ELECTROACTIVE MATERIALS FOR ENERGY HARVESTING

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SUMMARY

- Introduction
  - Materials and devices
- Piezoelectrics
  - Physical properties/fabrication
  - ZnO microrods
- Electrets
  - Physical properties/fabrication
  - SiO_2 micro particles as electrets

TRANSDUCTION MECHANISMS AND MATERIALS

Mechanical action

Strain (cantilever, etc)

Motion («free» inertial mass,)

Strain conversion

- Piezoelectrics
- Electroactive polymers
- Magnetostrictive mat.
- Magnetoelectrics

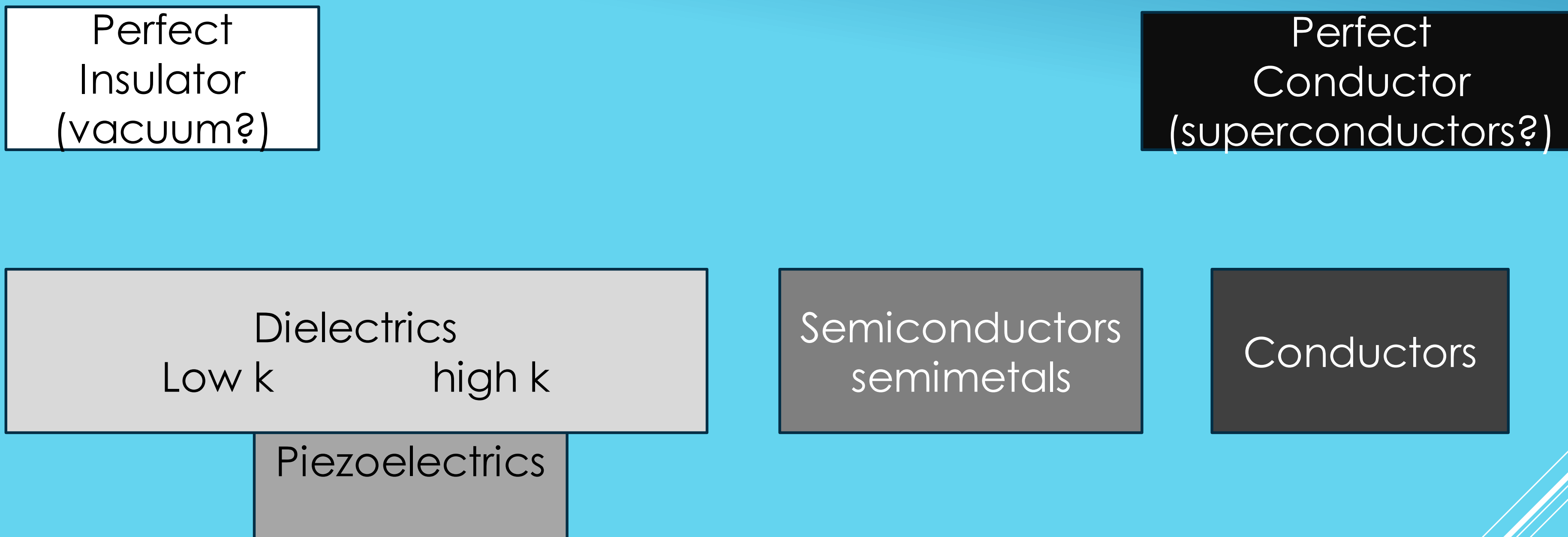
Electrostatic

- Electrets

Electromagnetic Induction

- Magnets

ELECTRIC BEHAVIOR OF MATERIALS



Depending on the external conditions (electric field intensity or frequency, temperature, shape, strain) the behaviour of real materials can move between these extrema

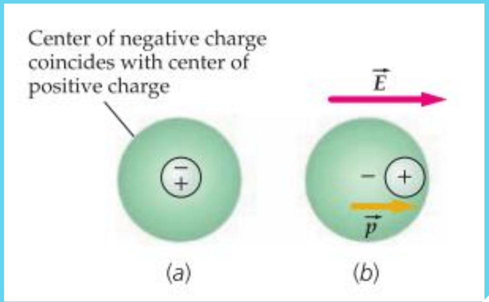
ELECTRIC POLARIZATION

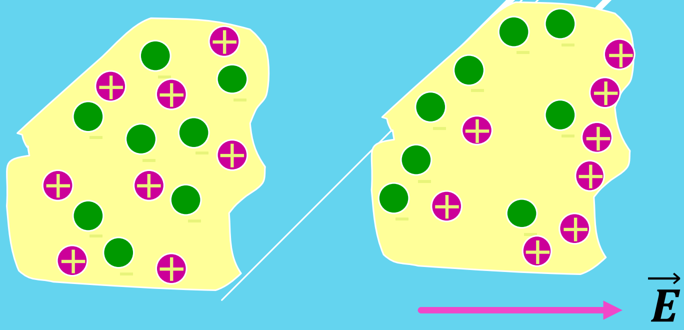
$$P = \frac{\varepsilon - 1}{4\pi} E$$

In an external electric field, materials acquire an induced dipole moment or POLARIZATION

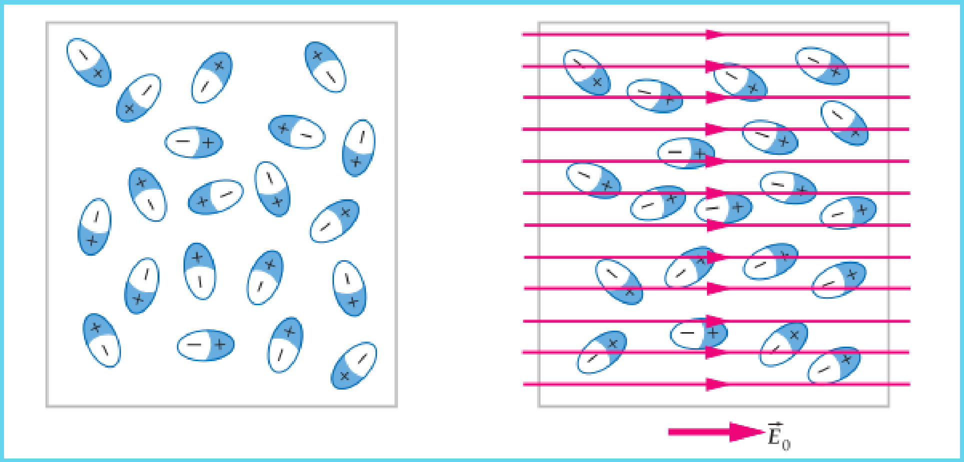
It can have different origins

Deformation (of electron or ions)

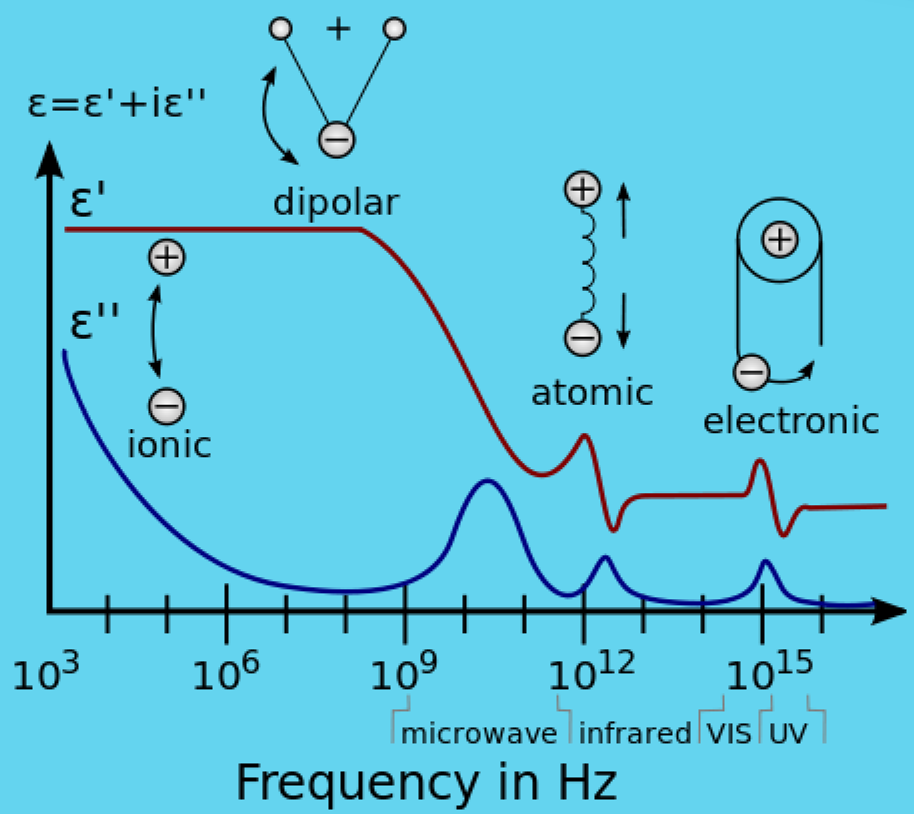




Orientation (of pre-existing dipoles)



FREQUENCY DEPENDENCE



- The response of the electroactive materials is strongly frequency dependent.
- They work best at resonance when the trasferred power is maximum.
- They still react at lower frequency, while at higher frequency they cannot rearrange following the external field

MATERIALS IN MAGNETIC OR ELECTRIC FIELDS

Diamagnetic

Its atoms have no permanent magnetic moment. The induced moment opposes the external field.

Paramagnetic

Its atoms have permanent magnetic moment, which aligns with the external field

Ferromagnetic

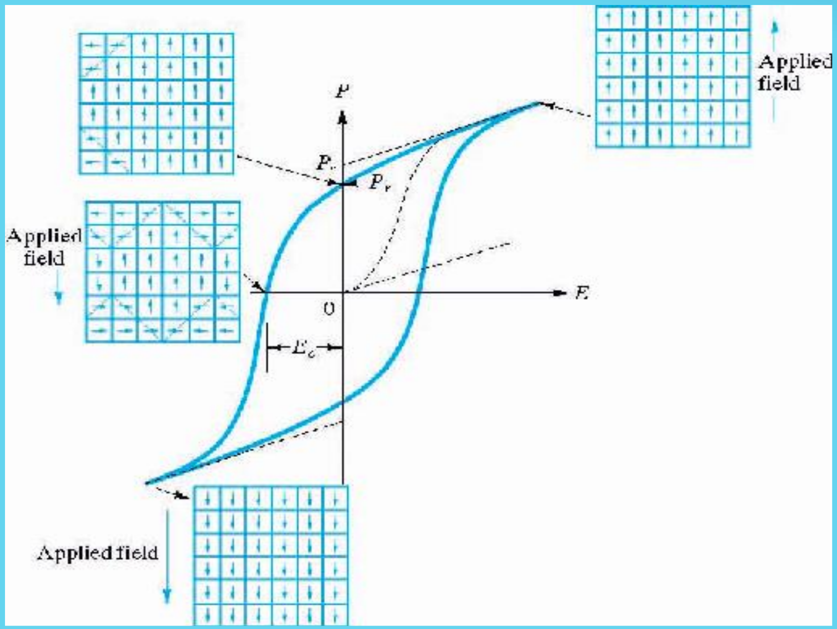
Its atoms have permanent magnetic moment and strong exchange energy connects them into domains

Paraelectric

Also the induced dipole in dielctrics is aligned with the external field

Ferroelectric

HYSTERESIS



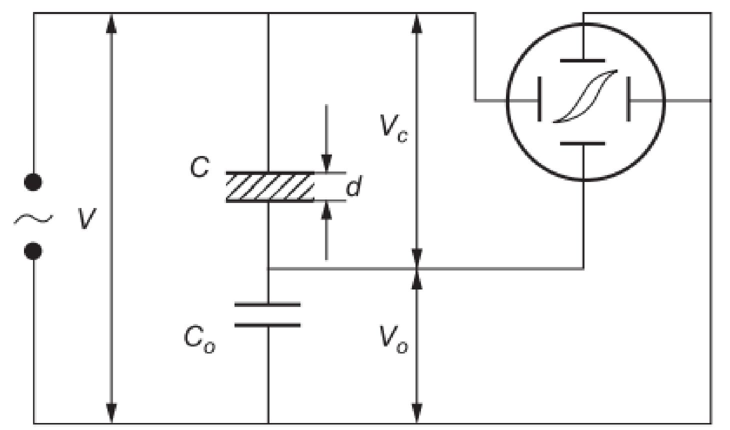


Figure 4-3 The Sawyer–Tower method for the measurement of the polarization-electric field (P–F) characteristics.

In Ferroelectrics (Ferromagnetics) materials, the thermal agitation cannot overcome the alignement of the domains. A coercive field is needed to reverse polarization (magnetization).

THE MICROSCOPIC ORIGIN

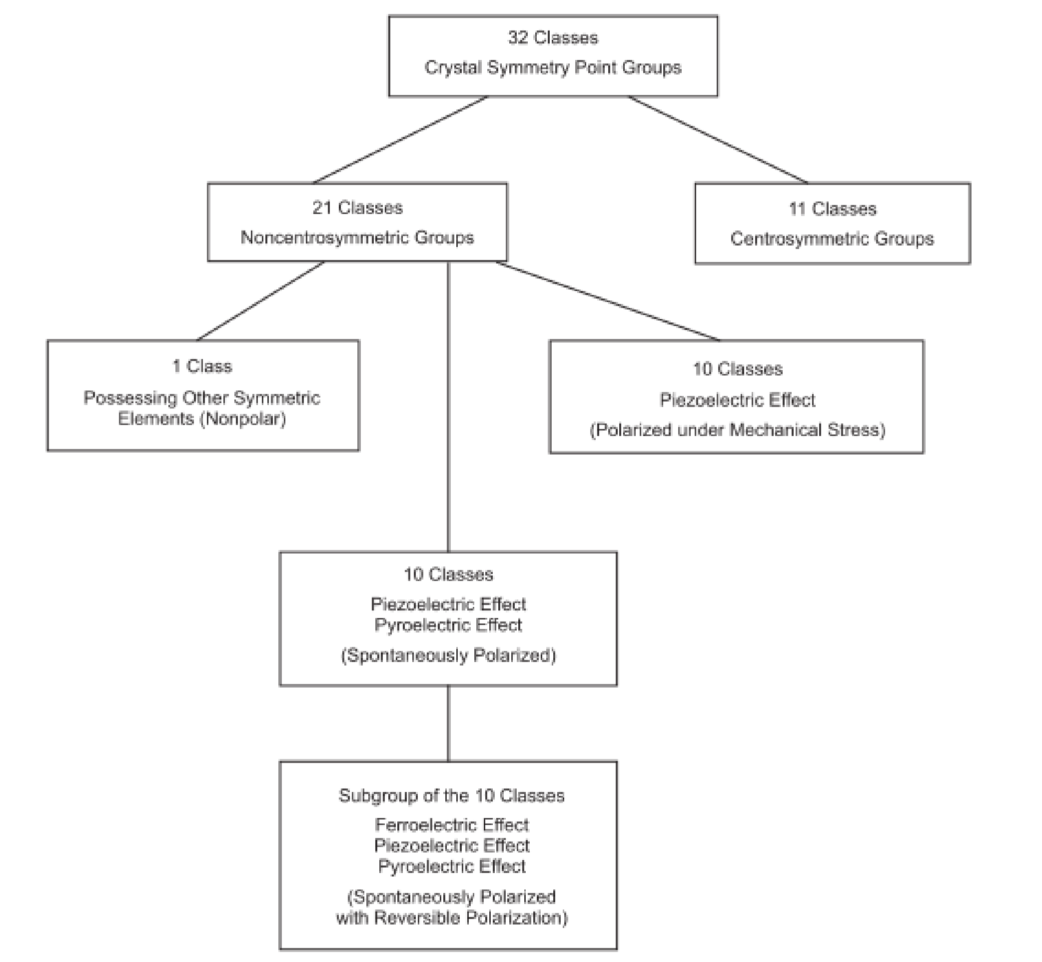
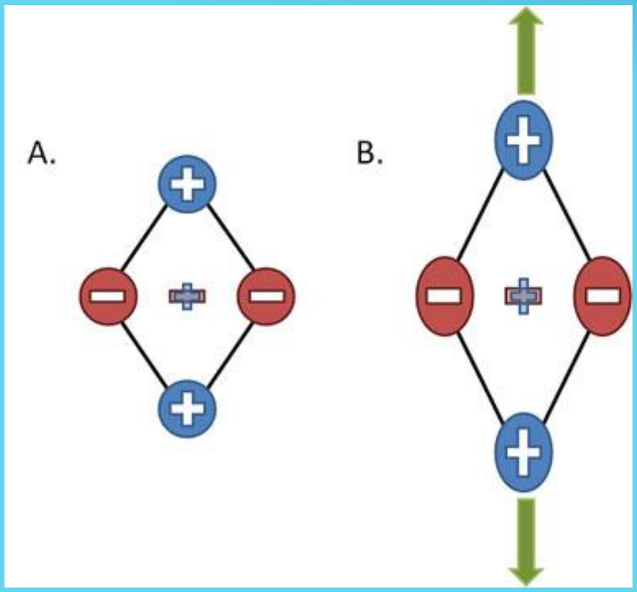


Figure 4-1 Classification of crystals showing the classes with piezoelectric, pyroelectric, and ferroelectric effects.

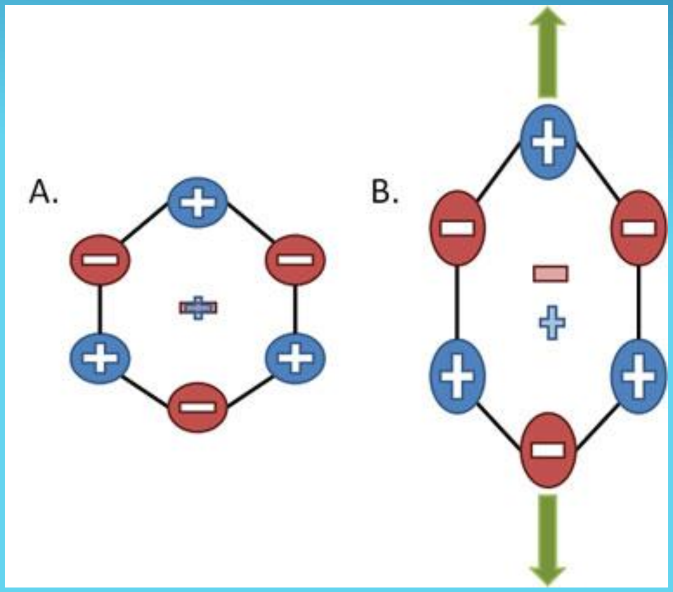
Simmetry of the unit cell is a necessary, but not sufficient condition.

Different charge distributions can cancel or strongly decrease the piezoelectric effect

PIEZOELECTRICITY



Centro-symmetric

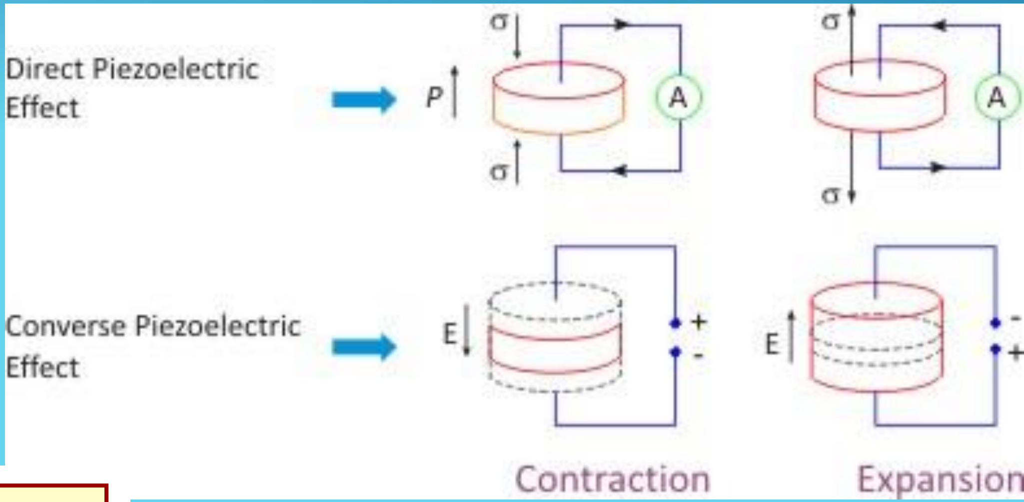


Non Centro-symmetric

In centrosymmetric crystals the strain does not move the center of charge of the positive or negative charges. On the other hand, in in non centro-symmetric crystals, if the atoms have different charges because of the strain provokes the formation of an electric dipole.

PIEZOELECTRIC COEFFICIENTS

- $P = d\,\sigma$
- $\varepsilon = d^t\,E$



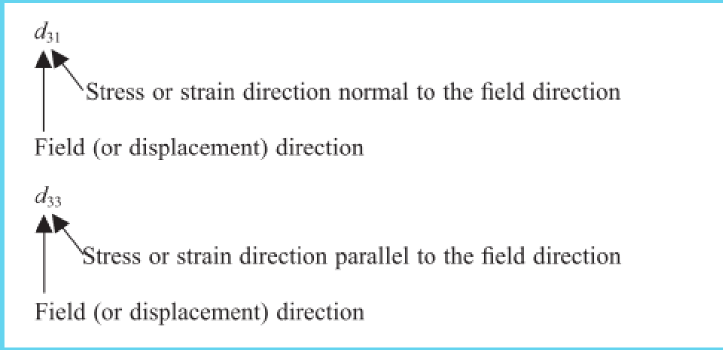
Material	Piezoelectric Constant, d (pm/V)
Quartz	2.3
Barium Titanate	100-149
Lead Niobate	80-85
Lead zirconate titanate	250-365

The direct piezoelectric effect is used as the basis for ENERGY HARVESTING (and force, pressure, vibration and acceleration sensors) while converse effect is used as a basis for actuator and displacement devices.

PIEZOELECTRIC COEFFICIENTS

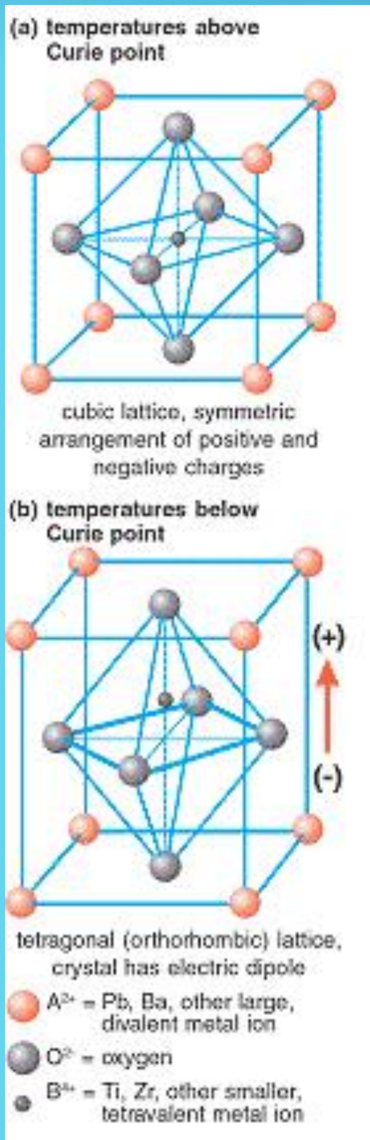
d is third-rank tensor (d_{ijk} 3x3x3) , as it links the effect of strain/stress (second order tensor) to the induced Polarization/Electric field (vector).

However, it is often written in a contract matrix form (3x6), where 4,5,6 index are used to express shear stress/strain



Axis «3» is usually the anomalous axis of uniaxial piezoelectric crystals and the one where the effect is stronger

FERROELECTRICITY

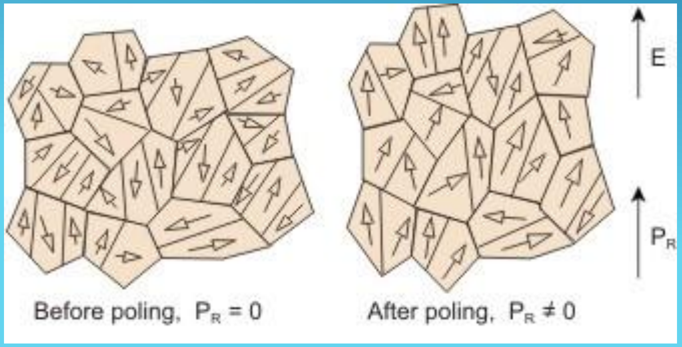


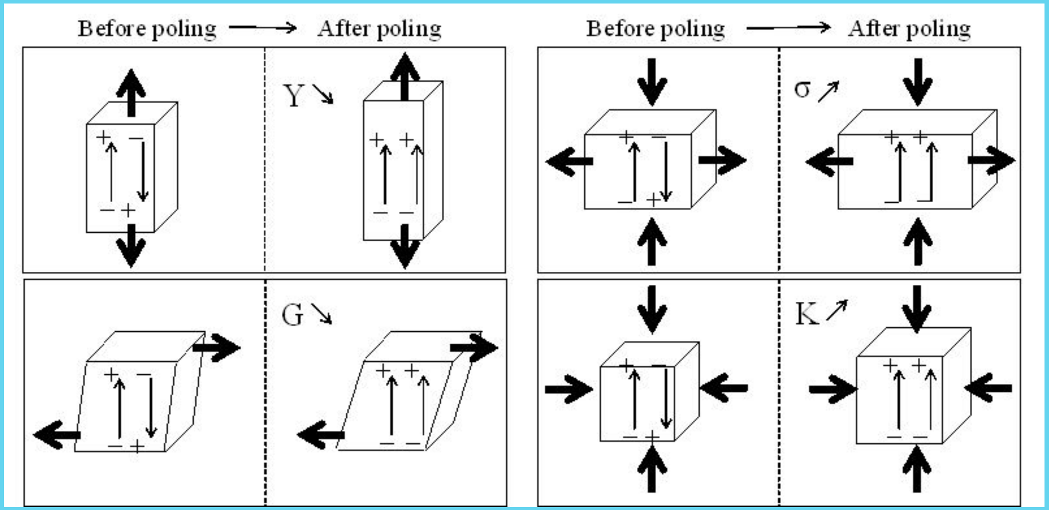
In BaTiO3 at room temperature the stable phase has the Ti4+ ion displaced form the center of the cell. It has two stable positions: above and below the 4 central oxygens.
Depending on its position, the dipole will be reversed.

Name (Abbreviation)	*Chemical Formula*	*Curie Temperature, T_c (°C)*	*Spontaneous Polarization P_s(μC m^{-2}) at [T (°C)]*	*Crystal Structure*	
				Above T_c	*Below T_c*
Barium Titanate	$BaTiO_3$	120	26.0 [23]	Cubic	Tetragonal
Lead Titanate	$PbTiO_3$	490	50.0 [23]	Cubic	Tetragonal
Potassium Niobate	$KNbO_3$	435	30.0 [250]	Cubic	Tetragonal
Potassium Dihydrogen Phosphate (KDP)	KH_2PO_4	−150	4.8 [−177]	Tetragonal	Orthohombic
Triglycine Sulfate (TGS)	$(NH_2CH_2COOH)_3$• H_2SO_4	49	2.8 [20]	Monoclinic (Centrosymm.)	Monoclinic (Noncentrosymm.)
Potassium-Sodium Tartrate-Tetrahydrate (Rochelle salt)	$KNaC_4H_4O_6$•$4H_2O$	24	0.25 [5]	Orthorhombic (Centrosymm.)	Monoclinic (Noncentrosymm.)
Antimony Sulfo-iodide	SbSI	22	25.0 [0]	Orthorhombic (Centrosymm.)	Orthorhombic (Noncentrosymm.)
Guanidinium Aluminium Sulfate Hexahydrate (GASH)	$C(NH_2)_3Al(SO_4)_2$•$6H_2O$	None	0.35 [23]	Trogonal	—

POLING

- Under a strong external field it is possible to induce the poling of the ferroelectric material (i.e. polarize)



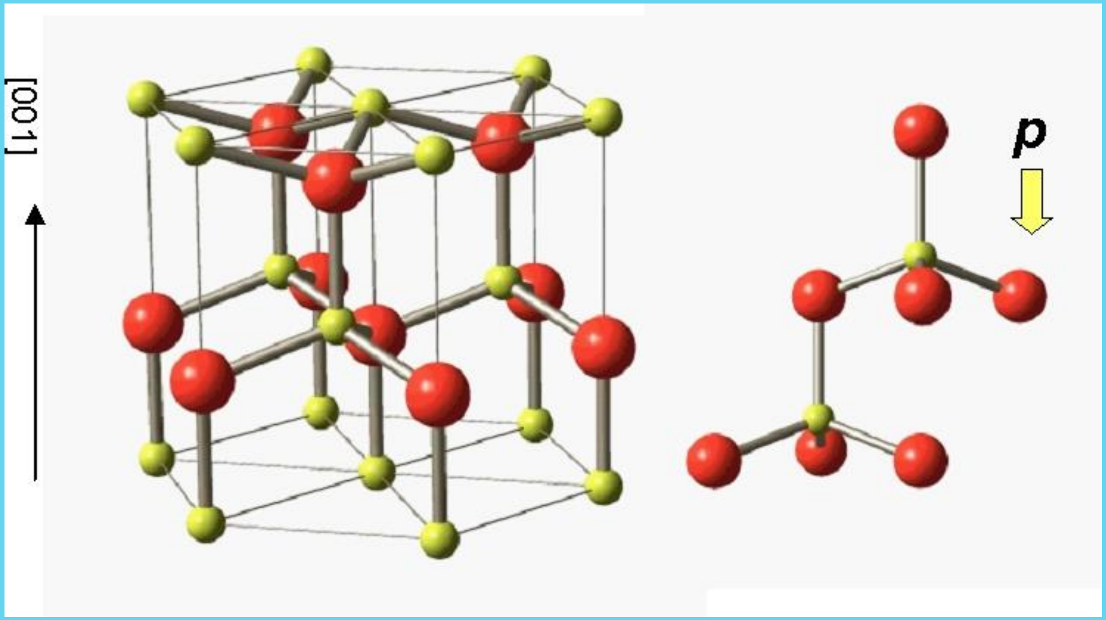


If the material is poled, the stress acting on it can generate an intense change of the electric dipole (usually stronger than in common piezolectric materials)

PYROELECTRICS

Crystal with a permanent dipole, not reversible.

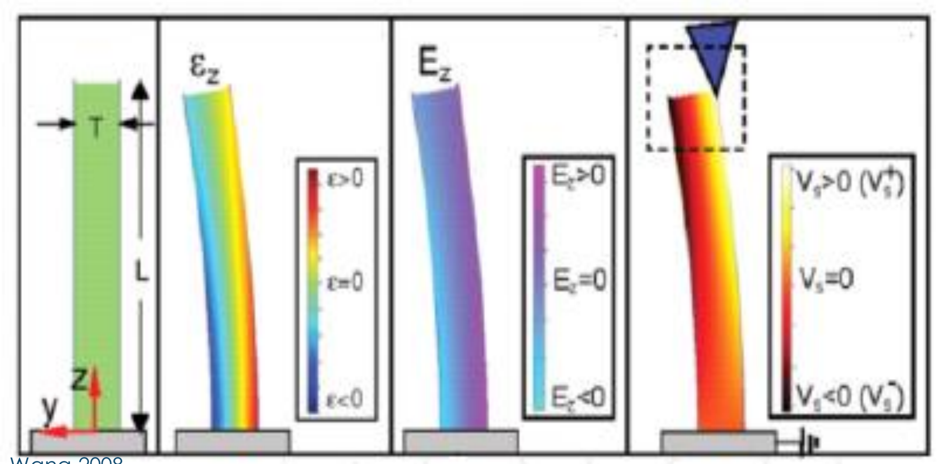
They have to be grown as single crystals.



Wurtzite structure crystals, such as ZnO, are asymmetric along the [001] axis, ([001] is different from [00-1])

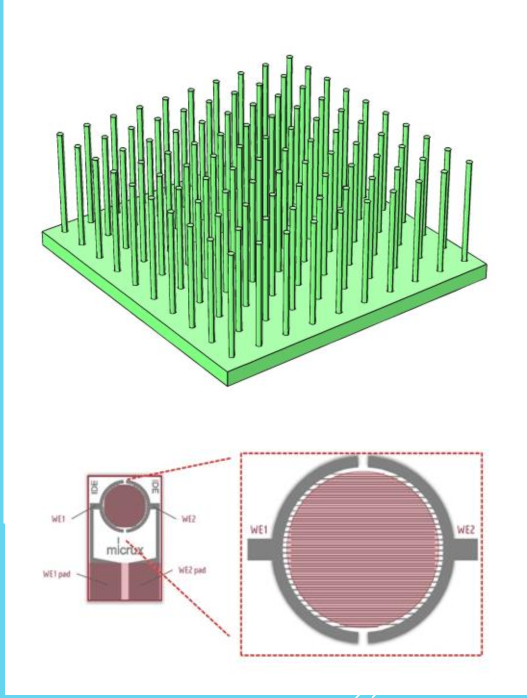
Because of thermal dilatation, the electric dipole increases

ZINC-OXIDE MICRORODS



Wang 2008

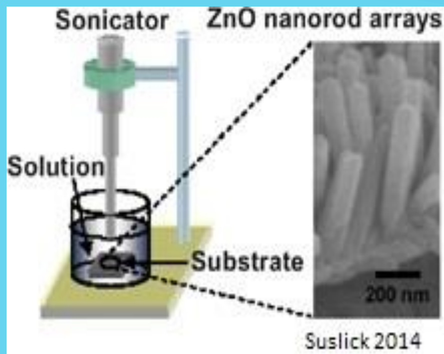
Growth of ZnO pillars on IDE



Objective: exploiting the difference of potential at the base of the pillar induced by the bending

FABRICATION

Sonochemical synthesis



$$(CH_2)_6N_4 + 6\,H_2O \rightarrow 4\,NH_3 + 6\,HCHO \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

$$Zn^{2+} + 2OH^- \xrightarrow{)))} ZnO + H_2O \quad (3)$$

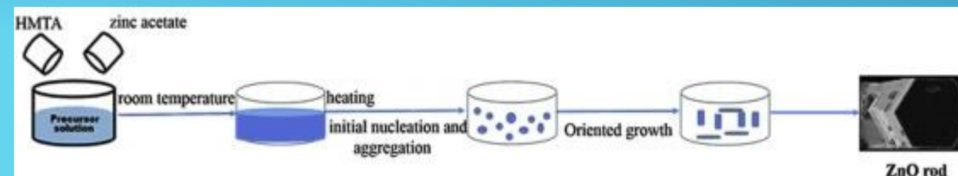
$$Zn^{2+} + 2\,O_2^- \xrightarrow{)))} ZnO + {}^3\!/_2O_2 \quad (4)$$

Reagenti:

HMTA, $(CH_2)_6N_4$

Acetato di Zinco, $Zn(CH_3COO)_2$

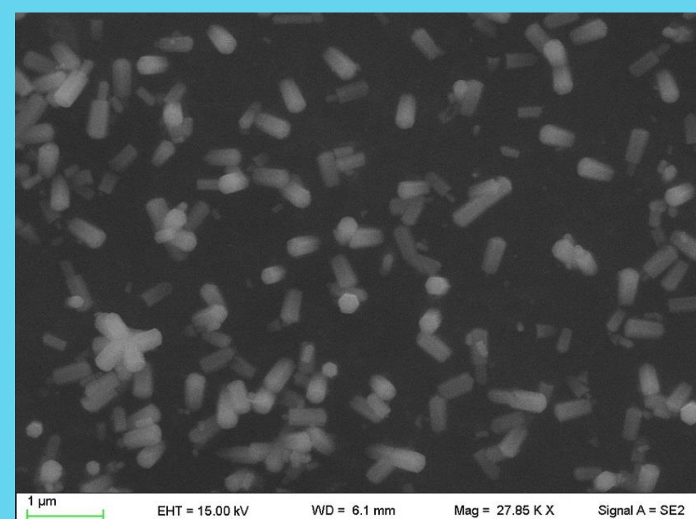
Hydrothermal synthesis



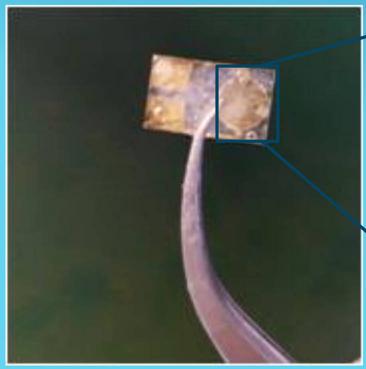
$$C_6H_{12}N_4 + 6H_2O \rightarrow 6CH_2O + 4NH_3 \quad (1)$$

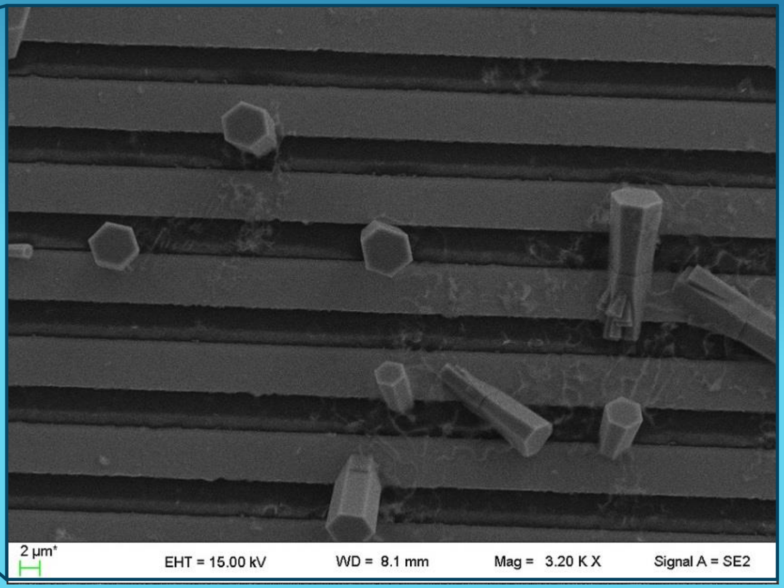
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

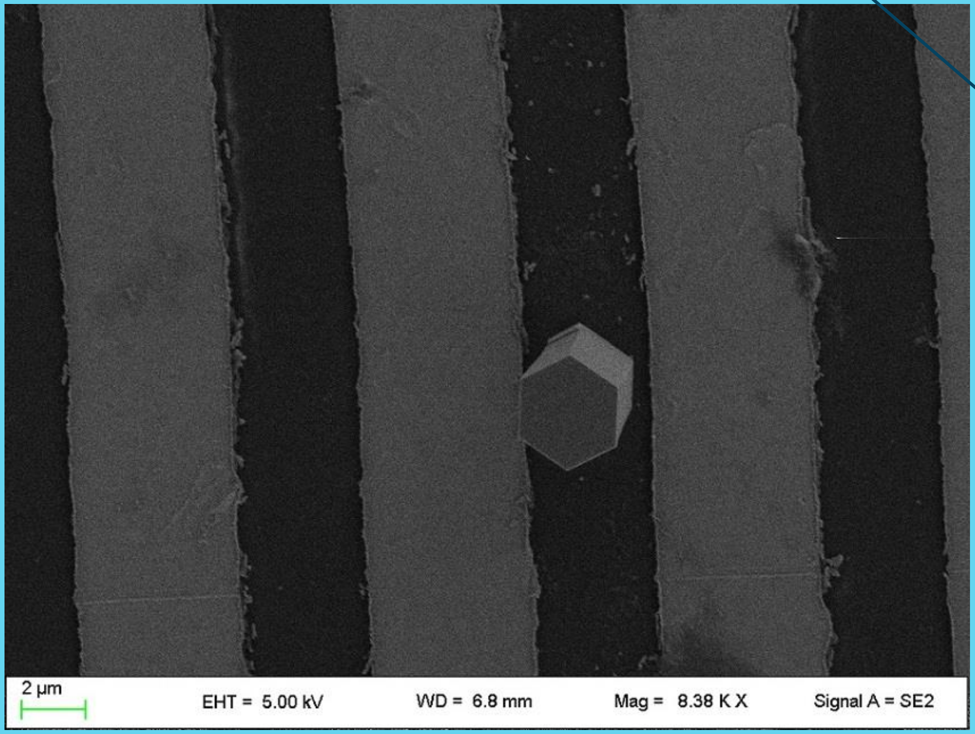
$$2OH^- + Zn^{2+} \leftrightarrow ZnO + H_2O \quad (3)$$



HYDROTHERMAL SYNTHESIS ON IDE



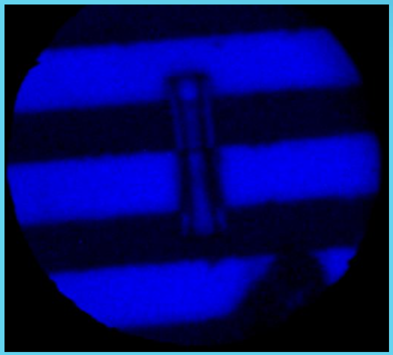


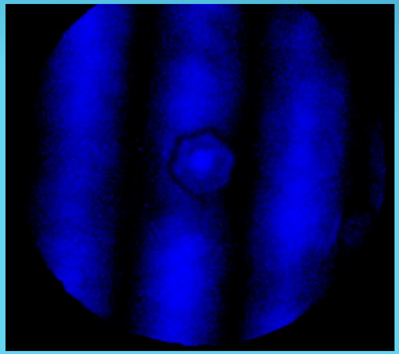


Reagents:

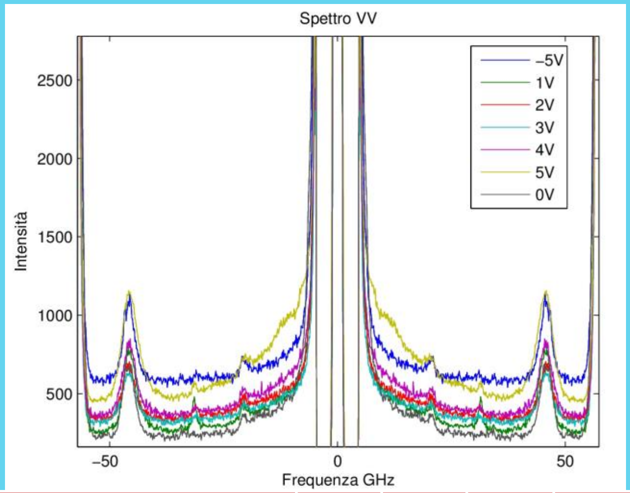
- HMTA e Acetato di Zinco (Rapporto molare 4:1)
- Temperatura 85°C (5h)
- Substrato IDE

SPECTROSCOPIC CHARACTERIZATION

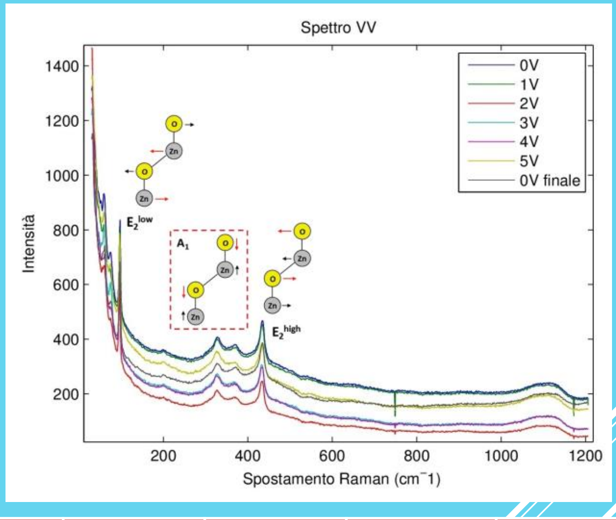




Raman and Brillouin spectroscopy on single crystals

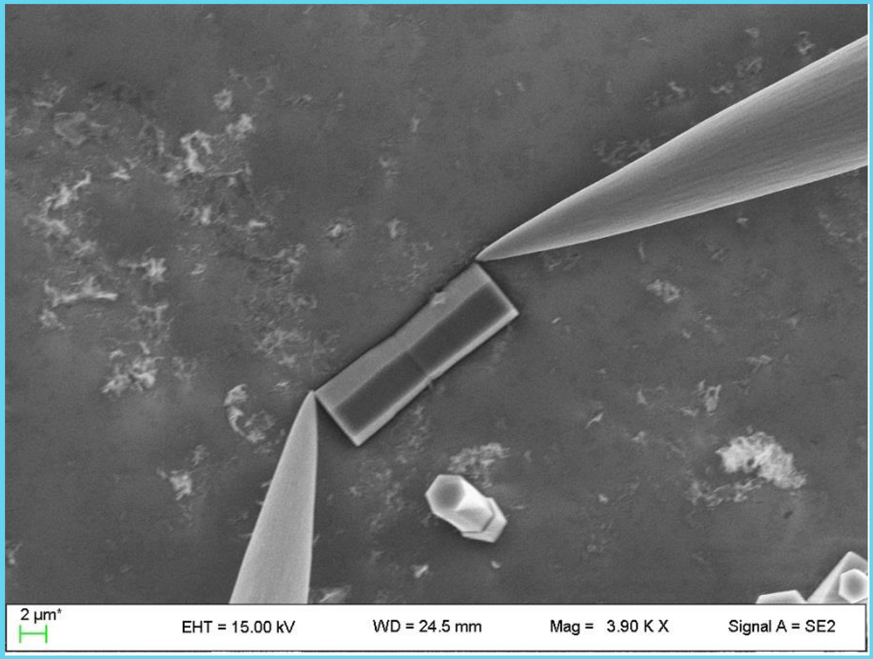


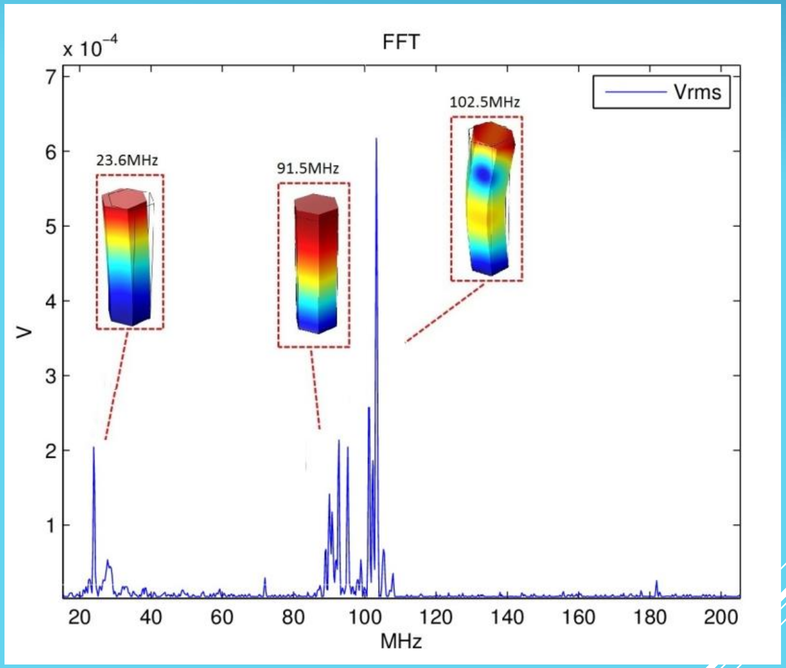
Elementi Matrice C (GPa)	C_{11}	C_{33}	C_{44}	C_{66}
Ref. Bhat et al.	209	210	42	44
Risultati	209	198	42	43



Raman Shift (cm^{-1})	E_2^{low}	$A_1(E_2)$	$A_1(E_1,E_2)$	A_1	E_2^{high}
Ref. Damen et al.	101	208	332	380	437
Risultati	101	205	332	379	438

SEM CHARACTERIZATION





Electrical measurements on single crystals in the SEM environment.
It is possible to observe the normal mode of vibrations of the crystal inducing electrical signa at the borders

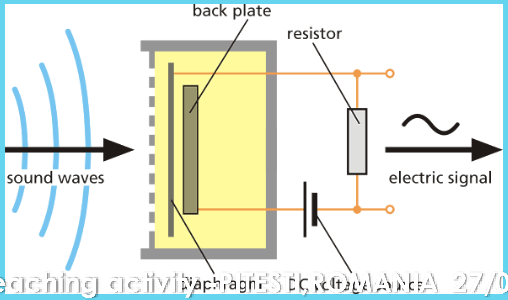
ELECTRETS

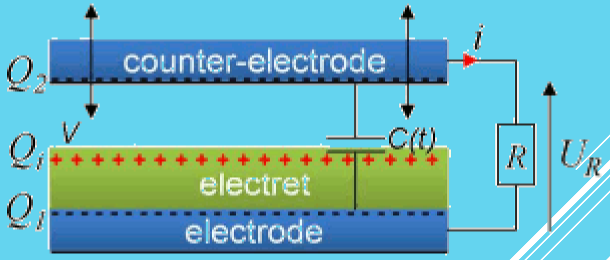
Dielectrics with unbalanced charge (permanent oriented electric dipoles or a net charge.)

Electrical analogue of a magnet: able to generate an electric field

MATERIALS: dielctrics (polymers, oxides) with high dielectric strength and low conducibility

Old applications: microphone





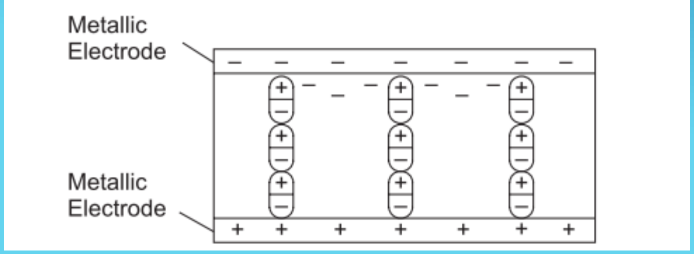
S Boisseau et al. Smart Materials and Structures 20, 105013, 2011

New ones : energy harvesting devices

FORMATION OF ELECTRETS

Two types of electrical charges in an electret :

- monocharges (also called real charges)
- dipolar charges (such as in ferroelectrets)

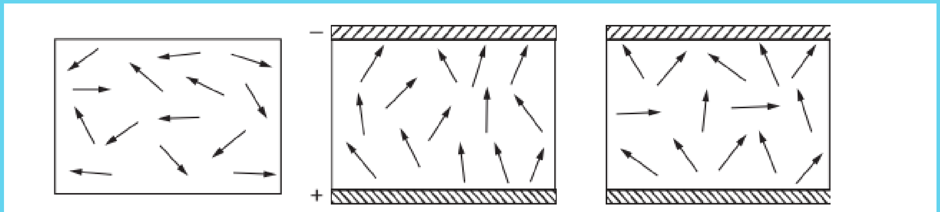


Several fabrication techniques:

- Thermo-Electrical Method (dipolar)
- Electromagnetic Radiation Method (dipolar)
- Liquid-Contact Method (real charges)
- Corona Discharge Method (real charges)
- Electron-Beam Method (real charges)

THERMO-ELECTRICAL METHOD

Dipolar molecules are randomly arranged but they will actively orient under an electric field at a temperature higher than the glass transition temperature, Tg



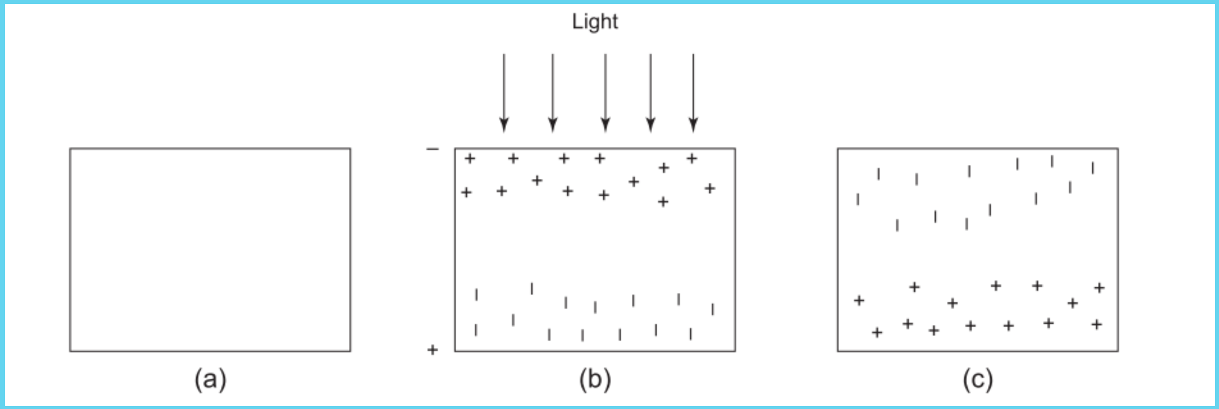
Typycal materials is the Carnauba wax–beeswax (first electret, made by Eguchi in 1919)

Drawback: stability

Ferroelectrets can be considered electrets obtained by thermoelectrical method (the poling) but with, possibly, much higher Tg

ELECTROMAGNETIC RADIATION METHOD

Displacement of the charge carriers generated by penetrating radiation (x-rays or ultraviolet light), under an externally applied electric field.

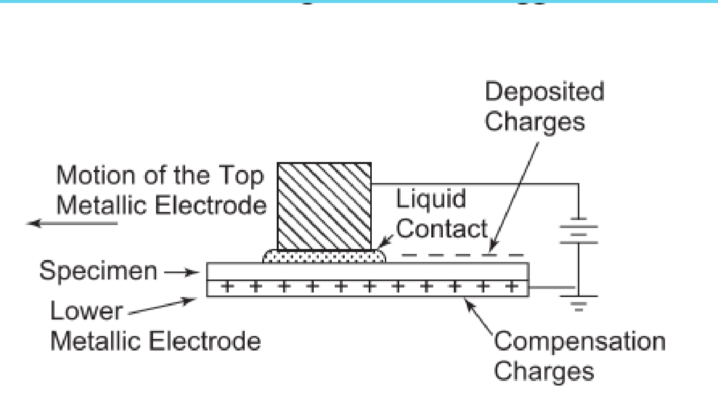


These carriers can be trapped near the electrodes to create a space charge polarization.

The polarization remains after the external field removal

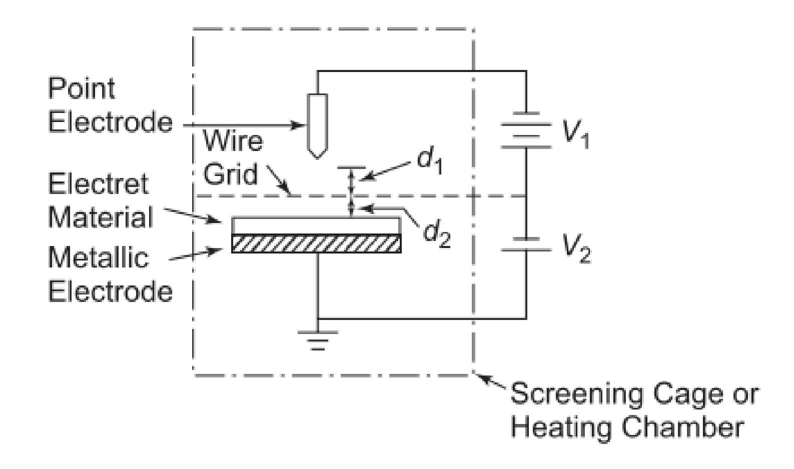
(LIQUID) CONTACT METHOD

Transfer of real charges into the material, by a conductive contact. This can be made at large scale down to the nanoscale (AFM)



The advantage of the conductive liquid is in the possibility to move the metallic contact all over a large surface

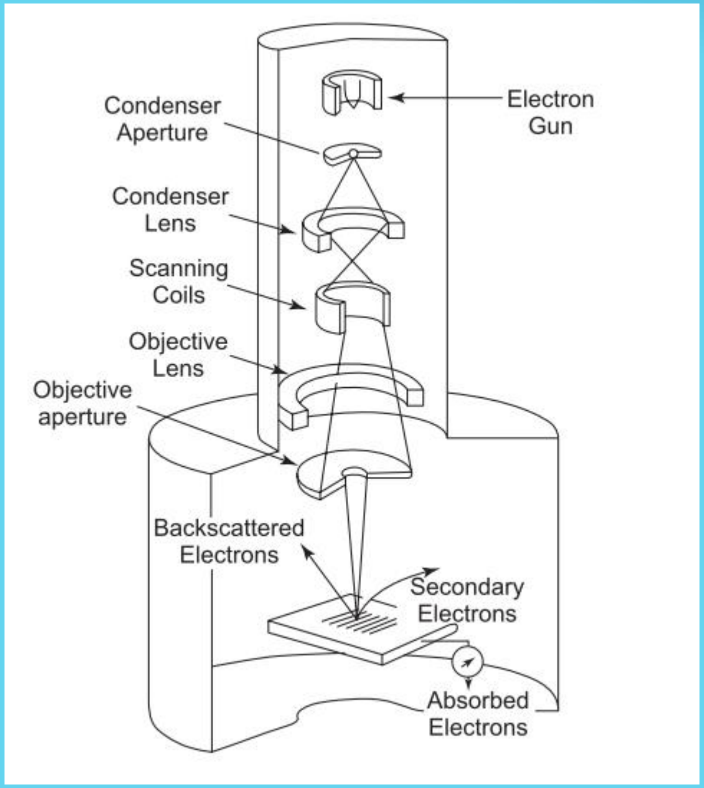
CORONA DISCHARGE



The bottom electrode is a vacuum-deposited metallic film on the material surface, and the top forming metallic electrode is usually made of a metallic wire

Around the point electrode it is possible to exceed
the breakdown strength of the air in a region of a few millimeters.
The so formed ions/free electrons can be accelerated toward the grid
and so be implanted in the target dielectric material

ELECTRON BEAM METHOD

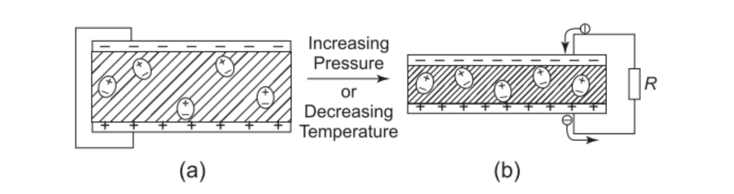


It is possible to inject/extract real charges (electrons) into the electret by SEM

The energy of the electron beam (<50 keV) should be controlled according to the structure and thickness of the material specimens to be used for forming electret

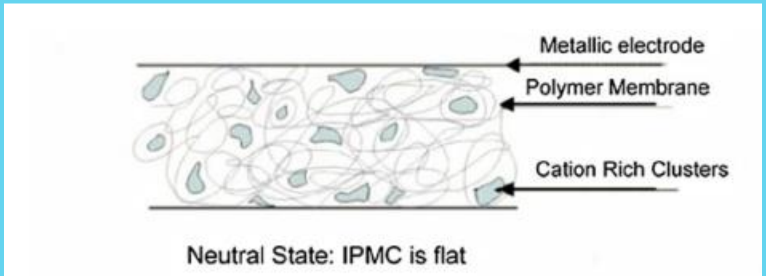
A similar mechanism can be used with ion implantation instrument

ELECTROACTIVE POLYMERS
(ARTIFICIAL MUSCLES)

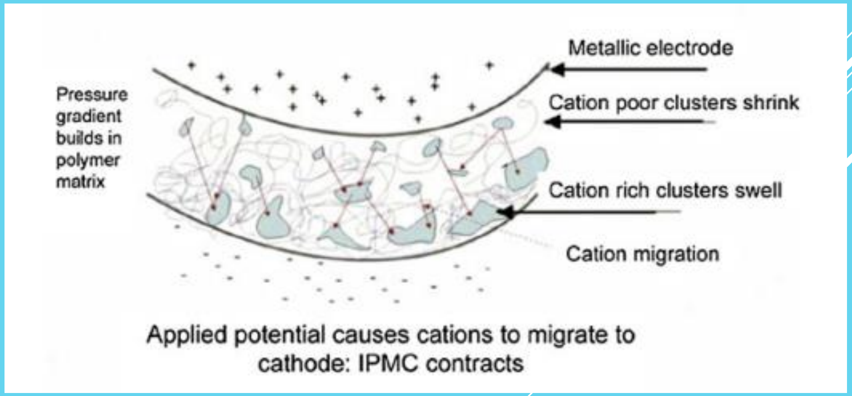


Dipolar «soft» electrets have interesting properties similar to piezolectric materials . They can react to external field changing shape or , viceversa, change their own dipolar field because of a change in shape

More complex structures can be engineered. Polymer are especially intersting.



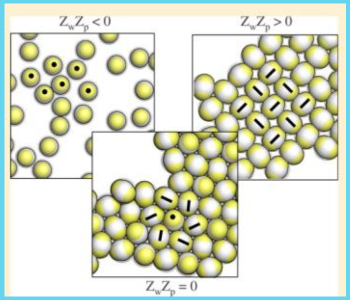
Neutral State: IPMC is flat



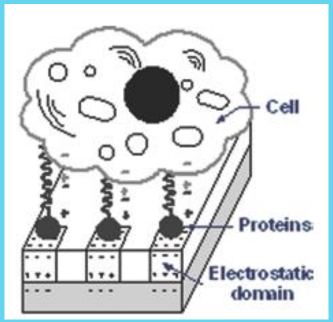
Applied potential causes cations to migrate to cathode: IPMC contracts

SIZE REDUCTION OF ELECTRETS

- **Miniaturization** of devices (EH, MP)
- The charge provides a further way to **functionalize** the nano/micro- material



Bianchi et al, Nano Lett. 2014, 14, 3412 − 3418



Tofail, Biological Interactions with Surface Charge in Biomaterials (RSC Publ.)

Drawbacks

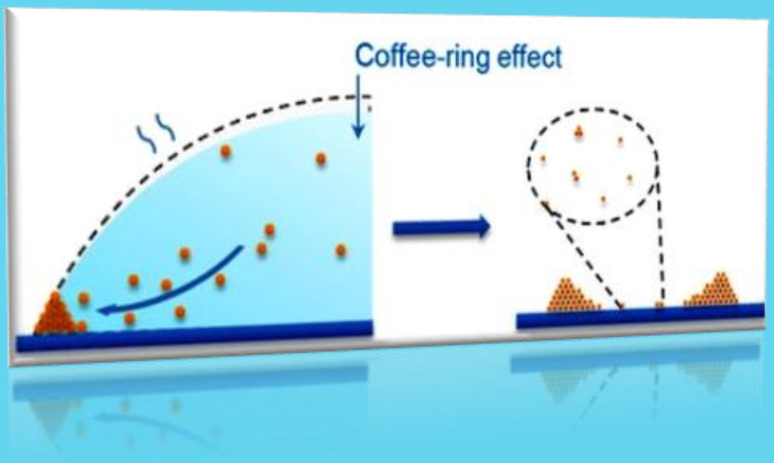
Stability of charging (surface vs space)
Control of charging

But also dynamic applications

Electro-Mechanical resonators

SAMPLES

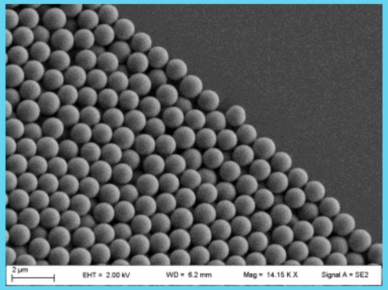
- SiO_2 particles (0.5 e 1 µm) deposited by drop casting on a polished copper substrate

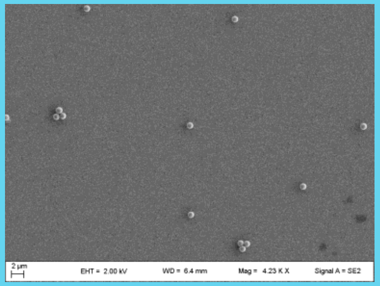


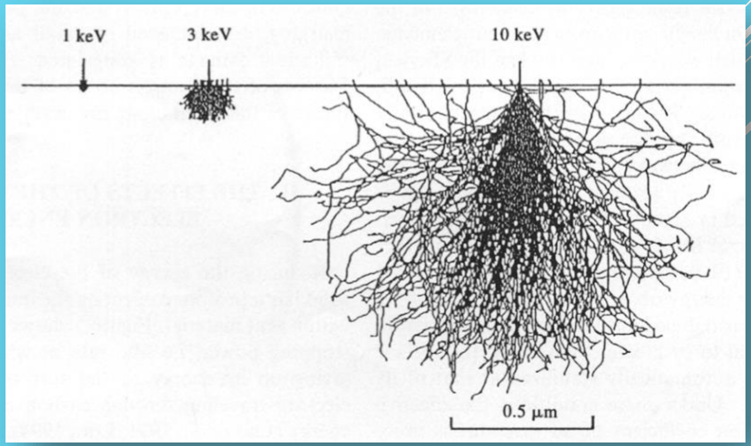
Fabrication by SEM

1) ***High lateral resolution (5 nm at 20 keV)***
2) ***Energy dependent penetration***

$$R = (76/\rho)E_0^{1.67}$$







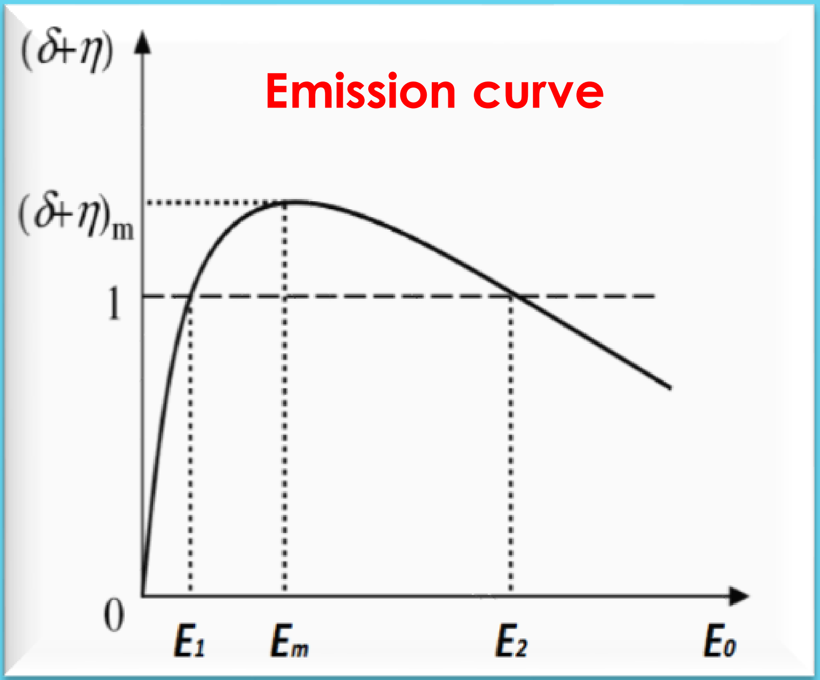
CHARGING MECHANISM

Total Yield Approach

$$\frac{\partial Q}{\partial t} = \left(1-\sigma(E_0)\right)\cdot I_B - I_L$$

1) **Crossover energies** (E_1 e E_2)

2) **Three chraging region: (σ>1 e σ<1)**



Charge effect:
$E_L = E_0 - eV_s$

Small size material:
1) Leakage current I_L can be significant

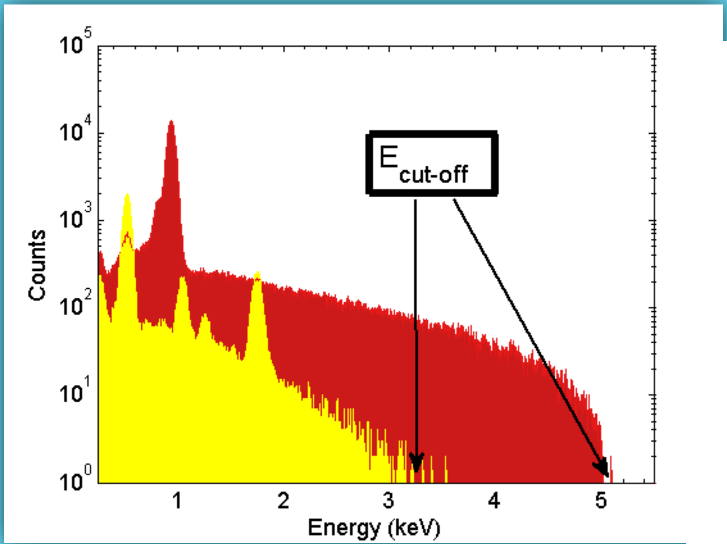
2) Surface potential V_S up to 200-300 V

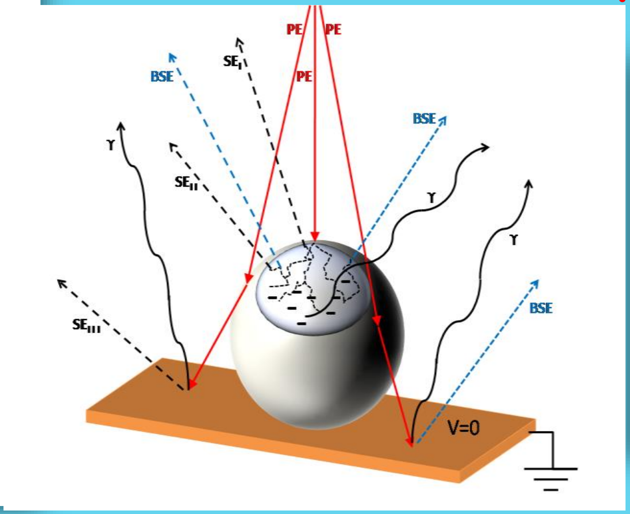
DUANE-HUNT LIMIT SHIFT

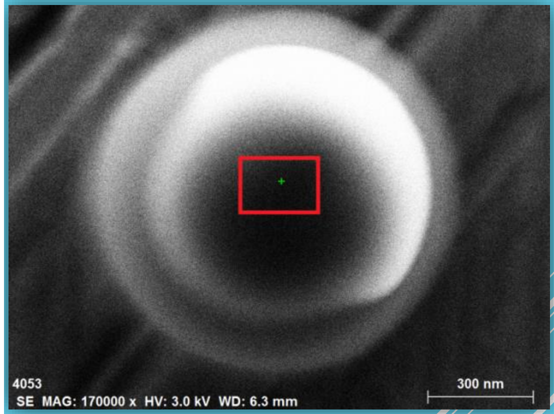
$E_L = E_0 - eV_s$

Bremsstrahlung x-ray spectrum

$$V_S = \frac{E_0 - E_{cut-off}}{e}$$





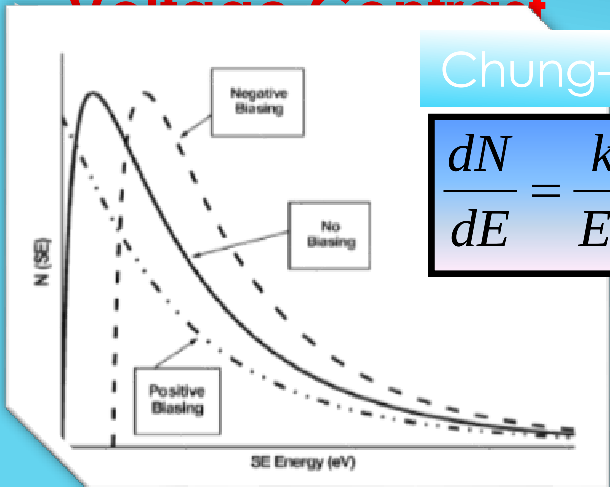


$\eta(\pi/2) \rightarrow 1$

$$V_S < 2R \cdot r.d. \approx 350V \Rightarrow Q \approx 10^5 e^-$$

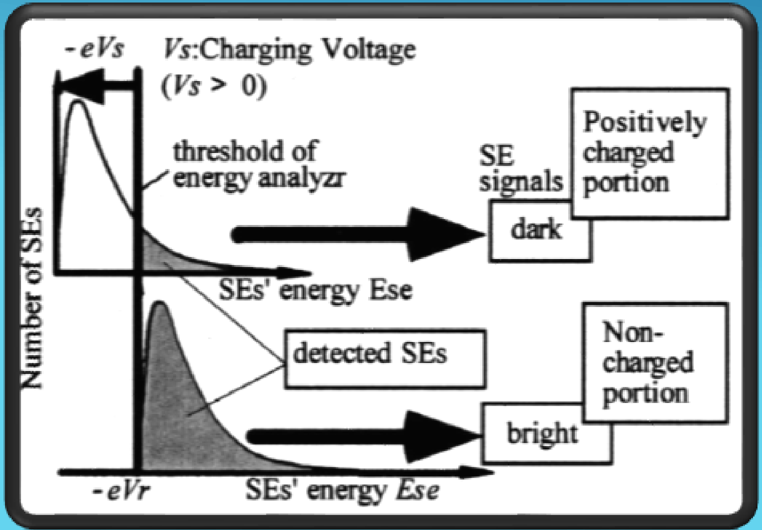
ELECTRONIC SPECTROSCOPY

Voltage Contrast



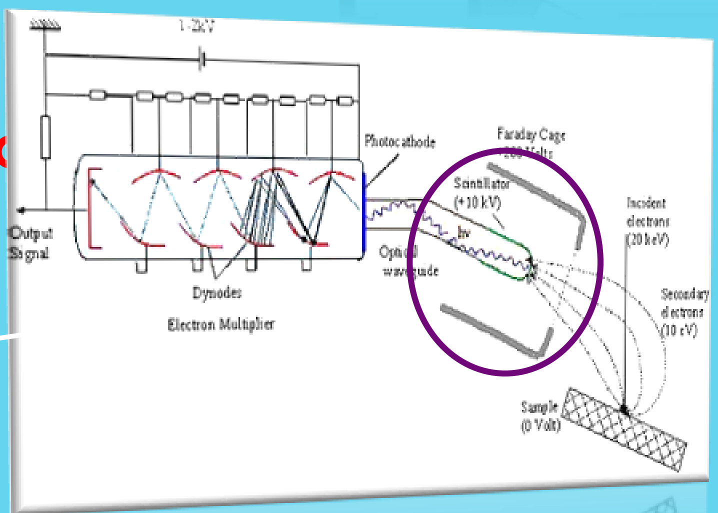
Chung-Everhart

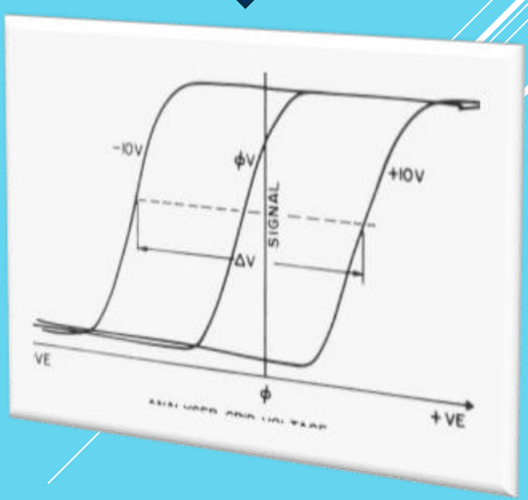
$$\frac{dN}{dE} = \frac{k}{E_0} \frac{E}{(E+\phi)^4}$$



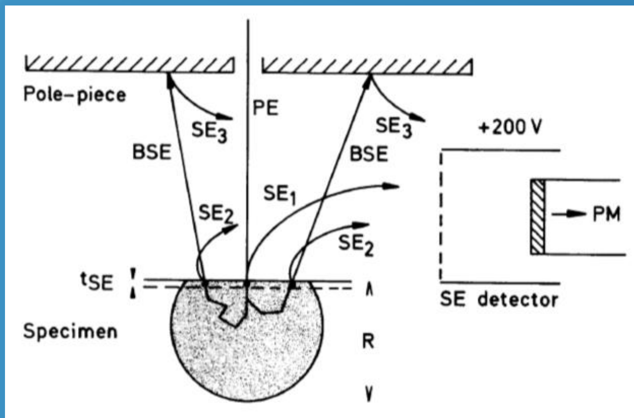
- Output depends o
potential

Everhart-Thornley detector (E-T)





ELECTRONIC SPECTROSCOPY



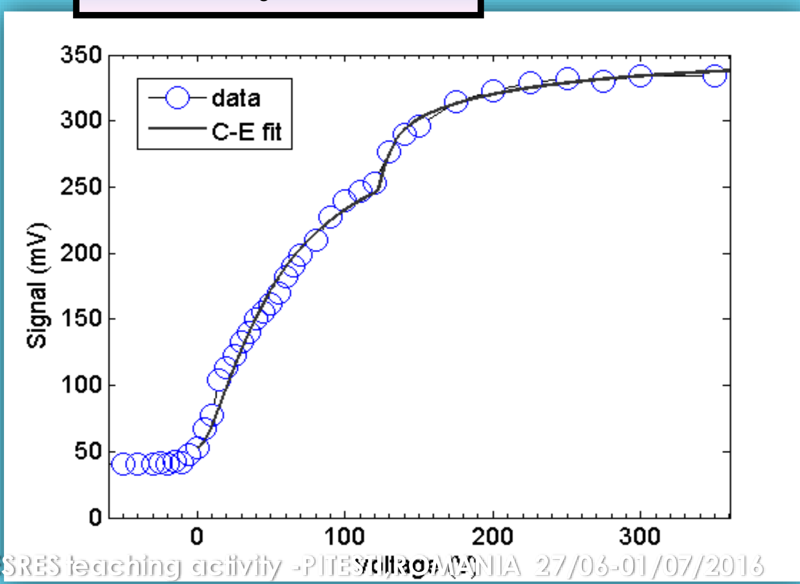
Strong background from the SEM chamber

Increasing Working Distance WD

Increasing Φ

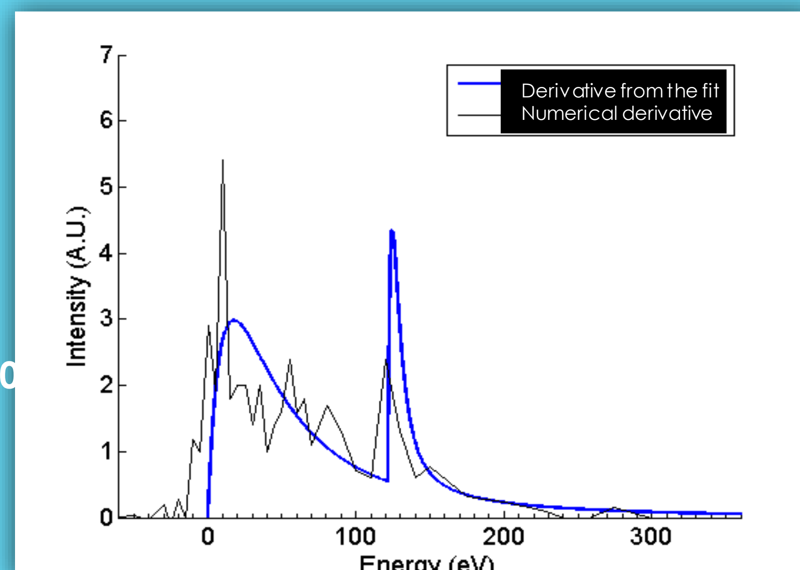
$$\frac{dN}{dE} = \frac{k}{E_0}\frac{E}{(E+\phi)^4}$$

$$S_{SE} = f_1(\delta \sec(\phi) + \delta\eta\beta) + f_2\delta_{ext} + f_3(d\eta / d\Omega)\Delta\Omega$$

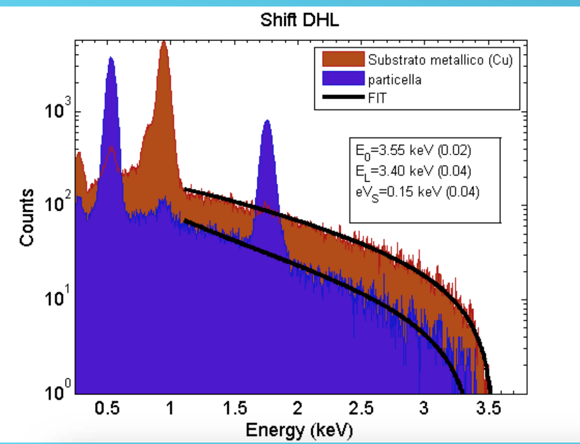


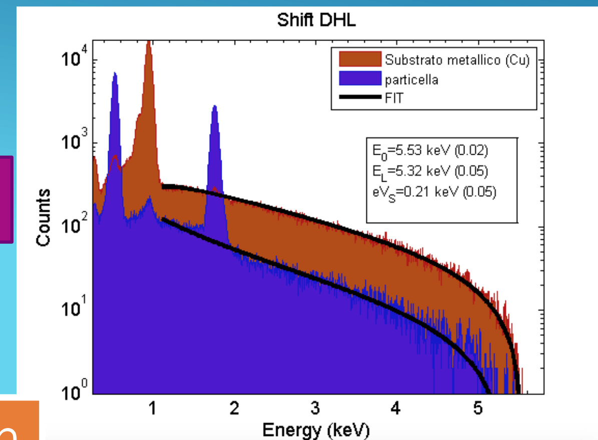
=1.8 keV
D=6.8mm
ag=150KX

=(121±19)V
prems=(130 ±50



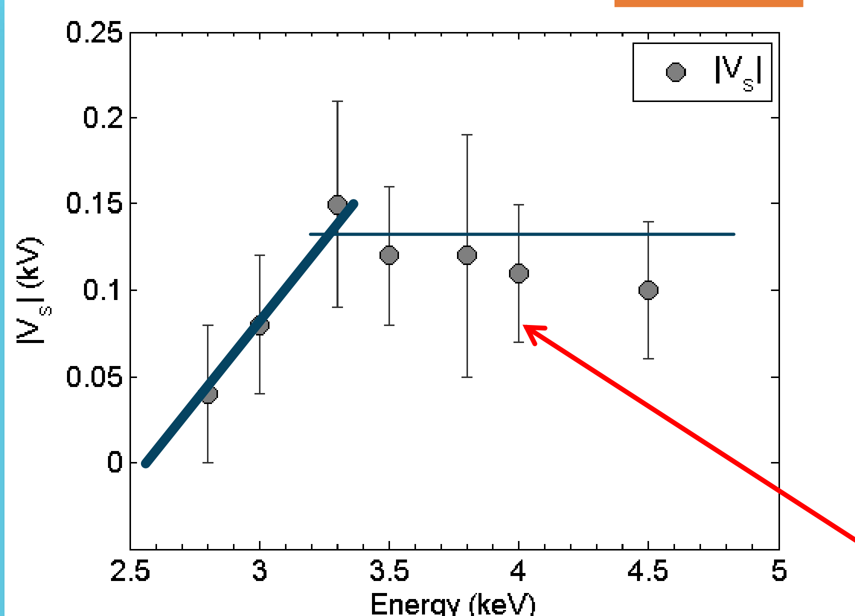
CHARGING VS ENERGY



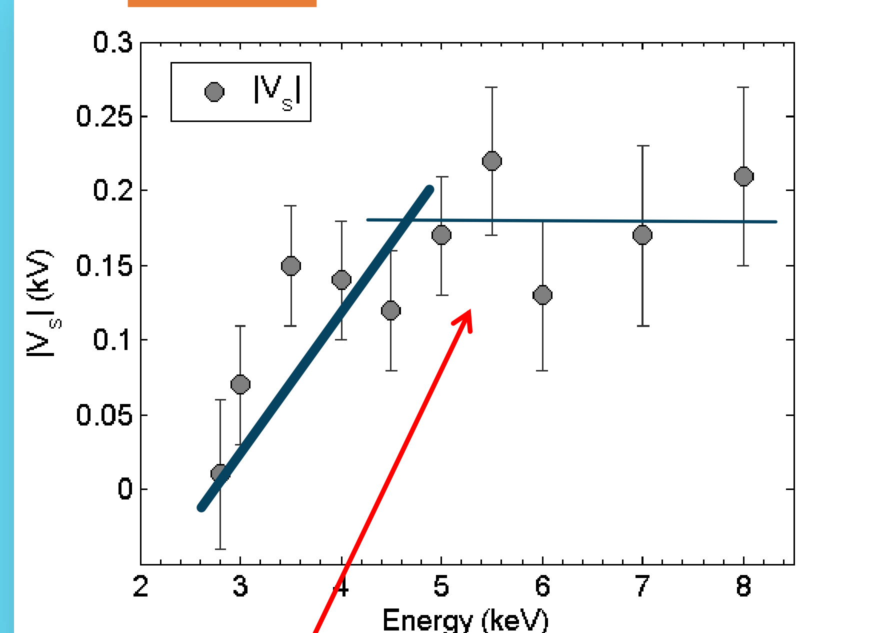


Initial linear increase

0.5 µm



1.0 µm



Potential saturation

CHARGE TEMPORAL EVOLUTION

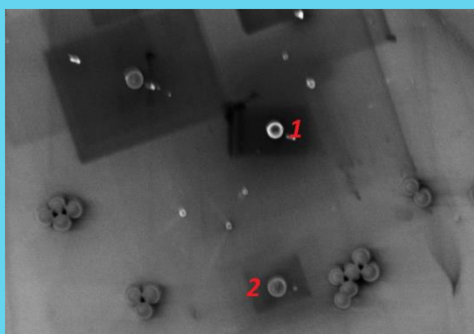
Samples in air

Monitoring charge by non penetrating electrons (0.5-1.5 keV)

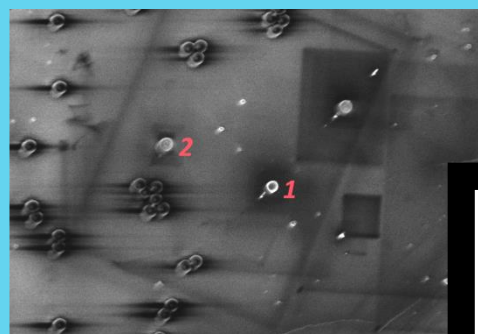
Observations by In Lens detector

→ More electrons detected from charged particles

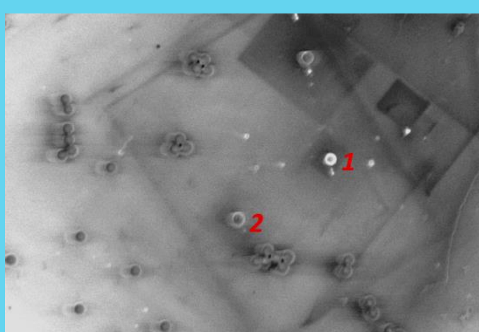
$$\Delta N(V_s) = N_{charged}(V_s) - N_{neutral}$$



13 days



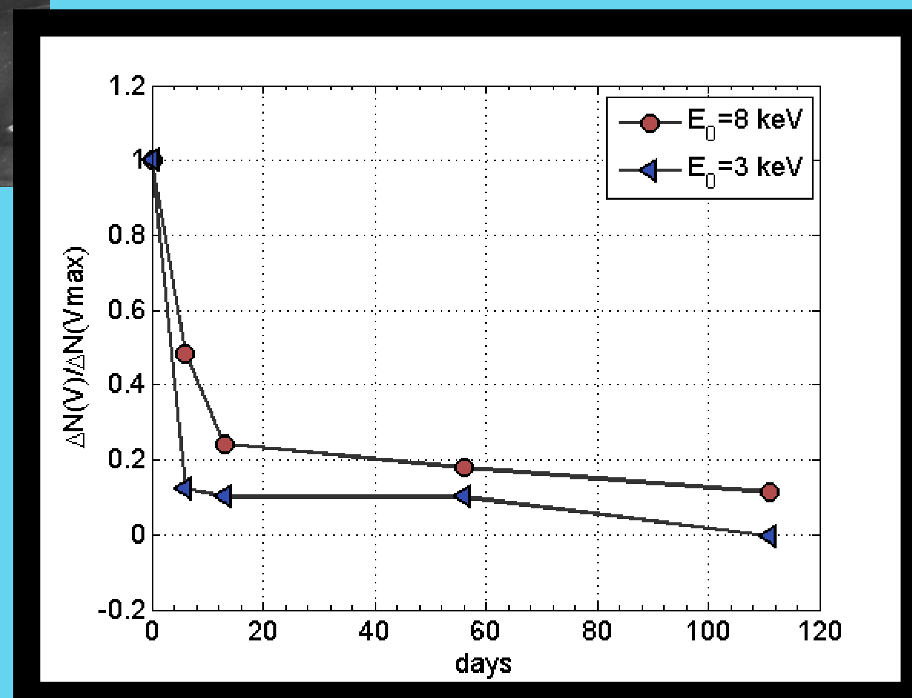
56 days



111 days

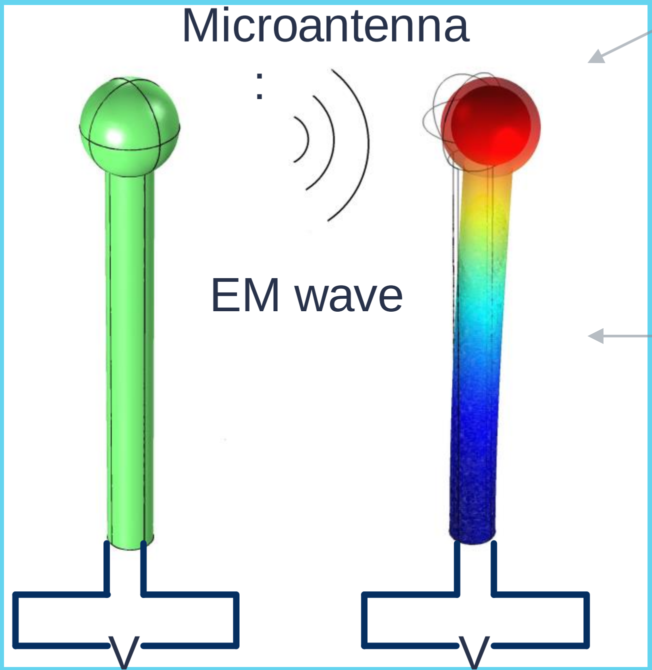
Two characteristic lifetimes:

1) ***fast*** (***surface***)
2) ***Slow*** (***space***)



A «MIXED» DEVICE

A useful commistion of the properties of electrets particles and piezoelectric rod



Electret particle

ZnO Microrod

The particle works as a (em)force collector.

The force impulse is trasnferred into electrical form by means of the piezo transduction

FINAL COMMENTS

- Device and materials are strongly correlated
- Electro active mterials are effective ways to harvest mechanical energy (noise vibration and direct forces)
- Piezoelectric properties depend on the asymmetric structure of the crystal
- Electrets are artificial materials which provide significant external electric field