Highly sensitive ion sensors using charge transfer technique

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Abstract

Accumulation method ion sensor (AMIS), an expected high sensitive ion sensor, is proposed and prototype one is fabricated using a charge coupled device (CCD) process. The principle of the accumulation method ion sensor is based on the charge transfer techniques. The AMIS is operated in a signal integration mode. Charges corresponded to an ion concentration is transferred from a sensing part to the floating diffusion region on several times, and the signal charges are accumulated in the floating diffusion region. It is expected that the signal-to-noise ratio (SNR) of the chemical potential information increases \( n^{0.5} \) times, as the signal is integrated \( n \) times. The output signal was measured by using the equivalent signal. It was found that the output signal from AMPS, which was integrated five times, was linearly changed to the input signal and the total sensitivity was 450 mV/pH. This sensitivity is about nine times higher than that of ion sensitive field-effect transistor (ISFET).

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1. Introduction

Most familiar ion sensor using semiconductors is an ion sensitive field-effect transistor (ISFET). The ISFET based biosensor has a very proper configuration to in situ monitoring of various chemical processes, in vivo medical diagnosis and many other fields [1].

The ISFET is a combined structure of an ion-selective electrode (ISE) and a metal–insulator–semiconductor field-effect transistor (MISFET). The normal metal or polysilicon gate electrode of MISFET is replaced by the electro-chemical reference electrode in electrolyte solution and an ion-sensitive membrane on the top of the gate insulator. For proper operation of the ISFET, a gate voltage is applied to the gate insulator via the reference electrode and the electrolyte solution. An electro-chemical potential by ions is developed at the surface of the ion-sensitive membrane and can be measured as a shift in drain current or threshold voltage of the ISFET according to the bias method. The sensitivity of the ISFET is derived from site-biding model. From this model, the maximum sensitivity is 59.2 mV/pH for monovalent reaction at 25 °C, which is well known the Nernst value [2].

In this paper, a highly sensitive ion sensor used a charge transfer technique is proposed. The charge transfer technique is widely used in the charge coupled devices (CCDs) [3].

2. Principle and basic operation

It can be supposed that measurements of a small pH fluctuation are difficult by ISFET because the theoretical maximum sensitivity is only 59 mV/pH and the small output signals are buried in the 1/f noise component of the MISFET. Even if the small output signal from ISFET is amplified using a low noise amplifier, the output signal and the output noise (main component is 1/f noise) are amplified on a same time, and the signal-to-noise ratio (SNR) is not increased.

In this paper, we propose an accumulation method ion sensor (AMIS) that has new ion sensing principle. A schematic diagram of the AMIS is shown in Fig. 1. The AMIS consists of six parts: an input diode (ID), an input gate (IG), an ion sensing part, an output gate (OG), a floating diffusion (FD) and a source follower part. The ion sensing part of the AMIS consists of Si3N4/ SiO2/p-type Si substrate. The Si3N4 film is a sensing membrane for the hydrogen ions or the pH sensing. Its structure is almost same as the ISFET. However, the output signal of the proposed ion sensor is different from that
Fig. 1. Schematic diagram of AMIS. AMIS consist of six parts: an input diode (ID); an input gate (IG); a pH sensing part; an output gate (OG); a floating diffusion (FD); and a source follower part.

Fig. 2. Schematic measurement system of AMIS.

The output signal from the ISFET is the shift of the voltage between the gate and the source. On the other hand, the signal from the sensing part is a charge whose density varies according to the depth of the potential well under the ion sensing parts. This schematic measurement system is shown in Fig. 2. The reference electrode is inserted in the electrolyte to keep the potential of electrolyte constant. Reference electrode is biased at a voltage \( V_{RS} \). As the pH value in a solution is varied, the density of the hydrogen ions on the Si3N4 film is changed. Consequently, the potential on the Si3N4 film is shifted according to Nernst equation (theoretically, 59 mV/pH at room temperature), and the depth of the potential well in the p-type Si under the sensing part is varied.

The schematic structure of the AMIS and its potential well diagram is shown in Fig. 3. The ion sensing part is constructed with Si3N4/SiO2/Si structure. The Si3N4 film acts as the hydrogen ion-sensitive membrane. The potential well is formed in the Si substrate surface under the sensing part. As the density of the hydrogen ions in a solution (i.e. the value of the pH) is changed, the depth of the potential well is also changed. As the pH value on the sensing part becomes lower, the depth of this potential well is deeper.

An operation procedure of the AMIS is described. The clock cycle is initiated by turning off the output gate (Fig. 3a). Next, the potential of the input diode decreases and the electric charge is flowed into a potential well under a sensing part. The depth of the potential well is determined by the value of the pH. The potential of the input gate is fixed optionally, and is determined by the lowest sensing value. If this potential was higher than the potential under sensing part, the charge could not be stored. A depth of the charge packet is created by potential difference between the control electrode and the sensing part and the area of sensing part. The input diode is initially reverse biased over the input gate potential. Next, the input diode is briefly pulsed from \( V_{D1} \) to \( V_{D2} \) (Fig. 3b) and kept...
again $V_D$ (Fig. 3c). The well under the sensing part floods with charge and the excess charge beyond the control gate potential overflows to the input diode part. The charge corresponding to the pH value at the sensing part is remained in the charge packet. Next, the output gate is turned on, and the charge is transferred to the floating diffusion part (Fig. 3d). The procedure from Fig. 3a to Fig. 3d is repeated several times (Fig. 3e). This cycle is called “signal integration cycle.” As the signal integration cycle is repeated, the potential in the floating diffusion part is decreased and the signal charges are accumulated. By this integration operation, the potential under the ion sensing part is integrated in the floating diffusion part. The floating diffusion part is connected to a gate electrode of the source flower circuit, and the potential of the floating diffusion part is read from $V_{out}$ node of the source flower circuit. After the signal is measured, the floating diffusion part is rested using a reset transistor.

The AMIS is operated in a signal integration mode. Charges corresponded to chemical potential value are transferred from a sensing part to the floating diffusion region for several times and the signal charges are accumulated in the floating diffusion region. It is expected that the SNR of the chemical potential information increase to accumulate the signal charges. As a chemical potential signal $S_0$ is accumulated $n$ times, total quantity of the signal $S$ is described as follows:

$$S = n S_0$$

The total quantity of the noise $N$ is described as follows:

$$N = \sqrt{N_1^2 + N_2^2 + \cdots + N_n^2}$$

where $N_1, N_2, \ldots, N_n$ are the noise components of each integration stage. If these components are same, above equation is simplified as

$$N = \sqrt{n N_0^2}$$

Therefore, the total SNR is given by

$$\frac{S}{N} = \frac{n S_0}{\sqrt{n N_0^2}} = \sqrt{\frac{S_0}{N_0}}$$

From this equation, SNR increases $n^{0.5}$ times, as the signal is integrated $n$ times. The $1/f$ noise component of the source flower circuits is not influenced because the input signal of the source flower circuit increases by the integration.

Moreover, the signal voltage is able to be amplified by the capacitance amplification principle during the charge transfer procedure if a capacitance of the ion sensing part ($C_{ion}$) is bigger than a capacitance of the floating diffusion part ($C_{diff}$). When a potential depth under the sensing part is $\Delta V_{ion}$, the signal charges ($Q_{ion}$) exist under the sensing part. After the charges ($Q_{ion}$) are transferred from the sensing part to the floating diffusion part, a potential in the floating diffusion ($\Delta V_{diff}$) decrease. The relationship is found as

$$\Delta V_{diff} = \frac{C_{ion}}{C_{diff}} \Delta V_{ion}$$

It is found that the output increase by $(C_{ion}/C_{diff})$ ratio.

3. Fabrication and characteristics

The prototype AMIS is fabricated using 5 μm rule unrefined 2-poly, 1-aluminum CCD process. The thickness of the gate oxide (SiO$_2$) and the hydrogen ion-sensitive membrane (Si$_3$N$_4$) is 50 nm, respectively. The device photograph is shown in Fig. 4. The size of the sensing part is 100 μm × 80 μm and the gate length is 50 μm. The measurement of the device was carried out applying “equivalent voltages” to the sensing parts instead of chemical potential signals in electrolyte. The equivalent voltage was previously decided by using ISFET type chemical potential sensor in the test element group. To use ISFET, the change of the potential on the Si$_3$N$_4$ film is easily speculated. From the results obtained by changing the potential on the Si$_3$N$_4$ film, it was found that the potential on the Si$_3$N$_4$ film is linearly changed and this slope is about 50 mV/pH. These results were utilized as equivalent voltage.

The output signal of the sensing part was measured by using the equivalent voltages. The equivalent voltage was applied by changing a voltage of reference electrode instead of the changing the pH value in this experiment. The AMIS was dipped in a buffer solution and operated on a clock frequency of 1000 Hz in this measurement. The integration cycle dependence of output voltage is shown in Fig. 5. It is found that the output signal multiplies to increase the integration cycle.

![Fig. 4. The photographs of the fabricated prototype AMIS. The sensing area is 100 μm × 80 μm.](image-url)
Fig. 5. Integration cycle dependence of output voltage. The output signal is multiplied to increase integration cycle.

The measurement results are shown in Fig. 6 as a function of the pH value. In this figure, the output signals from one integration cycle and five integration cycles are indicated. The output signal from one integration cycle is equal to that from ISFET. The output signal from AMIS, which was integrated five times, was lineally changed and this sensitivity of output voltage was 1.75 V/pH. However, this value includes the amplification by the capacitance amplifier. The real sensitivity without capacitance amplification factor was 450 mV/pH. This sensitivity is about five times higher than that of ISFET. A noise characteristic of the AMIS is thus estimated.

4. Conclusions

AMIS, which is expected as high sensitive ion sensor, is proposed and prototype one is fabricated using a CCD process. The principle of the AMIS is based on the charge transfer techniques. The AMIS is operated in a signal integration mode. The charges corresponded to the pH value are transferred from a sensing part to the floating diffusion region for several times and the signal charges are accumulated in the floating diffusion region. It is expected that the SNR of the pH information increases $\sqrt{n}$ times, as the signal is integrated $n$ times. The output signal of the sensing part was measured by using the equivalent voltages. It was found that the output signal from AMIS, which was integrated five times, was lineally changed and the total sensitivity was 450 mV/pH. This sensitivity is about five times higher than that of ISFET.

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