CMUT as a Chemical Sensor for DMMP Detection

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***Abstract*— We present an 18-MHz capacitive micromachined ultrasonic transducer (CMUT), used as a chemical sensor for detection of a common simulant for chemical weapons, dimethyl methylphosphonate (DMMP), in air. CMUTs are attractive for chemical sensor applications because of their unprecedented mass sensitivity per membrane area, low motional impedance, and high quality factor compared to other flexural-mode resonators. The device is composed of 1000 individual cells operating in parallel, which provides a robust operation with low false alarm rate and low motional impedance comparable to that of Quartz crystal resonators. We designed a CMUT-based oscillator with a phase noise of -84.8 dBc/Hz and -136.6 dBc/Hz at offset frequencies of 1 kHz and 1 MHz, respectively. The oscillator exhibits an Allan deviation of 0.6 Hz with a one-sigma error of 0.037 Hz, which translates to a theoretical limit of mass detection of 16.2 ag. The 18-MHz CMUT is functionalized with a 50-nm thick polymer layer, polyisobutylene (PIB). The described CMUT sensor demonstrates a volume sensitivity of 37.38 ppb/Hz to DMMP.**

I. Introduction

Chemical and biological sensor systems have a wide range of applications, including consumer, military, and medical applications. Portable, yet sensitive and reliable sensors can replace bulky equipment, extending the range of applications beyond in-laboratory detection. For example, system-on-chip sensors can save lives of soldiers in the battlefield by detecting explosives or chemical warfare agents. Moreover, such sensors can also enrich our daily life by detecting spoilage of food, monitoring our environment, and identifying diseases detectable from our breath.

These chemical sensor systems must demonstrate reliability, portability, sensitivity, and selectivity. Recent advances in MEMS resonant devices, such as cantilevers [1], FBAR [2] and SAW [3] resonators, allow the realization of miniaturized chemical sensors, which all utilize the mass-loading mechanism. For all these sensors the successful system integration is essential.

The CMUT technology is an ideal candidate for a miniaturized sensor realization. Recently, a 6-MHz CMUT-based resonant chemical sensor system has been demonstrated with a promising volume sensitivity and a theoretical limit of mass loading detection on the order of 10^{-15} g per membrane [4]. A CMUT operated as a resonator for a chemical sensor has various advantages compared to existing resonant MEMS devices. The device inherently provides a multi-resonator configuration resulting in low motional impedance and a low false alarm rate. The array structure facilitates an easy implementation of a multi-channel chemical sensor with each resonating channel coated with a

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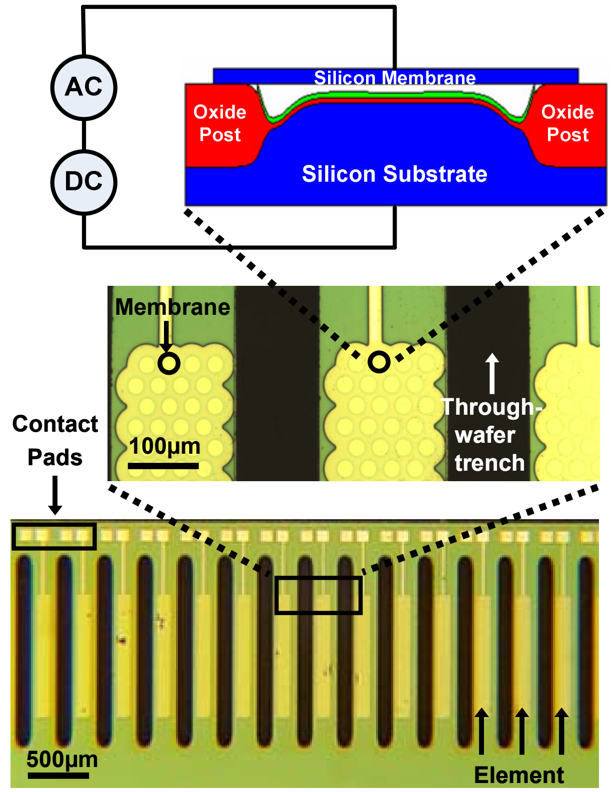
(b)
(c)


Figure 1. (a) Schematic of a single cell of a CMUT device. (b) Optical picture of the fabricated device. A single elements is composed of multiple cells and each element is separated by through-wafer trenches to reduce element-to-element cross-talk through the substrate (c) Optical picture of a single die, showing an array of multiple elements.

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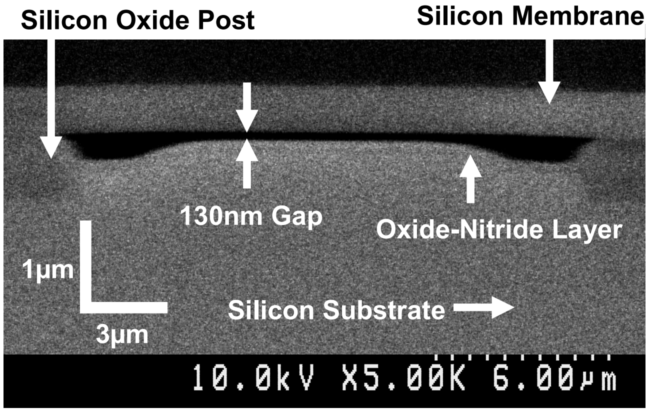


Figure 2. SEM photograph of the cross section of a single CMUT cell. The photograph is stretched 3.2 times in vertical direction for better visibility [4].

different polymer. Compared to cantilever based sensors with similar active detection area, the vacuum-sealed cavity of a CMUT is subject to smaller damping, thus translates into significantly higher quality factor. In addition, CMUT technology is a mature technology that has been topic of research for various applications in the last 15 years [5, 6]. Not only CMUTs can be fabricated with great control and yield, but also numerous design tools, such as finite element models, exist to predict the device characteristics.

Motivated by the goal of improving the limit of mass detection and the volume sensitivity, we use a CMUT with a higher resonant frequency of 18 MHz, compared to the device used in [4]. Further, we demonstrate the sensor performance by detecting a common simulant for chemical weapons, dimethyl methylphosphonate (DMMP) in air. In addition, we also present results of long-term tests to verify the reliability of the CMUT sensor.

II. Methodology

A. Operation

The basic building block of our CMUT, designed for chemical sensor applications, is a capacitive cell as depicted in Fig. 1. We use a circular single crystal silicon membrane as the top electrode, which is separated by a vacuum gap and an insulation layer from the bottom electrode (conductive substrate). When a voltage is applied between the two electrodes, the top membrane is attracted by electrostatic force. Due to the small separation between the two electrodes, a high electric field strength and in turn an efficient electromechanical coupling is achieved.

The material properties and dimensions of the membrane, and the applied bias voltage determine the resonant frequency (f_0) of the CMUT. For a circular membrane, f_0 is inversely proportional to the square-root of the mass (m) of the membrane [4]. Thus, the loaded mass on the resonant membrane can be detected by tracking the shift in resonant frequency. The expected frequency shift of a mass-loading system can be calculated by

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

B. Structure

The 18-MHz CMUT elements used for this work are composed of 1000 circular cells with 500-nm thick silicon membranes with radii of 9 µm (Fig. 2). The membrane is supported by the 0.9-µm thick oxide posts and separated from the bottom electrodes by 130-nm large vacuum gaps. In total, 32 elements are placed in a 10 mm x 5 mm die to form an array structure. The elements share a common ground through a highly conductive silicon substrate and each element is separated by through-wafer trenches to reduce acoustic cross-talk through the substrate (Fig. 1). The details of the fabrication processes of this CMUT are described in [7].

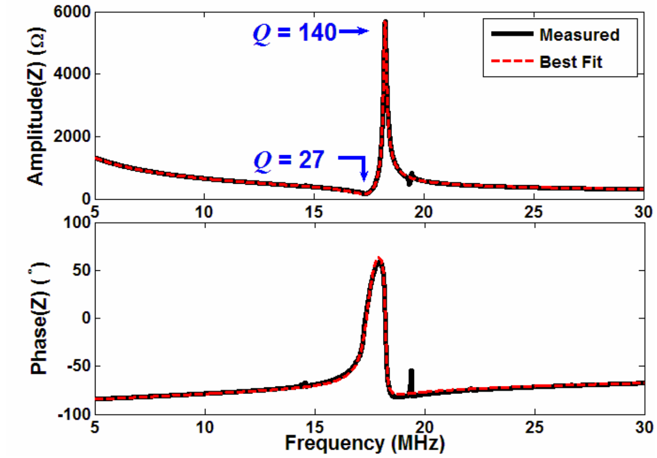
The CMUT structure was designed to maximize the sensitivity of the sensor. First, we use a thin membrane (500 nm) made of single crystal silicon to reduce the mass, m. The calculated mass of a single membrane is 2.3×10^{-10} g. Furthermore, highly conductive silicon was used for the membrane layer to completely omit metal electrodes on the membrane, which are generally deposited on top of CMUT membranes. Second, by using extended oxide posts (0.9 µm) [8], a thin vacuum gap height (130 nm) is realized. The high ratio between oxide post thickness and the gap height improves the coupling coefficient, the breakdown voltage, and the parasitic capacitance of the CMUT.

III. Practical Advantages of the CMUT

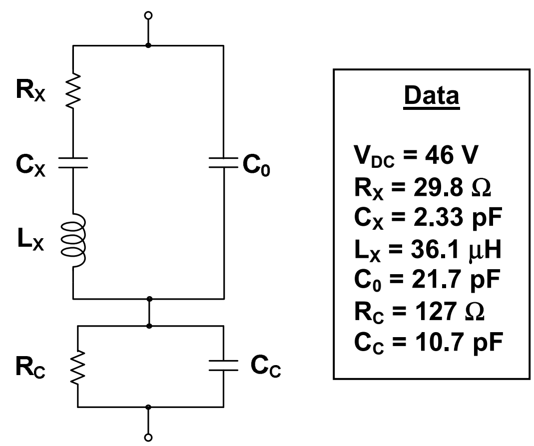
CMUTs have many practical advantages as a resonant chemical sensor: array structure, vacuum cavity, and massive parallelism. The CMUT elements are fabricated in an array, which allows for the implementation of a multi-channel sensor. In a multi-channel configuration, we can use one channel as a reference to compensate for the long-term drift. Moreover, elements can be functionalized with different polymers for a more reliable detection of various chemicals.

The second advantage is the vacuum cavity. As resonant chemical sensors must be exposed to the medium, flexural-mode resonators are subject to significant damping caused by the medium. The CMUT device is less subject to the medium damping because one side of the membrane faces vacuum. Thus, the vacuum-sealed cavity of a CMUT translates into a significantly higher quality factor compared to cantilever based sensors with similar active detection area.

Another advantage of the CMUT is the inherent parallelism. Each CMUT element is a multi-resonator structure with 100s to 1000s of capacitor cells, all operating in parallel. The massive parallelism of resonators not only reduces thermal noise of the oscillator [9], but also reduces the effective motional impedance, which allows using a simpler oscillator circuit with less gain requirement. Further, the parallelism enhances the robustness of the device. For examples, a CMUT device with defects on some of the cells, e.g. due to mechanical impact during operation or fabrication, can still stay functional as long as the majority of cells are intact (Fig. 1 (c)).



(a)



(b)

Figure 3. (a) Measured and fitted impedance characteristics of the 18-MHz CMUT biased at 46 V. (b) 6-element equivalent circuit model used to fit the input impedance of the CMUT. The values for each component are shown.

IV. System Level Design

We designed a free-running oscillator circuit using the 18 MHz CMUT as the frequency selective device to track the frequency shift due to mass-loading in real-time. The CMUT elements are coated with a chemically sensitive layer of polyisobutylene (PIB). The resulting frequency shift due to DMMP detection is read out by a frequency counter (SRS 620).

A. *Design and Characterization of Oscillator Circuit*

The resonant characteristics of the CMUT are first measured as the basis for the oscillator design. The electrical input impedance of the CMUT, biased at 46 V shows a resonance at around 18 MHz with quality factors of 27 and 140 at series and parallel resonances, respectively (Fig. 3 (a)). The impedance is then modeled as a 6-element equivalent circuit (Fig. 3 (b)), which includes parasitic effects of the substrate and electrode contacts in addition to the conventional

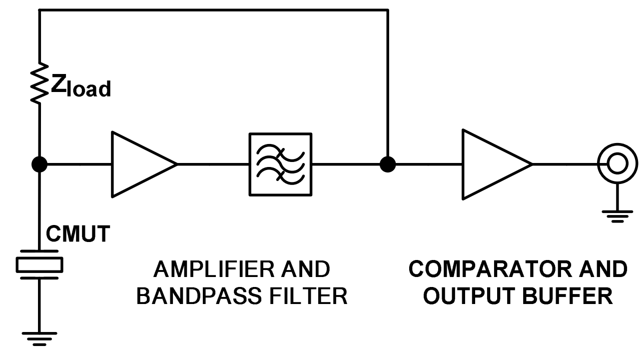


Figure 4. Block diagram of the parallel-resonant CMUT oscillator.

4-element RLC model (Van Dyke circuit) [10]. The standard Van Dyke circuit consists of a series combination of an inductor (L_X) representing the mass of the membrane, a capacitor (C_X) representing the stiffness of the membrane, and a resistor (R_X) modeling the motional resistance, in parallel to the electrical capacitance (C_0) of the structure. A good fit is obtained between the measured and modeled parameters, as illustrated in Fig. 3 (a).

Fig. 4 shows the block diagram of the oscillator circuit. The two main challenges in designing a CMUT-based low-noise oscillator are a five times lower Q at the series resonance compared to the parallel resonance (Fig. 3 (a)) and the constraint set on the applicable circuit topologies due to the ground electrode common to all CMUT elements in an array. For this work, we designed an oscillator circuit based on the Colpitts topology, which benefits from the higher Q at the parallel resonance (Fig. 3(a)). To maximize the gain at the parallel resonance, the resonator is connected as a shunt element in a voltage divider. The value of the Z_{load} is chosen to optimize the trade-off between the in-circuit Q and the gain. The voltage divider output is further amplified and filtered with a second-order non-inverting bandpass filter centered at the parallel-resonant frequency. The closed-loop signal is

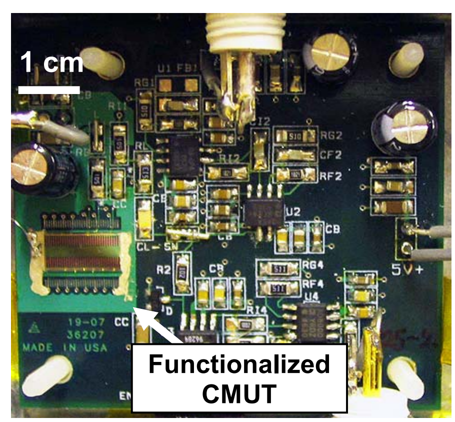
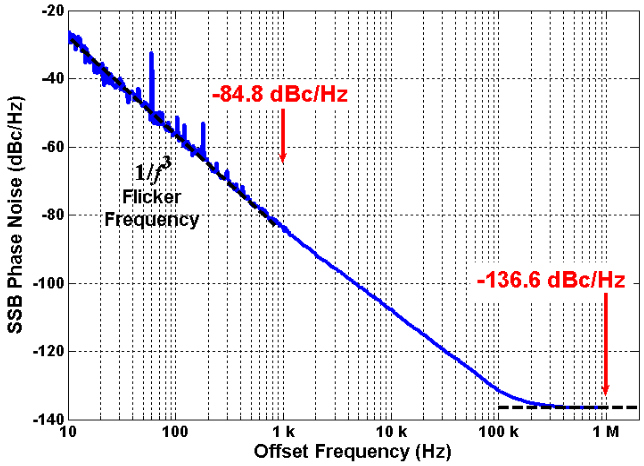
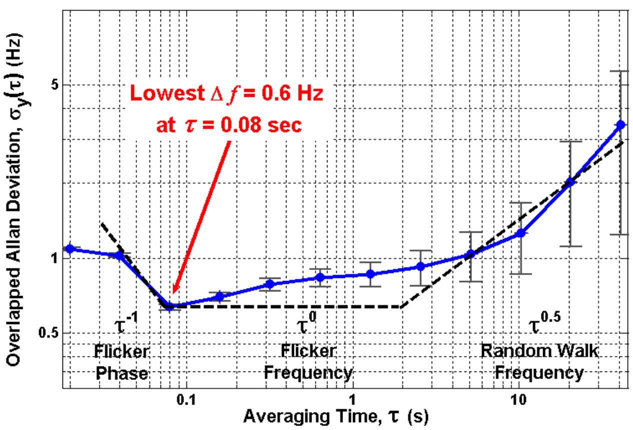


Figure 5. Photograph of the PCB showing oscillator circuits with the wire-bonded 18-MHz CMUT. The PCB is shielded in a metal box for noise measurements and chemical experiments.



(a)



(b)

Figure 6. (a) Measured single side band (SSB) phase noise using Agilent E5052A Signale Source Analyser. Oscillator has a floor noise of -136.6 dBc/Hz at offset frequency of 1 MHz. (b) Overlapped Allan's deviation [11] for different averaging times calculated from the frequency counter data with a gate time of 20 ms. The error bars indicate a 1-sigma confidence level.

sampled and outputted through a buffer to shield the loop from variations in the external load.

The circuit is implemented on a PCB (Fig. 5) with the CMUT directly wire-bonded to minimize parasitic effects of the bond-wire. The CMUT is biased at 46 V to obtain a f_0 of 18.2 MHz. As the detection limit of the sensor (1) is primarily set by the short-term frequency stability of the oscillator, Δf, the stability of the oscillator is characterized in the frequency and time domains using a signal source analyzer (Agilent E5052A) and a frequency counter (SRS 620), respectively. The stability measurements are conducted after 30 minutes of stabilization at a constant temperature of 40°C.

The measurements indicate a phase noise level of -84.8 dBc/Hz and -136.6 dBc/Hz at offset frequencies of 1 kHz and 1 MHz, respectively (Fig. 6 (a)). The overlapped Allan deviation [11] is calculated for different averaging times based on the frequency data measured at a sampling rate of 20 ms (Fig. 6 (b)). The curve shows dominant flicker phase and frequency noise components in the time domain which corresponds to $1/f^1$ and $1/f^3$ phase noise, respectively. The curve denotes the lowest Allan deviation of 3.5×10^{-8} and a frequency noise of 0.6 Hz at an averaging time of 0.08 s. Using (1), we predict an unprecedented mass resolution of 0.077 attogram per μm^2 (i.e. $0.077 \times 10^{-18} / \mu m^2$).

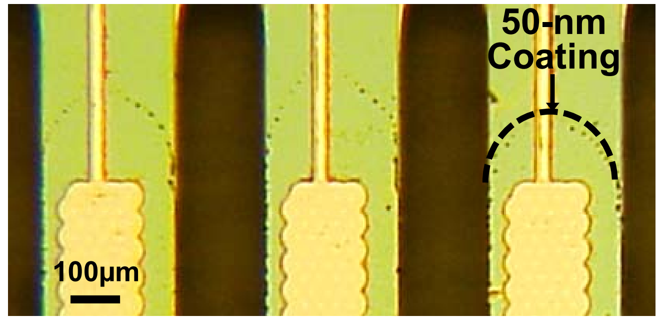


Figure 7. Optical picture of the CMUT elements functionalized with a 50-nm thick layer of PIB.

B. *Functionalization*

For DMMP detection, the CMUT array is coated with a 50-nm thick layer of polymer, polyisobutylene (PIB), using an inkjet dispensing system (Model MD-P-705, Microdrop, Norderstedt, Germany) [12]. 0.2-nl droplets of diluted polymers are ejected on the pre-cleaned CMUT elements, leaving a uniform polymer film on top of the CMUT membranes (Fig. 7).

There is more room for improving the current 50-nm thick PIB polymer. The thin coating did not significantly perturb the device impedance because the oscillation frequency difference before and after the coating was insignificant. Thus, we can still increase the coating thickness to increase the volume sensitivity further. In addition, in retrospect, PIB polymer is known to be inadequate for highly sensitive detection of DMMP, thus, we can expect orders of magnitude improvement in our volume sensitivity using more sensitive polymers, such as synthesized polymer developed for DMMP. Our CMUT sensor with PIB coating, however, already shows excellent volume sensitivity.

C. *Chemical Experiement Setup*

The goal of our chemical experiment is to test the volume sensitivity and reliability of our sensor system. To estimate volume sensitivity, the frequency shift due to various DMMP vapor concentrations must be measured. We use a mass flow controller and a bubbler to control the vapor concentration of DMMP. Purified air generated from a zero air generator (Balston Parker Model 76-803) is first bubbled through a test tube containing DMMP at a flow rate ranging from 1 to 10 ml/min (Fig. 8). The saturated outgoing mixture then merges with the air carrier flowing at a rate of 500 ml/min. The resulting small volume concentrations of DMMP vapor is then delivered to a chamber enclosing the coated CMUT device. In order to reduce the effect of the experimental set-up

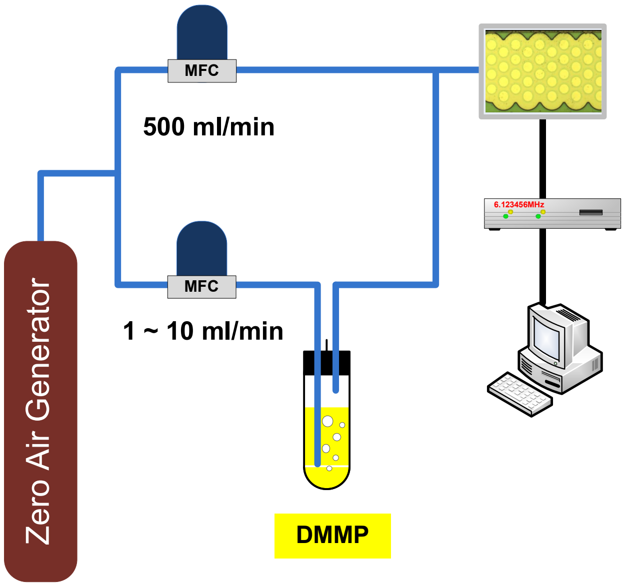


Figure 8. Schematic of the chemical experiemental setup. Mass flow controllers and a bubbler are used to adjust the vapor concentration of DMMP. The saturated mixture from the bubbler then merges with the purified air generated from a zero air generator (Balston Parker Model 76-803). The final mixture is then delivered to a chamber enclosing the coated CMUT device.

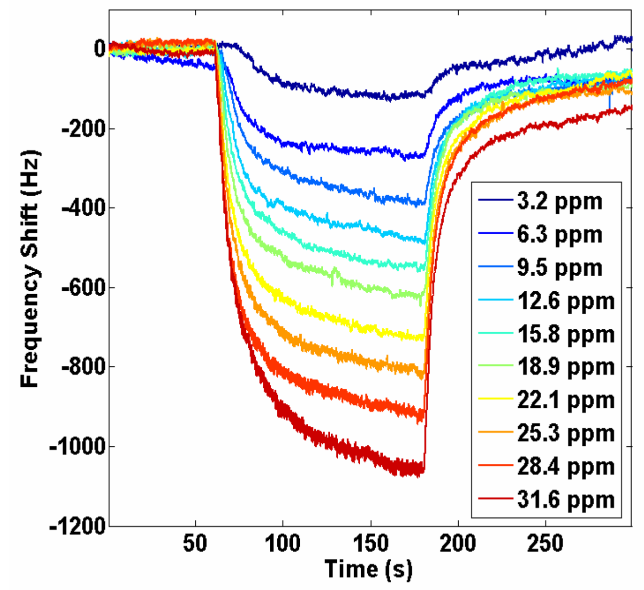
on the time constant, the size of the chamber was designed small (3 cm^3).

V. Experimental Results

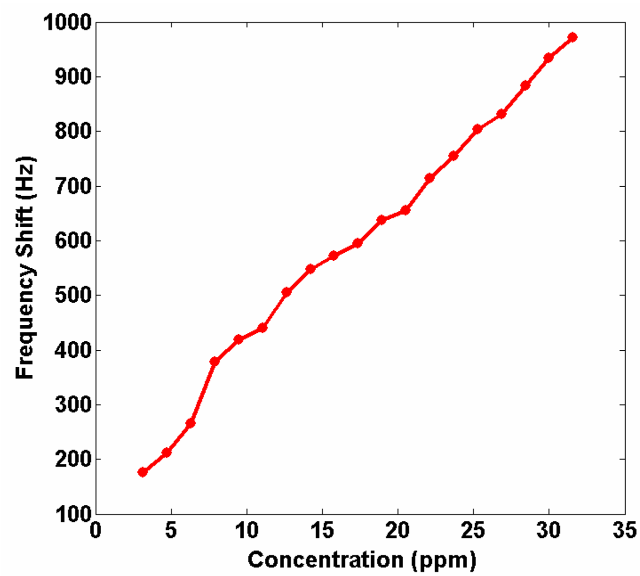
The volume sensitivity of our CMUT sensor to DMMP is characterized by varying the analyte concentration from 3.2 ppm to 31.6 ppm with a step of 1.5 ppm. Here, we assume that the outgoing mixture from the bubbler is completely saturated to the vapor concentration of DMMP. Fig. 9 (a) shows the transient 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. Our sensor system shows a fast response time. For example, in response to 31.6-ppm DMMP injection, the fall time and rise time are 45.4 s and 37.3 s, respectively.

The maximum frequency shift is approximately a linear function of the DMMP concentration (Fig. 9 (b)). Thus, linear regression is used to estimate the volume sensitivity. By taking the inverse of the slope, the estimated volume sensitivity of our CMUT sensor to DMMP is 37.38 ppb/Hz. The estimated sensitivity is promising because we used non-optimal PIB polymer layer and we expect orders of magnitude improvement in volume sensitivity with polymers such as BSP3 [13].

We tested the reliability of our CMUT sensor by applying 200 pulses of 50-ppm DMMP over 26 hours. Fig. 10 shows the maximum frequency shift observed at each pulse. The mean frequency response to the 50-ppm DMMP pulses is 1.018 kHz with a variation of 8%. The variation is mainly



(a)



(b)

Figure 9. (a) Transient frequency shifts of the PIB-coated CMUT in response to various concentration of DMMP. DMMP vapor starts to flow in at 50 s and stops at 180 s. (b) Plot of maximum frequency shift observed at different DMMP concentrations.

attributed to the changes in the environment, such as temperature, pressure and humidity. The 8% variation is not critical to our sensor system because differential detection can be readily implemented using a reference oscillator. The reference oscillator based on a neighboring element is exposed to the same environment and thus the long-term drift can be subtracted out.

In addition, the CMUT sensor exhibited an extremely low false alarm rate not only during the reliability test, but also

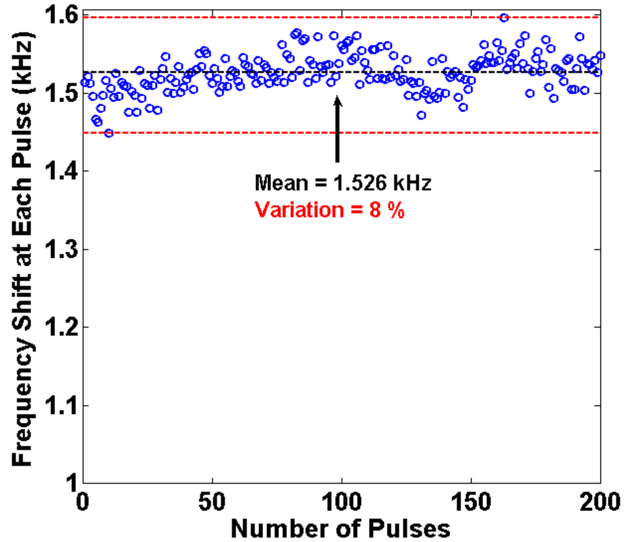


Figure 10. Maximum amplitude of frequency shift at each pulse. 200 pulses of 50-ppm of DMMP were applied over 26 hours.

during other chemical experiments to detect different analytes, such as water and ethanol. Zero failure in the system was observed during 120 hours of testing with 8000 pulses. Thus, the CMUT sensor has a good potential for the DMMP detection with high sensitivity as well as extremely low false alarm rate.

VI. CONCLUSION

We demonstrated a robust resonant chemical sensor based on an 18-MHz CMUT, with high sensitivity to DMMP. With our current oscillator design, we also predict an unprecedented mass resolution per membrane area of 0.077 attogram per μm^2. The inherent features of the CMUT devices: higher quality factor compared to cantilevers due to vacuum cavity, massive parallelism of resonators, the array structure, and large surface area, make the CMUT devices an excellent candidate for future chemical sensor system with stringent requirements.

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