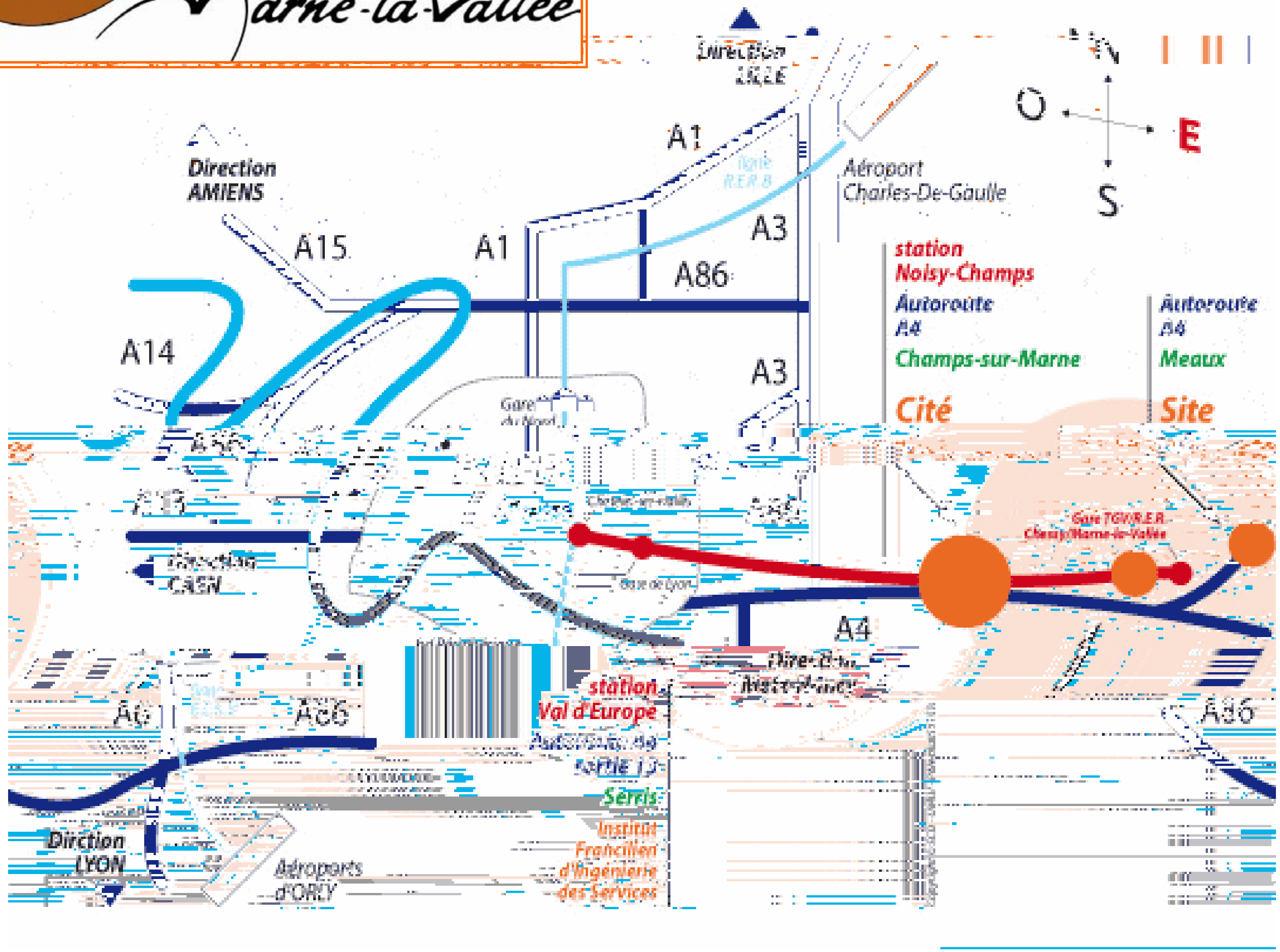
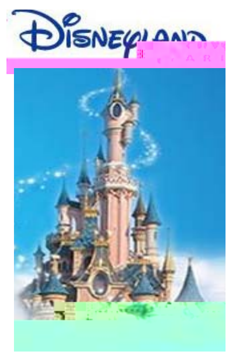
巴黎东部马恩河谷大学 (UPEMLV)
(巴黎东大联盟 UPE)





Our Campus of Cité Descartes

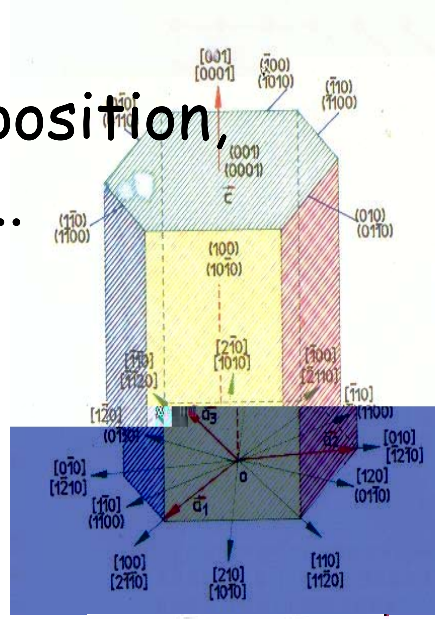
始建于1991年的巴黎东部马恩河谷大学现在已有超过11000名学生，17个研究实验室.
UPEMLV

ESIEE

ZnO:

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

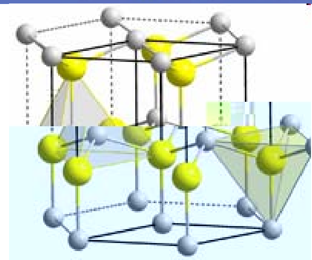
a = 0.325 nm et c = 0.512 nm.



- **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;*

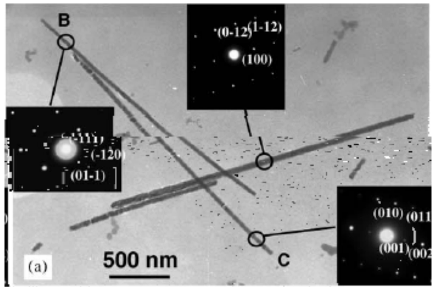
  …



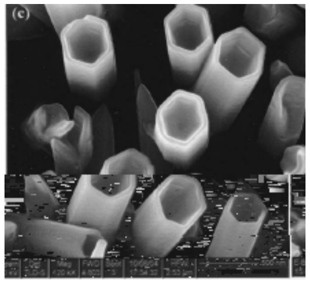
Applications :

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

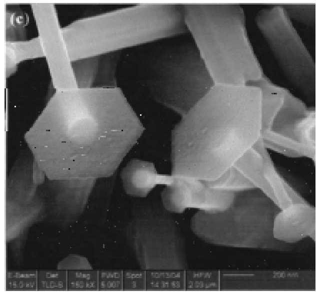
Morphologies :



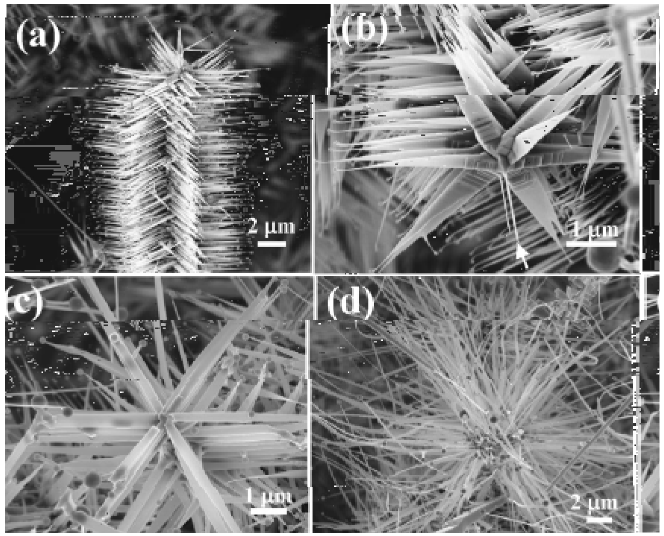
Nanowires



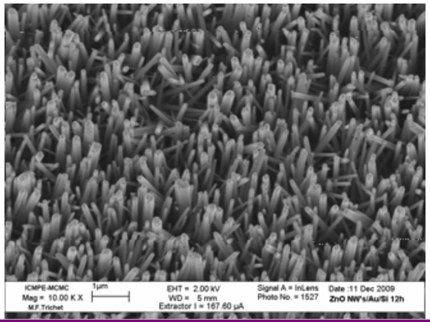
nanotubes

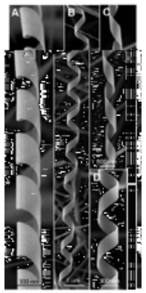


nanopins

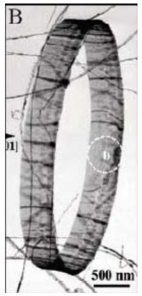


nanosbrushs



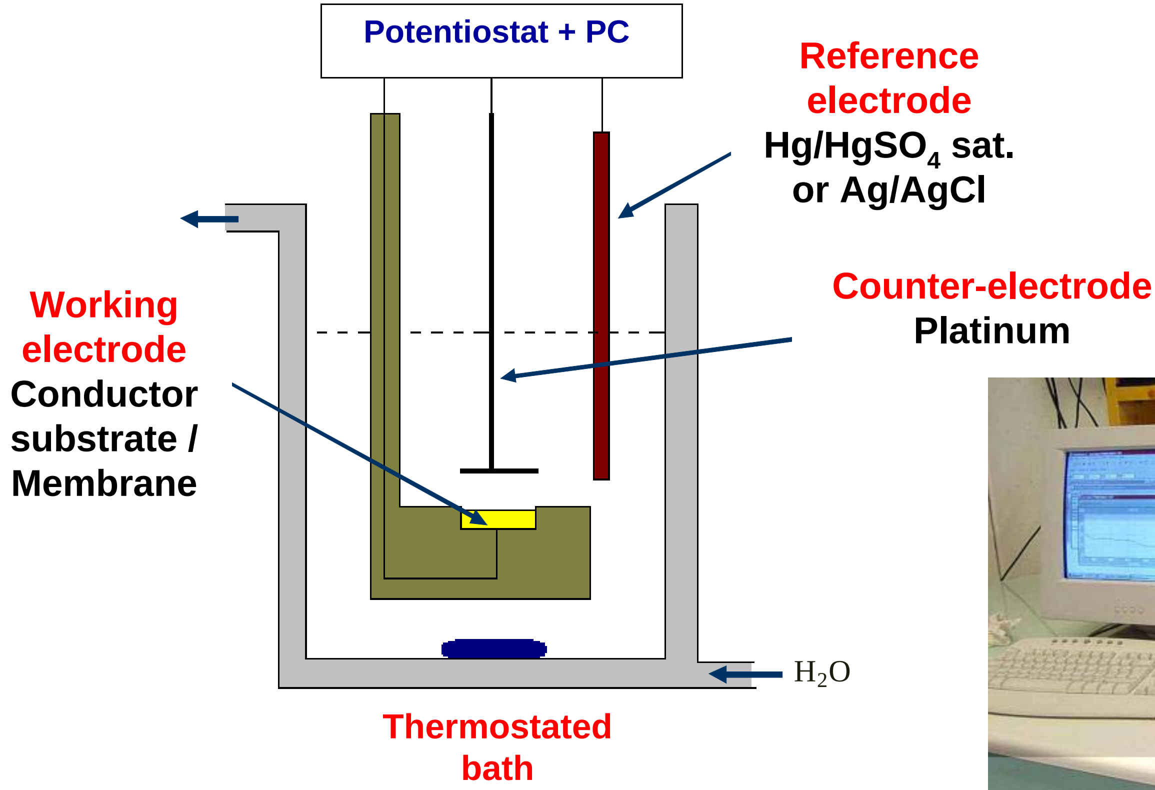


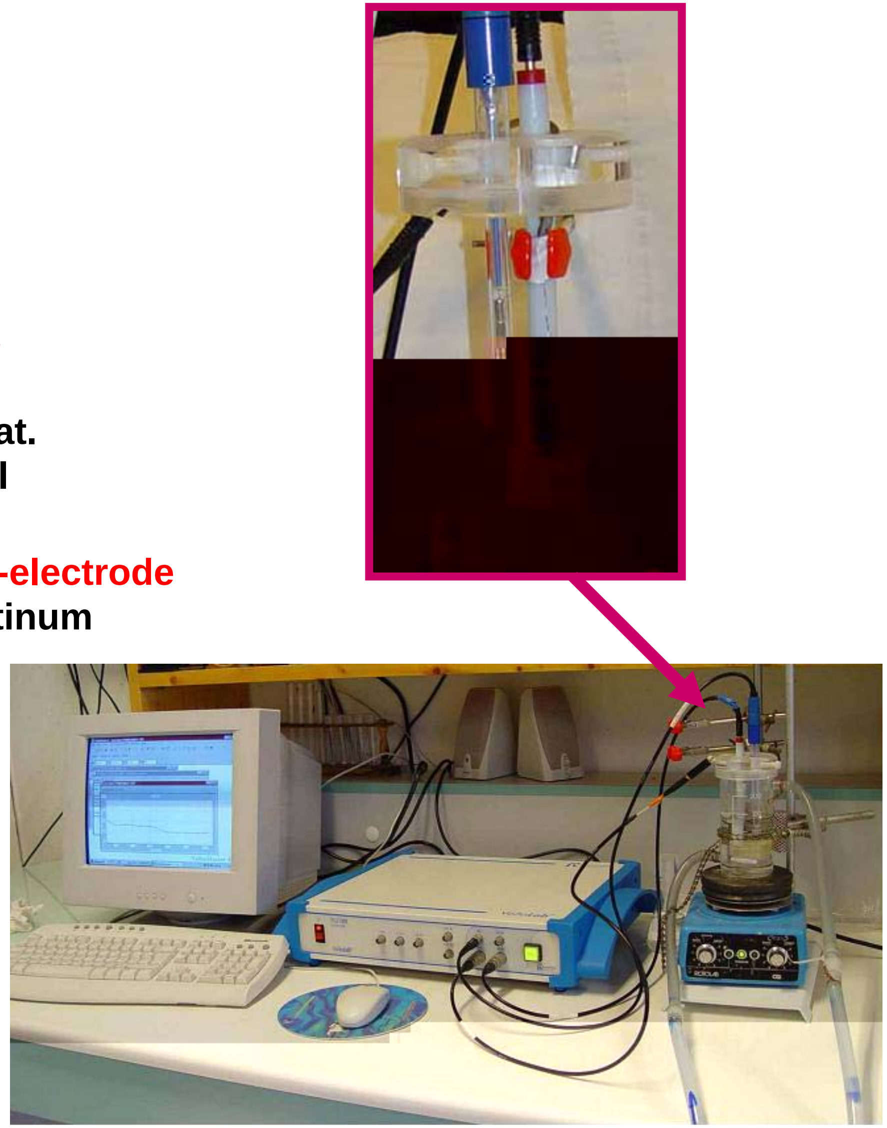
nanohelix



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:

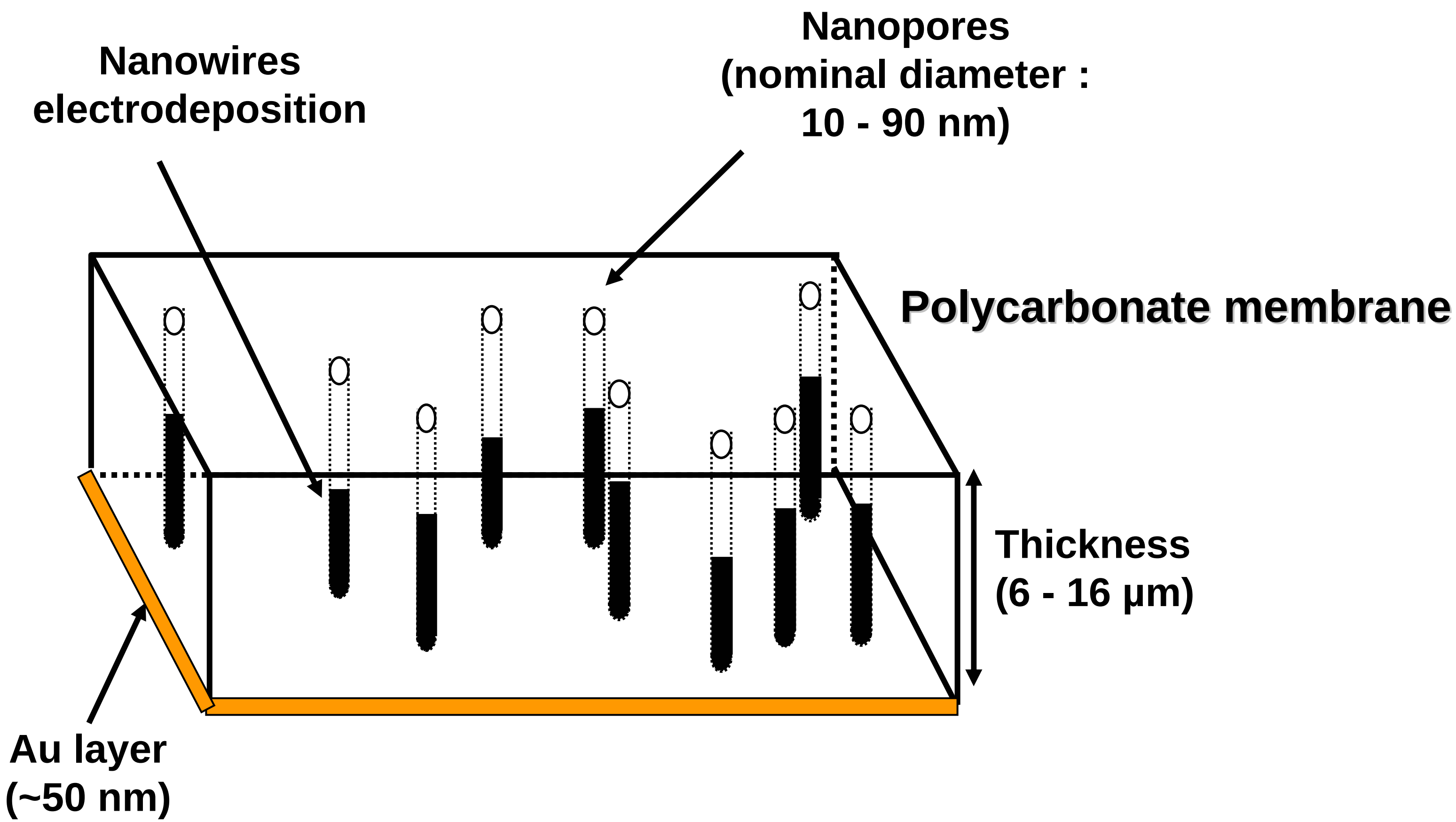
$$H_2O_2 \quad 2e \quad o \quad 2OH$$

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

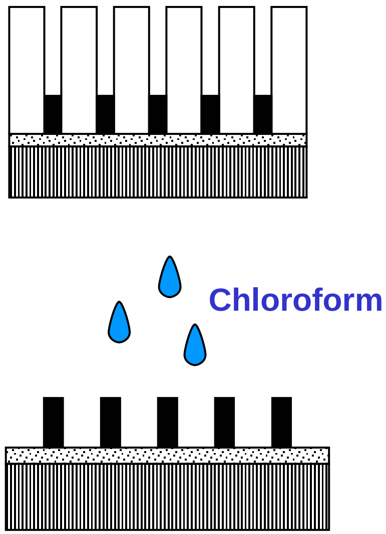
$$Zn^{2} \quad H_2O_2 \quad 2e \quad o \quad ZnO \quad H_2O$$

K. Laurent, Y. Leprince-Wang et al. , 517 (2008) 617-621.
K Laurent, Y. Leprince-Wang et al. , 41(2008) 195410.

Template method:



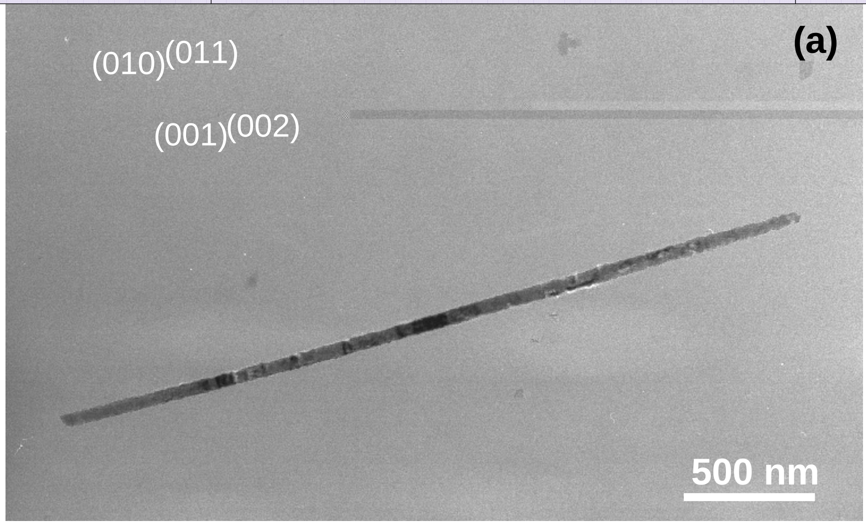
Pore density: ~ 6 $x10^8$ - 2 $x10^9$ pores/cm^2



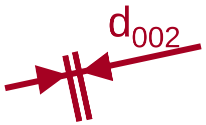
TEM Grill

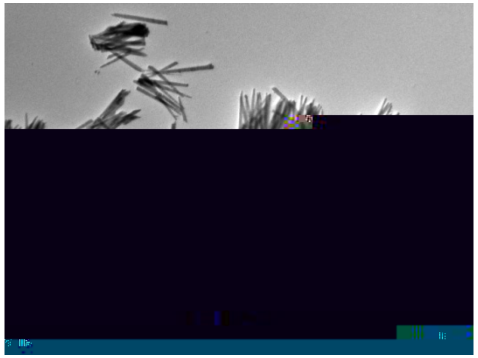
TEM images showing a general morphology of the electrodeposited ZnO nanowires from M type membranes (d ~ 150 nm).

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.



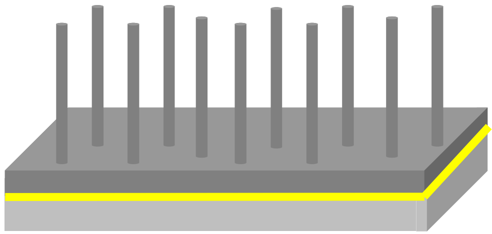
Both TEM observation (a) and HRTEM image (b) showing a M30 type individual nanowire with near <1 0 0> growth direction.



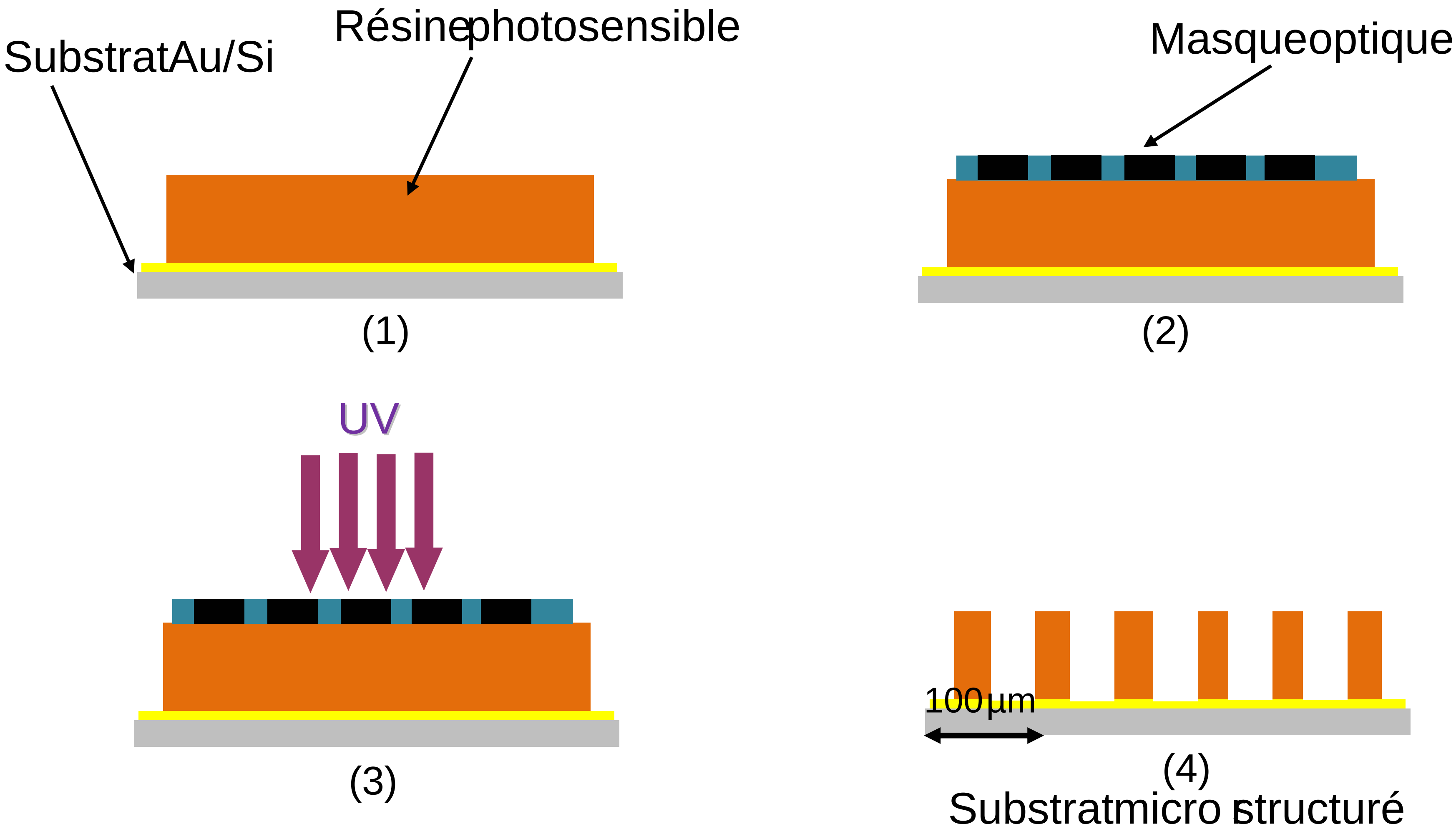


In chaos ➔ Well-ordered

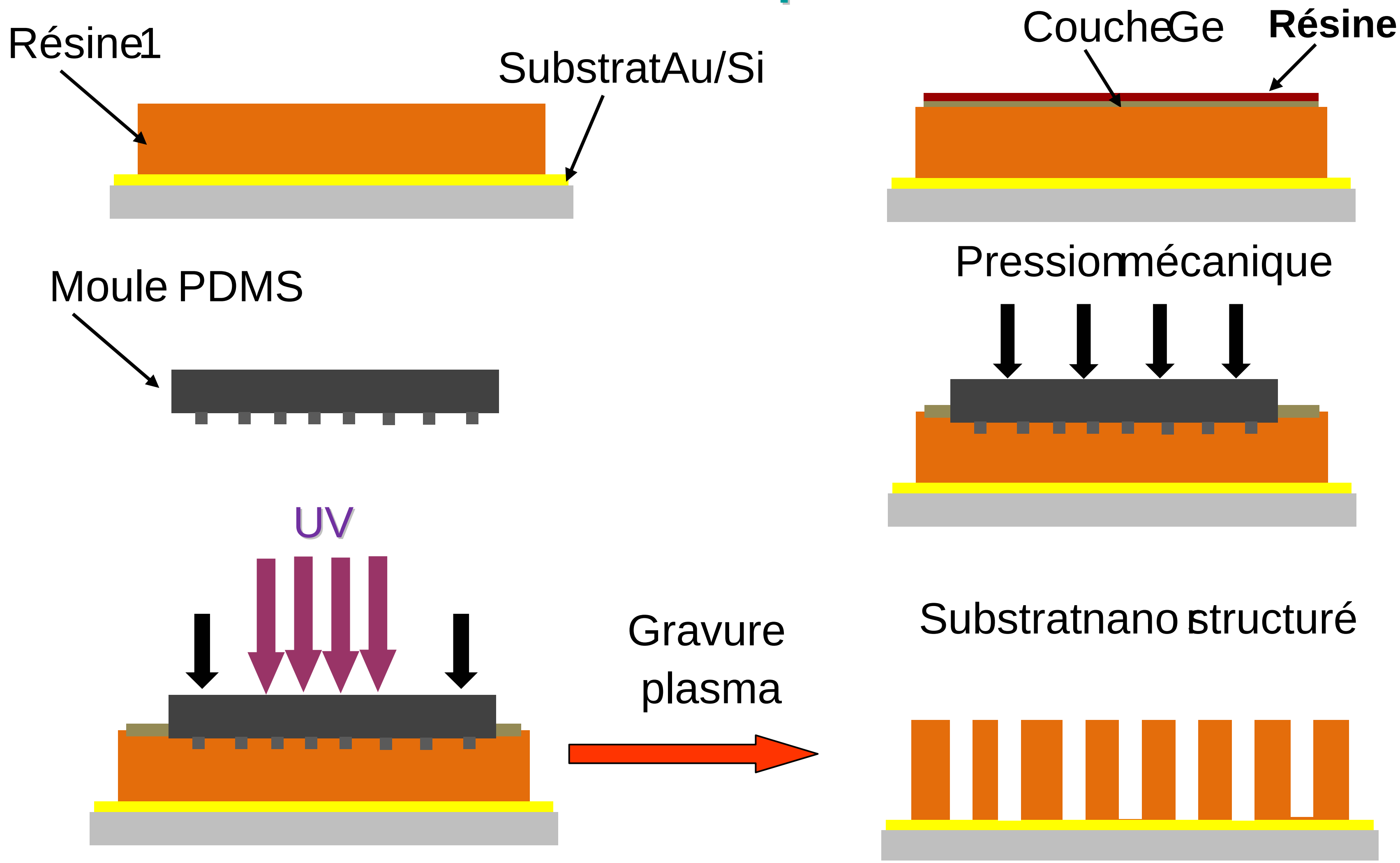
(using template method)



Optical lithography



Nanoimprint



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

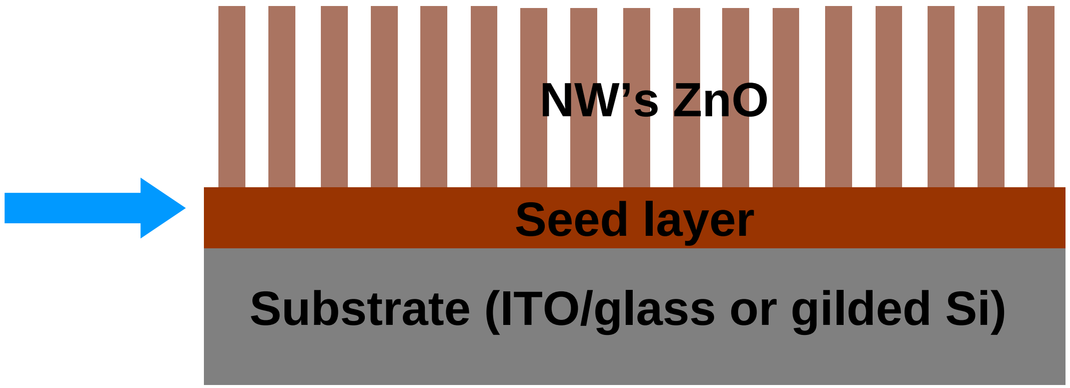
ZnO micro- and nano-rods using lithography defined templates:

Micro-structured photoresist
obtained by optical lithography.

Nano-structured PMMA using
ultraviolet nanoimprint lithography.

Y. Leprince-Wang et al. , (2010).

ZnO nanowire arrays:
(electrodeposition & hydrothermal method)



1. [illegible]

1) Electrodeposition of a seed layer:

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

(at room temperature) $I = -0{,}15\ mA/cm^2$ $t = 45min.$

$$\tfrac{1}{2}\,O_2 + H_2O + 2e^- \ :\ 2OH^-$$

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

Seed layer

Au layer

Si

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 •~1 µm

1 µm

Dependence of the ZnO NWs' morphology:

[$ZnCl_2$] 9 ➔ d 9

Thickness$_{\text{seed layer}}$ 9 ➔ d 9

[KCl] 9 ➔ • 9 [KCl] 9 9 ➔ d 9

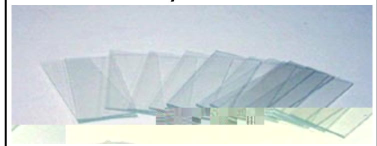
2. [illegible]

1) The seed layer deposition:

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

Spin-coating

Annealed at
350°C, 20min.



100 nm

Homogenous layer & small grain size (~ 20 nm)

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 ➔ •~ 0.7 µm.

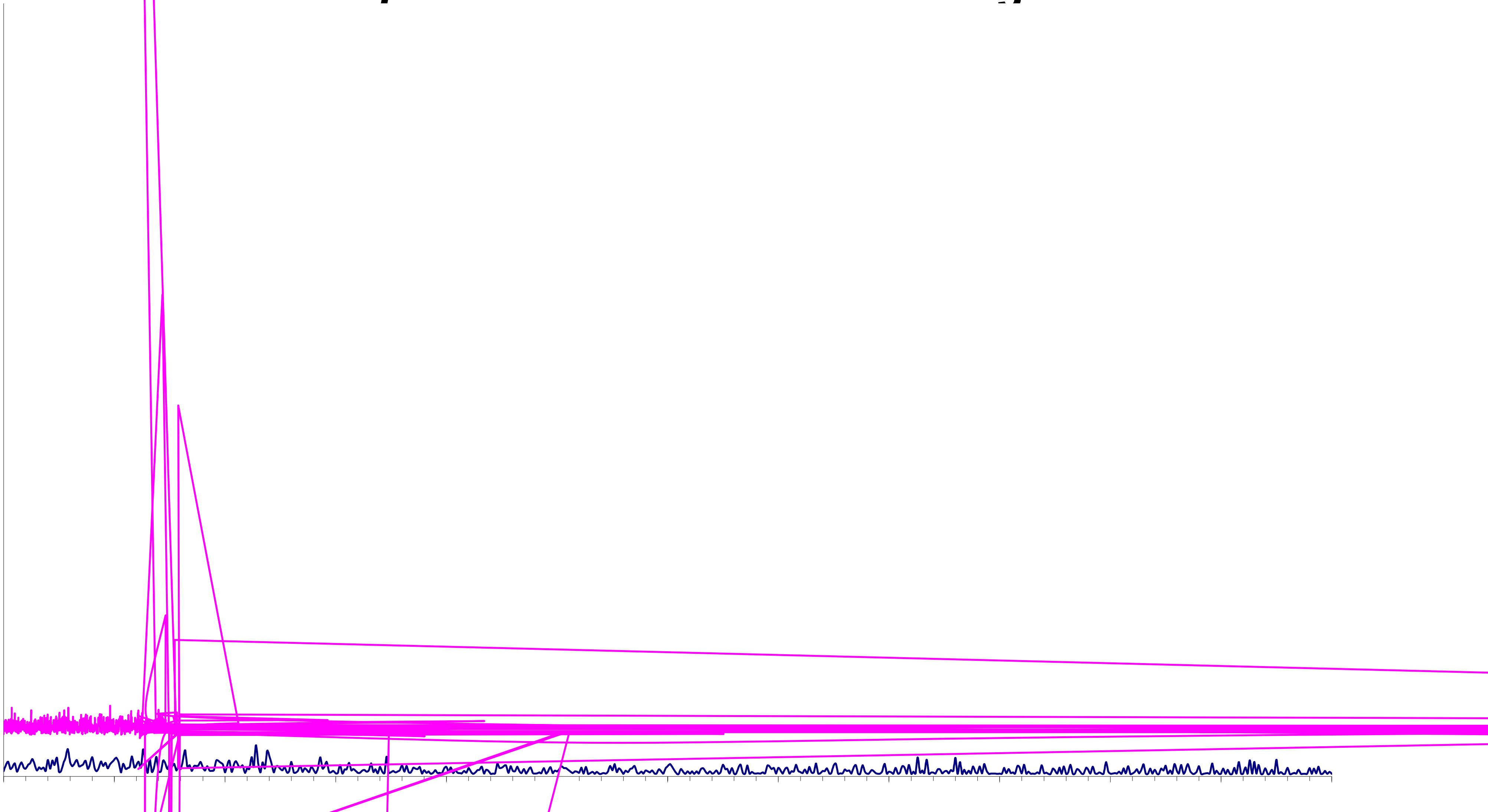
30 µm

200 nm

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 (•~350 nm)

(c) 80°C (•~550 nm)

(d) 90°C (•~850 nm)

t = 2h

Influence of the growth time on the length

t = 30 min

t = 45 min

t = 1h

t = 2h

3h

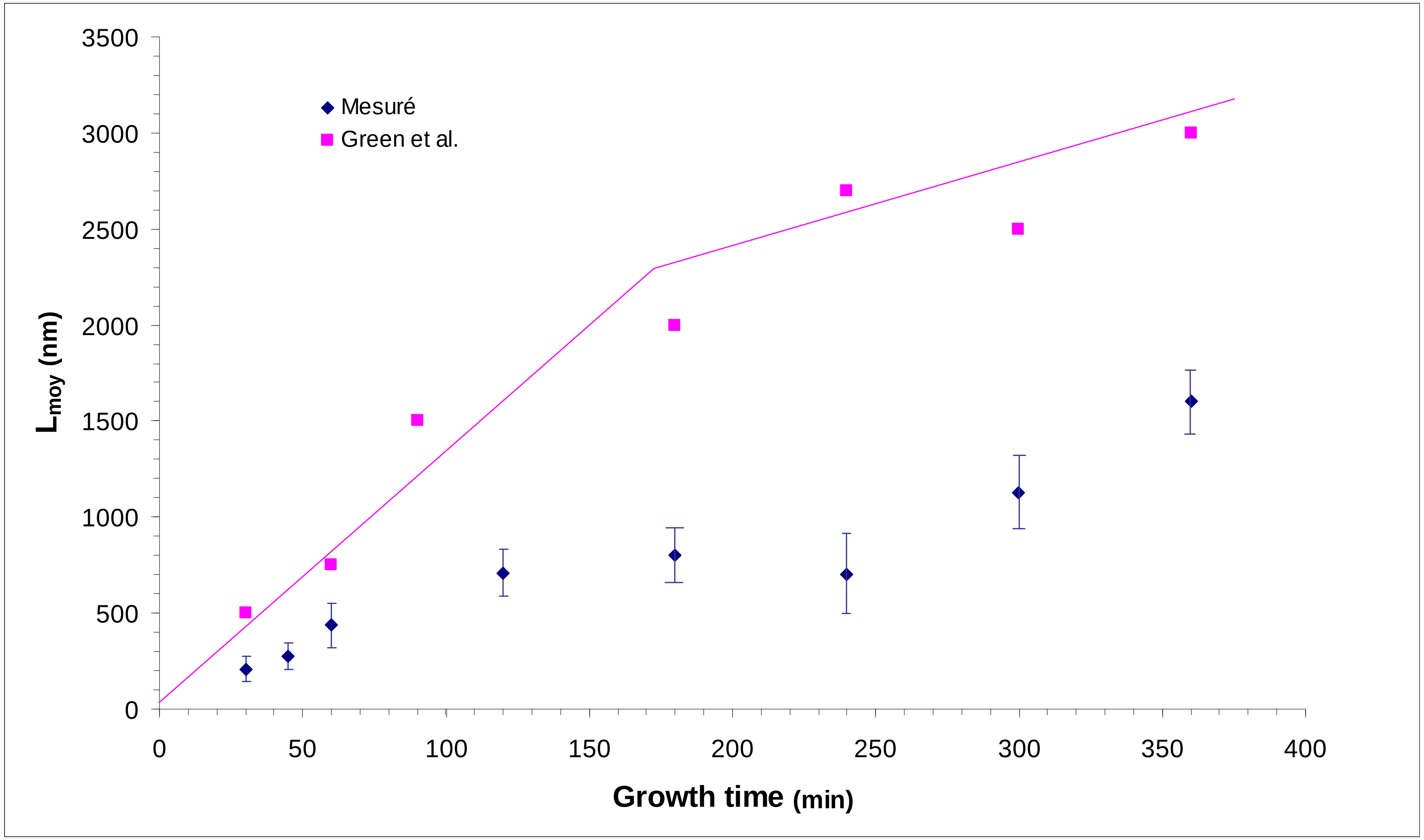
4h

5h

6h

T = 90°C.

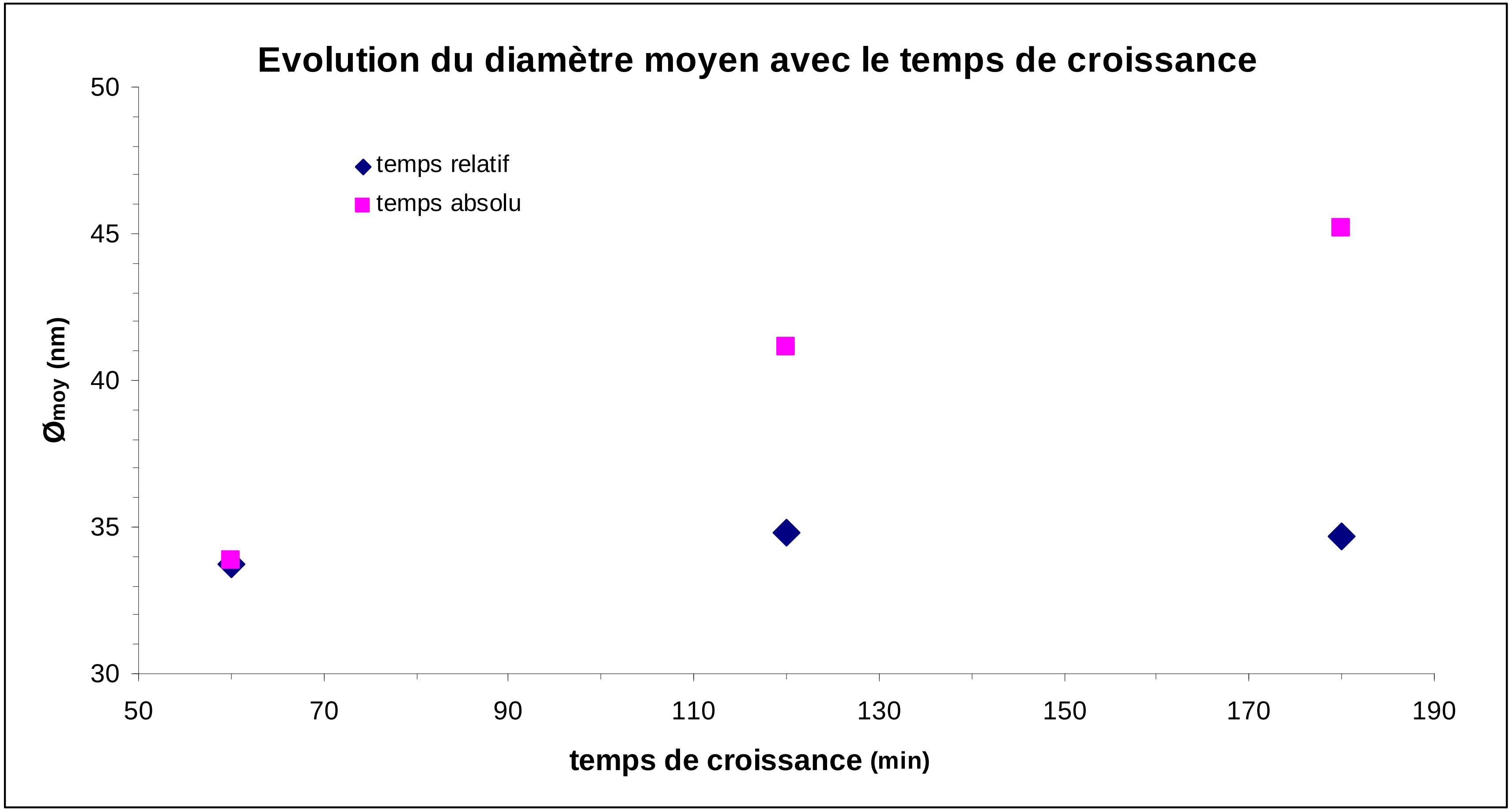
Influence of the growth time on the length



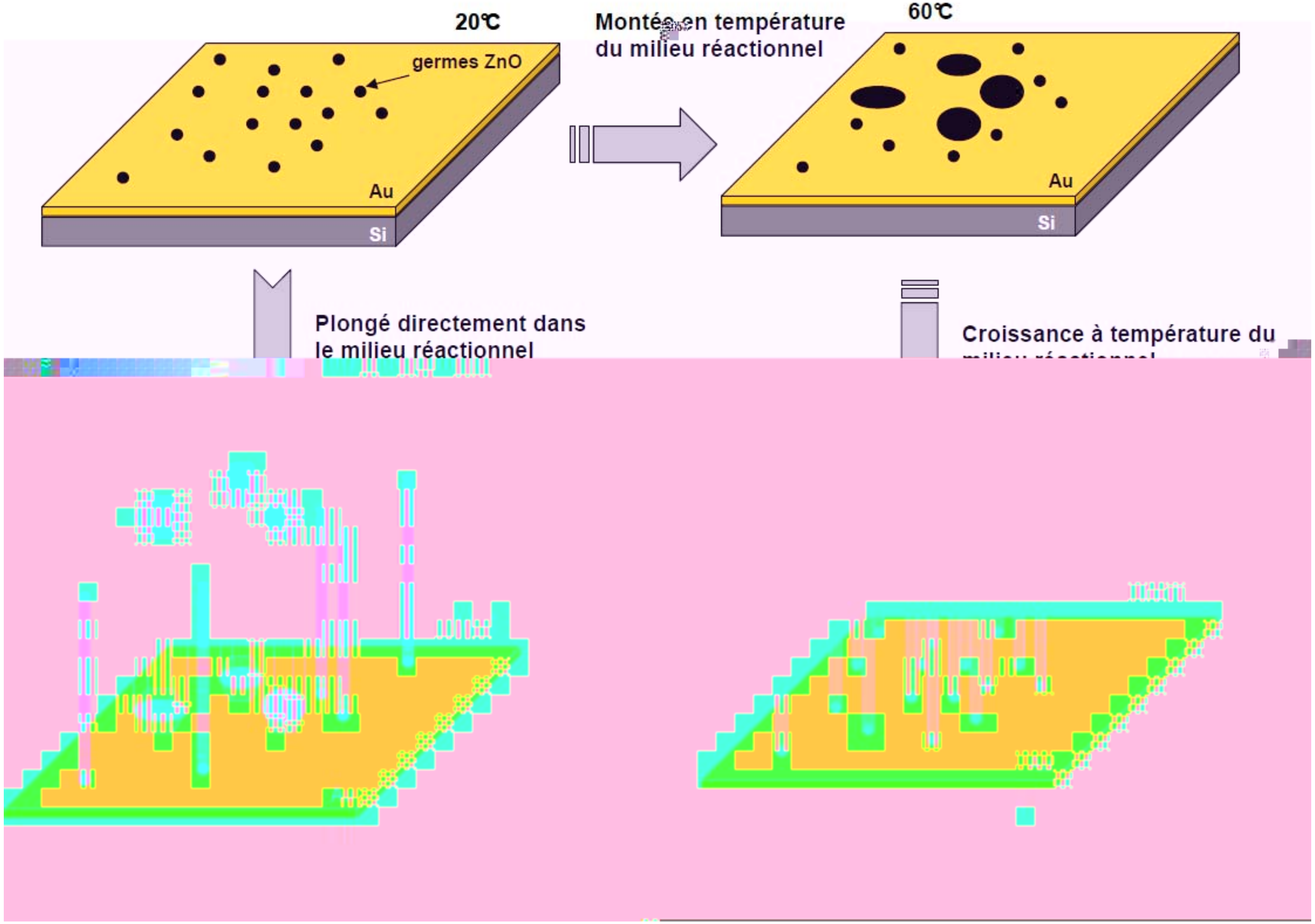
Green et al.: phase rapide 11,1 nm/min, phase lente 5,5 nm/min.

Measurements: v ~ 5 – 6 nm/min.

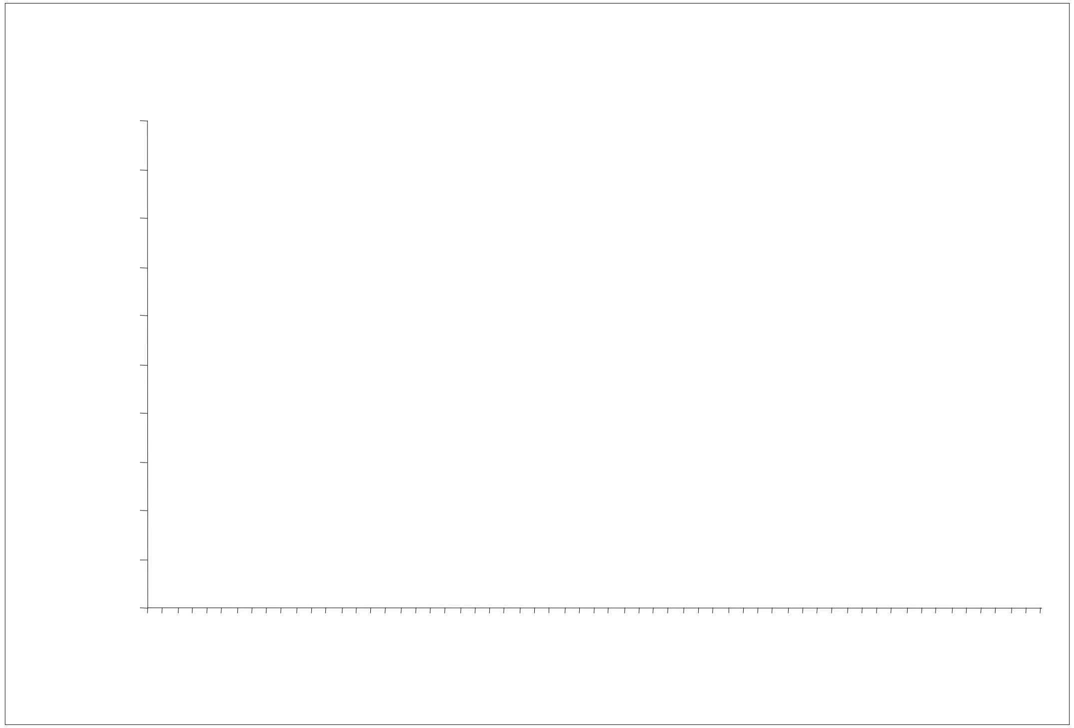
Influence of the growth time on the diameter



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
Croissance à température du

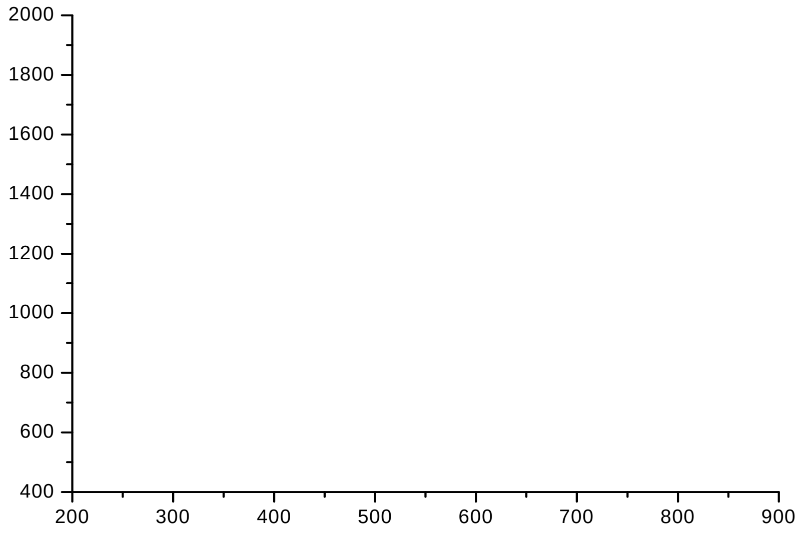
XRD measurements:



(HR)TEM observations:

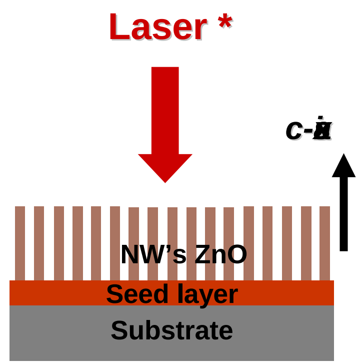
Monocrystalline structure with excellent crystallinity, along c-axis growth.

Raman & PL measurements:



(1) E_2: 437 cm^{-1} in nanowires ~ ZnO bulk ➔ stress-free;
439 cm^{-1} in thin film ➔ under compressive stress **
' Q V en cm^{-1} ' Q et V en GPa***

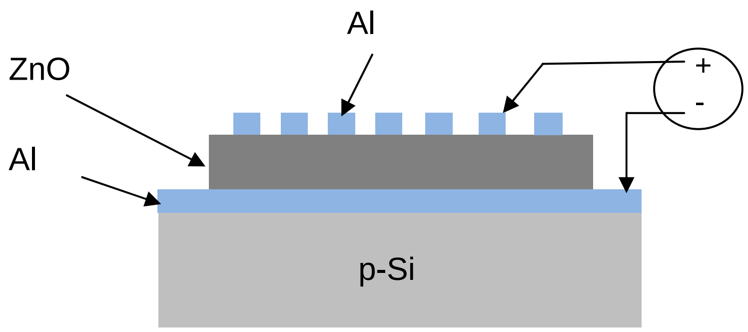
(2) Oxygen vacancy (defects) ↗ ➔ conductivity of ZnO ↗.



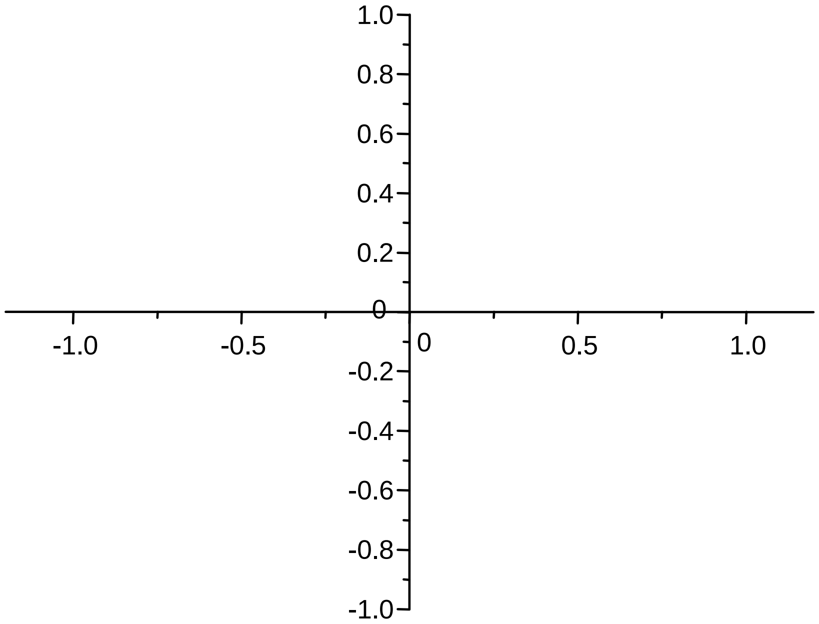
** K. Laurent, Y. Leprince-Wang *et al.* [illegible], 517 (2008) 617-621.
*** F. Descremps *et al.* **Physical Review B**, 65 (2002) 092101.

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

Ohmic contact ZnO thin film / Al



Couche mince contact ohmique
(Al/ZnO/Al)



$$! \quad \frac{S\,R}{L}$$

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

Resistivity of ZnO:

! = 0.06 ± 0.02 cm

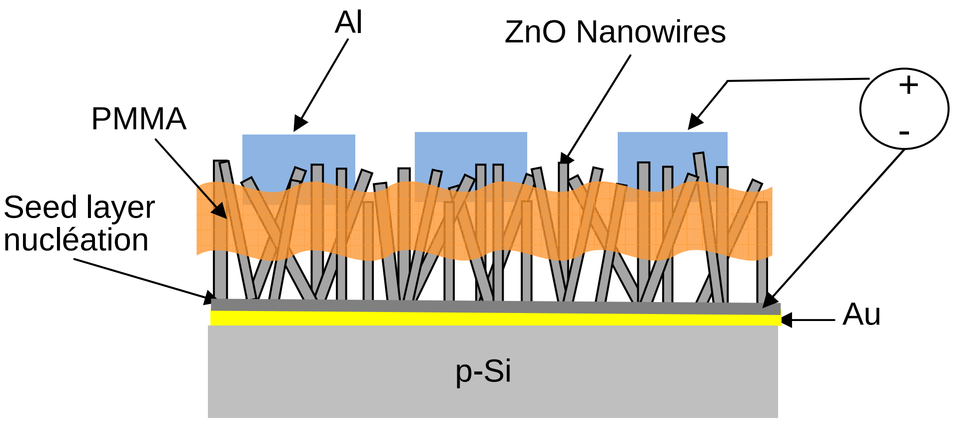
Literature* :

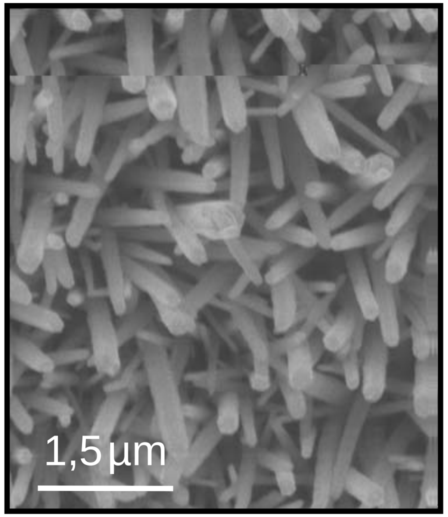
! = 0.001 – 0.1 cm

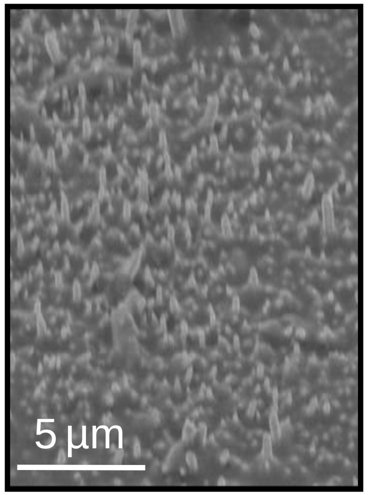
* T. Schuler, M.A. Aegerter, Thin Solid Films **351** (1999) 125.
* Ozgur et al Journal of Applied Physics, **98** (2005) 041301.

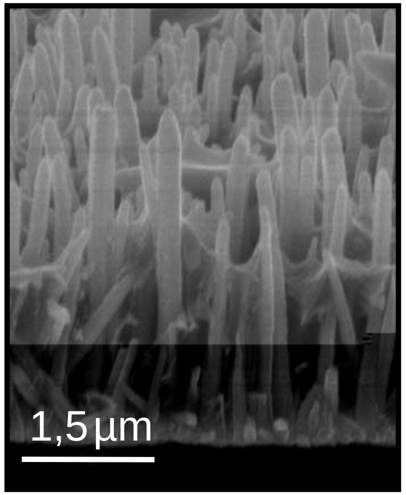
Schottky junction – ZnO nanowires/Au

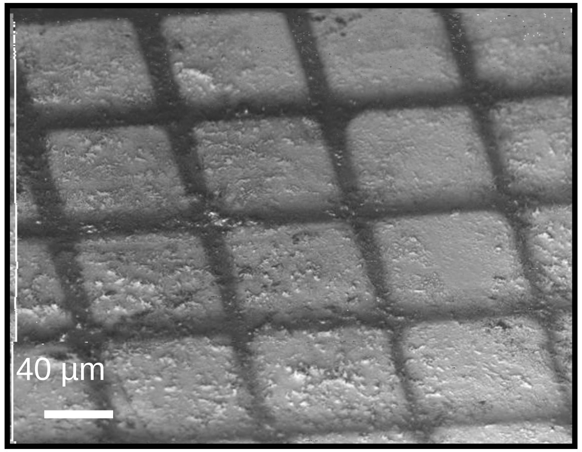
* Samplepreparation:





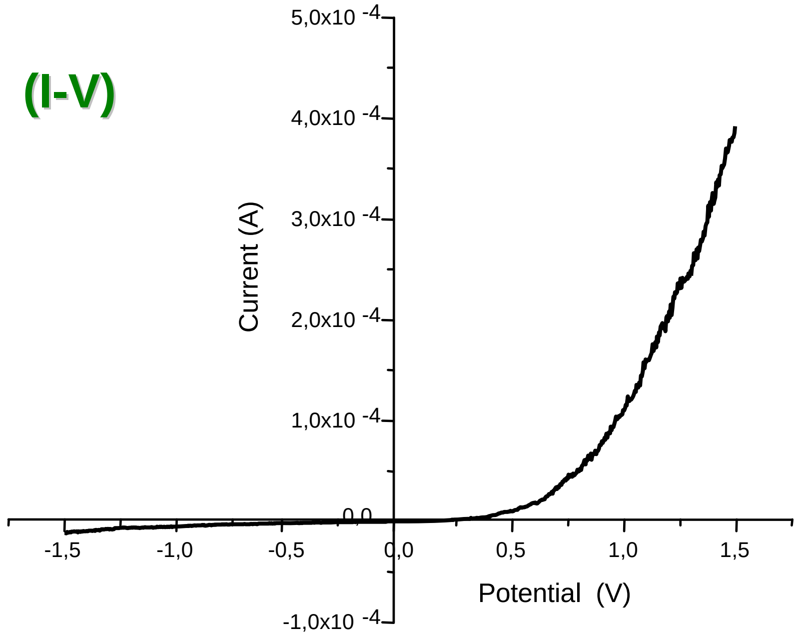


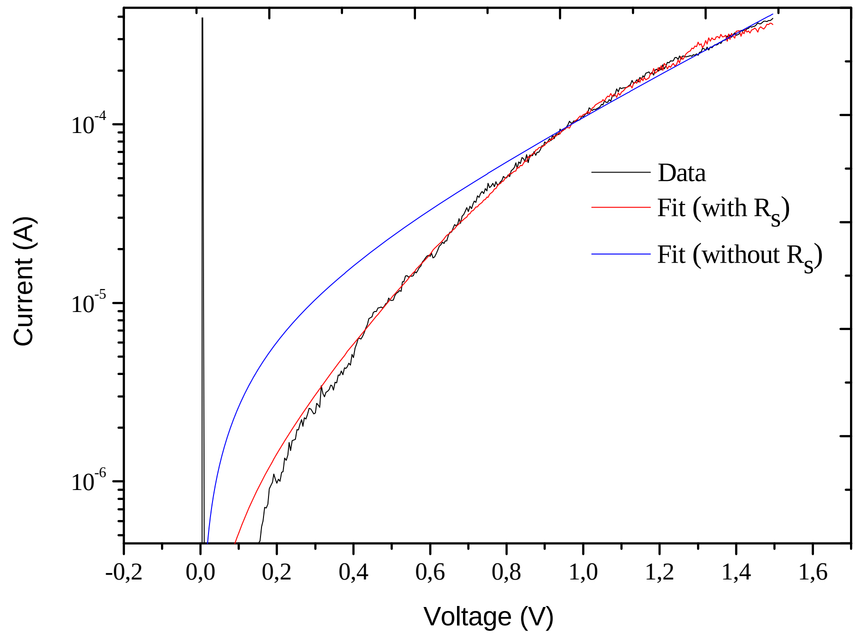




Contact Schottky – ZnO nanowires /Au

(I-V)





$$I = I_s \left[\exp\left(\frac{qV}{nk_B T} \right) - 1 \right]$$ No adequate

$$I = I_s \left[\exp\left(\frac{q(V - R_S I)}{nk_B T} \right) - 1 \right]$$ Our model with series resistance R_S.

Schottky contact parameters:

$R_s = 800 \pm 50$

$n = 10 \pm 1$

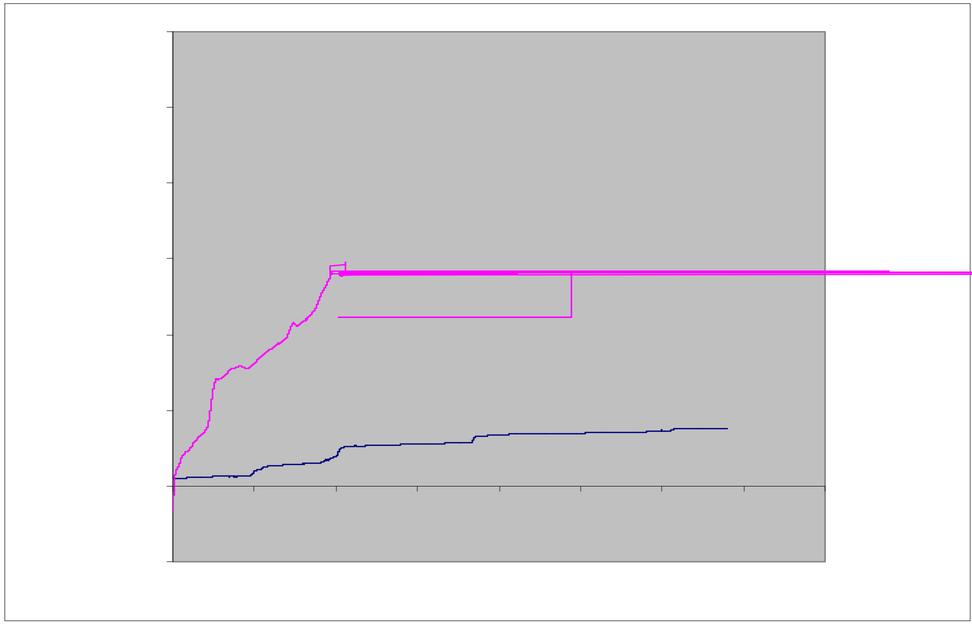
$L_{sb} = 0,36 \pm 0,02\,eV$

R_s 0 ± 15 Ω

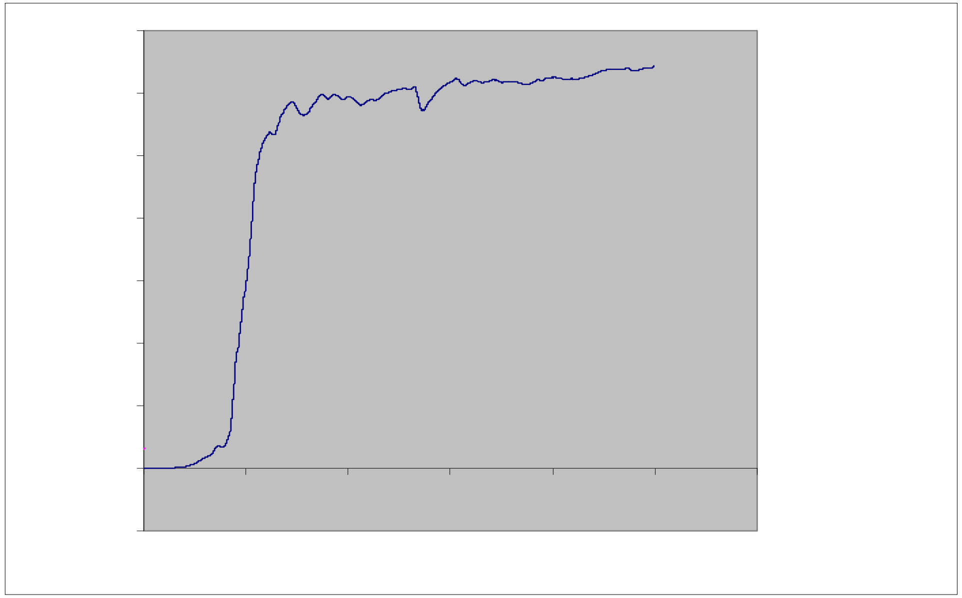
n 10 ± 1

Φ_b ± 0 eV

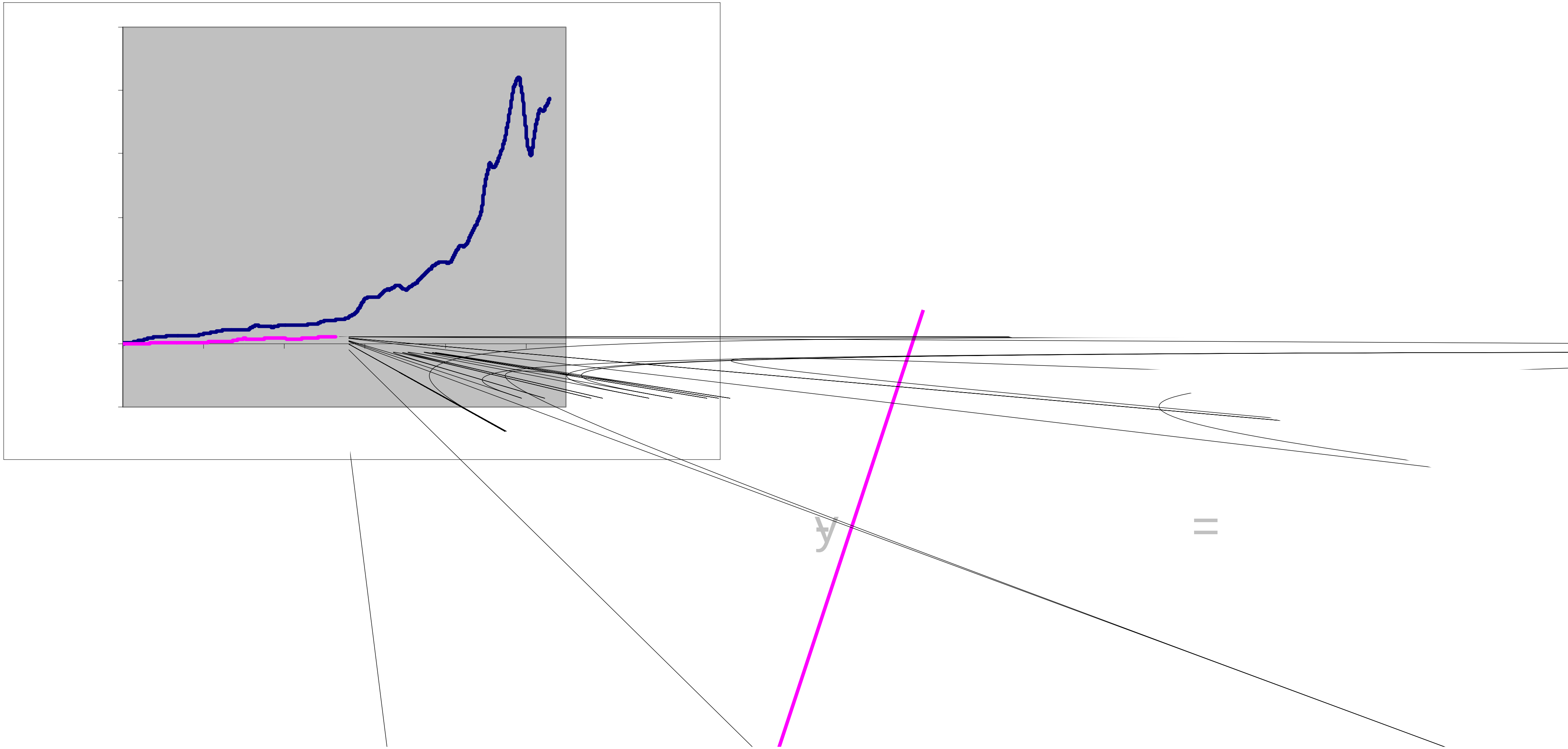
1. µ-pillars



2. Black Silicon



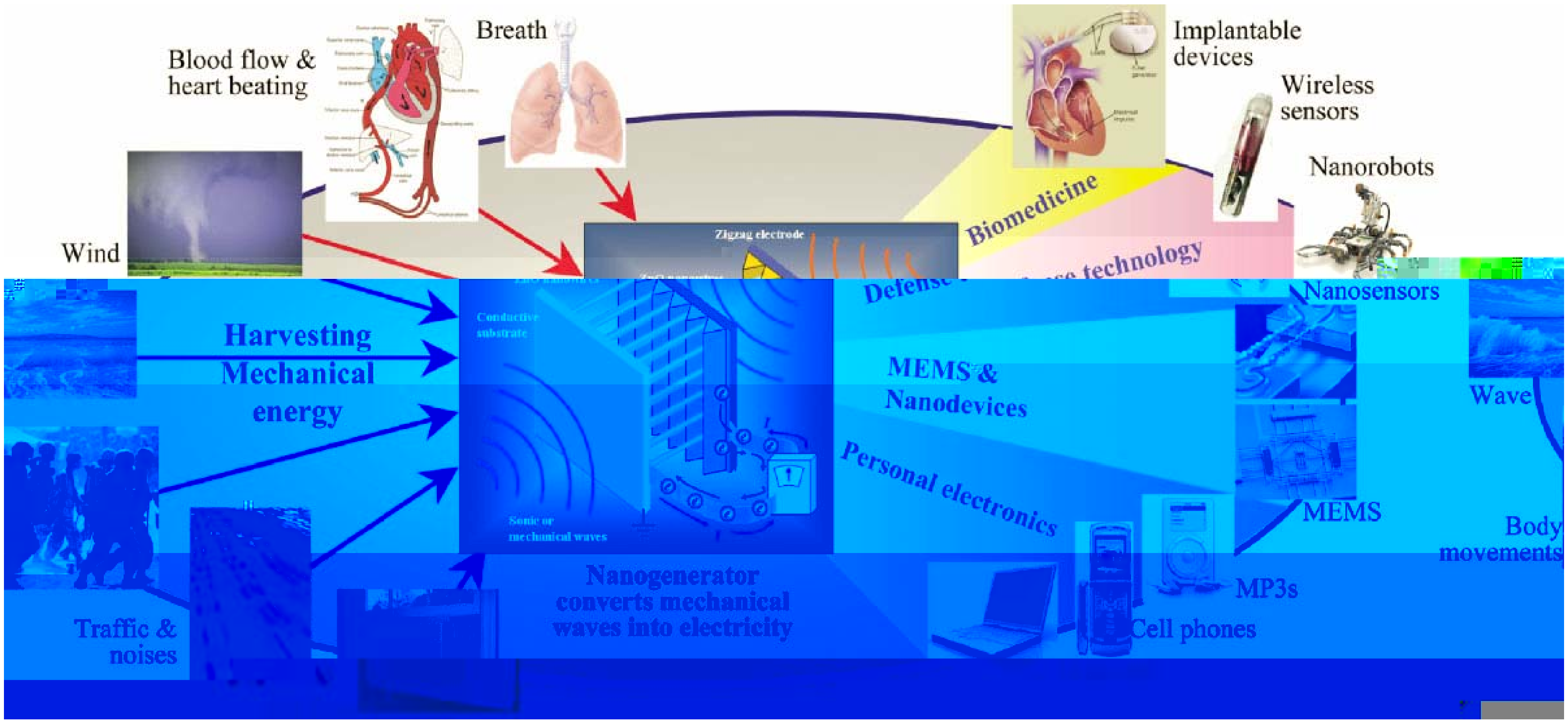
3. ZnO NW/Au

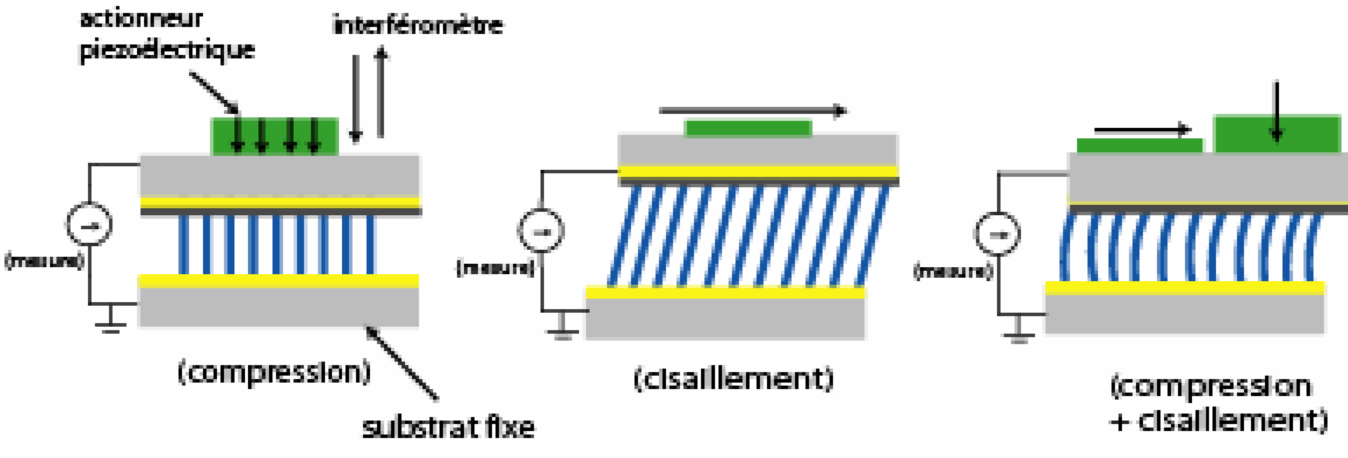


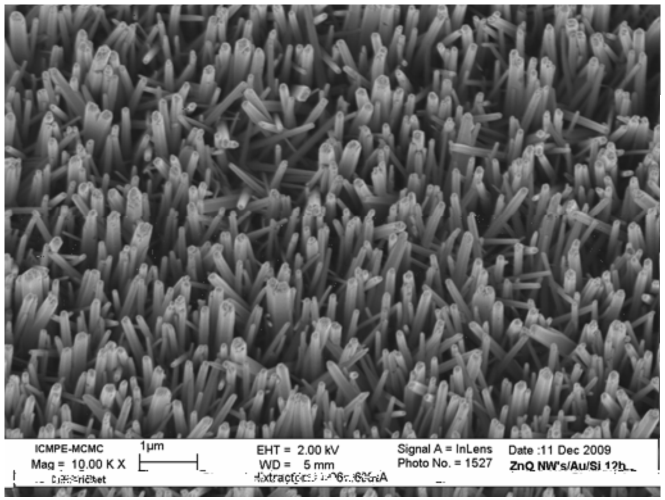
Application 1: [illegible]

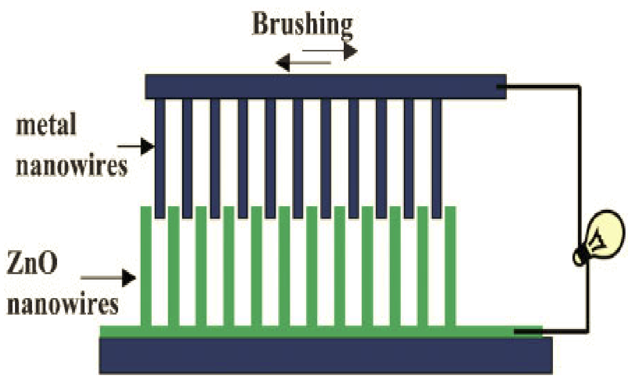
[illegible]

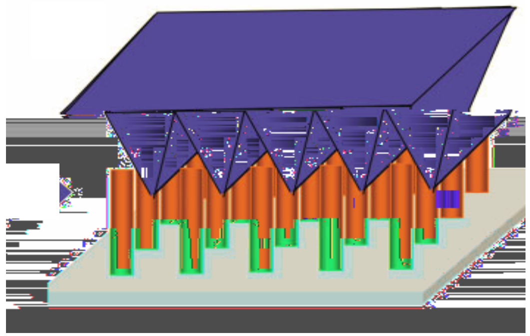
Perspectives







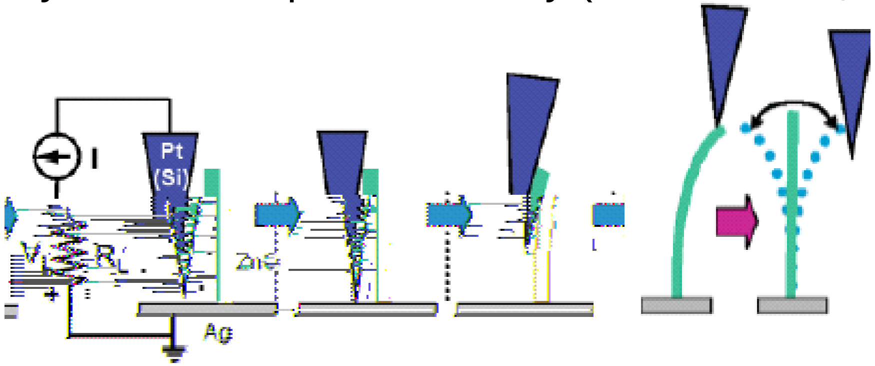




Under studding: coupling electro-mechanics properties of ZnO nanowires.

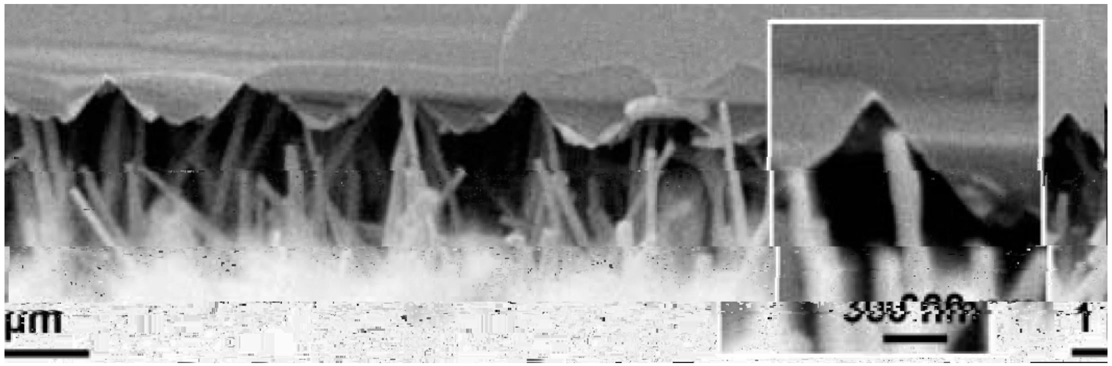
State of the art : nanopiezoelectric system

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



ZL Wang, B (2006)

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

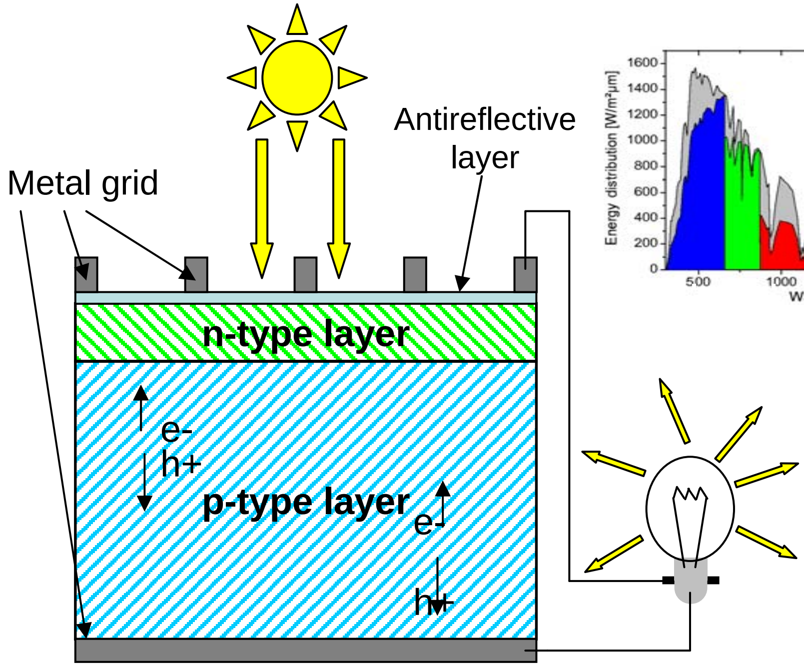


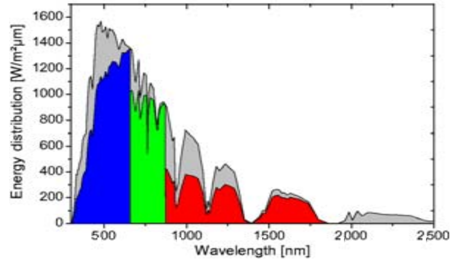
ZL Wang, B (2007)

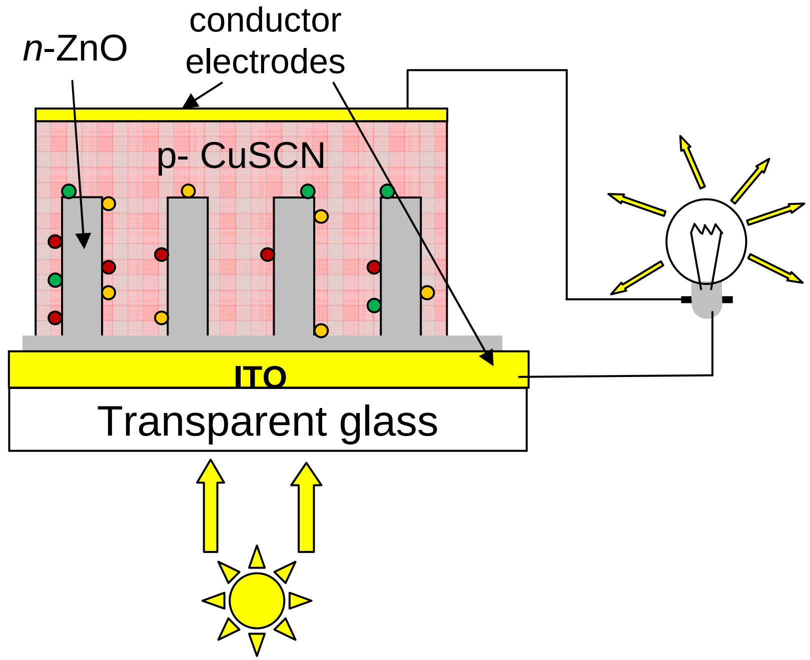
Collective signal: ~ 10 mW, ~ 800 nA / ~ 6 mm²

0 5% ➔

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

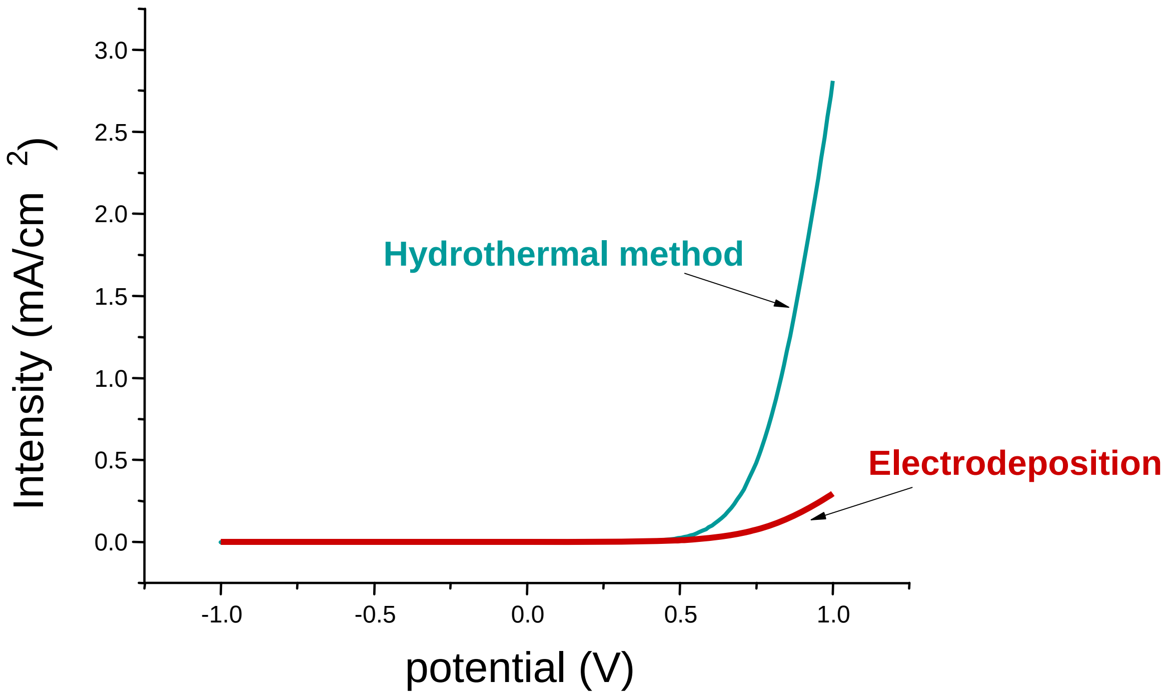
Conception

- ZnO nanorods array
- semi-conductors nanoparticles

➔ η ↑

STF Program in China (2009-2011)

p n junction between CuSCN & ZnO:



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

Electrodeposition of CdS NPs:

Chemical bath*:

37 cm^3 of 1M Cd(Acet)

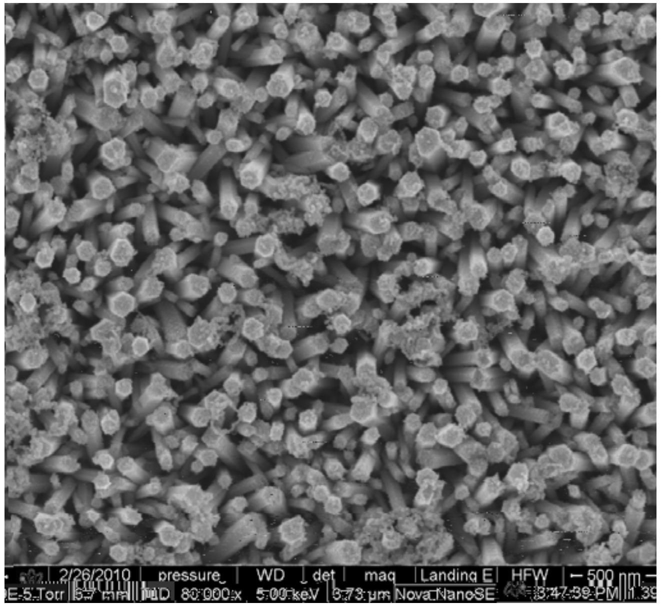
20 cm^3 of 13M ammonia

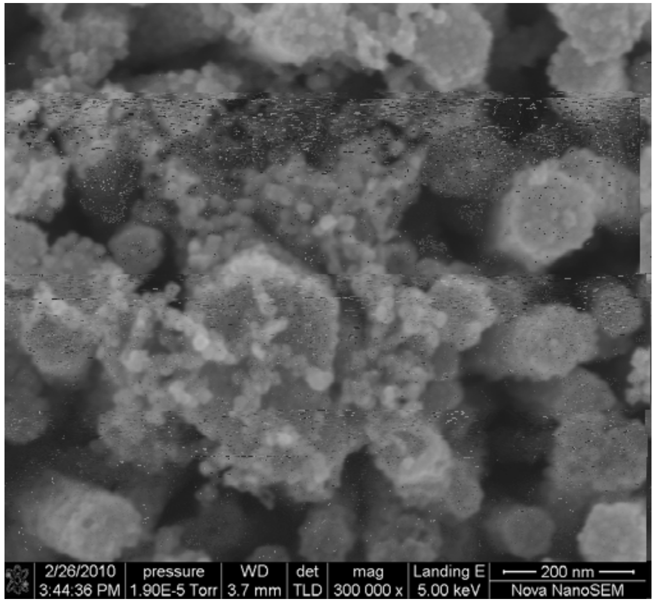
10 cm^3 of 7.2M triethanolamine

100 cm^3 of deionized water

37 cm^3 of 2M thiourea

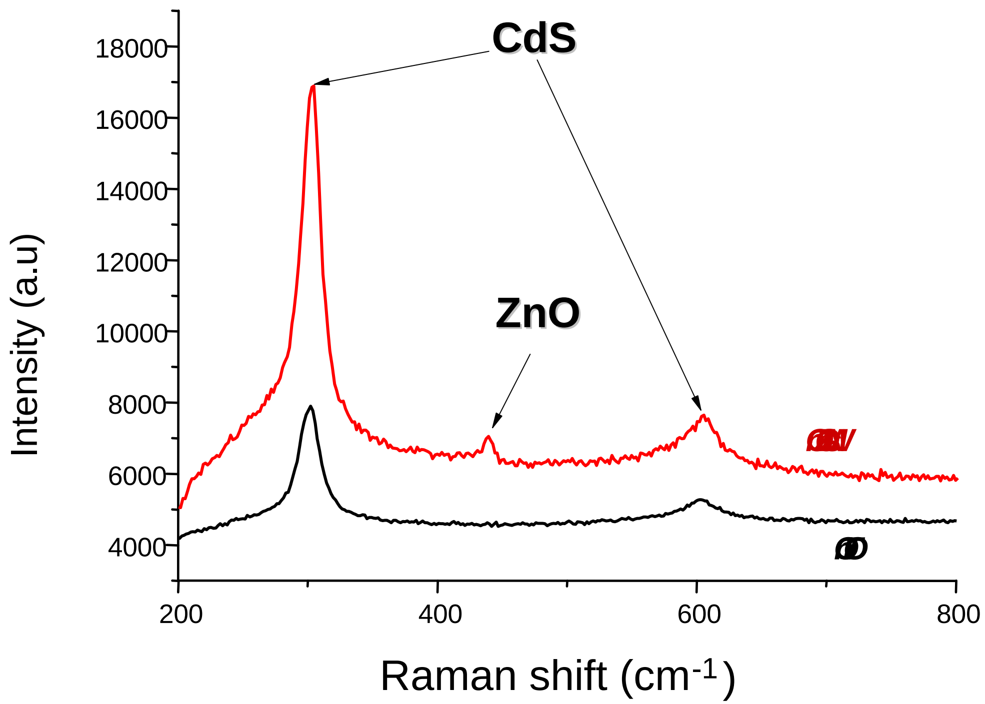
{* Method: Tetsuhiko ISOBE, Materials research bulletin, 30 (1995) 975}

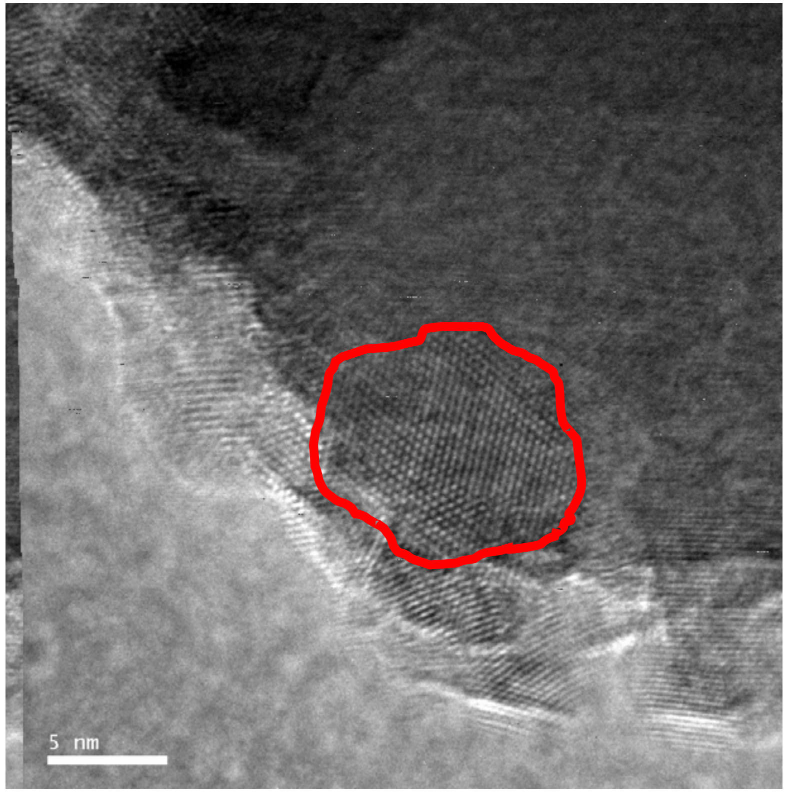




- Homogenous coverage
- Nanoparticles ~15-20 nm size

Raman & HRTEM characterizations of CdS NPs:

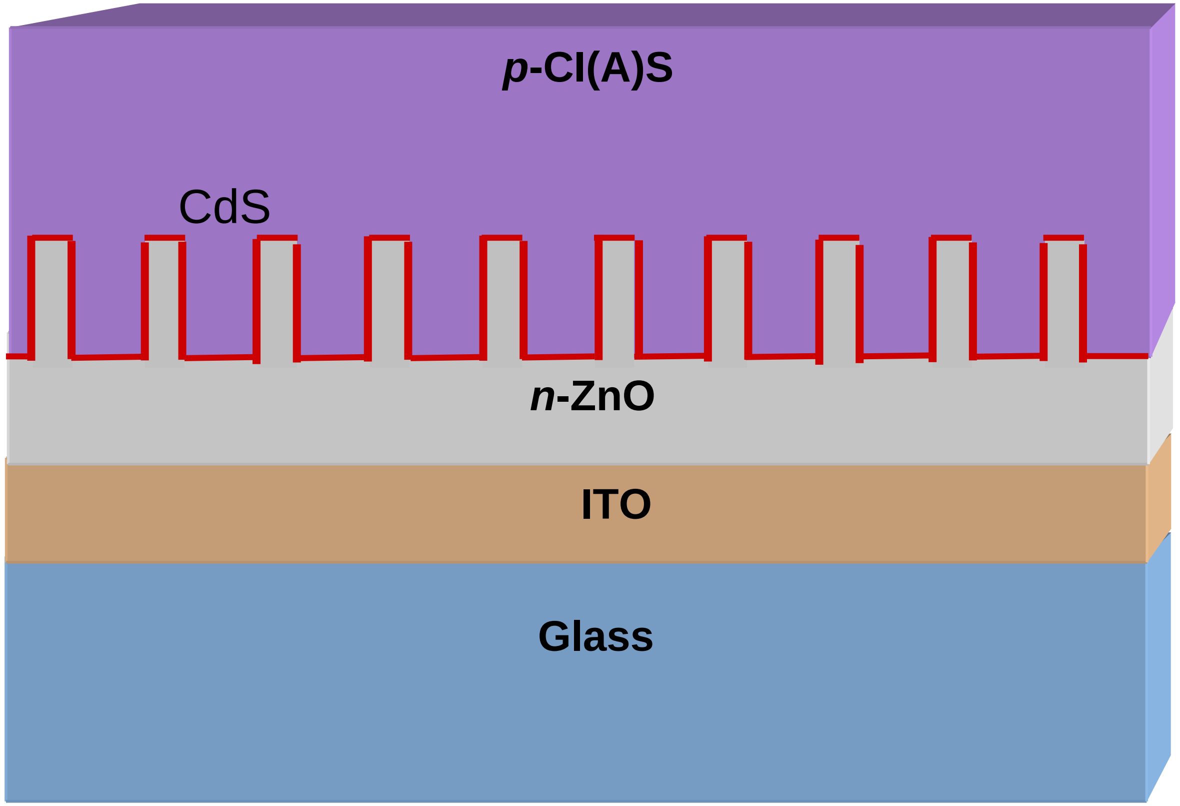




Perspective:

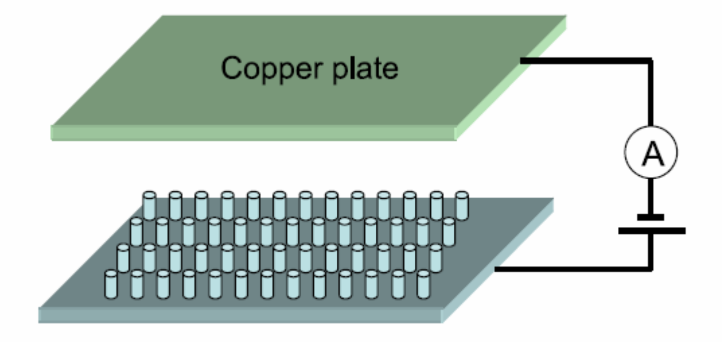
1) Chemical bath deposition of PbCdS nanoparticules ➔ large absorption band
2) The third step : CuSCN on NPs + ZnO NWs

New Project on $CuIn(Al)S_2$

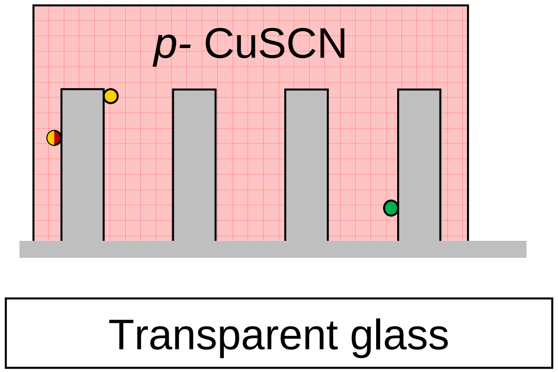


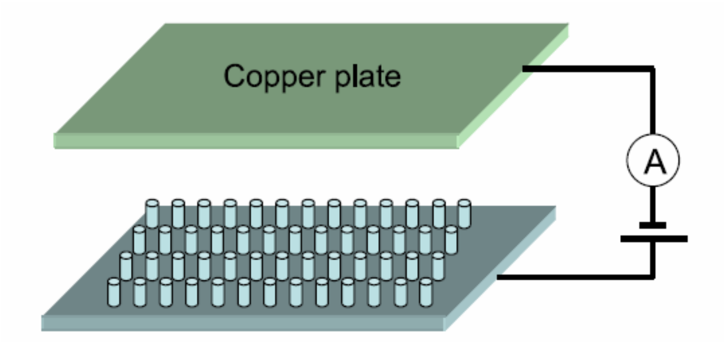
gap_{CIS} ~1.5 eV & gap_{CIAS} ~1.1 – 1.7 eV

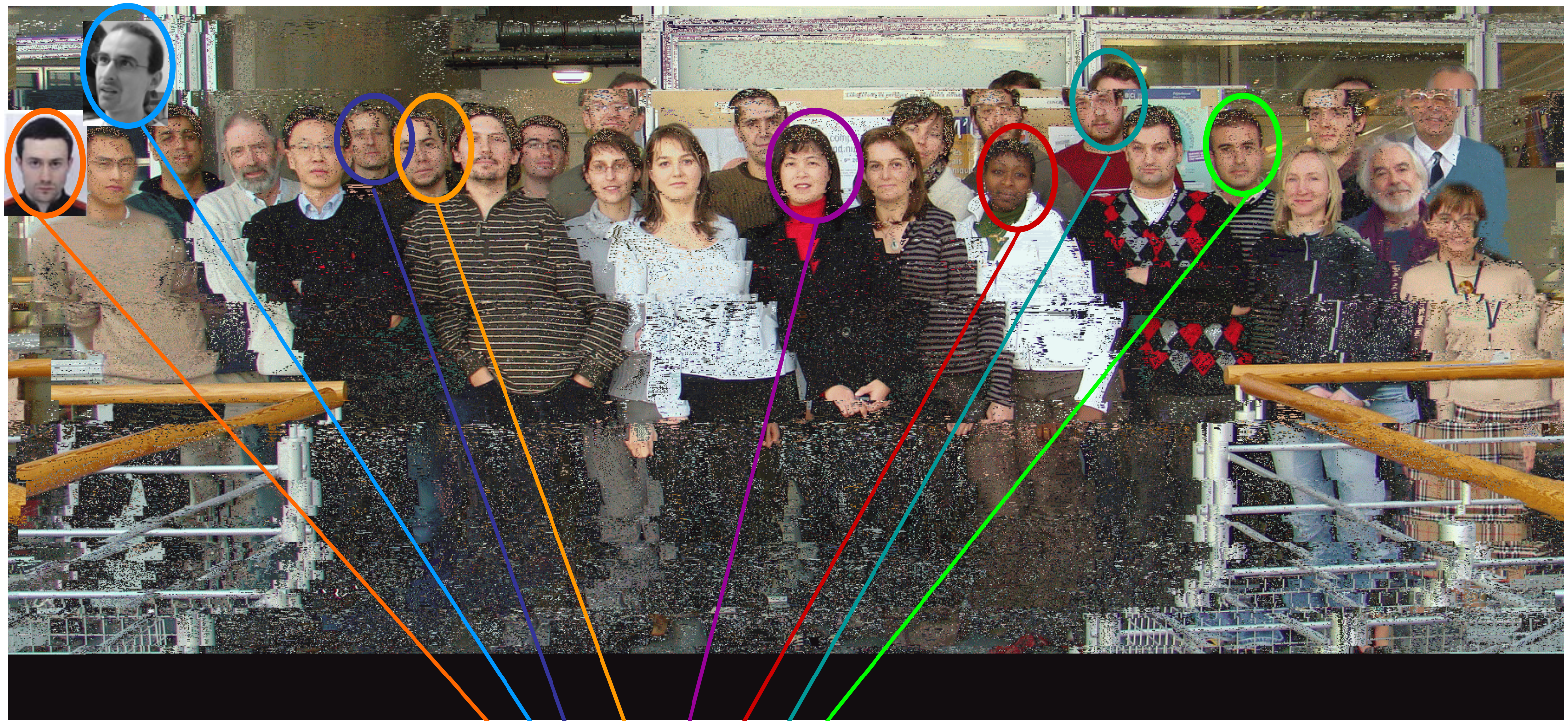
Applications 3 ➔ Nanostructured gas sensor



The nanowire sensor devi


p- CuSCN
Transparent glass


Copper plate
A



"Nanomaterials" Team

* **LEPRINCE Yamin** (Pr.)
* **CAPOCHICHI Martine** (Ing.)
* **BROURI Tayeb** (Ph.D, 2007-2011)
* **CESAR-CHAVALIER Clotaire** (Ph.D)
* **LEOPOLDES Julien** (Assitant Pr.)
* **LAURENT Kevin** (Postdoc – PKU 2009-2011)
* **BOUCHAIB Salah** (Ph.D)
* **CONRAD Guillaume** (Ph.D)

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Thanks