

Marquette University
e-Publications@Marquette

Civil and Environmental Engineering Faculty
Research and Publications

Civil and Environmental Engineering, Department
of

6-1-2011

On the Relative Sensitivity of Mass-sensitive Chemical Microsensors

Luke A. Beardslee

Georgia Institute of Technology - Main Campus

S. Truax

Georgia Institute of Technology - Main Campus

J.-J. Su

Georgia Institute of Technology - Main Campus

Stephen M. Heinrich

Marquette University, stephen.heinrich@marquette.edu

Fabien Josse PhD

Marquette University, fabien.josse@marquette.edu

See next page for additional authors

Accepted Version Published as part of the proceedings of the conference, *16th International Solid-State Sensors, Actuators and Microsystems Conference*, 2011: 1112-1115. DOI. © Institute of Electrical and Electronics Engineers. Used with permission.

Authors

Luke A. Beardslee, S. Truax, J.-J. Su, Stephen M. Heinrich, Fabien Josse PhD, and O. Brand

On the Relative Sensitivity of Mass-Sensitive Chemical Microsensors

L. A. Beardslee

*School of Electrical and Computer Engineering, Georgia Institute of Technology
Atlanta, Georgia*

S. Truax

*School of Electrical and Computer Engineering, Georgia Institute of Technology
Atlanta, Georgia*

J.-J. Su

*School of Electrical and Computer Engineering, Georgia Institute of Technology
Atlanta, Georgia*

Stephen. M. Heinrich

*Department of Civil and Environmental Engineering, Marquette University
Milwaukee, Wisconsin*

Fabien Josse

*Department of Civil and Environmental Engineering, Marquette University
Milwaukee, Wisconsin*

Oliver Brand

*School of Electrical and Computer Engineering, Georgia Institute
of Technology
Atlanta, Georgia*

Abstract: In this work, the chemical sensitivity of mass-sensitive chemical microsensors with a uniform layer sandwich structure vibrating in their lateral or in-plane flexural modes is investigated. It is experimentally verified that the relative chemical sensitivity of such resonant microsensors is -to a first order- independent of the microstructure's in-plane dimensions and the flexural eigenmode used, and only depends on the layer thicknesses and densities as well as the sorption properties of the sensing film. Important implications for the design of mass-sensitive chemical microsensors are discussed, whereby the designer can focus on the layer stack to optimize the chemical sensitivity and on the in-plane dimensions and mode shape to optimize the resonator's frequency stability.

Keywords, IEEE Keywords: Sensitivity, Resonant frequency, Chemicals, Strontium, Polymers, Silicon, Geometry

INTRODUCTION

Micromachined resonators, in particular cantilever beams, have been extensively investigated for application as mass-sensitive biochemical sensors in both the gas and liquid phase [1]. Typically, these devices have a layered structure and are coated with a uniform sensitive layer (e.g., a polymer film for chemical sensors or a protein layer for biosensors), which binds analyte from the surroundings, increasing the device's mass and thus shifting its resonance frequency.

The limit of detection (LOD) of such resonant sensors, i.e., the lowest possible (ambient) concentration of analyte that will produce a discernable sensor response, may be expressed as three times the ratio of the relative frequency stability σ_{min} (evaluated using, e.g., the Allan variance method) to the relative chemical sensor sensitivity SR (describing the relative frequency change per change in analyte concentration). Alternatively, the LOD can be written as three times the ratio of the minimal detectable frequency change f_{min} and the

absolute chemical sensitivity S (describing the absolute frequency change per change in analyte concentration). Thus,

$$(1) \quad LOD = 3 \frac{\sigma_{min}}{S_R} = 3 \frac{f_{min}}{S}.$$

As described in [2], the chemical sensitivity (S) (as well as the relative chemical sensitivity (S_R)) may be written as the product of the gravimetric sensitivity (G) (or the relative gravimetric sensitivity (G_R)) of the coated resonant sensor, i.e. the change (or relative change) in frequency f with respect to a change in coating density ρ_m , and the analyte sensitivity (S_A), i.e. the change in coating density ρ_m with respect to a change in analyte concentration c_A in the surrounding medium:

$$(2) \quad S = G \cdot S_A = \frac{\partial f}{\partial \rho_m} \frac{\partial \rho_m}{\partial c_A}$$

$$(3) \quad S_R = G_R \cdot S_A = \left(\frac{1}{f} \frac{\partial f}{\partial \rho_m} \right) \frac{\partial \rho_m}{\partial c_A}$$

If the analyte concentration is given in ppm, the analyte sensitivity S_A may be calculated as [2][3]

$$(4) \quad S_A = \frac{\partial \rho_m}{\partial c_A} = \begin{cases} M_A \cdot K \cdot \left(\frac{p}{RT} \right) \cdot 10^{-6} & \text{in gas} \\ \rho_{A} \cdot K \cdot 10^{-6} & \text{in liquid} \end{cases}$$

where ρ_A is the density of the (liquid) analyte, M_A its molar mass, p , R , and T are gas pressure, gas constant and temperature, respectively, and K is the partition coefficient (gas or liquid phase) of the particular analyte/coating combination, i.e., the ratio of the steady-state analyte concentration in the sensitive film to the analyte concentration in the surrounding medium. The factor 10^{-6} accounts for the fact that c_A is given in ppm.

In this work, the chemical sensitivity of resonators vibrating in their lateral or in-plane modes is investigated. The use of in-plane over out-of-plane modes yields advantages of reduced viscous damping and, in the case of liquid-phase sensors, reduced mass loading by the surrounding fluid [4][5]. For this reason, cantilever sensing platforms utilizing the in-plane modes are a promising solution for low-cost or embedded sensors for either biomedical or environmental sensing applications.

THEORY

Assuming a layered cantilever of uniform cross section vibrating in one of its flexural in-plane modes (motion parallel to the planes of the layers), one obtains the resonance frequency by solving the Euler-Bernoulli differential equation, yielding

$$(5) \quad f_i = \frac{\lambda_i^2}{2\pi\sqrt{12}} \frac{W}{L^2} \sqrt{\frac{E_{\text{eff}}}{\rho_{\text{eff}}}}$$

where W and L are the width and length of the cantilever (see schematic in Fig. 1), and E_{eff} and ρ_{eff} are its effective Young's modulus and effective mass density, respectively. The derivation of Eq. (5) assumes that the cantilever experiences bending deformation only, which is generally fulfilled for $L \ll W$ for in-plane vibrations.

Since micromachined cantilevers are often not single-material structures, but layered structures, E_{eff} and ρ_{eff} must be calculated from the (weighted) averages of the different material properties. Assuming a layered beam cross-section (Fig. 1) and operation in an in-plane flexural mode, E_{eff} and ρ_{eff} are simply calculated as:

$$(6) \quad E_{\text{eff}} = \frac{\sum_n h_n E_n}{\sum_n h_n} = \frac{1}{h} \sum_n h_n E_n$$

$$(7) \quad \rho_{\text{eff}} = \frac{\sum_n h_n \rho_n}{\sum_n h_n} = \frac{1}{h} \sum_n h_n \rho_n$$

Assuming that the m -th (and last) layer is the chemically sensitive layer, e.g., a polymer layer, which absorbs analyte molecules from the environment, the density of this layer changes in proportion to the analyte concentration c_A in the environment. For low analyte concentrations, we can assume that the change in ρ_m is proportional to the change in c_A , i.e.,

$$(8) \quad \rho_m(c_A) = \rho_m(0) + S_A c_A$$

$$(9) \quad \rho_{\text{eff}} = \frac{1}{h} \left[\sum_{n=1}^m h_n \rho_n + h_m S_A c_A \right]$$

with the analyte sensitivity SA being the proportionality factor, which is characteristic for the particular recognition film and analyte combination. For simplicity, we assume here that the analyte sorption only affects the cantilever's effective density but not its Young's modulus. Especially for higher analyte concentrations, this might not be a valid assumption [6], but does not affect the conclusions drawn here.

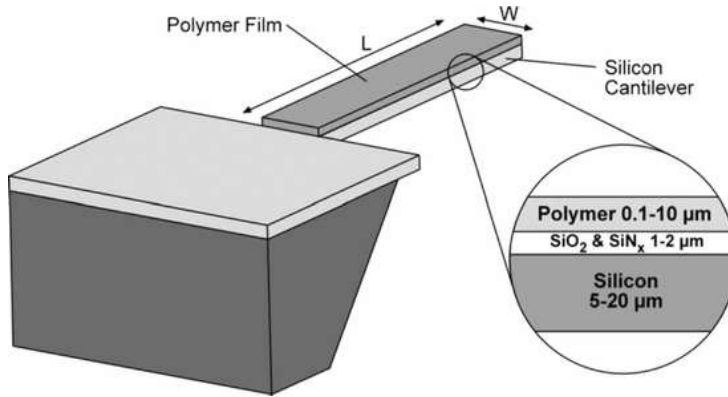


Figure 1: Schematic of prismatic beam and layered structure of the microresonators used in this work.

With analyte sorption only affecting ρ_{eff} (and not E_{eff}), one may easily show that the relative chemical sensitivity for in-plane cantilevers of a given uniform layer sandwich structure is independent of the in-plane dimensions W and L and the mode shape, i.e. λ_i .

$$(10) \quad S_R = \frac{1}{f} \frac{\Delta f}{\Delta c_A} \approx -\frac{1}{2} \frac{h_m S_A}{\sum_{n=1}^m h_n \rho_n}$$

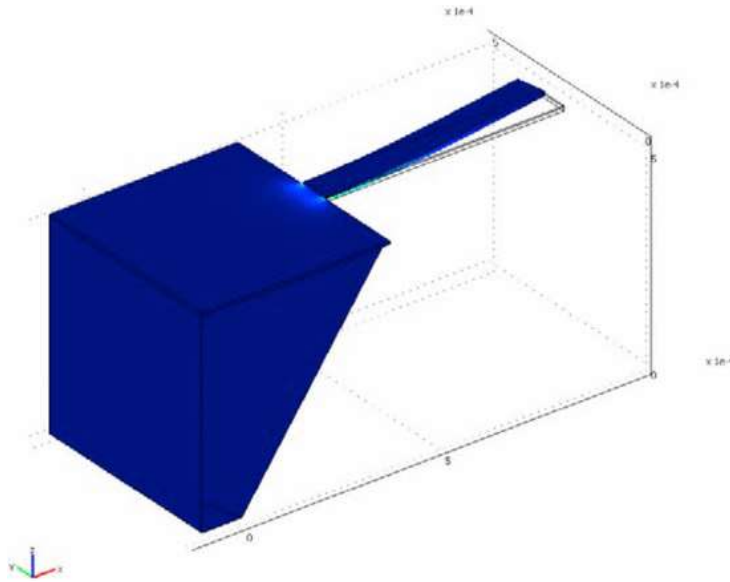
Thus, the relative gravimetric sensitivity GR is simply

$$(11) \quad S_R = \frac{1}{f} \frac{\Delta f}{\Delta c_A} \approx -\frac{1}{2} \frac{h_m S_A}{\sum_{n=1}^m h_n \rho_n}$$

If the in-plane beam dimensions and the employed flexural mode do not affect the (relative) chemical sensitivity' how can we improve the limit of detection of mass-sensitive microsensors? The answer is two-fold: from Eq. (10), we see that increasing the thickness of the sensitive film h_m will increase SR . This increase is linear for small h_m (i.e., as long as the denominator is not increased appreciably

by the increase in hm), but levels off for thicker sensing films. In the limit of a cantilever consisting only of the sensing film, the denominator becomes hm μm and the relative chemical sensitivity SR becomes independent of hm . On the other hand, the effect of the short-term frequency stability on the LOD must be considered. The short-term frequency stability is closely linked to the quality factor of the resonance, with higher Q -factors yielding better (lower) f_{min} . We have, e.g., recently demonstrated the advantages of using in-plane rather than out-of-plane resonance modes when studying the Q -factor of the resonators in air or in water [7].

The finite element modeling (FEM) software COMSOL (Stockholm, Sweden) has been used to simulate the relative gravimetric sensitivity GR of cantilever beams, hammerhead structures and disk-type resonators (see Fig. 4) with a uniform layer structure. For the simulations, a modal analysis was used, the density of the polymer coating on top of the in-plane microresonator was varied, and the resulting shift in resonance frequency was extracted. The structures were not re-meshed when the polymer density was altered. As an example, Fig. 2 shows the finite element model for a $600 \times 75 \times 8 \mu\text{m}$ cantilever coated with a $4 \mu\text{m}$ polyisobutylene (PIB) film as sensitive layer. Part of the silicon support structure is included in the model to account for the non-ideal clamping of the cantilever [5][7].



with those of the hammerhead structure shown in Fig. 4. One also observes that GR is not only constant for the different in-plane (IP) flexural modes, but for the fundamental out-of-plane (OOP) flexural mode as well.

	Mode	f_0 (kHz)	Δf (Hz)	G_R ($10^{-5} (\text{kg m}^{-3})^{-1}$)
45W 200L	1 st OOP	216.1	196.7	9.10
	1 st IP	1163.4	1076	9.25
HH	1 st OOP	98.53	89.80	9.11
	1 st IP	333.5	333.5	9.08

Table 1: Simulation results comparing the relative gravimetric sensitivity of a 45×200 μm cantilever to that of a hammerhead device with a radius of 200 μm . For the simulations, the devices were assumed to have a Si thickness of 8 μm with a 4 μm polymer film ($\rho_{\text{p}}=840 \text{ kg m}^{-3}$) on top. The polymer density was changed by 10 kg m^{-3} . OOP/IP = out-of-plane/in-plane mode.

EXPERIMENTAL VERIFICATION

To experimentally verify that the relative gravimetric sensitivity is, in fact, independent of the in-plane resonator geometry and is only a function of the thicknesses of the layer stack for in-plane excitations, we have exposed PIB-coated microresonators with different in-plane dimensions to different toluene concentrations in a custom gas set-up and extracted their relative chemical sensitivity SR. The resonators themselves are fabricated using a CMOS compatible bulk micro-machining process [4]. The beams consist of a silicon layer, coated with two dielectric layers and the polymer film. The dielectric layers on the beam's surface are composed of (1) a thermal oxide for electrical isolation of the metal lines used to connect the on-chip resistors and (2) a PECVD passivation stack on top of the metal lines (see Fig. 1). The polymer film is deposited onto the beams using a spray-coating system. The polymer thickness is measured using a Tencor P15 contact profilometer; a step is created for this purpose by masking off a portion of each die with tape during spray-coating. The silicon beam thickness is defined by the thickness of an epitaxial layer on the surface of the wafer used for fabrication. Membranes of uniform thickness are released during a potassium hydroxide etching step from

the back of the wafer using an electrochemical etch stop; then, cantilever-type microstructures are defined by reactive ion etching. The thickness of the silicon layer was measured for each tested device using an SEM.

The three different geometries tested are shown in Fig. 4. All of the tested resonators use electrothermal excitation and piezoresistive detection [5], and were fabricated on the same wafer. For the cantilever beams and the hammerhead devices the heating resistors and piezoresistive Wheatstone bridge are at the base of the device, while for the disk-type microresonator they are located at the center of the device. Locating the resistors at the base of the cantilevers and hammerheads minimizes the static temperature increase of the microstructure. A temperature increase of the polymer film reduces the partition coefficient of the analyte in the polymer layer and thus reduces SA (see below).

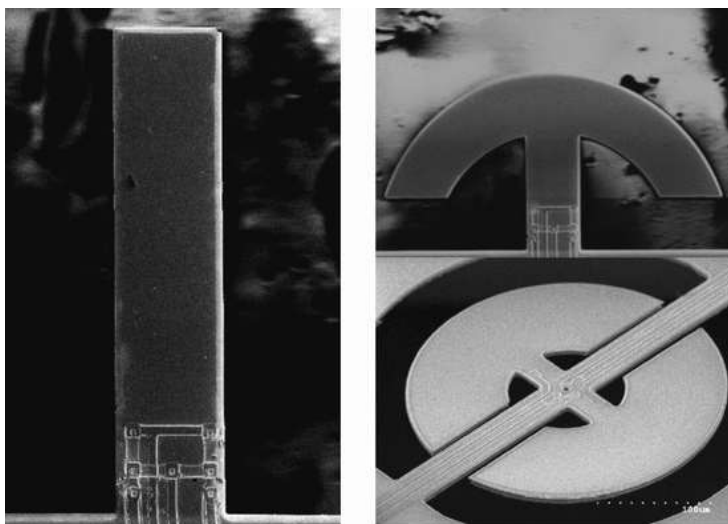


Figure 4
Figure 4: Micrographs of a 45 μm wide, 200 μm long cantilever (left), a hammerhead device (top, right), and a microdisk resonator (bottom, right). For all three devices the resistors for thermal excitation and piezoresistive detection are visible.

Figure 5 shows an example measurement, in this case the first in-plane resonance frequency of a PIB-coated hammerhead structure as a function of time, subject to four injections of toluene with increasing analyte concentration. The chemical sensitivities (SR and S)

can simply be extracted from the observed frequency changes at given analyte concentrations.

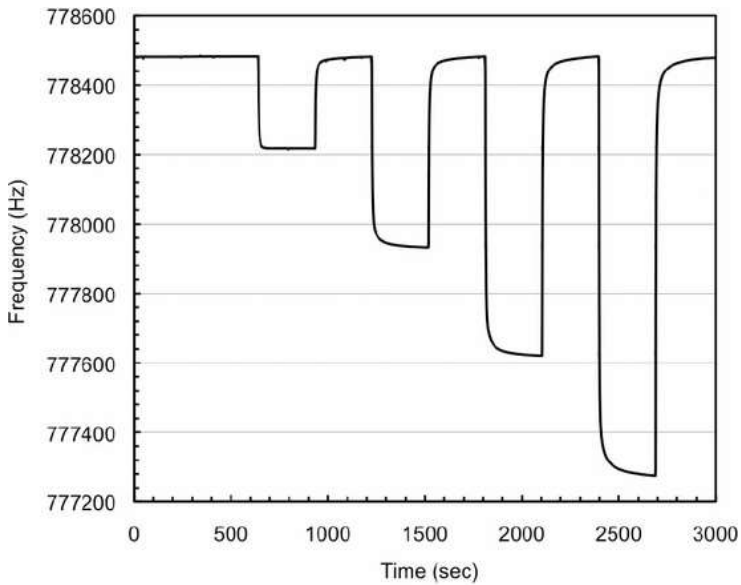


Figure 5

Figure 5: Measured resonance frequency of hammerhead resonator (see Fig. 4) coated with a 0.55 μm thick PIB film as a function of time subject to 4 subsequent exposures to different toluene concentrations (4000, 8000, 12000 and 16000 ppm).

Since the PIB thickness on each device was not identical, the results were normalized by the polymer thickness using Eq. (10). Table 2 compares the normalized sensitivities S/hm and SR/hm of the tested resonators. While S/hm varies by a factor of >20 , SR/hm for the tested beams and hammerhead structures agrees within 50%. For the disk resonator, a distinctly lower SR is found, which is believed to stem from the increased static temperature elevation of this particular device and the resulting lower partition coefficient. The micro-disk experiences a higher static temperature rise compared to other geometries because of the placement of the excitation and detection resistors in the center of the beam.

	f_0 (kHz)	h_m (Å)	Δf (Hz)	S/h_m (Hz/ppm/ μm)	S_R/h_m (1/ppm/ μm)
45W 200L	1249.0	1683	230	0.342	2.74×10^{-7}
45W 800L	89.7	1188	6.97	0.0147	1.64×10^{-7}
HH	778.5	5470	265.5	0.121	1.56×10^{-7}
μDisk	755.2	5945	65.7	0.0276	3.66×10^{-8}

Table 2: First in-plane resonant frequency, polymer thicknesses, frequency shift for 4000 ppm toluene exposure, and relative chemical sensitivities normalized to a $1\mu\text{m}$ polymer thickness for 4 different in-plane resonator geometries. All tested devices have a silicon thickness of approx. $18.8\mu\text{m}$.

One other possible source of error, which could account for the differences between the simulations and experimental results is the non-uniform polymer thickness caused by the spray coating. Although the polymer thickness is measured on the die itself, variations over the die surface can occur as a result of the spray coating, and the thickness of each individual device could not be measured with the profilometer used in this work.

CONCLUSIONS

The present work confirms that the relative gravimetric and chemical sensitivities of in-plane resonant chemical microsensors with a given layer stack are independent of the in-plane device geometry and only dependent on the thicknesses of the layers. This result has important implications when choosing cantilever geometries for sensing applications. Two important points are that (1) for a fixed silicon thickness, the designer can choose a geometry, which maximizes the frequency stability or Q-factor (lowers the noise in the output signal). Alternatively, (2) the designer can pick a fixed in-plane geometry and find the device thickness that will give the largest frequency shift without a significant degradation in frequency stability.

Ultimately, the important figure of merit in sensor design is the limit of detection, which is a function of both the short-term frequency stability and the frequency shift due to analyte uptake in the sensitive layer (see Eq. (1)). The frequency stability is correlated with the

[2011 16th International Solid-State Sensors, Actuators and Microsystems Conference, (June 2011): pg. 1112-1115. [DOI](#). This article is © Institute of Electrical and Electronics Engineers and permission has been granted for this version to appear in e-Publications@Marquette. Institute of Electrical and Electronics Engineers does not grant permission for this article to be further copied/distributed or hosted elsewhere without the express permission from Institute of Electrical and Electronics Engineers.]

resonator' s Q-factor, which decreases as the thickness of the device decreases. Knowing that the relative sensitivity is only dependent on the layer thicknesses allows the designer to determine how selecting a given silicon thickness to optimize Q will in turn effect the sensitivity of the sensor. This can therefore be done without comparing several different in-plane geometries individually.

ACKNOWLEDGEMENTS

The authors would like to thank the staff of the Georgia Tech Nanotechnology Research Center for their help. This work has been funded in part by the National Science Foundation under award ECCS-0824017.

References

- P. S. Waggoner, H. G. Craighead, *Lab Chip*, vol. 7, pp. 1238-1255, 2007.
- D. Lange, C. Hagleitner, A. Hierlemann, O. Brand, H. Baltes, *Analytical Chemistry*, vol. 74, pp. 3084-3095, 2002.
- L. A. Beardslee, K.S. Demirci, Y. Luzinova, B. Mizaikoff, S.M. Heinrich, F. Josse, O. Brand, *Analytical Chemistry*, vol. 82, pp. 7542-7549, 2010.
- J. H. Seo, O. Brand, *Journal of Microelectromechanical Systems*, vol. 17, pp. 483-493, 2008.
- L.A. Beardslee, A.M. Addous, S.M. Heinrich, F. Josse, I. Dufour, O. Brand, *Journal of Microelectromechanical Systems*, vol. 19, pp. 1015-1017, 2010.
- Z.H. Li, Y. Jones, J. Hossenlopp, R. Cernosek, F. Josse, *Analytical Chemistry*, vol. 77, pp. 4595-4603, 2005.

NOT THE PUBLISHED VERSION; this is the author's final, peer-reviewed manuscript. The published version may be accessed by following the link in the citation at the bottom of the page.

L.A. Beardslee, A.M. Addous, K.S. Demirci, S.M. Heinrich, F. Josse, O. Brand, *Proceedings of the 9th IEEE Sensors Conference*, pp. 1996-1999, 2010.

[2011 16th International Solid-State Sensors, Actuators and Microsystems Conference, (June 2011): pg. 1112-1115. [DOI](#). This article is © Institute of Electrical and Electronics Engineers and permission has been granted for this version to appear in e-Publications@Marquette. Institute of Electrical and Electronics Engineers does not grant permission for this article to be further copied/distributed or hosted elsewhere without the express permission from Institute of Electrical and Electronics Engineers.]