Highly Sensitive Detection of DMMP Using a CMUT-based Chemical Sensor

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Abstract— **We present ppt-level detection of dimethyl methylphosphonate (DMMP), a common simulant used in detector calibrations for sarin gas, using a new capacitive micromachined ultrasonic transducer (CMUT) design with a mass sensitivity improved from 130 zg/Hz/μm^2 to 48.8 zg/Hz/μm^2. A low-noise oscillator using the CMUT as the frequency selective component exhibits an Allan deviation of 0.55 Hz at the presence of air flow. The CMUT resonant sensor was functionalized with a 50-nm thick proprietary polymer layer (Sandia National Laboratory, Albuquerque, NM). Our sensor performance was reliably measured at the MIT Lincoln Laboratory where the accurate delivery of low concentrations of gases was ensured through stringent calibrations. Our sensor response to various concentrations of DMMP in air (10 ppb-1 ppm) showed an excellent volume sensitivity of 30.6 pptv/Hz. Based on the system noise floor, we achieved a mass resolution of 26.9 zg/μm^2 and a limit of detection of 16.8 pptv. In addition, the sensor showed good selectivity to DMMP.**

I. INTRODUCTION

Miniaturized chemical and biological sensor systems have a wide range of emerging applications for consumer, military, and medical use. Portable sensors with high sensitivity and reliability can replace the bulky equipment, expanding the potential applications beyond the conventional use of in-laboratory detection. For example, portable yet highly sensitive chemical sensors are desired in military and counter terrorism applications to detect a small trace of explosives and chemical warfare agents. Such a system-on-chip chemical sensor will also be a crucial component in a smart home application, detecting spoilage of food and monitoring the air quality. Recent advances in MEMS resonant devices, such as cantilevers [1], FBAR [2] and SAW [3] resonators, and CMUTs [4] allow the realization of such miniaturized chemical sensors by utilizing the mass-loading mechanism.

The CMUT technology is a good candidate for a miniaturized sensor system with various advantages compared to existing resonant MEMS devices. First, one side of the resonating structure is backed by a vacuum-sealed cavity, resulting in a higher quality factor compared to cantilevers with similar detection area. Second, the device is composed of thousands of resonating structures connected in parallel, which reduces the thermal noise of the oscillator. The multi-resonator configuration facilitates matching the impedance of the sensor to the interface electronics by producing a large range of motional impedances. Third, the array structure allows an easy implementation of multi-channel detection to enhance selectivity. Moreover, CMUT technology has been a topic of research for the last 15 years, and thus CMUTs can be designed and fabricated with great control and high yield.

We have previously demonstrated 6-MHz [4] and 18-MHz [5] CMUT-based resonant chemical sensor systems with a promising volume sensitivity of 37.38 ppb/Hz to DMMP and a theoretical limit of mass-loading detection on the order of 10^{-21} g per unit area (μm^2). Motivated by the goal of improving the limit of detection and the volume sensitivity, we use a CMUT with smaller plate mass and operating at a higher resonant frequency of 47.7 MHz. In this work, we demonstrate the improvement in the sensor performance by detecting a common simulant for sarin gas, dimethyl methylphosphonate (DMMP) in air. The sensor performance was measured at the MIT Lincoln Laboratory where the accurate delivery of low concentrations of gases in the 10 ppb to 1 ppm range was ensured through stringent calibrations. We also present results of our sensor responses to other analytes to show selectivity to DMMP.

II. METHODOLOGY

The sensing mechanism of a CMUT chemical resonant sensor is mass loading. Thus, the CMUT sensor used in this work is designed to operate at a higher frequency to provide a higher mass sensitivity compared to previous CMUT sensors [5]. Array structure, vacuum cavity, and massive parallelism are additional advantages a CMUT offers as a chemical sensor.

A. Operation

The basic building block of the CMUT used as a resonant sensor is a capacitor [Fig. 1(c)]. A highly-doped, circular

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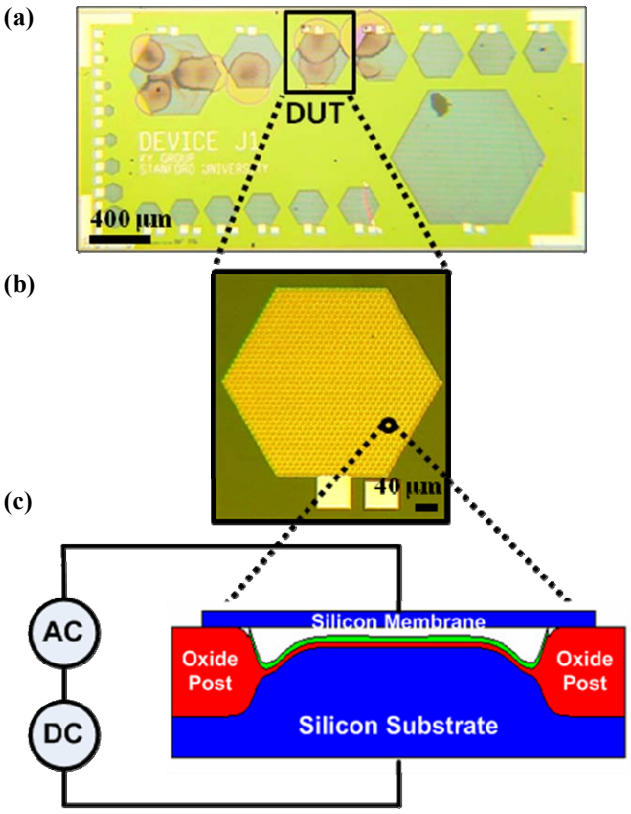

Figure 1. (a) Photograph of a single die, showing the array of CMUT resonant sensors with a 50-nm of polymer coating. (b) Photograph of a single element with 1027 cells. (c) Schematic of a single cell of a CMUT device.

single-crystal silicon plate forms the top electrode and the conductive silicon substrate acts as the bottom electrode. The top electrode is supported by thick oxide posts and is suspended over a thin evacuated cavity (vacuum gap) formed on top of an insulation layer. The structure is actuated by electrostatic force where an efficient electromechanical coupling is achieved due to the high electric field established over the narrow vacuum gap.

The resonant frequency (f_0) of a circular plate is inversely proportional to the square-root of the mass (m) of the plate. Thus, the additional mass on the resonant structure can be quantified by measuring the negative shift in the resonant frequency. More specifically, f_0 of the circular plate is estimated by [6]

$$f_0 = \frac{0.83}{a}\sqrt{\frac{Et^3}{m(1-\nu^2)}}, \qquad (1)$$

where a is the radius, E is the Young modulus, t is the thickness, and υ is the Poisson ratio. The negative frequency shift due to mass loading can then be estimated by

$$\Delta f_0 = -\frac{1}{2}\frac{\Delta m}{m} f_0 . \qquad (2)$$

B. Sensor Structure

22 hexagonal CMUT elements composed of a different number of circular cells are placed in a 2.5 mm x 5 mm single die to form an array structure [Fig. 1(a)]. The elements share a common ground through an electrical conductive silicon substrate. The 47.7-MHz CMUT elements used in this work are composed of 1027 circular cells with a 500-nm thick silicon plates and radii of 5.3 µm [Fig. 1(b)]. The plates are supported by the 1-µm thick oxide posts and separated from the bottom electrodes by a 50-nm vacuum gap. These CMUT structures were fabricated based on high temperature assisted direct wafer-bonding and LOCOS technique [7].

The 47.7-MHz CMUT resonant sensor is designed to achieve a higher mass sensitivity compared to that of an 18-MHz CMUT [5]. The increase in frequency is achieved by reducing the radii of the circular plates from 9 µm to 5.3 µm (1), which also results in a reduction of mass from 0.23 ng to 0.1 ng. Overall, the mass sensitivity has improved from 33.6 ag/Hz to 4.31 ag/Hz.

C. Practical Advantages of CMUT

In addition to high mass sensitivity, CMUTs have various practical advantages as a resonant chemical sensor: array structure, vacuum cavity, and massive parallelism. Each die is composed of an array of 22 CMUT elements, which allow for the implementation of a multi-channel sensor. In a multi-channel configuration, elements can be functionalized with different polymers to detect various chemicals and to enhance selectivity through pattern recognition. Moreover, one channel can be used as a reference to compensate for any environmental effects other than mass loading, such as atmospheric pressure, vibrations, and temperature, on the base-line frequency.

The second advantage is the vacuum gap. In general, flexural-mode resonators used as a chemical sensor must be exposed to a gaseous medium and thus are subject to significant medium damping. The CMUT resonant plate is less affected by such medium damping because one side of the CMUT resonant plate faces vacuum. Thus, compared to a basic cantilever structure, surrounded by the gaseous medium under test, a CMUT resonant sensor with a similar active detection area has a higher quality factor, and thus, it can provide significantly increased active sensing area.

In addition to the multi-channel configuration and the higher quality factor, another advantage of CMUT is the inherent massive parallelism. Each CMUT element is composed of 100s to 1000s of capacitor cells operating in parallel to form a multi-resonator structure [Fig. 1(b)]. The parallel multi-resonator structure has the advantage of lower effective motional impedance, which not only reduces the thermal noise of the oscillator [8], but also provides a better impedance match to the interface electronics. Moreover, the parallelism increases the robustness of the sensor. For example, a CMUT device can remain functional despite few defective cells, such as caused by mechanical impact during the sensing operation or fabrication steps, as long as the majority of the cells are intact.

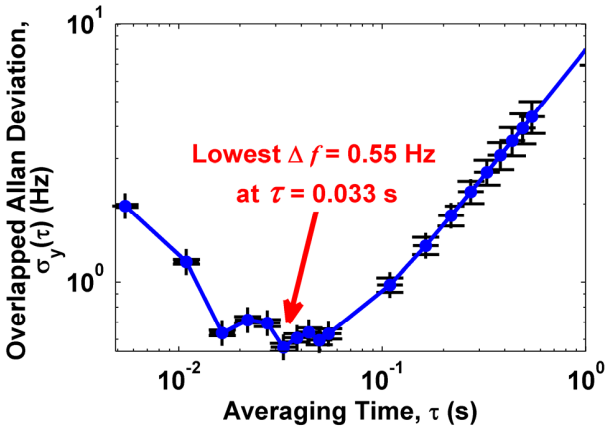

Figure 2. Overlapped Allan deviation for different averaging times calculated from the frequency counter data with a gate time of 5 ms. The error bars indicate 1-sigma confidence level.

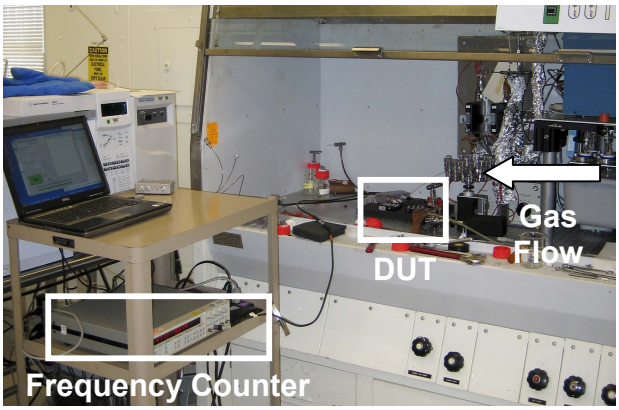

Figure 3. Test setup at the MIT Lincoln Laboratory. The setup is calibrated for accurate delivery of low concentrations of various gases from 10 ppm to 10 ppb.

III. System Level Design

We designed a free-running oscillator circuit using the 47.7-MHz CMUT as the frequency selective device to track the frequency shift due to mass loading in real time. The CMUT elements were coated with a layer of chemically sensitive proprietary polymer developed in the Sandia National Laboratory. The chemical experiments were conducted at the MIT Lincoln Laboratory, where accurate delivery of ppb-level concentrations of DMMP was ensured through stringent calibrations.

A. Design and Characterization of the Oscillator Circuit

The electrical input impedance of the CMUT was first measured to model the resonator for the oscillator design. The CMUT was biased at 36.5 V (70% of the pull-in voltage) that resulted in a f_0 of 47.7 MHz. The impedance was then modeled by the Butterworth-van-Dyke (BvD) equivalent circuit, the conventional 4-element model consisting of RLC motional impedance branch in parallel with the parasitic capacitance of the device [9]. A free-running oscillator circuit was designed to satisfy the Barkhausen criterion with the CMUT used as the frequency selective component in its feedback loop. The closed-loop signal was then sampled and outputted through a buffer. The circuit was implemented with discrete components on a PCB with the CMUT directly wire-bonded to PCB pads to minimize parasitic effects of the chip-carrier.

The limit of detection of a mass-loading based resonant sensor, Δm, is primarily set by the short-term frequency stability of the oscillator, Δf (2). This parameter was measured in the time domain using a frequency counter (SRS 620) at the presence of air flow to estimate the realistic noise floor of the system that includes the effects of fluctuations in the flow due to the mass flow controller. The overlapped Allan deviation [10] was calculated for different averaging time based on the frequency data measured at a sampling rate of 200 Hz (Fig. 2). The curve denotes the lowest Allan deviation of 1.15×10^{-8} and a frequency noise of 0.55 Hz at an averaging time of 0.033 s. Using (2), we estimate an unprecedented mass resolution of 48.8 zg/μm^2 (i.e. 48.8×10^{-21} g/ μm^2).

B. Functionalization and Chemical Experimental Setup

The CMUT elements were coated with an approximately 50-nm thick layer of proprietary polymer, developed by Sandia National Laboratory to be highly sensitive to DMMP. The diluted polymer was pipette-dropped on top of four elements [Fig. 1 (a)]. Approximately 50-nm thick coating on top of the 500-nm CMUT resonant plate did not significantly perturb the device impedance as observed by the insignificant change in the resonant frequency before and after the coating.

Previously, we demonstrated a high volume sensitivity of 37.38 ppb/Hz to DMMP using our 18-MHz CMUT chemical resonant sensor coated with polyisobutylene polymer layer [5]. For the 18-MHz chemical sensor system, we used in-house chemical setup that could control the vapor concentration from 32 ppm down to 3.2 ppm [5]. To test the current sensor system composed of an improved sensor with a higher mass sensitivity and a better polymer layer, an advanced chemical setup was required that could deliver very low concentrations in ppb range and also to guarantee the accurate concentration through stringent calibrations.

Thus, we conducted the sensitivity test of the 47.7-MHz sensor system at a certified lab (MIT Lincoln Laboratory), where such a chemical system is established through the Micro Gas Analyzers (MGA) program sponsored by Defense Advanced Research Projects Agency (DARPA). The chemical setup at the MIT Lincoln Laboratory can deliver low range of concentrations of DMMP from 1 ppm down to 10 ppb, generated from a DMMP permeation tube placed in a constant-temperature oven (Fig. 3). The carrier gas to control various concentrations of DMMP was air which was first dehydrated and then purified through a zero-air generator (Model 76-803, Balston Parker, Haverhill, MA). The mixed gas containing the purified air and DMMP was then delivered to a small chamber (3 cm^3) enclosing the functionalized CMUT device.

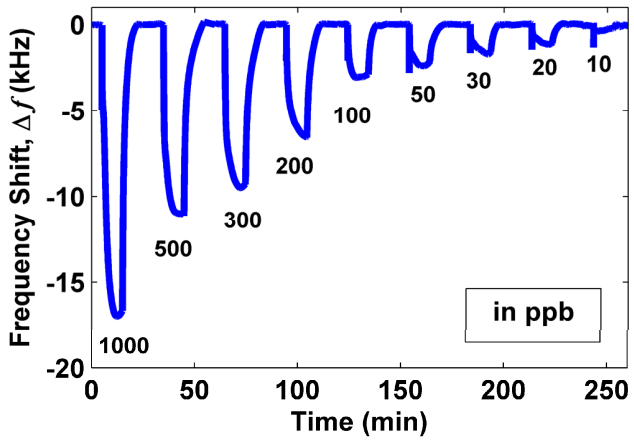

Figure 4. Transient frequency shifts in response to various concentrations of DMMP. DMMP vapor was added for a duration of 10 min followed by 20-min purging with the carrier gas.

IV. Experiemental Results

The volume sensitivity of the 47.7-MHz CMUT sensor to DMMP was characterized for nine different analyte concentrations ranging from 1 ppm down to 10 ppb. Fig. 4 shows the transient frequency shifts in response to various DMMP concentrations. As the polymer layer absorbs DMMP molecules, the oscillation frequency drops as a function of volume concentration. The response time to ppb-level and ppm-level concentrations are approximately 1 and 2 min, respectively. The sharp peaks observed at the start of each pulsing (Fig. 4) for the concentrations from 10 to 50 ppb are due to pressure shock from the mass flow controller used in the experimental setup.

The maximum frequency shifts between 10 ppb and 100 ppb are a linear function of the analyte concentration (Fig. 4). Using the best-fit linear regression, the volume sensitivity of 30.6 ppt/Hz can be estimated by taking the inverse of the slope, which is orders of magnitude improvement in volume sensitivity compared to [5]. Based on the system noise floor of 0.55 Hz, we achieved a mass resolution of 26.9 zg/μm^2 and an unprecedented limit of detection of 16.8 pptv, which outperforms the state-of-the-art resonant chemical sensors developed for DMMP detection (Table 1).

TABLE I. Comparison of the performance of 47.7 MHz CMUT sensor to that of the state-of-the-art resonant chemical sensors

	This Work	*Work [11]*	*Work [12]*
Sensor	CMUT	Cantilever	SAW
Outside Laboratory	Yes	No	No
Demonstrated DMMP Concentration	10 ppb ~ 1 ppm (in air)	0.5 ppb (in He)	0.19 ppm ~ 19 ppm (in N_2)
Limit of Detection	16.8 pptv	30 pptv	0.1 ppmv
Response Time	~ 240 s	~ 60 s	~ 900 s
Interference Test	Yes	None	None

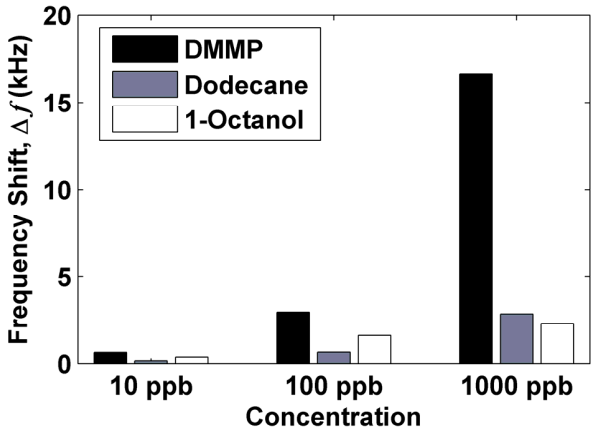

Figure 5. Frequency shifts in response to Dodecane, 1-Octanol, and DMMP at various concentrations.

Finally, the CMUT sensor coated with the proprietary polymer was exposed to different analytes, such as Dodecane and 1-Octanol, at various concentrations (Fig. 5). The sensor shows much smaller responses to Dodecane and 1-Octanol in comparison to the response to DMMP.

V. Conclusion

We demonstrated a robust resonant chemical sensor based on a 47.7-MHz CMUT with very high sensitivity to DMMP, verified by the experiments conducted at the MIT Lincoln Laboratory. With the low noise floor of the system, we also predict an unprecedented mass resolution per plate area of 0.048 ag/μm^2. The inherent features of the CMUT devices including higher quality factor compared to cantilevers due to vacuum gap, massive parallelism of resonators, and the array structure, make the CMUT devices a great candidate for future chemical sensor systems.

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