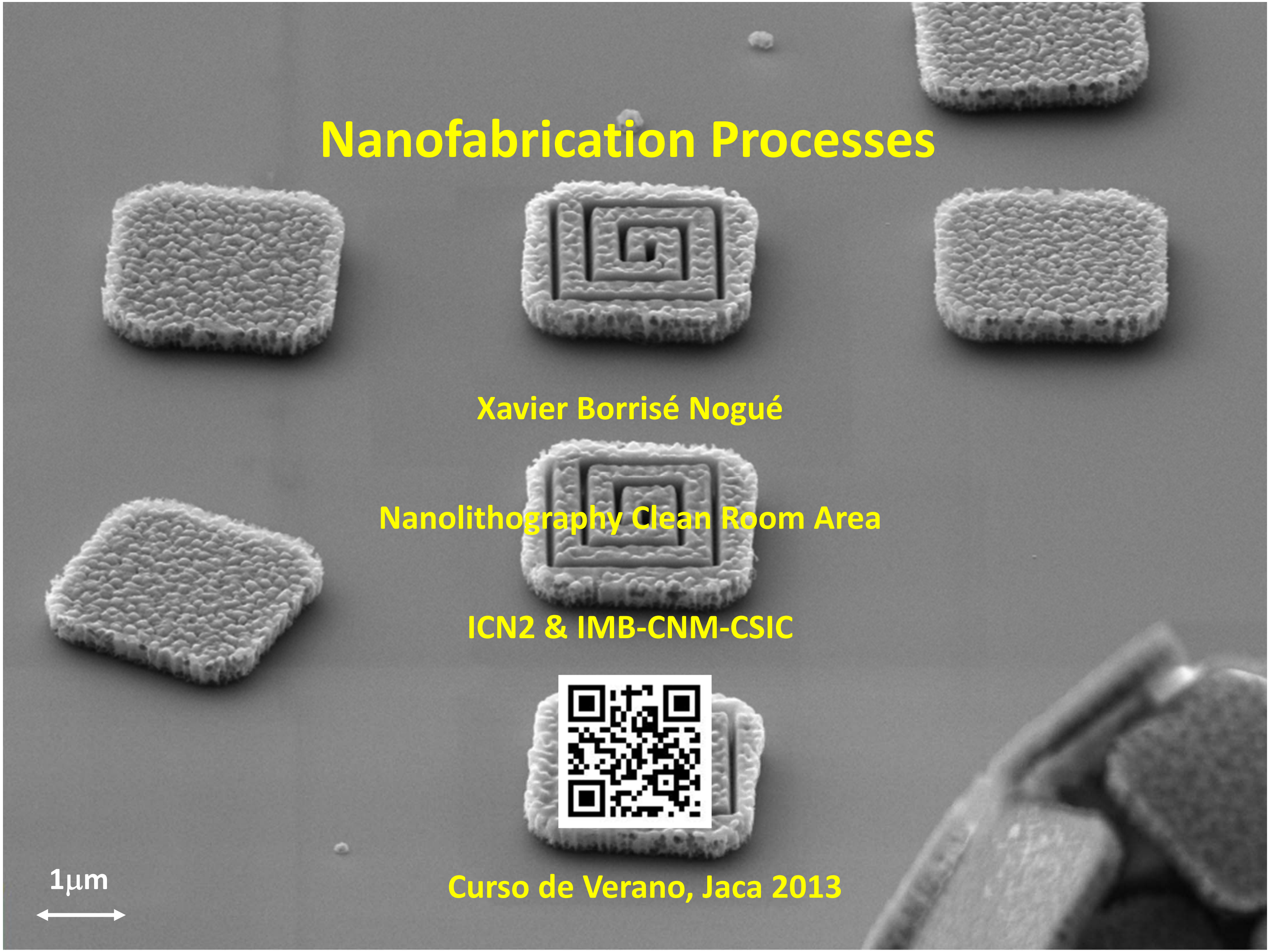

Nanofabrication Processes
Xavier Borrisé Nogué
Nanolithography Clean Room Area
ICN2 & IMB-CNM-CSIC
Curso de Verano, Jaca 2013
1μm

Outline

Intro to Clean-Room Processing

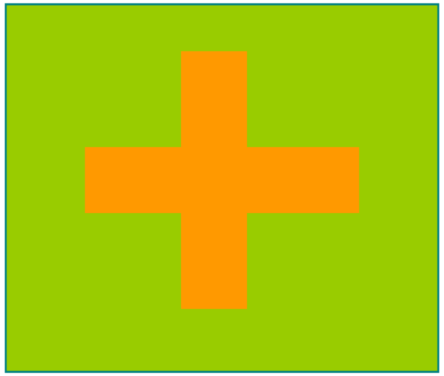
Electron Beam Lithography (EBL)

Focused Ion Beam Patterning (FIB)

NanoImprint Lithography (NIL)

Ending

The Basic Nanofabrication Process

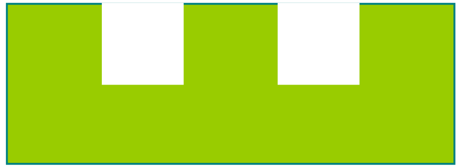


LITHOGRAPHY

Features definition

DEPOSITION

Metalization
Thermal Processes, CVDs,
Implantation,…



SELECTIVE ETCHING

Wet & Dry Etching

Pattern Transfer

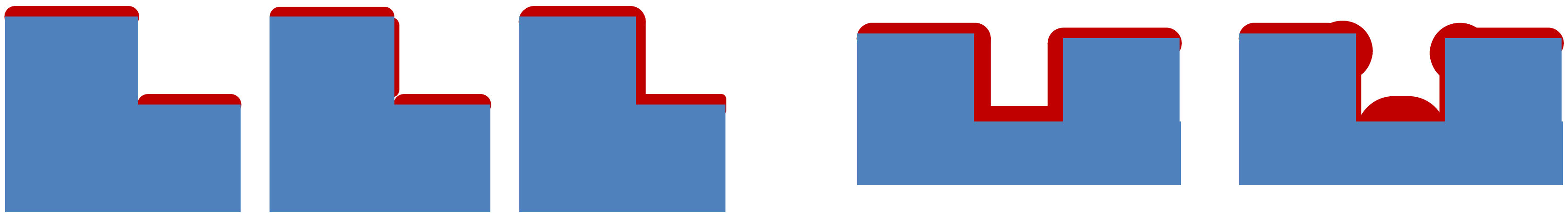
Metalization

Metalization is used for different purposes:

- Surface metal coating (as for creating contacts and metal tracks)

- Metal patterns defined by litography
  - Mask Fabrication
  - Metal features.

Quality of the coating

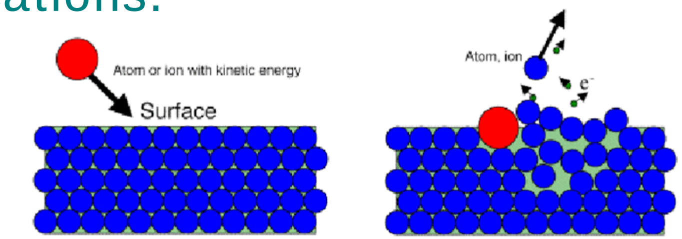


"Step-like coating" Conformal coating

Metalization: Evaporation or Sputtering?

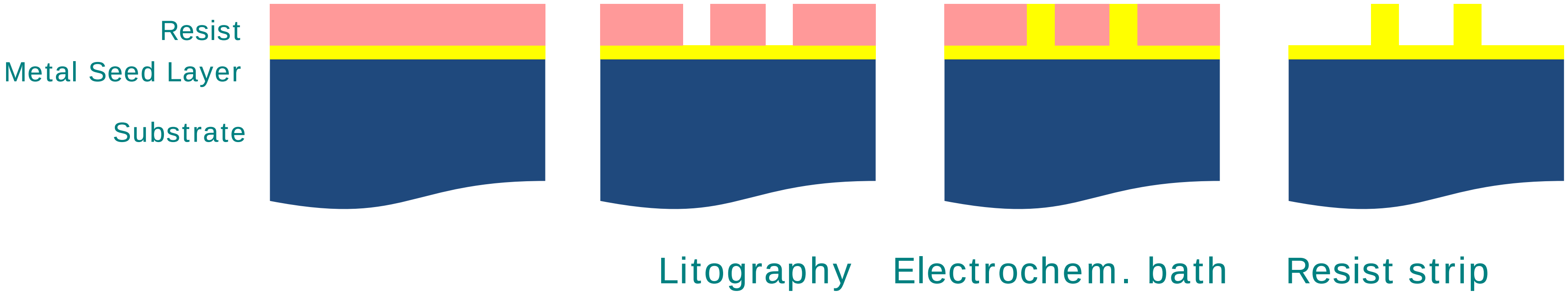
Evaporation: In a high-vacuum chamber, a metalic target creates a cloud of atoms directed to the sample (either by thermal or electron beam heating). Due to the high vacuum level and the geometry of the chamber, the mean-free path of the atoms is large, achieving a high directional coating (non-conformal and step-like coating) which make it ideal for lift-off applications.

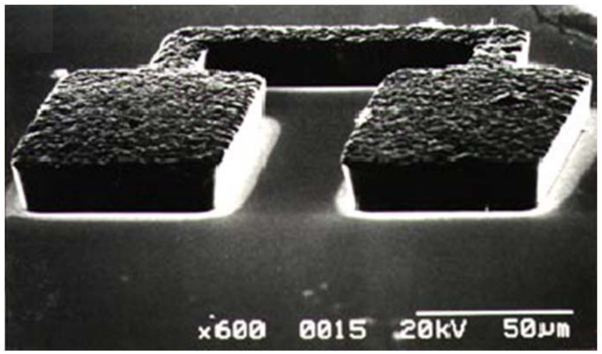
Sputtering: In a low-pressure chamber a plasma is created, which generates the ion sputtering of the metallic target, directed to the sample by voltage difference. In this case the metal atoms suffer from a lot of collisions while crossing the plasma in the way to the sample. The coating is the highly conformal, good for contacts, but less for lift-off applications.



Metalization: to create a new structure

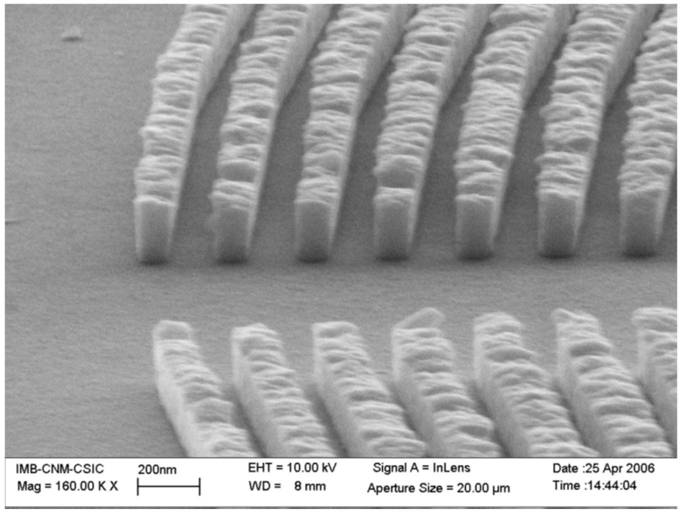
Electroplatting: Selective Depositon of a metal in an electrochemical bath from a seed layer (metal)





Used in µ-electroncis to create vias/contacts

NANO →



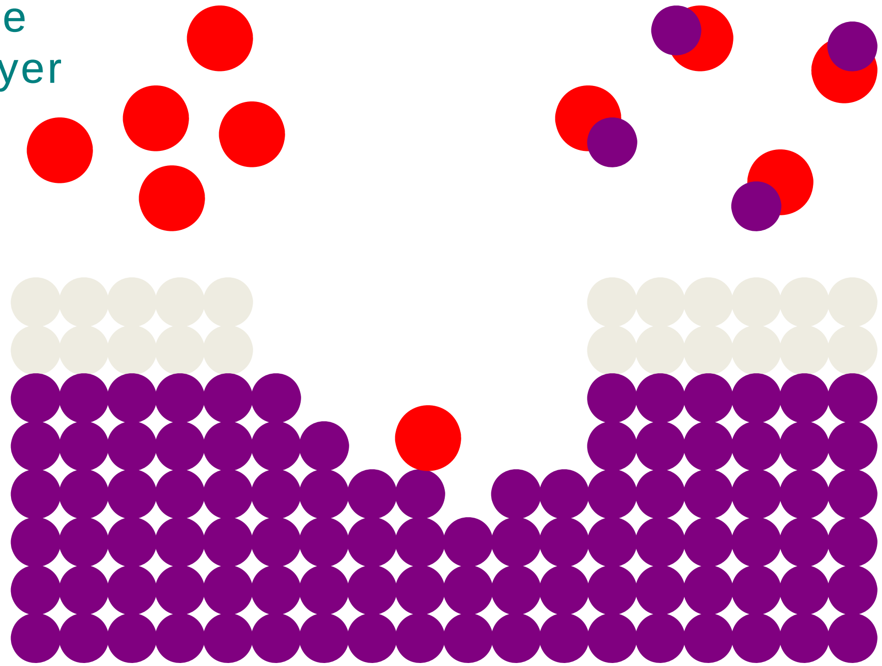
Transfering features: Etching

Definition: Selective Partial or Complete layer removal

Reactive: Molecule able to etch the layer

Product: resulting molecule from the process

Mask



Layer to etch

Etching Reaction: interaction between the reactive and the layer with resulting products and the etched layer.

Transfering features: Etching

Etching Process

Pure Physic — RIE — Pure Chemical

Pure Physic
- Ion Bombardment
- High Anisotropy
- Low Selectivity

RIE: Dielectrics, Si, Metals

Pure Chemical
- Chemical Reaction
- Mainly Isotropic
- High Selectivity

What are they used for?

Etching Layer
- Total
- Partial

Surface Conditioning
- Surface layer removal
- Cleaning procedures

Wet etching

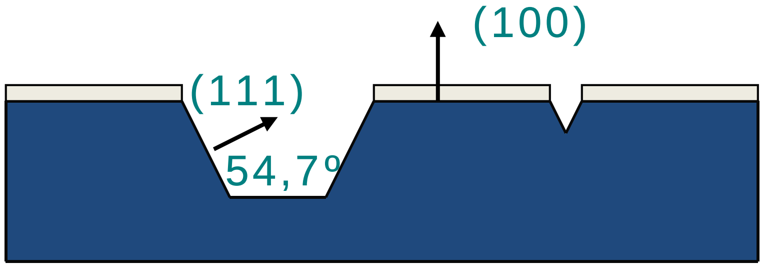
Cleaning
HF, IPA, Piranha, Acetone...

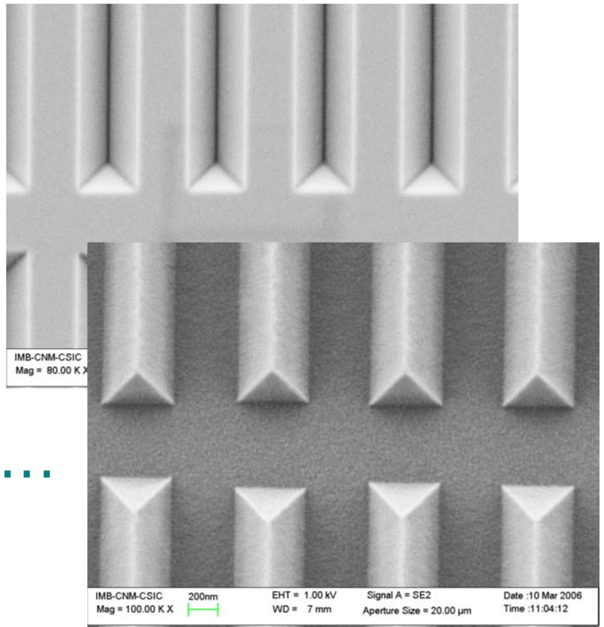
Silicon Etching
Si-etch, KOH, TMAH, EDP

Oxides and Si derivates (Si_3N_4)
SiO etch, HF, BFH, H_3PO_4...

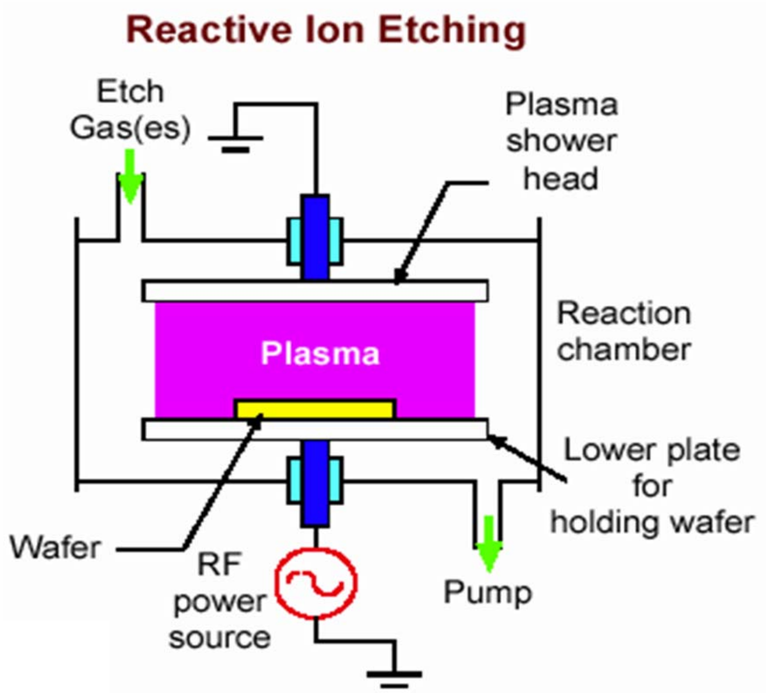
Etching Metals
Al-etch, Ti-etch, Cr-etch, Ni-etch, Au-etch...

Example: Si etch following planes (KOH, TMAH)



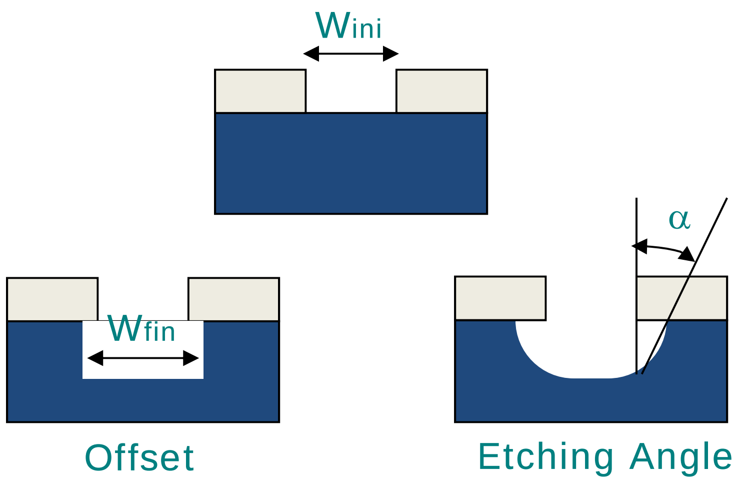


Dry Etching



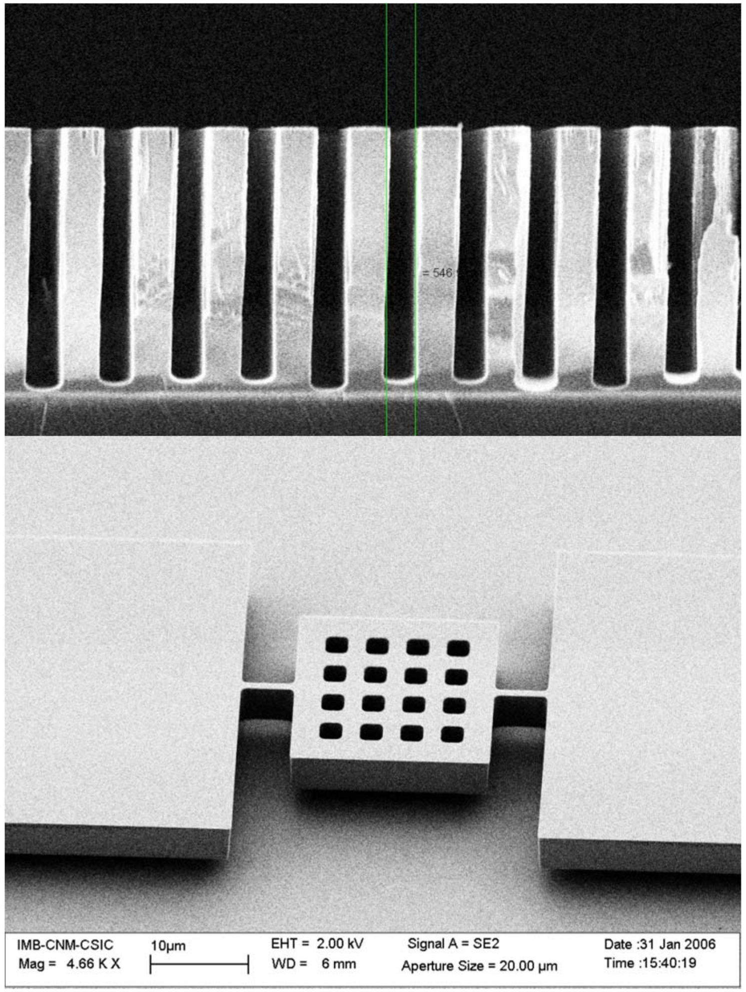
Important parameters to characterize

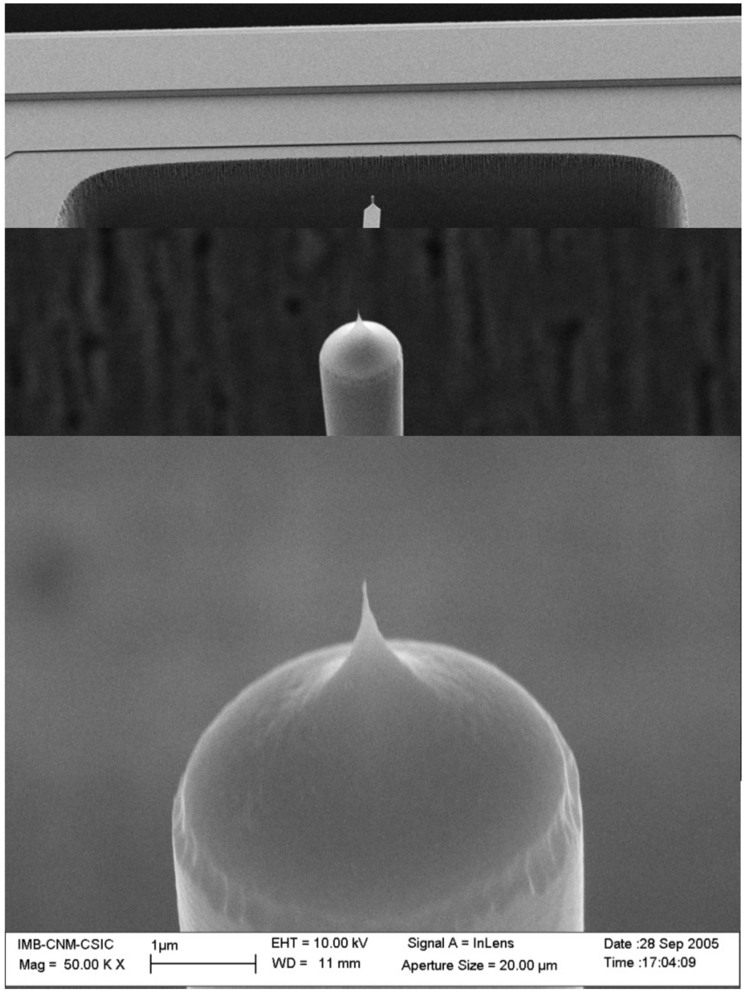
- Speed
- Selectivity
- Homogeneity
- Anisotropy



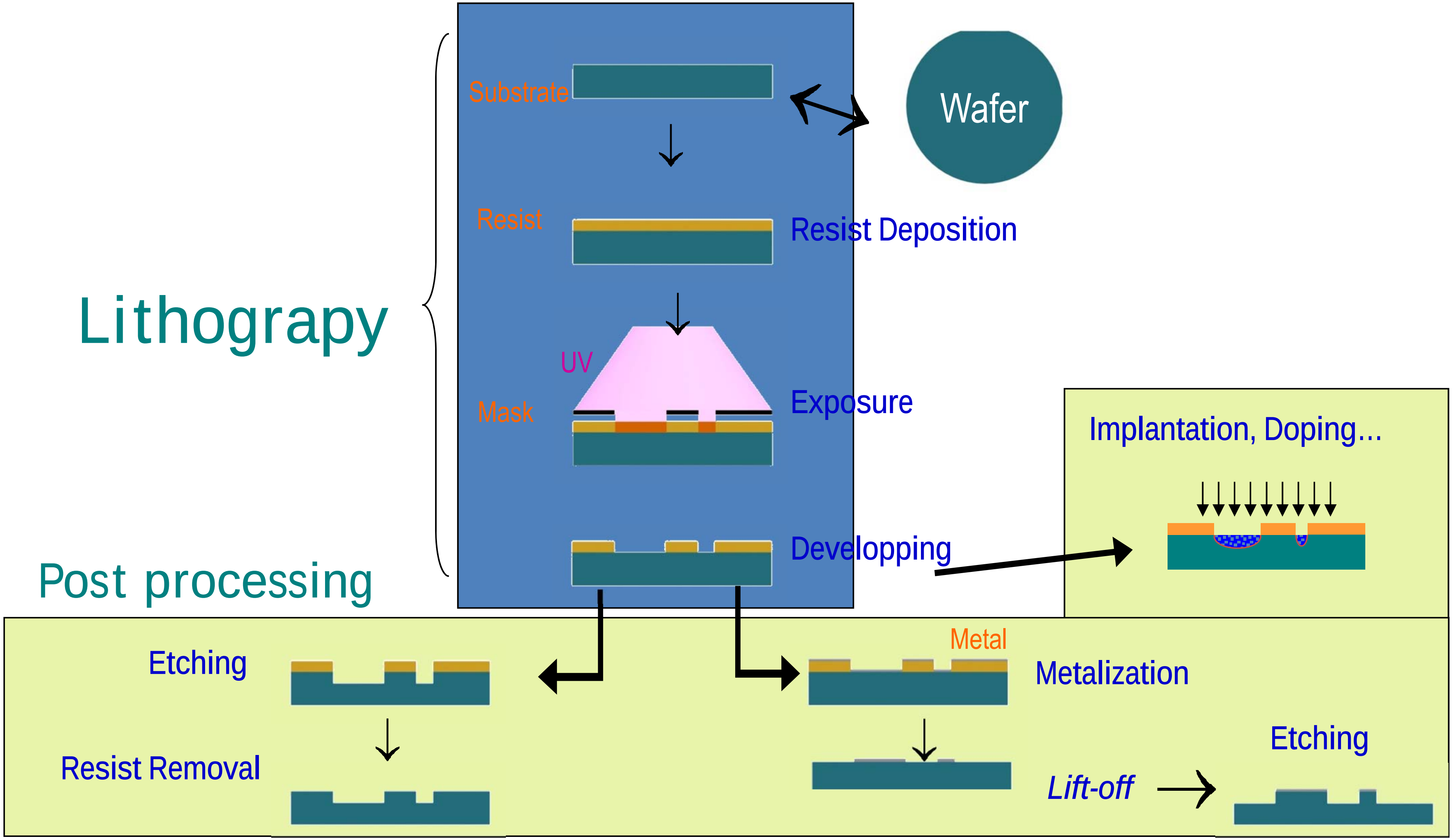
Si	CF_4, SF_6/O_2, Cl_2...
SiO_2	CHF_3, CF_4/CHF_3...
Si_3N_4	CHF_3/CF_4, SF_6/H_2...
Orgànics	O_2, SF_6/O_2...
Al	BCl_3, $BCl_3/Cl_2/N_2$...

Dry Etching: Examples



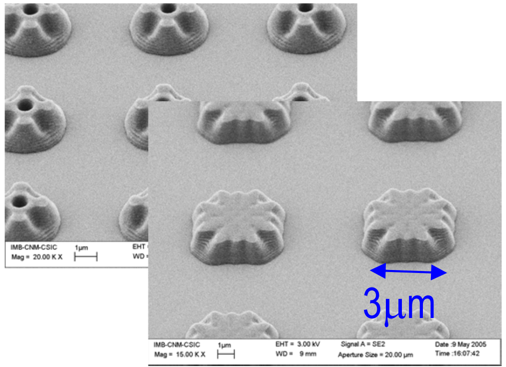


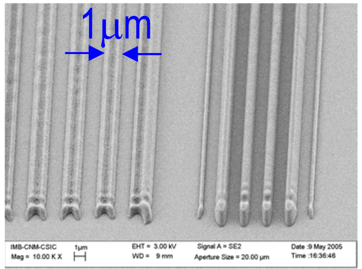
Summary: The Nanofabrication Process



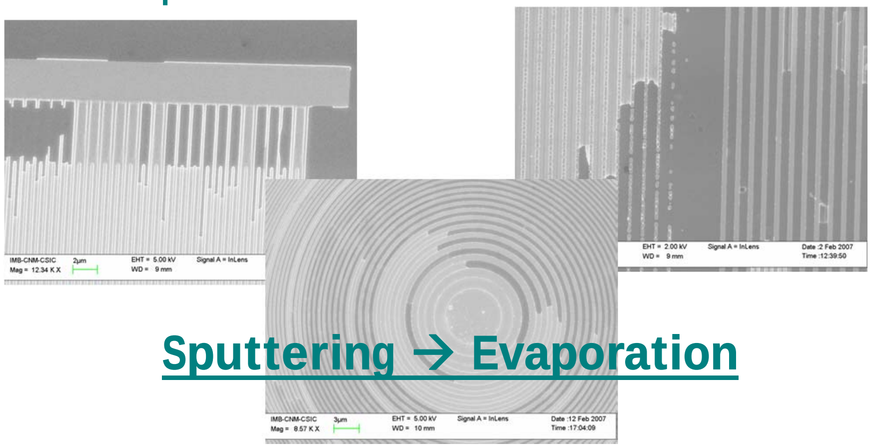
When reducing dimensions...

Lithography: difraction effects





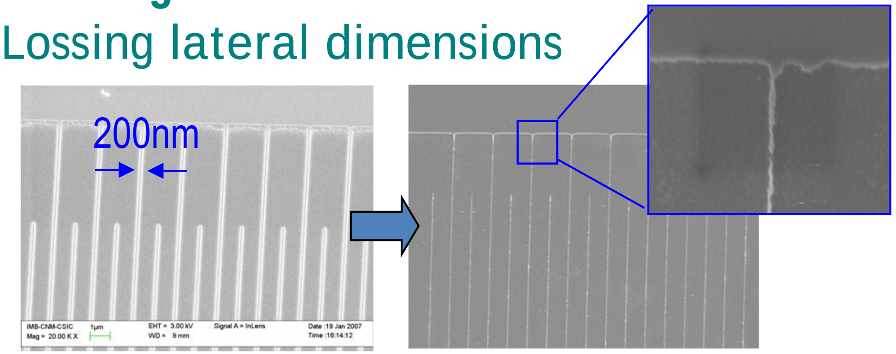
Lift-off: problems in small and dense patterns.

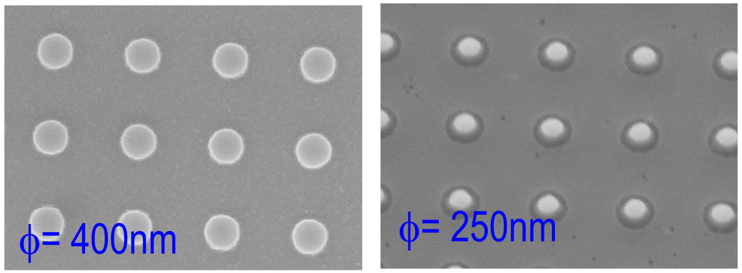


Sputtering → Evaporation

Etching features

Lossing lateral dimensions



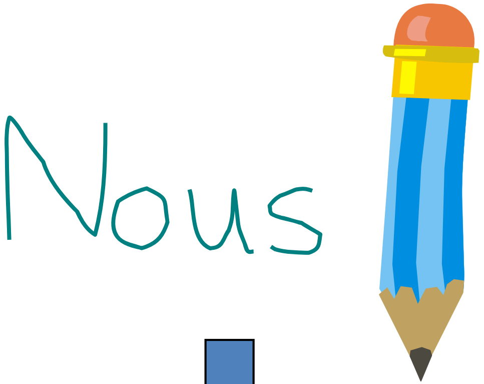


Finding "new recipes"

Lithography: Alternatives needed!!

To define features: Nanolithography

Creating new patterns



- Serial
- Flexible
- Slow

Pattern Replication

- Paralel
- Fast

Local Probe Interaction

STM, AFM, SNOM, ND…

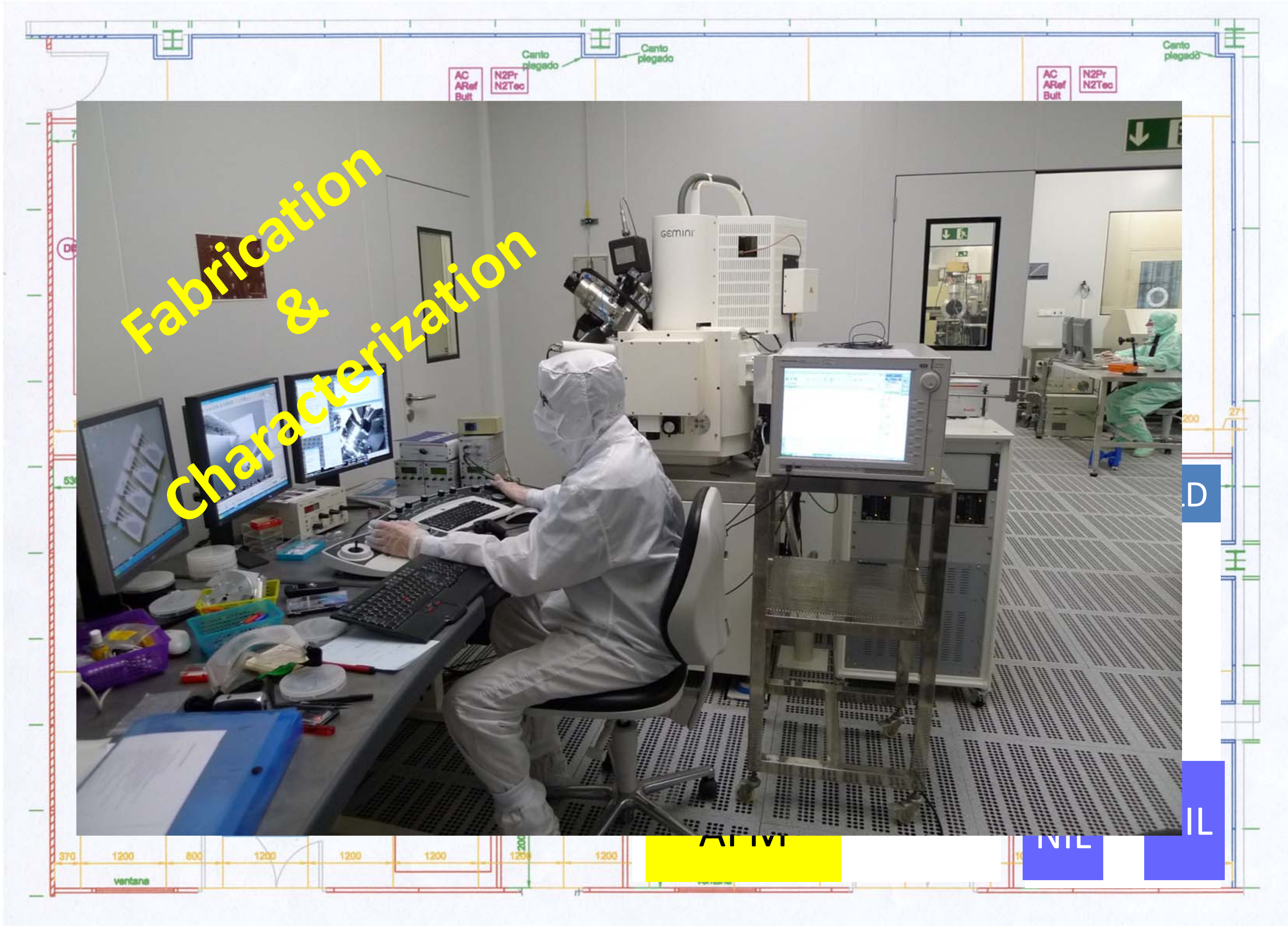
Reducing Wavelength

EBL, FIB, LaserLitho DUV, EUV, X-RAY…

Mold Replication

NIL, SFIL, uCP, Stencil…

The “Nano-Area”



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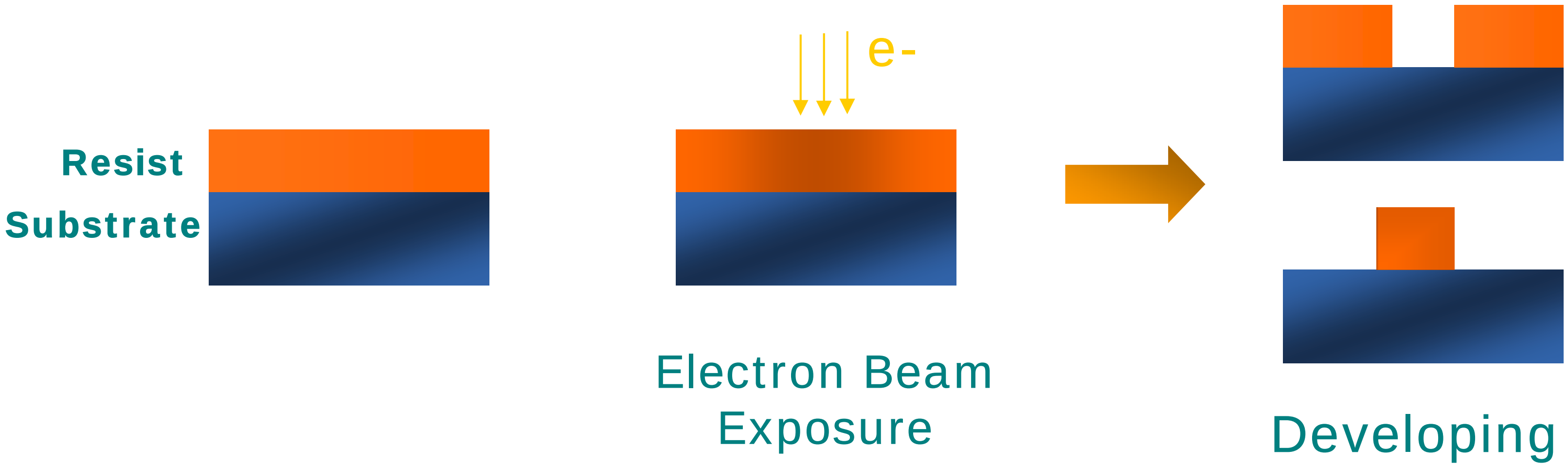
Electron Beam Lithography

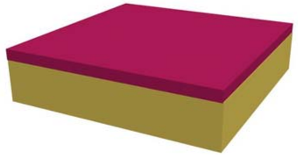
<u>Definition</u>: A **focused electron beam** is conducted by electromagnetic forces through a **material sensible** to electronic radiation, defining simple or complex 2D-patterns. The radiated material (or the complementary) will be **selectively eliminated** creating a contrast on the sample for pattern transfer.



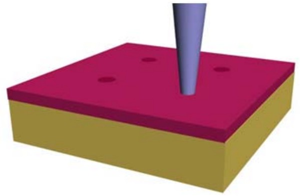
Electrons wavelength: $\lambda_e = \frac{1.226}{\sqrt{V}}(\text{nm})$ < 0,1Å!!

Complete Process

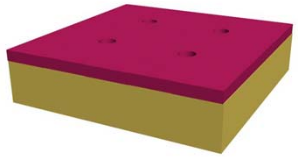
Raith 150TWO



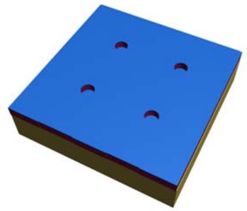
Spinning
100nm PMMA



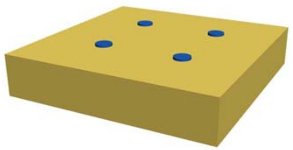
EBL Exposure



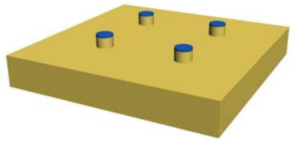
PMMA Developing



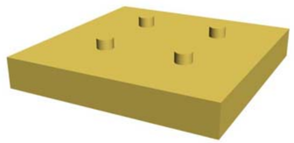
Al Evaporation



Lift-off PMMA

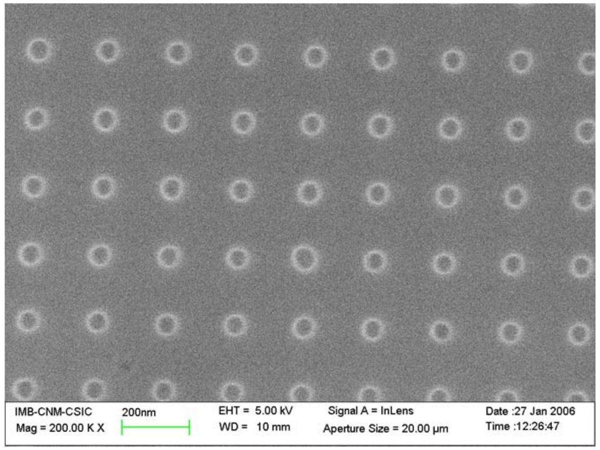


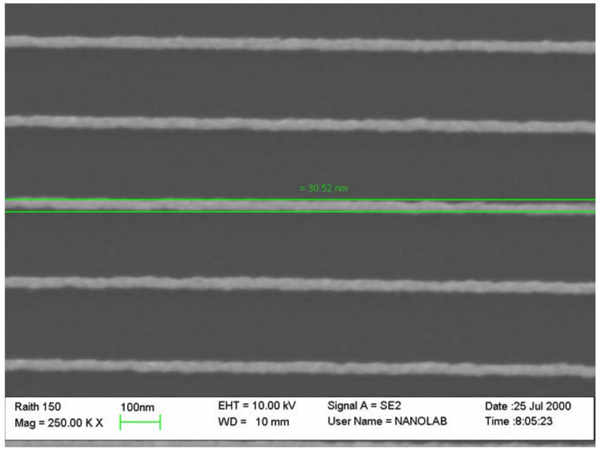
RIE SiO2

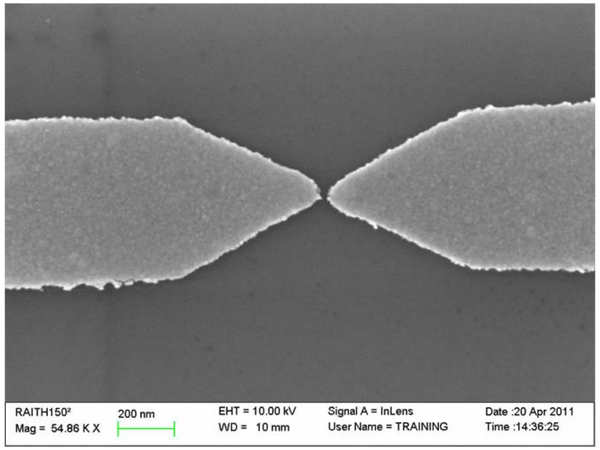


Al Etching

Some Examples

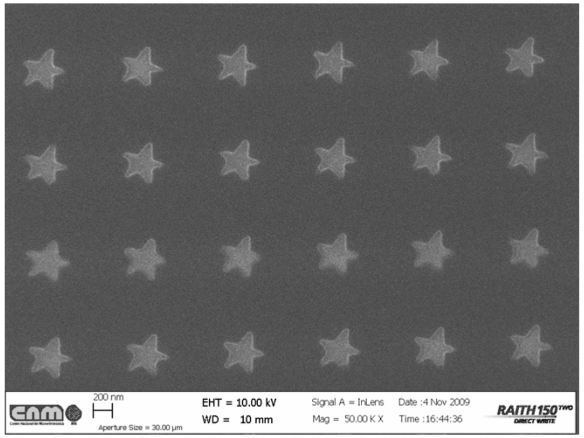




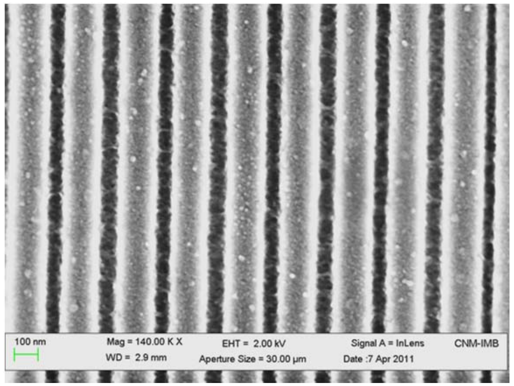


Positive Resist (PMMA)

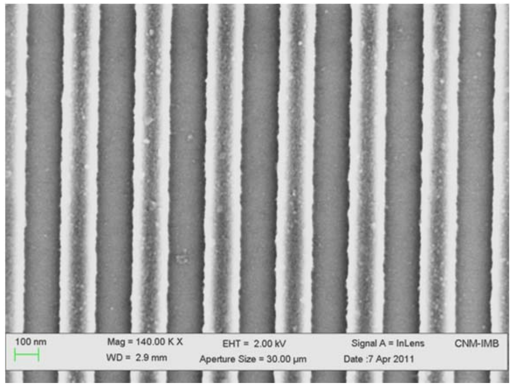
Negative Resist



155 nm line / 78 nm spacing

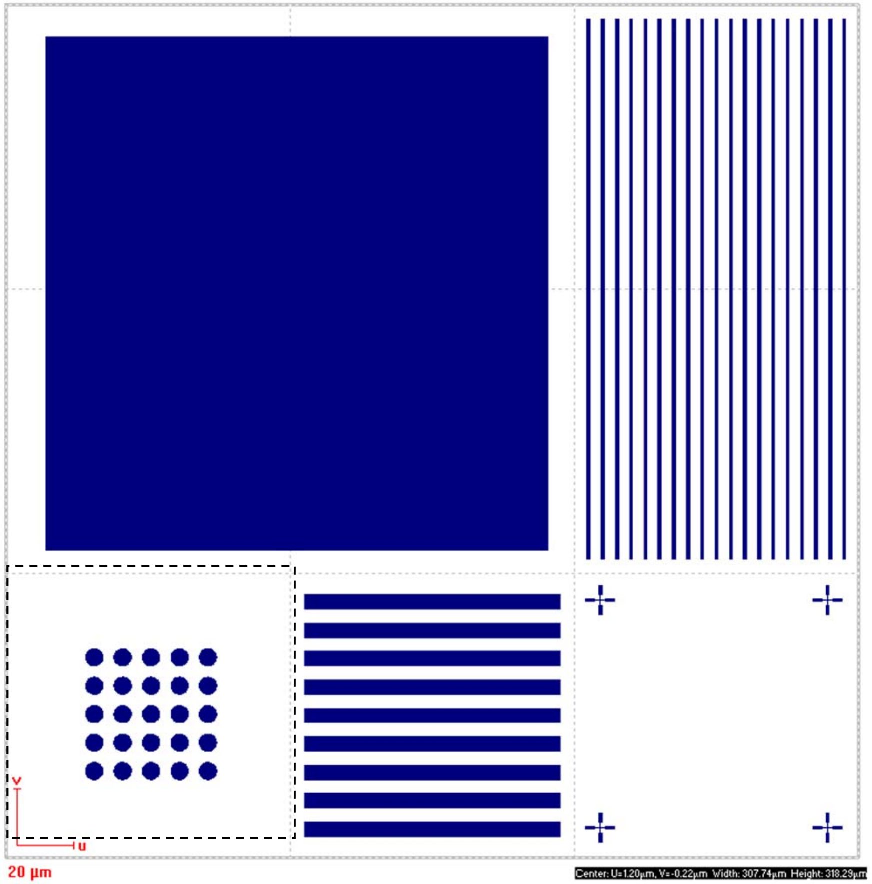


217 nm line / 108 nm spacing

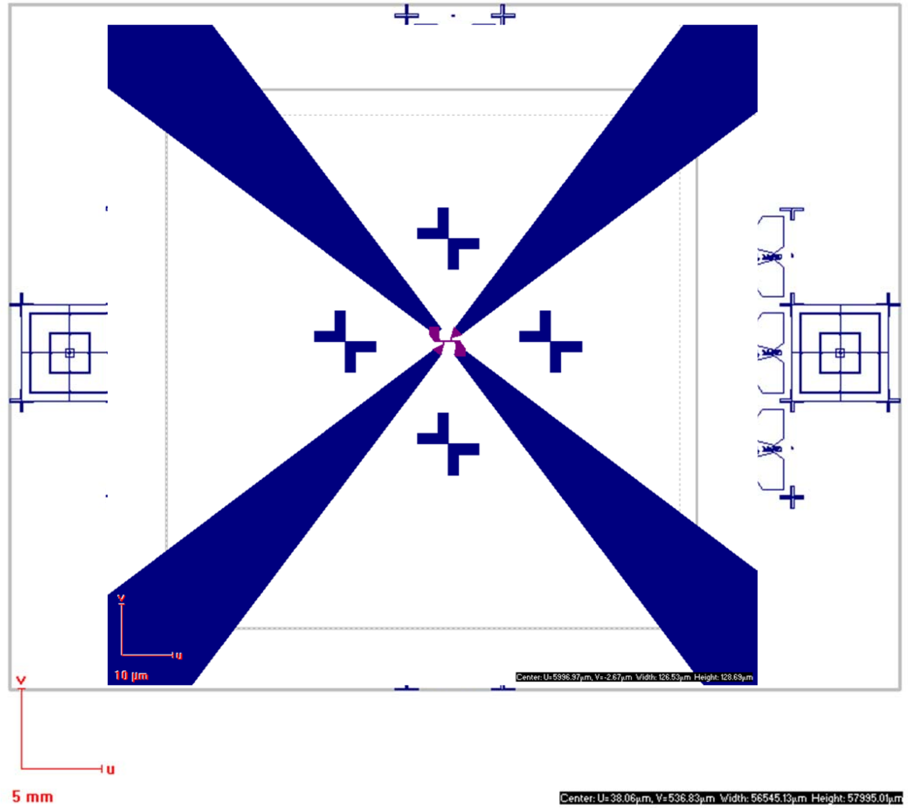


How do we do it?

gaussian beam, vector scan, fixed stage



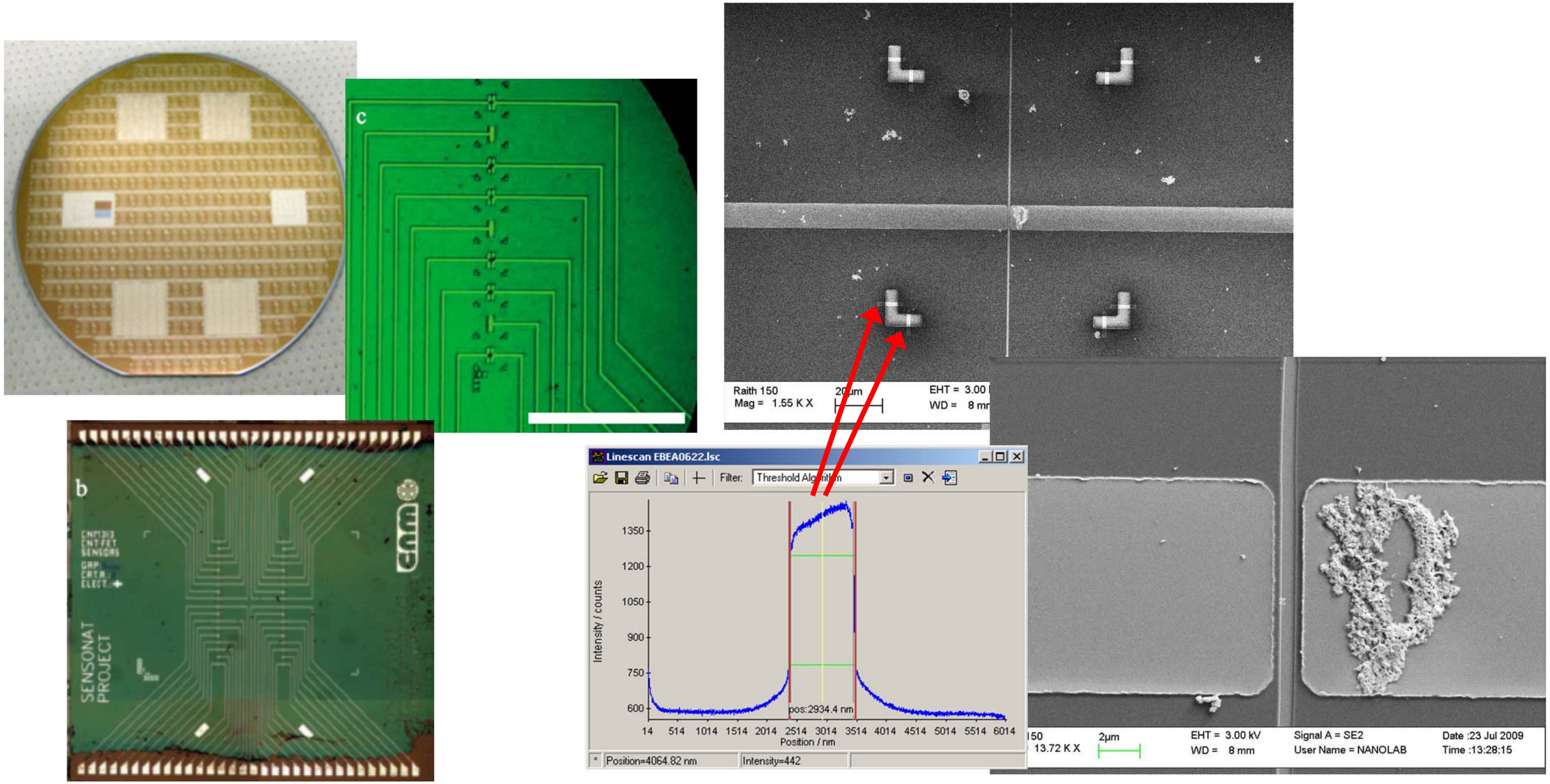
gdsII design



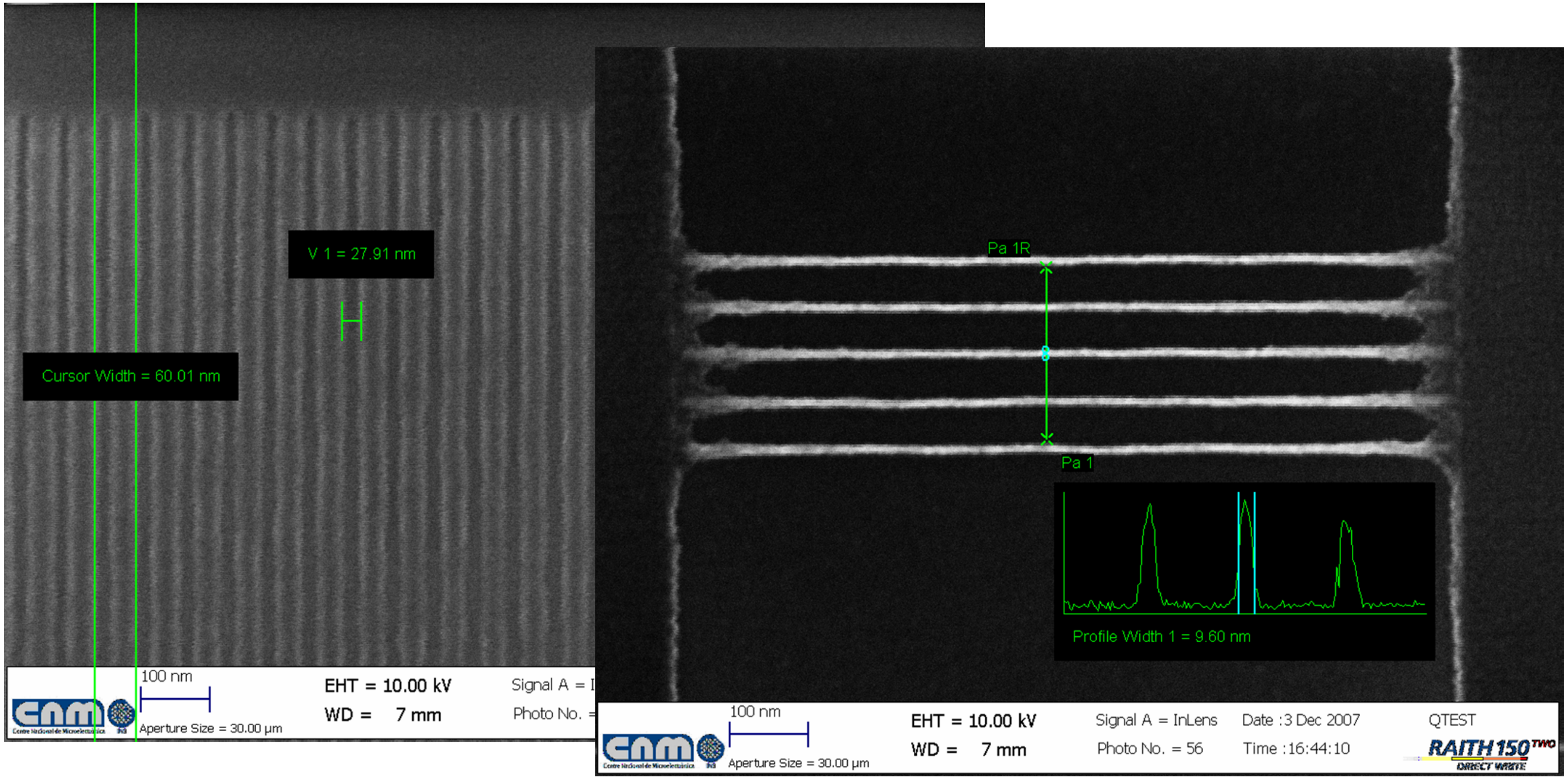
Mix & Match with OL

Overlay

Expose over an existing pattern: necessary a pre-aligment before exposing



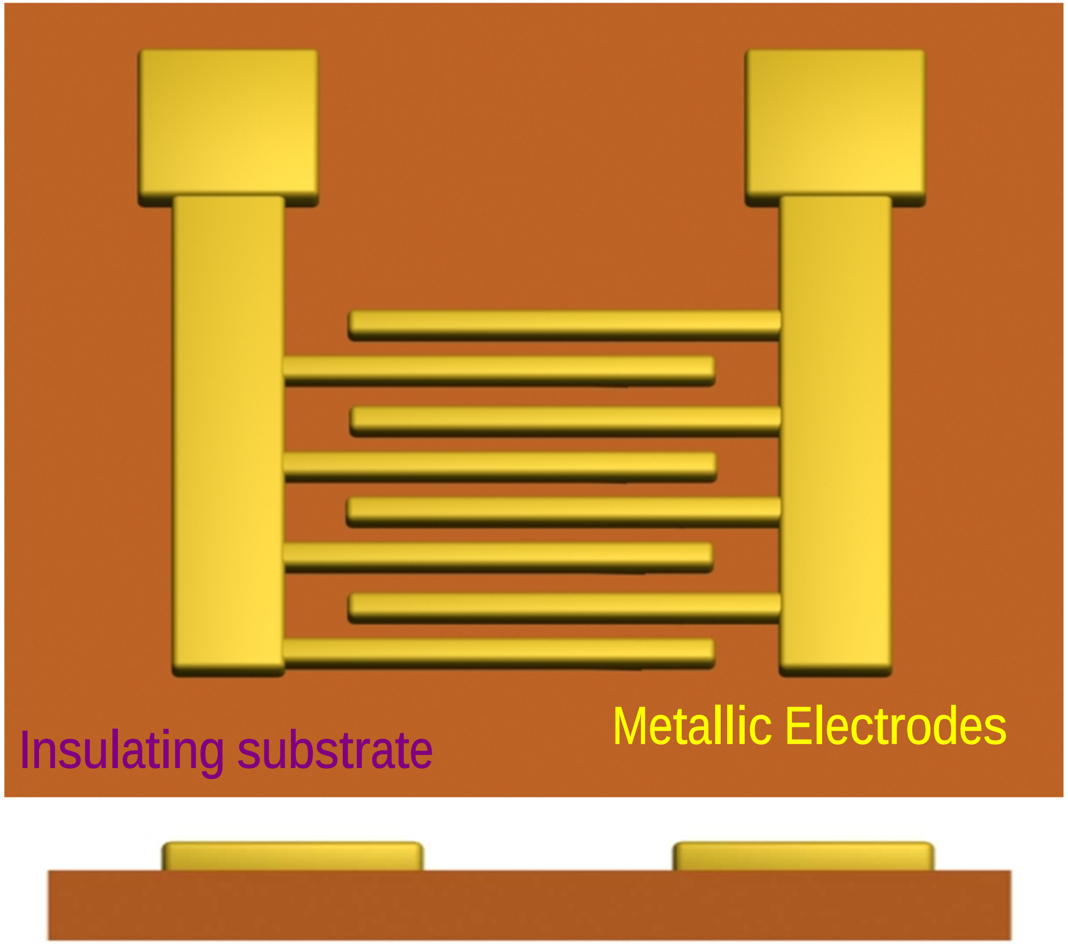
Raith 150TWO: High Resolution



Higher Column Performance (Current Stability and Beam Drift)

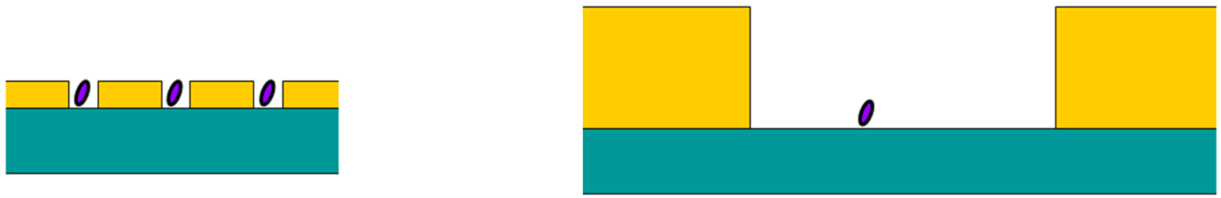
Interdigitated nanoelectrodes (IDEs)

Electrochemical sensors, biosensors, nanoparticle detection, etc



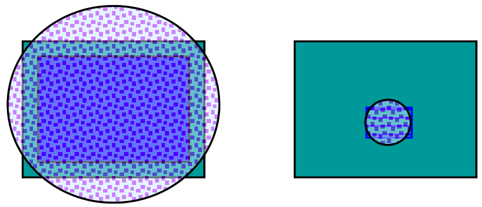
Why Nano-Electrodes?

- **Improved sensitivity** for electrodes/gap with size similar to the target.



- Faster **response.**

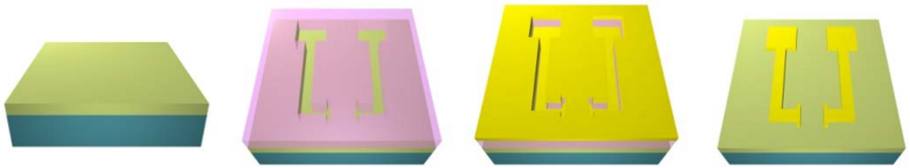
- **Less quantity of analyte.**



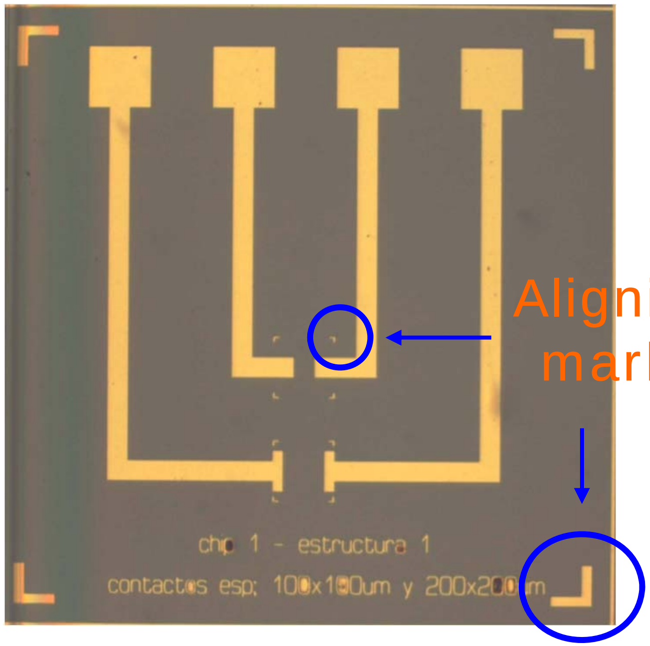
- Miniaturization -> Possibilities for **Integration**

Fabrication: **Optical Lithography + EBL**

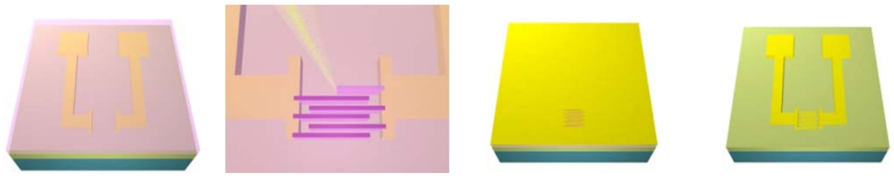
1. Contacting Pads



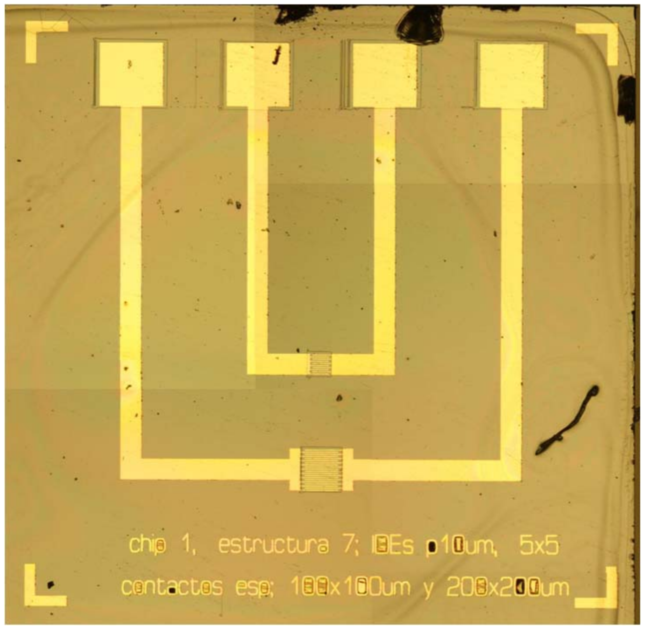
Optical Litography, metalization (gold), lift-off



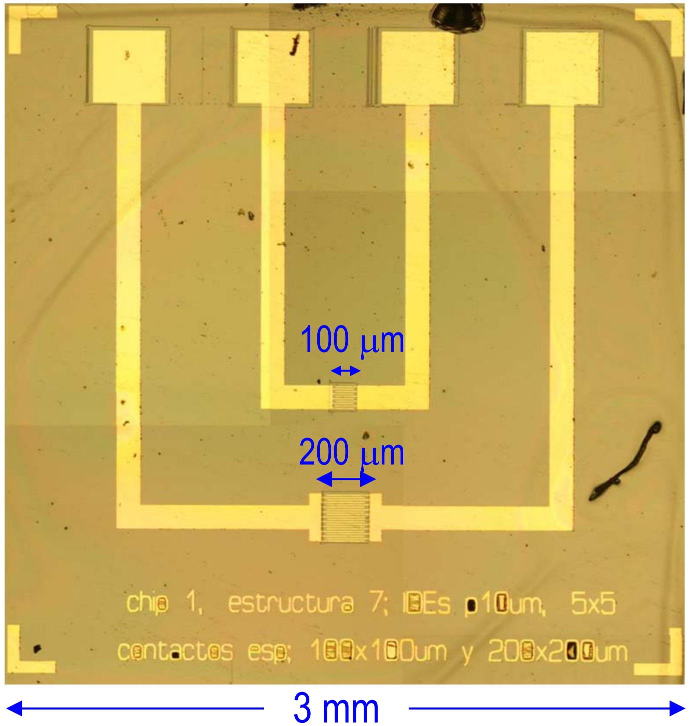
2. Digits

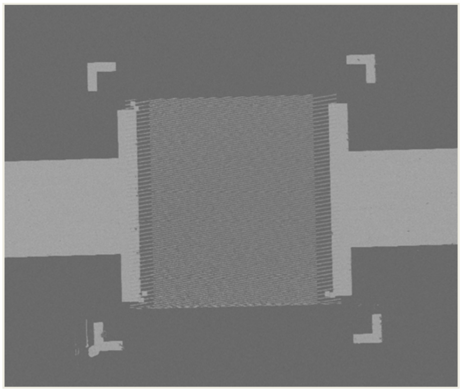


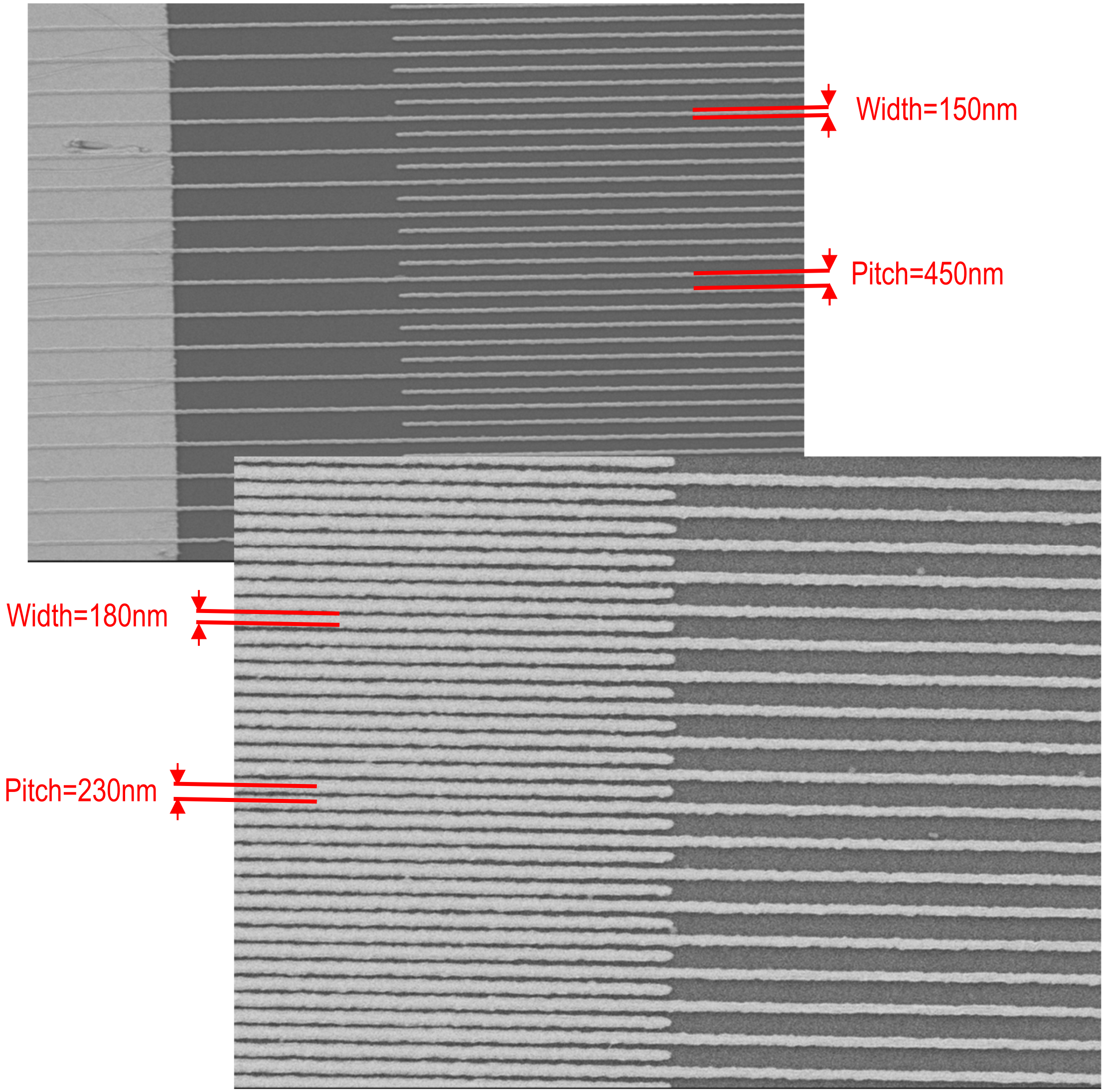
EBL, metallization (gold), lift-off

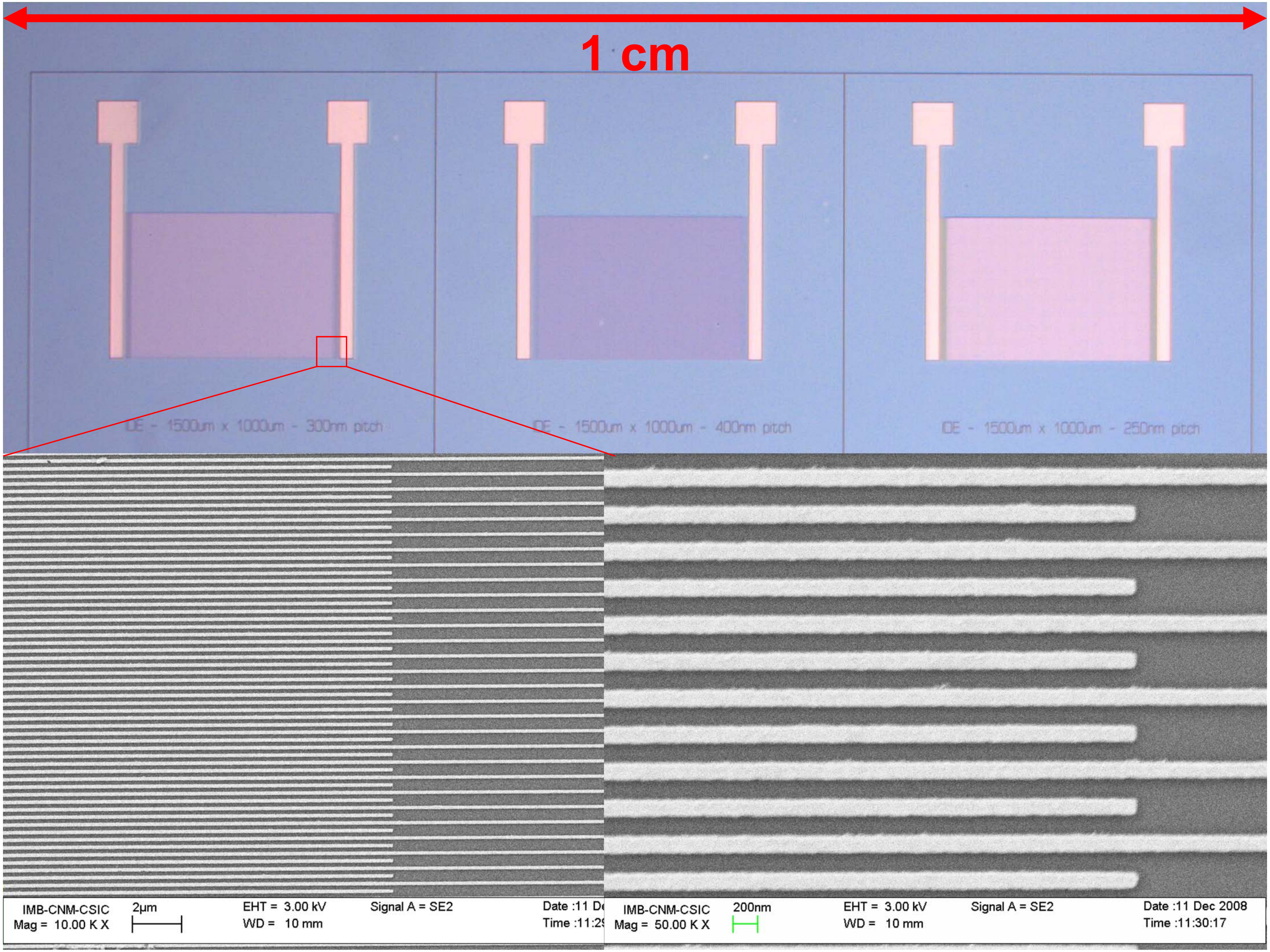


Devices


100 µm
200 µm
3 mm

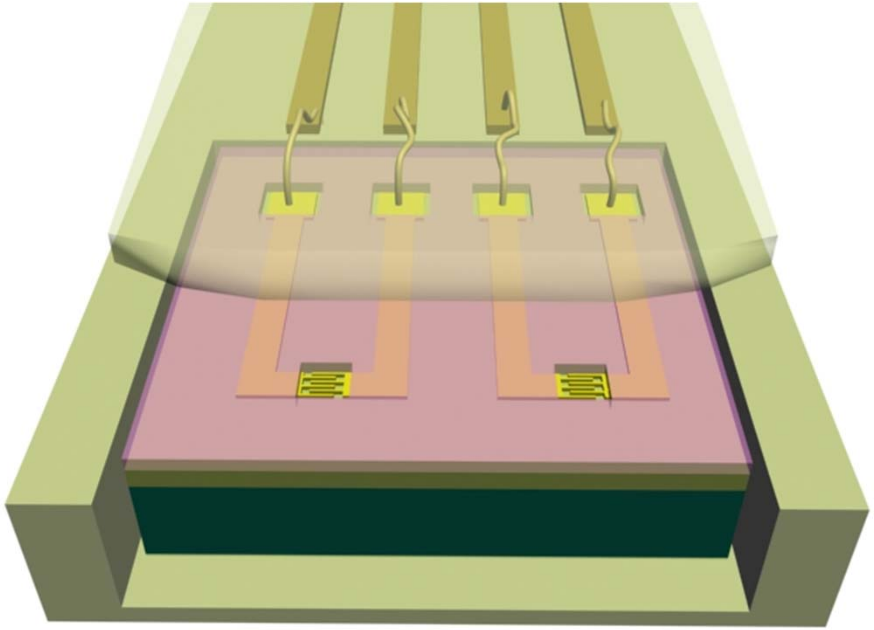


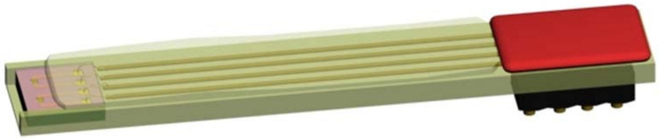

Width=150nm
Pitch=450nm
Width=180nm
Pitch=230nm

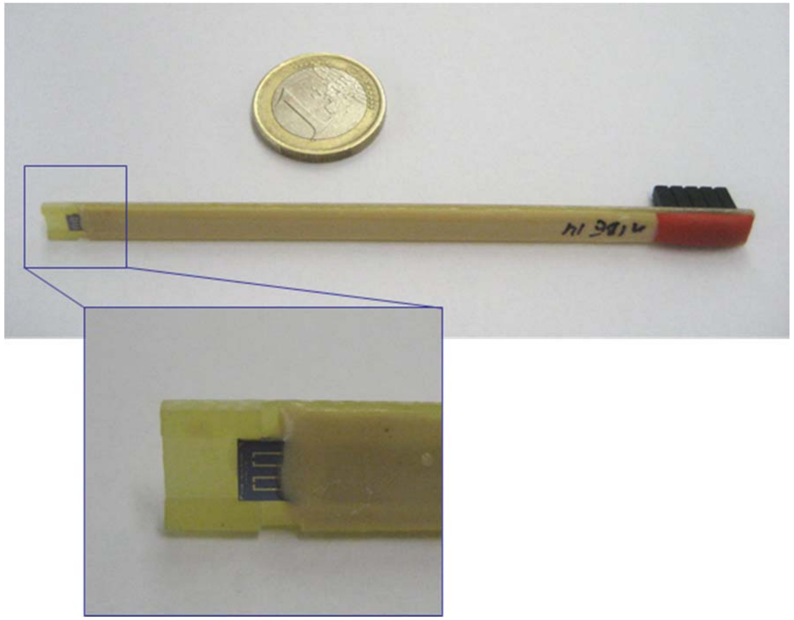

1 cm
IDE - 1500um x 1000um - 300nm pitch
IDE - 1500um x 1000um - 400nm pitch
IDE - 1500um x 1000um - 250nm pitch
IMB-CNM-CSIC
Mag = 10.00 K X
2µm
EHT = 3.00 kV
WD = 10 mm
Signal A = SE2
IMB-CNM-CSIC
Mag = 50.00 K X
200nm
EHT = 3.00 kV
WD = 10 mm
Signal A = SE2
Date :11 Dec 2008
Time :11:30:17

Packaging

The chip is passivated with PMMA, and only some areas left open.



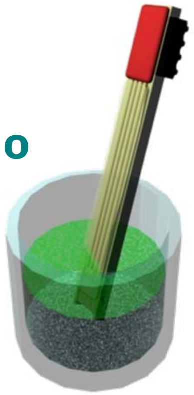




The chips are bounded and encapsulated to a **PCB strip**.

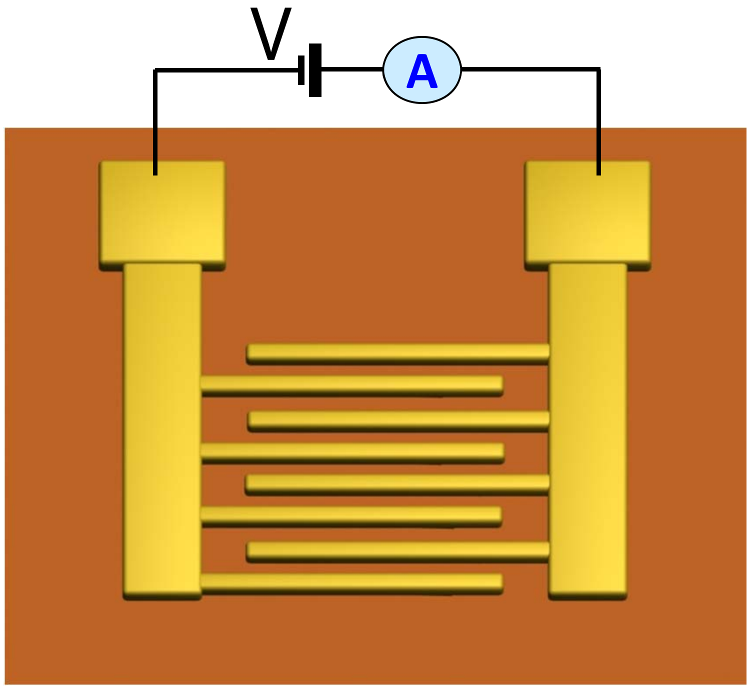
- Facilitates the **connection to equipments** for characterization.

- Enables working **in liquid media.**

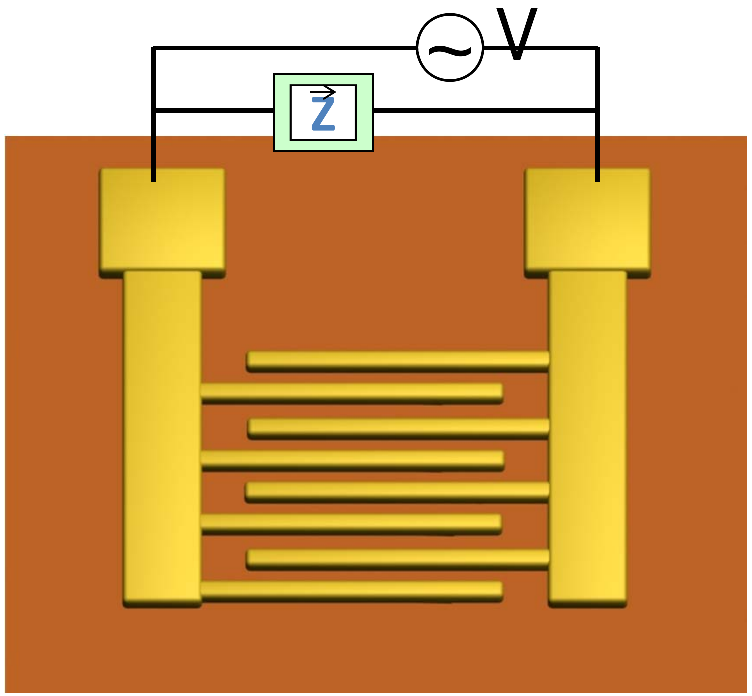


Device Performance

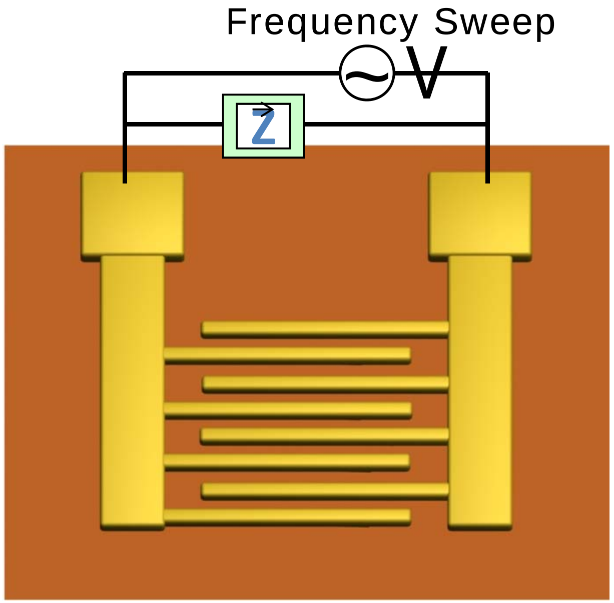
1.Voltamperometry: Electrochemical current coming from the redox reactions of the active species in the solution.

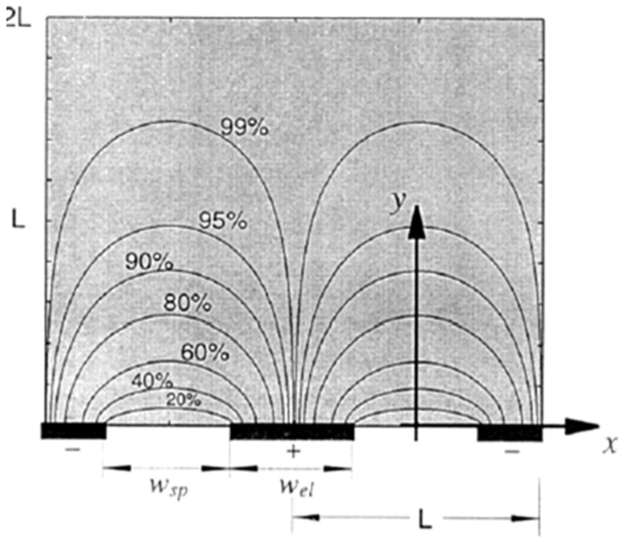


2. Impedance Spectroscopy: measurements of the impedance of the media as a function of the frequency. This is, the resisitivity and capacitance.



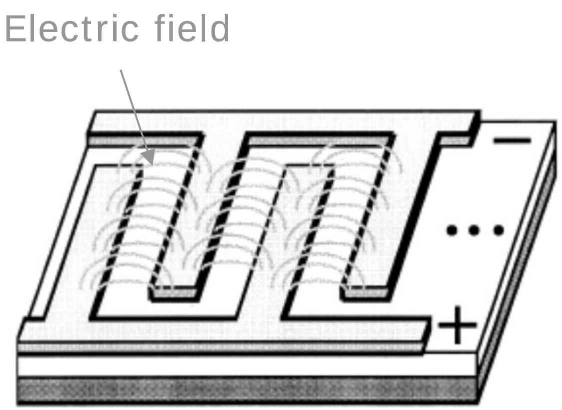
Impedance Spectroscopy





95% of the activity takes place below L

Nanoelectrodes (L<<)

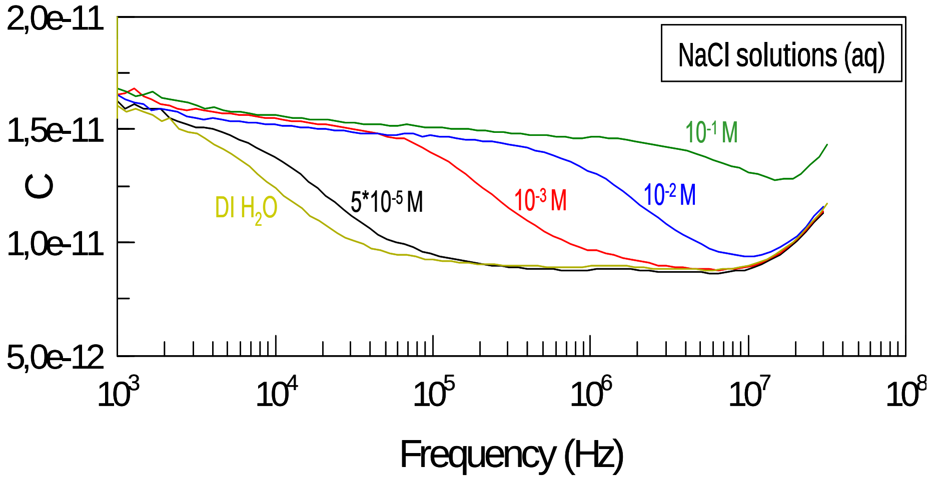


- Changes in the capacitance or resistivity of the media can be detected.

- The presence of elements in-between the digits can be detected.

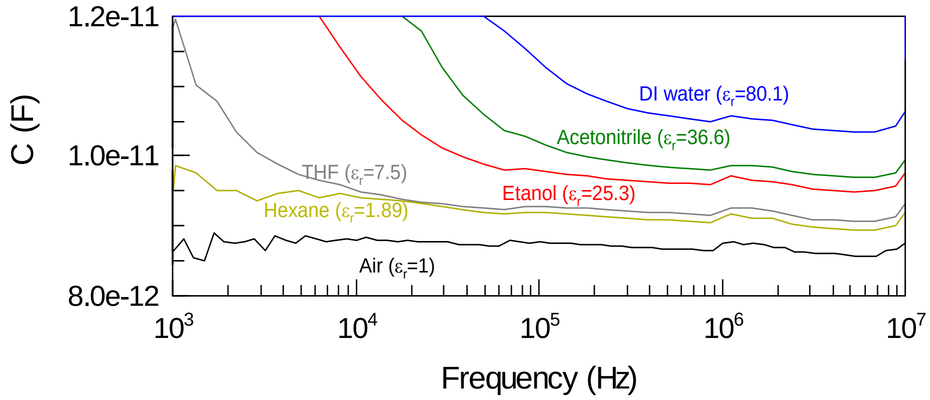
Validation of the Model

Dependence on the conductivity



Higher ionic concentration -> The double layer is still created for high frequencies.

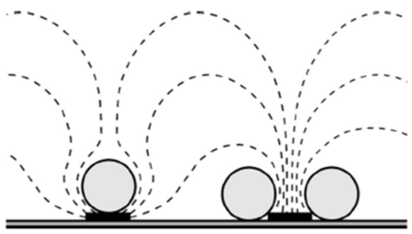
Dependence on the permittivity

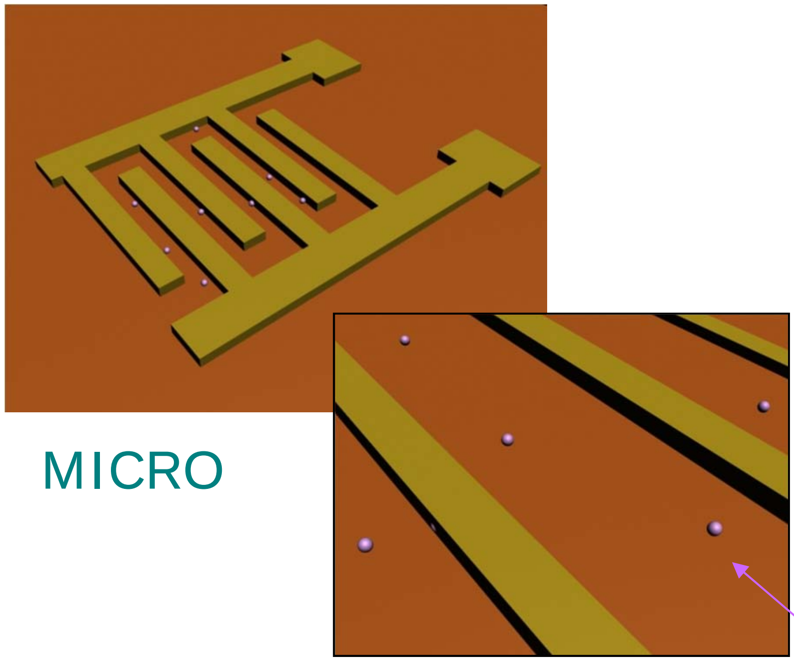


Non-polar liquids do not form double layer

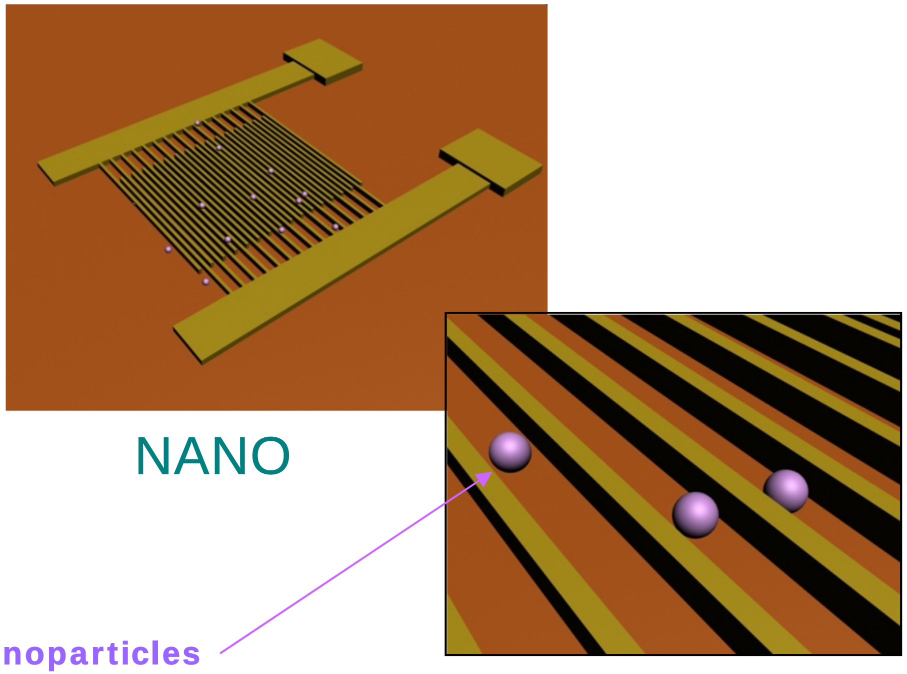
Nanoparticles

For the detection of nano particles, it is necessary that the gap in-between digits has a similar size: nanometric. The field lines are more affected -> increased sensitivity.



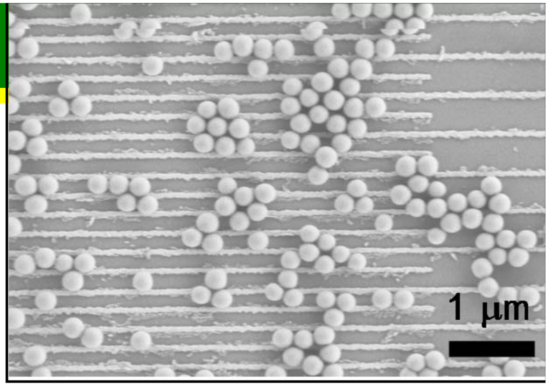


MICRO

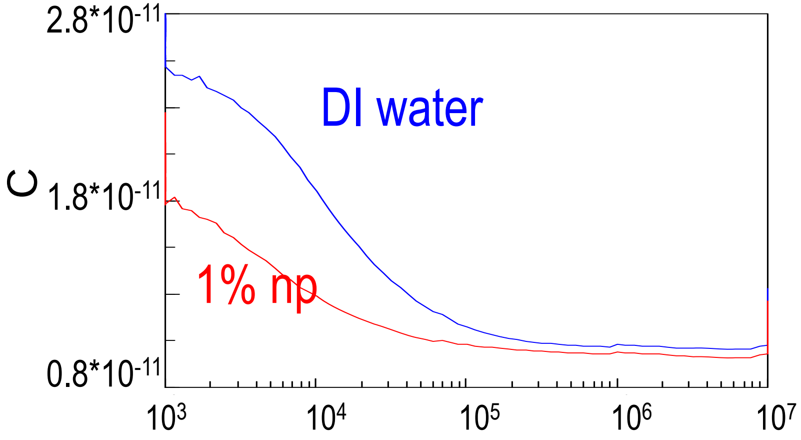


NANO

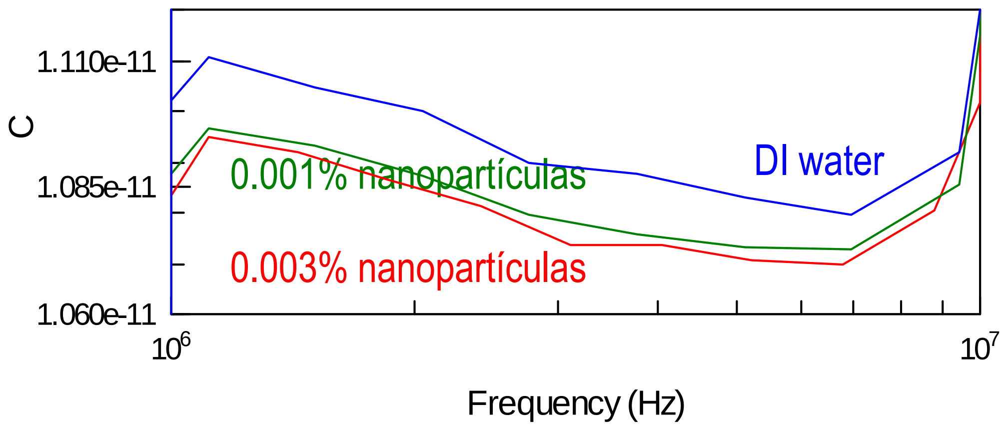
1. Detection of Insulating nanoparticles
(Latex, Silica, f=300nm)



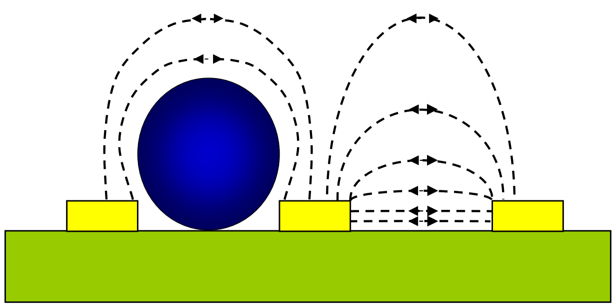
High concentration



Low concentrations

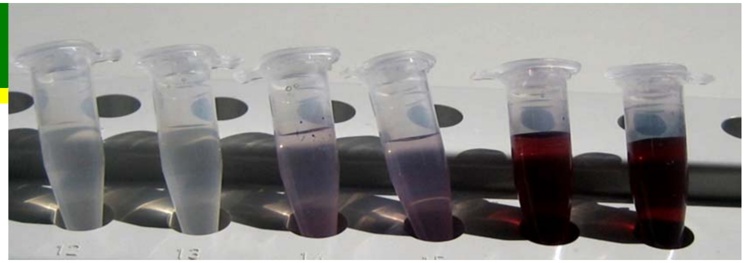


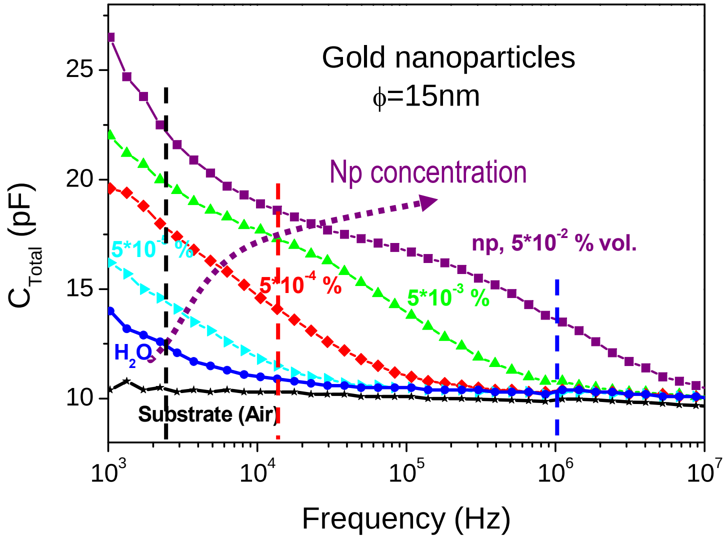
The inactive particles reduce the effective area of the sensor -> The capacitance measured decreases as a consequence.



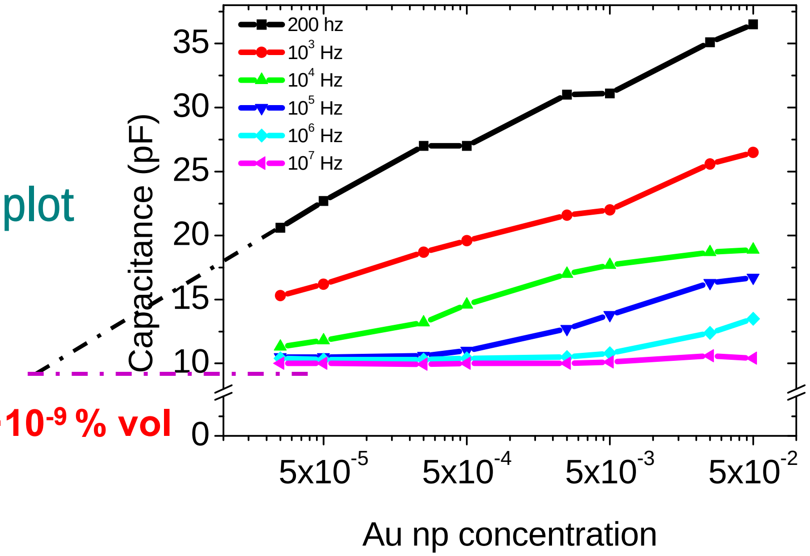
2. Quantification of conductive nanoparticles

(Gold, f = 15 nm)



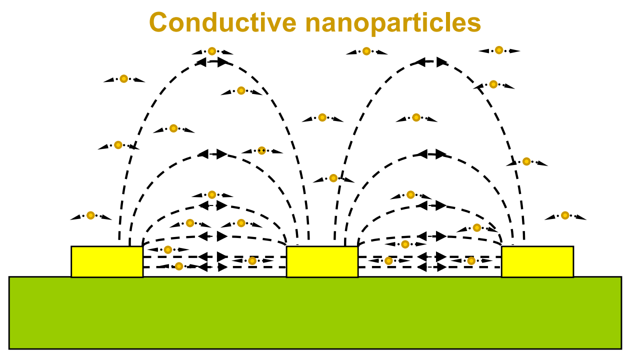


Calibration plot



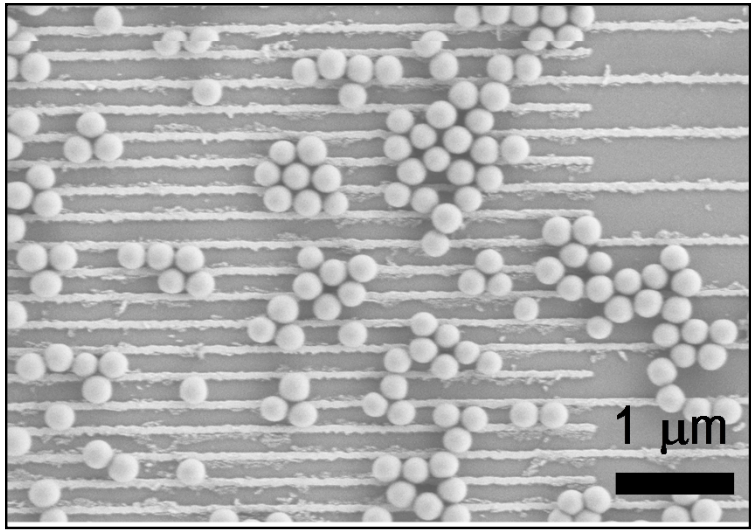
[np]$_{min}$ = 3.4·10^{-9} % vol

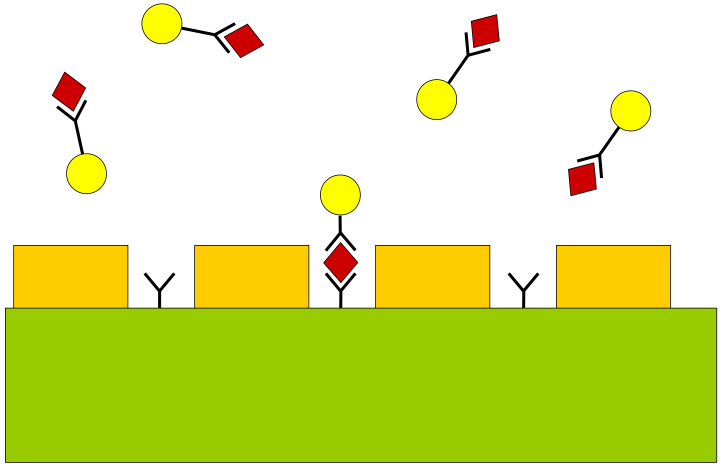
The gold nanoparticles are conductive and very small: they follow the a.c. electric field, thus, increasing the capacitance. The curves are similar to those measured for Na^+ Cl^- ions in aqueous solutions.



Functionalization of the nanoparticles

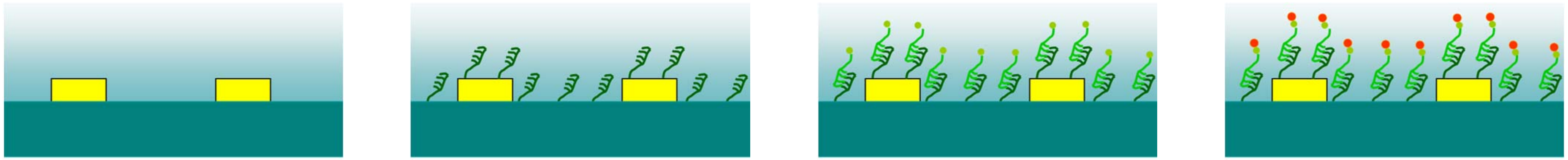
Specific recognition






Example:
Specific
detection of DNA

First essay: specificity of np adhesion

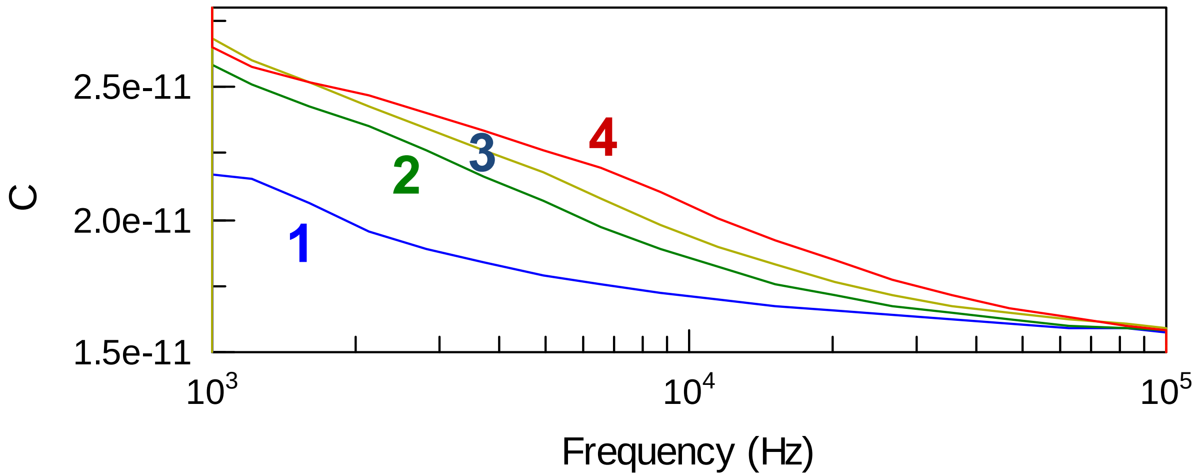


1. Blank
(bare electrode, in DI water)

2. Adsorption of DNA
(probe)

3. Hybridization
(Complementary DNA, with biotin)

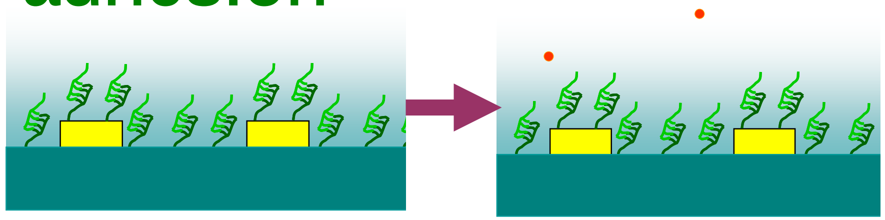
4. Gold nanoparticles
(Φ=15nm)

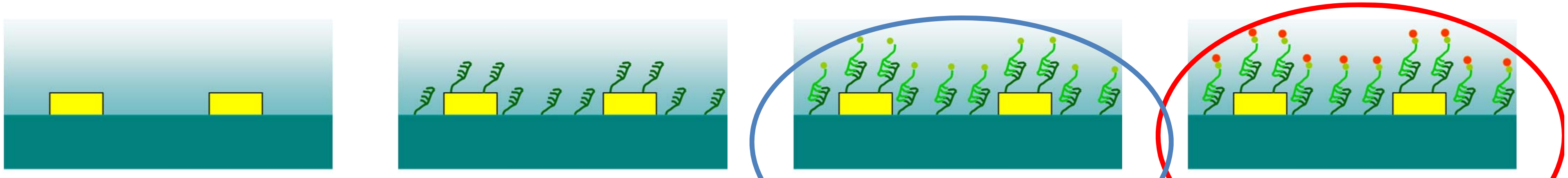


Charged DNA moves in-between the digits, increasing the total capacitance of the system.

First essay: specificity of np adhesion

Negative control





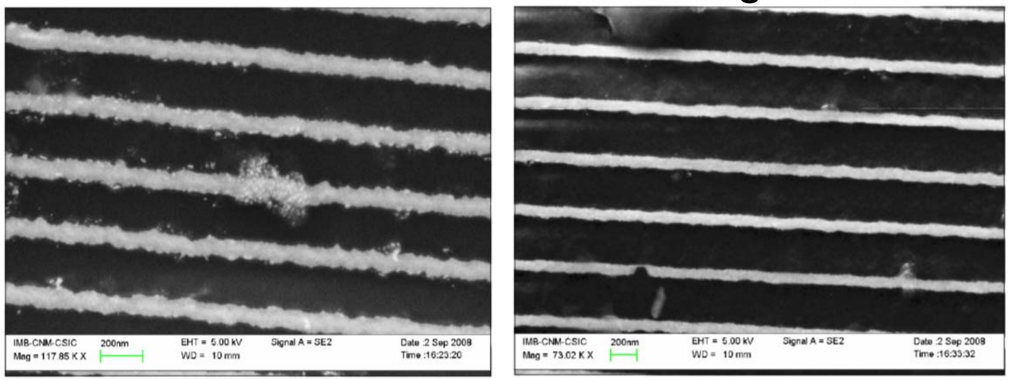
1. Blank
(bare electrode, in DI water)

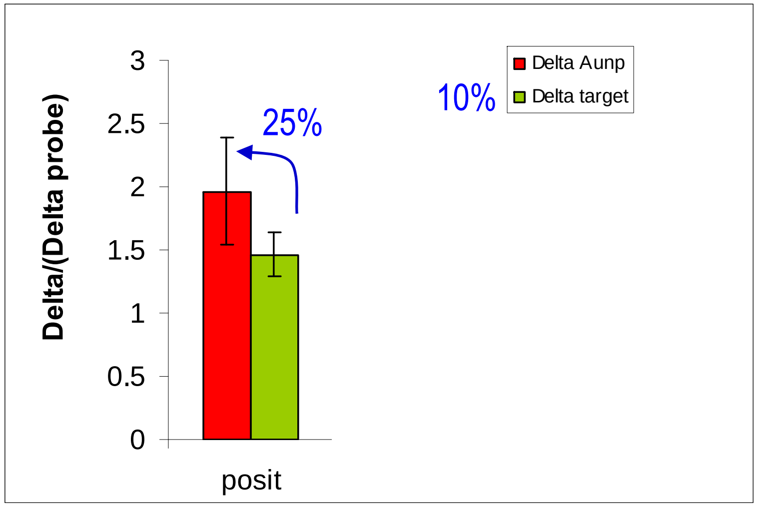
2. Adsorption of DNA
(probe)

3. Hybridization
(Complementary DNA, with biotin)

4. Gold nanoparticles
(Φ=15nm)

Positive Negative





Detection of mutant gene of BRCA1

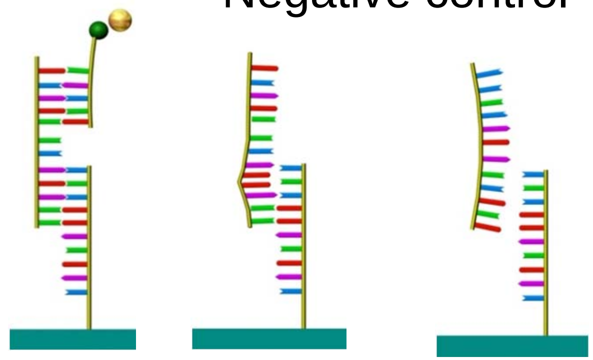
Wild gene

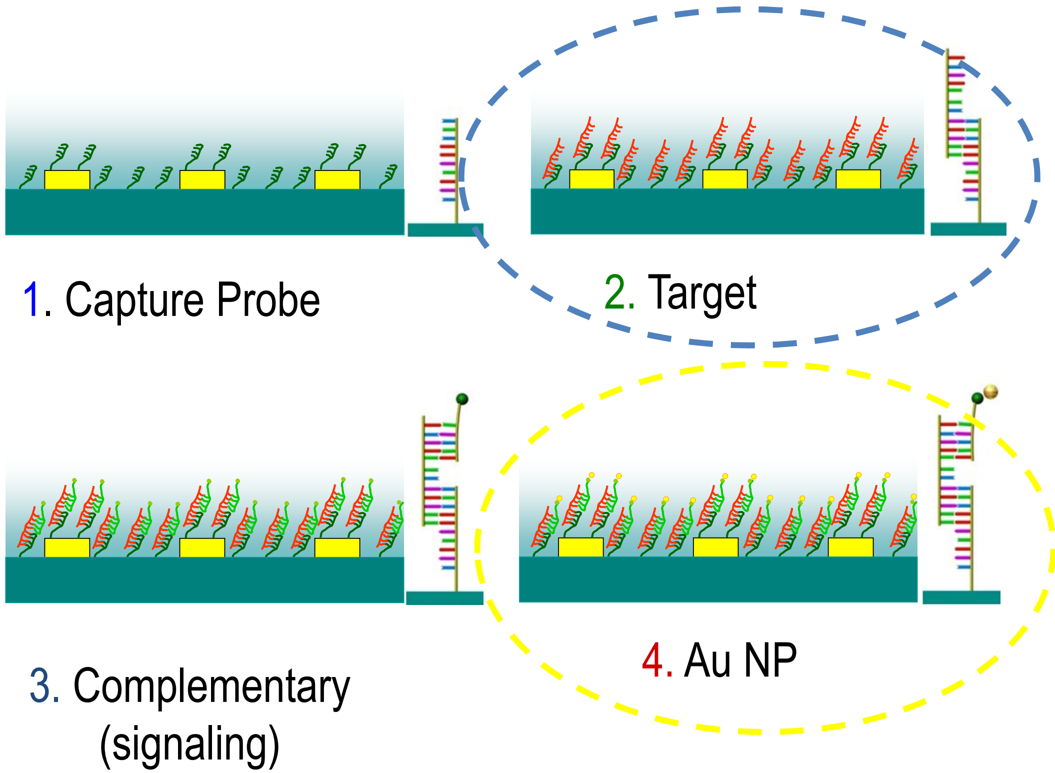
5'-caccactttt tcccatcaag tcatttgtta aaactaaatg taagaaaaa-3'

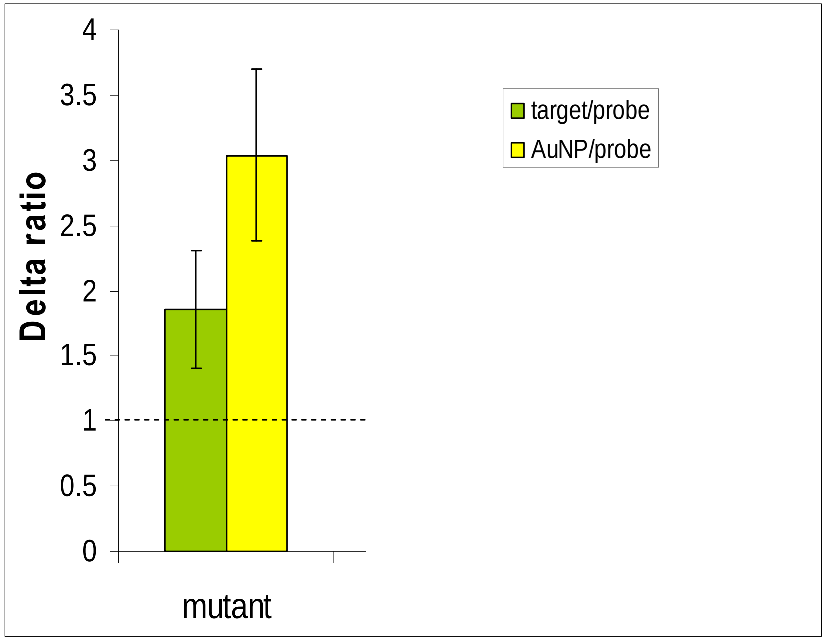
Mutant

5'-caccactttt tcccatcaag tcatttgtta aaactaaag taagaaaaa-3'

Negative control







Summarizing

•A technology was developed for the fabrication of electrochemical sensors basen on interdigitated nanoelectrodes, ranging rom the lighographic process to the encapsulation.

• Impendance spectroscopy characterizations showed the good performane of the devices. The improved sensitivity compared to micrometric devices was shown.

• Succesful detection of the complementary hybridization event with the nanoIDEs has been proved (MicroChim.Acta 170, 275 (2010))

Outline

Intro to Clean-Room Processing

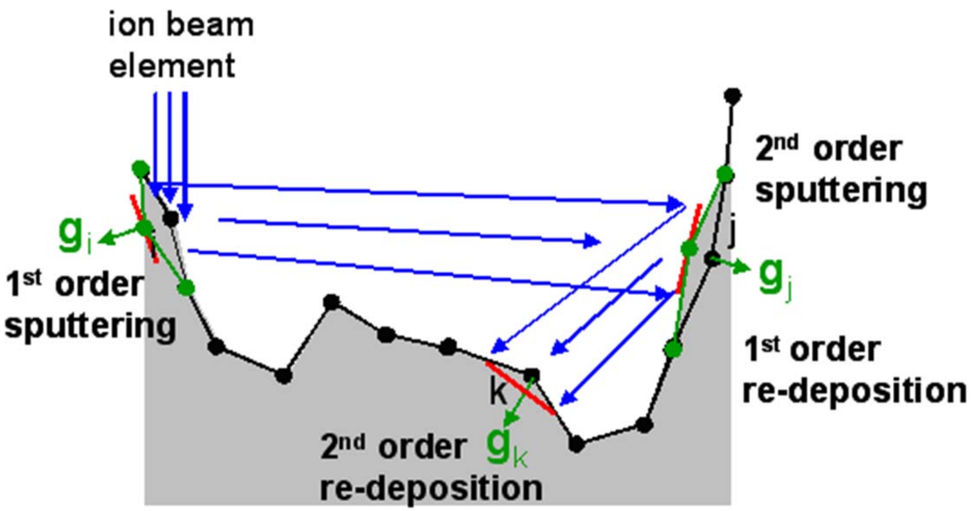
Electron Beam Lithography (EBL)

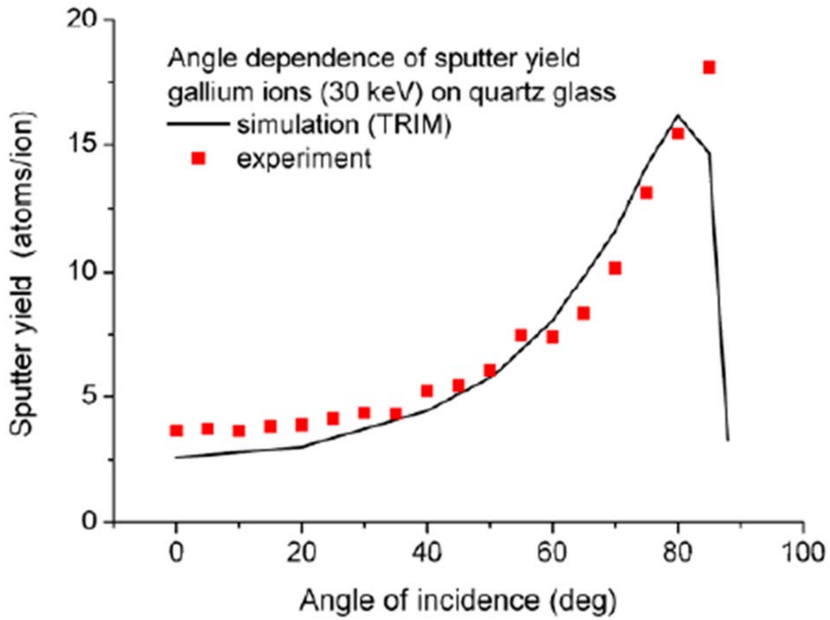
Focused Ion Beam Patterning (FIB)

More Nanolithographies

Ending

Principles of Ion Sputtering



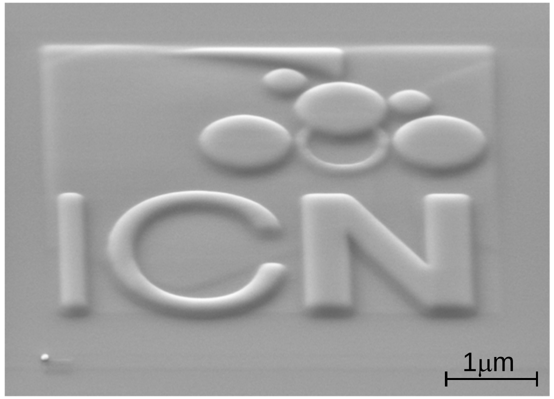


"Sputter rate" per diferent materials (30kV):

Si = 0,27 $\mu m^3/nC$; Si3N4 = 0,2 $\mu m^3/nC$; C = 0,18 $\mu m^3/nC$;
Al = 0,3 $\mu m^3/nC$; Au = 1,5 $\mu m^3/nC$; Ni = 0,14 $\mu m^3/nC$

Zeiss Crossbeam 1560XB

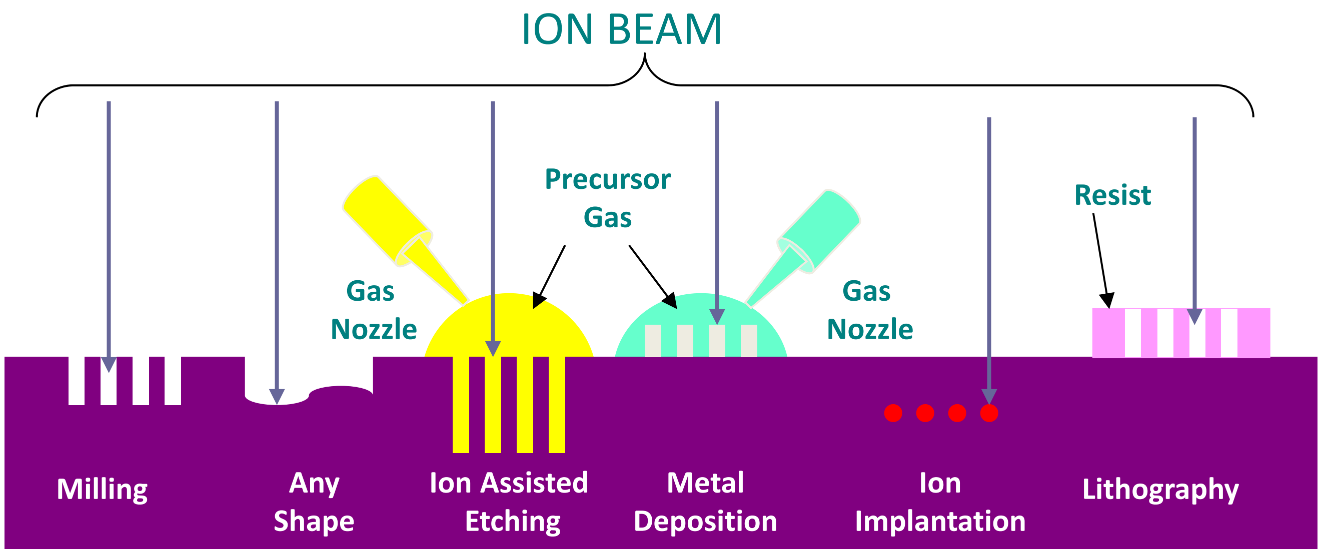
CROSS BEAM: Combination of electron and ion columns which allows "real-time" SEM monitoring of FIB modifications



3D TEOS depo using Raith software

- FE-SEM column (0,1-30kV)
- FIB column (5-30kV)
- 6" chamber
- GIS (5 precursors)
- 3 Nanomanipulators
- Raith lithography

Operation Modes



Milling (most used)
Imaging

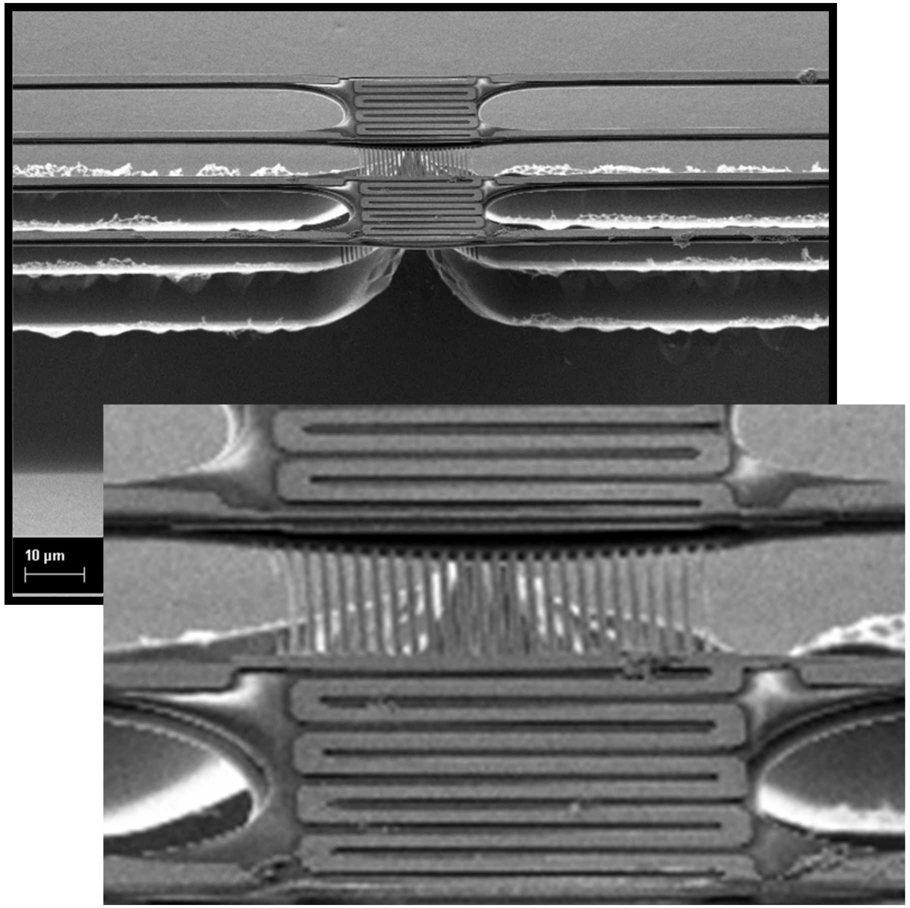
Chemical induced reactions
- Deposition
- Etching

Ion Implantation
(doping or damaging)

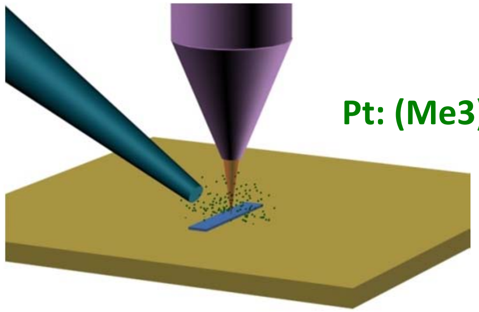
Lithography
(resist exposure)

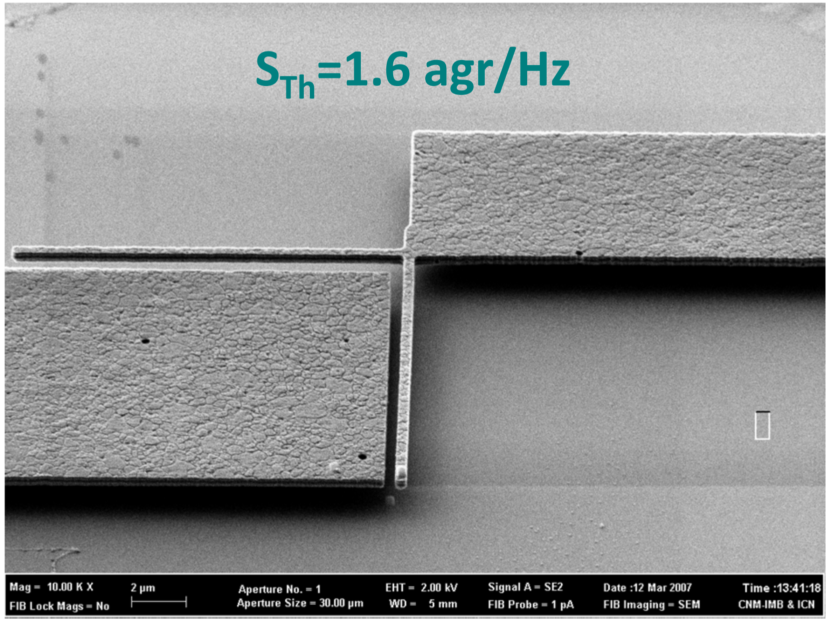
GIS (Gas Injection System)
- Deposition: C, Pt, TEOS
- Etching: XeF_2, H_2O

Many applications



Nanostructuring membranes nanowires for thermal measurements

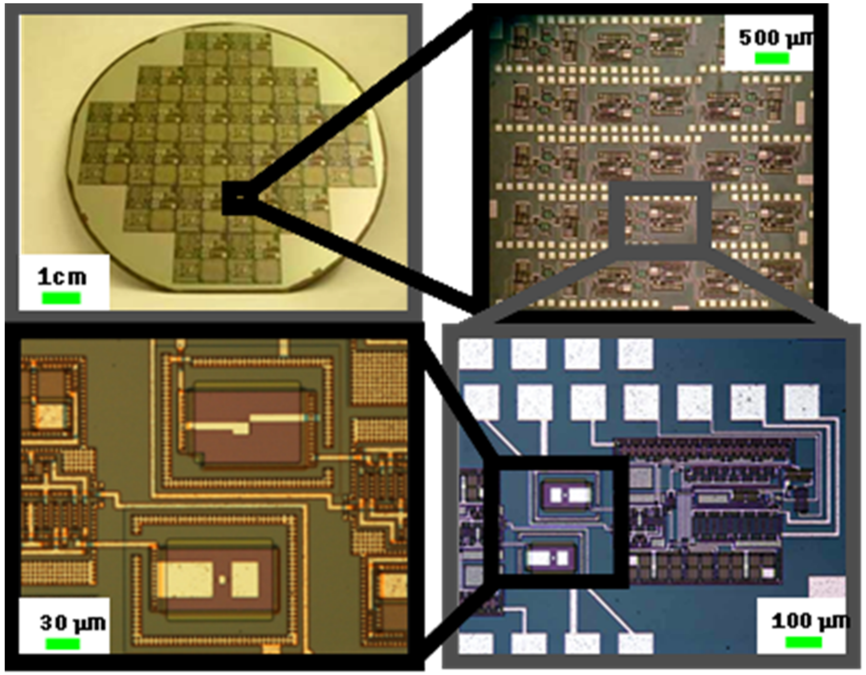


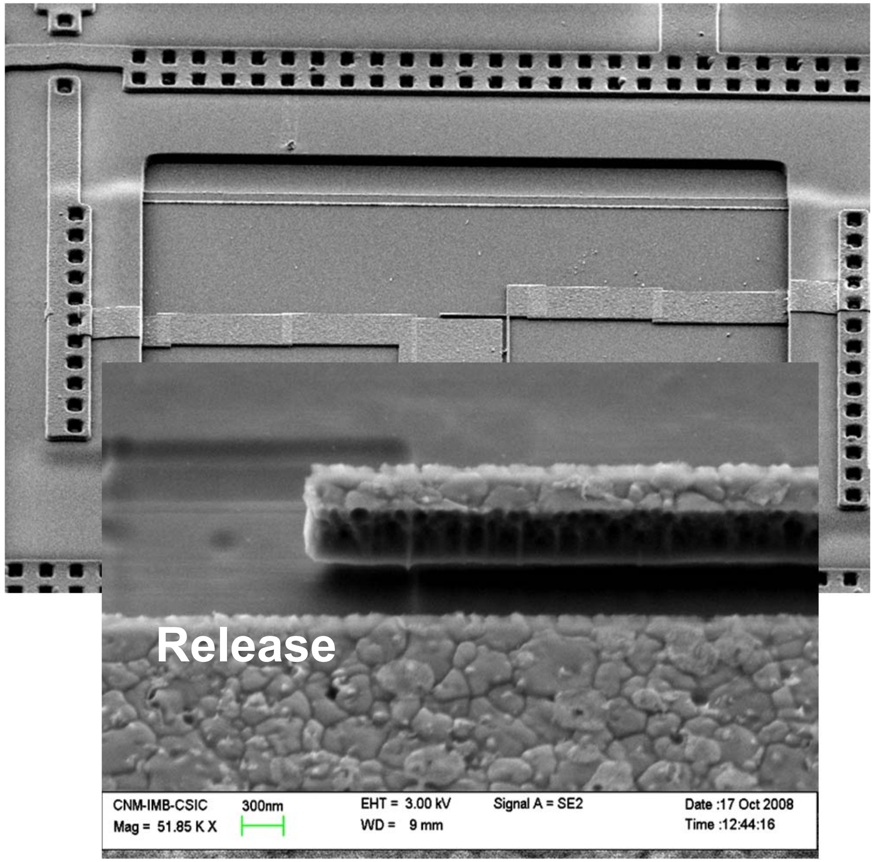


FIBID on nanocantilevers (200fg)

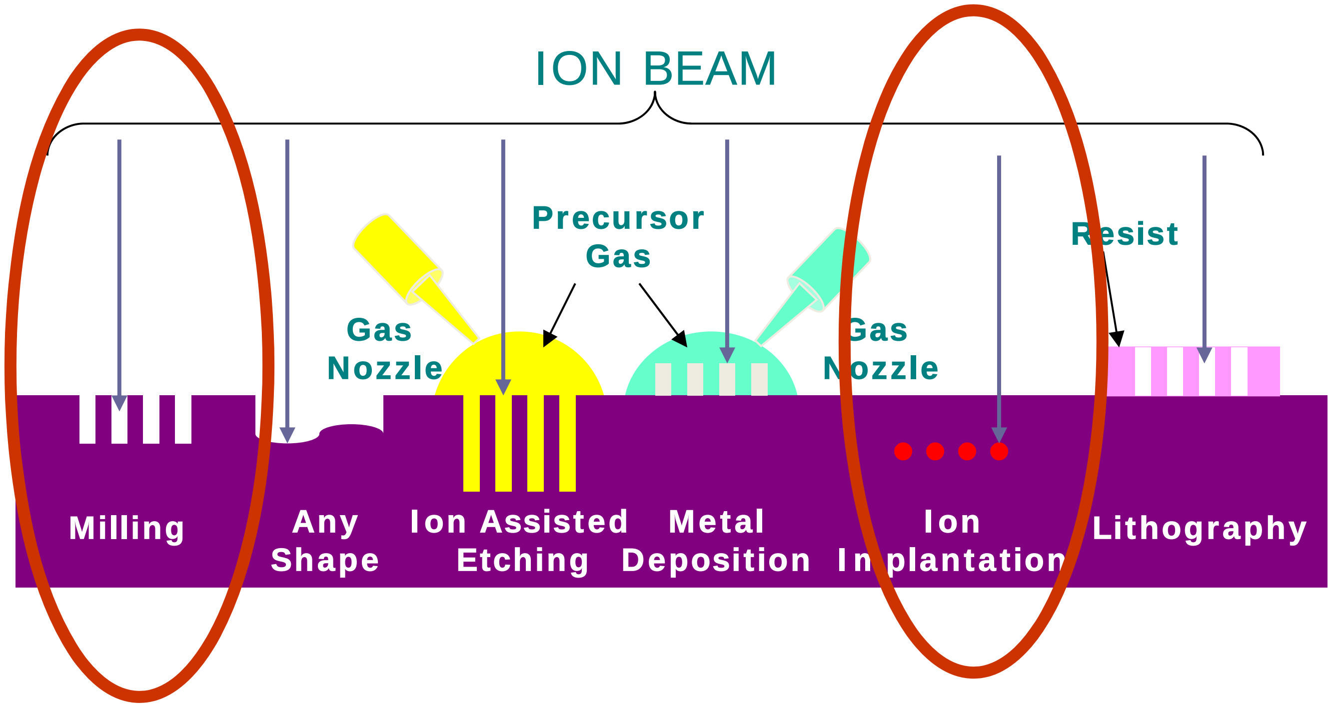
NEMS by FIB: Intro

OBJECTIVE: Development of a focused ion beam based process for the **simple and rapid prototyping of nanomechanical devices**



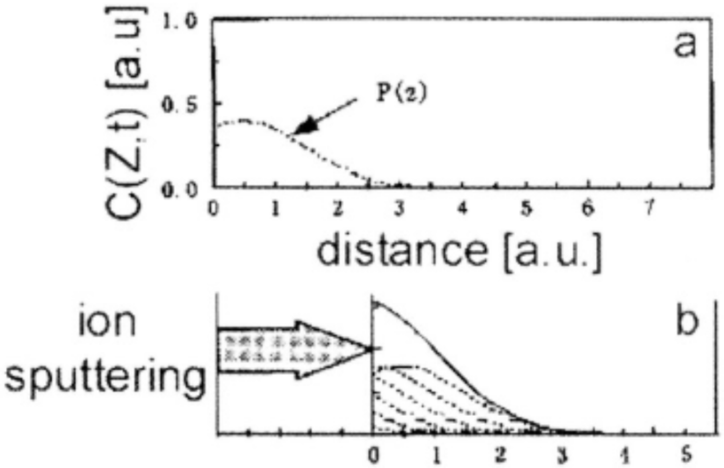


Focused Ion Beam Based Processes



Ga^{+} ions; 5-30 keV; 1 pA-50 nA

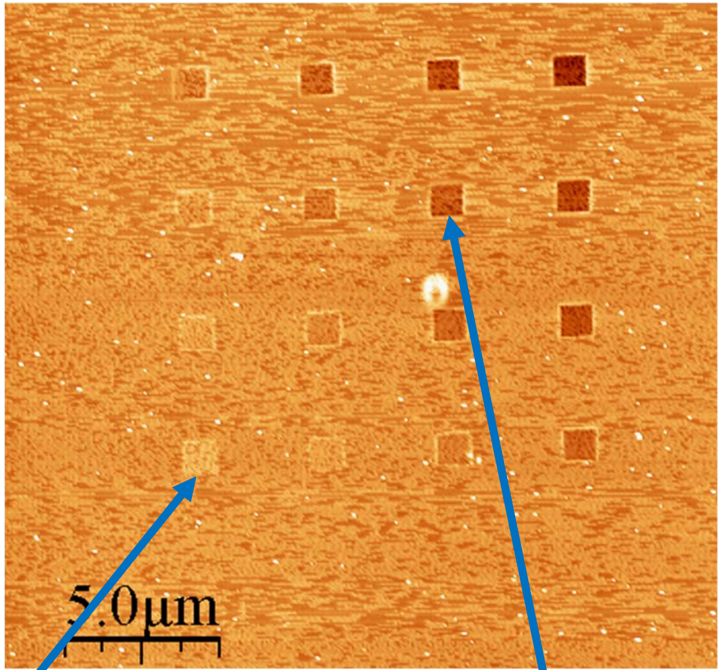
Concept of the Processs: FIB Implantation



Implant profile without sputtering

Implant profile With steady state sputtering

Increasing dose does not implant more ions to the surface, but rather, only recedes the “same” steady state surface with time



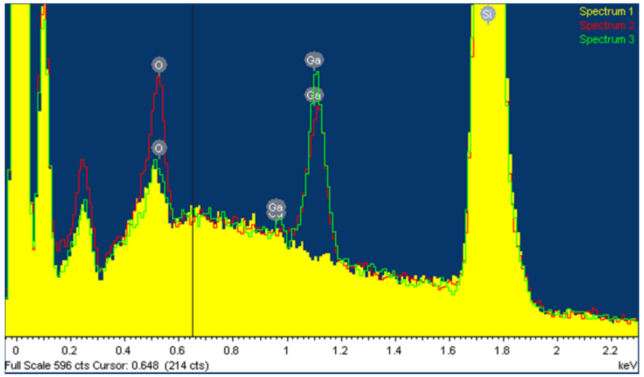
Ga⁺ exposure
Dose: $1.5\cdot10^{16}$ Ions/cm²
1-2 nm height

Ga⁺ exposure
Dose: $2\cdot10^{16}$ Ions/cm²
1-2 nm depth

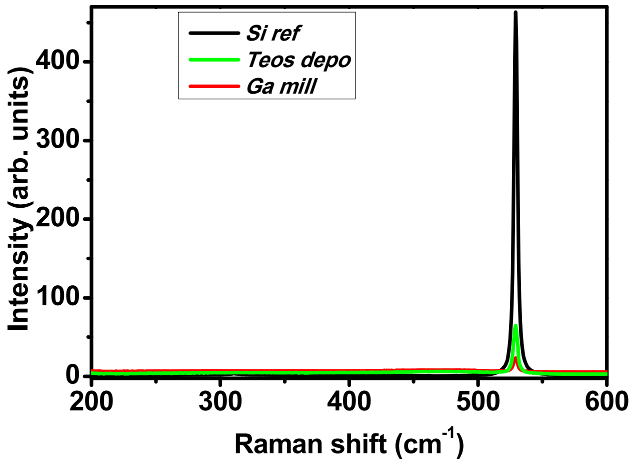
30 keV Ga Ion Range at 0 degrees on silicon: 30-50nm

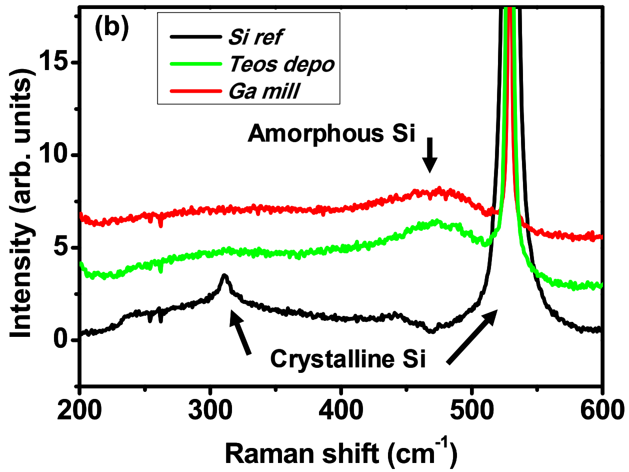
Material Characterization

EDX analysis



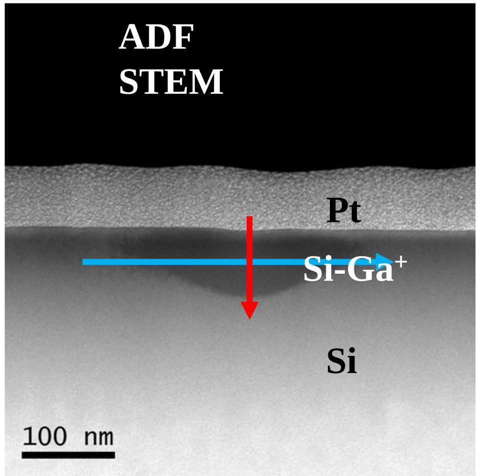
Raman analysis

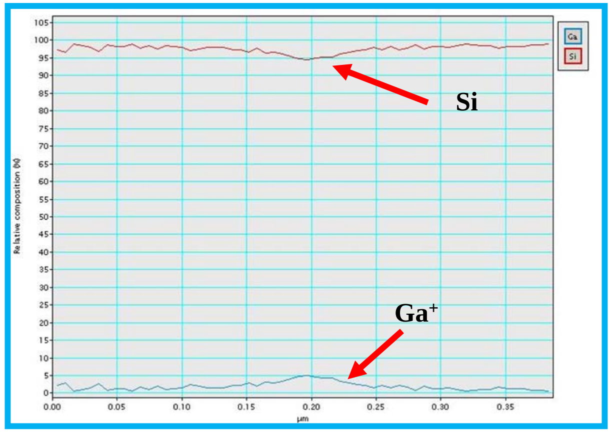


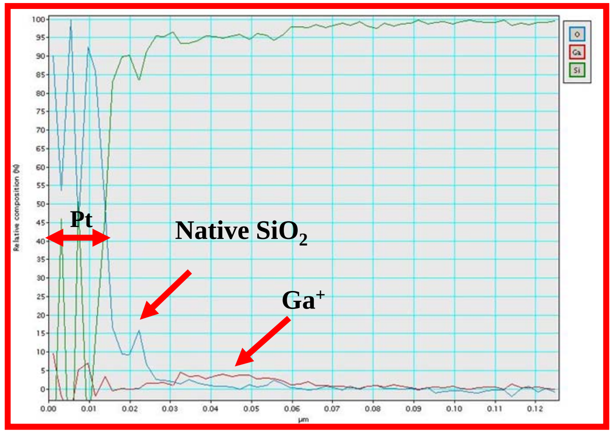


Material Characterization

EELS elemental analysis profiles obtained along the width and depth of a Ga+ implanted wire section.

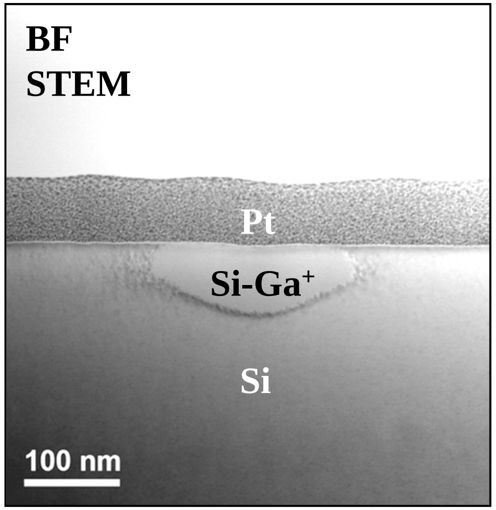


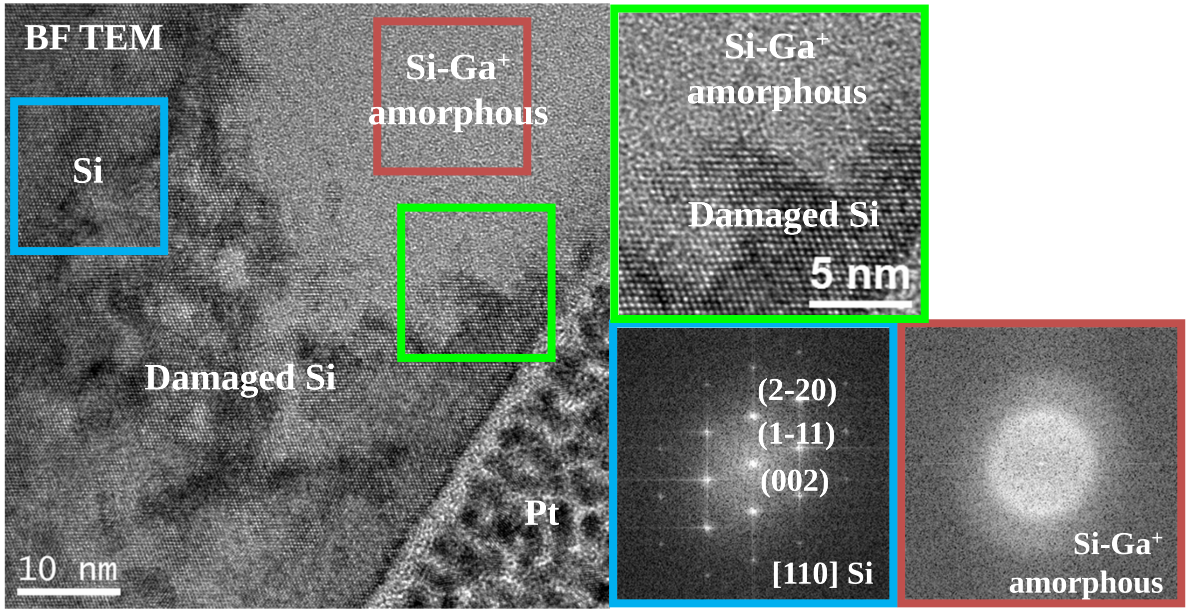


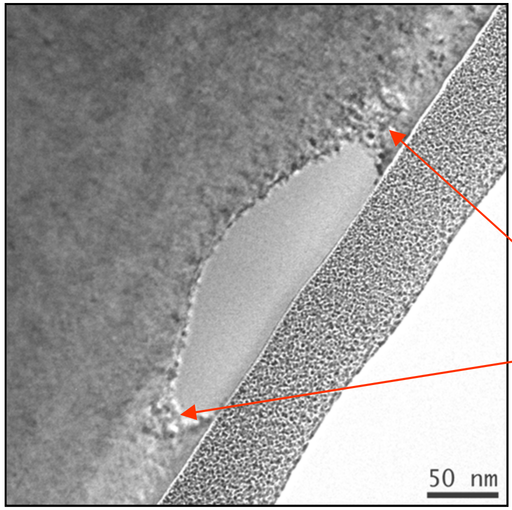


The material in the implanted region is mainly composed of Si, with contents up to 5% in Ga+ and residual O content

HRTEM Characterization

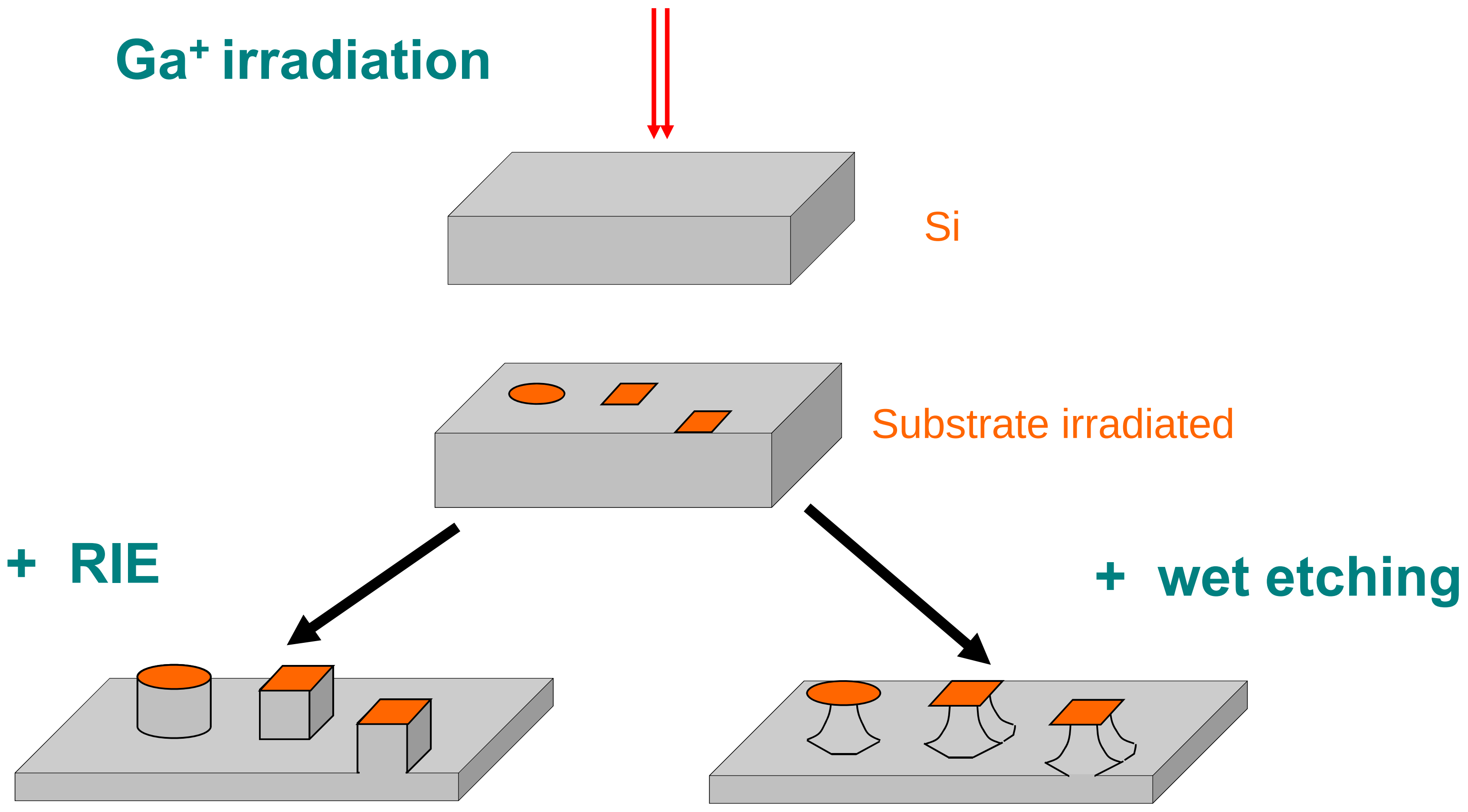






- Crystallization of the Si in the substrate far away from the Ga+ implanted area.
- In the Ga+ implanted area, the material is amorphous.
- Next to the borders, the Si structure is damaged with rough areas of mixed amorphous and crystalline Si.

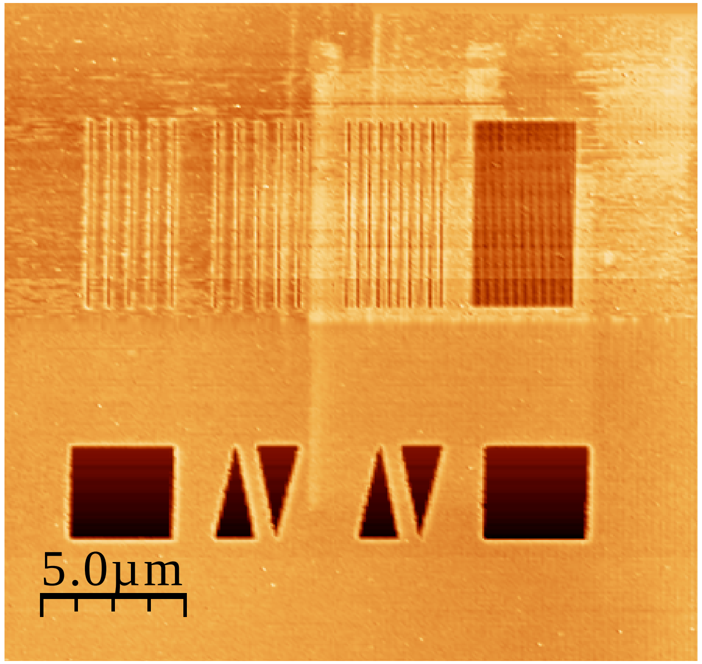
Using Implantation as Mask for Etching

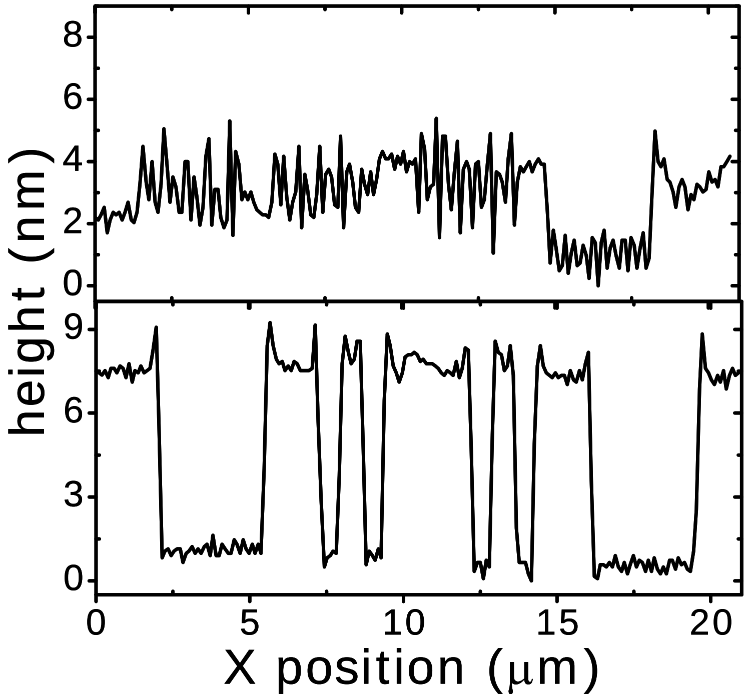


FIB implantation and RIE

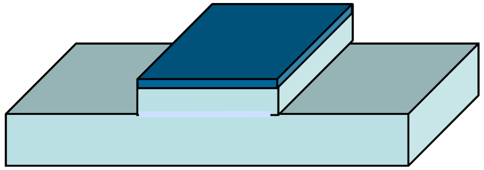
After FIB

Irradiation :30 keV Ga^{+}
5000 mC/cm^2; 50 – 100 nc/cm



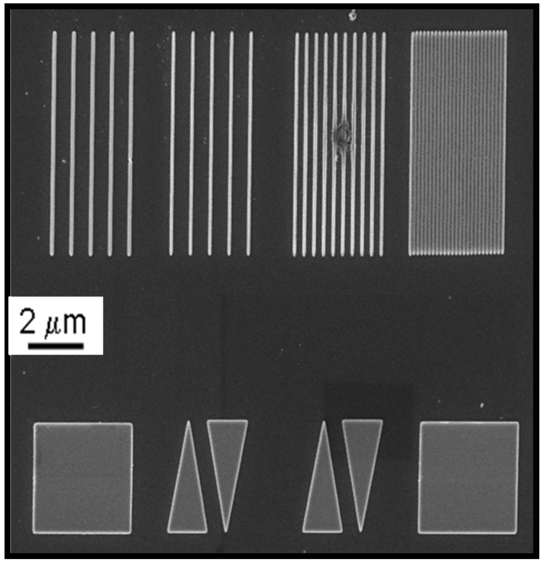


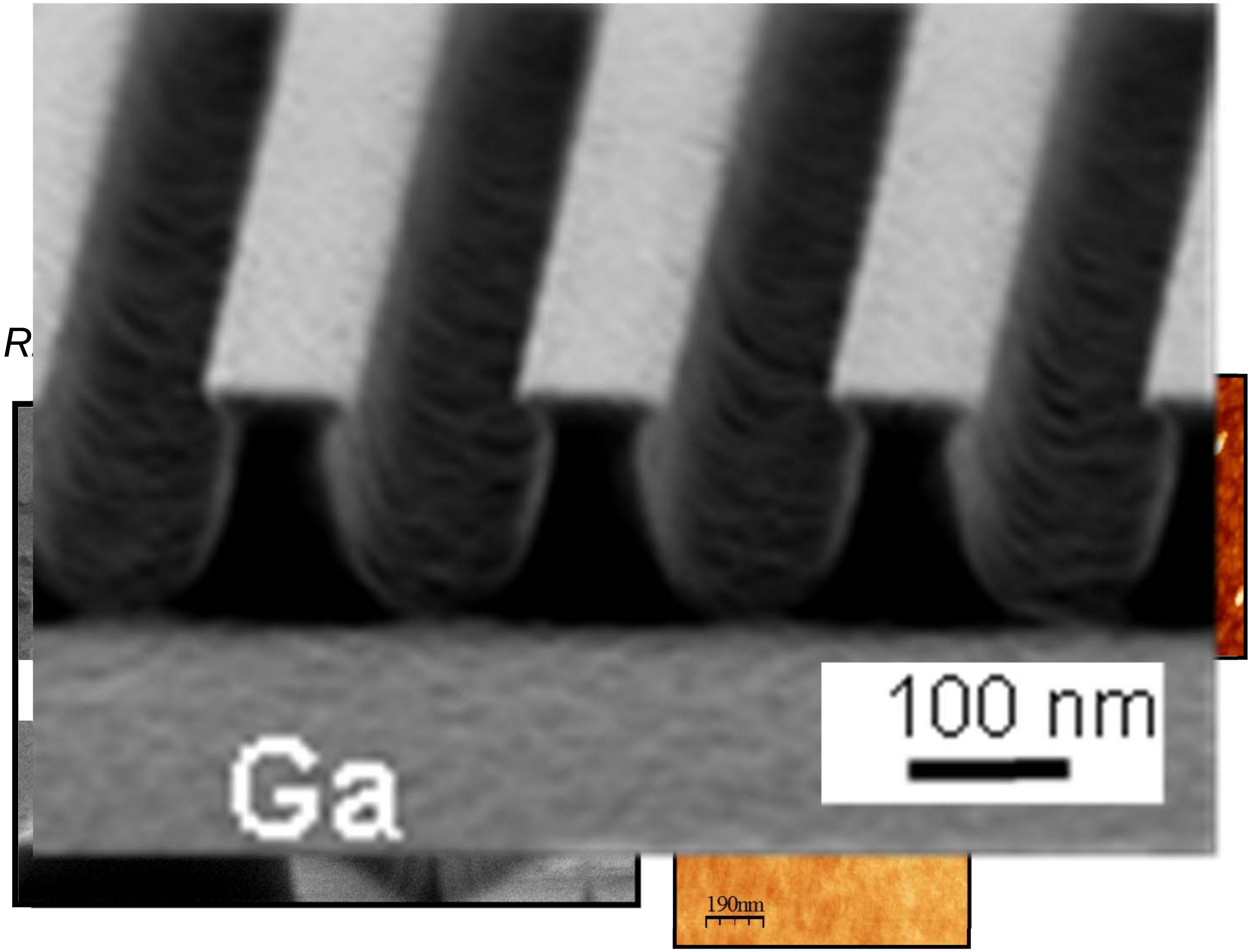
FIB implantation and RIE



After RIE

SEM and AFM images after R

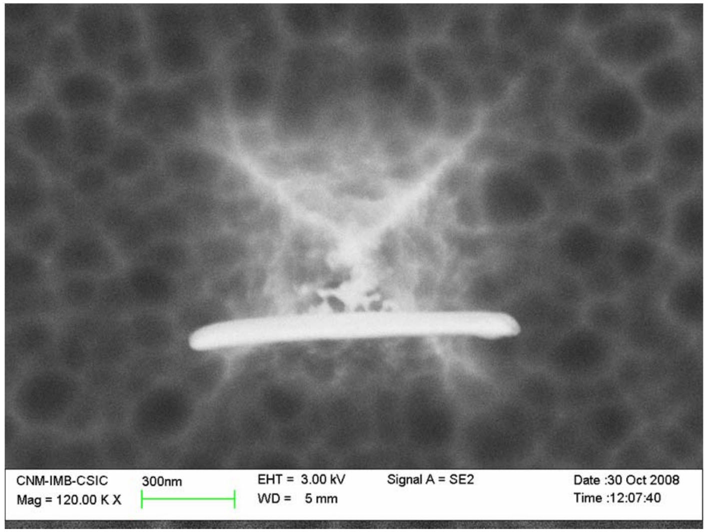


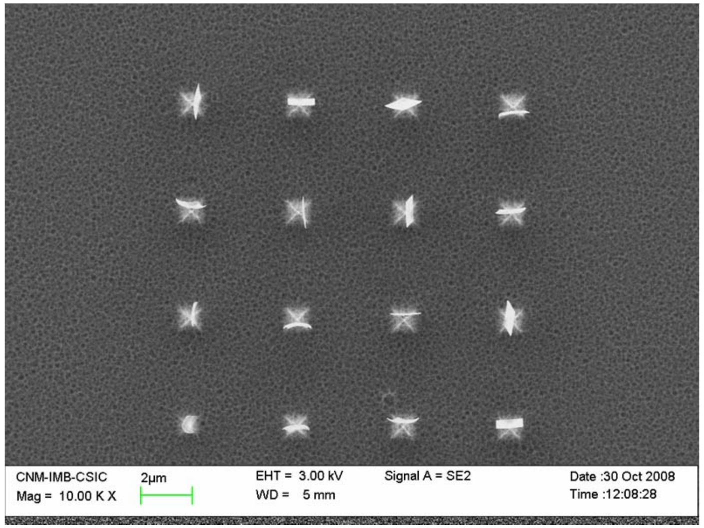


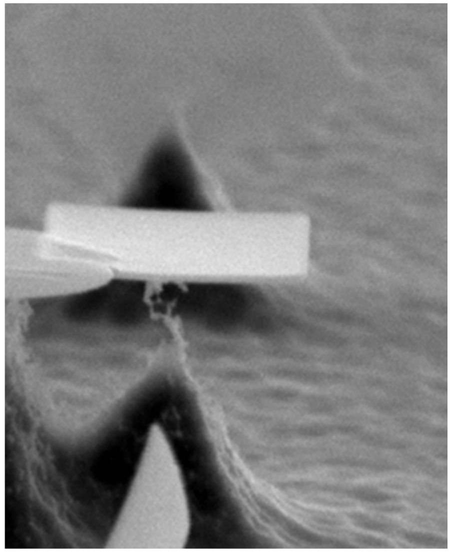
Mask Robustness

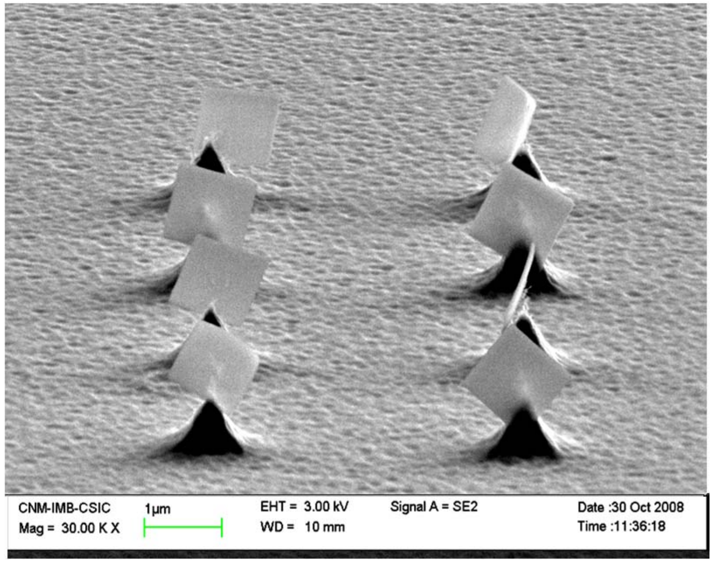
Isotropic RIE reveals:

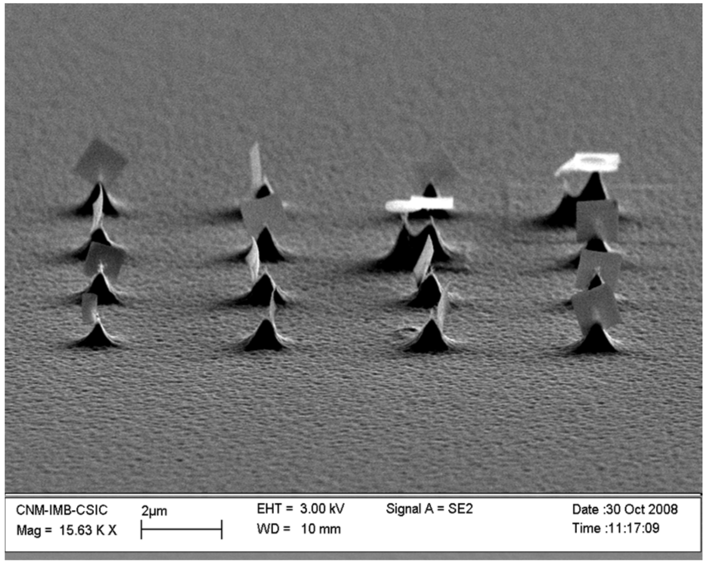
- **mask robustness**
- **thickness**
- **selectivity**











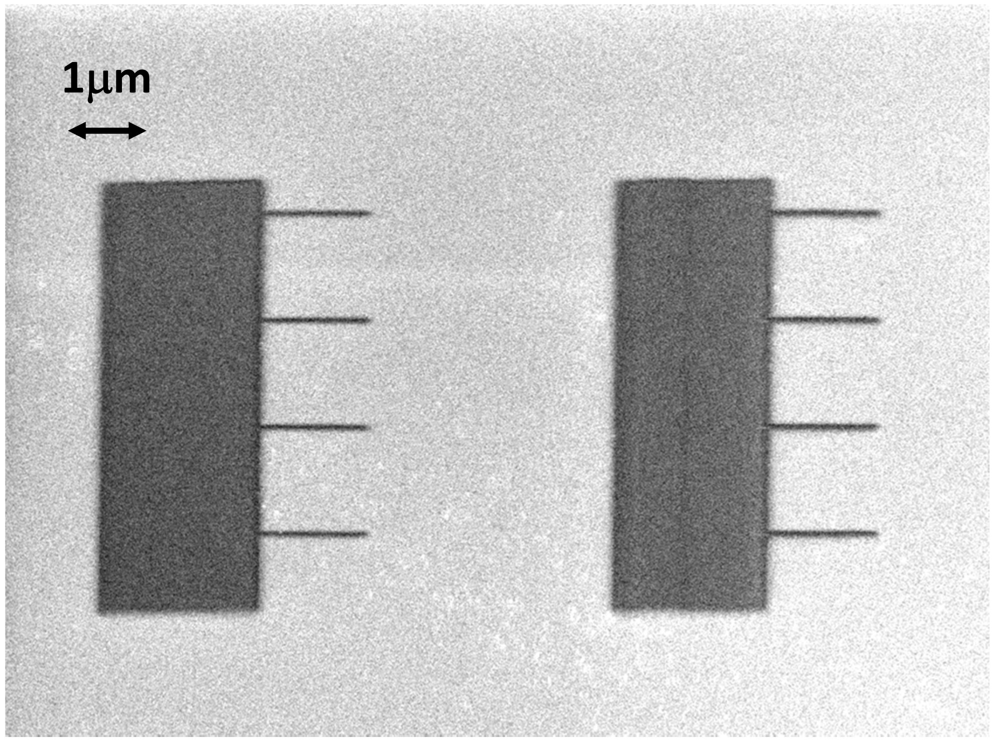
FIB implantation and wet etching

Si (bulk)

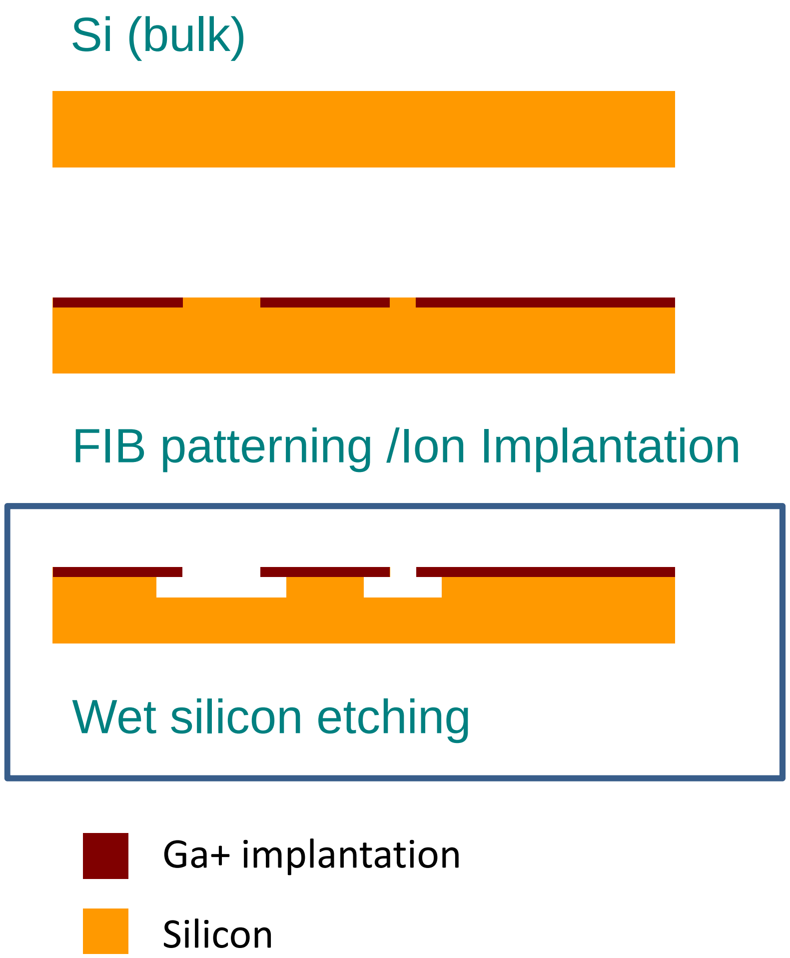
FIB patterning /Ion Implantation

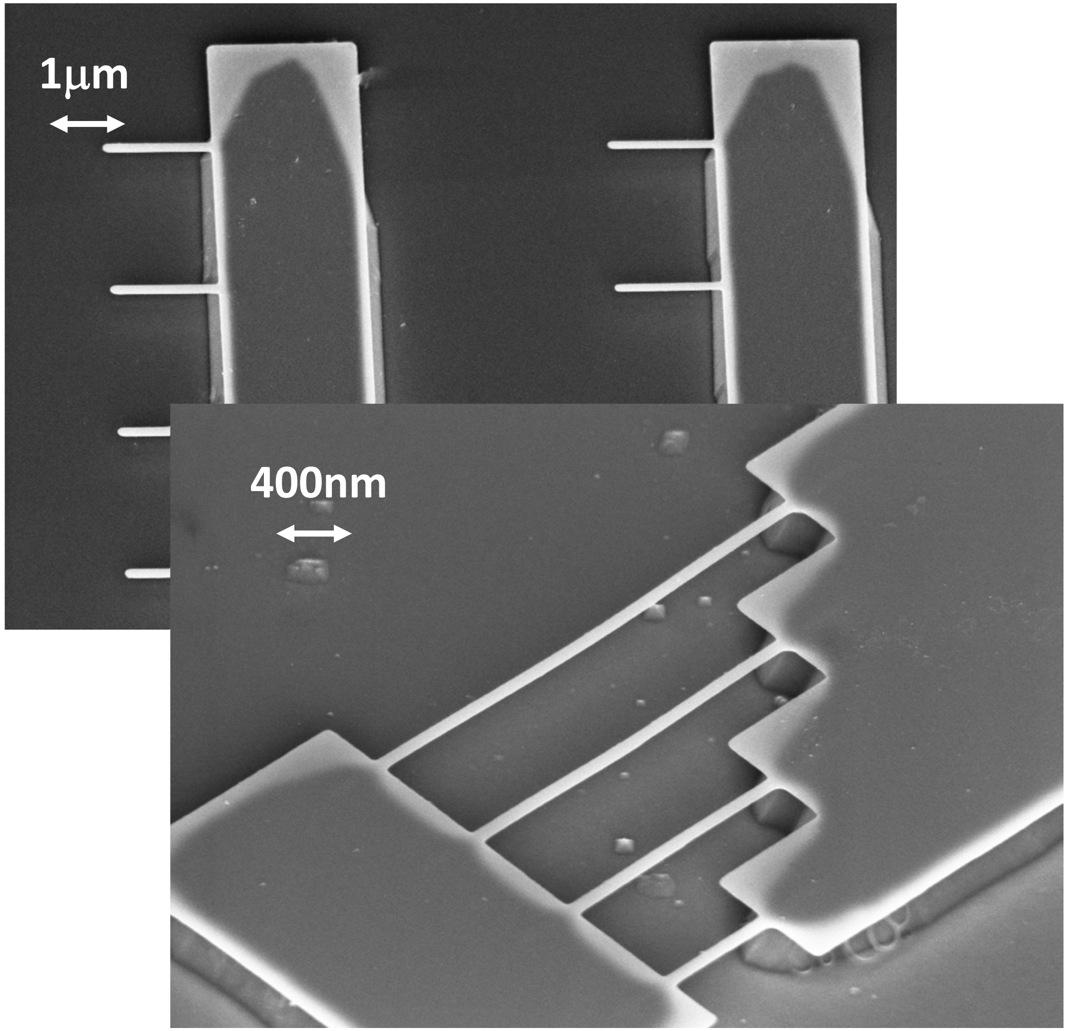
Ga+ implantation

Silicon



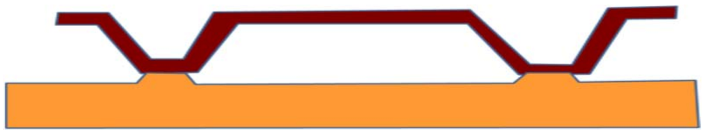
Direct Nanomechanical Devices by Implantation





FIB implantation + milling and wet etching

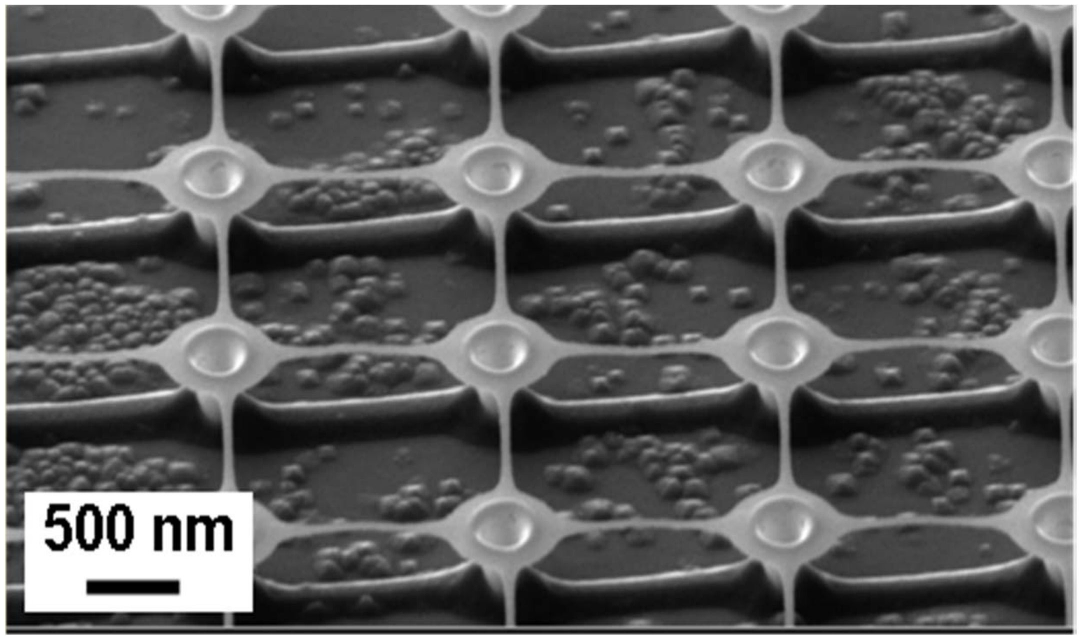
FIB implantation + milling



Wet silicon etching

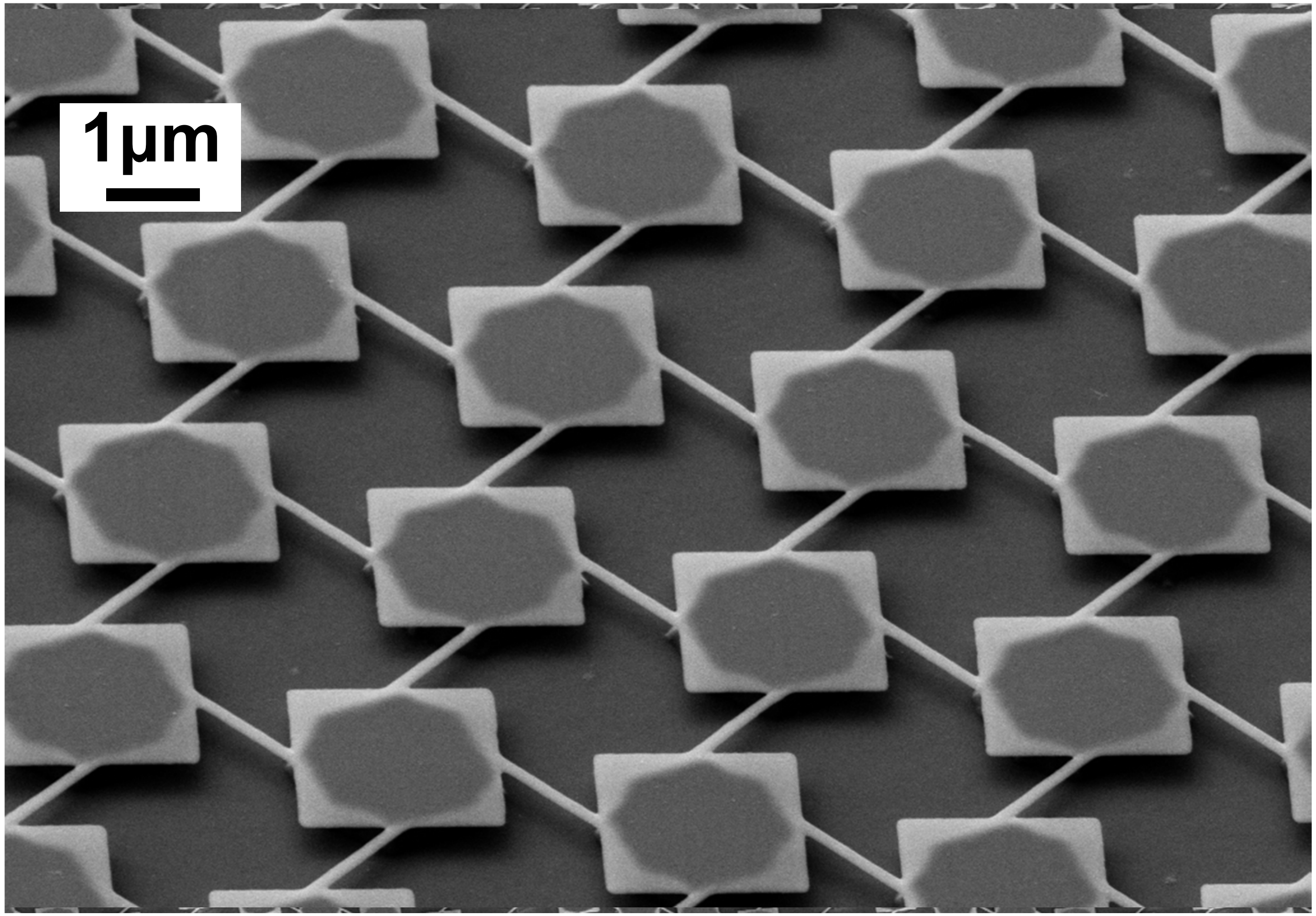
Ga+ implantation

Silicon



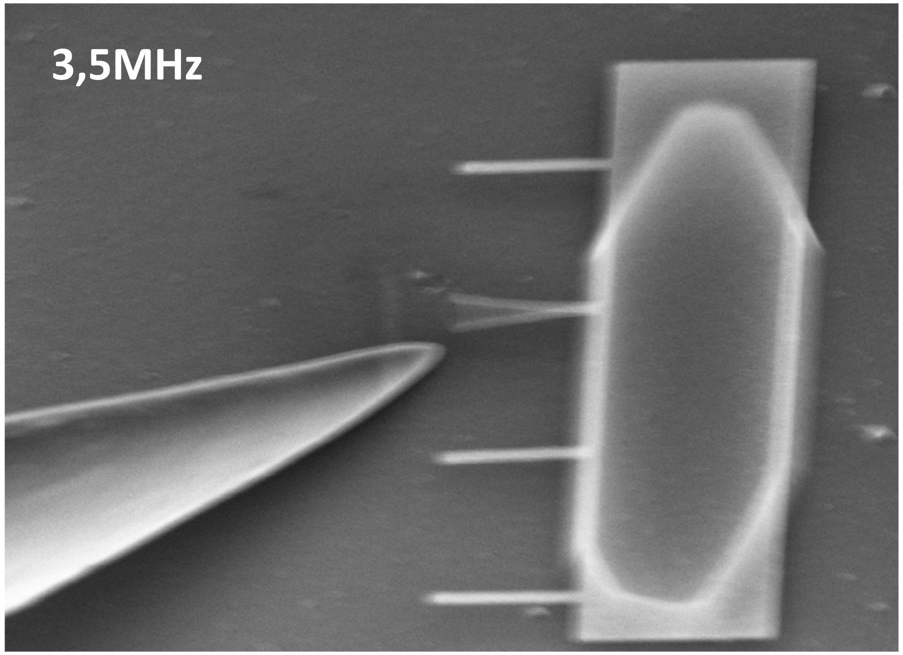
Fabrication of 3D structures combining FIB implantation and milling

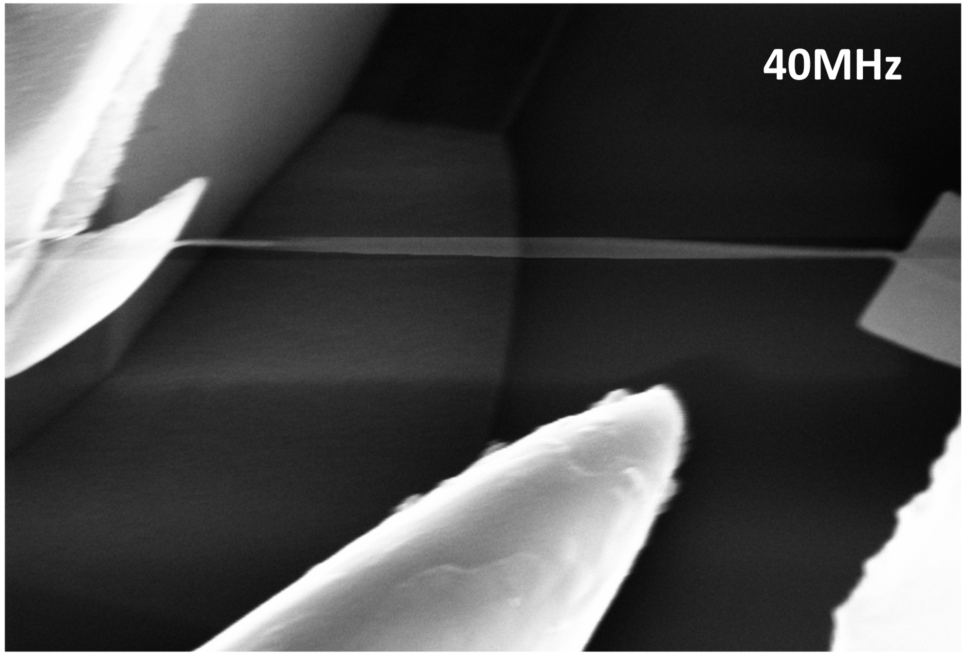
Large Scale Fabrication



SEM images of a large-scale array of doubled clamped beams. (The orientation of the beam has been selected to optimize the release during the under- etching process.

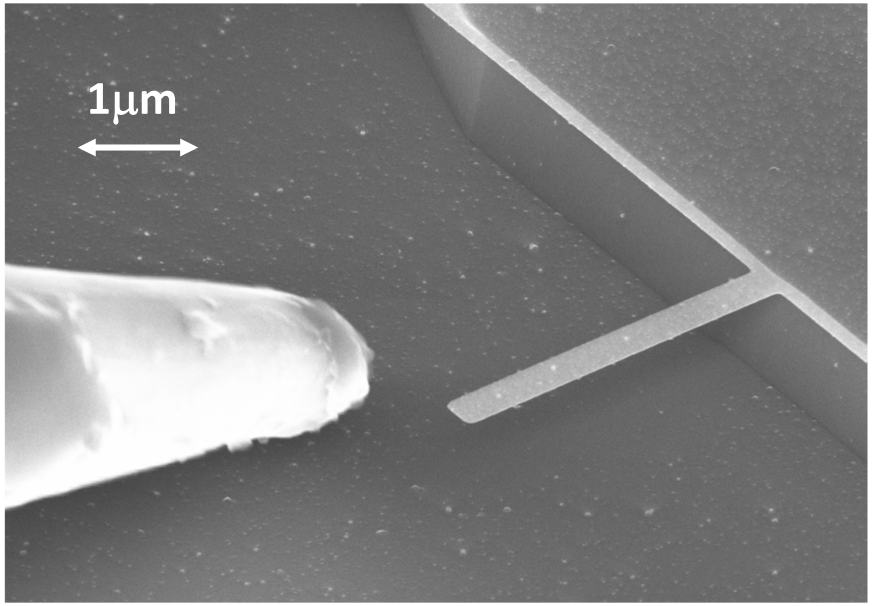
Dynamical Response

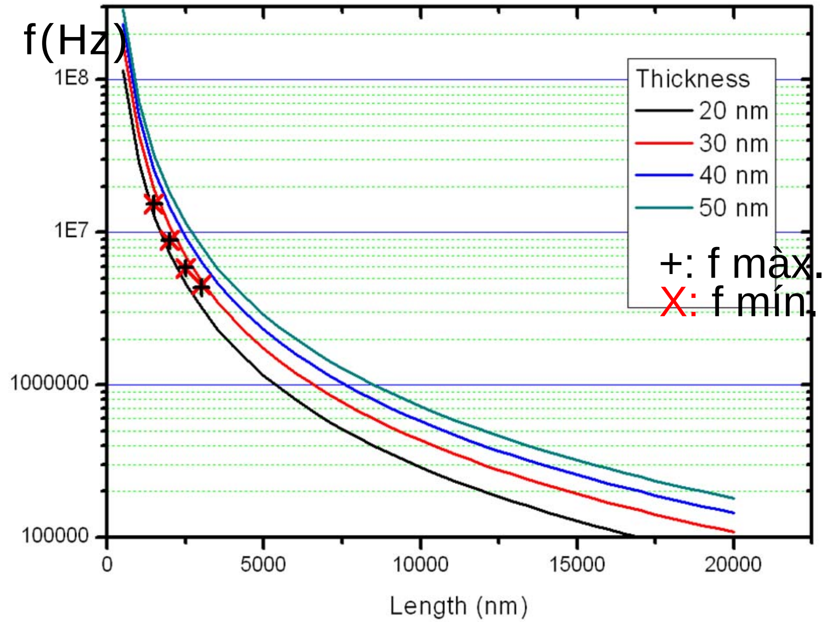




Ultra-thin single and double clamped beams fabricated by FIB exposure and TMAH etching. Their dynamical response has been characterized inside an SEM chamber by approaching a sharp needle to the beams using micromanipulators and applying an AC voltage. The resulting oscillating electrostatic force induces the movement of the beam. The images show the moment in which the frequency of the oscillating force matches the mechanical resonance frequency of the beam.

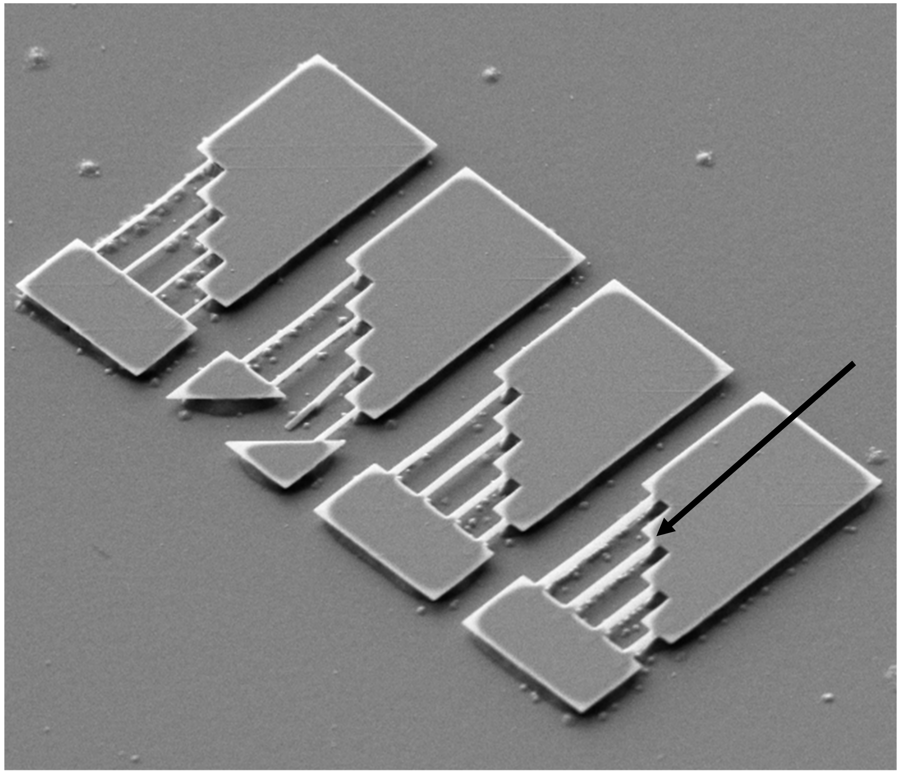
Dynamical Response

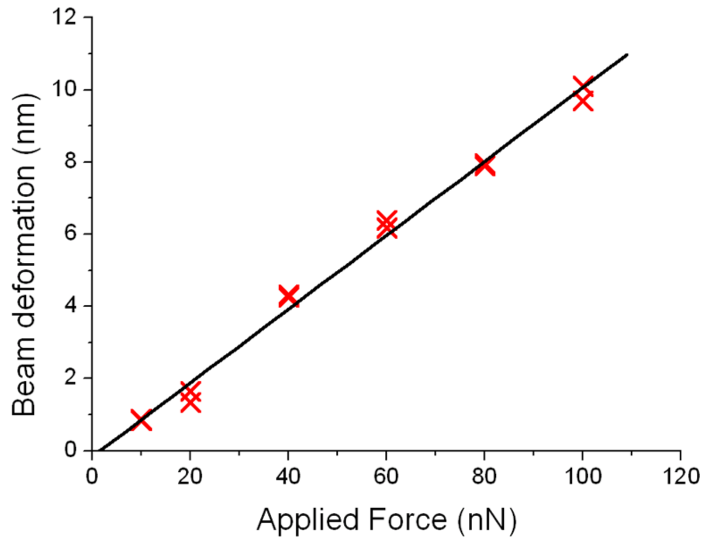




Study of the resonance frequency of thin cantilevers as a function of their dimensions.
Dimensions: 1µm<length<4 µm; width= 300nm; thickness=35nm.
The SEM image (left) shows a cantilever of 3 µm length and a sharp needle close to it that causes the electrostatic actuation of the cantilever.
The right figure shows the experimental value of the resonant frequency of several cantilevers (black crosses for the maximum measured and red for the minimum) as a function of length. Solid curves show the theoretical resonant frequency as a function of length and thickness and fixed width of 300nm.

Elastic Properties measured by AFM





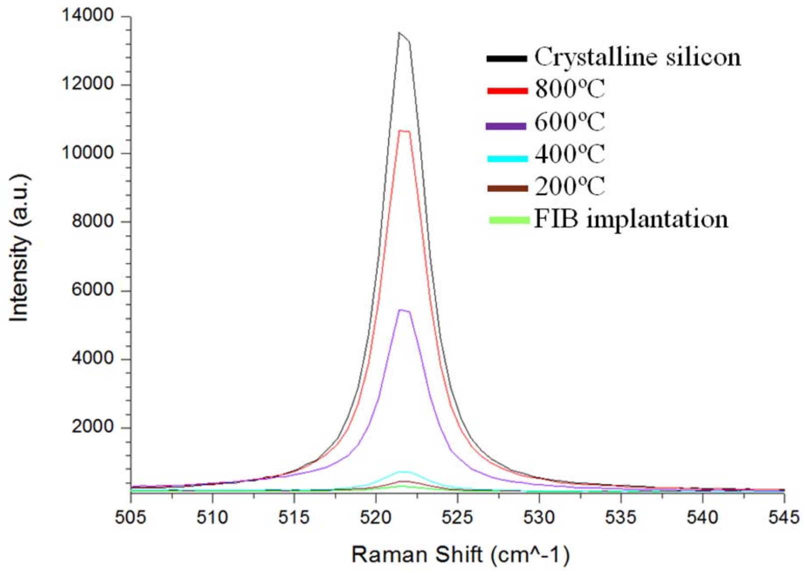
Experimental k = 9.77(N/m)

Theoretical k = 1.11 (N/m)

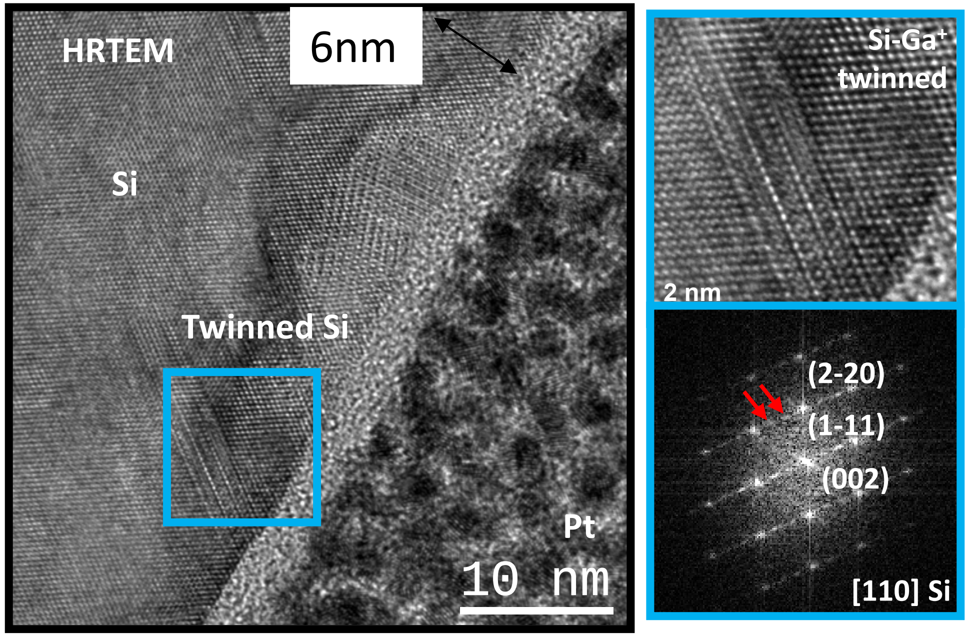
AFM measurement of a double clamped beam (DCB). The dimensions of the beam are 3um x 230nm x 35nm. In the right figure is plotted the deformation measured on the center of the DCB as a function of the force applied using the AFM-tip. The experimental value of the beam spring constant (k) is obtained from the figure and the theoretical value is calculated according the dimensions of the beam and assuming bulk crystalline silicon as structural material.

Ongoing Work: Annealing

Annealing

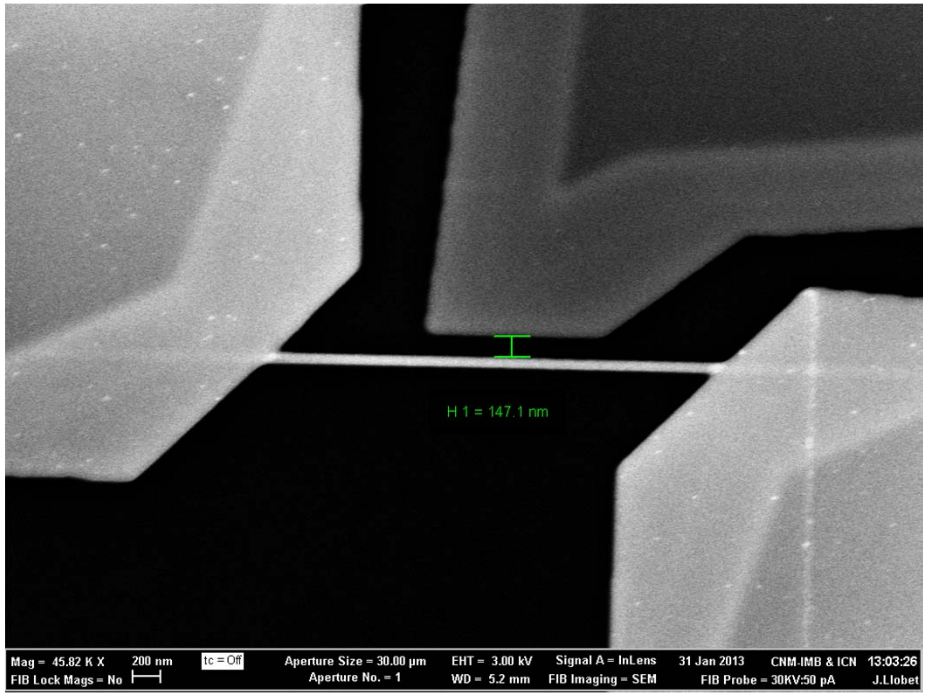


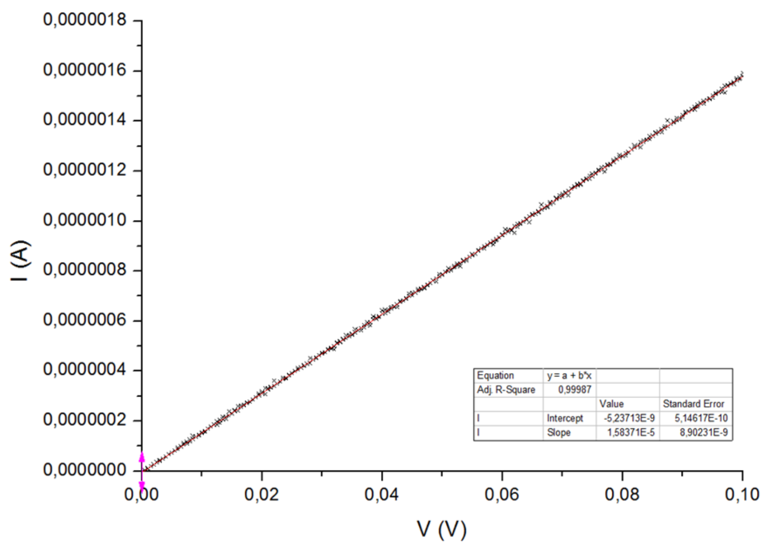
Cristallinity Recoverning
(Doping during Annealing)



HRTEM micrographs showing the recrystallized areas after annealing (600ºC).

Ongoing Work: Electrical Measurements





SEM image of free suspended DCB. The dimensions are 1.2µm length, 80nm weight and 40nm thickness. Electrical behavior of the DCB in right figure. The resistance is about 63kΩ and the resistivity **$1.68\cdot10^{-4}$ Ω·m** (equivalent to Si (B-doped $10^{.18}$at/cm^3))

Summarizing

• A simple, fast and flexible method to fabricate ultra-thin nano-mechanical devices and 3D nanostructures at large scale by the combination of ion beam implantation and silicon etching is presented.

• The characterization of the dynamic response shows an experimental resonance frequency close to the theoretically expected.

• The elastic properties of the double clamped beam show an experimental spring constant higher than the theoretically expected that suggests an increase of the beam stiffness.

• Actually working in the electrical measurements of the structures

Outline

Intro to Clean-Room Processing

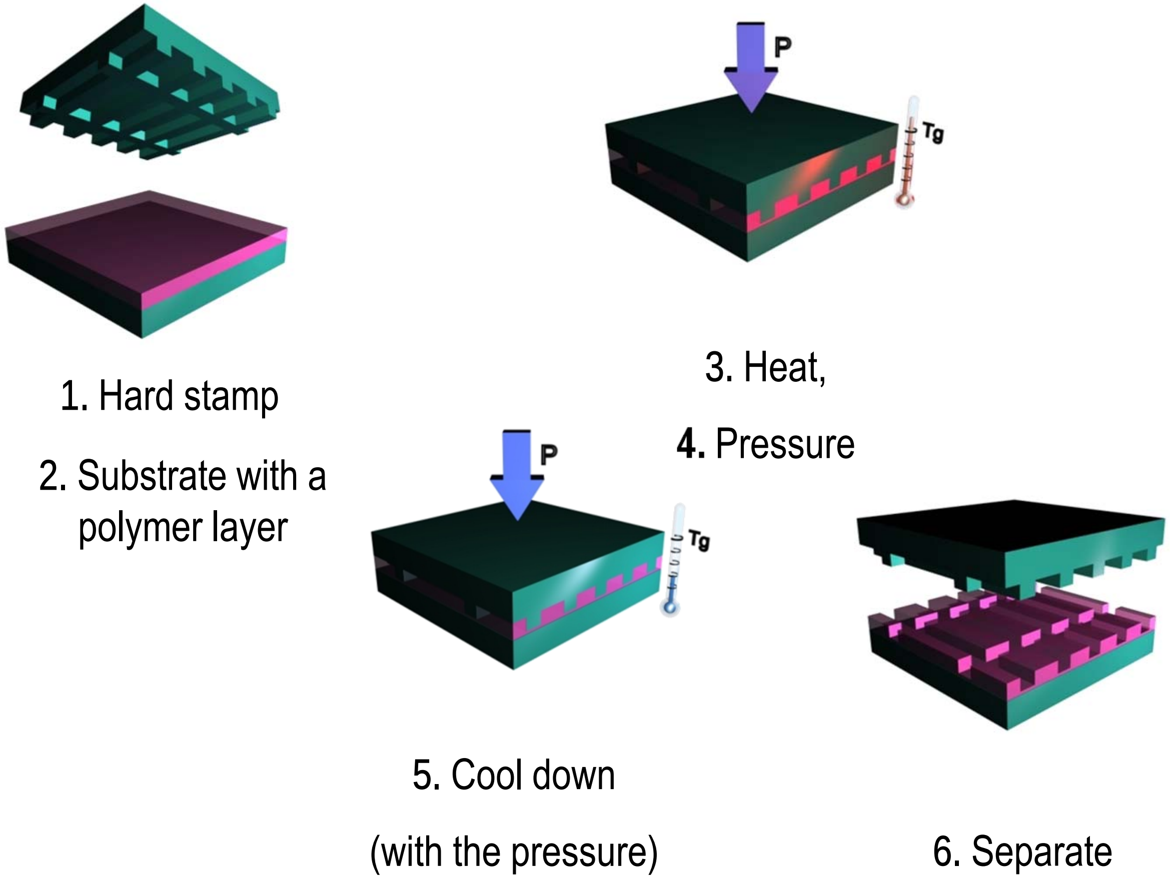
Electron Beam Lithography (EBL)

Focused Ion Beam Patterning (FIB)

NanoImprint Lithography (NIL)

Ending

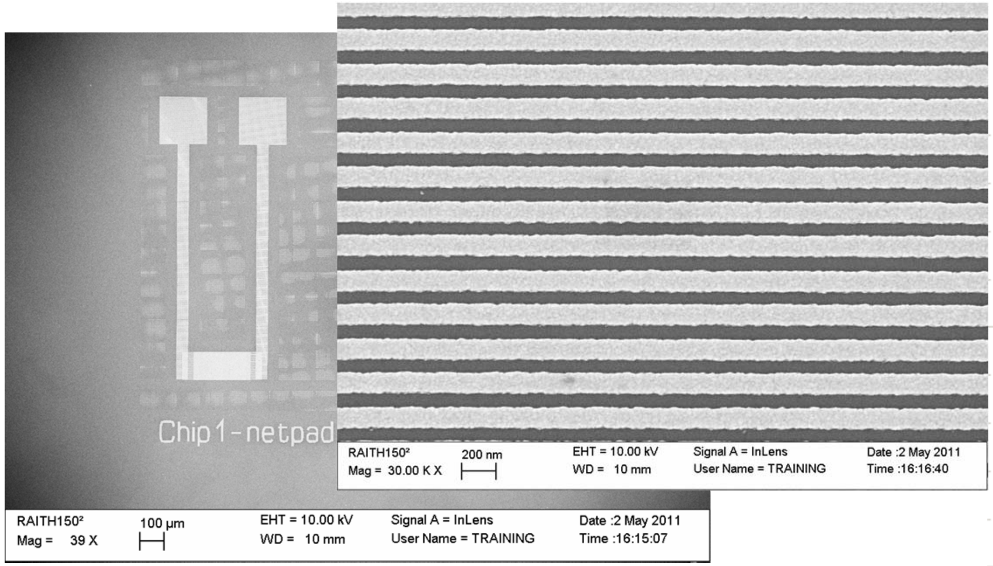
NanoImprint Lithography: “Thermal NIL”

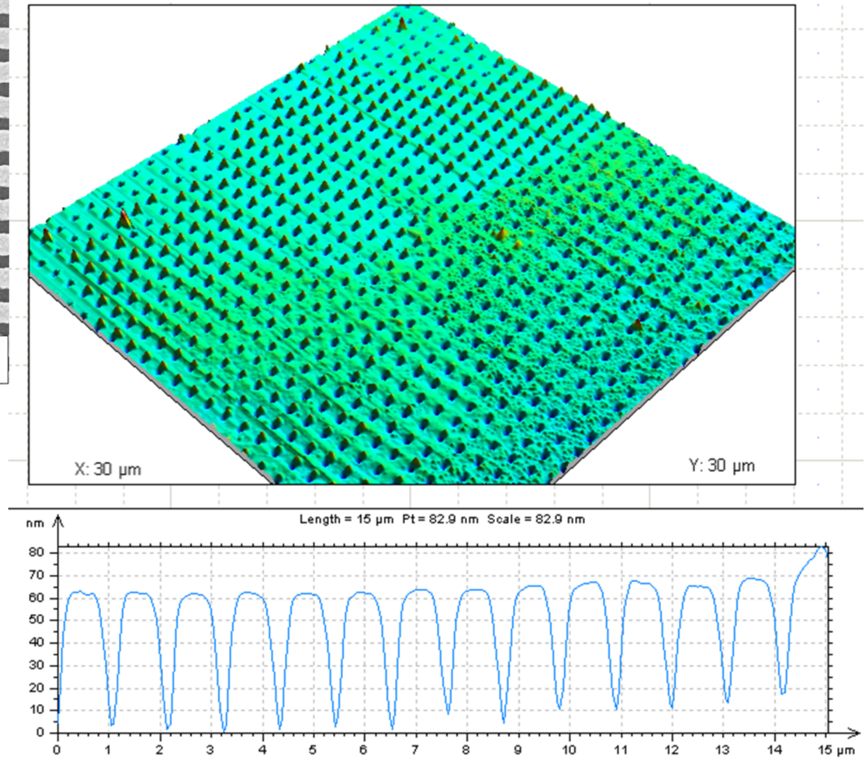


- Stamp Dependant Resolution
- Paralel Fabrication

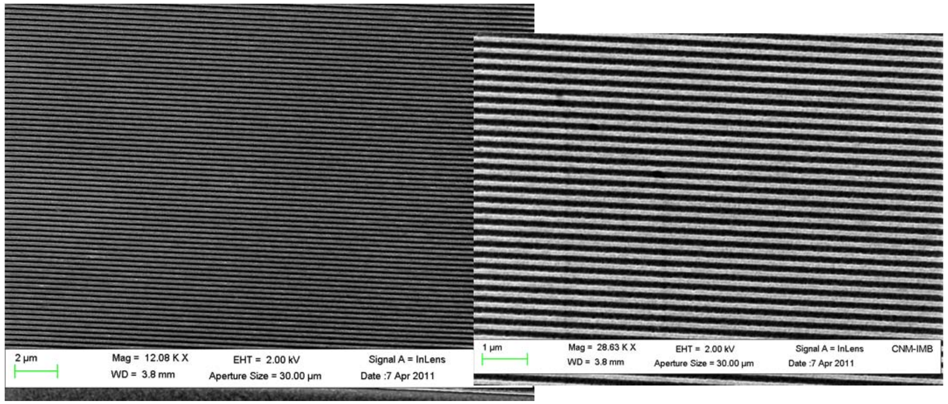
NIL: Examples and Materials

Silicon



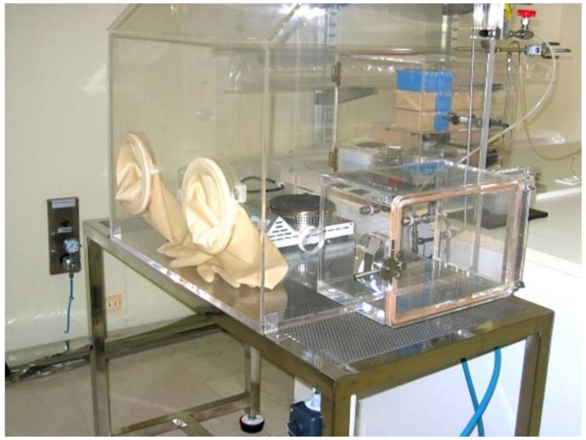


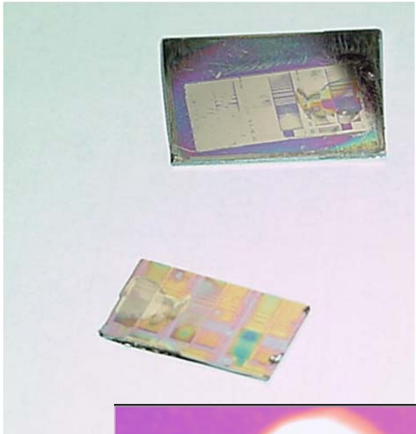
PTT Foil: poly(trimethylene terephthalate)

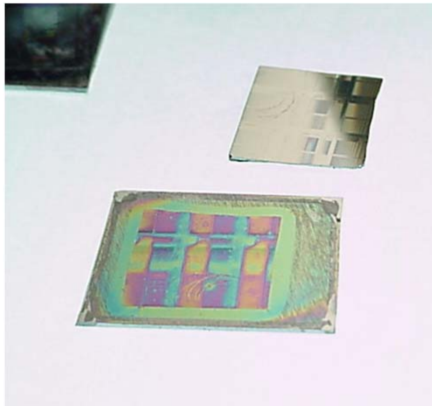


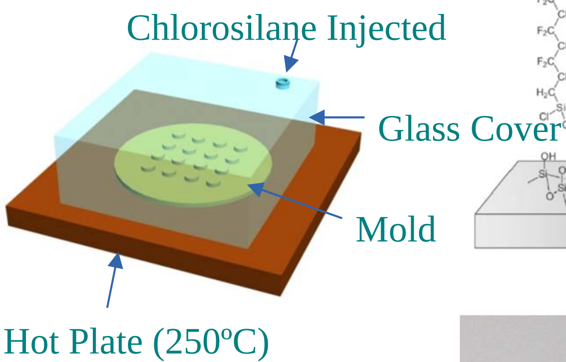
LSMO on PVA matrix over STO

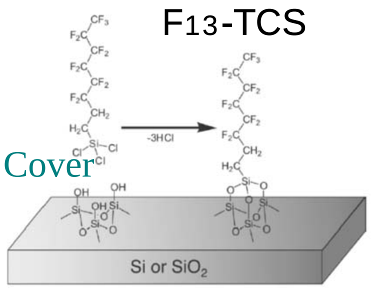
Anti-sticking layer deposition

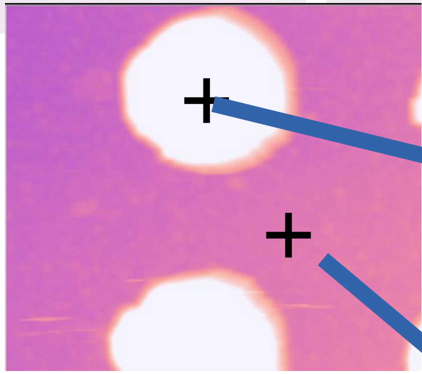


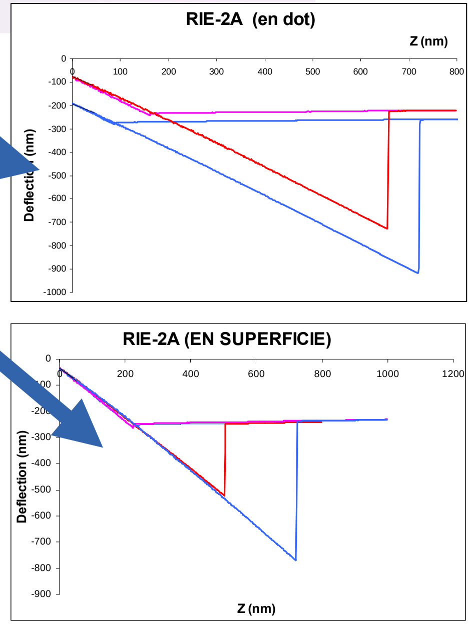




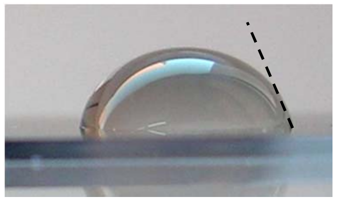




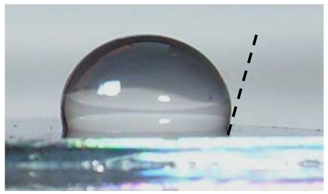




Contact Angle

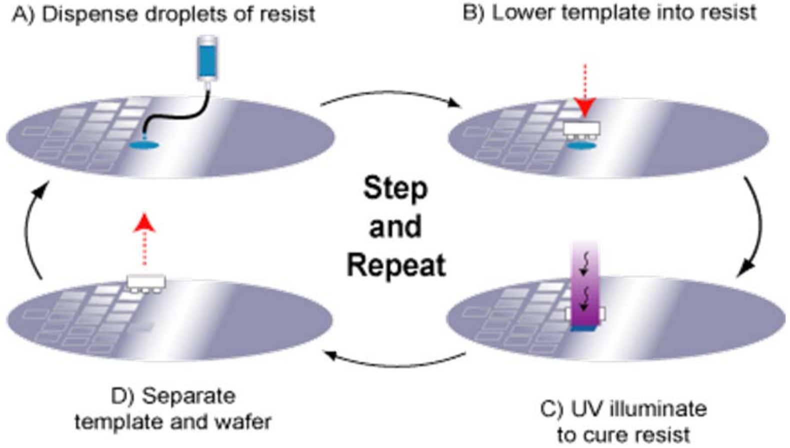


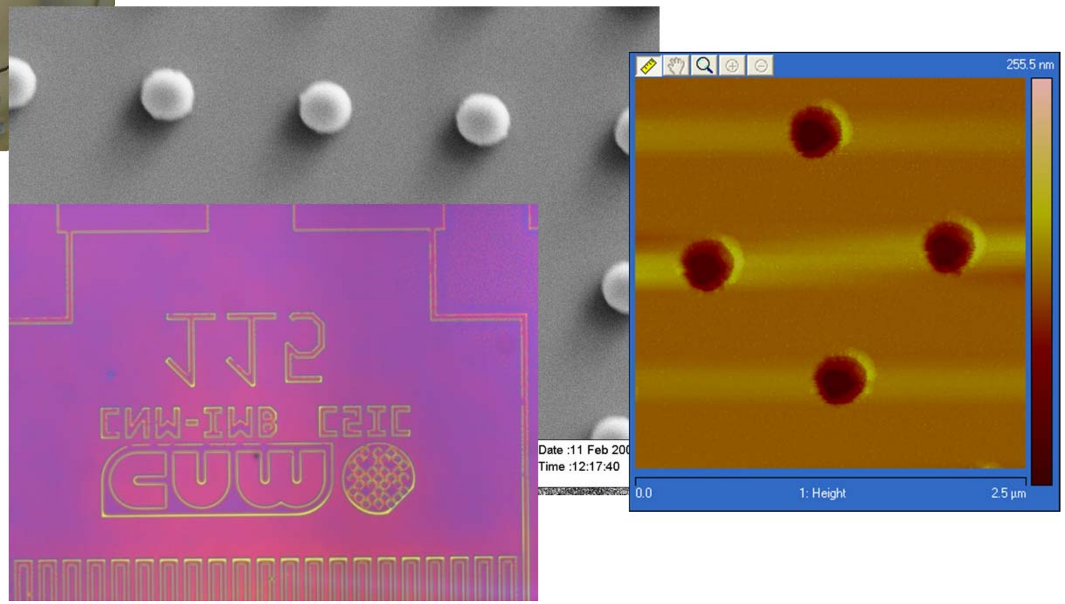
Silicon



Treated Silicon

UV-NIL: NPS300





NIL future…

- Combination of NIL techniques possible (HSQ as structural layer for UV-NIL, combination of thin films for lift-off, use of step&repeat NIL for enhancing mold capabilities, roll-to-roll NIL capabilities…)

- Main drawbacks: as a 1-1 transfer dimensions, defects and uniformity plays an important role for final success of the process.

- Alignment possible but… change your way of thinking with NIL!. Easier to achieve semi-3D imprints where several levels corresponds to different lithography levels (OLEDs fabricated with only 1-lithography NIL step).

- Driving Key applications: LEDs, flexible substrates (OLEDs, displays, PVs), lenses (mobile phone cameras), μ-fluidics…


ENDING...
500nm