Nanolitografías basadas en el uso de un AFM

Tip-based Nanolithographies

Scanning Probe Lithography

Oxidación scanning Probe lithography oSPL

(Local Oxidation Nanolithography o AFM oxidation nanolithography)

Nanomachining

nanoshaving and Nanografting

Field-assisted SPL

Dip Pen Nanolithography

Thermomechanical SPL

Ricardo Garcia

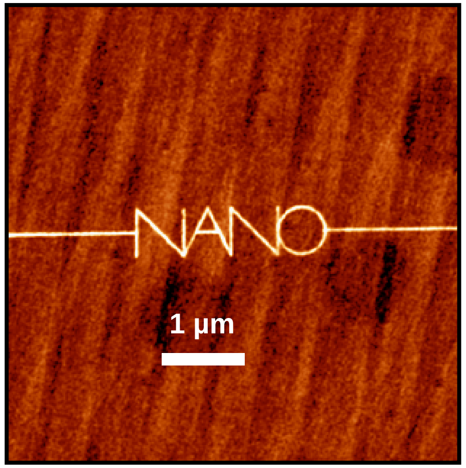
Definition: Lithography

"Printing process in which the image to be printed is rendered on a flat surface, and treated to retain ink while the nonimage areas are treated to repel ink."

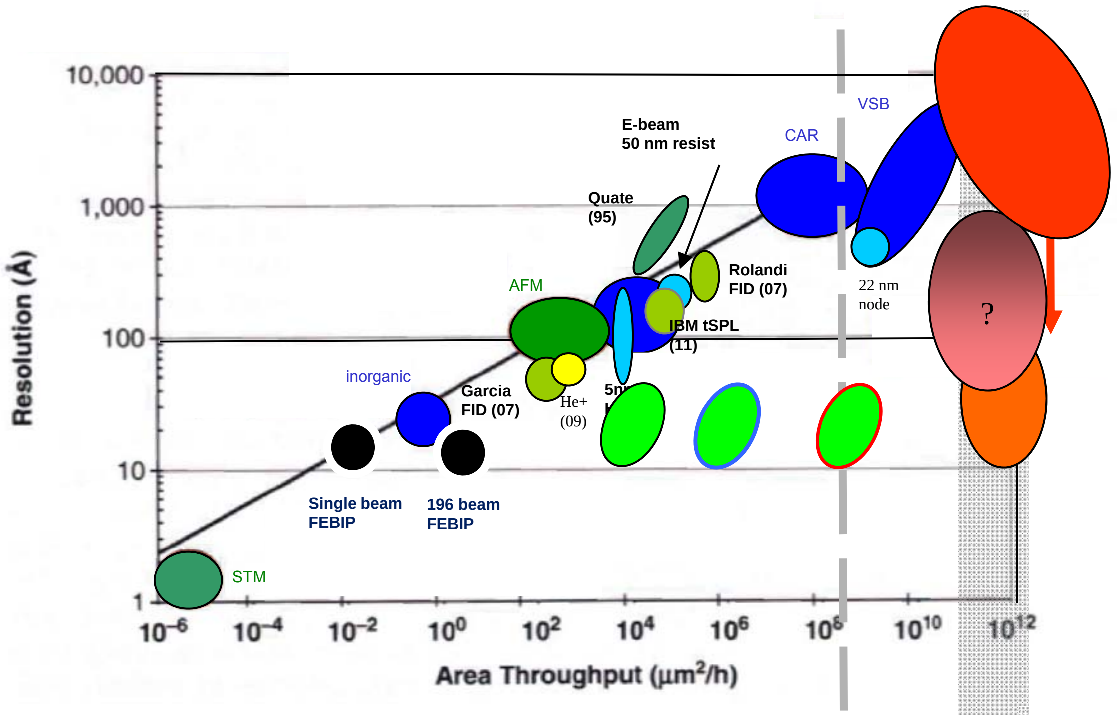
(The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2004)

'Muchacha en la ventana' by Salvador Dalí

Nanolithography: **Proceso o conjunto de procesos que permite la fabricación de nano-estructuras y nano-dispositivos con una precisión espacial por debajo de los 100 nm.**



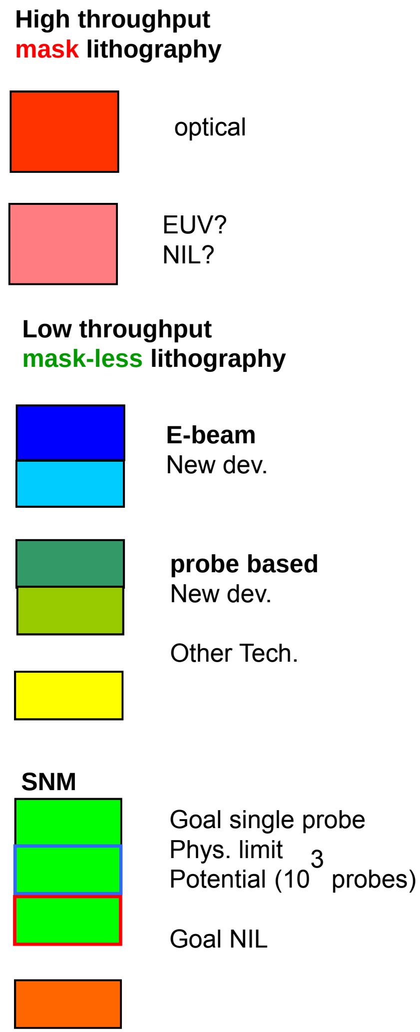
Nanolithographies: Resolution and throughput



Mask prod.:
0.005 cm²/s
1 mask in 8h

Wafer scale:
1 – 20 cm²/s
5 – 100 wph

Adapted from:
C. Marrian, D. Tennant, *J. Vac. Sci. Technol., A*, 2003, 21, S207
S.V. Sreenivasan, *MRS Bulletin*, Sept. 2008;

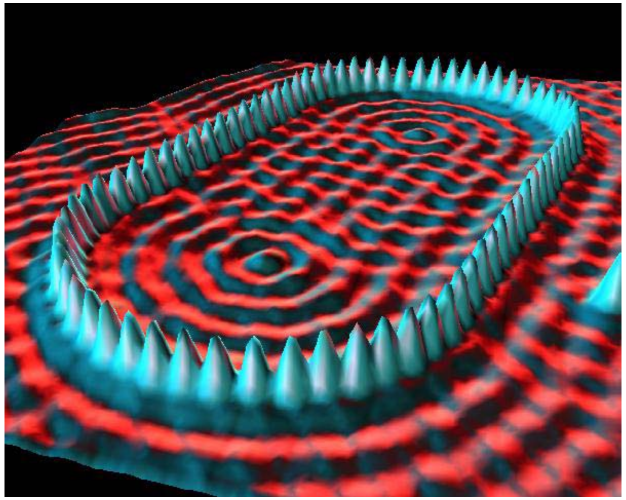


VSB: variable shaped beam; CAR: chemically amplified resist; FID: field induced deposition;

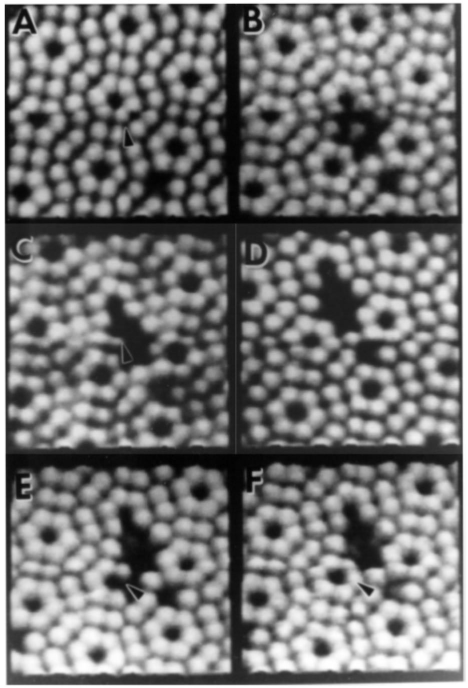
Tecnología: Rapidez, tamaño y coste son los factores relevantes
Ciencia: El tamaño es lo más importante

STM 1982

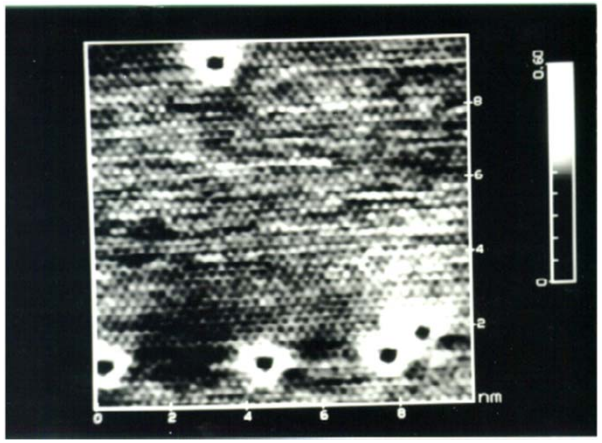
AFM 1986



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



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



García, WSe (1992)

Nanolithography: Requirements

Nanometer-scale motives

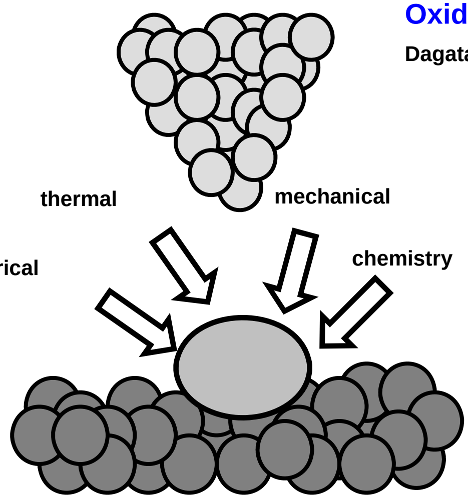
Reproducibility

Compatible with technological environments

Scalable

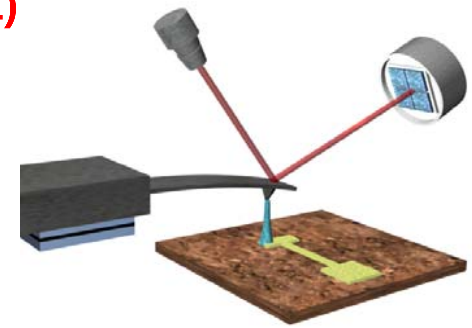
Throughput

Scanning Probe Lithographies (SPL)

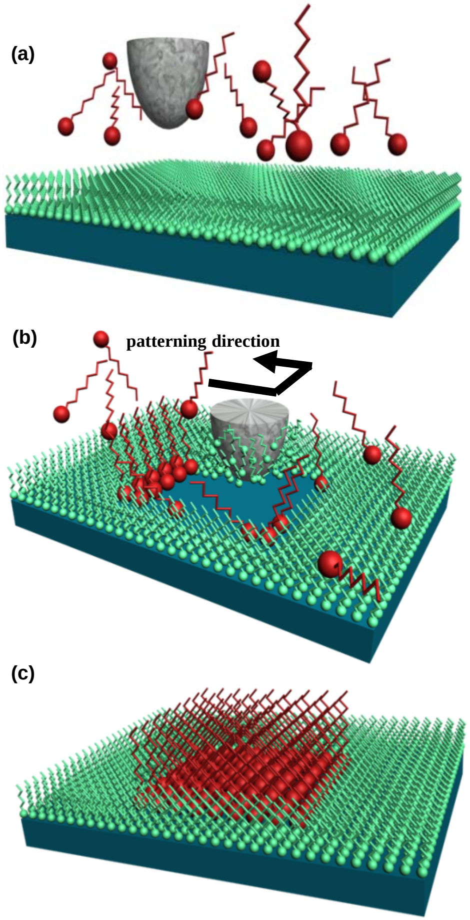


Oxidation SPL

Dagata (1990)

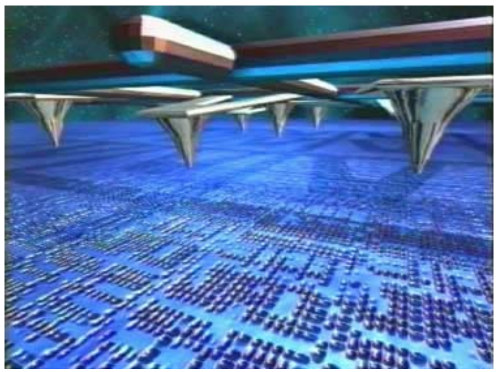


Nanomachining



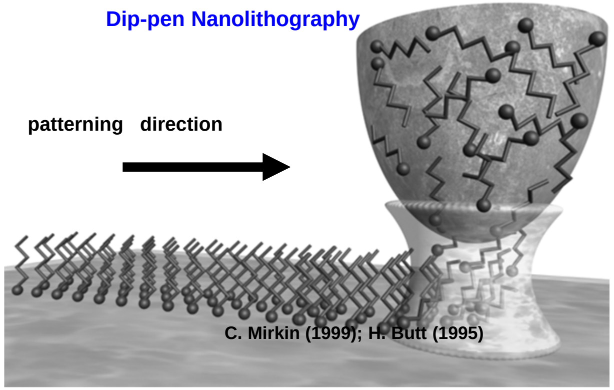
G. Liu (1997)

Thermomechanical SPL



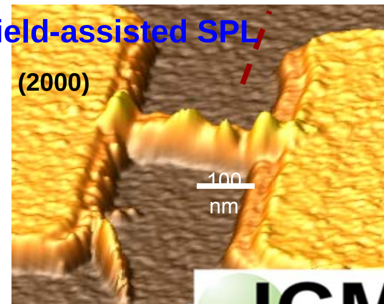
Binnig et al. (1999)

Dip-pen Nanolithography



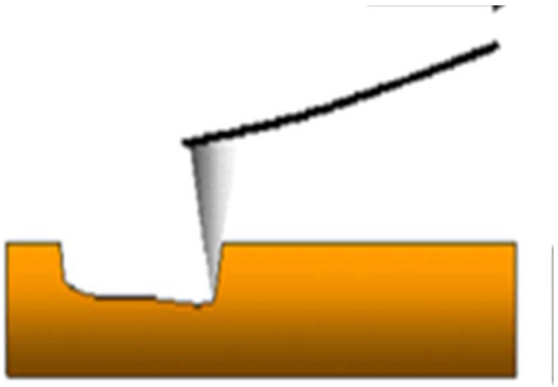
Field-assisted SPL

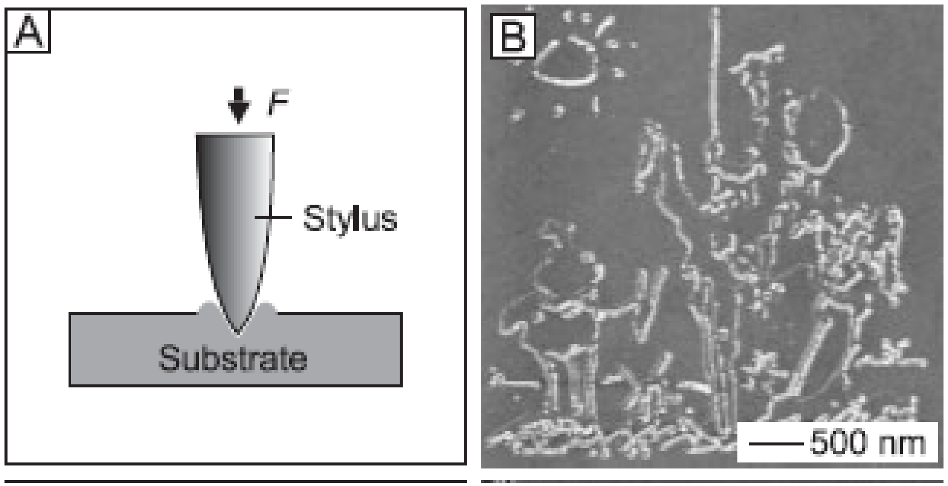
(2000)



Nanomachining

Force: Probe tip used to "plough" a soft layer





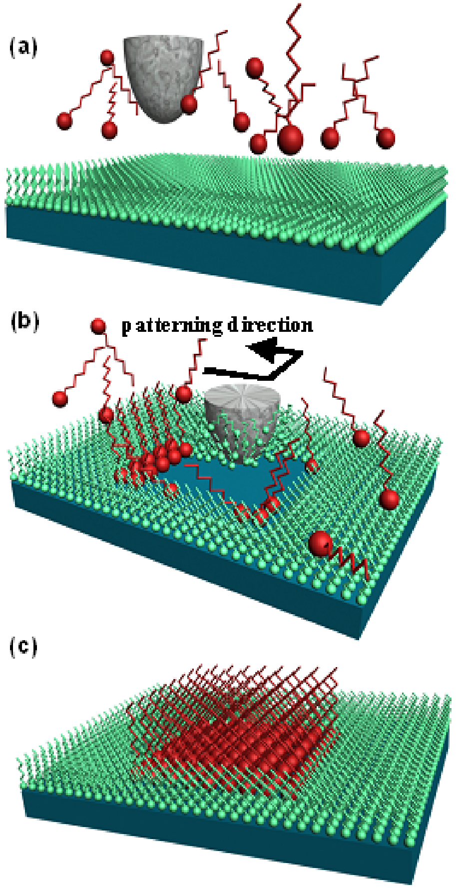
B) The AFM topographic image of Pablo Picasso´s ' Don Quixote' that was carved in the surface of a polycarbonated film with an AFM tip

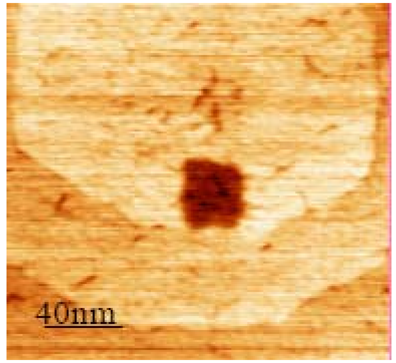
Nanomachining: nanoshaving and nanografting

A Sam is assembled on the surface

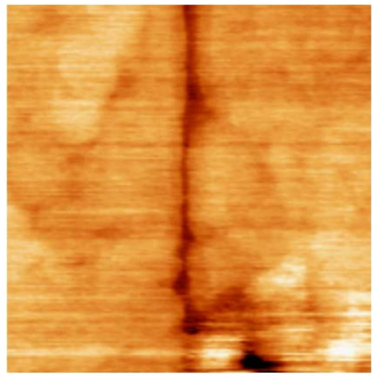
The AFM tip exerts a force on the SAM and removes the monolayer in a certain region (nanoshaving)

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





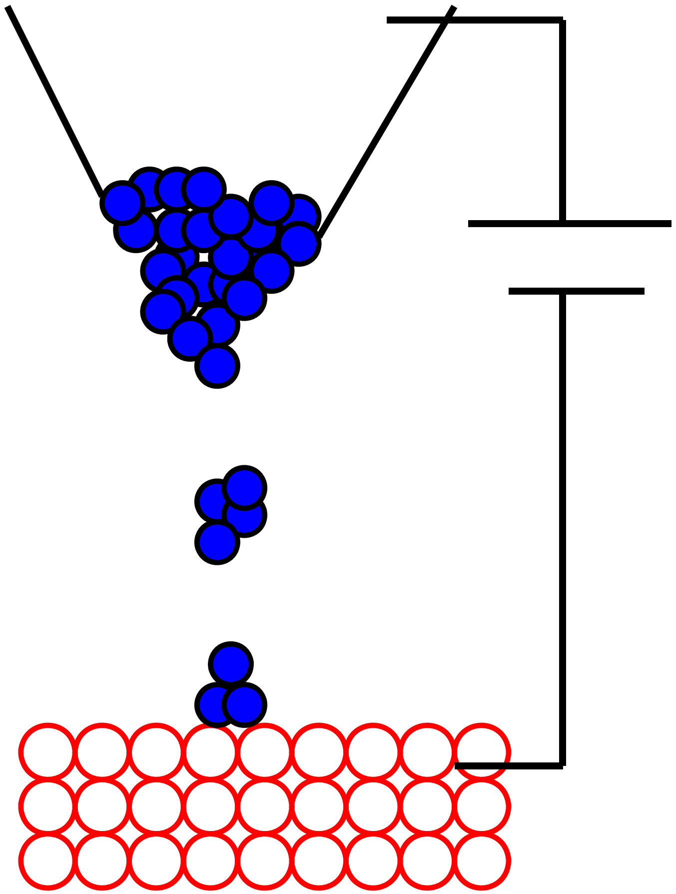
CH3-(CH2)9-SH nanografted into a CH3-(CH2)17-SH SAM (400Å×400 Å)



A 70 Å “line” of CH3-(CH2)9-SH nanografted into a CH3-(CH2)17-SH SAM(800 Å ×800 Å)

Field evaporation

in an atomic force microscope interface



E_{tip}~1/k (V/R)

Exp. fields for Au evaporation

Field ion microscopy: 35 V/nm

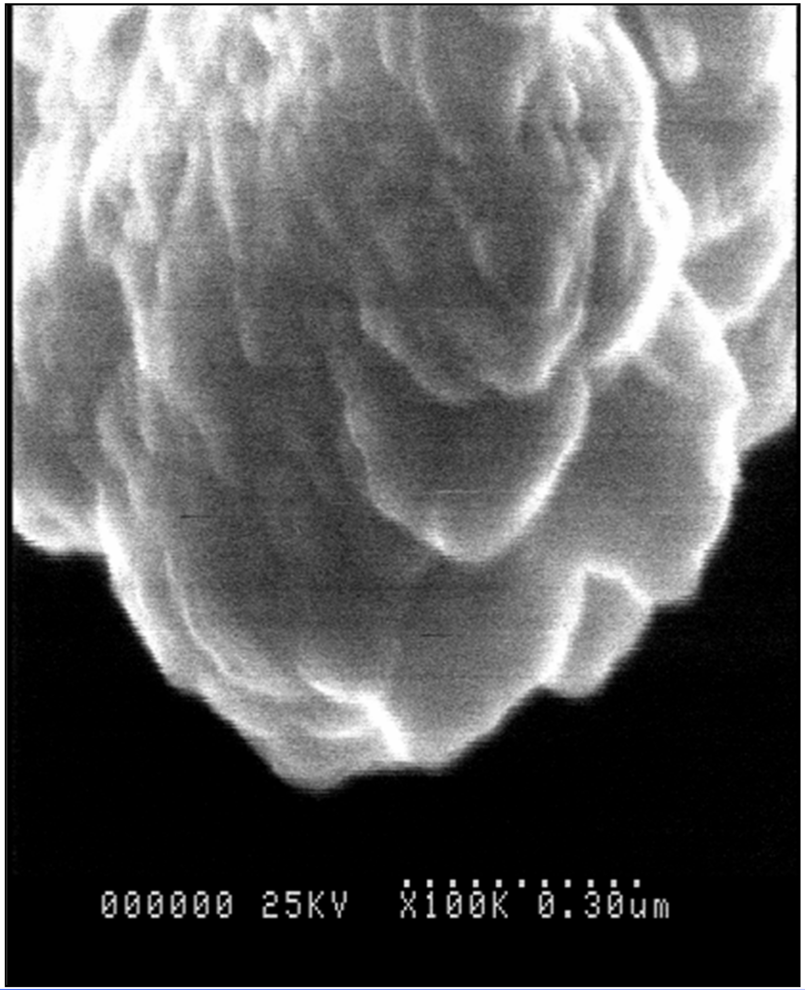
STM (Mamim et al.) 4 V/nm

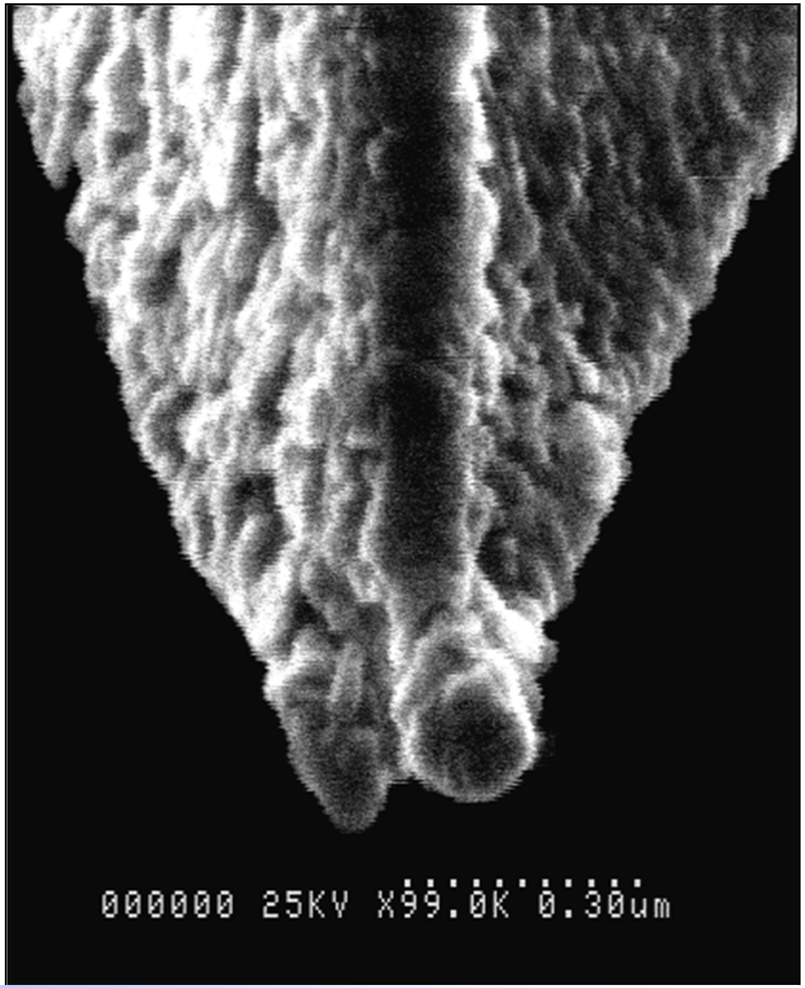
C-AFM (Hosaaka et al. Jpn. J. Apl. Phys. 33, L1358 (1994)

5.5 V/nm

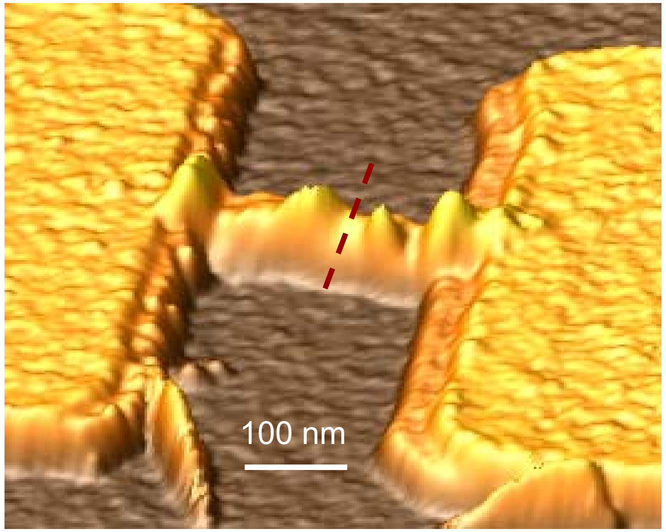
Scanning Probe Lithography: Gold Deposition

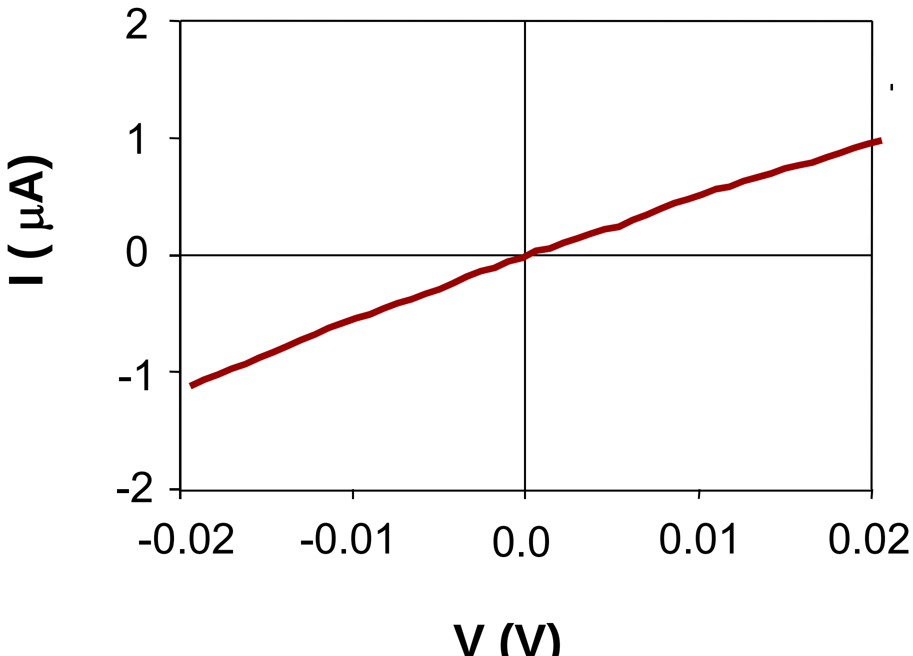
SEM images of gold tips (Au on n-Si)





Fabrication of gold Nanowires by SPL





Cross-section

Height = 5 nm

Width = 40 nm

Length = 250 nm

$R_{hilo\ AFM} = 359\ \Omega$

$\rho_{hilo\ AFM} = 2.87 \times 10^{-7}\ \Omega\ m$

$\rho_{bulk\ Au} = 2.44 \times 10^{-8}\ \Omega\ m$

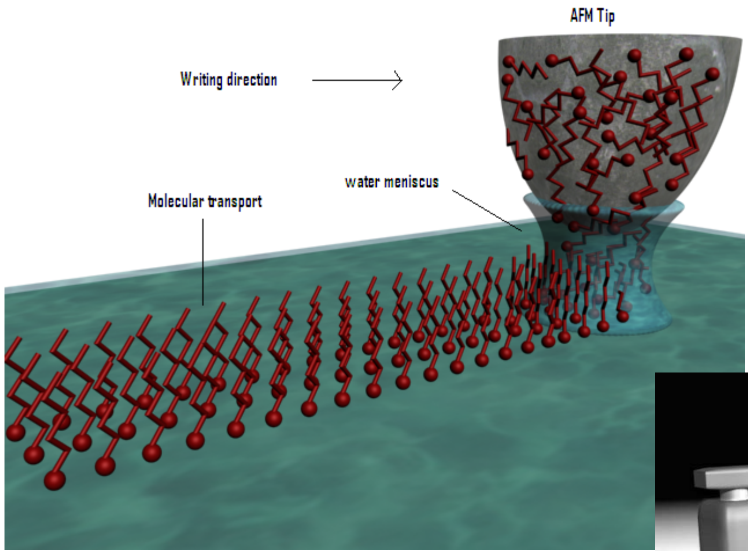
M. Calleja et al., Appl. Phys Let.. 79, 2471, (2001).

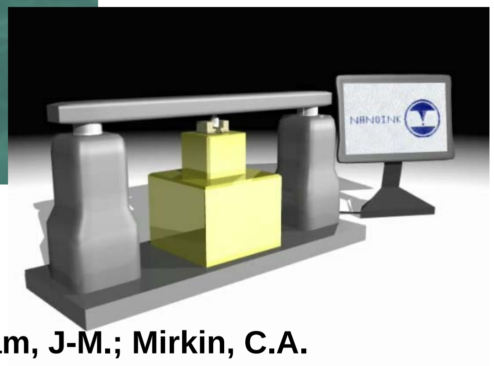
Dip Pen Nanolithography

Transport of molecules to the surface via water meniscus

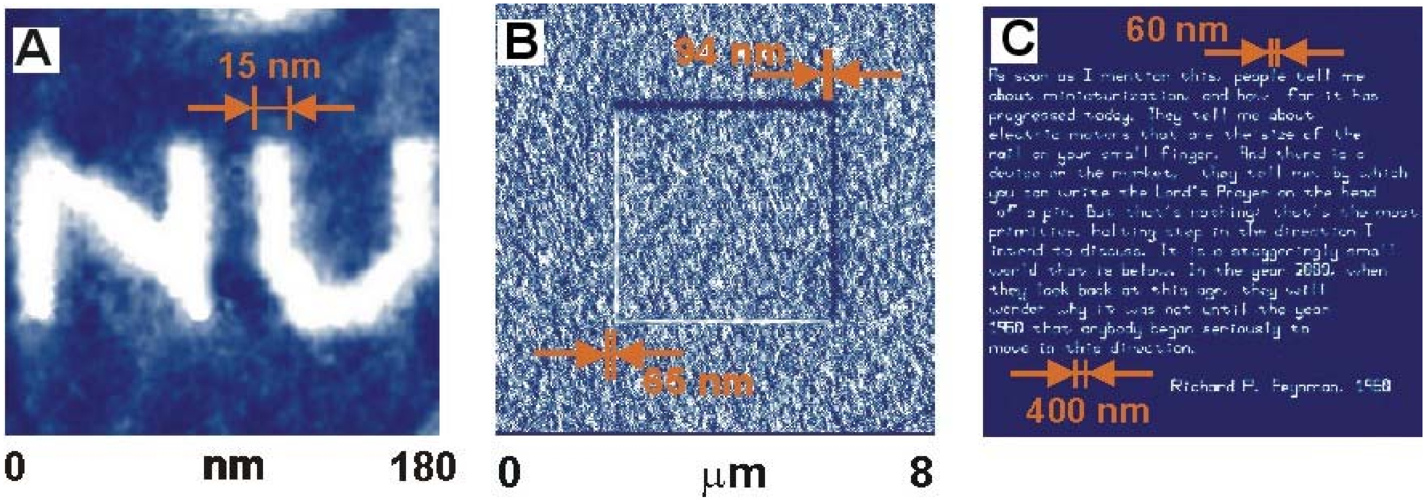
‘Bottom-up’ aproximation : Writing of a pe

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

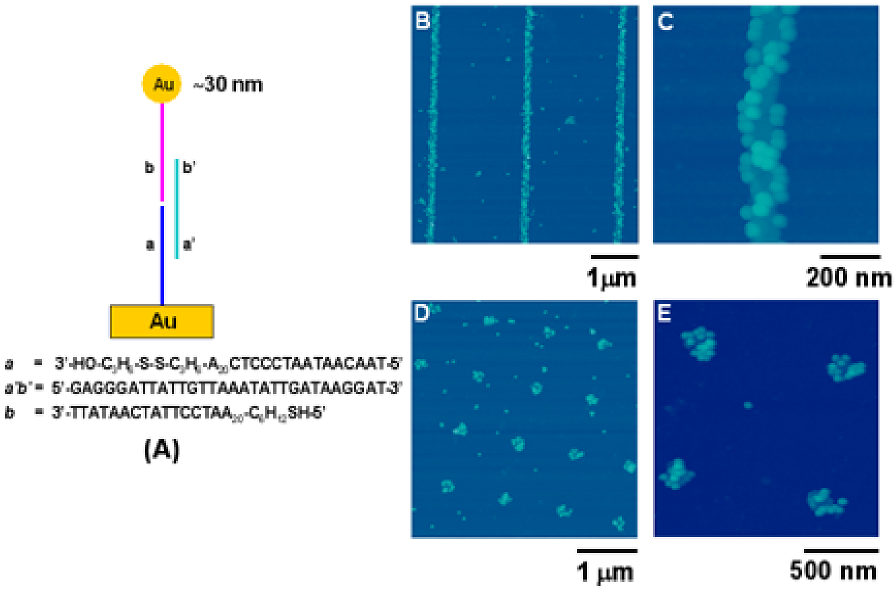




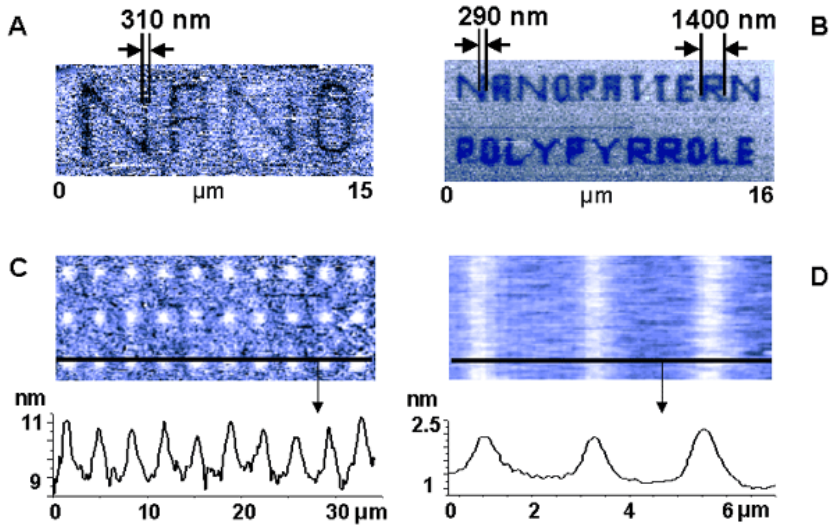
Lim, J-H.; Ginger, D.S.; Lee, K-B.; Heo, J.; Nam, J-M.; Mirkin, C.A. *Angew. Chem. Int. Ed.* 2003, *20*, 2411-2414.



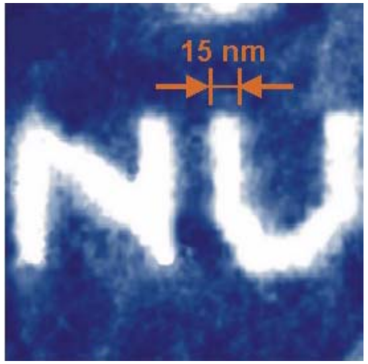
A
15 nm
0
nm
180
B
94 nm
65 nm
0
μm
8
C
60 nm
400 nm



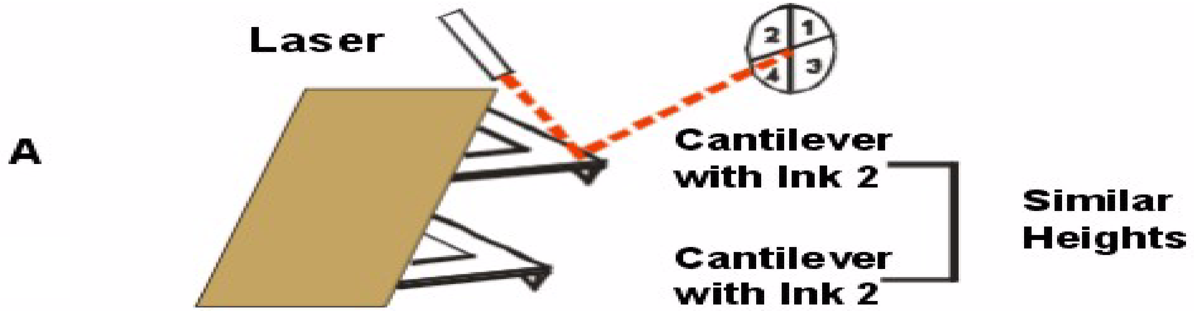
Au
~30 nm
b
b'
a
a'
Au
a = 3'-HO-C3H6-S-S-C3H6-A20CTCCCTAATAACAAT-5'
a'b' = 5'-GAGGGATTATTGTTAAATATTGATAAGGAT-3'
b = 3'-TTATAACTATTCCTAA20-C6H12SH-5'
(A)
B
C
1μm
200 nm
D
E
1 μm
500 nm

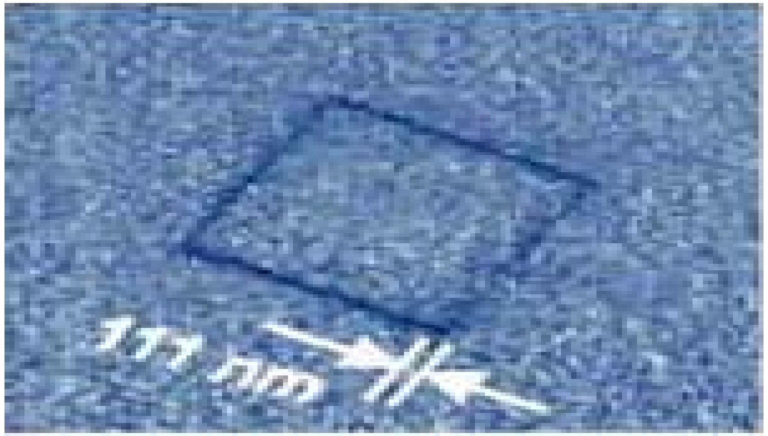


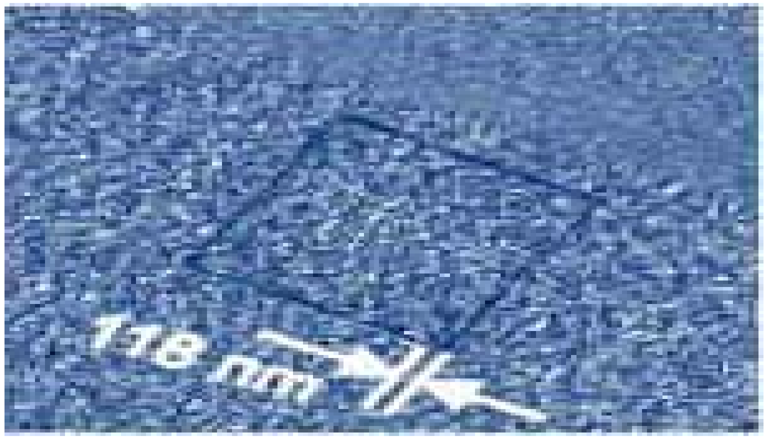
A
310 nm
0
μm
15
B
290 nm
1400 nm
NANOPATTERN
POLYPYRROLE
0
μm
16
C
D
nm
11
9
0
10
20
30 μm
nm
2.5
1
0
2
4
6 μm



Parallel nanolithography







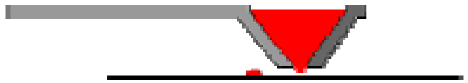
Nanoscale Dispensing (NADIS)

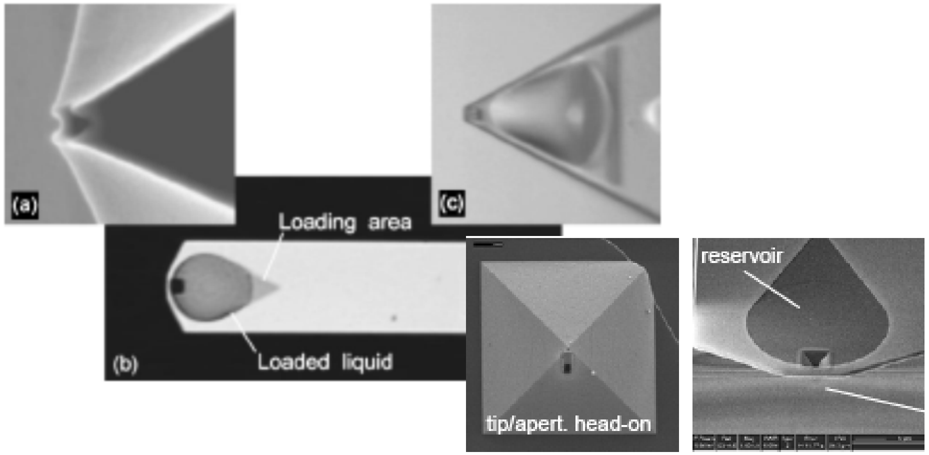
Tip with a 200 nm aperture at its apex made it by focused-ion-beam milling

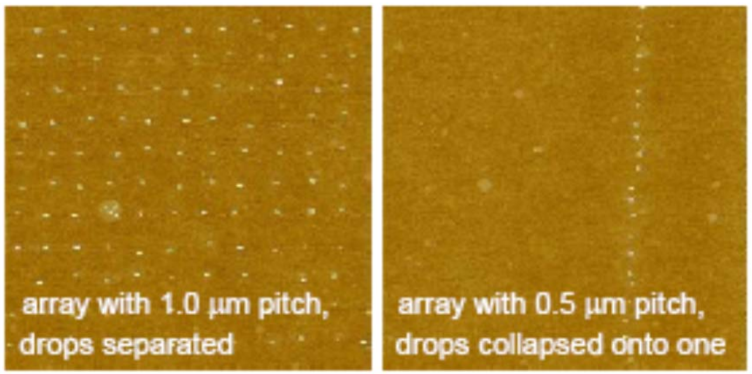
Pattern ‘liquids’

Versatile (ambient condition)

Integration of fluidic system possible



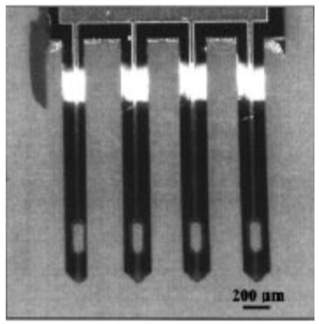




Glycerol on $SiO_{2,}$ image size (10 x 10) μm^2

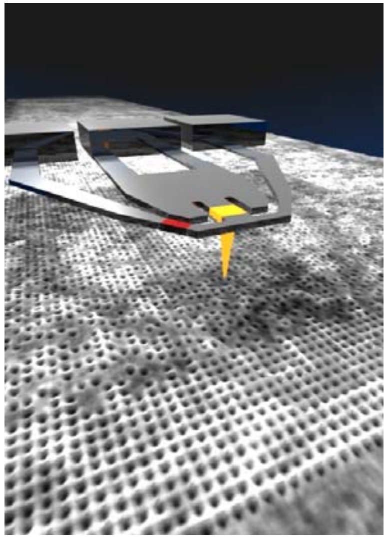
A. Meister et al. APL 85, 25 (2004)

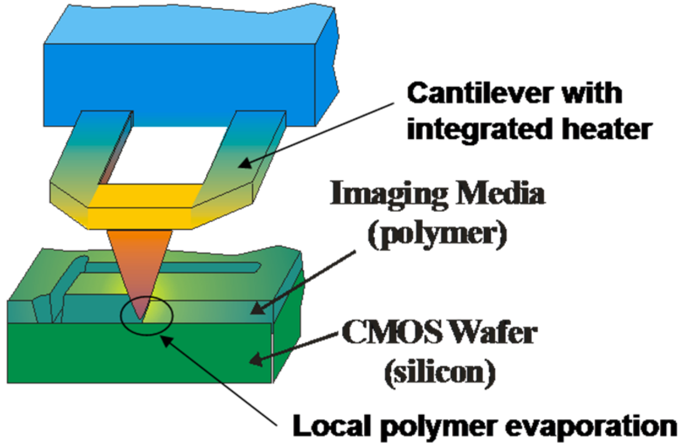
Parallel probes for multi-material deposition



thermomechanical SPL (t-SPL)

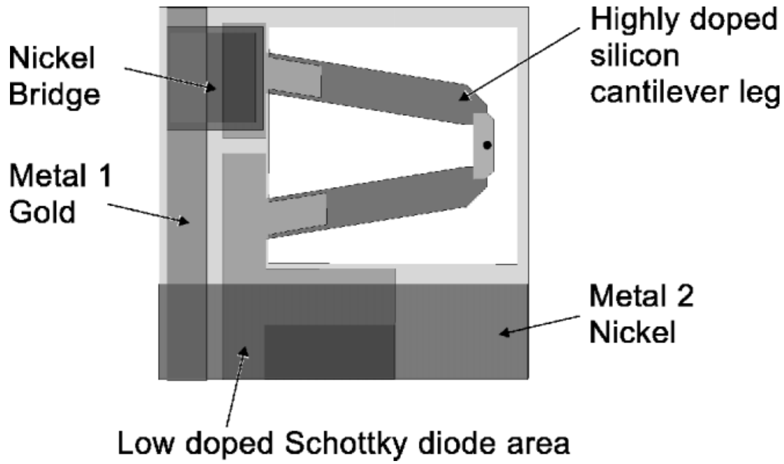
Process where a resistive cantilever tip, which is in contact with a polymer storage medium, is heated by current pulses. As a result, indentations representing data bits are formed by a combination of applying a local force to the polymer layer and softening it by local heating



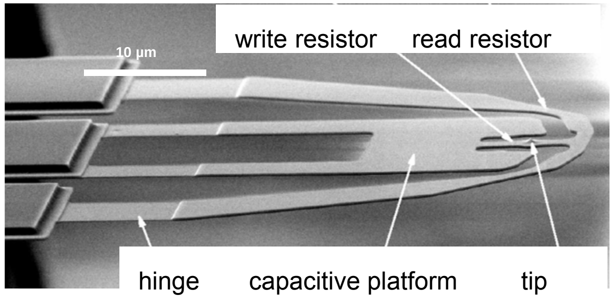


Bits: Fuerza y Temperatura

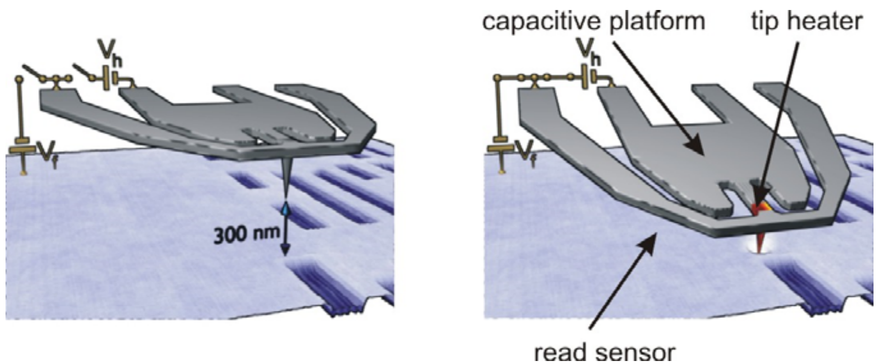
G. Binnig, M. Despont, U. Drechsler, W. H¨aberle, M. Lutwyche, P. Vettiger, H.J. Mamin, B.W. Chui and T.W. Kenny, Appl. Phys. Lett. 74 (1999) 1329.
P. Vettiger, M. Despont, U. Drechsler, U. D¨urig, W. H¨aberle, M.I. Lutwyche, H.E. Rothuizen, R. Stutz, R. Widmer and G.K. Binnig, IBM J. Res. Develop. 44 (2000) 323.



Heatable Probes

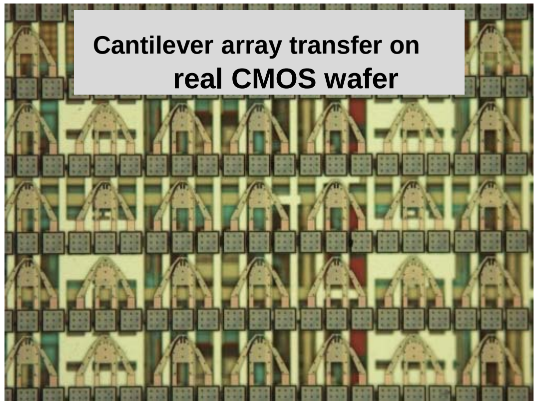


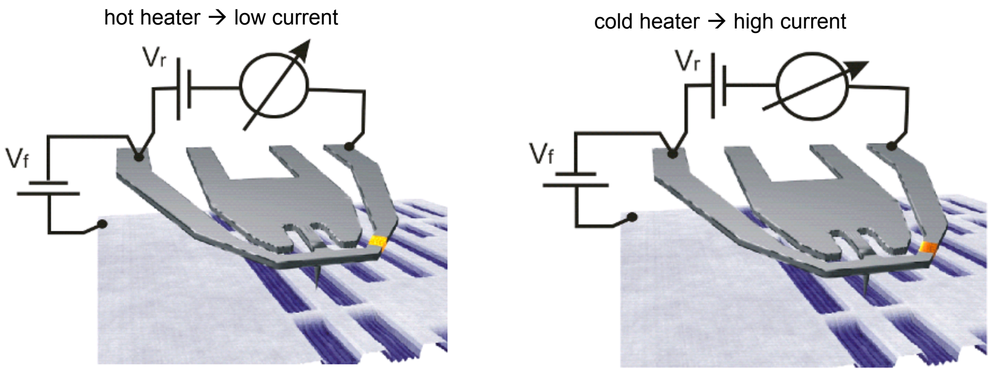
Current design:
- Stiffness ~ 0.1…1 N/m
- Resonance frequency ~ 50..150 kHz
- Thermal time constant ~ 5 µs
- Apex radius of tip ~ 5 nm



Thermo-mechanical writing:
- Efficient electrostatic actuation: up to 1 µN
- Resistive tip heating: up to **700 C**
- **no feedback => fast**

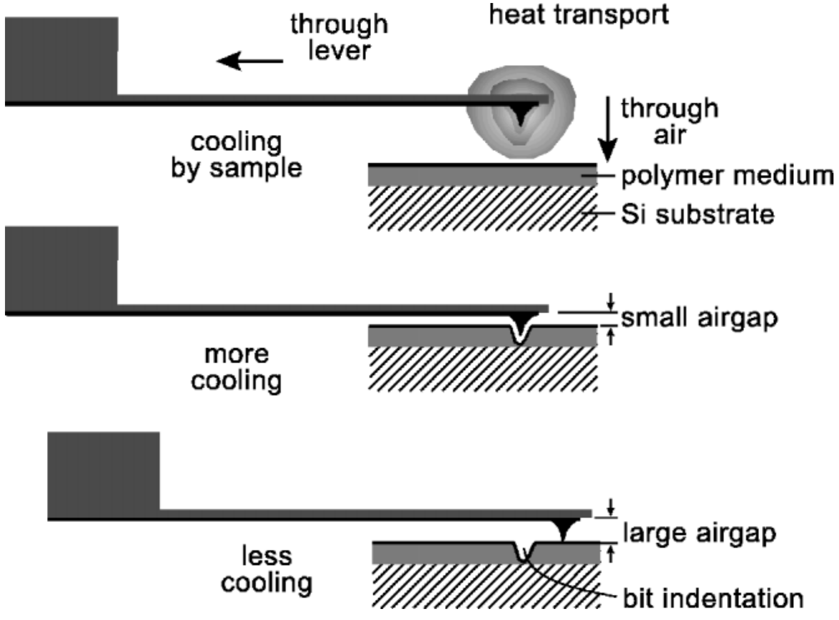
Thermo-resistive reading:
- Read resistor heated to ~ 200C
- **Sensitivity ~ 0.1 nm @ 50 kHz BW**
- in contact
- **no feedback => fast**





Pantazi et al., IBM J. Res. & Dev. (2008) 52, 493--511
Gotsmann et al., Adv Funct. Mater. (2010), 20, 1276-1284

AFM thermomechanical lithography



Principle of AFM thermal sensing. The tip of the cantilever is continuously heated by a DC power supply. A bit is sensed via a tiny change of the resistance of the heater stage induced by a modulation of the heat conductance through the air gap as the tip follows the contour of an indentation.

Dithering Force Microscopy

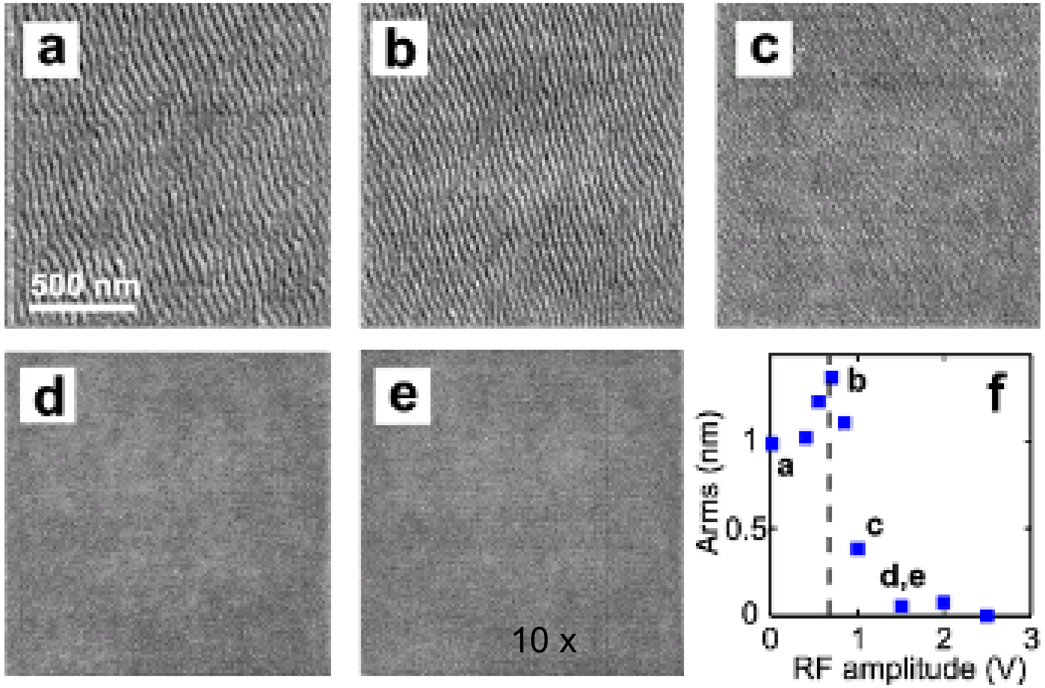
Effect on friction:
- Socoliuc A et al., Science, **2006**, 313, 207

Effect on tip wear:
- Lantz M A, Wiesmann D and Gotsmann B, *Nat. Nanotechnol.*, **2009**, 4, 586

Features:
- soft lever follows topography
- no feed-back → fast scanning

Mechanism:
- Stiffness of high modes (>10 N/m) is sufficient to overcome adhesion
- Rippling stops, when tip gets out of contact

Consequence:
Imaging speed only limited by sensor bandwidth (~ 6 μs/pixel)



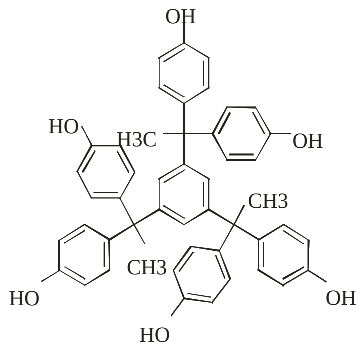
A. Knoll et al., *Nanotechnology* **2010**, *21*, 185701.

Material Strategy

Direct removal of organic material
- – Versatile
- – Compatible to CMOS
- – In-situ inspection

- **Efficient thermally activated process**
  - – Thermal process active at ~ 150 C
- **Stability**
  - – Imaging and etching

Molecular glass

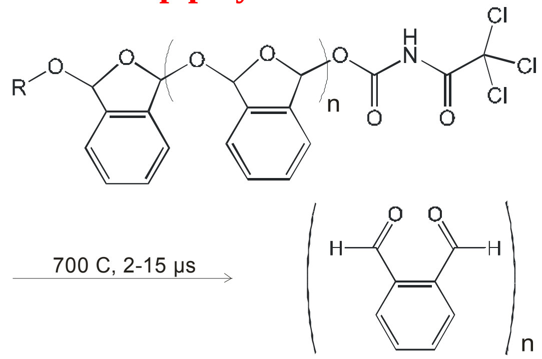


- Mw = 715 g/mol
- physical inter-molecular bonds
- **complete molecules are removed**

- 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)

Unzip polymer



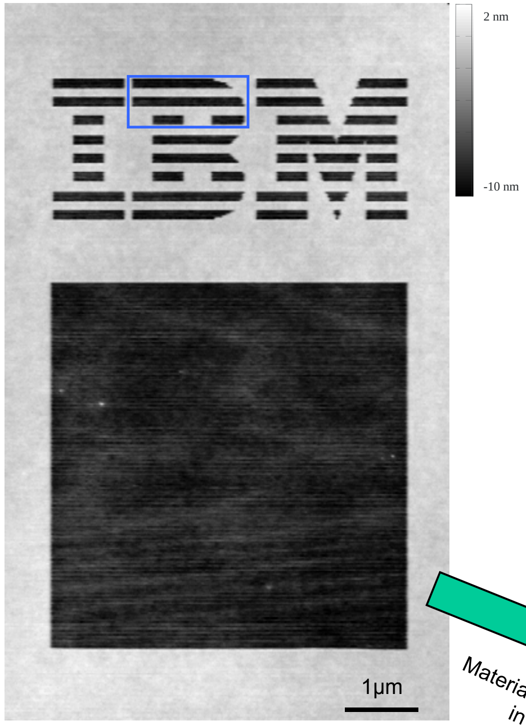
Polyphthalaldehyde (PPA)

- thermodynamically unstable backbone
- synthesis at -78 °C
- **unzips into monomers upon bond breakage**

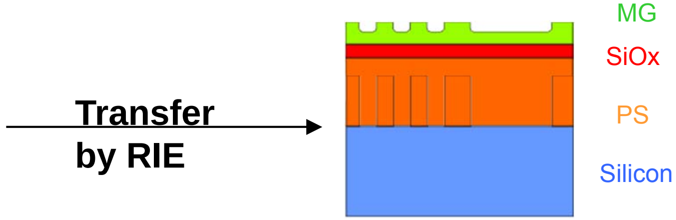
- Tg = Tunzip ≈ 150 °C

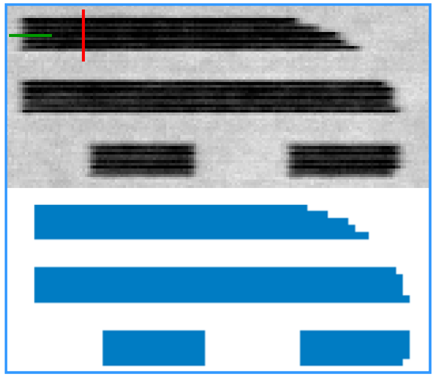
H. Ito, C. G. Willson,
Technical Papers of SPE Regional Technical Conference on Photopolymers, 1982, 331

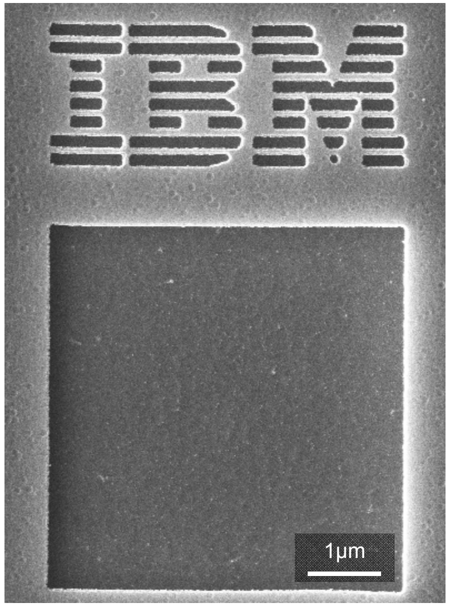
Molecular Glass: Patterning Results



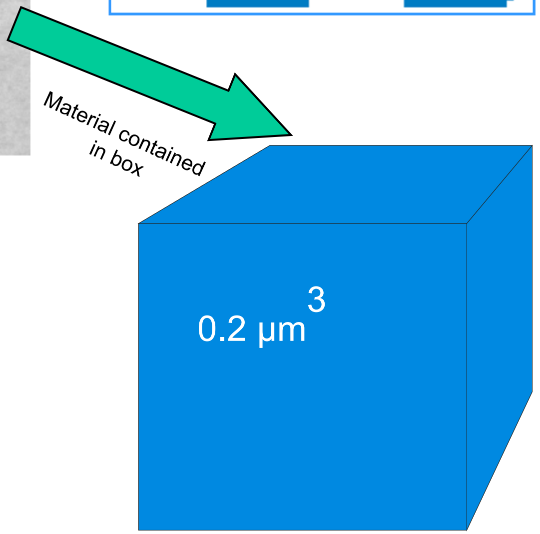
Pitch 29 nm
8 nm depth



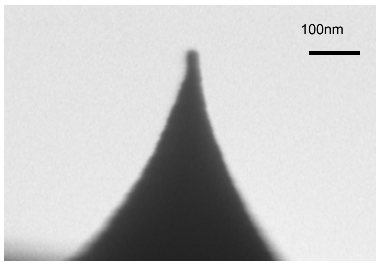




Pattern in Si after transfer:
400 nm depth (50x)



Tip after patterning
several fields:
same scale:

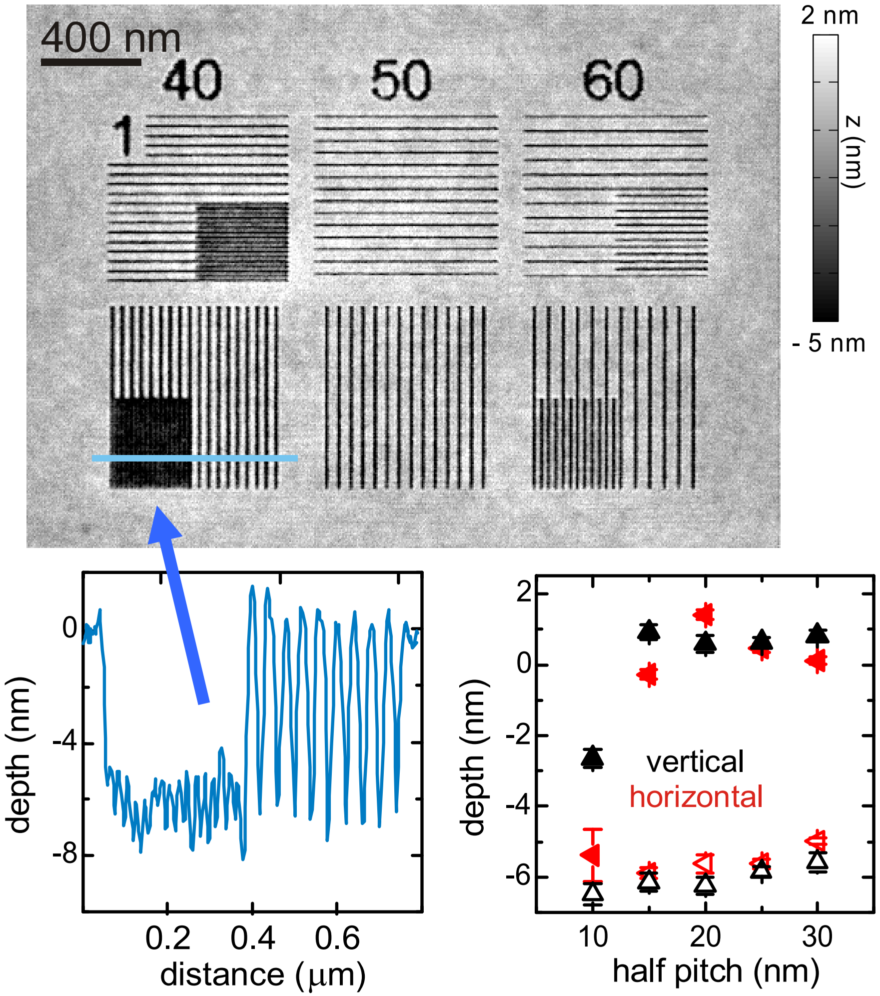


SEM of the tip
after $2 \cdot 10^5$ written pixels

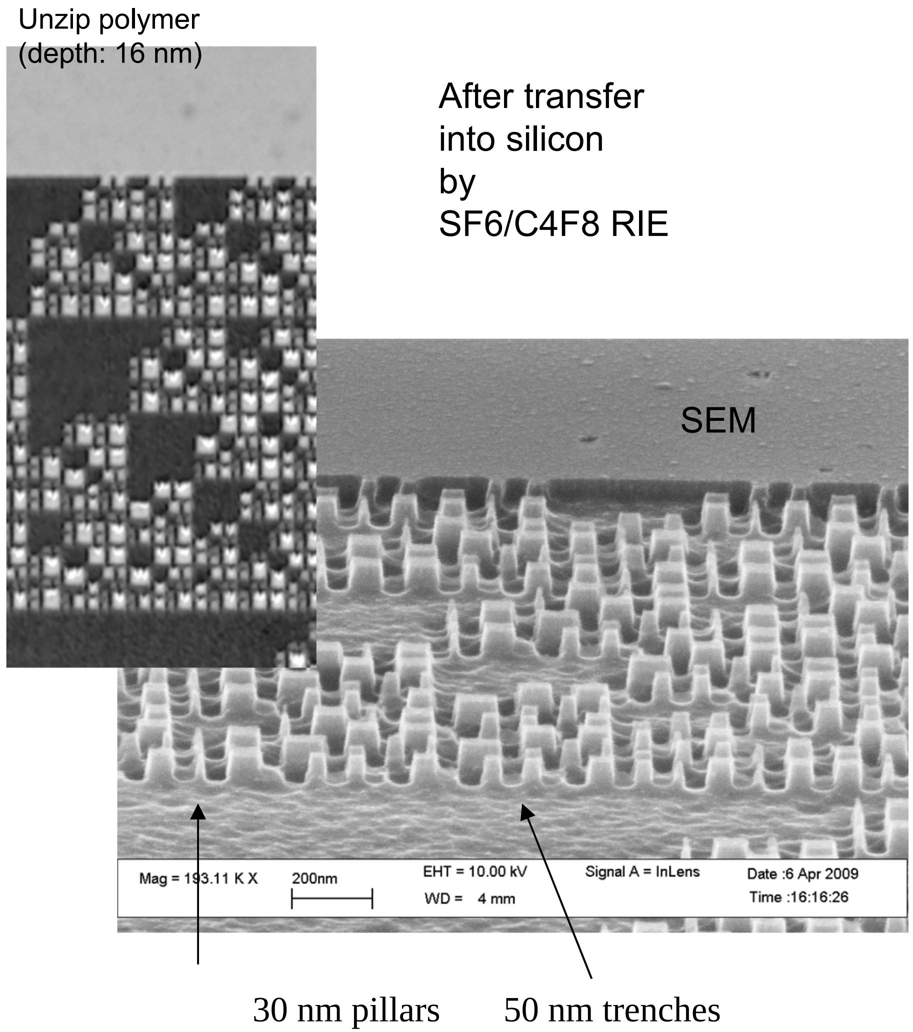
Parameters:
- # Pixels: $4\ 10^4$
  - Heater temperature: 300°C
  - Load force: 80nN
  - Pulse duration: 5.5µs

15 nm half pitch resolution

Molecular Glass



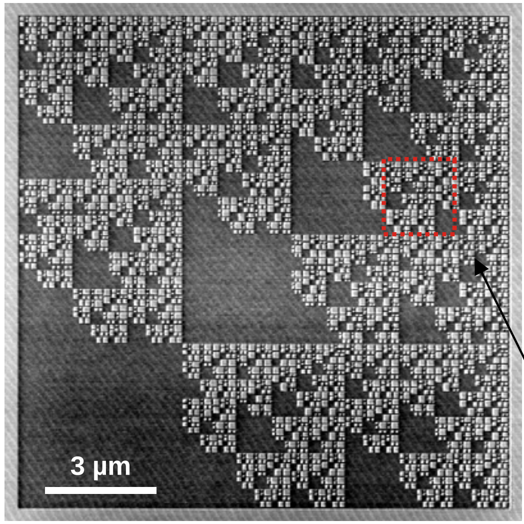
Direct transfer into silicon



AK et al., *Adv. Mater.*, ***22***, 3361, (2010)

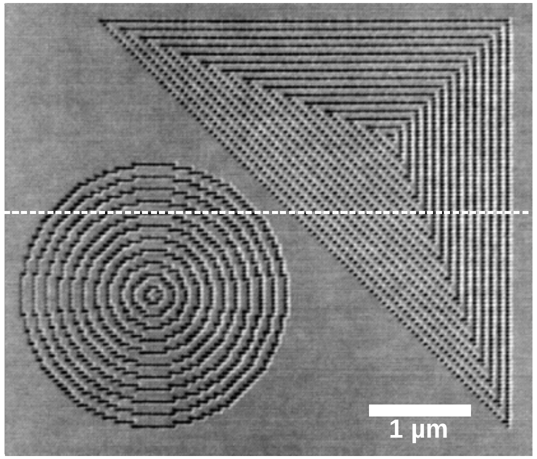
D. Pires et al. , *Science*, ***328***, 732 (2010)

500 KHz writing in unzip polymer



Fractal pattern

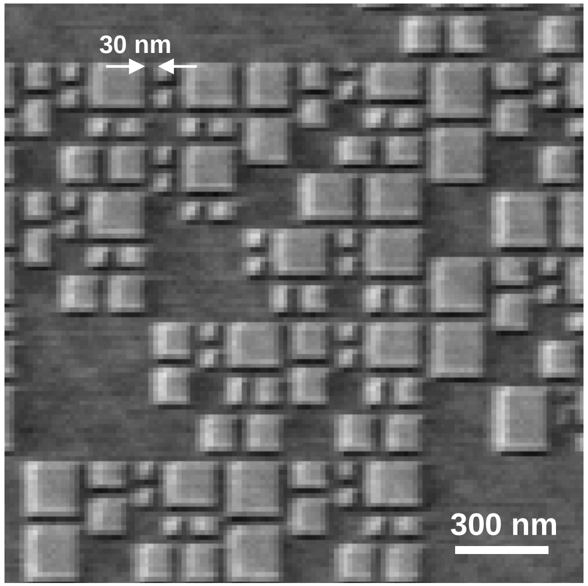
Write duration: 11.8 s



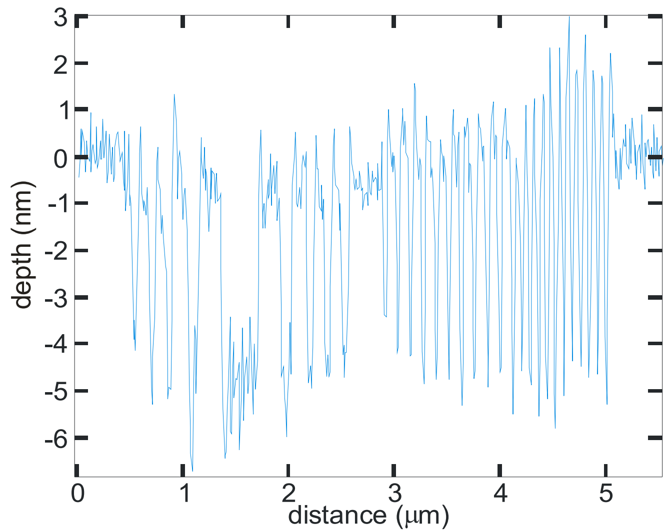
Circles and lines

Write duration: 0.8 s

- Size 13.2 x 13.2 μm^2
- 7.5 mm/s
- 880 x 880 pixels (15 nm)



- 5 x 4 μm^2
- 20 mm/s
- 125 x 100 pixels
- Read: 10x slower (2 mm/s)

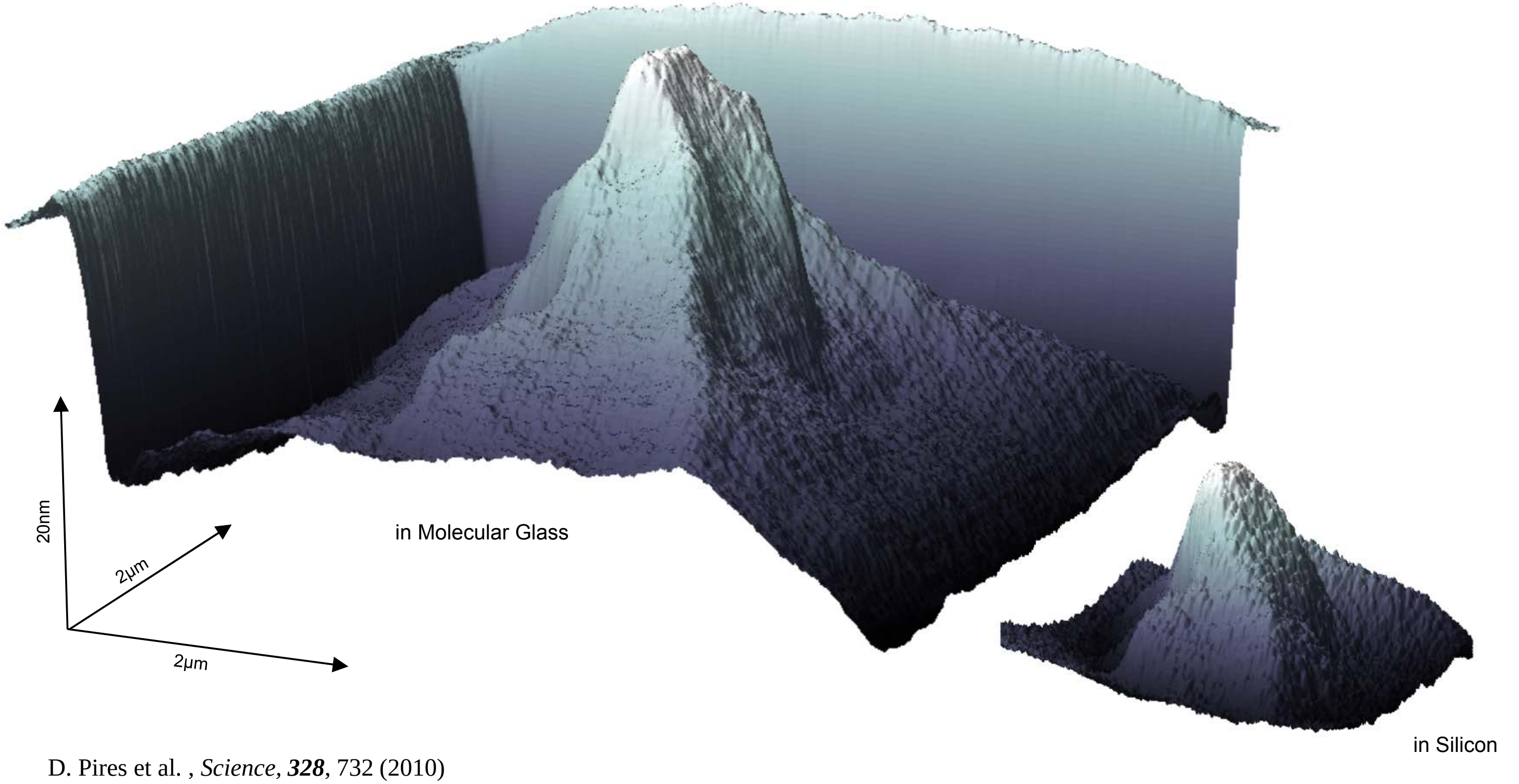


P. Paul et al, *Nanotechnology* **2011**, *22*, 275306

Molecular Glass: Complex 3D-Structures

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

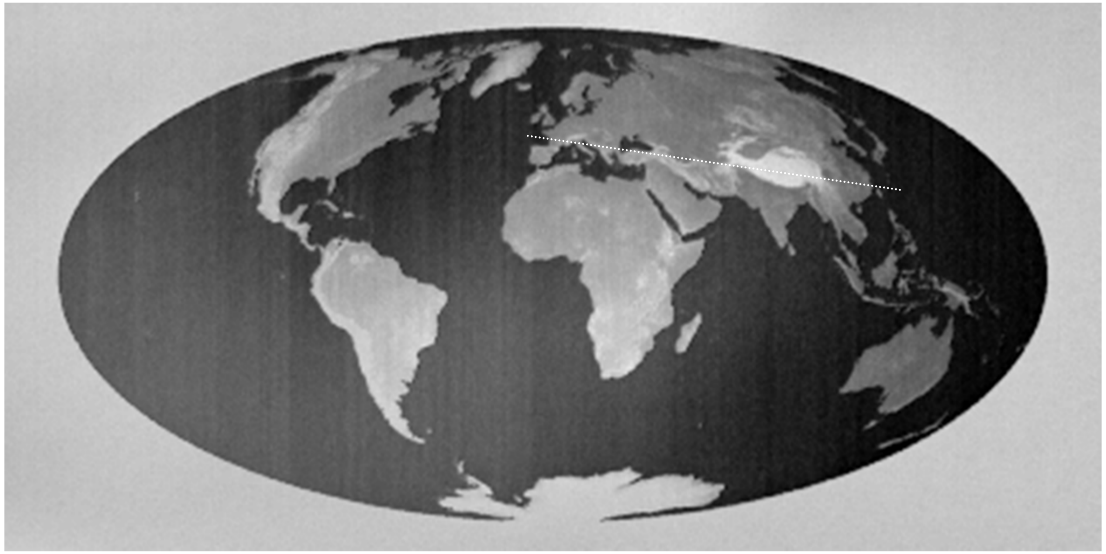
(photographer: Marcel Wiesweg; source: Wikimedia)

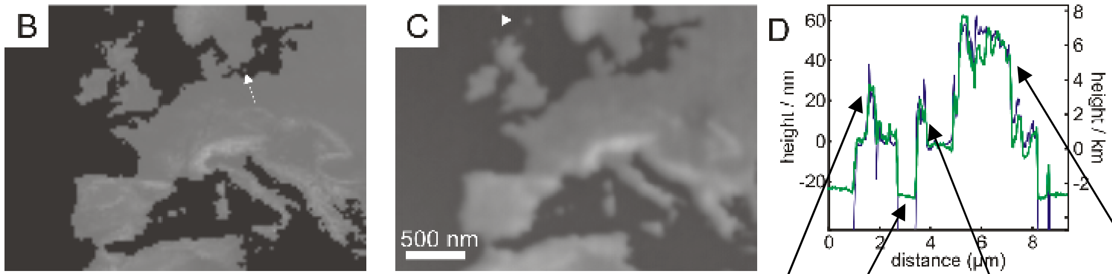


D. Pires et al. , *Science*, ***328***, 732 (2010)

3-D Direct Writing Using Unzip Polymers

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





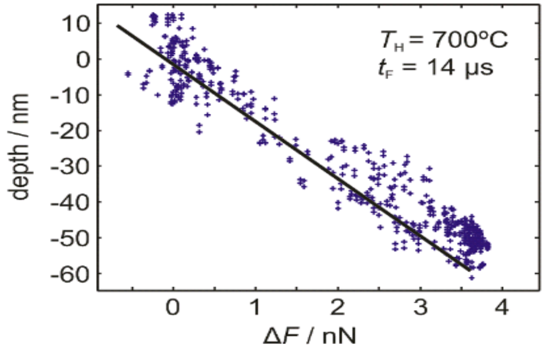
Bit map

Written replica

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

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

Alps
Black Sea
Caucasian Mountains
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

AK et al., *Adv. Mater.*, ***22***, 3361, (2010)

oxidation Scanning Probe Lithography
o-SPL

Outline

i). Background

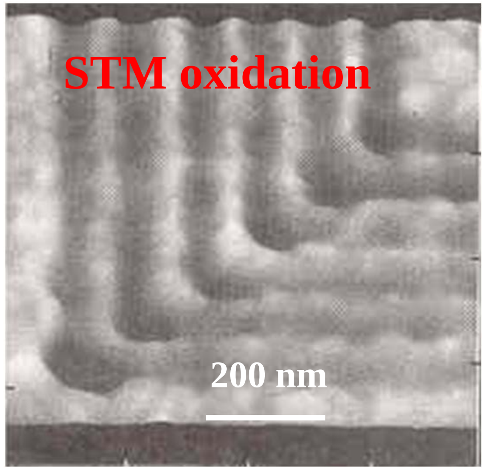
ii). Kinetics and Mechanism

iii). Liquid Bridge Formation

iv). Resolution

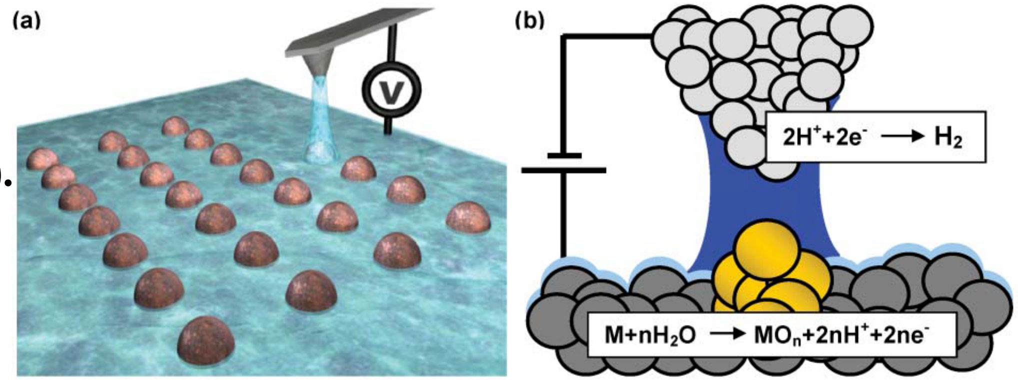
v). Applications

- Template growth
- Transistors
- Sensors

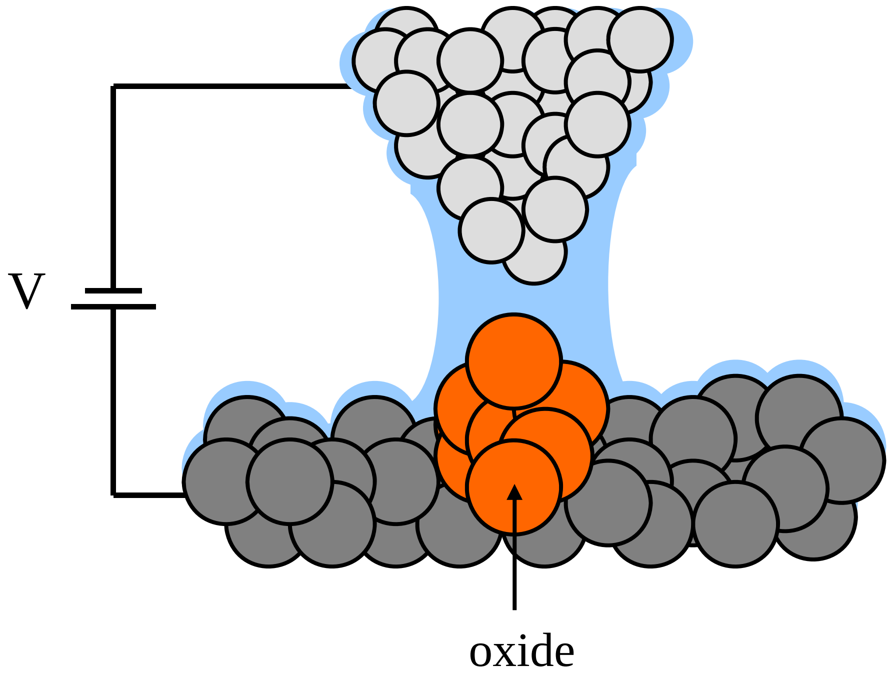


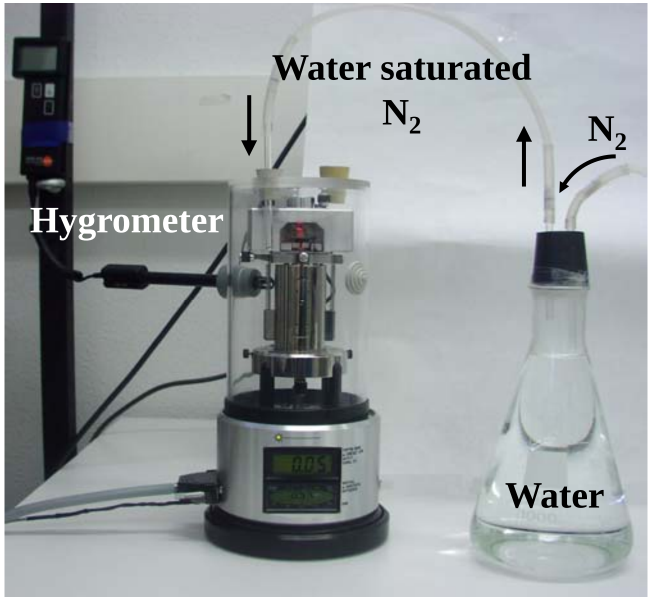
Dagata et al. Applied Physics Letters 56, 2001 (1990); Thundat et al. J. Vac. Sci. Technol. A 8, 3527 (1990)

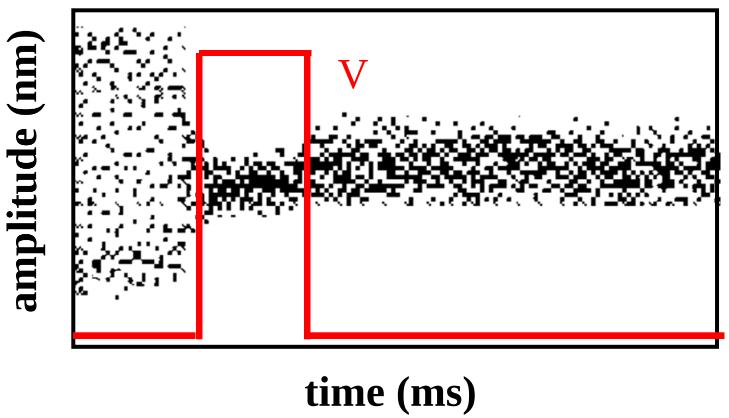
v).

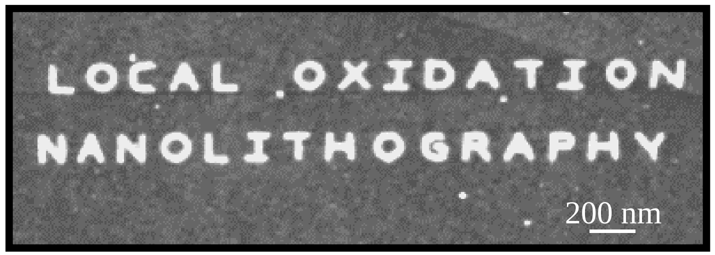


LOCAL OXIDATION NANOLITHOGRAPHY

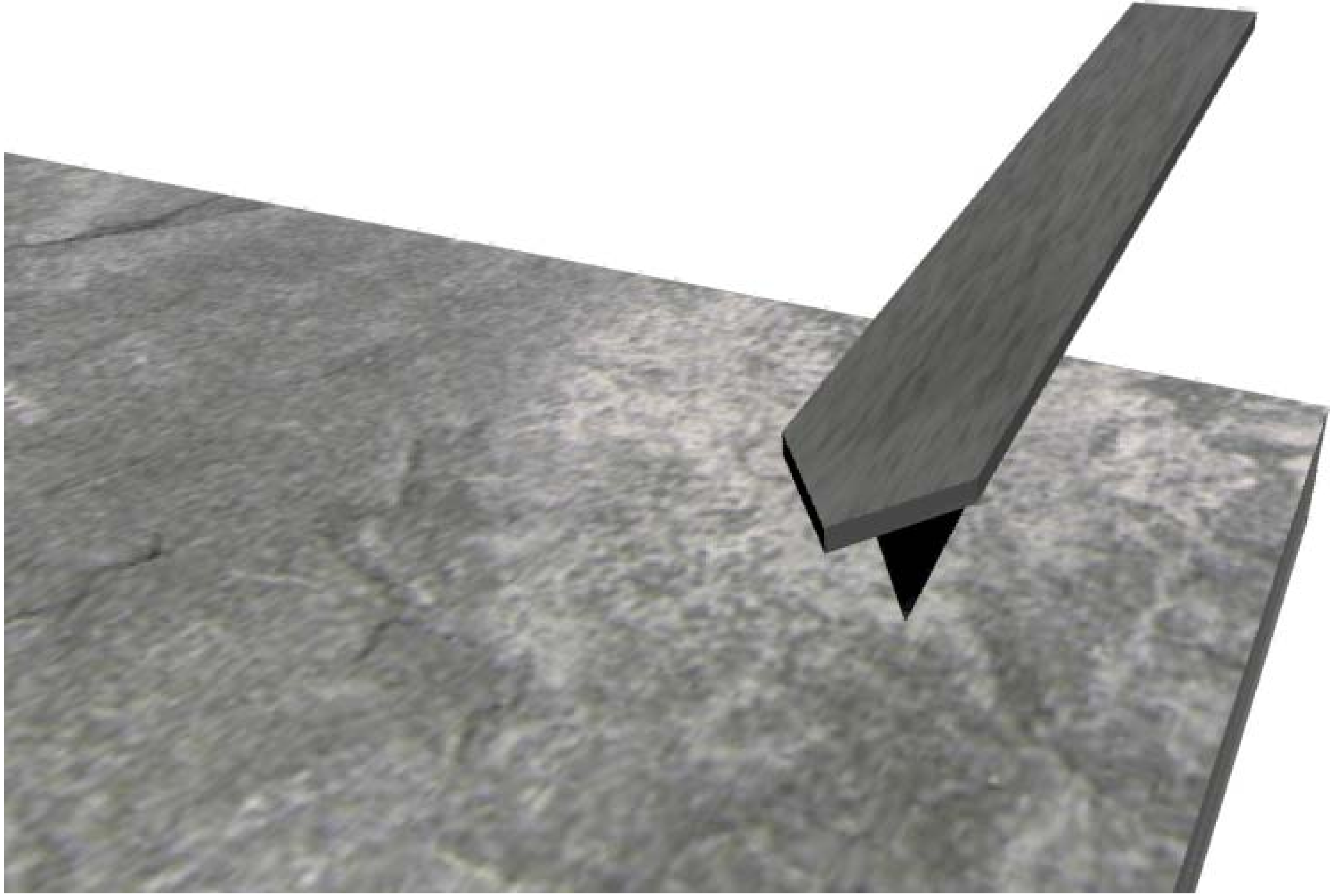


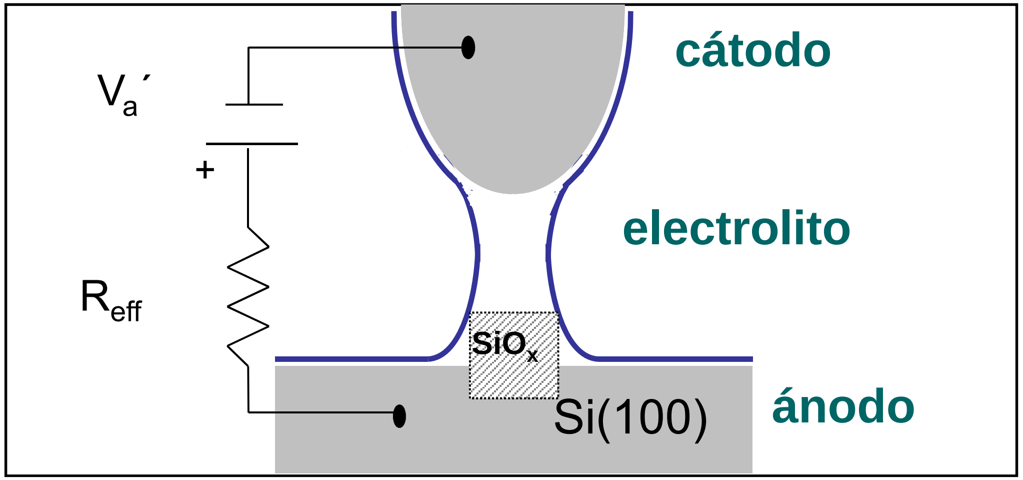






García, Calleja, Perez-Murano, Appl. Phys. Lett. (1998)
Martínez et al., Nano Lett. 5, 1161 (2007)





Electrolyte

$$2H_2O \rightleftharpoons 2H^+ + 2(OH^-)$$

Anode

$$Si + 2h^+ \longrightarrow Si^{2+}$$

$$Si^{2+} + 2(OH^-) \longrightarrow Si(OH)_2$$

$$Si(OH)_2 \longrightarrow SiO_2 + H_2$$

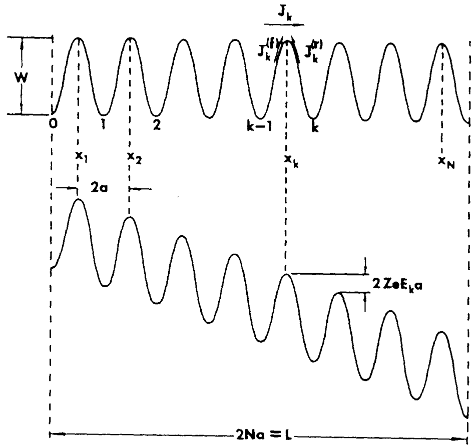
Cathode

$$2H^+ + 2e^- \longrightarrow H_2$$

Global Reaction

$$Si + 2h^+ + 2H_2O \longrightarrow SiO_2 + 2H^+ + H_2$$

Local Oxidation



E = electric field

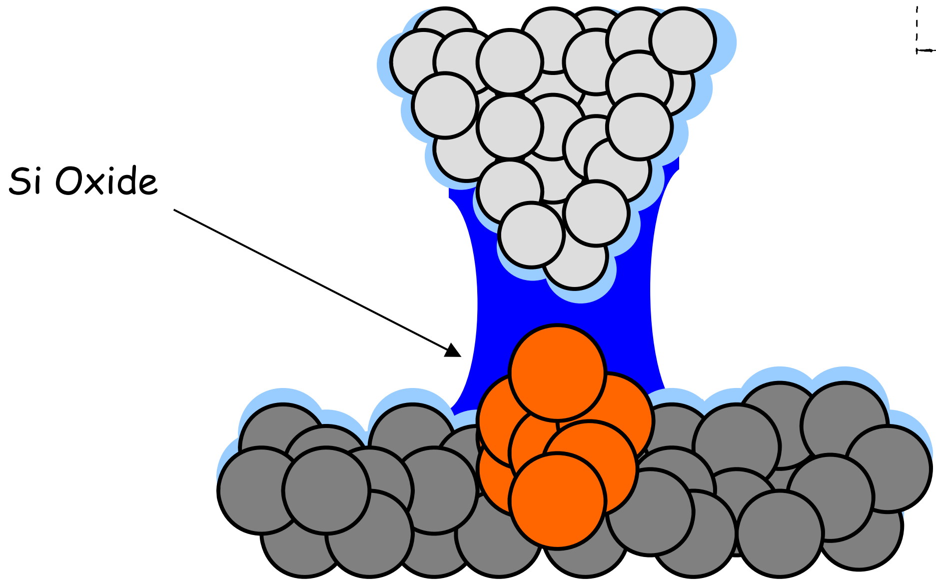
a=interatomic distance

ν= vibrational frecuency

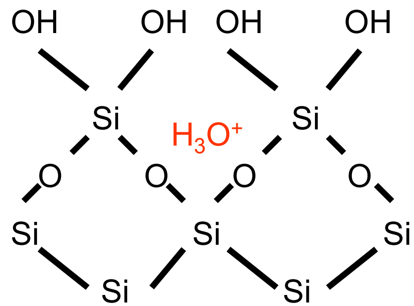
Ionic current

$$J = n\nu e^{\frac{-W}{\kappa_B T}} e^{\frac{zeEa}{\kappa_B T}}$$

N. Cabrera, N. F. Mott, *Rep. Prog. Phys.*, 12, 163, (1949)

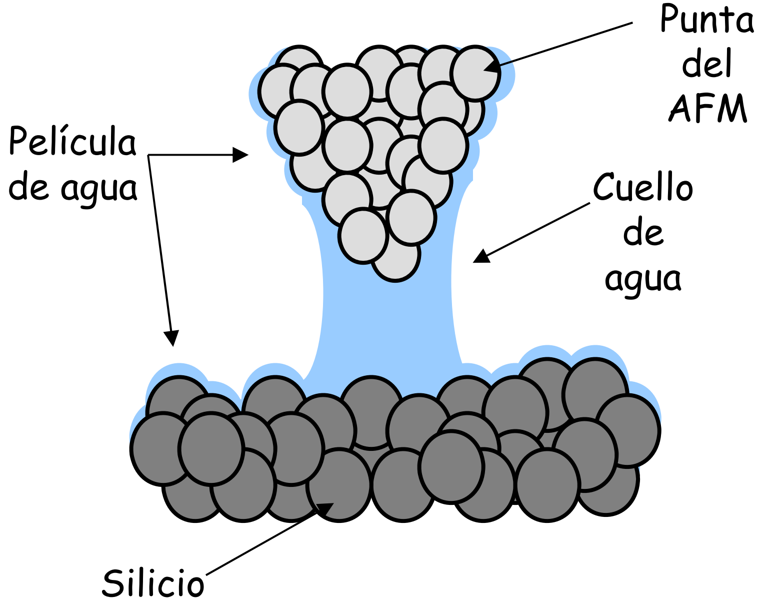


$V_{ox.}$



García, Calleja, Pérez-Murano APL 72, 2295 (1998); García, Calleja, Roher, J. Appl. Phys. 86, 1898 (1999); Tello, García APL 79, 424 (2001);

Puentes de agua para fabricar chips



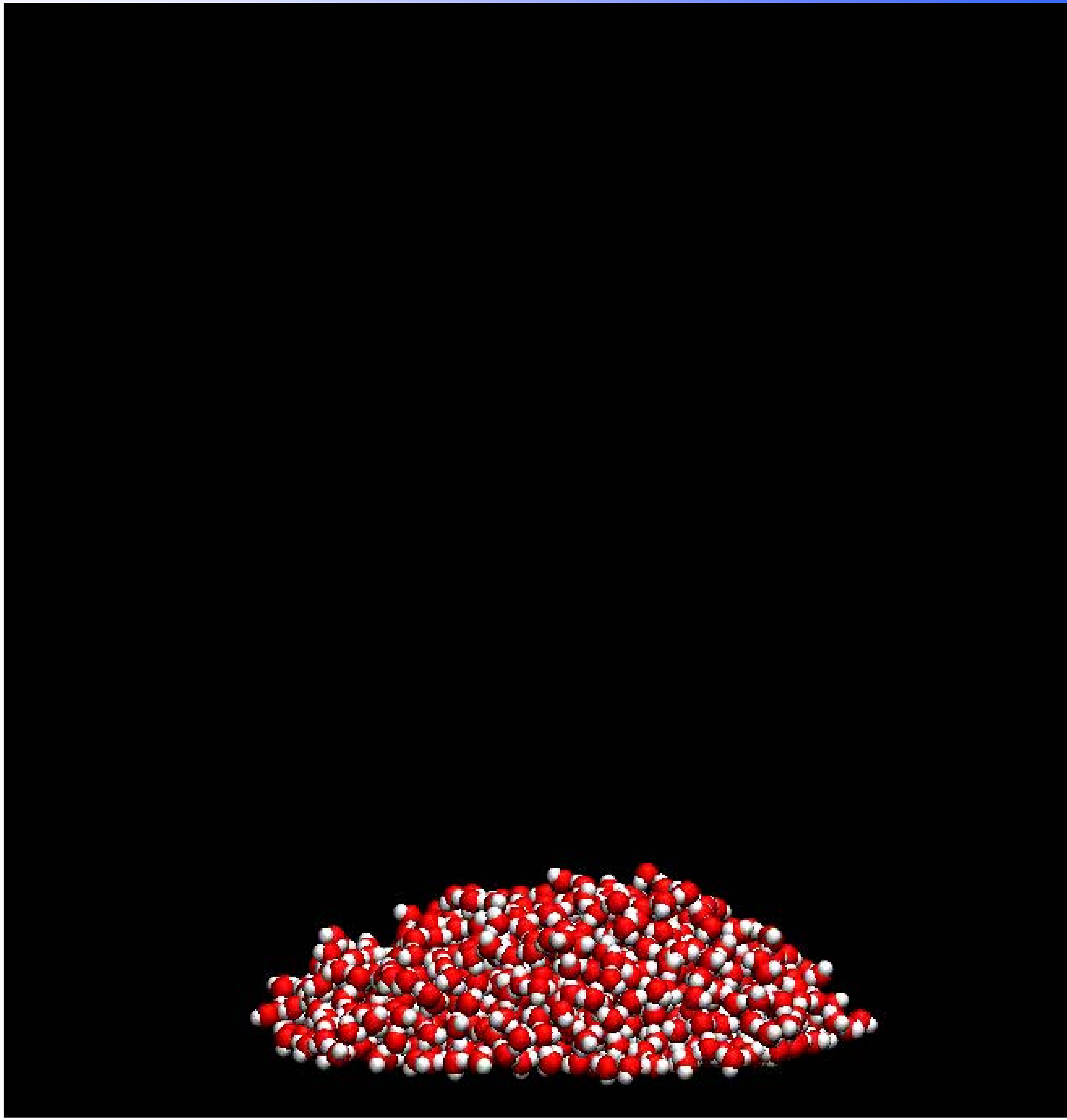
V > V$_{umbral}$

ΔU= {surface+condensation+electrostatic energies}= $\Delta U_s + \Delta U_c + \Delta U_e$

$\Delta U = \pi W^2 d[(RT/\upsilon)Ln(1/H)-2\gamma/d-1/2d^2(\varepsilon-1)\varepsilon_0 V^2]+2\pi\gamma Wd$

Gómez-Moñivas et al. PRL 91, 056101 (2003)

Gracía-Martín, García, APL 88, 123115 (2006)



E=2 GV/m= 2 V/nm

time=75 ps

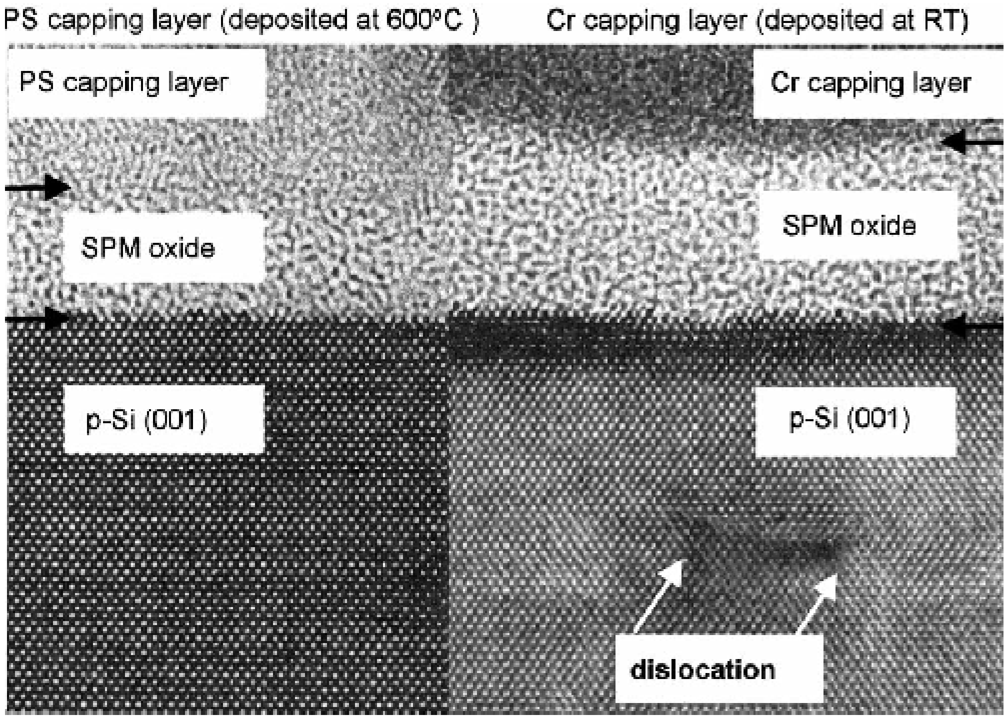
Meniscus height 3 nm

1014 molecules

MD by F. Zerbetto and T. Cramer, UBologna

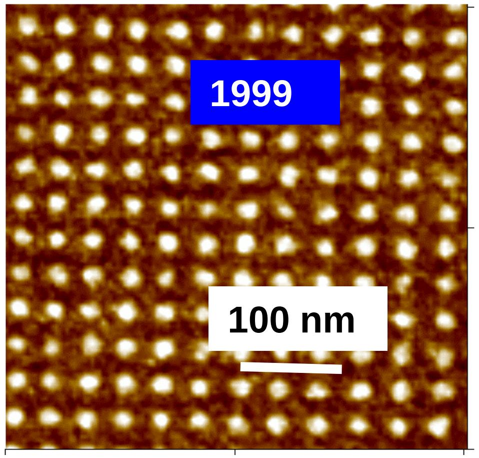
Cramer, Zerbetto and Garcia, Langmuir 24, 6116 (2008)

Cross-Section TEM images of Local Oxides

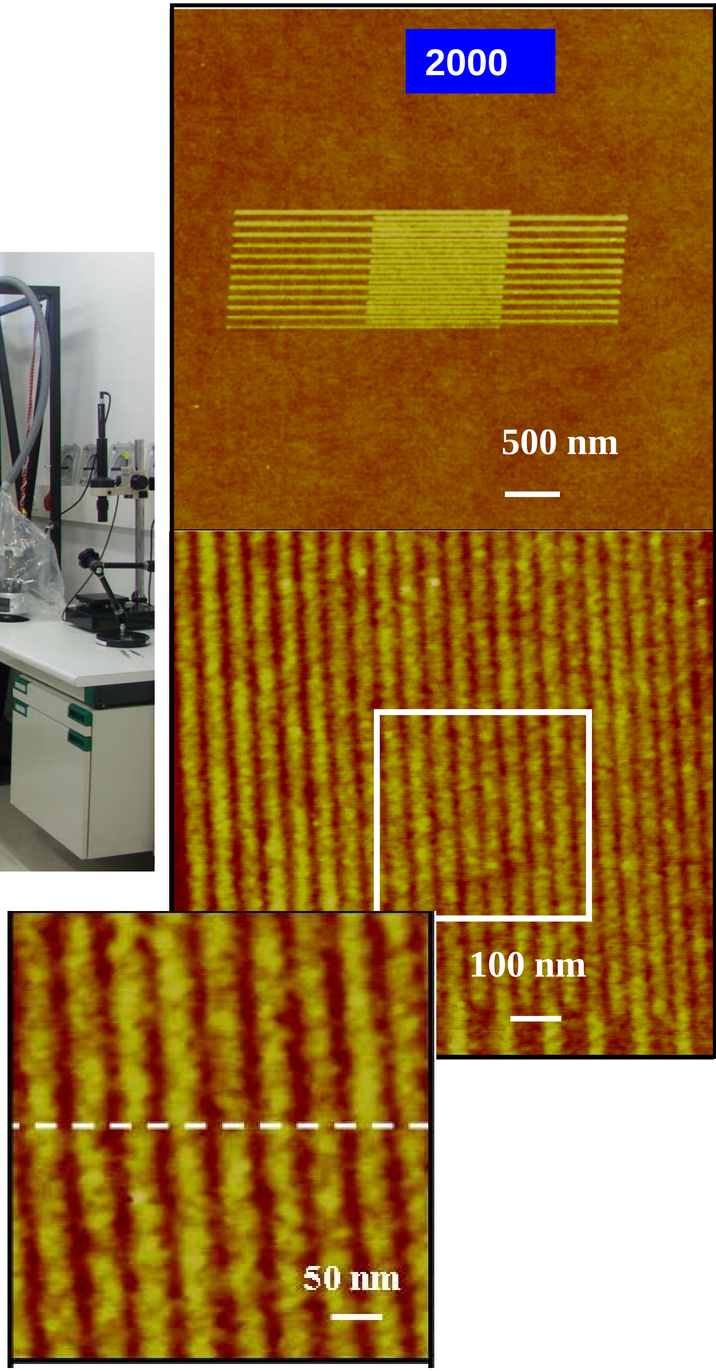


Morimoto et al. Appl. Surf. Sci. 158, 205 (2000)

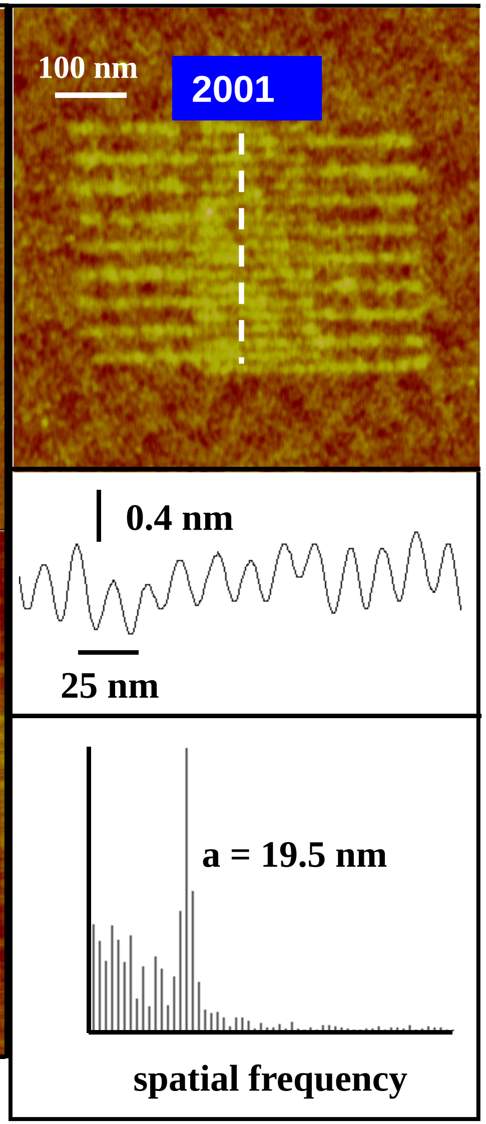
CSIC



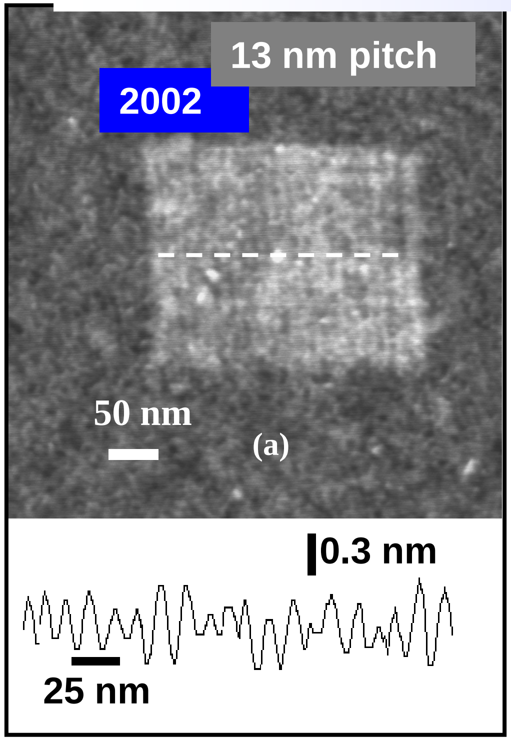
1999
100 nm

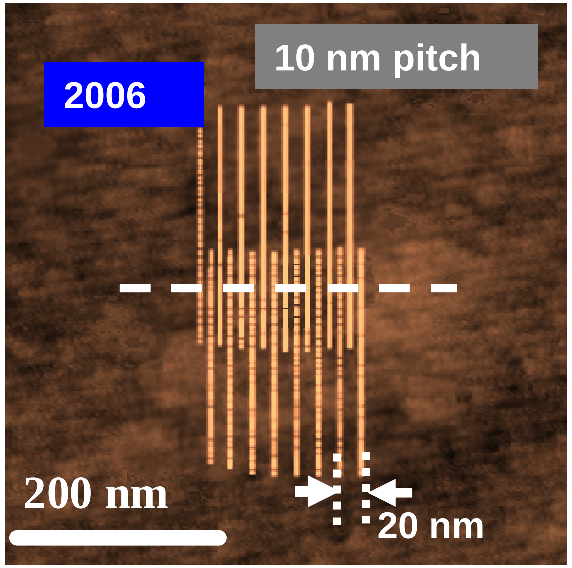


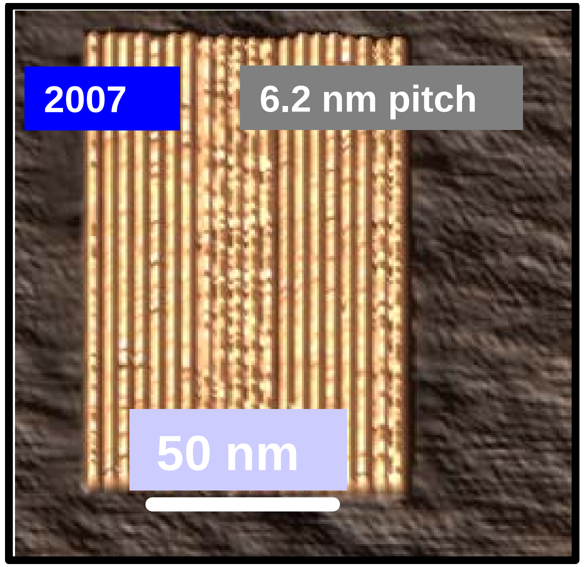
2000
500 nm
100 nm
50 nm

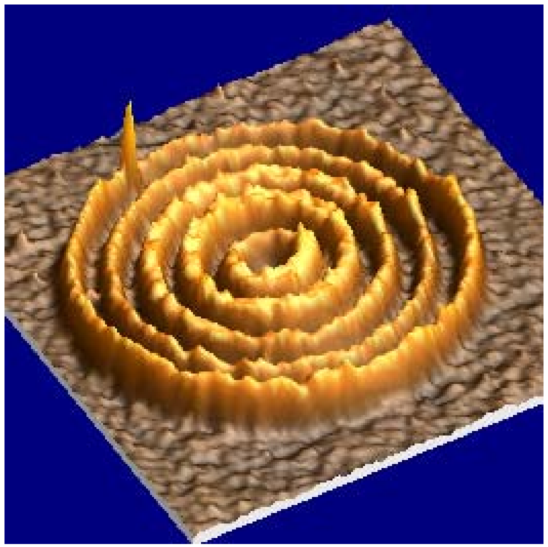


100 nm
2001
0.4 nm
25 nm
a = 19.5 nm
spatial frequency

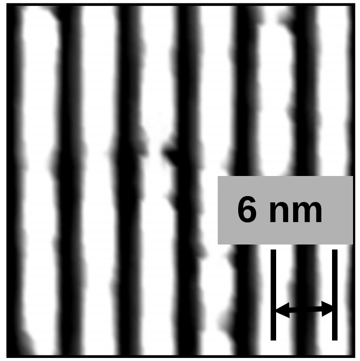


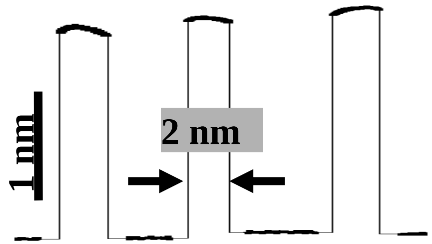






Year	Lattice periodicity nm	Feature size nm
1999	40	20
2001	20	10
2002	13	10
2006	10	4
2007	6	2



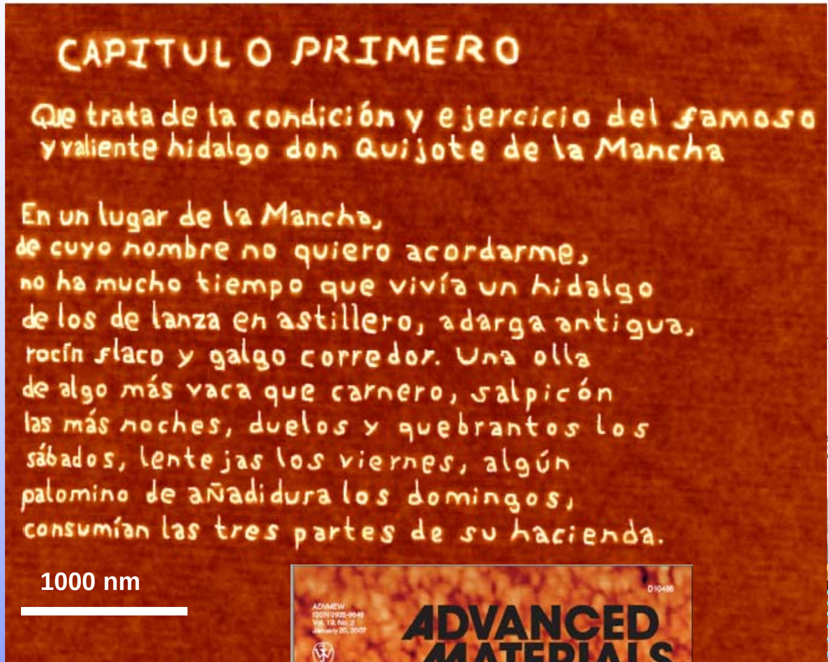


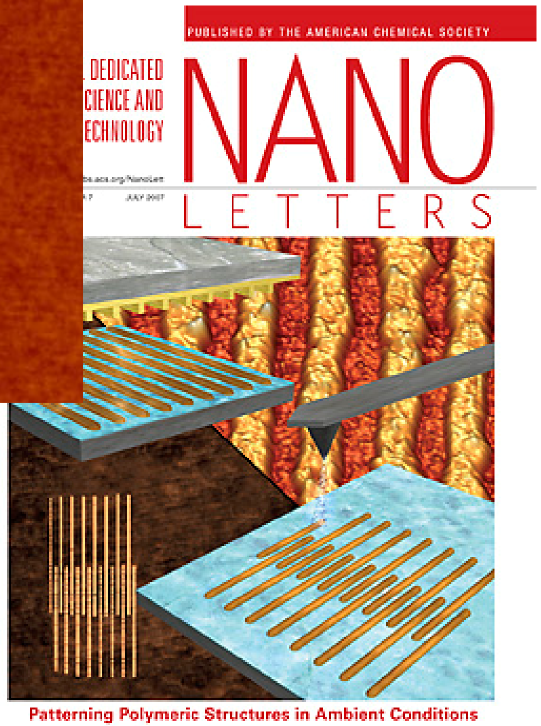
Pitch record at ambient conditions ?

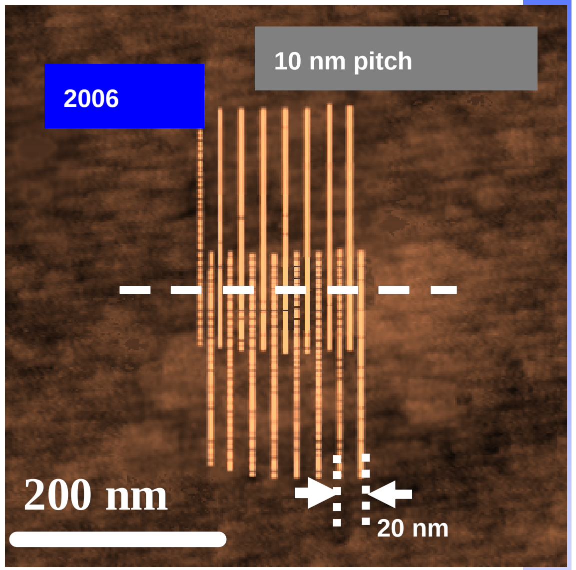
CSIC

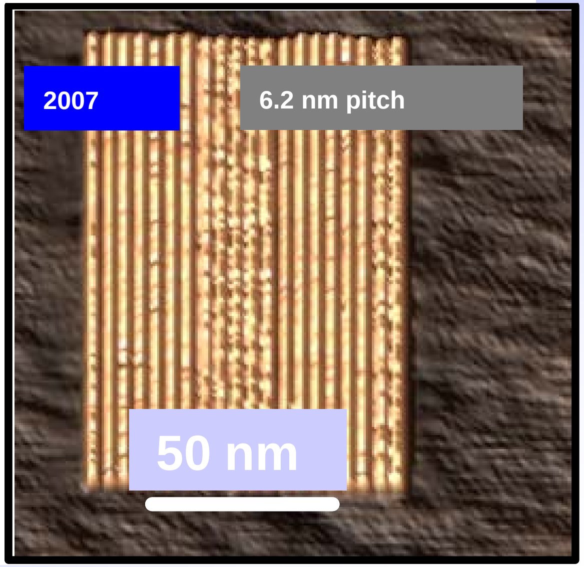
i). Nanometer-size liquid Bridges

ii). Minimum Feature Size

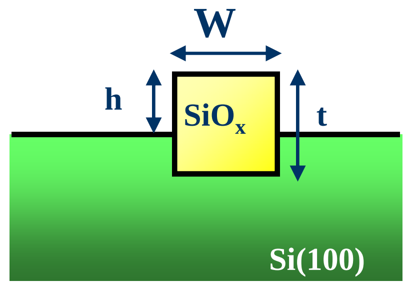




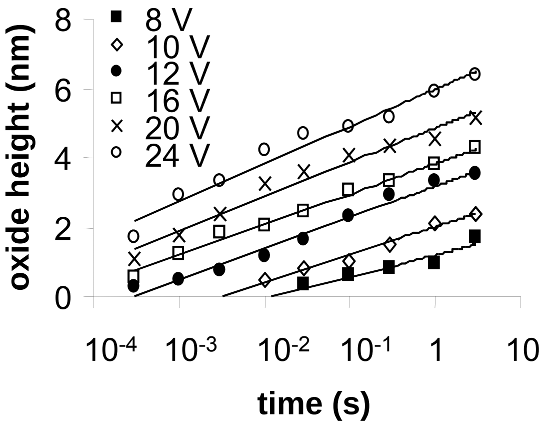


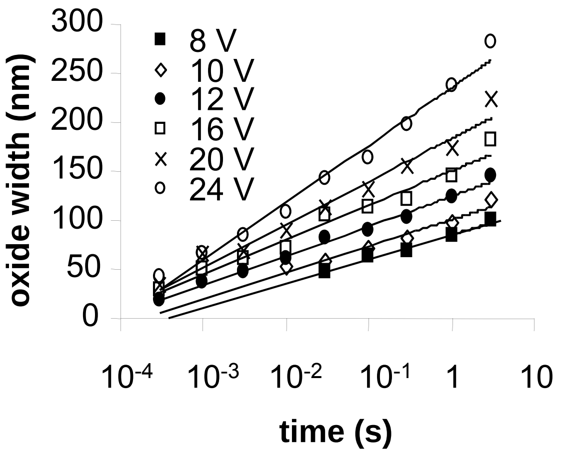


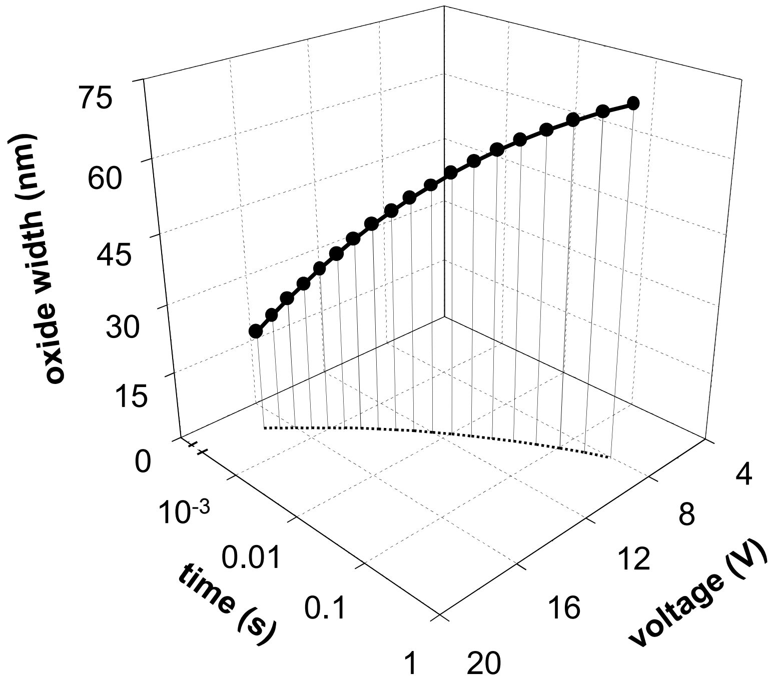
Oxidation Kinetics



h=cte=1 nm

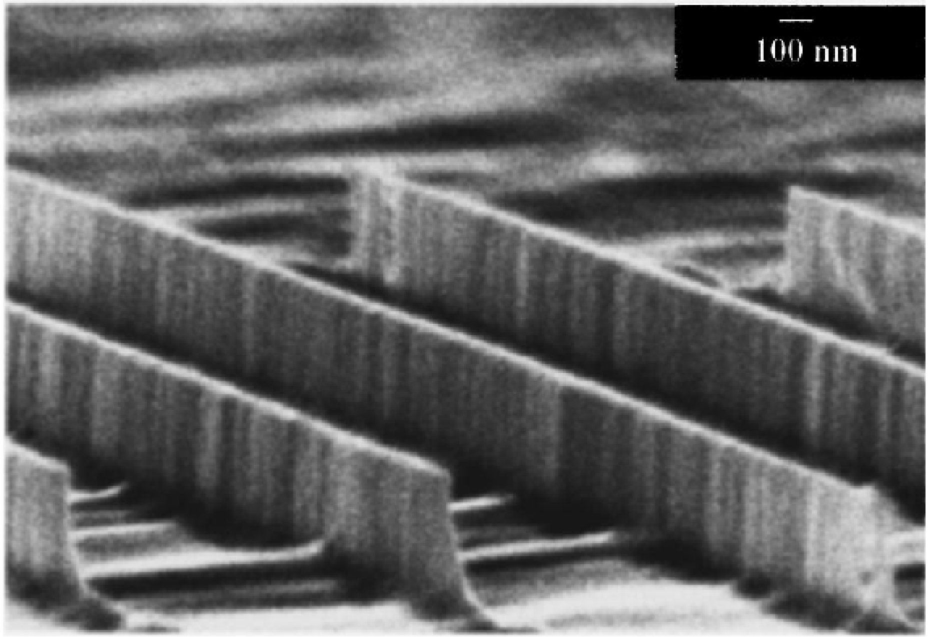


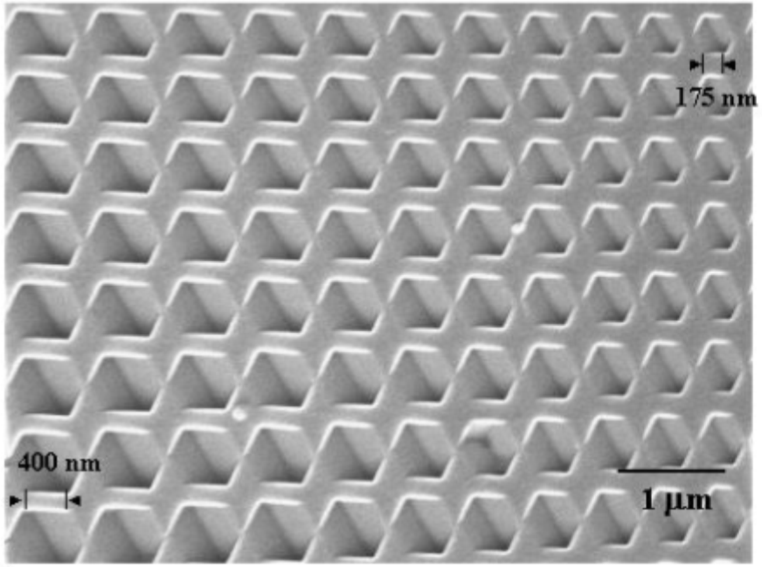




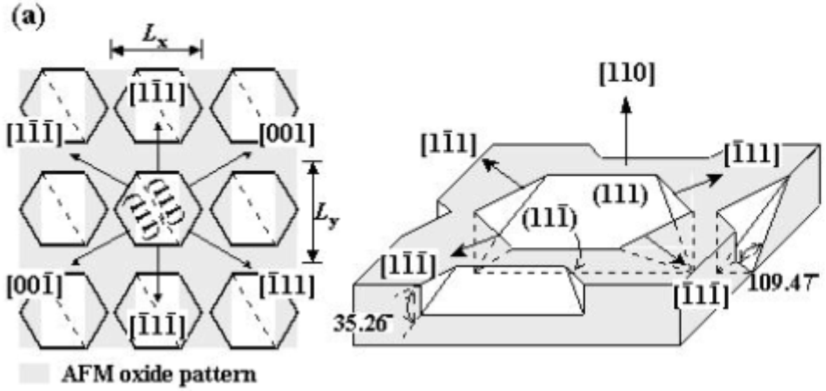
Calleja, García, APL 76, 3427 (2000)

3D Nanostructures





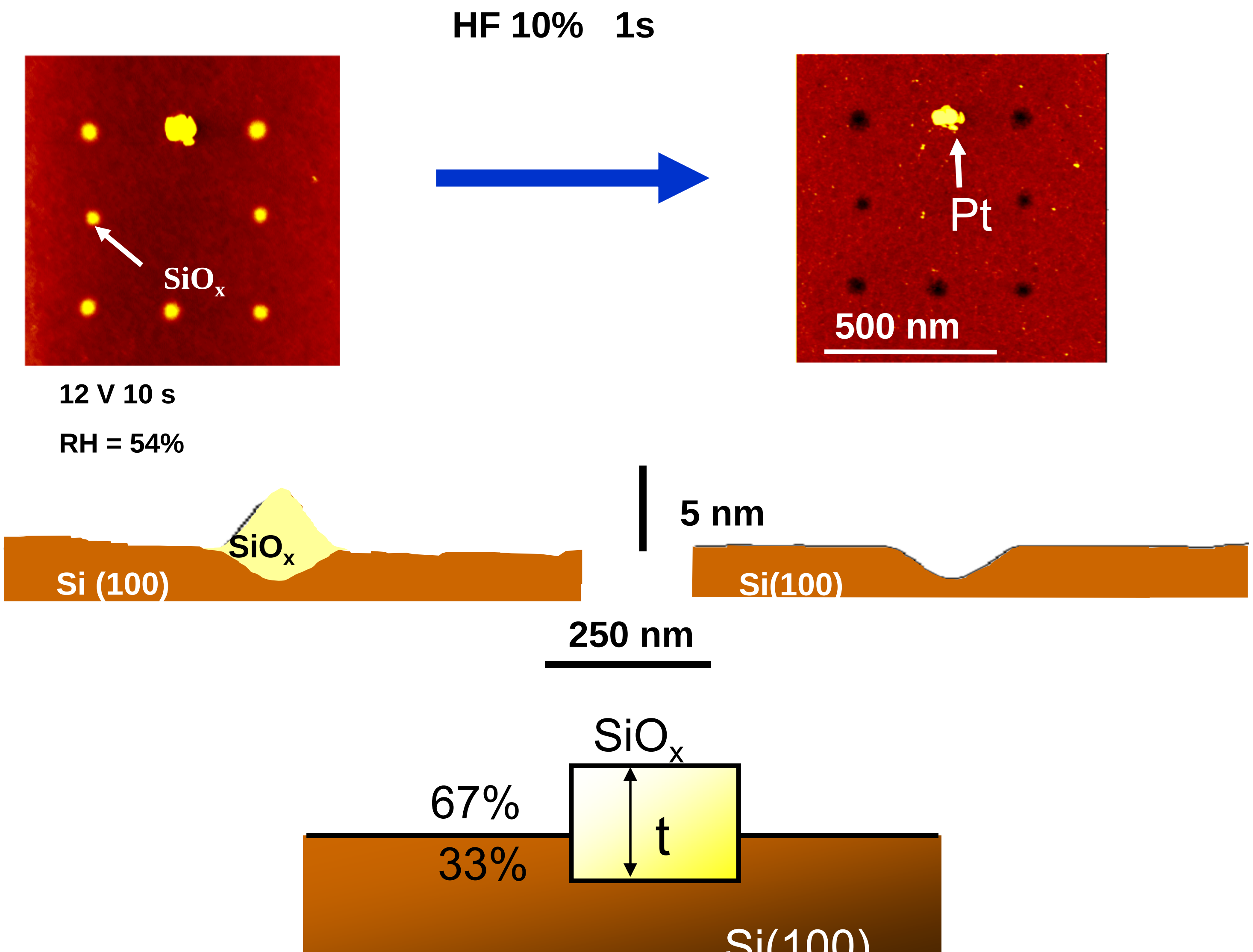
(a)



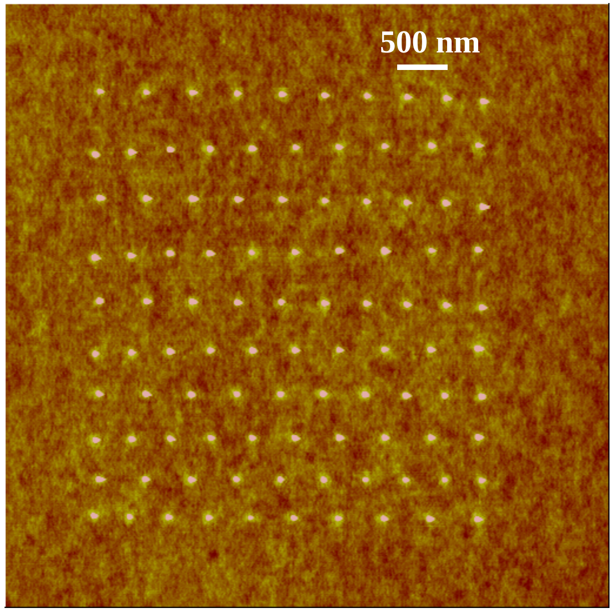
(b) (c)

S. Gwo et al. APL 75, 2429 (1999)

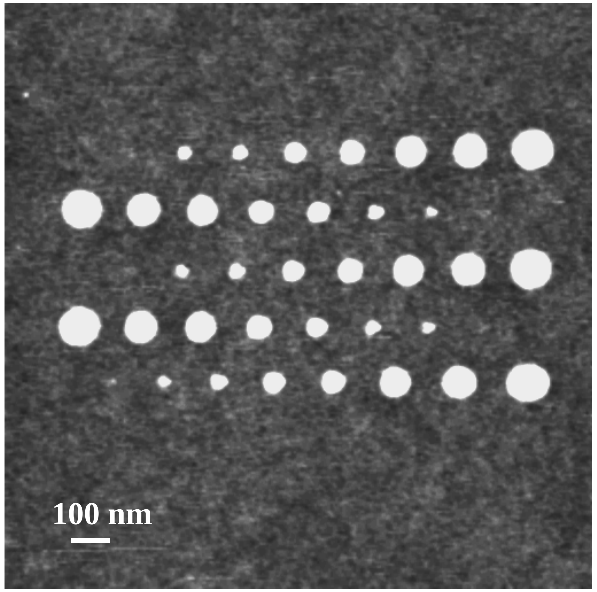
HF wet etching of oxidized surfaces



GaAs



Niobium



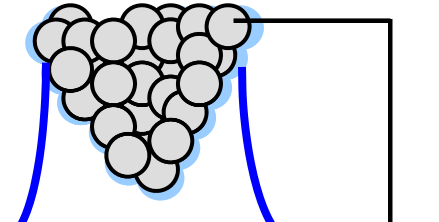
Titanium, Aluminum, carbon films, silicon nitride, InP, GaAs, Organosilanes...

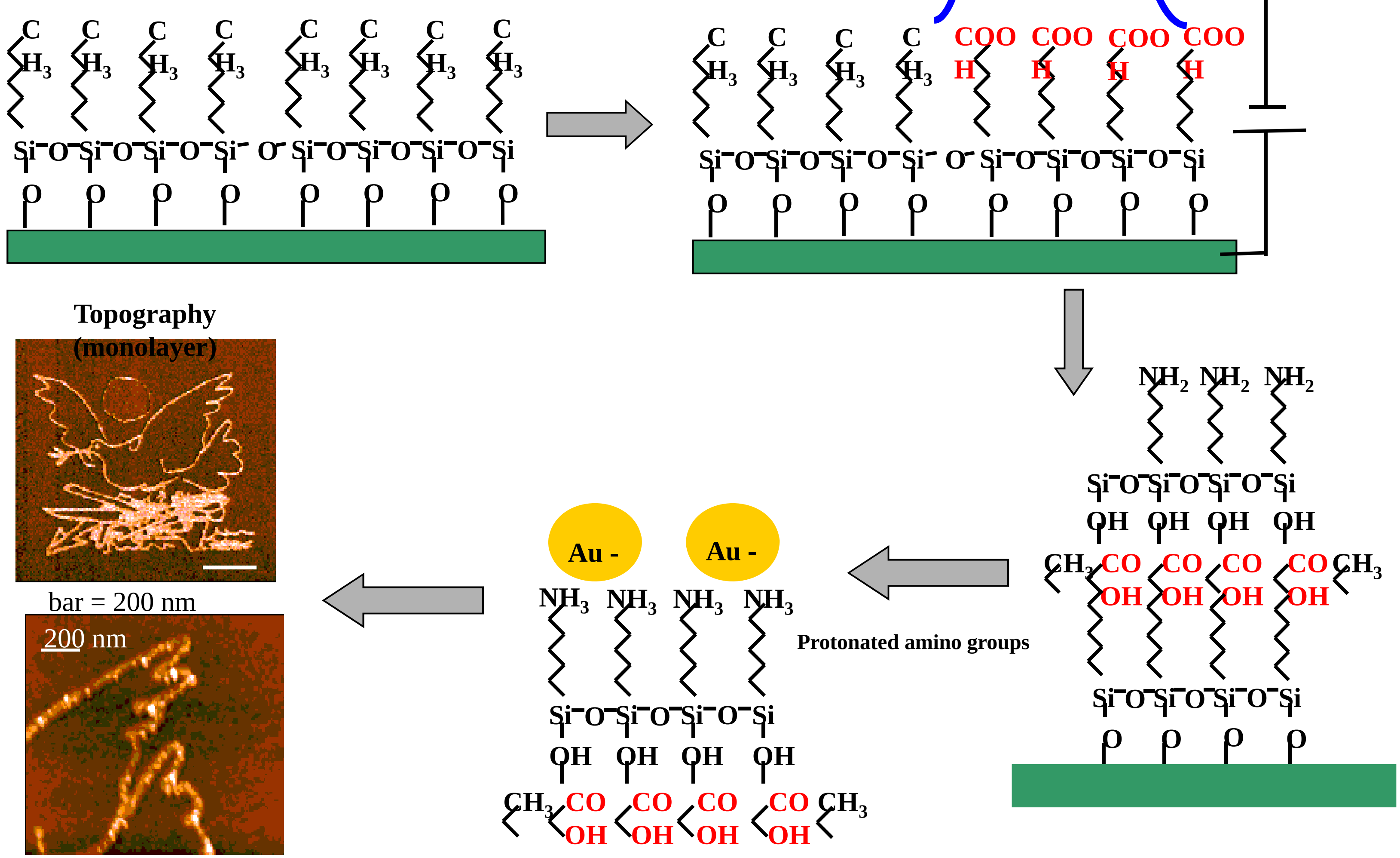
o-SPL: Self-assembled monolayers

Patterned templates for in-situ nanofabrication of metal-semiconductor-organic interfaces

Sagiv et al., Adv. Mat. 725, 12 (2000); Nano Letters 4, 845 (2004)

OTS= n-octadecyltrichlorosilane CH_3-$(CH_2)_{17}$-$SiCl_3$)

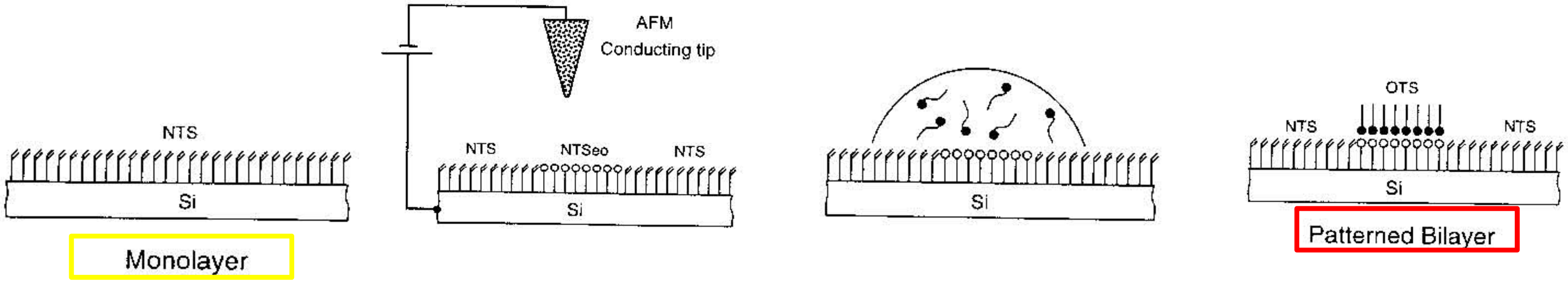




Local Oxidation Nanolithography on self-assembled monolayers (1/3)

Fabrication steps:

(1) (2) (3) (4)



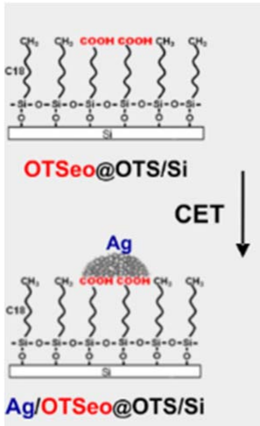
Functionalization of Si substrate with a self-assembled Silane (NTS) monolayer.

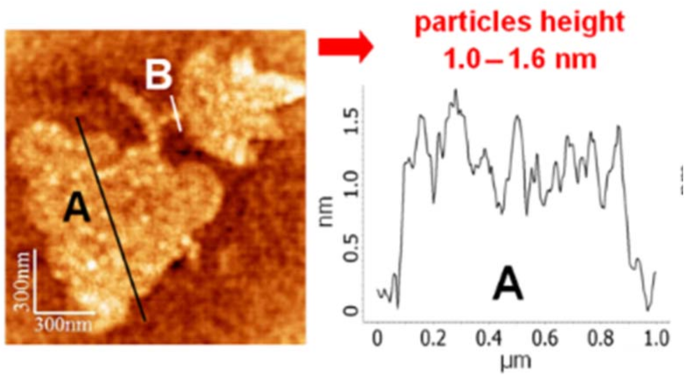
Electrooxidation of the monolayer in selective sites with an AFM tip.

Second functionalization with another silane monolayer (OTS).

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

It is possible to oxidized the OTS monolayer to deposit selectively different metals such as silver, creating localized patterns with any shape

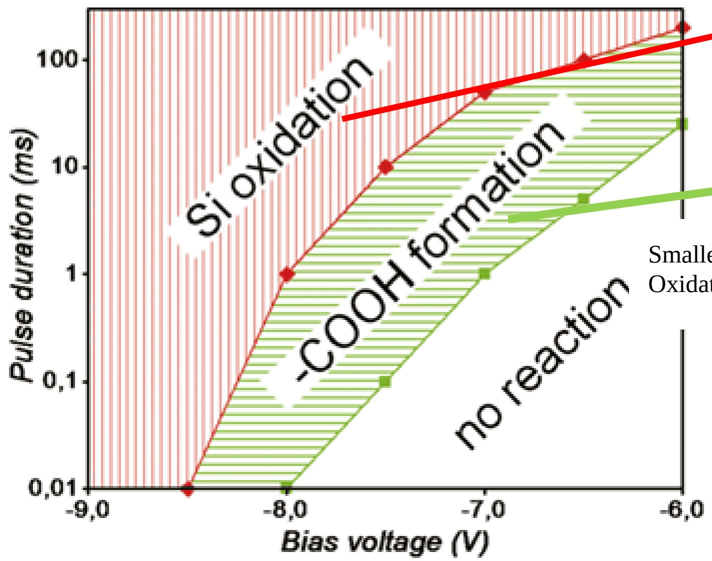




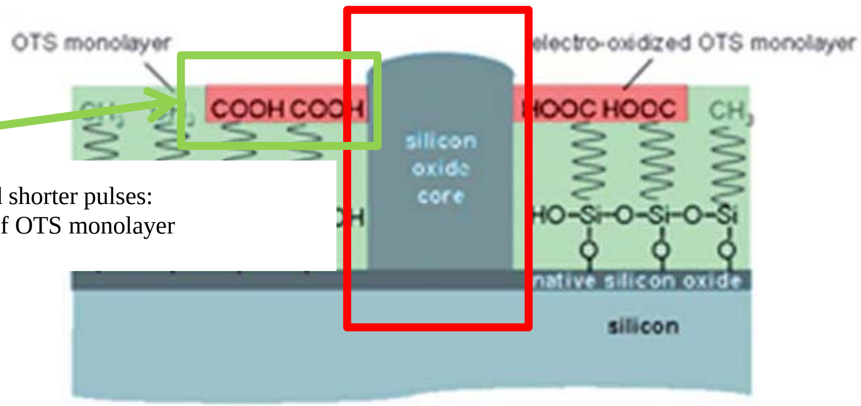
R. Maoz, S.R.Cohen and J. Sagiv. *Advanced Materials* **1** (1999)
J. Berson, A. Zeira, R. Maoz and J. Sagiv. *Beilstein Journal of Nanotechnology* **3** (2012)

Local Oxidation Nanolithography on self-assembled monolayers (2/3)

Regimes of oxidation:

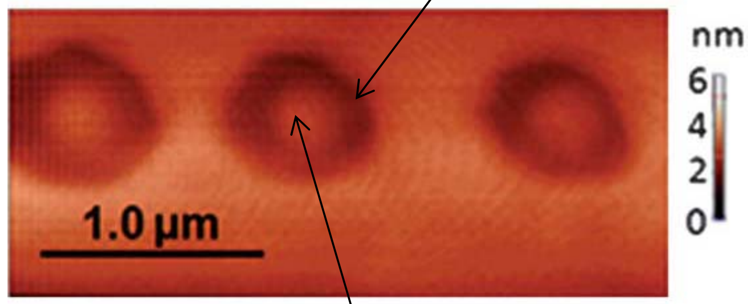


Larger and longer pulses:
Oxidation of Si substrate



Smaller and shorter pulses:
Oxidation of OTS monolayer

OTSox

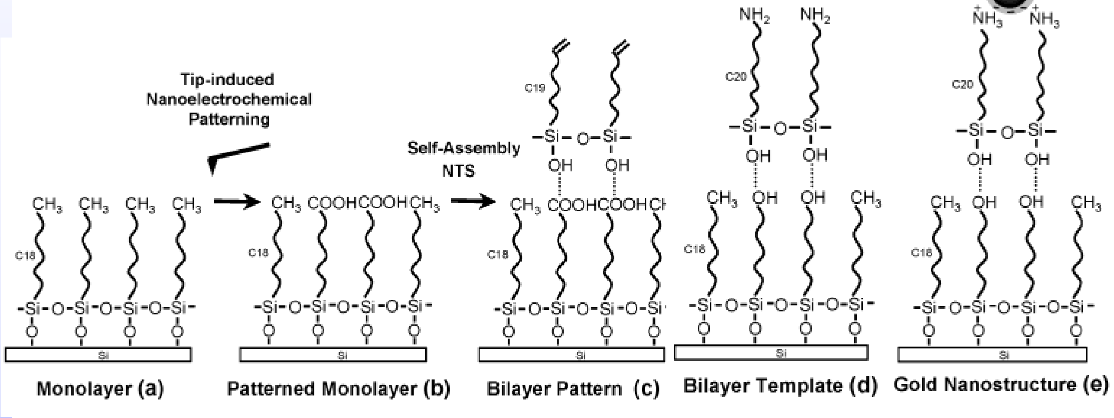


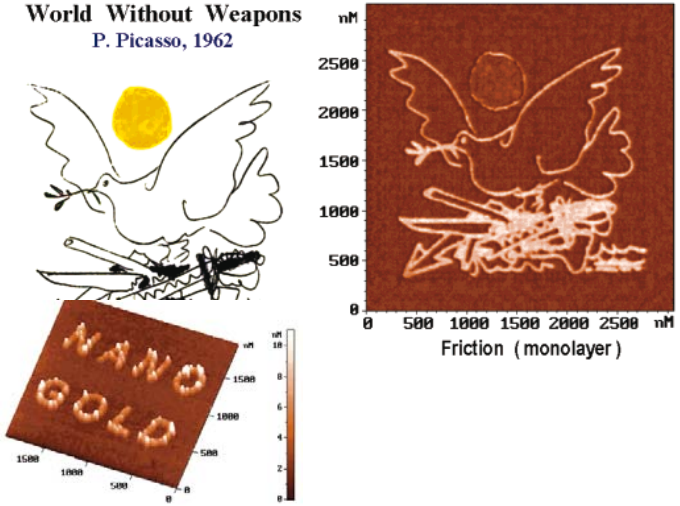
SiO2

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

Local Oxidation Nanolithography on self-assembled monolayers (3/3)

Serial approach

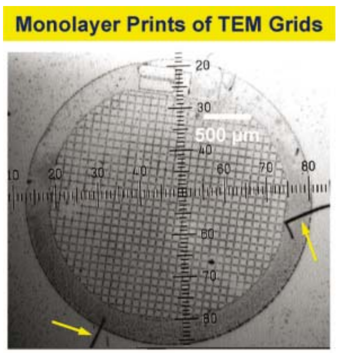




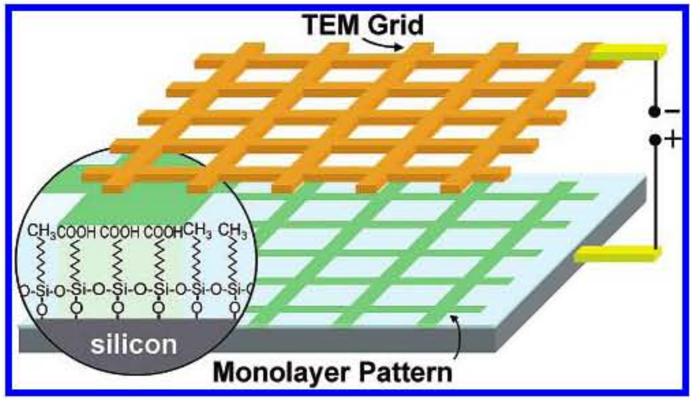
S. Liu, R. Maoz and J. Sagiv. *Nano Letters* **4** (2004)

Parallel approach

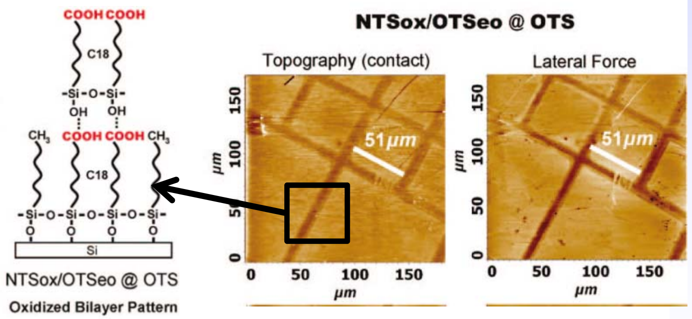
Stamp



Oxidation process



Replica pattern



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

Nanolitografía de oxidación local

oxidation Scanning Probe Lithography (o-SPL)

Masks	**Máscaras**
Templates	**Moldes**
Dilectric barriers	**Barreras Túnel (dieléctricos)**