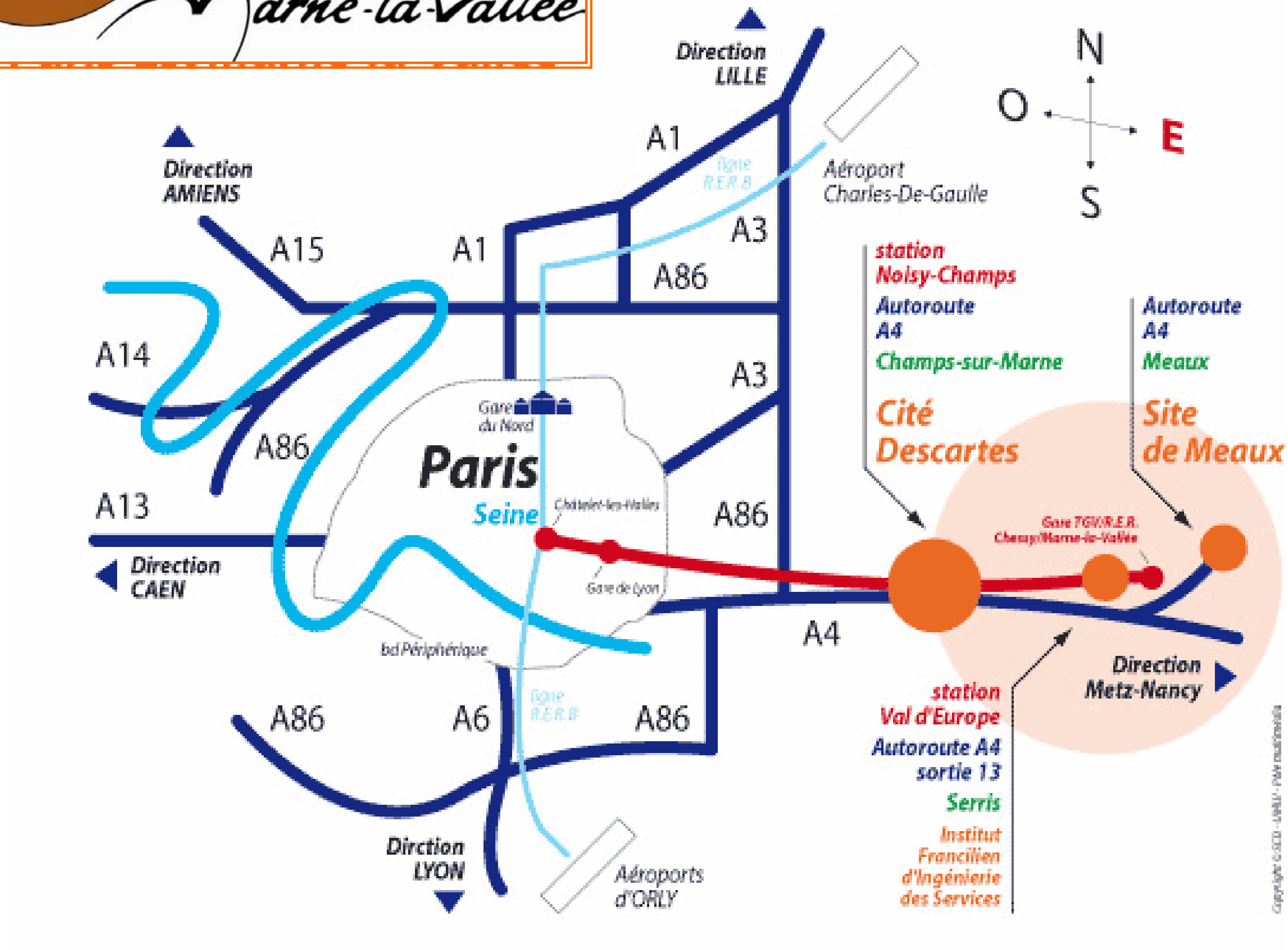
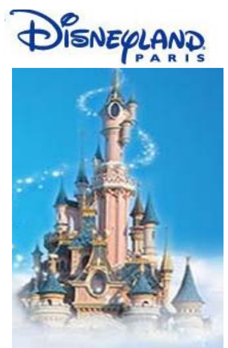
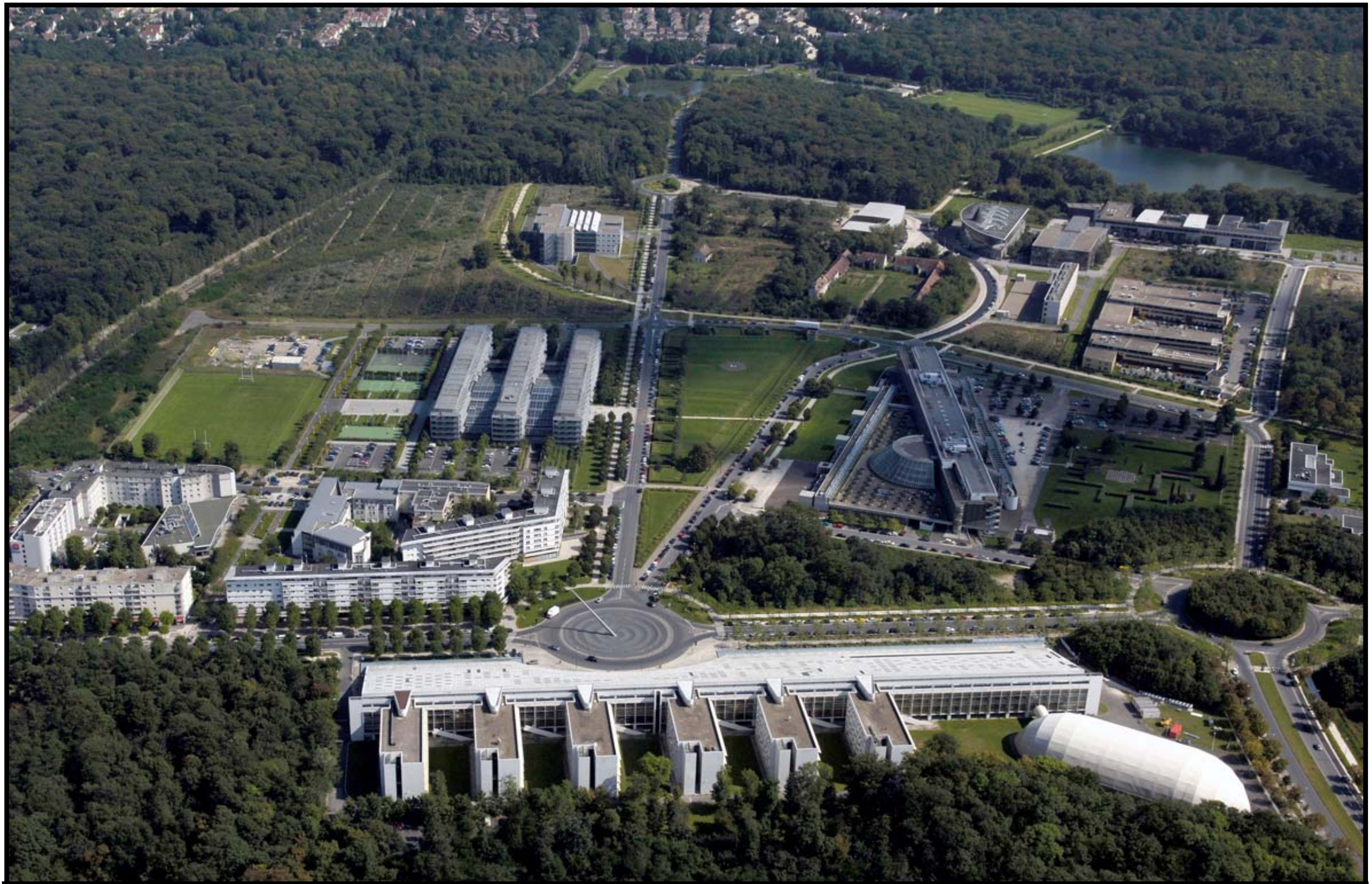
巴黎东部马恩河谷大学 (UPEMLV)
(巴黎东大联盟 UPE)

NİVERSİTÉ PARİS-EST
Marne-la-Vallée







Our Campus of Cité Descartes

始建于1991年的巴黎东部马恩河谷大学现在已有超过11000名学生，17个研究实验室. UPEMLV是巴黎东部大学的创始成员之一，巴黎东部大学联盟是由许多致力于高等教育与研究的学院所组成的（路桥学院，ESIEE学院，巴黎第十二大学等）。

Laboratoire de Physique des
Matériaux Divisés et des Interfaces (LPMDI)

Elaboration of ZnO Nanowire Arrays and their Applications on Green Energy and Environment

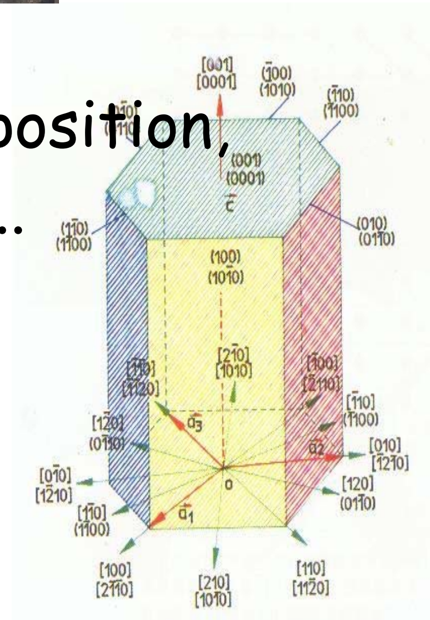
Outline:

- Introduction
- Elaboration & Structural characterization
- Electrical measurements
- Applications

ZnO:

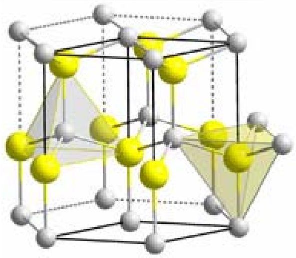
- **Semiconductor II-VI:**
- **Wurtzite structured:**

a = 0.325 nm et c = 0.512 nm.



- **Elaboration methods:** PVD, CVD, Sol-gel deposition, Electrodeposition, hydrothermal…

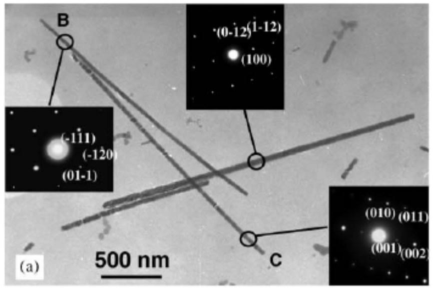
- **Properties:**
  - *direct wide bandgap (3.37 eV or 368 nm);*
  - *large exciton* binding *energy (60 mV);*
  - *piezoelectric properties;*
  - *high isoelectric point (IEP = 9.5);*
  - *high electrons transfer capacity*;
  - *biocompatible;*
  - *high chemical stability;*
  - …



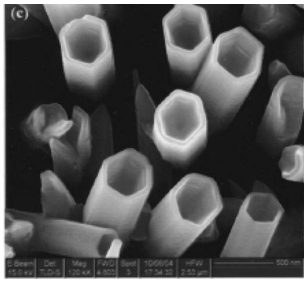
Applications :

- Bio-sensor
  Bio-devices
- Gas sensor
- UV/Blue emission devices
- Nanogenerator of electricity
- Laser diodes
- Solar cells

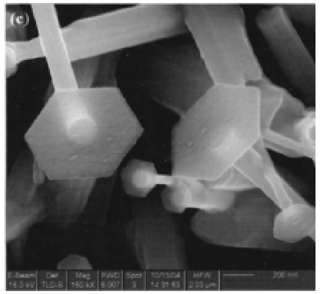
Morphologies :



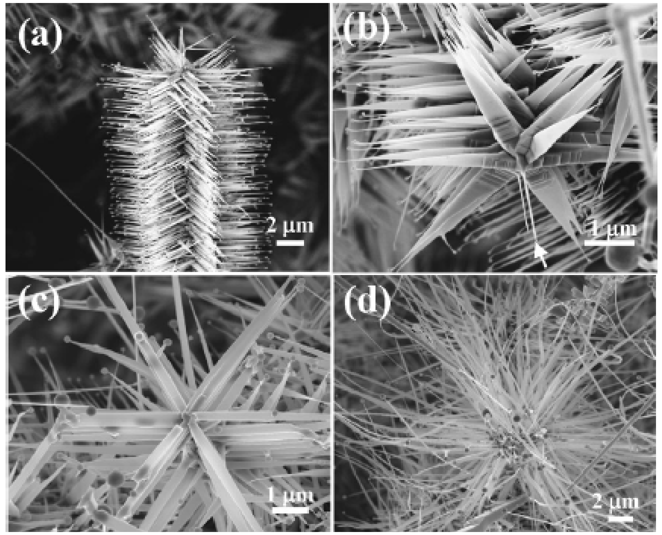
Nanowires



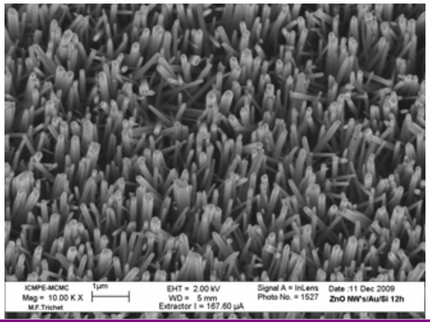
nanotubes



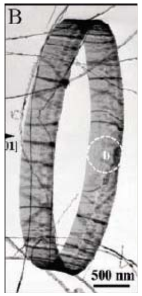
nanopins



nanosbrushs

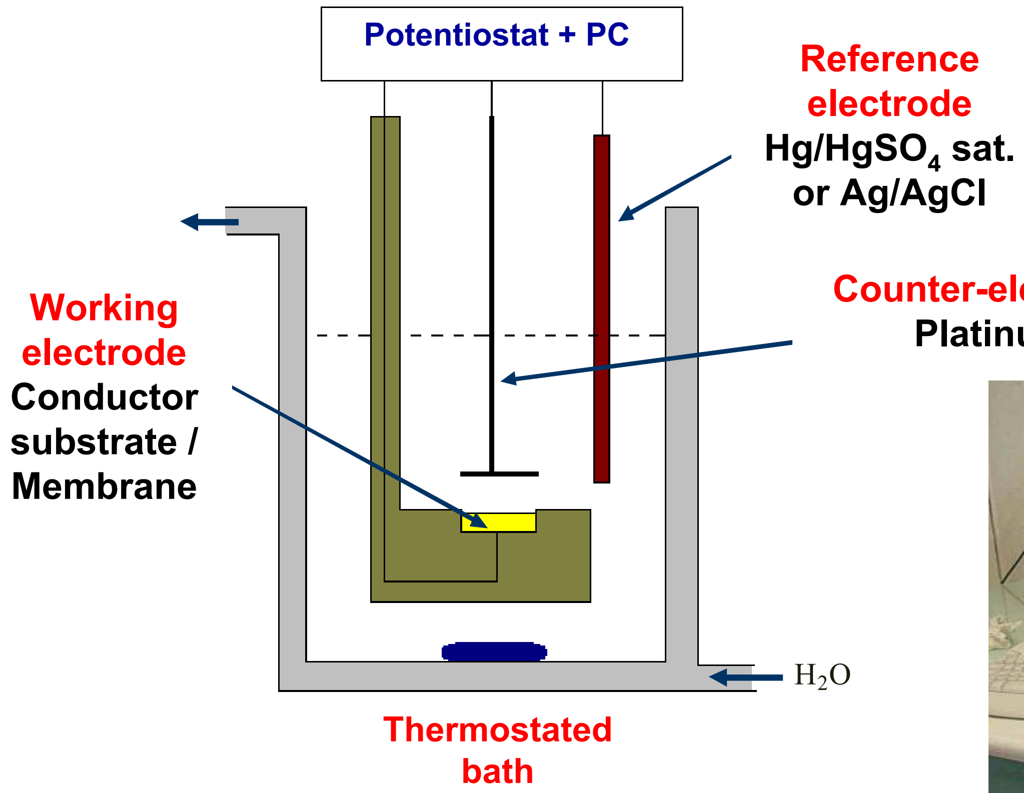


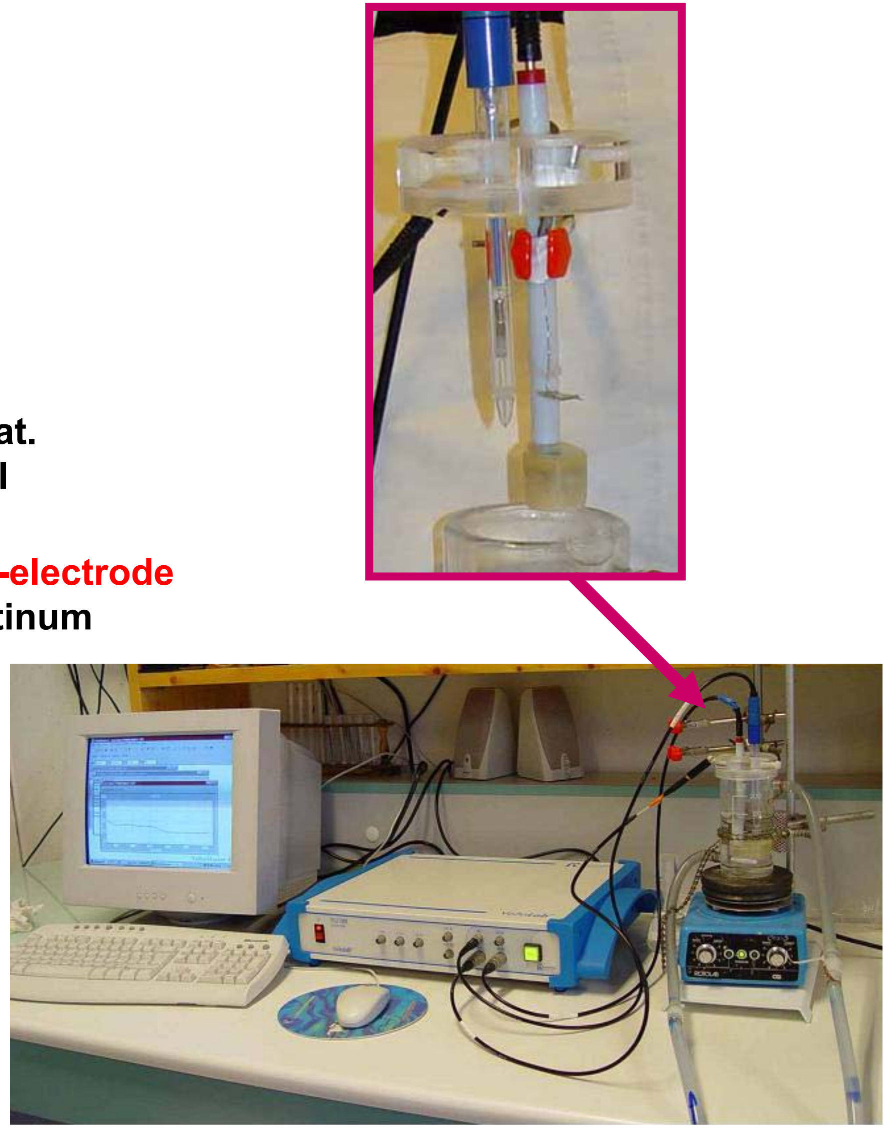
nanohelix



nanoring

Single nanowires obtained by electrodeposition:





Classical three-electrode electrochemical cell for ZnO deposition: thin films & nanowires

❖ Electrolyte :

* 0.1 M KCl * 5 mM $ZnCl_2$ * 5 mM H_2O_2 (30%)

❖ Experimental details:

- **Temperature:** T = 70°C.
- **Substrates:** Metallic discs, gilded Si, ITO
  (➔thin films & NW arrays)
  Polycarbonate membranes, PMMA
  (➔ micro-plots & single NW's).
- **Counter-electrode:** Platinum. * $V = -1{,}5\ V_{/MSE}$

❖ Electrochemical mechanism:

1. The reduction of hydrogen peroxide leads to the formation of hydroxide ions:

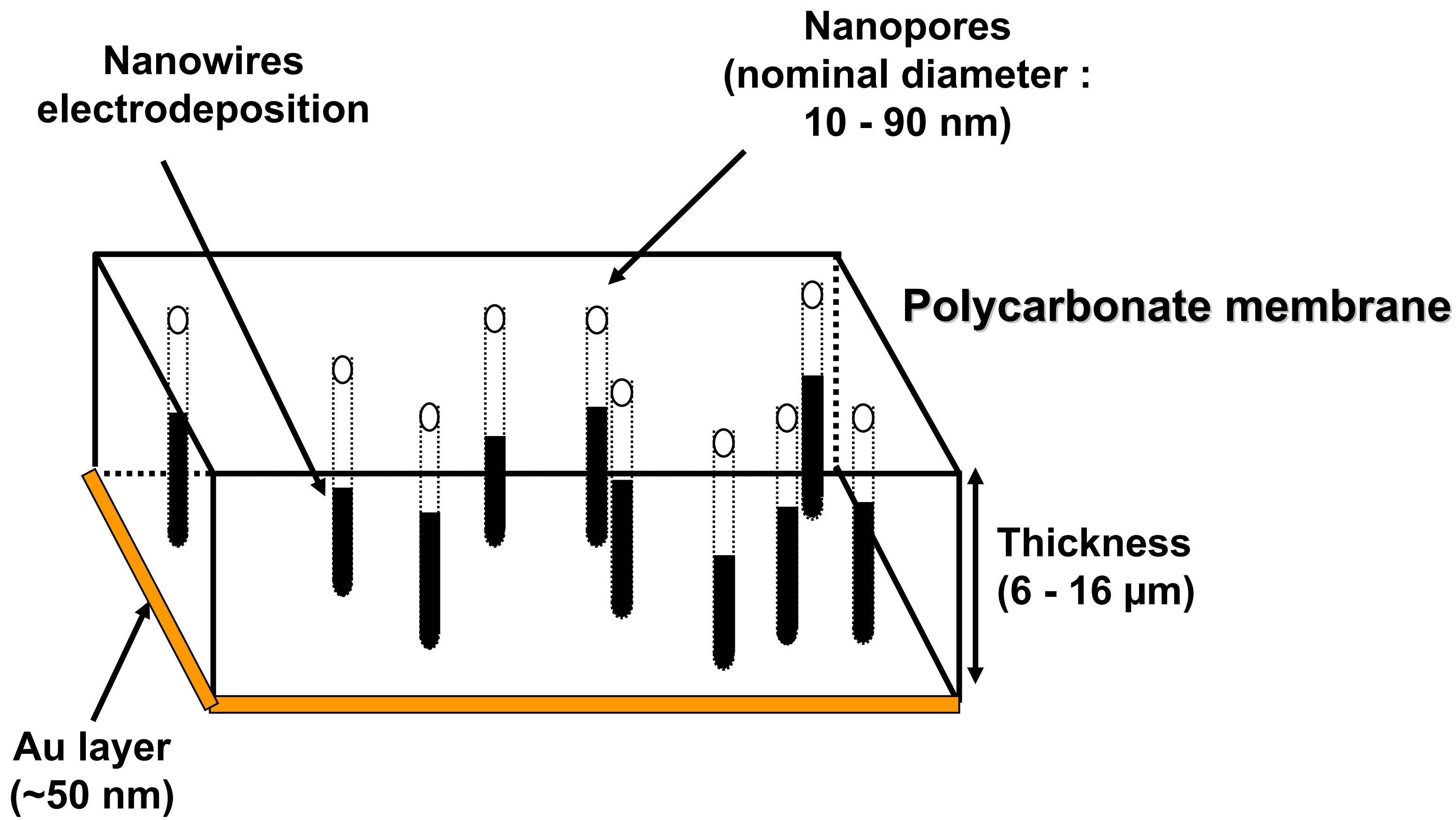
$$H_2O_2 + 2e^- \rightarrow 2OH^-$$

2. The overall deposition reaction of ZnO in the presence of H_2O_2 can be reasonably written as:

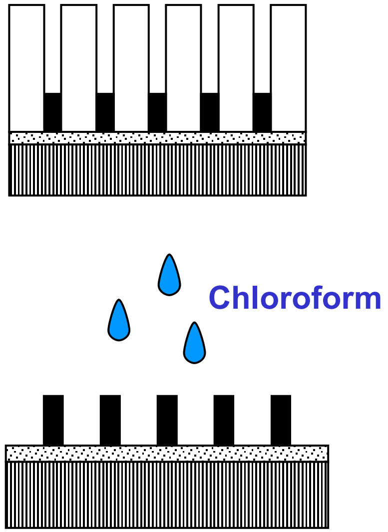
$$Zn^{2+} + H_2O_2 + 2e^- \rightarrow ZnO + H_2O$$

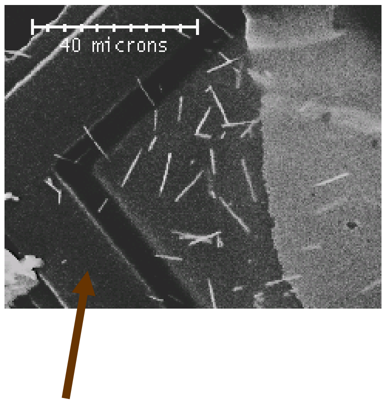
K. Laurent, Y. Leprince-Wang et al. ***Thin Solid Films***, 517 (2008) 617-621.
K Laurent, Y. Leprince-Wang et al. ***J. of Physics D: Applied Physics***, 41(2008) 195410.

Template method:

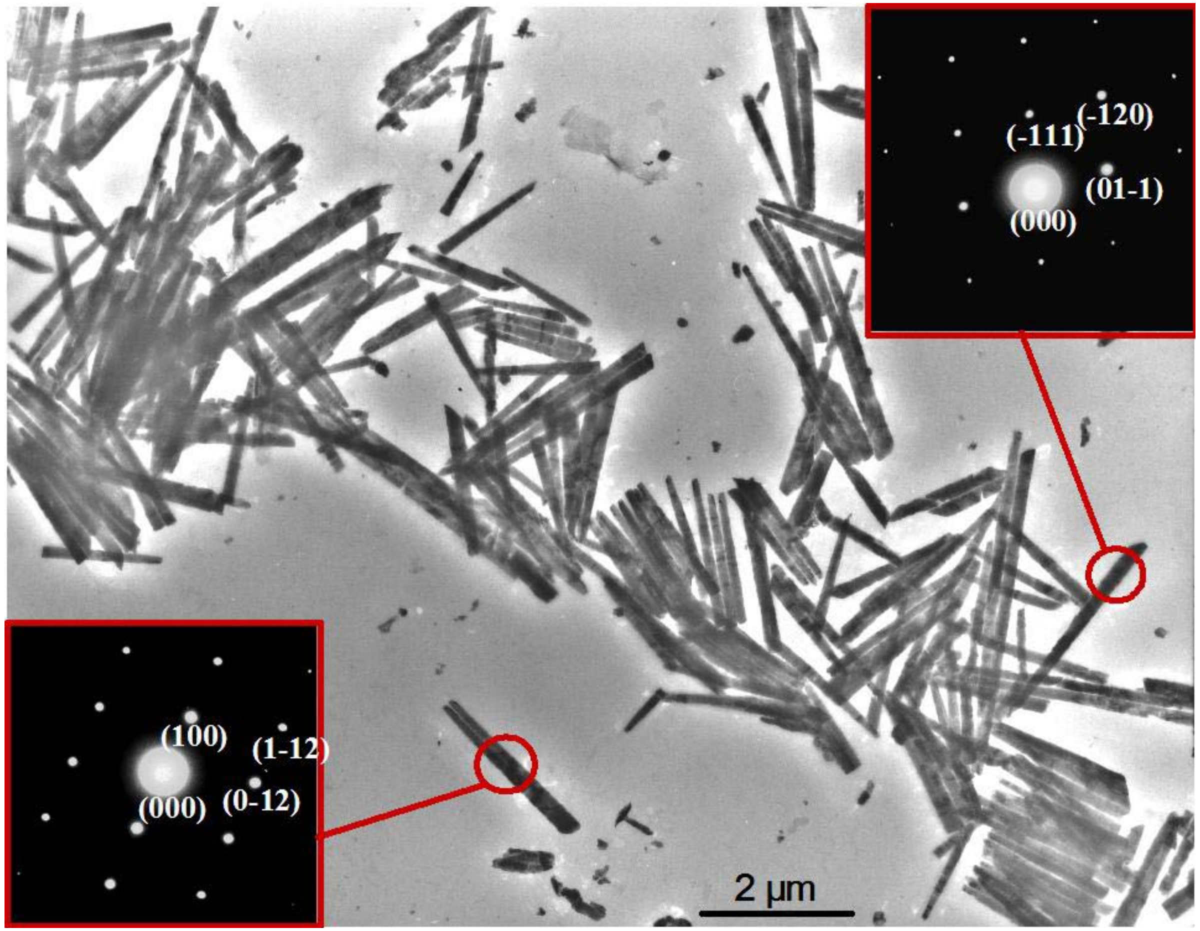


Pore density: ~ 6 x10^8 - 2 x10^9 pores/cm^2



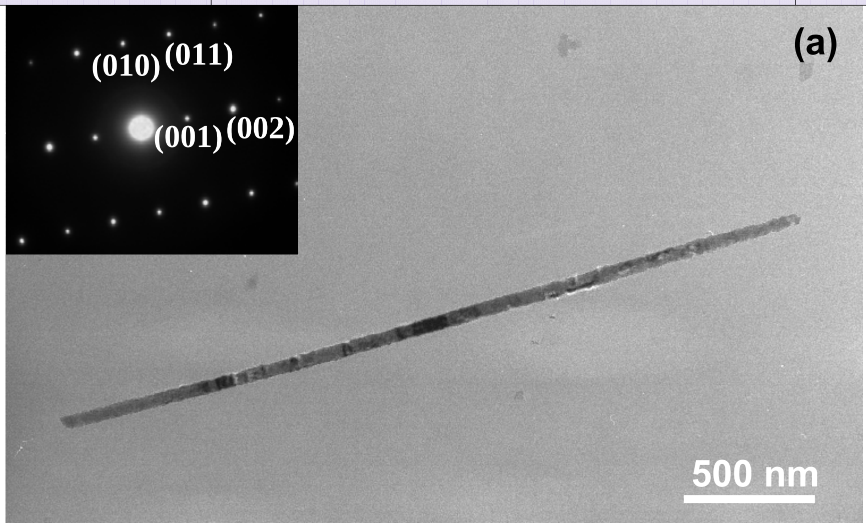


TEM Grill

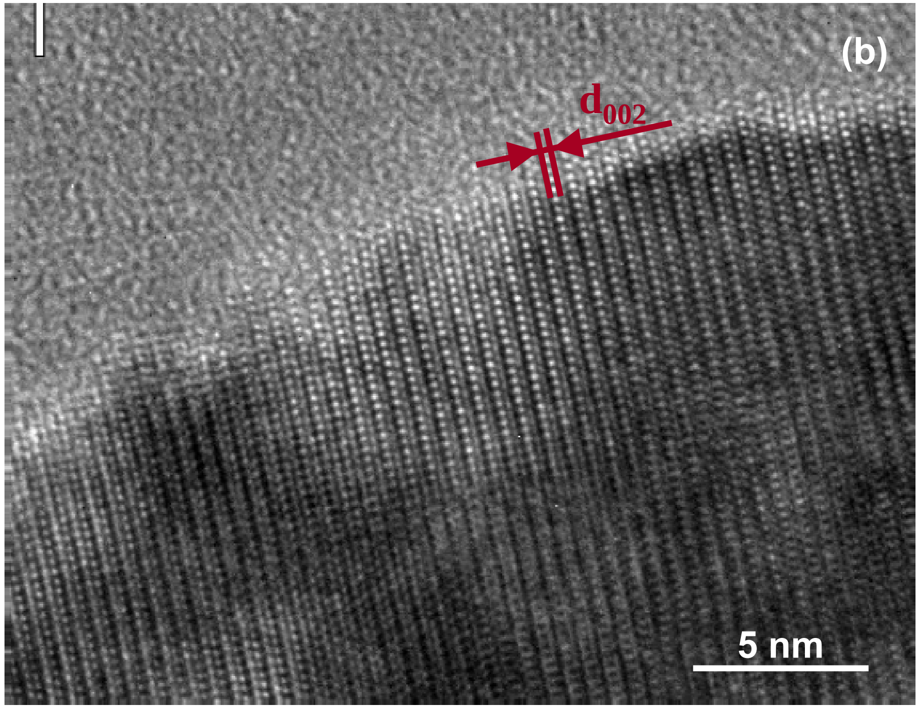


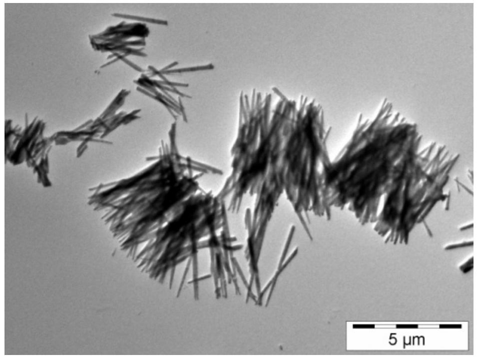
TEM images showing a general morphology of the electrodeposited ZnO nanowires from ***M90*** type membranes (d ~ 150 nm).

Y. Leprince-Wang et al. *Microelectronics Journal*, **36** (2005) 625-628.
Y. Leprince-Wang, D.P. Yu et al. *Journal of Crystal Growth*, **287** (2006) 89-93.



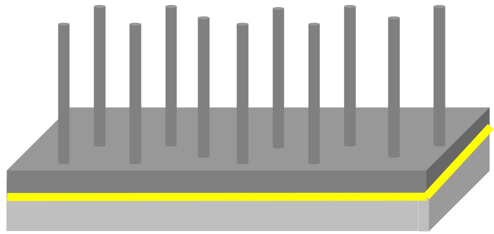
Both TEM observation (a) and HRTEM image (b) showing a M30 type individual nanowire with near <1 0 0> growth direction.



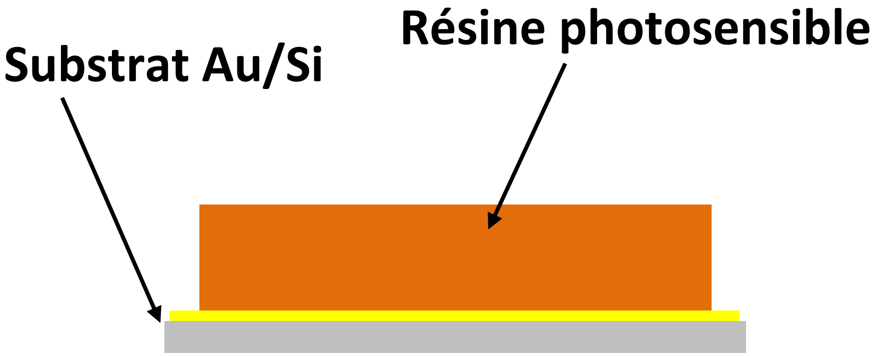


In chaos ➔ Well-ordered

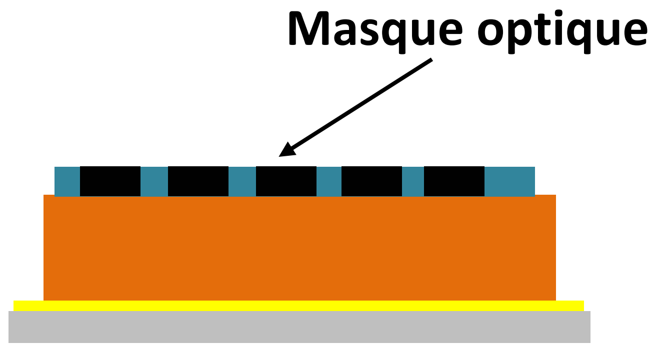
(using template method)



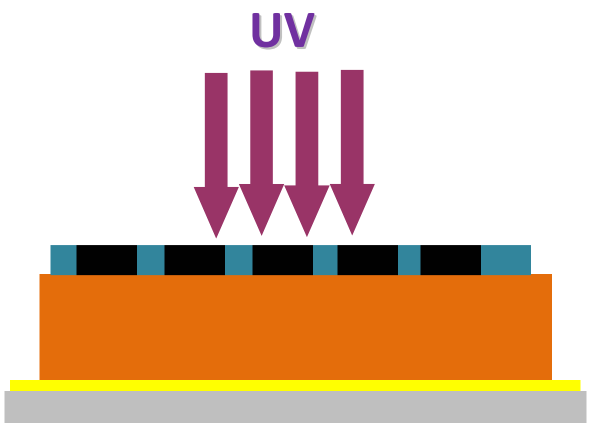
Optical lithography



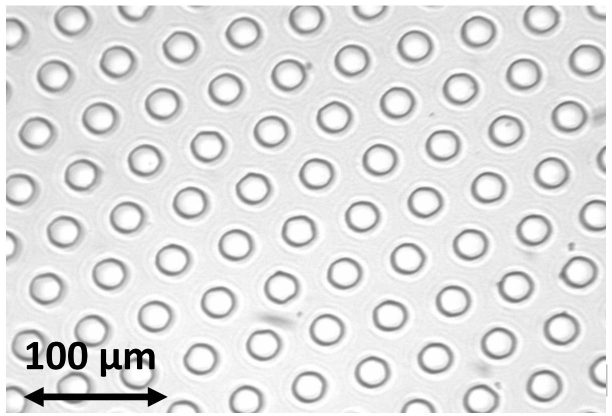
(1)



(2)



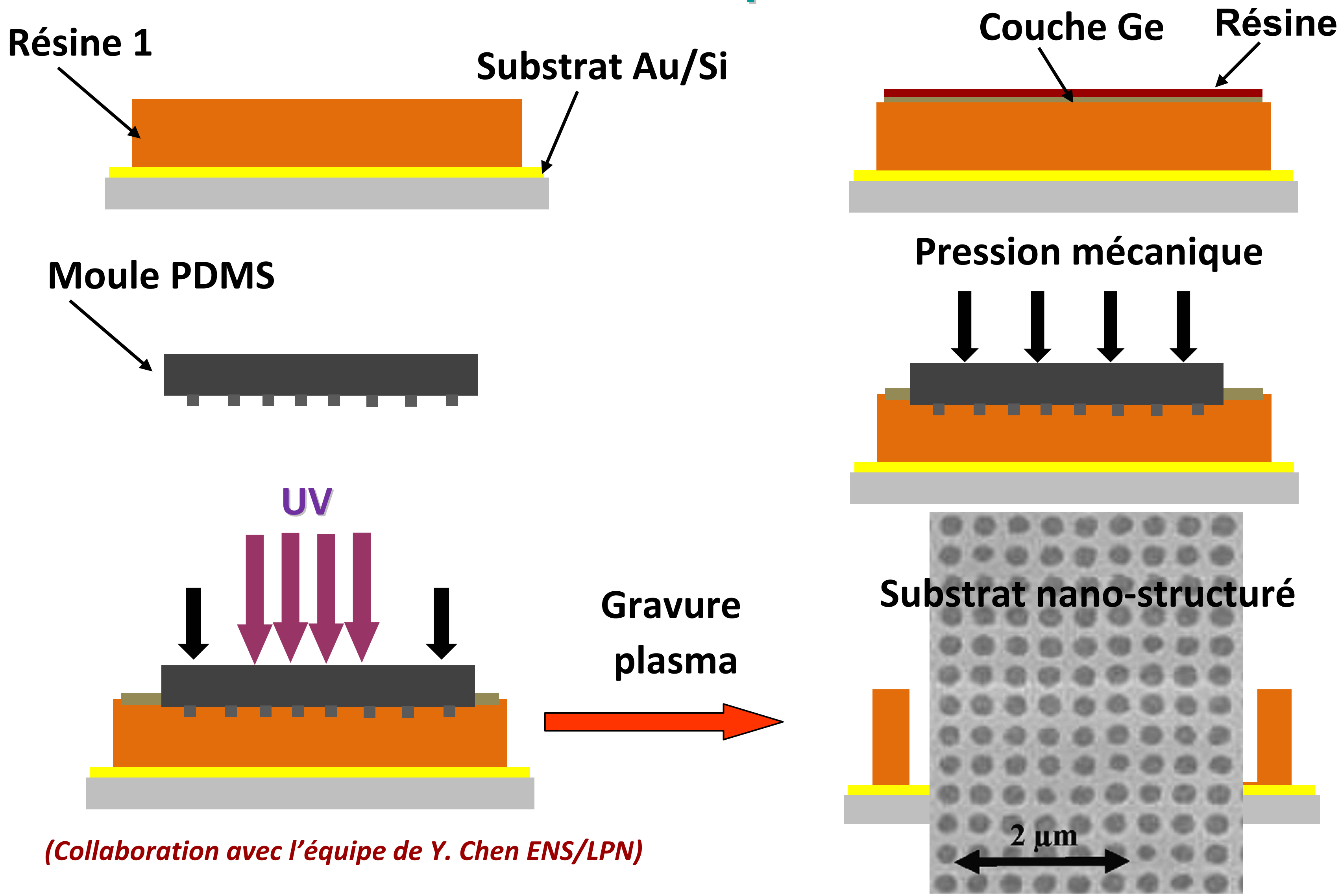
(3)



(4)

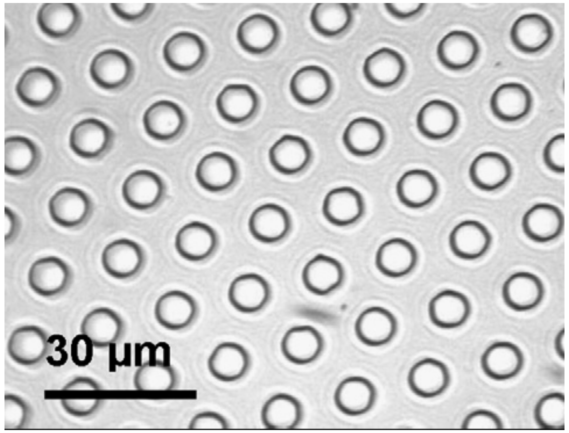
Substrat micro-structuré

Nanoimprint

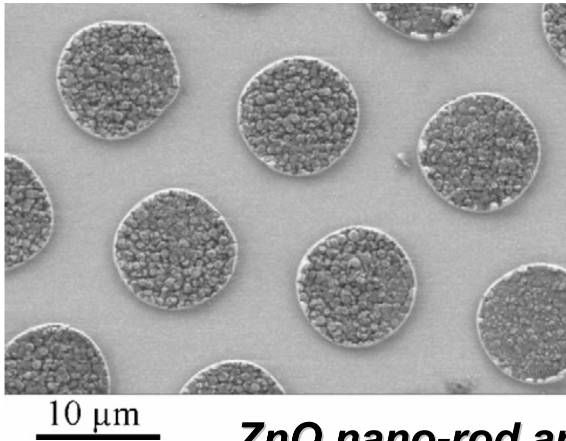


(Collaboration avec l'équipe de Y. Chen ENS/LPN)

ZnO micro- and nano-rods using lithography defined templates:

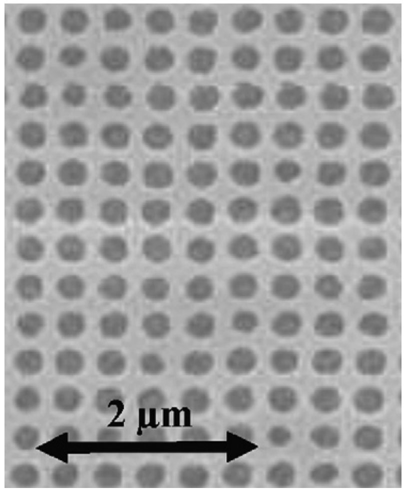


Micro-structured photoresist obtained by optical lithography.

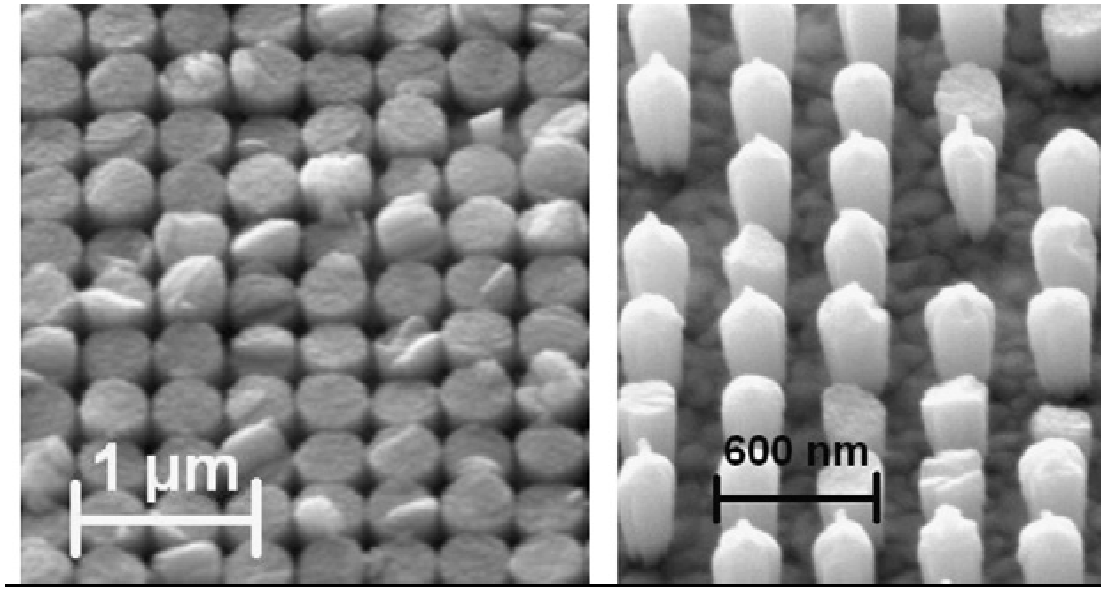


ZnO micro-rod arrays

ZnO nano-rod arrays

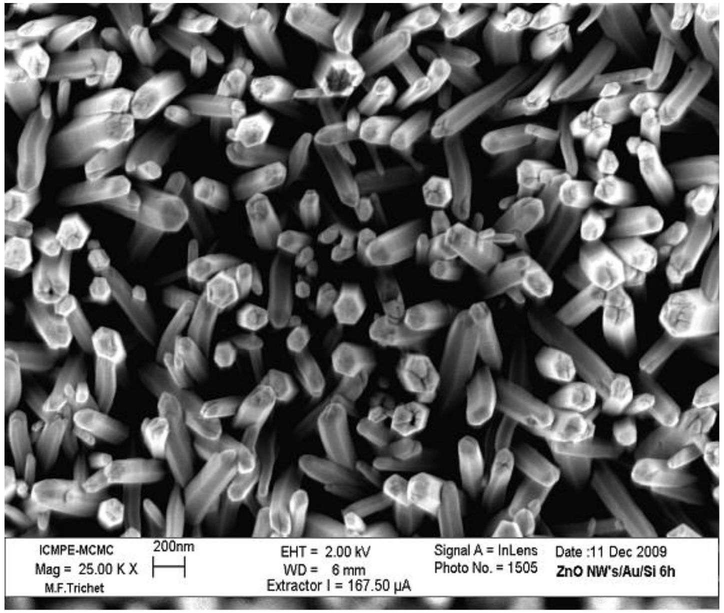


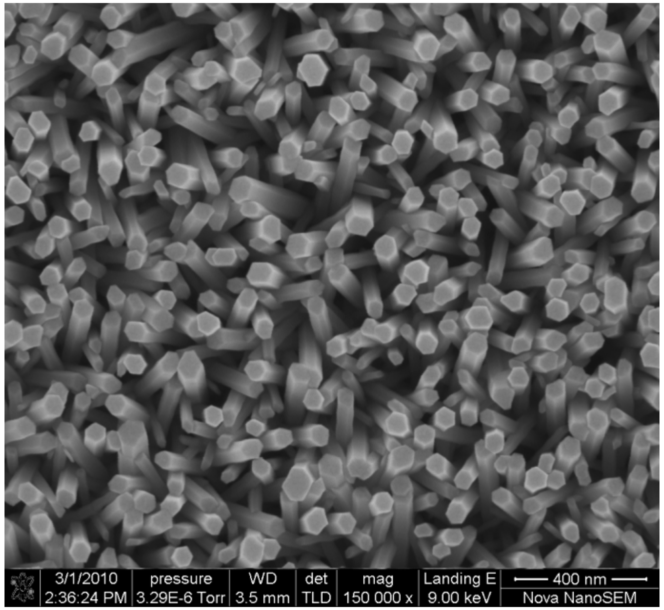
Nano-structured PMMA using ultraviolet nanoimprint lithography.

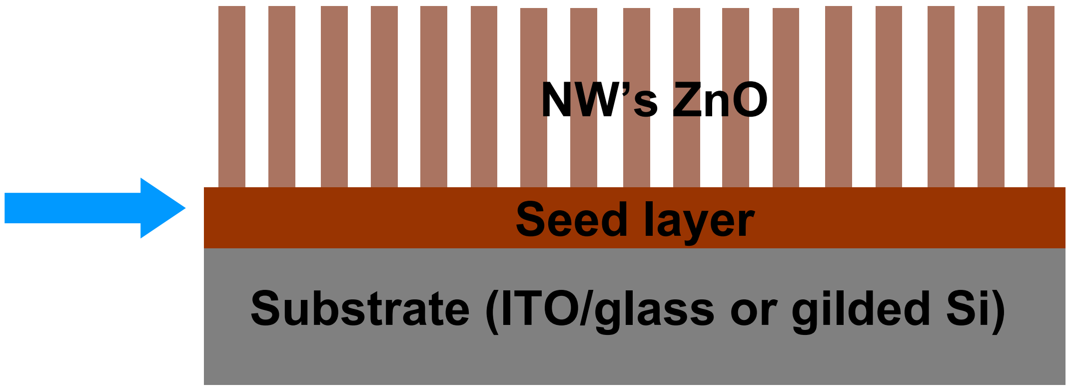


Y. Leprince-Wang et al. ***Materials Sciences & Engineering B***, (2010).

ZnO nanowire arrays:
(electrodeposition & hydrothermal method)







1. Electrodeposition of ZnO nanowire arrays

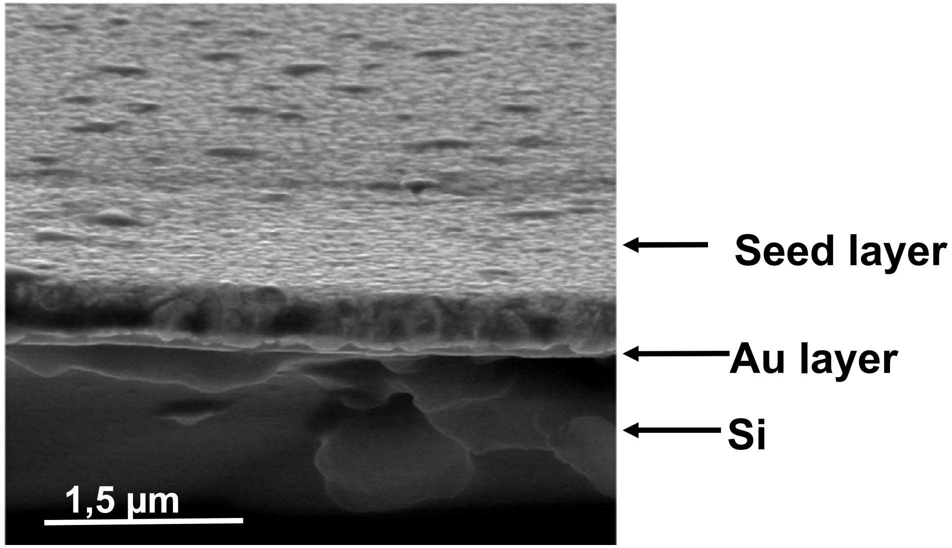
1) Electrodeposition of a seed layer:

Electrolyte: [$ZnCl_2$] = 5 mM; [KCl] = 0,1M; and O_2 saturated

(at room temperature) I = – 0,15 mA/cm^2 t = 45min.

$$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

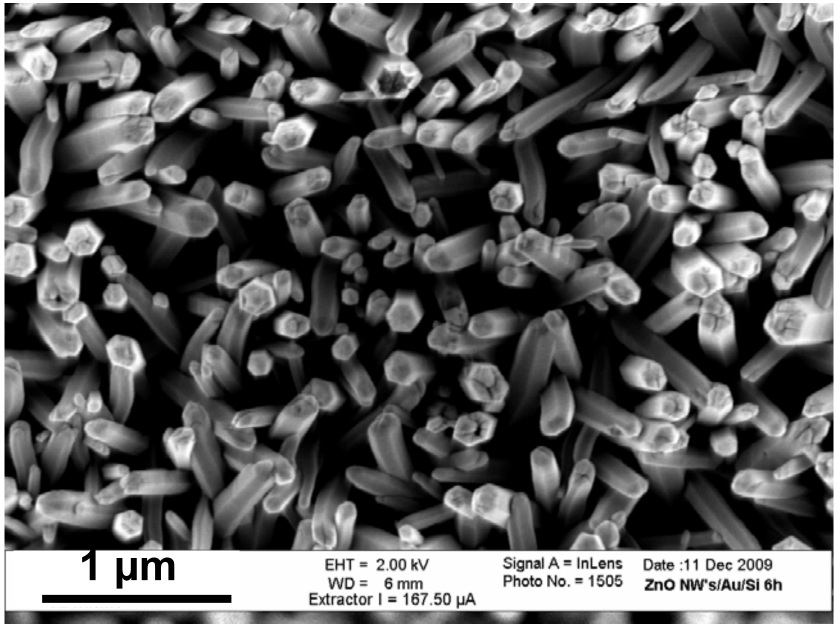
$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

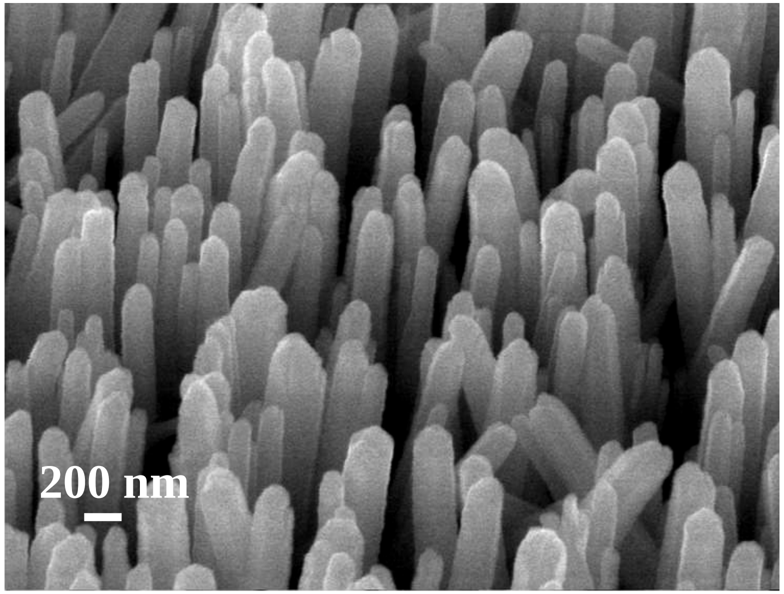


2) Electrodeposition of the nanowires:

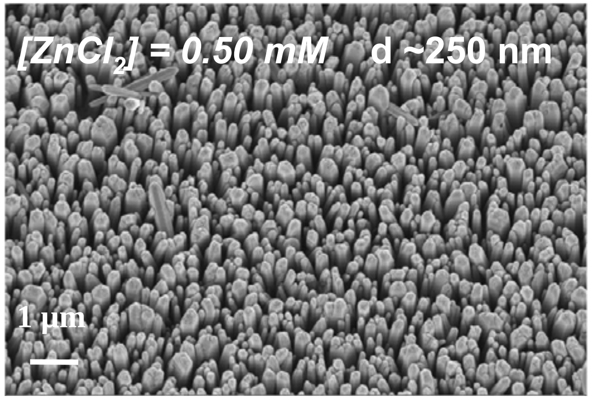
Electrolyte: $[ZnCl_2]$ = 0.5 mM; [KCl] = 0,1M; and O_2 saturated

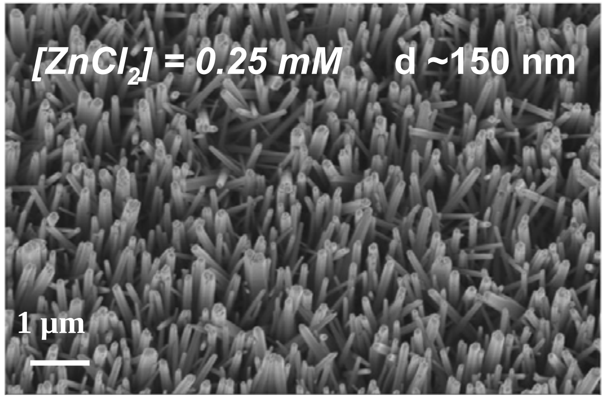
(at 80°C) * V = – 1,5 $V_{/SCE}$ t ~ 2h for ℓ~1 µm

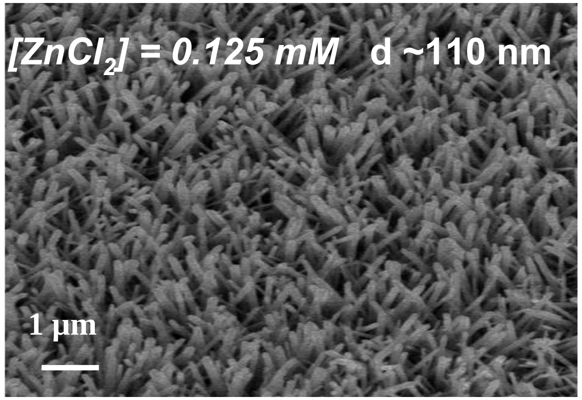




Dependence of the ZnO NWs' morphology:



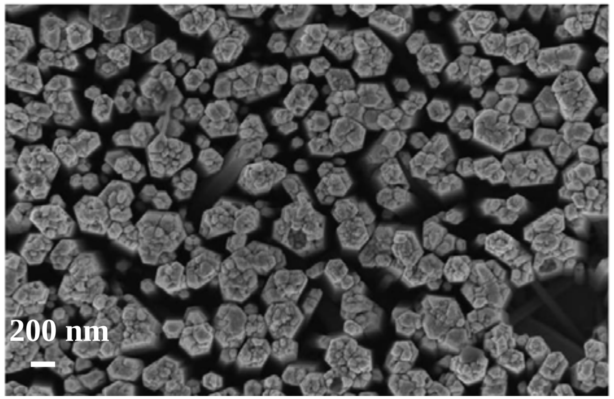




$[ZnCl_2] \uparrow \Rightarrow d \uparrow$

$Thickness_{seed\ layer} \uparrow \Rightarrow d \uparrow$

$[KCl] \uparrow \Rightarrow \ell \uparrow$ $[KCl] \uparrow\uparrow \Rightarrow d \uparrow$



{T. Brouri, Thesis of Université Paris-Est, May 2011}

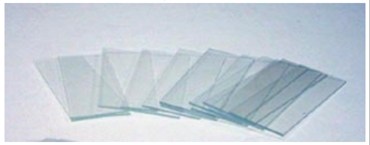
2. Hydrothermal method for ZnO nanowire arrays

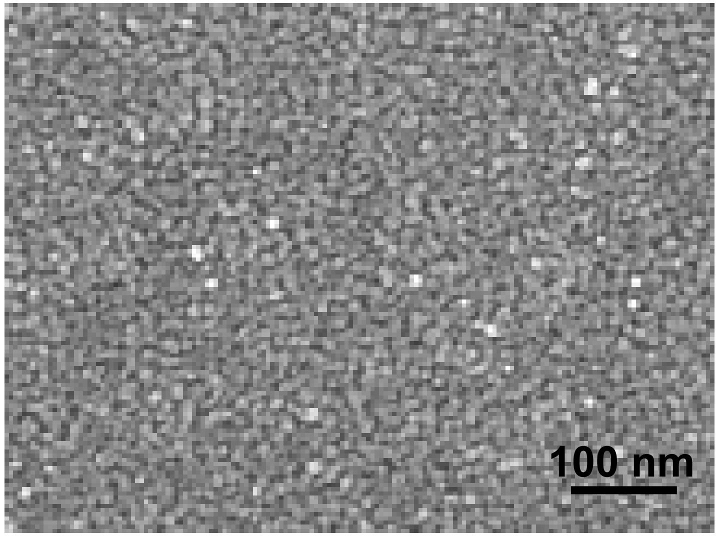
1) The seed layer deposition:

Solution:
0.01 M $Zn(Acet)_2$
in ethanol

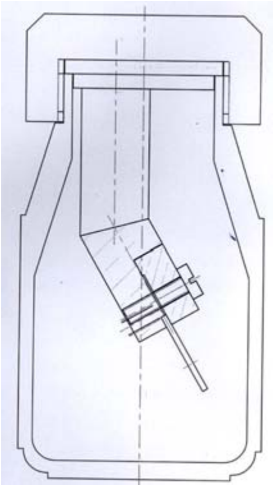
→ Spin-coating

→ Annealed at 350°C, 20min.





Homogenous layer & small grain size (~ 20 nm)



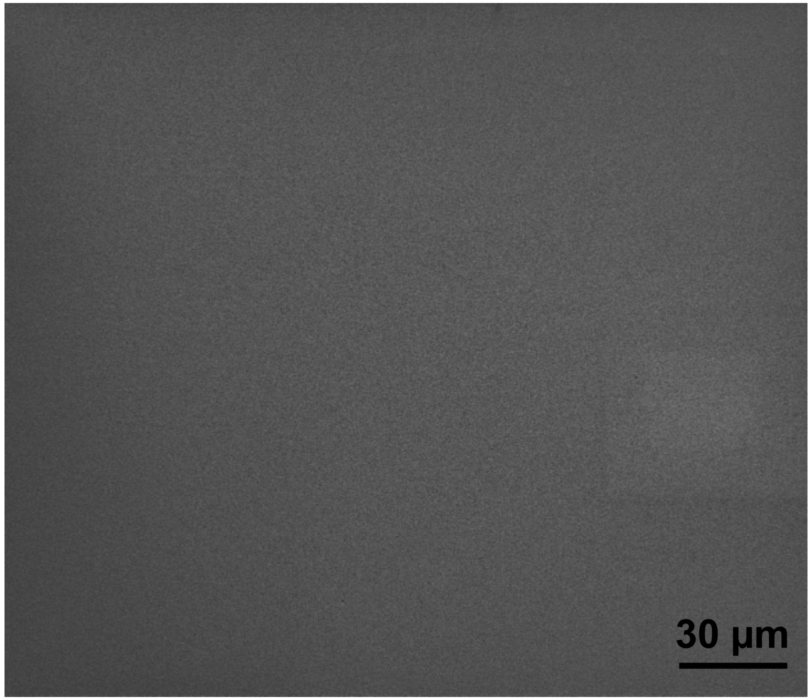
V_{sol}= 50 mL

2) The nanowires growth:

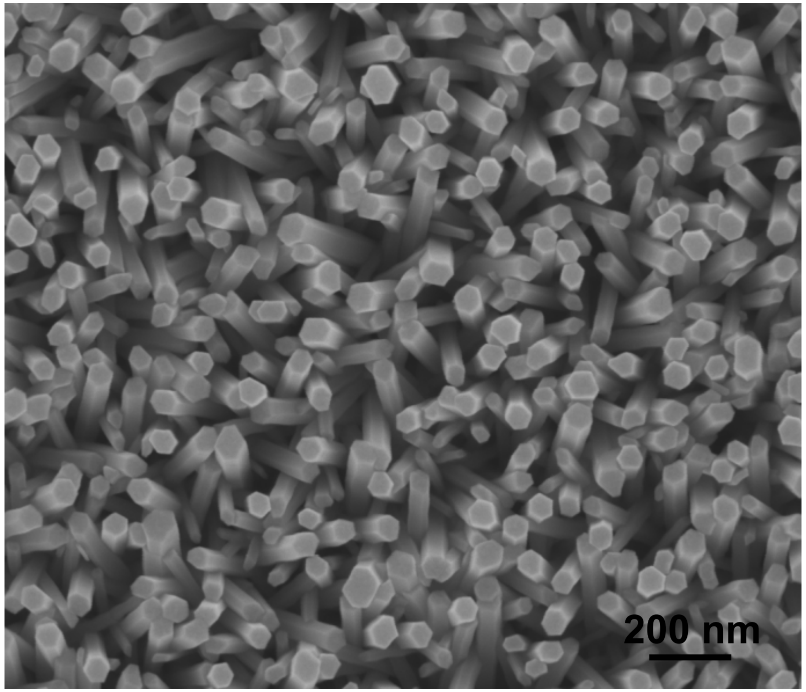
ZnO nanowires synthesis:

Solution: 0.025 M $Zn(NO_3)_2$, 0.025 M HMTA $\{(CH_2)_6N_4\}$.

Conditions: 90°C, 2 hours ➔ ℓ ~ 0.7 µm.

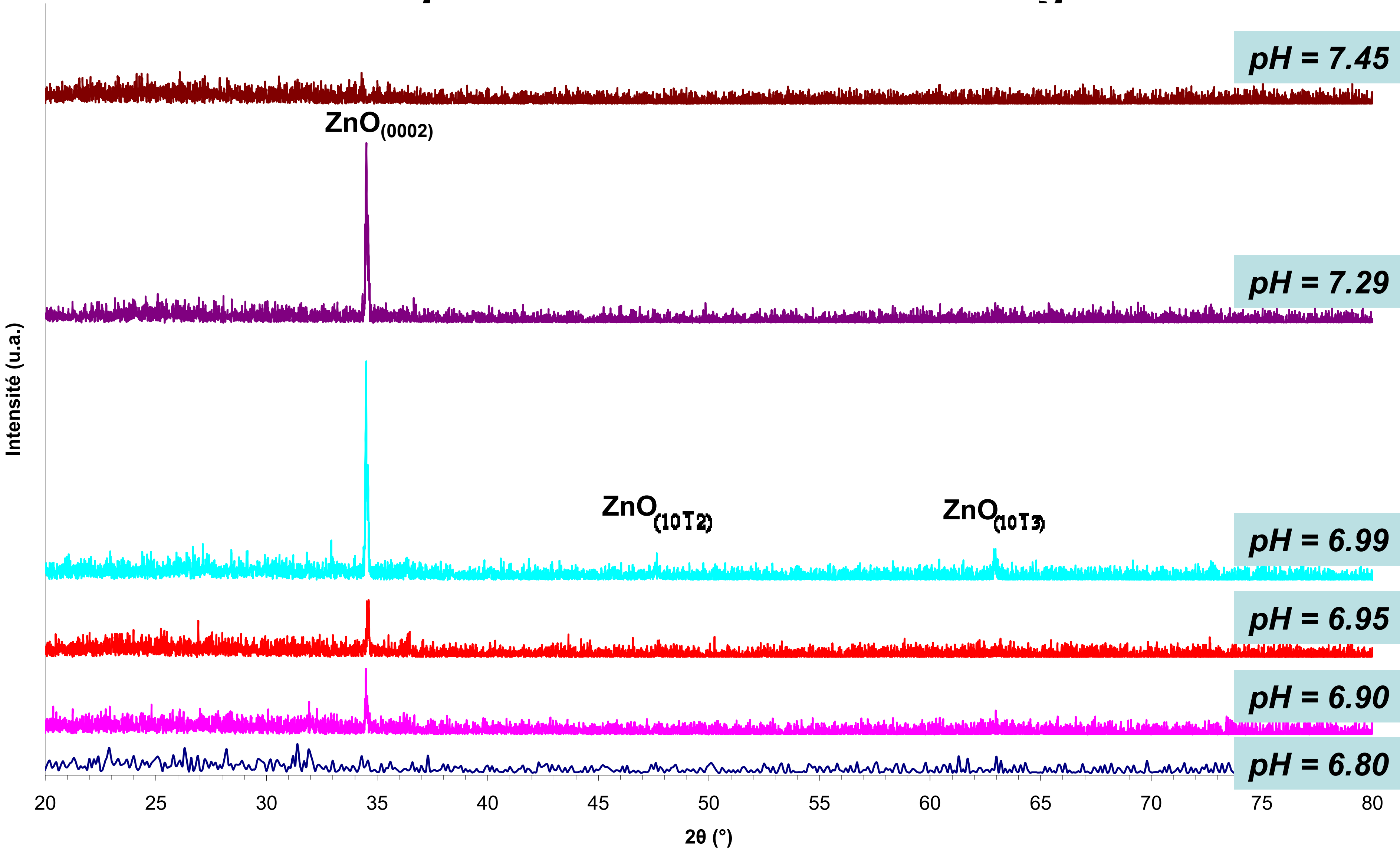


Excellent homogeneity on large scale.



Well crystallize ZnO & homogeneity in diameter (50-70 nm).

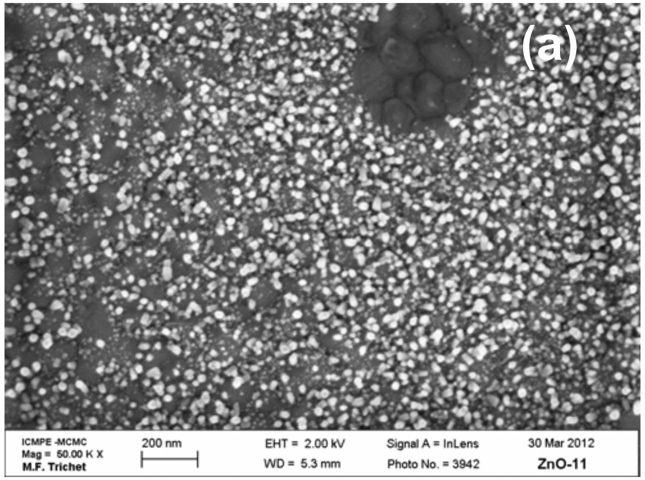
Influence of *pH* value on the nanowires growth



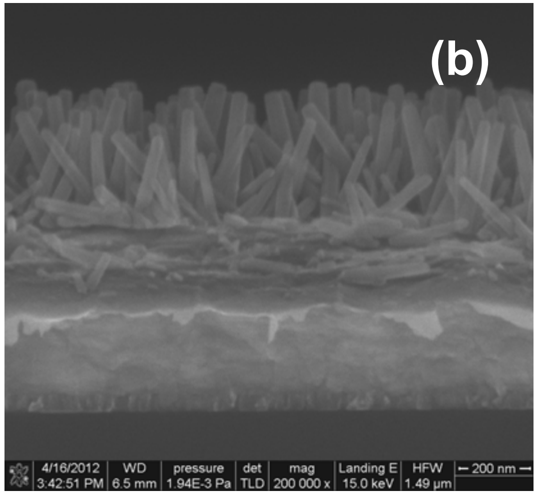
Narrow window: 6,80 < pH < 7,45

JCPDS card n°36-1451

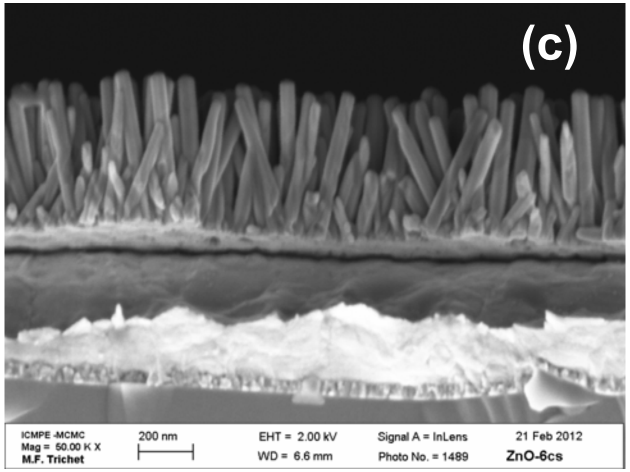
Influence of temperature on the nanowires growth



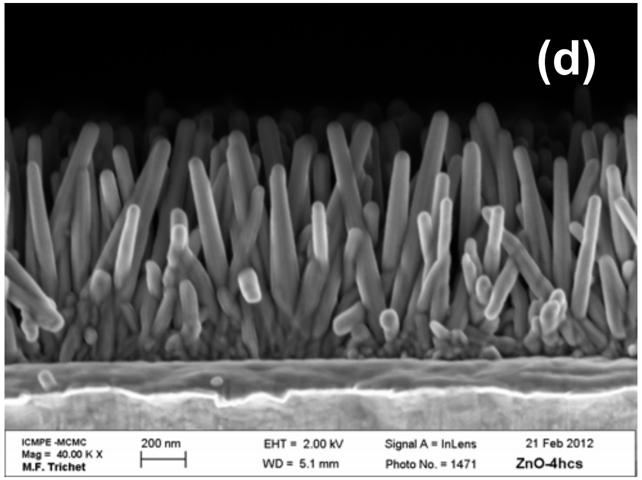
(a) 60°C (no NWs growth)



(b) 70°C (ℓ ~350 nm)



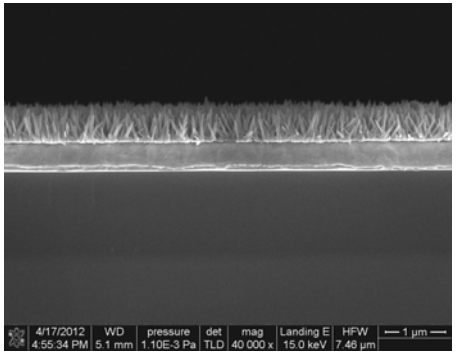
(c) 80°C (ℓ ~550 nm)



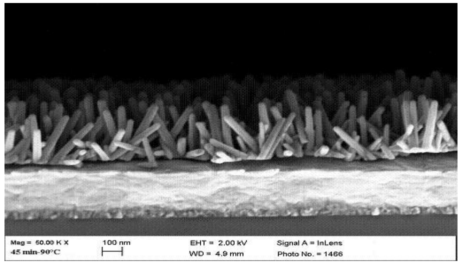
(d) 90°C (ℓ ~850 nm)

t = 2h

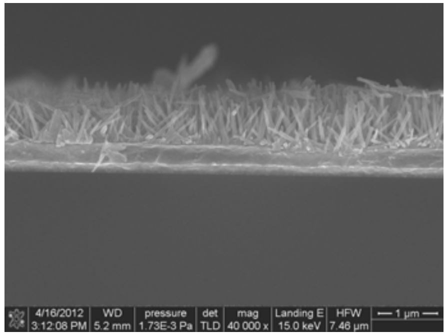
Influence of the growth time on the length



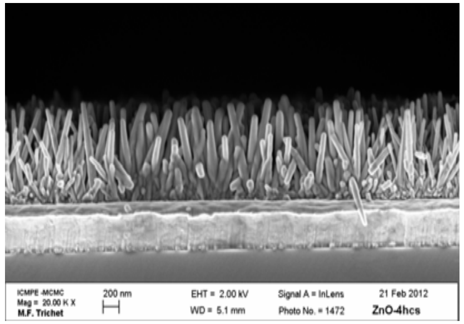
t = 30 min



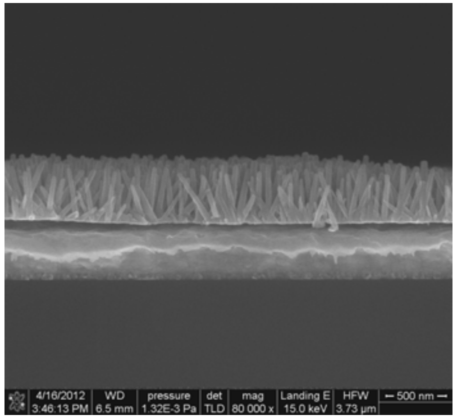
t = 45 min



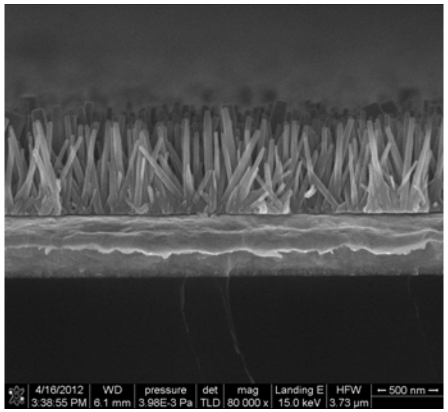
t = 1h



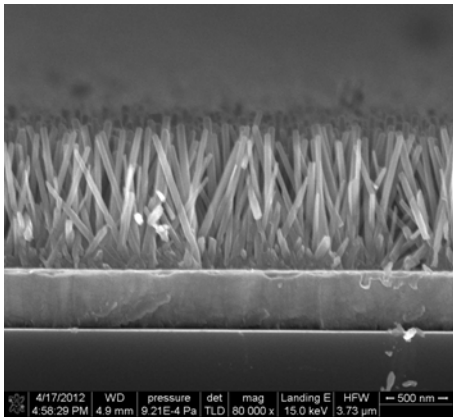
t = 2h



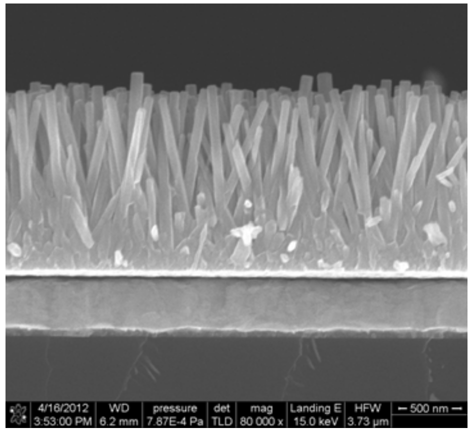
3h



4h



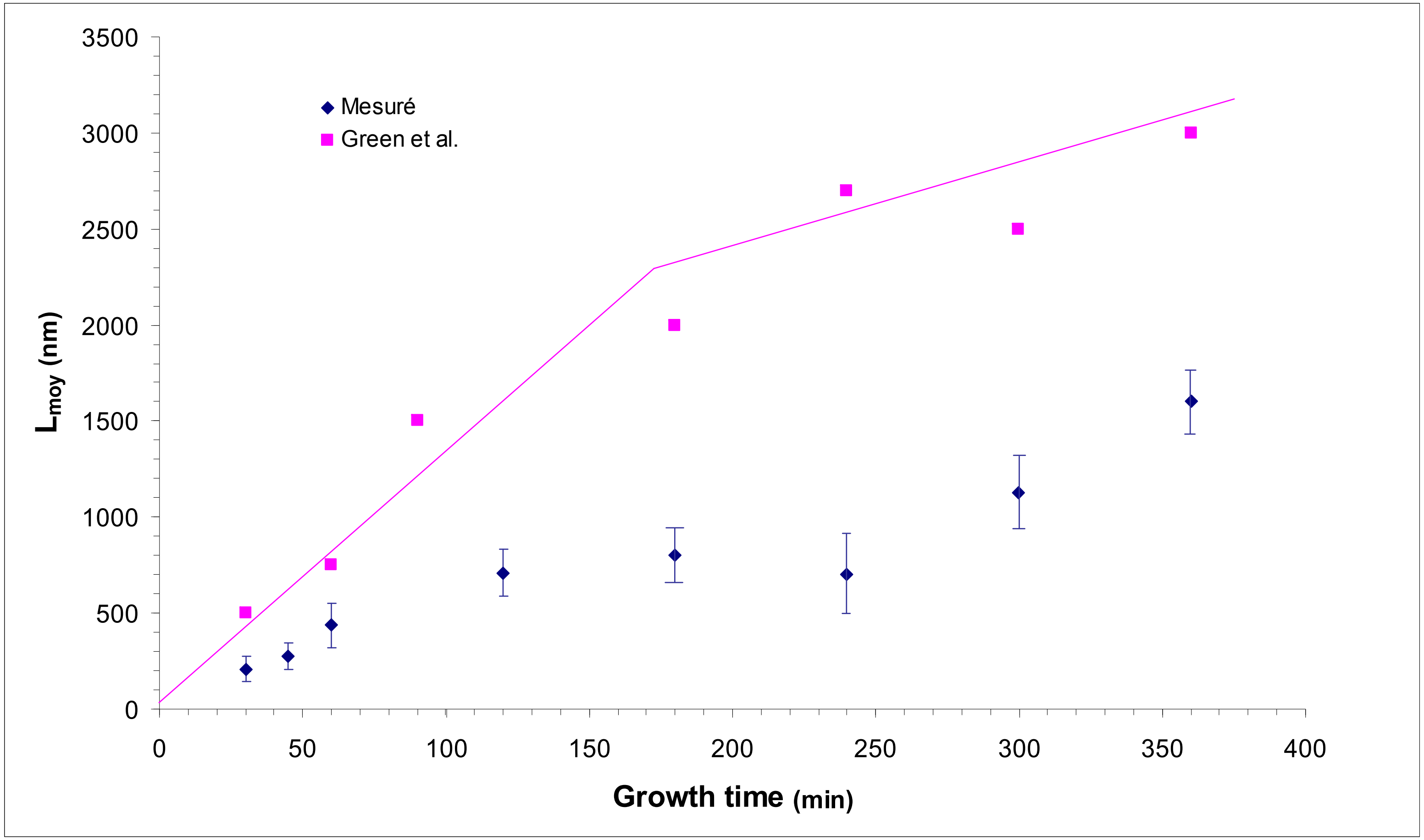
5h



6h

T = 90°C.

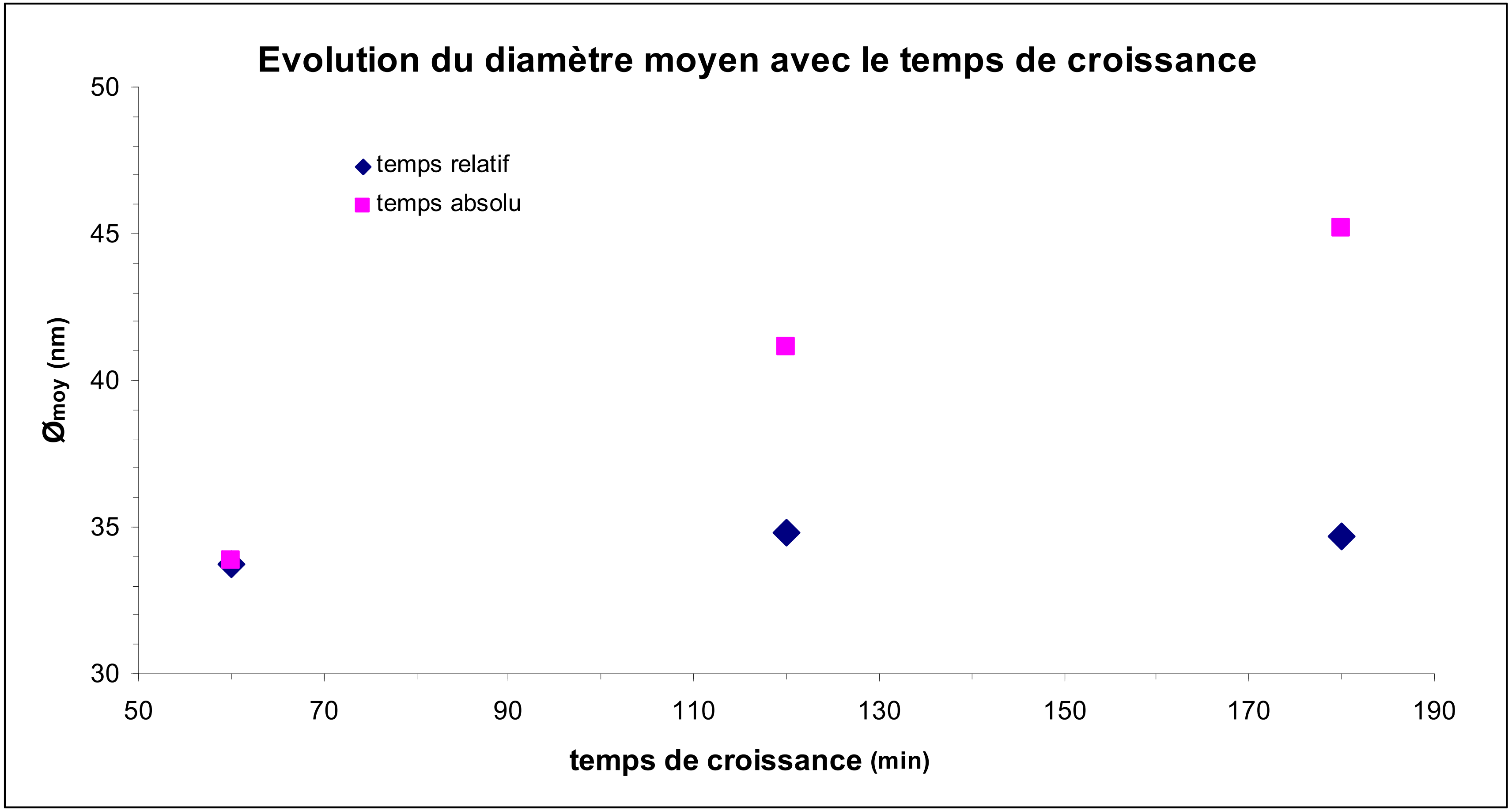
Influence of the growth time on the length



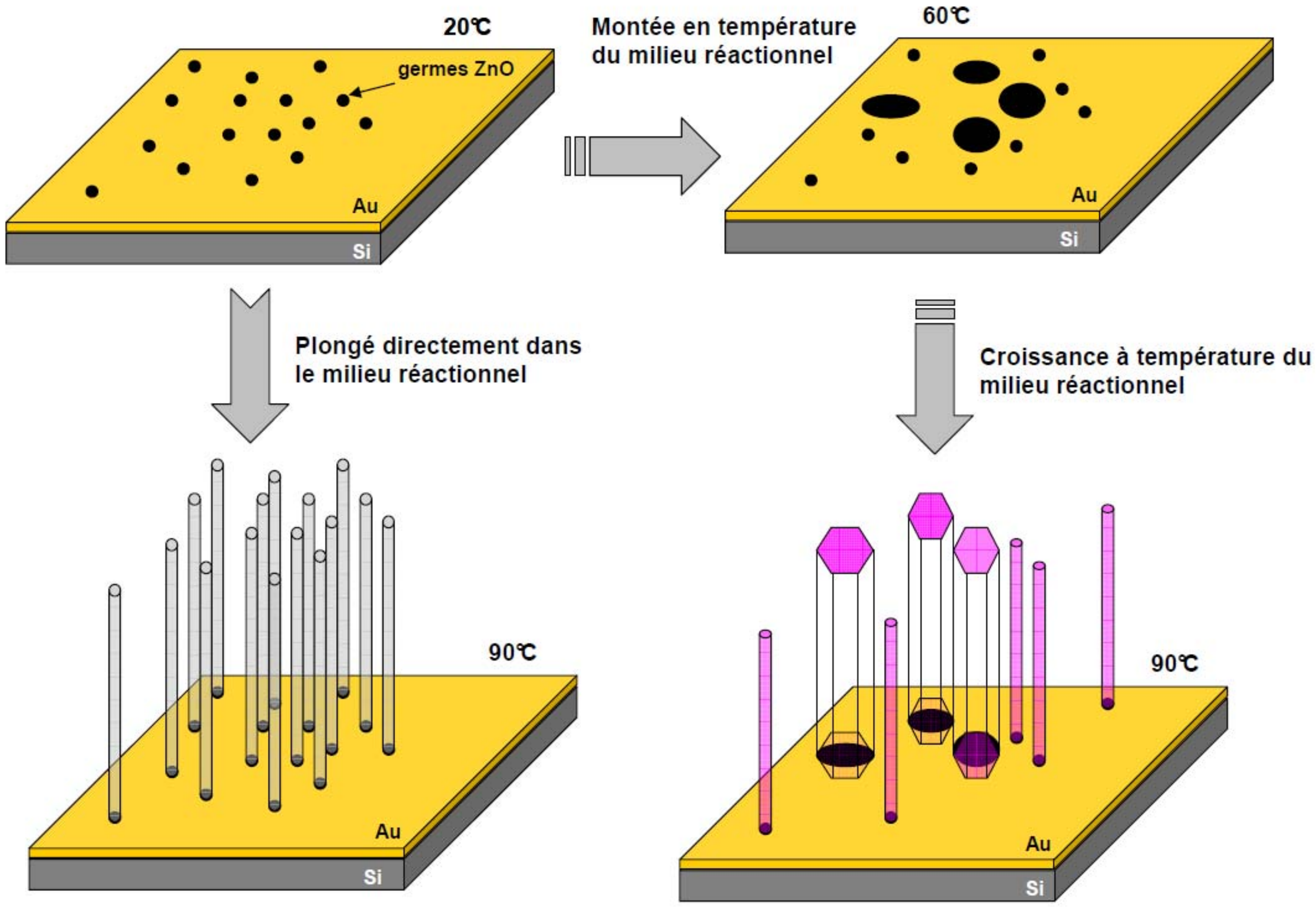
Green et al.: phase rapide 11,1 nm/min, phase lente 5,5 nm/min.

Measurements: v ~ 5 – 6 nm/min.

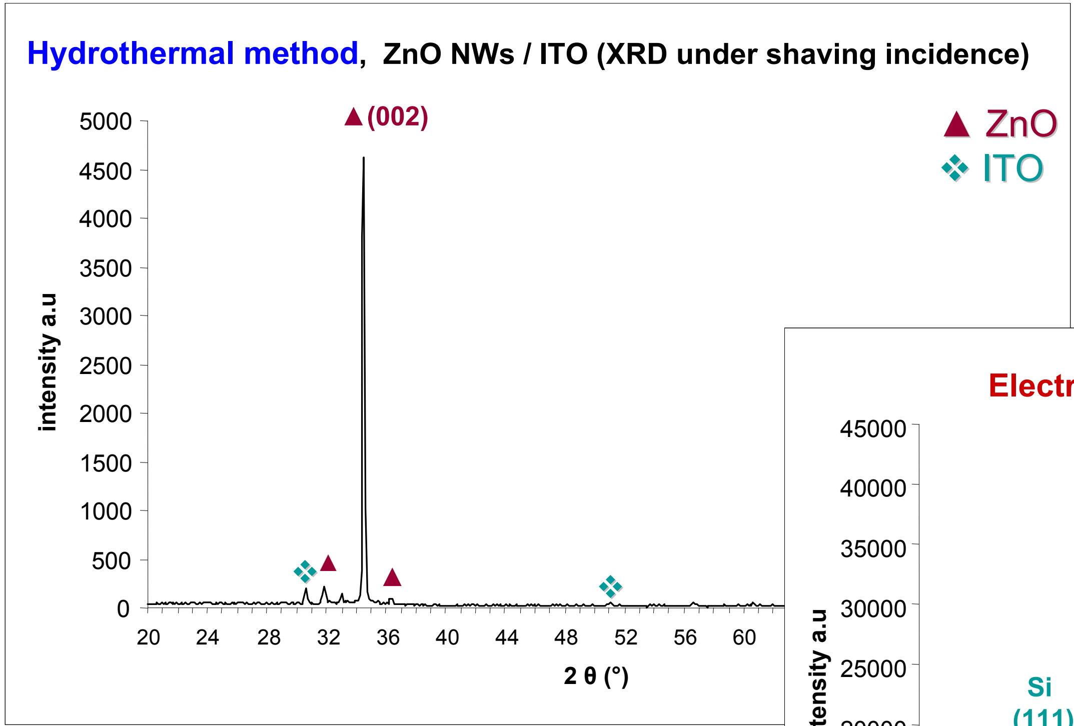
Influence of the growth time on the diameter

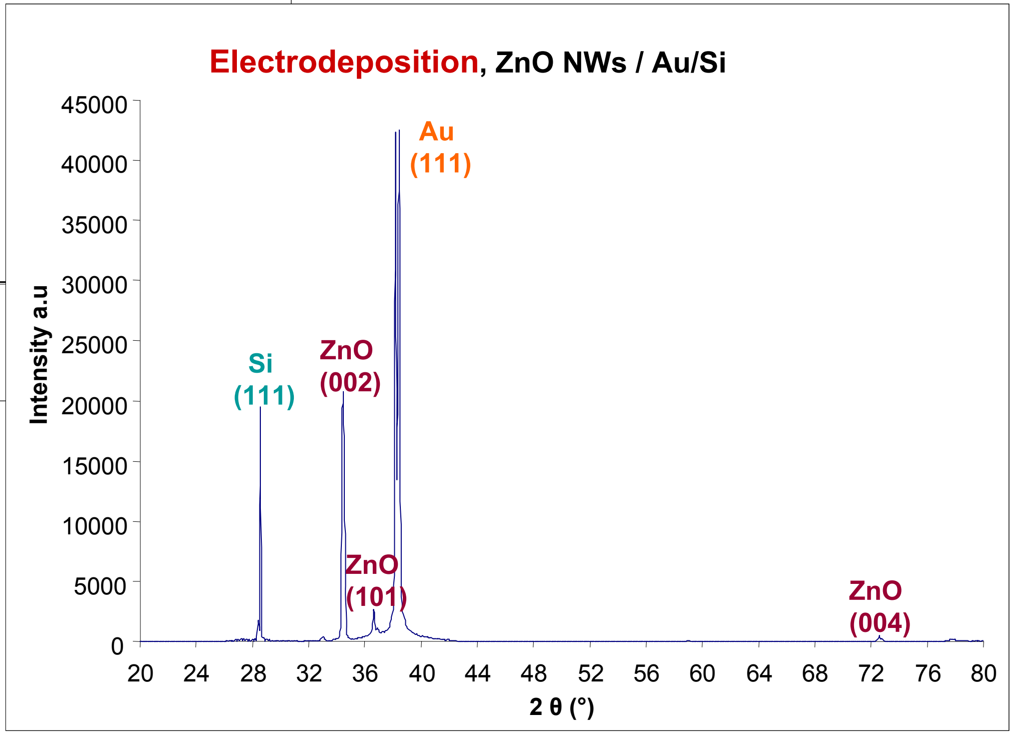


Diamètres constants pour les échantillons plongés directement à température


20℃
germes ZnO
Au
Si
Montée en température
du milieu réactionnel
60℃
Au
Si
Plongé directement dans
le milieu réactionnel
90℃
Au
Si
Croissance à température du
milieu réactionnel
90℃
Au
Si

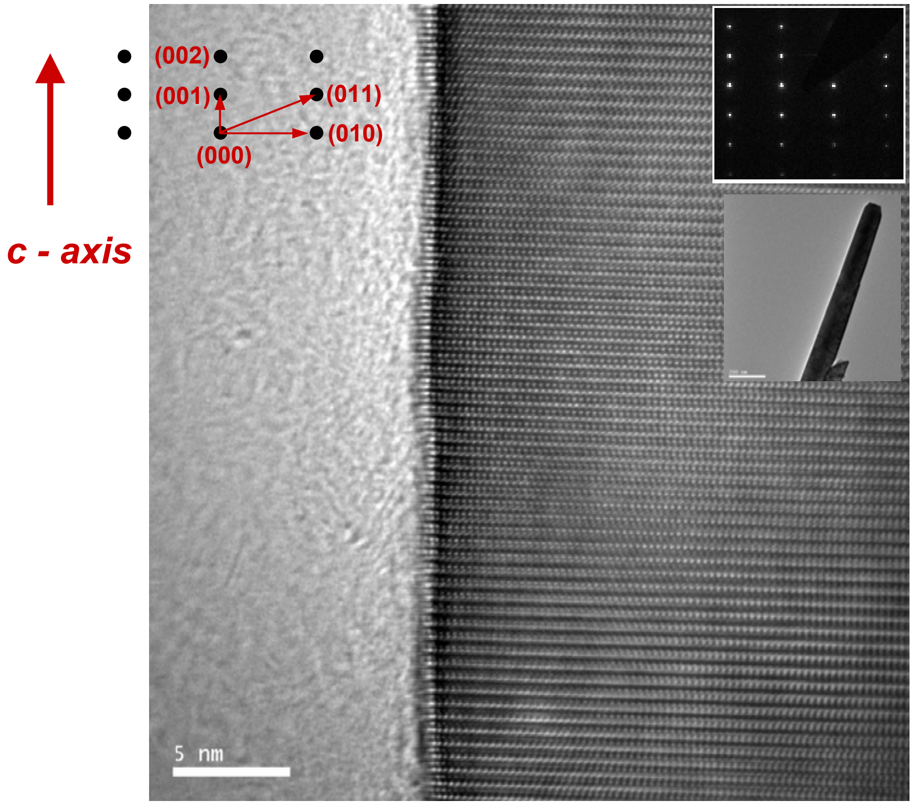
XRD measurements:

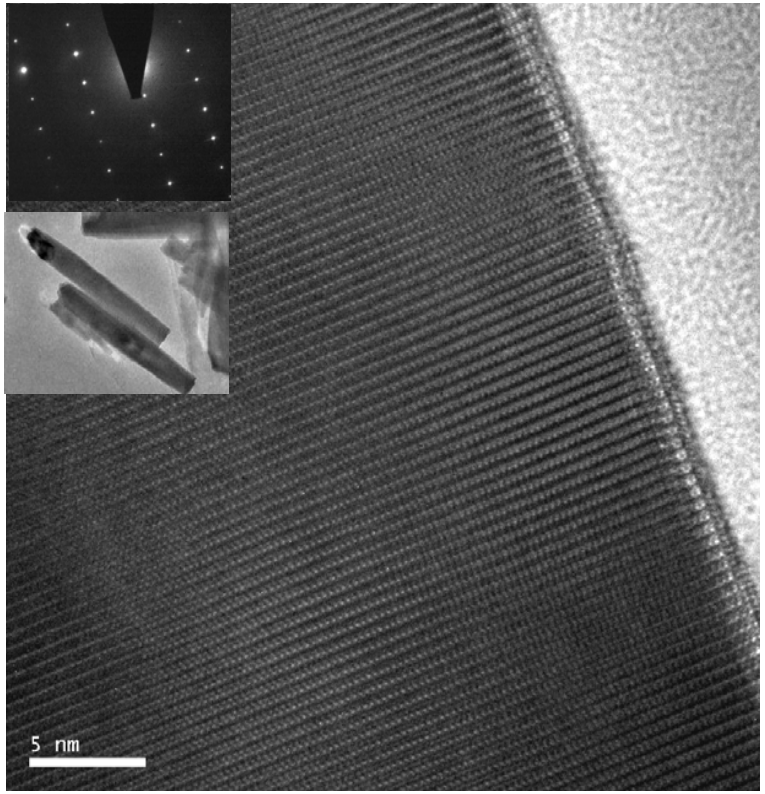




(HR)TEM observations:

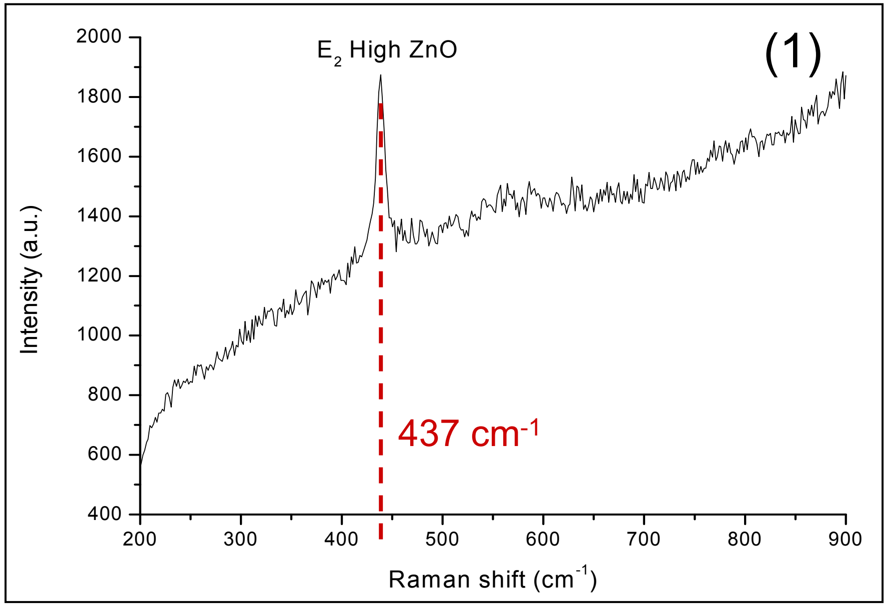
Electrodeposition ***Hydrothermal method***

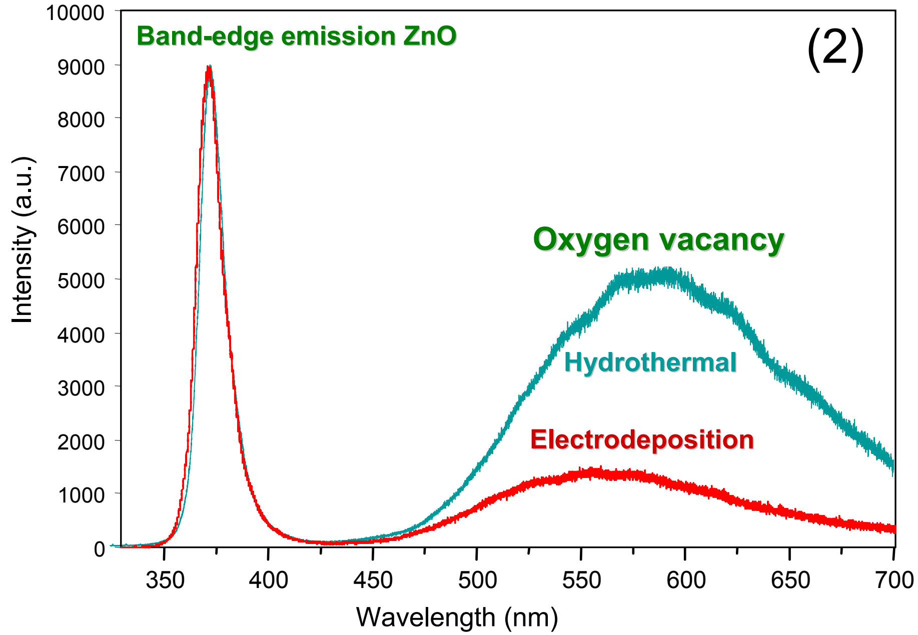




Monocrystalline structure with excellent crystallinity, along c-axis growth.

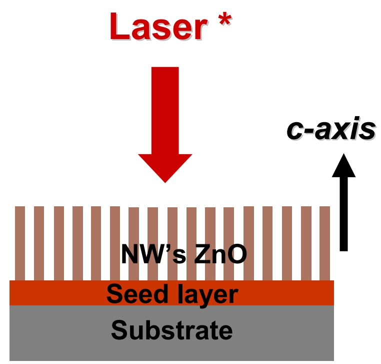
Raman & PL measurements:





(1) E_2: 437 cm^{-1} in nanowires ~ ZnO bulk ➔ stress-free;
439 cm^{-1} in thin film ➔ under compressive stress **
$\Delta\nu = -4{,}4\ \sigma$ $\Delta\nu$ en cm^{-1} et σ en GPa ***

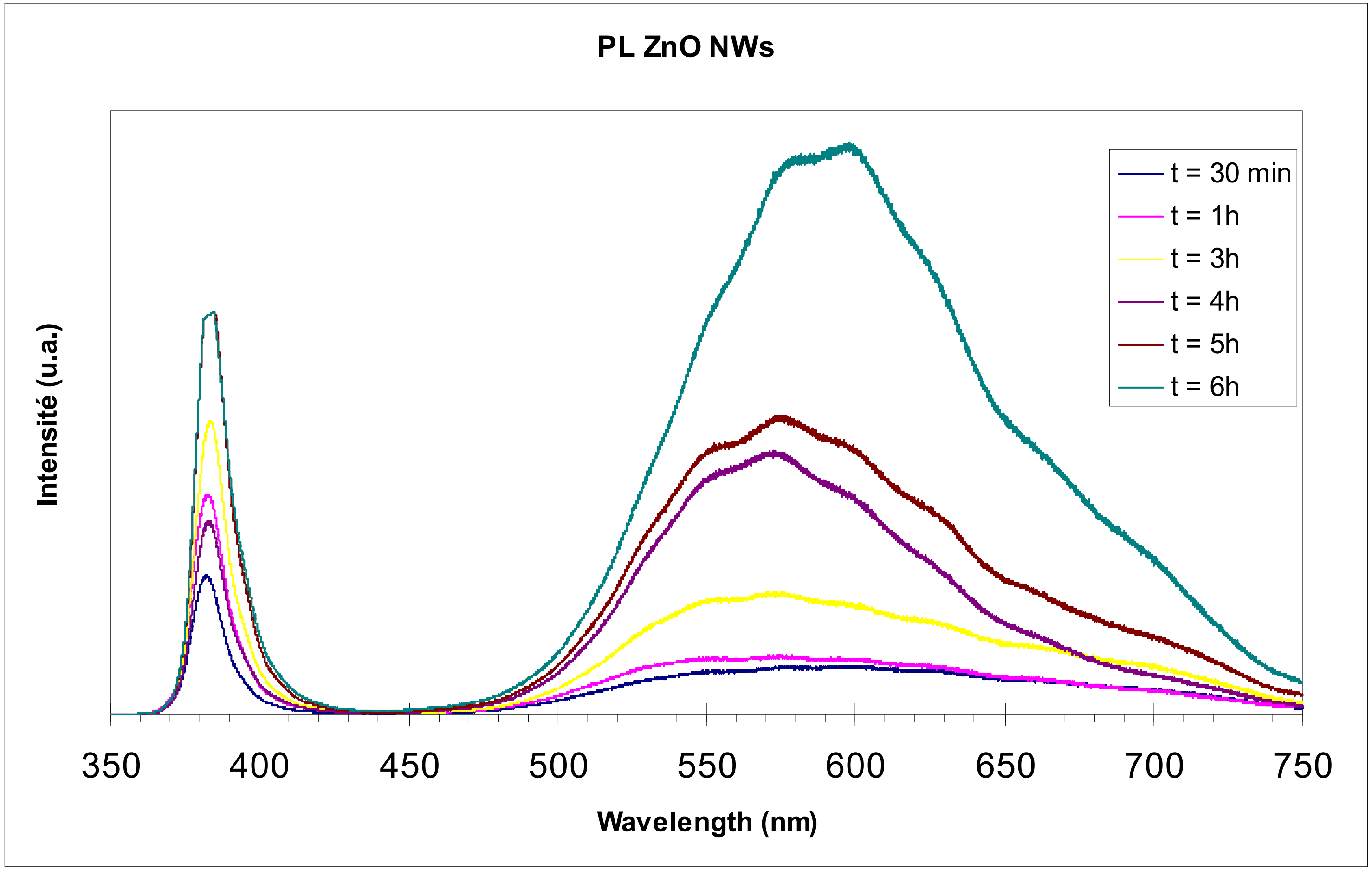
(2) Oxygen vacancy (defects) ↗ ➔ conductivity of ZnO ↗.



** K. Laurent, Y. Leprince-Wang *et al.* ***Thin Solid Films***, 517 (2008) 617-621.
*** F. Descremps *et al.* **Physical Review B**, 65 (2002) 092101.

* Laser : λ = 515 nm for Raman
λ = 325 nm for PL

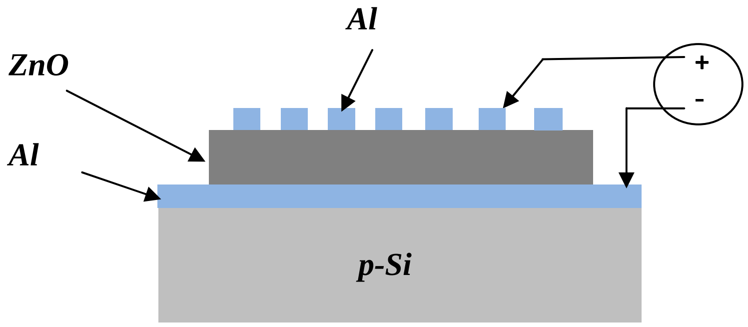
PL Measurements

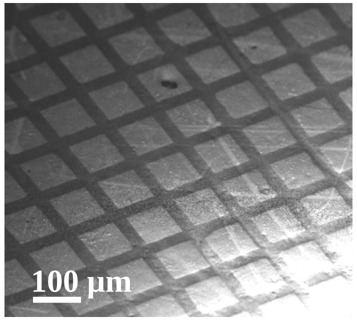


$V_{(solution)}$ = 50mL fixed

Ohmic contact ZnO thin film / Al

{T. Brouri, Thesis of Université Paris-Est, May 2011

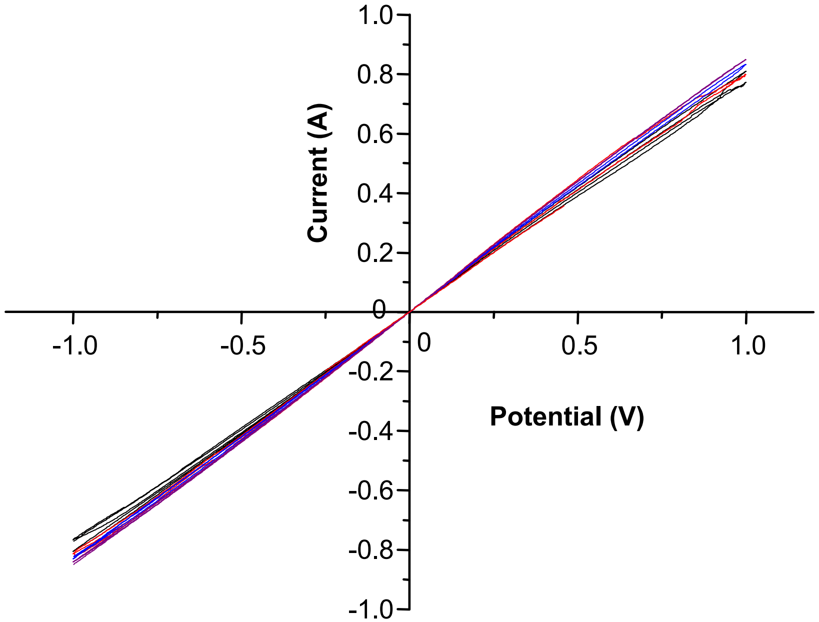




$$\rho = \frac{S\,R}{L}$$

ρ : electrical resistivity
S : µ-electrode air
L : thin film thickness

Couche mince contact ohmique (Al/ZnO/Al)



Resistivity of ZnO :

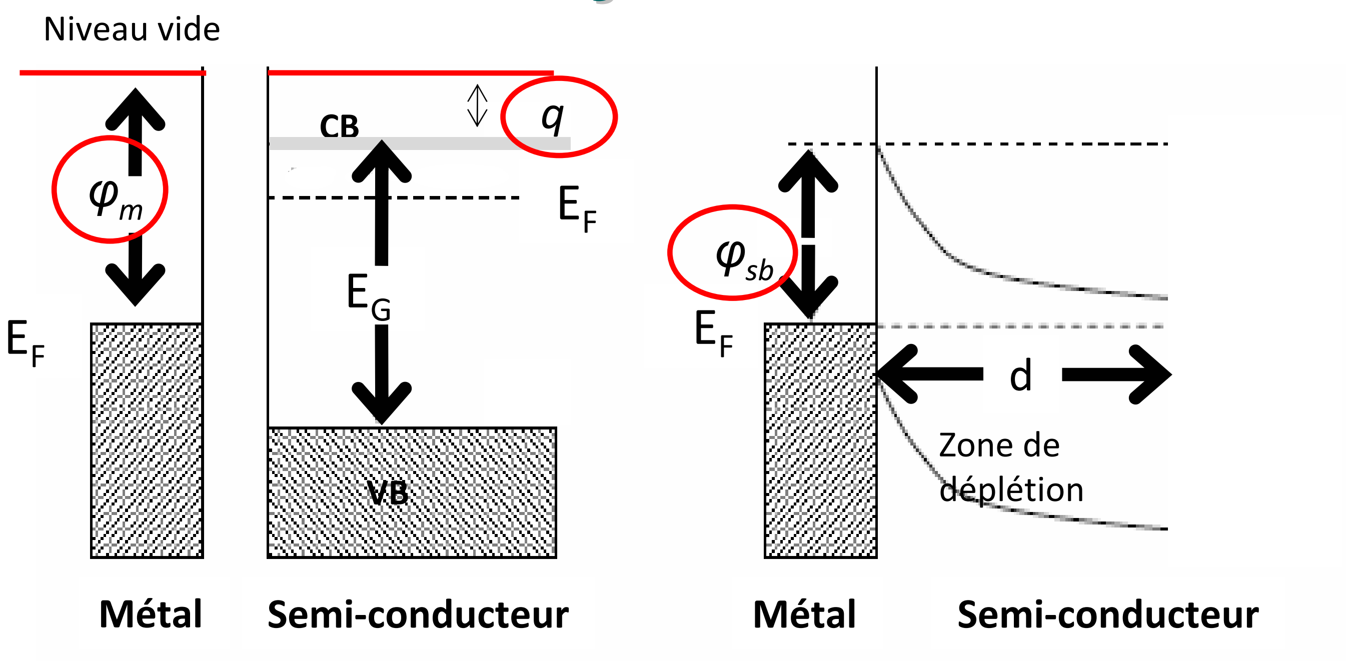
ρ = 0.06 ± 0.02 Ω·cm

Literature * :

ρ = 0.001 – 0.1 Ω·cm

* T. Schuler, M.A. Aegerter, Thin Solid Films **351** (1999) 125.
* Ozgur et al Journal of Applied Physics, **98** (2005) 041301.

Schottky contact ZnO thin film / Au

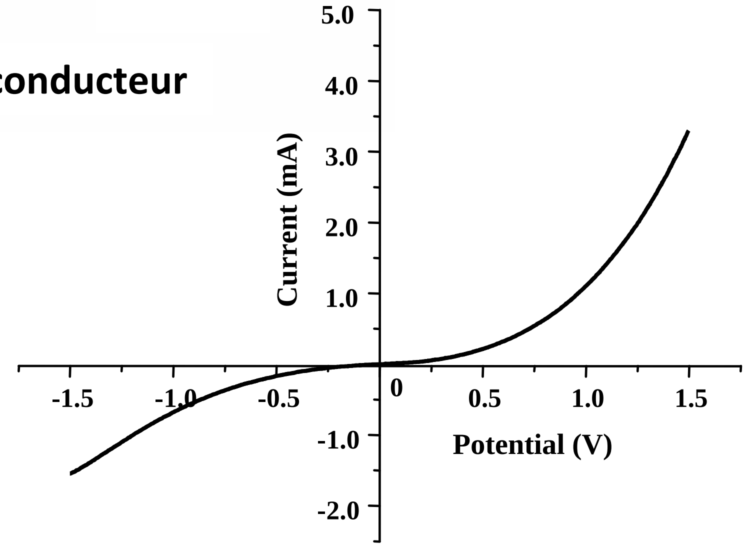


ZnO thin film:

R_s = 90 ± 15 Ω

n = 10 ± 1

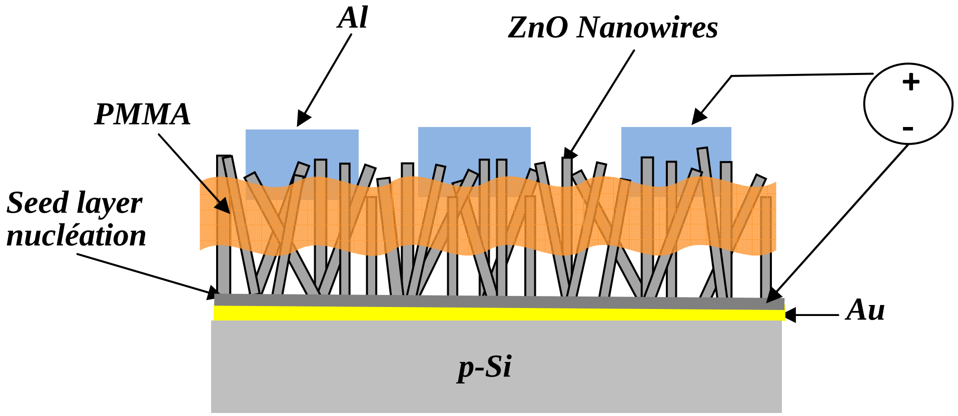
Φ_{sb} = 0,39 ± 0,01 eV

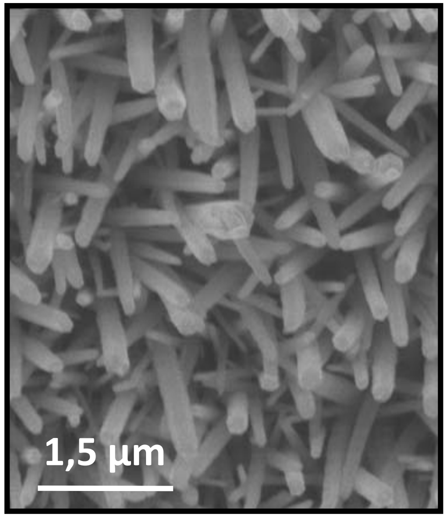


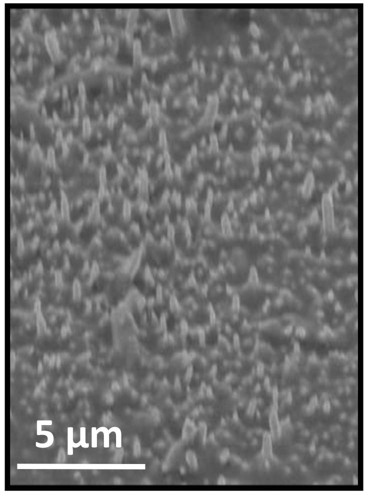
Schottky barrier : $\varphi_{sb}=\varphi_m-\chi_s$

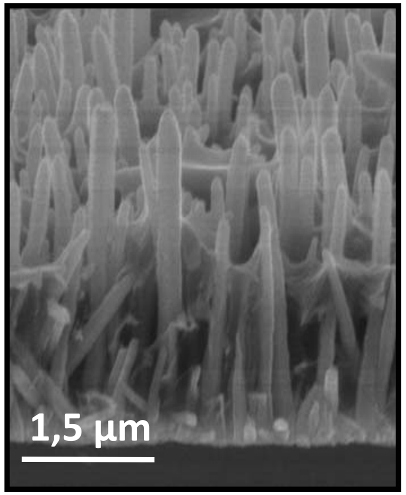
Schottky junction – ZnO nanowires/Au

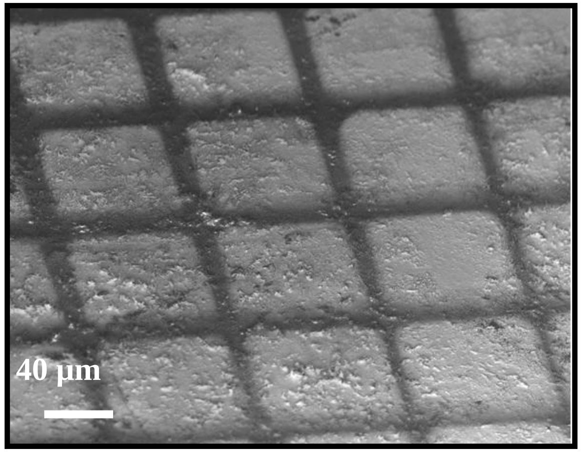
*** Sample preparation:**





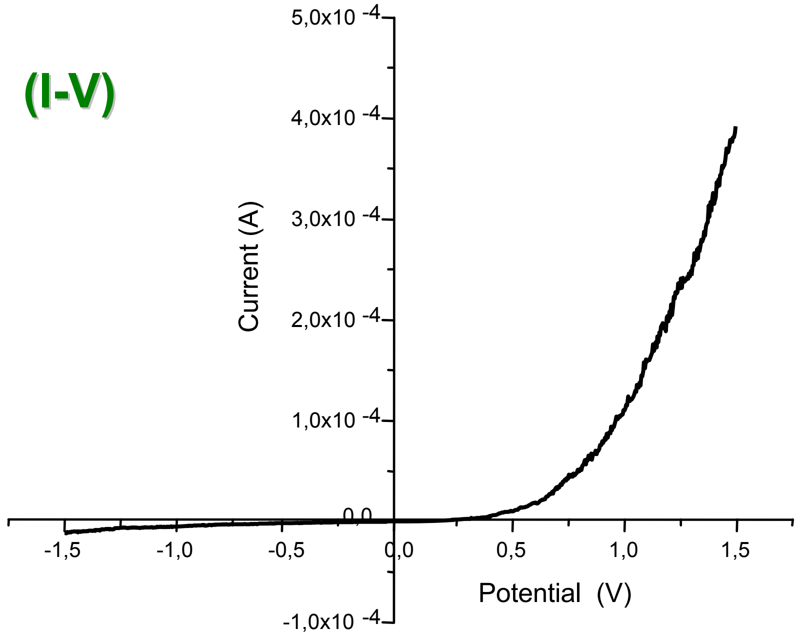


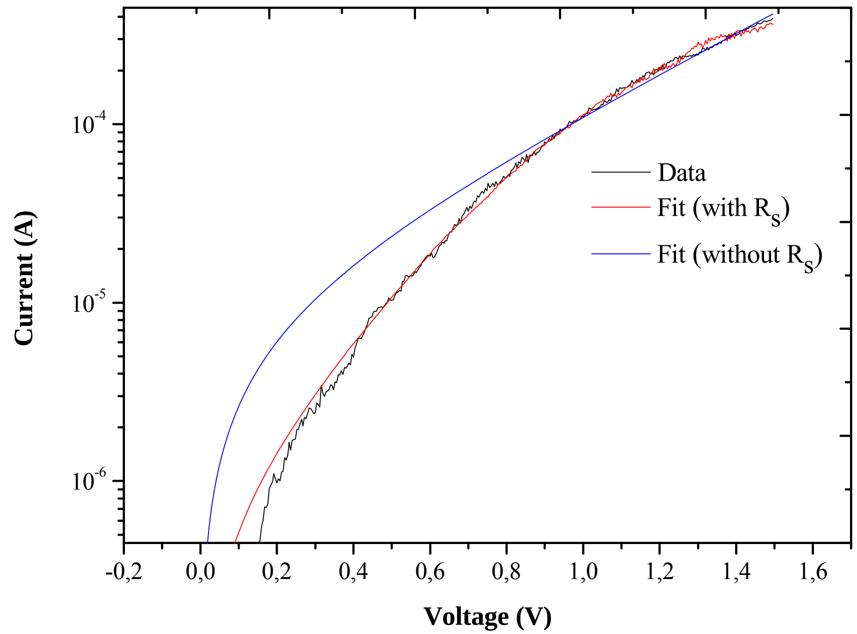




Contact Schottky – ZnO nanowires /Au

(I-V)





$$I = I_s\left[\exp\left(\frac{qV}{nk_BT}\right)-1\right]$$

No adequate

$$I = I_s\left[\exp\left(\frac{qV - R_S I}{nk_BT}\right)-1\right]$$

Our model with series resistance R_s.

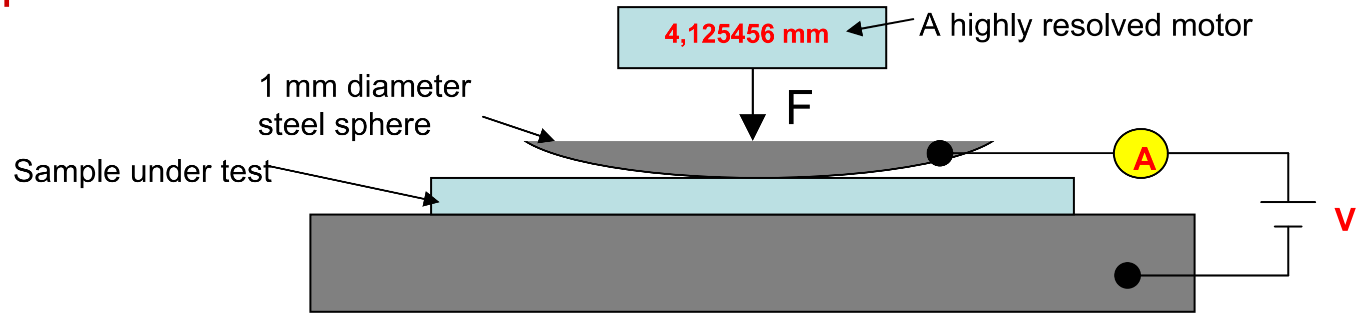
Schottky contact parameters :

R_s = 800 ± 50 Ω
n = 10 ± 1
Φ_{sb} = 0,36 ± 0,02 eV

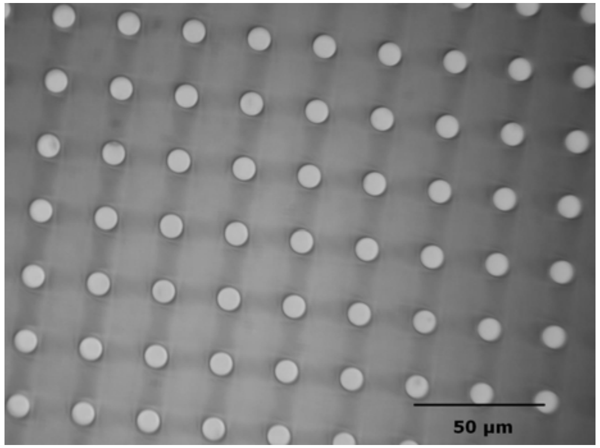
ZnO thin film:
R_s = 90 ± 15 Ω
n = 10 ± 1
Φ_{sb} = 0,39 ± 0,01 eV

Collective measurements on a ZnO nanowire network: Qualitative results

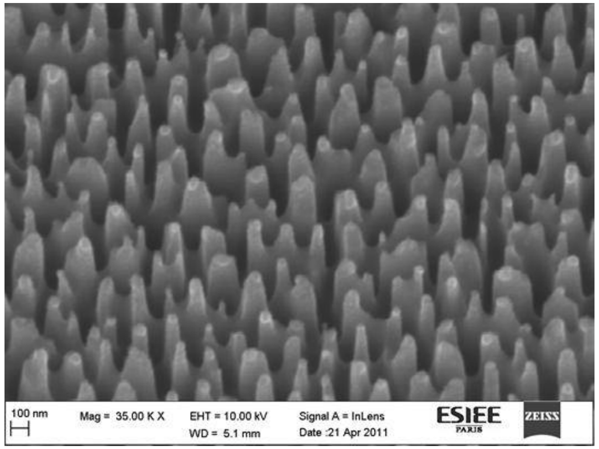
Experimental setup



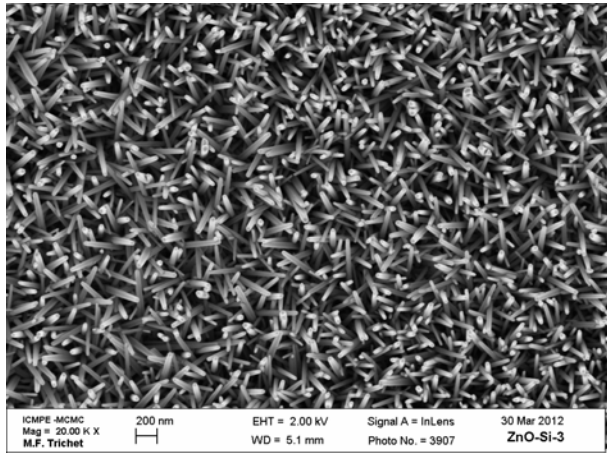
Understanding the electrical response → Three sample categories



Si µ-pillars

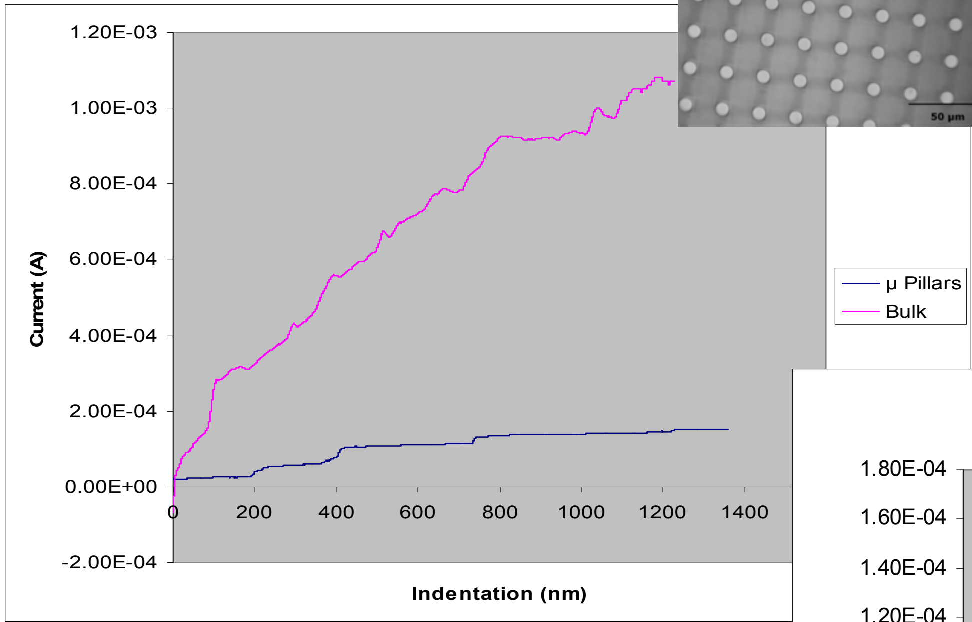


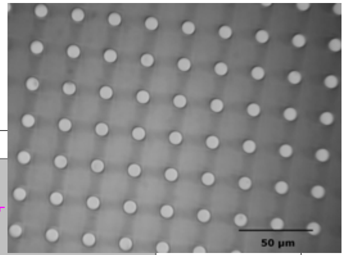
Black Silicon



ZnO NW/Au

1. μ-pillars



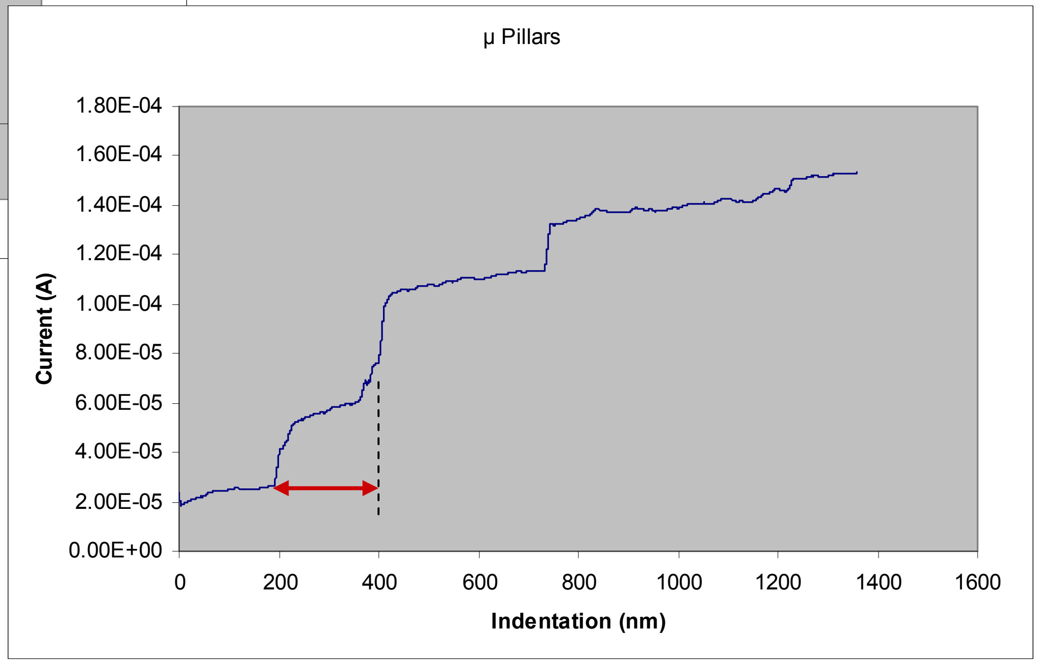


Current values measured on bulk are around 8 times those on the μ pillars

Pillars area density = 12.5% = **1/8**

➔ Contact is Hertzian

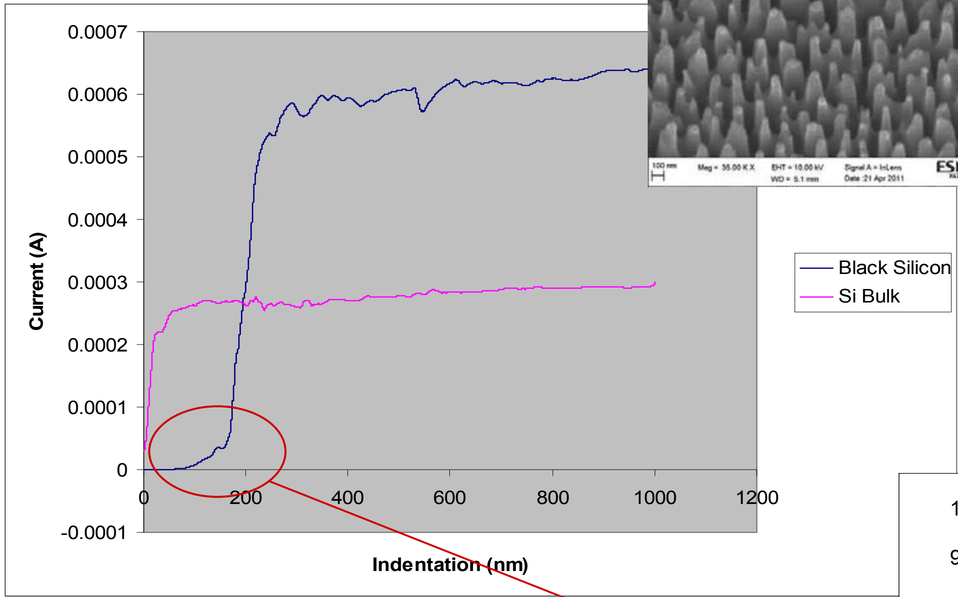
➔ $R_{contact} = \sqrt{R_{sphere}.Depth_{Indentation}}$

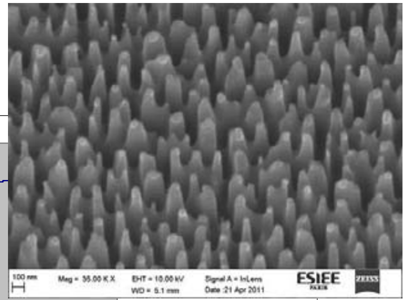


- Discrete current steps!

- Step width in good agreement with pillar-to-pillar distances (>15 μm)

2. Black Silicon

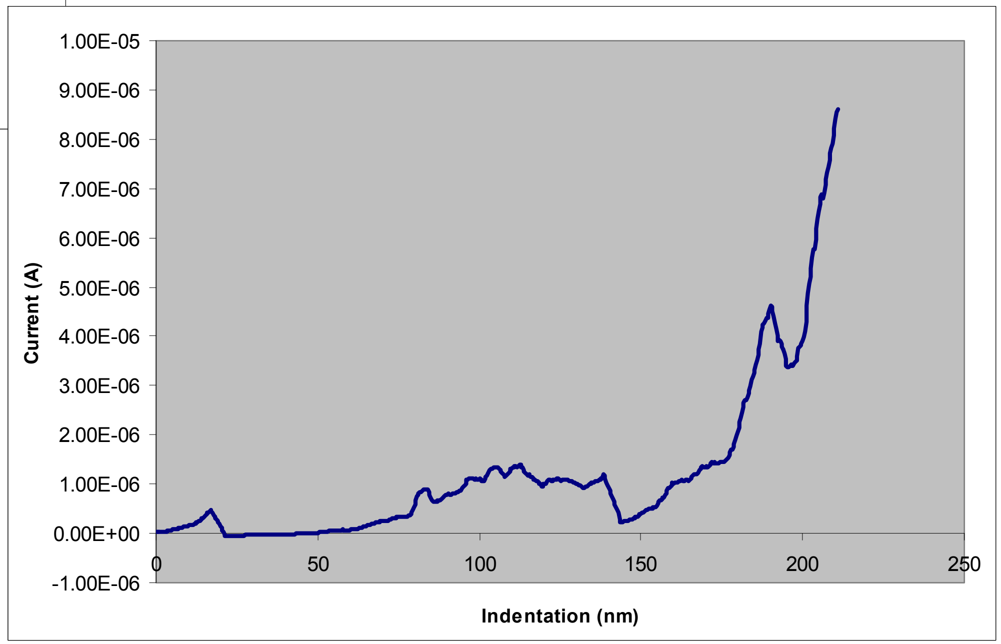




- Black silicon is destroyed by the test!

- Saturation value of the current in BS > in Si Bulk → effect of the BS destruction?

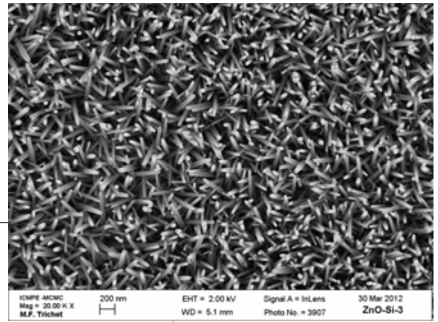
- BS current grows slowly.

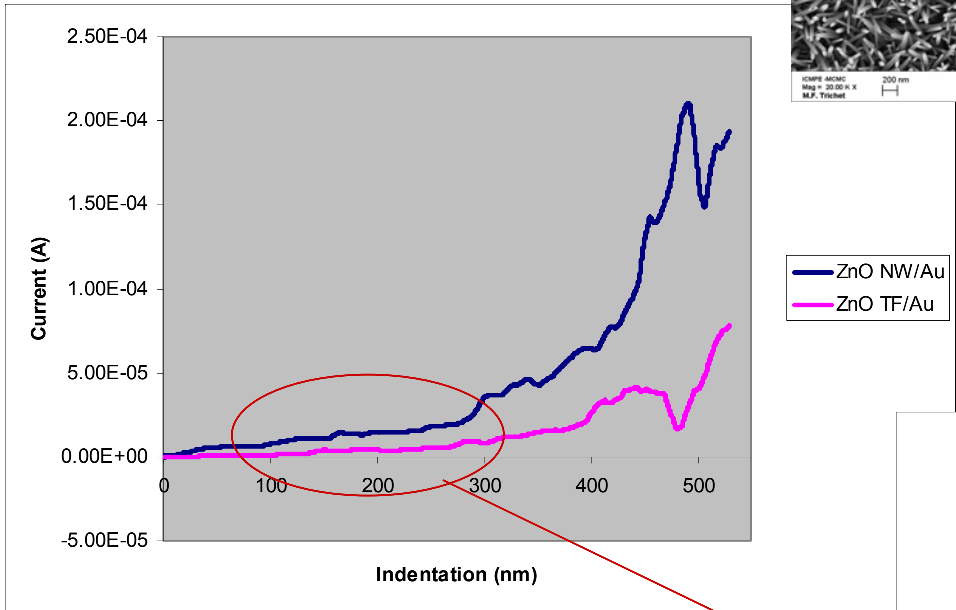


- Current growth in a sawtooth fashion→ An indentation of few nanometers is enough to destroy each spike!

➔ Will be the region of interest in NW measurements.

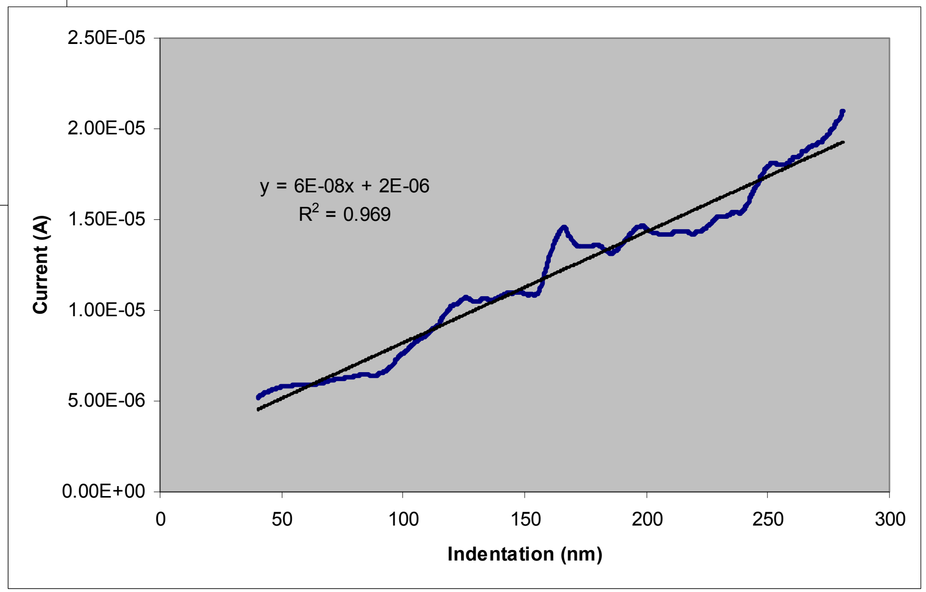
3. ZnO NW/Au





- Bulk current is lower than NW's (as previous case)

- No visible steps in NW's curve (as can be expected since typical NW-to-NW distance is few 10's nm)



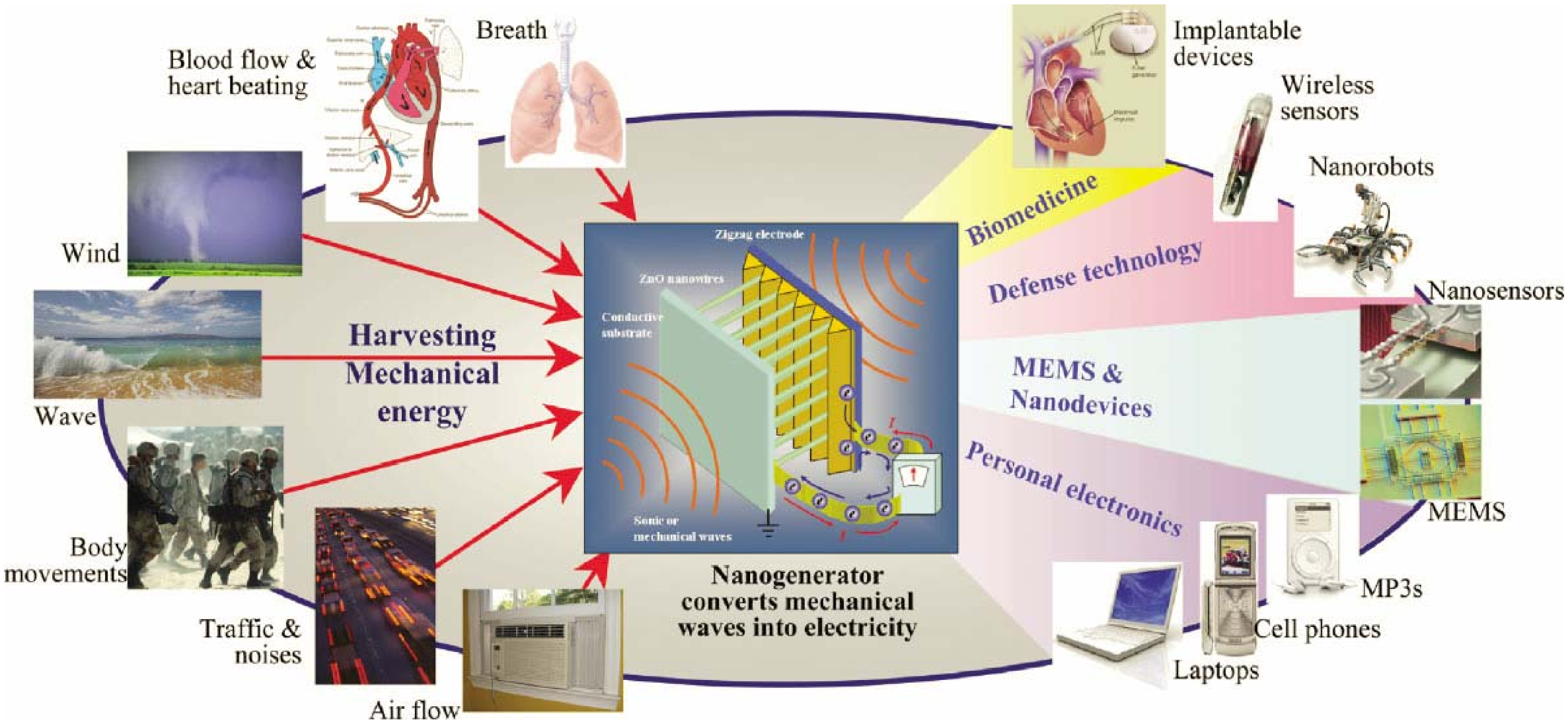
- Current proportional to indentation depth

➔ Hertzian contact + NWs act as a network of parallel resistors

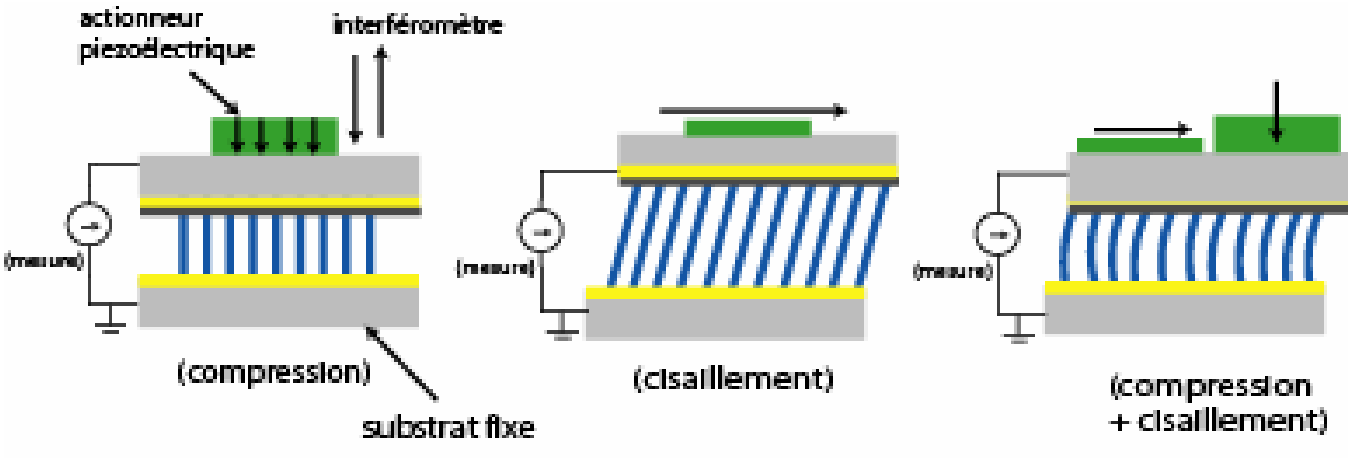
Application 1: *Electric nanogenerator*

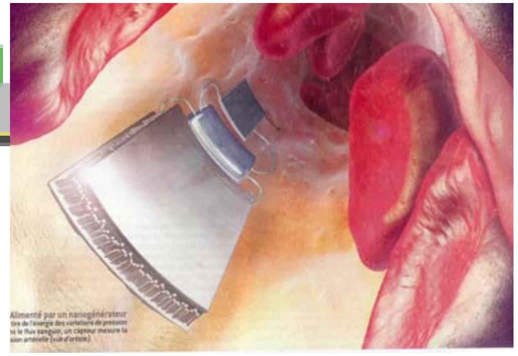
(Objective: convert surrounding energy into electrical energy)

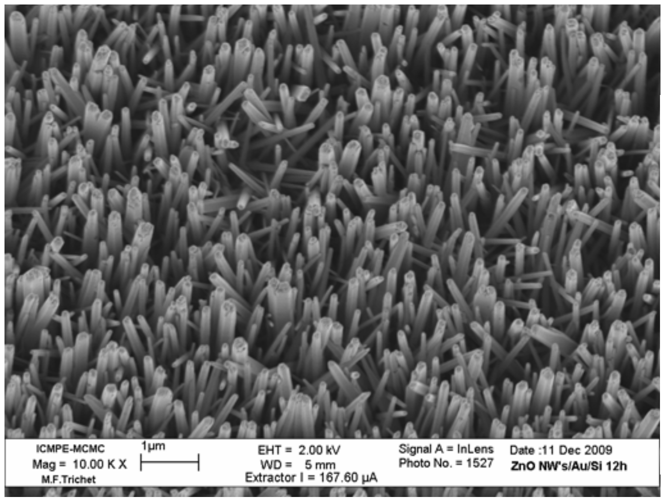
Perspectives of nanogenerators for harvesting mechanical energy and potential future applications.

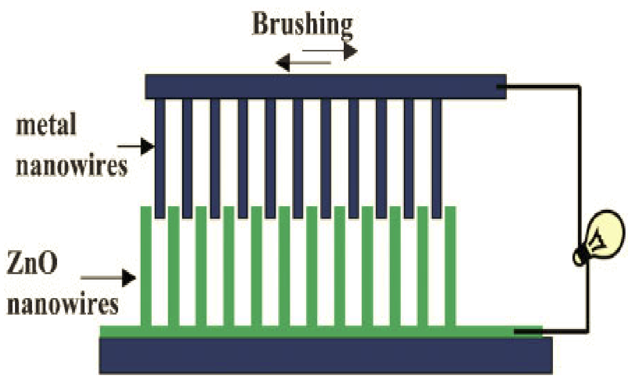


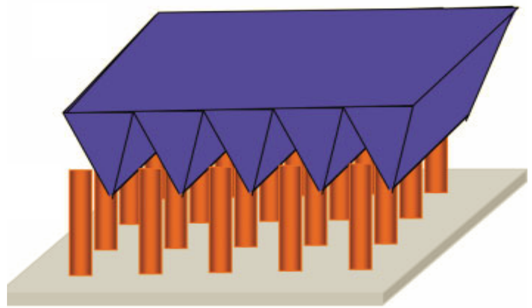
*Z. L. Wang "Self-Powered Nanosystems", Adv. Funct. Mater. 2008, **18**, 3553–3567.*







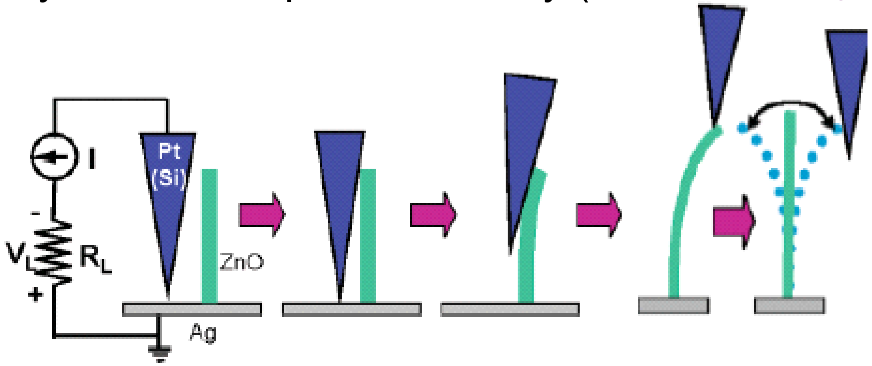




Under studding: coupling electro-mechanics properties of ZnO nanowires.

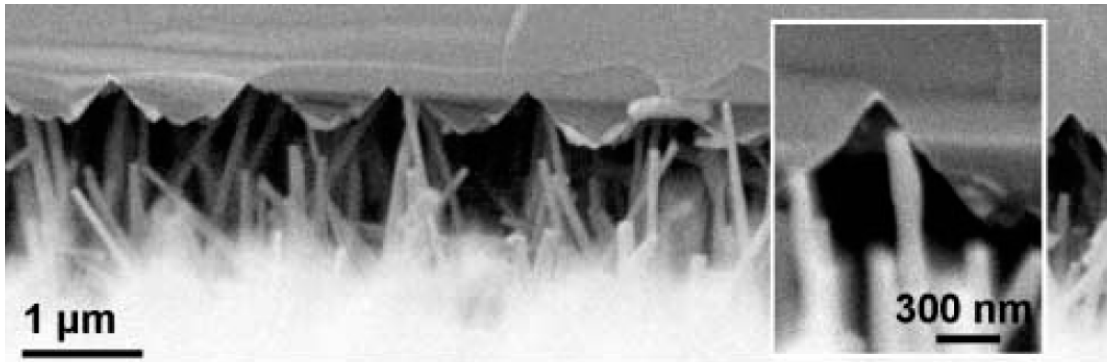
State of the art : nanopiezoelectric system

Study of the nanopiezoelectricity (*ZL. WANG, Georgia Tech. USA)*



*ZL Wang, **Science** (2006)*

1 ZnO nanowire ➔ ~ 10 mV (necessary force: ~ nanoNewton / nanowire)

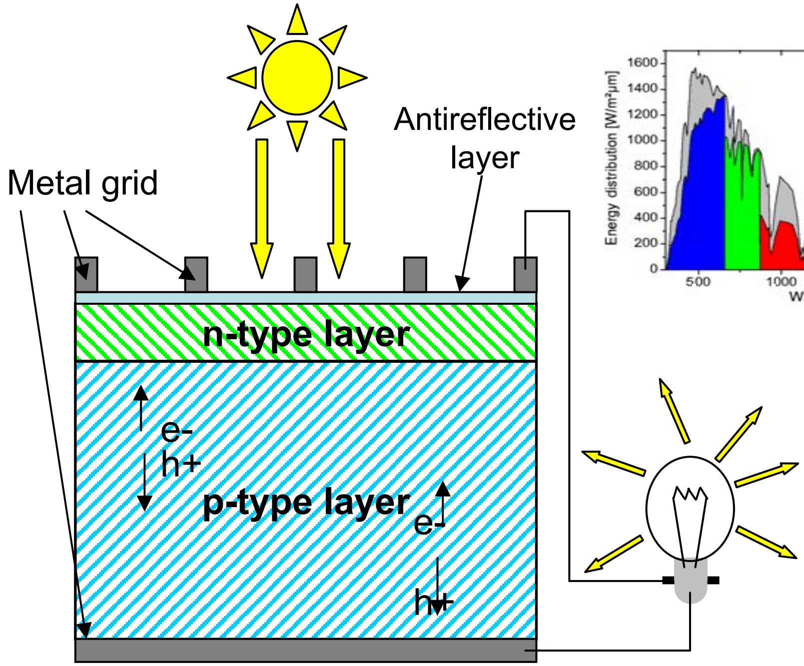


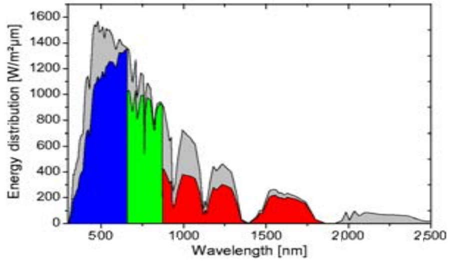
*ZL Wang, **Science** (2007)*

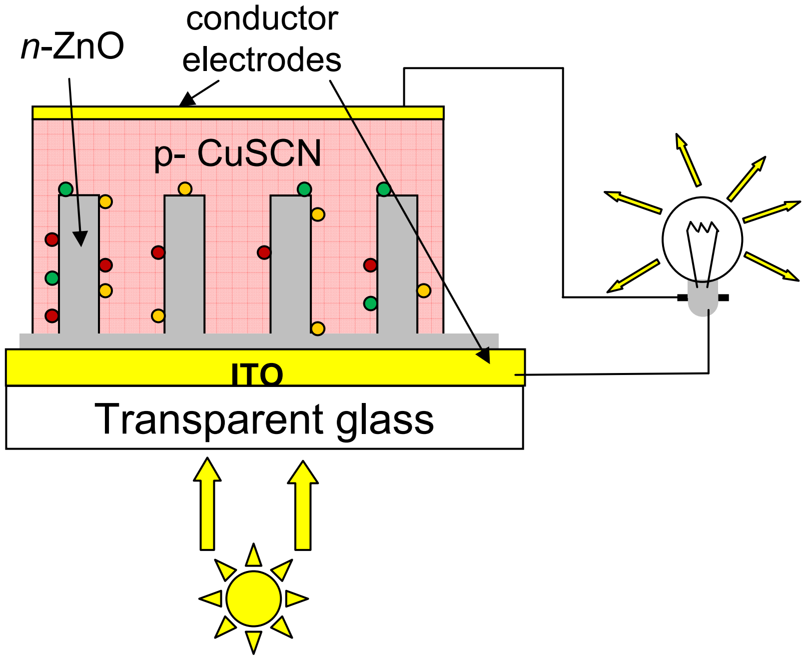
Collective signal: ~ 10 mW, ~ 800 nA / ~ 6 mm²

0.5% of the nanowires are active ➔ Control of the network

Application 2 ➔ Multi-nanostructured Solar Cells







Si based devices :

- 98 % of the world market
- Fabrication process
- Non-friendly to environment

η : ~ 16%

Alternative to Si

Conception

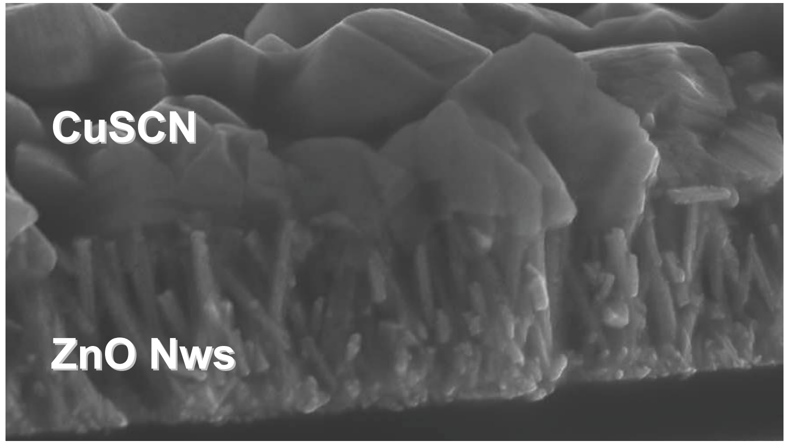
- ZnO nanorods array
- semi-conductors nanoparticles

➔ $\eta \uparrow$

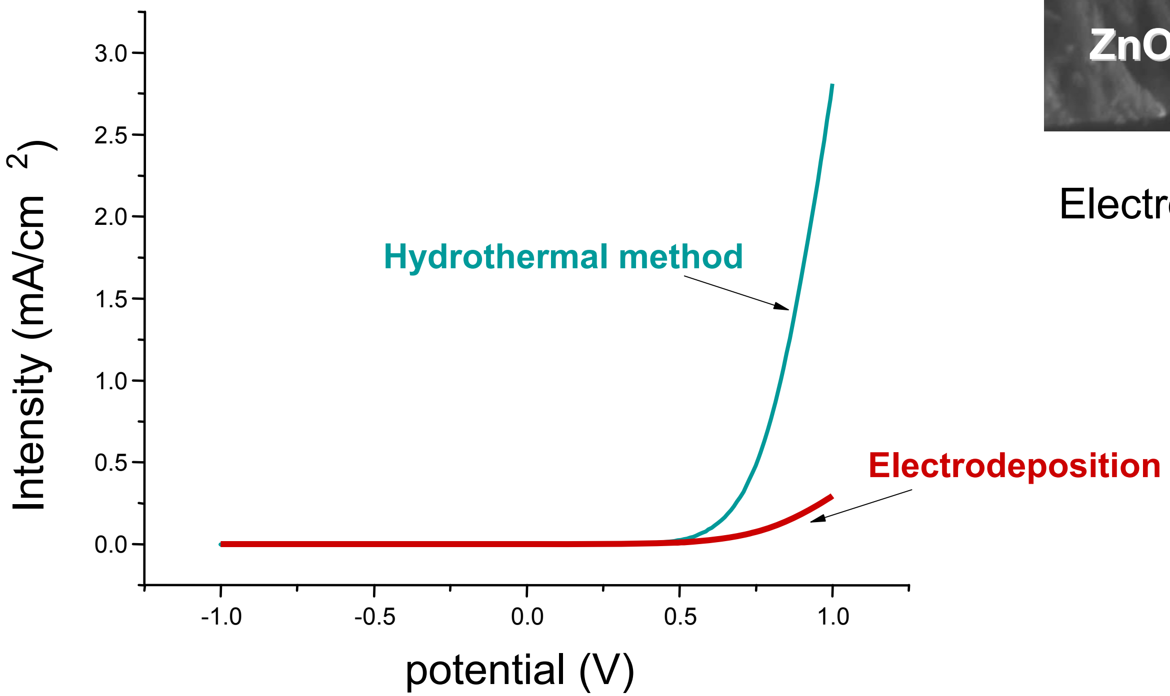
STF Program in China (2009-2011)

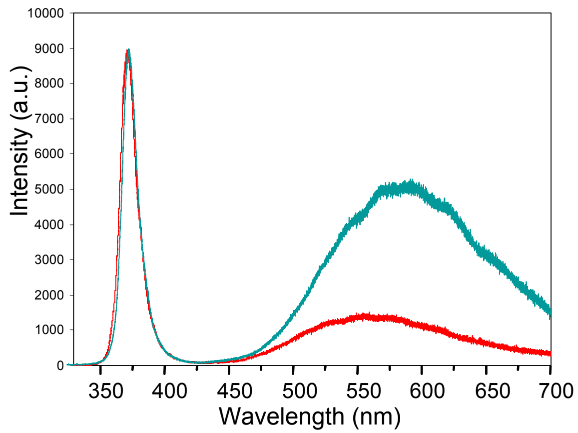
p-n **junction between CuSCN & ZnO:**

p-CuSCN: E_g =3.4 eV ; *n*-CdS: E_g =2.4 eV



Electrodeposited CuSCN on ZnO NWs.





K. Laurent, D.P. Yu, Y. Leprince-Wang *et al. Journal of Applied Physics*, 110 (2011) 094310.

Electrodeposition of CdS NPs:

Chemical bath*:

37cm^3 of 1M Cd(Acet)

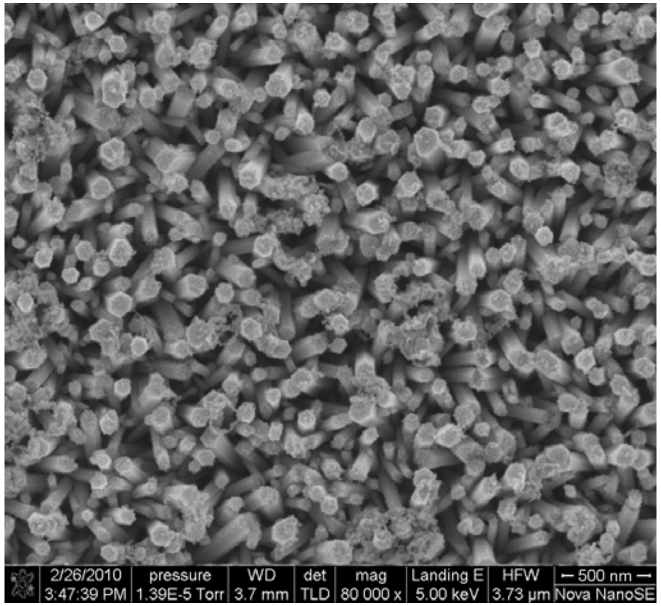
20cm^3 of 13M ammonia

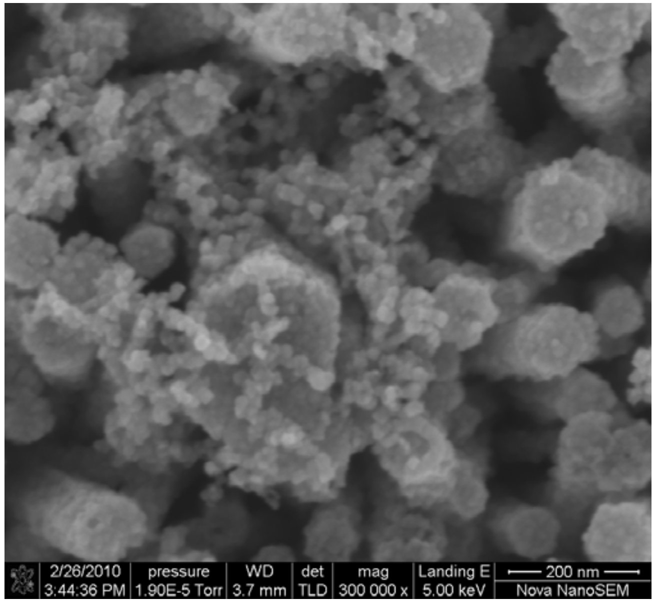
10cm^3 of 7.2M triethanolamine

100cm^3 of deionized water

37cm^3 of 2M thiourea

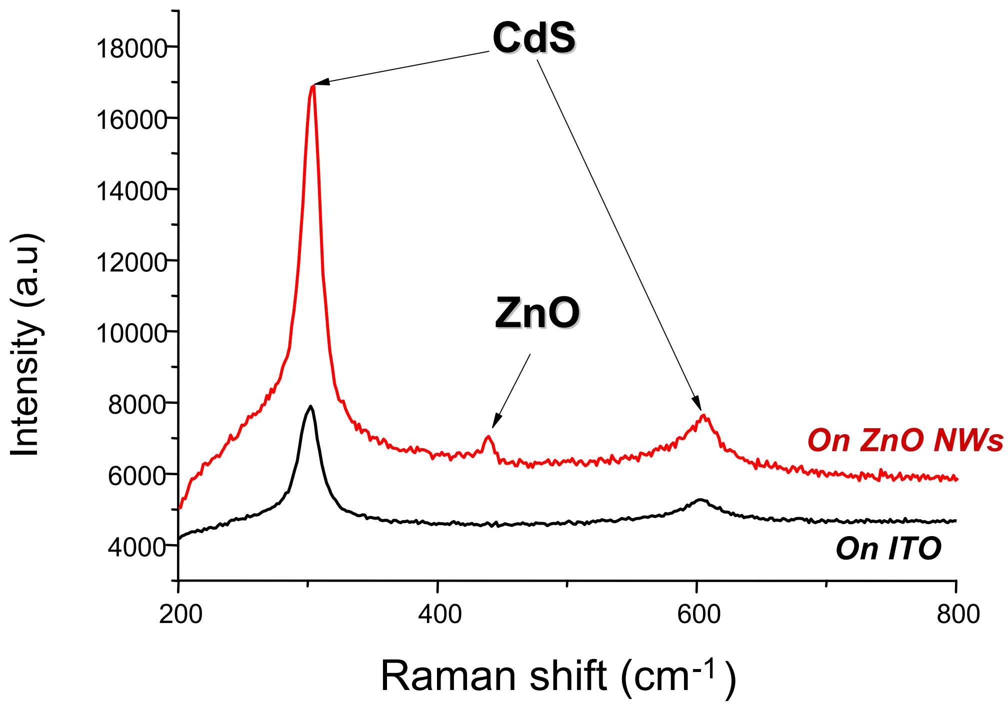
{ Method: Tetsuhiko ISOBE, Materials research bulletin , **30** (1995) 975}*

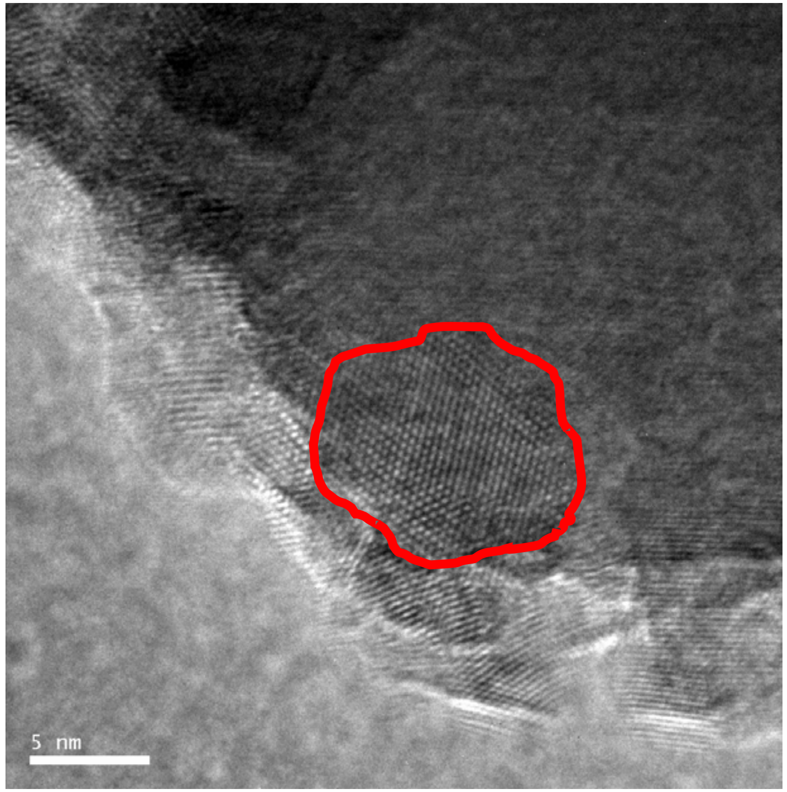




- Homogenous coverage
- Nanoparticles ~15-20 nm size

Raman & HRTEM characterizations of CdS NPs:

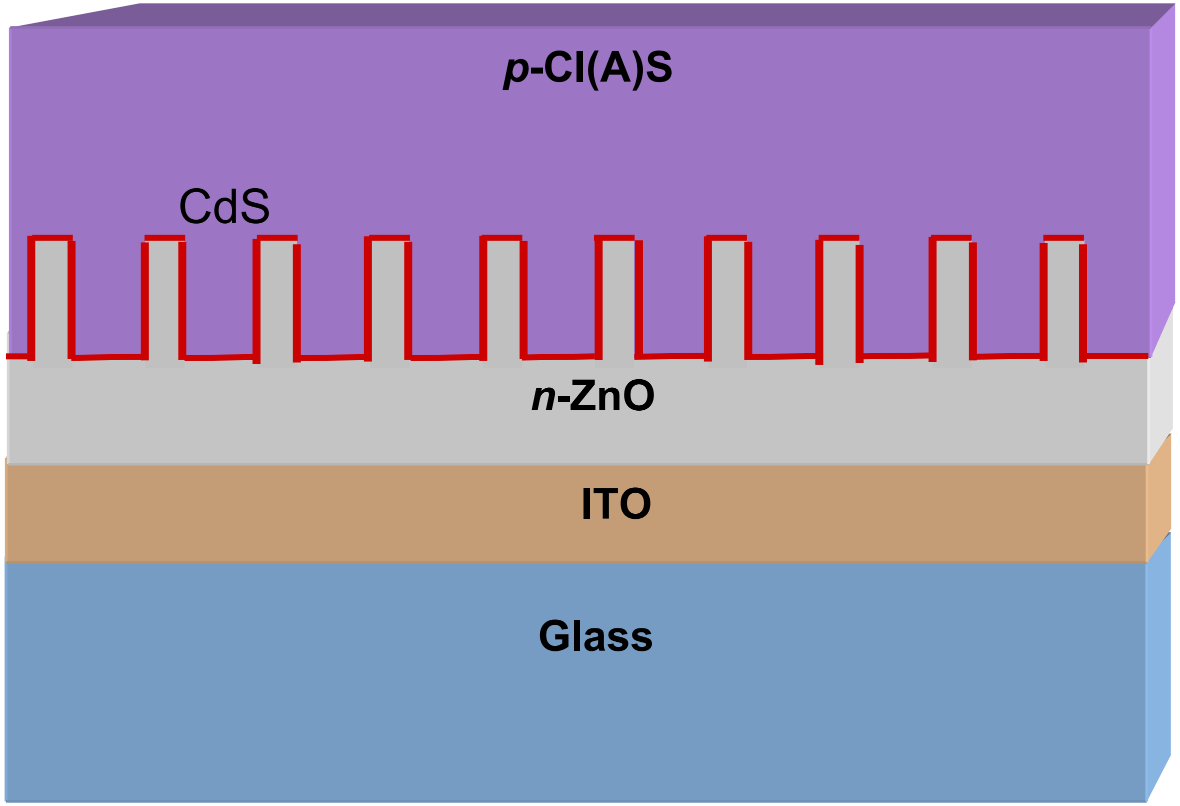




Perspective:

1) Chemical bath deposition of PbCdS nanoparticules ➔ large absorption band
2) The third step : CuSCN on NPs + ZnO NWs

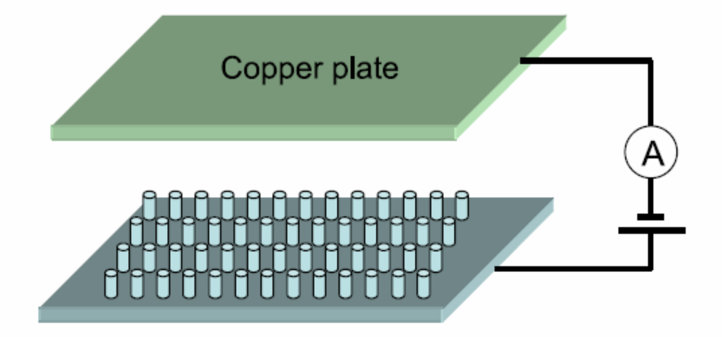
New Project on $CuIn(Al)S_2$



gap_{CIS} ~1.5 eV & gap_{CIAS} ~1.1 – 1.7 eV

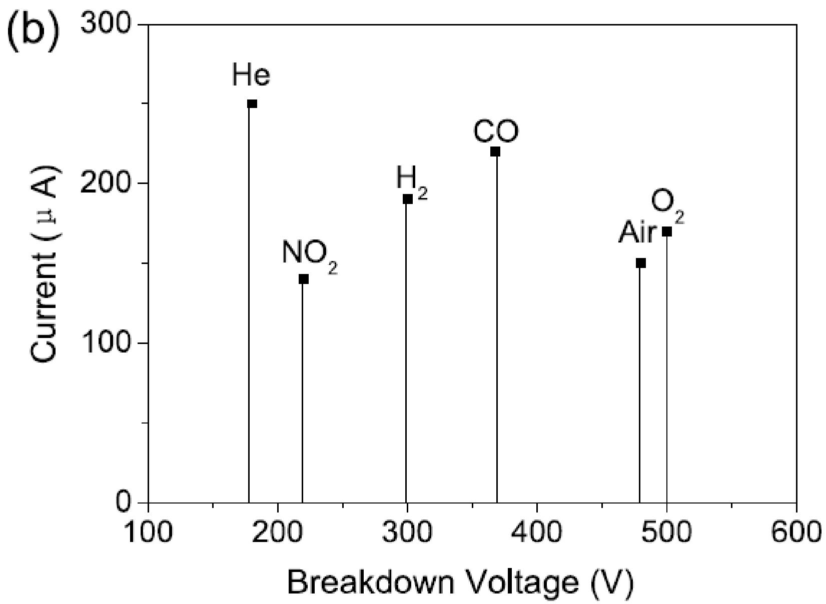
Applications 3 ➔ Nanostructured gas sensor

ZnO: promising materials for gas sensor.
ZnO nanowire arrays: large surface area ➔ high detection sensitivity

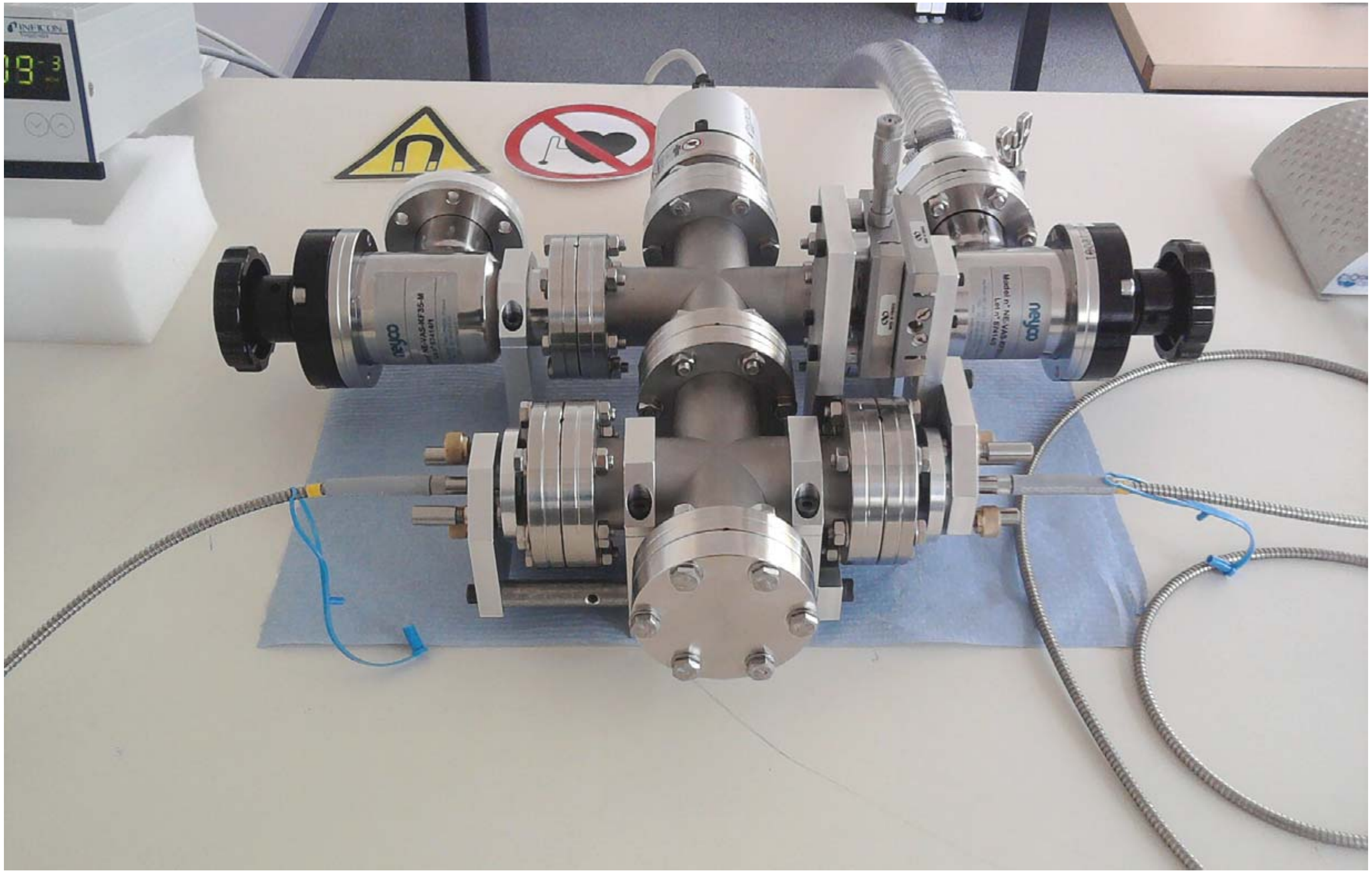


The nanowire sensor device. Exploded view of the sensor showing a ZnO nanowire film as the anode and a Cu plate as the cathode.

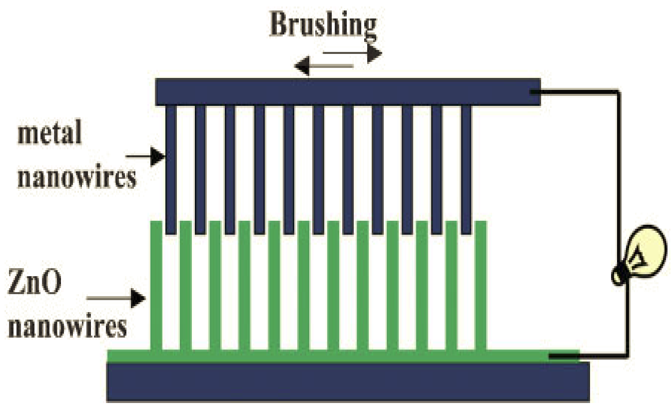
* *L. Liao et al. Nanotechnology* ***19*** *(2008) 175501*

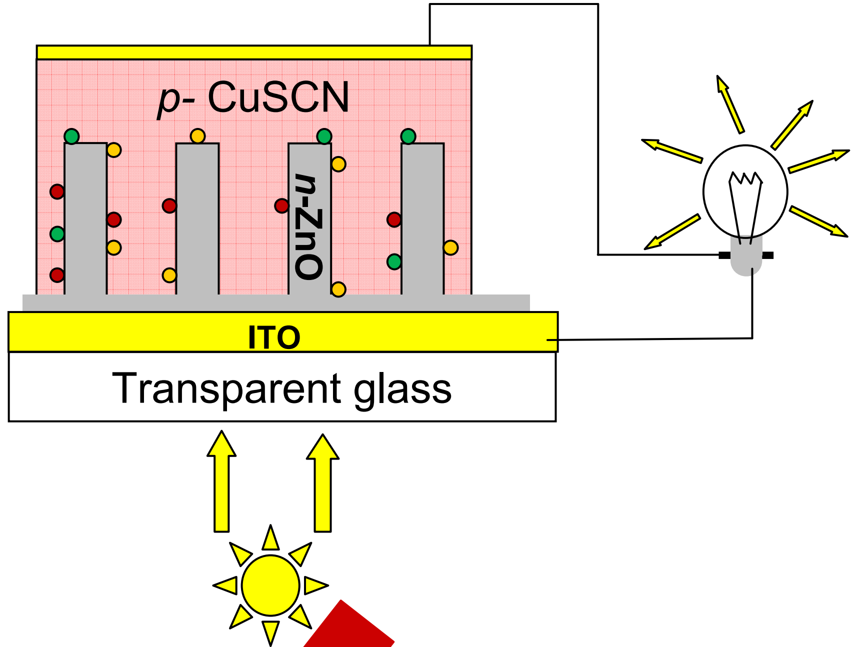


I–V curves for He, NO_2, CO, H_2, air and O_2, showing distinct breakdown voltages.

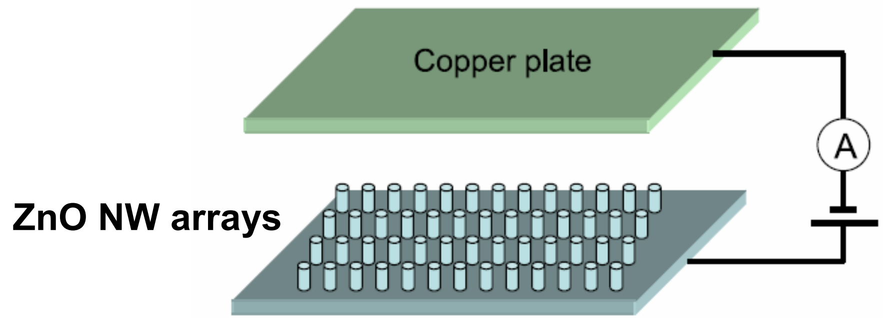


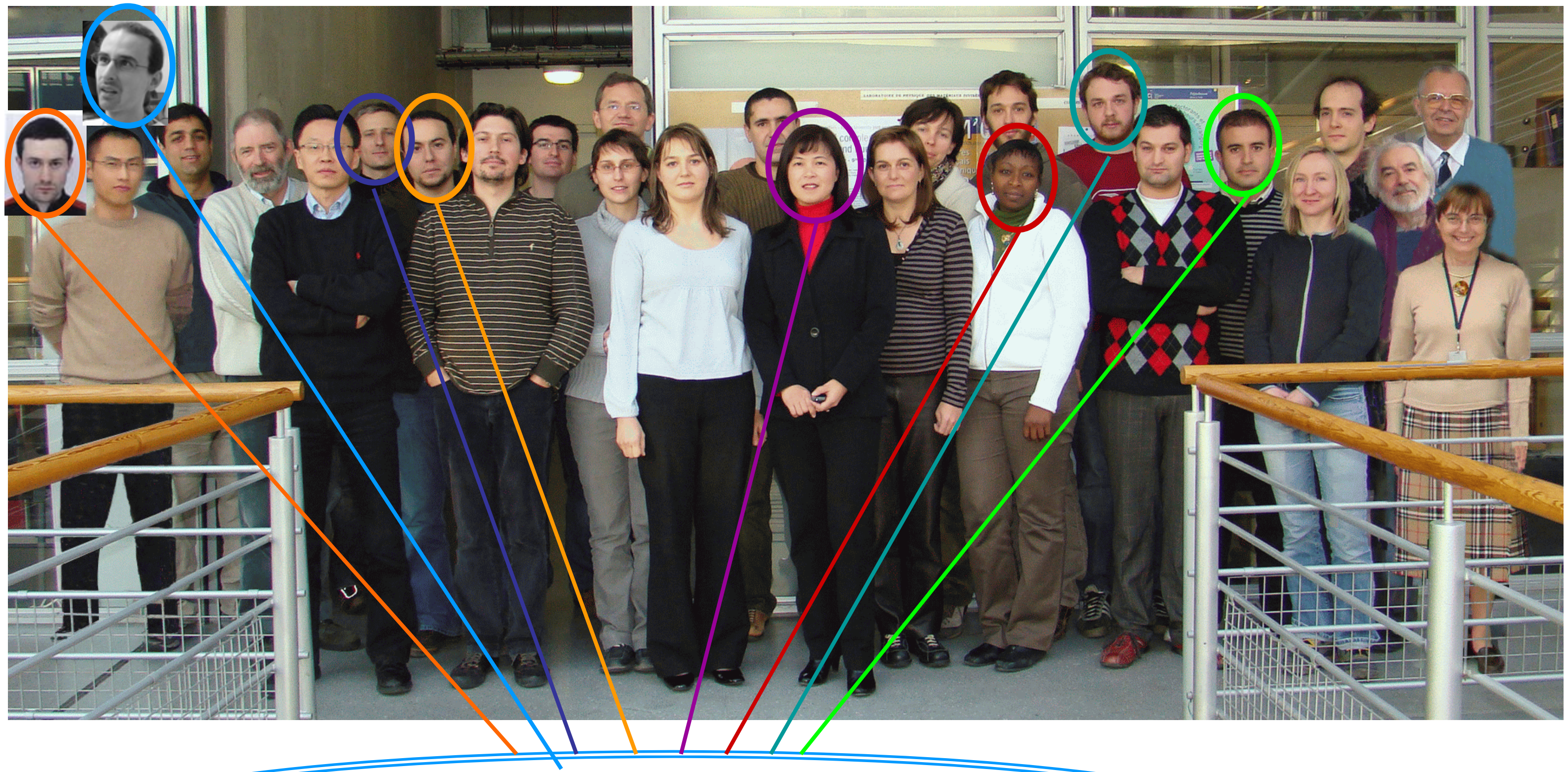
Summary





(via Capacitor)





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