Solvent Detection and Water Monitoring With a Macroporous Silicon Field-Effect Sensor

Jeffrey P. Clarkson, Philippe M. Fauchet, Fellow, IEEE, Vimalan Rajalingam, and Karl D. Hirschman

Abstract—Integration of electrical and fluidic systems for the design and fabrication of a system-on-chip (SOC) capable of sensing various liquid phase solvents is reported. A monolithic integration strategy makes use of macroporous silicon (MPS) as a gateway to interface the electrical and fluidic domains. In this application, the MPS material, acting as a sensing membrane, is used in a flow-through structure to transport an analyte from fluidic channels on one side of the chip to sensing electrodes on the other. A fluid–oxide–semiconductor interface results in the modulation of a space charge region in the semiconductor where real-time measurements are used to detect and distinguish between the presences of various solvents. The fluidic system has delivered sample volumes as small as 2 μL. Selected test solvents (i.e. acetone, ethanol, isopropyl alcohol, methanol, and toluene) have generated a measured change in capacitance up to 11%. A practical application of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations of this sensor was demonstrated by monitoring various cations.

Index Terms—Chemical sensing, field-effect sensor, flow-through, fluidics, macroporous silicon, membrane, porous silicon, solvent detection.

I. INTRODUCTION

SEVERAL types of chemical sensors have been developed, each with their own specific advantages and disadvantages with respect to sensitivity, selectivity, power consumption, size, cost, and application. Chemi-resistors and chemFETs are among the available solid-state devices that have advantages over other classes (e.g., optical) in size and portability, but often have issues related to selectivity and sensitivity [1]. This is, in large part, a result of the limited surface area available for sample interaction in the gate region of the device.

One way to maximize the amount of surface area available for sample interaction is to make use of porous silicon (PS) [2], [3]. A number of applications involving porous silicon in chemical and biological sensing have been reported [4]–[10]. Porous silicon can take various forms including microporous (pore with ≤ 2 nm), mesoporous (pore width 2–50 nm), and macroporous (pore with > 50 nm) [2]. In this paper we use macroporous silicon (MPS) with pore diameters between 1–2 μm and a center-to-center spacing of ~ 2.5 μm. Porous silicon of this form was chosen because it does not impede analyte flow during sample delivery. The surface area of a MPS sensing membrane (100 μm thick and a pore diameter of 1 μm) increases by approximately 130× compared with an equivalent planar chemFET sensing region. This paper reports on the use of a new device architecture, which utilizes an MPS flow-through sensing membrane and an integrated microfluidic system for detection and discrimination of liquid phase solvents.

II. EXPERIMENTAL

A. Device Design

The sensor design consists of an MPS region connected to a KOH etched fluidic channel as seen in Fig. 1(a) and (b). The KOH etched fluidic channels are monolithically integrated with the sensing membrane causing the analyte delivery sites and fluidic channels to be self-aligned. The frontside MPS region serves as the sensing membrane for solvent detection. When a solvent is delivered into this region, it behaves similar to well-understood electrolyte/insulator/semiconductor (EIS) sensors where localized field effects modulate a semiconductor space charge region [11]. Electrodes are placed on non-flow-through portions of the MPS, which run adjacent to the flow-through sensing membrane region. This configuration allows for electrical connection directly to the MPS membrane, while minimizing the risk of a short-circuit pathway between the analyte and sensing electrodes.

Complex sensing operation of multiple solvents can take place with an arrayed sensor design. This allows for faster solvent screening as more than one measurement could be taken simultaneously. Fig. 2(a) and (b) show the frontside and backside views of four linearly aligned electrode pairs placed along a MPS flow-through membrane as seen in (c). Four individual backside KOH fluidic channels define the arrayed locations where solvent analytes are delivered.

B. Device Fabrication

MPS sensor devices were fabricated on 4-in (100) oriented boron-doped p-type silicon wafers within a resistivity range ρ ~
The MPS layer was formed by electrochemical lining throughout the pores. It m-thick aluminum lining of approximately 50 nm provided the greatest sensitivity and are used for the work presented herein. Contact cuts through the passivation oxide were patterned and etched, and 2-μm-thick aluminum electrodes were deposited via dc sputtering and subsequently patterned. This design allows the sensor contacts, and potentially integrated microelectronics, to be isolated from the backside fluidics. The placement of the electrical and fluidic systems on separate sides of the chip ultimately eases packaging concerns.

C. Electrical Characterization

A computer was networked with a HP 4275A multifrequency LCR meter and LabVIEW software was used to collect real-time sensing data. All measurements taken in this work were completed in a parallel capacitive mode with an ac signal of 10 kHz and an oscillation voltage amplitude of 60 mV. This waveform was observed to successfully detect biological samples in previous related research [9]. Ambient conditions including temperature, humidity, and light were controlled to ensure any generated signal was insignificant compared to the sensors response to a test solvent. Various solvents such as acetone, ethanol, isopropyl alcohol (IPA), methanol, and toluene were selected for testing in this work. These solvents were chosen because they are readily available, pose minor safety concerns, and quickly evaporate.

Both conductive epoxy and probe contacts were used to establish wire connections to the electrodes of the sensing device and resulted in a similar sensor response. Sensors were connected to the LCR meter with the backside fluidic channel facing up. Collection of real-time capacitance across the sensing membrane began and a pipette was used to dispense approximately 33 μl of solvent into the backside channel. The solvent immediately filled the channel and an instantaneous increase in capacitance was observed. Data collection continued until the solvent evaporated out of the sensing membrane and the measured capacitance returned to a baseline value.

III. RESULTS AND DISCUSSION

Successive exposures to liquid phase solvents were conducted to investigate the long-term behavior of the device. Separate sensors were exposed to acetone and IPA 100 times over the course of nine days. Fig. 3 shows ten repeated exposures to acetone taken on the ninth day. The graph contains ten spikes in capacitance, each representing the introduction of solvent into the backside channel. The solvent immediately filled the channel and an instantaneous increase in capacitance was observed. Data collection continued until the solvent evaporated out of the sensing membrane and the measured capacitance returned to a baseline value.
Fig. 3. Measured capacitive response to successive deliveries of acetone to the sensor. Each peak represents one delivery for a total of ten deliveries.

Fig. 4. Different measured capacitive signals for different sample sizes of acetone. The large and small peaks result from delivery of 10- and 4-μl sample volumes, respectively.

Fig. 5. Successive ~ 33-μl deliveries of IPA to a sensor. As samples are delivered to the device, a change in baseline capacitance occurs.

to which the sensor returns is slightly different. For the case of acetone, the baseline capacitance typically increases over successive exposures. The most dramatic shifts in baseline capacitance are seen with IPA. Fig. 5 shows real-time capacitance measurements taken during ten successive IPA deliveries. Baseline shifts in chemical sensors have been routinely observed [13]. The variation in baseline capacitance for this type of sensor is probably due to modification of the oxide surface and complex interaction kinetics of subsequent solvent deliveries. In addition, the lack of a well-defined analyte reference potential may also contribute to this baseline shift. While this device structure ensures analyte/semiconductor electrical isolation and two-terminal testing simplicity, a drifting baseline requires data normalization for signal comparison.

Fig. 6 shows the $C-V$ characteristic of a large-area test structure, which offers a tenfold increase in the capacitance of an individual sensor. This dual-sweep characteristic was obtained using the frontside electrode contacts to MPS as reference ground, and a saline solution as the working gate electrode. Aside from the peculiar structure in accumulation mode, the characteristic represents a typical MOS capacitor in accumulation, depletion (flatband), and inversion modes of
While this is not the standard electrode configuration for sensing, this demonstration of charge modulation is qualitatively consistent with the proposed mechanism of sensor operation. The measured increase in the sensor capacitance upon the infiltration of solvents is explained by the semiconductor charge distribution initially near flatband (without solvent), shifting toward accumulation mode (with solvent).

Table I shows average and standard deviation values for IPA and similar tests conducted with acetone, ethanol, and methanol. Although one sensor is capable of detecting all the solvents listed in Table I, each solvent was detected with a separate device.

It is important to note the MPS depth across an Si substrate varies slightly and this can lead to minor variations in the size of the sensing membrane of each device. This variation can affect the average capacitive of a particular solvent measured in one device to the next.

The next study investigated the sensor’s ability to discriminate between different solvents. Fig. 7 shows acetone, ethanol, IPA, methanol, and toluene detected by the same sensor. This test was conducted by placing a 33-μl sample into the backside channel and allowing it to completely evaporate before the next sample was delivered. From left to right, the four obvious peaks are acetone, IPA, ethanol, and methanol with a final less obvious hump indicating toluene. This test demonstrates that a single device can discriminate between these five solvents. Toluene was tested last because it was found that it permanently desensitized the sensors and rendered them useless in most cases.

It is believed that this degradation is caused by a permanent modification of the oxide liner within the MPS where subsequent interactions between the fluid and semiconductor are...
greatly hindered. When acetone was delivered to the sensor after exposure to toluene, a change in capacitance was not observed. This is an indication that capacitive measurements are not detecting explicitly the presence of a liquid in the membrane, but rather the modulation of the space charge from a given liquid interfaced with the semiconductor.

The changes in capacitance for acetone, ethanol, IPA, and methanol are 0.300, 0.250, 0.225, and 0.305 nF, respectively. These capacitance values are not identical with those of Table I; as mentioned before, this is a result of differences in the sensing membrane size. It is important to note that the largest peak experienced in each sensor was created by methanol. In addition, the rank of signal amplitude from largest to smallest (from methanol, to acetone, ethanol, and IPA) is consistent between sensors with different size membranes.

By investigating the physical properties of the various solvents, information pertaining to the characteristic capacitive response in the sensor can be found. Table I displays important physical properties of each solvent [14]. The duration of the capacitive response depends on the vapor pressure of the solvent as shown in Fig. 8. A more convenient way to show this is seen in Fig. 9, where the indirect linear relationship between the duration of signal and the vapor pressure of the tested solvent is obtained. Acetone has the highest vapor pressure of 233 torr and, as expected, exhibits the shortest signal duration of approximately 30 s. This strongly suggests that our sensor can be used to quantify the vapor pressure of various solvents.

Investigation of the signal response as a function of dielectric constant was conducted by exposing a sensor to liquids seen in Table I. Based on the capacitive response of the sensor to acetone, isopropanol, ethanol, methanol, and toluene, one might conclude that the capacitive change is directly related to the dielectric constant of the analyte. However, when exposed to water, a liquid with a dielectric constant much higher than the test solvents, the average change in capacitance is the smallest at 0.007 nF. If the capacitive response was directly related to dielectric constant one would expect the signal response from water to cause the largest capacitive change. Based on this observation, the dielectric constant appears to have no direct correlation to the signal strength. This further reinforces the argument that the capacitive response is a result of modulation of the space charge region in the semiconductor and not from the addition of a material with a different permittivity. The extent of this modulation depends on many parameters, including the properties listed in Table I, the geometry of the molecule being detected, the presence of semiconductor–oxide surface states, the configuration of the electric double layer, etc.

The signals obtained from the five test solvents in Figs. 7 and 8 have distinct features. This is an important property of the sensor because discrimination between various solvents can be achieved. Toluene generates a very small signal much unlike any other present in the tests. Acetone is different because of its short signal duration. Methanol stands out because it has two characteristic peaks. Both ethanol and IPA are similar; however, the top portion of the peak of IPA is irregular while ethanol is smooth and ramped towards a peak value. It was consistently observed that the capacitive signal tends towards a maximum just prior to final solvent evaporation and signal drop.

To achieve reliable discrimination between signatures they must be reproducible on a day-to-day basis. Fig. 10(a) and (b) shows normalized acetone and IPA signatures taken over a period of eight days. The normalized signatures of acetone and IPA change slightly on a day-to-day basis which may result from minor variations in ambient conditions and sample size. Overall, the signatures do exhibit a similar response on a day-to-day basis, and this strongly suggests that computational analysis can be used to analyze characteristic signals generated by various solvents for discriminative and identification purposes.

To demonstrate practical application of our sensor, real time water monitoring was conducted with a packaged sensor as seen in Fig. 11. The package consists of lased glycolized polyethylene terephthalate (PETG) sheets, which were assembled to form a fluidic system that consisted of an input port, an interface to chip level fluidics, and an output port. Real-time capacitive measurements were taken while sample volumes of 70 µl were injected into the packaged device. After approximately 80 s, the sample was pumped out of the package with N₂ gas. The flow of N₂ gas through the sensor resulted in a large rise in the measured capacitance with the sensor. This region, as indicated by

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**Fig. 8.** Overlay of normalized capacitive signals of various test solvents.

**Fig. 9.** Linear relationship between duration of signal and vapor pressure for acetone, methanol, IPA, and ethanol has been observed.
resulting in a stronger localized field modulating the space charge region in the semiconductor. Additional investigation is needed to realize the lower limit detection of this sensor.

Although not presented in this paper, it is feasible that various solvent contaminants could result in different measured capacitance. This is based on the fact that each of the pure solvents tested resulted in a different capacitive response. It is clear from the figures presented in this work that visual inspection of signature characteristics can be used to distinguish between different solvents. Computer-based analysis with arrayed sensors may have potential to rapidly identify and discriminate various solvents while minimizing human error. Above all, integration with on-chip sensing circuitry is feasible [15], and this could ultimately lead to lab-on-a-chip technology for solvent screening.

IV. CONCLUSION

Various solvents including acetone, ethanol, isopropyl alcohol, methanol, and toluene were detected with specificity in their liquid phase. The measured capacitive response is a result of localized field effects that modulate a space charge region in the semiconductor. The use of MPS greatly increased the amount of surface area available for sensing operation while allowing integration of backside fluidics for sample delivery. Measured capacitive signatures from the test solvents are shown to be repeatable and reproducible. Distinction between contamination levels of IPA in water was demonstrated with a packaged sensor. This sensor, which has successfully integrated a basic fluidic delivery system on the backside and sensing electrodes upon the frontside, ultimately defines macroporous silicon flow-through membranes as a prime candidate for integration with on-chip circuitry that is suitable for lab-on-chip technology capable of solvent detection.

REFERENCES

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