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Deposition of Thin Films of Aluminum Oxide-H_2O System from Aqueous Solutions at Room Temperature

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Abstract:
Room temperature deposition of aluminum oxide-H_2O films was attempted by dripping the $NaAlO_2$ solution to the substrate. The thin films showing interference fringes were obtained on the silicon substrate in the concentration range of 0.05-0.18 mol/l of $NaAlO_2$, in which CO_2 gas was blew into the $NaAlO_2$ solution to lower the pH from 11.7-12.7 to 10.6-11.6 beforehand. The thickness of the films was 0.05-0.15 μm, which depended on the concentration of $NaAlO_2$. The film surface consisted of small particles of 50-150 nm. The dripping was essential for the film deposition. It was deduced from the results of XRD and chemical analysis that the deposited films were amorphous aluminum oxide containing hydroxyl group. According to the IR spectrum, hydroxyl group was not detected in the films obtained from the solution with the concentration of 0.08-0.11 mol/l. Excellent adhesion was confirmed by cross cut tape test (JIS K5400), in which any piece was not peeled. Mohs hardness was measured as 4, which corresponded to that of böhmite. It is concluded that böhmite like amorphous films were deposited at room temperature, using a dripping system. This process will expected to be applicable to the surface hardening of some plastics.
Key words: thin film, böhmite, alumina, aqueous solution, sodium aluminate

1. INTRODUCTION

Thin films of aluminum oxide have been used as dielectric film, insulator, filter for ultra-violet, protection films for reflection, wear resisting films, corrosion-resisting films, etc. The thin films of aluminum oxide are prepared by sol-gel method and chemical vapor deposition (CVD) method. In the sol-gel method, alkoxide such as $Al(iso\text{-}OC_3H_7)_3$ is hydrolyzed [1]. Heating at above 500°C is inevitable to remove carbides and hydroxl group to obtain aluminum oxide films. Thermal and plasma CVD methods also need high temperatures above 1000°C [2, 3]. If aluminum oxide films were prepared at near the room temperature, excellent properties of aluminum oxide would be utilized more extensively, e.g. coating on plastics. Only one example for the room temperature preparation of aluminum oxide film is the anordic oxidation of aluminum. However, aluminum oxide film has not been deposited other substrates.

We previously obtained SiO_2 amorphous film at room temperature, using sodium silicate and hydrochloric acid [4];

$$Na_2SiO_3 + 2HCl \rightarrow SiO_2 + 2NaCl + H_2O \quad (1).$$

Generally, equation (1) produces gel-like material of $SiO_2{\cdot}nH_2O$, which contains a large amount of hydroxil group and water [5]. However, the amount of water or hydroxil group in the obtained film was very small enough to make a hard film. Dripping of the mixed solution of Na_2SiO_3 and HCl was essential to obtain the SiO_2 film. On the other hand, it is well known that böhmite ($\gamma\text{-}Al_2O_3{\cdot}H_2O$) is precipitated by blowing CO_2 into an aqueous solution of sodium aluminate [6];

$$2NaAlO_2 + CO_2 + H_2O \rightarrow Al_2O_3{\cdot}H_2O + Na_2CO_3 \quad (2).$$

In this study, our dripping technique was applied to prepare the aluminum oxide films with a small amount of water, using equation (2).

2. EXPERIMENTAL

Reagent grade $NaAlO_2$ produced by wako pure chem. Ind. Ltd. was used. The substrate used was mainly silicon wafer (10 x 20 x 1 mm^3). MgO single crystal ((100), 10 x 10 x 0.5 mm^3), polycarbonate (S300, P300, 30 x 30 x 3 mm^3) and acryl resin (MMA, 20 x 20 x 2 mm^3) were also used as substrates. The substrates were washed with methanol or acetone for 20 min.

$NaAlO_2$ was dissolved in water to make an aqueous solution with the concentration of 0.03-0.20 mol/l. The pH of the solution was controlled by blowing an air to the solution with air bubles. CO_2 in the air was used to control the pH value. The solution was then charged into a buret to drip with a rate of 0.1-5 ml/min for 4-10 h on the substrate.

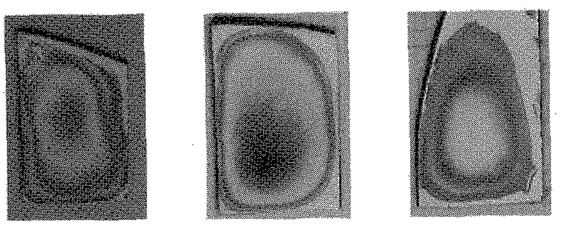
In order to confirm the presence of aluminum in the deposited films, they were dissolved in water by hydrochloric acid. Sodium hydroxide solution was added to the solution to make an alkali solution. Aluminon solution with ammonia was dripped into the solution to detect aluminum in the film.

Distribution of aluminum in the film was examined by glow discharge – optical emission spectrometry (GD-OES). Induction coupled plasma analysis was applied to analyze the aluminum quantitatively. Film thickness was measured by stylus profile measuring system (DEKTAK-3ST). The hydroxil group in the film was estimated by FT-IR. Pencil test and measurement of Mohs hardness were performed to estimate the film hardness. Adhesion test was done by cross cut tape test [7].

3. RESULTS AND DISCUSSION

3.1 Film deposition

The $NaAlO_2$ solution controlling pH at a prescribed value was dripped for 4h on the silicon substrate with a dripping rate of 0.5 ml/min. The substrate was initially repelling the drops of solution. After 20 min, wet area appeared on the substrate and it gradually spread on the substrate. The wet area was extended to all over the substrate in 1h. The dripping was continued up to 4h. The thin films showing interference fringes appeared in the concentration range of 0.05-0.18 mol/l of $NaAlO_2$ (controlled pH: 10.8-12.3), as shown in Fig. 1. Especially, homogeneous fringes were obtained in the concentration range of 0.08-0.11 mol/l, in which pH of the solution was controlled to 10.6-11.6. The films were not scraped off by microspatula. On the other hand, the film obtained by dripping for over 4 h was not homogeneous.



(a) (b) (c)

Fig.1. The films deposited at room temperature. (Flow rate; 0.5 ml/min, Substrate; Si, Concentration of $NaAlO_2$;(a):0.06 mol/l, (b):0.10 mol/l, (c):0.13 mol/l)

When the flow rate of the solution was larger than 0.5 ml/min, films were not obtained. Dip coating, spin coating and flowing the solution on the substrate did not deposit any film on the substrate. It is concluded that the dripping is essential for the film deposition.

The thin films showing interference fringes also deposited on polycarbonate and MgO substrates. However, reproducibility was not obtained in these substrates. Film was not obtained on an acryl resin. Surface modification may be required for these substrates.

The optimum conditions for the film deposition are summarized as follows; Concentration of the $NaAlO_2$ solution: 0.08-0.11 mol/l, pH before dripping: 10.6-11.6, Dripping rate: <0.5 ml/min. These films seemed to be deposited by the polymerization of $Al(OH)_3$, which was caused on the substrate by the absorption of CO_2 in the air. Further investigation is required to clarify the deposition mechanism.

3.2 Estimation of deposited film

There was no peak in the XRD patterns of the film. It was confirmed by aluminon test that the film contained aluminum. Figure 2 shows the distribution of aluminum in the film by GD-OES analysis. From these results and equation (2), the film seemed to be amorphous alumina containing hydroxyl group.

Table 1 shows the film thickness measured by stylus profile measuring system and that calculated by aluminum content in the film, assuming the film was α-Al_2O_3. The thickness increased with the increase of the concentration of $NaAlO_2$. The calculated thickness was in agreement

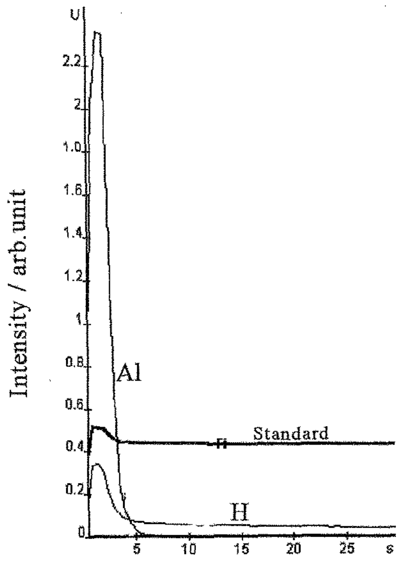


Fig.2. GD-OES depth profiles of deposited film. (Concentration:0.10 mol/l, Flow rate:0.5 ml/min)

with the thickness obtained by stylus profile measuring system up to 0.10 mol/l of $NaAlO_2$ concentration. When the $NaAlO_2$ concentration was 0.12 mol/l, the calculated thickness was different from the thickness measured by stylus profile measuring system. The amount of hydroxyl group in the films obtained with 0.06-0.10 mol/l is deduced to be small, compared to that in the film obtained with 0.12 mol/l of $NaAlO_2$.

Figure 3 shows FT-IR spectra of the films obtained

Table.1. Comparison of the film thickness measured by stylus profile measuring system and ICP

Concentration of $NaAlO_2$aq. (mol/l)		0.06	0.08	0.1	0.12
Film thickness (μm)	ICP*	0.0301	0.0585	0.121	0.179
	Stylus profile	0.0339	0.0585	0.127	0.217

* Assuming the film was α-Al_2O_3

from $NaAlO_2$ solutions with the concentrations of 0.10 mol/l and 0.12 mol/l, respectively. The absorption based on OH stretching band of the film obtained with 0.10 mol/l of $NaAlO_2$ was very small, whereas the absorption was recognized in the film obtained with 0.12 mol/l of $NaAlO_2$. It is concluded that the favorable concentrations of $NaAlO_2$ are 0.08–0.10 mol/l. This may be related to the CO_2 absorption of dripped solution.

Figure 4 shows the surfaces of the films obtained from 0.10 mol/l and 0.13 mol/l of $NaAlO_2$ solutions. The film surface obtained from 0.10 mol/l solution consisted of the grains with 50-150 nm, whereas rough surface was observed in the case of 0.13 mol/l.

Excellent adhesion was confirmed by cross cut tape test (JIS K5400), in which any piece was not peeled off.

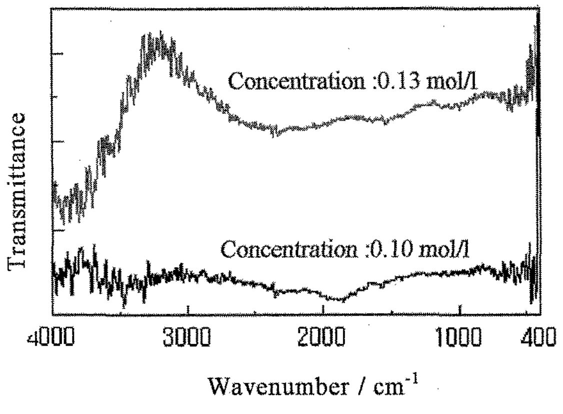
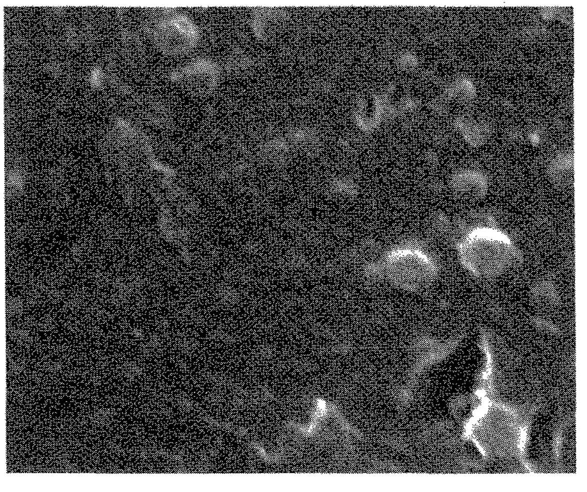
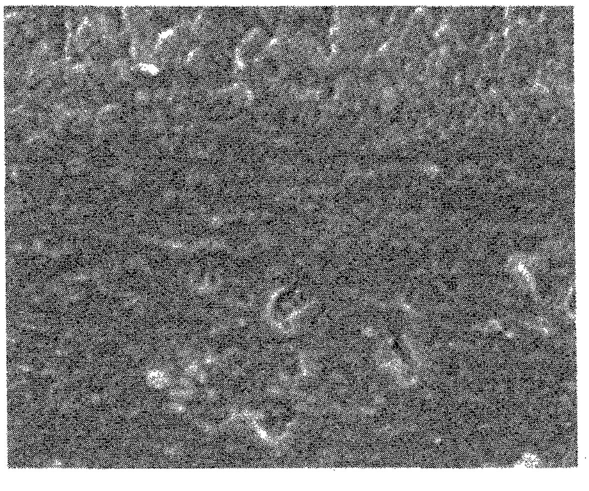


Fig.3. FT-IR spectra (Flow rate; 0.5 ml/min).



(a) Concentration:0.13 mol/l 500nm



(b) Concentration:0.10 mol/l 500nm

Fig.4. Surface of deposited films (SEM). (Flow rate; 0.5 ml/min, Substrate; Si)

Pencil test was done for the film obtained. However, the scratch was not observed even by the use of 9H. The mohs hardness was measured to be 4, which is in agreement with that of böhmite. It is concluded that böhmite like amorphous films were deposited at room temperature, using a dripping system.

4. CONCLUSIONS

In this study, the room temperature deposition of aluminum oxide-H_2O film was attempted, using aqueous solution of $NaAlO_2$. The thin films showing interference fringes were obtained on silicon substrate in the concentration range of 0.05-0.18 mol/l of $NaAlO_2$. The films consisted of homogeneous fine grains were obtained in the concentration range of 0.08-0.11 mol/l, in which pH of the solution was controlled to 10.6-11.6. The films were obtained only by dripping the solution with a rate of <0.5 ml/min. This is because the solution on the substrate needs the absorption of CO_2 in air to deposit a film. The films were also obtained on the polycarbonate and MgO substrates.

From the results of XRD and chemical analysis, the films were deduced to be amorphous aluminum oxide films containing hydroxyl group. The absorption based on OH stretch band in FT-IR spectrum was hardly observed for the film obtained from the $NaAlO_2$ solution with 0.08-0.11 mol/l. The film had an excellent adhesion. Mohs hardness of the films was 4, corresponding to that of böhmite. Therefore, it is concluded that böhmite like amorphous films were deposited at room temperature, using a dripping system.

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