Functionalization of screen-printed PZT microcantilevers for gas detection

Riadh Lakhmi(1), Rosa M. Vázquez(2), Carlos R. Zamarreño(3), Hélène Debéda(1), Claude Lucat(1), Raul Calavia(2), Eduard Llobet(2), RoFrancisco J. Arregui(3), Marc Delgado(4)

(1) Université de Bordeaux, Laboratoire IMS, Groupe Microsystèmes , 33405 Talence Cedex, France
(2) Universitat Rovira i Virgili, 26 Av. Països Catalans, 43007 Tarragona, Spain
(3) Public University of Navarra, IEE Department 31006, Pamplona, Spain
(4) Sensotran, 31 Av. Remolar- 08820 El Prat de Llobregat, Spain

Summary

I. Introduction

II. Sensor principle

- ❖ Self-actuated cantilever
- ❖ Electro-mechanical model

III. Sensor realization

- ❖ Self-actuated cantilever
- ❖ Polarization
- ❖ Evidence of piezoelectric properties
- ❖ Sensitive layer deposition
- ❖ Frequency shift measurements

IV. Gas detection

- ❖ Toluene detection with PEUT
- ❖ Benzene detection with SnO_2

V. Conclusion

I. Introduction

❖ Gas detection issues :

- Guarantee safe environments (free from NOx, benzene…)
- Detect toxic gases at low concentration (… to ppb)

❖ Device issues :

- Gas detection function
- Vibrating structure
- Self-actuated device
- Low power consumption
- Process cost effective, simple

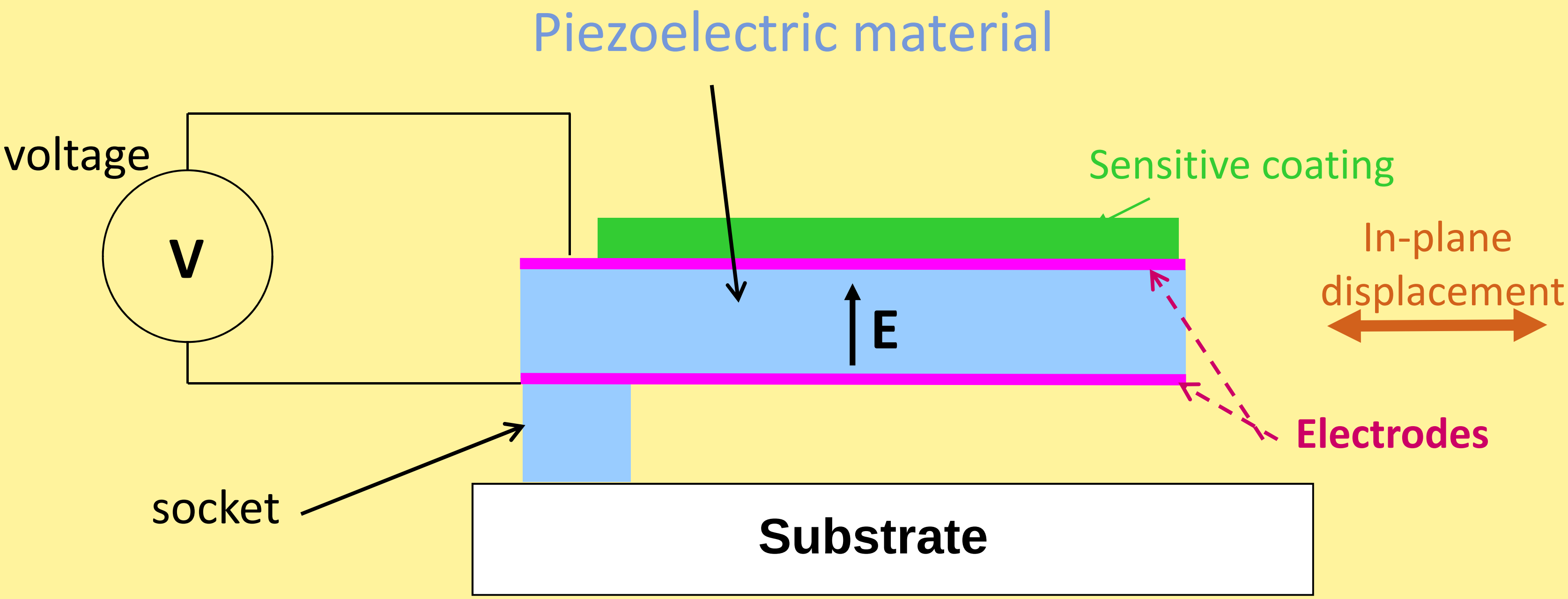
❖ Technological choices :

- Cantilever structure
- Piezoelectricity (actuation and sensing)
- Screen-printing + sacrificial layer technique
- Adsorbent layer (SnO_2, polypyrrole, PEUT…)

→ Dispenser, Spray, Electrodeposition

II. Sensor principle

❖ Self-actuated PZT cantilever* for gas sensors



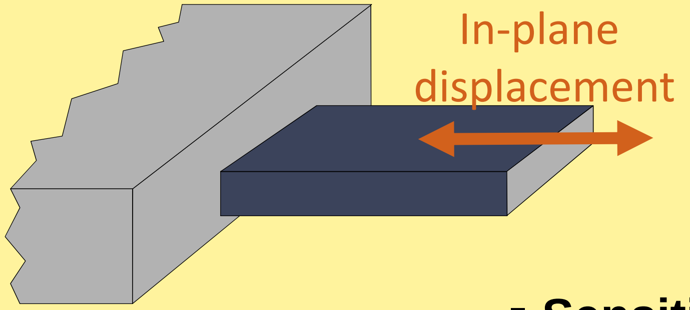
“In-plane” Longitudinal mode (31 mode)

*C. Castille PhD Thesis (2010)

II. Sensor principle

❖ Electro-mechanical model

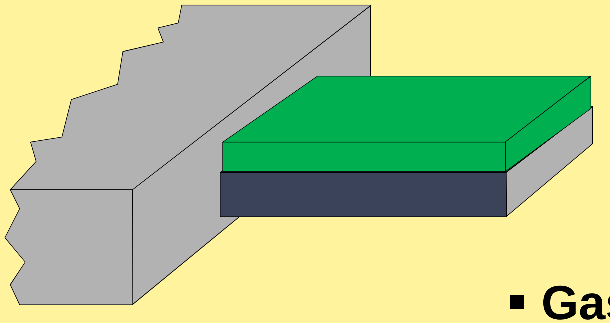
- **31-longitudinal resonance frequency**



$$f_{31}^{(n)} = \frac{\lambda_{31}^{(n)}}{2\pi}\sqrt{\frac{k_p}{m_p}}$$

k_p : cantilever's spring constant
m_p : cantilever's mass
λ_{31} : eiger value $\lambda_{31}^{(n)} = \frac{2n-1}{2}\pi$

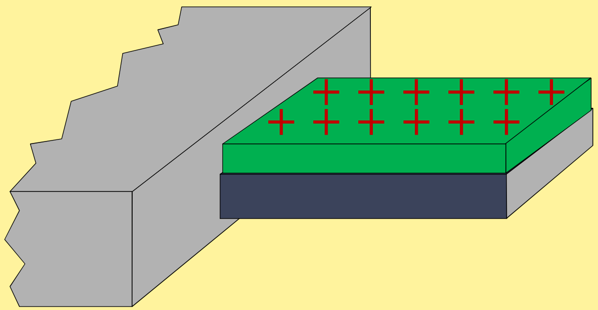
- **Sensitive layer effect**



$$f_{31}^{(n)} = \frac{\lambda_{31}^{(n)}}{2\pi}\sqrt{\frac{k_p + k_{sl}}{m_p + m_{sl}}}$$

k_{sl} : sensitive layer's spring constant
m_{sl} : sensitive layer's mass

- **Gas adsorption effect**



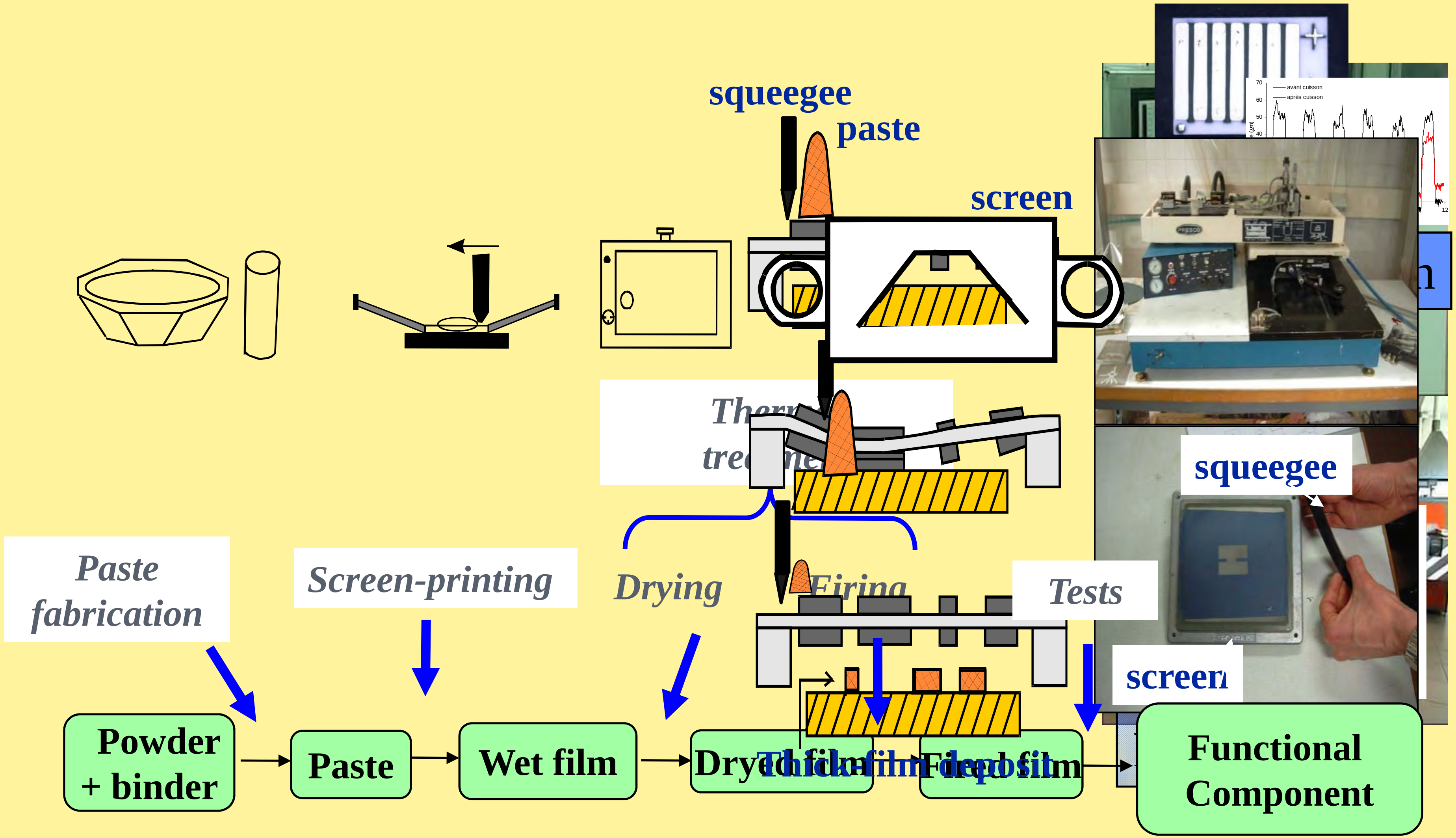
$$f_{31}^{(n)} = \frac{\lambda_{31}^{(n)}}{2\pi}\sqrt{\frac{k_p + k_{sl}}{m_p + m_{sl} + h_{sl}.K.C_g}}$$

h_{sl} : sensitive layer's thickness
C_g : sensitive layer's mass
K : partition coefficient

Sensitivity : $S = \frac{\Delta f}{\Delta Cg}$

III. Sensor realization

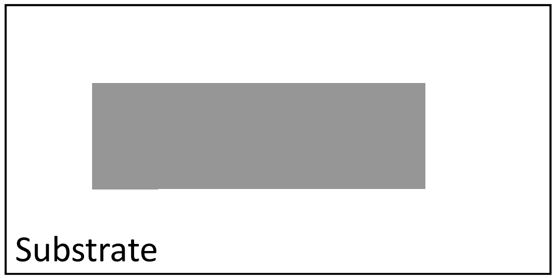
Screen-printing process



III. Sensor realization

Screen-printing process + sacrificial layer process (*)

Cross-section



Top view

- ✓ Sacrificial layer deposition ($SrCO_3$+epoxy)
- ✓ Consolidation
- ✓ Structural layer deposition
- ✓ Final firing
- ✓ Removal of sacrificial layer in a weak acidic solution

** PhD thesis P. GINET (Déc. 2007)*

** CNRS Patent WO07077397 (Jan. 2007)*

III. Sensor realization

❖ Self-actuated PZT cantilever

1. Screen-printing inks fabrication

PZT = {PZT + eutectic} + ESL organic binder

Sacrificial ink = $SrCO_3$ + epoxy binder

Gold = commercial ESL ink

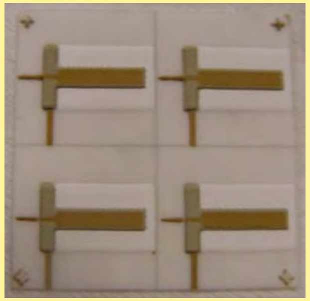
2. Layers screen-printing and drying (120°C,20min)

Sacrificial layer

Gold (bottom electrode)

PZT

Gold (top electrode)



Dimensions
6 < L(mm) < 10
1 < w(mm) < 2
100 < t(µm) <150

3. Isostatic pressure (1min,1kbar)

4. Firing 2 hours at 900°C

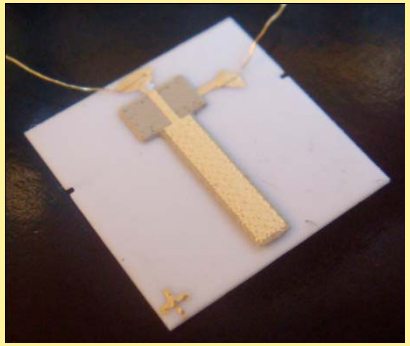
III. Sensor realization

❖ Polarization

Objective : give its piezoelectric properties to PZT

Polarization cell

- 1st step: Vacuum (0.1 mbar)
- 2nd step: Helium atmosphere
- High temperature polarization
  (280°C – 500V for 15 minutes)
  Until breakdown voltage (500V)



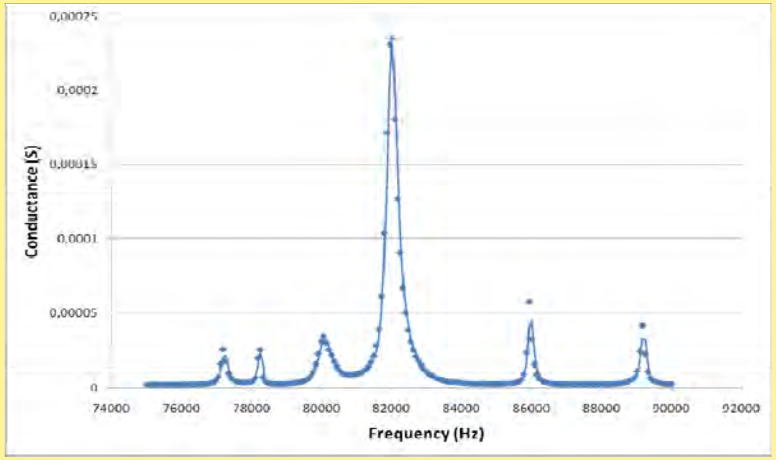
Sample with wires

*** Polarization have been carried out at ICMCB Bordeaux**

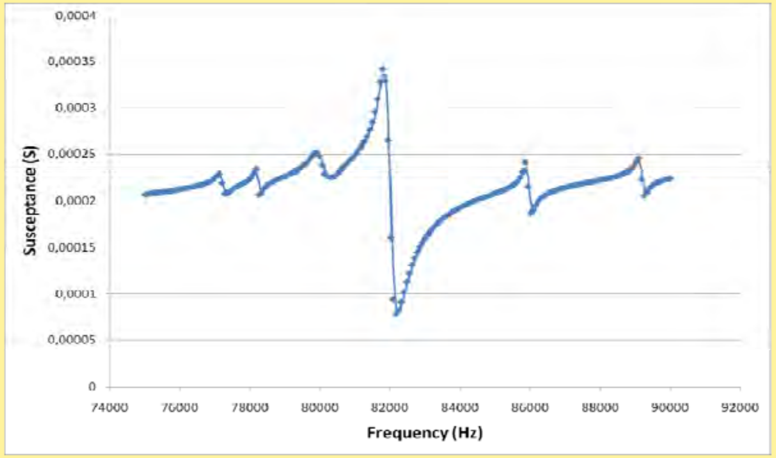
III. Sensor realization

❖ Evidence of piezoelectric properties

Impedance/ Admittance measurements



*Longitudinal mode - **G(f)***



*Longitudinal mode - **B(f)***

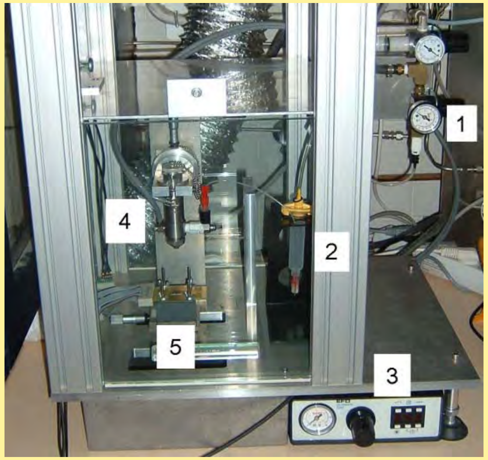
In plane 31-longitudinal resonance:

- 60KHz < f_{res} < 100KHz
- 300 < Q < 450
- tan(δ)≈ 0,4 - 0,6%

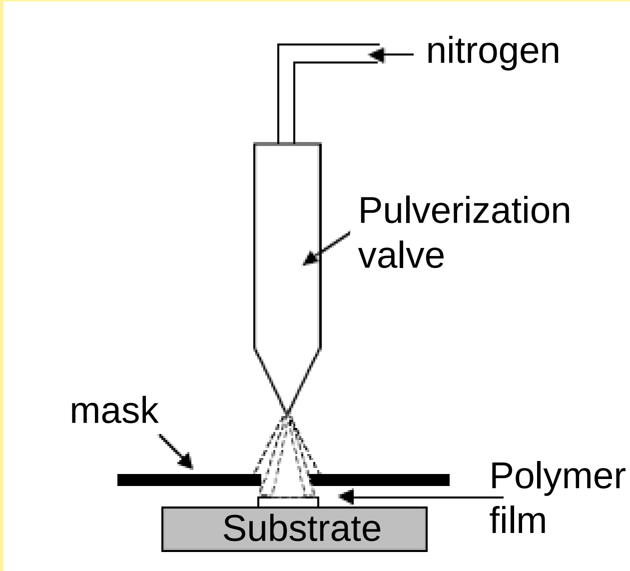
III. Sensor realization

❖ Sensitive layer deposition : PEUT

Spray coating



Photography of pulverization bench



1. Pressure supply setting.
2. Syringe containing a mixture polymer-solvant.
3. Controller allowing the adjustment of pulverization time and pressure
4. Pulverization valve
5. Wired micro cantilever

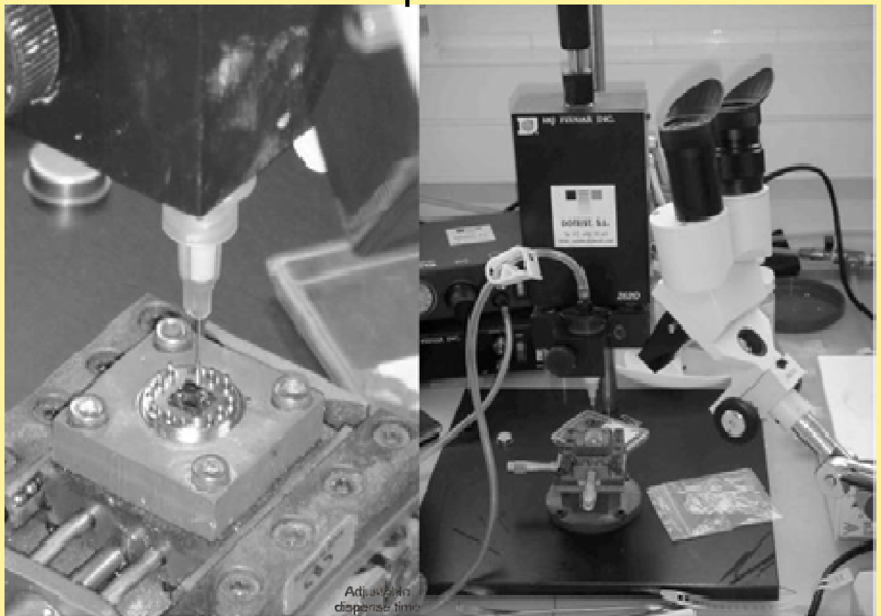
1 – Solution preparation (**polymer + solvant**)
2 – Syringe supplied with solution
3 – Pressure / time of pulverization setting
4 – Spray until desired film thickness

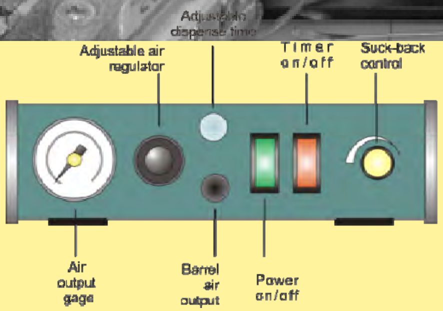
III. Sensor realization

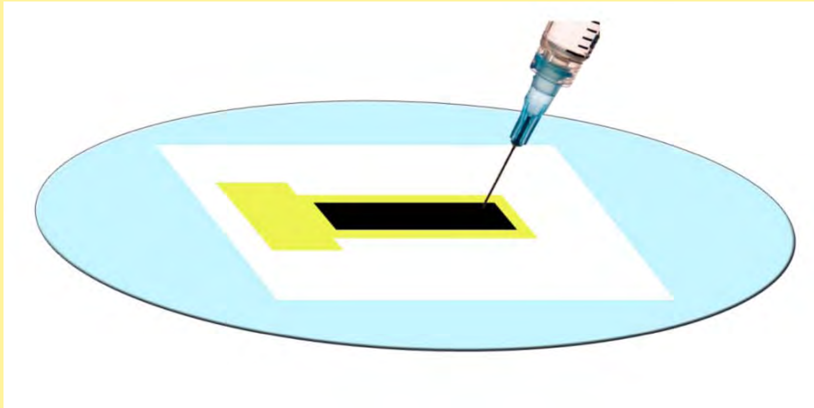
❖ Sensitive layer deposition : SnO_2 and active carbon

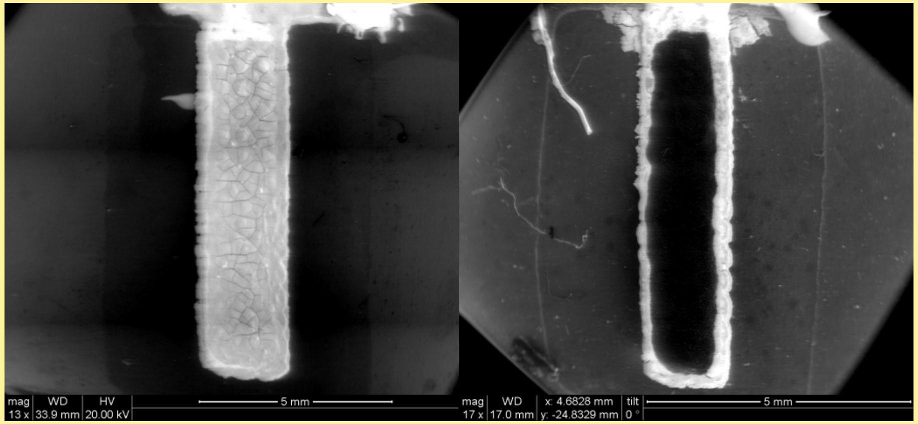
Drop coating system

Semi-automated micro-dispenser with x-y micro positioner









SnO_2 and active carbon coated PZT cantilevers

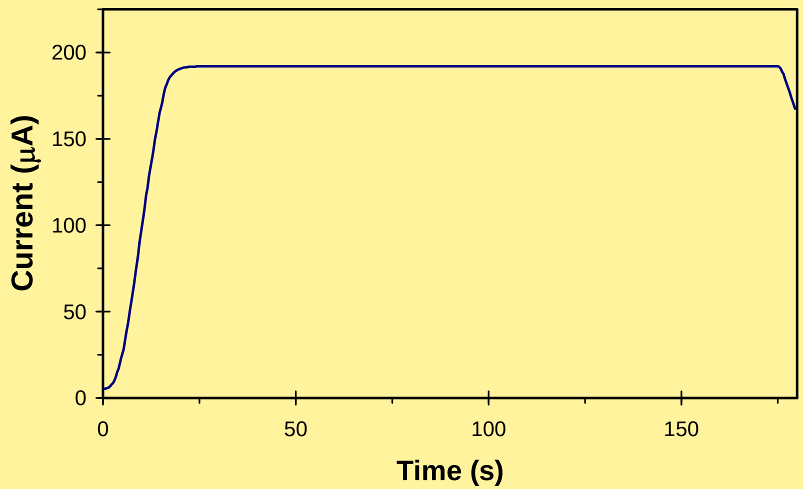
III. Sensor realization

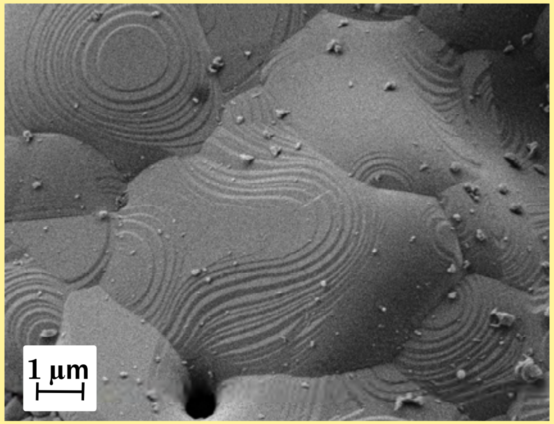
❖ Sensitive layer deposition : Polypyrrole

Electrodeposition : chronoamperometry

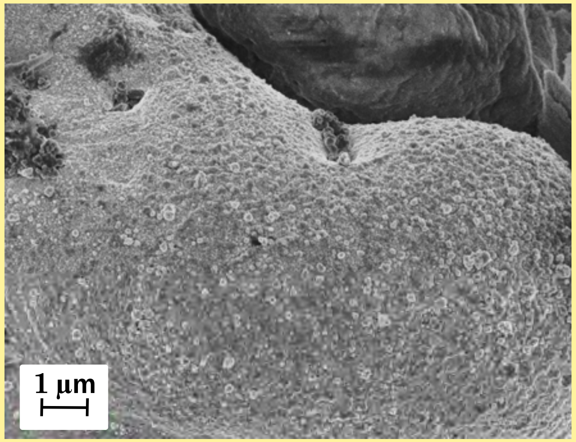
Electrodeposition from 0.1 M PPy and 0.1 M LiCl solution at pH 2.2.

- Deposition time = 180 s
- Voltage = 0.9 V





Electrode before deposition



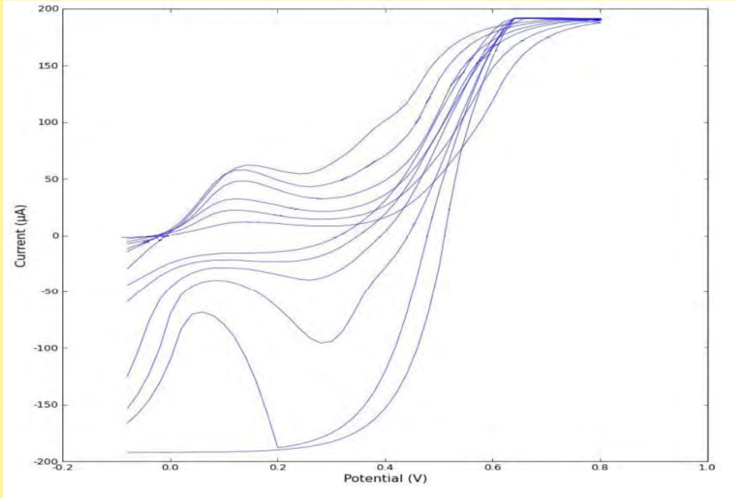
Electrode after deposition

Based on: Yu-Chuan Liu et al., "Evidence of Chemical Effect on Surface-Enhanced Raman Scattering of Polypyrrole Films Electrodeposited on Roughened Gold Substrate," *Langmuir* **28**, 174-181 (2002).

III. Sensor realization

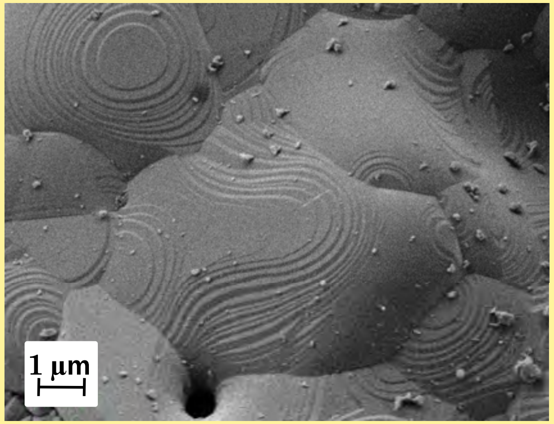
❖ Sensitive layer deposition : Polyanniline

Electrodeposition :
cyclic voltammetry

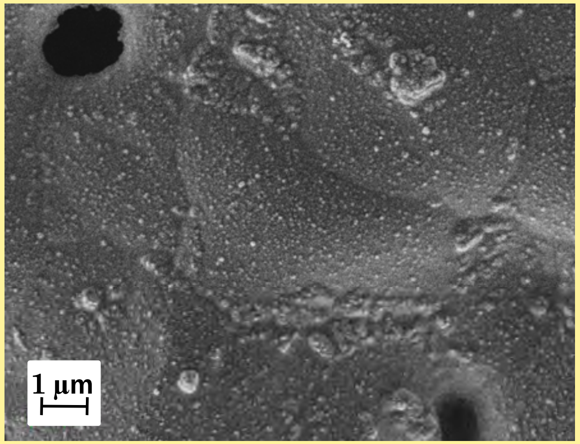


Electrodeposition from 0.2 M H_2SO_4, 0.1 M PSS and 0.1 M aniline

- Voltage sweep from -0.1V to 0.8 V.
- Voltage step: 0.25 V/s.
- Cycles: 6



Electrode before deposition



Electrode after deposition

Based on: M. Zhang et al (2008).

III. Sensor realization

❖ Frequency shift measurements

	Before Deposition (KHz)		After Deposition (KHz)		Shift (KHz)	
	1st mode	*2nd mode*	*1st mode*	*2nd mode*	***1st mode***	***2nd mode***
PEUT	67.935	205.19	66.32	202.87	**- 1.615**	**- 2.32**
Polyaniline	69.380	205.704	74.297	218.994	**4.917**	**13.29**
Polypyrrole	70.607	211.184	71.830	212.414	**1.223**	**1.23**
SnO_2	69.614	207.451	73.333	220.987	**3.719**	**13.536**

$$f_{31}^{(n)} = \frac{\lambda_{31}^{(n)}}{2\pi}\sqrt{\frac{k_p + k_{sl}}{m_p + m_{sl}}}$$

k_{sl} → Stiffness effect of the sensitive layer deposit

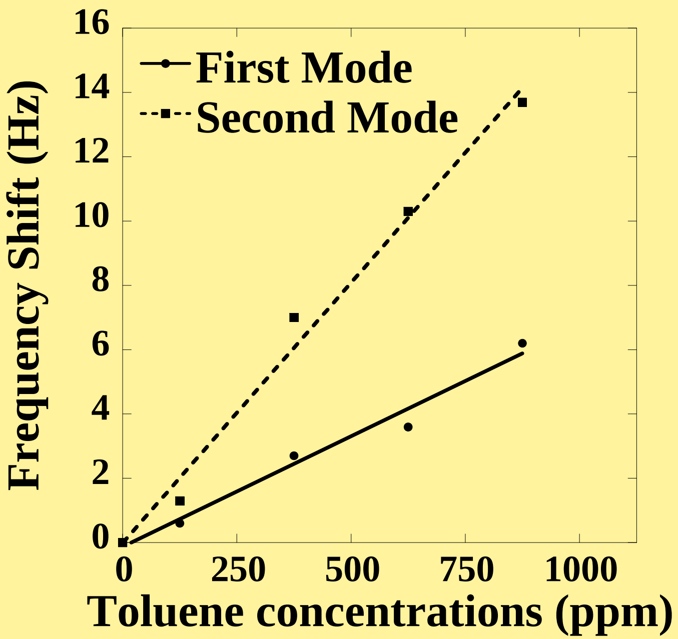
m_{sl} → Mass effect of the sensitive layer deposit

- **- shift** in the case of PEUT (mass effect more important than stiffness effect)
- **+ shift** in the other cases (stiffness effect more important than mass effect)

IV. Gas detection

❖ Toluene detection with PEUT

Experimental : → carrier gas : **nitrogen** (100mL/min)
→ different concentrations of toluene (0 to 850ppm)



1st mode

$$\frac{\Delta f}{\Delta C_g} \approx 7\,\mathrm{mHz/ppm}$$

2nd mode

$$\frac{\Delta f}{\Delta C_g} \approx 16\,\mathrm{mHz/ppm}$$

Sensitivities 2 times better for the second longitudinal mode

Limit of detection : (Res = 0.1Hz)

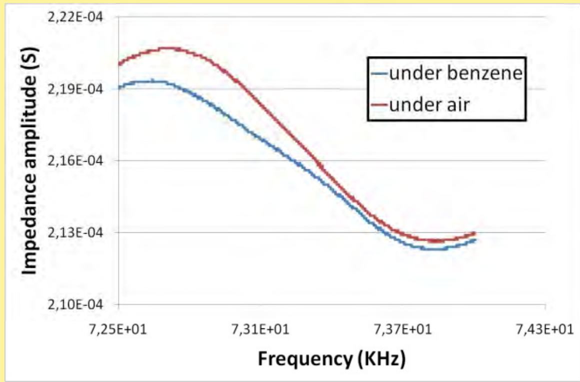
1st mode → 14ppm
2nd mode → 5ppm

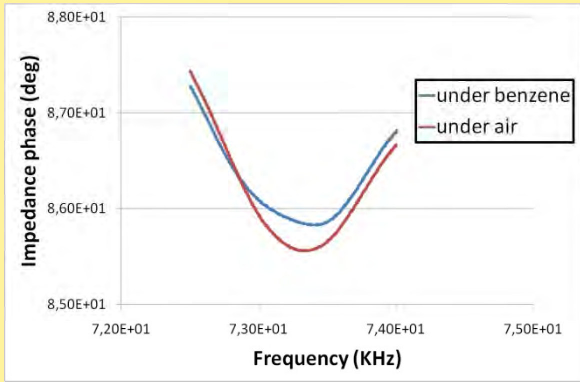
PhD Thesis C. Castille (2010)

IV. Gas detection

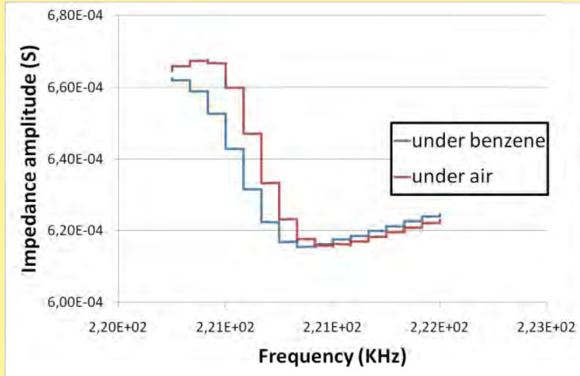
❖ Benzene detection with SnO_2

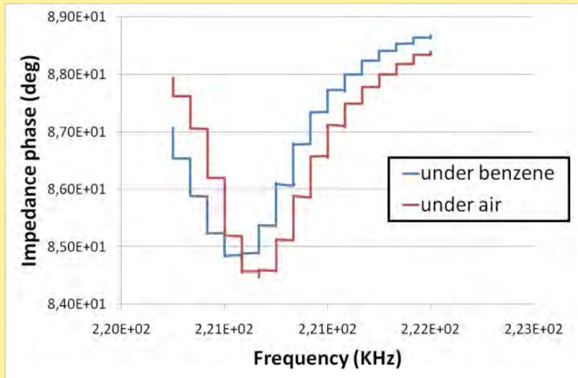
- **Impedance shifts :** (amplitude and phase)





First 31-longitudinal mode





Second 31-longitudinal mode

Experimental:

→ carrier gas : **synthetic air** (100mL/min)

→ 1ppm of benzene

Good sensitivities

- 60Hz/ppm (1st mode)
- 100Hz/ppm (2nd mode)

Detection at ppb level expected

V. Conclusion

- ❖ Cantilever shaped micro-sensors realized by screen-printing
- ❖ Self-actuated PZT cantilever
- ❖ In plane 31-longitudinal vibration mode
- ❖ Sensing mode : frequency shift ⟷ mass adsorption
- ❖ Measurement performed with PEUT and SnO_2
- ❖ Results much better for SnO_2 (factor ~ 10^4)

Current work:

→ Gas detection with active carbon, polypyrrole and polyanniline
→ Detection of other gases (selectivity?)