Current development of Energy Harvesting Techniques with focus on Thermoelectric, Piezoelectric and Photovoltaic technologies

UNIVERSITÀ
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ENERGY HARVESTING

THE NEW ERA OF GREEN POWER

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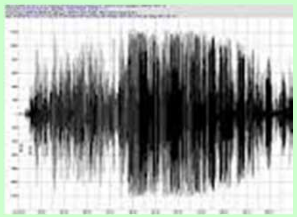
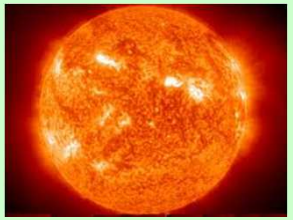
Energy Harvesting

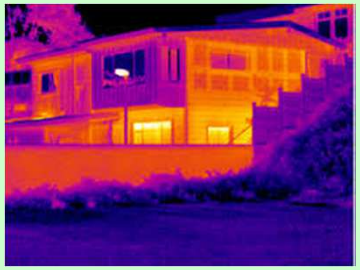
Energy Harvesting = the process of capturing minute amounts of energy naturally-occurring energy sources, accumulating them and storing them for later use.

Mechanical Vibrations




Solar Light




Thermal Energy

Electromagnetic radiation

But also (very intriguing) **biological sources.**

Why Energy Harvest?

For small electronic devices and sensors:

- Remote locations deployment
- Low manteinance
- Inextiguishable energy sources
- No battery disposal

For large scale or industrial purposes:

- Energetic independence
- Reduced costs and possible profits
- Respecting EU established goals (Roadmap)

- Clean energy: **NO ENVIRONMENTAL IMPACT**

EU Road Map

''This Road Map, an integral part of the Strategic European Energy Review, sets out a long-term vision for renewable energy sources in the EU. It proposes that the EU establish a mandatory (legally binding) target of 20% for renewable energy's share of energy consumption in the EU by 2020''

(Communication from the Commission to the Council and the European Parliament - Renewable energy road map - Renewable energies in the 21st century: building a more sustainable future)

National overall targets for the share of energy from renewable sources in gross final consumption of energy in 2020 (1)

A. *National overall targets*

	Share of energy from renewable sources in gross final consumption of energy, 2005 (S_{2005})	Target for share of energy from renewable sources in gross final consumption of energy, 2020 (S_{2020})
Belgium	2,2 %	13 %
Bulgaria	9,4 %	16 %
Czech Republic	6,1 %	13 %
Denmark	17,0 %	30 %
Germany	5,8 %	18 %
Estonia	18,0 %	25 %
Ireland	3,1 %	16 %
Greece	6,9 %	18 %
Spain	8,7 %	20 %
France	10,3 %	23 %
Italy	5,2 %	17 %

Purpose of this work

Photovoltaic

- Working principles: the p-n junction based solar cell
- Hybrid-Organic solar cells: Dye sensitized cells (DSC)

Piezoelectric

- Working principles: the direct piezoelectric effect
- Research on self-powered nanodevices

Thermoelectric

- Working principles

Photovoltaic (I)

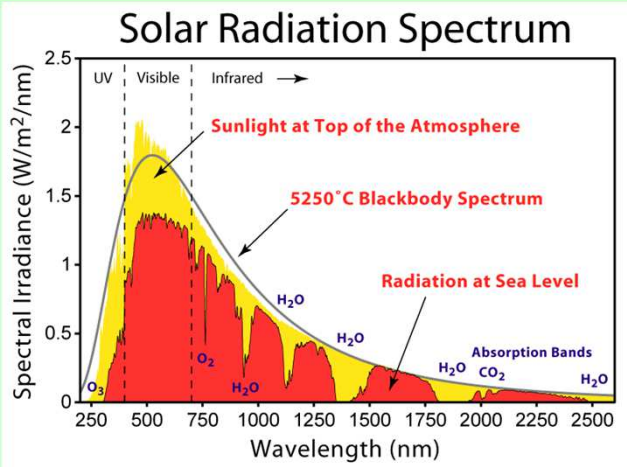
The sun is the greatest source of energy for our planet.
More than 10^{24} J/year are absorbed by the atmosphere, oceans and lands

Photovoltaics = direct conversion of light into electrical energy

Solar energy may also be converted to thermal energy (Solar thermal route) or even to chemical energy through photo-electrochemical devices (solar fuels). Even fossil fuels are the result of millions of years of solar energy being converted to chemical energy.

The sun emits energy in the form of electromagnetic radiations, we can consider this energy to be carried by quantum particles called photons, whose energy depends on the wavelength of the radiation.

$$E_{ph} = \frac{hc}{\lambda}$$

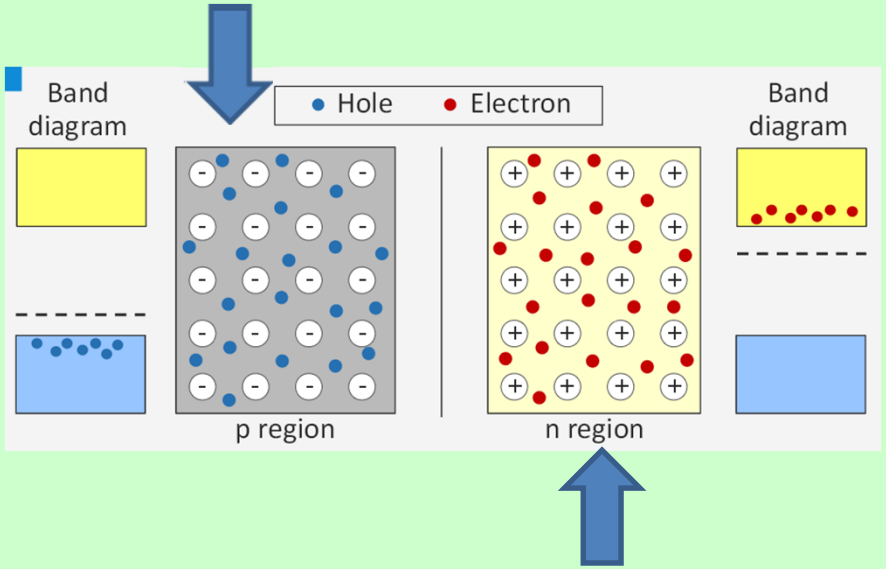


The simplest working block of a photovoltaic system is the solar cell.

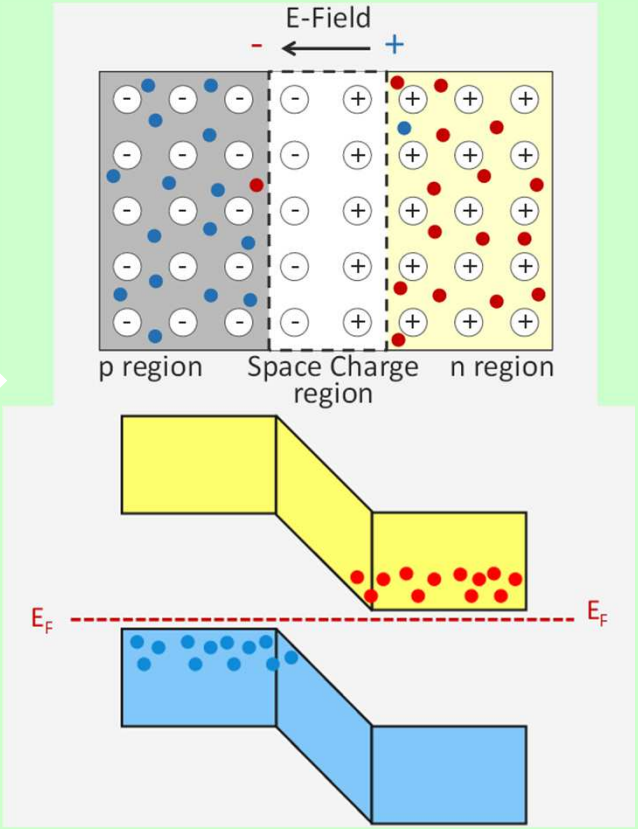
Photovoltaic (II)

The basic solar cell is realized using a p-n junction: the union of a p-doped semiconductor with an n-doped one. Let's take, for example, silicon:

Adding Boron atoms to the lattice of silicon adds extra holes (majority carriers): p-doping

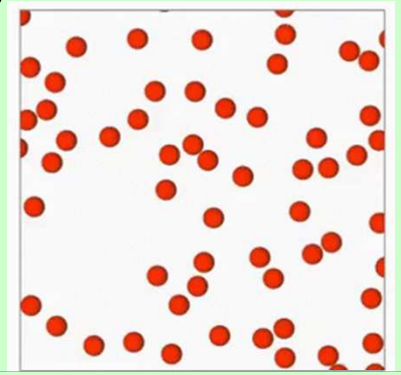


Adding Phosphorus atoms introduces more electrons (majority carriers): n-doping



Photovoltaic (III)

In general, electrons dispersed in a material move randomly in the lattice: their kinetic energy depends on the temperature of the material (thermal velocity). Even though no particle is still, there is no net movement, hence no flow of current (**Brownian motion**).

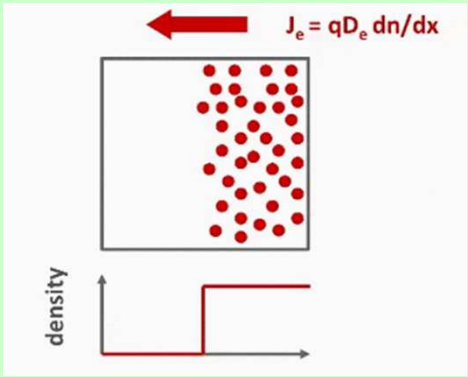


We have a **diffusion current** when we have a different concentration gradient of particles across the material:

$$J_{n-diff} = qD_n \frac{\partial n}{\partial x} \qquad D_n = \frac{kT}{q}\mu_n$$

In which

$$J_{p-diff} = -qD_p \frac{\partial p}{\partial x} \qquad D_p = \frac{kT}{q}\mu_p$$



The **drift current** is, instead, due to an electric field (E) accelerating the charge:

$$J_n = qn\mu_n E$$

$$J_p = qp\mu_p E$$

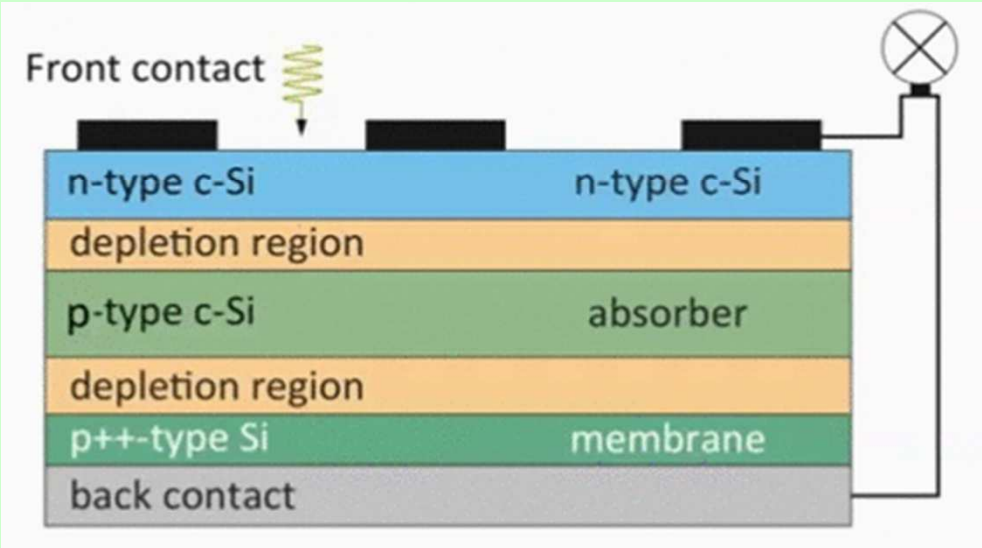
μ = mobility of carrier
D = diffusion coefficient
T = temperature in K
k = Boltzmann constant
q = elementary charge

Diffusion current involves majority carriers, while drift current usually involves minority charge carriers

Photovoltaic (IV)

We look at the response of the junction to a uniform illumination:

- A **photon is absorbed** by the semiconductor. If the $E_{photon} \geq E_{band-gap}$ it will **excite an electron** in the valence band to go to the conduction band and leave an hole behind.
- In both, p and n regions the increase of majority carriers because of excitation is negligible with respect to the concentration due to doping, while **the increase in minority carriers is significant** (low injection).
- The **drift current** ($J = q\boldsymbol{n}\mu E$) has a direct dependence on the concentration of carriers, hence the number of minority charge carriers drifting from one side to the other increases:
  - If we short circuit the two sides of the semiconductor we observe a net current (**short circuit current I_{sc}**): an electron moves from the p-type to the n-type region and diffuses all the way to the metal contact, enters the circuit and is **recombined** with a hole **at the metal contact** of the p-type.
  - If instead we had left the circuit open, charges would have accumulated on the two sides yielding an **open circuit voltage V_{oc}**.



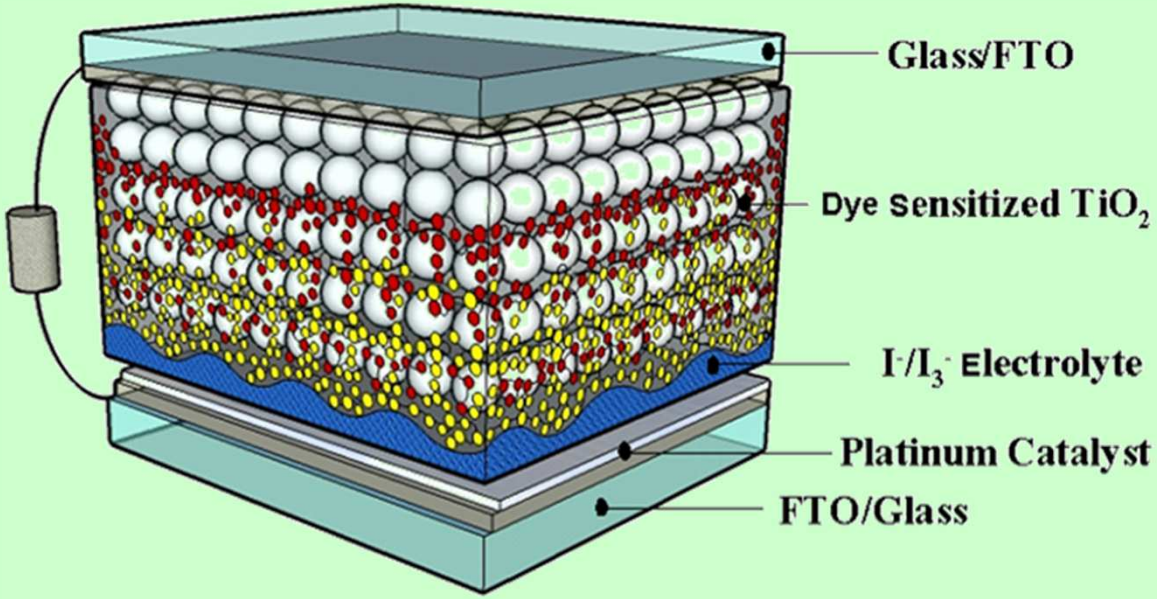
Hybrid-organic cells

Using organic materials sometimes along semiconductors.

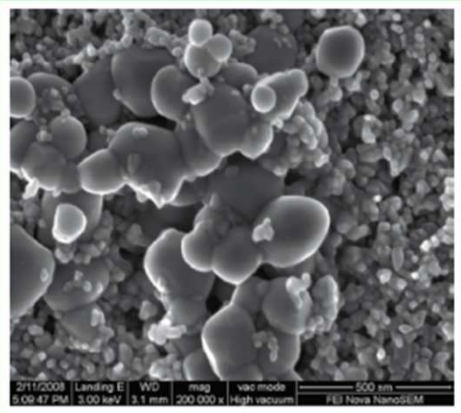
Flexible devices are ideal for energy harvesting: modules could be applied anywhere

Dye sensitized solar cells (DSC)

Their working principle is based directly on the photosynthesis.

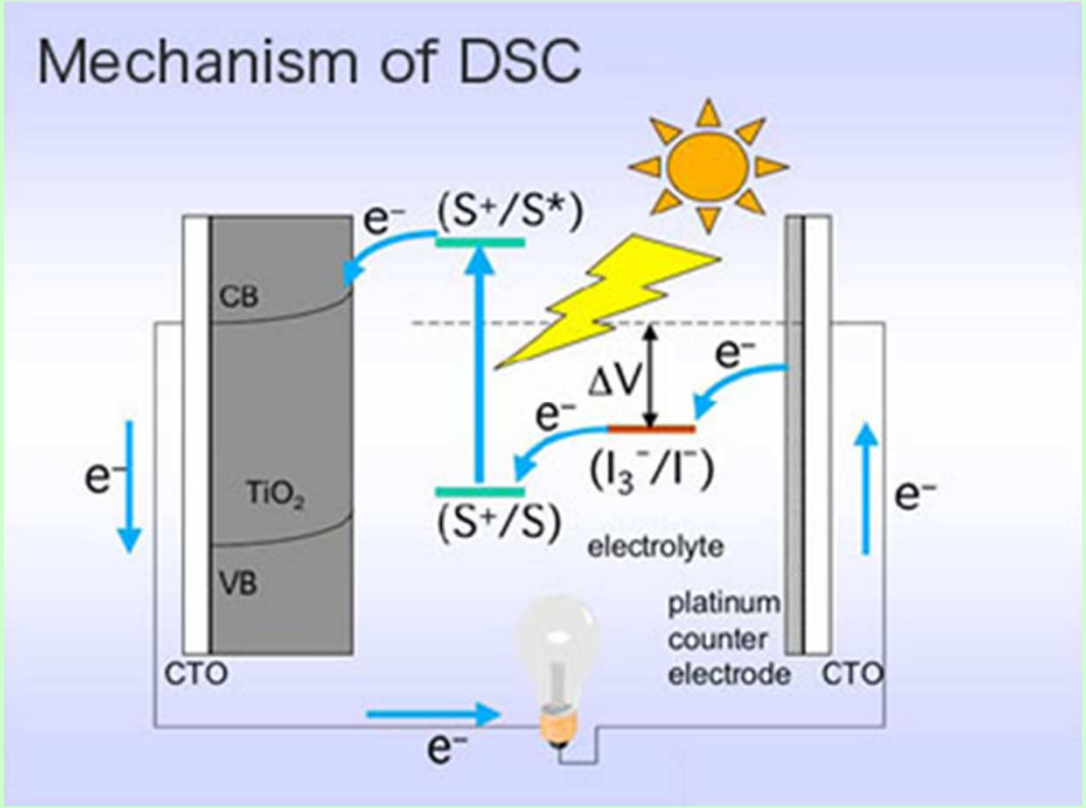


TiO2 is a semiconductor. Mesoporous growth allows greater binding surface with the dye (a rutinum based metalorganic molecule)



FTO is a transparent conducting oxide (TCO). ITO is also used as an alternative. Making it thinner (hence flexible) reduces conductivity.

Organic or hybrid-organic cells

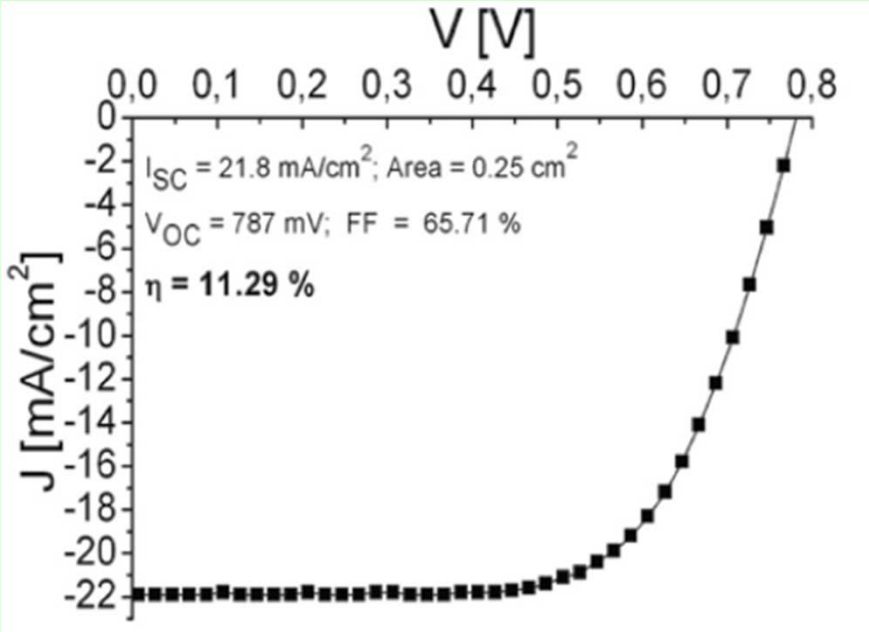


1. The **dye absorbs the photons** and **excites an electron** from a bonding to an empty antibonding state
2. The electron is quickly **transferred to** the conduction band of the **TiO_2**
3. The **electrolytes I^-/I_3^- give back to the dye** the released electron.
4. The **regeneration of the electrolyte** happens **at the counter electrode** and platinum acts as a catalyst to this regeneration.

No permanent chemical reaction takes place

Problems: **I^-/I_3^- is corrosive** and attacks the platinum electrode but also the metallic collection grids which boost the TCO conductance, **absorbs a lot of photons** and is **not a suitable choice for all weathers**. The aim is to look for different redox couples like cobalt based electrolytes or more importantly organic electrolytes.

Results and improvements



The electrical characteristics of an optimized DSC of area 0,25 cm^2 under an illumination of 1000 W/m^2 (1 sun) and an AM 1.5 solar spectrum.
V_{OC} is the open circuit voltage,
I_{SC} Is the short circuit current density
FF is the fill factor.
Results obtained by the *Centre for Hybrid and Organic Solar Energy (CHOSE)*
Aldo Di Carlo, Andrea Reale, Thomas M. Brown, Francesca Brunetti
***Università degli Studi di Roma "Tor Vergata", Roma, Italia*.**

A challange for Engineers, Physicists and Chemists:

Turn to completely **organic dyes**:

- higher extinction coefficients
- easily synthesized
- can be molecularly engineered
- cheaper than rutinium based dyes
- allow to tune the color of the dye for aesthetical or architectonic needs

At the moment they are **very unstable**

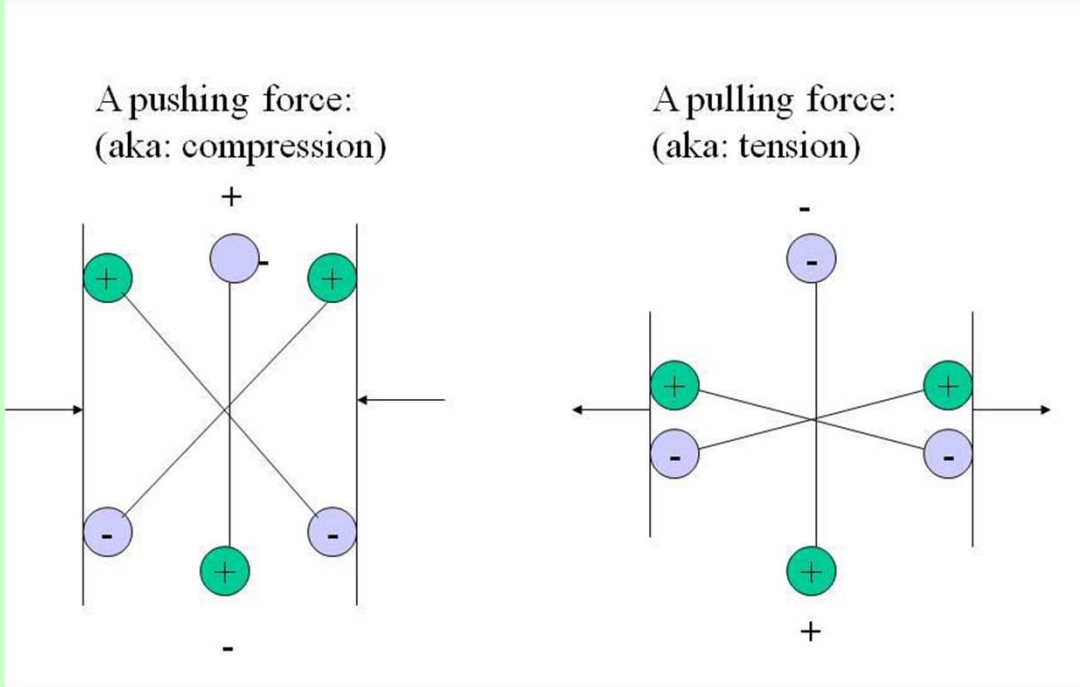
SAMSUNG in a 2012 press-release announced that they managed to industrialize **graphene** thin film production. Graphene is resistant and flexible and is suitable as conductive material instead of ITO (Indium Tin Oxide) which is very expensive. Graphene has also higher transparency.

Piezoelectric (I)

Piezoelectricity = an applied stress or vibration on particular materials generates an output voltage (direct piezoelectric effect)

This effect was observed by Pierre Curie in 1880. It is present in some **natural crystals** (like quartz) and in artificial materials called **piezoceramics**.

The piezoelectric effect is related to the dipoles present in the materials lattice. If, upon applying a stress, the dipoles become aligned, then we have the generation of a potential difference among the opposite ends of the sample.



Piezoelectric (II)

Piezoelectric materials are characterized by several coefficients, usually packed in matrix form:
d_{ij}: Strain coefficients: polarization generated per unit of mechanical stress (T) applied to a piezoelectric material or, alternatively, is the mechanical strain (S) experienced by a piezoelectric material per unit of electric field
g_{ij}: Voltage coefficients or field output coefficients: electric field generated by a piezoelectric material per unit of mechanical stress applied or, alternatively, is the mechanical strain experienced by a piezoelectric material per unit of electric displacement applied

The first subscript gives the direction of the excitation, the second describes the direction of the system response.

To go from [d] to [g]: $[g] = [\varepsilon_T]^{-1} * [d]$

The subscript T indicates that the dielectric constant has been measured when no stress is applied

Other important parameter is the Young's modulus Y (describing the elastic properties of the material).

$$\{D\} = [\varepsilon] * \{E\} + [d] * \{T\}$$

D = electric displacement vector (3 components)
T = stress tensor (6 components)
E = applied electric field (3 components)
d = piezoelectric contants (3x6 matrix)
ε = dielectric contant (3x3 matrix)

Piezoelectric (III)

Common applications of the piezoelectric effect are:

- The electric cigarette lighter

- The portable sparkers used to ignite gas stoves.
- Modern gas burners now have built-in piezo-based ignition systems.

The Defense Advanced Research Projects Agency in the United States began a project called *Energy Harvesting*, whose main objective was finding means to power up battlefield equipment through piezoelectric generators embedded in soldiers' boots.
Other possible piezoelectric energy harvesting applications are:

- Converting a dance floor to generate electricity
- Harvesting **vibrations from industrial machinery** to charge batteries for backup supplies or for other low-power devices
- Self-powered remote controls upon pressing button or bending them

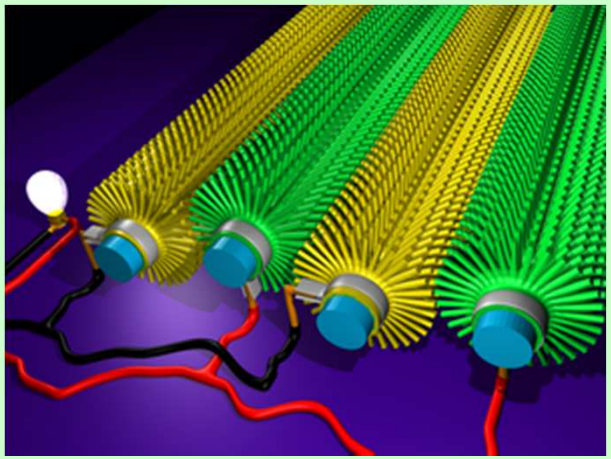
A possible **medical application**, would be applying piezoelectric materials to the joints of patients with a pace-maker in order to recharge it.
Challange: realizing biocompatible piezoceramics

Self powered nanowire devices

DARPA also supported a research on autonomous devices powered through piezoelectric materials.
At the Georgia Institute of Technology, a group of researchers (S. Xu, Y. Qin, C. Xu, Y. Wei, R. Yang and Z. L. Wang) realized in 2009 a UV sensor and a pH sensor which are powered by Zinc Oxide (ZnO) nano-wires.

Their work was published online on «Nature» (an international weekly journal on science) in 2010 and shows promising results.

The power source is called Vertical nanowire array integrated nanogenerator (VING).



Fabrication process

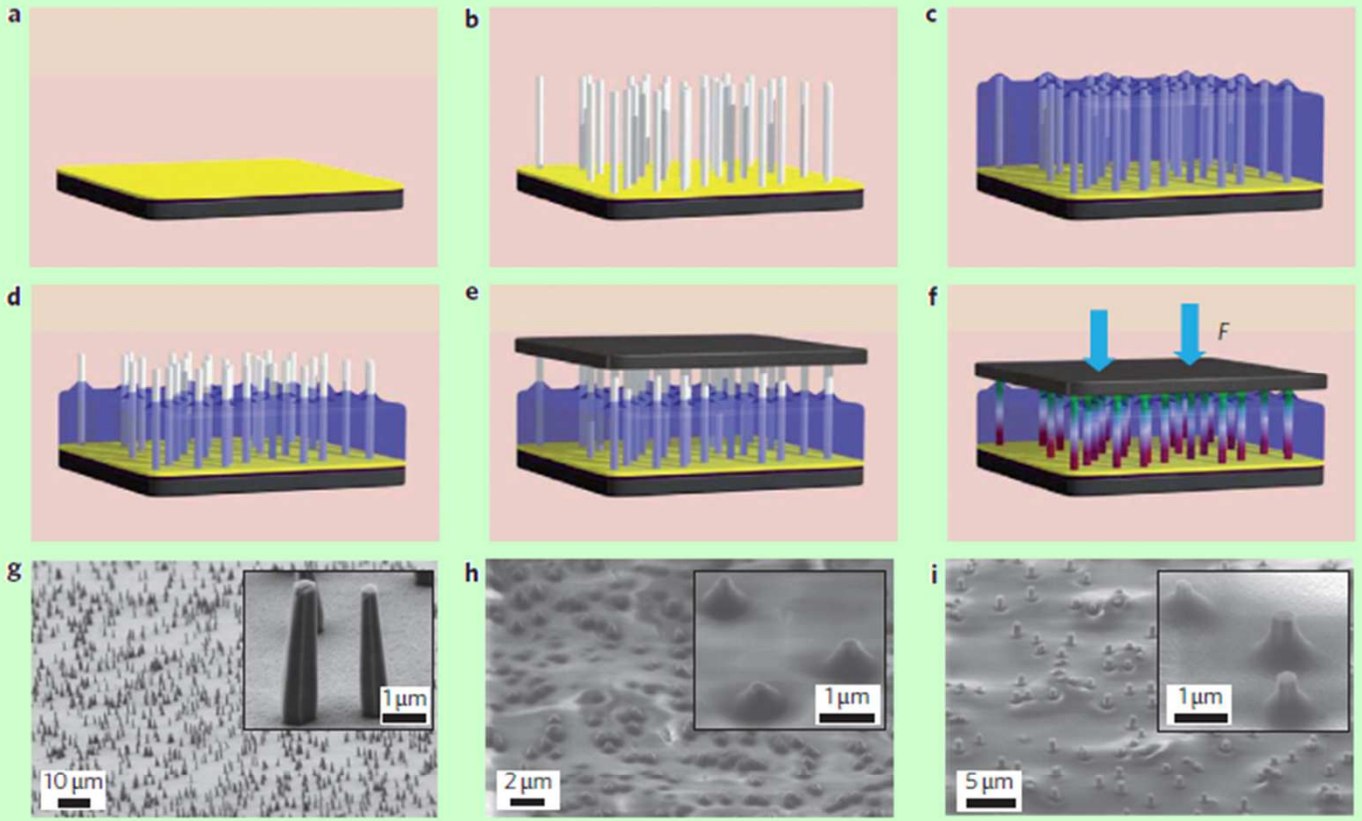
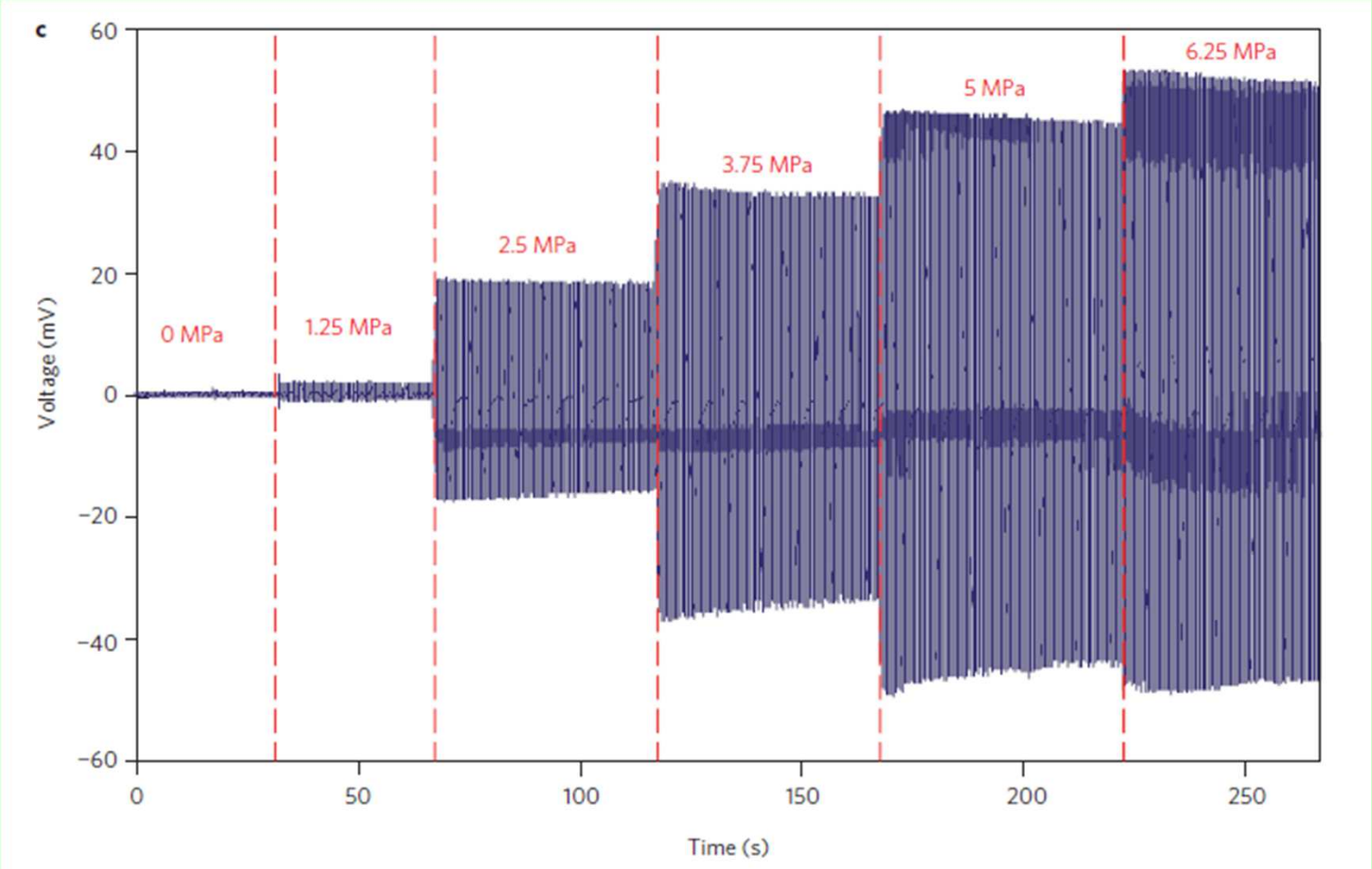


Figure 1 | Steps for fabrication of VING. a–f, On a gold-coated silicon wafer (**a**), ZnO nanowire arrays (**b**) are grown by low-temperature hydrothermal decomposition. PMMA, applied by spin coating (**c**), covers both the bottom and tips of the nanowire arrays. After oxygen plasma etching (**d**), the tips of the nanowires are exposed, fresh and clean, but the main body and bottoms of the nanowires are still fully enclosed, greatly improving the robustness of the structure. A platinum-coated flat electrode is placed on top of the nanowires (**e**) to form a firm Schottky contact. When a uniaxial stress is applied at the top electrode (**f**), the nanowires are readily compressed, the straining of the crystallographically aligned nanowires generating a macroscopic piezoelectric potential along the *c*-axis growing direction of the nanowires. **g–i**, SEM images of the as-grown ZnO nanowire arrays on the substrate (**g**), after spin-coating with PMMA (**h**) and after oxygen plasma etching (**i**).

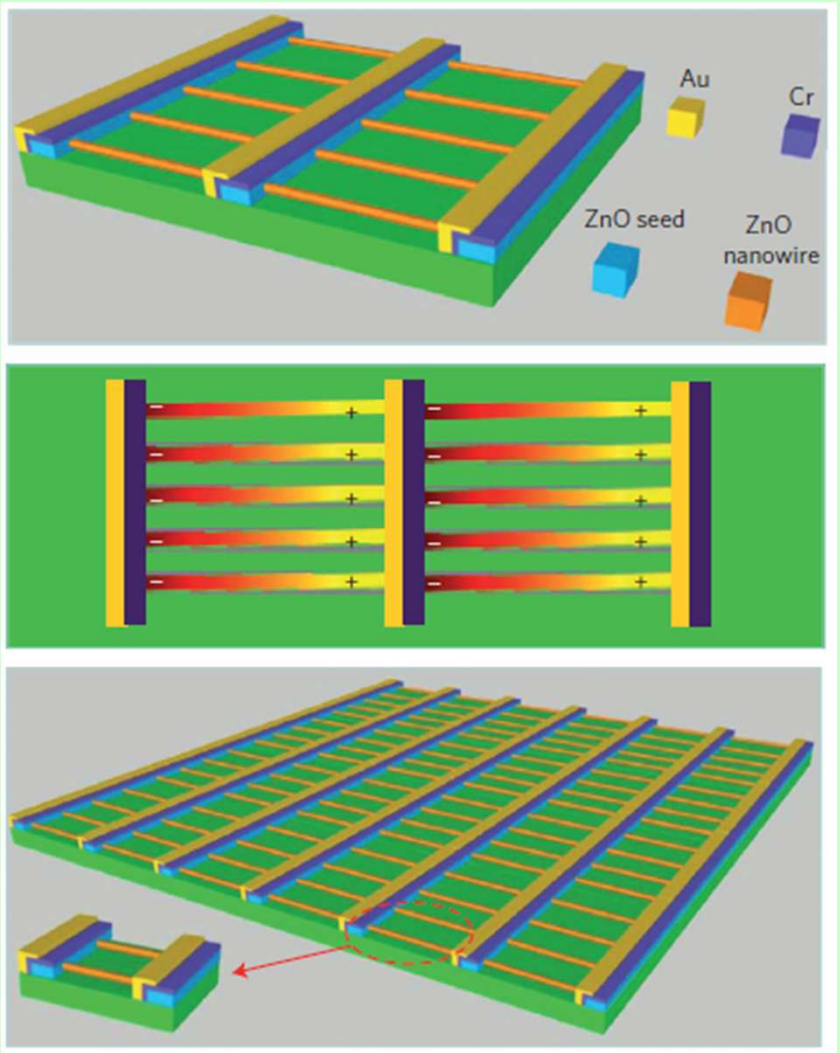
Results



As we can see the response (output voltage) of the system increases linearly with the applied stress, and this agrees with the theory on the matter.

Future objectives

The main challange is trying to integrate these nanogenerators to a **flexible substrate**, so that they could be driven by mechanical agitations present in our living environment, including human motion. It would also be ace to have higher output generators. A proposed design is the Lateral-nanowire-array Integrated Nano-Generator (LING) which presents some problems in the realization, mostly related to growing the nanowires with exactly aligned crystallographic polarity, which can't be done by chemical assembly. Further more, the junction between the nanowires and the substrate will have to be very strong, so not to break when undergoing an excessive stress. Temptative lab results showed an output voltage of 1.26 V and an output current of approximately 28.8 nA with a strain of 0.19%



Thermoelectric (I)

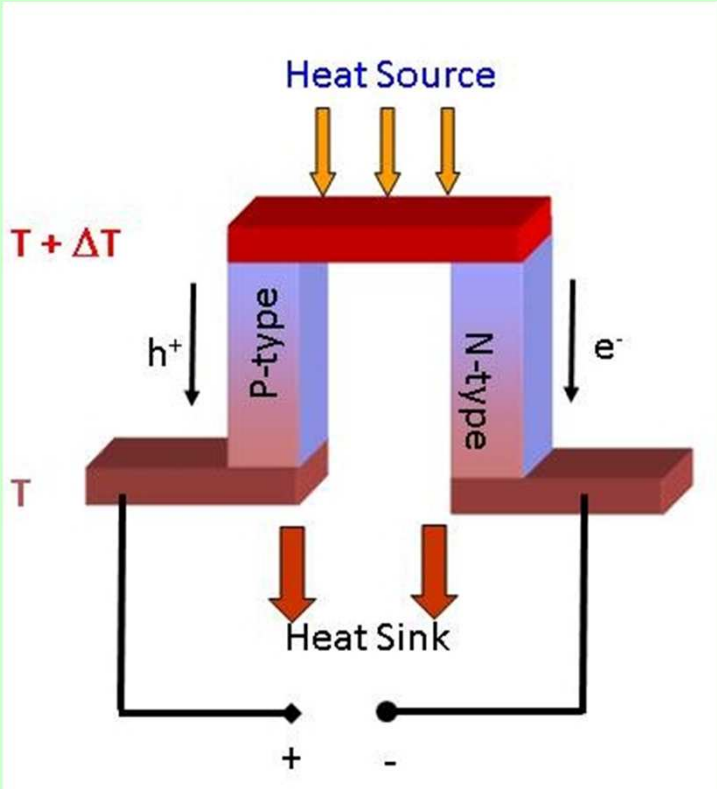
Thermoelectricity = the direct conversion of a temperature difference into an electromotive force (emf)

All materials can exhibit the thermoelectric effect, however those in which it is stronger are called **thermoelectric materials**.

The thermoelectric effect is based on three distinct effects:

- **Seebeck effect**
- Peltier effect (the reverse Seebeck effect)
- Thomson effect (negligible effect)

Seebeck observed how, if we create a loop of distinct materials and expose the junctions to different temperatures, we can observe a current flowing in the loop, even though no voltage is applied. The current flows in order to re-establish thermal equilibrium between the junction ends. If the circuit were open we would observe an emf at the ends. This effect is used in temperature sensors called thermocouples.

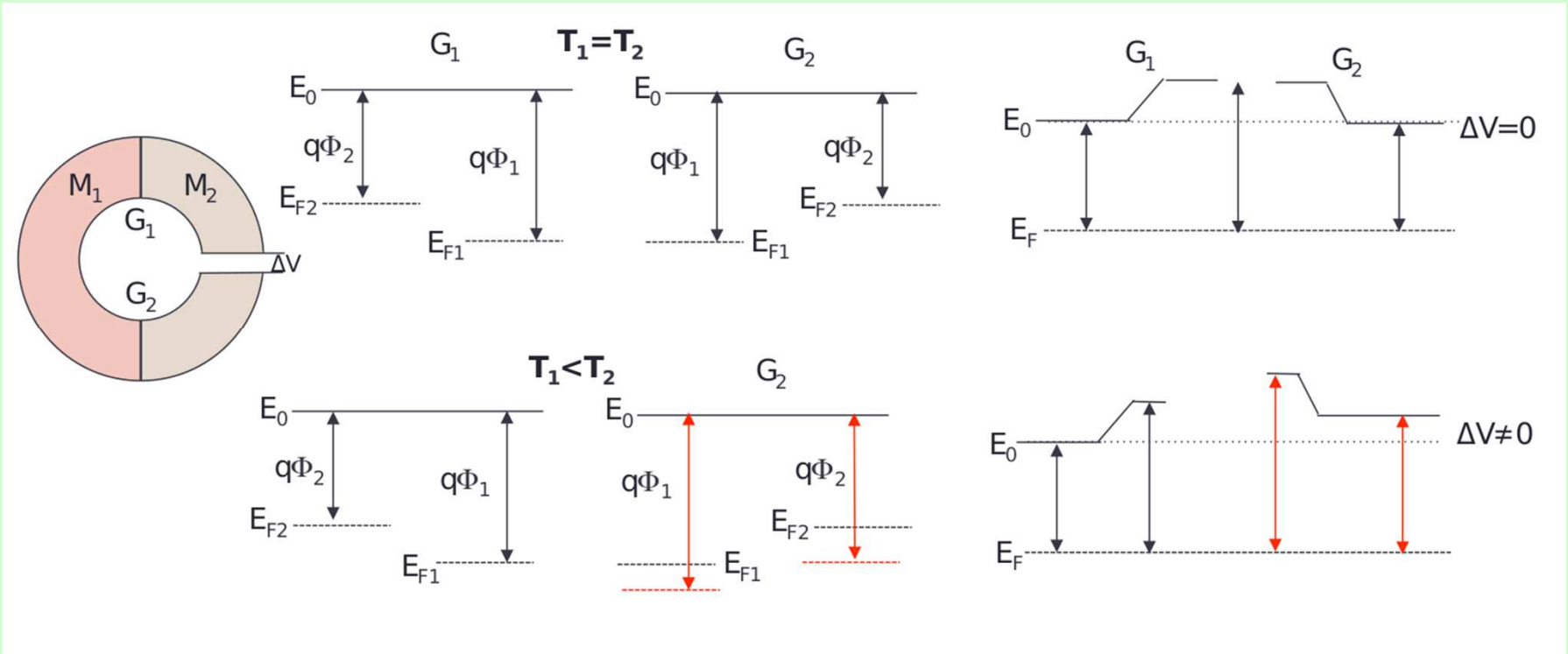


Thermoelectric (II)

The Fermi level (or electrochemical potential) is related to the absolute temperature of the material:

$$\epsilon = \epsilon_0 + kT\ ln(n) + qV$$

Since the two junctions are at different temperatures, equilibrium will be reached when the Fermi levels are the same, and this causes charge carriers diffusion (current).



Thermoelectric (III)

Good thermoelectric materials must have very high **Seebeck's coefficient** (S), high **electrical conductivity** (σ), but as low as possible **thermal conductivity** (λ), in order to maintain the thermal gradient between the two junctions. In this regard doped semiconductors would, again, be very suitable, but problems rise because of the difficulties in making semiconductor wires.

Seebeck's coefficient (S) is a temperature dependent quantity which could be either positive or negative (depending on which type of carriers are dominant in the electric transport)

$E_{emf} = -S\,\nabla T$ or $-\nabla V = S\,\nabla T$ Once equilibrium (J=0) is reached

It is best to use two of materials with **Seebeck's coefficient of opposite sign** (e.g. n-doped and p-doped semiconductors), in order to improve the performance of the device.

In literature there is usually a **unit less figure of merit ZT** which is used to evaluate the thermoelectric performance of the material:

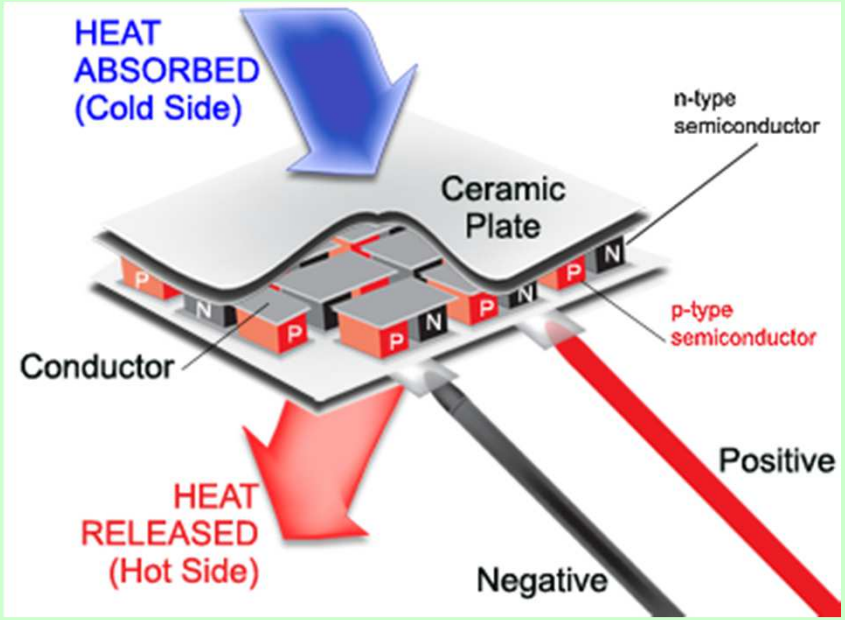
$$ZT = \frac{\sigma S^2 \mathrm{T}}{\lambda}$$

It is used is because it has a direct relationship with the expression for the maximum efficiency obtainable from a thermoelectric device, taking into account Seebeck's coefficient, electrical conductivity and thermal conductivity.

Thermoelectric (IV)

The best application of the thermoelectric effect comes from the **Peltier cell**, used for thermoelectric cooling (through the Peltier effect)

A **TE power generator** device consists of p and n legs which are connected electrically in series and thermally in parallel. The p and n legs are joined by a metal interconnect and the series of legs are placed in between a heat source and a heat sink. Problems in power generators industrialization are due to **very low efficiencies** (below 10%), even though, on the plus side, such devices have a **very long life time.** A major problem for the TE community is the lack of standards in efficiency measurements, which makes some experimental conditions hardly reproducible.



The main objective for researchers is increasing the ZT figure of merit and research is now focusing on **modulation-doping on nanocomposites** to do so.

Conclusion

There is much room for improvement in each of these technologies, in particular on the efficiency point of view, but tackling the energy problem is an issue that must be addressed by the entire scientific community: engineers, physicists, chemists and biologists must work together to make sure that our way of living becomes more and more

sustainable

Thank you for your attention!