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Depletion-Mode Field Effect Semiconductor Sensor with Cation-Sensitive Polymer Membranes

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Semiconductor ion sensors based on the surface conductance change due to a variation in the depletion layer thickness have been constructed. An n-SnO_2 electrode was coupled with four kinds of cation-sensitive polymer membranes (Fe^{3+}- and Cu^{2+}-exchanged Nafion membranes and poly(vinyl chloride)-supported dioctyl phthalate membranes containing a neutral carrier, valinomycin or nonactin), and its surface conductance was measured under depletion conditions as a function of the cation concentration. The sensor exhibited sensitivity to Fe^{3+}, Cu^{2+}, K^+, or $NH_4{}^+$ at levels higher than 10^{-4} mol dm^{-3} within 10 s. The sensor response was analyzed in terms of (1) the dependence of the surface conductance on the surface band bending and (2) the potential difference at solution/membrane interfaces. From the analysis, it is confirmed that the membranes show nearly Nernstian behavior and that the semiconductor acts as a potentiometric transducer. The applicability of the depletion-mode semiconductor sensor is discussed.

Semiconductor devices with low output impedance have been extensively studied recently in view of micro and multifunctional sensor fabrication. Many of such devices are of the ISFET (ion-sensitive field effect transistor) type, introduced by Bergveld,[1,2] with an insulator/semiconductor structure. The device is a modification of the MISFET (metal-insulator-semiconductor FET) and is based on the variable thickness of the inversion layer (channel) of a semiconductor substrate.[3,4] A variety of chemically sensitive membranes has been coupled with this device to develop effective sensors.[4]

There are another type of field effect devices, namely, the metal-semiconductor FET (MESFET) and junction FET (JFET), in which a change in the depletion layer thickness is utilized.[5] However, application of these devices for chemical sensor construction has scarcely been studied.

A field effect chemical sensor can be constructed also by use of semiconductor/electrolyte interfaces as follows. When an anodic bias is applied to an n-type semiconductor in contact with an electrolyte solution, a depletion layer is formed in the semiconductor. The conduction electrons are driven away from the surface region of the semiconductor. A change in the depletion layer thickness, caused for instance by ionic adsorption, alters the surface conductance of the semiconductor. Since the depletion layer acts as an insulating layer, no insulator needs to be placed on the semiconductor surface, and the device has no p-n junction in the semiconductor substrate. Thus, the structure of the sensor based upon the above principle is much simpler than that of the conventional ISFET.

In a previous paper,[6] we used n-type SnO_2 as a semiconductor and a perfluorinated sulfonate cation-exchange polymer, Nafion, as an ion-sensitive layer, to fabricate the first example of a "depletion-mode field effect sensor." The present work has been conducted to explore further the applicability of the depletion-mode sensor. By combining an SnO_2 electrode with four kinds of cation-sensitive polymer membranes, sensors for Fe^{3+}, Cu^{2+}, K^+, and $NH_4{}^+$ have been developed.

Experimental

Materials. Nafion (a 5% alcoholic solution, equivalent weight 1100), valinomycin, and nonactin were obtained from Aldrich Chemical Co., Sigma Chemical Co., and Boehringer Mannheim GmbH, respectively. Poly(vinyl chloride) (PVC, degree of polymerization 1100), dioctyl phthalate (DOP) as a plasticizer, and spectro-grade tetrahydrofuran (THF) were from Wako Pure Chemicals. $FeCl_3 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, KCl, NH_4Cl, LiCl, NaOH, and HCl were of reagent grade. All these chemicals were used without further purification. Distilled water, or deionized water purified with Milli Q-II (Millipore Ltd.) was used.

Preparation of Sensors. SnO_2-coated glass plates were used as semiconductor substrates. The SnO_2 layer had a thickness of about 50 nm and a donor density of 10^{21} cm^{-3}. Two terminals, W and D, were placed on the SnO_2 layer with the ohmic contacts of indium metal, which were insulated with an epoxy resin. The effective surface area of the sensor was 1×1 cm^2.

The Nafion membrane was prepared as follows.[6] A Nafion solution was spread on the SnO_2 surface and dried; the thickness of the membrane was estimated to be 1—2 μm from the weight gain. The Nafion-coated semiconductor was then immersed in a 0.2 M (1 M=1 mol dm^{-3}) $FeCl_3$ or $CuCl_2$ aqueous solution for at least 16 h to obtain ion-exchanged Nafion.

The neutral carrier-PVC membranes were cast from a THF solution containing 12 mg of PVC, 2.5 mg of a neutral carrier, and 35 μl of DOP.[7] The membrane formed on the semiconductor was air-dried overnight, then placed in a vacuum desiccator for 1 h. The thickness of the membranes was roughly 0.1 mm. The membranes were conditioned by immersing them in 0.2 M KCl and NH_4Cl aqueous solutions for valinomycin and nonactin, respectively.

The sensor construction is illustrated in Fig. 1.

Operation of Sensors. The electrical conductance of the sensor at a constant electrode potential, V_W, was measured as reported in the previous paper.[6] The electrode potential was

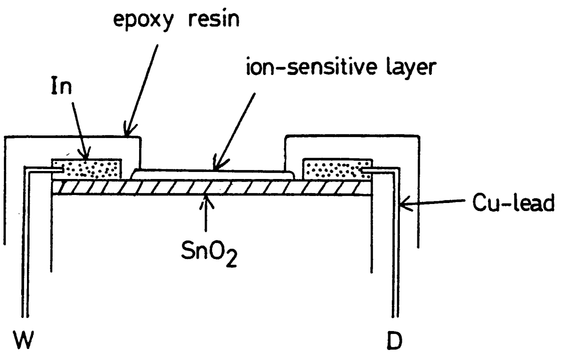

Fig. 1. Schematic representation of sensor construction.

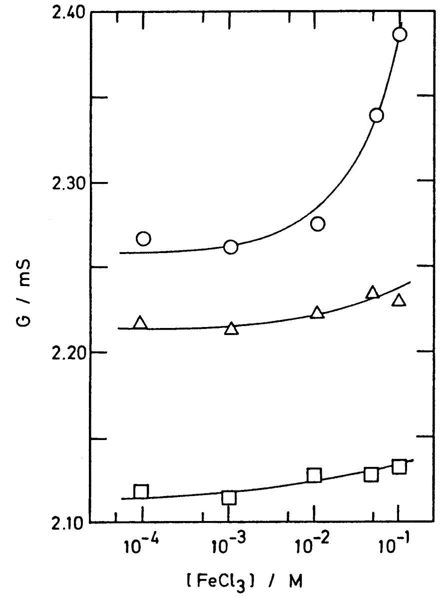

Fig. 2. Response of the Fe^{3+}-sensor (Fe^{3+}-Nafion/SnO_2). V_W=+400 (○), +500 (△), +1000 mV (□) vs. Ag/AgCl.

controlled by a Toho Technical Research potentiostat Model 2000 against an Ag/AgCl (KCl saturated) reference electrode. A small voltage (1—5 mV), V_D, was applied with a Yokogawa voltage supply Model 2553 between the two terminals, W and D, and the current, I_D, was measured by a Takeda Riken electrometer Model TR 8651. The electrical conductance, G, was calculated from the relation;

$$G=\partial I_D/\partial V_D.$$

For measurements of the time response to a concentration step, the voltage supply and the electrometer were replaced with a Yokogawa-Hewlett-Packard low frequency impedance analyzer Model 4192A operated at 1 kHz and 5 mV.

All the measurements were carried out at room temperature and in solutions flushed with nitrogen.

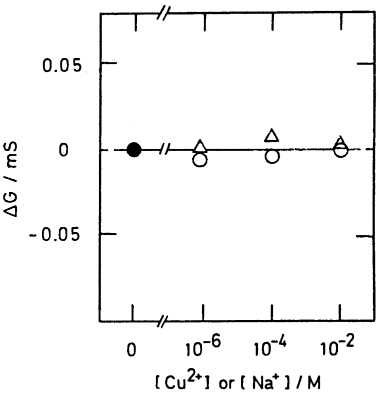

Fig. 3. Effect of coexisting Cu^{2+} (○) and Na^+ (△) on the Fe^{3+}-sensor. $[FeCl_3]=1\times10^{-3}$ M (pH 1.5); V_W=+400 mV vs. Ag/AgCl.

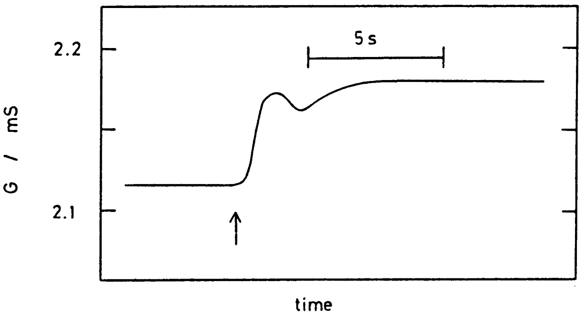

Fig. 4. Time response of the Fe^{3+}-sensor to a Fe^{3+} concentration step (0→0.1 M). V_W=+400 mV vs. Ag/AgCl.

Results

Nafion-Based Fe^{3+}- and Cu^{2+}-Sensors. Figure 2 shows a typical response of the Fe^{3+}-sensor carrying an Fe^{3+}-exchanged Nafion membrane in the aqueous solutions containing $FeCl_3$ in the concentration range from 10^{-4} to 10^{-1} M at pH 1.5. The conductance of the sensor changed with a change in the $FeCl_3$ concentration. The sensitivity is higher at more negative electrode potentials. At an appropriate electrode potential, the Fe^{3+}-sensor can detect Fe^{3+} ions at levels higher than 10^{-4} M.

The Fe^{3+}-sensor shows no pH dependence.[6] Addition of Na^+ or Cu^{2+} to a 10^{-3} M $FeCl_3$ test solution did not alter the sensor response, as depicted in Fig. 3, where a change in surface conductance, ΔG, upon addition of these interfering ions is plotted against their concentration. This result ensures a good selectivity of the Fe^{3+}-sensor.

Figure 4 shows a time response of the Fe^{3+}-sensor to a stepped change in Fe^{3+} concentration from 0 to 0.1 M under vigorous stirring. Though the trace is perturbed in the initial phase probably due to non-uniform mixing of the solution, the response of the sensor is completed within 10 s, which is short enough for practical use.

Use of the Cu^{2+}-exchanged Nafion membranes gave electrodes sensitive to Cu^{2+}. A typical response of the Cu^{2+}-sensor in the aqueous solutions containing $CuCl_2$ at pH 1.5 is given in Fig. 5. Similar to the Fe^{3+}-sensor, the sensitivity is higher at more negative electrode potentials. The effective potential range for

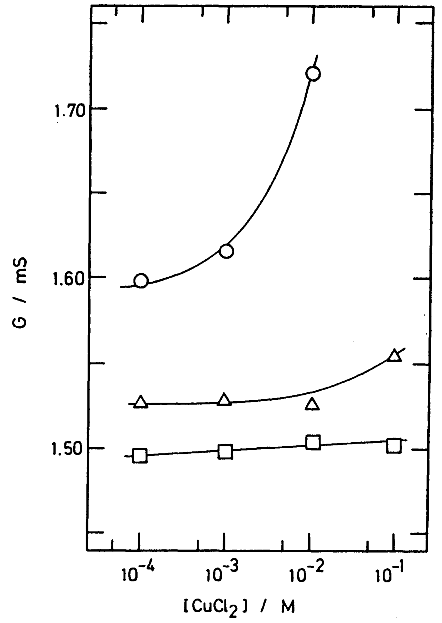

Fig. 5. Response of the Cu^{2+}-sensor (Cu^{2+}-Nafion/SnO_2). V_W=+150 (○), +300 (△), +400 mV (□) vs. Ag/AgCl.

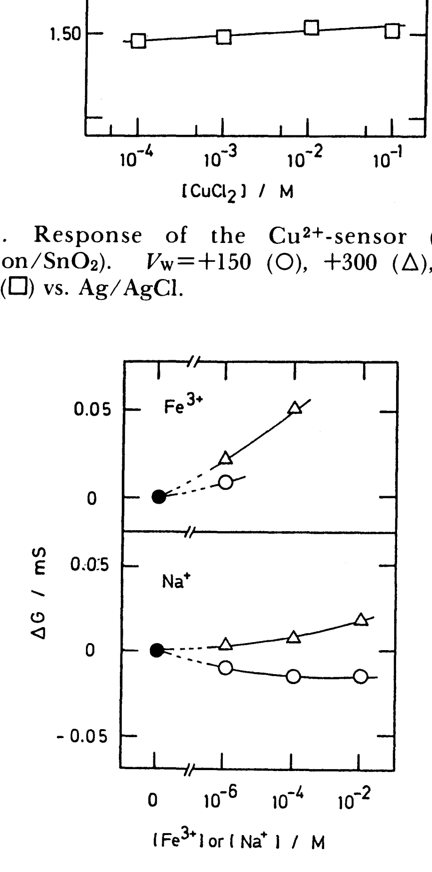

Fig. 6. Effect of coexisting Fe^{3+} and Na^+ on the Cu^{2+}-sensor. $[CuCl_2]=1\times10^{-3}$ M (pH 1.5); V_W=+150 (○), +300 mV (△) vs. Ag/AgCl.

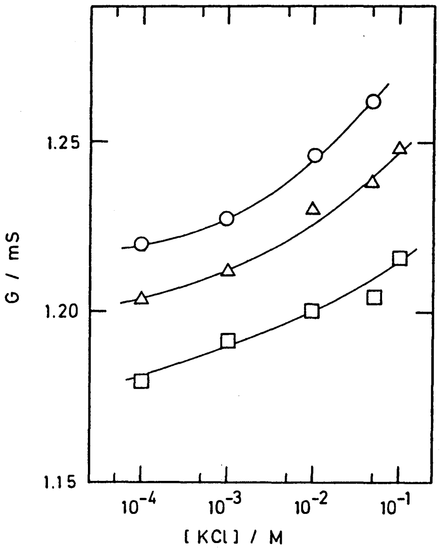

Fig. 7. Response of the K^+-sensor (valinomycin-DOP-PVC/SnO_2). V_W=−200 (○), −100 (△), +100 mV (□) vs. Ag/AgCl.

the Cu^{2+}-sensor is negative of that for the Fe^{3+}-sensor.

Figure 6 shows the effect of interfering ions (Na^+ and Fe^{3+}) to the response of a Cu^{2+}-sensor (in 10^{-3} M $CuCl_2$, pH 1.5). The conductance of the sensor was affected by the addition of these ions, and hence the selectivity of the Cu^{2+}-sensor is not sufficient.

Since the semiconductor used in this work is highly doped, the depletion layer is correspondingly thin; for example, about 1.0 and 1.4 nm at electrode potentials 0.4 and 1.0 V vs. Ag/AgCl, respectively, for the case of the SnO_2 in direct contact with a pH 1.5 electrolyte solution. The conduction electrons may tunnel to the solution through the depletion layer,[8] giving rise to a cathodic current reducing Fe^{3+} or Cu^{2+}.[9] The utilization of this current for the sensor signal was discussed in the previous work.[6] In the case of the Cu^{2+}-sensor, the current reducing Fe^{3+} was too large to carry out a stable conductance measurement, because the effective operational range for the Cu^{2+}-sensor is negative enough to reduce Fe^{3+}.[9]

Neutral Carrier-Based K^+- and NH_4^+-Sensors. Several macrolide antibiotics are known to exhibit highly selective complexing ability to certain cations.[10] Valinomycin for K^+ [11] and nonactin for NH_4^+ [12] are typical examples, and have been used as cation carriers in liquid membrane systems.[10,13] Combination of a polymer-supported liquid membrane containing a carrier and a semiconductor transducer gives an ion sensor.[14] In view of this, we have attempted to construct K^+- and NH_4^+-sensors by use of PVC-supported DOP membranes.[15]

The valinomycin-based sensor showed K^+-sensitivity, as illustrated in Fig. 7. The solution was a KCl aqueous solution containing 0.1 M NaCl (pH 6.2). The K^+-sensor did not respond to Na^+ and Li^+ at concentrations below 10^{-2} M, and to H^+ for pH value ranging from 4 to 10.

The response of a nonactin-based NH_4^+-sensor is shown in Fig. 8. Here an NH_4Cl aqueous solution containing 0.1 M NaCl was used. The sensor did not respond to Na^+ and K^+ at concentrations below 10^{-2} M.

Discussion

Under depletion conditions, the surface conductance of a semiconductor depends on the space charge layer thickness, which in turn is related to the surface band bending. This situation is described by the following equation for n-type semiconductors;[6]

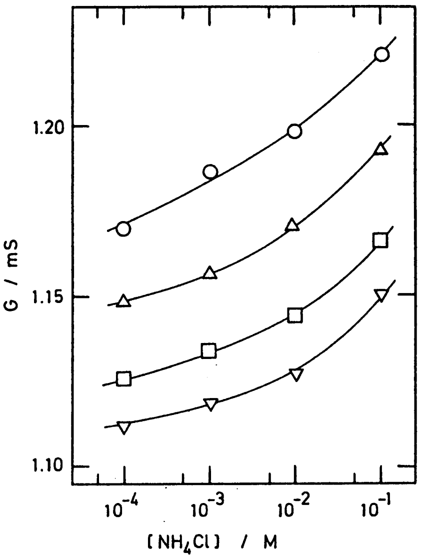

Fig. 8. Response of the NH_4^+-sensor (nonactin-DOP-PVC/SnO_2). V_W=−100 (○), +0 (△), +100 (□), +200 mV (▽) vs. Ag/AgCl.

$$\Delta\sigma_S = -(2\varepsilon e N_D \mu_e^2)^{1/2}(-V_S)^{1/2}. \quad (1)$$

Here V_S is the band bending at surface ($V_S = V_{fb} - V_W$; V_{fb} is the flatband potential), $\Delta\sigma_S$ the difference between the surface conductivity under a depletion condition ($V_S < 0$) and that at the flatband state ($V_S = 0$), ε the dielectric constant of the semiconductor, μ_e the mobility of the conduction electrons, N_D the donor density, and e the elementary charge.

As the potential drop in the Helmholtz layer of an oxide semiconductor surface changes in general with pH of the solution,[16] V_{fb}, and hence V_S and the surface conductance, of the semiconductor in direct contact with an electrolyte solution depend on pH of the solution under potentiostatic conditions. For the sensors developed in this work, however, the semiconductor surface is covered with an ion-sensitive polymer membrane. In such a case a change in V_S via the cation concentration change in solution should be caused by the potential difference at the membrane/solution interface. This has been confirmed previously by flatband potential measurements for the Nafion/SnO_2 system.[6] The flatband potential is generally estimated from the Mott-Schottky plot of the depletion capacitance. However, this procedure is difficult to apply to the high-resistance and low-capacitance membrane/semiconductor system as in the present study.

If the potential difference at the membrane/solution interface exhibits the Nernstian behavior, a plot of G against $[V_W - (RT/nF)\ln a]$, where n is the valency of the cation and a is its activity, should give a single curve for a variety of V_W-a combinations. The term $(RT/nF)\ln a$ is approximated by $(0.059/n)\log c$ (V) at T=300 K, where c is the cation molarity. Figures 9 and 10 show the G vs. $[V_W - (0.059/n)\log c]$ plots for the Fe^{3+}- and NH_4^+-sensors, respectively. Each plot gives a single curve, and the above-mentioned point is thus verified. Similar results were also obtained both for Cu^{2+}- and K^+-sensors.

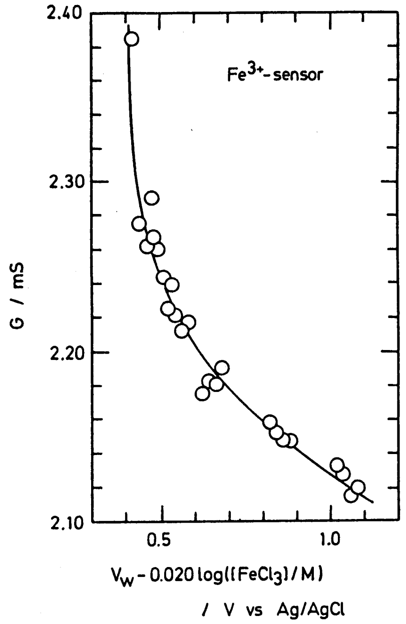

Fig. 9. Plot of the surface conductance against $V_W - (0.059/n)\log c$ for the Fe^{3+}-sensor (n=3).

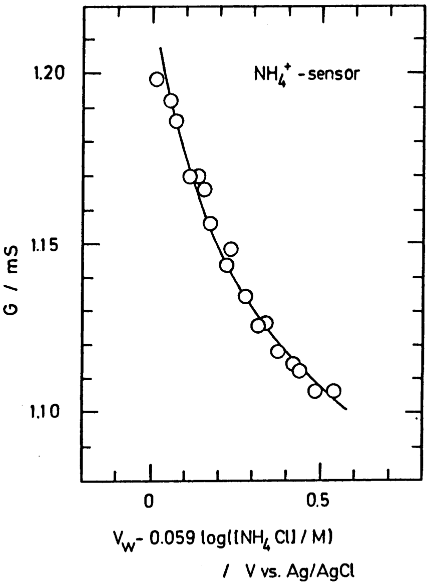

Fig. 10. Plot of the surface conductance against $V_W - (0.059/n)\log c$ for the NH_4^+-sensor (n=1).

The dependence of the sensitivity on the electrode potential is explained with reference to Eq. 1. A more negative electrode potential gives a smaller band bending for a given cation concentration (the band edge is fixed to the solution at the given cation concentration). At a more negative potential, therefore, the change in the surface conductance is greater for a change in the cation concentration, thus resulting in higher sensitivity.

Our measurements have shown that the selectivity of the Cu^{2+}-sensor is poorer than that of the Fe^{3+}-sensor.

This could be accounted for by invoking a higher affinity of the sulfonato groups in Nafion to Fe^{3+} than to Cu^{2+}, as has been suggested also for Nafion-based ion-selective electrodes.[17] In contrast, valinomycin and nonactin are ionophores highly selective to K^+ and NH_4^+, respectively.[11,12] This is corroborated by the excellent selectivities of the K^+- and NH_4^+-sensors developed in this work.

The Nafion-based Cu^{2+}-sensor required application of a more negative electrode potential than the Fe^{3+}-sensor for the sufficient sensitivity. This observation is explained qualitatively as follows. As the affinity of the sulfonato groups is higher to Fe^{3+} than to Cu^{2+}, the difference in the chemical potential of Fe^{3+} between in Nafion and in the solution is larger than in the case of Cu^{2+}. The electrochemical potentials of the cation in Nafion and in the solution are equal at equilibrium. On a reasonable assumption that the electrical potential drop in the solution is zero, the electrical potential in Nafion is more positive for Fe^{3+} than for Cu^{2+}. Hence the band edge of the semiconductor contacting Nafion is more lowered, or V_{fb} is more positive for Fe^{3+} than for Cu^{2+}. Thus the Cu^{2+}-sensor required application of a more negative electrode potential for the sufficient sensitivity.

The performance of the sensors constructed in this work is based mainly on the properties of the membrane used, and the semiconductor is acting as a potentiometric transducer under depletion conditions. Incorporation of other chemically sensitive layers into this simple yet effective transducer may introduce new useful chemical sensors.

Further, the present system could find potential application for the electrochemical characterization of thin layers on solid substrates, including Langmuir-Blodgett films.

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