



Evaluation of Key Factors for Preparing High Brightness Surfaces of Aluminum Films Electrodeposited from AlCl_3 -1-Ethyl-3-Methylimidazolium Chloride–Organic Additive Baths



Kazuma Uehara^a, Keitaro Yamazaki^a, Takao Gunji^a, Shingo Kaneko^b, Toyokazu Tanabe^a, Takeo Ohsaka^b, Futoshi Matsumoto^{a,*}

^a Department of Material and Life Chemistry, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama, Kanagawa 221-8686, Japan

^b Research Institute for Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama-shi, Kanagawa 221-8686, Japan

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ABSTRACT

The effects of additives, such as 4-pyridinecarboxylic acid hydrazide (4-PCAH) and its analogs, and organic solvents, such as toluene, benzene and xylene, on the brightness of aluminum (Al) prepared using constant-current deposition from an ionic liquid of ethyl-3-methylimidazolium chloride (EMIC)-aluminum chloride (AlCl_3) were investigated by light spectroscopy, scanning electron microscopy (SEM), reflectivity tests, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy. In order for the deposited Al films to exhibit high brightness, a combined use of 4-PCAH and toluene is effective. Moreover, the relationship between the brightness (i.e., reflectance) of the prepared Al films and the molecular structure of a variety of additives was clarified. Both a pyridine ring and an acetyl hydrazine group are necessary for constituting an effective additive. The structural isomers of a given additive bring about different surface brightness, e.g., for PCAHs the reflectance at 450 nm is in the order of *para*-isomer > *meta*-isomer > *ortho*-isomer. It was considered that in 4-PCAH electron-withdrawing acetyl hydrazine group is bounded to the pyridine ring, and consequently the electron density around the nitrogen atom in the pyridine ring is decreased, which is conducive to the adsorption of 4-PCAH on the cathode of deposited Al films. In addition, the reflectance was found to increase with decreasing the crystalline domain size of Al deposits and with increasing the reaction resistance for Al electrodeposition. The reaction mechanism of Al electrodeposition from the present ionic liquid media containing various additives is also discussed briefly.

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1. Introduction

Aluminum (Al) is the second most abundant metallic element in the Earth's crust. Al has been widely used as a coating material because Al has the ability to resist corrosion due to passivation and a high visible light reflectivity. Thin layers of Al are typically deposited onto a flat surface using physical vapor deposition [1], chemical vapor deposition [2] or hot-dip coating processes [3]. The electrochemical deposition of Al at ambient temperature in coating processes has been extensively investigated for many years, because this deposition process does not require expensive equipment and the size of the Al film deposited with a uniform thickness can be easily scaled-up or scaled-down and can be

prepared on surfaces with various shapes. Much attention has been devoted to the electrochemical deposition of Al using organic solvents [4–8] and ionic liquids [4,9–11] containing Al(III) ions to prevent a preferential hydrogen evolution in aqueous solutions. However, even in organic solvents and ionic liquids, the deposition of Al occurs with a low efficiency and the uniformness of the Al film deposited is still inadequate with poor smoothness and brightness [12]. Recently, the electrochemical deposition of smoother Al films composed of nanocrystalline deposits has been reported with several organic solvents [8] and ionic liquids [13,14], i.e., they possess high reflectance values ranging from 70 to 80% in the visible light region [15–19]. If a high deposition efficiency and a smooth Al film formation can be achieved using electrochemical deposition, Al films would be applicable to a wide range of decorative coatings and optoelectronic materials. To form smooth surface with a high deposition efficiency, in many researches [16–25], additives such as organic and inorganic molecules have

* Corresponding author. Fax: +81 45 4139770.

E-mail address: fmatsumoto@kanagawa-u.ac.jp (F. Matsumoto).

been added to the electrodeposition bath, typically polyethylene amines [16] and dimethylammonium chloride [17] in dimethylsulfone- AlCl_3 baths, 1,10-phenanthroline and nicotinic acid in ionic liquids as well as mixtures of ionic liquids and organic solvents [20–22] and also organic solvents such as toluene are added to the baths [23]. In addition, more recently, systematic studies on the additives, which are selected in the viewpoint of electron-donating or –withdrawing properties in their molecules [24] and which are alkali metal chlorides, rare earth chlorides, small organic molecules, and surfactants [25] to clarify the key factors for fabricating Al films with bright surfaces, have been carried out.

In our recent studies, we have demonstrated that the addition of 4-pyridinecarboxylic acid hydrazide (4-PCAH) to an EMIC/ AlCl_3 /toluene mixture improves the brightness of the deposited Al film [26,27]. The prepared Al films possess surface characteristics of the degree that the characters reflected on the surfaces are readable. The reflectivity of the Al film prepared in EMIC/ AlCl_3 /toluene/4-PCAH was 84% at 450 nm. To the best of our knowledge, this reflectivity is the highest reported value. In the present study, to clarify how the addition of 4-PCAH to the EMIC/ AlCl_3 /toluene bath effectively improves the brightness of electrodeposited Al films, a systematic series of organic molecules were studied as molecular additives, and based on the SEM image, reflectance, XRD profile and reaction resistance data of the films obtained by adding the individual additives, the relationship between the brightness of the prepared Al films and the molecular structure of the additives was examined and based on the results obtained, the reaction mechanism of Al electrodeposition was discussed. In this paper, the additive is defined as the organic molecules added to the EMIC/ AlCl_3 ionic liquid, although, generally, the additive is defined as the molecules that are added to the solutions by small amount. The small molecules such as 4-PCAH and its analogues and solvents such as toluene and xylene are classified in the category of additives in this study. Generally ionic liquids are known as so-called green solvents and the EMIC/ AlCl_3 ionic liquid is also considered to be environmentally benign. The addition of organic solvent to the ionic liquids produces a negative effect in the viewpoint of environment. However, as mentioned below, the addition of organic solvent is required to achieve high brightness of electrodeposited aluminum surface.

2. Experimental

The electrolytic baths were prepared by the stepwise addition of anhydrous AlCl_3 grains (0.19 mol, Fluka, crystallized, 99%; used as received) into EMIC (9.5×10^{-2} mol, Wako Pure Chemicals Co. Ltd. (Wako), 99%; used as received) at 25 °C in an argon-filled glove box (MDB-1KXV, Miwa, Japan). After mixing AlCl_3 and EMIC (molar ratio EMIC: AlCl_3 = 1: 2) for 6 h at room temperature, toluene (0.87 mol, 99.0+%, Wako) was added to the pretreated EMIC/ AlCl_3 electrolyte bath prior to the final addition of each additive (1.8 mM) at 25 °C. The detailed procedure for preparation of the bath solutions for the Al electrodeposition is described in the Electronic Supplementary Information (ESI). The following organic molecules were used as additives without further purification: 4-pyridinecarboxylic acid hydrazide (4-PCAH, 98%), 3-pyridinecarboxylic acid hydrazide (3-PCAH) and 2-pyridinecarboxylic acid hydrazide (2-PCAH) (98%, Tokyo Chemical Industry (TCI)), 4-pyridinecarboxaldehyde (4-PCA, 98%, Alfa Aesar), 3-pyridinecarboxaldehyde (3-PCA) and 2-pyridinecarboxaldehyde (2-PCA) (98%, TCI), 4-methoxypyridine (4-MP), 3-methoxypyridine (3-MP) and 2-methoxypyridine (2-MP) (97%, Wako), 4-aminopyridine (4-AP, 98%, Kanto Chemicals Co. Ltd. (Kanto)), 3-aminopyridine (3-AP) and 2-aminopyridine (2-AP) (99%, Wako), benzoyl hydrazine (BH, 98%, TCI), pyridine-4-carboxamide (P-4-CA, 99%, Junsei Chemicals Co. Ltd.), pyridine-3-carboxamide (P-3-CA, 98%, Wako), pyridine-2-

carboxamide (P-2-CA, 95%, TCI), acetyl hydrazide (AH, 98%, Kanto), acetamide (AA) and 4-pyridyl hydrazide (4-PH) (98%, TCI), 4-(aminomethyl)pyridine (4-AP) and pyridine (PY) (99.5%, TCI).

The pretreated Cu plates were served as the working electrodes. Aluminum (99.999%, $5 \times 5 \text{ cm}^2$) sheets and Al wire (99.999%, 3 cm in length, 1 mm in diameter) were used as the counter and reference electrodes, respectively. The electrochemical deposition of Al was carried out with a constant-current mode of 8.0 mA cm^{-2} using an electrochemical analyzer (Hokuto Denko, HZ-5000). The method for pretreatment of Cu plates and the procedure for the electrochemical deposition of Al are explained in the ESI.

Field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS) were used to characterize the prepared Al films (see the ESI for the FE-SEM, XRD, XPS and EIS procedures).

3. Results and discussion

3.1. Optimization of the bath composition

Fig. 1(A–F) show the micrographs of the Al film surfaces obtained by the electrodeposition of Al in the EMIC/ AlCl_3 /toluene bath containing different concentrations (0.45–3.6 mM) of the 4-PCAH additive. The EMIC/ AlCl_3 /toluene composition was fixed as mentioned in the Experimental section. A constant current density of 8.0 mA cm^{-2} and a deposition time of 2 h were used for all of the Al electrodeposition. To determine the brightness differences between the Al films, pictures were taken of the Al films on which the characters “KUKU UNIV” were reflected (upper part: Al film, lower part: printed-out characters). The visibility of the characters reflected on the Al films was considered as a measure indicating the surface brightness. As the concentration of 4-PCAH was increased, the “KUKU UNIV” characters became clearer (A–C), indicating an improvement in the surface brightness. At the concentration of 1.8 mM, the highest reflectance was observed (D). Then, the visibility decreased gradually due to the formation of yellow deposit. As can be readily seen from Fig. 1(G), the reflectance of visible light (450 nm) of the Al films indicates the similar 4-PCAH concentration dependence to that of the visibility, i.e., the reflectance increases from 69 to 78% with increasing the 4-PCAH concentration from 0.45 to 1.35 mM, and it attains its maximum (84%) at 1.8 mM and further increasing the concentration leads to a gradual decrease in the reflectance.

In Fig. 2, is shown the dependence of the reflectance of the Al films electrodeposited from EMIC/ AlCl_3 /4-PCAH bath upon the concentration of organic solvents added (i.e., toluene, benzene and xylene) in the concentration range of 4.96 to 10.79 M, in which the bath solutions containing benzene (or xylene) of 10.41 and 10.79 M could not be used as a uniform solution. Interestingly, we can see from Fig. 2 that the visibility of the characters reflected on the Al films largely depends on the organic solvent added, that is, among the solvents examined the addition of toluene brings about the significant improvement in the surface brightness and in addition, the visibility largely depends on the concentration of toluene and the highest visibility was obtained at 9.25 M. Fig. 2(E) demonstrates the dependence of the reflectance of visible light (450 nm) upon the toluene concentration. The maximum reflectance was obtained at 9.25 M. The reflectance maximum observed is considered to result from the dependence of the solution viscosity (η) and the concentration ($C(\text{Al}^{3+})$) of electroactive Al^{3+} species (Al_2Cl_7^- , mentioned below) in the bath solution on the amount of toluene added. Then η and $C(\text{Al}^{3+})$ increases and decreases, respectively, with increasing the added amount of toluene. The low ion-conductivity due to the low viscosity of the bath solution induces the deposits of the Al films at high overpotential, leading to low

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