

Development of a Novel Micro-FIA-ISFET Integrated Sensor

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Based on the principle of flow injection analysis (FIA), we report that a novel micro-FIA-ISFET integrated sensor comprising four pairs of long-arm pH-ISFET(Si₃N₄/SiO₂ gate)/REFET(SiO_xN_y/Si₃N₄/SiO₂ gate) units and a symmetric Ti/Au pseudoreference electrode has been integrated on a chip, thereby achieving integrative configuration of a transducer and micro-flow-through cell. The sensor chip size is 6 × 8 mm². The initial results of our experiment indicate that the liquid to be measured, which is driven by a peristaltic pump, flows with great fluency and that the amount of test sample needed for dynamic measurement is greatly reduced. The differential sensitivity of the sensing units is in the range of 32 – 44 mV/pH. The response time of the integrated sensor is less than 1 second, and its reliability and stability are considerably improved.

1. Introduction

Ion-sensitive field-effect transistors (ISFETs) have potential advantages over conventional ion-selective electrodes (ISEs) such as their small size, rapid response, low output impedance, low cost, and suitability for mass production. These advantages give ISFETs great potential in the fields of chemical analysis, biomedical research, and industrial manufacture and monitoring; however, there are also some problems. In the practical application of ISFETs, a standard reference electrode is required to provide a reference electric potential. Because the standard reference electrode is relatively large, it is very

inconvenient to use, particularly when the sample is small or when it is used in a special place, such as in the human body. In addition, in conventional static measurements, the electrode potential of reference electrodes can change the concentration of ions surrounding them. This effect, together with long-term drift, hysteresis, and other undesirable responses, reduces the accuracy and stability of the measurement. Some studies have shown that the former can be solved by fabricating micro-reference electrodes,^(1,2) using microprocessing technology and adopting differential circuits,^(3,4) and that the latter can be solved by adopting a flow injection analysis (FIA) system.^(5,6) Using flow injection measurement, not only can the precision and stability of the measurement be improved, but also consecutive and in-line measurements can be conducted, which can greatly improve the efficiency of measurement.⁽⁷⁻⁹⁾

In this paper, the fabrication process and features of a novel micro-FIA-ISFET integrated sensor is reported. This sensor comprises a micro-flow-through cell, four pairs of ISFETs, and a symmetric Ti/Au pseudoreference electrode. Its fabrication process is compatible with NMOS IC technology and all components are integrated on a single chip. The sensor, together with the extra flow-through driven system and measurement electronics, constitutes a micro-FIA-ISFET integrated sensor system.

2. Experiment

A pattern micrograph of a sensor chip of size $6 \times 8 \text{ mm}^2$ is shown in Fig. 1. Four pairs of long-arm ISFETs are aligned on the chip, each of which acts as a unit. Each unit comprises a pH-ISFET and a REFET with common sources. Using this configuration, differential signal output can be easily achieved through differential sensing between pH-ISFET and REFET; thus the sensor can effectively reject common mode noise. If the four

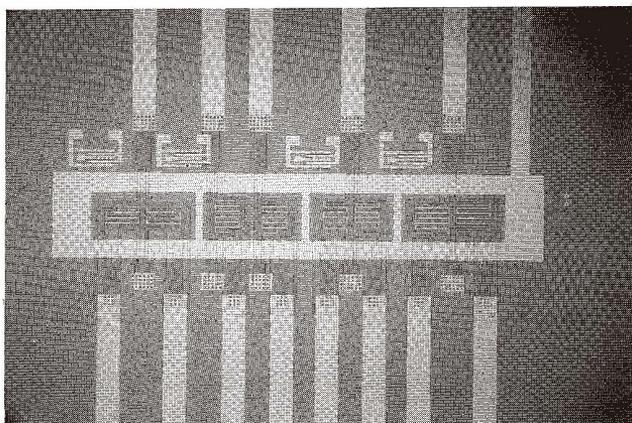


Fig. 1. Pattern micrograph of an integrated ISFET sensor chip.

units are mounted on different sensitive and insensitive membranes, a sensor array, which is sensitive to four kinds of ions, can be obtained. The long-arm structures are heavily doped areas which are connected to the ISFETs and extra electronics.

The substrate of the sensor chip is a p-type (100) silicon wafer with a resistivity of 5–9 Ω -cm. The W/L of the ISFETs is 80, 60 and 40. In the preliminary experiment, all four units are H⁺ ion-sensitive. Their pH-sensitive gates have a two-layer configuration of Si₃N₄ (50 nm) and SiO₂ (40 nm), whereas their pH-insensitive gates have a three-layer configuration of SiO_xN_y (6–8 nm), Si₃N₄ (50 nm) and SiO₂ (40 nm). Si₃N₄ is deposited by LPCVD, followed by the outer SiO_xN_y layer thermal growth at 950 °C in dry oxygen for 30 min. The Ti/Au pseudoreference electrodes and electrical pads with thicknesses of 100 nm and 500 nm, respectively, are formed using electron beam evaporation and the lift-off process. The entire fabrication process is compatible with NMOS IC technology.

A micro-flow-through cell is formed on glass (7740) by micro-machining technology. At end of the cell, two holes with a diameter of 0.5 mm are bored, which act as inlet and outlet of the flow-through cell. In order to protect FET on the chip from destruction by high voltage, the chip is first sintered on a header. Then, each pad of source and drain and the Ti/Au pseudoreference electrode are bonded by wires and connected to a positive potential. Finally, 300°C and 800 V are applied to bond the silicon chip and glass together. For the reason of the Ti/Au pseudoreference electrode, the chip temperature is set below 350°C. A large Ti/Au area on the chip facilitates bonding. After electrostatic bonding of the silicon chip and glass, a special paste is used to adhere the two stainless steel pipes to the holes of the glass. The package is finally sealed by filling the areas around the glass, wires and pads with paste. The fabricated sensor is shown in Fig. 2.

Figure 3 shows the block diagram of the measurement system. The sample and the calibrating solution are driven by a peristaltic pump through the micro-flow-through cell and the ISFETs, and are then drained via the outlet. The sensor signal is amplified by

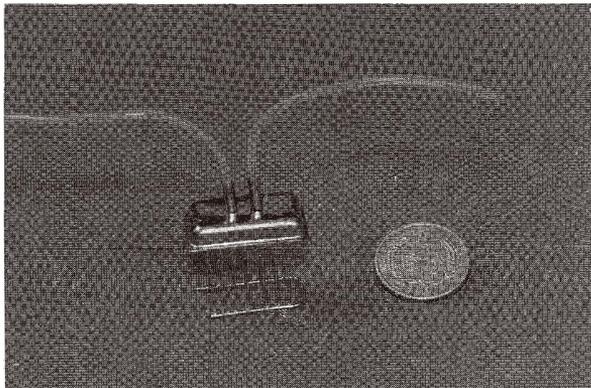


Fig. 2. Micrograph of the micro-FIA-ISFET sensor.

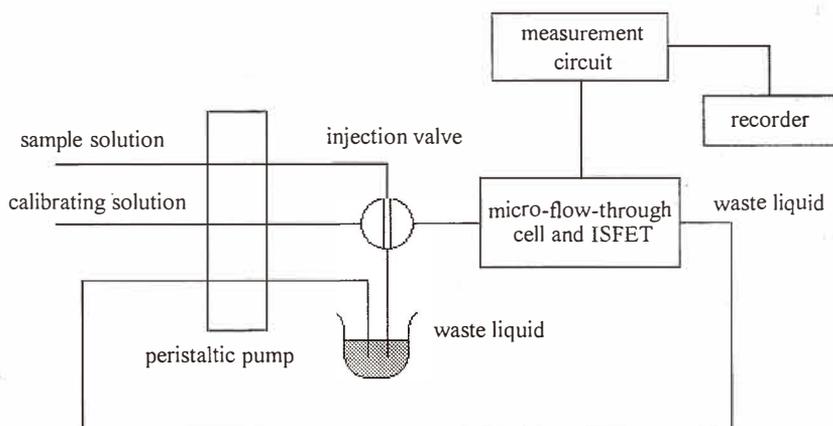


Fig. 3. Block diagram of the measurement system.

measurement electronics, and is then recorded by a function recorder. Each sensor unit is connected to a differential amplifier and the potential of the pseudoreference electrode is 0.5 – 1.0 V. The signal output by the differential amplifier is selected using a multichannel switch, and is then amplified by a preamplifier, the total amplification of which reaches 1.5. Finally, the response curves are plotted by the function recorder.

3. Results and Discussion

Figure 4 shows the SIMS result for the $\text{SiO}_x\text{N}_y/\text{Si}_3\text{N}_4/\text{SiO}_2$ structure. We can see that the oxygen content on the surface of SiO_xN_y is higher than that in the SiO_2 layer. Therefore, the pH sensitivity of the $\text{SiO}_x\text{N}_y/\text{Si}_3\text{N}_4/\text{SiO}_2$ gate ISFET is more similar to that of the SiO_2 gate ISFET than that of the Si_3N_4 gate ISFET.^(10,11) With the $\text{SiO}_x\text{N}_y/\text{Si}_3\text{N}_4/\text{SiO}_2$ gate ISFET as the REFET and $\text{Si}_3\text{N}_4/\text{SiO}_2$ gate ISFET as the pH-ISFET, the pH sensitivity of the four units shown in Fig. 5 can be measured with an on-chip Ti/Au pseudoreference electrode. The sample is driven by a peristaltic pump into the micro-flow-through cell, until the micro-flow-through cell is full of sample solution. The unstable electrolyte-Ti/Au electrode potential is a signal commonly detected in the differential system and thus will not interfere with the final output signal. Its measurement circuit is of a constant-current pair transistor differential mode. From Fig. 5, it can be seen that the sensitivity of the four units is in the range of 32 – 44 mV/pH where linear regression coefficients are between 0.956 and 0.987.

The size of the micro-flow-through cell is $0.4 \times 5.0 \times 0.3 \text{ mm}^3$. The inner and outer diameters of the inlet and the outlet of the stainless steel pipes are 0.4 mm and 0.5 mm, respectively. The entire FIA system is shown in Fig. 3. When samples ($2 \mu\text{l}$ per run) with

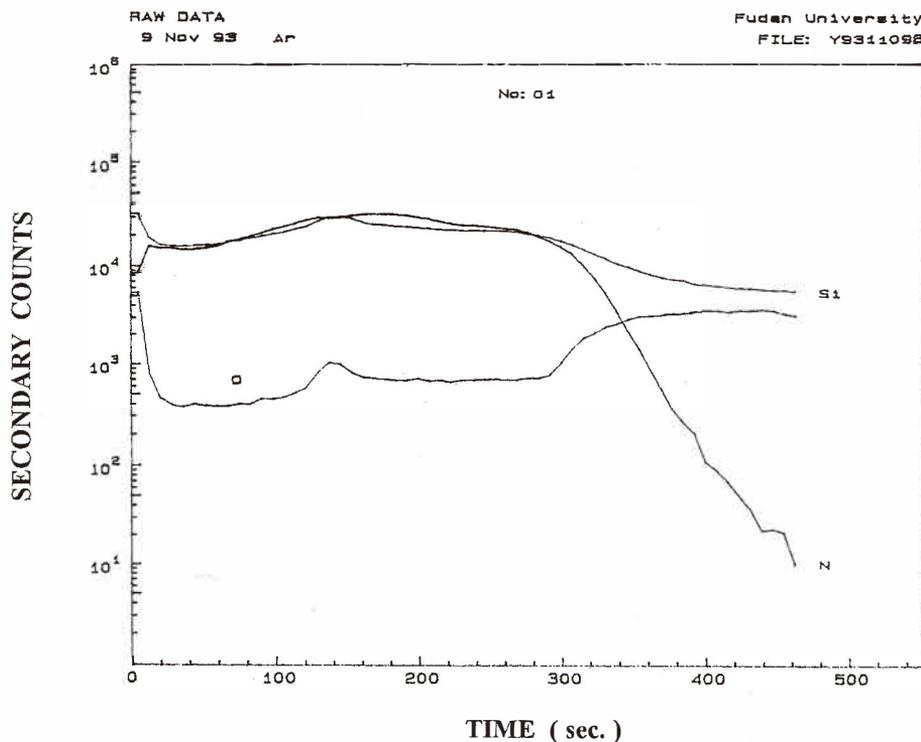


Fig. 4. SIMS result for the $\text{SiO}_x\text{N}_y/\text{Si}_3\text{N}_4/\text{SiO}_2$ structure.

various pH values are injected into the system, and the flow rate of the calibrating solution is 0.3 ml/min, in order to achieve reproducibility of measurement, the response of each sample is recorded four times. The response features are shown in Fig. 6. It can be seen from the width of the peaks that the response is very fast and uniform. The rise time is less than 0.1 second, and the whole response time of each sample is nearly 1 second. The fall time depends on the sample dispersity. When the flow rate of the calibrating solution is low, the response time increases to several seconds. Figure 7 shows the effect of different flow rates on the output response. The pH values of the carrier solution and the measured solution are 3.71 and 9.18, respectively. The injected sample is also 2 μl per run.

Figure 8 shows the standard curve obtained from measurement of samples whose pH values are known. It can be seen that standard curve is a straight line. According to this standard curve, the pH value of the sample measured (pH = 5.84) is 5.82. The absolute error is ± 0.02 . In practical measurements, the appropriate calibrating solution should be selected on the basis of the estimated pH value of the sample. The pH value of the sample can then be determined from the standard curve.

In the flow injection measurement system, because a known standard solution is

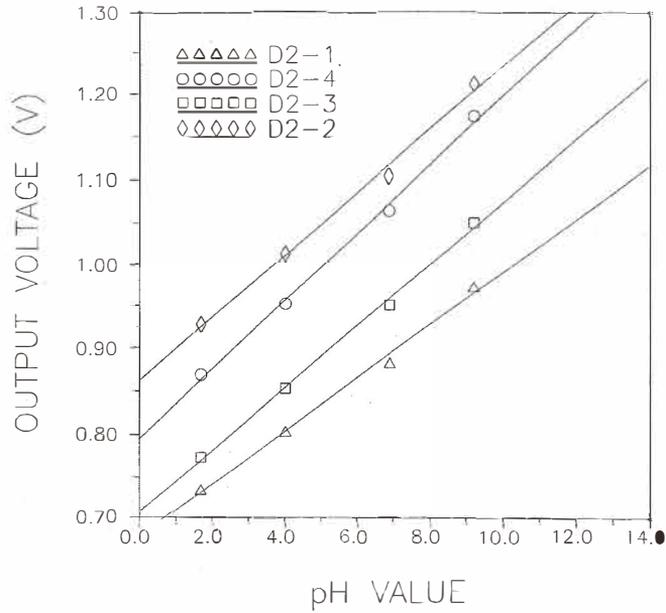


Fig. 5. pH sensitivity of the four units.

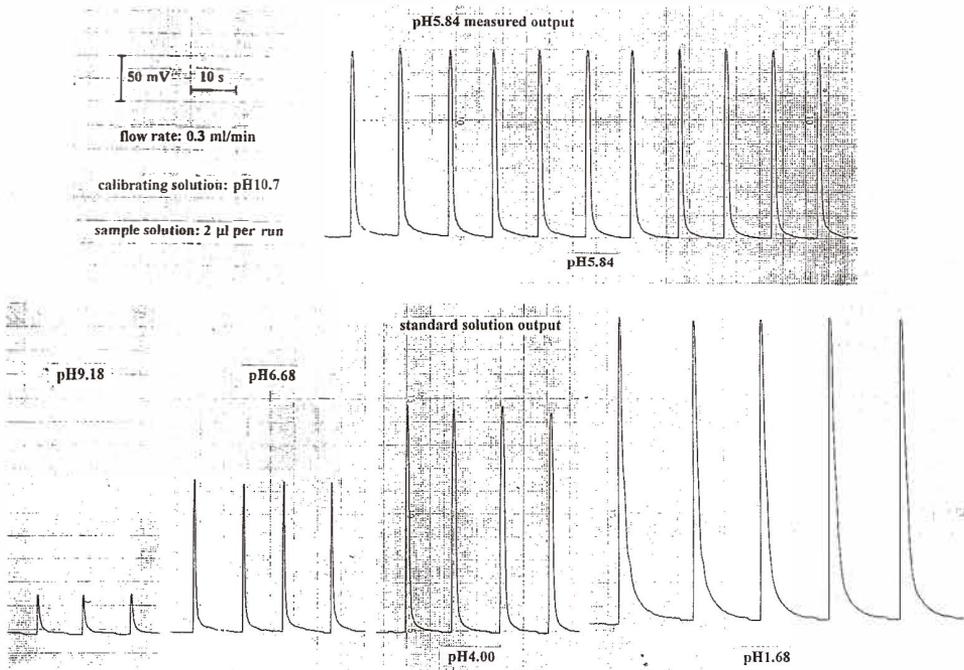


Fig. 6. Typical output response from the FIA system.

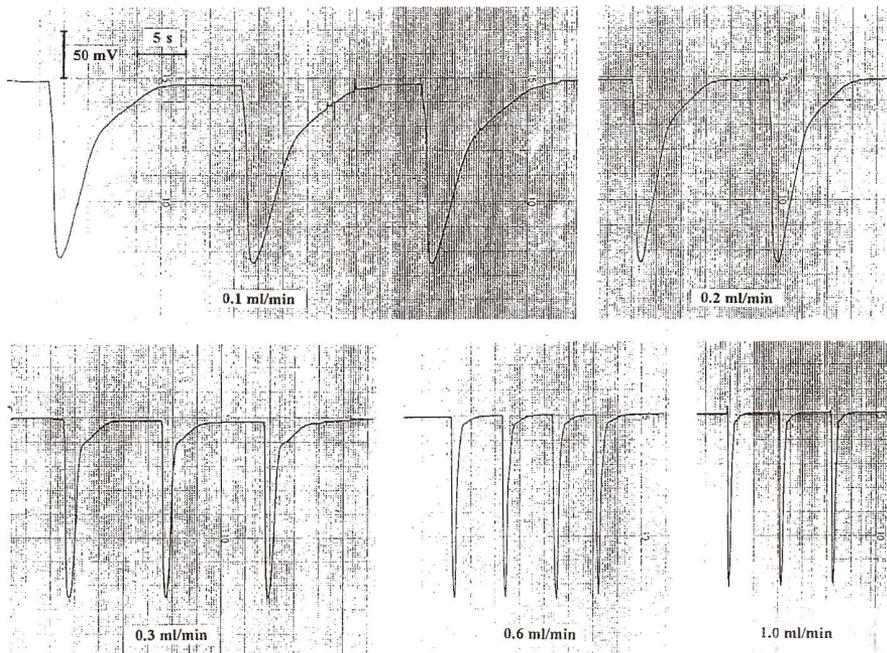


Fig. 7. Effect of different flow rates on output response(carrier solution: pH 3.71, measured solution: pH 9.18, 2 μ l per run).

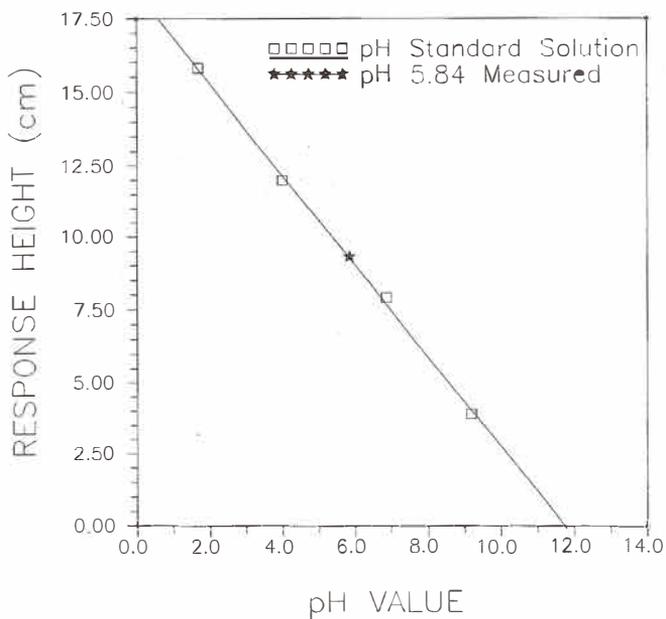


Fig. 8. pH value standard curve of the FIA-ISFET system.

calibrated and the measurement time is very short, the drift and the poor stability of the ISFET become irrelevant. Conversely, the fast response of the ISFET is an extremely important feature that improves measurement precision and efficiency. The use of a micro-flow-through cell and a symmetric Ti/Au pseudoreference electrode greatly decreases sample consumption (10 μ l for four runs), which has great significance in the study of biomedicine and clinical medicine.

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