Capacitive micromachined ultrasonic transducers for chemical detection in nitrogen

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(Received 11 May 2007; accepted 5 August 2007; published online 28 August 2007)

The authors present the prototype of a chemical sensor using a capacitive micromachined ultrasonic transducer array. Each element in the array consists of a large number of resonating membranes connected in parallel. A five-channel oscillator circuit operates at the resonant frequency around 6 MHz in this prototype. The surface of the elements in the array is coated by polymers such as polyallylamine hydrochloride, polyethylene glycol, and polyvinyl alcohol to detect different chemicals. By measuring shift in oscillation frequencies due to the mass-loading effect, analytes, e.g., water and isopropanol, with concentrations around 20 ppbv (parts per 10^9 by volume) range can be detected. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2776348]

Chemical and biological sensors can be implemented by combining a mechanically resonant device with a thin layer of chemically sensitive material on which molecules of targeted chemicals interact. The adsorbed or bound molecules alter the mass of the resonant device, resulting in a resonant frequency shift. High sensitivity, specificity to targeted molecules, robustness, and fast response time are some of the important figures of merit of a chemical/biological sensor. Various mass sensing systems have been developed based on devices such as micromachined cantilevers,[1] thin film bulk acoustic wave resonators,[2] surface acoustic wave resonators,[3] and quartz crystal microbalances.[4] The sensor responses of these devices are often evaluated by functionalization such as polymer coating.[1,3,4]

In this study, capacitive micromachined ultrasonic transducers (cMUTs), originally developed for conventional medical and underwater ultrasonic imaging,[5] are used as a mass sensing device. A cMUT typically consists of a large number of vacuum-backed resonating membranes connected in parallel. CMUTs have inherent performance and manufacturing advantages that make them attractive devices for use in mass sensing applications compared to cantilevers and piezoelectric resonators. Small membrane mass and high resonant frequencies in the range of tens of megahertz combined with quality factors in the range of several hundreds provide excellent sensitivity; arrays with multiple channels can be easily fabricated allowing the implementation of systems that can detect a variety of chemical agents in parallel; the multimembrane, multichannel arrangement improves the reliability, especially for applications with minimum tolerance for false alarms; robust device structure allows reliable operation in harsh environments. In this letter, we present the results from a prototype mass-sensing system employing a cMUT array.

Resonant characteristics of a cMUT are mainly determined by the mechanical properties and dimensions of the resonating membrane. For a circular membrane, the resonant frequency is estimated by

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

where t is the thickness, a is the radius, E is the Young modulus, v is the Poisson ratio, and m is the mass of the membrane.[6] The sensitivity is defined by the relative frequency shift due to mass loading, which is commonly defined as

$$\frac{\Delta f}{f_0} = -\frac{1}{2}\frac{\Delta m}{m}. \tag{2}$$

The membrane structure of the cMUT used in the described mass-sensing system is illustrated in Fig. 1. This structure is fabricated using a surface micromachining process on a silicon substrate.[7] Each element in the array is comprised of 750 circular silicon nitride membranes with a radius of 18 μm and a thickness of 0.85 μm. There is a vacuum gap between the two electrodes; electric field strengths in the gap between the two electrodes are on the order of 10^9 V/m.

DC voltage is applied between the two electrodes; under the applied bias voltage, the membrane is attracted toward the bottom electrode. Efficient electromechanical coupling is achieved as a result of the strong electric field in the gap.[8]

An electrical equivalent circuit model is used as the basis for the design and analysis of the cMUT (Ref. 9) [Fig. 2(a)]. In its simplified form, the equivalent circuit consists of the electrical capacitance of the structure (C_0) in parallel with a series combination of an inductor representing the

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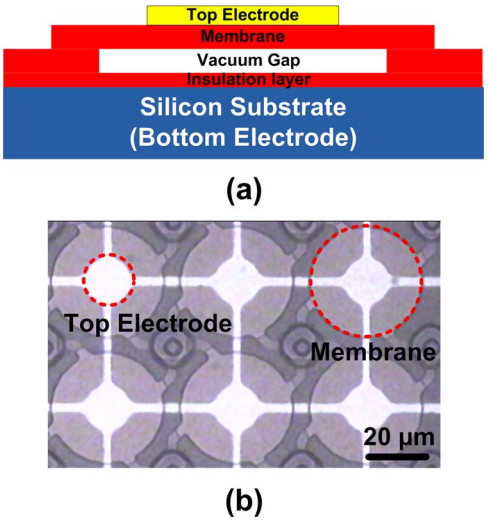

FIG. 1. (Color online) (a) Schematic of a single membrane of a cMUT device. (b) Optical image of a portion of a cMUT array element.

mass of the membrane (L_x), a capacitor representing the stiffness of the membrane (C_x), and a resistor modeling the motional resistance including the radiation into the medium (R_x). A good fit is obtained between the measured and modeled parameters [Fig. 2(b)].

The design of the oscillator circuit using the cMUT as a resonator is illustrated in Fig. 3. In this circuit, the cMUT is used as a frequency selective device in the feedback loop of the oscillator. Furthermore, a bandpass filter in the loop ensures the oscillation frequency to be confined around the resonant frequency of the cMUT, 6 MHz for the prototype presented here.

An important goal for the design of multichannel systems is to minimize the interaction between different channels, especially the adjacent ones. The electrical and mechanical cross couplings between adjacent resonators in the array increase the frequency noise of the system. To minimize the mechanical cross coupling through the silicon substrate, 120 μm wide through wafer isolation trenches are formed between five resonators used in this prototype system. Electrical cross coupling is also minimized by a careful layout of the signal traces and by ground shielding. Furthermore, the resonant frequencies of different channels are set to slightly different values by adjusting the dc bias voltages, so that the frequency locking between adjacent resonators

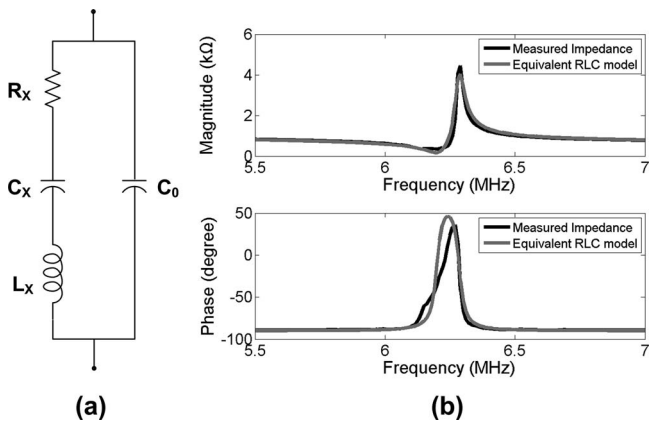

FIG. 2. (a) Equivalent *RLC* model of a cMUT. (b) Magnitude and phase of the input impedance.

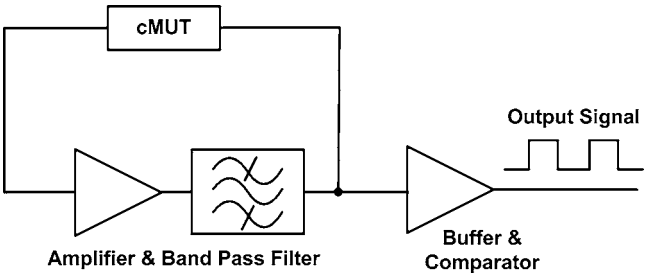

FIG. 3. Simplified block diagram of the oscillator circuit.

can be prevented. As a result of the use of these frequency separation and trench isolation techniques, cross coupling and thus the frequency noise is reduced. When five channels are simultaneously oscillating, a low noise level of 0.4, 1.6, and 13 Hz is achieved for a gate time of 1, 0.1, and 0.01 s, respectively.

To functionalize the five-channel cMUT array, three channels are coated with three polymers, polyallylamine hydrochloride (PAAM), polyethylene glycol (PEG), and polyvinyl alcohol (PVA), while two channels are left uncoated to be used as reference channels. 0.2 nl droplets of diluted polymers (1 mg/ml PAAM or PEG in nanopure water and 1 mg/ml PVA in DMSO) are ejected on the UV/ozone-cleaned cMUT array using an inkjet dispensing system (model MD-P-801, Microdrop, Norderstedt, Germany).[10] As the ejected droplets dry out on the surface of cMUT membranes, a uniform thin polymer film is formed. When the analyte diffuses into the polymer layer, the increased mass of the polymer coating shifts the resonant frequency of the cMUT downward. When the chamber is purged with nitrogen, analyte molecules diffuse out of the polymer coating and then the resonant frequency is recovered.[3]

To test the functionality and sensitivity of the system, a series of experiments is performed by detecting widely used solvents such as isopropanol, acetone, ethanol, and water as an analyte. To reduce the volume concentration of the analytes, a small amount of nitrogen gas is bubbled through the analyte, so that the analyte evaporates into the nitrogen gas. This mixture is then combined with the nitrogen carrier flowing at a rate of 500 ml/min. The nitrogen gas carrying the analyte is then delivered to a small chamber with a volume of 27 cm^3 that contains the functionalized cMUT array (Fig. 4). The frequency shifts of the five oscillators are measured

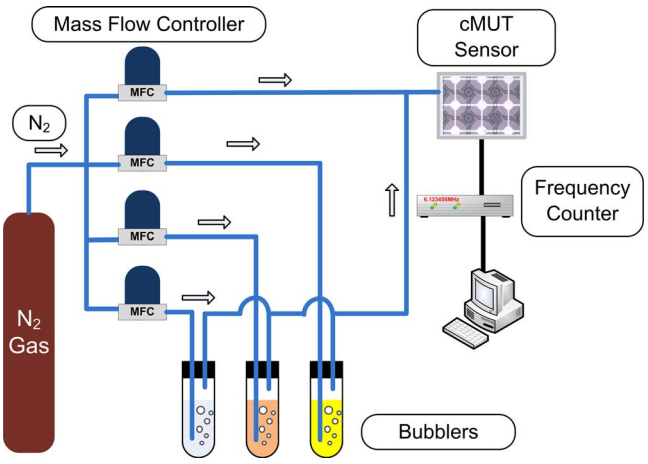

FIG. 4. (Color online) Schematic of the experimental setup.

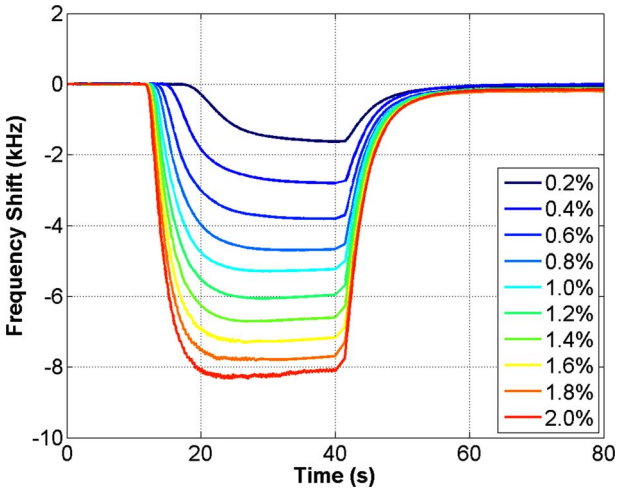

FIG. 5. (Color online) Frequency shift of PAAM coated channel due to the vapor of isopropanol. Analytic vapor starts flowing at the point of 10 s and stops at 40 s.

simultaneously using five frequency counters (model SR620, Stanford Research Systems, Sunnyvale, CA).

Figure 5 shows the frequency shift of the channel coated with PAAM due to the isopropanol vapor. Assuming that nitrogen through the bubbler is fully saturated with the analyte, volume concentration of the analyte is calculated based on the vapor pressure of the analyte. The results show that the system has a fast response time. A time constant of 4.8 s (falling) and 7.3 s (rising) is measured at 2% vapor concentration. Furthermore, the functionalized channels have different sensitivities to various chemicals as demonstrated in Fig. 6.

Although the frequency shift due to the mass loading is not a linear function of the concentration of the analytes, a linear fit is used to compute the approximate sensitivity of each channel (Fig. 6). The sensitivity of functionalized array can be calculated as

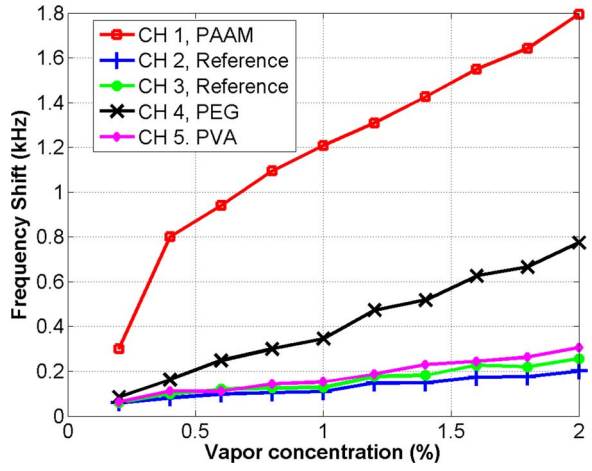

FIG. 6. (Color online) Frequency shift of several channels coated with different polymers in the presence of acetone vapor.

TABLE I. Sensitivity of functionalized channels to several analytes. All values are in the unit of ppb/Hz.

	Water	Isopropanol	Acetone	Methanol
PAAM	41.6	101	3508	2150
PEG	410	1060	6420	2020
PVA	399	988	18800	5450

$$S = \frac{\Delta C_V P_0}{\Delta f P_{\text{atm}}}, \tag{3}$$

where S is the sensitivity (ppm/Hz or ppb (parts per 10^9)/Hz, volume concentration), ΔC_V is the analyte vapor concentration, P_0 is equilibrium vapor pressure of the analyte, Δf is the frequency shift, and P_{atm} is the atmospheric pressure. As summarized in Table I, relative sensitivities of the functionalized channels to various analytes are different, demonstrating that identification of a target chemical in the presence of an interfering chemical is possible. It is worth noting that the theoretical limit of detection based on the noise level of 0.4 Hz is 16.6 ppb for water using PAAM, which proves the excellent sensitivity of the sensor. Though not independently demonstrated, the calculated limit of the detection of mass loading is on the order of 10^{-15} g.

In conclusion, the functionality of cMUTs as resonating devices for use in mass sensing systems is demonstrated. In specific, the ability to diversely functionalize parallel sensor channels, fast response time, and high sensitivity are achieved in a compact design. Even though commonly available polymers are used, the prototype system is capable of detecting several analytes with concentrations in the ppb range.

This work was funded by DARPA, Microsystems Technology Office under Grant No. N66001-06-1-2030.

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