Proceedings of the 2003 IEEE International Frequency Control Symposium and PDA Exhibition
Jointly with the 17th European Frequency and Time Forum

COUPLED DETERMINATION OF GRAVIMETRIC AND ELASTIC EFFECTS ON TWO RESONANT CHEMICAL SENSORS: LOVE WAVE AND MICROCANTILEVER PLATFORMS

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Abstract – **The field of chemical microsensors for both gas and liquid sensing has been widely investigated in recent years. Several technologies have been utilized which include Love-wave acoustic sensors and silicon microcantilevers. Those structures are both used as chemical sensors by adding a sensitive coating to the device surface. Perturbations of the sensitive coating properties induce frequency drift in both devices, thus making chemical detection possible. Microcantilevers are essentially sensitive to the coating mass changes which modify the resonant frequency of the structure. However, the acoustic wave device is sensitive to all types of propagation perturbations which include mass loading and mechanical properties changes of the coating. One of the difficulties in acoustic sensor field is to separate each contribution from the induced frequency shifts. The aim of this paper is to couple experimental results from microcantilevers and Love-wave devices in order to identify and separate the two effects. At last, this coupled study is also interesting for gas and liquid phase detection applications, as it will permit to determine the elasticity evolution during the detection process, i.e. the analyte sorption.**

Keywords – Microcantilevers, Love-wave sensors, Resonant frequency, Coating mass effect, Mechanical properties.

I. INTRODUCTION

In the recent years, miniaturization of chemical sensors becomes an important requirement for industrial applications. Indeed, development of such microstructures for both gas and liquid constitutes a stake in fields as various as environment (analyte detection), food industry, biology, continuous quality and process chemical reaction control. Among the several technologies, there is a potential interest in the development of acoustic Love-wave and silicon microcantilevers sensors.

Acoustic wave chemical sensors have been widely studied for a large number of applications and have demonstrated their ability to detect hazardous compounds in gas or liquid environments [1, 2]. Among piezoelectric substrate based sensors, Love-wave ones are now known as the most sensitive [3]. They are based on a piezoelectric substrate covered by a thin guiding layer (Fig. 1). As the waves are guided in the top layer, their energy is confined in this layer, and then the waves are very sensitive to surface perturbations. For detections in gas or liquids, a chemically active coating, added on the sensor surface, interacts with the surrounding environment and causes acoustic waves perturbations. Love-wave sensors as all acoustic wave sensors are known to be sensitive to surface mass accumulation, or mass loading effect. But they can respond to a variety of the coating layer properties.

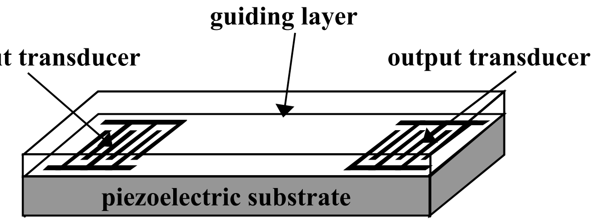
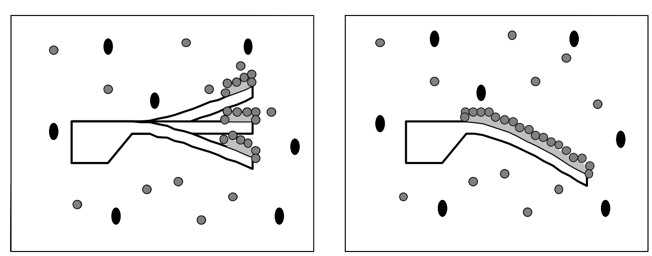


Fig. 1. Schematic of Love-wave device

More recently, another approach to implement chemical microsensors utilizes silicon microcantilevers. The physical effect used by this new type of sensor is also based on perturbations of the sensitive coating properties. In fact, the sorption of specific species by the coating modifies its physico-chemical characteristics and consequently the mechanical properties of the cantilever. The two principal modifications used within the framework of chemical sensors are the variation of the resonant frequency resulting essentially from the mass modification of the system [4, 5] (Fig. 2a) or the bending variation due to the difference of the mechanical surface stress between microcantilever and sensitive layer after sorption [6, 7] (Fig. 2b).



(a) modification of the resonant frequency

(b) modification of the deflection

Fig. 2. Microcantilever sensor principles:
(a) microbalance, (b) surface stress sensor

In the case of resonant frequency measurement (Fig. 2a), silicon microcantilevers are essentially sensitive to the coating mass changes. However, for Love-wave devices, frequency shift is not directly linked to a resonance phenomenon but to perturbation of the wave propagation velocity. As a result the acoustic wave device is sensitive to all types of propagation perturbations which include mass loading and mechanical properties changes (e.g. viscoelasticity) of the coating. Very often, mass loading effect and elastic changes are coupled in the sensor response, which makes identification and quantification of each contribution very difficult. Consequently, one of the difficulties in acoustic sensor field is to separate each phenomenon from the induced frequency shifts.

In the present study, experimental results from microcantilevers and Love-wave devices are coupled in order to identify and separate the two effects. The coupling of measurements from the two sensors, combined with a numerical analysis taking into account elastic properties of the sensitive coating, allows to estimate the polymer elasticity contribution. Latter, this coupled study will also be interesting for gas and liquid phase detection applications, as it will permit to determine the elasticity evolution during the detection process, i.e. the analyte sorption.

II. SENSORS DESIGN

A. Love-wave devices

The base of Love-wave device is the Surface Skimming Bulk Wave (SSBW) device consisting in a piezoelectric substrate with two interdigital transducers (IDT) separated by the wave propagation path (delay line). Using quartz substrate, the IDTs are realized with their fingers parallel to X crystallographic axis in order to generate pure shear horizontal polarized waves. To obtain the Love-wave device, a thin layer is added on the top of the substrate; under certain conditions the SSBW is trapped and guided in the top layer, which is called guiding layer. The main characteristics of Love-wave devices are substrate material and cut, guiding layer thickness and wavelength (IDTs periodicity). A theoretical modeling using analytical resolution of motion equations allowed to determine the characteristics which give the best results in term of mass loading sensitivity [8]. According to these results, different devices were realized (Fig. 3). For these devices, working frequency is in the range from 87 MHz to 115 MHz.

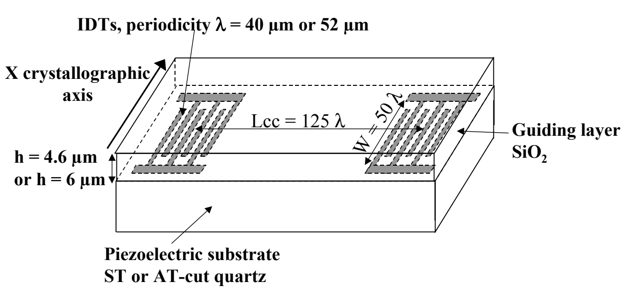


Fig. 3. Experimental Love-wave devices characteristics

Love-wave propagation is characterized by the phase velocity and the attenuation. In order to measure accurately the wave phase velocity changes, the Love delay line is inserted in the retroaction loop of an amplifier to constitute an oscillator system. The output signal is then the oscillator frequency which is measured with a counter. The best accuracy needs an oscillator as stable as possible. With a good choice of electronic devices, we can achieve oscillator short time stability about a few hertz per second at a working frequency close to one hundred megahertz.

B. Microcantilevers devices

Usually in such microsensors, the microstructures are parallelepiped-shaped or standard AFM V-shaped microcantilevers with sensitive coating at the free-end or over the whole structure [9,10]. In order to improve the performances of such sensors, and to assure easier measurement with maximal sensitivity, various shapes have been studied. Then, the resonant frequency and sensitivity expressions have been derived and an optimization of the material, size and shape has been performed [11]. After all, to facilitate the frequency measurement and to have a large sensitive surface, it is interesting to set up a rectangular plate at the free-end of the cantilever (Fig. 4).

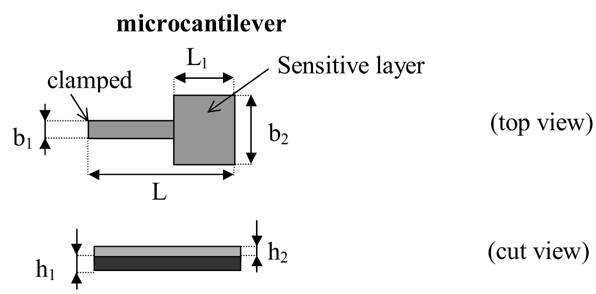


Fig. 4. Microcantilever geometrical parameters

Cantilever sensors have been realized at ESIEE group [12] from silicon, using photolithography, DRIE (Deep Reactive Ion Etching) and metallization techniques. Fig. 5 illustrates two kinds of structures labelled **IIC5** (L=2mm, b_1=400µm, b_2=1mm, h_1=66µm) and **IIC8** (L=3mm, b_1=400µm, b_2=2mm, h_1=66µm). According to Fig. 4, L is the total length, b_1 the cantilever width, b_2 the square plate width and h_1 the cantilever thickness.

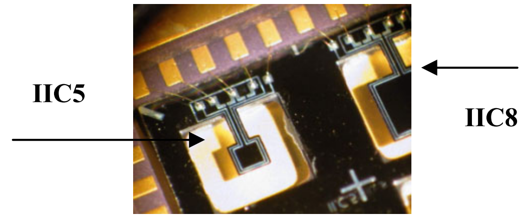


Fig. 5. Microstructure realized at ESIEE group [12]

Targeting a full compact microsystem, the excitation of the cantilever in the resonant mode is performed by applying piezoelectric material or by making use of a magnetic field. For the piezoelectric excitation, the piezoelectric material is a ceramic glued under the chip which permits the cantilever oscillation. Concerning the electromagnetic excitation, a magnetic field created by a magnet placed close to the chip interacts with an electrical current (passing through a conducting strip placed on the microcantilever) and allows to obtain an electromagnetic force (Laplace force) which sets up the structure in motion.

In order to detect the cantilever oscillation, semiconductor strain gauges are etched on the device surface.

Like for the Love-wave devices, the microcantilever is inserted in the retroaction loop of an amplifier to constitute an oscillator (Fig. 6) and according to the Barkhausen conditions, the resonant frequency is monitored. Using this electronic circuit, shifts in the frequency are observed when the structure mass changes, e.g., by addition of a sensitive coating or later by the sorption of vapor into a surface coating.

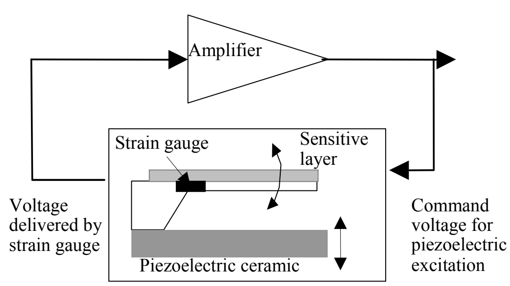


Fig. 6. Block diagram of the electrical oscillator with piezoelectric excitation and piezoresistive measurement

III. Experimental Set Up and Procedure

A. Coating material

A wide range of partial selectivity and sorption properties can be recovered by careful selection of the polymeric coating materials [13]. In our particular case, to detect humidity and organic volatile compounds (alcohols vapors: ethanol, propanol….) the investigated microsensors were coated with a slightly polar poly(etherurethane) PEUT film. This polymer, received from Thermedics Inc.(Tecoflex EG-80A), presents a high porosity and a low glass transition temperature (Tg). Indeed, a low Tg is an interesting property when sorption and diffusion phenomena are studied.

B. Layer deposition

The polymeric film PEUT is deposited onto the sensing structures by spray coating with a controlled time to obtain a layer which can be reproduced. Before spraying, the polymer PEUT is dissolved in dichloromethane solvent (concentration 25mg/mL) and may be continuously agitated. Then, the solution is sprayed onto the cleaned devices with an airbrush system (Dosage 2000, model Valmemate™ 7040) using pure nitrogen as carrier gas, and shadow mask.

C. Measurement procedure

Hence, the experiments consist in recording in real time, the frequency shift of both devices in oscillator configuration. The solution (PEUT+solvent) is sprayed during 0.1s and between each layer deposition a time of oscillator stabilisation is necessary (Figs. 7, 8).

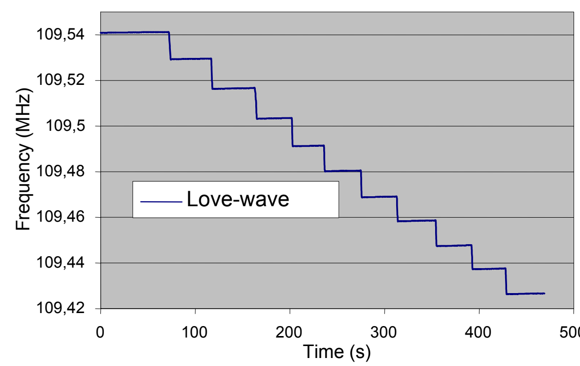


Fig. 7. Frequency versus time for Love-wave device working at 109MHz (ST-cut quartz substrate, wavelength $\lambda = 40$ µm, SiO_2 guiding layer, thickness h = 6 µm). 10 depositions of PEUT (during 0.1 s).

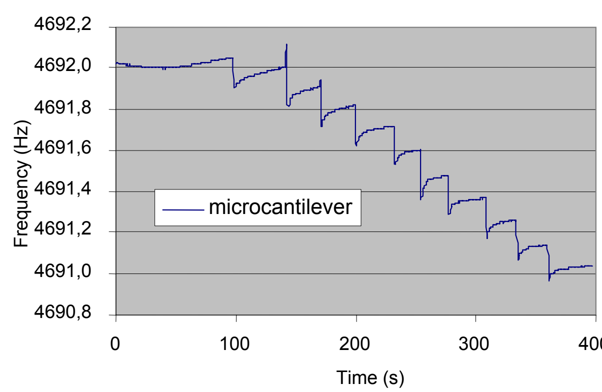


Fig. 8. Frequency versus time for microcantilever device (IIC8). 10 depositions of PEUT (during 0.1 s)

According to Figs. 7 and 8, we can notice that the frequency shift is important at the beginning of spraying time. In fact, this high value corresponds to the mass effect of both polymer and solvent. Then, the frequency rises again because of solvent evaporation and so mass structure decreasing.

IV. RESULTS AND DISCUSSION

A. PEUT thickness evaluation with Love-wave

To evaluate the coating thickness, in case of Love-wave devices, we use the theoretical modeling consisting in an analytical resolution of propagation equations in the considered structure. Details for this model could be find in [8]. The analytical resolution uses a multilayer structure (Fig. 9). Each layer is described by its mechanical parameters (shear elastic modulus μ for isotropic material, elastic stiffness constants c_{ij} for anisotropic), its density (ρ), its shear bulk velocity (V_i) and its thickness (h, b) if relevant.

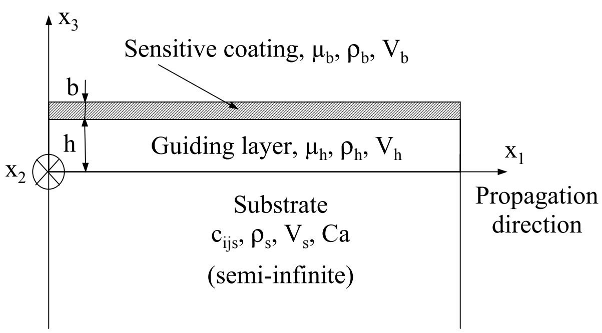


Fig. 9. Love-wave multilayer structure

The analytical resolution allows to obtain the dispersion relation which links the wave phase velocity with all the structure parameters. It is then possible to calculate the wave phase velocity of the two layers structure (substrate and guiding layer) without coating, and of the three layers structure taking into account the coating layer. The difference between these two quantities gives the velocity shift due to coating deposition. As we measure a frequency shift in oscillator configuration, we have to link the frequency shift with the velocity shift. The relation is given by the expression:

$$\frac{\Delta f}{f_0} = \frac{V_g}{V_0}\frac{\Delta V}{V_0} \quad [14]$$

Δf and ΔV are respectively the frequency and the phase velocity shifts due to coating deposition, f_0 and V_0 are the frequency and the phase velocity without coating layer, and V_g is the group velocity.

It is then possible to evaluate the coating thickness. The Love-wave oscillator frequency has been recorded during PEUT deposition (Fig. 7), and the frequency shift at steady-state is extracted. PEUT parameters (density and shear modulus) are given by the provider and, using the theoretical modeling and the above expression, the coating thickness is evaluated to fit experimental curves. A thickness of about 40 nm is found for ten successive PEUT depositions during 0.1 s.

B. PEUT thickness evaluation with microcantilever

The microstructure resonant frequency can be expressed by the classical expression :

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{0.24\,m}}$$

with m the microstructure mass and k the microstructure stiffness.

For a cantilever composed of two different materials, the mass and stiffness expressions are:

$$m = (\rho_1 h_1 + \rho_2 h_2)\Sigma$$

and

$$k = \frac{\alpha\Sigma}{L}\left(\frac{\hat{E}_1 h_1^3}{12} + \frac{\hat{E}_2 h_2^3}{12} + \frac{h_1 h_2 \hat{E}_1 \hat{E}_2 (h_1 + h_2)^2}{4\left(h_1 \hat{E}_1 + h_2 \hat{E}_2\right)}\right)$$

with α a constant depending on the shape of the microcantilever, Σ the upper-surface of the microcantilever, L the length, h_1 and h_2 the thicknesses of the two materials, ρ_1 and ρ_2 the mass densities, $\hat{E}_1 = E_1 / \left(1-\nu_1^2\right)$ and $\hat{E}_2 = E_2 / \left(1-\nu_2^2\right)$ with E_1 and E_2 the Young's moduli and ν_1 and ν_2 the Poisson's coefficients.

For silicon microcantilever with PEUT coating the relative variations of the stiffness k and of the mass m have been plotted in Figs. 10 and 11.

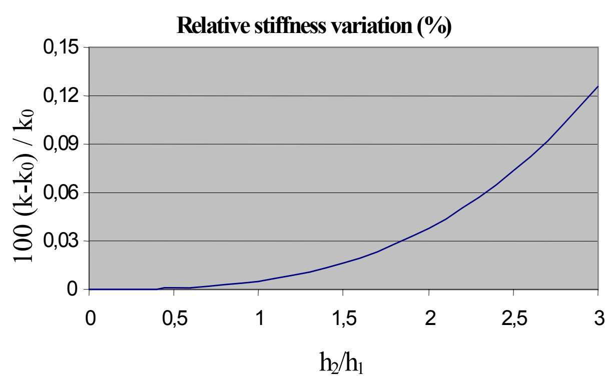


Fig. 10. Relative stiffness variation as a function of the PEUT thickness
silicon: E_1=150GPa, ν_1=0.273, so $\hat{E}_1 = E_1 / \left(1-\nu_1^2\right)$ =162GPa
PEUT: E_2=6.89MPa, ν_1=0.2, so $\hat{E}_2 = E_2 / \left(1-\nu_2^2\right)$=7.18MPa

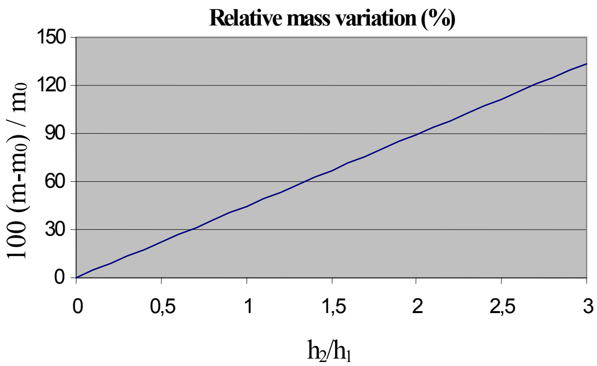


Fig. 11. Relative mass variation as a function of the PEUT thickness silicon: ρ_1=2330kg/m^3, PEUT: ρ_2=1040kg/m^3

Considering Figs. 10 and 11, for silicon and PEUT materials, we can conclude that the relative mass variation during the polymer deposit is at least thousand times more important than the relative stiffness variation. So, during the sensitive coating deposit the structure stiffness can be considered constant and only the mass is modified. Consequently, the frequency expression f with coating is linked to the frequency without coating, f_0, as follows:

$$f = f_0 \frac{1}{\sqrt{1+\frac{\rho_2 h_2}{\rho_1 h_1}}}$$

Using this expression and the frequency shift (Fig. 8) the PEUT film thickness is estimated by the expression:

$$h_2 = \frac{\rho_1 h_1}{\rho_2}\left(\frac{f_0^2}{f^2}-1\right)$$

The polymer thickness extracted from experimental frequency shift is about 60 nm for a time deposition of 0.1s. This result is very different from the 40 nm thickness obtained with Love-wave device results. It is then necessary to confirm the polymer thickness by direct measurement and to go further in the experimental results exploitation.

C. Comparison and results ascertaining

For the calibrations of the spray coating system, and in order to verify that microcantilevers are essentially sensitive to the coating mass change, the thickness of the deposited film has been characterized by optical profilometry (Fig. 12).

According to Fig. 12, the results obtained by optical profilometry are in agreement with experimental results. So we can conclude that the thickness evaluated with microcantilevers is correct and then that these devices are essentially mass sensitive, whereas the thickness evaluated with Love-wave devices is wrong.

This discrepancy between acoustic devices and microcantilevers can be explained by the fact that, as mentioned in the introduction, Love-wave devices can respond to a variety of properties of the coating layer. In particular changes in the shear modulus, can affect the device response. Moreover, the polymers shear modulus is strongly frequency dependant, and Love-wave devices work at high frequency (about 100 MHz). So it is obvious that the data sheet value given by the provider for the PEUT shear modulus is not correct for the Love-wave devices frequencies.

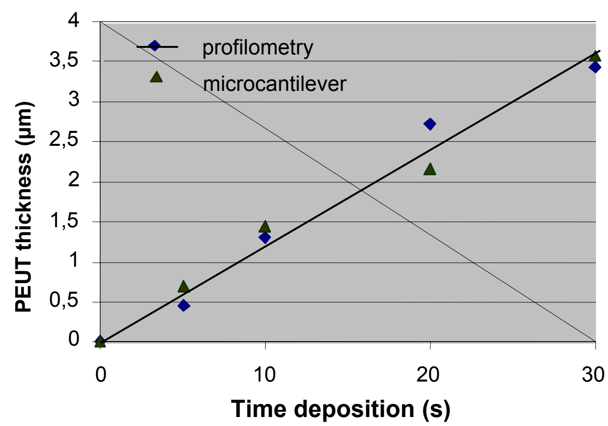


Fig. 12. PEUT thickness versus time deposition

We propose to use the results of microcantilevers to evaluate the polymer thickness and then to find the new shear modulus value which fit experimental curves. Fig. 11 shows the relative frequency shift obtained for two Love-wave devices. We present experimental results, directly extracted from the oscillator records, and theoretical results using analytical modeling. The polymer thickness is those given by microcantilevers results.

The discrepancy revealed by results comparison in previous paragraph is visible on Fig. 13. Using the provider's value for the PEUT shear modulus (2.87x10^6 N/m²), the theoretical relative frequency shift is not in agreement with experimental results. Moreover, this result using a rubbery material shows an exponential evolution whereas the evolution of experimental relative frequency shift is linear versus polymer thickness.

To explain these differences and to rectify the theoretical results, we take into account the frequency dependence of polymer shear modulus. Studies of the viscoelastic properties of polymers bring to light the evolution of polymer shear modulus versus frequency of excitation [15]. A rubbery polymer at low frequency could appear to be glassy if it is excited at high frequency. This leads us to increase the PEUT shear modulus value to fit experimental curves (Fig. 13).

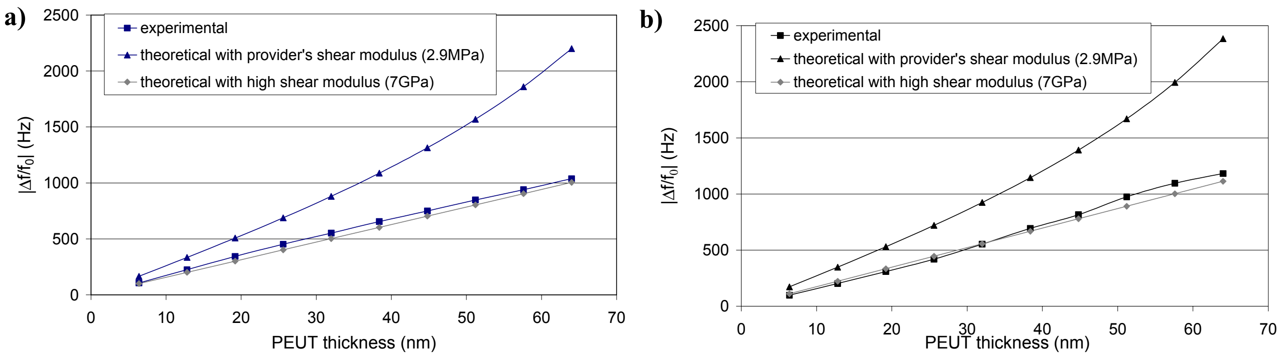


Fig. 13. Relative frequency shift versus PEUT thickness for two Love-wave devices. a) Love-wave device working at 109 MHz (ST-cut quartz substrate, λ = 40 µm, SiO_2 guiding layer, h = 6 µm). b) Love-wave device working at 115 MHz (AT-cut quartz substrate, λ = 40 µm, SiO_2 guiding layer, h = 4.6 µm)

The new value found for shear modulus is about $7x10^9$ N/m², which is a glassy value. We have to note that we consider only the elastic part of polymers mechanical properties in this study. The imaginary part of shear modulus representing the viscosity contribution is not taken into account. This choice is driven by no additional attenuation measured on Love-wave devices during polymer deposition (insertion losses (S_{21}) measured with a network analyzer at the end of the coating process).

This result is very interesting for the understanding of Love-wave sensors response. Indeed, previous results in gas detections showed an experimental mass loading sensitivity lower than theoretical predictions [16]. This element could now be explained by a wrong sensitive coating shear modulus value. For future chemical detections, it is of primary importance to characterize the sensitive coating at high frequency in order to improve our theoretical predictions.

V. Conclusion

In this paper, an original approach to couple both Love-wave and microstructure platforms has been proposed to identify and separate gravimetric and elastic effects.

First, the experimental tests comparison shows a discrepancy thickness value between the two devices but the difference is explained. Indeed, the Love-wave device is sensitive to mass loading and mechanical properties changes (e.g. elasticity) of the coating. So, the coupling of measurements from the two sensors combined with a numerical analysis allow first, to demonstrate that microcantilevers are essentially mass sensitive. As a result, we can estimate the polymer elasticity contribution and so rectify the theoretical values of Love-wave device, taking into account the frequency dependence of polymer shear elastic modulus.

Finally, this coupled study is also interesting for gas and liquid phase detection applications, as it will permit to determine the elasticity evolution during the detection process, i.e. the analyte sorption.

Acknowledgment

The authors thank Olivier Français, from the ESIEE group for the technological process setup concerning the microcantilever sensors.

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