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Vessel Gate and Diamond Solution Gate Field-Effect-Transistors (SGFETs) for Aiming for Measuring pH of Elevated Temperature

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Abstract

All solid glass-less pH sensor has been required in the food industry. We report a new pH sensing system utilizing stainless-steel vessel (vessel gate) instead of the glass electrode in this work. We investigate the pH sensitivity utilizing vessel gate with either a silicon ISFET or a hydrogen-terminated diamond SGFET, and the temperature dependence of silicon ISFET and oxygen-terminated diamond SGFET are also. In conclusion, the combination of vessel gate and pH insensitive diamond SGFET showed high pH sensitivity (-54 mV/pH), and diamond SGFETs could operate in solution at 95 °C.

1. Introduction

All-solid-state pH sensors are of great interest in the food industry. Conventional pH sensing systems with glass electrodes (Ag/AgCl electrodes) have the risks of leakage of KCl internal solution or breakage of the glass electrode. Due to these problems, glass electrode pH sensor is not suitable for in process monitoring for food production line. Therefore, silicon ISFETs have not been put to practical use in the food industry despite a lot of research, and there has been a demand for a pH sensing system that does not require a glass electrode [1].

We have reported diamond solution gate FETs (SGFETs) operated in electrolyte solution environment (Fig.1) [2]. Diamond has many appealing properties including biocompatibility, ease of surface modification, and chemical-physical stability and, therefore, are suitable for biosensing applications. Diamond SGFETs are also good candidates for pH sensing applications since the hole concentration of diamond SGFETs varies with different ion concentrations of solutions [3]. However, diamond SGFETs require a glass electrode as the gate electrode. To solve this problem, we utilized a stainless-steel vessel named "Vessel Gate" as the gate electrode instead of the glass electrodes. We found that the stainlesssteel surface exhibits a high pH sensitivity of 57 mV/pH. The high pH sensitivity is equivalent to that of Nernst equation (59 mV/pH). In addition, the pH of the entire solution can be measured because the sensing is on the stainless-steel surface.

To take advantage of this high pH sensitivity and stability of stainless-steel, we conducted two experiments: a) measuring the pH sensitivity of the combination of a vessel gate and silicon ISFET or a pH insensitive hydrogen-terminated (C-H) diamond SGFET [2], and b) measuring the temperature dependence with a silicon ISFET and an oxygen-terminated (C-O) diamond SGFET from room temperature to 95°C.

2. Experimental methods

SUS304 stainless steel was used as the vessel gate because SUS304 is widely used in the food industries. C-H surface without boron delta-doped layer was conducted by plasma treatment in a hydrogen atmosphere, and C-O surface on boron delta-doped layer was carried out by a plasma reactor in an oxygen atmosphere. First, I_{DS} - V_{GS} characteristics of the silicon ISFET were measured from pH 2 - 12 with glass electrode. I_{DS} - V_{GS} characteristics of the silicon ISFET with vessel gate were also measured from pH 2 - 12. The pH sensitivity was computed by calculating V_{GS} at the same drain current. The same procedure was conducted to C-H diamond SGFET as well. Then, I_{DS} - V_{DS} characteristics of silicon ISFET and C-O diamond SGFET were measured using Ag/AgCl electrode and vessel gate at 20, 40, 60, 80, 95°C.

3. Results and Discussion

Fig. 3 shows pH sensitivities of (a) Silicon ISFET (+ 48 mV/pH) and (b) C-H diamond SGFET (-6 mV/pH) when using the glass electrode as the gate electrode. This indicates the successful preparation of pH sensitive and insensitive FETs. When the vessel gate was used instead of the glass electrode, silicon ISFET and C-H diamond SGFET showed -5 mV/pH and -54 mV/pH, respectively, as shown in Fig.4. The result indicates that the combination of vessel gate and pH insensitive diamond SGFETs with low pH sensitivity, can changed to a high pH sensitive system when compared with the case of using glass electrodes.

We then investigated the effect of elevated temperature. Fig.5 shows that Silicon ISFET had a distorted waveform at 60°C and became inoperable thereafter. On the other hand, C-O diamond SGFET was able to operate at 95°C as shown in fig.6. This result show that diamond SGFETs are great candidates for high temperature pH measurements.

4. Conclusion

To eliminate the use of glass electrodes, we utilized stainless-steel vessel (vessel gate) as a gate electrode instead of glass electrode with diamond SGFETs. The combination of vessel gate and pH insensitive diamond SGFET showed a high pH sensitivity (-54 mV/pH). In addition, the diamond SGFETs could operate under solutions of 95 °C. As the result, vessel gate and diamond SGFETs can be a great candidate for pH sensing system in the food industry. In the future, we will investigate terminations with stable pH sensitivity in high temperatures.

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Fig.1 The cross sectional view of diamond SGFETs in electrolyte solution. One of the features of diamond SGFET is that the electric double layer formed can replace the use of an insulating film often seen in ISFETs



Fig.2 The measurement schematic images: (a) Ag/AgCl electrode and (b) Vessel Gate. In case of (a) Ag/AgCl electrode, gate voltage is applied between the tip of the electrode and FET_o channel which is sensing surface. In the case of (b) Vessel Gate, the entire stainless-steel surface also becomes the sensing surface.



Fig.3 I_{DS} - V_{GS} characteristics and pH sensitivity of (a) Si ISFET and (b) C-H diamond SGFET when using Ag/AgCl electrode. Silicon ISFET and C-H diamond SGFET show pH high sensitivity and low sensitivity, respectively.



Fig.4 I_{DS} - V_{GS} characteristics and pH sensitivity of (a) Si ISFET and (b) C-H diamond SGFET when using Vessel Gate. The result indicates that the combination of vessel gate and pH insensitive diamond SGFETs with low pH sensitivity, can changed to



Fig.5 The temperature dependence of STISFET. (a) Room temperature operation, (b) A collapsed I_D - V_{DS} characteristics at 60 °C indicates inoperable.

C-O Diamond SGFET (a) Ag/AgCl electrode



Fig.6 The temperature dependence of C-O diamond SGFET: (a) Ag/AgCl electrode and (b) vessel gate. C-O diamond SGFET was able to operate at 95°C.

References

- [1] P. Bergveld, IEEE Transactions on Biomedical Engineering, 70-71 (1970).
- [2] H. Kawarada et al., Phys. Status Solidi A 185, 1, 79-83(2001).
- [3] K.S. Song et al., Analytica Chimica Acta, 573-574, 3~8 (2006).