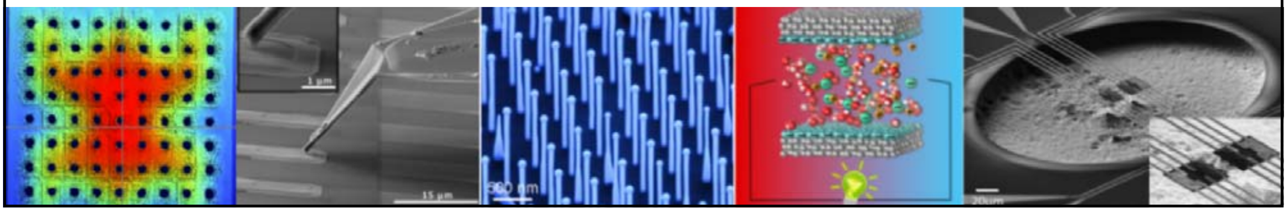
Journées du GDR-NAME 19-21 mai 2021

GDR NAnoMaterials for Energy applications
ELABORATION
MESURES METROLOGIE
SIMULATIONS THEORIE
APPLICATIONS

Atelier #6
Micro-Nano-Devices
(for energy applications)



Outline

1. Thermo-Photo devices

- Integration of Thermoelectric micro-nano devices
- Photovoltaics devices
- Thermophotovoltaic devices (with nanoscale gaps)

2. Kinetic devices

- Piezoelectric Kinetic Energy Harvesters
- Electrostatic Kinetic Energy Harvesters

3. Other devices

- Nano LED
- Adiabatic logic with micro/nano devices
- Piezoelectric energy converters

4. Metrology

- Metrology for thermal properties of thermoelectric micro/nano devices
- Metrology & standardization for kinetic energy harvesters

Integration of Thermoelectric micro-nano devices

Dimitri Tainoff (Inst. Neel, MOIZ)
Katir Ziouche (IEMN)

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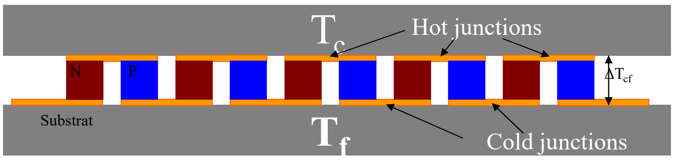
Vertical technology

Bulk → micro devices



Thermocouples perpendicular to both surfaces

- Most widespread technology,
  → miniaturization is challenging.
- The heat flows directly through the thermoelectric materials
  → The device efficiency depends only on thermoelectric materials

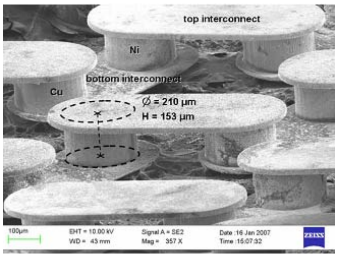
➔ **Figure of merit improvement ZT**

⇒Maximise the power factor $\alpha^2.\sigma$

⇒Minimise the thermal conductivity κ

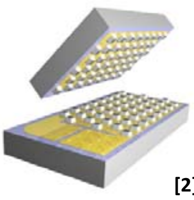
Materials and ZT # group 3

Examples of vertical technology integration

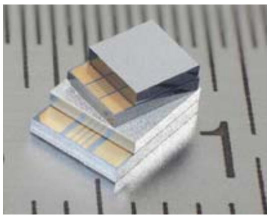


[1]

- Made on flexible substrate
- Thermoelectric microgenerator (µTEG) and thermal microfluxmeter
- GreenTEG company created from Swiss Federal Institute of Technology (ETH)



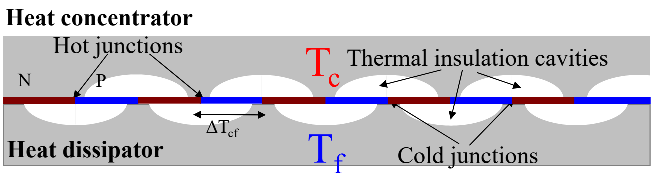
[2]



- Vertical technology of µTEG or fluxmeter (marketed products, MPG-D751 made by “micropelt”)
- Sensitivity of de 140 mV/K at 23° C (dimension 14 mm^2, electrical resistance 300Ω)

Planar technology

Micro-nano devices



Thermocouples parallel to both surfaces

- Easier to integrate onto nano/micro TE device fabricated on silicon
- Heat flows not only through TE materials (support, concentrator and dissipator)

Efficiency improvement :

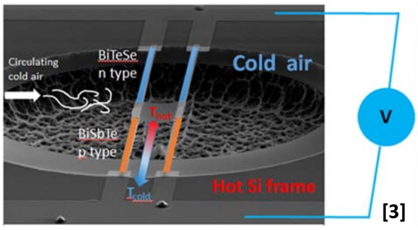
⇒ Maximise the **figure of merit ZT of materials**

Materials and ZT
group 3

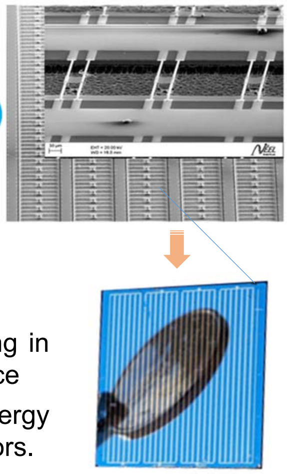
⇒ **Design optimization to collect heat and limit losses**

group 6

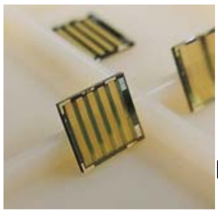
Examples of planar technology integration *(micro-nano devices)*



[3]



- Planar technology
- Numerous nanoTEG are coupling in parallel → low electrical resistance
- Application : micro-source of energy for autonomous connected sensors.



[4]

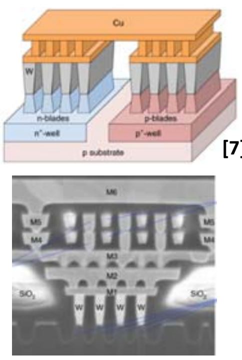
Suspended thermopile (onto multi membranes)

Planar monolithic µTEG

- Technology of µTEG
- High thermal planar resistance
- Out power ~300 µW/cm² for 1 W injected

NAMe GDR Nanomaterials for Energy Applications

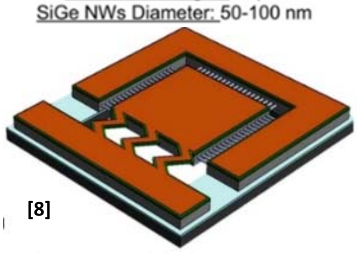
Others examples of TE micro-nano devices



[7]

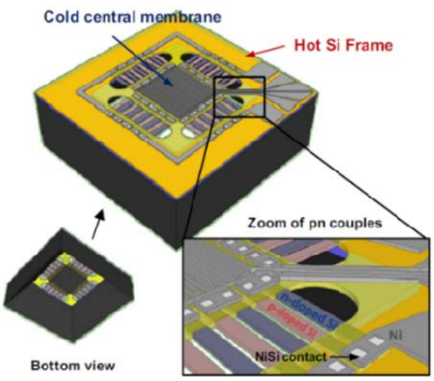
- Si integrated TE generators
- Vertical nanostructures

Single device area: 2 mm²
SiGe NWs Length: 10 µm
SiGe NWs Diameter: 50-100 nm



[8]

- Top down micromachining
- Growth of SiGe nanowires



[5,6]

- Micropower TE generator from thin Si membranes

NAMe GDR Nanomaterials for Energy Applications

Photovoltaics devices

Jean-Paul Kleider (GeePs, FedPV)

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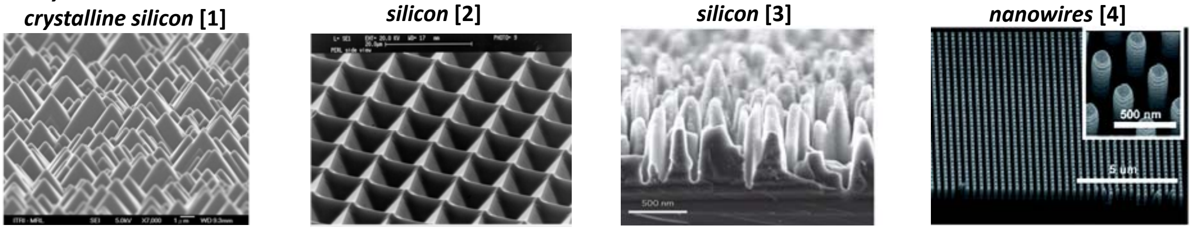
Nano aspects: different levels, in different technologies

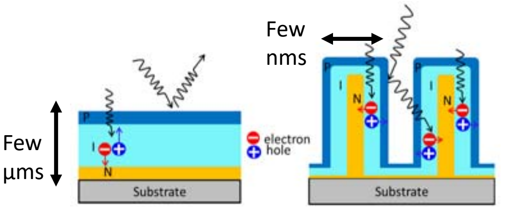
- Nanostructured architectures
  nanophotonics → increase light absorption through patterning
  nanowires, radial junction nanowire solar cells
  → decouple light absorption and electrical transport/carrier extraction

- Nanometric layers acting as passivation/buffer layers or enhancing collection of one type of carriers
  → concept of passivating selective contacts (e.g. in silicon PV)
  → transport/extraction layers in perovskite PV (e.g. NiO_x as hole transport layers, TiO_x as electron transport layers, self-assembled monolayers)

Silicon nanowires: as an ultimate of texturing

Pyramid textured crystalline silicon [1] | *Inverted pyramid silicon* [2] | *Black silicon* [3] | *Silicon nanowires* [4]





planar junction | *radial junction*

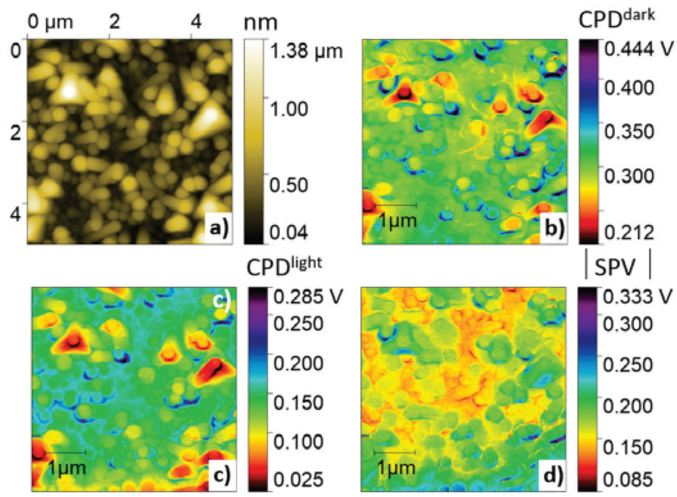
Radial junction nanowire structures enable [5,6]

- Strong light trapping and anti-reflection
- Short distances to extract carriers

→ Potentially higher open-circuit voltage and better performance for defective materials as compared to planar junction solar cells

Main issues: passivation of nanowires → at present, record efficiencies < 20%

Characterization of nanowire solar cells from AFM/C-AFM/KPFM



KPFM measurements performed at the same location on NWs [7] illustrating:

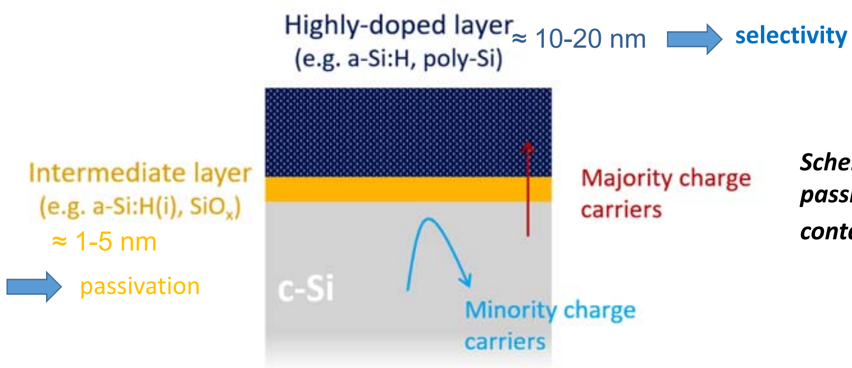
a) the topography

b) the contact potential difference (CPD) under dark conditions,

c) the CPD under white LED illumination and

d) the surface photovoltage (SPV) → V_{oc} of individual nanowires

Concept of full area passivating selective contacts: example in Si



Schematic view of a passivation selective contact [12]

- **Silicon heterojunctions solar cells: (p)a-Si:H/(i)a-Si:H/c-Si**

→ 25.6% efficiency [8], world record of 26.7% in the IBC configuration [9]

- **Poly-Si based selective contacts: (p+)poly-Si/SiO_x/c-Si**

→ 25.8% efficiency on 2x2 cm^2 area [10], 24.6% for 6"x6" [11]

Thermophotovoltaic devices with nanoscale gaps

Rodolphe Vaillon (IES)

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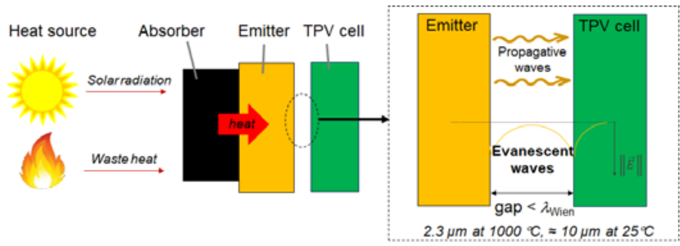
Thermophotovoltaic (TPV) devices with nanoscale gaps

- **Principle:**

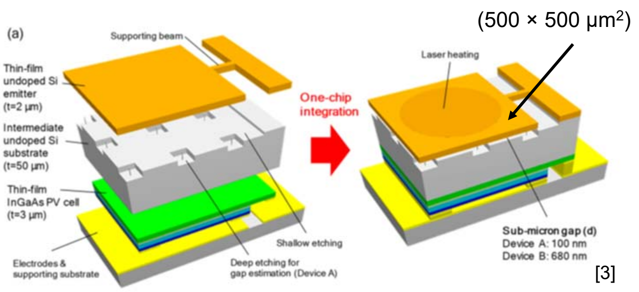


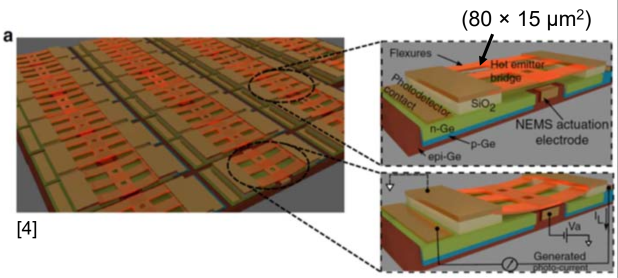
➡ Higher generated electrical power at nanoscale gaps

- **Main parameters/materials and influence of nanomaterials:** structures and fabrication techniques for building a nanoscale (< 1 µm) vacuum gap between the hot (> 500 °C) and cold (room temp.) sides (see also near-field radiative heat transfer devices ([1] but ΔT < 200 °C))

Recent first convincing experimental demonstrations [2-5]

- Among them, **two devices**:





- **Performances:** < 1 mW.cm^{-2}; <u>estimated</u> efficiency < 1%
- **Applications:** thermal energy harvesting. Research stage (TRL <4)
- **Future challenges:** devices with much larger areas, temperature differences and performances (emitter/cell design challenges: see Working Group 3)

Piezoelectric Kinetic Energy Harvesters

Guylaine Poulin-Vittrant (GREMAN)
Gustavo Ardila (IMEP-LAHC)
Vincent Consonni (LMGP)
Hélène Debéda (IMS)
Noelle Gogneau (C2N)
Maria Tchernycheva (C2N)

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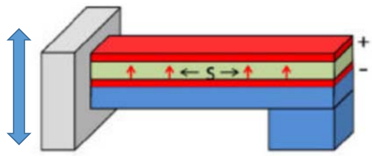
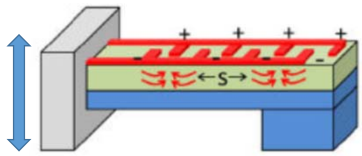
MEMS cantilever-type piezoelectric harvesters

- **Principle:** Vibration applied to a bending cantilever (piezo layer on a passive substrate, Si or metal)
- **Piezo films:** various deposition methods [3]
  - ✓ **Thin films** (< a few μm): sputtering, MOCVD, laser ablation processes, sol-gel process
  - ✓ **Thick films** (> 10μm): hydrothermal method, aerosol-deposition, granule spray in vacuum, electrophoresis [4], screen printing, tape-casting…



Piezoelectric unimorph in 31-mode

[1]

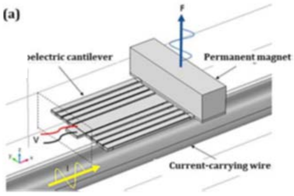


Piezoelectric unimorph in 33-mode

MEMS cantilever-type piezoelectric harvesters

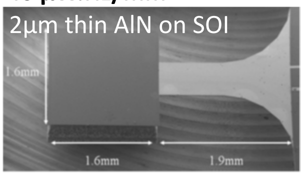
- **Key issues:** for integration in MEMS technology
  - ✓ Growth of oxide films on Si or metal substrates : inter-diffusion, large lattice & thermal expansion mismatch
  - ✓ Clamping effect on the substrate ⇨ lower effective piezo coefficient
  - ✓ Proper texturing of electrode layers
  - ✓ If piezo layer thickness < 1µm ⇨ low generated voltage

9µW, 60Hz, **3 µW.Hz/mm³**
(depends on current and distance to wire)



- **Performances:**
  10^{-3} to 10 µW/(cm².Hz.g²)
  or 10^{-4} to 10^{-1} µW/(mm³.Hz.g²)
  on a frequency range: 100-1000Hz [3]

0.5µW, 212Hz, 0.68g [2]
40 µW.Hz/mm³



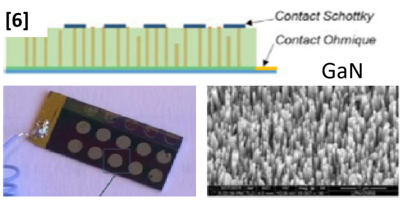
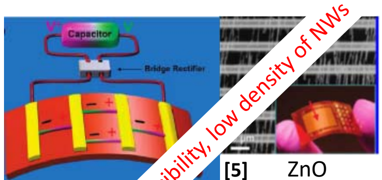
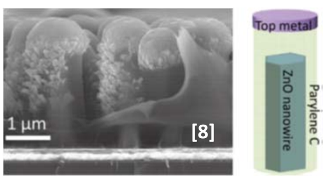
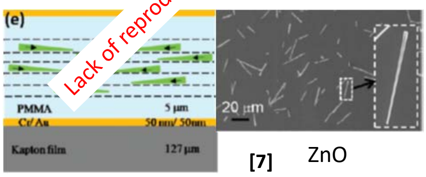
50µm thick PZT by screen printing on stainless steel

[1]

Gold ball-bonding connection

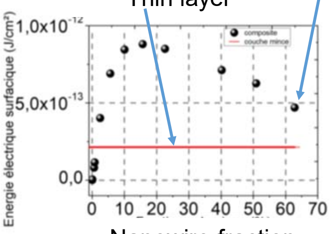
Piezo-semiconducting nanowire based nanogenerators

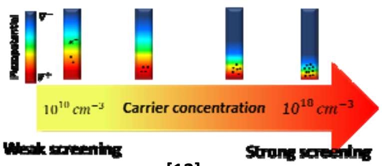
A **NW array** embedded in a polymer matrix, between electrodes and on a rigid or flexible substrate. Various configurations :

	NWs orthogonal to the substrate	NWs parallel to the substrate
Electrodes are in contact with the NWs	[6]  GaN	 [5] ZnO
Capacitive coupling between NWs and electrode via insulating layer	 [8] ZnO	 [7] ZnO

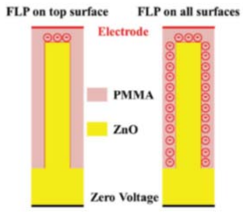
Main parameters / influence of nanostructured device

NW should have [9,10,11]: high aspect ratio, optimal density, low doping (charges screening), polarity uniformity.



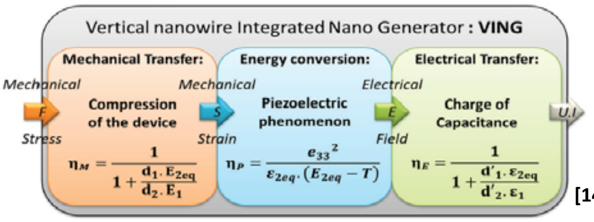


+ effect of Fermi Level Pinning [13]



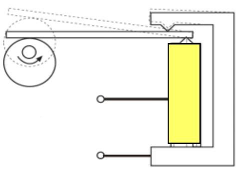
+ other electrification effects (tribo, flexo…) under debate

NW environment:
Electrodes
and encapsulating layer
electrical and mechanical properties

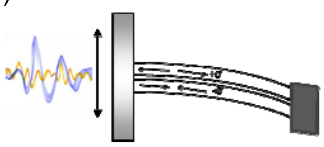


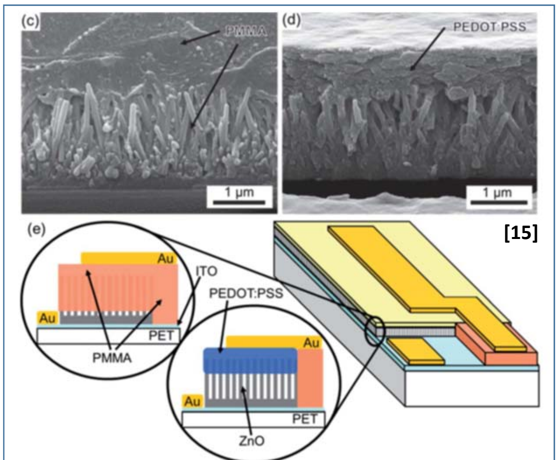
Performances and applications of nanogenerators

- Large variety of mechanical testing conditions (compression, bending) [15]
- Mostly under compression:
  1-10 µW/cm² @ a few N force
  @ 0.3 to 5 Hz [16]



- Comparison with bending cantilevers:
  10^{-3} to 10 µW/(cm².Hz.g^2)
  (base of a machine tool : 10 m/s² [3] ≈ 1g)





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

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

Electrostatic Kinetic Energy Harvesters

Philippe Basset (ESYCOM)
Alain Sylvestre (G2ELAB)
Elie Lefeuvre (C2N)
Dimitri Galayko (LIP6)

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Main requirements for electrostatic transducers

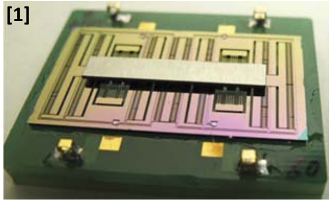
→ Need (high) capacitance variations + polarization

- Spring-mass system (inertial or direct-pressure)
- Soft polymer covered by electrodes (direct-pressure)

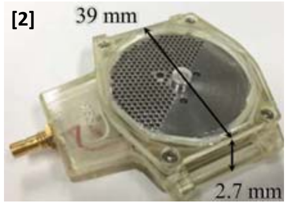
- External DC source
- Charged electret
  - ✓ Injection
  - ✓ Poling
  - ✓ Tribo-electrification

Inertial Si-based MEMS KEH

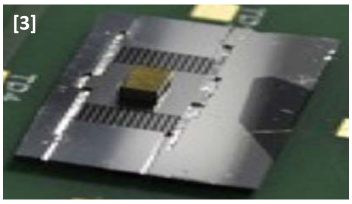
- External mass for low frequency / low *g* applications
- Bias from
  - ✓External DC source
  - ✓Corona discharge
  - ✓“Solid-state” electret
- Typ. 1-10 µJ / mechanical cycle / *g* / cm²



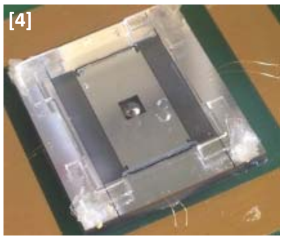
For SHM (50 Hz)



For smart watch (rotation)



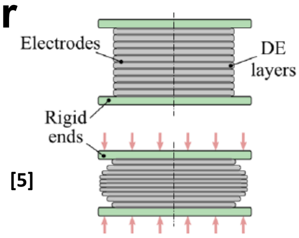
For pacemaker (10-20 Hz)

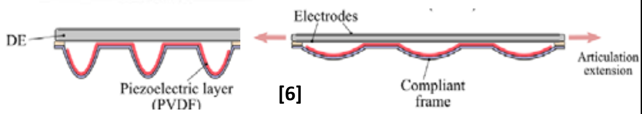


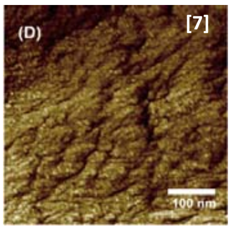
For RFID tag (1-10 Hz)

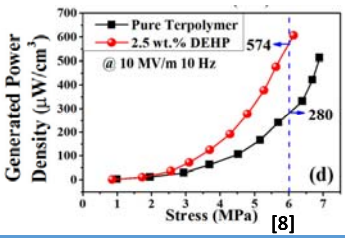
Dielectric elastomer & electrostrictive polymer

- Capacitance variation is obtained with a deformable elastomeric dielectric material
- Polarization:
  - ✓Include an electret or a piezoelectric layer
  - ✓Or need an external electric field
- Upto mJ / cm^3 / mech. cycle @ few kV and few 100’s% of deformation
- Applications: high-pressure/ extension systems (shoe sole, water waves…)

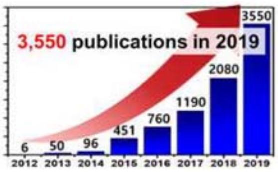






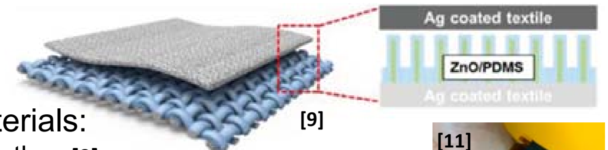


Triboelectric (nano)generators (TENG)



→Polarization by contact electrification of an electret layer

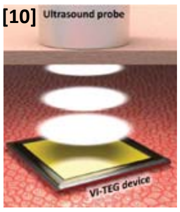
→Mostly direct-pressure devices



[9]

- Lot of possible flexible materials:
  - ✓ Harvesting from textile in clothes **[9]**
  - ✓ Power transfer through ultrasound waves **[10]**
  - ✓ Patches for "2nd skin" applications **[11]**
  - ✓ Air flow harvesting **[12]**

[10]



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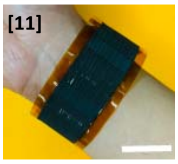

- Typ. tens of nJ to a few µJ / mech. cycle / cm²
- Applications: smart textile, energy transfer to implant…

[12]

Nanowire Light Emitting Diodes

Maria Tchernycheva (C2N)

- Integration of Thermoelectric micro-nano devices
- Photovoltaics devices
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- Piezoelectric Kinetic Energy Harvesters
- Electrostatic Kinetic Energy Harvesters
- Nano LED
- Adiabatic logic with micro/nano devices
- Piezoelectric energy converters
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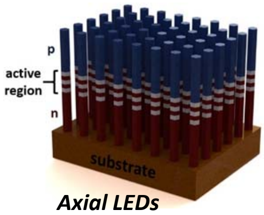
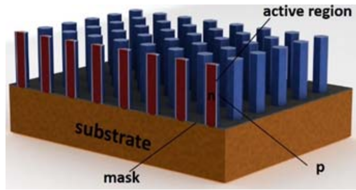
Potential benefits of nanowire-based LEDs

- Efficient strain relaxation – **dislocation-free nanocrystals**, higher QE
- Growth on **low-cost substrates**



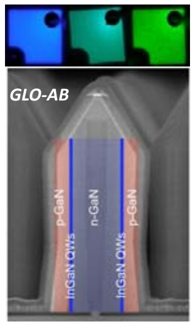
Axial LEDs

[1]

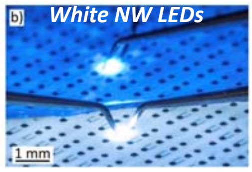


Radial LEDs

Core/shell InGaN NW LED



[6]



✓ *Dislocation free highly mismatched active region (e.g. In-rich InGaN/GaN QDiscs to cover the **green gap**)*

✓ *Increase of the emitting surface - decrease of current density – **reduction of droop***

✓ *Lateral surface is non-polar – **no field***

- Strong effort on NW LEDs to compete with planar LEDs
- Small size – mechanical flexibility. Good for alternative applications : **flexible light sources**

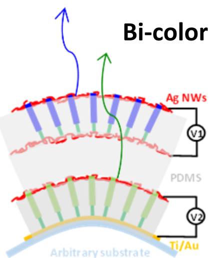
Flexible nanowire LEDs

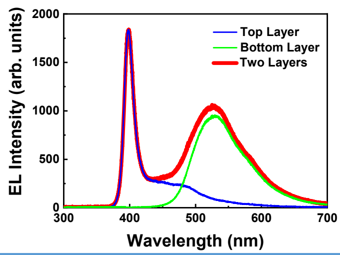
Flexible blue, green and white light sources and high brightness displays using nanowire/polymer membranes

- Combine crystalline III-V **materials** with flexible polymers
  - ✓Flexibility of polymers and high efficiency and long lifetime of crystalline materials
  - ✓Modularity – combination of “incompatible” materials

Flexible blue, green and white NW LEDs

Bi-color flexible LEDs





Adiabatic logic with micro/nano devices

Gaël Pillonnet (CEA)

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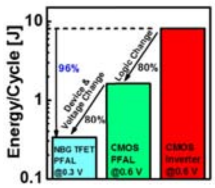
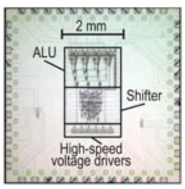
Devices for near zero-power Boolean operations

- **Fundamental limitation of FET approaches [1]**
  - ✓ Ultimate power consumption (~kBT) is not achievable using nano-scale transistors [2,9]



[7]

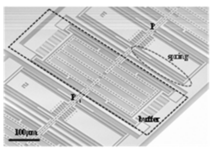
- **Adiabatic Operations**
  - Reduce current flows and recycle energy by reducing the speed [3]
  - ➔ Enable near zero-power operations from energy-reversible micro-scale devices



[6]

- **Candidate to be a « Landauer switch » :**
  - ✓ MEMS w/ or w/o mechanical/electrical contact [4,5,8]
  - ✓ Solid state devices: Josephson [6], tunnel junction [7]

- **Applications**
  - ✓ Processing in IoT devices
    - + fundamental : explore the minimal energy floor of Boolean operations



[5]

Piezoelectric energy converters

Gaël Pillonnet (CEA)
Dejan Vasic (SATIE)

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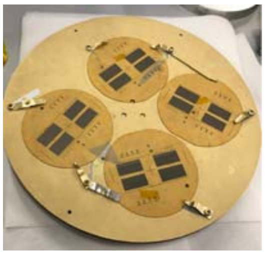
Piezo Resonators for Power Converters

- **Motivation:**
  1/ Magnetic devices have a sub-linear scaling-law in miniaturization [1,2]
  2/ Piezoelectric resonators are inductive behavior and can be scaled down without penalty [3]
  ➔Revival piezo MEMS devices for power conversion
- **Ideal candidate [4]:**
  ✓high coupling (k^2>10%),
  ✓high quality (Q>1000),
  ✓MHz frequency (>> harvesting)
- **State of art:**
  ✓macro-scale PZT [5],
  ✓LnO MEMS [6]



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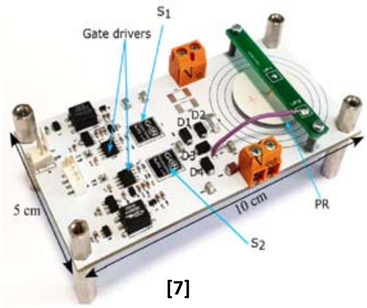


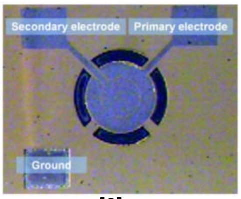
[7]

- **Applications**
  ✓DC-DC converters
  ✓1's Watt @MHz with cm^2-scale devices could be achieved

Micro Transformers for Power Converters

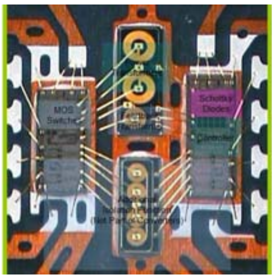
- **Motivations:**
  1/ Need to supply micro-systems @high voltage and @low-power
  2/ Find a alternative to bulky magnetic transformers with poor scale-down property
  3/ Piezo Devices is almost a planar devices
  ➔ Piezo devices are a key enabler to achieve low form factor and scale down the size vs power requirements

- **SoA candidate:**
  ✓PZT transformer [8],
  ✓AlN [9],
  ✓Coreless [10]



[8]

[9]



[10]

- **Applications:**
  ✓DC-DC converter from µW to mW, MHz, 100's V

Metrology for thermal properties of thermoelectric micro/nano devices

Nolwenn Fleurence (LNE)

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What is metrology and why is it useful ?

Reliability, reproducibility and comparability

physical value

number

unity

$$Q = (\{Q\} \pm \{u\})\ [Q]$$

uncertainty

Challenge: Measurement techniques at macroscale not suitable for nanoscales!

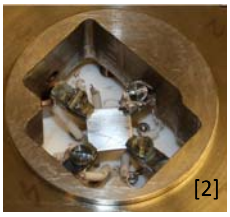
Need: characterise thermoelectric conversion efficiency

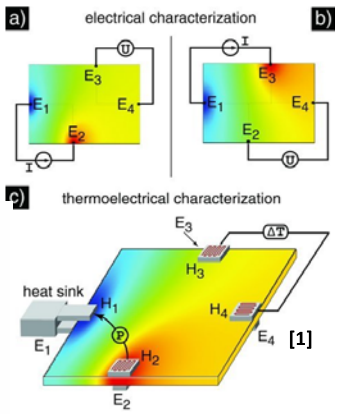
- Dimensionless figure of merit:

$$ZT = \frac{S^2.\sigma}{k}T$$

➡ Suitable for material characterization

Combined van der Pauw Approach
Uncertainty: 5 to 10% **[2]**



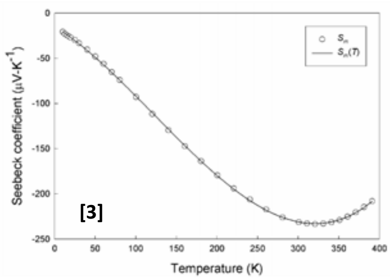


- Certified materials:

VAMAS TWA 38 Thermoelectric Materials

✓ SRM® 3451

✓ SRM® 3452

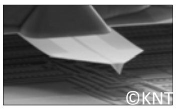


Need: characterise thermoelectric conversion efficiency

- **At device level**:

Influence of design, heat losses, thermal boundary resistances

- **Techniques:**
  - ✓modulated photothermal radiometry
  - u = 10% for $\lambda < 5 W/m^{-1}.K^{-1}$
- **Applications:** thin films structured TE devices
  - ✓scanning thermal microscopy (for $\lambda<10W/(m^{-1}.K^{-1})$)
  - u: currently 20% in best case, need to be improve
- **Applications:** nanostructured TE devices



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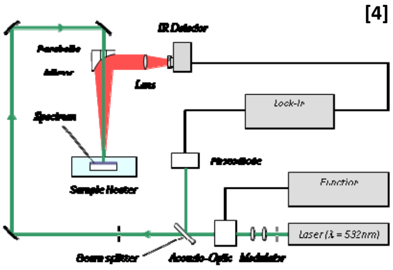

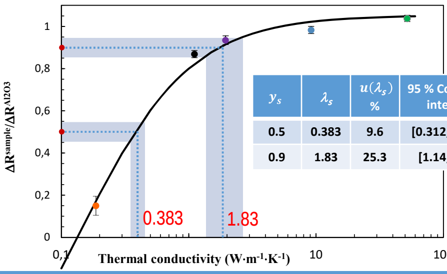

y_s	λ_s	$u(\lambda_s)$ %	95 % Coverage interval
0.5	0.383	9.6	[0.312;0.456]
0.9	1.83	25.3	[1.14;2.69]

[5]

Metrology & Standardization for kinetic energy harvesters

Elie Lefeuvre (C2N)
Mickaël Lallart (LGEF)
Philippe Basset (ESYCOM)
Guylaine Poulin-Vittrant (GREMAN)

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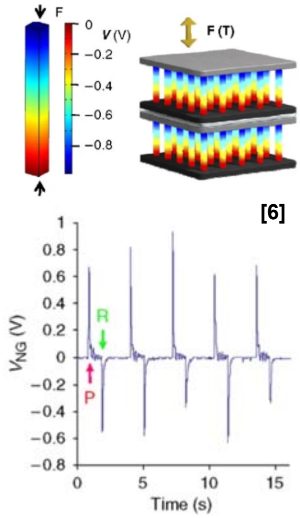
Metrology – Standardization: Mechanical EH

Characteristics of nanodevices

- Current works use various "standards" for performance evaluation
- Trend to "oversell" the performances of (nano)materials & devices:
  - ✓ ***Peak Power*** (instead of average power)
    Or even worse:
  - ✓ ***Power*** = ***Voc***$_{peak}$ x ***Isc***$_{peak}$
- **Need for common definitions, unified methods and protocols**



Metrology – Standardization: Mechanical EH

International Standard: IEC 62830

https://www.iec.ch/ [1]

International Electrotechnical Commission

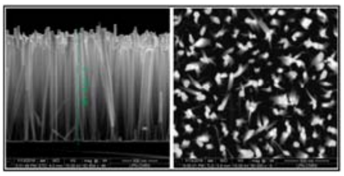
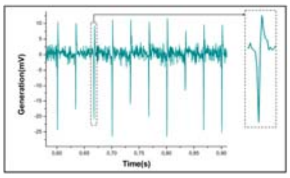
- Part-1: Vibration based piezoelectric energy harvesting
- Part-2: Thermo power based thermoelectric energy harvesting
- Part-3: Vibration based electromagnetic energy harvesting
- Part-4: Test and evaluation methods for **flexible piezoelectric** energy harvesting devices
- Part-5: Test method for measuring generated power from **flexible thermoelectric** devices
- Part-6: Test and evaluation methods for **vertical contact mode** triboelectric energy harvesting devices
- Part-7: Linear **sliding mode triboelectric** energy harvesting

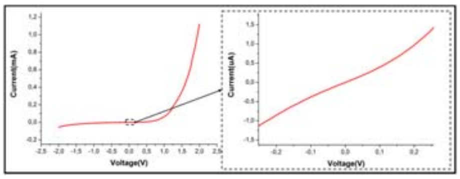
Metrology – Standardization: Mechanical EH

International Standard for Nanomaterials?

- **Thin films:**
- IEC 62830-2: **thermoelectric thin film** EH devices
- IEC 62047-30: MEMS **piezoelectric thin film** EH devices

- **Standardized Metrology for Piezoelectric Nanowires? Not yet**

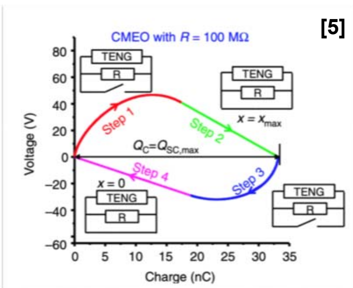





[7]

Metrology – Standardization : Mechanical EH

Need for “fair” characterization methods for nanomaterials/nanodevices used by all



- At the material level
  → figures of merit (Priya [2])
  → energy density J/m^3, J/kg... and test conditions

- At the device/system level
  → figures of merit (Mitcheson [3], Badel [4], Zi [5])
  → energy per mechanical cycle, per m^3 of "real volume"...

Metrology – Standardization : Mechanical EH

- Differentiating between
  - ✓ Inertial
    - Need a feedback control, at least for frequency sweep
    - Frequency-sweep back-and forth
    - Definition of bandwidth
  - ✓ Normal excitation
    - Need a force sensor
  - ✓ Direct friction
    - How evaluate the mechanical input?
- Electrostatic KEH
  - ✓ Normalization from QV-max for given C_{max}, C_{min} & V_{bias}
  - ✓ Breakdown voltage
  - ✓ DC output voltage
- Output power
  - ✓ in "steady-state" (at optimum operating point)
  - ✓ or from scratch (all cap/induct discharged)?

Conclusion

- Presentation far from being exhaustive
- In particular, we are looking for contributions for electromagnetic kinetic energy harvesters
- Metrology could be a workshop by itself
- Please join us if you want to contribute

Thank you for your attention!

Animateurs:
- Philippe Basset (ESYCOM)
- Skandar Basrour (TIMA)
- Nolwenn Fleurence (LNE)

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- Maria Chernycheva (C2N)
- Dimitri Galayko (LIP6)
- Noëlle Gogneau (C2N)
- Jean-Paul Kleider (GEEPS)
- Mickaël Lallart (LGEF)
- Elie Lefeuvre (C2N)
- Gaël Pillonnet (CEA)
- Guylaine Poulin-Vittrant (GREMAN)
- Alain Sylvestre (G2ELAB)
- Dimitri Tainnof (MOIZ & Inst. Neel)
- Rodolphe Vaillon (IES)
- Dejan Vasic (SATIE)
- Katir Ziouche (IEMN)

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