DOI 10.5162/IMCS2012/P1.2.12

Uncoated PZT thick film cantilever for chemical species detection in gaseous phase

Riadh LAKHMI, Hélène DEBEDA(*), Claude LUCAT
University of Bordeaux, Laboratoire IMS, 33405 Talence Cedex, France
Contact: helene.debeda@ims-bordeaux.fr

Abstract :
Coated silicon cantilevers functioning with flexural mode are classically used for chemical species detection. Recently, new types of entirely screen-printed piezoelectric ***PZT cantilevers*** operated with the unusual "in-plane" ***31-longitudinal*** mode have been shown to be good candidates for actuation, sensing or energy harvesting applications. In order to prevent from ageing phenomena linked to the sensitive layer, the cantilever sensors may be used without any coating. ***Detection*** of water and ethanol is successfully performed using the 31-longitudinal mode of uncoated PZT cantilever sensors giving respectively negative and positive frequency shifts. As the viscosity and density of those gases don't allow explanation of such high values of frequency shifts, responses have to be found in the competition between mass and stiffness effects. Differences between the cantilever's response to water and ethanol can be explained by the higher wettability of gold towards ethanol. Indeed, whereas the main effect of water onto the gold surface seems to be linked to mass effects, only stiffness effects can justify the positive shifts observed in the case of ethanol vapour.

Key words: PZT cantilevers, 31-longitudinal mode, water sensitivity, ethanol detection.

Introduction

The field of cantilever-based sensors is relatively recent since it only emerged in the beginning of the 1990's to offer a cheap, rapid portable solution to the chromatographic and spectroscopic techniques. They have been attractive for gas sensing because of their high sensitivity at room temperature and the reversibility of their detection principle [1]. This last one makes it possible for them to measure phenomena as changes in surface stress, temperature and mass.

Due to the cantilever geometries and the mainly used electromagnetic actuation, the flexural vibration mode appears to be the most classically chosen. However, modes working at higher frequencies are interesting since they will offer better sensitivities and potentially better detection limits to given species. Here, a symmetrical cantilever beam piezoelectrically actuated favors the so-called 31-longitudinal, mode at higher frequencies, thus enabling higher detection sensitivity. More, actuation and detection are both performed with the same PZT layer simplifying the fabrication process compared to silicon cantilever where the electromagnetic actuation and piezoresistive detection are generally used. Furthermore, the cost-effective and time-sparing fabrication process chosen combines different screen-printing steps with the use of a sacrificial layer.

To perform detection of chemical compounds, specific sensitive layer is usually deposited on the cantilever to trap the different species. This sorption phenomenon affects the cantilever mass and its stiffness inducing cantilever bending for gas detection in static mode. Besides, the dynamic mode remains largely used. In this case, a frequency shift is measured as a result of mass and stiffness changes due to species sorption [2]. Even if polymers like PEUT, PDMS or PVA [3,4] remain the most used sensitive layers, inorganic ones like zeolites have been successfully used for a few years because of their high specific surface area [5]. Nevertheless, the major drawback of those sensitive layers is their ageing process, especially for polymers and inorganic layers like SnO_2 [6] working at high temperature. Therefore, in this study, the potentialities of uncoated cantilevers for gas detection are studied. In the case of uncoated silicon cantilever, it has been observed that the detection relies on the density and viscosity influence of gas medium on the resonant frequency [7].

PZT cantilever sensors' fabrication

The simple design of PZT cantilevers used for this study is shown in figure 1. Thanks to the combination of the standard screen-printing technology with a sacrificial layer process, free-standing piezoelectric beams are fabricated and released from the substrate.

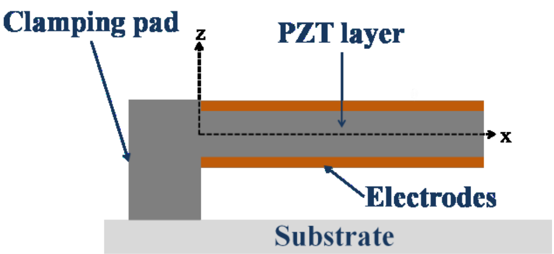
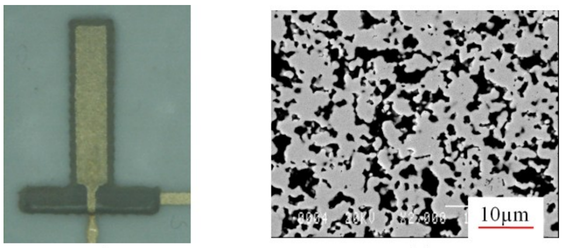


Figure 1. Design of the PZT cantilever

This multilayered component is achieved by deposition of successive layers (sacrificial, gold and PZT layers) subsequently dried or polymerized 20min at 120°C after each printing step. Once all the layers are deposited and dried, the samples are isostatically pressed 1min at 1kbar to improve the densification. The samples are then co-fired 2h at 900°C with a heating rate of 20°C/min and a cooling rate of 20°C/min. Finally, the removal of the sacrificial layer is performed in a diluted acidic solution and thus allows free movement of one extremity of the two-face electroded beam while the other one is clamped on the substrate. The samples obtained exhibit a porosity of about 25% as it can be seen on figure 2.



a) b)

Figure 2. a) 8x2x0.1mm3 PZT cantilever b) SEM of the PZT porous layer

The piezoelectric ink is based on a PZT powder (Pz26 from Ferroperm) mixed with 3wt% LBCu (25wt% Li_2CO_3, 40wt% Bi_2O_3, 35wt% CuO) sintering aid. The sacrificial layer paste is composed of $SrCO_3$ dispersed in an epoxy binder CV59 from Electro-Sciences Laboratories. Concerning the bottom and top electrode, commercial gold paste ESL8836 from Electro-Science Laboratories is used. The dimensions used in this study are for the length L=8mm, width b=2mm and thickness h~100µm. The symmetrical electrodes (e~7µm) have a slightly smaller area than those of PZT beam in order to prevent short-circuits.

Prior to detection, the PZT cantilevers are poled to confer them their piezoelectric properties by applying an electric field of 5kV.cm^{-1} between the electrodes for 15min at 280°C under helium atmosphere. The temperature is then lowered to room temperature before turning off the electric field.

PZT cantilever sensing principles

The vibration mode used to perform detection is referred as in-plane 31-longitudinal mode. The main advantage of this vibration mode compared to the classical flexural mode is the higher resonant frequency for typical cantilever geometries, leading to improved sensitivities.

- *Density and viscosity effects*

When a cantilever vibrates in a viscous fluid (gas or liquid), the latter imposes an inertial force proportional to the cantilever's acceleration and a viscous force proportional to its velocity. In the case of a cantilever immersed in a fluid, the viscous losses are dominant. Then, according to Sader [8], the quality factor is expressed by:

$$Q = \frac{2\pi\sqrt{1 + Lg_2/m}}{Lg_1/m} f_{0,31} \qquad (1)$$

$$g_1 = w\sqrt{2\eta_{fluid}\rho_{fluid}\omega} \qquad (2)$$

$$g_2 = w\sqrt{\frac{2\eta_{fluid}\rho_{fluid}}{\omega}} \qquad (3)$$

where *L*, w, *m* are respectively the length, width and mass of the cantilevers, g_1 and g_2 to the hydrodynamic parameters. η_{fluid}, ρ_{fluid}, ω are respectively the viscosity, the density of the surrounding fluid and the pulsation of the cantilever.

Finally, the resonant frequency of the cantilever, depending on Q, is described by following equations:

$$f_{r,31} = f_{0,31}\frac{1}{\sqrt{1 + \frac{Lg_2}{m}}}\sqrt{1 - \frac{1}{2Q^2}} \qquad (4)$$

$$f_{0,31}^{(n)} = \frac{(2n-1)}{4L}\sqrt{\frac{E_p t_p + 2E_{Au}t_{Au}}{\rho_p t_p + 2\rho_{Au}t_{Au}}} \qquad (5)$$

where indexes *p* and *Au* refer to PZT and gold, *E* and *t*, referring respectively to Young's modulus and thickness values.

- *Mass and stiffness effects*

The frequency variation ($\Delta f_{r,31}$), related to the gas sorption, is proportional to the resonant frequency and linked to the gas effect on both the mass (m_c) and the stiffness (k_c) of the cantilever (eq. (6))

$$\Delta f_{r,31} = \frac{f_{r,31}}{2}\left[\frac{\Delta k_c}{k_c} - \frac{\Delta m_c}{m_c}\right] \quad (6)$$

The mass effect related to the gas sorption induces a negative frequency shift whereas the stiffness effect can induce either positive or negative shift. In this paper, tests have been performed with PZT layers having porosity of 25-30% and without any sensitive layer.

Humidity and ethanol detection

Humidity detection is performed at 25°C with controlled relative humidity (%RH) from 10% to 80% in vapor generator cell (*VGI MEMS* from *Surface Measurement Systems*). Ethanol vapors are produced with a vapor generator *PUL110* type. Ethanol concentration inside the chamber is varied from 0.5% to 8% in a 100mL/min nitrogen flow.

In figure 3, frequency shifts measured under different relative humidity levels are observed. In this case, negative frequency shifts are obtained with a good relative sensitivity ($S_{rel} = \frac{\Delta f_{r,31}}{f_{r,31} C_g}$ where C_g is the gas concentration) of 0.11m^3/kg.

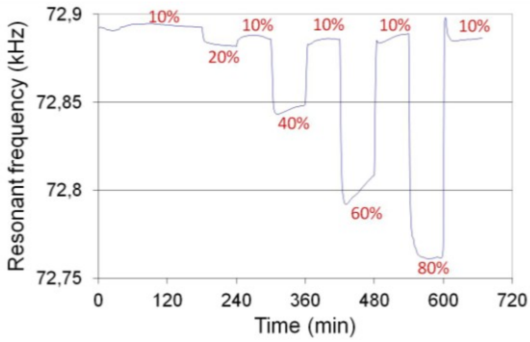


Figure 3 – Resonant frequency variation of uncoated screen-printed PZT cantilever (8x2x0.1mm^3) with water vapor (60min steps at different humidity levels)

In figure 4, positive frequency shifts are observed for 4 different ethanol concentrations (0.5% to 8%) with relative sensitivity of 0.009m^3/kg.

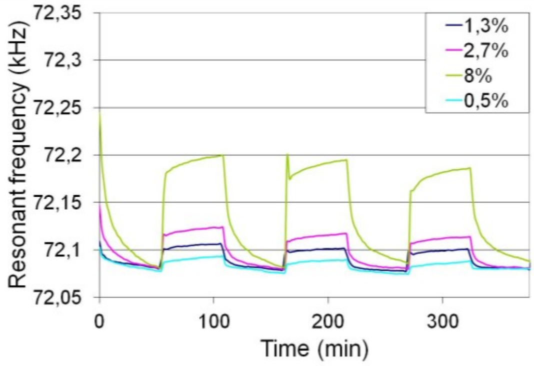


Figure 3 – Resonant frequency variation of uncoated screen-printed PZT cantilever (8x2x0.1mm^3) with ethanol gases (steps of 54min of alternatively nitrogen and x% ethanol concentrations)

Discussion

The difference in the sign of the frequency shift between the two gases tested indicates that the gas influence on the stiffness cannot be neglected, especially in the case of ethanol (Tab. 1). Contrary to uncoated silicon cantilevers where gas inertial and viscous effects are sufficient to explain the amplitude and sign of the frequency shifts [7], they do not explain the shift amplitudes observed in our cases. Indeed, frequency shifts up to more than 100Hz are obtained for 80% relative humidity or 8% ethanol whereas inertial and viscous effects of water and ethanol would induce frequency variations lower than 0,1Hz.

Therefore, the frequency shifts should be linked to sorption phenomena. The first effect of vapor sorption onto a cantilever, occurring either for water or ethanol, is the increase of its effective mass inducing a decrease of the resonant frequency. Nevertheless, mass effect cannot explain the positive frequency shifts observed in the case of ethanol. Such positive frequency shifts, resulting from cantilever stiffness modification, have already been observed in previous works [9-11]. Surface stresses occurring during vapors sorption can induce either positive of negative frequency shifts, depending on interactions between the coating and the vapor. Indeed, Thundat et al [9] observed that V-shaped cantilevers, both-side coated with phosphoric acid, overcome a negative resonant frequency shift while cantilevers, both-side coated with gelatin, exhibit positive frequency shifts. Besides, bare gold coatings usually have a low wettability towards water and a higher affinity to alcohols. Namely, gold is a preferred coating in combination with thiols which are, in terms of chemical reactivity, similar to alcohols. In 2001, Hansen et al [10] demonstrated that the high surface stresses generated inside the gold coating can be modulated by the cleanliness of the gold surface.

Based on these results, frequency shifts due to water sorption are attributed to mass effects. Conversely, the predominant stresses generated by ethanol sorption on the cantilever explain the positive shifts measured.

Tab. 1:Comparison of the sensitivity obtained for ethanol and humidity

	Humidity	**Ethanol**
Concentration range	10-90 %RH	0.5%-8%
Frequency shift sign	**-**	**+**
$S_{relative}$ $\left(S_{rel} = \frac{\Delta f_{r,31}}{f_{r,31} C_g}\right)$	0.081	0.017
$S_{relative}$ (m^3/kg)	**0.110**	**0.009**

Moreover, it is noticed that sensitivity values more than 10 times better for water compared to ethanol are obtained.

Conclusion

PZT cantilevers have been successfully realized thanks to the association of screen-printing and sacrificial layer. The cantilever's symmetrical geometry and the piezoelectric actuation and read out favor the unusual 31-longitudinal mode. This last one is particularly interesting for its higher sensitivity compared to the classical flexural mode. Water and ethanol vapor detection have been successfully performed without any sensitive layer to prevent from ageing phenomena. In both cases, frequency shifts proportional to the vapor concentration in nitrogen are obtained. High amplitude shifts measured are not justified by density and viscosity effects. Besides, differences in the sorption behavior are observed between the two tested vapors. Indeed, ethanol vapors induce positive frequency shifts due to a higher effect of cantilever stiffness modification compared to adsorbed mass impact. However, water induces negative frequency shifts mainly linked to mass effect.

For a better understanding of the phenomena happening during vapor sorption, further work will consist in decoupling the mass loading and the spring constant variations influences. This can be realized by simultaneously measuring the bending and the resonant frequency [11].

References

[1] M. Goeders et al., “Microcantilevers: Sensing Chemical Interactions via Mechanical Motion”, Chem. Rev., 2008, 108, 522-542, doi: 10.1021/cr0681041.

[2] Q. Zhu et al., Microcantilever Sensors in Biological and Chemical Detections, Sensors & Transducers Journal, 2011, 125, 1-21.

[3] D. Lange et al., Complementary metal oxide semiconductor cantilevers arrays on a single chip: mass sensitive detection of Volatile Organic Compounds, Anal. Chem., 2002, 74, 3084-3095, doi:10.1021/ac011269j.

[4] Y. Dong, Characterization of the gas sensors based on polymer-coated resonant microcantilevers for the detection of volatile organic compounds, Analytica Chimica Acta, 2010, 671, 85-91, doi:10.1016/j.aca.2010.05.007.

[5] M.A. Urbiztondo et al., Zeolite modified cantilevers for the sensing of nitrotoluen vapours, Sensors and actuators B, 2009, 137, 608-616, doi:10.1016/j.snb.2009.01.047.

[6] B. Ghaddab et al., Benzene monitoring by micro-machined sensors with SnO_2 layer obtained by using micro-droplet deposition technique, Sensors and Actuators B, 2011, 152, 68-72, doi:10.1016/j.snb.2010.09.046.

[7] S.Tétin et al, Modeling and performance of uncoated microcantilever-based chemical sensors, Sensors and Actuators B, 2010, 143, 555-560, doi:10.1016/j.snb.2009.09.062.

[8] E. Sader., Frequency response of cantilever beams immersed in viscous fluids with applications to the atomic force microscope. Journal of Applied Physics, 1998, 84, 64-76, doi:10.1063/1.368002.

[9] T. Tundat et al., Vapor Detection Using Resonating Microcantilevers, Anal. Chem. 1995, 67,519-521, doi:10.1021/ac00099a006.

[10] A. Hansen et al., Stress formation during self-assembly of alkanethiols, Probe Microscopy, 2001, 2, 139-149.

[11] G.Y. Chen et al., Adsorption-induced surface stress and its effects on resonance frequency of microcantilevers, Journal of Applied Physics, 1995, 77, 3618-3622, doi:10.1063/1.359562.