



Novel Sensor Using ISFET and Pt Electrodes for Water pH and Flow Speed Measurement

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Abstract—Multiple water quality sensors are required to construct a network for continuous and precise monitoring of water quality in natural environments. Therefore, low-cost sensors are necessary for guaranteeing scalability and widespread adoption. In this letter, we developed a sensor that can measure natural water pH and flow speed using only one ion-sensitive field-effect transistor (ISFET) and two Pt electrodes. The proposed sensor does not require an external reference electrode (RE) or electrolyte, because one of the Pt electrodes temporally acts as a reference electrode by electrolysis.

Therefore, the sensor system for a reference electrode is omitted, and the electrode does not undergo electrolyte deterioration. Furthermore, the fabrication process is much simpler than that of pH sensors integrated with reference electrodes. We experimentally verified the proposed sensor. We confirmed that its pH measurements showed roughly similar tendency to those obtained using an Ag/AgCl reference electrode and achieved the sensitivity at least 20 mV/pH. In addition, we could measure flow speed from 5 to 25 cm/s by measuring the time variation of the Pt electrode potential.

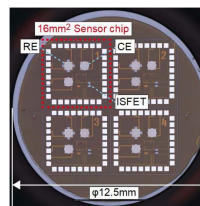
Index Terms—Sensor applications, flow speed sensor, ion-sensitive field-effect transistor (ISFET), pH sensor, Pt electrode, reference electrode (RE), water quality sensor.

I. INTRODUCTION

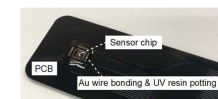
Monitoring natural water resources, such as rivers, lakes, and the sea, is important for protecting fishery resources and conserving the living environment. Using a system based on a wireless sensor network for monitoring the natural water environment is effective for the early detection of abnormalities, which could be observed in real time over the large area using this system. Hence, various sensor nodes have been proposed according to different applications [1], [2], [3]. To obtain more accurate and extensive data when large-area natural water resources are monitored, many sensor nodes are required. Therefore, the manufacturing and operation costs per sensor node must be minimized. However, existing systems are expensive and unsuitable for installation on a large scale. Integration of sensors in a wireless sensor network can effectively reduce costs. However, it is difficult to integrate various sensors for monitoring water quality as the working principles differ among sensors.

In this letter, we propose an integrated sensor for wireless monitoring of natural water quality that simultaneously measures pH and flow speed. The sensor consists of an ion-sensitive field-effect transistor (ISFET) and two Pt electrodes. The pH is the basic quantity to monitor water quality, whose measurement can be conducted using the ISFET [4]. As an ISFET is fabricated on a Si substrate by using

The fabricated sensor devices



Sensor probe installed with a sensor chip



We proposed and verified a sensor to simultaneously measure the pH and flow speed of natural water flow using an ISFET and two Pt electrodes.

CMOS-compatible fabrication processes [5], its integration with other Si-based sensors is simple. However, a reference electrode (RE) is generally required for ISFET operation. Although several studies have addressed the miniaturization of the RE using microelectromechanical system (MEMS) technology [6], [7], [8], deterioration of the chemical in the RE is unavoidable and adversely affects the long-term continuous usage of the sensor. Alternatively, Ag nanoparticles can be used as pseudo-RE [9]. However, in this method, Ag nanoparticle ink was inkjet-printed on a printed circuit board (PCB) and requires the sintering process; thus, it has limit in sensor miniaturization. In contrast, we focused on producing a sensor that is as simple as possible, does not use external REs or chemicals, and requires only one type of ion-sensitive membrane. To this end, we integrated two Pt electrodes to serve as an RE and enable the simultaneous measurement of water flow speed.

II. WORKING PRINCIPLE

The proposed sensor comprises an ion sensor, an RE, and a counter electrode (CE). Specifically, an ISFET is used as an ion sensor, and Pt electrodes are used as RE and CE. Fig. 1 depicts the working principle of the proposed sensor. Fig. 1(a) shows the initial sensor state. A constant current is applied to the RE and CE as setup action, and the RE and CE serve as cathode and anode, respectively. The water to be measured is electrolyzed on the RE and CE. Then, hydrogen is produced on the RE, whereas oxygen is produced on the CE. Furthermore, given that electrolytes are present in water in natural

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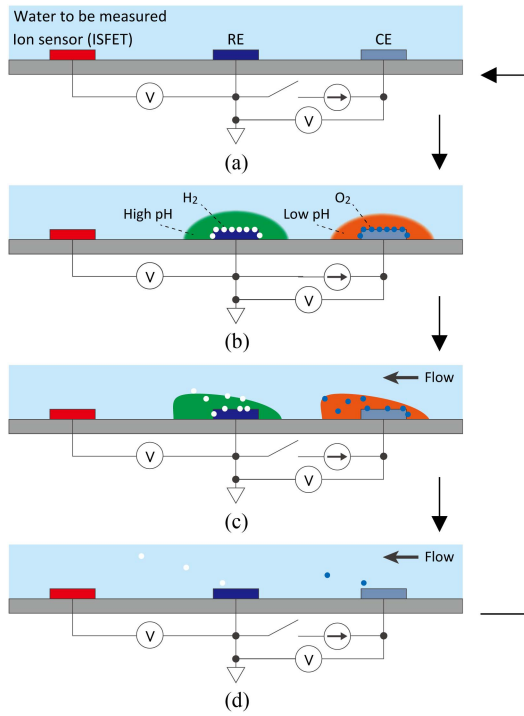


Fig. 1 Illustration of the flow speed sensing principle. (a) Initial state. (b) Electrolysis state. (c) Release state. (d) Desorption state.

environments, the pH around the RE increases and that around the CE decreases, as illustrated in Fig. 1(b). Then, we stop applying current between the RE and CE, as shown in Fig. 1(c). Next, hydrogen and oxygen respectively pass through the RE and CE according to the water flow. As the surface electric potential of Pt changes when it adsorbs hydrogen [10], the RE acts as reference for the ISFET, and the ISFET source voltage changes depending on the hydrogen adsorption or desorption on the RE.

The hydrogen adsorbed by the RE is desorbed and diffused gradually according to the water flow, as shown in Fig. 1(d). Finally, hydrogen is completely desorbed, and the sensor returns to its initial state. The hydrogen desorption speed changes according to the flow speed of the measuring water. The time between the beginning of hydrogen desorption (i.e., end of electrolysis) and complete desorption depends on the flow in the surrounding areas. Consequently, the proposed sensor can also measure flow speed. On the other hand, the pH can be measured immediately after the switch-OFF shown in Fig. 1(c). Usually, the RE is required as it provides a surface potential that does not change according to pH. In the proposed sensor, we use the hydrogen adsorbed in our RE as a pseudo-standard hydrogen electrode. Surface potential E of the pseudo-standard hydrogen electrode can be expressed using the Nernst's equation as

$$E = E^0 + \frac{RT}{F} \ln \frac{a_{H^+}}{\sqrt{P_{H_2}}} \quad (1)$$

where E^0 is the potential of the standard electrode, R is the gas constant, T is the absolute temperature, F is Faraday's constant, a_{H^+} is the activity of hydrogen ions, and P_{H_2} is the partial pressure of hydrogen. A conventional hydrogen RE realizes $E = E^0$ by maintaining $P_{H_2} = 1$ and $a_{H^+} = 1$. In the proposed sensor, we achieve $P_{H_2} = 1$ around RE by generating hydrogen during electrolysis. Moreover, by maintaining the hydrogen ion concentration around RE, we also achieve a constant a_{H^+} . Thus, letting A be defined by (2), the surface potential of the RE

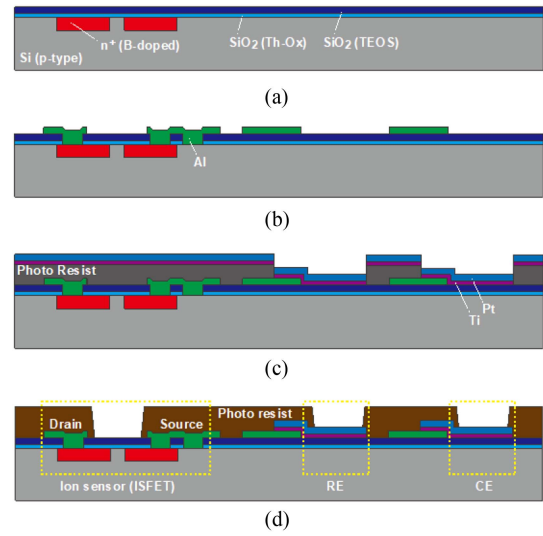


Fig. 2 Fabrication of ISFET and Pt electrodes for the proposed sensor: formation of (a) n-well and oxide films, (b) Al wiring layer, (c) Pt electrodes, and (d) protective coating layer.

in the proposed sensor is given by (3), and therefore, this electrode can function as RE after correcting for the temperature

$$A = \frac{R}{F} \ln \frac{a_{H^+}}{\sqrt{P_{H_2}}} \quad (2)$$

$$E = E^0 + AT. \quad (3)$$

By using the sensing method described earlier, the pH, the flow speed, and electrical conductivity can be simultaneously measured. Electrical conductivity can be measured using the electric potential across RE–CE under an applied current. Electrical conductivity σ during current application can be expressed as

$$\sigma = a \frac{I_{\text{const}}}{V} \quad (4)$$

where a is a constant determined by the electrode areas and distance between the RE and the CE, I_{const} is the applied current, and V is the measured potential of the CE.

III. DEVICE FABRICATION

We fabricated the ISFET and Pt electrodes on a p-type Si substrate. For fabrication, we adopted Minimal Fab, which is a specific semiconductor/MEMS device fabrication platform [11]. In Minimal Fab, a 12.5-mm wafer is used, and an extremely clean room facility is not necessary. Hence, it is suitable for fabricating a small quantity of diverse devices in a short period.

Fig. 2 illustrates the fabrication process. First, an n-doped region, which serves as source and drain of the ISFET, is prepared using thermal diffusion and Boron as dopant. Furthermore, a 60-nm-thick SiO_2 layer is formed through thermal oxidation. Then, a 100-nm-thick SiO_2 layer is formed through tetraethyl orthosilicate (TEOS) plasma chemical vapor deposition on top of the aforementioned layer [see Fig. 2(a)]. The TEOS oxide film serves as an ion-sensitive layer. Thereafter, a contact hole is formed on the oxide film through buffered HF wet etching. Furthermore, a 300-nm-thick Al layer is formed through sputtering and then patterned [see Fig. 2(b)]. Subsequently, lift-off resist is patterned, and a 50-nm-thick Ti layer and a 100-nm-thick Pt layer are sputtered [see Fig. 2(c)]. Note that the Ti and Pt layers

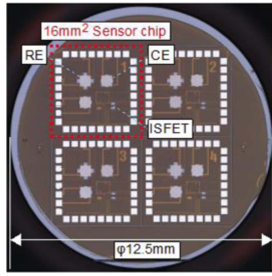


Fig. 3 Fabricated sensor device.

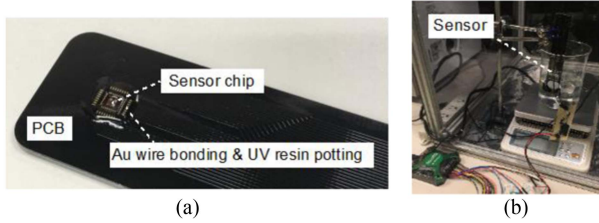


Fig. 4 Measurement setup for sensor evaluation. (a) Sensor probe installed with a sensor chip. (b) Photograph of the pH measurement setup.

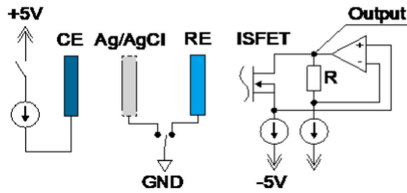


Fig. 5 Overview of the measurement circuit. A current regulative diode is used to generate constant current. When either the RE or the Ag/AgCl RE is being used, the other is disconnected from the measurement circuit.

are formed using the conventional sputter. Finally, photoresist for packaging is formed for waterproofing [see Fig. 2(d)].

Fig. 3 depicts the four fabricated sensor devices before dicing. The sensor consists of an ISFET and Pt electrodes. Other devices, such as pressure sensor, temperature sensor, and MOSFET, are simultaneously fabricated on the same substrate and will be discussed in detail in a separate report. The area of one sensor chip is 16 mm² and contains 32 pads for external connections.

IV. EXPERIMENTAL RESULTS

A. Measurement Setup

We performed measurements to verify the sensor operation. First, we bonded the sensor on a PCB, which was designed for the proposed sensor evaluation, as shown in Fig. 4(a). To prevent short circuit by the water, an ultraviolet-cured resin was coated on the wire-bonded area of PCB. Fig. 4(b) shows a photograph of the measurement setup. The sensor probe and an Ag/AgCl RE were immersed in a beaker, in which pH standard solutions were used to clarify the relationship between ISFET output and pH value. Here, the Ag/AgCl RE was used for comparison. When the proposed RE was being used, the Ag/AgCl RE was disconnected from the measurement circuit shown in Fig. 5. The ISFET was implemented as a source-follower circuit, and its drain voltage was controlled using an operational amplifier (JRC,

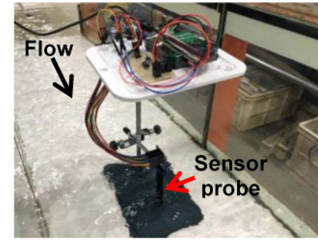


Fig. 6 Photograph of the measurement setup for flow speed measurement. A sensor probe was immersed in the experimental water flow channel and set in parallel to flow to reduce the influence of PCB on flow speed measurement.

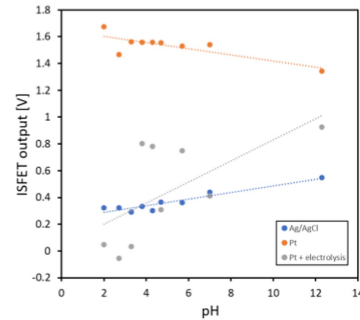


Fig. 7 Output characteristics of the ISFET by pH. The output voltages were averaged from three to five times measurements. In the measurement, we focused on acidity measurement.

NJM2119) to maintain the ISFET resistance equal to that of resistor R . Power supply to operational amplifier, current apply to electrode, and output data logging were performed by a measurement instrument (Digilent, Analog Discovery 2). Current regulative diodes (SEMITEC, E-101) were used to supply constant current by delivering 100 μ A, and resistor R was set to 10 k Ω . Therefore, the ISFET voltage between the source and the drain was maintained at 1 V, and output voltage V_{out} is given by

$$V_{out} = V_{offset} + V_g \quad (5)$$

where V_g is the ion-sensitive surface potential, and V_{offset} is the threshold voltage plus the source-drain voltage of the ISFET.

On the other hand, to verify the working principle as the flow speed sensor, a sensor probe with the same measurement setup shown in Fig. 4(a) was used. To detect water flow speed, the sensor probe was immersed in the experimental water flow channel with flow speed variation function, as shown in Fig. 6. In the measurement, the probe of conventional electromagnetic flowmeter (KENEK, VE-10) was also immersed near the ISFET in the experimental water flow channel to clarify the relationship between hydrogen desorption time at the electrode and water flow speed.

B. Measurement Results and Discussion

The output voltages between the ISFET and the RE before electrolysis [see Fig. 1(a)], RE after electrolysis [see Fig. 1(c)], and Ag/AgCl RE are shown in Fig. 7. When the Ag/AgCl RE was used, the ion sensitivity of the ISFET was approximately 20 mV/pH. However, this value was lower than the sensitivity expected from the Nernst's equation in (1) (approximately 50 mV/pH). Such low sensitivity is caused by the deterioration of the TEOS oxide layer, because its film is less dense than the thermal oxide film. Before electrolysis, when the

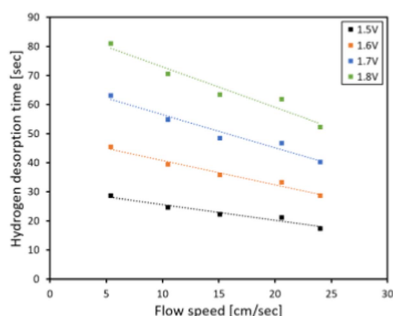


Fig. 8 Relationship between hydrogen desorption time (time until surface potential of Pt electrode is recovered after electrolysis) and water flow speed. The water flow speed was measured with an electromagnetic flowmeter. At the present measurement condition, the maximum flow speed can be measured was 25 cm/s.

proposed Pt RE was used, the characteristics were opposite to those of the Ag/AgCl RE use. Thus, we demonstrated that before electrolysis, the RE is influenced by pH and unsuitable for use as an RE. In contrast, after electrolysis, when the proposed Pt RE was used, the response of the ISFET showed roughly similar tendency to that of the Ag/AgCl RE use. The lower output voltage compared when the Pt RE used is due to reverse electric field caused by adsorbed hydrogen ions. As a summary, after electrolysis, the fabricated Pt electrode can be applicable as an RE, although its accuracy remains to be increased by improving the ion-sensitive layer, as well as the surface roughness of the Pt electrode and optimizing the duration time of electrolysis.

To verify the sensing principle as a flow speed sensor, we measured time variation of the Pt electrode potential. In other words, hydrogen desorption time was measured, and we obtained relevance to water flow speed. The measurement results are shown in Fig. 7, where the release time (i.e., time after switch-OFF in Fig. 1(c) until the surface potential of RE is recovered) was measured until the ISFET output become constants of 1.5, 1.6, 1.7, and 1.8 V. The pH was fixed to 7 during these measurements. The electrolysis in the step of Fig. 1(b) was conducted for 10 s. As shown in Fig. 8, we found that the surface potential of Pt RE recovery time is shorten progressively as the flow speed increased. We also confirmed the linearity between surface potential recovery time and flow speed because the correlation coefficients (R^2) were 0.95, 0.98, 0.96, and 0.94 when the ISFET output voltages were 1.5, 1.6, 1.7, and 1.8 V, respectively. These relations suggest the effectiveness of the proposed sensor to measure water flow speed. Namely, when both the amount of hydrogen adsorbed by the electrode immediately after electrolysis and the partial pressure of hydrogen on the surface are postulated to remain constant, the outflow speed of hydrogen is determined to depend on the thickness of the concentration boundary layer. As the thickness of the concentration boundary layer varies according to the flow around the electrodes, the flow speed could be measured effectively. A further quantitative study to clarify the relationship between Pt electrode potential change and flow speed is necessary. The thickness of adsorbed hydrogen depends on water type

that will be thicker when seawater is used due to various electrolytes. In principle, the proposed sensor can be applicable to seawater; however, packaging must be critical to prevent algae attachment and corrosion.

V. CONCLUSION

In this letter, we proposed a novel sensor to simultaneously measure the pH and flow speed of natural water flow using an ISFET and two Pt electrodes. After electrolysis, a Pt electrode acts as an RE. By using the Pt RE, we could obtain pH measurements showing roughly similar tendency to those obtained by using an Ag/AgCl RE. Therefore, we verified the possibility to construct a pH sensor into a single chip integrated with an RE. Moreover, we demonstrated that the proposed sensor can be used to measure water flow speed by measuring the time required for the sensor output to return from the state after electrolysis of water to that before electrolysis. In conclusion, the proposed sensor can be applicable for a low-cost large-scale water quality monitoring system.

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REFERENCES

- [1] D. Kandris, C. Nakas, D. Vomvas, and G. Koulouras, "Application of wireless sensor networks: An up-to-date survey," *Appl. Syst. Innov.*, vol. 3, no. 1, 2020, Art. no. 14, doi: [10.3390/asi3010014](https://doi.org/10.3390/asi3010014).
- [2] K. Gulati, R. S. K. Boddur, D. Kapila, S. L. Bangare, N. Chandnani, and G. Saravanan, "A review paper on wireless sensor network techniques in Internet of Things (IoT)," *Materialstoday: Proc.*, vol. 51, no. 1, pp. 161–165, 2022.
- [3] E. T. de Camargo et al., "Low-cost water quality sensors for IoT: A systematic review," *Sensors*, vol. 23, no. 9, 2023, Art. no. 4424, doi: [10.3390/s23094424](https://doi.org/10.3390/s23094424).
- [4] P. Bergveld, "Development, operation, and application of the ion-sensitive field-effect transistor as a tool for electrophysiology," *IEEE Trans. Biomed. Eng.*, vol. BME-19, no. 5, pp. 342–351, Sep. 1972.
- [5] M. Douthwaite, N. Moser, and P. Georgiou, "CMOS ISFET array for integrated electrochemical sensing and imaging applications: A tutorial," *IEEE Sens. J.*, vol. 21, no. 20, pp. 22155–22169, Oct. 2021.
- [6] R. Komiyama, H. Miyashita, T. Kageyama, K. Ohmi, S.-S. Lee, and H. Okura, "A microfluidic device fully integrated with three pH sensing electrodes and passive mixer for nanoparticle synthesis," in *Proc. IEEE SENSORS Conf.*, 2015, pp. 1–4.
- [7] N. Roy, D. Verma, and A. Prabhakar, "Cost-effective MEMS fabrication and electrode alignment in microfluidic devices for biological detection," in *Proc. Int. Conf. Elect., Comput. Energy Technol.*, 2021, pp. 1–4.
- [8] Z. Zhao, H. Tu, E. Kim, B. Sloane, and Y. Xu, "A flexible Ag/AgCl micro reference electrode based on a parylene tube structure," *Sens. Actuators B: Chem.*, vol. 247, pp. 92–97, 2017.
- [9] S. Papamatthaiou, U. Zupancic, C. Kalha, A. Regoutz, P. Estrela, and D. Moschou, "Ultra stable, inkjet-printed pseudo reference electrodes for lab-on-chip integrated electrochemical biosensors," *Sci. Rep.*, vol. 10, 2020, Art. no. 17152.
- [10] D. A. J. Rand and R. Woods, "A study of the dissolution of platinum, palladium, rhodium and gold electrodes in 1 m sulphuric acid by cyclic voltammetry," *J. Electroanalytical Chem. Interfacial Electrochem.*, vol. 35, no. 1, pp. 209–218, 1972.
- [11] S. Khumpuang, F. Imura, and S. Hara, "Analyses on cleanroom-free performance and transistor manufacturing cycle time of minimal fab," *IEEE Trans. Semicond. Manuf.*, vol. 28, no. 4, pp. 551–556, Nov. 2015.