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

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Piezoelectricity

Part of the Heckman Diagram

Direct effect

Inverse effect

Effect of polarity orientation

centrosymmetric crystal

non-centrosymmetric crystal
Piezoelectric materials

32 classes de symétrie

21 non centro-symétriques

20 Piézoélectriques

Polarisés sous contraintes

11 centro-symétriques

10 Pyroélectriques

Polarisés spontanément

Ferroélectriques

Polarisation réversible

AB_3O_6

ABO_3

A_2B_2O_7

A_4B_3O_12

Perovskite

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Piezoelectric materials

Quartz

PZT ceramics (50’s)

PVDF film (1969)

Macro Fibre Composites (1993) [Wilo4]

Piezocomposites (early 90’s)
Piezoelectric materials

- Quartz
- PZT ceramics (50’s)
- PVDF film (1969)
- Macro Fibre Composites (1993) [Wil04]
- Piezocomposites (early 90’s)

- Total thickness: 290 µm
- Piezo fibre section: 350 µm x 175 µm
- Piezo fibre spacing: 60 µm
- IDE finger width: 100 µm
Piezoelectric materials

- Quartz
- PZT ceramics (50’s)
- PVDF film (1969)
- Monocristals (early 2000)
- Macro Fibre Composites (1993) [Wilo4]
- Piezocomposites (early 90’s)
- Nanowires (2006)
- Thin films (early 2000)

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Piezoelectric materials

- Quartz (50's)
- PZT ceramics (50's)
- PVDF film (1969)
- Piezocomposites (early 90's)
- Macro Fibre Composites (1993) [Wilo4]
- Marzencki et al.
  Thin films (early 2000)
- Monocristals (early 2000)
- Nanowires (2006)
- PZN-9PT
- AlN
- KNN

<table>
<thead>
<tr>
<th>Material</th>
<th>Quartz</th>
<th>PbTiO₃</th>
<th>BaTiO₃</th>
<th>PZT</th>
<th>MFC</th>
<th>PVDF</th>
<th>PZN-9PT</th>
<th>AlN</th>
<th>KNN</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₃₃</td>
<td>2.3</td>
<td>120</td>
<td>90</td>
<td>300 à 700</td>
<td>400 (PZT-SA : 440)</td>
<td>30</td>
<td>2500</td>
<td>7</td>
<td>200</td>
</tr>
</tbody>
</table>

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Mechanical energy harvesting

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

- 2 THUNDER (76×51×0.635mm³) 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

\[
\langle P \rangle = 8.4 \text{ mW}
\]
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

Wang, Georgia Tech:
ZnO nanowires
∅ = 0.03 to 0.10 µm
L = 1 to 3 µm
6 mm² 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.

Mechanical excitation modes:
2 main modes, or a combination of both

Electrical configurations: Schottky contact or capacitive coupling

AFM excitation principle
Schottky contact between metal tip and NW

Strain Electric field Electric potential


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Piezo-semiconducting nanowire based nanogenerators

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

<table>
<thead>
<tr>
<th>NWs orthogonal to the substrate</th>
<th>NWs parallel to the substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrodes are in contact with the NWs</td>
<td>Capacitive coupling between NWs and electrode via insulating layer</td>
</tr>
<tr>
<td>[6]</td>
<td>[5]</td>
</tr>
<tr>
<td>GaN</td>
<td>ZnO</td>
</tr>
<tr>
<td>Lack of reproducibility, low density of NWs</td>
<td></td>
</tr>
</tbody>
</table>

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1. **Piezo-semiconducting nanowire based nanogenerators**
2. **NW array** embedded in a polymer matrix, between electrodes and on a rigid or flexible substrate. Various configurations:
   - Electrodes are in contact with the NWs.
   - Capacitive coupling between NWs and electrode via insulating layer.
   - [6]: GaN
   - [5]: ZnO
   - [7]: ZnO
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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
Nanogenerators structure

Wish list

- Top contact
- Polymer matrix
  - Fully conformal
  - Strong adhesion
  - Simple deposition
  - Allow NWs to flex
- ZnO NWs

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

Wish list

Top contact
- Good adhesion on polymer
- Electrically conductive
- Mechanically robust
- Flexible if the whole NG is

Example:
Ti/Al electrode deposited by sputtering

Polymer matrix

ZnO NWs


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Nanogenerators functional characterization

Example of dedicated test benches

Test bench in compression [1]

Test bench in flexion [2]

• **Compressive force** in contact or impact mode
• **Variable resistive load**

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

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

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Nanogenerators functional characterization

**Typical output characteristics**

- **Power vs load resistance**
  - 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

- **Durability test**
  - Pressure = 50 kPa
  - Area of device = 1.2 cm²
  - Frequency = 5 Hz
  - Resistance@128 MΩ

- **Experimental data**
  - Linear fitting
  - S = 0.09 V/kPa

**Varying compressive Force**

- Pressure = 50 kPa
- Frequency = 5 Hz
- Resistance@128 MΩ


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Nanogenerators functional characterization

Typical output characteristics

Power vs load resistance

Under a defined mechanical excitation:

<table>
<thead>
<tr>
<th>$V_{peak}$ (V)</th>
<th>$V_{RMS \max}$ (V)</th>
<th>$I_{sc {RMS}}$ (nA)</th>
<th>$P_{av {max}}$ (nW)</th>
<th>$W$ (nJ)</th>
<th>$R_{opt}$ (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.9</td>
<td>1.8</td>
<td>15</td>
<td>29</td>
<td>5.8</td>
<td>&gt;100</td>
</tr>
<tr>
<td>6.8</td>
<td>2.7</td>
<td>28</td>
<td>64</td>
<td>12.8</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

RMS and average values should be preferred to peak values

- 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

To move toward standardization!
Nanogenerators performances

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

✓ Mostly under compression:

\[1-10 \, \mu W/cm^2 \atop <10 \, \mu W/(cm^2.Hz.g^2)\]

@ a few N force @ 0.3 to 5 Hz

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

✓ Comparison with bending cantilevers:

\[10^{-3} \, \text{to} \, 10 \, \mu W/(cm^2.Hz.g^2)\]

(base of a machine tool : \(10 \, \text{m/s}^2 \approx 1 \text{g}\))


Applied force:

- Bending at 1Hz 0.9ms\(^2\)
- Energy: \(40\text{nJ/cm}^2\) per cycle
- Average power \(5\mu W/cm^2\)

J. Briscoe et al., Energy Environ. Sci. 6 (2013) 3035
Nanogenerators: how to choose the right material?

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

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:

<table>
<thead>
<tr>
<th>Matériaux</th>
<th>Matériaux massif (expérimental)</th>
<th>Matériaux massif (expérimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d33 (10^-12 m/V)</td>
<td>E (GPa)</td>
</tr>
<tr>
<td>ZnO</td>
<td>9.93</td>
<td>164</td>
</tr>
<tr>
<td>GaN</td>
<td>1.86</td>
<td>397</td>
</tr>
<tr>
<td>PZT</td>
<td>650</td>
<td>N/A</td>
</tr>
<tr>
<td>PVDF</td>
<td>-25</td>
<td>N/A</td>
</tr>
</tbody>
</table>

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

\[
F_{oM} = \frac{d_{31}^2}{\varepsilon_{33} \tan \delta} = \frac{d_{31} g_{31}}{\tan \delta}
\]


<table>
<thead>
<tr>
<th>Material</th>
<th>Bulk</th>
<th>Nano</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
<td>d31 [m/V]</td>
<td>epsilon33r</td>
</tr>
<tr>
<td>PZT</td>
<td>-2,30E-10</td>
<td>2900</td>
</tr>
<tr>
<td>PVDF</td>
<td>3,98E-12</td>
<td>6,8</td>
</tr>
<tr>
<td>ZnO</td>
<td>-5,43E-12</td>
<td>12,6</td>
</tr>
<tr>
<td>GaN</td>
<td>-1,50E-12</td>
<td>8,9</td>
</tr>
</tbody>
</table>

⇒ 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?
Nanomaterials properties

- Higher mechanical properties: Young modulus

Nanomaterials properties

- Higher mechanical properties: Young modulus, fracture strength

**ZnO**

Nanomaterials properties

- Higher mechanical properties: Young modulus, fracture strength
- Exhalted piezoelectric coefficients at smallest diameters \(\Rightarrow\) 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.

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
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**

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

- \( n_e \): 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

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

In situ TEM and micromanipulator to measure the NW resonance frequency

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


Piezo-semiconducting nanowires characterisation

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

Piezoelectric properties


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.

**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. Jamond et al., Nanoscale, 9 (2017) 4610-4619
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


Topographic image and electric signal

2D mapping @ different forces

Statistical study

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Nanogenerators: parameters of influence

NW should have: High aspect ratio

Transverse Force

Longitudinal Force
Nanogenerators: parameters of influence

NW should have: Uniform polarity

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.

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

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

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


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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

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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 $\Rightarrow$ intrinsic N-type doping, high conductivity, both lowering nanogenerator performance

S. Boubenia, Thèse Univ. Tours, 2019, hal.archives-ouvertes.fr/tel-02975514
Nanogenerators: parameters of influence

**NW should have:** Low doping

Defects imply intrinsic N-type doping & high conductivity, both lowering nanogenerator performance.

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?

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

A. J. Lopez Garcia, Nanomaterials 2021, 11, 941
Nanogenerators: parameters of influence

**NW environment:**
Electrodes and encapsulating layer electrical and mechanical properties

\[ \eta_M = \frac{1}{1 + \frac{d_1}{d_2} \cdot \frac{E_{2eq}}{E_1}} \]

\[ \eta_p = \frac{e_{33}^2}{\varepsilon_{2eq} \cdot (E_{2eq} - T)} \]

\[ \eta_E = \frac{1}{1 + \frac{d'_1}{d'_2} \cdot \varepsilon_{2eq}} \]

⇒ 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.

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.

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 \(10^{18}\text{cm}^{-3}\)), significant levels of voltage are measured across the nanogenerator.

\[
\text{FLP : commonly exists at the surface of III-V and II-VI semiconductor compounds}
\]

\[
\text{At the surface of n-type ZnO NWs, oxygen molecules get negatively charged by capturing the free electrons from NW core.}
\]

\[
\Rightarrow \text{low-conductivity depletion layer near the surface}
\]

\[
\Rightarrow \text{screening of piezoelectric potential is suppressed.}
\]

Nanogenerators: last trends

✓ Additional surface charges

Fermi Level Pinning (FLP)

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

Conclusion: ZnO, a multifunctional material

Mechanical sensor

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

UV sensor


Gas sensor


Water depollution device


pH sensor

Conclusion: ZnO, a multifunctional material

... and much more...