UNIWERSYTET ŁÓDZKI

FACULTY OF PHYSICS AND APPLIED INFORMATICS
University of Lodz

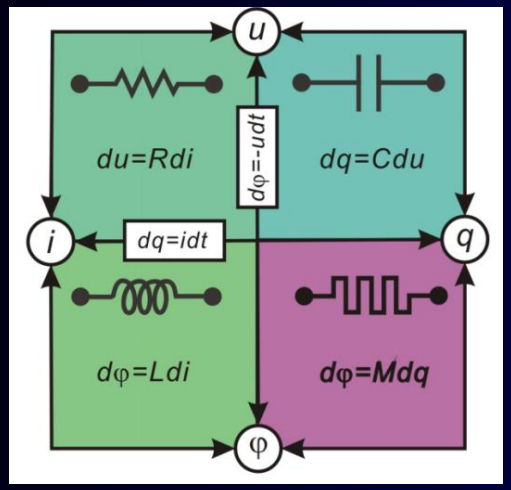
prof. Zbigniew Klusek

The mystery of resistive switching - from TiO_2 to graphene oxide.

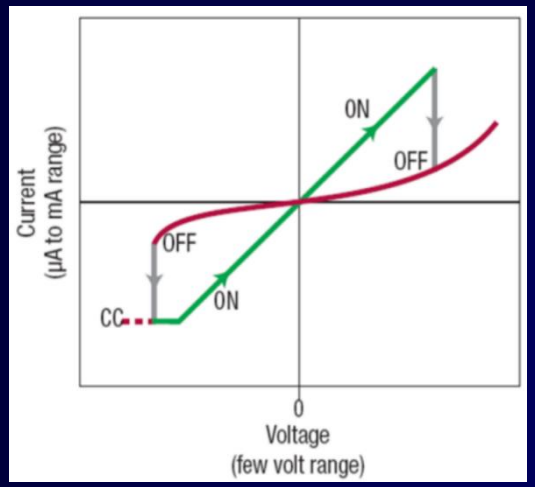
Motivation

Understanding switching phenomena in titanium dioxide and graphene oxide

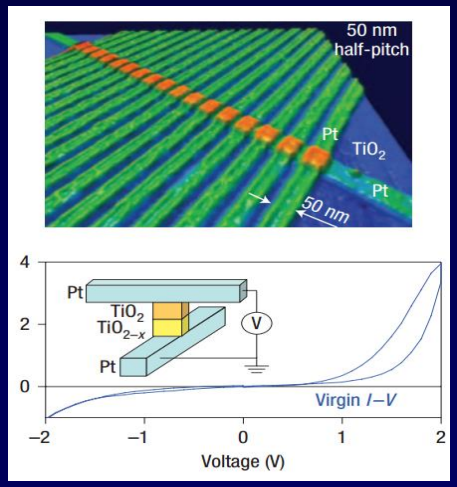
Connect people working on oxides with graphene community



Leon Chua
Memristor-The missing circuit element
(1971)

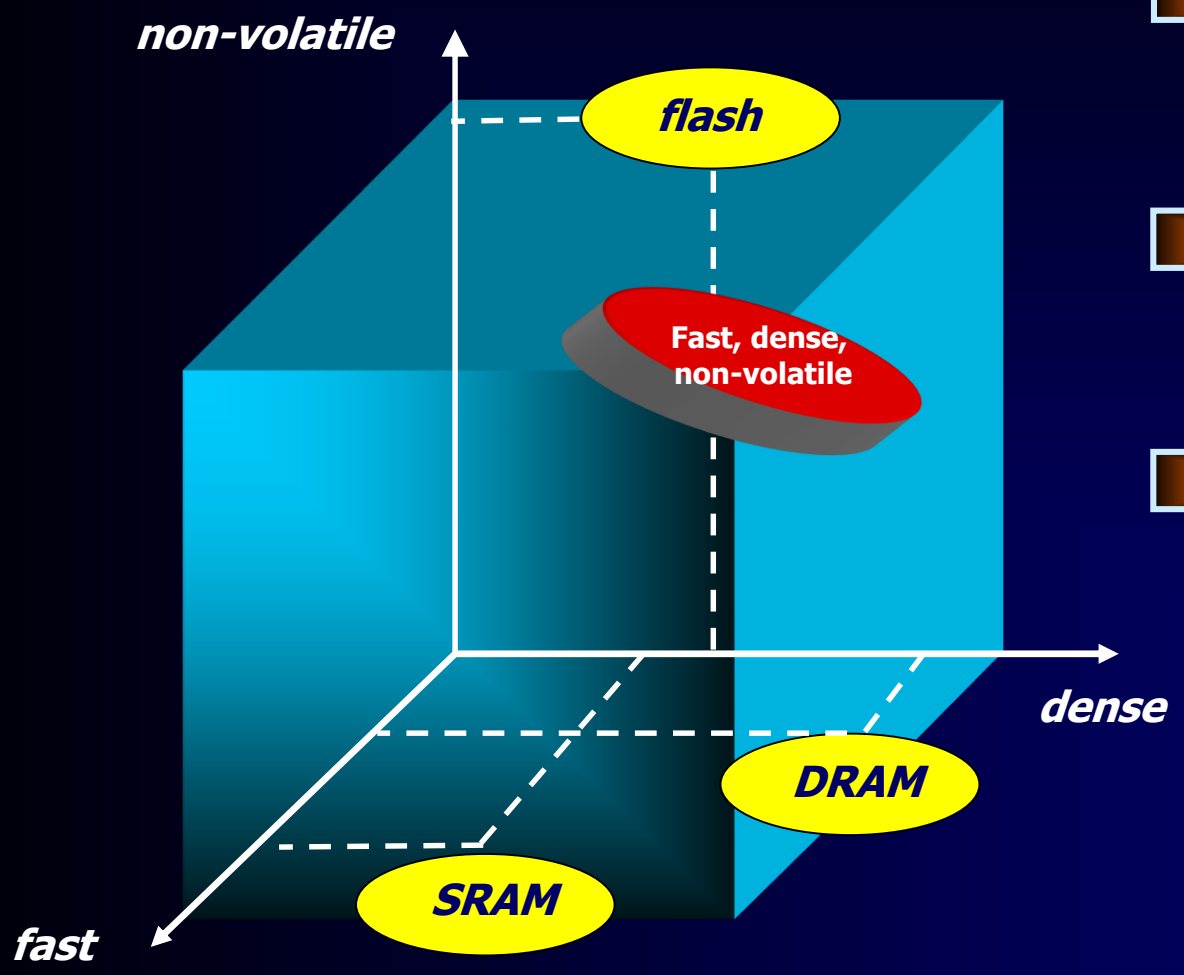


Rainer Waser
Nanoionics-based resistive switching memories
(2007)



R. Stanley Williams
Memristor-The missing circuit element
(2008)

New types of memories



flash

They are:
non-volatile but
slow and
not to dense

DRAM

They are:
dense but
non-volatile and
not to fast

SRAM

They are:
fast but
non-volatile and
not to dense

Resistive switching

scaling process in memory devices (new physical phenomena)

- ferroelectric — **FRAM**
- resistance — **ReRAM**
- phase — **PRAM**
- magnetoresistnce — **MRAM**

ReRAM

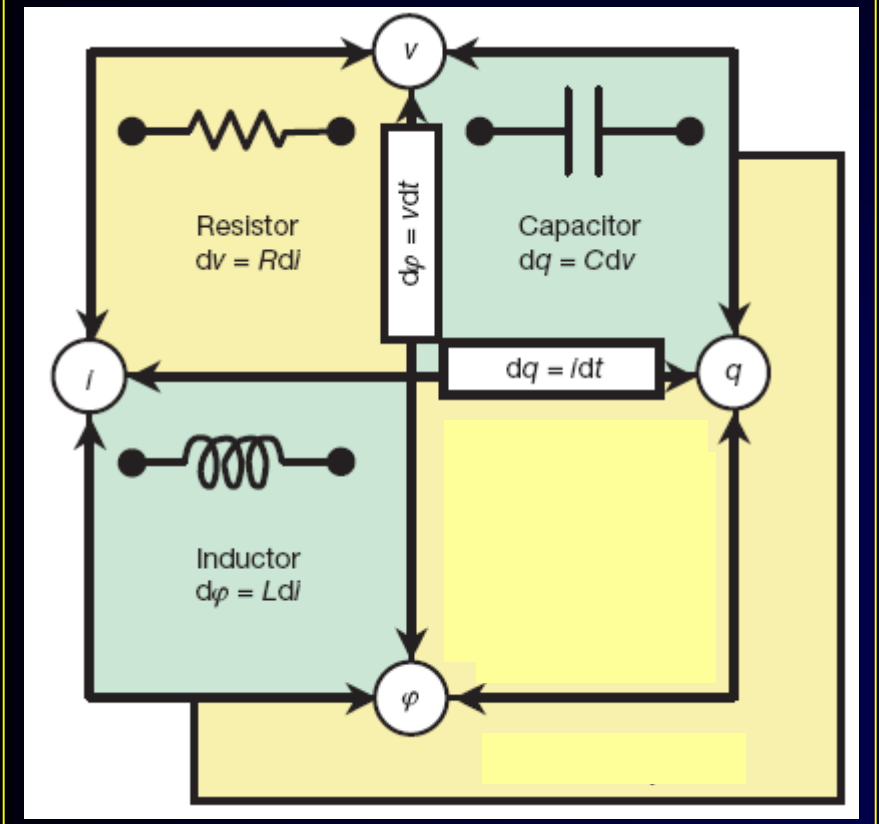
$SrZrO_3$
$SrTiO_3$
TiO_2
NiO
Cu_2O

amorphous
polycrystalline

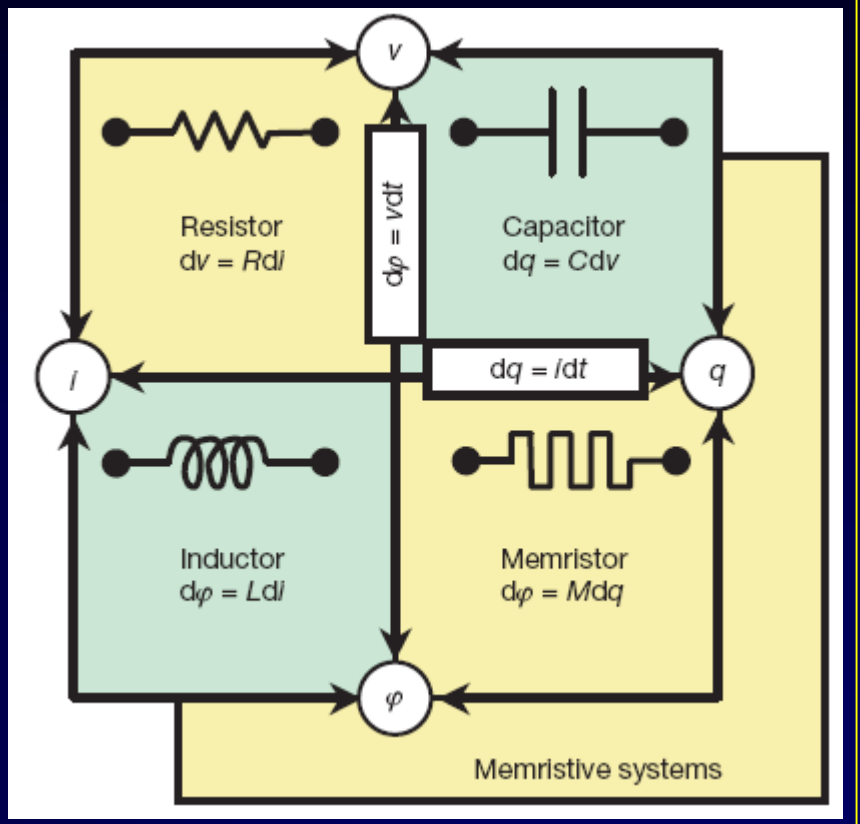
MOCVD
ALD

resistive switching memristive materials

Resistive switching

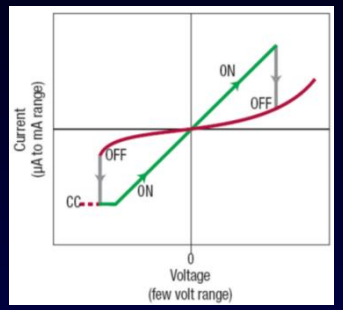


Chua, IEEE Trans. Circuit Theory (1971), 18, 507



Resistive switching

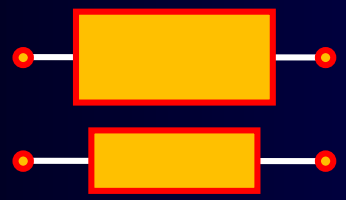
Flow of current through an element changes its resistance



High resistance (OFF) and low resistance (ON) states are well distinguishable

Logical 0

Logical 1

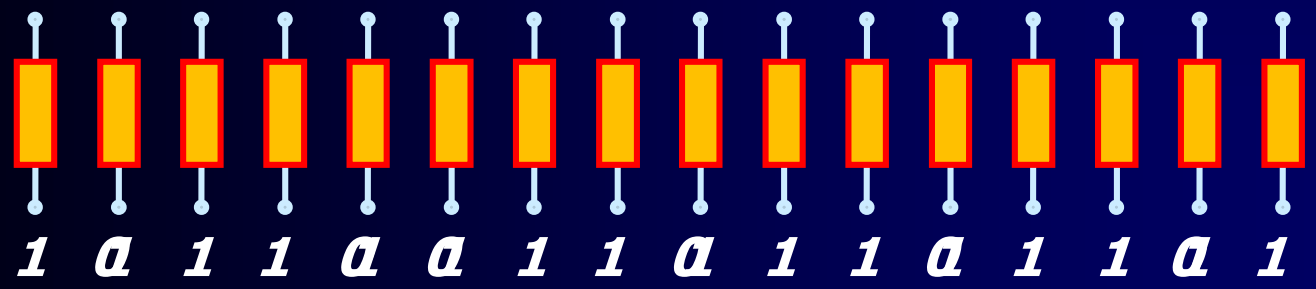


K. Szot, M. Rogala, W. Speier, Z. Klusek, A. Besmehn, and R. Waser Nanotechnology 22 , 254001 (2011).

M. Rogala, Z. Klusek, C. Rodenbücher, R. Waser, and K. Szot Appl. Phys. Lett. 102 , 131604 (2013).

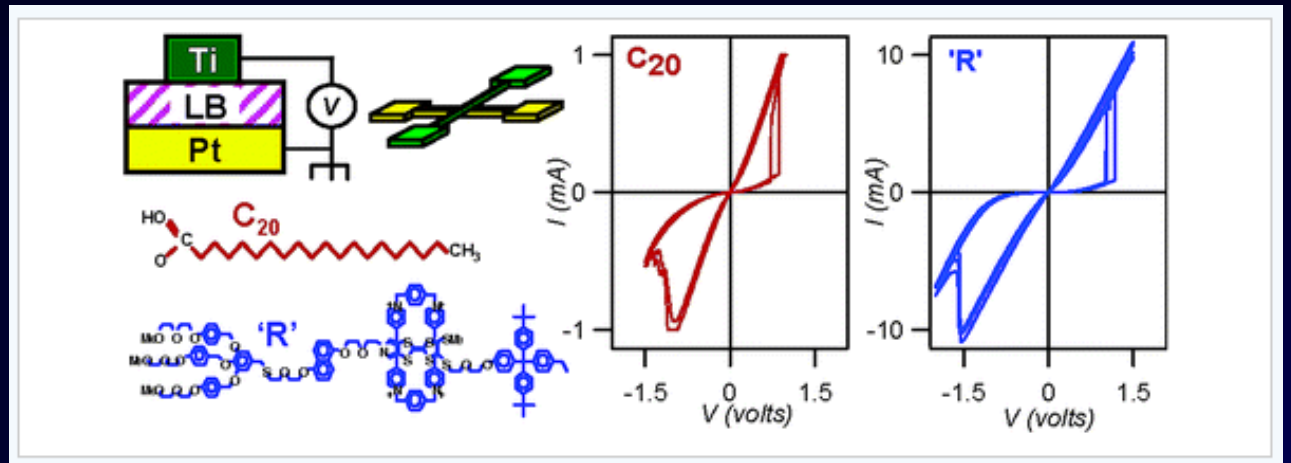
M. Rogala, G. Bihlmayer, W. Speier, Z. Klusek, C. Rodenbücher, K. Szot Adv. Func. Mat. 25, 6382 (2015).

Matrix composed out of such elements can be used as a memory (ReRAM)



Resistive switching

Prof. Stan Wiliams



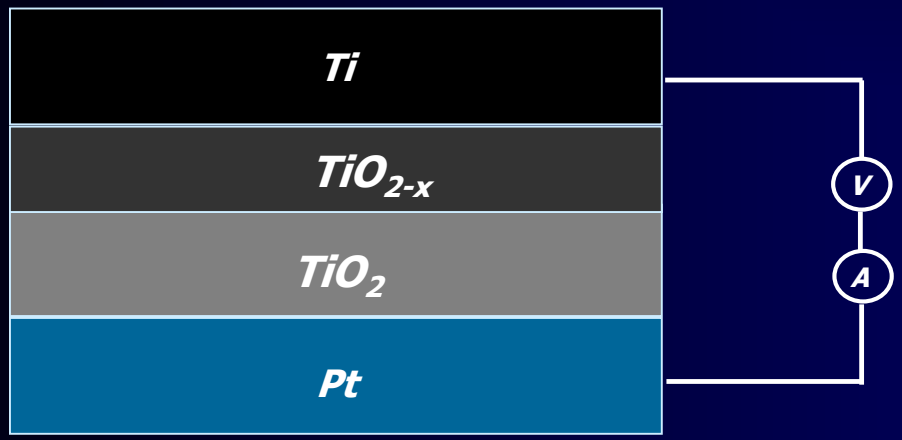
Electronic devices comprising a Langmuir–Blodgett molecular monolayer sandwiched between planar platinum and titanium metal electrodes functioned as switches and tunable resistors over a 10^2–10^5 Ω range under current or voltage control. Reversible hysteretic switching and resistance tuning was qualitatively similar for three very different molecular species, indicating a generic switching mechanism dominated by electrode properties or electrode/molecule interfaces, rather than molecule-specific behavior.

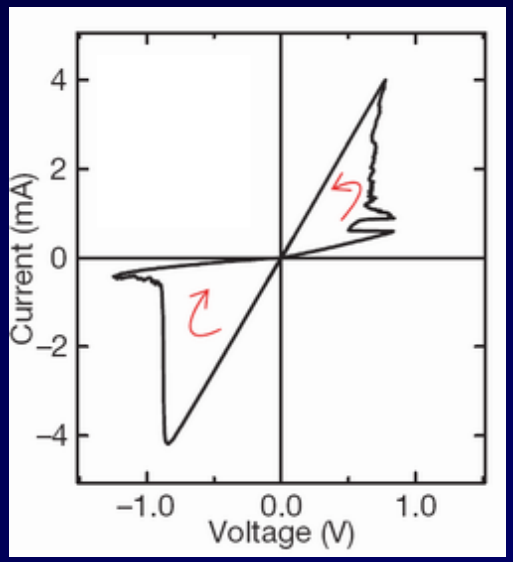
D.R. Stewart, D. Ohlberg, P. Beck, Y. Chen, S. Wiliams at al.
Nano Letters (2004), 4, 133

Resistive switching

nature International weekly journal of science

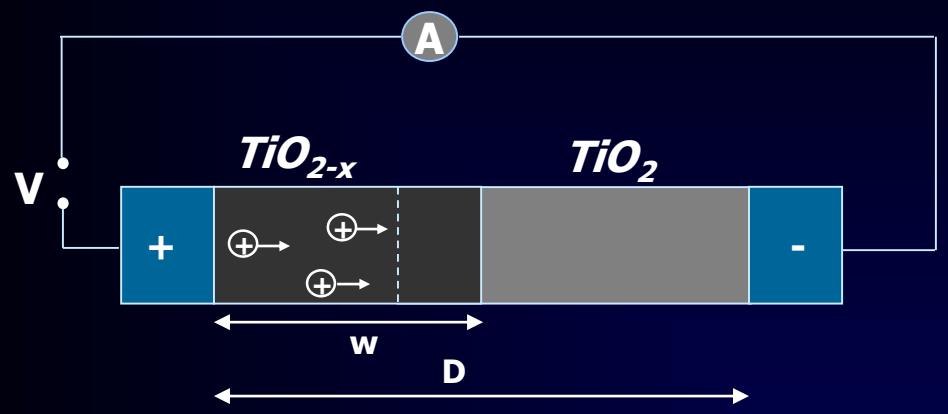
The missing memristor found





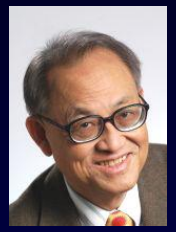
D. Strukov, G. Snider, D. Stewart, , S. Williams
Nature (2008), 453, 80.

Resistive switching



$$U = R(w)i$$

$$\frac{dw}{dt} = Ai$$

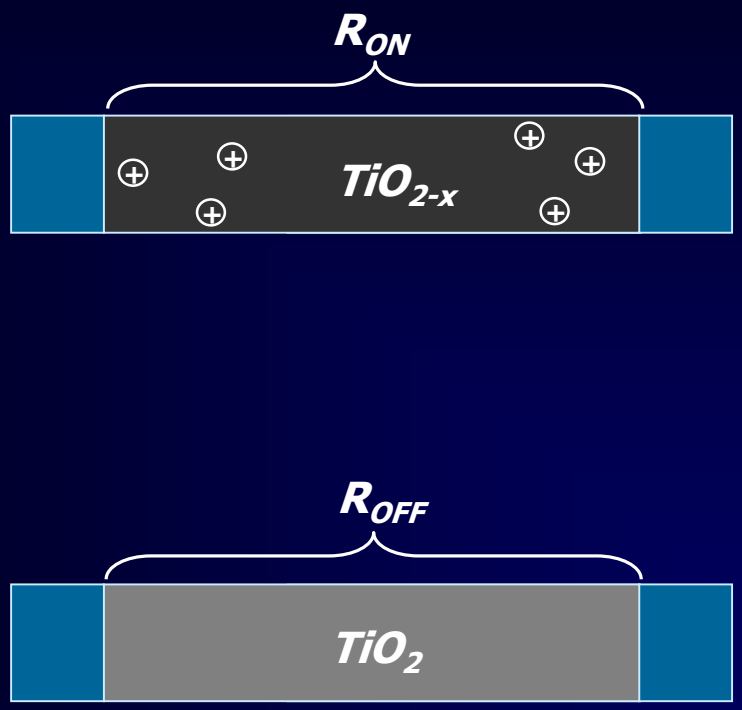


$$U(t) = \left(R_{ON}\frac{w(t)}{D} + R_{OFF}\frac{D - w(t)}{D} \right) i(t)$$

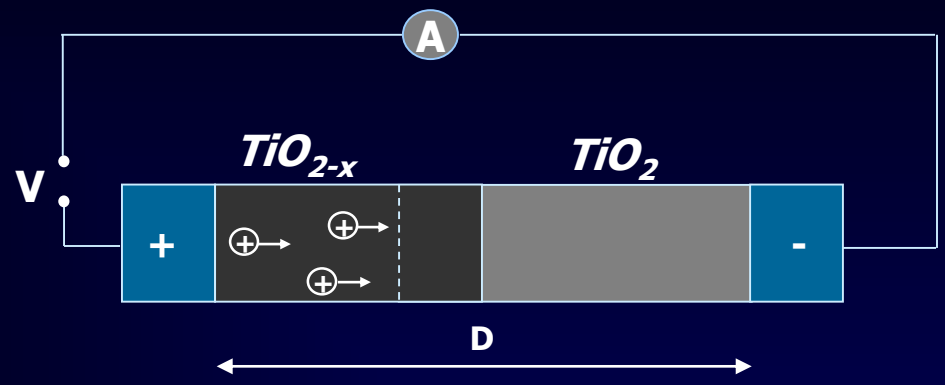
$$\frac{dw(t)}{dt} = v_D(t) = \mu E(t) = \mu \frac{U(t)}{w(t)} = \frac{\mu}{w(t)} \left(\frac{w(t)}{D} R_{ON} i(t) \right) = \mu \frac{R_{ON}}{D} i(t)$$

D. Strukov, G. Snider, D. Stewart, S. Williams
Nature (2008), 453, 80.

Resistive switching



Problems to solve



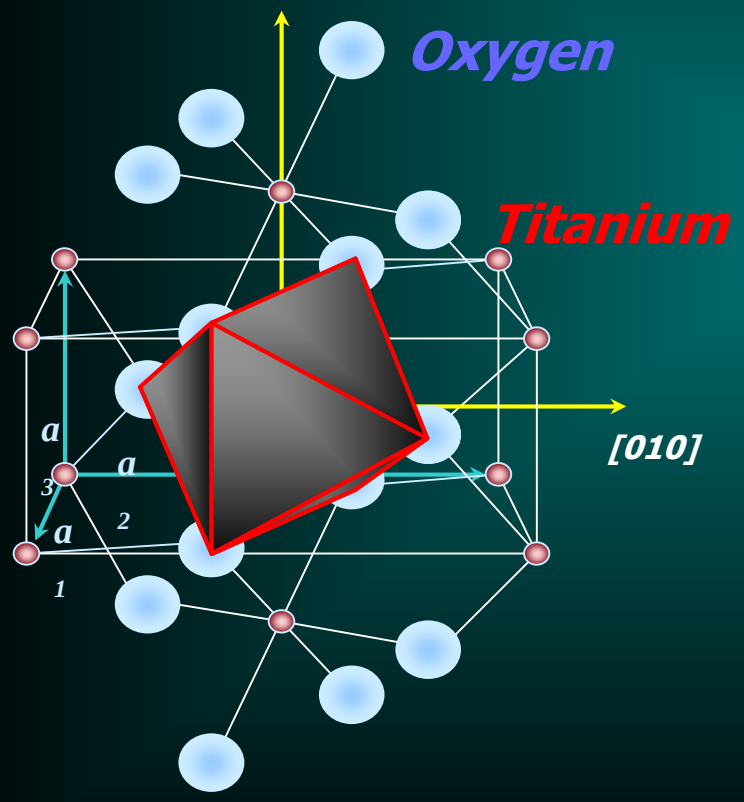
$$U = M(q) \cdot i$$

$$M(q) = R_{OFF}\left(1 - \frac{\mu R_{ON}}{D^2} q(t)\right)$$

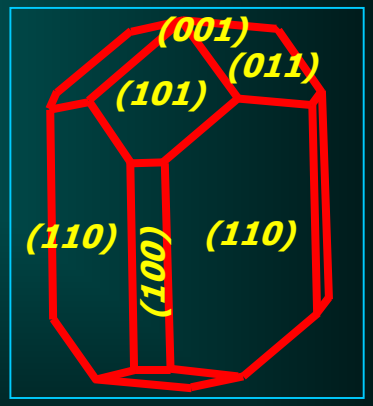
Whether electric current can change chemical stoichiometry ?

Titanium dioxide TiO_2

TiO_2 as a model material for memristive studies

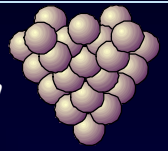


Rutile TiO_2



STM/STS - Tersoff-Hamann theory

Tip wave function



$$\Psi_\mu = \frac{1}{\sqrt{\Omega_T}} c_T \cdot \kappa \cdot R \cdot e^{\kappa \cdot R} \frac{1}{\kappa \left| \vec{r} - \vec{r}_0 \right|} e^{-\kappa \left| \vec{r} - \vec{r}_0 \right|}$$

surface wave function

$$\Psi_\nu = \frac{1}{\sqrt{\Omega_S}} \sum_{\vec{G}} A_G e^{-z\sqrt{\kappa^2 + \left|\vec{\kappa}_G\right|^2}} e^{\left(i\vec{\kappa}_G \cdot \vec{x}\right)}$$

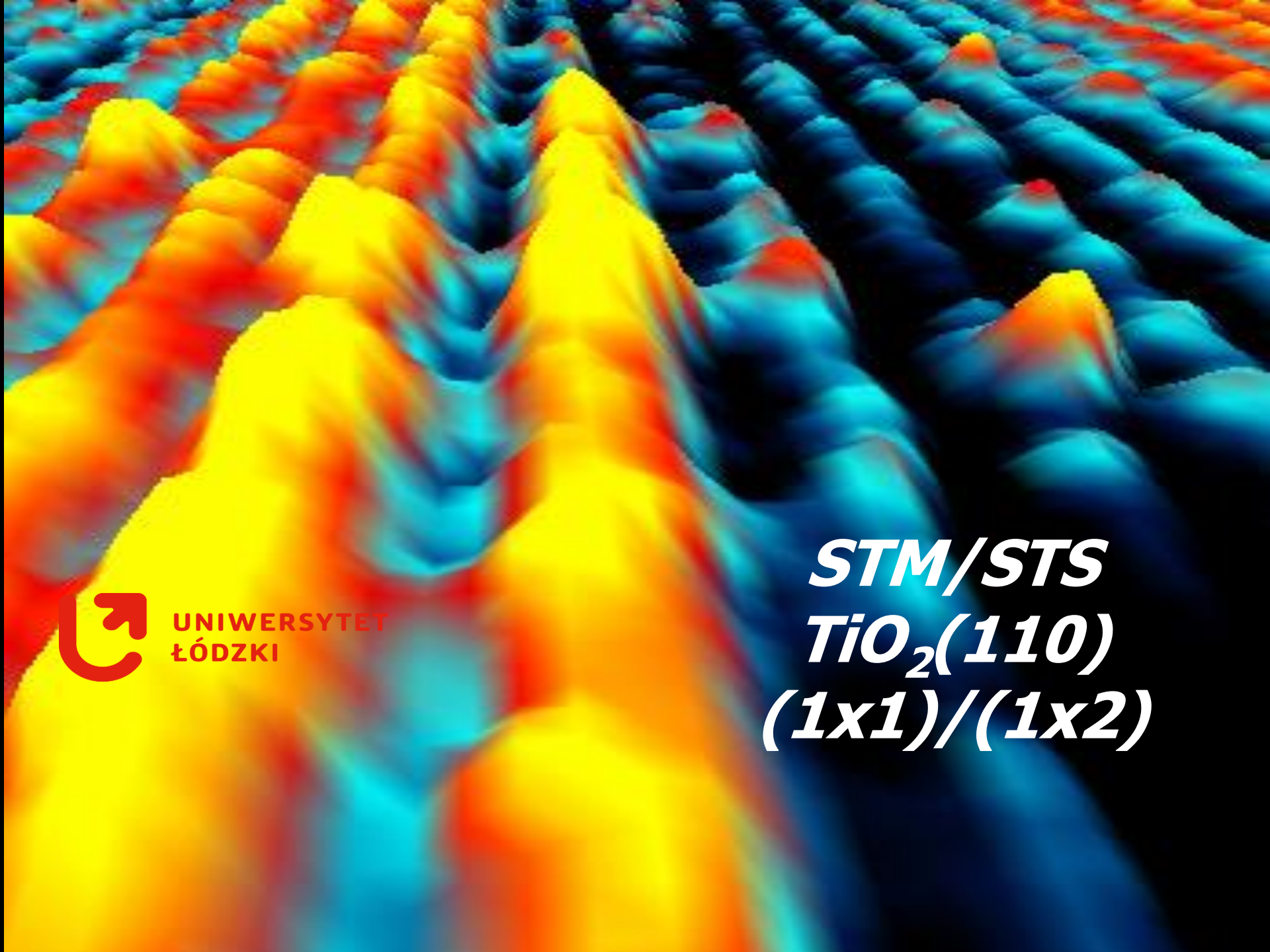
Perturbation theory

$$M_{\mu,\nu} = \frac{h^2}{2m} \int \left(\Psi_\mu^* \nabla \Psi_\nu - \Psi_\nu \nabla \Psi_\mu^* \right) dS$$

$$I = \frac{2\pi e}{h} \sum_{\mu,\nu} f\left(E_\mu\right)\left[1 - f\left(E_\nu + eV\right)\right] \left|M_{\mu,\nu}\right|^2 \delta\left(E_\mu - E_\nu\right)$$

Tunnelling current expression

$$I \propto \sum_\nu \left|\Psi_\nu\left(\vec{r}\right)\right|^2 \delta\left(E_\nu - E_F\right) \equiv \rho\left(\vec{r}, E_F\right)$$



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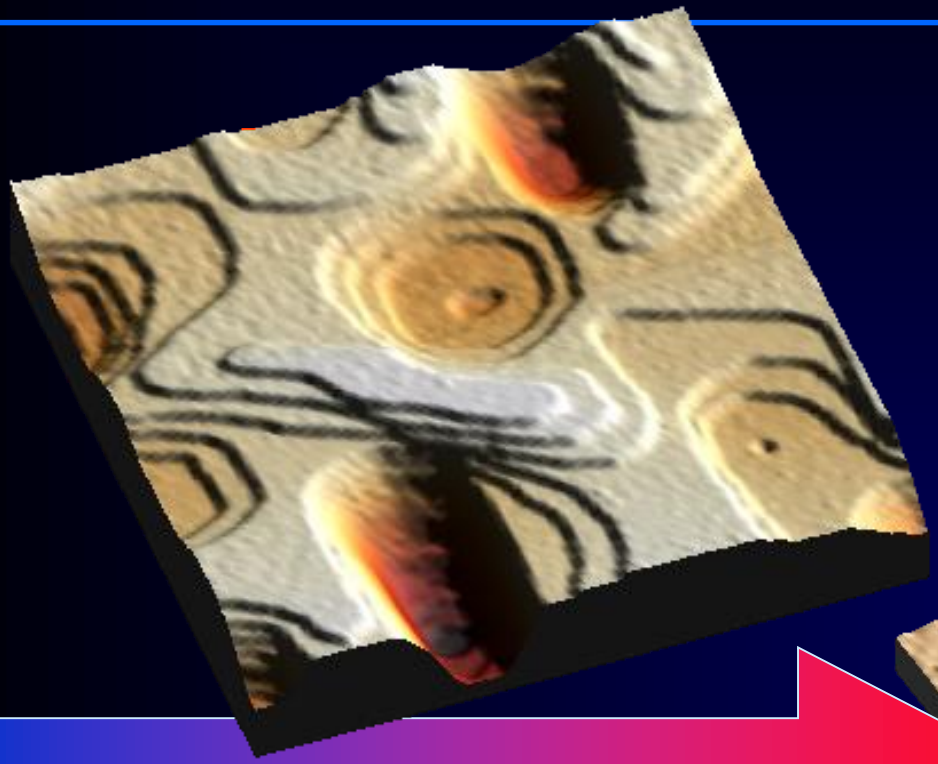
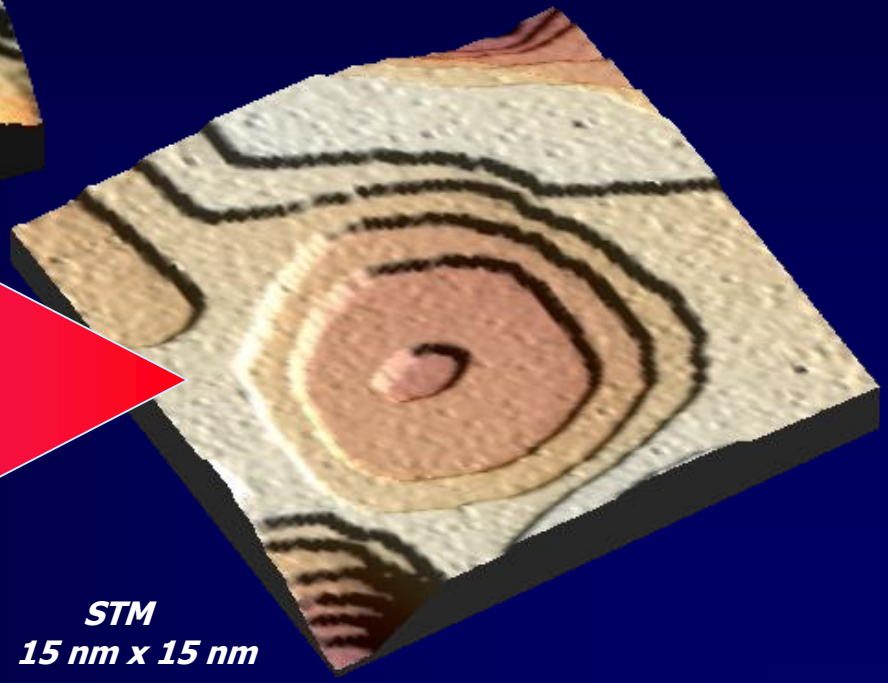
STM/STS TiO_2(110) (1x1)/(1x2)

TiO_2(110)-(1x1) & (1x2)



Reduction

Ti^{4+} --> Ti^{3+}



sputtering + heating

STM
15 nm x 15 nm

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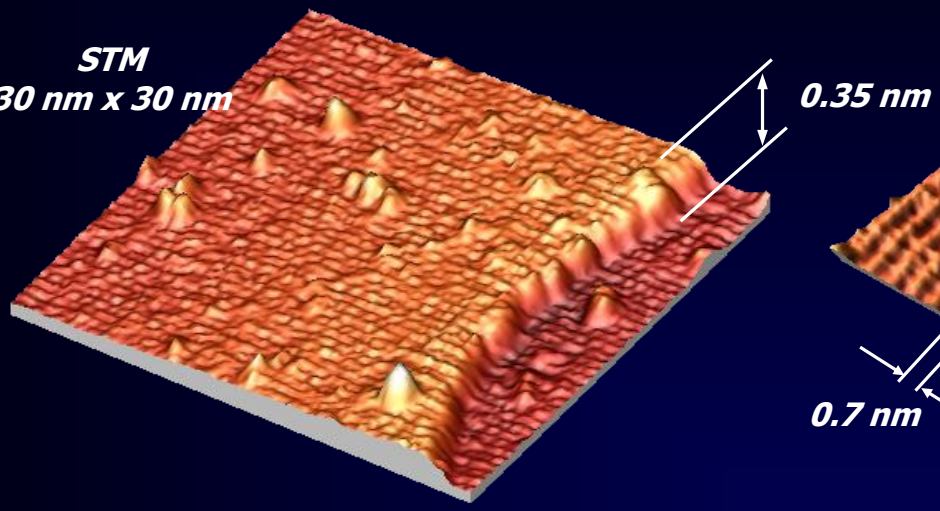
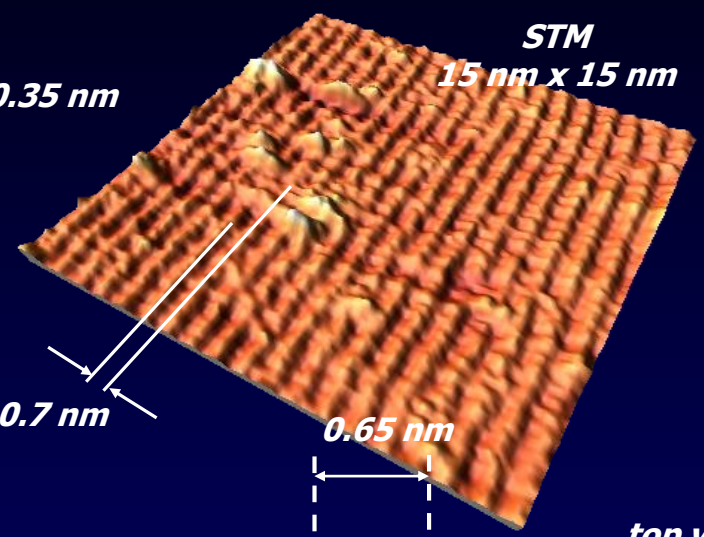
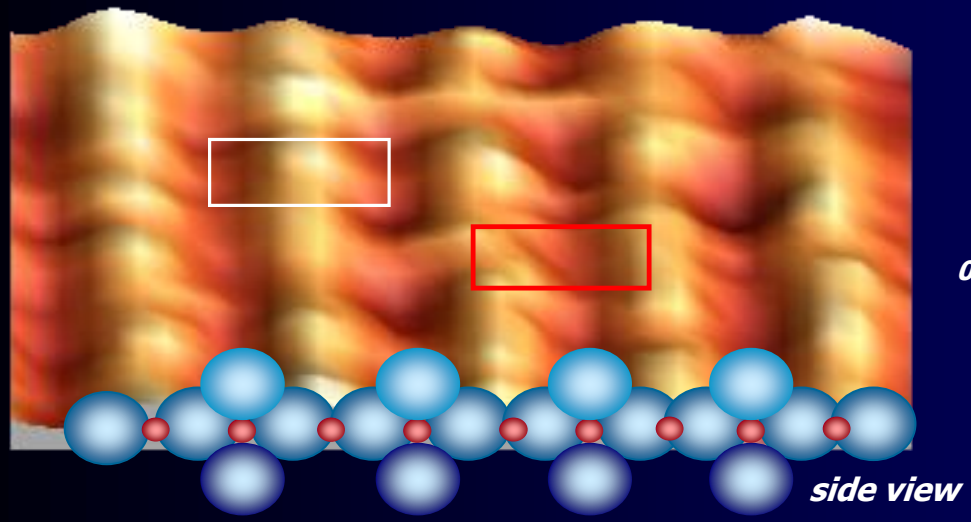
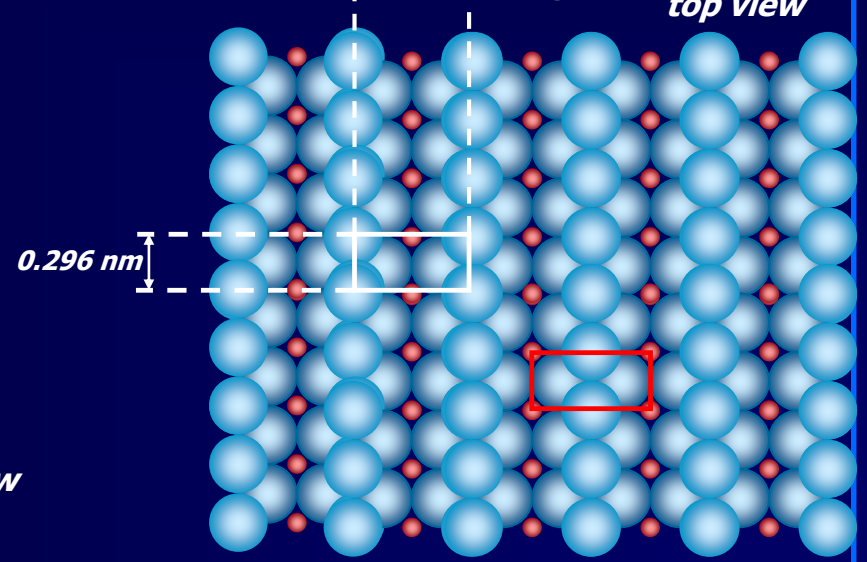
TiO_2(110)-(1x1) & (1x2)









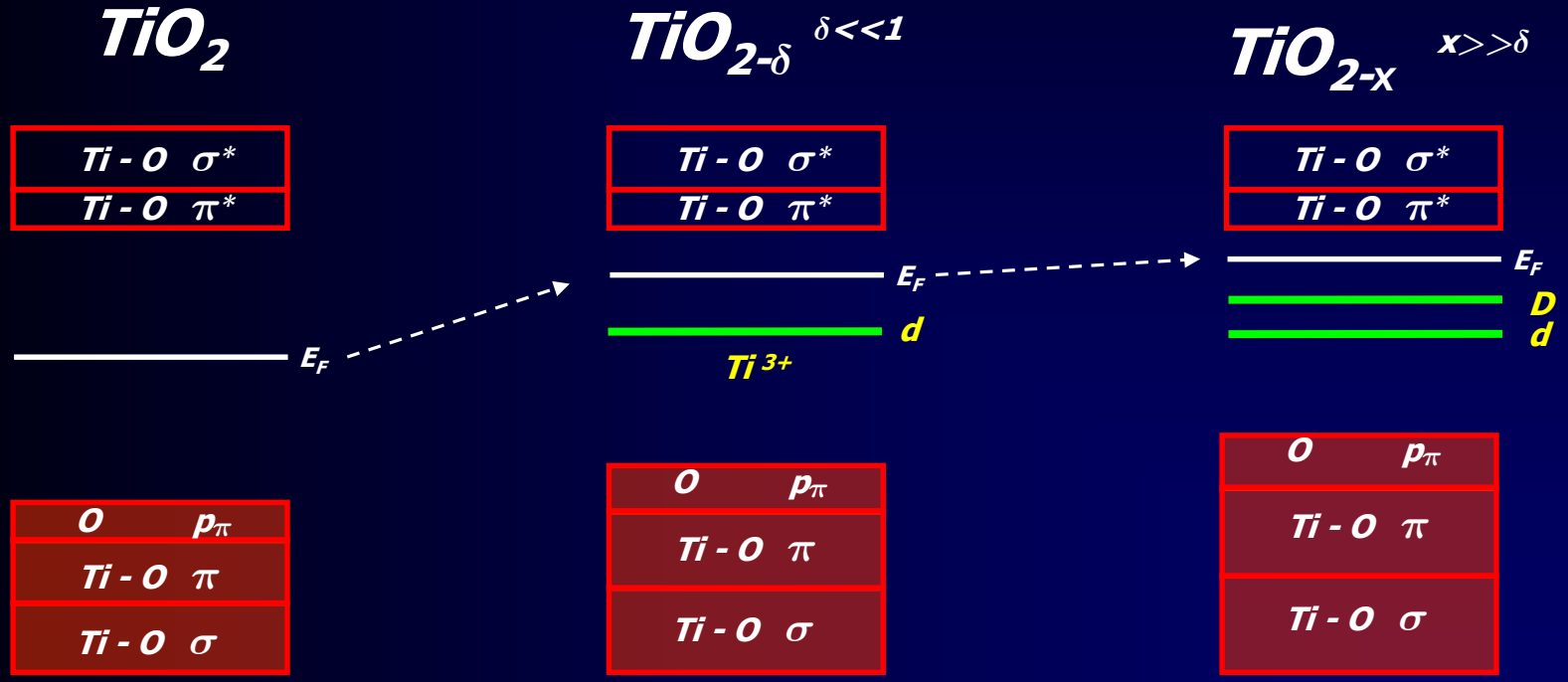
STM image, sample bias=+2V (unoccupied states)

Electronic structure of TiO_2

$Ti^{4+} \rightarrow Ti^{3+}$ i.e. $TiO_2 \rightarrow Ti_2O_3$

K. E. Smith, V. E. Heinrich, Phys. Rev. B. 38, 5965, (1988).
H. Nakatsugawa, E. Iguchi, Phys. Rev. B. 56, 12931, (1997).
A.I. Poteryaev, A.I. Lichtenstein, G. Kotliar, Phys. Rev. Lett. 93, 86401-1, (2004).

Reduction →

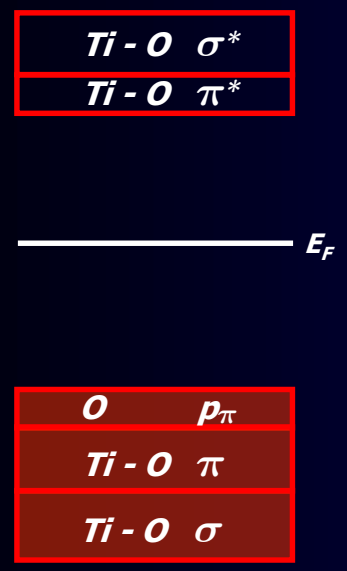


d - defect state related to Ti^{3+}
1.4 –1.0 eV below E_F

D - defect state related to clusters of Ti^{3+}
0.7-0.4 eV below E_F

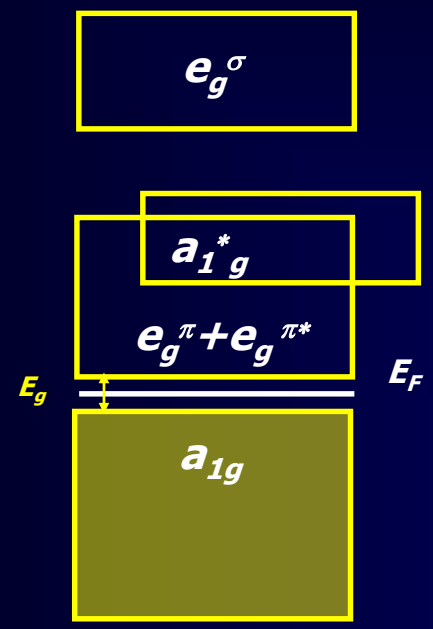
TiO_2(110)-(1x1) & (1x2)

TiO_2

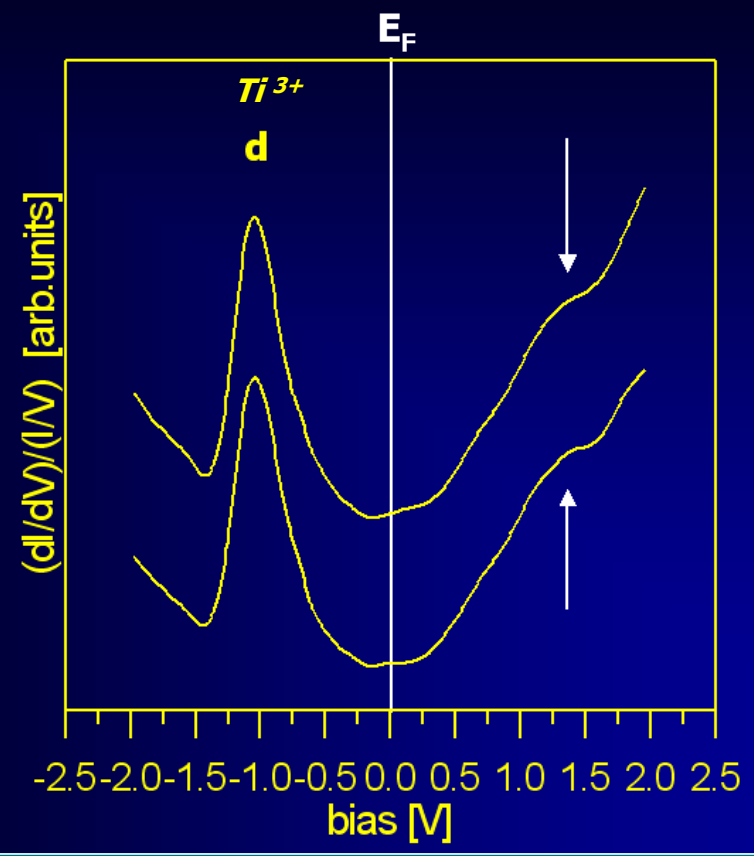


insulator

Ti_2O_3

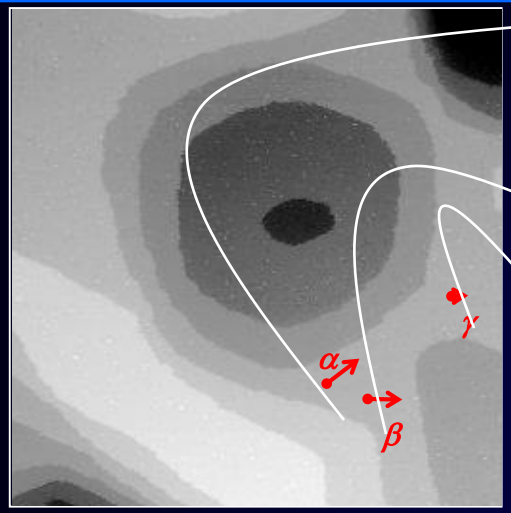


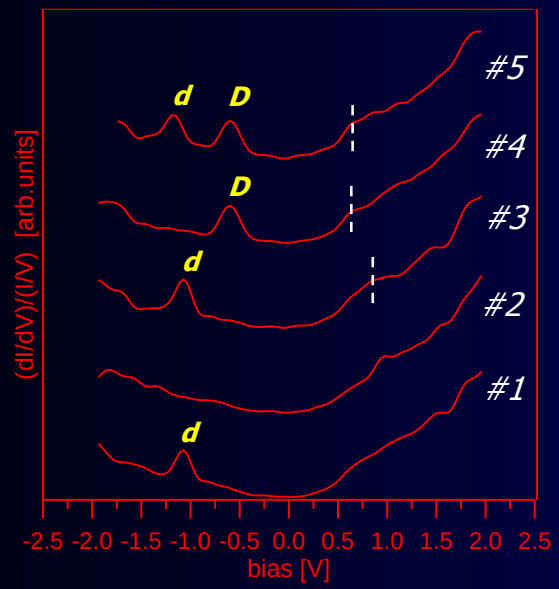
small-gap semiconductor

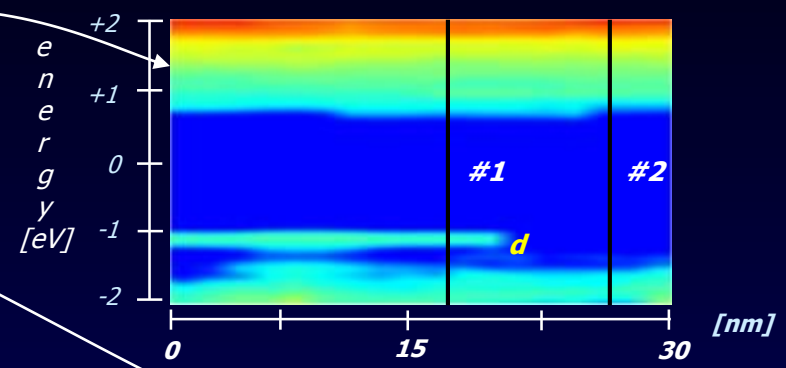


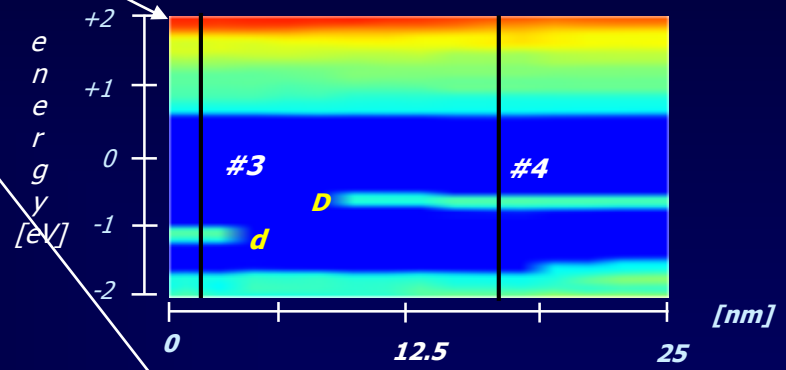
Scanning Tunneling Spectroscopy

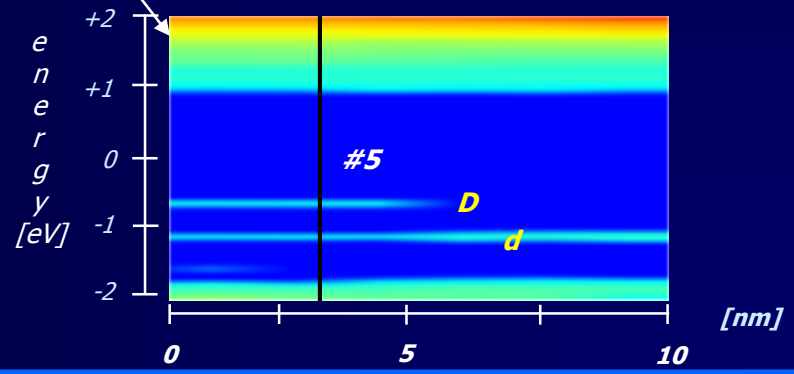
Electronic structure heterogeneity











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Influence of STM tip on TiO_2

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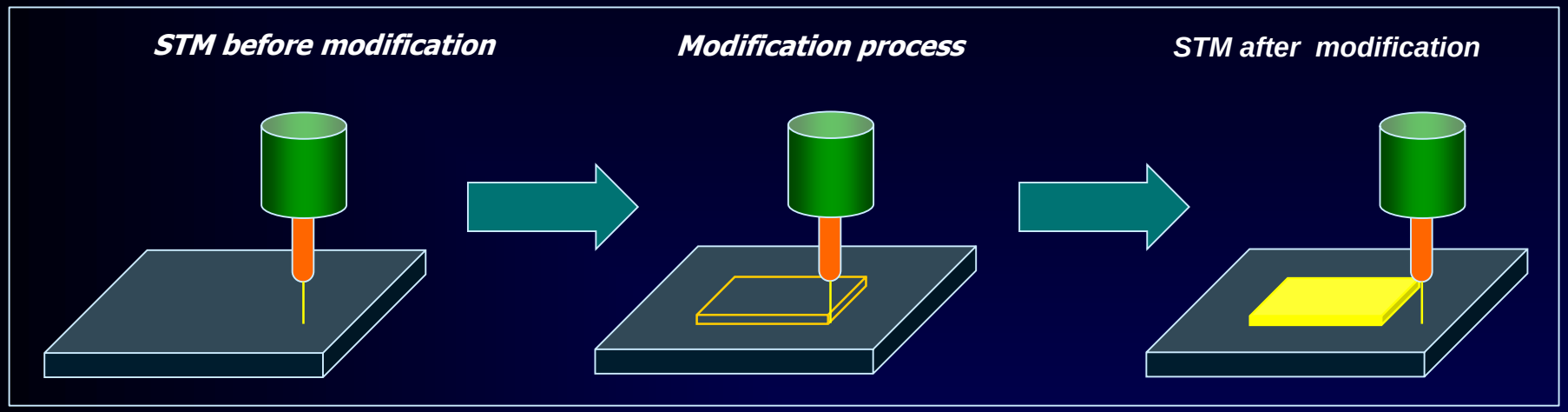
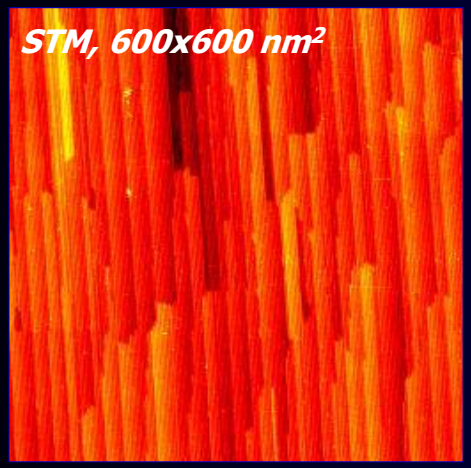
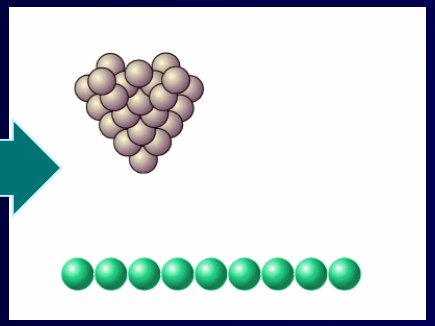
Influence of STM tip on TiO_2

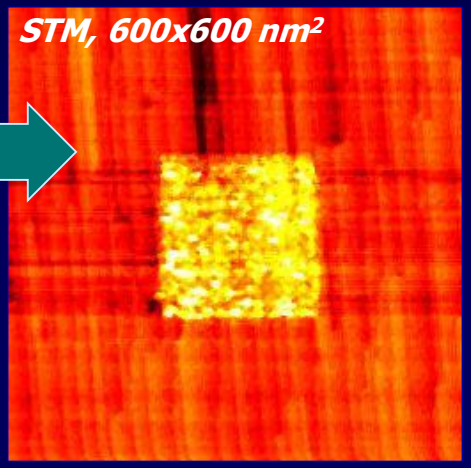




U_s=+2.5 V, 0.1 nA



$|U_s| \geq 4$ V, $I \geq 1$ nA



U_s=+2.5 V, 0.1 nA

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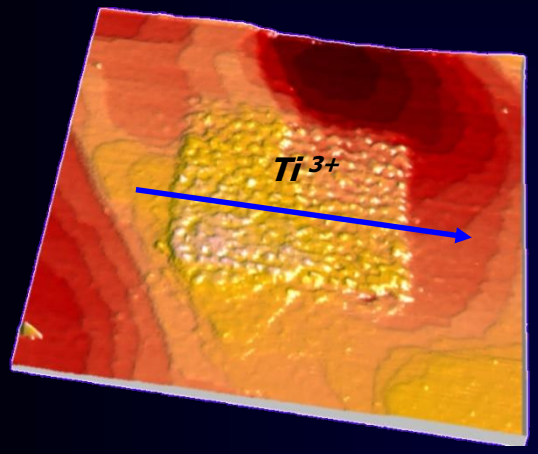
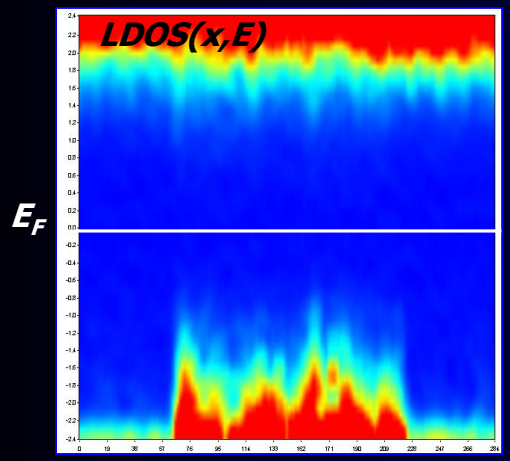
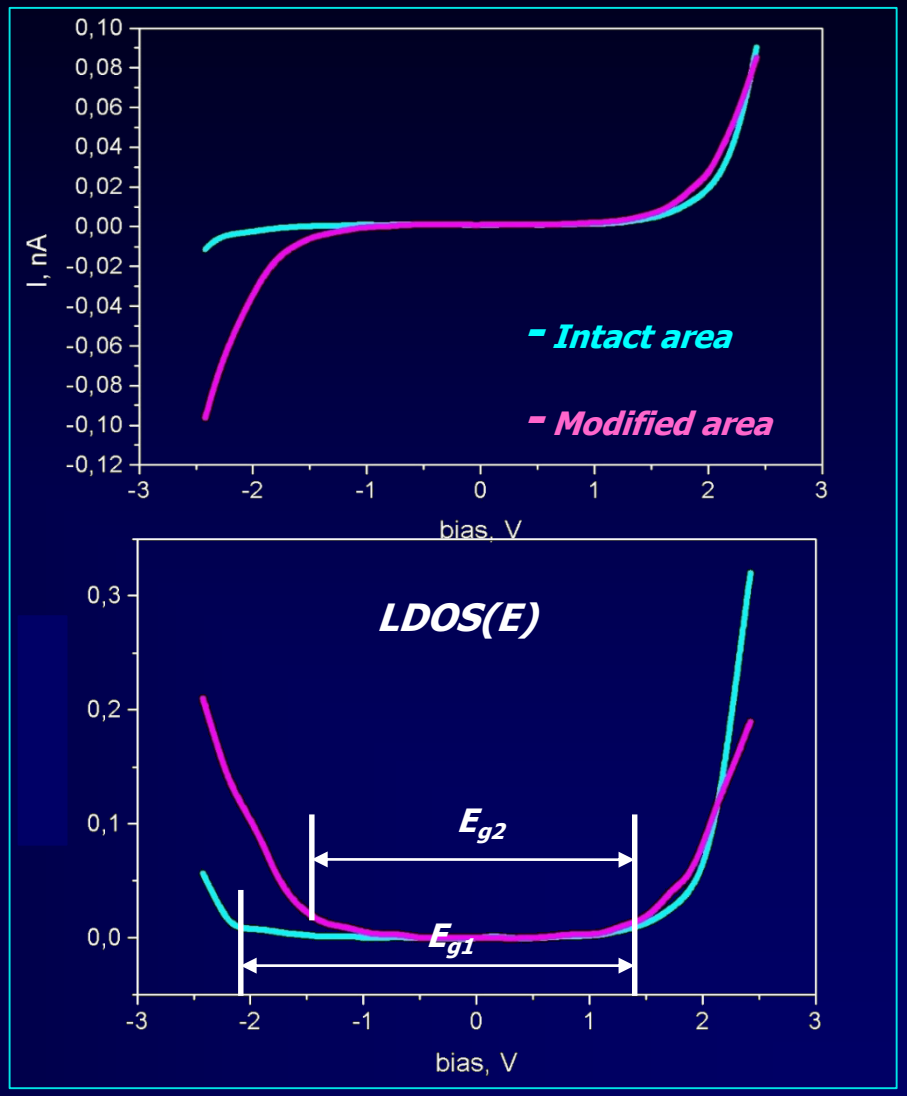
Influence of STM tip on TiO_2(110)



300 x 300 nm² STM image of TiO_2 (110) surface showing 150 x150 nm² modification



LDOS map showing different electronic structure of intact and modified areas



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STM/STS $TiO_2(100)$ (1x3)/(1x7)

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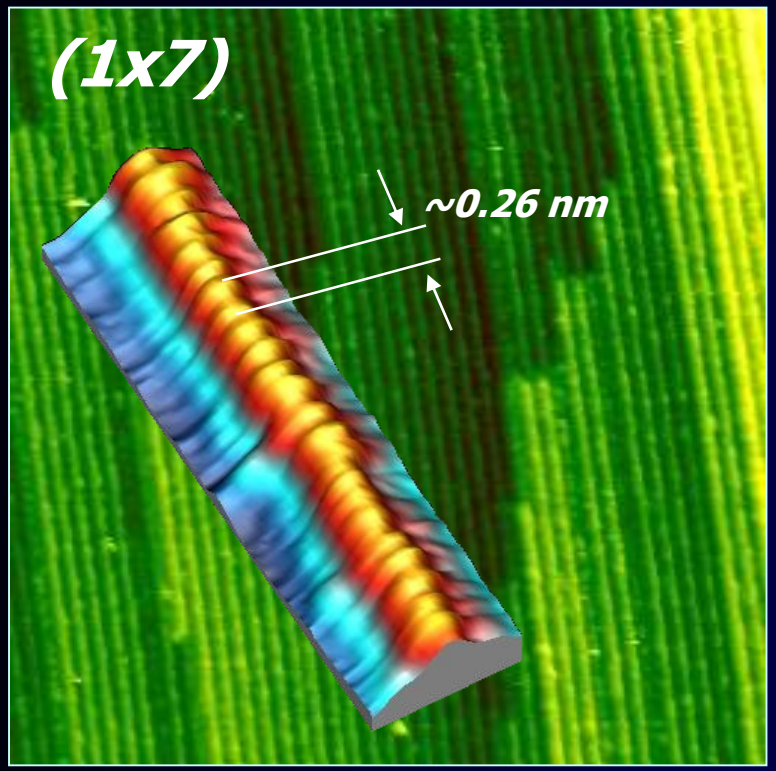
Influence of STM tip on TiO_2(100)

Z. Klusek, A. Busiakiewicz, P.K. Datta, Surf. Sci. 600, pp. 1619-1623, (2006).
Z. Klusek, A. Busiakiewicz, P.K. Datta, et al. Surf. Sci. 601, pp. 1513-1520, (2007).



STM topography - 69 nm x 69 nm

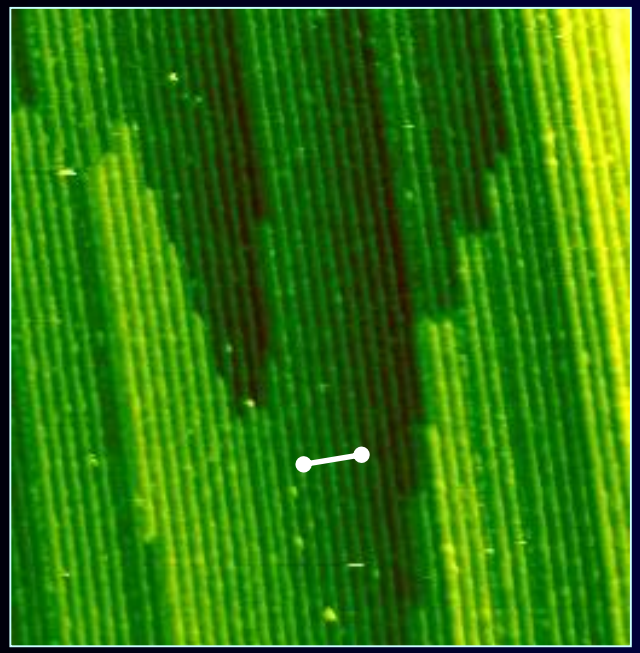
STM topography – 68 nm x 68 nm

Heating T=1070K, t=7-15 h

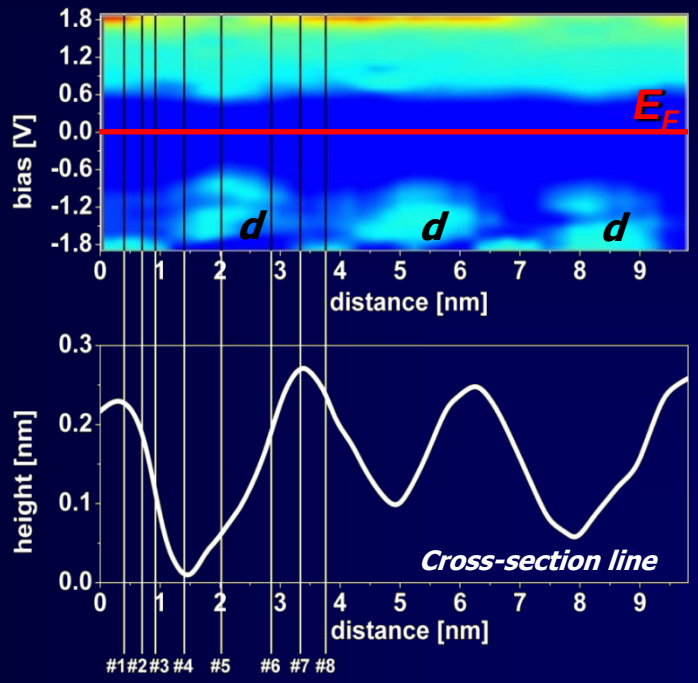
TiO_2(100)-(1x7) reconstruction CITS results

Z. Klusek, A. Busiakiewicz, P.K. Datta, Surf. Sci. 600, pp. 1619-1623, (2006).
Z. Klusek, A. Busiakiewicz, P.K. Datta, et al. Surf. Sci. 601, pp. 1513-1520, (2007).

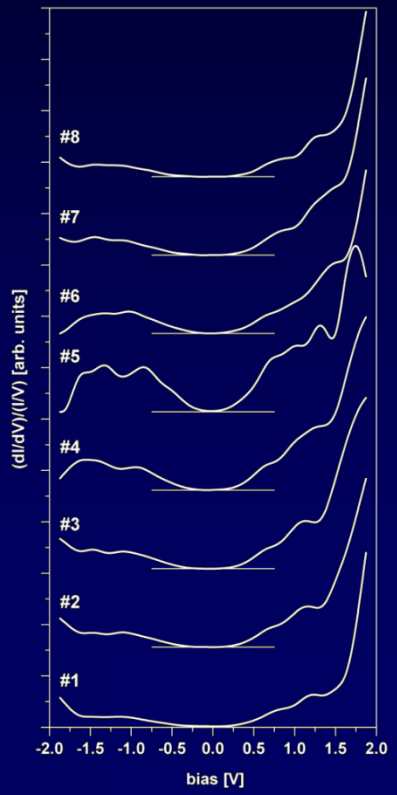
TiO_2(100)-(1x7)



LDOS map



LDOS curves



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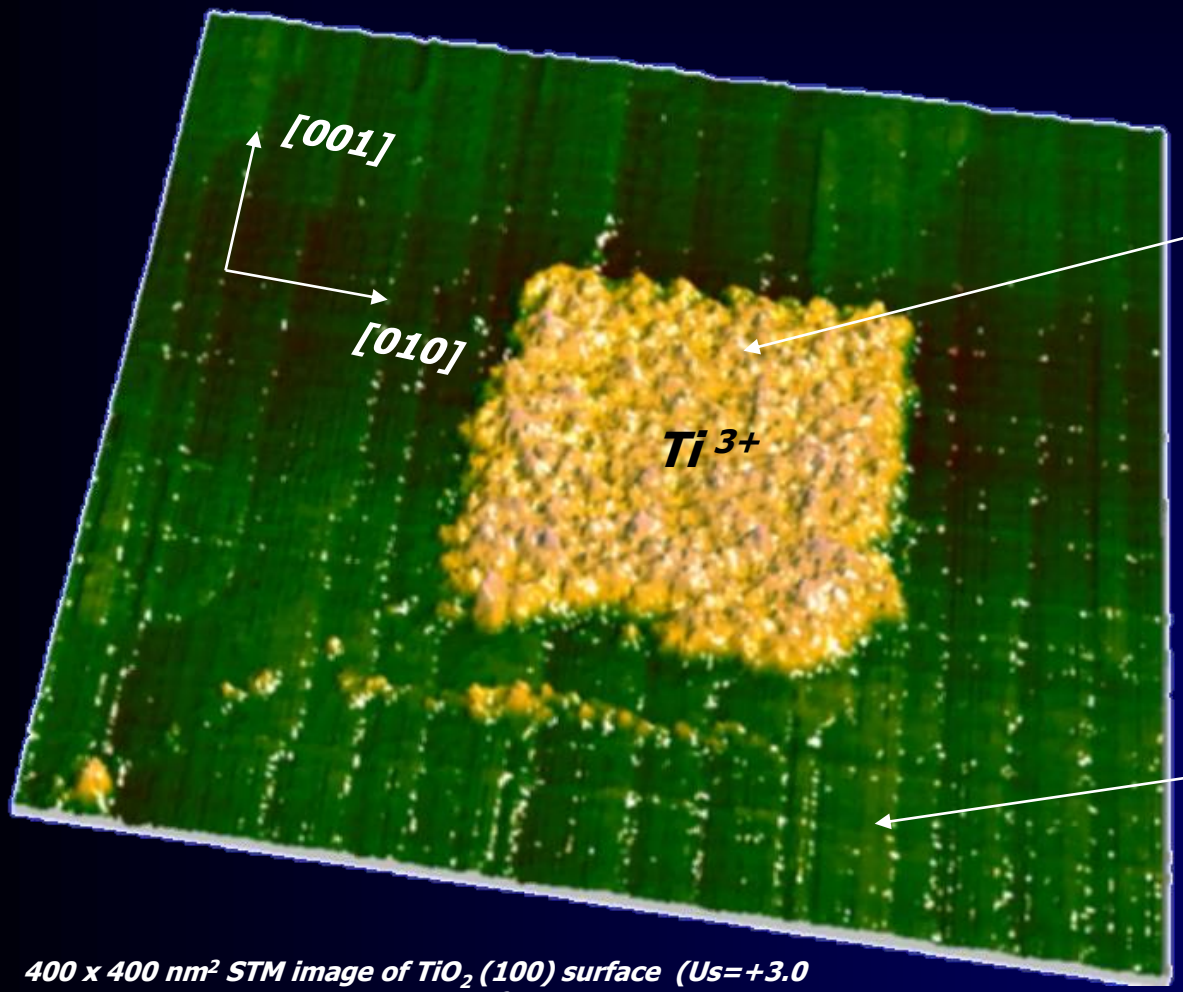
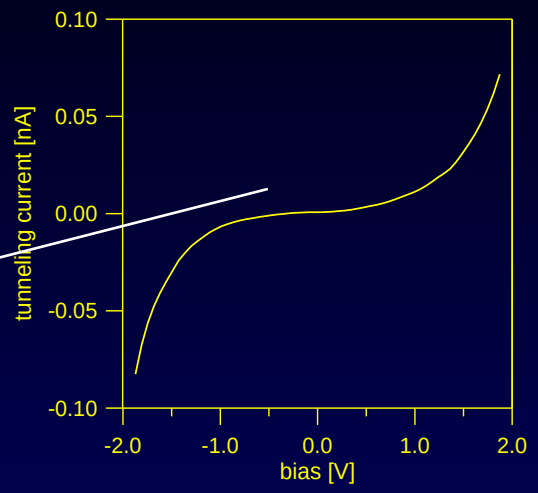
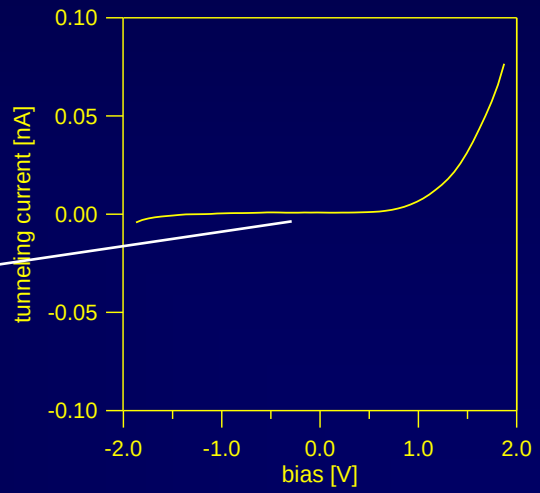
Influence of STM tip on TiO_2(100)







400 x 400 nm² STM image of TiO_2 (100) surface (Us=+3.0 V, I=0.1 nA) showing 150 x150 nm² modification obtained with Us=+5.0V and I=2 nA

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STM/STS $TiO_2(001)$

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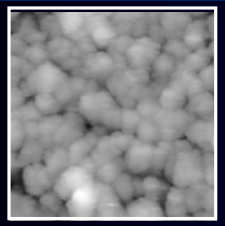
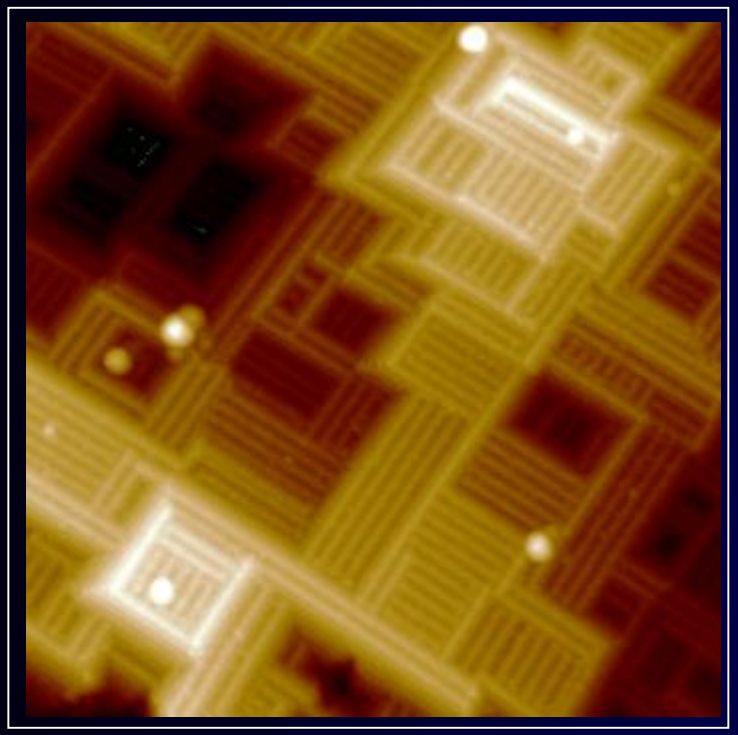
Influence of STM tip on $TiO_2(001)$

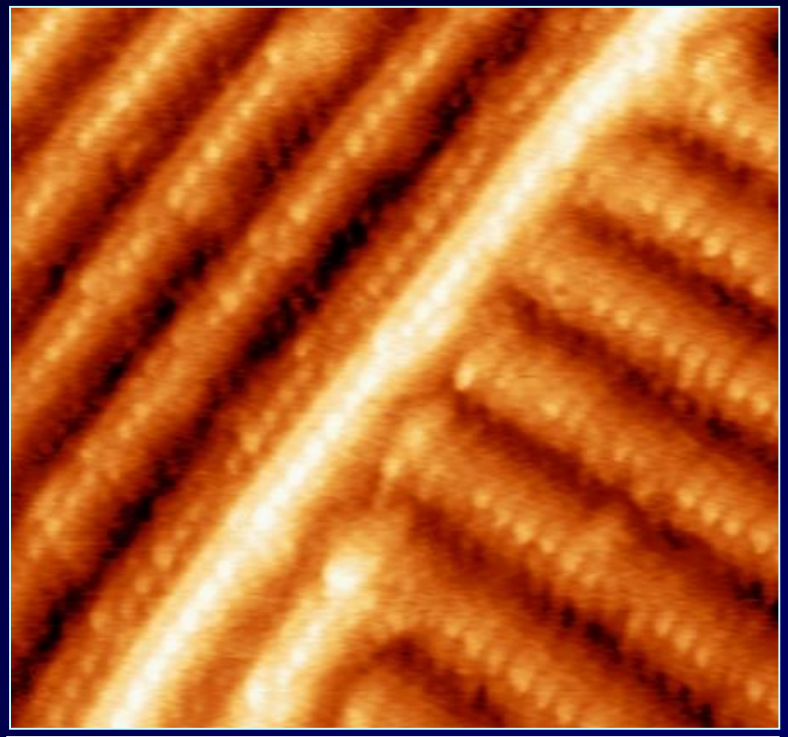
A. Busiakiewicz, Z. Klusek, M. Rogala et al. J. Phys. Cond. Matt. 22, 395501 (2010).



100 nm x 100 nm STM image of the $TiO_2(001)$ surface after sputtering.



STM, 150 nm x 150 nm after 1173 K



STM, 20 nm x 20 nm

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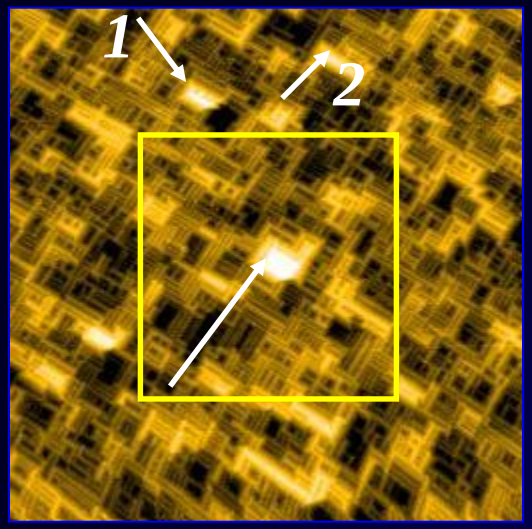
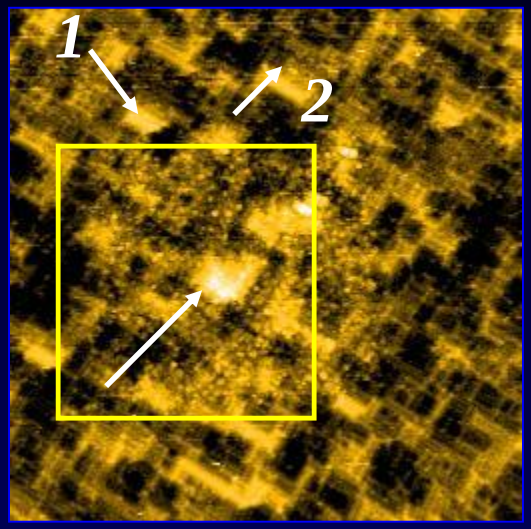
Influence of STM tip on TiO_2(001)



300 x 300 nm² STM image of TiO_2 (001) surface (Us=+2.8 V, I=0.1 nA) – topography obtained before modification attempt

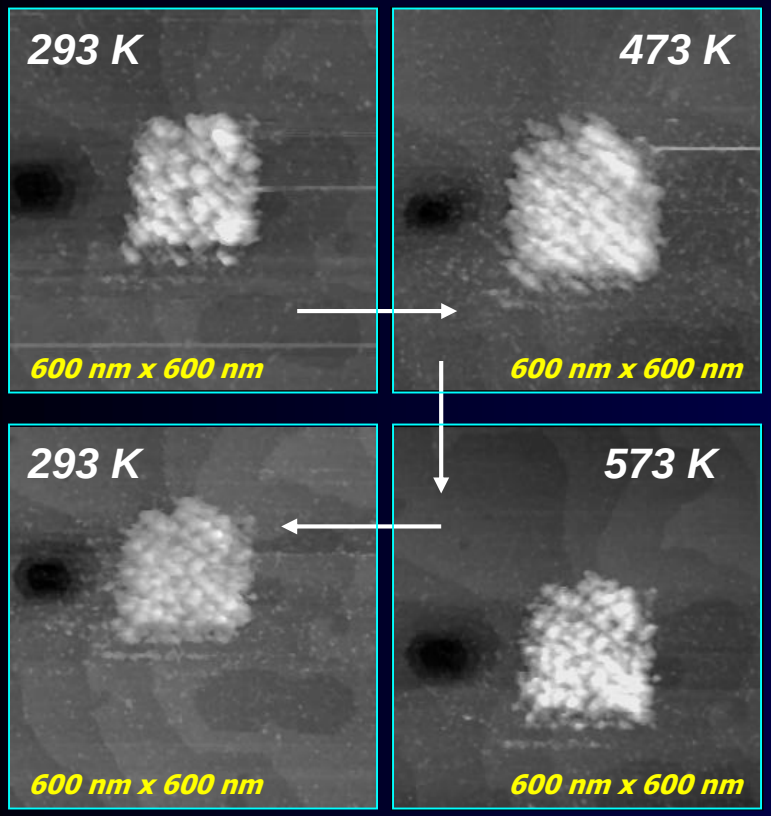


300 x 300 nm² STM image of TiO_2 (001) surface (Us=+2.8 V, I=0.1 nA) after 150 x 150 nm² modification attempt (scanning parameters: Us=+5.0 V, I=3 .0 nA)

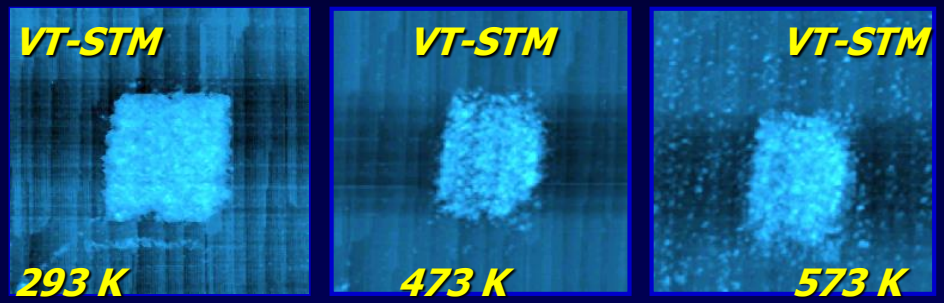
No significant STM induced changes on TiO_2 (001) surface were observed even for high bias voltages and big values of tunneling current.

Modification stability

$TiO_2(110)$



$TiO_2(100)$



An in-situ HT-STM topographies recorded at different temperatures.

The total time in which temperature was raised from 293 K to 573 K was 24 h.

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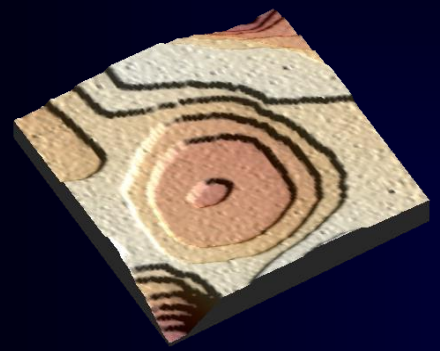
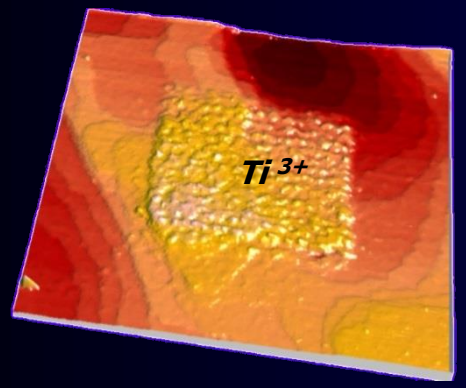
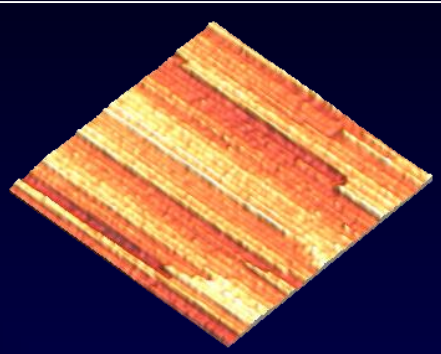
Influence of STM tip on TiO_2



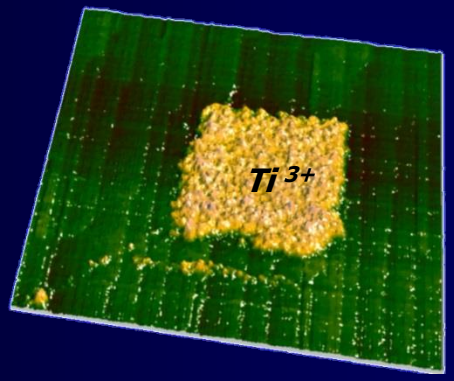
TiO_2 (110) - (1x1)
TiO_2 (110) - (1x2)



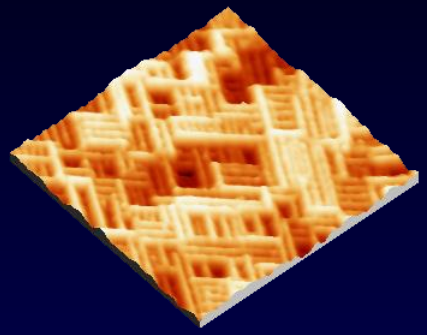
TiO_2 (110) - (1x1)
TiO_2 (110) - (1x2)



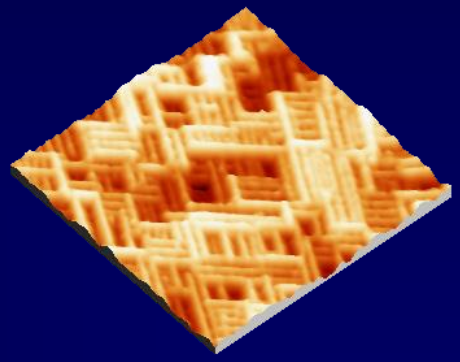
TiO_2 (100) - (1x3)
TiO_2 (100) - (1x7)



TiO_2 (100) - (1x3)
TiO_2 (100) - (1x7)



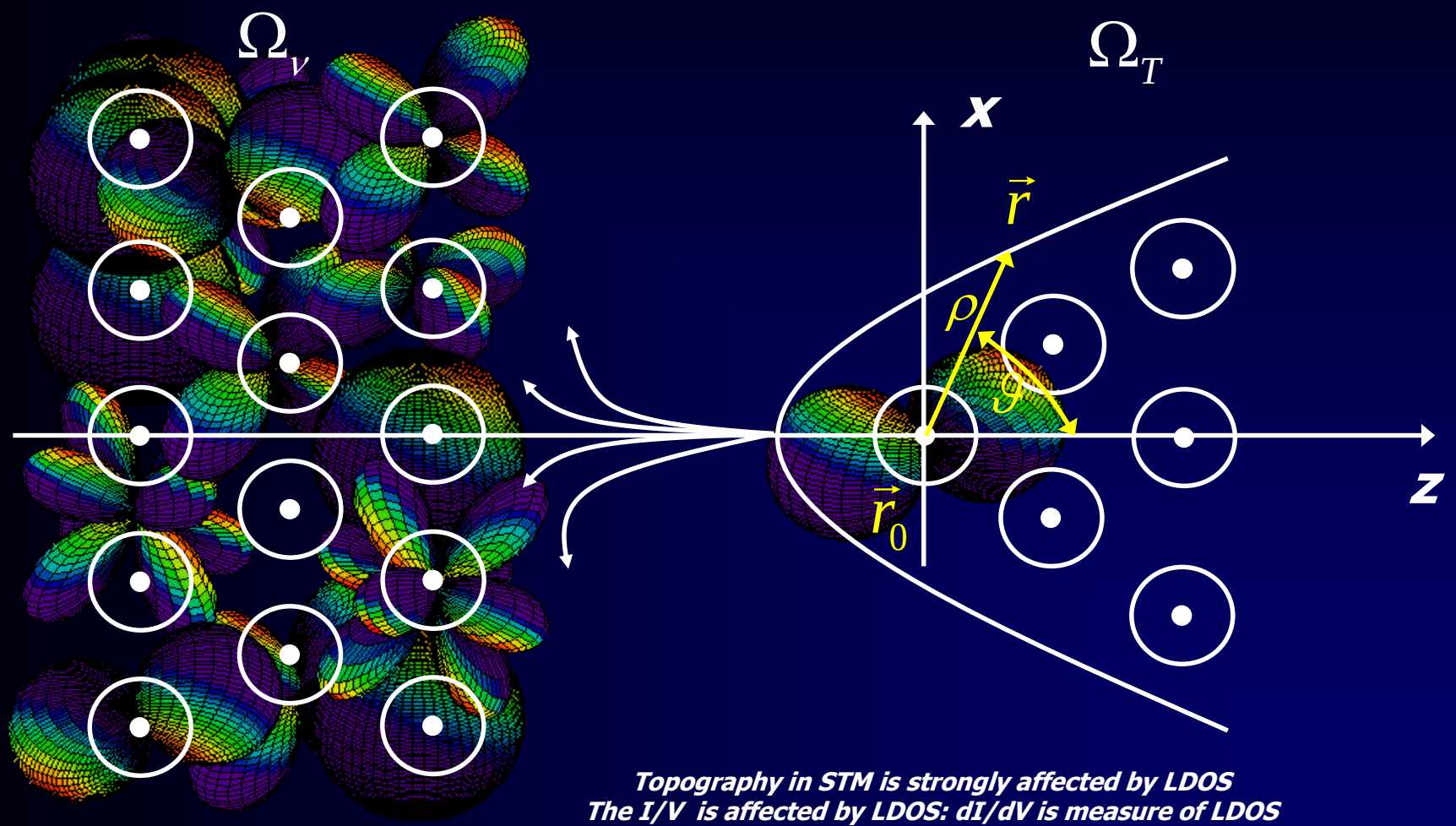
TiO_2 (001)



TiO_2 (001)

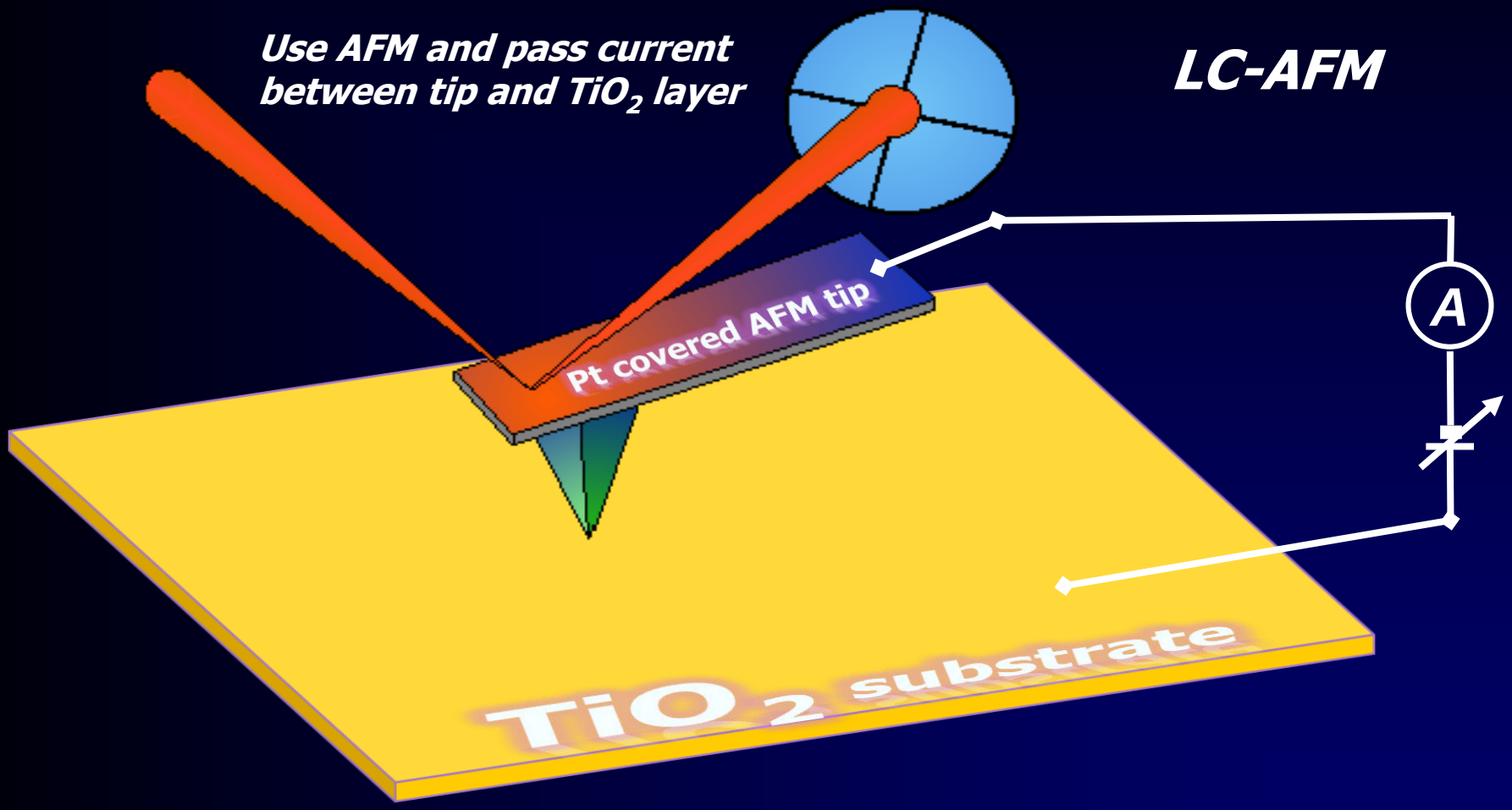
STM versus LC-AFM

We do not observe hysteretic behavior on I/V curves



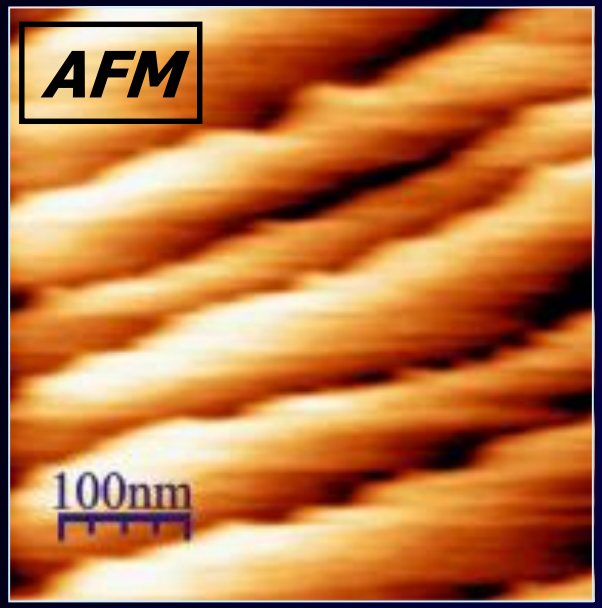
Topography in STM is strongly affected by LDOS
The I/V is affected by LDOS: dI/dV is measure of LDOS

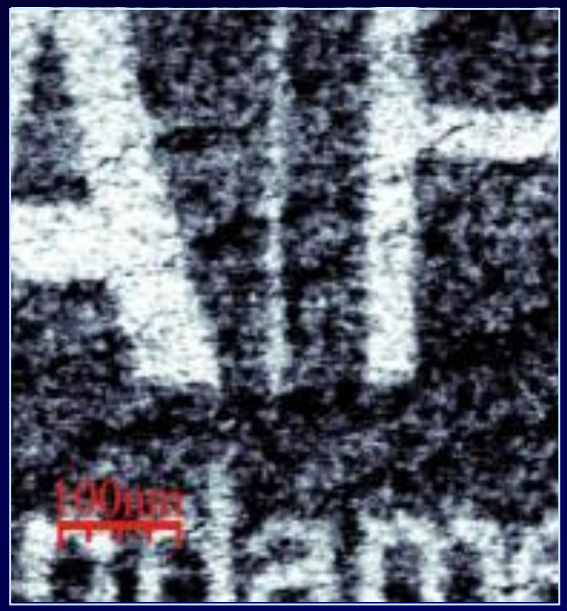
Resistive switching in $TiO_2(110)$



Modification of TiO_2 by LC-AFM

This is the same region of surface



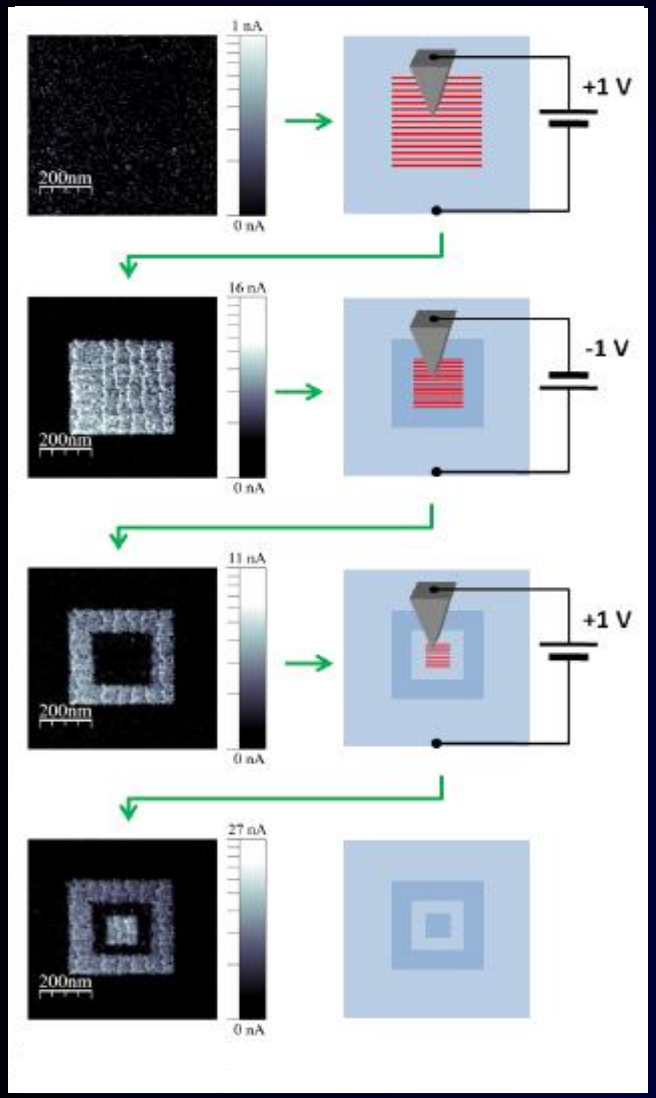


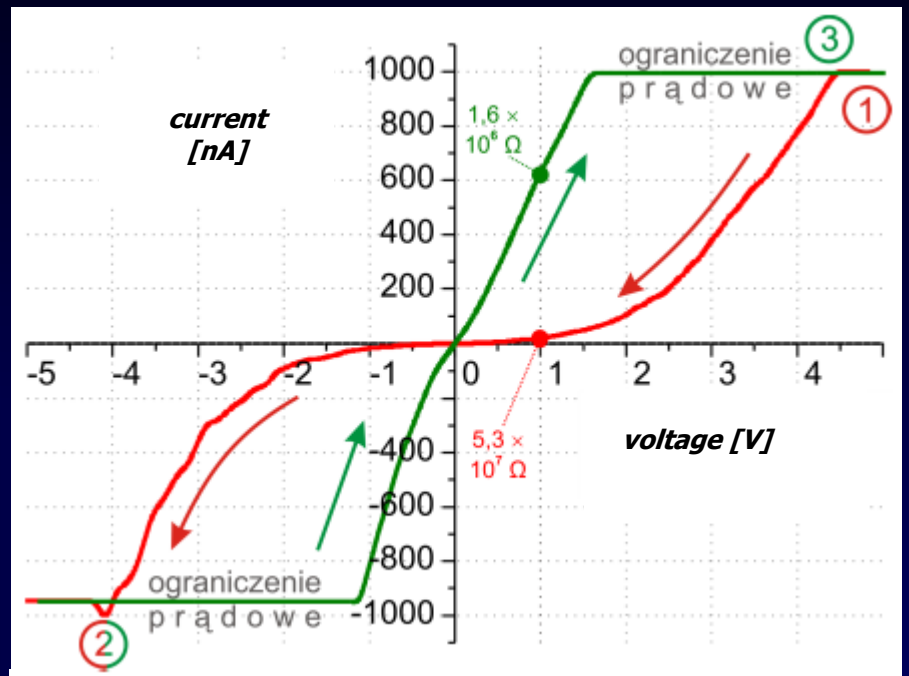
topography [nm]

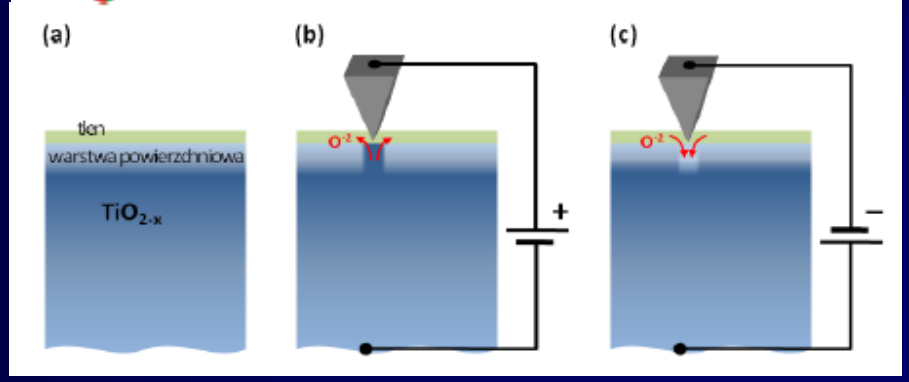
resistance

current [nA]

Resistive switching in $TiO_2(110)$







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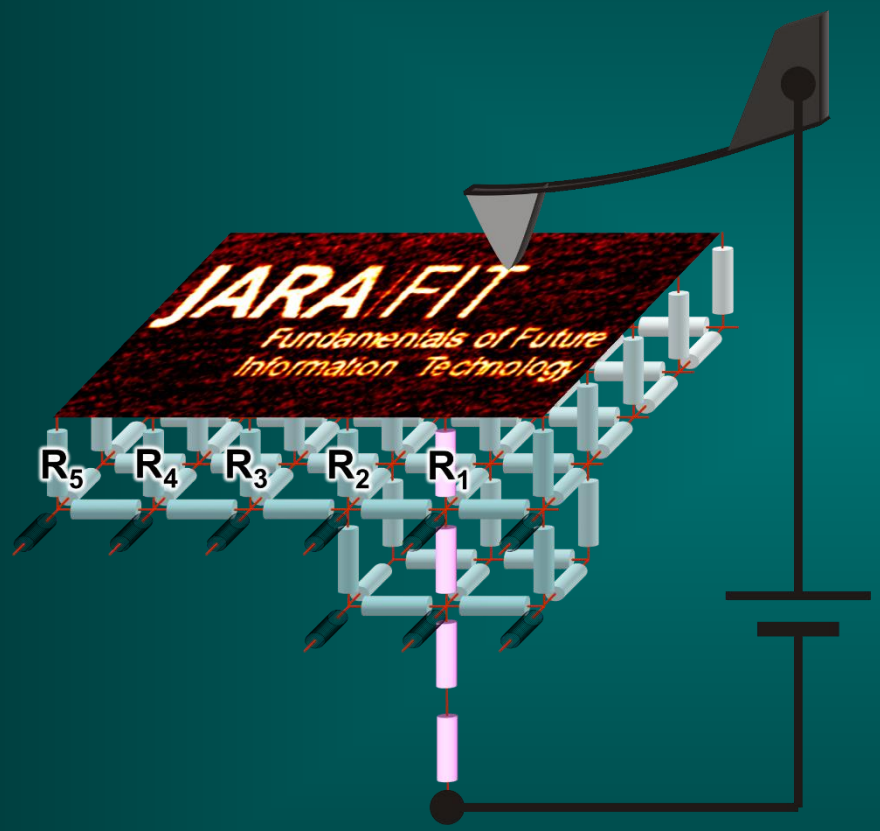
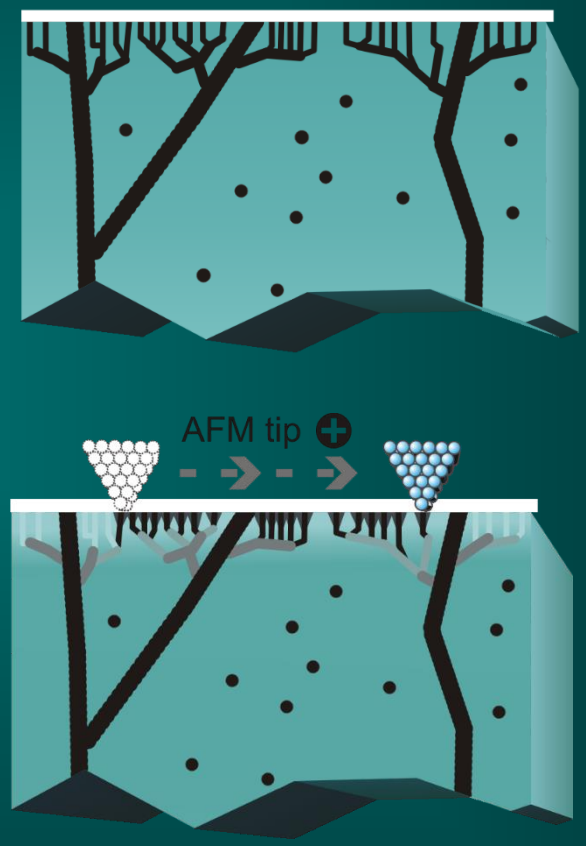
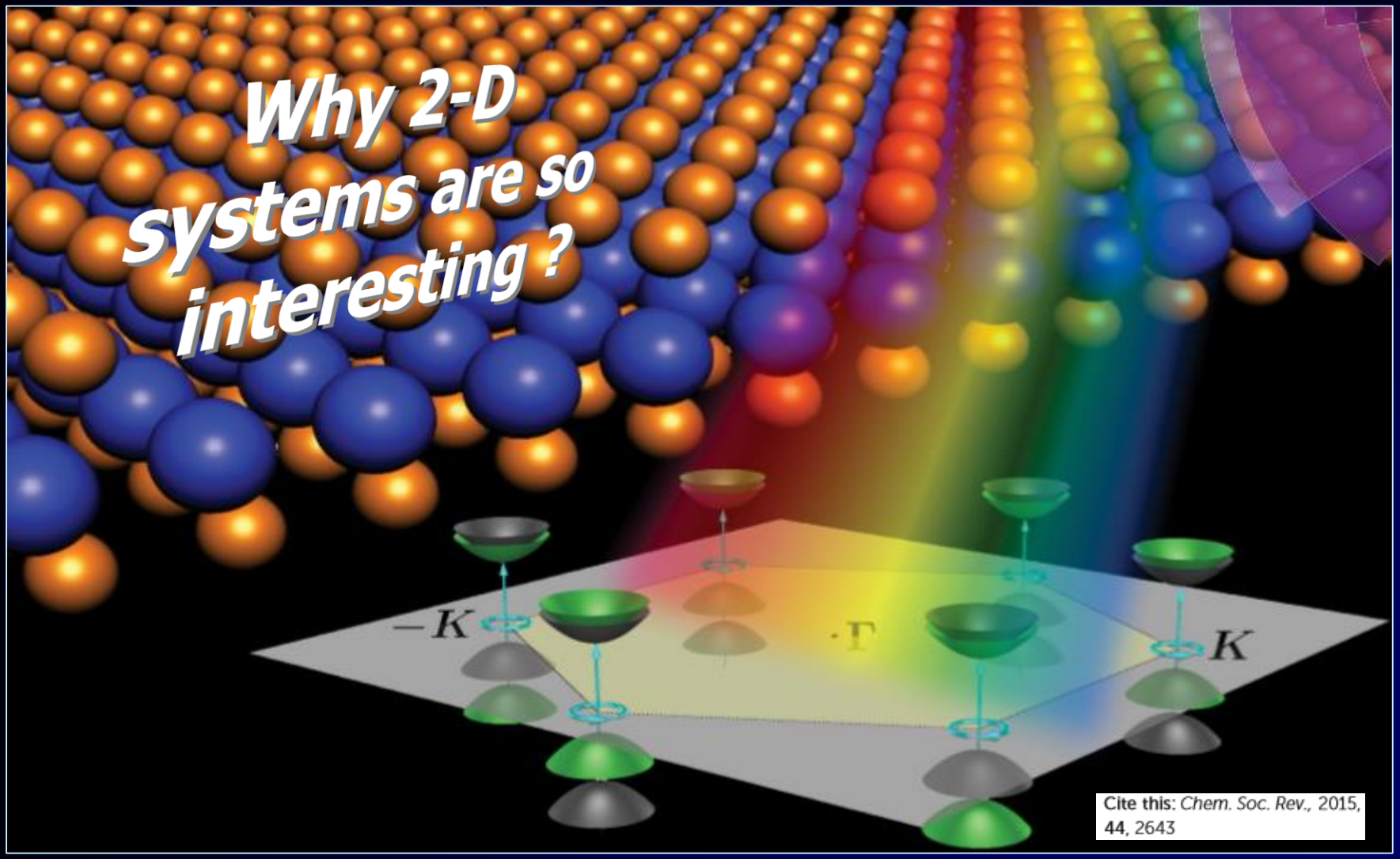
Resistive switching in $TiO_2(110)$





K. Szot, M. Rogala, W. Speier, Z. Klusek, A. Besmehn, R. Waser Nanotechnology 22, 2540001 (2011).
M. Rogala, Z. Klusek, K. Szot, Appl. Phys. Lett. (2013).

Two dimensional systems



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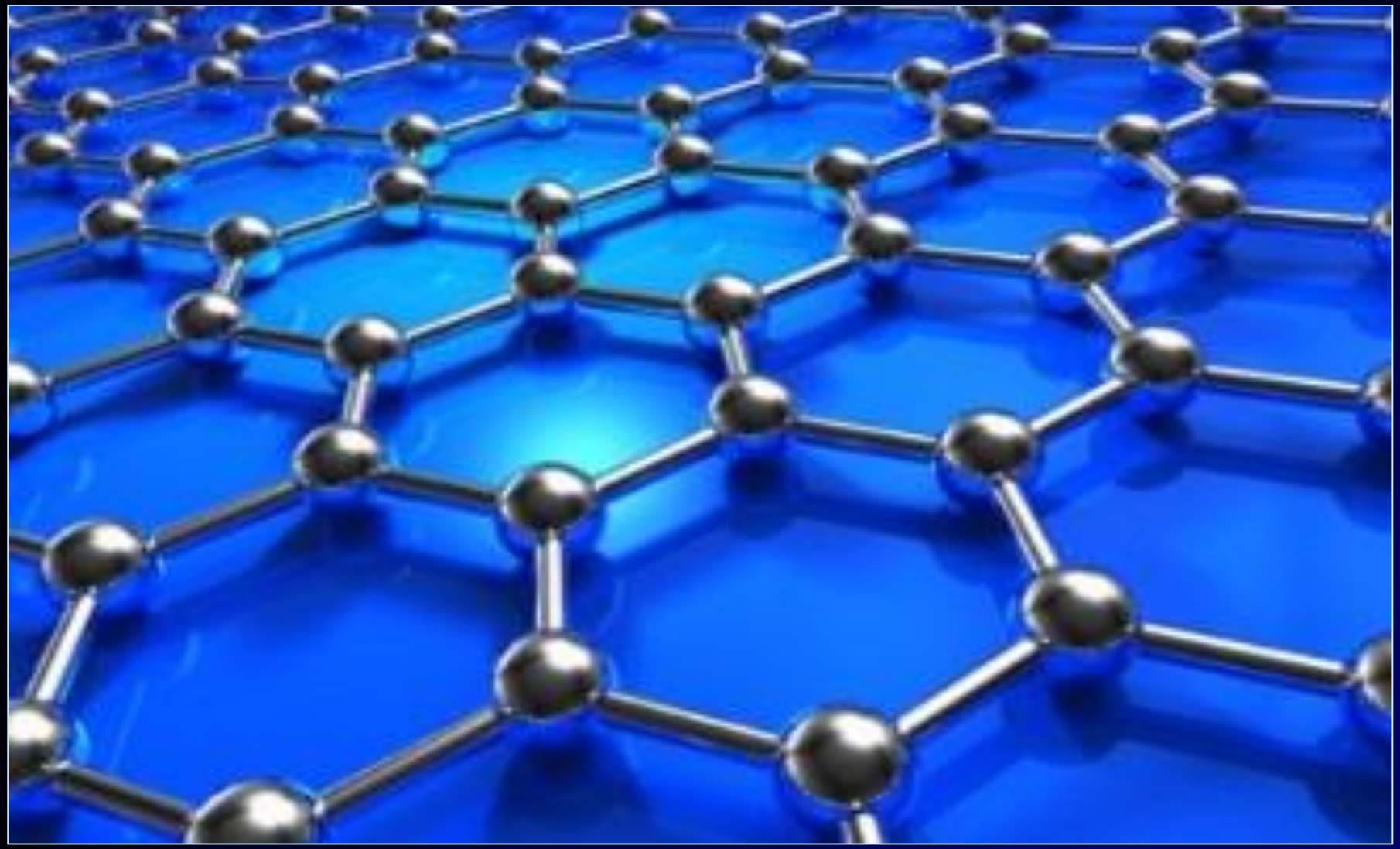
Graphene

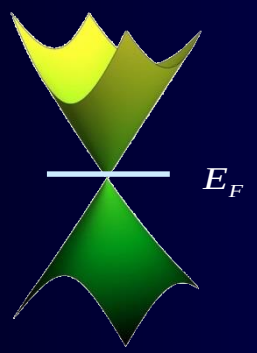


Physics of graphene

Electron properties

$$H = v\begin{pmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{pmatrix} = v\begin{pmatrix} 0 & \pi^+ \\ \pi & 0 \end{pmatrix} = v\left(\sigma_x p_x + \sigma_y p_y\right) = v\vec{\sigma}\cdot\vec{p}$$

$$\psi = \begin{pmatrix} \psi_{AK} \\ \psi_{BK} \\ \psi_{AK'} \\ \psi_{BK'} \end{pmatrix}$$



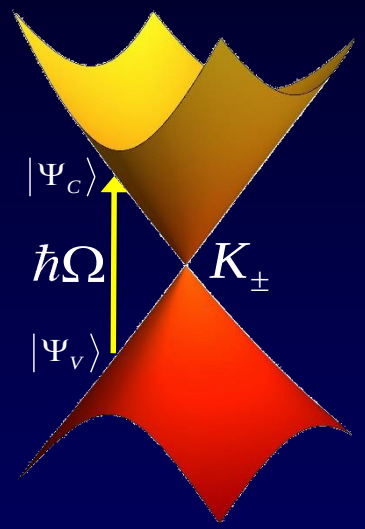
pseudospin conservation
->
lack of backscattering

Optical properties

$$E\left(\vec{k},\Omega\right) = E_0 e^{i\left(\vec{k}\vec{r} - \Omega t\right)}$$

$$H = v_F \sigma\left(\vec{p} - \frac{e}{c}\vec{A}\right)$$

$$\vec{A} = \left(ev_F / i\Omega\right)\vec{E}_0$$



$$W_i = \left(c / 4\pi\right)\left|\vec{E}_0\right|^2$$

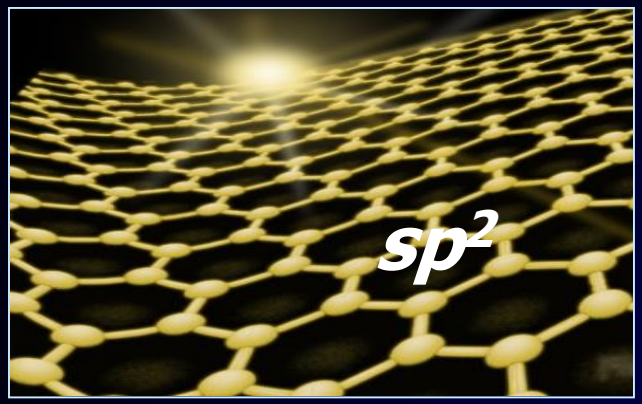
$$W_a = \frac{2\pi}{\hbar}\left|\langle\Psi_c|\left(ev_F / i\Omega\right)\sigma\cdot\vec{E}_0|\Psi_V\rangle\right|^2 \times \rho\left(\hbar/2\right)\times\hbar\Omega$$

$$\rho = \left(E/2 = \hbar/2\right) = \hbar\Omega / \pi\hbar^2 v_F^2$$

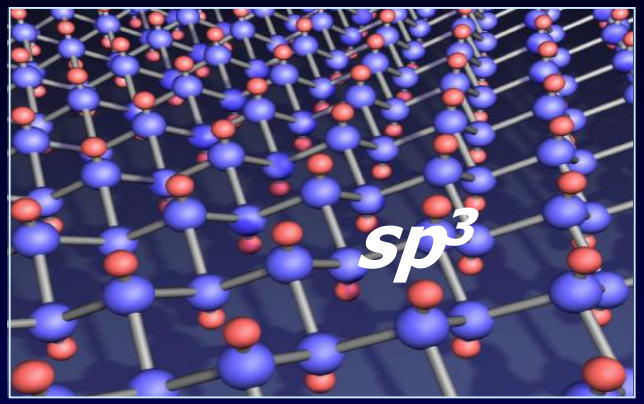
$$W_a = \frac{e^2}{4\hbar}\left|E_0\right|^2$$

$$P = \frac{W_a}{W_i} = \frac{\pi e^2}{\hbar c} = \pi\alpha \qquad T = \left(1 + 0.5\pi\alpha\right)^{-2} \approx 1 - \pi\alpha \approx 97.7\%$$

Graphene and graphene derivatives

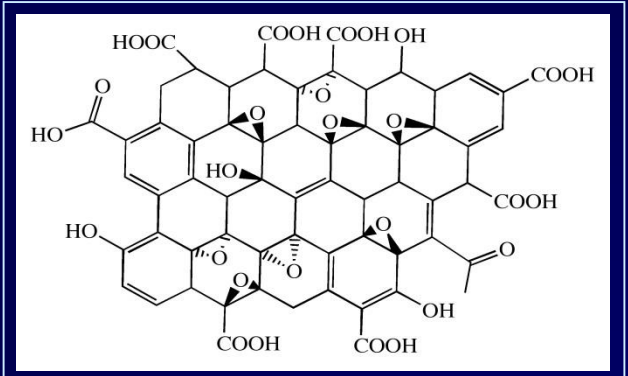


graphene



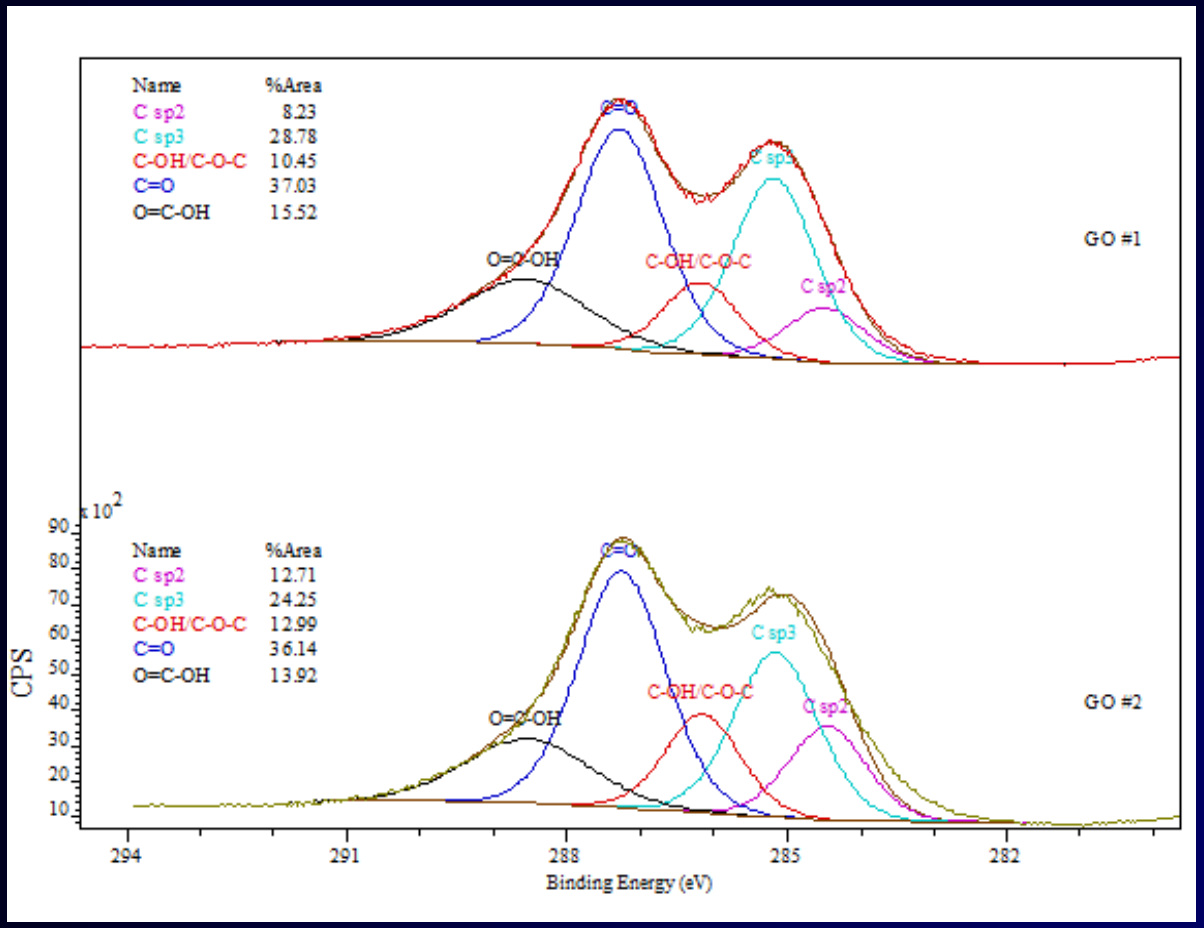
graphane

graphone

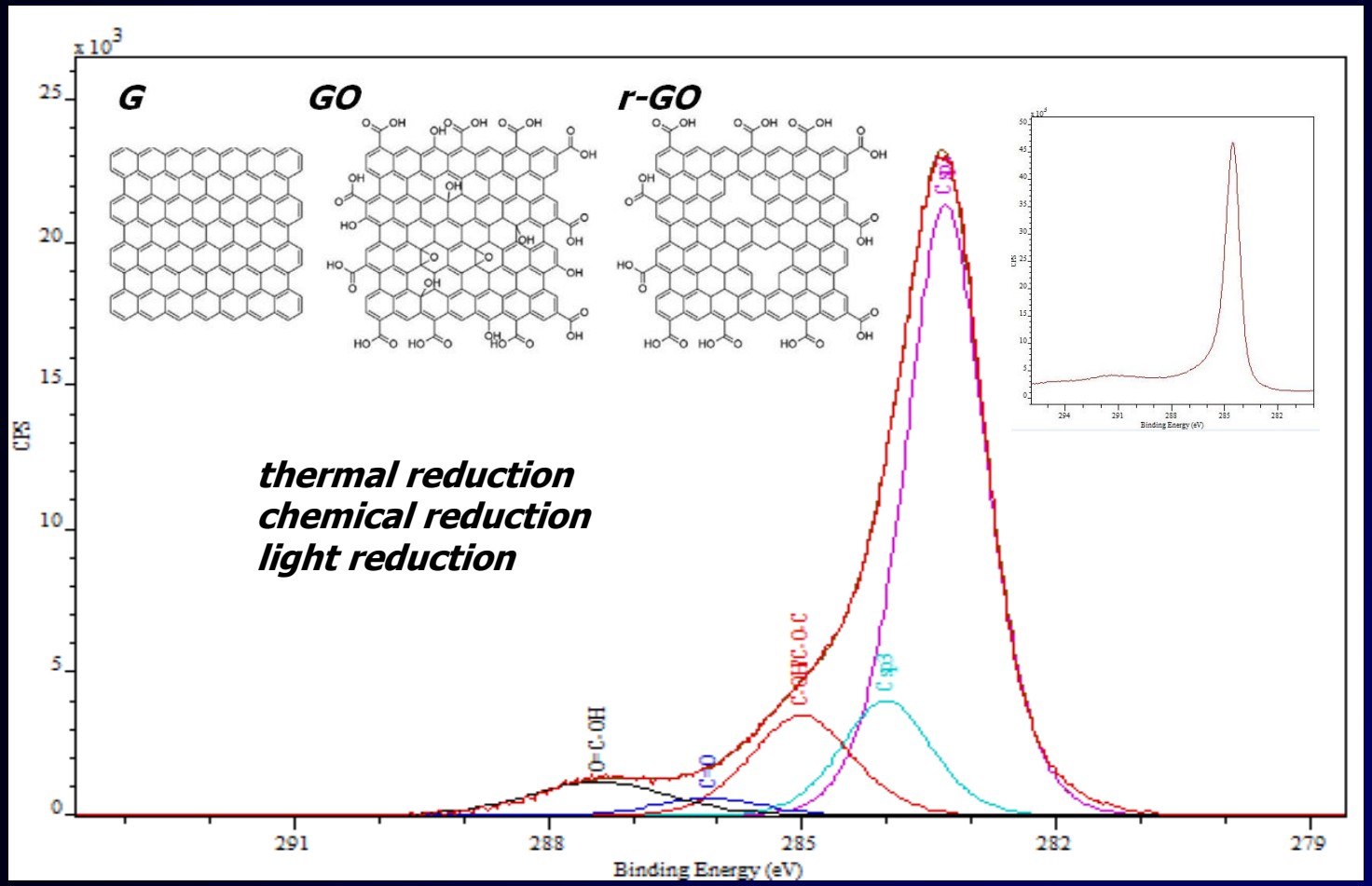


graphene oxide

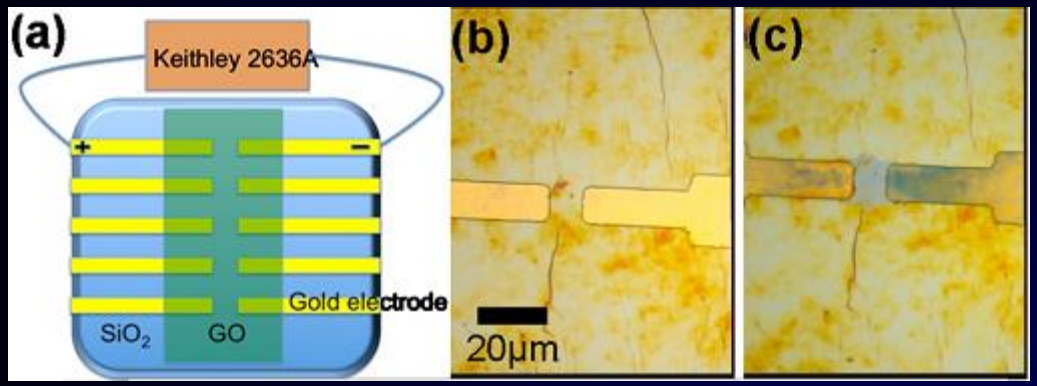
Graphene oxide – XPS results



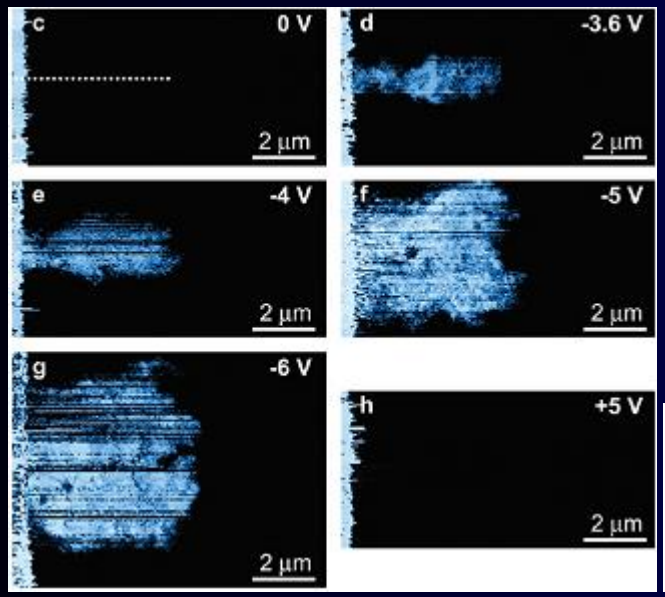
Reduced graphene oxide – XPS results



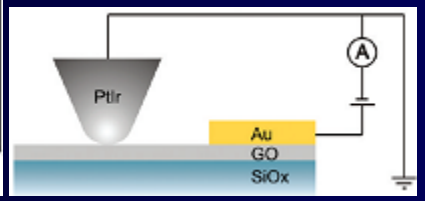
Resistive switching in GO



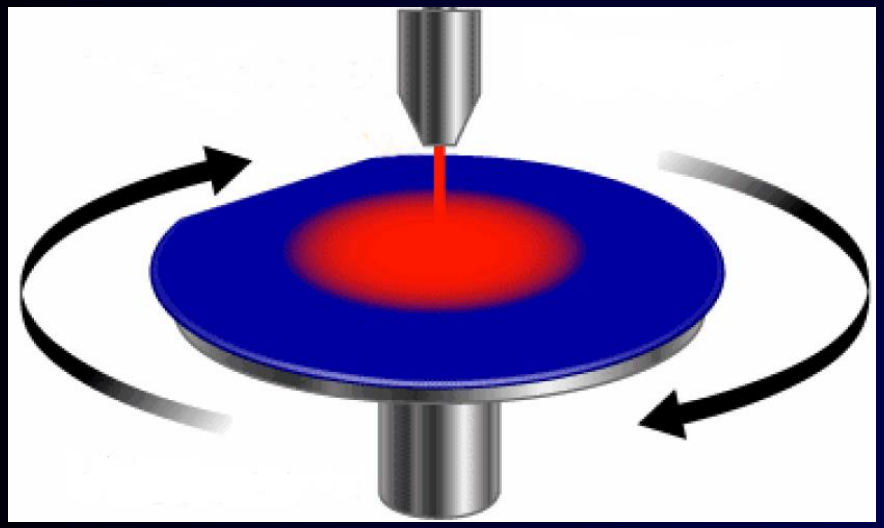
Teoh, et al., APL 98, 173105 (2011)



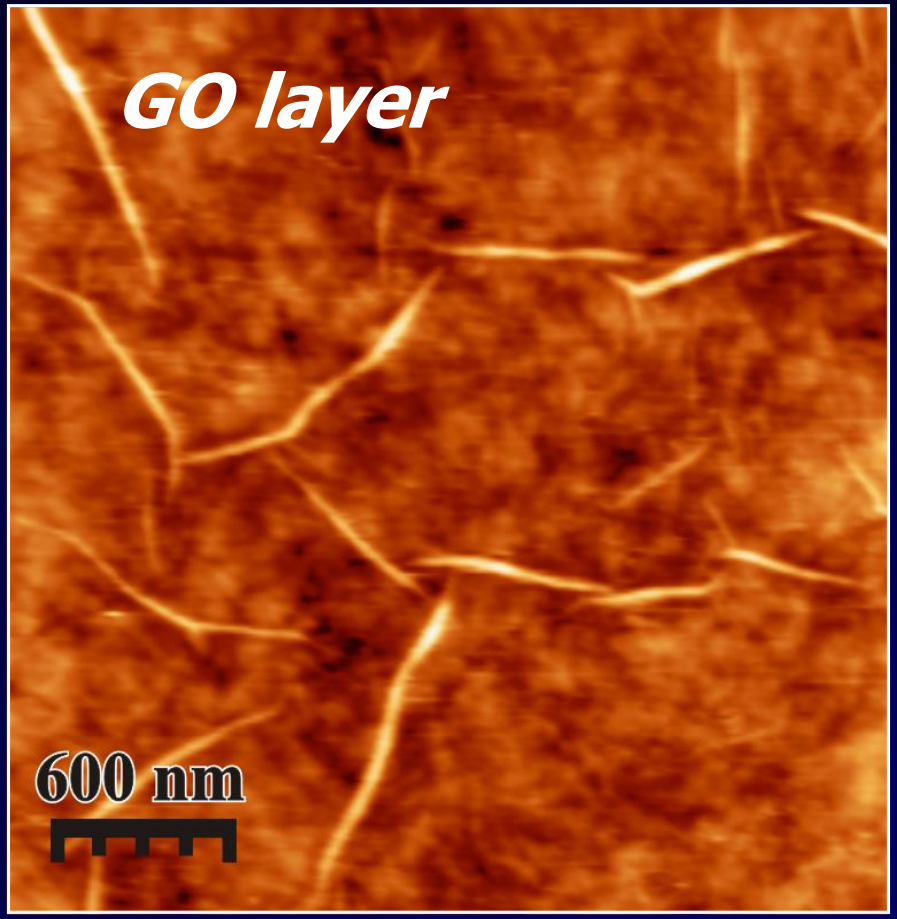
Mativetsky, et al. JACS 132, 14130 (2010)



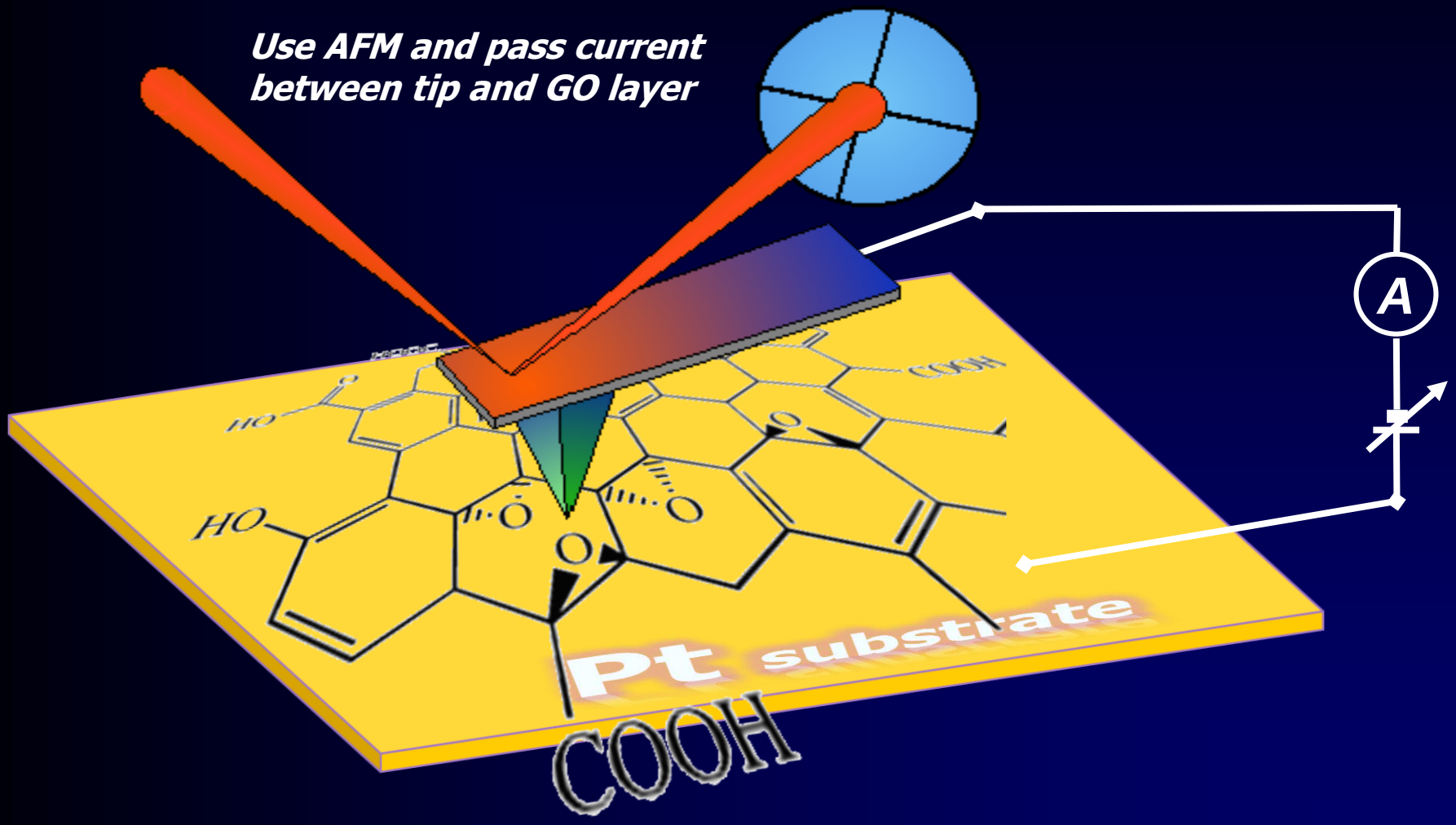
Resistive switching in GO



Thickness of GO film:
20 – 100 nm



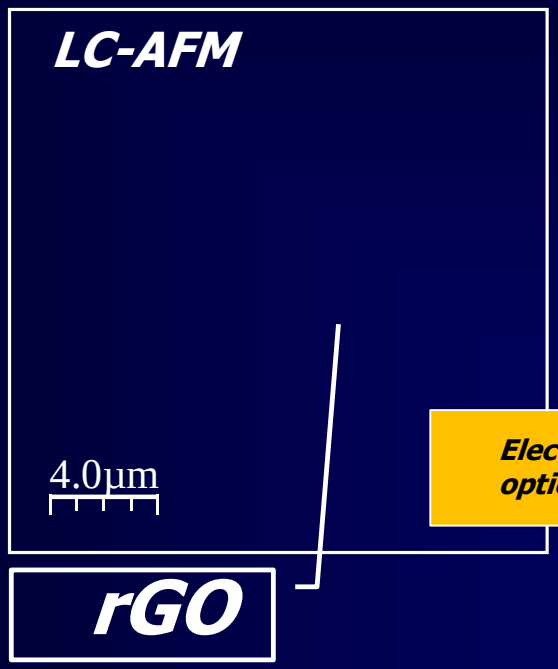
Resistive switching in GO

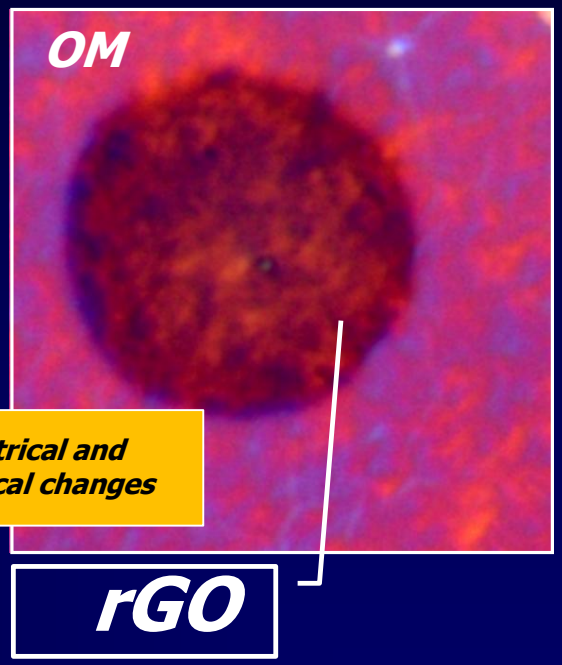


GO reduction -> rGO

ambient

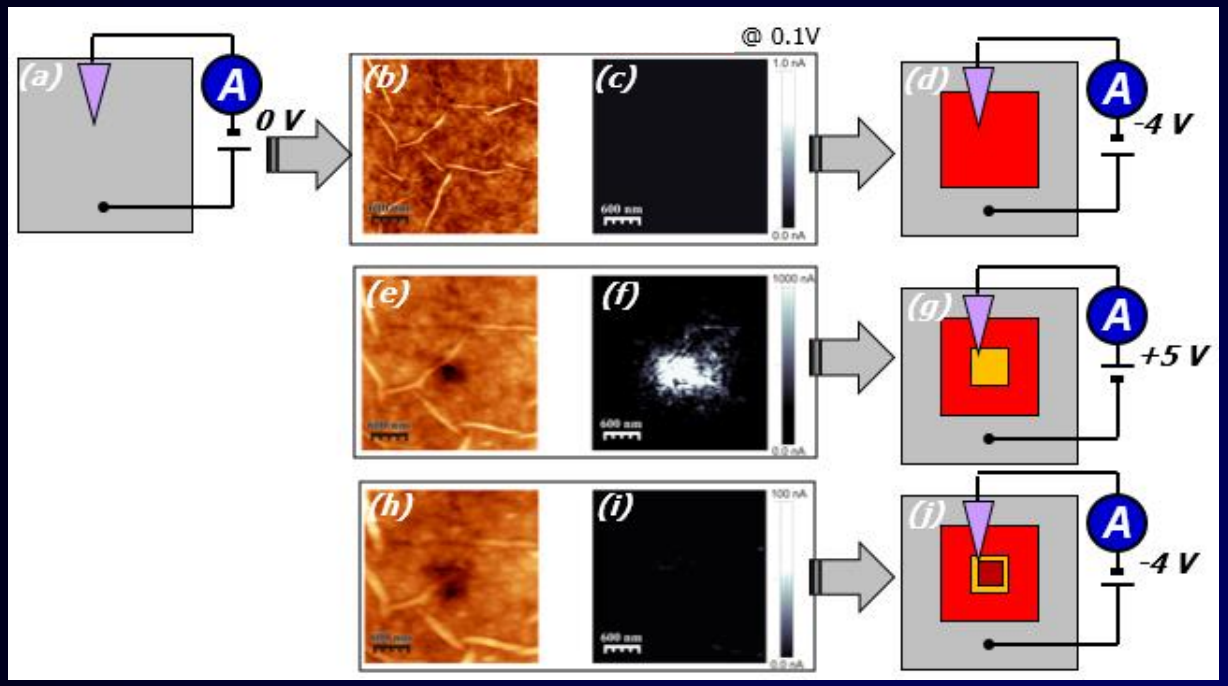
Electric field





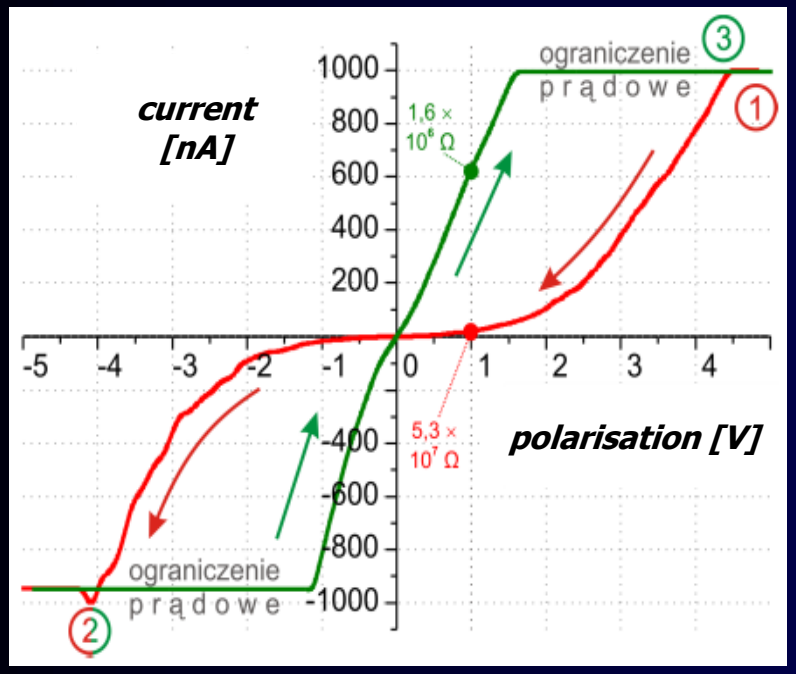
Electrical and optical changes

Resistive switching in GO



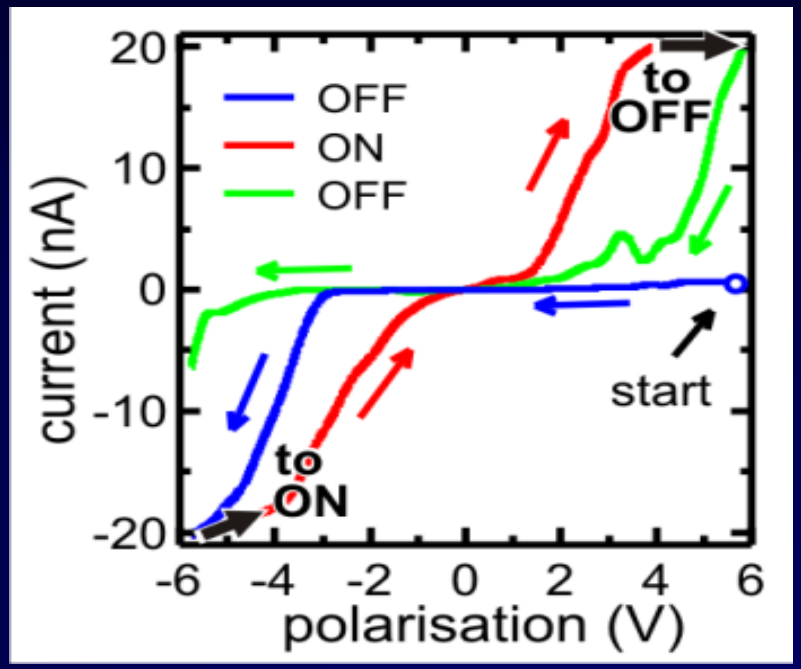
Resistive switching in GO

Resistive switching – TiO_2



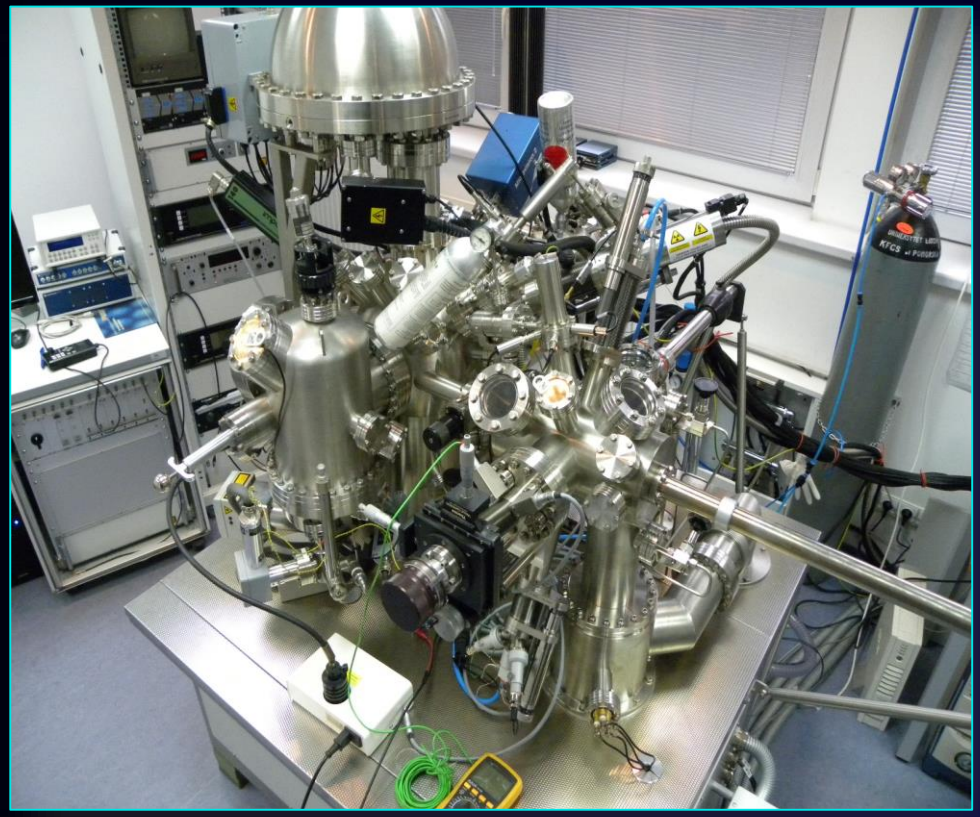
UHV

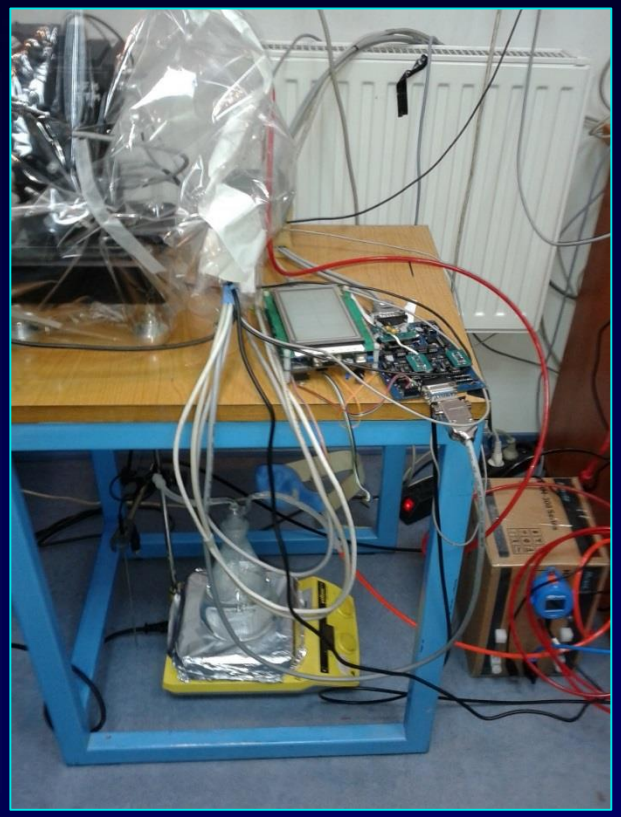
Resistive switching – GO



ambient

Resistive switching in GO

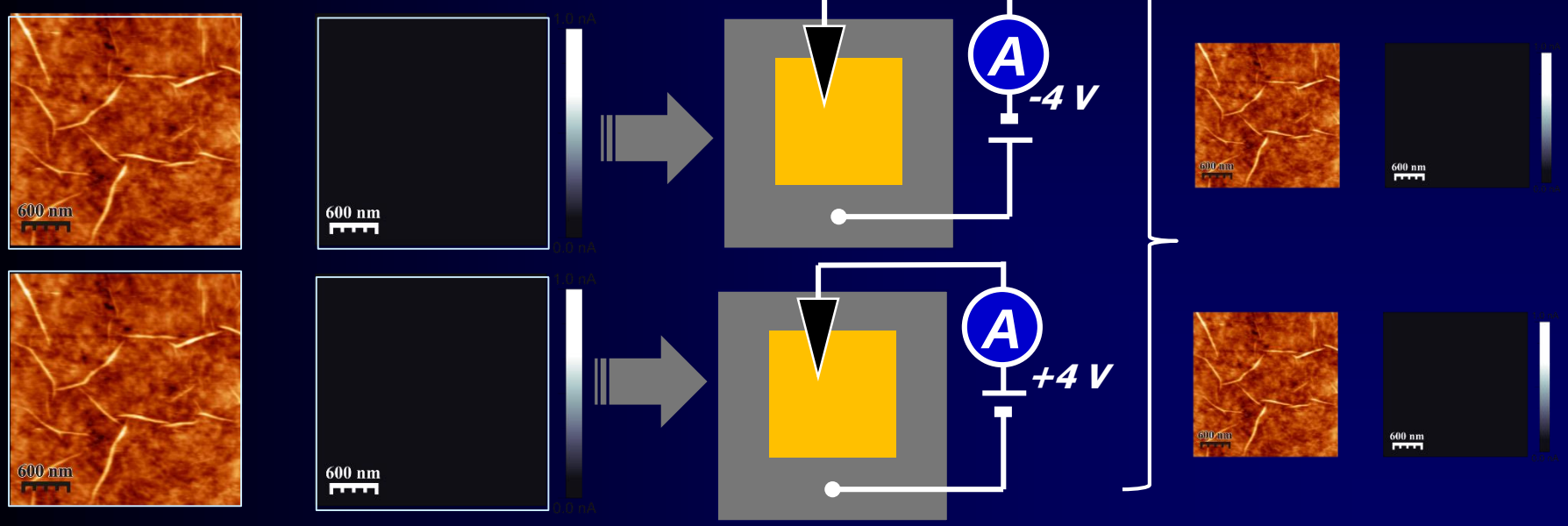




Resistive switching in GO

UHV O_2 N_2 CO_2 Ar

topography conductivity



Resistive switching in GO

UHV O_2 N_2 CO_2 Ar

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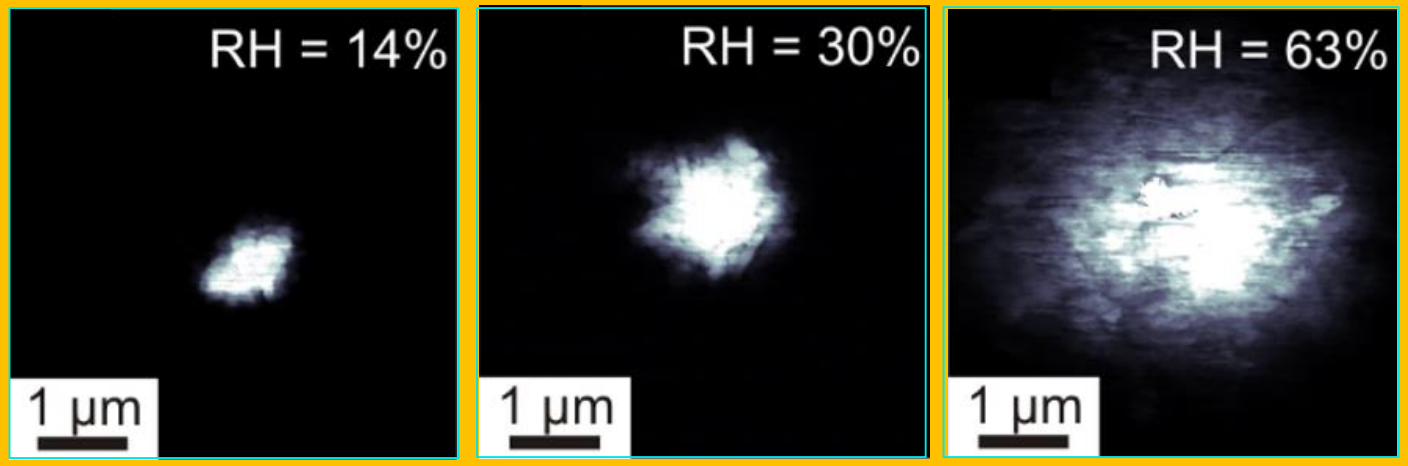
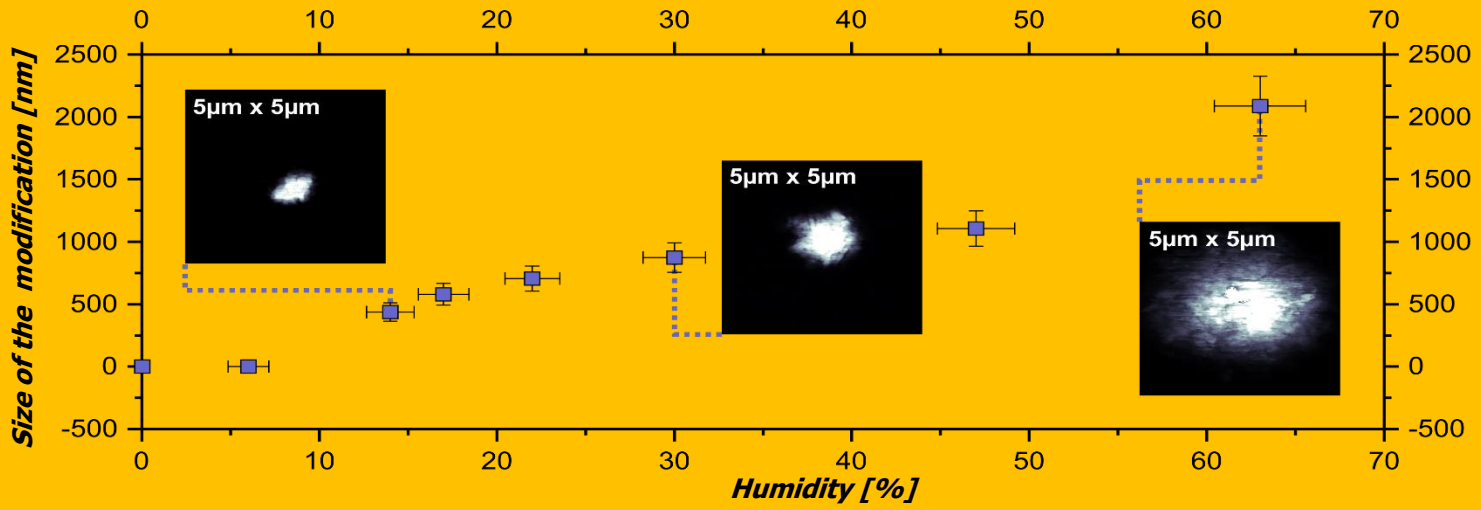
GO reduction -> rGO

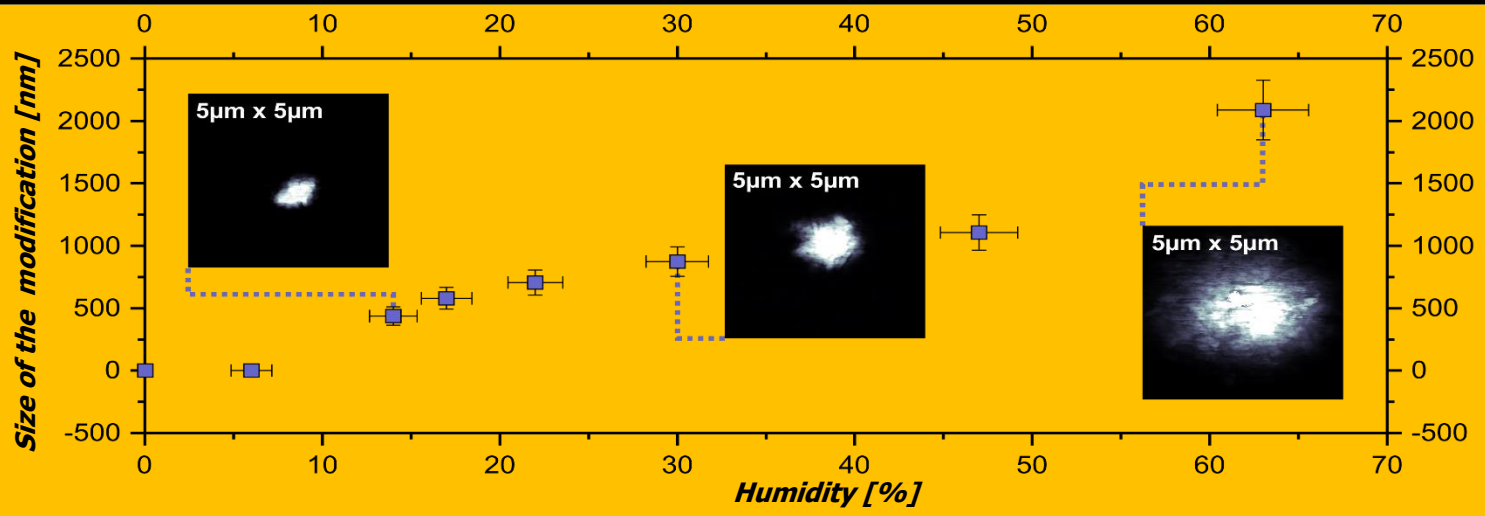


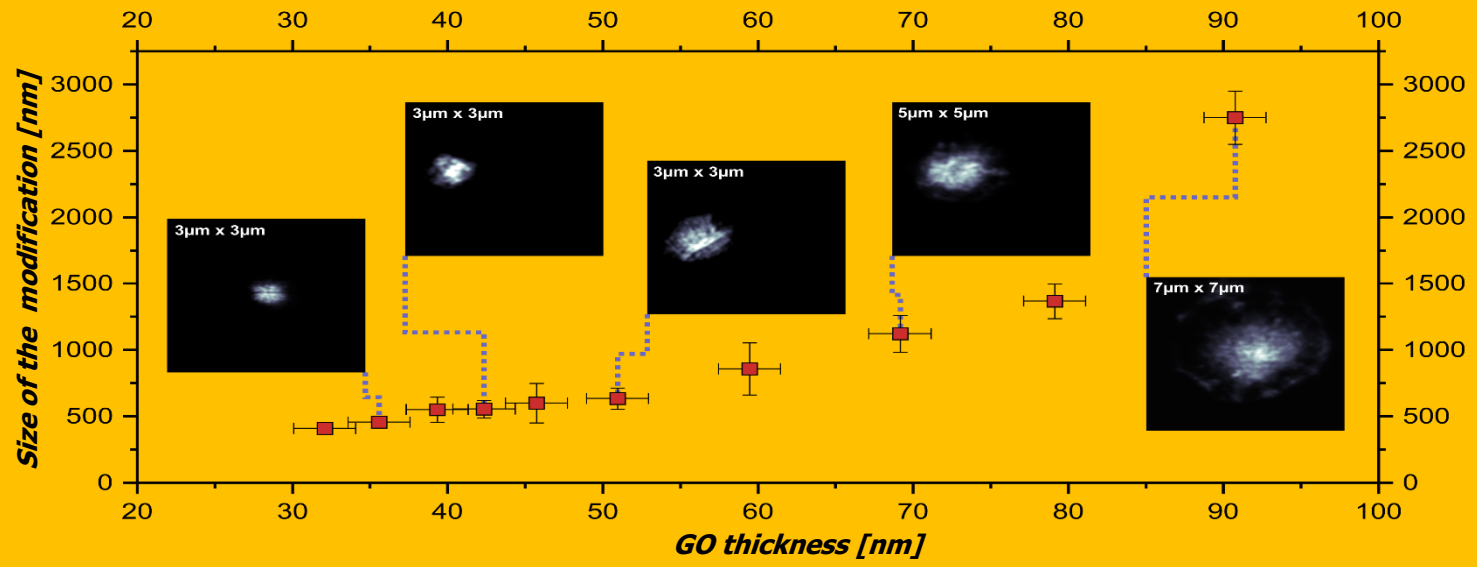
Modification area increase as a function of increasing humidity



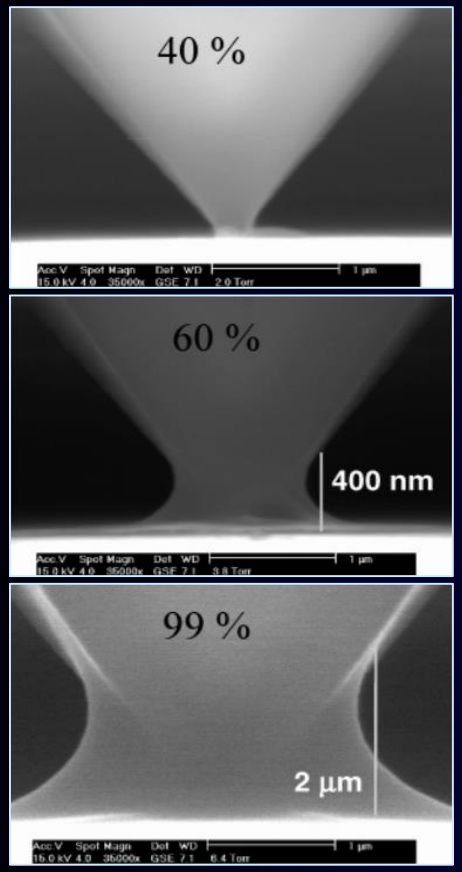
UNIWERSYTET ŁÓDZKI

GO reduction -> rGO





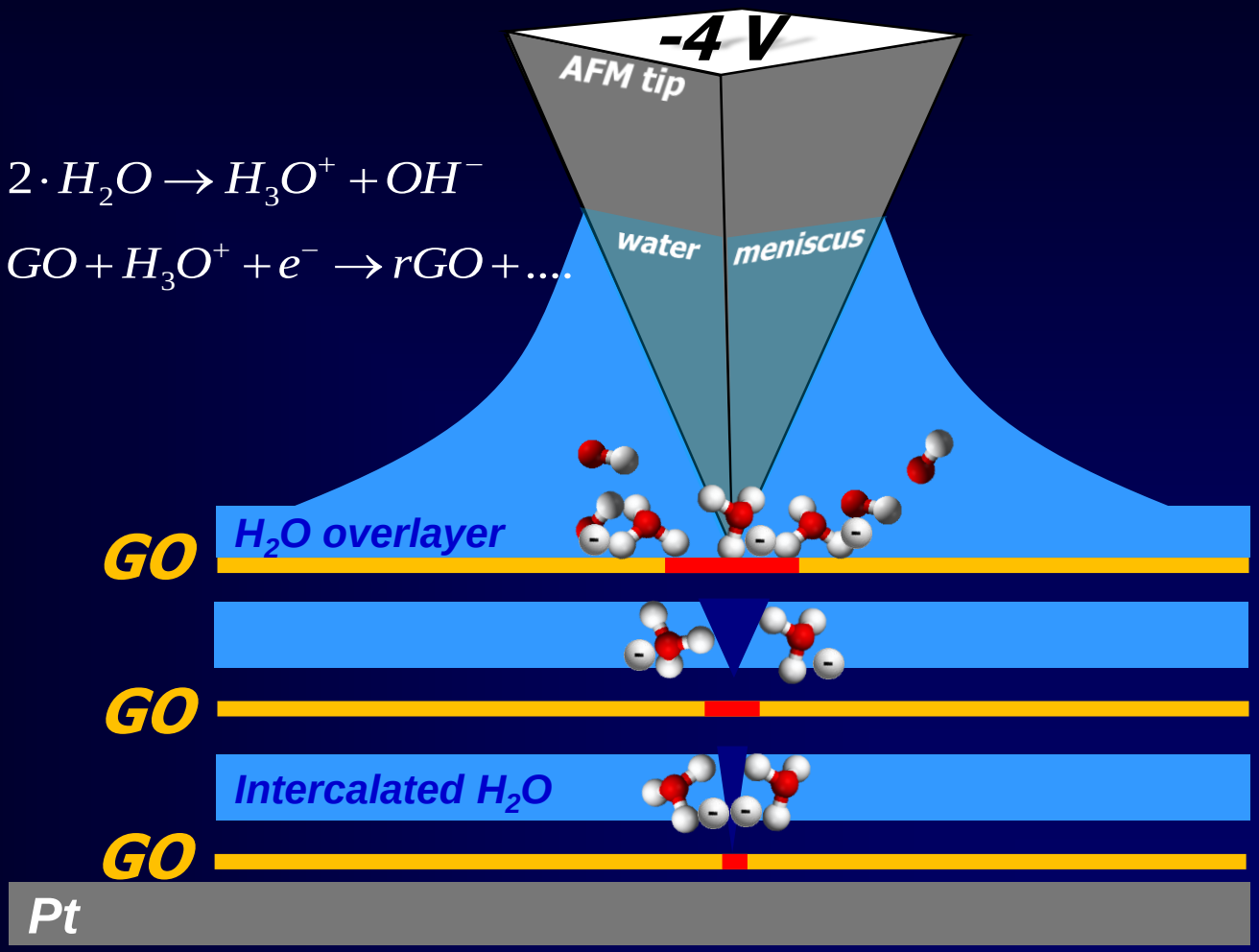
GO reduction -> rGO



Weeks et al.; Langmuir 21 8096 (2005)

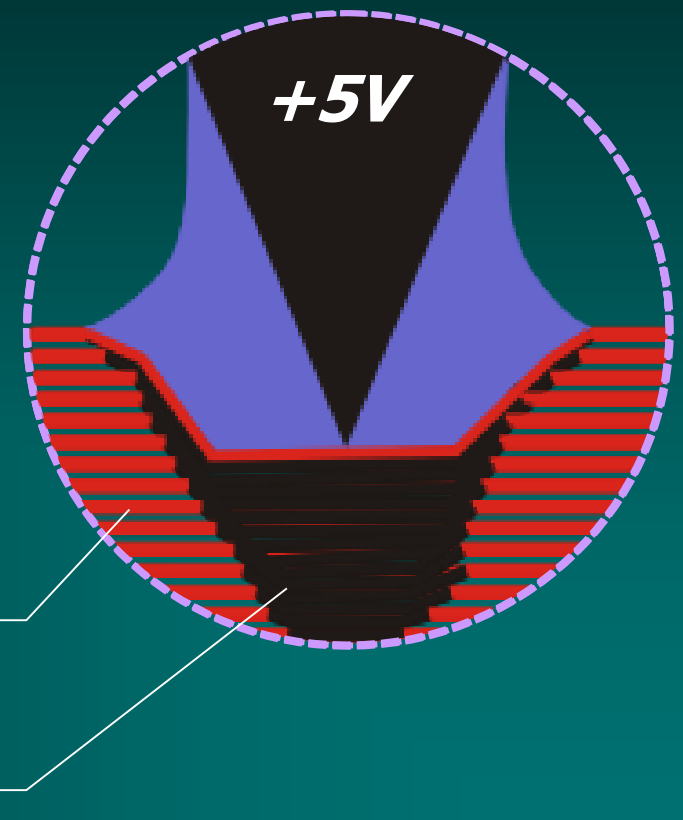
$$2 \cdot H_2O \rightarrow H_3O^+ + OH^-$$

$$GO + H_3O^+ + e^- \rightarrow rGO + \ldots$$



Resistive switching model in GO

- RS – restricted to GO/H_2O interface
- Negatively biased tip starts reduction proces
- e^- are transfered to GO in H_2O
- reduced GO – new electrode
- Possible role of H+ ions
  - $2\,H_2O \rightarrow 4\,H^+ + 4\,e^- + O_2$
  - $GO + a\,H^+ + b\,e^- \rightarrow rGO + c\,H_2O$

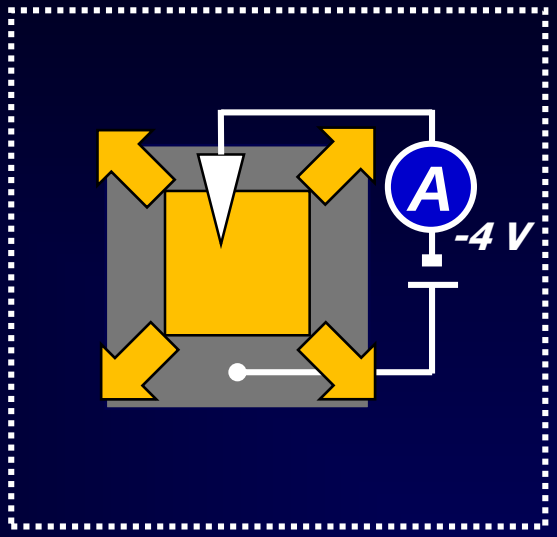


Rogala et al., Appl. Phys. Lett. 106 263104 (2015)

GO reduction -> rGO

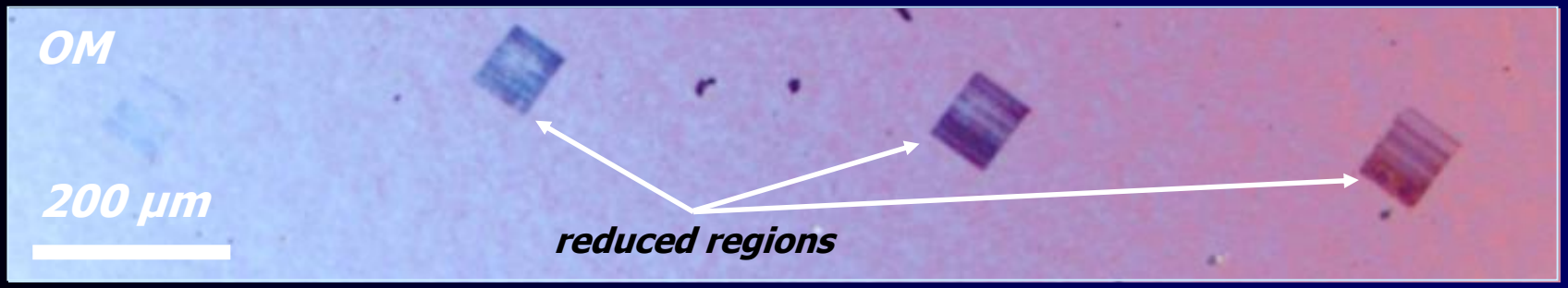
XPS

Sample preparation



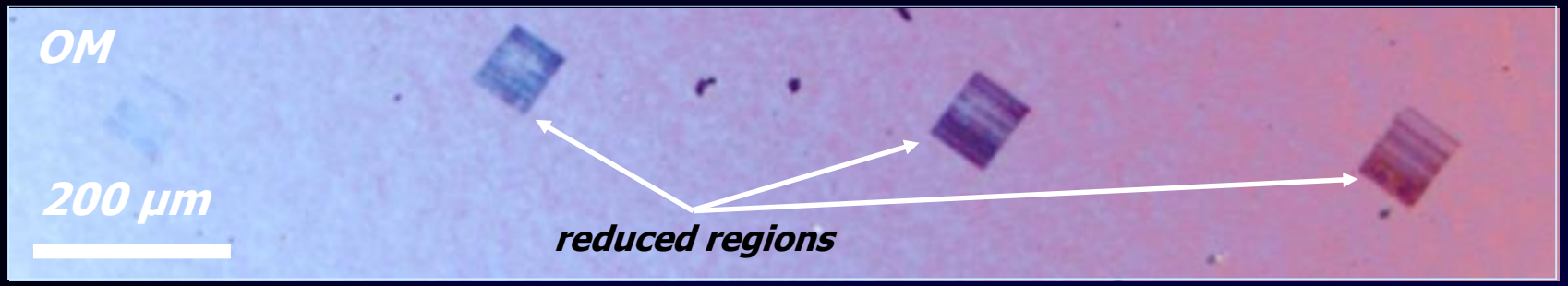
Typical modification size
0.5×0.5 μm²

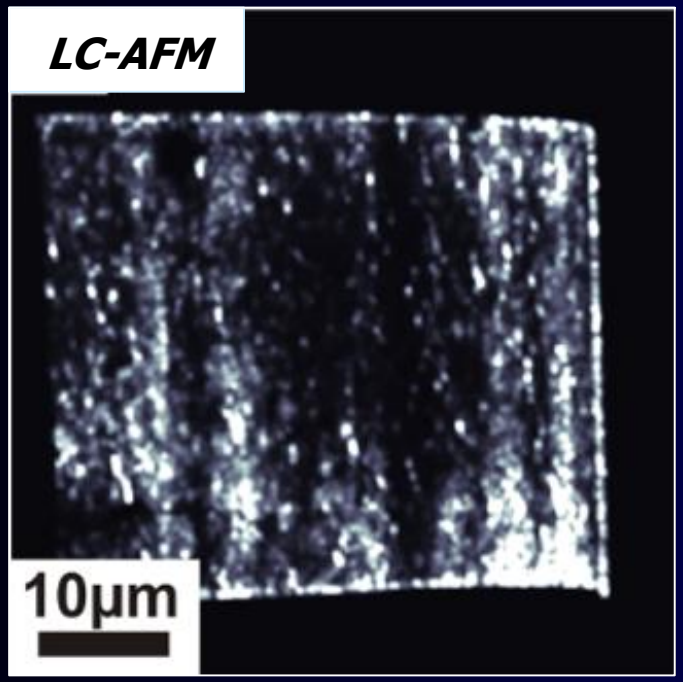
40×40 μm²

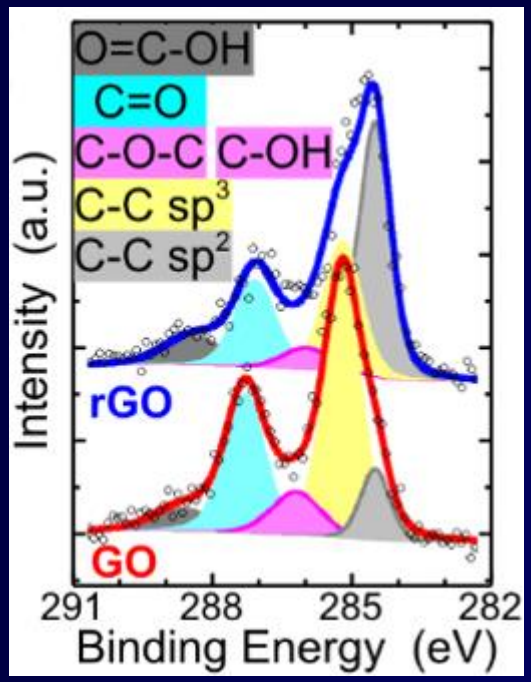


UNIWERSYTET ŁÓDZKI

GO reduction -> rGO







Decrease of carbonyl group

sp^2 larger then sp^3

GO is further reduced

XPS

Resistive switching

RS = TiO_2 + BIAS

RS = GO + BIAS + H_2O

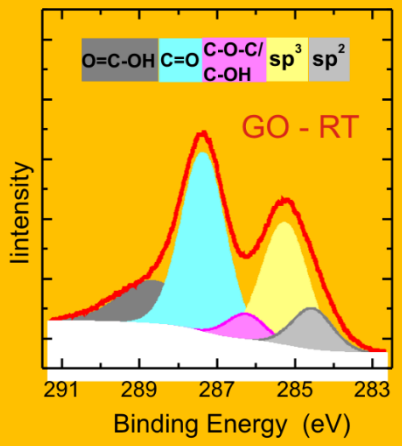
PROBLEMS

- GO is modified during standard experiments
- Literature dose not give coherent description of method of chemical composition measurement in the case of GO

UNIWERSYTET ŁÓDZKI

Influence of measurements on ...

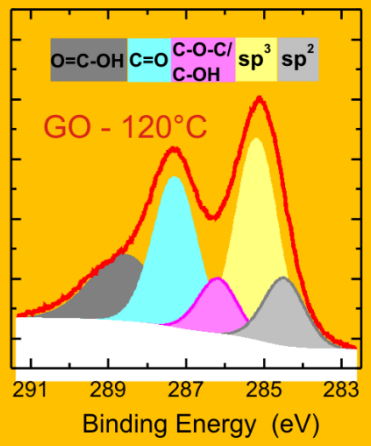
Before preparation

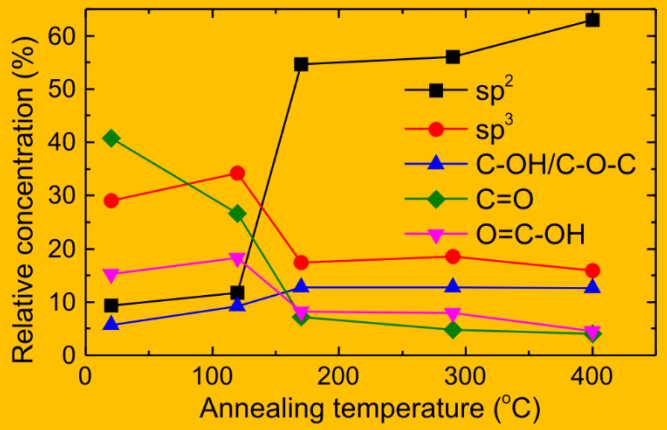


120°C

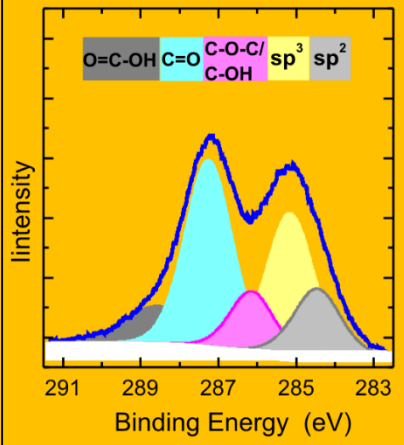
30 min

After heating





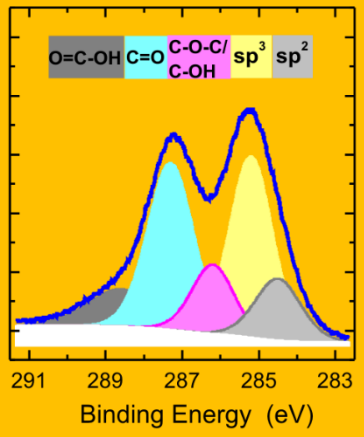
Before irradiation

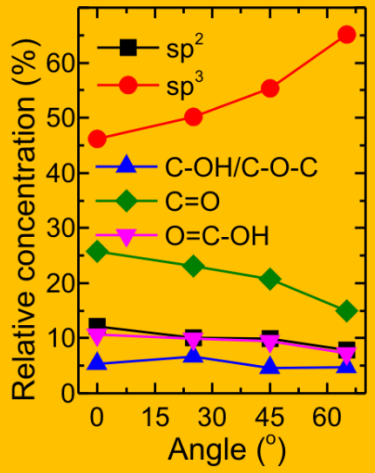


X- ray

370 min

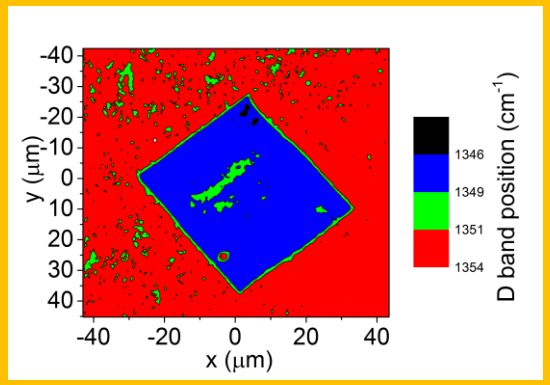
After irradiation

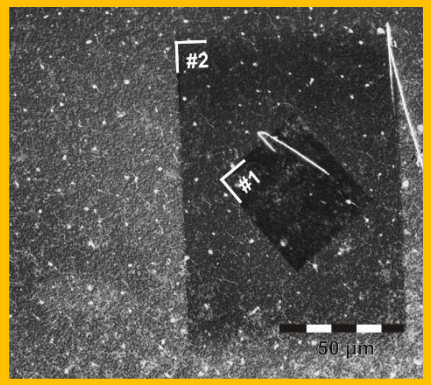


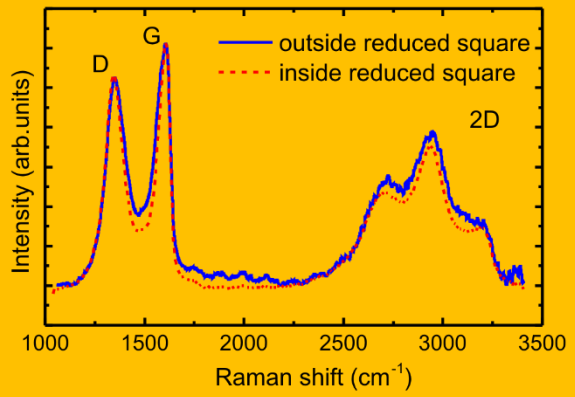


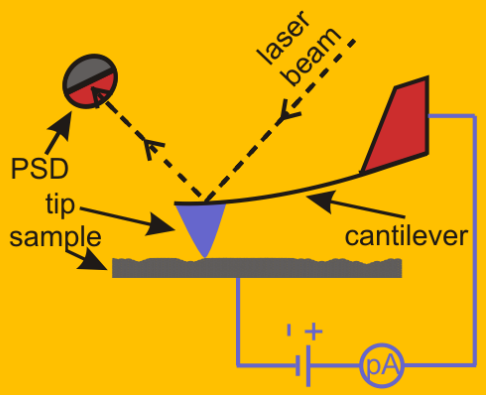
UNIWERSYTET ŁÓDZKI

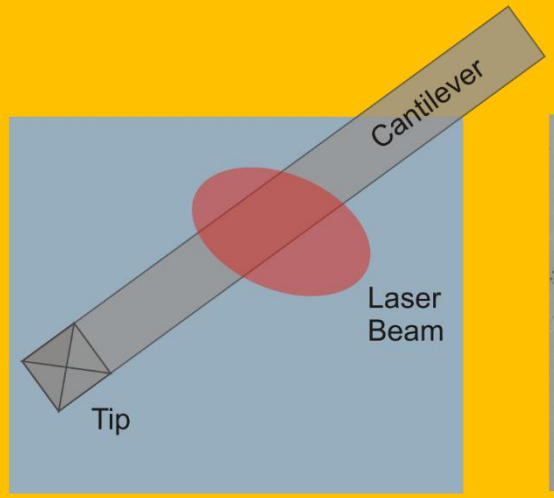
Influence of measurements on ...

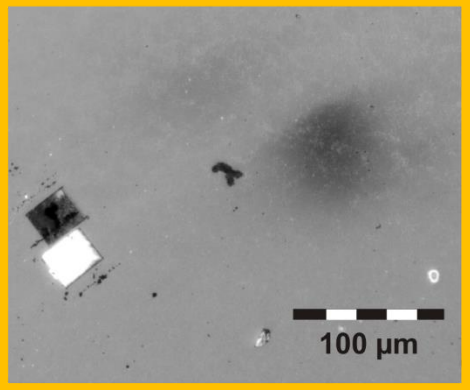




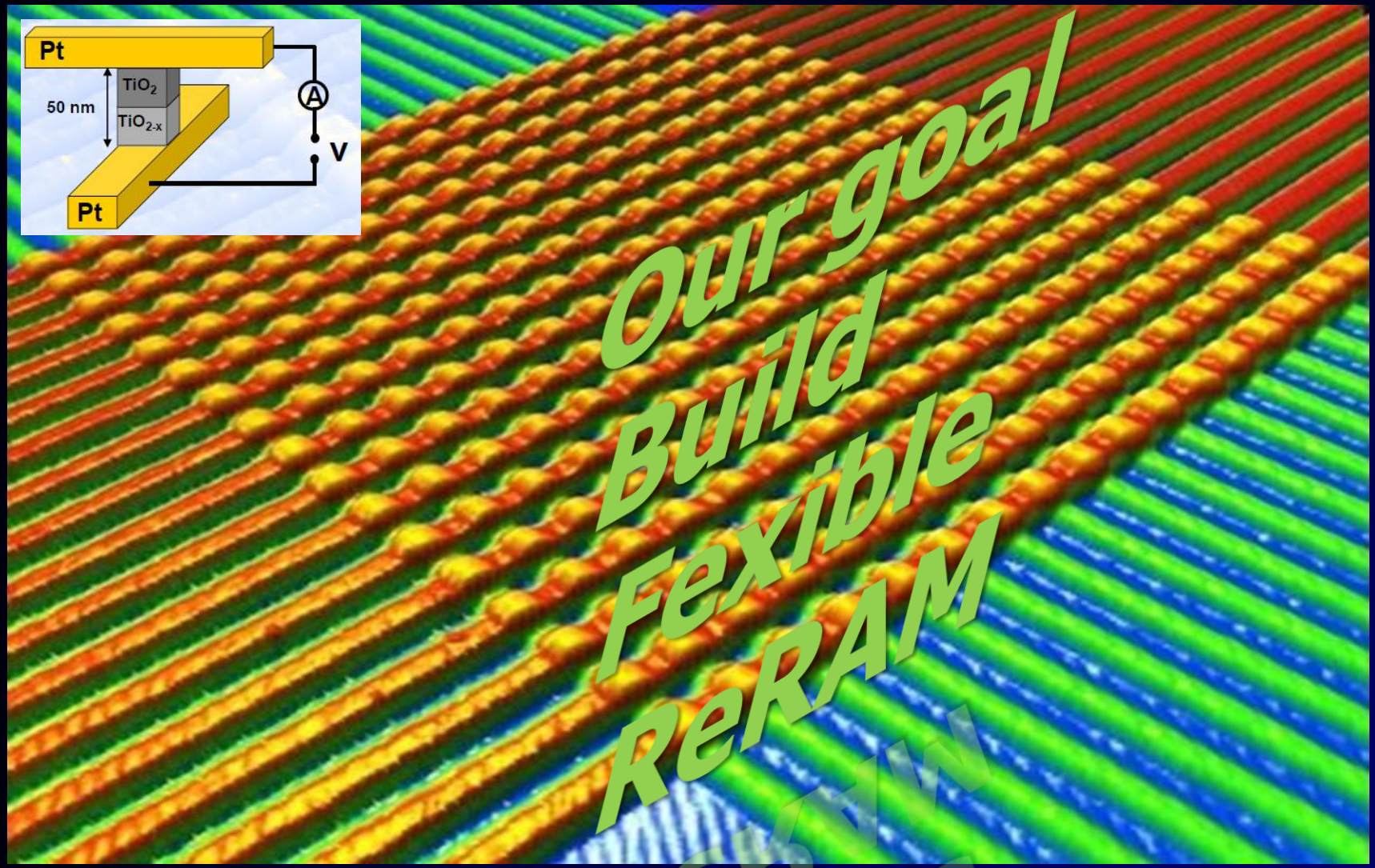








Resistive switching in TiO_2



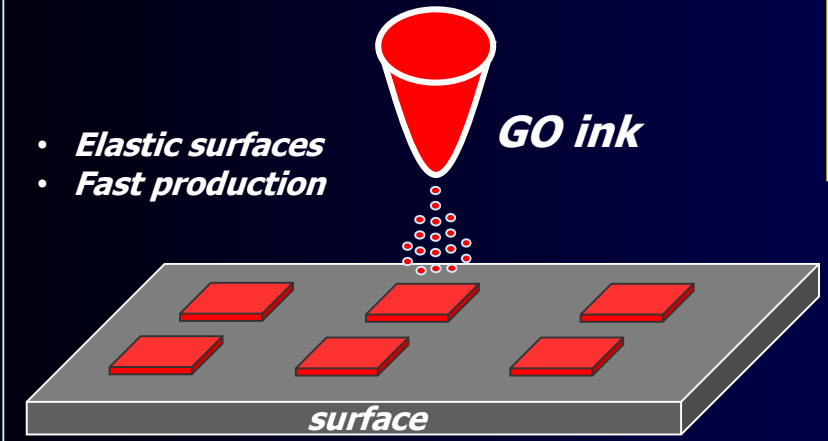
Ink-Jet printing

photolitography

- Very expensive equipment
- Highly complicated production – HV, UHV

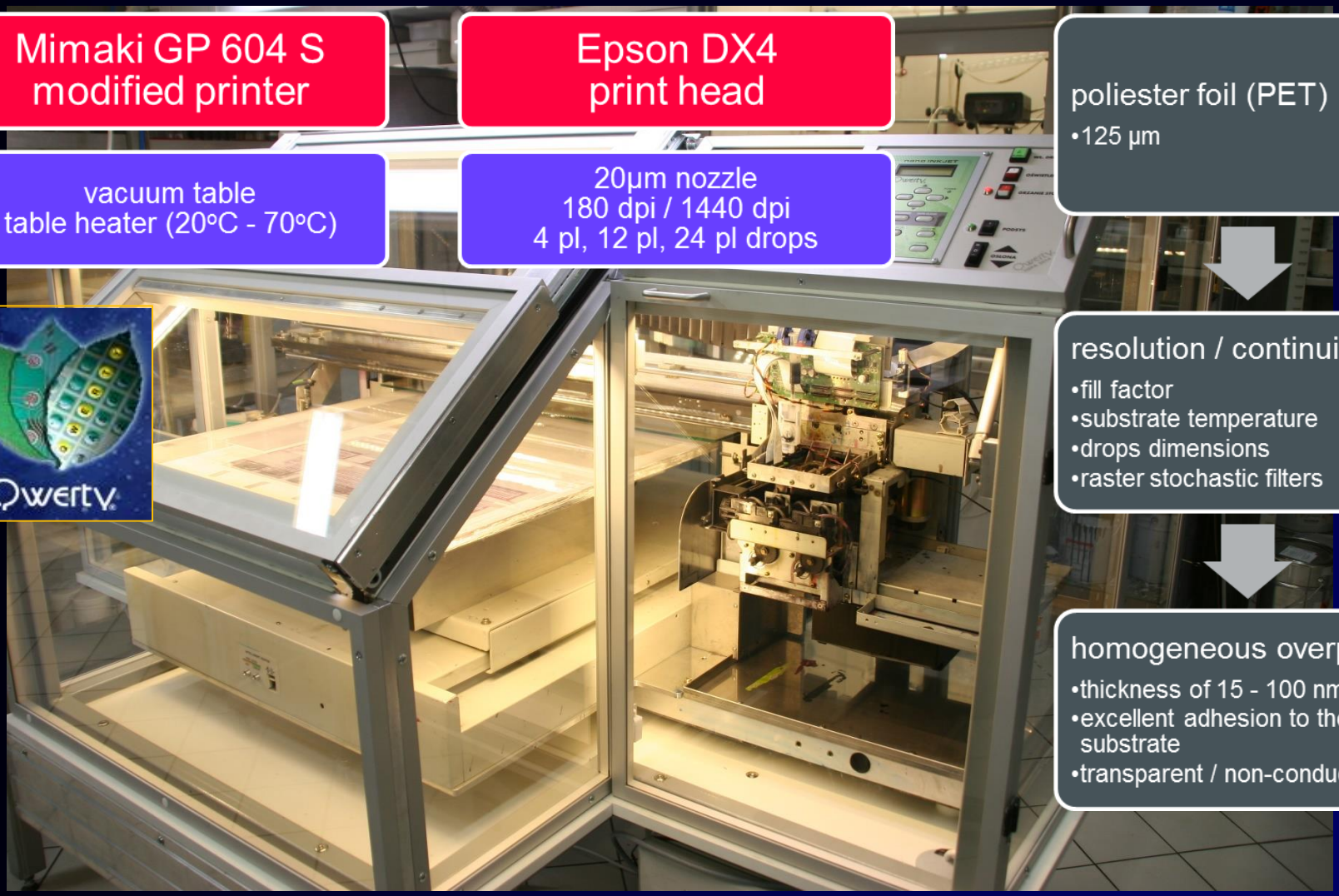
Ink-Jet

- Elastic surfaces
- Fast production



UNIWERSYTET ŁÓDZKI

Mimaki GP modyfied printer



Mimaki GP 604 S
modified printer

Epson DX4
print head

vacuum table
table heater (20°C - 70°C)

20µm nozzle
180 dpi / 1440 dpi
4 pl, 12 pl, 24 pl drops

Qwerty

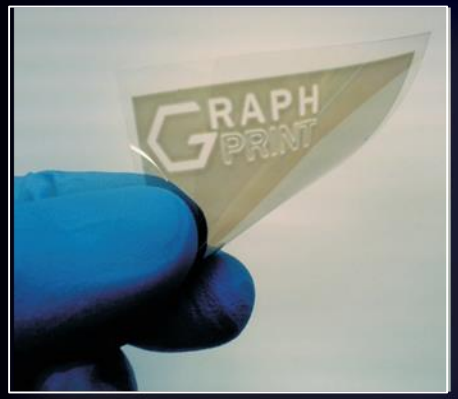
poliester foil (PET)
- 125 µm

resolution / continuity
- fill factor
- substrate temperature
- drops dimensions
- raster stochastic filters

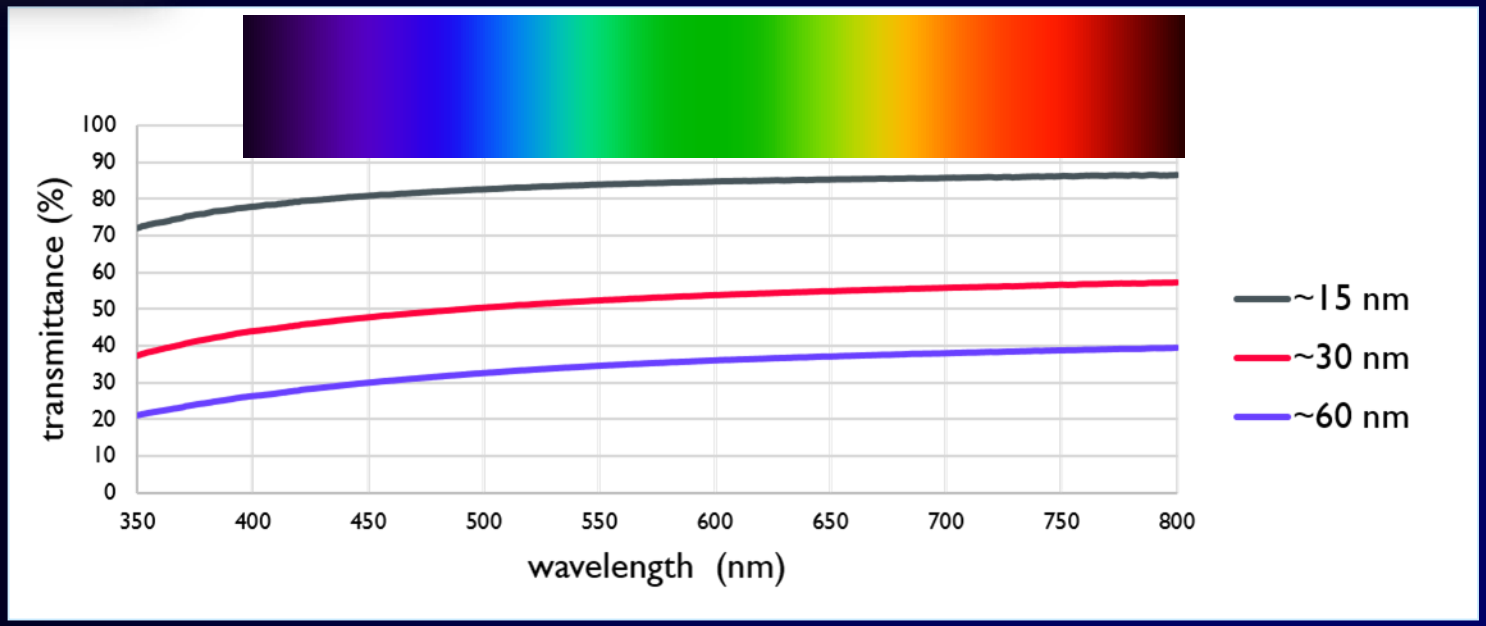
homogeneous overprints
- thickness of 15 - 100 nm
- excellent adhesion to the substrate
- transparent / non-conductive

UNIWERSYTET ŁÓDZKI

Ink-Jet printing

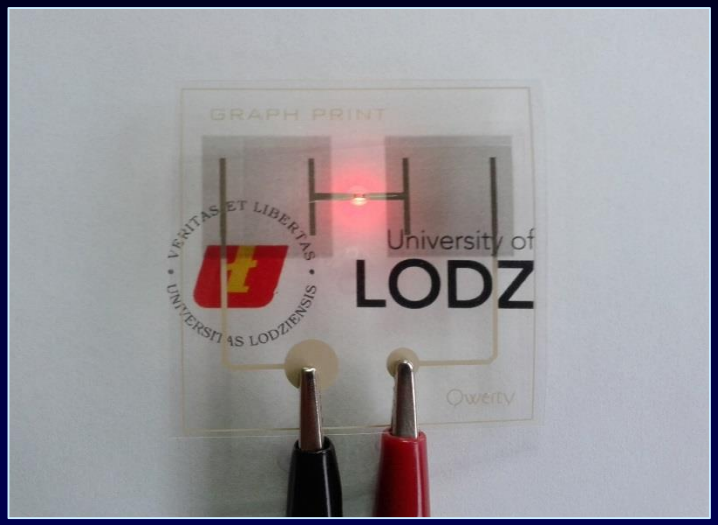


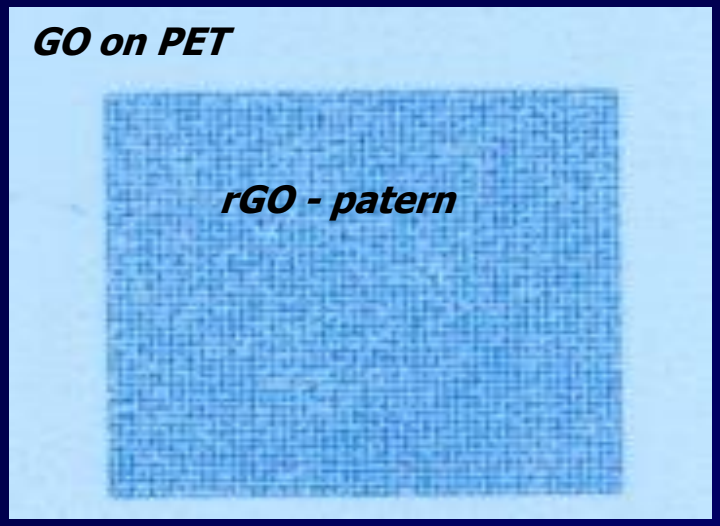
thikness	Transmitance @ 550 nm	Resistance per square
10 – 15 nm	84 %	150 kΩ/sq
30 – 35 nm	52 %	10 kΩ/sq
55 – 65 nm	34 %	4 kΩ/sq



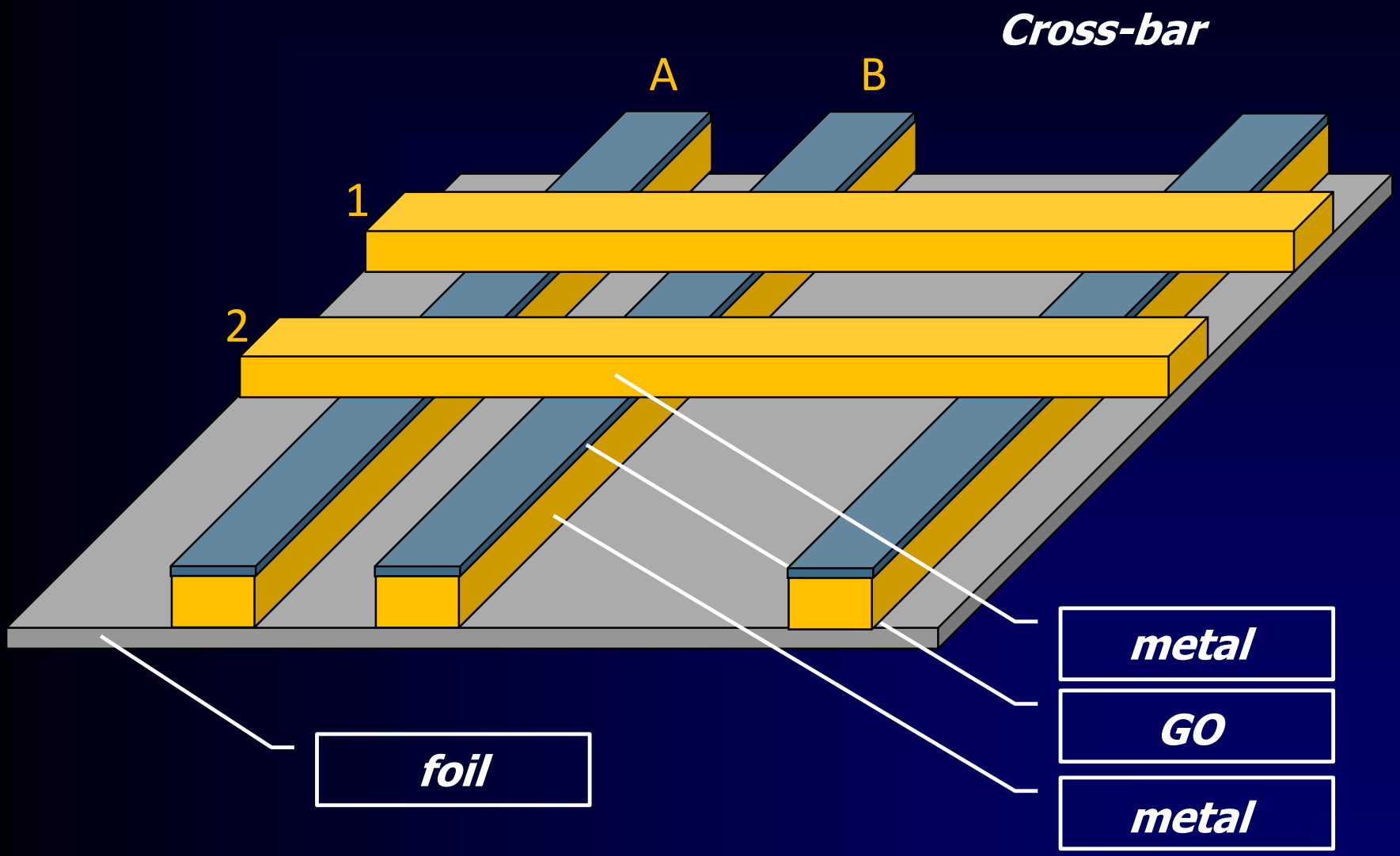
UNIWERSYTET ŁÓDZKI

Ink-Jet printing





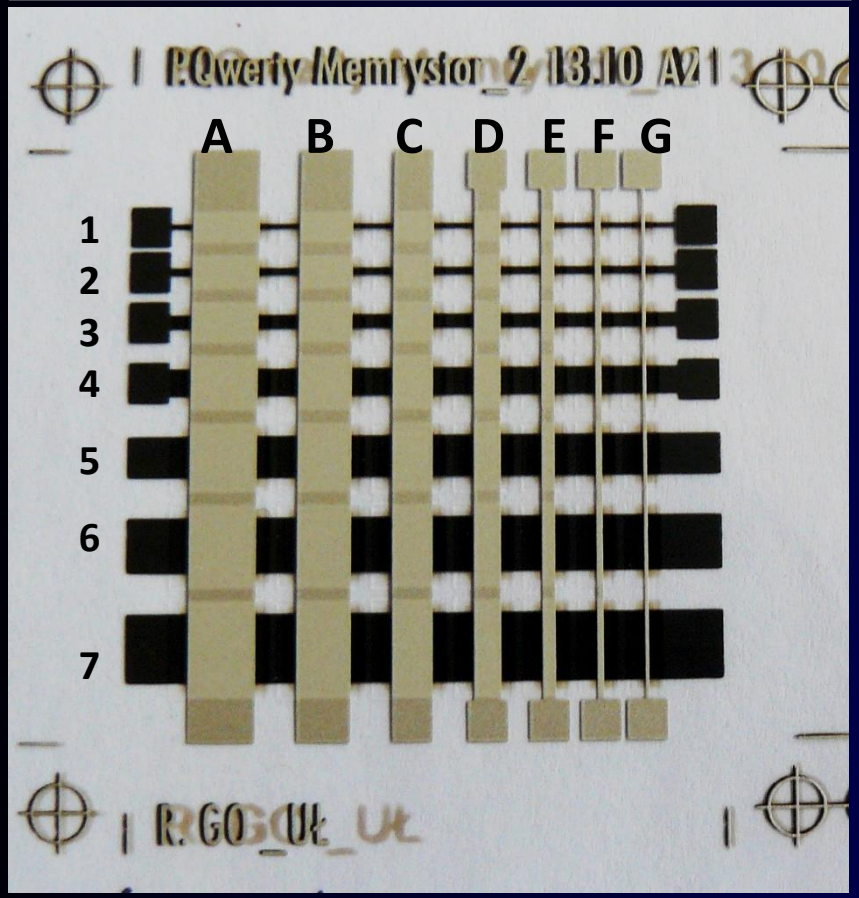
Flexible resistive switching devices



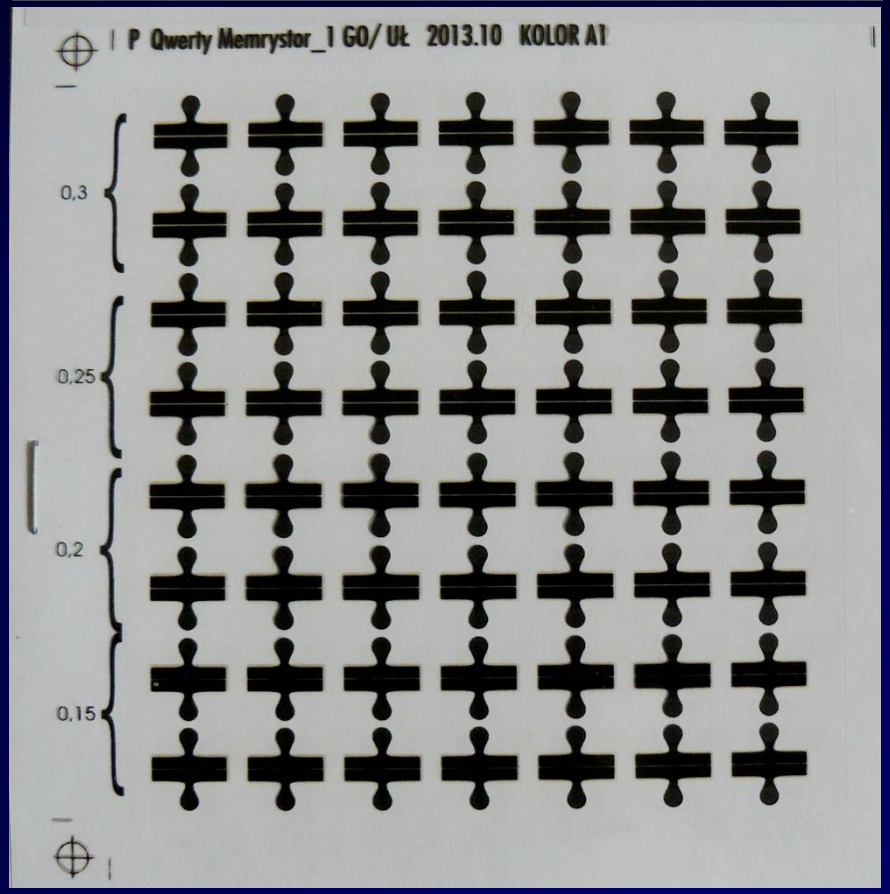
UNIWERSYTET ŁÓDZKI

Flexible resistive switching devices

Cross-bar structure



Capacitor structure



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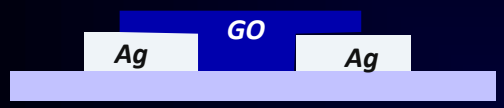
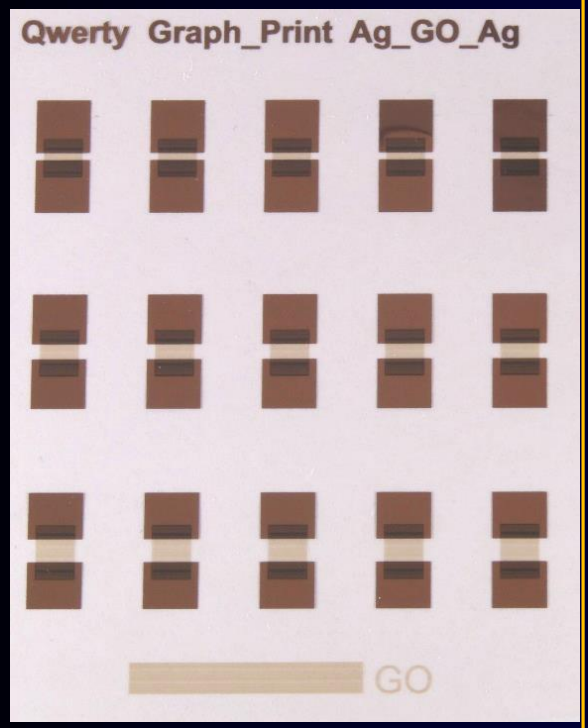
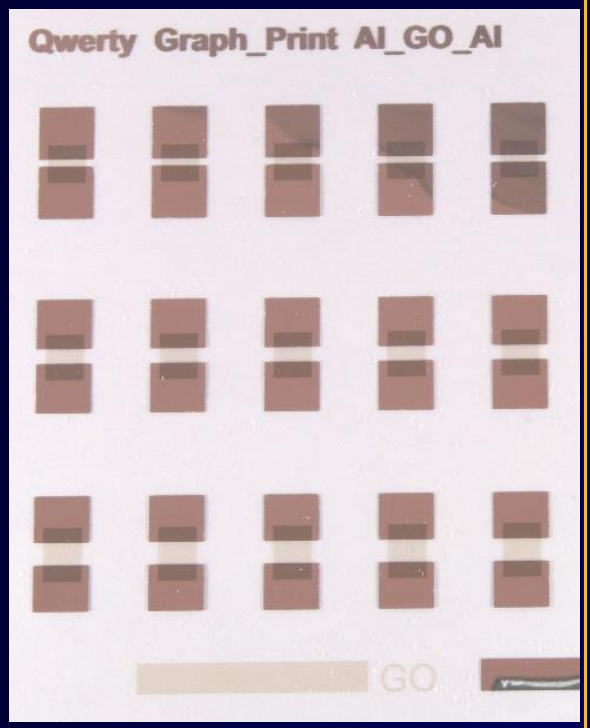
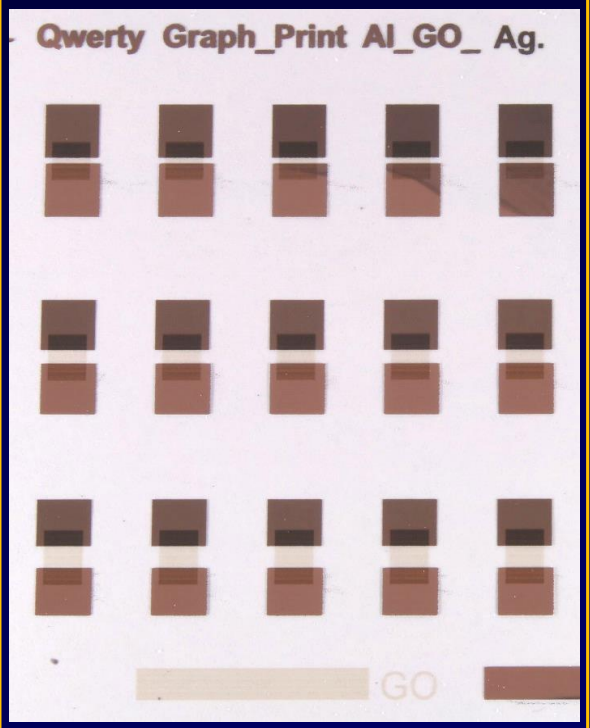
Flexible resistive switching devices

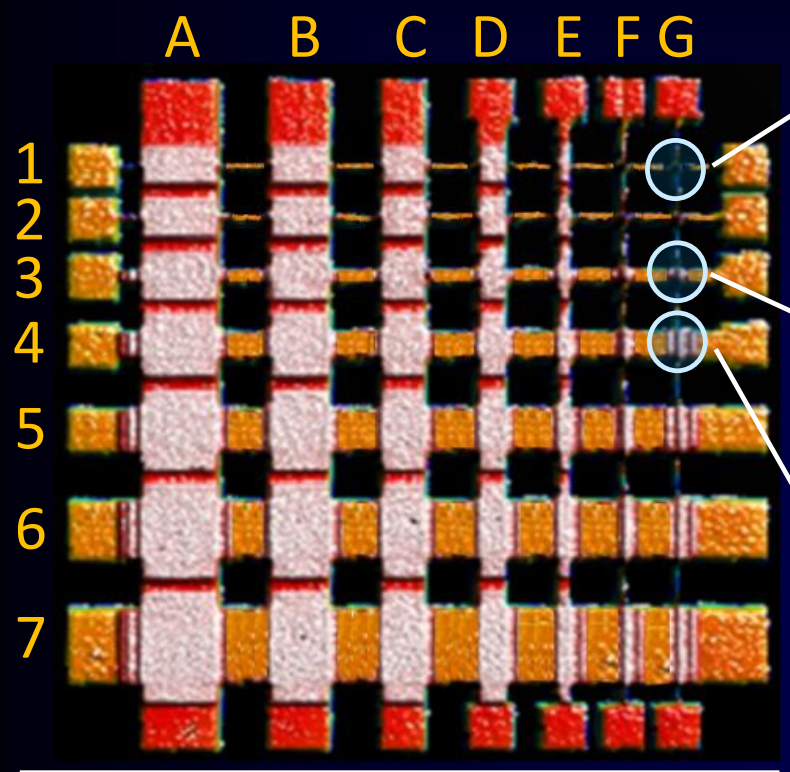




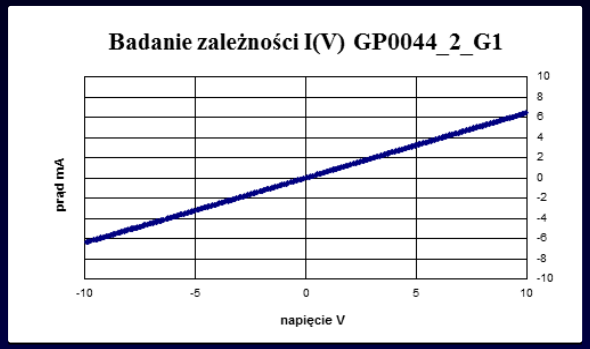


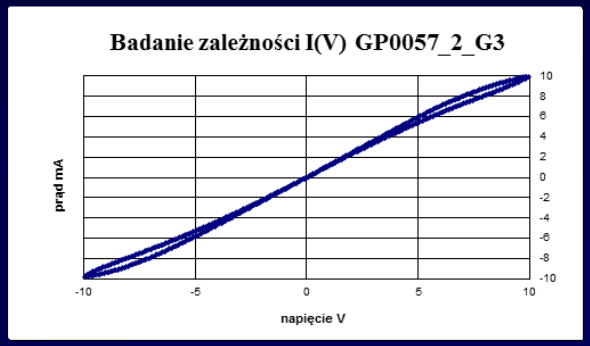


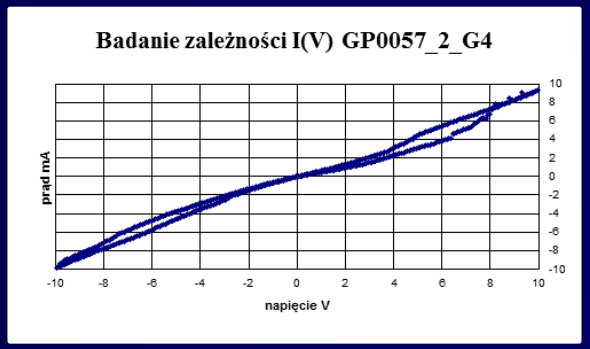
Flexible resistive switching devices



Cross-bar structure







Conclusions

Understanding of basic properties of resistive switching in titanium dioxide and graphene oxide

towards application

UNIWERSYTET ŁÓDZKI

Projects

GRAPH MET-IN

GRAPH HYBRID

ML InkJet

GRAPH PRINT

GRAPH RESIST

GRAPH INTERA

Financial support

National Center for Scientific Research

National Center for Research and Development