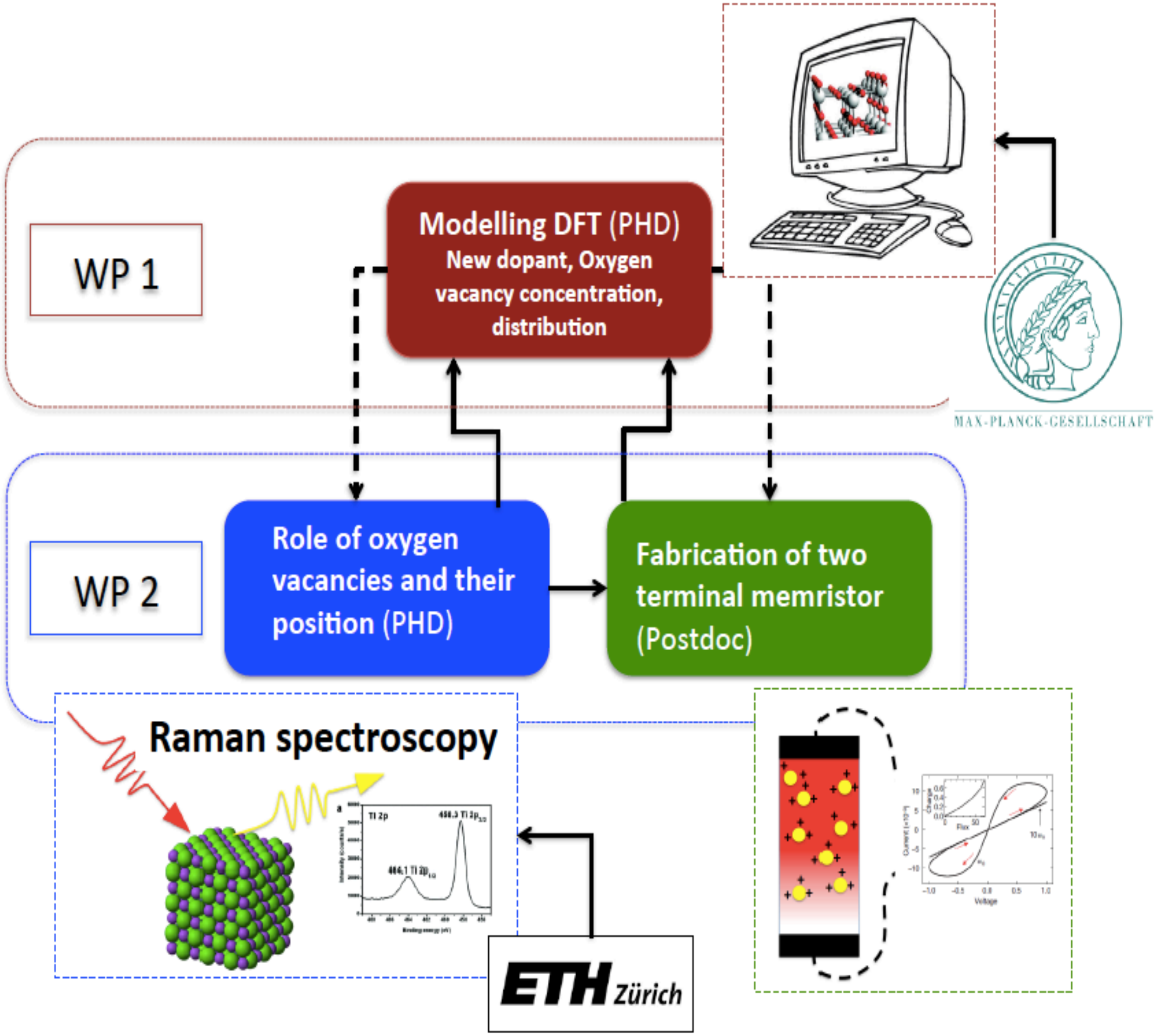
3D XPoint



Cross Point Structure
Perpendicular wires connect submicroscopic columns. An individual memory cell can be addressed by selecting its top and bottom wire.
Stackable
These thin layers of memory can be stacked to further boost density.
Non-Volatile
3D XPoint™ Technology is non-volatile—which means your data doesn't go away when your power goes away—making it a great choice for storage.
Selector
Whereas DRAM requires a transistor at each memory cell—making it big and expensive—the amount of voltage sent to each 3D XPoint™ Technology selector enables its memory cell to be written to or read without requiring a transistor.
High Endurance
Unlike other storage memory technologies, 3D XPoint™ Technology is not significantly impacted by the number of write cycles it can endure, making it more durable.
1
Memory Cell
Each memory cell can store
bit of data.

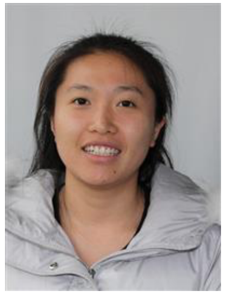


Nano Ionic Conducting Engineered materials for information application (NICE)



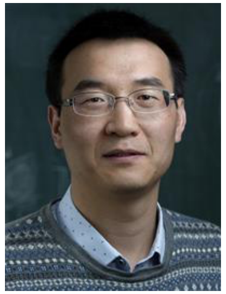
Acknowledgment


Yulin Gan


Yang Li

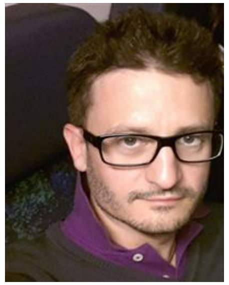

Merlin Von-Soosten


Vincenzo Esposito


Yunzhong Chen


Yu Zhang


Dennis V. Christensen


Simone Sanna

…..off course also our international collaborators…..

INDEPENDENT RESEARCH FUND DENMARK

THANK YOU FOR YOUR ATTENTION!!