Advanced Scanning Probe Lithographies

i). Scanning Probe Lithography/ies

Force Microscope
Context
NanoLithographies

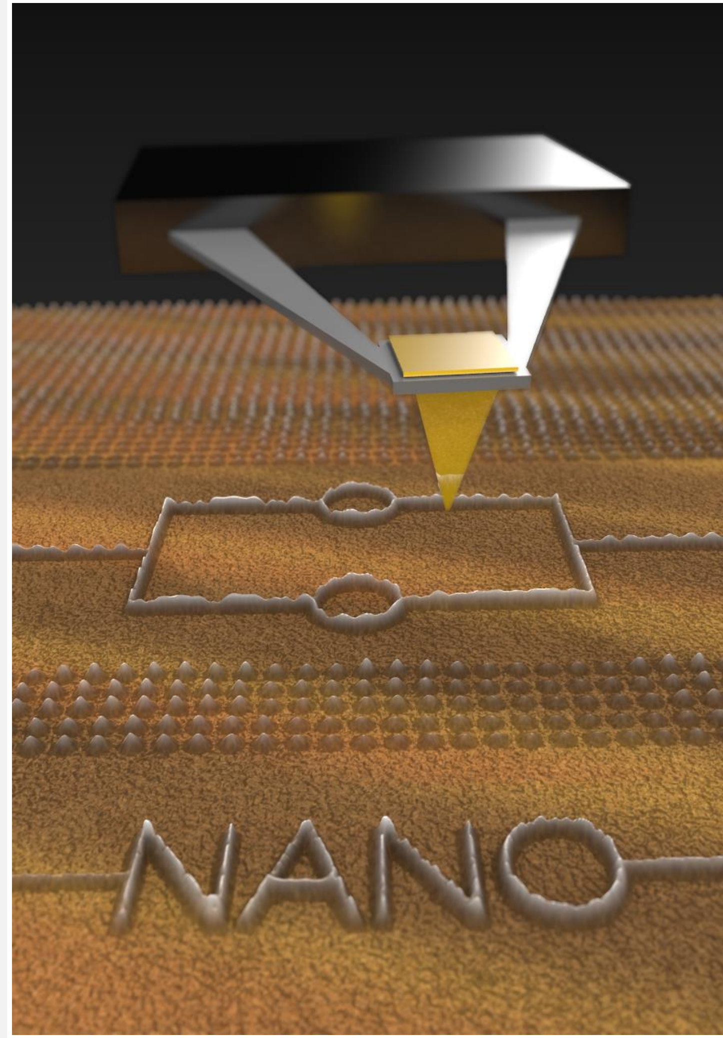
a. oxidation SPL

Principles
Protein & soft matter patterning
Patterning 2D materials
nanoscale FET transistors

b. thermal and thermochemical SPL

3D Patterning
Graphene transistors

iv). Summary



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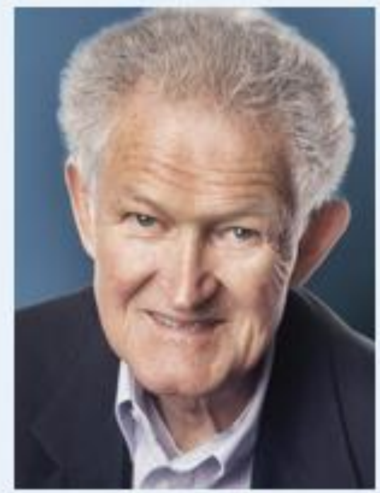
VOLUME

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

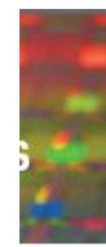
Christoph Gerber
University of Basel, Switzerland



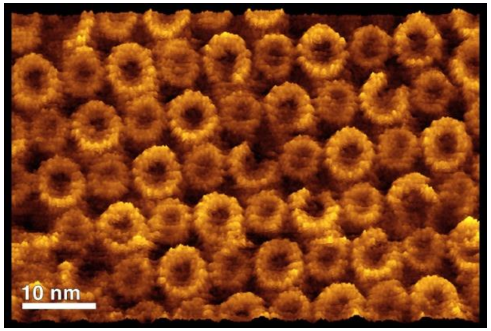
Calvin Quate
Stanford University, USA

Top

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

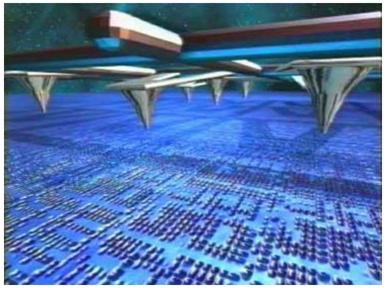


Wood, J. The top ten advances in materials science. *Mater. Today* **11**, 40 (2008).
Ball, P. Material witness: Greatest hits. *Nature Mater.* **7**, 102 (2008).



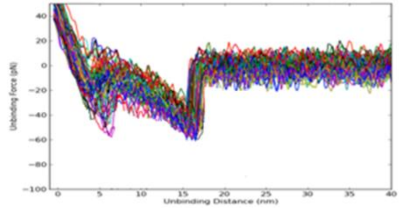
Molecular motors, H Seelertet, A. Engel, D.J. Muller (2000)

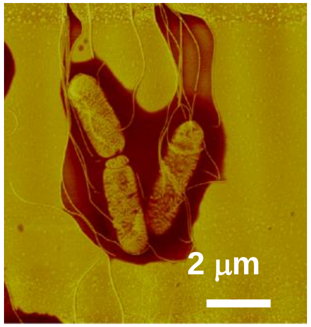
Polymers, R. Magerle (2004)



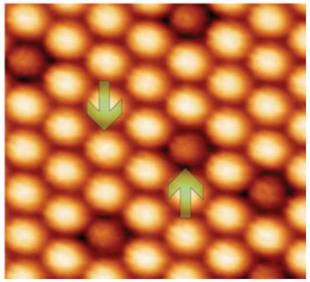
Nanopatterning, G. Binnig (1999)

Force spectroscopy

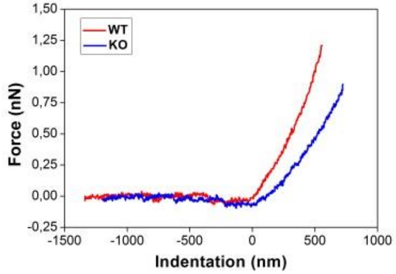


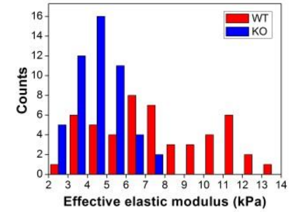


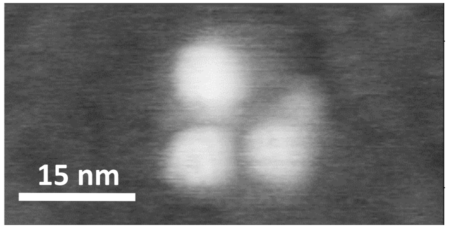
Cells, R. Acvi (2007)



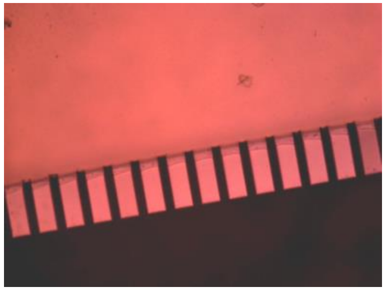
Atom identification, O. Custance, S. Morita et al. (2007)



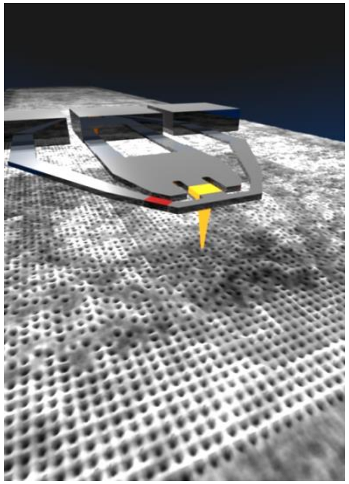




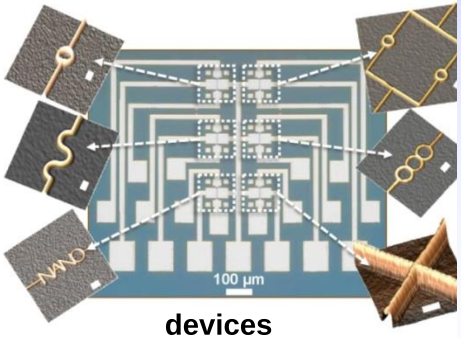
Antibodies, A.S. Paulo, R. Garcia (2000)



Nanomechanical sensors J. Tamayo (2007)



Probe lithography

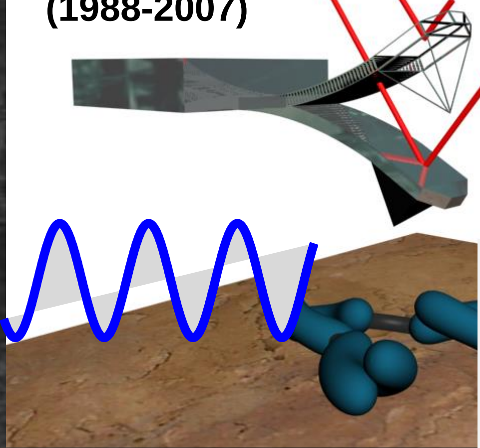


devices

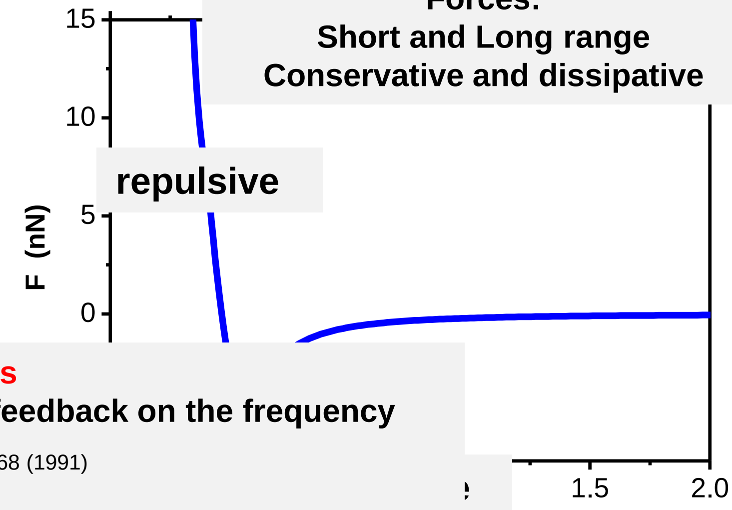
Dynamic AFM:

amplitude, frequency, phase shift

(1988-2007)



Forces:
Short and Long range
Conservative and dissipative



Two main dynamic AFM modes

Frequency Modulation AFM **feedback on the frequency**

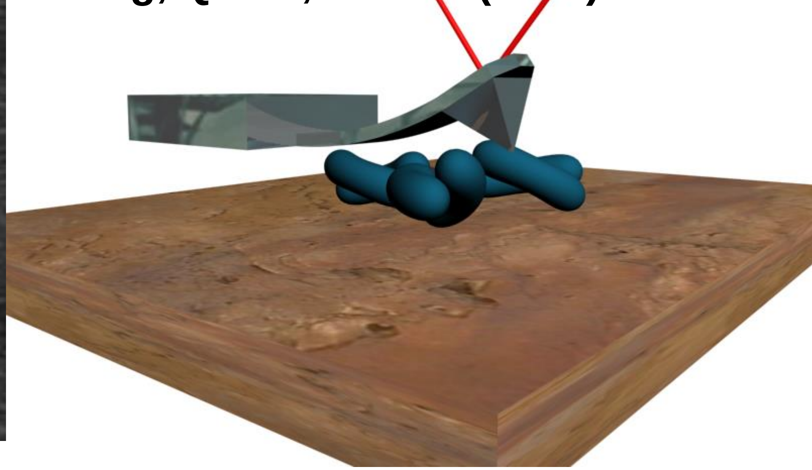
T.R. Albrecht, P. Grütter, D. Rugar, JAP 69, 668 (1991)

Amplitude Modulation AFM **feedback on the amplitude**

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

Contact : static deflection, *F=kΔz*

Binnig, Quate, Gerber (1986)



Contact AFM

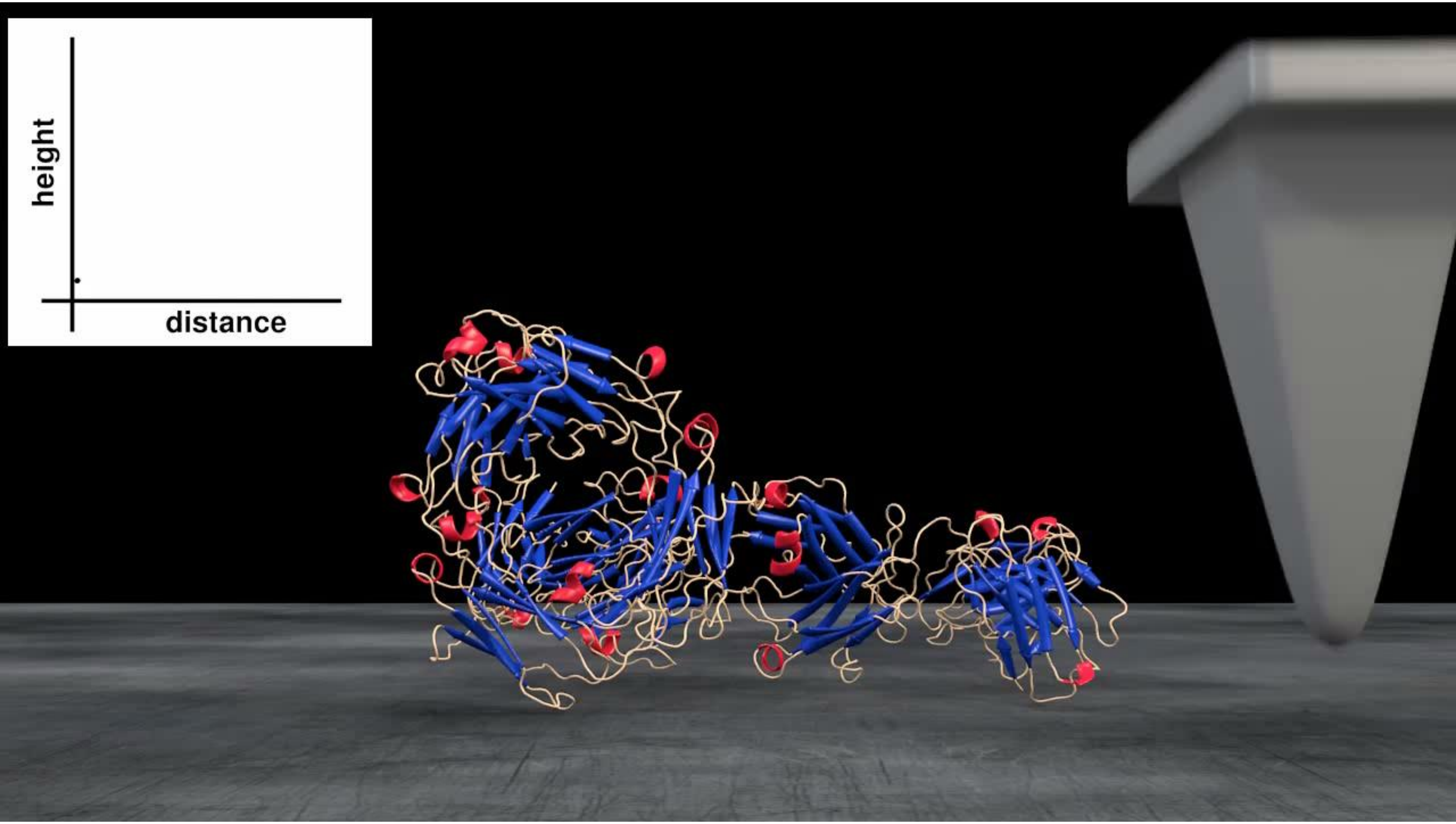
- **a single observable**
- **hard to control the force**

Dynamic AM methods

- **multiple data acquisition**
- **different feedback controls**
- **better control of the force**
- **fast**

Amplitude modulation AFM (tapping mode AFM):

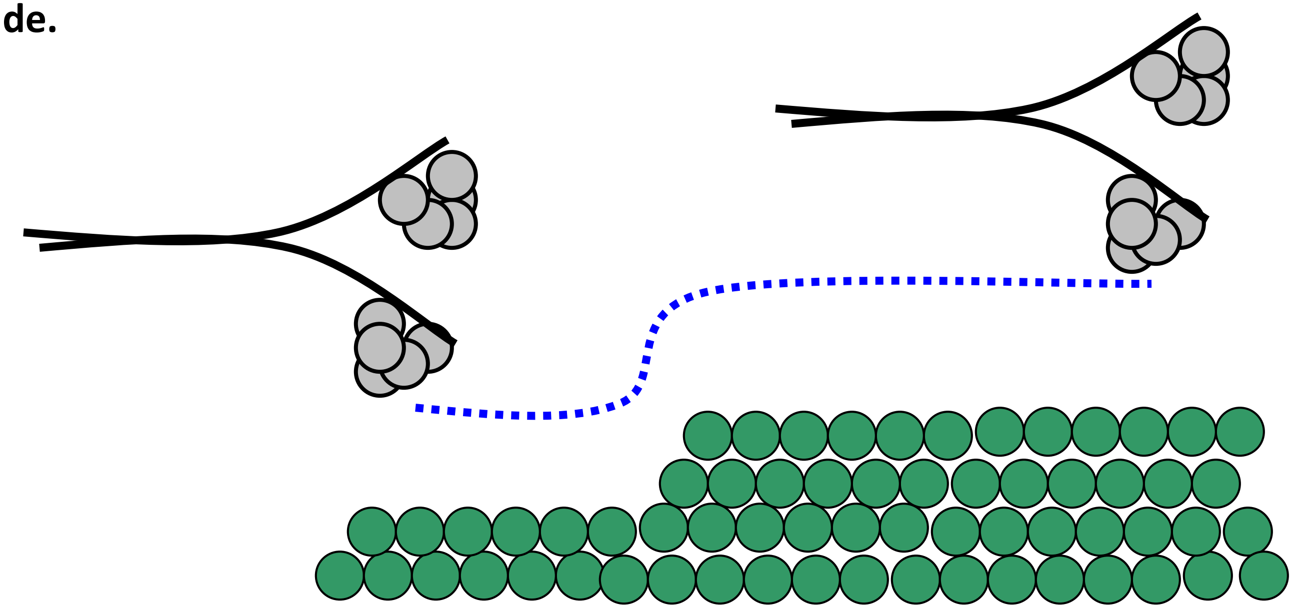
an image is formed by scanning the tip across the surface at a fixed oscillation amplitude.



R. Garcia, Amplitude modulation atomic force microscopy, Wiley 2011

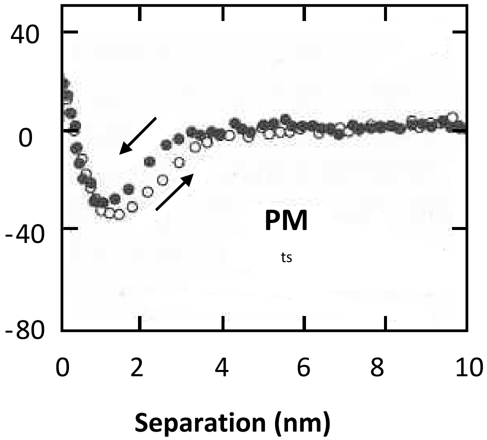
An image is acquired by displacing the tip across the sample and keeping one or severables observables at a fixed value (amplitude, frequency, phase shift, dissipation). The choice of the observable determines the name: Tapping mode AFM, frequency modulation AFM…

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



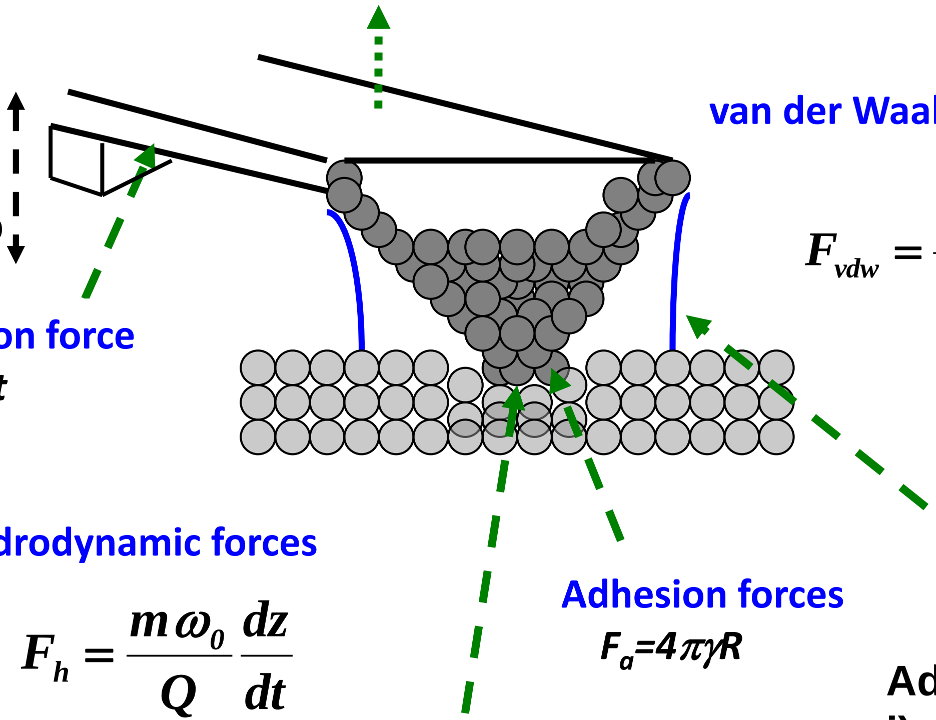
Zhong et al. Surf. Sci. 290, L688 (1993);
Anselmetti et al. Nanotechnology 5, 87 (1994);
García, Pérez, Surf. Sci. Rep. 47, 197 (2002).

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

$F_a=4\pi\gamma R$

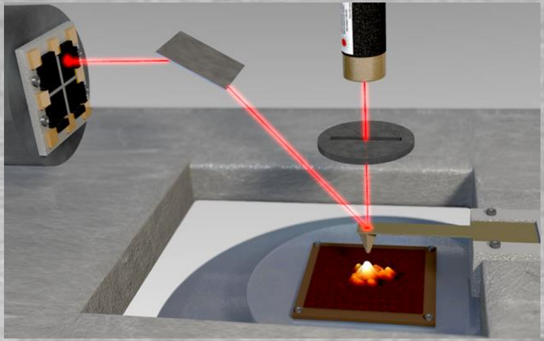
Adhesion forces
i). Unspecific
ii). specific

Short range repulsive forces (DMT)

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

Some steps in the evolution of AFM (1986-1996)

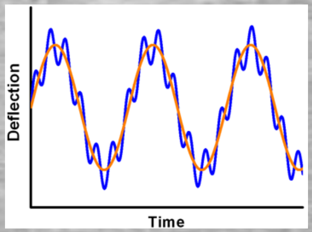
Integrated tip-microcantilevers: T.R. Albrecht, C. Quate (1990); J. Greshner (1991)

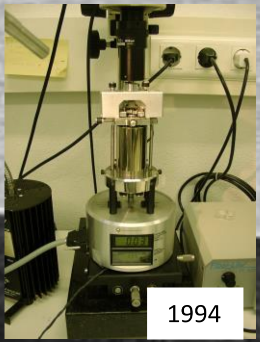


Optical beam deflection: G. Meyer, N.M. Amer (1998);

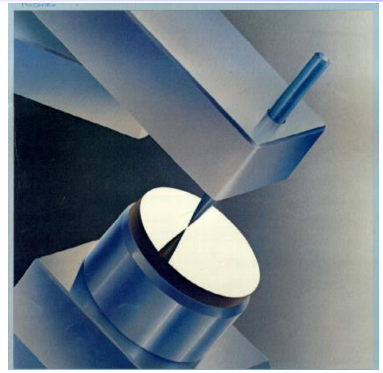
Dynamic AFM

Y. Martin, C. Williams, H.K. Wickramasinghe (1987);
T.R. Albrecht, C. Quate (1990); P.K. Hansma (1994);
W. Han, S.M. Lindsay (1996); J. Tamayo, R. Garcia (1996)



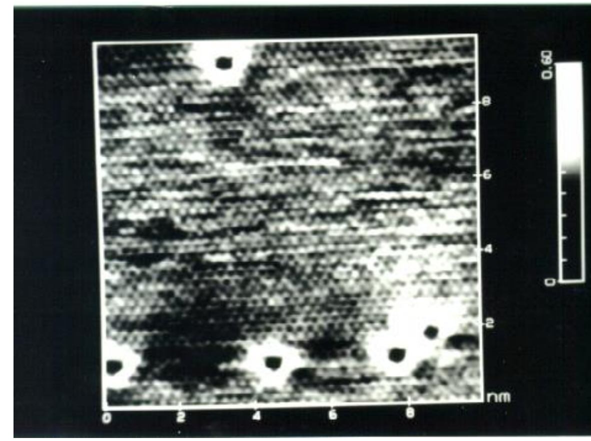


Commercial AFMs: Digital Instruments (1990)

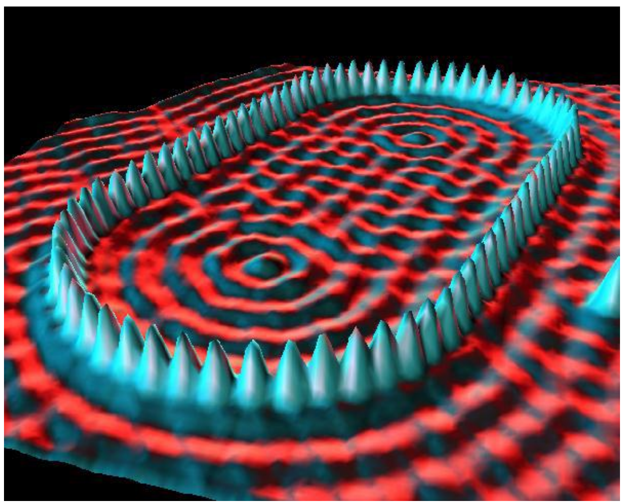


STM 1982

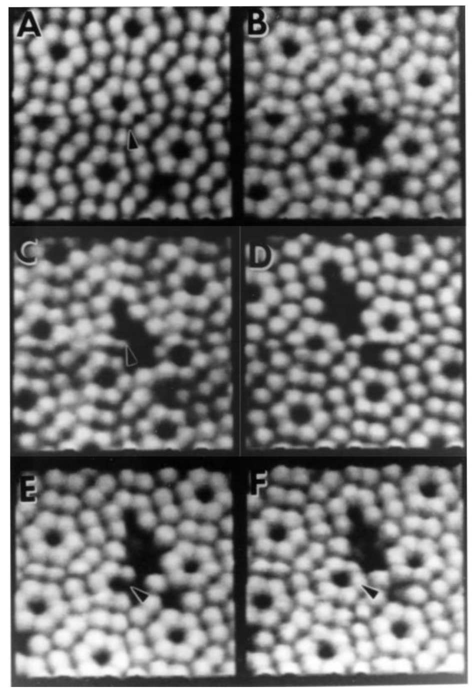
AFM 1986



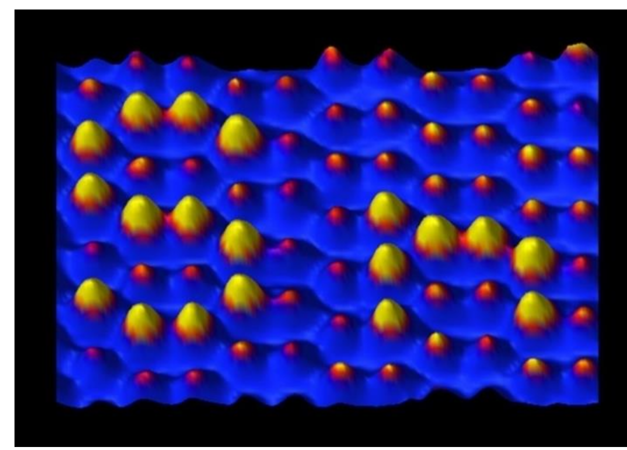
García, WSe_2 (1992)



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



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



Morita et al. (2005)

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

Nanolithography: Requirements

Nanometer-scale motives

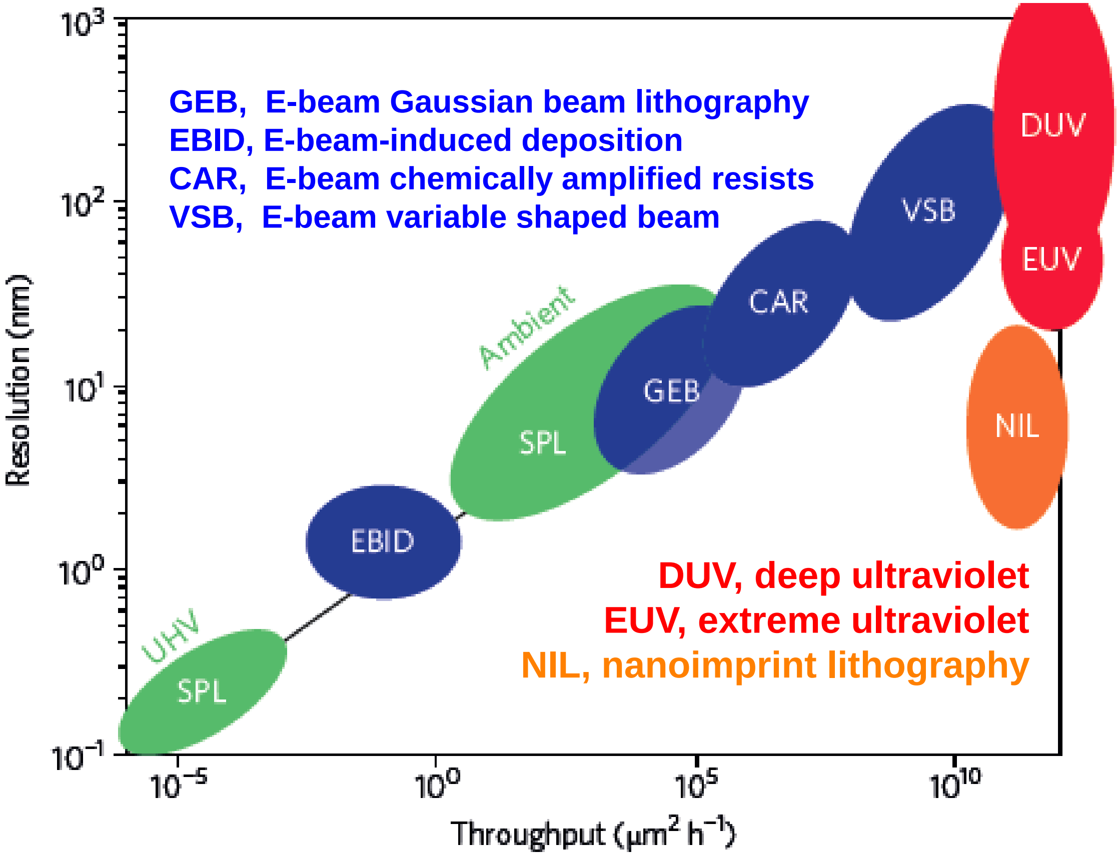
Reproducibility

Compatible with technological environments

Scalable

Throughput

NanoLithography: Throughput versus Feature Size



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

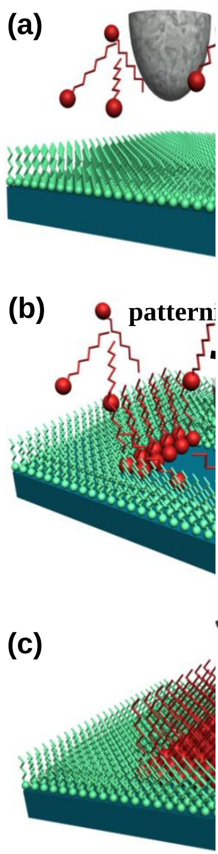
SPM based Nanolithographies

Nanoshavi

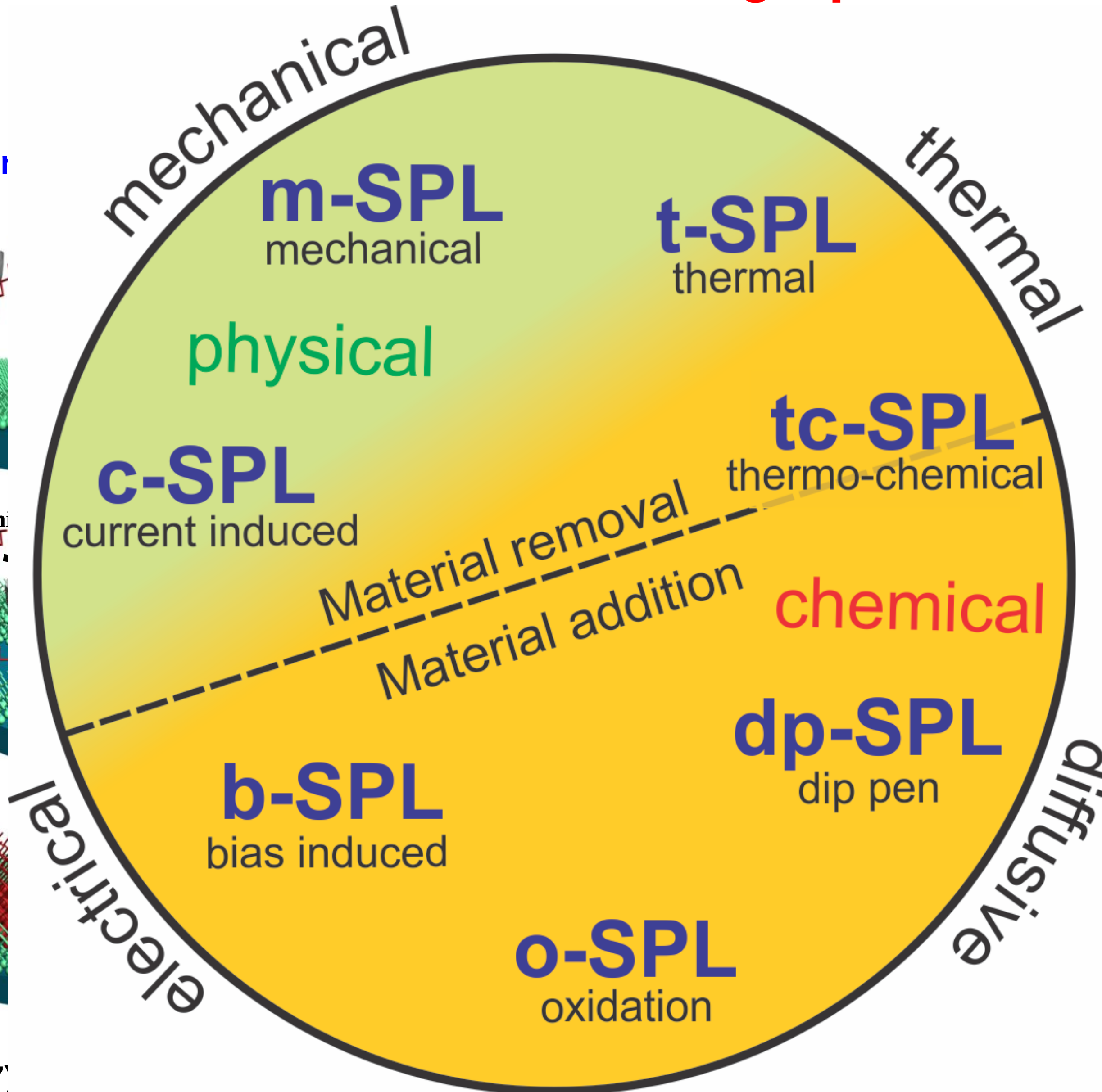
(a)

(b)

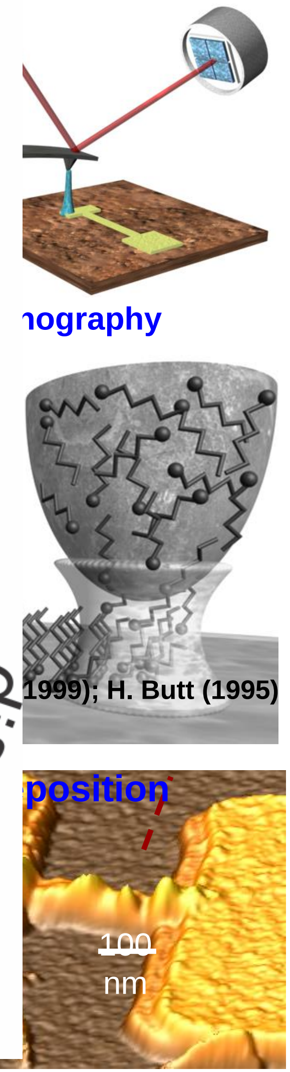
(c)



G. Liu (1997



ning Probe
phy

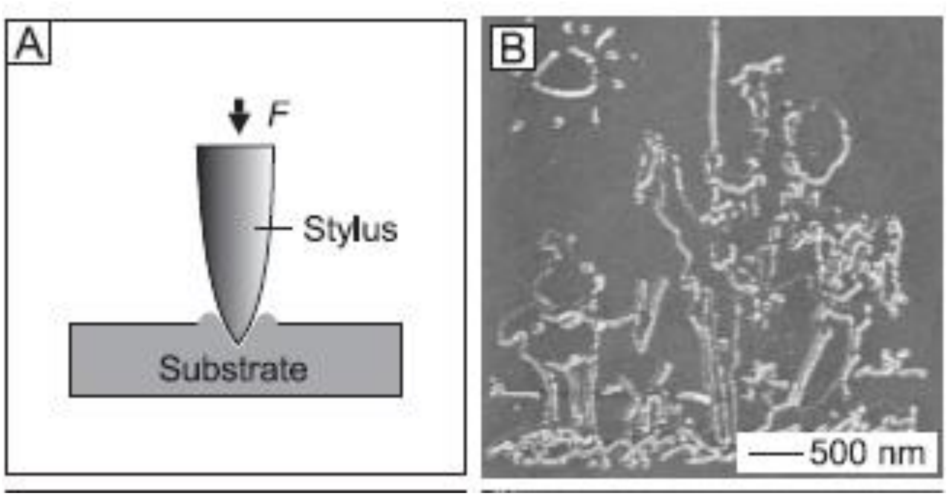


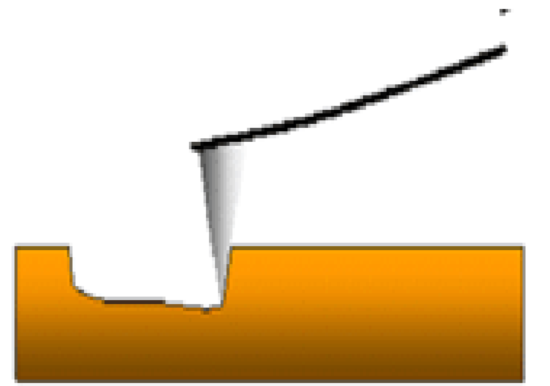
R. Garcia, A.W. Knoll, E. Riedo, *Nature Nanotechnology* **9**, 577 (2014)

mechanical-SPL

Nanomachining

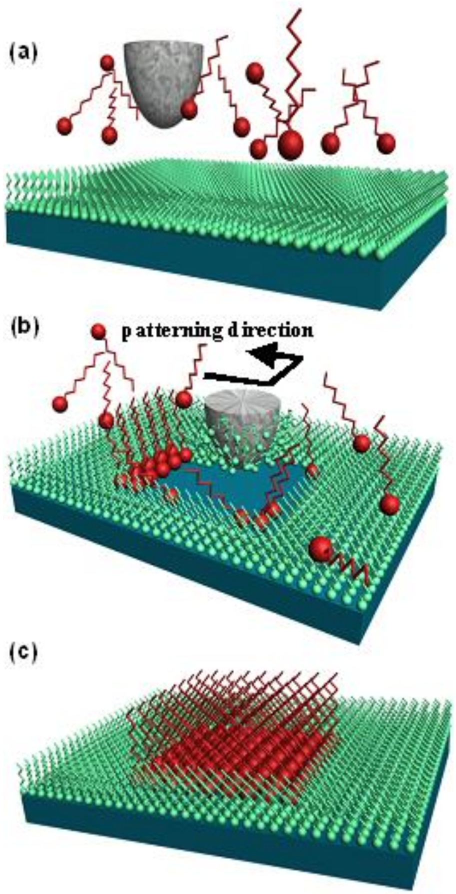
Mechanical Force: Probe tip used to “plough” a soft layer





B) The AFM topographic image of Pablo Picasso´s ‘ Don Quixote’ that was carved in the surface of a polycarbonated film with an AFM tip

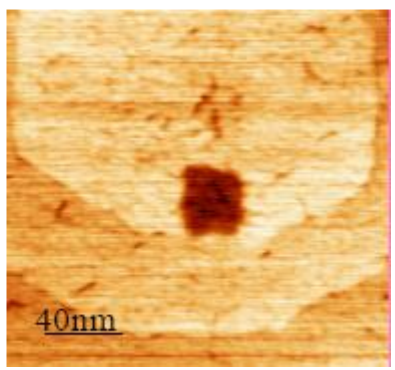
m-SPL
nanoshaving and nanografting



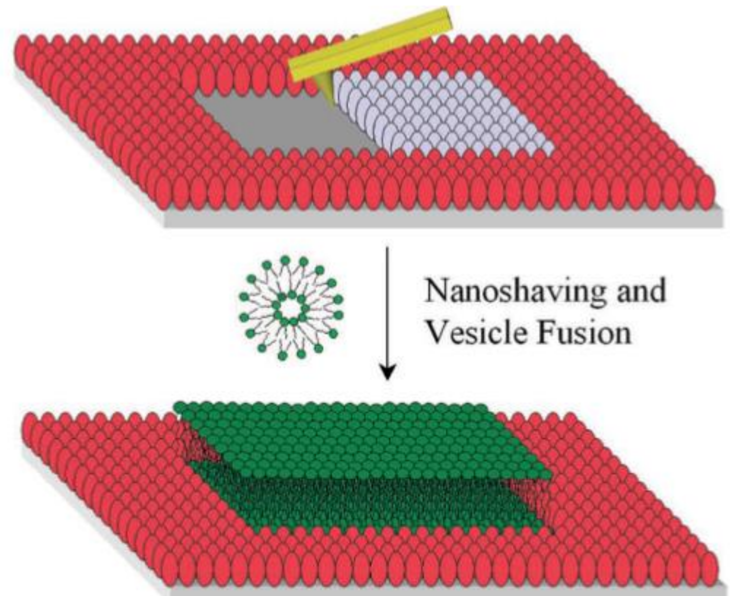
A SAM is assembled on the surface

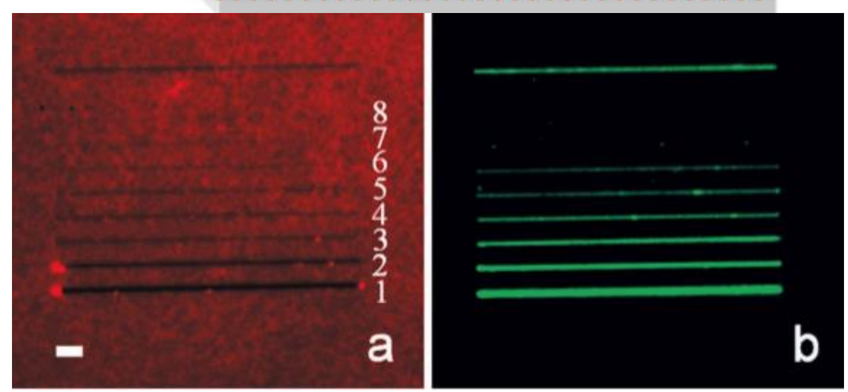
The AFM tip exerts a force on the SAM and removes the monolayer in a certain region (nanoshaving)

A diferent monolayer can be self-assembled in the swept region



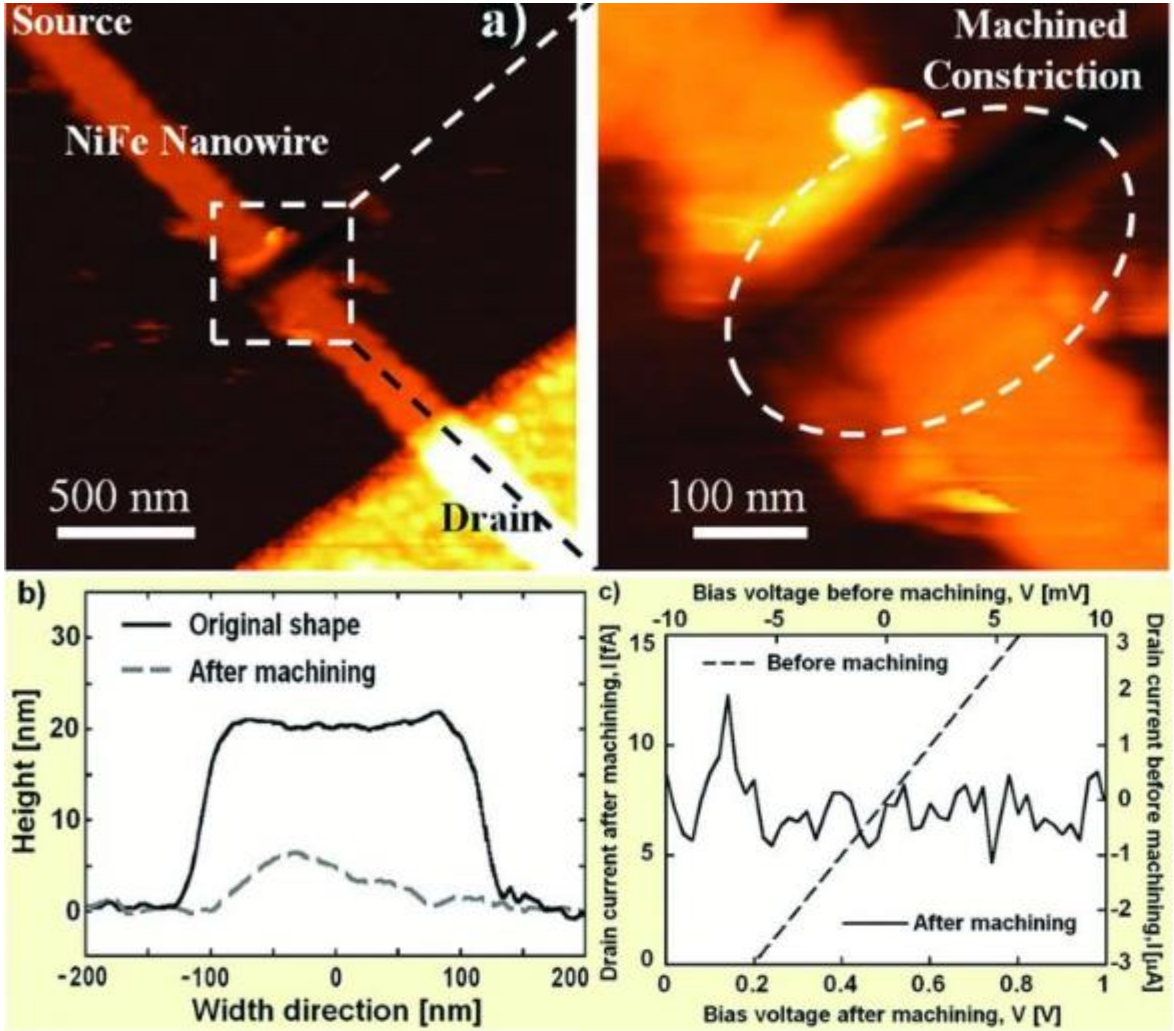
CH3-(CH2)9-SH nanografted into a CH3-(CH2)17-SH SAM (400Å×400 Å)





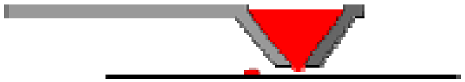
Epifluorescence images of (a) a nanoshaved BSA monolayer and (b) SLB lines. The top line, which is ~200 nm in width, was used as a reference marke

J.J. Shi, J.X. Chen, P.S. Cremer, JACS 130, 2718 (2008)



A.A. Tseng et al. Small7, 3409 (2011)

Nanoscale Dispensing (NADIS)

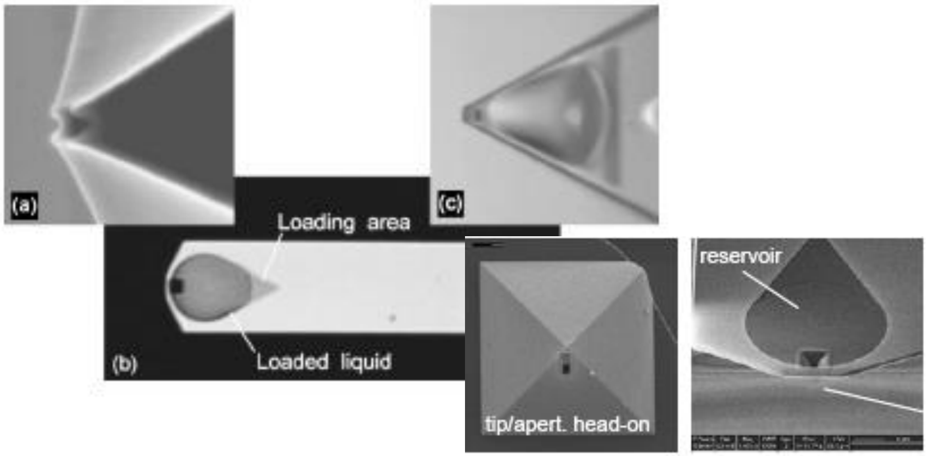


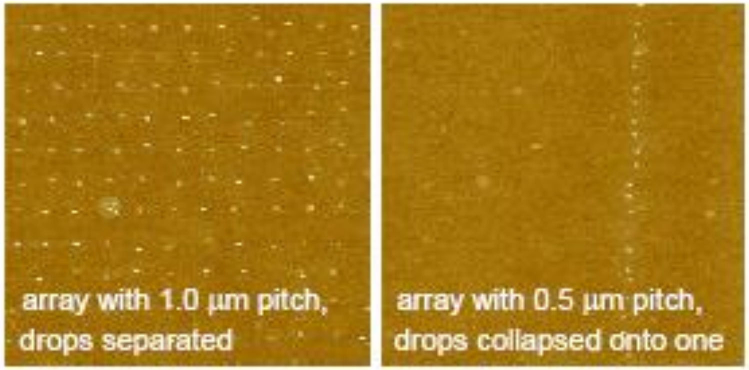
Tip with a 200 nm aperture at its apex made it by focused-ion-beam milling

Pattern ‘liquids’

Versatile (ambient condition)

Integration of fluidic system possible

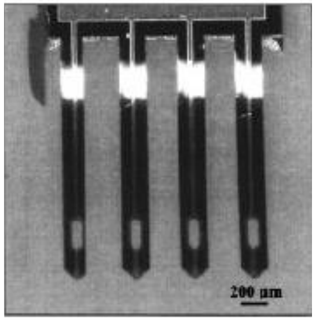




Glycerol on SiO2, image size (10 x 10) μm^2

A. Meister et al. APL 85, 25 (2004)

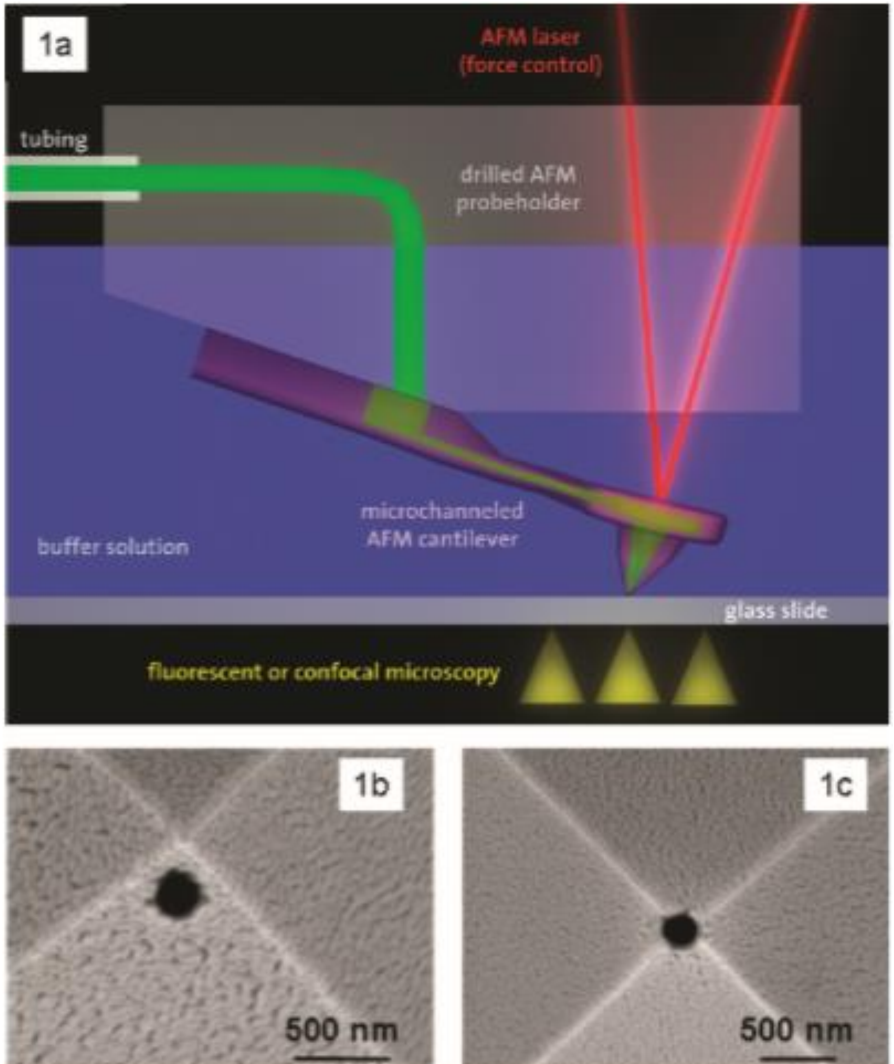
Parallel probes for multi-material deposition

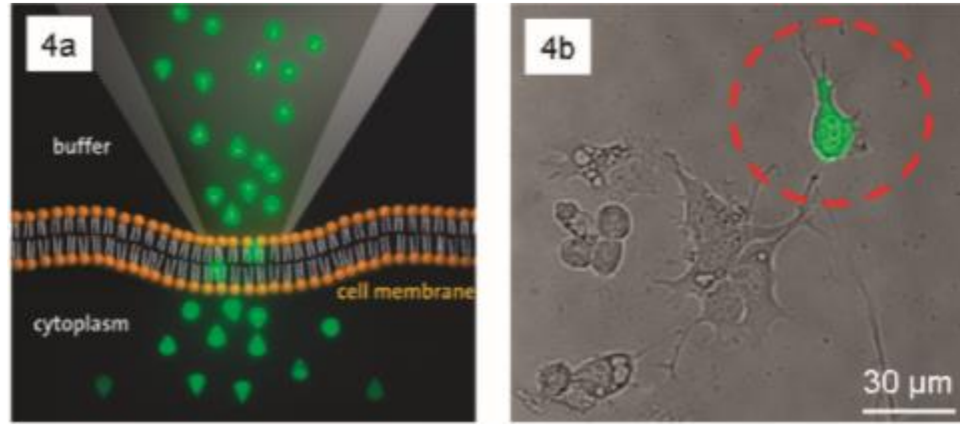


NANO LETTERS
2009
Vol. 9, No. 6
2501-2507

FluidFM: Combining Atomic Force Microscopy and Nanofluidics in a Universal Liquid Delivery System for Single Cell Applications and Beyond

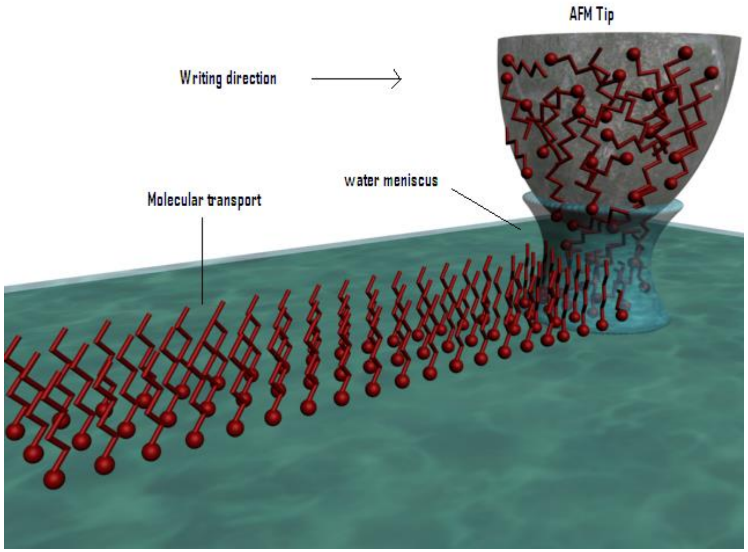
André Meister,[†,§] Michael Gabi,[‡,§] Pascal Behr,[‡] Philipp Studer,[‡,∥] János Vörös,[‡] Philippe Niedermann,[†] Joanna Bitterli,[†] Jérôme Polesel-Maris,[†,⊥] Martha Liley,[†] Harry Heinzelmann,[†] and Tomaso Zambelli*[,‡]





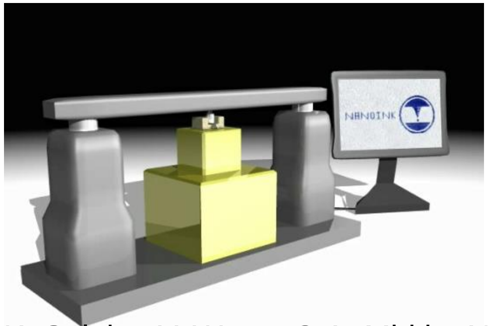
Dip Pen SPL (dp-SPL)

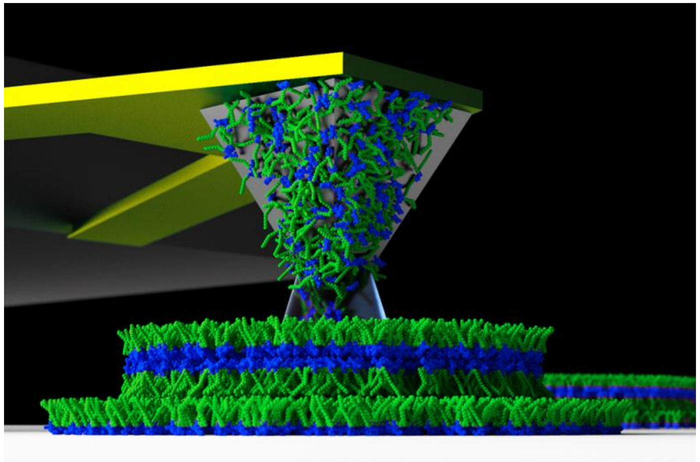
Transport of molecules to the surface via water meniscus



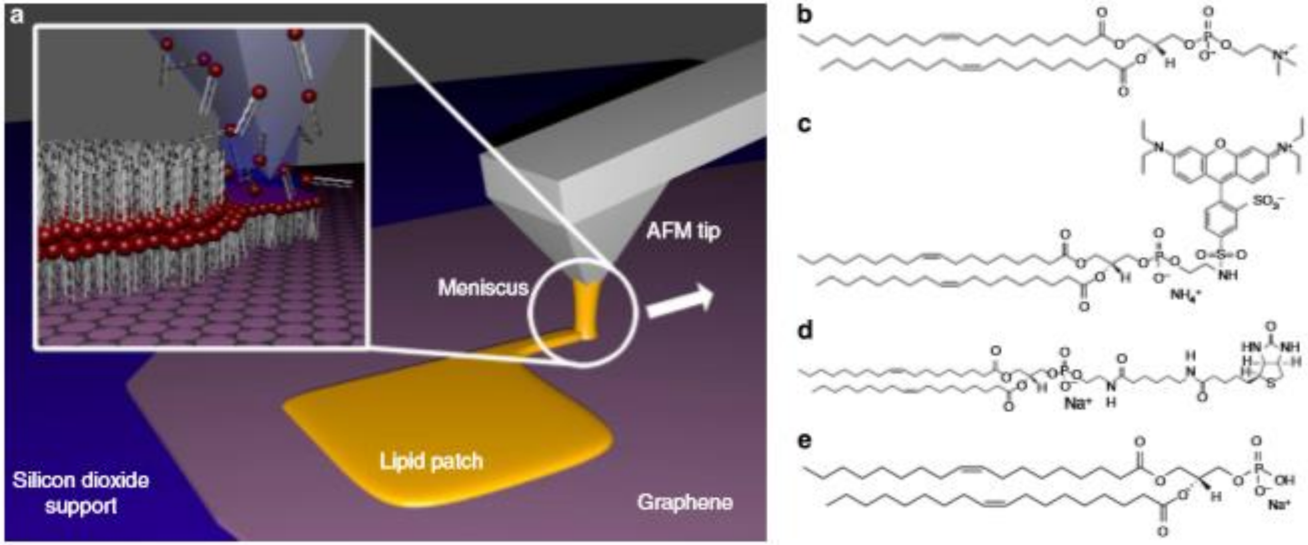
'Bottom-up' aproximation : Writing of a pen

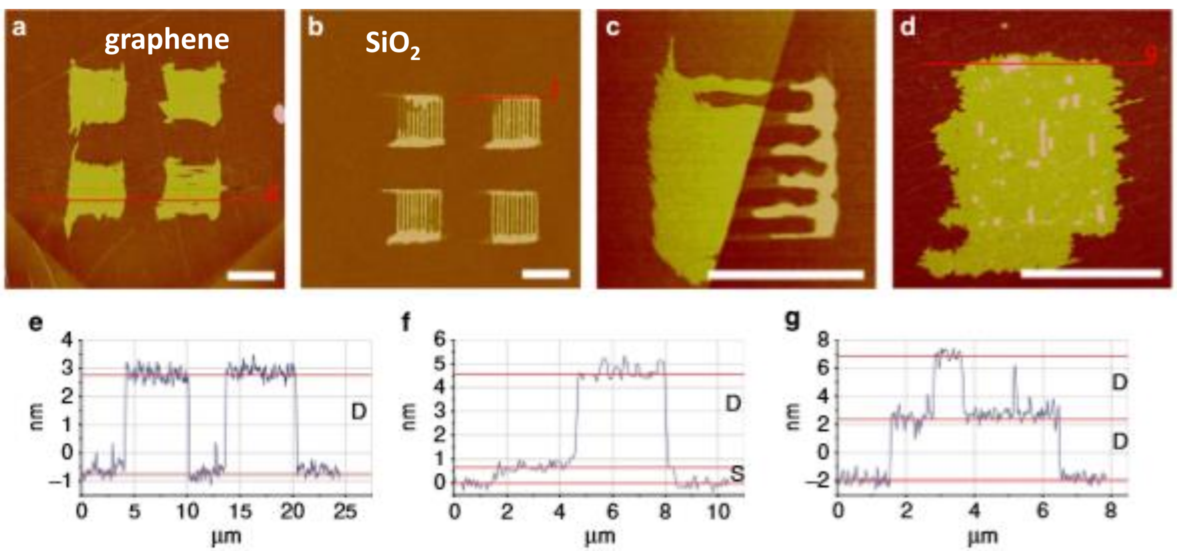
Pen	→	AFM Tip
Ink	→	Molecular solution
Paper	→	Surface substrate





K. Salaita, Y. Wang, C.A. Mirkin, Nat. Nanotechnol. 2, 145-155 (2007);
R.D. Piner,…, C.A. Mirkin, Science 282, 661 (1999)





M. Hirtz et al. Nat. Commun. 4, 2591 (2013)

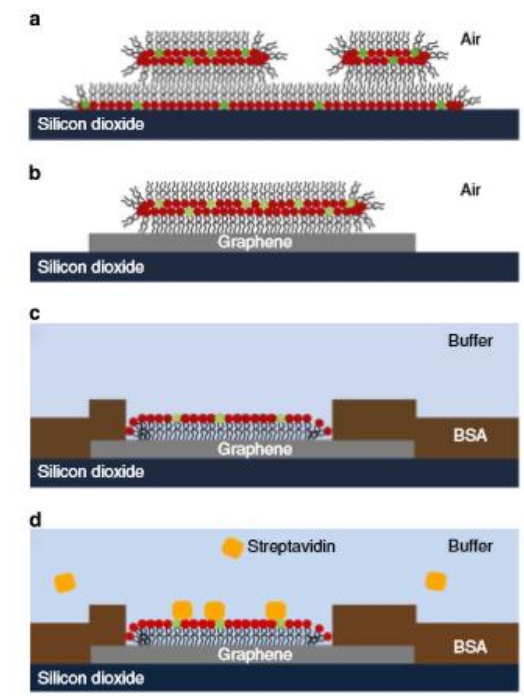
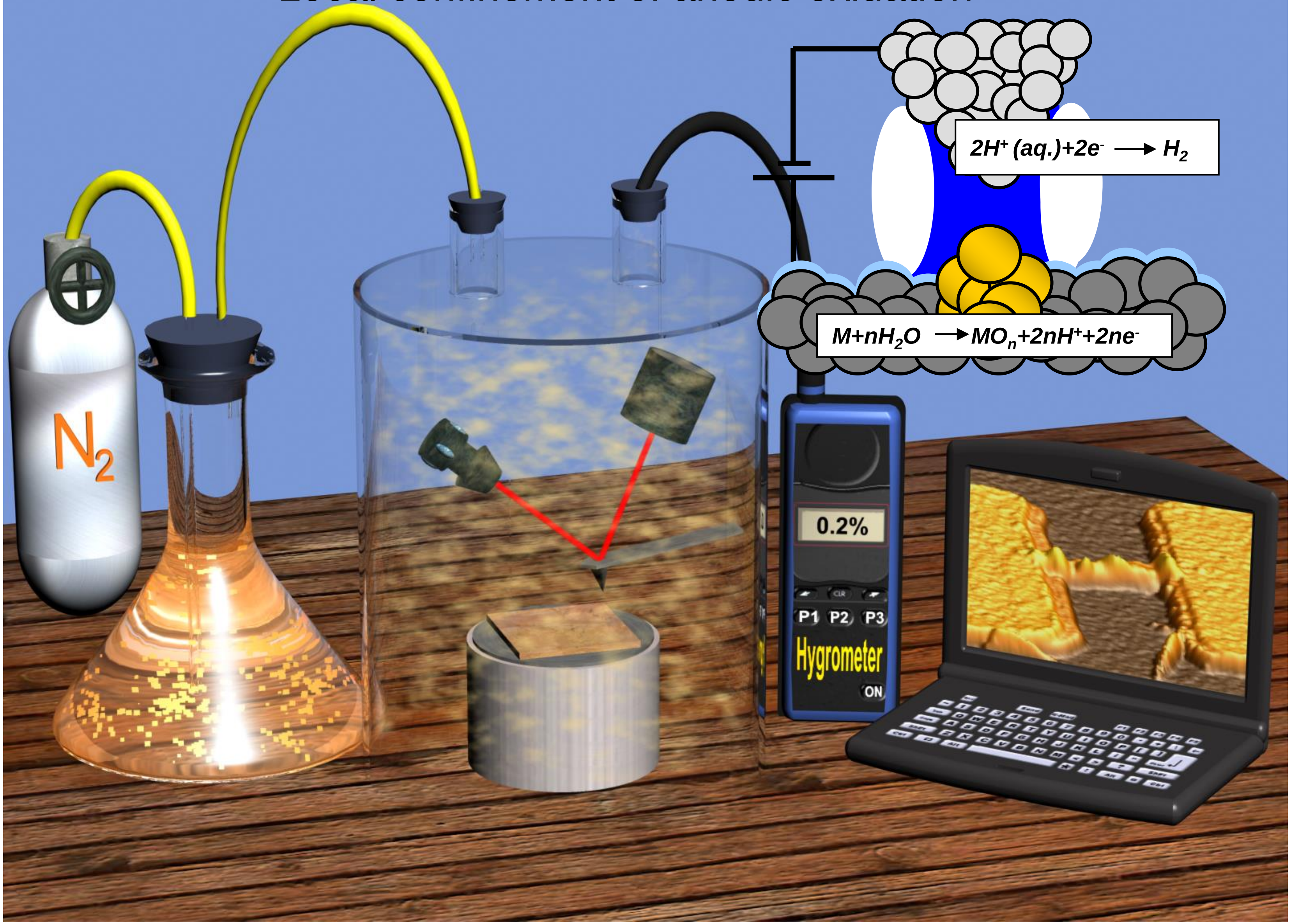


Figure 7 | Proposed membrane organization on silicon dioxide and graphene. DOPC headgroups are marked in red, Biotin-PE headgroups in green. **(a)** Base monolayer and additional bilayer on silicon dioxide in air, **(b)** single bilayer on graphene in air and **(c)** monolayer of phospholipids on graphene surrounded by BSA layer under water. Streptavidin can later be bound to the biotinylated headgroups of the phospholipids from solution **(d)** with BSA and DOPC preventing unspecific binding to the substrate.

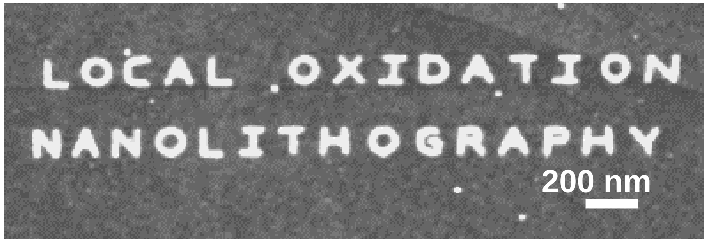
Oxidation SPL:

Local confinement of anodic oxidation

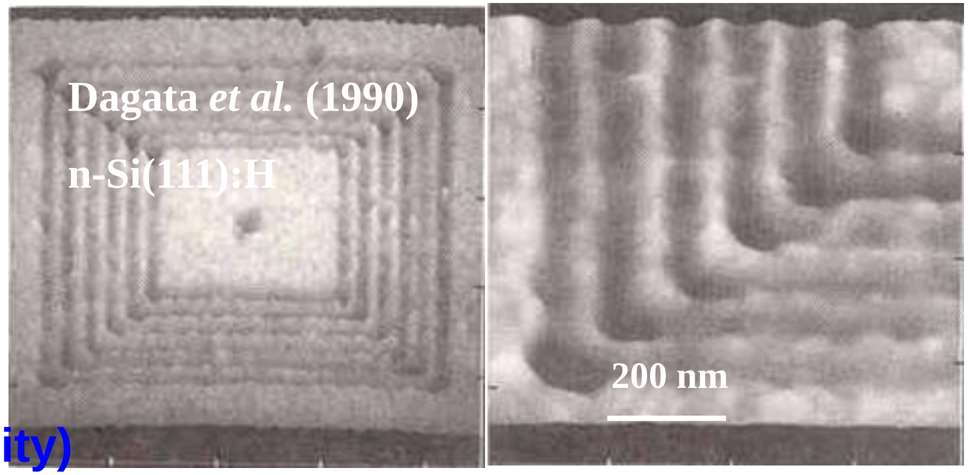


García, Calleja, Perez-Murano, Applied Physics Letters (1998)

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)

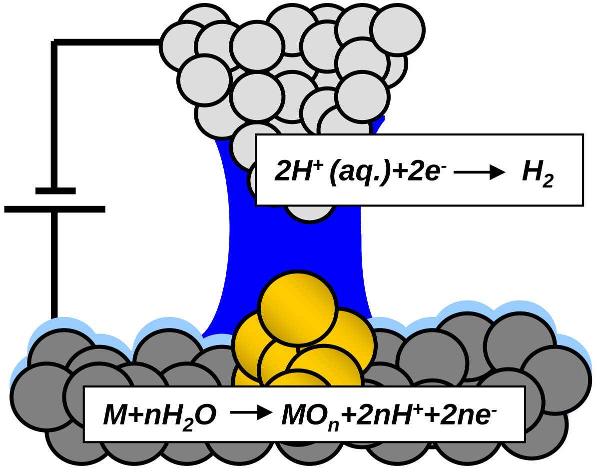
R. Garcia, M. Calleja, F. Pérez-Murano, Appl. Phys. Lett. (1998)

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.



Oxidation SPL

dielectric barriers
Templates
Masks

STM	contact AFM	dynamic AFM	meniscus	kinetics	high speed AFM
1990	1993	1994-1998	1993-1999	1998-2004	2009

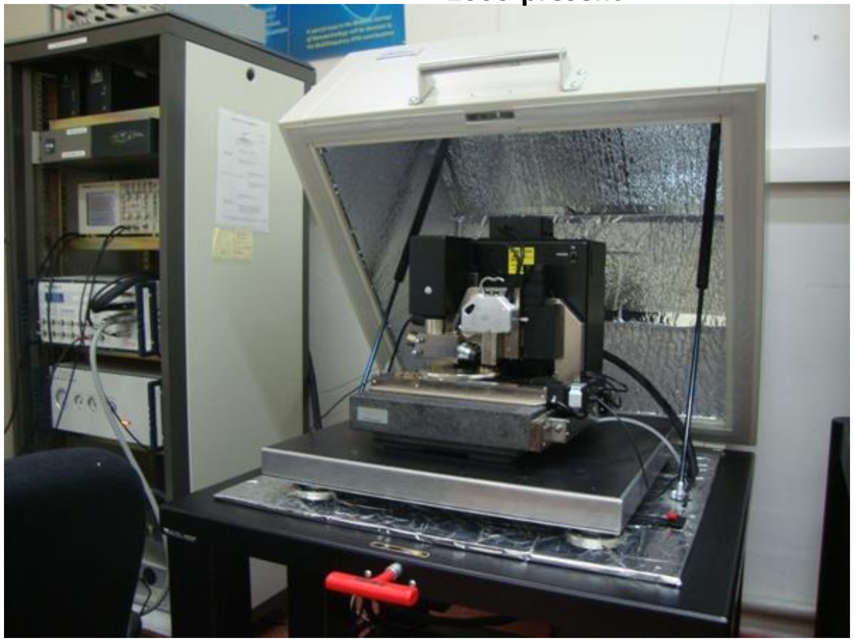
Si, Ta. Nb, Ti, GaAs	SAM	graphene	Protein, macromolecules patterning	transition metal dichalcogenides	Grey-scale patterning
1990-1998	1995-2005	2008-2011	2003-2010	2015-2016	2016

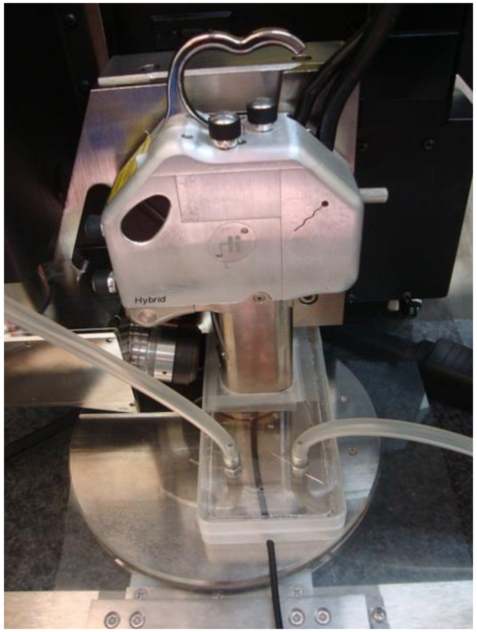
Metal-oxide transistors	Single electron transitors	Quantum devices (III-V compounds)	Si nanowire devices	graphene devices	TMD devices	optical devices
1995-1998	1997-2008	1998-2002	2002-2011	2008-2013	2015-2016	2007-2012

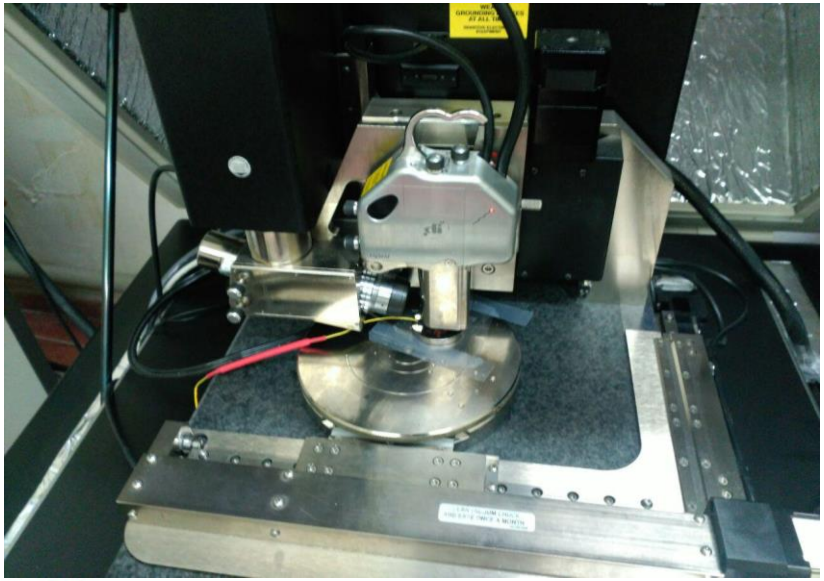
Y.K. Ryu, R. Garcia, *Nanotechnology 28, 142003*(2017);
R. Garcia, RV. Martinez, J. Martinez, Chem. Soc. Rev. (2006)

O-SPL instruments

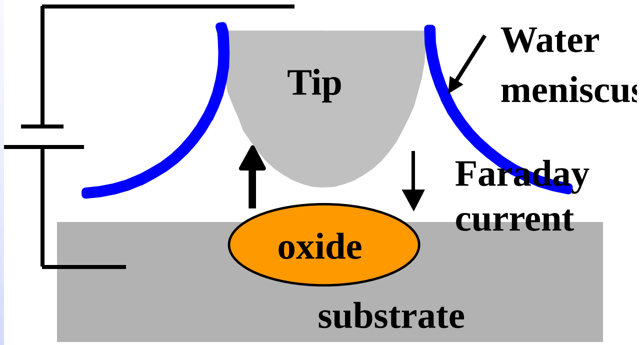
2006-present

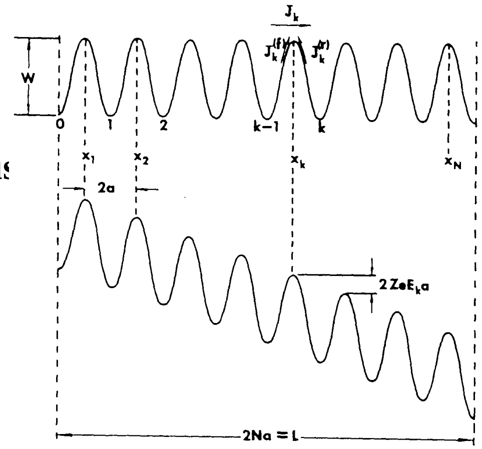






SPACE CHARGE MODEL FOR LOCAL OXIDATION





Silicon case

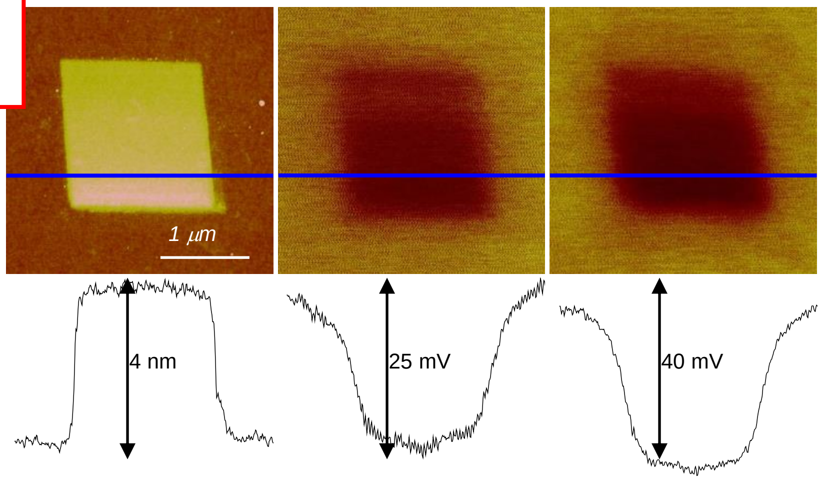
Electrolyte: $2H_2O \rightarrow 2H^+ + 2(OH^-)$

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

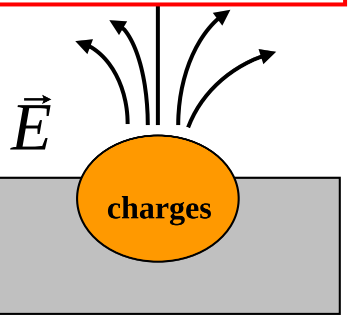
Cathode: $2H^+ + 2e^- \rightarrow H_2$

Kelvin Probe AFM measurements

The local oxidation process
negative space charge build-up



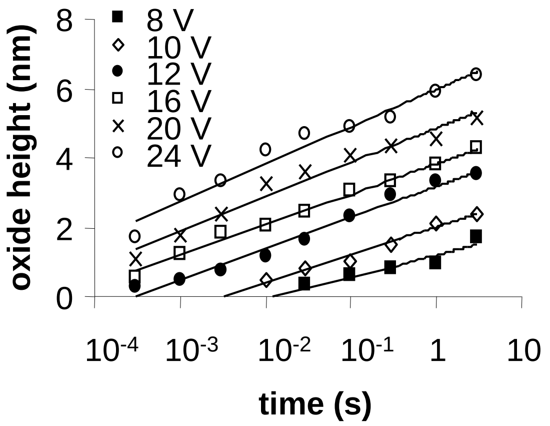
Negative Space charges

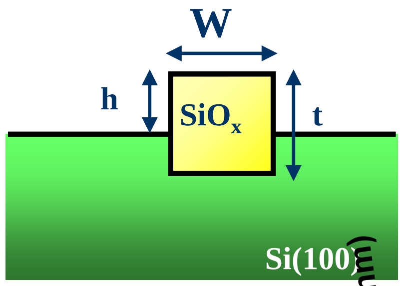


$$\rho = \frac{2\varepsilon\varepsilon_0}{d^2} V$$

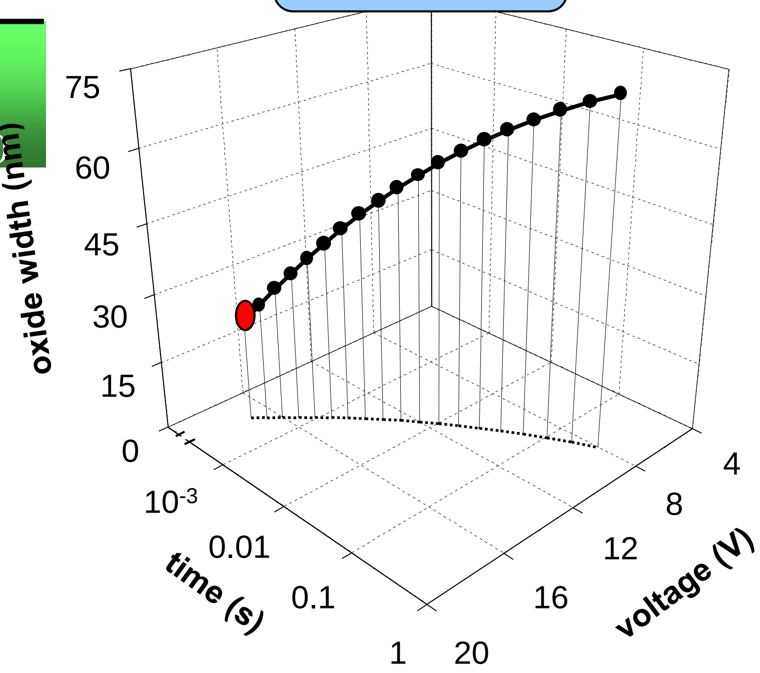
M. Chiesa, R. Garcia, APL 96, 263112 (2010)

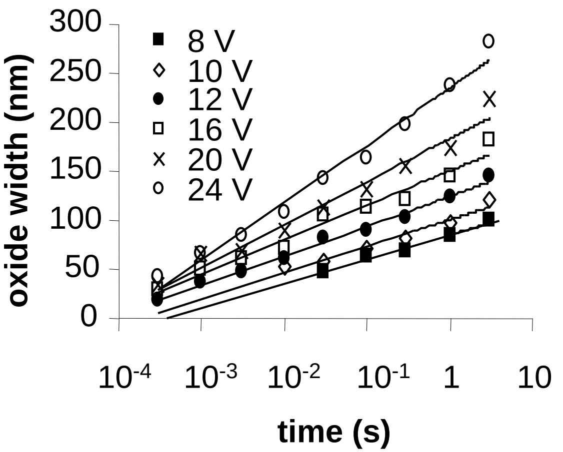
Oxide size vs voltage and pulse duration





h=cte=1 nm

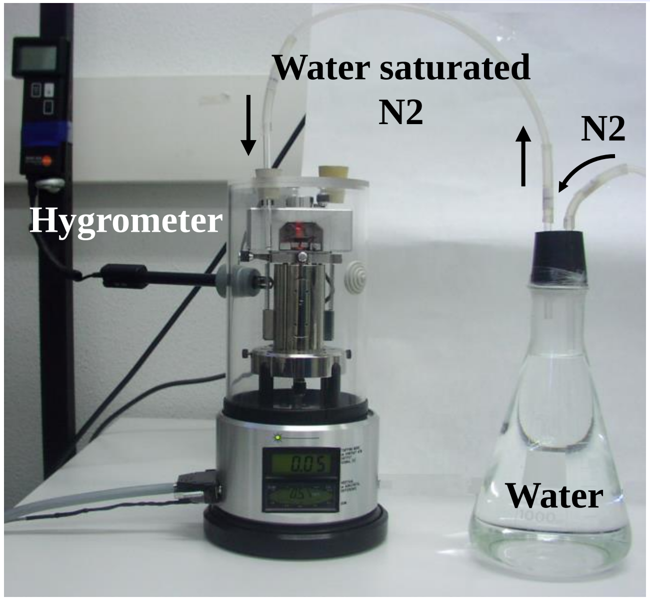




$h \sim V\,(t/t_0)^{\gamma}$

Short pulses and high voltages generate the best aspect ratio features

Calleja, García, APL 76, 3427 (2000)



Field-induced formation of water bridges

E=2 GV/m= 2 V/nm

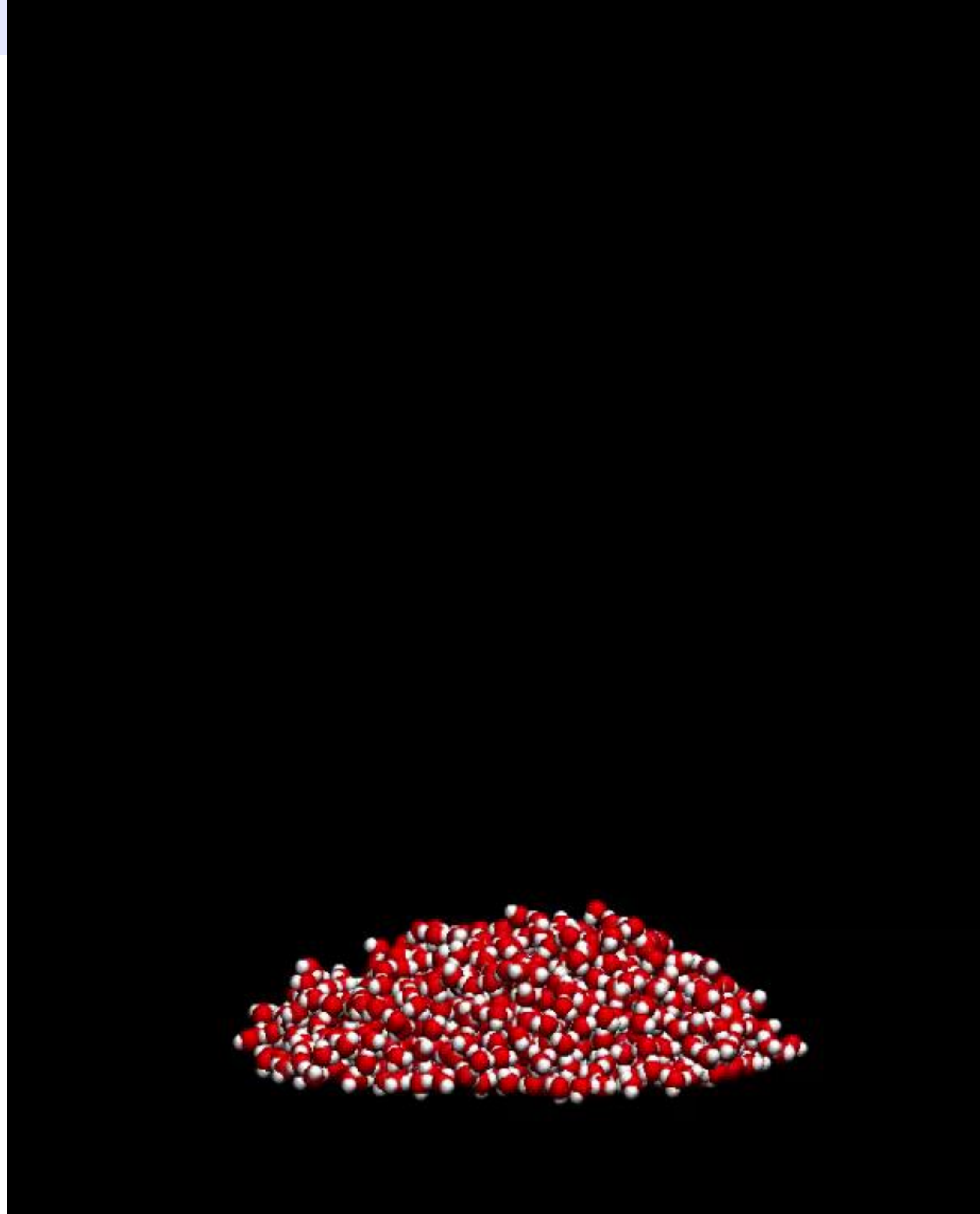
time=75 ps

Meniscus height 3 nm

MD by F. Zerbetto and T. Cramer, UBologna

1014 molecules

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



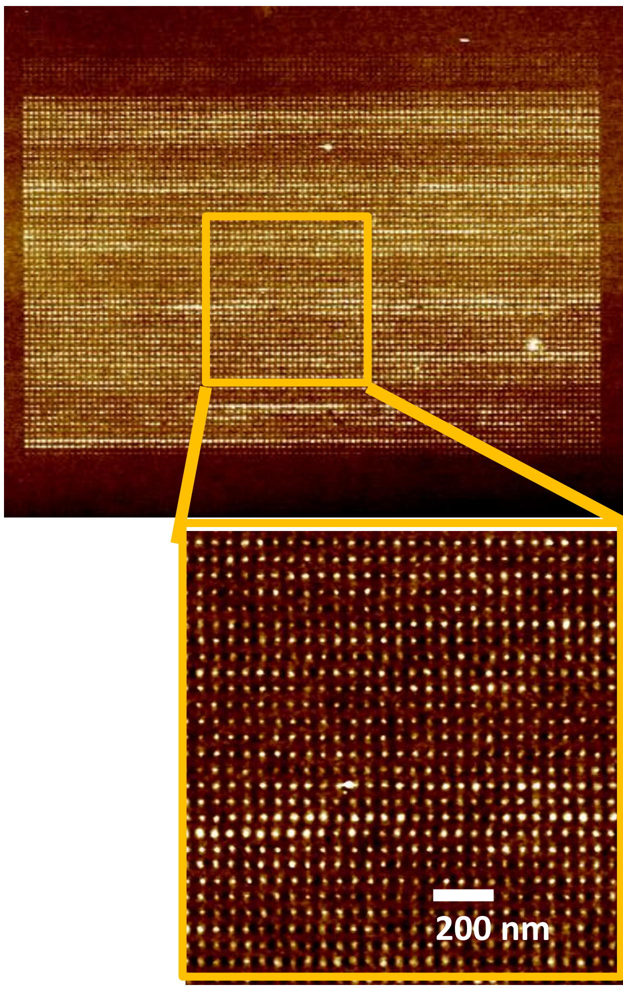
Oxidation Scanning Probe Lithography

Reproducibility

array of 6000 dots

(45%, 1 ms, 27V, A_0~ 5 nm)

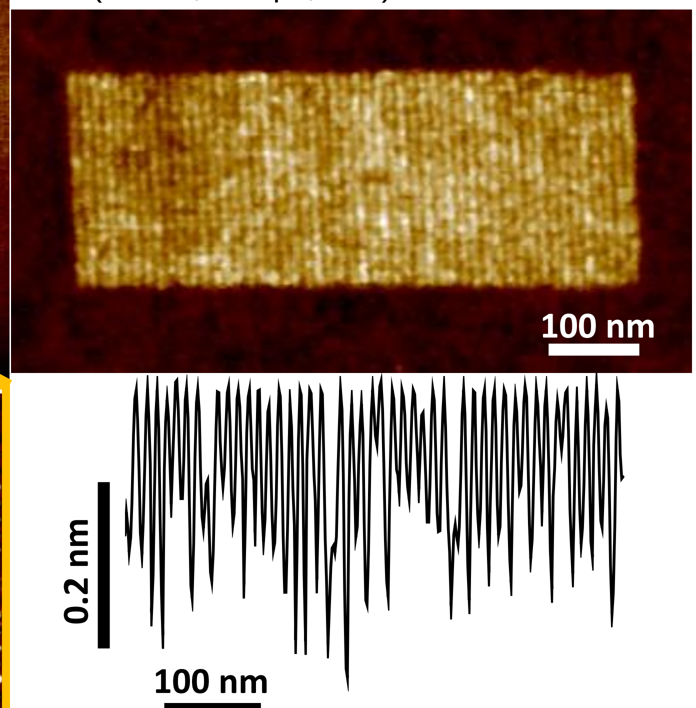
50 nm periodicity



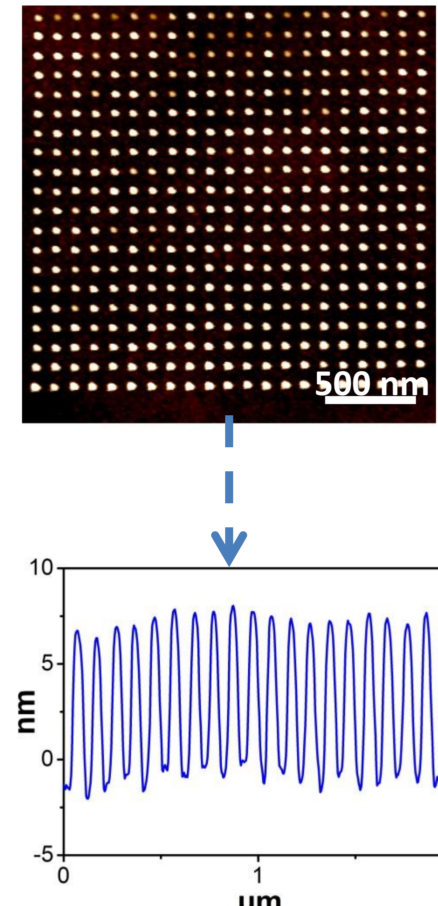
Resolution

Array of 50 lines with 15 nm periodicity

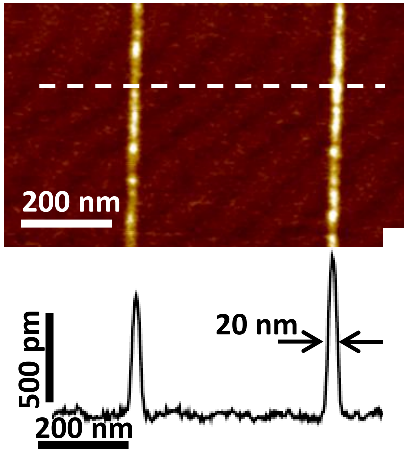
(42.7%, 500 µs, 24V)

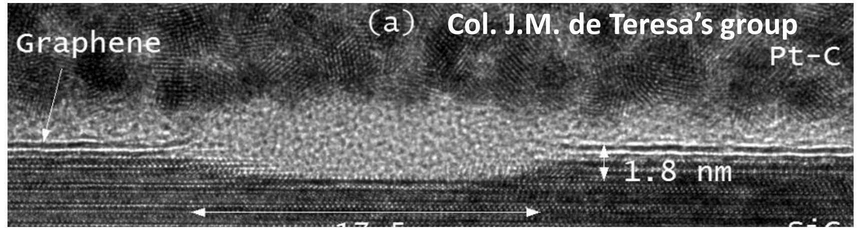


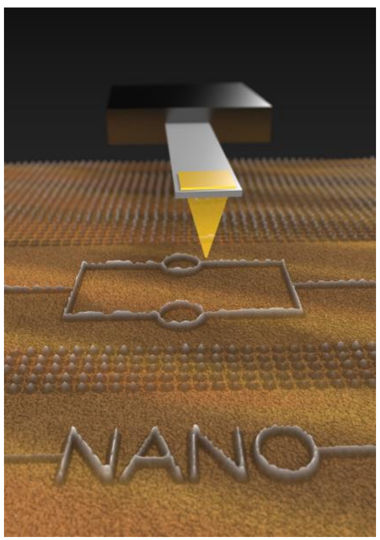
Si nanopillars

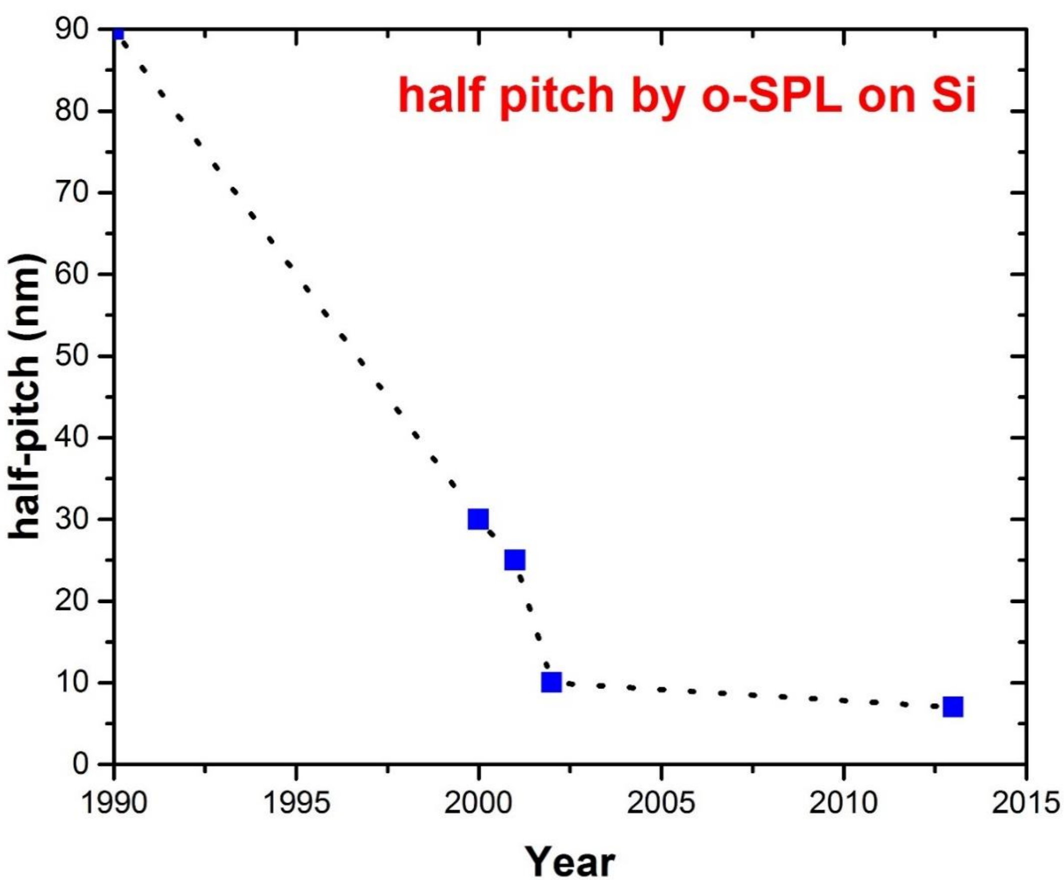


Oxidation Scanning Probe Lithography: Minimum feature size





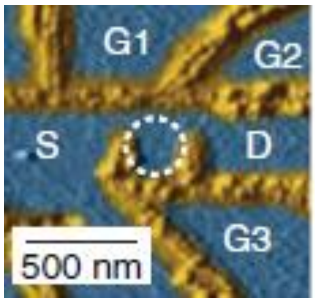




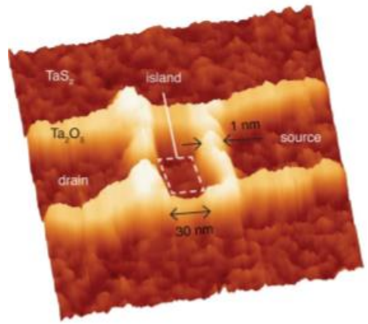
o-SPL:

Direct Nanppatterning a large variety of materials

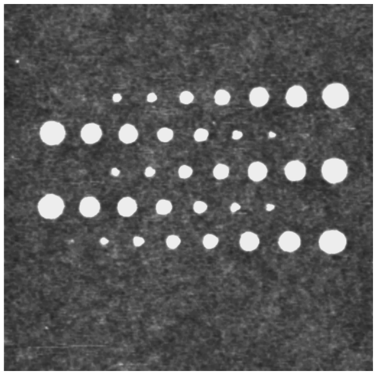
GaAs



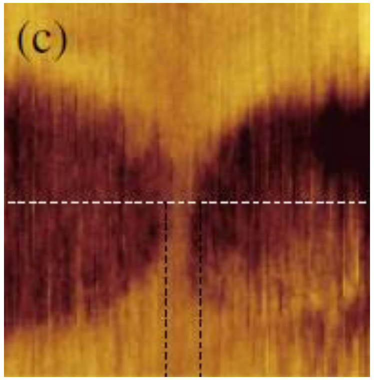
Ta



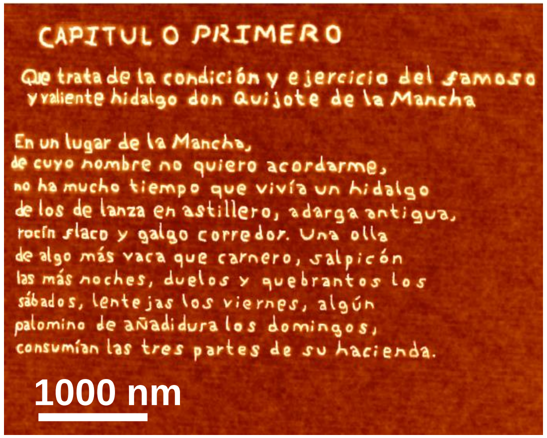
Niobium



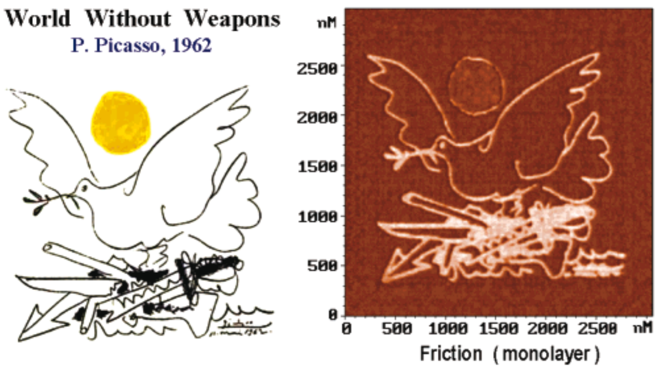
graphene



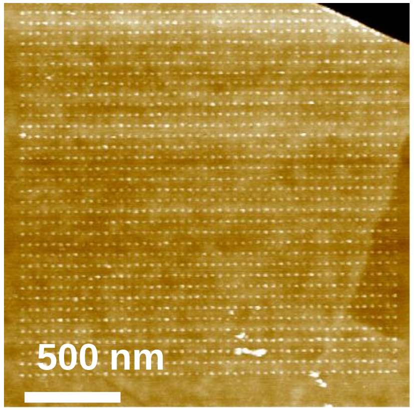
silicon



SAM templates



WSe2



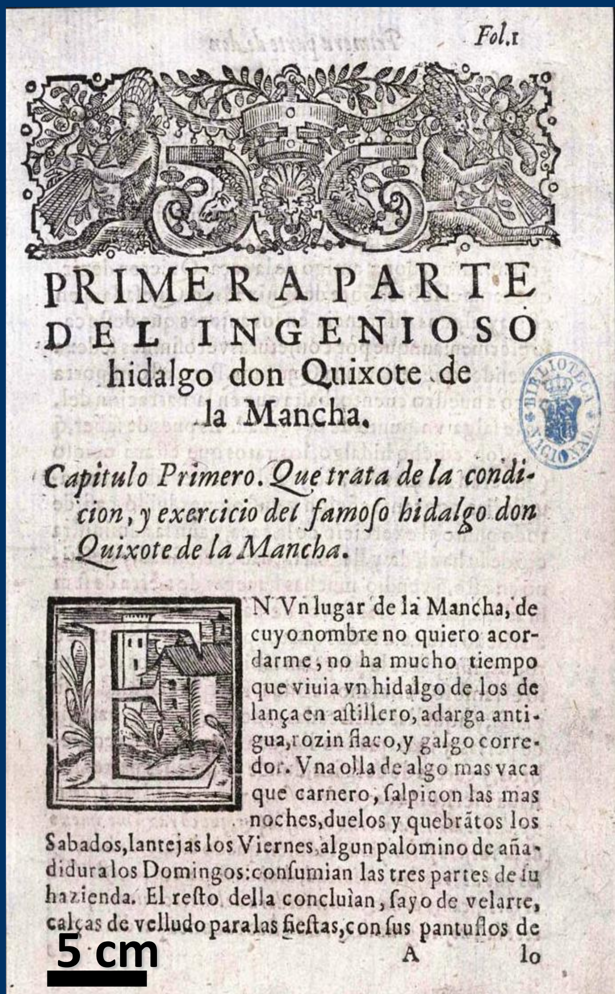
Metals, semiconductors, Organosilanes...

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

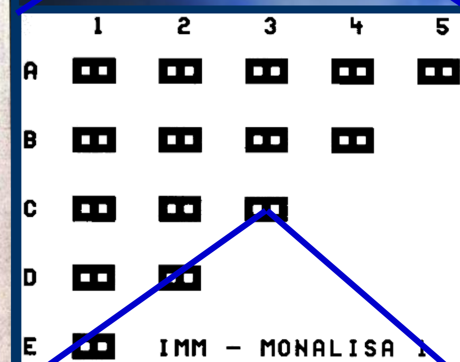
PRIMERA PARTE DEL INGENIOSO hidalgo don Quixote de la Mancha.

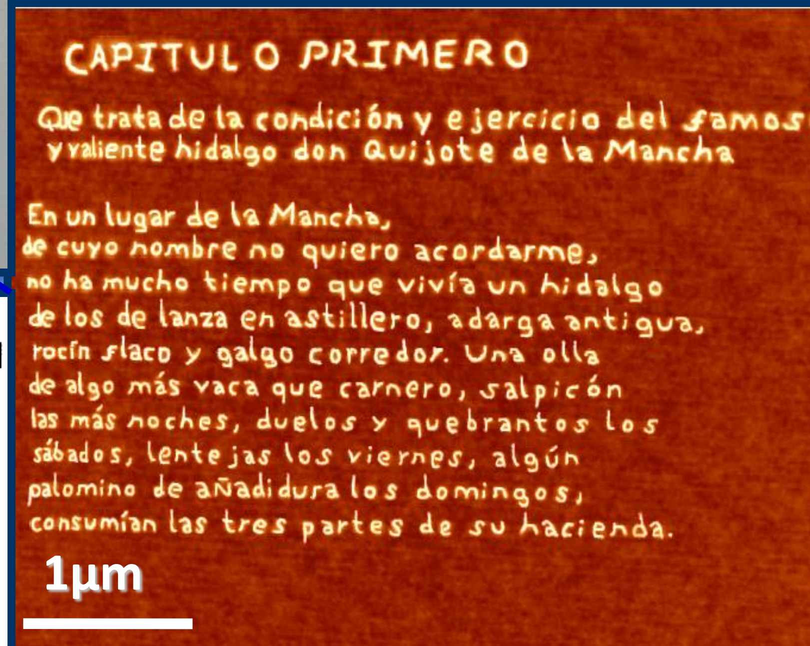
Capitulo Primero. Que trata de la condicion, y exercicio del famoso hidalgo don Quixote de la Mancha.

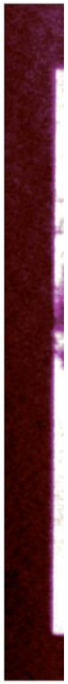
EN Vn lugar de la Mancha, de cuyo nombre no quiero acordarme, no ha mucho tiempo que viuia vn hidalgo de los de lança en astillero, adarga antigua, rozin flaco, y galgo corredor. Vna olla de algo mas vaca que carnero, salpicon las mas noches, duelos y quebrātos los Sabados, lantejas los Viernes, algun 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

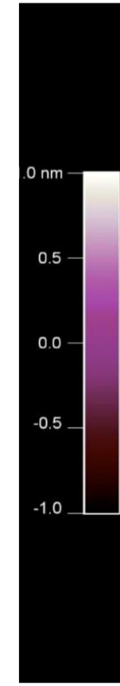
A lo

5 cm

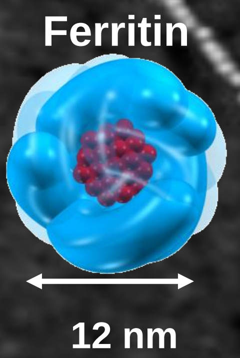








R. Proksch (2016)



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

Ferritin

FERRITIN

- **Spherical Iron Storage Protein, Hollow Shell Containing Iron Atoms**

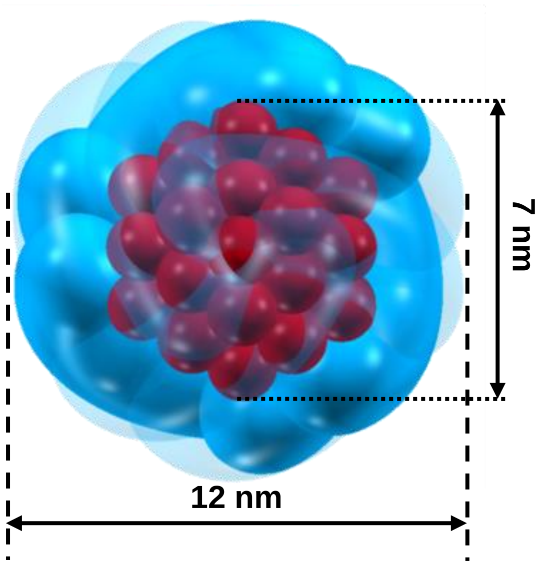
- **Shell Consists of 24 Subunits (apoferritin)**

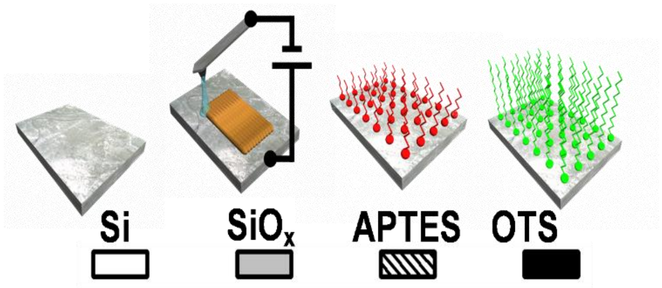
with an ferrihydrite core $(FeOOH)_8(FeOOPO_3H_2)$

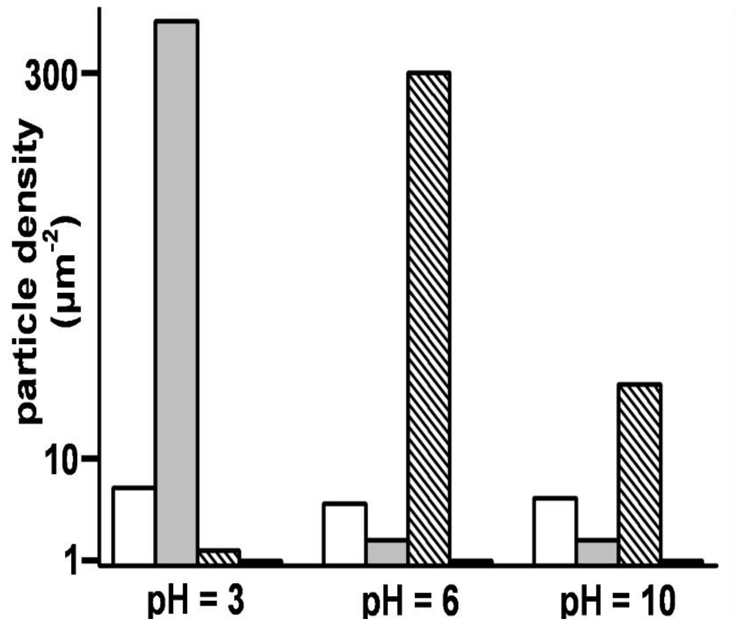
- **Superparamagnetic Properties**

Isolectric point at pH=4.5

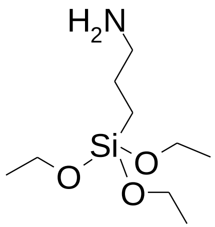
- **Apoferritin → Hollow Shell without Magnetic Core**

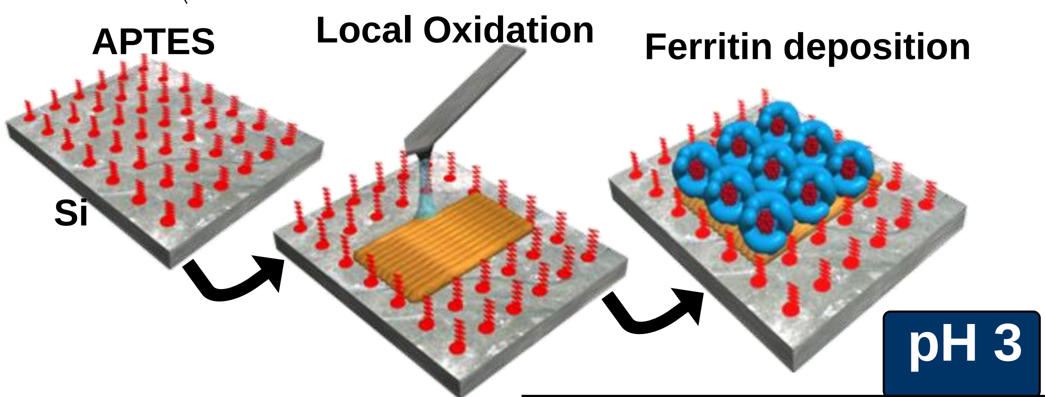


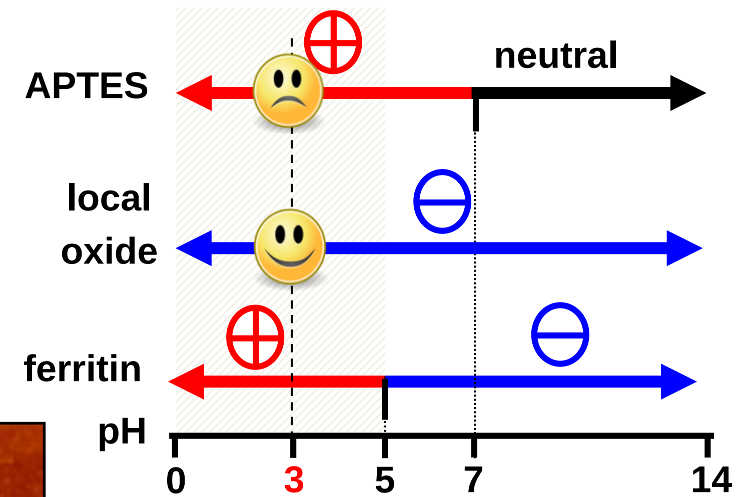


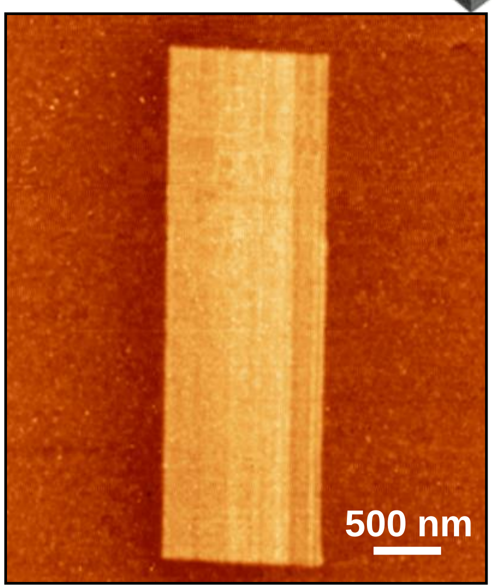


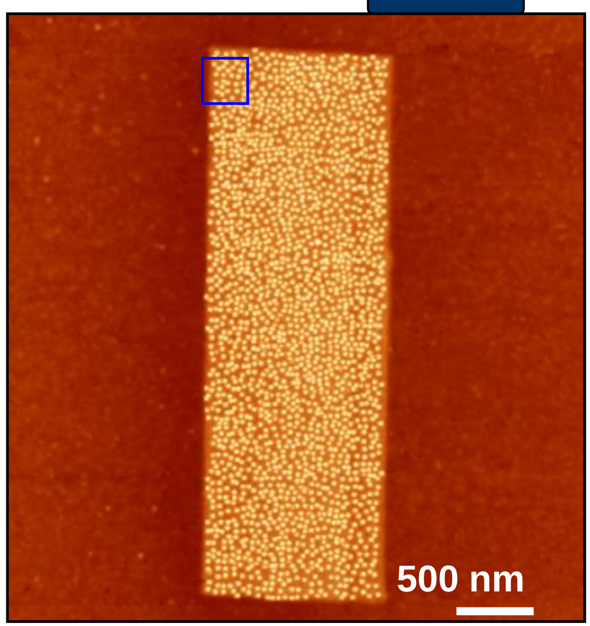
Nanoscale positioning of ferritin (low pH)

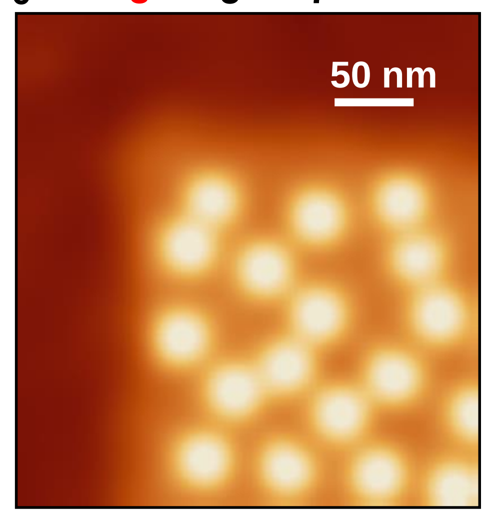








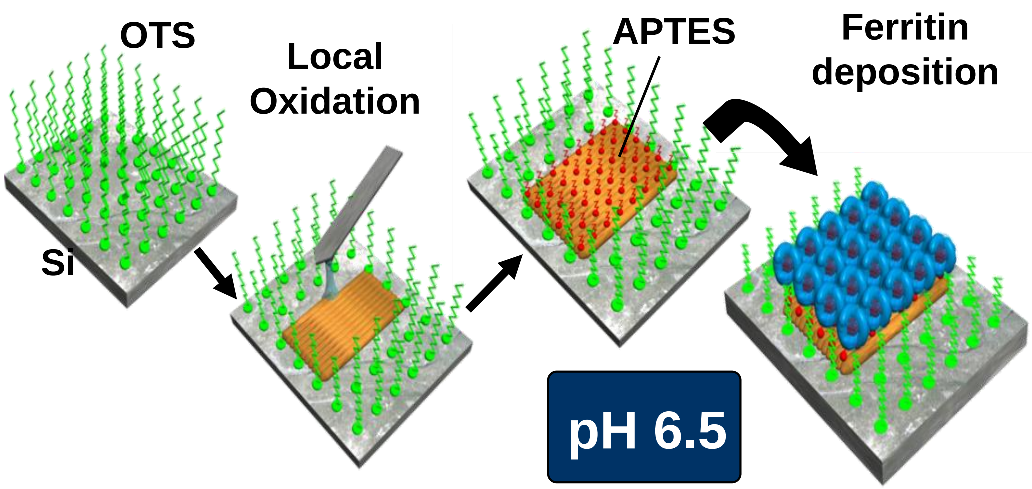


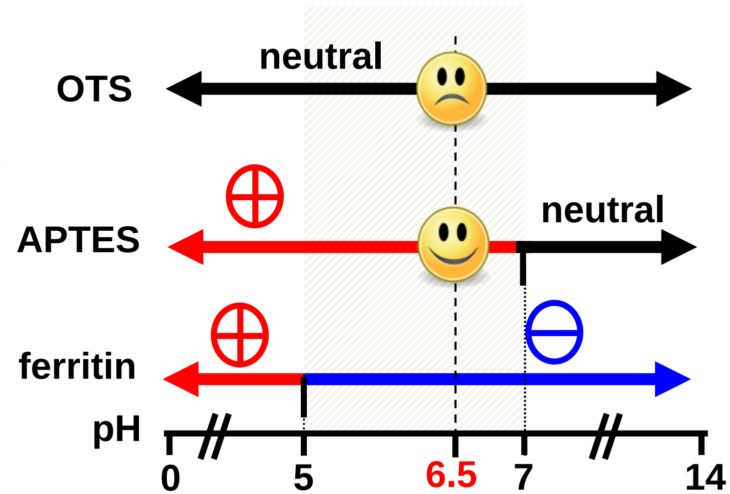


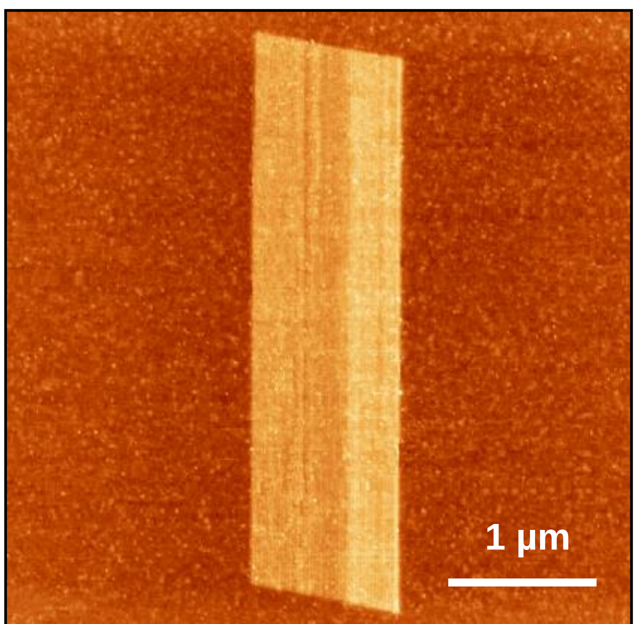
Ferritin isoelectric point 4.5

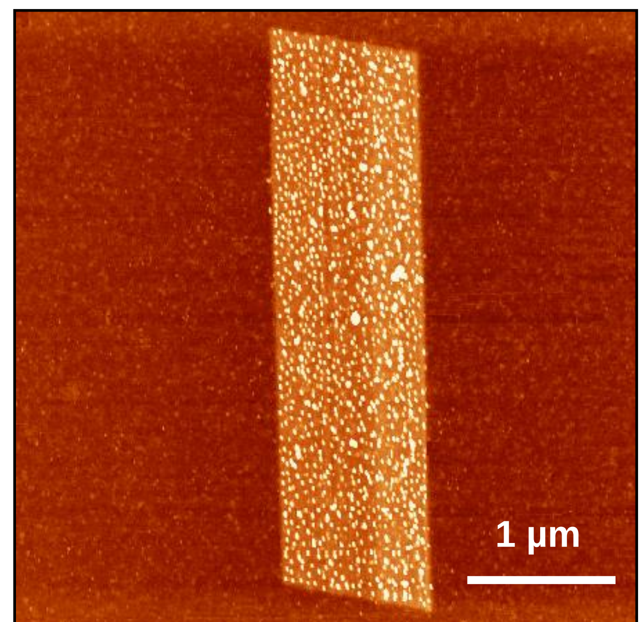
R.V. Martinez , J. Martinez, M. Chiesa, R. Garcia, E. Coronado, E. Pinilla-Cienfuegos, S. Tatay, *Adv. Mater*. **22**, 588 (2010)

Controlled positioning at neutral pH

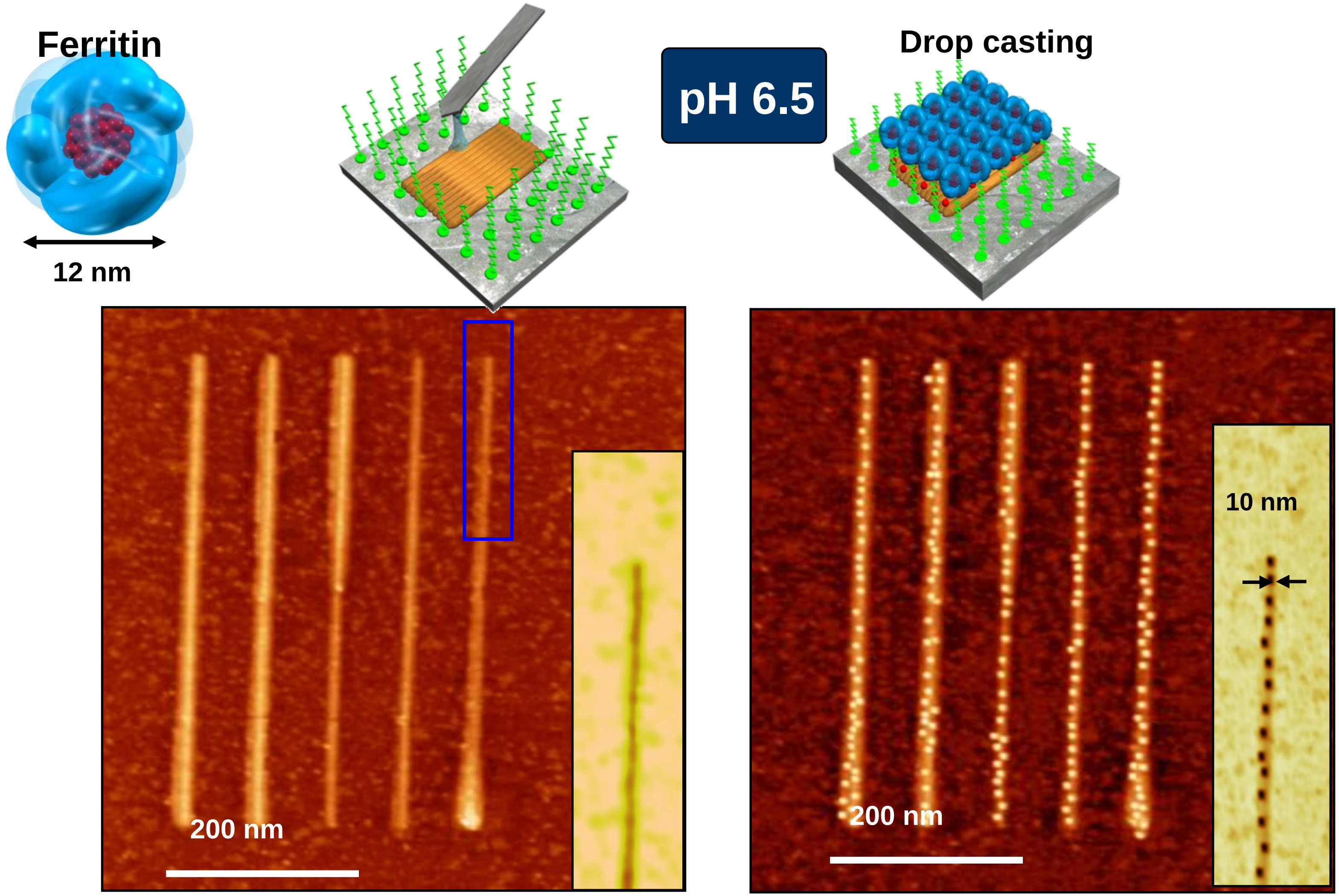








Protein patterning with 10 nm feature size



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)

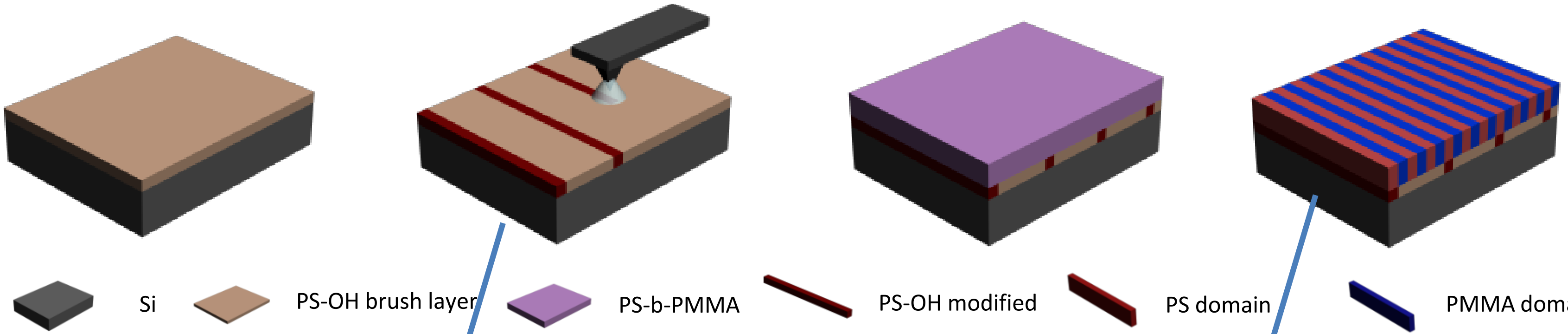
Creation of guiding patterns for directed self assembly of block co-polymers by O-SPL

1. Brush grafting + Annealing

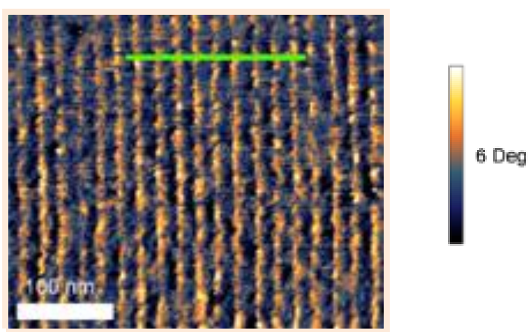
2. Chemical surface modification by AFM

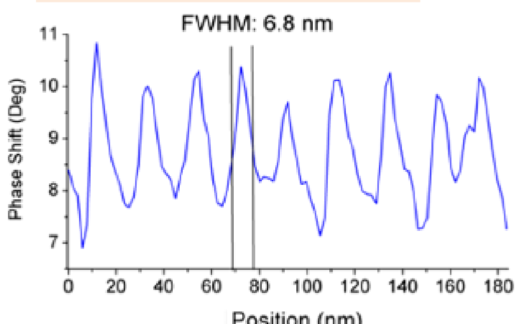
3. PS-b-PMMA deposition + Annealing

4. BCP directed self-assembly

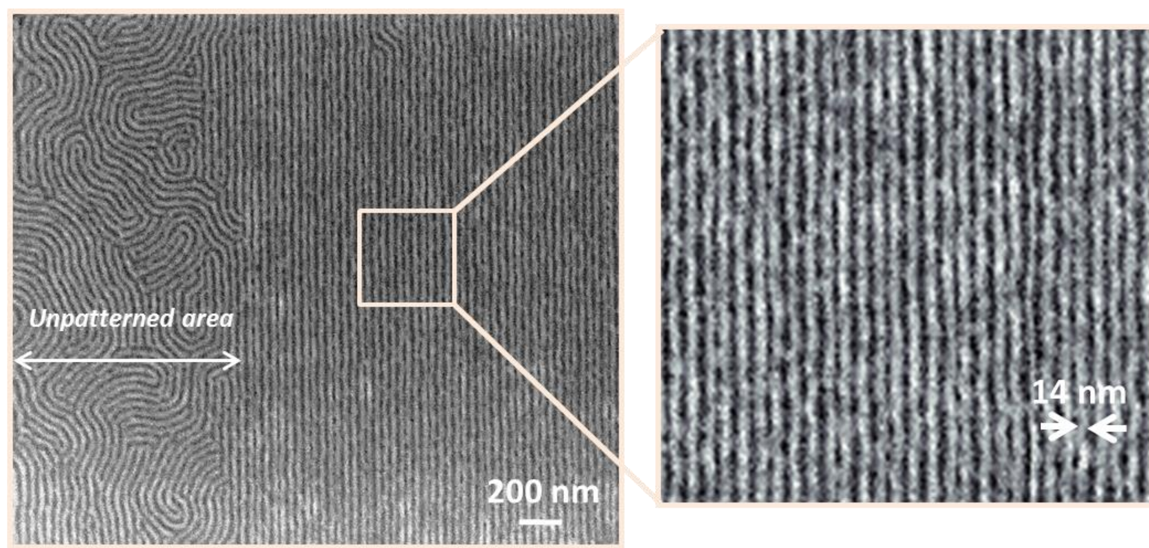


➔ Sub-10 nm guiding patterns





AFM phase image

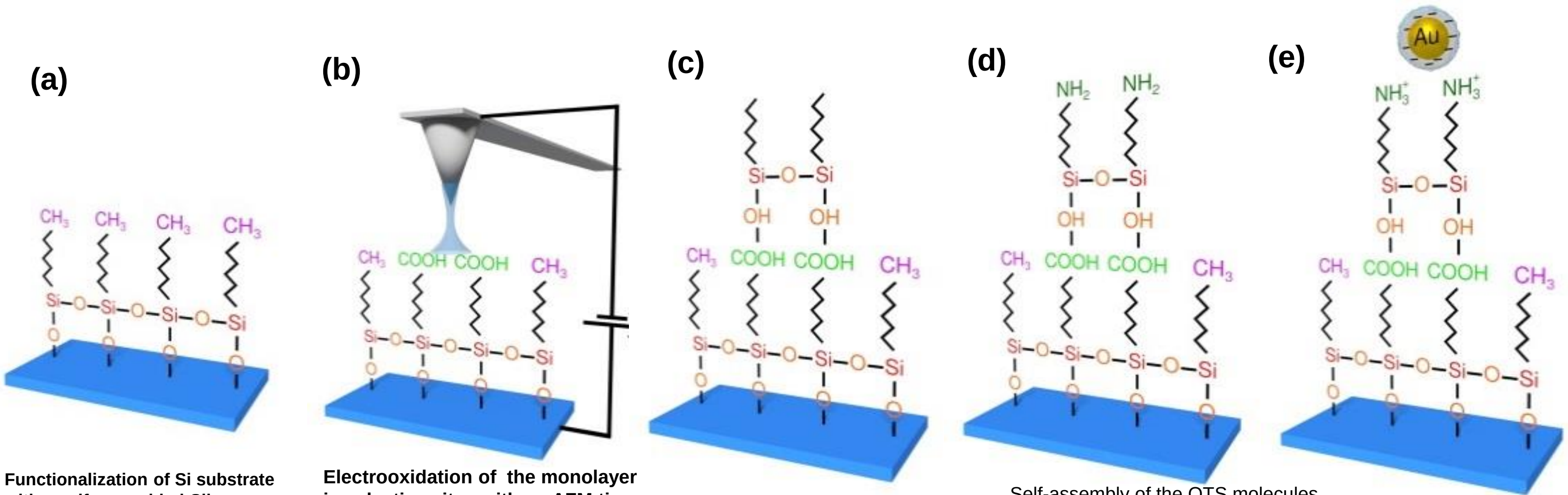


M. Fernández-Regúlez; L. Evangelio, M. Lorenzoni, J. Fraxedas, F. Pérez-Murano, ACS Appl. Mater. Interfaces 6, 21596 (2014)

CSIC cnm

in-situ nanofabrication of metal-semiconductor-organic interfaces

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

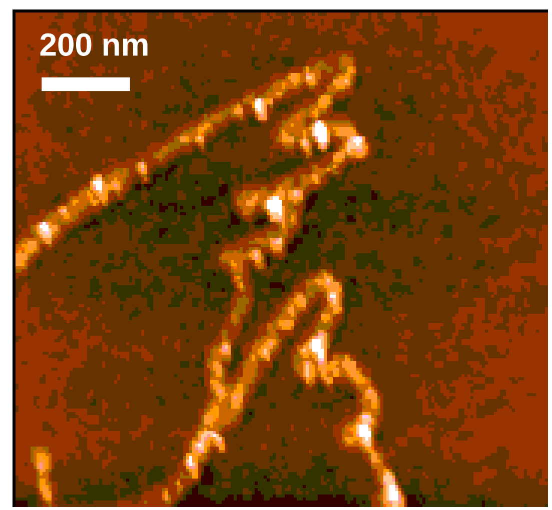


Functionalization of Si substrate with a self-assembled Silane monolayer.

Electrooxidation of the monolayer in selective sites with an AFM tip.

Second functionalization with another silane monolayer (OTS).

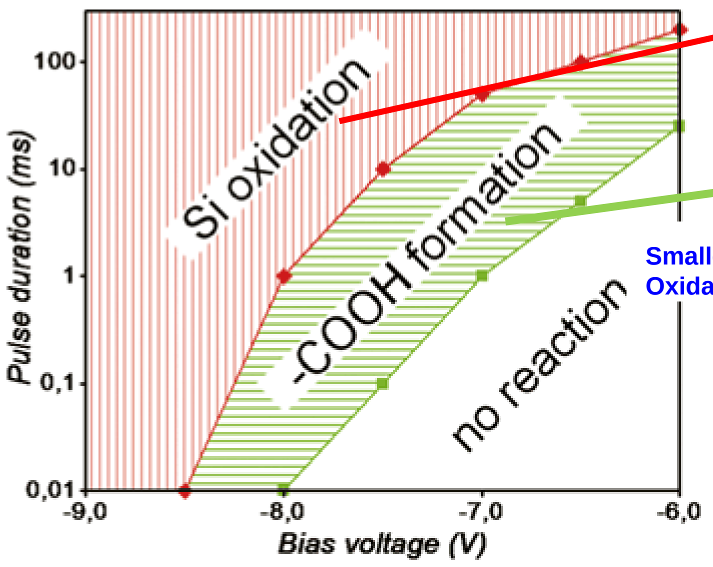
Self-assembly of the OTS molecules only in the oxidized sites



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)

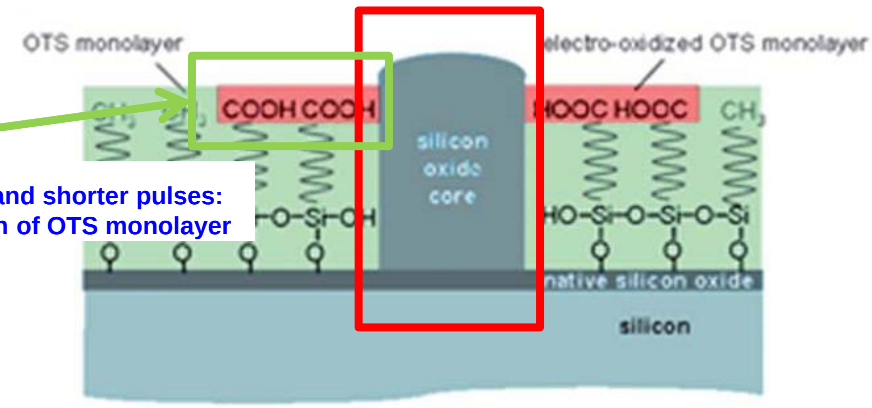
o-SPL on self-assembled monolayers: Interplay SAM vs. Silicon oxidation

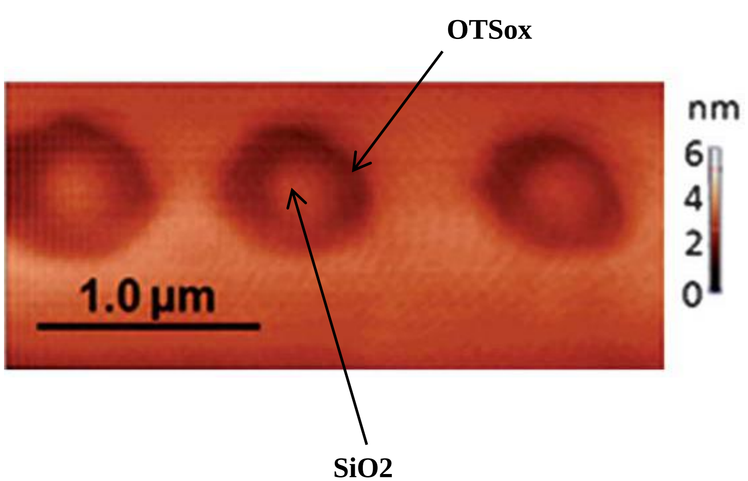
Regimes of oxidation:



Larger and longer pulses:
Oxidation of Si substrate

Smaller and shorter pulses:
Oxidation of OTS monolayer



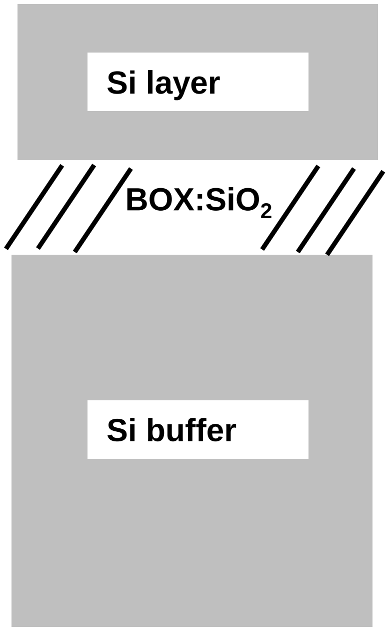


T.Druzhinina, S. Hoeppener, N. Herzer and U.S. Schubert. *Journal of Materials Chemistry* 21 (2011)

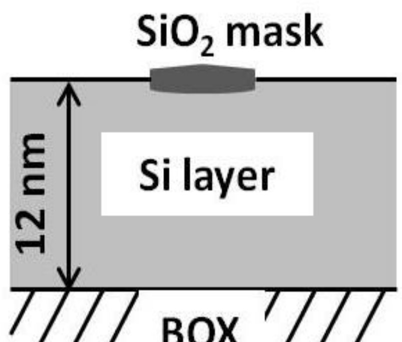
Mask Fabrication

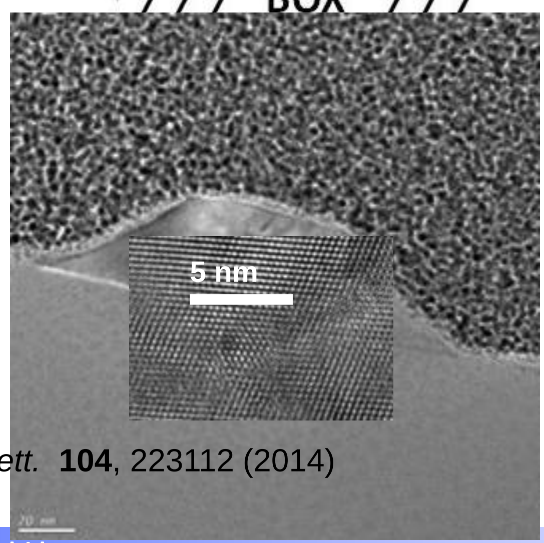
I: substrate

SOI: Silicon on insulator

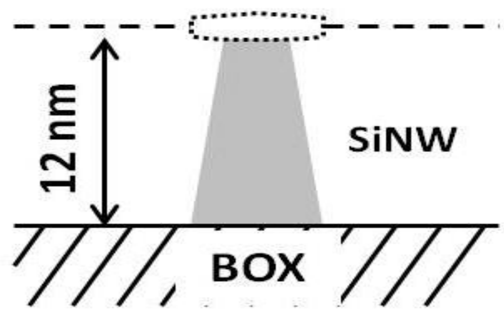


II: o-SPL





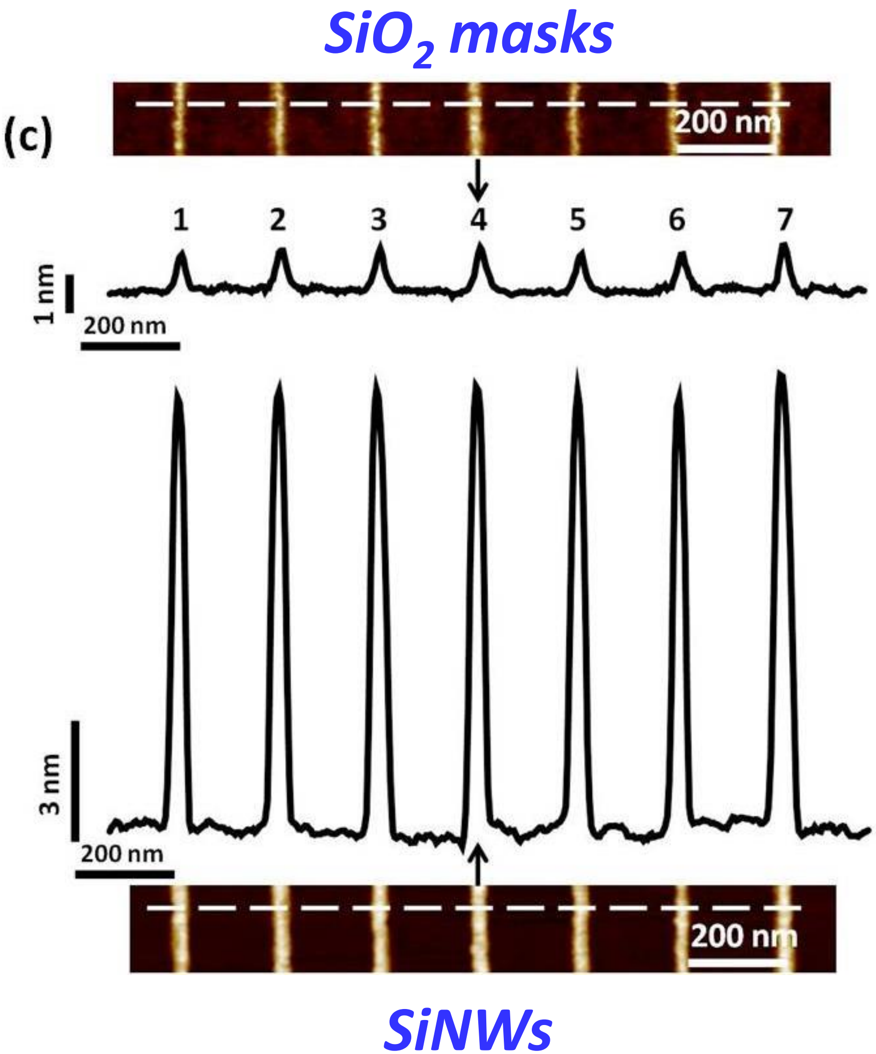
III: Etching



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)

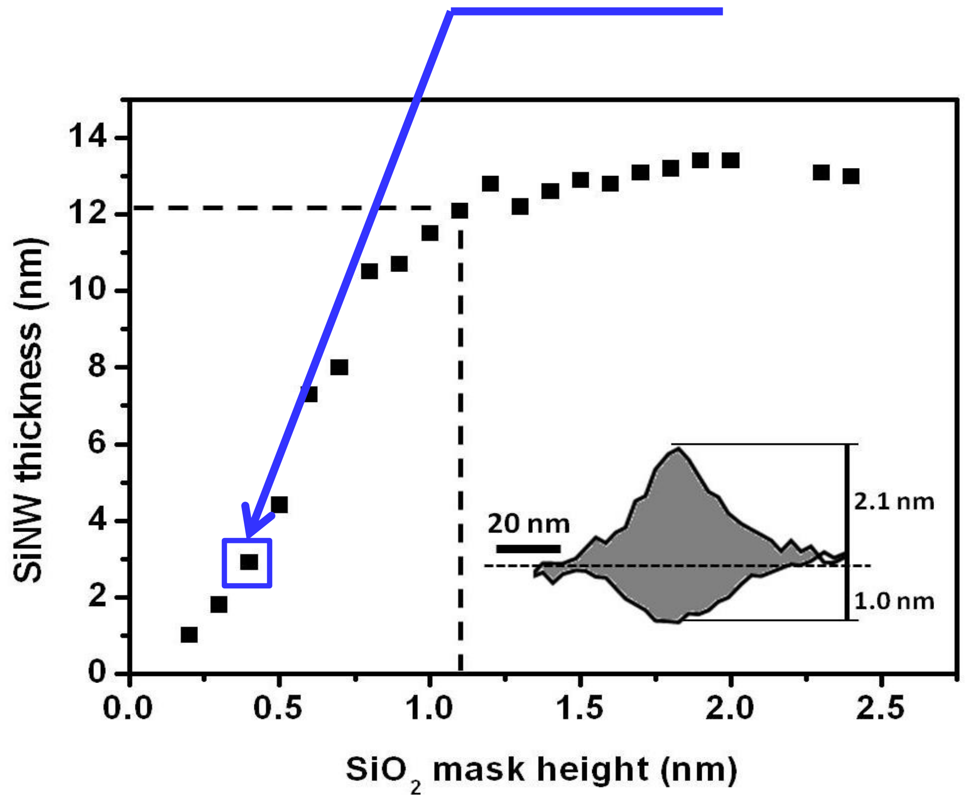
SiNWs after pattern transfer

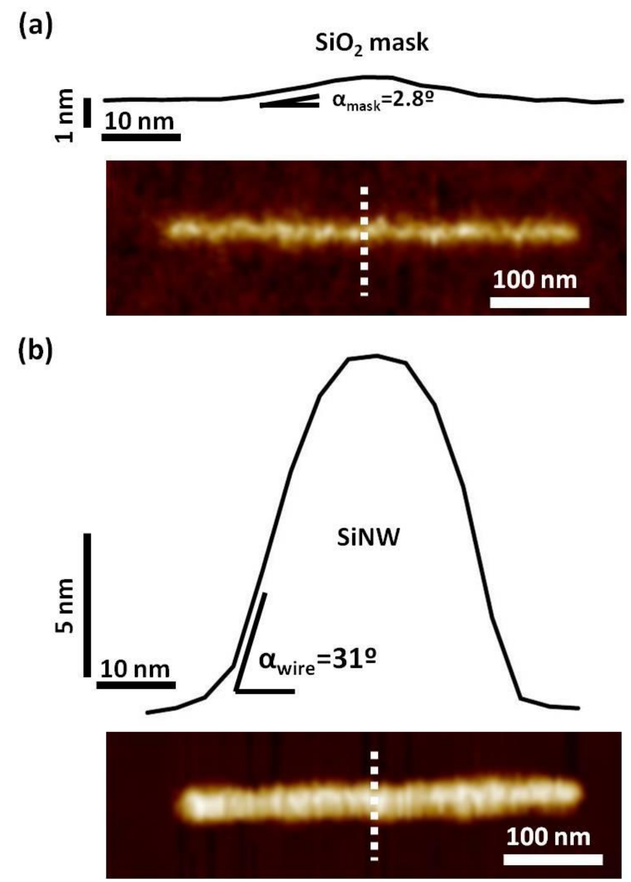


Nº	h(nm) SiO_2 mask	h(nm) SiNW	w(nm) SiO_2 mask	w(nm) SiNW
1	1.1	12.7	24	27
2	1.1	13.0	24	34
3	1.3	13.0	34	35
4	1.4	13.1	33	30
5	1.2	12.9	35	33
6	1.1	12.7	29	24
7	1.4	13.5	25	39

SiNW thickness as a function of the thickness of the mask

Section of the SiNW≈ 3x30 nm²





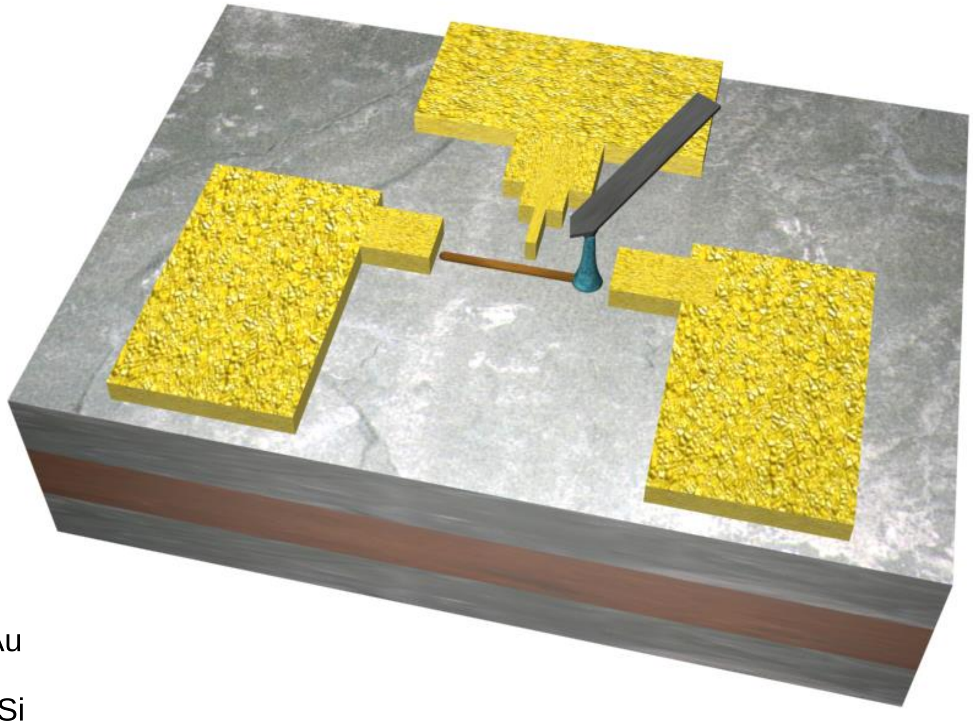
The oxide mask height is controlled by the voltage amplitude

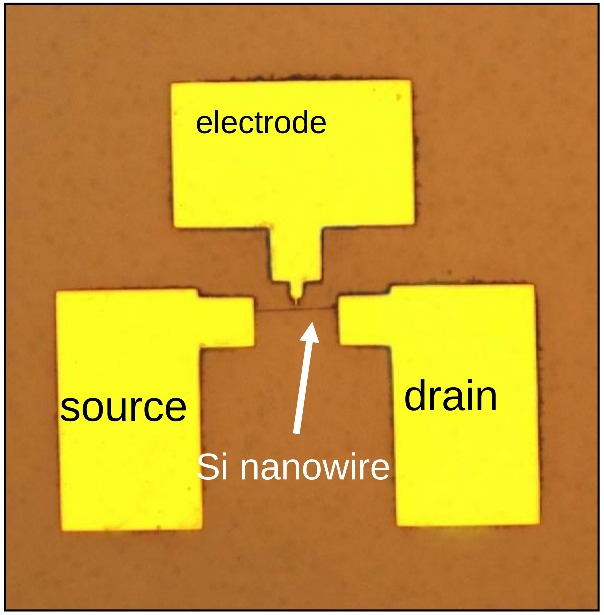
$$\textit{Selectivity} = \frac{\tan \theta_{nw}}{\tan \theta_{mask}} \approx 11$$

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

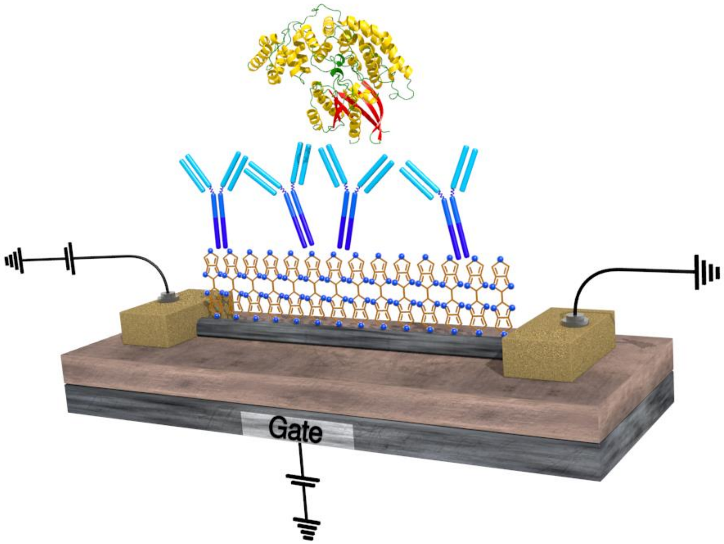


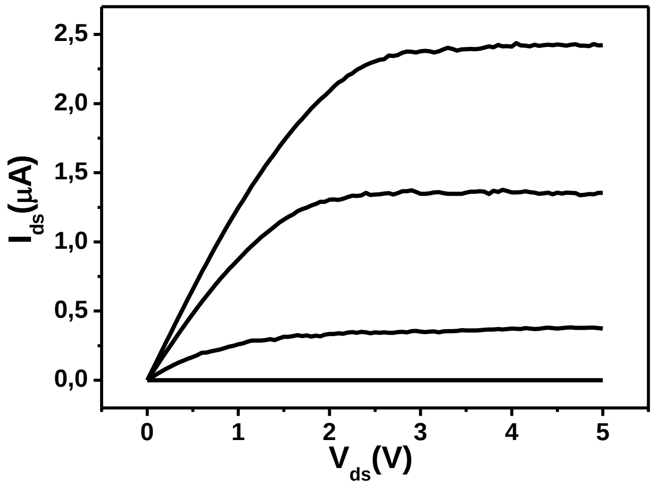


Au
Si
SiO_2

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)

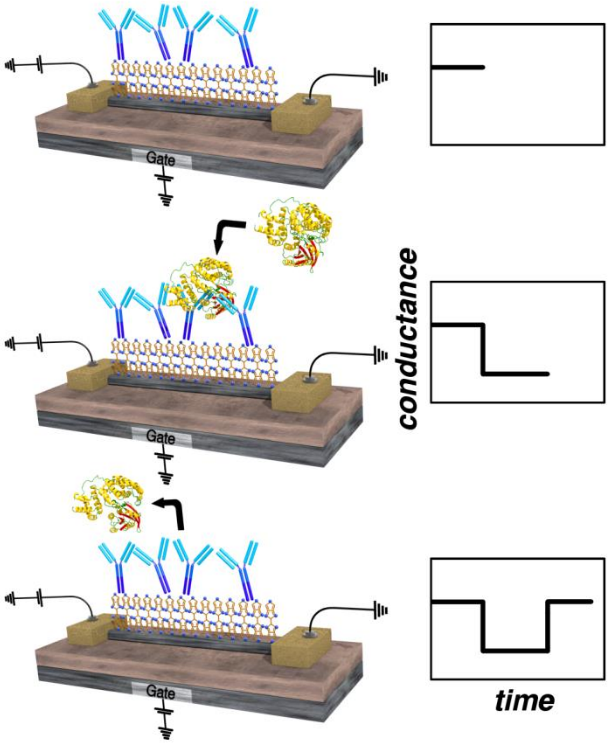
Transistor: three terminal device
Field-effect transistor: The current is modified by the electrical field of the gate

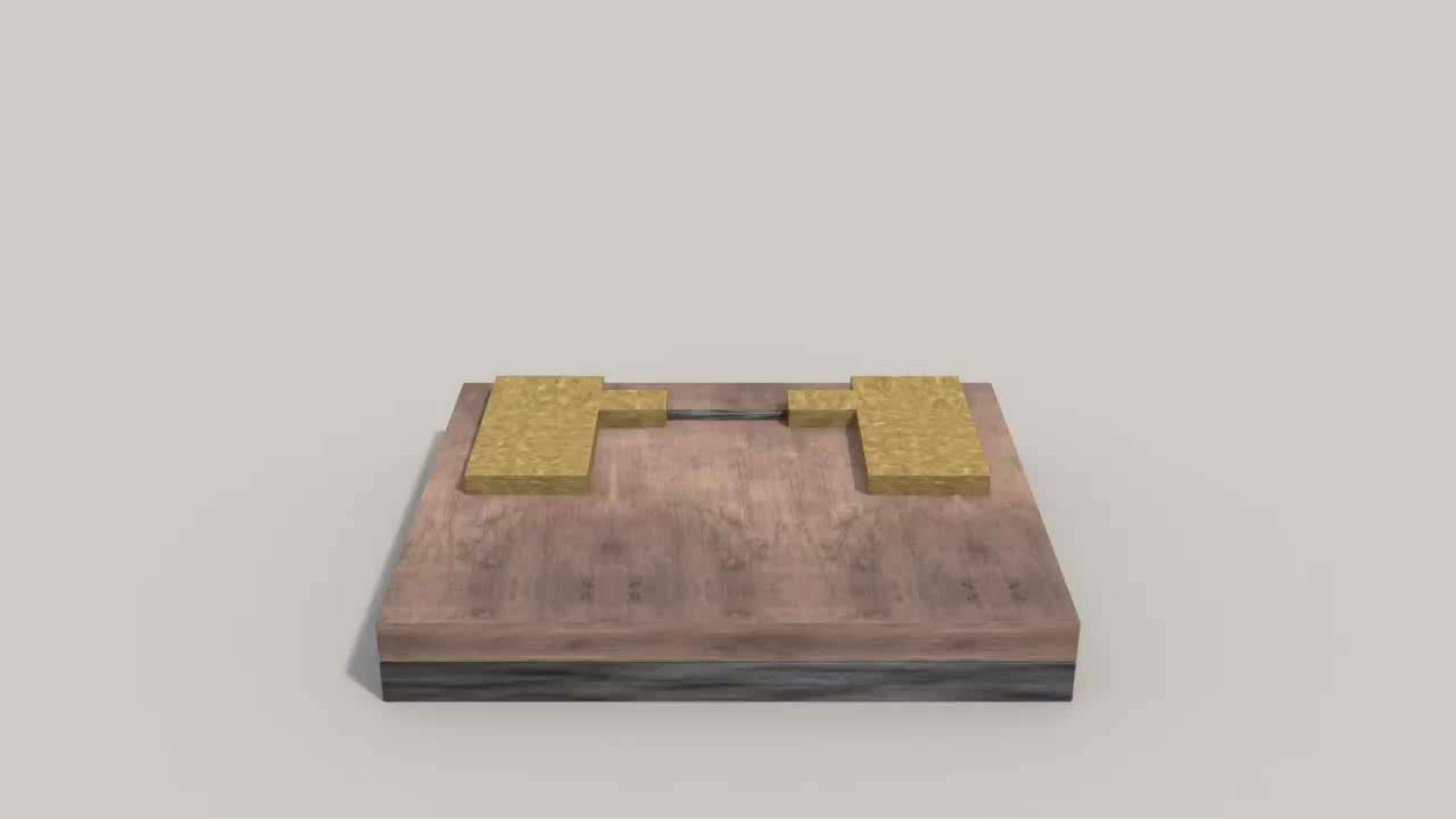




SiNW biosensors
general sensing principle

the current measured is affected by the molecular interactions



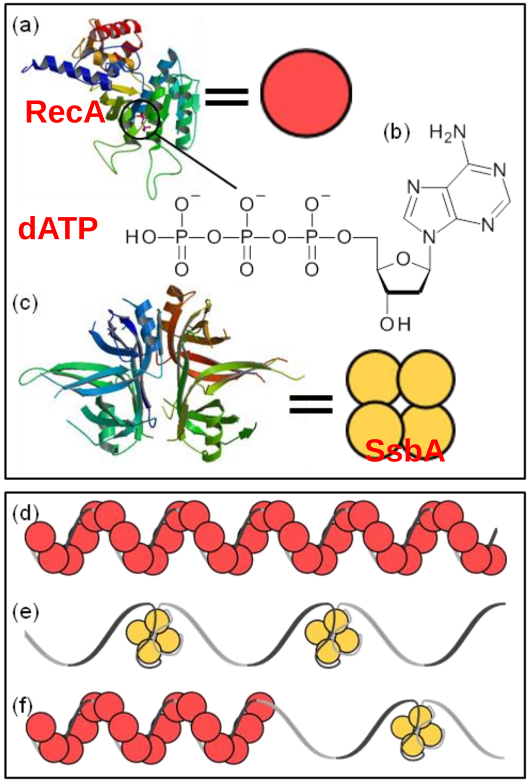


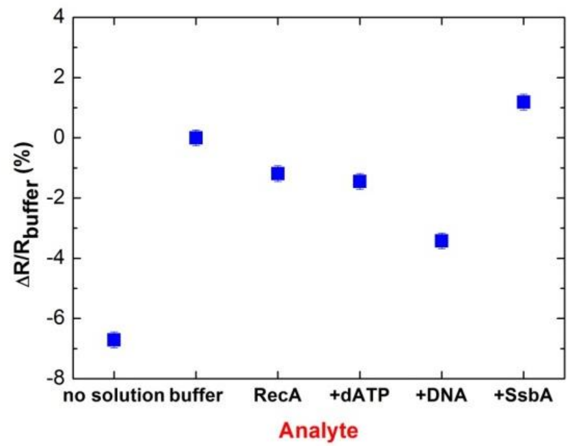
M. Chiesa et al. Nano Letters 12, 1275 (2012)

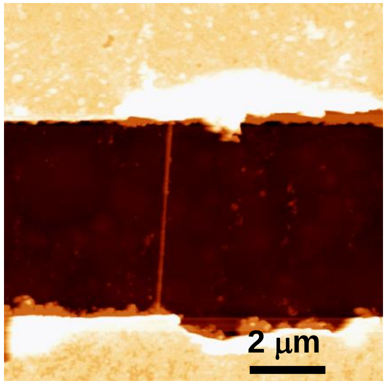
NANO LETTERS
Letter
pubs.acs.org/NanoLett
12, 1275-1281 (2012)

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

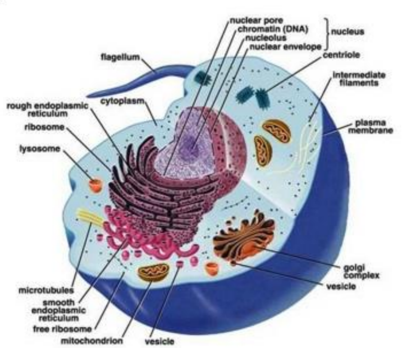
Marco Chiesa,[†] Paula P. Cardenas,[‡] Francisco Otón,[§] Javier Martinez,[†] Marta Mas-Torrent,[§] Fernando Garcia,[†] Juan C. Alonso,[‡] Concepció Rovira,[§] and Ricardo Garcia*,[†]







f



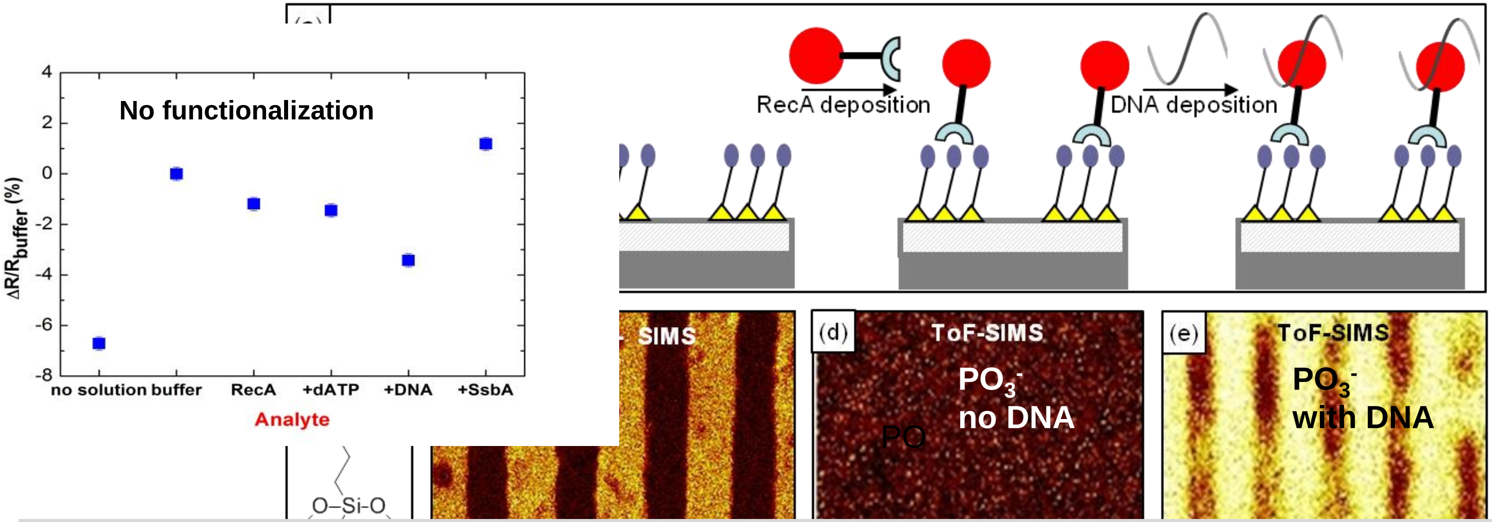
RecA forms a polymorphic right-handed helix around the DNA with approximately six monomers per helix turn

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

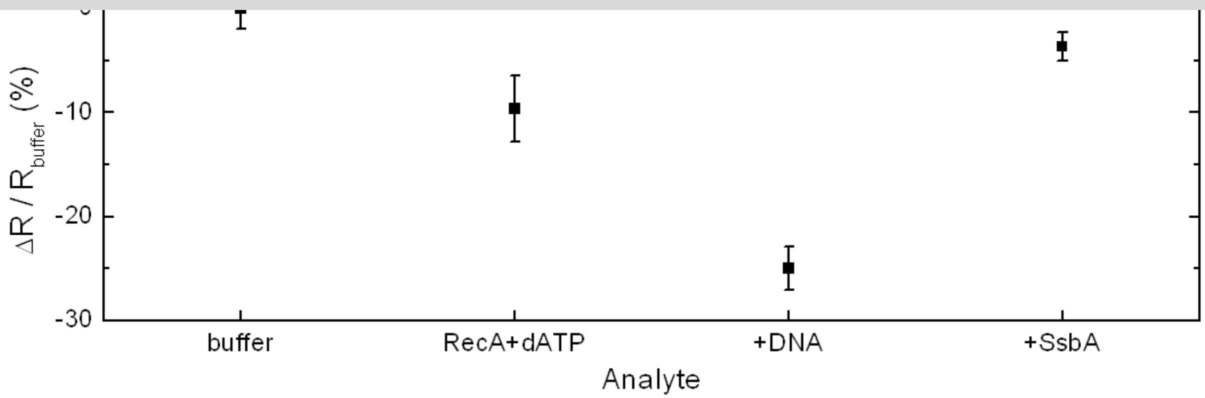
RecA: M_w = 38 kDa, d=27Å
SsbA: M_w = 18.8 kDa per subunit

SiNW functionalization to improve selectivity

with SAM amine terminations

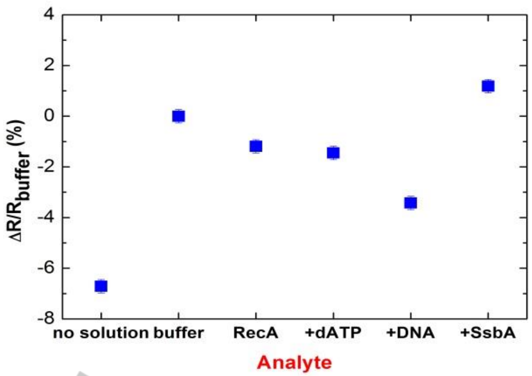


SiNW functionalization improves molecule adsorption and selectivity which improves reproducibility



CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

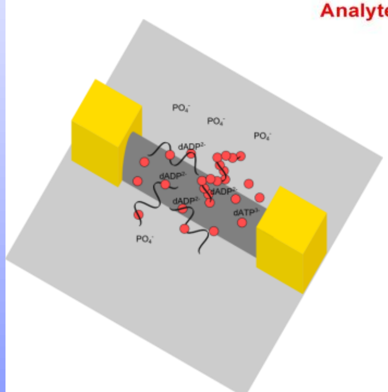
Biosensing Principle

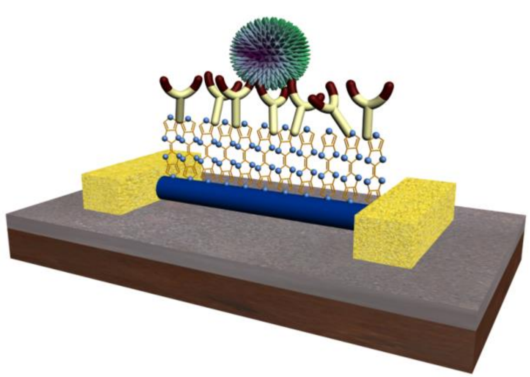


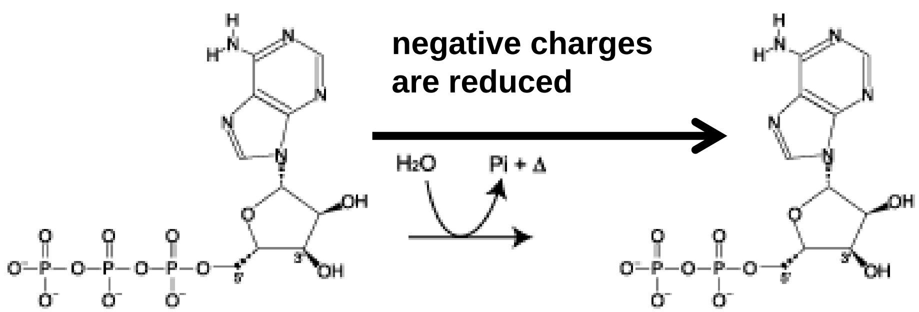
- SiNW measures changes in the resistance

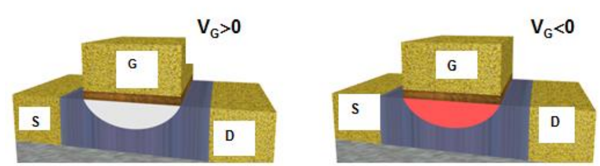
- The resistance of the SiNW is sensitive to changes in the charges in the nanowire-liquid interface

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



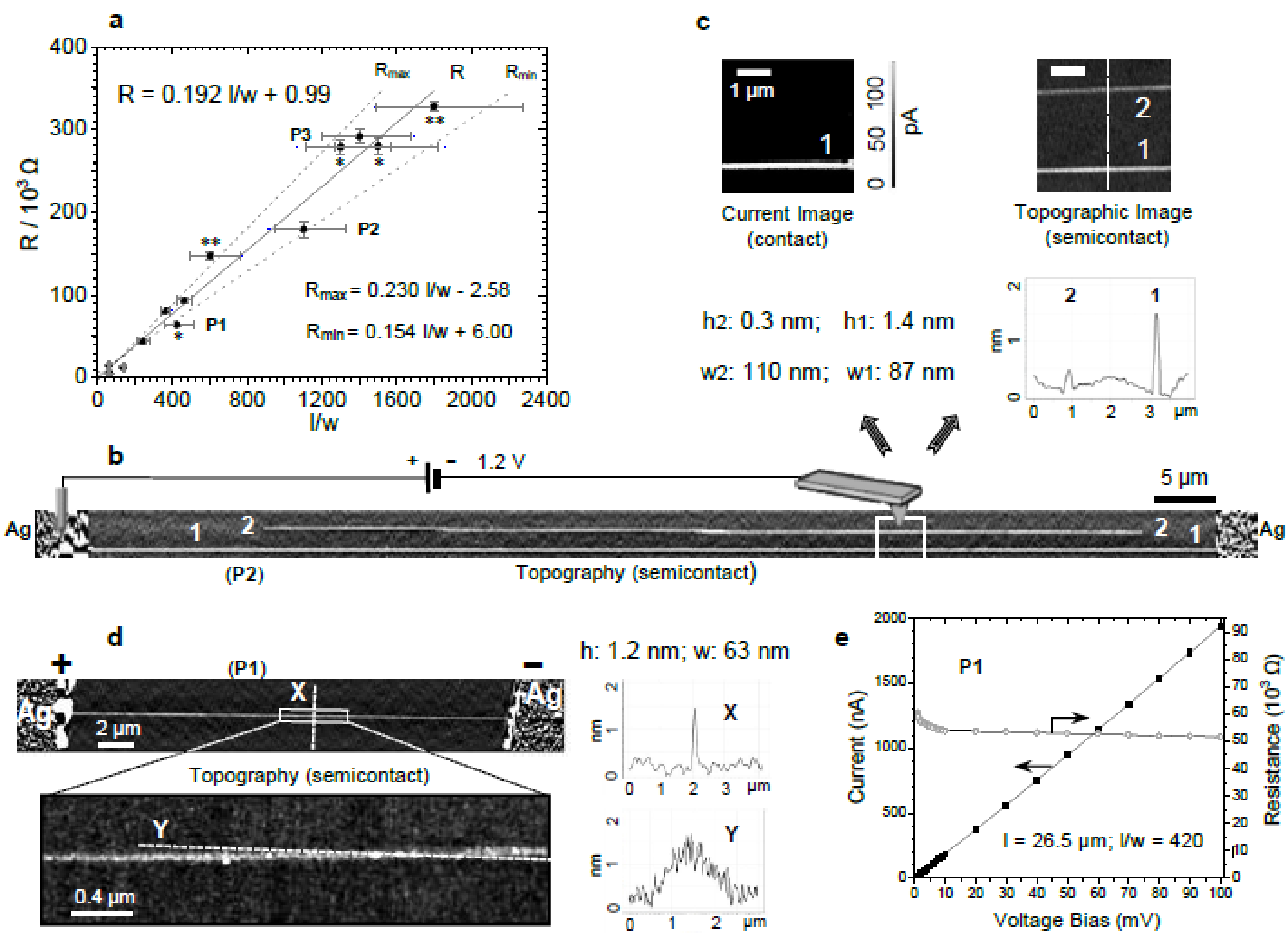




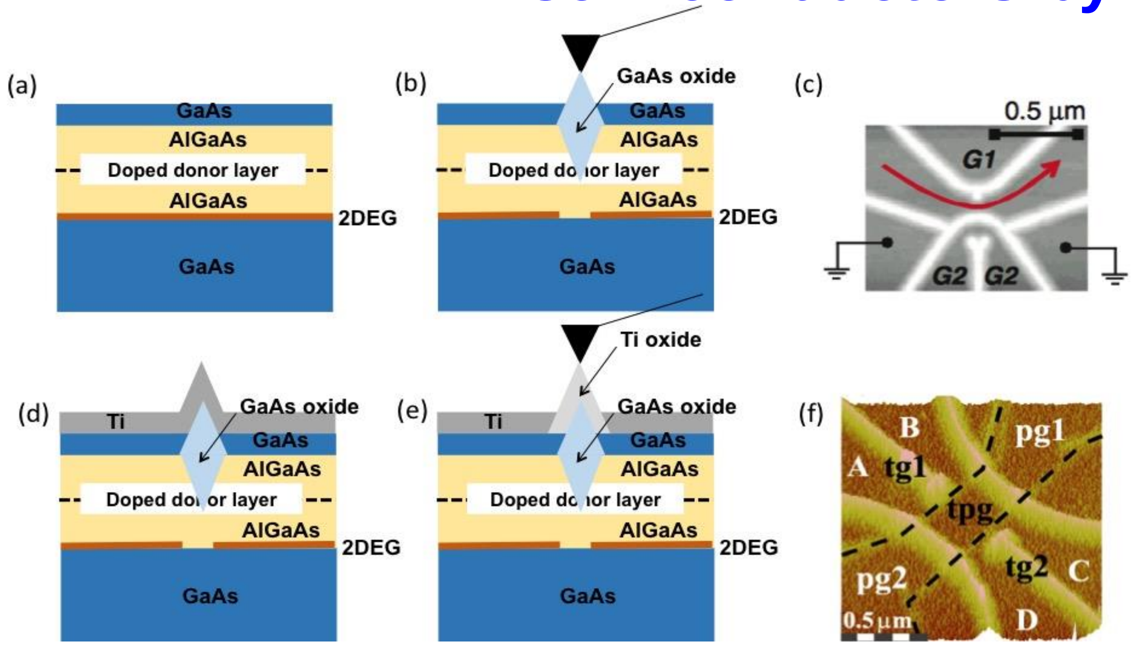


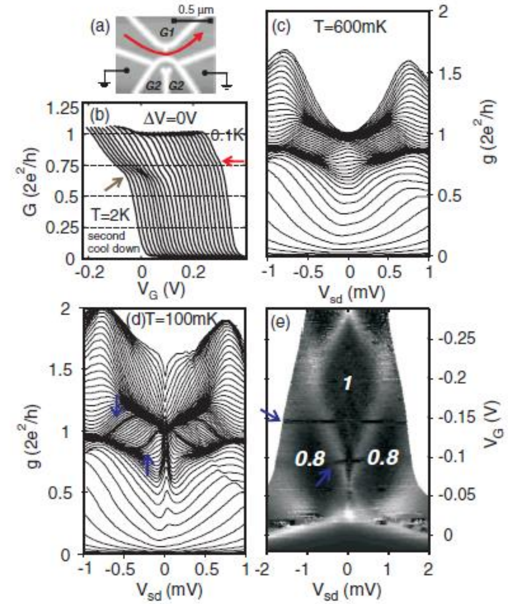
ICMM

Ion-transport device patterned by constructive lithography

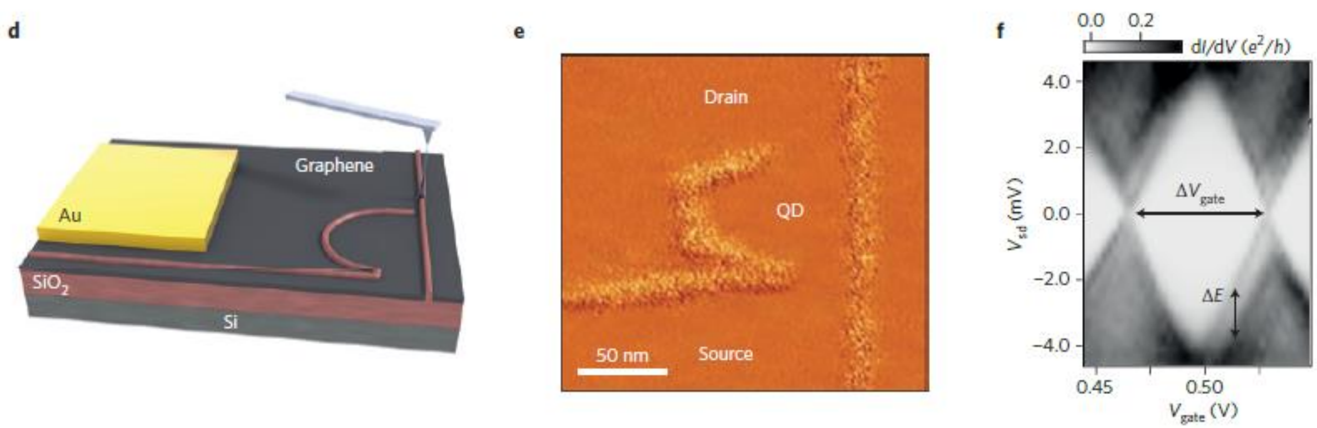


Quantum devices on crystalline semiconductors by o-SPL



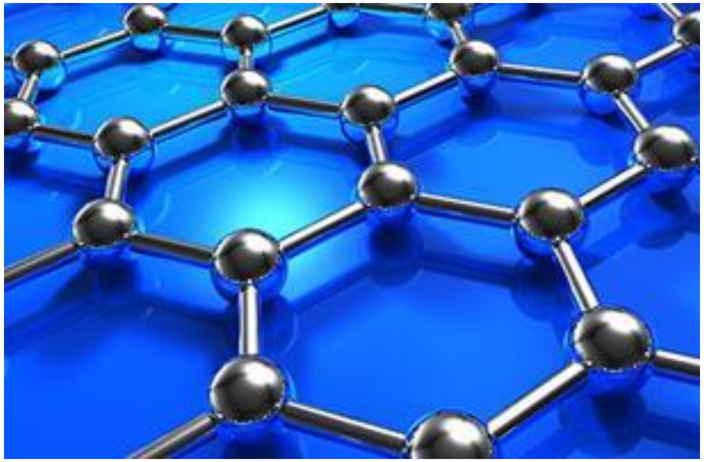


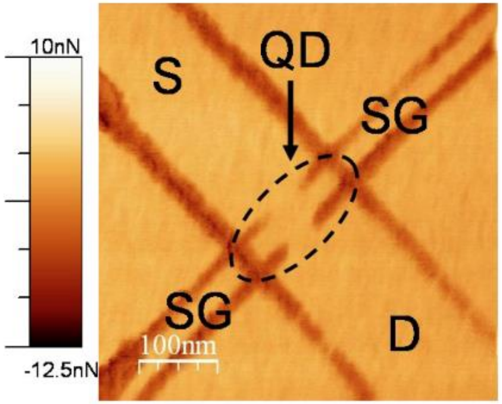
K. Ensslin et al. PRB 87, 245406 (2013); R.J. Haug et al. PRL 116, 096802 (2016)

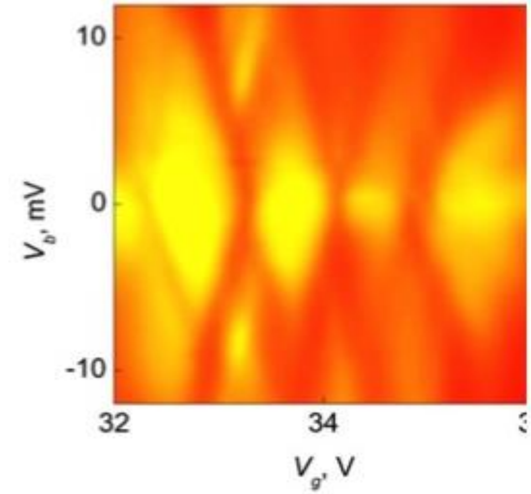


M. Buitelaar et al. APL 103, 18117 (2013)

Direct patterning of 2D electronic materials

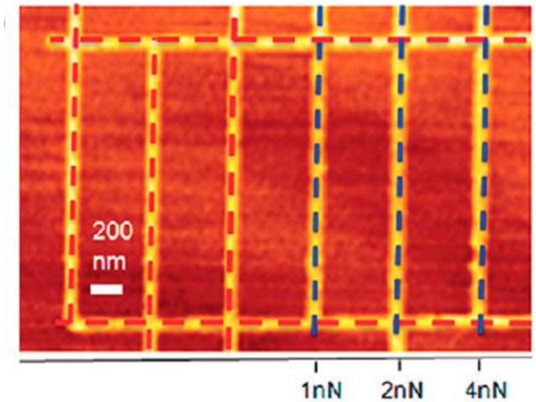


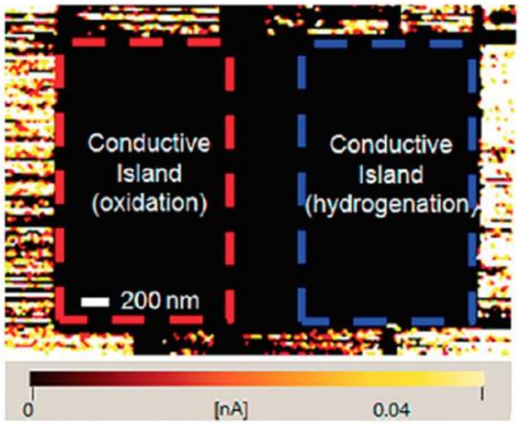




S. Neubeck , A.K Geim, K.S. Novoselov et al. Small 6, 1469 (2010)

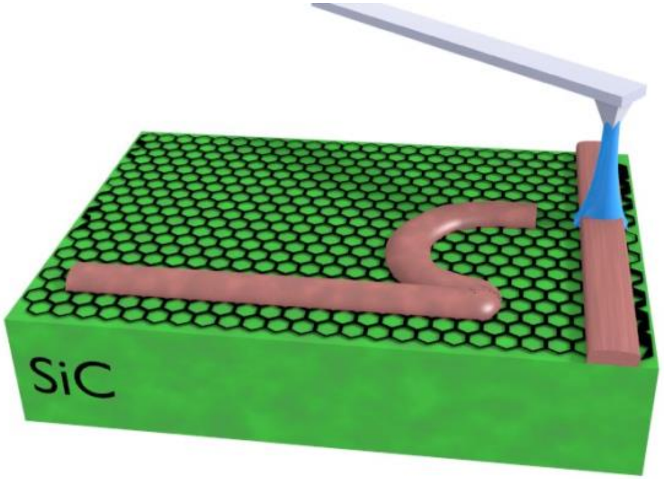
L-S. Byun et al., ACS Nano 5, 6417 (2011)

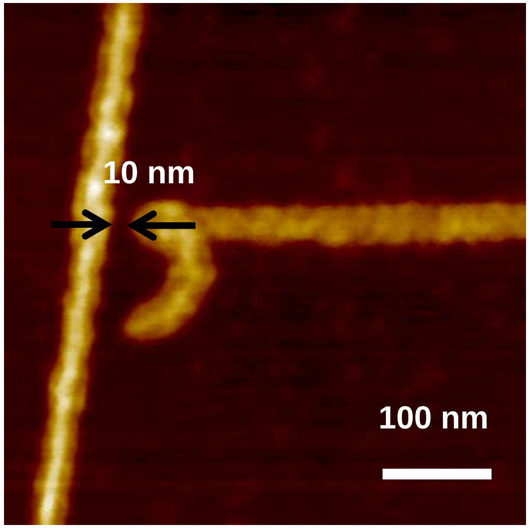




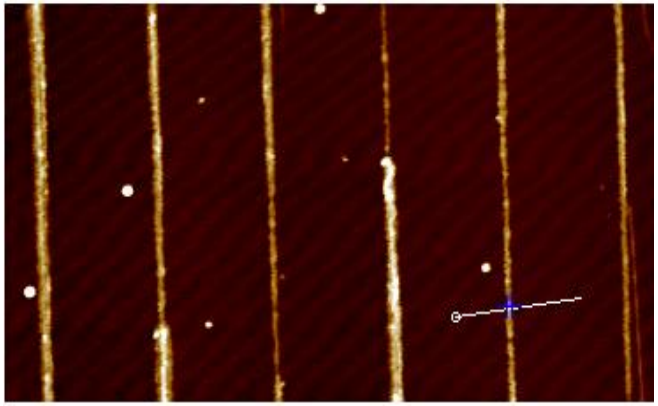
o-SPL GARAPHENE PATTERNS

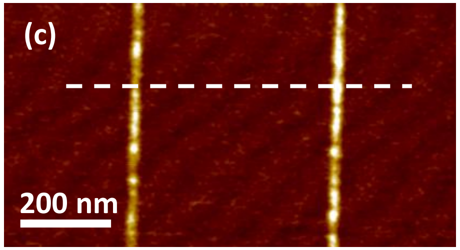
Chemical & structural characterization

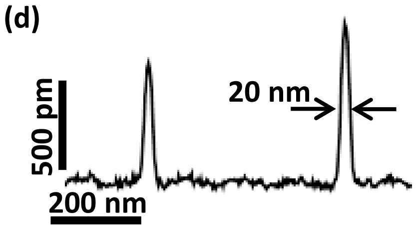




(b) RH=46,7%
Tip-sample distance ≈7 nm
V=37V
t=1 ms
2 nm step

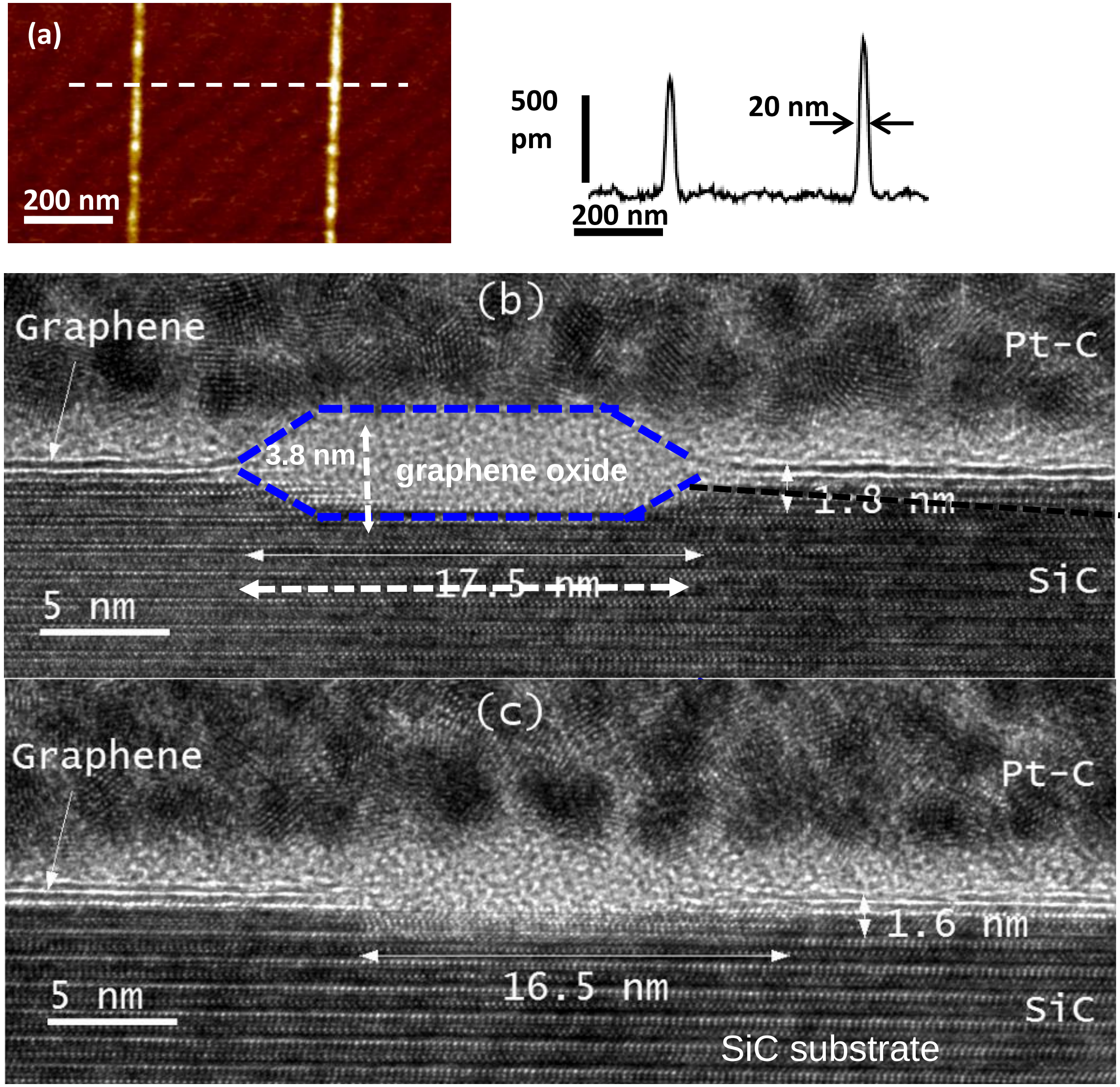


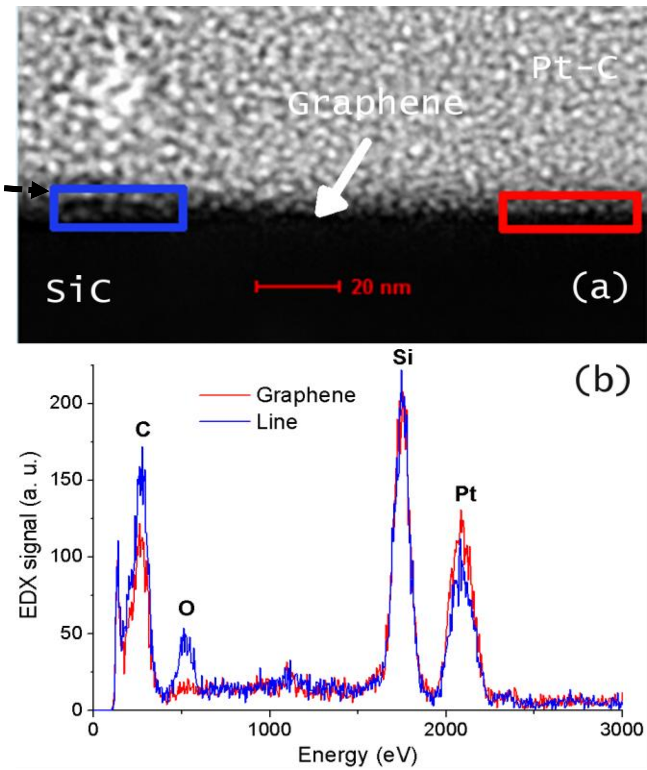




(c) RH=57%
V=20,4-20,1 V
t=0,7 ms
A0≈7-8 nm
1020 points → 2 nm limit in lateral resolution

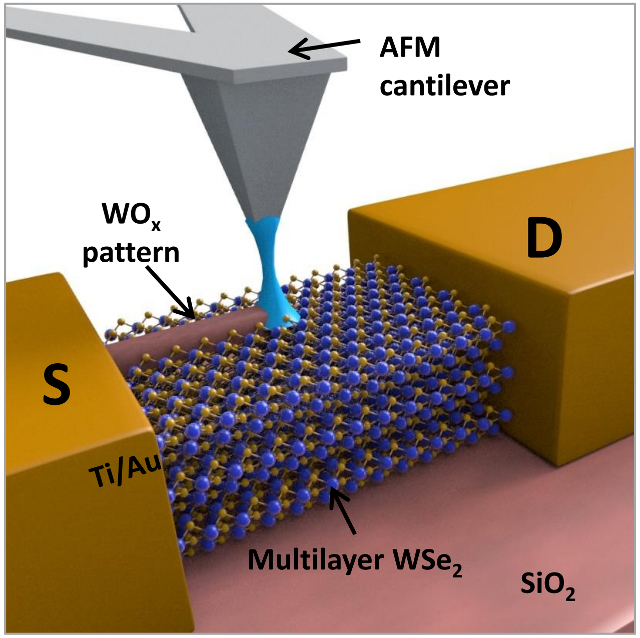
A. I. Dago, S. Sangiao, F. Rodriguez, J.M. de Teresa, R. Garcia, *Carbon* **129**, 281 (2018)

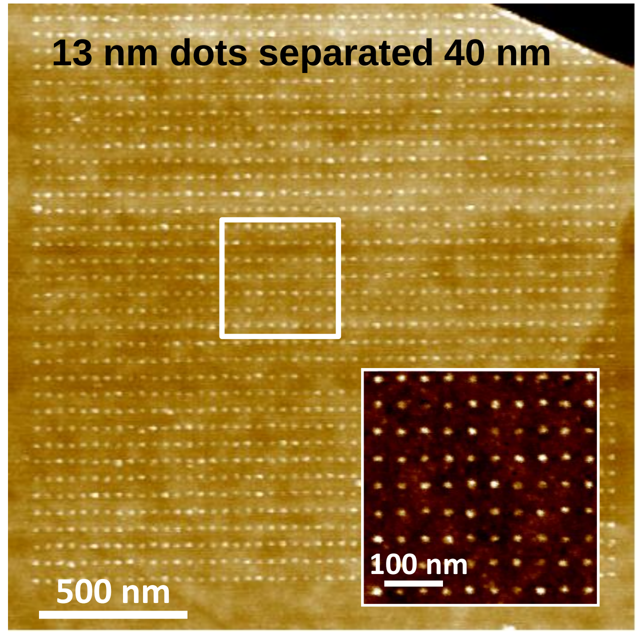




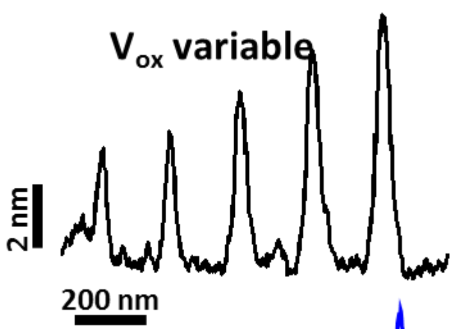
A. I. Dago, S. Sangiao, F. Rodriguez, J.M. de Teresa, R. Garcia, *Carbon* **129**, 281 (2018)

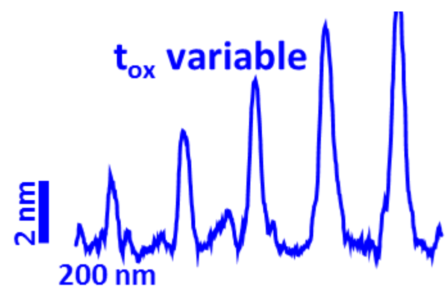
Direct fabrication of 2D Transition Metal Dichalcogenides devices: WSe_2





V=29.1 V t=1.8 ms
38.5% RH



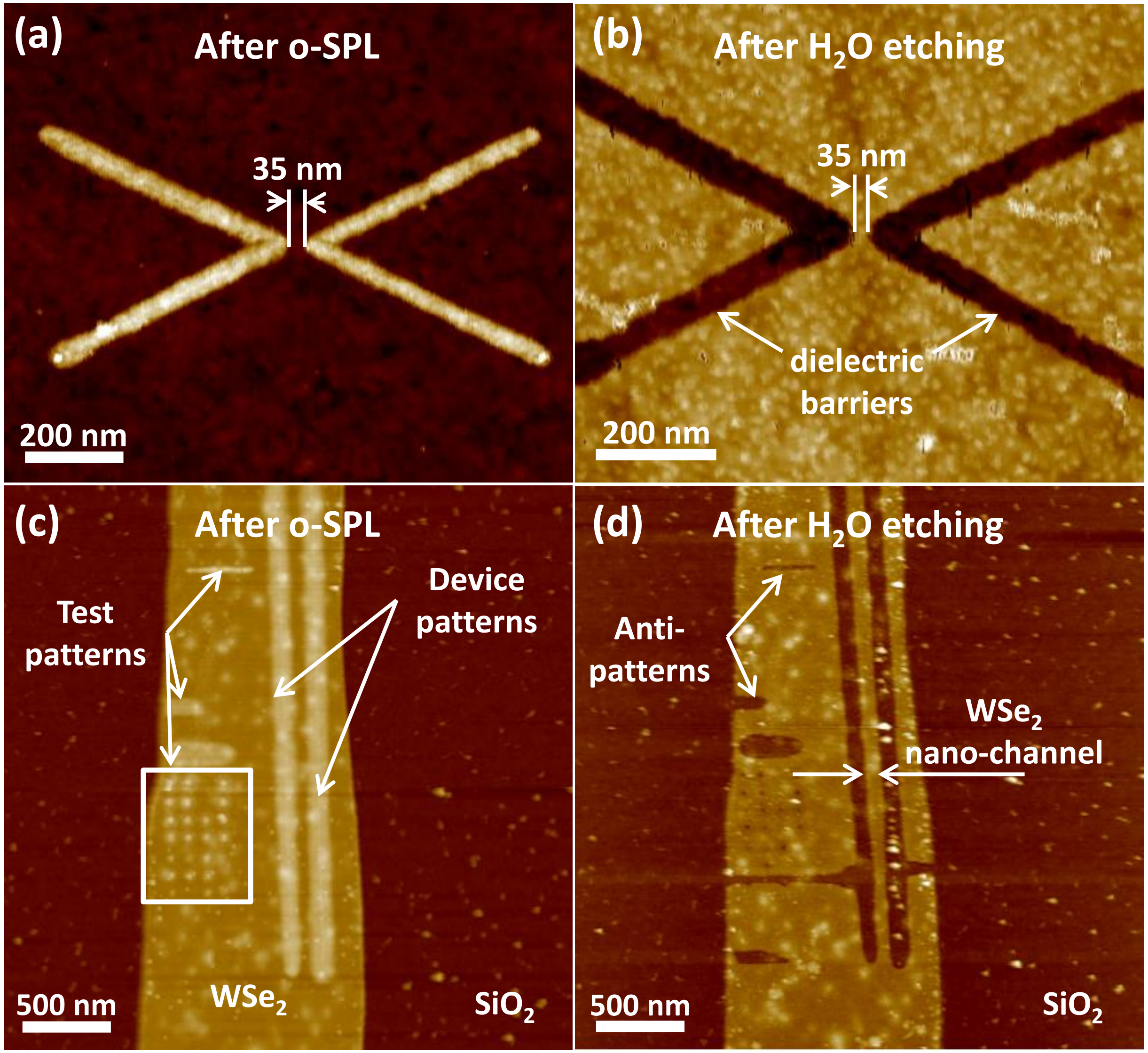


t=0.3, 0.6, 0.9, 1.2, 1.5 ms

V=9, 10.5, 12, 13.5, 15 V

A. I. Dago, Y.K. Ryu, R. Garcia, *Appl. Phys. Lett.* *109,* 163103 (2016)

Devices



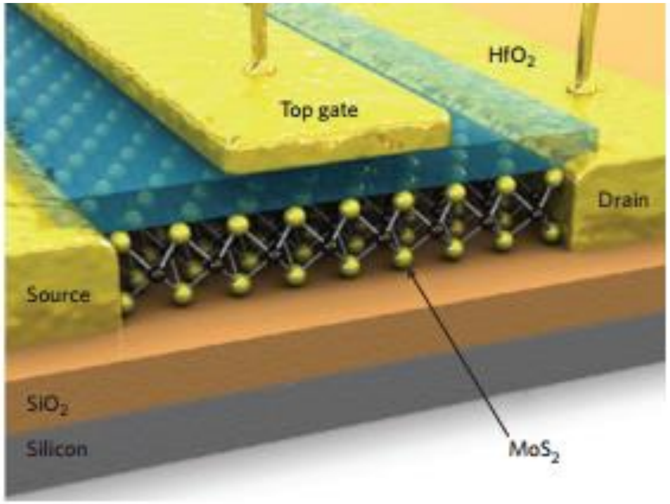
(a) Vox=18 V tox=0,2 ms
38%RH
2 nm step
Flake thickness ≈5nm

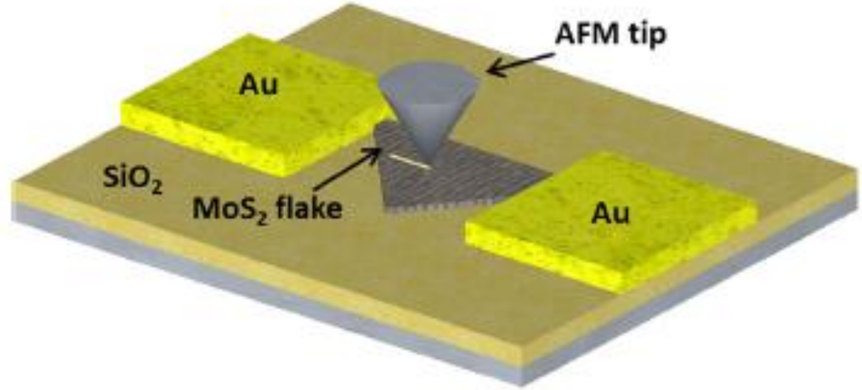
(c)&(d) Initial width 1,25µm → Final Width 80 nm
Flake thickness ≈ 5 nm

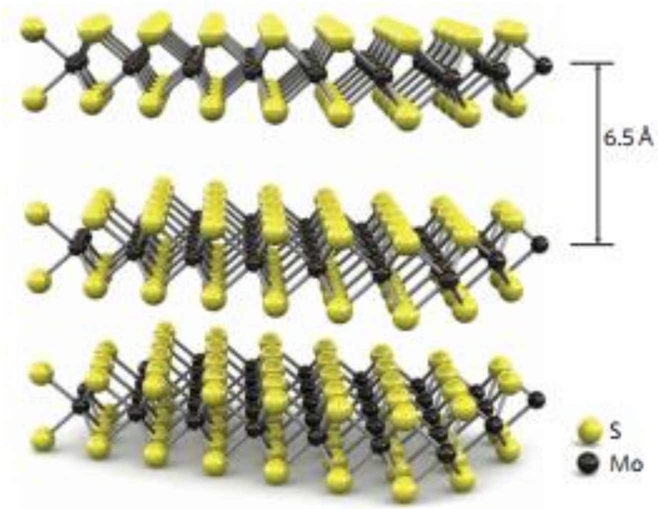
(c) Device patterns:
Lines along the channel
Asp=95 mV Da=23 mV A0≈110 mV
43,5% RH
Vox=16,5 V tox=0,5 ms
Step 3 nm separation 200 nm

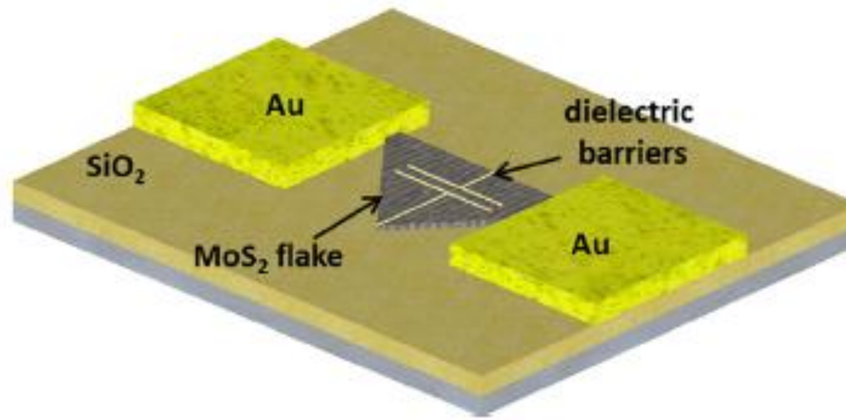
Lines perpendicular to the channel
Asp=90 mV Da=60 mV
44,6%-42%
Vox=16,5 V tox=0,5 ms
Step 3 nm

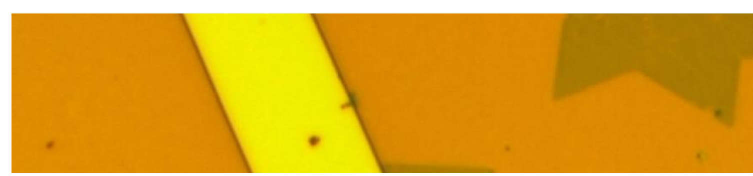
Direct fabrication of 2D Transition Metal Dichalcogenides devices: MoS_2



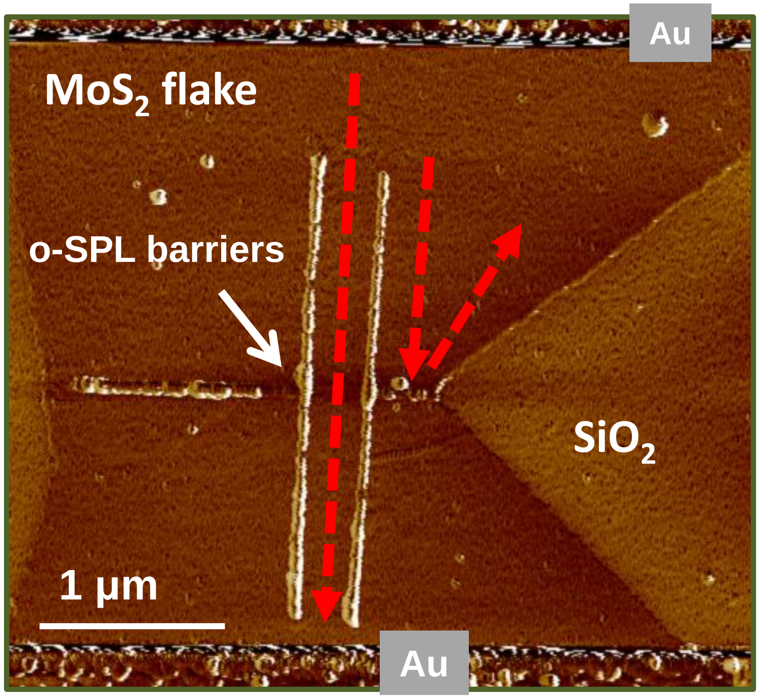


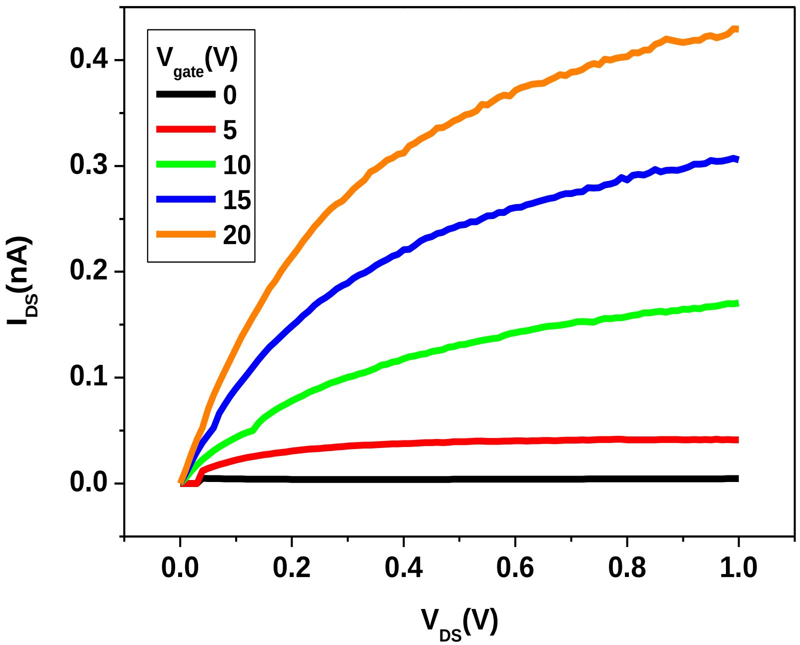






Electronics and optoelectronics of two-dimensional transition metal dichalcogenides, Qing Hua Wang,Kourosh Kalantar-Zadeh, , Andras Kis, Jonathan N. Coleman and Michael S. Strano. *Nature Nanotechnology* **7**, 699 (2012)

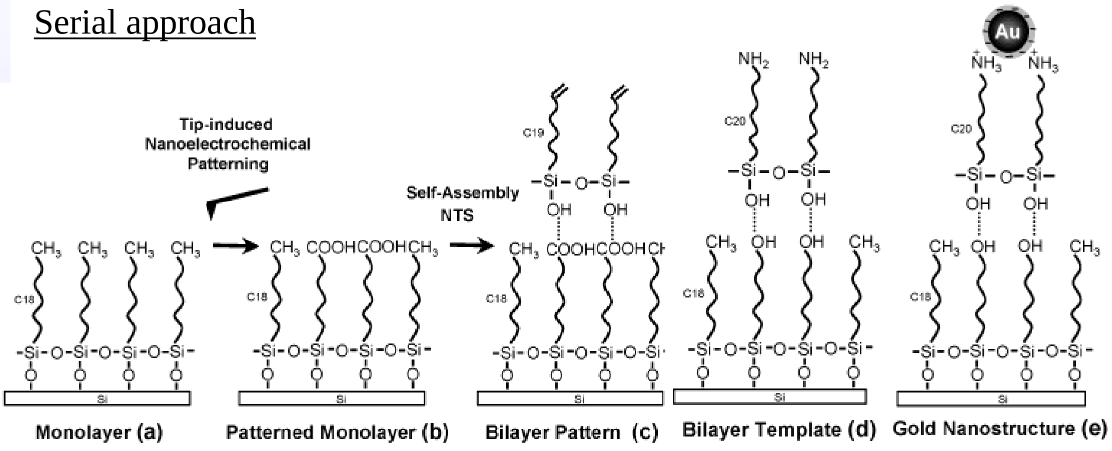


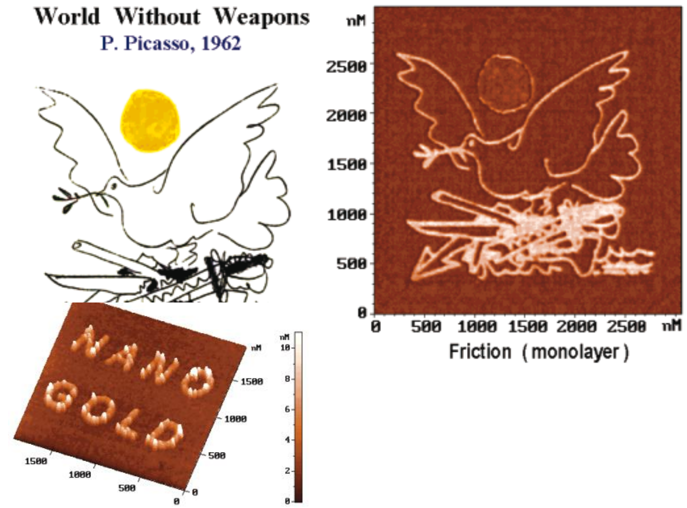


F.M. Espinosa *et al.* APL **106**, 103503 (2015)

o-SPL on self-assembled monolayers:

Serial approach

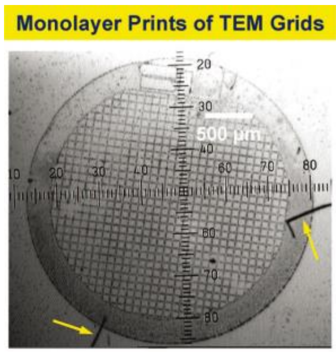




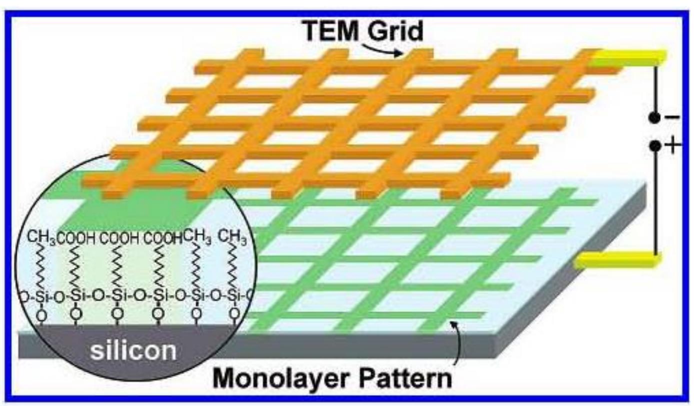
S. Liu, R. Maoz and J. Sagiv. *Nano Letters* **4** (2004)

Parallel approach

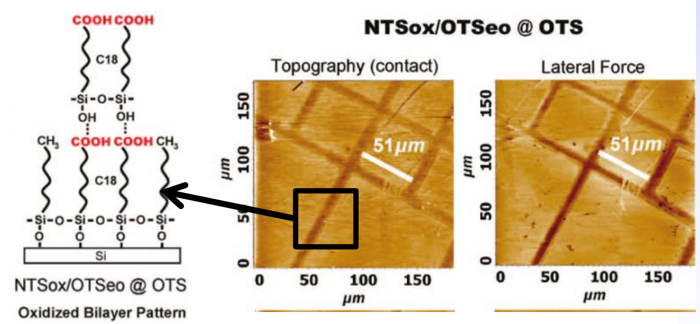
Stamp



Oxidation process

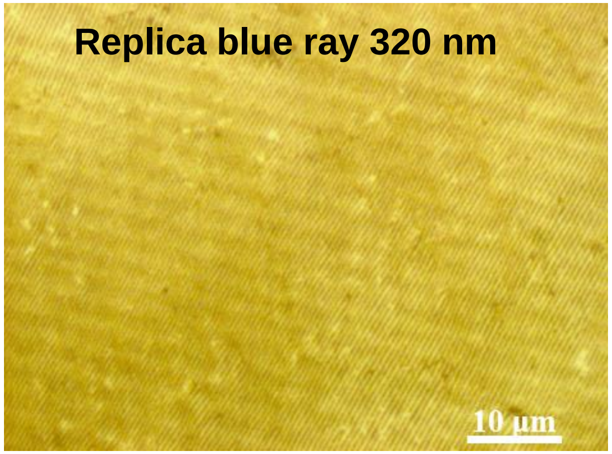


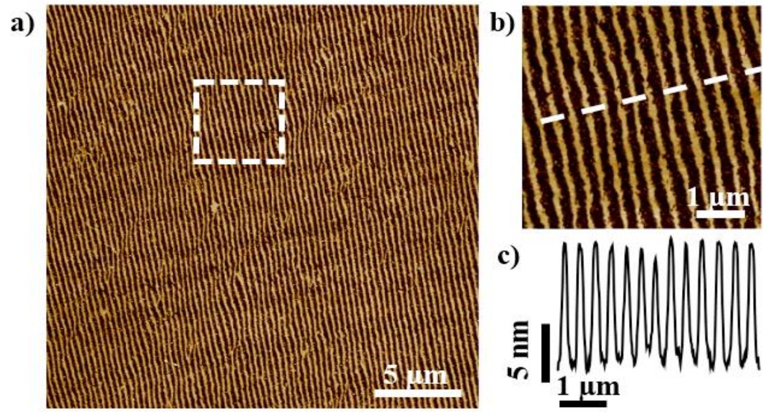
Replica pattern

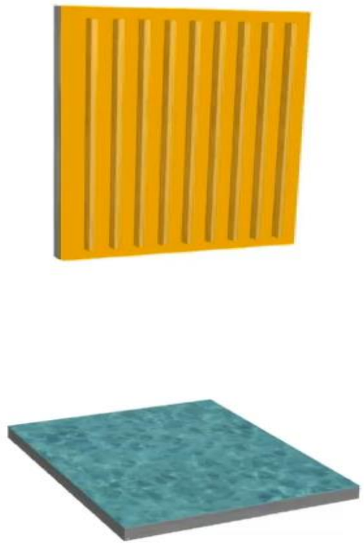


S. Hoeppener, R. Maoz and J. Sagiv. *Nano Letters* **3** (2003)

Up-scaling: Parallel oxidation SPL

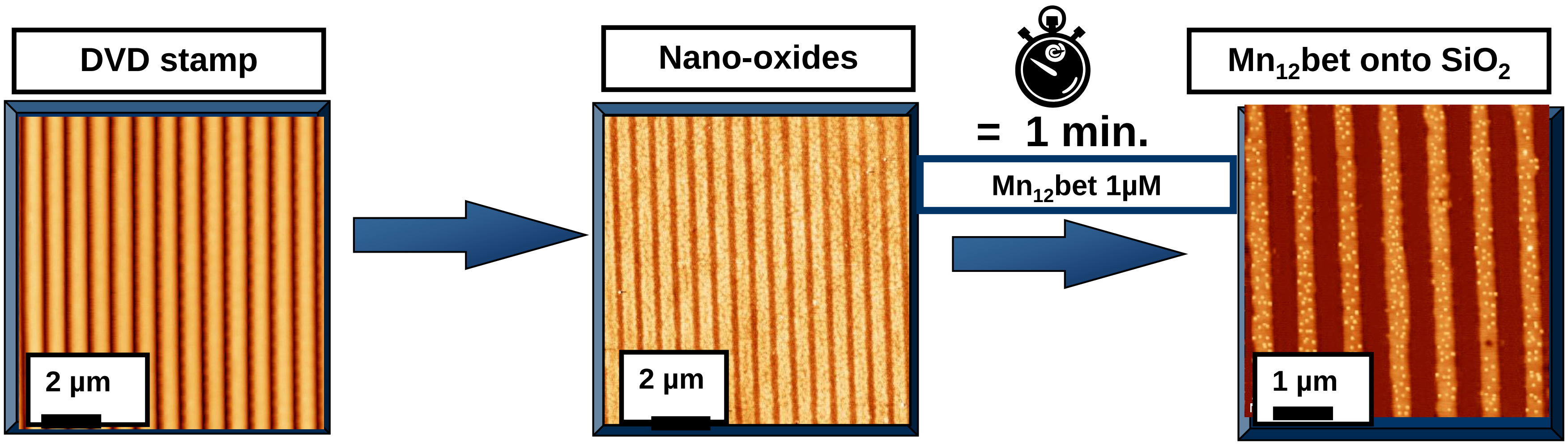




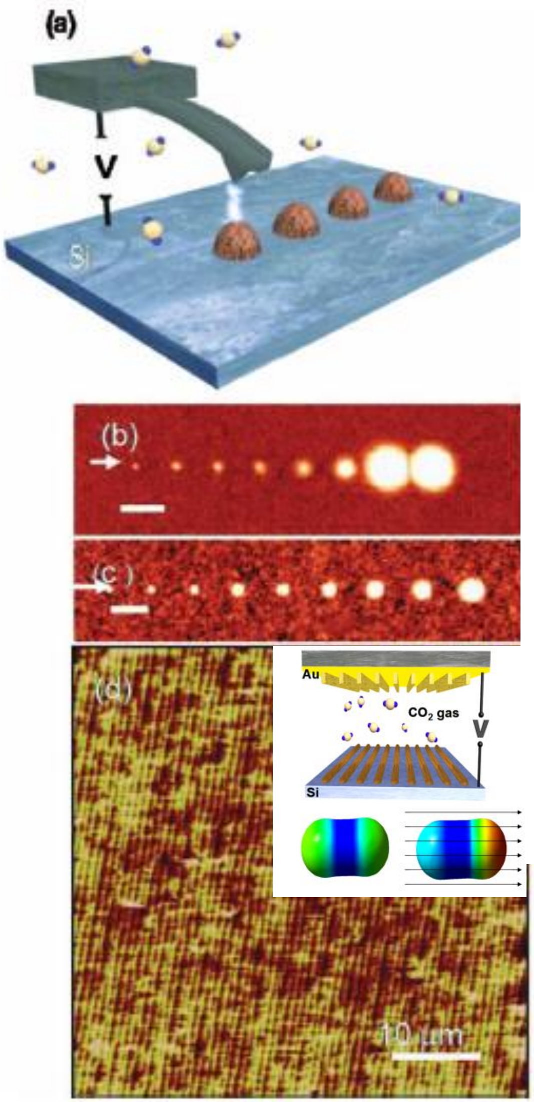


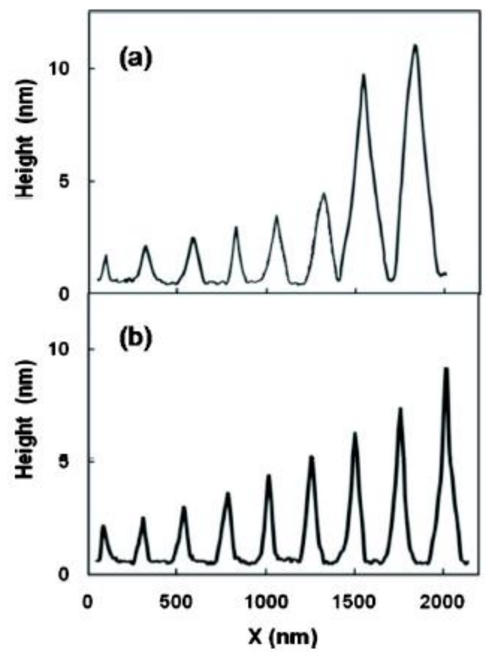
Molecular architectures: Parallel patterning

Template growth Mn_{12}bet (on nano-oxides) and ferritin:

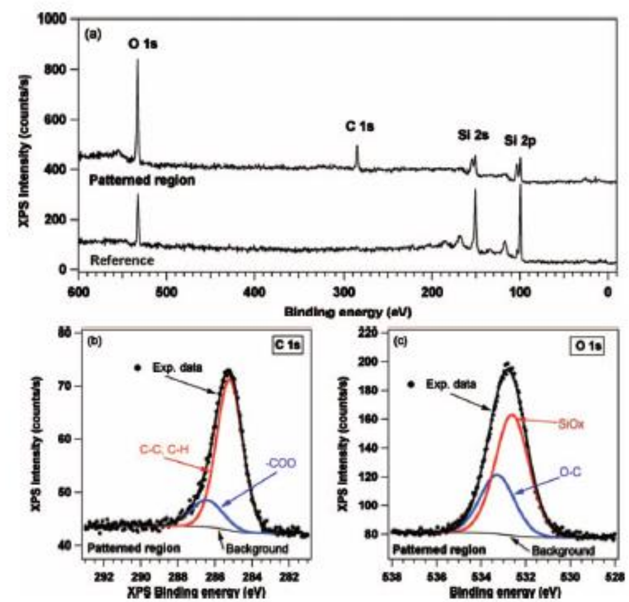


Field-induced chemical reactions
Carbon Dioxide reduction





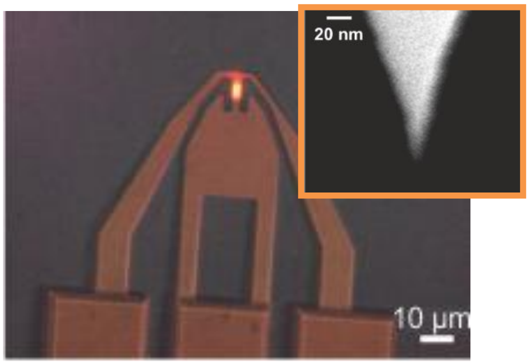
XPS



R. Garcia et al. Appl. Phys. Lett. 96, 143 (2010)

Thermal Scanning Probe Lithography: Method

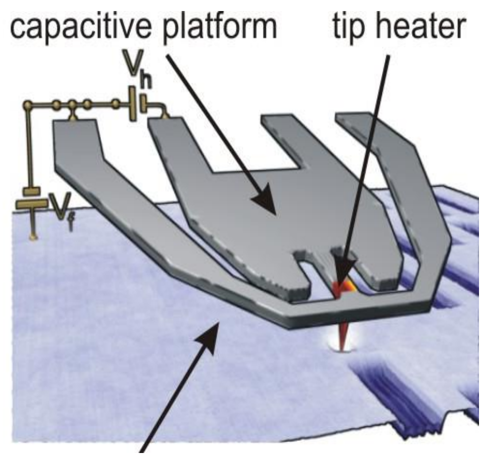
Silicon cantilever
- Microheater: 2x4 µm^2
- → up to 1000 ºC heater T



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

Writing
Heated tip evaporates resist

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



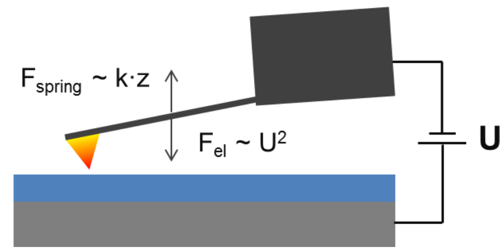
Thermal sensor for height signal

Wear less imaging:

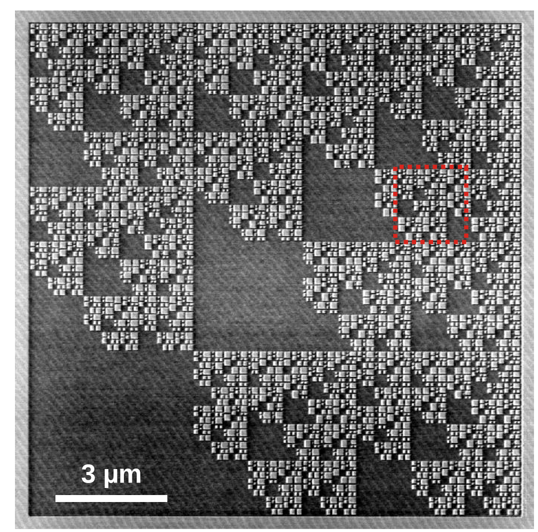
AC modulation >1 MHz

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

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



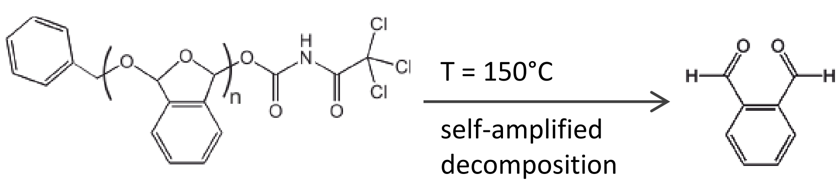
High speed patterning
880x880 pixels in 11.8s



500 kHz pixel clock

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

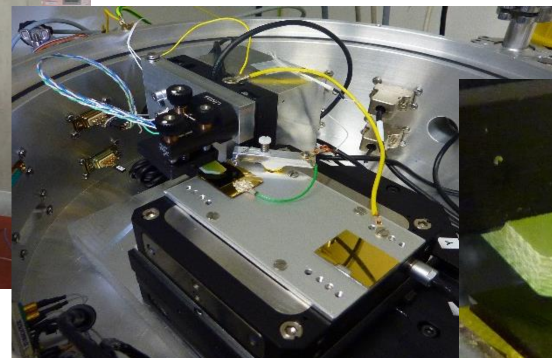
Resist
Unzipping polymer PPA (polypthalaldehyde)



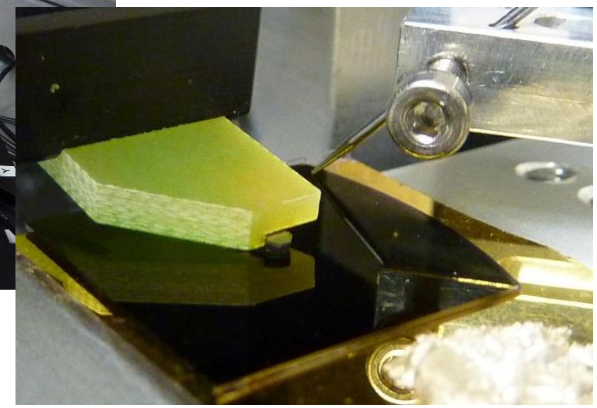
Coulembier et al., *Macromolecules*, **43**, 572-574 (2010)

Thermal Scanning Probe Lithography: The set-up

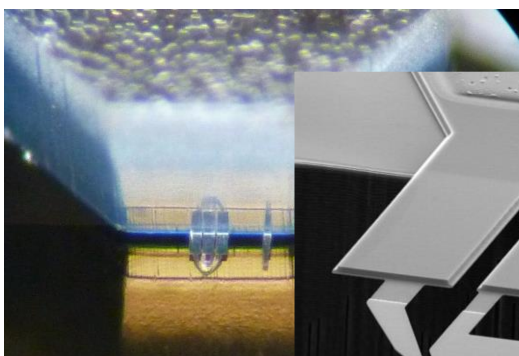
50 cm



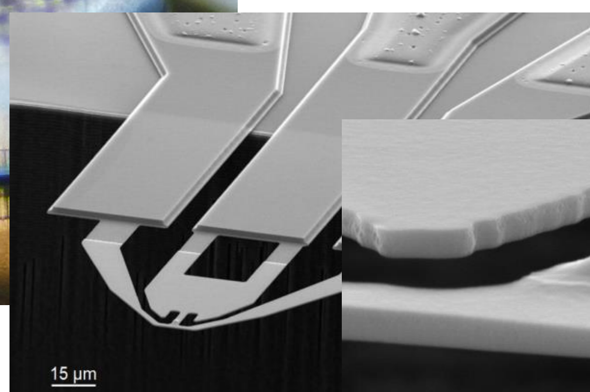
3 cm



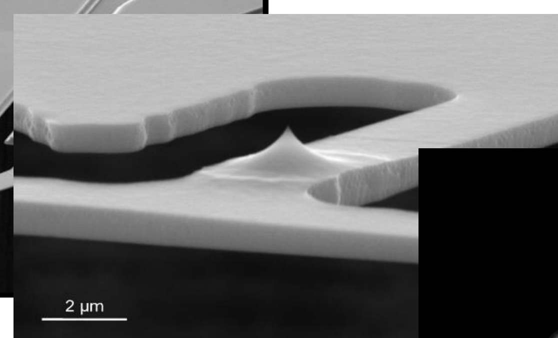
5 mm



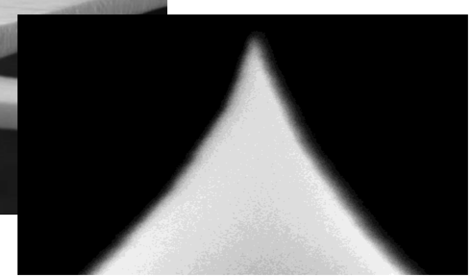
0,2 mm



0,03 mm

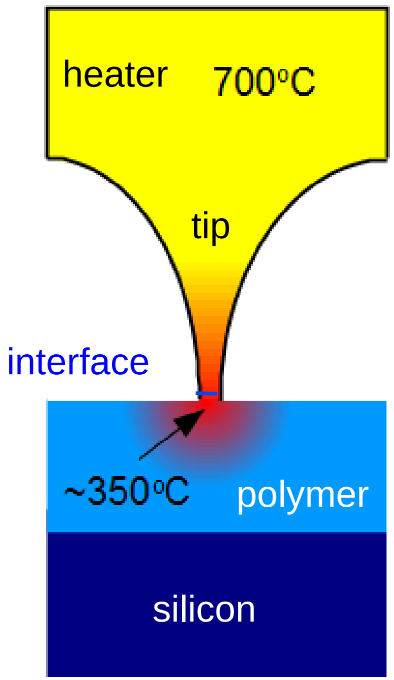


0,002 mm



0,00005 mm = 50 nm

Thermal 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

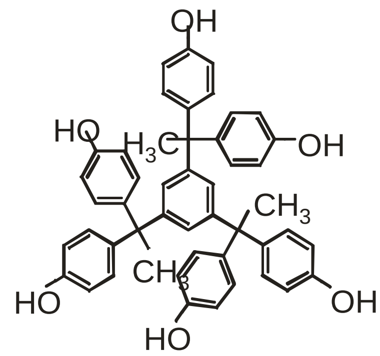
Chemical reaction:
thermally activated process ←→
time temperature superposition

1 s to 1 µs → ΔT ~ 200°C !

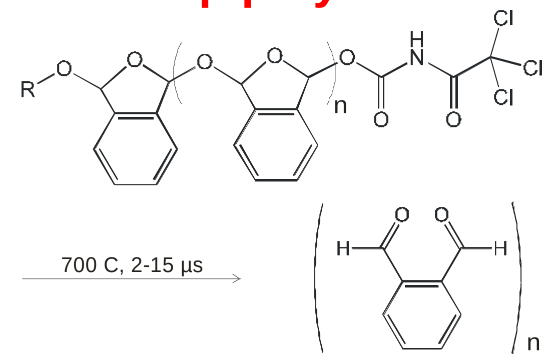
Thermally sensitive material required !
T_{conv} ~ 150..200 C

Material Strategy

Molecular glass



Unzip polymer

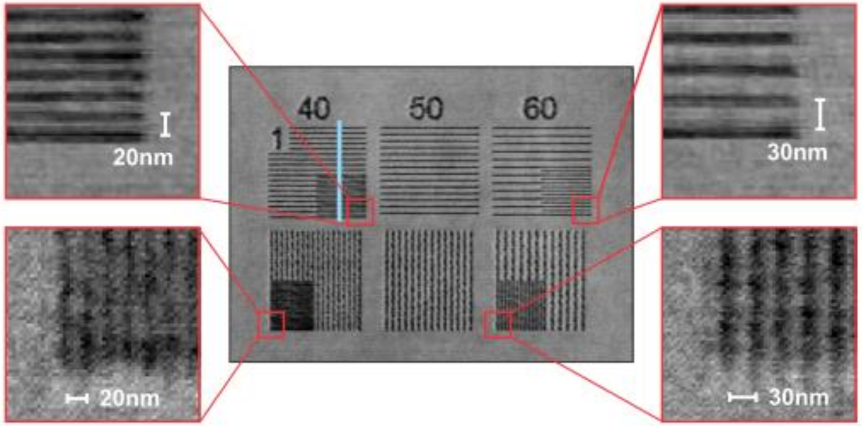


Polyphthalaldehyde (PPA)

	Molecular glass	Unzip polymer
▪ **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*

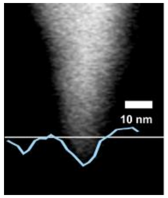
Features of tSPL

Resolution: 10 nm HP



Depth: 4 nm

Corresponds to tip shape:



Features:

Resolution: ~ 10 nm

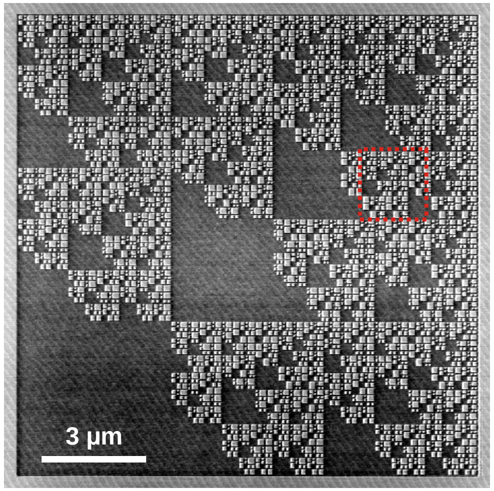
Speed:

→ 500 MHz imaging (2 us pixel time)

→ 666 kHz imaging (1.5 us pixel time)

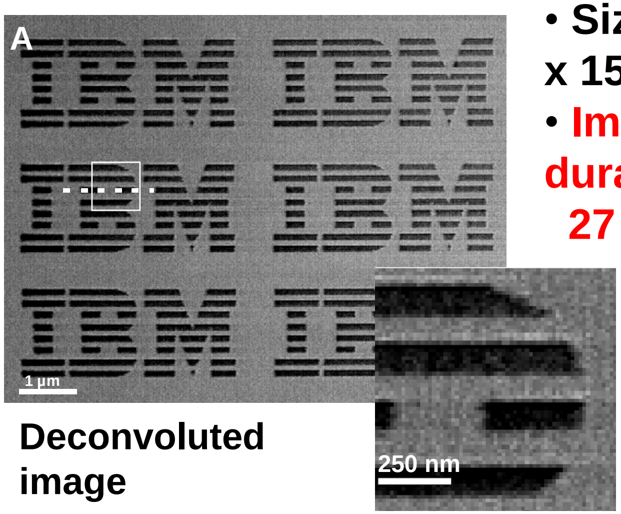
Resonance frequency : 150 kHz

500 kHz patterning



Fractal pattern
Size 13x13 µm^2
7.5 mm/s
880x880 pixels
Write duration: 11.8 s

666 kHz imaging

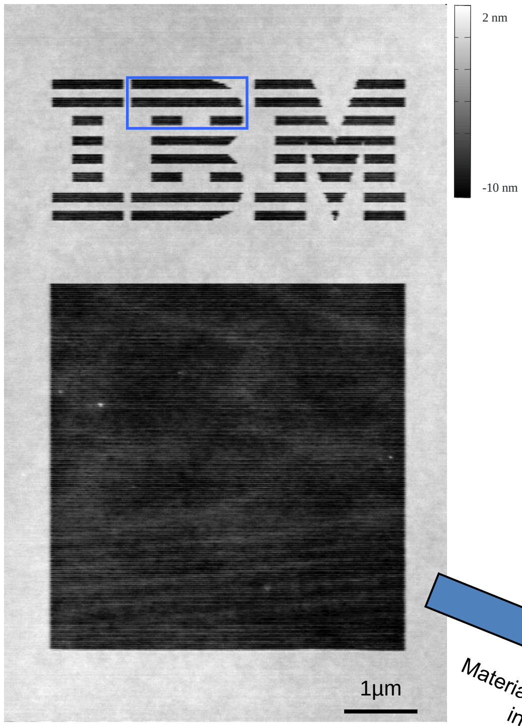


Deconvoluted image

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

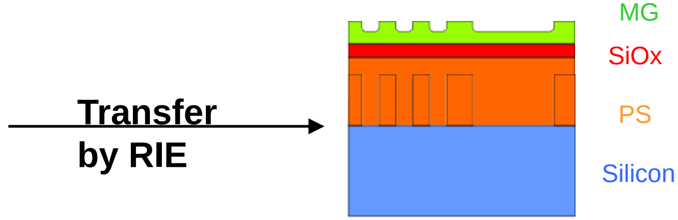
Paul et al., *Nanotechnology* 22, 275306 (2011).

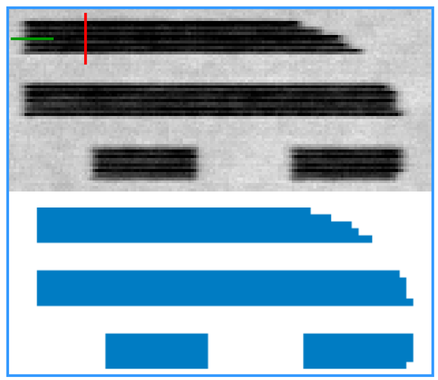
Molecular Glass: Patterning Results

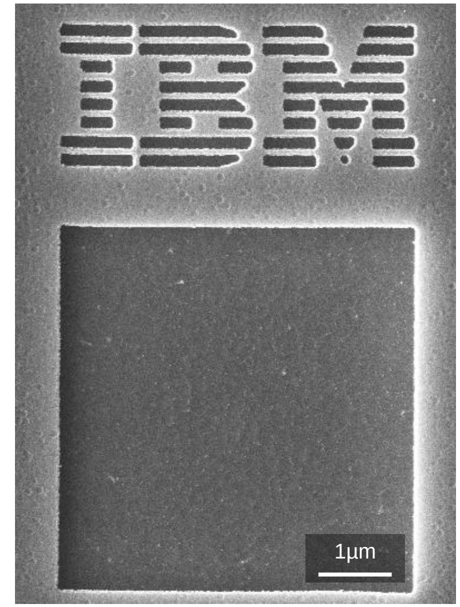


Pitch 29 nm
8 nm depth

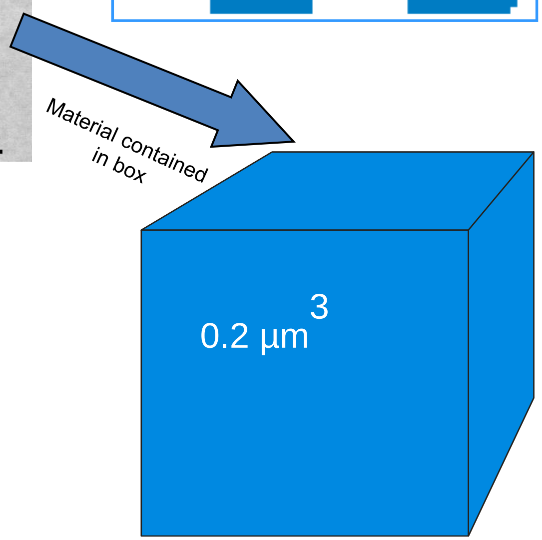
Parameters:
Pixels: 4 10^4
Heater temperature: 300°C
Load force: 80nN
Pulse duration: 5.5µs



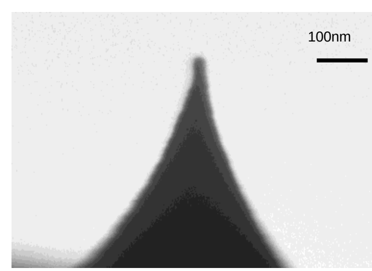




Pattern in Si after transfer:
400 nm depth (50x)

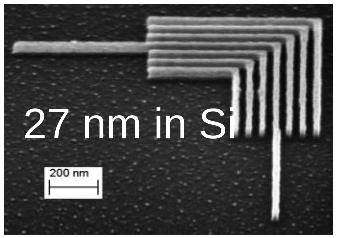


Tip after patterning
several fields:
same scale:



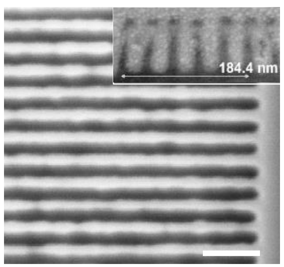
SEM of the tip
after $2 \cdot 10^5$ written pixels

Half Pitch Resolution after Pattern Transfer

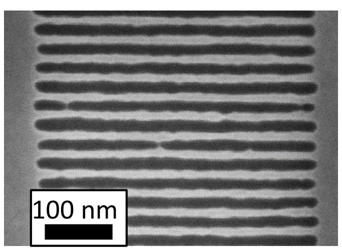


Transfer stack:
20 nm PPA
4 nm SiO_2
50 nm HM

18 nm in Si

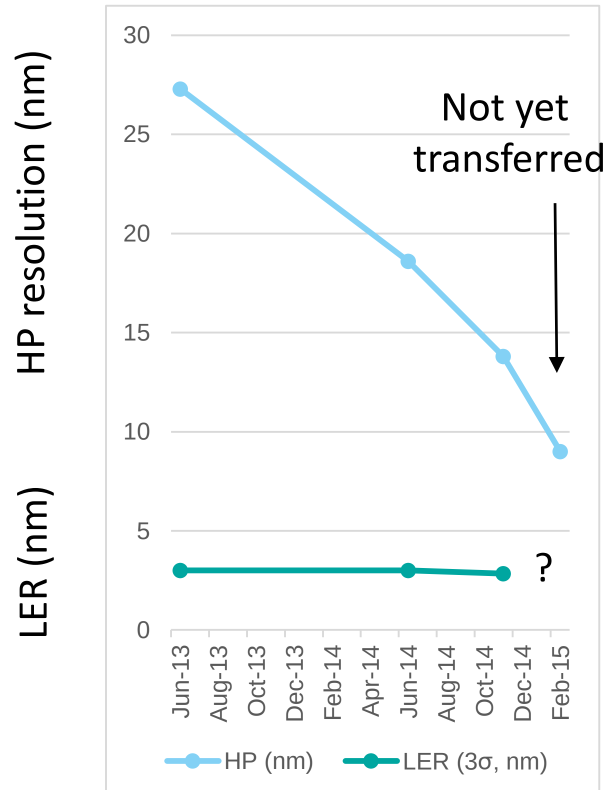


9 nm PPA
3 nm SiO_2

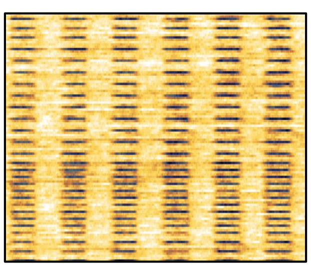


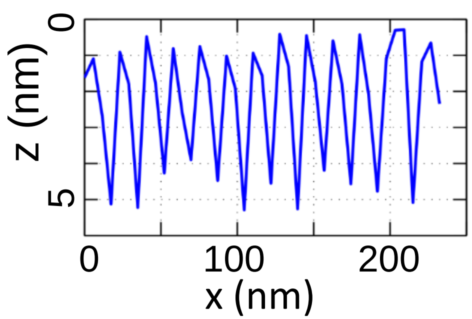
14 nm in HM (30 nm)

2 nm SiO_2
30 nm HM



9 nm in PPA

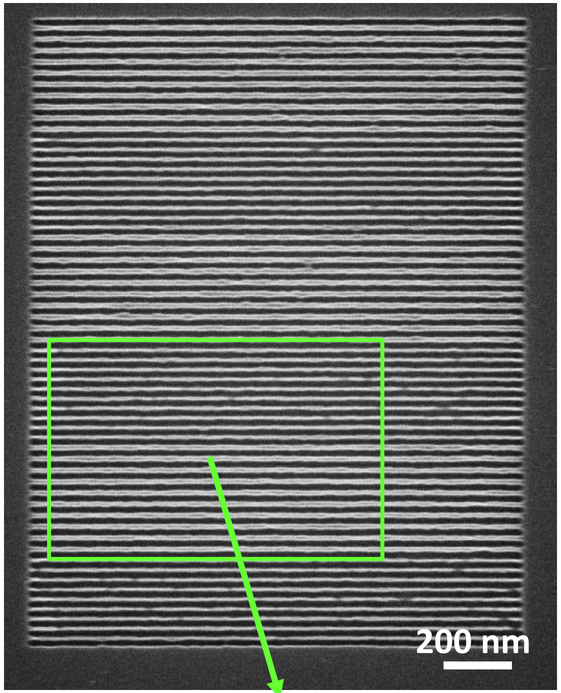


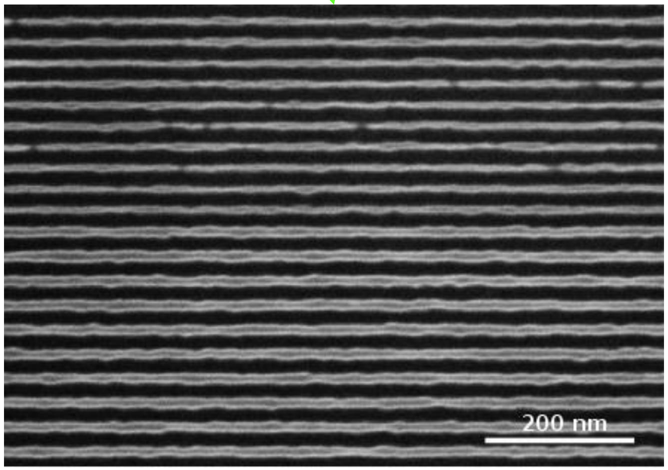


[1] L. Cheong et al., *Nano Lett.*, **13**, 4485 (2013). [2] Wolf et al., *J. Vac. Sci. Technol. B*, 33, 02B102 (2015).

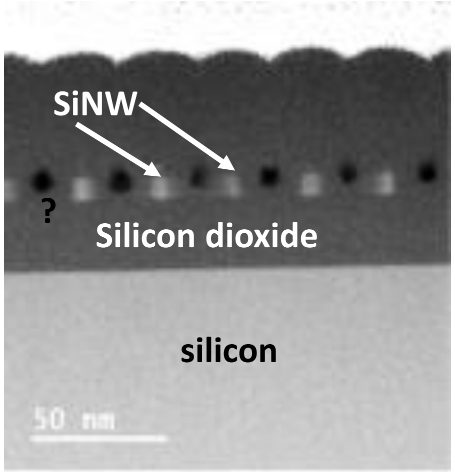
High resolution thermal scanning probe lithography

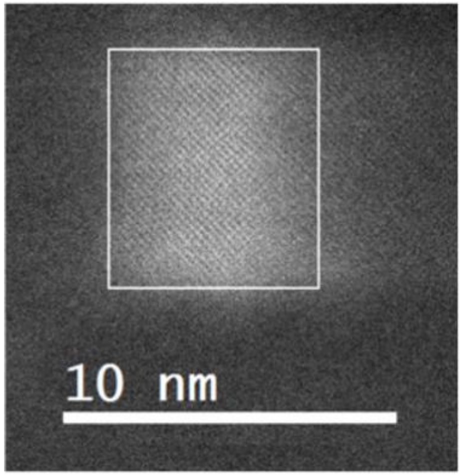
SiNWs 14 nm and 16 nm half-pitch



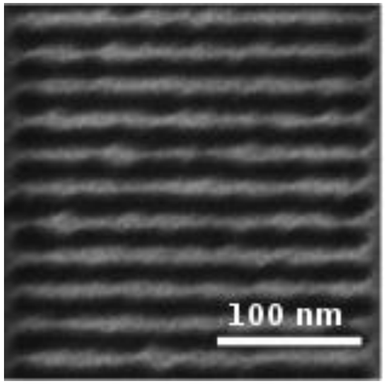


STEM cross sections from one of the arrays of 14 nm half-pitch SiNWs
Atomic resolution, line width approx 7 nm,
height approx 7.7 nm

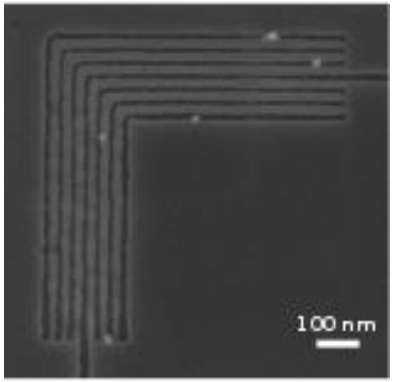




11 nm HP transferred
into 20 nm HM8006



14 nm HP L-shaped SiNWs

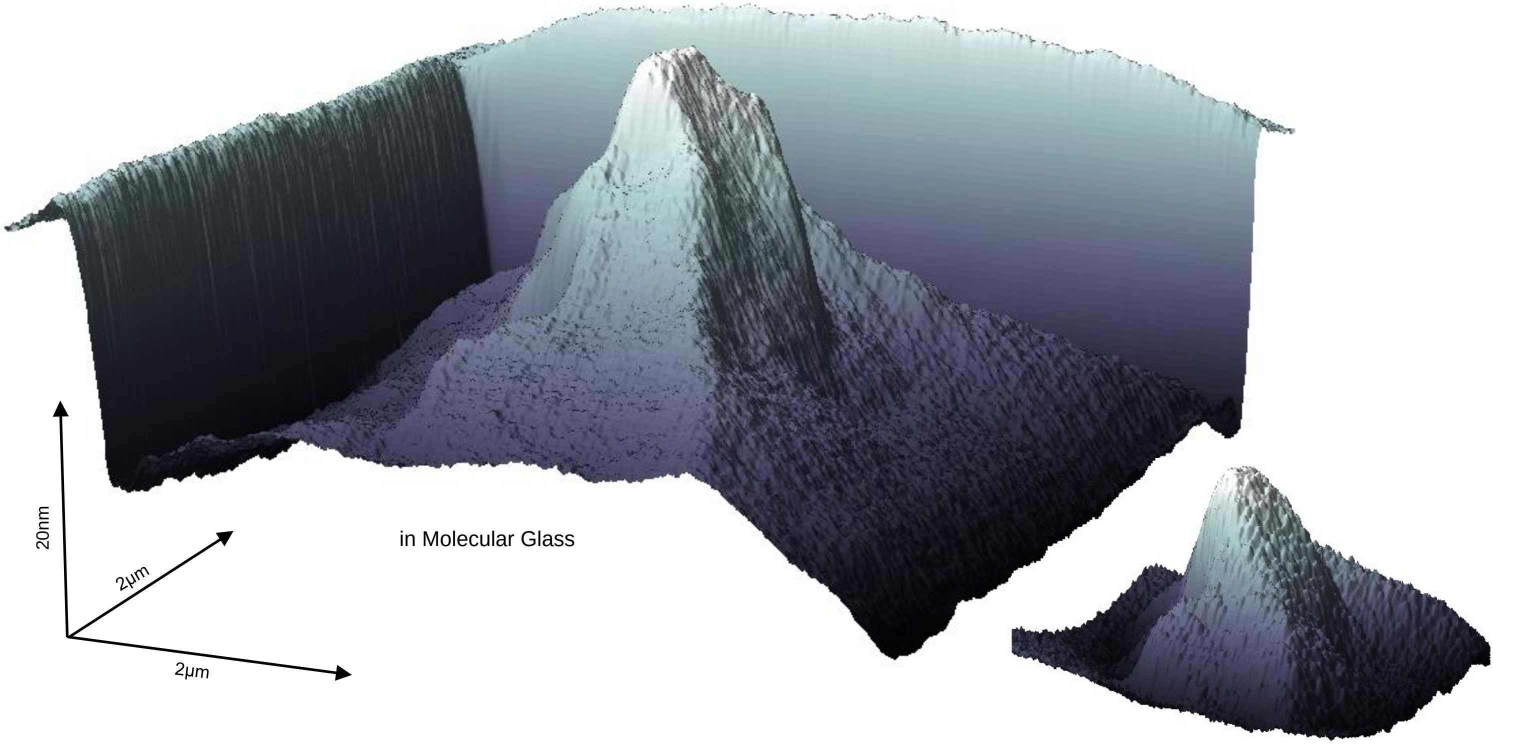


'Sub-10 nanometer feature size in silicon using thermal scanning probe lithography'
Y.K.R.Cho, C. D. Rawlings, H. Wolf, M. Spieser, S. Bisig, S. Reidt, M. Sousa, S. R. Khanal, T. D. B. Jacobs, A. W. Knoll
ACS Nano **11**, 11890 (2017)

Molecular Glass: Complex 3D-Structures


(photographer: Marcel Wiesweg; source: Wikimedia)

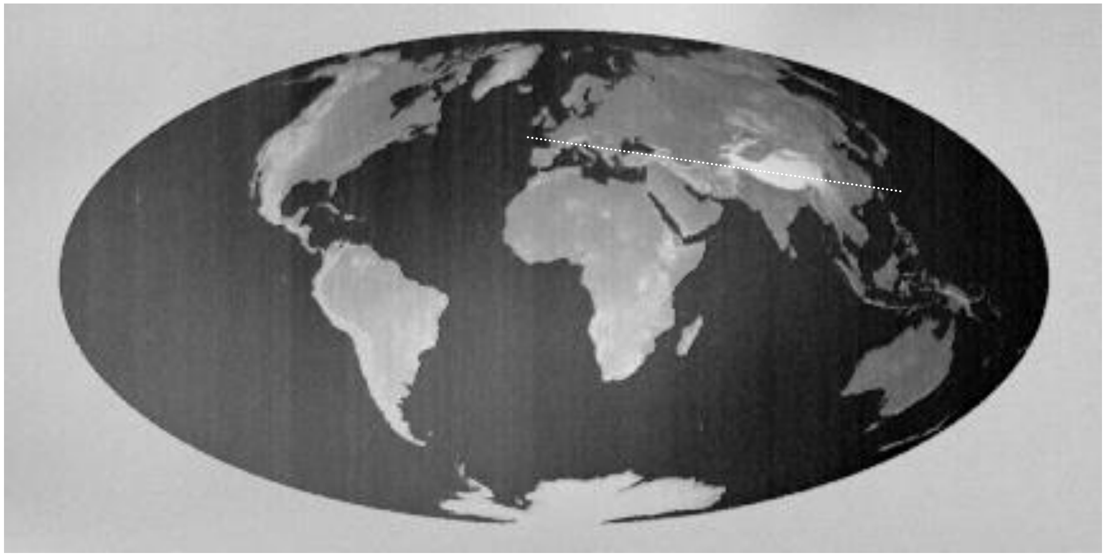
- *Matterhorn* (Swiss Alps)
  Topographical data from geodata © Swisstopo
- Multilevel patterning
  - 120 levels

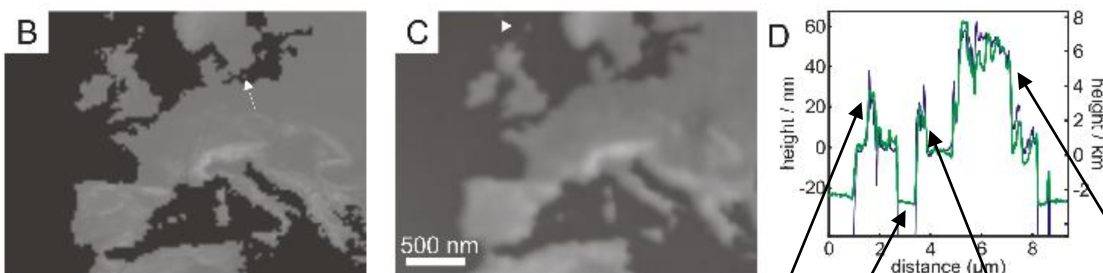


D. Pires et al. , *Science*, ***328***, 732 (2010)

3-D Direct Writing Using Unzip Polymers

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





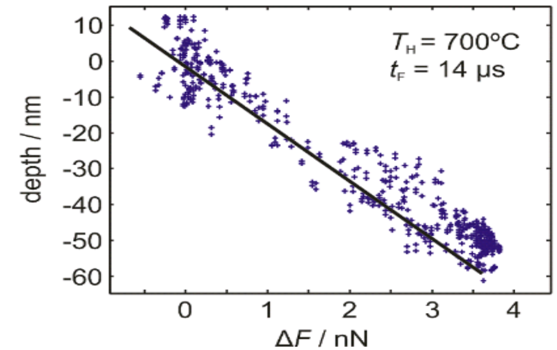
Bit map

Written replica

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

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

Alps
Caucasian Mountains
Black Sea
Himalaya



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

World Map:
250 nm of SAD polymer on Si

5x10^5 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

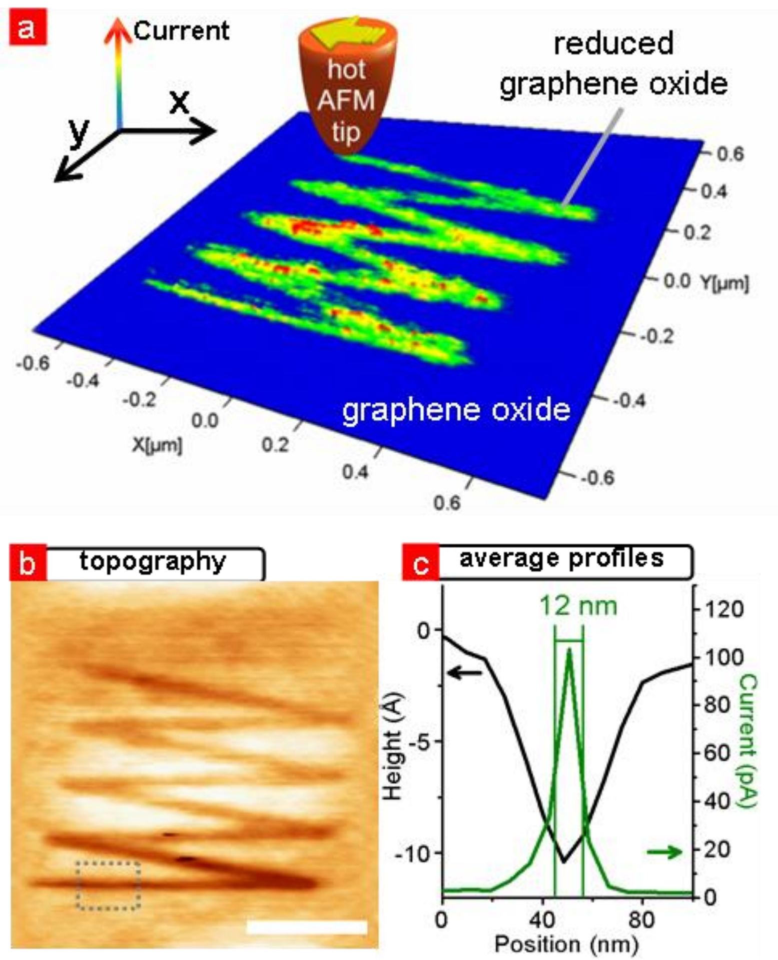
Scanning probe lithography pattern and image: Area= 12×10^{-8} cm^2

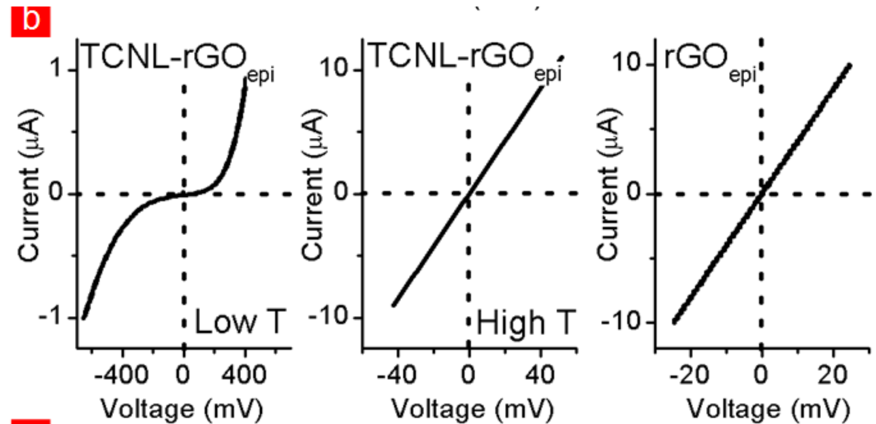
A. W. Knoll,

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

tc-SPL to perform Nanoscale tunable reduction of graphene oxide

E. Riedo et al. Science (2010)





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-rGO_{epi} Low T	9174 ± 2 KΩ	N/A
TCNL-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
- True 3D nanoscale patterning

Limitations

Requires specific cantilevers

Requires resist

Acknowledgements

Thank you for your attention !

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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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