

Electrical Properties of Alcohol Vapor Sensors Based on Porous Silicon

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Abstract

In this work, we fabricated a gas-sensing device based on porous silicon(PS), and its C-V properties were investigated for sensing alcohol vapor. The structure of the sensor consists of thin Au/oxidized PS/PS/p-Si/Al, where the p-Si is etched anisotropically to be prepared into a membrane-shape. We used alcohol gases vaporized from different alcohol (or ethanol) solutions mixed with pure water at 36°C, similarly with an alcohol breath measurement to check drunk driving. As the result, I-V curves showed typical tunneling property, and C-V curves were shaped like those of a MIS (metal-insulator-semiconductor) capacitor, where the capacitance in accumulation was increased with alcohol vapor concentration

Key Words : Porous silicon MIS alcohol sensor

1. INTRODUCTION

As drinking alcohol affects the ability to safely operate dangerous equipment such as automobiles, motorboats and industrial equipment, it is strictly prohibited by the law to operate an automobile if one is so under the influence of alcohol that he cannot safely operate the motor vehicle. When one drinks alcohol, alcohol is absorbed into blood stream. If the alcohol level in blood is greater than 0.1%, one is presumed to be too intoxicated to safely operate an automobile and punished in most countries. Therefore, various test meters have

been developed to measure the level of alcohol in blood to check drunk driving.

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, the porous silicon has also received much attention as a material applicable to chemical sensors[2-4] based on its large internal surface area, while metal oxide[5] or polymer[6] has been used as typical detecting layer.

In this work, we fabricated a gas-sensing device based on porous silicon, and its C-V properties were investigated for sensing alcohol vapor. Our porous silicon sensors can be regarded as MIS capacitors due to thin oxidized porous silicon layer formed rapidly at high temperature. We measured C-V curves as a function of alcohol solution concentration which provide information such as the flat-band voltage shift and the magnitude of the oxide capacitance.

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2. EXPERIMENTAL

Boron-doped, (100) p-type, Si wafers with resistivity of 20cm were used as substrates. The substrates were deposited with nitride layer by LPCVD with a thickness of $0.4\mu\text{m}$ at 750°C . After patterning the nitride layer, they were etched anisotropically to reduce thickness as shown in a schematic diagram of Fig.1(a). The wet etching was carried out in 20% TMAH (Tetramethyl ammonium hydroxide) solvent for 14 hours at 85°C . Consequently the remaining thickness of the substrates was about $150\mu\text{m}$, and the bottom area of membrane structure was 9mm^2 . These etched substrates were prepared to form porous silicon layer by anodization in a 1:4 volume solution of HF (49% in water)-ethanol, where the applied current density was $100\text{mA}/\text{cm}^2$ and the anodization was performed for 4 minutes. Next, the surface of the porous silicon layer was oxidized shortly to improve stability with regard to ageing effects of porous silicon. The oxidation of the porous silicon layer was carried out by use of rapid thermal oxidation at 1000°C for 30 seconds. Metallization was carried out with thin Au/Cr (300nm thickness) to make an electrode and a guide ring on the top, and the Au/Cr layer at the center was removed by $1.5\times 1.5\text{mm}^2$ to disclose porous silicon layer into the air, and then an Al electrode was formed on the backside of the substrates to ensure ohmic contact. In this work, thin gold contact was used as semitransparent electrode, allowing vapor to pass through the micro pores in the gold film. A completed sample is shown in Fig.1(b).

Figure 2 indicates a set of measurement equipment. To adjust our experiment with conditions of typical breath alcohol measurement, it was fed with gas mixture vaporized from alcohol solution at 36°C close to the temperature of human body. As shown in this figure, gas vaporized from alcohol solution warmed up by a heater is injected to a chamber with N_2 gas as carrier gas through a tube. Every measurement was carried out after 30 seconds from exposure

to gases. Current-Voltage (I - V) measurement was carried out with a dc power meter to observe the current under bias to Au electrode from -2 to 2V . C - V curves were measured using a LCR meter and a power supply unit which provides both dc bias voltage and ac signal, where the bias was applied from zero to 2V .

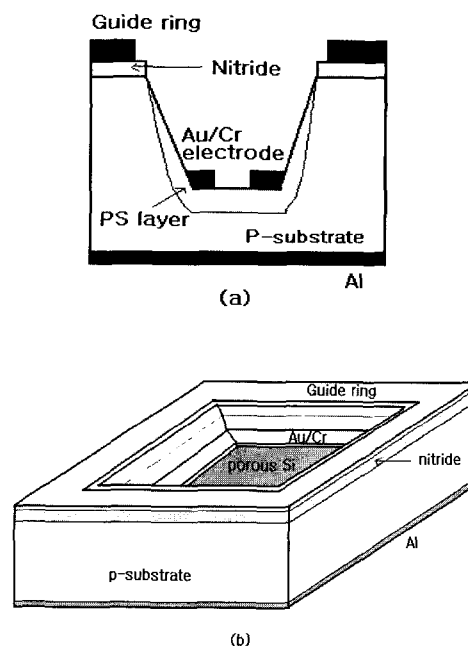


Fig. 1. Schematic diagram of the cross section (a) and the structure(b).

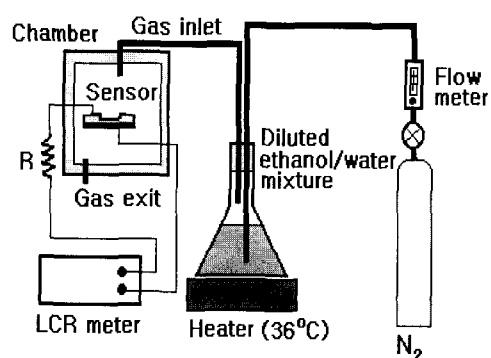


Fig. 2. Scheme of the apparatus for gas sensing measurement.

3. RESULTS AND DISCUSSIONS

The structure of our device consists of Au/oxidized PS/PS/p-Si/Al. Since the thickness of the oxidized porous silicon layer formed by rapid thermal oxidation is very thin, the device can be regarded electrically as a MIS (metal-insulator-semiconductor) tunnel diode. However, as the thin insulating layer (oxidized porous silicon layer) is formed on a nondegenerate semiconductor substrate, no negative resistance is expected. Fig.3 shows current and capacitance measured as a function of bias to Au electrode at room temperature without any injection of vaporized gas. As shown in Fig. 3(a), I-V curves were determined by tunneling current I_t which is expressed as

$$I_t \propto T e^{-q\phi_n/kT} (e^{qV/kT} - 1), \quad (1)$$

where T is the tunneling probability, B the barrier height, and V the applied bias. Under forward bias (negative bias to Au electrode), dominant current is an electron tunnel current from metal to the conduction band, and increases monotonically with the increasing energy difference between two Fermi levels (of metal and p-type Si) which is directly proportional to the applied voltage. However, under reverse bias (positive bias to Au electrode), the surface is in depletion, and the rate of carrier supply is reduced. As a result, the current was limited by reverse saturation current, lowered considerably than under the forward-bias.

Figure 3(b) shows C-V curves measured as a function of bias with frequency (500Hz and 1MHz) of the ac small-signal voltage as parameter, where the axis of capacitance indicates a normalized capacitance divided by the capacitance measured at $V=0$. C-V curves were shown similarly to those of a typical MIS(metal-insulator-semiconductor) capacitor with the p-type substrate. At the low frequency(500Hz) C-V curve, stretch-out,

lowering of the slope in C-V curve, was found in depletion due to moderate response time of interface-trapped charges. The high-frequency (1MHz) C-V curve was saturated into a minimum value in strong inversion, almost independent of the bias because minority carrier density does not change with rapidly varying ac signal.

We observed the flat-band voltage shift from the measured C-V curves. The experimental capacitance-voltage curve is shifted from the ideal theoretical curve by an amount

$$V_{FB} = \phi_{ms} - \frac{Q_o}{C_{ox}}, \quad (2)$$

where V_{FB} is the flat-band voltage shift, ϕ_{ms} the work-function difference between metal electrode and silicon substrate, and Q_o the oxide charge, and C_{ox} the oxide capacitance. The oxide charges include oxide fixed charge, oxide trapped charge and mobile ionic charge. V_{FB} is dependent on the work-function difference as seen in Eq.(2). The metal-to-insulator work function is 4.15V for the Au-SiO₂ system, while the work function for p-type Si (about $20\Omega\text{cm} \cong 5 \times 10^{14} \text{cm}^{-3}$) is calculated to be about 4.1V. Therefore the work function difference ϕ_{ms} is a little positive, close to zero. In our samples, since V_{FB} is observed about 0.4~0.5V as shown in Fig. 3(b), it turns out that the shift is caused dominantly by oxide charges. Generally the flat-band voltage shift is affected by both the magnitude and polarity of oxide charges. As most oxide charge has positive polarity by dangling bonds near the SiO₂-Si interface or mobile alkali ions such as sodium, it results in a shift of the C-V curve toward more negative bias. However, in our case the flat-band voltage was shifted to more positive voltage which might be caused by trapped negative oxide charge. In our case the existence of the negative oxide charges is supposed to originate from HF-treated process during anodization. Generally under anodization, positive bias is applied to p-type substrate to supply hole charges from

semiconductor into surface, while to move fluorine ions from solution into surface. That is, there exist abundant fluorine ions at surface, and it is inferred that fluorine ions which are not removed completely in pores during cleaning process are trapped during the following oxidation process, and consequently they play a role as negative oxide charges.

Figure 4 shows high-frequency C-V curves measured with no vapor, and under exposure of alcohol gases vaporized from 0, 0.1 and 0.2 % alcohol solutions, respectively. Since at high-frequency(1MHz) interface traps do not respond to the ac signal voltage, high-frequency C-V measurement can provide stabilized C-V curves. The measurement was carried out similarly to breath alcohol measurement used at testing drinking and driving violation.

The total capacitance C_{HF} of a MIS capacitor at the high frequency(1MHz) is given as the series combination of the silicon capacitance and the oxide capacitance.

$$C_{HF} = \frac{C_s C_{ox}}{C_s + C_{ox}}, \quad (3)$$

where C_{ox} is the oxide capacitance and C_s is the silicon capacitance. For a given insulator thickness, the value of C_{ox} is constant and corresponds to the maximum capacitance of the system in accumulation. Generally porous silicon layer can be regarded as a complicated dielectric material, where its dielectric constant is affected by various components such as air, water vapor and alcohol vapor impregnated in pores. Therefore the oxide capacitance in this work means an equivalent capacitance which includes additive dielectric components by air, water vapor and alcohol vapor in pores as well as the oxide.

In accumulation, the total capacitance is nearly determined by the oxide capacitance. In Fig. 4 it is found that the total capacitance increases from 2800 to 4400pF at applied bias $V=0$, when the alcohol solution concentration is changed from 0 to 0.2%. Instead, under no exposure of

any vapor, the capacitance is observed to be 660pF at $V=0$. In principle, the vapor adsorption at porous silicon layer leads to a change of the dielectric constant of the porous silicon layer (including oxidized porous silicon layer) because the vapor adsorbed in pores can easily condense into a liquid in the micro capillaries of the porous silicon layer. Alcohol has a high relative permittivity (24 at 25 °C) and is very volatile, so it becomes strongly vaporized even at low temperature of 36°C and then the capacitance can be largely changed for small variation of alcohol solution concentration.

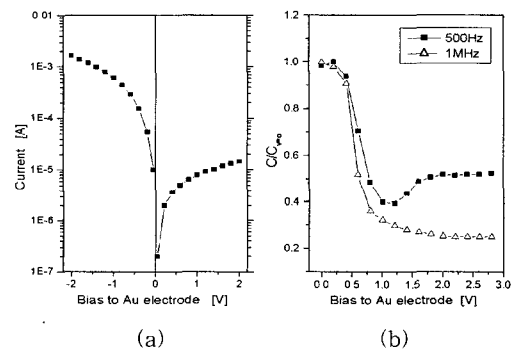


Fig. 3. Current (a) and normalized capacitance (b) measured without any injection of vapor.

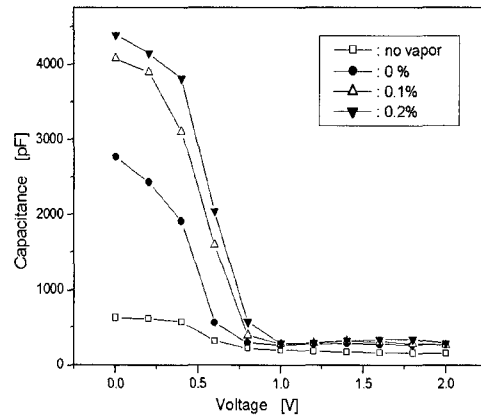


Fig. 4. C-V curves in different alcohol solution concentrations.

We also observed the change of the flat-band

voltage shift from C-V curves. From Eq.(1), it is found that the flat-band voltage is influenced by both the oxide charges and oxide capacitance. By vapor adsorption, the magnitude of interface oxide charge and trapped oxide charge may be changed. However, since they cannot respond to rapidly varying ac signal in high-frequency C-V measurement, the change in V_{FB} by these components is hardly expected, and rather the negative shift of the flat-band is supposed to be due to the increase of the equivalent oxide capacitance with increasing dielectric constant. The flat-band voltage shift was moved approximately to zero voltage when the alcohol solution concentration was increased to 0.2%.

4. CONCLUSIONS

This study based on the variations of the electrical properties of porous silicon by vapor adsorption has demonstrated that porous silicon can be used for alcohol vapor sensing. From the C-V curves in accumulation, about 160% increase in capacitance in response to a small change of alcohol solution concentration from 0 to 0.2% proves that porous silicon sensors provide sufficient sensitivity for alcohol vapor with low concentration. Property of the flat-band voltage shift provided information about the existence of negative oxide charge and dependence on alcohol vapor concentration. In conclusion, we showed that the variation in C-V curves is measurable and detectable when low-concentration alcohol vapor is exposed to the porous silicon surface.

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