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Outline

1. Bordeaux, University and IMS Laboratory
2. IMS Lab - PRIMIS team activities
3. Printed technologies for electronics and MEMS
4. Screen-printed PZT MEMS
5. Printed gas sensors: toward RT detection
6. Organic MEMS



Bordeaux, University and Lab...



BORDEAUX AND ITS UNIVERSITY



~730 000 inhabitants

- **3rd rank in France**
53 000 students and 5600 employees
- **3 departments**
 - Science and technology,
 - Law, political science and economy
 - Medicine



Academic Laboratories



IMS-Bordeaux LABS



IMS-BORDEAUX LABS

Laboratoire d'Intégration du Matériau au Système



400 people working in the field of Engineering
(material sciences, electrical engineering, biology, humanities)

10 000 m²: 40% dedicated to experimental facilities



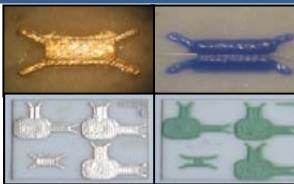
IMS-BORDEAUX LABS



4 Departments

10 Groups

27 Teams

Systems and Interactions B. Veyret	BIOELECTRONICS S. Renaud	Bio-EM I. Lagroye	ELIBIO N. Lew	ims ghi
	COGNITICS J-M André	CIH J-M André	ESC E. Daniellou	
Systems X. Moreau	SIGNAL Y. Berthoumieu	MO	PRIMS team PRInted Microelectromechanical Systems (MEMS) 4 permanent positions and 6 PhD	
	PRODUCTION ENGINEERING Y. Ducq	ME		
	AUTOMATIC CONTROL A. Oustaloup	ARI		
Hardware Integration Y. Deval	CIRCUIT DESIGN J-B Bégueret	EC2	D. Le	C. Maneux N. Malbert
	DEVICES RELIABILITY E. Woirgard	PAC		
	NANOELECTRONICS T. Zimmer	LAS		
From Materials to Devices L. Vignau	ORGANIC ELECTRONICS & MEMS L. Hirsch	ELORGA L. Hirsch	PRIMS I. Dufour	MIM V. Vigneras
	WAVES C. Dejous	MDA D. Rebière	EDMINA L. Béchou	

420 members including 150 researchers, 160 PhDs, 15 Post-docs, 70 technical staff, 25 administrative staff



IMS Lab-PRIMS team activities



PRIMS: PRInted MEMS Team

www.ims-bordeaux.fr/fr/recherche/groupe-recherche/58-organique/prims/41-PRIMS

➤ 4 Permanent positions

2 professors

1 junior researcher

1 associate professor



Cédric
Ayela



Hélène
Débéda



Isabelle
Dufour



Claude
Pellet

➤ 6 PhD students

Frank Bokeloh

Pierre-Henri Ducrot

Simon Grall

Marco Pereira

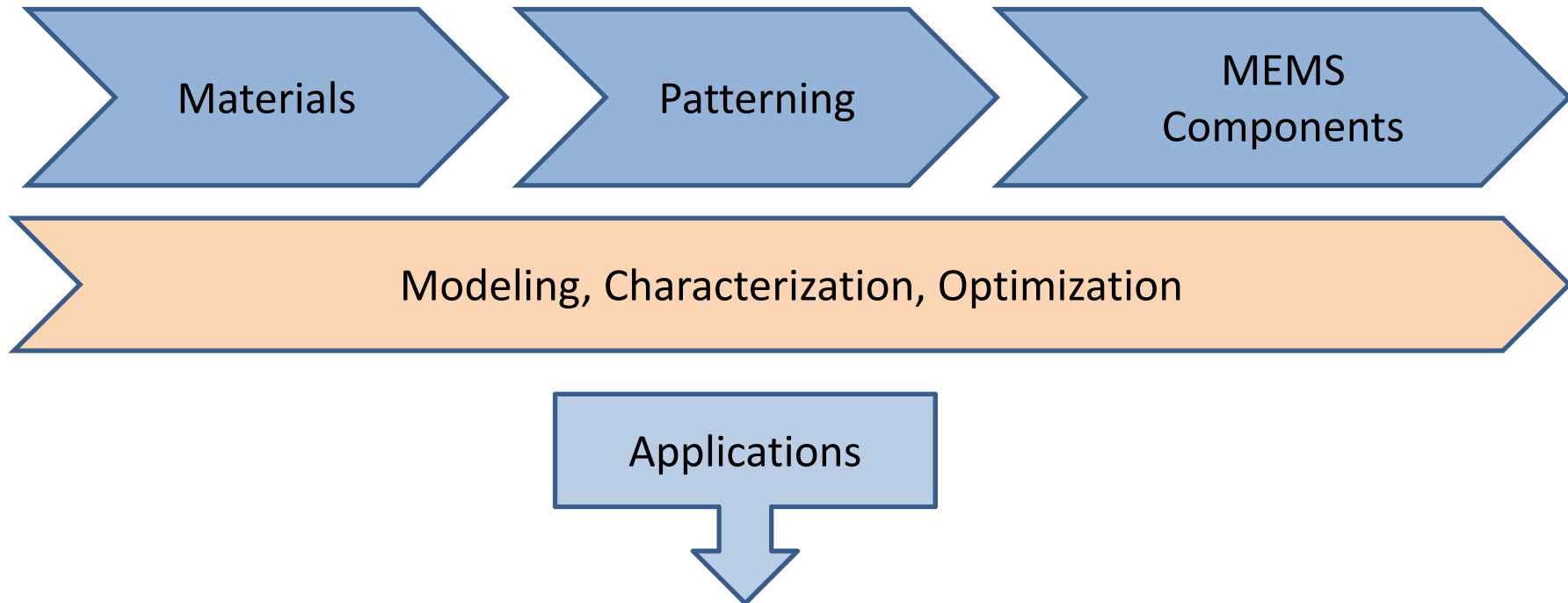
Maria Isabel Rua Taborda

Onuma Santawitee

PRIMS: PRInted MEMS Team

From materials to devices ... in the MEMS field

Alternative solution to all-silicon MEMS ('home-made' → 'printed')
or **silicon MEMS** (processed in other Labs)



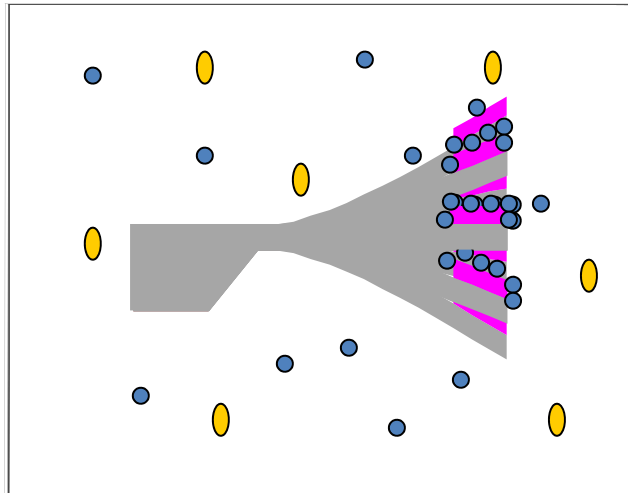
**Chemical sensors, Materials characterization, Physical Sensors, Actuators,
Energy Harvesting, Structural Health Monitoring, Cell Mechanics**

(Chemists, Physicists, Technologists and Electronics Engineers)



Silicon cantilever: from design to gas detection

Dynamic mode

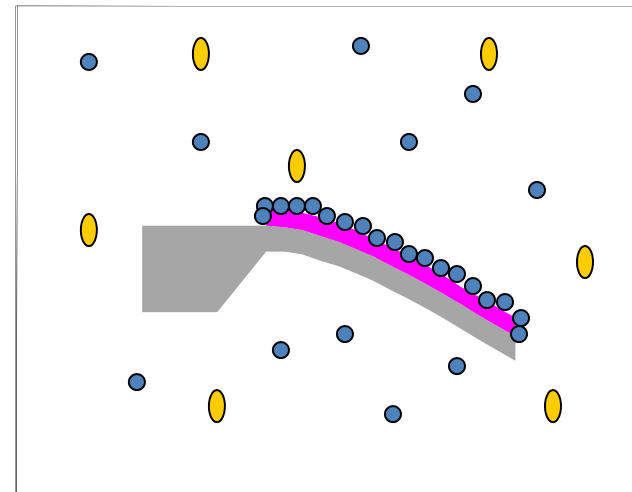


Mass modification

Variation of the resonant frequency



Static mode



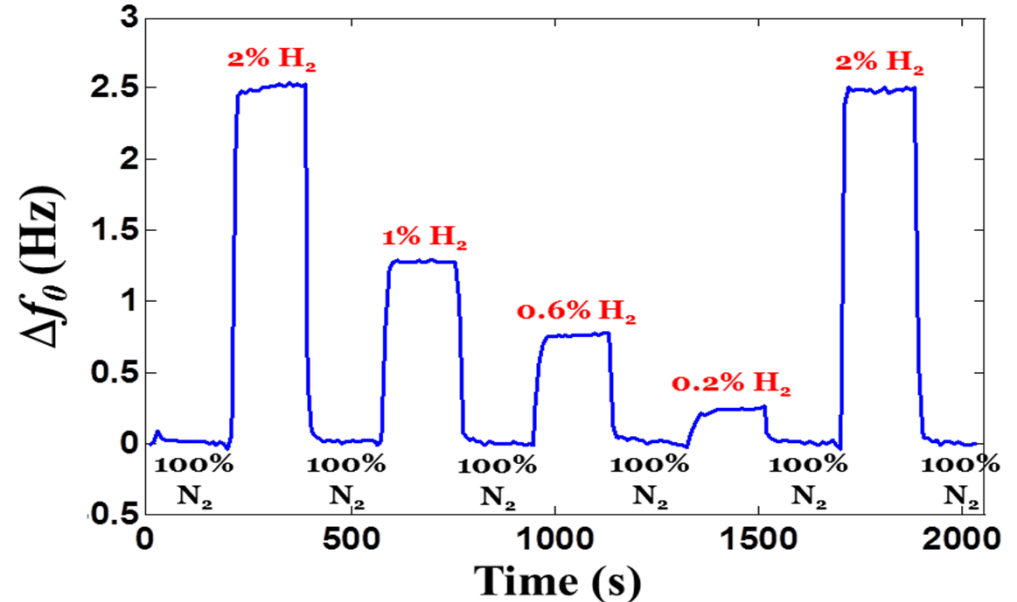
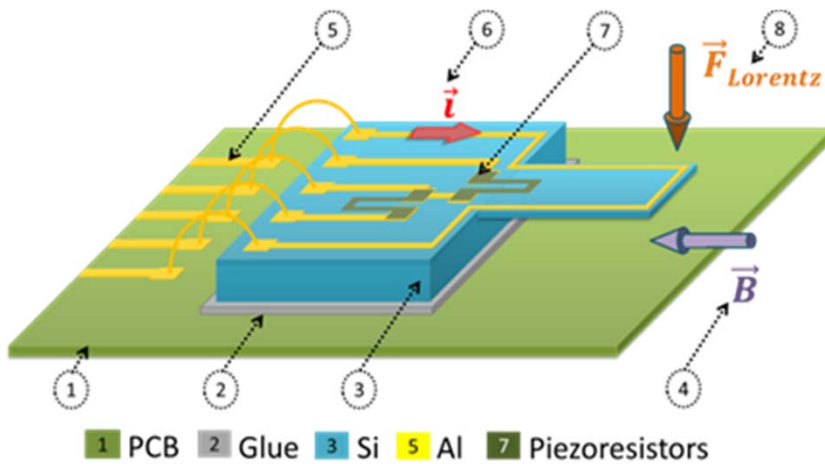
Stress/strain modification

Variation of deflection

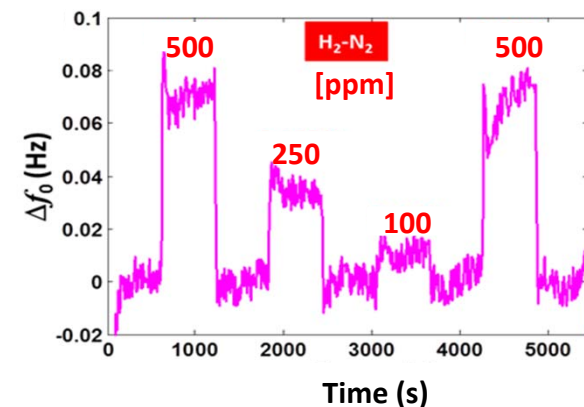
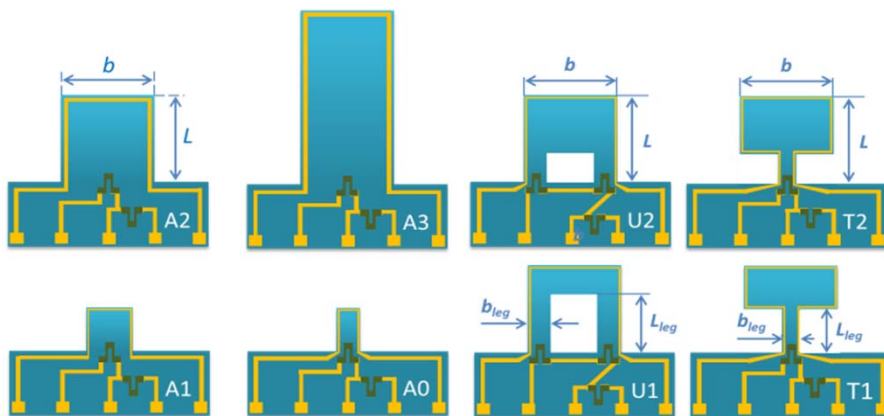


Silicon cantilever: from design to gas detection

Dynamic mode: Detection with uncoated microcantilevers

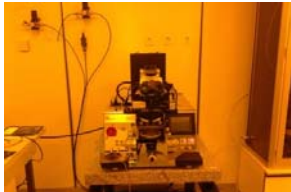


$L=1\text{mm}$, $b=1\text{mm}$, $h=5\mu\text{m}$, $f_0=4.5\text{kHz}$



Sensors and MEMS patterning

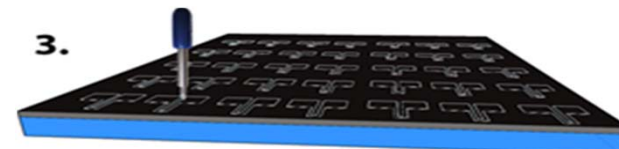
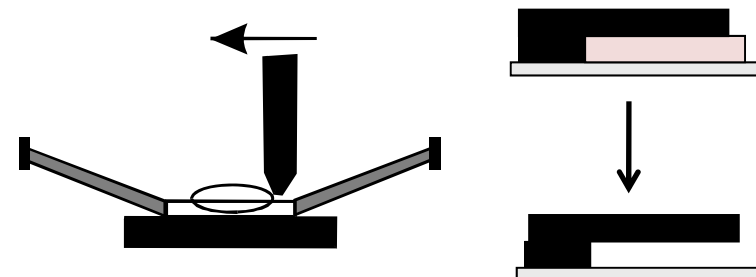
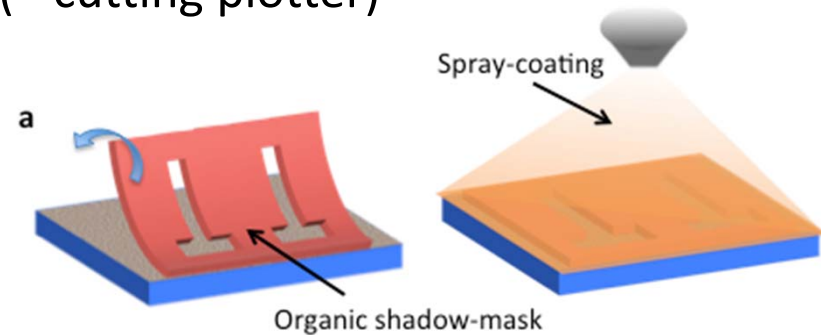
Clean room facilities , class 10000 (TAMIS)



- Screen-printing (+ sacrificial layer)
- Spray + stencil (+ sacrificial layer)



- Spin-coating + Xurography (= cutting plotter)



ADVANTAGES :

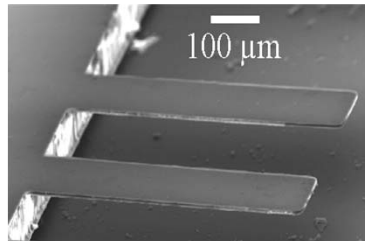
- *low cost*
- *collective fabrication*
- *large choice of substrates and starting materials*
- *components and electronics*
- *bio-compatibility (organic)*
- *harsh environment (inorganic)*

...

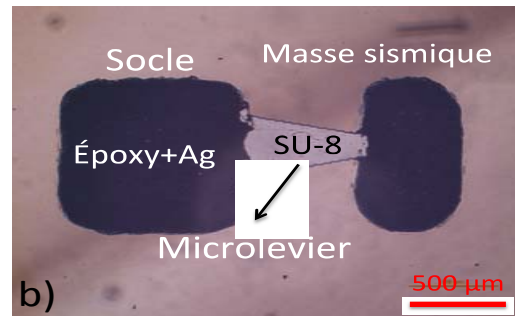


Examples of printed components

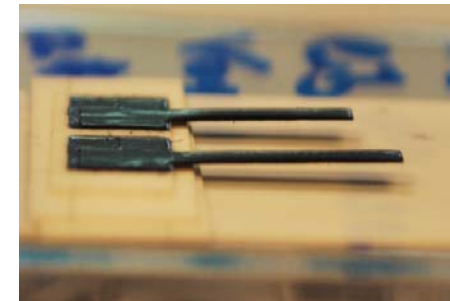
Photolithography + wafer bonding: SU8



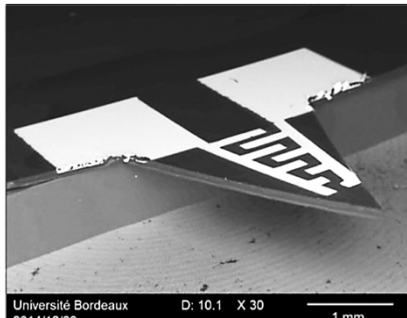
Screen-printing + Photolithography: SU8 + Ag/époxy



Screen-printing: Cu, Pt, vitrocéramique, PZT, epoxy/C



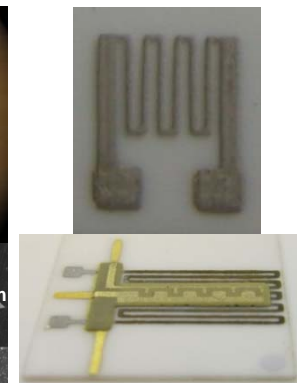
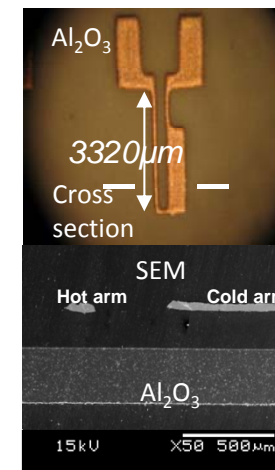
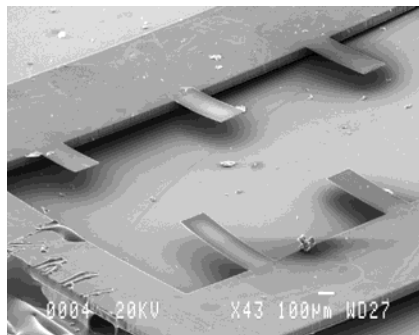
Photolithography: CNTs/SU8



Xurography: CNTs/SU8



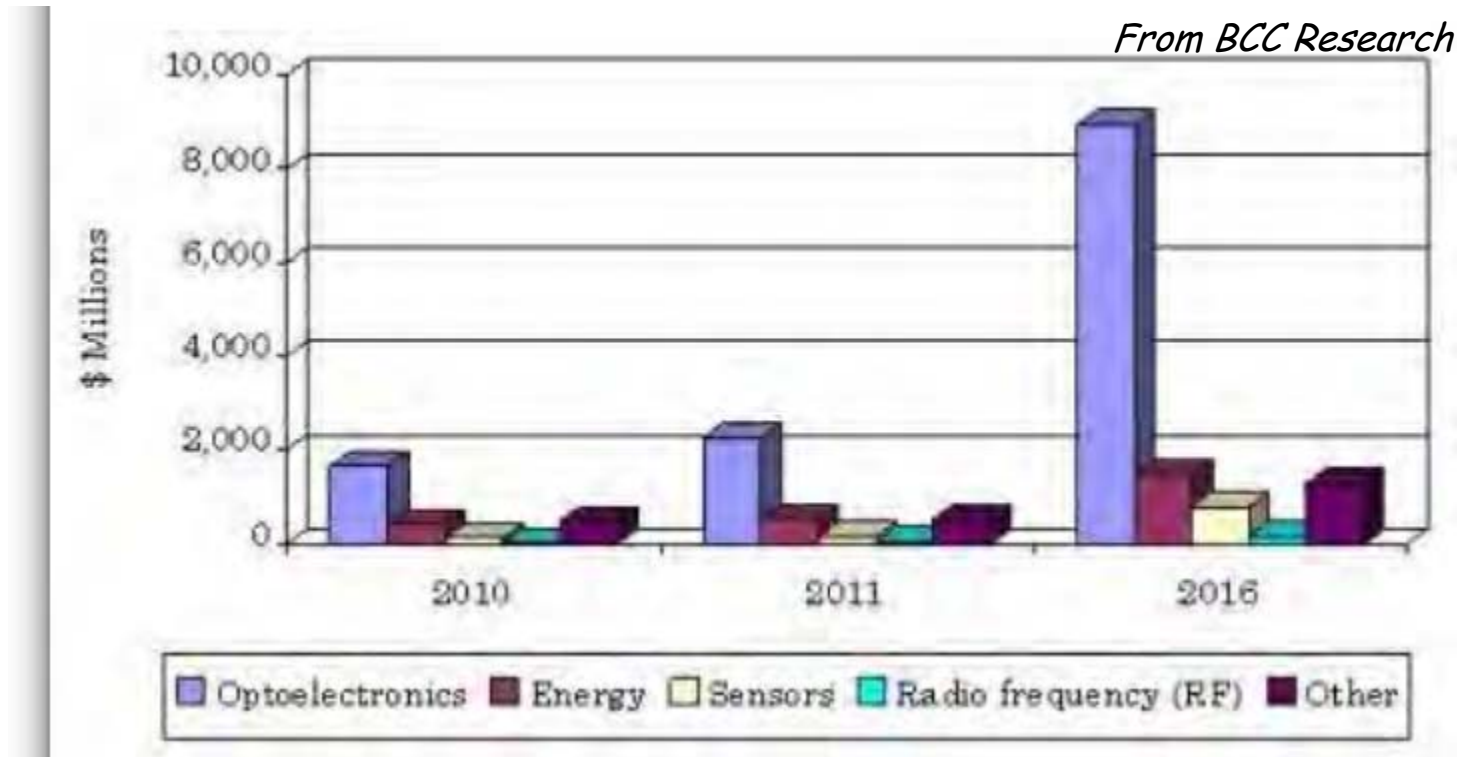
Stencil + spray: MIP



Printed technologies for Electronics and MEMS



Printed technologies → growing demand of the electronic market



- ✓ **Low cost:** additive process, fast/high volume, low capital investment
- ✓ **Good enough quality:** repeatable, good resolution
- ✓ **Capabilities:** printed layers, substrates, form factors, temperature process

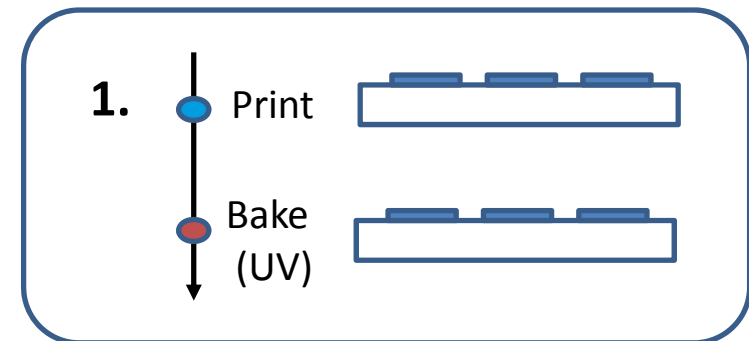
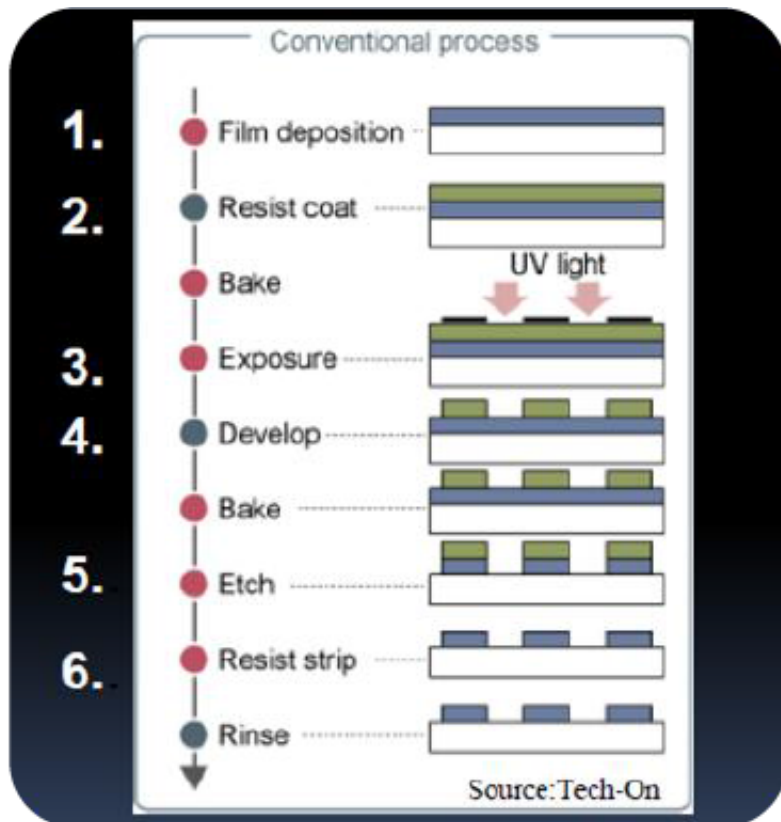
Printed technologies →

Additive process (≠ subtractive process)

Conventional layer application:
6 steps

Simpler

Printing layer application:
« 1 » step

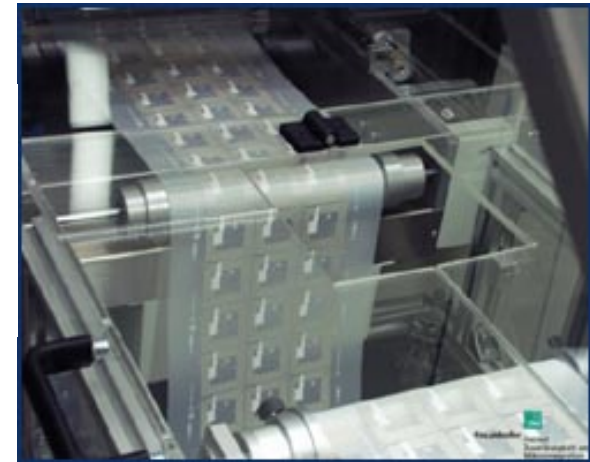


High speed printing

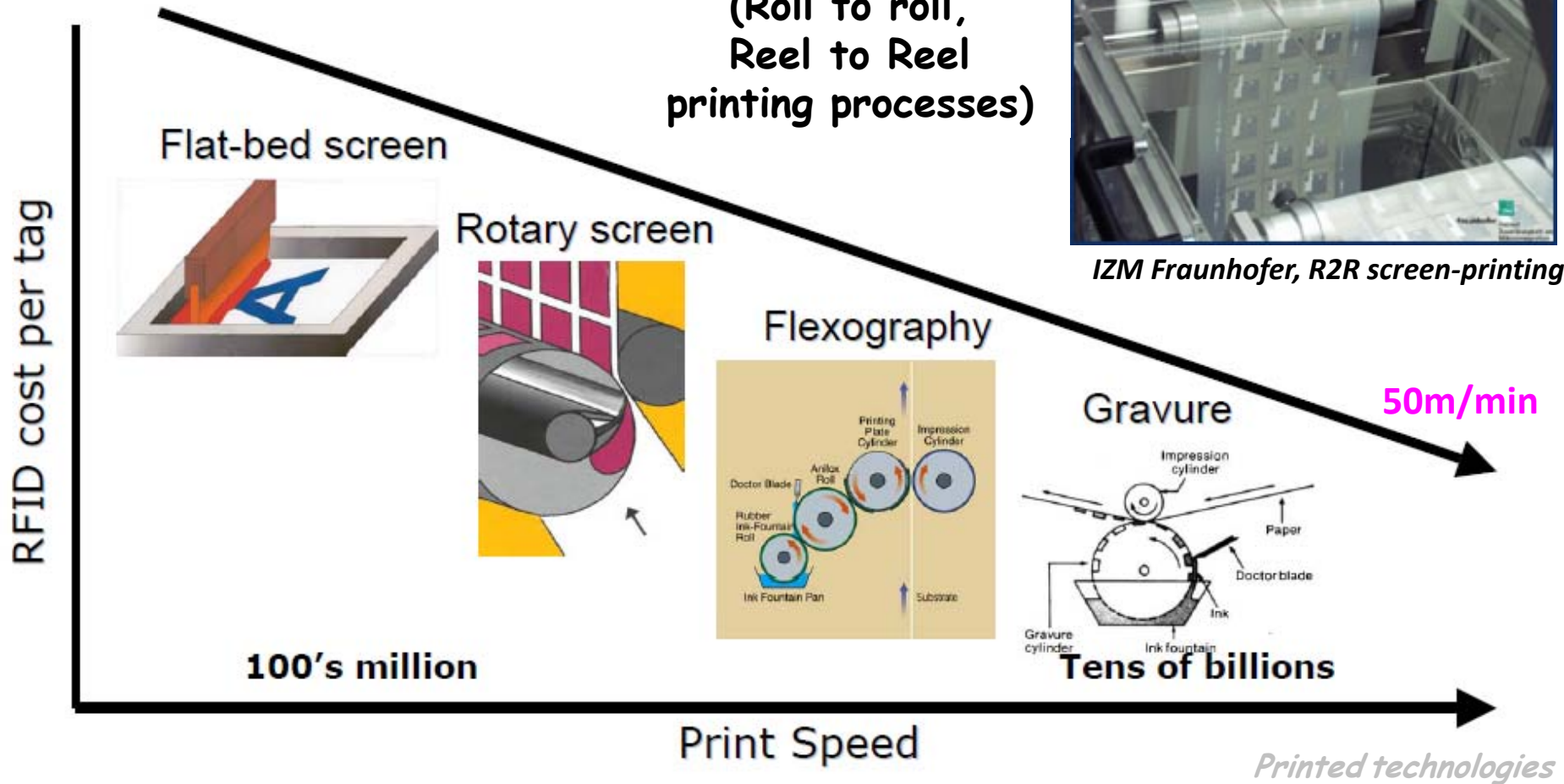
- High speed printing ⇒ Low cost



R2R
(Roll to roll,
Reel to Reel
printing processes)

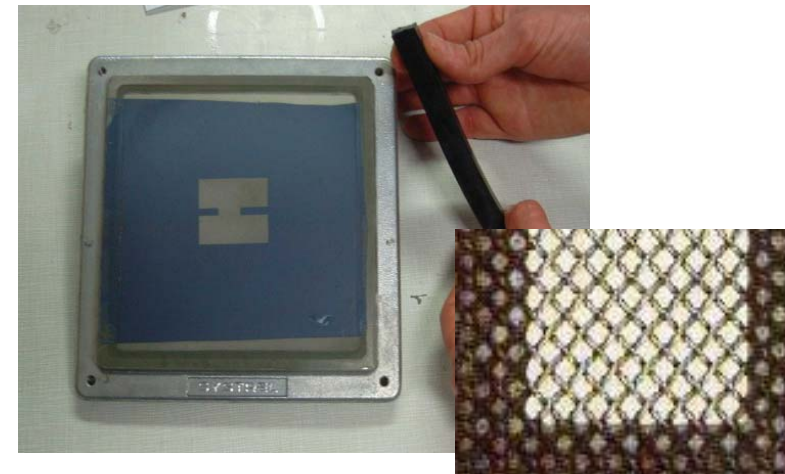
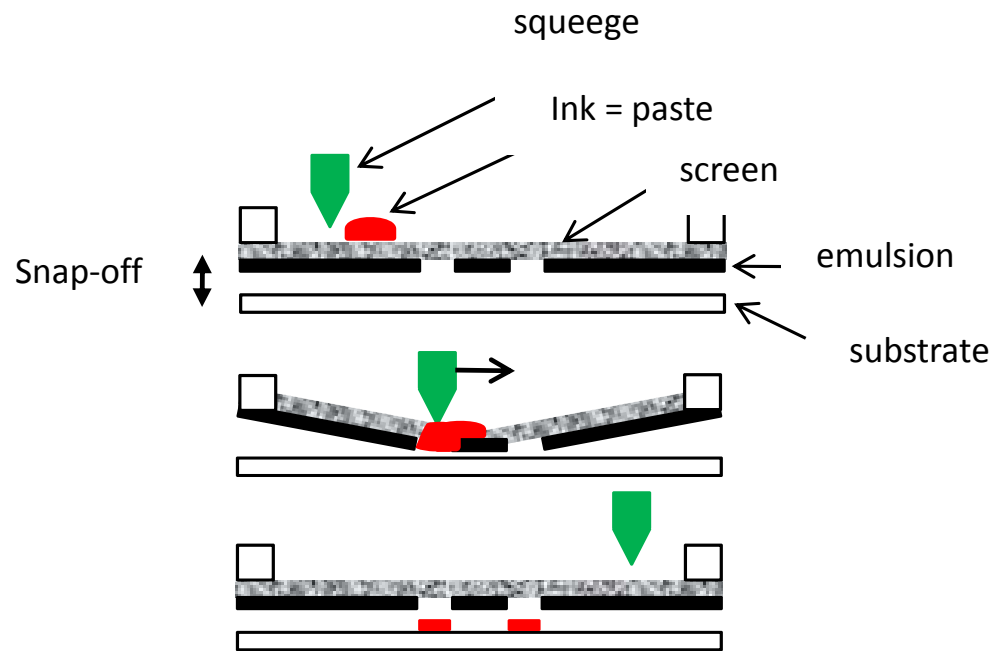


IZM Fraunhofer, R2R screen-printing



Screen-printing

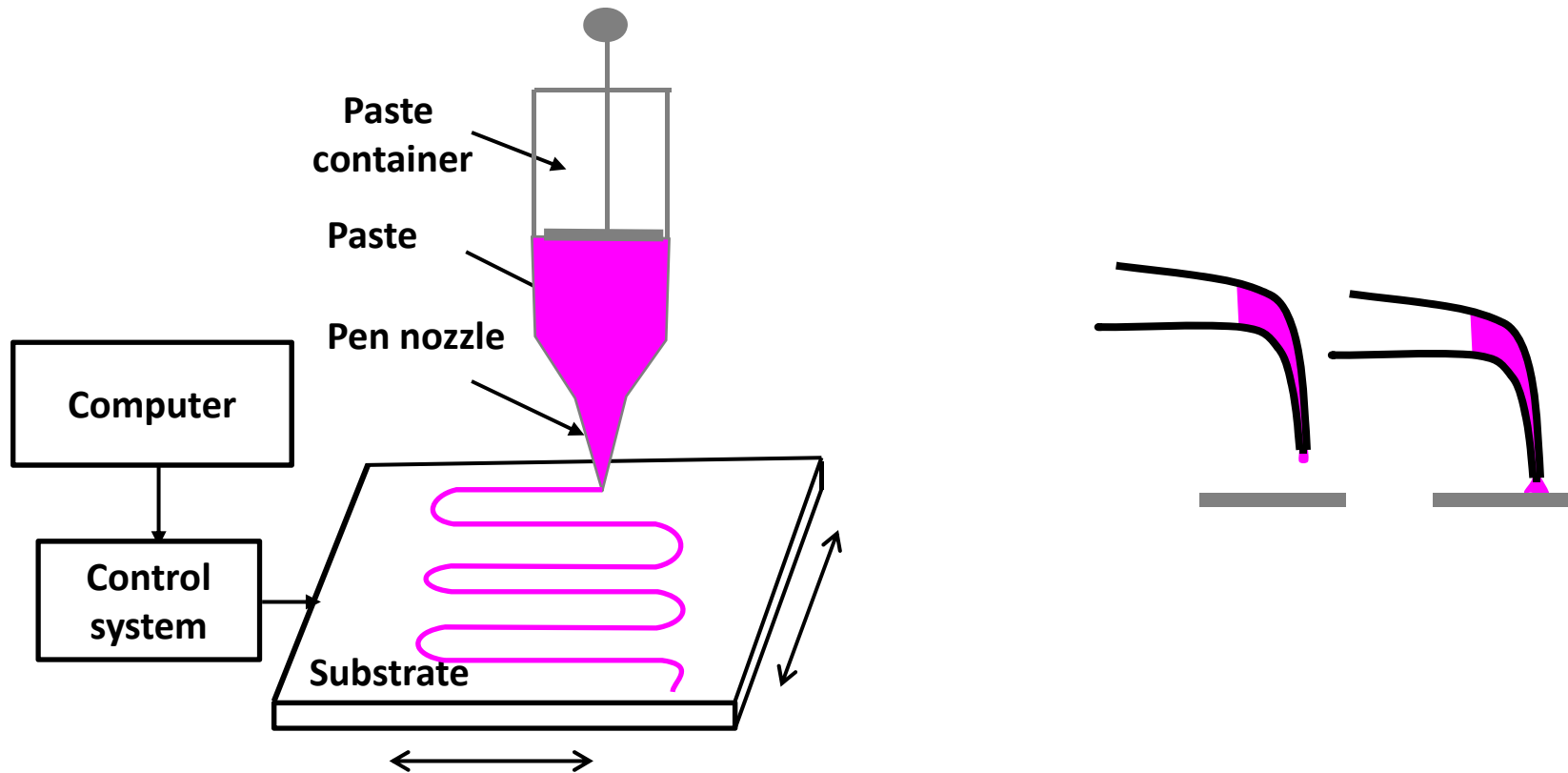
- ❑ Most simple, flexible and cheap



1. Patterning of a screen by photo-lithography
2. Paste transfer onto a substrate through the screen by a squeegee

Direct printing techniques

❑ Filament microdispensing systems (Micropen®)



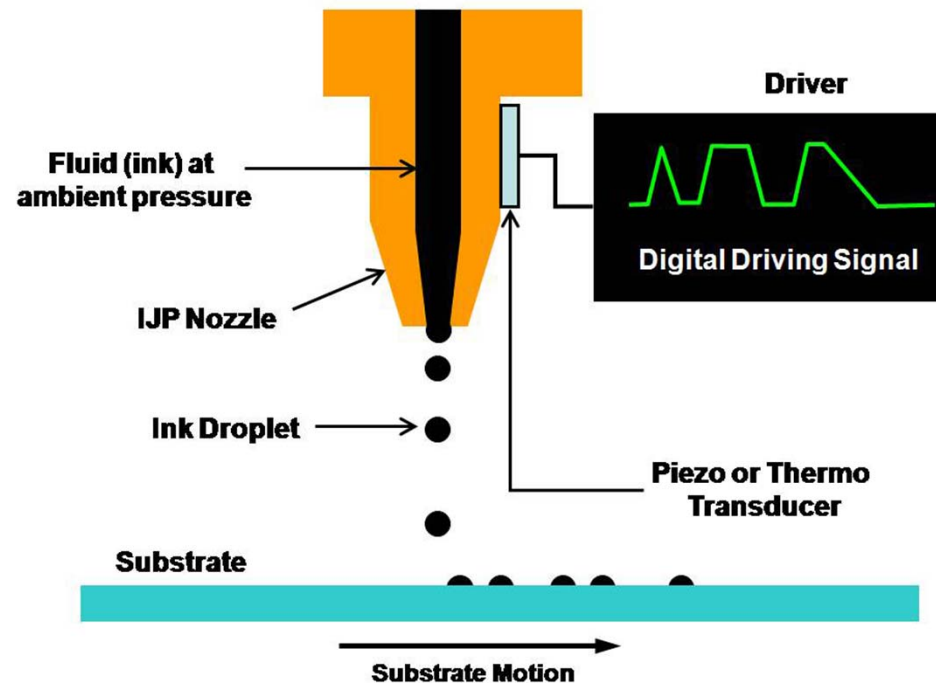
1. Printing pattern created on software

2. Printing via capillarity action

3. Ink loaded in a syringe, compressed and squeezed out into the writing head by controlled pressure

Direct printing techniques

□ Inkjet technology (DOD Drop On Demand *)



<http://spie.org/x18497.xml?ArticleID=x18497>

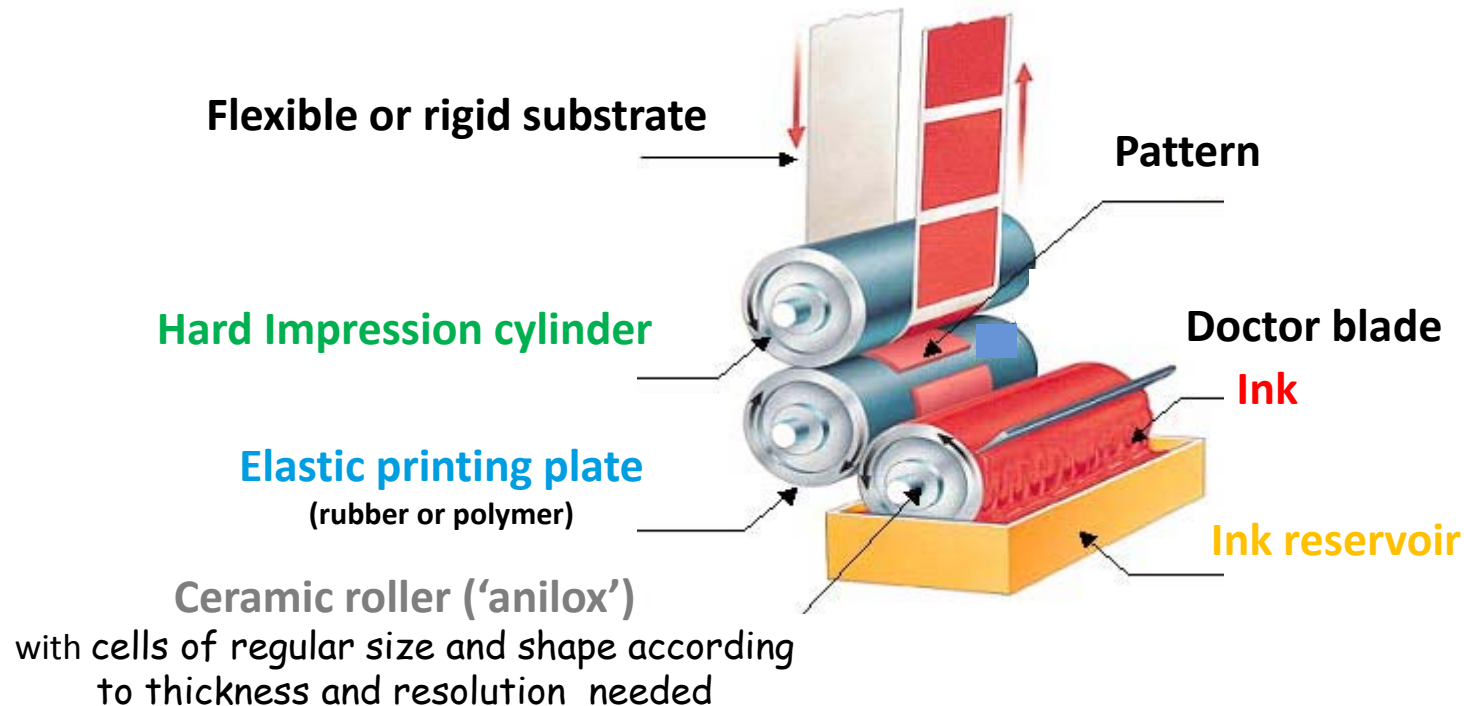
Direct projection of drops ($\varnothing 15-200\mu\text{m}$) on localized area

* CIJ continuous inkjet exists



Reel to reel printing techniques (R2R)

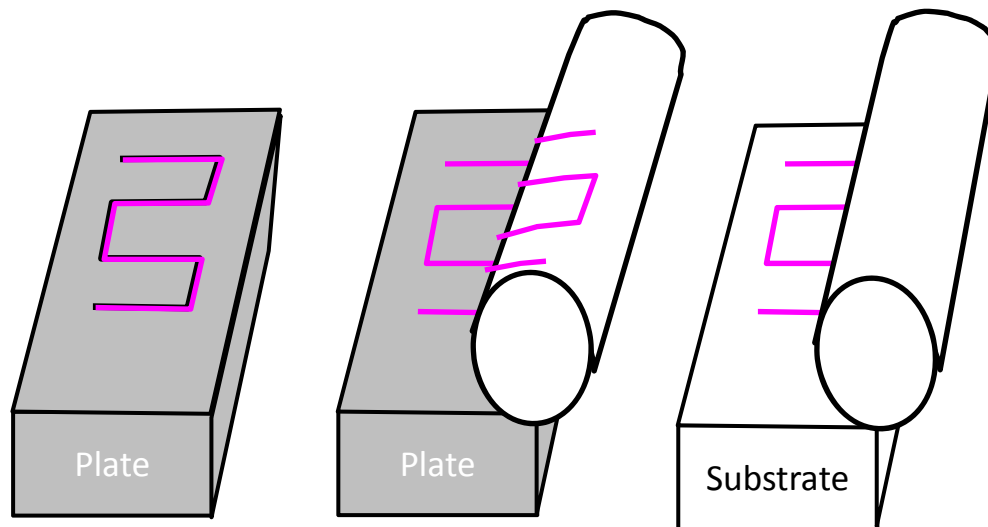
□ Flexography printing (flexo)



1. Pattern engraved on an elastic printing plate
2. Ink in contact with the anilox /scraping off any excess of ink with the doctor blade
3. Ink transfer on the elastic printing plate
4. Printing on the travelling substrate thanks to the hard impression cylinder

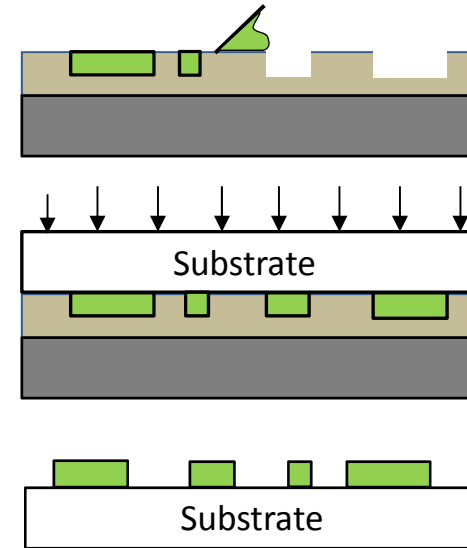
Gravure off set printing

□ Gravure printing process



1. Pattern to be printed engraved on the plate
2. Filling of engravings by doctor-blade method
3. Picking up the ink by rolling action
4. Transfer of the ink to the substrate by similar rolling action

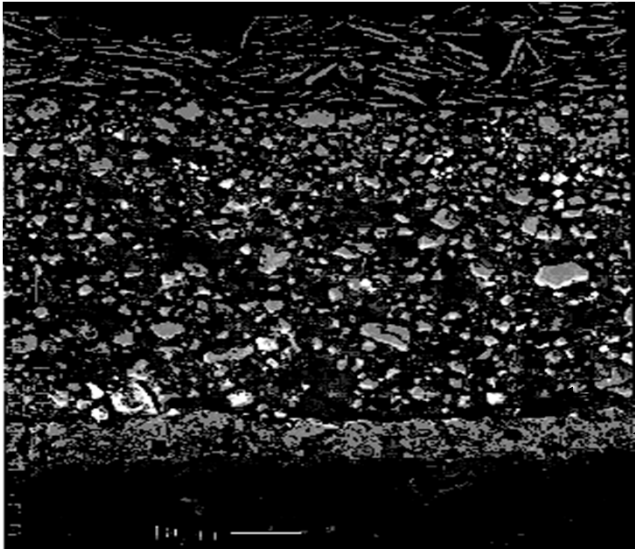
□ Direct gravure printing process



1. Patterned silicone polymer fastened on a smooth metal plate
2. Filling of the grooves in the silicone
3. Transfer of ink by pressing the substrate against ink

Kittilä et al, IEEE transactions on electronics packaging manufacturing, 2004

Printed technologies : summary

	Resolution / Thickness	Substrates	Pastes/inks	Viscosity *
 <p>(from Southampton University)</p>			Conductive, resistive, dielectric...	0.1-10 Pa.s
			Polymer inks ($T_{\text{curing}} < 200^{\circ}\text{C}$) - Organic polymers, - Composites (polymer + powders)	0.005-500 Pa.s
			Inorganic inks ($400^{\circ}\text{C} < T_{\text{sintering}} < 1000^{\circ}\text{C}$) = temporary organic binder + powder	<20m Pa.s
				0.1-10 Pa.s
				0.01-0.5 Pa.s

* Water = 1mPa.s, olive oil = 0.1 Pa.s, Honey= 10Pa.s



Screen-printed PZT MEMS



Processing of piezoelectric MEMS

Thin films

- ☺ Combination with Si micro-machining, precise frequency
- ☹ Poor piezoelectric properties, small displacement, insufficient forces

Thick films

- ☺ Good piezo. properties
- ☺ Force > force with thin films

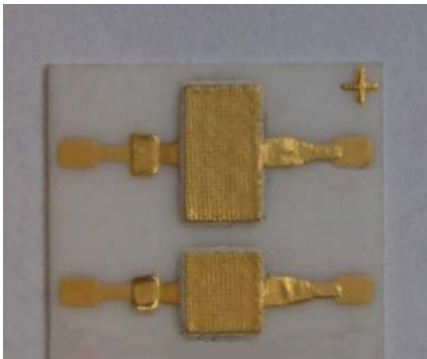
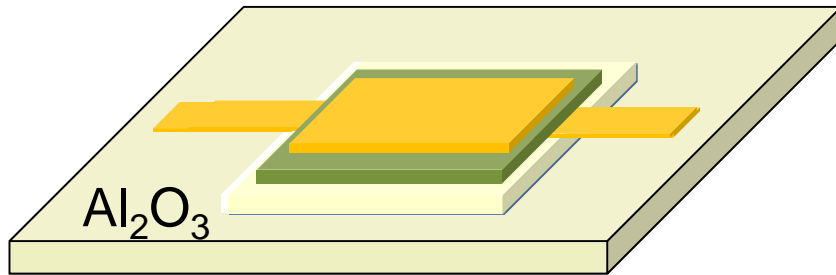
towards free-standing thick films

Ceramics

- ☺ Good piezoelectric properties
- ☹ Thickness, component assembly



Processing of piezoelectric MEMS

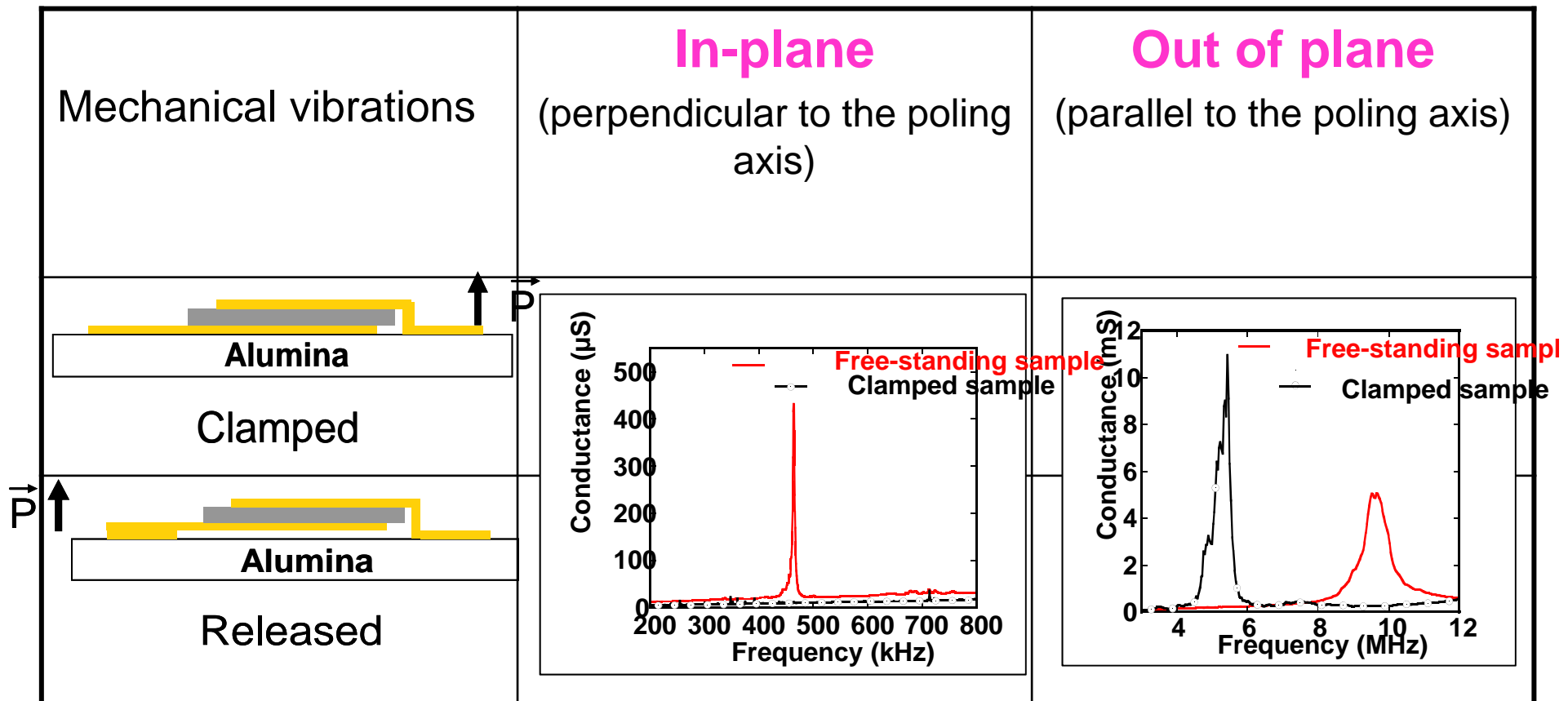


1. Sacrificial layer (epoxy+ SrCO_3)
curing 20min 120°C
2. Bottom electrode (Au),
drying 20min 120°C
3. PZT+ sintering aid
drying 20min 120°C
4. Top Electrode (Au),
drying 20min 120°C
5. Isostatic pressure
(1kBar= 100MPa, 1min)
6. Cofiring 2h, 900°C
→ [3.3x3.3x0.08mm³]
7. Sacrificial layer removal
(0.9mole.L⁻¹ H_3PO_4)
8. Poling (270°C, 5kV.mm⁻¹)
9. Characterization

Comparison clamped/free-standing PZT



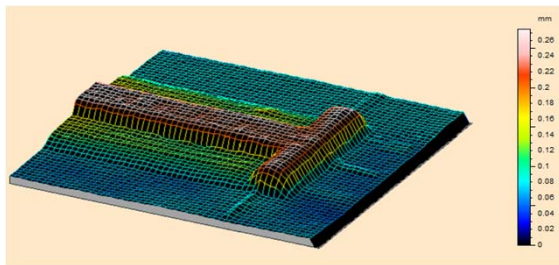
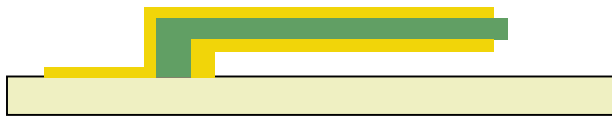
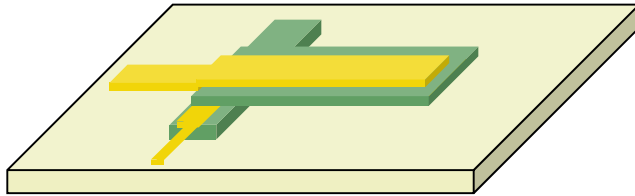
3.3x3.3x0.08mm³



✓ Admittance analysis (HP4194A)

Au/PZT/Au realizations

Cantilever

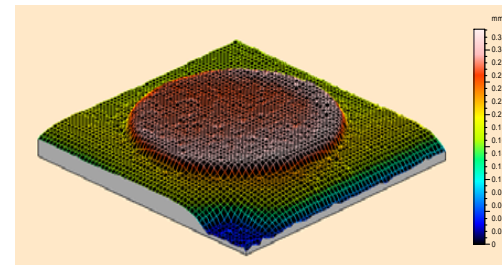
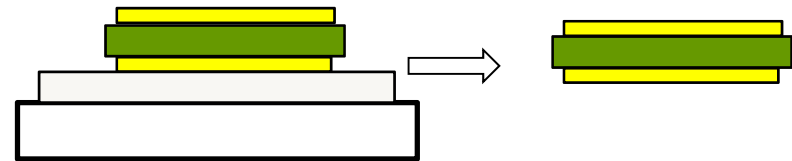


8x2x0.1mm³



↪ Gas detection and viscosity measurement

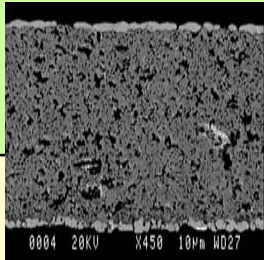
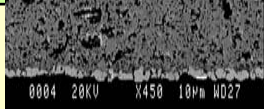
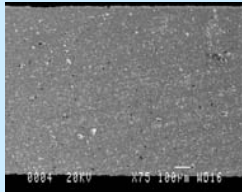
Disk



∅9.5mm x0.2mm

↪ Actuation and damage detection (SHM)

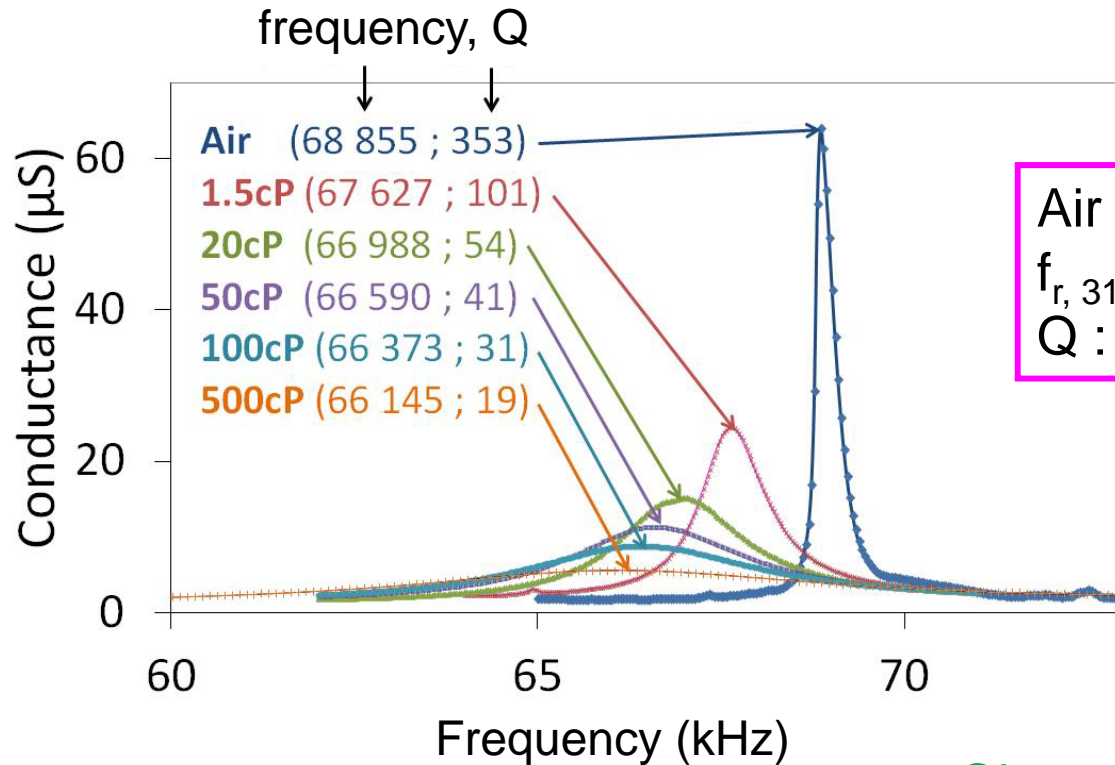
Characterizations (μ structure et electromechanical)

	Porosity	Density (g/cm ³)	K_T^{33}	k_p (%)	$-d_{31}$ (pC/N)	Q	f_{res} (kHz)
Au/PZT/Au disk Ø9.5mm, t=190 μ m		5.5	410	15	40	350	170
Au/PZT/Au cantilever 8x2x0.1mm			330	-	80	400	70
Au/PZT/Au pellet Ø11.5mm, t=950 μ m		7.2	900	46	80	280	140
PIC151 commercial Ø10mm, t=0.3mm	-	7.7	2900	66	200	90	240

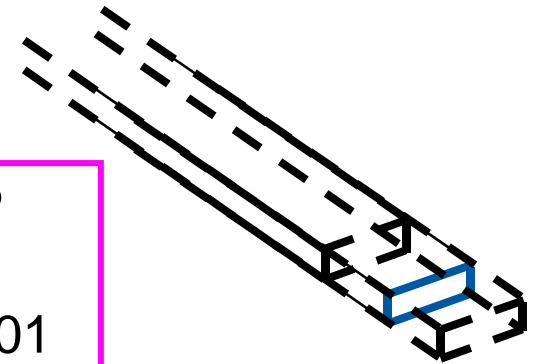
Thick-films properties < ceramics ... MEMS tests

Au/PZT/Au cantilever: sensor

↪ Viscosity measurement, use of longitudinal mode, uncoated



Air to 1.5 cP
 $f_{r, 31} \rightarrow 1.8 \%$
 $Q : 353 \rightarrow 101$

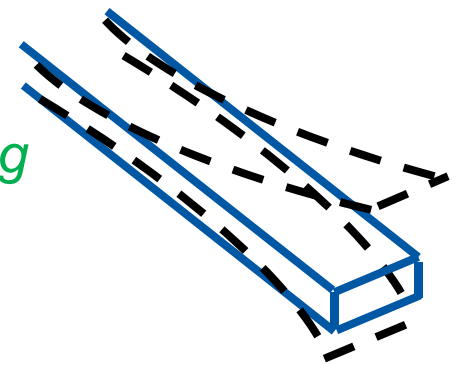


Si cantilever, bending

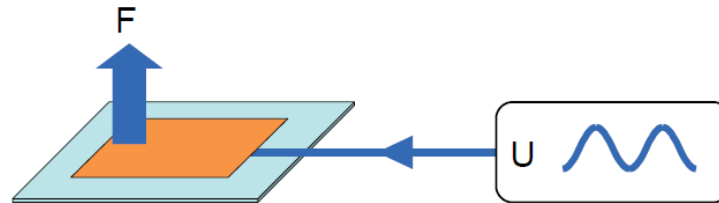
Air to 1cP (water)

$f_{r, flexural} \rightarrow 50 \%$

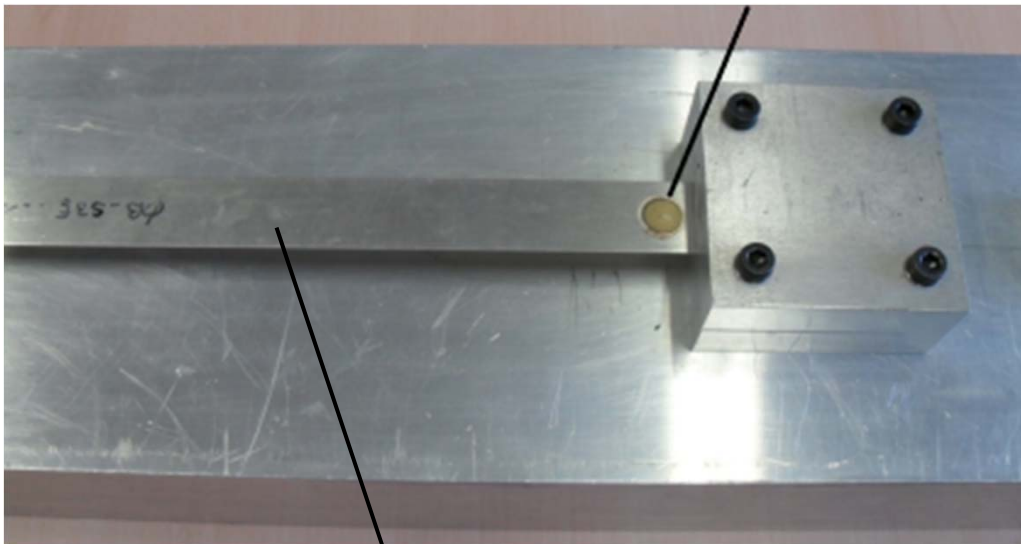
$Q = 1500 \rightarrow \approx 10$



Au/PZT/Au disk: actuator



Au/PZT/Au disk $\varnothing 9.5\text{mm}$, $t=190\mu\text{m}$



Steel beam ($200 \times 20 \times 0.48\text{mm}^3$)

$U=100\text{ V}$ (peak to peak)
 $f=10\text{ Hz}$ (beam's resonance)



Oscillations: speed= 73 mm/s
Max amplitude 1.16 mm (tip)

PI ceramic ($\varnothing 10\text{ mm}$, $t=300\mu\text{m}$)

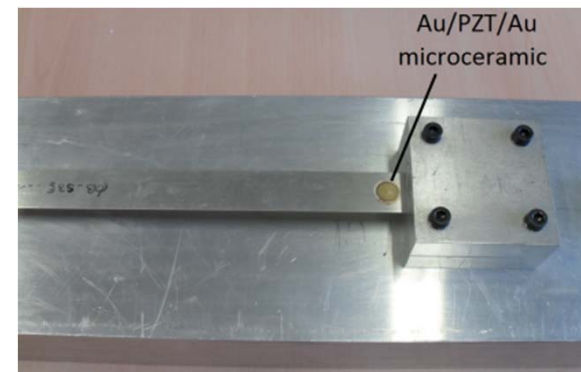
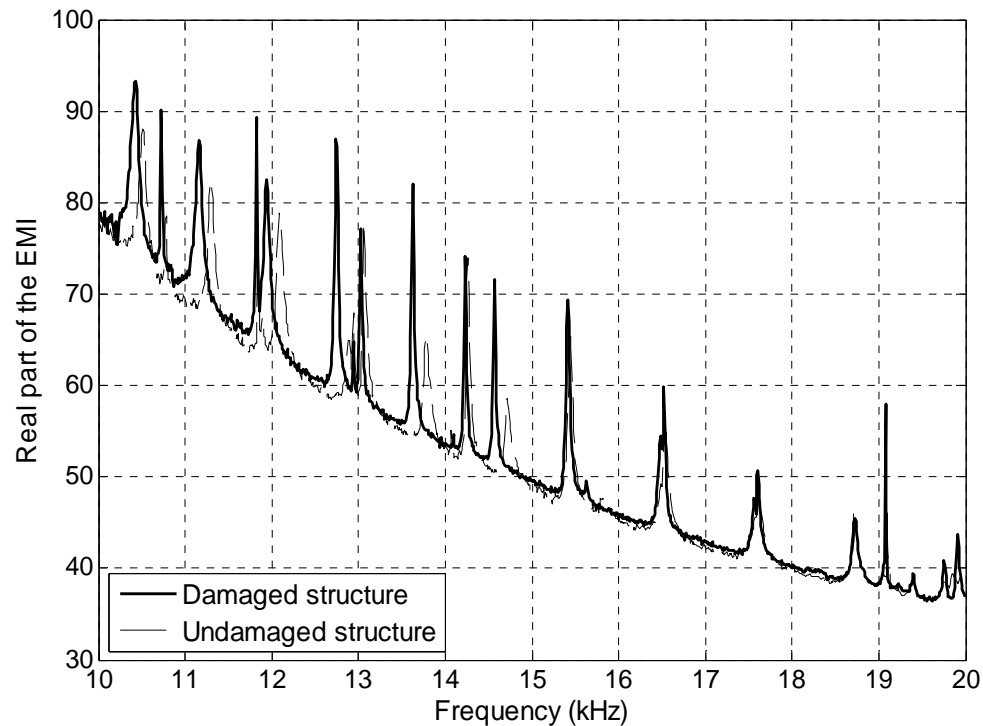
Oscillations: speed= 380 mm/s
Max amplitude 6.02 mm

Au/PZT/Au disk: sensor

↳ Structural health monitoring

Electro-Mechanical Impedance method (EMI):

damage \Rightarrow change of the electromechanical coupling of the ceramic bonded or embedded in structure

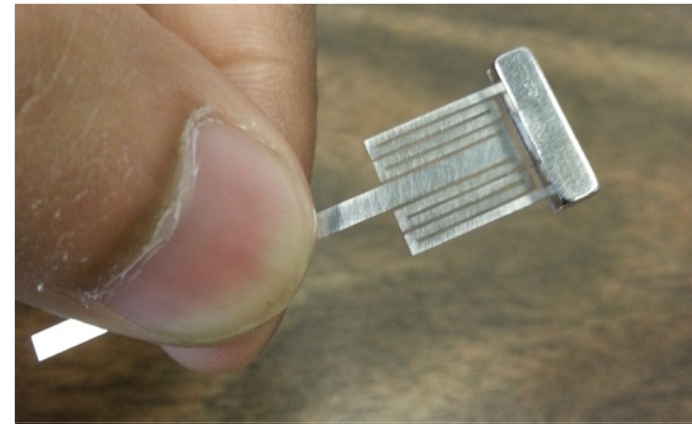
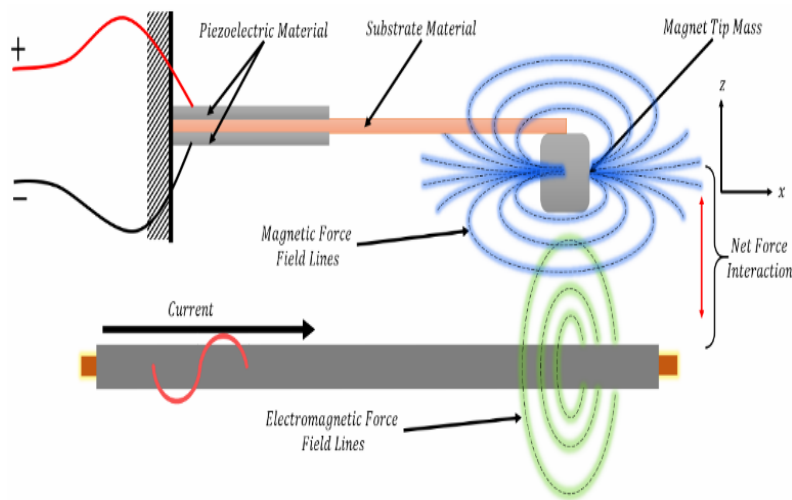


$$\Delta f_{\text{mean}} (\%) = \frac{\sum_{n=1}^{N_{pks}} |f_n^D - f_n^{UD}| / f_n^{UD}}{N_{pks}} * 100\%$$

Alternative to free-standing PZT: PZT supported on stainless steel

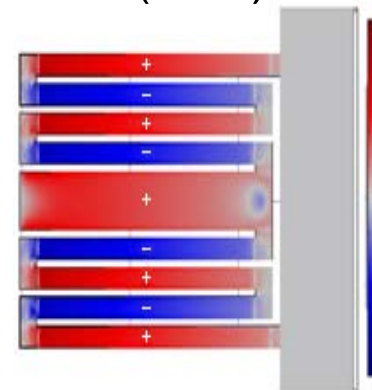
➤ Energy harvesting for smart grid

Piezoelectromagnetic cantilever beam



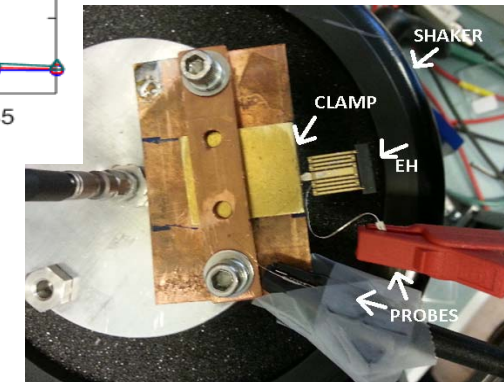
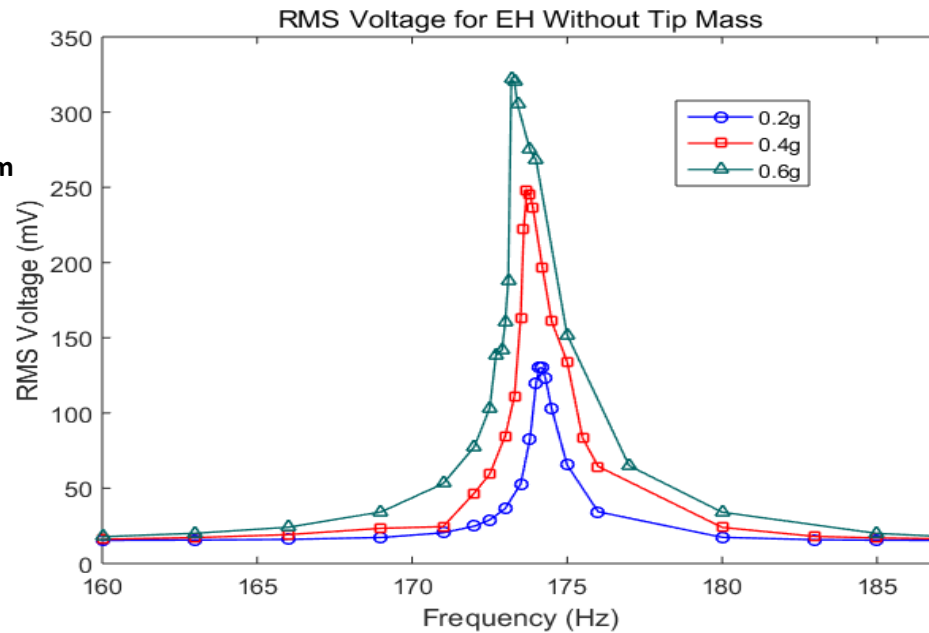
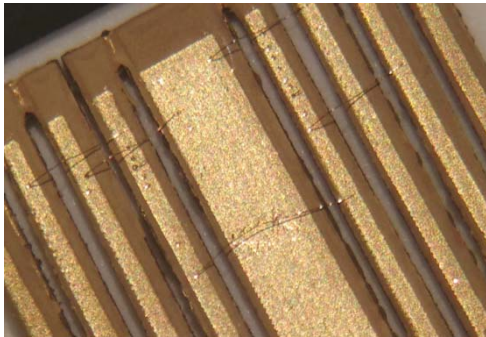
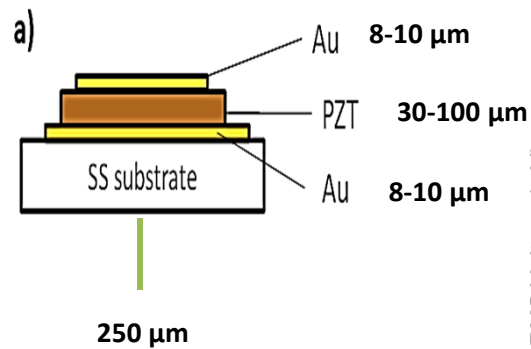
Optimized **meander shaped beam** and Strain contour plot showing tension (red) and compression (blue).

- In North America AC power transferred at 60 Hz
- Need to tune system to 60 Hz for resonance resulting in maximum power output



Alternative to free-standing PZT: PZT supported on stainless steel

Energy harvesting for smart grid



A large blue shape that is a right-angled triangle with its hypotenuse facing the bottom-left, positioned in the top-left corner of the slide.

Printed gas sensors:
toward RT detection



université
de BORDEAUX

Gas sensor requirements



○ Low cost



Screen-printed gas sensors

○ Portable

○ Good sensitivity



Nano-materials

○ Selective



Multi-sensors

○ Stable

○ Low consumption



Toward room temperature

○ User friendly operation

- Nano-materials

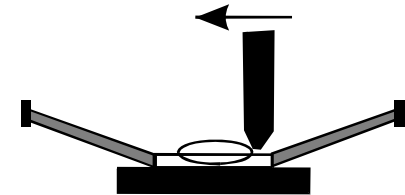
○ Easy calibration

- UV activation

○ Cheap and easy maintenance

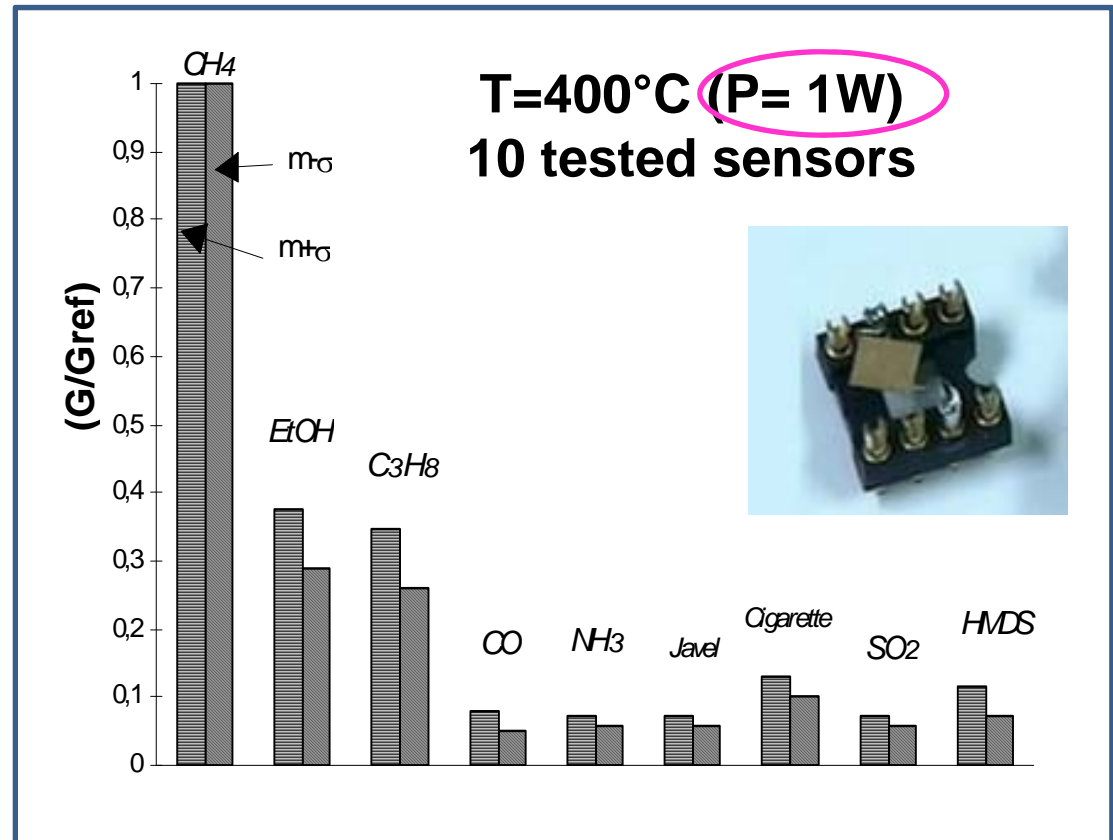
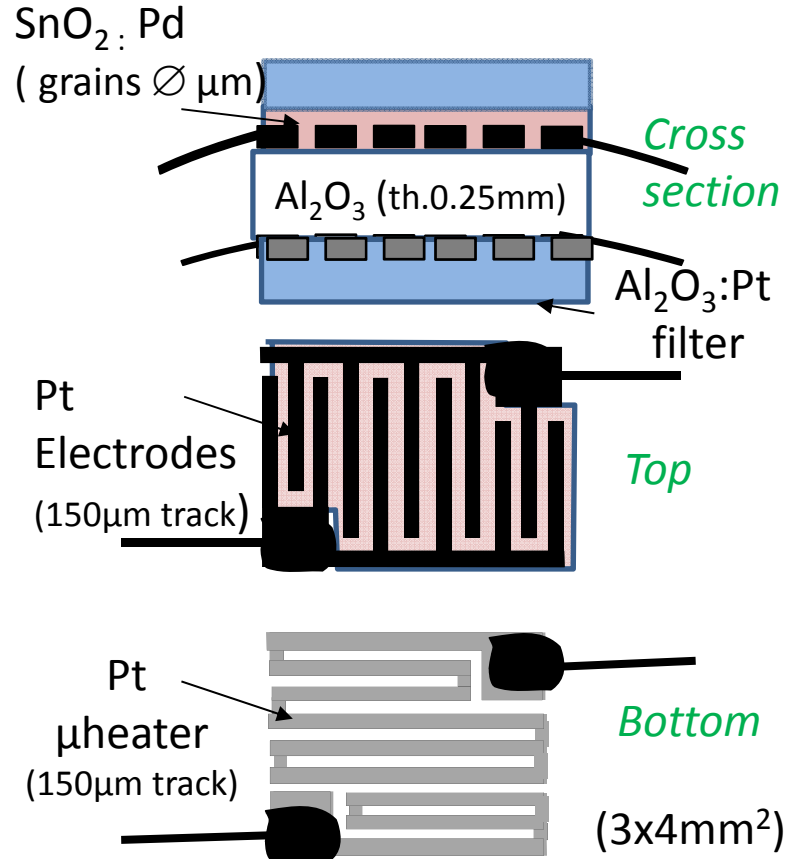
- Cantilever gas sensors

○ Flexible and biocompatible if possible ...



Selectivity toward CH₄: multi-sensors

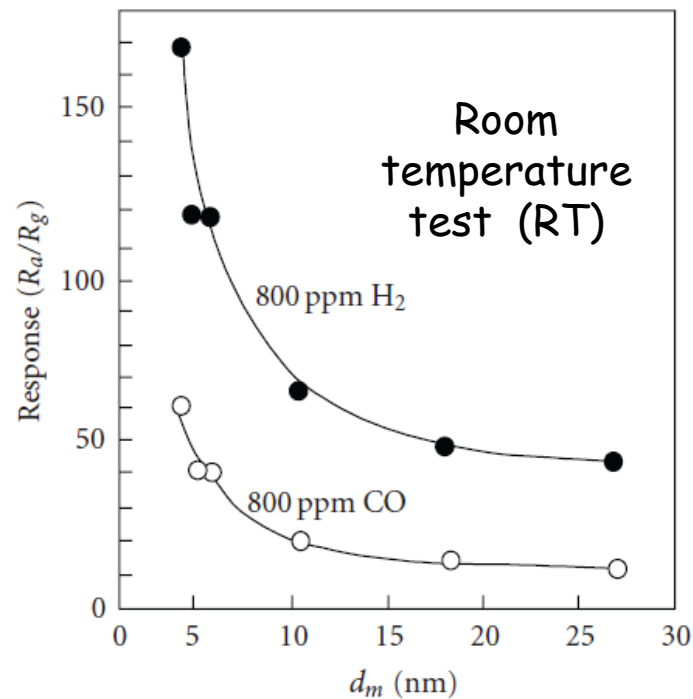
Resistive (SnO₂) and catalytic sensors (Pd, Pt)



⇒ Sensitive ($R_{air}/R_{CH_4} \sim 6$), selective and stable
≡ Figaro MOX sensors (GDF tests)

Reduction of operating T ? \Rightarrow nanomaterials

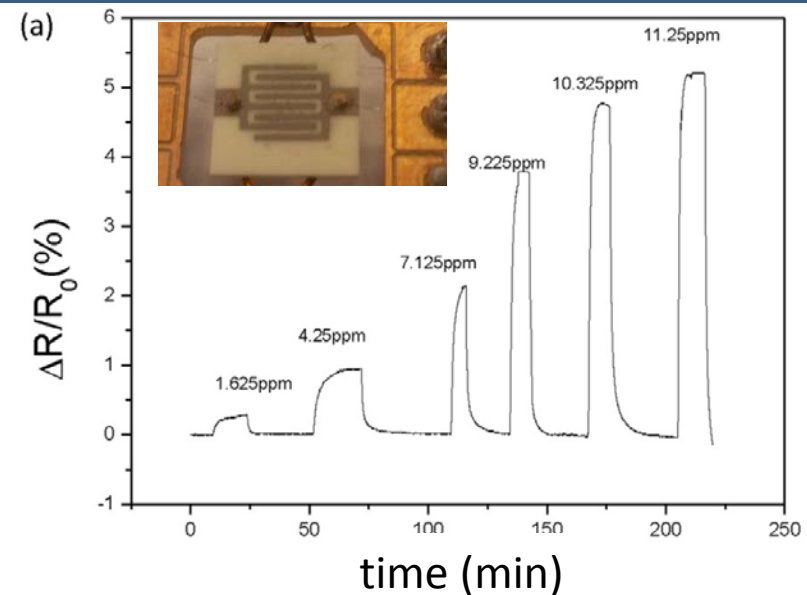
- Metal Oxide Semiconductors
MOX (SnO_2 , ZnO , WO_3 ...)



Brush coated SnO_2 thick film,
influence of nanoparticle size

Journal of Sensors, 2009
N. Yamazoe and K. Shimano

- Carbon nanotubes CNTs



Benzene detection at
room temperature

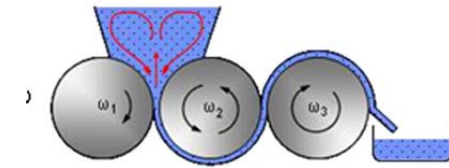
Sensors and Actuators B: Chemical, 2013
I. Hafaiedh, W. Elleuch, P. Clément,
E. Llobet, A. Abdelghani

Nanoceramics, H₂ resistive ZnO sensors

1. ZnO nanopowder (Nanotech ®, APS 40-100nm, S.A. 10-25m²/g)

2. Paste preparation

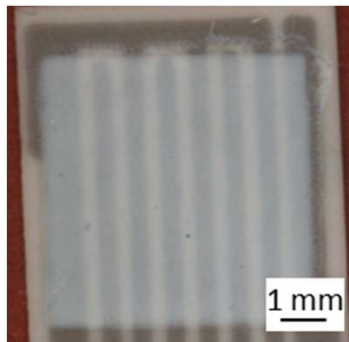
- 30%wtZnO + organic binder (ESL400)
- 3 roller mill → viscosity 0.1-10 Pa.s



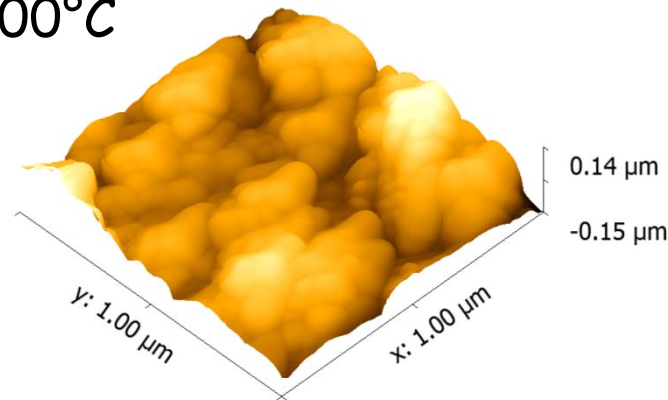
3 roller mill

3. Printing on Al₂O₃ substrate (Pt IDTs + Pt μ heater)

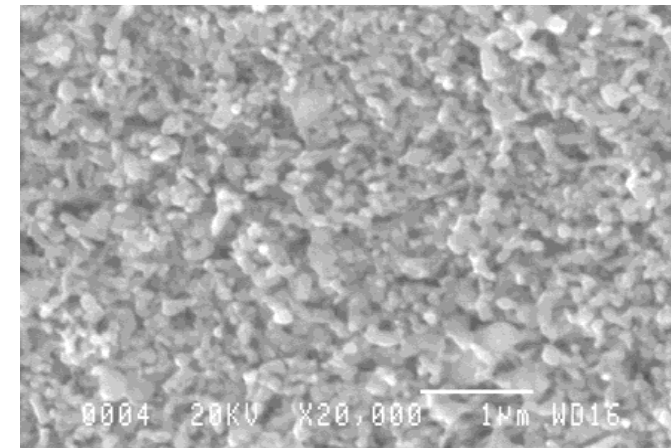
4. Firing 30min 400°C



8.5x6.3x0.6mm³



AFM image

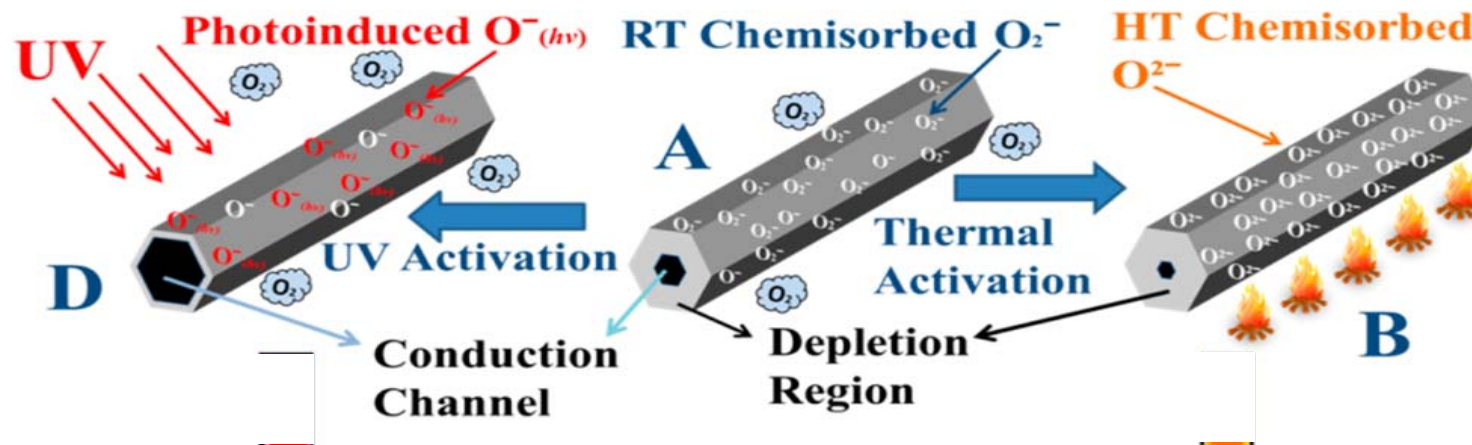


SEM image

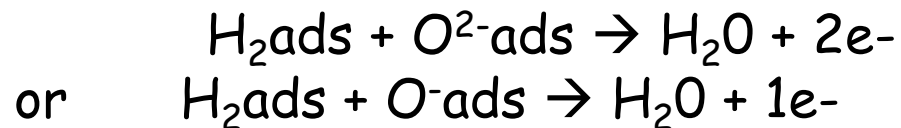
Nanograins ~ 100nm

ZnO nanoceramics, RT H₂ detection

Higher sensitivity \Rightarrow Energy activation, UV or T

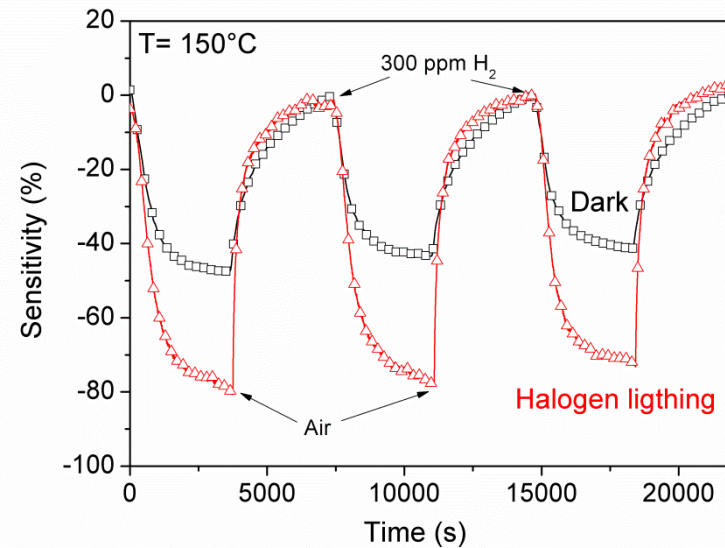
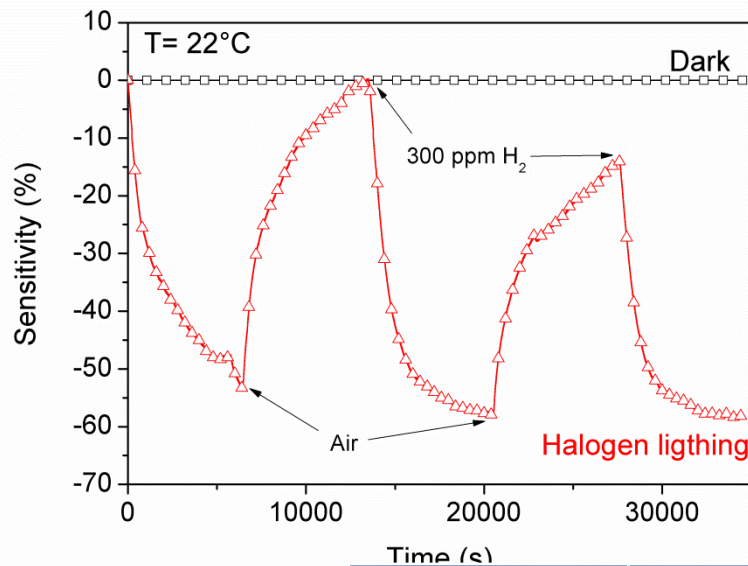


J. Phys. Chem. 2013, M. R. Alenezi



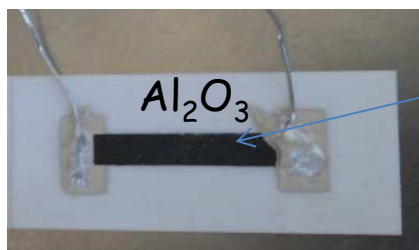
ZnO nanoceramics, RT H₂ detection

Halogen lighting (15 μW/mm²)



Temperature	Light	Sensitivity (%)
RT	No	0
	Halogen (15 μW/mm ²)	44
150°C	UV (7.7 mW/mm ²)	43
	No	38
	Halogen (15 μW/mm ²)	71
	UV (7.7 mW/mm ²)	94

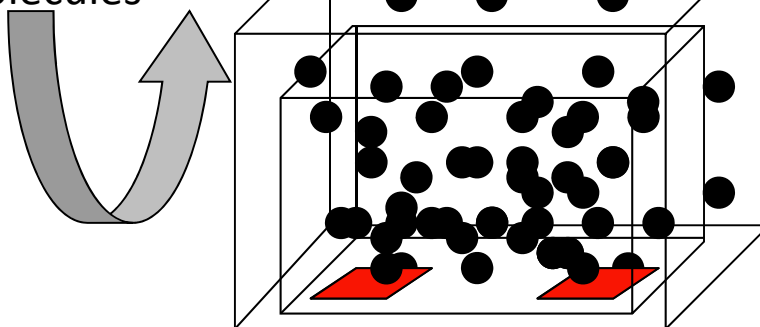
Nanocomposite based resistive sensor



- Black carbon + epoxy + bistable nanoparticles (NPs \varnothing 45nm, $\text{Fe}(\text{Htrz})_2\text{trz}] \text{BF}_4 \cdot \text{H}_2\text{O}$ SCO complex)
- Printing, drying 120°C , curing 150°C
- Ag contact

■ Gas sensor principle

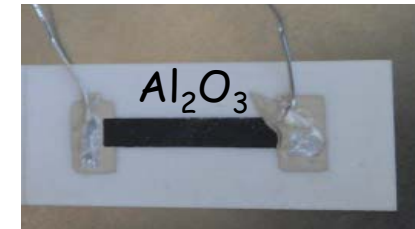
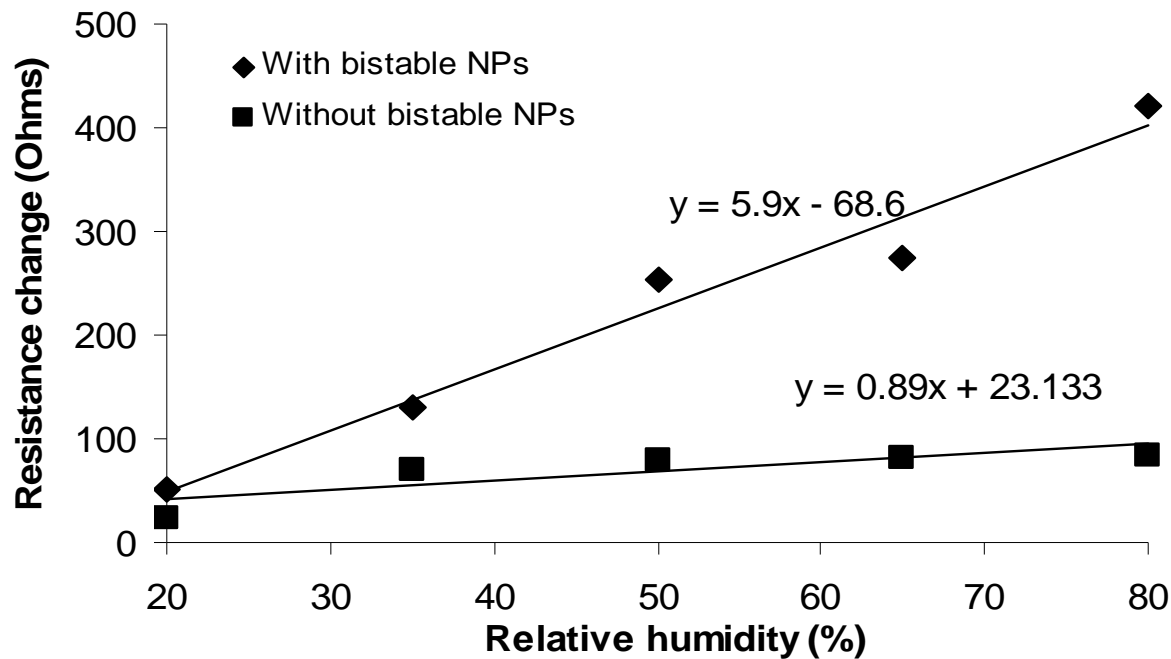
H_2O
molecules



$\text{H}_2\text{O} \Rightarrow$ Swelling of epoxy + bistable NPs
 \Rightarrow Resistance \downarrow (percolation phenomena)

Nanocomposite based resistive sensor

■ RT tests



3x15x0.02mm³

$$R_{\text{without NPs}} = 5.2\text{k}\Omega$$
$$R_{\text{with NPs}} = 9.4\text{k}\Omega$$

- ⇒ 6x higher with bistable nanoparticles
- ⇒ Possibility to use organic substrate

Gas sensor requirements



○ Low cost

○ Portable

○ Good sensitivity

○ Selective

○ Stable

○ Low consumption

○ User friendly operation

○ Easy calibration

○ Cheap and easy maintenance

○ Flexible and biocompatible if possible ...

Screen-printed gas sensors

Nano-materials

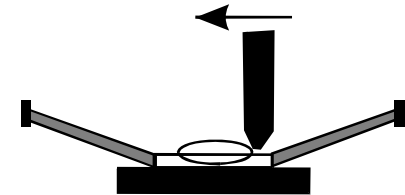
Multi-sensors

Toward room temperature

- Nano-materials

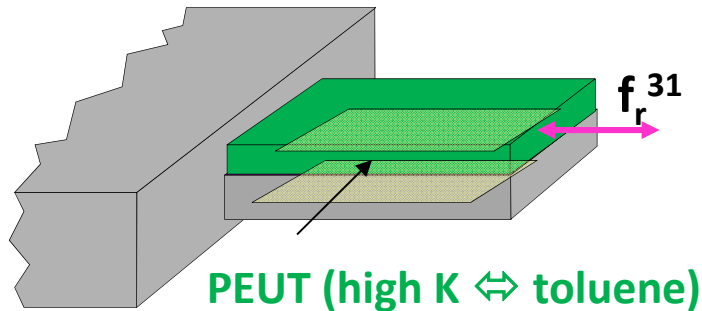
- UV activation

- Cantilever gas sensors



Screen-printed cantilever gas sensors

Toluene detection with Au/PZT/Au cantilever



- Piezoelectric effect \Rightarrow actuation and detection
- In plane 31 Longitudinal resonant mode \Rightarrow high resonant $f_r \Rightarrow$ high sensitivity S

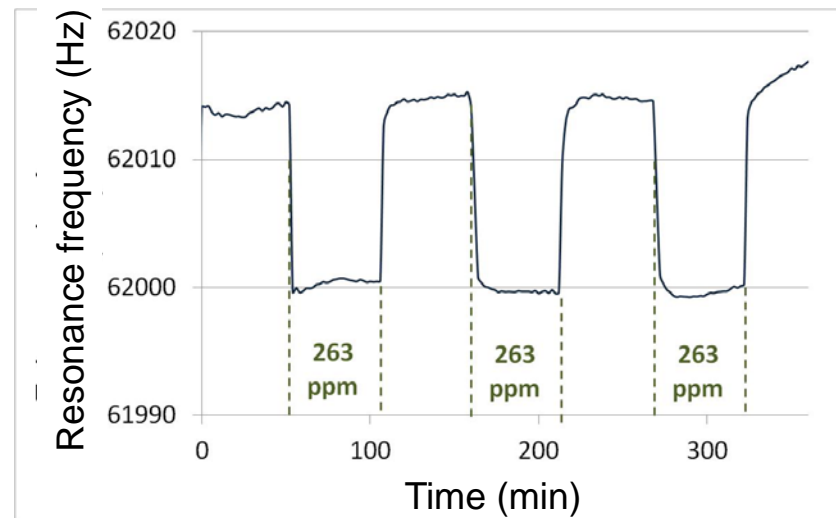
$$S = \frac{\Delta f_{31}}{\Delta C_g}$$

with:

$$f_{31}^{(n)} = \frac{\lambda_{31}^{(n)}}{2\pi} \sqrt{\frac{k_p + k_{sl}}{m_p + m_{sl} + L_{sl} \cdot b_{sl} \cdot h_{sl} \cdot K \cdot C_g}}$$

- k_p : cantilever's spring constant
- k_{sl} : sensitive layer's spring constant
- h_{sl} : sensitive layer's thickness
- b_{sl} : sensitive layer's width
- L_{sl} : sensitive layer's length
- K : sensitive layer's partition coefficient
- C_g : gas concentration

H. Debéda et al, Sensors and actuators B, 2013



$$S = 465 \cdot 10^{-4} \text{ Hz/ppm, LOD} = 80 \text{ ppm}$$

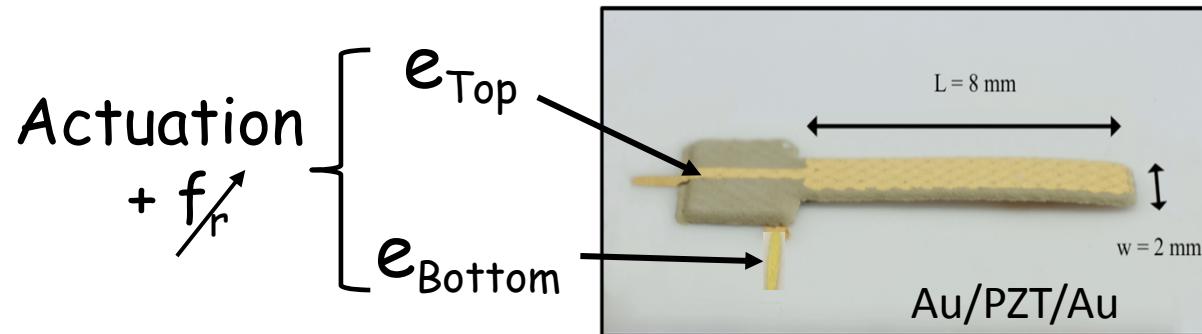
Si cantilever + PEUT, bending, $f_r = 3 \text{ kHz}$

$$S = 9 \cdot 10^{-4} \text{ Hz/ppm, LOD} = 47 \text{ ppm}$$

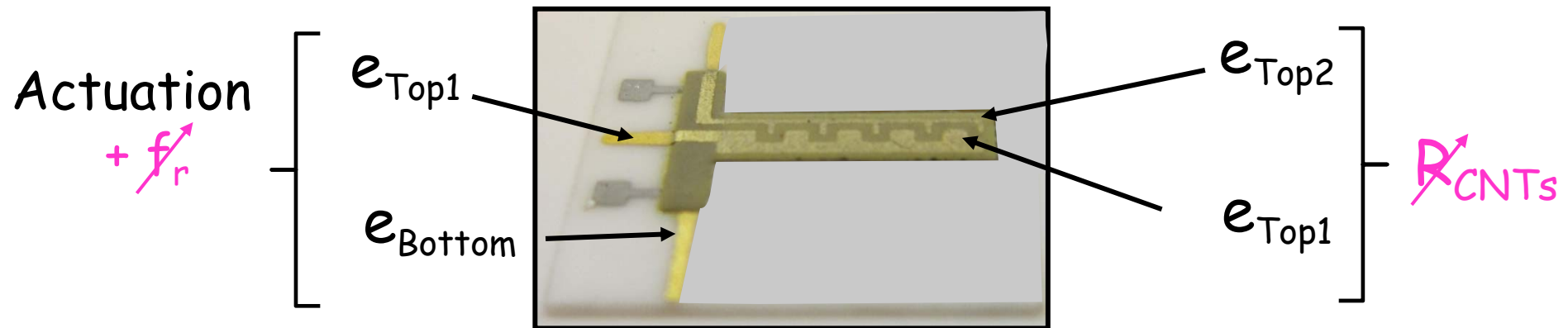


Double transduction : PZT + CNTs

- Simple transduction: *resonant*



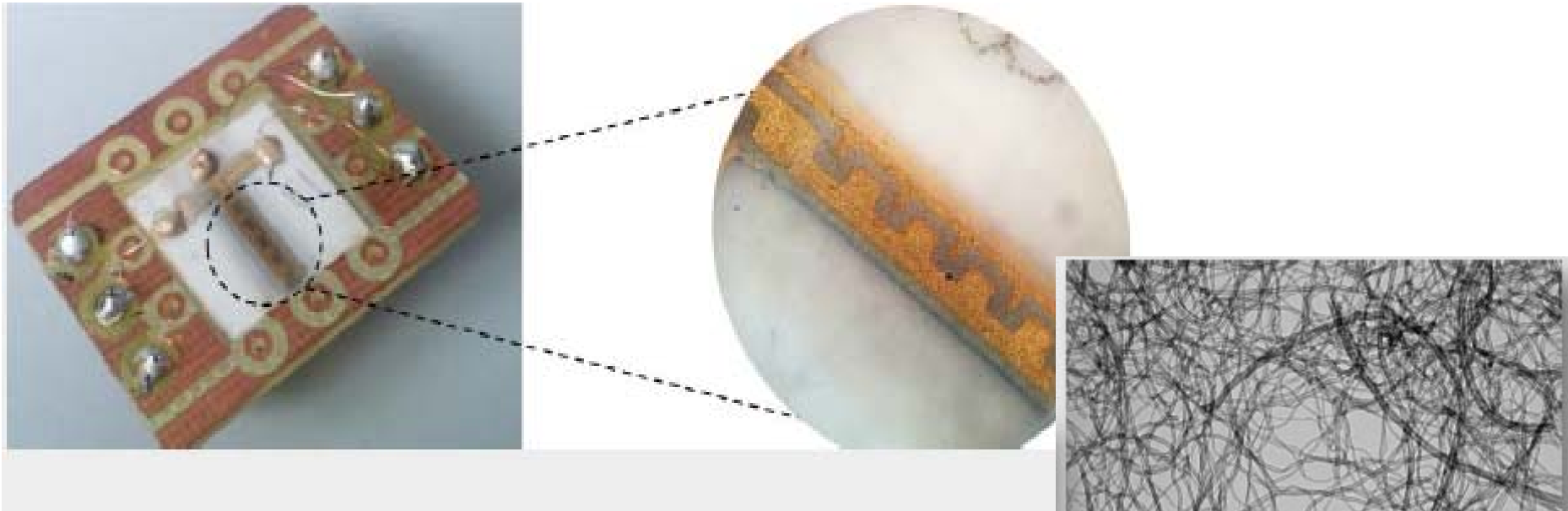
- Double transduction: *resonant + resistive*



Double transduction: all printed

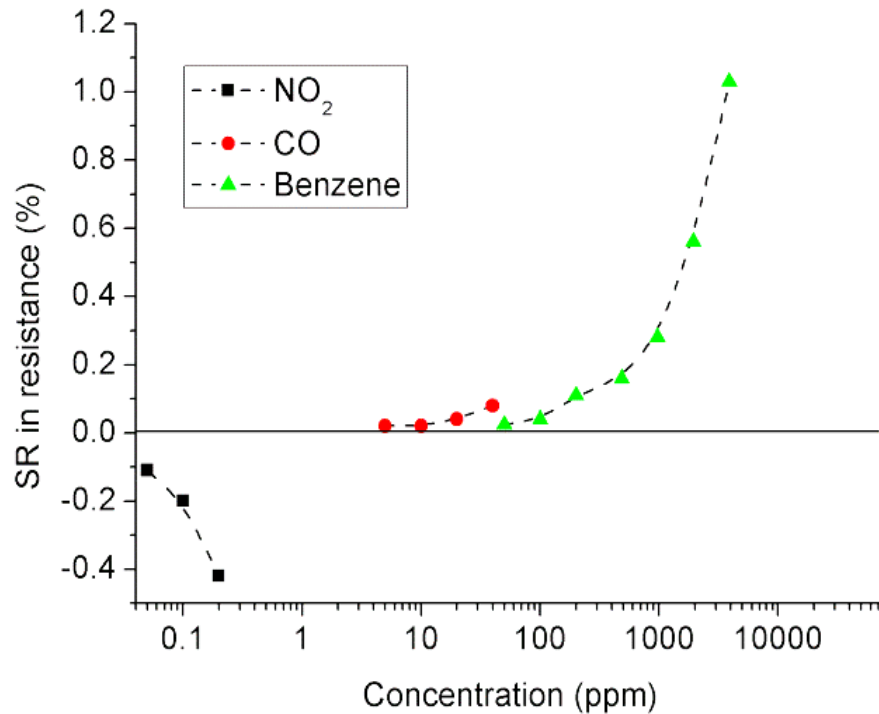
Sensitive coating deposition

- MWCNTs air brushing



Length $50\mu\text{m}$, Outer
 \varnothing 3-15nm, Inner \varnothing 3-7nm (Nanocyl) \rightarrow $300\text{m}^2/\text{g}$

Double transduction: PZT + CNTs



- Discrimination between oxidizing and reducing gases with the resistive sensor response

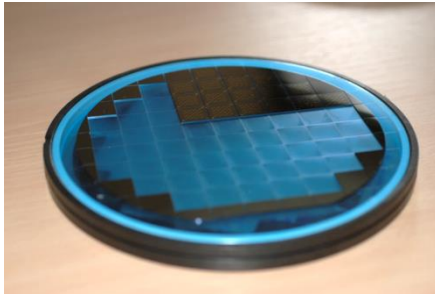
Limit of detection (ppm)	<i>Benzene</i>	<i>CO</i>	<i>NO₂</i>
Resistive	2	30	0.05
Mass	1	5	0.05

Organic MEMS

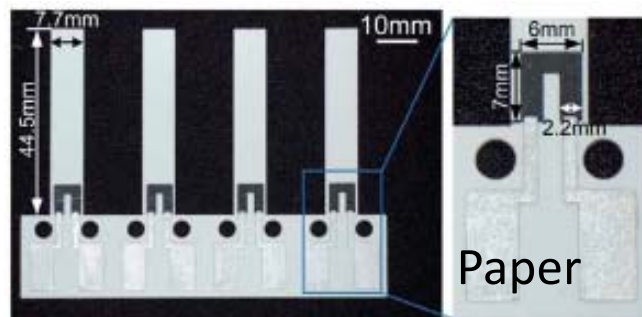


Attraction of organic electronics

Inorganic

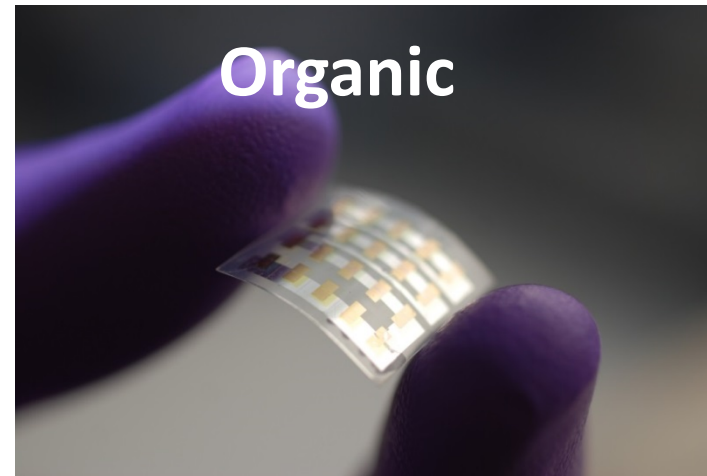


- Rigid, hard, heavy
- Expensive
- Confined in wafer
- Requires clean-room facilities
- Time and energy consuming



X. Lui *et al*, Lab. Chip., (2011)

Organic



- Flexible, stretchable, lightweight
- Low-cost
- High throughput, large surface
- Non-toxic, abundant
- Solution process, low temperature

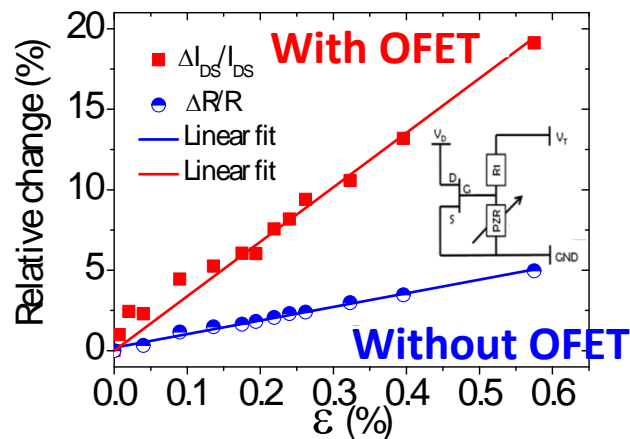
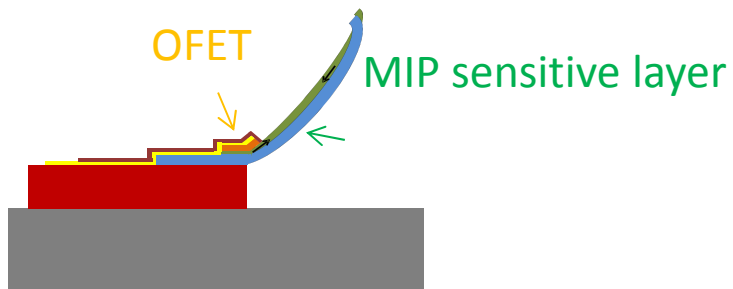
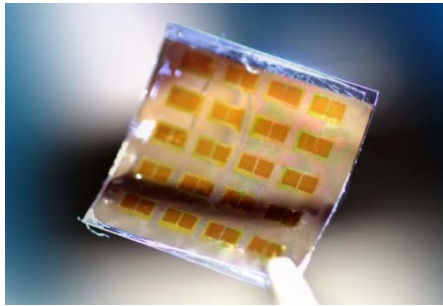


K. Bourzac *et al*, Nature News, (2012)

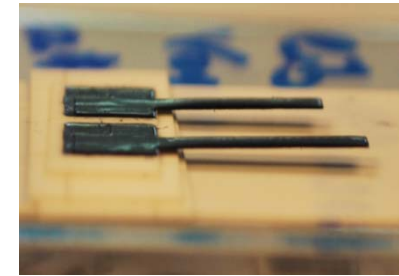
Organic MEMS: gas sensors

Cantilever: static mode

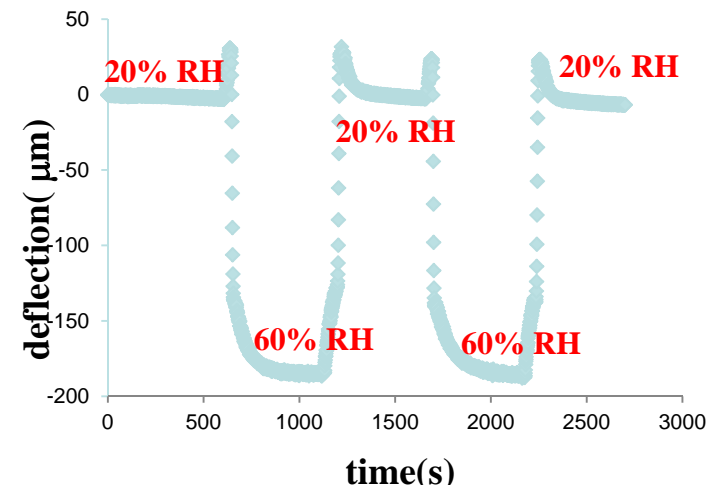
Molecular Imprinted Polymer (MIP) / OFET



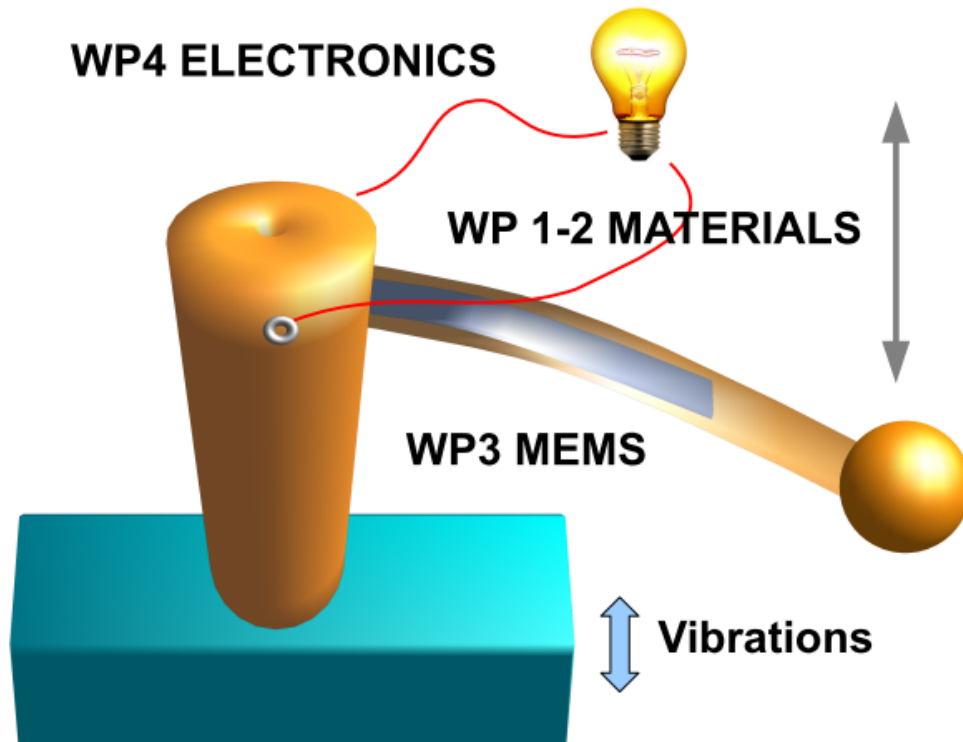
EPOXY/carbon / agarose coating



$L=10\text{mm}$, $b=2.5\text{mm}$, $h=80\mu\text{m}$



Organic MEMS: energy harvesting



ORGANIC CANTILEVER

High mass part (composite)

Low stiffness part (organic)

Electrostrictive layer (CNT composite)

Electrodes

PRINCIPLE

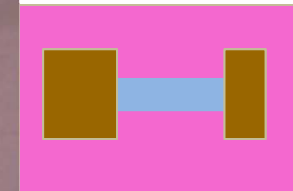
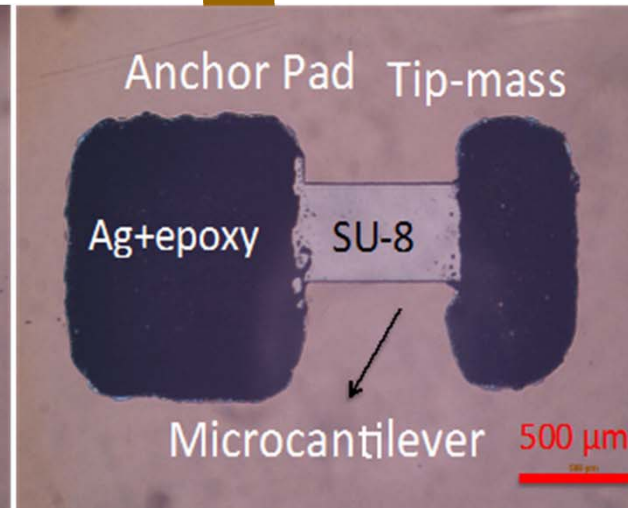
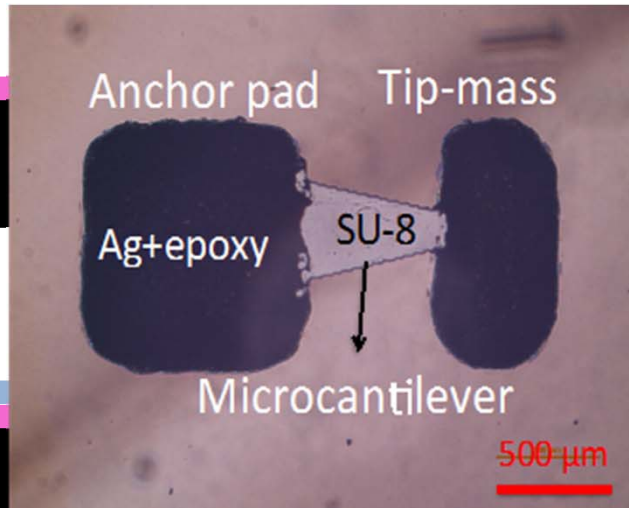
Environmental vibrations \rightarrow stress/strain \rightarrow permittivity change of electrostrictive layer \rightarrow capacity change \rightarrow electronics for energy harvesting

Organic MEMS: energy harvesting

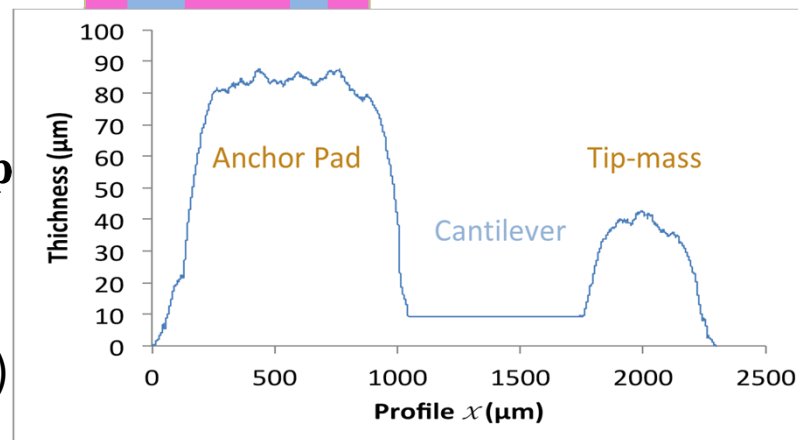
Processing

Spin coating

Screen-printing



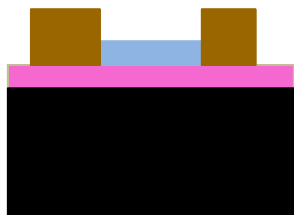
omnicoat



c)

e)

Screen-p



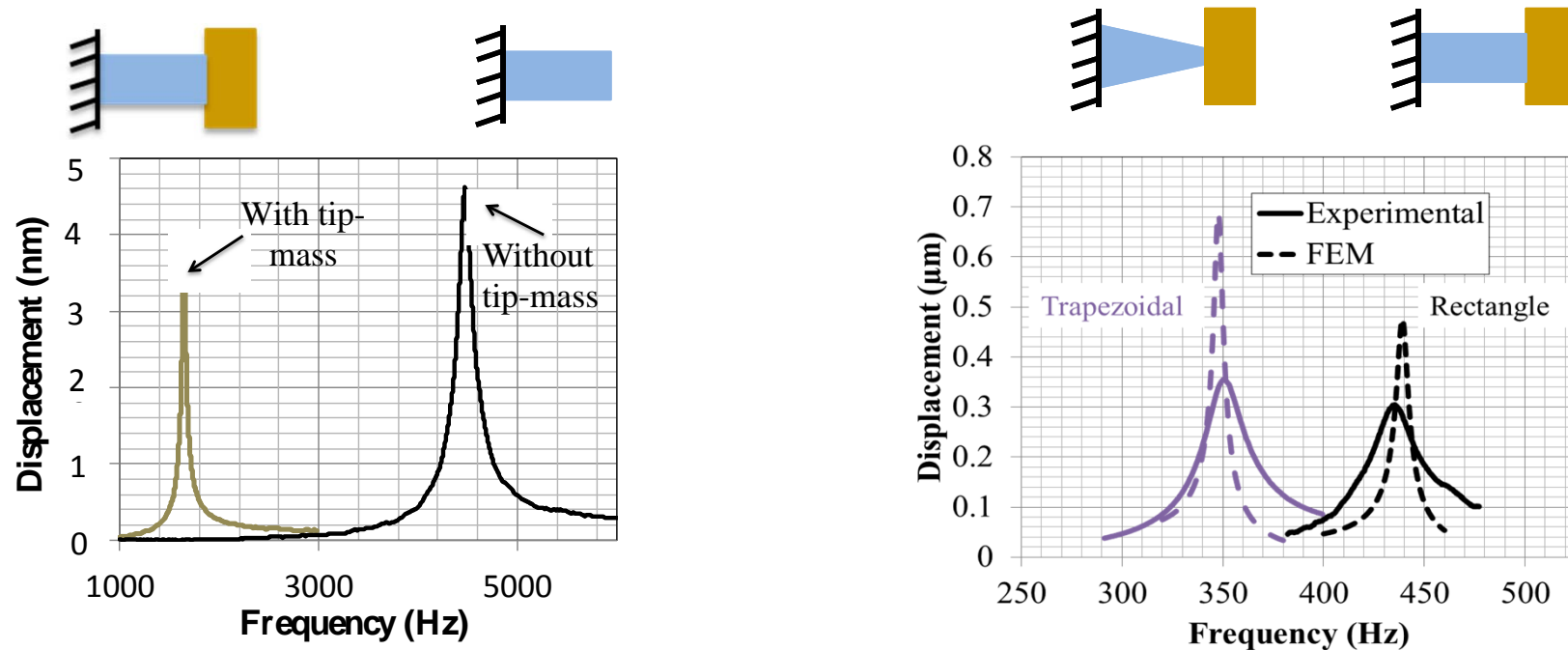
ver (Omnicoat)

SU-8)

Anchor pad and tip-mass (Ag-polymer)

Organic MEMS: energy harvesting

Resonance frequency



1st vibration mode (out of plane)

- Influence of tip-mass: f_r (with tip-mass) = $1/3 f_r$ (without tip-mass)
- Influence of the geometry of the micro-beams + tip-mass: < 10 times
- Repeatability: $f_r = 372\text{Hz} \pm 16\text{Hz}$

Organic MEMS: xurography processing

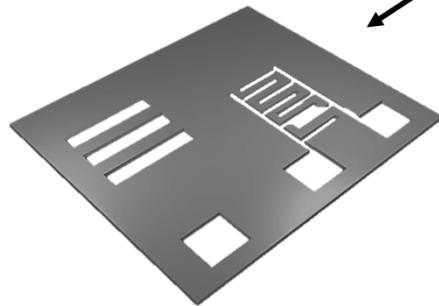
Xuron (blade, razor) and *Graphe* (to write)



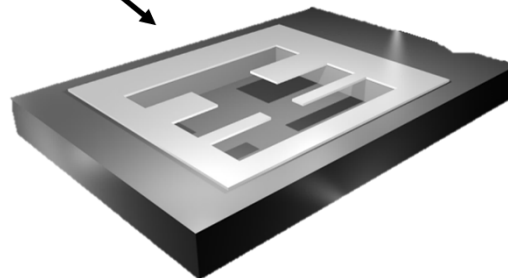
Characteristics:

- Devices can be designed in any CAD program
- Software opens DXF files
- Lateral resolution of 5 μm
- Handle a variety of material
- Cut material up to 250 μm thick
- Large choice of blade

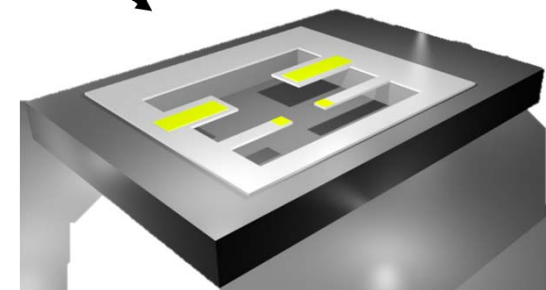
Cutting plotter \longrightarrow Deposition techniques



Flexible masks



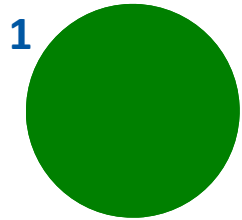
Monolayer MEMS



Multilayer MEMS

Organic MEMS: xurography processing

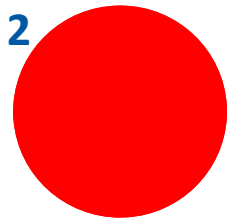
Piezoelectric micro-cantilever resonator



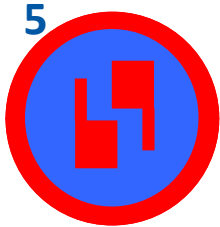
PEN substrate
(50 μ m)



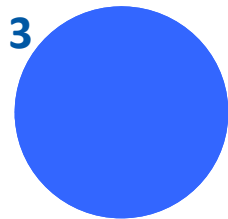
PET Shadow mask



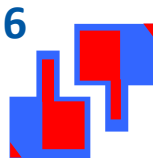
Deposition of the
first layer of
aluminum (140nm)



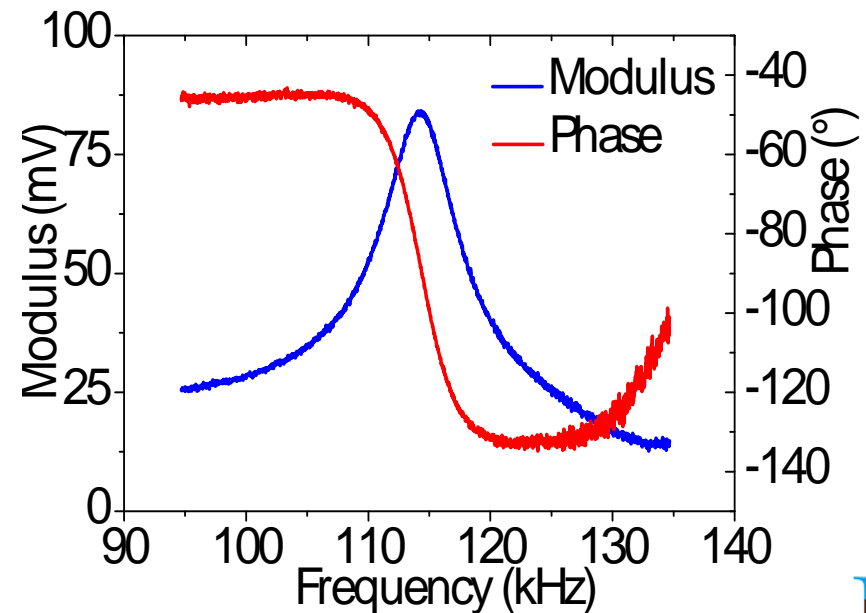
Deposition of the
second layer of
aluminum (140nm)



PVDF-TrFE spin-
coating and
annealing

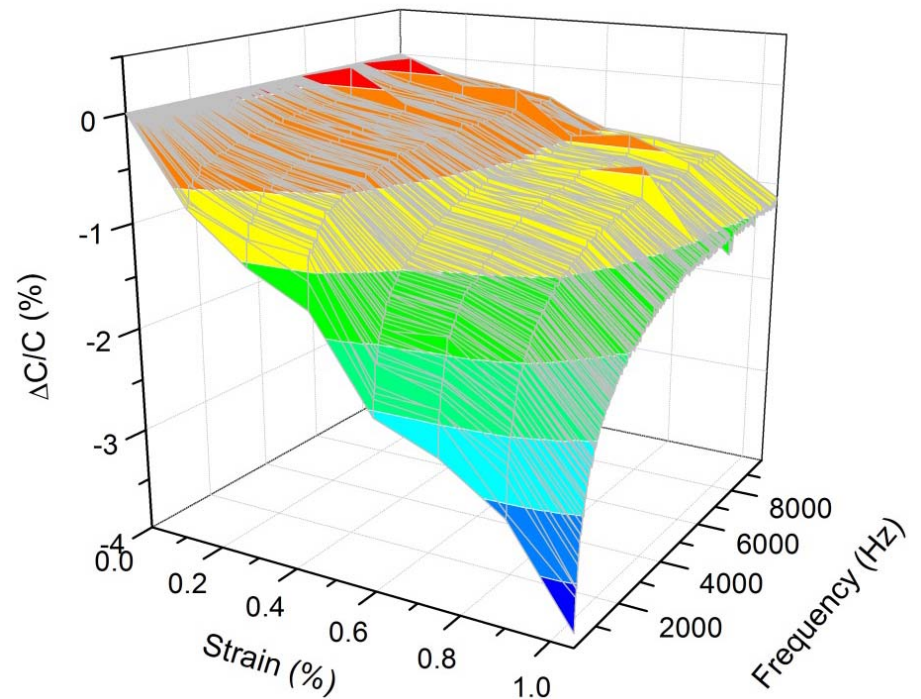
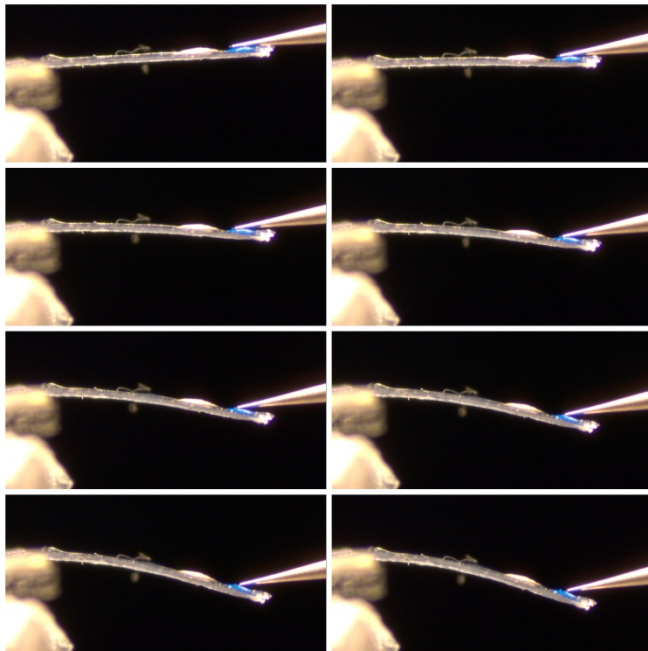
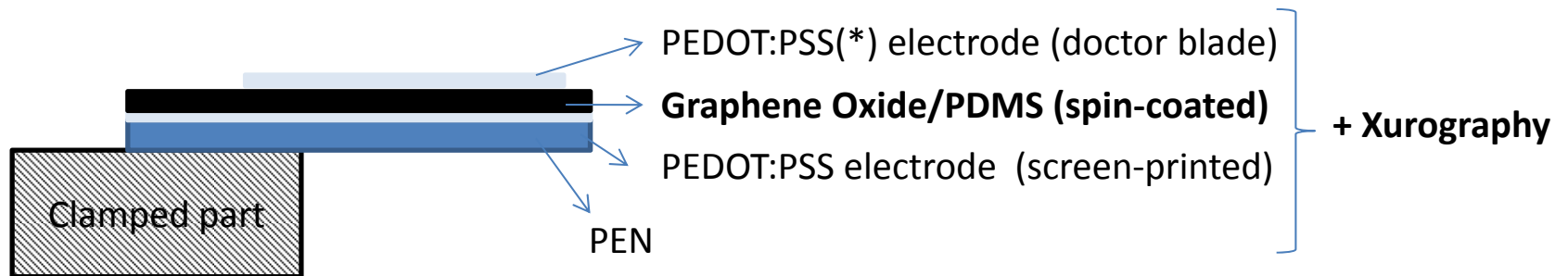


Cutting of the shape
with the cutting
plotter (Xurography)



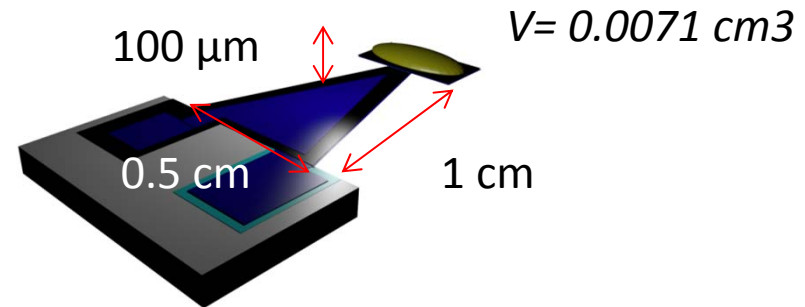
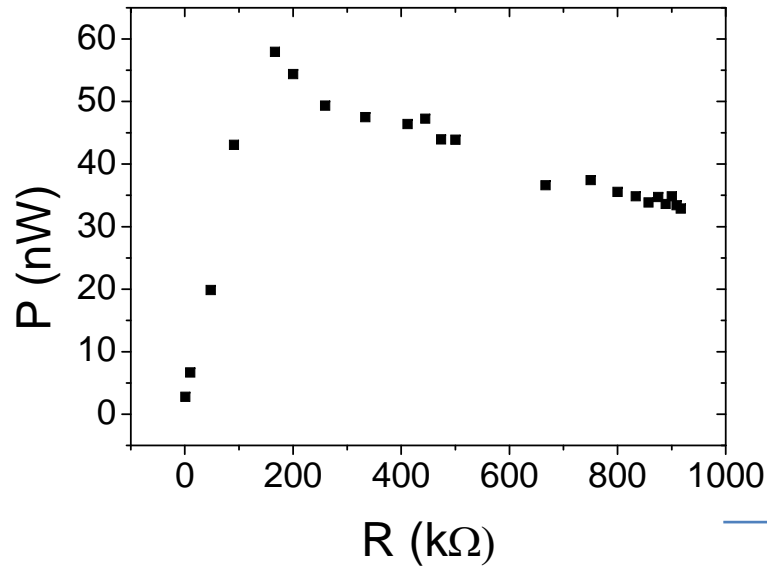
Organic MEMS: xurography processing

↳ Electrostrictive MEMS energy harvester



(*) PEDOT:PSS = poly(3,4-éthylènedioxythiophène) : poly(styrène sulfonate)

Electrostrictive MEMS energy harvester



	Electrostrictive polymer	Power density ($\mu\text{W}/\text{cm}^3$)
<i>D Jaaoh et al, 2016</i>	PU	1.11
<i>D Jaaoh et al, 2016</i>	PU/PANI 2wt%	1.54
<i>P.J. Cottinet et al, 2011</i>	P(VDF-TrFE-CFE)	280.00
<i>Our micro-cantilever</i>	PDMS/rGO 3.7wt%	8.15
PU: Polyurethane, PANI : polyaniline conducteur		

Outline

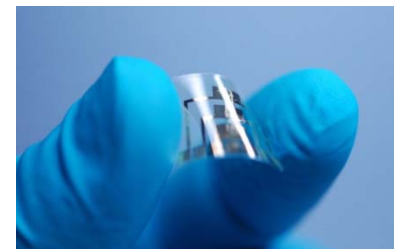
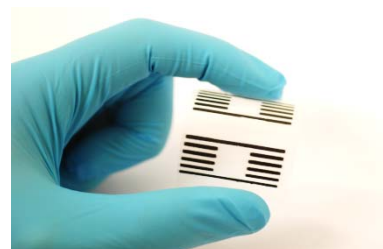
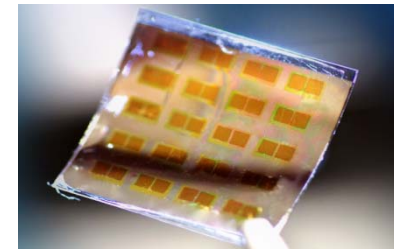
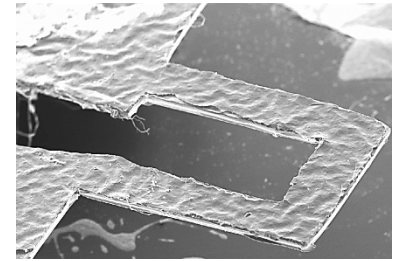
1. Bordeaux, University and IMS Laboratory
2. IMS Lab - PRIMIS team activities
3. Printed technologies for electronics and MEMS
4. Screen-printed PZT MEMS
5. Printed gas sensors: toward RT detection
6. Organic MEMS

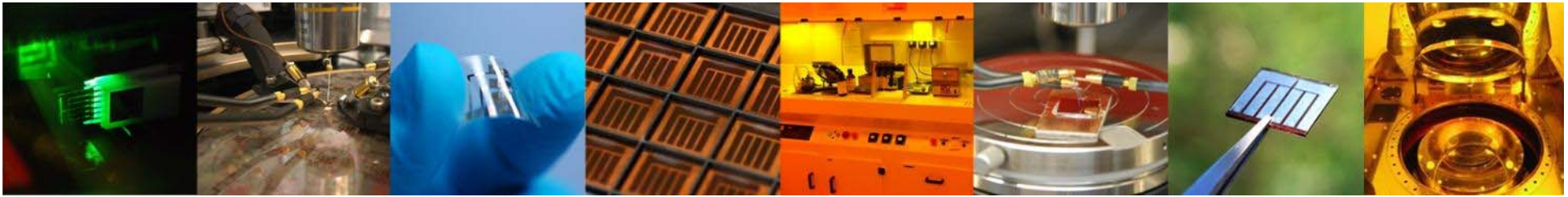
... Conclusion



Conclusion

- Use of simple, low-cost, versatile and fabrication processes (screen-printing, xurography, spray, etc...).
- It led to successful achievement of state-of-the-art printed MEMS devices
- Toward "green" and flexible electronic: no lead, organic, bio-compatible ...





**Thank you.
Merci!**

Aknowledgements

C. Lucat,
I. Dufour, C. Ayela,
D.Thuau, P.Clément, R. Lakhmi,
H. Nesser, PH. Ducrot, ...



Laboratoire de l'Intégration du
Matériau au Système



université
de **BORDEAUX**