

Development of a Wide Range pH Sensor based on Electrolyte-Insulator-Semiconductor Structure with Corrosion-Resistant Al₂O₃-Ta₂O₅ and Al₂O₃-ZrO₂ Double-Oxide Thin Films

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In order to develop a pH sensor having a wide pH response range from strong acid to strong alkali, electrolyte-insulatorsemiconductor capacitors using corrosion-resistant Al_2O_3 - Ta_2O_5 and Al_2O_3 - ZrO_2 double-oxide films as the insulator were fabricated and their response characteristics to H⁺ and alkali metal ions were examined. The sensors with Al_2O_3 - Ta_2O_5 and Al_2O_3 - ZrO_2 films having an Al^{3+} cationic fraction of about 0.4 showed a wide linear pH response range of -1.5 to 13.0 and a small alkali metal ion sensitivity. The use of the Al_2O_3 - Ta_2O_5 film is suitable for increasing pH sensitivity and that of the Al_2O_3 - ZrO_2 film is promising for increasing corrosion resistance against strong alkali solutions. © 2004 The Electrochemical Society. [DOI: 10.1149/1.1643074] All rights reserved.

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In the last three decades, much attention has been paid to the research and development of chemically sensitive field-effect devices such as ion-sensitive field-effect transistors (ISFETs). electrolyte-insulator-semiconductor (EIS) capacitors, and lightaddressable potentiometric sensors (LAPS).¹ These devices can measure changes in the surface potential at the insulator/electrolyte interface. When the insulator is an oxide or a nitride, such as Al₂O₃, Ta2O5, and Si3N4, the field-effect devices show almost Nernstian pH sensitivities.² This type of pH sensor has several advantages such as rapid initial response, high input impedance, strong solidstate construction, and the possibility of miniaturization. It is therefore expected to find use in a variety of applications and to replace conventional pH-glass electrodes. However, pH-sensitive fieldeffect devices up to now have been limited to some applications such as *in vivo* use of catheter-tip ISFETs,¹ so that the glass electrodes are still dominant pH sensors in most applications. This is because the field-effect device pH sensors have some disadvantages, such as hysteresis,²⁻⁵ drift^{2,5-7} and photo-sensitivity,⁸⁻¹⁰ which lower the accuracy of the sensors. Furthermore, alkali metal ion sensitivity¹¹ and corrosion¹² hinder the application to pH measurement in strong acid and alkali solutions. In these solutions, ordinary pH-glass electrodes cannot be used due to large acid and alkali errors, though the alkali error arising from sodium ion sensitivity can be reduced by using a specially formulated lithium ion conductive glass. The field-effect device sensors will be applicable in strong acid and alkali solutions if insulator materials having low alkali metal ion sensitivity and high corrosion resistance are developed. Recently, several companies have offered pH-ISFET sensors, which achieve almost Nernstian response over a wide pH range of 1-13, small acid and alkali errors (*e.g.*, $\Delta pH < 0.2$ in 1 M HCl and 1 M NaOH), and high stability. In hot NaOH solution, however, the lifetime of commercially available pH-ISFETs is greatly reduced by the dissolution of insulator materials. In order to extend the application area of field-effect device pH sensors, it is still required to develop insulator materials having high corrosion resistance, high pH sensitivity, low alkali metal ion sensitivity, and high stability.

It has been reported that in the absence of alkali metal ions an ISFET with a Ta_2O_5 insulator film shows an ideal Nernstian pH response in the pH range of -7 to 13.7.¹¹ However, a deviation from Nernstian response is observed when Li⁺ ions exist in solutions of pH > 7, and Na⁺ and K⁺ ions in those of pH > 12. The sensitivity

of metal oxide (MO) to alkali metal ions should be related to the association of surface hydroxyl groups (MOH) with alkali metal ions $(X^{\rm +})^{13\text{-}15}$

$$MOH + X^{+} = MO^{-} - X^{+} + H^{+}$$
 [1]

or

$$MO^{-} + X^{+} = MO^{-} - X^{+}$$
 [2]

where MO^- is a negatively charged surface site formed by the dissociation of the MOH group. The above ion exchange reactions occur at pH higher than the point of zero charge (pH_{pzc}) of the oxide. Therefore, if an oxide with a high pH_{pzc} value is used as an insulator, the alkali metal ion sensitivity should be lowered. This will be realized by using Al₂O₃ as an insulator because the pH_{pzc} value of Al₂O₃ (8.8-9.4)¹⁶⁻¹⁸ is higher than those of Ta₂O₅ (2.8-5.2)^{16,17,19} and ZrO₂ (5.5-8.1).^{16,17,20} We have previously reported that the alkali metal ion sensitivity of an EIS capacitor pH sensor with a ZrO₂ film is lower than that of the sensor with a Ta₂O₅ film.²¹ This reveals that the use of an oxide with a high pH_{pzc} value such as Al₂O₃ is effective in reducing alkali metal ion sensitivity.

The corrosion resistance of Al_2O_3 in alkaline solutions is, however, lower than those of Ta_2O_5 and ZrO_2 .^{22,23} Because the thickness of insulator film of the field-effect device pH sensor is typically less than 100 nm, chemical dissolution of the film significantly shortens the lifetime of the sensor.¹² The corrosion resistance of the insulator oxide should be improved for use of the sensor over a wide pH range. The improvement of the corrosion resistance by combining Al_2O_3 and Ta_2O_5 or ZrO_2 is thought to be promising because our previous studies show that Al_2O_3 - Ta_2O_5 and Al_2O_3 - ZrO_2 double-oxide films having Al^{3+} cationic fractions of less than 0.4 have good corrosion resistance comparable to single Ta_2O_5 and ZrO_2 films.^{22,23}

The objective of the present study is to develop field-effect device pH sensors having a wide pH response range and a low alkali metal ion sensitivity by using Al_2O_3 - Ta_2O_5 and Al_2O_3 - ZrO_2 double-oxide films as the pH-sensitive insulator. A metallorganic chemical vapor deposition (MOCVD) technique was employed to form the double-oxide films, and EIS capacitors to examine sensing characteristics of the films. ISFETs seem to be more suited as practical sensors because of their possibility of miniaturization and compatibility with integrated circuit technology. However, it is necessary to make a good encapsulation for protecting electrical connections of FETs from the attack of corrosive solutions including strong acid and alkali. EIS capacitors can avoid such a limitation and their fab-

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Table I. Composition and pH of solutions used for pH response tests. The pH values were measured at 25°C by using a platinumhydrogen electrode and a pH-glass electrode.

Composition	pH
10 M H ₂ SO ₄	-1.90
$3 \text{ M H}_2 \text{SO}_4$	-0.49
$1 \text{ M H}_2 \text{SO}_4$	0.13
$0.1 \text{ M H}_2 \text{SO}_4$	1.01
0.15 M H ₃ PO ₄	1.54
$0.03 \text{ M H}_3\text{PO}_4 + 0.12 \text{ M NaH}_2\text{PO}_4$	2.63
$0.15 \text{ M NaH}_2 PO_4$	4.44
$0.075 \text{ M NaH}_2\text{PO}_4 + 0.075 \text{ M Na}_2\text{HPO}_4$	6.79
0.15 M Na ₂ HPO ₄	9.17
$0.03 \text{ M Na}_{2}\text{HPO}_{4} + 0.12 \text{ M Na}_{3}\text{PO}_{4}$	11.11
0.15 M Na ₃ PO ₄	12.47
0.1 M NaOH	13.10
1.0 M NaOH	13.93
3.0 M NaOH	14.39
10.0 M NaOH	15.53

rication processes are simpler than those of ISFETs. 24 It has been proved that the results obtained by using EIS capacitors are transferable to ISFETs. 7

Experimental

Fabrication of EIS capacitor pH sensors.—A p-type (100) silicon wafer with a specific resistivity of 10-12 Ω cm was used as the substrate of the EIS capacitors. The gate insulator had a double layer structure composed of a lower layer of SiO₂ and an upper layer of Al₂O₃-Ta₂O₅ or Al₂O₃-ZrO₂. The SiO₂ layer was grown to a thickness of 50 nm by thermal oxidation at 950°C in a wet-oxygen atmosphere. After removing the SiO₂ on the back-side of the wafer with a 10% HF solution, gold was evaporated to form an ohmic contact and the wafer was annealed for 30 min at 350°C under a nitrogen flow. The Al₂O₃-Ta₂O₅ and Al₂O₃-ZrO₂ films were then deposited on the front side of the wafer by using a cold wall lowpressure MOCVD apparatus described in a previous paper.²² Aluminum triisopropoxide $[Al(O-i-C_3H_7)_3]$, tantalum penta-methoxide $[Ta(OCH_3)_5]$, and zirconium tetraisopropoxide $[Zr(O-i-C_3H_7)_4]$ were used as precursors and heated at 100, 120, and 170°C, respectively. Nitrogen (99.999 vol %) was used as a carrier gas of the precursors and oxygen (99.9 vol %) as a reactant gas. The composition of the films was controlled by the flow rate of carrier gas for each precursor. The thickness of the films was adjusted to about 100 nm by ellipsometric monitoring of the film growth.²² All the films were deposited at 350°C and used without post-heat-treatment. The chemical composition of the films was determined by chemical analysis.^{22,23} The cationic mole fraction of constituent metal elements, $X_{\rm M}$, was calculated from their mass in the films, $W_{\rm M}$. For example, the cationic mole fraction of Ta in the Al₂O₃-Ta₂O₅ film, X_{Ta} , is defined by the following equation

$$X_{\rm Ta} = (W_{\rm Ta}/M_{\rm Ta})/(W_{\rm Al}/M_{\rm Al} + W_{\rm Ta}/M_{\rm Ta})$$
[3]

where M_{Al} and M_{Ta} are atomic weight of Al and Ta, respectively.

Micro- and crystal structures of the Al₂O₃-Ta₂O₅ and Al₂O₃-ZrO₂ films have been examined in previous studies using transmission electron microscopy and electron diffraction.^{22,23} The results show that the Al₂O₃-Ta₂O₅ films with X_{Ta} values between 0.0 and 1.0 have homogeneous amorphous structures.²² The Al₂O₃-ZrO₂ films of X_{Ta} = 0.0-0.85 are also amorphous and homogeneous, while those of X_{Ta} = 0.86–1.00 consist of fine crystal grains having a tetragonal structure.²³

Electrolytes.—The pH response of the EIS capacitor sensor was examined in H_2SO_4 , NaOH and phosphate buffer solutions, whose composition and pH values are listed in Table I. The pH values of



Figure 1. Schematic of apparatus used for pH response test.

these solutions were measured by using a platinum-hydrogen electrode and a pH-glass electrode. Alkali metal ion sensitivity was examined in mixed solutions of 0.1 M Na₂B₄O₇ and 0-1000 mM LiCl. The solutions containing 0-100 mM LiCl have the same pH value of 9.3, and that containing 1 M LiCl has a slightly lower pH value of 8.8. All the solutions were used without deaeration.

Examination of pH and alkali metal ion sensitivities.—Figure 1 illustrates a schematic of the apparatus used for pH response tests. A glass vessel with a hole at the bottom was used as a test cell. The sensor was held to the bottom of the cell by a Viton O-ring and a clamp. Capacitance-voltage (C-V) and constant capacitance (CON-CAP) measurements were performed by use of a setup consisting of a frequency response analyzer, a potentiostat, a personal computer, and a feedback control circuit. The gate voltage to the EIS structure was applied through a Ag/AgCl(3.33 M KCl) reference electrode. In the measurement of C-V curves the gate voltage was scanned from -2 to 2 V at a rate of 15.26 mV/s. An ac voltage with an amplitude of 100 mVp-p and a frequency of 1 kHz was superimposed on the gate voltage to measure the capacitance. The change of the surface potential at the electrolyte/insulator interface can be evaluated as a voltage shift of the C-V curve. In the present study the voltage required to achieve a preset capacitance, $C_{\rm ps}$, which is approximately 60% of the maximum capacitance, \vec{C}_{max} , is defined as the response voltage, $V_{\rm R}$. The response voltage can be recorded directly by the CONCAP method,²⁵ in which the feedback control circuit adjusts the gate voltage to keep the measured capacitance at a constant value of $C_{\rm ps}$.

The sensor was first stabilized for a few hours in a neutral phosphate buffer solution of pH 6.79, after which the C-V curve was measured and a preset capacitance value for the CONCAP method was determined. The pH was then changed stepwise in the acid or alkali direction. The response voltage was recorded by the CONCAP method for five minutes at each intermediate pH value. After the measurement at the extreme pH value of -1.90 or 15.53, the pH was stepped to the initial value of 6.79. The C-V curve was measured again and compared with the initial one. The measurements of alkali metal ion sensitivity started after the sensor was stabilized in the neutral phosphate buffer solution. The change in the response voltage was measured as a function of LiCl concentration in 0.1 M Na₂B₄O₇ solutions by the CONCAP method. All measurements were performed at 25°C in the dark.

Results and Discussion

pH response characteristics of sensors with Al_2O_3 , Ta_2O_5 and ZrO_2 single-oxide films.—The C-V curves of EIS capacitor pH sensors with Al_2O_3 , Ta_2O_5 and ZrO_2 films were measured in solutions having different pH values. As reported in a previous paper,²¹ the C-V curves of the sensors with Ta_2O_5 and ZrO_2 films shifted along with the voltage axis towards higher values with increasing solution



Figure 2. C-V curves of EIS capacitor sensor with Al_2O_3 insulator film in solutions with different pH values.

pH. There was little or no change in the maximum capacitance, $C_{\rm max}$, which corresponds to the capacitance of the oxide film. It is therefore suggested that Ta₂O₅ and ZrO₂ films do not dissolve when exposed to the test solutions listed in Table I for a short period of time. In contrast to these oxide films, Al₂O₃ films undergo dissolution when exposed to alkali solutions. Figure 2 shows the change in C-V curves with solution pH for the sensor with an Al₂O₃ film. The



Figure 3. Response voltage, V_R , as a function of solution pH for EIS capacitor sensors with Al_2O_3 , Ta_2O_5 , and ZrO_2 films.



Figure 4. Change in response voltage, ΔV_R , as a function of LiCl concentration, *x*, in 0.1 M Na₂B₄O₇ + 0-1000 mM LiCl solutions for EIS capacitor sensors with Al₂O₃, Ta₂O₅, and ZrO₂ films.

pH was changed stepwise in the alkaline direction. When the pH is increased in the range of 6.79-11.11, the C-V curve shifts to higher voltages due to pH response. The $C_{\rm max}$ value remains constant for the change in pH from 6.79 to 9.17, but increases slightly for that from 9.17 to 11.11, suggesting that dissolution of the Al₂O₃ film starts around pH 11. When the pH is increased from 11.11 to 12.47, the $C_{\rm max}$ value increases significantly. A further increase in pH has no influence on C-V characteristics. It is therefore suggested that the Al₂O₃ film dissolves away around pH 12.5, and the underlying SiO₂ film is exposed to the solutions having pH values higher than 12.5.

The response voltage, $V_{\rm R}$, which is defined as the voltage required for achieving a preset capacitance $C_{\rm ps}(=0.6C_{\rm max})$, was measured by the CONCAP method described in the experimental section. Figure 3a, b, and c show the value of $V_{\rm R}$ as a function of pH for the sensors with single oxide films of Al₂O₃, Ta₂O₅, and ZrO₂, respectively. Linear pH response ranges can be seen for all the films examined. To determine the pH response range of each sensor, we define the acidic and alkaline pH limits as the pH values at which errors due to the deviation from a linear $V_{\rm R}$ vs. pH relationship



Figure 5. C-V curves of EIS capacitor sensor with Al_2O_3 - Ta_2O_5 insulator film in solutions with different pH values.



Figure 6. Response voltage, $V_{\rm R}$, as a function of solution pH for EIS capacitor sensors with Al₂O₃-Ta₂O₅ insulator films having various Ta cationic fractions, $X_{\rm Ta}$.

exceed 0.2 pH unit. Thus determined linear pH response ranges are shown in Fig. 3. The linear pH response ranges for Ta_2O_5 (pH -2.0-11.5) and ZrO₂ (pH 0.0-12.0) are wider than that for Al₂O₃ (pH 0.5-11.0). The pH sensitivity of Ta_2O_5 (56.2 mV/pH) is higher than those of Al₂O₃ (51.5 mV/pH) and ZrO₂ (51.0 mV/pH). Among the three oxide films examined, the Ta_2O_5 film is the most promising insulator because it has a relatively wide pH response range and a high pH sensitivity. However, the alkaline pH limit for the sensor with Ta_2O_5 (pH 11.5) is comparable to that for ordinary pH-glass electrodes (pH 11-12). It is therefore required to improve pH response characteristics in alkaline solutions without deteriorating corrosion resistance.

The deviation from a linear $V_{\rm R}$ vs. pH relationship for the Al₂O₃ film in alkali solution was due to dissolution of the film. The corresponding deviation observed for Ta₂O₅ and ZrO₂ films should arise from alkali metal ion sensitivity. However, it is difficult to evaluate the magnitude of alkali metal ion sensitivity from Fig. 3, because both the Na⁺ ion concentration and pH value are changed simultaneously in the alkali solutions used for the pH response test (Table I). Therefore, alkali metal ion sensitivity was examined in mixed solutions of 0.1 M Na₂B₄O₇ and 0-1000 mM LiCl having approxi-



Figure 7. Change in response voltage, $\Delta V_{\rm R}$, as a function of LiCl concentration, *x*, in 0.1 M Na₂B₄O₇ + 0-1000 mM LiCl solutions for EIS capacitor sensors with Al₂O₃-Ta₂O₅ insulator films having various Ta cationic fractions, $X_{\rm Ta}$.

mately the same pH value (8.8-9.3). The change in the response voltage due to an increase in LiCl concentration, $\Delta V_{\rm R}$, was evaluated with respect to the $V_{\rm R}$ value measured in the solution containing no LiCl (pH 9.3). The solution containing 1 M LiCl had a low pH value (pH 8.8) compared with those containing less than 100 mM LiCl (pH 9.3), so that the $\Delta V_{\rm R}$ values measured in the former solution include the component due to pH response. This component can be evaluated from the pH sensitivity determined in Fig. 3, and then subtracted from the measured $\Delta V_{\rm R}$ value to provide the component due to the response to Li⁺ ions. Figure 4 shows thus corrected $\Delta V_{\rm R}$ values as a function of LiCl concentration for the sensors with single oxide films of Al₂O₃, Ta₂O₅, and ZrO₂. It is evident from this figure that Al₂O₃ is insensitive to Li⁺ ions around pH 9, while Ta₂O₅ and ZrO₂ are sensitive. Among the three oxides examined, Ta₂O₅ has the highest sensitivity to Li⁺ ions. These results can be explained in terms of the difference in pH_{pzc} among the three oxides. The pH_{pzc} value increases in the following order

$$\begin{split} Ta_2O_5(2.8\text{-}5.2)^{16,17,19} &< ZrO_2(5.5\text{-}8.1)^{16,17,20} \\ &< Al_2O_3(8.8\text{-}9.4)^{16\text{-}18} \end{split}$$

Because the pH_{pzc} value of Al₂O₃ is very close to the pH value of the test solution (pH 8.8 to 9.3), this oxide should have a trace amount of positively charged surface sites (MO⁻ sites in Eq. 1 and 2), at which alkali metal ions adsorb. In contrast, Ta₂O₅ has a low pH_{pzc} value and thus serves a significant amount of MO⁻ sites for

Table II. Summary of pH response characteristics for EIS capacitor pH sensors with Al₂O₃-Ta₂O₅ films.

Film composition X_{Ta}	pH sensitivity (mV/pH)	Liner pH response range ^a	Li^+ ion sensitivity ^b (mV)	Thinning rate (nm/s) ²²	
				6 M HCl	1 M NaOH
0.00 (Al ₂ O ₃)	51.5	0.5-11.0	0	2×10^{-2}	4
0.34	55.9	0-13.5	-7	3×10^{-5}	1×10^{-3}
0.63	56.8	-1.5-13.5	-18	<3 $ imes$ 10^{-6}	$8 imes 10^{-6}$
0.80	56.9	-1.5-12.5	-32	<3 $ imes$ 10^{-6}	$8 imes 10^{-6}$
$1.00 (Ta_2O_5)$	56.2	-2.0-11.5	-48	$<3 \times 10^{-6}$	8×10^{-6}

^a pH range in which measurement error is less than 0.2 pH unit.

^b Response to Li⁺ ion concentration change from 0 to 1 M at pH 8.8.



Figure 8. Response voltage, $V_{\rm R}$, as a function of solution pH for EIS capacitor sensors with Al₂O₃-ZrO₂ insulator films having various Zr cationic fractions, $X_{\rm Zr}$.

adsorption of alkali metal ions. This should be responsible for the observed high Li⁺ ion sensitivity of Ta_2O_5 . Although Li⁺ ions are normally not in sample solutions and Na⁺ and K⁺ ions cause smaller interference than Li⁺ ions,¹¹ it is feared that the sensors with Ta_2O_5 and ZrO_2 films may cause large errors in measured pH in an alkaline solution containing concentrated alkali metal ions.

pH response characteristics of sensors with Al_2O_3 - Ta_2O_5 double-oxide films.—The change in C-V curves with solution pH for the sensor with an Al_2O_3 - Ta_2O_5 film of $X_{Ta} = 0.63$ is shown in Fig. 5. The C-V curve shifts to higher voltages with increasing solution pH. The C_{max} value remains constant in the pH range of -0.49 to 13.93, indicating no dissolution of the film. The Al_2O_3 - Ta_2O_5 and Al_2O_3 - ZrO_2 films with X_{A1} values lower than 0.5 did not dissolve in the test solutions having pH-1.90-15.53. On the other hand, the films with X_{A1} values larger than 0.4 underwent dissolution in strong alkali solutions having pH values higher than 14.

Figure 6 shows the response voltage, $V_{\rm R}$, as a function of solution pH for the sensors with Al₂O₃-Ta₂O₅ films having different $X_{\rm Ta}$ values. The measured $V_{\rm R}$ values were normalized in such a way that



Figure 9. Change in response voltage, $\Delta V_{\rm R}$, as a function of LiCl concentration, *x*, in 0.1 M Na₂B₄O₇ + 0-1000 mM LiCl solutions for EIS capacitor sensors with Al₂O₃-ZrO₂ insulator films having various Zr cationic fractions, $X_{\rm Zr}$.

at pH 6.79 the $V_{\rm R}$ value of each sensor is equal to that of the sensor with pure Al₂O₃ film. The sensors with Al₂O₃-Ta₂O₅ films of $X_{\rm Ta}$ = 0.34-0.80 show wide pH response ranges. Among them, the film of $X_{\rm Ta}$ = 0.63 has the widest pH response range of pH-1.5-13.5.

Figure 7 exhibits the change in the response voltage, ΔV_R , measured as a function of LiCl concentration in 0.1 M Na₂B₄O₇ solutions for the sensors with Al₂O₃-Ta₂O₅ films. The ΔV_R value increases with increasing LiCl concentration. At a given LiCl concentration the alkali metal ion sensitivity becomes larger with increasing X_{Ta} . The sensitivity of the films with $X_{Ta} = 0.34$ -0.63 is, however, less than 7 mV in the Li⁺ concentration range of 1-100 mM. The response voltage of 7 mV leads to an error of about 0.1 in measured pH values.

The pH response characteristics of the sensors with Al₂O₃-Ta₂O₅ films are summarized in Table II, where pH sensitivity, linear pH response range, alkali ion sensitivity for 1 M Li⁺ at pH 8.8, and film thinning rates in 6 M HCl and 1 M NaOH at 25°C²² are listed. The best film composition for a wide range pH sensor is thought to be $X_{\text{Ta}} = 0.63$ because the film with this composition unites a high pH sensitivity, a wide pH response range, a low alkali metal ion sensitivity, and good corrosion resistance.

The pH sensitivity is low for the film of $X_{\text{Ta}} = 0$ (Al₂O₃), while it increases toward the Nernstian value (59.1 mV/pH at 25°C) with increasing X_{Ta} up to 0.63. According to the models developed to describe the pH response of a field-effect device sensor with an oxide insulator film, the pH sensitivity of the sensor is primarily determined by the following oxide-dependent parameters: the number of surface groups, N_s , and the equilibrium constants of disso-

Table III. Summary of pH response characteristics for EIS capacitor pH sensors with Al₂O₃-ZrO₂ films.

Film composition $X_{\rm Zr}$	pH sensitivity (mV/pH)	Liner pH response range ^a	Li ⁺ ion sensitivity ^b (mV)	Thinning rate (nm/s) ²³	
				1 M HCl	1 M NaOH
$0.00 (Al_2O_3)$	51.5	0.5-11.0	0	2×10^{-2}	4
0.37	52.7	0.0-13.5	-6	7×10^{-5}	5×10^{-3}
0.52	52.8	-1.0-13.0	-15	<3 $ imes$ 10^{-6}	3×10^{-4}
0.63	52.3	-1.5-13.0	-15	$<3 \times 10^{-6}$	$<3 \times 10^{-6}$
1.00 (ZrO ₂)	51.0	0.0-12.0	-31	<3 $ imes$ 10^{-6}	$<3 \times 10^{-6}$

^a pH range in which measurement error is less than 0.2 pH unit.

^b Response to Li⁺ ion concentration change from 0 to 1 M at pH 8.8.

ciation and protonation reactions of surface hydroxyls (MOH in Eq. 1), $K_{\rm a}$ and $K_{\rm b}$.²⁶⁻²⁸ A high pH sensitivity is achieved as the oxide has a large value of $N_{\rm s}$ or a large value of $K_{\rm a}K_{\rm b}$, which is equivalent to a small value of $\Delta p K (=pK_{\rm a} + pK_{\rm b})$.²⁶⁻²⁸ The sub-Nernstian response of the sensor with $X_{\rm Ta} = 0$ can be explained in terms of low $N_{\rm s}$ and high $\Delta p K$ values for Al₂O₃ ($N_{\rm s} = 8 \times 10^{18}$ cm⁻³, $\Delta p K = 4$)^{27,28} and a marked increase in the pH sensitivity with increasing $X_{\rm Ta}$ is attributed to the effect of Ta₂O₅ having high $N_{\rm s}$ and low $\Delta p K$ values ($N_{\rm s} = 10 \times 10^{18}$ cm⁻³, $\Delta p K = 2$).^{27,28}

pH response characteristics of sensors with Al_2O_3 - ZrO_2 double-oxide films.—Figure 8 shows the response voltage, V_R , as a function of solution pH for the sensors with Al_2O_3 - ZrO_2 films having various X_{Zr} values. The sensors with Al_2O_3 - ZrO_2 films of X_{Zr} = 0.37-0.63 show wide pH response ranges. Among them, the film with X_{Zr} = 0.63 has the widest linear response range of pH-1.5-13.0.

Figure 9 exhibits the change in the response voltage, $\Delta V_{\rm R}$, measured as a function of LiCl concentration in 0.1 M Na₂B₄O₇ solutions for the sensors with Al₂O₃-ZrO₂ films. The alkali metal ion sensitivity becomes larger with increasing $X_{\rm Zr}$. The sensitivity of the films with $X_{\rm Zr} = 0.37$ -0.63 is, however, close to that of pure Al₂O₃ in the LiCl concentration range of 1-100 mM. The use of these films as insulators should minimize errors due to alkali metal ion sensitivity.

The pH response characteristics of the sensors with Al₂O₃-ZrO₂ films are summarized in Table III, where pH sensitivity, linear pH response range, alkali ion sensitivity for 1 M Li⁺ at pH 8.8, and film thinning rates in 1 M HCl and 1 M NaOH at 25°C²³ are listed. The best composition for a wide range pH sensor is thought to be X_{Zr} = 0.63 because the film with this composition unites a high pH sensitivity, and good corrosion resistance. A comparison between the data listed in Tables II and III suggests that the linear pH response range and alkali metal ion sensitivity for the sensor with the Al₂O₃-Ta₂O₅ film of X_{Al} = 0.37 (X_{Ta} = 0.63) are comparable to those for the sensor with the Al₂O₃-Ta₂O₅ film of X_{Al} = 0.37 (X_{Ta} = 0.63) are comparable to those for the sensor with the Al₂O₃-ZrO₂ film having the same X_{Al} (X_{Zr} = 0.63). However, the former sensor has higher pH sensitivity, and the latter one better corrosion resistance against strong alkali solutions.

The results of the present study strongly suggest that the use of a double-oxide film as a pH-sensitive insulator is effective in satisfying different requirements such as high pH sensitivity, low alkali metal ion sensitivity, and high corrosion resistance, which cannot be united by using a single oxide film.

Conclusion

1. EIS capacitor pH sensors using $Al_2O_3\mbox{-}Ta_2O_5$ and $Al_2O_3\mbox{-}ZrO_2$ double-oxide films as insulator layers have been developed.

2. The sensor with the Al₂O₃-Ta₂O₅ film of $X_{Ta} = 0.63$ shows a wide pH response range of -1.5 to 13.5, a high pH sensitivity of 56.7 mV/pH and a low alkali metal ion sensitivity.

3. The sensor with the Al_2O_3 - ZrO_2 film of $X_{Ta} = 0.63$ shows a wide pH response range of -1.5 to 13.0, a high pH sensitivity of 52.3 mV/pH and a low alkali metal ion sensitivity.

4. The Al_2O_3 - Ta_2O_5 and Al_2O_3 - ZrO_2 films provide comparable pH response range and alkali metal ion sensitivity if the oxide composition is optimized, while the former film is effective in increasing pH sensitivity and the latter one effective in increasing corrosion resistance against strong alkali.

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References

- 1. P. Bergveld, Sens. Actuators B, 88, 1 (2003).
- 2. T. Matsuo and M. Esashi, Sens. Actuators, 1, 77 (1981).
- L. Bousse, H. H. Van den Vlekkert, and N. F. de Rooij, Sens. Actuators B, 2, 103 (1990).
- L. Bousse, S. Mostarshed, B. van der Schoot, and N. F. de Rooij, Sens. Actuators B, 17, 157 (1994).
- 5. T. Mikolajick, R. Kühnhold, and H. Ryssel, Sens. Actuators B, 44, 262 (1997).
- 6. L. Bousse and P. Bergveld, Sens. Actuators, 6, 65 (1984).
- 7. S. Jamasb, S. Collins, and R. L. Smith, Sens. Actuators B, 49, 146 (1998).
- 8. W. Wlodarski, P. Bergveld, and J. A. Voorthuyzen, Sens. Actuators, 9, 313 (1986).
- 9. J. A. Voorthuyzen and P. Bergveld, Sens. Actuators B, 1, 350 (1990).
- P. Gimmel, K. D. Schierbaum, W. Göpel, H. H. Van den Vlekkert, and N. F. De Rooij, Sens. Actuators B, 4, 135 (1991).
- 11. P. V. Bobrov, Yu. A. Tarantov, S. Krause, and W. Moritz, Sens. Actuators B, 3, 75 (1991).
- 12. U. Guth, W. Oelssner, and W. Vonau, Electrochim. Acta, 47, 201 (2001).
- 13. C.-P. Huang and W. Stumm, J. Colloid Interface Sci., 43, 409 (1973).
- D. E. Yates, S. Levine, and T. W. Healy, J. Chem. Soc., Faraday Trans. 1, 70, 1807 (1974).
- 15. J. A. Davis, R. O. James, and J. O. Leckie, J. Colloid Interface Sci., 63, 480 (1978).
- 16. M. A. Butler and D. S. Ginley, J. Electrochem. Soc., 125, 228 (1973).
- 17. A. K. Vijh, Appl. Phys. Commun., 13, 275 (1994).
- 18. G. Gonzalez and S. M. Saraiva, J. Dispersion Sci. Technol., 15, 123 (1994).
- 19. M. Kosmulski, *Langmuir*, **13**, 6315 (1997).
- 20. S. Ardizzone and S. Trasatti, Adv. Colloid Interface Sci., 64, 173 (1996).
- 21. F. Tamura, N. Akao, N. Hara, and K. Sugimoto, Boshoku Gijutsu, 46, 243 (1997).
- Y. Handa, N. Hada, N. Hada, and K. Sugimoto, *Dostoral Optics,* **77**, 275 (1997).
 N. Hara, S. Nagata, N. Akao, and K. Sugimoto, *J. Electrochem. Soc.*, **146**, 510 (1999).
- E. Takahashi, N. Akao, N. Hara, and K. Sugimoto, in Organic and Inorganic Coatings for Corrosion Prevention, L. Fedrizzi and P. L. Bonora, Editors, p. 299, The Institute of Metals, London (1997).
- M. J. Schöning, M. Thust, M. Müller-Veggian, P. Kordos, and H. Lüth, Sens. Actuators B. 47, 225 (1998).
- 25. M. Klein, Sens. Actuators B, 1, 354 (1990).

(1996).

- 26. L. Bousse, N. F. de Rooij, and P. Bergveld, IEEE Trans. Electron Devices, ED-30,
- 1263 (1983). 27. R. E. G. van Hal, J. C. T. Eijke, and P. Bergveld, *Sens. Actuators B*, **24/25**, 201
- (1995).
 28. R. E. G. van Hal, J. C. T. Eijkel, and P. Bergveld, *Adv. Colloid Interface Sci.*, 69, 31