Civil and Environmental Engineering Faculty Research and Publications

Civil and Environmental Engineering, Department of

1-1-2016

Transient Analysis of Analyte Desorption Due to Thermal Cycling with Varying Pulse Duration

Patrick Getz
Georgia Institute of Technology - Main Campus

Christopher Carron
Georgia Institute of Technology - Main Campus

Stephen M. Heinrich
Marquette University, stephen.heinrich@marquette.edu

Fabien Josse
Marquette University, fabien.josse@marquette.edu

Oliver Brand
Georgia Institute of Technology - Main Campus

TRANSIENT ANALYSIS OF ANALYTE DESORPTION DUE TO THERMAL CYCLING WITH VARYING PULSE DURATION

Patrick Getz[1], Christopher Carron[1,2], Stephen M. Heinrich[3], Fabien Josse[3] and Oliver Brand[1]

[1]School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, GA, USA

[2]Harris Corporation, Melbourne, FL, USA

[3]Marquette University, Milwaukee, WI, USA

patrick.getz@gatech.edu

INTRODUCTION

This paper introduces heating pulse duration modulation on a chemically sensitive, polymer-coated resonant cantilever platform for analyte discrimination during the desorption phase. As in our previous work, the embedded heaters enable real-time measurements of analyte sorption into the polymer film, without the need for traditional valve systems and reference gases [1-2]. This work particularly looks at the effects of varying pulse lengths on the sensor responses, while holding the heating power constant. A model differential equation is developed for the sensor response based on both the device sensitivity and transient response. This model can then be used together with estimation theory for analyte identification and quantification, even in mixtures.

DEVICE DESIGN

The microresonator with semicircular head region (Fig. 1, [1]) used in this work is excited into its fundamental in-plane mode by a diffused resistor at a corner of the anchor point. Four diffused resistors, forming a U-shaped Wheatstone bridge, selectively sense the in-plane mode and enable closed-loop operation [3]. The
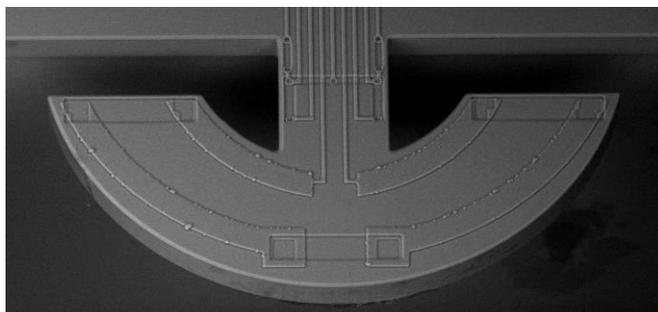
Fig. 1: SEM micrograph of resonant microstructure with semicircular head with 200 μm outer radius supported by a 75 μm wide and 100 μm long cantilever. Resistors for thermal excitation and piezoresistive detection of in-plane flexural vibrations are located at the cantilever base. Three heating resistors for rapid thermal modulation are embedded on the semicircular head [1].

three heating resistors are connected in series and located along the edges of the head region, providing a uniform temperature profile over the heated area and a temperature elevation of approx. 71°C for 100 mW of applied heating power [1].

CHEMICAL MEASUREMENTS

Two resonators on the same die, one coated with a 2.6 μm polyisobutylene (PIB) sensing film and one uncoated reference, are used for the experiments. The devices are chosen such that the resonant frequencies and half power regions do not overlap, avoiding any mechanical or electrical cross-talk during simultaneous excitation. The coated and uncoated resonators have in-plane resonant frequencies of 723.22 kHz and 750.19 kHz, respectively.

Fig. 2 shows a typical chemical measurement with applied heating pulses, where the sensing system is exposed to 800 ppm o-xylene in nitrogen. A rapid drop in frequency from the temperature dependence of the Young's modulus for silicon occurs at the beginning of
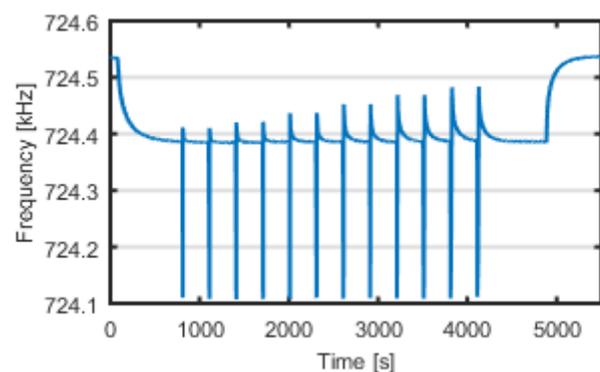
Fig. 2: In-plane resonance frequency of a PIB-coated resonator after thermal compensation using reference resonator. The sensing system is exposed to carrier gas and subsequently o-xylene at 800 ppm. Six pairs of heating pulses of various duration and 38mW of applied power are spaced five minutes apart allowing for full re-absorption.
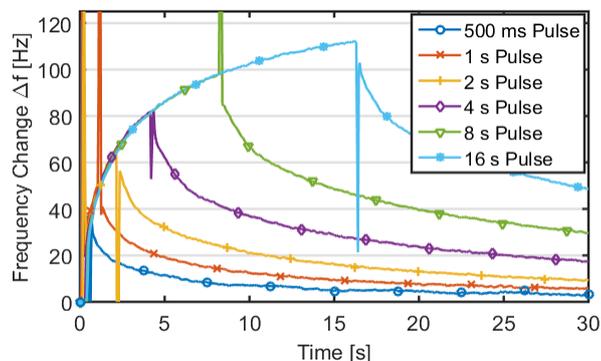
Fig. 3: Frequency change stemming from analyte desorption (during heating with different pulse duration) and subsequent re-absorption of 800 ppm o-xylene into the 2.6 µm PIB film. Frequency changes due to temperature effects have been subtracted using a reference measurement, resulting in signal small artifact/spikes at the beginning and end of the pulse.

each heating pulse. This temperature effect can be compensated for by measuring and subtracting the sensor response to heating pulses without analyte exposure.

Fig. 3 shows the resulting temperature-compensated signal transients for the different heating pulse duration. Clearly, the shape of the desorption transient is not dependent on the heating duration, while the re-absorption transients get shorter with shorter pulse length. This can be explained by the analyte distribution in the sensing film, but makes the desorption transients more suitable for analyte analysis. Fig. 4 demonstrates the possible discrimination between analytes using the transients generated by the heating pulses. The process of analyte desorption of an n-analyte system can be represented by the following equations:

$$\dot{C}_i(t) = -\frac{1}{\tau_i} C_i(t) + \frac{\gamma_{p,i}}{\tau_i} C_{amb,i}(t)$$

$$\Delta f(t) = \sum_{i=1}^{n} a_i C_i(t)$$

where $C(t)$ is the analyte concentration in the coating at time t, $C_{amb}(t)$ is the ambient analyte concentration at time t, τ is the response time constant for a given analyte/coating combination, and subscript i refers to analytes in the mixture. γ_p is the polymer partition coefficient for a given analyte, $\Delta f(t)$ is the frequency shift observed at time t, and a is the equilibrium frequency shift. For analyte desorption, the coefficient a_i will be a positive value and for analyte absorption process the coefficient a_i will be a negative value. This model can be used with estimation theory for analyte identification and quantification, even in mixtures.
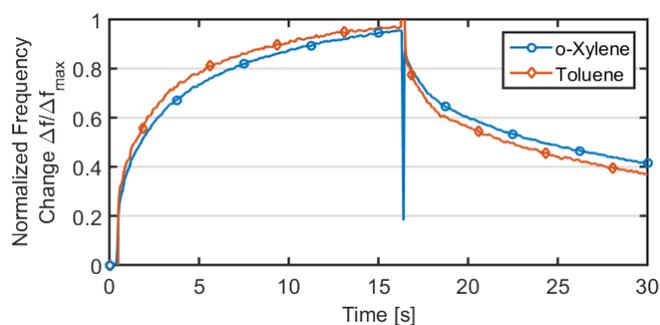
Fig. 4: Comparison of the thermal desorption of analyte due to 16 second heating pulses on 800 ppm o-xylene and 3600 ppm toluene after processing in a manner identical to Fig. 3.

REFERENCES

[1] Beardslee, L. A., et al. (2010). Thermal excitation and piezoresistive detection of cantilever in-plane resonance modes for sensing applications. *Journal of Microelectromechanical Systems*, 19(4), 1015–1017.

[2] Carron, C., Getz, P., Heinrich, S. M., Josse, F., & Brand, O. (2015). Cantilever-based resonant microsensors with integrated temperature modulation for transient chemical analysis. In *Transducers 2015, 18th International Conference on Solid-State Sensors, Actuators and Microsystems* (pp. 1511–1514).

[3] Lange, D., Hagleitner, C., Hierlemann, A., Brand, O., & Baltes, H. (2002). Complementary metal oxide semiconductor cantilever arrays on a single chip: mass-sensitive detection of volatile organic compounds. *Analytical Chemistry*, 74(13), 3084–3095.

[4] Su, J.-J., Carron, C., Truax, S., Demirci, K. S., Beardslee, L. A., & Brand, O. (2011). Assessing polymer sorption kinetics using micromachined resonators. In *2011 16th International Solid-State Sensors, Actuators and Microsystems Conference* (pp. 1420–1423).