# Characteristics of Semiconductor and Ion-Sensitive Layers That Affect Response of Ion-Sensing Devices Based on n-$SnO_2$/Ion-Exchange Membrane Junction

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**Synopsis.** The carrier density and thickness of both the semiconductor and ion-sensing membrane were found to significantly affect the sensitivity of ion-sensing devices with a junction of n-type $SnO_2$ and cation-selective plasticized polymeric membranes. When an anion-selective membrane was employed instead, the resulting device responded in a different way from the corresponding cation-sensing device.

Ion-selective electrodes constitute a group of the most developed ion sensors. They, however, still have some drawbacks, such as high membrane impedance and limited miniaturization. Semiconductors are useful materials for various sensors as well as for ion-sensing devices. Ion-sensitive field-effect transistors are typical ion-sensing devices based on semiconductor/insulator/ion-sensitive membrane/solution junctions,[1-3] which allow the use of high-impedance membranes and the construction of miniaturized multi-ion sensors. Recently, Okawa et al. fabricated ion-sensing devices with semiconductor/ion-sensitive layer junctions, using n-type $SnO_2$ as the inorganic semiconductor and a polymeric cation-exchanger,[4] valinomycin-containing poly(vinyl chloride) (PVC) film,[5] or crown ether Langmuir–Blodgett film[6] as the cation-sensitive layer. The stimulating research got us interested in the type of ion-sensing device, to which various materials can be applied, while being easy to fabricate.

We have fabricated n-$SnO_2$-based ion-sensing devices, using the semiconductors with various thicknesses and carrier densities and a typical cation-selective membrane. An anion-selective membrane was also tested as an ion-sensing layer of the device. This paper is concerned with the effects of the semiconductor characteristics and the ion-sensing membranes on the $SnO_2$-based ion-sensing device.

## Experimental

**Materials.** Dibenzo-30-crown-10 (DB30C10) was prepared according to Pedersen's procedure.[7] Trioctylmethylammonium chloride (TOMACl) was employed as received from Tokyo Kasei. Poly(vinyl chloride) (PVC, polymerization degree of 1100) was purified by reprecipitation from tetrahydrofuran (THF) in methanol. Dioctyl sebacate (2-ethylhexyl sebacate, DOS) was distilled under vacuum. The semiconductors, n-type $SnO_2$ with thickness of 12—41 nm and carrier density of $1\times10^{20}$ and $4\times10^{20}$ $cm^{-3}$, which were formed on glass substrates (2×2.5 cm) by chemical mist deposition, were kindly supplied by Taiyoyuden Corporation. The metal salts employed here were of analytical grade. Water was deionized.

**Device Fabrication and Measurements.** The $SnO_2$-based ion-sensing devices were constructed with reference to a procedure from the literature.[5] A cutaway view of the device is illustrated in Fig. 1. The $SnO_2$ layer on the glass was etched to a 1×2.5 cm strip in the center of the glass substrate by treating with dil HCl–Zn powder. The ion-sensing membranes were cast separately. The typical cation- and anion-sensitive membranes of about 0.2 mm thickness were cast by pouring THF solutions (4 ml) of 100 mg PVC/200 mg DOS/10 mg DB30C10 (32.3/64.5/3.2 wt%) and 100 mg PVC/200 mg TOMACl (33/67 wt%) into a flat Petri dish of 43 mm inner diameter, followed by air drying of the THF at room temperature. A square of 1.3×1.3 cm was cut out from the membrane and then placed just at the center of the semiconductor substrate. The thinner cation-sensitive layers were cast or spin-coated directly on the substrate from THF solutions with the same composition as those for the thick membrane. Copper leads were contacted ohmically to each end of the $SnO_2$ strip by Ag paste and then fixed by an epoxy resin. The resulting device was covered by encapsulation with a silicon rubber (Shin-Etsu, KE44T), except for the ion-sensitive membrane section, the exposed area being about 1×1 cm. The device was soaked in $1\times10^{-3}$ M (1 M=1 mol $dm^{-3}$) KCl solution in order to condition the ion-sensitive membrane. Electrical conductance measurements were carried out at room temperature according to a reported procedure.[4] The sample solutions did not contain any special pH buffer. The current between the two terminals of the semiconductor part ($I_D$) was measured with a small applied voltage ($V_D$), while the electrode potential ($V_W$) vs. Ag–AgCl was controlled potentiostatically using a double-junction reference electrode (1 M $CH_3CO_2Li$/3 M KCl/AgCl-Ag). The $I_D$ readings were made in 2 min after changing the applied voltages. Since the relationship between $I_D$ and $V_D$ is ohmic in the $V_D$ range of 0—100 mV, the conductance (G) was calculated from $I_D$ values at $V_D$ of 10 mV. The percent variation of the conductance was

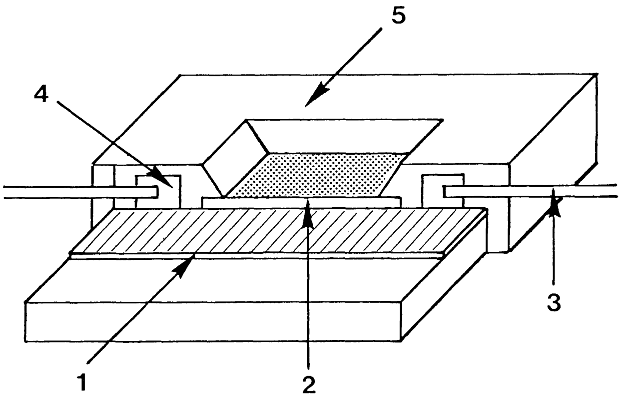

Fig. 1. Cutaway view of schematic diagram for ion-sensing device. 1: semiconductor, 2: ion-sensitive membrane, 3: copper lead, 4: Ag paste, 5: encapsulation.

obtained as 100×[G(at $1\times10^{-1}$ M KCl)−G(at $1\times10^{-4}$ M KCl)]/G(at $1\times10^{-4}$ M KCl). The membrane potentials were measured by using a cell assembly of Ag–AgCl/$1\times10^{-3}$ M KCl/membrane/test solution/1 M $CH_3CO_2Li$/3M KCl/AgCl–Ag and an electrometer. The flatband potentials were measured by using Mott–Schottky plots.[8)]

## Results and Discussion

A typical response to the $K^+$ concentration in measured aqueous solutions for the cation-sensing device based on a $SnO_2$–DB30C10/DOS/PVC membrane junction is shown in Fig. 2. Increasing the cation concentration enhanced the electrical conductance of the device; a greater positive electrode potential resulted in a lower conductance. This was the case in previous $SnO_2$-based cation-sensing devices.[4,5)] It was then proposed that their conductance response to the cation concentration is ascribable to a thickness change in a space-charge layer of the semiconductor, which is in turn caused by a cation-concentration-induced potential change of the ion-sensitive layer. If this response mechanism is reasonable, the sensitivity of ion-sensing devices based on a $SnO_2$–ion-sensitive membrane junction must appreciably depend upon the characteristics of the semiconductors and ion-sensitive membranes employed. We applied $SnO_2$ with different thicknesses and carrier densities to our cation-sensing device, using a DB30C10/DOS/PVC membrane with a thickness of 200 μm as the ion-sensitive membrane. The percent variations of conductance for the cation-sensing devices are summarized as a measure of device sensitivity in Table 1. The thinner $SnO_2$ layers generally afforded a higher percent variation of the conductance in the $SnO_2$-based cation-sensing device. This suggests that the conductance for thin semiconductors (12—19 nm thickness) are more sensitive to a potential-drop-induced change of the space-charge layer thickness than that for thick types (41 nm thickness). Moreover, low-carrier-density $SnO_2$ with 12 nm thickness gave better results regarding device sensitivity than did the high-donor-density type with the same thickness. This result may reflect the general observation that the higher carrier density in n-type semiconductors results in a thinner space-charge layer.

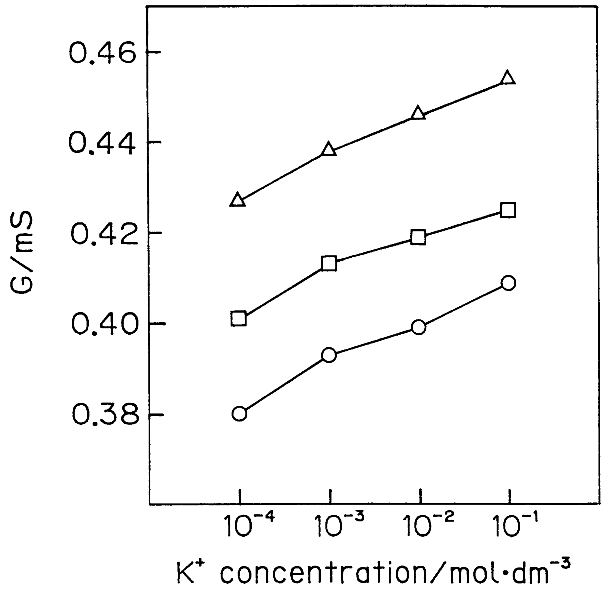

Fig. 2. Conductance response to $K^+$ concentration for cation-sensing device with $SnO_2$–DB30C10/DOS/PVC junction. $V_w$: 0.3 V (○), 0.1 V (□), −0.1 V (△) vs. Ag–AgCl. $SnO_2$: 19 nm thickness and $4\times10^{20}$ cm$^{-3}$ carrier density. PVC membrane: 200 μm thickness.

Table 1. Dependence of Characteristics of Semiconductor and Ion-Sensitive Layer upon Sensitivity of Ion-Sensing Devices Based on $SnO_2$–DB30C10/DOS/PVC Junction

| Semiconductor | | Ion-sensitive layer | Percent variation of conductance[a)] |
|---|---|---|---|
| Donor density | Thickness | Thickness | |
| $10^{20}$ cm$^{-3}$ | nm | μm | % |
| 4 | 19 | 200 | 6.1 |
| 4 | 19 | 10 | 1.2 |
| 4 | 19 | 0.5 | 1.2 |
| 4 | 19 | 0.05 | 1.5 |
| 4 | 12 | 200 | 14.4 |
| 1 | 41 | 200 | 5.7 |
| 1 | 14 | 200 | 20.0 |
| 1 | 12 | 200 | 21.2 |

a) At an electrode potential ($V_w$) of −0.1 V vs. Ag–AgCl.

The characteristics of the ion-sensitive membrane also affected the response of the $SnO_2$-based ion-sensing device. Cation-sensitive membranes of DB30C10/DOS/PVC with various thicknesses were tested regarding their conductance response of the resulting device to a $K^+$ concentration change (Table 1). Only an ion-sensitive membrane of 200 μm thickness allowed good sensitivity (high percent variation of conductance) in the ion-sensing device. Much thinner membranes brought about only poor sensitivity. In separate experiments for measuring the membrane potential, the 200-μm membrane exhibited a near-Nernstian response on the $K^+$ concentration in test solutions, whereas the thinner ones did not. A substantial thickness of the ion-sensitive layer of the plasticized PVC is, therefore, required to realize a potential drop comparable to the Nernstian response, which in turn causes a significant conductance change accompanied by a space-charge-layer thickness change. The ion selectivity of the ion-sensitive layer should be naturally reflected in the device selectivity, since its potential drop is essentially governed by its ion-exchange selectivity. An ion-sensing device based on $SnO_2$–DB30C10/DOS/PVC membrane junction is, thus, highly selective to $K^+$, as shown in Fig. 3.

It is of much interest to see how the $SnO_2$-based device responds when the cation-sensitive membrane is replaced by an anion-sensitive one. Increasing the $Cl^-$ concentration diminished the electrical conductance in an anion-sensing device based on a $SnO_2$–TOMACl/PVC junction (Fig. 4). This anion-concentration

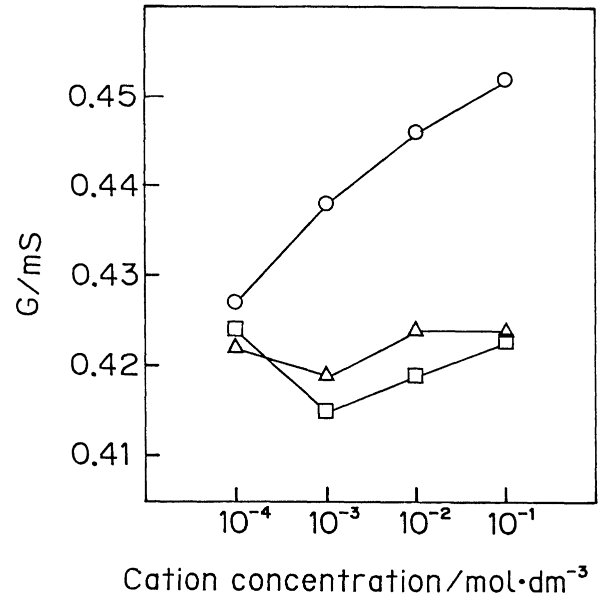

Fig. 3. Ion selectivity of cation-sensing device with SnO$_2$-DB30C10/DOS/PVC junction. K$^+$ (○), Na$^+$ (□), Li$^+$ (△). $V_w$: −0.1 V (△) vs. Ag-AgCl. The characteristics for the semiconductor and ion-sensitive layers are the same as for Fig. 2.

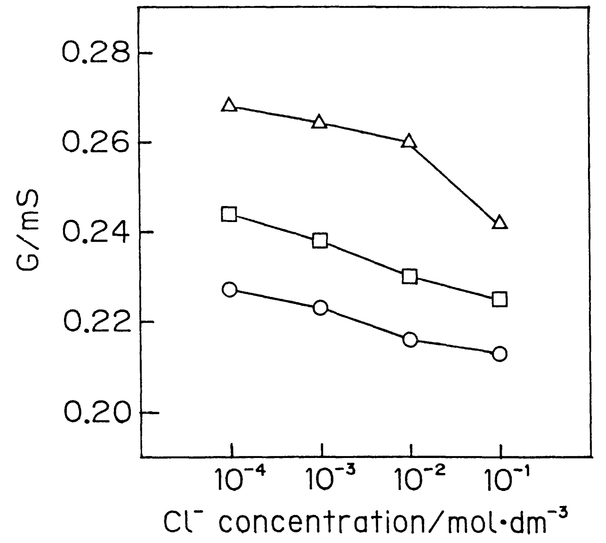

Fig. 4. Conductance response to Cl$^-$ concentration for anion-sensing device with SnO$_2$-TOMACl/PVC junction. $V_w$: 0.3 V (○) 0.1 V (□), −0.1 V (△) vs. Ag-AgCl. SnO$_2$: 19 nm thickness and $4\times10^{20}$ cm$^{-3}$ donor density. PVC membrane: 200 μm thickness.

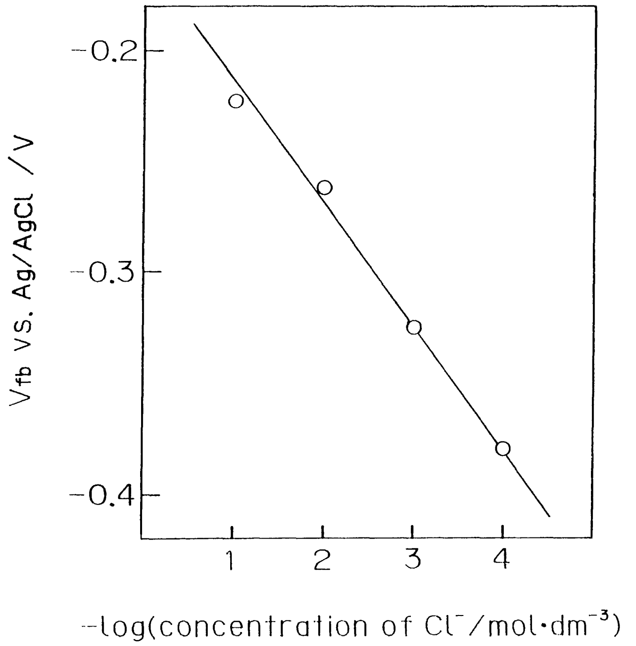

Fig. 5. Dependence of flatband potential of semiconductor upon Cl$^-$ concentration in anion-sensing device with SnO$_2$-TOMACl/PVC junction. The characteristics for the semiconductor and ion-sensitive layers are the same as for Fig. 4.

dependence of the conductance was contrary to the cation-concentration dependence found in the cation-sensing devices, i.e. the conductance decreased with increasing the anion concentration. The anion-sensing device, however, showed the same relationship between the electrode potential ($V_W$) and the conductance, i.e. the positive shift in the electrode potential diminished the conductance. The near-Nernstian response in the flatband potential of the semiconductor, as depicted in Fig. 5, confirms a response mechanism that the semiconductor conductance change is induced by a potential change in the anion-sensitive layer and, thereby, the space-charge-layer thickness change in the semiconductor.[4)]

In conclusion, the characteristics of the semiconductor and ion-sensitive layer significantly alters the sensitivity of ion-sensing devices based on SnO$_2$-ion-sensitive PVC membrane junctions; the choice of materials for the semiconductor and ion-sensitive membrane seems to be quite important for designing this type of ion-sensing device.

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### References

1) P. Bergveld, *IEEE Trans. Biomed. Eng.*, **BME-17**, 70 (1970).

2) H. Abe, M. Esashi, and T. Matsuo, *IEEE Trans. Electron Devices*, **ED-26**, 1939 (1979).

3) S. D. Moss, C. C. Johnson, and J. Janata, *IEEE Trans. Biomed. Eng.*, **BME-25**, 49 (1978).

4) M. Sukigara, Y. Aikawa, M. Kimura, and Y. Okawa, *Nippon Kagaku Kaishi*, **1987**, 484.

5) Y. Okawa, M. Sukigara, S. Yoshida, and T. Watanabe, *Bull. Chem. Soc. Jpn.*, **61**, 1175 (1988).

6) S. Yoshida, Y. Okawa, T. Watanabe, S. Inokuma, and T. Kuwamura, *Chem. Lett.*, **1989**, 243.

7) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).

8) J. M. Bolts and M. S. Wrighton, *J. Phys. Chem.*, **80**, 2641 (1976).