“Nanomatériaux pour l’énergie”
“Instrumentation multifonctionnelle à l’échelle nano”

Noelle Gogneau

NanoVIBES

Nanomaterials and nano-structured architectures for micro-devices harvesting mechanical energies

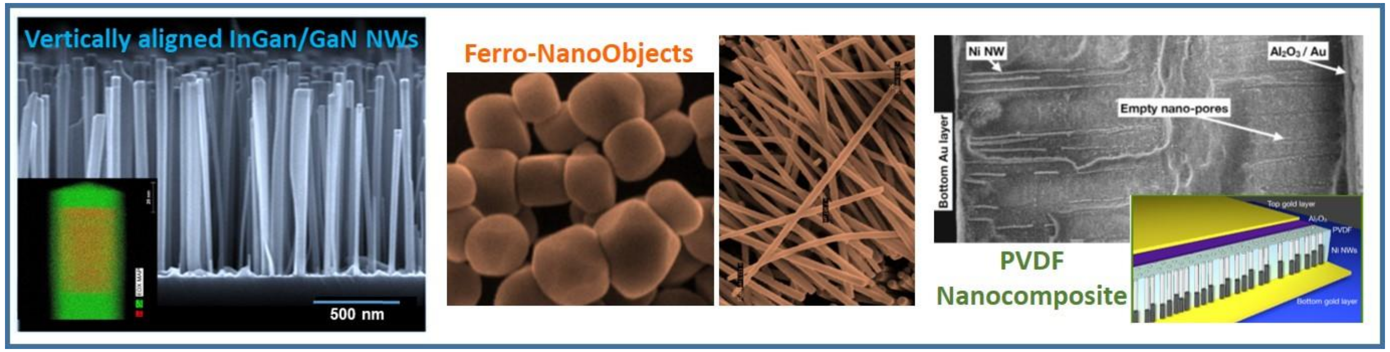
« Imagine a world where the micro-devices could draw the energy they need to operate from their direct environment! »

Involved Industrial Partners

NanoVIBES Challenge

Development of efficient electromechanical generator

Integrating nanomaterials showing piezo- ferro- tribo-electric properties *(exalted due to the reduced dimensions)* **…**



Materials structured at nanometer scale to enhanced electromechanical coupling of the active layer

… Able to convert mechanical energy *(vibrations and mechanical deformation)* **into readily available electricity**

To supply micro-devices such as sensors or implantable medical devices

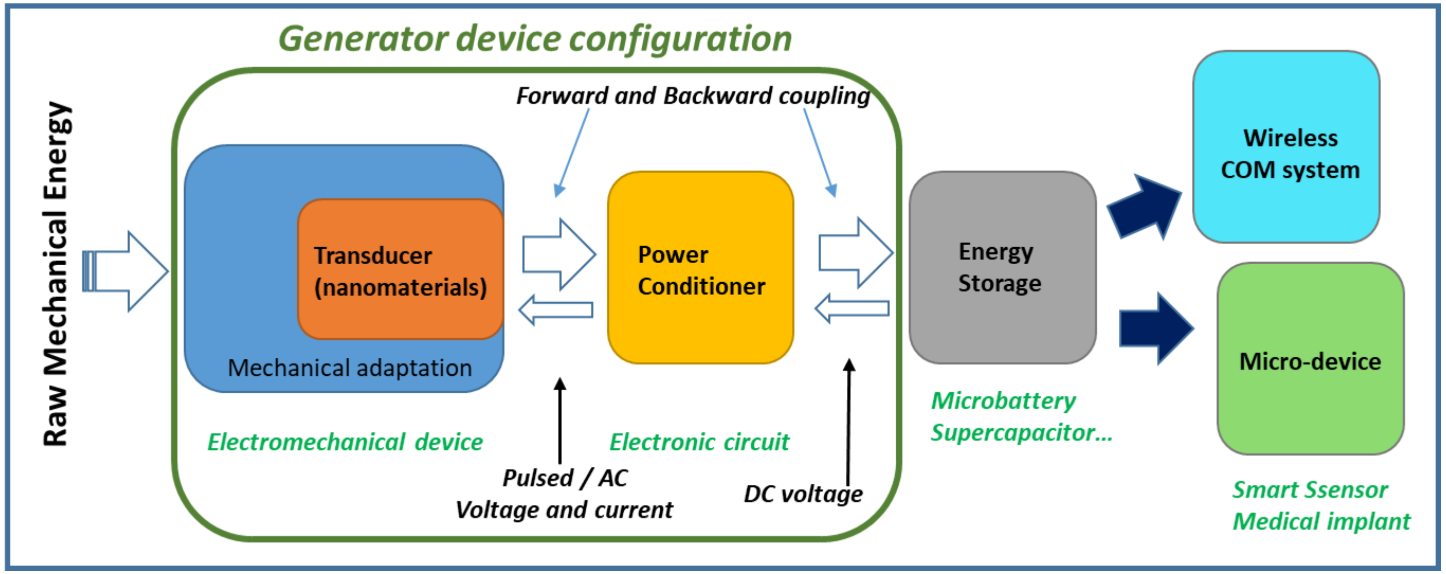
Smart Objects

- ✓ *with long lifetime (> 2 years)*
- ✓ *Working in non-accessible or hostile environment*

NanoVIBES Challenge

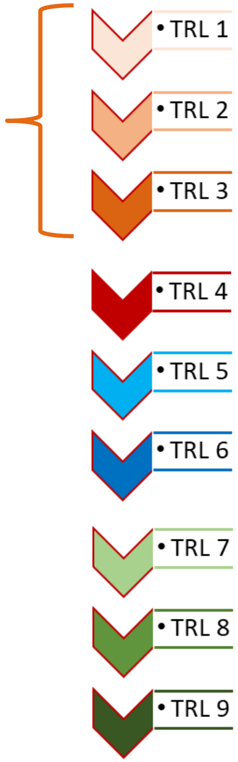
Criteria to replace batteries in Micro-devices with Energy Harvesting System:

- Ultra-compact and integrable, without increasing their size or weight
- Generating sufficiently power to supply the µ-systems
- Providing, under environmental conditions, sustainable energy while operating independently and presenting an important lifetime



Integration of the active layer into MEMs With optimized architecture
Investigation of the generator performances, robustness & durability in real conditions

Academic research on EM systems for Energy Harvesting



NanoVIBES Challenge

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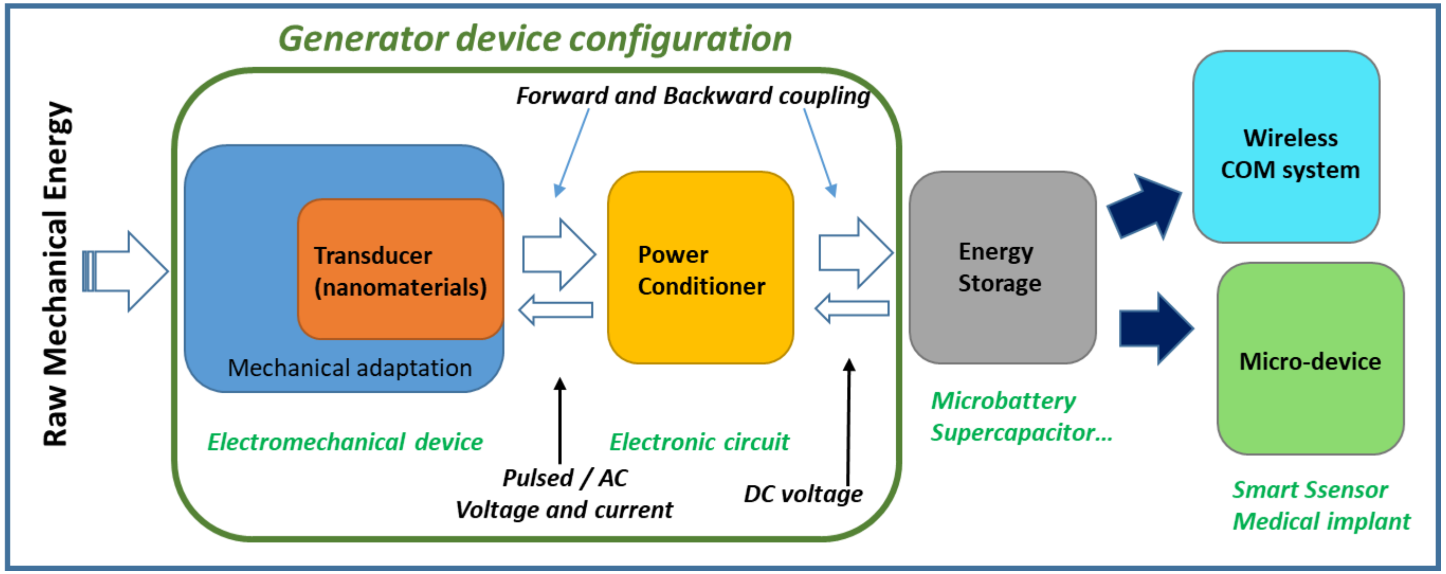
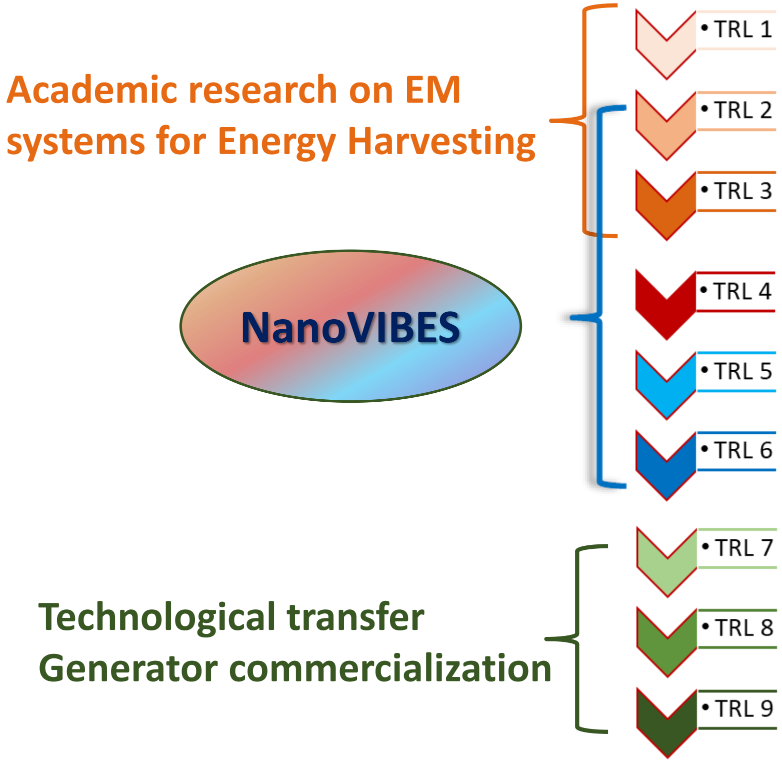




Integration of the active layer into MEMs With optimized architecture
Investigation of the generator performances, robustness & durability in real conditions

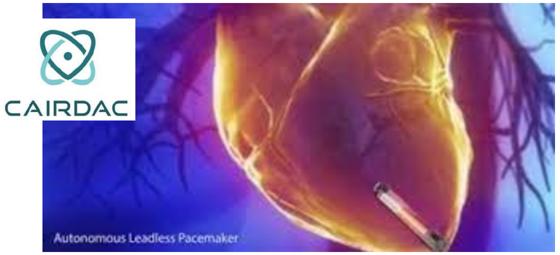
Identification of the application and definition of the specificities

Nature and the amplitude of the mechanical deformations
Dimensional constraints and energy needs (micro-device and possible COM module)

NanoVIBES Objectives

Investigation of 3 families of generators
Bringing common objectives

Family	Low cost generators without strong volume constraints	Ultra-compact generators	Generators for hostile environments
Objective	**Structural Health Monitoring of** bridges (SERCEL comp.), aging of railway (SNCF comp.)	Module to supply **medical implant devices**, such as pacemaker (CAIRDAC startup)	**Monitoring sensors** evolving in hostile environments (high T°, large range of T° or radiation (SAFRAN, CNES companies))
Requirements	Generators sensitive to the own **vibrations** of the infrastructures/bodies while being cost competitive	**Ultra-compact, integrable, bio-compatible**, robust and durable generators	Materials with properties supporting **hard environment** and supplying electrical energy in a given size
Proposed solution	**Few cm² large generator integrating $BaTiO_3$ or ZnO/PDMS or PVDF composite**	**Generator size < 1 cm3 integrating GaN or ZnO NWs**	**cm² generator integrating GaN NWs with specific matrix and contacts; or $BaTiO_3$/metal foils**



Fundamental challenges oriented by real application aims defined with industrial partners

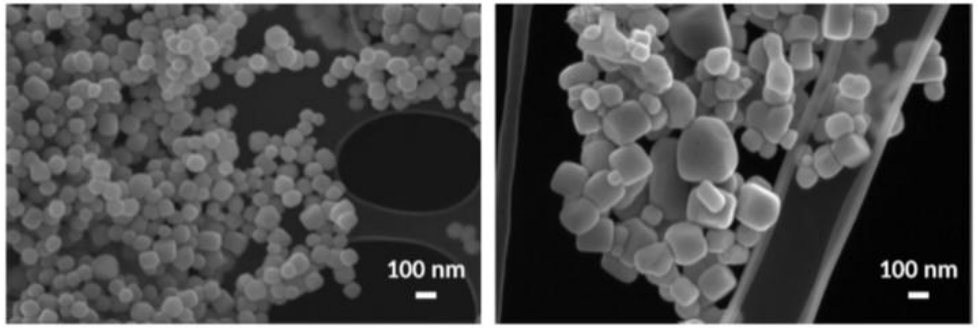
NanoVIBES 1st Results

t0 — t12 — t24 — t36 — t48 — T60

- ❖ Improvement of the conversion efficiency of transducers by working on nanomaterials synthesis
- ❖ Investigation of the electromechanical conversion properties at the nanoscales and microscales
- ❖ Integration transductor into generator device: - MEMs integration
  - Influence of the electric reading system
- ❖ Testing of piezo-generators in real conditions in close collaboration with industrial/startup partners
- ❖ Durability & robustness investigation

Structures Properties Modeling of Solids

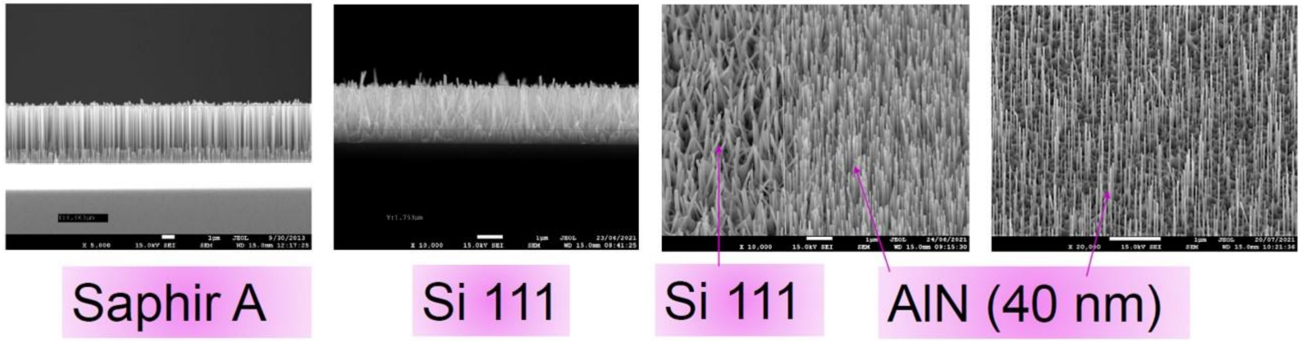
Synthesis of ferroeletric nanoparticles ($BaTiO_3$) by Solvo-Thermal Process



→ Enhancement of the Ferroelectric properties

GEMaC
Groupe d'Etude de la Matière Condensée

Optimization of the growth of ZnO NWs



→ Enhancement of the ZnO NW piezoelectric conversion

NanoVIBES 1st Results

t0 — t12 — t24 — t36 — t48 — T60

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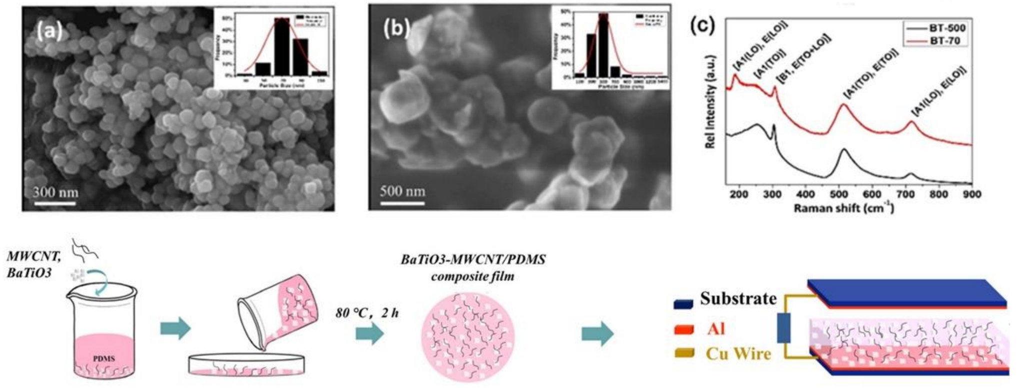
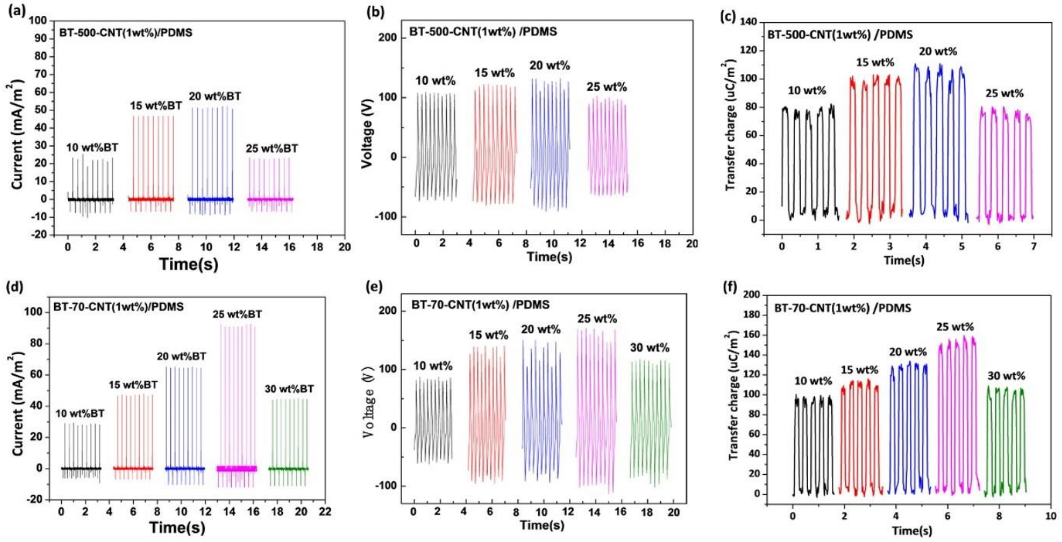
Triboelectric transducer based on BaTiO3/MWCNT/PDMS composite films





Centre de Nanosciences & de Nanotechnologies (C2N)

GeePS Génie électrique et électronique de Paris

- Improvement of the conversion efficiency of transducers by working on nanomaterials synthesis
- **Investigation of the electromechanical conversion properties at the nanoscales and microscales**
- Integration transductor into generator device: - MEMs integration
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- Testing of piezo-generators in real conditions in close collaboration with industrial/startup partners
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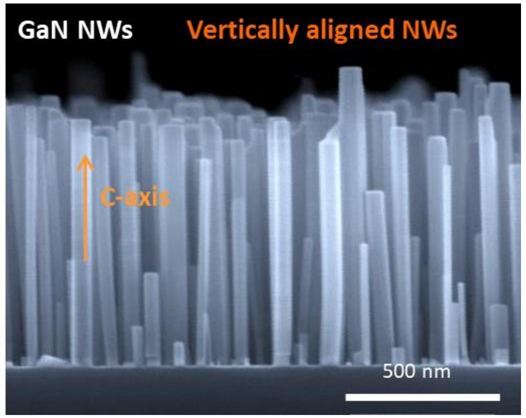
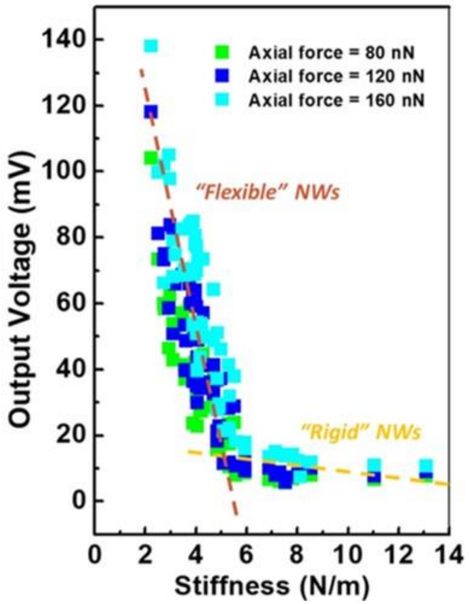
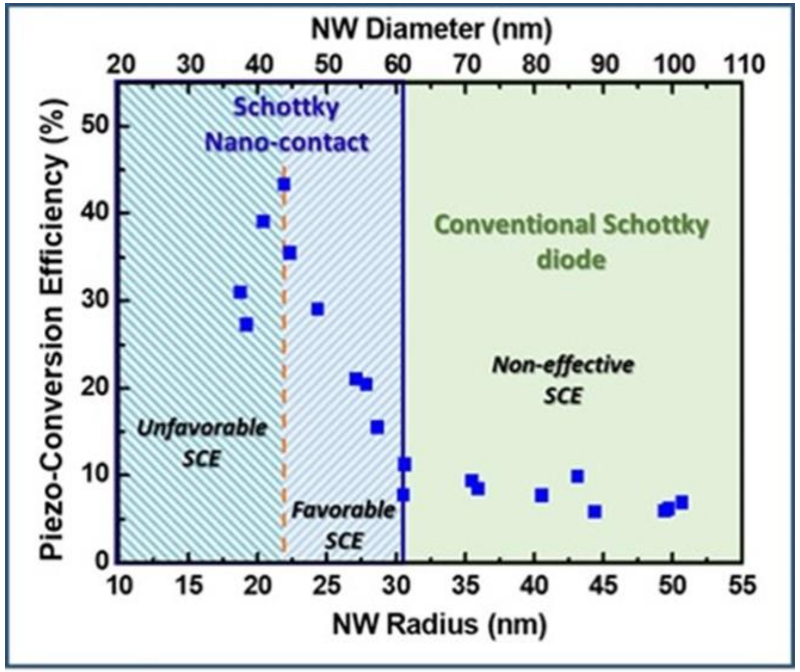
Piezoelectric properties of GaN NWs at the nanometer scales







→ Strong influence of properties specific to nanometer scales t0 t12 t24 t36 t48 T60

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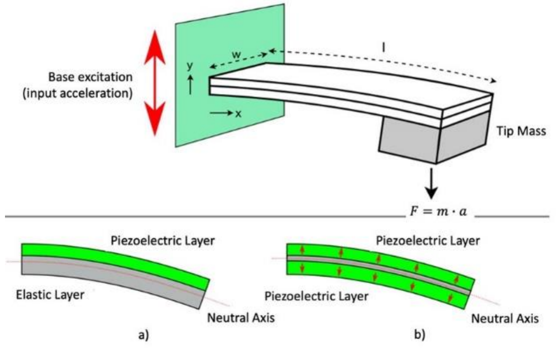
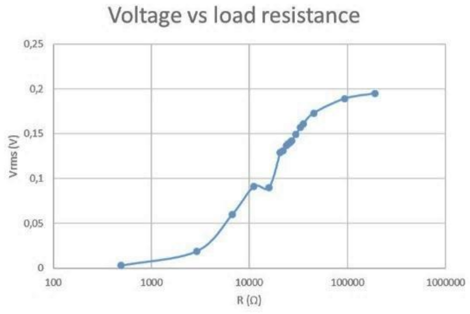
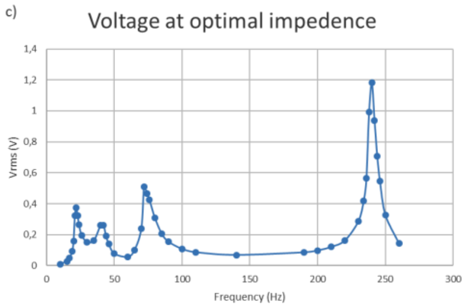
Transducer properties based on ferro- or Tribo-electric system at the macroscales

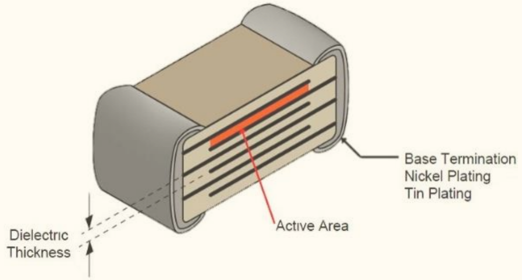
Ferroelectrics for multi-energy harvesting







Create and optimize structure to maximize energy output



Structures Properties Modeling of Solids

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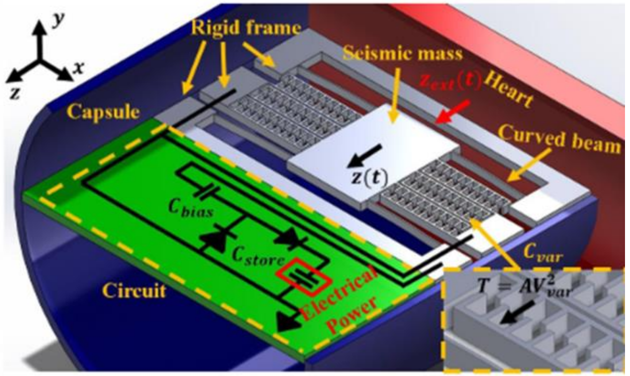
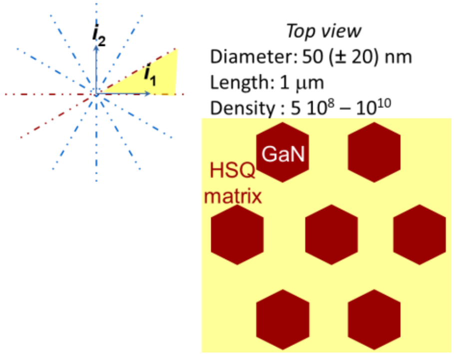
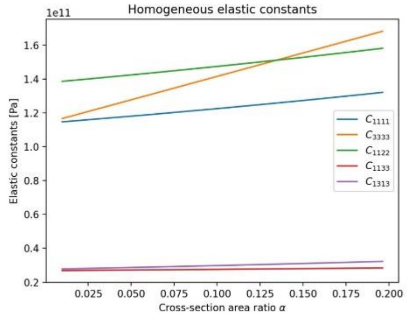
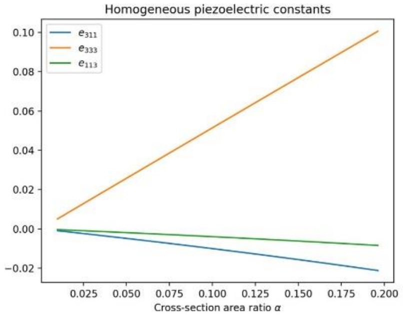
MEMS integration to maximize the generator performances
Simulations/predictions

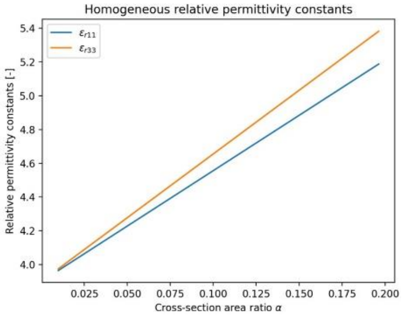


Manuscrit de thèse B.Vysotskyi
Université Paris-Saclay (2018)









NanoVIBES 1st Results

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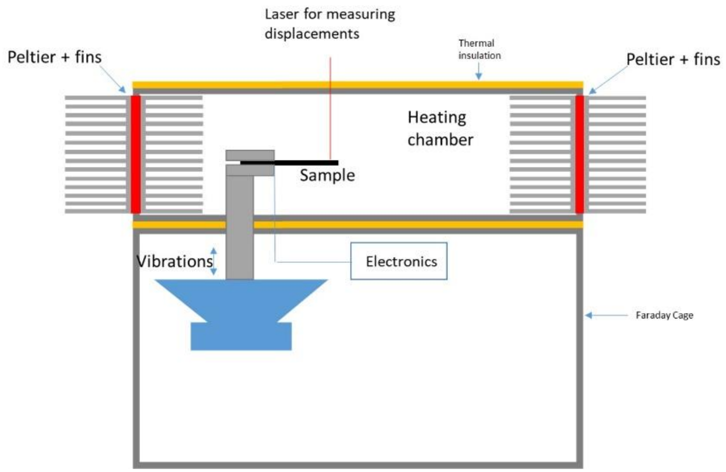
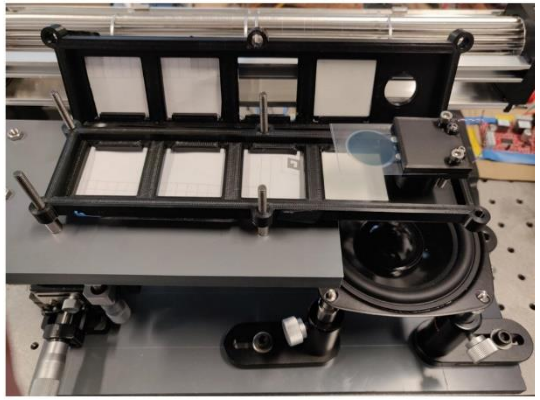
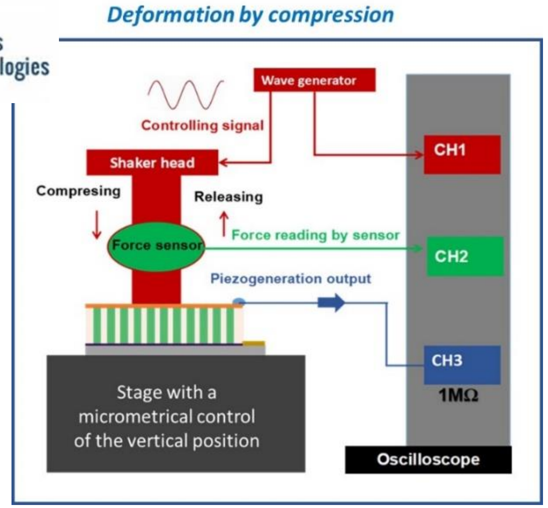
Different setup in laboratories of NanoVIBES project

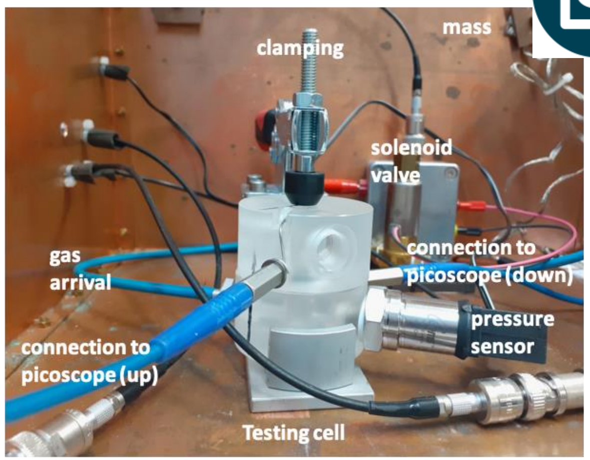
Structure Properties Modeling Solids





Centre de Nanosciences & de Nanotechnologies (C2N)





NanoVIBES project: The NanoVIBES team is growing !

PhD student   Post-doc   CIFRE fellowship

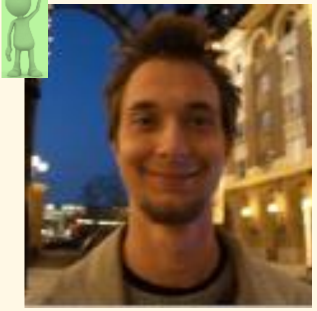
Already recruited !

Monika PARIHAR
PhD Nano-characterization – GeePs / C2N
From October 2020
Characterization at the nanometer scale of the electro-mechanical conversion properties of piezoelectric nanostructures

Dr. Potrzebowska Natalia
18-month post-doc at CEA/DRF/IRAMISLSI
From July 2020 to December 2021
Fabrication and study of innovative flexible piezoelectric nanostructured generator based on poly(vinyldifluoride) (PVDF) thin films

Matthieu Fricaudet
PhD student at SPMS
From October 2020
Multi-energy harvesting

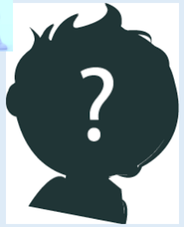
PhD Student - C2N
January 2021
Development of InGaN/GaN NWs based transductors for piezoelectric applications



Dr. Andraz Bradesko
Post-doc at SPMS
From summer 2020 to October 2021
Energy harvesting using nanoferroelectrics

Mathilde Lavanant
CentraleSupélec student (2^{nd} y)
Research program on Energy harvesting at the nanoscale

They will arrive !!!



PhD Stud. – CIFRE CAIRDAC/C2N
As soon as possible !
Robustness and fatigue of Energy Harvester system

Dr. Samiran Garain
Post-doc at MSSMAT
soon 2022
Polymer nanocomposites and their Piezo/Triboelectric proprieties for Energy Harvesting applications

NanoVIBES project

3 publications …

Materials Today Communications 28 (2021) 102528

Contents lists available at ScienceDirect

Materials Today Communications

journal homepage: www.elsevier.com/locate/mtcomm

ELSEVIER

Mixing nanostructured Ni/piezoPVDF composite thin films with e-beam irradiation: A beneficial synergy to piezoelectric response

Natalia Potrzebowska[a], Olivier Cavani[a], Ozlem Oral[a], Olivier Doaré[b], Giuseppe Melilli[a,c], Jean-Eric Wegrowe[a,*], Marie-Claude. Clochard[a,*]

Polymer Degradation and Stability 195 (2022) 109786

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polymdegradstab

ELSEVIER

Molecular dynamics between amorphous and crystalline phases of e-beam irradiated piezoelectric PVDF thin films employing solid-state NMR spectroscopy

Natalia Potrzebowska[a], Olivier Cavani[a], Slawomir Kazmierski[b], Jean-Eric Wegrowe[a], Marek J. Potrzebowski[b,*], Marie-Claude Clochard[a,*]

ACS APPLIED NANO MATERIALS

www.acsanm.org Article

Local Immiscibility Control on Shape and Size of Nano-objects in the Solvo-Thermal Process: Implications for Ferroelectric Nanoparticles

Christine Bogicevic* and Pierre-Eymeric Janolin*

NanoVIBES Event : Annual day !

October 7, 2021

Centre de Nanosciences & de Nanotechnologies (C2N) · MSSMat · Structures Properties Modeling of Solids · GeePs · GEMaC · LSI

NanoVIBES

Quand Académiques et Industriels se rencontrent !

Sercel · Schlumberger · SNCF · cnes · CAIRDAC · SAFRAN

NanoVIBES website

NANOVIBES

Nanomaterials and nano-structured architectures for micro-devices harvesting mechanical energies

NANOVIBES PARTNERS · INDUSTRIAL PARTNERS · RESULTS · PUBLICATIONS · VULGARIZATION

Welcome !

NanoSaclay · université PARIS-SACLAY

Journée annuelle Projet NanoVIBES

"Nanomaterials and nano-structured architectures for micro-devices harvesting mechanical energies"

7 Octobre 2021

News

- Journée annuelle Projet NanoVIBES
- Presentation of NanoVIBES project at the Annual LabEx NanoSaclay Day – October 13, 2020
- NanoVIBES Kick-Off meeting – February 5, 2020

Events

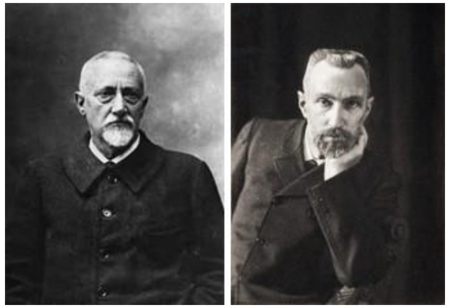
- septembre 2021
- octobre 2020

nanovibes.c2n.universite-paris-saclay.fr

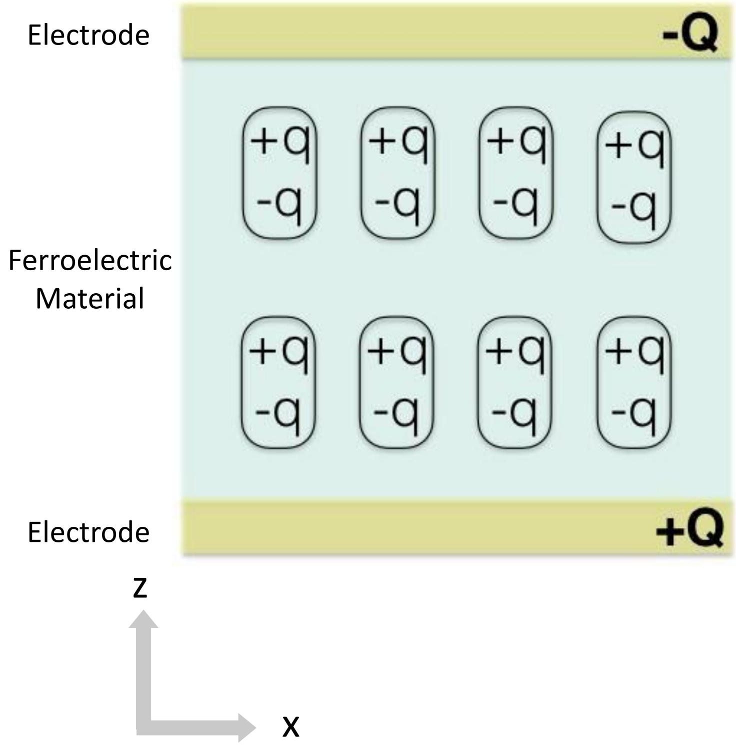
Mixing nanostructured Ni/piezoPVDF composite thin films with e-beam irradiation: a beneficial synergy to piezoelectric response

Natalia Potrzebowska, Olivier Cavani, Ozlem Oral, Jean-Eric Wegrowe,
Marie-Claude Clochard

Piezoelectric effect



Curie Brothers
Direct piezoelectric effect
1880



Piezoelectricity is defined as the aptitude to convert mechanical strain in electrical charge and vice versa.

Constitutive equations

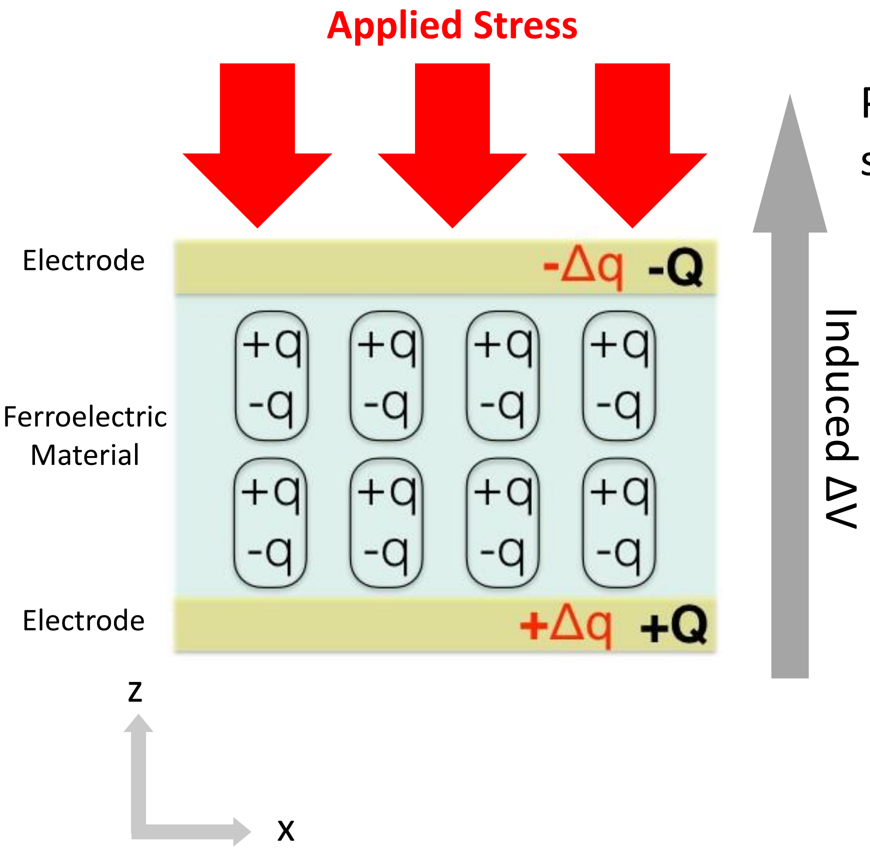
$$D = \varepsilon^T E + d_{33} T$$

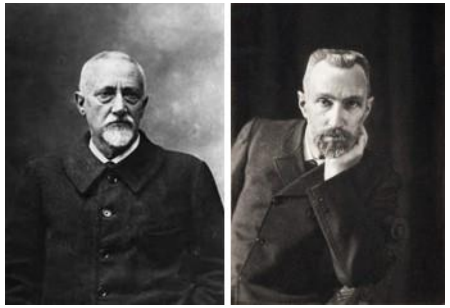
$$S = d_{33} E + s^E T$$

D : electric displacement ($C.m^{-2}$)
E : electric field ($V.m^{-1}$)
T : stress ($N.m^{-2}$)
S : strain
ε^T : dielectric constant
s^E : compliance (inverse of the young's modulus)
d_{33} : piezoelectric constant ($m.V^{-1}$ or $C.N^{-1}$) in z direction

Piezoelectric effect

Direct piezoelectric effect (Generator/Sensor)





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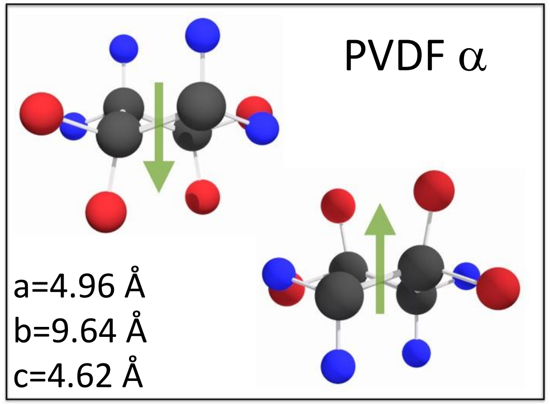
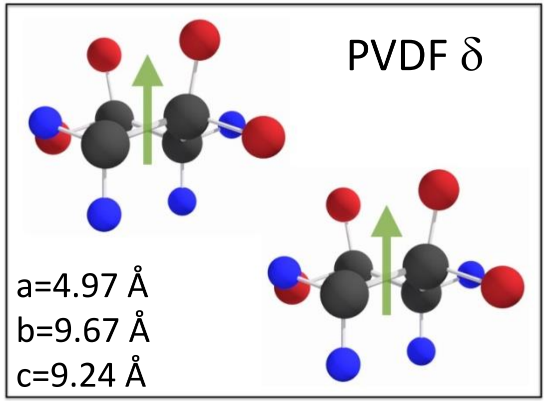
Ferroelectric polymer: Poly(Vinylidene DiFluoride)

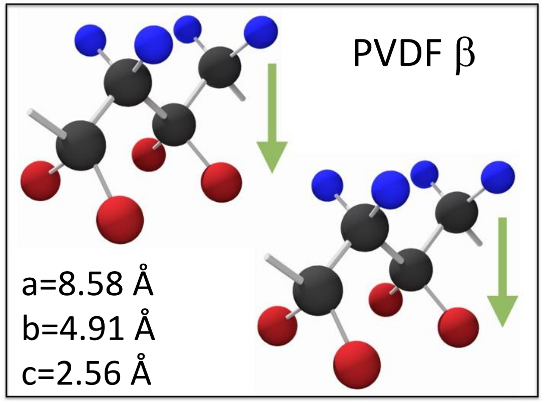
PVDF polymorphism : crystalline phases (40%) α, β, δ and γ phases.



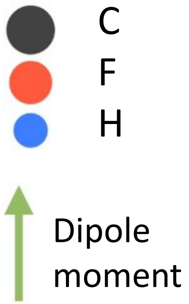
Monoclinic cell
Non net dipole moment

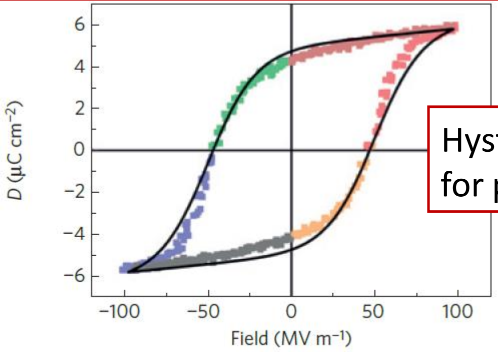


Monoclinic cell
net dipole moment



Orthorombic cell
net dipole moment



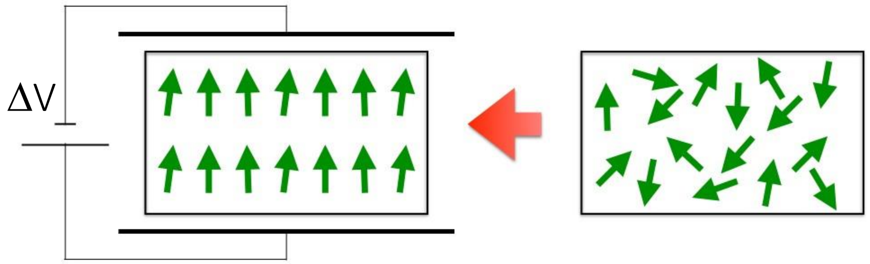


Hysteresis loop for piezo- PVDF

Poling process

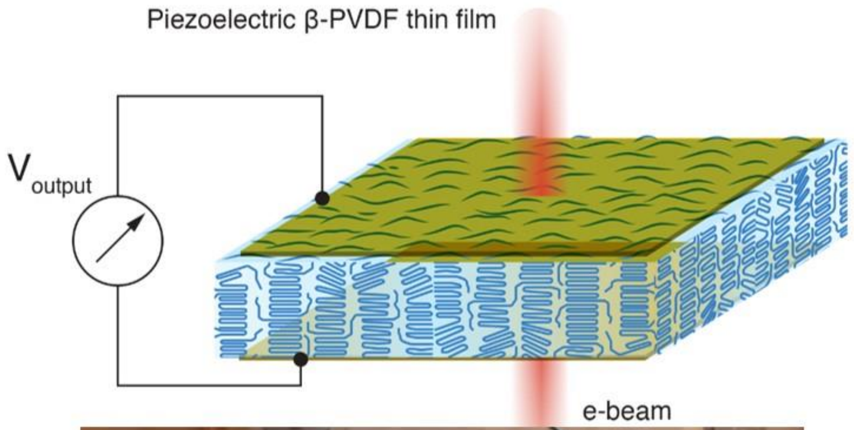
(T≈ 95°C , ΔV=50 ÷ 100 $MV.m^{-1}$)

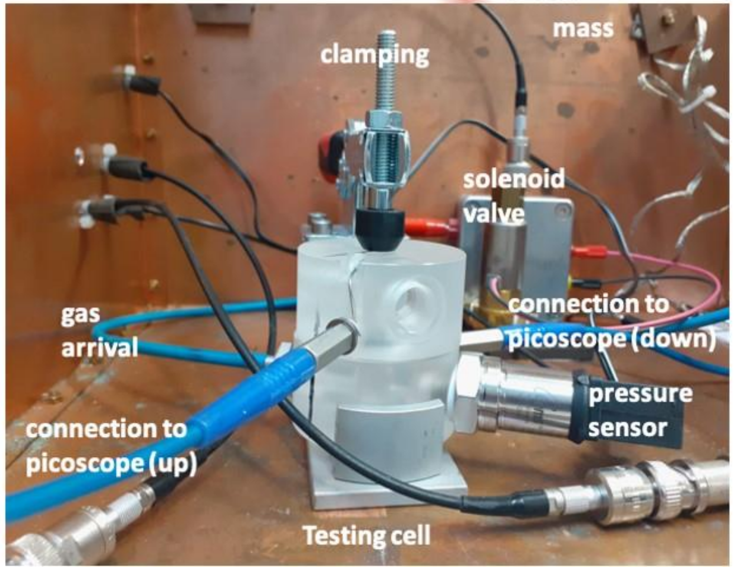
Dipole moments are randomly oriented (β and δ phase)

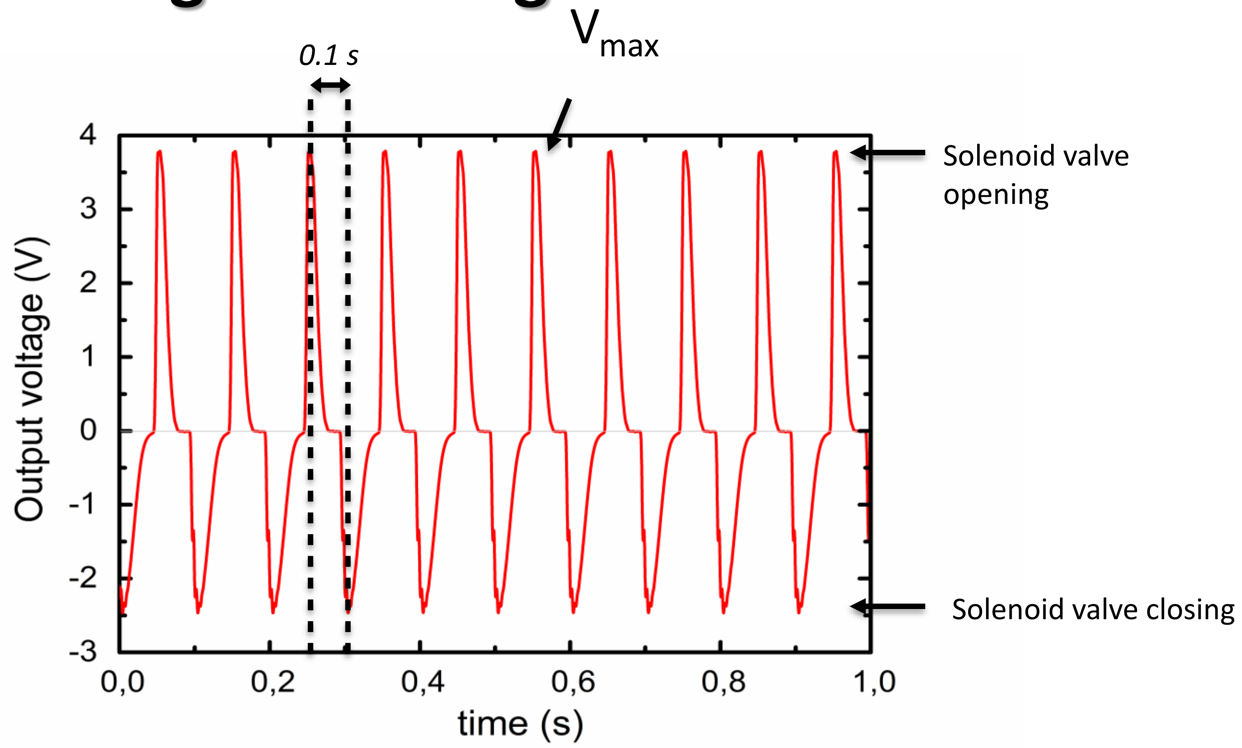


* Ilias Katsouras *et al.* Nature Materials 15, 78–84 (2016)

β-PVDF performances
to exploit Energy Harvesting in bending mode

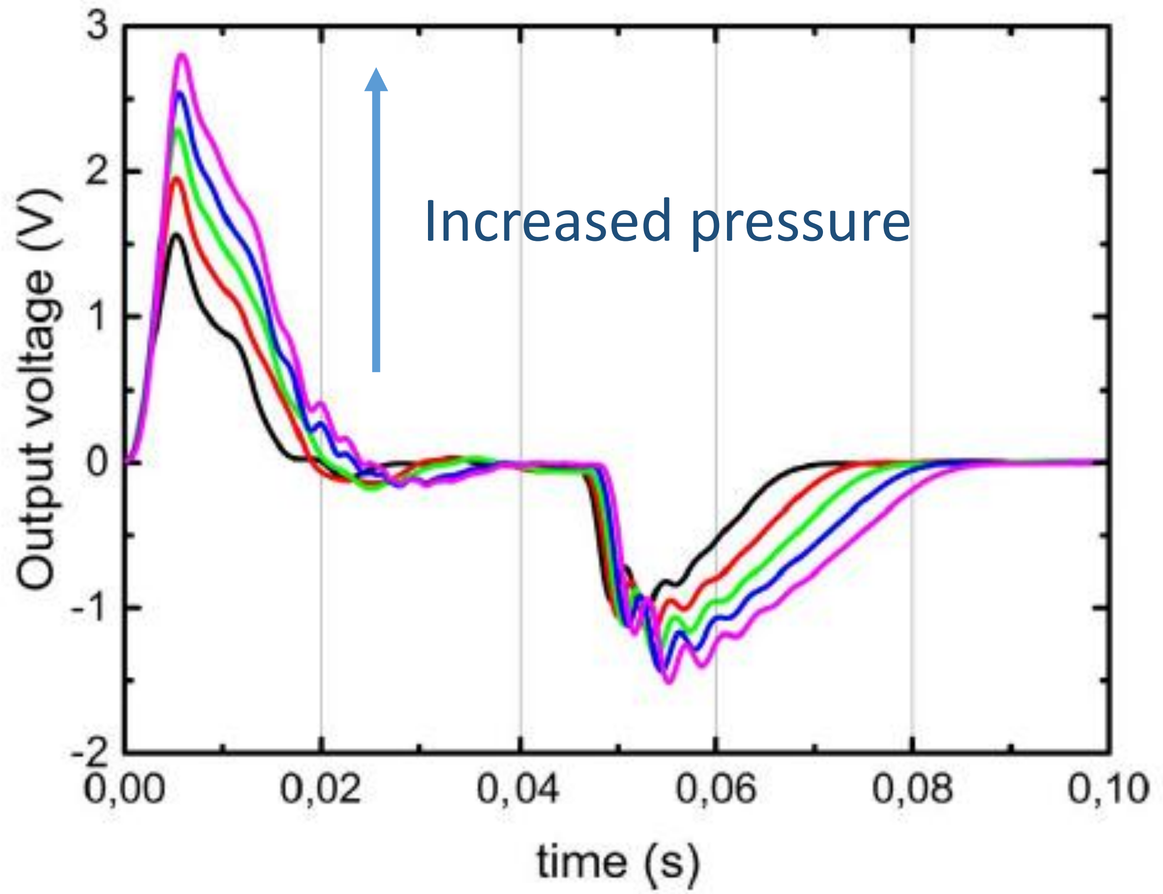


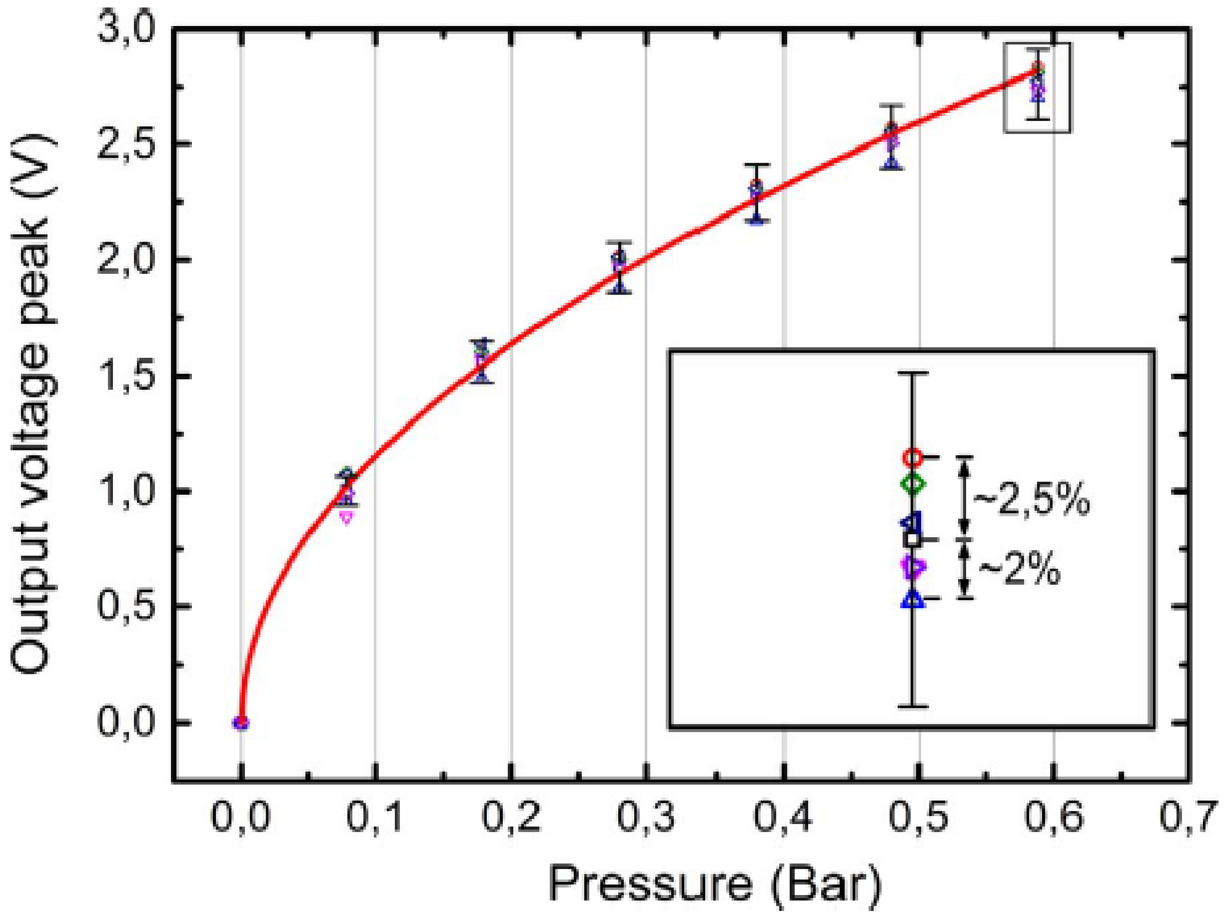




experimental set-up developed by Didier Lairez at LSI allowing the simultaneous registration of the pressure and the output voltage; bottom: open cell of 0.78 cm² with a gold sample in place

β-PVDF performances
to exploit Energy Harvesting in bending mode





Robust (thin films of 10micron thick)

no fatigue observed after more than 100 of cycles when keeping the material in its elastic region

➡ reversibility of voltages output increasing and decreasing the pressure in the chamber

Piezoelectric coefficient d_{33} of various ferroelectric materials

$$D = \epsilon^T E + d_{33} T$$

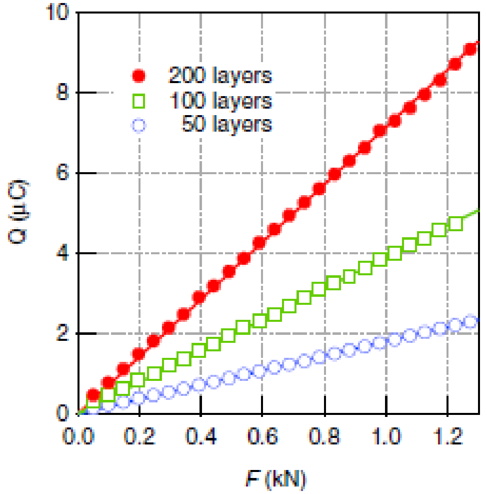
$$S = d_{33} E + s^E T$$

	Material	d_{33}(pC/N)		
		Gao et al. 2019	Vatansever et al. 2011	Vacca et al. 2014
polymer	PVDF	24-23	35	33
	P(VDF-TrFE)	25-40		
Inorganic material	ZnO	12-13		5.9
	PZT	225-590	220	50-150
	$BaTiO_3$	191		82

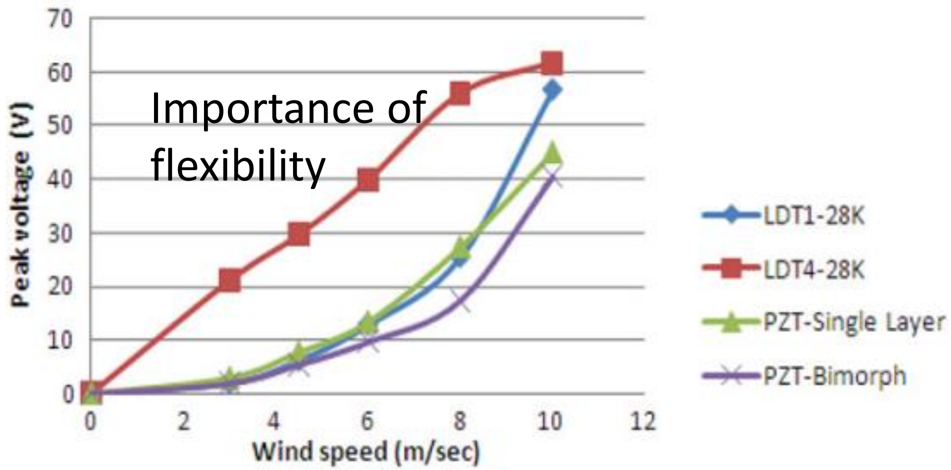
In context of fabricating piezogenerator:

D_{33} higher for ceramics and PZT BUT

- Problem of mechanical breakdown for PZT [Nakajima et al. 2011]
- PVDF is robust, flexible and cheap
- PVDF allows to work on large surface
- Multilayers of PVDF



Press stress dependence of generated charge of rolled PVDF film
[Nakajima et al. 2011]

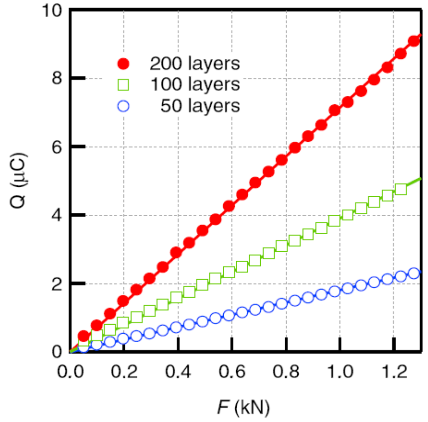


Voltage responses of PVDF and PZT composite films with respect to various wind speed. [Vatansever et al 2011]

State of the art: Architectural strategies for flexible piezogenerators

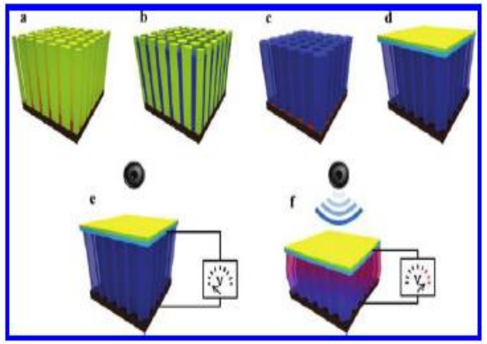
Inclusion of 1D nano-objects

Multilayers



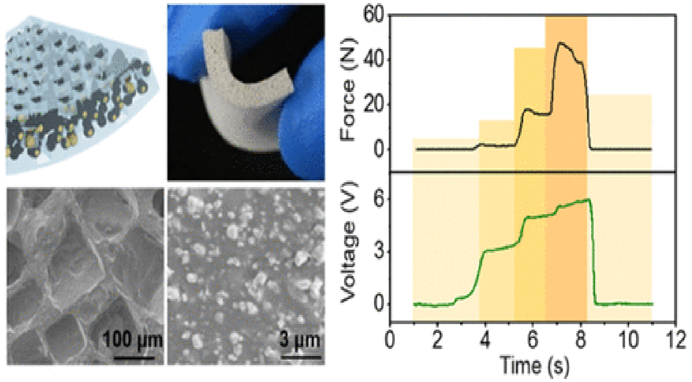
Jpn.J.Appl.Phys (2013)

Nanostructuration



Corea; Samsung, Nano Lett. 2011

Composite



China; Appl. Mater. Interfaces, 2018

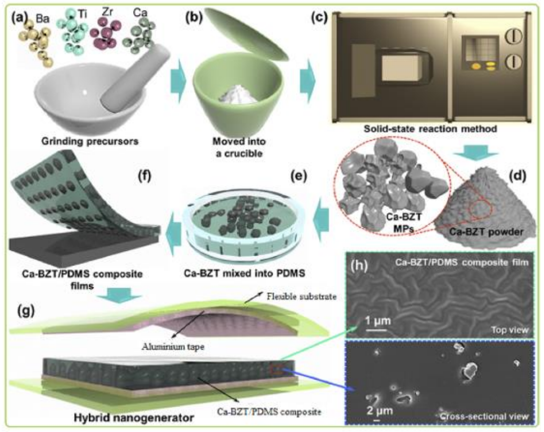


Fig. 5. Fabrication of Ca-BZT MPs composite [71].

Compos Sci Technol., 2020

Increased performances playing both with d_{33}, permittivity and flexibility

$$D = \epsilon^T E + d_{33} T$$

$$S = d_{33} E + s^E T$$

Melilli et al., J Material Sci Eng 2018, 7:2
DOI: 10.4172/2169-0022.1000444

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Commentary Open Access

Enhanced Piezoelectric Response in Nanostructured Ni/PVDF Films

Melilli G[1], Lairez D[1,6], Gorse D[1], Galifanova A[1], Oral O[1], Balanzat E[2], Doaré O[3], Tabellout M[4], Bechelany M[5], Wegrowe JE[1] and Clochard MC[1]*

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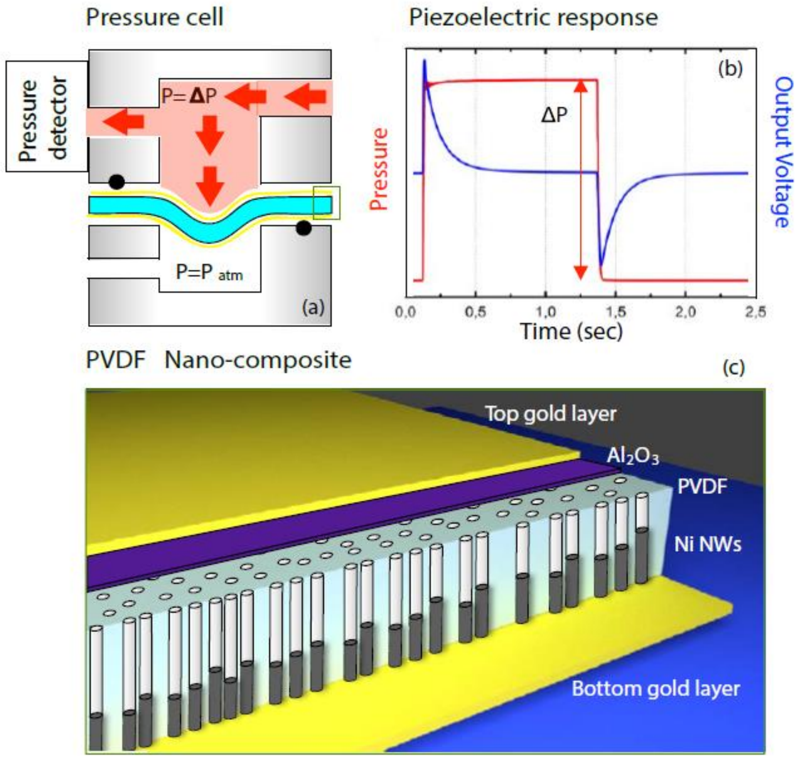
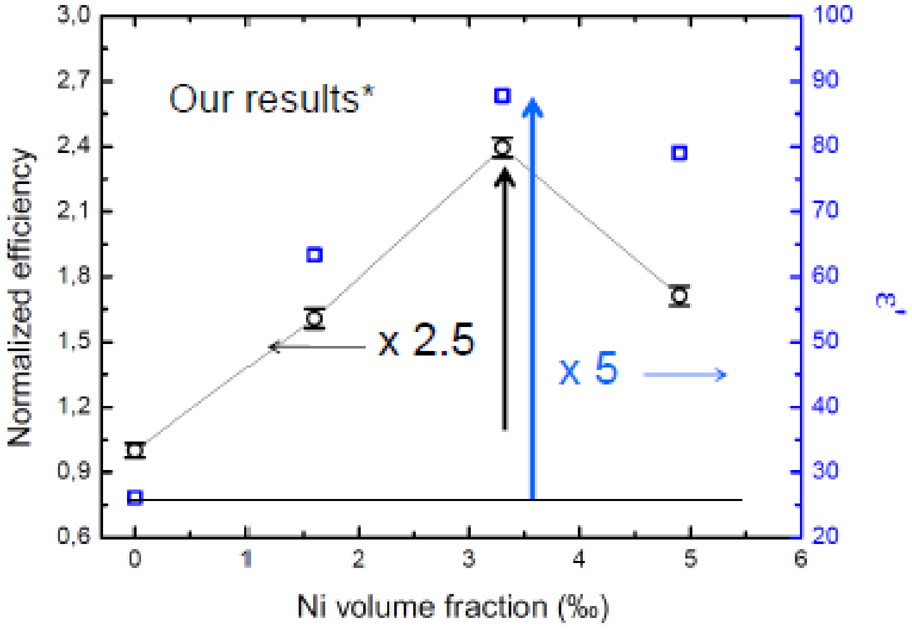
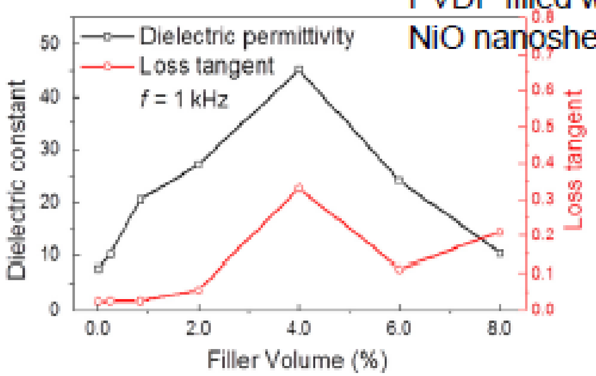


4,5 µm length



From Amoresi et al. Ceramics (2015)

PVDF filled with NiO nanosheets



Maxwell-Wagner-Sillars interfacial polarization

. Static permittivity x 5

. **Piezoelectric efficiency x 2.5**

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Mixing nanostructured Ni/piezoPVDF composite thin films with e-beam irradiation: A beneficial synergy to piezoelectric response

Natalia Potrzebowska [a], Olivier Cavani [a], Ozlem Oral [a], Olivier Doaré [b], Giuseppe Melilli
Jean-Eric Wegrowe [a,*], Marie-Claude. Clochard [a,*]

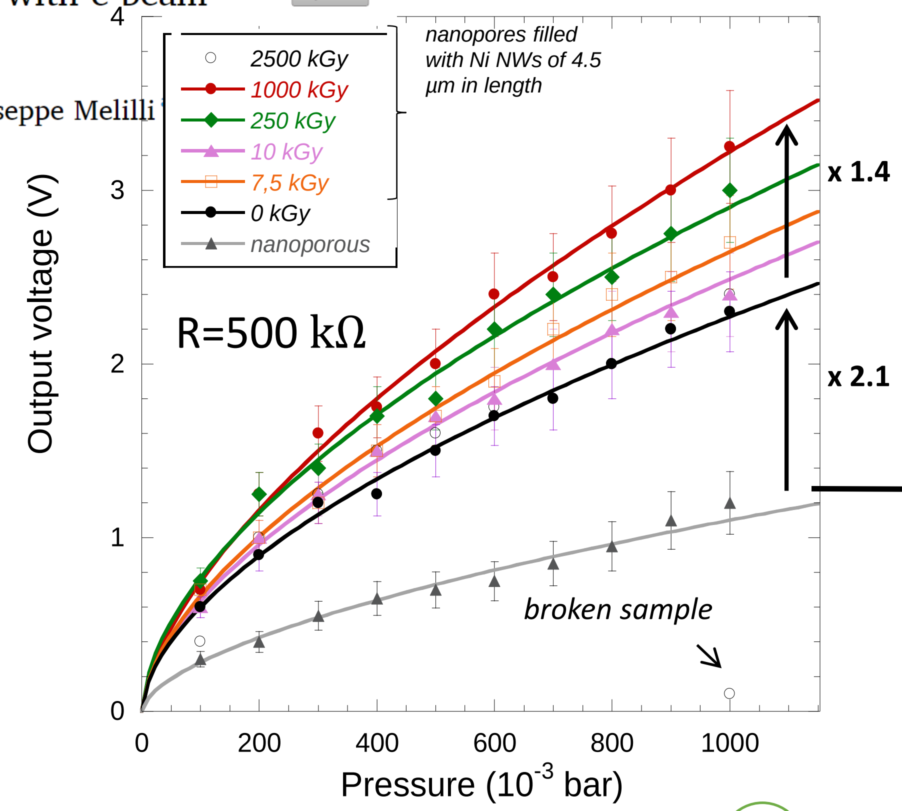
$^{136}_{54}Xe^{43+}$ 7,0024 MeV/A

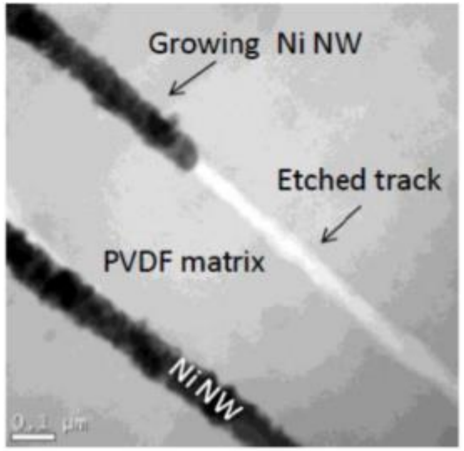
D1/SME

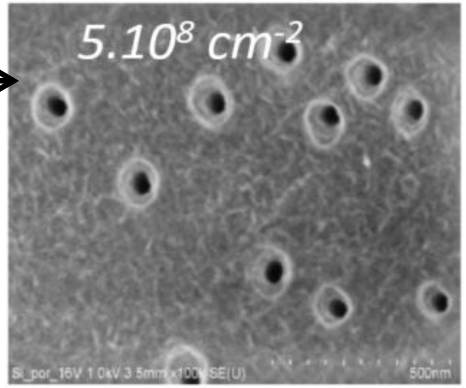
Technological locks:

. weak capacity for small pieces

Solution: insertion of inorganic nanostructures in polymer bulk to enhance the permittivity + irradiation damages to increase the material flexibility







➔ increase of both the permittivity ε^T x 5 and the compliance $\mathbf{S^E}$ x 1.125

➔ piezoelectric response **x 3.5**

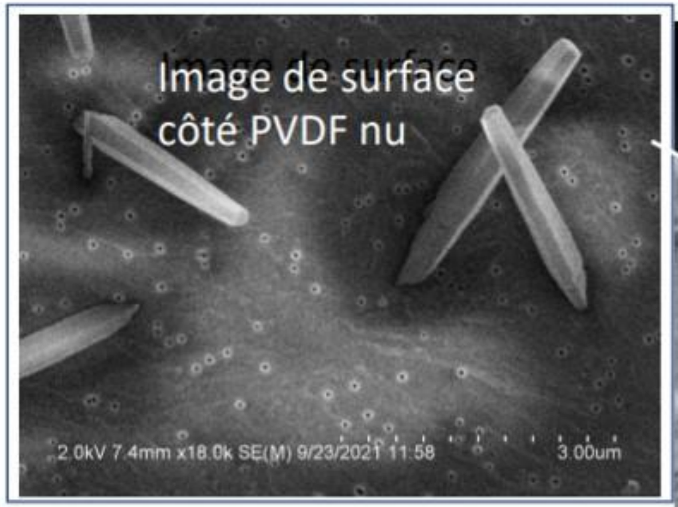
P_{max}=24µW/cm² for 1 film of 10μm thick

$$D = \epsilon^T E + d_{33} T$$

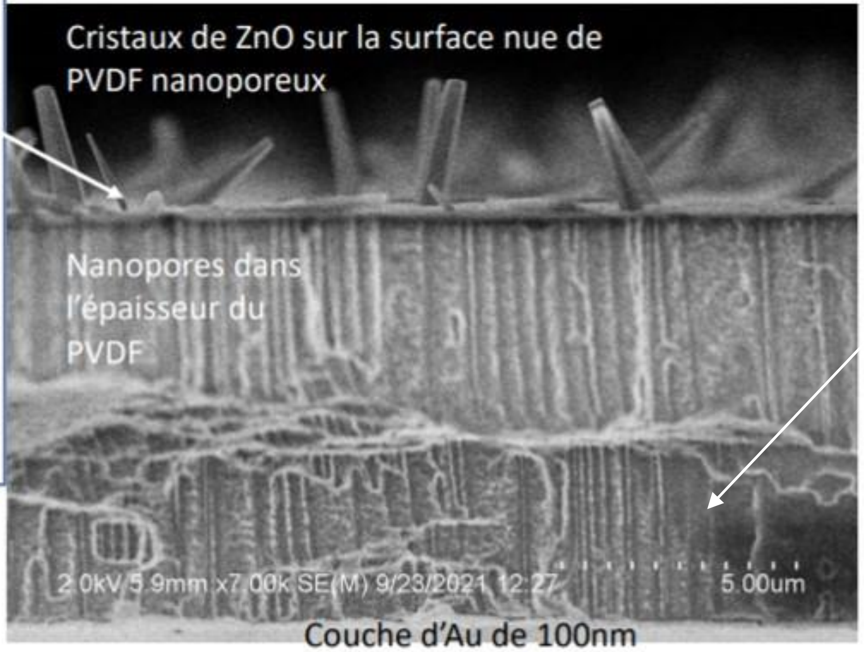
$$S = d_{33} E + s^E T$$

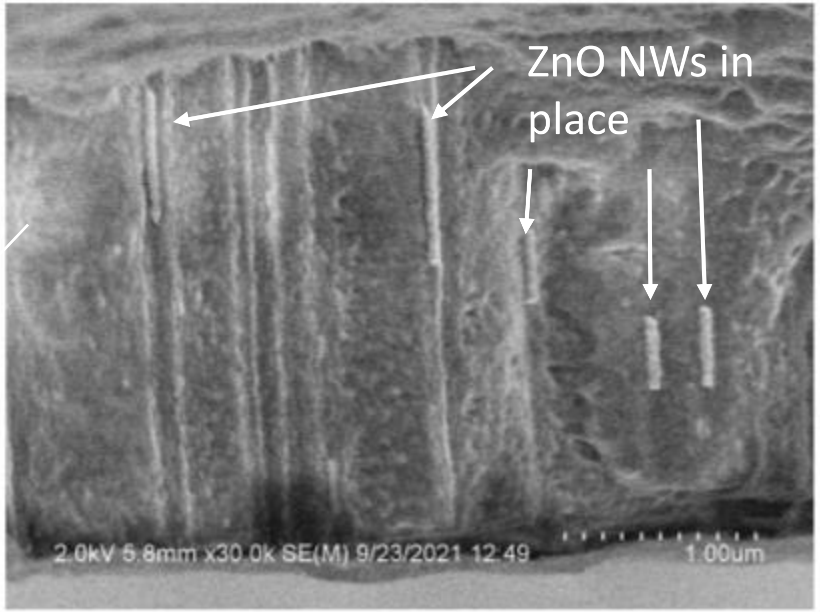
NanoSaclay
Laboratoire d'Excellence

Preliminary results: piezoPVDF/ZnO NWs



Diamètre des nanopores env. 80-100nm; densité 5.10^{8} cm^{-2}

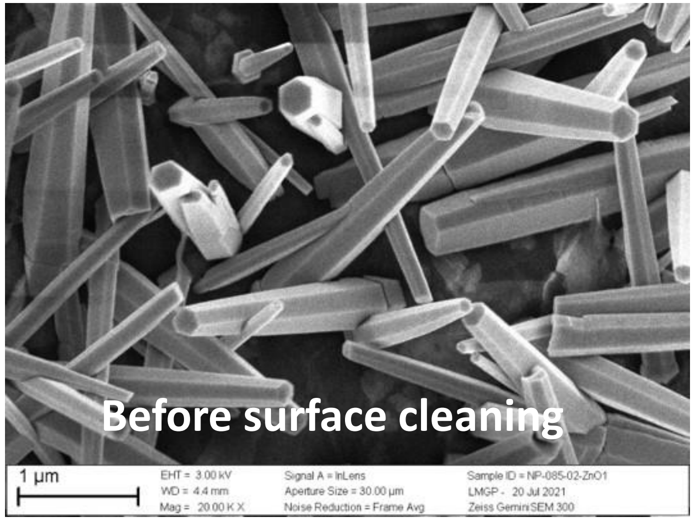


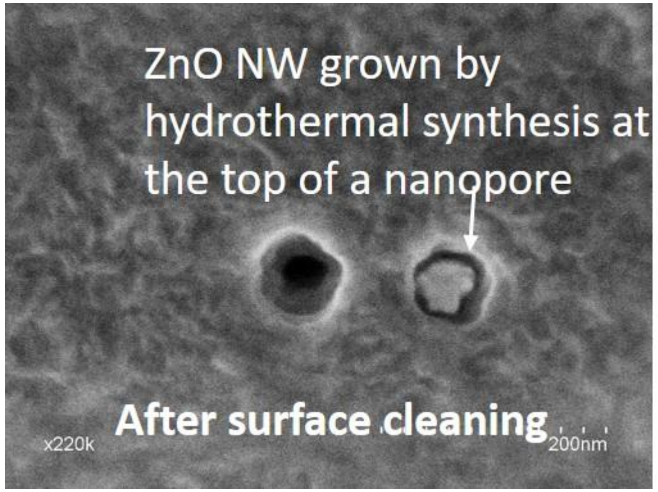


Collaborative work with

GEMAC (V. Sallet / J. Scola)

LMGP (V. Consonni)

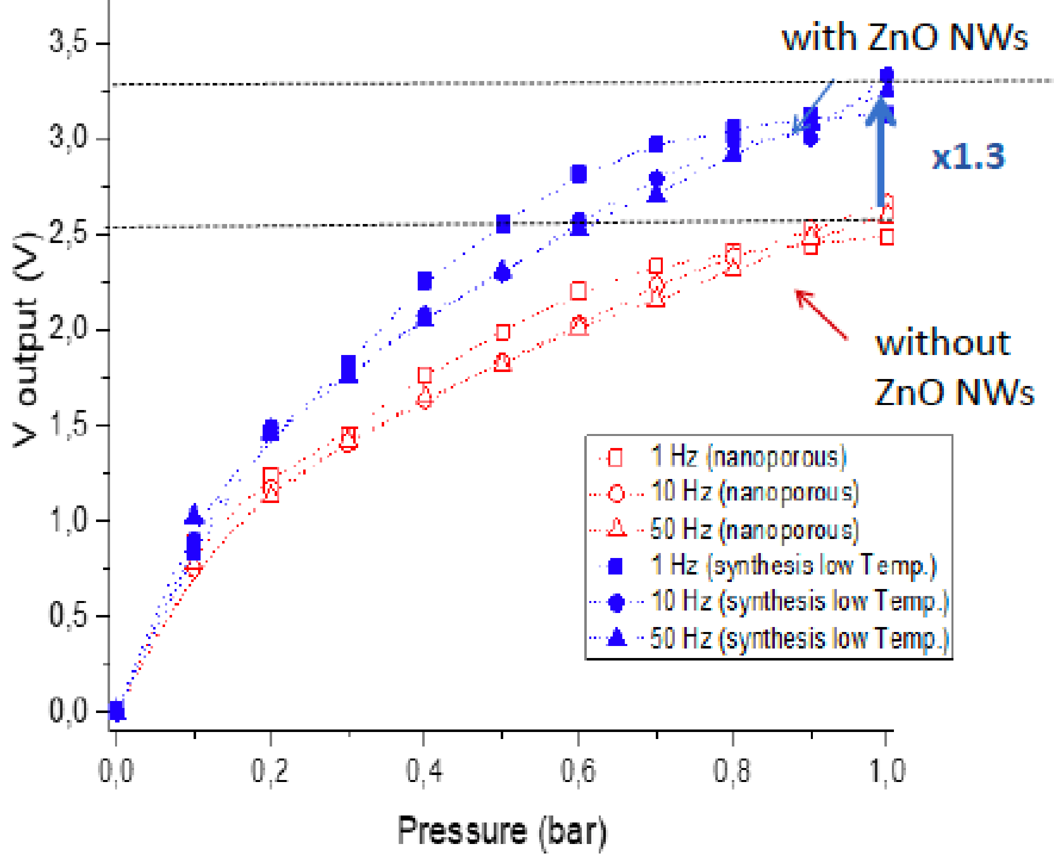


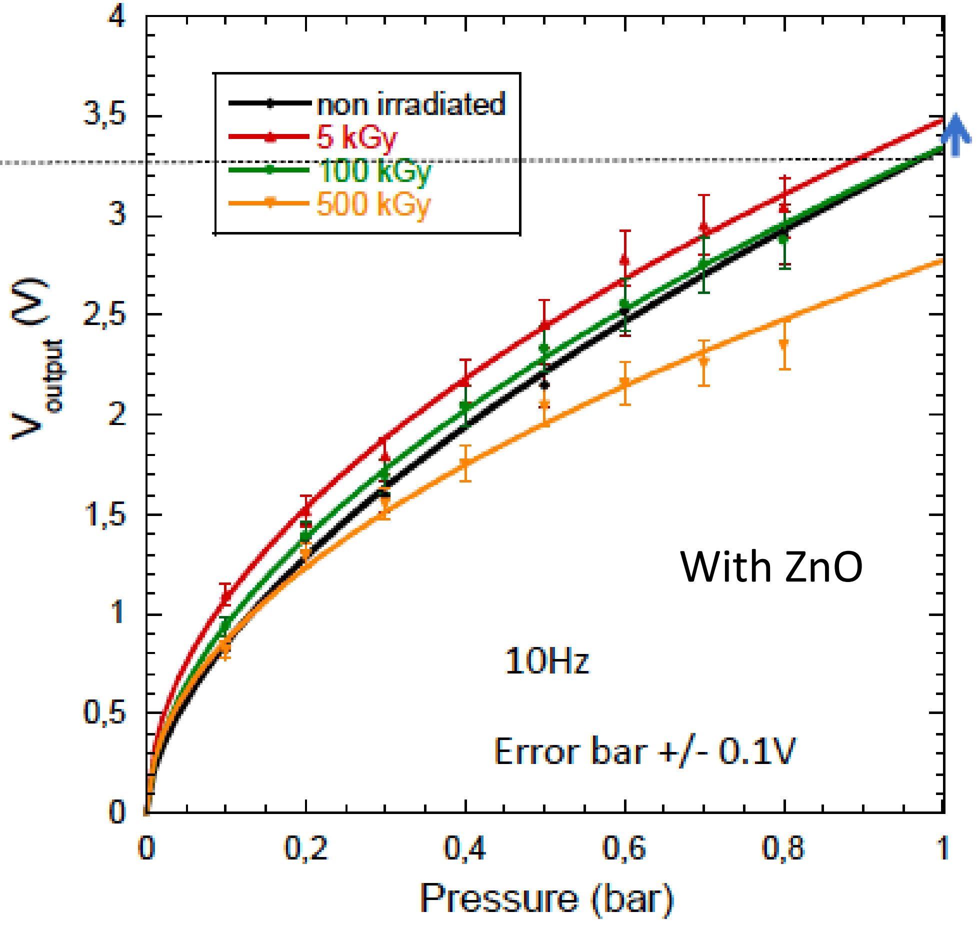


Axe de nucleation section hexagonale 001

Preliminary results: piezoPVDF/ZnO NWs composites

$V_{output(ZnO)} \approx V_{output(Ni+e\text{-}beam)}$





R=1 MΩ, 50 cycles; Diameter of pores ca. 80-100 nm; Fluence 10^9 cm^{-2}

Next = more work on ZnO growing synthesis, NWs density and ZnO doping

Thank you for your attention

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CPM Sebastien Ceste

GANIL: Yvette Ngono-Ravache

Platform XRD: Sandrine Tusseau-Nenez

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