Development of Glassless All-solid-state pH Sensor

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Glass electrode pH meters are the de-facto standard for measuring pH and Yokogawa offers pH meters of this type, which are widely used by many customers in various industries including chemicals, water and sewerage, petrochemicals, and biotechnology. However, glass electrode pH meters involve inherent risks: glass is fragile and the internal liquid may leak and contaminate samples. Therefore, we have been working with Waseda University to develop a next-generation all-solid-state pH sensor. This paper describes the key technologies and reports the characteristics of a prototype.

INTRODUCTION

pH (hydrogen ion concentration) index is a fundamental and important factor as a solution property parameter and governs many chemical characteristics. A glass electrode pH meter, whose measurement principle was proposed in 1906 and research and development has progressed since then, is currently the industry standard for pH sensing. Yokogawa also manufactures and distributes glass electrode pH meters, which are widely used by many customers in various industries including chemicals, water and sewerage, petrochemicals, and biotechnology. However, glass electrode pH meters involve the risk of contamination of sample by foreign matters as a result of damage to the working glass electrode. In particular, food industry customers have pointed out that this is a serious problem in food production processes. Another important issue for the glass electrode pH meters is that a silver/silver chloride electrode containing internal liquid (potassium chloride (KCl) solution) is used as a reference electrode. In general, the reference electrode establishes a reference potential by leaking the KCl solution into the test liquid sample while pH sensing. Therefore, the contamination-sensitive industries such as pharmaceutical industry and the semiconductor industry that uses ultra-pure water with extremely low anion/cation concentration point out that sensor-derived components may become mixed with the sample as a problem.

To overcome these issues regarding the pH measurement, an ion-sensitive field-effect transistor (ISFET) pH sensor using a silicon semiconductor was proposed in the 1970s and has been developed since then. However, the electrode containing internal liquid is still employed as a reference, so that the contamination problem remains unsolved.

For a next-generation glassless all-solid-state pH sensor, Yokogawa has collaborated with Waseda University to research and develop a pH sensor using a semiconductive diamond that possesses a physical robustness and chemically stableness. This paper describes the key technologies needed to realize the glassless all-solid-state pH sensor and reports the characteristics of a prototype.

DIAMOND FET SENSOR

Advantages of Diamond as a Sensor

Diamond is a highly robust p-type semiconductor material. Compared to the traditional silicon semiconductor, the band gap is approximately five times greater, the heat conductivity is about 13 times greater, and the breakdown electric field strength is about 33 times greater. Furthermore, diamond is a chemically stable electrochemical material. Compared to a traditional metal electrode such as gold, the potential window of diamond is about twice wider while the background current is smaller by one digit (the sensitivity is about 10 times higher in terms of S/N ratio). Yokogawa has collaborated with Waseda University to research and develop a

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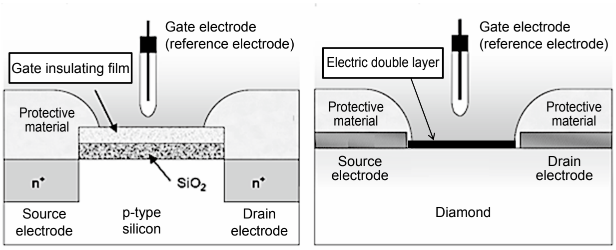
pH sensor employing such a singular material, diamond, as an ISFET chemical sensor.

Figure 1 shows the structure of a silicon-type ISFET (Si-ISFET) and a no-gate-insulator diamond FET (also called diamond SGFET).



(A) Silicon-type field-effect transistor (B) Non-gate-insulator diamond field-effect transistor

Figure 1 Structure of a Si-ISFET and a non-gate-insulator diamond FET

Typical issues of Si-ISFET include a short-term and/or long-term drift caused by the liquid-contacting silver/silver chloride (Ag/AgCl) electrode as a gate electrode. Since the diamond FET is no-gate-insulator, there is a possibility that it can solve the above-mentioned Si-ISFET problem. Furthermore, another feature of the no-gate-insulator diamond FET is that the terminal element of wetted diamond surface can control the pH sensitivity which is essential for a pH sensor. Table 1 shows the relationship between the type of the termination of the diamond and its properties. The working electrode of the all-solid-state pH sensor uses a partially oxygen-terminated diamond FET (C-O diamond). Meanwhile, the reference electrode uses a partially fluorine-terminated diamond FET (C-F diamond) to form a differential FET in order to remove the influence of temperature and achieve a stable measurement system.

Table 1 Relationship between the diamond surface and properties(1)(2)(3)(4)(5)

Type	Hydrogen-terminated diamond	Partially oxygen-terminated diamond	Partially fluorine-terminated diamond
	C-H diamond	C-O diamond	C-F diamond
Surface condition	C-H	C-OH C-O-C C-OOH C-H	C-F C-F2 C-F3 C-H
Wettability	Hydrophobicity	Hydrophilicity	Hydrophobicity
Treatment	Hydrogen plasma	Ozone treatment	Fluorine plasma
pH sensitivity	–	High pH sensitization	Low pH sensitization
	ca. 10 mV/pH	20 to 50 mV/pH	3 to 8 mV/pH

All-solid-state Diamond pH Sensor

Figure 2 shows the all-solid-state diamond pH sensor composed of a boron-doped polycrystalline diamond FET that we prototyped. It is composed of a pH-sensitive FET (partially oxygen-terminated diamond), a pH-insensitive FET (partially fluorine-terminated diamond) and a quassi-reference electrode.

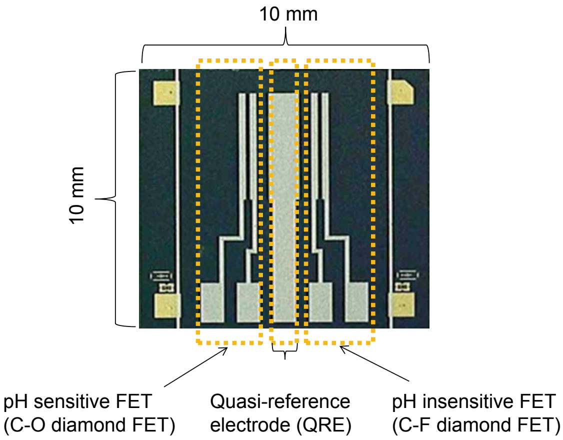


Figure 2 All-solid-state diamond pH sensor under development

The following (i) to (v) steps show an outline of the manufacturing process of the diamond FET. For more information, refer to reference (3) and (4).

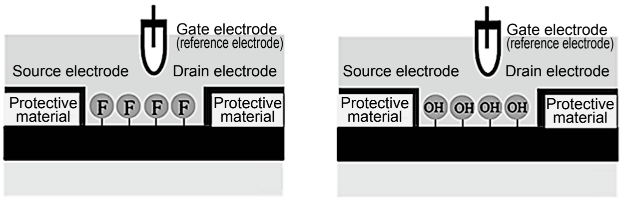
(i) Use a polycrystalline diamond substrate of up to 10 mm square with the thickness of 0.3 to 1.0 mm as the start substrate and a quartz-type microwave chemical vapor deposition (CVD) reactor and synthesize a boron-doped diamond layer on the substrate using a homoepitaxial growth method.

(ii) Position titanium/gold (Ti/Au) pads for a drain electrode and a source electrode to ensure a channel length of 1 to 10 mm and a channel width of up to 0.1 mm.

(iii) Connect metal wires to the drain and source electrodes for applying external bias voltage.

(iv) Encapsulate the drain and source electrodes with nonconductive material to protect them from the solution; only the area of the boron-doped diamond surface between the pads was exposed to the buffer solutions.

(v) Modify the diamond termination so that it works as a diamond FET sensor with pH-sensitivity controllability. Obtain the partial fluorine-terminated diamond (C-F diamond) from C-H diamond substrate using an ICP-RIE with perfluoropropane (C_3F_8) gas source. Meanwhile, for the partial oxygen-terminated diamond (C-O diamond), modify the C-H diamond surface using an ozone oxidation method. Figure 3 shows diagrammatic illustrations of surface-modified diamond FET sensor.



(A) pH insensitive fluorine-terminated diamond FET (B) pH sensitive fluorine-terminated diamond FET

Figure 3 Schematic diagram of surface-modified diamond FET sensor(4)

RESULTS AND DISCUSSION

Characterization of Diamond FET Sensor

We used Yokogawa's Model GS820 source measure unit to drive FETs. We applied drain-source voltage (Vds) and gate-source voltage (Vgs) with a common source method and measured the drain-source current (Ids) to characterize the FETs. The gate voltage was applied via the silver/silver chloride reference electrode. Figure 4 shows the FET current/voltage characteristics of C-H diamond as an example of the basic performance of a diamond FET sensor. The obtained FET I-V curves follow MOSFET theory, which verifies the function of the diamond FET sensor. Furthermore, the saturation is confirmed in the range of Vgs from −0.5 V to −1.0 V, where the FET sensor can be used as pH sensor with good linearity.

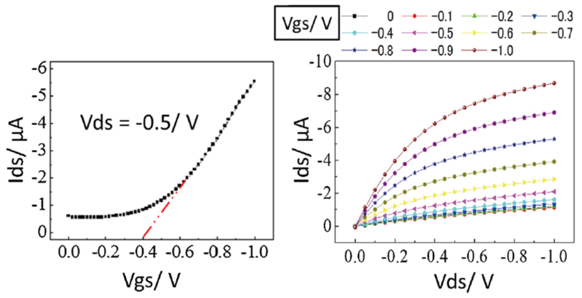


Figure 4 FET current-voltage characteristics of hydrogen-terminated diamond(3)

Characteristics of a pH Sensitive FET and pH Insensitive FET

Figure 5 shows the evaluation results of the partially oxygen-terminated diamond FET which is classified as pH-sensitive FET. The threshold voltage shifts corresponding to the pH value in solution (pH shift) so that it was employed as a pH sensor. A good linearity is shown in the pH range from 2 to 12 with $R^2>0.99$. The pH sensitivity depends on Ids and is the range from 21 to 31 mV/pH.

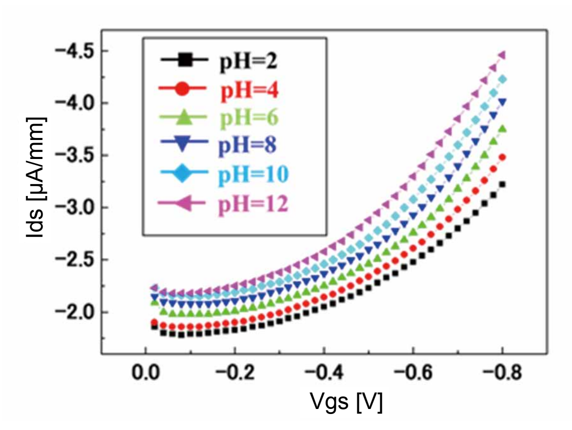


Figure 5 Characteristics of partially oxygen-terminated diamond FET sensor(3)

Figure 6 shows the evaluation results of the partially fluorine-terminated diamond FET (C-F diamond) which is classified as pH insensitive FET. For the partial C-F diamond FET, the FET I-V curves along the MOSFET theory are also obtained.

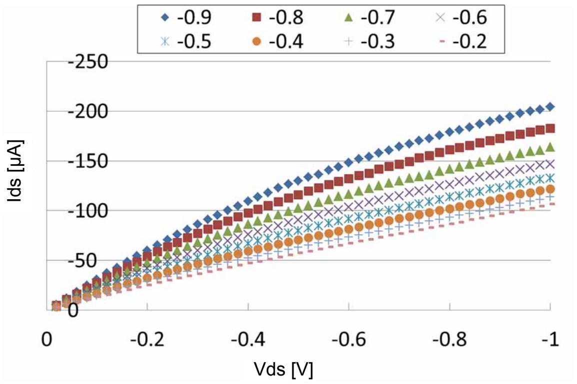


Figure 6 Characteristics of a partially fluorine-terminated diamond FET sensor
(Ids-Vds characteristics when Vgs is −0.2 to −0.9 V)

Characteristics of an All-solid-state pH Sensor

We examined the characteristics of the all-solid-state pH sensor using a differential FET detection technique that employs the C-O diamond and C-F diamond as pH-sensitive FET and pH-insensitive FET respectively. Figure 7 shows the pH sensitivity of the pH-sensitive C-O diamond FET and pH-insensitive C-F diamond FET. We used an evaluation method that complies with the Japanese Industrial Standard (JIS) K0802 and we used pH standard solutions (pH 4.01 phthalate buffer solution, pH 6.86 phosphate buffer solution, pH 9.18 borate buffer solution, and pH 10.01 carbonate buffer solution). In case of using pH-sensitive FET (indicated by ☐), linearity depending on the pH value was obtained. Meanwhile, in case of pH-insensitive FET (indicated by ◆), the Vgs values do not correspond to the pH values. These results suggested that the differential FET measurement technique to obtain output values of the pH-sensitive FET by referring to the output values of the pH-insensitive FET is feasible.

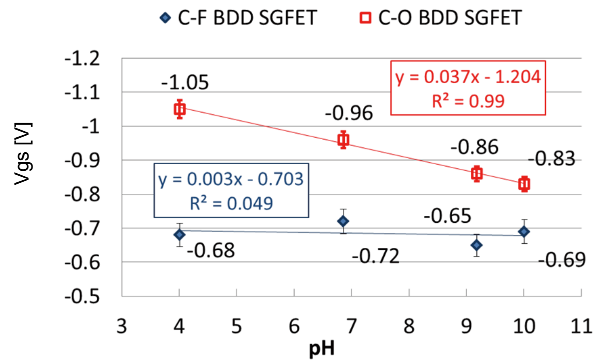


Figure 7 pH sensitivity of a pH-sensitive partially oxygen-terminated diamond FET and pH-insensitive partially fluorine-terminated diamond FET(4)

Figure 8 shows the configuration of the developed all-solid-state pH sensor. It measures differential FET output values using a pH-sensitive FET (partially oxygen-terminated diamond FET) and pH-insensitive FET (partially fluorine-terminated diamond FET) by applying drive voltage via a quassi-reference electrode.

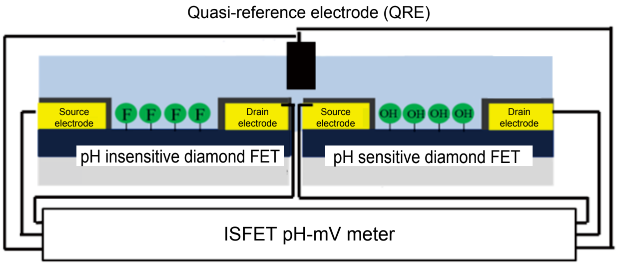


Figure 8 Configuration of the developed all-solid-state pH sensor(4)

Figure 9 shows the FET characteristics using an ISFET pH-mV meter equipped with a source follower circuit. The horizontal axis shows the pH values in solution adjusted by Carmody wide range buffer solution and the vertical axis shows the output values of the prototyped all-solid-state pH sensor using differential FET method. In the range of pH 2 to pH 10, and pH sensitivity of 27 mV/pH were obtained with a good linearity (R^2=0.99).

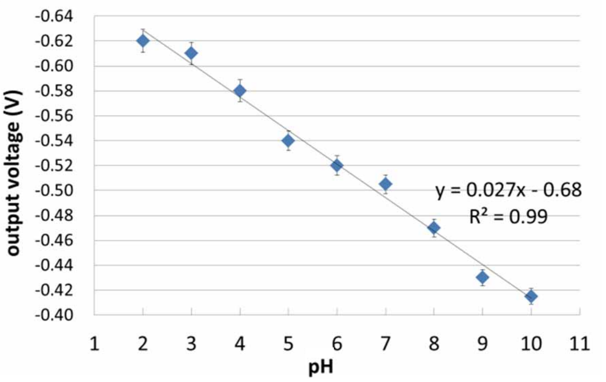


Figure 9 Characteristics of the developed all-solid-state pH sensor(4)

CONCLUSION

We prototyped a no-gate-insulator diamond FET to implement a glassless all-solid-solid pH meter to replace a glass electrode pH meter that meets the customers' request. By performing differential FET detection using a pH-sensitive partially oxygen-terminated diamond FET and pH-insensitive partially fluorine-terminated diamond FET, we verified that the prototype worked as an all-solid pH sensor. We will further improve the performance and increase the reliability. Furthermore, we will continue development of a next-generation pH sensor that enables customers to perform contamination-free pH measurement and control in any production environment and in any place customers wish.

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