POLYMER WICKING TO MASS LOAD CANTILEVERS FOR CHEMICAL GRAVIMETRIC SENSORS

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ABSTRACT

Achieving size reduction with electrostatic capacitive detection in cantilever resonant gravimetric microsensors necessitates use of narrow gaps and beams, which are incompatible with polymer addition using techniques such as ink jet, spray coat, dip cast, and dip pen deposition. A method is introduced to wick controlled amounts of polymer onto narrow grooves. Polystyrene dissolved in toluene and xylene is deposited onto a target well area using drop-on-demand ink jetting. The solvent with polymer is wicked into a 2 μm wide groove running the length of a 4 μm wide cantilever. Sidewall 1 μm-wide gaps to electrostatic actuation and sensing comb fingers remain free of polymer and operate as intended. The resonator with 410 pg of polymer and sensitivity of 76 fg/Hz is self-excited in a feedback oscillation loop. Initial measurements of saturated concentrations of acetone, ethanol and 2-propanol provide 20 Hz to 130 Hz shifts.

Keywords: chemical sensor, CMOS-MEMS, gravimetric sensor, polymer wicking

INTRODUCTION

Single-chip electronic noses, enabled by full on-chip integration of gas chemical microsensors with signal-conditioning electronics has tremendous medical, environmental and safety applications. Gravimetric detection is an important sensing modality for these microsystems. Commercially available mass-sensitive devices for volatile organic compound detection use piezoelectric quartz substrates. Thickness shear mode resonators (TSMR), also known as quartz micro-balances (QMB) [1][2], and Rayleigh surface acoustic wave (SAW) devices [3] are examples of such devices. However, these piezoelectric devices have not been fully integrated with on chip electronics. In contrast, resonant cantilever chemical microsensors integrated with CMOS has been demonstrated [4]. Prior work on cantilever mass sensors includes detection of humidity, mercury vapor, and volatile organic compounds [5] as well as biomolecular recognition in a liquid media [6]. Post-CMOS micromachining has been used to make fully integrated mass sensitive oscillators with pico-gram resolution [7]. These devices were formed through deposition of precise amounts of a chemically sensitive layer onto relatively wide cantilevers.

Another example of a CMOS-MEMS resonant gas sensor used electrostatic actuation and detection to form a free-running oscillator [11]. A cantilever beam suspended

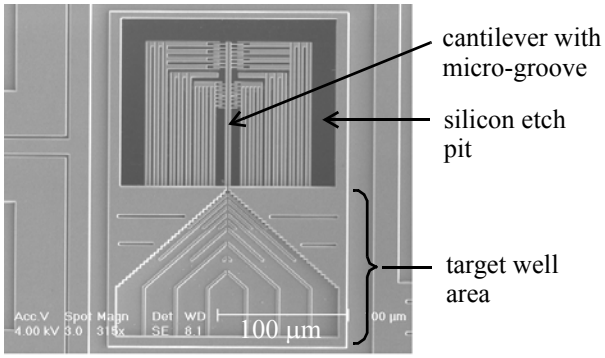

Fig 1: Gravimetric micro-cantilever resonant sensor.

a plate made large enough to accommodate drops of chemically sensitive polymer placed directly onto the plate using drop-on-demand ink jet deposition. Ink jet deposition can functionalize each cantilever in an arrayed structure with a separate polymer. This non-contact technology is scalable for large arrays, easy to use, versatile, and faster than other means of coating such as from micro-capillaries and drop casting from pipettes [9]. Other thin film application methods include dip pin and shadow mask processing which are both time consuming processes.

It is beneficial to further scale down the size of the resonant microstructure to achieve a higher mass sensitivity. Scaling cantilevers down to micro- and nano-scale dimensions is achievable with optical or piezoresistive resonant detection. However, microstructures with low-noise electrostatic actuation and detection require narrow air gaps that are generally incompatible with existing polymer deposition techniques. This work presents a method to mass load a microstructure with polymer without affecting nearby gaps. Precise amounts of polymer are wicked onto the microstructure through capillary action of micro-grooves formed along the length of the beam. The technique enables design of low-mass polymer-loaded cantilevers with electrostatic actuation and capacitive sensing for integrated gas chemical detector arrays.

MICRO-CANTILEVER DESIGN

The gravimetric micro-cantilever sensor is shown in Fig 1 with a close up view of the beam microstructures in Fig 2. The resonant structure is a simple 120 μm-long, 4 μm-wide beam with a 2 μm-wide micro-groove running along the length of the beam. Motion is parallel to the surface of the silicon substrate. Differential comb drives with 7 rotor fingers are located near the end of the

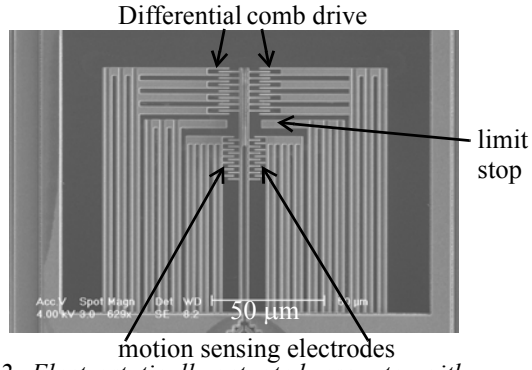

Fig 2: Electrostatically actuated resonator with differential comb drive and sensing electrodes.

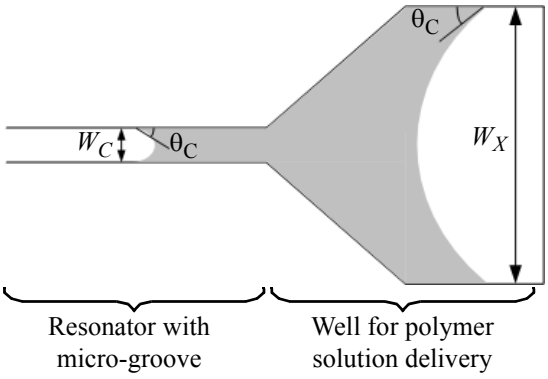

Fig 3: Illustration of solution delivery to the resonator

beam for lateral electrostatic actuation. The stator fingers are suspended by three cantilever beams connected in parallel and sized identically to the resonator cantilever beam. Any curl from vertical stress gradient is matched to ensure the stator and movable comb fingers are aligned in the same plane. Motion sensing of the plate is implemented using capacitive comb electrodes placed on both sides of the main beam and located further toward the base from the actuation combs. A limit stop is located between the actuator and sense combs.

A target well area is located at the base of the cantilever to collect the jetted drops. The well has an approximate depth of 9 μm and a maximum width of 165 μm. The well narrows in width toward the base of the cantilever at a 45° angle on each side.

A schematic of the transition region between the well and the micro-groove is shown in Fig 3. A pressure difference exists between the two surfaces of the liquid/gas interface [8]. This differential pressure is

$$\Delta P_{XC} = 2\gamma\cos\theta_C\left(\frac{1}{W_X} - \frac{1}{W_C}\right) \qquad (1)$$

where γ is the surface tension, θ_C is the contact angle, W_X is the width of the well and W_C is the width of the micro-groove running along the length of the cantilever. This causes a flow of the solution by capillary action from the well to the resonator. Once the solvent dries polymer is left in the micro-channel in the resonator.

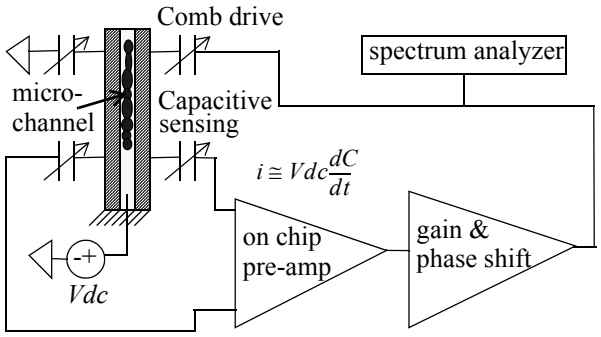

Fig 4: Oscillator gas sensor schematic. The electrostatically actuated resonator is placed in a feedback loop with off-chip electronics for oscillation.

OSCILLATOR DESIGN

A block diagram of the closed-loop feedback system to sustain the resonant oscillation is shown in Fig 4. A dc polarizing voltage, V_{dc}, is applied to the movable beam. The resonator velocity is detected by measuring the motional displacement current, $V_{dc}\ dC/dt$, through the comb finger capacitors. An on-chip preamplifier produces a voltage, V_s, that is proportional to the difference of the current through the differential capacitors formed by the sense comb electrodes.

An external amplifier placed in series with the on-chip pre-amplifier provides 40 dB of gain and -90° of phase shift at the mechanical resonance. This phase compensation is needed for free running oscillation. In this implementation, only one side of the differential actuator is used. During free oscillation, the actuator voltage amplitude is 0.2 V with a dc polarizing voltage of 23.0 V.

The calculated resonant frequency from layout dimensions and prior to polymer deposition is 250 kHz. With analyte addition, a change in the mass of the cantilever changes the resonance frequency. The mass sensitivity (gm/Hz) is

$$\frac{\Delta m}{\Delta f} = -\frac{2(m_b + m_{poly})^{\frac{3}{2}}}{\sqrt{0.25k}} = -\frac{4(m_b + m_{poly})}{f_o} \qquad (2)$$

where m_b is the mass of the beam, m_{poly} is the mass of the polystyrene, k is the spring constant of the cantilever, and f_o is the resonance frequency of the cantilever. The calculated mass sensitivity for this device is 76 fg/Hz. The sensitivity (Hz/ppm) of the micro-balance due to analyte concentration is [11]

$$\frac{\Delta f}{\Delta C_{air}} = \frac{\Delta f}{\Delta m}\frac{\Delta m}{\Delta C_{air}} = -\frac{f_o}{4(m_b + m_{poly})}K_{PG}V_{poly} \qquad (3)$$

where C_{air} is the concentration of the analyte in air, K_{PG} is the partition coefficient associated with the particular polymer/analyte combination, and V_{poly} is the volume of

the polymer on the beam. The volume of polymer to fill the micro-groove is 7.2 x 10^{-16} m^3. Assuming that the micro-groove is filled with polystyrene the concentration sensitivity to ethanol, 2-propanol, and acetone is calculated to be 0.006 Hz/ppm, 0.005 Hz/ppm, and 0.01 Hz/ppm, respectively.

FABRICATION

The sensor was fabricated in the SiGe 0.35 μm BiCMOS technology from Jazz Semiconductor (Newport Beach, CA) followed by post-CMOS micromachining [10]. After foundry CMOS fabrication, three dry etch steps are used for definition and release of the structures, as illustrated in Fig. 5. The intermetal dielectric layers are etched using an anisotropic CHF_3/O_2 reactive-ion etch (RIE) (Fig. 5(b)) where the top metal layer acts as a mask defining the pattern of the structure. A subsequent undercutting of the structures by a Si etch is performed using an anisotropic deep reactive-ion etch (DRIE) (Fig. 5(c)) followed by an SF_6/O_2 isotropic etch (Fig. 5(d)) of the bulk silicon for structural release of the metal and dielectric stack. The sidewalls and bottom of the micro-grooves are defined by the metal-3 and metal-1 layer, respectively, in the CMOS technology.

In the last stage of manufacturing, the chemically sensitive polymer dissolved in solvent is deposited using a piezoelectric drop-on-demand ink jet (Fig. 5(e)) purchased from MicroFab Technologies (Plano, Texas). The orifice of the ink jet is 30 μm in diameter and the average drop size is 31 μm in diameter. An x-y stage (Aerotech Inc.) that moves the device under the ink jet provides positional accuracy of 0.2 μm.

POLYMER DELIVERY RESULTS

Polymer deposition tests used 2 mg/mL polystyrene mixed in a 1:1 mixture of HPLC grade toluene and xylene at room temperature. The solution was then sonicated for 10 minutes.

As expected, attempts to directly deposit onto cantilevers result in the destruction of the devices, as shown in Fig 6, This occurs because the ink-jetted drop volume

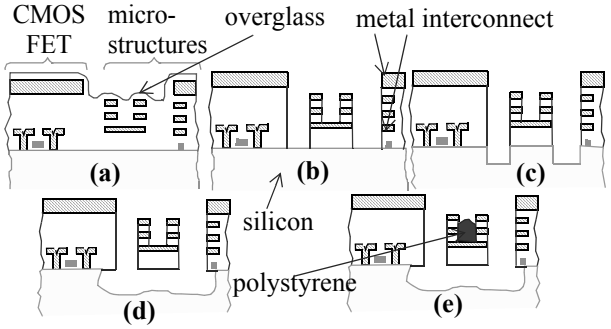

Fig 5: Post CMOS processing steps; (a) CMOS chip from foundry, (b) Reactive-ion etch of dielectric layers, (c) DRIE of silicon substrate, (d) isotropic etch of silicon substrate, (e) Ink jet deposition

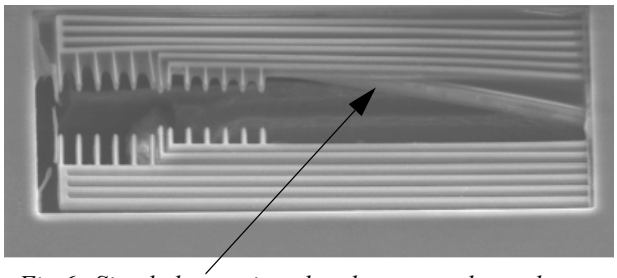

Fig 6: Simple beam pinned under stator electrodes after direct ink jet deposition onto cantilever.

(~33 pL) greatly exceeds the target cantilever size. The device is pinned under the actuating electrodes due to surface tension effects rendering it inoperable.

To successfully load the cantilever with polymer, six drops of solution (2 mg/mL polystyrene in 1 toluene:1 xylene) were deposited onto the target area at the base of the cantilever beam. The polymer wicks onto the cantilever beam and the solvent then evaporates. A view at the base of the cantilever micro-channel is shown in Fig 7(a) and Fig 7(b) before and after polystyrene deposition, respectively. The tip of the micro-channel resonator with and without polystyrene is shown in Fig 7(c) and Fig 7(d), respectively. The device was successfully operated with electrostatic actuation. The frequency response of the cantilever before and after polystyrene loading is shown in Fig 8. The resonance frequency shifted down by 5400 Hz. This corresponds to an added polymer mass of 410 pg. The calculated mass of polystyrene in six drops of solution is 396 pg.

GAS TEST MEASUREMENTS

Gas analytes are introduced with nitrogen as the carrier gas in the system shown in Fig. 9. The nitrogen supply is connected through an adjustable flow-meter and a 2-way ball valve. The flow-meter has a minimum flow rate of 0.21 liters per minute (Lpm) and a maximum rate

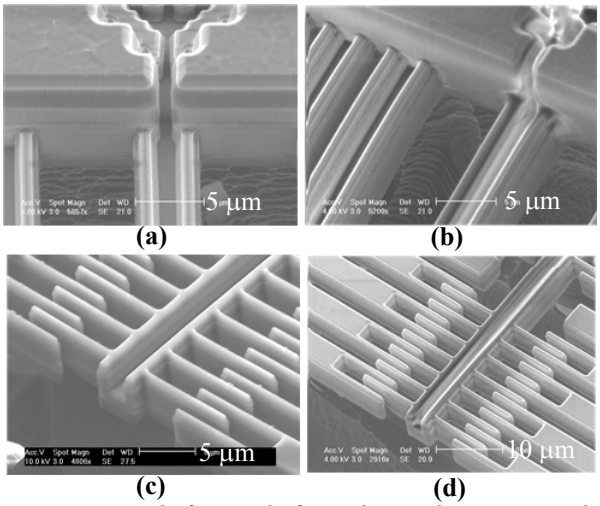

Fig 7: Device before and after solution deposition in the well; (a) entrance from well to micro-channel, (b) resonator at the base with polystyrene, (c) tip of resonator without polystyrene, (d) tip of resonator with polystyrene

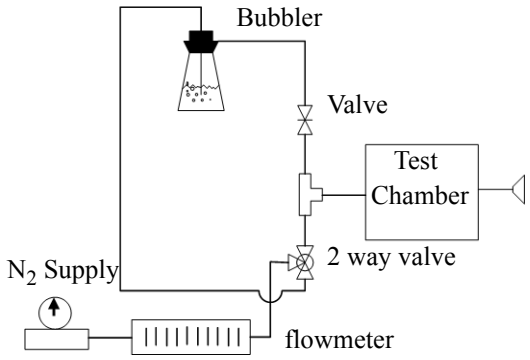

Fig 9: Gas test setup

of 1.21 Lpm. One outlet of the ball valve connects to a T-connector for direct connection of the carrier gas and analyte vapor to the test chamber. The other outlet of the ball valve is connected to the inlet of a bubbler which is submersed in the liquid form of the analyte of interest.

Tests were performed with ethanol, 2-propanol, and acetone. N_2 was flowed at 1 Lpm through the chamber using an external bubbler until an equilibrium concentration is reached. In these initial tests, the equilibrium concentration was not measured but is assumed to be at or close to the saturation concentration of the corresponding vapor at a temperature of 300 K and a pressure of 1 atm.

Free-running oscillator responses to ethanol, 2-propanol, and acetone flows are shown in Fig 10. The mechanical resonance frequency with no exposure to analyte is 204.499 kHz. The oscillator signal has a 65 dB SNR and a 3 dB width of 3 Hz limited by the 3 Hz resolution bandwidth of the spectrum analyzer. From the frequency shifts in Fig 10, the amount in grams of ethanol, 2-propanol, and acetone loaded into the polystyrene is calculated to be approximately 1.5 pg, 2.6 pg, and 9.9 pg, respectively.

CONCLUSIONS

The gas tests successfully demonstrate an organic vapor detector using the CMOS-MEMS self-excited resonator oscillator. The polymer loading method that exploits capillary action in the micro-groove enables

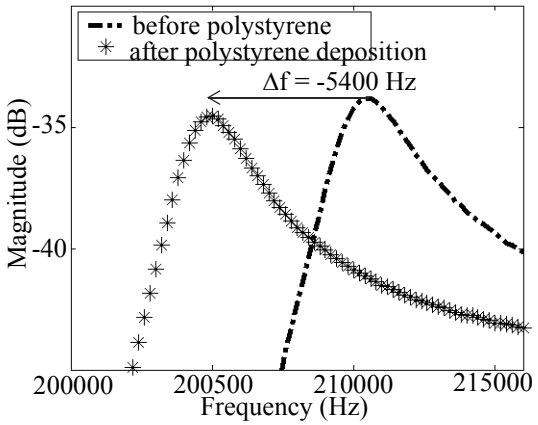

Fig 8: Frequency response of device before and after polystyrene deposition.

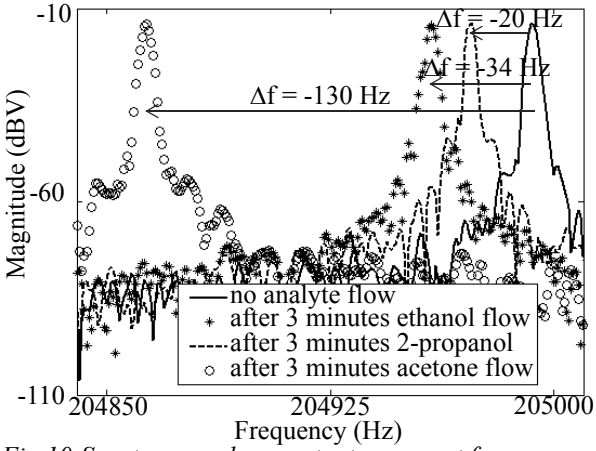

Fig 10:Spectrum analyzer output: resonant frequency shifts due to ethanol, IPA, and acetone gas flows.

design of narrow-gap electrostatic combs alongside the micro-cantilever. Compatibility with ink jet polymer delivery enables loading of different polymers to individual cantilever sensors. The precise amount of polymer loading with this method should lead to repeatable results from device to device.

Scaling down the cantilever size led to a high mass sensitivity of 76 pg/Hz for the 4 μm-wide cantilever design. With further design maturation, the technology should lead to highly sensitive gas chemical gravimetric sensor arrays on chip.

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