Prototyping of a Microsensor for Organic Vapours and Solutions

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Abstract

The cost and requirement of special devices and clean room are limitations for microfabrication technique. This paper addresses the low cost method for prototyping and fabrication of micro-chemisensor for the detection of organic molecules. Porous silicon layer is fabricated on the (100) plane of p-type silicon wafer using metal assisted chemical etching method. According to the characterization results the metal assisted chemical etching method gives good porous morphological structure which is suitable for sensor fabrication. The microelectrodes for the sensor were prepared on the porous layer using cost effective microfabrication technique. The electrode patterns to be fabricated are designed using free design software to generate the high resolution image file. Transparency-based photo-masks are made by offset printing technique which is very cost effective for rapid prototyping. The contact mask aligner provides the transferring of pattern onto the substrates. The fabricated sensor exhibits very sensitive and reversible response during the real-time measurements of capacitance in ethanol vapour. The change in surface charges upon ethanol infiltration into the porous structure produces the response in electrical properties of sensor.
Keywords: chemisensor, microfebrication, MEMS, photo lithography.

I. Introduction

In the past decade, Micro-electro-mechanical sensors (MEMS) technology has attracted increasing attention because of its capability of downsizing electronics using highly integrated micro-devices. Common functions required by MEMS devices include microfluidics, micro-optics, micromechanics, and micro-electrodes. However, conventional MEMS fabrication techniques use the same semiconductor manufacturing systems that are used to produce large and small scale integrated circuits and they require several tens of processes. Therefore MEMS fabrication requires large capital investment and has high production costs. The cost of fabrication of MEMS devices is very expensive. To provide cost effective method for researchers and students to conduct microfabrication techniques is one of the objectives of this research.

Organic vapor sensors have been a very active research area, since organic vapors are among the most harmful gases [1]. Almost all organic vapors are potentially toxic to the liver and kidneys. Even brief exposure to these vapors can result in a variety of serious effects in both the peripheral nervous system and the central nervous system [2]. The current work addresses how to prototype microsensor for the detection of organic compound using cost effective fabrication technique. Sensors based on semiconductor technology are most attractive because they are compact, sensitive, low cost, and have low power consumption [3]. The simplest and most commonly accepted theory of the semiconductor sensor operation mechanisms is that atoms and molecules of the gases interact with semiconductor surfaces to influence surface conductivity and surface potential. Surface conductivity changes are mainly due to changes in the free electron concentration due to charge exchange between adsorbed species from the gas and the semiconductor surface. The charge exchange occurs in a thin layer below the gas solid interface. Therefore, for a high sensitivity gas detection the semiconductor must have a large specific area (surface area to volume ratio) to produce a higher charge exchange rate. This can be realized in practice by using porous materials due to their large specific area. Since, porous silicon (PS) has very high surface to volume ratio, it is

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a promising candidate for gas sensing. Traditional method of detecting of the organic gas concentrations is mostly gas chromatography, but it is expensive and takes a long time and needs professional laboratory facilities with specialized staff [4]. Therefore, it is needed new modern sensors cheap and capable quickly sensing of organic vapors and harmful gases. Porous silicon-based vapor sensor could be the most attractive choice since it would be compact, sensitive and low cost.

The second section explains the experimental of porous silicon fabrication and characterization, and the third section describes how to prepare the microelectrodes for the sensor using cost effective method. The cost benefit analysis of the current technique of prototyping microelectrodes and the characterization and performance analysis of a prototyped sensor are discussed in the fourth section and finally, the current research is concluded.

II. Fabrication of Porous Silicon

Two technologies are involved in the prototyping of a microsensor which are the fabrication of porous silicon and microfabrication technology. Boron doped silicon substrates with (100) crystallographic orientation and resistivity of 1-10Ωcm were used as the starting materials. Metal assisted chemical etching method is used to optimize the porous formation for microsensor fabrication. It is immersed in a tank of solution of 5:5:10:1 (volume ratio) 50%HF:30%H_2O_2:H_2O:4.7mM of $AgNO_3$ for different hours in metal assisted chemical etching method. The etched silicon wafers were rinsed thoroughly with deionized water. The remaining Ag from the PS surface is removed by room temperature cleaning in aqueous solution of 30% HNO_3 for 20 minutes. Then PS substrates were washed with deionized water, ethanol and acetone, respectively, under ultrasonic agitation and dried in oven.
According to the characterization results the metal assisted chemical etching method gives better porous morphological structure as shown in Figure 1 which is suitable for sensor fabrication. Therefore, it method was used to fabricate microsensor.

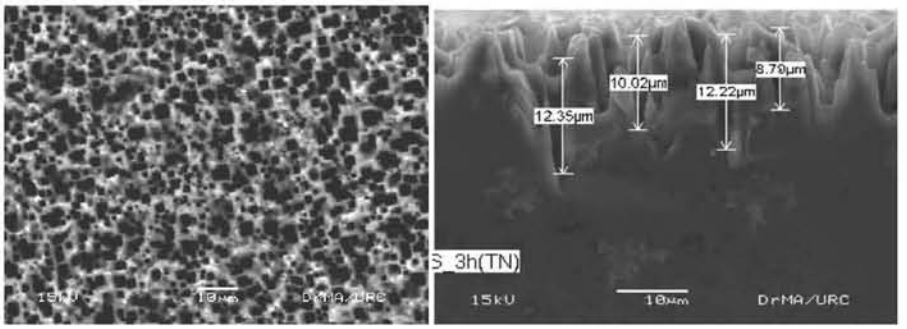


Figure 1. SEM images of porous formation by metal assisted chemical etching

Surface chemical composition of PS is best probed with Fourier Transform Infrared (FTIR) spectrophotometer. The FTIR spectra of the p-type porous silicon are shown in Figure 2. In the transmittance spectrum, peak at 624.96 cm^{-1} represents Si-H bending (Si_3SiH), peak at 852.56 cm^{-1} shows Si-H_2 wagging mode and peak at 910.23 cm^{-1} illustrates Si-H_2 scissor mode [5]. The peak at around 1074.30 cm^{-1} is due to Si–O–Si stretching modes [6], which are depended on the oxidation degree of porous silicon. Furthermore, 2096.69 cm^{-1} and 2922.25 cm^{-1} are, respectively, related to Si–H stretch (Si_3-SiH) and C-H stretch (CH_2) [7]. Chemical bonds and their IR resonance positions detected in PS are shown in Table 1. Si-H bonds play

an important role in regulating optical electrical and gas sensing properties of porous silicon [5].

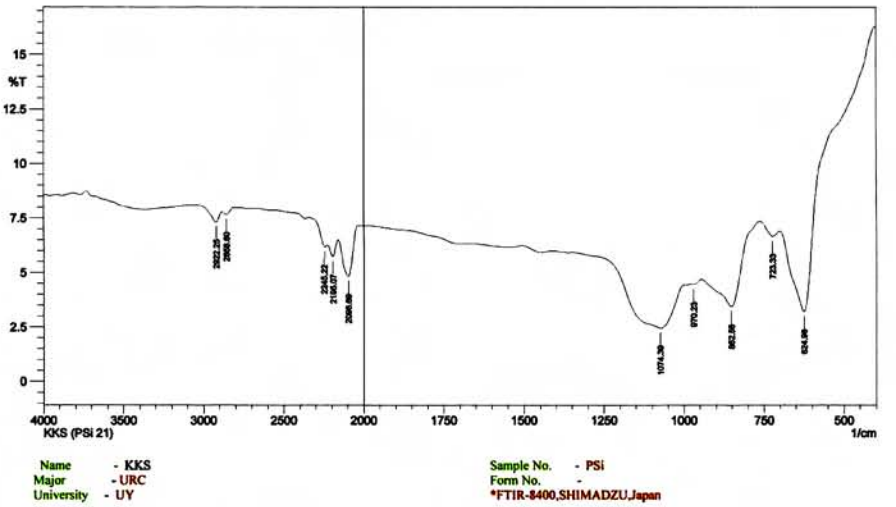


Figure 2. FTIR transmittance spectrum of a PS

Table 1 IR absorption peaks and their corresponding functional groups

Peak position (cm^{-1})	Attribution
624.96	Si-H bending
852.56	Si-H_2 wagging
910.23	Si-H_2 scissor
1074.30	Si–O–Si stretching
2096.69	Si–H stretch (Si_3-SiH)
2922.25	C-H stretch (CH_2)

III. Preparation of Microelectrodes

Microelectrode patterns are prepared on the porous silicon layer as given in Fig xxx. Mask for electrode is designed in L-Edit software that can produces various mask design in micro level scale (line width in μm) as a GDS file. GDS file is then converted to postscripts file with Link-CAD software. Next, the postscripts file is converted to PDF file with PDF converter.

Before starting the lithography process, thermal SiO_2 layer is prepared by annealing the porous Si wafer in 800 degree C for 1 hour. The RZJ-304 photoresist layer is coated on the wafer using spin coater. Next, the photoresist layer is exposed to ultraviolet (UV) light through the mask. This step is done on a mask aligner in which mask and wafer are aligned with each other before the exposure step is performed. Photoresists is removed using RZX-3038 aqueous based developers. The aluminum electrode is deposited on substrate using

vacuum evaporator (JEOL JEE-4X). Then photoresist layer is removed by immersing into the RBL-3368 photoresist remover for 3 minutes.

IV. Results and Discussion

This paper describes not only to fabricate microsensor but also to find the way for cost effective microfabrication technique for researchers and university students. Transparency-based photo-masks by offset printing technique is very cost effective for rapid prototyping.

The cost comparison of standard microfabrication and the method used in this work is shown in Table 2. It is an estimate cost for one times process. The cost is significantly reduced in clean room facilities and mask making process. It is about $500 cheaper than standard microfabrication for one times process. But this technique can fabricate the microelectrodes patterns with 20 µm in line width. This resolution is enough for most proto typing levels.

Figure 5 shows capacitance-frequency characteristics of the sensor for without and with ethanol solvent at an applied ac voltage of 100 mV and zero dc bias. It is observed that the value of the measured capacitance decreases with increase in frequency from 500 Hz to 50 kHz. The reactive part of the effective impedance shows between 500 Hz to 5 kHz. The real time response of the sensor that connected with capacitance meter was tested by putting the sensor to the top of the beaker containing ethanol and then it was removed. The infiltrated ethanol molecules into the macropores are accompanied by a rapid, significant increase in capacitance. Once the porous layer is completely filled with ethanol vapor, the capacitance reached the maximum values. After removing the sensor from ethanol environment, reducing of ethanol vapor from the device started to take place, down-arrow branch of Figure 6 giving a rapid return of the capacitance to its original values (dry sensor state).

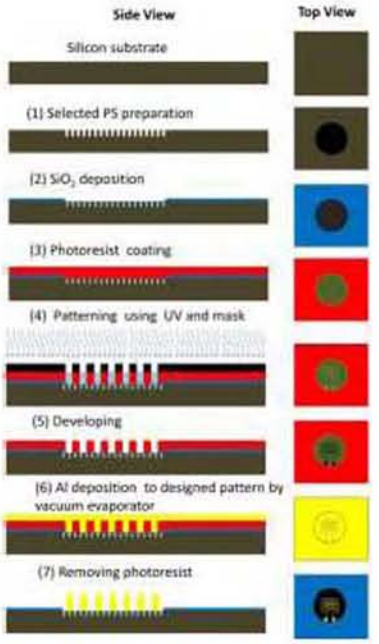
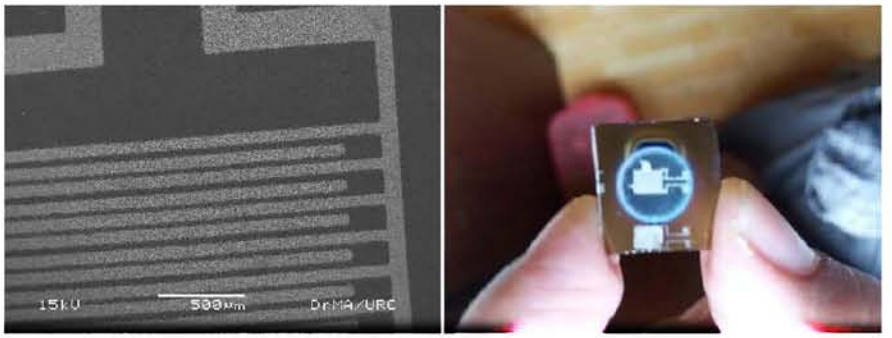


Figure 3. Fabrication procedure for microsensor



(a) (b)

Figure 4 (a) SEM images of microsensor with microelectrodes pattern on PS
(b) Photograph of microsensor

Table 2 Comparison of estimated cost for microfabrications techniques

No	Requirements	Cost for standard microfabrication	Cost for microfabrication used in this work
1	Clean room facility	$ 4.2	$ 0.1
2	Mask	$ 500	$ 1.5
3	Photoresist	$ 3.3	$ 3.3
4	Developer	$ 4.7	$ 4.7
5	Remover	$ 4.7	$ 4.7
	Total	$ 516.9	$14.3

The observed sensing response could also be understood by considering the change in surface charge during the infiltration process. Ethanol is an electron donor molecule and may inject an electron to the surface states of the PS layer that are available at the Si-SiO_2 interface. This leads to a modification of the surface charge distribution, which finally results in a change in capacitance. Change in surface charge by electron donating molecules has been reported previously by Farid A. Harraz in terms of electrical properties of PS [8].

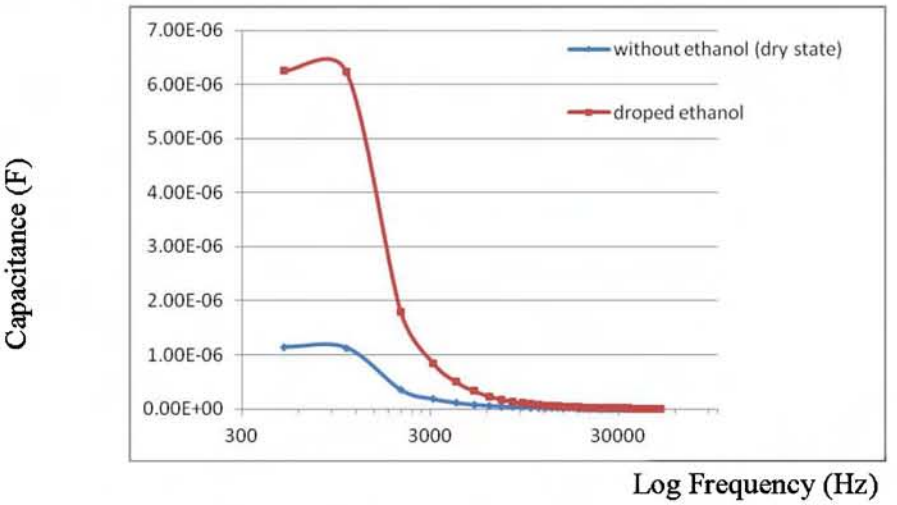


Figure 5. Variation of capacitance with frequency

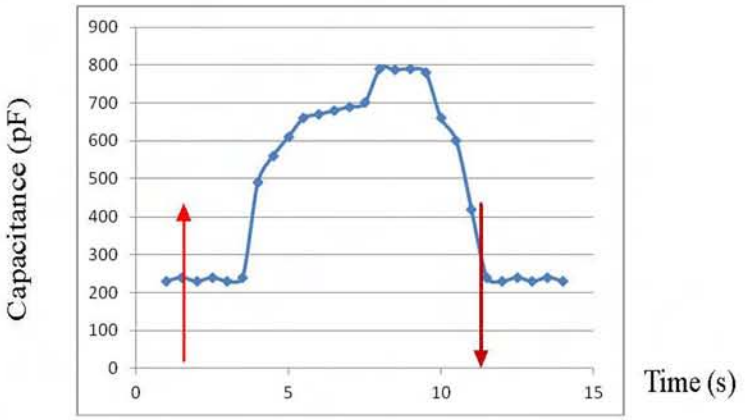


Figure 6 Sensor response with ethanol vapour

To analyze the response of the sensor in the ethanol vapor it was placed in vapor test chamber together with Humidity sensor (DHT11) and alcohol sensor (MQ-3) as shown in Figure 7. The ethanol vapor is generated by blowing the air into the ethanol bubbler and air was used as vapor carrier. The amount of ethanol vapor is controlled by the flow of air into the bubbler. Real-time capacitance values of the sensor were measured by LCR meter at applied frequency of 1kHz and a DC bias of 0 V. The relative humidity (RH%), temperature (°C) from humidity sensor and readings from the uncalibrated alcohol sensor which is interfaced by Arduino controller are recorded.

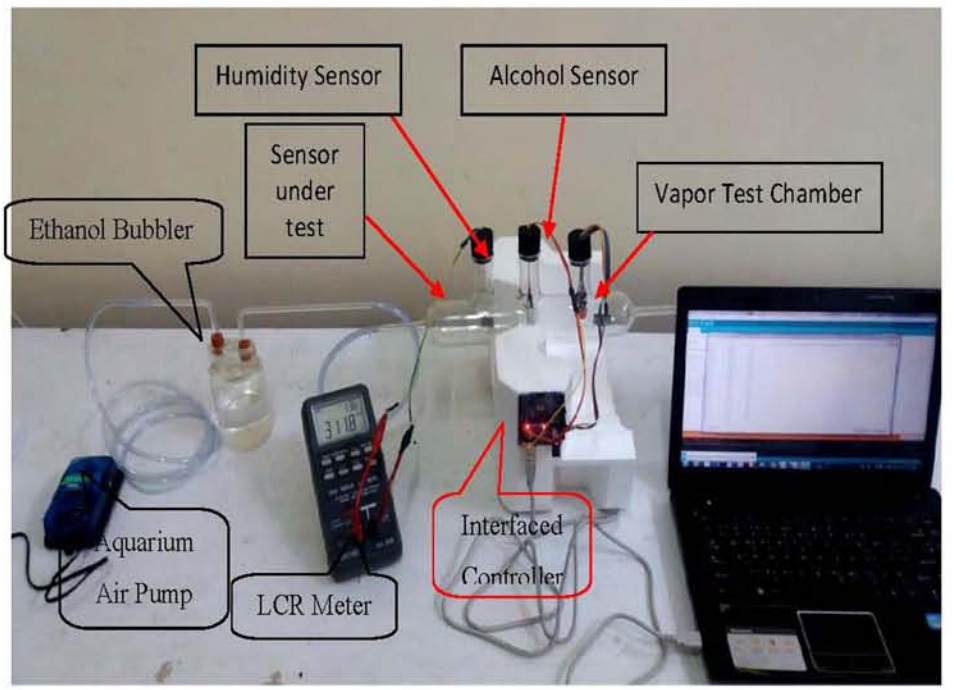


Figure 7 Experimental set up for ethanol vapour sensing

The capacitance of the fabricated sensor is increased with the amount of ethanol vapor as shown in Figure 8. Figure 9 shows the response of our device and the alcohol sensor with the relative humidity. It is assume that the humidity is increased with the amount of ethanol vapor. It is found that both sensors show similar characteristics with amount of humidity.

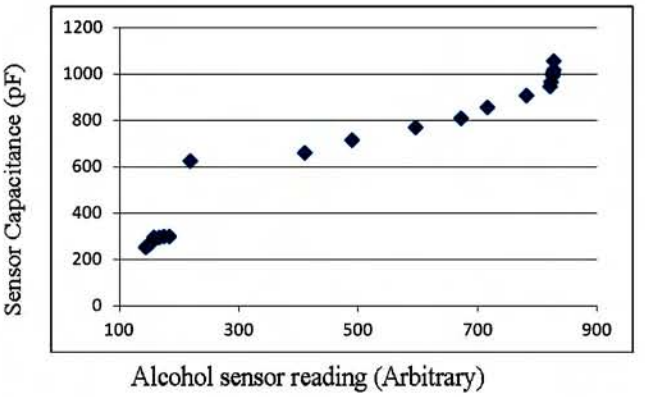


Figure 8 Change in capacitance of fabricated sensor with alcohol sensor reading

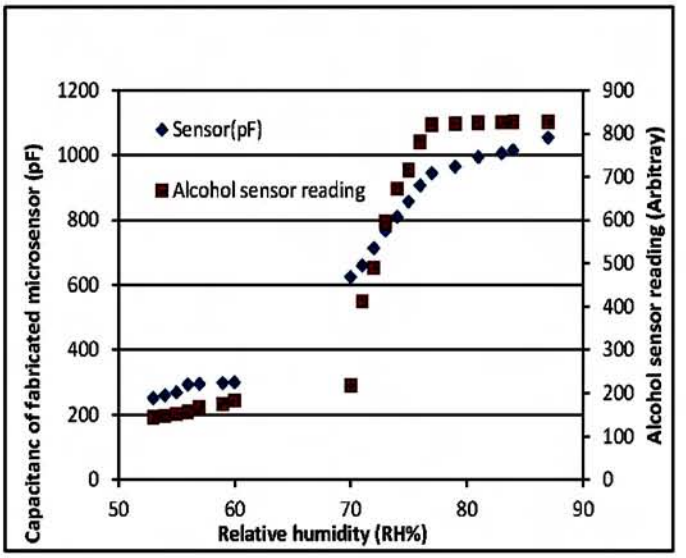


Figure 9 The response of organic sensor and alcohol sensor with the relative humidity

Table 3 illustrates the change in capacitance of fabricated sensor with other organic solutions and water. 10µl of solutions are dropped onto the sensor in turn and the change in capacitance is observed. It is found that sensor is the most sensitive for ethanol liquid and least sensitive for water.

Table 3 Change in capacitance for different organic solutions

Solution	Capacitance for dry sensor	Capacitance after dropping organic solution	Change in capacitance
Ethanol (95%)	268 pF	1401 pF	1133 pF
Methanol (95%)	278 pF	1302 pF	1024 pF
Isopropyl alcohol (91%)	289 pF	1206 pF	917 pF
Water	268 pF	466 pF	198 pF

V. Conclusion

Porous silicon is prepared by different methods and optimized for microsensor. It is found that metal assisted chemical etching method is better than electrochemical etching (anodization) method for sensor fabrication. The contact micro metal electrodes on PS were prepared using cost effective microfabrication. The cost of proposed fabrication method has been compared with standard method. A spin coater, a mask aligner, a vacuum evaporator and mask design software are the minimum requirements for current method. After testing for different organic solutions and ethanol vapour, the developed sensor has high sensitivity, fast response and long term stability. Moreover easy realization of array sensors using silicon based method provides the development of system-on-chip integration with microprocessor system for environmental monitoring, food processing and E-nose for robotic applications.

Acknowledgements

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