Silicon micro-nanotechnologies and compatible materials for the energy autonomy of small devices

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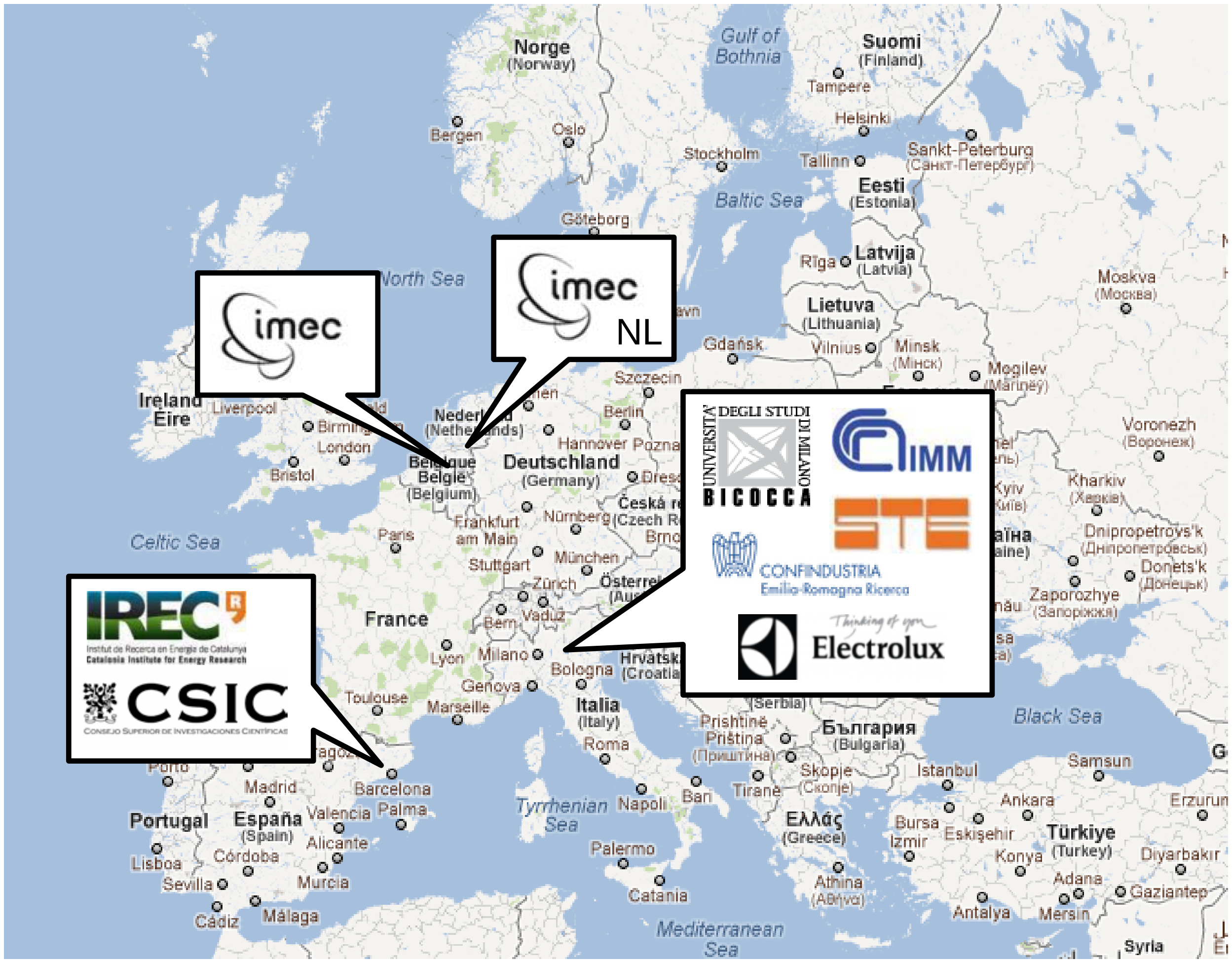
IMB-CNM (CSIC)

sinergy-project.eu

Partners

Silicon Friendly Materials and Device Solutions
for Microenergy Applications



9 partners
(ES, IT, BE, NL)

Coordinator:
CSIC
(IMB-CNM)

Title: Silicon Friendly Materials and Device solutions for Microenergy Applications

Acronym: **SiNERGY**

Call/topic: NMP.2013.2.2 -4 Materials solutions for durable energy harvesters

Duration: 36 months

Funding: 3,794,913.00 € (4.824.460.00 €)

Partners: 9 (4 countries) - **coordinated by** Luis Fonseca (CSIC)

Goal: Silicon materials and Silicon technologies & architectures for long term autonomy microenergy solutions

Focus: (1) Technology development at device level (2) Systems integration feasibility

Devices: (1) Harvesters based on thermoelectrics (2) Harvesters based on mechanical vibrations (3) thin film / 3D batteries energy

Silicon

(compatible)

technology

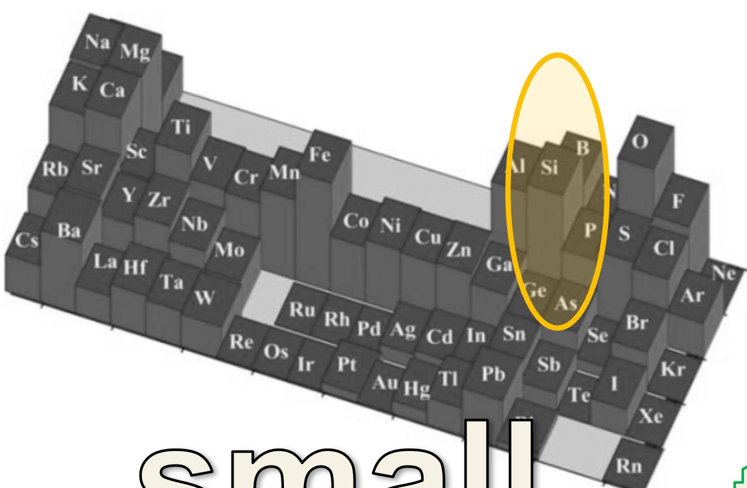
small

devices

In the wide open skies of material research.. Why to restrict to the silicon family?

Chains do not only restrain...

Enabling aspects of Silicon materials and architectures:



Abundant material
Mature fabrication technology
Cost effectiveness and economy of scale
Miniaturized systems and dense architectures

small technology devices

... Silicon friendly?

- Silicon and close Silicon relatives thin film substractive and top-down standard technologies

- Materials/processes compatible with the Si devices or the Si fab infrastructure:
  - Post-processing
  - Processing temperature
  - Wafer level
  - Include bottom-up

Silicon
(compatible)
technology

Why microenergy solutions:

Small Power for the next Big Thing

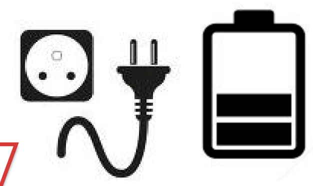
IoT

energy

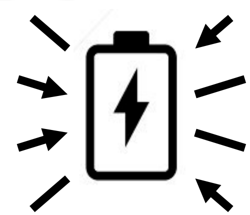
devices

Functional autonomy

Energy autonomy



grid off-grid

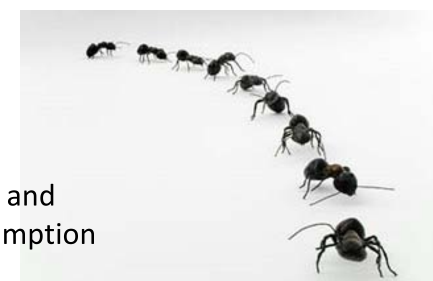


Energy harvesting

Get the energy, or replenish the battery, from the environment

If many (sensors), better...

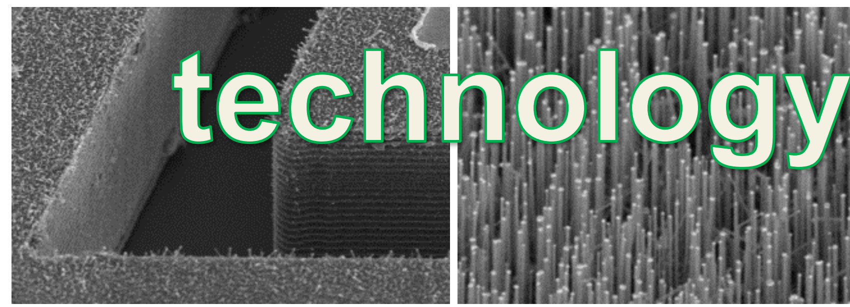
- Small



Less material and
energy consumption

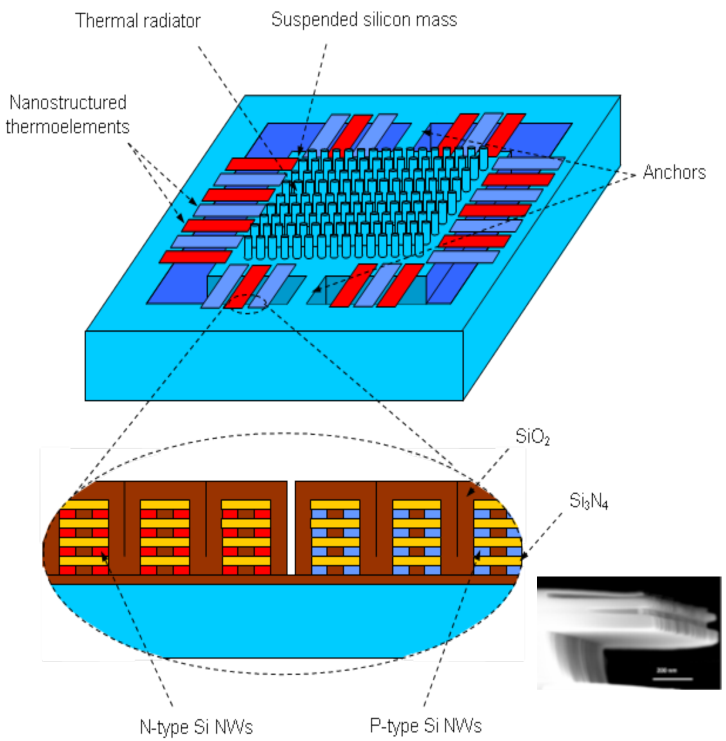
small

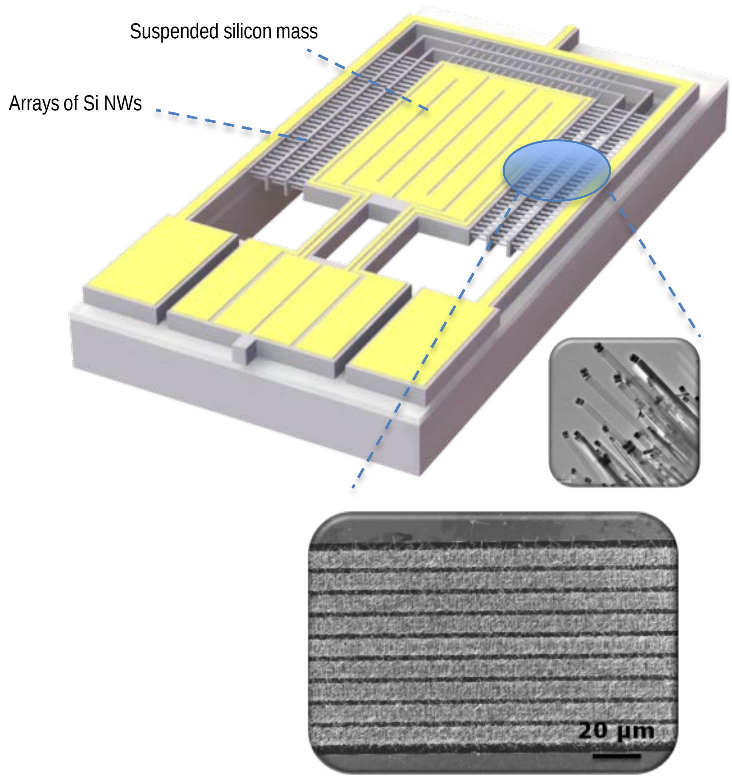
- but internally 'dense'



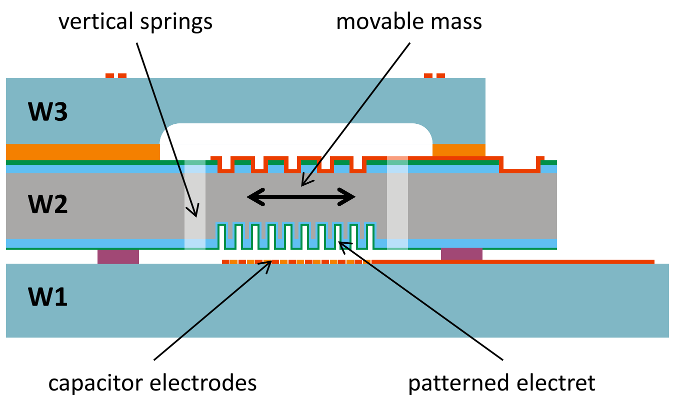
– Micromachining: free surfaces & volumes (<u>coupling</u> with the environment)
– 3D architectures (where to <u>integrate</u> nanomaterials)
– high aspect ratios / high density features

- 3D microstructures
  + top-down Si NWs
- 3D microstructures
  + bottom-up Si NWs

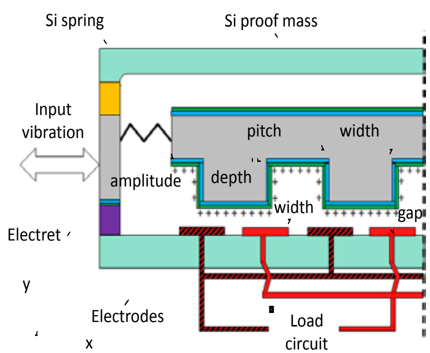




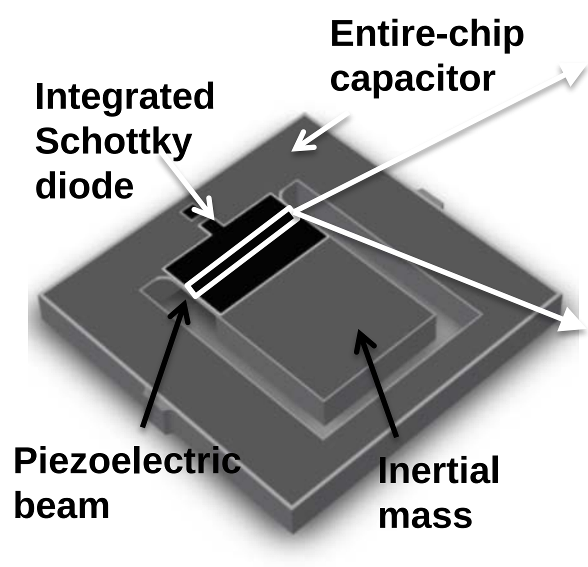
- 3D microstructures
  + thin films



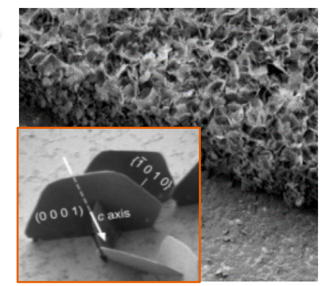
Electrostatic action

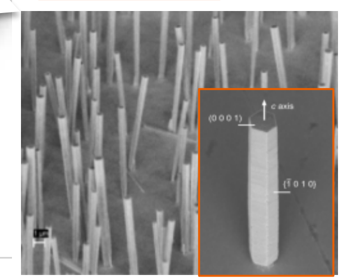


- 3D microstructures
  + bottom-up ZnO nanoX



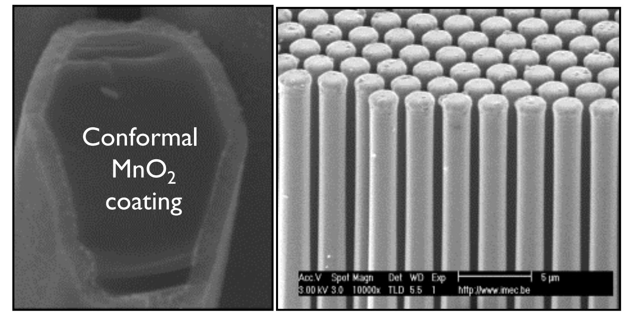
nanosheets



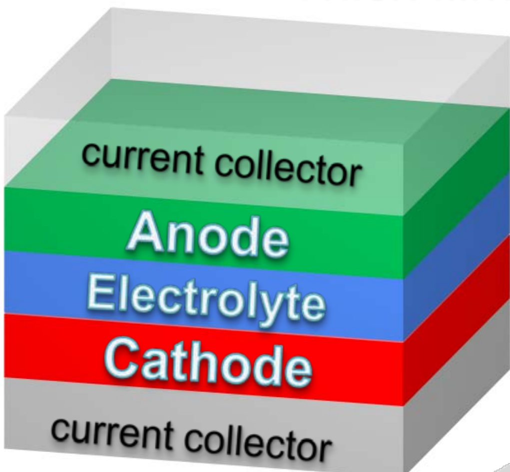


nanowires

- Materials for Si compatible batteries
- 3D microstructures

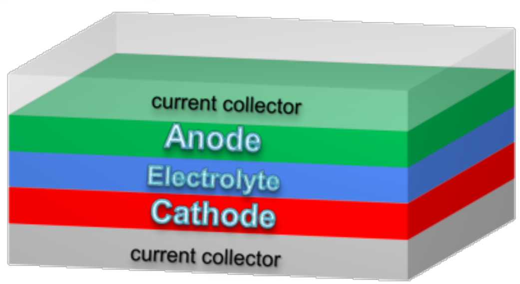


Thick film



High capacity
Low power

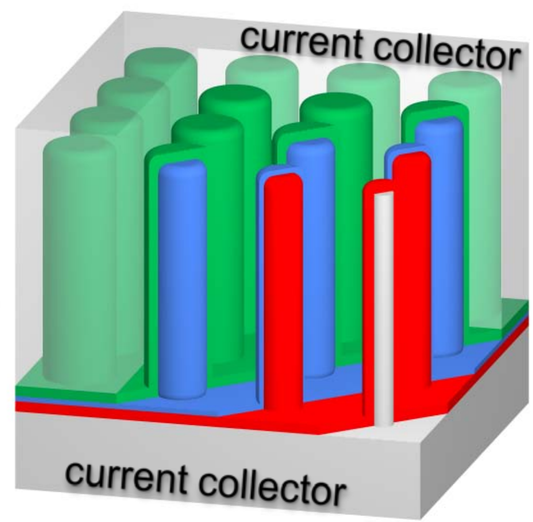
Thin film



Low capacity
High power

3D

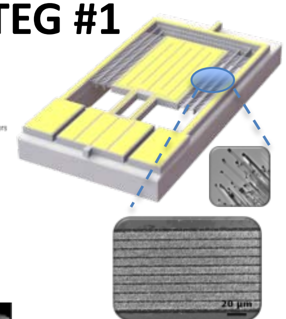
High capacity & power



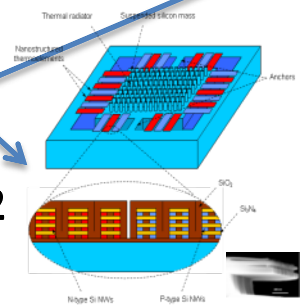
3D microstructures + materials

- Thermal contrast

TEG #1



TEG #2



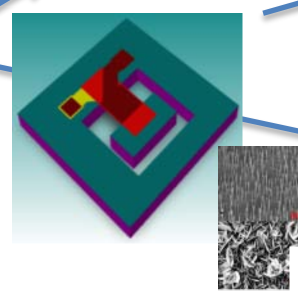
- Nanomaterials:

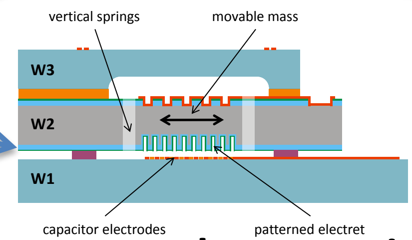
**post-growth*

- •*Bottom-up*
- •*Top-down*

- Moving masses

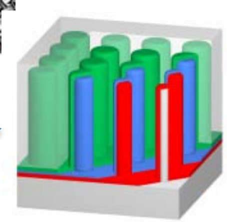
piezoelectric





electrostatic

- high aspect ratio support



Solid state battery

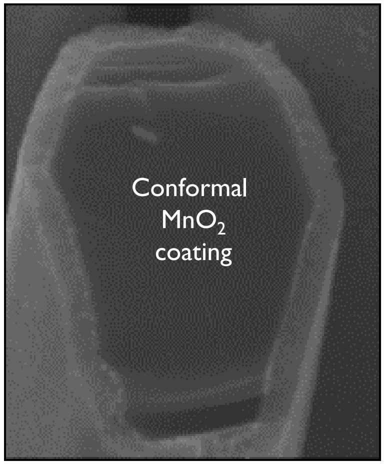
- Thin film materials

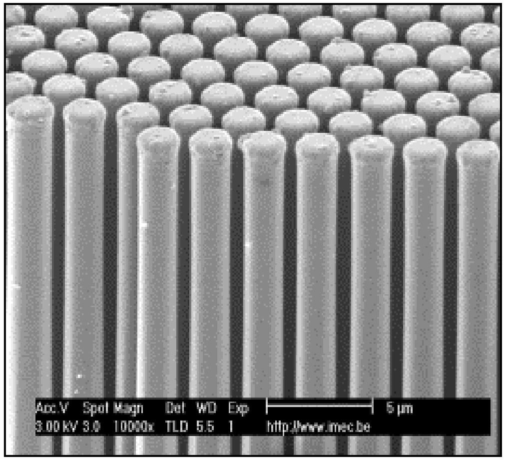
**post-lithiation*

Solid State microbatteries

Post-lihtiation

- Li is instrumental in batteries electrodes and electrolytes
- Li is not a Silicon compatible material





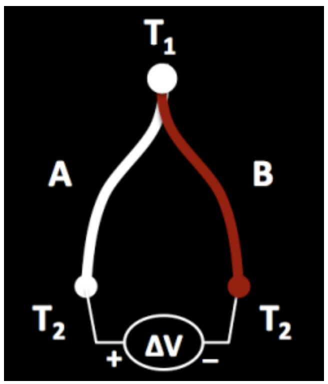
- Li-free conformal deposition (e.g. MnO_2, TiO_2) by ALD or ECD
- Lithiation (into LTO or LMO) by a solid state reaction as a post-process

Thermal Energy Harvesting

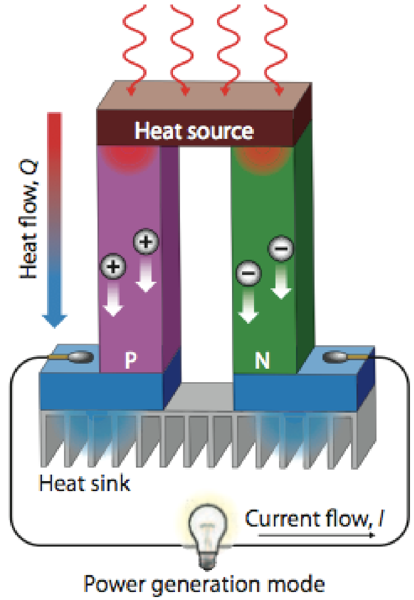
Integration of SiNWs

Thermal energy harvesting: heat into electricity

$$V=(S_A-S_B)\bullet\Delta T$$

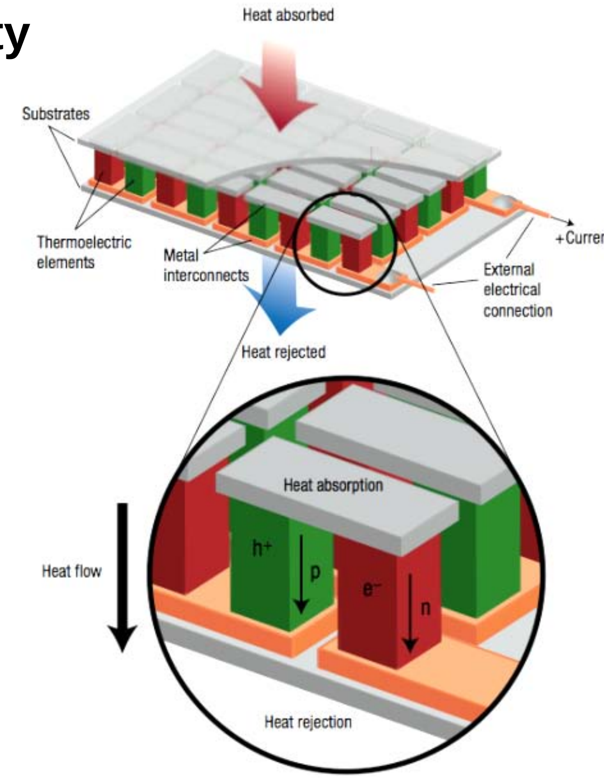


Thermoelectric generation (TEG)



Schematic illustrations of a thermoelectric element for power generation (Seebeck effect).

Li *et al*. NPG Asia Mater. 2, 152 (2010)



Snyder and Toberer Nature Mater. 7, 105 (2008)

- Efficiency of a thermoelectric material → *ZT*
- Good thermoelectric materials → *ZT* >1

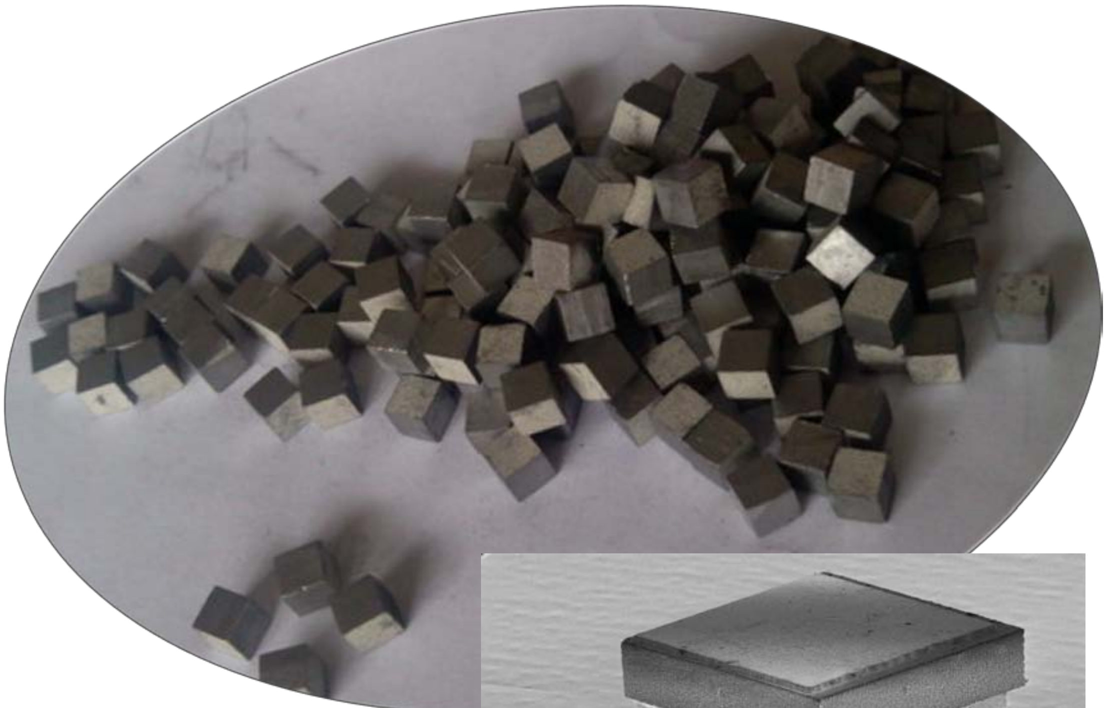
$$ZT = (S^2\sigma/\kappa)T$$

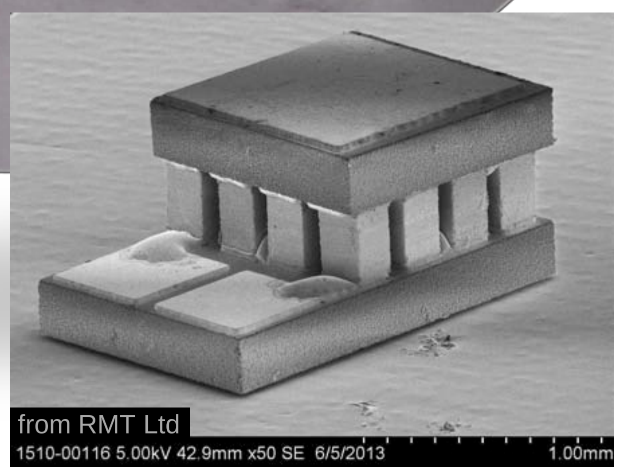
European Union

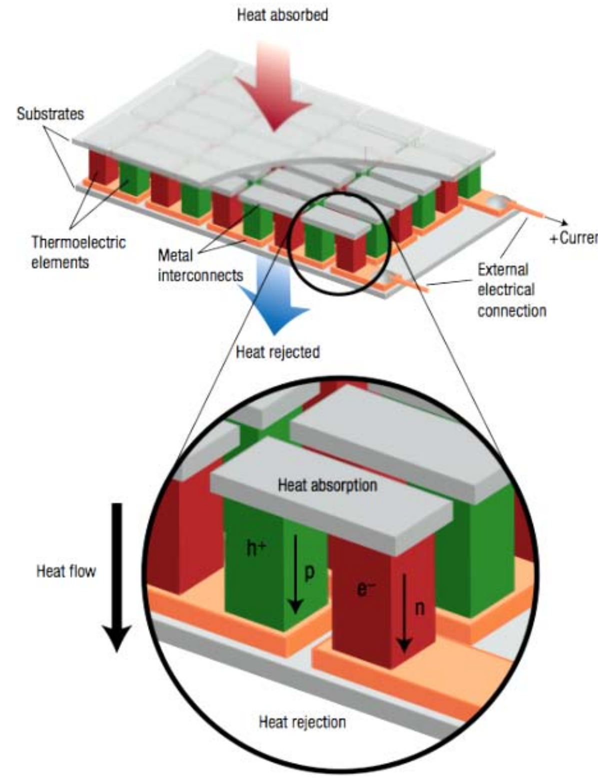
SEVENTH FRAMEWORK PROGRAMME

Thermal harvesting

The Seebeck effect



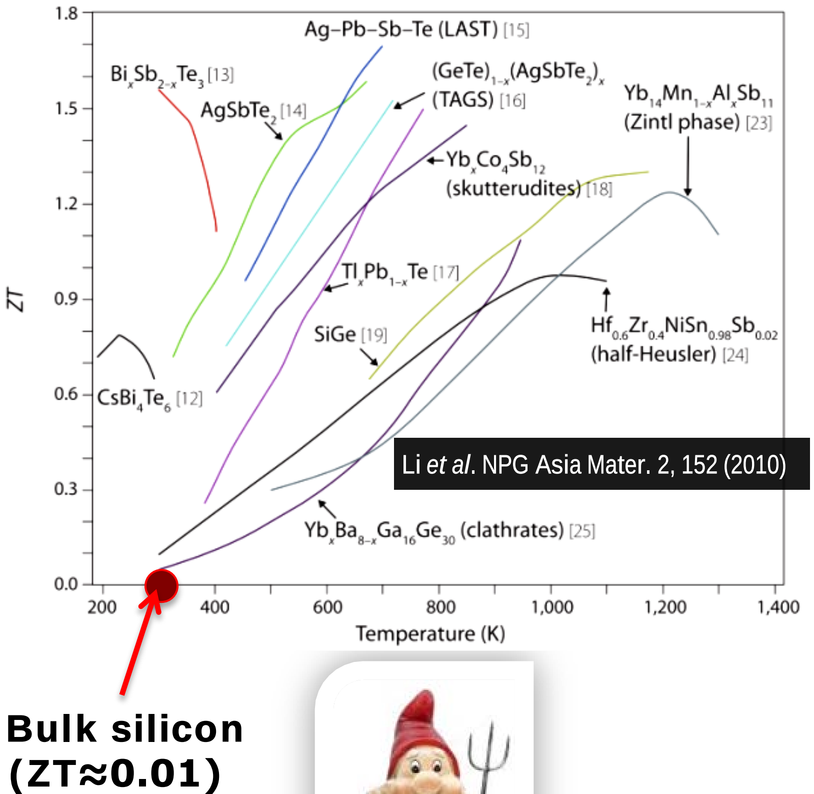




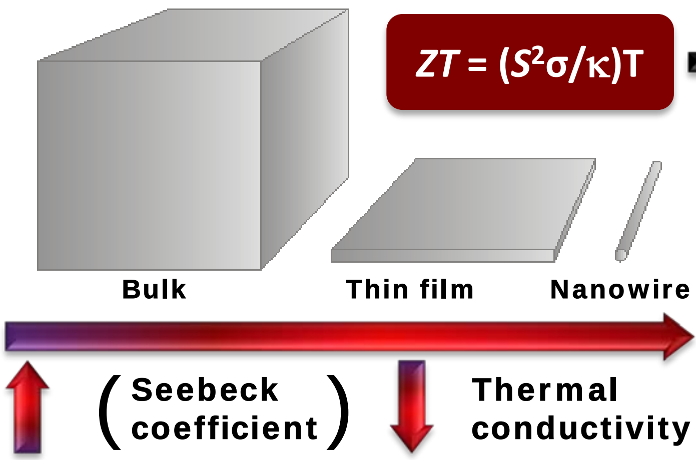
Snyder and Toberer Nature Mater. 7, 105 (2008)

$$ZT = (S^2\sigma/\kappa)T$$

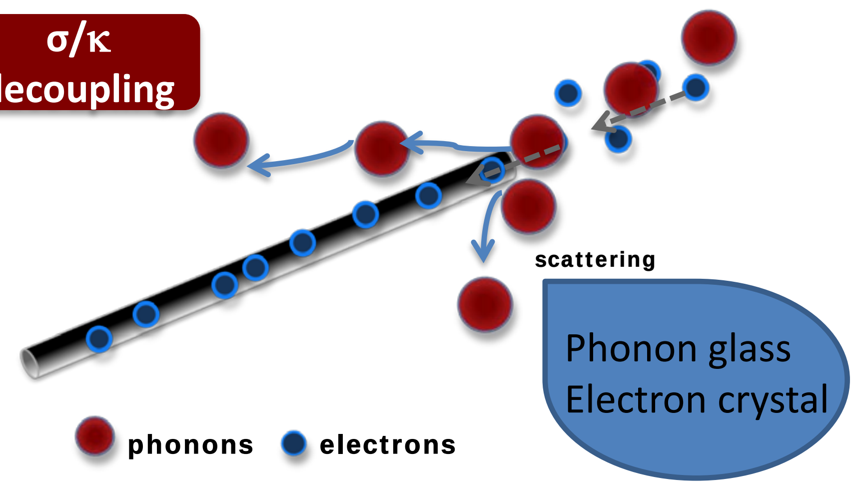
- Silicon: technology giant - thermoelectric dwarf



$ZT = (S^2\sigma/\kappa)T$ → **σ/κ decoupling**

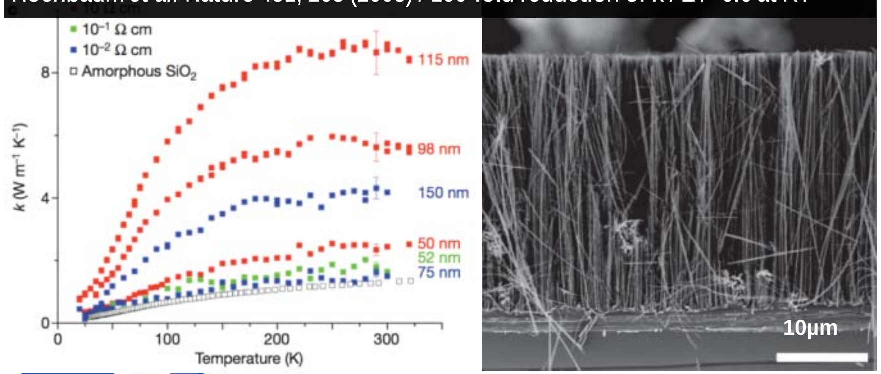


Hicks & Dresselhaus, Physical Review B, 47, (1993)

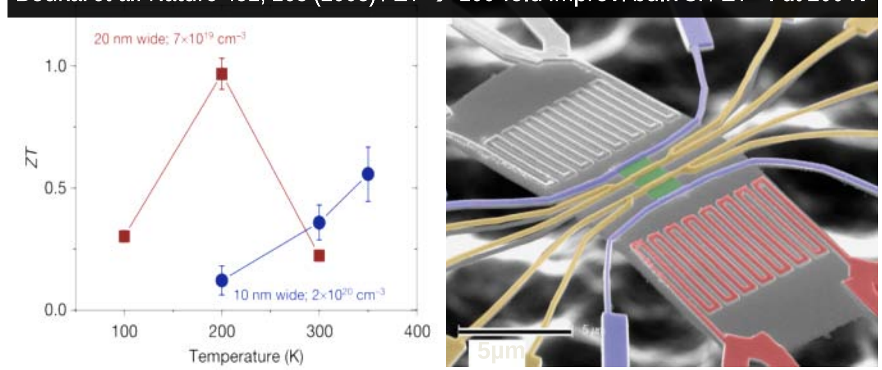


SINGLE SILICON NANOWIRES with $ZT \approx 1$ → (2008)

Hochbaum *et al.* Nature 451, 163 (2008) / 100-fold reduction of k / ZT=0.6 at RT



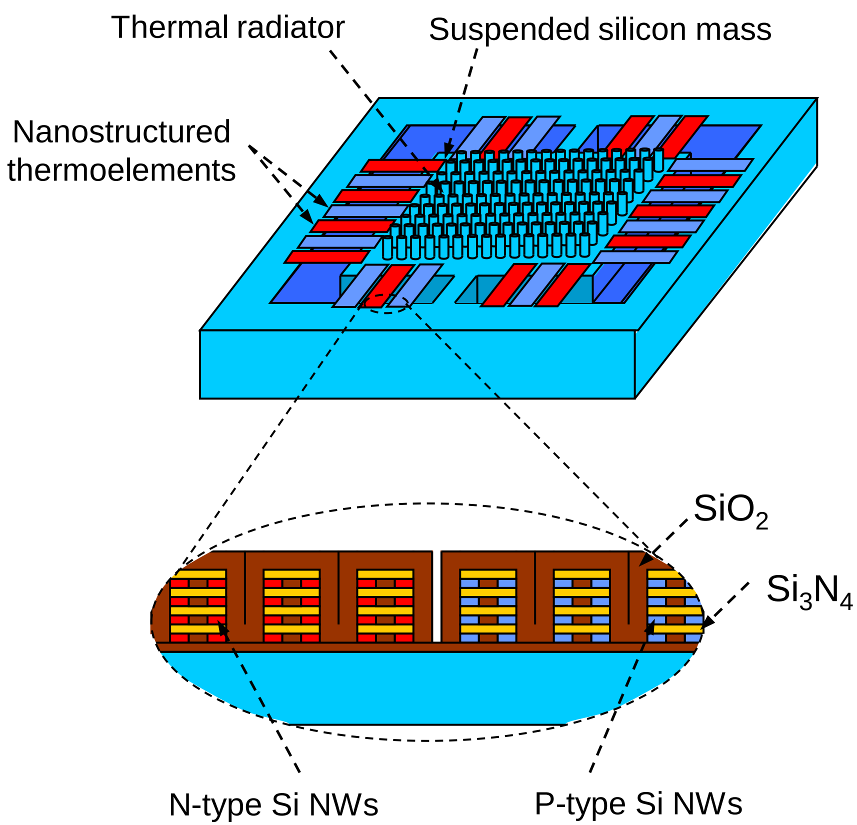
Boukai *et al.* Nature 451, 168 (2008) / ZT → 100-fold improv. bulk Si / ZT≈**1 at 200 K**

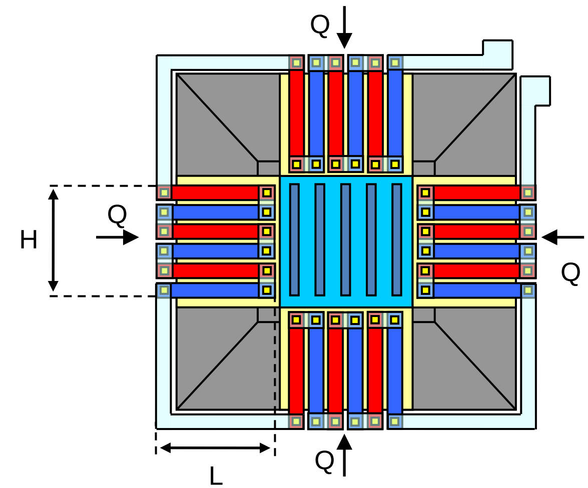


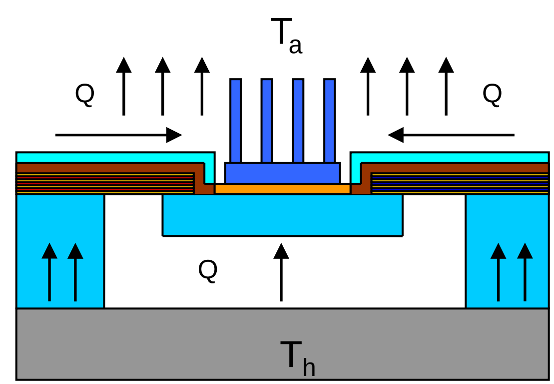
Thermal Energy Harvesting

Silicon compatible
TOP-DOWN nanomaterial
(Si NWs)

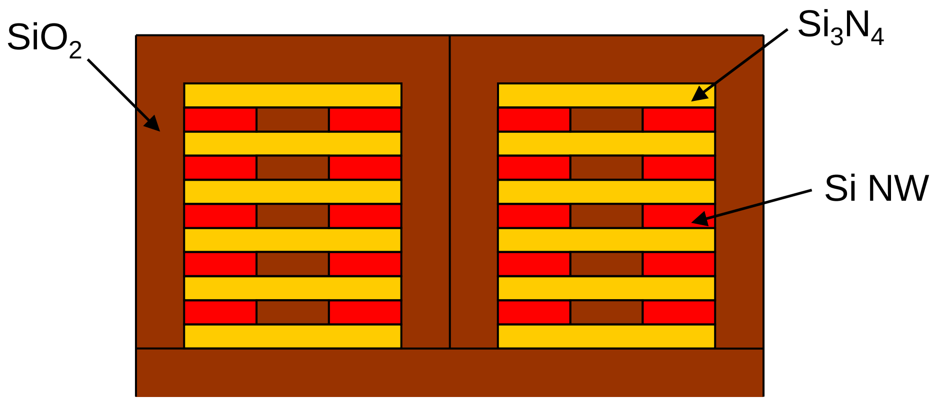
Planar architecture (suspended platform to force a lateral gradient)

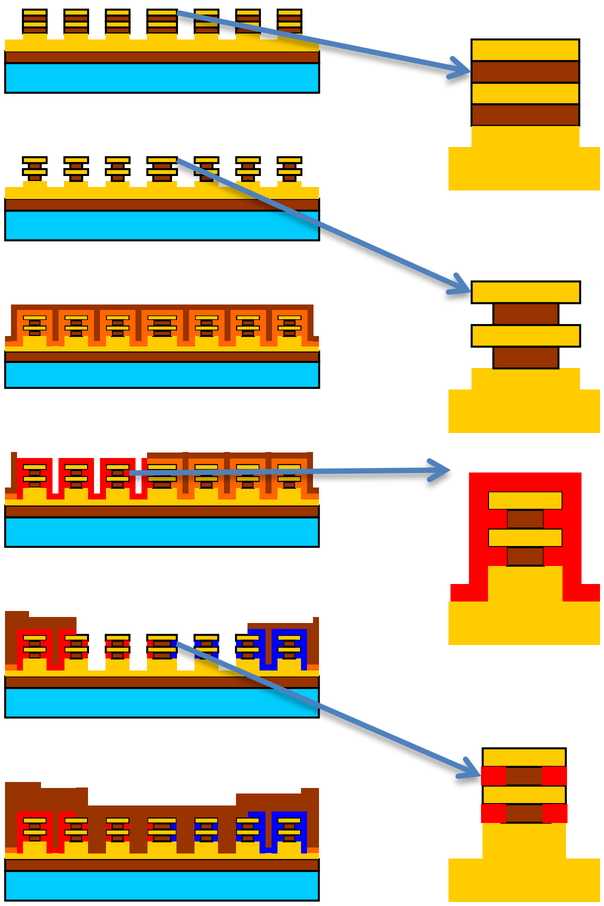






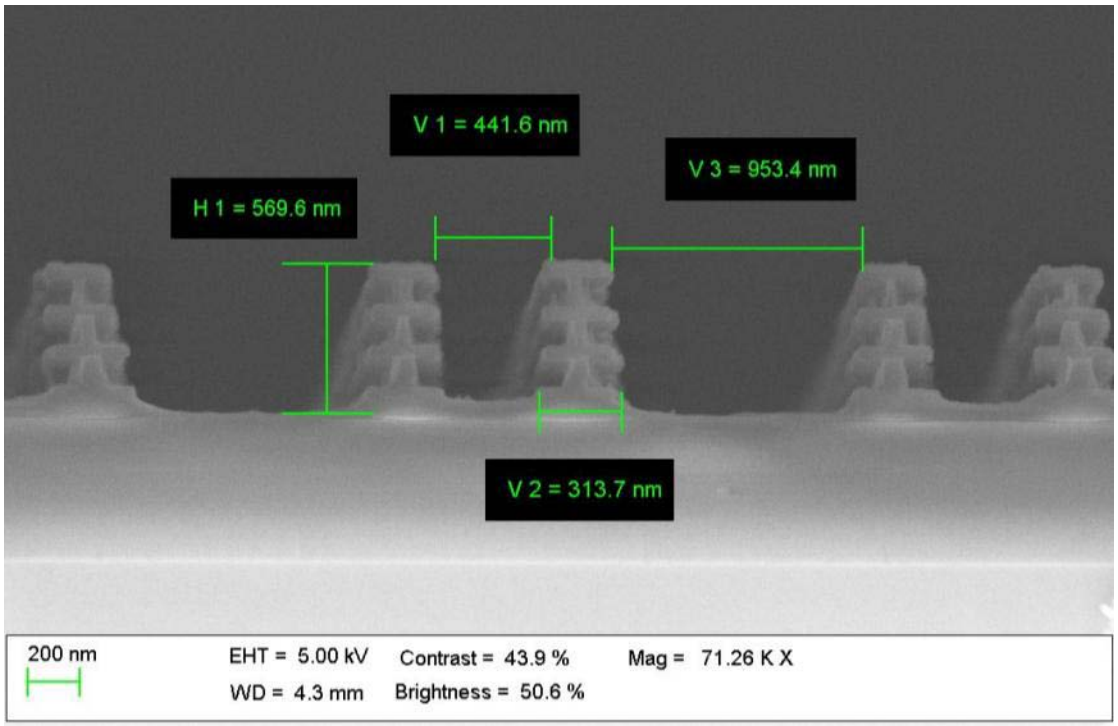
Cross-section of nanostructured thermoelement

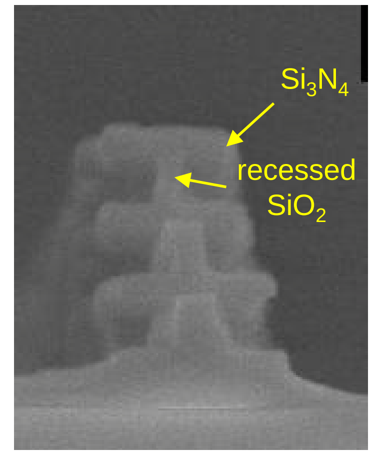




Stacked SiNWs **arrays** created by **polysilicon** conformal deposition and subsequent etch-back into lateral recessed oxide cavities defined by differential wet etch into multilayered sandwiches of oxide and nitride ... without nanolithography

NMP3-SL-2013-604169





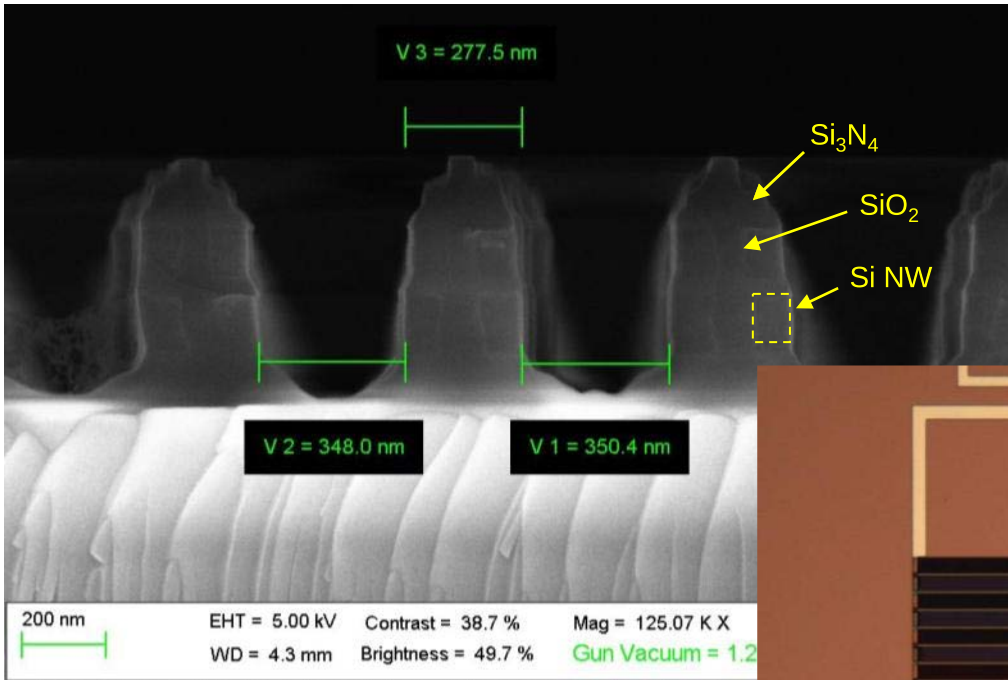
70x120 nm^2

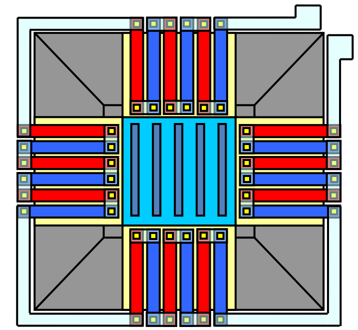
Arbitrary length (several hundred microns)

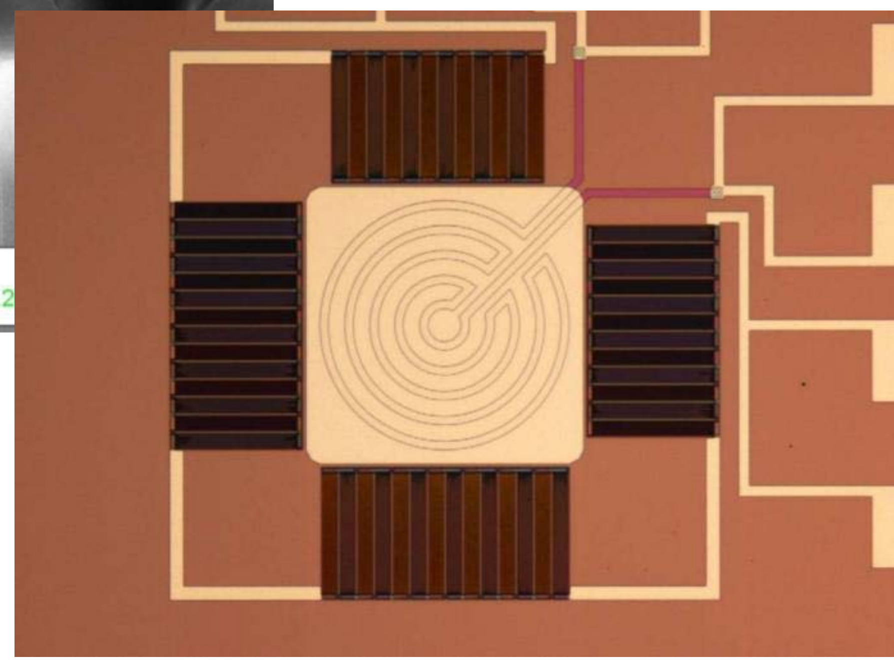
1.0×10^4 NWs/mm

Thermal harvesting

Top-down μ-generators







Thermal Energy Harvesting

Silicon compatible
BOTTOM-UP nanomaterial
(SiNWs)

Top-down

<u>Si micromachining:</u>

- 2.5D ‘planar’ structure
- Areas with thermal contrast

Maximum topographical flexibility at a minimum technological cost

Maximum material flexibility at a minimum technological cost

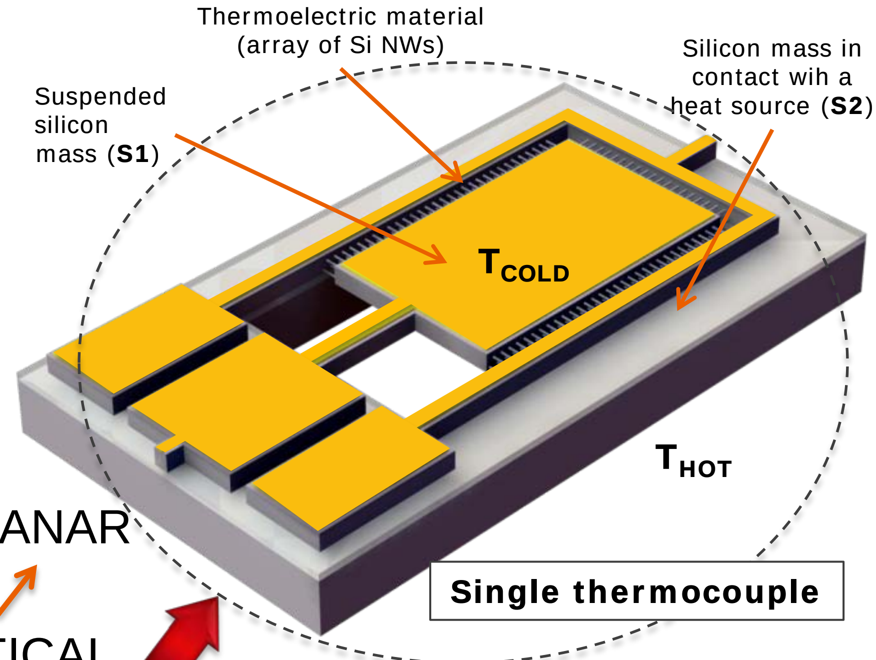
<u>Si NWs growth</u>

-Parallel integration of large numbers of nano-objects

Bottom-up

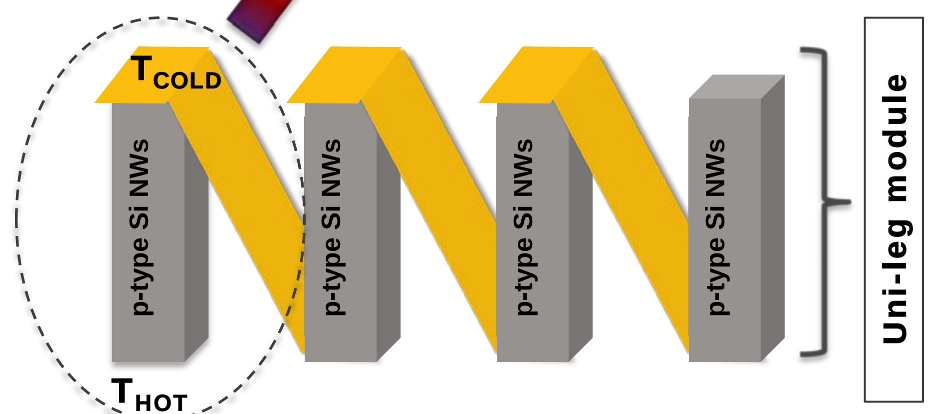
Unique features:

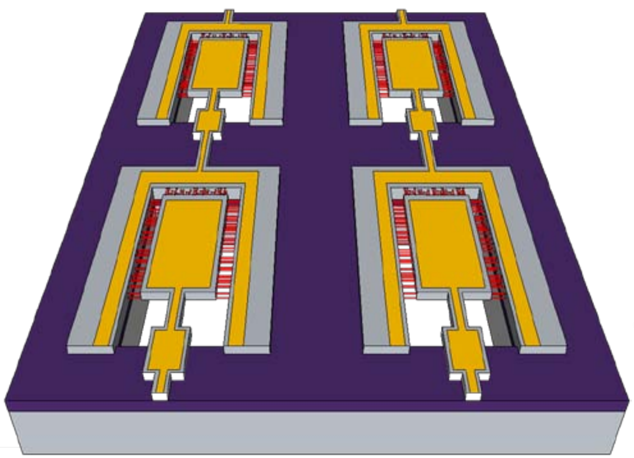
- **Uni-leg** architecture
- Material → (**all**) **silicon**
- **“3D”** SiNWs arrangement **(10^6)**
- **Planar architecture**
- Scalability → series and/or parallel connections



PLANAR

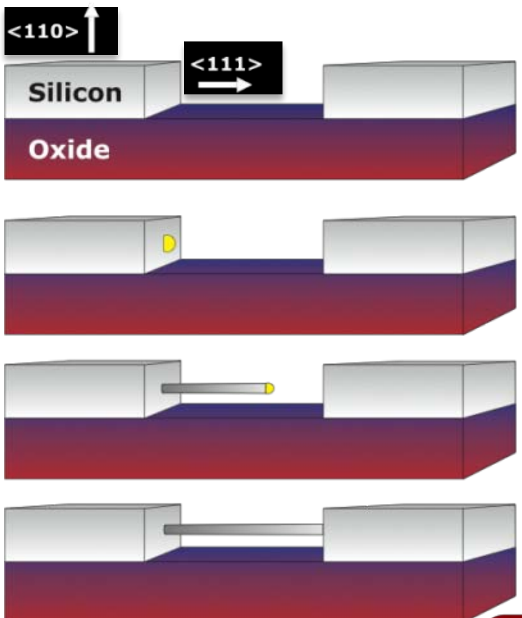
VERTICAL



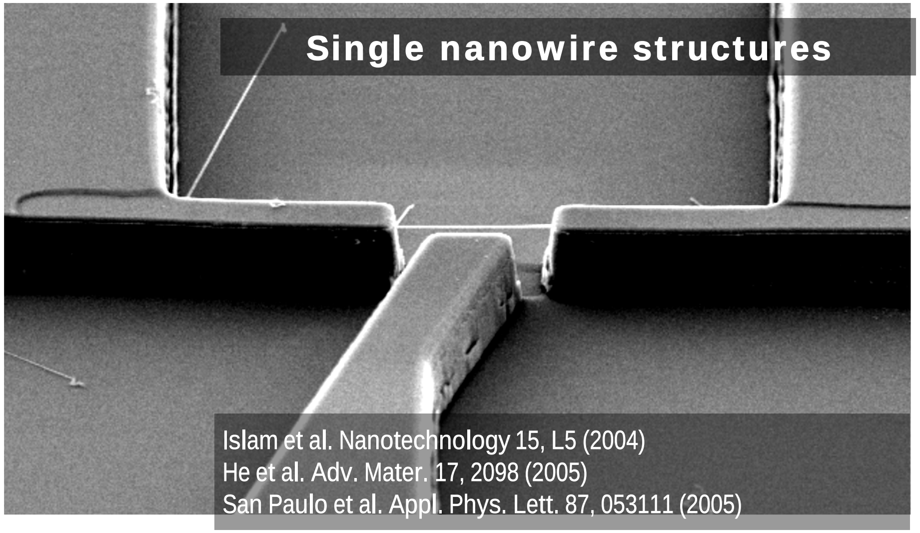


Horizontal growth of Si nanowires

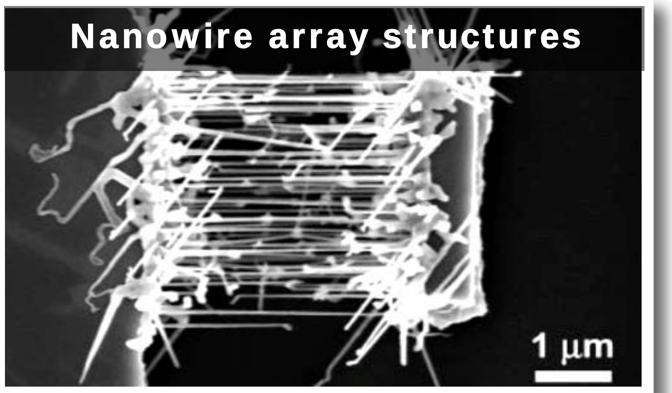
- **Selective** deposition of Au nanoparticle
  - Control of nanoparticle size
  - Deposition only on Si surfaces
- VLS growth method (**quasiepitaxial**)



SiH_4
Over 700° C
(Ø 80-100 nm)



Islam et al. Nanotechnology 15, L5 (2004)
He et al. Adv. Mater. 17, 2098 (2005)
San Paulo et al. Appl. Phys. Lett. 87, 053111 (2005)

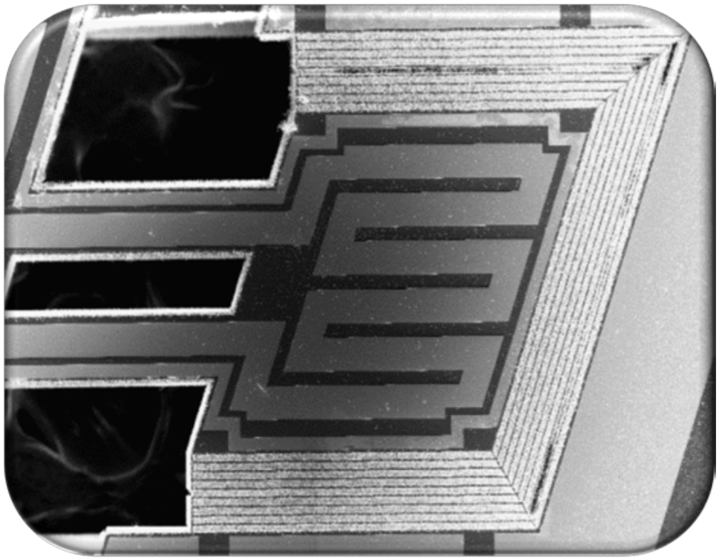


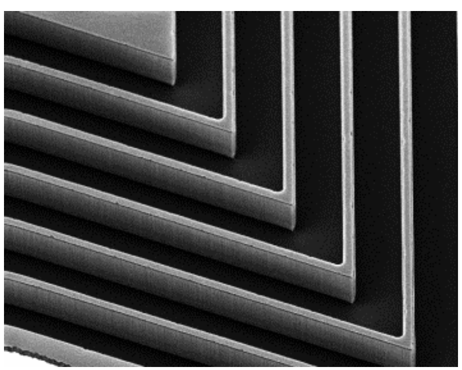
San Paulo et al. Nano Letters 7, 1100 (2007)

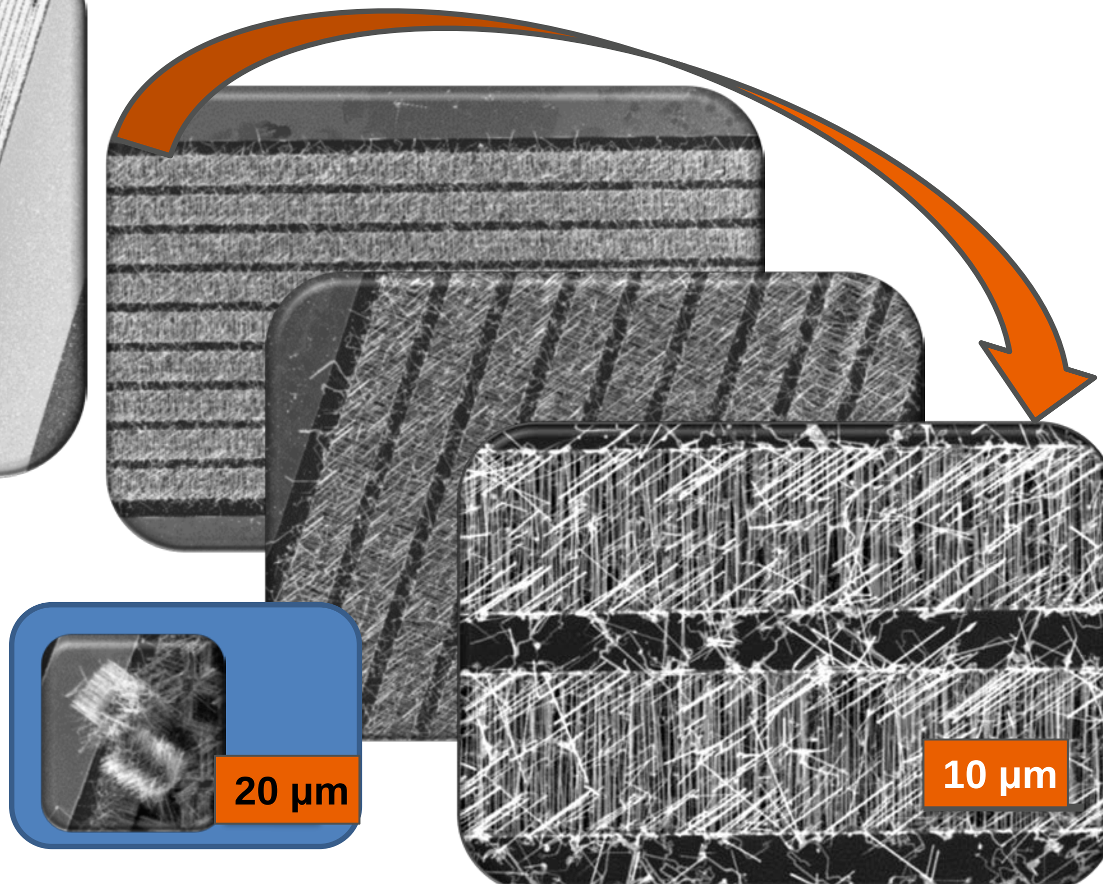
- Mechanically robust
- Electrically continuous

Multiarray of Si NWs

- Microspacers: Si lines (3um)
- Multiple linked arrays of Si NWs 10 µm-long







Mechanical Energy Harvesting

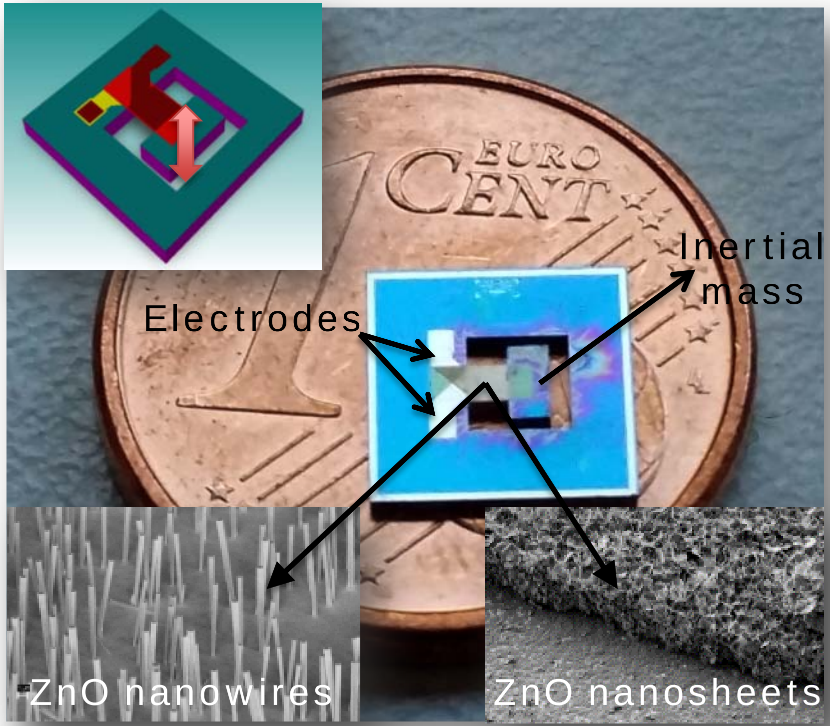
Silicon compatible
Bottom-up piezoelectric nanomaterial
(ZnO nanoobjects)

Mechanical energy harvesting: vibrations to electrical energy

- Electrostatic
  - Charged variable capacitor
- Piezoelectric
  - Electric charge due to applied stress in piezoelectric material
- ~~Electromagnetic~~
  - Induction by variable magnetic field

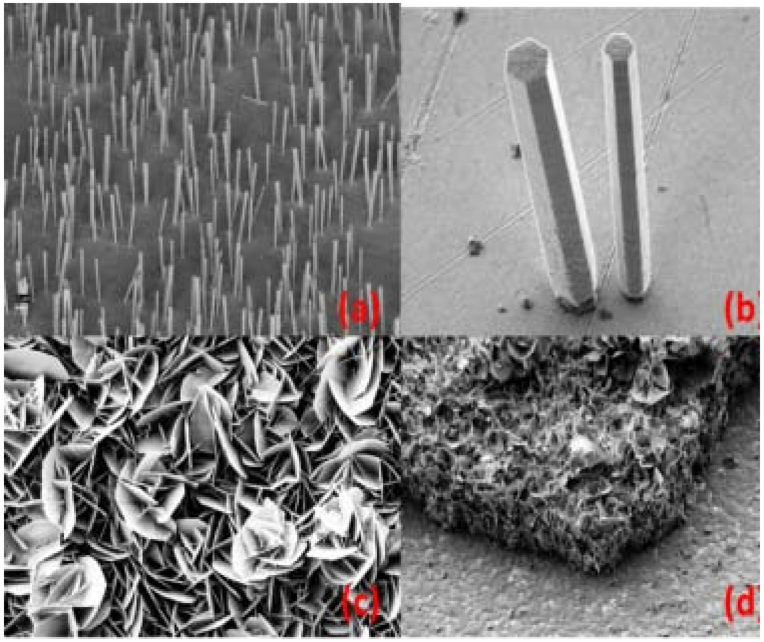
$$P \approx dQ/dt$$

- Piezoelectric energy harvesters – what do we need?
- Inertial mass & cantilevered spring
  - Mass
  - Flexible spring
- Piezoelectric material
  - ZnO nanowires & nanosheets
  - Polymer coating of piezo layer
  - Electrodes



Piezoelectric materials - ZnO nanostructures

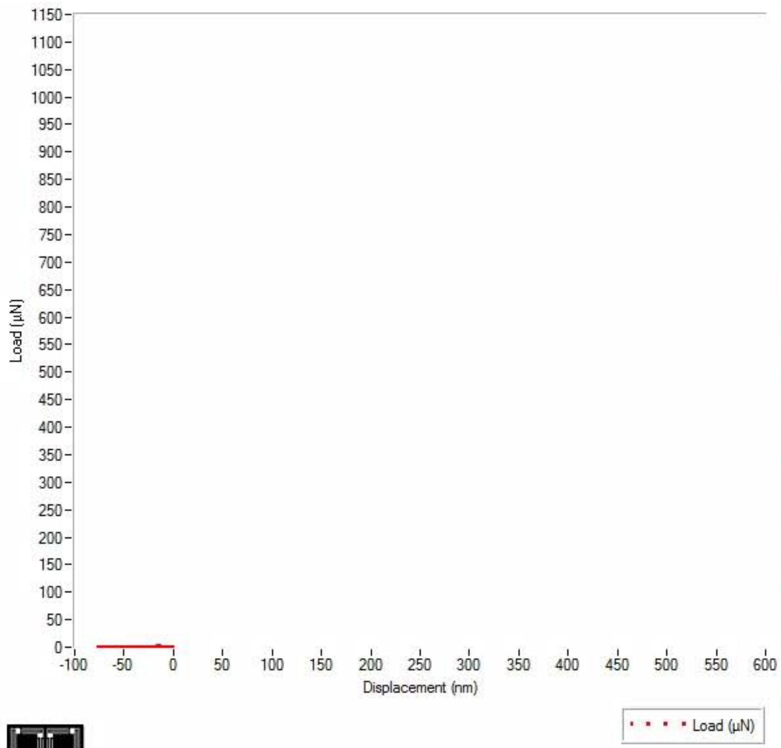
- ZnO nanowires & ZnO nanosheets:
  - Inherent piezoelectric behavior of ZnO
  - More flexible and robust than thin-films
  - Easy to grow and integrate with silicon, low-cost solution (Hydrothermal synthesis)
  - High novelty provided by ZnO nanosheets

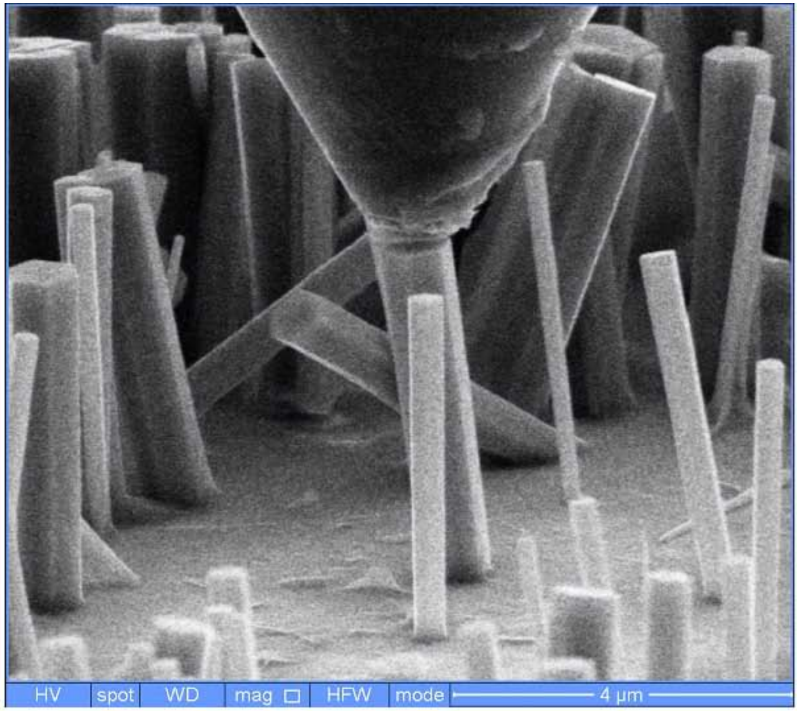


ZnO nanowires (overall view (a) and detailed view (b)), and nanosheets (top view (c) and tilted view (d)). NW lengths rate from 2 to 5 µm and thicknesses from 100 nm to 900 nm.

Detailed growth being patented

- ZnO nanostructures allow higher compression without fracture.
- It has been demonstrated that a single ZnO NW can stand for a compressing force of more than 1mN!





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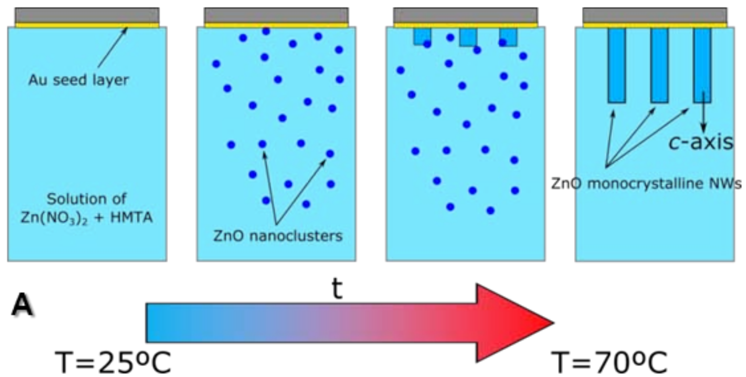
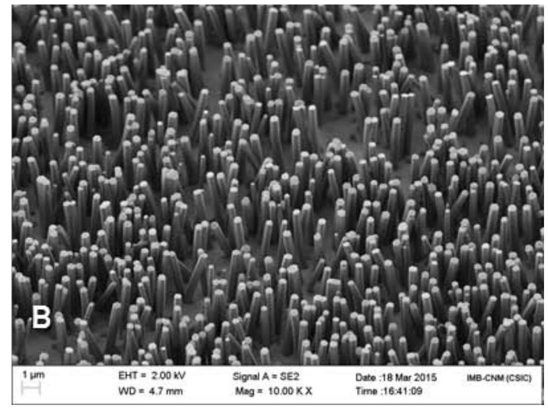
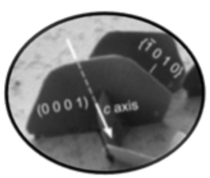
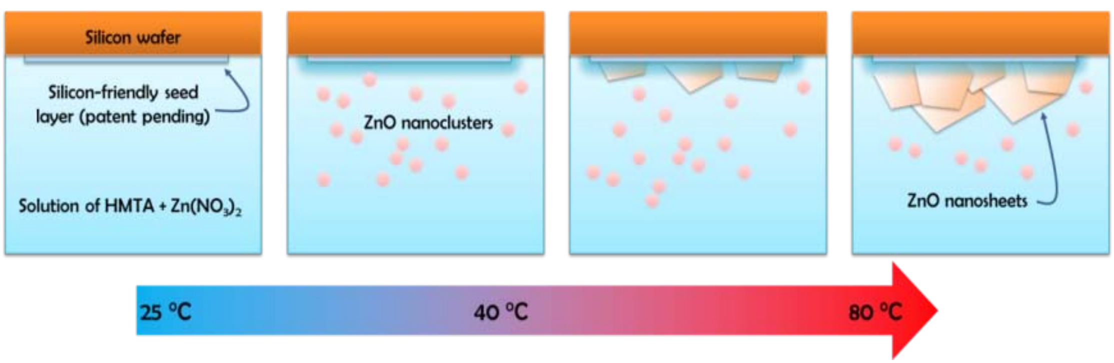
Hydrothermal process (cheap, low T, wafer level and selective)

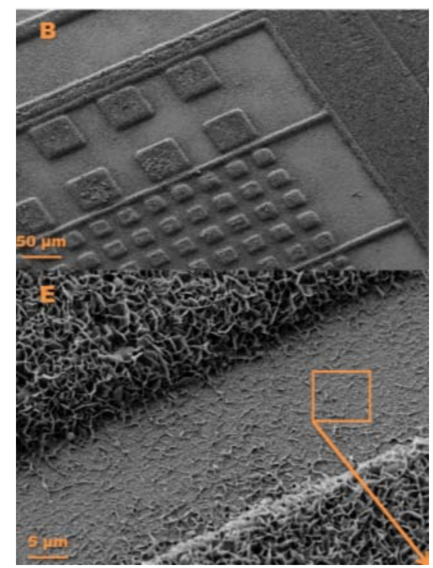




NW



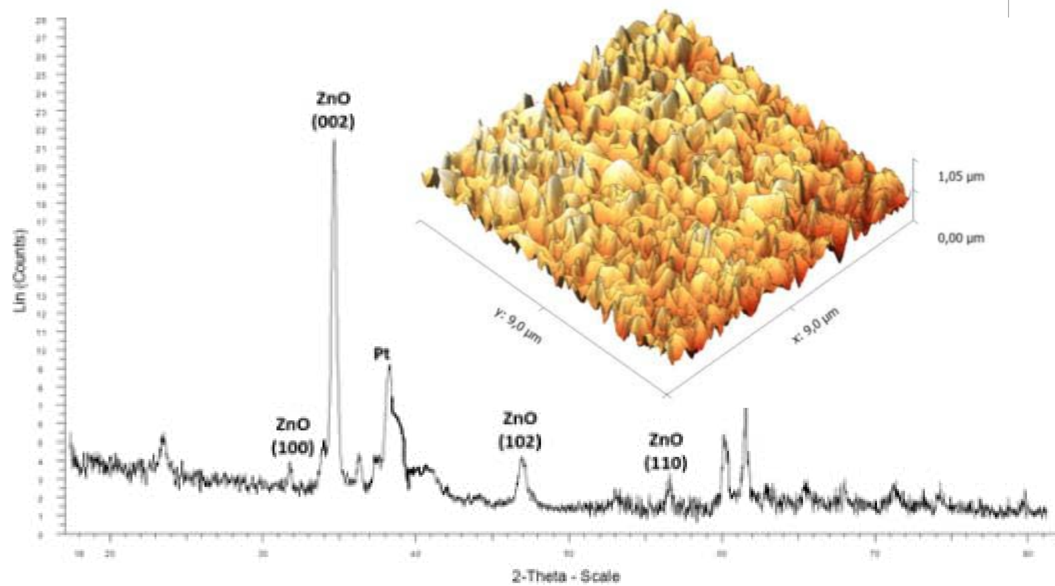


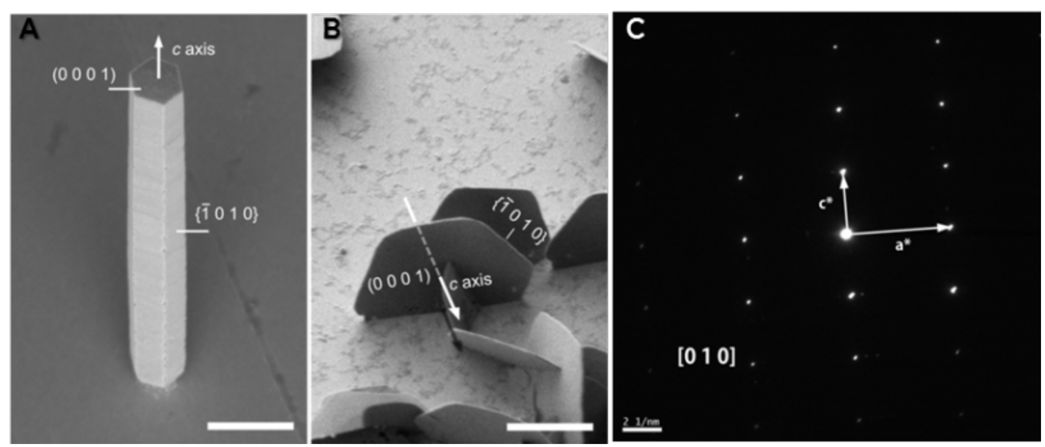


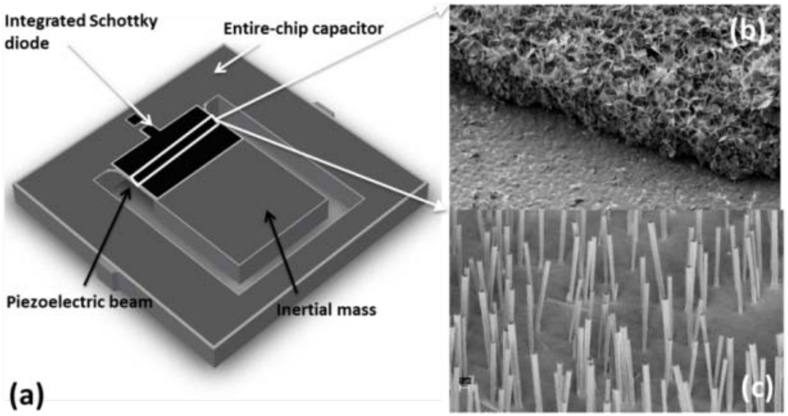
NS

ZnO nanomaterial characterization by TEM, SEM and XRD:

- ZnO NWs & NWs show a **good crystalline** structure.
  - oriented along c-axis (NW) and perpendicular to it (NS)
- **Good piezoelectric coefficient** (measured by PFM: NW: 8.6 pm/V; NS: 4.2 pm/V)
- NS: Thickness < 20 nm, several µm long; **high aspect ratios**
- NS: Extremely high-density, **reproducible and fast**

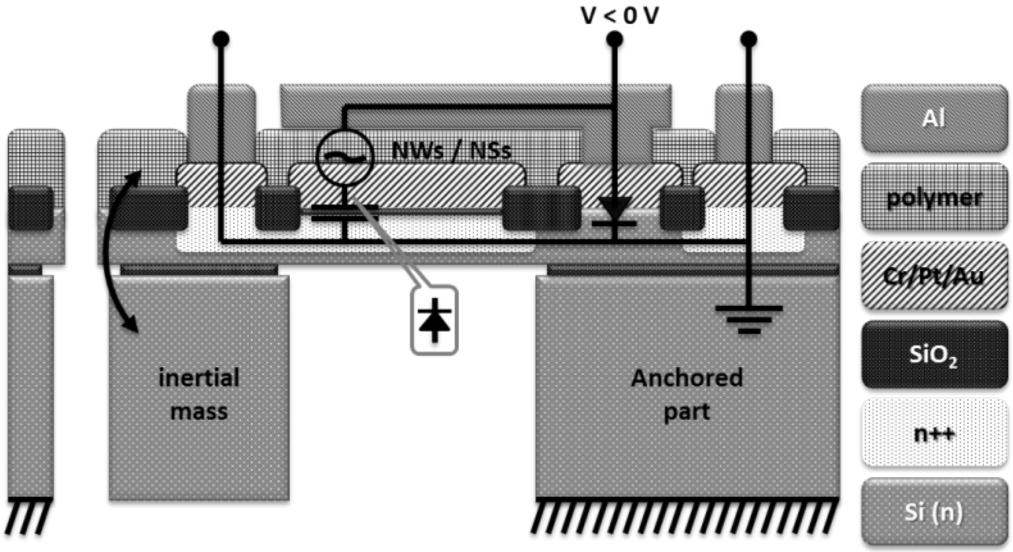






Integration of ZnO nanomaterial into Si micromachined bending structures

Si device:
On-chip pre-rectification



- Without an 'install and forget' approach IoT/TS may not happen → (micro)energy autonomy is required
- Energy/power does not (down)scale well → high density features (3D architectures) need to be handled
- Let's try do harvesters/batteries **with the same technologies that are already used for fabricating miniaturised sensors reliably, cost-effectively and in high numbers** → Si micro-nanotechnologies
- As an example, top-down integration of Si NWs in thermal harvesters has been presented, as well as compatible integration of bottom-up nanomaterials in thermal (Si NWs) and vibrational harvesters (ZnO NW&NS)

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sinergy-project.eu
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- 2016 E-MRS Spring meeting
  - Symposium W: **Materials and systems for micro-energy harvesting and storage**
    - Materials and system issues for thermal energy microharvesters
    - Materials and system issues for mechanical energy microharvesters
    - Materials and systems issues for microbatteries
    - Materials and system issues for micro supercapacitors

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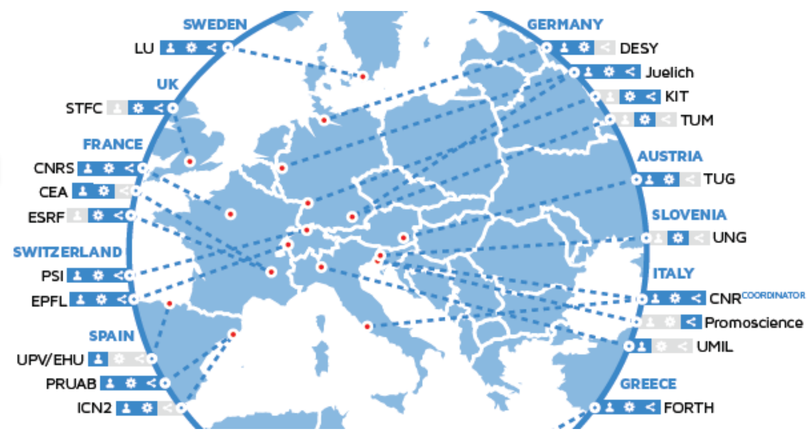

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