Piezoelectric nanogenerators based on nanowires

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Outline

I. Introduction

- Context : piezoelectricity
- Interest of Nanowires (NWs)

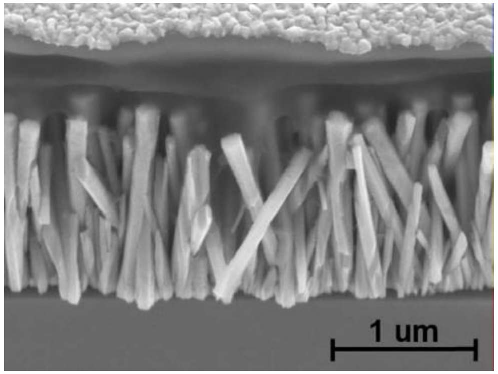
II. Nanogenerators : Experiments and theory

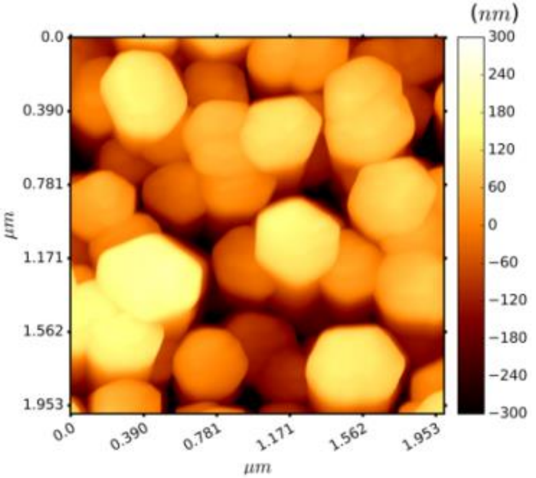
- Origin, working principle
- Theory
- Doping and Surface traps

III. Individual NWs: Experiments and theory using AFM

- NWs vs. thin films (PFM)
- Theory vs. experiments

IV. Conclusions





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Introduction

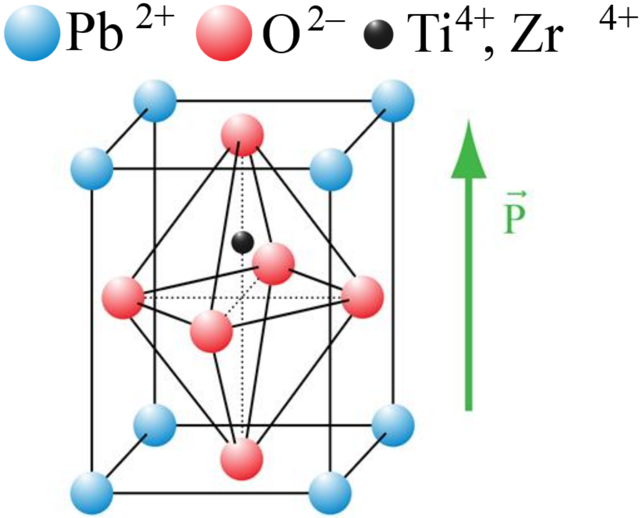
Introduction (1/9)
Piezoelectricity

What is the piezoelectric effect?

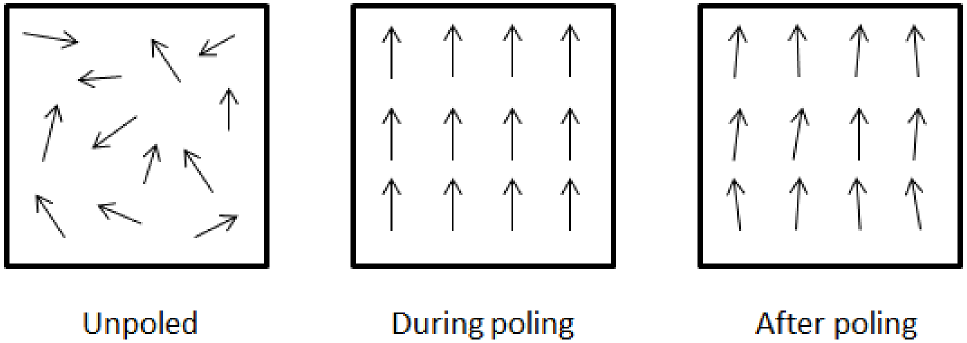
Pierre & Jacques Curie (1880)

Materials with non centro-symmetric crystal structure
(ex: Quartz, PZT, GaN, ZnO, AlN, etc)

PZT crystal structure

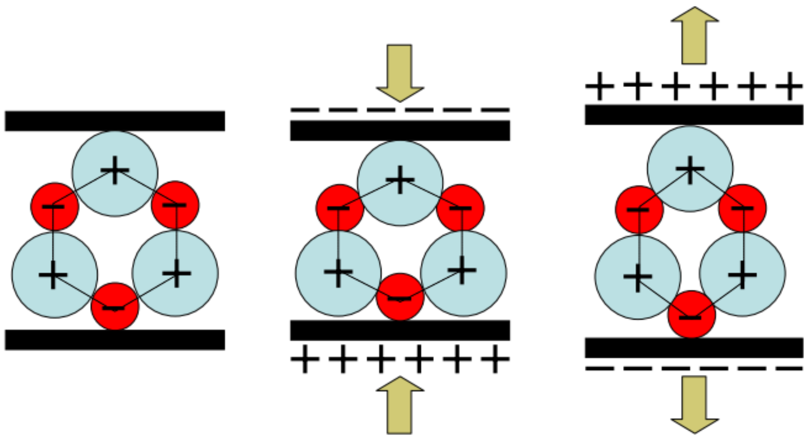


Sometimes "poling" is necessary
(High electric field at high T.)
Ex: PZT @ ~200°C and 1MV/m

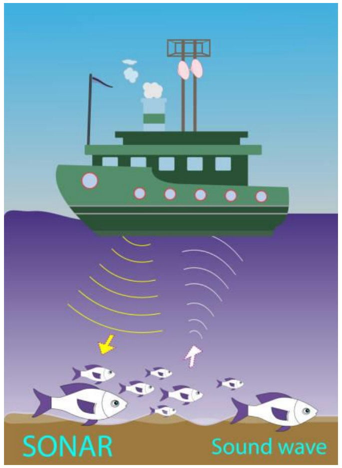


Context : Piezoelectric energy conversion

Materials with nonsymmetric crystal structure
(ex: Quartz, PZT, AlN, GaN, ZnO, etc) → wurtzite structure



d[m/V]
or
d[C/N]



1) Direct effect : Force → Electric field

Sensors and energy harvesting

2) Reverse effect : Electric field → strain

Actuators

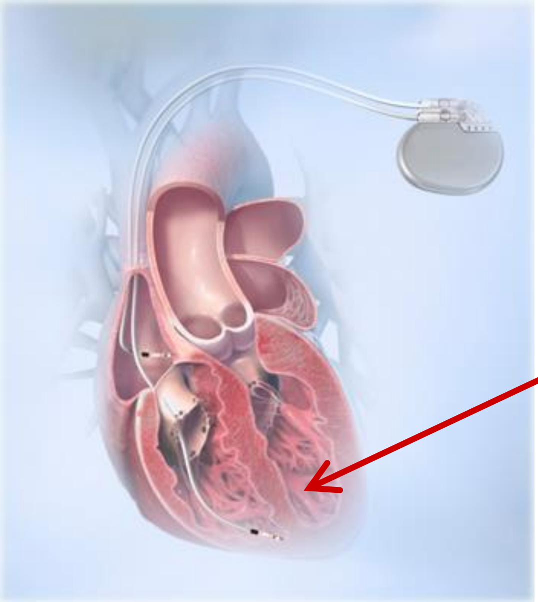
And many others…

Introduction (3/9)
Energy harvesting applications

Portable devices

Batteryless TV remote control
(Arveni for Philips, 2011)

Pacemakers
(source: St. Jude Medical inc., Medtronic)



1gr, $1cm^3$

Introduction (4/9)
Materials and properties

- Electromechanical coupling factor (efficiency in the energy conversion):

$$W = \frac{1}{2} E S^2 V \qquad E_c = \frac{1}{2} E^2 \frac{d_{33}^2 S^2}{\varepsilon} V \qquad k^2 = \frac{E_c}{W} = E \frac{d_{33}^2}{\varepsilon}$$

Material	Bulk material parameters			
	d_{33} [pm/V]	E [GPa]	$\varepsilon/\varepsilon_0$	k^2
PVDF	-25	0.39	13	0.002
PZT	650	50	3800	0.62
AlN	4	330	9	0.06
ZnO	9.93	140	10.9	0.14
GaN	1.86	300	8.9	0.013
PMN-PT	1400	18	4713	0.84

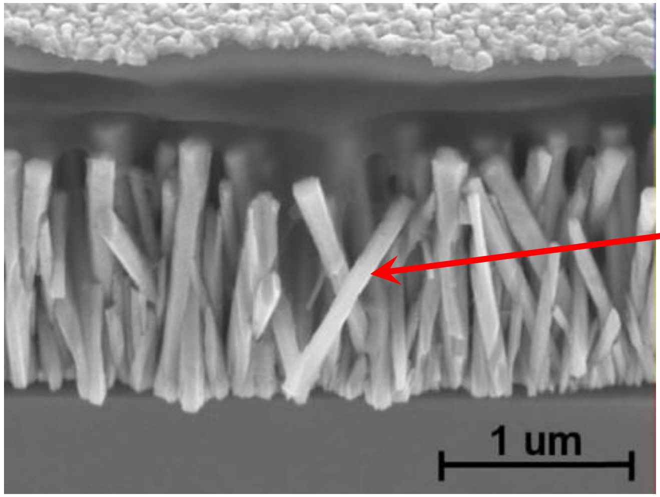
Most used! → PZT

PZT → Lead, ~1000°, ~750°

AlN, ZnO, GaN: Lead free low T (<400°C)

PMN-PT → Lead, ~750°

Nanogenerators Based on piezoelectric nanowires



Nanowires:
- A few µm long
- A few 10-100nm wide

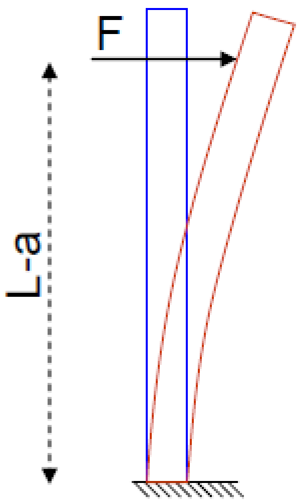
Different names :
- *Nanogenerators*
- *Piezogenerators*
- *Nanocomposites*

Based on different piezo NWs:
- *ZnO, GaN*
- *$BaTiO_3$, $ZnSnO_3$*
- *Lead-free Niobates: $NaNbO_3$…*
- *Lead based: PMN-PT, PZT*

Introduction (6/9)
Why nanowires ?

Rough estimates - analytical modeling

Cylindrical beam, linear, elastic model



Main strain along z

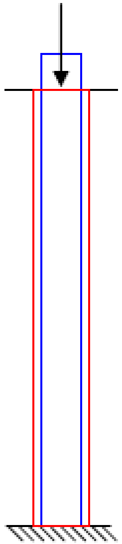
$$\varepsilon_{zz-\max} = \frac{F}{E} \cdot \frac{4}{\pi \cdot R^3} \cdot (L-a)$$

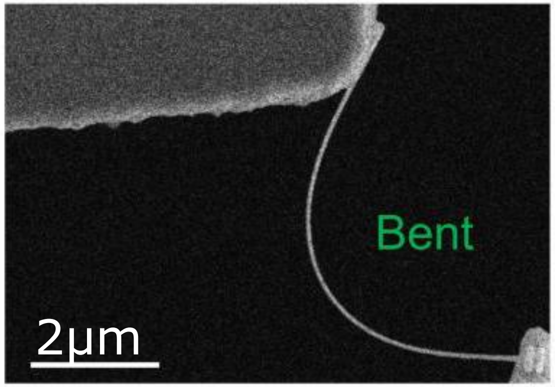
Why nanowires are interesting

Strain along z

$$\varepsilon_{zz} = \frac{F}{E} \cdot \frac{1}{\pi \cdot R^2}$$

$$P = \frac{F}{\pi \cdot R^2}$$

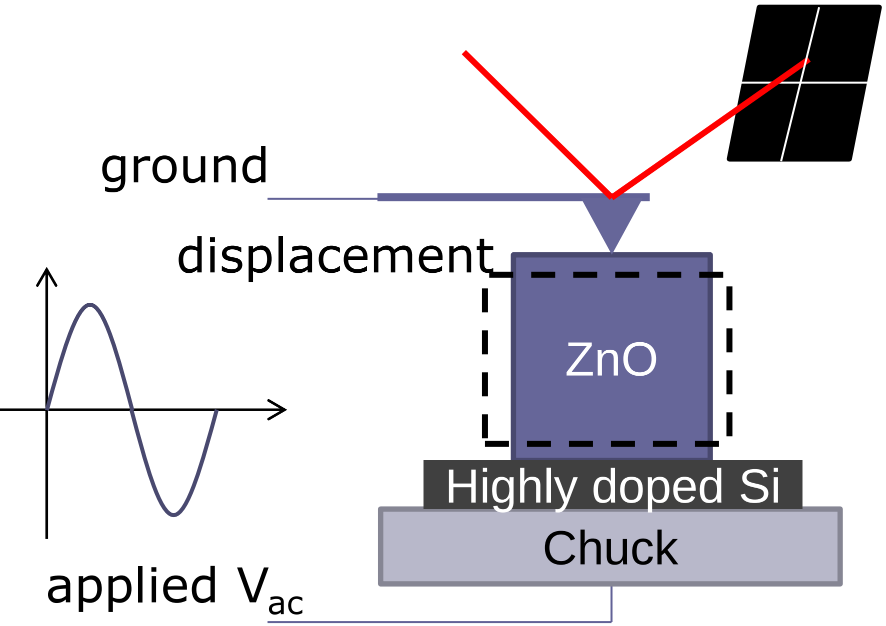




ZnO nanowires, G. Cheng et al., Nature Nanotech. , 2015

More deformation → More voltage or energy

Introduction (7/9)
Why nanowires ?
Experiments - Atomic Force Microscopy



AFM - Piezoelectric Force Microscopy

An AC voltage is applied between an AFM Conductive tip and the bottom electrode or substrate

By the converse piezoelectric effect the meterial will deform vertically.

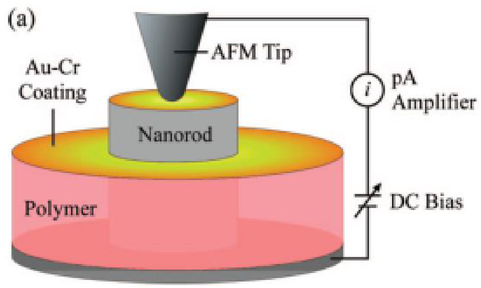
This deformation is measured by the AFM.

Deformation / voltage → Piezoelectric properties

Why nanowires ?

PFM

- Improved piezoelectric properties (PFM) d_{33} **(quantitative)**



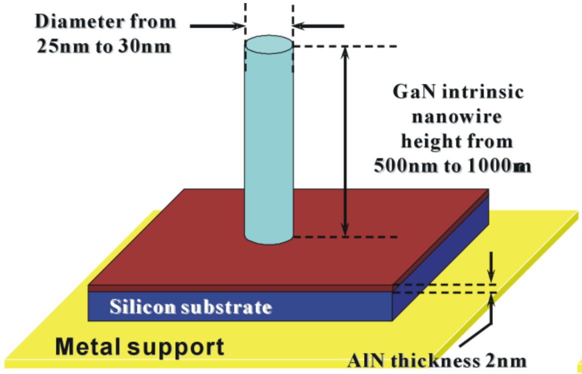
D. Scrymgeour et al., Nano Lett. 8, 2008

Piezoelectric coefficients measured in m/V

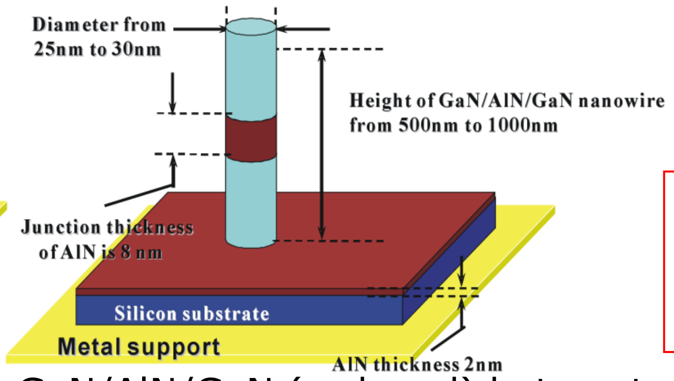
ZnO NWs ~2x better than bulk (300nm wide)

GaN NWs ~7x better than bulk (150nm wide)

- Heterostructures X. Xu, et al., Nanotechnology 22 (2011)



GaN intrinsic NW

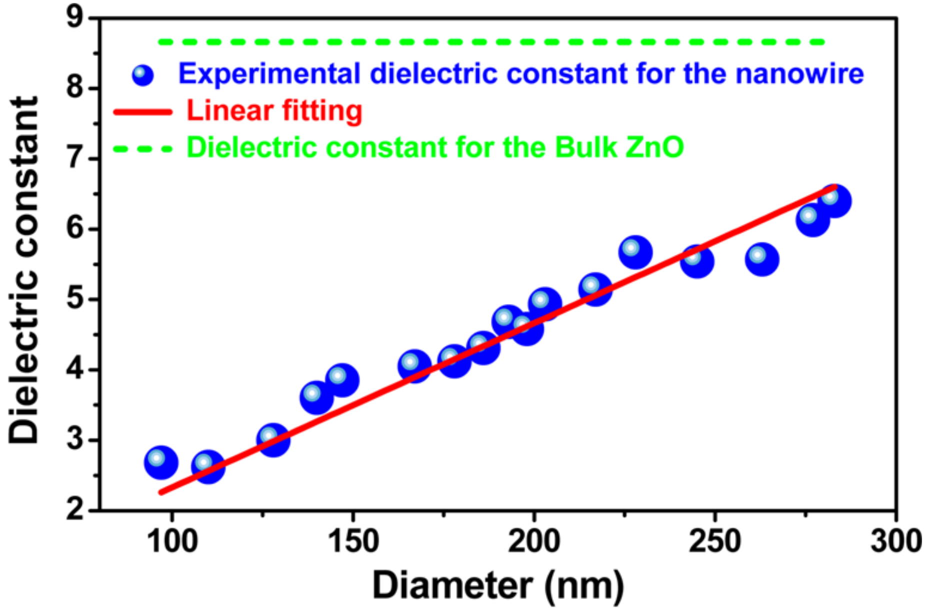


GaN/AlN/GaN (n-doped) heterostructured NW

Heterostructures provide ~9x more potential than Intrinsic counterparts

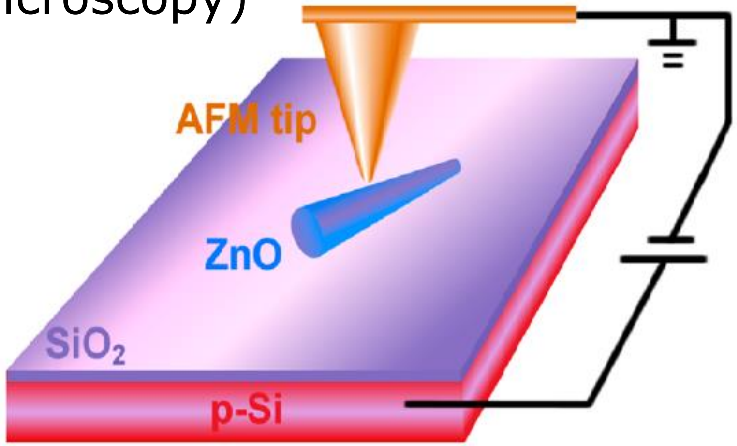
Introduction (9/9)
Why nanowires ?

- Dielectric properties of ZnO Nanowires (Experimental)



Y. Yang et al., Nanoletters 12, 2012

SCM (Scanning Conductance Microscopy)



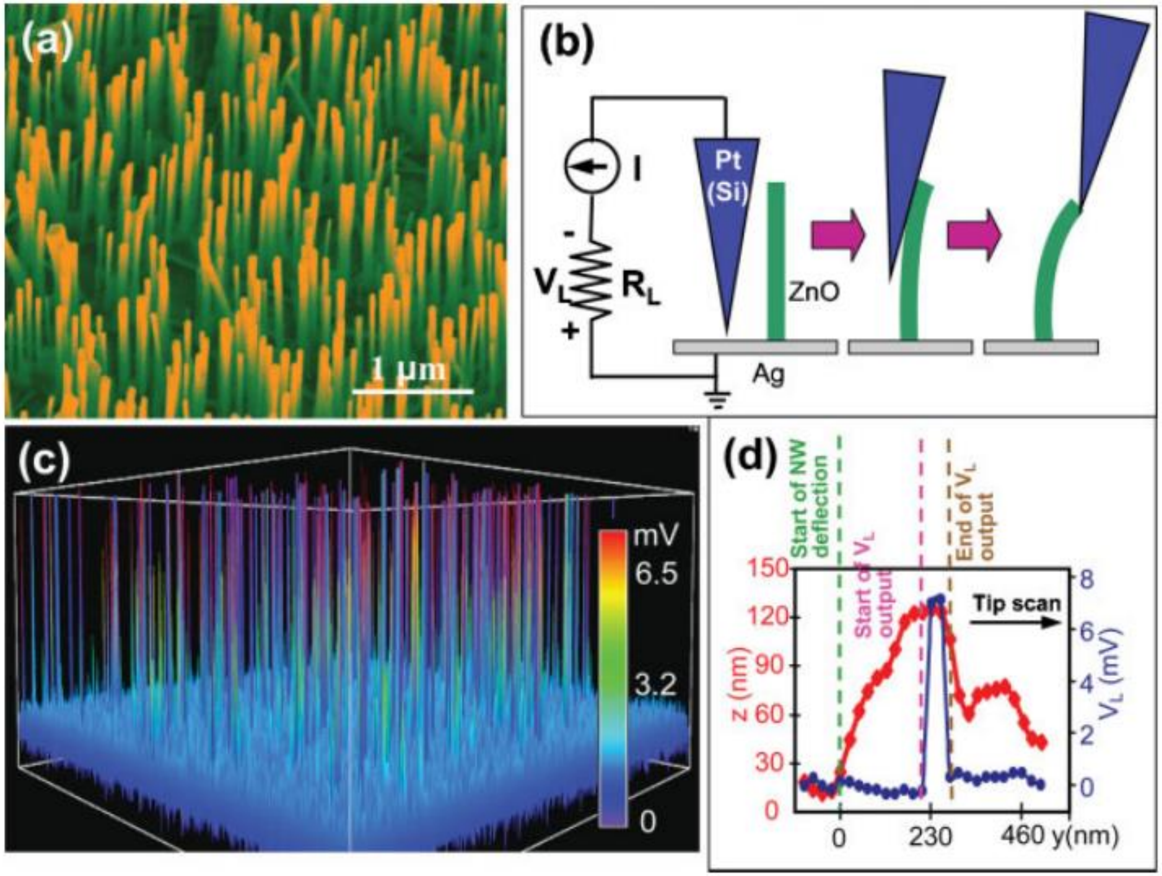
- Energy conversion
  - ✓ Mechanical properties
  - ✓ Piezoelectric properties ↗
  - ✓ Dielectric properties ↘

$$k^2 = \frac{E_c}{W} = E\frac{d_{33}^2}{\varepsilon}$$

Nanogenerators / piezogenerators: experiments

Nanogenerators
Origin and early devices (1/3)

2006

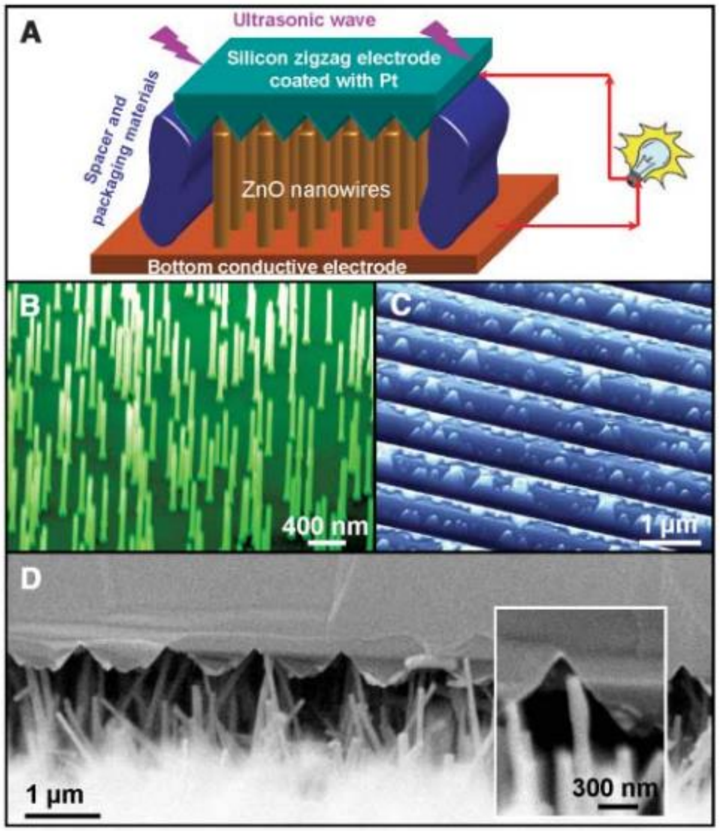


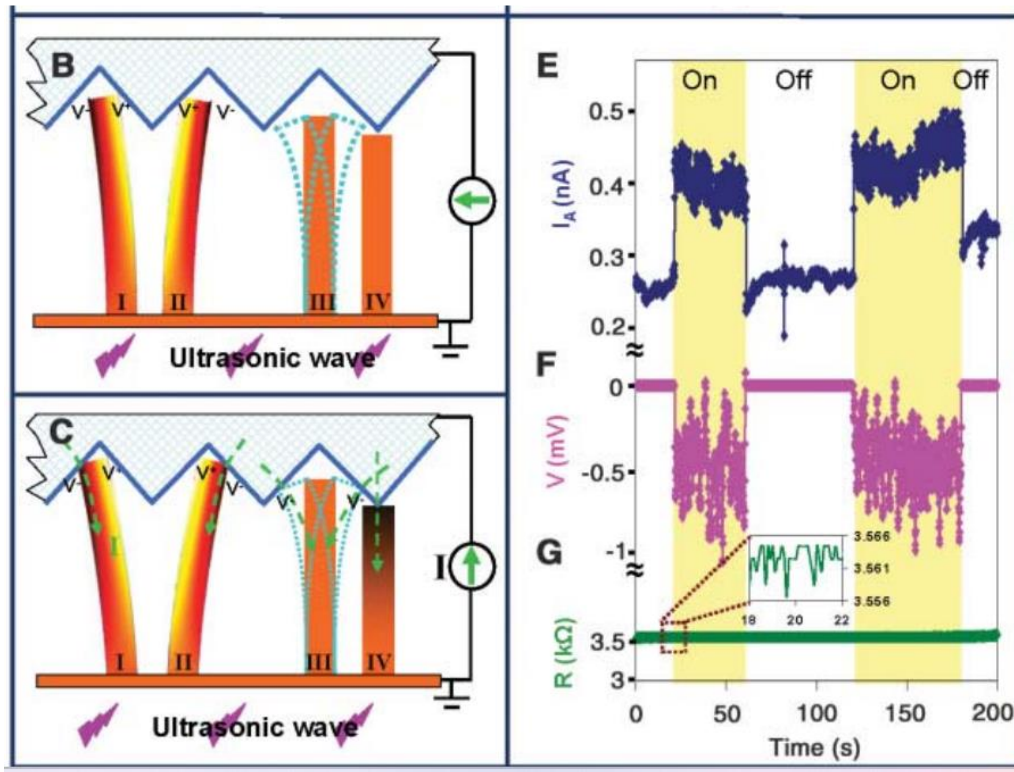
AFM experiments on ZnO NWs

Z. L. Wang, Science, 2006, GeorgiaTech, USA

Nanogenerators
Origin and early devices (2/3)

2007: First devices – based in AFM experiments and Schottky contacts



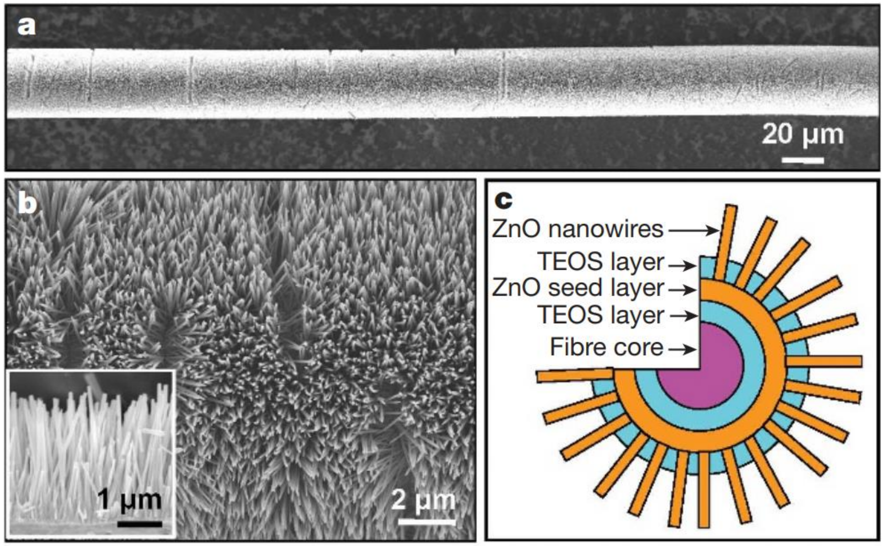


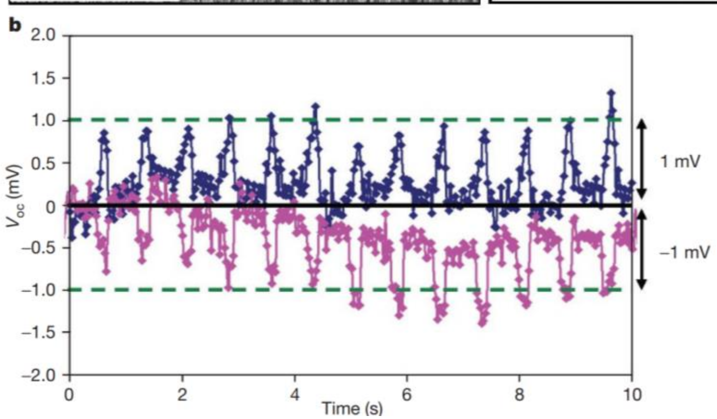
Generation of ~1mV under ultrasonic bath

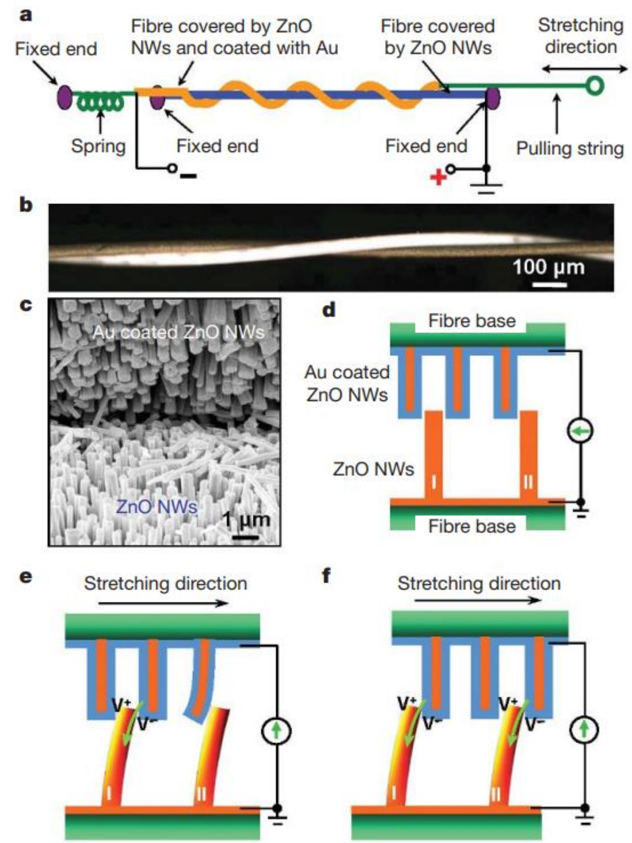
X. Wang et al., Science 316, 2007, GeorgiaTech, USA

Nanogenerators
Origin and early devices (3/3)

2008: Radially integrated ZnO NWs
50-200nm wide, 3.5µm long







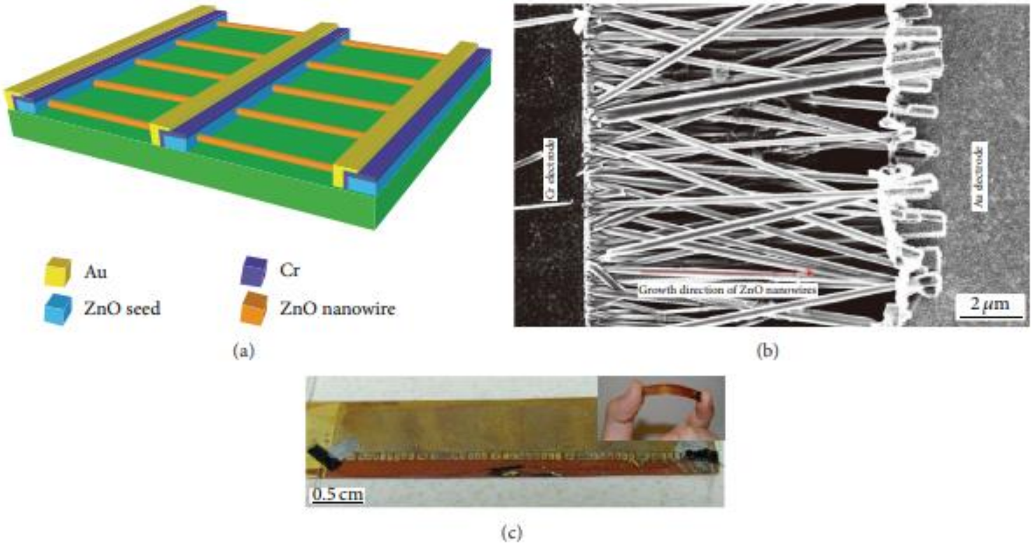
Generation of ~1mV under stretching

Y. Qin et al., Nature letters 451, 2008, GeorgiaTech, USA

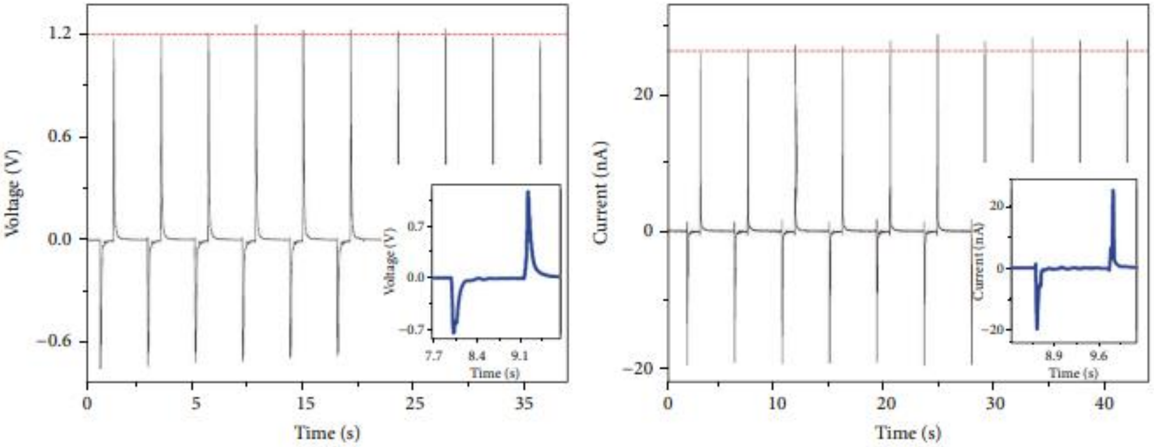
Nanogenerators
Classical structures (1/3)

2010:
Laterally integrated Nanogenerators (LING)

~200nm wide, 5µm long ZnO NWs



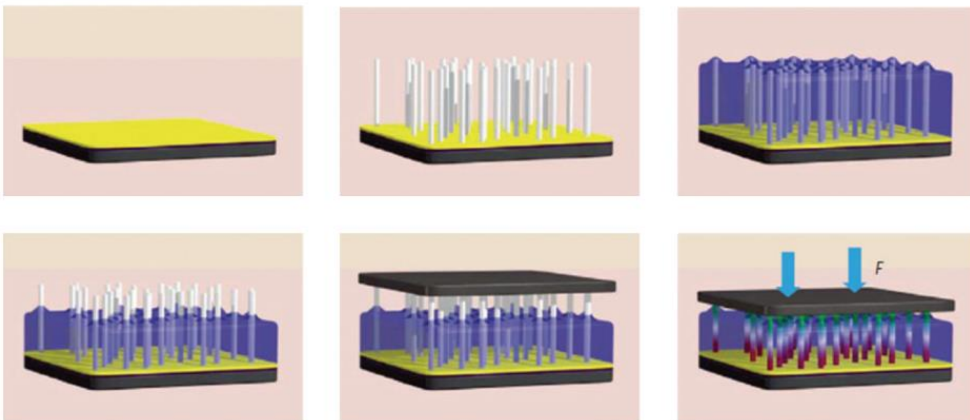
Generation of ~1.2V under bending



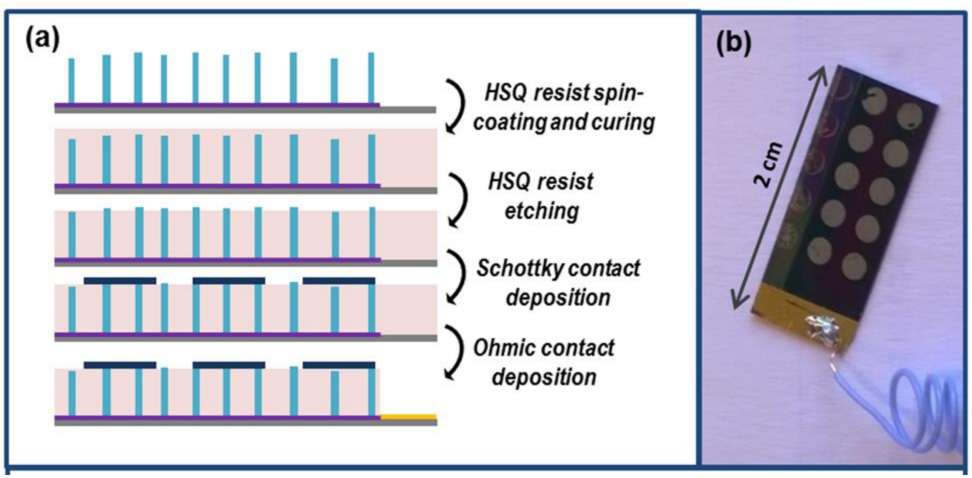
S. Xu et al., Nature Nanotechnology 5, 2010, GeorgiaTech, USA

Nanogenerators
Classical structures (2/3)

2010 : Vertically Integrated Nano Generators (VING)

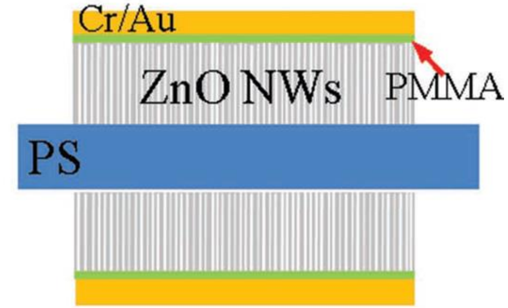


S. Xu et al., Nature Nanotechnology 5, 2010, GeorgiaTech

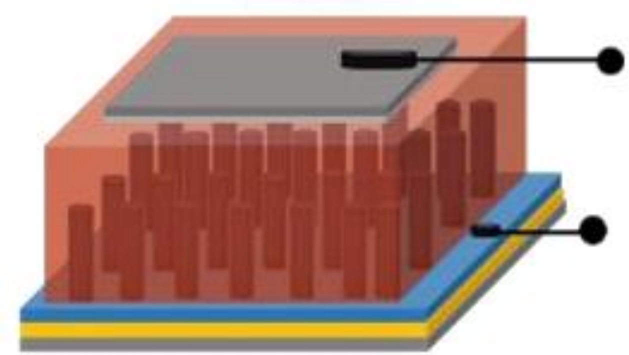


N. Jamond et al., Nanotechnology 27, 2016
C2N, Palaiseau, France, GaN NWs.

2011: Capacitive devices



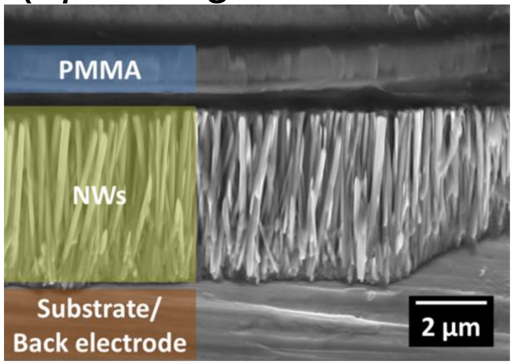
Y. Yang et al., Nanoletters 12, 2012, GeorgiaTech, USA



T. Slimani et al., Nanomaterials, 2021
GREMAN, Tours, France

Nanogenerators
Classical structures (3/3)

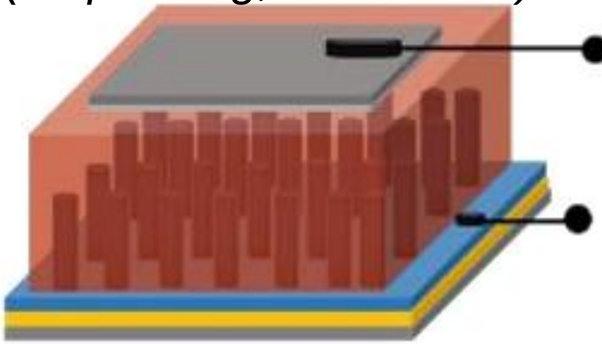
ZnO NWs integrated into Si (3µm long, 200nm wide)



~15nW/cm^2
~0.3V

R. Tao et al., Semicond. Sci. Technol., 2017
IMEP-LaHC, Grenoble, France

ZnO NWs integrated on PDMS (0.7µm long, 70nm wide)



~50nW/cm^2
~7V

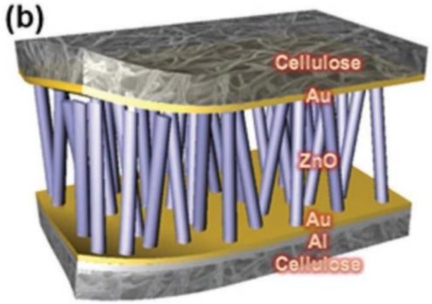
T. Slimani et al., Nanomaterials, 2021
GREMAN, Tours, France

ZnO NWs on Polystyrene (2µm long, 150nm wide)

0.2W/cm^3
20V

Y. Hu et al., Adv. Mat., 2011 GeorgiaTech, USA

ZnO NWs integrated into paper



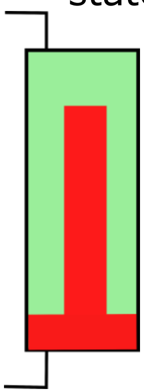
2µA/cm^2
75mV

K-H. Kim et al., Small, 2011
Sungkyunkwan University, Republic of Korea

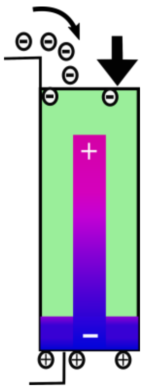
Capacitive structure operation (compression)

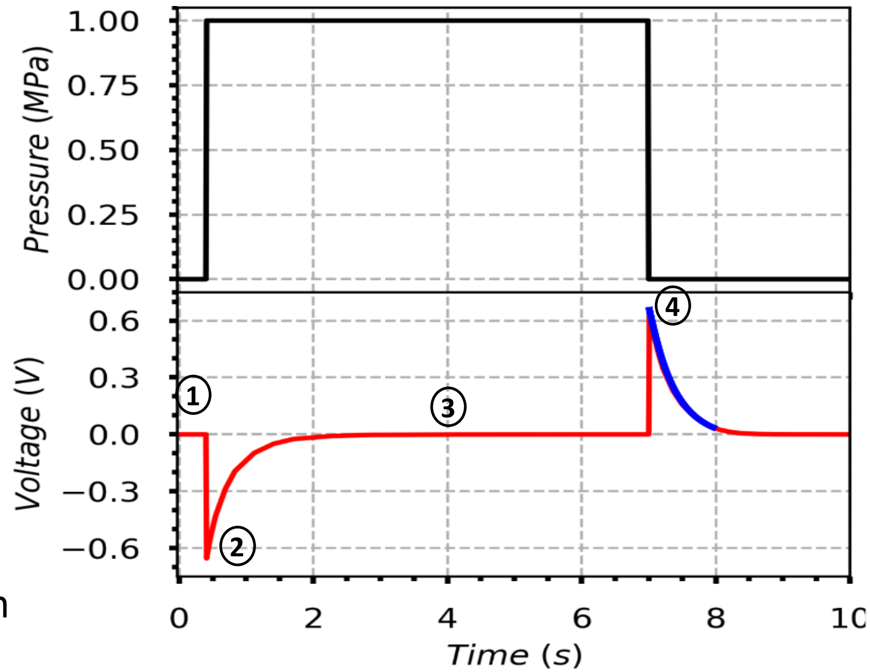
Transient response of mechanical system

① Initial state

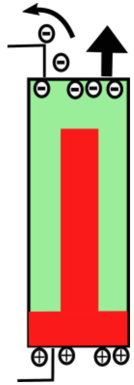


② Press action

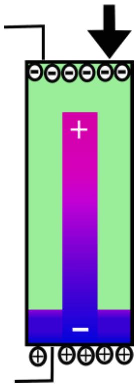




④ Release action

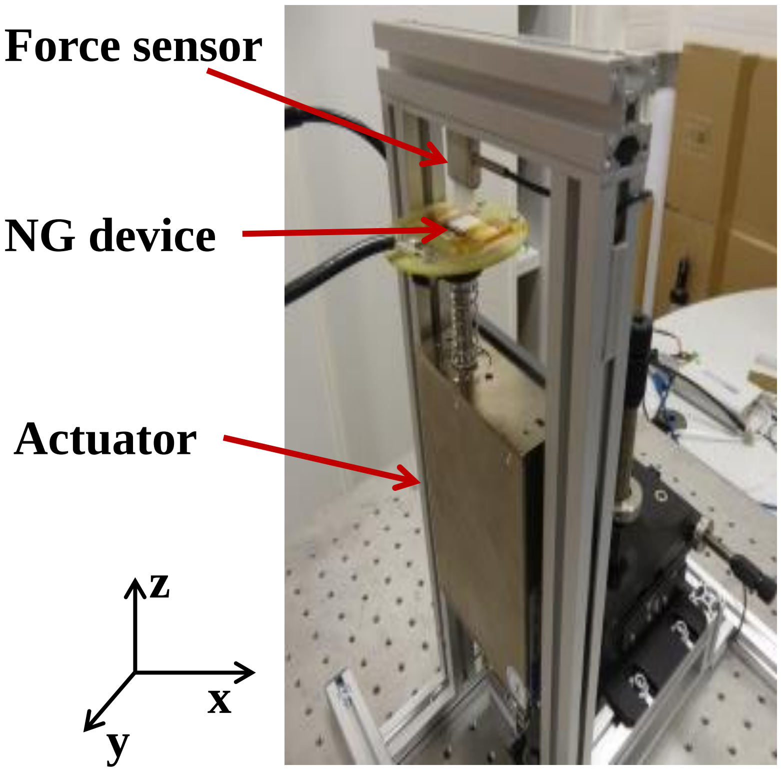


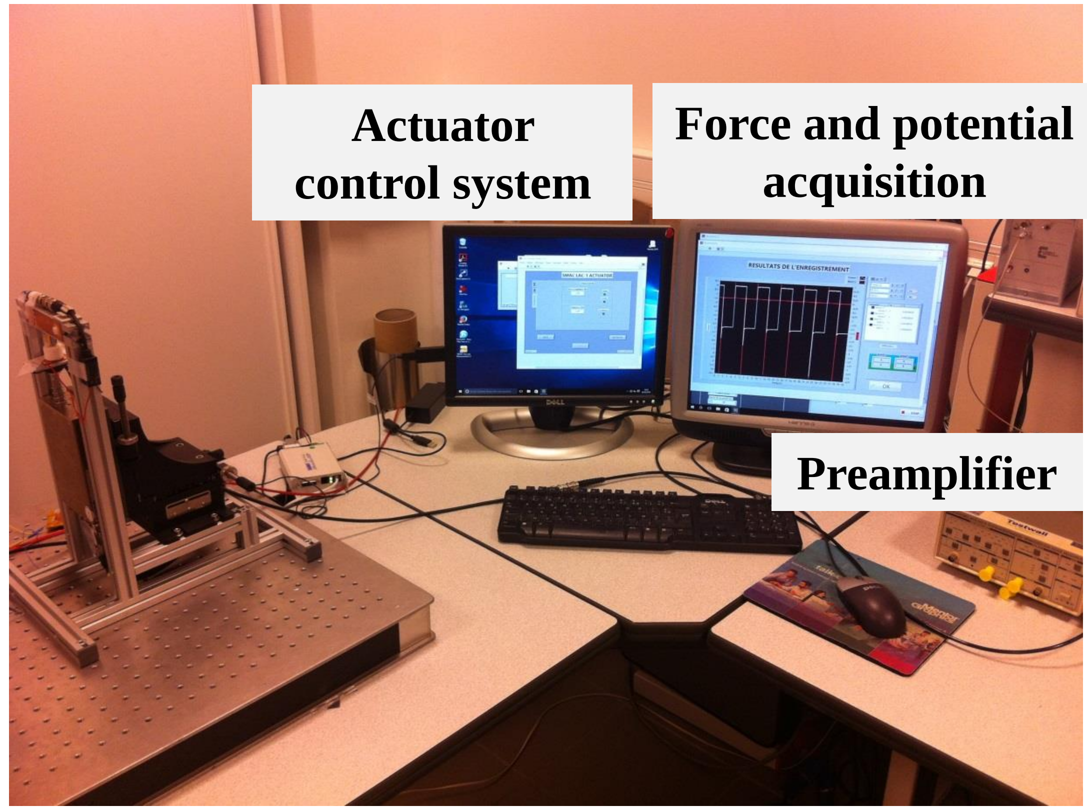
③ Holding pressure



Experiments under compression (1/4)

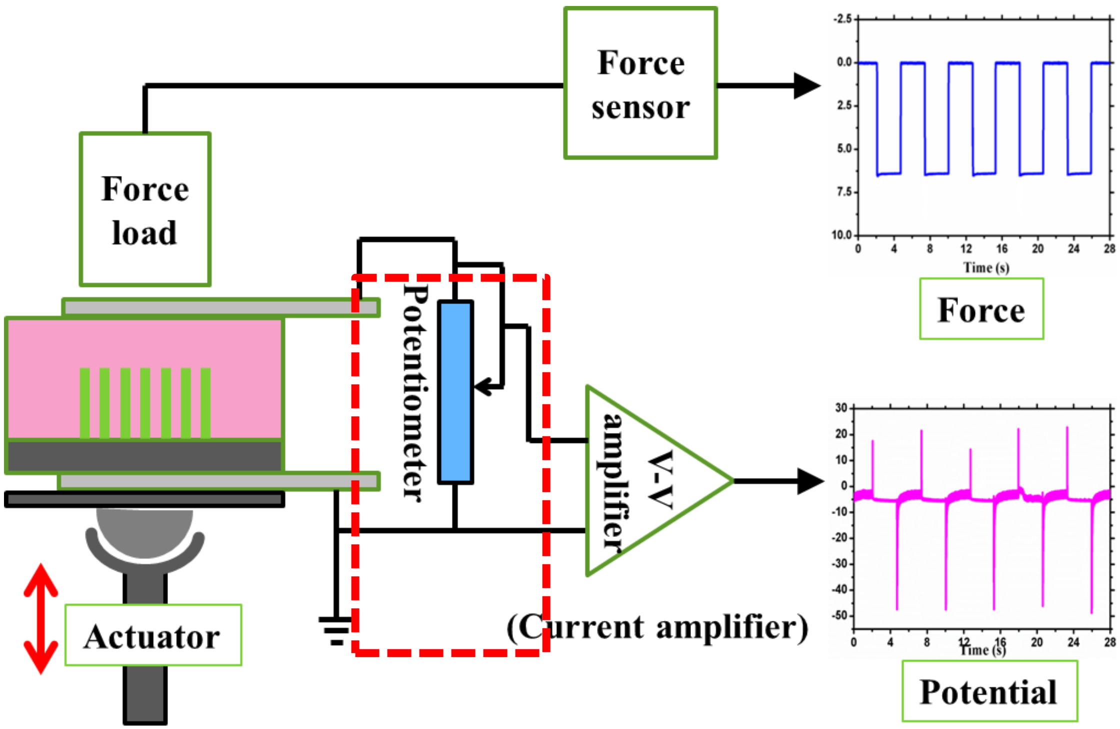
- **Example of a home-made set-up (IMEP-LaHC)**



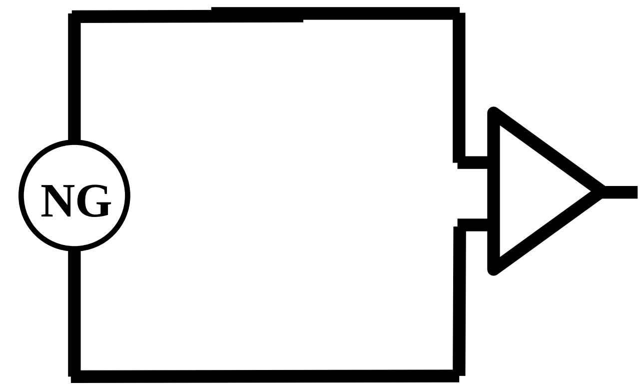


Nanogenerators
Experiments under compression (2/4)

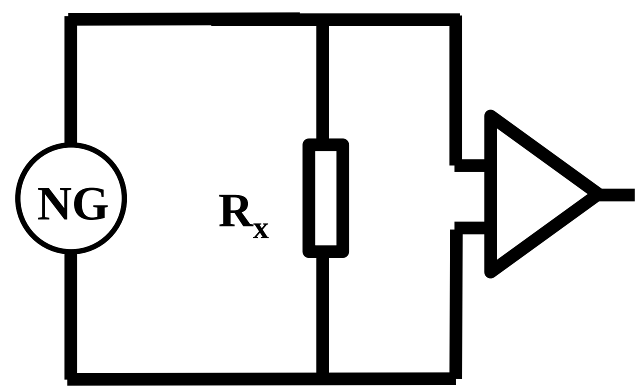
- **Schematics of set-up**



Measurement without load

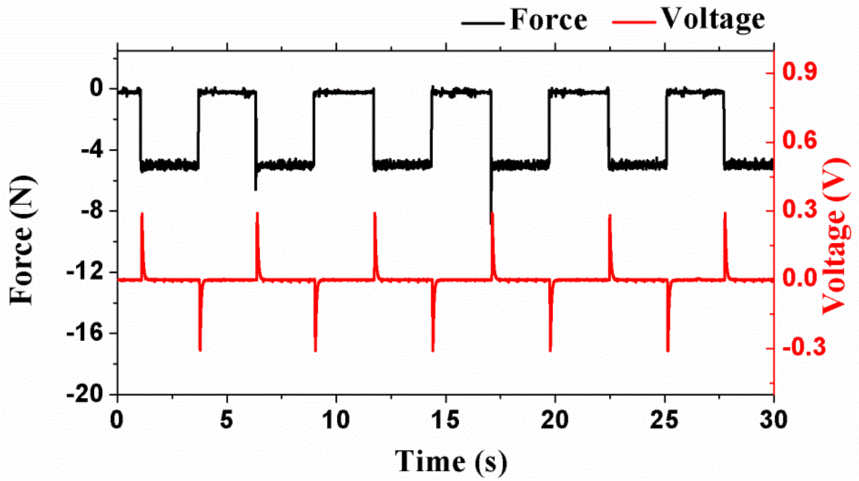


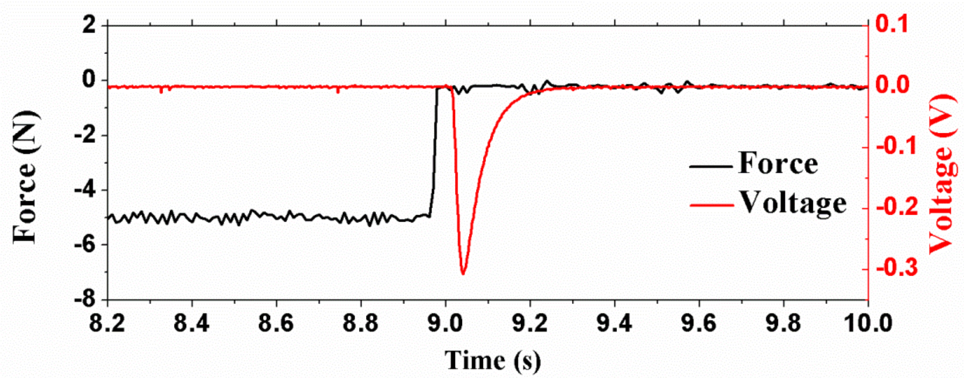
Measurement with load

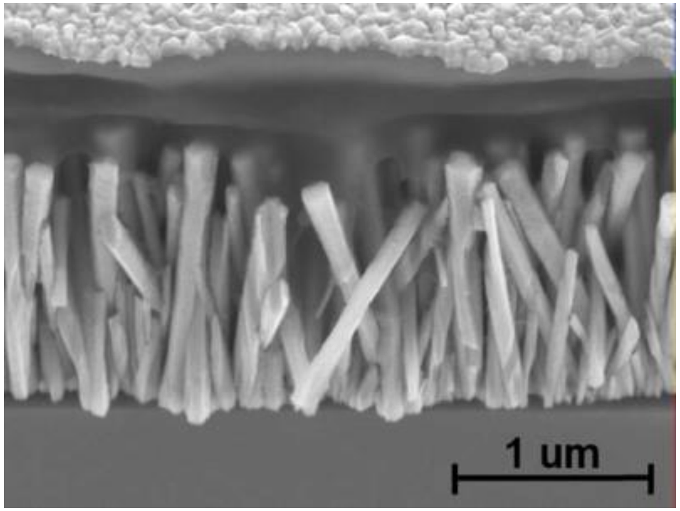


Nanogenerators
Experiments under compression (3/4)

- VING under compression
  - Force: 5 N Frequency: 0.2 Hz







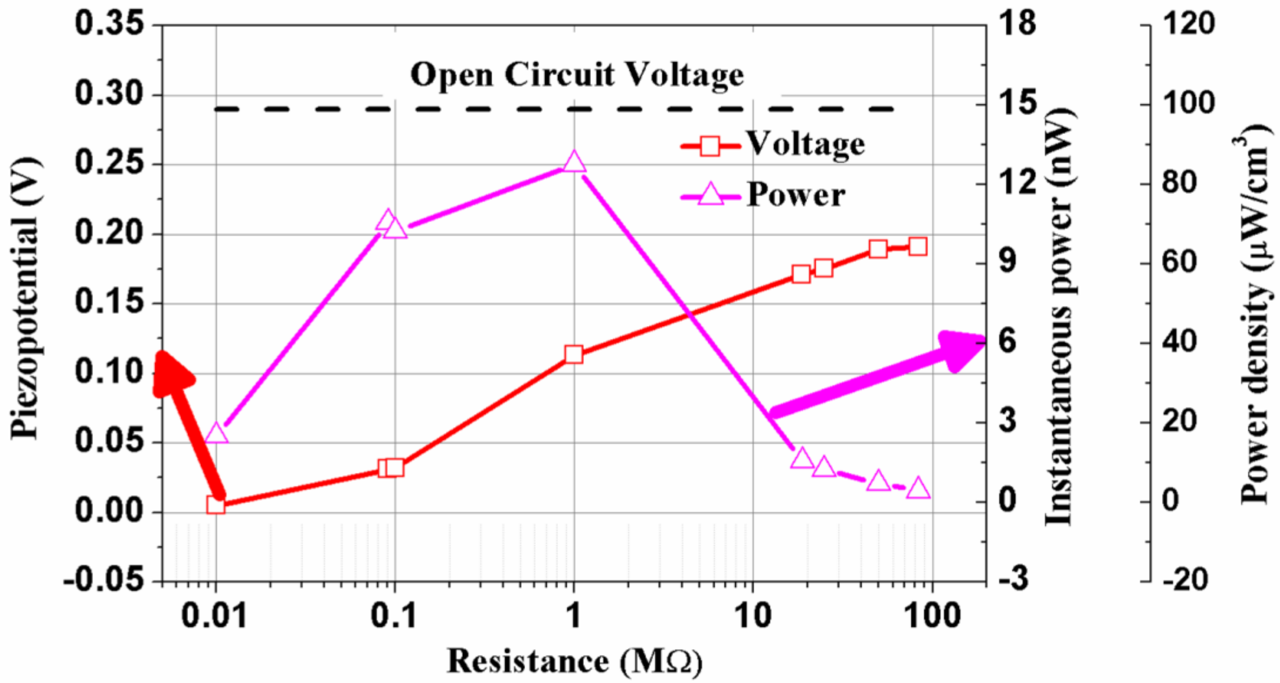
R. Tao et al., Semicond. Sci. Technol., 2017
IMEP-LaHC, Grenoble, France

Open circuit voltage: ~ 0.3V

Experiments under compression (4/4)

Power generated with electric load

- Force: 2 N Frequency: 0.2 Hz



$$P = \frac{V^2}{R}$$

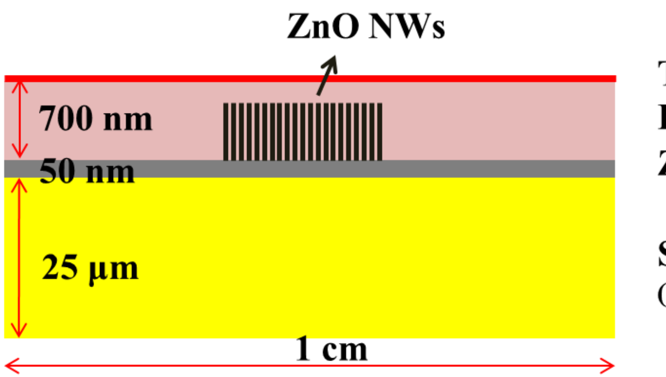
- Maximum power of the NG device: 13 nW (optimum load R=1MΩ)

R. Tao et al., Semicond. Sci. Technol., 2017
IMEP-LaHC, Grenoble, France

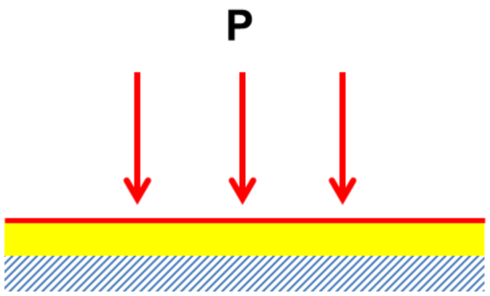
Nanogenerators : Theory

Modeling of piezoelectric nanocomposites
VING: Vertical Integrated NanoGenerators

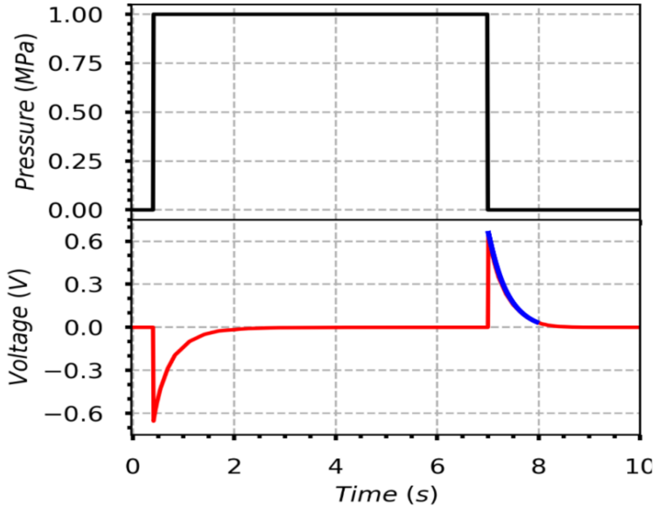
VING sandwiched by two electrodes
(composite material)



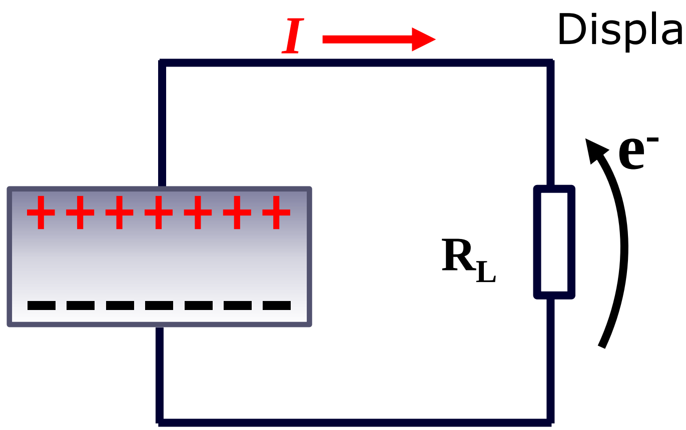
Compression



Transient response



Basic models : Insulating piezoelectric material



Displacement current

Ex: PZT, PVDF

Our models : composite based on ZnO NWs
3D unit cell approach

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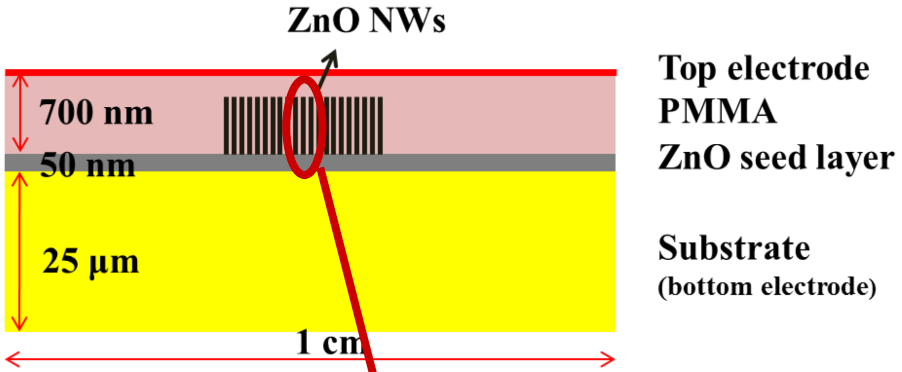
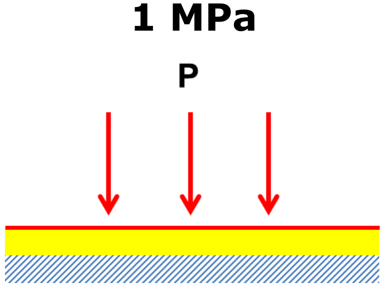
composite sandwiched by two electrodes



Density: $10^{10}\,cm^{-2}$

Working mode

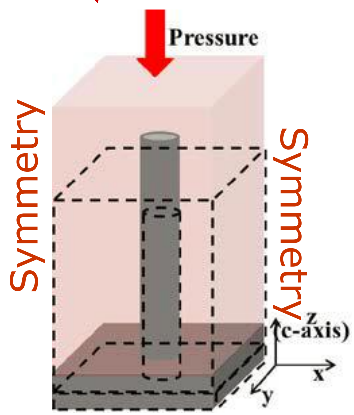
Compression



Mechanical

Linear elasticity
Bulk properties

$d = 50\ nm$
$L = 600\ nm$
$Ratio = d/w$
(density)

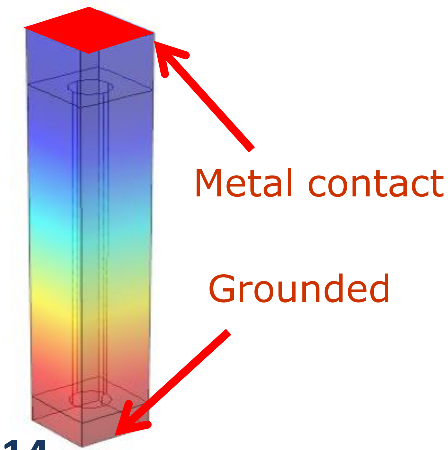


Fixed constraint

Electrical

Intrinsic ZnO (low doping)

No Semi-conducting properties



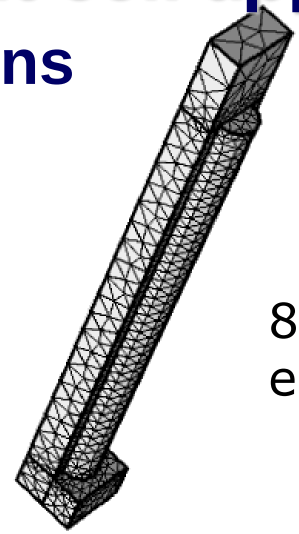
R. Hinchet et al., Adv. Funct. Mater. 2014

Our models : composite based on ZnO NWs 3D unit cell approach

NG cell structure and boundary conditions

Hypothesis :

- *Linear regime (mechanical, piezoelectric)*
- *Bulk properties*
- *No semiconducting properties (dielectric material)*



8k elements

Equations to be solved

Piezoelectric equations :

$$[\sigma] = [c][\varepsilon] - [e]^T[E]$$
$$[D] = [\kappa][E] + [e][\varepsilon]$$

Standard terms

Coupling terms

Poisson equations :

$$-\nabla\sigma = 0$$
$$\nabla D = 0$$

$[c]$: elasticity matrix
$[e]$: piezoelectric coefficient
$[\kappa]$: dielectric constant

$[\sigma]$:stress
$[\varepsilon]$: strain
$[E]$: electric field
$[D]$: electric displacement

Modeling of piezoelectric nanocomposites

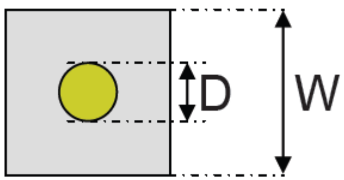
IMEP-LAHC

Parametric study (3/4)

Parameters varied:

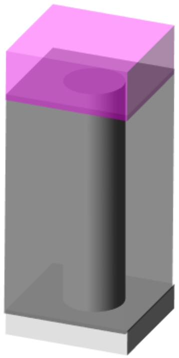
NWs density

D/W (D=50nm, W varies)

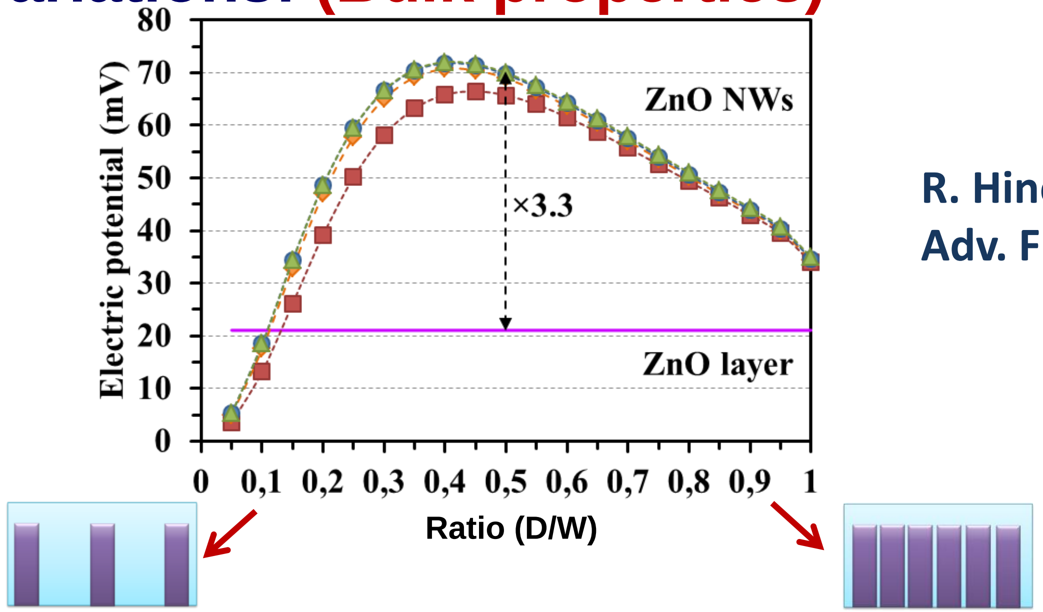


Top insulating materials

Material	PMMA	SiO_2	Si_3N_4	Al_2O_3
Young modulus (GPa)	3	70	250	400
Dielectric constant	3.9	4.2	9.7	5.7



Potential variations: (Bulk properties)

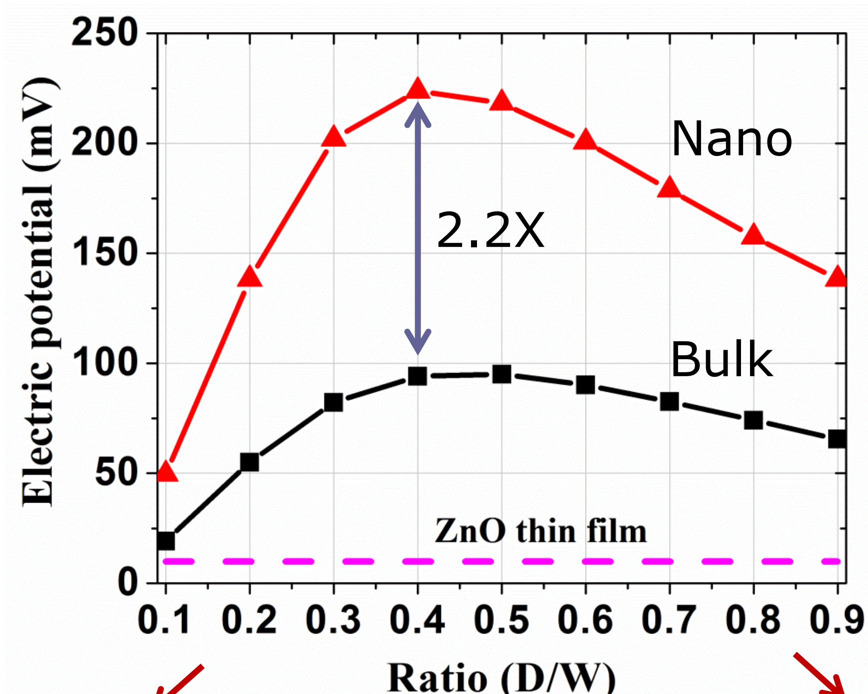


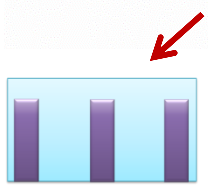
R. Hinchet et al.,
Adv. Funct. Mater. 2013

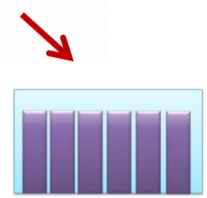
Modeling of piezoelectric nanocomposites

Parametric study (3/4)

- **Potential variations and energy: (nano properties)**







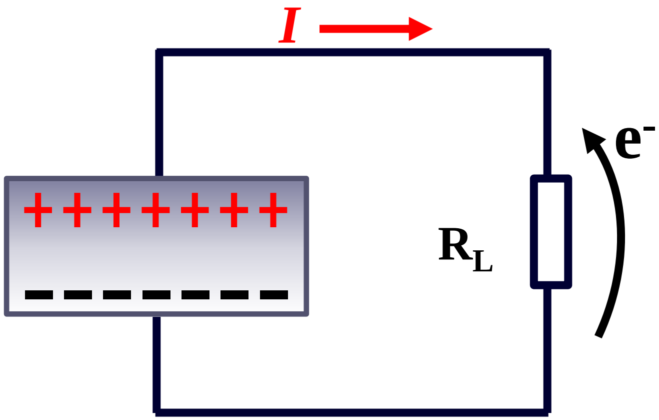
Nano properties:
Piezo: x2
Dielectric: /5

R. Tao et al., Future Trends on Microelectronics 2016

Screening effects

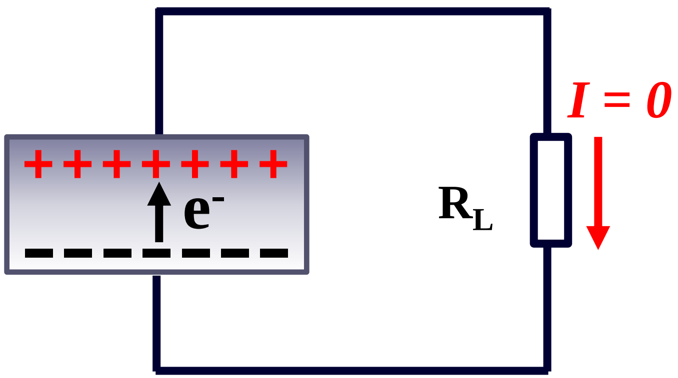
ZnO as semiconductor: rarely intrinsic (very low doping)

Insulating piezoelectric material



With free carriers

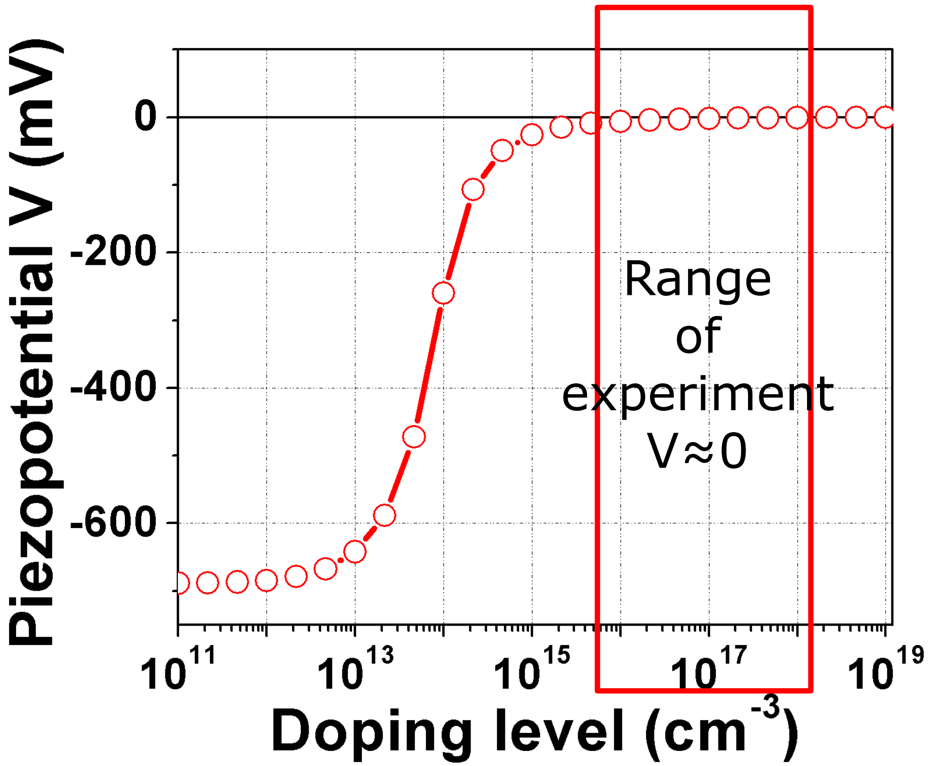
Semiconductor (GaN, ZnO…)



- Unintentionally doped in the growth (~10^{17} cm^{-3})

$$\nabla D = -\rho$$

$$\rho = q(n - p + N_A^- - N_D^+)$$

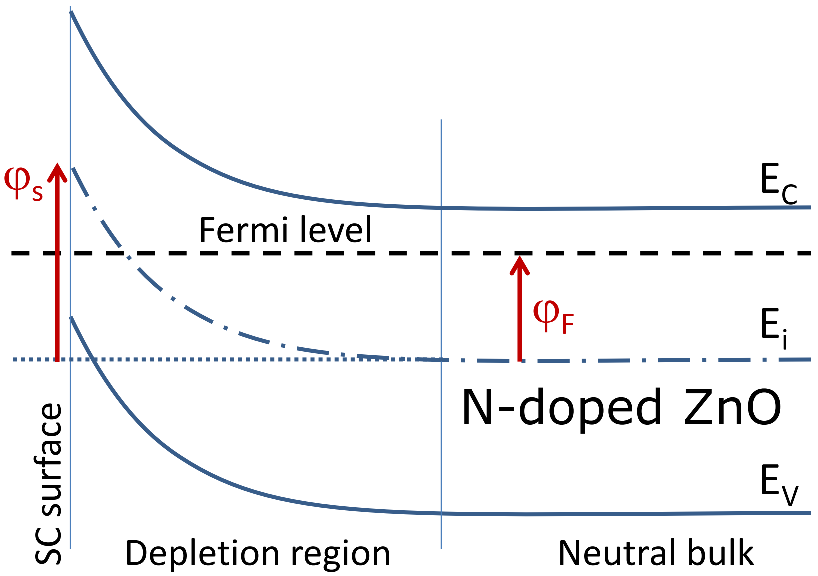


- Close to **0V** at doping **10^{15} cm^{-3}**

Origin of Surface Traps and their consequences

Surface Traps : In ZnO, presence of O_2 molecules at the surface (capture free electrons), surrounding material…

SFLP:
Surface Fermi Level Pinning



- Hypothesis : $N_{it} \sim 5 \times 10^{11}$ cm^{-2}eV^{-1} (medium range)

$$Q_{dep} = \sqrt{2\, q\, \varepsilon\, N_D \varphi_s} \longrightarrow Q_{dep} + Q_s = 0$$

Boundary condition :

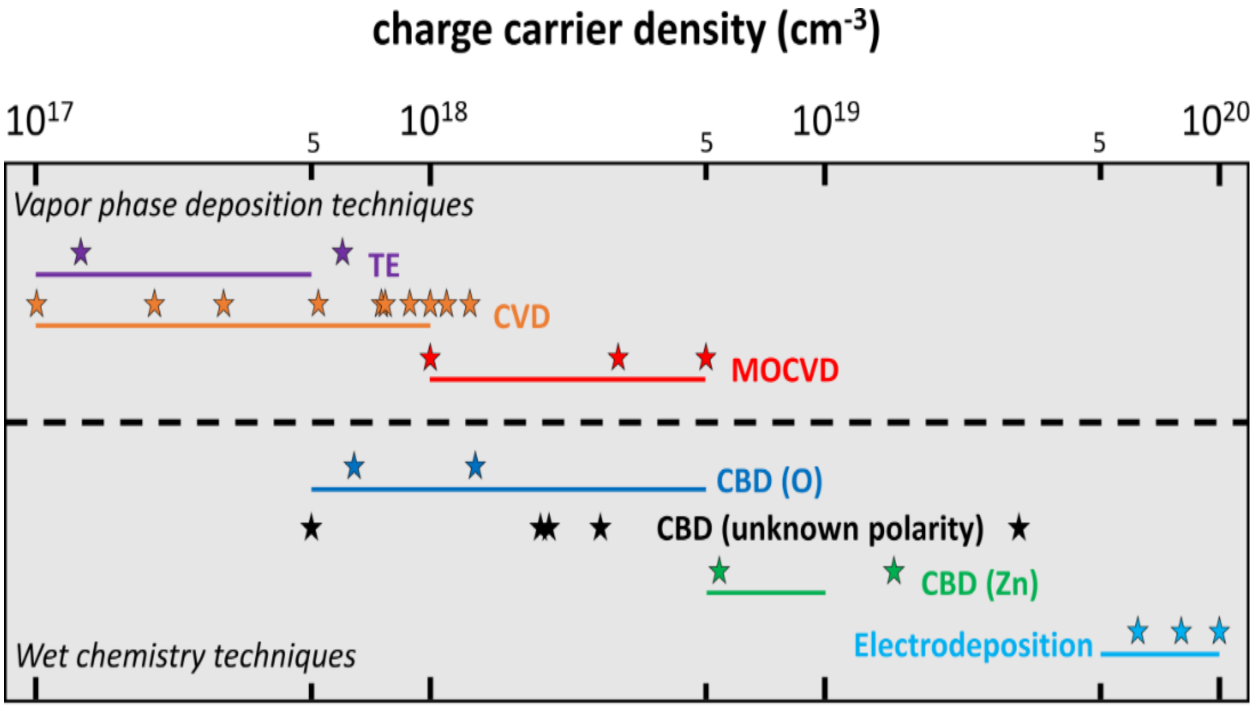
$$\vec{n} \cdot \kappa \vec{\nabla} V = Q_s$$

R. Tao et al., Adv. Electron. Mat. 2018

Influence of Surface Fermi Level Pinning (1/3)

Semiconducting parameters from experiments

Dr. Vincent CONSONNI



$N_{it} = 10^{12}\ eV^{-1}cm^{-2}$

$N_{it} = 10^{13}\ eV^{-1}cm^{-2}$

- Different growth techniques lead to different level of doping and surface states

A. Lopez et al., Nanomaterials 2021

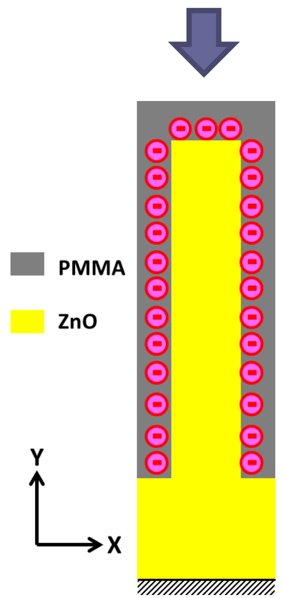
Influence of Surface Fermi Level Pinning (2/3)

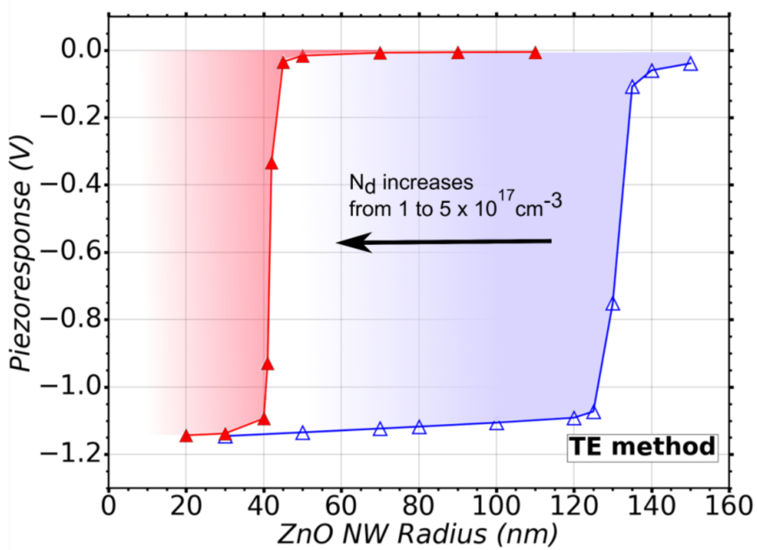
IMEP-LAHC

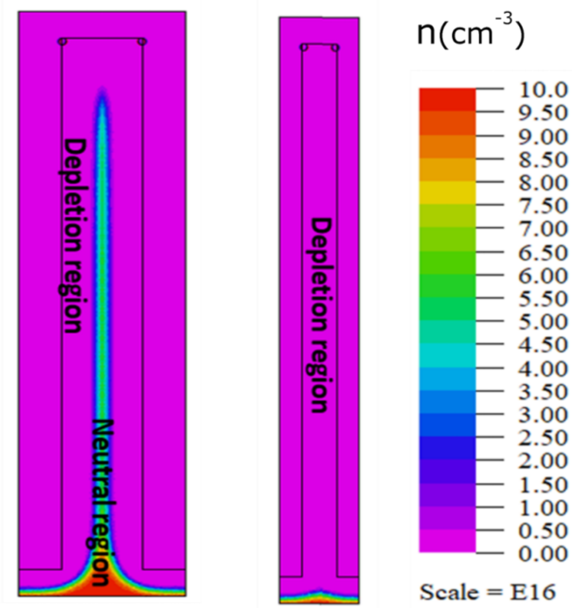
Effect of NW growth method: radius, doping, surface traps

P = 1MPa L= 5µm

Compression







Thermal Evaporation (TE):

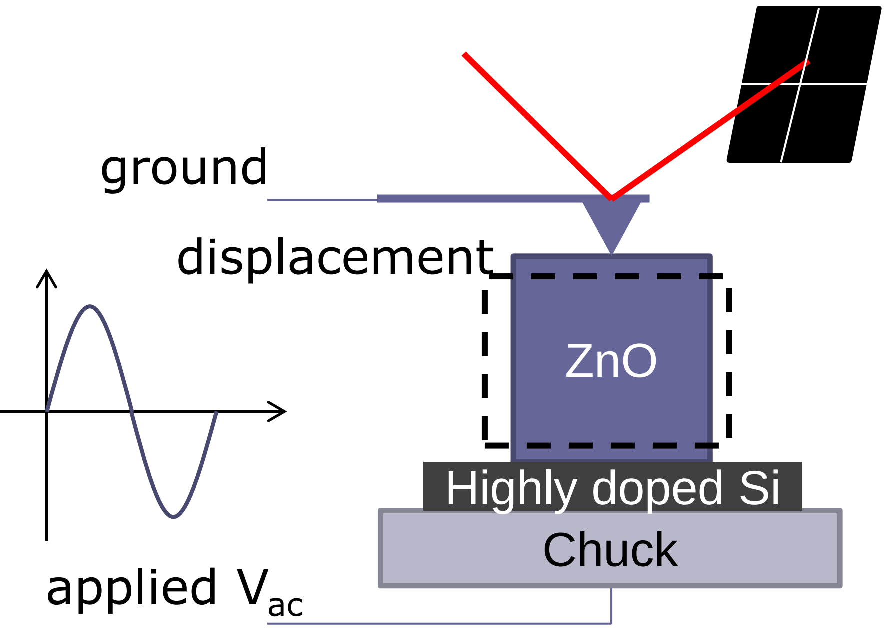
- Doping (N_D): Range $10^{17} – 5×10^{17}$ cm$^{–3}$
- Surface trap density (N_{it}): About 10^{12} eV$^{–1}$ cm$^{–2}$

- Existence of a critical radius leading to fully depletion (optimal performance)
- Dependance on doping and surface trap density
- Guidelines for performance optimization

A. Lopez et al., Nanomaterials 2021

Individual NWs: Theory and experiments using AFM

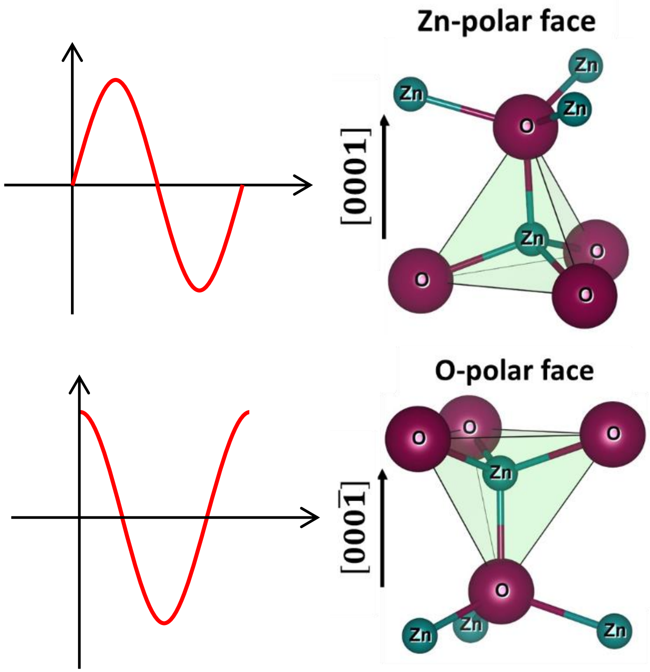
AFM - Piezoelectric Force Microscopy
ZnO NWs vs thin film



An AC voltage is applied between an AFM Conductive tip and the bottom electrode or substrate

By the converse piezoelectric effect the meterial will deform vertically.

This deformation is measured by the AFM.

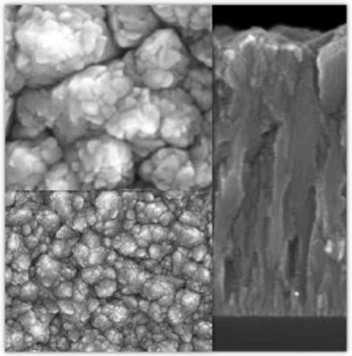


Deformation / voltage → Piezoelectric properties

Phase between signals → c-axis orientation

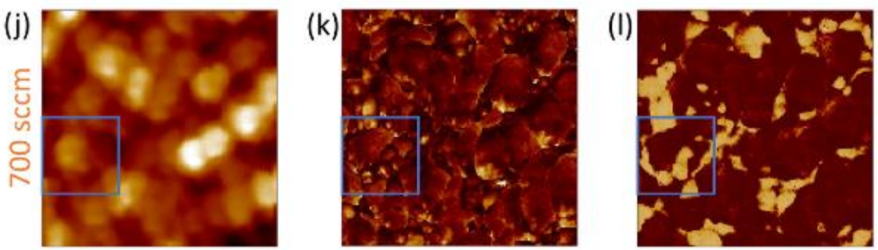
AFM - Piezoelectric Force Microscopy
ZnO NWs vs thin film

Thin films (MOCVD)



900nm thick

Conditions:
O_2 700sccm
DEZn 0.5g/min
T = 500°C



Topography Amplitude Phase

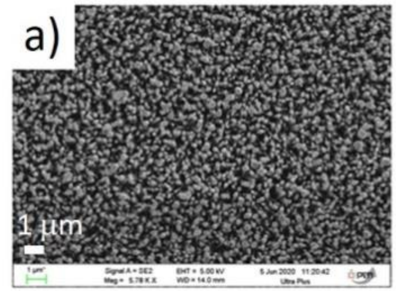
d_{33}^{eff}~1.6pm/V

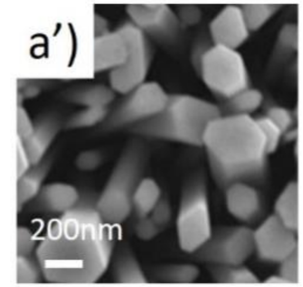
Zn and O polarity

Q. Ch. Bui et al., Mater. Adv. 2021

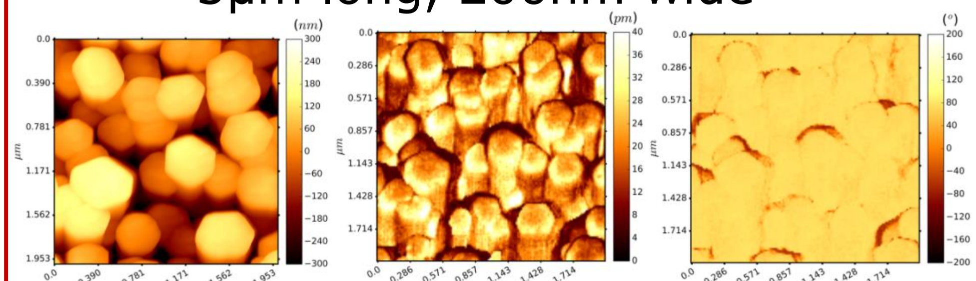
Overall, better performance from NWs vs. Thin films

ZnO NWs (CBD and MOCVD)





3µm long, 200nm wide



Topography Amplitude Phase

d_{33}^{eff}~4.6pm/V Zn polarity

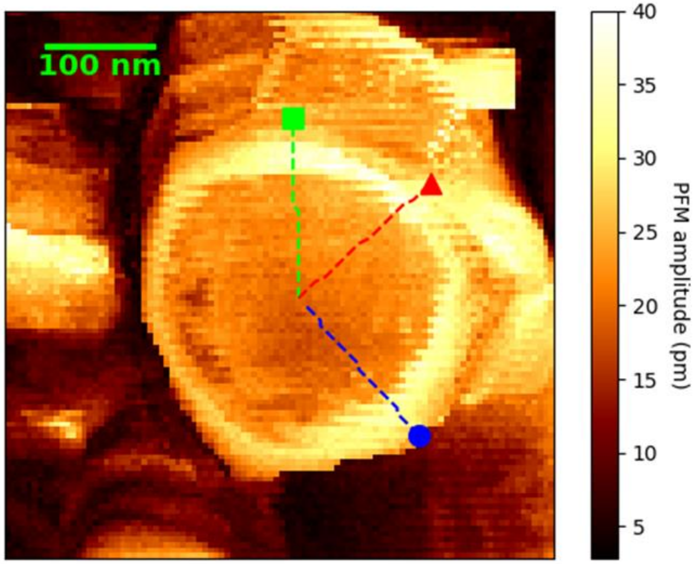
A. Lopez et al., Nanomaterials 2021

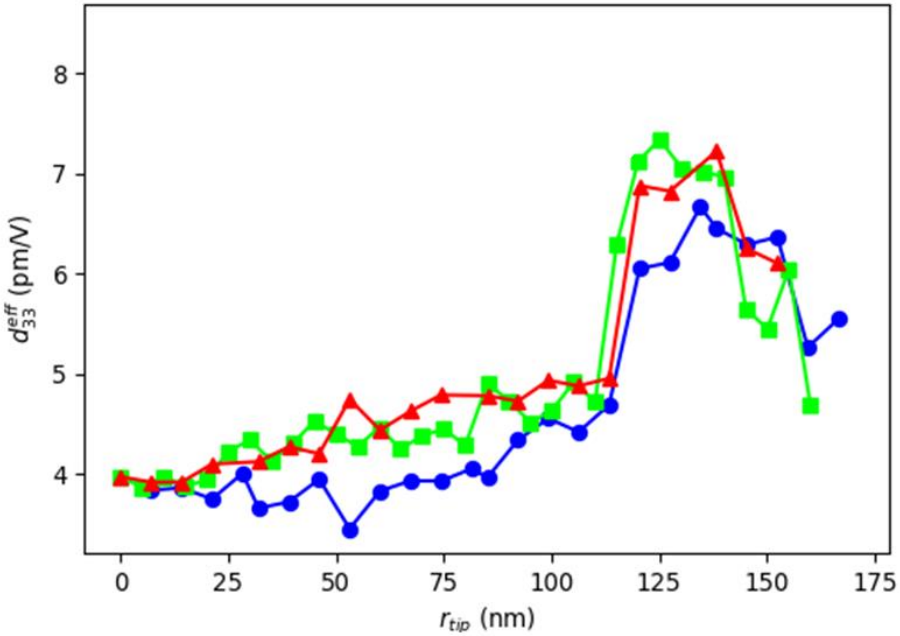
d_{33}^{eff}~4.4pm/V and Zn polarity
1µm long, 60nm wide NW (MOCVD)

Q. Ch. Bui et al., Appl. Mater. Interfaces 2020

AFM - Piezoelectric Force Microscopy
Piezoresponse distribution at the NW surface

ZnO NWs (CBD)

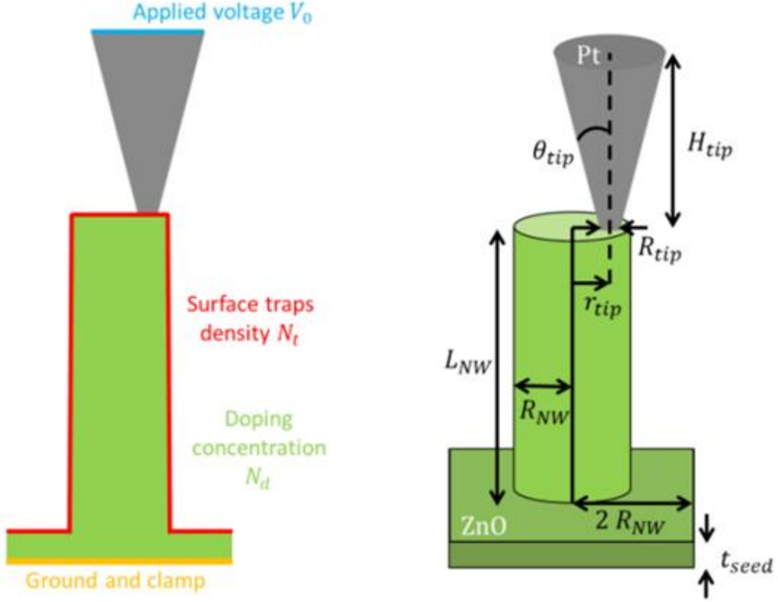


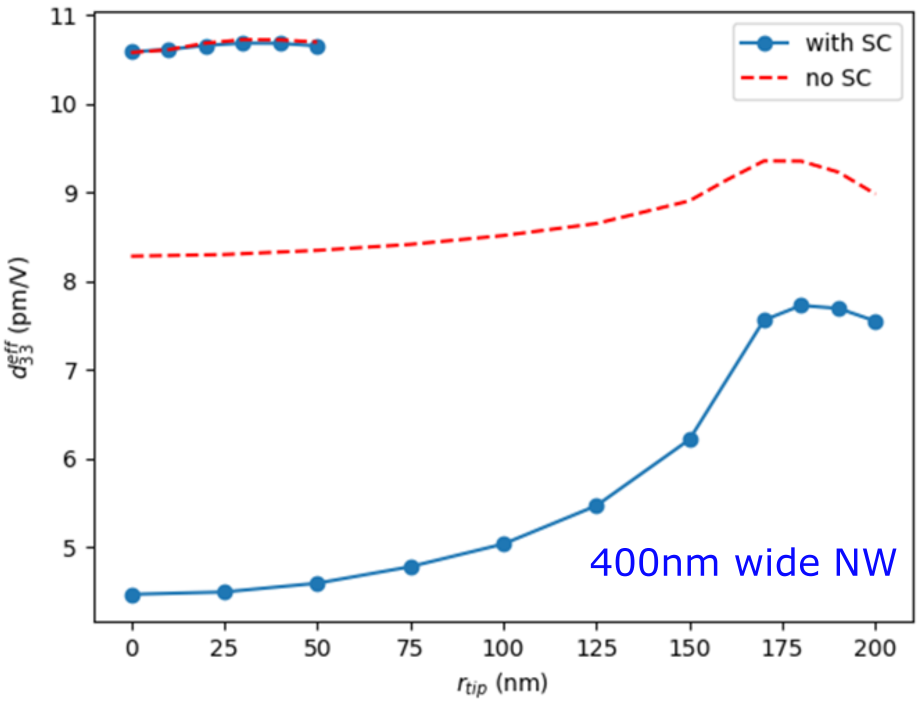


- Piezoresponse increases as the AFM tip approaches the NW border
- Can this effect be explained by simulations?

T. Jalabert et al., Smart Materials for Opto-Electronic Applications, SPIE 2023

AFM - Piezoelectric Force Microscopy
piezoresponse distribution at the NW surface





Simulation parameters (CBD):

$N_{it}=10^{13}\ eV^{-1}.cm^{-2}$
$N_d=10^{17}\ cm^{-3}$

- 3D models including semiconducting properties
- Improvement compared to previous 2D models
- Piezoreponse explained by semiconducting properties (surface traps)

T. Jalabert et al., SPIE 2023

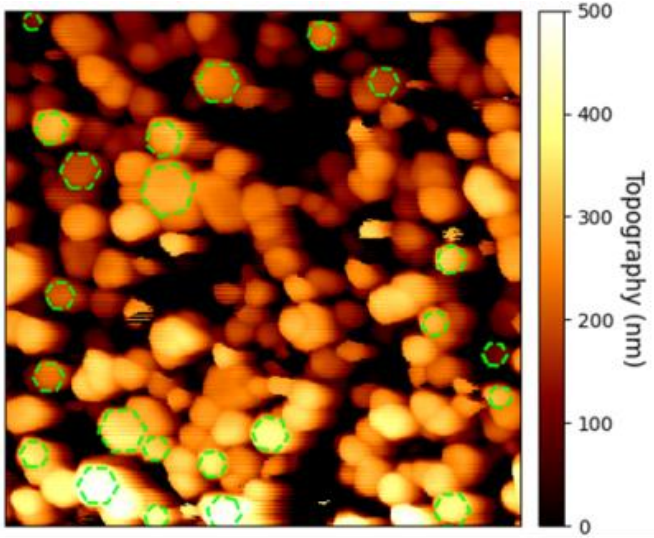
IMEP-LAHC

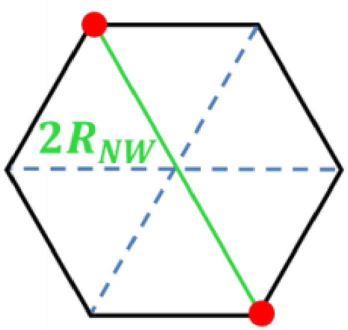
Tyndall National Institute

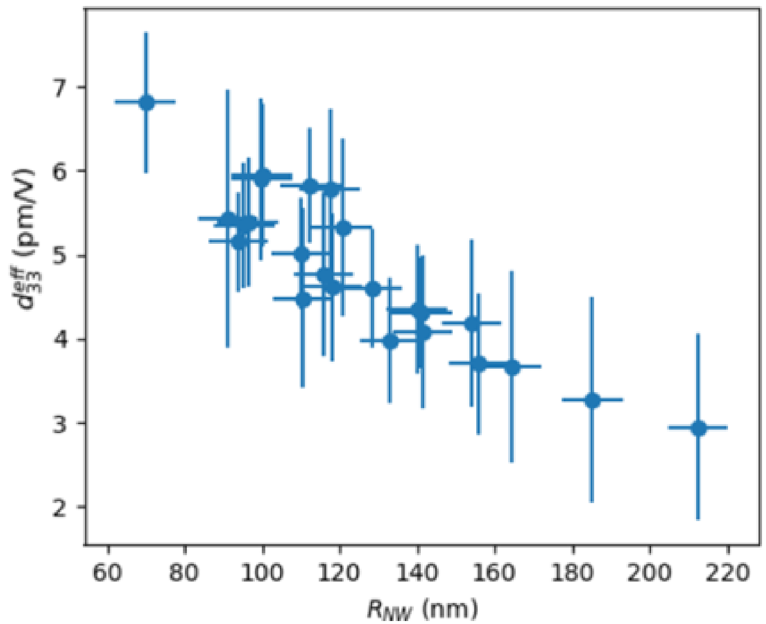
AFM - Piezoelectric Force Microscopy

Effect of ZnO NWs radius Experiments

ZnO NWs (CBD)







- Clear trend in function of the NW radius

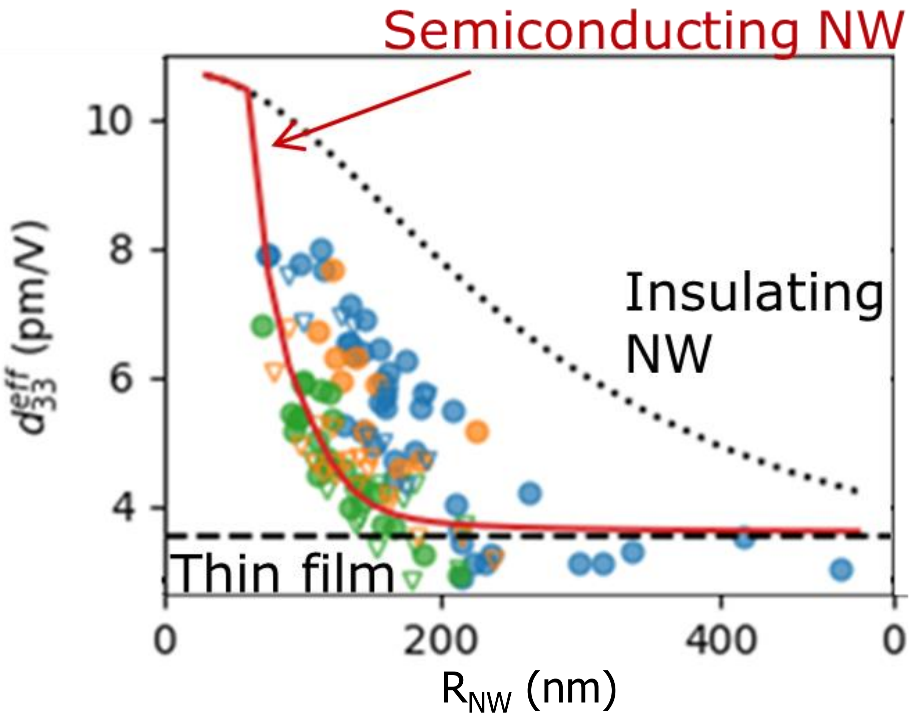
T. Jalabert et al., Nanotechnology 2023

IMEP-LAHC

Tyndall National Institute

AFM - Piezoelectric Force Microscopy
Effect of ZnO NWs radius
Experiments vs. simulations

Seed layer deposition conditions (Evaporation)



Simulation parameters (CBD):

$N_{it}=10^{13}$ $eV^{-1}.cm^{-2}$
$N_d=10^{17}$ cm^{-3}

Challenge:
- Mesure doping, surface traps
- Validate the models

T. Jalabert et al., Nanotechnology 2023

IMEP-LAHC

Conclusions

- **Interest of piezoelectric semiconducting NWs in energy conversion applications: flexibility, sensitivity, enhanced properties**

- **Nanocomposites : easy to fabricate and integrate in multiple substrates**

- **Surface traps could explain the high performance reported in experiments of piezo nanocomposites and PFM (NWs vs. thin films)**

Conclusions

- **Simulations provide important optimization guidelines :**
  - Nanocomposite performance depends on the NWs growth method, length and radius
  - Reduction of doping, control of surface traps density
  - It is better to use long and thin NWs

- **Piezoelectric composite based on semiconducting NWs could outperform piezo thin films**

Thank you for your attention…

Acknowledgements:

- **Colleagues:** L. Montès, M. Mouis, A. Cresti, G. Ghibaudo
- **Students/post-docs:** R. Hinchet, R. Tao, A. Lopez, Q. C. Bui, M. Parmar, M. Pusty, T. Jalabert
- **Technical staff:** X. Mescot, M. Gri, A. Bouchard
- **Clean Room staff:** PTA/CIME
- **Collaborators:** Prof. Z. L. Wang (GeorgiaTech/BINN), R. Songmuang (I. Néel), E. Paulliac-Vaujour (CEA-Leti), V. Consonni (LMGP), B. Salem (LTM), N. Cordero (Tyndall)
- **Funding:**

National French funding : SCENIC - ANR-20-CE09-0005
LATINO - ANR-21-CE50-0026

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 863227.