Development of Wide Range EIS Capacitor pH Sensor Using Corrosion-Resistant Al_2O_3-Ta_2O_5 and Al_2O_3-ZrO_2 Thin Films as Insulator Layer

K. Sugimoto, S. Yoshida, N. Akao, and N. Hara
Department of Metallurgy, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Introduction

An EIS capacitor pH sensor has an electrolyte / insulator / semiconductor structure and the one with Ta_2O_5 or ZrO_2 as the insulator has been known as a good pH sensor for an acid - neutral pH range (1-5). In an alkaline pH range, however, the sensor has high sensitivity to alkali metal ions and shows a large error in a measured pH value. This demerit of the sensor is thought to be improved by adding Al_2O_3 to Ta_2O_5 or ZrO_2 because Al_2O_3 has low sensitivity to alkali metal ions. The objective of the present study is to develop an EIS capacitor pH sensor with a wide pH response range which covers from strong acid to strong alkali.

Experimental

A p-type Si(100) with a thermal SiO_2 film of 50 nm thickness was used as the substrate of sensor. A Ta_2O_5-Al_2O_3 or ZrO_2-Al_2O_3 layer of 100-120nm thickness was formed on the substrate by MOCVD. $Ta(OCH_3)_5$, $Zr(O\text{-}i\text{-}C_3H_7)_4$ and $Al(O\text{-}i\text{-}C_3H_7)_3$ were used as precursors for Ta_2O_5 ,ZrO_2 and Al_2O_3, respectively.

The schematic of apparatus used for pH measurement is shown in Fig. 1. Capacitance-potential curves (C-V curve) were measured using a frequency response analyzer and a potentiostat. A potential value ,V_R ,at a capacitance, $C_{0.6}$, of 60% of the maximum capacitance measured at a given pH value was used as a pH response potential. Solutions of known pH values between –2 and 15 were used as test solutions. 0.1M $Na_2B_4O_7$ solutions of pH9.3 containing 0-1000mM LiCl were used for alkali metal ion sensitivity tests.

Results and Discussion

Figure 2 shows pH response potential, V_R , as a function of solution pH for the pH sensors with Ta_2O_5-Al_2O_3 films having different Ta cationic fractions, X_{Ta}. The pH sensors with Ta_2O_5-Al_2O_3 films having X_{Ta} = 0.34 – 0.80 show a wide pH response range of –2 to 13. Alkali ion sensitivities of these sensors were 5 - 15 mV at 100mM LiCl. The best composition is X_{Ta} = 0.67 because the film with this composition has a wide pH response range, high corrosion resistance(6) and low alkali metal ion sensitivity. A pH sensor with a ZrO_2-Al_2O_3 film having a Zr cationic fraction, X_{zr}, of 0.63 also showed a wide pH response range of –2 to 12. An alkali ion sensitivity of this sensor was 20mV at 100mM LiCl. This film also has good corrosion resistance(7).

Conclusion

An EIS capacitor pH sensor with a Ta_2O_5 - Al_2O_3 film of X_{Ta} = 0.67 has a wide pH response range of –2 to 13 , a low alkali metal ion sensitivity of 5mV at 100mM LiCl, and high corrosion resistance.

References

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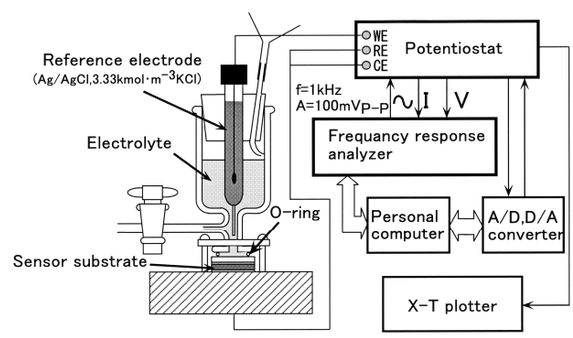

Fig. 1 Schematic of apparatus used for pH measurement.

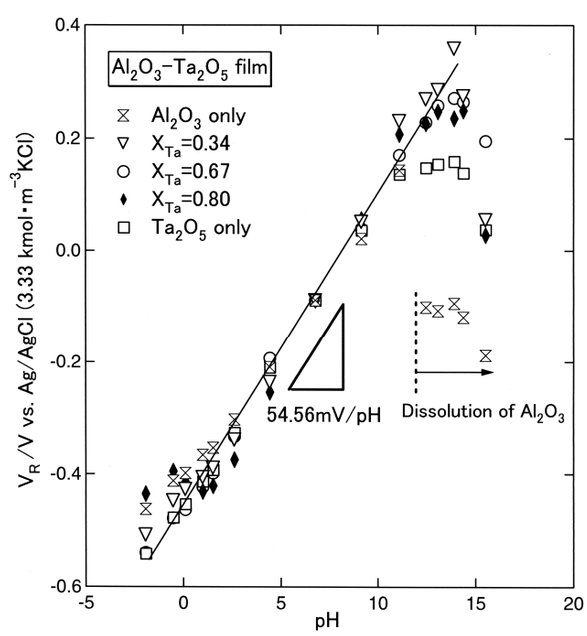

Fig. 2 pH response potential V_R as a function of solution pH for the sensors with Ta_2O_5-Al_2O_3 films.