논문 97-6-2-07

Improvement of reliability of an ISFET pH-meter by employing multiple sensors

Kee-Seok Chang*, Byung-Woog Cho**, Chang-Soo Kim***,
Sang-Bok Choi*, Byung-Ki Sohn**

Abstract

The ISFET(ion sensitive field effect transistor), a semiconductor ion sensor, has many advantages over conventional ion sensors. Various single-sensor type ISFET pH-meters have been developed. However, they could not be applied in fields because their performances are directly affected by the sensor condition. With only one sensor, the system could be easily damaged from environmental factors, and reliability of it is decreased. Therefore, a 4-channel pH-meter system is proposed to improve the reliability of ISFET pH-meter. It has 4 ISFETs as ion sensor, and a software which contains a new calibration and measurement algorithm appropriate to the system. The reliability of the system was proved by measuring hydrogen ion concentration in the pH standard solutions and buffer solutions.

Ⅰ. Introduction

The pH-meters which measure the hydrogen ion concentration in a solution have been used in the fields of analytical chemistry, biomedical instrumentation, and environment monitoring.

For the measurement of hydrogen ion concentration in a solution, ISE(ion selective electrode) type pH-meters have been used widely. It is, however, reported that ISEs are slow in response, relatively large in size, expensive in cost, and difficult in handling. ISFET[1-3], a solid state semiconductor device, has many advantages such as fast response, small dimension, and easy standardization and mass production due to the fabrication based on the integrated circuit technologies. These potential advantages allow unique application possibilities such as *in-situ* measurement or microelectronic integration.

For the application of pH-ISFET, various pH-meters[4-5] have been developed with only one sensor. But with a single sensor, the system can be easily damaged and deteriorated by electrostatic discharge or other environmental causes, that results in the decrease in reliability and stability of the measurement system.

Accordingly, in order to improve the reliability of the pH measurement system, it is desirable to design a multi-channel pH-meter which consists of several pH-ISFETs for measurement, and the sotftware to do the processing of the multi-channel sensor signals.

* Dept. of Sensor Eng., Kyungpook Nat'l Uni.
** School of Electronic and Electrical Eng., Kyungpook Nat'l Uni.
*** Sensor Technology Research Center, Kyungpook Nat'l Uni.
<접수일자 : 1996년 11월 30일>

In this paper, a 4-channel pH-meter system utilizing 4 pH-ISFETs is proposed. Each of the sensors is operated by the null-balance method. This method yields a signal which directly reflects the interfacial potential at the chemically active gate of the pH-ISFET. Hardware of the system consists of bias and preamplification circuit, signal processing circuit, and LCD(liquid crystal display) panel. The software for the system also has been developed. It has a new calibration and measurement algorithm appropriate to the proposed 4-channel pH-meter.

The performance of the realized system was tested in the pH buffer solutions and the pH standard solutions.

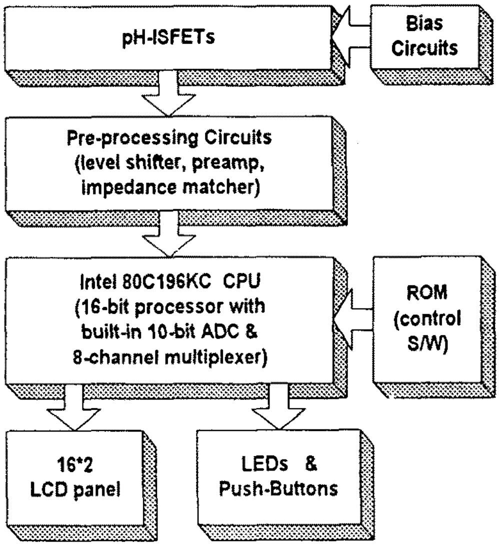

Fig. 1. Block diagram of the system.

II. Design of the hardware

The block diagram of the designed 4-channel pH-meter is represented in Fig. 1. The system uses 4 ISFETs as transducer, 80C196KC(Intel Co.) as CPU(central processing unit). And it displays program steps and measurement results on LCD panel. The conditions of individual sensors are exhibited by on/off the LEDs. Considering average response time of the pH-ISFETs, sampling of the output signals was begun after 10 seconds from putting sensors into the solution, and was continued. The output voltages of the sensors were accepted and stored when they were not varied more than 1 LSB(least significant bit) for 2 seconds.

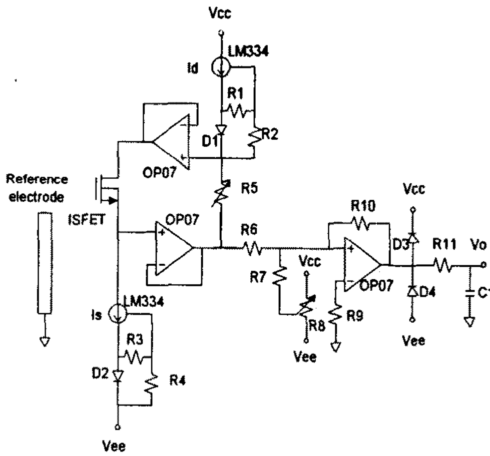

Fig. 2. Processing circuit of the system.

The circuit, represented in Fig. 2, is for preprocessing. It shows one channel of the system. As shown in figure, null-balance circuit is used, in which the drain current and drain-to-source voltage can be held constant so that the bias of the ISFET does not change. The source voltage changes linearly with the pH dependent changes in the threshold voltage, while the reference electrode is grounded. Thus, the transfer of this method is practically linear and the application of the pH-ISFETs is not restricted. The output voltage levels of the pH-ISFETs are as high as about 58mV/pH that is sufficient to detect the variance of the pH. However, if they were transferred to the A/D converter as they are, the quantization error[6] would be increased because of the quantization level of the A/D converter. *U3* of Fig. 2 is the level shifter and amplifier to balance threshold voltages of each sensors and reduce the quantization error. The gain is determined as 8.2, considering sensitivity of the sensor, measurement range, and input level of the A/D converter. As a result, the resolution of the system is 0.01 pH and measurement range is pH 3~11. D_3 and D_4 is a voltage clipper to protect input unit of the CPU and R_{11} and C_1 is a impedance matcher to full charge up the sampling capacitor in the A/D converter.

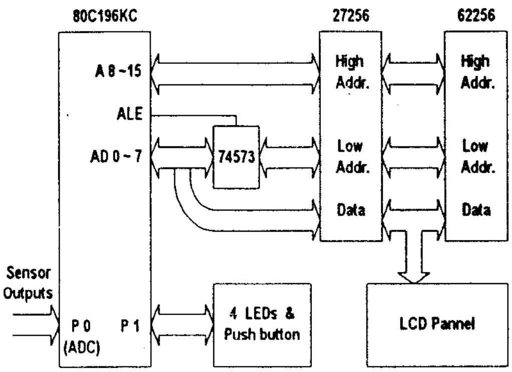

Fig. 3. Block diagram of the CPU interface.

The CPU in the control circuit has five 8bit input/output ports, 10bit A/D converter, and 8-channel multiplexer. The block diagram of the CPU interface is exhibited in Fig. 3. As shown in the figure, the CPU receives the output signals of the sensors through the port 0, controls the LEDs, represent the conditions of the sensors, the and push-buttons through the port 1. The LED is lighted when the sensor operates normally, otherwise it is put out. The push-buttons take the role of menu selection, alternation of the program step, or reset of the system. EPROM(erasable programmable read only memory) and RAM (random access memory) are connected to the address-data bus to transplant the software and to store the data respectively. And the LCD panel is controlled through the address-data bus.

III. Design of the software

The signal processing software suitable for the system was programmed and its main flow diagram is described in Fig. 4. After the power is supplied, the software initializes the system, operating mode of the CPU and peripheral ICs. Because there are deviations of the sensitivities and the threshold voltages, level shift of the output signals is required. After then, 3-point calibration is done, and calculated sensitivities are compared with a standard sensitivity to determine whether they could be used for measurement or not.

It is well known that calibration plays a key role in sensors. Signal processing circuit for a sensor requires a suitable calibration that has to provide a reliable sensor representation. Although the pH-ISFET has excellent linearity and reproducibility with wide pH range, 3-point calibration method was used for more precise measurement, which linearizes the output signal in acid region and base region separately. Therefore, 8 sensitivities are stored at the calibration routine.

At the sensitivity checkup routine, the calculated sensitivities at calibration routine are compared with the standard one. The sensors that have lower sensitivity than the standard sensitivity are extracted from the measurement, which is also represented by LEDs.

After then, it begins measurement routine. It computes the pH value of voluntary pH solution from the output voltages of the sensors and the stored values at calibration routine. Because the sensors could be damaged by electrostatic discharge or other environmental causes during the measurement, the output voltage levels of the sensors are continuously monitored. If some sensors were not working, they should be extracted from the measurement and computation in next step.

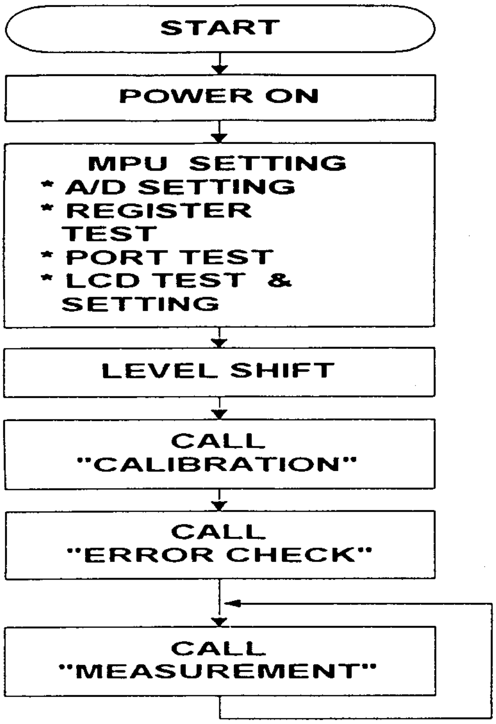

Fig. 4. Flow chart of main control S/W.

Ⅳ. Experiments and results

A sketch of the experimental set-up is given in Fig. 5. The software was transferred from the personal computer to the hardware. The results of the measurement were displayed at the LCD panel. Sensor conditions were shown by the LEDs.

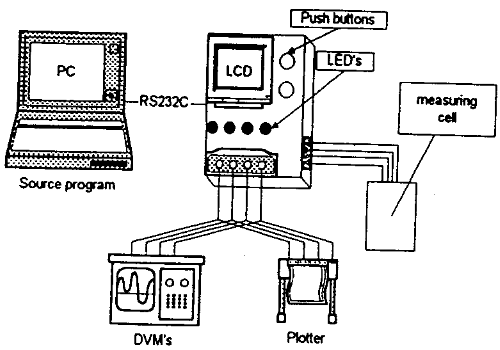

Fig. 5. Sketch of the experimental set-up.

The output signals of each sensors could be monitored individually by digital multimeters or plotter.

The solutions used for testing designed pH-meter were pH standard solutions(Aldrich, pH 3~11). The hydrogen ion concentration is measured 5 times in the standard solutions as the sequence of pH 11 to 2 after calibration. To make comparison with commercialized pH-meter, a ISE type pH-meter(ORION, EA940) was tested in the same procedure and environment. The results are exhibited in Fig. 6. It shows the variance of the measured pH values of two pH-meters. The variance, represents repeatability of the output values at the same pH solution, is considered to be caused by the hysteresis[7-8] characteristics of the sensors. As shown in Fig. 6, designed pH-meter stands comparison with commercialized one.

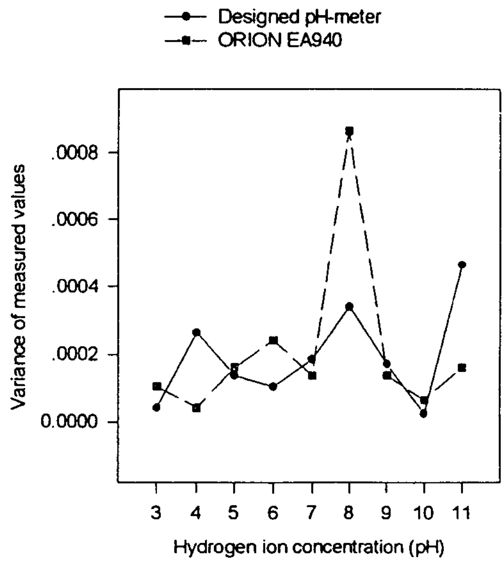

Fig. 6. Variations of measured values.

The deviations of two pH-meters from the real values are shown in Fig. 7. The deviation does not, however, directly indicate mere difference between measured value and real value. It could be seen that the designed 4-channel pH-meter

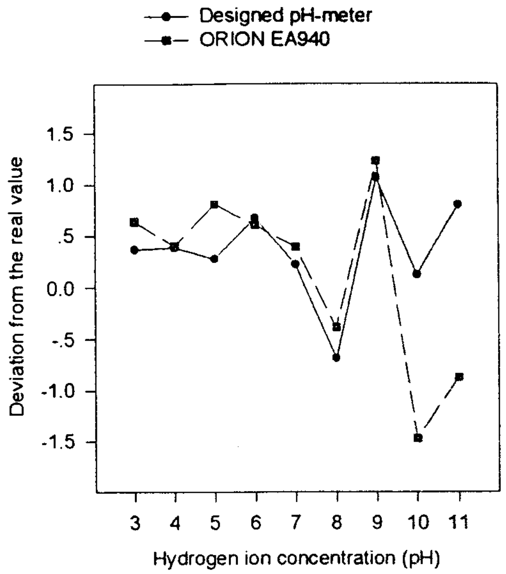

Fig. 7. Deviation of the measured pH value from the real value.

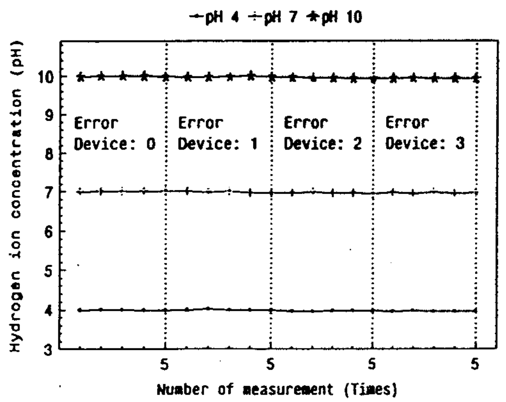

Fig. 8. Reproducibility of the designed pH-meter on occurrence of sensor error.

shows better performance than commercialized one as shown in the figure.

When some sensors do not work during measurement, the misconducting sensors have to be extracted from the measurement not to affect the measuring operation of the system. For the purpose of testing the reliability of the system on occurrence of damaged sensors, the normal sensors were replaced by the misconducting sensors one by one during the measurement. Then, the displayed values of the system were continuously monitored. We can see that the system has excellent measurement reproducibility and stability as shown in Fig. 8. It must be noticed that the measured values are little less than the real values after several measurements which is due to slow response(9-10) property of the sensors, not to the decrease of reliability by the misconducting sensors.

V. Conclusion

The 4-channel pH-meter hardware with 4 pH-ISFETs as the pH detector and appropriate processing software have been developed to improve the reliability and the stability of the pH measurement system. The software which has a new calibration and measurement algorithm could extract abnormal sensors from the measurement of pH after discriminating between normal sensors and others. The functions of the system showed satisfactory results as designed. The reliability of the system was proved by measuring hydrogen ion concentration in the pH standard solutions and buffer solutions.

It is expected that this system could be used in various fields, and applied for any other ion sensors whose output signals are voltage

References

[1] P. Bergveld, "Development, operation, and application of the ion-sensitive field-effect transistor as a tool for electro-physiology", *IEEE Trans., BME-19, 342-351, 1972*

[2] J. N. Zemel, "Ion-sensitive field effect transistors and related devices", *Anal. Chem., vol. 47, 255A-268A, 1975*

[3] P. W. Cheung, W. H. Ko, D. J. Fung, and S. H. Wong, "Theory, fabrication, testing and

chemical response of ion-sensitive field effect transistor devices", *Workshop on Theory design, and biomedical application of solid state chemical sensors, CRC Press, 91-118, 1978*

[4] F. V. Perezgasga, A. K. Covington, "Multisensor operation of ion-sensitive field effect transistors in the constant current mode", *Sensors and Actuators B, vol. 6, 219-222, 1992*

[5] M. Bove, A. Cambiaso, M. Grattarola, S. Martinoia, G. Verreschi, "An array of H+ FETs for space-resolved electrochemical measurements in microenvironments", *Sensors and Actuators B, vol. 24-25, 218-221, 1995*

[6] D. Martinez, D. Esteve, "Adaptive quantization and fault detection in smart sensors", *Sensors and Actuators A, vol. 46-47, 530-533, 1995*

[7] L. Bousse, P. Bergveld, "The role of buried OH site in the response of inorganic-gate pH-sensitive ISFETs", *Sensors and Actuators, vol. 6, 65-78, 1984*

[8] L. Bousse, S. Mostarshed, B. Schoot, N. F. Rooij, "Comparison of the hysteresis of Ta_2O_5 and Si_3N_4 pH-sensing insulators", *Sensors and Actuators B, vol. 17, 157-164, 1994*

[9] Yu Dun, Wei Ya-dong, Wang Gui-hua, "Time-dependent response characteristics of pH-sensitive ISFET", *Sensors and Actuators B, vol. 3, 279-285, 1991*

[10] L. Bousse, D. Hafeman, N. Tran, "Time-dependence of the chemical response of silicon nitride surface", *Sensors and Actuators B1, 361-367, 1990*

著 者 紹 介

장 기 석

1972년생. 1995년 경북대학교 전자공학과 졸업 (공학사). 1997년 경북대학교 센서공학과 석사과정 졸업 (공학석사). 현재 (주)한국전자(KEC) 연구원 . 주관심분야 : 반도체 센서 및 센서 시스템.

최 상 복

1967년생. 1996년 경북산업대학교 전자공학과 졸업 (공학사). 현재 경북대학교 센서공학과 석사과정. 주관심분야 : 센서 시스템.

조 병 욱

『센서학회지 제1권 제1호』 논문 92-08, p.101 참조.
현재 경북대학교 전자공학과 박사과정

김 창 수

『센서학회지 제1권 제1호』 논문 92-08, p.101 참조.
현재 경북대학교 센서기술연구소 연구원

손 병 기

『센서학회지 제1권 제1호』 논문 92-08, p.101 참조.
현재 경북대학교 전자전기공학부 교수, 센서기술연구소 소장