

INTEGRATED VOC VAPOR SENSING ON FBAR-CMOS ARRAY

Matthew L. Johnston, Hassan Edrees, Ioannis Kymissis, and Kenneth L. Shepard
Columbia University, New York, NY, USA

ABSTRACT

This paper reports first results of volatile organic compound (VOC) detection on a monolithically integrated film bulk acoustic resonator (FBAR) array on a silicon integrated circuit substrate. The combined sensor platform uses thin polymer layers as gas absorbers for individual FBAR functionalization, and frequency shifts are measured on-chip in response to changing VOC concentration. Integrating sensors, drive, and read-out functionality on a single CMOS die enables a robust, multiplex sensor platform and obviates external measurement equipment.

INTRODUCTION

Volatile organic compounds (VOC) are released to the air as a byproduct of industrial solvents, and measuring both environmental release and human exposure to these vapors is critical to their safe, long-term use [1]. In each of these applications, analytical quantification has typically been performed by gas chromatography and mass spectrometry, techniques that are sensitive and precise but cannot be employed in real-time monitoring or portable sensing applications.

Acoustic wave devices, which enable both real-time detection and portable platforms, have been demonstrated for the detection and quantification of VOC content in air and water [2]. Approaches developed for the quartz crystal microbalance have been extended to surface acoustic wave devices, contour mode resonators, and cantilevers in the micro- and nanoscale regimes [3,4]. In this paper, this technique is now applied to a monolithic FBAR-CMOS oscillator array, which enables direct, simultaneous measurement of all sensors for parallel multiplex detection.

MEASUREMENT PRINCIPLE

Like the macroscopic quartz crystal microbalance, an FBAR sensor demonstrates a decrease in resonant frequency in response to mass loading. For small shifts, this behavior is governed by the Sauerbrey Equation, $\Delta f = (-f_o^2 \Delta m)/(NA\rho)$, where f_o is the resonant frequency, Δm is the mass loading, N is the material-derived sensitivity constant, A is the resonator surface area, and ρ is the density. There is a clear incentive to increase resonator frequency, as the sensitivity scales with its square. In practice, however, measurement resolution does not scale with sensitivity, which limits attainable improvement in terms of limit of detection.

As applied to VOC sensing, the change in mass is caused by the absorption of an ambient organic vapor into an applied polymer layer. For certain classes of rubbery polymer films, there is a high affinity between target VOC compounds and the polymer material. Commonly employed polymers include polydimethylsiloxane (PDMS), polyisobutylene (PIB), and polyetherurethane (PEUT) for the detection of aromatic hydrocarbons, alcohols, and alkanes [5]. The

inherent difficulty in using polymer-sensing layers is that they mechanically damp the FBAR resonance, degrading the quality factor; a compromise between sensitivity and loading must be reached.

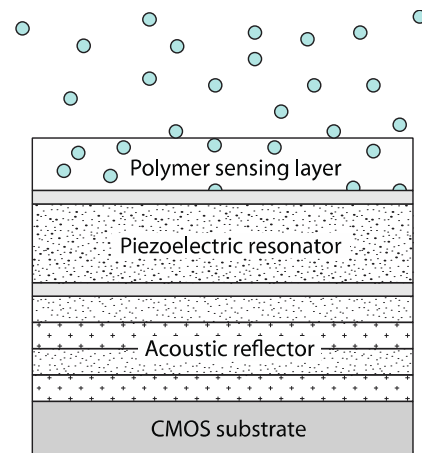


Figure 1: Illustration of basic sensing principle. A thin polymer layer is applied to a solidly mounted FBAR device, which is in turn built monolithically atop a CMOS substrate for drive and readout. Absorbed organic vapors cause a frequency shift, which is measured by the underlying integrated circuits.

Replacing an individual VOC sensor with an array of detection sites enables multiplex vapor detection. Sensors can be functionalized with different polymers, each of which has a separate set of affinities for classes of compounds; this enables classification and quantification of unknown multi-component vapor samples [6]. Additionally, a dense sensor array supports sensor replicates and non-functionalized controls, the latter of which may prove useful in correcting for thermal drift and other common-mode system noise sources.

By combining resonant VOC sensors with direct CMOS integration, a portable, low-cost, low-complexity detection system can be built. The small size and high frequency of FBAR devices are well aligned for building dense arrays on modern CMOS platforms; sensors typically operate in the low gigahertz regime and may measure 100 μ m or less on a side.

Measurement of the resonant frequency is accomplished by using the FBAR as the resonant tank for a simple oscillator. The frequency of oscillation is determined with a digital frequency counter. This is the same measurement topology employed in a standard megahertz-regime quartz crystal microbalance, and collocation of resonator, oscillator, and counter allow this to be extended well into gigahertz frequencies.

FBAR-CMOS SENSOR DESIGN

Active CMOS Substrate

The integrated circuit substrate was designed and fabricated in a $0.18\mu\text{m}$ RF CMOS process. The chip enables a 6×4 array of FBAR-based Pierce oscillators; both oscillator and frequency counting hardware are replicated at each array site. A more detailed description of the circuits and architecture has been previously reported [7]. The chip measures $3\text{mm} \times 5\text{mm}$, and it enables simultaneous interrogation of all sensors with a simple digital interface.

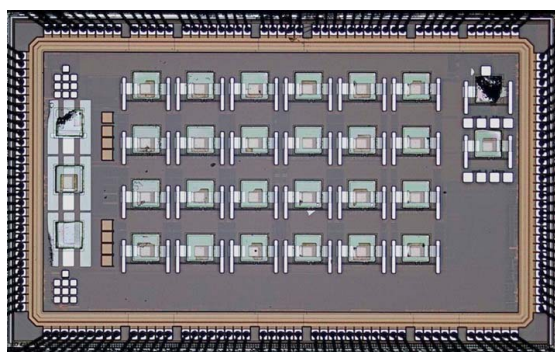


Figure 2: Die photo of the active CMOS substrate after resonator fabrication and wire bonding. Die measures 3mm by 5mm and supports a 6×4 sensor array.

Monolithic FBAR Fabrication

Resonators are built directly atop the active CMOS substrate in a solidly mounted structure, as illustrated in Figure 1. Mechanical isolation is achieved with a multi-layer acoustic mirror, analogous to an optical Bragg stack. In this case, alternating layers of tungsten and silicon dioxide are used to build a broadband acoustic mirror around the target resonant frequency. The die photo of the complete chip is shown in Figure 2. A cross-section scanning electron micrograph of this structure is depicted in Figure 3.

For the array, acoustic reflectors are patterned as isolated structures; this allows open access to the CMOS top metal layers exposed through passivation openings, and it also mitigates mechanical cross-talk among FBAR devices. Mirror layers and piezoelectric zinc oxide resonator layer are deposited using RF magnetron sputter deposition, and gold electrodes and chrome adhesion layers are deposited by evaporation. All features are defined through a photolithographic lift-off process, and fabrication is carried out on individual dice.

POLYMER APPLICATION

To increase sensitivity to organic vapors, a thin polymer layer is applied to the top surface of each FBAR sensor. Choosing an appropriate layer thickness is guided by a desire to significantly increase vapor sensitivity while negligibly degrading the resonator quality factor. Additionally, for an array of sensors, leveraging multiplex detection also requires individual functionalization of neighboring devices. Polymer application for a resonant gas sensor is typically done by spin-coat or spray-coat methods [8], which are not suited

for coating individual devices in a dense array. In this work, glass micropipettes are used for precise, small-volume application of dilute polymer solutions.

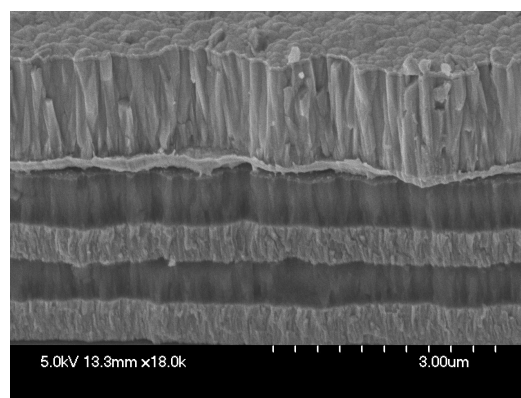


Figure 3: Tilted scanning electron micrograph of a fabricated FBAR cross-section. Alternating tungsten and silicon dioxide layers form the acoustic reflector, and the columnar zinc oxide layer is visible on top.

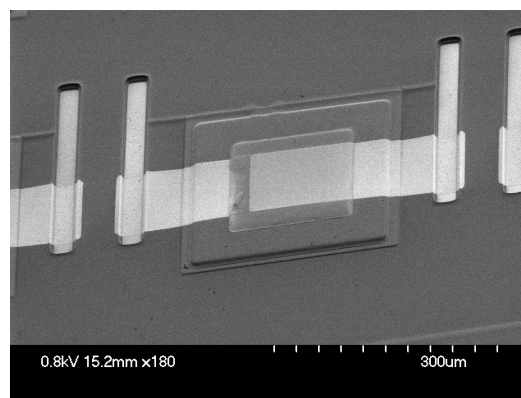


Figure 4: Tilted micrograph of a single FBAR device fabricated directly on the active CMOS substrate. Electrical connection to underlying circuits is made through openings in the CMOS passivation.

Pulling a small-diameter glass capillary tube down to a micron-scale tip diameter creates a micropipette, which is commonly used for the injection or extraction of small volumes of material to or from individual cells. In this work, a capillary with a pulled tip diameter of approximately $100\mu\text{m}$ is used with a precision pneumatic injector and manipulator arm to apply small volumes of dilute polymer solutions to individual FBAR top surfaces.

Uncured polydimethylsiloxane (PDMS) is mixed in a 10:1 ratio by weight with its curing agent and diluted many-fold in an organic solvent; typical dilution ratios used span 100:1 to 500:1 (solvent:PDMS) by weight. Film thickness and spot diameter can be controlled as a function of dilution ratio, solvent selection, and injection pulse. For thinning, PDMS is commonly diluted with hexane, toluene, or tert-butyl alcohol (TBA)[9], all of which have been tested here for use with FBAR devices. Toluene and hexane have proven effective for use in the micropipette setup. It was found that hexane wets more readily to the chip surface and evaporates quickly,

whereas toluene creates smaller-area spots (for a given dilution ratio) and significantly increases PDMS curing time. The use of TBA as a diluent for micropipette application of PDMS yielded poor results; with a melting point near room temperature, very dilute solutions tend to solidify in the capillary and clog the pipette tip. For the results shown, a hexane-PDMS solution with a 500:1 dilution ratio was applied, yielding polymer spots 200 μ m to 400 μ m in diameter. These were cured overnight at 100°C. Degradation in quality factor (Q) after application of a thin PDMS layer is small, with a typical resonator showing a decrease from 211 to 171 after spotting. A sample PDMS application test on a standalone FBAR device is shown in Figure 5.

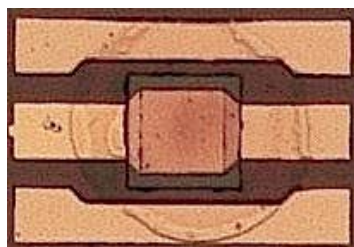


Figure 5: Optical microscope image of a standalone FBAR device on glass. A 400 μ m diameter PDMS spot is visible after micropipette application of a dilute hexane-PDMS solution.

EXPERIMENTAL SETUP

Dosing Chamber

Vapor sensing experiments were conducted in a dedicated dosing apparatus, illustrated in Figure 6. The chamber was constructed from a three-liter glass reaction vessel with a multi-input glass top section. Standard ground-glass fittings are used for gas inlet and exhaust, and a rubber septum is used for the solvent injection port and electrical feed-through.

To perform a concentration experiment, the chamber is first purged with nitrogen until a steady-state response is achieved, at which point the purge line is closed and the chamber has a sealed nitrogen environment. A small volume of liquid organic sample is then injected into the chamber, where it evaporates in the fixed volume to a calculable vapor concentration. So long as the target concentration is below the saturating vapor concentration for the organic compound, it will evaporate fully. A small fan assists evaporation and uniform steady-state vapor concentration. After steady-state frequency shift has been reached, the chamber is again purged with a nitrogen flow.

FBAR-CMOS Electrical Interface

A post-processed CMOS die is wire-bonded to a 144-pin ceramic PGA package. This is socketed on a custom printed circuit board (PCB). The PCB also includes necessary voltage sources, a temperature-compensated quartz crystal resonator for frequency reference, an FPGA for all-digital interfacing with the CMOS chip, and a USB bus for communication and data

export. The system consumes approximately 0.9W while in operation, and it can be powered from the USB bus directly. No additional hardware is required for operation of the sensor array.

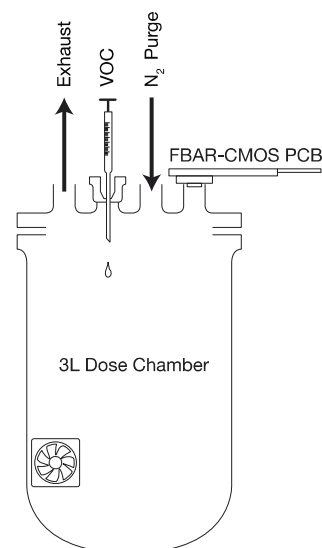


Figure 6: Illustration of static dose apparatus used for vapor testing. A small volume of organic solvent is injected through a septum and evaporates to a fixed vapor concentration.

EXPERIMENTAL RESULTS

Transient Sensor Response to VOC Exposure

A typical sensor response is shown in Figure 7, which plots the transient frequency shift of a PDMS-coated 1.44 GHz FBAR-CMOS sensor after an injection of toluene into the dose chamber. This measurement comprises frequency recordings at approximately one-second intervals; these are taken with the on-chip digital frequency counter located beneath the sensor. For the concentration shown, the sensor response begins to stabilize after 60 seconds, and recovery occurs on a comparable timescale.

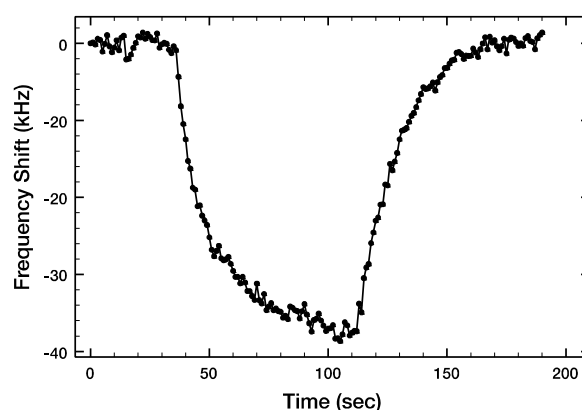


Figure 7: Transient response of PDMS-coated FBAR-CMOS sensor to 5200 ppm toluene vapor, as measured with on-chip frequency counter. Sample injection occurs at 40 seconds, and nitrogen purge occurs at 110 seconds.

During nitrogen purge, the sensor frequency returns to baseline, which demonstrates the reversibility of toluene absorption into the PDMS film. The settling time of the initial frequency shift is a function of both solvent evaporation rate and vapor absorption rate, which in a static system cannot be observed independently.

Toluene Concentration Series

A more extended toluene concentration series is shown in Figure 8, demonstrating a sensitivity of -7.29 Hz/ppm for a PDMS-coated 1.44 GHz FBAR-CMOS oscillator. For an inferred PDMS layer thickness of 8 nm, the partition coefficient for PDMS-toluene is used to calculate a sensor sensitivity of 31.3 kHz/pg, which is 313 kHz $\cdot\mu\text{m}^2$ /fg when normalized to sensor area. As sensitivity scales with the square of resonant frequency, these results are commensurate with other resonant VOC work, with 41.6 kHz $\cdot\mu\text{m}^2$ /fg reported at 220 MHz [4] and 10 MHz $\cdot\mu\text{m}^2$ /fg at 8 GHz [10].

The calculated Allan deviation is used to determine a minimum detectable frequency shift of ~ 440 Hz, which corresponds to an LOD of 60 ppm toluene for the sensor shown. This limit will depend closely on the polymer thickness and partition coefficient.

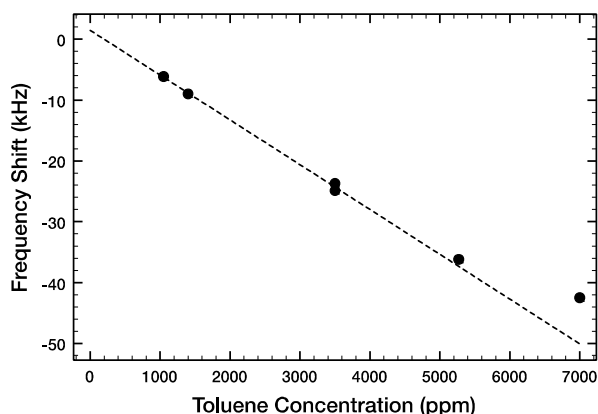


Figure 8: Toluene concentration series on integrated 1.44 GHz FBAR-CMOS oscillator coated with ~ 8 nm PDMS sensing layer. This shows sensitivity in the linear region of -7.29 Hz/ppm, and a non-linear saturation behavior above 5000 ppm.

CONCLUSIONS

The experimental results shown here demonstrate the use of monolithic FBAR-CMOS oscillators for VOC sensing applications. A method for small-volume polymer application has been developed, and reversible sensor response to toluene vapor has shown a frequency shift proportional to concentration with a sensitivity of 313 kHz $\cdot\mu\text{m}^2$ /fg.

The integration of monolithic FBAR devices with a CMOS platform yields a dense, self-contained sensor array. This work will enable the development of a multiplex vapor fingerprint array and can additionally be extended to broader chemical and biological sensing applications.

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REFERENCES

- [1] S. D. Piccot, J. J. Watson, and J. W. Jones, "A Global Inventory of Volatile Organic Compound Emissions From Anthropogenic Sources," *Journal of Geophysical Research*, vol. 97, no. 9, pp. 9897–9912, Jan. 1992.
- [2] J. W. Grate et al., "Determination of partition coefficients from surface acoustic wave vapor sensor," *Analytical Chemistry*, vol. 60, no. 9, pp. 869–875, May. 1988.
- [3] Y. Li, C. Vancura, D. Barretino, and M. Graf, "Monolithic CMOS multi-transducer gas sensor microsystem for organic and inorganic analytes," *Sensors and Actuators B, Vol 126 (2)*, 2007.
- [4] M. Rinaldi, B. Duick, C. Zuniga, C. Zuo, and G. Piazza, "SS-DNA functionalized ultra-thin-film ALN Contour-mode Resonators with self-sustained oscillator for volatile organic chemical detection," in *Micro Electro Mechanical Systems (MEMS), 2010 IEEE 23rd International Conference on*, 2010, pp. 132–135.
- [5] K. Bodenhofer, A. Hierlemann, G. Noetzel, U. Weimar, and W. Göpel, "Performances of Mass-Sensitive Devices for Gas Sensing," *Analytical Chemistry*, vol. 68, no. 13, Jan. 1996.
- [6] M. Horrillo, M. Fernandez, J. Fontecha, and I. Sayago, "Detection of volatile organic compounds using surface acoustic wave sensors with different polymer coatings," *Thin Solid Films*, 2004.
- [7] M. L. Johnston, I. Kymissis, and K. L. Shepard, "FBAR-CMOS Oscillator Array for Mass-Sensing Applications," *Sensors Journal, IEEE*, vol. 10, no. 6, pp. 1042–1047, 2010.
- [8] R. Gabl, E. Green, M. Schreiter, and H. Feucht, "Novel integrated FBAR sensors: a universal technology platform for bio-and gas-detection," *Sensors*, 2003.
- [9] K. Choonee, R. R. A. Syms, M. M. Ahmad, and H. Zou, "Post processing of microstructures by PDMS spray deposition," *Sensors & Actuators: A. Physical*, vol. 155, no. 2, pp. 253–262, Oct. 2009.
- [10] S. Rey-Mermet, R. Lanz, and P. Muralt, "Bulk acoustic wave resonator operating at 8GHz for gravimetric sensing of organic films," *Sensors & Actuators: B. Chemical*, vol. 114, no. 2, pp. 681–686, Apr. 2006.

CONTACT

M.L. Johnston, mlj@ee.columbia.edu