Advanced Scanning Probe Lithographies

i). Scanning Probe Lithography/ies

Force Microscope
Context
NanoLithographies

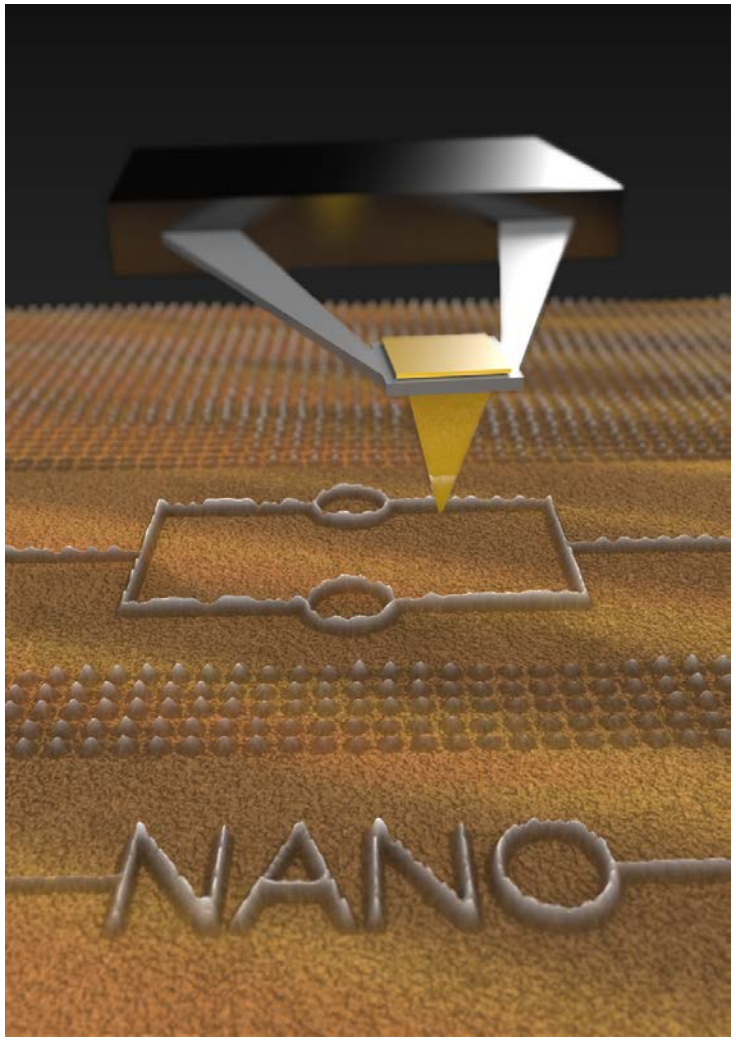
a. oxidation SPL

Principles
Molecular Architectures
nanoscale FET transistors

b. thermal and thermochemical SPL

3D Patterning
Graphene transistors

iv). Summary



30 years after the invention of force microscopy

VOLUME

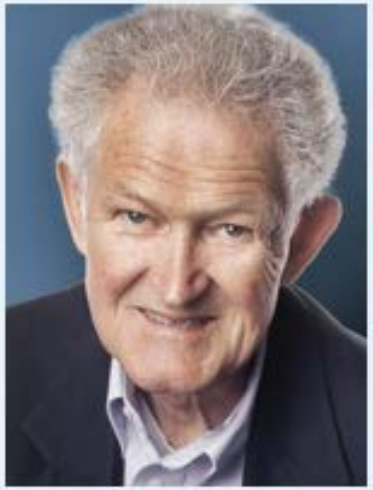
THE KAVLI PRIZE
2016 Laureates

2016 KAVLI PRIZE NANOSCIENCE

Recognized "for the invention and realization of atomic force microscopy, a breakthrough in measurement technology and nanosculpting that continues to have a transformative impact on nanoscience and technology."

Gerd Binnig
Former member of IBM Zurich Research Laboratory, Switzerland

Christoph Gerber
University of Basel, Switzerland

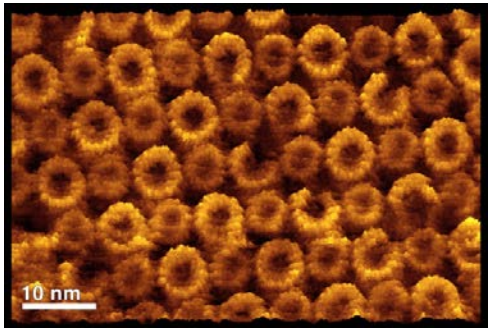


Calvin Quate
Stanford University, USA

Top

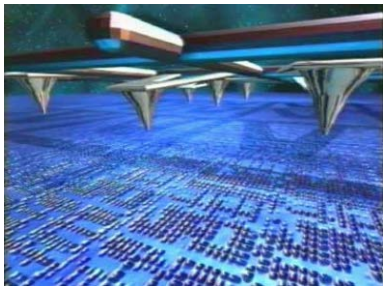
1. I
2. S
3. C
4. S
5. N

Wood, J. The top ten advances in materials science. *Mater. Today* **11**, 40 (2008).
Ball, P. Material witness: Greatest hits. *Nature Mater.* **7**, 102 (2008).

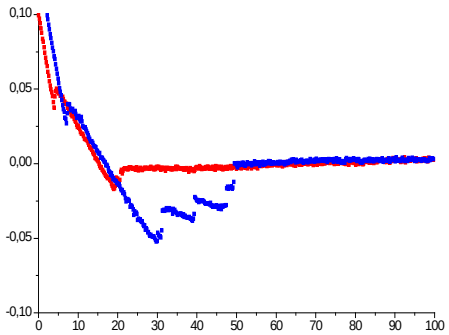


Molecular motors, H Seelertet, A. Engel, D.J. Muller (2000)

Polymers, R. Magerle (2004)

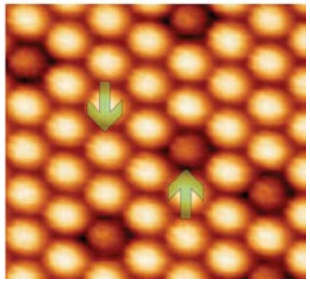


Nanopatterning, G. Binnig (1999)

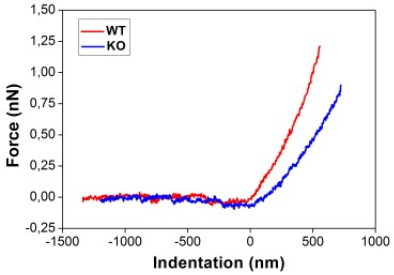


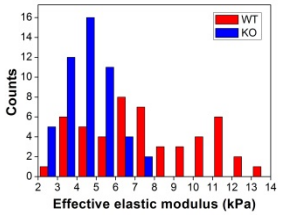
Force spectroscopy

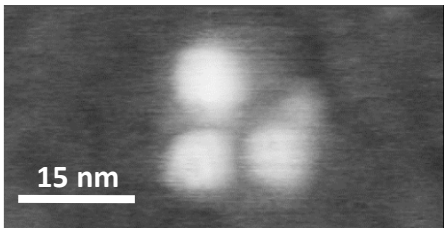
Cells, R. Acvi (2007)



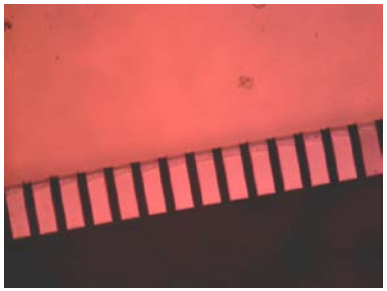
Atom identification, O. Custance, S. Morita et al. (2007)



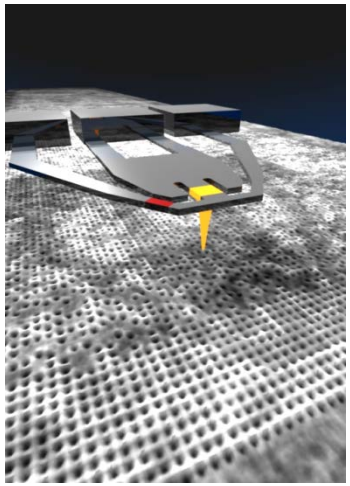




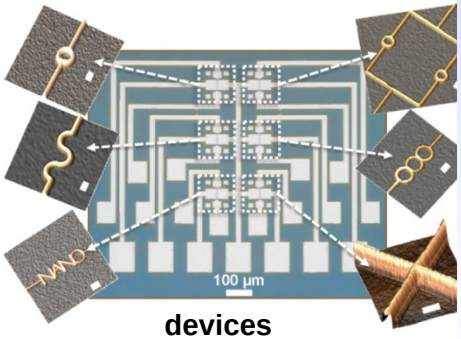
Antibodies, A.S. Paulo, R. Garcia (2000)



Nanomechanical sensors J. Tamayo (2007)



Probe lithography



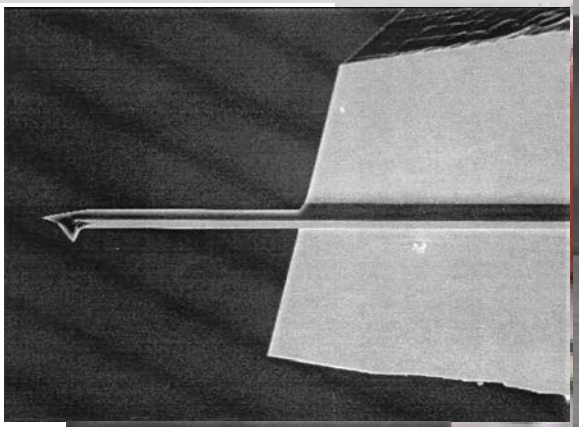
devices

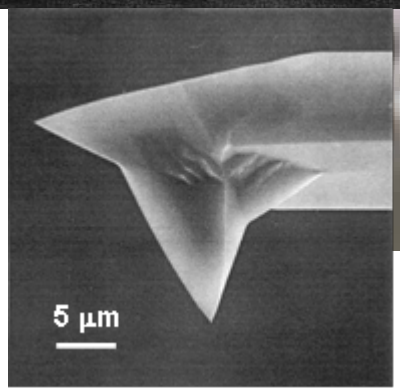
Atomic Force Microscope:

Use mechanical forces to build a atomic resolution microscope

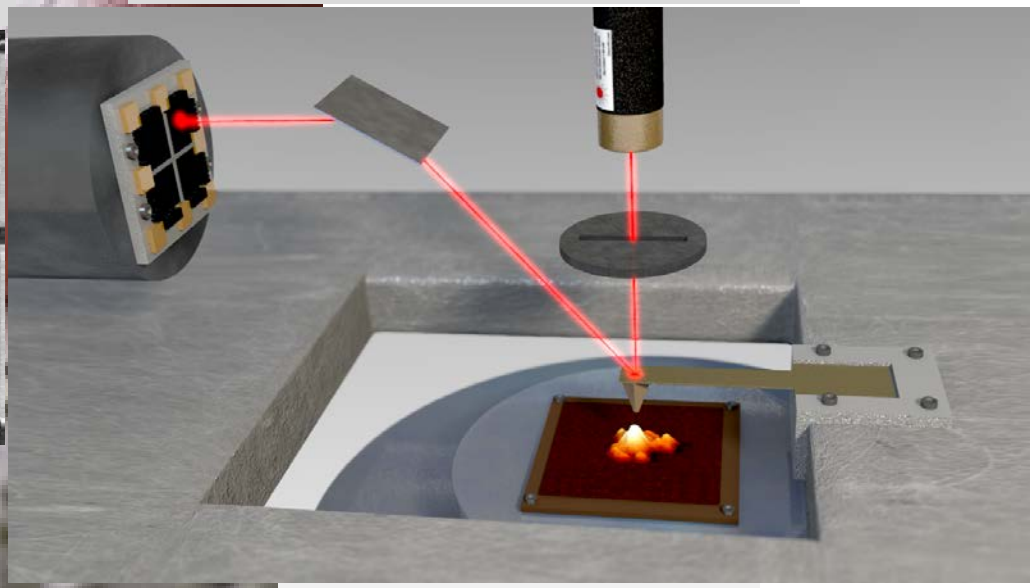
G. Bining, C. Quate, C. Gerber (1986)

Integrated microcantilevers
T.R. Albrecht, C. Quate (1990)
J. Greshner (1991)





Optical beam deflection
G. Meyer, N.M. Amer (1989)

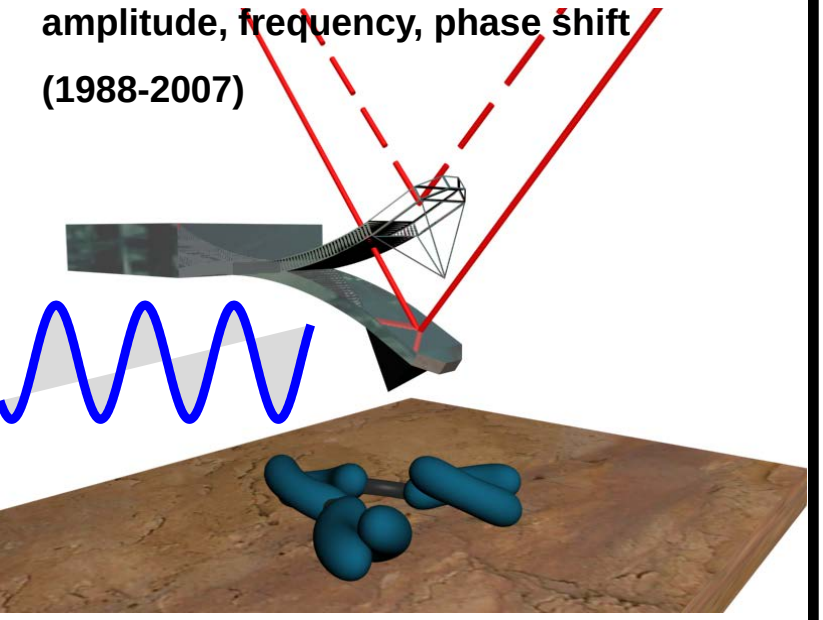


$$z(L) = \frac{2L}{3}\frac{dz(L)}{dx}$$

Dynamic AFM:

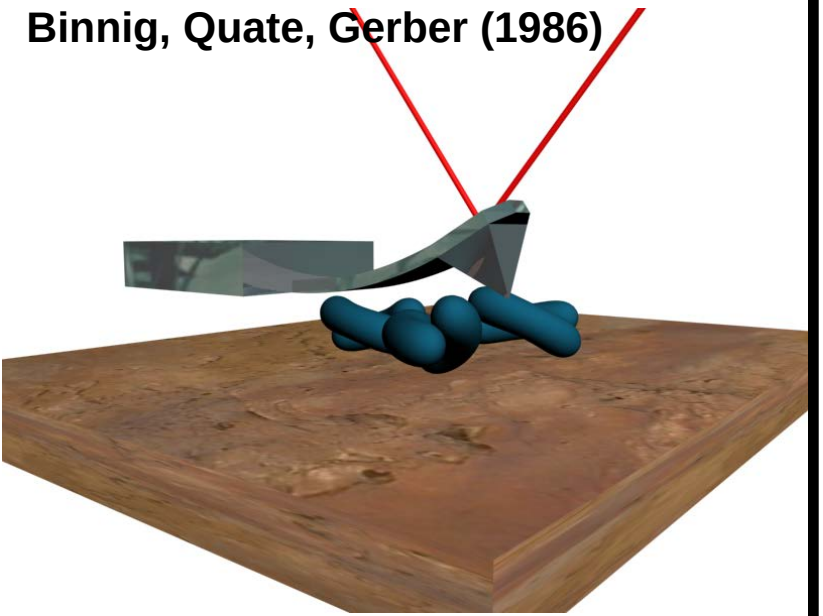
amplitude, frequency, phase shift

(1988-2007)

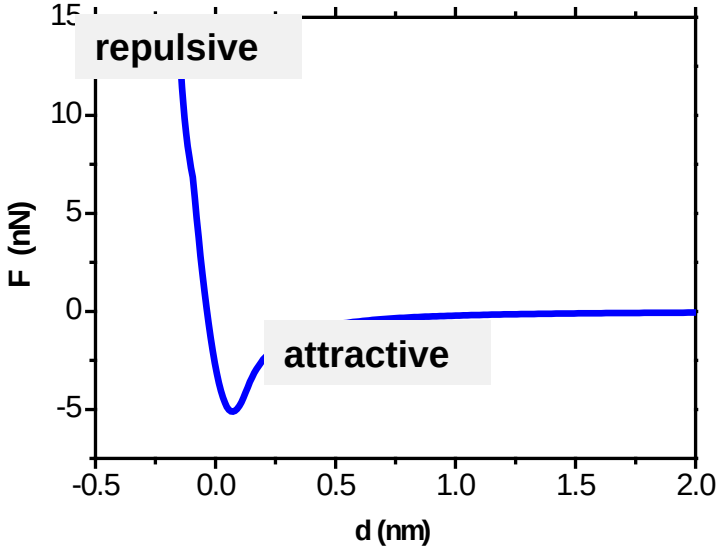


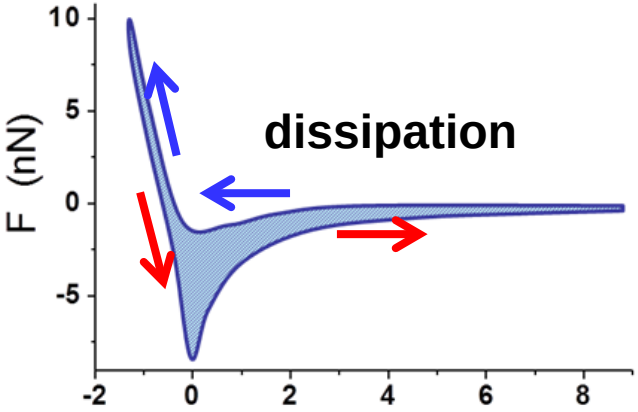
Contact : static deflection, $F=k\Delta z$

Binnig, Quate, Gerber (1986)



Forces:
Short and Long range
Conservative and dissipative



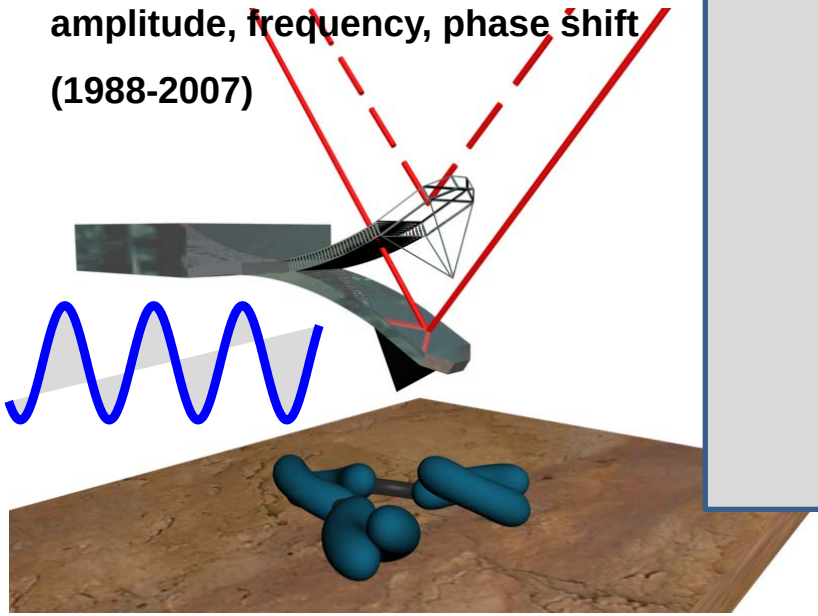


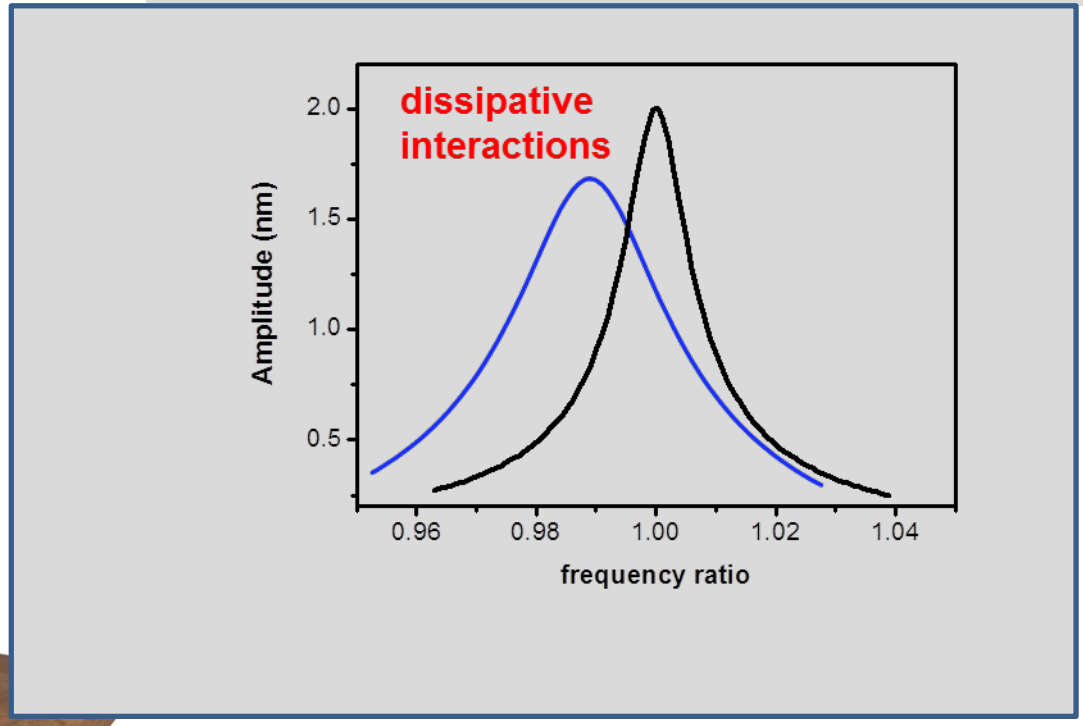
A force acting on a vibrating cantilever changes its **resonant frequence** and **reduces its amplitude**

Dynamic AFM:

amplitude, frequency, phase shift

(1988-2007)





Two main dynamic AFM modes

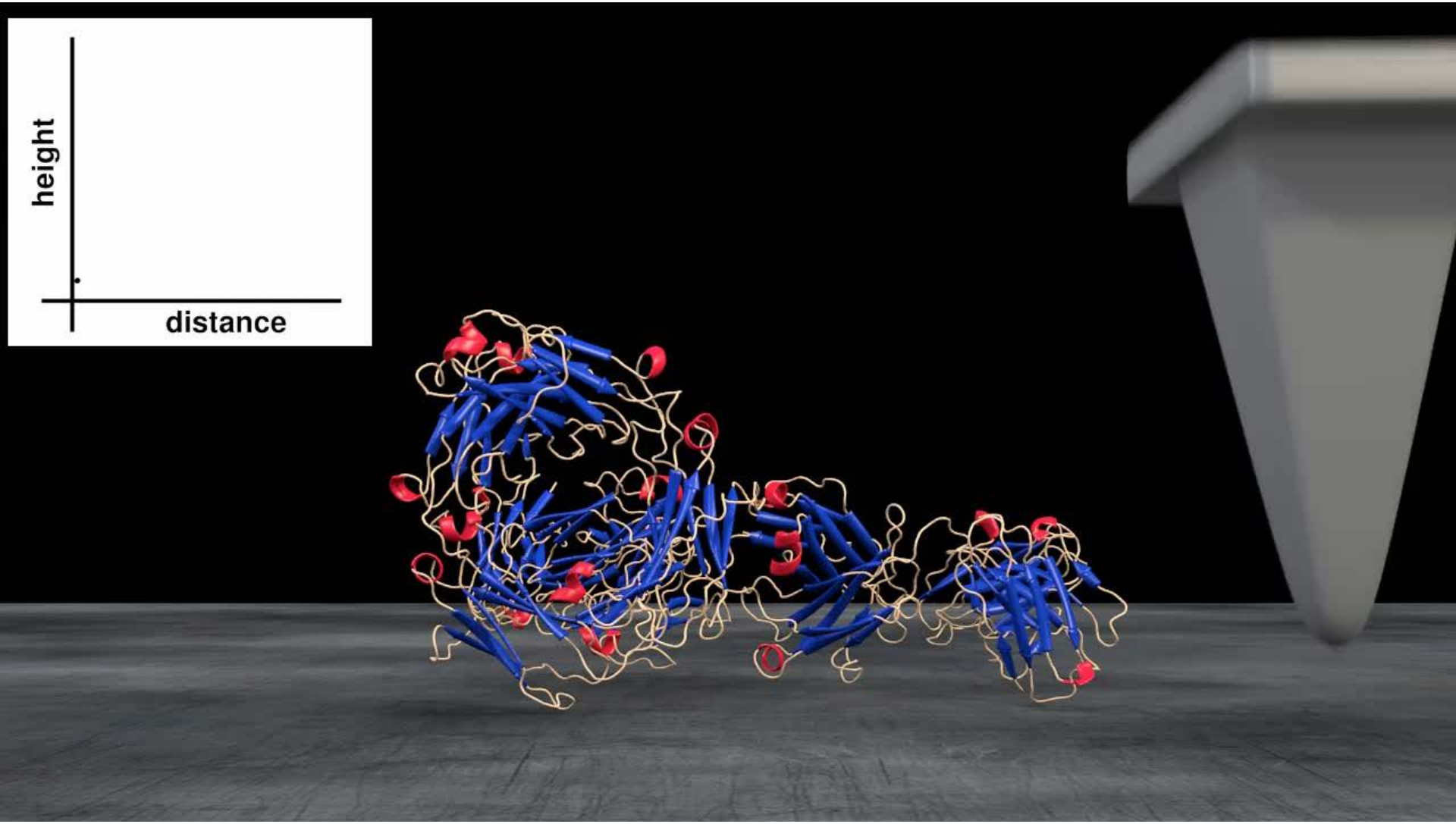
Frequency Modulation AFM **feedback on the frequency**

T.R. Albrecht, P. Grütter, D. Rugar, JAP 69, 668 (1991)

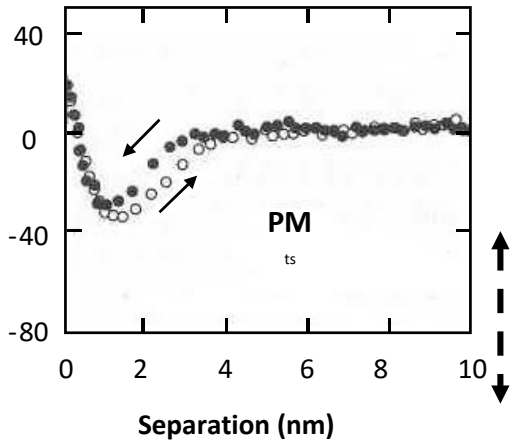
Amplitude Modulation AFM **feedback on the amplitude**

Martin, Williams, Wickramasinghe JAP 61, 4723 (1987)

Amplitude modulation AFM (tapping mode AFM):
an image is formed by scanning the tip across the surface at a fixed oscillation amplitude.



Forces in AFM



Restoring force cantilever

$F_c = -kz$

van der Waals forces

$$F_{vdw} = \frac{HR}{6d^2}$$

Excitation force

$F_0 \cos \omega t$

Capillary forces

Hidrodynamic forces

$$F_h = \frac{m\omega_0}{Q}\frac{dz}{dt}$$

Adhesion forces

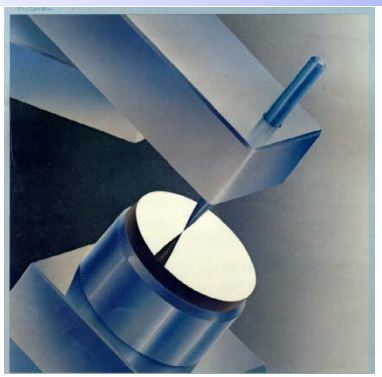
$F_a = 4\pi\gamma R$

Short range repulsive forces (DMT)

$$F_{DMT} = E^* \sqrt{R}\delta^{3/2}$$

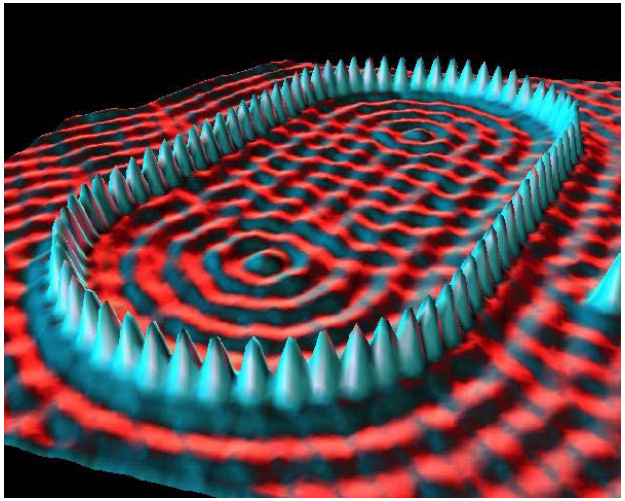
Adhesion forces
i). Unspecific
ii). specific

R. García, R. Pérez, Surf. Sci. Rep. 47, 197 (2002).

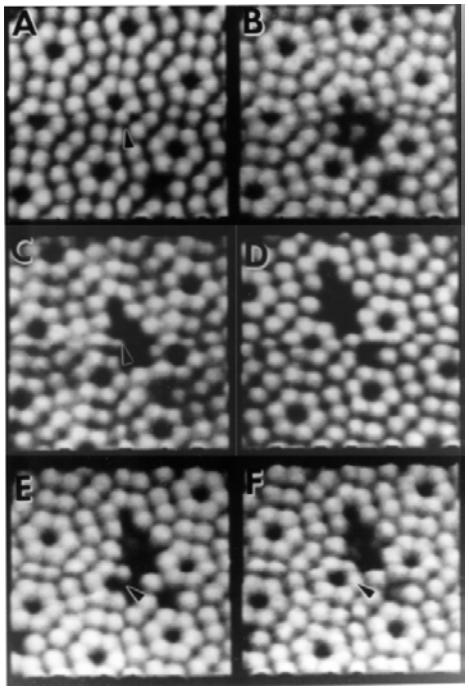


STM 1982

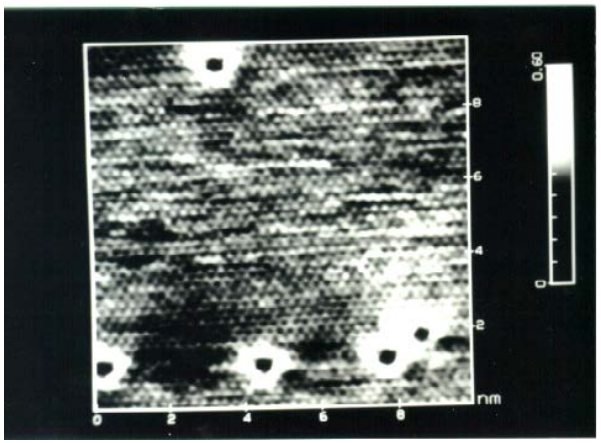
AFM 1986



Quantum corral, Fe on Cu(111)
Crommie, Lutz, Eigler (1993)



Lyo and Avouris, Si(111)7x7 (1991)



García, WSe_2 (1992)

Review atomic-scale manipulation by SPL: O. Custance, R. Perez, and S. Morita, *Nature Nanotechnology* **4**, 803-810 (2009).

Nanolithography: Requirements

Nanometer-scale motives

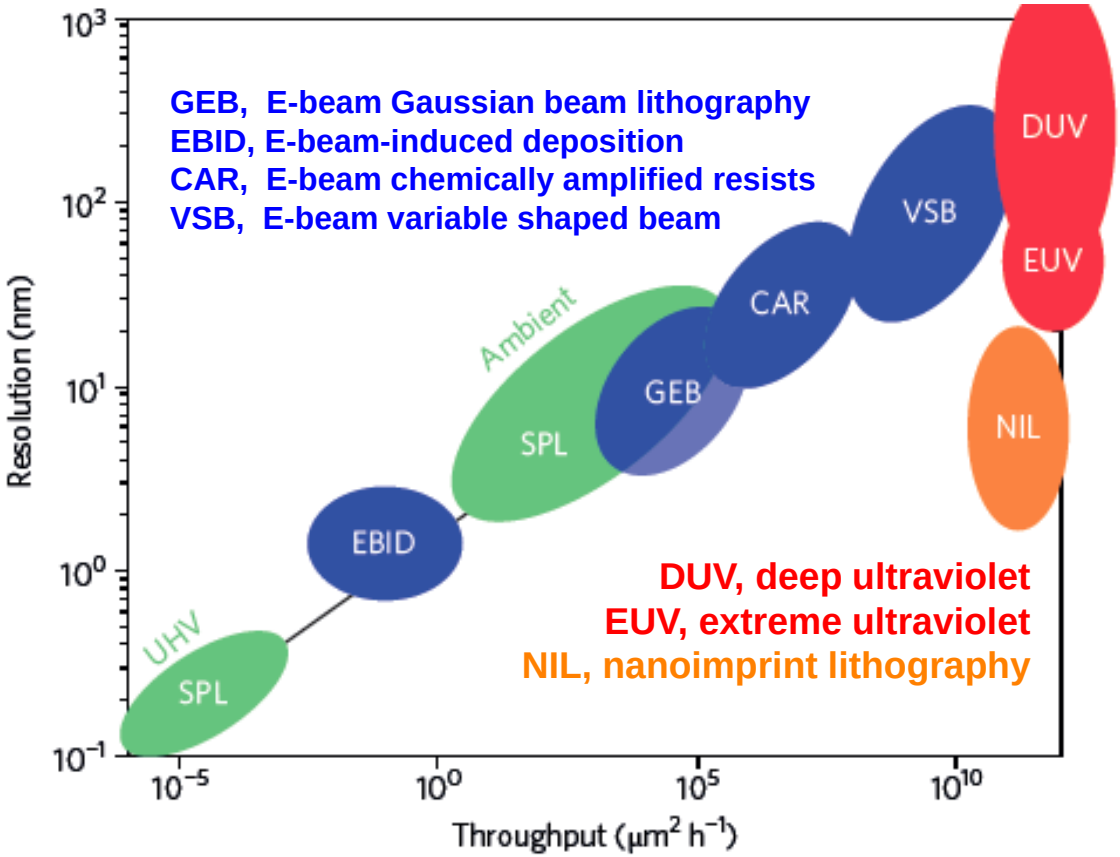
Reproducibility

Compatible with technological environments

Scalable

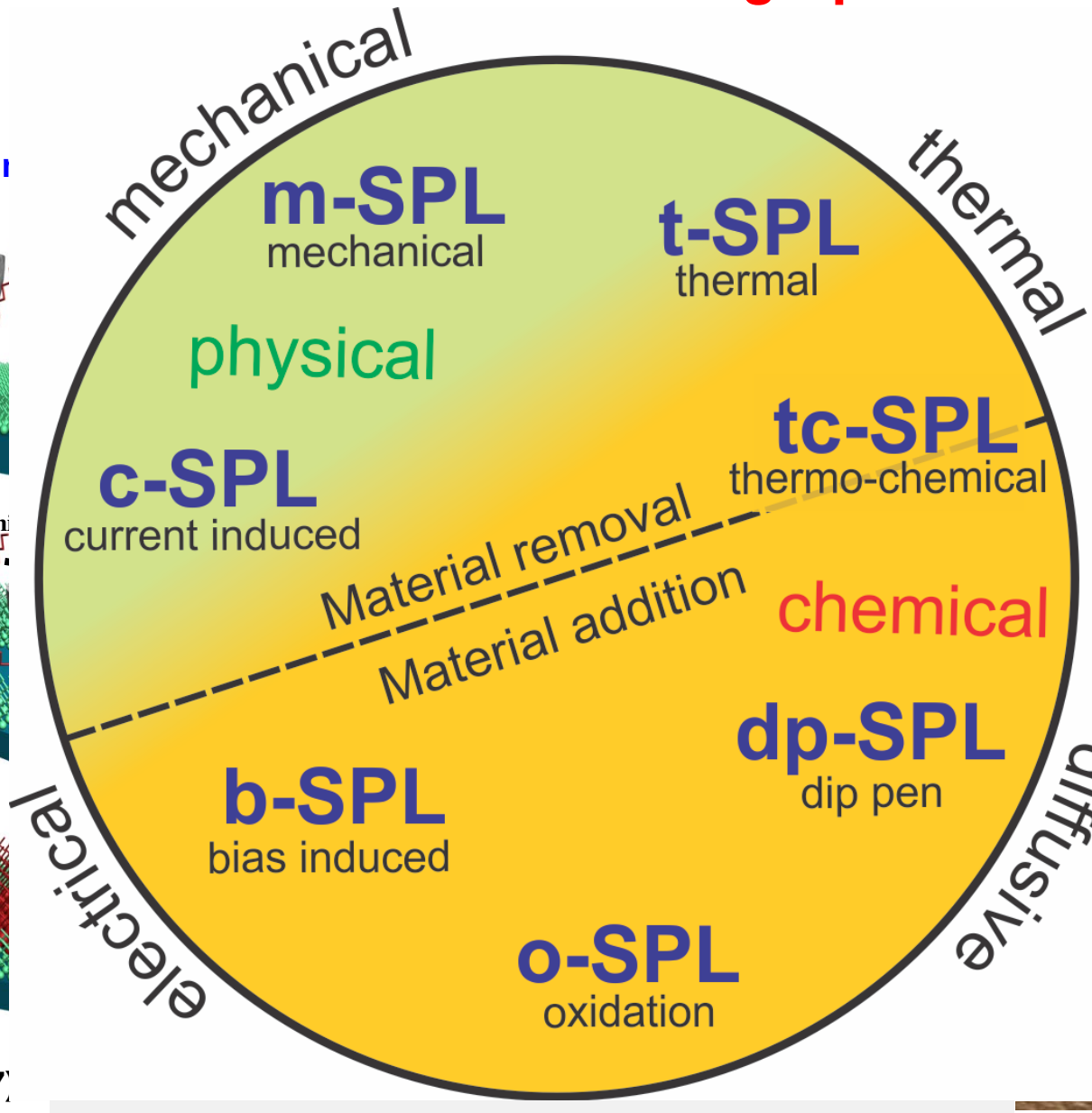
Throughput

NanoLithography: Throughput versus Feature Size



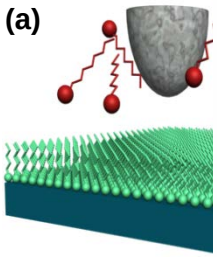
R. Garcia, A.W. Knoll, E. Riedo, *Nature Nanotechnology* **9**, 577 (2014)

SPM based Nanolithographies

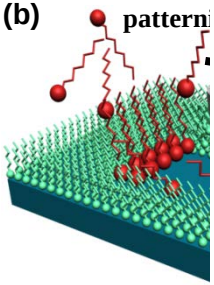


Nanoshavi

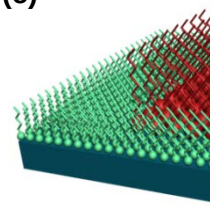
(a)



(b)

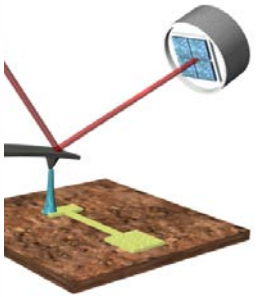


(c)



G. Liu (1997)

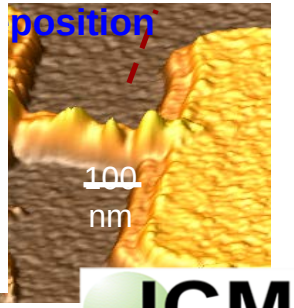
ning Probe
phy



nography

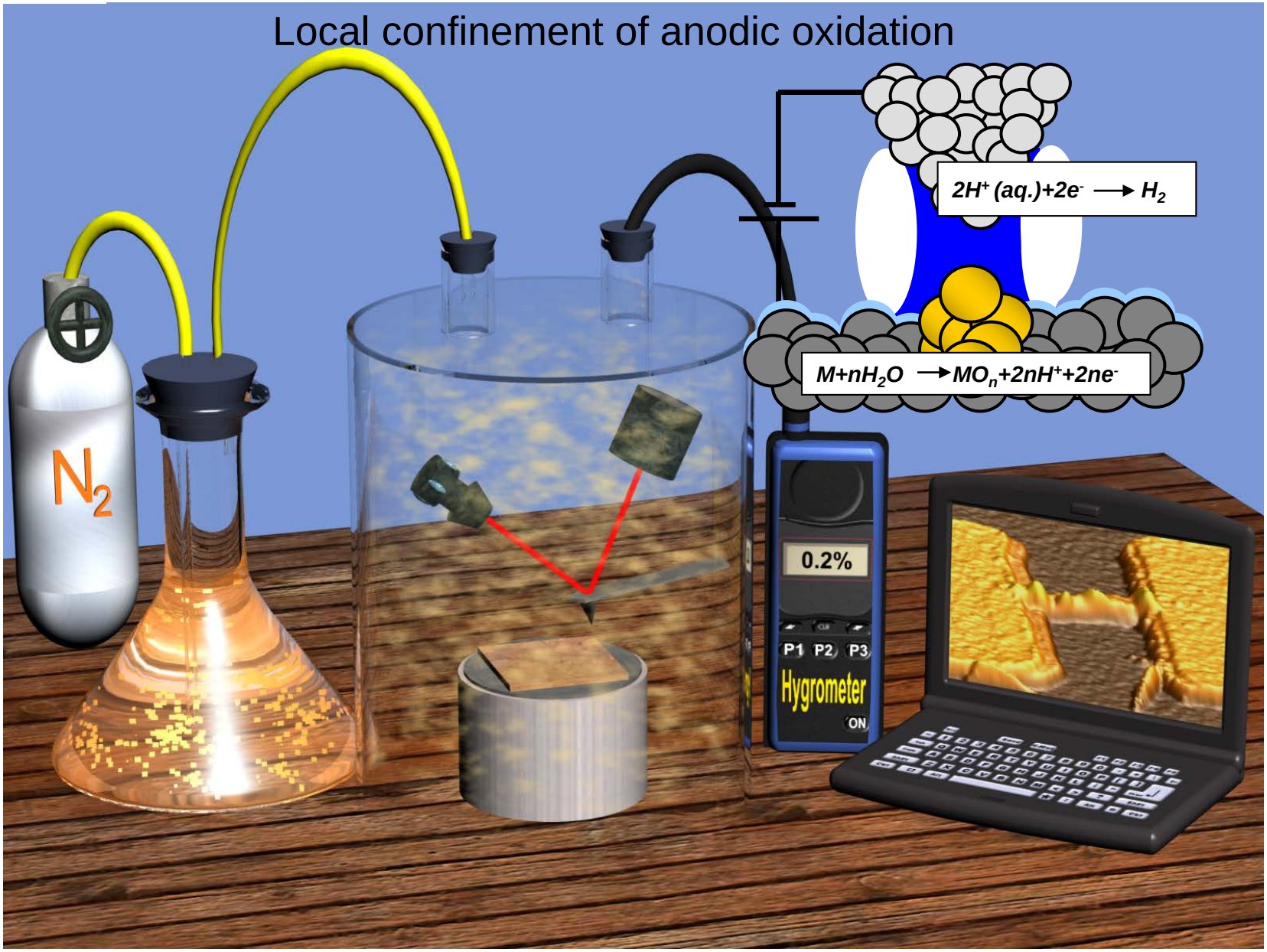
1999); H. Butt (1995)

position



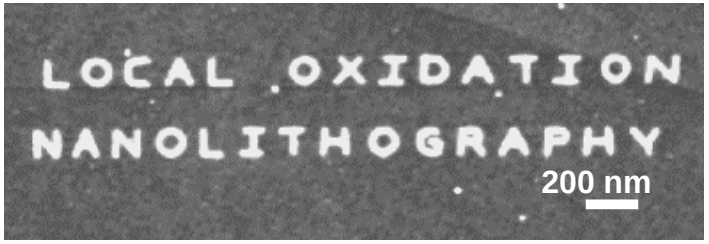
R. Garcia, A.W. Knoll, E. Riedo, *Nature Nanotechnology* **9**, 577 (2014)

Oxidation SPL:

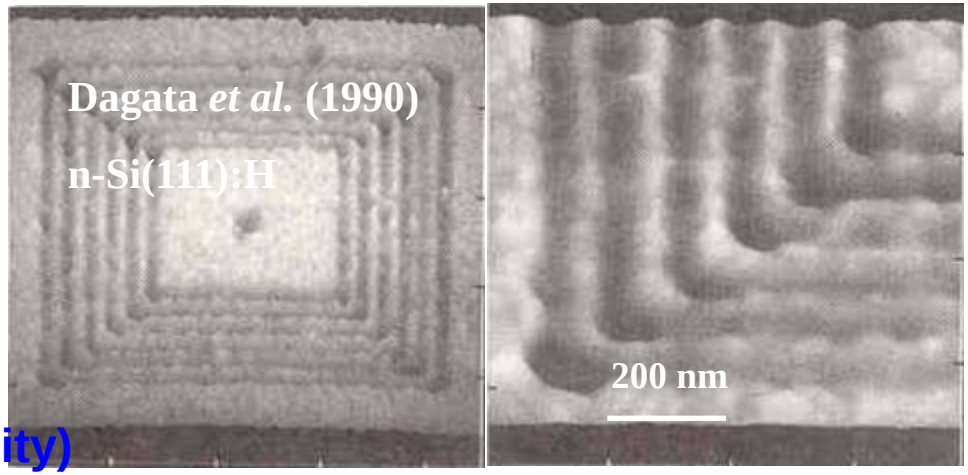


García, Calleja, Perez-Murano, Applied Physics Letters (1998)

Oxidation SPL: basics



STM oxidation of surfaces



1st observations with STM (serendipity)

J.A. Dagata et al. Appl. Phys. Lett. 56, 2001 (1990)

T. Thundat et al. J. Vac. Sci. Technol. A 8, 3527 (1990)

o-SPL with AFM (contact mode)

H. C. Day and D. R. Allee, Appl. Phys. Lett., 1993, 62, 2691.

o-SPL in AFM non-contact mode (extended tip lifetime)

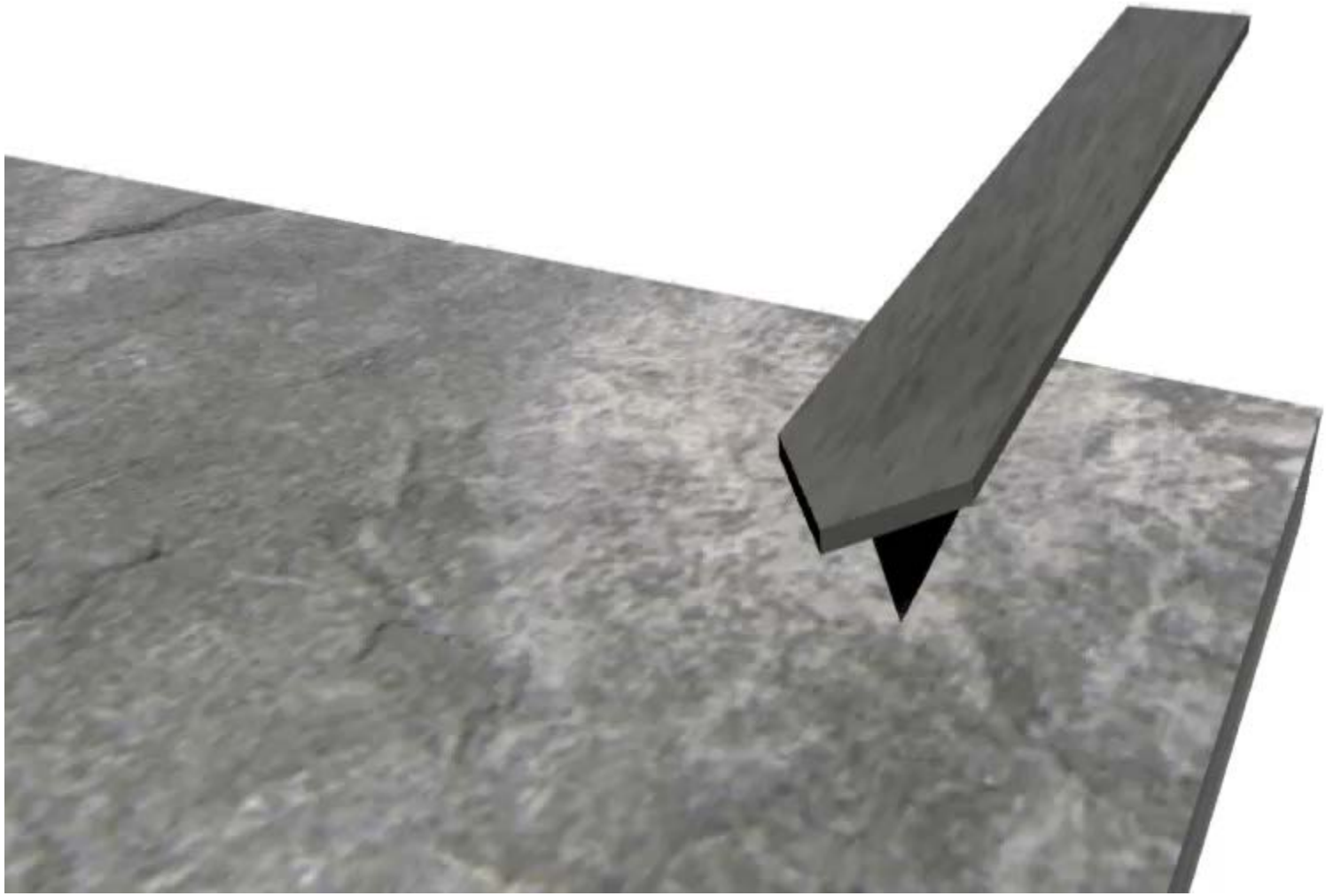
R. Garcia, M. Calleja, F. Pérez-Murano, Appl. Phys. Lett. (1998)

Role of humidity

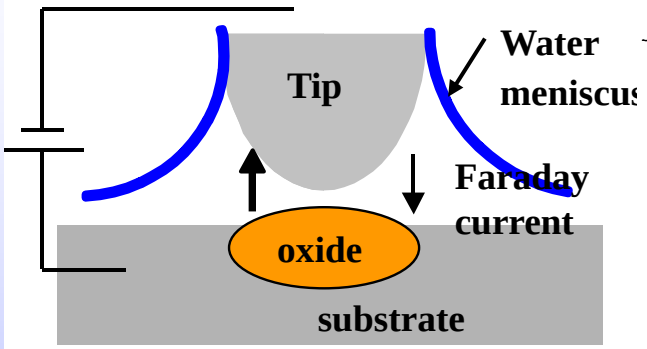
P. Avouris, T. Hertel and R. Martel, Appl. Phys. Lett., 1997, 71, 287.

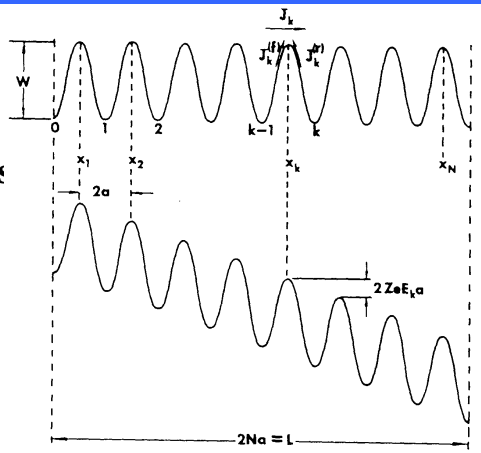
Liquid meniscus

R. Garcia, M. Calleja and H. Rohrer, J. Appl. Phys., 1999, 86, 1898.



SPACE CHARGE MODEL FOR LOCAL OXIDATION





Silicon case

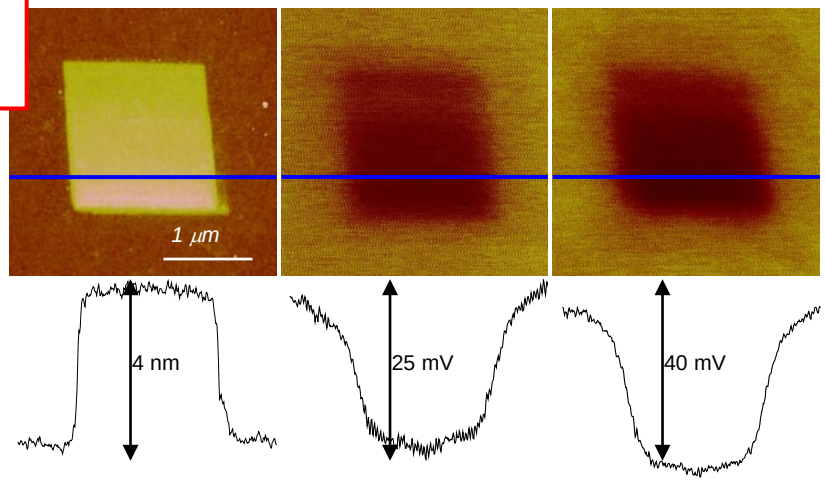
Electrolyte: $2H_2O \rightarrow 2H^+ + 2(OH^-)$

Anode: $Si + 2h^+ + 2(OH^-) \rightarrow SiO_2 + H_2$

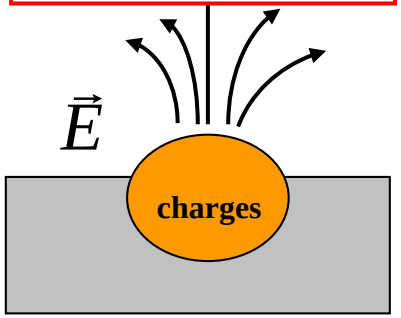
Cathode: $2H^+ + 2e^- \rightarrow H_2$

Kelvin Probe AFM measurements

The local oxidation process negative space charge build-up

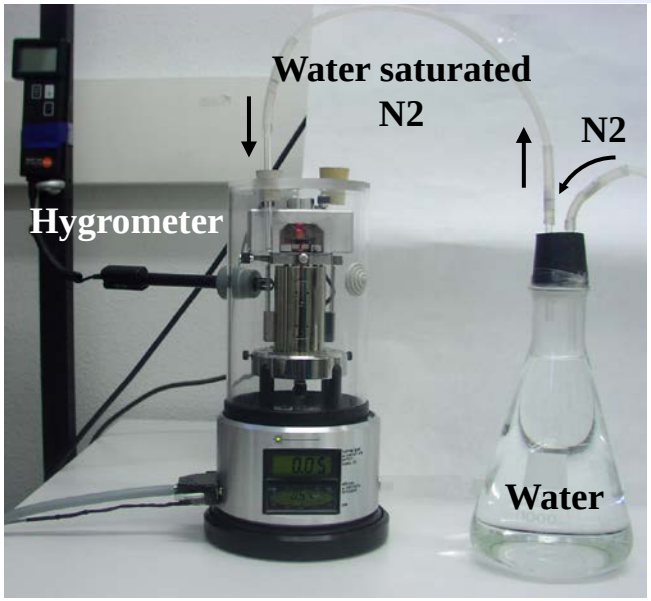


Negative Space charges



$$\rho = \frac{2\varepsilon\varepsilon_0}{d^2}V$$

M. Chiesa, R. Garcia, APL 96, 263112 (2010)



Field-induced formation of water bridges

E=2 GV/m= 2 V/nm

time=75 ps

Meniscus height 3 nm

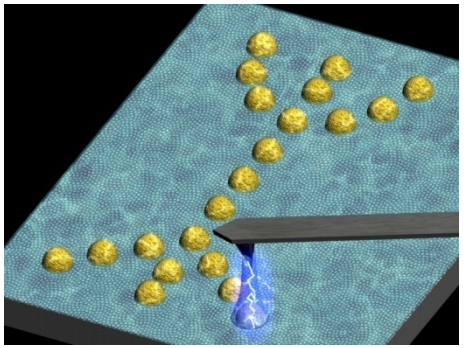
MD by F. Zerbetto and T. Cramer, UBologna

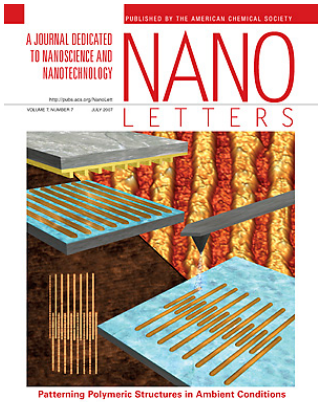
1014 molecules

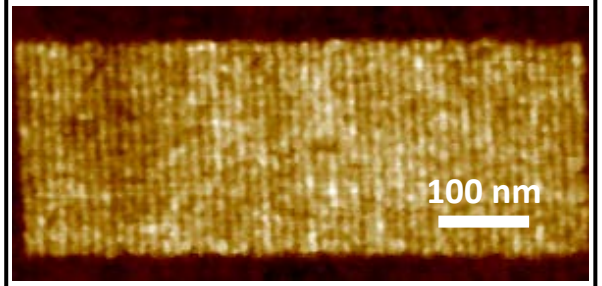
Cramer, Zerbetto and Garcia, Langmuir 24, 6116 (2008)

TIP-BASED NANOFABRICATION

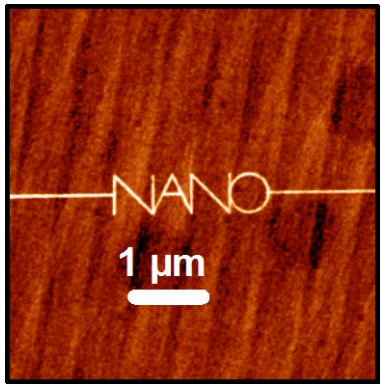
Nanopatterning

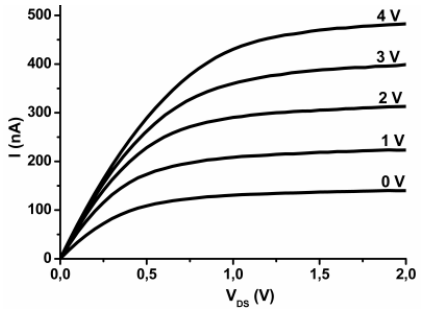




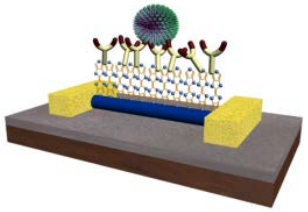


Nanoelectronic devices

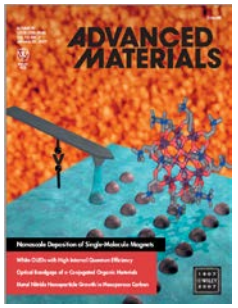


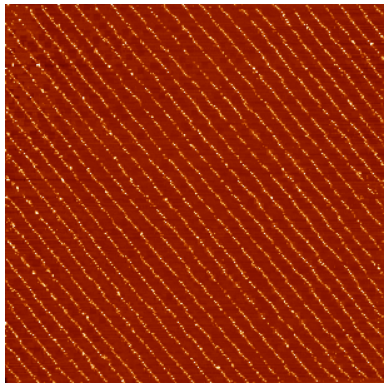


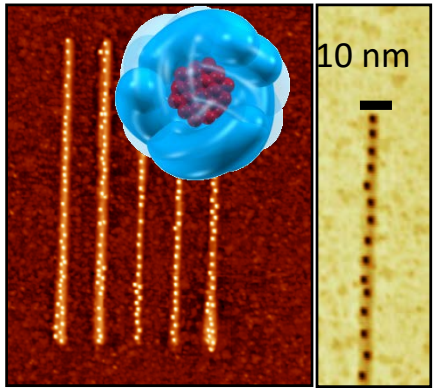
Nano Letters 11, 3636 (2008)



Molecular Architectures



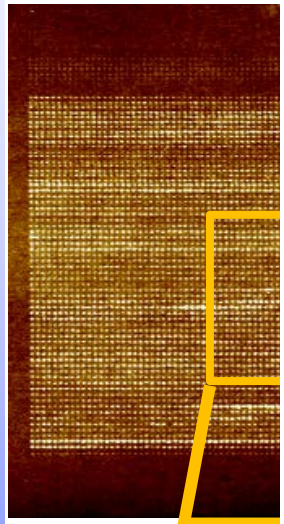


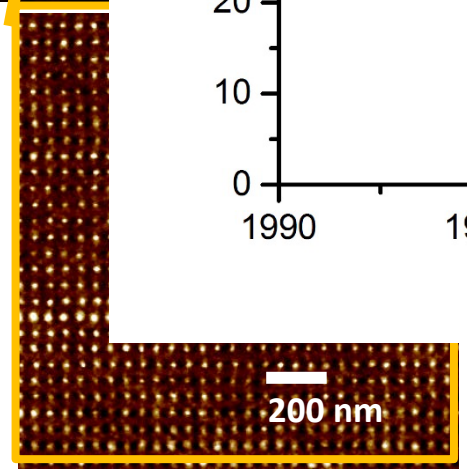


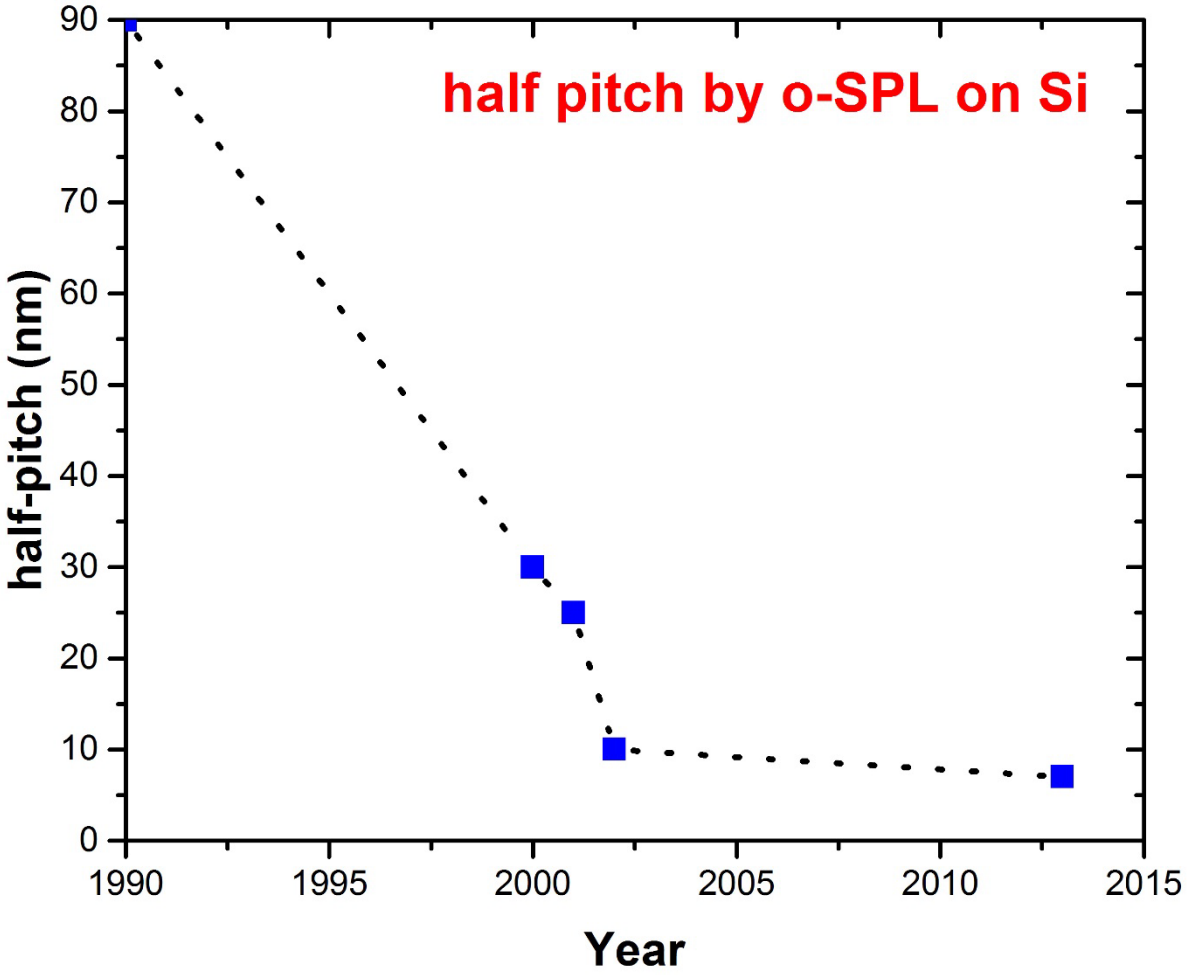
Oxidation Scanning Probe Lithography

Reproducibility

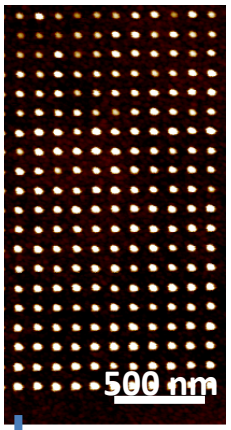
array o
(45%, 1 ms
50 nm

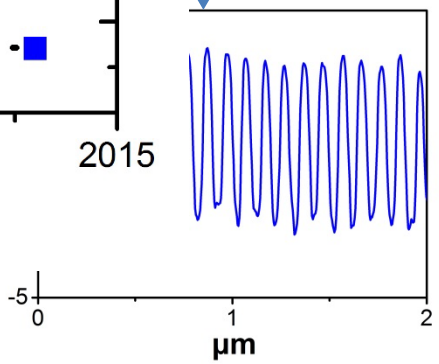






opillars

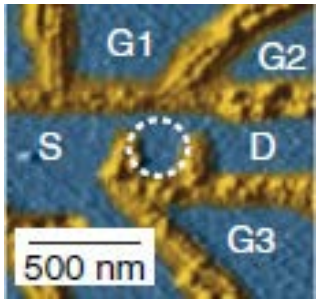




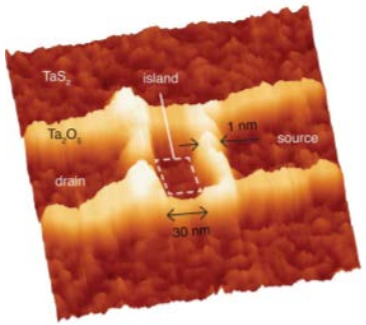
o-SPL:

Direct Nanppatterning a large variety of materials

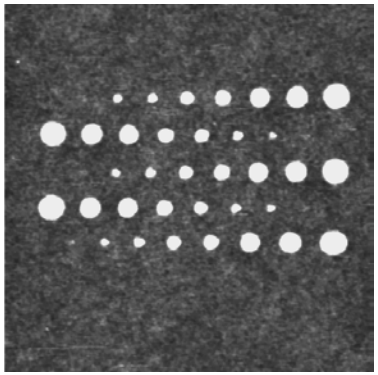
GaAs



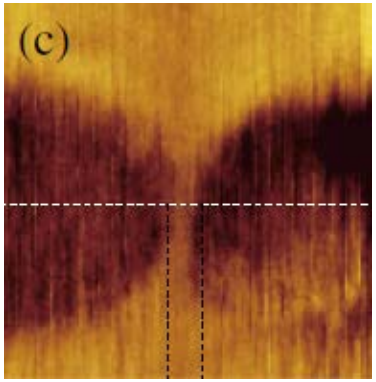
Ta



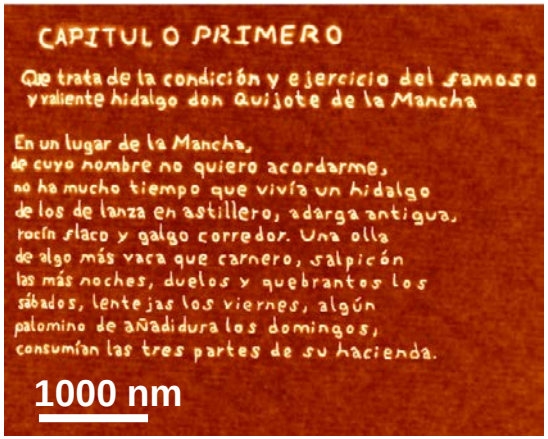
Niobium



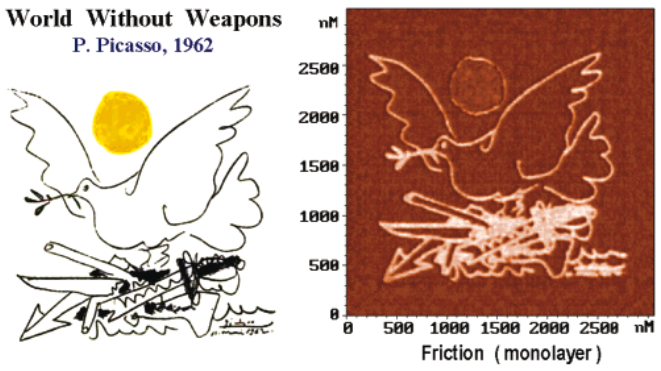
graphene



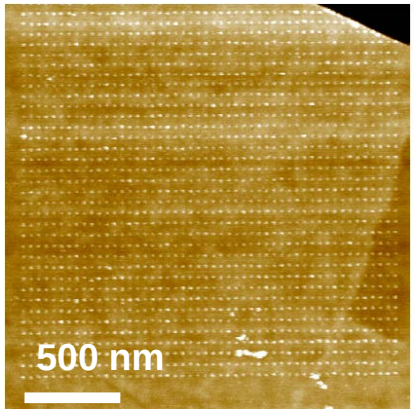
silicon



SAM templates



WSe2



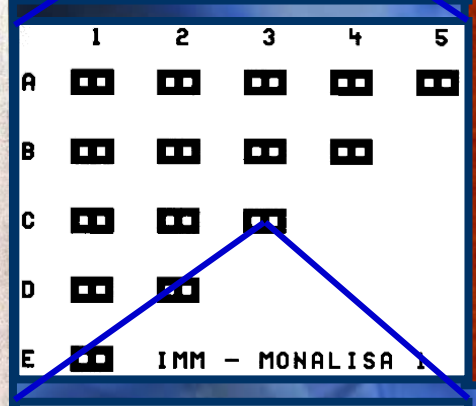
Metals, semiconductors, Organosilanes...

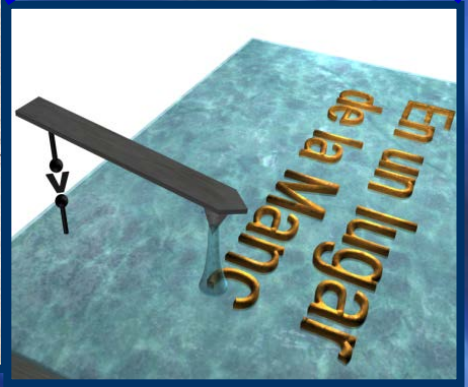
TECHNOLOGY CNN.com

'Don Quixote' paragraph fits on a chip

Thursday, April 7, 2005 Posted: 7:48 AM EDT (1148 GMT)

MADRID, Spain (AP) -- Physicists in Spain are celebrating the 400th anniversary of publication of "Don Quixote" in a very small way: they wrote the first paragraph on a silicon chip in letters so tiny the whole 1,000-page book would fit on the tips of six human hairs.





Fol. 1

PRIMERA PARTE
DEL INGENIOSO
hidalgo don Quixote de
la Mancha.

Capitulo Primero. Que trata de la condicion, y exercicio del famoso hidalgo don Quixote de la Mancha.

EN Vn lugar de la Mancha, de cuyo nombre no quiero acordarme, no ha mucho tiempo que viuia vn hidalgo de los de lança en astillero, adarga antigua, rozin flaco, y galgo corredor. Vna olla de algo mas vaca que carnero, salpicon las mas noches, duelos y quebrantos los Sabados, lantejas los Viernes, algun palomino de añadidura los Domingos: consumian las tres partes de su hazienda. El resto della concluian, sayo de velarte, calças de velludo para las fiestas, con sus pantuflos de A lo

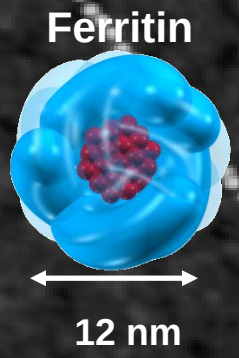
5 cm

CAPITULO PRIMERO

Que trata de la condición y ejercicio del famoso y valiente hidalgo don Quijote de la Mancha

En un lugar de la Mancha,
de cuyo nombre no quiero acordarme,
no ha mucho tiempo que vivía un hidalgo
de los de lanza en astillero, adarga antigua,
rocín flaco y galgo corredor. Una olla
de algo más vaca que carnero, salpicón
las más noches, duelos y quebrantos los
sábados, lentejas los viernes, algún
palomino de añadidura los domingos,
consumían las tres partes de su hacienda.

1µm



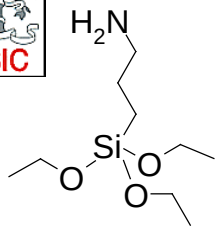
Template growth of Molecular Arquitectures

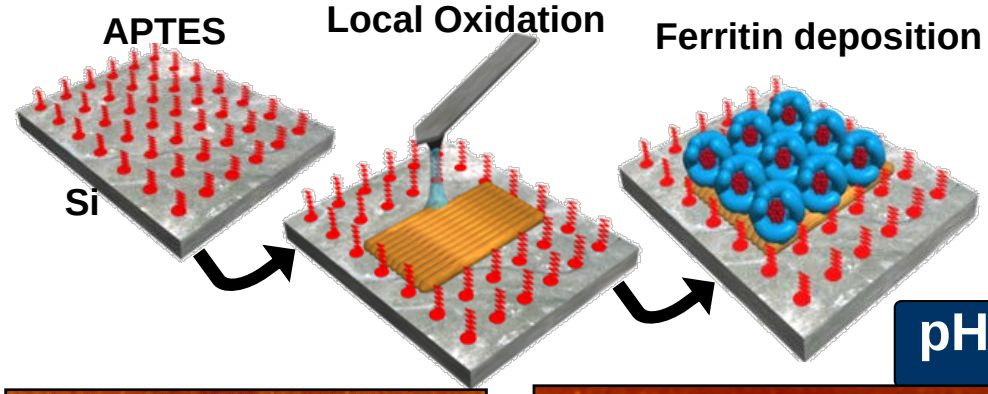
, Ramsés V. Martínez[1], Marco Chiesa[1] Javier Martínez[1], Ricardo Garcia[1], Eugenio Coronado[2], Elena Pinilla-Cienfuegos[2], Sergio Tatay[2]

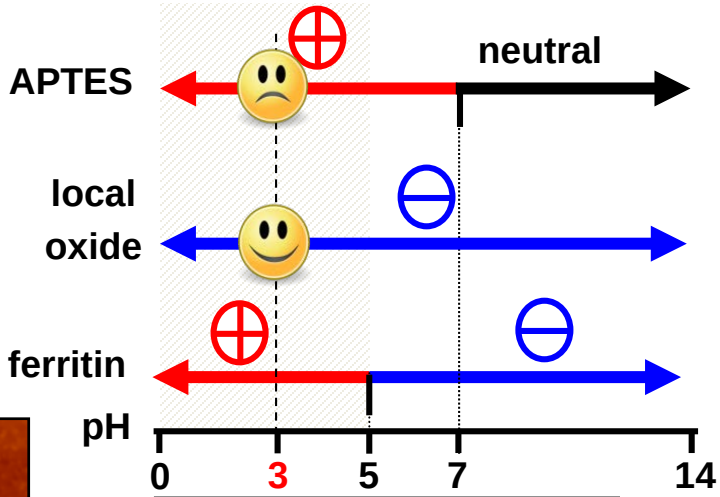
[1]Instituto de Microelectrónica de Madrid, CSIC, Spain

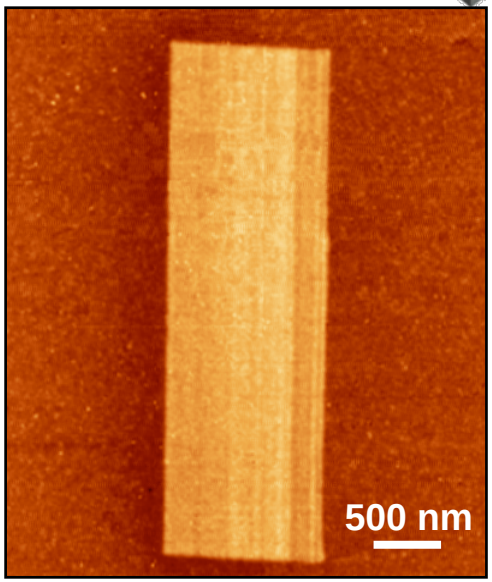
[2]Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, Spain

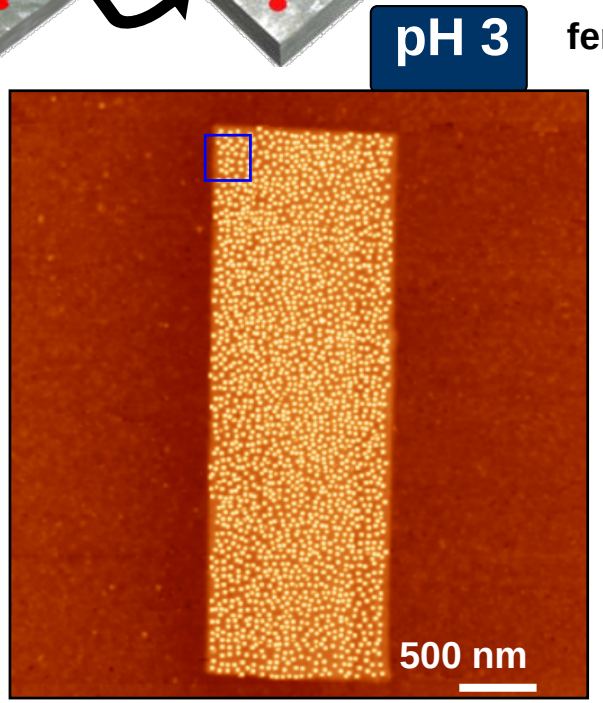
Nanoscale positioning of ferritin (low pH)

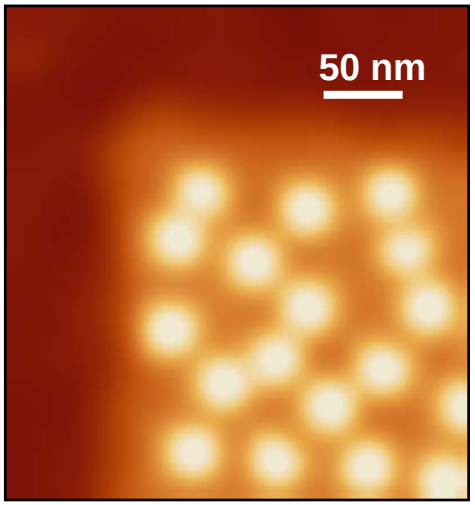








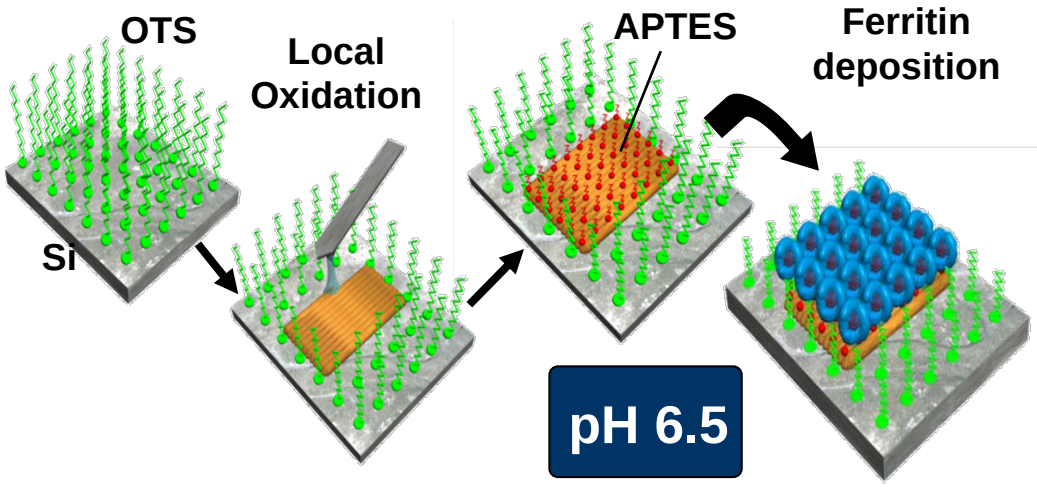


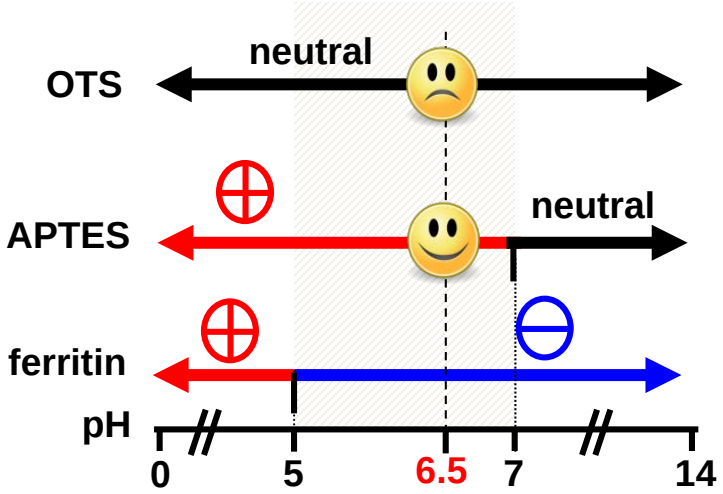


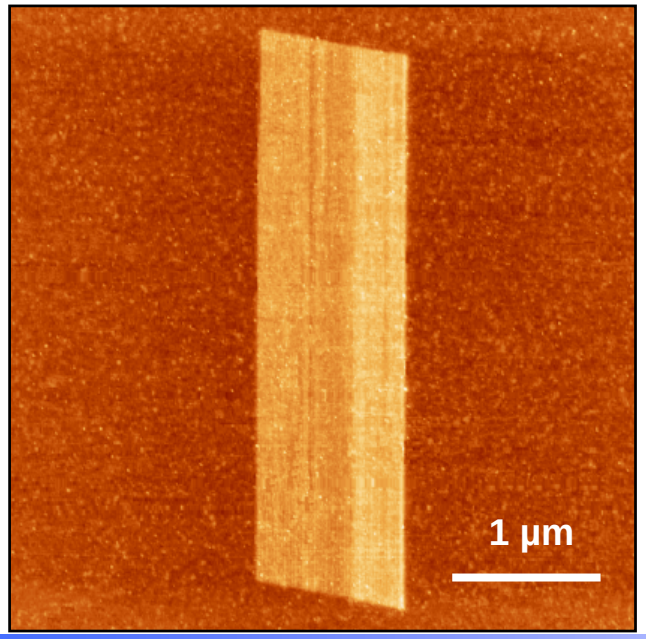
Ferritin isoelectric point 4.5

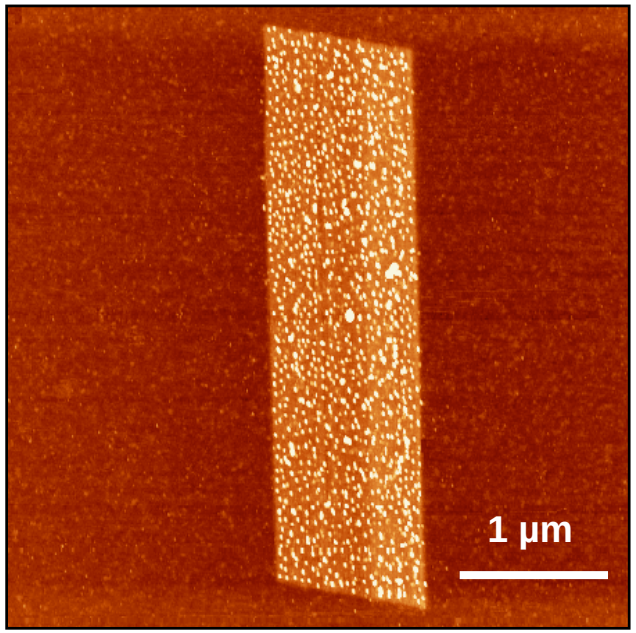
R.V. Martinez , J. Martinez, M. Chiesa, R. Garcia, E. Coronado, E. Pinilla-Cienfuegos, S. Tatay, Adv. Mater. 22, 588 (2010)

Controlled positioning at neutral pH

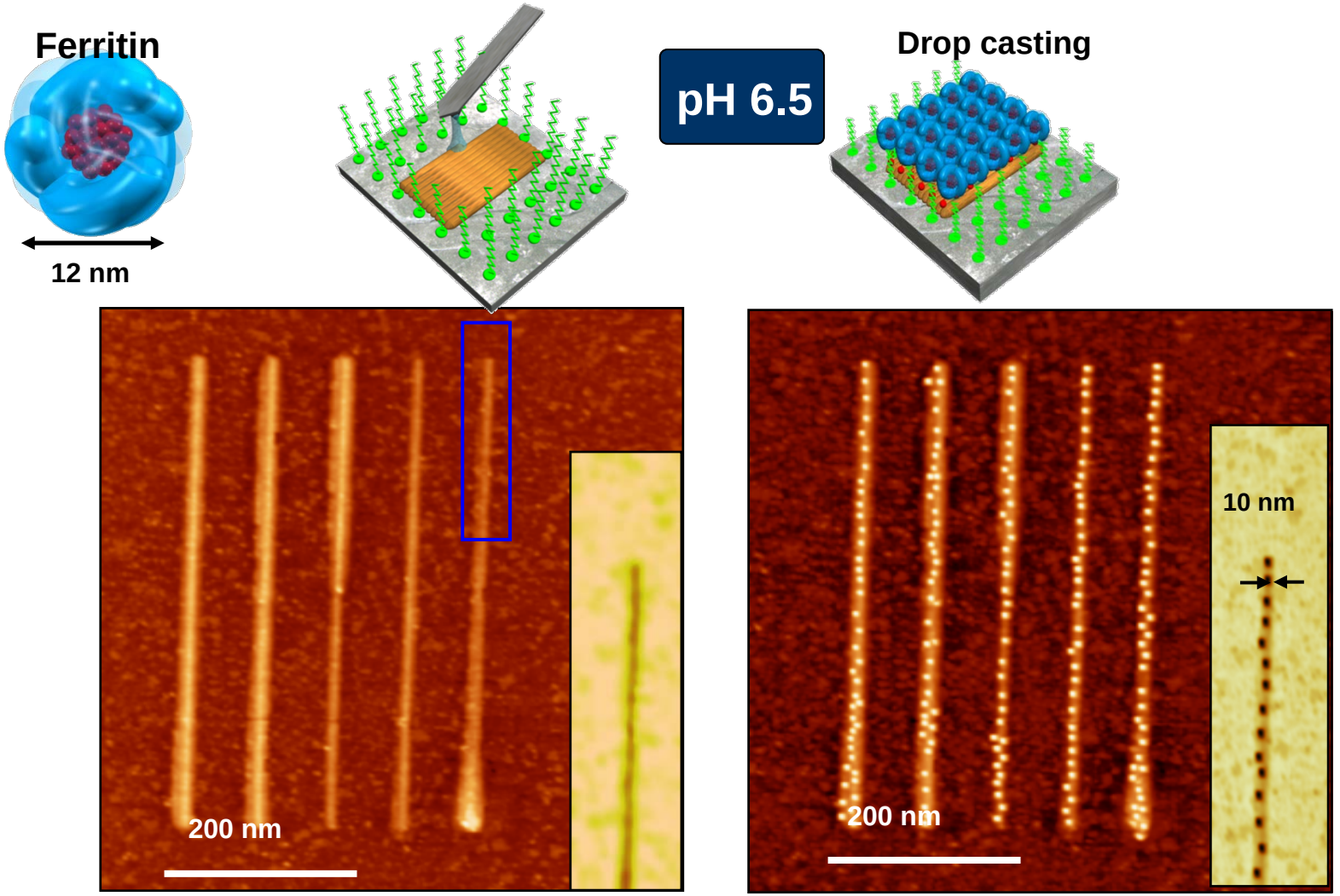








Protein patterning with 10 nm feature size



R.V. Martinez , M. Chiesa, R. Garcia, Small 7, 2914 (2011)
R.V. Martinez *et al*., Adv. Mater. 22, 588 (2010)
R.V. Martinez et al., Adv. Mater. 19, 291 (2007)

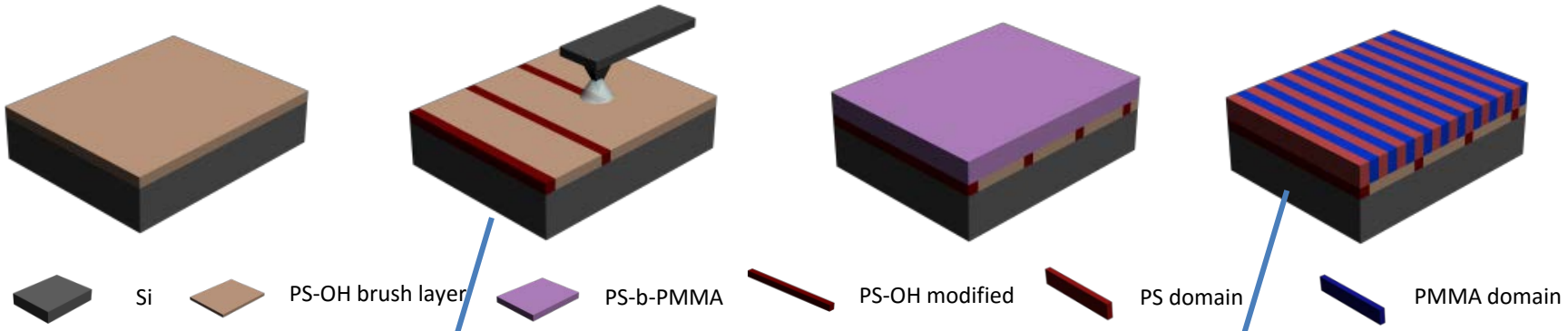
Creation of guiding patterns for directed self assembly of block co-polymers by O-SPL

1. Brush grafting + Annealing

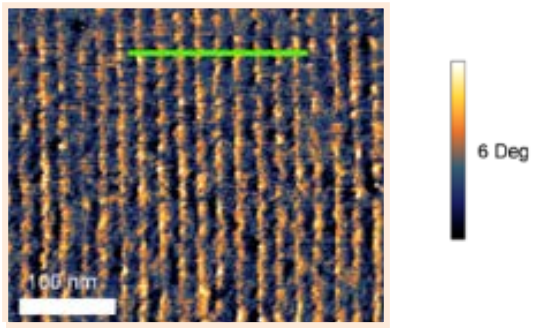
2. Chemical surface modification by AFM

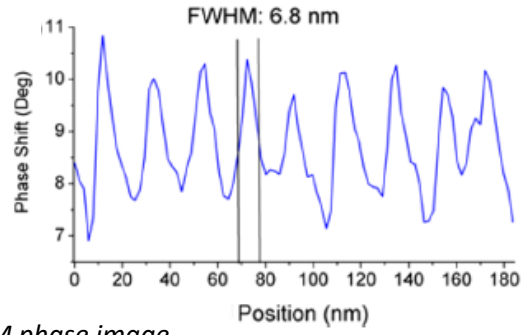
3. PS-b-PMMA deposition + Annealing

4. BCP directed self-assembly

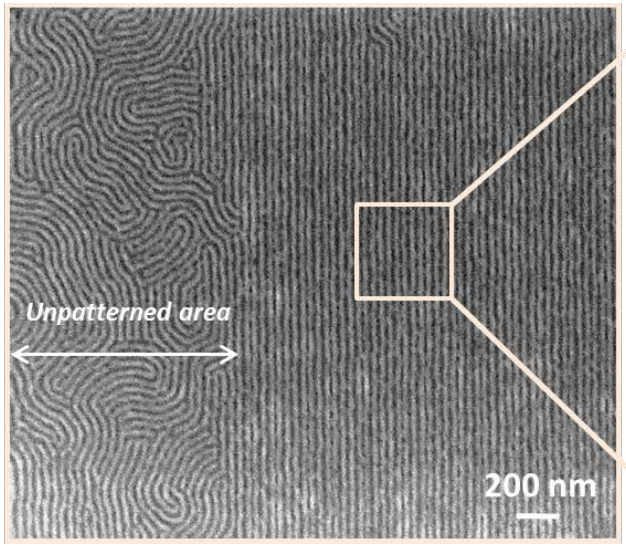


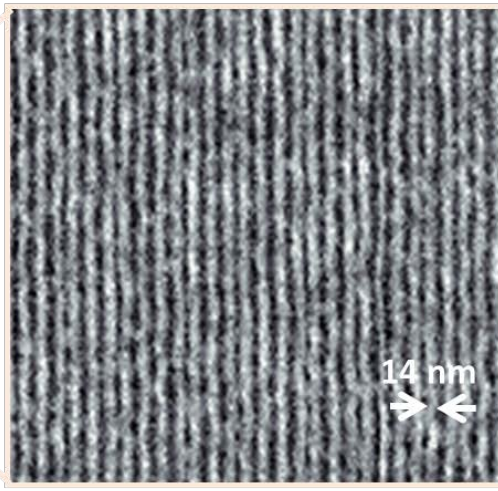
➔ Sub-10 nm guiding patterns





AFM phase image

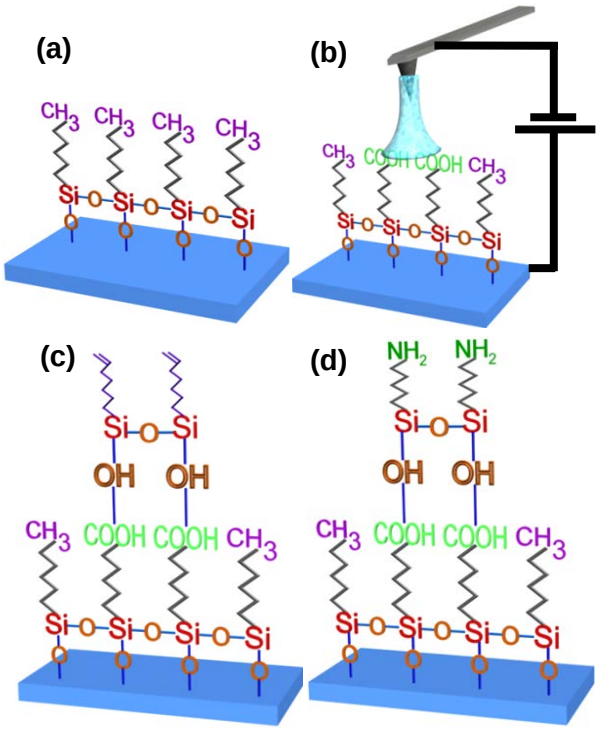


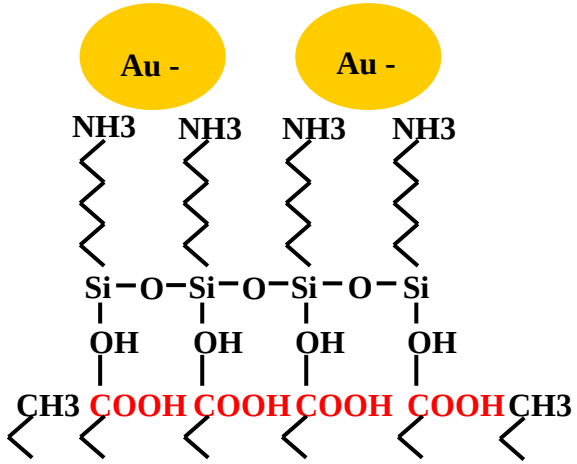


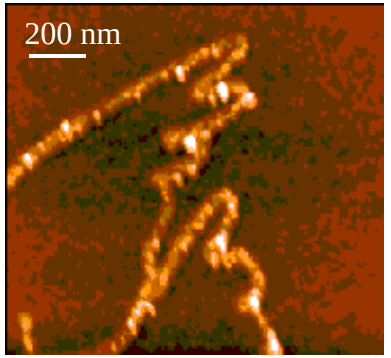
M. Fernández-Regúlez; L. Evangelio, M. Lorenzoni, J. Fraxedas, F. Pérez-Murano, ACS Appl. Mater. Interfaces 6, 21596 (2014)

in-situ nanofabrication of metal-semiconductor-organic interfaces

OTS= n-octadecyltrichlorosilane CH3-(CH2)17-SiCl3)



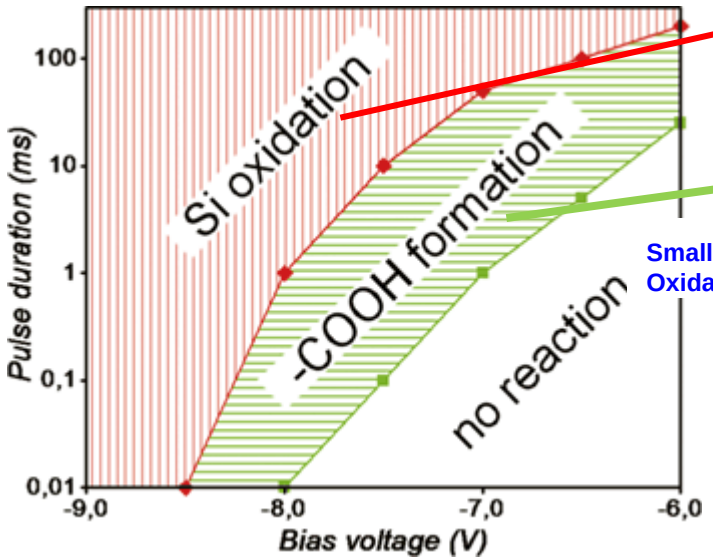




R. Maoz, S.R.Cohen and J. Sagiv. *Advanced Materials* 1 (1999)
J. Berson, A. Zeira, R. Maoz and J. Sagiv. *Beilstein Journal of Nanotechnology* 3 (2012)

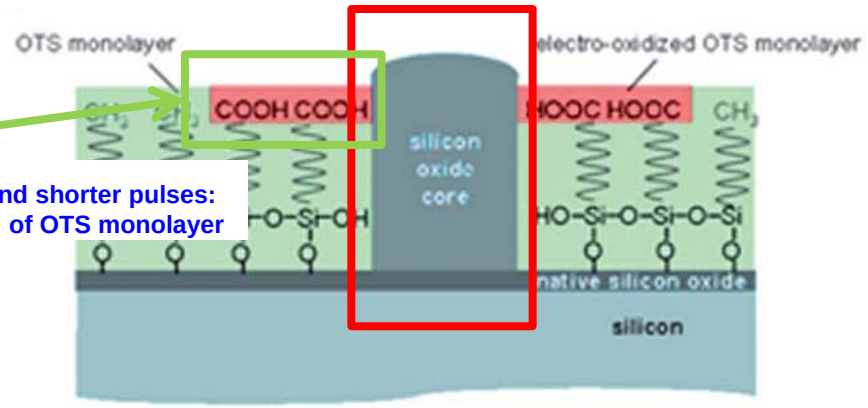
o-SPL on self-assembled monolayers: Interplay SAM vs. Silicon oxidation

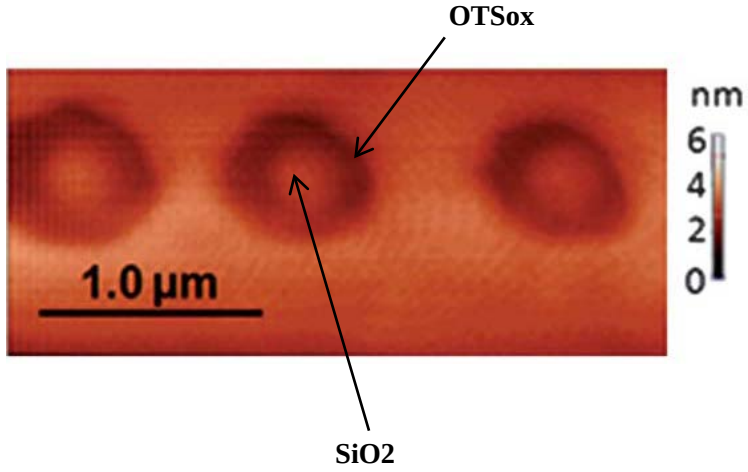
Regimes of oxidation:



Larger and longer pulses:
Oxidation of Si substrate

Smaller and shorter pulses:
Oxidation of OTS monolayer



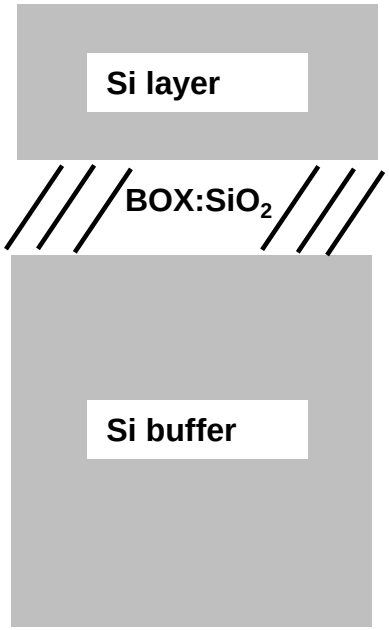


T.Druzhinina, S. Hoeppener, N. Herzer and U.S. Schubert.
Journal of Materials Chemistry 21 (2011)

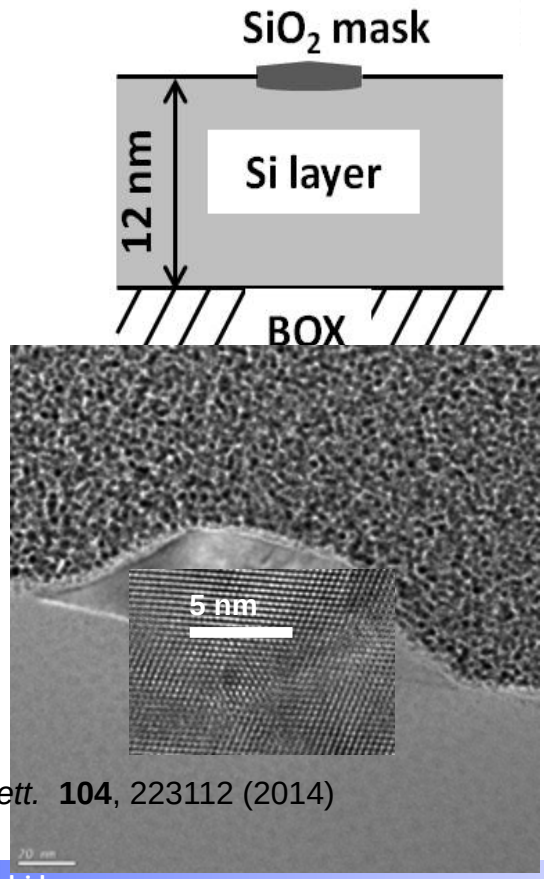
Mask Fabrication

I: substrate

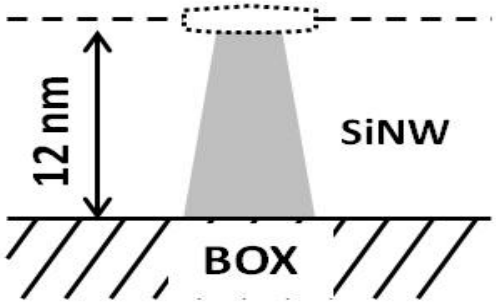
SOI: Silicon on insulator



II: o-SPL



III: Etching

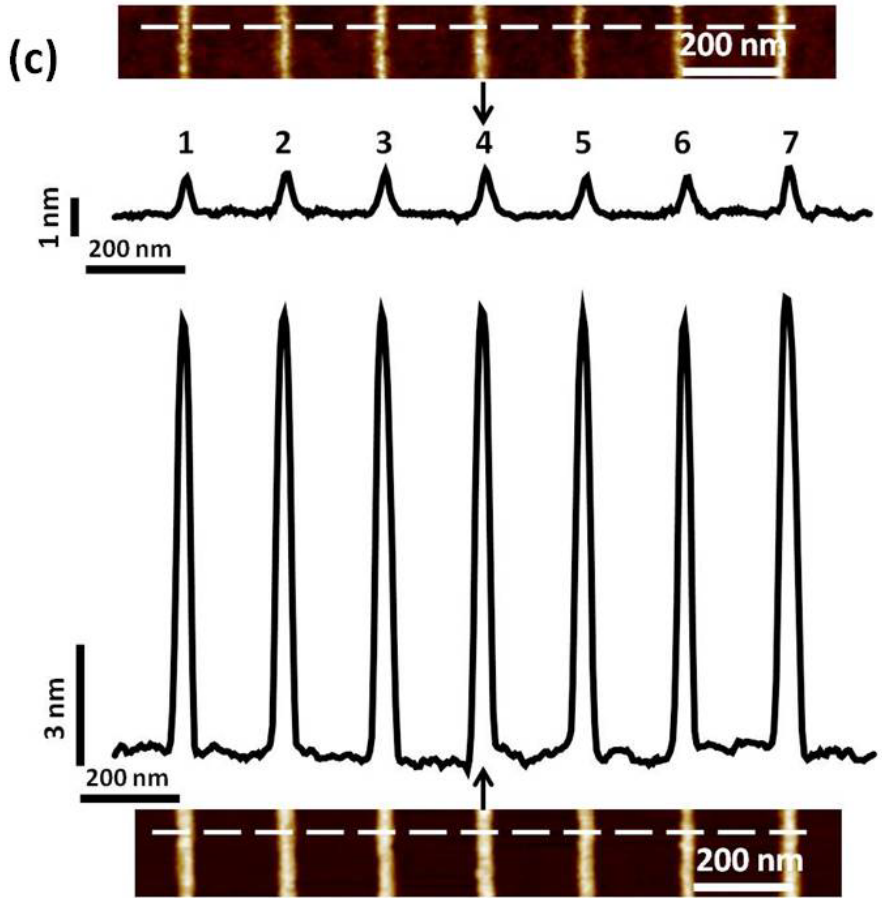


RIE Parameters	Value
rf-power	10 W
Chamber pressure	90 mTorr
SF_6:O_2 proportion	12:3 sccm
Etching time	126 s

Y.K. Ryu et al. *Appl. Phys. Lett.* **104**, 223112 (2014)

SiNWs after pattern transfer

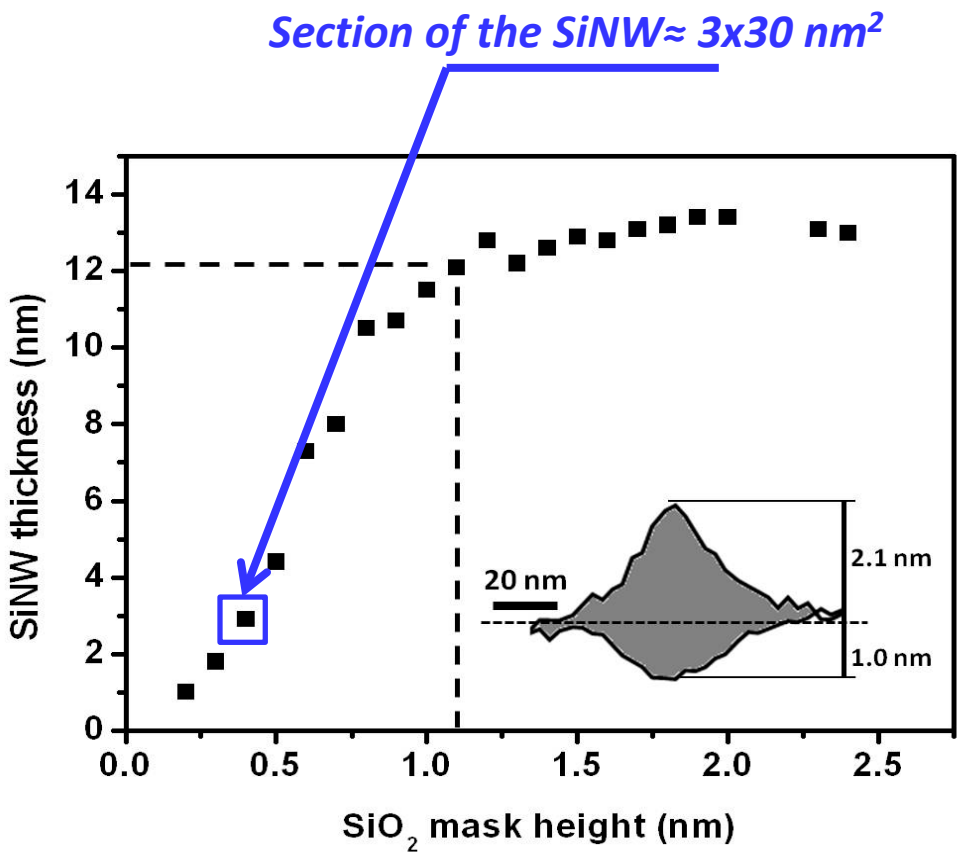
SiO_2 masks

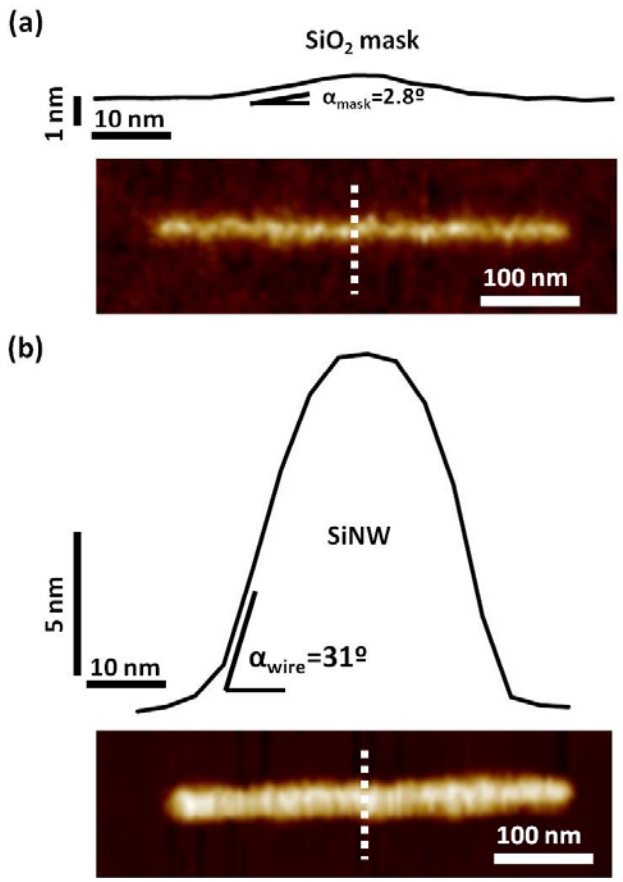


SiNWs

Nº	h(nm)		w(nm)	
	SiO_2 mask	SiNW	SiO_2 mask	SiNW
1	1.1	12.7	24	27
2	1.1	13.0	24	34
3	1.3	13.0	34	35
4	1.4	13.1	33	30
5	1.2	12.9	35	33
6	1.1	12.7	29	24
7	1.4	13.5	25	39

SiNW thickness as a function of the thickness of the mask





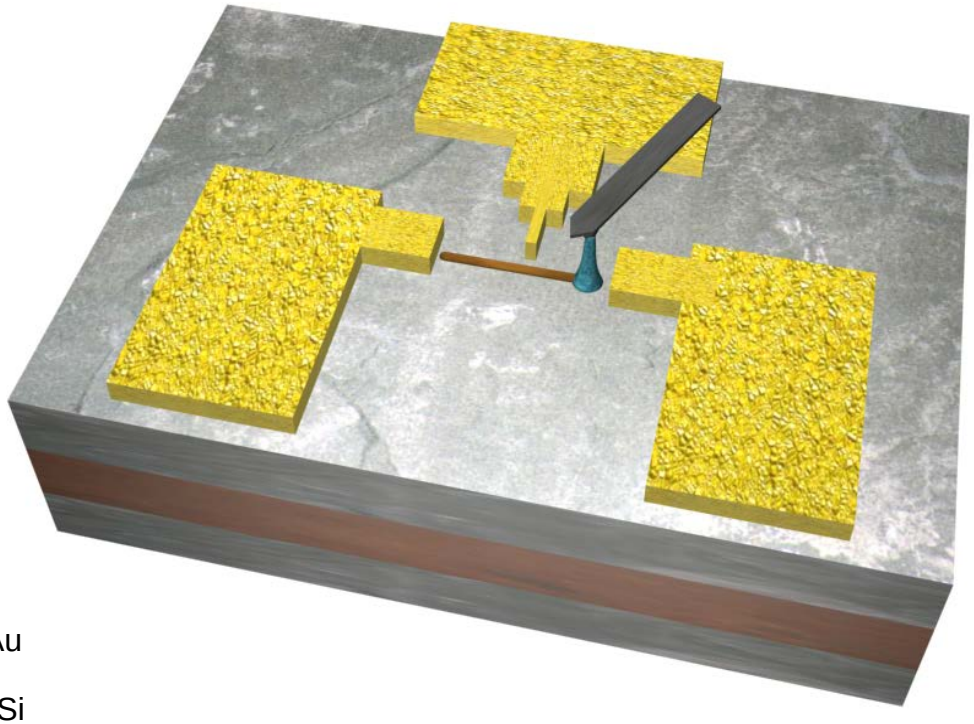
The oxide mask height is controlled by the voltage amplitude

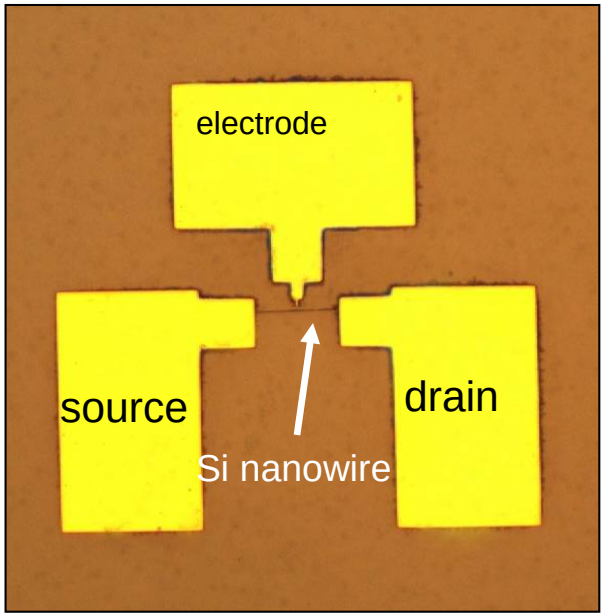
$$\textbf{\textit{Selectivity}} = \frac{\tan\theta_{nw}}{\tan\theta_{mask}} \approx 11$$

Y.K. Ryu et al. *Appl. Phys. Lett.* **104**, 223112 (2014)

Silicon Nanowires by Oxidation SPL

Steps:
1: SOI wafer, 2: Intitial metallization, 3: Oxide mask; 4: dry etching; 5: 2nd metallization



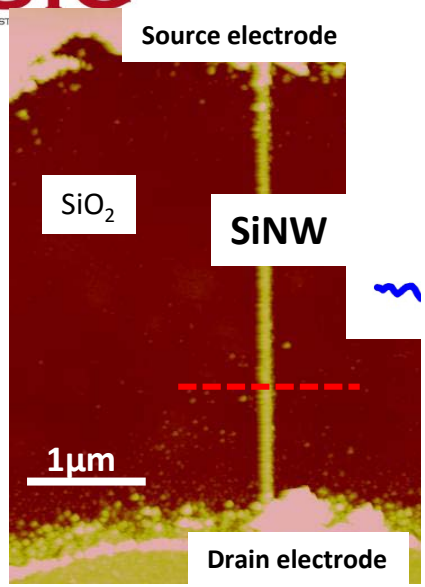


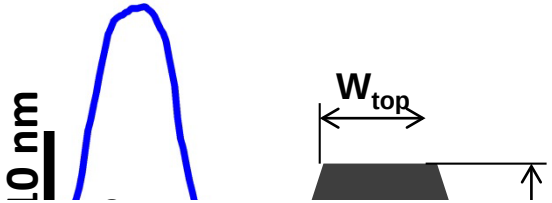
Au

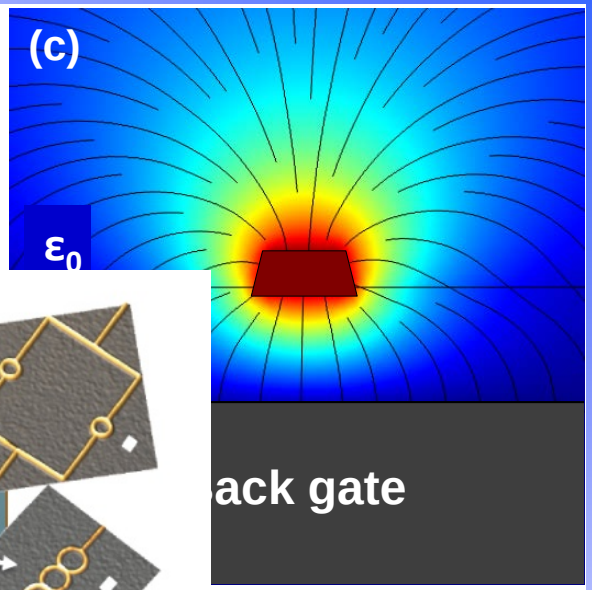
Si

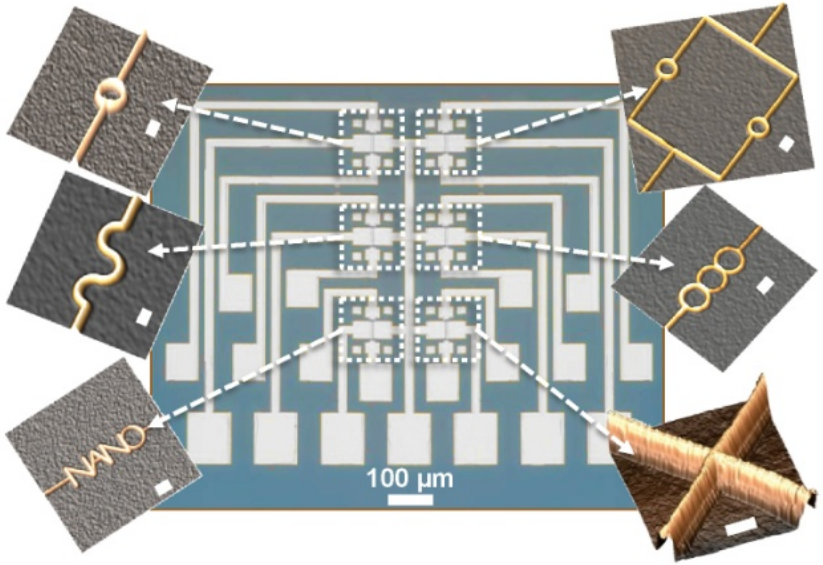
SiO_2

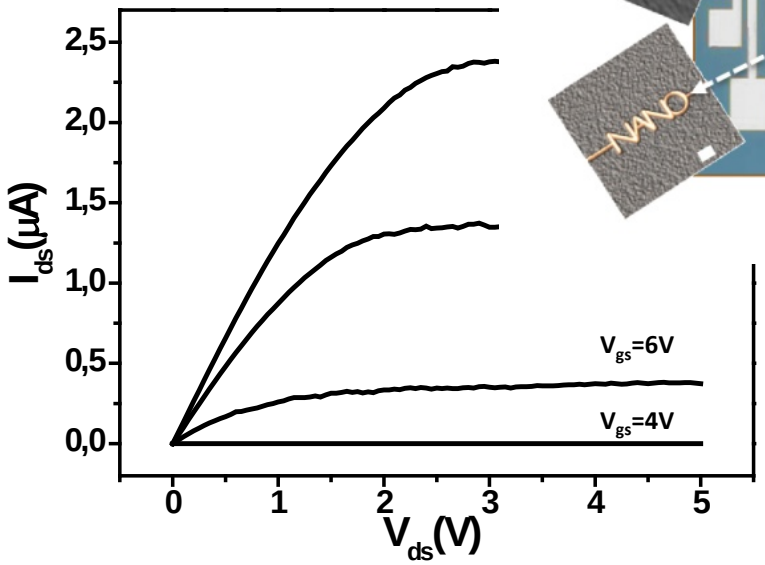
Y.K. Ryu, M. Chiesa, R. Garcia, Nanotechnology 24, 313205 (2013)
R.V. Martinez, J. Martinez, R. Garcia, Nanotechnology 21, 245301 (2010)
J. Martinez, R.V. Martinez and R. Garcia, Nano Letters 8, 3636 (2008)

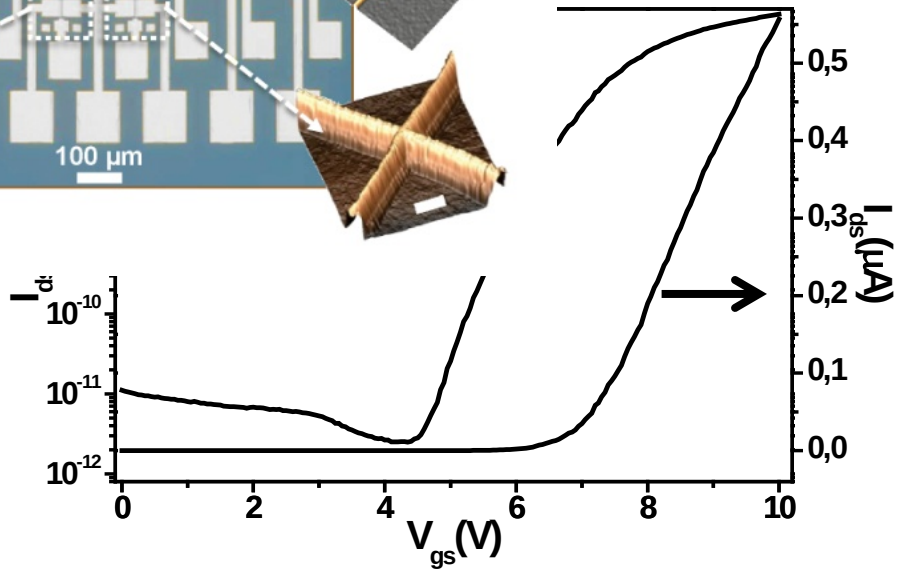








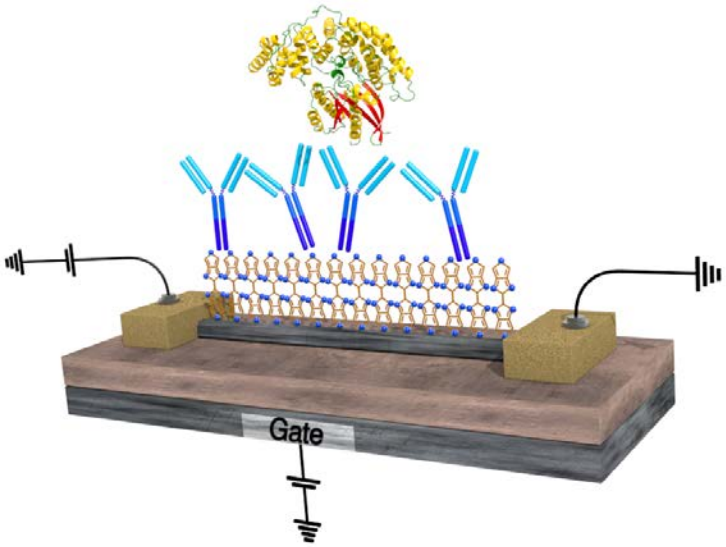


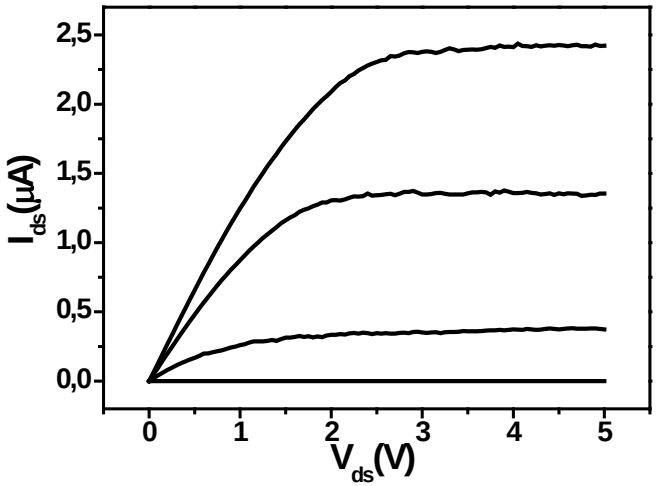


subthreshold swing is close to the theoretical limit for device of this geometry

electron mobility 230 cm^2/Vs

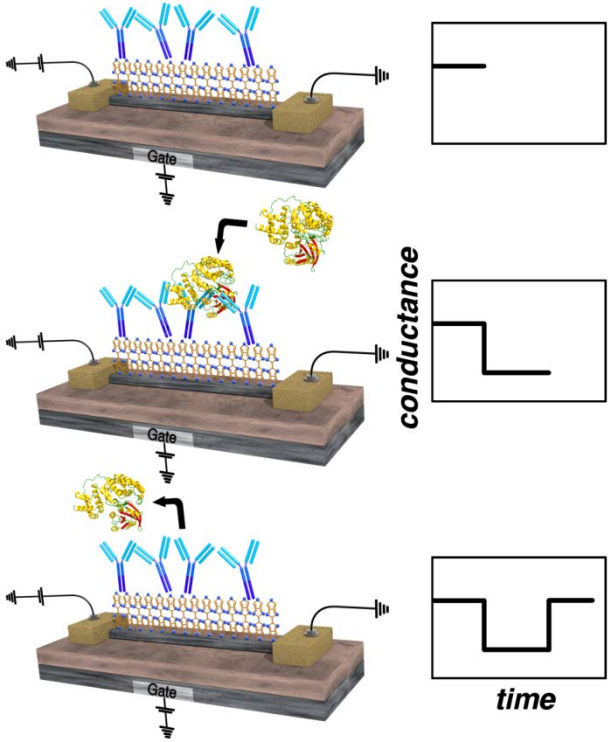
Transistor: three terminal device
Field-effect transistor: The current is modified by the electrical field of the gate





SiNW biosensors general sensing principle

the current measured is affected by the molecular interactions

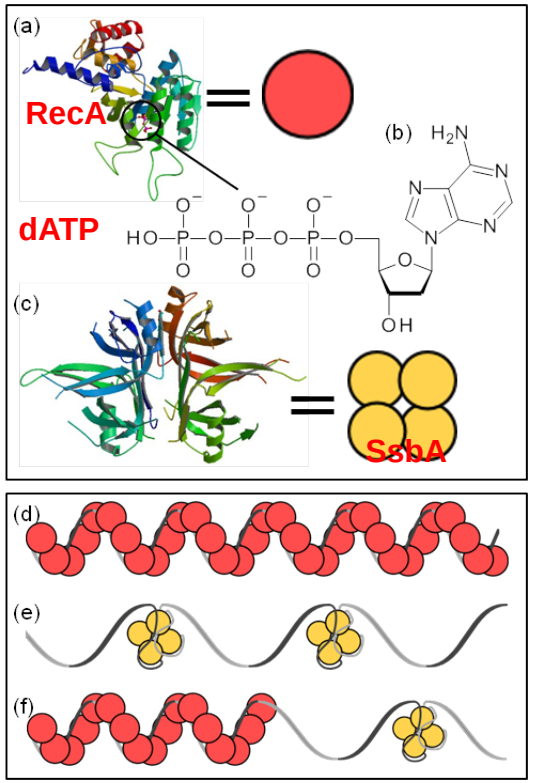


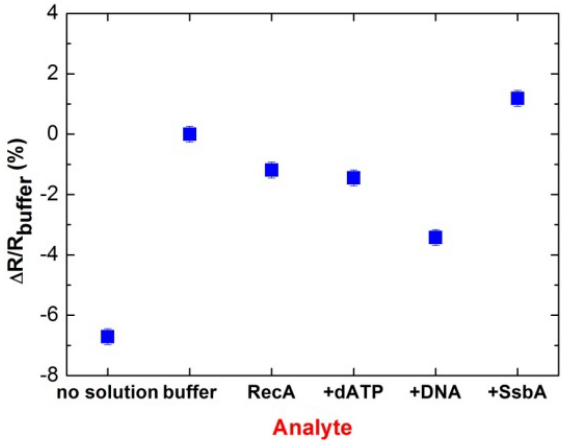
M. Chiesa et al. Nano Letters 12, 1275 (2012)

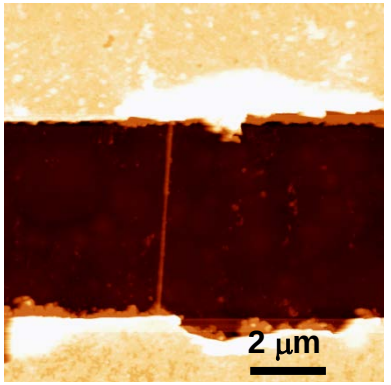
NANO LETTERS
Letter
pubs.acs.org/NanoLett
12, 1275-1281 (2012)

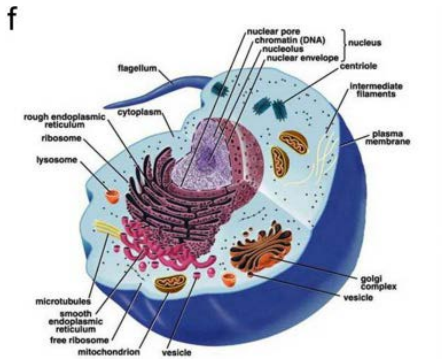
Detection of the Early Stage of Recombinational DNA Repair by Silicon Nanowire Transistors

Marco Chiesa,[†] Paula P. Cardenas,[‡] Francisco Otón,[§] Javier Martinez,[†] Marta Mas-Torrent,[§] Fernando Garcia,[†] Juan C. Alonso,[‡] Concepció Rovira,[§] and Ricardo Garcia*[,†]







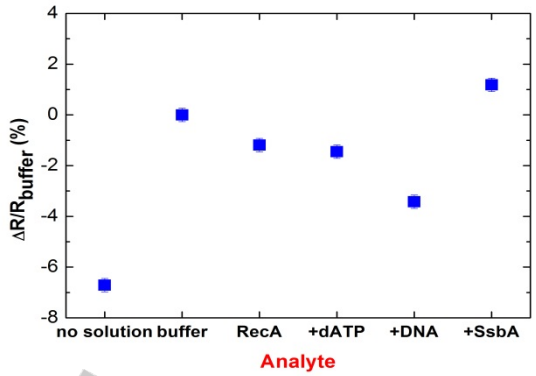


RecA forms a polymorphic right-handed helix around the DNA with approximately six monomers per helix turn

SsbA is a protein that competes with RecA for the binding sites along the DNA chain

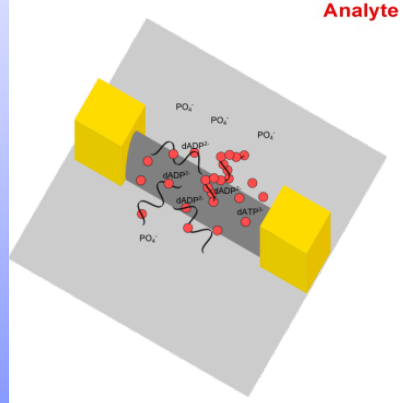
RecA: M_w = 38 kDa, d=27Å
SsbA: M_w = 18.8 kDa per subunit

Biosensing Principle

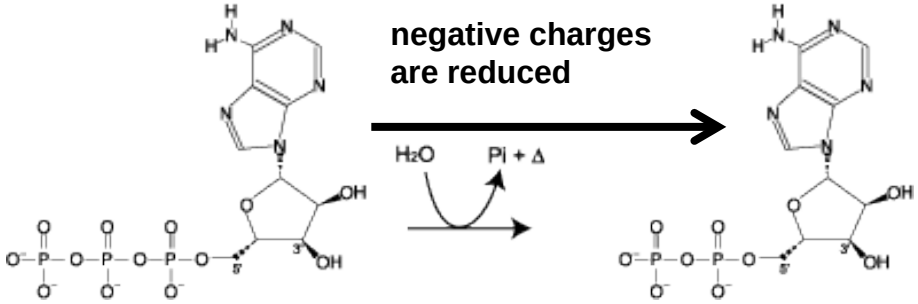


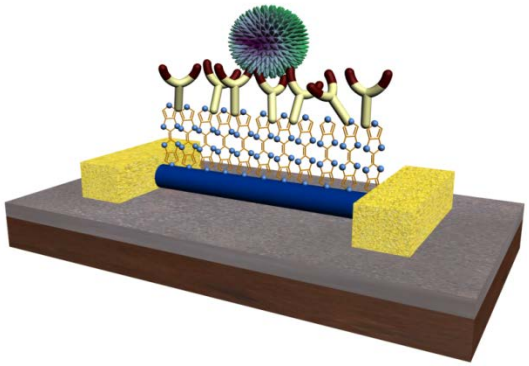
- SiNW measures changes in the resistance

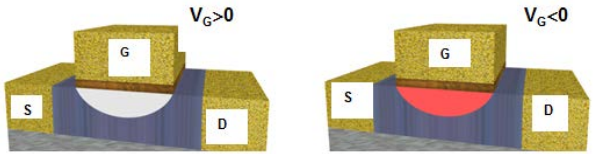
- The resistance of the SiNW is sensitive to changes in the charges in the nanowire-liquid interface



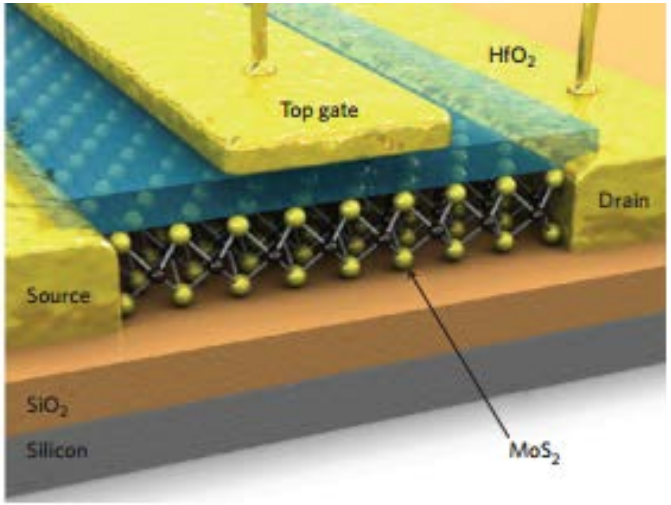
- The minimum in R is due to dATP hydrolysis (dADP+ Pi) This reaction reduces the negative charge surrounding the SiNW (like a positive gate)

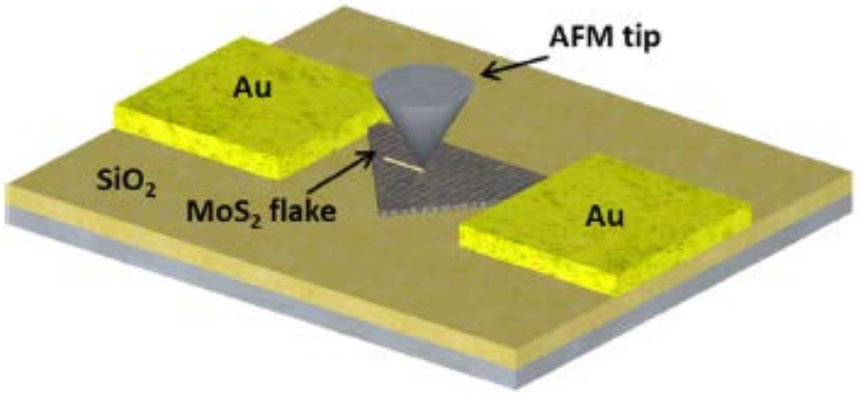


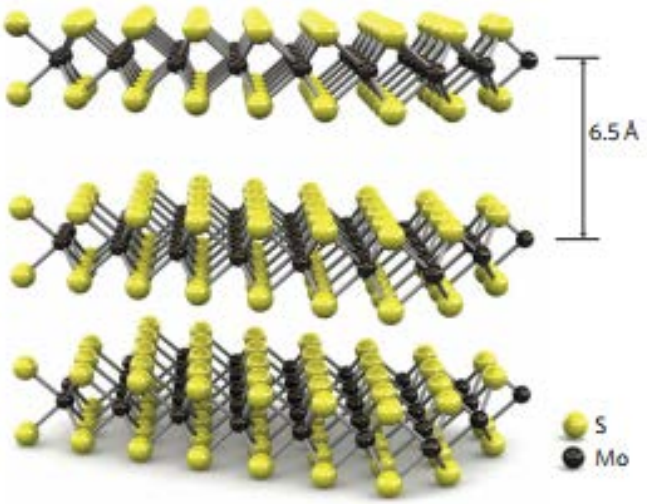


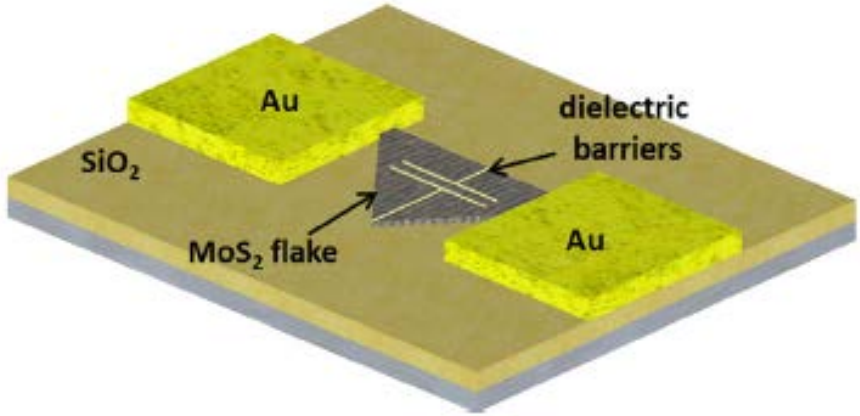


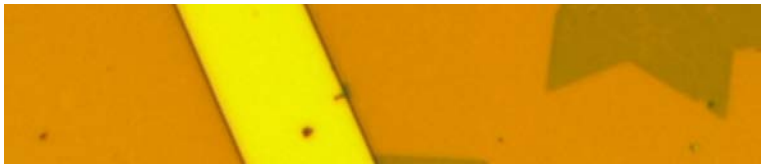
Direct fabrication of 2D Transition Metal Dichalcogenides devices: MoS_2



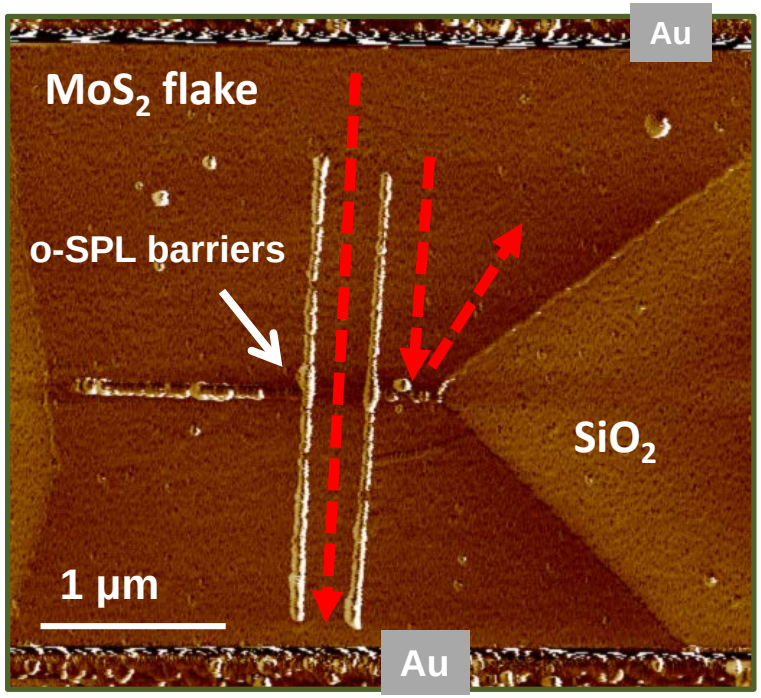


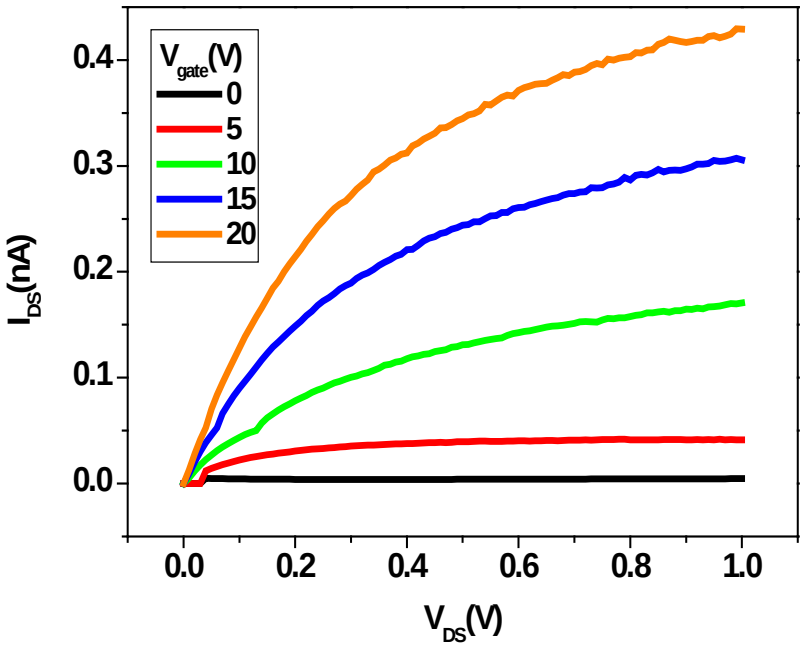




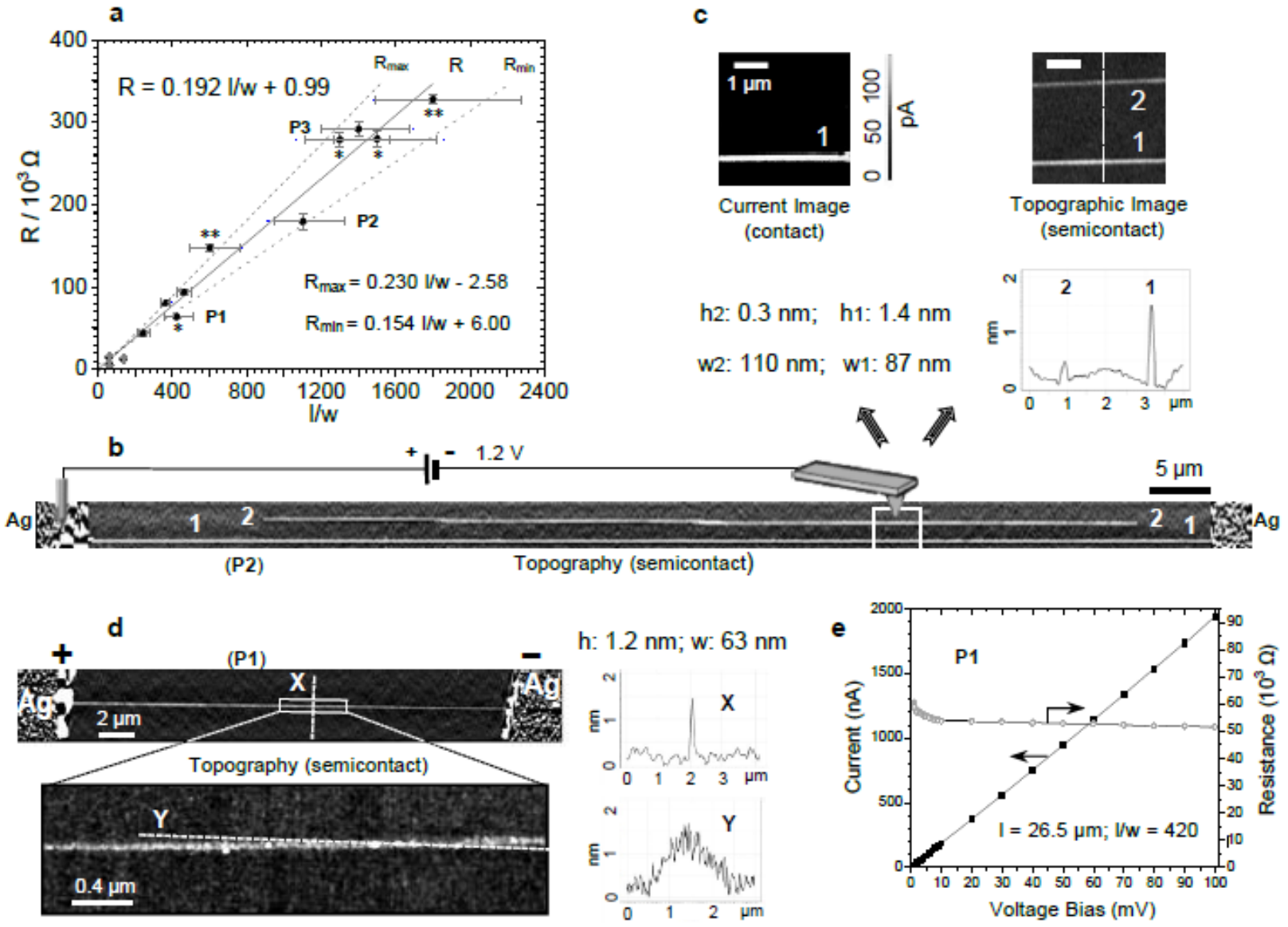


Electronics and optoelectronics of two-dimensional transition metal dichalcogenides, Qing Hua Wang,Kourosh Kalantar-Zadeh, , Andras Kis, Jonathan N. Coleman and Michael S. Strano. *Nature Nanotechnology* **7**, 699 (2012)



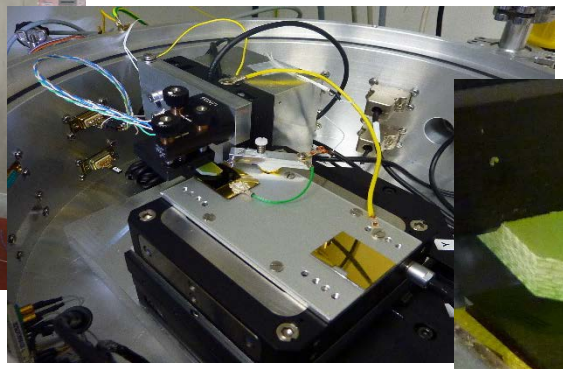


F.M. Espinosa *et al.* APL **106**, 103503 (2015)

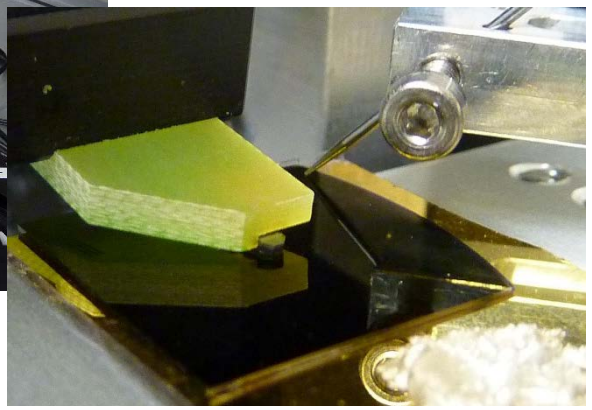

a
R = 0.192 l/w + 0.99
R_max
R
R_min
P1
P2
P3
R_max = 0.230 l/w - 2.58
R_min = 0.154 l/w + 0.00
R / 10^3 Ω
l/w
b
+
-
1.2 V
5 μm
Ag
Ag
1
2
2
1
(P2)
Topography (semicontact)
c
1 μm
1
0 50 100 pA
Current Image (contact)
2
1
Topographic Image (semicontact)
h2: 0.3 nm; h1: 1.4 nm
w2: 110 nm; w1: 87 nm
nm
μm
d
+
(P1)
-
Ag
Ag
X
2 μm
Topography (semicontact)
Y
0.4 μm
h: 1.2 nm; w: 63 nm
X
Y
nm
μm
e
P1
Current (nA)
Resistance (10^3 Ω)
l = 26.5 μm; l/w = 420
Voltage Bias (mV)

Thermal Scanning Probe Lithography: The set-up

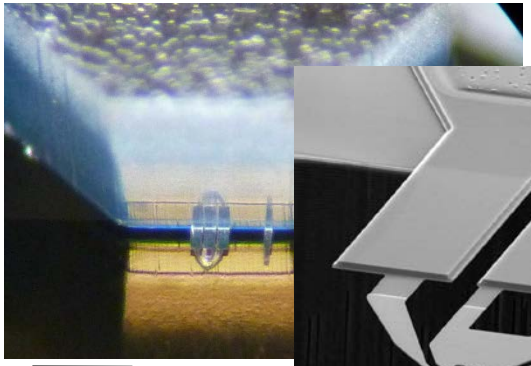
50 cm



3 cm

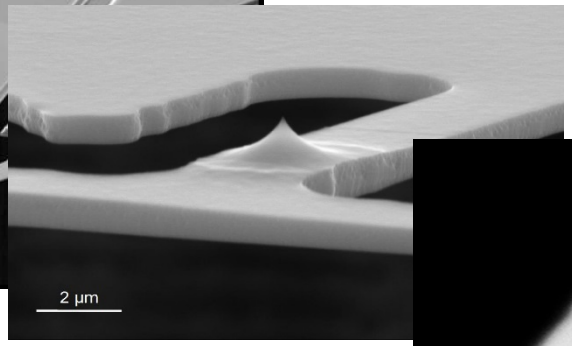


5 mm

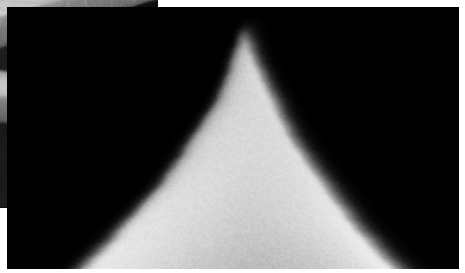


0,2 mm

0,03 mm



0,002 mm

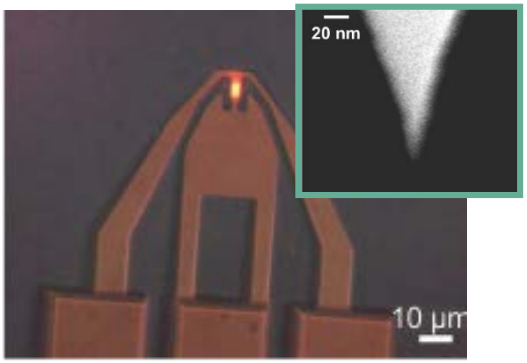


0,00005 mm = 50 nm

Thermal Scanning Probe Lithography: Method

Silicon cantilever

- Microheater: 2x4 µm²
- → up to 1000 ºC heater T

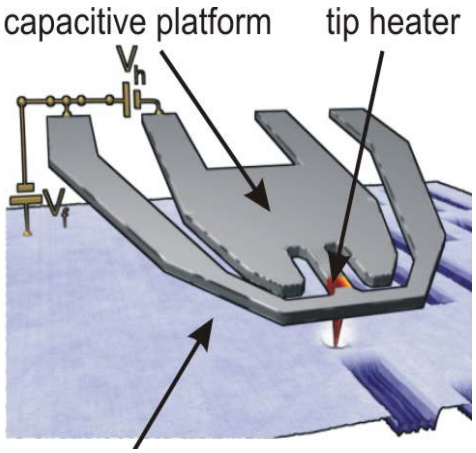


- Stiffness ~ 1 N/m
- Resonance frequency 150 kHz

Writing

Heated tip evaporates resist

D. Pires et al., *Science,* **328**, 732-735 (2010)



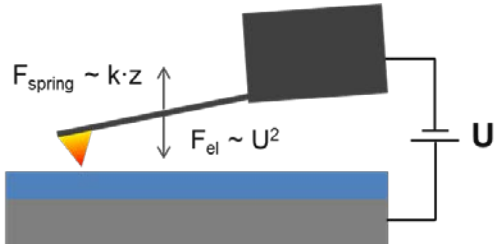
Thermal sensor for height signal

Wear less imaging:
AC modulation >1 MHz

A. Knoll et al., *Nanotechnology,* **21**, 185701 (2010)

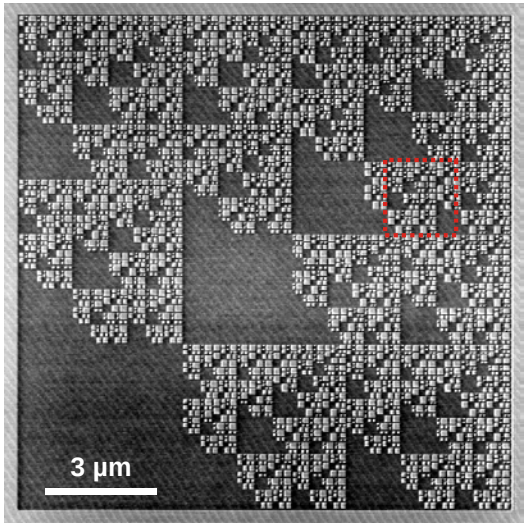
Force control

- electrostatic actuation (~1 µs pull-in time)



High speed patterning

880x880 pixels in 11.8s

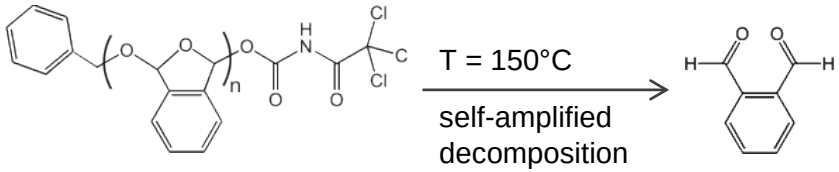


500 kHz pixel clock

A. W. Knoll et al., *Adv. Mater.,* **22**, 3361-3365 (2010)

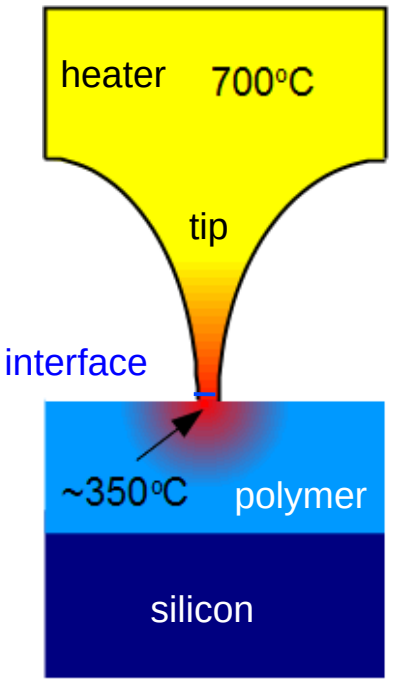
Resist

Unzipping polymer PPA (polypthalaldehyde)



Coulembier et al., *Macromolecules*, **43**, 572-574 (2010)

Thermal Cascade



T_{heater}

$T_{polymer}$

~ 350°C

RT

Limitation in heater temperature:
Dopant diffusion vs. Silicon diffusion
→ Phosphorous

Thermal bottleneck:
Assumptions:
5 nm silicon tip, opening angle 30...60°
Result:

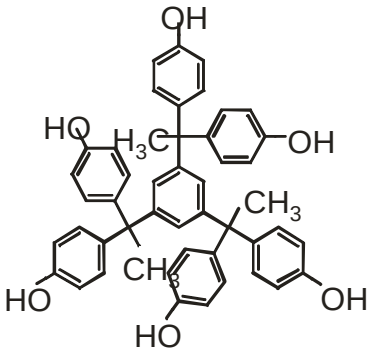
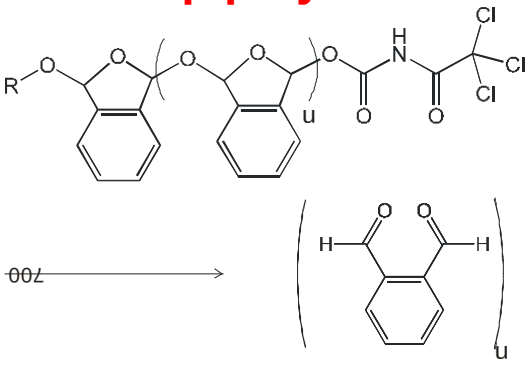
- $T_{polymer}$ ~ 0.3...0.6 T_{heater}
- $T_{polymer,max}$ ~ 300-400°C

Chemical reaction:
thermally activated process ←→
time temperature superposition

1 s to 1 µs → ΔT ~ 200°C !

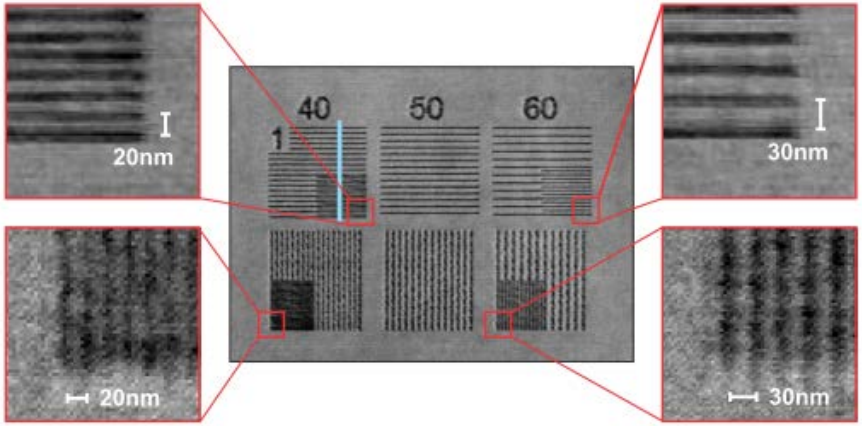
Thermally sensitive material required !
T_{conv} ~ 150..200 C

Material Strategy

	Molecular glass	Unzip polymer
		 Polyphthalaldehyde (PPA)
▪ **Efficient thermally activated process** – Thermal process active at ~ 150 C	• M_w = 715 g/mol • physical inter-molecular bonds • **complete molecules are removed**	• thermodynamically unstable backbone • synthesis at -78 °C • **unzips into monomers upon bond breakage**
▪ **Stability** – Imaging and etching	• H-bonds: Tg 126 °C A. De Silva; J. Lee, X. André, N. Felix, H. Cao, H. Deng & C. Ober *Chem. Mater.,* ***20***, 1606 (2008)	• Tg ≈ Tunzip ≈ 130 °C H. Ito, C. G. Willson, *Technical Papers of SPE Regional Technical Conference on Photopolymers, 1982, 331*

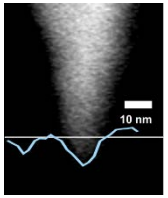
Features of tSPL

Resolution: 10 nm HP



Depth: 4 nm

Corresponds to tip shape:



Features:

Resolution: ~ 10 nm

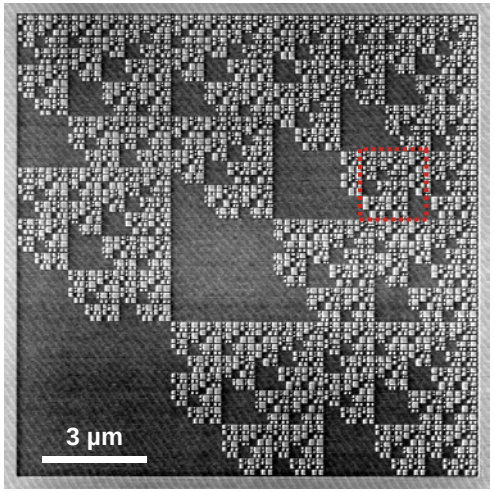
Speed:

→ 500 MHz imaging (2 us pixel time)

→ 666 kHz imaging (1.5 us pixel time)

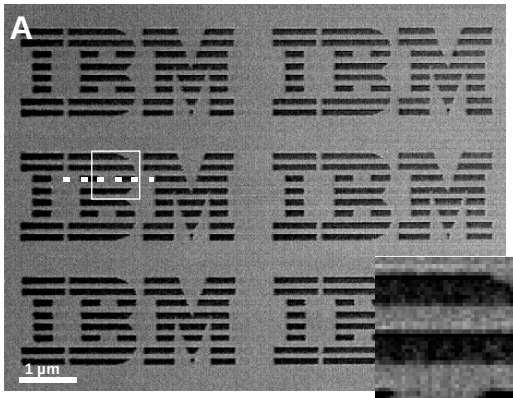
Resonance frequency : 150 kHz

500 kHz patterning

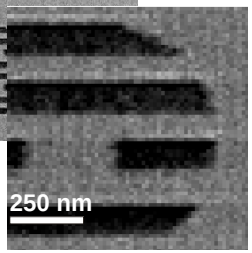


Fractal pattern
Size 13x13 µm²
7.5 mm/s
880x880 pixels
Write duration: 11.8 s

666 kHz imaging



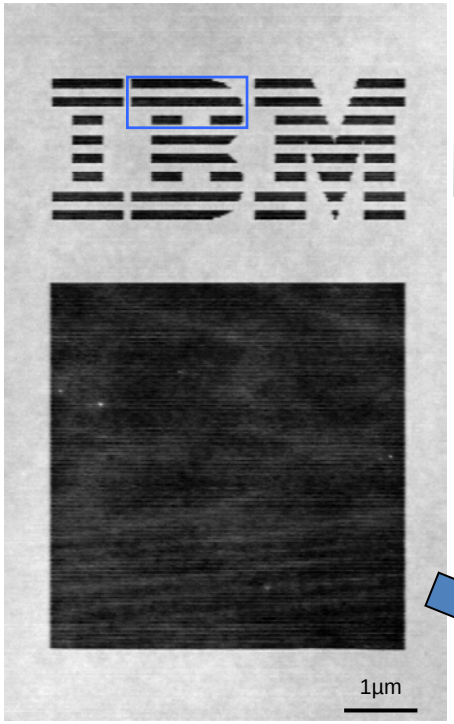
- **Size: 1500 x 1500 pixels**
- **Imaging duration: 27 s**



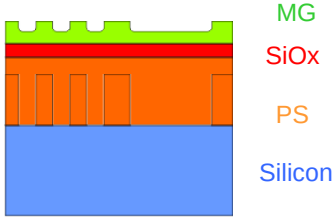
Deconvoluted image

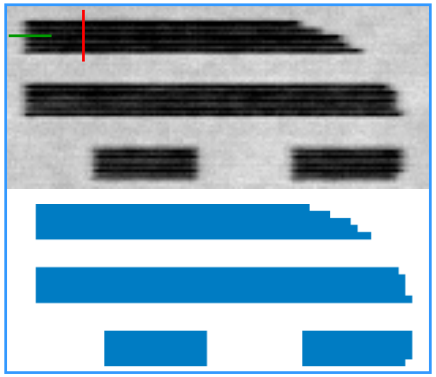
Paul et al., *Nanotechnology* 22, 275306 (2011).

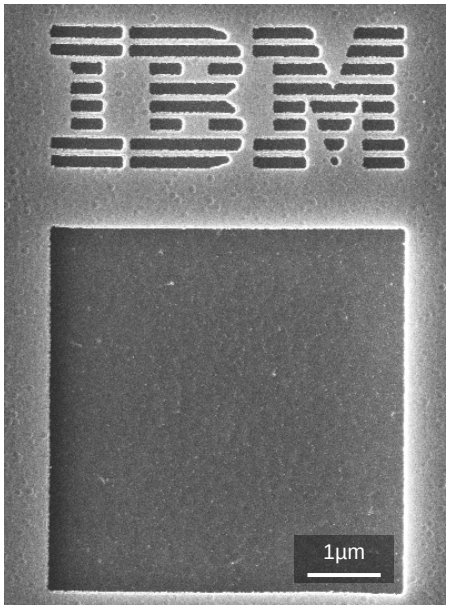
Molecular Glass: Patterning Results



Transfer
by RIE

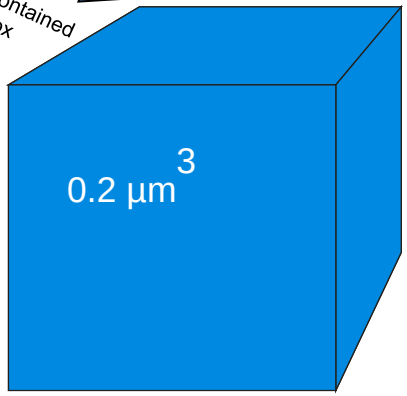




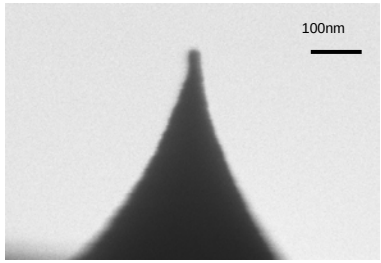


Pattern in Si after transfer:
400 nm depth (50x)

Material contained in box



Tip after patterning
several fields:
same scale:

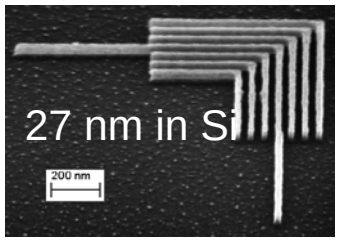


SEM of the tip
after $2 \cdot 10^5$ written pixels

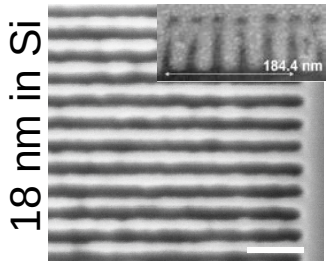
Pitch 29 nm
8 nm depth

Parameters:
Pixels: $4\ 10^4$
Heater temperature: 300°C
Load force: 80nN
Pulse duration: 5.5µs

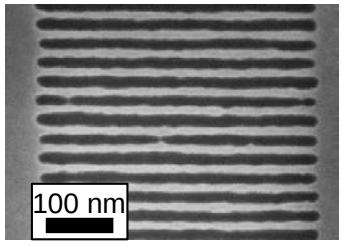
Half Pitch Resolution after Pattern Transfer: Progress since 2013



Transfer stack:
20 nm PPA
4 nm SiO2
50 nm HM

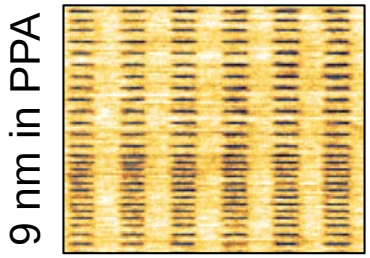


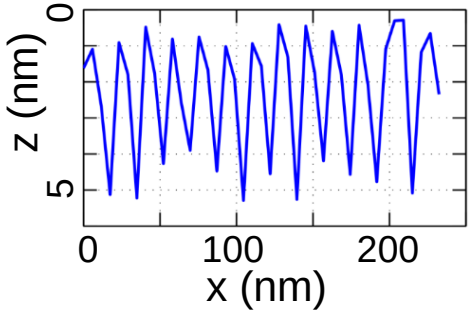
9 nm PPA
3 nm SiO2

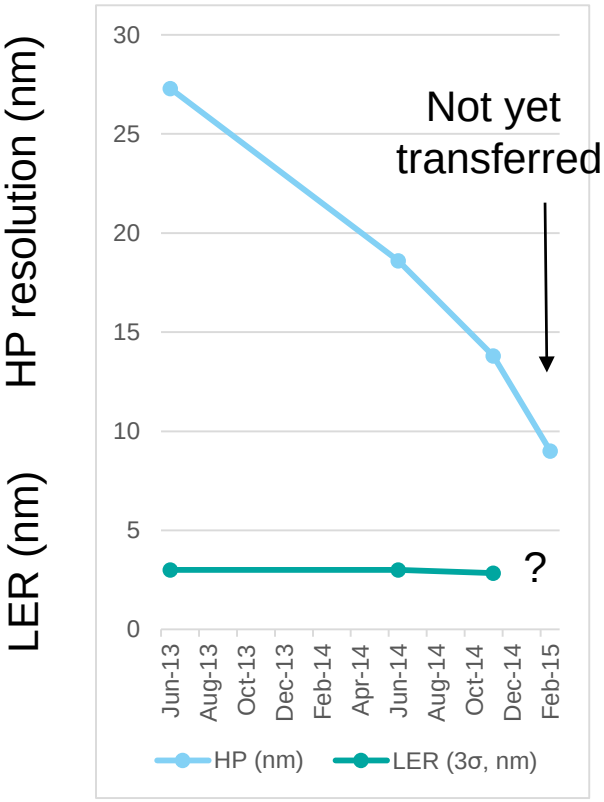


14 nm in HM (30 nm)

2 nm SiO2
30 nm HM





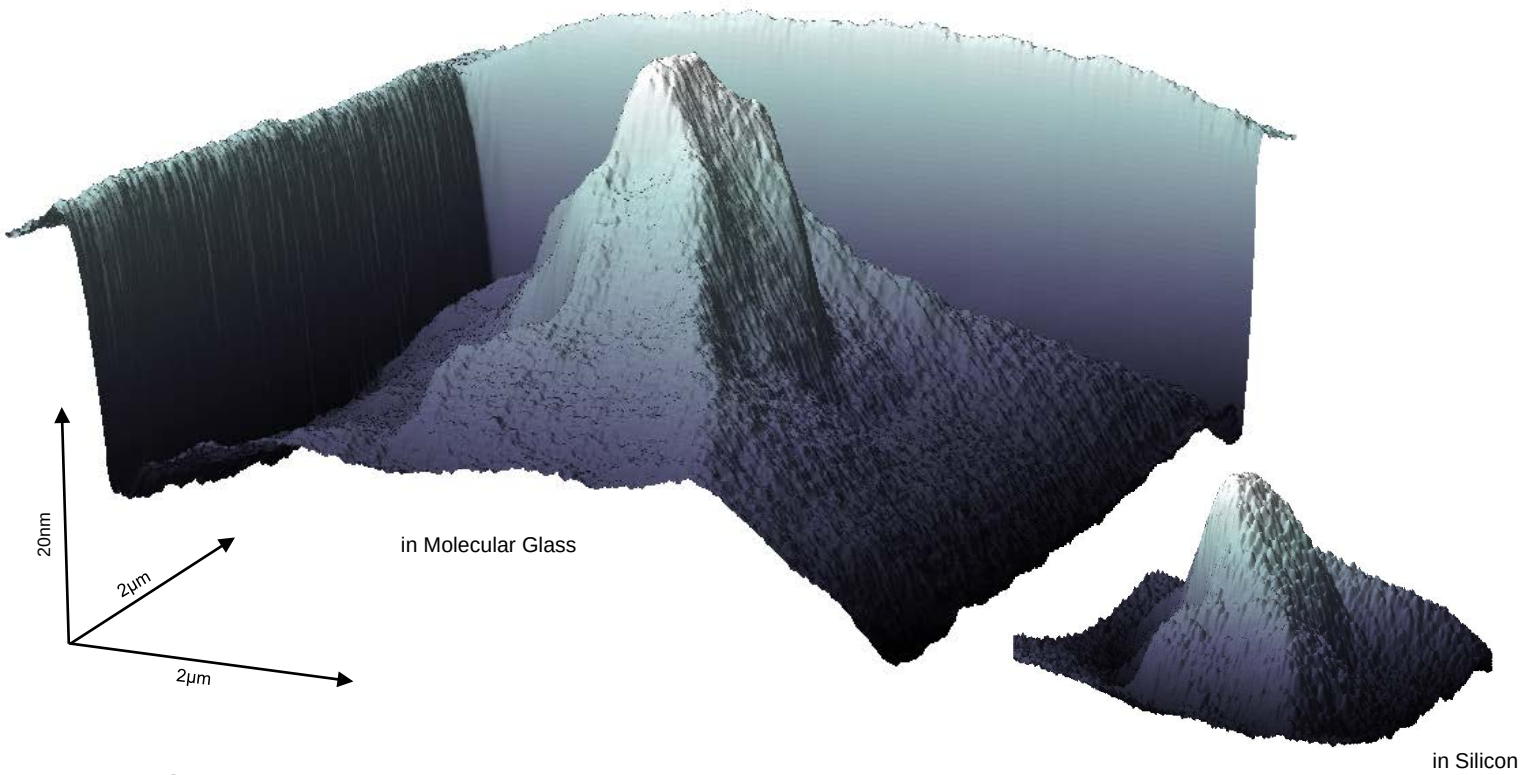


[1] L. Cheong et al., *Nano Lett.,* **13**, 4485 (2013). [2] Wolf et al., *J. Vac. Sci. Technol. B*, 33, 02B102 (2015).

Molecular Glass: Complex 3D-Structures

(photographer: Marcel Wiesweg; source: Wikimedia)

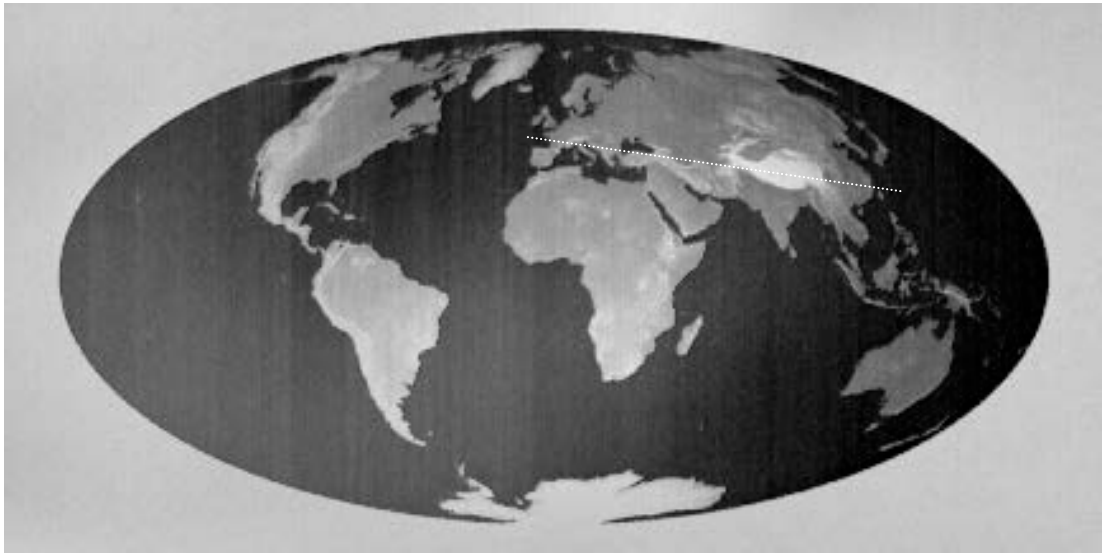
- *Matterhorn* (Swiss Alps)
  Topographical data from geodata © Swisstopo
- Multilevel patterning
  - 120 levels

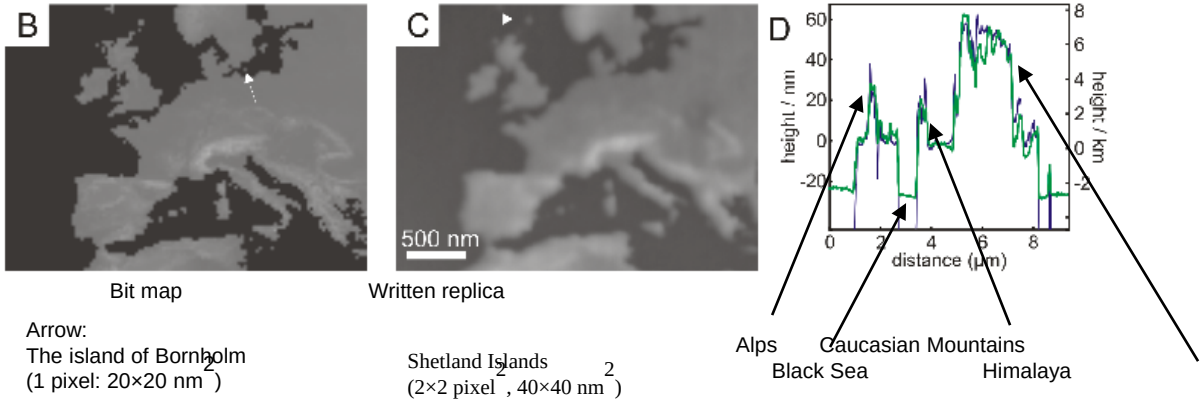


D. Pires et al. , *Science*, ***328***, 732 (2010)

3-D Direct Writing Using Unzip Polymers

Adapted from GTOPO30, U.S. Geological Survey, http://eros.usgs.gov



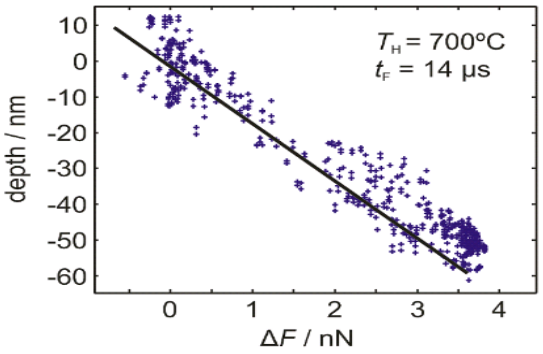


Bit map

Written replica

Arrow:
The island of Bornholm
(1 pixel: 20×20 nm^2)

Shetland Islands
(2×2 pixel^2, 40×40 nm^2)



Patterning depth controlled by writing force
→ **direct writing of 3D relief structures in one shot**

World Map:
250 nm of SAD polymer on Si

5×10^5 pixels

60 µs pixel

Total patterning time 143 s

A.W. Knoll et al., *Adv. Mater.*, ***22***, 3361, (2010)

Photo portrait Area= 6 cm^2

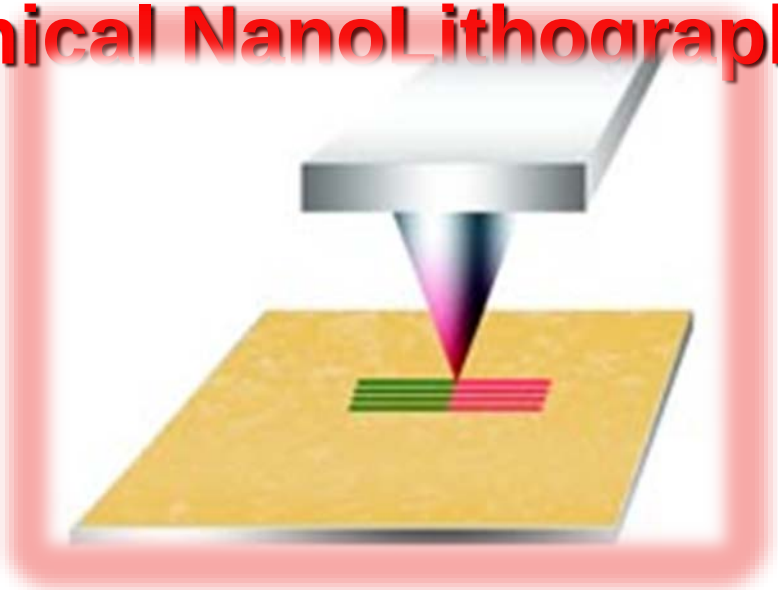
Richard Feymann

Scanning probe lithography pattern and image: Area= 12x10^{-8} cm^2

A. W. Knoll,

R. Garcia, A. Knoll, E. Riedo, Nature Nanotechnol. 9, 577 (2014)

ThermoChemical NanoLithography (tc-SPL)

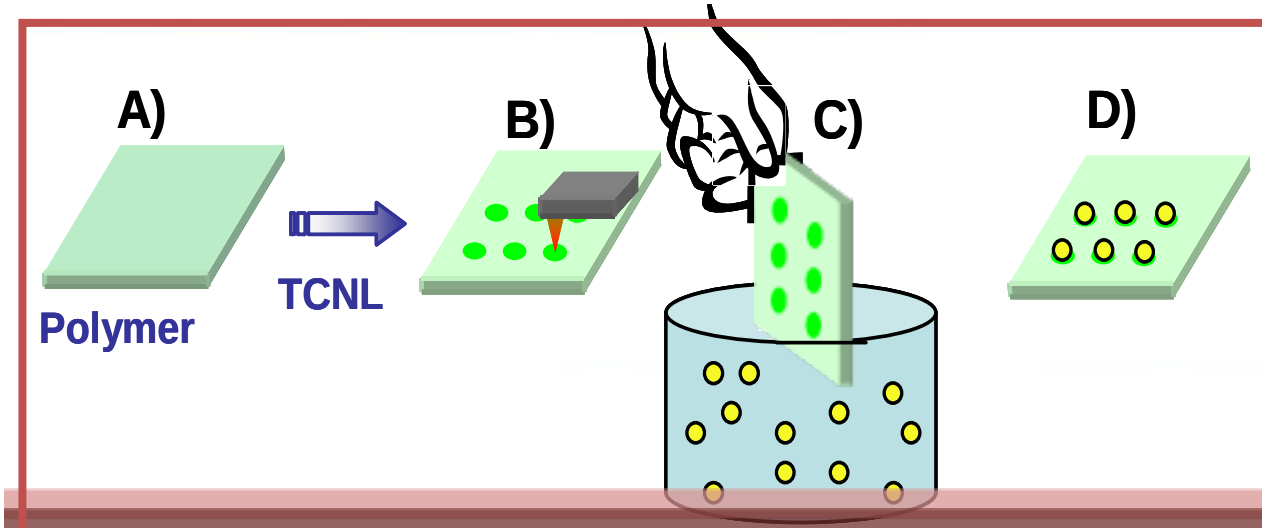


Elisa Riedo,
Georgia Institute of Technology

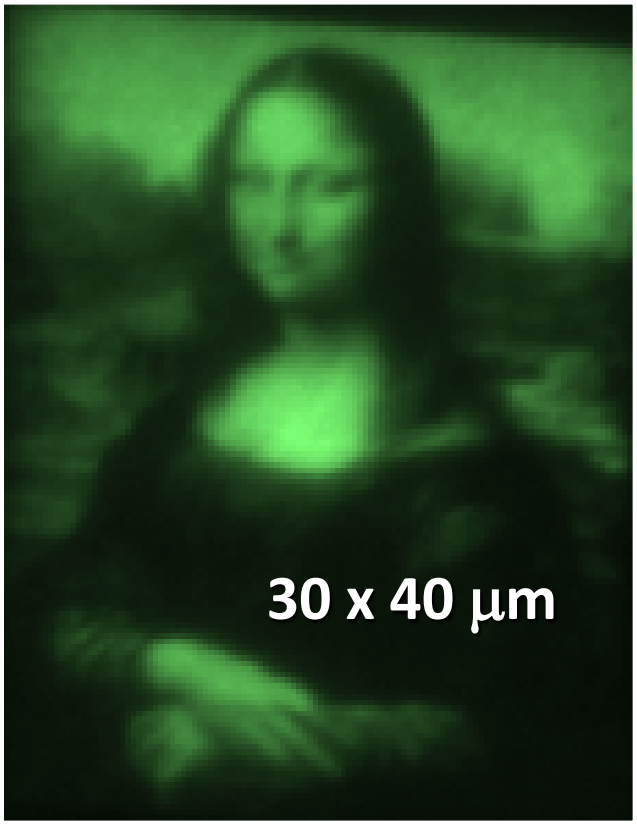
ThermoChemical Nanolithography (tc-SPL):
Local Thermal Activation of a Chemical Reaction

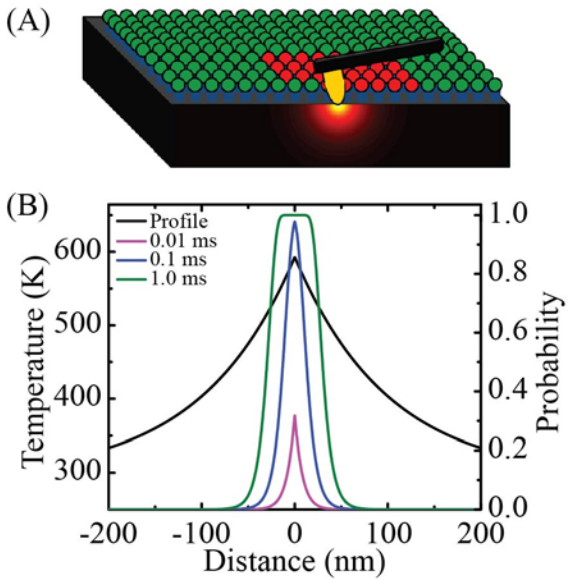
- **High resolution control of topography (from nm to mm)**
- **Unprecedented control of chemistry and function at nm-scale**

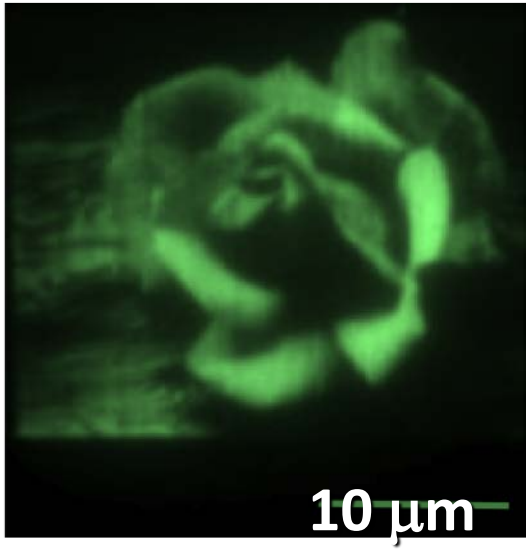
Wetting and Chemical Functionality



Nanoscale Chemical Gradients







$$\frac{dP}{dt} = k(P_0 - P)$$

$$k = A \cdot e^{\frac{-E_A}{RT}}$$

T(*x*,*y*)

Fluorescent image

Complex Gradients → Functional Gradients

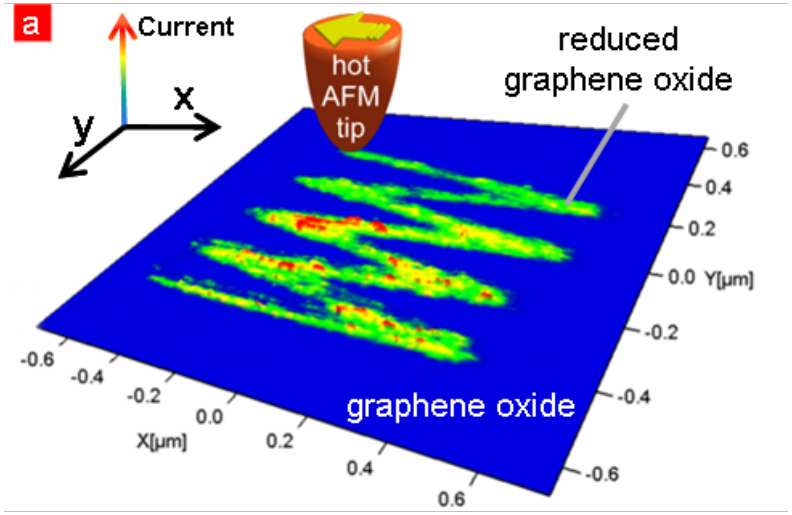
Eg. Wetting gradient, protein gradients…

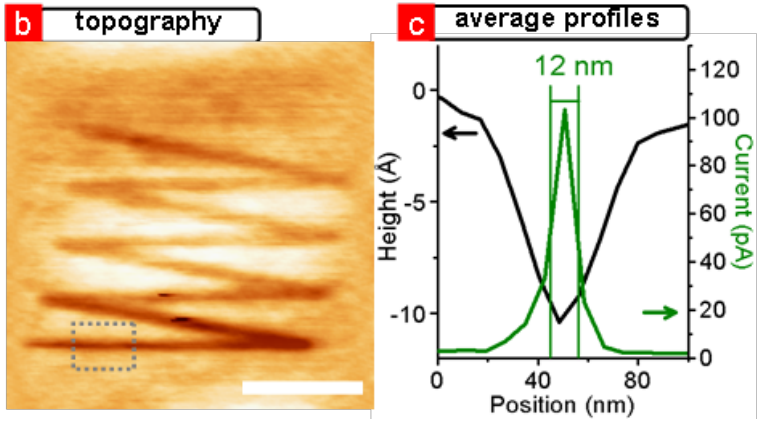
Thermal activation leads to cleavage of tetrahydropyran and carbon dioxide to expose amines

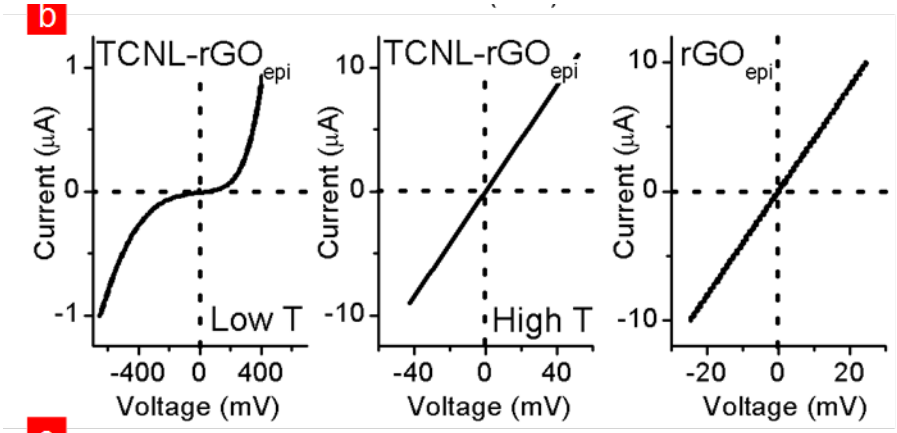
Carroll et al. *Langmuir* 29, 8675 (2013).

tc-SPL to perform Nanoscale tunable reduction of graphene oxide

E. Riedo







c

Micro 4-point transport measurement and KPFM data

Sample	R_{sheet}	Δ Φ
EG	50 ± 50 Ω	290 ± 60 mV
GO_{epi}	427 ± 10 MΩ	0
$TCNL\text{-}rGO_{epi}$ Low T	9174 ± 2 KΩ	N/A
$TCNL\text{-}rGO_{epi}$ High T	30 ± 3 KΩ	168 ± 50 mV
rGO_{epi}	18 ± 10 KΩ	188 ± 90 mV

Scanning Probe Lithographies

Variety of approaches
Research friendly
Incorporates Intrinsic metrology

o-SPL Advantages

- Direct nanopatterning of materials
- Applicable to many materials: semiconductors, metals, organics, biomolecules
- Low-cost approach for nanoscale device fabrication

Limitations

- Extensive patterning requires the use of several tips (slow)

t-SPL Advantages

- Fast writing and large areas
- 3D nanoscale patterning

Limitations

Requires specific cantilevers

Requires resist

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J. Martinez

R.V. Martinez

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Concepció Rovira, ICMB-CSIC

Single Nanometer Manufacturing for beyond CMOS devices (SNM)

Funded by the European Union

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MINISTERIO DE CIENCIA E INNOVACIÓN