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2001 J. Phys. D: Appl. Phys. 34 3505

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Organic vapour sensing by current response of porous silicon layer

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Received 8 June 2001, in final form 7 September 2001

Published 5 December 2001

Online at stacks.iop.org/JPhysD/34/3505

Abstract

In this paper, a porous silicon (PS) layer is investigated as a sensing material to detect organic vapours with low concentration. To do this, PS sensors with membrane structure were designed and fabricated. The sensors were made by applying the technologies of membrane formation by anisotropic etching of silicon and PS formation by anodization in HF solution. From fabricated sensors, current–voltage (I – V) curves were measured for ethanol (called alcohol), methanol and acetone gases evaporated from 0.1–0.5% solution concentrations at 36°C. As a result, all curves showed rectifying behaviour due to a diode structure between Si and the PS layer. The conductance of our sensors mostly increased along with the organic solution concentration at a high voltage of 5 V, but the built-in potential on the measured I – V curve was lowered with it by the adsorption effect of the organic vapours with high dipole moment.

1. Introduction

Since porous silicon (PS) was suggested as a potential optical material after the observation [1] of specific photoluminescence phenomena, it has invoked much interest in the development of new silicon light emitting devices. In addition, PS has also received much attention as a material applicable to chemical sensors as well as the electronic material or sacrificial layer [2] in current fabrication technologies. In recent years, papers dealing with the sensing characteristics of PS layers have been published owing to the high sensitivity due to their large internal surfaces. Many of them proposed to monitor the variations of electrical conductivity or capacitance by gas adsorption on the PS layer. The first gas sensors suggested were humidity sensors [3], where the capacitance variation of the PS layer was studied throughout the range of 0–100% relative humidity, consequently resulting in a 440% increase in capacitance. A high sensitivity of the PS layer was also shown for organic vapours such as ethanol, methanol or acetone with high dipole moments [4–7].

In this paper, the current response of a pure PS layer against organic vapours such as ethanol, methanol and acetone is quantitatively discussed. Generally, the applications of PS gas sensors are suitable for detecting organic gases with high

dipole moment and high vapour pressure. But the electrical response of the PS layer for these organic gases can lead to remarkable differences depending on the oxidation of the PS surface. Silicon treated in HF is hydrophobic while an oxidized PS layer is hydrophilic.

Our sensors were fabricated as a membrane structure available for blocking some heat transport into neighbouring circuits in chemical sensor systems that often use a heater to enhance the sensitivity. In the future, research on membrane structure will be activated further in view of current trends toward integrated sensors that include a variety of on-chip signal processing functions on a substrate.

2. Experimental

Owing to the doping dependence at forming PS layers, double-side polished p-type (100) 4 inch silicon wafers with a resistivity of 0.1 Ω cm were used as substrates to fabricate PS layers and membrane structures. In our fabrication process, the formation of PS layers was done as the final step to maintain a clean PS layer without accumulation of any contamination layer on it.

As the first step, a p-type epitaxial layer of 10^{15} cm⁻³ concentration with a thickness of 20 μ m was grown on the

wafers at 1120°C. An n⁺-layer was made by ion implantation after forming a patterned oxide with a thickness of 0.5 μm as a mask layer, and then annealed at 800°C for 12 h in nitrogen atmosphere. Therefore, the front-side surface of the substrates is divided into p and n⁺ areas. Next, to form a membrane structure by back-side etching, a thermal oxide was grown to a thickness of 0.6 μm to be used as a mask layer during anisotropic wet etching. The anisotropic etching for the membrane structure was performed in 20% tetramethyl ammonium hydroxide (TMAH) solution heated to 85°C for 14 h. TMAH solution is often used to replace KOH which may introduce contaminations by alkali metal, or ethylene diamine pyrochatechol (EDP) which is harmful to the human body. After back-side etching, the thickness of the membrane was about 90 μm, and the membrane structure still maintained enough mechanical strength. After the remaining oxide was stripped, a nitride layer was deposited by low pressure chemical vapour deposition (LPCVD) with a thickness of 0.4 μm at 750°C to passivate both sides of the wafers. After contact holes at the front side of the wafers were formed, Al metallization was followed. Finally, a PS layer was formed by anodization at conditions shown in table 1, after positive photoresist was used as a mask layer on the wafers. Figure 1 indicates a schematic diagram of our designed sensors. In this work, 25 (5 × 5) sensors per wafer were fabricated, and the size of a sensor is 3.5 × 3.5 mm². A fabricated sensor which is completed up to wire bonding is shown in figure 2.

Figure 3 indicates a set of measurement equipment. As shown in this figure, organic gases were generated by evaporation from organic solution diluted from 0.1% to 0.5%

concentrations by distilled (DI) water. The experiment is aimed at estimating the sensitivity of our sensors against organic vapours such as ethanol (called alcohol), methanol and acetone. Before exposure to organic vapours, the sensors were cleared with nitrogen gas, and then gas mixture containing these organic vapours was blown on the PS surface. Here, to adjust our experiment with conditions of typical breath alcohol measurement, the sensors were fed with gas mixture evaporated from organic solution at 36°C close to the temperature of the human body. Formally, the traffic violations about drinking and driving are defined as alcohol concentration included in blood, and the penalty is imposed when the alcohol concentration in blood usually exceeds 0.05% even though the regulations are different in each country.

The measurement of electrical properties was carried out with a semiconductor analyser to observe *I-V* curves under the bias voltage from 0 to 5 V, where a serial resistor of 1 kΩ was connected to prevent overshooting. *I-V* curves were measured after 30 s from exposure to gases. Since the organic vapours treated in our work have very low concentration and strong volatility, the sensors were returned to the original state after our sensors were purged by nitrogen.

Table 1. Anodization conditions for the formation of PS layer.

Parameters	Conditions
Substrate	0.1 Ω cm, (100) p-type 4 inch Si wafer
HF concentration	25%
Current density	120 mA cm ⁻²
Anodization time	2 min

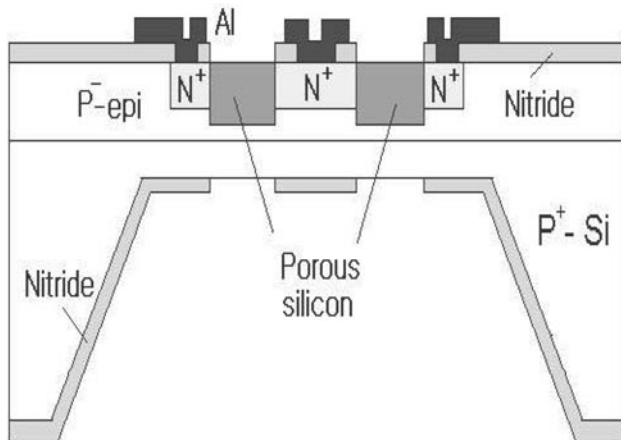


Figure 1. Schematic structure of our PS sensor.

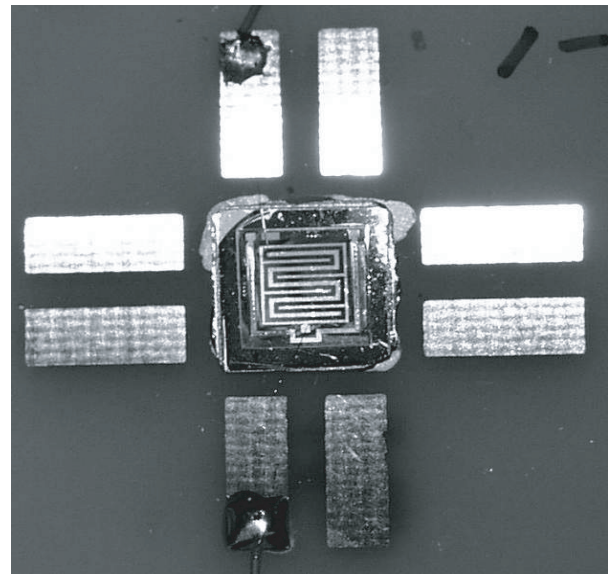


Figure 2. Photograph of a fabricated sensor.

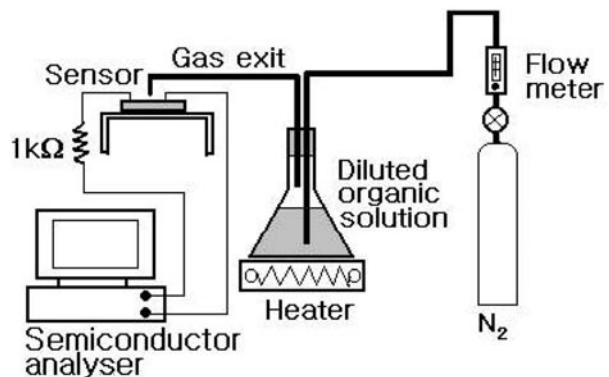


Figure 3. A set of equipment for measuring *I-V* curves.

3. Results and discussions

All the properties of the PS layer, such as porosity, thickness, pore diameter and microstructure, strongly depend on the anodization conditions. The data given here were obtained by anodizing wafers in the dark at room temperature without stirring the HF solution. First, we examined a PS layer formed on a p-type epitaxial layer of 10^{15} cm^{-3} concentration under the conditions mentioned in table 1 with a SEM as shown in figure 4. Most pores were shaped irregularly with large porosity as shown in figure 4(a), and the thickness of the PS layer was found to be about $3 \mu\text{m}$ as shown in figure 4(b). As shown in these figures, since the size of pore diameter is found to be over $0.1 \mu\text{m}$ as a whole, there are no quantum effects expected in our PS layers. Therefore, the mechanism of the current response can be explained by both the electrical transport properties in a PS-Si diode structure and the charge transfer reaction that occurs during the adsorption at the PS surface.

Chemical sensors based on PS layers are generally used to examine chemical concentrations in the liquid or gas phase by observing a variation of conductance or capacitance of these devices. In this paper, the current response was analysed

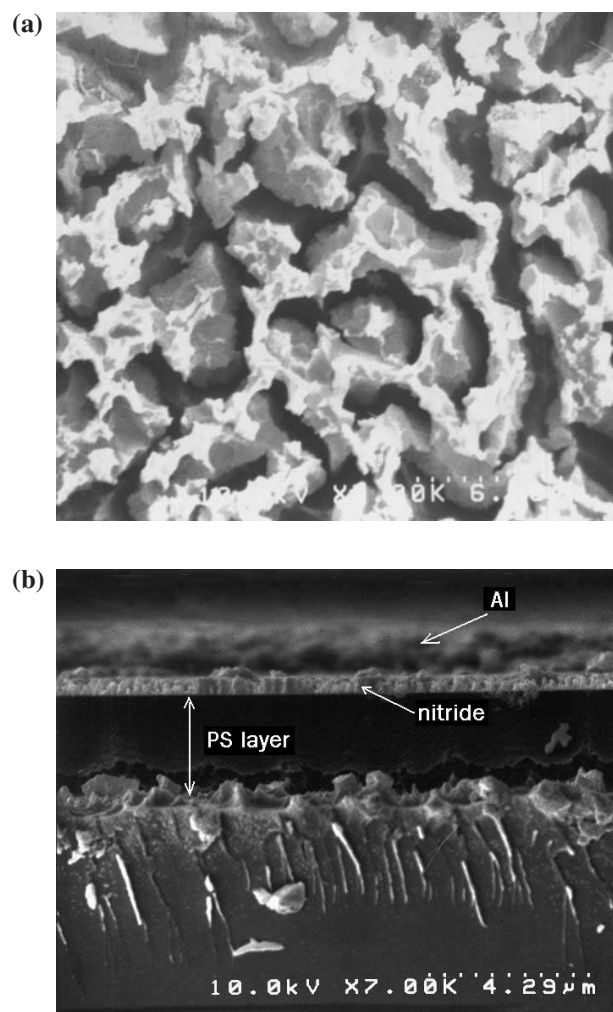


Figure 4. SEM photographs of a PS layer: (a) top view and (b) cross section.

for 0–5 V bias voltage against ethanol, methanol and acetone vapours evaporated from 0.1–0.5% solution concentrations. The measurement was carried out according to the same principle applied to breath alcohol meters usually used at testing drinking and driving violation, except that nitrogen gas was supplied via water kept to 36°C instead of blood. Figure 5 indicates I – V curves measured for ethanol, showing a non-linear shape. While I – V curves had quite a small slope below the applied voltage of 3 V (or below the electric field of $1 \times 10^4 \text{ V m}^{-1}$), the current increased rapidly above an applied voltage of 3 V. Such a rectifying nature in the current response is caused by a diode structure between the p-type PS and the n-type Si layer. At the maximum applied voltage of 5 V, the current rose from 15 to $125 \mu\text{A}$ when the ethanol concentration increased from 0% to 0.5%. Figure 6 indicates the magnitude

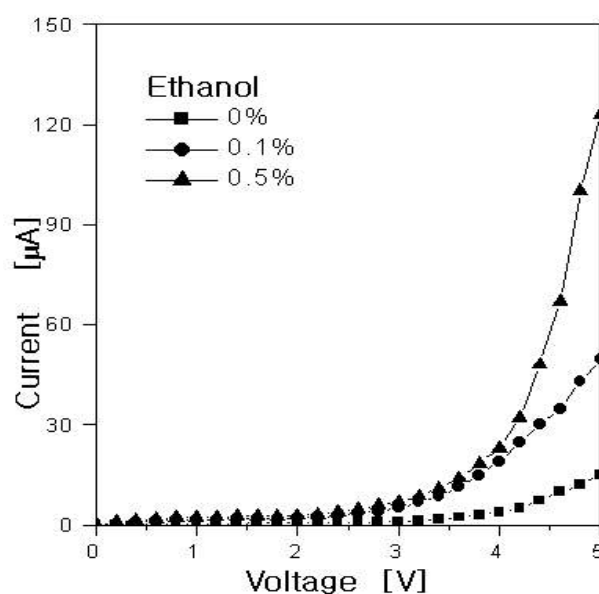


Figure 5. I – V curves measured for ethanol.

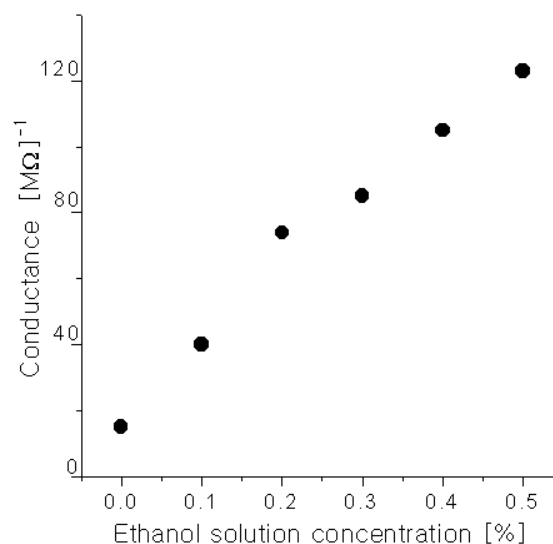


Figure 6. Dependence of conductance on ethanol solution concentration at 5 V.

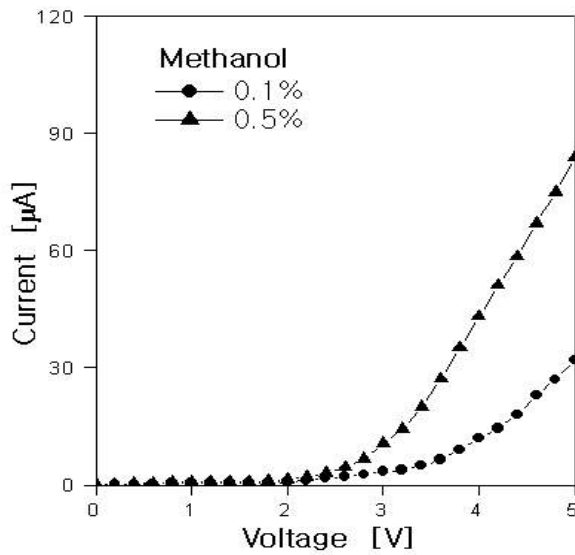


Figure 7. I - V curves measured for methanol.

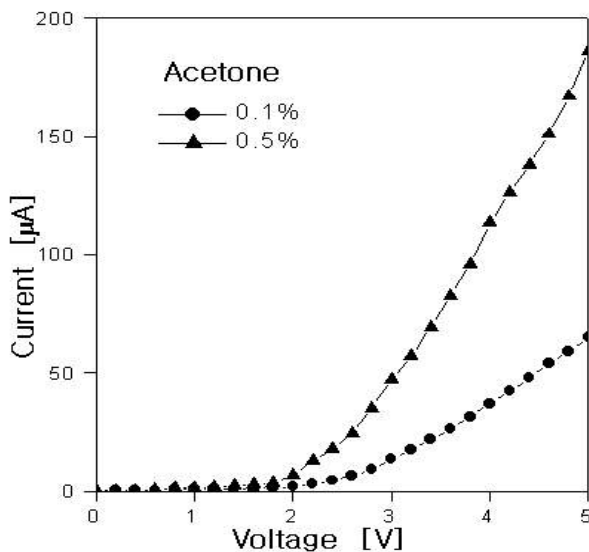


Figure 8. I - V curves measured for acetone.

of the conductance measured in concentration intervals of 0.1% at an applied voltage of 5 V, showing nearly a linear increase. Such results show that the sensitivity is enhanced effectively at high voltages, and that our sensors possess efficient sensitivity to detect even concentrations below 0.1%. We tried the same measurements for methanol and acetone as performed for ethanol. The results also showed rectifying behaviour in I - V curves similar to the ethanol case, as shown in figures 7 and 8, respectively, in which the built-in potential was lowered somewhat in comparison with that of ethanol.

If the PS layer provides high adsorption to certain organic vapours, the current response will be further enhanced. However, the adsorption magnitude of organic vapours at the PS surface is different according to surface state and types of organic vapours. Especially it has been known that the oxidation treatment of PS surfaces has a considerable effect

Table 2. Dipole moment and vapour pressure of organic materials used in this study.

Compound	Dipole moment (debye)	Vapour pressure (torr)
Ethanol	1.69	59
Methanol	1.7	128
Acetone	2.88	233

on the adsorption due to the fact that HF-treated silicon layers [5] are hydrophobic in nature while oxidized PS layers [4] are hydrophilic. For the latter the conductivity response is negligible to methanol and acetone vapours, while for the former it is sensitive to all of these organic vapours. Ethanol is very permeable into the silicon wafer, so that high sensitivity is observed in both cases. The PS layers in our sensors were not oxidized, and therefore a high current response was observed for all of these organic vapours due to large dipole moment and high vapour pressure as shown in table 2.

In principle, the vapour adsorption at the PS layer leads to a change of the dielectric constant of the PS layer because the adsorbed vapours can easily condense into a liquid in the microcapillaries of the PS layer. In the paper [5], it has been reported that a many-fold of current increase appears at exposing the PS layers to organic vapours with large dipole moment. In addition, we found from I - V curves that the built-in potential was reduced somewhat when the vapour concentration was increased. The built-in potential in a p-n junction can be expressed as equation (1) by the depletion approximation.

$$V_{bi} = \frac{qNx^2}{2\epsilon_r\epsilon_0}, \quad (1)$$

where V_{bi} is the built-in potential, q the electron charge, N and x the doping density and the depletion-layer width respectively, ϵ_0 the permittivity of free space and ϵ_r the relative dielectric constant of the conductor. From equation (1), we can see that the built-in potential is inversely proportional to the relative dielectric constant. Therefore, in the case of acetone with the highest dipole moment among organic vapours treated here, the built-in potential becomes smallest, and close to 2 V as shown in figure 8.

However, the dipole moment and vapour pressure are not the only physical factors that affect the conductivity. As mentioned before, we should consider the adsorption effect of molecules as a supplementary reason for the enhancement of PS conductivity. Even though methanol has a higher dipole moment than ethanol, the relatively low response is probably due to a weak physical adsorption to silicon.

4. Conclusions

PS sensors possess many merits of the characteristics required for chemical sensor development. Among them, the fact that PS sensors can be constructed on a standard silicon wafer and process is sufficient to attract attention with other silicon-based devices.

This study is based on the variations of the electrical conductivity when a PS layer is exposed to organic vapours. From fabricated sensors, I - V curves were measured from

0 to 5 V against ethanol, methanol and acetone gases evaporated in 0.1–0.5% solution concentrations. As a result, I – V curves showed a rectifying behaviour and it was found that the built-in potential in I – V curves was lowered with the increase of vapour concentrations. Since the built-in potential is dependent inversely on the relative dielectric constant of the PS layer, its values were decreasing in the order of ethanol, methanol and acetone according to the magnitude of their dipole moment. In addition, we discovered significant changes in the electrical conductivity at applying high voltage, where the adsorption effect to the PS surface should be considered additionally.

In conclusion, the current response of our PS sensors provided not only enough sensitivity for organic vapours with low concentration, but the shift of the built-in potential for various organic vapours might allow a way to distinguish among different organic vapours.

Acknowledgments

This study was supported by the academic research fund of Kyungnam University and the Share-ISRC Program

through Inter-University Semiconductor Research Center in 2000.

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