Piezo-semiconducting nanowires integration into flexible nanogenerators for mechanical energy harvesting

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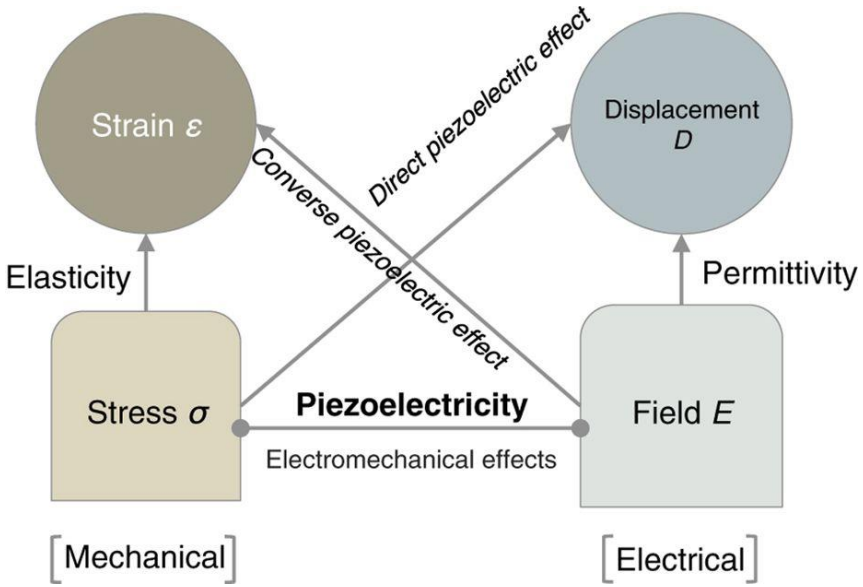
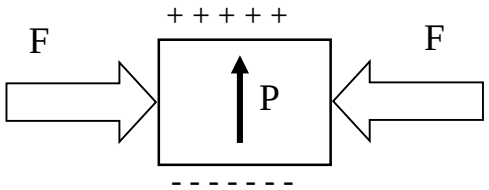
Piezoelectricity

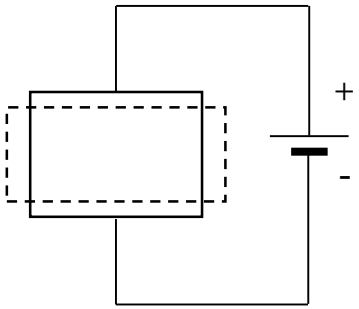


Part of the Heckman Diagram
Jong et al., Sci. Data 2:150053 (2015)

Direct effect

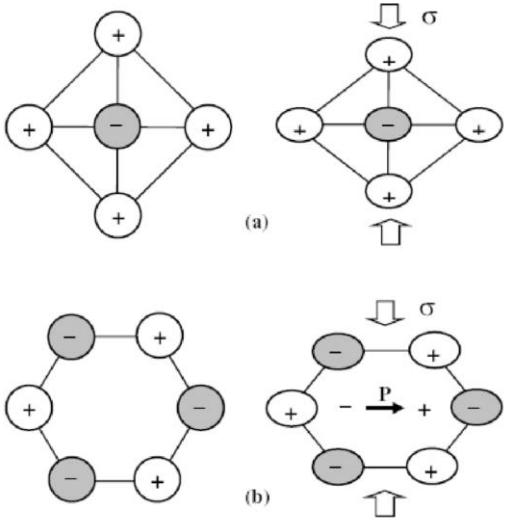


Inverse effect

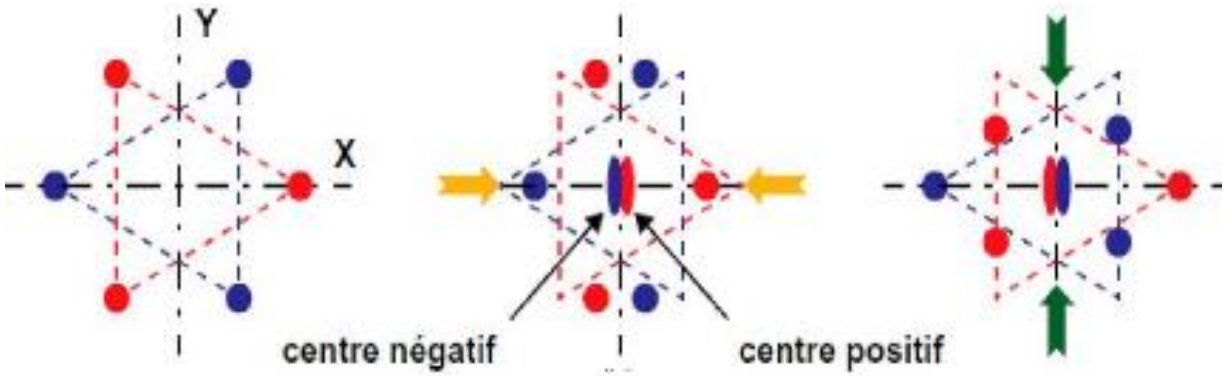


centrosymmetric crystal

non-centrosymmetric crystal



Effect of polarity orientation



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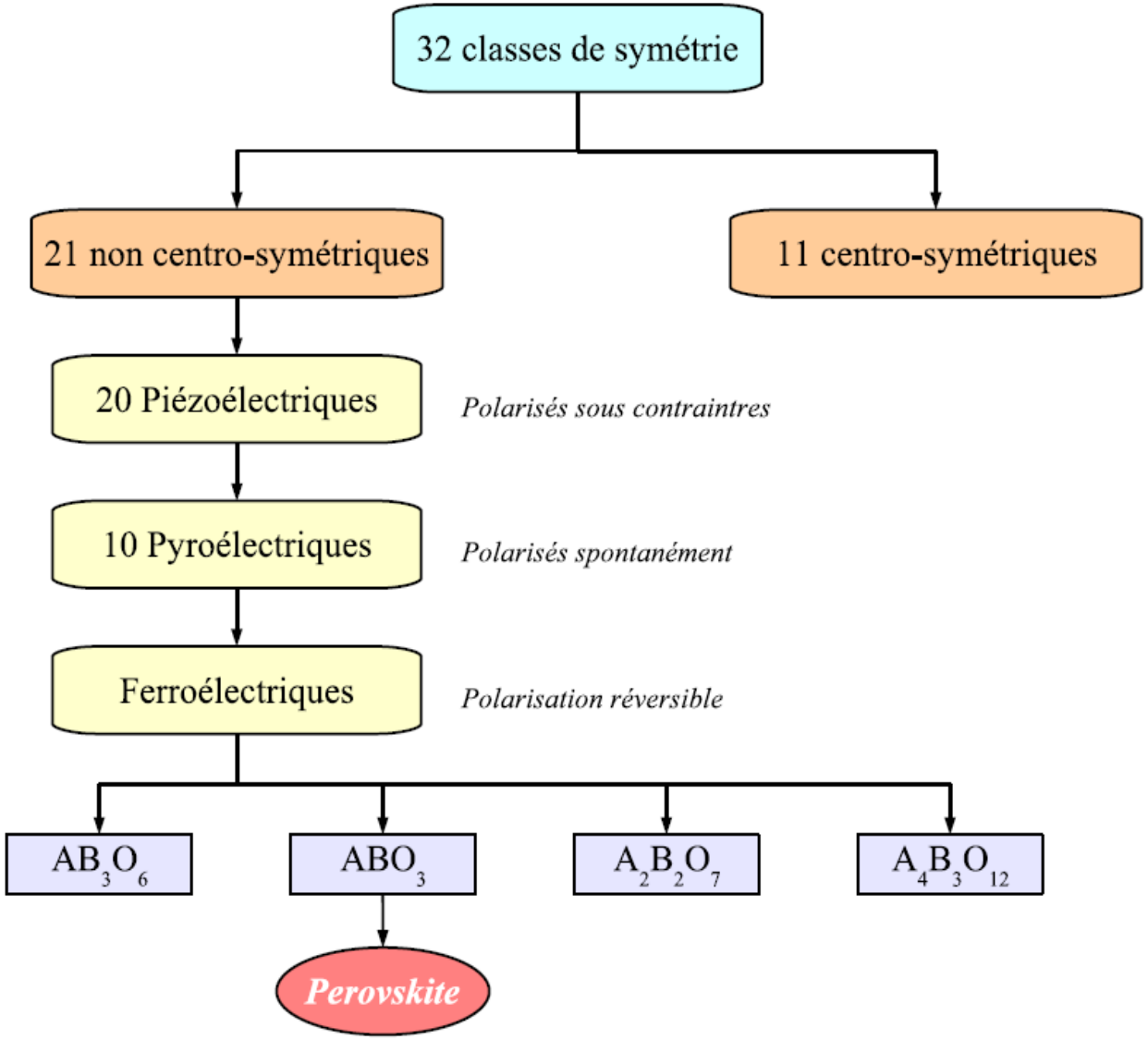
Piezoelectric materials



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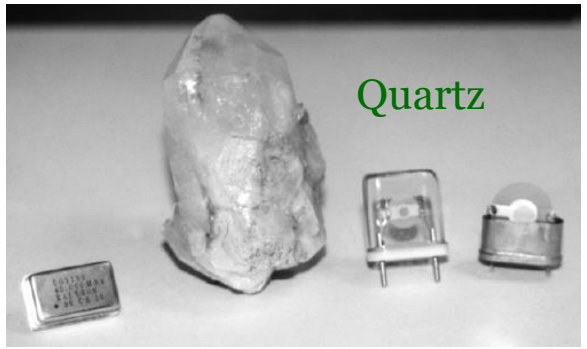
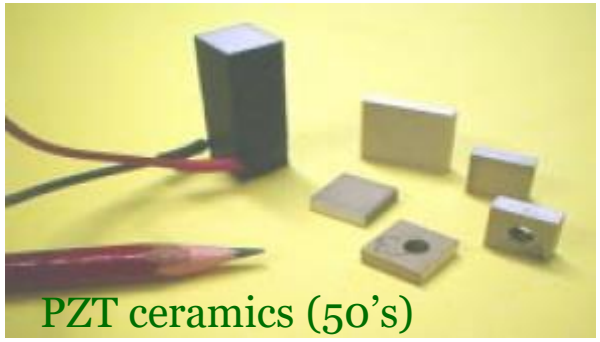
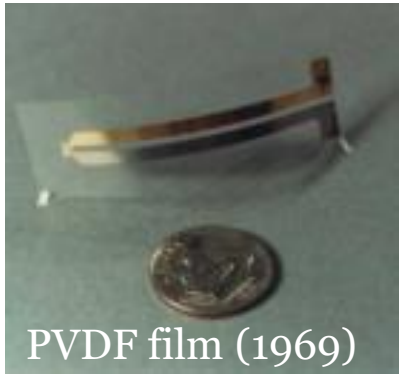
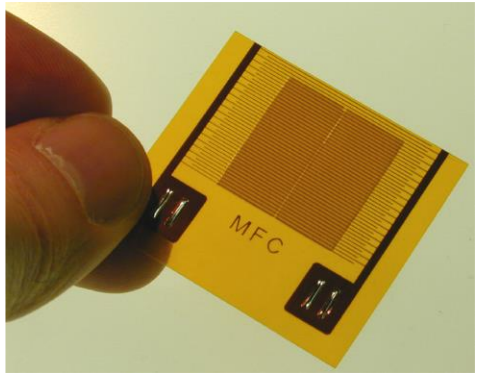
Piezoelectric materials

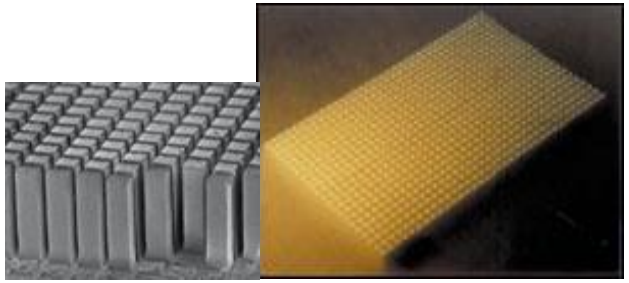






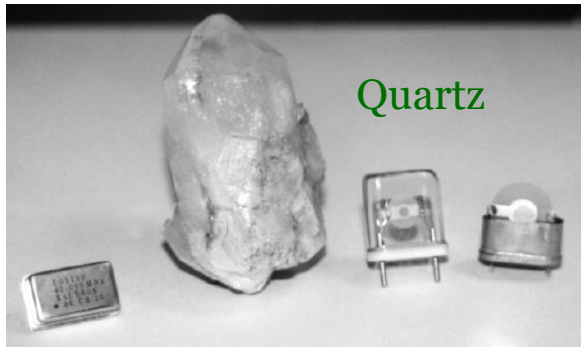


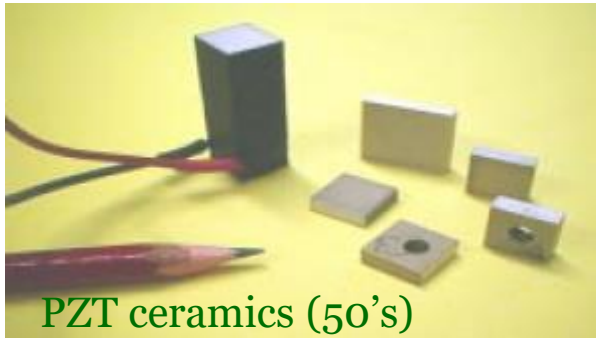
Macro Fibre Composites (1993) [Wil04]

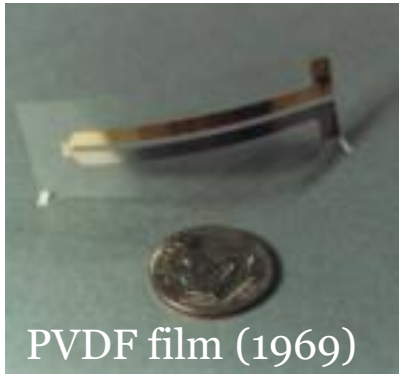


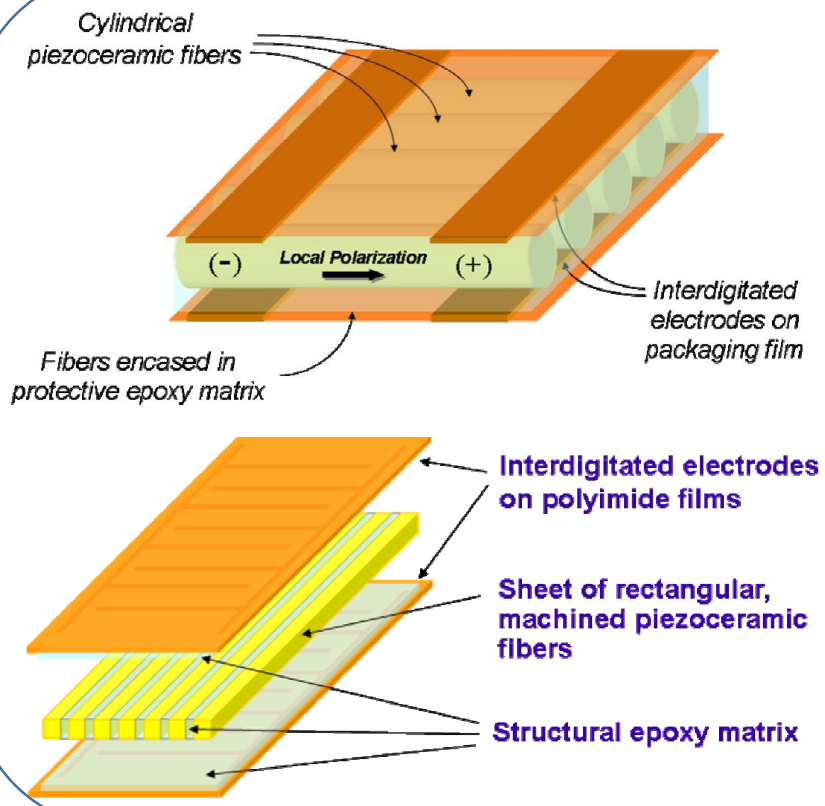
Piezocomposites (early 90's)

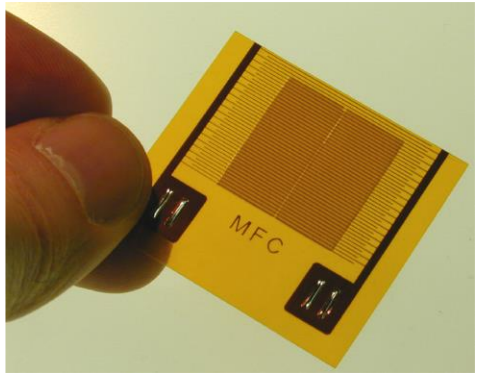
Piezoelectric materials











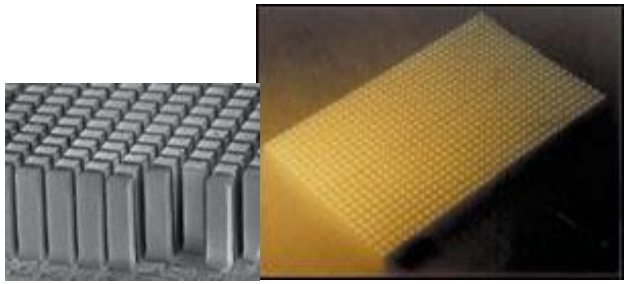
Macro Fibre Composites (1993) [Wil04]

Total thickness: 290 µm

Piezo fibre section: 350 µm x 175 µm

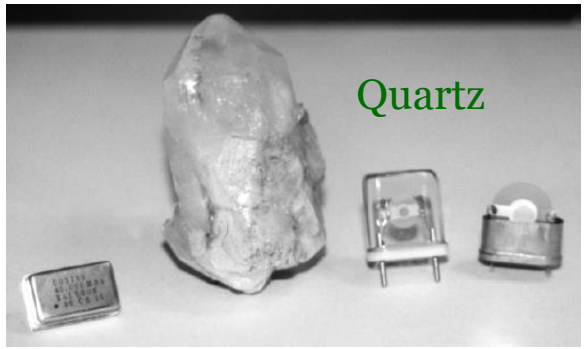
Piezo fibre spacing: 60 µm

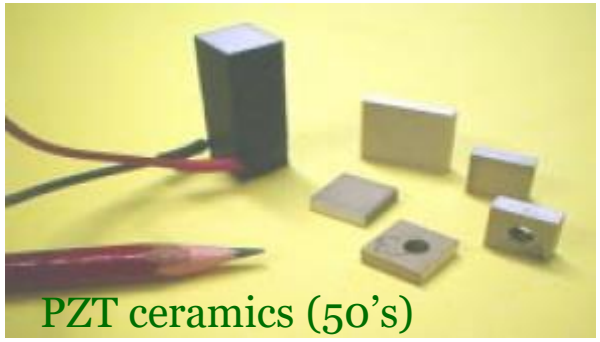
IDE finger width: 100 µm

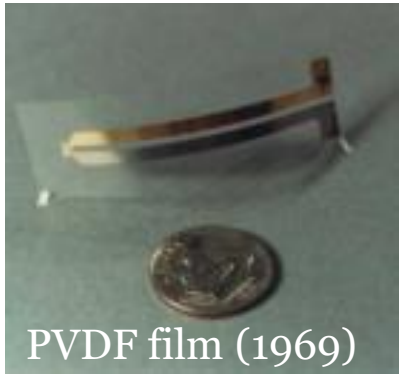


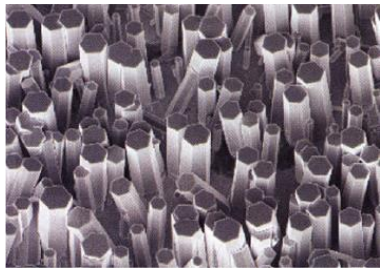
Piezocomposites (early 90's)

Piezoelectric materials

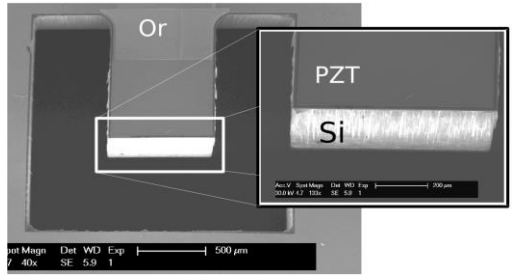




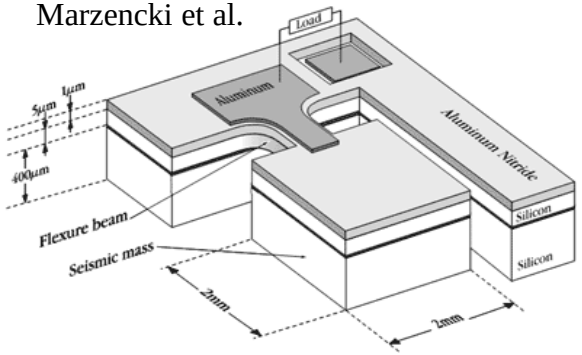




Nanowires
(2006)

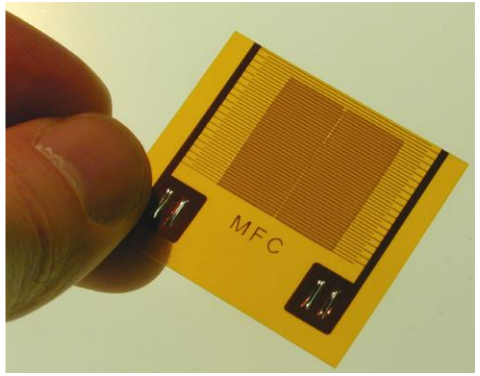


Marzencki et al.

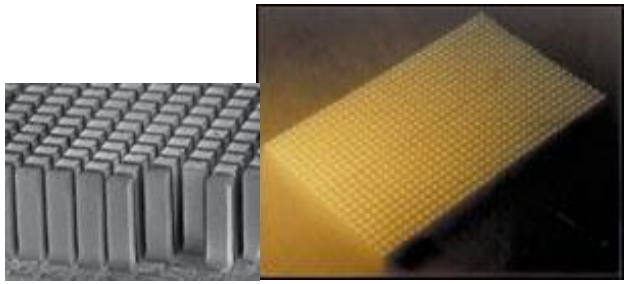


Thin films
(early 2000)

Monocristals
(early 2000)



Macro Fibre Composites
(1993) [Wil04]



Piezocomposites (early 90's)

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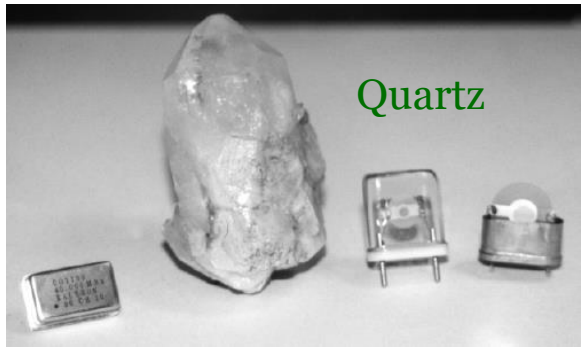
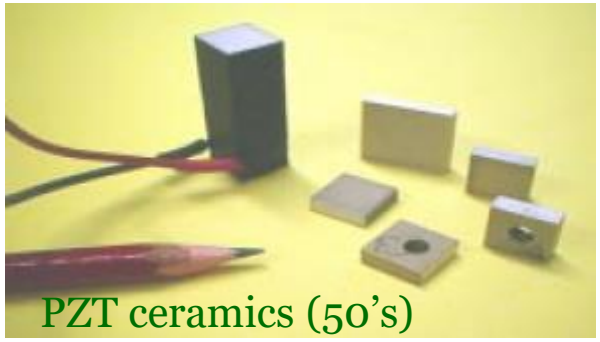
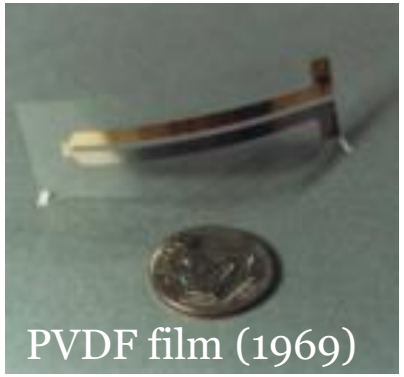
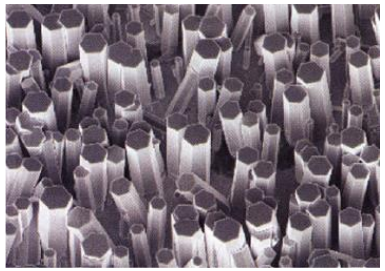
Piezoelectric materials

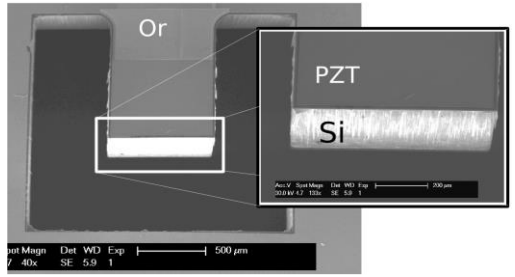








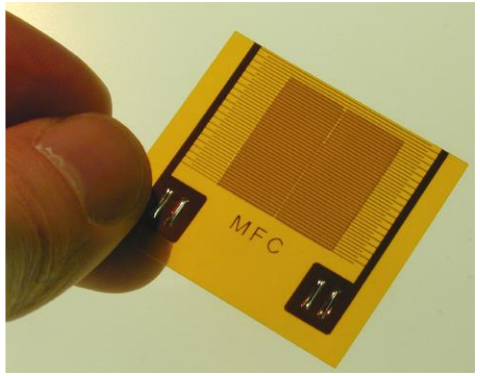
Nanowires (2006)



Marzencki et al.

Thin films (early 2000)

Monocristals (early 2000)



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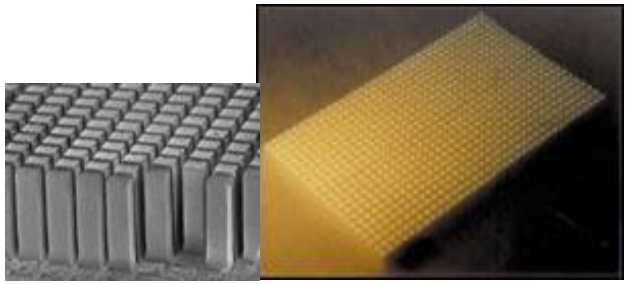


Piezocomposites (early 90's)

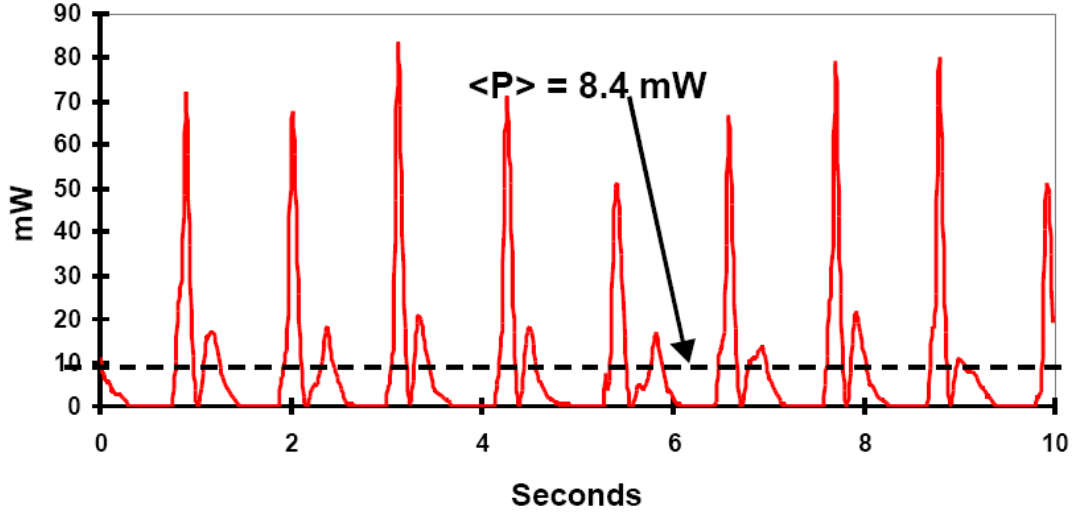
Material	Quartz	$PbTiO_3$	$BaTiO_3$	PZT	MFC	PVDF	PZN-9PT	AlN	KNN
d_{33} (10^{-12} m/V)	2,3	120	90	300 à 700	400 (PZT-5A : 440)	30	2500	7	200

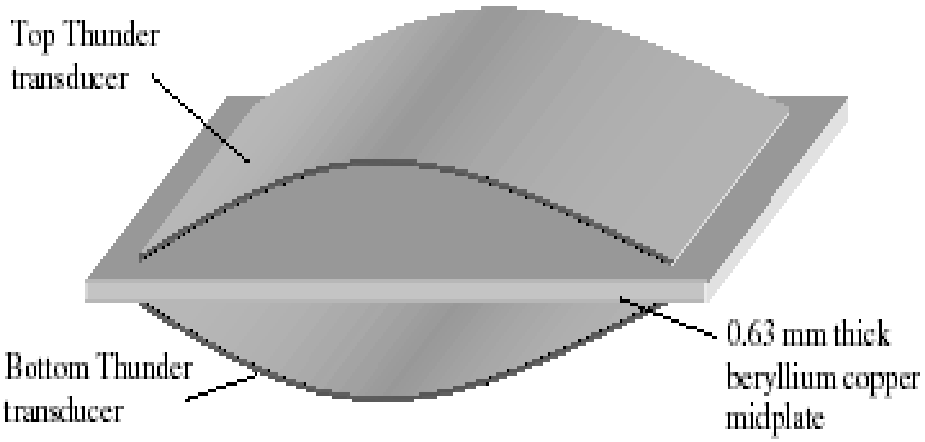
Mechanical energy harvesting

Example: Human power – shoe insert (Shenck, MS Thesis, 1999)

- 2 THUNDER (76×51×0.635mm^3) PZT unimorphs connected in parallel and mounted on opposing sides of a Be-Cu backplate
- 8.4 mW at 0.9 Hz into 500 kΩ

Power delivered to a 500 kW resistor





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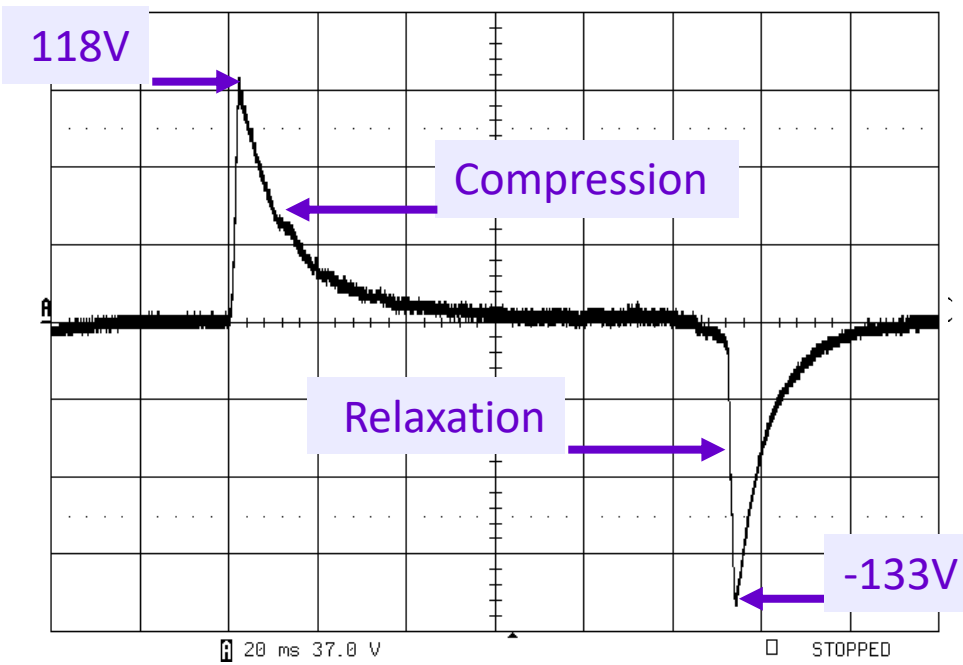
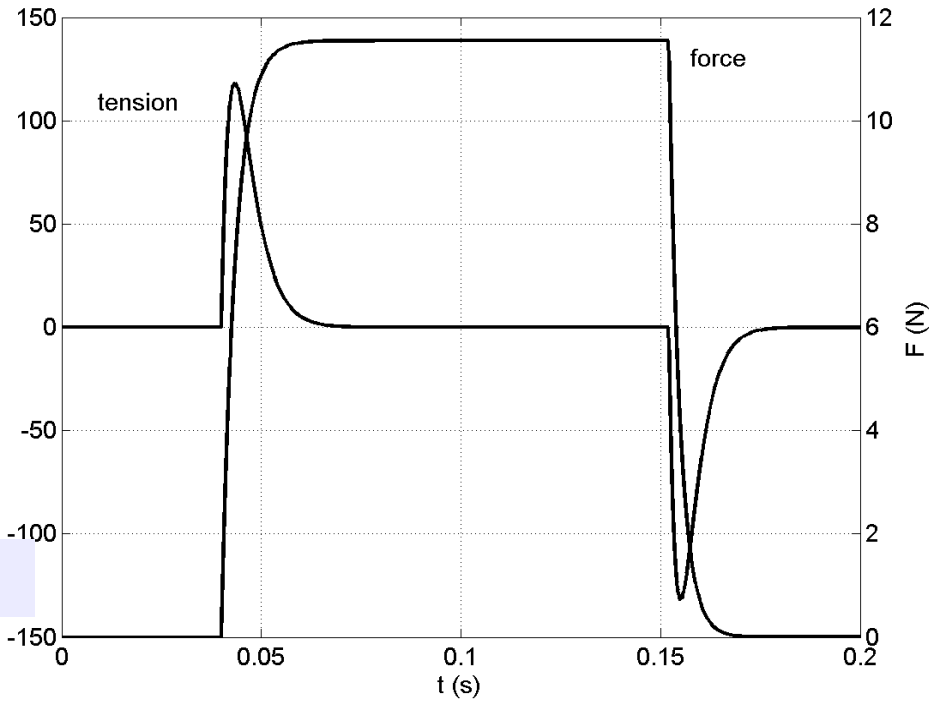
Output of a piezoelectric rod when submitted to a slow compressive stress

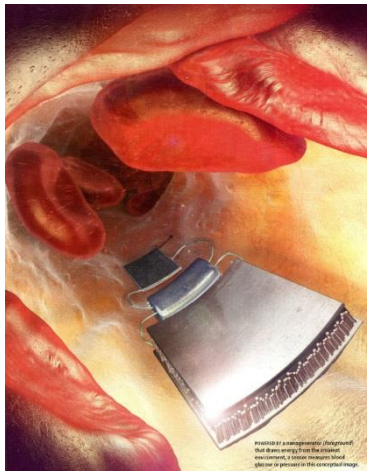


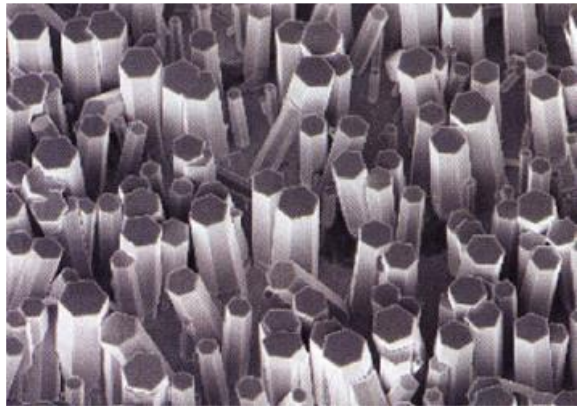


3mm×3mm×1cm PZT ceramic rods

Poulin G. et al., 9th Internat. ELECTROCERAMICS 2004

Piezo-semiconducting nanowire based nanogenerators





Z. L. Wang and J. Song, Science 312 (2006) 242-246

Wang, Georgia Tech :

ZnO nanowires

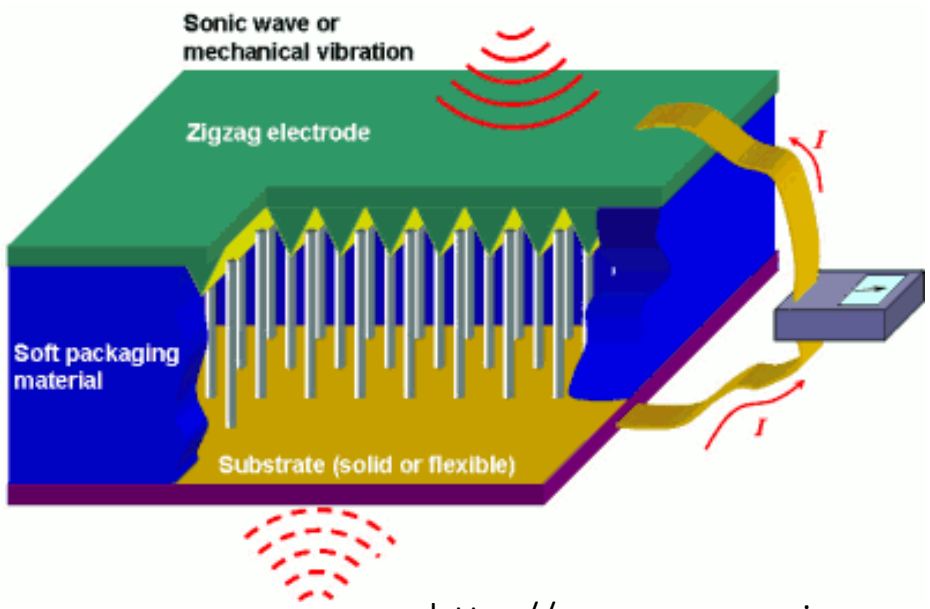
∅ = 0.03 to 0.10 µm

L = 1 to 3 µm

6 mm^2 device

→ 10 mV, 800 nA

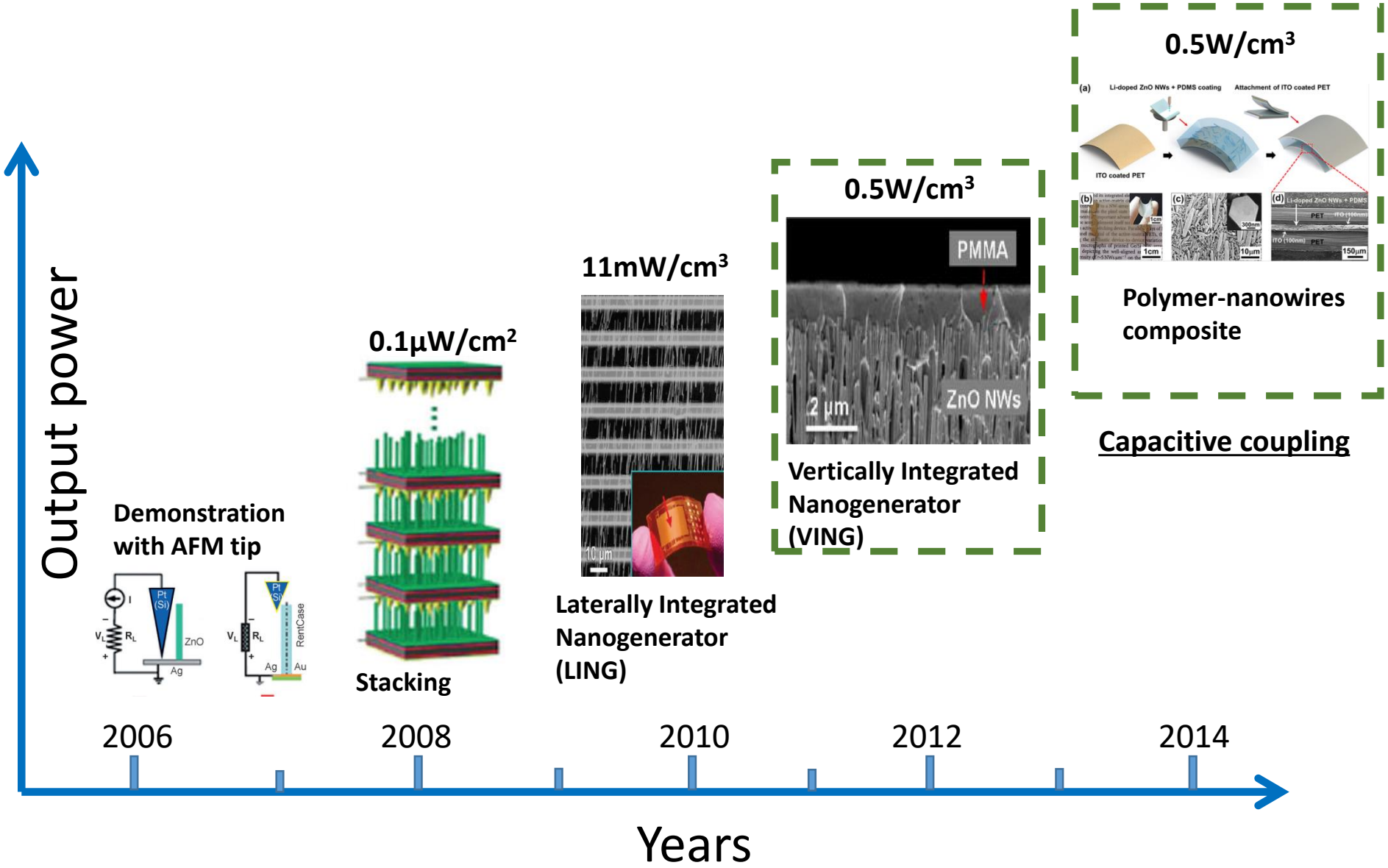
→ power of a few nW



http://www.nanoscience.gatech.edu/

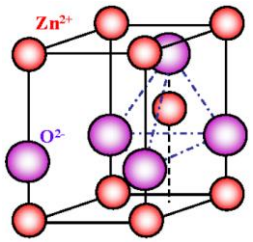
Piezo-semiconducting nanowire based nanogenerators

History

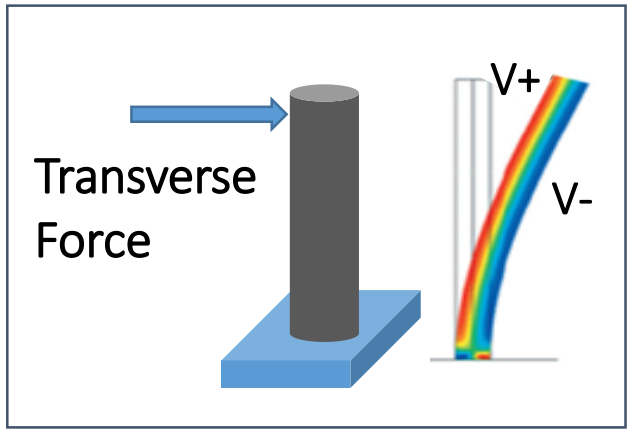


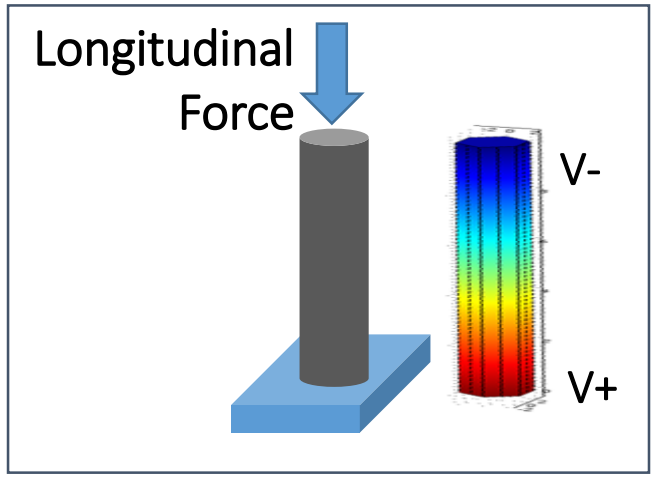
Adapted from ZL Wang et al., Angew. Chem. Int. Ed. 51 (2012) 2–24

Piezo-semiconducting nanowire based nanogenerators



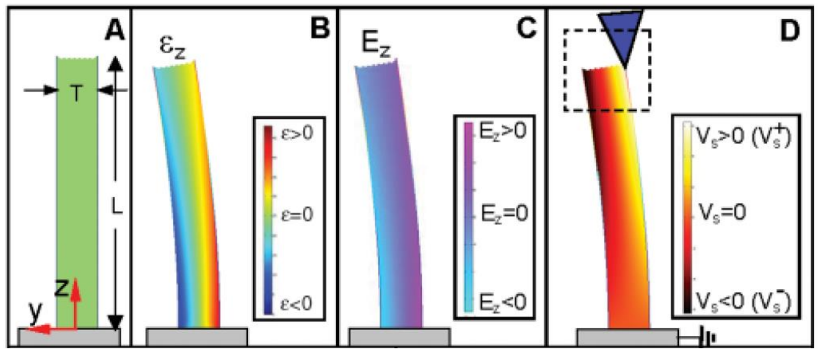
Owing to non-center symmetric crystal structure of the wurtzite semiconductors, **piezo polarization direction is parallel to c axis.**





<u>Mechanical excitation modes:</u>
2 main modes, or a combination of both

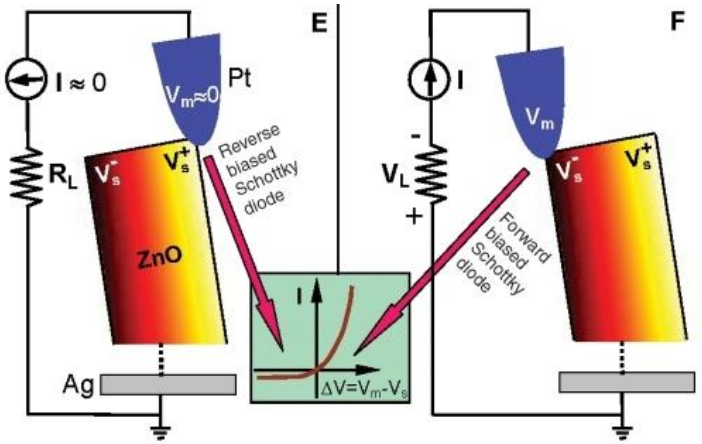
<u>Electrical configurations:</u> Schottky contact or capacitive coupling



Strain

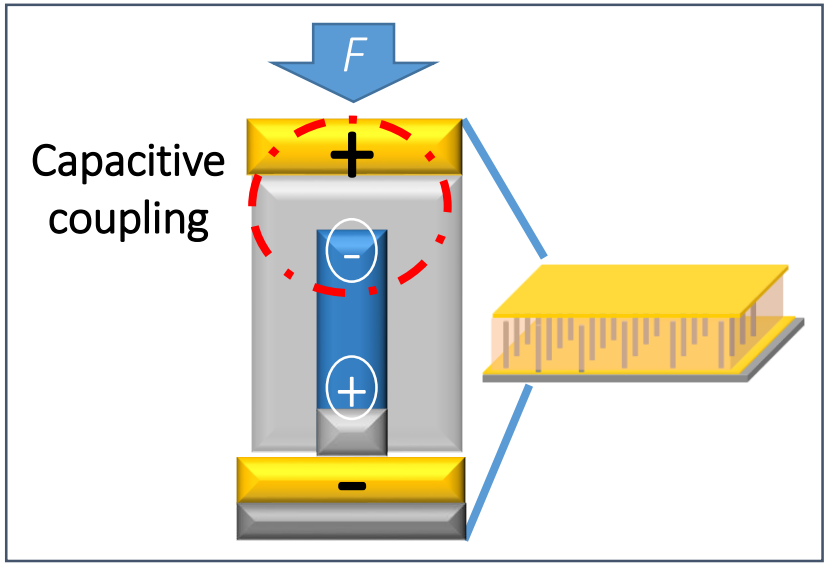
Electric field

Electric potential



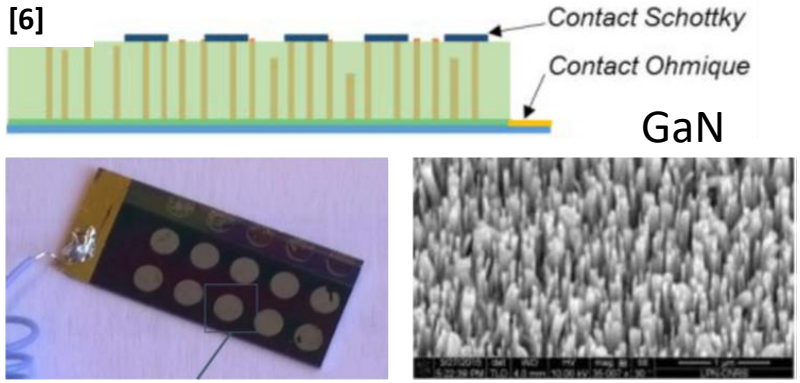
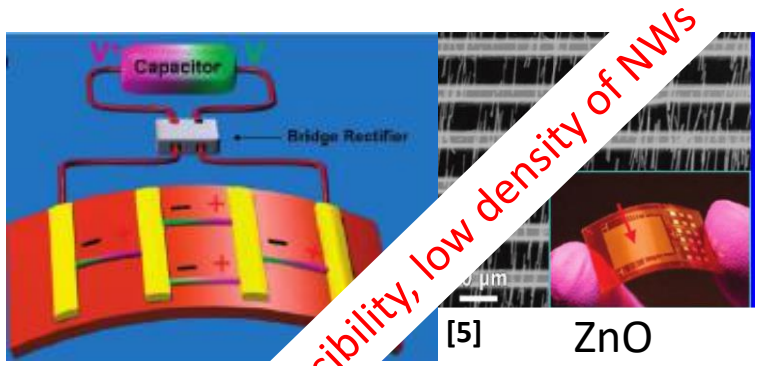
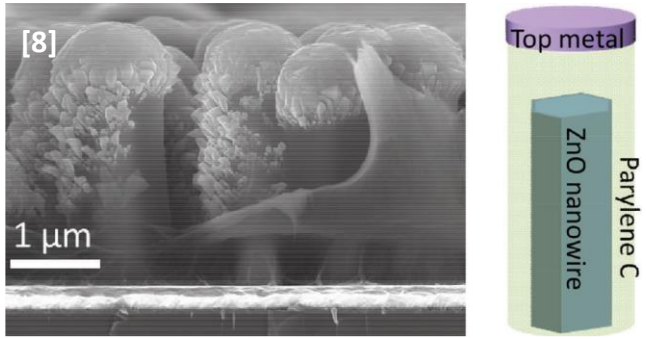
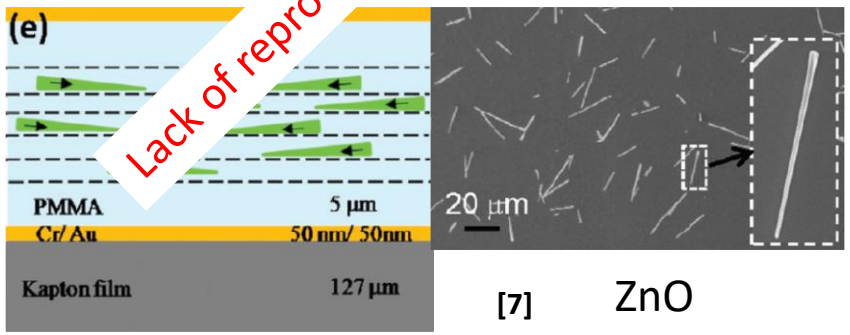
AFM excitation principle
Schottky contact between metal tip and NW

Z. L. Wang et al. Science (2006)
doi:10.1126/science.1124005



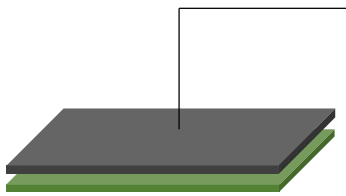
Piezo-semiconducting nanowire based nanogenerators

A **NW array** embedded in a polymer matrix, between electrodes and on a rigid or flexible substrate. Various configurations :

	NWs orthogonal to the substrate	NWs parallel to the substrate
Electrodes are in contact with the NWs	[6]  GaN	 [5] ZnO Lack of reproducibility, low density of NWs
Capacitive coupling between NWs and electrode via insulating layer	 ZnO	 [7] ZnO

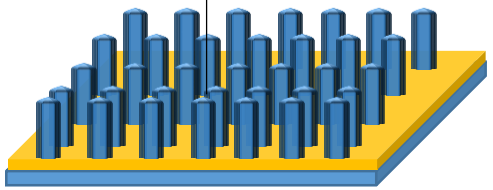
Nanogenerators structure

Wish list



Top contact

Polymer matrix



ZnO NWs

✓Highly orientated along polar axis

✓Strong NW adhesion to substrate

✓High quality ZnO NWs : intensive research on how to decrease the intrinsic N-type doping of ZnO NWs (usually $10^{18}cm^{-3}$) by 1 or 2 decades

✓ If flexible substrate : low temperature process

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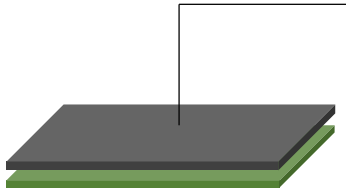
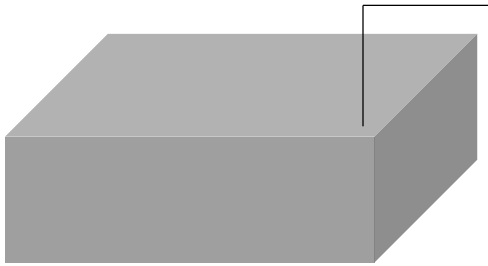
Nanogenerators structure

Wish list

Top contact



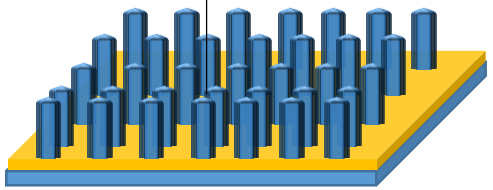


Polymer matrix

- ✓Fully conformal
- ✓Strong adhesion
- ✓Simple deposition
- ✓Allow NWs to flex

Examples:
PMMA deposited by spin-coating
Parylene C deposited by CVD (Chemical Vapor Deposition)

ZnO NWs



Nanogenerators structure

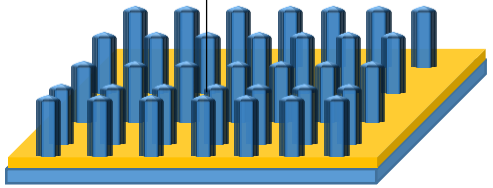
Wish list

Top contact

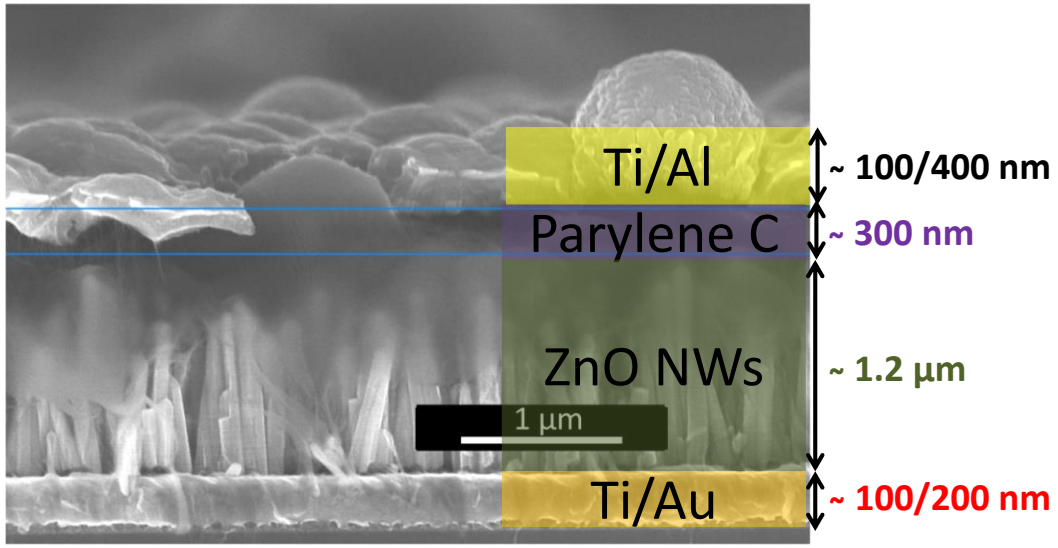
- ✓Good adhesion on polymer
- ✓Electrically conductive
- ✓Mechanically robust
- ✓Flexible if the whole NG is ⇨ research on flexible electronics

Example:
Ti/Al electrode deposited by sputtering

Polymer matrix



ZnO NWs



Dahiya, et al., Adv. Mat. Tech. (2017) 1700249

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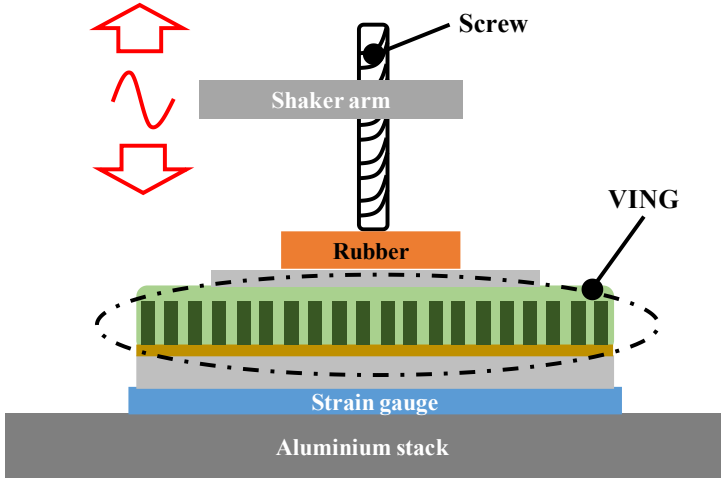
Nanogenerators functional characterization

Example of dedicated test benches

Test bench in compression [1]

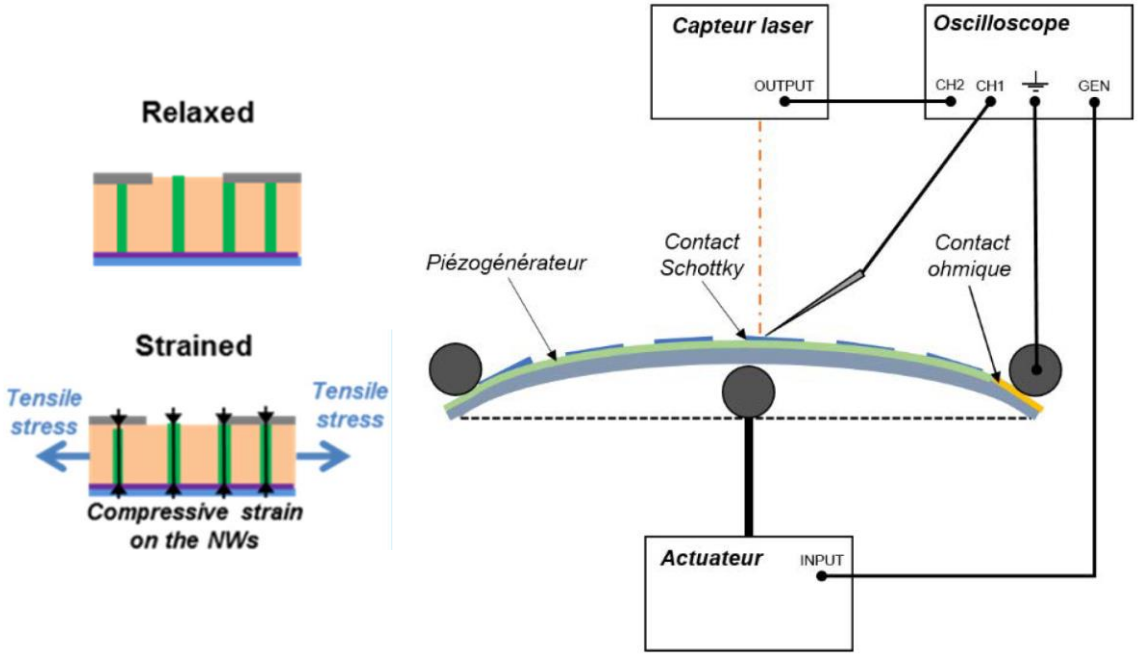


- **Compressive force** in contact or impact mode
- Voltage measured via a high input impedance circuit

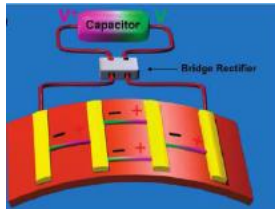
[ex: Nadaud et al. Appl. Phys. Lett. 112 (2018) 063901]

- Variable resistive load

Test bench in flexion [2]



- **Bending force** but the force seen by NWs depends on their orientation and environment (properties of the substrate and encapsulating layer)



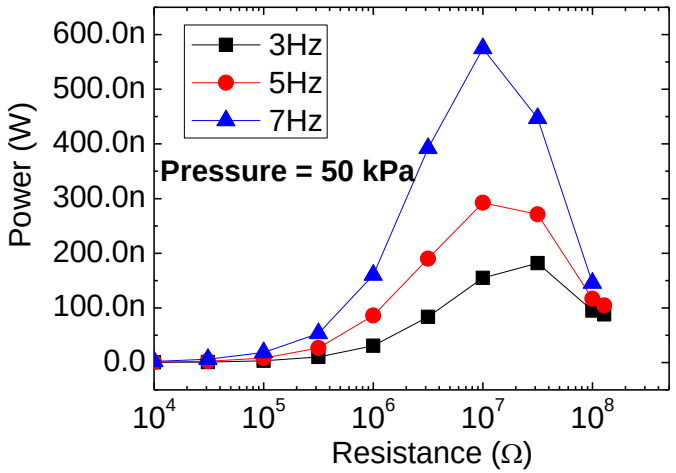
G. Zhu et al., Nano Lett. 2010, 3151-3155

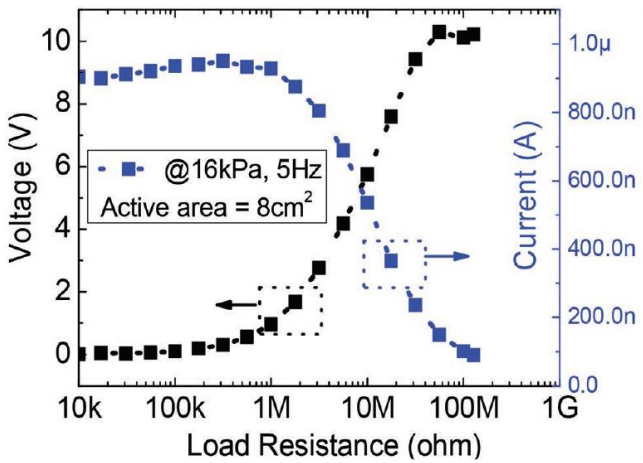
[1] A. S. Dahiya, et al., Adv. Mat. Tech. (2017) 1700249
[2] N. Gogneau et al., Semicond. Sci. Technol. 31 (2016) 103002

Nanogenerators functional characterization

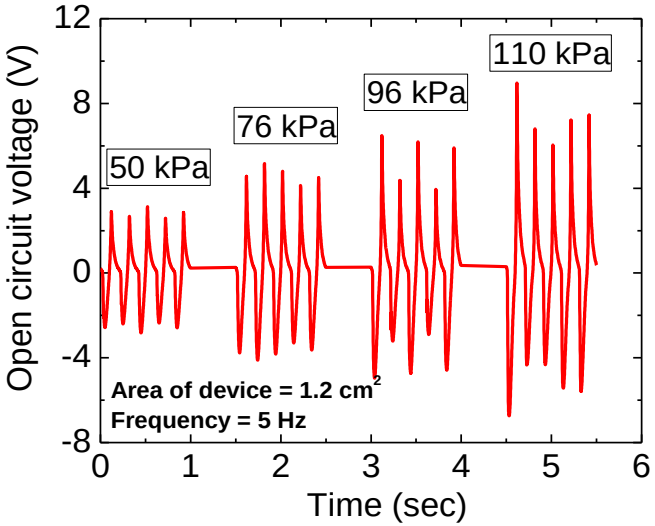
Typical output characteristics

Power vs load resistance

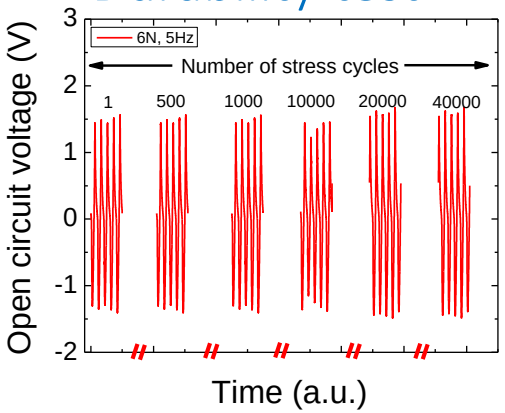




Varying compressive Force



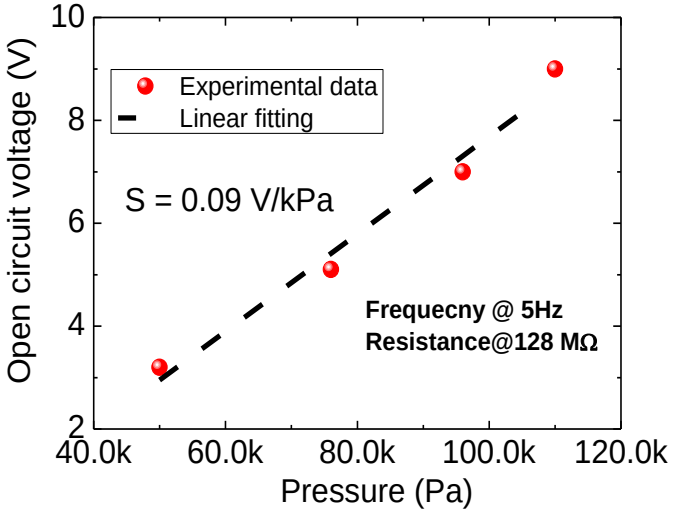
Durability test



- Pressure sensitivity in V/kPa

And for a given force (shape, frequency, amplitude):

- Short circuit current and open circuit voltage
- Output peak power @ given load
- Average peak power @ given load

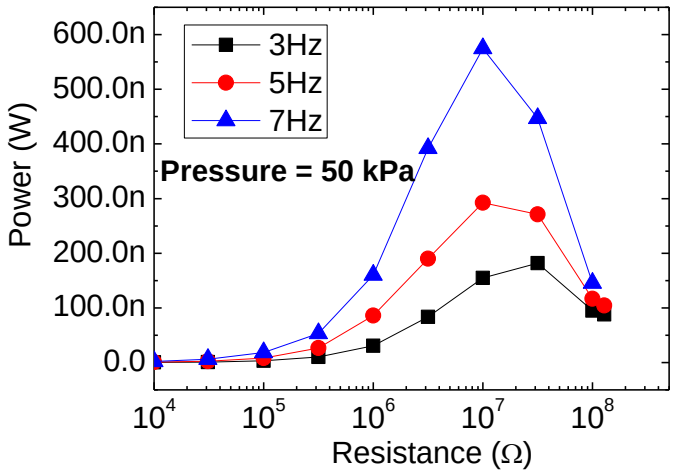


A. S. Dahiya, et al., Adv. Mat. Tech. (2017) 1700249

Nanogenerators functional characterization

Typical output characteristics

Power vs load resistance



Under a defined mechanical excitation:

V_{peak} (V)	$V_{RMS\ (max)}$ (V)	$I_{sc\ (RMS)}$ (nA)	$P_{av\ (max)}$ (nW)	W (nJ)	R_{opt} (MΩ)
3.9	1.8	15	29	5.8	>100
6.8	2.7	28	64	12.8	>100

RMS and average values should be prefered to peak values

To move toward standardization!

- Pressure sensitivity in V/kPa

And for a given force (shape, frequency, amplitude):

- Short circuit current and open circuit voltage
- Output peak power @ given load
- Average peak power @ given load

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Nanogenerators performances

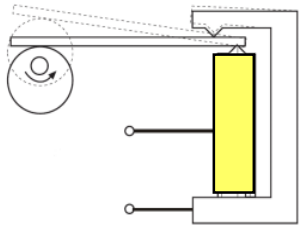
✓ Large variety of mechanical testing conditions (compression, bending)

✓ Mostly under compression:

1-10 µW/cm² @ a few N force

@ 0.3 to 5 Hz

[S. S. Indira et al., Nanomaterials 9 (2019) 773]

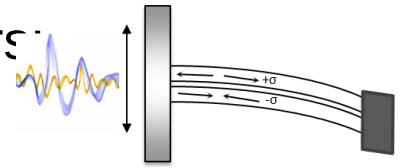


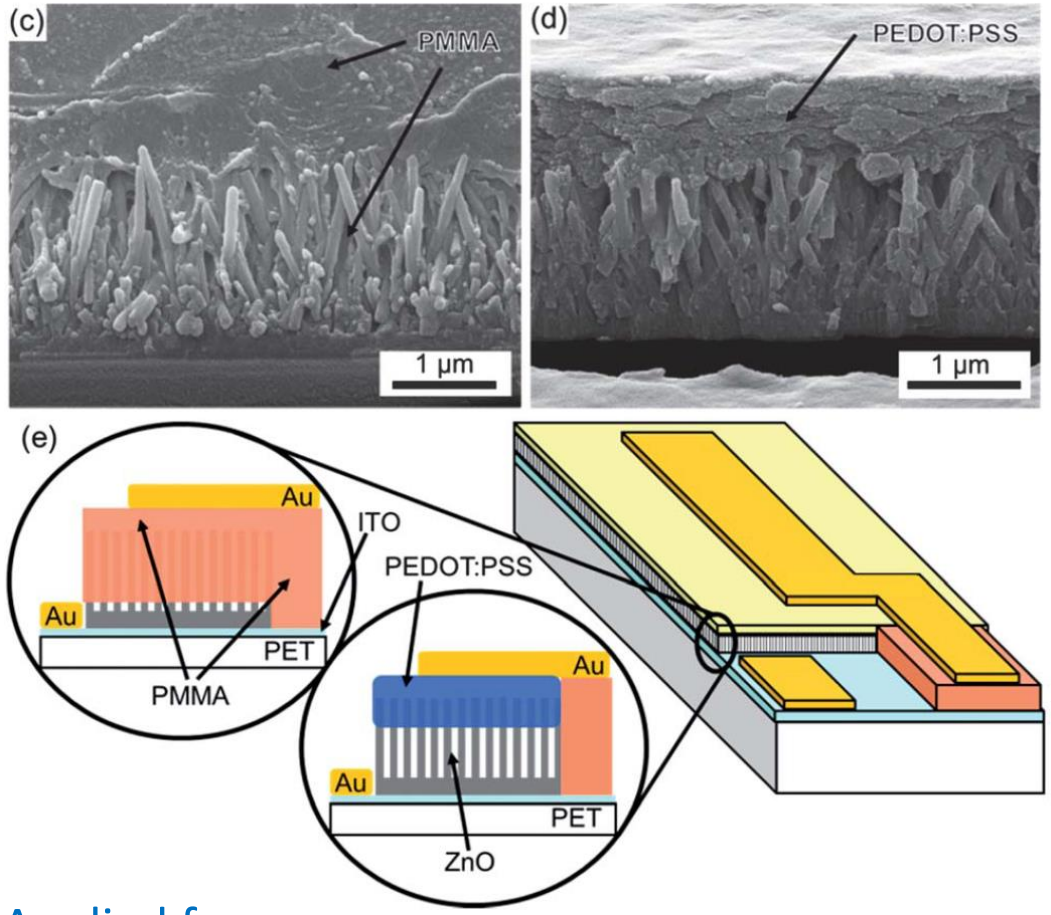
✓ Comparison with bending cantilevers:

10^{-3} to 10 µW/(cm².Hz.g²)

(base of a machine tool : 10 m/s² ≈ 1g)

[S. Priya et al.,Energy Harvesting and Systems 2017; 4(1): 3–39]





Applied force:
Bending at 1Hz
0.9ms^{-2}

Energy: **40nJ/cm²** per cycle
Average power **5µW/cm²**

J. Briscoe et al., Energy Environ. Sci. 6 (2013) 3035

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Nanogenerators: how to choose the right material?

- ✓ Large literature on ZnO nanowires /nanorods grown by **chemical or physical methods**

H. D. Espinosa et al., Adv. Mater. 24 (2012) 4656-4675
A. J. L. Garcia, M. Mouis, V. Consonni, G. Ardila, Nanomaterials, 11(4) (2021) 941

- ✓ Other piezo materials with various synthesis methods: **GaN, PZT, CdS, CdSe, PVDF** (electro-spinning)…

Effect of nanostructuration:

Matériau	Matériau massif (expérimental)		Echelle nanoscopique (expérimental)	
	d_{33} (10^{-12} m/V)	E (GPa)	d_{33} (10^{-12} m/V)	E (GPa)
ZnO	9.93	164	14-26.7	100
GaN	1.86	397	12.8	43.9
PZT	650	N/A	101	46.4-99.3
PVDF	-25	N/A	-38	0.39

R. Hinchet et al., In IEEE 2012 Int. Electron Devices Meeting, 6.2.1-6.2.4
E. L. Perez, PhD Univ. Grenoble Alpes (2016)

Nanogenerators: is there a figure of merit?

✓ **Figure of merit:** a numerical expression based on one or more characteristics of a device, material or procedure, that represents its performance or efficiency

$$FoM = \frac{d_{31}^2}{\varepsilon_{33} tan\delta} = \frac{d_{31} g_{31}}{tan\delta}$$

From S. Priya, IEEE Trans. Ultrason. Ferro. Freq. Control 57(12) (2010) 2610-2612

Material	**Bulk**				**Nano**			
Property	d31 [m/V]	epsilon33r	tan(delta) [%]	FoM [1e-12]	d31 [m/V]	epsilon33r	tan(delta) [%]	FoM [1e-12]
PZT	-2,30E-10	2900	2	108	-3,83E-11	2900	2	3
PVDF	3,98E-12	6,8	20	1	6,05E-12	6,8	20	3
ZnO	-5,43E-12	12,6	1	26	1,4E-11	12,6	1	176
GaN	-1,50E-12	8,9	1	3	1,28E-11	8,9	1	208

⇨ Low permittivity can benefit to materials having lower piezo coefficients.

Downscaling does not have the same effect for all materials!

✓ But: established on specific quasi-static mechanical cycle…

… and is it applicable to nanomaterials?

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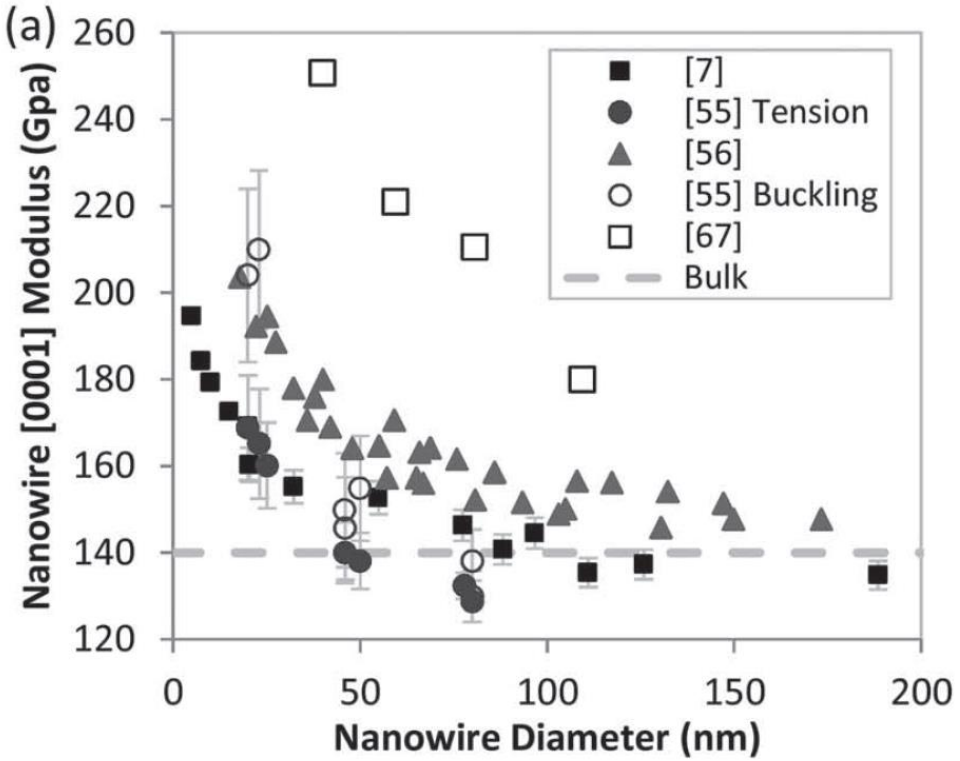
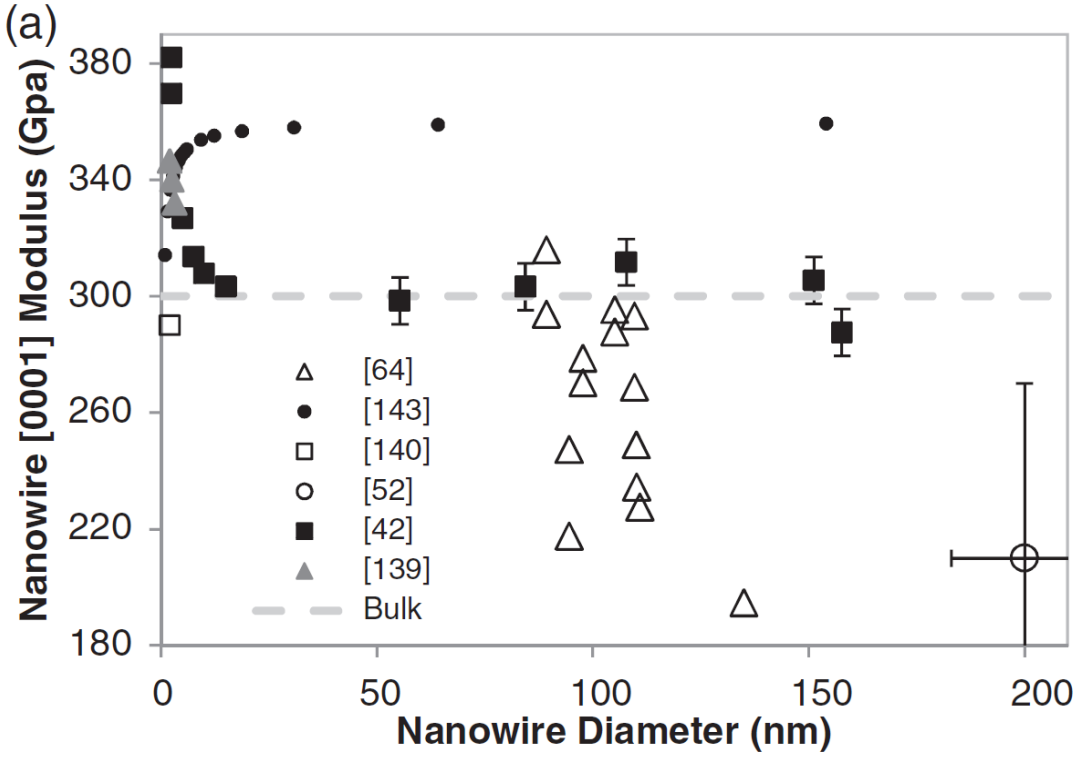
Nanomaterials properties

- Higher mechanical properties: Young modulus

ZnO



GaN

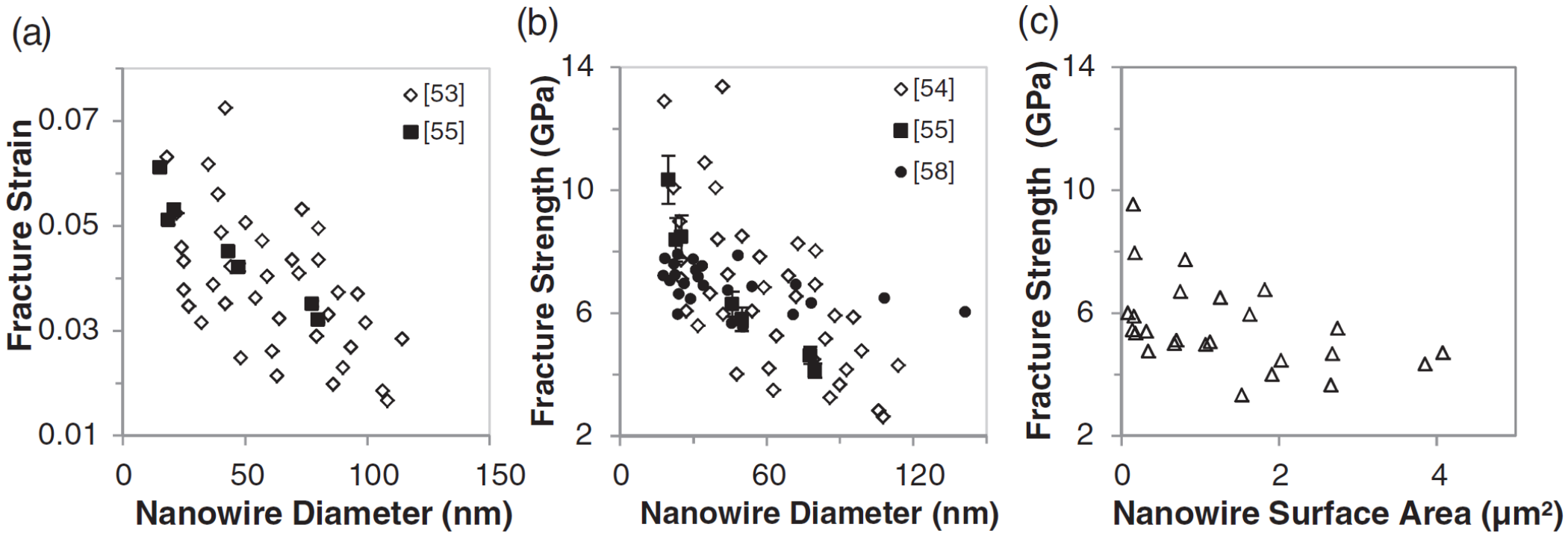


Experimental / Review: H. D. Espinosa et al., Adv. Mater. 24 (2012) 4656-4675

Nanomaterials properties

- Higher mechanical properties: Young modulus, fracture strength

ZnO



Experimental / Review: H. D. Espinosa et al., Adv. Mater. 24 (2012) 4656-4675

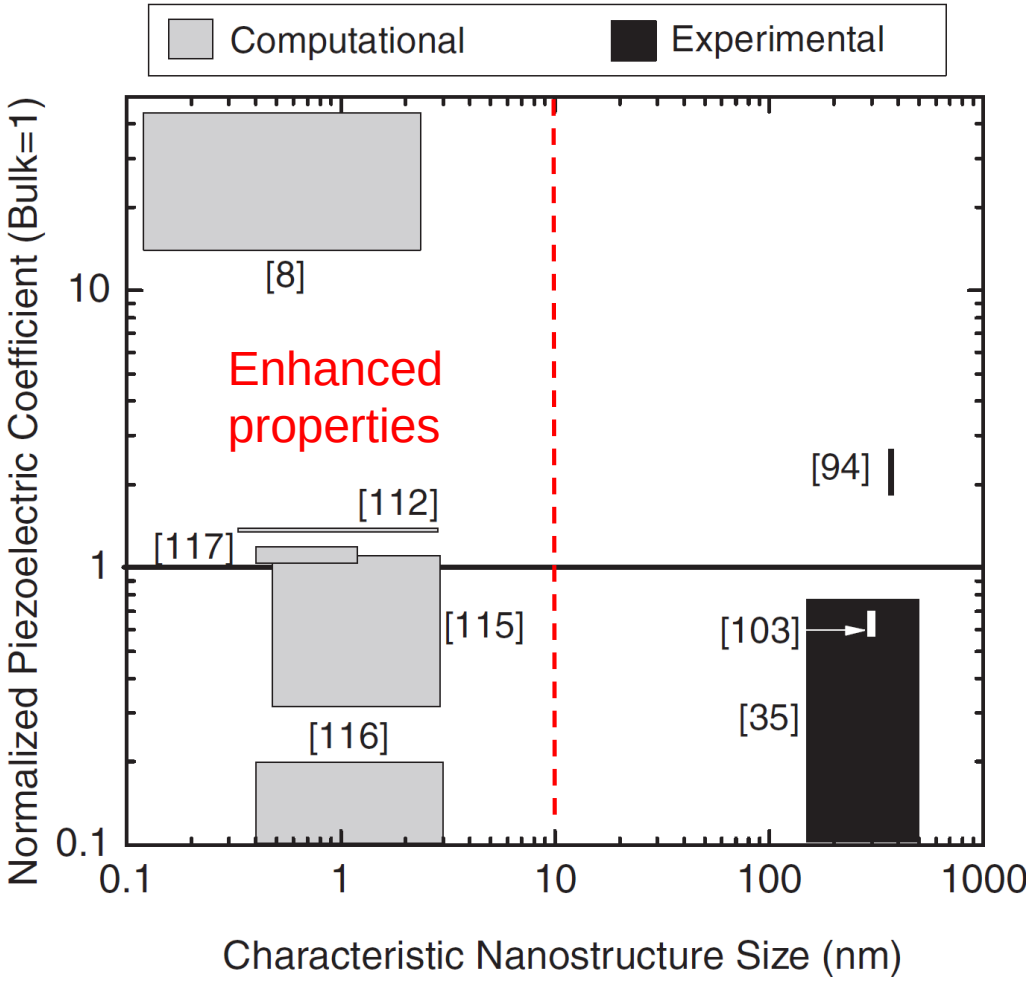
Nanomaterials properties

- Higher mechanical properties: Young modulus, fracture strength
- Exhalted piezoelectric coefficients at smallest diameters ⇨ Higher sensitivity to deformation without plastic damage

ZnO

Piezoelectric coefficients (experimental and computational) for different characteristic sizes.

Values are normalized with respect to the corresponding value for bulk ZnO, indicated by a horizontal line.

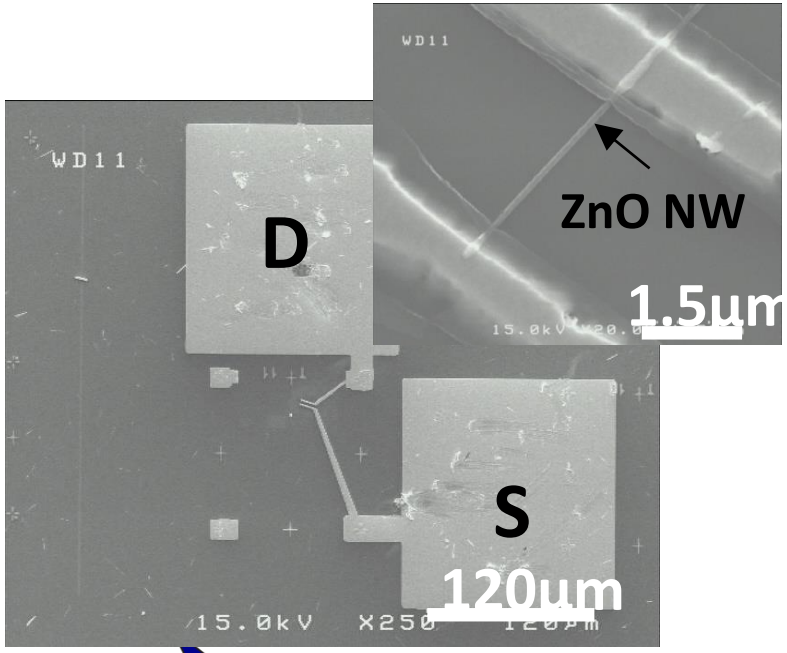


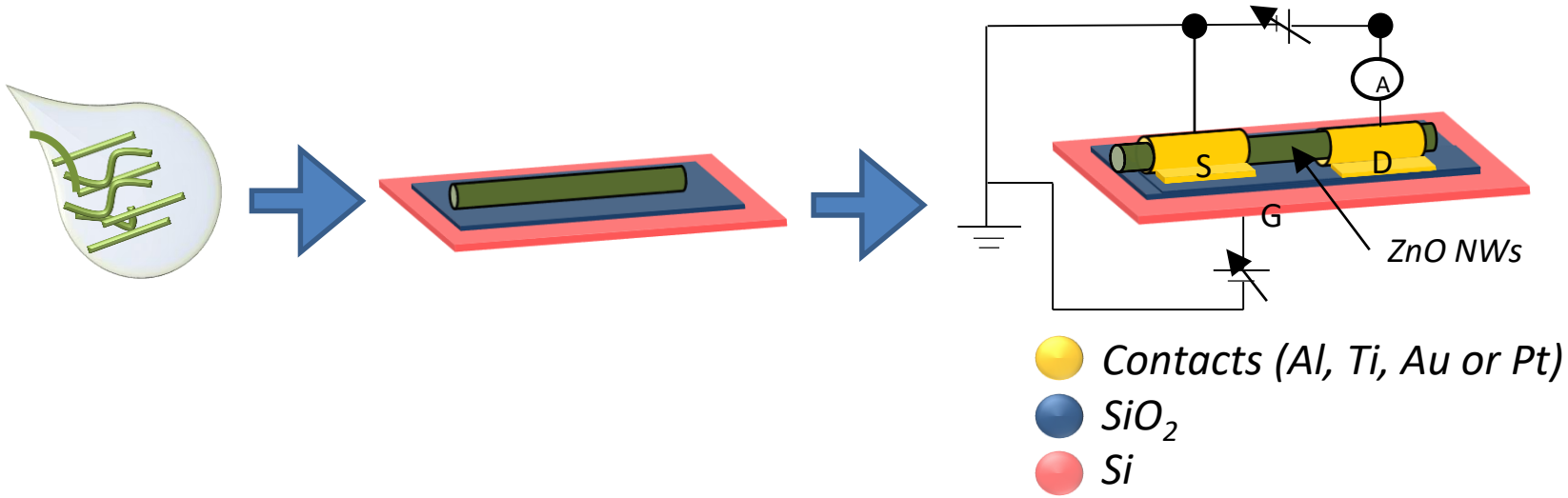
H. D. Espinosa et al., Adv. Mater. 24 (2012) 4656-4675

Piezo-semiconducting nanowires characterisation

- Experimental evaluation of **mechanical, electrical and piezoelectric properties** of NWs by dedicated methods

Electrical properties: single nanowire based Field Effect Transistors characterization





A way to evaluate the free charge carriers density in the NWs:

- Carrier transport type (p- or n-type?)
- Carrier concentration & Mobility

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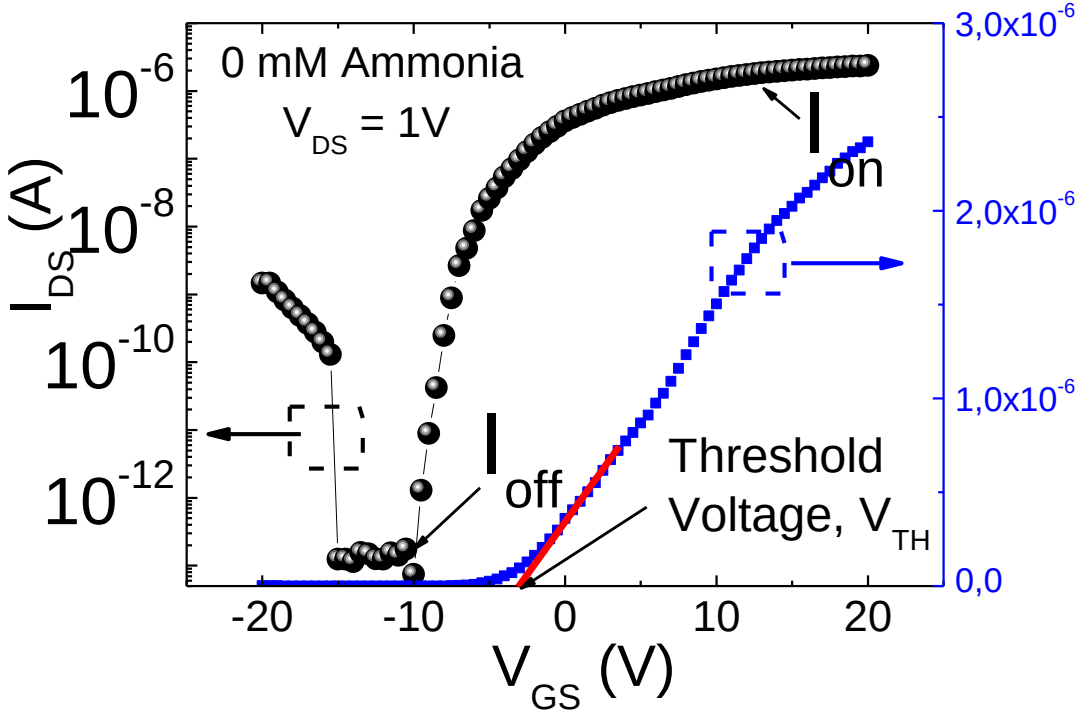


$$n_e \approx \frac{C_{NW} V_{TH}}{2\pi r^2 L}$$

n_e : free charge carriers density
C_{NW} : channel capacitance (nanowire)
V_{TH} : threshold voltage
r : nanowire radius
L : channel length

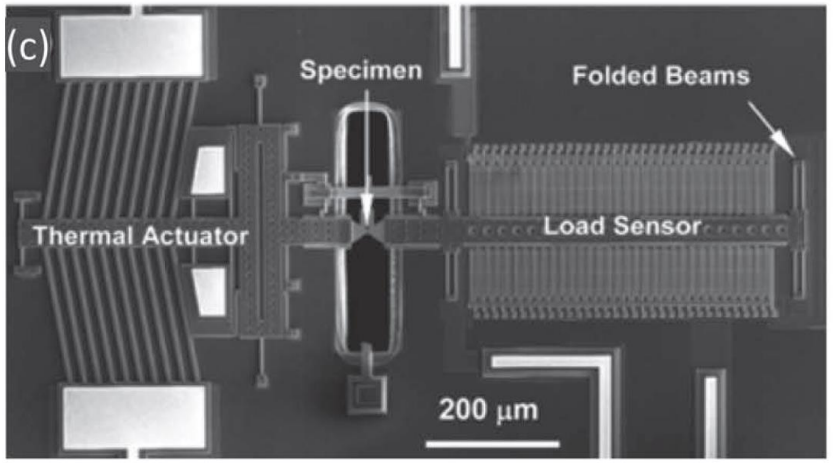
C. Opoku et al., RSC Adv., 2015, 5, 69925–69931

Piezo-semiconducting nanowires characterisation

- Experimental evaluation of **mechanical, electrical and piezoelectric properties** of NWs by dedicated methods

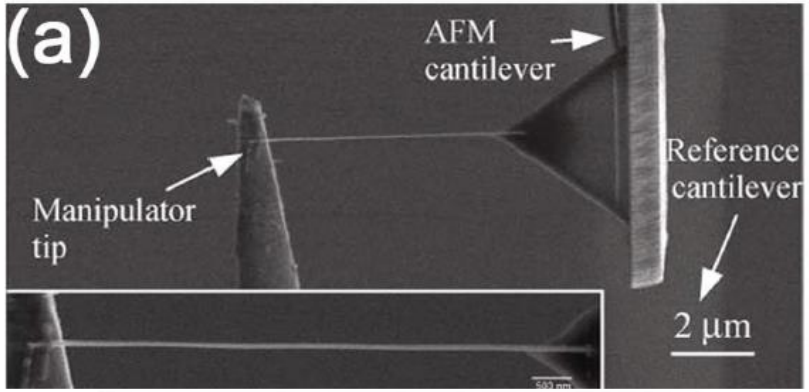
Mechanical properties

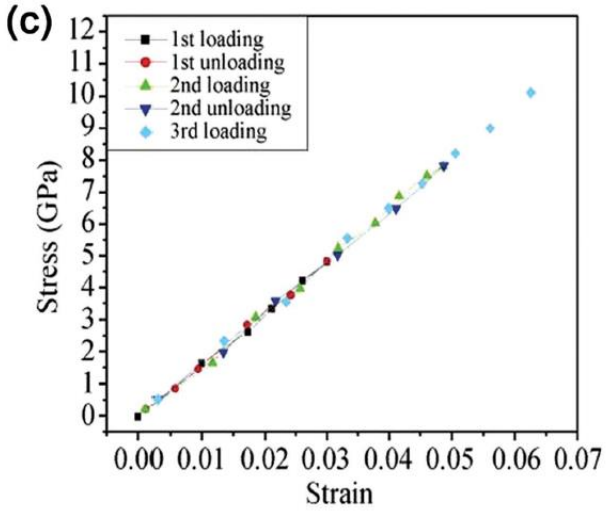
In situ TEM experiments and MEMS testing platform coupled with atomistic simulations



R. Agrawal et al., Nano Lett 2008, 8, 3668-3674

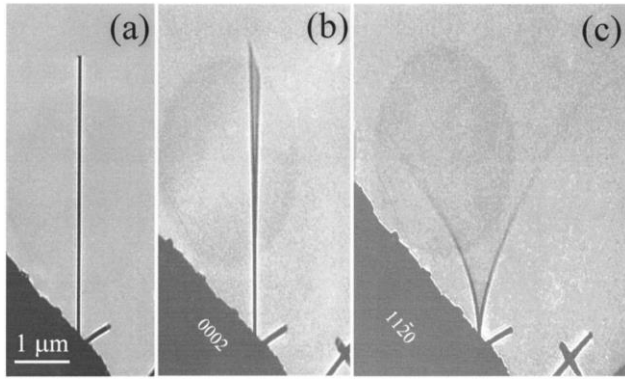
Nanowire loading (tension or buckling) by AFM cantilever and micromanipulator





S. Wang et al., Adv. Science 4 (2017) 1600332

In situ TEM and micromanipulator to measure the NW resonance frequency



X D. Bai et al., Appl. Phys. Lett. 82 :4806, 2003.

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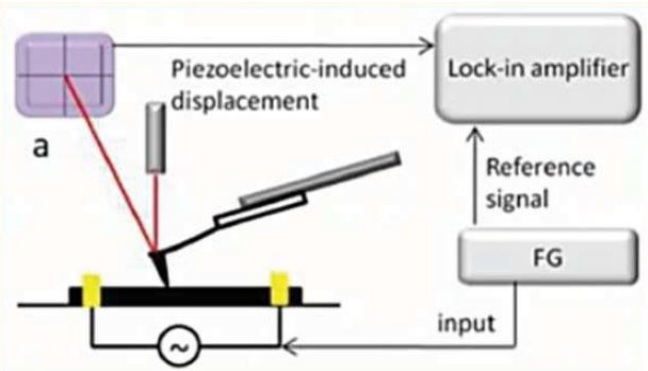
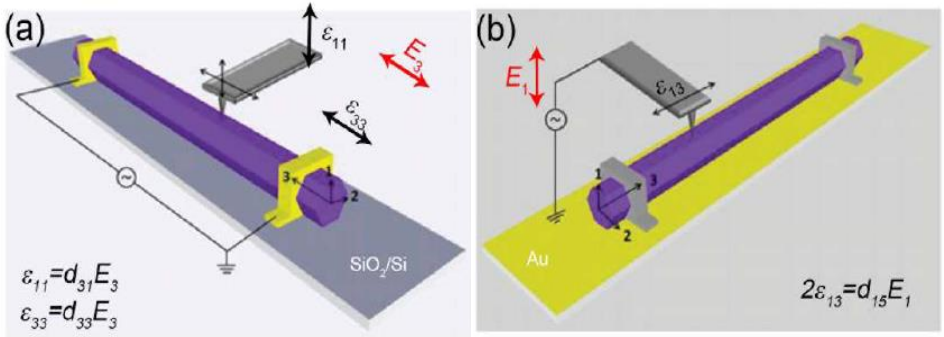
Piezo-semiconducting nanowires characterisation

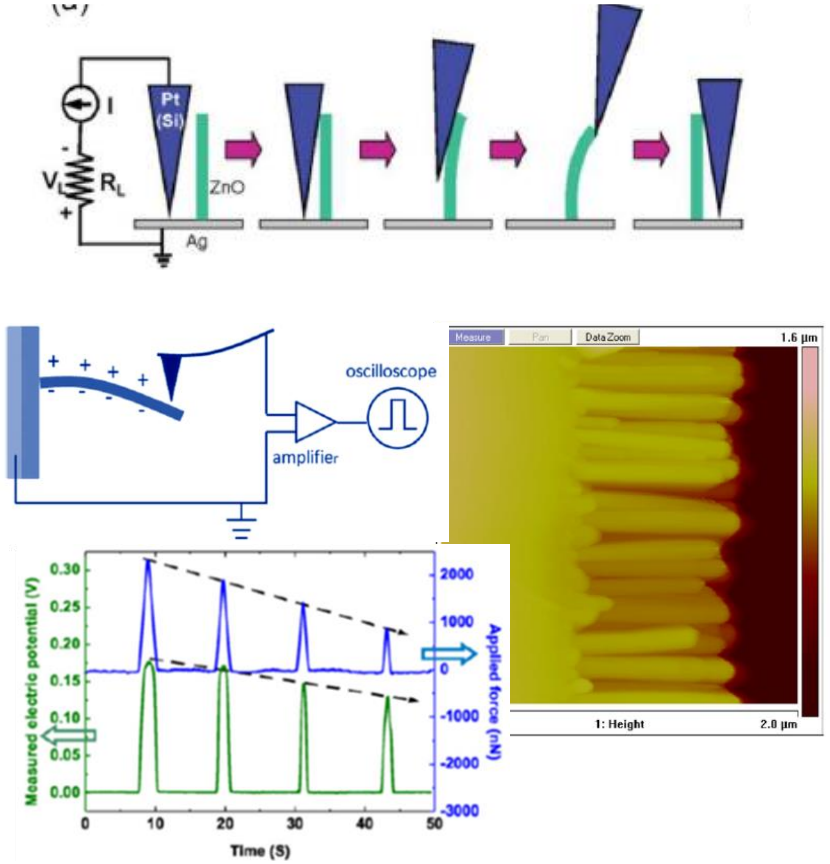
- Experimental evaluation of **mechanical, electrical and piezoelectric properties** of NWs by dedicated methods

Piezoelectric properties





M. Minary-Jolandan et al., NanoLett. 12 (2012) 970-976



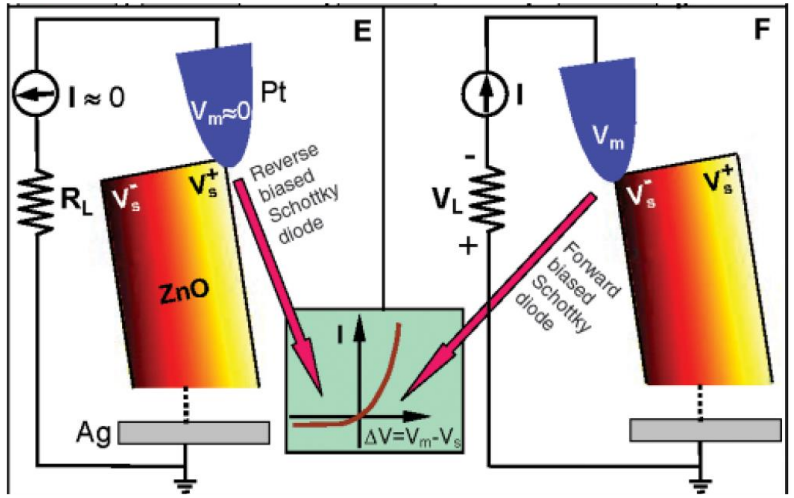
Z.L. Wang, Science 2006; X. Xu et al. , Nanotechnology 22 (2011) 105704 (8pp)

Piezo-semiconducting nanowires characterisation

- Experimental evaluation of **electromechanical conversion properties** of NWs

AFM with electrical module: The main used technique to characterize NWs as energy harvesters

Measurement based on Schottky diode which regulates the charge flow
⇒ NW bending/releasing creates an alternating flow of charges in the external circuit.



Z. L. Wang et al. Science (2006)
doi:10.1126/science.1124005

Schottky diode influenced by material characteristics

- ❖ Semiconductor material polarity
- ❖ Type of doping
- ❖ Applied deformation

Schottky diode influences the energy harvesting efficiency

Nano-contact effects

N. Gogneau et al. Semicond. Sci. Technol. 31 (2016) 103002
N. Jamond et al., Nanoscale, 9 (2017) 4610-4619

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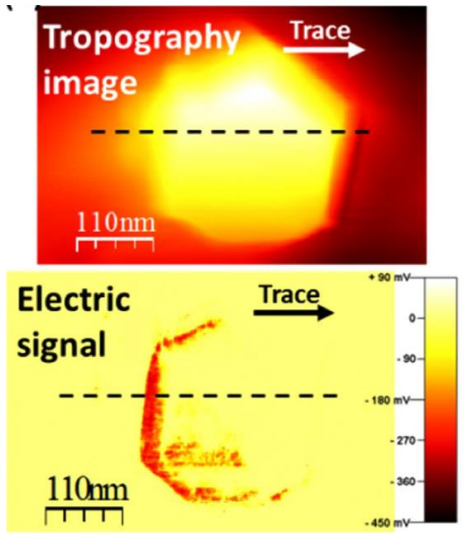
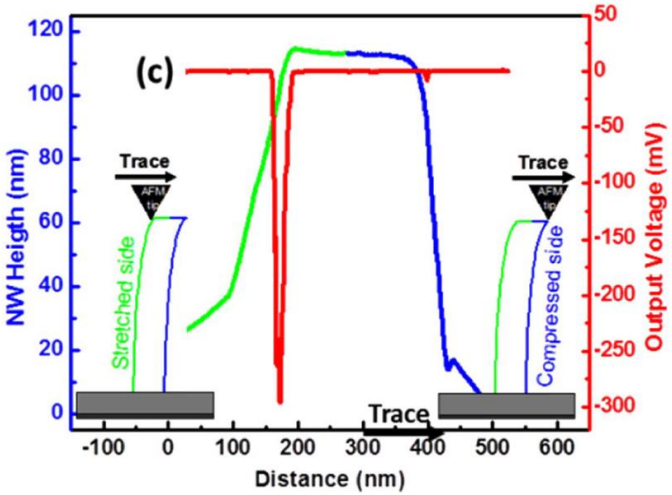
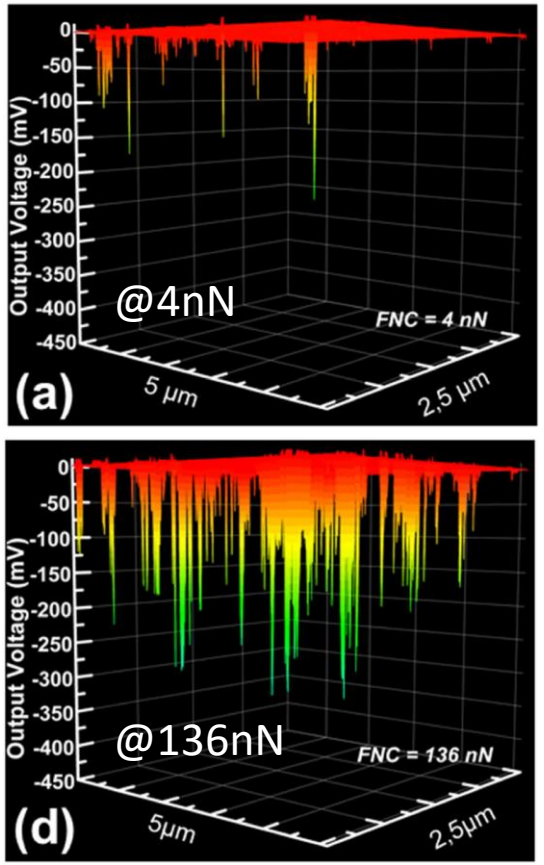
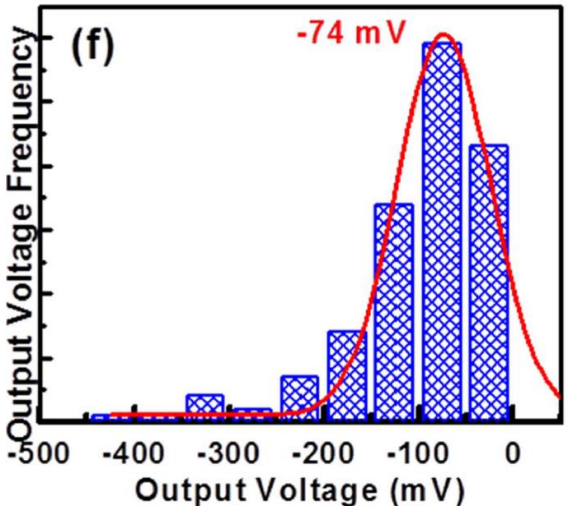




Topographic image and electric signal



2D mapping @ different forces



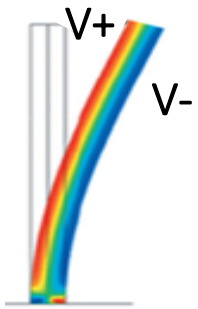
Statistical study

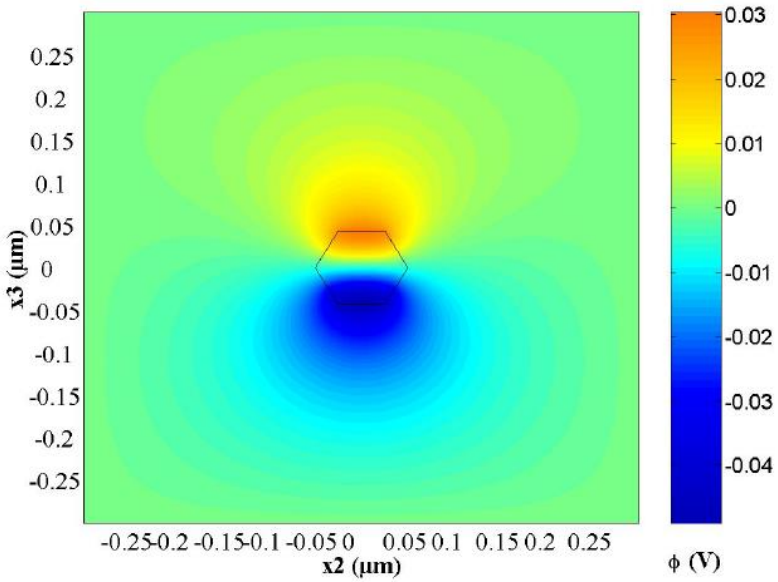
N. Gogneau et al., Semicond. Sci. Technol. 31 (2016) 103002

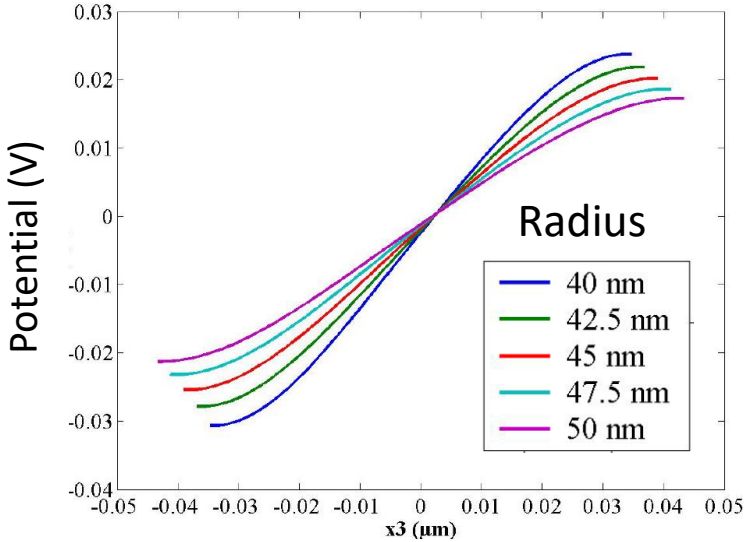
Nanogenerators: parameters of influence

NW should have: High aspect ratio

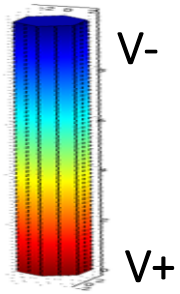
Transverse Force

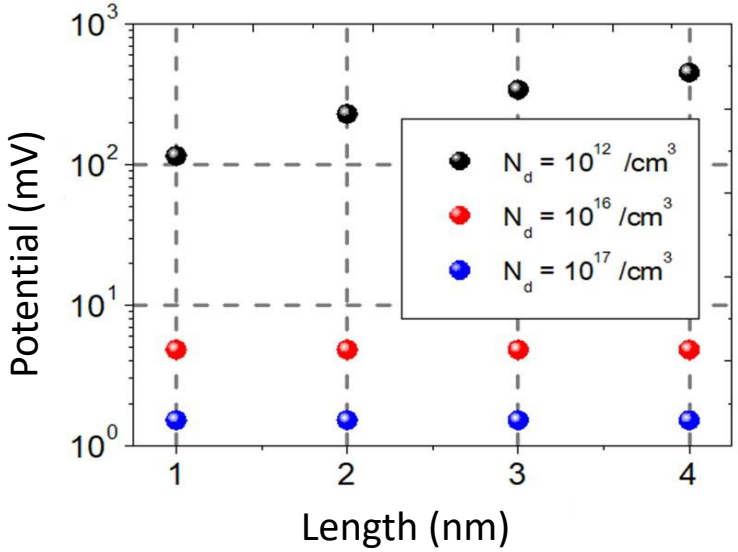


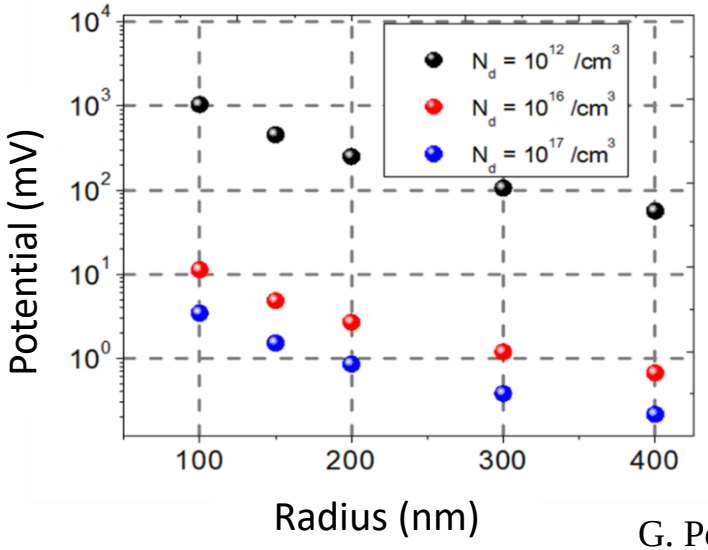




Longitudinal Force







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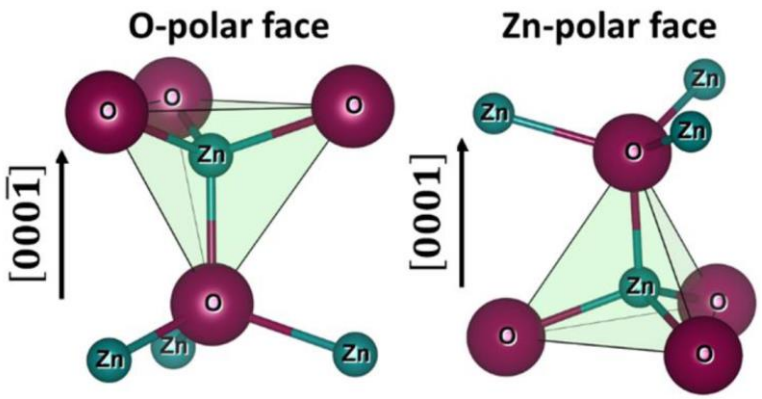
G. Poulin-Vittrant

Nanogenerators: parameters of influence

NW should have: Uniform polarity

ZnO

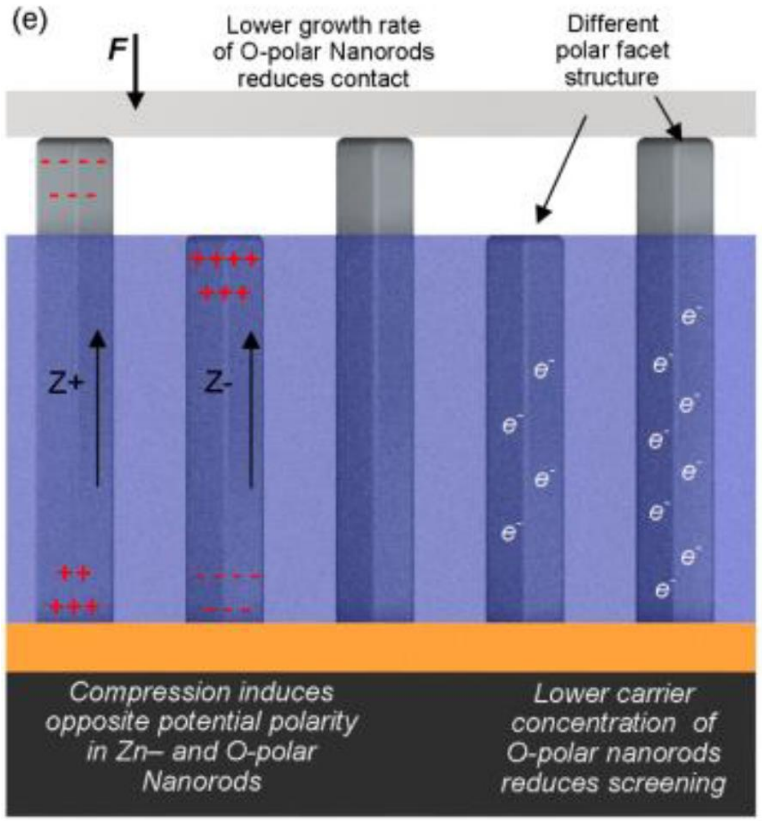


With Chemical Bath Deposition (CBD), the polarity of ZnO NWs **depends on the polarity of** patterned c-plane ZnO single crystals of **the nucleation layer.**

With vapor-phase deposition techniques, ZnO NWs are Zn-polar even on a O-polar seed layer.

V. Consonni et al., ACS Nano vol. 8, no. 5, 4761–4770 (2014)

The NW array should have uniform polarity to have a cumulative effect on the electric potential of the full device.



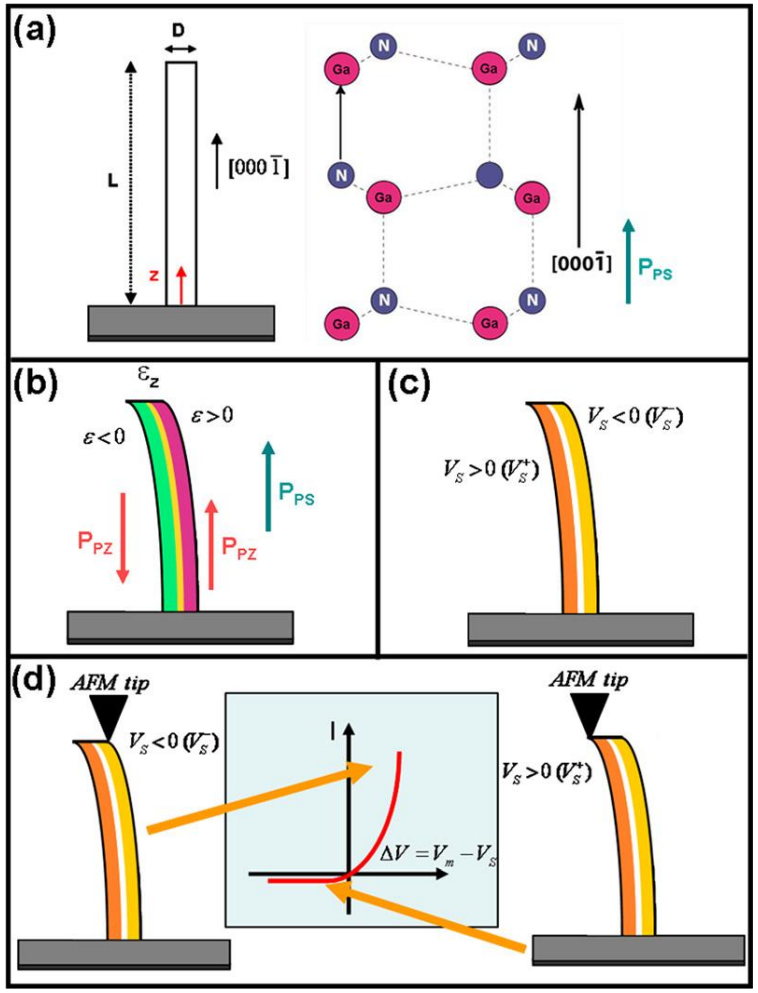
V. Consonni and A. M. Lord, Nano Energy (2020) https://doi.org/10.1016/j.nanoen.2021.105789

Nanogenerators: parameters of influence

NW should have: Uniform polarity

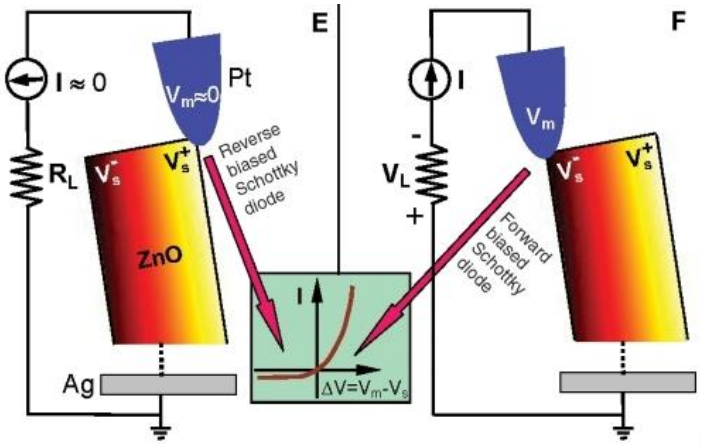
GaN

N-polar GaN NWs were grown by plasma-assisted molecular beam epitaxy (PAMBE)
On 2.5-nm-thick AlN covered Si(111) substrates
Substrate temperature: 800°C
Growth under N-rich condition with an N/Ga ratio of about 1.36



N. Gogneau et al., Appl. Phys. Lett. 104, 213105 (2014)

Opposite behavior to **Zn-polar ZnO NWs:**



Z. L. Wang et al. Science (2006)
doi:10.1126/science.1124005

Nanogenerators: parameters of influence

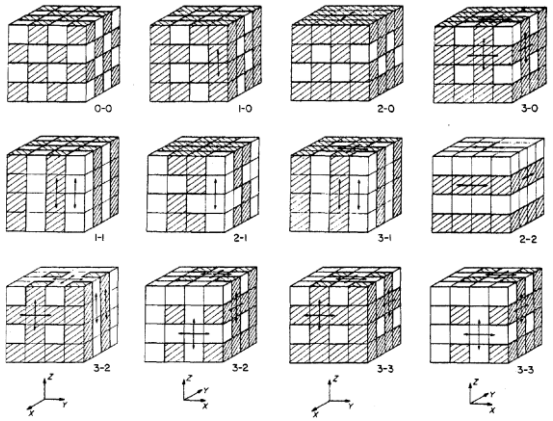
NW should have: Optimal density

- Literature:

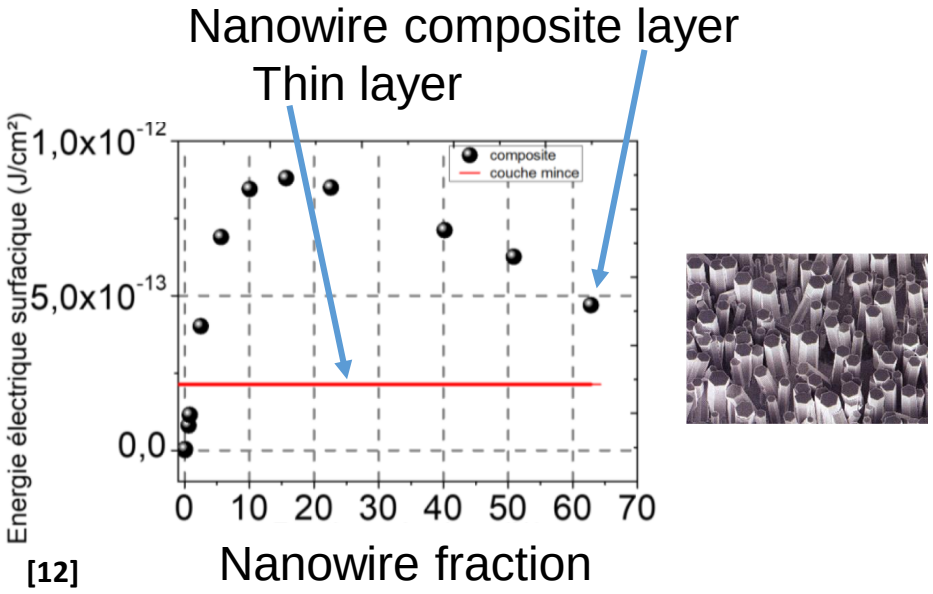
1-3 piezo composite ultrasonic transducers : higher converted energy than bulk piezo material.

Existence of an optimal density (ratio of NWs over total volume or surface).

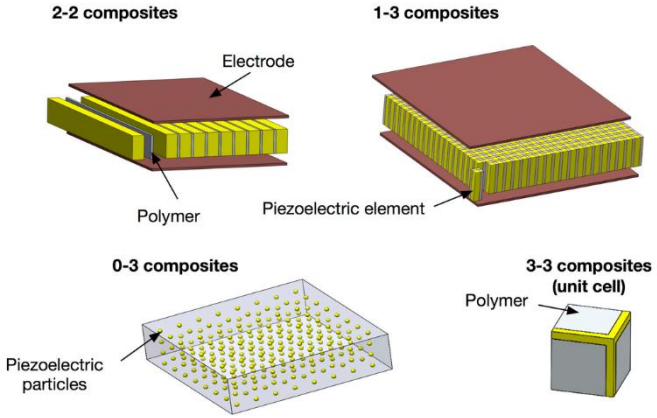
- Same tendency for piezo composite harvesters



R.E. Newnham et al., Mat. Res. Bull. 13 (1978) 525-536



S. Boubenia, Thèse Univ. Tours, 2019



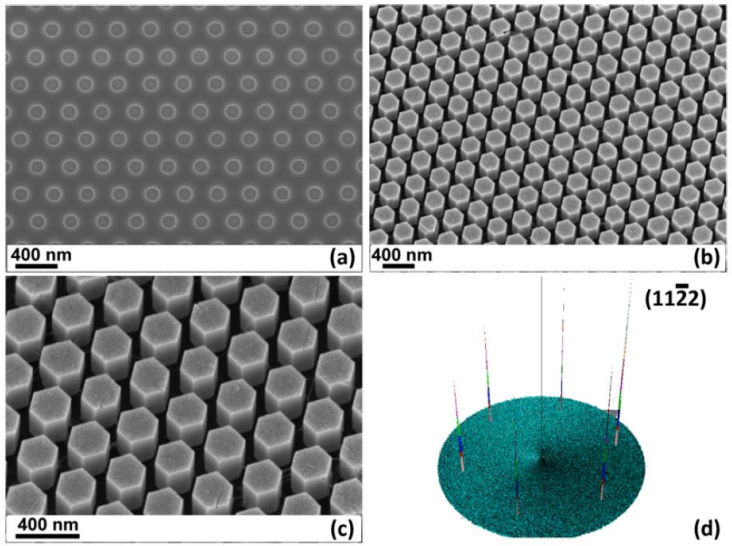
H J Lee et al., Sensors 2014, 14, 14526-14552

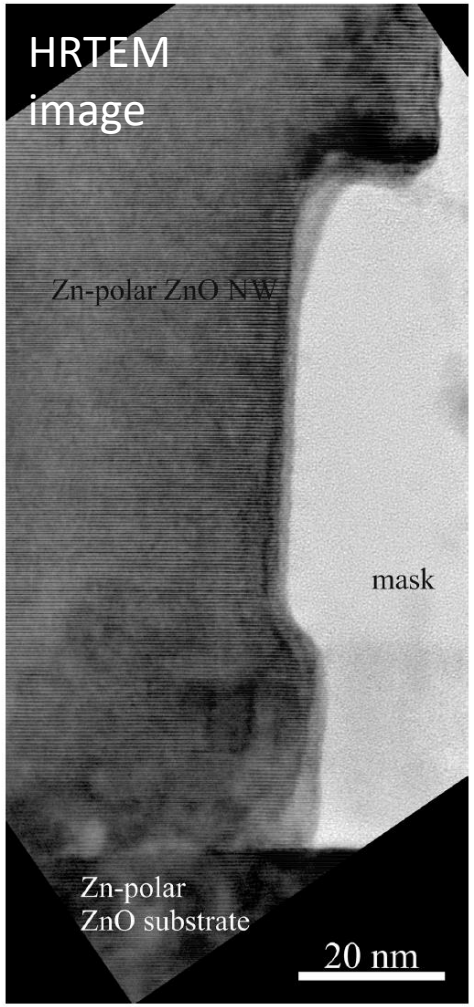
Nanogenerators: parameters of influence

NW should have: Good alignment and uniformity… up to selective area growth

How to grow well-organized nanostructures? Using prepatterned polar c-plane ZnO single crystals

Example:
Substrates : ZnO bulk single crystals from Crystec with O-polar and Zn-polar crystal orientations
+ silicon dioxide SiOx layer with a thickness of 30 nm (by plasma-enhanced CVD)
+ silicon nitride Si_xN_y layer (acting as a selective mask) with a thickness of 60 nm (by plasma-enhanced CVD)
+ holes (from 50 nm to 1 µm) in the mask defined and opened by Electron beam lithography (EBL) followed by reactive ion etching (RIE)





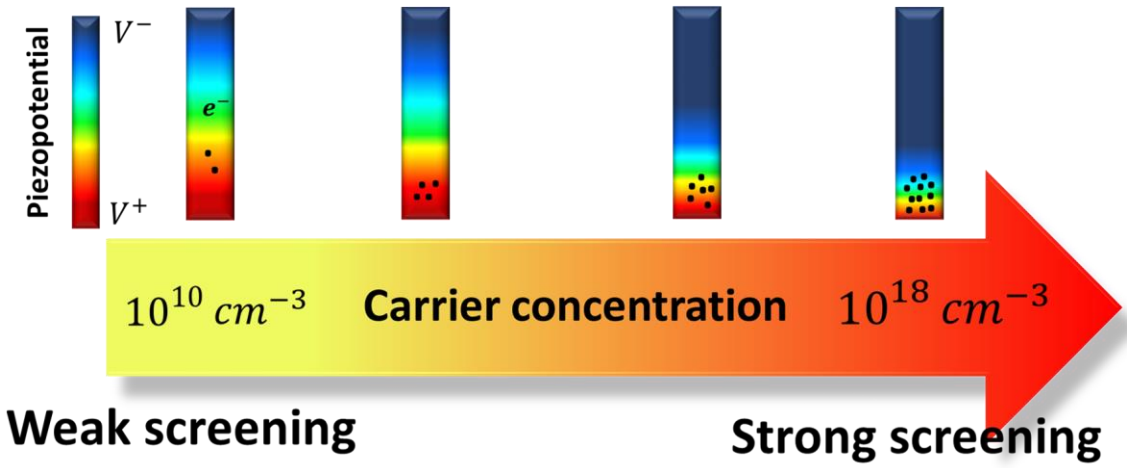
Other seed layers (Au) and methods (Block copolymers) to prepare patterned seed layers…

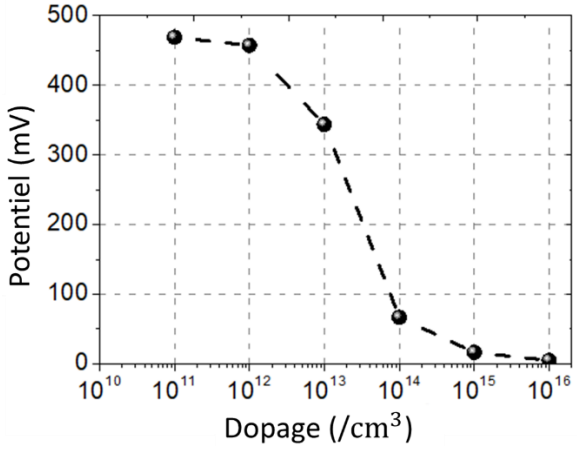
V. Consonni et al., ACS Nano vol. 8, no. 5, 4761–4770 (2014)

Nanogenerators: parameters of influence

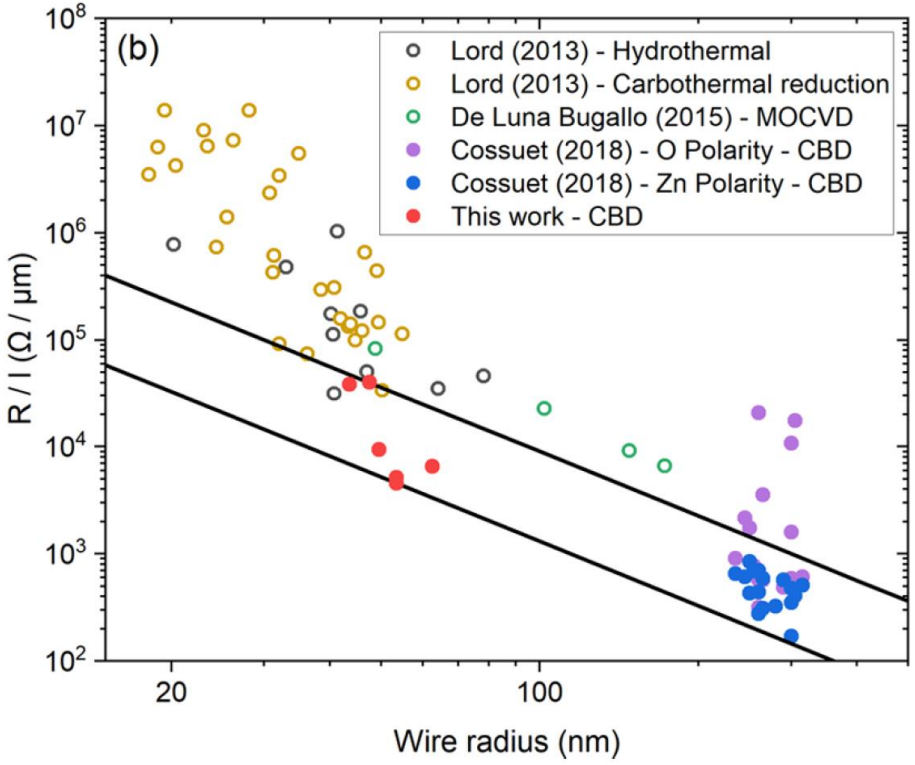
NW should have: Low doping

Defects ⇨ intrinsic N-type doping, high conductivity, both lowering nanogenerator performance





S. Boubenia, Thèse Univ. Tours, 2019, hal.archives-ouvertes.fr/tel-02975514



J. Villafuerte et al. The Journal of Physical Chemistry C 124, 16652-16662 (2020)

Nanogenerators: parameters of influence

NW should have: Low doping

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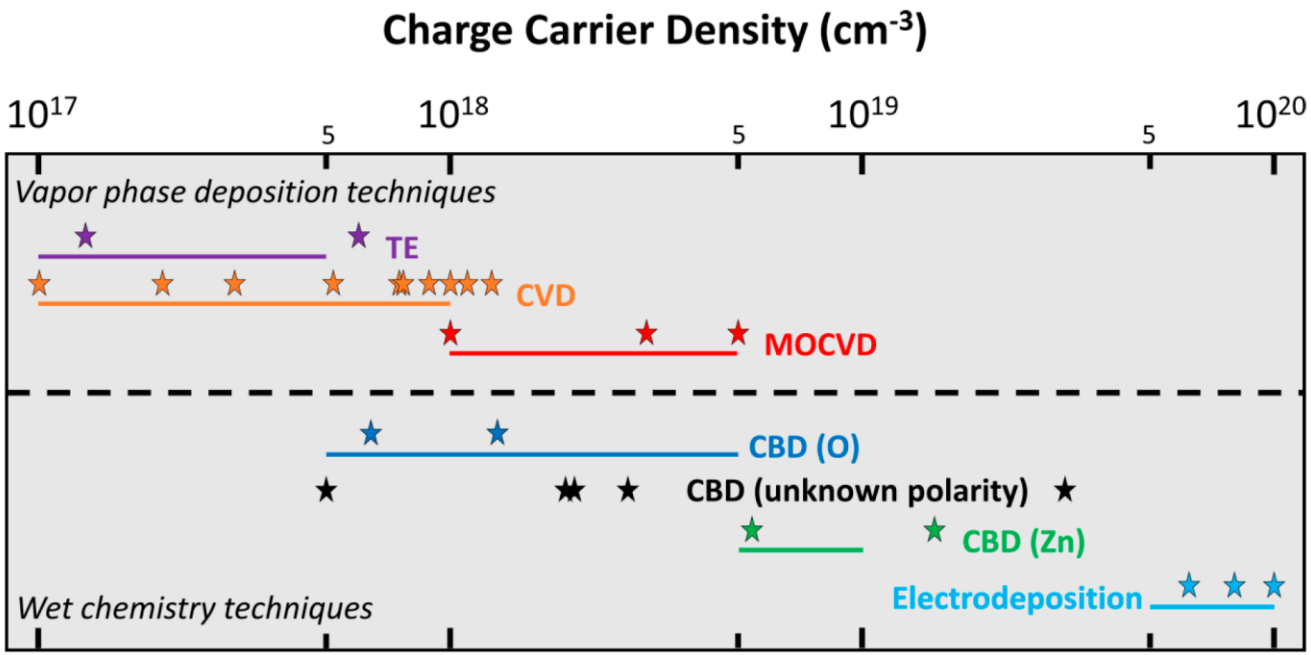
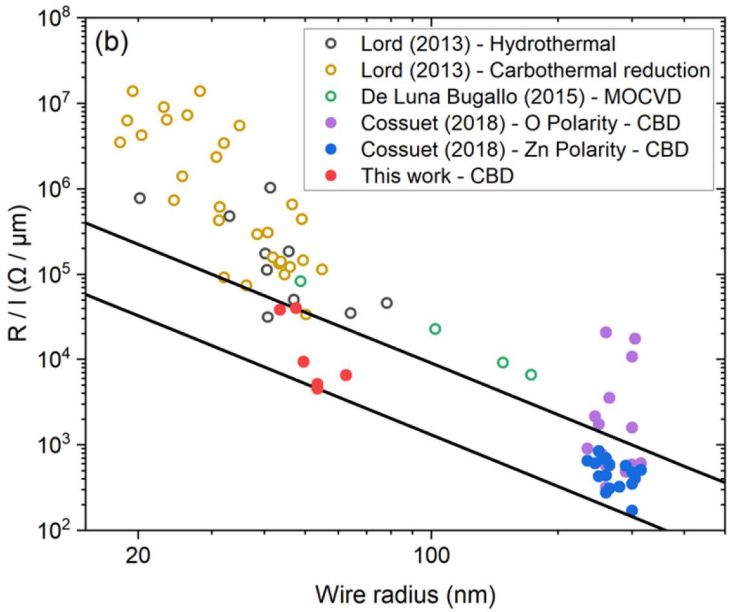


Stars: experimental data
Solid lines: range used for simulation
TE = thermal evaporation

A. J. Lopez Garcia, Nanomaterials 2021, 11, 941



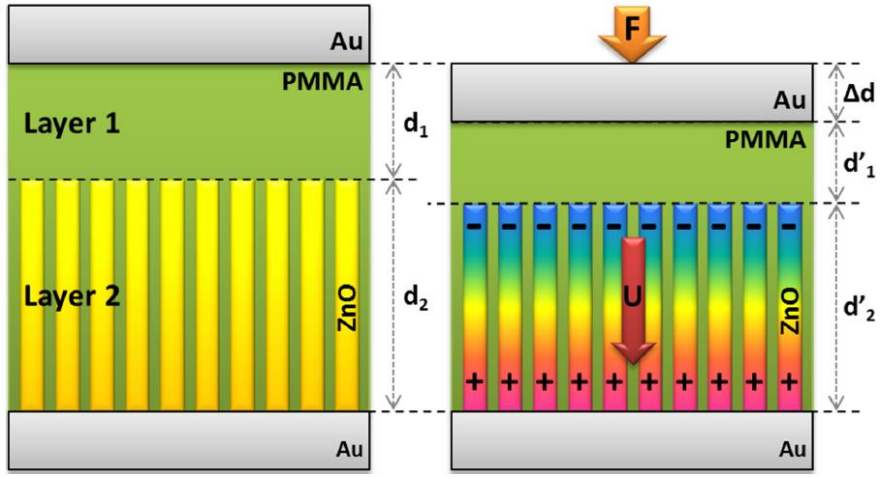
J. Villafuerte et al. The Journal of Physical Chemistry C 124, 16652-16662 (2020)

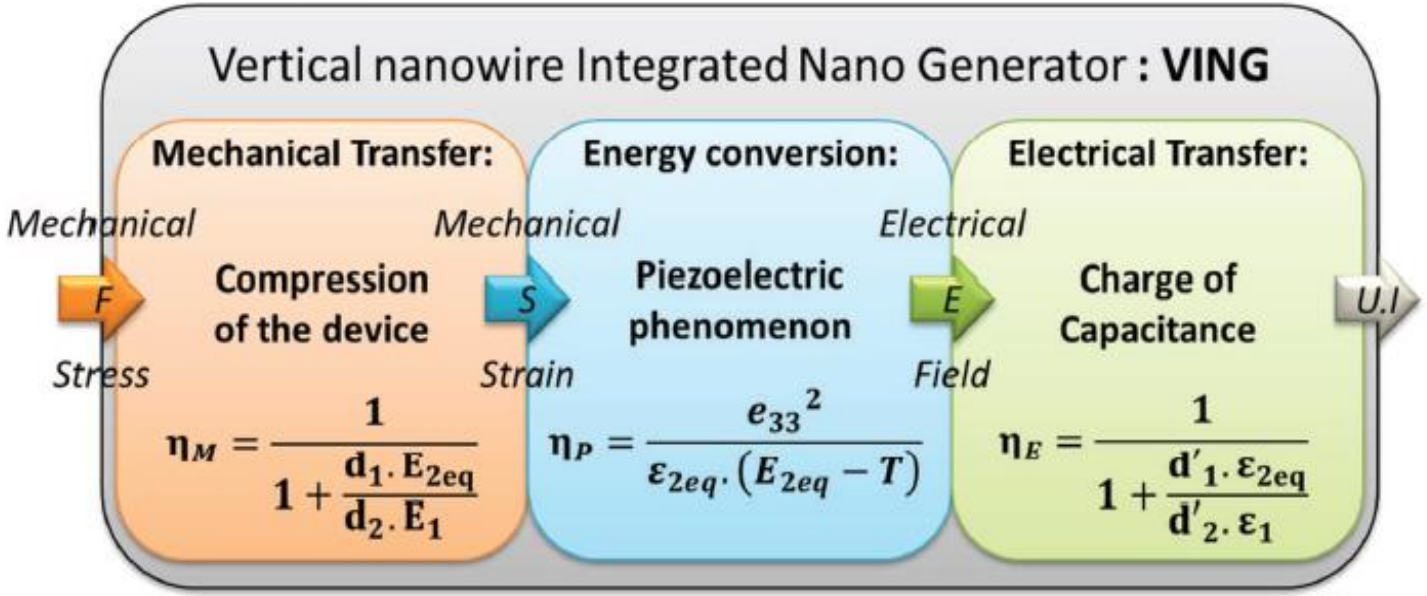
Nature and origin of defects? Still in debate.
During CBD, incorporation of hydrogen in the center of ZnO NWs during growth? Carbon and nitrogen contained in chemical precursors?

Nanogenerators: parameters of influence

NW environment:

Electrodes and encapsulating layer electrical and mechanical properties



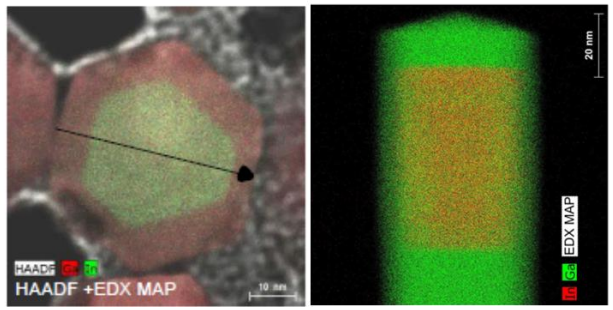


⇨ Design and guideline rules

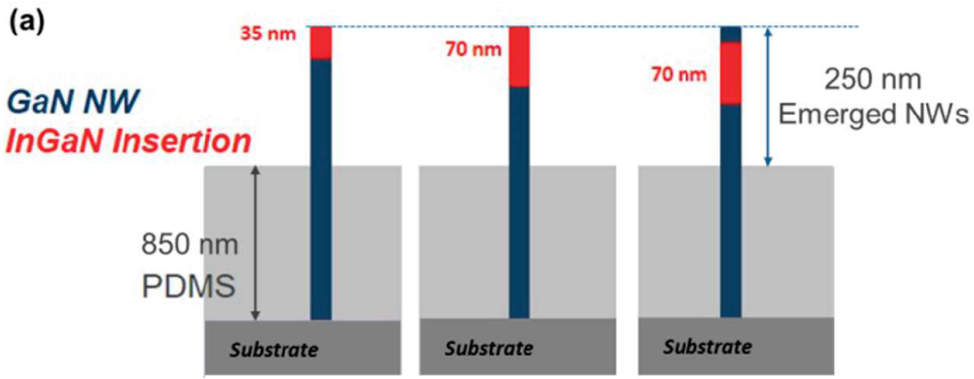
R. Hinchet et al., in Proc. of PowerMEMS 2012

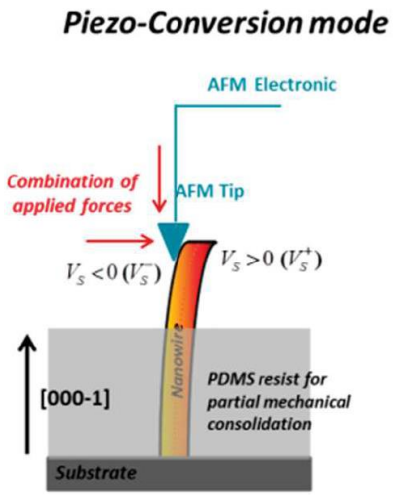
Nanogenerators: last trends

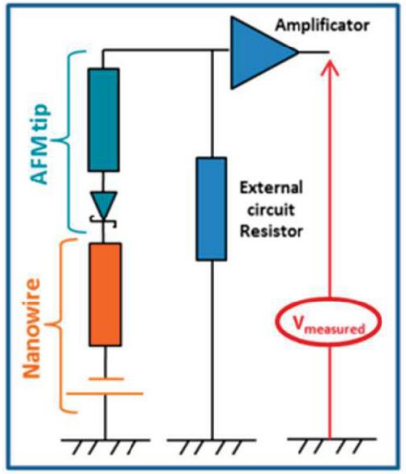
✓ Heterostructured NWs

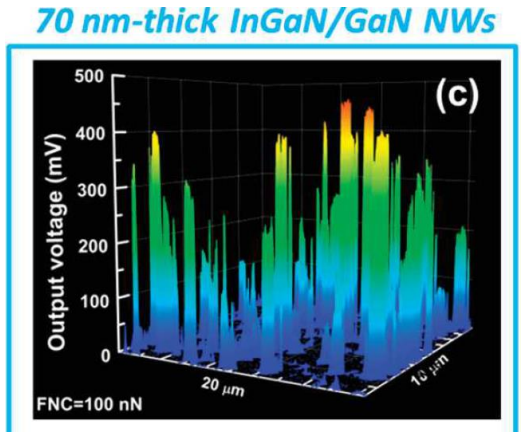


Highly homogeneous In-rich $In_{0.35}Ga_{0.65}N$ insertions in GaN nanowires









The piezo-conversion of InGaN/GaN NWs is 30% more efficient than GaN.

N. Jegenyes et al., Nanomaterials 8(6) (2018) 367, doi: 10.3390/nano8060367

Nanogenerators: last trends

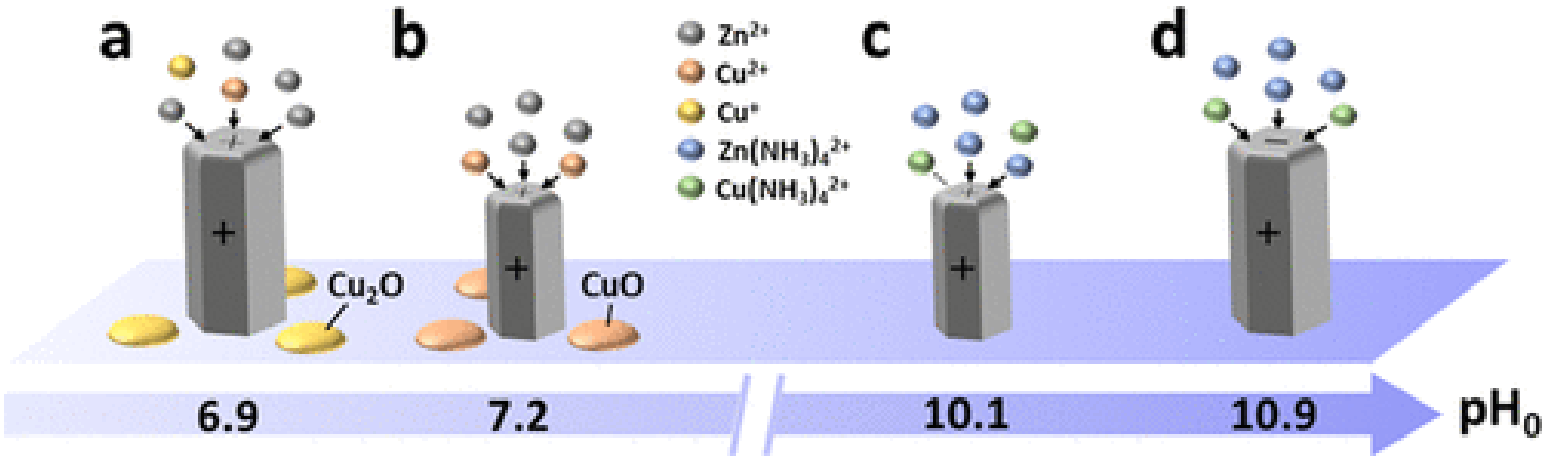
✓ Doping of NWs

Intentional doping for further enhancement of piezoelectric conversion properties

X. Li et al., Nanomaterials 2018, 8, 188, doi:10.3390/nano8040188
S. Goel, B. Kumar, J. of Alloys and Compounds 816 (2020) 152491

In ZnO: the high free electron density coming mainly from hydrogen should be decreased.

Ex: Compensating doping with Cu to decrease the free electron density in ZnO NWs grown by chemical bath deposition.



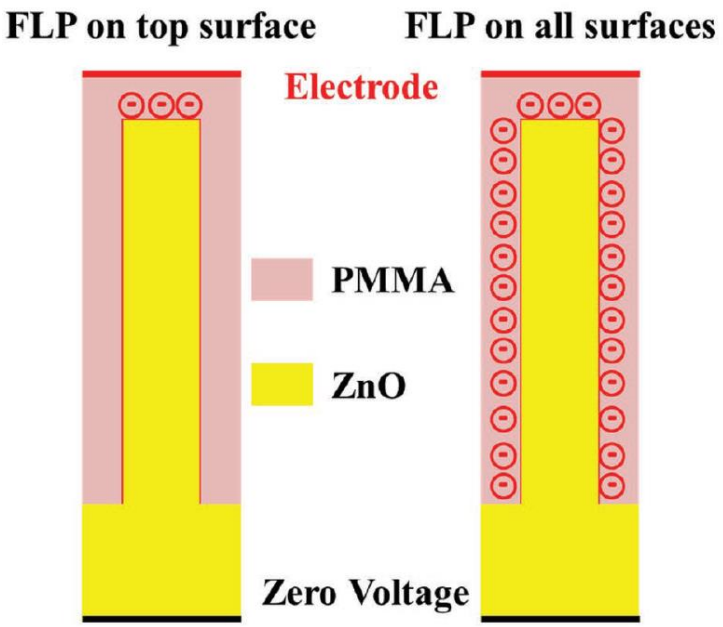
C. Lausecker et al. Inorganic Chemistry 60, 1612-1623 (2021)

Nanogenerators: last trends

✓ Additional surface charges

Fermi Level Pinning (FLP) is an hypothesis to explain the **contradiction between experimental and theoretical results**
(at realistic doping levels ($10^{18}cm^{-3}$), significant levels of voltage are measured across the nanogenerator).

FLP : commonly exists at the surface of III-V and II-VI semiconductor compounds
At the surface of n-type ZnO NWs, oxygen molecules get negatively charged by capturing the free electrons from NW core.
⇨ low-conductivity depletion layer near the surface
⇨ screening of piezoelectric potential is suppressed.



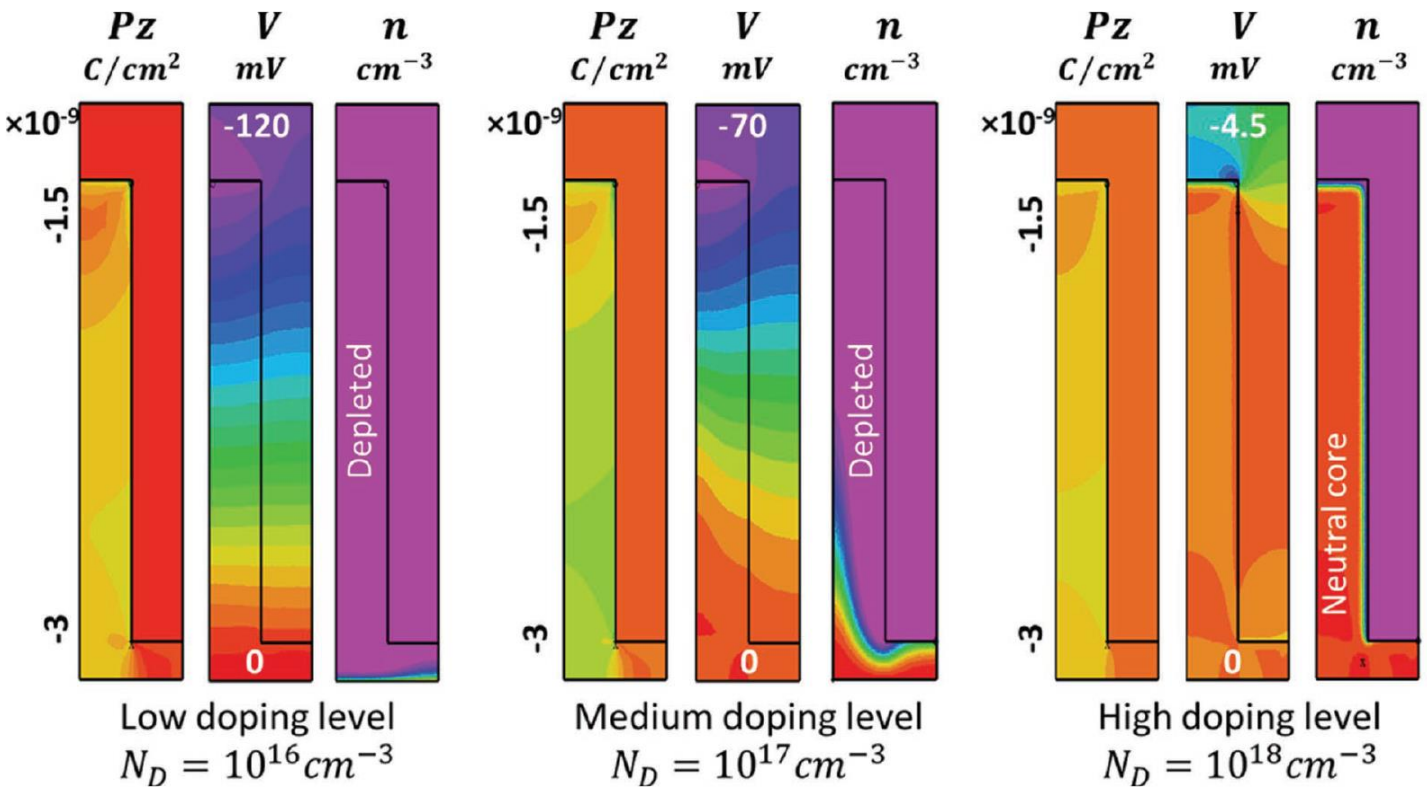
[14]

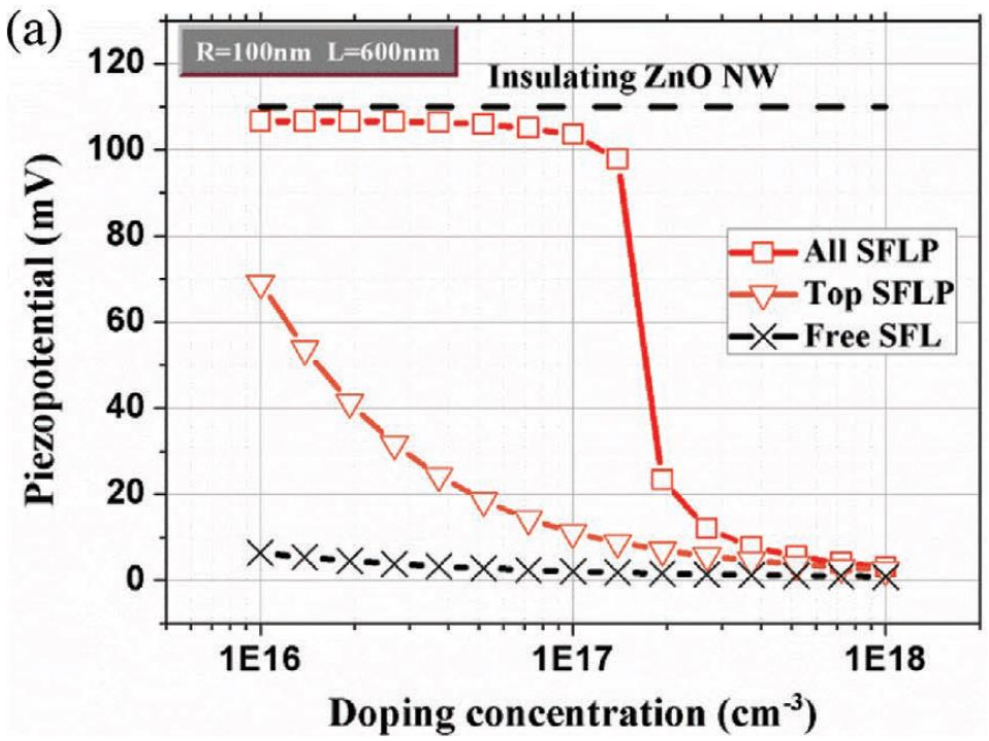
R. Tao et al., *Adv. Electron. Mater.* 2017, 1700299

Nanogenerators: last trends

✓ Additional surface charges

Fermi Level Pinning (FLP)



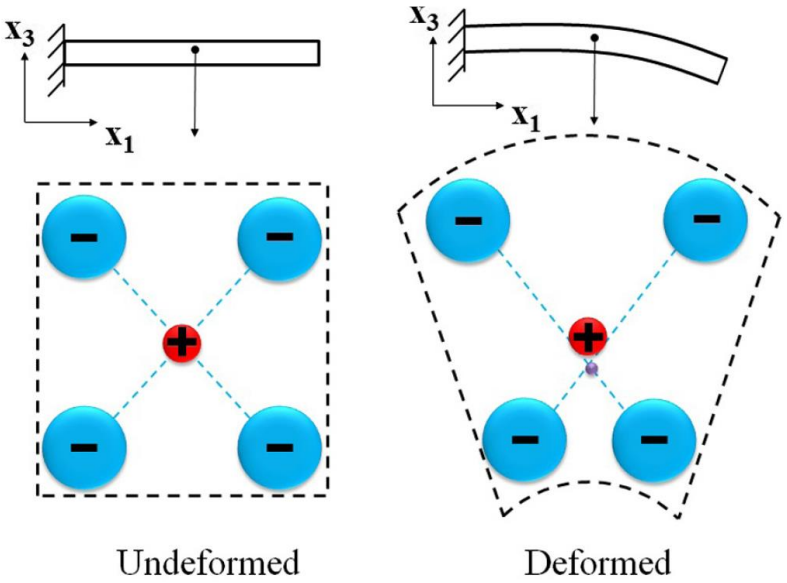


R. Tao et al., *Adv. Electron. Mater.* 2017, 1700299

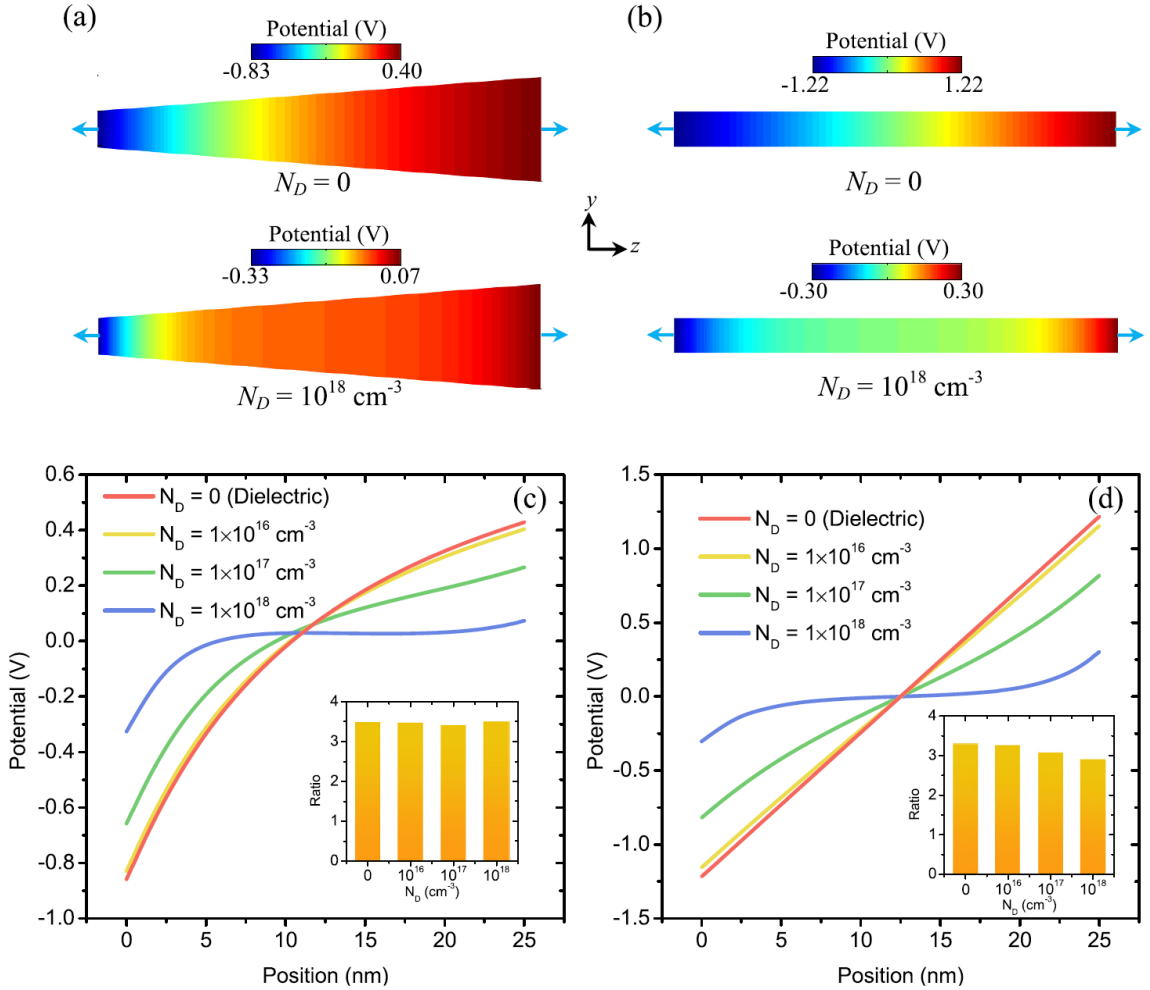
Nanogenerators: last trends

✓ Flexoelectricity

Links **strain gradients** to polarization.
Exists in all dielectrics, even in non-piezoelectric materials.



Q. Deng et al., Int. J. of Solids and Structures 51 (2014) 3218–3225



J. Zhang et al. Nano Energy (2021) doi: 10.1016/j.nanoen.2020.105489

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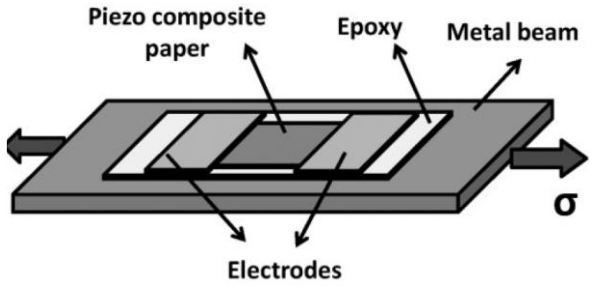
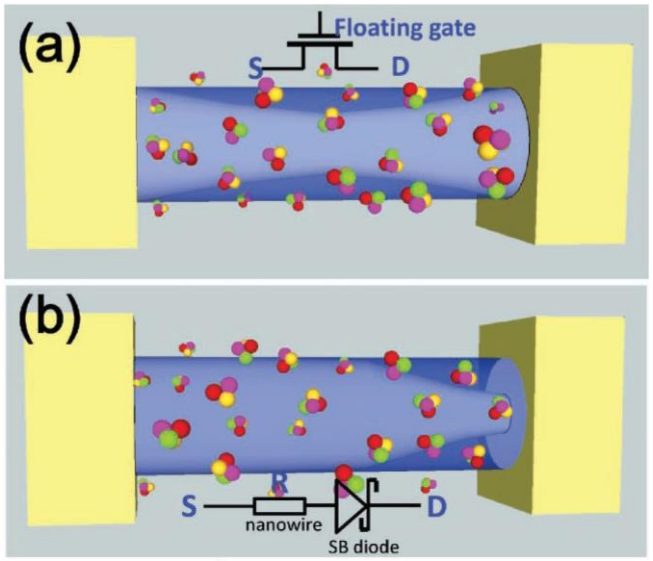
Conclusion: ZnO, a multifunctional material

Mechanical sensor



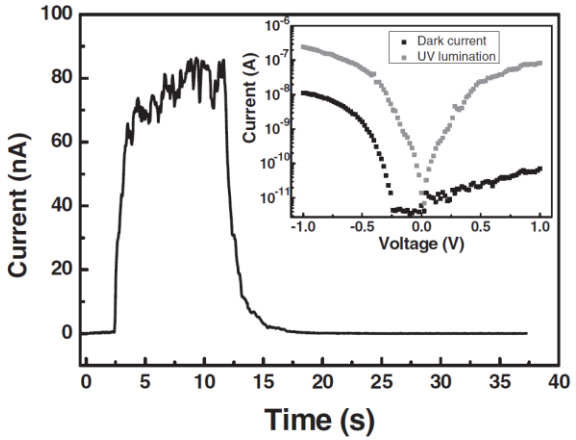
H. Gullapalli, Small 2010, 6, No. 15, 1641–1646

Gas sensor



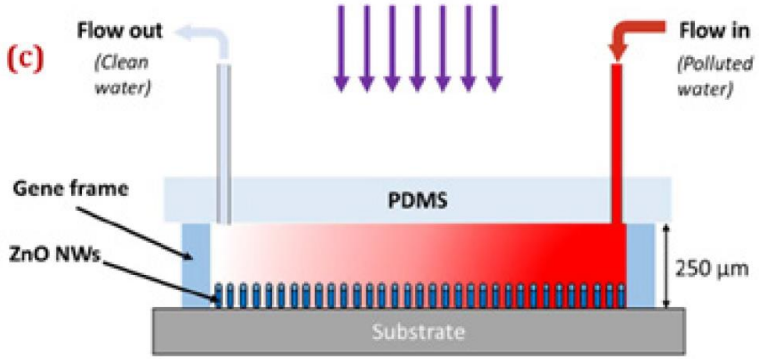
Y. Hu, Adv. Mater. 2010, 22, 3327–3332

UV sensor



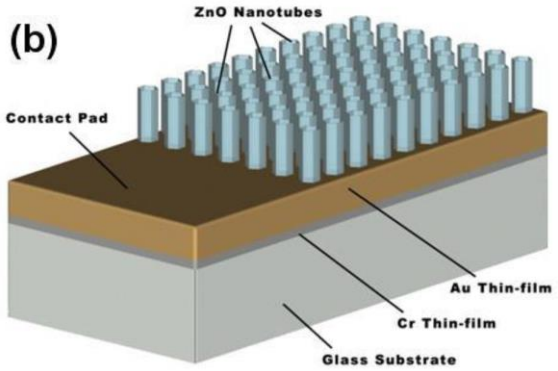
Y. Hu, Adv. Mater. 2010, 22, 3327–3332

Water depollution device



Y. Leprince-Wang et al., NanoWorld J 6(1): 1-6 (2020)

pH sensor



A. Fulati, MSc thesis 2010, ISBN: 978-91-7393-369-8

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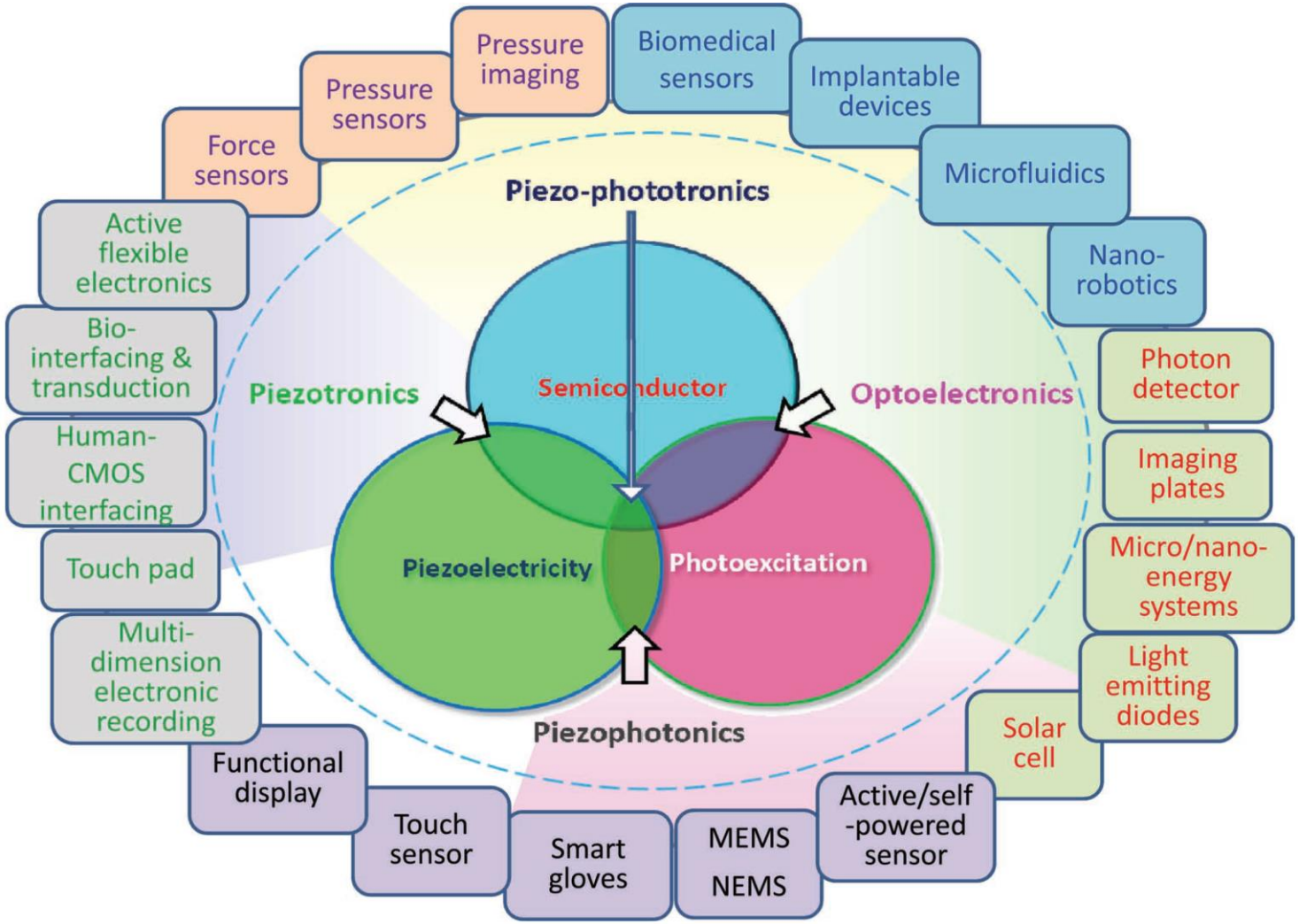
Conclusion: ZnO, a multifunctional material

… and much more…



Z. L. Wang, Adv. Mater. 2012, 24, 4632–4646