Effect of moisture concentration on electrodeposition of aluminum in dimethylsulfone

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Abstract

The influence of moisture on Al electrodeposition was investigated in 23.3 mol% AlCl_3 -DMSO₂ bath at 403 K. Cyclic voltammetry measurement and electrodeposition at constant current were carried out in baths containing 67–174 ppm moisture. The deposits obtained under 40 mA cm⁻² for 1 h was characterized in terms of their surface appearance, surface microstructure, and cross section in SEM observation, XRD analysis and surface hardness, and film thickness (current efficiency). In addition, NMR spectroscopy was used to clarify the effect of moisture on the relative abundance of $\text{Al}(\text{DMSO}_2)_3^{3+}$ and AlCl_4^- species in the bath. When the AlCl_3 -DMSO₂ bath was kept at 403 K in the glove box, its moisture content decreased gradually up to 5 h, and increased between 6 and 72 h with the elapse of heating time. A high current efficiency of c.a. 100% was observed, the low surface hardness was improved, and the surface was uniform for Al deposits obtained after 5 and 6 h or drying when the abundance of $\text{Al}(\text{DMSO}_2)_3^{3+}$ was relatively high.

Keywords Electrodeposition · Aluminum · Nuclear magnetic resonance · Dimethylsulfone · Moisture concentration

1 Introduction

Aluminum (Al) is widely used in aircrafts, aerospace, optical, and automobile industries due to its excellent corrosion resistance and physicochemical properties. Several methods are now available to obtain Al deposits in ionic liquids [1–9], molten salts [10–12], physical vapor deposition [13, 14], chemical vapor deposition, spray coating [15, 16], cementation [17, 18], sputtering [19, 20], hot dipping [21, 22], and electrodeposition [23–25].

As Al is highly reactive ($E^\circ = -1.67$ V vs. NHE), it cannot be electrodeposited in aqueous solutions [24, 26]. In recent years, the development of ionic liquids has opened a door for the electrodeposition of Al and many other elements, such as Mg, Ti, Ta, Si, and Ge that cannot be obtained from aqueous solutions at moderate temperatures. Whereas the electrolysis of alumina used to be the only way to produce Al [27], the electrodeposition of Al and its alloys in

chloroaluminate ionic liquids, which are considered first-generation ionic liquids has been intensively studied. Also, coating methods using organic compounds such as nonaqueous solvent and ionic fluid have been examined. These compounds are nonvolatile ionic solvents: AlCl_3 -N-ethylpyridinium bromide, AlCl_3 -N-ethylpyridinium chloride, AlCl_3 -1,3-dialkylimidazolium chloride, and AlCl_3 -1-butyl-1-methyl pyrrolidinium [8, 28, 29]. Recently, these ionic liquids have been proposed as alternative electrodeposition solutions [30–32]. In comparison with ionic liquids, a lower vapor pressure, a higher electric conductivity, a wider electrochemical window, and its high flammability hinders its widespread use in many applications. To solve this problem, AlCl_3 /dimethylsulfone has been employed for electrodeposition at low temperature [33–41]. Dimethylsulfone (DMSO₂ or $(\text{CH}_3)_2\text{SO}_2$) is a non-toxic white crystalline powder with high solubility in AlCl_3 and in organic solvents such as acetone and ethyl alcohol,

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and it exhibits a low melting point of 382 K [42]. Moreover, compared to other ionic liquids and molten salts, electrodeposition in an AlCl_3 – DMSO_2 bath is an economic and straightforward technique that produces a uniform and smooth Al electrodeposit. In addition, it is possible to electroplate Al at close to 380 K in an AlCl_3 – DMSO_2 bath [42, 43]. Previous studies have clarified conditions for the electrodeposition of a dense and smooth Al film from this bath. In the AlCl_3 – DMSO_2 bath, the Al ions are present as $\text{Al}(\text{DMSO}_2)_3^{3+}$ and AlCl_4^- by the reaction of Eq. (1).

AlCl_4^- is stable in DMSO_2 bath and cannot be reduced directly to metal Al. Meanwhile, $\text{Al}(\text{DMSO}_2)_3^{3+}$ has a weaker binding force between metal and ligand than AlCl_4^- , and it is thought to be the source of the electrodeposited Al. In other words, Al electrodeposition can be written according to Eq. (2).

When using the DMSO_2 bath, it is important to control its C_m for Al electrolysis. Moisture contamination has been reported to cause reduced current efficiency, rougher surface of the electrodeposit, and increased burn area [44]. However, the detailed relationship between water concentration in the bath and its influence has not been clarified. Clarifying this relationship is important for quality control of the electrodeposited Al film.

To answer this question, in this study electrodeposition was carried out in a DMSO_2 bath with intentionally added moisture, and the appearance and microstructure of the deposit and the current efficiency were analyzed. In addition, for a bath that was dried under an inert atmosphere, the change of its moisture level over time was monitored for 72 h. Changes in the amounts of $\text{Al}(\text{DMSO}_2)_3^{3+}$ and AlCl_4^- species in the DMSO_2 baths were also evaluated by ^{27}Al NMR spectra.

2 Experimentals

2.1 Bath preparation and electrochemical measurements

Preparation of the electrolytic baths and electrochemical experiments were carried out in an argon-filled glove box (Cosmo, GBTV-065) that was equipped with a circulation system (Sinkukiko, GLD-200). A purifier was used to make the atmosphere in the glove box up to 1 PPM. (Operation under moisture/oxygen concentration 1 PPM in an inert gas atmosphere).

The electrolytic baths were prepared by stepwise addition of anhydrous AlCl_3 grains (Nacalai, crystallized, 99 mass%) into DMSO_2 (Tokyo Chemical Industry, 99 mass%). After pretreatment, the DMSO_2 powder was heated in a 100-cm³ glass beaker at 403 K to remove water by holding the powder at 333 K for at least 48 h in vacuum. Dimethyl sulfoxide ($(\text{CH}_3)_2\text{SO}$, DMSO, Nacalai, 98 mass%) and dimethyl sulfide ($(\text{CH}_3)_2\text{S}$, DMS, Nacalai, 98 mass%) were also used to confirm that DMSO_2 stably existed without decomposition in the AlCl_3 – DMSO_2 bath.

Electrochemical properties were measured in the Ar-filled glove box with a potentiostat/galvanostat (BioLogic, SP 150). Cyclic voltammetry (CV) was carried out using a Pt electrode and Pt coil as the working and counter electrodes, respectively, between -2 V and 2 V versus Al/Al^{3+} at a scan rate of 100 mV s^{-1} . An Al wire directly soaked in the electrolytic bath was used as the reference electrode. The temperature was maintained at 403 K using a hot-plate. Galvanostatic electrodeposition was performed at a current density of 40 mA cm^{-2} on a Cu plate, which was previously polished with SiC paper and then cleaned by sonication in ethanol.

A part of the plate was covered with Nitoflon insulating tape so that only an area of 1 cm^2 was exposed. During the electrodeposition process, the bath was agitated with a stirrer (As-one, FLHS-A-PRO) at 150 rpm. The distance between the Cu plate and the Al counter electrode was c.a. 14 mm.

2.2 Bath characterization

^{27}Al NMR spectra were measured at 130.3 MHz using a 500 NMR spectrometer (Agilent Technology). All chemical shifts were referenced to D_2O containing 1.5 M $\text{Al}(\text{NO}_3)_3$ as an external reference. Samples were placed in 10 mm NMR tubes with a 5-mm coaxial tube filled with $\text{DMSO}-d_6$ as a lock solvent. The temperature of DMSO_2 was kept at 403 K, the same as in the electrochemical measurements.

0.2 mL (about 0.26 g) was taken from a AlCl_3 – DMSO_2 bath immediately before electrodeposition with a syringe and charged into the Karl Fischer moisture meter, whereby the C_m in the AlCl_3 – DMSO_2 bath was measured.

As will be described later, the C_m measured by the Karl Fischer moisture meter is the total concentration of H_2O , AlOCl_2^- , and $\text{Al}(\text{OH})\text{Cl}_3^-$ but in the present paper this value of C_m is defined as H_2O . It was used as an index of concentration. In addition, the concentration of hydrogen chloride gas generated from the bath was measured using a passive deutyube (GASTECH).

2.3 characterization of deposits

After electrolysis, the deposits were characterized by means of X-ray diffraction (XRD; Rigaku Ultima IV; 40 kV–30 mA, $0.4^\circ \text{ min}^{-1}$) and field emission scanning electron microscopy (FE–SEM; NeoScope JCM–5000, JEOL), in order to check the crystal orientation and surface morphology. Before the XRD and SEM observations, the deposits were washed with AlCl_3 – DMSO_2 solution and vacuum dried.

3 Results and discussion

3.1 Stability of DMSO_2

When DMSO_2 as a solvent is reduced, DMSO and DMS are produced as shown in Fig. 1. Therefore, in addition to the AlCl_3 – DMSO_2 bath, two other baths of AlCl_3 –DMSO and AlCl_3 –DMS were prepared to confirm that DMSO_2 was chemically stable in the bath, and the electrochemical behavior was conducted.

DMSO has a high dielectric constant ($\epsilon=47$), it is difficult to oxidize and reduce, and so its potential window is wide for an organic solvent. At 403 K, when AlCl_3 is dissolved in DMSO, the bath solidified. The photograph and XRD measurement result of the coagulum are shown in Fig. 2. The XRD data confirmed that it was mainly Al_2O_3 together with some

Fig. 2 Photograph of an AlCl_3 –DMSO coagulum (a) and XRD analysis (b)

AlClO . It is considered that DMSO and AlCl_3 undergo chemical reactions as shown in Eqs. (3) and (4).

Since DMSO reacted with AlCl_3 to produce solidified Al_2O_3 , electrochemical measurements could not be made. Therefore, Al electrodeposition cannot be performed in the AlCl_3 –DMSO bath. Meanwhile, the AlCl_3 – DMSO_2 bath maintained a liquid state at 403 K, and Al precipitation is obtained by galvanostatic deposition. In other words, in the AlCl_3 – DMSO_2 bath, there seemed to be no conversion of DMSO_2 to DMSO.

When DMSO_2 is reduced and loses both of its two oxygen atoms, it becomes DMS (Fig. 1). The electrochemical behavior was also examined using AlCl_3 –DMS bath at 293 K, since the boiling point of DMS is 310.3 K. When AlCl_3 particles were dissolved in the DMS bath at room temperature, the heat of dissolution caused the solution to boil. Therefore, a separable flask filled with AlCl_3 –DMS bath was kept at 293 K by using a water bath. A pseudo reference electrode with Al wire inserted was used in the bath. CV measurement was carried out in the 23.3 mol% AlCl_3 –DMS bath, and the resulting voltammogram is shown in Fig. 3. A rise in the anodic and cathodic currents was observed at around 0.8 V. A galvanostatic electrodeposition experiment was carried out for 1 h at 40 mA cm^{-2} and 293 K. However, no Al precipitation was observed according to XRD measurement of the cathode surface afterwards. Therefore, in the AlCl_3 – DMSO_2 bath, DMSO_2 is not converted to DMS (i.e., it is considered to exist stably).

Fig. 1 Redox reactions of dimethylsulfone

Fig. 3 Cyclic voltammograms of Pt electrode in 23.3 mol% AlCl_3 -DMSO baths at 293 K

3.2 Effect of moisture in the bath

The CV measurements were performed using two baths adjusted to different C_m in order to clarify the influence of moisture on Al reactions in AlCl_3 -DMSO₂. A bath of 23.3 mol% AlCl_3 -DMSO₂ (80 mL) at 403 K was prepared and designated as bath (a). Another bath (b) was prepared by dropping 100 μL (0.13 vol%) of distilled water into bath (a). The C_m of the dried DMSO₂ was measured to be 9 ppm, and that of the bath prepared by dissolving AlCl_3 in this DMSO₂ (i.e. bath (a)) was 67 ppm. After adding distilled water, the moisture was 390 ppm in bath (b).

CV experiments were carried out in the potential range from -2 to 2 V in 23.3 mol% AlCl_3 -DMSO₂ baths at 403 K. Figure 4 shows the cyclic voltammograms recorded after

Fig. 4 Cyclic voltammograms of Pt electrode in 23.3 mol% AlCl_3 -DMSO₂ baths at 403 K. **a** 67 ppm H_2O , **b** 390 ppm H_2O

20 cycles. The shapes of the curves did not change after three cycles. It is clear that the moisture affects the CV behavior.

The open circuit potential at the beginning of the CV scan is 0.2 V in bath (a) and 1.2 V in bath (b). The main electrochemical reaction in bath (a) is Al deposition, cathodic current, and Al dissolution, anodic current, changing in around 0.2 V. On the other hand, in bath (b) the redox reaction of water becomes dominant. It is considered that a large amount of H^+ ions is reduced to hydrogen gas, corresponding to the cathodic current below 1.0 V as shown in Eq. (5).

This cathodic current of hydrogen evolution accompanied with Al deposition leads to a high current of 60 mA cm^{-2} in bath (b), in comparison to the value of 48 mA cm^{-2} in bath (a) observed at -2 V. The anodic current corresponding to Al dissolution also decreases with increased water content in the bath.

After CV measurement, the galvanostatic electrodepositions were carried out for 1 h at 40 mA cm^{-2} and 403 K. Figure 5 shows photographs of the surface of Al film obtained in bath (a) and bath (b). When moisture was added in the bath, the Al surface was blackened and became much thinner. The thickness of Al film is 45 μm in bath (a) and 10 μm in bath (b), as measured from cross-sectional SEM observation, and the current efficiencies were 90% and 19%, respectively.

Fig. 5 Surface photographs and SEM images of Al electrodeposited on Cu substrate under 40 mA cm^{-2} for 1 h in 23.3 mol% AlCl_3 -DMSO₂ at 403 K, **a** 67 ppm H_2O , **b** 390 ppm H_2O

Considering the electrolysis at 40 mA cm^{-2} for 1 h, i.e., 144 C H_2O decomposition to hydrogen gas corresponds to 117 C, 81% current efficiency of 144 C. This consumes $(144 \times 0.81)/96500 = 1.21 \text{ mmol H}_2\text{O}$ from bath (b) containing 5.56 mmol H_2O . Therefore, it is considered that the remaining 81% current was all consumed for hydrogen generation.

In addition, the influence of moisture on ionic species in the bath and on the electrodeposition of Al was estimated by NMR spectroscopy, since ^{27}Al NMR spectroscopy allows unambiguous determination of the environment of Al atoms in most cases. In the literature, several regions of the NMR spectrum have been already assigned to Al species in different environments. For example, octahedral Al can be found at chemical shifts of around 0 ppm in the ^{27}Al NMR spectra, while tetrahedral Al can be found at around 100 ppm [45, 46].

The ^{27}Al NMR spectra obtained for the two electrolytes are shown in Fig. 6. AlCl_4^- and $\text{Al}(\text{DMSO}_2)_3^{3+}$ species were formed in AlCl_3 – DMSO_2 baths at 403 K with both bath (a) and bath (b). The sulfone-solvated Al^{3+} species are generated together with AlCl_4^- [32]. Since the source of Cl^- is AlCl_3 , asymmetric cleavage of AlCl_3 forms AlCl_4^- and $\text{Al}(\text{DMSO}_2)_3^{3+}$. It was confirmed that the chemical shift of AlCl_3 – DMSO_2 at 403 K included signals of AlCl_4^- (110 ppm) and $\text{Al}(\text{DMSO}_2)_3^{3+}$ (-10 ppm). The assignments of these chemical shifts were based on the work of Legrand et al. [32] It is known that AlCl_4^- is electrochemically inactive, while Al_2Cl_7^- is active in room-temperature ionic liquids. Since the anionic species in baths (a) and (b) is AlCl_4^- , we conclude that the cationic species $\text{Al}(\text{DMSO}_2)_3^{3+}$ is electrochemically active. The NMR peak of the ionic Al complex $\text{Al}(\text{DMSO}_2)_3^{3+}$ became more intense when water was added to bath (b). The concentration ratio of $\text{Al}(\text{DMSO}_2)_3^{3+}$ is 33.7% for bath (a) and decreases to 25.5% for bath (b). This is related to the remarkable reduction in current efficiency when moisture was mixed in the AlCl_3 – DMSO_2 bath.

Fig. 6 ^{27}Al NMR spectra of 23.3 mol% AlCl_3 – DMSO_2 electrolytes and involved Al species at 403 K. **a** 67 ppm H_2O , **b** 390 ppm H_2O

3.3 Moisture change with time and influence on electrodeposition

It was confirmed that the current efficiency was reduced and a black film was formed, when much H_2O was contained in the AlCl_3 – DMSO_2 bath. Therefore, it is desirable to keep the C_m in the bath as low as possible. The experimental results mentioned above were obtained by conducting electrodeposition immediately after adding distilled water to the bath. On the other hand, in this section, the AlCl_3 – DMSO_2 bath was kept at 403 K in an argon atmosphere, where the moisture in the bath will evaporate in time. The C_m in the bath over time was monitored, and the results are shown in Fig. 7. Okamoto et al. [44] reported that baths with a C_m of about 350 ppm or more gradually dry out with the lapse of time, while those with a lower C_m accumulate moisture to approach ca. 350 ppm. In this study, when the initial bath C_m was 67 ppm, its value decreased to 61 ppm after 6 h. However, from 6 to 72 h, the C_m increased again.

In the molten salt or ionic liquid containing AlCl_3 , any H_2O present will gradually react with AlCl_4^- to form $\text{Al}(\text{OH})\text{Cl}_3^-$ and HCl according to Eq. (6). It has been reported that HCl is released from $\text{Al}(\text{OH})\text{Cl}_3^-$ to produce AlOCl_2^- , as represented in Eq. (7) [44, 47].

Hence, it is considered that chemical species of $\text{Al}(\text{OH})\text{Cl}_3^-$, AlOCl_2^- , and HCl are formed in the bath when H_2O is present. The C_m in the bath was measured by the Karl

Fig. 7 Change in moisture content of DMSO_2 baths retained at 403 K in a glove box

Fischer Coulometric titration method in this experiment, utilizing the selective and quantitative reaction between water in the sample and iodine in the Karl Fischer reagent. However, when Al(OH)Cl_3^- or AlOCl_2^- is present in the sample, these ions react with components other than iodine in the Karl Fischer reagent to release H_2O in the same amount as Al(OH)Cl_3^- or AlOCl_2^- . [44].

Chemical species other than AlOCl_2^- among H_2O , Al(OH)Cl_3^- , AlOCl_2^- and HCl which are chemical species derived from water have protons, this proton is reduced to H_2 gas may occur as a side reaction on the cathode at the time of Al electrodeposition. On the other hand, AlOCl_2^- has no possibility of being reduced in addition to being reduced to metal Al. AlOCl_2^- is a chemical species derived from H_2O , the amount of which is included in a part of the C_m measured by the Karl Fischer moisture meter. However, since AlOCl_2^- has no possibility of being reduced only to metal Al, it does not contribute to reduction in current efficiency. Although the formation rate of AlOCl_2^- is slow, it is thought that a sufficient amount of AlOCl_2^- is produced when the bath is heated and kept for 24 h or more. (The measurement of the current efficiency is shown in Fig. 10).

The reason why the C_m of the bath rose after 6 h in Fig. 7 is that the AlOCl_2^- produced by the reaction with water in the argon atmosphere was measured by the Karl Fischer moisture meter.

To investigate how the gradual drying of the AlCl_3 -DMSO₂ bath affects Al electrodeposition in it, CV experiments were carried out in the potential range from -2 to 2 V for baths that had been dried for 0–72 h at 403 K in a glove box. The voltammograms recorded after 20 time cycles are shown in Fig. 8. The shape of the curves did not change after three cycles. The electrode potential was scanned from the open-circuit potential near 0 V in the negative direction, followed by scanning in the positive direction and then cycling. In each curve, the anodic current increased at approximately 0.2 V while the cathodic current decreased at -0.6 V. Therefore, the overvoltage for Al redox reaction in the anodic and cathodic reactions was 0.1 and 0.4 V, respectively, and so the dried solution slightly influenced the Al electrodeposition process. After drying for 72 h, when the bath reached the highest C_m , the current density required for Al deposition and dissolution was the smallest. In contrast, these current densities were the largest after drying the bath for 5–6 h.

In addition, to estimate the effect of ions in the bath on the deposit component, NMR spectra was recorded for all electrolytic AlCl_3 -DMSO₂ baths after they were kept at 403 K in glove box for 0 to 72 h (Fig. 9). The results clarified that AlCl_4^- and $\text{Al(DMSO}_2)_3^{3+}$ existed in the baths, while Al_2Cl_7^- was never observed. A peak corresponding to AlCl_4^- was detected in the vicinity of 104 ppm in all baths [32]. The peak of $\text{Al(DMSO}_2)_3^{3+}$ appeared between

Fig. 8 Effect of time on cyclic voltammograms of Pt electrode in 23.3 mol% AlCl_3 -DMSO₂ baths at 403 K in glove box. Number denotes time in hour

Fig. 9 ^{27}Al NMR spectra of 23.3 mol% AlCl_3 -DMSO₂ baths with time at 403 K in glove box

-10 ppm. For $\text{Al(DMSO}_2)_3^{3+}$, which is an Al complex ion, its peak is obvious until the drying time of 6 h. However, after 6 h, this peak becomes weaker and difficult to observe in the spectra, so the proportion of ion species was

Fig. 10 Abundance of Al(DMSO₂)₃³⁺ to AlCl₄[−] from NMR spectra of 23.3 mol% AlCl₃–DMSO₂ baths with time at 403 K in glove box and Al film thickness electrodeposited at 40 mAcm^{−2} for 1 h

investigated. Figure 10 shows the relative abundance of Al(DMSO₂)₃³⁺ to AlCl₄[−] and the Al film thickness measured from cross-sectional SEM images at each drying time. The current efficiency was calculated from the amount of current flow and the film thickness. After the bath was dried for 5 h, the current efficiency (Calculated from film thickness) was as high as 120%, whereas it was significantly reduced to 74% after 72 h.

In some cases, the contributions of underlying NMR peaks could be estimated by deconvolution of peak shoulders. The ratios from the integrated areas under the assigned peaks were compared to those measured by titration, in order to cross-check the composition. The concentration of Al(DMSO₂)₃³⁺ increased with drying time until 5 h, and remained almost unchanged afterwards.

When combined with the observation that AlCl₄[−] concentration increases with drying time, this finding indicates that the decreased current observed after 12 h results from a lower Al(DMSO₂)₃³⁺ concentration, which leads to reduced Al electrodeposition. Furthermore, increased viscosity of the bath may compromise the deposition. The results show that electrodeposition of Al is optimal in the AlCl₃–DMSO₂ bath that had been dried for 5–6 h.

The galvanostatic electrodepositions were carried out at a current density of 40 mA cm^{−2} for 1 h at 403 K. The surface and cross-sectional SEM images can be seen in Figs. 11 and 12.

At 0 h (without drying), significant cracking is found on the surface of the Al film, and the cross-section Al layer is approximately 45 μm in thickness with cracks inside, which may have contributed to its poor appearance. In the samples that had been dried for 5 and 6 h, a small number of cracks can be seen even though some regions appear entirely clear. After drying for more

than 12 h, an Al film was formed, but a small amount of DMSO₂ and some cracks were found to have formed.

The XRD profiles for the deposits, shown in Fig. 13, confirmed that the deposits consisted of crystalline Al metal without trace impurities such as Al₂O₃. Here, the intensities were normalized to the height of the (200) peak of Cu substrate at 51°.

In each of these patterns, diffraction peaks related to Al (111), (200), (220), and (311) were observed. The Al (200) reflection was notably high compared to Al (111), indicating that the preferential orientation of the Al deposit changed from (111) to (200). Also, the intensity of Al (200) diffraction peak increases for samples electrodeposited from baths with low *C_m*. So, the presence of moisture in the bath probably affected the crystal orientation of the electrodeposited Al. After drying the AlCl₃–DMSO₂ bath with moisture for 6 h in the argon-filled glove box, the current efficiency of Al electrolysis was improved, and a smooth Al electrodeposition film can be obtained.

Since the *C_m* in the Al electrodepositions decreased by the drying baths, the hardness of the Al electrodepositions was expected to decrease. Figure 14 shows the Vickers hardness values of Al electrodeposits obtained after drying the bath for different amounts of time. For the bath without drying, the Al films had a hardness of 1.50 GPa, while that with low moisture contents exhibited a low hardness of 0.27 GPa.

In Al electrodeposition from an AlCl₃–DMSO₂ bath, sulfur and chlorine derived from the bath are contained in the electrodeposition film as impurities [35]. In order to investigate the effect caused by the increase in *C_m*, the impurity concentration in the electrodeposited Al film was measured using EDX as shown in Fig. 15.

Sulfur and chlorine were contained in the electrodeposition film obtained from the bath with the drying for 5 h respectively at 1.10 and 0.95 mass%. These impurity concentrations increased with the increase in the *C_m* in the bath and chlorine and sulfur concentrations of the electrodeposited film obtained from the bath with the drying for 72 h were 2.57 and 1.97 mass%, respectively.

The impurity incorporation occurs by depositing Al atoms on impurity ions or molecules adsorbed on the surface of the Al deposit [48]. In the present case, the incorporation rate is thought to be limited by the slow adsorption of the impurity ions from the electrolyte onto the Al deposit. Since Cl is present in the electrolyte as negatively charged AlCl₄[−] ions, its adsorption rate onto the cathode surface must be small and further decrease as the cathode potential becomes more negative. Therefore, the hypothesis can be made that the adsorption rate of AlCl₄[−] onto the cathode surface limits the incorporation of Cl into the Al coating.

Fig. 11 Change in SEM images of Al films electrodeposited on Cu substrate under 40 mAcm^{-2} for 1 h in 23.3 mol% AlCl_3 -DMSO₂ at 403 K with time retained in glove box

As the C_m of the bath increases, the concentration of impurities incorporated into the electrodeposited Al film increases. The contamination of impurities in the electrodeposition film in this system is due to the fact that during electrodeposition, ions or molecules containing sulfur and chlorine present in the bath adsorb to the surface of the Al electrodeposition film and Al is further electrodeposited thereon. It is believed to happen. Therefore, when the current density during electrodeposition is lowered, the concentration of impurities incorporated in the electrodeposition film increases because the deposition rate of impurities remains unchanged while the electrodeposition rate of Al decreases. In other words, the rate at which impurities adsorb onto the electrodeposited film is not affected by the water concentration in the bath and is considered to be almost constant. Therefore, it is considered

that the impurity concentration in the electrodeposited film increased with an increase in C_m .

Although the hardness of metallic materials generally depends on the crystal grain size, there was no correlation between the morphology and the hardness of the Al electrodepositions in the present case; The lowest hardness obtained in this study was only slightly higher than that for pure Al (0.23–0.29 GPa), as reported in the literature [49, 50].

4 Conclusions

In this study, the influence of C_m on Al electrodeposition from AlCl_3 -DMSO₂ bath was investigated, and the current efficiency and the appearance/fine structure of the

Fig. 12 Change in SEM images of cross-section of Al films electrodeposited on Cu substrate under 40 mAcm^{-2} for 1 h in 23.3 mol% AlCl_3 - DMSO_2 at 403 K with time retained in glove box

Fig. 13 XRD patterns of Al electrodeposited on Cu substrate under 40 mAcm^{-2} for 1 h in 23.3 mol% AlCl_3 - DMSO_2 bath with time at 403 K in glove box

obtained Al film were analyzed. In addition, we measured the change of C_m in a heated AlCl_3 - DMSO_2 bath in argon atmosphere over time, as well as the corresponding effects on the Al electrodeposition. In the AlCl_3 - DMSO_2 bath, DMSO_2 was stable without decomposition into DMSO or DMS. The hydrogen generation reaction became more significant with increased water concentration, and it competed with the Al precipitation reaction. When the AlCl_3 - DMSO_2 bath was heated and kept in the glove box, its moisture content as measured by the Karl Fischer moisture meter decreased with time. It was revealed that, after 5–6 h of drying the bath, the current efficiency of Al electrodeposition improved, and an electrodeposited film with uniform surface could be obtained. The likely reason is that both moisture in the bath and HCl produced by reaction between water and AlCl_4^- gradually evaporated under heating. Minimizing the C_m in the bath is important

Fig. 14 Vickers hardness of Al film electrodeposited on Cu substrate under 40 mAcm^{-2} for 1 h from 23.3 mol% AlCl_3 -DMSO₂ at 403 K in glove box

Fig. 15 Impurity (chlorine and sulfur) contents in Al film electrodeposited on Cu substrate under 40 mAcm^{-2} for 1 h from 23.3 mol% AlCl_3 -DMSO₂ at 403 K in glove box

for obtaining high-purity electrodeposited Al films with uniform surface at high current efficiency.

Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflict of interest.

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