Corrosion Resistance of Al$_2$O$_3$-ZrO$_2$ Thin Films Prepared by Ion Beam Sputter Deposition

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INTRODUCTION

Al$_2$O$_3$-ZrO$_2$ thin films prepared by metalorganic chemical vapor deposition (MOCVD) have been known to have high corrosion resistance to both acid and alkali solutions. Takahashi et al. (1) reported that the films with cationic mole fraction of Zr, X_{Zr}, of larger than 0.47 hardly dissolved in 1M HCl and those with X_{Zr} of larger than 0.63 in 1M NaOH. Taking advantage of corrosion resistance in a wide pH range, these films have been applied to the gate material of EIS capacitor pH sensor. Sugimoto et al. (2) reported that the sensor with the film of $X_{Zr} = 0.63$ could be used in a pH range of –2 to 14 under low alkali ion sensitivity. The control of composition of the films by MOCVD is, however, not easy because the control of vapor pressure and flow rate of source materials are difficult.

The objective of the present study is to prepare Al$_2$O$_3$-ZrO$_2$ thin films by ion beam sputter deposition (IBSD) and to examine the corrosion resistance of the films in 1M HCl and 1M NaOH. In IBSD, the composition of films is easily controlled by the composition of target and high quality of films is expected because the films are formed in high vacuum under no direct irradiation of plasma. The comparison of corrosion resistances between the films prepared by IBSD and MOCVD will be performed.

EXPERIMENTAL

The Al$_2$O$_3$-ZrO$_2$ thin films were prepared by an IBSD system equipped with a Kaufman-type ion source. A complex sputtering target, which was consisted of an alpha Al$_2$O$_3$ plate (99.99 mass% purity) and small ZrO$_2$ tablets (98 mass% purity), was used. In order to obtain the film with desired composition, the number of ZrO$_2$ tablets on the Al$_2$O$_3$ plate was changed. Pt plates were used as substrates for film deposition. High purity Ar gas (99.9999 vol.%) was used for the sputter source. The base pressure of vacuum chamber was 1.87×10^{-4} Pa and the working pressure was 2.07×10^{-2} Pa. The thickness of the films was adjusted to about 70 nm by monitoring using QCM during deposition.

The corrosion resistance of the films was examined in 1M HCl and 1M NaOH at 293 K. The thinning rate of film thickness was measured in-situ by ellipsometry during corrosion tests. A rotating analyzer type automatic ellipsometer was used for the measurement. The relative phase retardation and the relative amplitude reduction were measured and the thickness and optical constant of the films were calculated from these parameters using Drude's exact optical equations.

RESULTS

Figures 1 (a) and (b) show the thinning rate of film thickness as a function of X_{Zr} for the Al$_2$O$_3$-ZrO$_2$ thin films in 1M HCl and 1M NaOH, respectively. The thinning rate attains the analytical limit at $X_{Zr} = 0.65$ in 1M HCl and $X_{Zr} = 0.55$ in 1M NaOH. Therefore, the films with X_{Zr} values larger than 0.65 should show high corrosion resistance in both the solutions. The

thinning rates of films prepared by MOCVD (1) were also given in the figures. The thinning rate of the films prepared by IBSD is lower than that by MOCVD at the same composition.

REFERENCES

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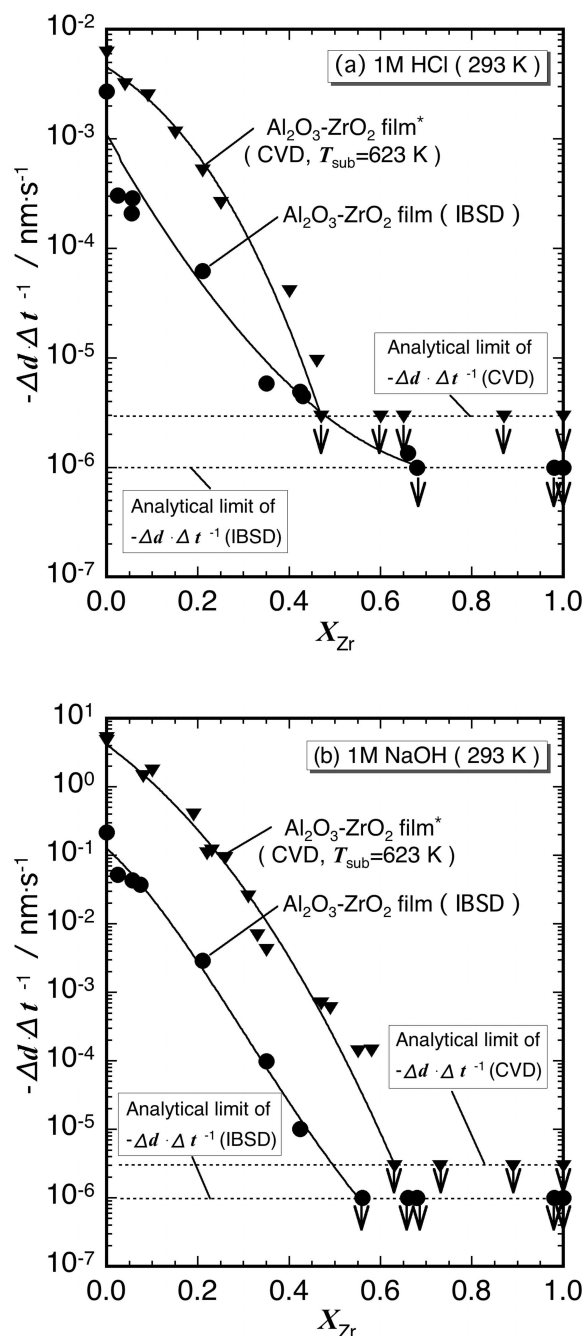

Fig. 1 Thinning rate of film thickness as a function of X_{Zr} for Al$_2$O$_3$-ZrO$_2$ thin films in 1M HCl (a) and 1M NaOH (b).