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New MOS-Type Glucose Sensor Using Sputtered LaF_3 Film

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INTRODUCTION

This report deals with a new semiconductor glucose sensor utilizing sputtered LaF_3 film as a gas-sensing material. It has been reported that LaF_3 solid electrolyte can be utilized for an all-solid-state oxygen sensor operative at T_r. The sensor, using LaF_3 single crystal or sputtered LaF_3 film, detects not only gaseous oxygen but also dissolved oxygen and H_2O_2 in solution, (*1–3*) and thus it has been incorporated successfully into a new type of all-solid-state enzyme sensors (*4,5*). Our recent work has shown that the use of sputtered LaF_3 thin film as a gate material gives a MOS-type micro-oxygen sensor workable at T_r (*6*). This has suggested to us that the MOS-type oxygen sensor may be applicable as a transducer of a micro-enzyme sensor to realize an enzyme sensor free from the use of an external reference electrode.

Experiments

Fig. 1 shows the cross-sectional view of the MOS-type glucose sensor fabricated here. An *n*-type Si of 4–6 Ω cm was thermally oxidized to an oxide layer about 100 nm thick, and an LaF_3 film (300 nm thick) was deposited on it by an RF magnetron-sputtering instrument. The LaF_3 sputtering was carried out in a pure Ar gas plasma at a pressure of 10.7 Pa, keeping the temperature of the substrate below T_r by water cooling. The acceleration voltage of the Ar plasma was adjusted to 16 kV and the deposition rate of the film was set at ca. 10 nm/min, so optimized previously, to prepare the LaF_3 film for the oxygen sensor (*5*). The LaF_3 film was then overcoated with a Pt-thin film (50 nm) by the same RF sputtering instrument, as an

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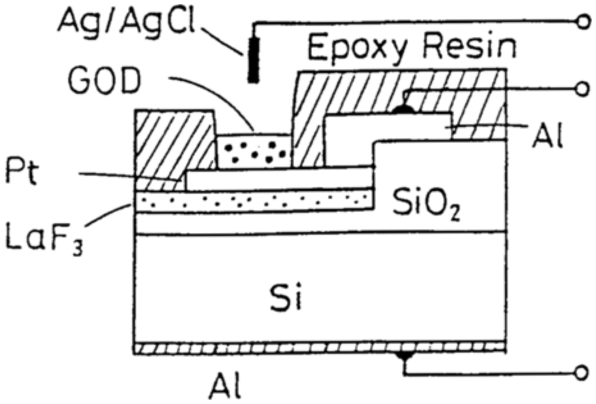

Fig. 1. Cross-sectional view of the MOS-type glucose sensor using sputtered LaF_3 film.

electrochemical catalyst as well as a gate metal electrode. The Pt gate was extended to the peripheral region of the thicker Al film (300 nm) to obtain good electrical contact. After the outside region of the gate electrode was covered with epoxy resin, a glucose oxidase (GOD) layer was overcoated on the gate electrode. The enzyme layer was formed on the MOS element as follows. A phosphate buffer solution (0.2*M*) containing GOD (100 mg/mL) and 15% bovine serum albumin was spin-coated (2000 rpm) on the Pt film and dried at T_r for 10 min. Then, 2% glutalaldehyde solution was dropped on the enzyme layer to immobilize GOD. The sensor was then washed with deionized water and was immersed into 0.1*M* glycine solution to get rid of excess glutaraldehyde. Glucose-sensing experiments were carried out by dipping the sensor element in the phosphate buffer solution into which a prescribed amount of glucose solution was poured while stirring with a magnetic stirrer. By controlling the capacitance of the MOS-type sensor at the flat band condition, the gate voltage that corresponded to the difference in surface voltage between the gate Pt electrode and the LaF_3 film was recorded as a sensor signal at T_t. In contrast, an external Ag/AgCl reference electrode was also used instead of the Pt gate electrode. In place of a conventional glass electrode having a high impedance, an Ag wire (diameter of 0.5-mm)-type electrode was fabricated by electrochemical coating of AgCl film on the Ag wire in a KCl solution. The contact impedance between the AgCl electrode and the electrolyte was < 1 KΩ.

RESULTS AND DISCUSSION

Fig. 2 shows the capacitance-voltage characteristics (C-V curves) of the MOS-type sensors measured at the frequency of 100 kHz. The solid line (a) and broken line (b) were recorded for the sensor fitted with a Pt

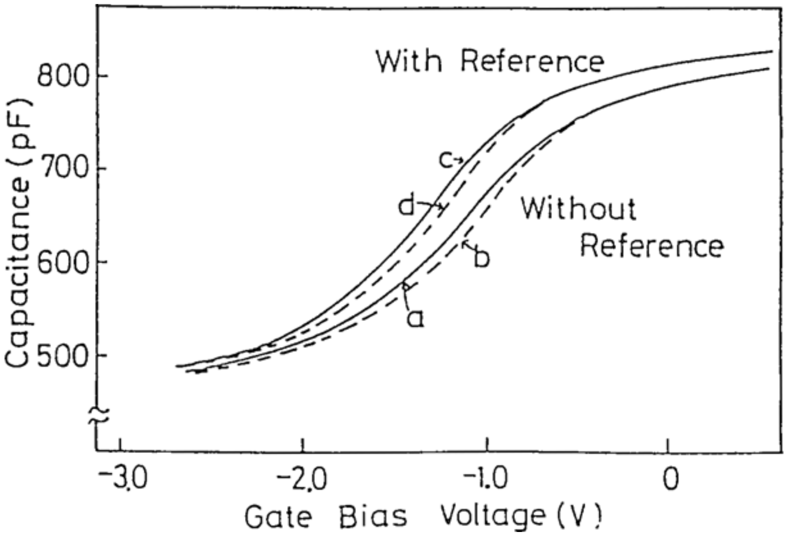

Fig. 2. Capacitance-voltage characteristics of a MOS-type glucose sensor before (solid line) and after (broken line) addition of 50 m*M* glucose into the buffer. (a), (b): with a Pt gate, (c), (d): with an Ag/AgCl reference electrode.

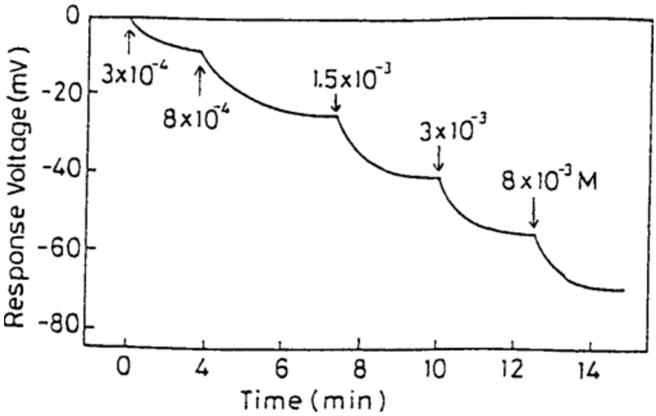

Fig. 3. Response transients of the MOS-type glucose sensor with a Pt gate electrode on the injection of various glucose concentrations.

gate before and after the addition of 50 m*M* glucose into the buffer, respectively. It is noted that the C-V curve shifts in the direction of less negative gate bias by the addition of glucose. Curves (c) and (d) were measured under identical conditions by using the external Ag/AgCl reference electrode. With the addition of glucose, the C-V curve is again seen to shift in almost the same manner as observed above. This result indicates that the enzymatic reaction of glucose induces a flat band shift in MOS structure. Fig. 3 shows the response transients of the MOS-type sensor fitted with a Pt gate electrode. At the point of each arrow, a measured amount of glucose was added to the buffer solution up to the

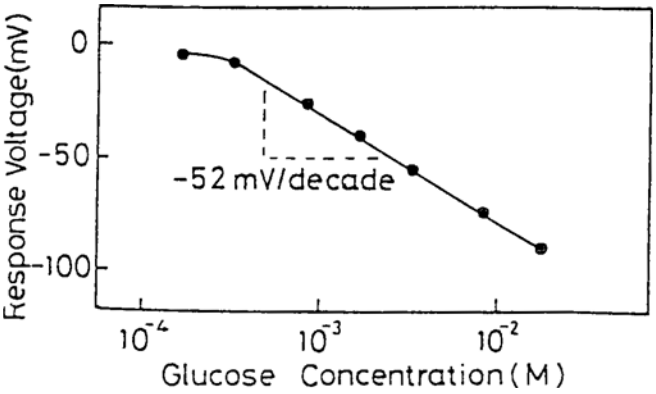

Fig. 4. Dependence of the response voltage of the MOS-type glucose sensor on glucose concentration in 0.1*M* phosphate buffer (pH 6.9).

glucose concentration indicated. Fig. 4 shows the stationary sensor output (response voltage) as a function of the logarithm of glucose concentration. Apparently, good linearity holds between the two quantities in the glucose concentration range 2×10^{-4}–$2\times10^{-2}M$ with a slope of −52 mV/decade. Glucose is oxidized with oxygen in the presence of GOD according to the following enzymatic reaction (1).

$$\text{glucose} + O_2 \longrightarrow \text{gluconolactone} + H_2O_2 \qquad (1)$$

It has been found that the LaF_3 solid electrolyte sensor respond to both dissolved O_2 and H_2O_2 in water at T_t. The present MOS-type glucose sensor also seems to respond to O_2 or H_2O_2, which is consumed or produced by reaction (1). The slope (−52 mV/decade) of the linear line in Fig. 4 suggests that the enzymatic reaction is associated with a one-electron electrode reaction (2) per glucose molecule consumed.

$$H_2O_2 = 2H^+ + O_2^+ + e^- \qquad (2)$$

An alternative possibility is that the sensor responds to the decrease of oxygen owing to the enzymatic reaction, but this possibility is far less plausible, as explained below. We have suggested previously (*4*) that the response reaction of a LaF_3 transducer to dissolved oxygen might be a two-electron reduction since the response had a logarithmical dependence on the oxygen concentration with a slope of ca. 30 mV/decade. A similar response was observed in the preliminary experiment on the present MOS type sensor. Thus, the sensing signal of Fig. 4 seems to be different from that of oxygen detection.

To confirm the above mechanism, the sensing signals (output voltage) of the sensor at various H_2O_2 concentrations were examined experimentally. As shown in Fig. 5, the response voltage was found to vary logarithmically, with a change of H_2O_2 concentration from 5×10^{-4} to $8\times10^{-2}M$ with a slope of ca. −52 mV/decade. It is noteworthy that this Nernst's

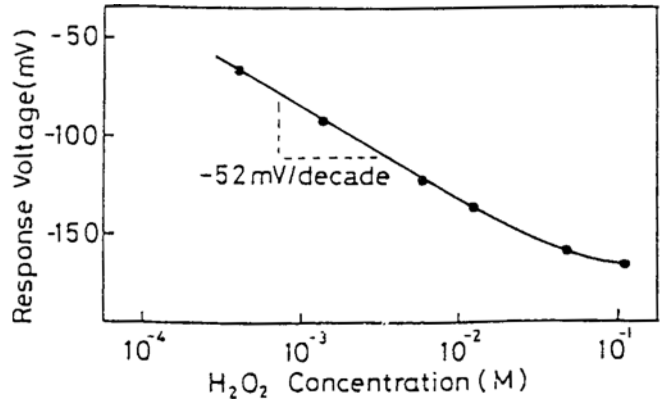

Fig. 5. Dependence of the response voltage of the sensor on H_2O_2 concentration in 0.1*M* phosphate buffer (pH 6.9).

slope coincides well with that observed in Fig. 4. These results support the theory that the glucose-dependent sensing signal of the present sensor is generated through its response to the H_2O_2 produced in the enzymatic reaction.

CONCLUSION

Sputtered LaF_3 film was applied to construct a new MOS-type glucose sensor. Unlike the conventional FET-type glucose sensor, the present sensor needed no external reference electrode to detect the change of H_2O_2 concentration. The sensor output varied logarithmically, with a change of glucose concentration ranging from 2×10^{-4} to $2 \times 10^{-2}M$ in a phosphate buffer solution of pH 6.9. Preliminary discussion on the sensing mechanism was presented.

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