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Unconventional uses of cantilevers for chemical sensing in gas and liquid environments

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Abstract

Microcantilevers used as (bio)chemical sensors are usually coated with a chemically sensitive layer. The coated devices operate either in a static bending regime or in a dynamic flexural mode. While the coated devices operate generally well in both the static and dynamic mode, they do suffer from certain shortcomings depending on the medium of operation and the application, including lack of selectivity and of reversibility of the sensitive coating and a reduced quality factor due to the surrounding medium. In particular, the performance of microcantilevers excited in their standard out-of-plane dynamic mode drastically decreases in viscous liquid media. Moreover, the responses of coated cantilevers operating in the static bending mode are often difficult to interpret. To resolve those performance issues, unconventional uses of microcantilever are reviewed in this paper, which consist of the use of the dynamic mode without sensitive coating, the use of in-plane (flexural and longitudinal) vibration modes in liquid media, and fully accounting for the viscoelastic effects of the coatings in the static mode of operation. The advantages and drawbacks of these unconventional uses of microcantilevers for chemical sensing in gas and liquid environments are discussed.

Keywords: Cantilever, chemical detection, resonant sensor, in-plane mode, viscoelasticity, static mode

1. Introduction

In recent years, interest in microcantilever-based chemical and bio-chemical sensing systems has risen due to their projected high sensitivity [1-5]. The large ratio of surface area to volume makes the microcantilever extremely sensitive to surface processes. For (bio)chemical detection, the microcantilever is usually coated with a (bio)chemically sensitive layer that aims to selectively sorb the analyte or molecule of interest. The sorbed substances can then be detected by monitoring either the resonant frequency (dynamic mode) or the quasi-static deflection (static mode). In the case of dynamic mode operation, the change in mass associated with the sorption of analytes into the sensitive coating causes a shift in resonant frequency, which may be correlated to the ambient

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concentration of the target substance. For static-mode operation, the sorption of analytes causes a cantilever deflection that is induced by the tendency of the sensitive coating to expand (or contract) upon analyte sorption.

While such cantilever-based sensors generally operate relatively well, they have shortcomings depending on the medium of operation and the application. The main performance issues can be summarized as follows:

- *Drawbacks due to the sensitive coating:* In addition to being subjected to environmental effects including temperature, humidity and aging effects, most chemically sensitive coatings, often polymers, only show partial selectivity to various analytes. Ideal selectivity is often achieved at the expense of reversibility. Moreover, the limited long-term stability of the coatings and the resulting aging affect the reliability of the sensor.
- *Drawbacks of the commonly used flexural out-of-plane dynamic mode in liquid media:* Dynamically excited microcantilevers are well suited for operation in low-viscosity media such as air. Their usefulness as a sensing platform is limited when operating in viscous liquid media. This is due to the large decrease in the device's quality factor caused by the additional viscous losses in the fluid. While the viscous damping reduces the quality factor the effective displaced fluid mass causes a significant decrease in the resonant frequency. The result is a decrease in the device sensitivity as well as an increase in the system's susceptibility to frequency noise, thus raising the sensor's detection limit. It is noted that the sensitivity of the sensors in dynamic mode increases with the resonant frequency, whereas the quality factor Q of the resonance mode influences the sensor resolution.
- *Drawbacks due to the interpretation of the static mode responses:* In static mode operation, polymer-coated microcantilevers may exhibit either a monotonic transient response or a response with overshoots [6]. Such differences in the sensor response make it difficult to easily interpret the measurements, analyze and predict the sensor's response, and perform signal processing for rapid and error free detection of chemical analytes.

In the present paper, we will review unconventional uses of microcantilevers as chemical sensors to solve some of the performance issues and avoid associated drawbacks. To eliminate problems associated with the sensitive coatings, an alternative method to detect and quantify chemical species without sensitive coating in certain applications will be presented (section 2). To resolve the drawbacks associated with the commonly used flexural out-of-plane dynamic mode in viscous liquid media, the characteristics of alternative vibrating modes, such as the in-plane (flexural and longitudinal) vibrating modes, will be described (section 3). Finally, an interpretation of the static-mode cantilever response taking into account the viscoelasticity of the sensitive coatings will be introduced in section 4.

2. Uncoated microcantilever-based chemical sensors operating in dynamic mode

2.1. Basic equation for dynamic mode operation

When a microcantilever vibrates in a viscous fluid (gas or liquid), the fluid offers resistance to the motion. The force per unit length, F_{fluid}, which is the consequence of all normal and tangential stresses (hydrodynamic pressure and viscous shear) exerted by the fluid on all the surfaces of the cantilever, can be written in the frequency domain (underlined notation) as [7]:

$$\underline{F_{fluid}} = -j\omega \underline{g_1}(\omega,x)\,\underline{w}(\omega,x) + \omega^2 \underline{g_2}(\omega,x)\,\underline{w}(\omega,x) \tag{1}$$

where x is the longitudinal coordinate, ω the radial frequency of the vibration, $\underline{w}(\omega,x)$ the microcantilever deflection, and $\underline{g_1}$ and $\underline{g_2}$ are functions specific to the fluid properties and the microcantilever cross-sectional geometry.

The fluid effects (viscous and inertial) influence the dynamic response of the beam, in particular, the resonant frequency f_r and the quality factor associated with viscous losses, Q_{visc}, as [8, 9]:

$$f_r = f_{0,vac} \frac{1}{\sqrt{1 + L\underline{g_2}/m}} \sqrt{1 - \frac{1}{2Q^2}} \tag{2}$$

$$Q_{visc} = \frac{2\pi\sqrt{1 + L\underline{g_2}/m}}{L\underline{g_1}/m} f_{0,vac} \quad (3)$$

where $f_{0,vac}$ is the undamped natural frequency of the microcantilever in vacuum, Q is the total quality factor of the cantilever/fluid system (incorporating all losses), m is the microcantilever mass and L is the microcantilever length.

The above equations illustrate the fact that in the general case of dynamic mode operation of a microcantilever, the resonant frequency depends on the fluid properties via the terms $\underline{g_1}$ and $\underline{g_2}$. Such dependency can be used to quantify the fluid, thus eliminating the need for a chemically sensitive coating.

2.2. Gas detection in binary mixture

Using the previous equations, analytical expressions for the relative frequency shift due to small changes in both mass density and viscosity of the fluid can be obtained. In the case of different binary mixtures (He / N_2, CO_2 / N_2 and H_2 / N_2), it has been shown that the predominant effect for the change in the microcantilever resonant frequency is due to the gas mass density variation [10]. The developed theory also allows to optimize the cantilever geometry with respect to the sensor sensitivity. In particular, the relative frequency shift due to the mass density of the gas increases with the ratio of the microcantilever width to the microcantilever thickness. Examples for the detection of hydrogen in air and carbon dioxide in nitrogen using silicon cantilevers with electromagnetic actuation and piezoresistive measurements are presented in Fig 2. The silicon cantilever has a length of 2mm, a width of 400µm and a thickness of 15µm. The resonance frequency of the uncoated sensor is approximately 5kHz.

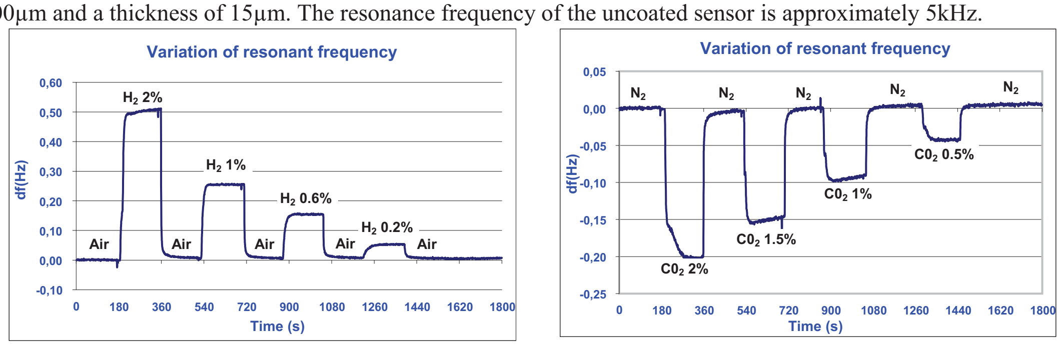

Fig. 2. Example of (a) detection of hydrogen in air and (b) carbon dioxide in nitrogen with an uncoated 2000 x 400 x 15µm^3 silicon cantilever

Compared to classical resonant microcantilever-based chemical sensors with sensitive coatings, the uncoated microsensors exhibit shorter response times because there is no analyte diffusion into the coating affecting the sensor response. Moreover, the absence of the sensitive coating leads to a more reliable and reversible behavior because there is no significant absorption and desorption phenomenon. The above results indicate that uncoated microsensors may serve as viable devices for the detection of specific concentrations of one gas in a binary mixture. The sensitivity and resolution of such sensors will be larger for those cases in which the difference between the mass densities of the two gases is higher. The major drawback of such sensor is that there is no intrinsic selectivity, thus these sensors can only be used for monitoring in environments where it is known that only one gas concentration can vary.

3. In-plane vibration modes in liquid media

From equation 2, it can be seen that the decrease of the resonant frequency when the microcantilever is immersed in a fluid is essentially due to the mass effect $\underline{g_2}$; this effect can be minimized if the term $\underline{g_2}$ is small in liquid. On the other hand, the strong decrease in the quality factor in liquid is due to the stronger influence of the viscous term $\underline{g_1}$ compared to the influence of the displaced fluid mass (term due to $\underline{g_2}$) in equation 3.

In order to limit the decrease of both the resonant frequency and the quality factor upon immersion in liquid media, alternative vibration modes that essentially shear the surrounding fluid rather than exerting normal stress on it have been studied and tested. In particular, two in-plane vibration modes (lateral flexural mode and elongation mode) have been theoretically studied [11, 12] in order to better understand the "intuitive" advantages offered by the in-plane mode of microcantilever-based sensors over their out-of-plane mode counterparts, as well as to quantify these advantages. Example measurements of the resonant frequency and quality factor associated with these two unconventional modes are presented in what follows.

3.1. In-plane (lateral) flexural mode

Exciting the microcantilever in the in-plane flexural vibration mode (or lateral vibration) rather than the out-of-plane flexural mode would reduce the amount of fluid resistance (combined effects of fluid-related inertial and viscous forces), which could potentially improve the sensitivity and limit of detection of microcantilever-based chemical sensors. The characteristics of the in-plane flexural mode can be obtained by evaluating the hydrodynamic forces ($\underline{g_1}$ and $\underline{g_2}$) acting on a laterally vibrating microcantilever as a function of both Reynolds number (fluid properties) and cantilever aspect ratio (thickness over width). Obtaining the hydrodynamic forces allows for the resonant frequency and *Q*-factor to be investigated as functions of both beam geometry and medium properties [11]. Trends in these characteristics can be used to optimize device geometry and maximize the frequency stability in sensing applications.

Several cantilevers with widths of 45, 60, 75 and 90µm, lengths of 200, 400, 600, 800, 1000µm and thicknesses 8, 12µm, corresponding to in-plane resonance up to about 3MHz have been characterized in air and water. The modeling of the fluid interaction terms, $\underline{g_1}$ and $\underline{g_2}$, for the lateral mode result in the resonant frequency being proportional to b/L^2 (where *b* is the cantilever width and *L* the cantilever length), the relative resonant frequency shift from air to water being proportional to $L/\sqrt{b}$ and the quality factor (in water) being proportional to $\sqrt{b}/L$ [11, 14]. These results of the modeling are in agreement with measurements made on the different cantilever geometries considered. Moreover, for the first lateral flexural mode, these microcantilevers exhibit quality factor in air up to 4300 and up to 67 in water (which usually doesn't exceed 10 in water for out-of-plane modes). Moreover, the resonant frequencies of the in-plane mode are only lowered by 5% to 10% in water compared to the values in air, whereas this reduction is approximately 50% for the out-of-plane modes. These two characteristics of the lateral mode operation are promising for future detection in liquid media.

For the microcantilevers designed and fabricated for operation in lateral flexural vibration mode, thermal excitation and piezoresistive detection based both on diffused resistors have been chosen as driving and sensing mechanisms, respectively. The design of the actuation resistors and integrated Wheatstone bridge allow a more efficient excitation of the in-plane flexural mode than the more classical out-of-plane flexural mode [13]. It is noted that, for example, at a given driving voltage, the free-end vibration amplitude, measured using a Polytec MSA-500 laser vibrometer, is 118nm at the first transverse flexural resonant frequency whereas it is 750nm for the first lateral flexural resonant frequency.

3.2. In-plane longitudinal mode

For the same reason as noted in the previous section, the longitudinal (axial) mode may be of potential interest for detection in liquid media. To assess the characteristics of this mode, self-actuated resonant-microcantilevers based on a thick-film piezoelectric layer associated with two electrodes have been processed and tested. Screen-printed microcantilevers comprising Au/PZT/Au layers are partially released from an alumina substrate (Fig.3) using a sacrificial layer process [15].

Using an impedance analyzer (HP4194A), frequency spectra have been measured for three different cantilever geometries (piezoelectric layers of $10x2x0.075mm^3$, $8x2x0.075mm^3$ and $6x1x0.075mm^3$ coated with 5-10µm thick symmetrical electrodes) in air and in various fluid with viscosities ranging from 1.55 to 300cP. Even though the quality factor in air is relatively low (probably due to internal mechanical losses and piezoelectric losses), ranging from 130 to 300, the quality factors in liquids are significantly higher compared to those of classical out-of-plane modes; the measured total quality factors for the three cantilever geometries range from 70 to 107, 41 to 51, and 20 to 22 for the 1.55, 20, and 300cP fluids, respectively. The decrease of the resonant frequency of the first longitudinal mode from air to dodecan (1.55cP) is only 1% and from air to 300cP silicone oil is a mere 2.8%.

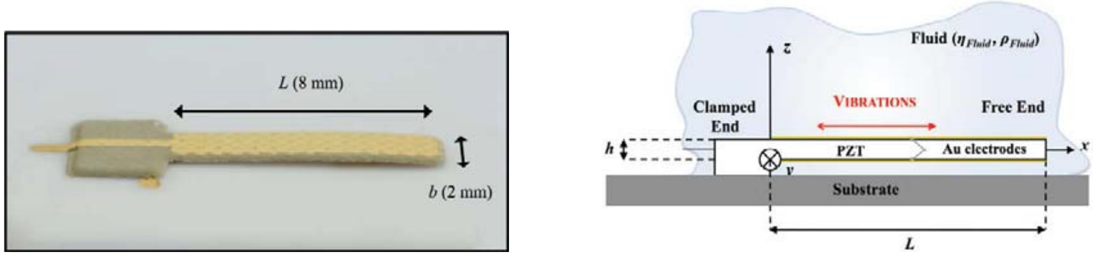

Fig. 3. (a) Example of screen printed piezoelectric cantilever; (b) schematic of the longitudinal mode [12]

As was the case with lateral-mode silicon cantilevers having an integrated scheme for actuation and measurement, these thick film piezoelectric cantilevers actuated in the longitudinal mode and utilizing impedance measurement are promising in terms of sensitivity and limit of detection for (bio)chemical detection in liquid media.

4. Influence of the viscoelasticity of polymer coatings on static mode cantilever response

A static-mode polymer-coated microcantilever undergoes a quasi-static deformation when analyte sorption causes either a change in the surface free energy (adsorption) or coating expansion (absorption). In either case, it is necessary to have an accurate model of the beam's deflection in order to design devices for high sensitivity, analyze and predict the sensor's response. The transient response in the static mode can be of various shapes when polymeric sensitive coatings are used, which include monotonic response and response with an overshoot. An analytical solution for predicting deflection and stress in a cantilever with viscoelastic coating when the coating is subjected to an exponential eigenstrain history (i.e., sorption-induced swelling strain) has been developed which provide an explanation for the different shapes observed in the transient responses [16]. The validation of this analytical model and its limitations has been made using finite element modeling [17].

Based on the results of the analytical model, an optimization of the choice of the mechanical viscoelastic properties of the polymer coating (instantaneous and asymptotic biaxial moduli and corresponding relaxation time) and of the coating thickness (determining the time constant of the chemical diffusion into the coating and then of the eigenstrain) can be envisaged in order to have larger transient deflection and an overshoot whose characteristics could possibly be used to perform more rapid chemical detection eliminating the need to wait for the steady state to be achieved. The reduction in detection time could be especially large in case of thick coatings and/or polymeric coatings that exhibit slow creep/relaxation.

5. Conclusion

The limitations of classical microcantilever-based microsensors are essentially due to the low selectivity and reliability of the sensitive coating, the limitation of the dynamic mode in liquid media, and the difficulty in interpreting static-mode response. In the present paper, some alternative uses of microcantilevers as chemical sensors have been proposed. The feasibility of these unconventional uses has been confirmed by physical analytical modeling, in addition to experimental observations and/or numerical validation. These unconventional uses have some advantages (shorter response time, better reliability when sensitive coatings are not used, higher quality factor and resonant frequency in liquid for in-plane resonant modes (relative to the classical out-of-plane mode), and higher signal and shorter response time utilizing the overshoot phenomenon in the static mode). However, these advantages are accompanied by some drawbacks, including lack of selectivity when sensitive coatings are not employed and the difficulty in determining the viscoelastic properties of polymer coatings for static- mode applications. The preliminary results are promising, but further measurements and modeling have to be performed in order to fully realize the benefits that these unconventional uses may offer.

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