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Potentiometric Response of Lipid Modified ISFET

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ABSTRACT

The gate surface of an ion-sensitive field effect transistor (ISFET) was modified with Langmuir-Blodgett (LB) film composed of fatty acid or crown ether amphiphiles to examine their potentiometric response to H^+ and K^+ ions. The results demonstrate the possible use of the lipid films for preparing ISFET ion sensors.

Index Entries: ISFET; LB film; ion sensors.

INTRODUCTION

The conventional type of pH-sensitive ISFET has been used to detect ionic species other than H^+ ion by coating the gate surface with ion sensitive membranes. For example, a poly(vinyl chloride) (PVC) membrane containing valinomycin has been used to prepare K^+-ion sensors (*1*). The PVC membrane-based ISFET ion sensor shows some advantages over conventional membrane electrode sensors; notably its small size and low output impedance. The disadvantages, however, such as slow response, short life, and so on, still must be improved. The polymer materials, such as polyacrylates and polysiloxanes have been employed to improve the potentiometric response of ISFET ion sensors (*2*). We have recently employed LB films composed of fatty acid or crown ether amphiphiles as sensitive layers of the ISFET ion sensors.

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Table 1
Effects of LB Membrane[a] Deposition of the pH Response of ISFETs

	pH response (mV pH^{-1})		
	Without LB layer	10 nm layer[b]	100 nm layer[c]
Si_3N_4 gate ISFET	45–50	45–50	12–25
Parylene gate ISFET	5–10	40–50	30–50

[a] Stearic acid was used as material
[b] 4-layer LB membrane
[c] 40-layer LB membrane

FATTY ACID-MODIFIED ISFET

It has been demonstrated that as a silicon nitride (Si_3N_4) gate, ISFET exhibits pH response potentiometrically owing to oxide formation at the uppermost layer of the Si_3N_4 surface (3). It is interesting to elucidate the effect of surface modification of the ISFET on the pH response. For this purpose, two types of ISFETs were used: Si_3N_4 gate and poly-*p*-xylylene (parylene) gate. Stearic acid LB films were deposited on the gate surface of both ISFETs by using a conventional type of Langmuir trough. The stearic acid LB film was deposited as Y type multilayers. The pH response of the LB film-modified ISFETs is summarized in Table 1. Before modification with the LB film, the Si_3N_4 gate ISFET exhibited a near Nernstain response to pH, whereas the pH response was suppressed to 5–10 mV/pH for the parylene gate ISFET. This is attributable to the reduced binding site to H^+ ion in the parylene surface (4). On the other hand, after modification with the 4-layer LB film (thickness: 10 nm), the pH response was enhanced for the parylene gate ISFET although the effect was negligible for the Si_3N_4 gate ISFET. The modification with 40-layer LB film (thickness: 100 nm) resulted in the reduced pH response to both ISFETs. These results clearly show two independent effects of the LB films, namely a barrier to the migration of H^+ or OH^- ions from bulk solution to the Si_3N_4 surface, and an ion-exchange site resulting from the carboxyl residues of stearate. The suppressed pH response of the Si_3N_4 gate ISFET with the thicker LB film originates from the former effect. The latter relates to the fact that the pH response of the parylene gate ISFET is enhanced from 5–10 mV/pH to 40–50 mV/pH or 30–40 mV/pH by the deposition of the LB film. These results provide a useful guiding principle for developing LB film-based ISFET sensors. The elimination of pH response may, if necessary, be attained by modifying the parylene gate ISFET with LB film composed of nonionic amphiphiles. This principle can be

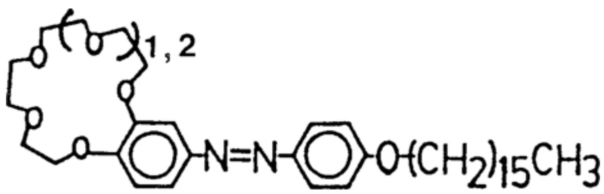

Fig. 1. Crown ether amphiphiles.

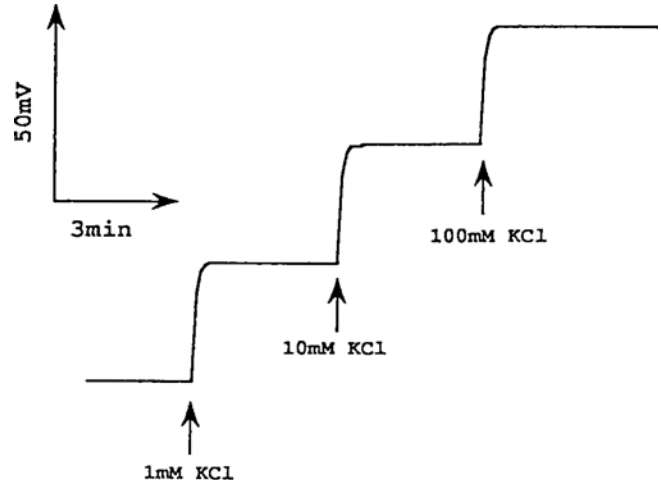

Fig. 2. Typical response of an ISFET ion sensor based on LB film composed of 18-crown-6 amphiphiles.

very important when preparing LB film-based ISFETs sensitive to, for example, Na^+, K^+, and Ca^{2+} ions, since ISFET ion sensors developed so far by the use of polymer membranes or chemical modification techniques often suffer from the potentiometric response to the H^+ ion, as well as to the ions being measured (*5*).

CROWN ETHER MODIFIED ISFET

In order to develop K^+ ion sensors based on lipid-modified ISFET, we prepared amphiphilic crown ethers, 4′-(*p*-hexadecyloxyphenylazo)benzo-15-crown-5 and its 18-crown-6 derivative (Fig. 1). These compounds form stable monomolecular layers on pure water that can be deposited in multilayers on the gate surface of ISFET by the LB technique.

The Si_3N_4 gate and parylene gate ISFETs were employed to develop the K^+ ion sensors by the use of the crown ether LB films. Fig. 2 shows typical response curves of the K^+ ion sensor prepared with parylene gate

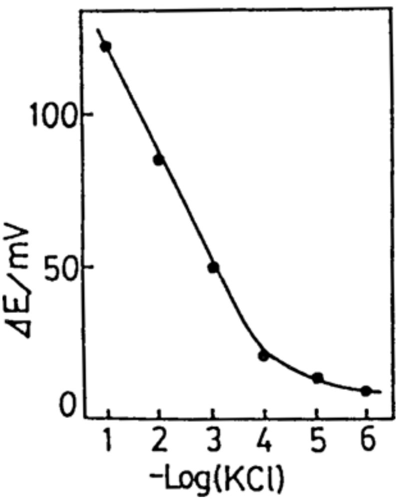

Fig. 3. The calibration graph of an ISFET K^+ ion sensor modified with an 18-crown-6 derivative LB membrane (40 layers).

ISFET modified with the 18-crown-6 derivative. The gate potential clearly depended on the KCl concentration in the sample solution, confirming the selective binding of the K^+ ion by the LB film. The response time of the sensor was satisfactorily fast. A typical calibration curve is depicted in Fig. 3. The sensor exhibited a potentiometric response to the K^+ ion above $10^{-4}M$, with the sensitivity of ca. 35 mV/decade. The relatively low sensitivity characteristics seem to be common to potentiometric sensors with surface sensitive layers of molecular dimension, in view of the fact that the sensitivity of ISFET ion sensors prepared by the chemical modification of the gate surface with crown ether is also 30–40 mV/decade (5). Fig. 4 shows the ion selectivity of the ISFET ion sensor based on 18-crown-6 amphiphiles. The sensor exhibited selectivity to the K^+ ion over Na^+ and Li^+ ions, which can be explained reasonably based on the K^+-ion selective nature of the crown ether. The ion sensor based on the 15-crown-5 derivative gave a similar but slightly inferior response to those with 18-crown-6 amphiphiles.

The Si_3N_4 gate ISFET was also modified with the crown ether amphiphiles, however, the response was inferior to those of parylene gate ISFET. This is probably owing to the effect of pH responses; i.e., the gate potential is thought to be determined by both H^+ and K^+ ions because of high sensitivity of the Si_3N_4 surface to the H^+ ion. Therefore, it is recommended that you use parylene gate ISFET to develop high performance ion sensors.

Table 2 summarizes the performance characteristics of ISFET K^+ ion sensors based on crown ether-doped PVC membranes, chemical modification of the gate surface, and LB membranes. At the present time, PVC

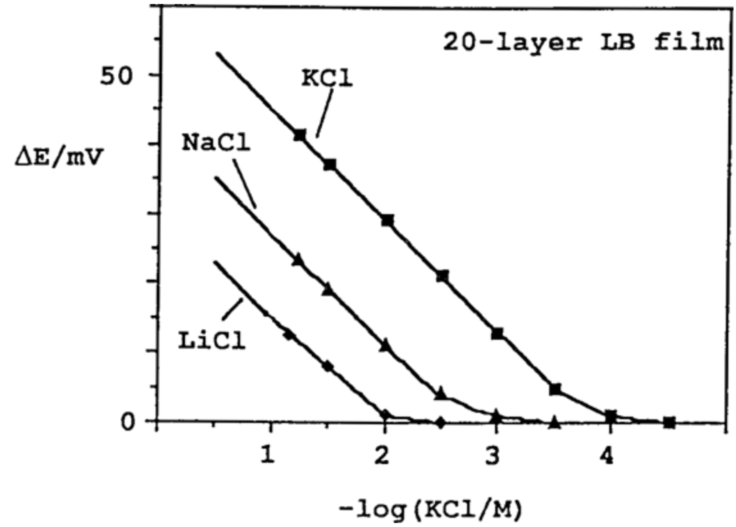

Fig. 4. The ion selectivity of an ISFET K^+ ion sensor modified with an 18-crown-6 derivative LB membrane (20 layers).

Table 2
Characteristics of Three Types of Sensitive Layers
of ISFET K^+ Ion Sensors Based on Crown Ethers

Ion-sensitive layer	PVC membrane	Chemical modification	LB membrane
Thickness	10–100 μm	5 nm <	5 nm <
Response time	slow	fast	depends on thickness
Sensitivity	55 mV pK^{-1}	35 mV pK^{-1}	35 mV pK^{-1}
Durability	poor	good	poor

membrane-based sensors are superior to others from the viewpoint of practical applications. The poor durability and low sensitivity of the LB film-based sensors are problems that must be improved.

Thus, LB film-based sensors have not yet been fully established as reliable sensors for practical use. Nevertheless, the LB film is currently attracting much attention in relation to the development of chemical sensors because of its promising characteristics, such as easy preparation under mild conditions (room temperature, atomospheric pressure, aqueous environment, and so on), ultra thin film and uniform thickness, and highly oriented biomembrane-related structure (*6,7*).

REFERENCES

1. Moss, S. D., Janata, J., and Johnson, C. C. (1975), *Anal. Chem.* **47,** 2238.
2. Van der Wal, P. D., Skowronska-Ptasinska, M., Verg, A. V. D., Bergveld, P., Shdholter, E. J. R., and Reinhauldt, D. N. (1990), *Anal. Chim. Acta* **231,** 41.
3. Matsuo, T. and Wise, K. D. (1974), *IEEE Trans. Biomed. Eng.* **BME-21,** 485.
4. Fujihira, M., Fukui, M., and Osa, T. (1980), *J. Electroanal. Chem.* **106,** 413.
5. Matsuo, T., Nakajima, H., Osa, T., and Anzai, J. (1986), *Sens. Actuators,* **9,** 115.
6. Anzai, J. and Osa, T. (1990), *Selective Electrode Rev.* **12,** 3.
7. Anzai, J., Lee, S., and Osa, T. (1991), *Sekiyu Gakkaishi* **34,** 399.