Interdisciplinary Research Institute
from interacting molecules to cellular regulatory networks

iemn UMR CNRS 8520 Recherche Formation Transfert

Silicon Nanowires, growth, functionalization and applications.

Y. Coffinier

Interdisciplinary Research Institute (IRI), Bio-Interface Group

Electronic, MicroElectronic and Nanotechnology Institute (IEMN)

Lille, France

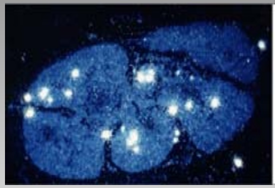
www.iri.cnrs.fr

www.iemn.univ-lille1.fr

Indo-French workshop 6-10 october 2008

CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

IRI@IEMN



Interdisciplinary Research Institute

from interacting molecules to cellular regulatory networks

IRI's theme : Studies on structure, dynamics and robustness of regulatory networks, in the context of multifactorial diseases

IRI research groups

Chromatinomics, Pierre-Olivier Angrand, Prof.Univ

Study of the functional network and the dynamics of the proteins that modify the histones and read these histone marks.

Systems epigenomics, Arndt Benecke CNRS

Identification of primary gene regulatory circuits, their plasticity, and their logical superposition a systemic approach to genomics, including chromatin dynamics, is required. Use of formal, numerical, and experimental methods in order to achieve such an integrated understanding.

Biointerfaces, Rabah Boukherroub CNRS

The aim of the research program is to take advantage of controlled surface chemistry, patterning (micrometer and nanometer scale), and surface analysis to study biomolecular interactions at a solid substrate

Biological nanosystems, Ralf Blossey (CNRSdirector of IRI)

Statistical mechanics and bioinformatics approaches to model artificial and natural nanosystems in biology. We are particularly interested in biosensors, regulatory networks and hydrodynamics on submicron scales.

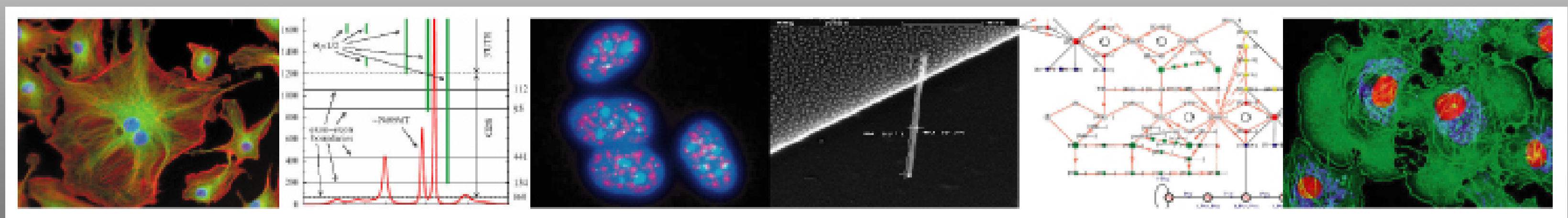
50 peoples

Biophotonics, Laurent Héliot, CNRS

The mission of the Biophotonics team is to imagine, develop and make available novel technologies and methods for real-time imaging of molecular events (dynamics, activities, interactions, assemblage,…) in living cells.

Multicellular dynamics, Yasuki Saka, CNRS

Aims to elucidate how cells decide their behaviours in response to the external queues in multicellular contexts such as embryogenesis. We are particularly interested in 1) how cells interpret extracellular signals and express a certain set of genes and 2) how cells interact each other during vertebrate development.



OUTLINE :

A) Silicon Nanowires growth

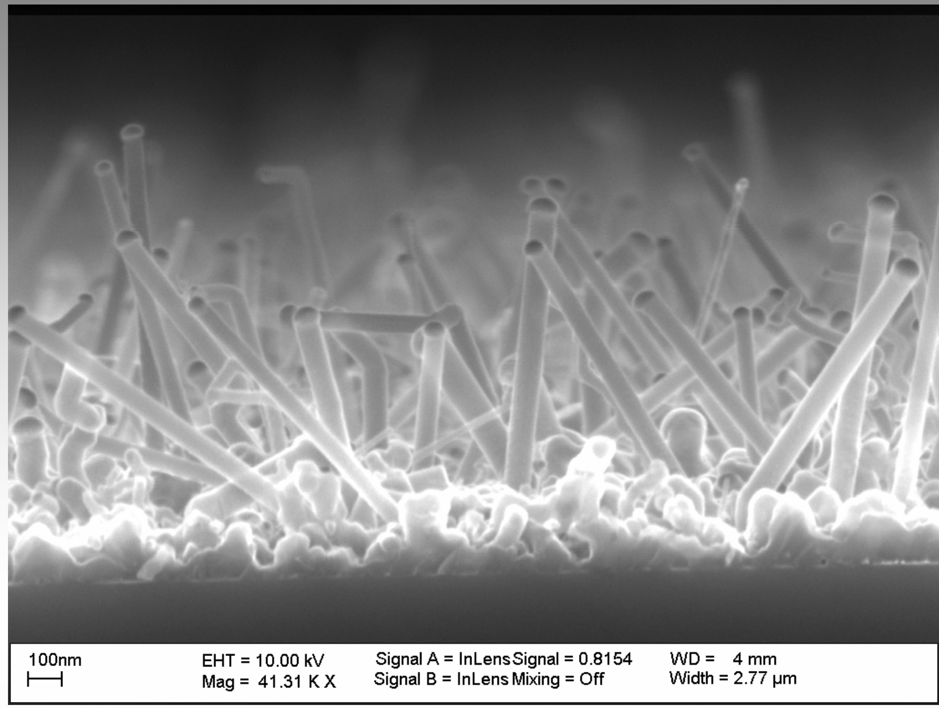
- **Chemical Vapor Deposition (CVD)**
- **Electroless (EE)**

B) Silicon Nanowires functionalization and applications

I) Desorption/Ionization On Silicon for Mass-Spectrometry (DIOS-MS)

II) Superhydrophobic surfaces and Electrowetting on Dielectric (EWOD)

Many Applications



- Field effect transistors (FET)
- Interconnects
- Nanoelectrode arrays
- Nano biosensors with high surface area
- Optical and electrical properties : Label-free sensors with high sensitivity

I) Synthesis

❖ **Lithography techniques**

❖ **Laser ablation of metal-containing silicon targets**
(Lieber *et al.* 1998; S. T. Lee *et al.* 1998)

❖ **"Oxide-assisted" technique:** it consists on thermal evaporation of highly pure powder mixture of silicon and silicon dioxide at 1200°C
(S. T. Lee *et al.* 1999)

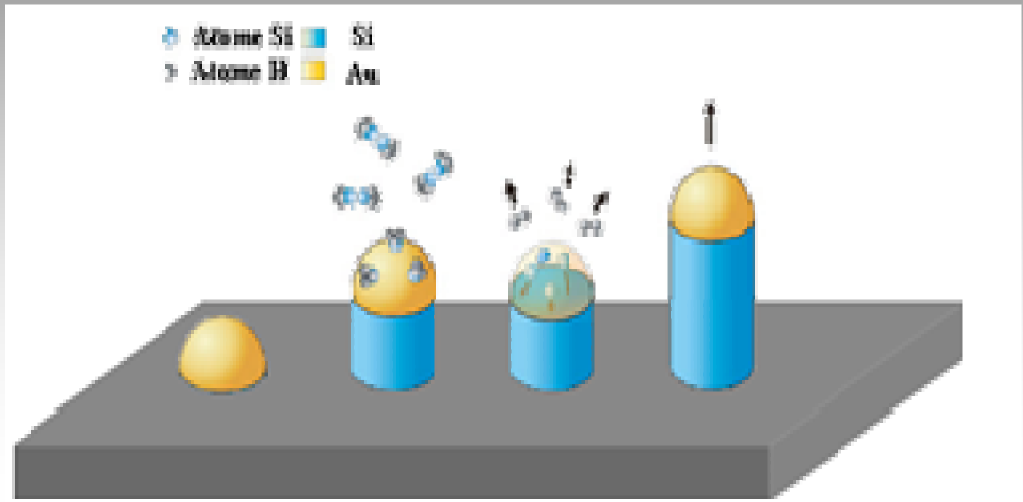
❖ **"Solution phase" technique (FLS: fluid-liquid-solid):** in this process, a precursor such as diphenylsilane was thermally degraded in supercritical fluid at 400 to 500°C in the presence of gold nanocrystals
(B. A. Korgel *et al.* 2000)

❖ **Solid-Liquid-Solid (SLS) technique**

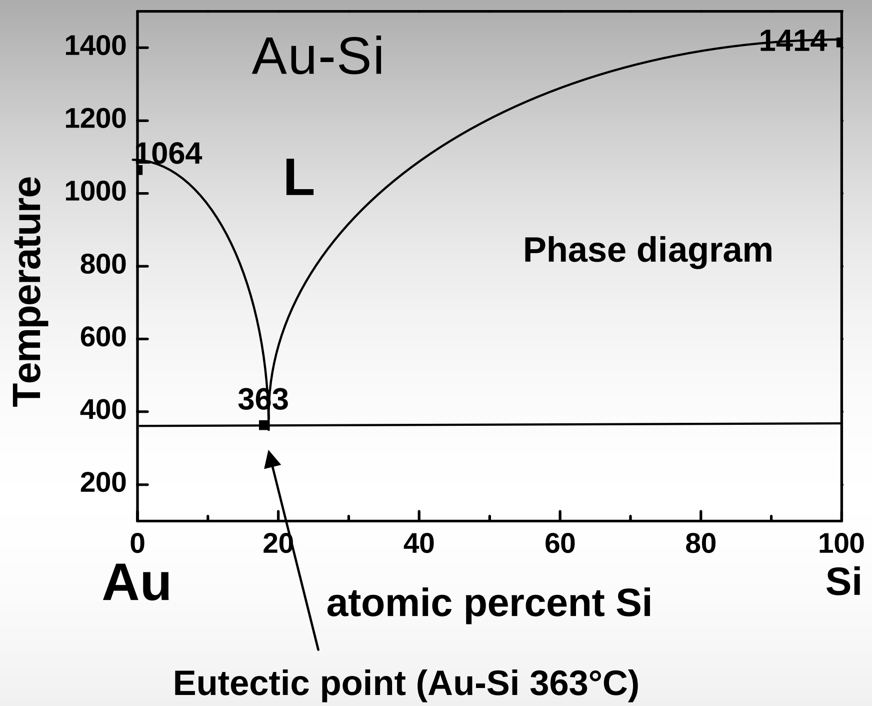
❖ **Vapor-Liquid-Solid (VLS) technique (CVD):** the fundamental process is based on metal catalyst directed chemical vapor deposition of silicon
(R. S. Wagner 1964).

❖ **Electroless etching (EE)** : The technique is based on the galvanic displacement of Si by Ag^+ *to* Ag^0 reduction on the wafer surface

I) Vapor-Liquid-Solid Nanowire Growth Mechanism

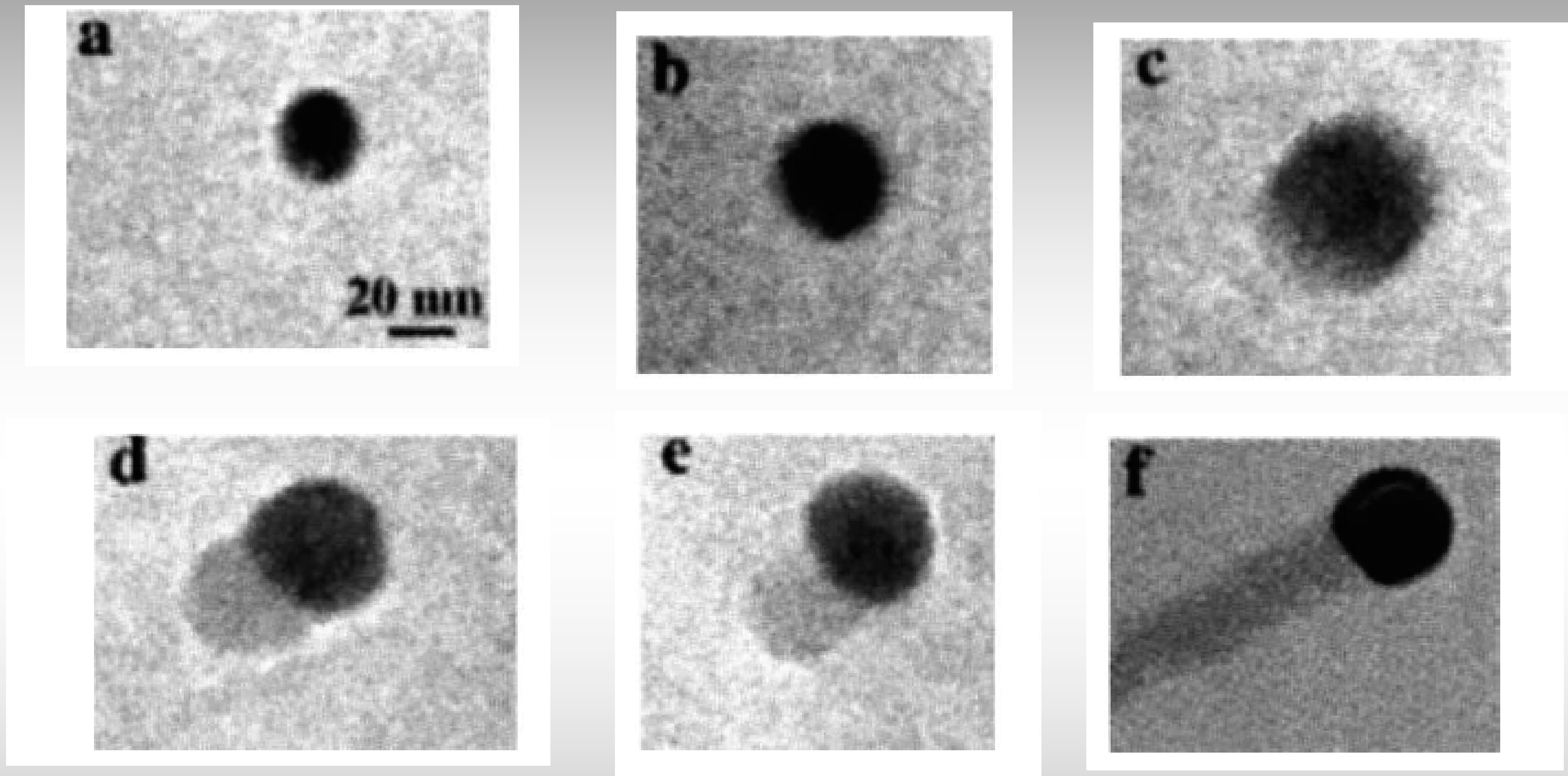


P 0.1-5mbar
T 440-500°C
Time 1- 60 min
SiH4 12-80 sccm



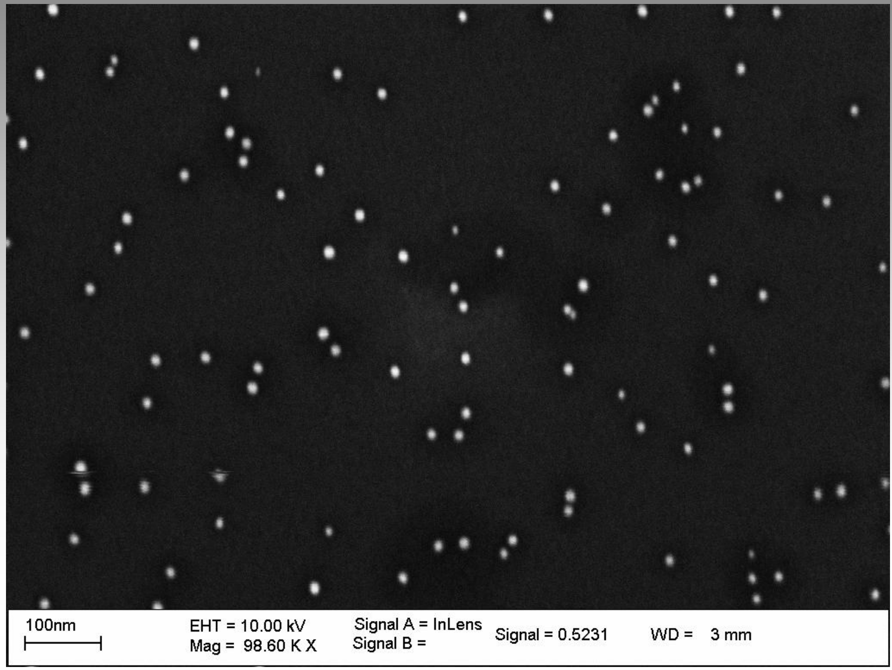
- Soon the liquid metal reaches saturation of silicon in solution and begins to precipitate out Si crystals against the substrate.
- As the crystal grows, it lifts the liquid catalyst up and a fiber crystal is formed.
- A longer time in the furnace produces a longer fiber.
- The diameter of the catalyst controls the diameter of the fiber. Fine metal catalyst powders produce fine fibers and larger diameter catalyst produce larger diameter fibers or rod–like crystals.

I) Real-time observations of nanowire growth in situ high-temperature TEM. Validation of the VLS growth mechanism.

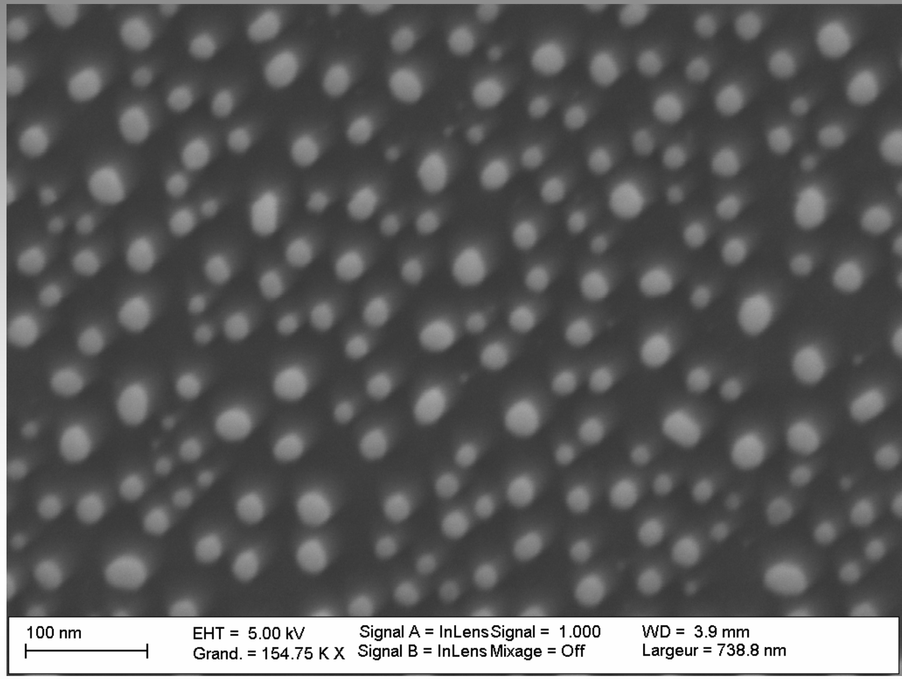


(a) Au nanoclusters
(b) Alloying initiated
(c) Nucleation at the solid-liquid interface
(d) and (e) nanocrystal elongates with further Si condensation
(f) Nanowire

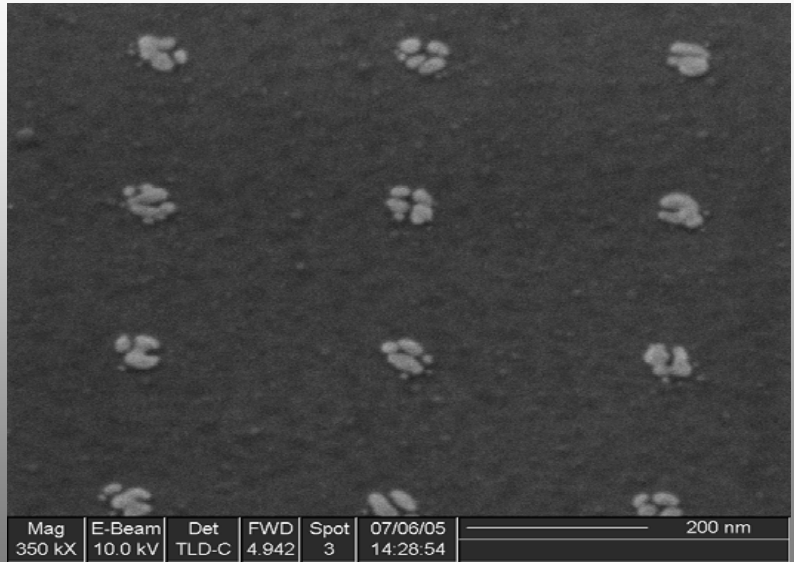
I) Gold catalysts deposition



Si-O-Si-$(CH_2)_3$-NH_3^+ + Gold NPs (5, 10, 20 nm)



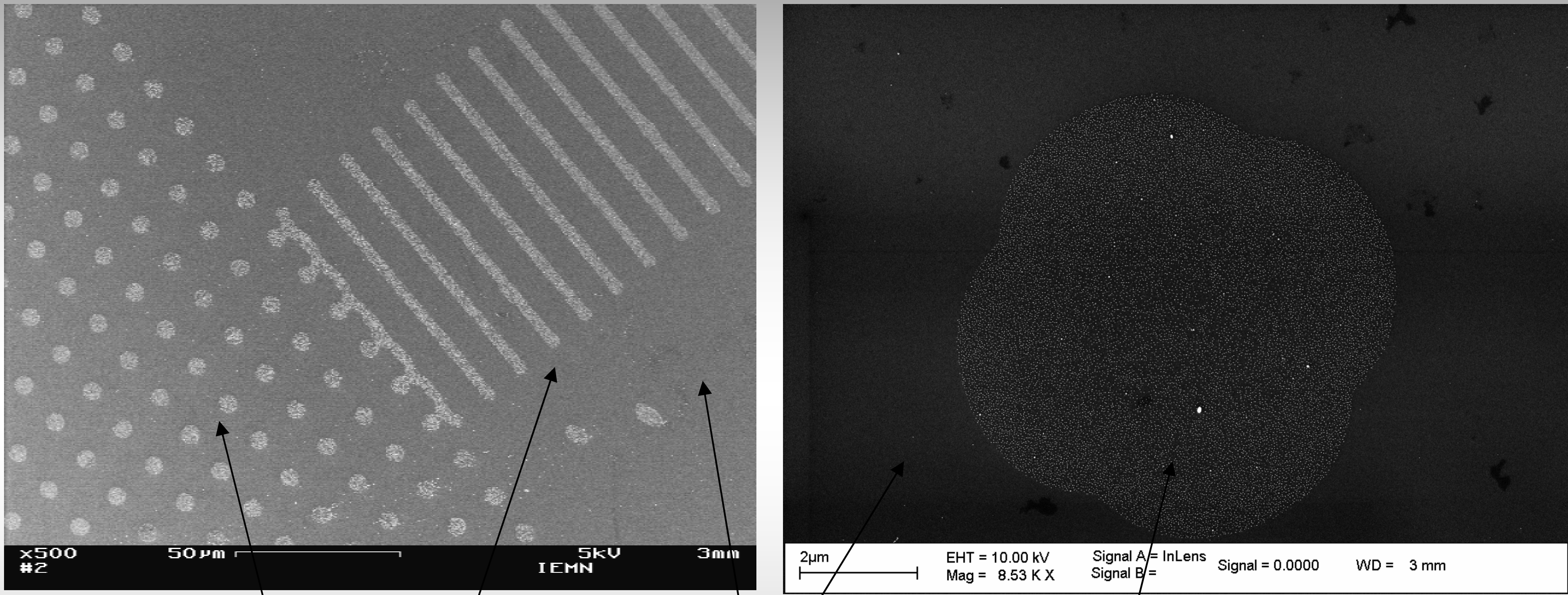
Dewetting of gold layer (15-40 nm)



Gold patterns made by EBL (15-…nm)

I) Gold catalysts deposition

By patterning the surface with hydrophilic/Hydrophobic contrast, we can selectively deposit gold NPs



Lines and dots of NPs on hydrophilic zone (APTS)

NPs

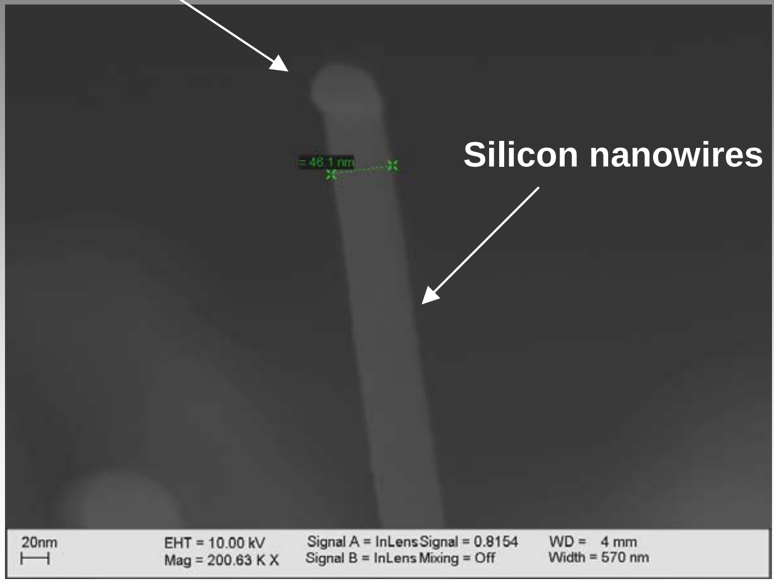
Hydrophobic zone (OTS)

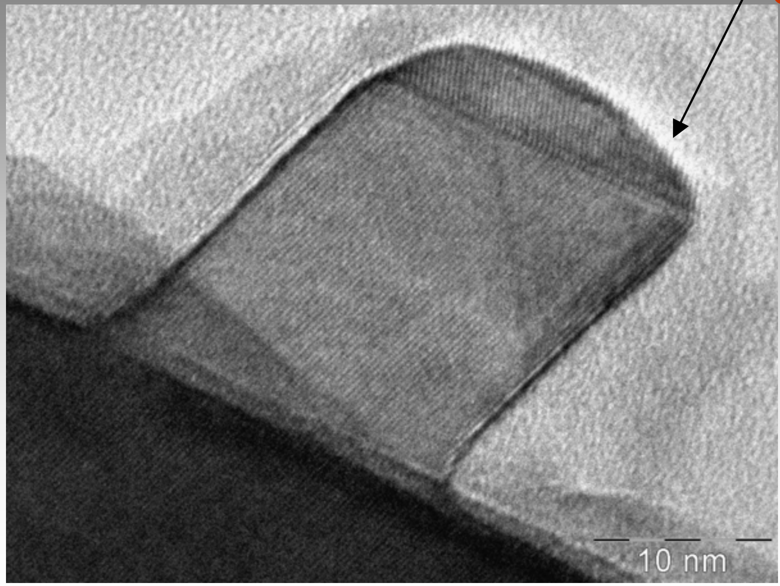
Patterns are designed by photolithography

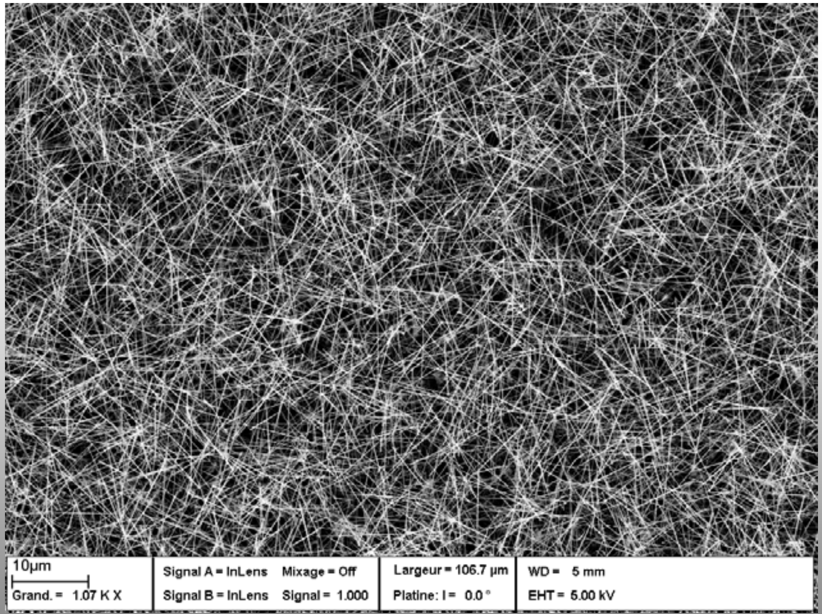
I) Large scale SiNWs

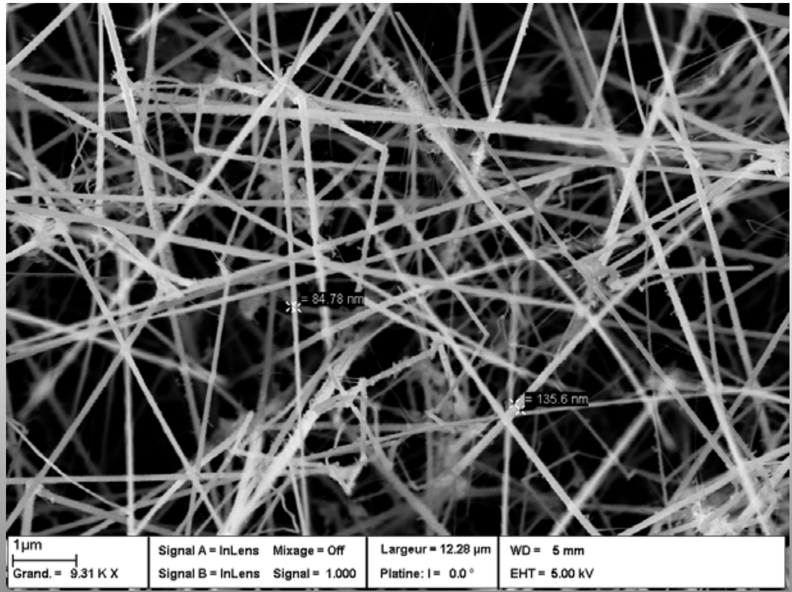
Gold catalyst

HRTEM of SiNWS



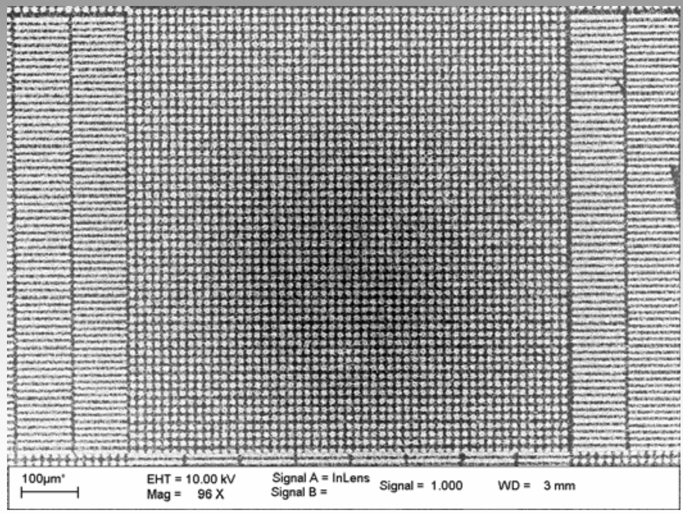


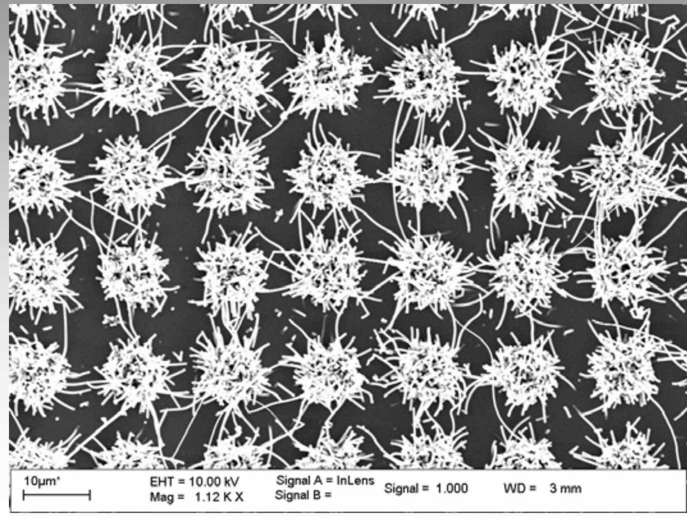


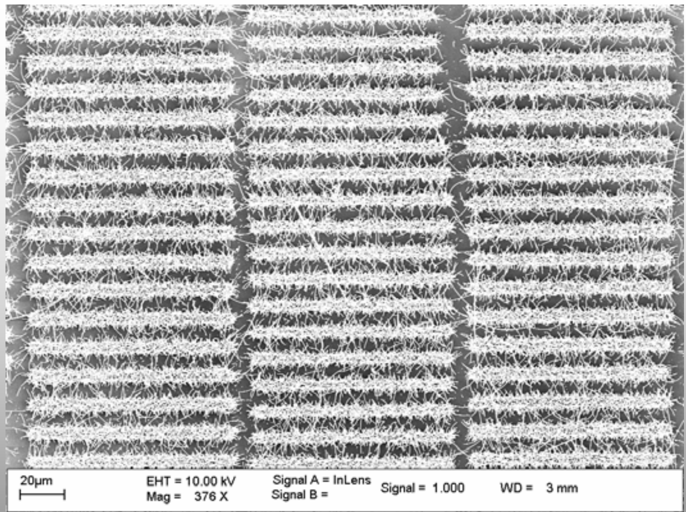


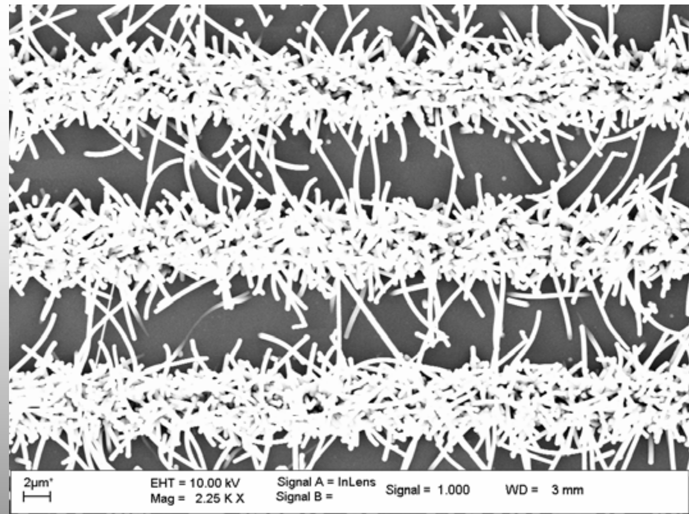
SEM pictures of Silicon nanowires

I) Patterned SiNWs



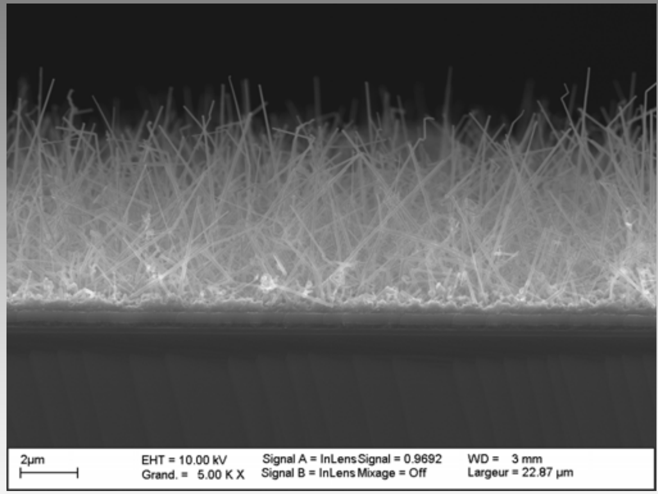


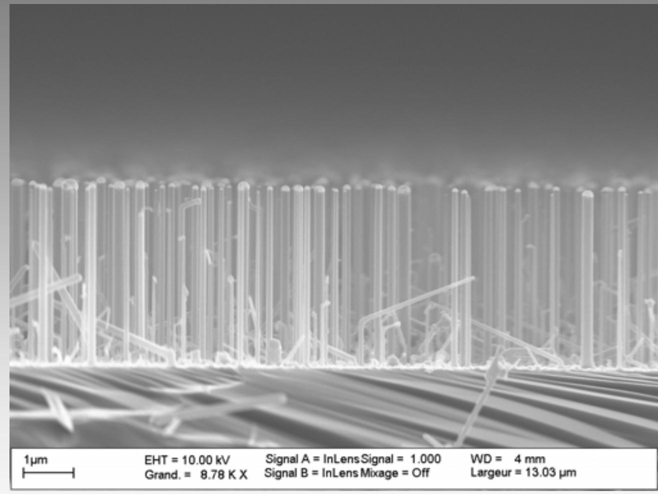


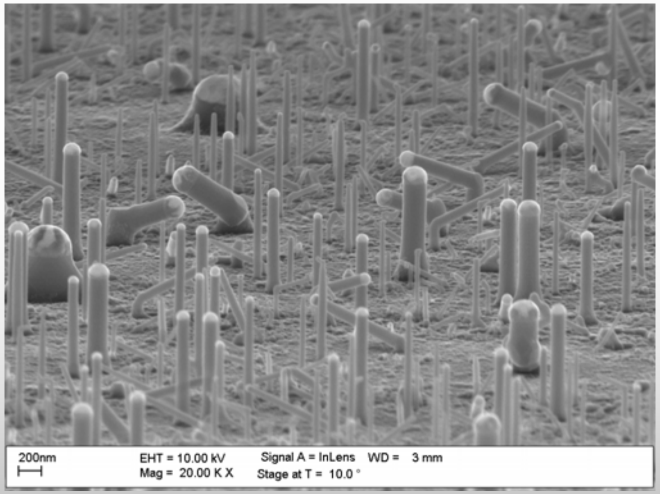


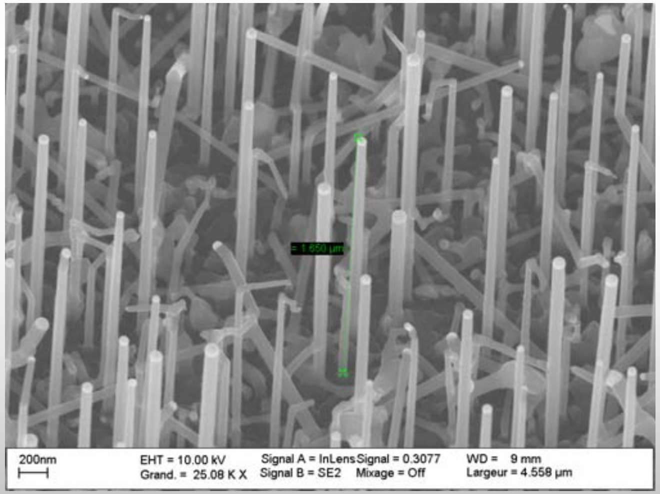
SEM pictures of Silicon nanowires

I) Orientation of SiNWs







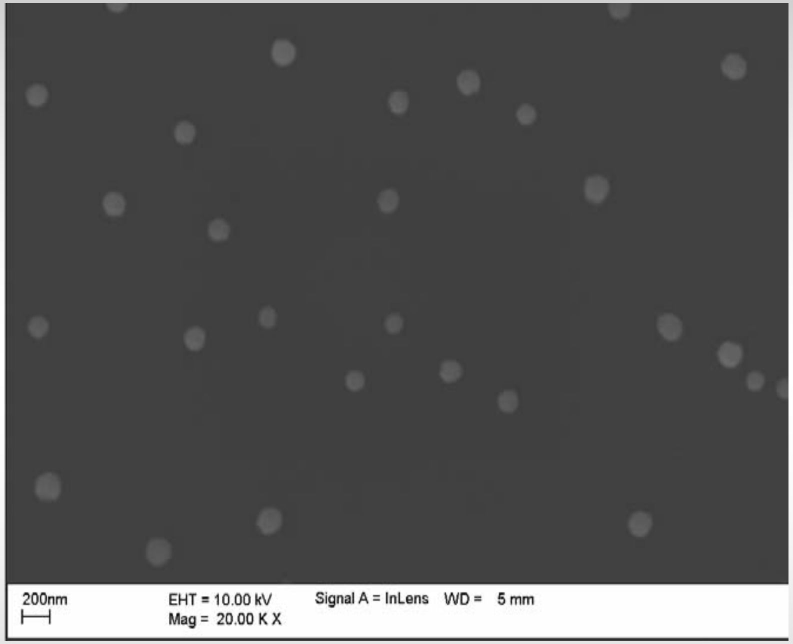


Playing on :

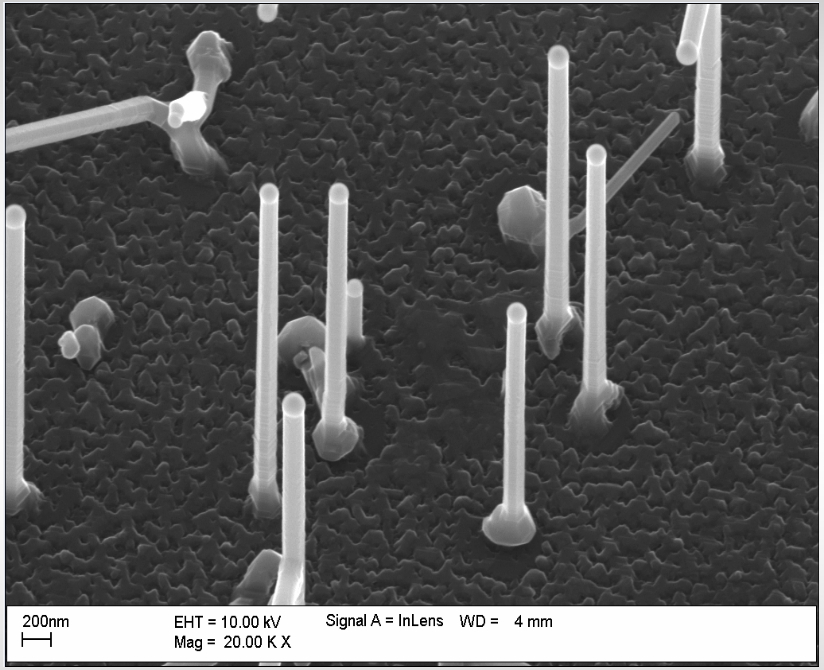
- **Growth temperature**
- **Pressure in furnace**
- **Silane flow, dilution H_2**
- **Time**
- **Surface interface (SiH, SiO2, cristalline orientation)**

I) Orientation of SiNWs

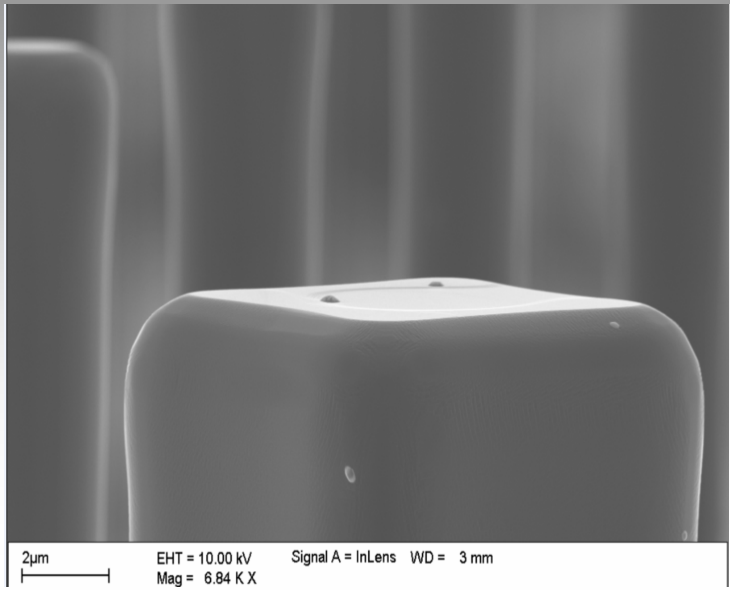
Au sur Si (111) under UHV conditions

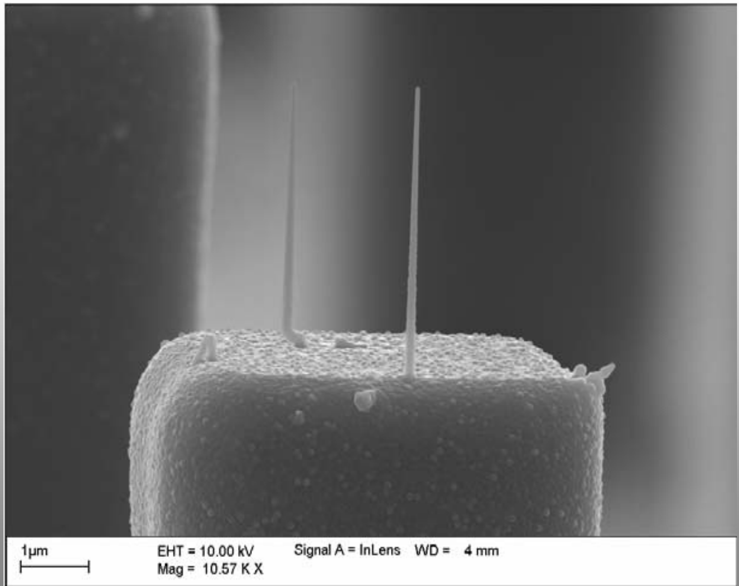


CVD



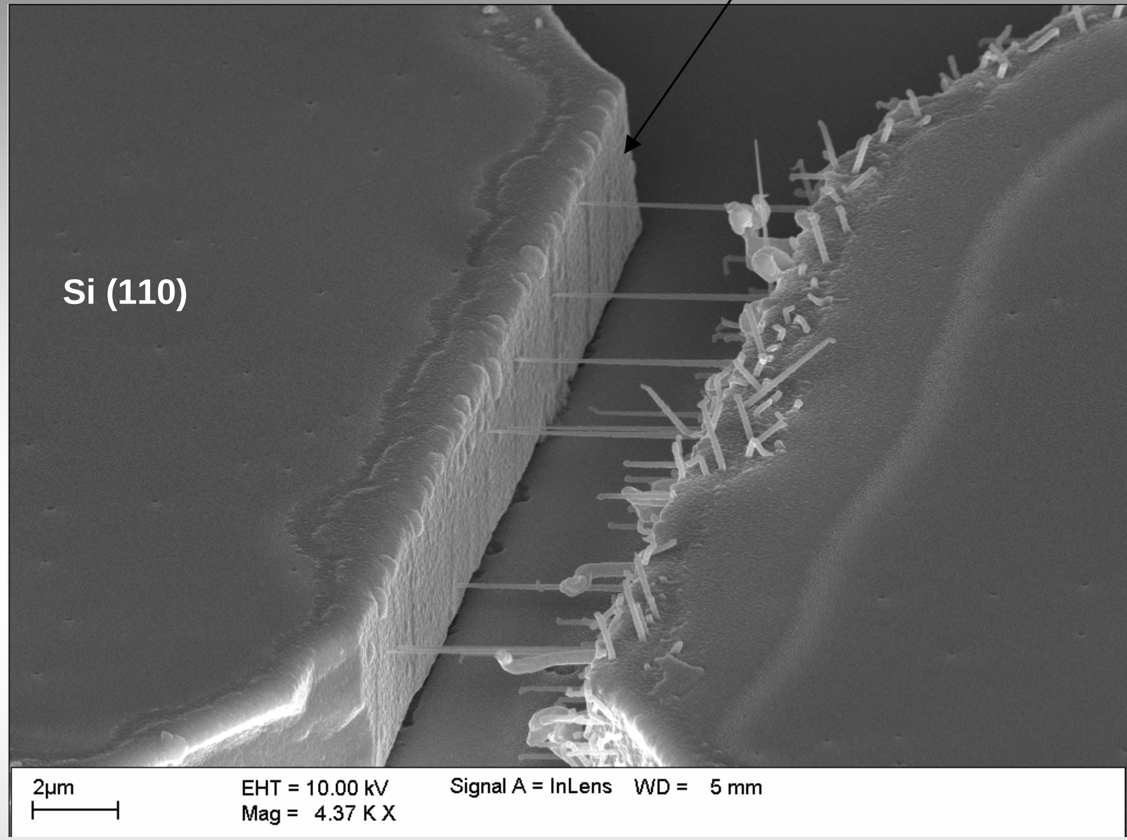
I) Localized growth of SiNWs



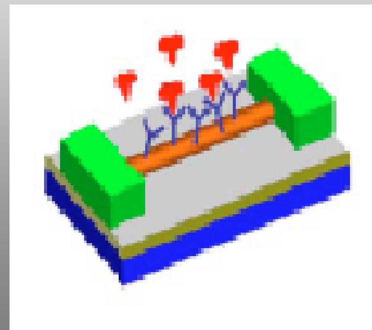


CVD growth

Si (111)

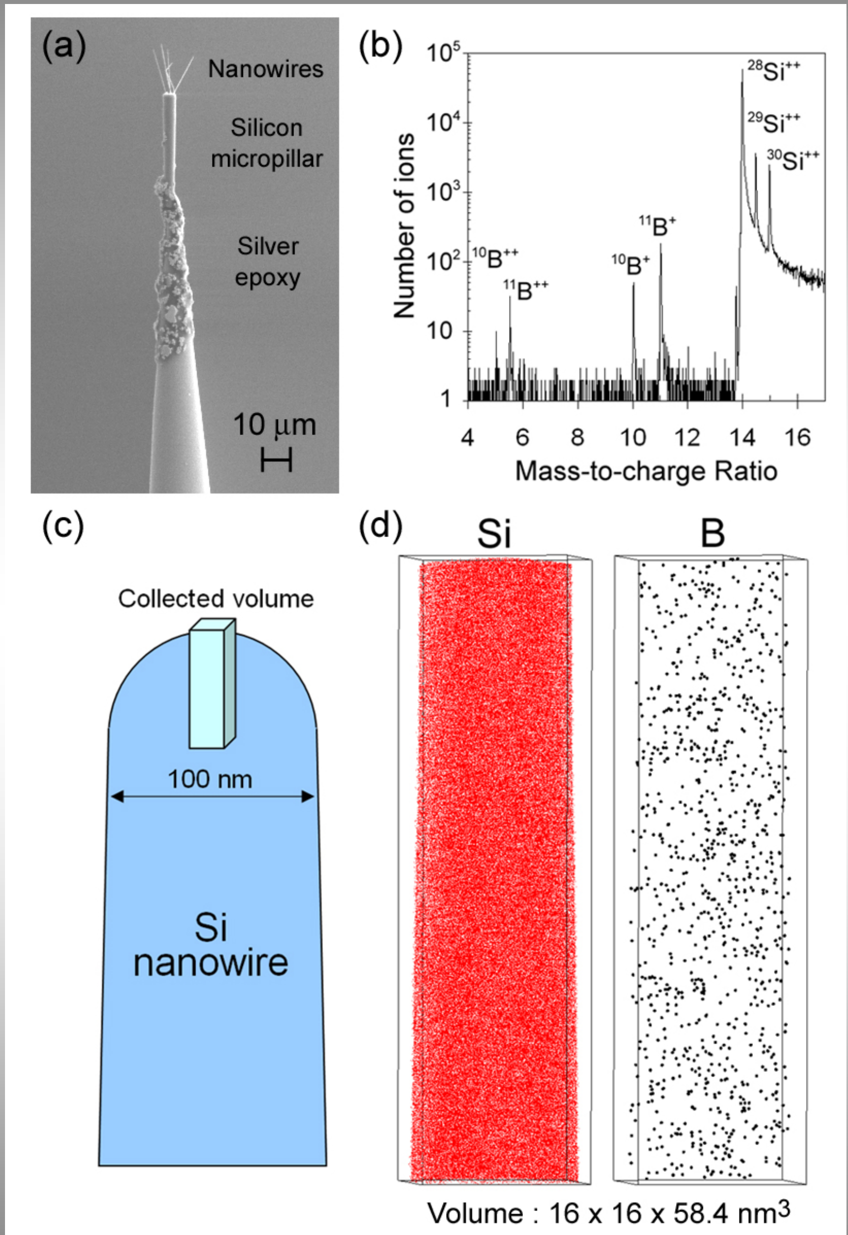


SOI (110)



Biosensors for label free detection of molecules, in progress!!!

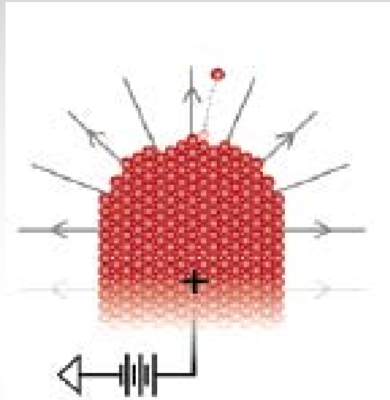
I) Study of SiNWs doping by 3D Atom Probe Tomography



Doping $1.3 \pm 0.3 \times 10^{20}$ $B.cm^{-3}$

Gold islands were deposited on Si µpillars (4µm* 60µm) under UHV
Au was evaporated from a W filament whereas Si surface was heated at T>450°C
During the growing step we added B_2H_6 for doping

Ions are expulsed from the wire
30 V/nm

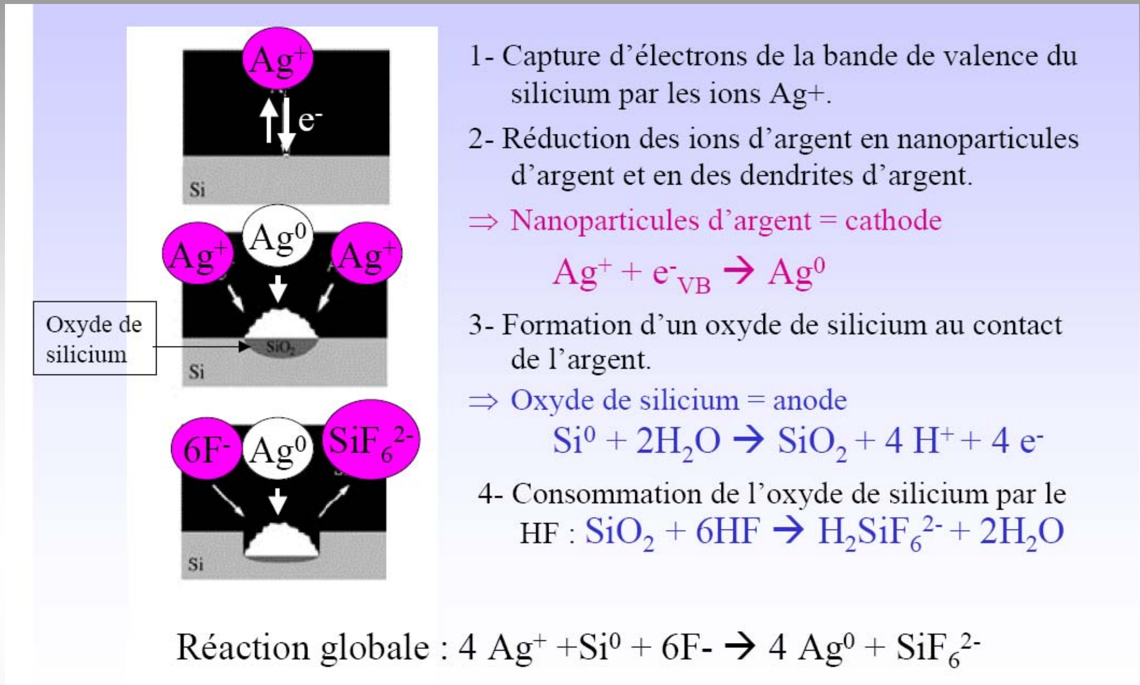


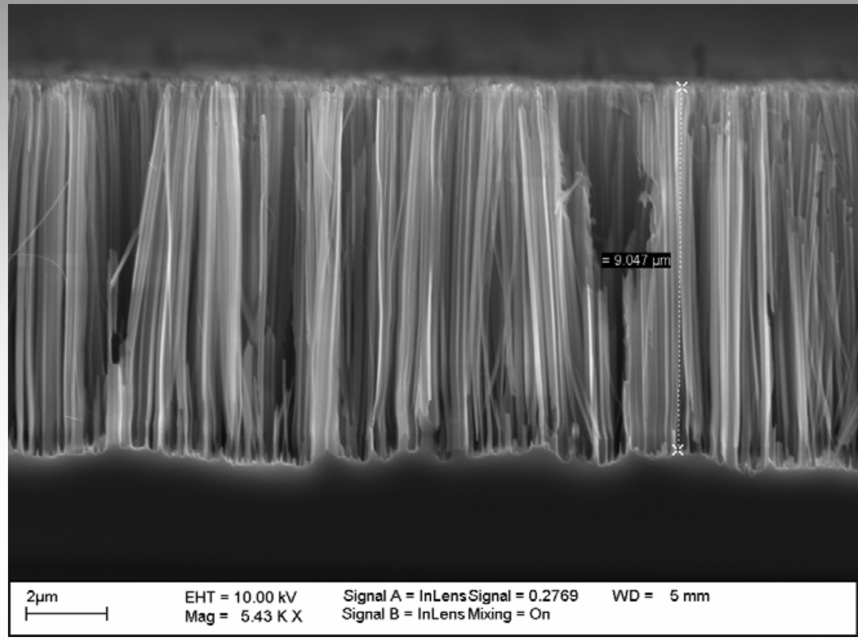
NW surface atoms are field-evaporated by means of high-frequency (2 kHz) laser pulses (100 nJ/350fs) superimposed on the DC voltage (15KV).
Only ions which are field-evaporated from a 20 nm wide area located in the center of the NW are mass-analyzed.
The 3DAP analysis was obtained at a collection rate of 0.4 million atoms/h.
During the evaporation process, the DC applied voltage remains constant due to the cylinder shape of the nanowire.

Collaboration IRI, IEMN and GPM (Rouen, Groupe of P. Pareige)

Tao Xu et al. To be published in JVST

II) SiNW synthesis by aqueous EE method



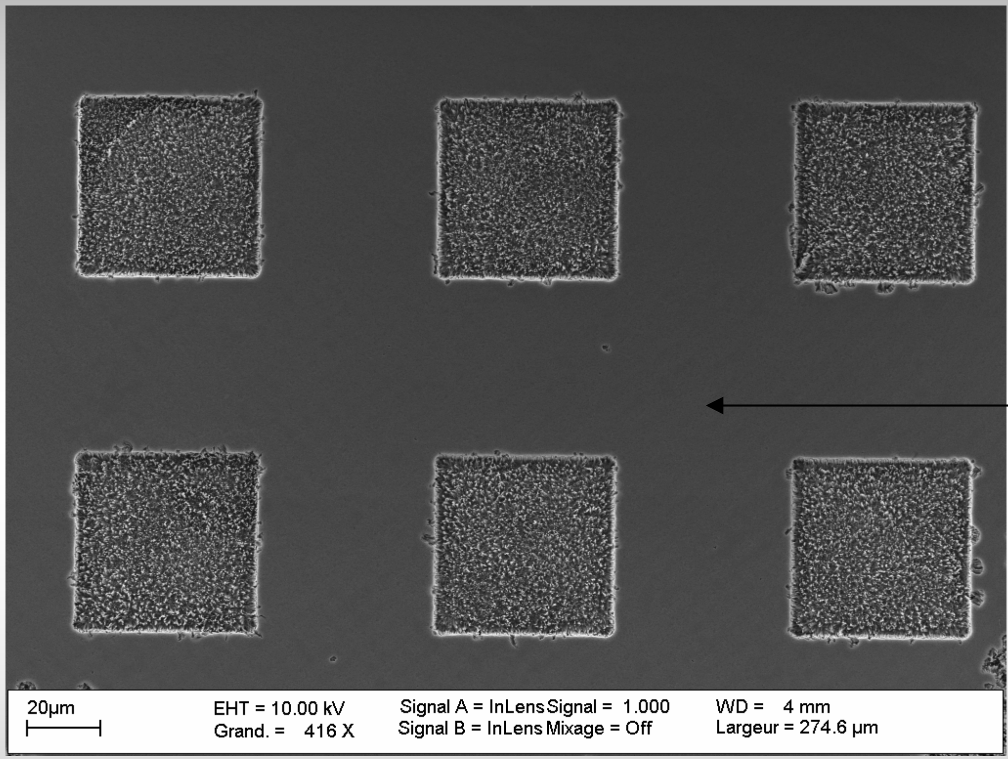


Nanowires synthesized by this approach were vertically aligned and consistent throughout batches across large areas up to wafer-scale.

Both etching time and AgNO3 concentration controlled nanowire length, roughly linearly, down to 5 µm at short immersion times (10 min).
At longer etching times, nanowire lengths were controllable up to 150 µm
Diameter 80-100nm

II) SiNW synthesis by aqueous EE method

Making patterns of SiNW *via* EE way



C18 or Resist
Removed after by acetone or plasma O2

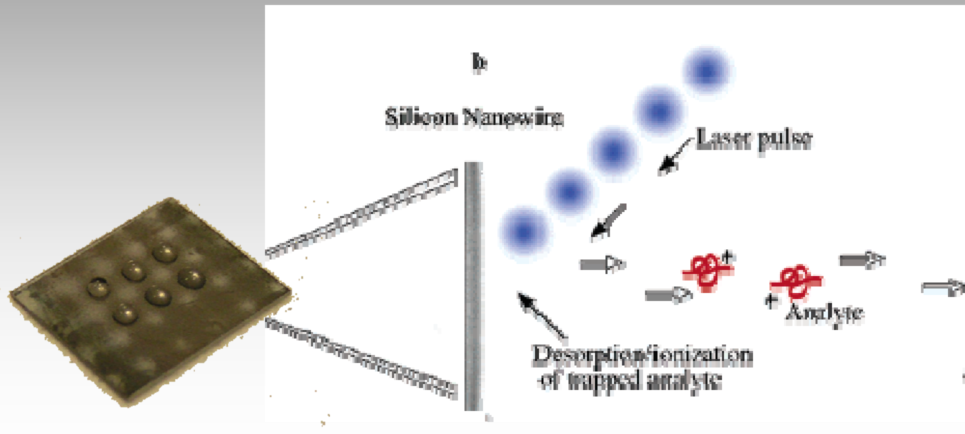
Si is protected by resist or organic layer (Octadecene)

Case of resist, patterns are made by classical photolithography and then dip in AgNO3/HF solution

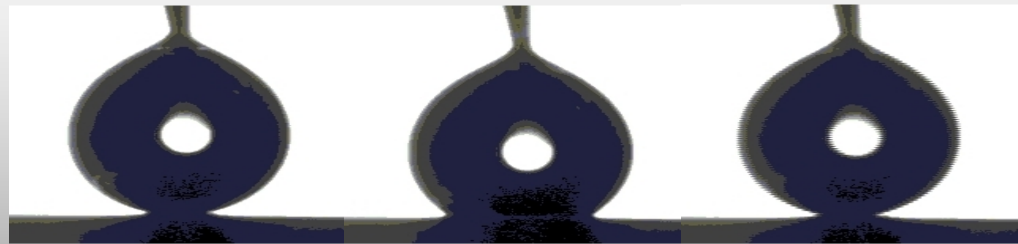
Case of organic layer, patterns are made by using optical mask and UV/O3 chamber, then dip in the AgNO3/HF solution

B) SiNWs functionalization and applications

- I) DIOS-MS

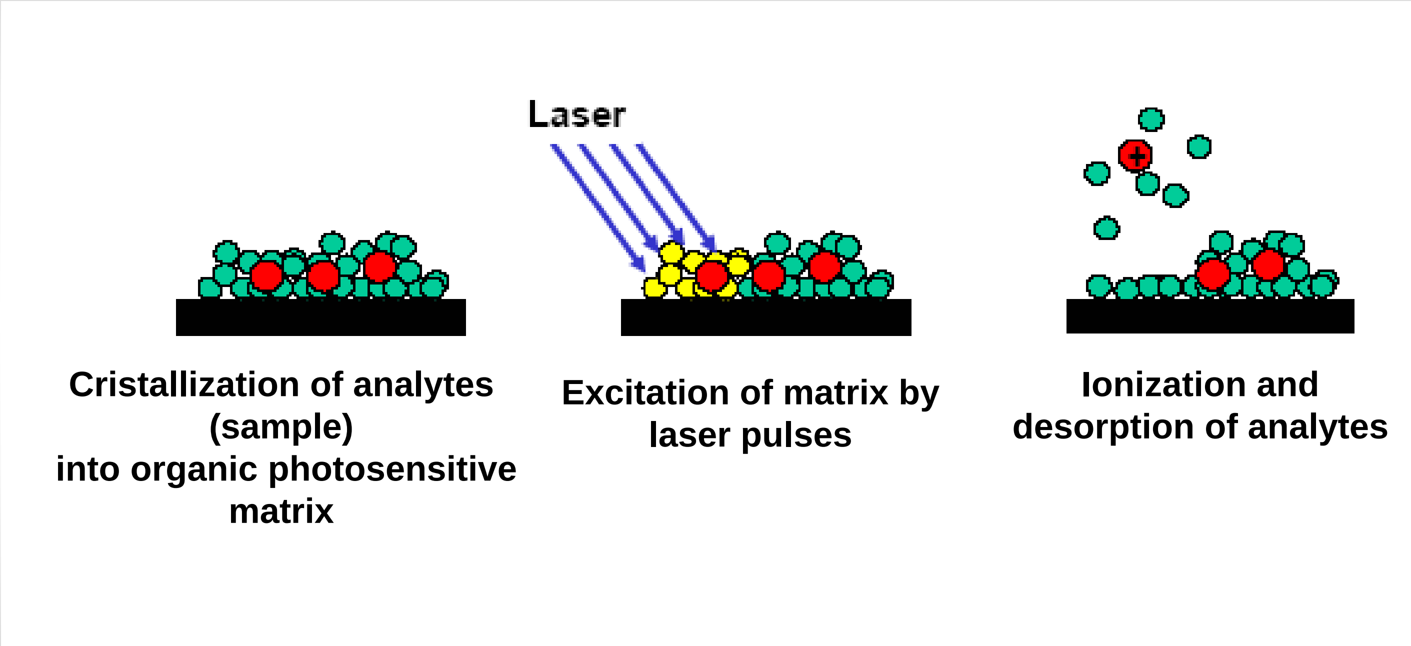


- II) EWOD

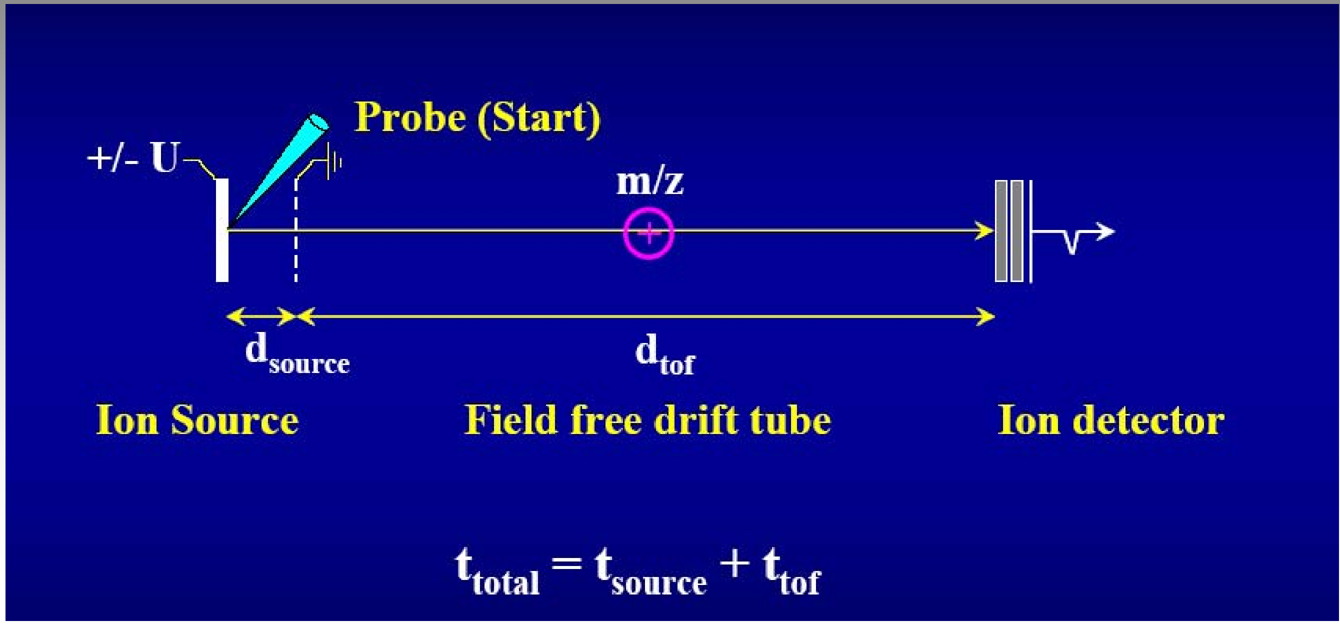


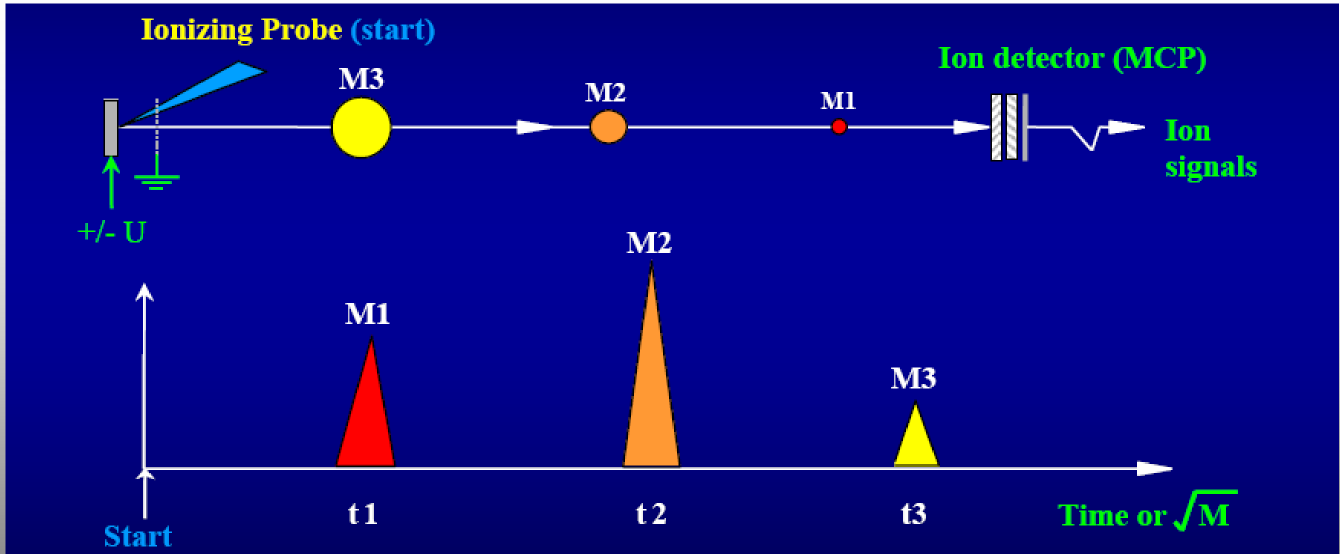
I) Desorption/Ionization On Silicon and Mass-Spectrometry (DIOS-MS)

In Biology, Mass Spectrometry analysis needs soft D/I step : MALDI for Matrix assisted Laser Desorption/Ionization



I) Time of Flight Mass Spectrometry (MS-TOF)





- Separation of analytes is function of m/z

Main drawbacks :

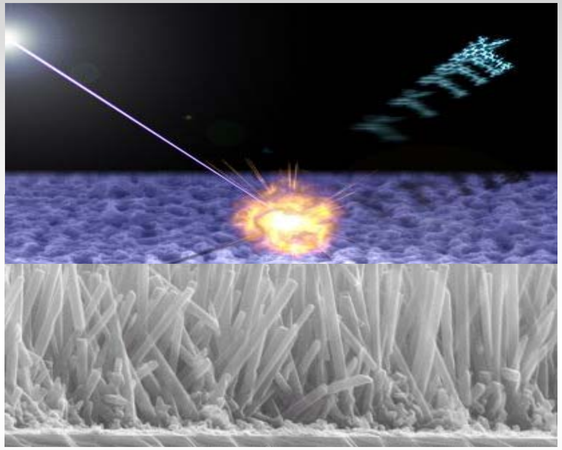
Analyte should :

-Soluble in the matrix

- Good cristallization : avoiding « hot spots »

- Small molecules (low molecular weight) detection (matrix ions).

To overcome these drawbacks



-**Optical properties**

- **Low thermic conductivity**

- **High surface area**

-**Control of their dimension, composition, density and location of nanowires**

- **Chemical modification (Target capture)**

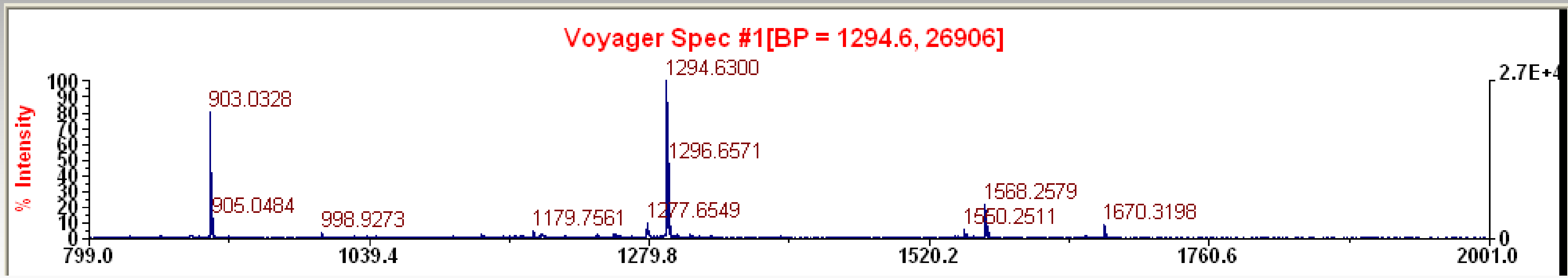
We expect

- **Reduction of background :**
Small molecules analysis (<500 Da)

Small laser fluence used
Limitations of analytes fragmentation

I) Preliminary results : DIOS-MS analysis of standard peptides

Ex.



MS analysis after D/I on SiNW

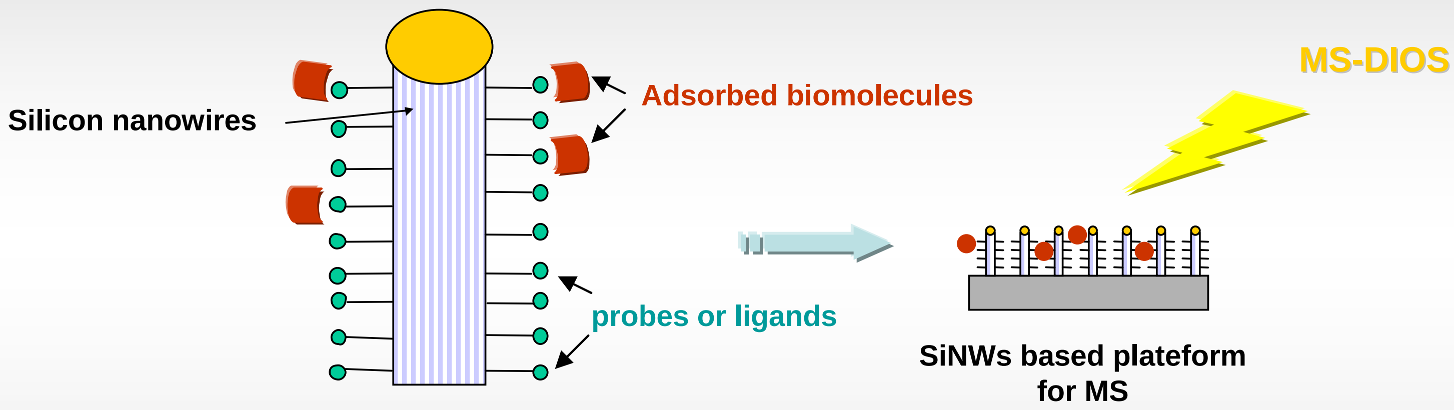
Peptides mix (Bradykinine (904Da), Angiotensine1 (1294Da), Fibrinopeptide (1565 Da) et Neurotensine (1671Da).

Femtomolar Detection

I) Chromatographic / MS plateform

- Specific adsorption of target molecules
- MS analysis

Same plateform



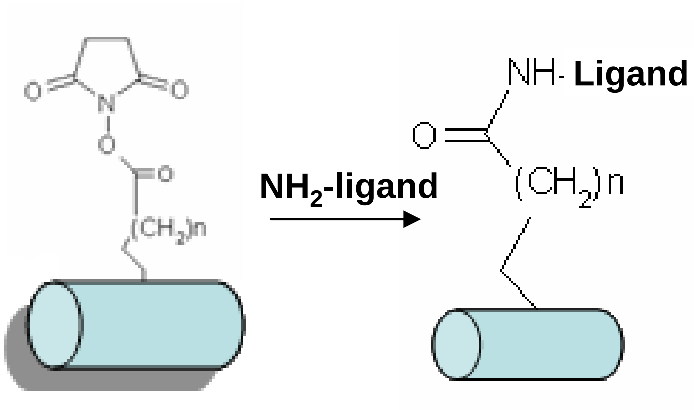
-Specific capture of target molecule from complex mix (chromatography)

- Higher Sensitivity for detection

-D/I directly on surfaces

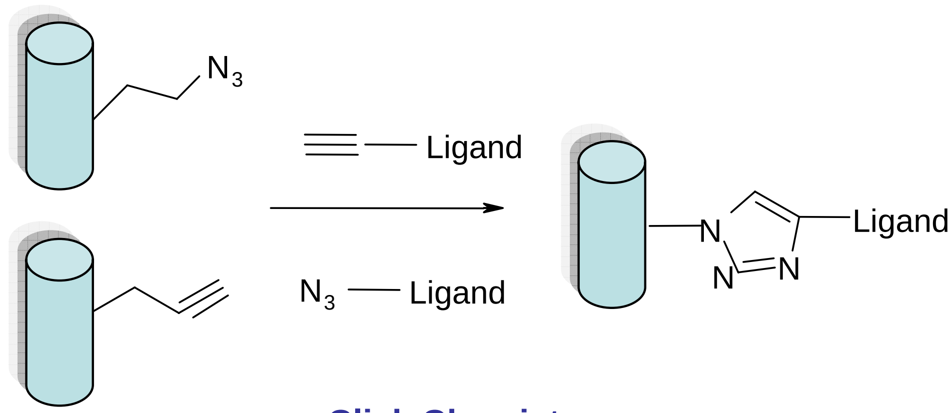
- Concentration of target molecules on surface in the case of low amount of these molecules

I) Several Chemistries are used for grafting specific ligands



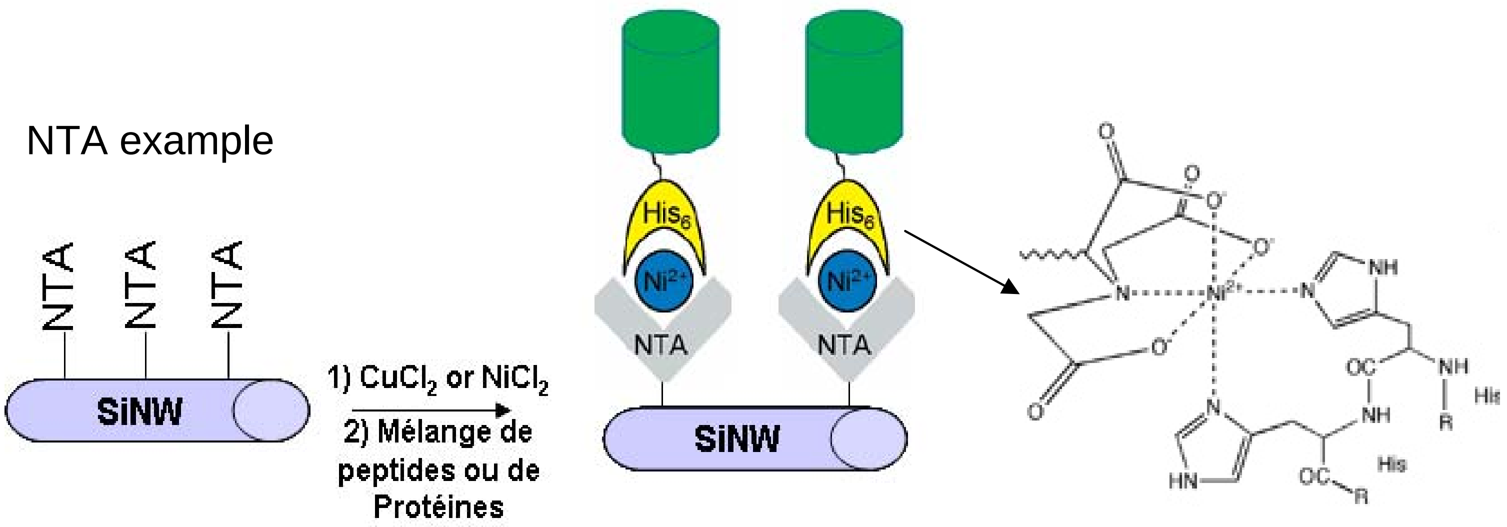
NHS ester acitvation

Amide bond

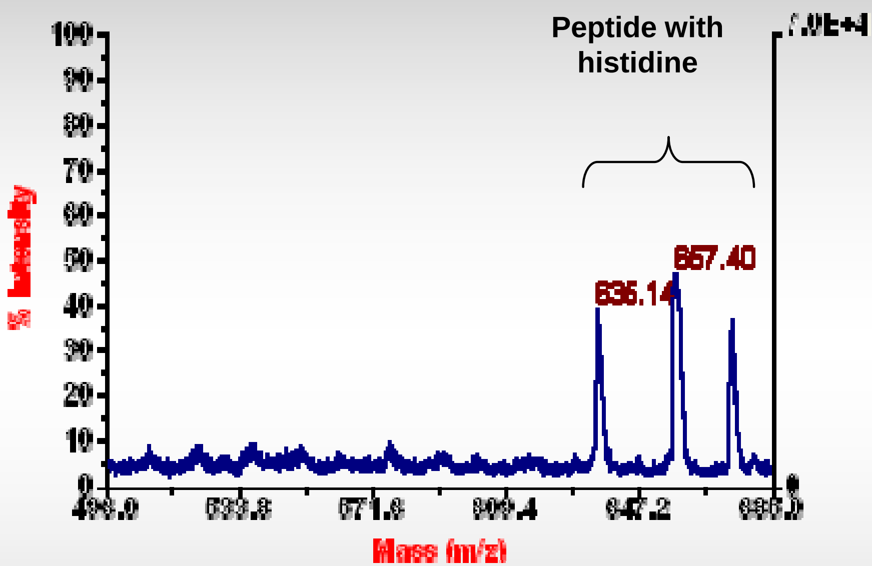


« Click Chemistry »

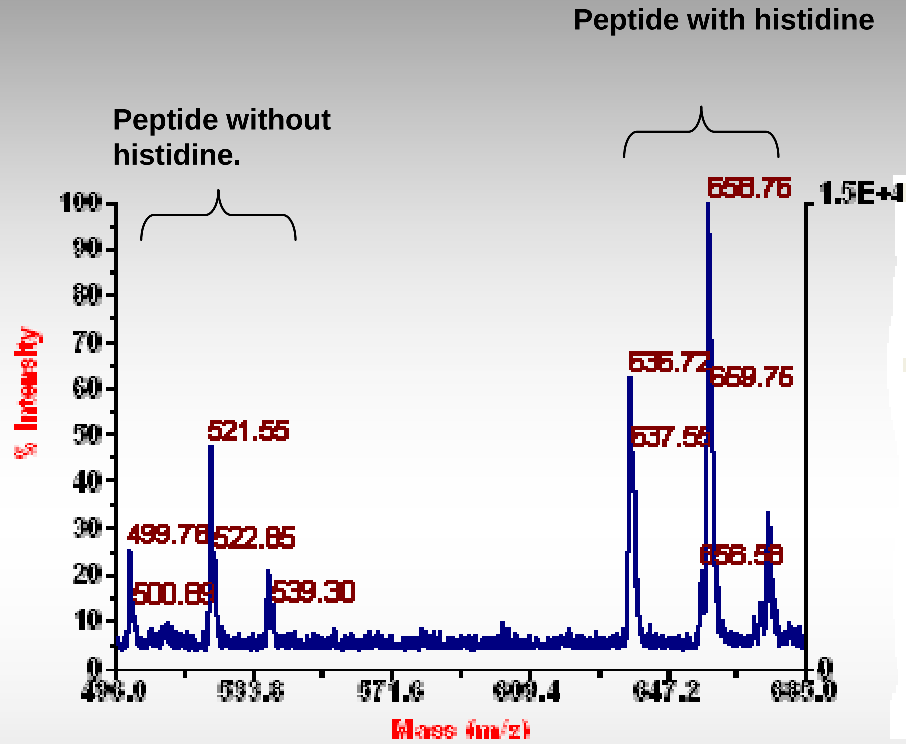
NTA example



I) MS analysis after specific capture of peptide



Detection of the specific peptide



Starting peptide mix

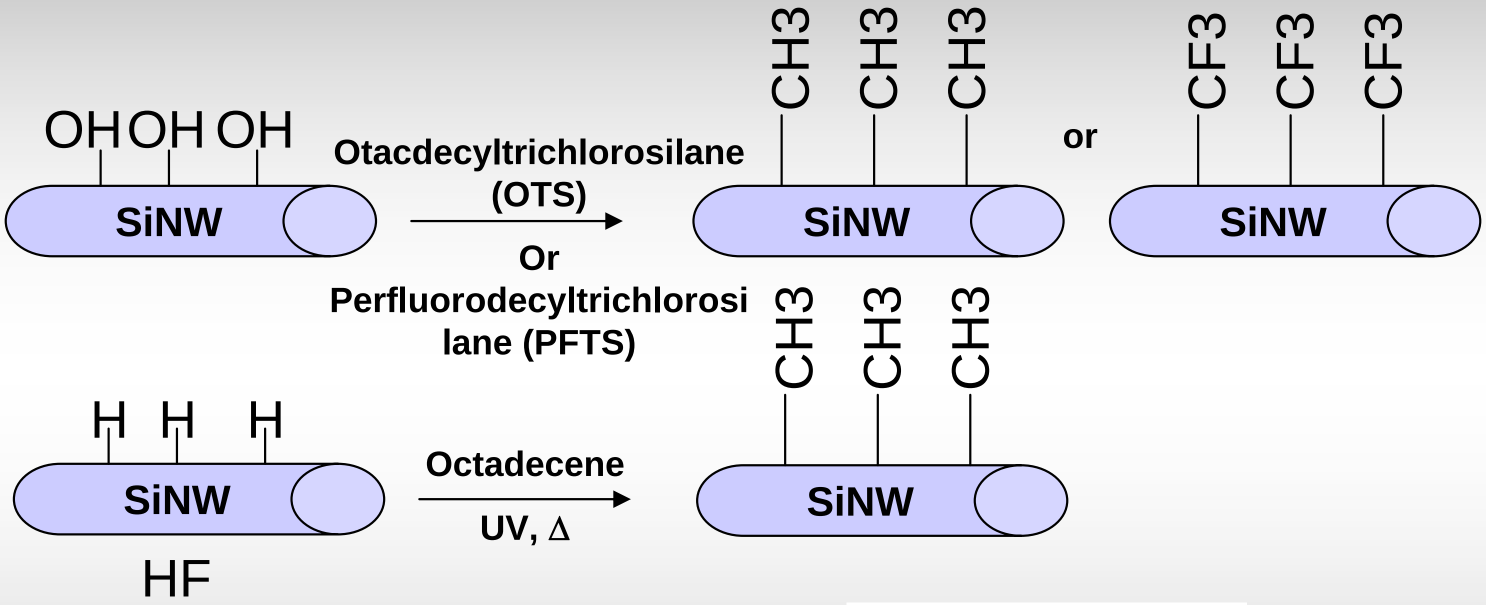
No detection of peptide without bivalent ions (Ni^{2+}) complex

II) Superhydrophobic surfaces

Roughness + hydrophobic chemistry (decreasing of surface energy)
= Superhydrophobic surface
« Lotus effect »

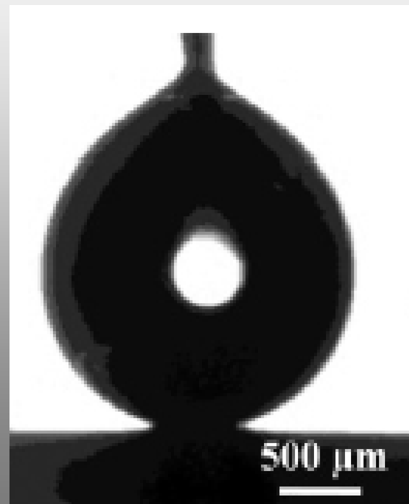
Silanization :

Hydrosilylation :

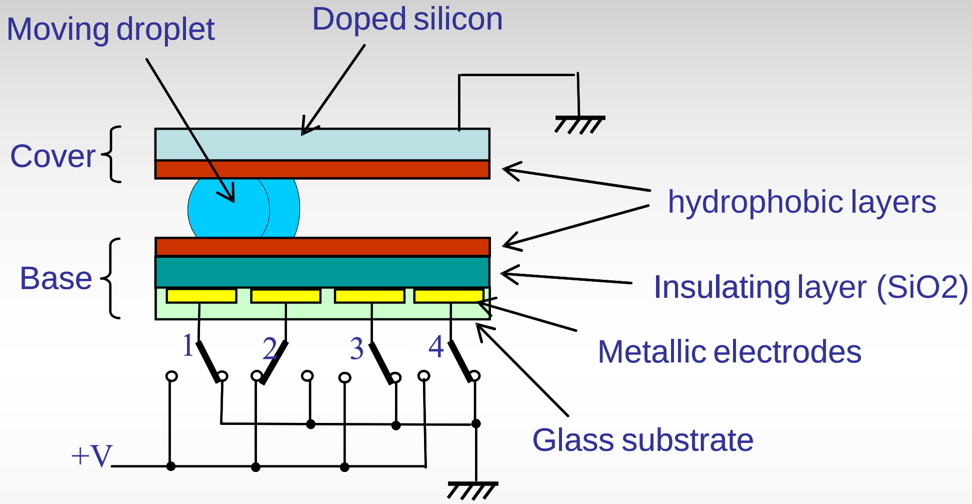


Or C_4F_8 plasma deposition (th. 60nm)

Contact angle = 160°

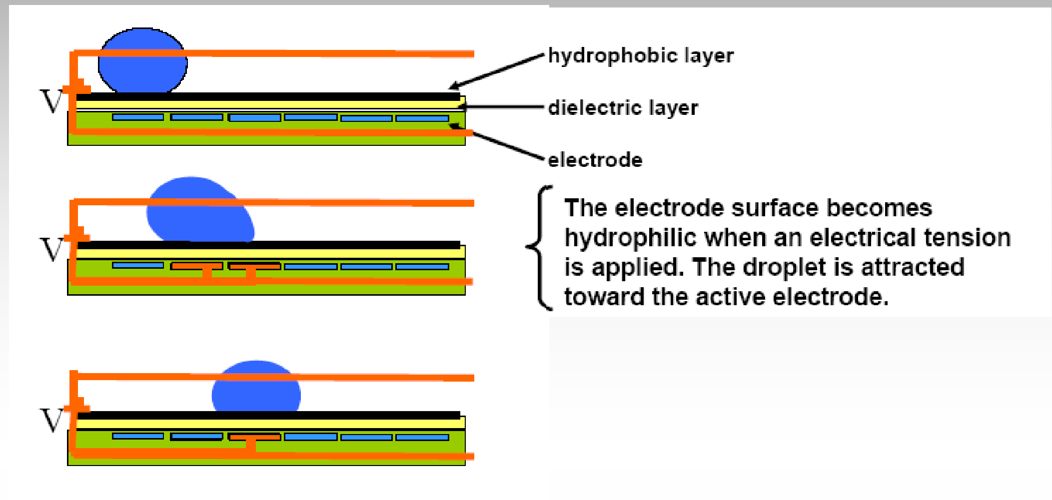


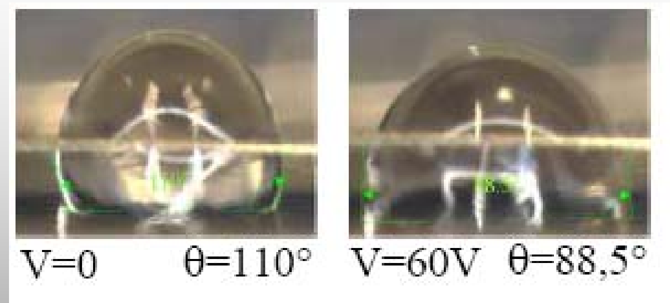
II) Principle of ElectroWetting On Dielectric (EWOD)



EWOD Set-up

Principle of EWOD

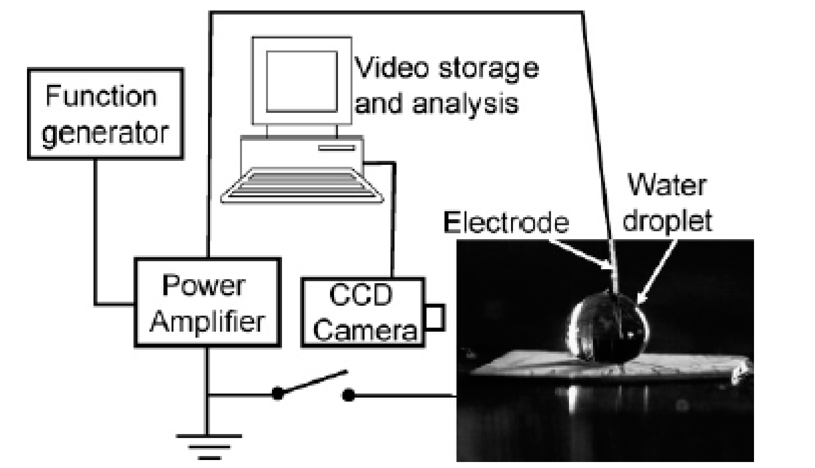


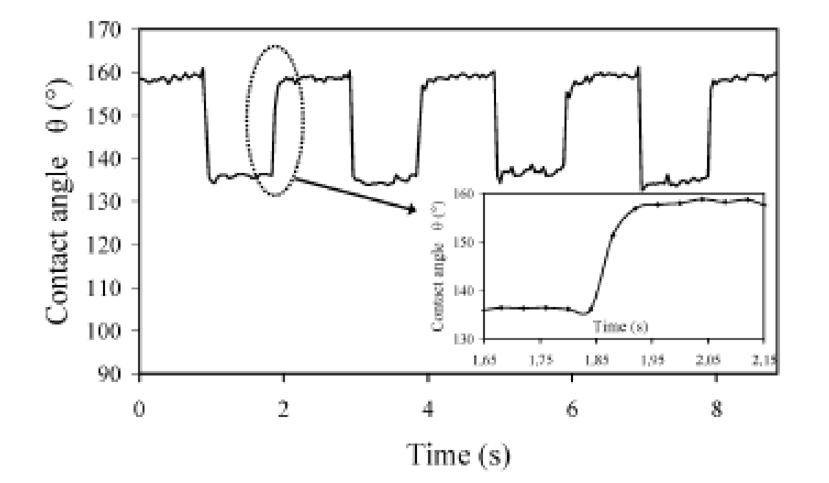


Ex. on Teflon coated surface

Used for Discrete actuation of liquid droplets in MF and Lab-on-Chip devices

II) Experimental set-up for the Electrowetting characterization of superhydrophobic surface on SiNW





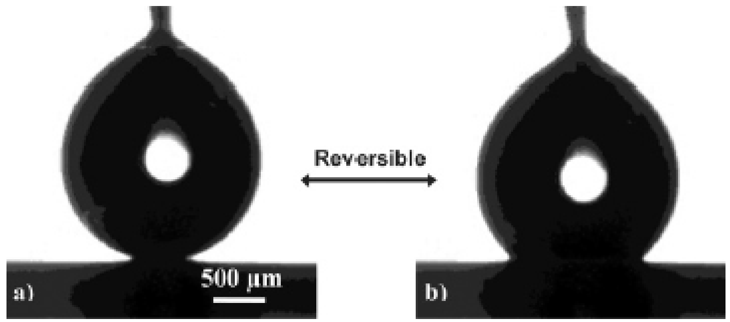
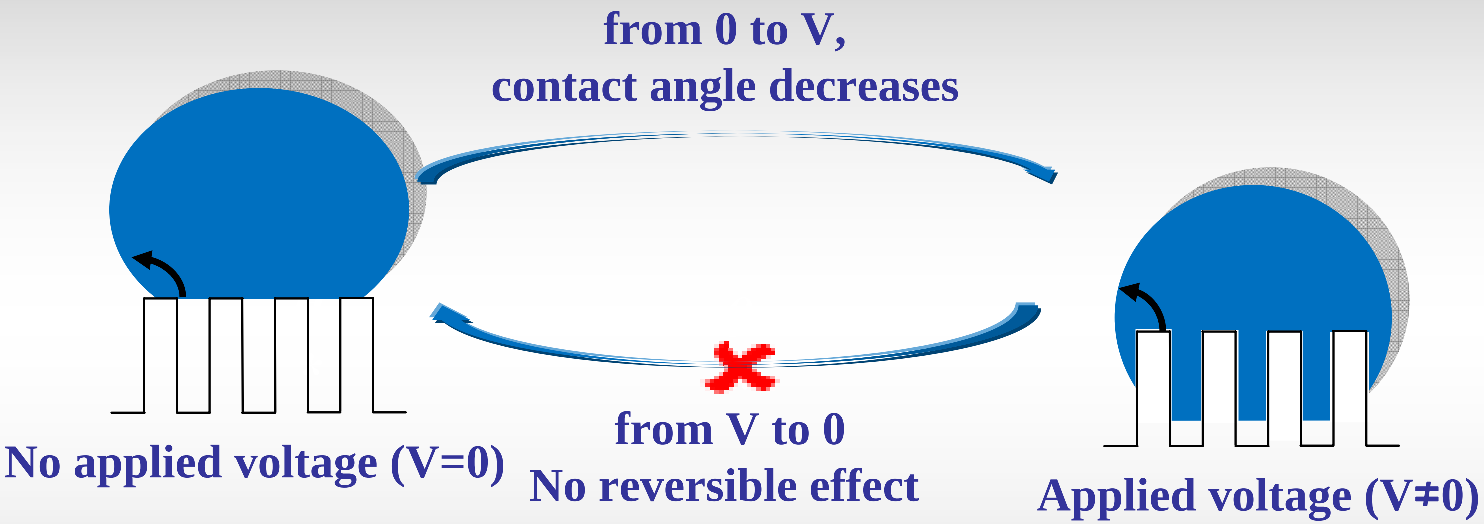


Figure 6. Electrowetting on silicon nanowires coated with hydrophobic fluoropolymer C_4F_8 displaying reversible electrowetting of a saline solution (100 mM KCl) in air : (a) contact angle = 160° at 0 V, (b) contact angle = 137° at 150 V_{TRMS}.

First example of total reversible electrowetting in air on superhydrophobic surface
Verplanck et al., Nanoletters, 2005 (State of the Art)

II) Why Electrowetting is reversible on our surfaces???

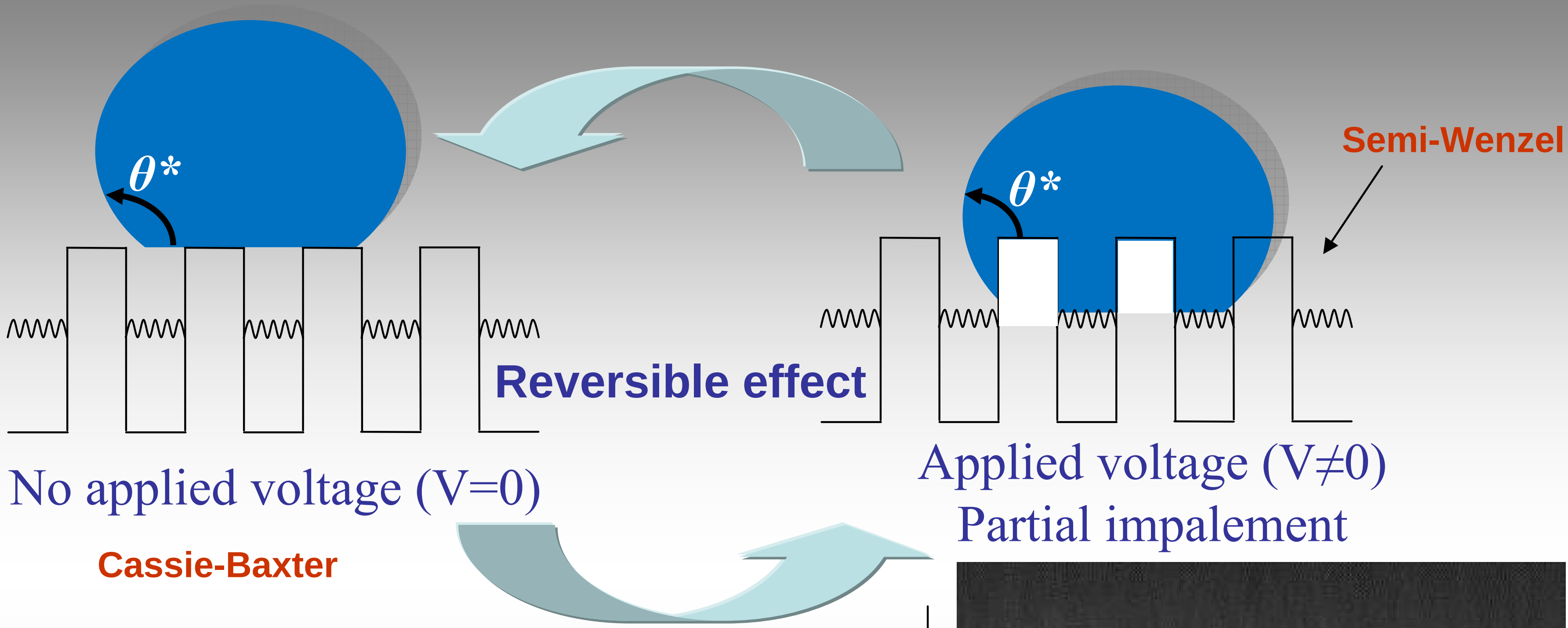
In the literature groups using structured surfaces (CNTs, Pillars…) for Electrowetting : no reversible effect in air



Cassie-Baxter
Hysteresis < 5°
Rolling ball effect
$$\cos \theta^* = -1 + \Phi_s(\cos \theta_E + 1)$$

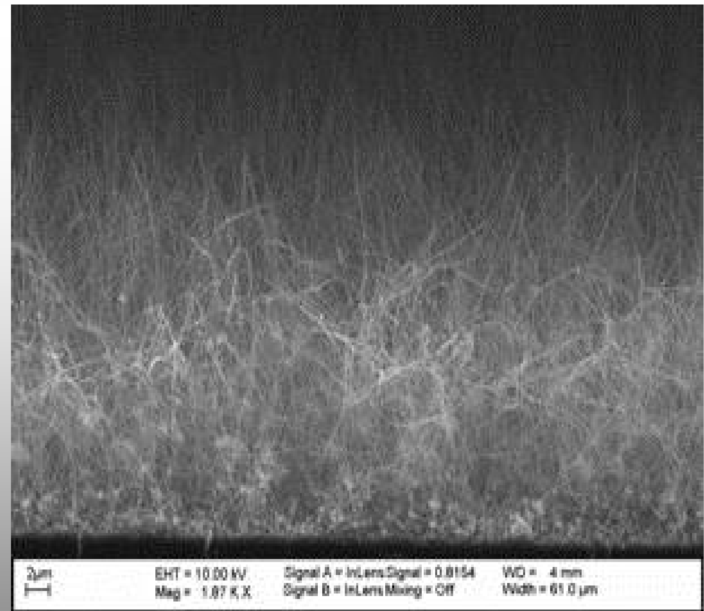
Wenzel
Hysteresis ~100°
$$\cos \theta^* = r\cos \theta_E$$
Total Impalement

II) Why Electrowetting is reversible on our surfaces???



Upper layer of SiNWs

Lower layer of SiNWs



Double layer of SiNWs prevents impalement of droplet after applying voltage
Making possible the reversibility!!!!

Other applications in the lab

-Scanning Enhanced Raman Spectroscopy (SERS)

- Label-free Biosensors

IV) Aknowledgements

IEMN Physic group :

Tao Xu, PhD Student

Bruno Grandidier, CNRS

Didier Stievenard, CNRS

IEMN microfluidic group :

Florian Lapierre, PhD Student

Vincent Thomy, MCF at USTL1

Philippe Brunet, CNRS

GPM Rouen Physic group :

Philippe Pareige, Prof.

IRI, Biointerfaces Group :

Rabah Boukherroub, CNRS

Gaëlle Piret, PhD student

Phuong Nhung Nguyen, PhD Student