SMART MICROFABRICATED CHEMICAL PRECONCENTRATOR

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ABSTRACT

The mass-sensitive smart preconcentrator (SPC) can determine when it has collected sufficient sample for analysis by a downstream chemical sensor system. The SPC consists of a Lorentz-Force-actuated MEMS resonator with an integral heater and surface coating for the collection of chemical analytes. The resonant frequency of the device varies with the mass of collected analyte. The limit of detection (LOD) of the SPC is less than 50 ppb for DMMP (dimethyl-methyl-phosphonate). At 1 ppm, 1 second collection of DMMP is sufficient to trigger analysis in a downstream microsystem. This paper gives a brief overview of the SPC and its integration into microanalytical systems. The theory of operation, which is applicable to other torsional oscillators, is used to predict a shear modulus of silicon(100) of $G = 57.0 \text{ GPa} \pm 2.2 \text{ GPa}$.

INTRODUCTION

Field Sensing and Preconcentration

A system approach, employing sample preconcentration, separation and detection functions, is necessary in reliable field detection units in order to separate target analytes from interferants [1-2]. Unlike previous microfabricated preconcentrators [3-7], this paper describes the first instance of a mass-sensitive microfabricated smart preconcentrator (SPC) for use in chemical detection microsystems [Fig. 1].

Figure 1: Top view photo and model dimensions.

Operation

The smart preconcentrator (SPC) combines mass sensing and preconcentration functions, permitting it to determine when it has collected sufficient analyte for analysis by a downstream chemical microsystem. The SPC consists of a MEMS resonator with an integrated heater, and is constructed by silicon-on-insulator (SOI) micromachining [8]. It is similar in form to the oscillators described by Howe and Muller [9] and Evoy et al. [10], except that here Lorentz-force driving and electrical impedance measurements are used. Fig. 2 shows that a free-standing paddle of silicon is suspended from a silicon frame by two torsional beams. An AC current, i , passes through a metal transducer line on the right side of the paddle. This current interacts with a transverse, in plane magnetic field, B , generated by a pair of miniature permanent magnets situated along the die edges (not shown). The Lorentz Force ($F \sim i \cdot B$) creates a torque on the paddle that changes sign

with the phase of the AC current oscillation. Sweeping the frequency of the drive current can be used to locate the resonant frequency of the SPC; the resonant frequency is measured via the induced current (i_p) on the transducer line, shown on the left side of the paddle in Fig. 2. During use, the SPC has a thin-film adsorbent layer deposited on its surface to collect chemical analytes of interest. As analytes are adsorbed, the mass change of the system is measured by a change in i_p . When the mass change is sufficient for a downstream detection system, the serpentine heater is pulsed with a square wave voltage to rapidly heat and desorb the collected analyte. The SPC reaches a desorption temperature of 200°C in 20 msec, consuming 100 mW steady-state at that temperature.

Figure 2: Solid model of the active area of the SPC. The drive current (i) and magnetic field (B) interact to create the Lorentz force (F) that causes rotation of the paddle about the long symmetry axis of the torsional beams, as indicated by the block arrow. The induced pickup current (i_p) is measured during operation.

THEORY

The equation of motion [11] for the SPC is

$$I_m \ddot{\theta} + \gamma \dot{\theta} + k\theta = \frac{BwLi}{2}, \quad (1)$$

where θ describes the angular motion around the central axis of symmetry generated by the Lorentz force. The right hand side of Eqn. 1 is the torque generated by the Lorentz force. The physical dimensions and parameters are shown in Figs. 1 and 2, with the exception of the oscillator thickness, c , which proceeds into the page in Fig. 1. Respectively, the moment of inertia, damping constant and torsion constant are

$$\begin{aligned} I_m &= \rho w c L \left(\frac{c^2 + w^2}{12} \right) \\ k &= 2 \frac{G}{a} b c^3 \beta \\ \gamma &= \frac{\sqrt{k I_m}}{Q} \end{aligned} \quad (2)$$

The Q of the oscillation appears in the denominator of the damping

constant. The density of the oscillator is ρ and the shear modulus of silicon is G . β is a dimensionless constant that depends on the ratio b/c , and has a limiting value of 1/3 for thin paddles. Eqn. (1) is solved in [11] in terms of the pickup impedance and current, and the sensitivity of the SPC to added mass is also derived. For the purposes of this discussion, we will restrict ourselves to the resonant frequency of the SPC:

$$\omega_o = \sqrt{\frac{k}{I_m}} = \sqrt{\frac{24\beta bc^2 G}{\rho w c a L (c^2 + w^2)}} \quad (3)$$

To easily account for the mass of the metal lines and a thin adsorbent ($t \ll c$), an effective density can be defined

$$\rho = \frac{M + \rho_{Si} w c L}{w c L} \quad (4)$$

M takes into account the collective mass of the metal lines and the adsorbent, and ρ_{Si} is the silicon density. Defining a surface adsorption density σ [g/cm²] of adsorbed analyte, the resonant frequency with adsorbed analyte becomes

$$\omega_n = \sqrt{\frac{24\beta bc^2 G}{\rho w a L (\rho c + \sigma)(c^2 + w^2)}} \quad (5)$$

Equation (3) can be used to determine the shear modulus of silicon based on measured resonant frequency. The amount of adsorbed mass can be determined from Equation (5).

FABRICATION

Microfabrication

The microfabrication process is illustrated in Fig. 3. Silicon on insulator wafers (SOI) are used for starting material. The wafers nominally have a 5 micron device layer, a 1 micron BOX and 400 micron handle (Figure 3a). The first step is deposition and liftoff patterning of the metal heater and transducer lines (solid black boxes in Figure 3b) over a thin dielectric isolation layer (not shown). Metal patterning is followed by etching of two ‘u’-shaped patterns through the device layer, stopping on the BOX (buried oxide). Figure 3c provides side and top views of this step. This step defines the lateral dimensions of the paddle and suspension beams, while the thickness of the resonator (c) is determined by the starting device layer thickness. In the final step, Figure 3d, the entire paddle is undercut by etching through the wafer, from the opposite side to the BOX. Alignment of the etch mask to the front side patterns is achieved using a Karl Suss MA/6 contact aligner. Both KOH and Bosch etching have been used for the latter etch step, though Figure 3d is indicative of Bosch etching given the sidewall angle illustrated. The choice of etching method does not influence device performance.

Adsorbent coating

Subsequent to microfabrication, layers of adsorbent and reference materials are applied to the SPCs. Hydrogen-bond acid modified sol gels, which are selective towards organophosphonate compounds, were mainly used in this work. An automated spray system was developed for this purpose. An electrically-heated, computer-controlled stepper stage was used to raster several shadow-masked SPCs at a time under an ultrasonic nebulizer (Sono-Tek Corp, Milton, NY). The number of passes under the nebulizer controlled the thickness of the adsorbent.

Throughout the course of testing it was discovered that

uncoated SPCs, intended as reference devices, had non-negligible sensitivity to low levels of analyte through non-specific adsorption. Aminosilanes were synthesized and applied to both sol gel coated and uncoated SPCs. These contained a fluorinated alkyl chain to provide a reagent that would both lower the surface energy of a surface and passivate the surface. This functionalization chemistry can be performed in solution or in the gas phase. A 10 wt%/vol solution of $\text{Me}_2\text{NMe}_2\text{SiCH}_2\text{CH}_2\text{C}_6\text{F}_{13}$ was generated in toluene. This solution was used to passivate reference SPCs, some of which were functionalized with a high surface area silica sol gel. The surfaces were allowed to react at room temperature for 30 minutes in solution followed by rinsing with toluene and air drying. The aminosilane functionalization of the silica gel did not appreciably affect its interaction with DMMP. Functionalization of bare resonators did, however, decrease the interaction of DMMP with the resonator, as seen below.

Figure 3: Microfabrication process steps illustrated in cross section and top views.

CONTROL CIRCUIT

To drive the oscillator and measure its response to analyte capture, the circuit of Fig. 4 was developed. In brief, a ring oscillator is used to drive the circuit into resonance by driving one of the transducer wires on the paddle. This driving scheme is also illustrated in Fig. 2. The trans-impedance amplifier (Trans.) produces an output voltage proportional to the pickup current in the other transducer line. This voltage is input into a phase-locked loop (PLL) and compared with the PLL's onboard oscillator frequency. The oscillator frequency is controlled by a digital potentiometer (Dig. Pot), allowing computer control of the oscillator circuit. During initial set up, the circuit is auto tuned using the micro-controller and digital pot to the resonant frequency of the SPC. In subsequent operation, frequency changes brought

on by analyte challenges move the circuit away from the PLL oscillator frequency and an error voltage is produced. The error voltage is thus proportional to the frequency changes with exposed analyte. The error is sent through a 4-pole active low pass filter (Filter) and coupled to an A/D converter (ADC) via a calibration amplifier. The circuit is set such that 1 mV of error is equivalent to 1 Hz of frequency. The microcontroller (PIC16C62B) also has the ability to measure the frequency directly via a multiplexed counter circuit implemented on the board. Interface with a host PC is accomplished using RS-232 and a host shell program written in Visual-Basic. The heater portion of the circuit (Heat) is activated by the PIC to rapidly heat the SPC to its desorption temperature once sufficient analyte has been collected. The electrical low connection on the heater is connected to ground (not shown).

Figure 4: Oscillator circuit for autotuning and mass loading measurements. The desorption heater circuit (Heat) is switched by the PIC when the mass loading is adequate for the downstream system.

TESTING

The SPC was inserted into drop-in test fixtures like those shown in Fig. 5. This packaging simultaneously creates a fluidic seal and electrical contact to the devices. When the plastic lids are fastened to the PEEK manifold, o-ring seals and miniature spring contacts are simultaneously compressed. A vapor generation system was developed to challenge the SPCs. A Lindberg-Blue oven (New Columbia, PA) was used to control the temperature of a diffusion vial containing DMMP. The flow rate of nitrogen through the system and the physical dimensions of the diffusion vial determined the concentration of DMMP delivered to the SPC. All flow lines exterior to the oven were heated in an insulated trunk line to prevent unwanted condensation. Test fixtures were connected to the output of the vapor system, while the control circuit of Fig. 4 was used for acquiring data. Raw data is shown in Fig. 6 for the response of an SPC to 400 ppbv of DMMP. The trace labeled 'sensor' is for an SPC coated with sol gel. The relatively flat response of the 'reference' device is due to the aminosilane treatment, mentioned above. After an initial precipitous drop, the sensor response tails off until the heater is pulsed at about 140 seconds and the response begins to return to baseline. The response of the SPC was tested down to 146 ppbv of DMMP, the minimum of the vapor system used.

In Figure 7, the time required for two devices to obtain a S/N ratio of 3:1 was determined as a function of concentration; the response times of the two devices were averaged to obtain the plot

of Fig. 7. This shows that as the concentration increases, the response time for the SPC to detect DMMP drops to less than 1 second. With typical preconcentrators an arbitrary collection time, normally set at one minute or greater, would be required. Therefore, the SPC diminishes collection times by a minute or more at high concentrations.

Figure 5: Packaging of a SPC (right), micro gas chromatograph with Minco heater (center), SAW array sensor (left) and Lee minivalve (far left). Electrical connections are made between the PCB and devices via miniature spring contacts. Miniature magnets (not shown) are placed in the recesses to either side of the SPC.

Figure 6: Response of an SPC to 400 ppbv of DMMP. The vertical axis is broken to allow simultaneous viewing of the sensor & reference response.

Figure 7: Response time required to reach 3:1 S/N as a function of concentration of DMMP.

DISCUSSION

Several design variations were fabricated, and their resonant frequencies were measured (Table 1). In all cases, $L = 1500$ micron, $a = 200$ micron and $c = 5$ micron were fixed. The values of β were taken from [12]. Based on Eqn. (3) the shear modulus of silicon (100) was predicted.

Table 1: Measured resonant frequency and predicted value of G .

Device	Resonant Frequency (kHz)	β	G Predicted (GPa)	w (micron)	b (micron)
1	19.6	0.318	56.0	500	180
2	17.0	0.316	55.0	500	140
3	14.6	0.317	60	600	160
4	11.9	0.318	56.0	700	180
5	9.8	0.316	47.5	700	140

The average shear modulus of Si (100) from this analysis is $54.9 \text{ GPa} \pm 5.5 \text{ GPa}$. If 47.5 GPa is treated as an outlier, the average shear modulus becomes $57.0 \text{ GPa} \pm 2.2 \text{ GPa}$. In an analysis of nanopaddle oscillators Evoy [10], predicted that the modulus of SOI silicon (100) is 1.5 to 2 times lower than literature values. In a more detailed analysis Dowell [13] predicted a Young's modulus of 122 GPa ; this is more consistent with commonly stated range of $E = 130 - 169 \text{ GPa}$, but is still up to 28% softer. With the exception of the results for device 5, the present work predicts a shear modulus of Si (100) that falls in the range reported by Kim [14] of $51 - 79 \text{ GPa}$. Indeed, the average shear modulus, including the outlier, is in this range. Li [15] did report that SOI Si (100) is about 20% softer than nominal bulk silicon values. If this degree of softening is applied to the range given by Kim, the acceptable range of shear modulus for Si (100) drops to $41 - 63 \text{ GPa}$. The average shear modulus predicted here is also in this range.

CONCLUSIONS

The SPC has the ability to detect when it has collected sufficient analyte for analysis by a downstream system. Ordinary preconcentrators, macro or micro-sized, would require an arbitrary collection time, wasting time at high concentrations. The SPC allows analysis times to be shortened drastically when ambient chemical concentrations are greatest, and most dangerous as in the case of toxic chemicals. Systems based on the SPC can have collection cycle times as short as 1 second with specificity at lethal concentrations. This is comparable, or shorter in duration than IMS-based systems. The existing SPC design has a LOD less than 50 ppb at 3:1 signal to noise. The theory of operation also allows for optimization of the SPC performance, and can be used in the measurement of the shear modulus of silicon.

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