Materials Science-Poland, Vol. 27, No. 2, 2009

A study of the gas specificity of porous silicon sensors for organic vapours

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A porous silicon sensor was investigated as a means to determine the response specificity for organic vapours. Porous silicon layers were fabricated by electrochemical anodization of p-type crystalline silicon in an HF ethanol solution under various conditions. The porous silicon sensors were placed in a gas chamber with various organic vapours, and the changes in electrical resistance under constant voltage of each sensor were used as detection signals. The sensors recorded various changes in resistivity for various organic vapours.

Key words: *porous silicon; response pattern; gas sensor; gas specificity*

1. Introduction

Porous silicon has been widely studied since the discovery of its strong visible photoluminescence [1]. The early research focused on fabrication methods, mechanical structures, electronic band structures, optical constants, and luminescence mechanisms, to name a few [2, 3]. Recent research focus has shifted to applications involving porous silicon based LEDs [4, 5] and various sensors [6–9]. Porous silicon is thought to be an ideal sensor material because of its large specific surface area of approximately 200–800 m^2/cm^3 [10].

To detect various substances including organic gases [11], NO_2 [9], L-glutamine [12], and humidity [13], changes in physical properties of the porous silicon layer, such as electrical resistance [11], photoluminescence intensity [7], capacitance [14], and optical reflectance [15], are used as response signals. Research thus far has focused on porous silicon capacity to detect gas and the properties of the response signal with respect to single gases. Such research has demonstrated porous silicon to be a good candidate for gas sensors. However, there is a paucity of research into the use of porous silicon for detecting gas mixtures. Due to differences in gas properties such

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as molecular weight, dipole moment, adsorption mechanisms on porous silicon surfaces, we can expect differences in electrical response for each gas, and that the intensity of these signals is proportional to the gas densities. Gas specificity of porous silicon sensors is taken from signal intensities specific to a certain gas. It seems more natural to say that different sensors have different specificities. Improvements in specificity can be obtained by using several different porous silicon samples. The results thus obtained are compared. Hence, gas specificity for one gas is acquired if a number of samples used thus allows obtaining precise gas fingerprints.

The acquired gas fingerprints can be incorporated into electronic sniffer systems, and gas composition can then be obtained through data processing. First, however, one should determine if porous silicon could indeed be used to detect a particular gas.

In this paper, we examine gas specificity of electrical signals obtained from the reaction of porous silicon samples prepared under various fabrication conditions, to specific organic vapours. Different electrical signal patterns thus obtained highlight the differences between the sample gasses.

2. Experimental

Porous silicon samples were prepared by the electrochemical anodization process in 10% ethanolic solution of HF using a (100)-oriented p-type single crystal silicon wafer of 0.06–0.12 Ω·cm. Table 1 presents the detailed fabrication conditions for the samples, and the labels given to each sample. The samples were fabricated at various current densities and anodization times with no change in the HF solution concentration. Porous silicon layers of various thicknesses and pore sizes were thus produced. These differences are expected to produce different responses of the porous silicon layers when brought into contact with the target organic gases.

Table 1. Fabrication conditions of porous silicon samples

Sample	HF concentration	Current density [mA/cm^2]	Anodization time [s]
A1	10%	5	1000 s
A2			2000 s
A3			4000 s
B1		10	200 s
B2			500 s
B3			1000 s
B4			2000 s
B5			4000 s
C1		20	100 s

A schematic diagram of our experimental set-up, showing only one sensor for simplicity sake, is shown in Fig. 1. Each sensor unit was biased with a constant 5 V dc between the top surface of the porous silicon layer and the bottom surface of the silicon substrate under the porous silicon layer. A tungsten tipped probe 600 μm in diameter served as a negative electrode (direct contact with the surface of the porous silicon layer), and Al conducting wire served as a positive electrode (attached to the back-side of the Si wafer). The movement of the probe tip over the porous silicon layer surface was precisely controlled by a micrometer to prevent surface damage.

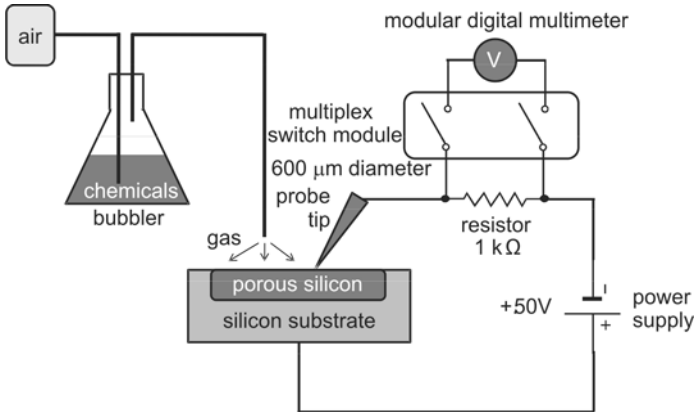

Fig. 1. Schematic diagram of the experimental equipment

The sensors were exposed to an organic gas under gas saturation conditions. Air was used as a carrier gas for the organic vapour, which was generated at room temperature in a vessel containing a liquid solvent such as isopropyl alcohol, ethanol, methanol, acetone, or xylene. The flow of the air introduced into the sample chamber was kept constant during the process and measurement stages. Under these experimental conditions, the gas concentration the samples were exposed to was considered to be nearly constant. The electrical response induced by the reaction between the porous silicon and the organic gas was recorded by measuring the voltage drop across a 1 kΩ resistor connected in a series circuit. The intensity of the measured response voltage increased as the resistance of a sample decreased, and vice-versa. To do this, a digital multimeter (National Instruments, PXI-4072) and a multiplex switch module (National Instruments, PXI-2503) were used.

3. Results and discussion

Cross-sectional scanning electron microscope (SEM) images of the porous silicon layers made with a current density of 10 mA/cm^2 for 100 s and 500 s show many pores between the silicon skeletons in the porous silicon layer (Fig. 2). Target organic va-

pours can penetrate into these pores. The ensuing interaction, under a constant bias voltage, results in an electrical response signal.

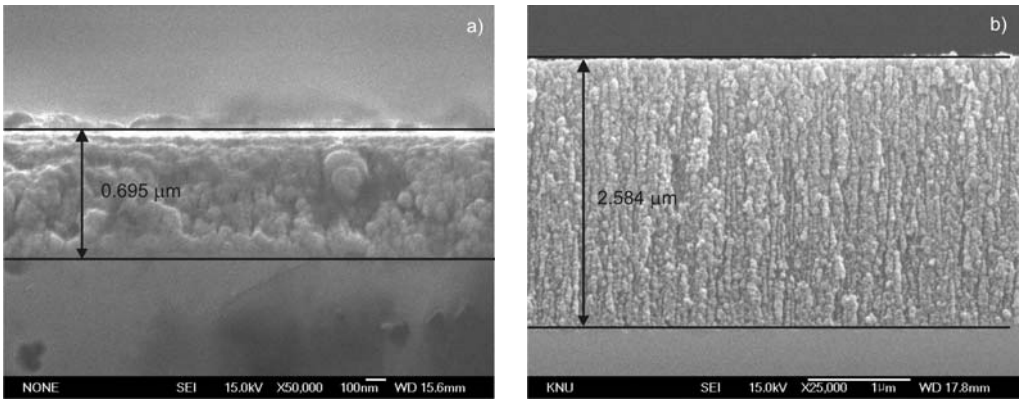

Fig. 2. Cross-sectional images of the porous silicon layers obtained with a 10 HF solution with the current density of 10 mA/cm^2 for: a) 100 s, b) 500 s

There are active studies on the change of the electrical signal when porous silicon is introduced by gas. For example, the conductivity of porous silicon layers increases for both NO_2 and ethanol gases. Measurements indicate that molecules of NO_2 act as acceptor centres [9]. Free carrier (hole) concentration in the porous silicon layers increases, thus increasing conductivity. Increasing conductivity for ethanol gas case is known to be correlated with oxidation of porous silicon layers [16]. Harper and Sailor have shown that reversible photoluminescence quenching of porous silicon is related to layer (molecular oxygen) oxidation [17]. Since O_2 molecules are absorbed into porous silicon layers by either physisorption or weakly chemisorption processes, photoluminescence quenching is due to transient nonradiative electron transfer from the luminescent chromophore in porous silicon by that same oxygen. From this point of view, the phenomenon of enhanced conductivity when porous silicon comes into contact with organic vapours is due to activation of the surface state via layer oxidation.

A typical time evolution of the electrical response signals (sample B5 for five types of organic gases) is shown in Fig. 3. All response signals were normalized to a base voltage in order to compare the signal intensities from various measurements. All response signals were higher than the base voltage during exposure to the gas; this effect indicates that the resistance of the porous silicon layer decreased and correspondingly its conductivity increased; this is consistent with the results of Baratto et al. [16]. Additionally, the response time or the time required to reach 90% of the steady state of the response curve ranged from 0.5 to 6.1 s depending on the organic gas type. These short response times indicate that the porous silicon sample could be used as a sensor, since the minimum response time required for a general sensor is within 20 s [18].

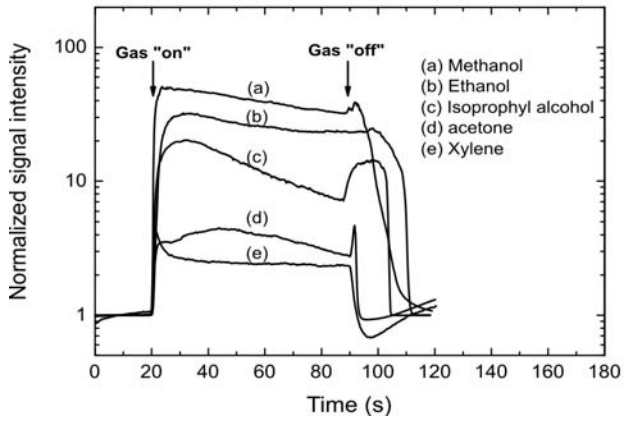

Fig. 3. Time evolution of the response signal
of sample B5 for various organic gases

The normalized intensity of the response signal from the porous silicon sensor differed for each of the gases (Fig. 3). It was the highest for methanol and the lowest for xylene vapour. This result indicates that porous silicon is capable of differentiating gases – an important factor for practical sensor applications using porous silicon. Note that gradual changes in the signals during exposure to the gases, as well as irregular signals that appeared soon after the gas was shut off, were observed. These phenomena, especially the change in signal intensity over time, have been previously reported [7, 9]. They must be resolved if porous silicon is to be used in practical sensing applications. Nevertheless, despite these limitations, the discovery of the gas selectivity of porous silicon is an important finding. For a given gas, electric signals obtained using different fabricated porous silicon samples can produce total specificity. In addition, comparison of electric signal patterns under specific instances can differentiate various organic gases.

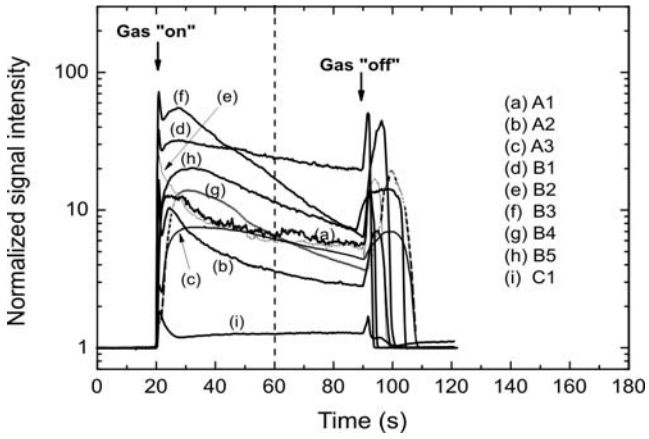

Fig. 4. Time evolution of the response signals measured
from the porous silicon samples for gaseous isopropyl alcohol

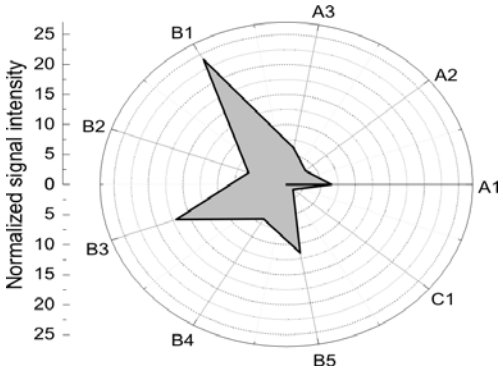

Fig. 5. Polar plot at the time of 60 s under conditions as in Fig. 4

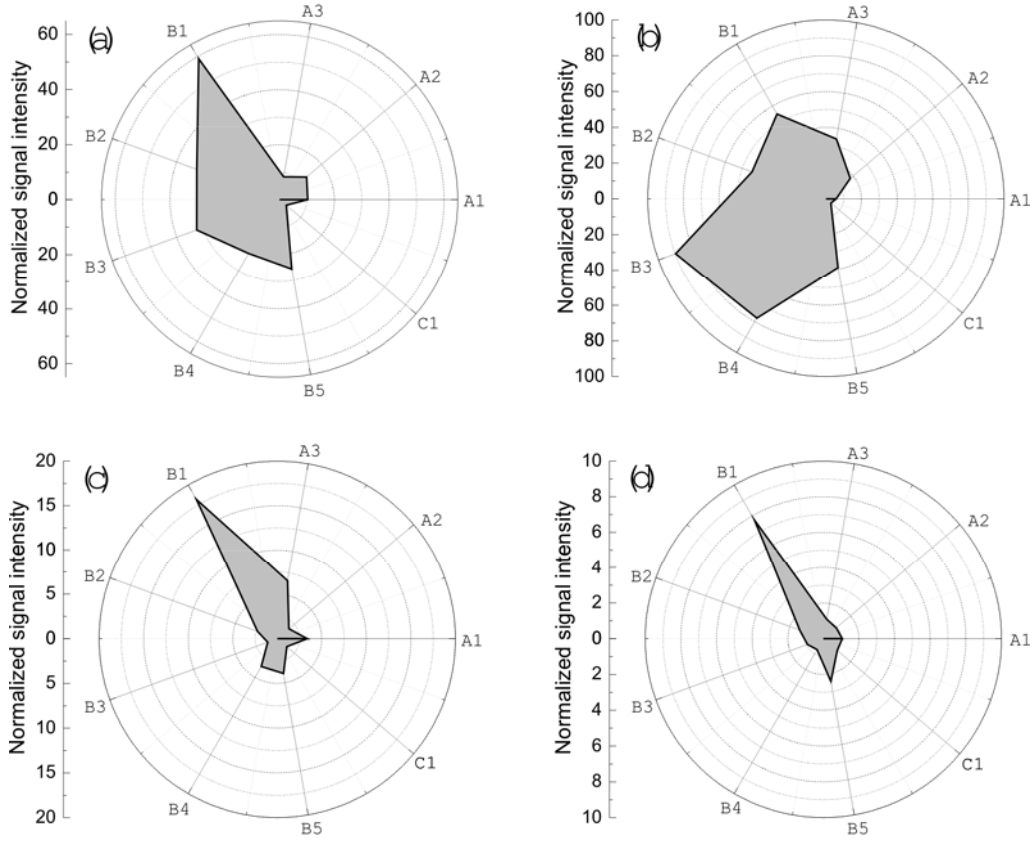

Fig. 6. The response patterns of various organic gases: a) ethanol, b) methanol, c) acetone, d) xylene

The time dependence of the measured response signals using porous silicon, made under various fabrication conditions (Table 1) and an isopropyl alcohol gas, was investigated (Fig. 4). As expected, different response signals were observed for different

sensors. For example, at 60 s, the intensity of the response signal is highest for B1 and lowest for C1. We visualized the gas specificity of sensors through the detection signals patterns. The pattern expressions of the gases are generally expressed in polar coordinates. The resulting image is typically referred to as the gas 'fingerprint'.

Figure 5 shows the results after 60 s under conditions as in Fig. 4. The electrical response signal in Fig. 4 changes in time while it is in contact with the gas, thus it is important to compare the pattern of each gas at the same time. Patterns for various organic gases used in this experiment are different (Fig. 6). These results indicate that porous silicon sensors have gas specificity.

4. Conclusions

The electrical detection specificity of porous silicon sensors have been investigated for various organic vapours. The porous silicon sensors, which were made under various fabrication conditions, were operated under a constant voltage without any modifications of sensing efficiency such as surface modification or heaters. The results indicate that the sensors produce different response signals and patterns for different gasses, indicating a gas specificity. However, an unstable nature of the response signals is an issue that should be addressed in future research.

Acknowledgement

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (No. KRF-2007-331-D00245).

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Received 23 April 2008
Revised 29 November 2008