Capacitive Micromachined Ultrasonic Transducer as a Chemical Sensor

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***Abstract* — We present a resonant chemical sensor based on a capacitive micromachined ultrasonic transducer (CMUT) technology. Depending on the frequency of the devices (18 to 32 MHz), the mass sensitivity per unit area ranges from 73 to 130 zg/Hz/μm^2. We functionalized the 18-MHz device with polyisobutylene (PIB) to detect dimethyl methylphosphonate (DMMP), a common simulant for the sarin nerve agent. Even with only a 50-nm thick coating layer, our sensor has a high volume sensitivity of 37 ppbv/Hz to DMMP in air. Taking advantage of multiple CMUT cells (100 to 2240), all resonating in parallel, the sensor achieves an equivalent volume resolution of 21 ppbv (parts per 10^9 by volume) to DMMP. In addition, 200 test cycles with DMMP applied over 26 hours revealed a zero false alarm rate and a 4.7% (3-σ) variation of volume sensitivity to DMMP. By using principal component analysis (PCA), we successfully classified all analytes in 21 experiments, and we present the results of pattern recognition. This work demonstrates that CMUT has a great potential for the sensitive, reliable, and yet portable chemical sensing systems.**

I. Introduction

There are many applications which require a reliable chemical detection of volatile compounds. Examples are the detection of explosive materials for homeland security and military applications, the detection of harmful industrial solvents, or simple household applications, such as the detection of spoiled food in a refrigerator. Existing chemical detection systems are often unsuitable for these applications, because of size, portability, and power consumption limitations. A reliable miniaturized chemical sensor will help to address all of these issues.

The microelectromechanical system (MEMS) technology is one of the most promising solutions to implement portable, sensitive, and reliable chemical sensors. Based on the scaling effect, MEMS devices can detect small changes in physical properties, such as permittivity [1], resistivity [2] and loaded mass [3-6].

Resonant chemical sensors, based on the mass loading effect, are widely researched in the MEMS community due to several advantages such as sensitivity and selectivity. By reducing the effective mass of the resonant structure, the mass sensitivity of these sensors has been considerably improved in the last couple of years. In addition, the resonant chemical sensors can be functionalized with a wide range of chemically sensitive layers, such as self-assembled monolayers (SAMs) and polymers. Recently, several types of resonant chemical sensors have been demonstrated, e.g. micro/nano cantilevers [3], FBARs [4], and SAW resonators [5]. While these devices have different resonant modes, they have one common property: the resonator itself consists of only one unit, i.e. a single resonator based oscillator system.

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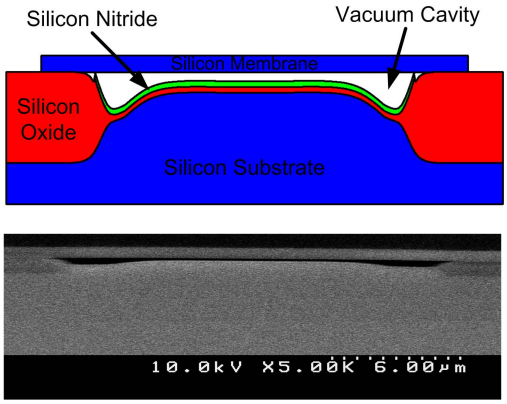

Figure 1. Schematic cross-section of a CMUT cell (top), and the corresponding SEM image (bottom).

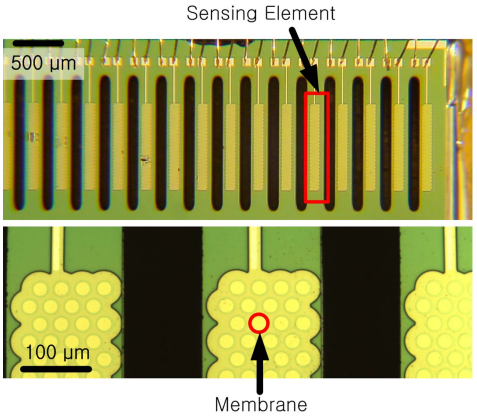

Figure 2. Photograph of the CMUT array (top) and multi-membrane elements (bottom).

Compared to these single resonator systems, a CMUT is made of 100s to 1000s of resonators, all connected in parallel. Each resonator is a circular shaped membrane, normally resonating at the first flexural mode. As a multi-resonator system, the CMUT has various advantages such as a good reliability and a lower noise, and, thus, a higher sensitivity performance. In previous work, we used a 6-MHz CMUT with a theoretical limit of mass detection of 10^{-15} g per membrane [6]. Motivated by high sensitivity and low limit of detection, we fabricated a higher frequency CMUT with an improved fabrication process [7]. Based on this new device we implemented a chemical sensor system to detect dimethyl methylphosphonate (DMMP), a common simulant for the chemical nerve agent sarin (GB).

II. Capacitive Micromachined Ultrasonic Transducer

A. *CMUT Structure and Operational Principle.*

The basic structure of a single cell of a CMUT element is shown in Fig. 1. The circular membranes are made of single crystal silicon. These membranes have radii ranging from 6 to 9 µm and a thickness of 0.5 µm. The membranes are permanently attached to a thermally grown silicon dioxide structure, by direct wafer bonding technique. The membrane is actuated by electrostatic force, i.e. by an applied voltage between the highly conductive silicon membrane and the silicon substrate. The resonant frequency is determined by measuring the electrical input impedance of the device. A single device with the size of 10 mm by 5 mm consists of 32 to 64 sensing elements. Each element is a multi-resonator structure, composed of 100 to 2240 membranes (Fig. 2). In order to remove crosstalk between each resonating element, through-wafer isolation trenches are etched between the elements.

B. *Theoretical Results*

The effective resonant frequency of each CMUT element is an average value of individual resonant frequencies of the membranes. Thus, for the estimation of the theoretical mass sensitivity of the sensor, it is enough to consider only one single membrane. If modeled as a mass-spring system, the resonant frequency of a single membrane is proportional to the square-root of the stiffness of the membrane and inversely proportional to the square-root of the mass of the membrane. This allows the theoretical derivation of the frequency shift Δf due to the loaded mass change Δm per unit area A from one membrane as

$$\frac{\Delta m}{\Delta f \cdot A} = -2\frac{m}{f \cdot A} = -2\frac{\rho \cdot t}{f}, \qquad (1)$$

where f is the resonant frequency, m is the mass of the membrane, ρ is the density of the membrane, and t is the thickness of the membrane. Based on the dimensions of the fabricated devices, mass sensitivities per unit area of the 18-MHz, and 32-MHz devices are 130 and 73 zg/Hz/µm^2, respectively.

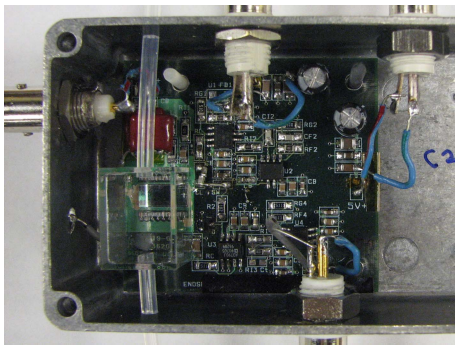

Figure 3. Photograph of the oscillator circuit. The CMUT array is enclosed in a glass chamber.

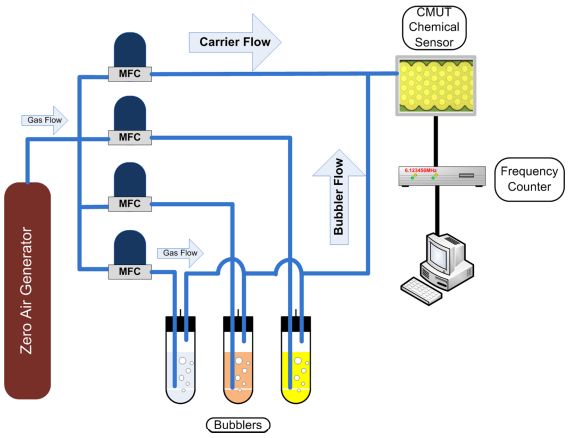

Figure 4. Schematic of the experimental setup

C. *Advantages of CMUT as a Resonant Chamical Sensor*

Flexural mode resonators used in chemical sensing applications dissipate energy because of the viscous damping introduced by the surrounding medium. Cantilevers used in chemical sensor systems, for example, are surrounded by air on all sides. Thus, the quality factor (Q) of a cantilever in air is limited, resulting in higher oscillator noise and thus worse limit of detection (LOD) level. A CMUT, however, has a vacuum cavity between the membrane and the bottom electrode (silicon substrate). Thus, energy is only dissipated to the medium on top of the membrane, resulting in a higher Q. The measured Q of the 18-MHz and 32-MHz devices ranges from 140 to 400 in air.

As a multi-resonator configuration, CMUTs allow for more a reliable and flexible sensor system. As 100s to 1000s of membranes oscillate in parallel, failure of a few membranes does not cause the whole device to fail, resulting in a low false alarm rate. In addition, the multi-resonator structure allows controlling the motional

impedance level, which makes the design of oscillator circuits easier.

In addition, CMUT technology has matured over the last decade as a result of the extensive research conducted on different applications such as underwater and diagnostic medical imaging [8] and airborne ultrasound transducers [9]. Using the existing technology, we fabricated CMUTs for chemical sensing with good dimension control and yield.

III. Functionalization

For chemical sensing in air, we coated a single element with a sorbent film to increase the selectivity and the sensitivity to DMMP. Using the inkjet printing technique, an 18-MHz element was functionalized [10]. Diluted droplets of polyisobutylene (PIB), each with a volume of 0.2 nl, were ejected on top of a device using an inkjet dispensing system (model MD-P-801, Microdrop, Norderstedt, Germany). After the solvent dried out, a 50-nm thick polymer film remained on top of the membrane. This thin coating did not change the resonant frequency and the quality factor significantly. Thus, there is more room for improvement in the volume sensitivity by optimizing the chemical coating thickness.

IV. Experimental Setup and Procedure

A. Oscillator Configuration

The frequency shift due to mass loading was detected by recording the frequency of a free-running oscillator circuit with a functionalized CMUT used as the frequency selective component in its feedback loop. For this work, we implemented a Colpitts oscillator. The functionalized CMUT is glued on and wire-bonded to a PCB (Fig. 3), which is enclosed in a metal box for RF shielding. The oscillation frequency is then measured by an external frequency counter (Model SR620, Stanford Research Systems, Sunnyvale, CA) in real time. With an optimal sampling time of 80 ms, we achieved a noise level of 0.6 Hz at 18.2 MHz oscillation frequency.

B. Chemical Experimental Setup

A schematic of the chemical experimental setup is shown in Fig. 4. A bubbler is used to evaporate a liquid-phase analyte into air. Purified air is generated by a zero air generator (Model 76-803, Balston Parker, Haverhill, MA) and separated into two flows; a carrier flow and a bubbler flow. When a small fraction of the purified air is injected into the bubbler, analyte molecules evaporate into the bubbler flow with a certain vapor concentration. These analyte molecules are diluted when mixed with the carrier flow. By adjusting the flow ratio between the carrier flow and the bubbler flow, vapor concentrations of the mixture can be controlled. In this work, we used a bubbler flow with a rate ranging from 1 to 10 ml/min with a constant carrier flow rate of 500 ml/min.

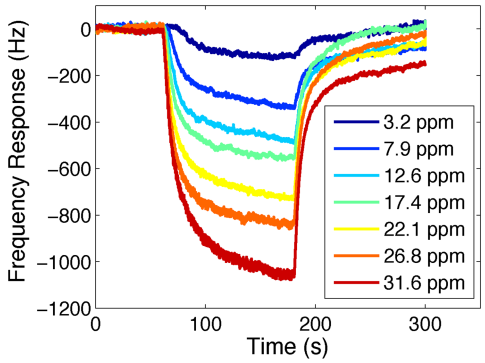

Figure 5. Transient response of the resonant frequency of the PIB-coated 18-MHz device to DMMP. DMMP is injected during the period between the 60-s point and the 180-s point.

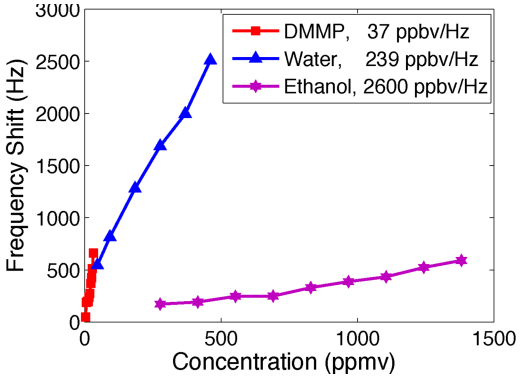

Figure 6. Frequency shift of the PIB-coated 18-MHz device in response to three analytes vs. the analyte concentration.

V. Experimental Results and Discussion

A. DMMP detection

The volume sensitivity of the CMUT chemical sensor is measured with various volume concentrations of three different analytes: water, ethanol and DMMP. Fig. 5 shows transient responses of frequency in response to different concentrations of DMMP vapor. At the 60-s point, the DMMP vapor is injected into the 3-cm^3 glass chamber, and then the coated PIB film absorbs DMMP molecules until it reaches an equilibrium condition. This chemi-absorption process is reversible and thus the original resonant frequency is recovered after the 180-s point, when the bubbler flow stops. Frequency shift as a function of the vapor concentration for different analytes is shown in Fig 6. The volume sensitivity of the sensor is inversely proportional to the slope. The calculated volume sensitivity of the 18-MHz device to DMMP is 37 ppbv/Hz. Based on the measured noise level of the oscillation circuit (0.6 Hz), the equivalent volume resolution is 21 ppbv.

B. Analyte Identification

In addition to the difference in the sensitivity, different analytes also exhibit different response times. Fig. 7 shows the normalized transient responses for the three analytes used in our experiments. This time constant information

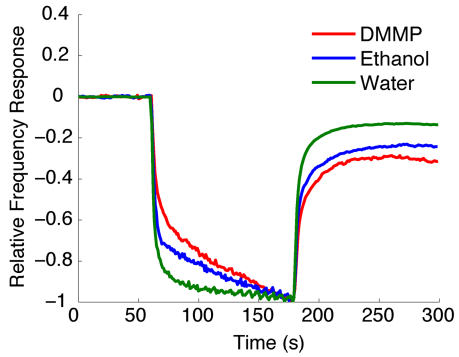

Figure 7. Relative frequency response of a PIB coated, 18-MHz element for three different analytes.

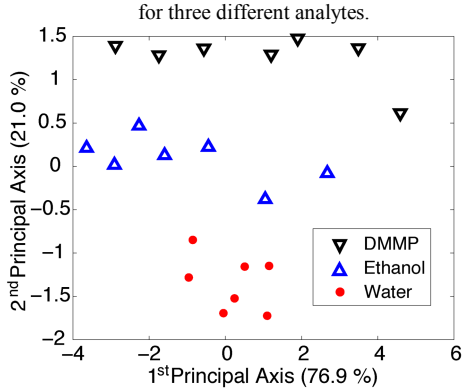

Figure 8. Principal component analysis of chemical experiments with a single element.

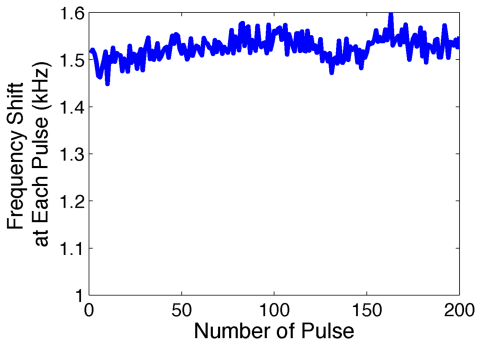

Figure 9. Repeatability test of the PIB-coated device. At each pulse cycle, DMMP vapor of 50 ppmv is injected for 120 s.

can be used for the analyte identification. Principal component analysis (PCA) is a common tool used for analyte classification in chemical sensor systems [11]. We used PCA on data we collected from 21 experiments and successfully separated three different analytes (Fig. 8).

C. *Repeatability*

In order to demonstrate the reliability of the sensor, we performed a long-term experiment by applying repeated pulses of DMMP. The DMMP vapor with a concentration of 50 ppmv was injected into the glass chamber for 120 s and then purged with air. During the 26-hour operation, 200 pulses were applied and the frequency shift for each pulse was measured. The CMUT chemical sensor successfully detected all chemical injections with no false alarms. In addition, during this experiment the volume sensitivity had a 3-σ variation of 4.7% as shown in Fig. 9.

VI. Conclusion

We presented a highly sensitive chemical sensor based on the CMUT technology with theoretical mass sensitivities of 130 zg/Hz/μm² and 73 zg/Hz/μm² for the devices operating at 18 MHz and 32 MHz, respectively. The multi-resonator configuration enables reliable operation and makes the design of the oscillator circuit easier. With the low-noise oscillator circuit design, we achieved an equivalent volume resolution of 21 ppbv to DMMP. Thus, this work demonstrates that CMUT technology has a great potential for the implementation of sensitive, reliable, and yet portable chemical sensing systems.

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