Characterization and modelling of piezoelectric semiconducting nanowires and transducers

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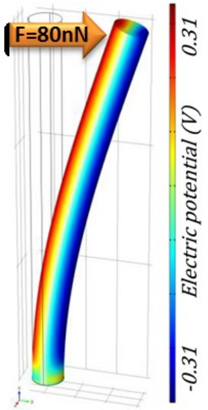
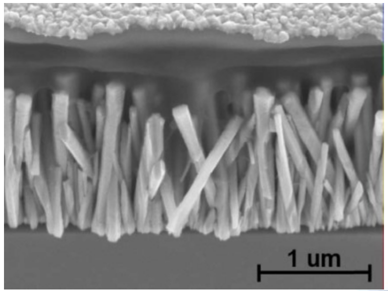
Grenoble, September 11 2019

Outline





I. **Introduction**

Piezoelectric materials

II. **Characterization of piezoelectric nanowires**

AFM techniques

III. **Modeling of piezo-NWs and nanogenerators**

Comparison vs. experiments

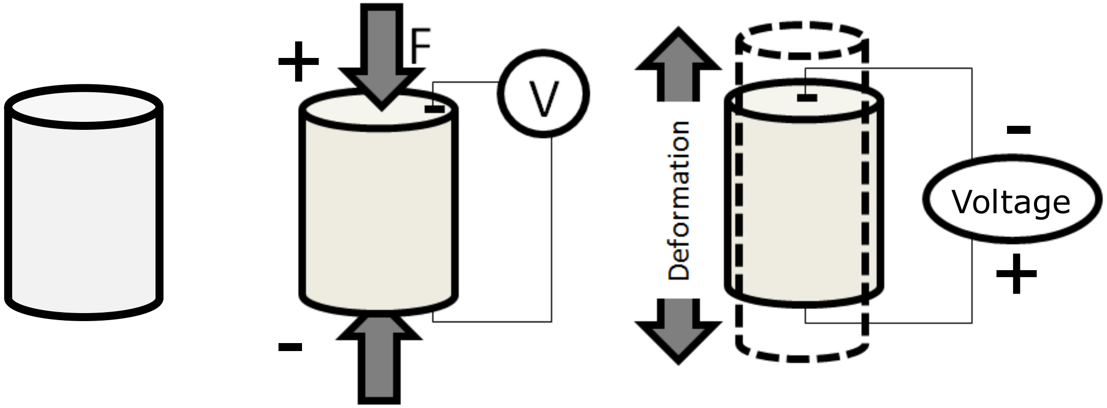
Surface traps and their effect on device performance

V. **Conclusions and perspectives**

Introduction (1/4)
Piezoelectricity

What is the piezoelectric effect?

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



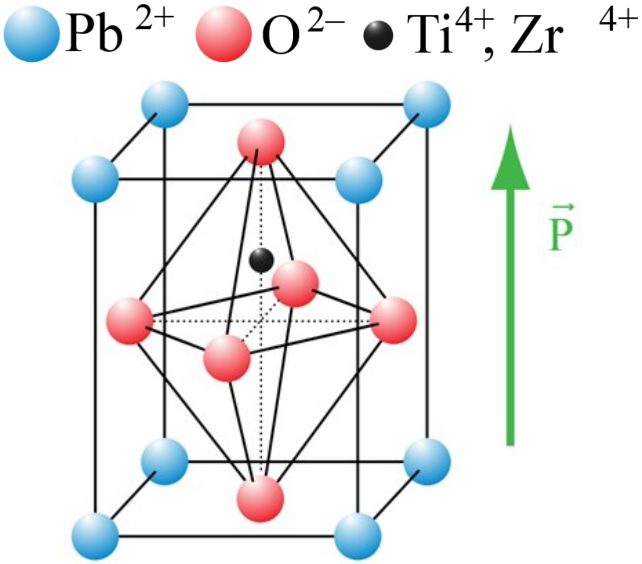
1) Direct effect : Force → Electric field

Sensors and energy harvesters

2) Reverse effect : Electric field → Strain

Actuators and haptic devices

PZT crystal structure

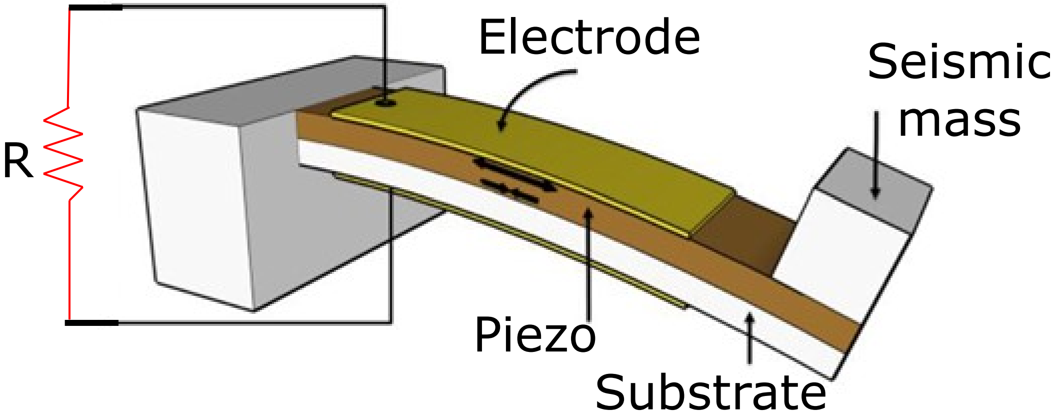


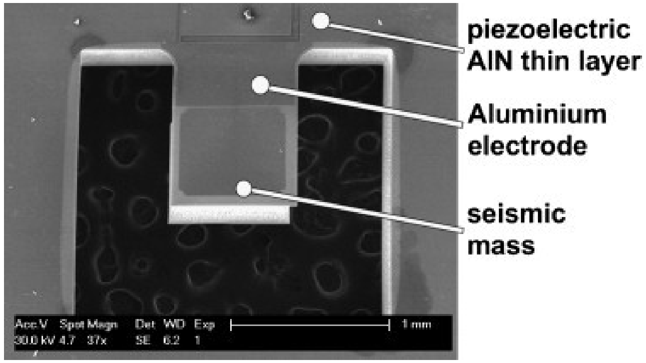
Introduction (2/4)

Piezoelectric materials for EH

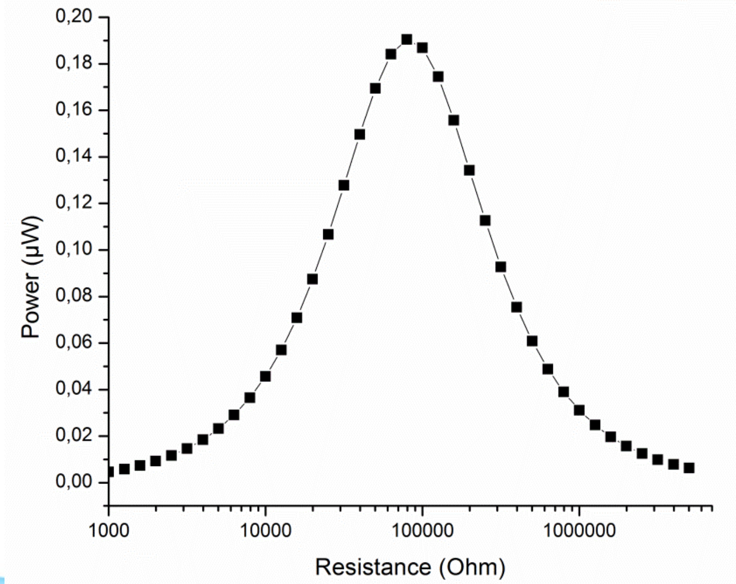
Basic resonant structure

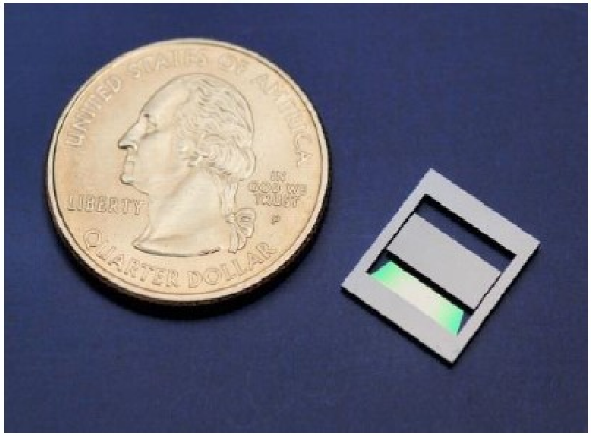
Uses mainly thin films (AlN, ZnO, PZT)





Marzenki et al. S&A 2008 (TIMA)



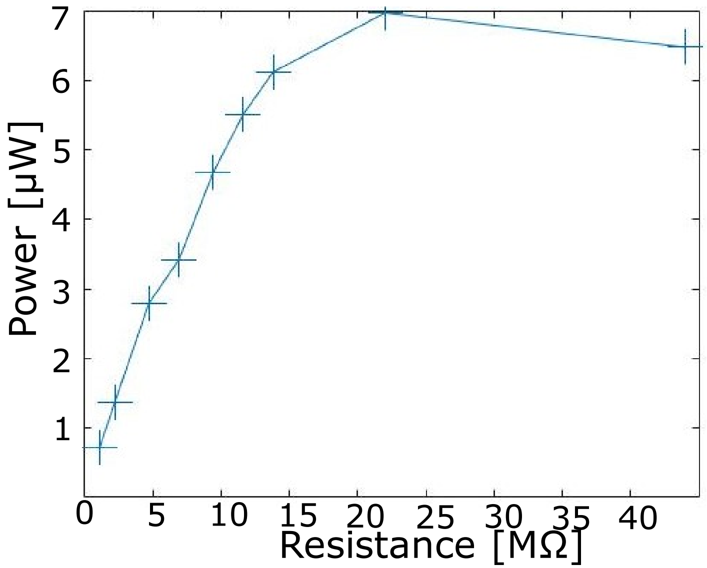


Microgen (USA) AlN based commercial MEMS harvesters

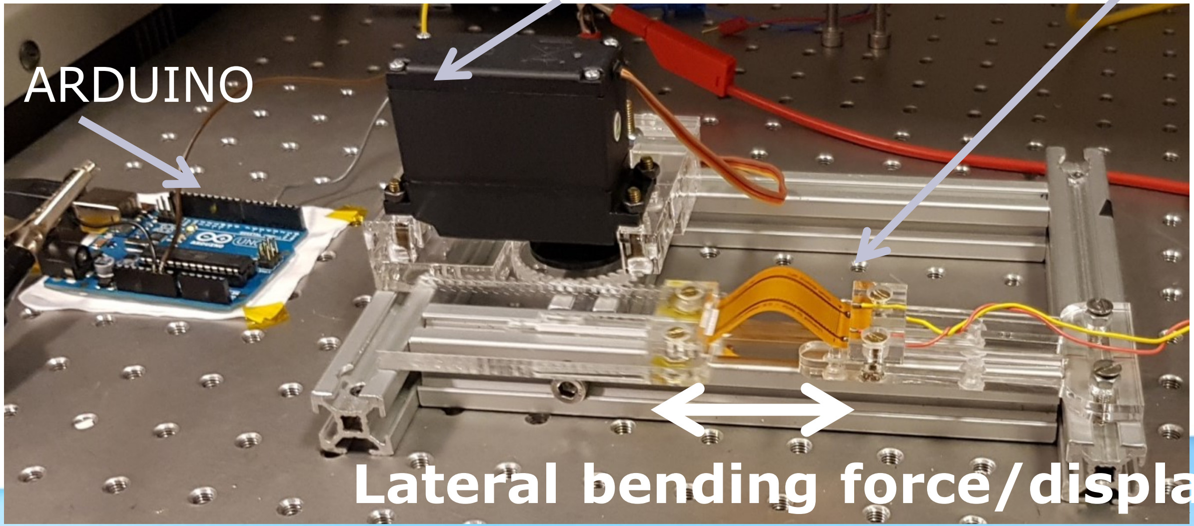
Introduction (3/4)
Piezoelectric materials for EH

Flexible non-resonant structures

Measurement example on a TE Connectivity device (@0.3Hz and 3mm of lateral displacement)



Characterization set-up



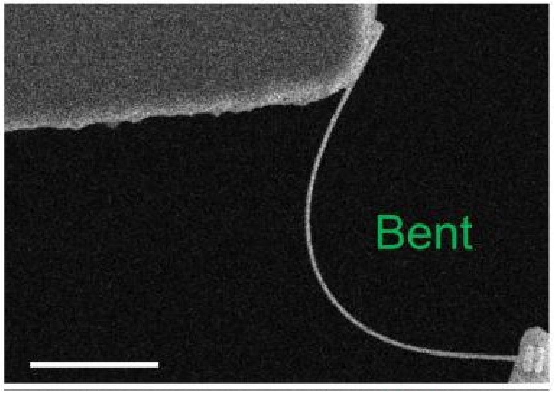
Introduction (4/4)

Nanowires and nanocomposites

Advantages of piezoelectric nanowires? (~ 10nm wide, > 500nm long)

- Higher flexibility
- High sensitivity to small forces
- Enhanced piezoelectric properties

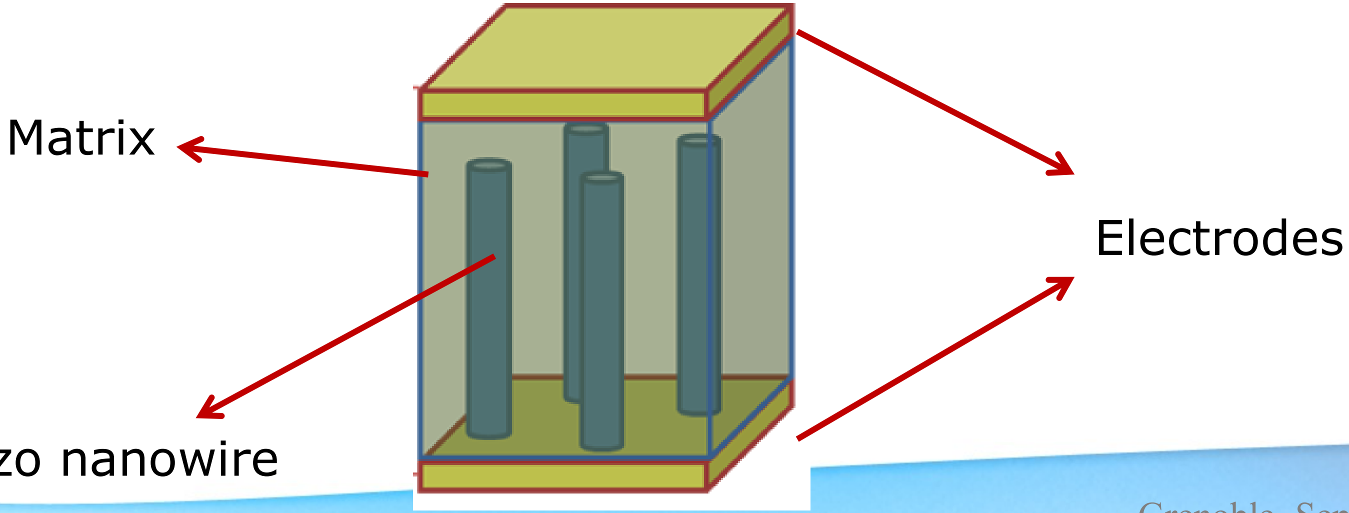
M-H. Zhao et al., Nanoletters 4, 2004



ZnO nanowires

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

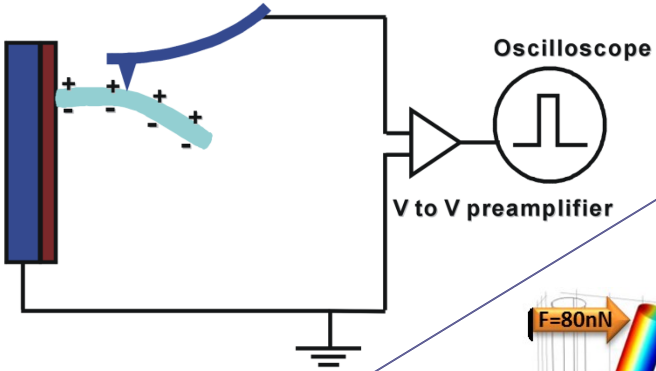
Piezoelectric Nanocomposites (NWs immerged in a dielectric)



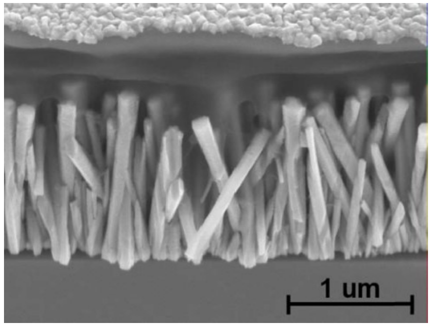
Our activities on piezoelectric NWs and piezo devices

NWs individual characterization

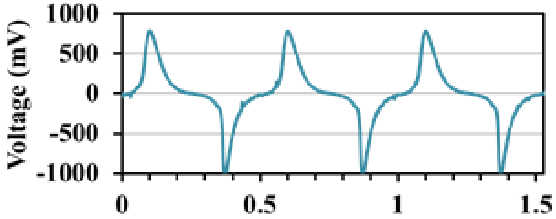
AFM techniques



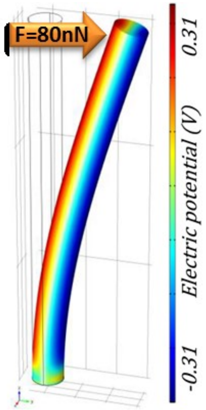
NW integration into devices and characterization

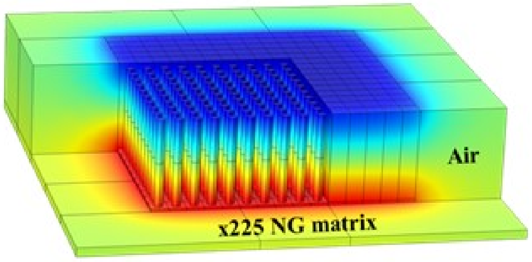


VING nanogenerator integration



Modeling





FEM and analytical models

Obj: Understand the physics + optimisation guidelines

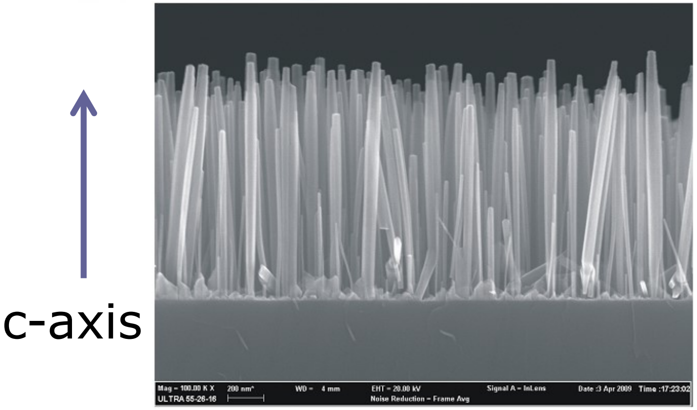
Individual nanowire characterization

AFM techniques and applications to sensing

Individual NW characterization

Electromechanical characterization

Near field characterization techniques

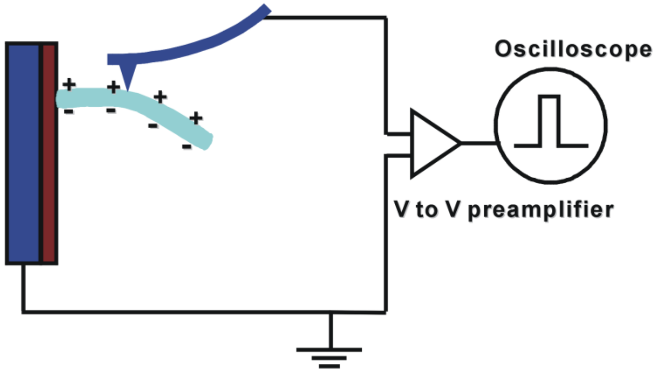


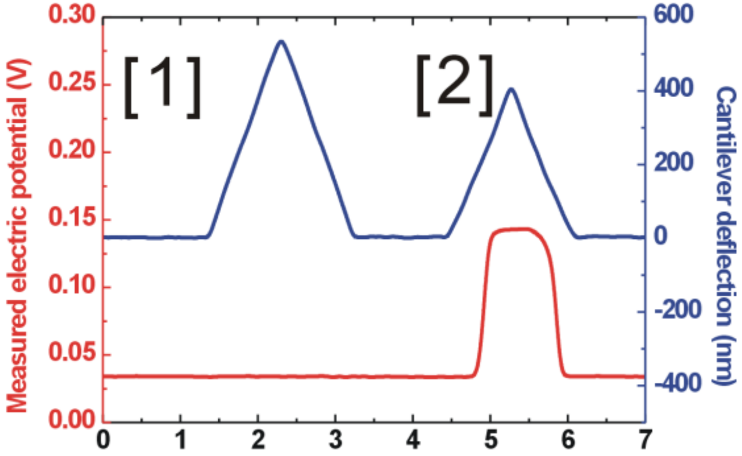
GaN NW (30nm wide, 1µm long)
Grown by MBE on AlN/Si substrate.

R. Songmuang et al., APL 91 2007

Selection of specific locations on the NW

*Collab.
Neel I.
and
LTM labs
(PhD X. Xu and
A. Potié)*





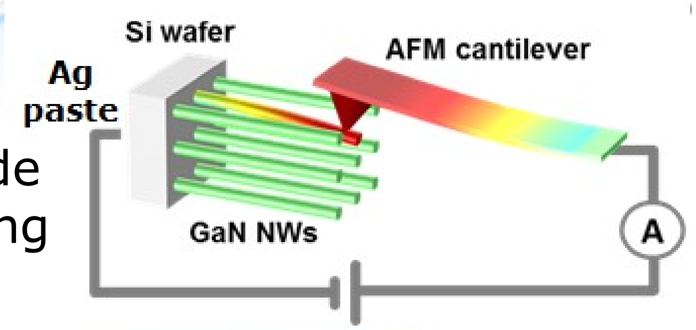
X. Xu, L. Montès et al., Nanotechnology 22 (2011)

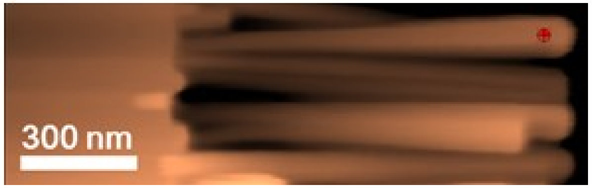
Individual NW characterization

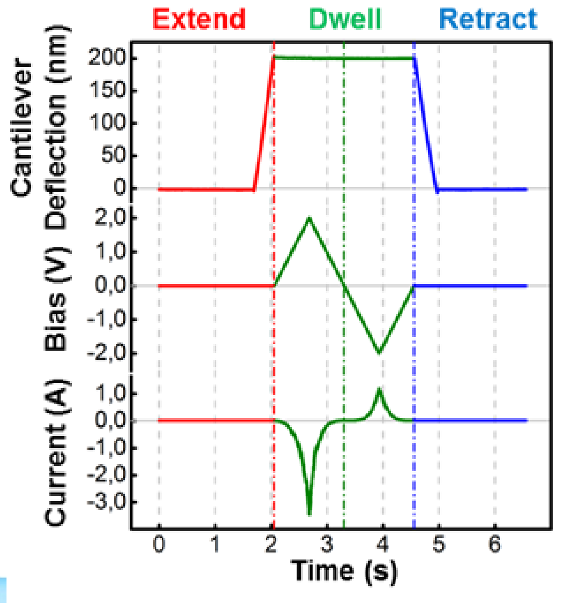
Mechanical sensor – piezotronic effect

60nm wide
1.5µm long

*Collab.
Neel I.
and
GeorgiaTEC*

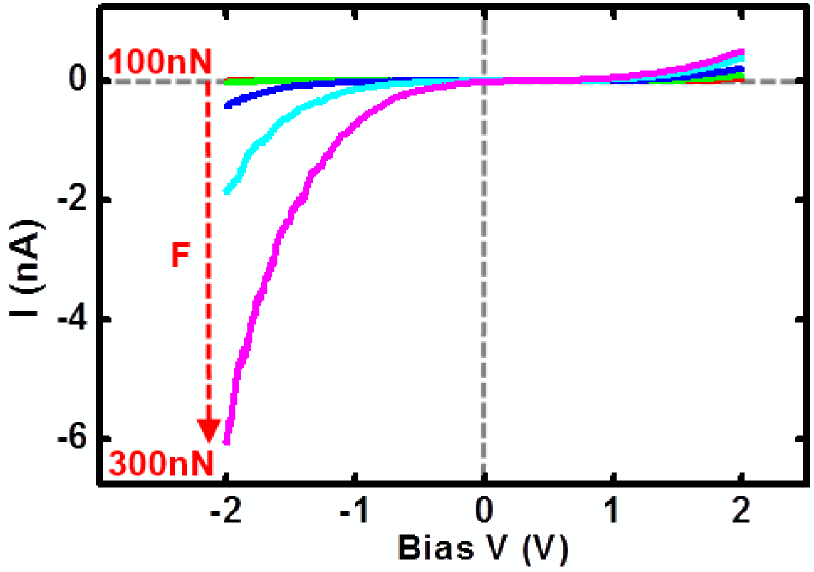






Experimental measurement:

- Current I through the Schottky junction GaN NW / Pt AFM tip
- I-V as function of F



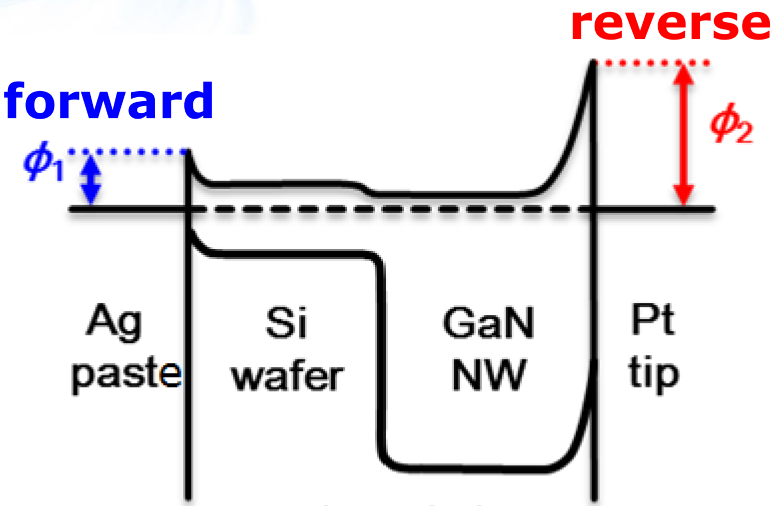
PhD R. Hinchet

Y. Zhou, R. Hinchet et al., Adv Mat, 2012

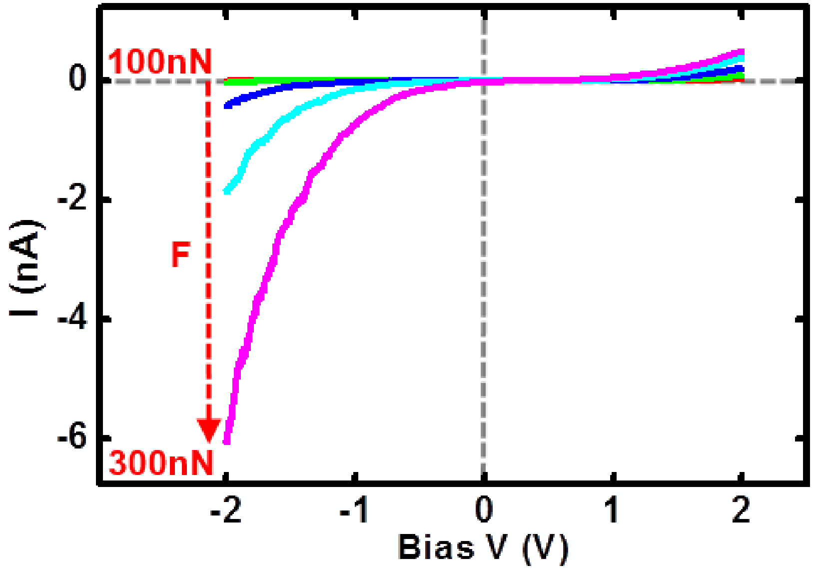
Individual NW characterization

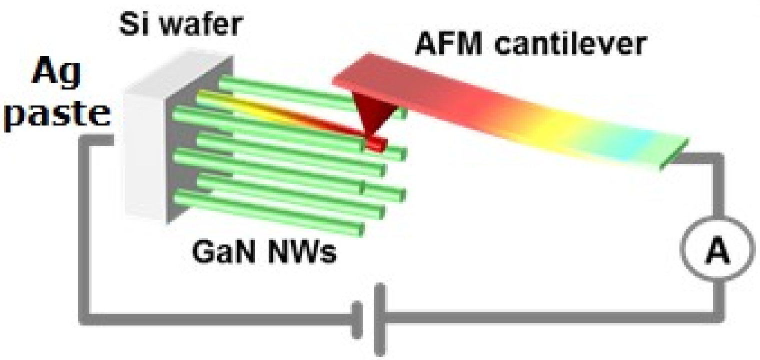
Mechanical sensor – what's behind?

Piezoelectric effect on Schottky diode:



energy band diagram





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Y. Zhou, R. Hinchet et al., Adv Mat, 2012

Individual NW characterization

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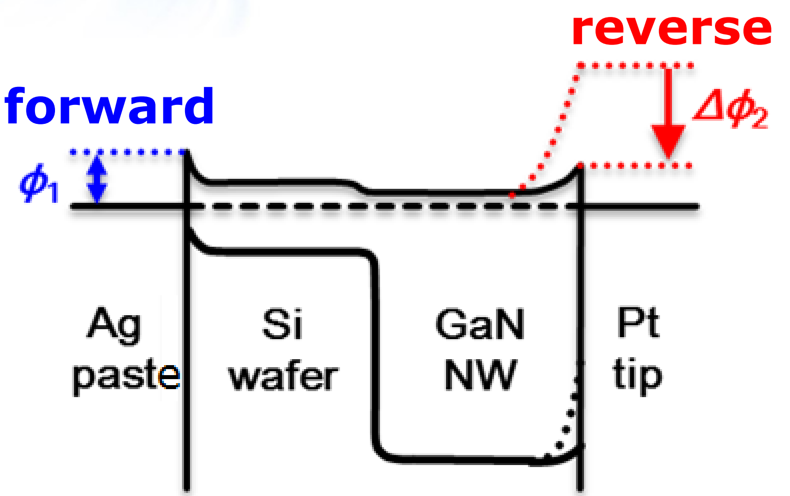
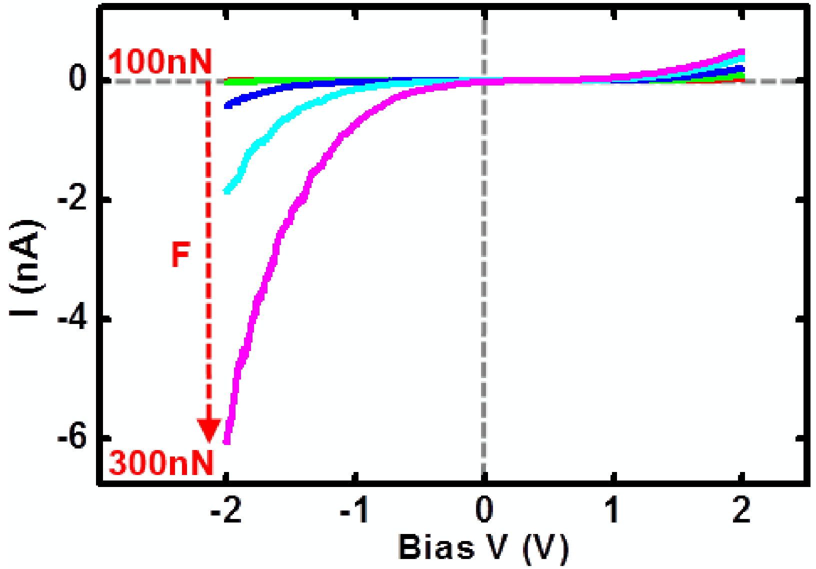


energy band diagram



- Local potential ↘ barrier height
- ↗ current through Schottky

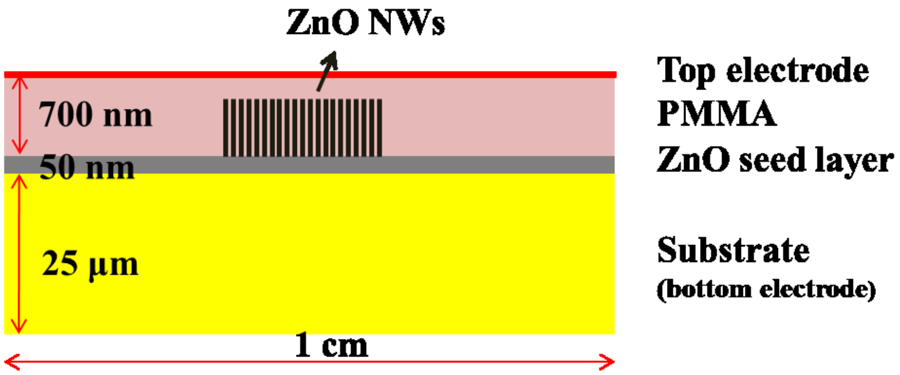
- **High sensitivity: 1.2 ln(A)/nN**
- **Resolution: better than 16nN**
- **Response time: τ < 5ms (200Hz)**

Y. Zhou, R. Hinchet et al., Adv Mat, 2012

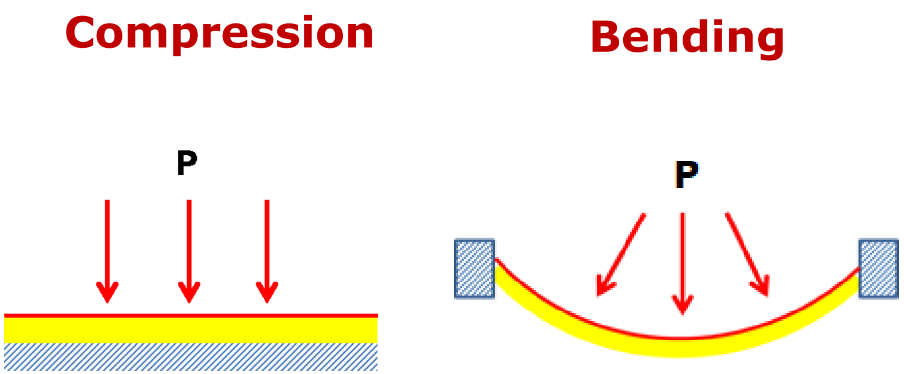
Devices modeling

Modeling of piezoelectric composites
VING: Vertical Integrated NanoGenerators

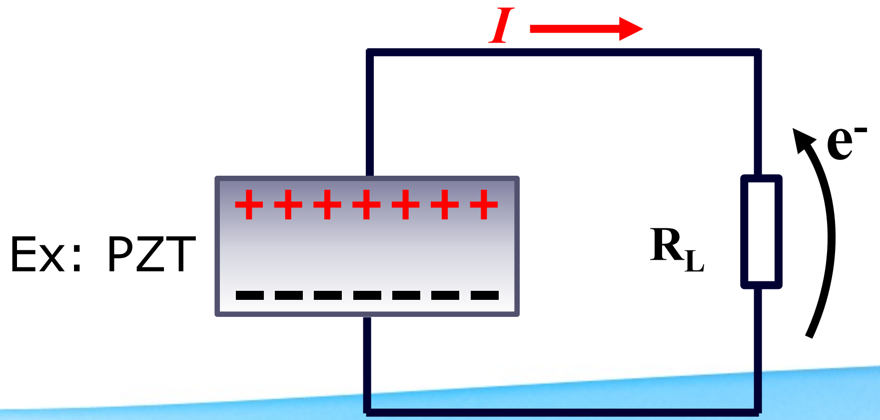
VING sandwiched by two electrodes
(composite material)



Working modes

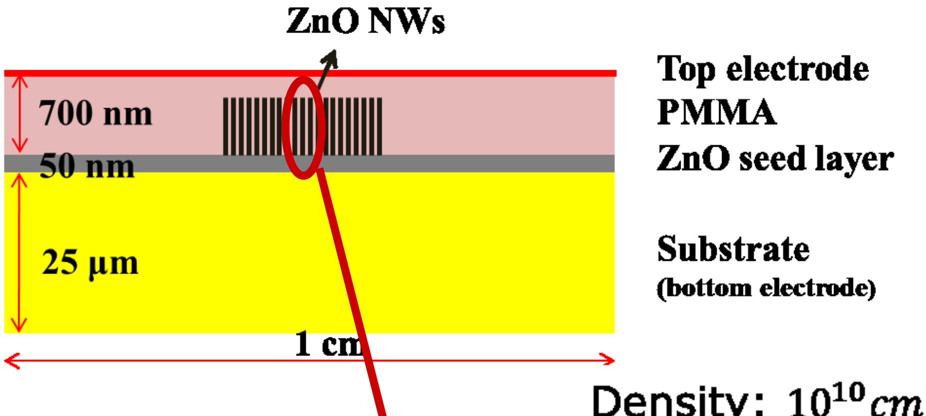


Basic models : Insulating piezoelectric material



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

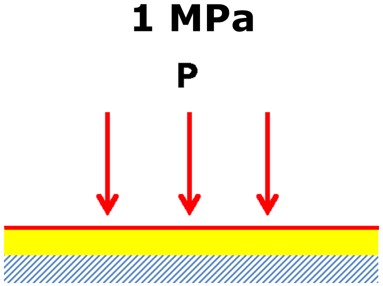
VING sandwiched by two electrodes



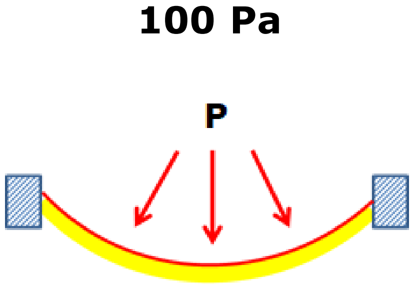
Density: $10^{10} cm^{-2}$

Working modes

Compression



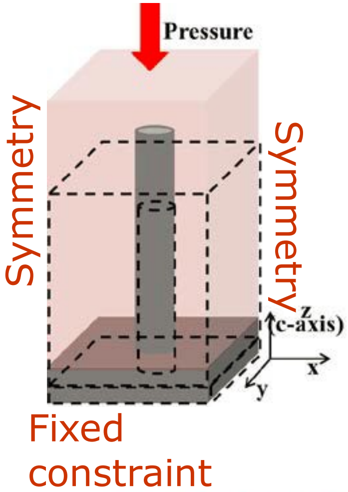
Bending

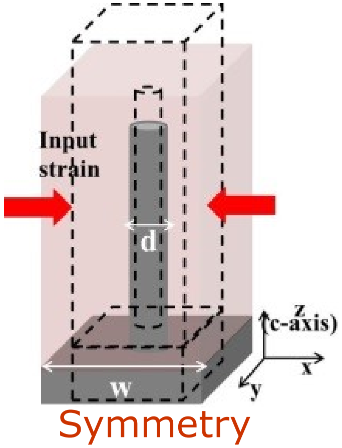


Mechanical

Linear elasticity
Bulk properties

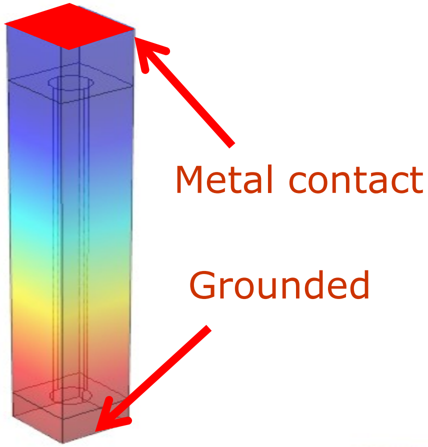
$d = 50\ nm$
$L = 600\ nm$
$Ratio = d/w$
(density)





Electrical

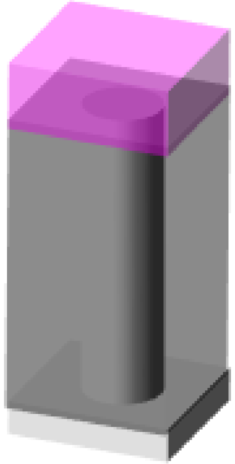
No Semi-conducting properties



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

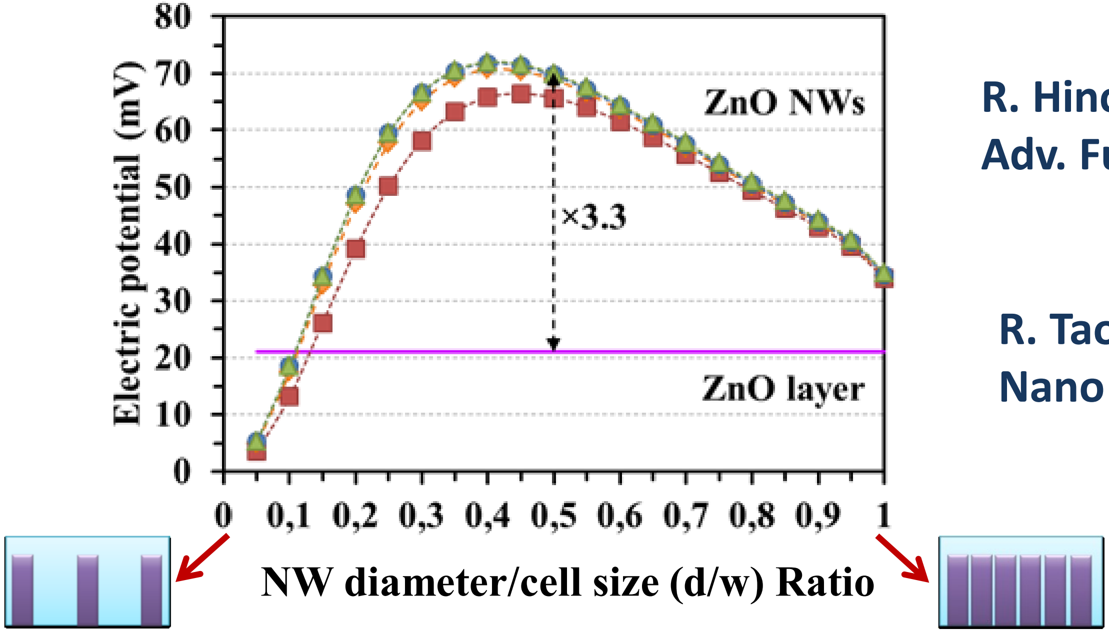
Our models : VING based on ZnO NWs

An example in compression mode



PMMA matrix
Top layer
varies

Material	**PMMA** □	SiO$_2$ ○	Si$_3$N$_4$ △	Al$_2$O$_3$ ×
E (GPa)	3	70	250	400
κ_{33}	3.9	4.2	9.7	5.7



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

**R. Tao et al.,
Nano Energy 2015**

Several ways to optimize the performance in compression mode:

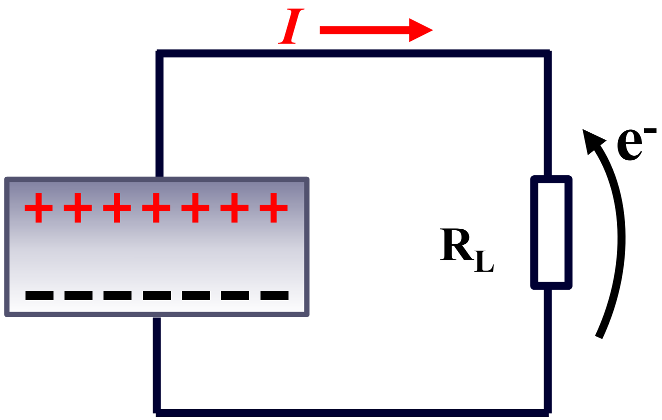
- Use a medium range of density
- Use hard materials as a top dielectric layer

Screening effects

ZnO as semiconductor :

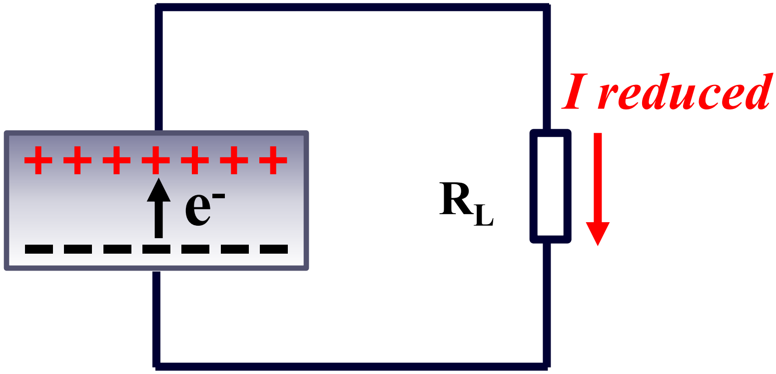
- ➢ Unintentionally doped in the growth (~ 10^{16} -10^{17} cm^{-3})

Insulating piezoelectric material



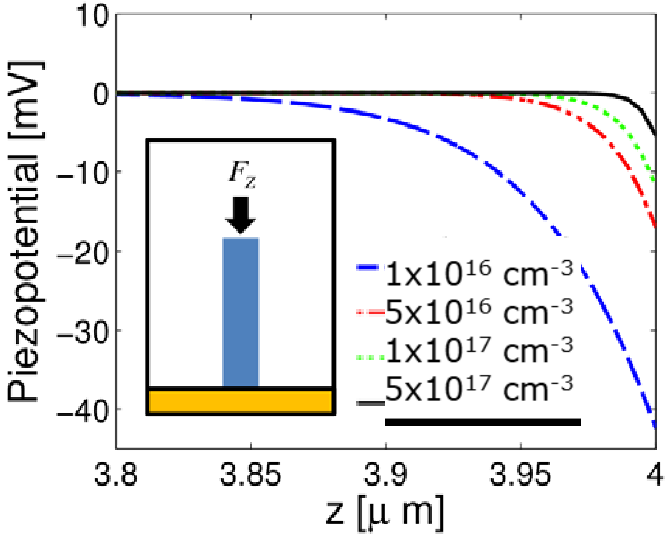
With free carriers

Semiconductor (GaN, ZnO…)



If an <u>individual ZnO NW</u> is n-doped,

- ➢ Depleted region at the top
- ➢ Length independent for NW longer than 200 nm
- ➢ Low output , heavily screened with higher doping



R=150nm
L= 4μm

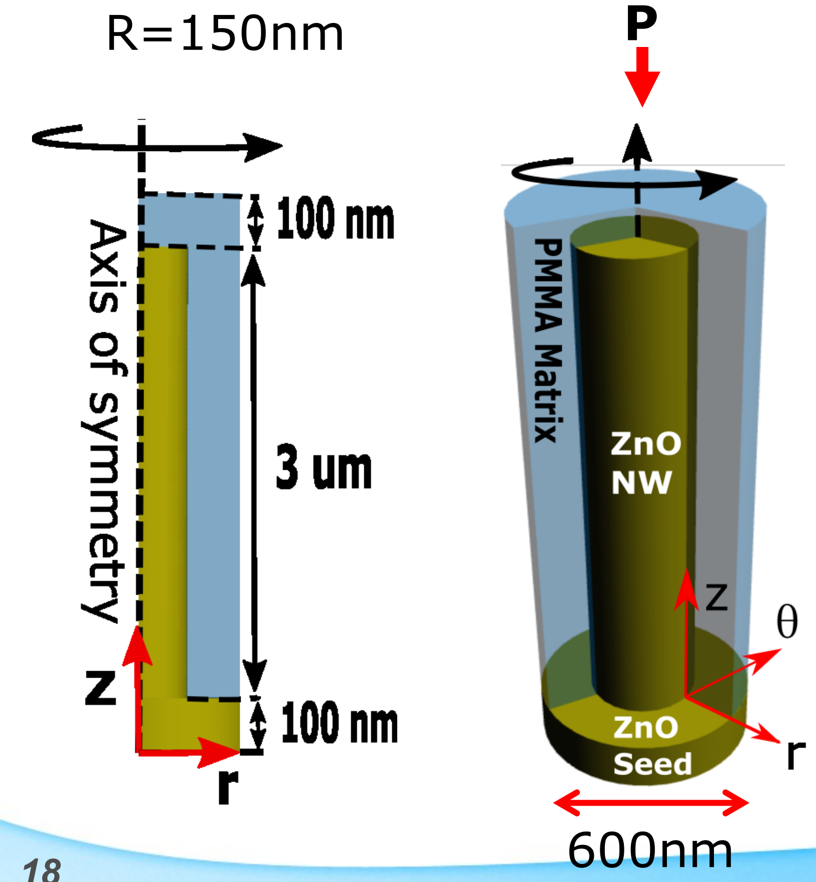
G. Romano et al. Nanotechnology 2011

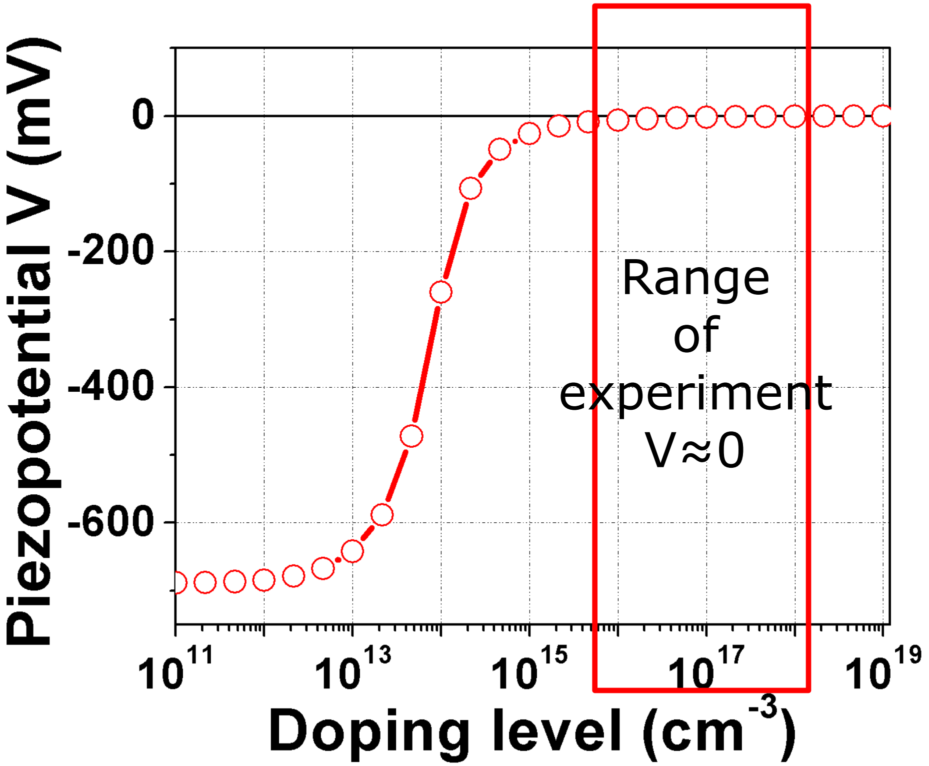
Screening effect in VING

2D axisymmetric approach : VING based in ZnO NWs immerged in PMMA

- **Unit cell :**
- ZnO/PMMA composite

R=150nm



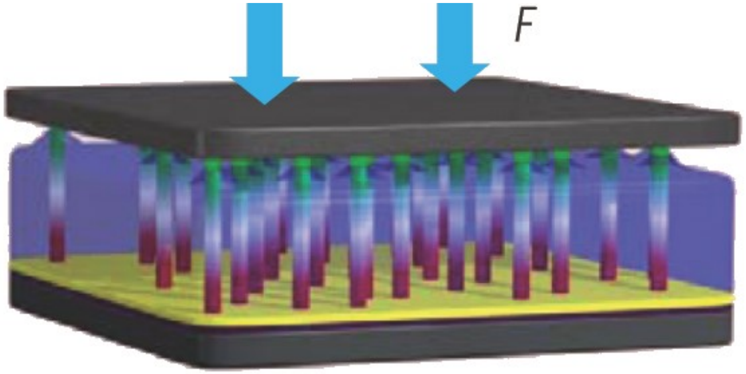


- Close to **0V** at doping **10^{15} cm^{-3}**

VING experimental results

How can we explain these results from a theoretical point of view ?

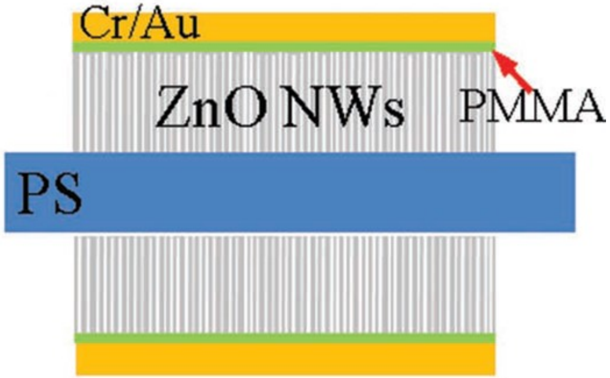
ZnO NWs integrated into Si
(4µm long, 300nm wide)



96mV
8.9nA/cm2

S. Xu et al.,
Nature Nanotech., 2010

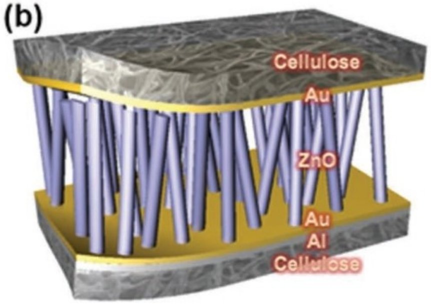
ZnO NWs (2µm long, 150nm wide)



20V

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

ZnO NWs integrated into paper



$2\mu A/cm^2$
75mV

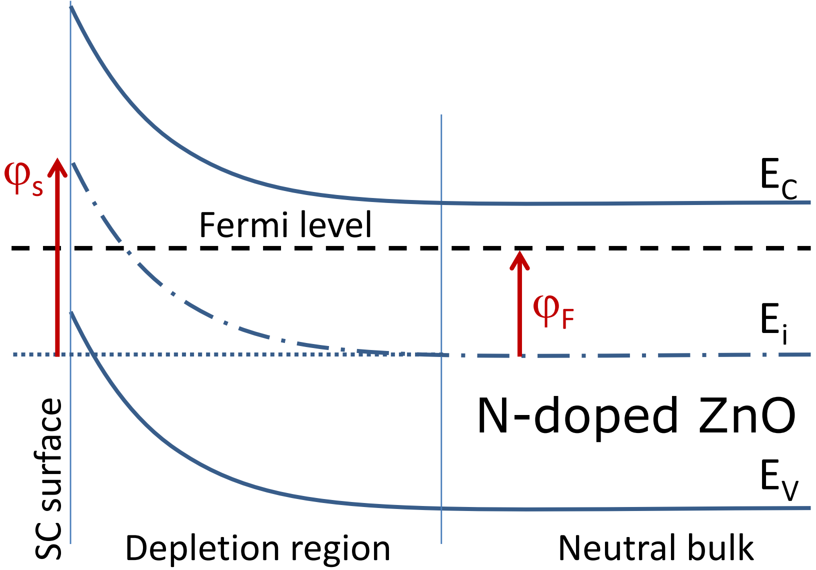
K-H. Kim et al., Small, 2011
Sungkyunkwan University, Republic of Korea

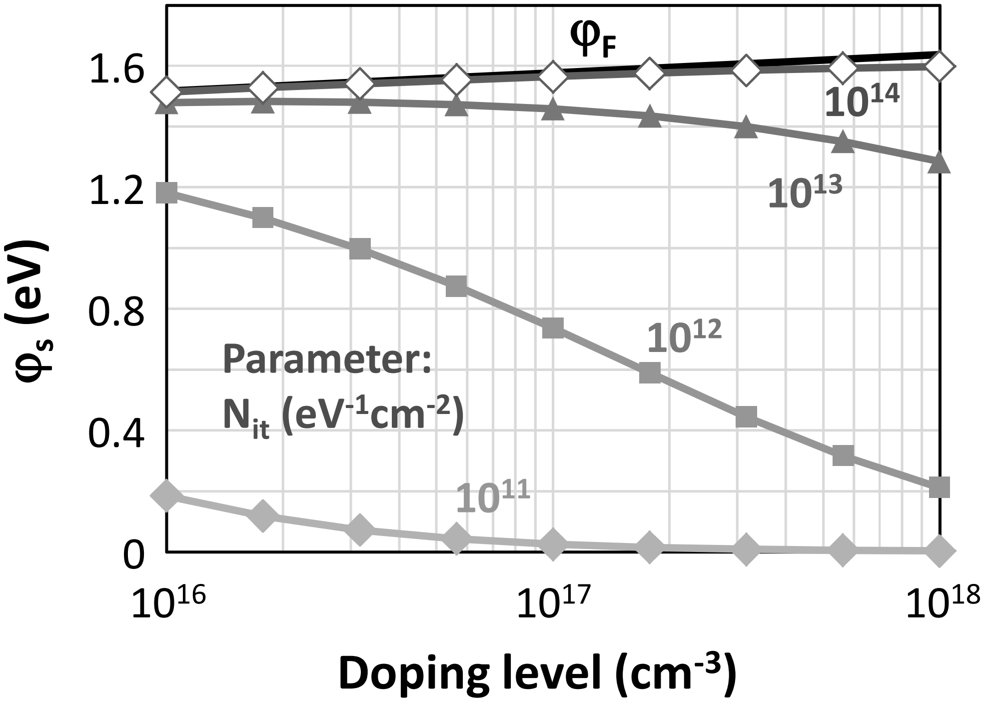
Surface traps

Influence in VING performance

Origin of Surface Traps and their consequences

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





SFLP: Surface Fermi Level Pinning

- For a high density of traps (N_{it}): $\varphi_s = \varphi_F$ → SFL pinned at mid-gap
- Hypothesis : $N_{it} \sim 5 \times 10^{11}$ $cm^{-2}eV^{-1}$ (medium range)

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

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

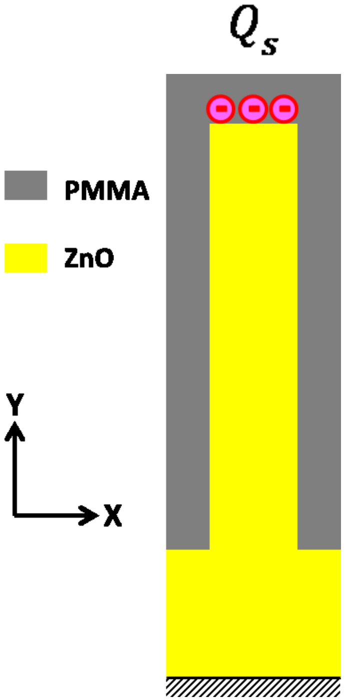
Influence of Surface Fermi Level Pinning (1/4)

SFLP on top vs. Doping (slow traps)

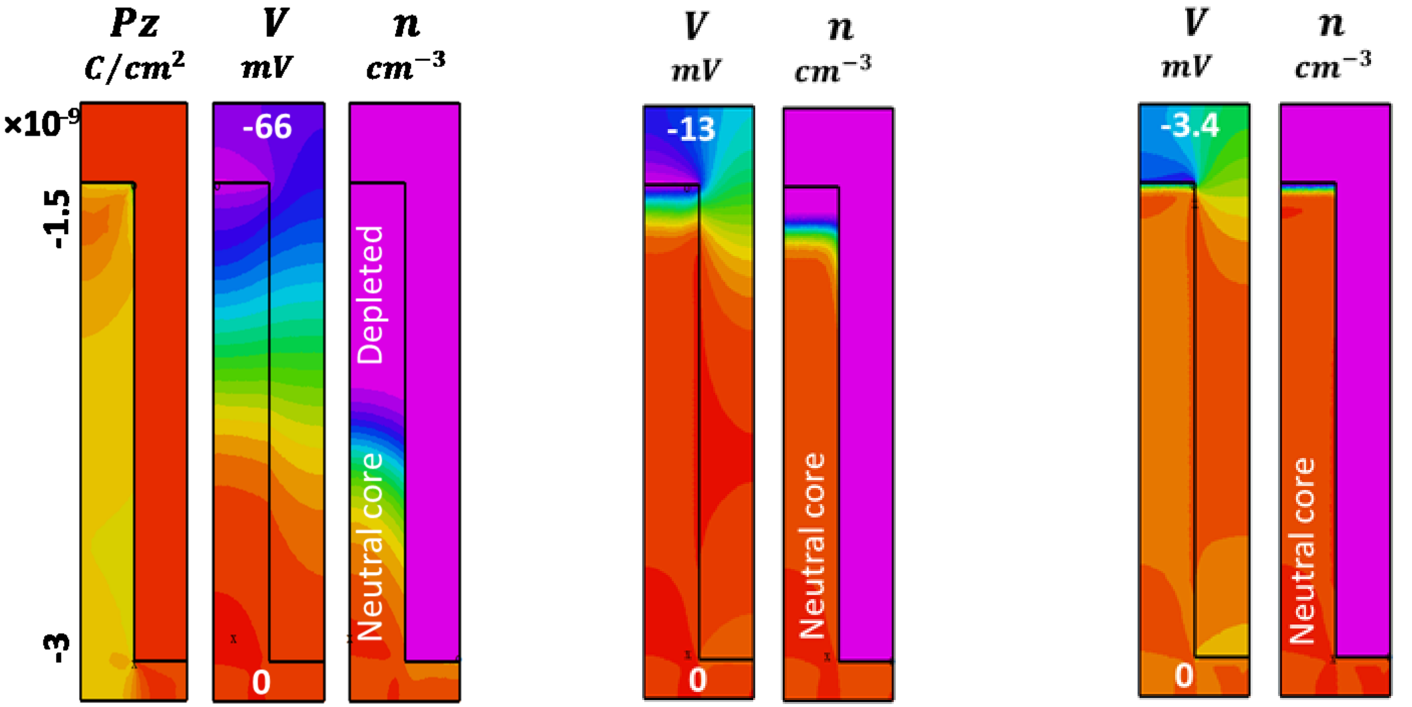
$P = 1MPa \quad R = 100nm \quad L = 600nm$

Unit cell :

SFLP on top



Bottom:
grounded and
constrained



Low doping level
$N_D = 10^{16} cm^{-3}$

Medium doping level
$N_D = 10^{17} cm^{-3}$

High doping level
$N_D = 10^{18} cm^{-3}$

- Depleted from the top, depending on doping level
- Allows much higher doping level to be used

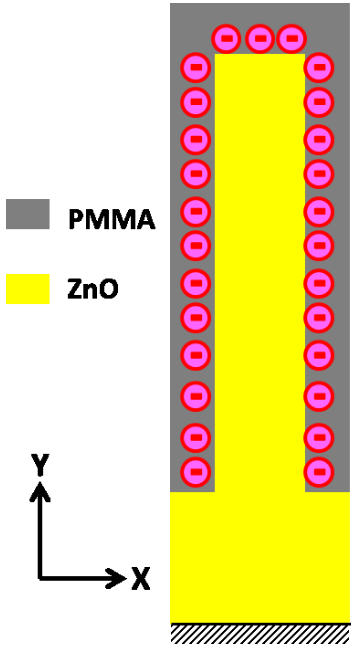
R. Tao et al., Adv. Electron. Mat. 2018

Influence of Surface Fermi Level Pinning (2/4)

SFLP at all interfaces vs. Doping (slow traps)

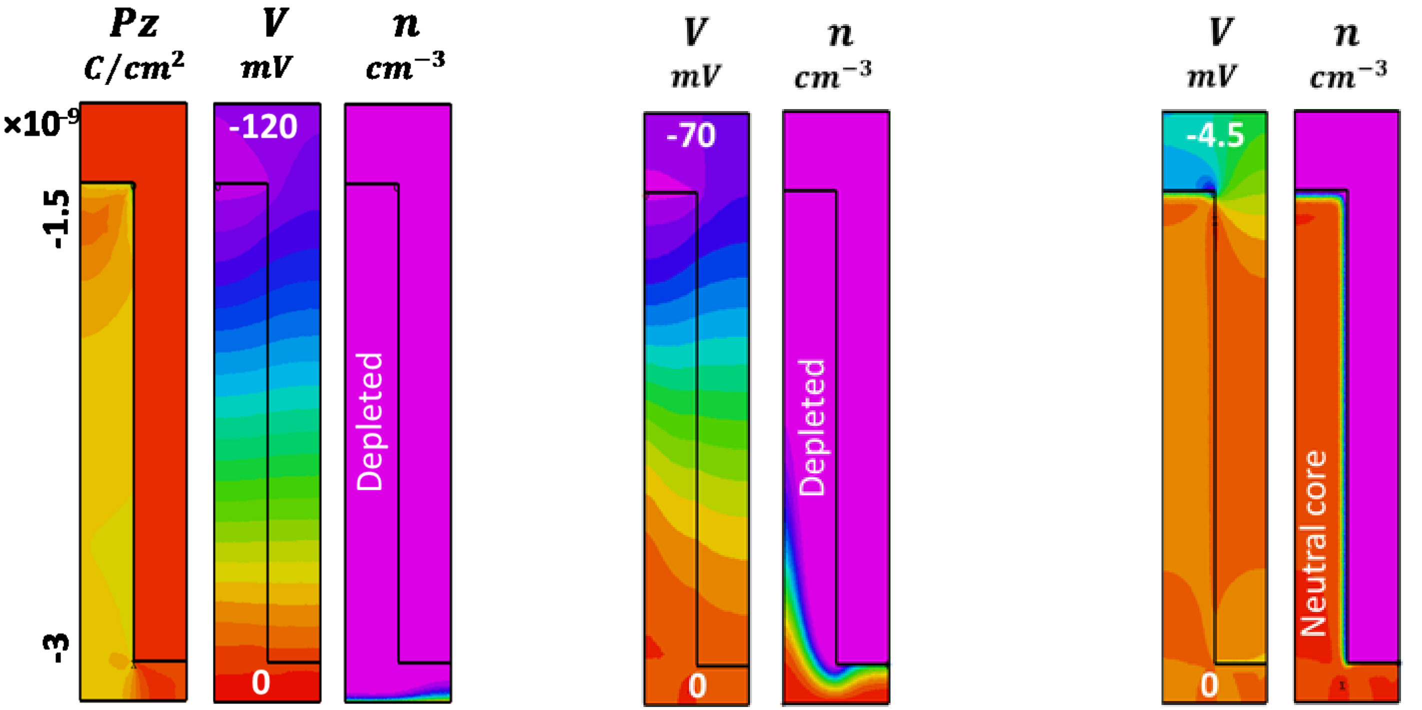
Unit cell :

SFLP on all surfaces



Bottom: grounded and constrained

$P = 1MPa \quad R = 100nm \quad L = 600nm$



Low doping level
$N_D = 10^{16} cm^{-3}$

Medium doping level
$N_D = 10^{17} cm^{-3}$

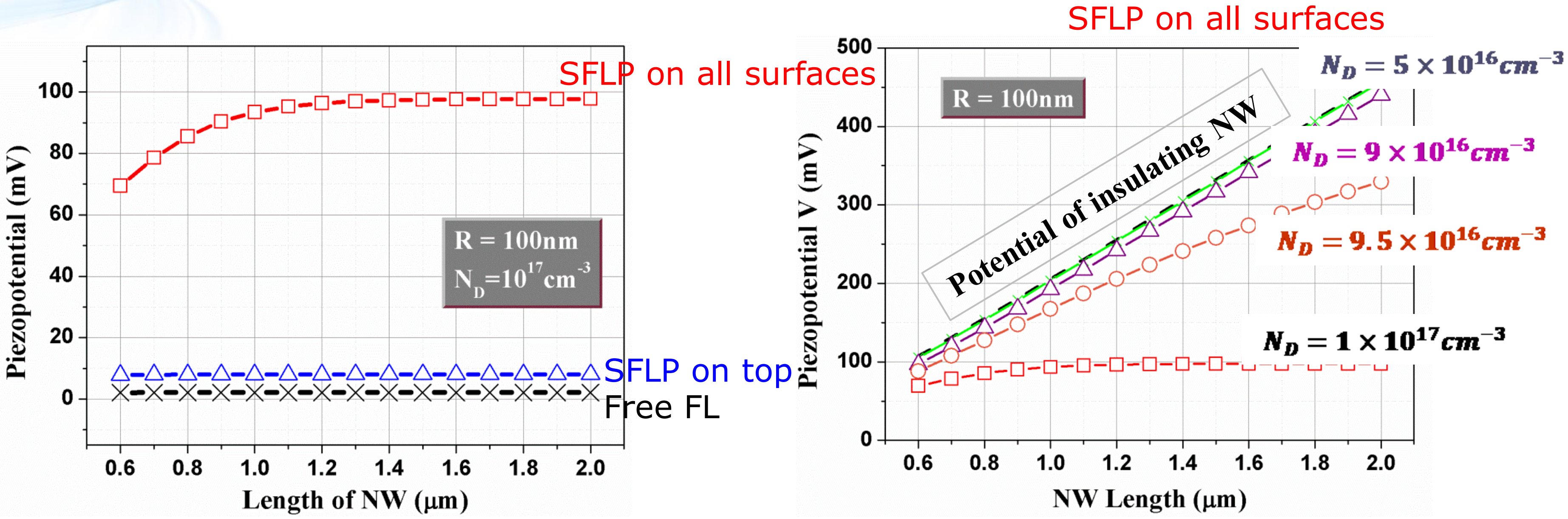
High doping level
$N_D = 10^{18} cm^{-3}$

- ➢ Depleted from all sides, depending on doping level
- ➢ Fully depleted at low doping and start to form neutral core at medium doping
- ➢ Allows much higher doping level to be used

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

Influence of Surface Fermi Level Pinning (3/4)

Effect of NW length



With free FL and SFLP on top only,

VING response is length-independent, consistent with Romano *et al.*

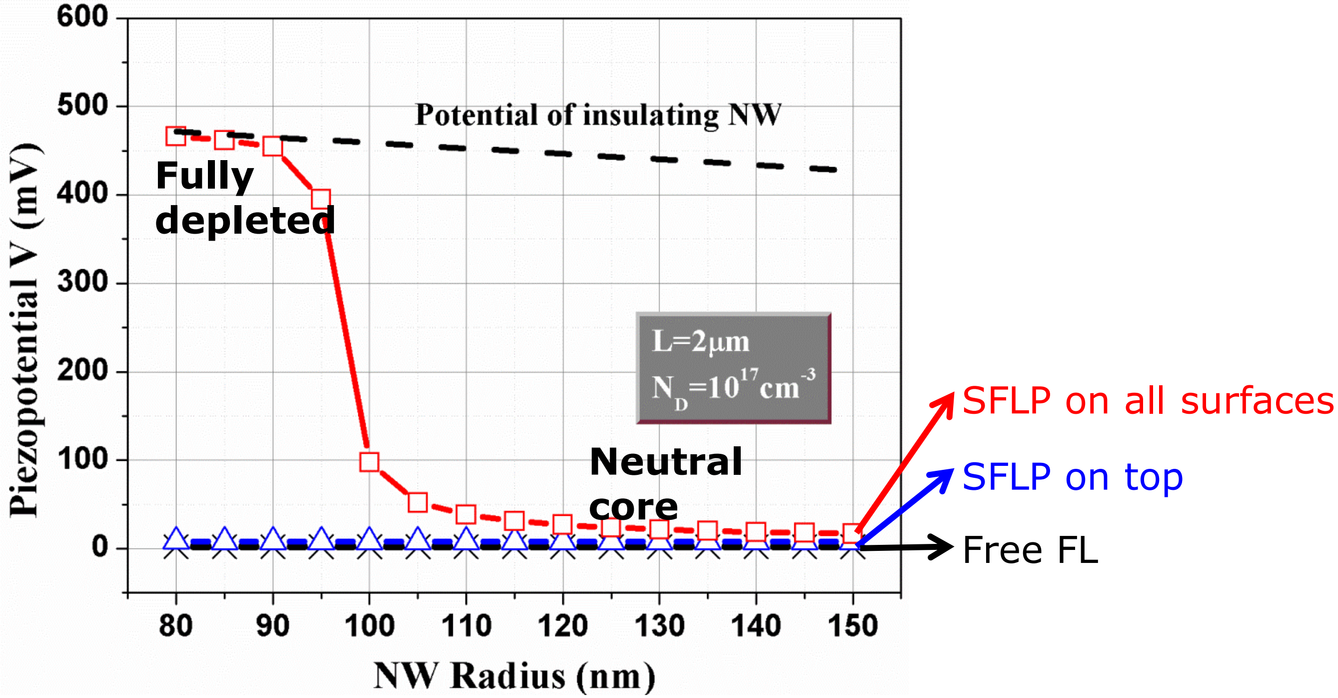
With SFLP at all interfaces,

VING response increases with length, length-dependency proved

It becomes interesting to increase NW length (as for piezoelectric insulators)

Influence of Surface Fermi Level Pinning (4/4)

Effect of NW radius



With free FL and SFLP on top only,

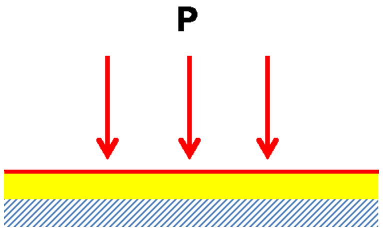
- ➢ VING response is radius-independent

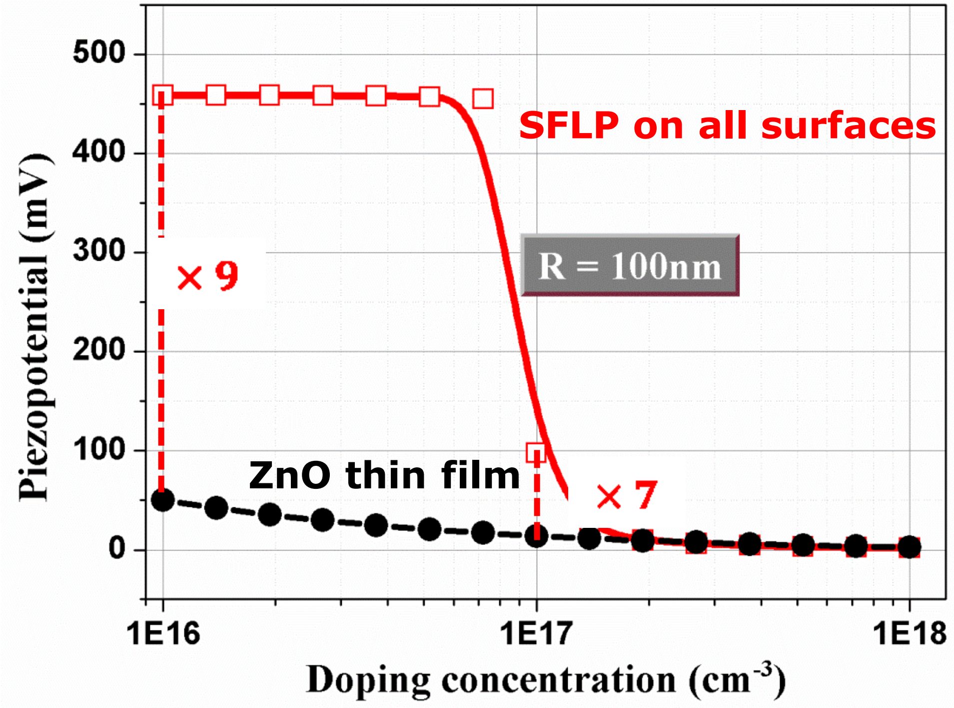
With SFLP on all interfaces,

- ➢ VING response increases with the decrease of NW radius, radius-dependency
- ➢ It becomes interesting to use thinner NW

NG cell vs thin film
Under compression

Thin film thickness: 2µm   NW length: 2µm   Doping level varied





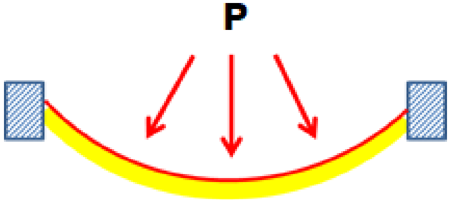
Compared with a ZnO thin film,

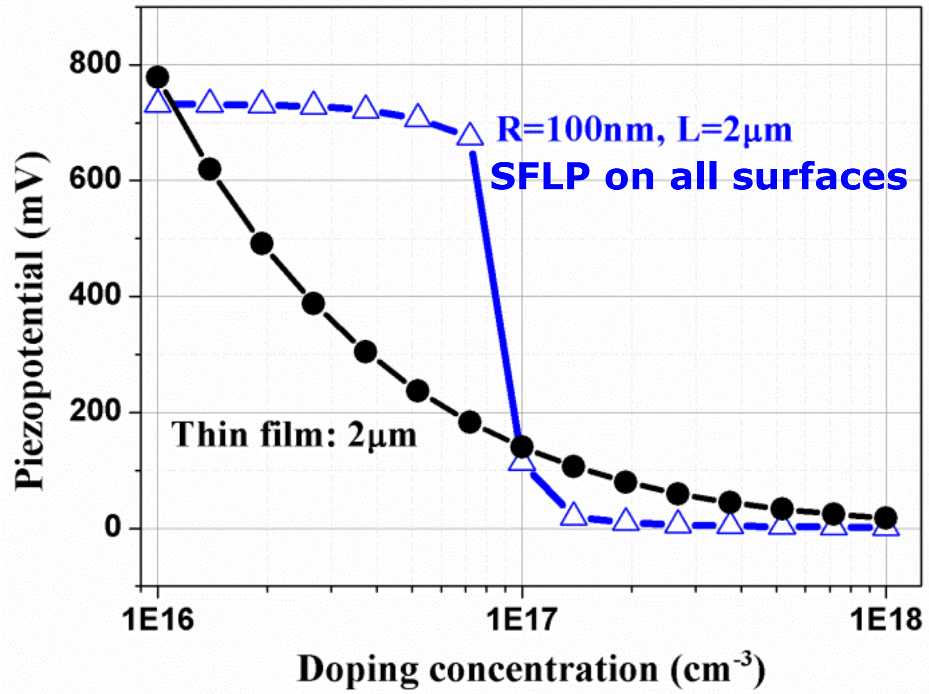
- ➢ Output of VING is higher than the thin film
- ➢ 6 times improved at medium doping level

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

NG cell vs thin film
Under bending

Thin film thickness: 2µm NW length: 2µm Doping level varied





Compared with a ZnO thin film,

- Similar maximum output
- Higher range of exploitable doping levels with NG

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

Conclusions

- **Piezo nanowires and nanocomposites are promising for mechanical energy harvesting and sensing**

- **SFLP could explain the high performance reported in experiments**

- **Important optimization guidelines :**
  - VING (composite) performance depends on the NWs length and radius
  - It is better to use long and thin NWs

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

Perspectives

- AFM characterization methods : combination of mechanical and electrical modes
- Studies of performance in function of traps densities, traps dynamics (slow and fast traps)
- Studies of the influence of traps to other devices based on piezoelectric semiconducting materials.
- Validation of the models through experiments

Thank you for your attention…

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