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Electroless plating of aluminum using diisobutyl aluminum hydride as liquid reducing agent in room-temperature ionic liquid

Isao Shitanda*, Atsushi Sato, Masayuki Itagaki, Kunihiro Watanabe, Nobuyuki Koura

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641, Yamazaki, Noda-shi, Chiba 278-8510, Japan

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ABSTRACT

We investigated an electroless aluminum plating based on using AlCl₃–1-ethyl-3-methylimidazolium chloride (AlCl₃–EMIC) ionic liquid with diisobutyl aluminum hydride (DIBAH) as a liquid reducing agent. The plating film was analyzed by measurements of X-ray diffraction, scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX) and glow discharge optical emission spectroscopy (GD-OES). Consequently, a thick aluminum plating film with high uniformity was prepared from AlCl₃–EMIC with DIBAH. No impurity phases were detected. Moreover, we discussed the reaction mechanism of the electroless aluminum plating.

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1. Introduction

Aluminum is used for many electronic-equipment, including hard disks, compact disks, high-density memory devices, semiconductor devices, electronic circuitry [1,2] since aluminum has a superior characteristic in corrosion resistance, thermal and electric conductivity. There are many uses of aluminum thin films but it is necessary to use large reactors utilizing methods such as sputtering and glow plasma in order to deposit aluminum on an insulating substrate such as silicon or glass.

Electroless plating is potentially useful method to produce aluminum thin films and aluminum wiring at the lowest cost. If the technique for electroless plating of aluminum is established, it will be able to obtain the thin and thick film coating on the substrates of insulating material and of quite complicated structures without the use of electricity.

It is impossible to obtain electrodeposition of aluminum in an aqueous solution because aluminum is a less-noble metal. Aluminum can be deposited from a room-temperature ionic liquid (RTIL) [3–6], but a practical technology for depositing aluminum from RTIL has not been established. Recently, we developed a technique for the electroless plating of aluminum based on using AlCl₃–1-ethyl-3-methylimidazolium chloride (EMIC) ionic liquid and lithium hydride (LiH) as the electrolyte and the solid reducing agent, respectively [7]. An aluminum film was formed on a glass surface without any impurity phase. On the other hand, the plating

* Corresponding author. E-mail address: shitanda@rs.noda.tus.ac.jp (I. Shitanda). bath containing LiH was difficult to control since LiH is only slightly soluble in the plating bath and accompanied with excessive fever at the deposition reaction.

We also found a liquid reducing agent: diisobutyl aluminum hydride (DIBAH, chemical structure: Fig. 1) [7]. They mentioned that a smoother plating surface was obtained in the case of DIBAH compared with the case of LiH. However, there were no reports of the details such as plating condition, film composition and reaction mechanism.

In the present study, we investigated the aluminum electroless plating based on using DIBAH which is highly soluble in AlCl₃–EMIC ionic liquid. We verified that a dense aluminum film with smooth surface could be plated uniformly by using DIBAH. The plating bath containing DIBAH was easier to control than that containing LiH. In addition, the reaction mechanism of electroless aluminum plating with DIBAH was discussed.

2. Experimental

A glass plate and a copper sheet were used as the substrates. We pretreated the substrates by the following procedures. First, the substrate was polished with Emery paper (#320) and then washed in turn with methanol and acetone. Second, the substrate was sensitized in acidic SnCl₂ solution (0.127 mol dm⁻³, pH 0.74) for 5 min. Third, the surface of the substrate was activated in acidic PdCl₂ solution (1.69 mmol dm⁻³, pH 0.77) for 5 min. The acidity of each solution was controlled by hydrochloric acid.

The AlCl₃-1-ethyl-3-methylimidazolium chloride ionic liquid, used as the electrolyte, was synthesized with the following procedures. First, AlCl₃ and 1-ethyl-3-methylimidazolium chloride

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Fig. 1. Chemical structure of diisobutyl aluminum hydride (DIBAH).

(EMIC) were mixed by stirring. Subsequently, this ionic liquid was treated by a substitution method in which aluminum wire was immersed in the liquid for more than 1 week. The aluminum wire was used to purify the mixture containing a slight amount of H_2O . H_2O is reacted with aluminum immersed in the mixture with the evolution of H_2 , and $Al(OH)_3$ is generated on the aluminum wire surface. Therefore, H_2O can be removed in the mixture by immersion of the aluminum wire. Then, we obtained a colorless and transparent ionic liquid. Mixture of $AlCl_3$ –EMIC ionic liquid and toluene containing DIBAH was used as a plating bath. At the same time, we immersed the substrate in the electrolyte for plating aluminum. The temperature of the electrolyte was kept constant with a thermocontroller. It is noted that preparation of $AlCl_3$ –EMIC ionic liquid and the electroless plating were performed in a glove box filled with dry nitrogen gas.

The crystal structure of the deposit was investigated using X-ray diffraction (XRD, Philips X'Pert Pro, CuK α radiation). The surface morphology and elemental analysis of the deposits were performed with scanning electron microscopy (SEM, SM200, Topcon) with energy-dispersive X-ray analysis (EDX, EDAX, Genesis2000). The depth profile of the film was analyzed with a glow discharge optical emission spectroscopy (GD-OES, JY-5000RF, Horiba-Jobin Yvon).

3. Results and discussion

Fig. 2 shows the surface analysis results of a deposit on the glass substrate using the SEM-EDX. The deposit was prepared in a mixture of 66.7 mol% AlCl₃-33.3 mol% EMIC ionic liquid and toluene containing DIBAH whose volume ratio was 80:20. The mixture was used as the plating bath in the following experiments unless otherwise noted. The SEM image (Fig. 2(a)) shows that the glass substrate was covered with the deposit uniformly. A precipitate due to aluminum reduction in solution bulk was not observed in the plating solution after the experiment. Fig. 2(b) shows the aluminum mapping result by the SEM-EDX, indicating that the aluminum was deposited uniformly. The XRD pattern of the deposit on glass substrate was shown in Fig. 3. A calculated lattice constant derived from observed peaks was 4.050 Å and that showed good agreement with the reported value of aluminum in the literature [8]. These results indicated that aluminum film was formed on the substrate in the room-temperature ionic liquid with DIBAH.



Fig. 3. XRD measurement result for electroless plating of aluminum from the mixture of 66.7 mol% AlCl₃–33.3 mol% EMIC and toluene containing DIBAH whose volume ratio was 80:20. The final concentration of DIBAH was 0.2 mol dm⁻³. Substrate: glass plate; temperature: 35 °C; plating time: 6 h.



Fig. 4. GD-OES depth profile of the electroless plating of aluminum from the mixture of 66.7 mol% AlCl₃–33.3 mol% EMIC and toluene containing DIBAH whose volume ratio was 80:20. The final concentration of DIBAH was 0.2 mol dm⁻³. Substrate: copper sheet; temperature: 35 °C; plating time: 12 h. Sputtering conditions: pressure: 900 Pa; power: 45 W; anode size: 4 mm.

The depth profile of the aluminum film on the Cu substrate was investigated using the GD-OES (Fig. 4). Only aluminum was detected from the surface to the boundary between Cu substrate and the deposit by GD-OES. No impurity phases such as C, H, Cl which were contaminants in the electrolyte, were detected. On the other hand, Sn and Pd, used for sensitization and activation, were not detected by GD-OES but slight amounts of Sn and Pd were



Fig. 2. (a) SEM measurements for the aluminum plating film surface. (b) Aluminum mapping result observed by SEM-EDX at the same observed position. The plating bath was the mixture of 66.7 mol% AlCl₃–33.3 mol% EMIC and toluene containing DIBAH whose volume ratio was 80:20. The final concentration of DIBAH was 0.2 mol dm⁻³. Substrate: glass plate; temperature: 35 °C; plating time: 3 h.



Fig. 5. (a) Dependence of plating time and electrolyte temperature on the amount of the deposit and (b-e) SEM images of surface morphology of aluminum plating from the mixture of 66.7 mol% AlCl₃-33.3 mol% EMIC and toluene containing DIBAH whose volume ratio was 80:20. The final concentration of DIBAH was 0.2 mol dm⁻³. Substrate: glass plate; temperature and time: (b) 35 °C and 1 h, (c) 35 °C and 3 h, (d) 35 °C and 6 h, (e) 55 °C and 30 min, (f) 55 °C and 1 h, (g) 55 °C and 6 h, (h) 65 °C and 30 min, (i) 65 °C and 1 h, and (j) 65 °C and 6 h.

detected when the aluminum film with Cu substrate was dissolved in nitric acid and analyzed by inductively coupled plasma emission spectroscopy. Therefore, Sn and Pd were found to remain in the aluminum film. There are several factors which determine the plating rate and surface morphology for electroless plating. Some of the factors are the plating temperature, the concentration of the reducing agent, and the concentration of the metal ion in the electrolyte. We have



Fig. 6. (a) Dependence of plating time and electrolyte composition on the amount of the deposit and (b and c) SEM images of surface morphology of aluminum plating from the mixture of AlCl₃–EMIC and toluene containing DIBAH whose volume ratio was 80:20. The final concentration of DIBAH was 0.2 mol dm⁻³. Substrate: glass plate; temperature: 55 °C; plating time: 6 h. Molar ratios of AlCl₃ and EMIC were (b) 52:48 and (c) 58:42, respectively.

investigated the effects of those factors on electroless aluminum plating on the glass substrate. First, we examined the dependence of plating temperature on both the amount of deposit and the surface morphology (Fig. 5). The amount of deposit increased with plating time (immersion time of the substrate) at 35 °C and 55 °C (Fig. 5(a)). Each data point is the average value calculated from

the three independent aluminum films prepared. In addition, the amount of deposit increased during the shorter period with higher temperatures, at the beginning of the plating. It suggested that the reaction rate increased with temperature [7]. Next, we investigated the surface morphology of the electroless aluminum plating. The size of the aluminum crystal grain at the surface became larger



Fig. 7. (a) Dependence of plating time and DIBAH concentration on the amount of the deposit and (b and c) SEM images of surface morphology of aluminum plating from the mixture of 66.7 mol% AlCl₃–33.3 mol% EMIC and toluene containing DIBAH whose volume ratio was 80:20. Substrate: glass plate, temperature: 55 °C; plating time: 6 h. The final concentrations of DIBAH were (b) 0.1 mol dm⁻³ and (c) 0.3 mol dm⁻³, respectively.

with longer plating time (Fig. 5(b)–(d)) at 35 °C. The surface morphology at 65 °C (Fig. 5(h)–(j)) was smoother than that at 35 °C and 55 °C (Fig. 5(e)–(g)) because the nucleation rate of aluminum increased with temperature. On the other hand, the amount of deposit decreased at 1–3 h at 65 °C.

In the same way, we studied the dependence of the aluminum concentration in the electrolyte on the amount of the deposit and the morphology of the electroless aluminum plating (Fig. 6). The electroless aluminum platings were carried out in three different electrolytes (66.7 mol% AlCl₃-33.3 mol% EMIC, 58 mol% AlCl₃-42 mol% EMIC, 52 mol% AlCl₃-48 mol% EMIC) with DIBAH. The final concentration of DIBAH was 0.2 mol dm⁻³. The amount of the deposited aluminum increased with the increase of molar ratio of AlCl₃ (Fig. 6(a)). Substrate surfaces were covered with deposit uniformly at all samples as shown in Figs. 5(g), 6(b) and 6(c). The alminum film deposited using 58 mol% AlCl₃-42 mol% EMIC was smoother than that deposited using 66.7 mol% AlCl₃-33.3 mol% EMIC. However, the thickness of the aluminum films deposited in 58 mol% AlCl₃-42 mol% EMIC was so thin that we recognize the scratched mark on the surface of the substrate. Furthermore, we examined the dependence of the reducing agent concentration on both the amount of deposit and morphology of the electroless aluminum plating (Fig. 7). The amount of deposit at the beginning of the plating and maximum amount of the deposit were increased with increasing the reducing agent (Fig. 7(a)). The size of the crystal grains increases with the increase of the DIBAH concentration according to the comparisons among Figs. 5(g), 7(b) and 7(c).

The characteristics of the aluminum film prepared using DIBAH, shown in Fig. 5(g), were compared with those prepared using LiH [7]. The aluminum film using DIBAH was more uniform, smoother than that using LiH. In addition, preparation of the plating bath and control of temperature using the DIBAH were easier because DIBAH was readily soluble and stable in the electrolyte.

The mechanisms of the aluminum electroless plating with DIBAH were discussed. An acidic $AlCl_3-EMIC$ ionic liquid, such as 66.7 mol% $AlCl_3-33.3$ mol% EMIC, contains $Al_2Cl_7^-$ which is ionic species for aluminum deposit [9]. Aluminum was deposited from the electrolyte by following reaction:

$$4\text{Al}_2\text{Cl}_7^- + 3\text{e}^- \rightarrow 7\text{Al}\text{Cl}_4^- + \text{Al} \tag{1}$$

It was also considered that the reducing agent, DIBAH, had a reaction indicated below since a H_2 gas was evolved during the electroless plating procedure:

$$(CH_3)_2$$
-CH-CH₂-AlH-CH₂-CH-(CH₃)₂
 $\rightarrow (CH_3)_2$ -CH-CH₂-Al⁺-CH₂-CH-(CH₃)₂+(1/2)H₂+e⁻ (2)

The electroless plating reaction mechanism might be described by the combination of the electrochemical reactions, indicated with Eqs. (1) and (2).

4. Conclusion

We succeeded in demonstrating the electroless aluminum plating from AlCl₃–EMIC ionic liquid with DIBAH. SEM-EDX and XRD results indicated that the deposited film was aluminum. GD-OES results showed that the placed film consisted of aluminum only, because only aluminum was detected from the surface to the boundary between Cu substrate and the deposit. No impurity phases such as C and H, which were considered to be likely contaminates from the electrolyte, were detected. The aluminum film deposited with DIBAH was more uniform and thicker than that with LiH. Preparation of the plating bath and control of temperature using DIBAH as the reducing agent were easier. In addition, we discussed the reaction mechanism of the electroless aluminum plating. Consequently, it was proposed that the electroless plating reaction consisted of oxidation reaction of DIBAH and reduction of Al₂Cl₇⁻.

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