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Capacitive micromachined ultrasonic transducer (CMUT) as a chemical sensor for DMMP detection

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ABSTRACT

We present a chemical sensor based on a capacitive micromachined ultrasonic transducer (CMUT) configured as a resonant mass sensor with a chemically selective polymer coating. The sensing unit of the CMUT consists of 100s to 1000s of resonators connected in parallel and acts as a single resonator. The high resonant frequency (18.2 MHz) and the small mass (296 pg) enable the CMUT to have a good mass sensitivity of 130 zg/Hz/μm^2. We functionalized the CMUT with polyisobutylene (PIB) as the sorbent film, which targets dimethyl methylphosphonate (DMMP), a simulant for nerve agent, sarin. An oscillator circuit was populated to trace the resonant frequency of the CMUT with a fast response time and low noise. We characterized the noise performance of the sensor system and identified the optimal gate time of the read-out frequency counter. Based on the noise measurement, the calculated limit of detection (LOD) of mass loading is 0.192 ag/μm^2 (3-σ confidence level). Chemical experiments were performed on the CMUT sensor with several analytes including DMMP, water, and ethanol. The limit of detection of the CMUT chemical sensor to DMMP vapor was measured as 56 ppb (3-σ confidence level).

1. Introduction

Demand for a highly sensitive, accurate, and portable chemical sensor system has been increasing over the recent years for a wide range of applications. Conventional applications in process control and chemical industry require high accuracy and sensitivity to monitor low-range concentrations of volatile compounds [1]. Recently emerging applications, including homeland security, smart home, and environmental monitoring require additional features such as portability and low-cost [2,3]. The existing chemical sensor systems, such as ion mobility mass spectrometers have high performance, but are not scalable because of the inherent working principle requiring ionization, a drift chamber and separate detectors [4]. Thus, new types of chemical sensor systems are necessary to address the emerging demand in both commercial and security applications.

Resonant chemical sensors based on the mass-loading effect (i.e., gravimetric sensors) with a chemical functionalization layer are promising candidates for such applications. These resonant systems have an advantage that a large selection of functionalization materials can be applied to detect various analytes, suitable for a wide range of applications. In addition, these resonant chemical sensors are not only scalable, but also the miniaturized sensors demonstrate comparable performance to bulky instruments [5]. Initial developments in quartz crystal microbalance (QCM) [6], surface acoustic wave (SAW) sensors [7] and film bulk acoustic resonator (FBAR) [8] have demonstrated the potential of a resonant chemical sensor with good mass sensitivity. However, when these sensors are implemented as an array to ensure selectivity, the size of the resulting device is still on the order of millimeters. To further reduce dimensions, various sensing devices based on the microelectromechanical system (MEMS) technology, such as MEMS resonators (e.g., micro-cantilevers), have been actively explored. Micro-cantilevers [9], which have the advantage of simple configuration show good sensitivity, but suffer from a low quality factor, Q, in air, which limits the sensor resolution. Several approaches to overcome these problems, such as fabricating nano-scale cantilevers [10], are under active investigation.

A capacitive micromachined ultrasonic transducer (CMUT) is another strong candidate for a MEMS resonant chemical sensor system [11] with three key advantages. First, a resonant thin plate is backed by a vacuum cavity where only the top side of the plate interacts with the surrounding medium; this reduces the overall energy loss and results in a higher quality factor compared to

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cantilevers. Second, the device is made of 100s to 1000s of resonators connected in parallel. This multi-resonator structure has two main advantages: a wide range of electrical impedance to match to electronics and an enhanced reliability compared to a single-resonator system. Moreover, a repeatable and reliable fabrication process [12] ensures that the lumped signal of the multi-resonator structure exhibits a single resonant frequency with a high quality factor (e.g., 100–400).

Our previous work demonstrated a multi-channel chemical sensor based on a CMUT array with 6 MHz operating frequency. The CMUTs, which were functionalized using various polymer layers [11], exhibited a mass sensitivity of 1 fg/Hz per a unit resonator and a volume sensitivity of 41.6 ppb/Hz to water vapor. In this work, we demonstrate a single-channel chemical sensor system, specifically designed to be highly sensitive to dimethyl methylphosphonate (DMMP), a common simulant for the chemical nerve agent, sarin (GB), which has an immediately dangerous to life or health (IDLH) concentration of 17.5 ppb [13]. The system is based on an improved CMUT sensor with a higher operating frequency of 18.2 MHz and a higher mass sensitivity of 33 ag/Hz. In addition, we present the response of the sensor system to other analytes and demonstrate a good repeatability through a long-term test.

2. Method

2.1. Working principle and design parameters

The transduction mechanism of our CMUT-based chemical sensor is the mass-loading effect; additional mass of analyte loaded on a functionalized resonant structure causes a shift in the resonant frequency. The basic building block of the CMUT resonator is a circular plate, which resonates in the first flexural mode. The dimensions and the material properties of the circular plate determine the resonant frequency, f_0, as

$$f_0 = 0.47\frac{t}{r^2}\sqrt{\frac{E}{\rho(1-\nu^2)}}, \quad (1)$$

where r, t, ρ, E, and ν are the radius, the thickness, the density, Young's modulus and Poisson's ratio of the plate, respectively [14]. Based on this equation, the resonant frequency, f_0, is inversely proportional to the density of the plate, and thus an increase in loaded mass due to analyte molecules linearly decreases the resonant frequency.

The critical figure of merit of a highly sensitive resonant sensor is mass sensitivity, which is defined as

$$S_m = \lim_{\Delta m \to 0} \frac{-1}{f}\frac{\Delta f}{\Delta m/A} = \frac{1}{2\rho t}, \quad (2)$$

where $\Delta m/A$ is the loaded mass normalized to the active sensor area, A [15]. The sensitivity is inversely proportional to the density and the thickness of the plate, and thus a light and thin plate is required to achieve high sensitivity. However, in practice, when the plate thickness becomes thinner, the radius of the plate needs to be smaller to maintain the resonant frequency and it will bring up the fabrication feasibility issue. The CMUT resonator used in this paper is made of a thin single crystal silicon plate of 0.5 μm thickness, and theoretical loaded mass per frequency shift ($1/S_m f$) is 130 zg/Hz/μm^2.

Another important factor is the minimum detection limit of loaded mass per unit area, defined as

$$\frac{\Delta m_{\min}}{A} = \frac{1}{S_m}\frac{\Delta f_{\min}}{f} = 2\rho t\frac{\Delta f_{\min}}{f}, \quad (3)$$

where $\Delta f_{\min}$ is the minimum detectable frequency change. $\Delta f_{\min}$ is typically characterized by the frequency noise of the system and highly depends on the quality factor, Q, of the resonant structure

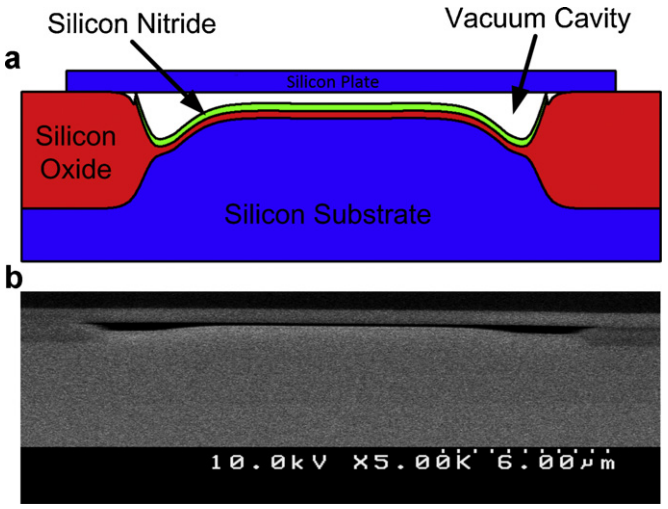

Fig. 1. (a) Cross-sectional schematic of a unit resonator of a CMUT. (b) SEM cross-sectional picture of a unit resonator.

[16]. The presented CMUT sensor system exhibits a low noise floor, resulting in a frequency resolution ($\Delta f_{\min}/f$) of 8.22×10^{-8} (3-σ confidence level) and a minimum detection limit of loaded mass per unit area ($\Delta m_{\min}/A$) of 0.192 ag/μm^2. This mass resolution is over an order of magnitude better than that of the state-of-the-art resonant chemical sensors based on nano-cantilevers (~4 ag/μm^2) [10]. The advantage of CMUT in the mass resolution is due to a low frequency resolution. The ρt of the CMUT is 5.3 times higher than the nano-cantilever, however, the CMUT has 110 times lower frequency resolution ($\Delta f_{\min}/f$) than the nano-cantilever.

2.2. Design of the CMUT resonant structure

2.2.1. Structure of the single resonator and its operation

Each resonant structure is a circular plate anchored around the edges to form a capacitor with a vacuum cavity (Fig. 1). The highly conductive single crystal silicon plate with a thickness of 0.5 μm is bonded on a pre-defined cavity to form a common top electrode. The radius of the resonant structure is 9 μm. When a DC bias voltage is applied between the plate (i.e., top electrode) and the substrate (i.e., bottom electrode), a high electric field built in the cavity provides sufficient electromechanical coupling between two electrodes. The AC voltage superimposed on the applied DC bias voltage excites the circular plate to vibrate.

There are several advantages of the CMUT-based resonant sensor over conventional capacitive resonant sensors such as capacitive micro-cantilevers [9]. First, the bottom side of the resonant structure faces a vacuum cavity, reducing the energy dissipation to the medium by half; only the top side of the resonant plate is subject to air damping. Therefore, Q of the CMUT resonator is approximately doubled compared to that of other flexural mode resonators with an equivalent size. Second, the encapsulated cavity makes the chemical functionalization easier. A typical MEMS resonator driven by electrostatic force has a thin gap between the electrode and the resonating structure, which must be protected from any chemical compounds during the functionalization step. The gap of our device is enclosed by the plate and oxide posts and is inherently protected during the chemical functionalization process (e.g., polymer coating).

In addition to these advantages, we adopt the LOCOS wafer bonding process [17] for the fabrication of CMUT in lieu of the conventional sacrificial release process [12]. In this new process, the nitride plate with an additional layer of metal traces is replaced with a highly conductive single crystal silicon plate, which has a

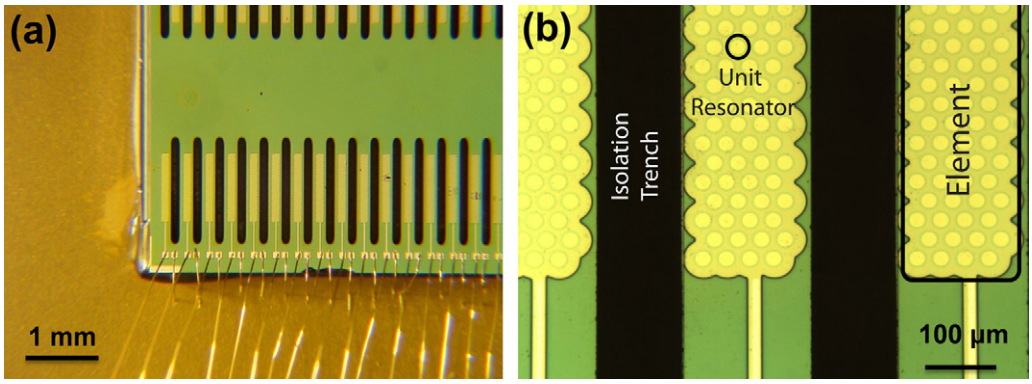

Fig. 2. Optical pictures of a CMUT array. (a) 64 sensing units (element) are located in a 5 mm × 2.5 mm die. (b) Top view of three elements. Circular pattern represents many unit resonators (Fig. 1) in a single element. In order to reduce the mechanical cross talk between elements, through-wafer isolation trenches are used between elements.

sheet resistance of 20 Ω/□. As a result the effective mass of plate is reduced. Moreover, the single crystal plate transferred from an SOI wafer has a better thickness uniformity and lower residual stress compared to the silicon nitride plate formed using the LPCVD process. The new process provides precise control of the plate dimensions, such as a plate thickness and a cavity shape, and also the process is capable of fabricating a very thin vacuum cavity as low as 40 nm. This low value for the cavity height reduces the required DC bias voltage to establish a high electric field strength that results in a good electromechanical coupling.

2.2.2. Structure of multi-resonators

A single CMUT sensor unit (channel) is composed of 100s to 1000s of identical resonant structures. These resonators in the channel are designed not to be mechanically coupled to each other, but to be electrically connected in parallel. Therefore, one can electrically access the parallel combination of all resonators through two bond pads, i.e., a signal and a ground pad (Fig. 2). The 18 MHz resonator used for the chemical detection is composed of 1000 resonators, each made of a single crystal silicon plate with a radius of 9 μm and a thickness of 0.5 μm.

This multi-resonator configuration has several benefits over the single resonator configuration. First, the effect on the lumped signal due to a failure of a few resonators during operation is not significant. As a result, the sensor is reliable and operational even with minor external damage. In addition, a larger number of resonators result in a larger total effective capacitance of the device. As a result, the ratio of unwanted parasitic capacitance due to electrical signal pads and external bond-wires to the active device capacitance becomes smaller. Moreover, the number of resonators can be used as an additional design parameter to adjust the lumped impedance of the device. For example, the lumped motional impedance is a critical parameter in the oscillator design in terms of thermal noise and impedance matching. This motional impedance is inversely proportional to the number of resonators and can be adjusted without changing the dimensions of individual resonators [18].

2.3. Device characterization

CMUT resonators are characterized electrically using an impedance analyzer (Model 4294A, Agilent Technologies, Santa Clara, CA). Important parameters of the resonant structure, such as the series and parallel resonant frequencies and *Q*, are extracted from this measurement. The measured input impedance of the CMUT (Fig. 3) shows a series resonant frequency of 17.3 MHz and a parallel resonant frequency of 18.2 MHz.

In an ideal resonator model, *Q* of both resonant frequencies should be comparable [16]. However, as the CMUT is made of multiple resonators connected in parallel, the resonator-to-resonator non-uniformity affects the quality factor. As Lee [19] discussed, the degradation of the quality factor of the series resonant frequency is more severe than that of the parallel resonant frequency, which is also observed in our measurement (Fig. 3). The measured quality factor of series resonant frequency (27) is much lower than

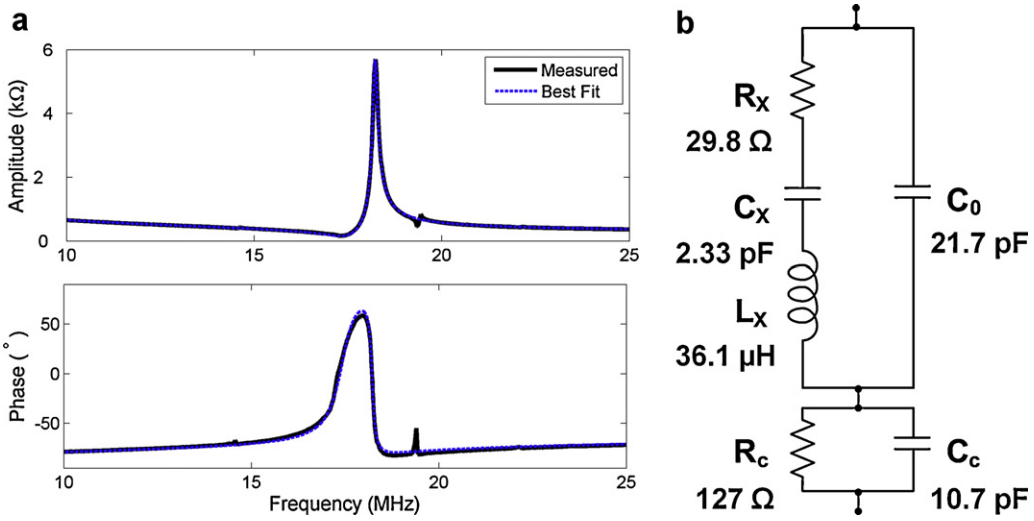

Fig. 3. (a) Measured input impedance of 18-MHz CMUT. (b) 6-elements equivalent circuit model with extracted component values from (a).

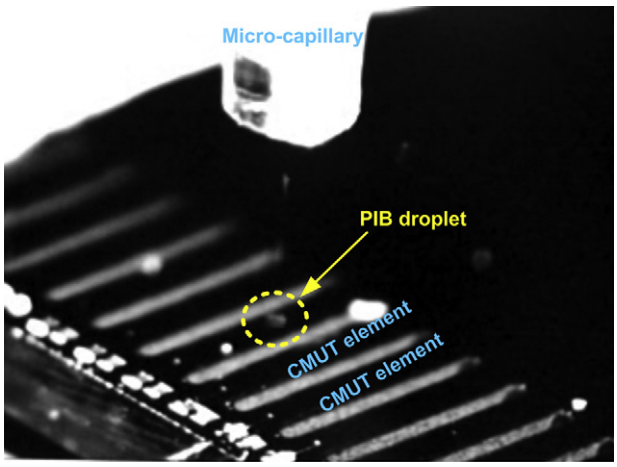

Fig. 4. Photograph of inkjet polymer coating. Cylinder on the top of the picture is micro-capillary used as droplet ejection. In this photograph, the solvent containing a polymer on the center element is not dried yet.

that of parallel resonant frequency (140) due to the resonator-to-resonator non-uniformity. To avoid low *Q* at the series resonant frequency, the oscillator circuit is designed to oscillate at the parallel resonant frequency.

2.4. Chemical functionalization

The resonators must be functionalized with a sorbent film to absorb analytes in air. This sorbent film should have high sensitivity and good selectivity to the analyte of interest. Among several commercially available polymers such as polyallylamine hydrochloride (PAAM), polyethylene glycol (PEG), and polyvinyl alcohol (PVA), we selected polyisobutylene (PIB) as the sorbent film to detect DMMP because of its availability and higher sensitivity to DMMP [20].

Diluted droplets of PIB (in toluene, 1 mg/ml), each with a volume of 0.2 nl, were ejected on the 18 MHz device using an inkjet-dispensing system (model MD-P-801, Microdrop, Norderstedt, Germany) [21]. The ejected droplets conformally coated the surface of the CMUT (Fig. 4). Then the solvent evaporated in a few seconds leaving a thin layer of polymer. It is challenging to measure the thickness of this polymer film using optical methods because the coated film is thin and optically transparent; only a particle pattern (Fig. 5) indicates the edge of the polymer coating. Thus, using atomic force microscope (AFM), operated in tapping mode, we measured the thickness of the polymer to be 50 nm. The effect

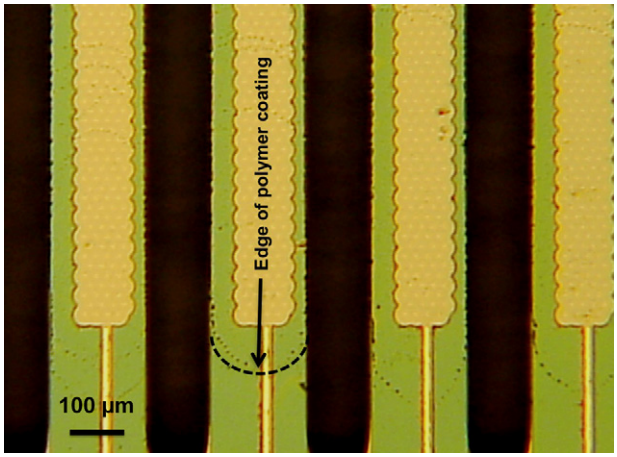

Fig. 5. Optical picture of a CMUT after functionalization. Small dotted line represents the edge of the polymer coating.

of a 50 nm polymer film on the quality factor and the resonant frequency of the device is negligible based on the input impedance measurement. The parallel resonant frequency slightly is increased by 0.64% while the quality factor is decreased by 7 after the polymer deposition.

Compared to the spin coating method, the inkjet-dispensing method tends to have less uniformity across the active area. However, the inkjet-dispensing method can selectively pattern areas of interest, e.g., top side of CMUT plates of a single device, and coat different polymers on multiple devices in a single die for array implementation [11].

2.5. Detection system

An accurate measurement of the resonant frequency is an essential part of a highly sensitive sensor system; lower frequency noise will result in lower limit of detection level of the system. The resonant frequency can be determined through the electrical input impedance measurement. However, this method suffers from limited frequency-sweep resolution and slow response time. Therefore, we designed a low noise oscillator circuit that tracks the resonant frequency of the device. This method allows for accurate real-time measurements using a digital frequency counter connected to the output of the oscillator circuit.

2.5.1. Oscillator circuit design

The oscillator circuit is composed of the CMUT as well as other discrete circuit components. For an optimal design, the circuit could be simulated and optimized in design steps. During these steps, the measured input impedance (Fig. 3a) could be modeled in an appropriate format and incorporated in the circuit simulation. In this work, we modeled the input impedance of the device as a 6-elements circuit model as shown in Fig. 3b. The model consists of the conventional 4-element RLC model (*Rx, Lx, Cx,* and *Co*) and additional two elements, *Cc*, and *Rc*. The 4-element RLC model is known as Butterworth Van Dyke model and commonly used as an equivalent circuit model for MEMS resonators. The additional two elements (i.e. *Cc* and *Rc*) represent the contact capacitance and the contact resistance to the substrate. The values of six elements were extracted from the measured input impedance based on a least squares fitting method (Fig. 3a).

Compared to other MEMS resonators and quartz-based resonators, CMUT resonators have two characteristics that govern the oscillator design. First, the CMUT is a one-port resonator, i.e., it has two electrical pads, a signal pad and a ground pad. This configuration gives more limitation of the topology of the oscillation circuit, compared to other two-port MEMS resonators [22,23]. Second, all the resonator units (elements) share the substrate as a common ground. Therefore the oscillator circuit, which is required to be compatible with the multi-channel oscillator, can access only one electrode of the CMUT, and leave the other electrode connected to ground. Last, as previously mentioned, the quality factor of the parallel resonant frequency of the CMUT is higher than that of the series resonant frequency. The circuit is designed to oscillate at the parallel resonant frequency to take advantage of higher *Q*.

Based on the above criteria, an oscillator circuit was designed and implemented (Fig. 6). The CMUT resonator was interfaced to the circuit through a voltage divider. The value of the capacitor in this stage was chosen to optimize the tradeoff between in-circuit *Q* and the gain of the voltage divider. The gain stage and band-pass filter were implemented using low noise op-amps (AD8045 and OPA657) to satisfy the Barkhausen criteria. The implemented circuit requires only two op-amps inside the oscillation loop, with a total power consumption of 80 mW. The loop gain is sufficiently larger than unity around the resonant frequency to start the oscillation from in-circuit noise components, and thus the system does

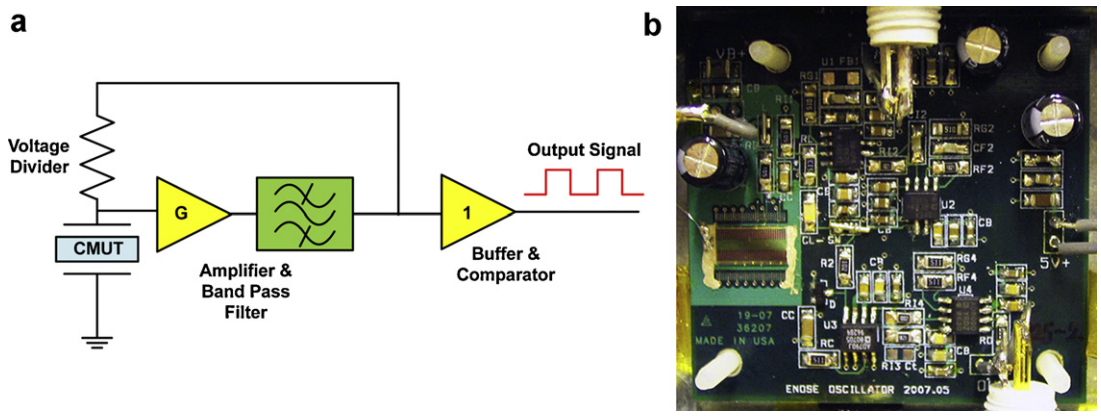

Fig. 6. (a) Schematic of the oscillator circuit including a CMUT. (b) Optical picture of a populated oscillator circuit on PCB.

not require an additional start-up circuit. The CMUT is directly mounted on a printed circuit board (PCB) without a chip-carrier and wire-bonded on the PCB to reduce parasitic capacitance.

2.5.2. Performance of the oscillator

The free running oscillation frequency of the circuit was measured using an external digital frequency counter (Model SRS620, Stanford Research System, Sunnyvale, CA) with a typical gate time of 10 ms, i.e., 100 frequency samples per a second. Frequency information is transferred to an external PC for signal processing. The time delay between the counter and the PC is less than 100 ms, which is short enough for a real-time measurement of the frequency shift due chemical absorption.

The amount of frequency shift is proportional to the amount of chemical absorption. As a result, the limit of detection of the output signal, i.e., frequency noise level, decides the limit of detection of analyte concentration in air. In order to quantify the frequency noise level, we used the Allan deviation method [24], which is a common method to measure the short-term frequency stability of timing references. The Allan deviation number, $\sigma_y(n\tau_0,M)$, for a given gate time, $n\tau_0$, is

$$\sigma_y(n\tau_0, M) = \sqrt{\frac{1}{2n^2(M-2n+1)} \sum_{j=0}^{M-2n} \left(\sum_{i=j}^{j+n-1} \bar{f}_{i+n} - \bar{f}_i \right)^2}, \quad (4)$$

where τ_0 is the gate time of the frequency measurement, M is total number of samples and $\bar{f}_i$ is the averaged frequency of n-samples. This method averages neighboring frequency samples to compute deviation at a given averaging time, $n\tau_0$, (i.e., effective gate time). In a short averaging time, the Allan deviation tends to decrease with more averaging time. However, the Allan deviation increases when the averaging time is larger than a certain value, because the drift of the resonant frequency (i.e., mid-term frequency noise) starts to dominate the frequency variation. We measured a large number of finely spaced frequency samples and computed the Allan deviation for various averaging times to find the optimal averaging time (Fig. 7). The oscillator has the lowest Allan deviation (σ_y/f) of 2.74×10^{-8} at 50 ms averaging time, which corresponds to a frequency noise level of 0.5 Hz. Based on Eq. (3), the sensor's minimum detection limit of loaded mass per unit area (Δ_{min}/A) is 1.92×10^{-11} kg/m^2 or 0.192 ag/μm^2 with 3-σ confidence levels.

2.6. Experimental setup

The volume sensitivity is measured using an in-house chemical set-up that can deliver low vapor concentrations of DMMP. The experimental setup consists of several mass flow controllers (MFC) and bubblers [11,25]. Purified air from a zero air generator (Model 76-803, Balston Parker, Haverhill, MA) was used to provide flow through two MFCs. These two MFCs separately control the flow rate of the carrier air and flow rate of the air injected into a bubbler. In the bubbler, the air flows through a liquid-phase analyte, resulting in evaporation of the analyte into the air. The air containing analyte molecules is then mixed with the carrier air. This mixture gas is transferred into a 3 cm^3 glass chamber, which encloses the polymer-coated CMUT resonator.

The typical flow rates of the bubbler air is 1–10 ml/min and the flow rate of diluted air is adjusted in 499–490 ml/min to regulate the total flow rate to 500 ml/min. The volume concentration of an analyte is calculated based on three parameters: the flow rate of the air through the bubbler, flow rate of the carrier air and the vapor pressure of each analyte, assuming the output of the bubbler is fully saturated with the analyte.

3. Results

3.1. Sensitivity and limit of detection

We chose DMMP as our main analyte and ethanol and water as reference analytes. Fig. 8 shows transient responses of the frequency to different concentrations of three different analytes. For each measurement, the analyte molecules were injected into the chamber at 60 s by flowing air through the bubbler containing DMMP. The PIB coating absorbs the analyte molecules until it reaches an equilibrium condition for the given analyte concentration. The mass of the absorbed molecules shifts the resonant

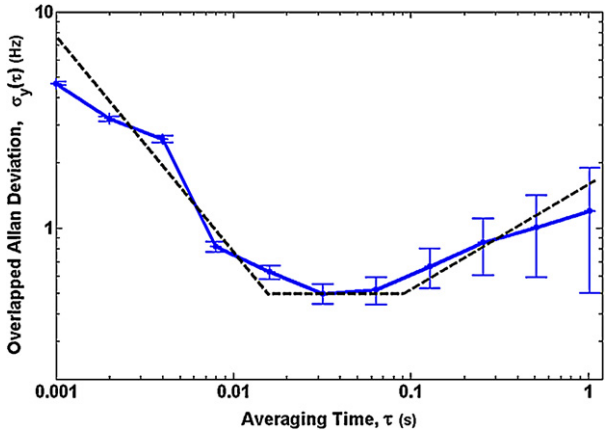

Fig. 7. Allan deviation σ_y of the oscillator circuit in Fig. 6(b).

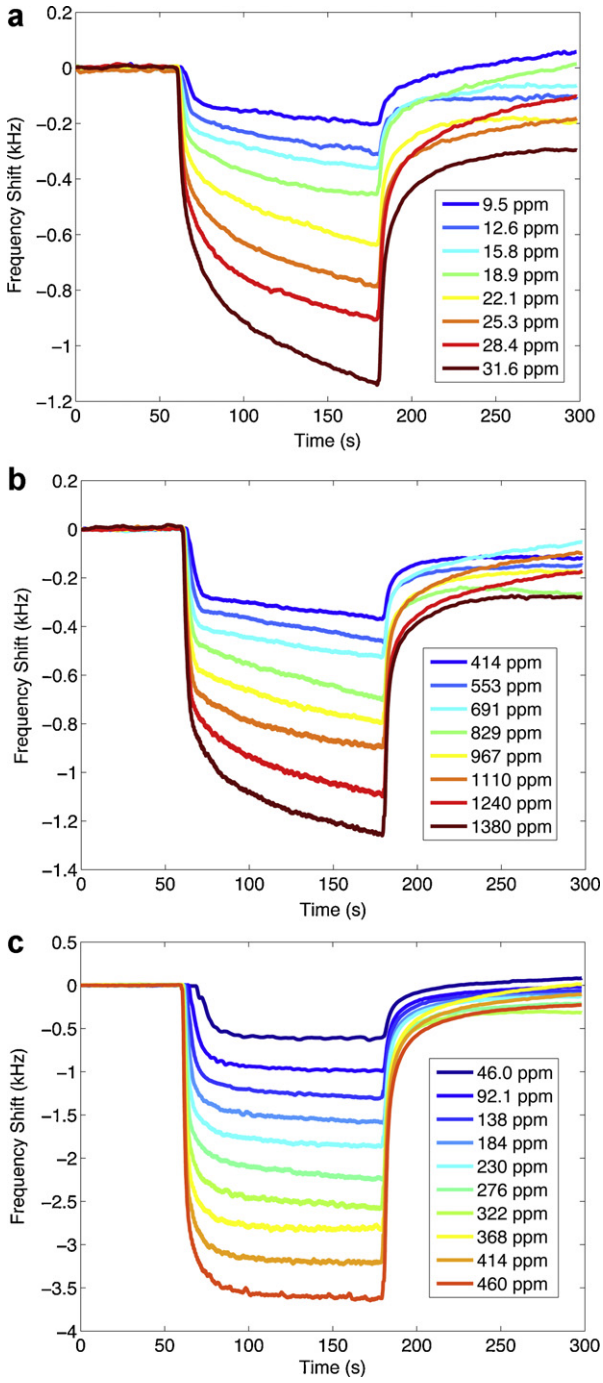

Fig. 8. Frequency response of the PIB coated CMUT chemical sensor to (a) DMMP (b) ethanol (c) water.

frequency downwards from its initial frequency of 18 MHz. This chemi-absorption process is reversible; the resonant frequency starts to recover back to the baseline when the flow through the bubbler is stopped at 180 s.

Fig. 9 demonstrates that the amount of frequency shift is proportional to different concentrations of the analytes (i.e., the amounts of the loaded molecules). The volume sensitivity is calculated based on the linear fitting between the amounts of frequency shifts with respect to various volume concentrations. The calculated volume sensitivities to DMMP, water, and ethanol are 37 ppb/Hz, 239 ppb/Hz, and 2600 ppb/Hz, respectively. The linearity in sensitivity illustrates that for the tested concentration range, the PIB coating (~50 nm) is not in the saturation region.

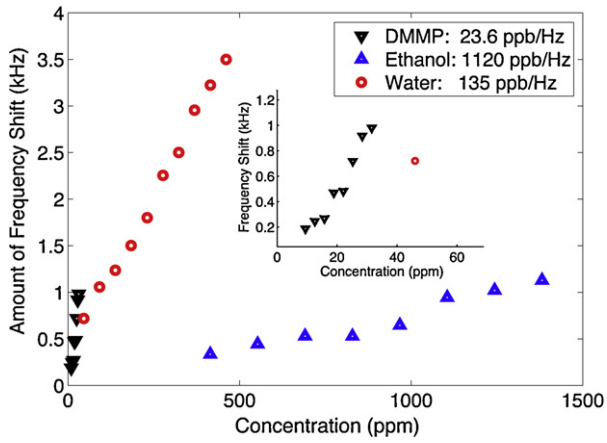

Fig. 9. Frequency shift of PIB coated CMUT in response to several analytes in different concentrations.

Based on the measured noise level of the oscillation circuit (0.5 Hz), the equivalent volume resolution of detection for DMMP is 56 ppb with 3-σ confident levels.

3.2. Analyte identification

We performed principal component analysis (PCA), a common pattern recognition algorithms used for analyte identification, to maximize the information extracted from the measurements. The transient frequency shifts for different analytes exhibit distinctive patterns (i.e., fingerprints), such as fall and rise time constants (Figs. 8 and 10) as observed in the chemical sensor based on a micro-cantilever array [26]. Five different data points between 60 s and 180 s were extracted from each curve and normalized by the maximum frequency shift (Fig. 8). These data points were used as an input dataset to the PCA [26]. The PCA of 21 experiments successfully separated three analytes (Fig. 11); the PCA plot shows a wide distribution of points for a single analyte because we use a single sensor. Accuracy of identification can be improved by using a functionalized array of sensors as we previously performed with the lower-frequency CMUT resonators [11].

3.3. Repeatability

Repeatability is another important figure of merit of a sensor system. We performed a long-term experiment to demonstrate

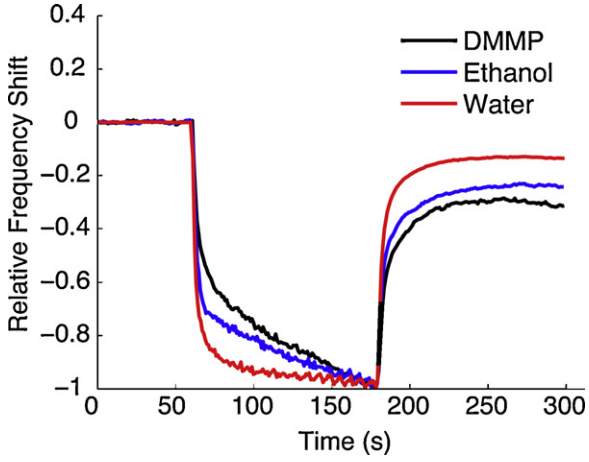

Fig. 10. Normalized frequency response of the PIB coated CMUT to three different analytes.

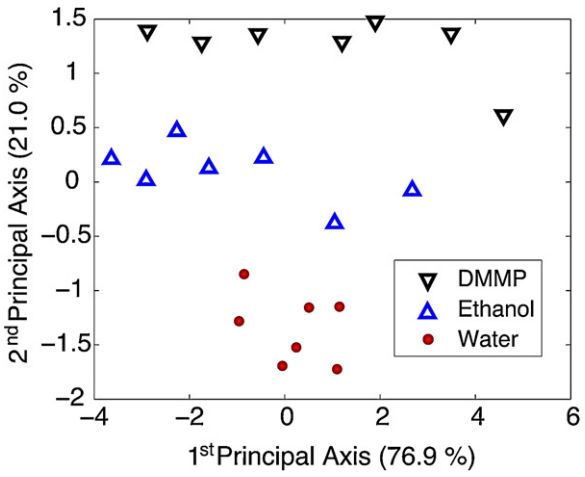

Fig. 11. PCA of three analytes from Fig. 8. Each point represents the different concentration of the analyte.

the repeatability of the sensor system, including the durability of the resonant structure and the polymer. The DMMP vapor with a concentration of 50 ppmv was injected into the glass chamber for 120 s and then the chamber was purged with purified air. This cycle was performed 200 times over a time period of 26 h (Fig. 12a). The CMUT chemical sensor successfully responded to all DMMP injections without any degradation of the output signal (Fig. 12b). The frequency shift of each pulse cycle showed that the volume sensitivity has a 3-σ variation of 4.7% over the 26 h operation, confirming negligible degradation effects from the resonator and the polymer.

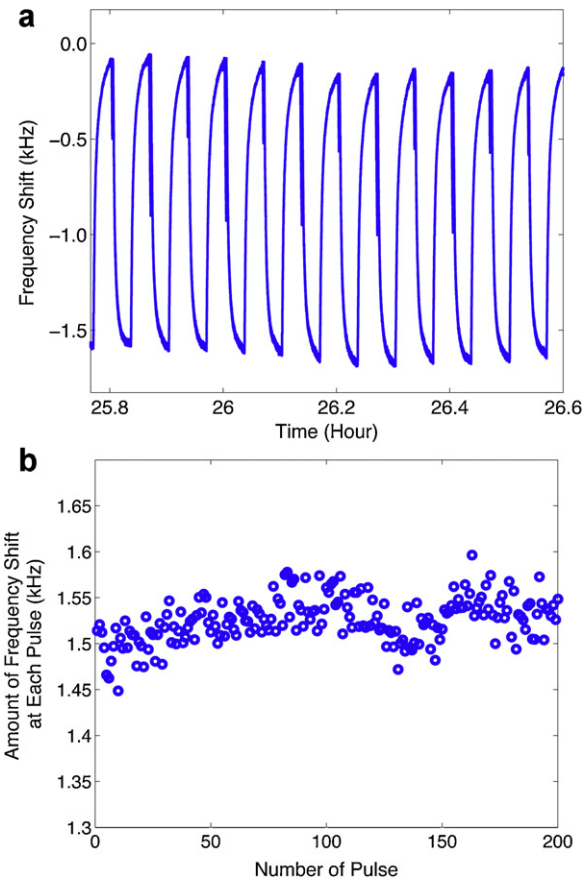

Fig. 12. (a) Frequency shift during repeatability tests. (b) Amount of frequency shift at each pulse in (a). 200 pulses correspond to 26.6 h.

The causes of the variation measured in the long-term experiment include systematic errors in the experimental setup. For example, the MFC has a limited accuracy of 1% flow rate and it has a variation of a response time in opening and closing valves.

4. Discussion

Our mass-loading sensor presented in this paper has improved in several ways from our previous work, which entailed the first demonstration of using a CMUT as a chemical sensor [11]. First, the mass sensitivity has been improved from 1 fg/Hz to 33 ag/Hz by optimizing the mechanical properties of the CMUT resonators. The device introduced in this paper is composed of a flexural plate that is less dense and thinner by factor of 1.37 and 1.70, respectively, compared to those of our previous CMUT sensor [11]. Based on (2), these modifications have improved the mass sensitivity per unit area by factor of 2.33. In addition, the higher operating frequency and the reduced size of the individual resonator in this work improved the mass sensitivity per a resonator approximately by another factor of 12. Second, despite the lower Q (140) than the Q of our previous work (250) at the parallel resonant frequency, improvements in the oscillator implementation, such as stringent ground shielding and reduction in parasitics that load the CMUT resonator, have allowed us to maintain a low noise level of 2.74×10^{-8} (Allan deviation, σ_y/f).

The CMUT still has much room for improvements as a resonant chemical sensor. The density and plate thickness can be further reduced to increase the mass sensitivity. In addition, the mass resolution can be improved by increasing the resonator Q. The limit of detection is determined by the frequency noise of the system (3), which is inversely proportional to the resonator Q. Therefore, a future resonator design must be optimized to achieve a higher Q. Moreover, the chemical sensitivity can be improved by using a more sensitive and selective functionalization material. In this paper, PIB was selected as the chemically selective layer due to its availability and known sensitivity to DMMP [20], which allowed us to achieve a limit of detection level of 56 ppb to DMMP. However, this resolution is still 3.2 times higher than IDLH of sarin (17.5 ppb). The volume sensitivity can be dramatically improved to meet the IDLH level of sarin by adapting synthesized polymers specifically developed for the nerve gases detection [27]. In addition, we coated the device with a very thin layer (50 nm) to minimize the effect of polymer coating on the device impedance. Applying a thicker layer of polymer may degrade Q of the device [28], but it can improve the volume sensitivity of the system. Therefore, the optimization of the polymer thickness is also a part of our future work.

5. Conclusion

We presented a highly sensitive chemical sensor based on the CMUT technology with theoretical mass sensitivity of 130 zg/Hz/μm^2 operating at 18.2 MHz. The inherent CMUT characteristics, such as the higher quality factor due to the vacuum cavity and the multi-resonator configuration, results in a lower frequency noise, a reliable operation, and a simple design of the oscillator circuit. In addition, the encapsulated gap allows the device to be not only fully compatible with the inkjet-dispensing method for the polymer coating, but also compatible with other general functionalization methods (e.g., spin-coating, dip-coating, and pipette-dropping). With the low noise oscillator circuit design, we achieved an equivalent volume resolution of 56 ppb to DMMP with 3-σ confident levels. This work demonstrated that a sensitive, reliable, and portable chemical sensing system could be achieved using an array of CMUT resonators. In addition, the CMUT resonator

with a higher resonant frequency and a synthesized polymer can achieve highly improved LOD in the order of ppt range.

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