MICROFABRICATED THERMAL PRE-CONCENTRATOR WITH INTEGRATED CANTILEVER-BASED RESONANT SENSORS

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ABSTRACT

This paper introduces the design, fabrication and initial testing of a smart MEMS-based micro thermal pre-concentration (μ TPC) system with integrated mass-sensitive chemical sensors for volatile organic compound (VOC) sensing. The presented suspended-membrane μ TPC design features a hybrid of a high surface-area-to-volume ratio and a low thermal mass, resulting in a potentially high pre-concentration factor and a short thermal time constant. Additionally, the system co-integrates upstream and downstream resonant cantilever sensors, operated in an in-plane resonant mode, to monitor the VOC uptake into the μ TPC in real time, but also offering the possibility of a fully integrated chemical sensing system with a dead volume of $<10\mu\text{L}$.

INTRODUCTION

Thermal pre-concentration is an effective approach for VOC detection at sub-ppm levels [1]. VOCs can be used to identify the state of many types of systems, e.g., the environment [2], personal health through breath analysis [3], [4], and plant health [5]. In each of these applications, accurate monitoring of certain VOCs is crucial to provide input for any corrective action. However, the concentrations for many analytes of interest in these systems are low ppm or ppb, with some trace VOCs existing in ppt concentrations [6], presenting a challenge for many types of chemical sensors with higher limits of detection (LOD). Pre-concentration can temporarily increase the concentration for many compounds allowing for low-concentration analyte identification by a variety of downstream sensing mechanisms, e.g., mass spectroscopy, gas chromatography, and MEMS based sensors [7].

Existing microfabricated pre-concentrators typically fall into two classes: (1) pre-concentrators that feature three-dimensional (3D) structures directly etched into the bulk (silicon) substrate [8], which often yields large sorbent volumes at the expense of long thermal time constants and large power consumption or (2) quasi-2D pre-concentrators based on thermally insulated suspended membranes, which allow for fast thermal rise times and low power consumption [9], but limit the sorbent volume. The proposed μ TPC is a hybrid of these designs, incorporating 3D high-aspect-ratio microstructures with a suspended membrane design, and coupling this sensor design with an effective packaging scheme that minimizes chamber dead volume.

Moreover, most microfabricated pre-concentration systems currently lack the ability to, in real-time, detect analyte uptake within the sorption film and, therefore, adjust the collection time based on the loading condition. An exception is the integration of a pre-concentrator on top of a pivot-plate-type mass-sensitive resonator [9], which can monitor the analyte uptake in the sorption film in real time. However, the integration of a pre-concentrator and sensor into one suspended microstructure limits the sorbent volume and the performance of the mass-sensitive sensor. Thus, in this work, micromachined resonant sensors were fabricated on the same chip next to the pre-concentrator to monitor analyte uptake upstream and downstream of the TPC. As the concentration of analyte within the μ TPC film starts to saturate, the detected concentrations at the

upstream and downstream sensors will converge due to less uptake by the TPC. While the detection of many analytes of interest (possibly ppt or low ppb in concentration) still remains a challenge with these sensors, other analytes remain at concentration levels, ppm or high ppb, that can be detected without pre-concentration [10], [11]. The signals from the optimized resonators can thus serve as a benchmark for the analyte uptake within the actual pre-concentrator and can be used to monitor and optimize the pre-concentration process in real time.

The achievable pre-concentration factor (CF) for an equilibrium-based pre-concentrator depends on the sorbent volume, the partition coefficient K of a particular sorbent-analyte combination, and the dead volume of the pre-concentration unit:

$$CF = \frac{K * \text{Absorption Volume}}{\text{Dead Volume}}. \quad (1)$$

To increase the CF, this work also presents ways to minimize the dead volume using wafer-bonding techniques.

DESIGN & FABRICATION

Figure 1 shows the system design, comprising of multiple resonant cantilevers and three μ TPC membranes on a single chip. The μ TPCs consist of a suspended membrane with integrated heating and temperature sensing resistors, defined in the device layer of a silicon on insulator (SOI) wafer and formed through boron diffusion with an oxide mask. The suspended membranes feature high-aspect-ratio pillars or ridges, etched in the handle layer of the SOI substrate, to increase the surface area by ~ 10 -100x.

Figure 1: CAD cutaway view of smart μ TPC fabricated on an SOI wafer through traditional MEMS bulk micromachining techniques with integrated upstream and downstream mass-sensitive chemical sensors.

The fabrication process of the μ TPC system follows a recent process used for resonant chemical sensors in our group [12], [13] and, thus, enables a smart, single-chip pre-concentration module with integrated chemical sensors. The high aspect-ratio deep-reactive-ion-etch (DRIE) from the backside of the wafer, used to

Figure 2: Simulated temperature distribution across heated 2x1 mm μ TPC with ridges using COMSOL. The applied heating power of 500 mW causes a fairly uniform 230 °C temperature elevation in the membrane and ridges.

release the resonant sensors in the previous work, now also serves to define the pillars and ridges used for pre-concentration [12]. Additionally, the device release etch, carried out from the top side of the wafer, now patterns the suspended membrane in addition to the sensing cantilevers. As such, no additional masks or fabrication steps are required to fabricate the pre-concentrators next to the resonant cantilevers.

The sensors are cantilever-based resonators with a semi-circular head region, which are coated with an appropriate sensing film after fabrication. Different implemented sensors designs have fundamental in-plane resonant frequencies of 300-800 kHz. Two

Figure 3: SEM micrographs of a fabricated μ TPC and resonant cantilever sensor die prior to polymer deposition. Three individually addressable and thermally isolated 1x2 mm μ TPCs, as well as the mass-sensitive sensors, are visible from both front side (top) and backside (bottom) of the chip.

sensors are placed at each inlet and outlet port to measure the analyte concentration in real time. The cantilevers are excited electrothermally, similar to our previous work, by a diffused resistor at a corner of the anchor. Four piezoresistors arranged in a U-shaped Wheatstone bridge preferentially detect the in-plane vibration mode and provide for continuous operation within an amplifying feedback loop [12], [14]–[16]. To compensate for temperature effects, one resonator is left uncoated to serve as a reference.

Figure 2 shows a thermal simulation of a pre-concentrator on top of a 1 mm by 2 mm suspended membrane with 20 μ m silicon thickness using COMSOL. The membrane, with an integrated 3-D ridge structure, is uniformly heated to approx. 230 °C using a heating power of 500 mW. Besides heat transport by conduction through the silicon, a constant heat transfer coefficient of 50 W/m²K was assumed to approximate the heat transfer through the surrounding air. The small thermal mass associated with the suspended membrane structure assures a short thermal time constant, simulated to be approx. 0.4 s for this device.

Figure 3 shows SEM images of a fabricated die with μ TPCs and mass-sensitive sensors. Each of the three suspended membranes is connected to the substrate by four legs connected to two anchor points. Various die configurations incorporate either two or three individually addressable μ TPCs with varying device geometries (with up to 2x2 mm membranes featuring a total surface area of 53 mm²) and incorporating either ridge or pillar like structures. The long supporting legs (1500-2250 μ m in length) provide thermal isolation, thus reducing the required heating power.

FUNCTIONALIZATION & PACKAGING

Maximizing the CF in Eqn. 1 necessitates a high absorption-volume to dead-volume ratio. Thus, special consideration must go into the post-fabrication functionalization and packaging steps. As already mentioned, the pillars/ridges significantly increase the surface area of the device; this allows for approximately 0.1 μ L of absorption volume per 2 μ m of polymer thickness for a 53 mm² device. Thin sorbent films allow for quick desorption from the film, causing a sharp increase in concentration under continuous flow testing. Thicker films, on the other hand, allow for larger CF. Figure 4 shows a typical coated device, which will have 5-20 μ m sorbent film deposited through a shadow-masked spray coating. The microresonator is functionalized with either the same or a different sorbent film. For the sample devices in this paper, the μ TPC pillars were coated with dimethyl silicone gum (silicone OV-1) and the microresonators were spray-coated with polyisobutylene (PIB).

Figure 4: SEM micrograph of polymer coated pillar structures. Shadow-masked pillars (bottom-left and top-right) are left uncoated, while pillars near the center are coated with a thick absorbing layer.

Figure 5: Fully packaged and wire-bonded device with ferrules aligned to laser ablated holes and epoxied to the borosilicate glass package for inlet and outlet ports.

The μ TPC is packaged by bonding borosilicate glass wafers, patterned with a layer of Microchem SU-8 3005 for thermo-compression bonding, to the μ TPC's top and bottom. This achieves a low dead volume, approx. $7\mu\text{L}$, which is required for a high CF. The borosilicate glass also thermally insulates the package, further minimizing the power required for sufficient temperature elevation ($100\text{--}200\text{ }^\circ\text{C}$). In addition to bonding, the SU-8 allows for appropriate spacing between the microresonator and the glass surface, which would otherwise prevent the resonator from oscillating. An additional epoxy layer is added outside the package in select areas to provide strength for high pressure testing.

After bonding, laser machining is used to form the inlet and outlet ports and ferrules are mounted with epoxy, providing for

Figure 6: (a) Measured average temperature elevation of $1\times 2\text{mm}$ μ TPC as a function of applied heating power. Dashed lines represent linear fits through the data sets up to $\sim 200\text{ }^\circ\text{C}$. (b) Measured and simulated thermal time constants for varying device geometries. Dashed lines represent the simulated data.

tubing access. Figure 5 shows a packaged device. The μ TPC can be operated in stop flow or continuous flow. While operating in stop flow, the μ TPC temporarily increases the concentration in the dead volume for downstream analysis by rapidly ejecting, through thermal desorption, analytes that had accumulated into the sorbent material over the sampling window. As the flow rate increases, the desorption window broadens, causing the maximum pre-concentration factor to decrease.

A sample device in this work was coated with approx. $0.31\text{ }\mu\text{L}$ of OV-1, resulting in an active volume to dead volume ratio of $\sim 1:23$. Thus for analytes with a partition coefficient greater than 23, pre-concentration will occur. With partition coefficients greater than 1000 for various aromatic compounds [17], we expect pre-concentration factors of 40 or higher based on Eqn. 1.

SYSTEM CHARACTERIZATION

To test the μ TPC, the two integrated $500\text{ }\Omega$ diffused resistors (connected either in series or parallel) are used for joule heating, while an additional meandering diffused resistor can be used for temperature sensing. The resistive temperature sensors of the μ TPC system are initially characterized in an environmental chamber up to $150\text{ }^\circ\text{C}$. The measured data was fit to a second order polynomial to extrapolate temperatures beyond $150\text{ }^\circ\text{C}$. Using this calibration data, the μ TPC heating using the embedded heating resistors is characterized with a source-meter unit. Figure 6a shows the average temperature of a fully-packaged and sorbent-coated pre-concentrator module with $2\times 1\text{ mm}$ membranes as a function of the heating power. As expected, the temperature elevation is linear with the applied heating power and approx. 700 mW are needed to heat to $\sim 200\text{ }^\circ\text{C}$, or $4.4\text{ mW}/^\circ\text{C}$ of temperature elevation, needed for VOC desorption. This is a larger power requirement than was simulated and it is thought to arise from the effect of the package on the thermal characteristics of the device. Figure 6b compares the simulated and measured thermal transients, indicating short thermal time constants of less than 1 sec even for the largest pre-concentrators. The continued increase in temperature after the initial rapid increase reflects the package and surrounding medium heating.

The resonant cantilevers were also characterized before and after functionalization/packaging. Figure 7 shows the successful integration of a cantilever sensor within the sealed package. The added polymer mass causes the shift in resonance frequency and slight drop in Q -factor.

Figure 7: Amplitude transfer characteristics of a resonant cantilever before and after functionalization and packaging with PIB. The added polymer mass contributes to a -4.2 kHz shift in resonant frequency while maintaining a high Q -factor, >1500 .

CONCLUSION

This paper demonstrates the design, fabrication, packaging and initial characterization of a smart μ TPC with integrated microresonators to sense VOC uptake in real-time. By utilizing pillar or ridge structures, a high surface-area is created allowing for large absorption film volumes compared to planar designs, while

still allowing for quick thermal rise times. The borosilicate glass packaging maintains an extremely low dead volume, which allows for higher pre-concentration factors.

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