Silicon Nanowires fabrication and surface nanostructuration by Metal Assisted Chemical Etching

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LCPM

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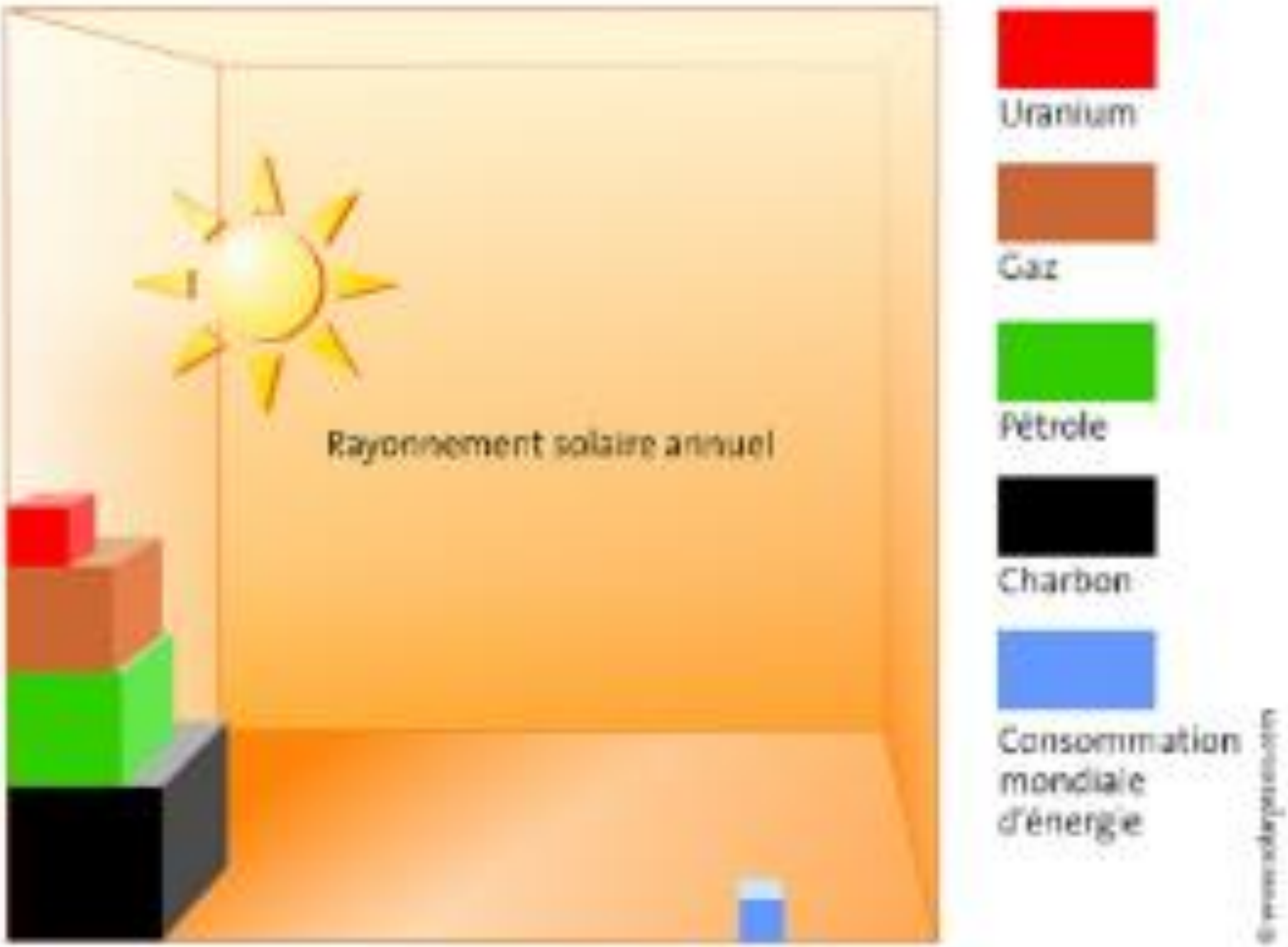


Figure 1 - Schematic distribution of global energy resources.
Source: Solarpraxis

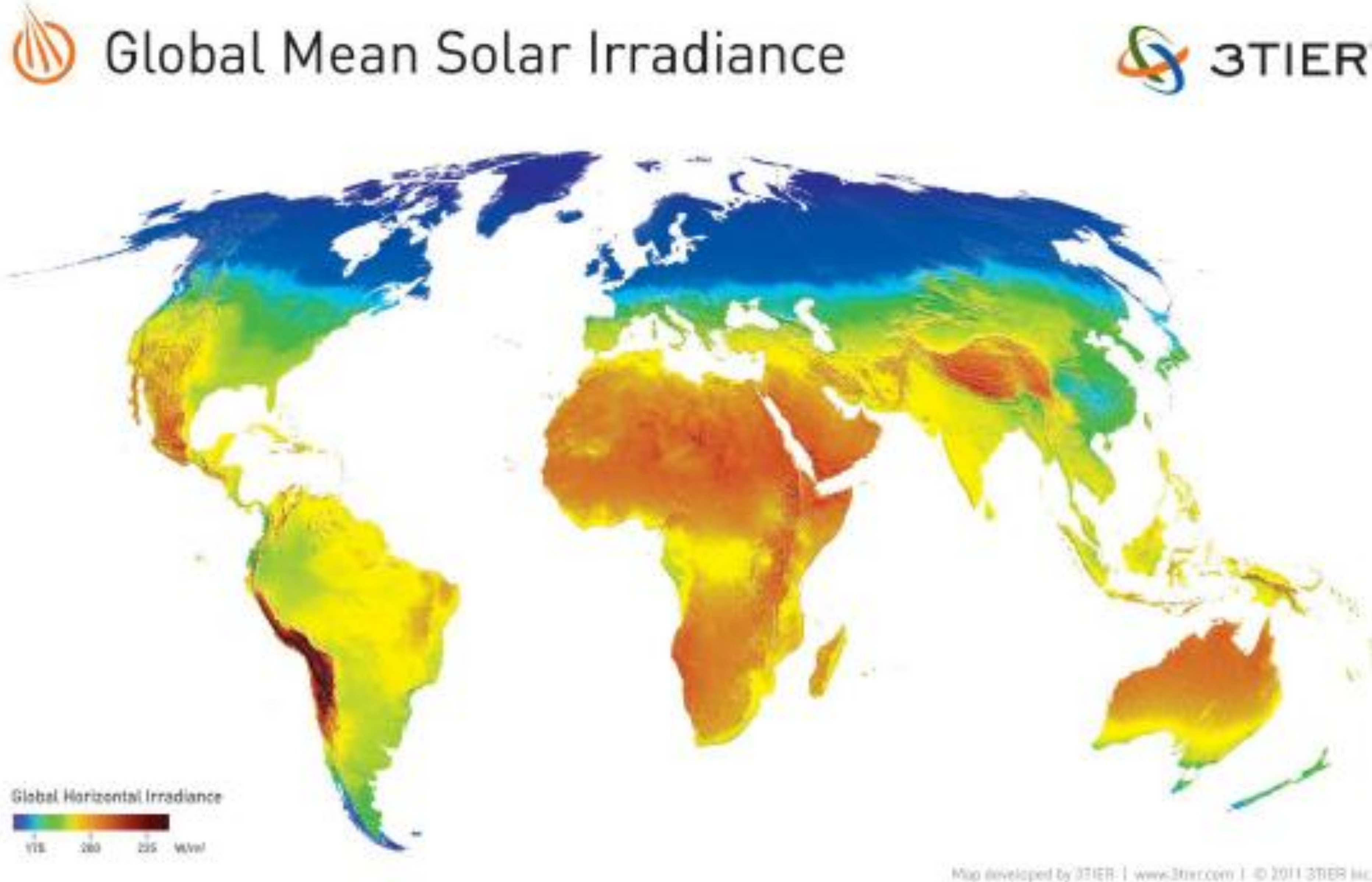


Figure 1.3 – *Carte de l'irradiance solaire sur la Terre, d'après 3TIER* (`http://www.3tier.com/static/ttcms/us/images/support/maps/3tier_solar_irradiance.jpg`)

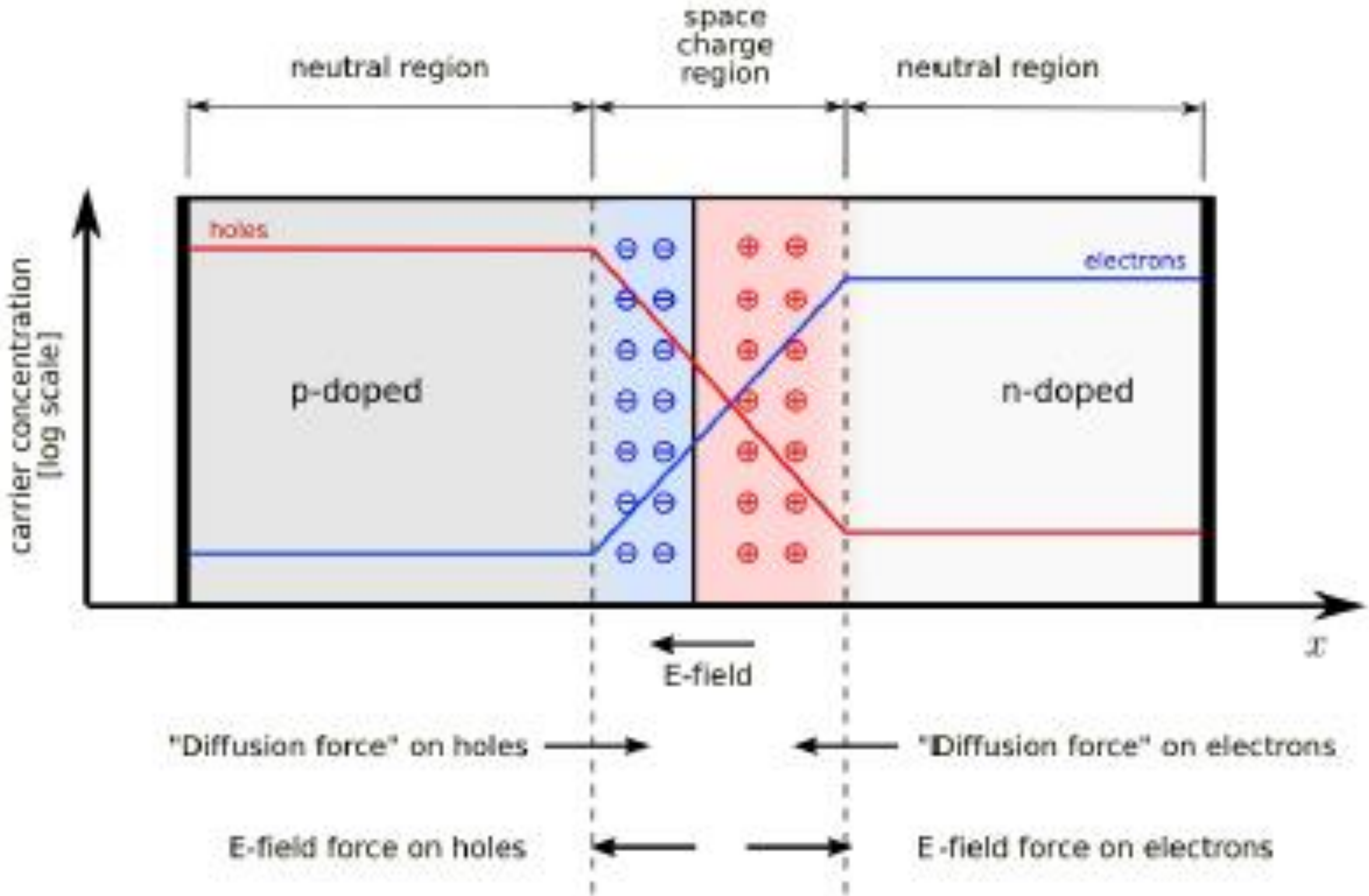


Figure 3 - Schematic of a p-n junction. Source: phD David Cohen

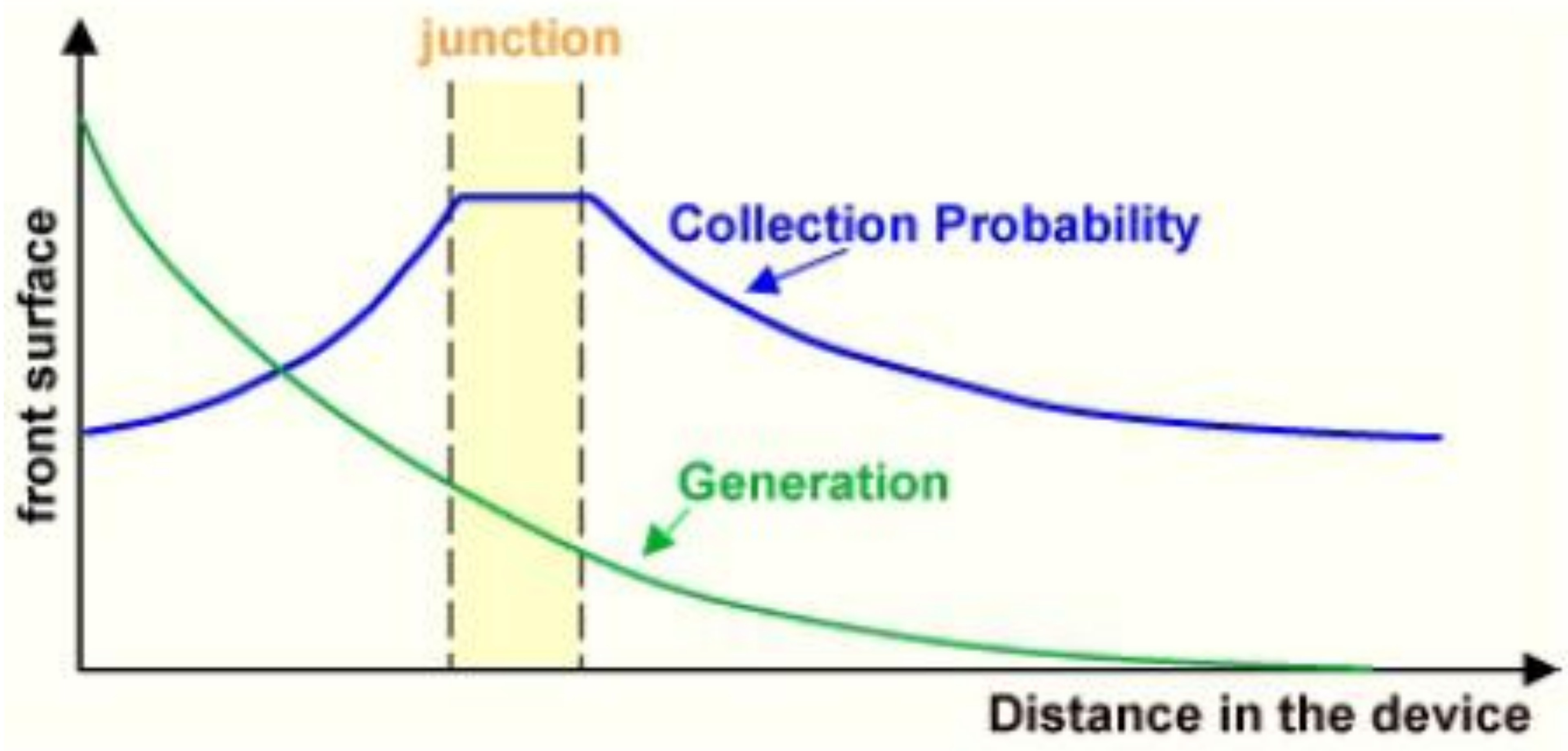


Figure 4 – carriers collection probability versus cell position. Source: phD David Cohen

Three types of recombinaison:

- Radiative recombinaisons: frequently present in direct

GAP material, so negligible in Silicon

AUGER Recombination: This type of recombination involves three carriers.

Traps Assisted Recombination: Also called Shockley-Read-Hall recombination, they are present in materials which contain defects (grain boundaries, impurities, etc.)

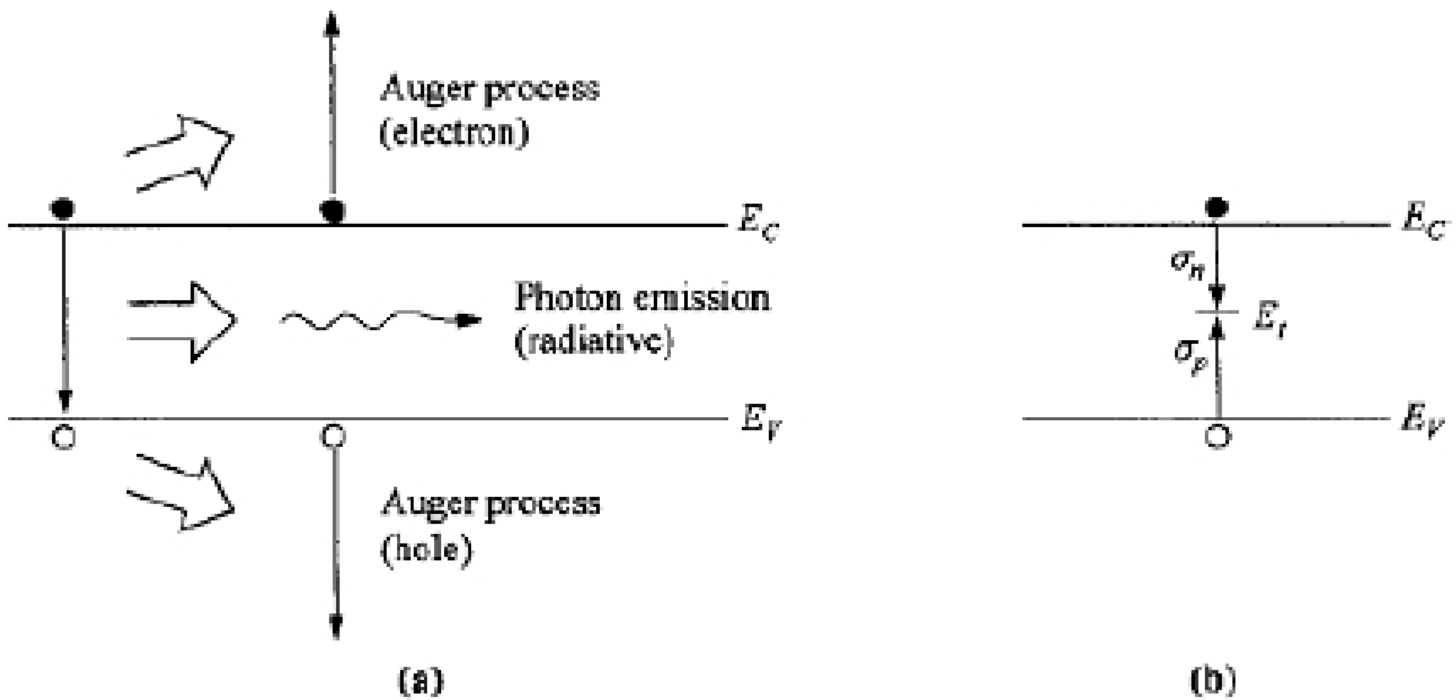


Figure 5 - Mechanisms of recombination. (a) radiative recombination resulting in the emission of a photon and Auger recombination resulting in the increase in energy of an electron or a hole. (b) Trap Assisted Recombination is the capture cross section of the trap. According Sze [1]

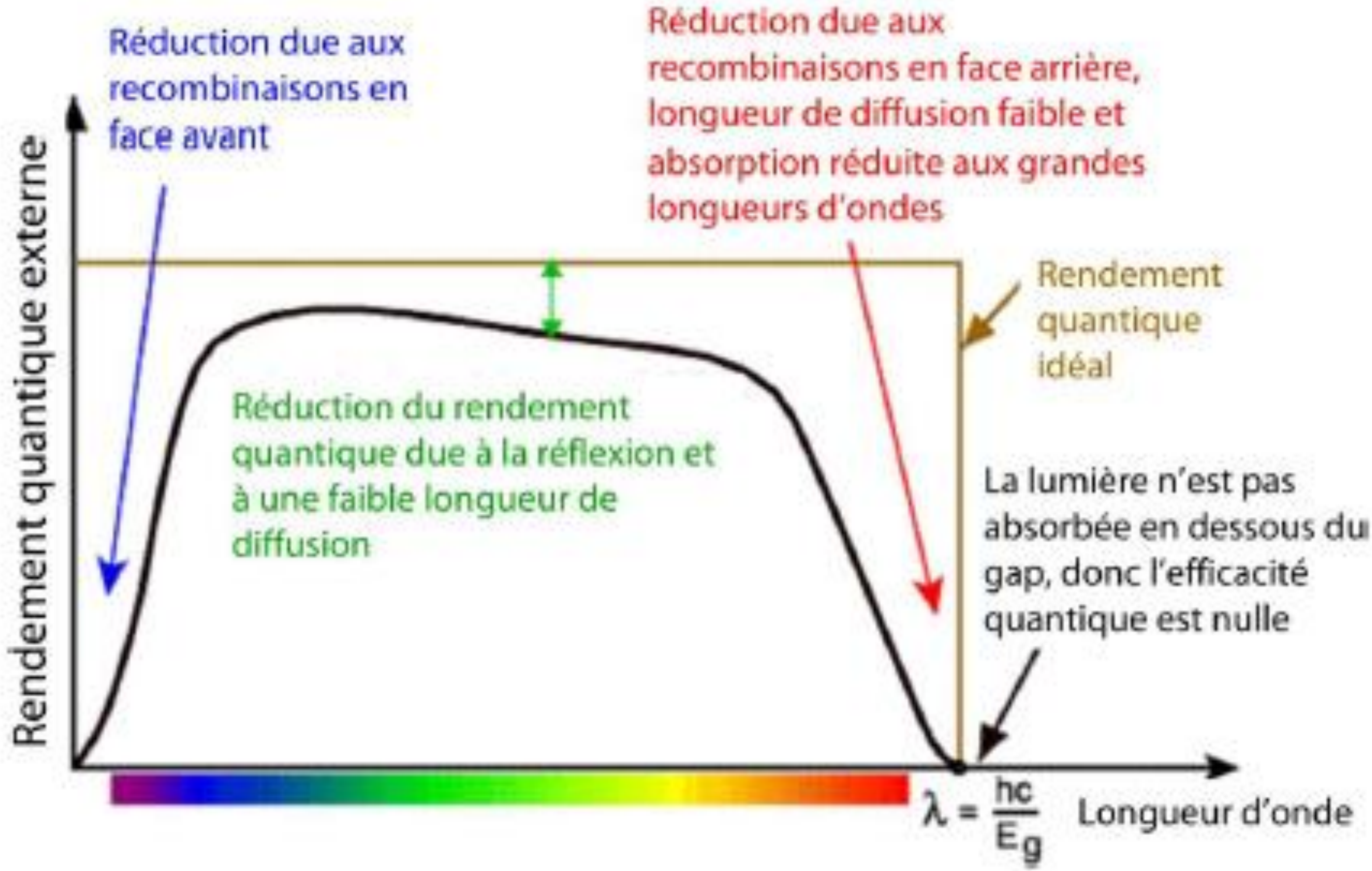


Figure 6 –External quantum efficiency of a solar cell and explanations of the various losses. Source : http: // www. pveducation. org/ pvcdrom/ solar-cell-operation/ quantum-efficiency

SOLUTIONS

Definition: What do we say nanostructure?
a nanostructure, according to be mono-, bi-or tri-dimensional, has at least one of its dimensions smaller than 100 nm.

Double interest:

- From a fundamental point of view, small size → new properties (electronic, magnetic, optical)
- From a technological point of view, nanostructures can increase the integration capacity of electronic components or memories stocking densities. . .

Outline

- Objective of the Work

- Why Silicon Surface Nanostructuration?

- Silicon Nanowires and Surface Nanostructuration Processes by MACE

- Results and Discussion

- Conclusion and Perpectives

Objective of the Work

Before using these nano-objects in technological applications, it is important to study in order to control their properties from their size, shape, interface, interaction with their environment. . .

The starting point of nanoscience and nanotechnology is therefore based on the realization of nano-structures, which are usable only if they are related to the macroscopic scale.

The objective is to reproducibly control the quality, properties, position and density of these nano-objects in order to study and use.

Why Silicon Surface Nanostructuration?

Issues and Context

- Silicon base material
- Why Si is unique?
- Same crystalline structural like diamond
- Indirect GAP: The maximum of the conduction band and the minimum of the valence band does not coincide in wave vector space
- Recent years: significant growth nanostructures: such as nanowires, columns or tubes → innovative devices in electronics, energy (PV), optics and biology.
- Nanostructuring of Silicon surface → manufacture quantum wells, quantum dots or quantum nanowires

additional advantage: confinement of carriers properties

Why Silicon Surface Nanostructuration?

«Small is beautiful»

- Richard feynman’s Idea: **“**There’s plenty of room at the bottom**”,** American Physical Society in 1959

- The challenge, even simple, is very important:

• make objects or structures,
• as smallest as possible,
• reproducible manner by controlling their size, their position. . .

What Application?

Why Silicon Surface Nanostructuration?

- Existing technologies → nanostructures: possibility
  * add or remove individual electrons,

  * turn on and off interactions,

 * tune the electronic state simply by changing the voltage on a gate electrode or an external magnetic field.

- In solar cells application, nanostructured surfaces: increasing photovoltaic conversion rate by the optical confinement

quantum effects

Quantum well:

When the dimensions of the material are smaller than the De Broglie wavelength associated to the electron,

Why Silicon Surface Nanostructuration?

quantum effects

properties of the material associated with the emergence of quantum effects. This wavelength □$_B$ is given by

$$\lambda_B = \frac{h}{p} = \frac{h}{\sqrt{2m_{eff}E}}$$

with m_{eff} the effective mass of the electron in the semiconductor material, the electron energy E and h Planck's constant.

- To be observed the quantization energy $E > k_B T$ (~ 26 meV at room temperature).
- The associated wavelength is called De Broglie thermal wavelength and given by:

$$\lambda_{th} = \frac{h}{\sqrt{3m_{eff}k_B T}}$$

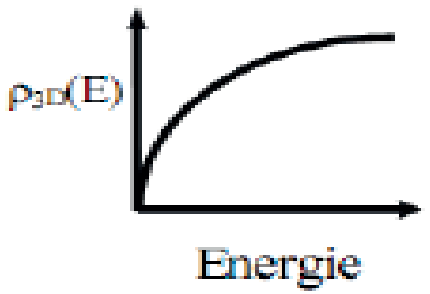
Why Silicon Surface Nanostructuration?

quantum effects

The interest in quantum confined structures is best summarized in the expressions for the density of states (DOS), $\rho(E)$ (number of states per unit volume per unit energy), defined as

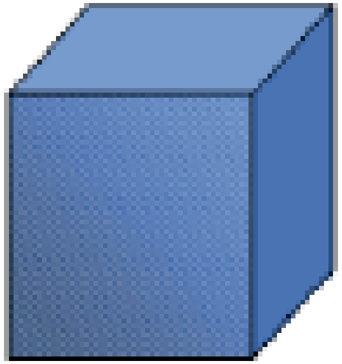
$$\rho(E) = \frac{\partial N}{\partial E},$$

where N is the total number of states per unit volume.

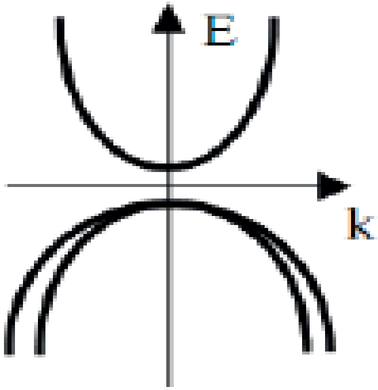


3D

$$N = \frac{k^3}{3\rho^2}$$



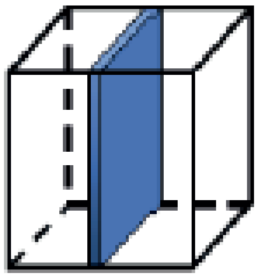
$$\rho_{3D}(E) = \frac{1}{\pi^2}\left(\frac{m^*}{\hbar^2}\right)^{3/2}\sqrt{2E},$$



Why Silicon Surface Nanostructuration?

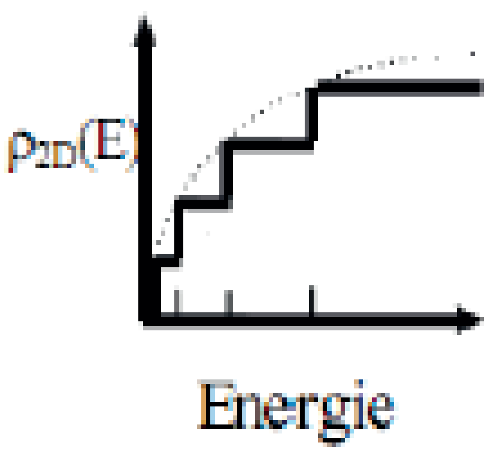
quantum effects

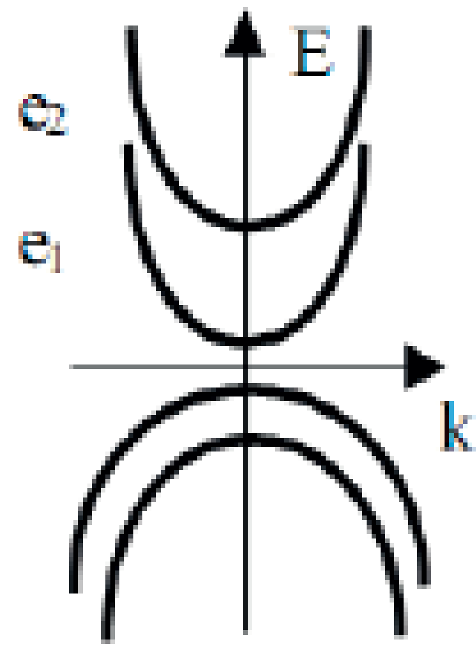
2D For a 2D system (i.e., two degrees of freedom):



$$N = \frac{k^2}{2p}$$

$$\rho_{2D}(E) = \frac{m^*}{\pi\hbar^2}\sum_{n_x}\Theta(E - E_{n_x}),$$



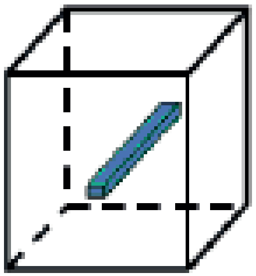


where □ is the step function and E_{nz} is the energy levels n discretized along z.

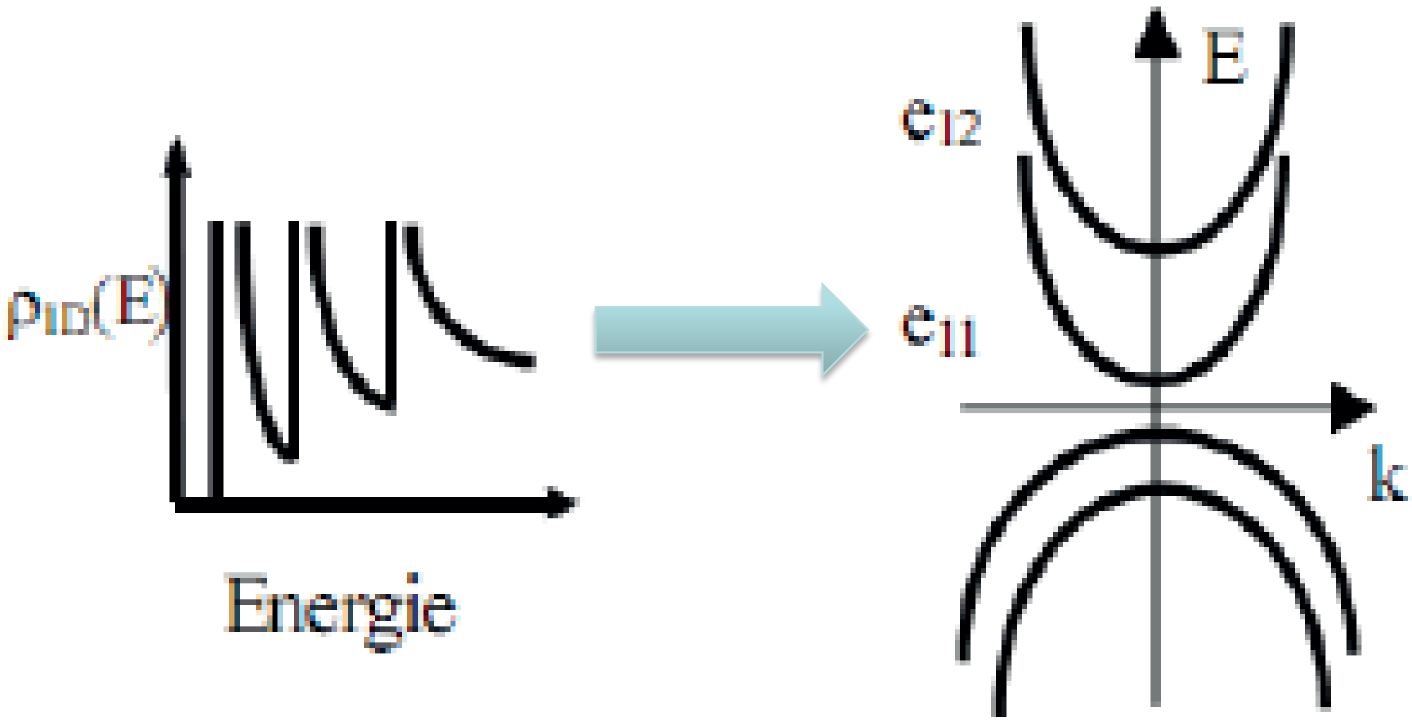
Why Silicon Surface Nanostructuration?

quantum effects

1D For a 1D system: $$N = \frac{2k}{p}$$

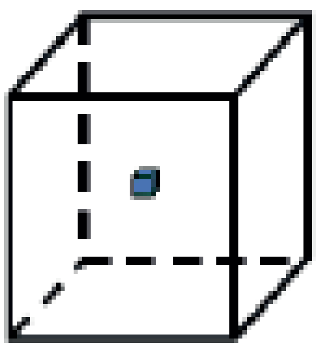


$$\rho_{1D}(E) = \frac{1}{\pi\hbar}\sqrt{2m^*}\sum_{n_x,n_y}\left(E - E_{n_x,n_y}\right)^{-1/2},$$

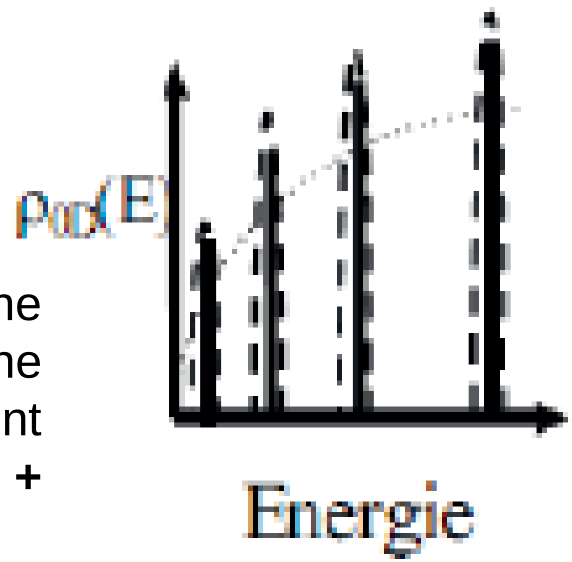


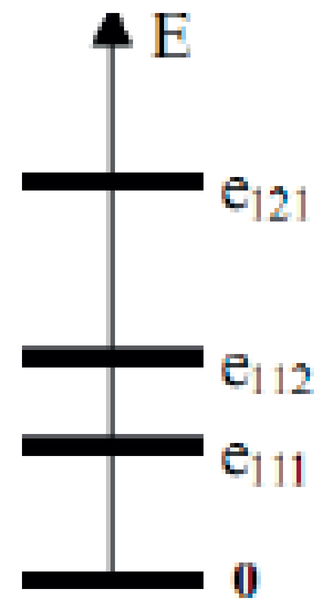
Finally, For a 0D system, there is no **k** -space to be filled and the number density is totally discrete

0D



$$\rho_{0D}(E) = 2 \sum_{n_x, n_y, n_z} \delta(E - E_{n_x, n_y, n_z})$$





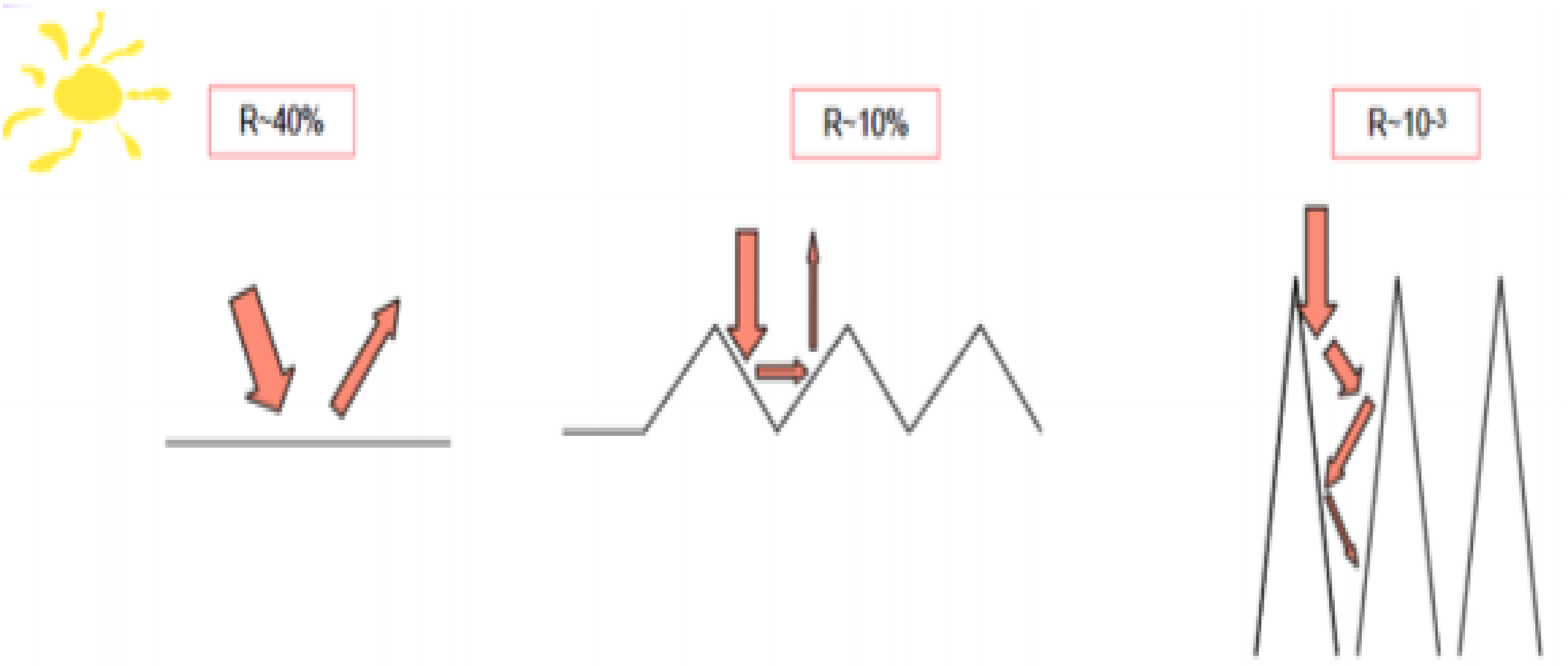
Eni with **I = x, y, z** is the quantized energy of the particular confinement direction, and **Enx,ny = Enx + Eny** , etc

To first order, in the infinite cubic potential confinement configuration,

$$E_{ni} = \frac{\hbar^2 p^2 n_i^2}{2m^* D_i^2}$$

Why Silicon Surface Nanostructuration?

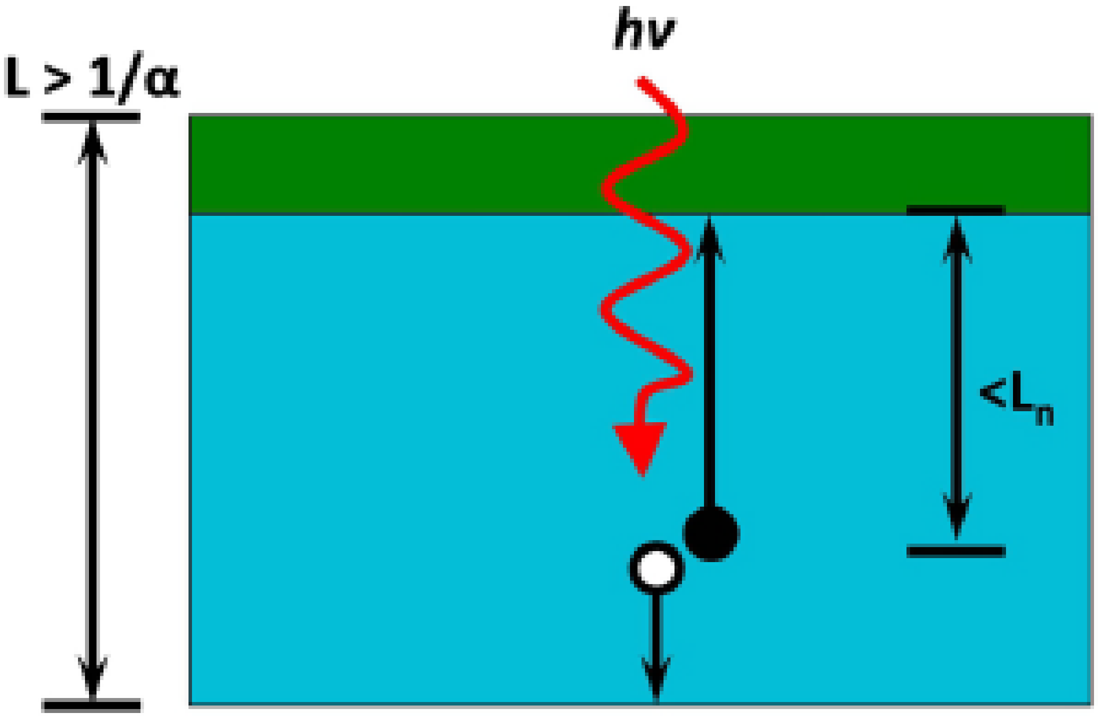
Effect on Solar Cells Optical Absorption



Reduction of reflection depending on the structure of the absorptive surface: increasing optical absorption compared to a thin layer of same thickness

Why Silicon Surface Nanostructuration?

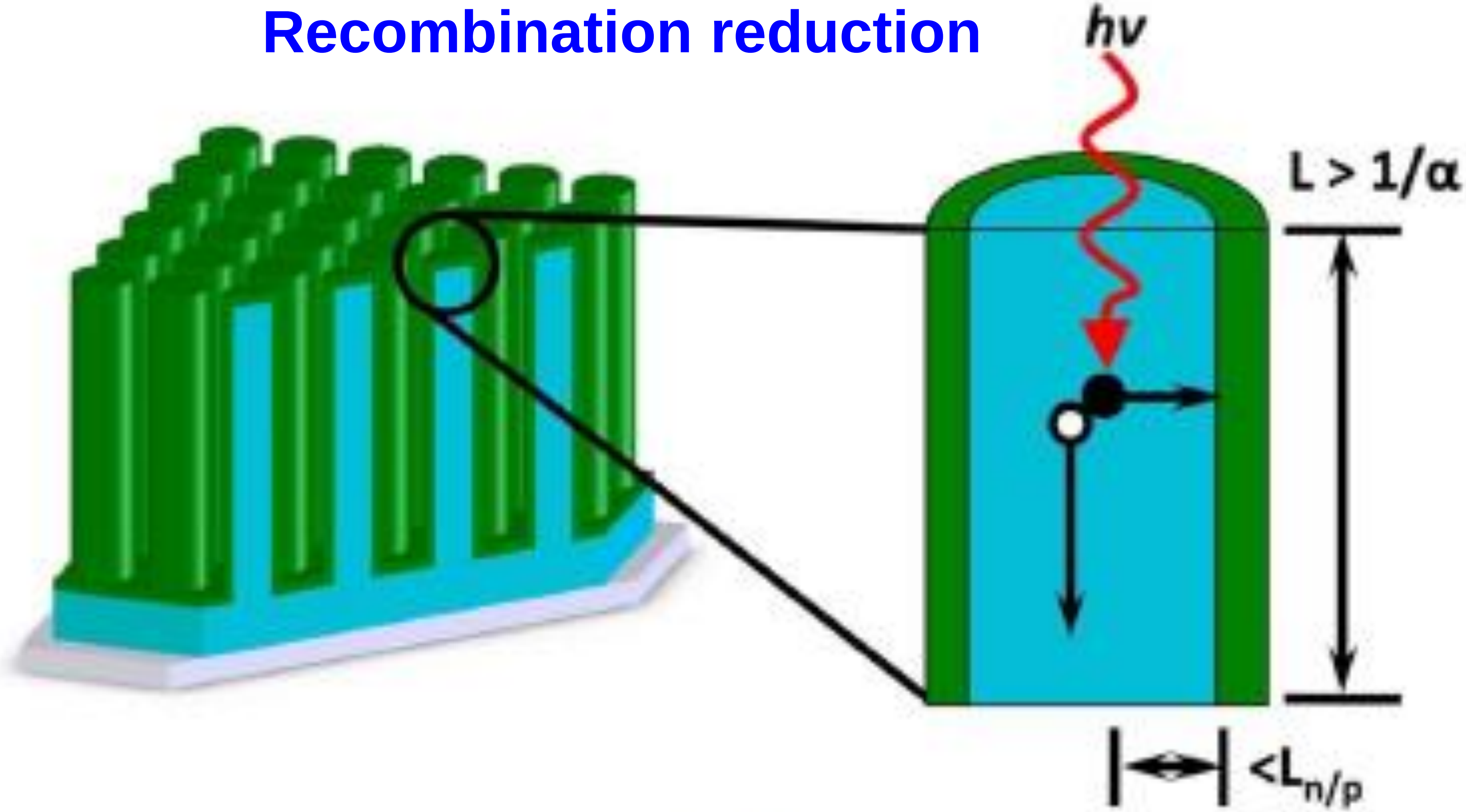
Recombination reduction



(a)

According to [1]. Diagram (a) an axial connection and (b) a radial junction.

Recombination reduction



(b)

The stress releasing on the electronic grade silicon for carriers efficient collection.

Silicon Nanowires and Surface Nanostructuration Processes by MACE

There are a number of techniques to produce nanostructures in Si. But all of these techniques are classified in two principle methods:

- Top - Down
- Bottom – Up

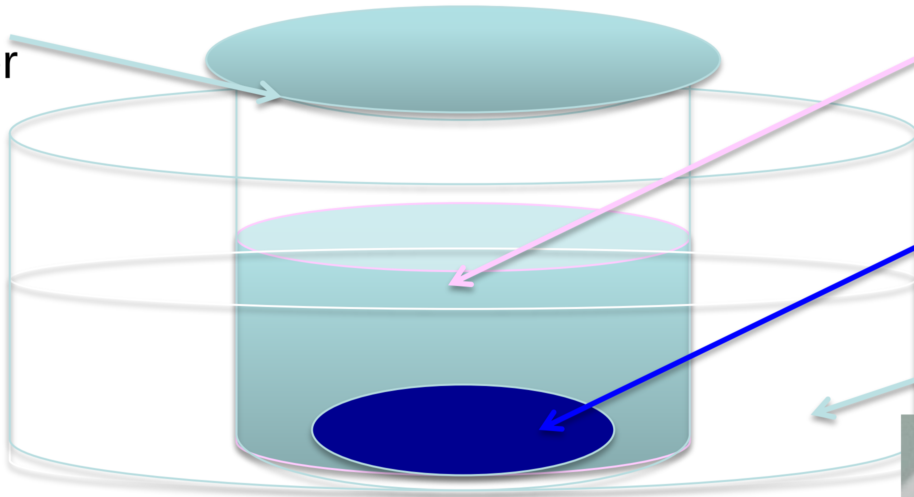
Metal-assisted wet-chemical Si etching (MaCE): promising solution → high aspect ratio nanostructures, well-defined shapes, and various complexity.

Metal catalyst: Au, Pt or Ag

- New tentative to use non noble metals: Cu, Zn, Al
- Principle and process used

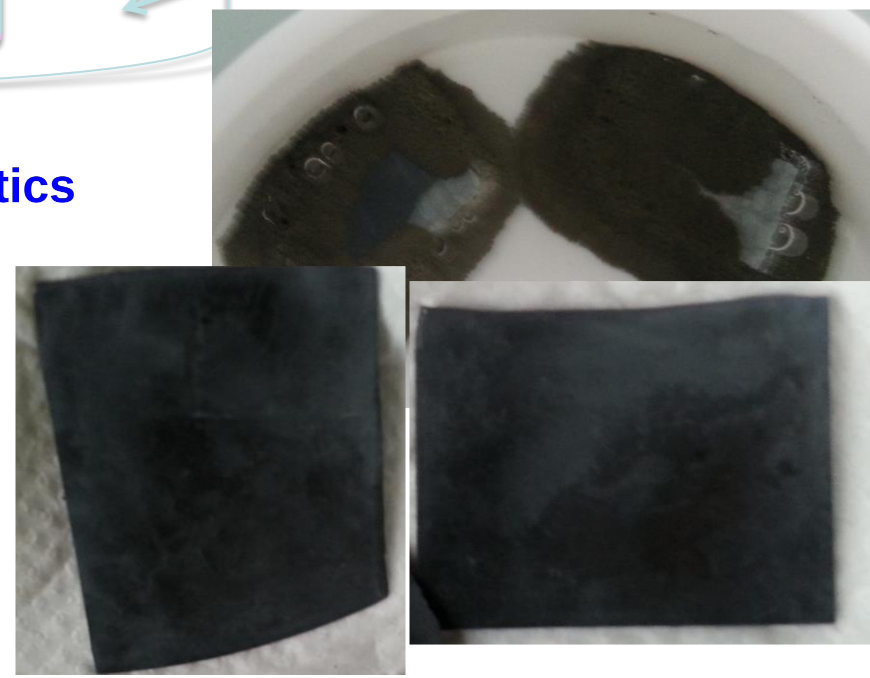
Silicon Nanowires and Surface Nanostructuration Processes by MACE

Process and Mechanism



Si wafer used characteristics

Fabricant	BT Electronics
Synthesised	CZ
Type	p, Borom doped
Orientation	<100>
Résistivité	1-5Ω.cm
Polissage	1 face
Thickness	600-650µm

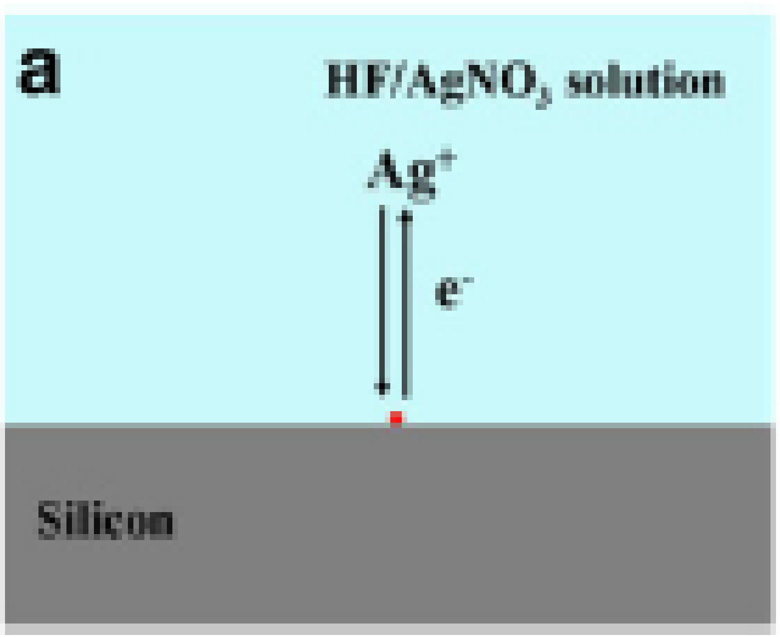


Photos: Wafers after etching

Silicon Nanowires and Surface Nanostructuration Processes by MACE

Process and Mechanism

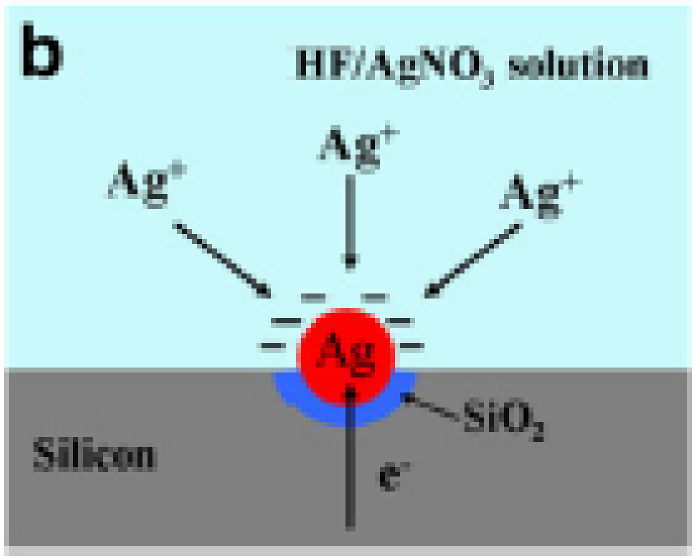
It can be divided into two processes (taking Ag as an example): 1.



Formation of Ag nucleation

a. Cathode reaction:

$Ag^+ + e^- = Ag$ $\mathbf{E}^{\theta} = 0.79$ V

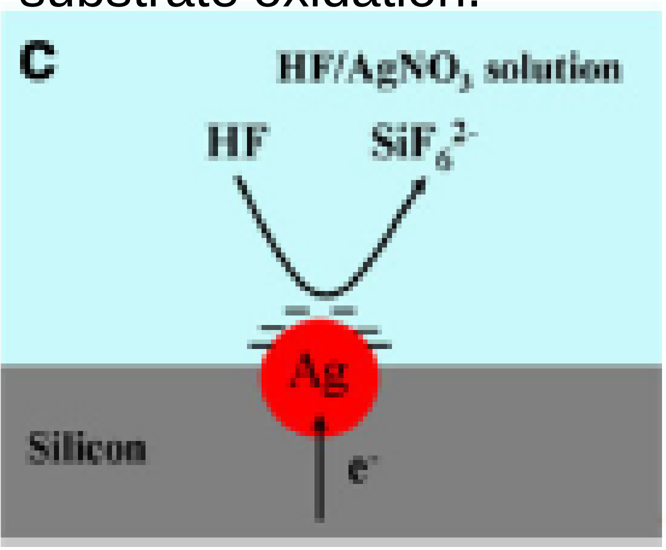


Ag particle growth and Si substrate oxidation.

b. Anode reaction:

$Si + 2H2O = SiO2 \;\; + 4H+ \;\; + 4e^{-}$

$\mathbf{E}^{\theta} \;\; = 0.91\ V$



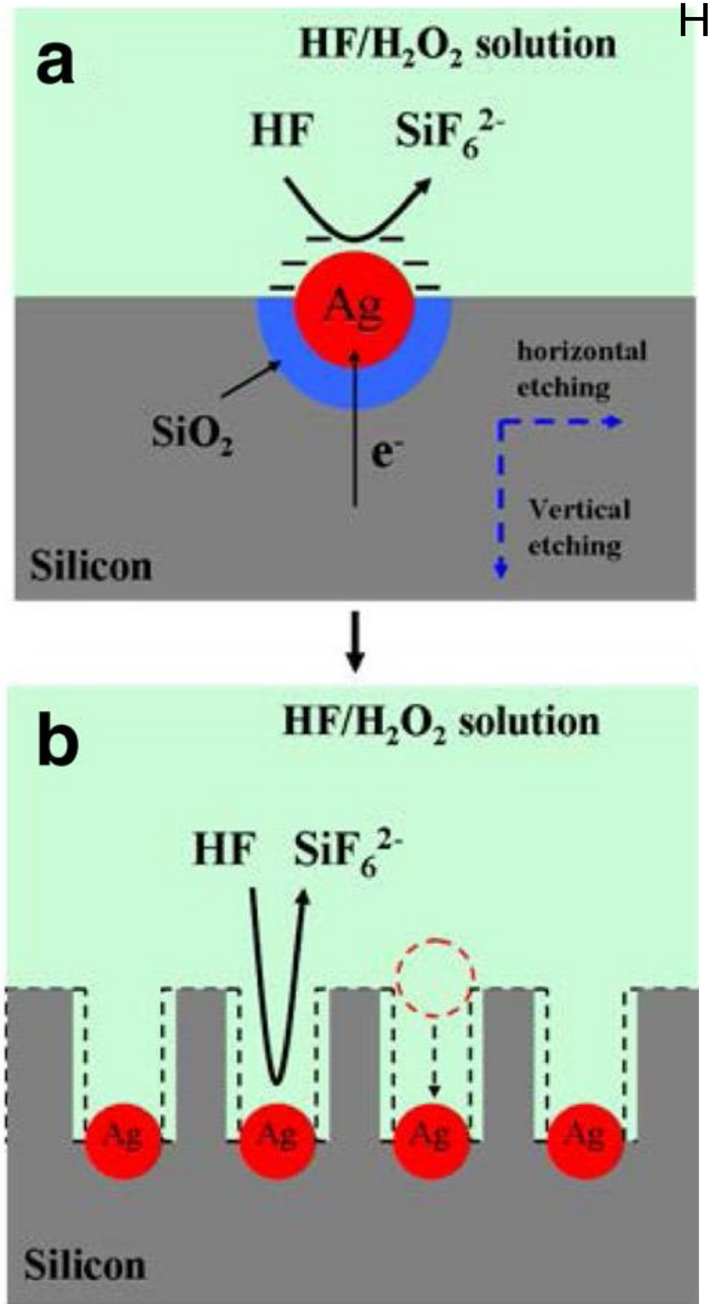
Ag particles trapped in the pits formed by the etching of SiO2 around it by HF

$SiO2 + 6HF = SiF_6^{2-} + 2H2O + 2H+$

c. Overall reaction:

$Si + 6HF + 4Ag^{+} = 4Ag + SiF_6^{2-} + 6H+$

H2O2 concentration effect on NWs morphology



H2O2 = 10 %

a. Cathode reaction:

$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+$

$\mathbf{E^{\theta}}$ = 1.76 V

b. Anode reaction:

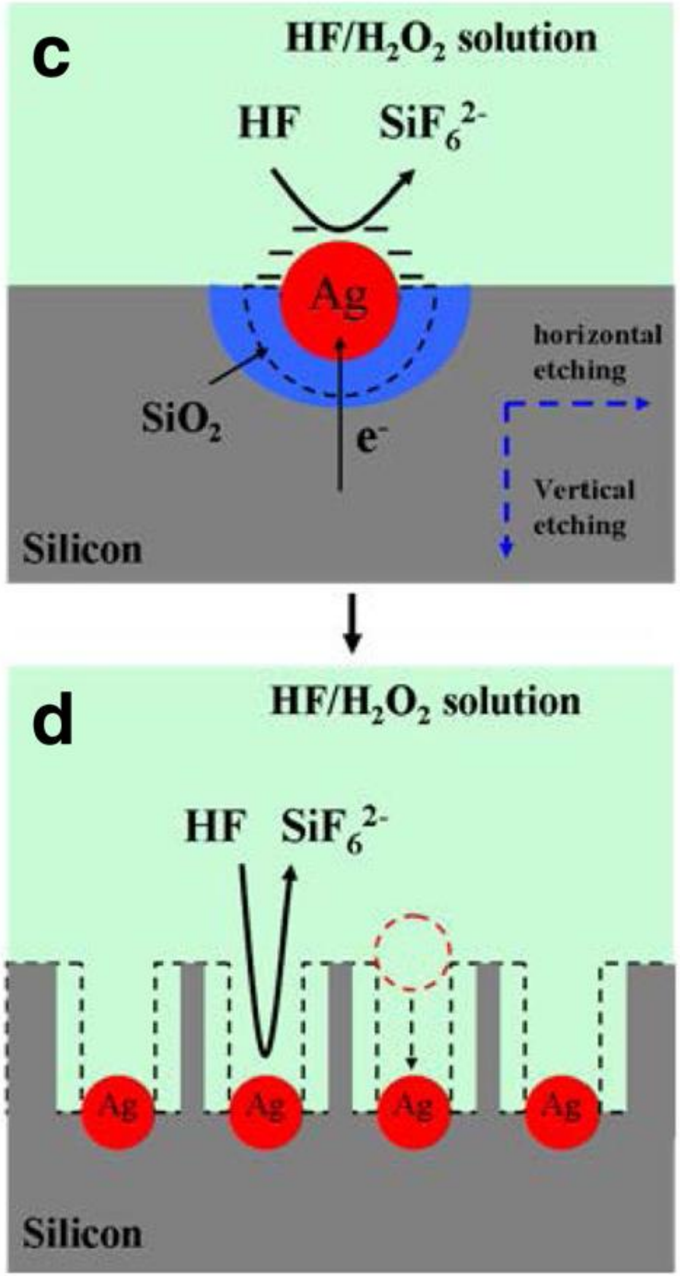
$Si + 6HF + nh^+ \rightarrow \mathbf{H_2SiF_6 + nH^+ + [n/2]H_2}$

c. Overall reaction:

$Si + 6HF + n/2\ H_2O_2 \rightarrow H_2SiF_6 + nH_2O + [2 - n/2]H_2$

H2O2 concentration effect on NWs morphology

H2O2 = 20 %



- In the process, AgNO3 plays an important role

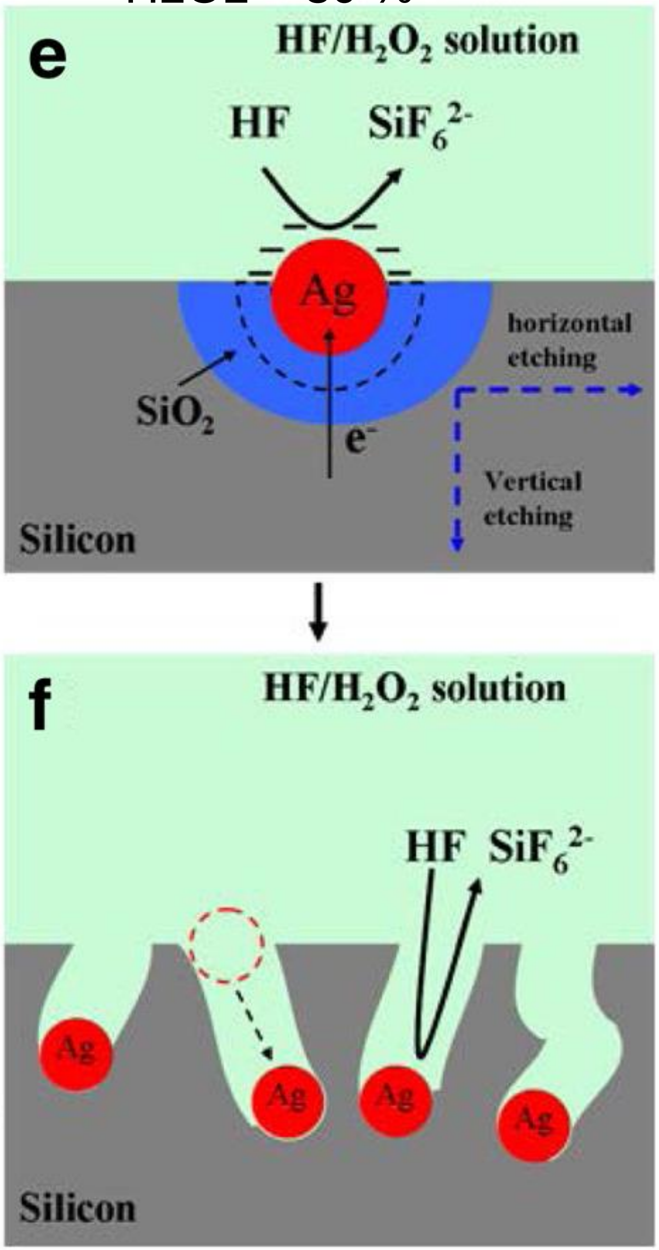
- the formation of vertical nanowires is relative to etching limitation around silver nanoparticle

- etching reaction is along the vertical direction

- H2O2 acts as hole donor and oxidant in the etching process

H2O2 concentration effect on NWs morphology

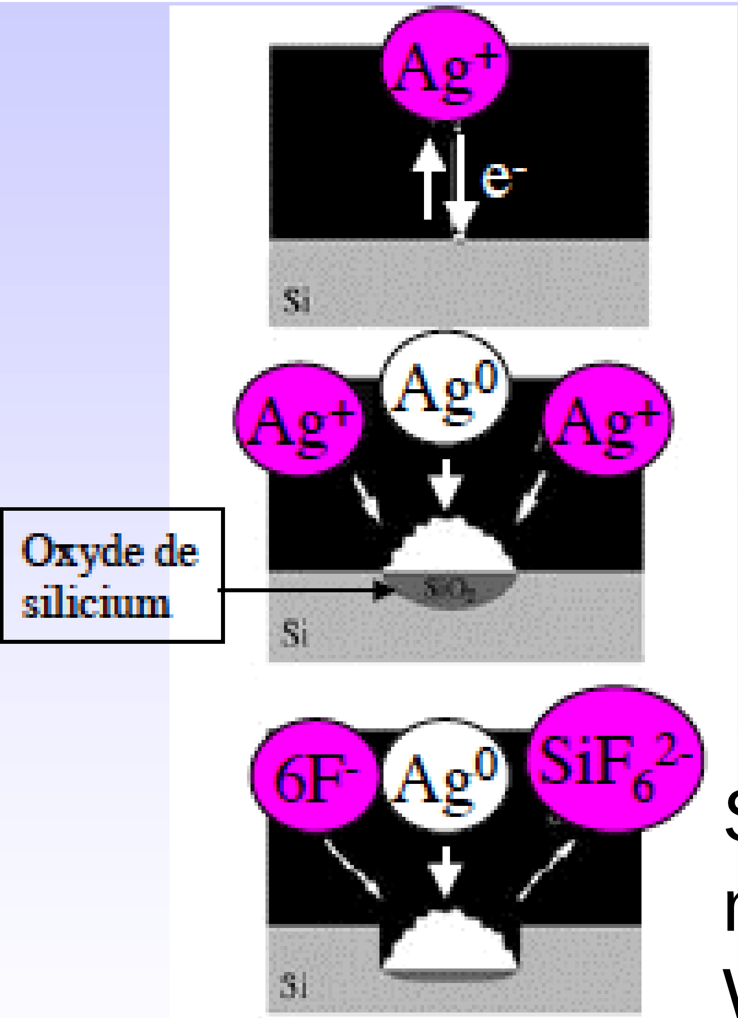
H2O2 = 30 %



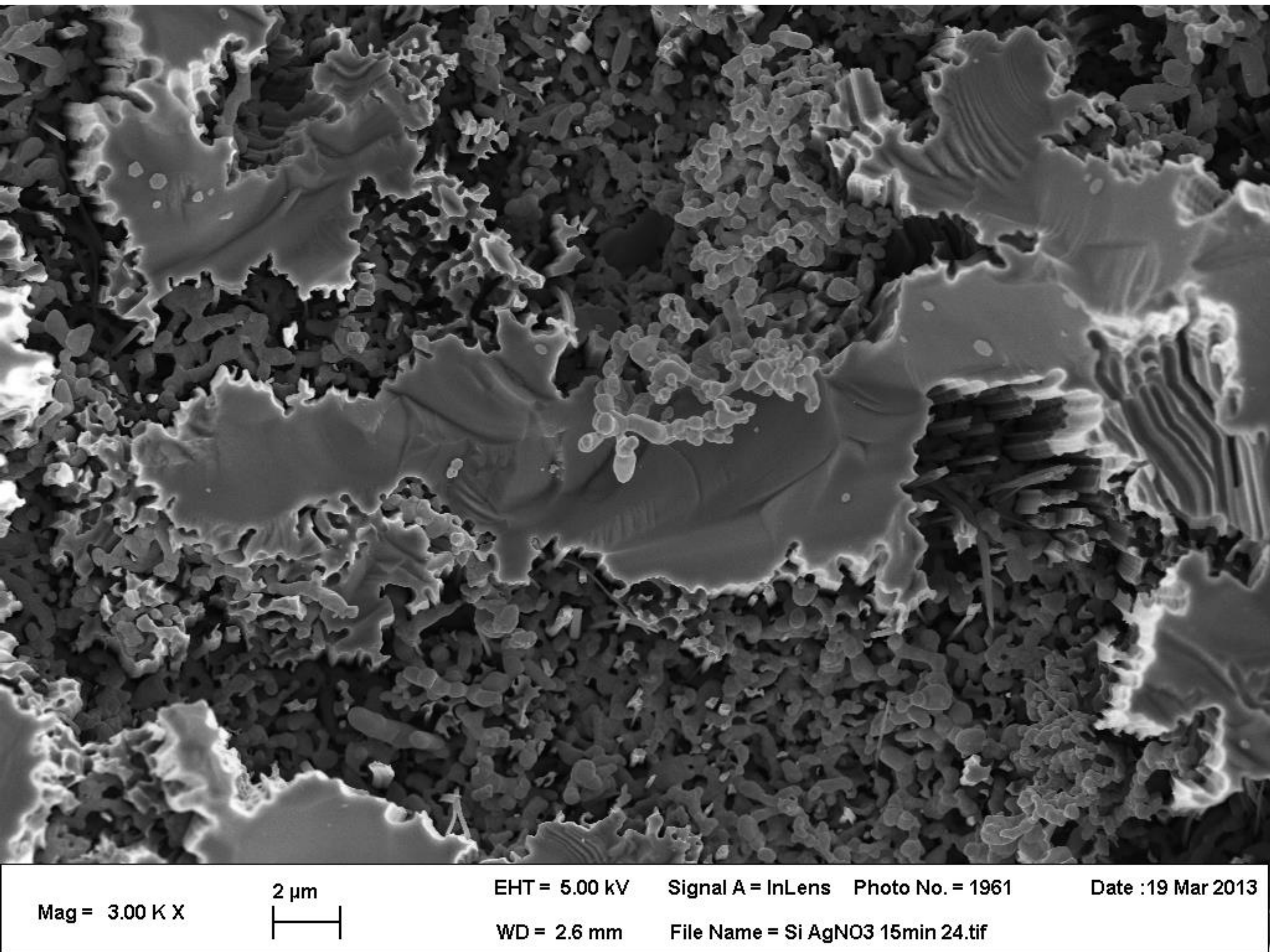
- H2O2 > 30 %, horizontal etching speed increases in a higher degree and overcomes the Ag nanoparticle gravity to shift its position

- Prepared SiNWs do not present an expected morphology of silicon nanowire arrays but a chaotic porous structure on the silicon substrate

Results and Discussion



Silver ions reduction to silver nanoparticles and dendrites.
We use: AgNO3, Cu(NO3)2 and Zn(NO3)2 as catalysts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2 µm
EHT = 5.00 kV
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Signal A = InLens
File Name = Si AgNO3 15min 24.tif
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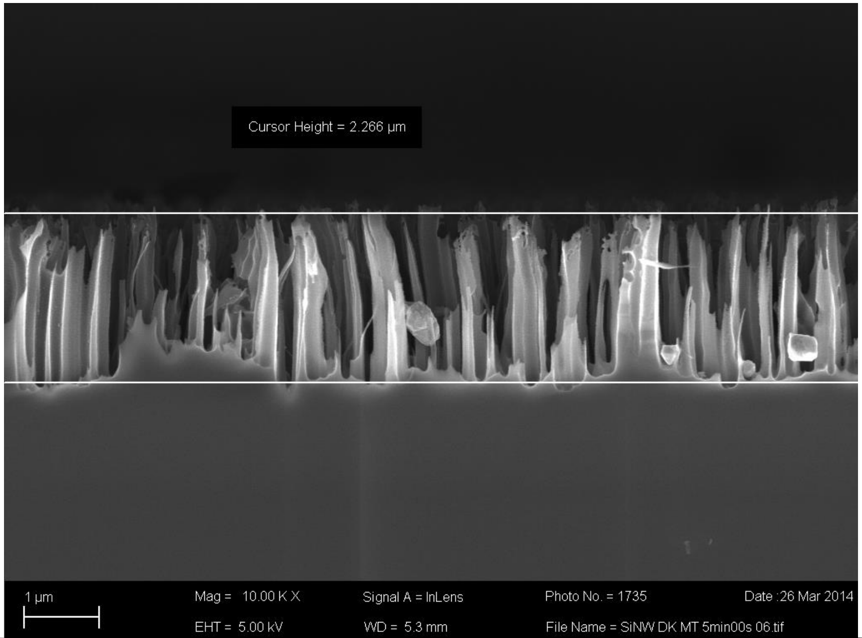
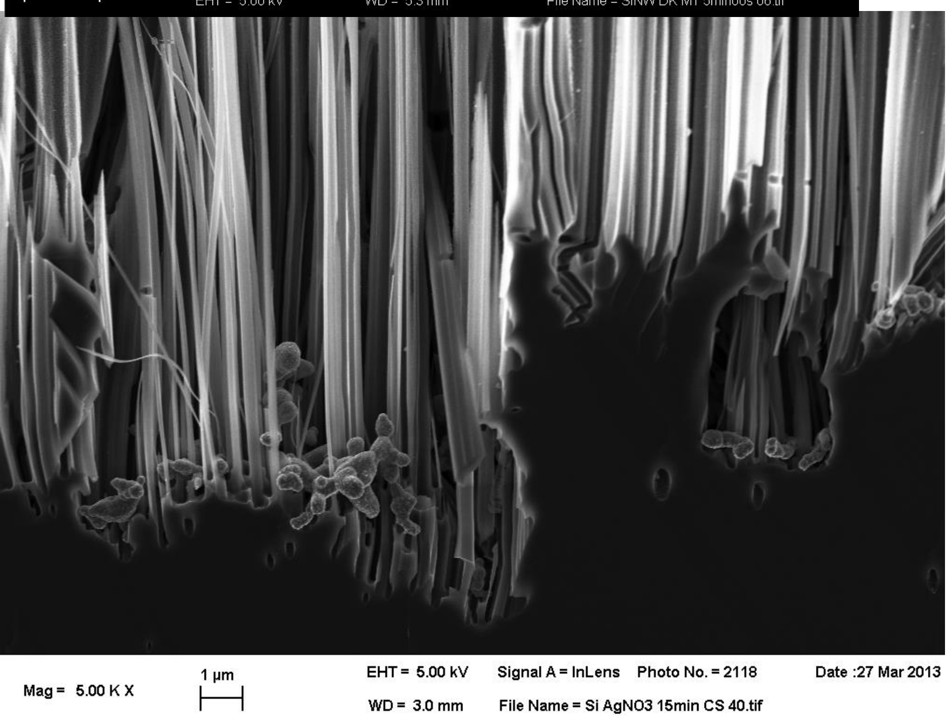
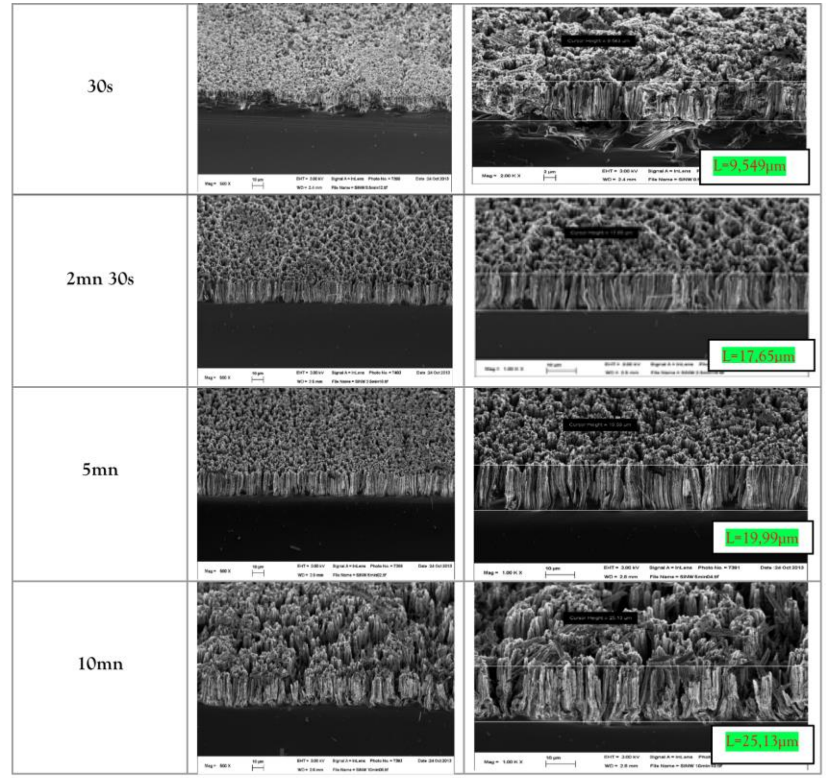
Results and Discussion for Ag catalyst



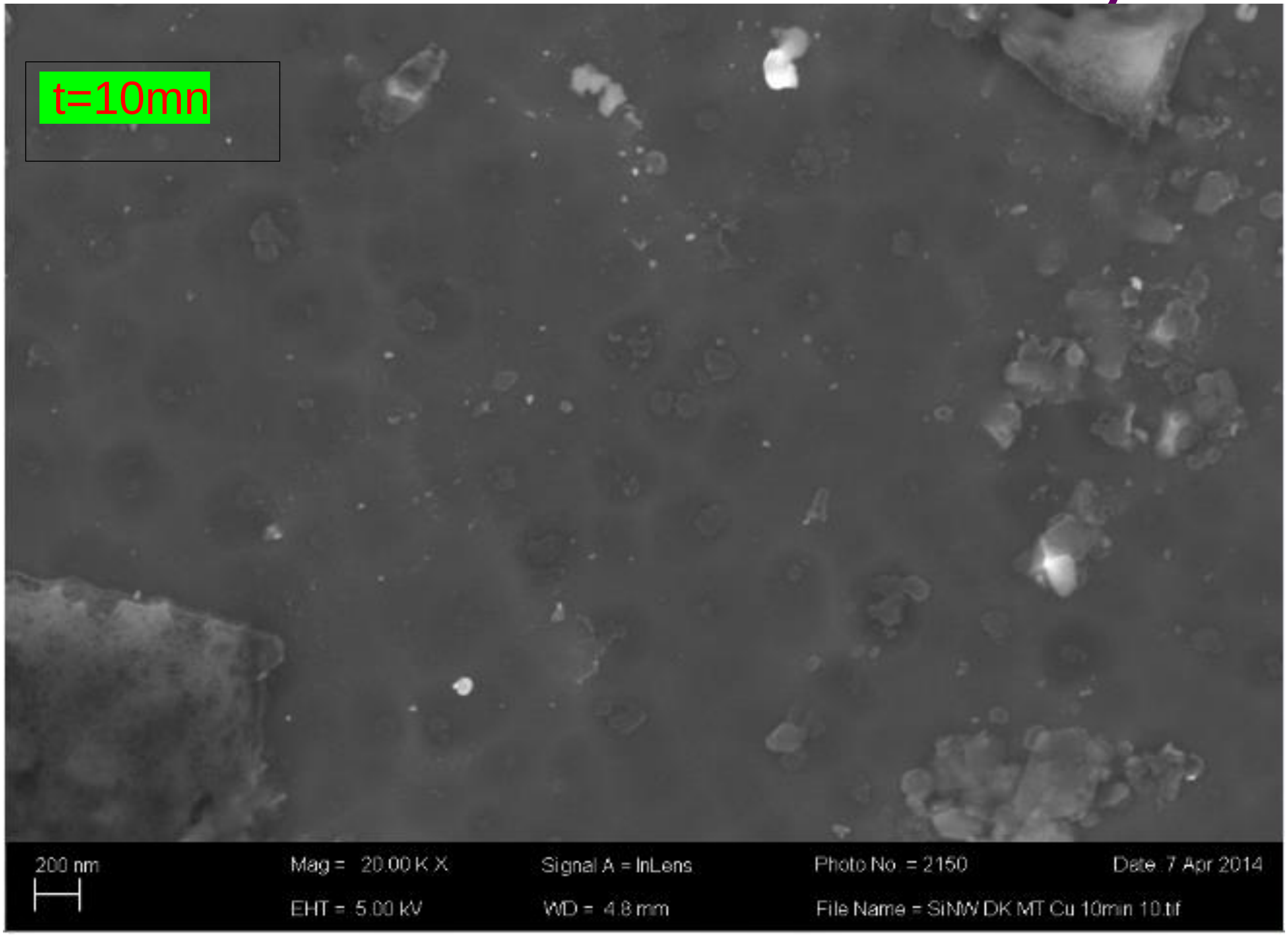




AgNO3 as catalyst:

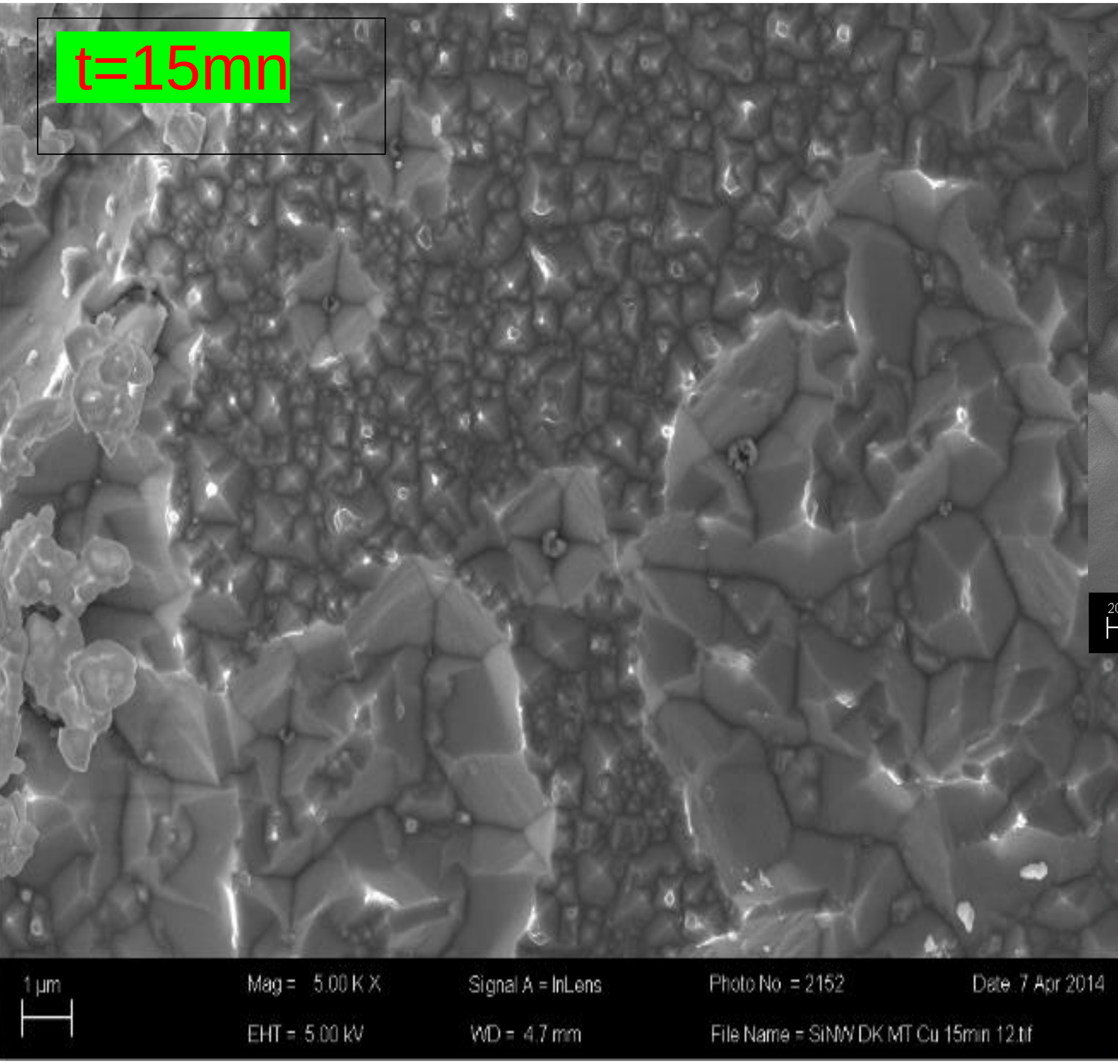
- Nanowires length increases as soon as the etching time

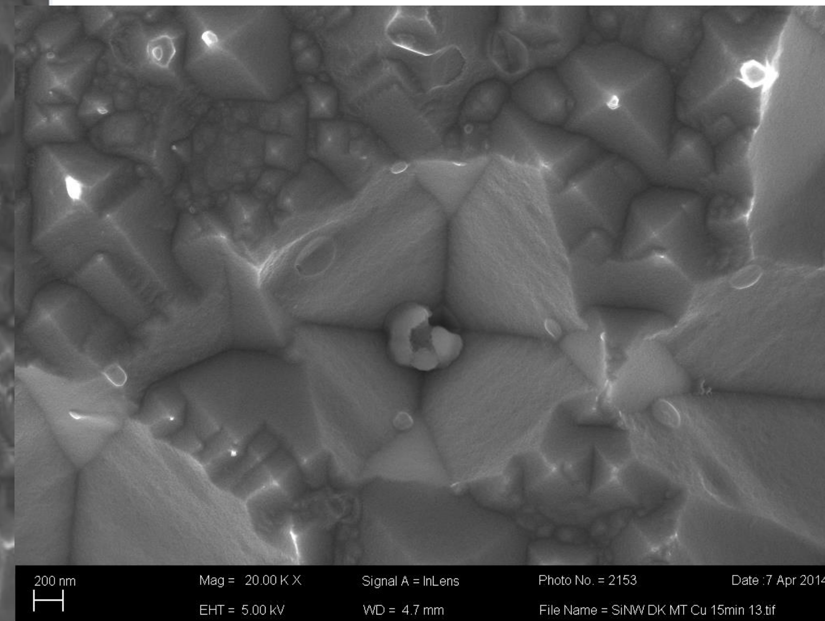
Results and Discussion for Cu catalyst



- For etching time below 10 mn, one can observe nuclei points around the surface

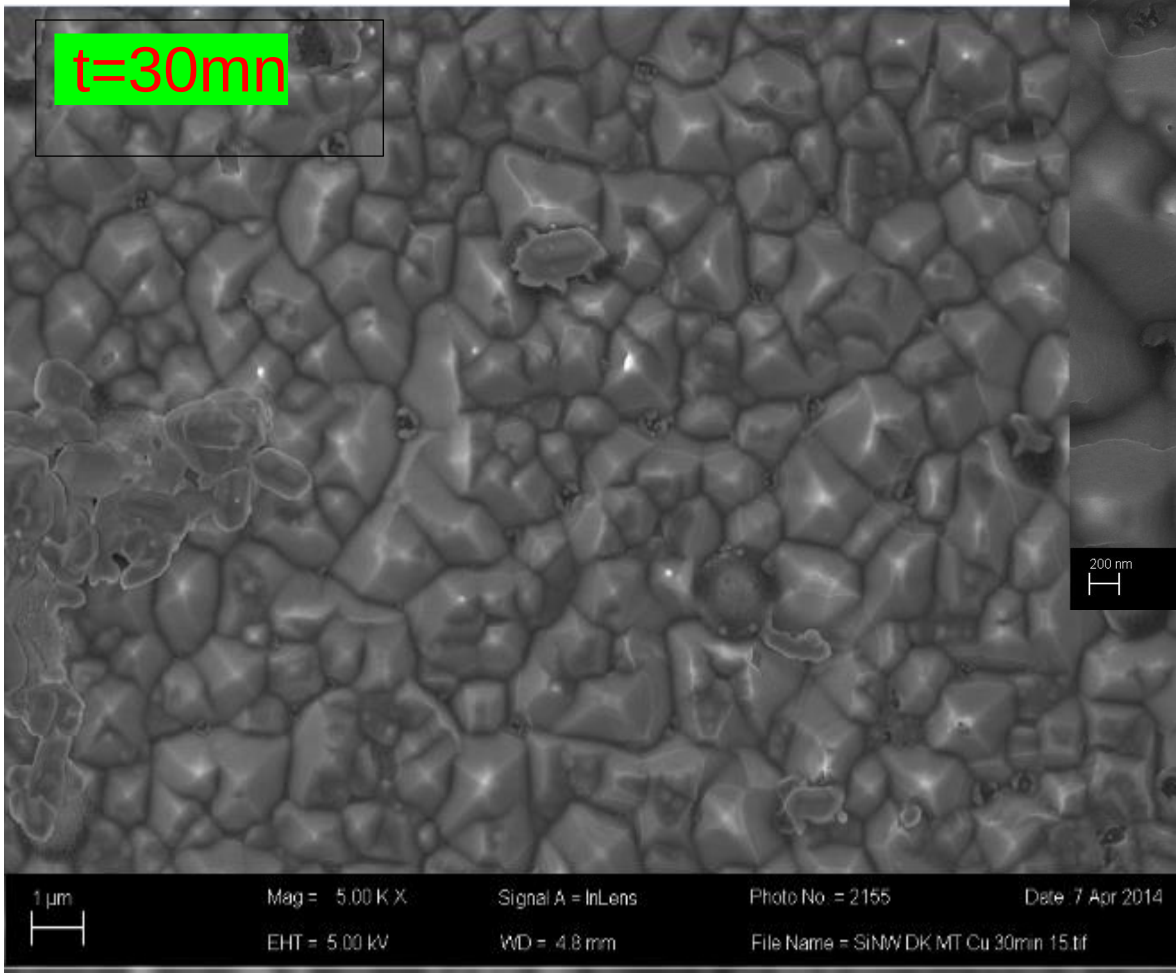
Results and Discussion for Cu catalyst

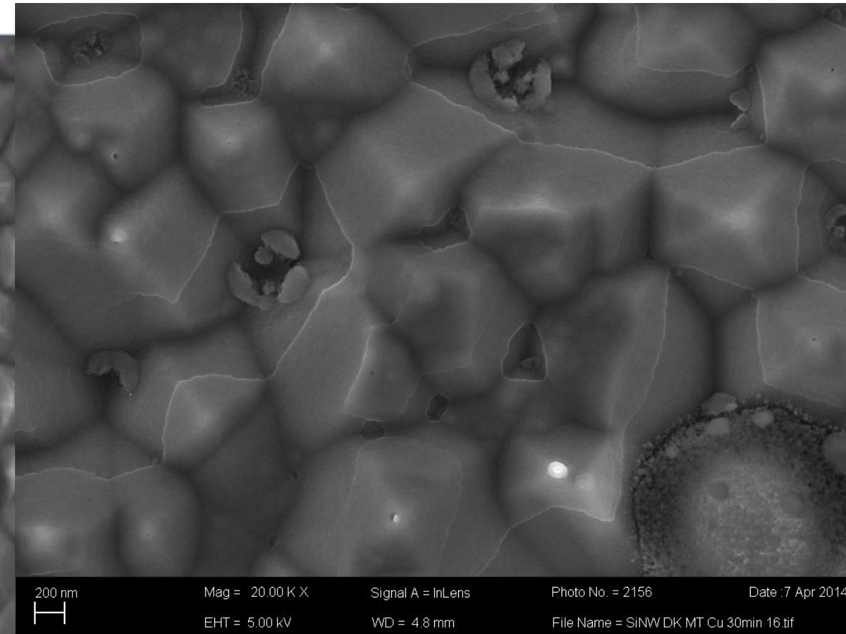




for 15 mn, the Silicon surface present non uniform pyramidal or conical forms

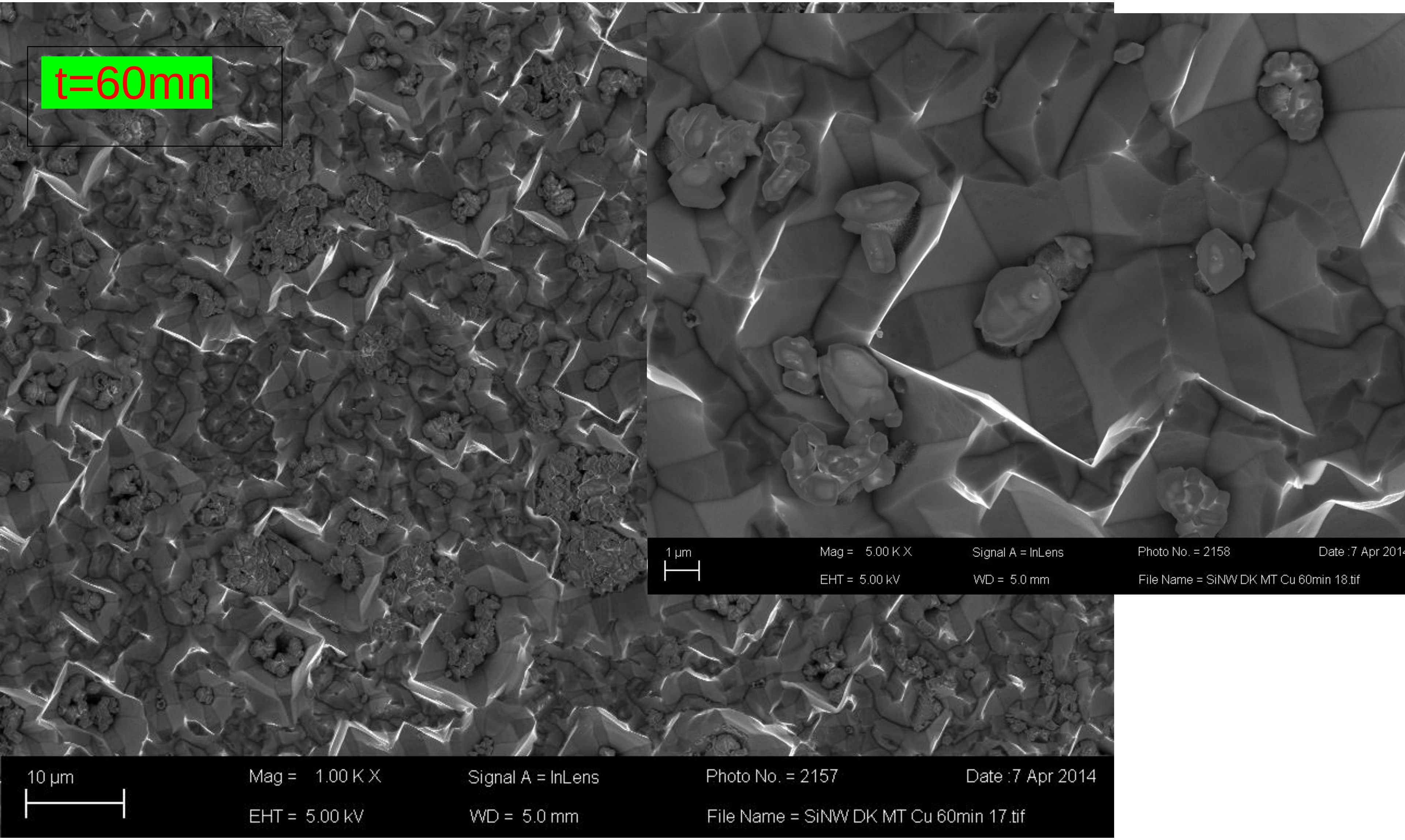
Results and Discussion for Cu catalyst





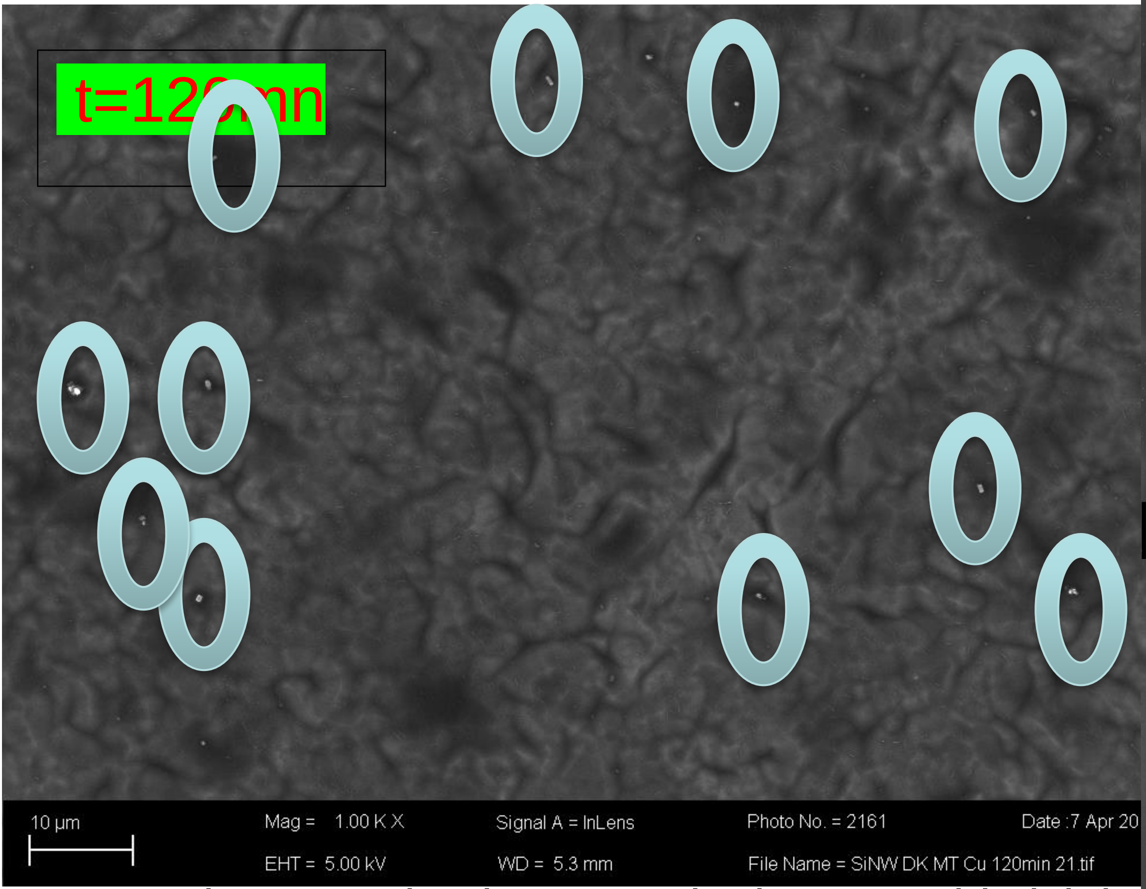
For 30 mn, the surface present uniform pyramidal forms

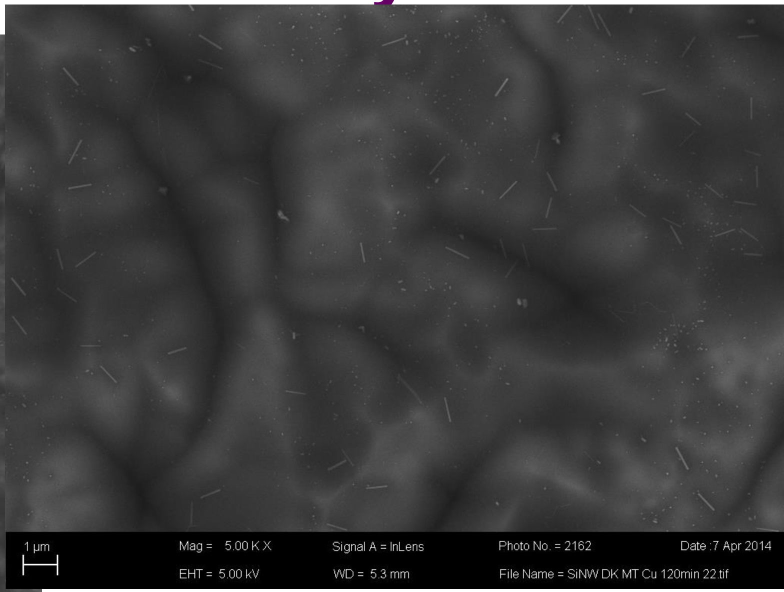
Results and Discussion for Cu catalyst

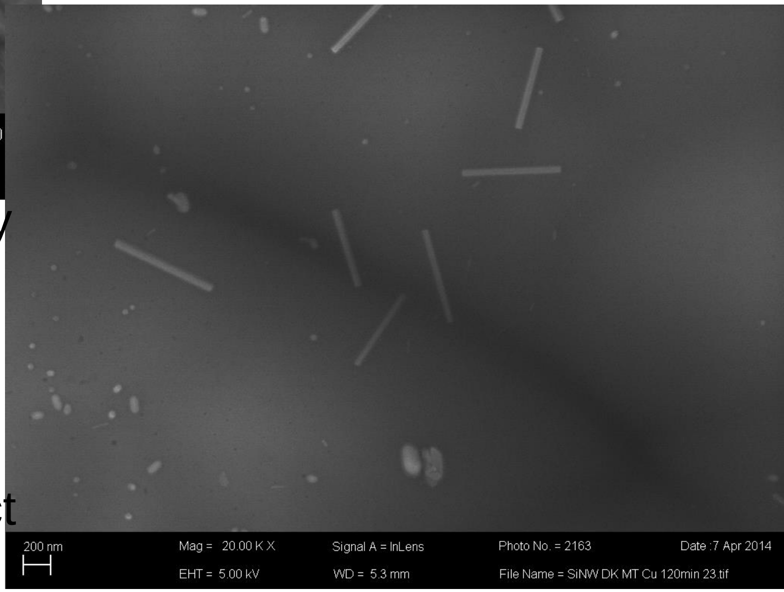


This structure becomes more symetric pyramidal and reverse pyramidal forms.
Presence of the Cu or CuO inside the pyramid coming from the Cu^{2+} reduction

Results and Discussion for Cu catalyst



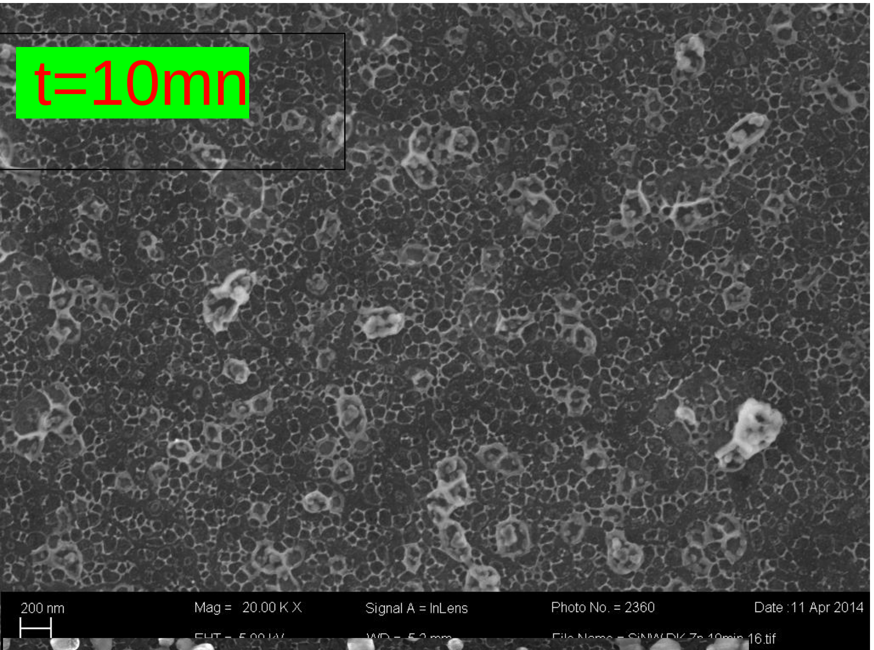


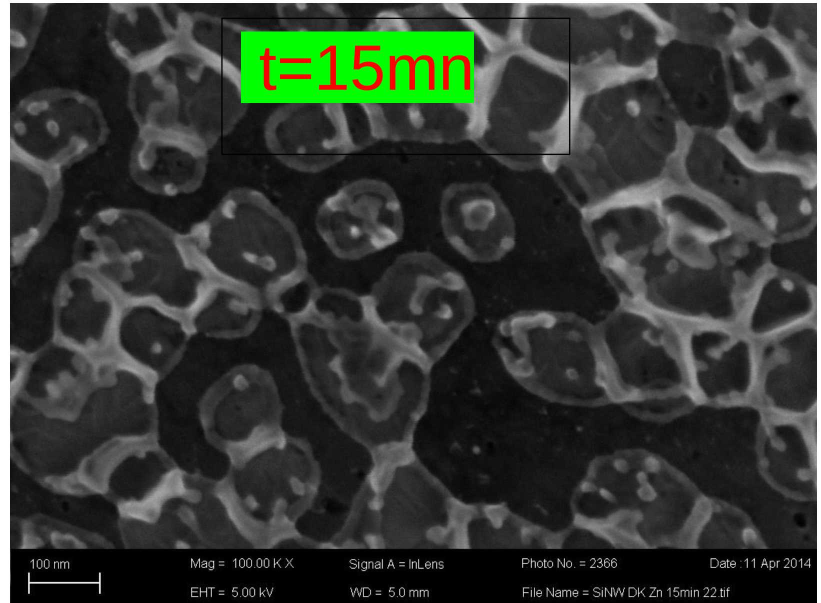


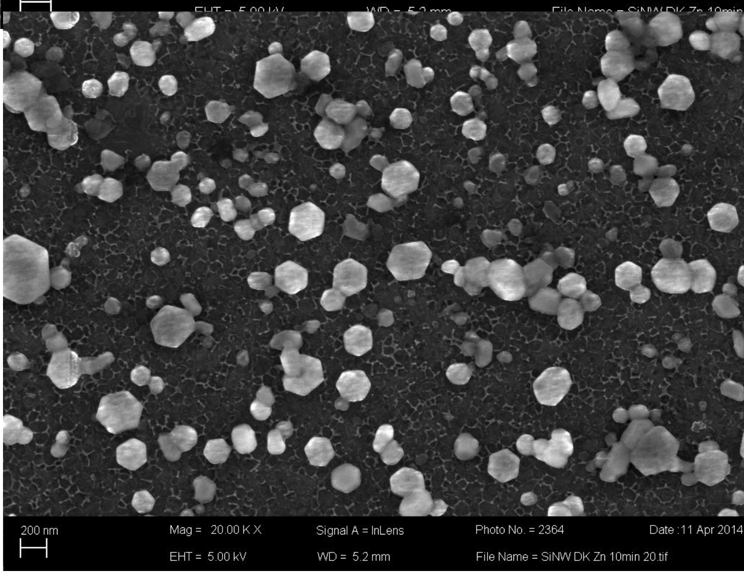
- Nanowires germination starts in the pyramid vicinity
- Growth of a pure and very distinctively Cu nanowires
- the surface present Cu nanowires coming from the Cu2+ reduction

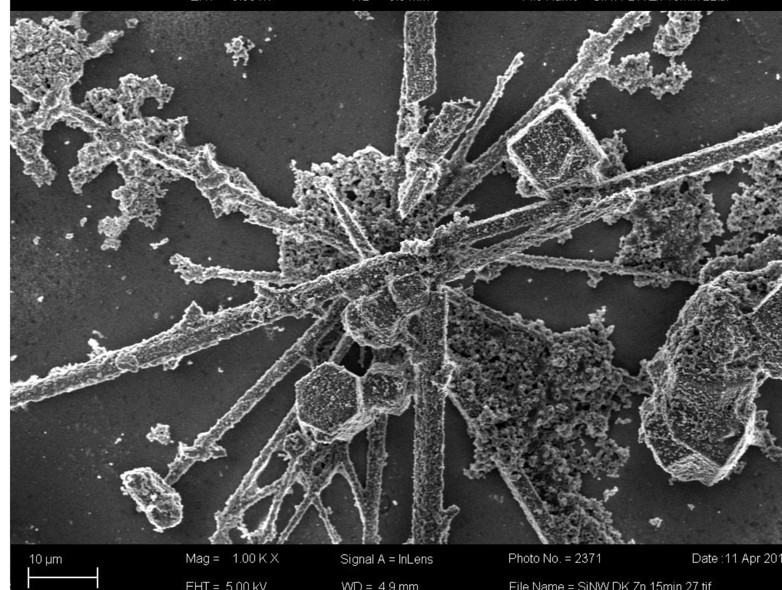
This result give a possibility to growth very perfect 1D Cu nanowires

Results and Discussion for Zn catalyst









- unlike other catalysts, Zn catalyst rather form a deposit of ZnO. This is explained by the hexagonal shape that comes from the Wurtzite structure of ZnO.

Conclusion and Perspectives

It is also possible to form nanostructures of spiro-conical nanoholes. This unique form could have potential applications in optoelectronics and biomedicine

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THANK YOU
FOR YOUR
ATTENTION
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EHT = 5.00 kV
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WD = 4.9 mm
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Date :28 Feb 2014