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New Glass-less pH Sensing System Using Diamond Electrolyte Solution Gate FETs (SGFETs) and Vessel Gate

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Abstract

In this work, we established new pH sensing system without a glass reference electrode. We fabricated partially O-terminated polycrystalline diamond SGFET. It has been operated in a stainless vessel (Vessel Gate) as a substitute for a glass reference electrode (Ag/AgCl). As a result, we found that the surface of a stainless vessel has high intrinsic pH sensitivity of 51~53 mV/pH, which is near Nernst response of 59 mV/pH, due to its oxide surface. However, the pH sensitivity of Vessel Gate compensate that of the SGFET. Thus, we propose that pH-insensitive SGFET is better in this pH sensing system.

1. Introduction

All solid glass-less pH sensor have been required. In 1970, Bergveld presented an ion-sensitive field-effect transistor (ISFET) as a substitute for glass pH sensor [1]. In 1974, Matsuo used a reference electrode as the gate electrode to apply gate voltage to an ISFET through electrolyte solution [2]. On the other hand, since 2001, we have reported diamond electrolyte solution-gate FETs (SGFETs) where the semiconductor surface was immersed in electrolyte solution directly and the drain current was controlled by electric double layer at the diamond surface [3]. Diamond has many advantages as a material for chemical and biosensors because of its wide potential window, physiochemical stability and simple chemical-modification.

A glass reference electrode (Ag/AgCl) is used for applying gate voltage. However, Ag/AgCl has any problems: the glass breakage and KCl solution leakage into sample solution.

In this work, we used a stainless vessel (Vessel Gate) to overcome the problems of Ag/AgCl. The stainless is SUS304 which is used widely in the food industry. The pH sensing system in this work consisted of SGFET and Vessel Gate.

2. Experimental methods

We fabricated partially O-terminated polycrystalline diamond SGFET. Fig.1 shows the cross-sectional view of the SGFET in electrolyte solution. The diamond SGFET shows p-type conductivity when it is H-terminated. After cleaning substrate, Ti/Au (30 nm/100 nm) were deposited on the surface as source and drain electrodes. After Hydrogen termination were modified on diamond surface, the isolation was performed by O_2 plasma ashing. Finally, the SU-8 as passivation film covered source and drain electrodes to protect them from electrolyte solution. Also, the channel area of SGFET was electrochemically oxidized to improve its pH sensitivity [4,5].

We measured the pH sensitivity of the SGFET using each Ag/AgCl and Vessel Gate as gate electrodes. Fig.2 shows our measurement systems in this work. Then, we analyzed the threshold voltage (V_T) shifts by pH change, and investigated the influence of Vessel Gate on the pH sensitivity of the SGFET. Similarly, we measured the pH sensitivity of commercially available Si ISFET (Winsense Co., Ltd.) to support more our claims that Vessel Gate affected the pH sensitivity of the SGFET.

Also, the measurements were performed in common gate. The main advantage of common gate mode is that drain current is saturated without applying drain-gate voltages. It indicates that the pH can be measured by only applying source-gate voltages.

3. Results and Discussion

Fig.3 (a) (b) show the $I_{DS} - V_{DG}$ characteristics of the SGFET at different pH in common gate. Fig.4 (a) (b) show the threshold voltage (V_T) shifts of the SGFET by pH change in common gate. Each figure compares different gate electrodes, which are Ag/AgCl and Vessel Gate. Their results imply that the Vessel Gate has a great effect on the pH sensitivity of the SGFET. As a result, when Ag/AgCl is used, the pH sensitivities of the SGFET are each -29 mV/pH and -11 mV/pH in each acid and alkaline area. On the other hand, when Vessel Gate is used, the effective pH sensitivities of the SGFET are each $+22$ mV/pH and $+42$ mV/pH in each acid and alkaline area. To one's surprise, the pH sensitivity of the SGFET measured using Vessel Gate is appear to be reverse sensitivity compared to the pH sensitivity measured using Ag/AgCl. This reverse phenomenon is assumed that Vessel Gate also has high intrinsic pH sensitivity because of its oxide surface.

Then, we estimate the intrinsic pH sensitivity of only stainless surface side (Vessel Gate) by cancelling the pH sensitivity of the SGFET using the following Eq. (1).

$$\Delta V_T^{Stainless\ surf} = \Delta V_T^{vs.\ Vessel\ gate} - \Delta V_T^{vs.\ Ag/AgCl} \quad (1)$$

Fig.4 (c) shows the calculation result of the SGFET using Eq. (1). As a result, the intrinsic pH sensitivities of only stainless surface side are each 51 mV/pH and 53 mV/pH in each acid and alkaline area. These values are near the Nernst response of 59 mV/pH.

Fig.5 (a) (b) show the $I_{DS} - V_{DS}$ characteristics of the Si ISFET at different pH in common source. Fig.6 (a) (b) show the threshold voltage (V_T) shifts of the Si ISFET by pH change. As a result, The Si ISFET has high pH sensitivity using Ag/AgCl. However, when Vessel Gate is used, the Si ISFET has a little effective pH sensitivity. Because the pH sensitivity of Si ISFET compensates that of stainless surfaces, the total pH sensitivity becomes very weak as a result. Fig.6 (c) shows the calculation result of the Si ISFET using Eq. (1).

4. Conclusion

To establish new glass-less pH Sensing System, we used the Vessel Gate (Stainless Vessel) as a gate electrode and the SGFET as a sensor. The stainless surface is found to be high intrinsic pH sensitivity of 51~53 mV/pH, because the effective pH sensitivity of Vessel Gate was compensated by that of the SGFET. Thus, we need pH insensitive SGFET. If the pH insensitive SGFET are fabricated, it is expected that the pH sensing system using Vessel Gate has higher pH sensitivity than this work.

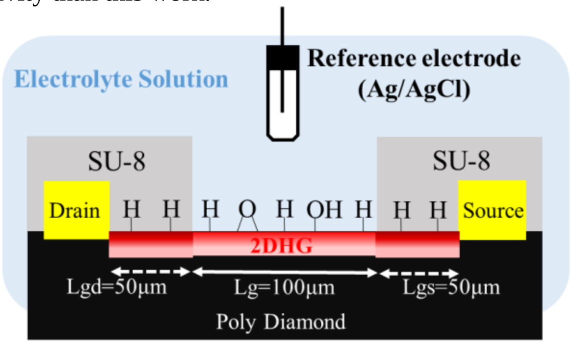

Fig.1 The cross-sectional view of partially O-terminated polycrystalline diamond SGFET in electrolyte solution.

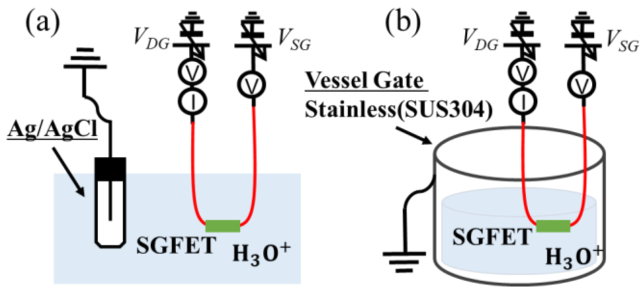

Fig.2 The measurement schematic images in common gate. (a) Ag/AgCl and (b) Vessel Gate (stainless vessel) are used as gate electrodes.

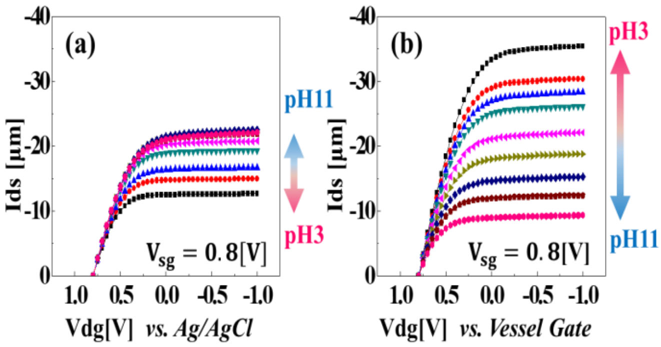

Fig.3 The $I_{DS} - V_{DG}$ characteristics of the SGFET for pH change in common gate. (a) Ag/AgCl and (b) Vessel Gate (stainless vessel) are used as gate electrodes.

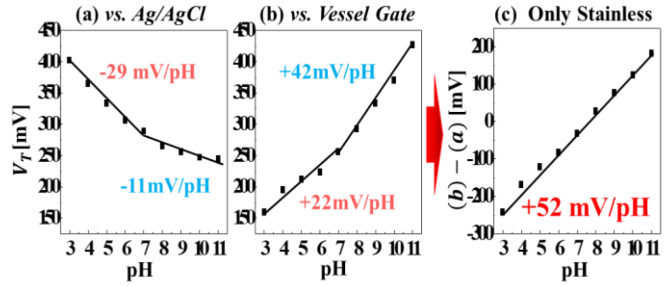

Fig.4 The threshold voltage (V_T) shifts of the SGFET by pH change in common gate. (a) Ag/AgCl and (b) Vessel Gate (stainless vessel) are used as gate electrodes. (c) means (b) - (a) .

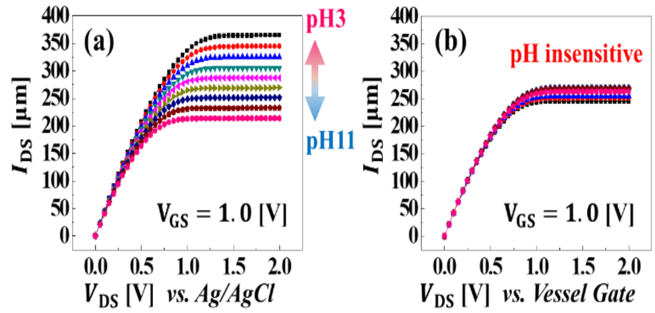

Fig. 5 The $I_{DS} - V_{DG}$ characteristics of the Si ISFET by pH change in common source. (a) Ag/AgCl and (b) Vessel Gate (stainless vessel) are used as gate electrodes.

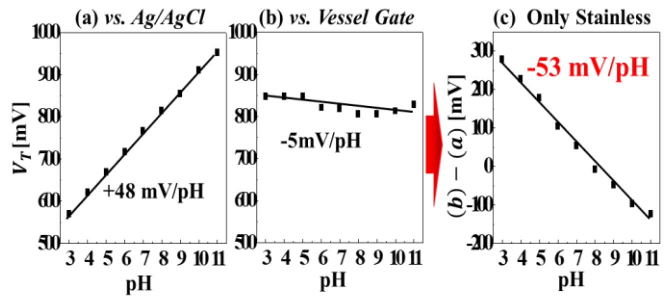

Fig.6 The threshold voltage (V_T) shifts of the ISFET by pH change in common source. (a) Ag/AgCl and (b) Vessel Gate (stainless vessel) are used as gate electrodes. (c) means (b) - (a).

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