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다공질 실리콘 구조를 이용한 화학 및 바이오 센서

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Porous silicon-based chemical and biosensors

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Abstract - In this study, two types of PS substrate were fabricated for sensing of chemical and biological substances.For sensing of the humidity and chemical analytes such as CH_3OH or C_2H_5OH, PS layers are prepared by photoelectrochemical etching of silicon wafer in aqueous hydrofluoric acid solution. To evaluate their sensitivity, we measured the resistance variation of the PS diaphragm. As the amplitude of applied voltage increases from 2 to 6 Vpp at constant frequency of 5 kHz, the resistance variation for humidity sensor rises from 376.3 to 784.8 Ω / %RH. And the sensitivities for CH_3OH and C_2H_5OH were 0.068 uA/% and 0.212 uA/%, respectively. For biological sensing application, amperometric urea sensors were fabricated based on porous silicon(PS), and planar silicon(PLS) electrode substrates by the electrochemical methods. Pt thin film was sputtered on these substrates which were previously formed by electrochemical anodization. Poly (3-methylthiophene) (P3MT) were used for electron transfer matrix between urease(Urs) and the electrode phase, and Urs also was by electrochemically immobilized. Effective working area of these electrodes was determined for the first time by using $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple in which nearly reversible cyclic voltammograms were obtained. The i_p vs. $\upsilon^{1/2}$ plots show that effective working electrode area of the PS-based Pt thin film electrode was 1.6 times larger than the PLS-based one and we can readily expect the enlarged surface area of PS electrode would result in increased sensitivity by ca. 1.6 times. Actually, amperometric sensitivity of the Urs/P3MT/Pt/PS electrode was ca. 1.55 uA/mM·cm^2, and that of the Urs/P3MT/Pt/PLS electrode was ca. 0.91 uA/mM·cm^2 in a linear range of 1mmol/L to 100mmol/L urea concentrations

1. Introduction

Porous silicon(PS) is a nanocrystalline material with a large specific surface area, making it an ideal candidate for gas- (or vapor) and liquid sensing applications.

Several types of porous silicon-based humidity sensors have been reported such as a capacitive type and a resistivetype. In the capacitive type, water vapor absorbed on the porous silicon surface causes capacitance change of sensing electrode due to an alteration of relative permittivity of dielectrics. Anderson et al. reported the beginning paper about the capacitive humidity sensor using porous silicon. They observed that the capacitance changed up to 440 % as the humidity varied from 0 to 100 %RH. On the other hand, in the resistive type, absorbed humid gas causes the conductivity change of sensing electrode to vary the I-V characteristics of the sensor. Tsu and Babic were discussed the conductivity increment in liquid. However, not only liquids but also polar vapor induces the conductivity of porous silicon layer to increase by orders of magnitude, as reported by Ben-Chorin et al. In this paper, we present bulk silicon-eliminated porous silicon diaphragm structure to show the conductivity variation only in the porous silicon layer Pt(Platinum)/Ti(Titanium) layers are used as a masking material to restrict the pore growth within a diaphragm region. Also, metal layers play a role of ohmic contact material that enable carrier to be injected into porous silicon layer.

The application fields of biosensor are extremely diverse for example, medical science, environmental engineering, food engineering etc. Among them medical sensor is widely investigated for the in-line, real-time, and in-vivo measurement of the patient's states. Recently, many research groups are interested in the micro-biosensors based on semiconductor technologies. However, provided that the micro-biosensors have very small areas of sensing electrode, its sensitivity would be deteriorated and the electrodeposition of polymer and enzyme becomes difficult. To resolve this kind of problems, PS biosensors have been represented. But, in case of coated PS biosensors, a drop of enzyme solution is just sprayed on the PS surface, so the bonding between them is too weak and the reproducibility is unsatisfactory. This paper reports the characteristics of Pt deposited PS based urea sensor as a basic experiments applicable to micro-biosensor. Urease is immobilized on the Pt deposited PS surface.

In this study, two types of PS substrate were fabricated for sensing of humidity/chemicals and biological substances.

2. PS-based humidity and chemical sensor

The starting material is a double side polished, (100) orientated n-type silicon wafer with a resistivity of 16 to 23 Ω·cm. A porous silicon diaphragm of 50 to 100 um thick is formed on n-type silicon wafer by anisotropic etching in TMAH (Tetra Methyl Ammonium Hydroxide) solution (20wt%) at 80 'C and

then electrochemical etching in HF : ethanol = 1 : 3 (by volume percentage) solution with an applied voltage of 15V at room temperature. UV illumination is used for the anodization . Pt/Ti films have a role of ohmic contact materials, and masking layers against HF solution in a process of anodization, as well. A Ti layer is introduced to promote the adhesion of Pt film to SiO2. Pt has some merits such as high thermal conductivity and stability at high temperature. Besides, its Schottky barrier height is high enough to reduce the leakage current. Ti and Pt layers are deposited by RF sputter in a vacuum chamber with 2 x 105 mbar of base pressure and temperature of 100 'C . Their thickness are 200 Å and 4,000 Å, respectively. Generally, the hillocks form on the Pt surface in case that the thickness of Ti layer exceed 200 Å. The lift-off process for the device patterning is followed by RTP(Rapid Thermal Process) at temperature of 700 'C for 30 sec, under Ar ambient. Fig. 1shows that a porous silicon layer has formed uniformly in the silicon surface. A porous silicon layer is not grown in the silicon region beneath Pt/Ti/SiO2 thin film.

Sensitivity dependence on the amplitude of applied voltage is shown in Fig. 2. The sensitivity of porous silicon diaphragm-based device varies from 376.3 to 784.8 /%RH. While on the other, that of a bulk silicon-based device is negligible.

We also fabricated PS-based chemical sensors, and their sensitivities for CH3OH and C2H5OH were 0.068 uA/% and 0.212 uA/%, respectively (data not be shown).

3. PS -based biosensor

In this work, we introduce a new type of PS-based amperometric urea sensors aimed for monitoring urea level with improved sensitivity, and long linear detection range.

A boron-doped, one-side-polished p-type silicon wafer(14~17 Ω·cm and (100) orientation) was employed as a starting material. Poly(3-methylthiophene)(P3MT) film was coated on a Pt thin film electrode by the anodical electropolymerization in an electrolyte solution composed of 0.1 mol/L 3-methylthiophene and 0.1mol/L NaClO4 at 20 times of potential scanning in a potential range of 0 1.8V vs. SCE. Figure 3 shows SEM images for the cross-section of a urease(Urs)-immobilized Pt thin film electrode based on a PS substrate. Urs molecules were chronoamperometrically immobilized on the P3MT modified Pt thin film electrode.

Calibration curves of Urs/P3MT/Pt/PS and Urs/P3MT/Pt/PLS electrodes are shown in the figure 4in which all data points are obtained from the chronoamperograms of both electrodes. Applied potential is 0.6 V vs. SCE at 35'in a buffered isotonic saline solution. Sampling time is 100 seconds after applying potential step. For both electrodes, current density is linearly proportional to the urea concentrations in the range of 1 100mmol/L urea concentrations. Measured sensitivity of the Urs/P3MT/Pt/PS electrode is ca. 1.55 uA/mM·cm^{2}and that of the Urs/P3MT/Pt/PLS electrode is ca. 0.91 uA/mM·cm^2. This implies that the Urs/P3MT/Pt/PS electrode shows larger sensitivity than the Urs/P3MT/Pt/PLS electrode by ca. 1.6 times and this is well matched to the results of the Randles plots for the determination of Aeff of PS- and PLS-based Pt thin film electrodes.

4. Conclusions

We have successfully fabricated two types of PS-based sensor. Both the chemical sensor and the biosensor, the PS substrates showed higher sensitivity than a planar silicon-based sensors. The use of PS as electrode substrates will offer better opportunity for obtaining high sensitivity not only in biosensors but also in the other types of sensors such as clinical applications, environmental monitoring, and neuroscience with a broad detection range.

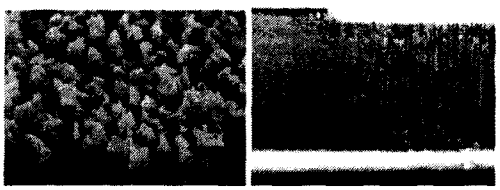

Fig. 1. SEM images of top view(left) and cross-sectional view(right) of PS diaphragm.

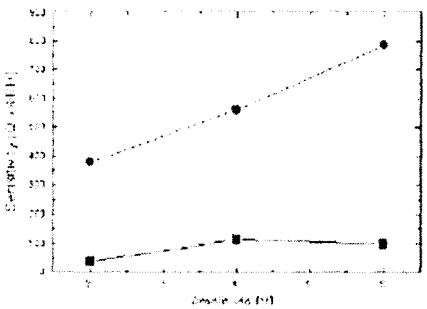

Fig. 2. Sensitivity (vs. amplitude) of humidity PS sensor. PLS-based(rectangle), and PS-based(circle)

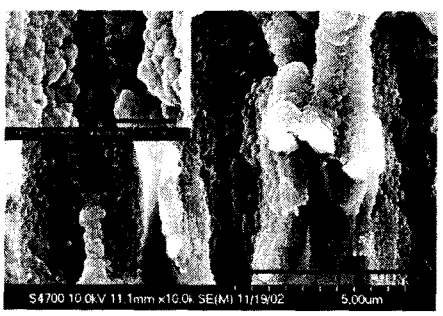

Fig. 3. SEM images for the cross-section of a PS-based urea sensor

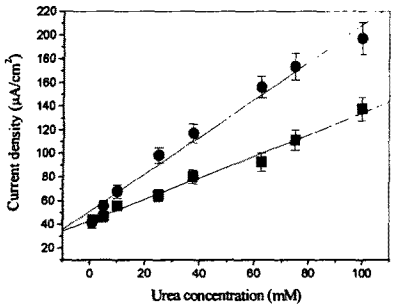

Fig. 4. Calibration curves of the P3MT-based urea senso rs. PLS-based(rectangle), and PS-based(circle)

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