

# Room Temperature Electrodeposition of Flat and Smooth Aluminum Layers from An $\text{AlCl}_3$ /diglyme Bath

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## 1. Introduction

Aluminum (Al) metal is an important material due to the light-weight, workability, and corrosion resistance, and is used as various forms such as bulk, foils, films, and composites. Also, Al is an anode candidate for next-generation battery, because of its negative electrode potential and high theoretical capacity.<sup>1,2)</sup> Such properties of Al makes electrodeposition of Al a fascinating subject of research, whereas electrodeposition of Al is not possible in aqueous electrolytes. Therefore, non-aqueous media, such as fused salts, organic solvents, and ionic liquids, are employed as solvents for Al electrodeposition.<sup>1-3)</sup> While the fused salts have been used for Al electrodeposition in smelters, the latter two solvents enable the electrodeposition at room temperature (RT). The organic solvents so far reported are, however, quite volatile and flammable (*e.g.* diethyl ether and tetrahydrofuran) or solid (*e.g.* dimethyl sulfone) at RT. Ionic liquids are less volatile and less flammable materials, which can solve these problems, but their material cost is still much higher than other Al plating baths.

Recently, we published two papers on RT electrodeposition of Al using a 1:5 (by mol) mixture of  $\text{AlCl}_3$  and diglyme (G2).<sup>4,5)</sup> G2 has a boiling point of 162 °C and is much less volatile at RT than both diethyl ether and tetrahydrofuran. It is true that G2 is somewhat more volatile than ionic liquids, but the material cost is less expensive. The Al layers obtained from the  $\text{AlCl}_3$ /G2 solution were uniform, but the appearance was jet-black due to rough surface morphology. To seek relationship between the color and surface morphology, in the present work, we tried to obtain flat and smooth silver-grayish Al deposits as is common with plated metal layers.

## 2. Experimental

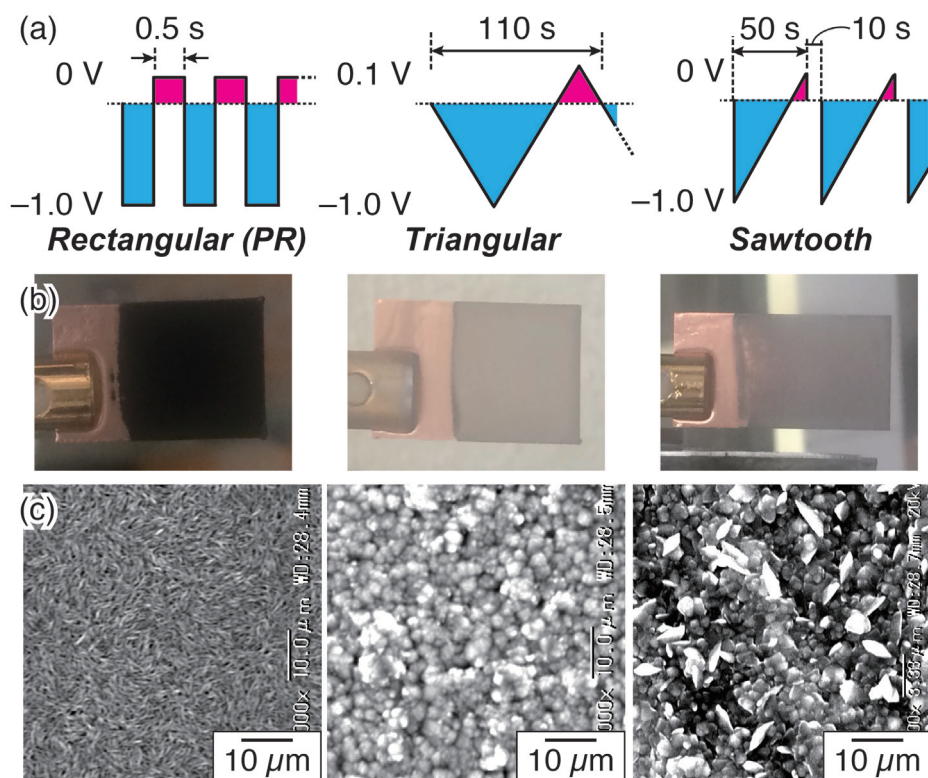
All electrochemical experiments were performed in an Ar-filled glove box. Anhydrous  $\text{AlCl}_3$  (Nippon Light Metal Company, Ltd.) was added little by little to G2 (electrochemistry grade, Kanto Chemical), which was well-dried by 3 Å molecular sieves to be less than 20 ppm  $\text{H}_2\text{O}$ , to obtain the  $\text{AlCl}_3$ /G2 (1:5 mol/mol) solution without noticeable degradation due to the heat of mixing. Cu sheet was used as a working electrode (WE), and Al sheets were used as a counter electrode (CE) and a quasi-reference electrode (QRE). The QRE was directly immersed in the same electrolyte. These electrodes were used for CV measurements after washing with acetone for 20 min.

## 3. Results and Discussion

We adopted three strategies to obtain the target Al deposit: (i) the use of additive(s), (ii) preliminary electrolysis to reduce impurities in the electrolyte, and (iii) the application of periodic potential change during electrodeposition. We tried several chemicals such as dimethylamine hydrochloride ( $\text{CH}_3)_2\text{NH}\cdot\text{HCl}$ , triethylenetetramine  $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_3\text{H}$ , and 1,10-phenanthroline, all of which have been reported as additive for Al electrodeposition from non-glyme baths.<sup>6-8)</sup> We found that dimethylamine hydrochloride with the concentration of 5  $\text{mg dm}^{-3}$  in the  $\text{AlCl}_3$ /G2 solution had an effect to improve the throwing power of the electrolyte. The preliminary electrolysis ( $-1$  V vs. Al QRE, 12 h, 3 times), which can reduce impurities in the electrolyte to make it colorless,<sup>4,5)</sup> was also found effective in promoting the nucleation and improving the smoothness of the deposits. These two strategies were, however, not enough to eliminate the black appearance. It is notable that the additive effect of dimethylamine hydrochloride on  $\text{AlCl}_3$ /G2 bath could be different from that on other Al electrodeposition baths.

Pulsed electrodeposition is widely used by the plating industry to improve the morphology (*e.g.*, finer grains).<sup>9-11)</sup> For further tuning of nucleation and subsequent grain growth through the modification of the Nernst diffusion layer, three different potential waveforms were employed as summarized in **Fig. 1**. Note that the maximal cathodic/anodic currents were the order of  $\text{mA cm}^{-2}$  in all cases. A commonly used rectangular pulse-reverse (PR) deposition (6 h) resulted in a more compact Al deposit compared to potentiostatic electrodeposition,<sup>4,5)</sup> while the appearance remained blackish (**Fig. 1b**), probably due to the flake-like surface structure as shown in SEM images (**Fig. 1c**). In contrast, a silver-grayish deposit was obtained using a triangular waveform with relatively long cathodic and anodic periods (100 cycles) as is used in cyclic voltammetry. The resulting layer was composed of compactly arranged spherical grains and the appearance was flat and smooth. We also tried a sawtooth waveform consisting of cathodic potential-step followed by a linear ramp-up toward anodic (10 cycles). The sawtooth waveform gave a mixed surface texture comprising the flake-like and spherical grains. This implies that the cathodic potential-step, by which the concentration of electrochemically active Al species *i.e.*  $[\text{AlCl}_2(\text{G}_2)_2]^+{}^{5)}$  near WE significantly decreases, is the cause of flake-like texture.

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**Fig. 1** Photographs (b) and scanning electron microscope images (c) of Al layers obtained with pulse potential waveforms (a). The potentials are in V vs. Al QRE. Note that 0 V vs. Al QRE is ca. 0.2 V positive to the equilibrium potential of  $\text{Al}^{3+}/\text{Al}$ , resulting in anodic dissolution of Al even at 0 V vs. Al QRE.<sup>4,5)</sup>

#### 4. Conclusions

Combination of bath conditions (preliminary electrolysis and additives) and electroplating conditions (pulse waveforms) gave Al layer with several appearances. While a rectangular pulse waveform gave flake-like Al grains, a triangular one gave spherical ones, resulting in flat and smooth Al layer with silver-grayish appearance.

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