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Mesoporous Silicon Layer as a Highly Sensitive Ethanol Sensor

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Mesoporous silicon (PSi) layer was used to create highly sensitive, electrically-based sensor for detection of liquid ethanol at room temperature. The PSi nanostructure that is generated in an electrochemical etching of crystalline silicon in HF-based solution was ≈ 4.5 μm thick with an average pore size of 30 nm. The as-fabricated sensor exhibits highly sensitive, reversible response during the real-time measurements of capacitance and conductance. Excellent repeatability of the devise was obtained after six cyclic tests, demonstrating stability of the sensor. Long-term stability for the sensor performance was also observed after four weeks storage. The observed response could be understood in terms of the change in surface charge upon ethanol infiltration into the mesoporous structure.

Keywords: Anodization; Electrochemical etching; Porous silicon; Electrical sensor.

1. INTRODUCTION

Significant research efforts have focused on the development of various sensing materials for the detection of organic molecules. Porous silicon (PSi), that is often produced by an electrochemical etching procedure [1-3], is a promising candidate due to ease of fabrication, large surface area [4], various accessible morphologies [5,6] and controllable surface modification and reactivity [7-12]. This actually allows the porous structure to be suited for use for specific sensing applications. The compatibility of PSi with conventional silicon processing technology adds another advantage compared to other sensing materials. The optical properties of PSi have been essentially used in many chemical and biological sensing applications using various porous structures, including rugate filters [13], Bragg mirrors [14], Fabry-Perot films [15], and microcavities [16]. In our previous works, we have fabricated 1-dimentional photonic crystal based on PSi rugate filters for optically sensing different types of organic vapors [13,17]. However, the experimental set-up is rather complicated with low device sensitivity. Thus, measuring the electrical properties would be an efficient alternative for enhanced sensitivity and a relatively lower-cost operation.

In contrast to the optical properties, there are limited reports on PSi chemical sensors dealing with its electrical properties [18-21]. For example, an electrical sensing of biochemical and organic chemical solutions using thermally oxidized macro-PSi sensor has been investigated [21]. In another report, the observed change in conductance upon exposure to different organic solvents using (~1 μm pore diameter, 20 μm pore thickness) of PSi layers with backside electrical contacts was described [19]. Their results illustrated a reversible response, however the sensor sensitivity was low with no investigation done on sensor durability. In this contribution, we demonstrate a simple method for electrical detection of liquid ethanol based on the electrochemical fabrication of meso-PSi layers with front electrical contacts. The underlying concept of our approach is based on that, the change in electrical properties upon infiltration of target analyte into the porous layer would enable the detection of organic molecules by recording the magnitude and time evolution of the conductance shift. Our findings indicate that the present sensor design is stable enough to retain high sensitivity and reversibility. Furthermore, the current approach could potentially be applied to create structures suitable for sensing a wide range of chemical and biological molecules.

2. EXPRIMENTAL

Mesoporous silicon (PSi) layers were fabricated, according to our previous procedures [22,23], by electrochemical etching of heavily doped *p*-type Si (100) wafer with a resistivity of 0.01-0.02 Ωcm; doping density: 7×10^{18} cm^{-3}. The anodizing solution composed of 28 wt.% HF/H_2O/EtOH with a Pt rod served as the counter electrode. The anodic current density was 50 mA/cm^2 for anodization time of 75 s.

Figure 1 shows FE-SEM images of cross-sectional view (image a) and top (b: inset micrograph) of the porous layer fabricated under the above conditions. Average pore size of 30 nm with 4.5μm depth could be recognized. The porosity of this sample is 48% as estimated from gravimetric measurement. Surface passivation was performed by anodic oxidation in 1 M H_2SO_4 electrolyte under galvanostatic condition of 5 mA/cm^2 for 20 min. The oxidation of PSi surface is required for stable and proper operation of the device. After oxidation, the porous layers are rinsed in deionized water and ethanol and left for drying naturally. The electrical contacts are then made on the front porous surface by colloidal Ag paint and Cu wires followed by baking at a temperature of 120 ºC for 2 h. The schematic cross-sectional view of the sensor with a close-up photograph are depicted in Fig. 1 (c) and (d), respectively.

Real-time capacitance (*C*) and conductance (*G*) of the sensor upon exposure to liquid ethanol, at room temperature were performed with the electrochemical workstation, ZahnerZennium, Germany, at applied frequency of 100 kHz, a dc bias of 0 V and an ac signal of 100 mV. The impedance as a function of frequency was also recorded for the dry sensor in a frequency range of 100 mHz to 100 kHz.

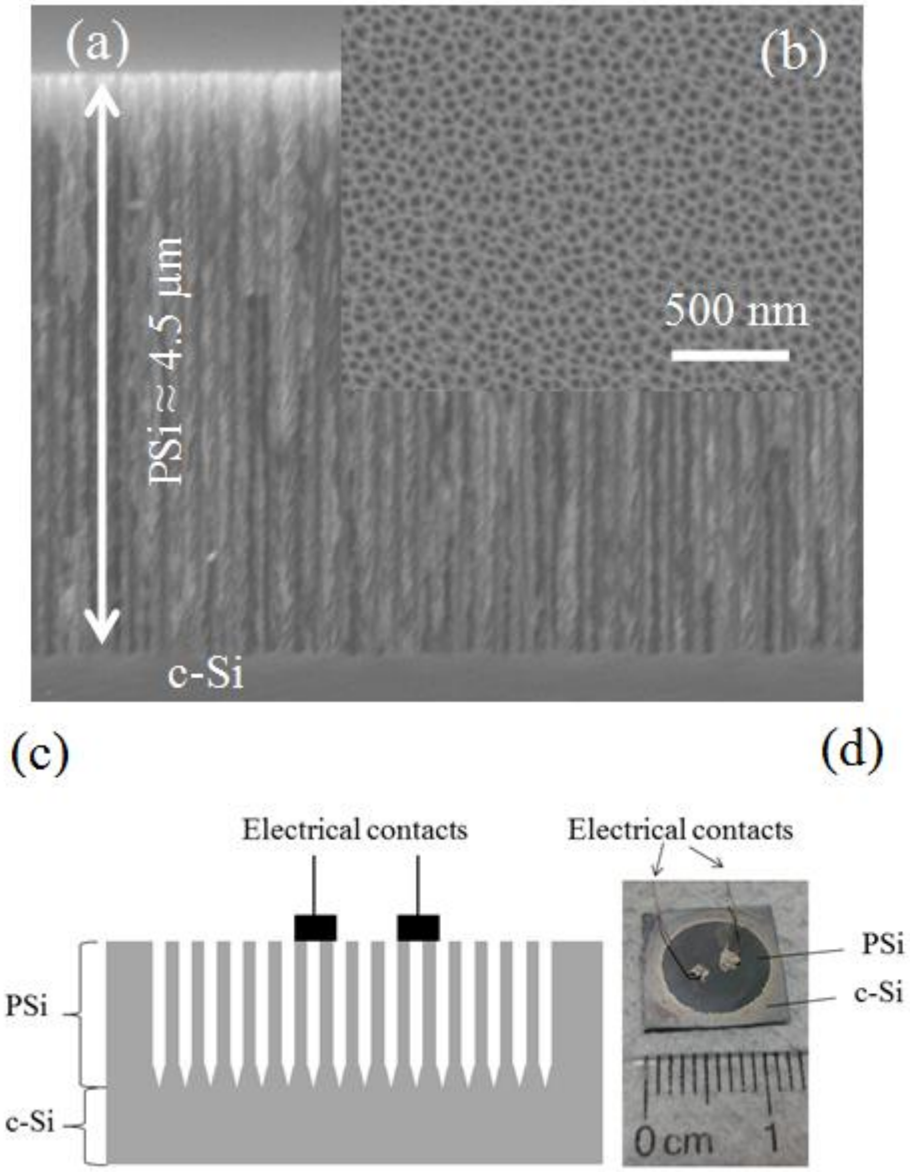

Figure 1. Scanning electron micrographs of (a) cross-sectional and (b) top-view as inset of mesoporous silicon layer produced from *p*-type silicon by galvanostatic anodization. (c) Schematic cross-sectional view of the porous silicon sensor. The electrical contacts are made on the front of the porous layer by colloidal Ag paint. (d) Close-up photograph of the sensor.

3. RESULTS AND DISCUSSION

The dependence of impedance and phase angle on applied frequency over a range of 100 mHz-100 kHz for dry PSi sensor was firstly evaluated at an ac signal of 100 mV and a dc bias of 0 V. The results are shown in Fig.2. The PSi-based device behaves as a resistor at low frequency, however as the frequency increases the impedance is reduced and the phase angle exhibits a capacitive behavior. The optimal frequency based on these results is 100 kHz.

The sensor was next used to examine its response to liquid ethanol. Experiments were performed by adding 10 µl ethanol solvent to the front porous layer. Figure 3 (a) shows the real-time evolution of the normalized capacitance and conductance after solvent exposure. The infiltrated ethanol molecules into the mesopores are accompanied by a rapid, significant increase in both capacitance and conductance. Once the porous layer is completely wetted with ethanol, the capacitance and conductance reached the maximum values. Afterwards, evaporation of ethanol from the device started to take place, down-arrow branch of Fig.3 (a), giving a rapid return of the capacitance and conductance to its original values (dry sensor state). It is likely that ethanol is sensed immediately at the pore opening, which may explain the fast conductance change of the device upon addition of ethanol target molecule. Such a rapid response is related to the placement of electrical contact onto the front porous layer, which is proved to be advantageous for enhancing the sensitivity compared to the rear side contact.

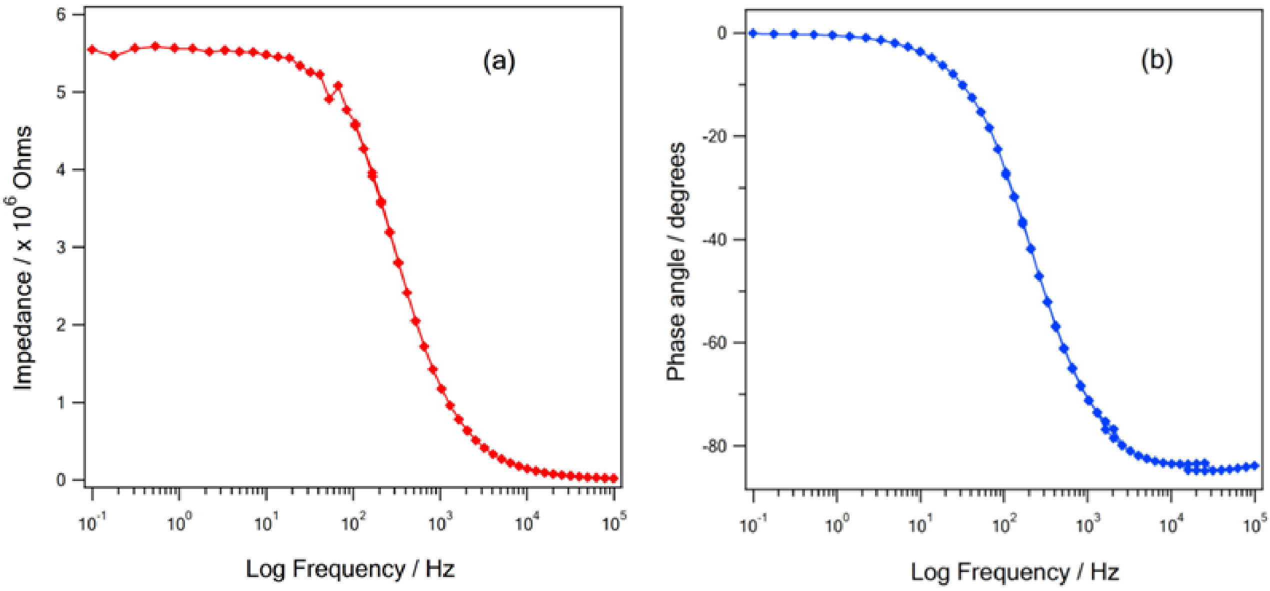

Figure 2. Impedance (a) and phase angle (b) as a function of frequency. The measurements were performed in a dry sensor device, with an ac signal of 100 mV and a dc bias of 0 V.

The observed sensing response could 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 PSi 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 and conductance. Thus, the increase in conductance could be attributed to an electron transfer from ethanol molecule to surface states of PSi. Change in surface charge by electron donating molecules has been reported previously by Lehmann et al [24] in terms of electrical properties of PSi. Conductance change was also observed as a result of change of surface charge for silicon nanowires sensor during the detection of biological and chemical species [25]. Space charge region modulation (SCRM) model has been proposed previously to describe the interaction mode and detection principle of organic solvent with PSi electrical sensor [19]. Briefly, an electrical double layer is formed when PSi surface is exposed to polar organic solvents. The presence of such charged molecules would modify the electrical double layer, and led to changes in the space charge region of silicon structure. Along with a change in dielectric constant inside the porous layer, an electrical signal is accordingly generated. Based on this model, similar sensing response could be induced by any molecule acting as either a negative charge or an electron donor.

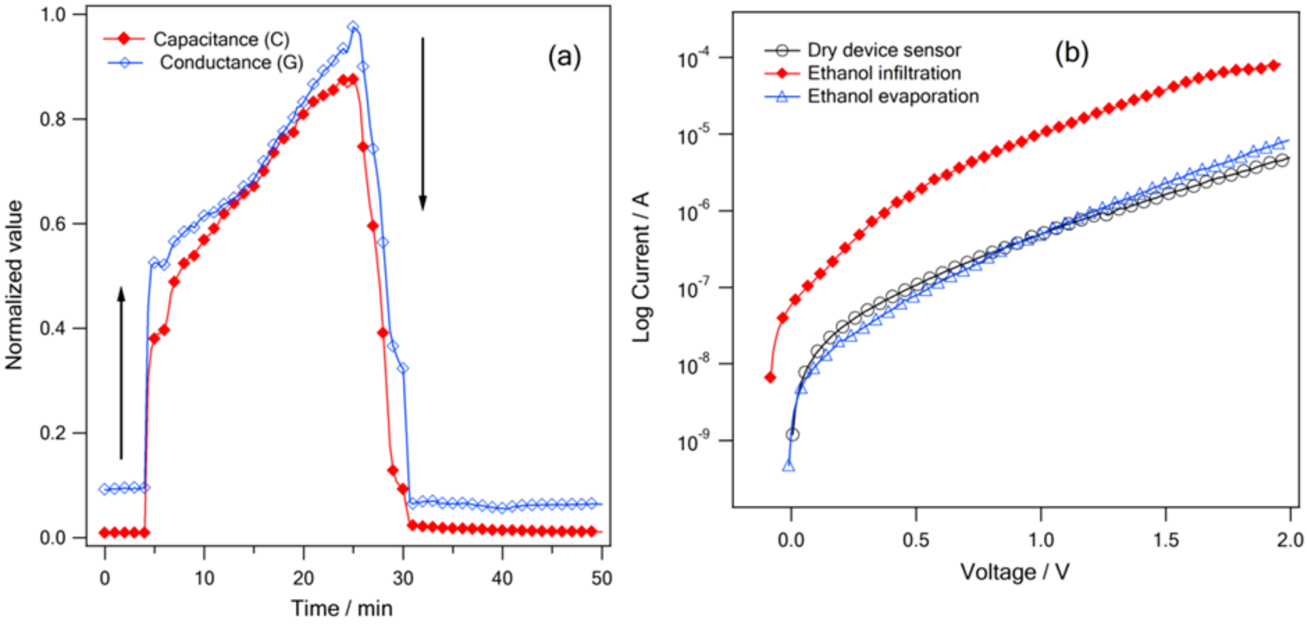

Figure 3. (a) Real-time capacitance (*C*) and conductance (*G*) of sensor measured at 100 kHz, 100 mV at room temperature after exposure to 10 μL ethanol. The vertical up-arrow indicates the injection of ethanol into the sensor device and the down-arrow indicates the evaporation of ethanol from device.(b) Current-voltage curves measured for dry device, after exposure to ethanol and after ethanol evaporation.

If this principally happens in our case, one should expect a reduction in resistance at the interface, which would facilitates the output current of the device. To support this point, we also measured the output current *vs.* bias voltage (*I-V* curves) for the dry device and for the device after ethanol injection. The results shown in Fig.3 (b) reveals an appreciable increase of current after solvent infiltration. The current decays again to its original value upon drying the device. Electron injection from ethanol molecule to PSi surface would build negative charge on the surface, hole accumulation would accordingly lower the resistance path at the interface, which finally led to a preferential current travel through this path. To further confirm such a scenario, we also tested the sensing behavior of the device towards liquid acetone as another electron donating molecule. In fact, an increase in capacitance is observed upon exposure of the surface to acetone, Fig.4. The sensing response towards acetone is found to be highly sensitive, reversible with a very rapid response time (infiltration and recovery times).

As explained above, the present PSi sensor shows a very sensitive and reversible response to liquid ethanol. The observed reversibility indicates no chemical reaction or surface modification has taken place during the sensing process. The sensitivity of the sensor, on the other hand, is defined as the maximum % changes in capacitance and conductance with respect to the reference value. Compared to a previous report of electrical macro-porous sensor [19], the present sensor response is much more sensitive ~10 times larger, but with longer response time ~5 times slower. The response time covers both infiltration and recovery times.

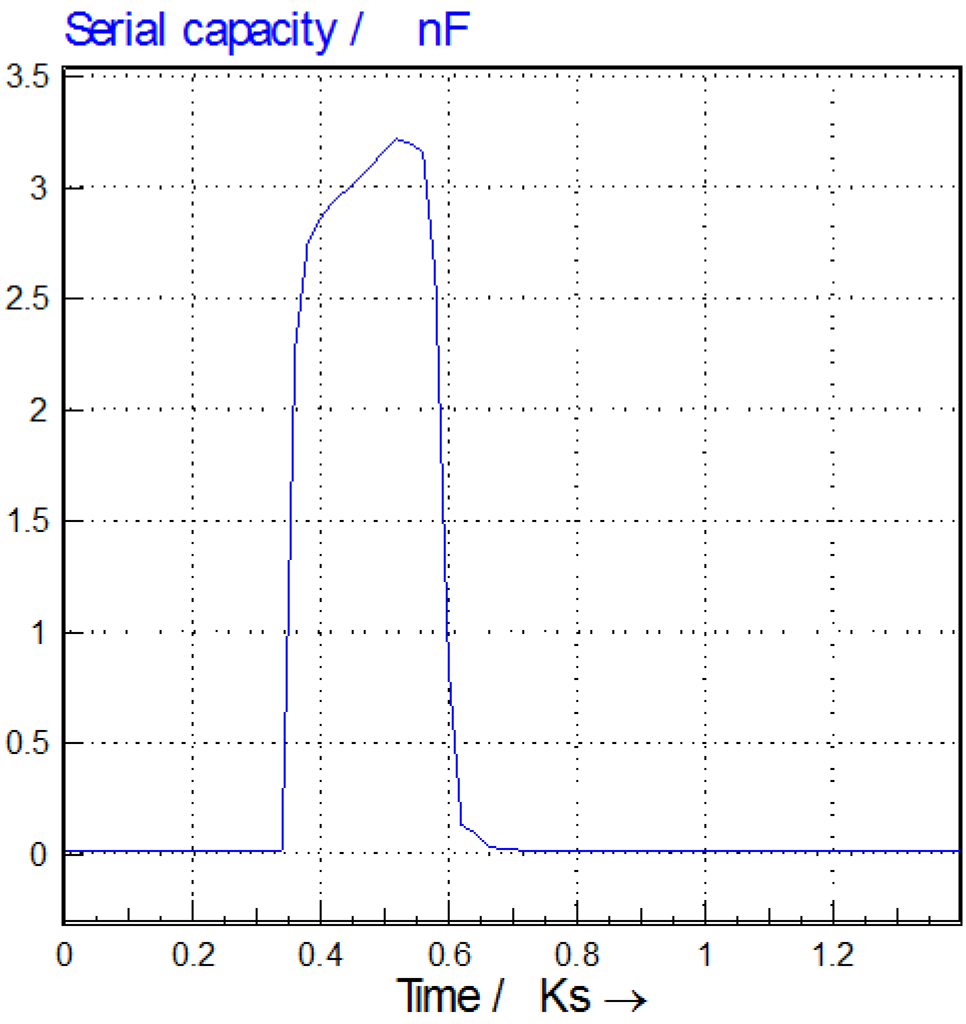

Figure 4. Real-time capacitance response of the sensor after exposure to 10 µL of liquid acetone.

The different behavior is likely related to the different porous structures and the metal contact placement. The present sensor has a mesoporous nature with a front metal contact to the porous layer, while the sensor design in Ref. [19] is a macro-porous structure with a metal contact at the underlying bulk silicon.

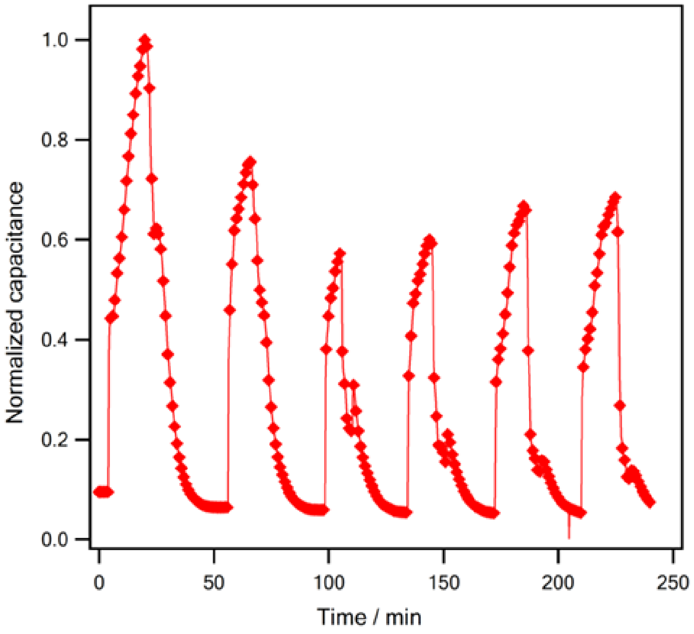

Figure 5. Cycling behavior of the sensor after injection of consecutive ethanol doses; six cyclic tests are shown only, demonstrating stability of the sensor.

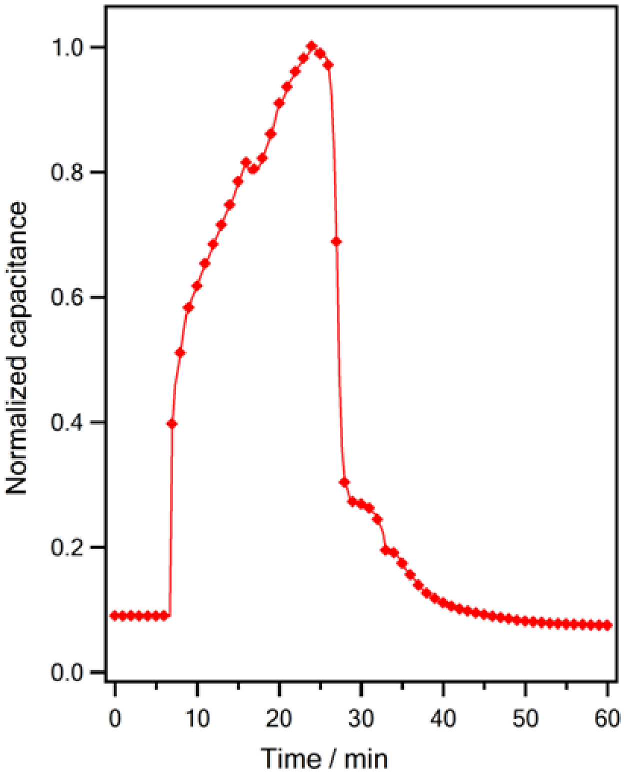

Figure 6. Long-term stability of the sensor towards ethanol sensing after 4 weeks storage.

The sensor response time is essentially affected by the characteristics of porous layer (pore size, porosity and pore thickness), the effective area of device as well as solvent volume and its physical properties. Hence, the response time of the present sensor may indeed be more rapid by considering and controlling the above parameters.

Figure 5 shows the cycling behavior of the sensor exposed to consecutive doses of liquid ethanol. Excellent repeatability of the devise with six different dynamic response curves is observed. For each cycle, complete recovery of the initial capacitance could be detected. The sensor is highly sensitive, exhibiting reliable and stable response-recovery characteristics.

In addition, the long-term stability is also a key factor for practical application and reliable sensor device. Our finding shown in Fig. 6 indicates that the sensor could presumably keep long-term stability over 4 weeks storage. Extending the scope of applications, the present sensor is expected to demonstrate a broad range of utility for detection of other chemical and biological species, which is being underway.

4. CONCLUSIONS

In summary, we have successfully produced an electrical sensor based on meso-PSi layers (30 nm pore size and 4.5 µm pore length) fabricated by electrochemical etching of crystalline silicon wafer. The PSi layers were easily infiltrated with and cleared of the liquid ethanol without damaging the porous matrix. Changes in capacitance and conductance of the device could be readily and repeatedly observed. The sensing response towards ethanol at room temperature was highly sensitive, and the process was reversible and reliable. Thus, the use of the present sensor device provides an inexpensive and easy-to-handle approach to detect a chemical reagent. In addition, the present sensor exhibits excellent long-term response after 4 weeks, indicating that the porous skeleton is stable enough to retain high sensitivity and reversibility.

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