Anion-Selective Field-Effect Transistor Sensor Using RF-Sputtering Film of Alkali Metal-Free Lead Phosphate Glass Containing Silver Oxide

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New ion-selective field-effect transistors (ISFET) for an anion responsive type probe are described. The gate surface of the ISFET was coated by radio-frequency sputtering with an alkali metal-free phosphate glass containing silver oxide. This ISFET responded to $S_2O_3^{2-}$, SCN^-, I^-, NO_2^-, SO_3^{2-}, and Cl^-, but not to NO_3^-, ClO_3^-, SO_4^{2-}, and HPO_4^{2-}. A radiation damage of sputtering products is generated in the dielectric layer and at the interface of the gate channel, and the static characteristics of the glass coated ISFETs were used to evaluate the radiation damage. Optimal RF sputtering gas composition, dc floating bias from anode to substrate, RF power density, and sputtering time were argon 90%/oxygen 10%, −70 V, 0.88 W cm^{-2}, and up to 4 h, respectively.

Since Bergveld[1] proposed a new type of electrochemical sensor, ion-selective field-effect transistors (ISFETs) have been fabricated by use of immobilized enzyme membranes,[2] heterogeneous membranes,[3] and ion-selective layers deposited on a gate surface.[4-6] An ISFET with an alkali ion-selective membrane fabricated by ion implantation on the gate insulator was examined.[7] ISFET sensor devices[8] have many advantages over conventional ISE such as very small dimensions and the solid-state nature at the gate surface.

According to Eisenman,[9] replacement of a 4-coordinated silicon atom in a sodium–alumino silicate glass with a 5-coordinated atom such as phosphorus generates a positively charged site which would exhibit anion-exchange properties and a response to anions. In previous work, alkali metal-free lead phosphate glasses containing silver oxide have been investigated as anion-selective electrodes.[10]

In this study, ISFETs as anion-selective electrodes were prepared by coating the gate surface with an alkali metal-free lead phosphate glass containing silver oxide by radio-frequency (RF) sputtering. Optimal sputtering conditions were sought for the sputtering gas composition, RF power density, sputtering time, and dc floating bias between anode and substrate. The response characteristics of the sensor to some anions are presented.

Experimental

Preparation of Target Glass Materials. To obtain the target materials of the alkali metal-free lead phosphate glass containing silver oxide, the following analytical reagents were used: ortho-phosphoric acid (85%), aluminum hydroxide, lead carbonate, and silver carbonate. A glass melt was poured into a circular hollow of about 60 mm in diameter on a graphite plate and was annealed overnight. The chemical composition of the target glasses was $5Ag_2O$: (47—55)P_2O_5 : (37—30)PbO : $10Al_2O_3$.

Fabrication of Glass Coated ISFET. Original n-channel ISFETs were obtained from Shindengen Electric Mfg.[11] The gate insulator of the ISFET was composed of two layers; the upper was chemical vapor deposited silicon nitride (100 nm), and the lower was thermally grown silicon dioxide (100 nm). The ion-selective gate area was 15 μm wide and 450 μm long.

A glass thin film was RF sputtered on the gate surface with an Ulvac SBR-1102E type RF (13.56 MHz) sputtering instrument. Unless otherwise noted, the RF power density, the sputtering gas composition, and its pressure were 0.88 W cm^{-2}, argon 90%/oxygen 10%, and 8×10^{-3} Torr (1 Torr=133.322 Pa), respectively, and the substrate temperature was around 50°C. The compositions of the target materials and the sputtered glass film were measured with an EDS type JEOL electron probe microanalyzer (EPMA) Model JCXA-733. The data obtained were corrected for adsorption, atomic number, and fluorescence factor (ZAF corrections). The thickness of the sputtered film was measured with a Sloan Dektak II-A type thickness meter with diamond-needle tracing. When the RF power density was 0.88 W cm^{-2} and the sputtering time was 4 h, the film was 0.73 μm thick.

Sputtering Gas Composition and dc Floating Bias on Substrate. Gas mixtures of argon (99.99%) and oxygen (99.99%) in varying ratios were used to control the composition of the sputtered glass film. When exposed to an argon or oxygen plasma by RF sputtering, the gate surface is hit continually by plasma-created species such as Ar^+, O_2^+, O^+, e^-, O_2^-, and O^- apart from the sputtered atoms. Bacause of this the positively charged trap in the SiO_2 layer gradually increases in the course of irradiation.[12] Since this bombardment caused radiation damage at the interface of the SiO_2 layer, the threshold voltage shifts were generated. Therefore, the minus dc floating bias between the anode and substrate was applied directly,[13] and anionic gas species or electrons created were removed.

Static Characteristics of ISFET. To investigate the radiation damage of the gate surface exposed to the plasma during RF sputtering, the drain current (I_D) of ISFET was measured both for the variation of the drain-source voltage (V_{DS}) and the gate-source voltage (V_{GS}), by immersing the devices in a standard pH buffer (pH 6.86).[14]

Measurements of Anion Activities with the Glass Coated ISFET. The output voltage was measured with a source-follower mode circuit purchased from Shindengen Electric Mfg. Unless otherwise specified, the voltage between the source and drain was held constant at 4.0 V. The test solution was stirred magnetically at 600 rpm at 25±0.2°C in a water bath. The output voltage was measured against an Ag/AgCl reference electrode.

Results and Discussion

Characteristics of Sputtered Films as a Function of RF Sputtering Condition. Table 1 summarizes the results of semi-quantitative elemental analysis of the target glass and the RF-sputtered films, as functions of gas mixture composition and sputtering power density. The elemental compositions of specimen prepared at an RF power density above 0.88 W cm^{-2} and an oxygen gas content above 10% were approximately the same as that of the initial target glass, with a slight decrease in the phosphorus and oxygen contents in the sputtered film. Actually, the sputtered film exhibited a pale purplish red color which is partially due to red phosphorus.[15] No crystal peaks were observed by X-ray diffraction with the sputtered film.

The chemical durability of a thick sputtered glass film was examined by measuring the decrease in the film thickness in distilled water as a function of time at about 30°C.

The effect of the exposure time on the decrease in the film thickness is shown in Fig. 1. Although a slight decrease in the film thickness was noted during the first 10 d, further decrease was negligible for over 60 d. The relative standard error of each measurement point was within 5%.

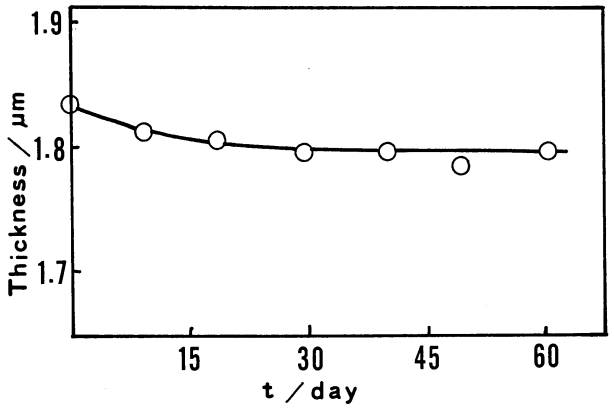

Fig. 1. Chemical durability of the sputtered glass film in distilled water.

The effective deposition rate of the RF sputtered phosphate glass film at various power densities was measured with a thickness meter. A roughly straight relationship was observed between the effective deposition rate and the power density.

Static Characteristics of the Phosphate Glass Coated ISFET. Figure 2 shows the static characteristics of the original ISFET (5) and the ISFETs prepared by sputtering at various Ar/O_2 gas compositions (1—4). For samples (1) and (2), the threshold voltage (V_{Th}) is in the

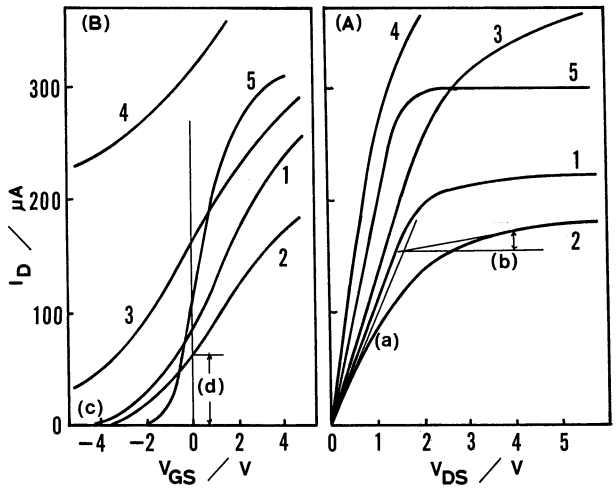

Fig. 2. Static characteristics of original and glass coated ISFET in the forms of V_{DS}–I_D relationship (A) (V_{GS}=0 V) and V_{GS}–I_D relationship (B) (V_{DS}=2 V). RF sputtering conditions: 0.88 W cm^{-2}, 4 h. Sputtering gas composition: 1, 100% Ar; 2, 90% Ar/10% O_2; 3, 60% Ar/40% O_2; 4, 100% O_2; 5, original ISFET. Evaluation of the sputtering damage; (a) initial slope, μA/V; (b) slope in the saturation region, μA/V; (c) threshold voltage, V; (d) I_D value at V_{GS}=0 V, μA.

Table 1. Results of Semi-Quantitative Elemental Analysis by EPMA of the Target Material and the Sputtered Films

Element	Target	RF sputtering conditions: 0.35	0.88				RF power density (W cm^{-2}) Gas composition (Ar %/O_2%): 1.77
		90/10	100/0	90/10	60/40	0/100	90/10
	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
Ag	6.57	6.58	7.11	5.67	5.19	6.37	6.64
		6.24	7.05	5.87	6.12	6.13	6.31
Pb	36.56	41.66	40.51	38.38	36.27	38.88	36.34
		42.22	40.15	38.36	37.97	40.21	36.46
P	20.46	17.95	17.83	19.30	19.50	18.11	19.64
		17.76	17.91	19.29	19.45	17.82	19.18
Al	3.24	3.69	4.17	4.46	5.73	4.83	4.65
		3.81	4.38	4.33	3.91	4.02	5.39
O	33.18	30.13	30.37	32.25	32.44	31.81	32.73
		29.96	30.56	32.16	32.04	31.82	32.67

range of −4.0 to −5.0 V, being shifted by about −2.0 V from that of the original ISFET. By sputtering in an Ar/O_2 mixture, the gate surface would be exposed to various ionic species, electrons, soft X-ray, and UV light.[16] The radiation damage on the ISFET gate surface would be caused mainly by bombardment of electrons, UV light, and soft X-ray radiation. Supply of a −70 V dc floating bias on substrate can eliminate the bombardment of electrons and anionic gas species.[17] When the bias voltage was zero or +70 V against the substrate, the static characteristics of ISFET was abnormally deteriorated due to these bombardments. The I_D value in the static characteristics is proportional to the gate capacitance for any value of V_{GS}. With an increase in the glass thickness on the gate surface, therefore, the I_D value decreases only to a small extent.

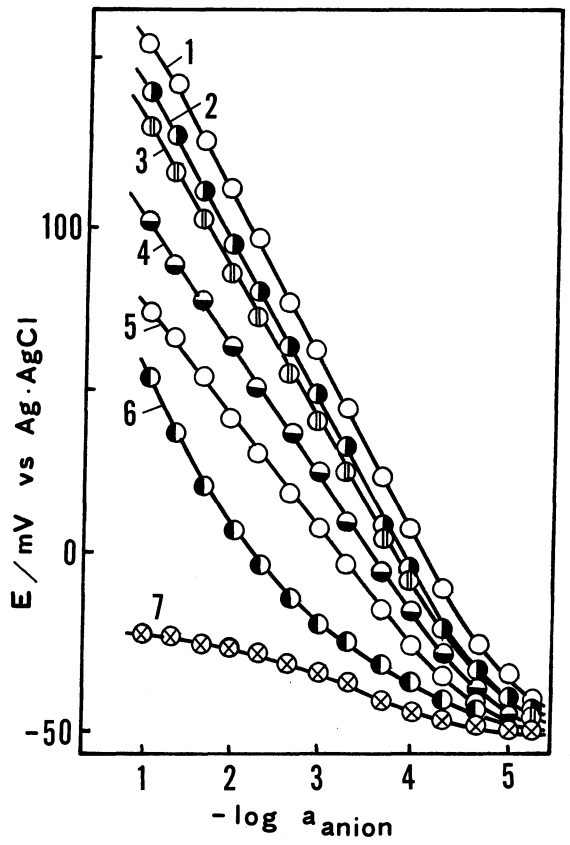

Fig. 3. Electrode response of glass coated ISFET as a function of ion activity. RF sputtering conditions: 0.88 W cm^{-2}, 4 h. Measurement conditions: V_{DS} 4.0 V, I_D 200 μA. 1, $S_2O_3^{2-}$; 2, SCN^-; 3, I^-; 4, Br^-; 5, NO_2^-; 6, ClO_4^-; 7, NO_3^-.

Response to Anions. Figure 3 shows typical potential response of a glass coated ISFET (ISFET No. 2 in Table 2) to various anions. The output voltage was measured at a drain-source voltage of 4.0 V and a drain current of 200 μA. The output voltage changed immediately on injection of anions and reached a steady state in about 60 s. The selectivity was in the order $S_2O_3^{2-} \geqslant SCN^- > I^- > Br^- > NO_2^- > SO_3^{2-} > Cl^-$. No response was found with NO_3^-, ClO_3^-, SO_4^{2-}, HPO_4^{2-}, and cationic species. The anion selectivites of this ISFET followed almost inversely to the Hofmeister series. The slope of the potential response ranged from 58 to 50 mV per decade change in $S_2O_3^{2-}$, SCN^-, and I^- activity. The detection limit for these three anions was as low as 5×10^{-6} mol dm^{-3} within a relative standard deviation of 2.3%. The potential response may result from adsorption of anions on the sputtered phosphate glass surface followed by a positive shift of the interface potential. By use of a silver oxide-free target glass, the slope of the potential response to $S_2O_3^{2-}$ and SCN^- decreased from 58 to 26 mV per decade change. This indicates that the silver ion in the glass plays a key role in the potential response.

Effect of Sputtering Conditions on the Static and Response Characteristics of Glass Coated ISFET. As seen in Fig. 2, a glass coated ISFET prepared by sputtering in 100% Ar (No. 1) or 90% Ar/10% O_2 (No. 2) has a small radiation damage and could be used for potential measurements. However, when the gas composition was 60% Ar/40% O_2 (No. 3) or 100% O_2 (No. 4), the threshold voltage and saturation region were not found out. Actually, the observed intensity of UV radiation in the plasma space became higher with an increase in the oxygen content.

The response behaviors of ISFETs, prepared under various RF sputtering conditions, to thiocyanate are shown in Fig. 4. The responses are nearly Nernstian for glass coated ISFETs sputtered in 100% Ar and 90% Ar/10% O_2. However, with increasing oxygen content in the sputtering gas, the response to thiocyanate became weaker and finally no response appeared at 100% O_2. These results are well in line with the static characteristics of the ISFETs.

As a measure of the RF sputtering damage, the static characteristics are given in Table 2 as a function of the

Table 2. Effect of Sputtering Gas Composition on the Radiation Damage

ISFET No.	Gas composition (Ar%/O_2%)	Initial slope (a) (μA/V)	Damage slope (b) (μA/V)	Threshold voltage (c) (V)	I_D value at V_{GS}=0 V (d) (μA)
1	100/0	80.8	3	−4.5	76
2	90/10	52.5	13	−4.0	46
3	60/40	124	32	—	165
4	0/100	275	133	—	490
5	Original	183	0	−2.0	138

Sputtering conditions: RF power density 0.88 W cm^{-2}, sputtering time 2 h.

Table 3. Effect of RF Sputtering Conditions on the Radiation Damage

ISFET No.	RF-sputtering conditions (W cm^{-2}, h)	Initial slope (a) (μA/V)	Damage slope (b) (μA/V)	Threshold voltage (c) (V)	I_D value at V_{GS}=0 V (d) (μA)
1	0.18, 20	323	226	—	470
2	0.35, 10	310	170	—	580
3	0.88, 4	52.5	13	−4.0	46
4	1.77, 2	23.6	28	−5.5	20
5	Original	183	0	−2.0	138

Gas composition: Ar 90%/O_2 10%.

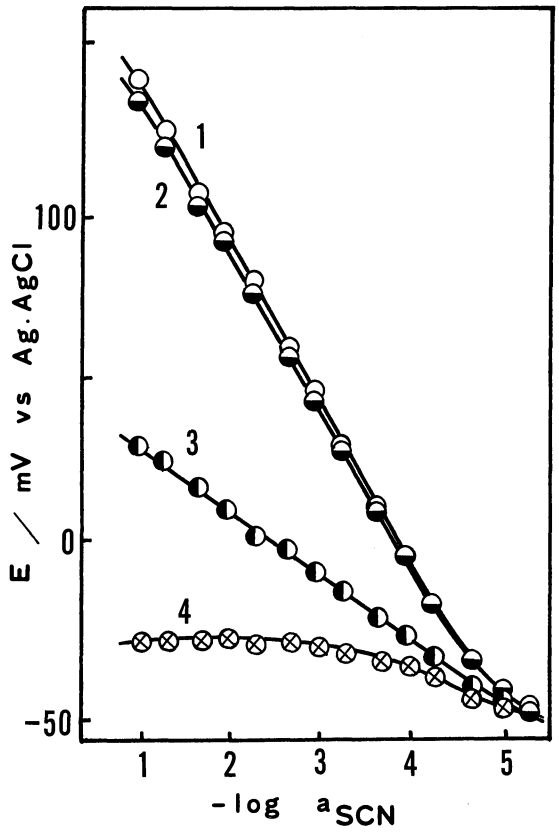

Fig. 4. Response to thiocyanate ion of glass coated ISFETs prepared with various sputtering gas compositions. Numbering is the same as in Fig. 2.

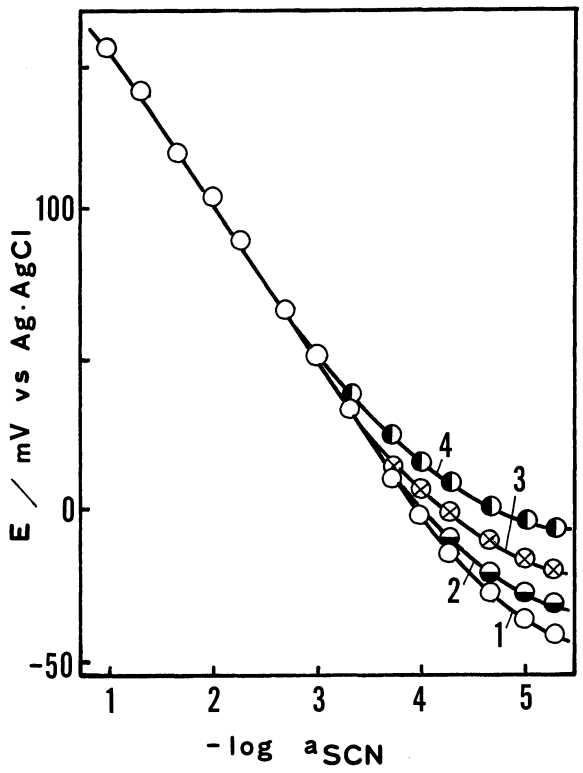

Fig. 5. Interference of nitrate on the thiocyanate response. 1, without NO_3^-; 2, 10^{-3} mol dm^{-3} NO_3^-; 3, 10^{-2} mol dm^{-3} NO_3^-, 4, 10^{-1} mol dm^{-3} NO_3^-.

sputtering gas composition. The initial slope of the I_D–V_{DS} curve is expressed in μA/V (a), the slope in the saturation region (as the damage factor of the device) of the I_D–V_{DS} curve in μA/V (b), the threshold voltage in V (c), and the I_D value at V_{GS} 0 V on the I_D–V_{GS} curve in μA (d). As seen, the (b) and (d) values are extremely high and the (c) value could not be determined for ISFETs No. 3 and 4.

For sputtered films of common thickness, the effects of RF power density and sputtering time on the radiation damage are summarized in Table 3. Although the radiation damage increase linearly with the plasma dose, the damage on the ISFET channel will be induced by prolonged RF sputtering even at a low power density. It is suggested that a higher RF power density is more favorable than a longer sputtering time to maintain the static characteristics of the ISFET at a good level.

Interferences and Long-Term Stability. The influence of nitrate on the thiocyanate calibration curves are depicted in Fig. 5. Except at very low thiocyanate concentrations, it is possible to determine thiocyanate ions in the presence of 10^{-1} mol dm^{-3} of nitrate. Potentiometric selectivity coefficients of the ISFET No. 2 in Table 2 for K_{SCN/NO_3}, K_{SCN/SO_4}, and $K_{SCN/Cl}$ are 1.3×10^{-4}, 6.3×10^{-5}, and 5.0×10^{-3}, respectively.

The shift of the output potential at a bromide concentration of 10^{-3} mol dm^{-3} for the ISFET No. 2 was less than 5 mV in 40 h. The potential response was maintained for over 3 moths.

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