Boron-doped Diamond Thin Film for Electrochemical Biosensors

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ABSTRACT

This paper describes the preparation of boron-doped polycrystalline diamond thin film whose electrical resistivity is lower than 10^{-1} Ω cm. The 1×1 mm^2 microelectrodes, its conducting line with 0.2 mm wide and 0.5×0.5 mm^2 pads was patterned by reactive ion beam etching. A glucose microsensor based on diamond film microelectrode and pyramidal containment produced on silicon by anisotropic etching was developed. Its advantages are high sensitivity and high stability.

1 INTRODUCTION

Diamond is an excellent material, having many unusual physical and chemical properties such as high resistivity, high corrosion resistance, chemical inertness etc.. Due to its special character, this material is extensively applied to high-electronic device, coating tools and other purposes.

The resistivity of polycrystalline diamond thin films made by chemical vapor deposition (CVD) can be decreased by doping with boron [1-3]. The synthesis of these low-resistivity diamond thin films lead to their application in electroanalysis as an electrode material. There are some papers describing the electrochemical properties of diamond films [4-5].

This paper describes the preparation of boron-doped polycrystalline diamond thin film(BDF), and its applications on glucose microsensor.

2 EXPERIMENTALS

2.1 PREPARATION OF MICROCHIPS

The BDF was deposited on a silicon wafer. Before deposition, the commercially polished silicon wafer was scratched with diamond powder in order to increase the nucleation density and a thorough chemical cleaning was accomplished. Boron doping and diamond growth were carried out in situ using a vertical hot filament assisted CVD system (see figure 1). The temperature of the filament and substrate were 2100℃ and 900℃, respectively. The reactant gas was a mixture of 0.5 sccm (standard cubic centimeter per min.) methane and 100 sccm hydrogen. Organoboranes ($BC_xH_yO_z$) were used as doping sources. The prossess no or low toxicity, good vaporization and transportation properties, are compatible with any carbon sources and are easily available. Figure 2 shows the resistivity of BDF as a function of the temperature of organoborane. After 6 h deposition, the BDF used in this work was grown to a thickness of 6 μm with a resistivity of 0.5 Ω·cm when the temperature of organoborane was 110℃. Owing to the difference in growth rate of diamond grains with different orientations, the surfaces of polycrystalline films were generally rough and this was favorable for increasing surface area. Figure 2 shows its morphology.The diamond grains can be clearly seen. The diamond structure for the film can also be confirmed by Raman spectra (Figure 3).

The schematic diagram of designed microchip is shown in Fig 5. Reactive ion beam etching technique patternized BDF including working electrodes (1.0 ×1.0 mm^2 in area), its conducting lines in 0.2 mm width and pads (0.5 ×0.5 mm^2 in area) (Figure 5a). A peice of 2 inch size and 300 mm thick p-type silicon (100) wafer with SiO_2 thin layer (1.5 μm) was used as the up-substrate.

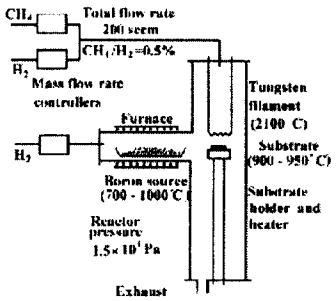

Fig 1. Schematic diagram of HFCVD apparatus

Fig. 2. SEM of diamond film

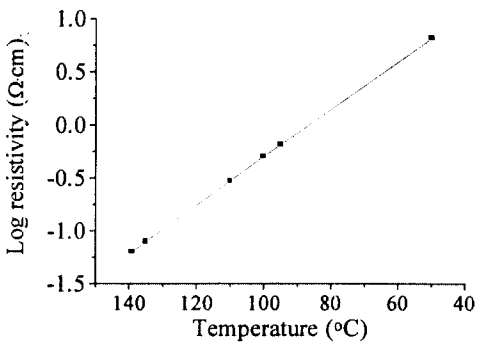

Fig. 3 Resistivity of the BDFs as a function of the temperature of organoborane.

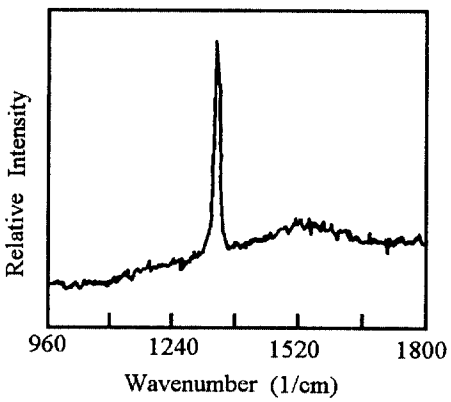

Fig 4 Raman spectra of BDF

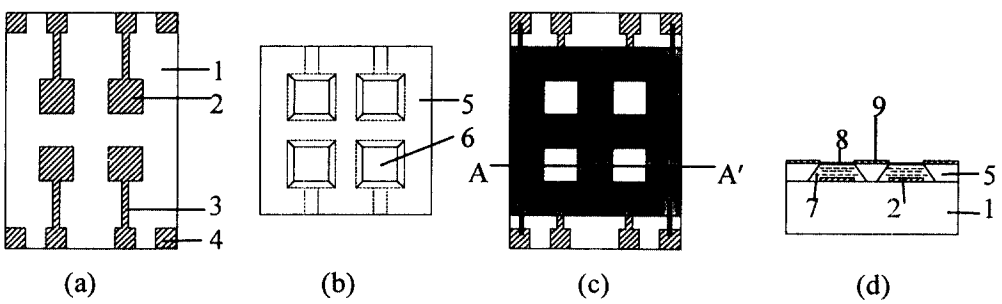

Fig. 5 Schematic diagram of designed microchip. 1.Silicon wafer down-substrate, 2. BDF working electrode, 3. conducting line, 4. pads, 5. silicon up-substrate, 6. quadratic hole, 7. emzyme membrane, 8. Nafion diffusion limit membrane, 9. Ag/AgCl reference electrode. (a) down-substrate, (b) up-substrate, (c) bonding up- and down-substrate, (d) cross section with A-A'.

A quadratic hole (1.2×1.2 mm^2 in area) on the SiO_2 layer was obtained by using photolithographic and etching processes successively. After the removing of photoresist and protective layers in the back side, silicon was etched anisotropically in 40% KOH solution at 50°C for 10 hr to create the four pyramidal cavities. A 1μm depth channel was also etched on the surface for the location of the conducting line. The SiO_2 thin layer was then removed by hydrofluoric acid (Figure 5b). A 400 nm thick silver layer was deposited on the back side of up-substrate. Partial chlorination of the silver layer was performed in 0.25 mol /L $FeCl_3$ solution to form the Ag/AgCl reference electrode on the back-side of silicon wafer. After the chip separating, anodic bonding between up-

and down-substrate was processed for each chips at 500°C and 300V for several minutes. The size of entire microchip is 7×5 mm (Figure 5c).

2.3 PREPARATION OF INCLUSION COMPLEX

0.05g β-cyclodextrin was added into 5ml of 5% glutaraldehyde and stirred for 20 minutes until it was solved. Left it overnight for the completion of inclusion process. Caculated amount of ferrocene was then added into β-CD solution and stirred thoroughly to form 1mM Fc-CD inclusion complex which could be used as a mediator in the construction of glucose-sensing microchip.

2.4 IMMOBILIZATION

5 μl of CD-Fc inclusion complex containing solution was added into the chamber of designed microchip and waiting for drying. It was followed by the adding of 5μl mixing solution of GOD, BSA and glutaraldehyde with optimal ratio. A thin film of Nafion was then covered on the surface of immobilized GOD membrane by adding of 5 μl 1% Nafion emulsion.

2.5 PREPARATION OF POTASSIUM ION SELECTIVE MICROELECTRODES

10 μl of valinomycin cotaining solution with optimal components of PVC resin powder and plasticizer was added into the chamber of designed microchip to form a potassium- sensing PVC membrane on the surface of Pt substrate electrode.

3.RESULTS AND DISCUSSION

3.1 CYCLIC VOLTAMMOGRAMS

The cyclic voltammograms for the glucose sensors with CD-Fc mediator in various concentration of glucose solution at a scan rate of 20 mV/s shows in Figure 6. The glucose sensor with CD-Fc mediator exhibits lower working potential (about 350 mV) than one without the mediator (about 650 mV), resulting in the avoidance of possible interferences at high working potential.

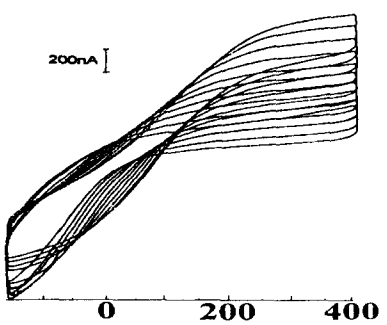

Fig. 6 Cyclic voltammograms for the glucose sensor

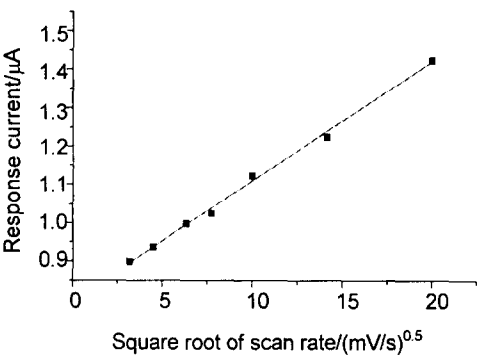

Fig. 7 The relationship between response current and scan rate for the glucose sensor

3.2 DEPENDANCE OF RESPONSE CURRENT ON POTENTIAL SCAN RATE

The cyclic voltammograms of 4 mmol/L glucose and bulk solution were recorded at 10, 20, 40, 60, 100, 200 and 400 mV/s, respectively. Figure 7 shows that the response current of the glucose sensor increases linearly with the square root of the scan rate, reflecting diffusion control process of the electrode reaction.

3.3 RESPONSE TIME

The response time, $t_{90\%}$, of the glucose sensor with 6 mmol/L glucose lay within 30 s estimated from the response-time curve using a potentiostat set at +400 mV. In other words, a stable mass transport was quickly established within 30s.

3.4 CALIBRATION CURVES

The calibration curves of the glucose sensors with various amount of GOD were shown in Figure 8. The sensor with 0.50 U GOD exhibits higher slope and narrower linear range than one with 0.25 U GOD.

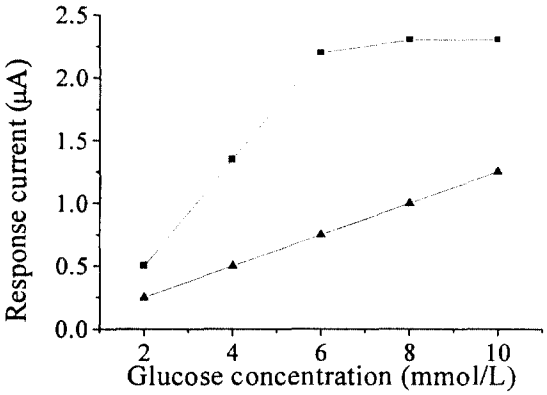

Fig. 8 Calibration curves for the glucose sensor with 0.50 U GOD (a) and with 0.25 U GOD(b)

3.5 APPLICATION

The glucose sensor was measured in a standard serum whose composition similar to normal human blood serum. The variation coefficient with ten consecutive determinations in the same sample is 1.6%. A comparison was carried out using the glucose sensor directly in serum of human blood with results obtained with spectrophotometry. Both measured values are identical.

4. CONCLUSIONS

A glucose sensor and based on BDF and pyramidal containments produced on silicon by anisotropic etching were developed. The structure of 2×2 cavity-array in a chip provide possibility of production of four-functional biosensor.

ACKNOWLEGEMENTS

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