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Ion-sensitive field-effect transistor for pK and pNa sensing

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Abstract-The ion-sensitive field-effect transistor (ISFET) is a new type of Ion Electrode. Up to now ISFET was usually fabricated by using a silicon wafer, but in this study a new ISFET is fabricated with an SOS--silicon film on a sapphire substrate. Using this structure, many types of ion-sensitive materials have been tested. For measuring pK, photoresist-valinomycin thin film has been examined, and a good response character was obtained. For pNa, SiNx-layer implanted with Li^{+} and Al^{+++} ions has been tested and its response character was discussed.

INTRODUCTION

Ion-sensitive field-effect transistors (ISFETs) (ref.1) have the capability of MIS-FETs with ion-selective electrodes, but the electrolyte solution, in which the ISFETs are immersed, and the reference electrode in the solution work as gate electrodes. The gate insulating films play the essential role in ion sensing.

Various new types of ion sensing material (refs.2,3) are adapted for a super miniaturized ISFET which is produced by applying the IC technique. The ISFET has the advantages of miniature size of the sensor and the sensor not needing any electrolytic or diffuse current. The readiness of operation for measuring a circuit becomes simple due to its low output impedance.

THEORY OF ISFET (ION-SENSITIVE FIELD-EFFECT TRANSISTOR)

The convenient MOSFET (or MISFET) device has metal connections to the source, drain and gate. The relationship between the drain current I_D, drain voltage V_D, gate voltage V_G, and the device threshold voltage V_T is given by the next expressions;

$$I_D = \beta\ [(V_G - V_T)V_D - 1/2V_D^2 \qquad \text{if} \quad |V_D| < |V_G - V_T| \qquad (1)$$

$$I_D = \beta\ [(V_G - V_T)^2/2] \qquad \text{if} \quad |V_D| \geq |V_D - V_T| \qquad (2)$$

where $\beta = C\mu W/L$, μ is surface carrier mobility, C is gate capacitance per unit area, W is channel width, and L is channel length.

The gate membrane of the ISFET is different from that of MOSFET; that is, the ion-selective membrane is coated on the insulated gate of FET. The ion-selectivity depends on the surface character of the ion-selective membrane. The interfacial potential between the membrane and the electrolytic solution is expressed as:

$$E_M = \text{constant} + RT/nF \cdot \ln\{([A] + K_{AB}[B])\} \qquad (3)$$

where [A], [B] : activity of A and B ions in the electrolytic solution, n : the ionic valency, K_{AB}: selectivity coefficient of A-ion electrode to B-ion.

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For measurement with ISFET, the drain current I_D depends on the potential of the gate membrane as shown in the next expression;

$$I_D = \beta\,(E_M - V_T + \text{const.})^2$$
$$= \beta\{\, RT/nF \cdot \ln([A] + K_{AB}[B]) - V_T + \text{const.}\}^2 \text{ in case of } |V_D| \geq |V_G - V_T| \quad (4)$$

PREPARATION OF ISFET

Two types of channel are used for MOSFET, and two types can be used for the production of ISFET also. For the preparation, both types of SOS--silicon on a sapphire plate can be used (ref.5).

The I_D - V_D Character of SOS-MOS-FET and SOS-MNOS-FET are shown in Fig. 1. MNOS is Metal-Nitride-Oxide-Semiconducor structure. The plasma treatments are available in the nitride process (refs.4,6).

The structure of ISFET prepared with SOS is shown in Fig. 2. The ion selective membrane covers the ion-sensing area on the insulated gate of the MNOS-FET.

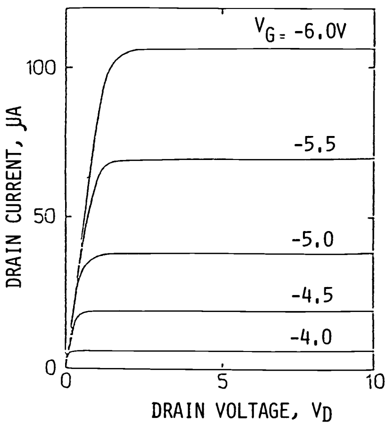

Fig. 1. I_D - V_D charaters of SOS-MNOS-FET

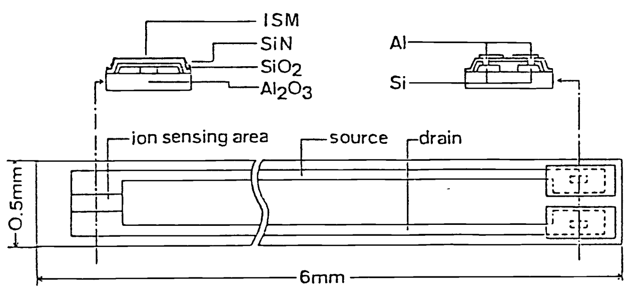

Fig. 2. Structure of SOS-ISFET

PREPARATION OF ISFET FOR pK AND ITS RESPONSE CHARACTER

For the ion-selective membrane on the gate of a K^+ ion ISFET, we first used PVC with crown ether. In many sorts of crown ether, di-hexyl-18-crown-6 was better in sensitivity and selectivity, but in this case of a thin membrane of ISFET, sensitivity decreased very fast as shown in Fig. 3.

Then valinomycin was used as a neutral carrier of the ion-selective membrane (ISM) of ISFET. To determine the composition of ISM, the next 3 composites were tested.

(1) PVC-valinomycin
(2) Photoresist-valinomycin-plasticizer
(3) Photoresist-valinomycin

(1) Valinomycin 10 mg, DOA (plasticizer) 660 mg, PVC 330 mg in the THF solvent were coated onto the insulated gate with a spinner so as to be a very thin film.
(2) Valinomycin 10 mg, DOA 120 mg, Photoresist (OMR-83) 800 mg in the THF are coated in a thin layer. After pre-baking at 80 °C for 30 min, the membrane was exposed for 10 sec to a UV lamp. Then, after post-baking at 80 °C for 15 min, it was exposed for 20 min. The thickness of the ISM was about 2 μ m.
(3) The same as the process used in (2) above but without DOA.

The drain current I_D of ISFET responds to K^+ ion activity. But it is not convenient to use the relationship between I_D and the K^+ ion concentration. The I_D can be changed to the equivalent gate potential $V_G$eq. The circuit shown in Fig. 4 is the source follower circuit,

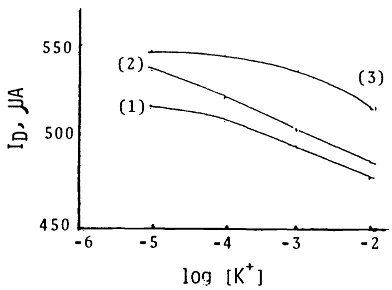

Fig. 3. The response character of pK ISFET with PVC-crown-ether (1) 30 min after being dipped in the test solution, (2) 3 hrs later, (3) 6 hrs later

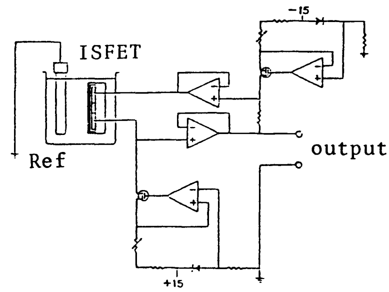

Fig. 4. Source follower circuit for the measurement of ISFET. $V_G$eq is gained from the output.

and the $V_G$eq is obtained from this output at constant I_D and V_D. The relationship of $V_G$eq to K^+ ion activity is the same as to that of the normal type of ion-selective electrode.

$$V_G eq = V_{IMS} + \text{constant} \qquad (5)$$

The constant includes the potential difference between the reference electrode used.

RESULTS OF pK ISFET

The response measurements for the K^+ ion 10^{-1} - 10^{-5} M in a Tris-buffer solution were tested with ISFET. The reference electrode was of the double junction type with Lithium Trichlor Acetate solution as an outer solution. The response character of pK ISFET is different — depending on the ISM used, as shown in Fig. 5.

The sensitivity of the ion-selective membrane of ISFET comes from valinomycin with DOA (plasticizer). The ISM without DOA has no or low sensitivity to the K^+ ion. The soundness of the photoresist membrane is better than that of the PVC membrane. The sensitivity of the ISFET with Photoresist-DOA-Valinomycin does not decrease for over 300 hrs. The slope of sensitivity is 52 - 58 mV/pK, and 90% response is achieved in several seconds.

The sensitivity of the ISFET with PVC-DOA-Valinomycin is the same as that of the ISFET with Photoresist-DOA-Valinomycin, but it decreases very rapidly during the time it's being used. The curves of the response character to the time of use are shown in Fig. 6.

Since the photoresist membrane is very tough and has a fine network structure, the plasticizer included in the membrane does not easily flow out. The valinomycin, which is soluble in the plasticizer, is a good ion-sensor over a long period of time.

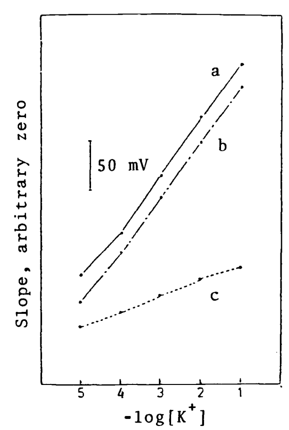

Fig. 5. Sensitivity of pK ISFET
(a) Plasticized photoresist
(b) Plasticized PVC
(c) Photoresist without plasticizer

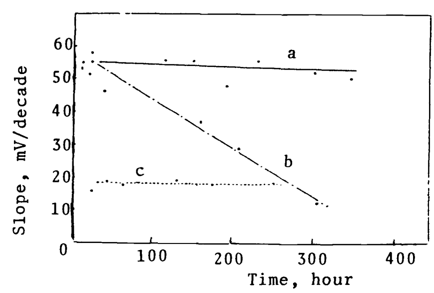

Fig. 6. Response character to elapsed time of pK ISFET. Sort of ISM of ISFET (a), (b) and (c) are as in Fig. 5.

PREPARATION OF pNa ISFET AND RESPONSE CHARACTER

The Na^+ ion ISFET was produced by a procedure similar to that used for ISFET with SOS--silicon film on sapphire. The ion-selective membrane on the gate was made by deposition a SiNx layer using plasma enhanced chemical vapor deposition onto the gate SiO_2 region, and the SiNx layer was implanted with Li^+ and Al^{+++} (refs.7,8) at room temperature. The total doses of Li^+ and Al^{+++} were 5 X 10^{14} ions/cm^2. The accelerating voltage were 50 KeV for Li^+ and 60 KeV for Al^{+++}. After implantation, the ISFET was thermally annealed at 773 K for 30 min in an argon atmosphere. The response character of the produced pNa ISFET is shown in Fig. 7. The slope of the response is about 30 mV/pNa, and full response is achieved in 1 min.

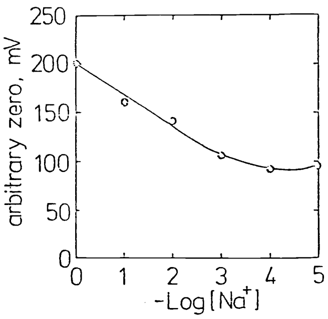

Fig. 7. The response character of pNa ISFET

SUMMARY

There are many types of ion-selective electrodes constructed with semi-conductive crystal (ref.9). One is the ion-selective electrode with an ordinary structure, and another is the ion-selective field effect transistor (ISFET). The ISFET has many advantages that ordinary types do not have (refs.10,11).

For the preparation of a pK ISFET, the ion-selective membrane on the insulated gate is the most important. The membrane composed of a photoresist and plasticizer with valinomycin has good characteristics as an ion-selective membrane on the gate when exposed to UV light and to baking.

K^+ ion-selective ISFET is very stable and able to be used for over 300 hrs. For pNa ISFET, the ion-selective membrane on the gate is prepared from a SiNx layer. The implantation of Li^+ and Al^{+++} ions into the SiNx layer is applied by plasma for the production of the ion-selective membrane, which has a low response but a tough character.

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