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Macro Porous Structure Silicon Capacitive Sensor for Aqueous Methyl Alcohol

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A very low-cost capacitive sensor device based on macroporous structure silicon has been used to detect and quantify the presence of an aqueous methyl alcohol solution. The porous structure silicon was fabricated by laser etching process using a commercial pulse fiber laser. The device has a large number of pores to sense different concentrations of the aqueous methyl alcohol solution. Experimental results prove the possible application of the porous structured silicon sensor to detect methyl alcohol in aqueous solutions up to 3.99 ppm based on the changes in the average dielectric constant within the area of the pores.

topics: laser etching (LE), limit of detection (LOD), pulse fiber laser (PFL), porous structured silicon (PSS)

1. Introduction

Sensors are used in many everyday life applications such as aeronautical industry, automotive industry, beverages production for composition or quality control, clinical diagnosis, diamond industry, environmental monitoring systems, food industry, clothing industry, maritime industry, safety and security industry [1]. Researchers continuously research sensor materials at low cost, easily fabricated, and compatible with present semiconductor technologies [1, 2]. Porous structured silicon (PSS) is a suitable material for sensor-making devices due to its advantages like low cost, easy fabrication, large surface area, and compatibility with present electronics technologies. The fabrication parameters of PSS allow for the easy control of the pore size and pore depth; when another material gets inserted into the pores, the optical and electrical properties of the PSS change. The advantages of optical sensing are the quick output response and the applicability in a hazardous environment. However, disadvantages include costly testing equipment that requires special training and the result may be affected by environmental interference, in contrast to electrical sensing that is done at low-cost and is easily compatible with electronics devices [3].

There are three types of etching processes for the fabrication of PSS: (i) electrochemical etching (ECE), (ii) dry etching, and (iii) laser etching (LE) [4]. Electrochemical etching is typically carried out in an aqueous electrolyte. The fabrication cost is low, but the ECE process uses hazardous chemicals like hydrofluoric acid. The dry etching process is either reactive ion etching (RIE) process or inductive coupled plasma (ICP). Etching rates are slow and the equipment used in dry etching is costly. In the LE process, we achieve high fabrication speed, accuracy and good resolution. Three types of lasers are used for the production of PSS: (i) CO_2 ($\lambda = 10.64$ μm), (ii) Nd:YAG ($\lambda = 1064$ nm), and (iv) pulse fiber laser (PFL) ($\lambda = 1064$ nm). The disadvantage of a CO_2 laser is that it requires Pyrex glass for etching in the silicon wafer. In Nd:YAG laser, the cost of equipment is high. CO_2 and Nd:YAG lasers require large cooling power and careful maintenance. Our earlier paper demonstrated that the PSS could be successfully fabricated on a silicon wafer using PFL [1–4].

Researchers used resistive, inductive, and capacitive principles for electrical sensing. The main disadvantages of resistive sensing are lower sensitivity and high power consumption. The main disadvantage of inductive sensing is a coil-size-shape fabrication, which is very difficult to design in an integrated circuit. The advantages of capacitive sensing are simple construction, lower cost, and operation at a low power supply. The change in the capacitance sensor is given by

$$C = \varepsilon_0 \, \varepsilon_r \, \frac{A}{d}, \tag{1}$$

where C — the capacitance, A — an area of the device, d — the distance between electrodes, $\varepsilon_0 = 8.854 \times 10^{-14}$ F/cm is the permittivity of free space, and $\varepsilon_r = 33.6$ is the relative permittivity of the aqueous methyl alcohol. By changing any value in (1) when the other two parameters are constant, the value of capacitive changes, as shown in Fig. 1.

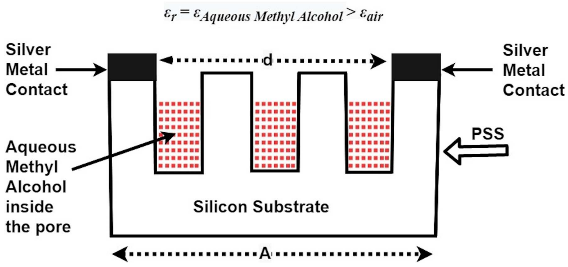

Fig. 1. Schematic cross-section of the PSS capacitive device as a function of relative permittivity.

TABLE I

The selective operation parameters of the PFL.

Parameter	Value
wavelength	1064 nm
speed	5 cm/s
output power	27 W
resolution frequency	0.2 MHz
loop count	1
operation mode	pulse mode

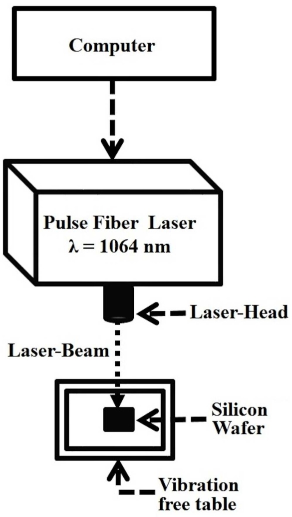

Fig. 2. Schematic setup for making the PSS using PFL.

Methyl alcohol (CH_4O) is also known as a wood alcohol and has the International Union of Pure and Applied Chemistry (IUPAC) name is Methanol. It is a colourless, volatile, flammable, and toxic organic aqueous solvent. It is used in the construction industries, automobile parts, and explosives in wastewater treatment plant to make a fuel cell in racing cars. So methyl alcohol is being continuously detected in our living environment, therefore the goal of this work is to measure the current response of PSS in sensing aqueous methyl alcohol.

2. Experimental

A two-inch single-side polished, boron-doped silicon wafer $\langle 100 \rangle$, with a 0.01 to 0.02 Ω cm resistivity and thickness of 275 μm, were selected. Silicon wafer immersed in piranha solution. Piranha solution is a mixture of sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) (3:1 ratio by volume) used for cleaning purposes before LE [1–4]. The silicon wafer was then cut into 1.5 cm^2. The cleaned wafer was etched using PFL micromachining of 1064 nm wavelength setup in the schematic diagram shown in Fig. 2. The total number of 7922 pores are fabricated in the area of 0.785 cm^2 using PFL. Table I illustrates the operation parameters of the PFL. Using PFL, the etching mechanism of pore formation fabrication was discussed in our earlier paper [4].

A thin layer of oxide is required for the operation of the sensor device and it is achieved with the help of hydrogen peroxide (H_2O_2) [1–3]. At standard ambient temperature and pressure, the PSS sample was soaked into the hydrogen peroxide (H_2O_2) 38 wt% for two days. The thin oxide layer makes the PSS hydrophilic and allows the infiltration of water-soluble molecules and other organic compounds into the pores. The last step involves the fabrication of the contact pads on PSS. Two contact pads are made using colloidal silver paste and Cu wires. The entire sample was then backed into the muffle furnace at 100°C for 20 min to permanently cure the silver conductive paste.

3. Results

Figure 3 shows the micrograph's top and cross-sectional views taken by Field Emission Scanning Electron Microscopy (FE-SEM) of fabricated PSS. The mean pore diameter of $\sim$ 55 μm, the mean distance of $\sim$ 20 μm, and pore depth of $\sim$ 99 μm were measured. The results show that the pores are etched uniformly across the silicon wafer area, which is essential for increasing device sensing performance because uniform aqueous solutions are going into the PSS. Our earlier paper [4] demonstrated that the pore diameter and depth can be controlled by PFL output power, speed, operation mode, resolution frequency, and pass number.

Figure 4 shows the X-ray Diffraction (XRD) measurement of oxidized PSS, which reveals that the peak diffraction is at $2\theta = 68.32$, and it corresponds to Si (400) plane reflection from 100 crystal orientation of the bulk silicon. The value of 2θ indicated in [3, 5] corresponds to the crystallinity of oxidized PSS. No additional boarding of the spectra near the peak were observed, confirming that the PSS is amorphous oxidized in nature [5]. Figure 5 shows the experimental setup involving the PSS capacitive sensor for the measurement of aqueous methyl alcohol. The next step is to standardize the device. We apply a 100 mV ac signal and 0.1 kHz to 100 kHz frequency to the bare sensor using an LCR meter.

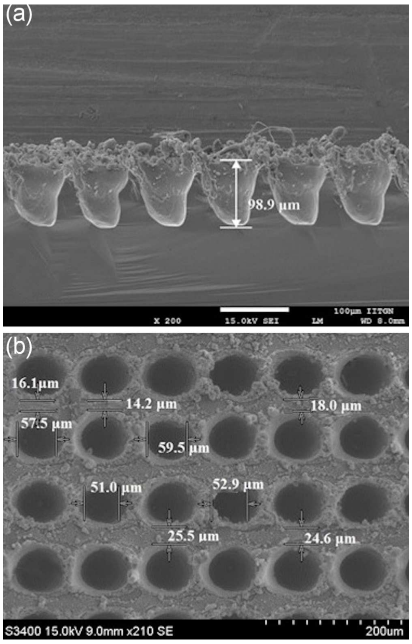

Fig. 3. FE-SEM image of micrograph (a) cross-sectional view, (b) top-View.

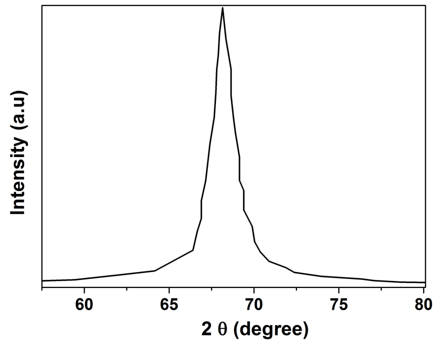

Fig. 4. XRD spectra of oxidized PSS.

Figure 6 as a plot of impedance and phase over frequency demonstrates that the device is capacitive at high frequency, whereas the device's impedance is high at low frequency. So, the experiment has performed at a frequency of 100 kHz and a voltage of 100 mV AC.

Figure 7 shows the concentration of methyl alcohol as a function of the change in capacitance value ΔC [nF], where ΔC is the value of each concentration difference of methyl alcohol and the initial value of the capacitance, i.e., air value.

The value of device capacitance increases due to the replacement of the air in the pores by aqueous methyl alcohol [5–11]. Figure 7 shows that the device response is linear up to 10 ppm. Above 10 ppm the response is non-linear due to saturation. The sensitivity (S) of the PSS sensor device is

$$S = \frac{\Delta C}{\Delta C_{\text{concentration}}}, \tag{2}$$

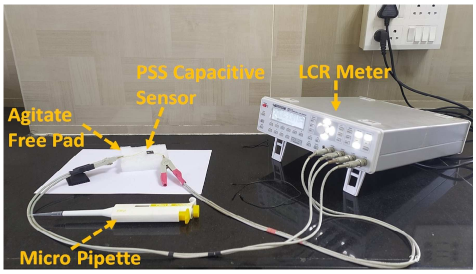

Fig. 5. Experimental Setup to sense aqueous methyl alcohol.

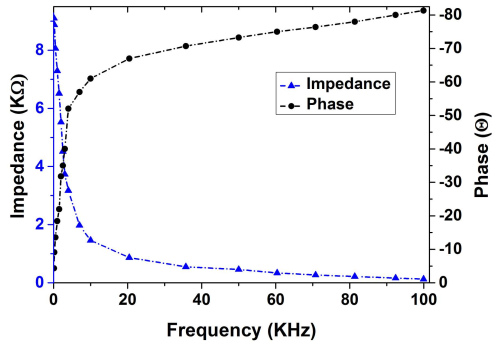

Fig. 6. Impedance and phase over the frequency.

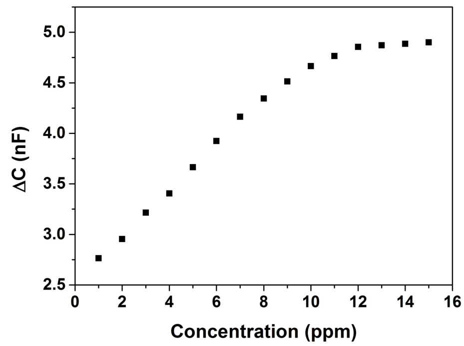

Fig. 7. Change in capacitance measured for different concentrations of methyl alcohol.

where ΔC denotes the change in the capacitance value, $\Delta C_{\text{concentrations}}$ indicates the change in the concentration level of the methyl alcohol aqueous solution. The calculated sensitivity value of the PSS sensor device is 0.27 nF/ppm.

Further, the limit of detection (LOD) is defined as

$$\text{LOD} = K\,\frac{\text{SD}}{S}, \tag{3}$$

where SD is the standard deviation, S denotes the measured sensitivity, $K = 3.3$ is a 95% confidence level [1–3]. From (3), the calculated LOD value is 3.99 ppm [1–3]. In Table II, a comparison of methyl alcohol LOD with other reported works [12–14].

TABLE II

Comparison of the LOD for methyl alcohol in the aqueous solution of the proposed PSS capacitive sensor with other reported works.

Method of detection	LOD [ppm]
nano-composite NiOOH and glassy carbon electrochemical method [12]	0.3204
graphene-based nano polyindole composites in situ method [13]	0.015
mesoporous α-Fe_2O_3 doped CdSe nano-structures glassy carbon electrode electrochemical method [14]	0.0013
macro porous silicon-based capacitive sensors [this work]	3.99

It is clear from Table II that our sensor device shows the highest value of LOD because our sensor structure size is in micro, whereas another sensor structure size is in nanoscales. After each experiment, the device was rinsed with deionized (DI) water.

Our experiment showed that the PSS capacitive sensor device can also be used as reversible sensor device applications. After each experiment, the aqueous methyl alcohol molecules inside the porous structure were removed by rinsing the sensor device in deionized (DI) water. Then the device was dried using nitrogen gas. The capacitance of the sensor device comes to its original value. This feature is very useful for the development of effective reversible PSS capacitive sensor device.

4. Conclusion

The paper presents laser-etched macro-porous structure silicon fabrication using a pulse fiber laser to develop a capacitive sensor device for different aqueous methyl alcohol concentration testing. FE-SEM characterized the surface morphology of the samples, and the mean pore diameter and depth were 55 μm and 99 μm, respectively. The device's sensitivity and the limit of detection (LOD) are 0.27 nF/ppm and 3.99 ppm, respectively. The proposed device can serve as a suitable technology for the low-cost bio-sensing application.

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