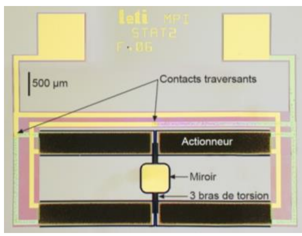
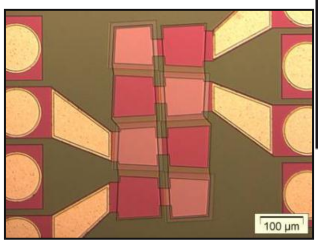
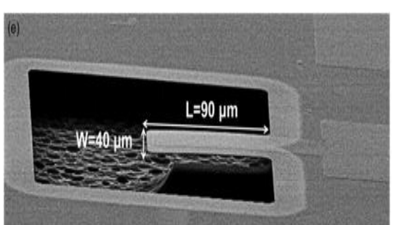
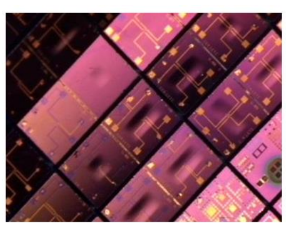
SENSORS AND ACTUATORS WITH FERROELECTRIC MATERIALS

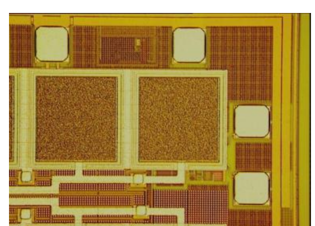




Emmanuel Defay







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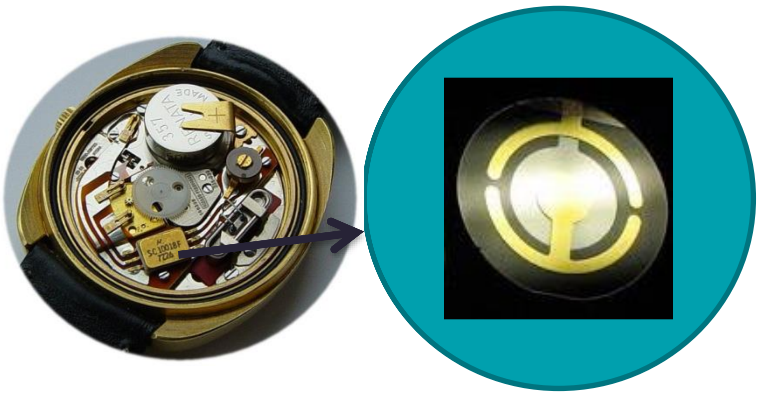
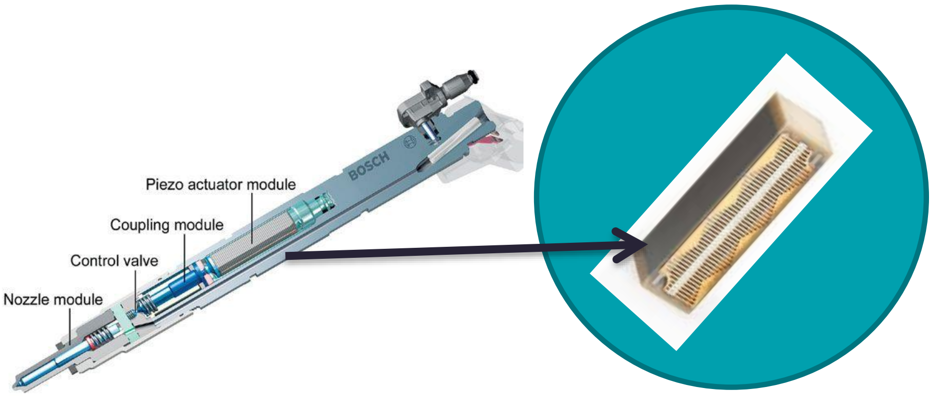
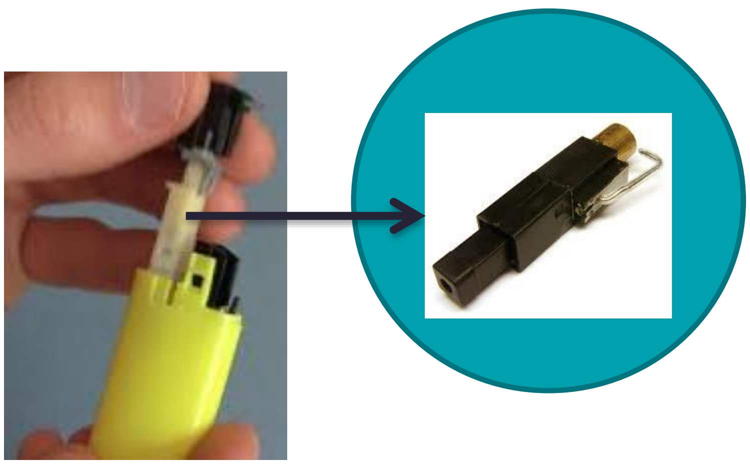
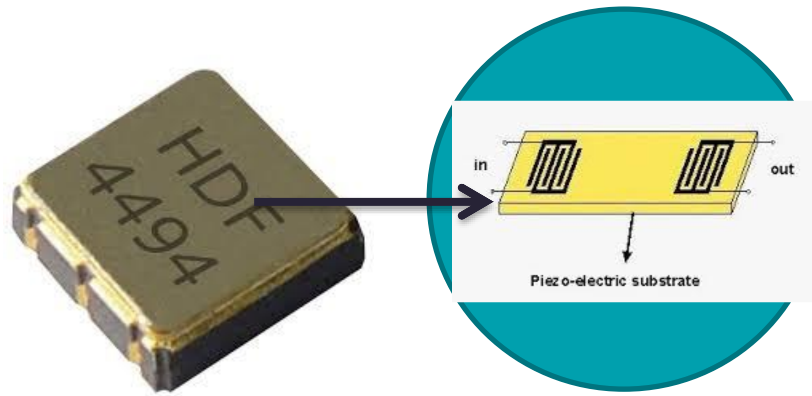
LIST

PIEZOELECTRIC DEVICES

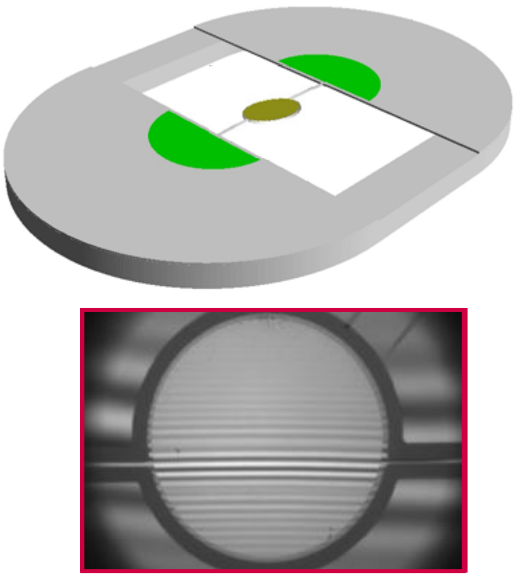




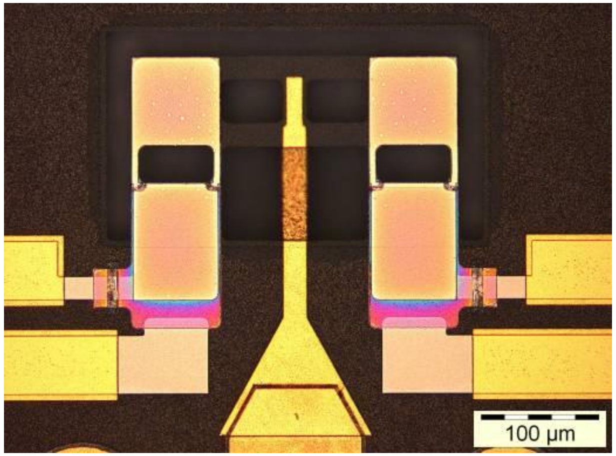




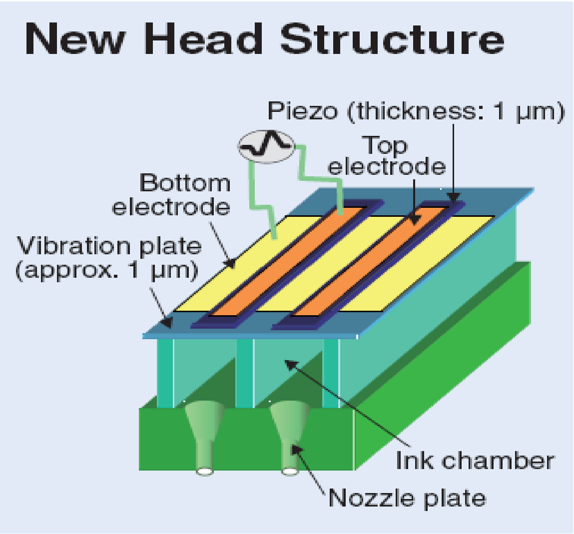
PIEZOELECTRIC DEVICES



Micro-mirror



RF MEMS Switches



Inkjet print-heads

FERROELECTRIC SENSORS AND ACTUATORS

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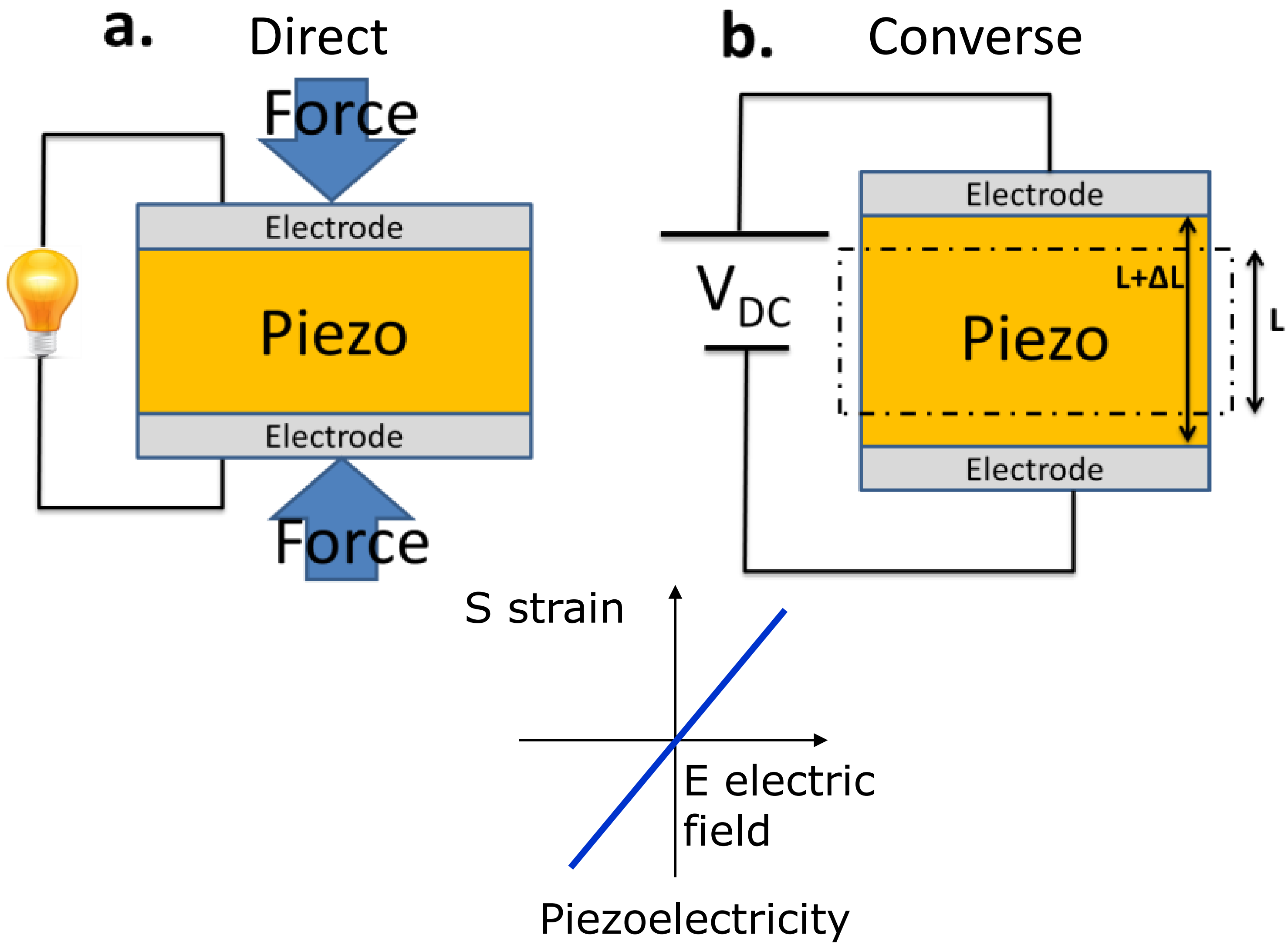
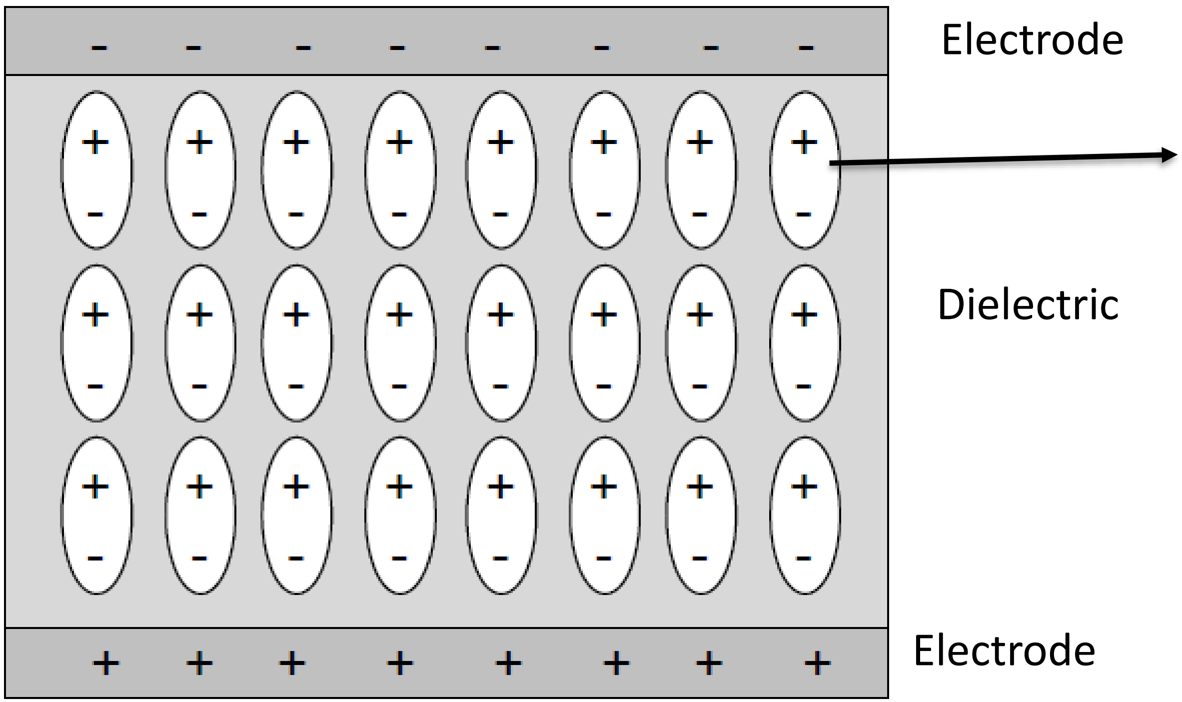
A materials approach

- Piezoelectricity and other effects
- Piezoelectric formalism
- Materials and depositions means
- Applications

Piezoelectricity



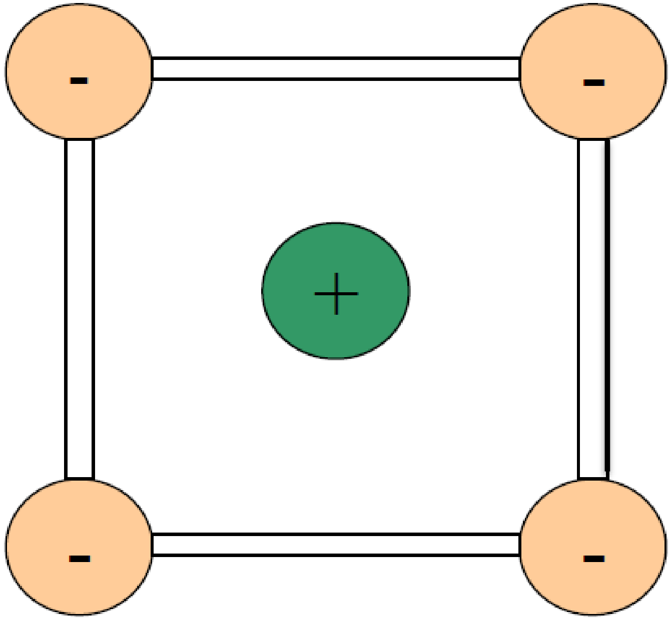
The dielectric effect

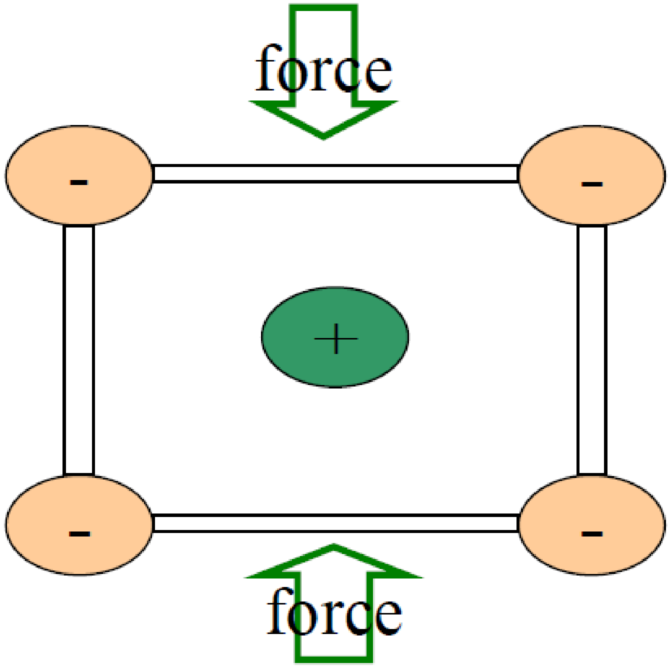


$$Q = CV$$

Q: electrical charge
V: voltage
C: capacitance

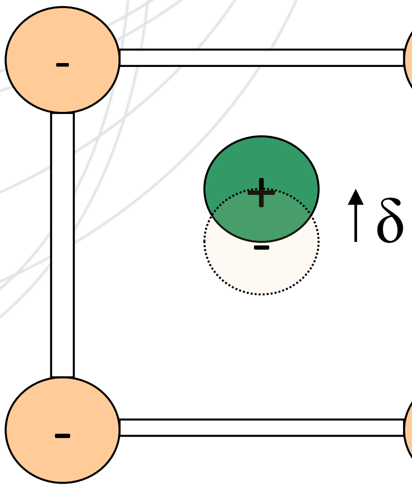
Non-piezoelectric dielectric



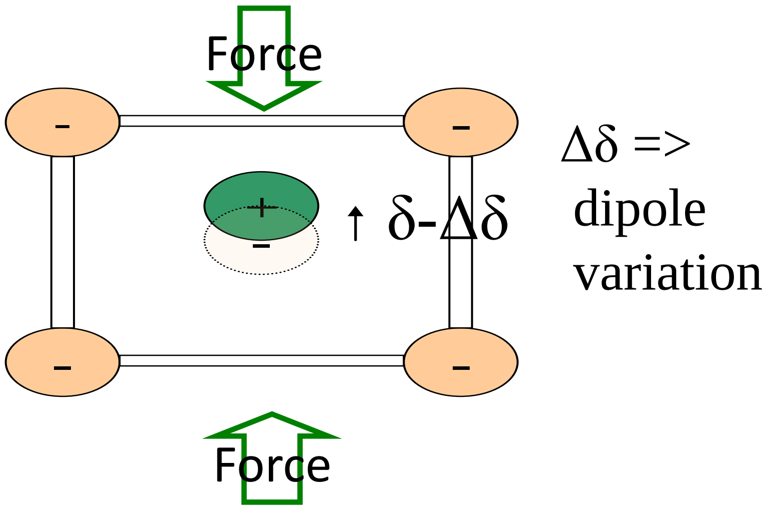


- When force is on, no dipole appears

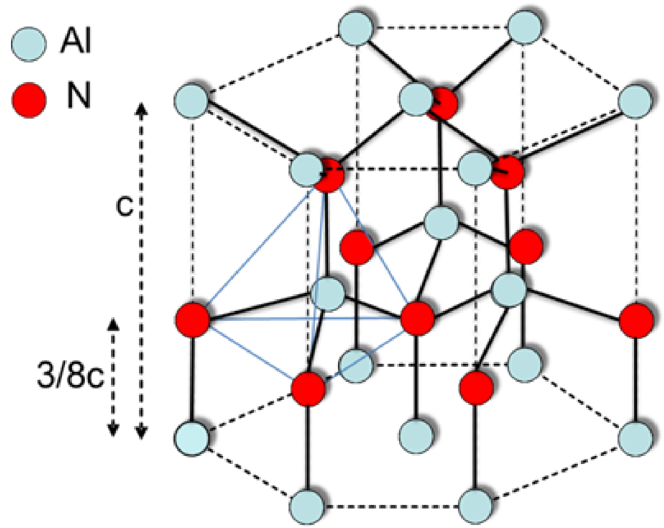
Piezoelectric (and pyroelectric)



Piezoelectric
Pyroelectric

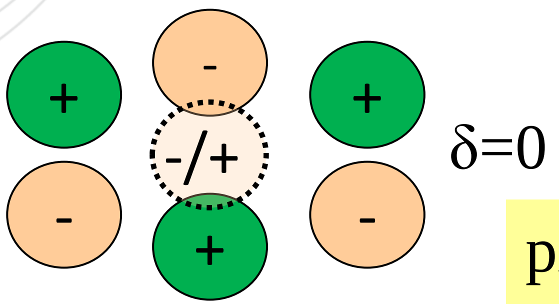


Example - AlN

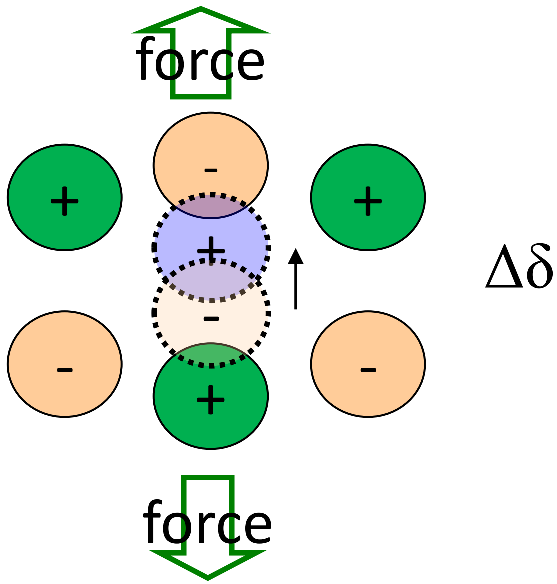


Piezoelectric (non pyroelectric)

Quartz: no dipolar moment at zero strain δ = 0

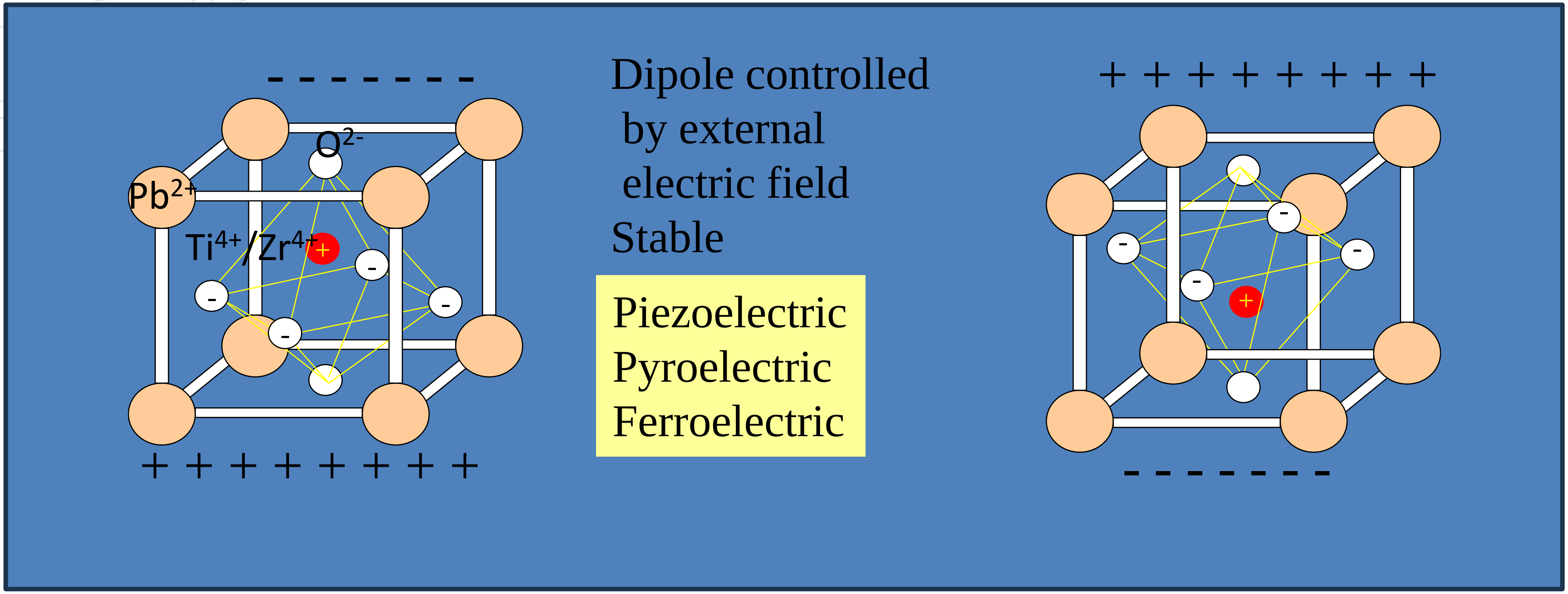


piezoelectric
non pyroelectric

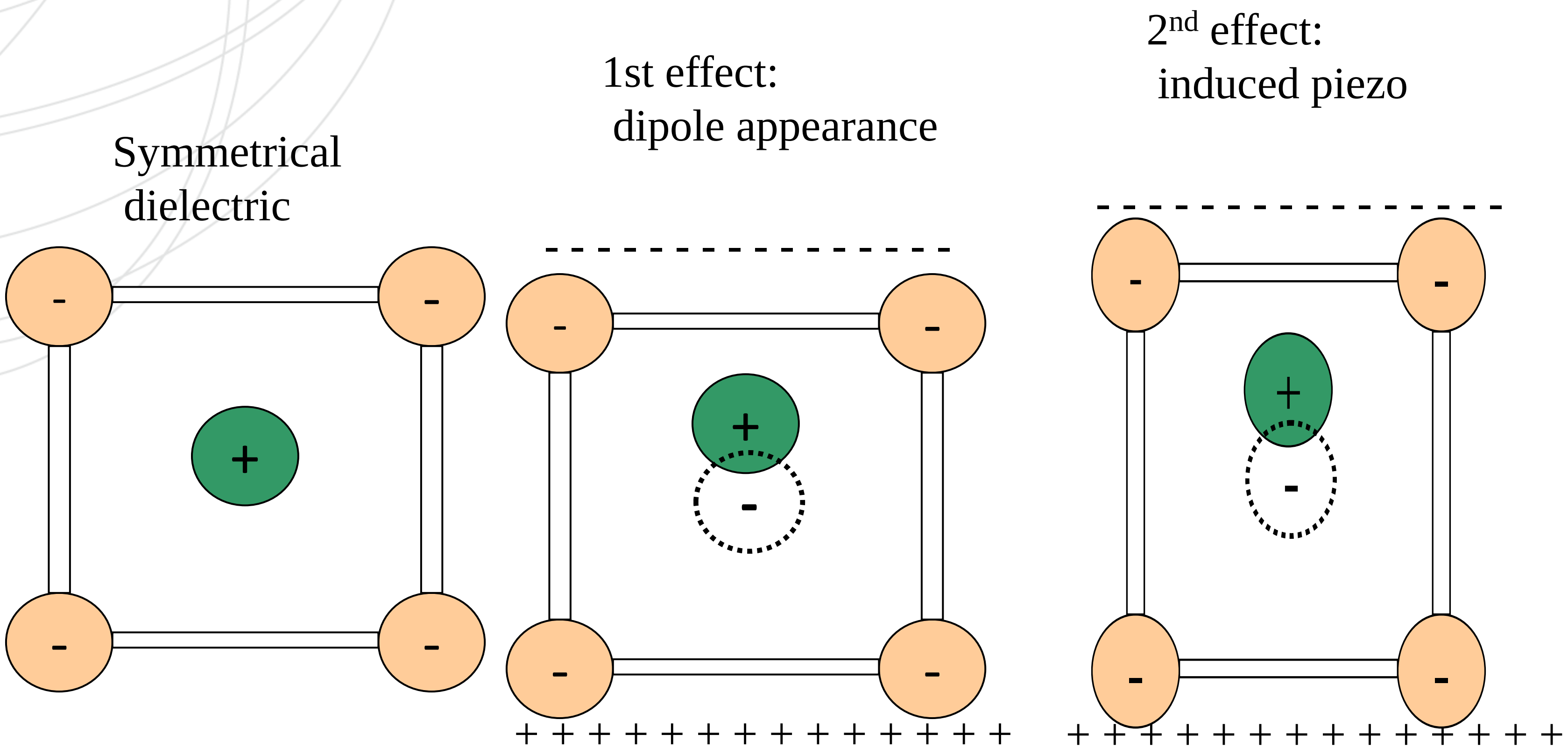


Piezoelectric (ferroelectric)

- Perovskite structure – Pb(Zr,Ti)O3



Electrostriction



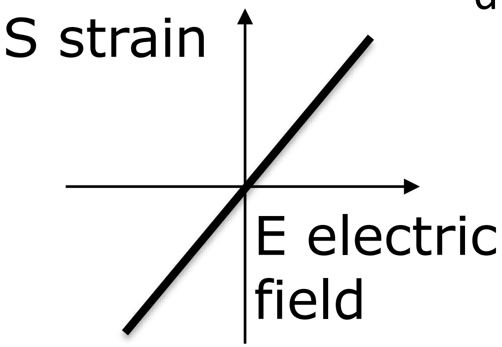
Quadratic effect

Electrostriction vs piezoelectricity

- Piezoelectricity

$S = dE$

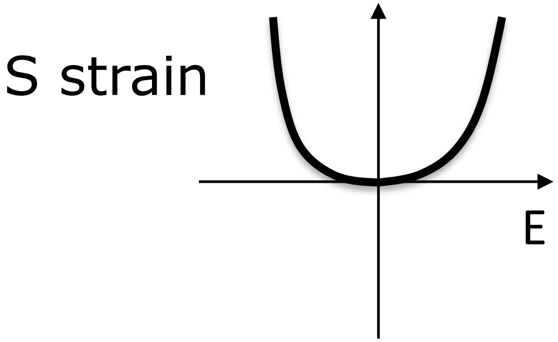
d - piezoelectric coefficient



- Electrostriction

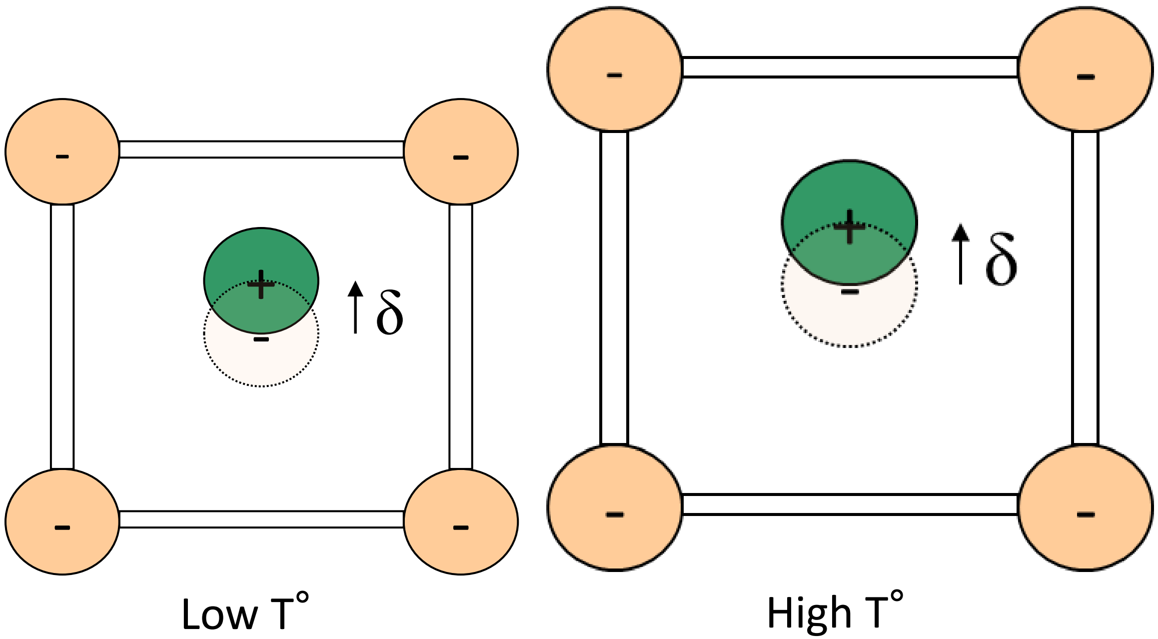
M - electrostrictive coefficient

$S = ME^2$



Pyroelectric effect

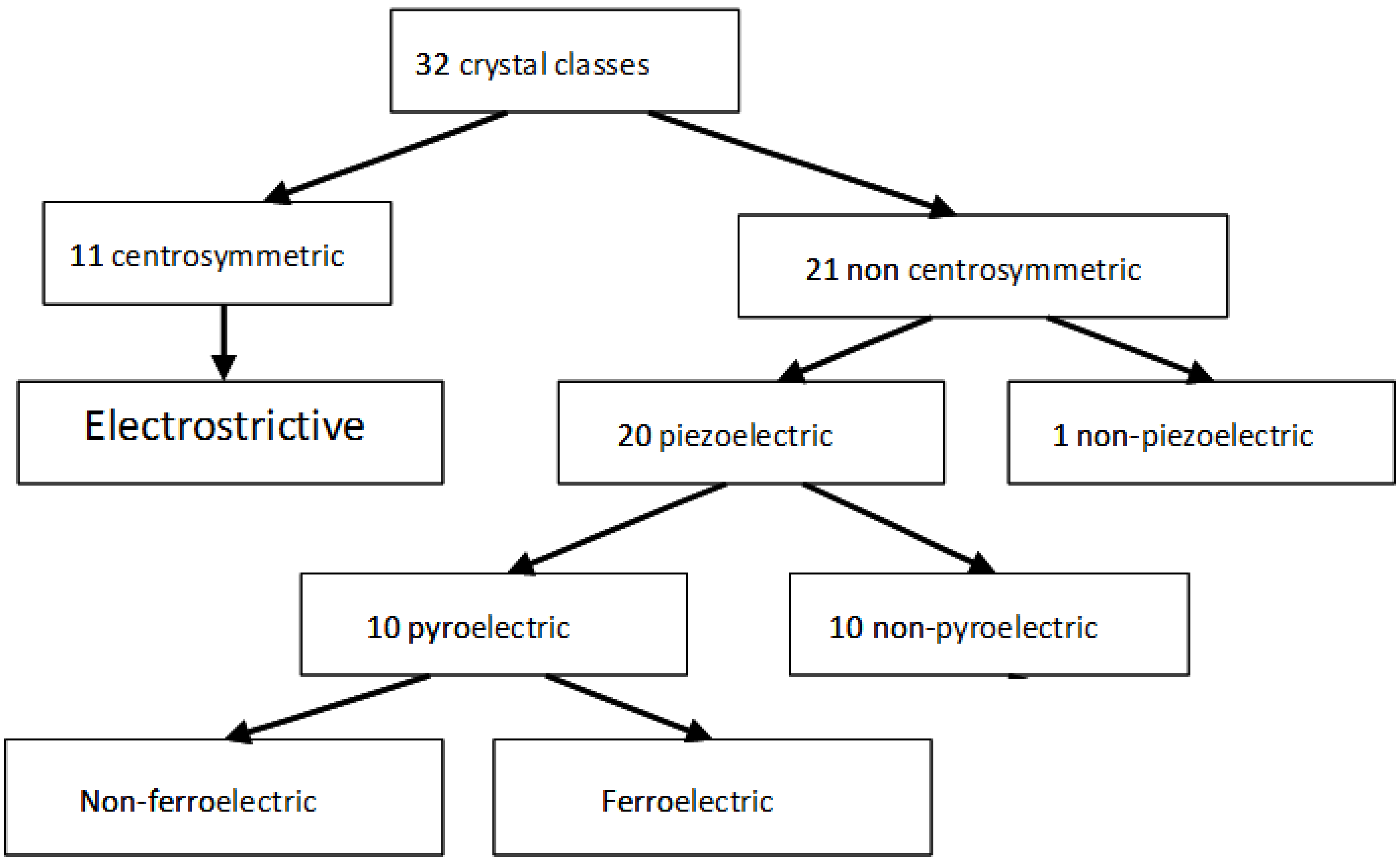
- Permanent spontaneous polarization δ
- Pyro, because δ changes with T°



$$\Delta Q = p\, A\, \Delta T$$

ΔQ: electrical charge variation
p: pyroelectric coefficient
A: electrodes area
ΔT: temperature variation

How to be piezoelectric



Thermodynamics for piezo

- Internal energy – state function ($\Delta U = \delta W + \delta Q$)

W: work Q: heat

- dU: total differential

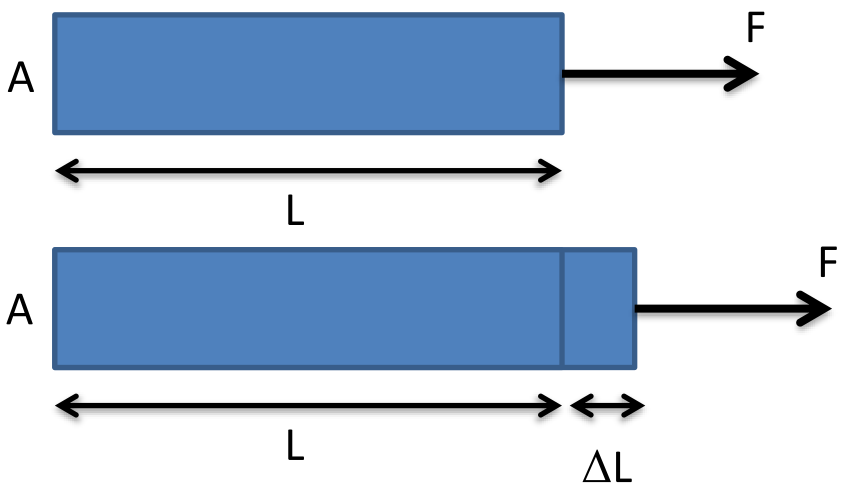
$$dU = \theta d\sigma + TdS + EdD$$

S: strain T: stress
D: electric displacement E: electric field
σ: entropy θ: temperature

- Intensive x d (extensive) in dU
- dU = 0 => equilibrium according to σ, S and D

Mechanical variables

- Strain $S = \Delta L/L$ (%)
- Stress $T = F/A$ (N/m^2 = Pa)
- L= length
- F = force
- A = area

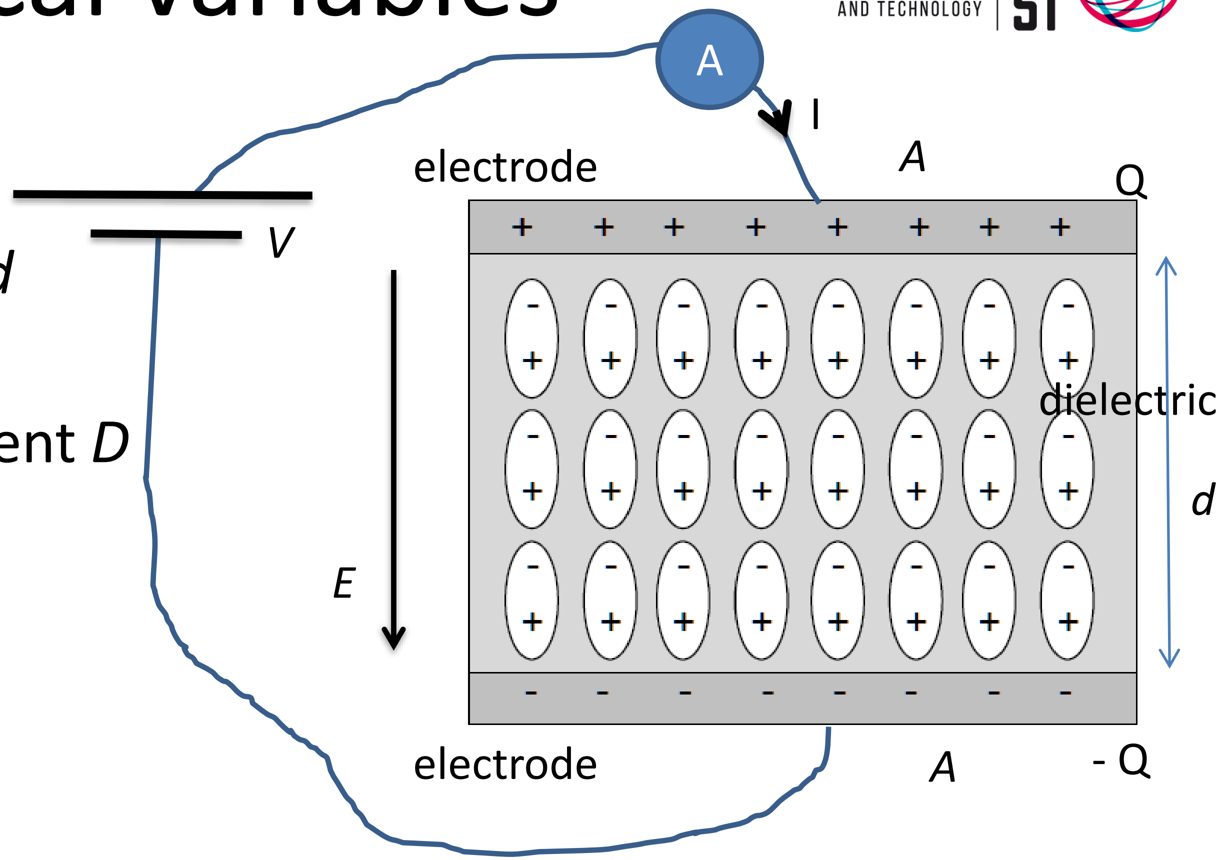


- Independent of sample size

- Hooke's law : F = k x (k: spring constant, x: extension)
- $T = c\ S$ (c : stiffness)

Electrical variables

- Voltage V
- Electric field $E = -V/d$
- Current I
- Electrical displacement D
- Electrode area A
- Q = D A
- I = dQ/dt
- Q = C V
- C = capacitance
- $C = \varepsilon_0 \varepsilon_r A/d$
- Electrostatic equation : $D = \varepsilon_0 \varepsilon_r E$



Legendre transform

- Other free energies to describe other equilibrium
  - Constant θ rather than constant σ
  - Constant *E* rather than constant *D*
  - Constant *T* rather than constant *S*
- Adding an energy term to internal energy: Legendre transform

- Helmholtz free energy $F = A = U - \sigma\theta$
- Gibbs energy: $G = U - \sigma\theta - TS - ED$
- Gibbs elastic energy: $G_1 = U - \sigma\theta - TS$
- Gibbs electric energy: $G_2 = U - \sigma\theta - ED$

Piezoelectric formalism

Internal energy U

$$dU = TdS + EdD$$

T,E – intensive
S,D – extensive
d - differential

S: strain T: stress

D: electric displacement E: electric field

Free energy G (if T and E main variables) – Legendre transform

$$G = U - TS - ED$$

$$dG = dU - TdS - SdT - EdD - DdE$$

$$dG = - SdT - DdE$$

→

Linear hypothesis
S depends on T
D depends on E

It means quadratic terms in energy + 1 coupling term (piezo)

$$G - G_0 = -\frac{1}{2} s^E T^2 - \frac{1}{2} \varepsilon^T E^2 - dTE$$

s^E material compliance at constant *E*
ε^T material dielectric constant at constant T
d piezoelectric coefficient

Piezoelectric formalism

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$dG = -SdT - DdE$

$$G - G_0 = -\frac{1}{2}s^E T^2 - \frac{1}{2}\varepsilon^T E^2 - dTE$$

$$\left.\frac{\partial G}{\partial T}\right)_E = -S \qquad \left.\frac{\partial G}{\partial E}\right)_T = -D$$

$$S = s^E T + dE$$
$$D = \varepsilon^T E + dT$$

S: strain
T: stress
E: electric field
D: electric displacement
s: compliance
ε: dielectric constant
d: piezoelectric coef

Three other possible formalisms (by using other free energies)

$$T = c^E S - eE \qquad S = s^D T + gD \qquad T = c^D S - hD$$
$$D = \varepsilon^S E + eS \qquad E = \beta^T D - gT \qquad E = \beta^S D - hS$$

The electromechanical coupling factor k

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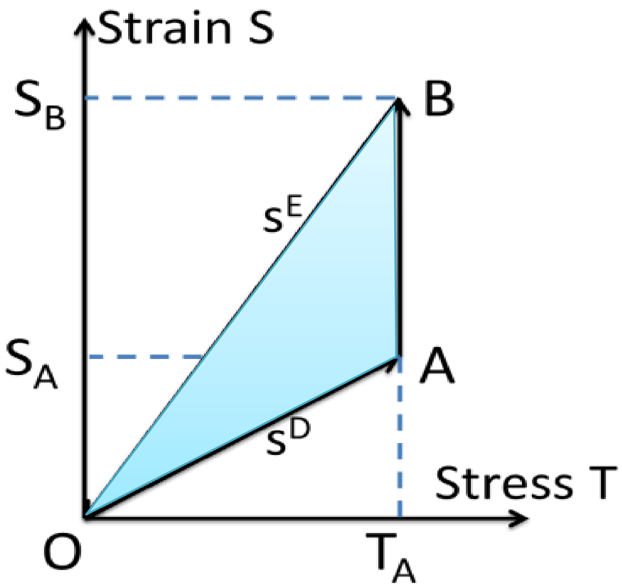
How to convert mechanical energy in electricity ?



Harvesting cycle

1. OA – stress piezo @ open circuit up to T_A
2. AB – Short circuit piezo @ T_A- harvesting
3. BO – release stress

$$Work_{OA} = \frac{1}{2} s^D T_A^2 \qquad W_{ork\,OB} = \frac{1}{2} s^E T_A^2$$

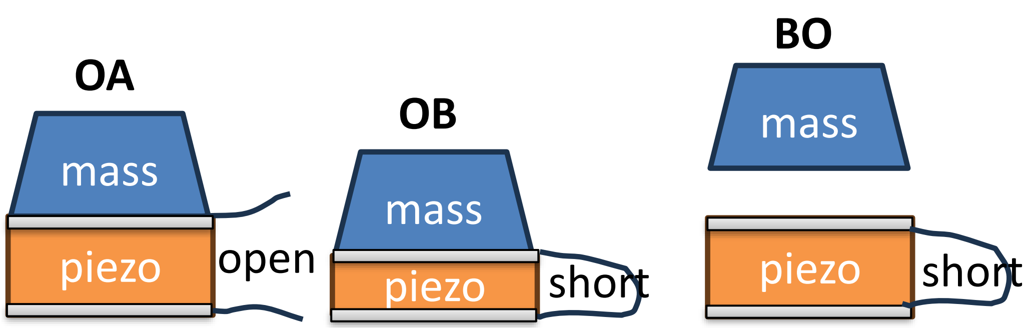
$$Work_{harvested} = Work_{OB} - Work_{OA}$$

s^D and s^E – piezo compliances at constant *D* and constant *E* ($s^D < s^E$)

$$k^2 = \frac{W_{OB} - W_{OA}}{W_{OB}} = 1 - \frac{W_{OA}}{W_{OB}}$$

$$k^2 = 1 - \frac{s^D}{s^E}$$

$$k^2 = \frac{d^2}{s^E \varepsilon^T}$$



k^2 can reach 85 % !

Ferroelectric formalism

- Laudau theory of phase transition
- Free energy description, as simple as possible
- Hypothesis
  - Free energy is the same between phases
  - Identify the order parameter that changes during a phase transition

Ferroelectric formalism

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- Order parameter - Polarisation
  - zero when cubic
  - Non-zero in tetragonal / rhombohedral phases
- Laudau free energy G_1, with only even terms in P

$$G_1(P,X,T) = \underbrace{\tfrac{1}{2} a (\theta - \theta_C) P^2 + \tfrac{1}{4} bP^4}_{\text{Electric terms}} \underbrace{- \tfrac{1}{2} s T^2}_{\text{Mechanical}} \underbrace{- Q P^2 T}_{\text{Coupling}}$$

G_1: Gibbs elastic energy
$dU = EdD + TdS$
$D \sim P$
$G_1(P,T)=U-ST$
$dG_1 = EdD - SdT$

Ferroelectric formalism

$$G_1(P,X,T) = \tfrac{1}{2}\, a\, (\theta - \theta_C)\, P^2 + \tfrac{1}{4}\, bP^4 - \tfrac{1}{2}\, s\, T^2 - Q\, P^2\, T$$

$dG_1 = EdP - SdT$

$$\left(\frac{\partial G_1}{\partial T}\right)_P = -S$$

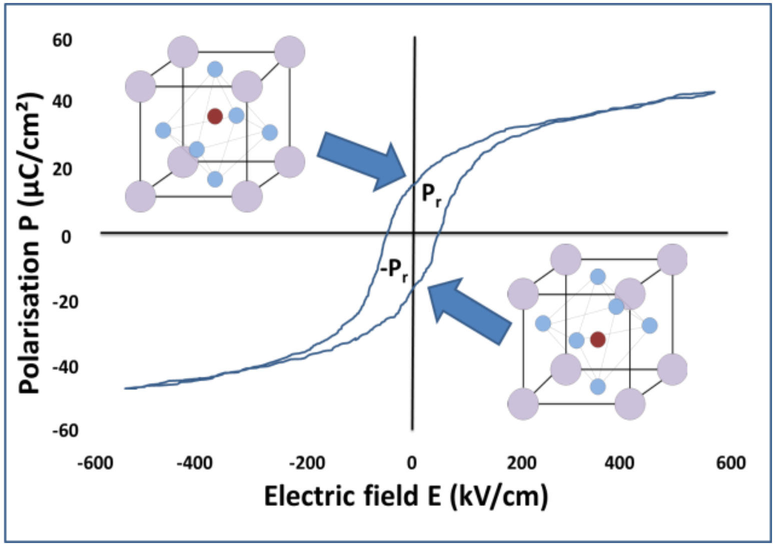
$$\left(\frac{\partial G_1}{\partial T}\right)_P = -S = -sT - QP^2$$

$$S = sT + QP^2$$

Pure piezo

$$S = s^E T + dE$$

Let's dig deeper



$$P = P_r + \varepsilon_0 \varepsilon_r E$$

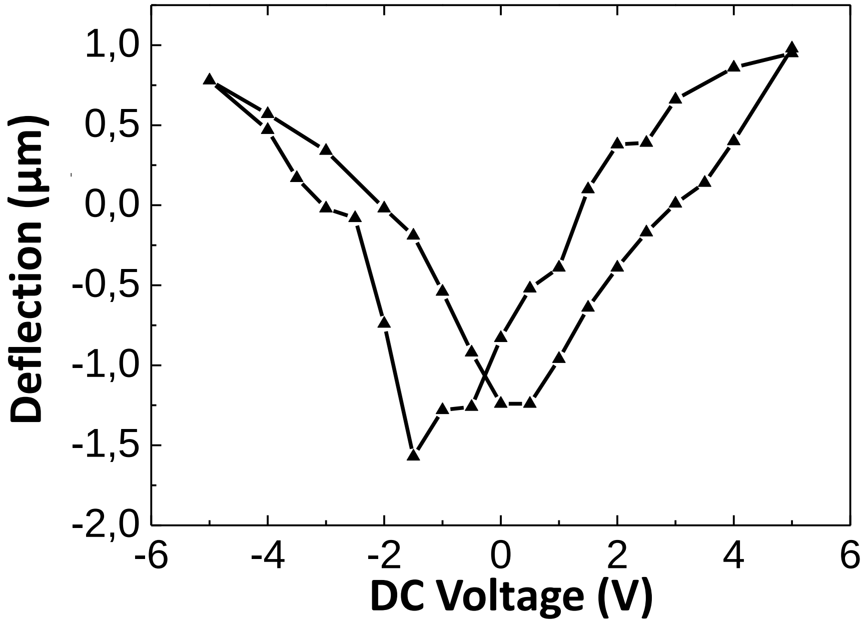
$$S = sT + Q(P_r + \varepsilon_0 \varepsilon_r E)^2$$

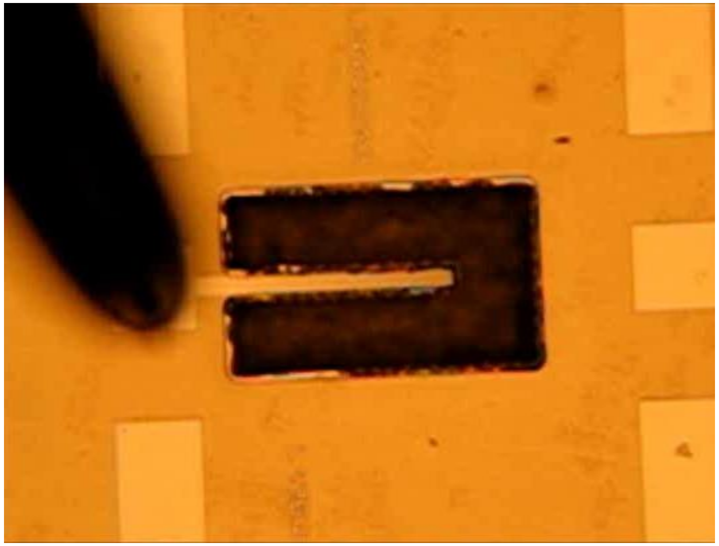
$$S = sT + QP_r^2 + \underbrace{2QP_r \varepsilon_0 \varepsilon_r}_{d \text{ piezo}} E + \ \ldots$$

$$d = 2QP_r \varepsilon_0 \varepsilon_r$$

Ferroelectric actuator

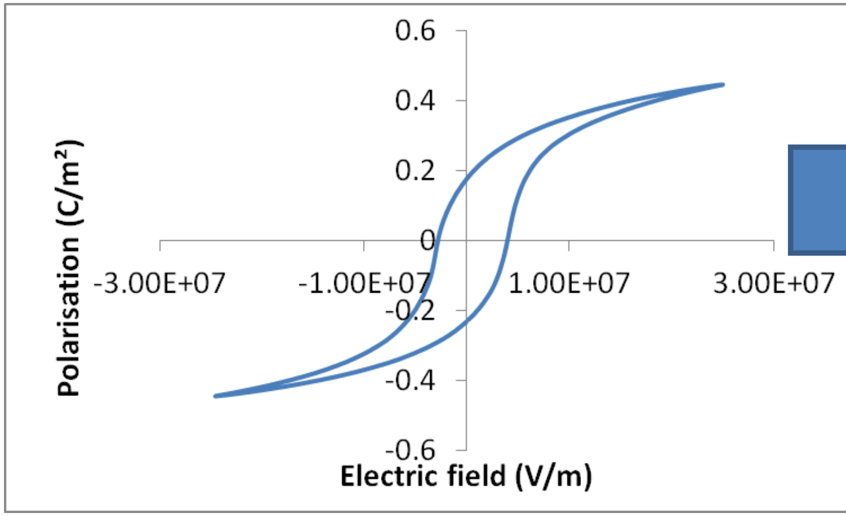
- PZT : if field < coercive field => linear
- If field > coercive field: one-way deflection !



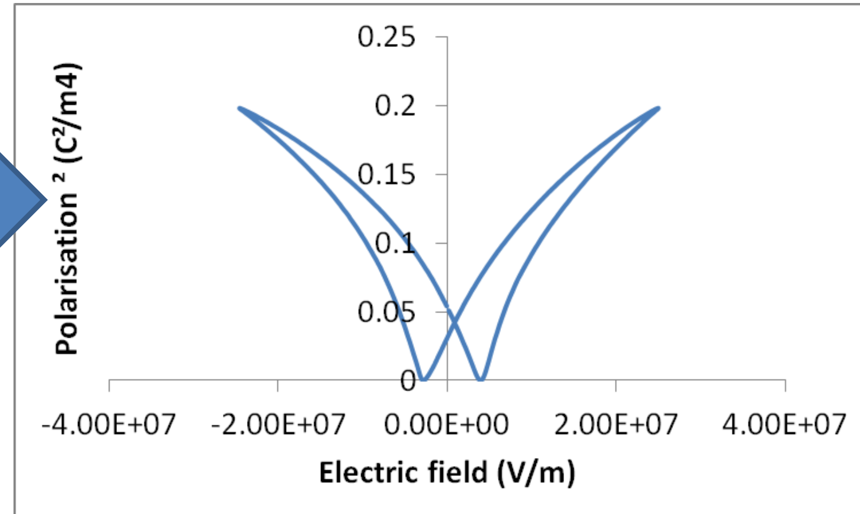


Ferroelectric actuator

- Electrostrition : strain S = Q (Polarisation P)²
- P = f(field E)



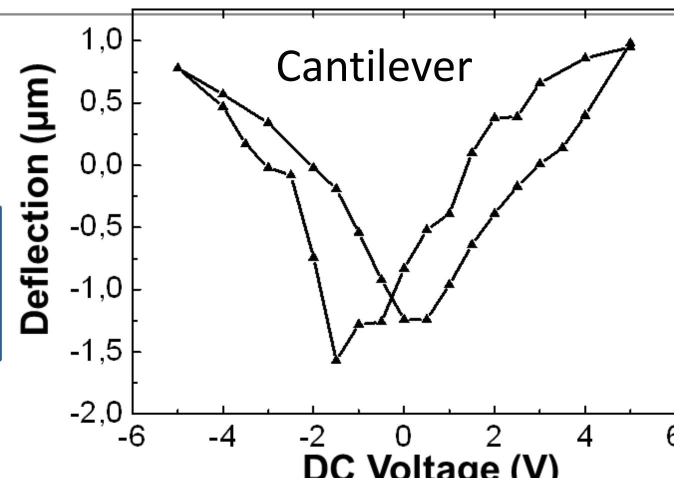
P²



Cantilever made of PZT

Deflection explained by electrostriction

S=QP²
Q=cst



PIEZOELECTRIC MATERIALS (FILMS)

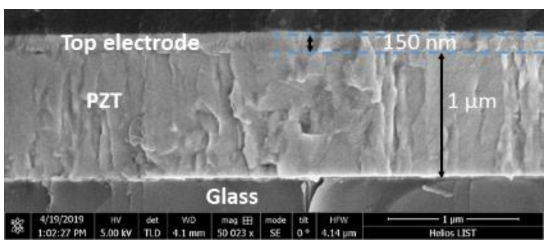
MATERIALS

Lead-based and lead free ferroelectric piezoelectric films

Lead zirconate titanate films (PZT)

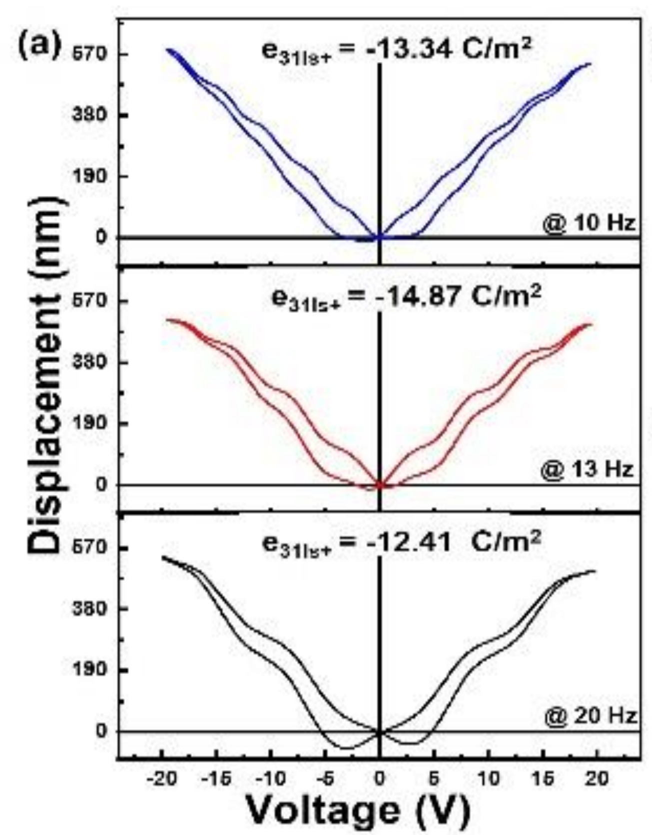
Grown by sol gel spin coating and inkjet printing

e31,eff = - 18 C/m²



L Song, S Glinsek, E Defay, Applied Physics Reviews 8 (4), 041315 (2021)

Best alternative to PZT – (K,Na)NbO_3 (KNN)

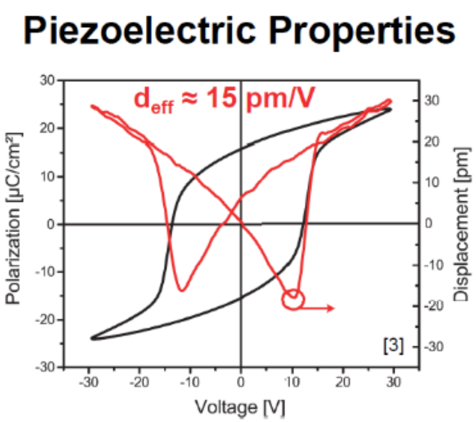


MATERIALS

Non perovskite lead free piezoelectric materials

Hafnia via sol gel

1 µm-thick films wit :
15 pm / V (> AlN)



T. Schenk et al., Applied Physics Letters 118 (16), 162902 (2021)

AlN via sputtering

d33 = 5 pm/V

Sc-AlN via sputtering

d33 = 25 pm/V

Akiyama et al., Adv. Mater. 2009, 21, 593

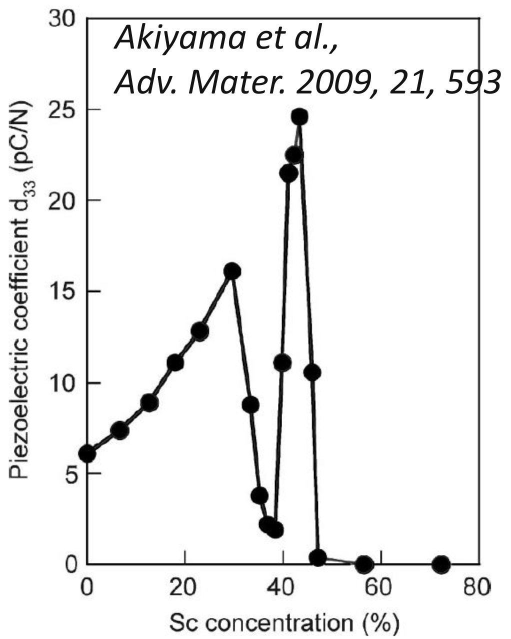


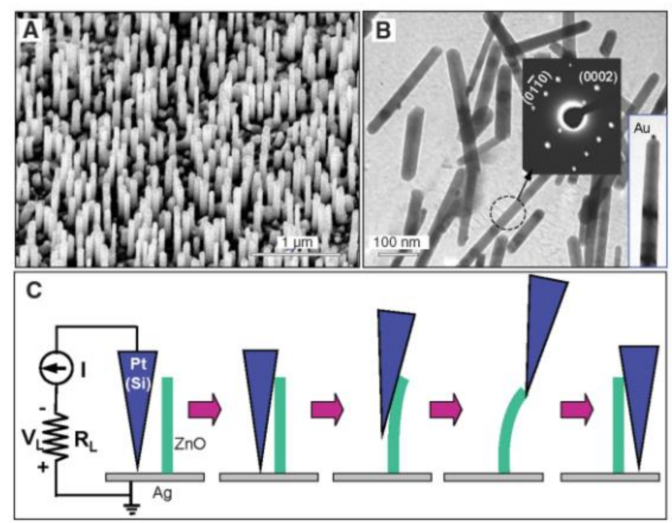
Figure 3. Dependence of piezoelectric coefficient d_{33} of $Sc_xAl_{1-x}N$ alloys on Sc concentration.

ZnO nanowires

14 APRIL 2006 VOL 312 **SCIENCE** www.sciencemag.org

Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays

Zhong Lin Wang[1,2,3]* and Jinhui Song[1]



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MATERIALS

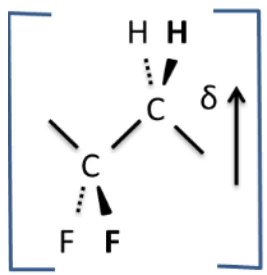
Giant Electrostriction and Relaxor Ferroelectric Behavior in Electron-Irradiated Poly(vinylidene fluoride-trifluoroethylene) Copolymer

Q. M. Zhang,* Vivek Bharti, X. Zhao

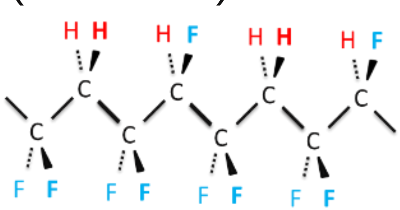
www.sciencemag.org • SCIENCE • VOL. 280 • 26 JUNE 1998

Piezoelectric polymers

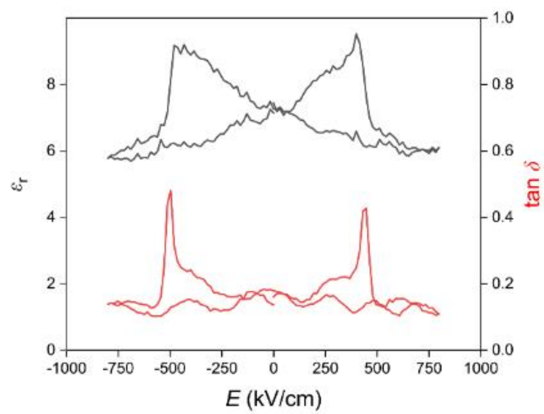
Polyvinylidene Difluoride



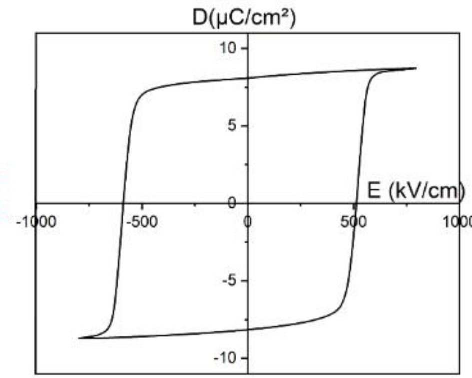
P(VDF-TrFE) => better piezo



Dielectric characterization



Ferroelectric characterization



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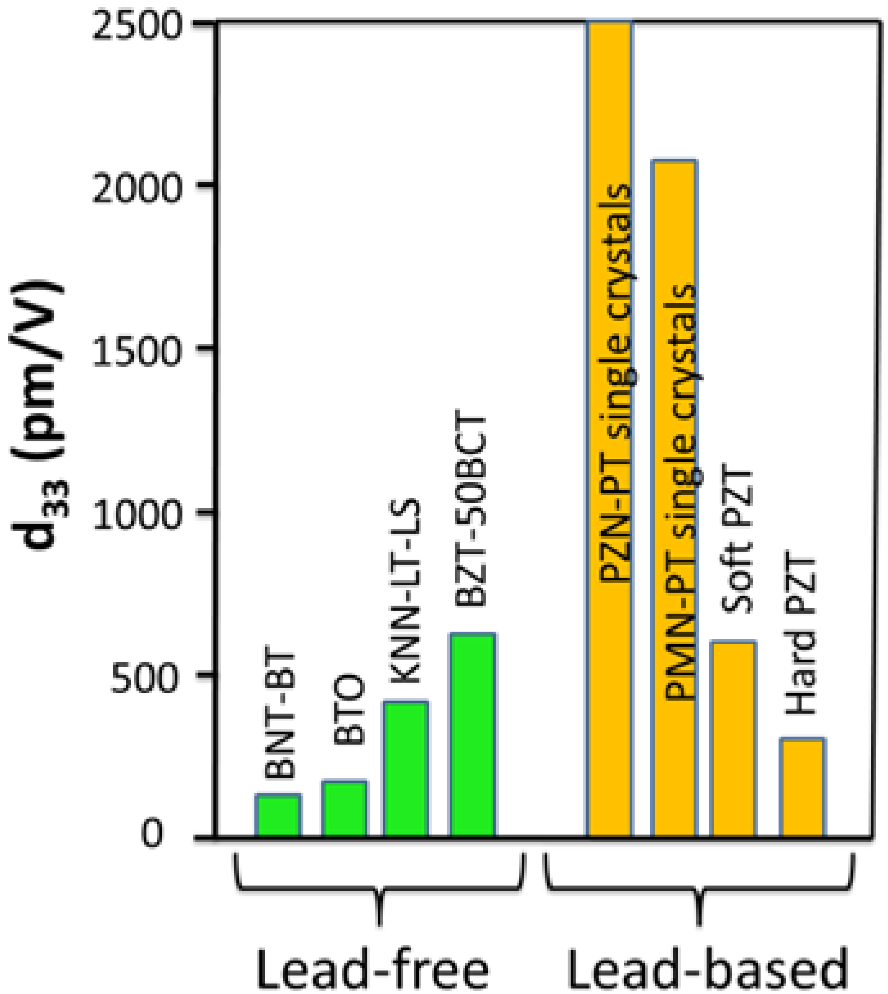
MATERIALS COMPARISON

3 types of materials

Perovskites (PZT) - large piezo properties
Wurtzite (AlN) – low acoustic losses
Polymers (PVDF) – low temperature fabrication

Material	Type	d_{33} (pm/V)	d_{31} (pm/V)	$-e_{31,eff}$ (C/m²)	ε	c_{33}^{E} (GPa)
PZT 5H	Ceramic	650	-320	25	3800	50
PZT	Poly –film	250	-150	20	1500	80
AlN	Poly-film	5	-2.5	1.0	10	300
ScAlN	Poly-film	20	-10	1.5	15	120
PVDF-based	Film / free standing films	-20	+6	0.01	10-30	2

Bulk perovskites



BNT - Bi0.5Na0.5TiO3
BTO – BaTiO3
KNN - (K,Na)NbO3
BZT-BCT – (Ba,Ca)(Zr,Ti)O3
PZN-PT - $Pb(Zn_{1/3}Nb_{2/3})O_3$ -$PbTiO_3$
PMN-PT – Pb(Mg,Nb)O3-PbTiO3
PZT- Pb(Zr,Ti)O3

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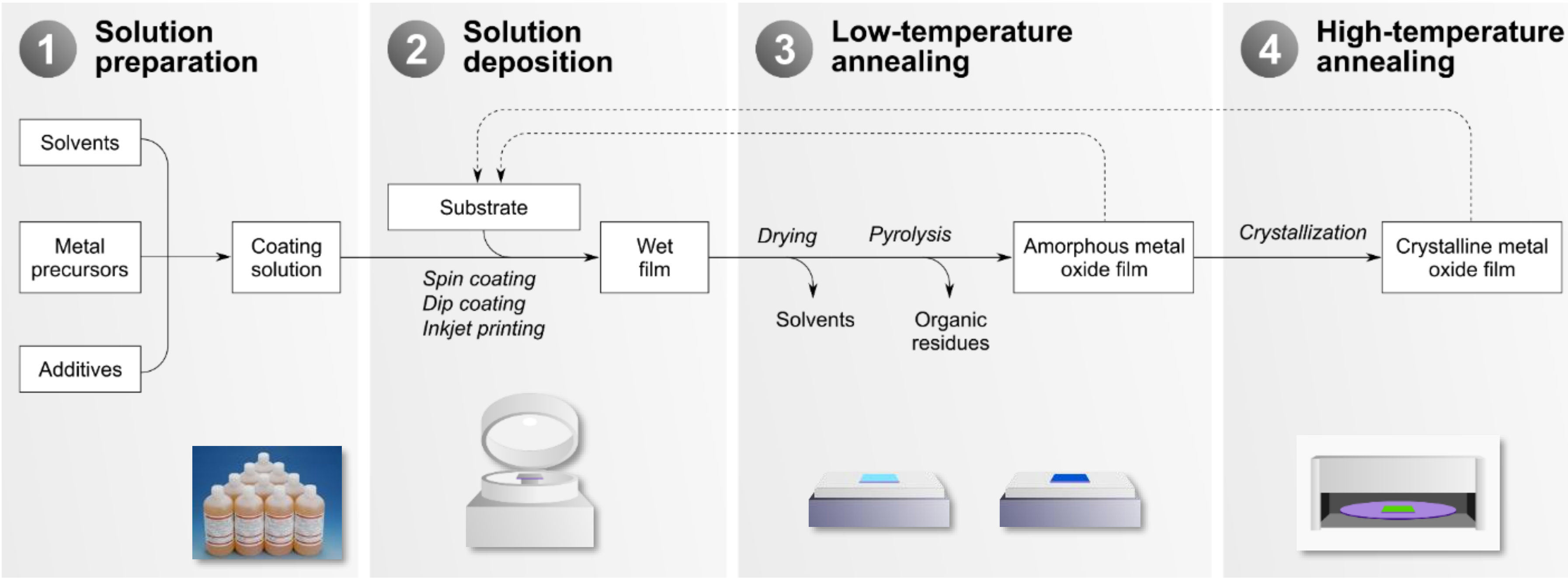
FABRICATION

(NON EXHAUSTIVE)

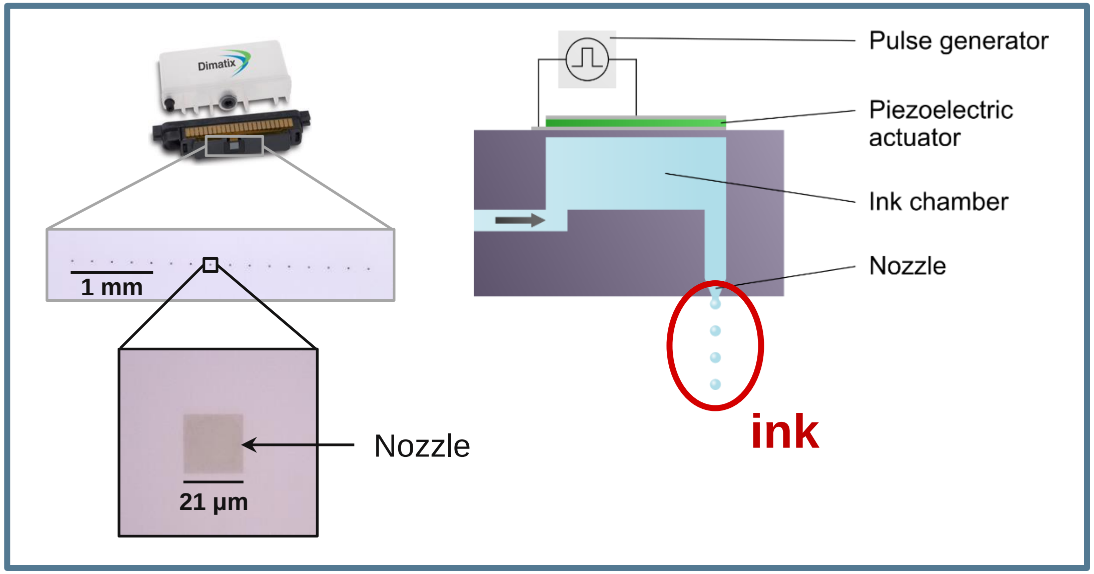
FABRICATION

Sol gel technology



FABRICATION

Inkjet printing



Low-cost

No vacuum deposition
No lithography

Eco-friendly

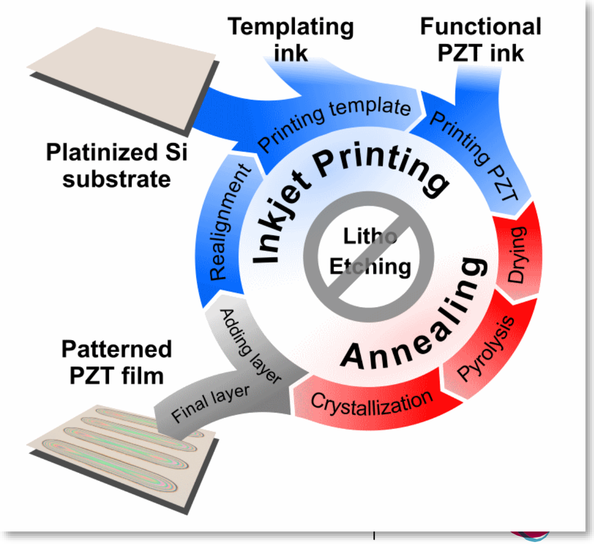
Additive manufacturing
Reduced waste

Versatile

Freedom of geometry
CSD-compatible

Up-scalable

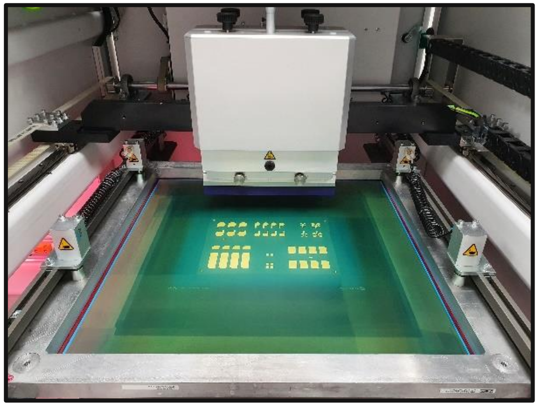
High potential for
industrial transfer

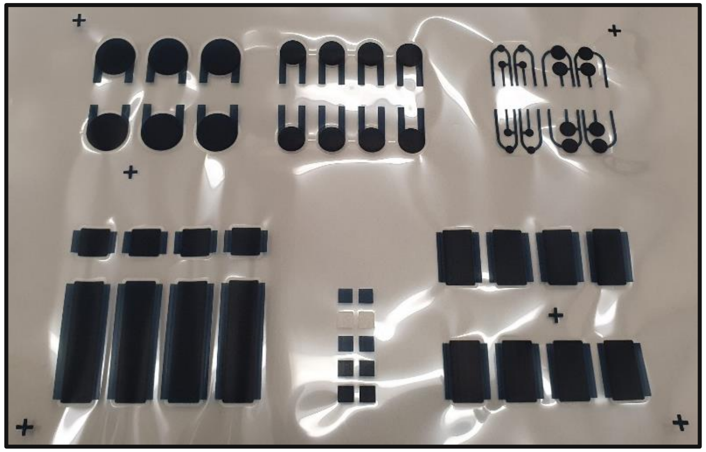


FABRICATION

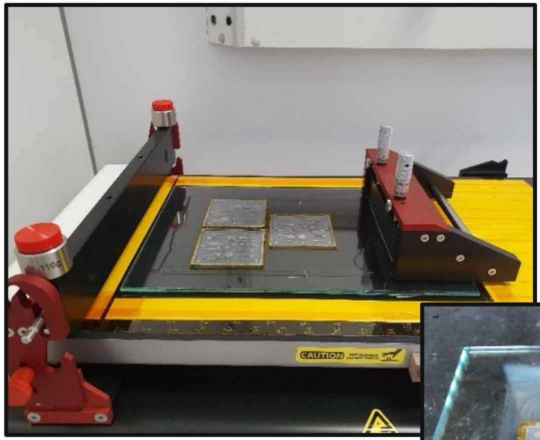
PVDF films

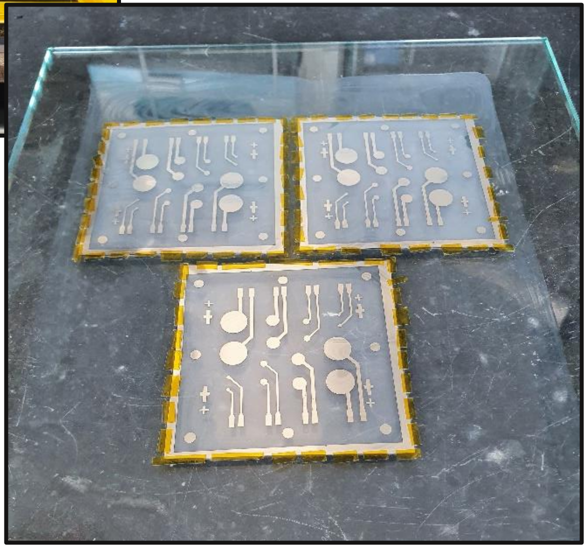
Screen printing





Bar coating

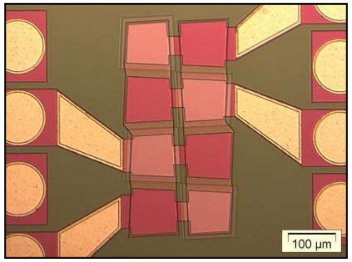


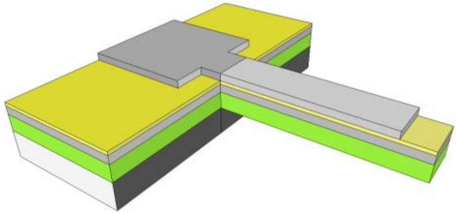


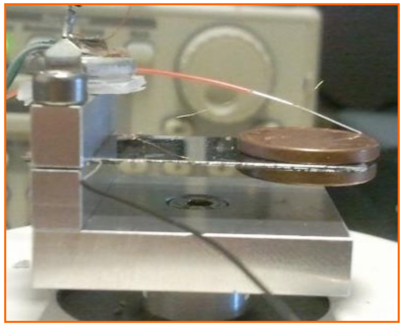
APPLICATIONS

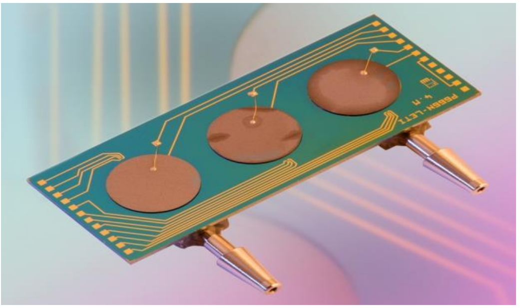
APPLICATIONS

- Acoustic resonators
  - Filters
  - Gas sensors
- Actuators
  - Micro-pump
- Energy harvester



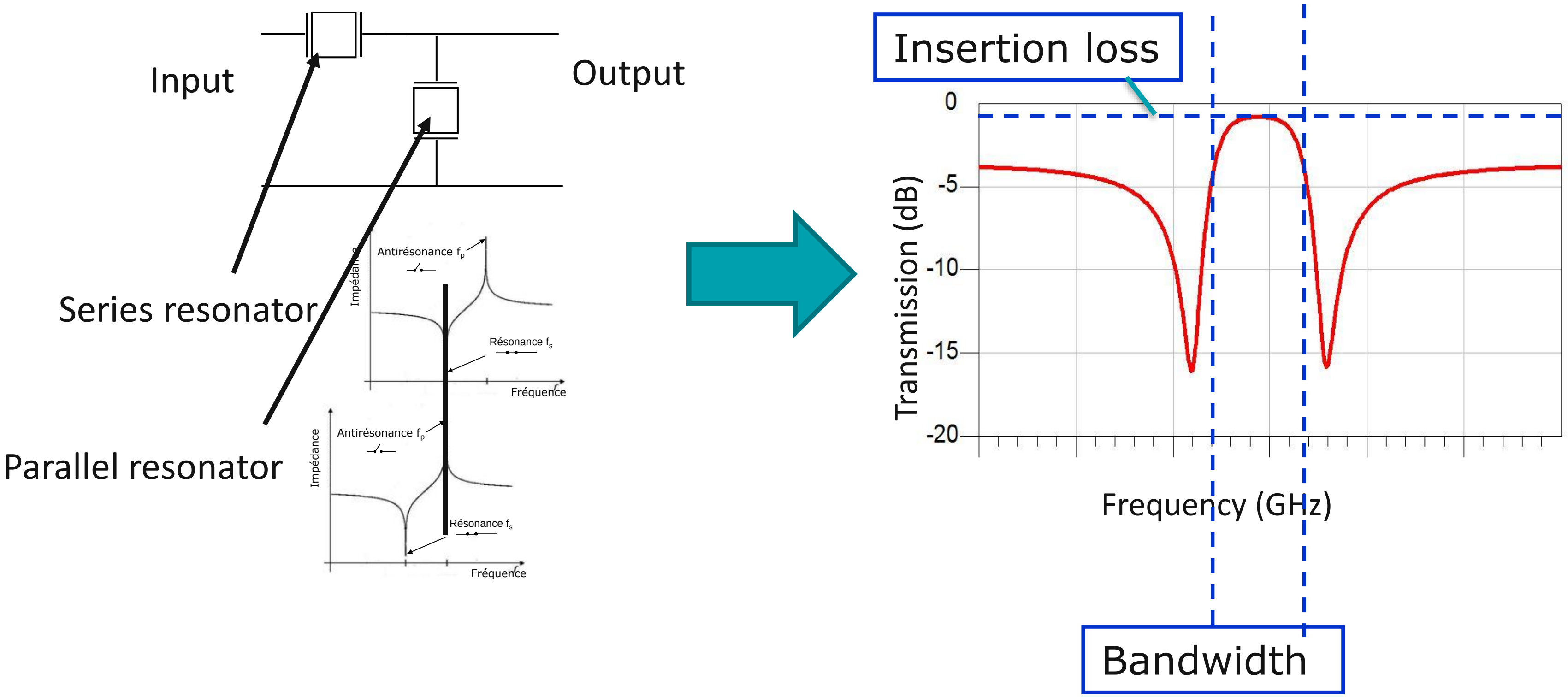




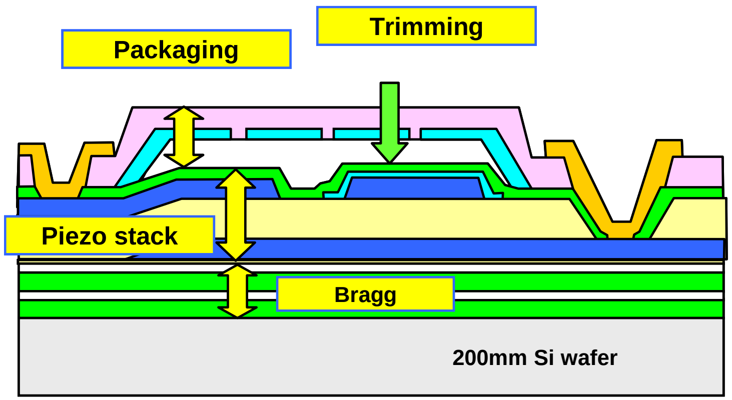


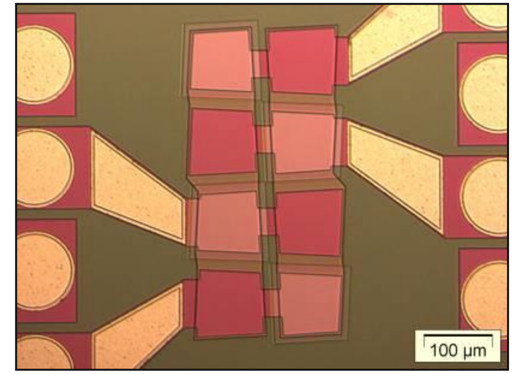
RF FILTERS

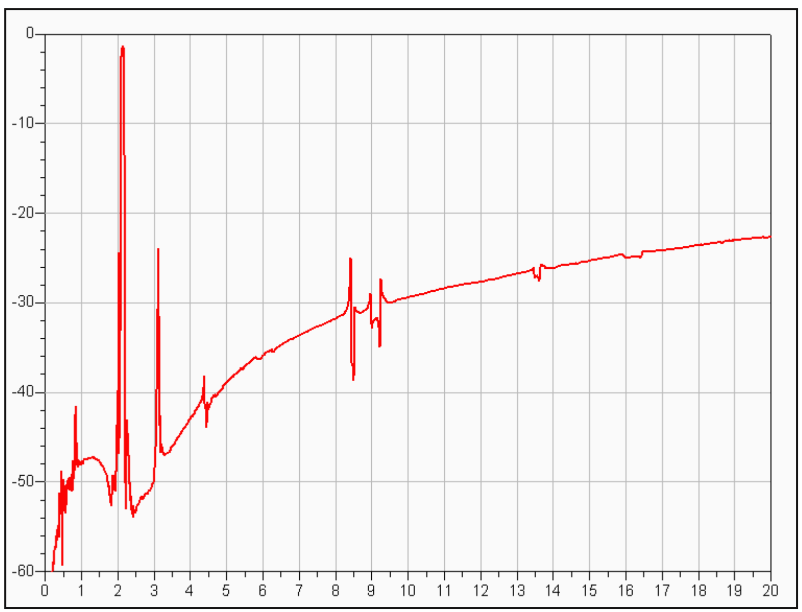
- Electrical coupling between acoustic resonators



RF FILTERS







Transmission (dB)

Frequency (GHz)

Resonator Quality factor= 1800

Insertion losses < 3 dB

Bandwidth = 80 MHz

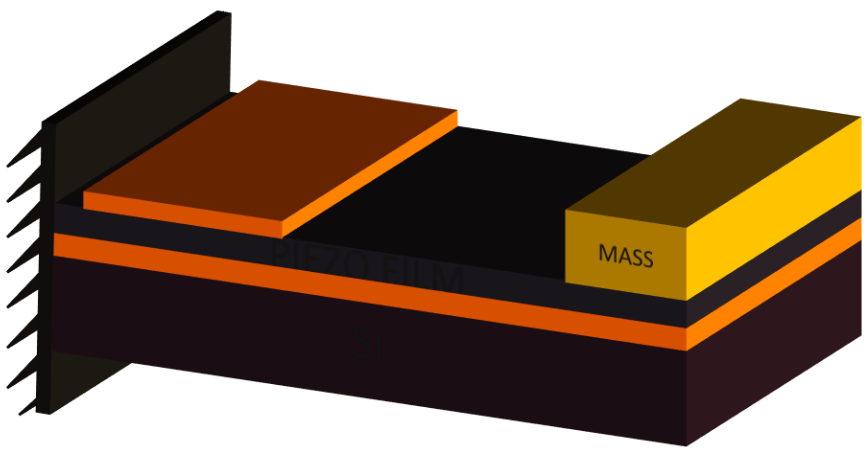
Central frequency = 2 GHz

Used in mobile phones

Duplexers

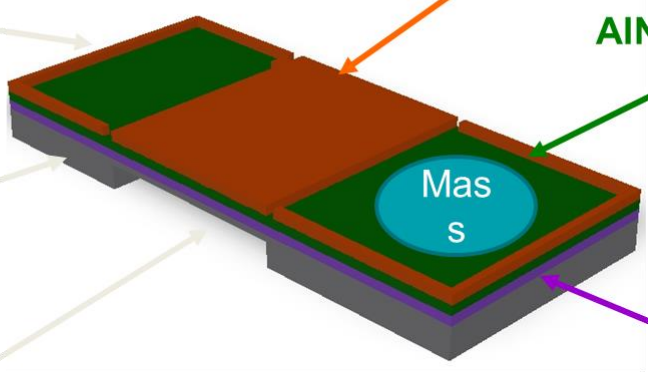
ENERGY HARVESTING

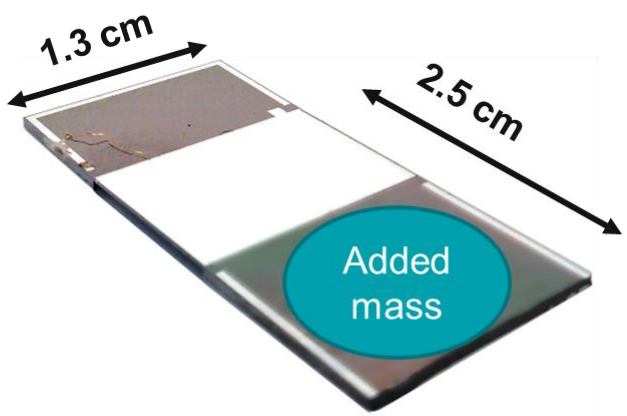
- AlN thin films
  - Low impedance compared to electrostatic harvesters
  - Simple electronic
- Silicon technology - Microsystems approach
- Added mass to reduce Si area
- Could reduce cost production compared to bulk



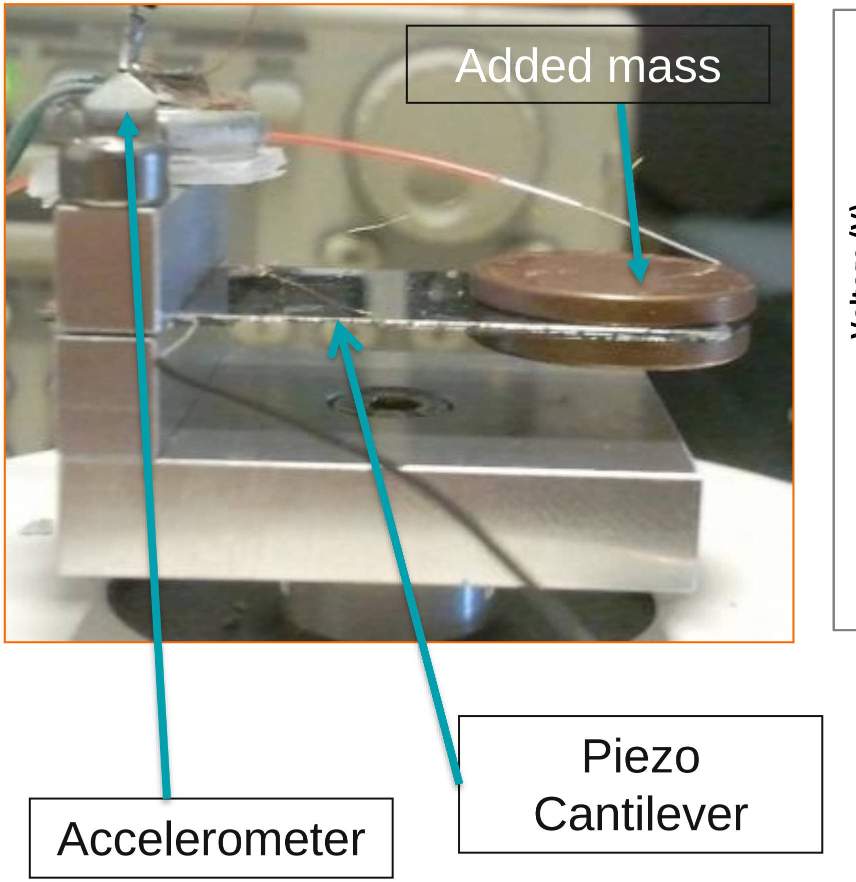
ENERGY HARVESTER

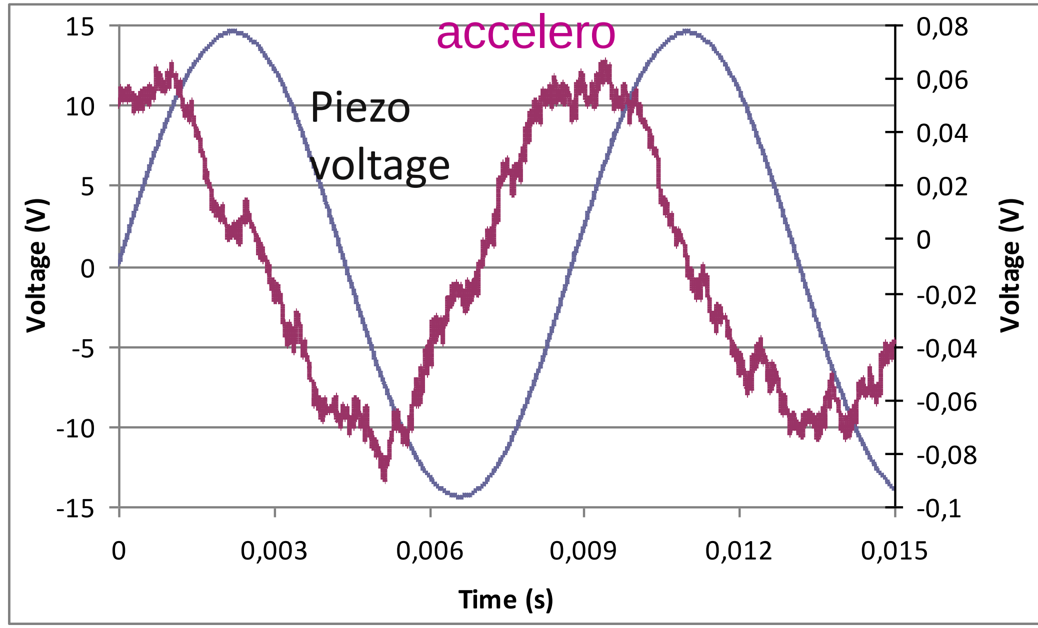
5 µm- AlN films





EXPERIMENTAL RESULTS





Total mass: 5 g

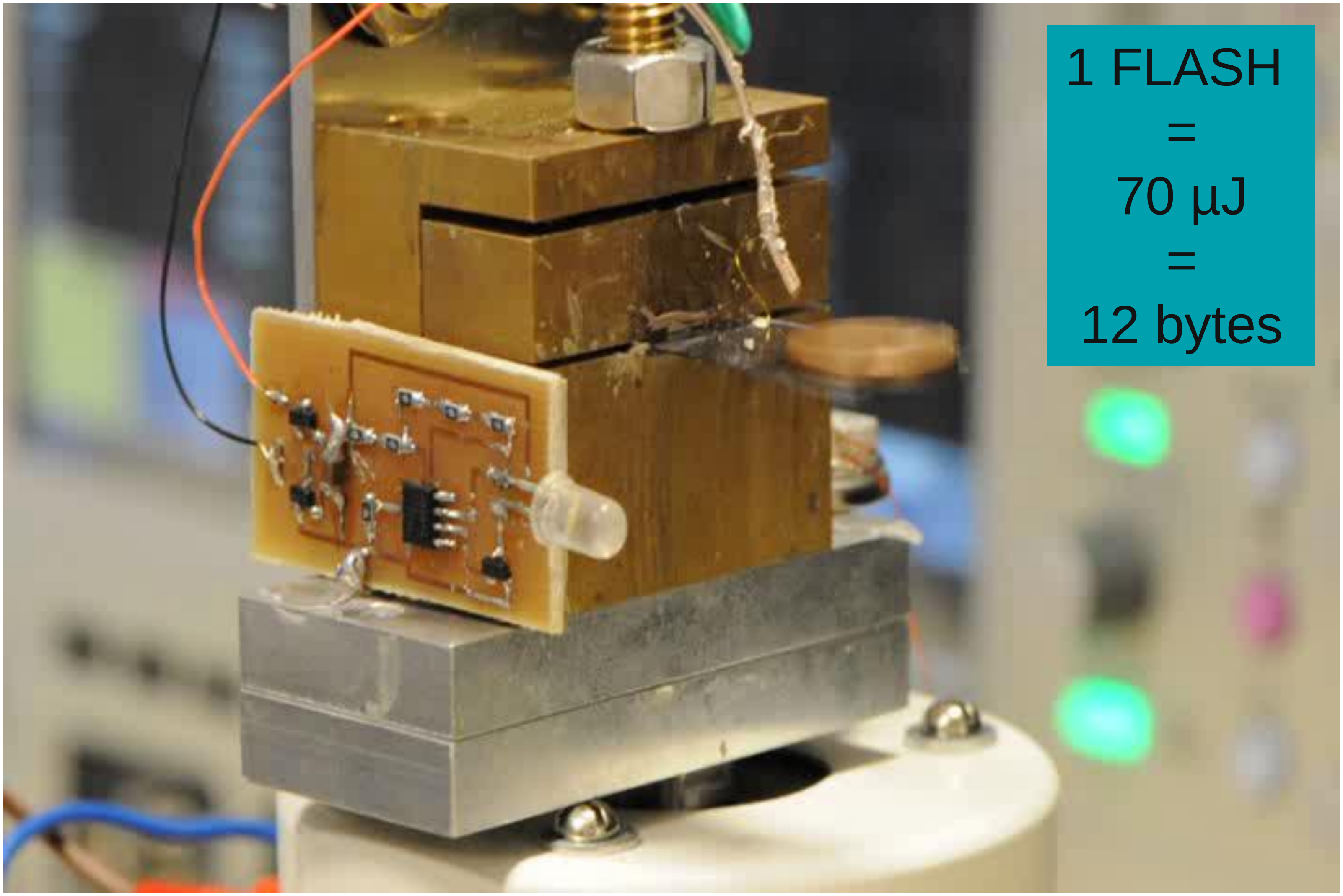
R_{load} =1 MOhm

Acceleration = 1.5m/s²

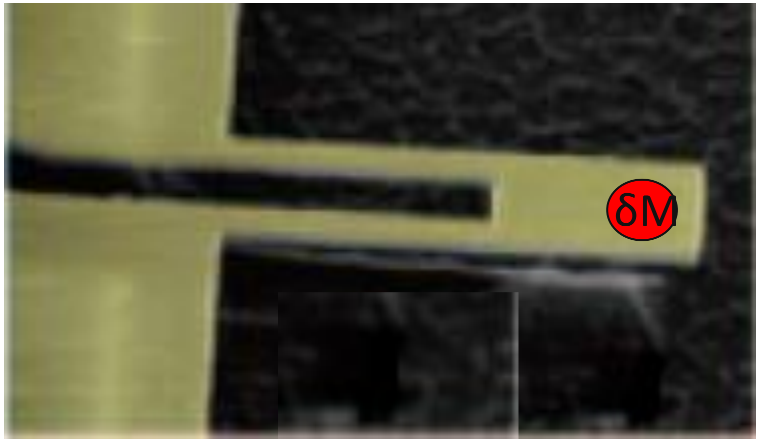
V=+/-15V @ 114Hz

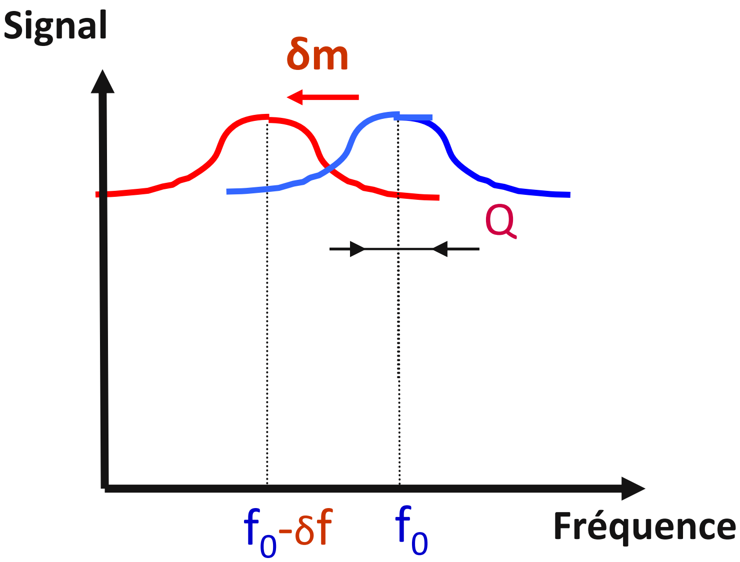
Harvested power = 110 µW

« AUTONOMOUS LED »



GAS SENSING

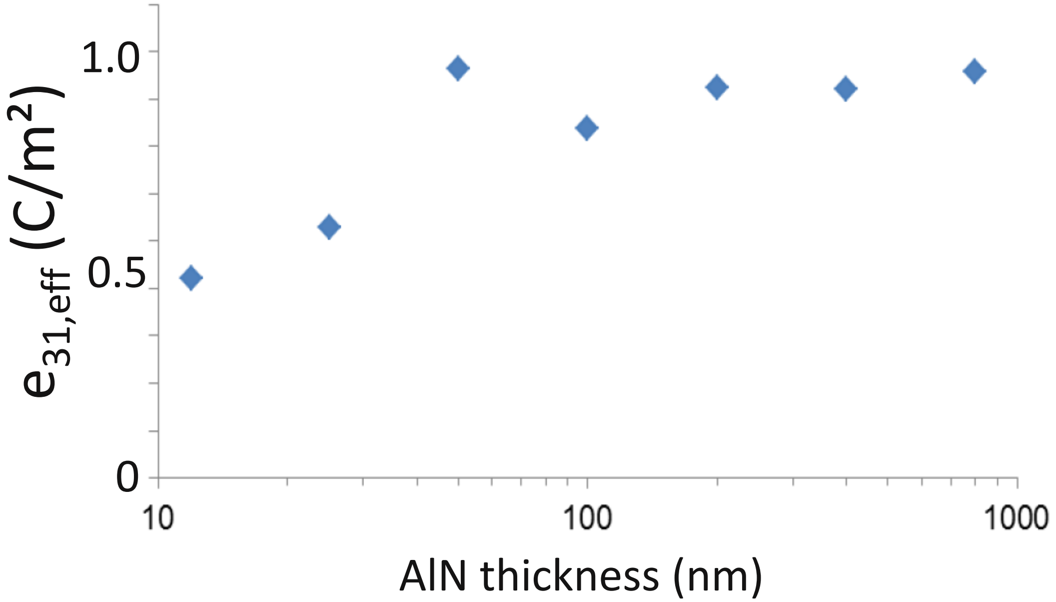


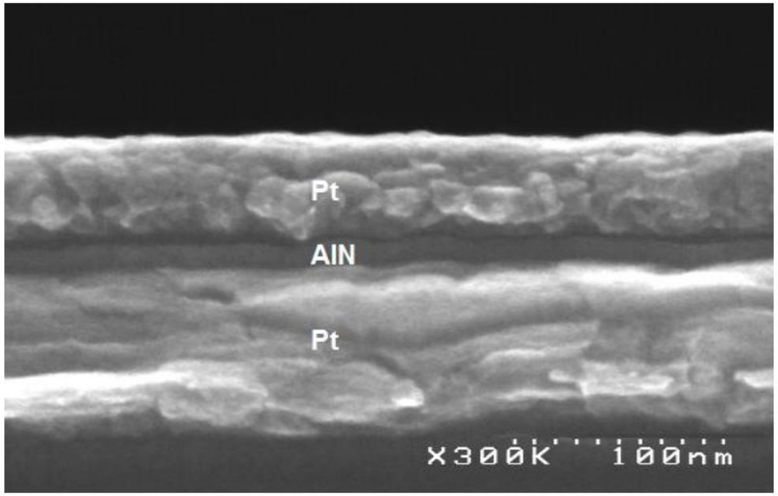


$$\frac{\delta f_0}{f_0} = -\frac{1}{2}\frac{\delta M}{M}$$

ULTRA THIN ALN FILMS

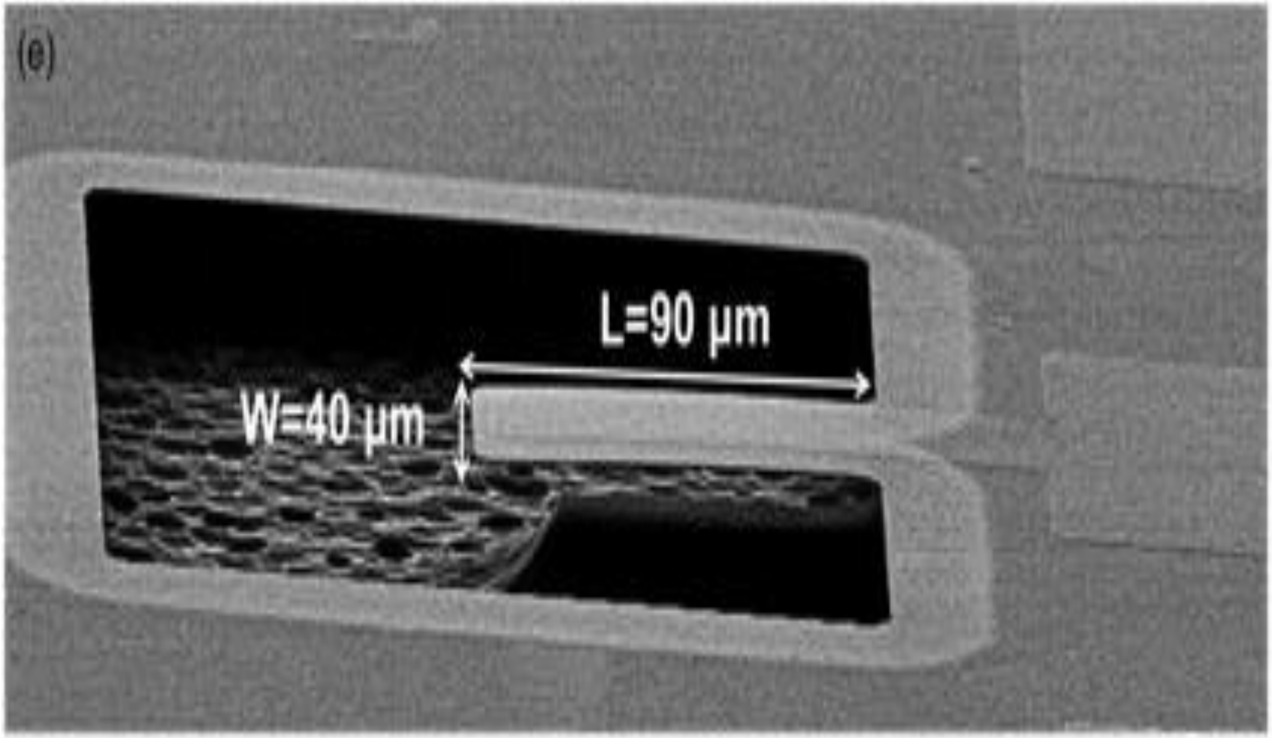
- 12 nm-thick AlN piezo !



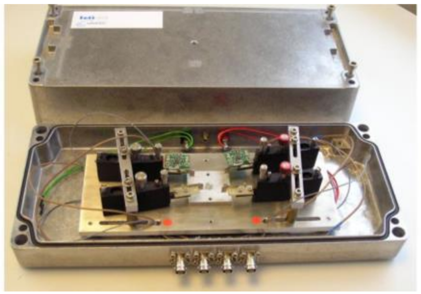


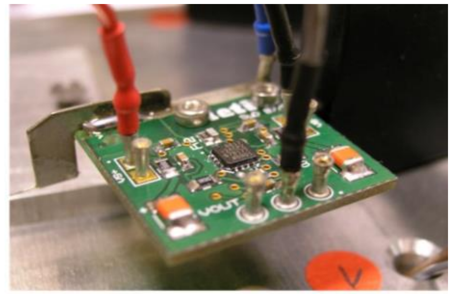
- ❑ $e_{31,eff}$ 50 nm = - 1.0 C.m^2
- ❑ Bottom electrode Mo, Pt, W
- ❑ Seeding layer AlN

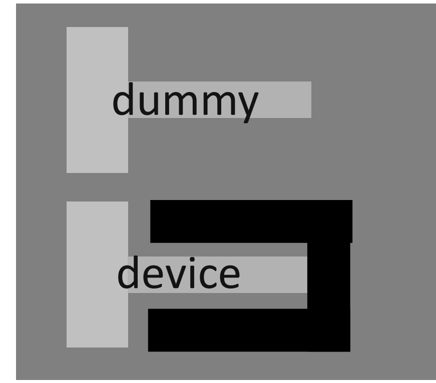
THIN ALN CANTILEVERS

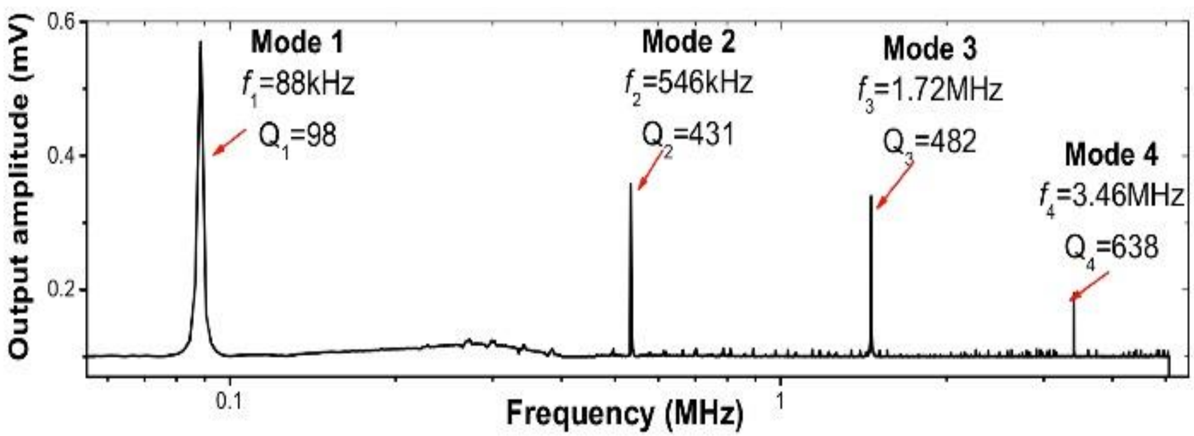


RESONANCE CHARACTERIZATION



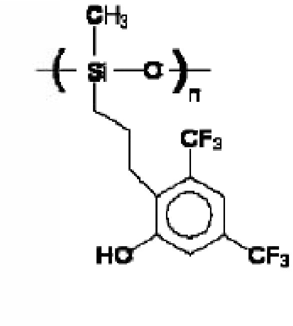




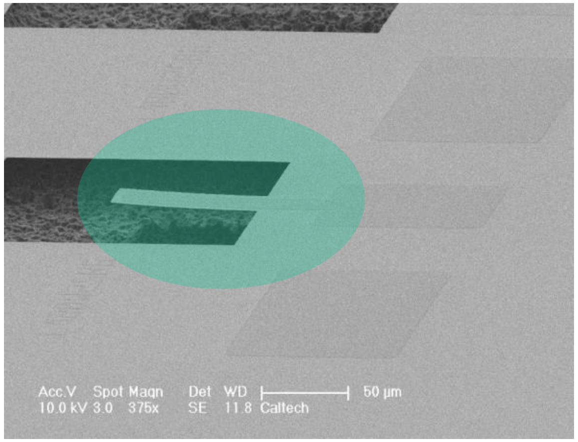


GAS SENSING

- Surface functionalisation



DKAP

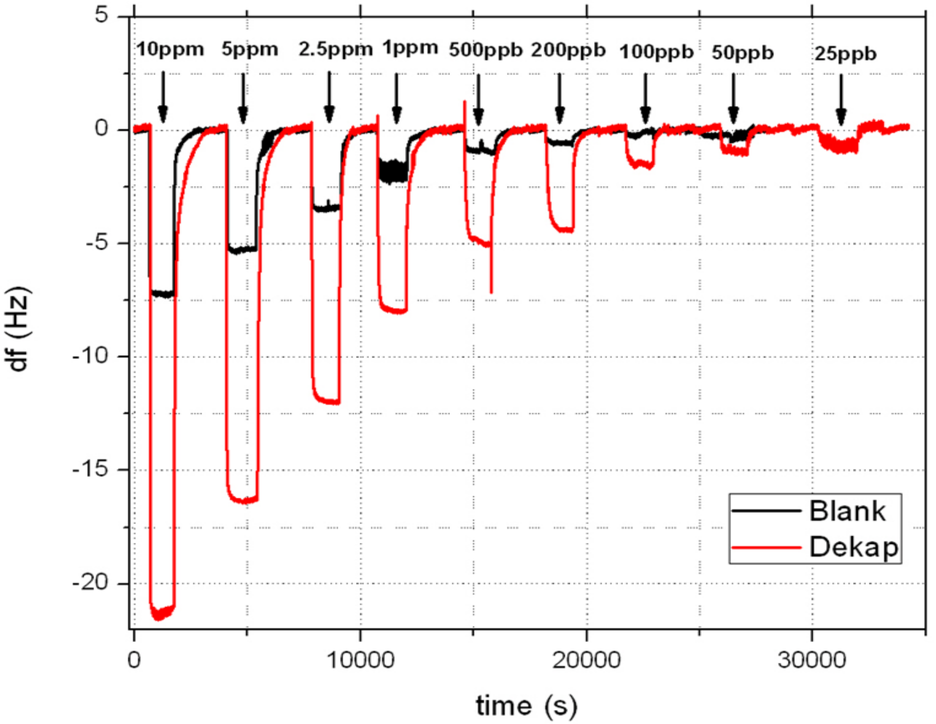


$$DMMP_{gas} + DKAP_{surf} \underset{k_{off}}{\overset{k_{on}}{\rightleftarrows}} DMMP - - DKAP$$

- DKAP added by drop coating

GAS SENSING OF DMMP

- 10 ppb resolution

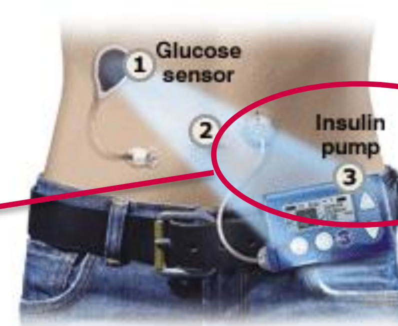


Ivaldi et al., JMM 2011

MICROFLUIDIC FOR HEALTH

- Main goals :
  - Reduce diagnostic time
  - Improve treatment efficiency
  - Improve patient comfort
  - Reduce treatement cost

- Lab-on-chip



Implantable
Piezo
Micro-pump

- Implemented devices

IMPLANTABLE MICROPUMP

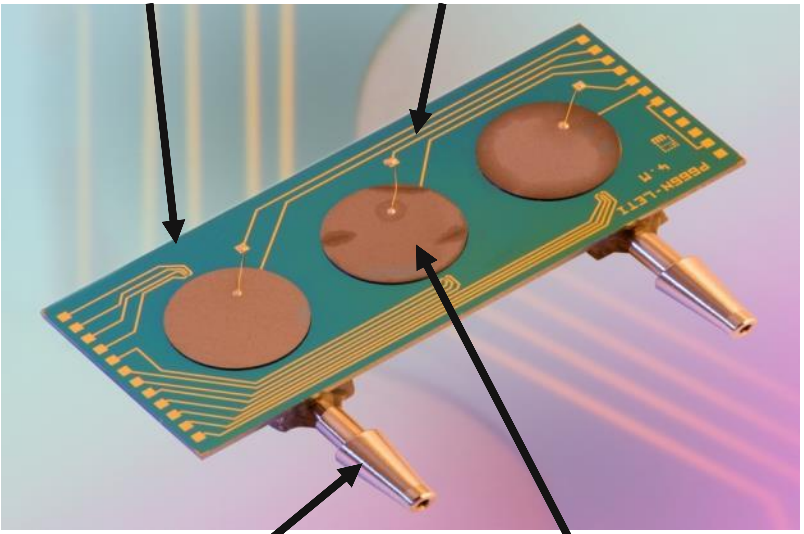
- Required specifications:

  Accurate flow rate control

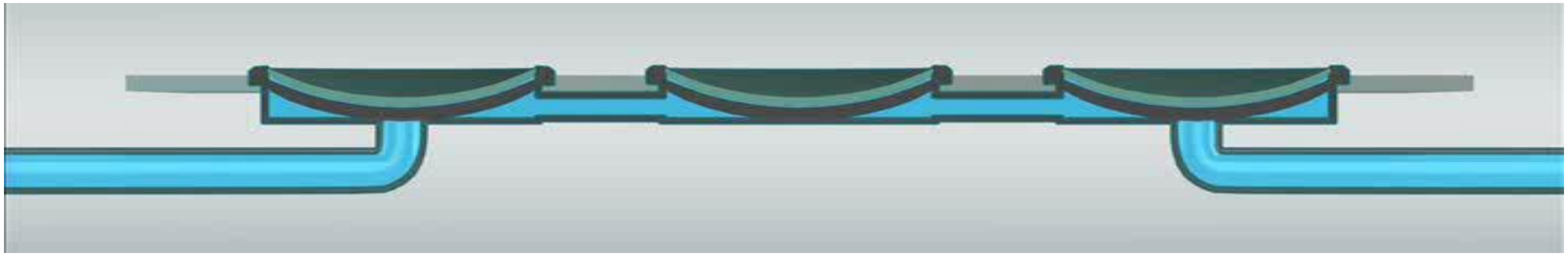
  Bio-compatibility

  Compactness

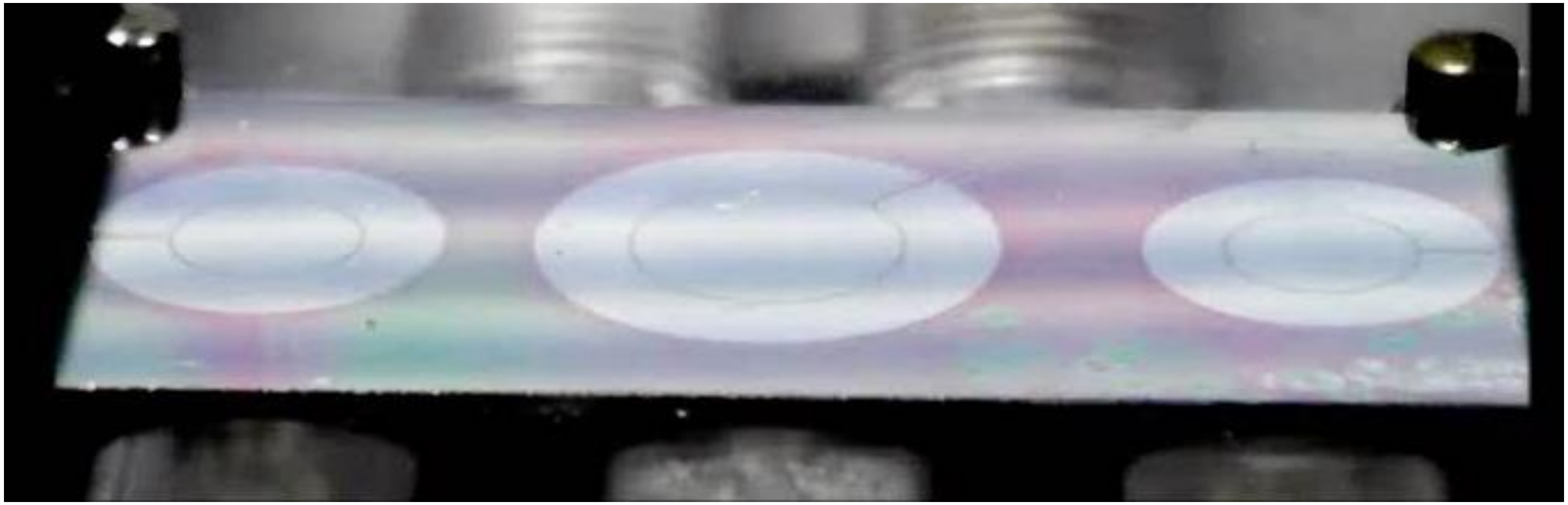
  Energy efficiency



- Peristaltic principle



PERISTALTIC PUMPING

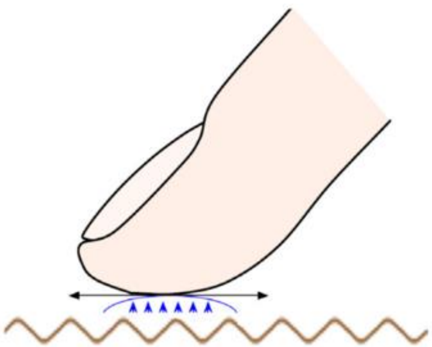


PIEZOELECTRIC HAPTICS

Lamb Waves

Antisymmetric zero-order A_0 mode in an infinite plate

Ultrasonic Vibration



Squeeze-film effect

Bernard et al., J. Micromech. Microeng., 2016

Finite plate – conditions for standing waves can be achieved (A_0).

Conditions for practical use

- Actuation frequency > 20 kHz
- Amplitude of normal displacement $A > 1$ µm
- Wavelength λ between 12 and 20 mm

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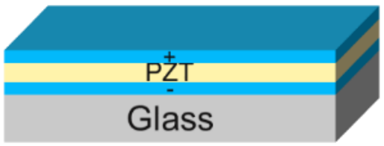
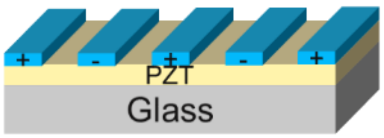
ACTUATOR DESIGN

Parallel plate (PPE)



InterDigital (IDE)

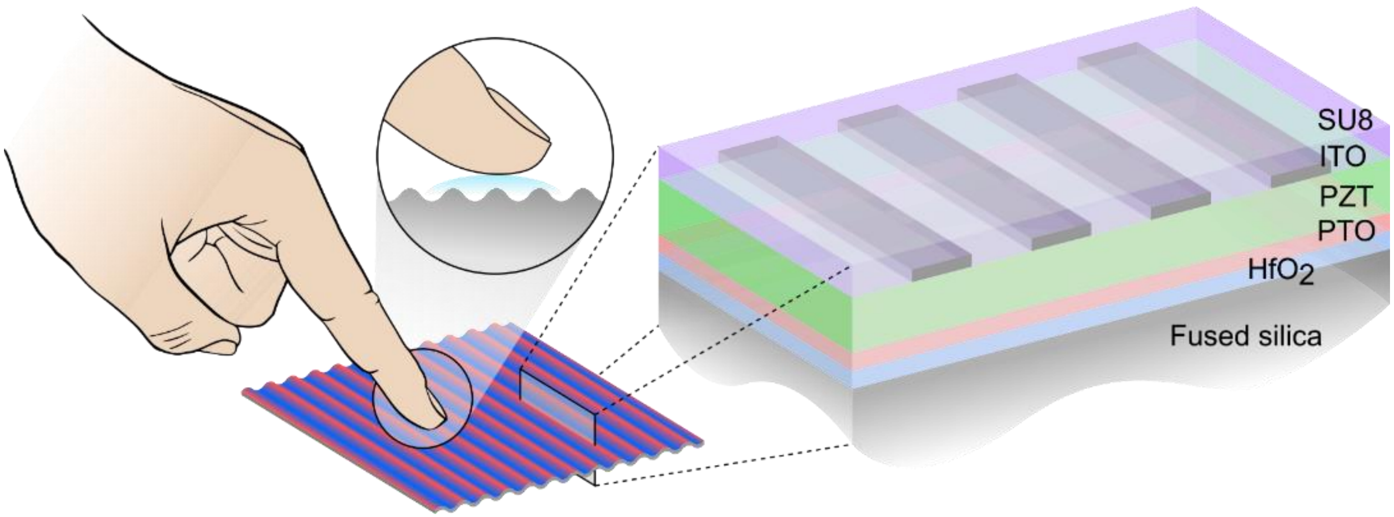


PPE vs. IDE

	d_{31} mode (PPE)	d_{33} mode (IDE)
Capacitance per unit surface (C/S)	High	Low
Area	Small	Large
Transmittance	Low	High

STRUCTURE

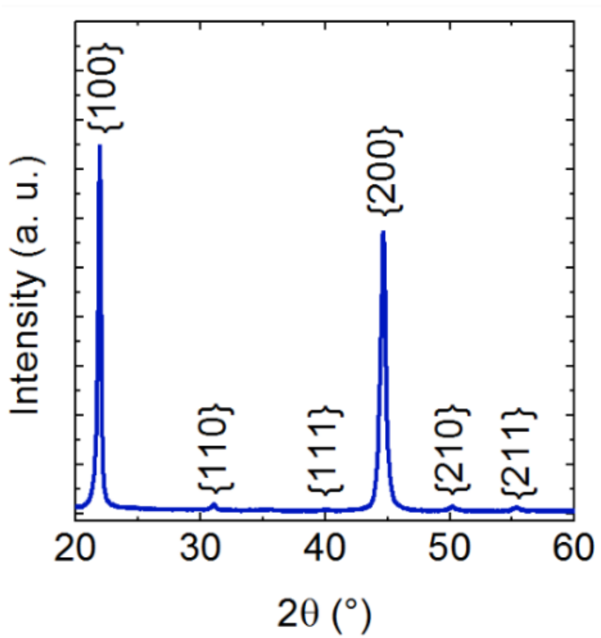
PTO: $PbTiO_3$
PZT: $Pb(Zr_{0.53}Ti_{0.47})O_3$
ITO: $In:SnO_2$
SU-8: epoxy-based negative photoresist

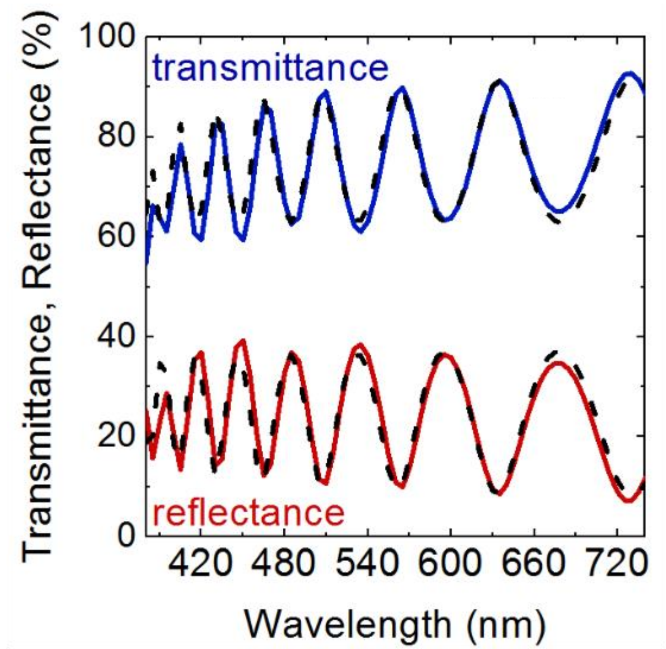


PZT thin-film processing method:
Chemical Solution Deposition

FULLY TRANSPARENT HAPTICS

Spin-Coated PZT Thin Films on Glass





{100} oriented perovskite phase. **Average transmittance in visible spectrum: 75 %.**

Glinsek et al., Adv. Funct. Mater., 30, 2003539 (2020)

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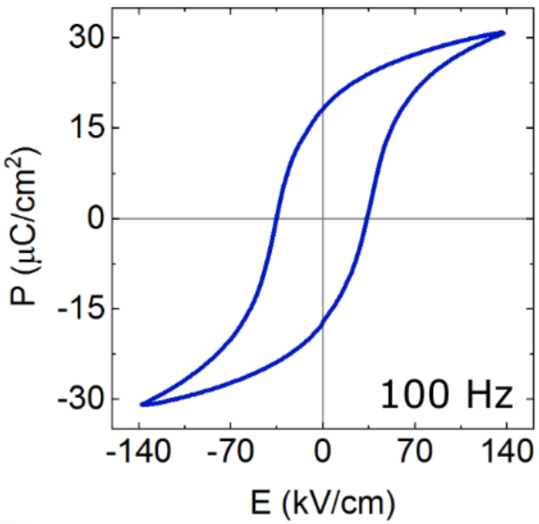
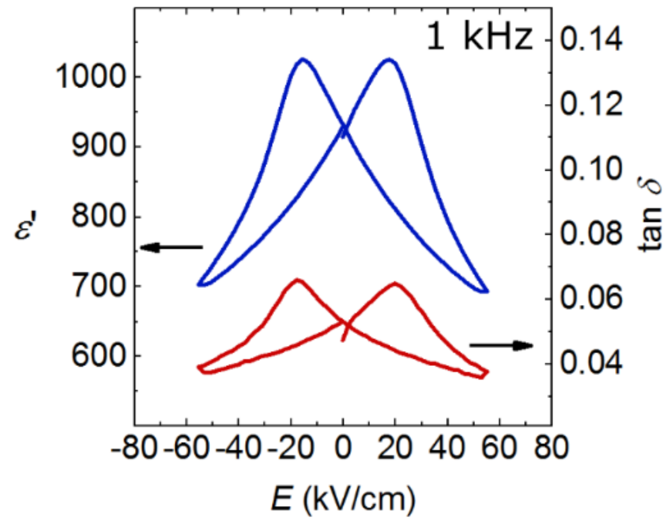
FULLY TRANSPARENT HAPTICS

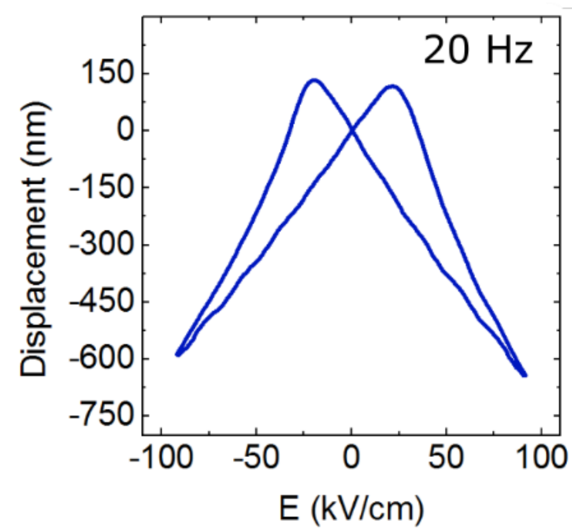
PZT Film on Glass



P_r = 18 μC/cm
E_c = 35 kV/cm



ε_r = 950
tanδ = 0.02



$e_{33,f}$ = 8 C/m^2

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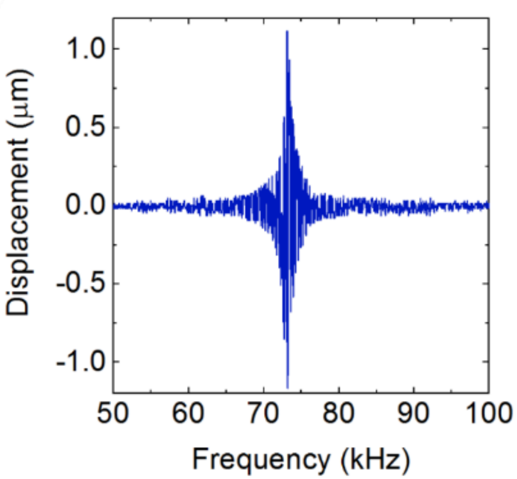
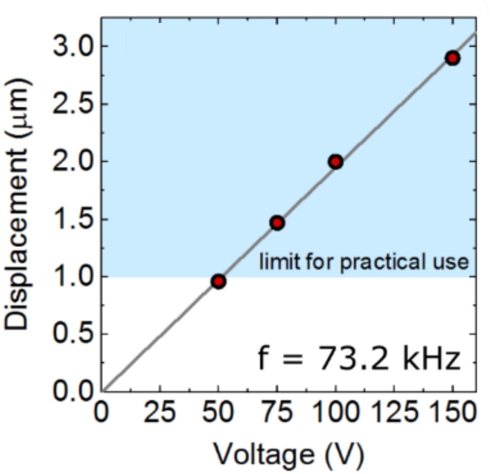
FULLY TRANSPARENT HAPTICS

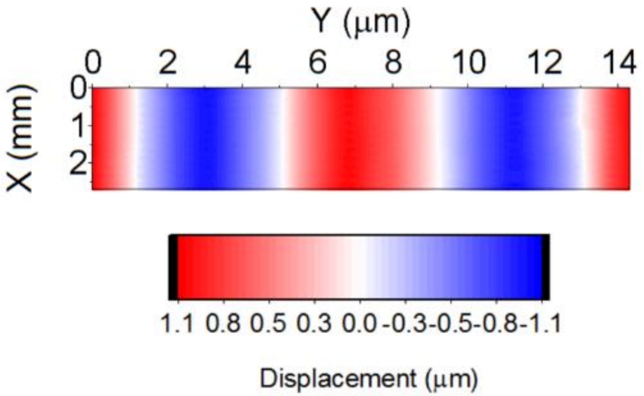
Characterization of the Device



Resonance: 73.2 kHz



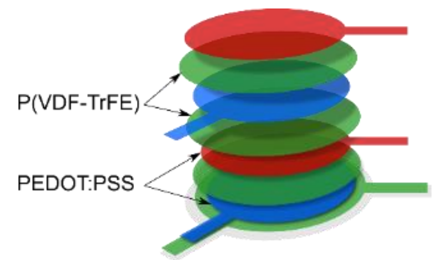
1 um displacement @60 V

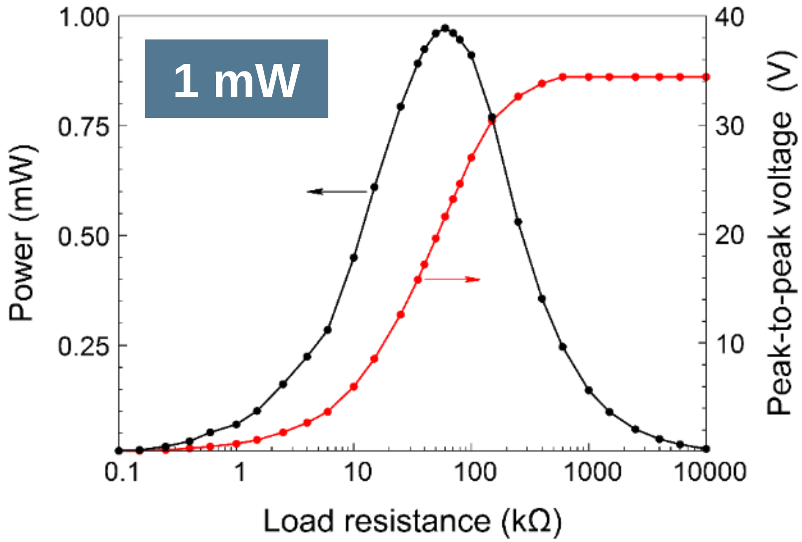


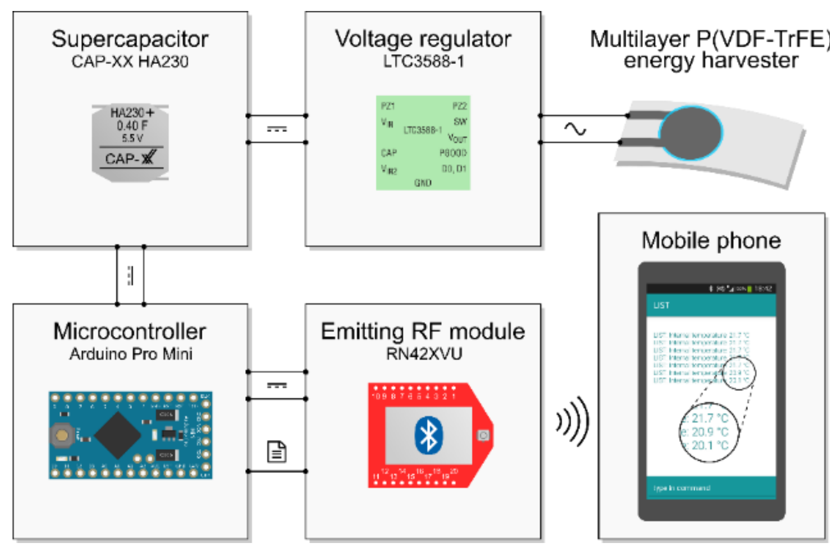
2D Map of the Lamb Wave

PVDF-based piezoelectric energy harvester

Piezoelectric polymer on flexible substrate: high strain (~1%)







Godard et al., Cell Reports Physical Science 1, 100068 (2020)

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CONCLUSIONS

CONCLUSIONS

- Ferroelectrics are peculiar piezoelectrics
- Well described by free energy approach
- Pb(Zr,Ti)O_3 is still leading the race for actuators
- Lead free materials – perhaps (K,Na)NbO3 (KNN), but difficult to replace PZT
- PVDF is excellent for energy harvesting
- Hafnia is of strong interest for ferro, but also for piezo
- Inkjet printing and associated methods should enable decreasing the cost
- It takes time to climb up the ladder of maturity

THANK YOU FOR YOUR ATTENTION

Fonds National de la Recherche Luxembourg

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