



HOKKAIDO UNIVERSITY

Title	Effect of Copper Pretreatment on the Double Zincate Process of Aluminum Alloy Films
Author(s)	Azumi, Kazuhisa; Egoshi, Shinnosuke; Kawashima, Satoshi et al.
Citation	Journal of The Electrochemical Society, 154(4), D220-D226 https://doi.org/10.1149/1.2436992
Issue Date	2007
Doc URL	https://hdl.handle.net/2115/22021
Type	journal article
File Information	JECS154-4.pdf





Effect of Copper Pretreatment on the Double Zincate Process of Aluminum Alloy Films

Kazuhisa Azumi,^{a,*} Shinnosuke Egoshi,^a Satoshi Kawashima,^{b,*} and Yuuichi Koyama^b

^aGraduate School of Engineering, Hokkaido University, N13W8, Kitaku, Sapporo, 060-8628, Japan

^bMeltex Incorporated, Research and Development Department, Kitaku, Saitama 331-0031, Japan

Etching pretreatment in $\text{H}_2\text{SO}_4 + \text{CuSO}_4$ solution was applied to magnetron sputter-deposited Al–Si alloy films formed on a glass plate to improve uniformity of Zn deposition in the double zincate process. In the etching process, a small amount of Cu was deposited on the alloy surface at a very high density to accompanying Al dissolution. These deposits acted as nucleation seeds for Zn deposition, resulting in uniform, fine and thin Zn layers on Al alloys in a zincate process. This effect was more prominent on Al alloys containing 2.0 or 2.6 atom % of Si than on those containing 0 or 1.0 atom % of Si. Such a discrepancy was caused by increased Cu deposition on Al–Si alloys with relatively high Si concentration.

© 2007 The Electrochemical Society. [DOI: 10.1149/1.2436992] All rights reserved.

Manuscript submitted August 18, 2006; revised manuscript received December 5, 2006. Available electronically February 8, 2007.

Plating on Al alloys is difficult due to the presence of a strong and chemically stable surface oxide film. Double zincate pretreatment has therefore been applied to remove the oxide film and to substitute the surface of Al with a thin Zn layer for the successive plating process.^{1–6} In this process, formation of a fine and uniformly deposited Zn layer is desirable to obtain smooth and pinhole-less plating layer with sufficient adhesivity. Plating technology has been intensively developed and applied to manufacturing of electronic devices because of its suitability for fabrication of thin and small components and because of its compatibility with photolithography. For example, plating on patterned Al deposition films used for internal connection in an LSI package such as a bond pad has been intensively investigated to achieve good dimensional accuracy and strong adhesivity. In this field, various kinds of preparation methods were examined to reduce dissolution damage on thin Al films caused by typical zincate pretreatment.^{7–12} Al–Si alloys have been widely used, for example, in manufacturing of electronic devices such as a lead frame used in an LSI. Application of double zincate pretreatment to Al–Si alloys, however, sometimes resulted in nonuniform Zn deposition probably due to nonuniformity of the surface condition induced by Si atoms.¹³ For example, Golby and Dennis reported that Zn deposits preferentially around eutectic Si.¹ Many studies have been carried out in an attempt to reduce the effects of such intermetallic compounds on electroless plating by using etching treatment,¹⁴ formation of a seed layer by using a dry process,^{13,15} and other techniques. Nano particles of Cu were also examined as seeds for plating on AlN.¹⁶ In order to reduce such nonuniformity in Zn deposition, an etching pretreatment method in which Al–Si alloys are immersed in etching solution of sulfuric acid containing low concentration of Cu^{2+} ions before the double zincate process has been developed (Cu pretreatment). In this process it is presumed that Cu deposits on an Al–Si alloy to accompanying Al dissolution as a substitution reaction and deposited Cu then acts as a nucleation site for Zn deposition in the zincate process. Since Cu deposition occurs in a dispersed manner and each deposit does not grow much in an etching solution with diluted Cu^{2+} ions, it is presumed that Zn deposition occurs densely and uniformly, resulting in a suitable zincated surface for plating. However, details of experimental results and discussion of this Cu pretreatment have not yet been presented as articles. In this study, therefore, the effect of Cu pretreatment on the double zincate process of Al–Si alloys was investigated using scanning electron microscopy (SEM) observation and electrochemical measurements. We used magnetron sputter-deposited Al–Si alloy

films as specimens because the concentration of Si in the alloys can be easily changed and the effects of impurities in alloy composition other than Al and Si can be minimized.

Experimental

Three kinds of magnetron sputter-deposited Al–Si alloys of 0.5 μm in thickness were formed on glass plates.⁶ The average atomic ratios of Si in alloys were estimated to be 1.0% (described as Al–Si(1) in this paper), 2.0% [Al–Si(2)] and 2.6% [Al–Si(3)], respectively, using an electron probe microanalysis (EPMA; JEOL Co., JXA-8900). For comparison, a magnetron sputter-deposited Al film and Al plate of 99.99% in purity (Al-4N, supplied by Nippon Light Metal Co., Ltd.) were also used. The pretreatment process used in this study is summarized in Table I. Three kinds of process conditions (Exp. A–C) were used to clarify the effect of etching pretreatment in the solution with or without Cu ions. During etching and zincate processes, immersion potential of the specimen was measured using an Ag/AgCl reference electrode in the Cu pretreatment and a Zn wire reference electrode in the zincate process. After each treatment, the specimen surface was observed using a field emission scanning electron microscope (FESEM; JEOL Co., model JSM-6300F). For Cu pretreatment, the specimen was immersed in etching solution containing $6.6 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 3.15 \times 10^{-4} \text{ mol dm}^{-3} \text{ CuSO}_4$ at 332–335 K (39–42°C) for 40 s. Temperature and immersion time for Cu pretreatment suitable for Al–Si films were experimentally obtained as described in the Results and Discussion section. Some specimens were also immersed in $6.6 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution for comparison. Solutions were not stirred during experiments except for experiments in which Cu ions were added to the solution. After Cu pretreatment, specimens were immersed in zincate solution containing $0.61 \text{ mol dm}^{-3} \text{ ZnO} + 5.8 \text{ mol dm}^{-3} \text{ NaOH}$ for the first zincate process, then immersed in 50 vol % HNO_3 solution for Zn stripping, and finally immersed in the same zincate solution again for the second zincate process. Double zincate pretreatment was done at room temperature around 296 K (23°C). The immersion time for the first and second zincate processes was short (10 s) in order to reduce damage to specimens caused by dissolution of Al in the zincate process.

Results and Discussion

Determination of Cu pretreatment condition.—The surface of Al–Si alloy films dissolves in concentrated H_2SO_4 solution during Cu pretreatment at high temperature, and further dissolution occurs in a highly alkaline solution during the double zincate process. Such a process causes considerable damage to thin Al–Si films used in this study. Therefore, a more suitable condition for Cu pretreatment was examined. In Fig. 1, change in the weight of the Al–4N plate in etching solution is plotted as a function of immersion time and temperature. In the figure, dissolution depth calculated from weight loss

* Electrochemical Society Active Member.

^z E-mail: azumi@eng.hokudai.ac.jp

Table I. Experimental procedure.

Process	Solution	Condition	Exp. A	Exp. B	Exp. C
1.	Degrease	Ethanol			
2a.	Cu preparation	6.6 mol dm ⁻³ H ₂ SO ₄ + 3.15 × 10 ⁻⁴ mol dm ⁻³ CuSO ₄	o	o	o
2b.	Etching	6.6 mol dm ⁻³ H ₂ SO ₄	o	o	o
3.	First zincate	0.61 mol dm ⁻³ ZnO + 5.8 mol dm ⁻³ NaOH	o	o	o
4.	Zn stripping	50% HNO ₃	o	o	o
5.	Second zincate	0.61 mol dm ⁻³ ZnO + 5.8 mol dm ⁻³ NaOH	o	o	o

is also indicated. Dissolution depths of the Al plate at 343–345 K (70–72°C) in H₂SO₄ solution with and without Cu²⁺ ions are around 2 μm at 100 s. An induction period for initiation of dissolution, corresponding to depassivation time caused by dissolution of the oxide film on Al, was observed. At this temperature, however, the dissolution rate is too large to adjust adequate dissolution depth of Al–Si alloy films of 0.5 μm in thickness. Therefore the dissolution rate at lower temperature (333–335 K, 60–62°C) was also examined. We assumed that dissolution depth of about 0.15 μm was acceptable in this study, and 40 s of etching at 333 K (60°C) was therefore chosen for Cu pretreatment. The actual dissolution rate of Al–Si alloy films, however, differed from the results shown in Fig. 1 depending on alloy composition.

SEM images of Al–Si surface after etching.— SEM images of Al–Si alloy films and Al film etched in H₂SO₄ solution with or without Cu ions are shown in Fig. 2. A magnetron sputter-deposited film showed a considerably flat surface as was found in a previous study.¹⁷ High-contrast images after etching, however, show a slightly granular shape of the Al film surface. This granular shape is probably reflected by columnar growth of magnetron sputter-deposited film and dissolution of Al film surface makes such a structure clearer. Such dissolution traces were not obvious in Al–Si(3) alloy films and became noticeable with a decrease in Si concentration as seen on an Al–Si(1) alloy film. Cu deposits were not detected by energy dispersive spectroscopy measurement on a Cu-prepared surface, and surface concentration of Cu was thus considerably low. A cyclic voltammogram obtained after Cu preparation showed that deposited Cu was about 3.2 ng cm⁻² for the Al–Si(3) alloy film, i.e., 0.0036 nm in thickness assuming uniform deposition. Cu ions are supplied under the condition of diffusion limit at a very low concentration and thus Cu deposits remained very small in size and were widely dispersed. Results of further analysis of Cu deposition in Cu preparation will be reported in the near future.

Immersion potential during Cu pretreatment.— Immersion potential, E_{im} , of the Al film and Al–Si alloy films during the etching process was measured to determine their electrochemical properties as shown in Fig. 3. In H₂SO₄ solution [Fig. 3a and b], H₂ gas evolution was observed after some immersion time and thus E_{im} is interpreted as a mixed potential of Al dissolution (anodic reaction) and H₂ gas evolution (cathodic reaction). E_{im} shifted in the less-noble direction and then reached around –1 V. Transition of E_{im} tends to be fast with increase in concentration of Si in the alloy films. The E_{im} curve of the Al–4N plate shows different behavior and is explained by preactivation of the surface for electrochemical reaction due to a small amount of elements added to improve the etching property, as discussed later. In Fig. 3c and d, E_{im} shifted in the negative direction and then moved in the noble direction during Cu pretreatment. The transition of E_{im} also became fast with increase in concentration of Si in the alloys. The steady-state E_{im} measured for alloy films during Cu pretreatment depended on concentration of Si and was more noble than that during H₂SO₄ etching. H₂ gas evolution was also obvious in this solution compared with that in H₂SO₄ solution.

From these results the electrochemical property of Cu-prepared Al–Si alloys is explained by the model described in Fig. 4. In etching solutions, dissolution of the surface oxide film is accompanied by a gradual increase in oxidation rate of the Al substrate, i.e.,

reformation of oxide or hydroxide and / or dissolution of Al through these states. In this stage, E_{im} shifts in the less-noble direction. H₂ gas evolution also becomes obvious with decrease in electrode potential. A considerably less-noble value of E_{im} in a steady state condition such as ~–1 V in H₂SO₄ solution indicates less activity of the surface for H₂ gas evolution reaction. Al is a less-noble metal and its surface is thus easily oxidized to be covered with a thin hydroxide layer in aqueous solution. Elemental processes of electrochemical reaction such as electron transfer and recombination of discharged H atoms to form H₂ molecule therefore cannot occur efficiently. On the other hand, in the Cu pretreatment process, a decrease in E_{im} causes not only H₂ gas evolution but also Cu deposition on the surface. Since the activity level of Cu as an electrochemical catalyst is considerably higher than that of Al, a small amount of Cu deposition on Al dramatically increases the reaction rate of the electrochemical process on the Al surface. A relatively noble value of E_{im} in a steady state in Cu pretreatment indicates that electrons formed by the Al dissolution reaction effectively transfer to protons to form H₂ gas on Cu deposits even with smaller overpotential. A relatively noble steady state potential also accelerates dissolution of the Al substrate. As a result, H₂ gas evolution and Al dissolution become noticeable in the etching solution containing Cu ions. For example, Al alloy films almost completely dissolved after about 300 s in Cu pretreatment solution but remained even after 400 s in H₂SO₄ solution.

The dissolution rate of Al films is considerably slower than that of the Al–4N plate shown in Fig. 1. This discrepancy is also explained by the difference in electrochemical activity of these materials. E_{im} of Al–4N shown in Fig. 3 is considerably noble compared with that of other specimens. Al–4N supplied by a company contains small amounts of other elements such as Cu and Pd, which improve

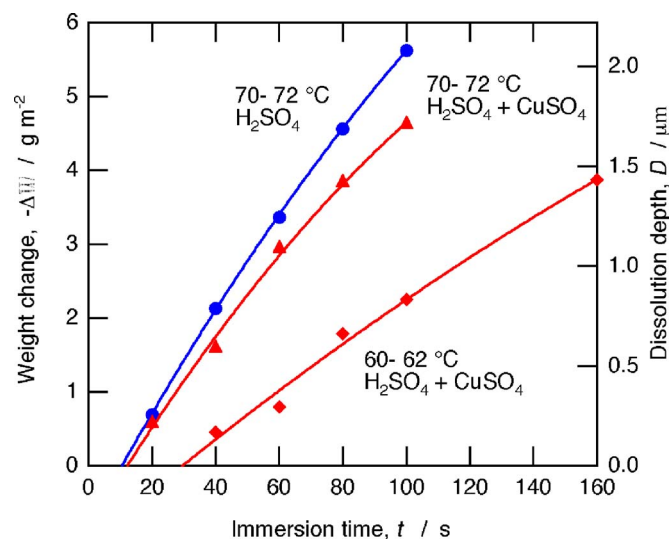


Figure 1. (Color online) Change in weight loss of Al plate (99.99% in purity, 0.3 mm in thickness) in (a) 6.6 mol dm⁻³ H₂SO₄ solution at 70–72°C, (b) 6.6 mol dm⁻³ H₂SO₄ + 3.15 × 10⁻⁴ mol dm⁻³ CuSO₄ solution at 70–72°C, and (c) 6.6 mol dm⁻³ H₂SO₄ + 3.15 × 10⁻⁴ mol dm⁻³ CuSO₄ solution at 60–62°C.

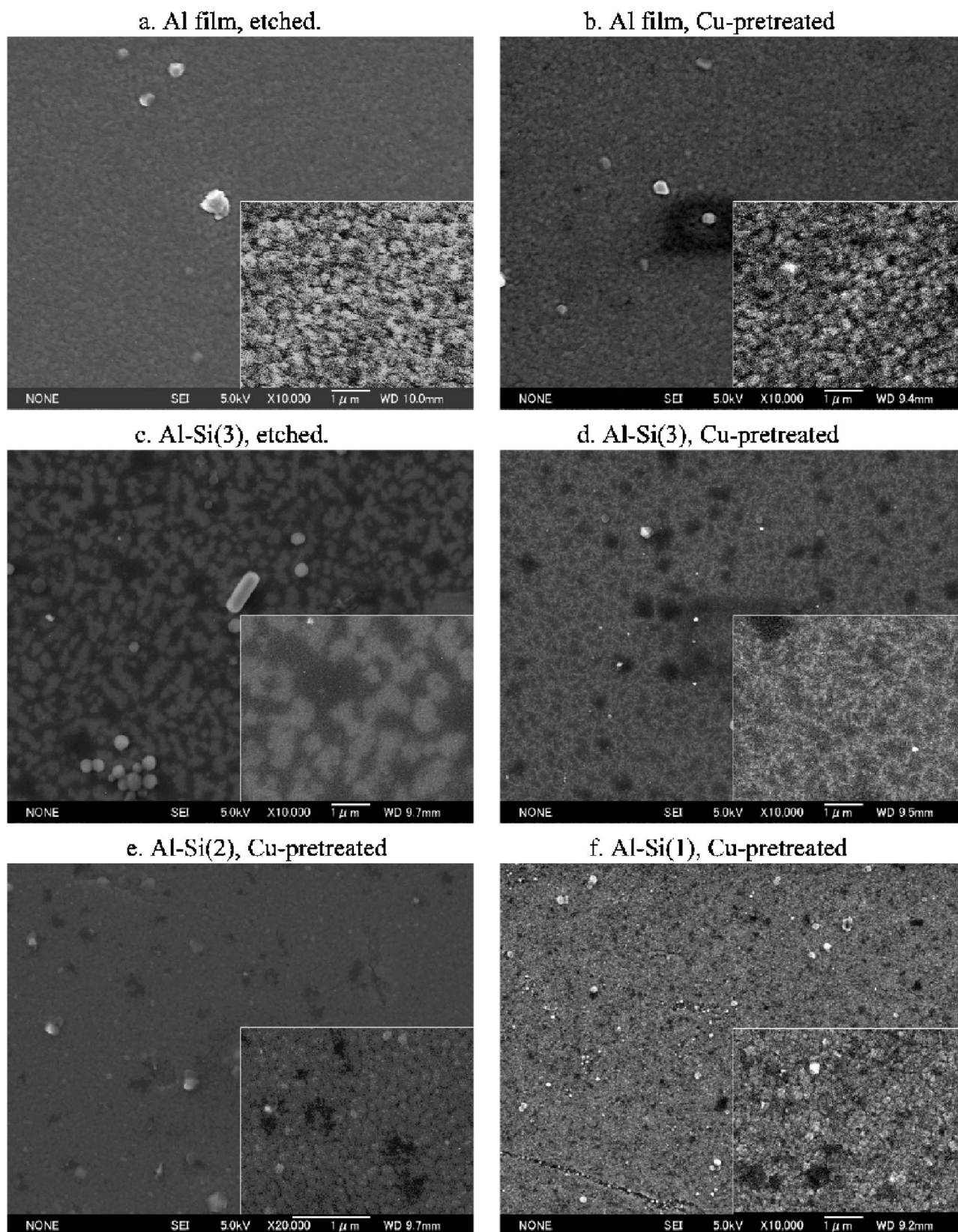


Figure 2. FESEM images of an Al film (a,b) and Al-Si(3) (c,d), Al-Si(2) (e) and Al-Si(1) (f) films after pretreatment in (a,c) $6.6 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution and (b,d,e,f) in $6.6 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 3.15 \times 10^{-4} \text{ mol dm}^{-3} \text{ CuSO}_4$ solution. Magnified (x4) image with enhanced contrast of each surface is superimposed at the lower-right position of each image.

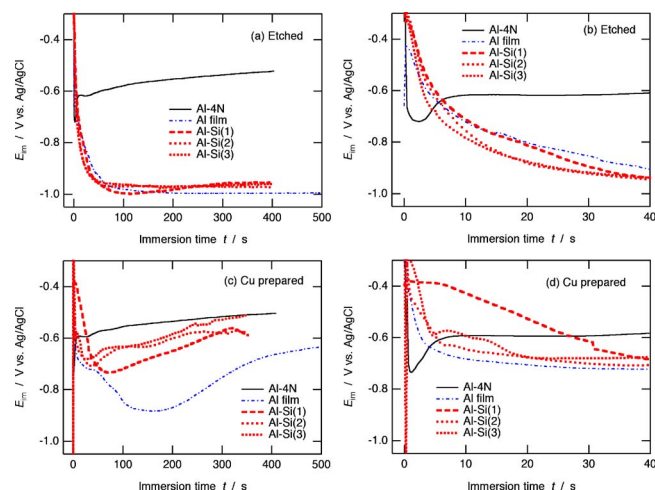


Figure 3. (Color online) Changes in immersion potential of various specimens in (a,b) $6.6 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution and (c,d) in $6.6 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 3.15 \times 10^{-4} \text{ mol dm}^{-3} \text{ CuSO}_4$ solution. (b,d) Expansion of initial stage of figures a,c.

the etching property of this material. Electrochemical activity of these additives is considerably higher than that of Al and thus they act as effective catalytic sites even if their concentrations are low. As a result, a higher anodic Al dissolution current can couple with H_2 gas evolution at lower overpotential. It was also reported that activity of Al-0.5% Cu alloy in etching process was considerably higher than that of Al-2% Si¹⁰ and was explained by higher electrochemical activity of Cu than that of Si for cathodic reaction, as discussed here.

The effect of Cu deposition depends on the concentration of Si in Al-Si alloy films. Figure 5 shows changes in E_{im} of the Al film [Fig. 5a] and Al-Si(3) alloy film [Fig. 5b] with addition of Cu^{2+} ions to H_2SO_4 etching solution as a function of concentration of Cu^{2+} ions. In the case of an Al-Si(3) alloy film, addition of Cu^{2+} ions of more than $1.57 \times 10^{-4} \text{ mol dm}^{-3}$ caused an immediate potential shift in the noble direction corresponding to Cu deposition, which increased electrochemical activity. Even addition of Cu^{2+} ions less than $0.315 \times 10^{-4} \text{ mol dm}^{-3}$ caused a potential shift after ~ 20 s of addition. Addition of Cu^{2+} ions at $0.315 \times 10^{-4} \text{ mol dm}^{-3}$ also affected E_{im} of the Al film, although its behavior is rather complicated as seen in Fig. 5a. After addition of Cu^{2+} ions, E_{im} shifted in the noble direction followed by temporary movement in the less-noble direction and then moved in the noble direction again. Although the origin of this behavior is not yet completely understood at the present time, electrochemical activation of the Al film is not prominent compared with that of the Al-Si(3) alloy. For example, addition

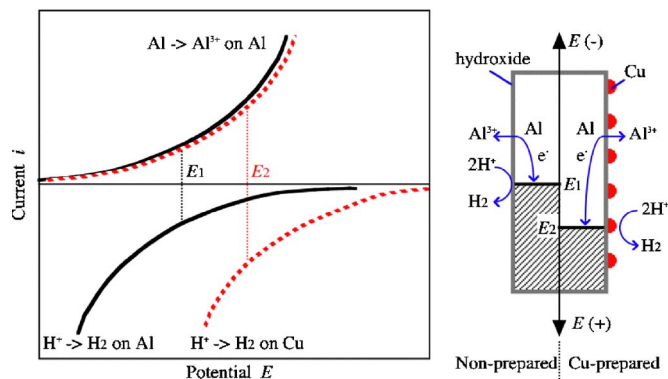


Figure 4. (Color online) Schematic representation of mixed potential of Al alloy during the etching process (E_1) and Cu preparation process (E_2).

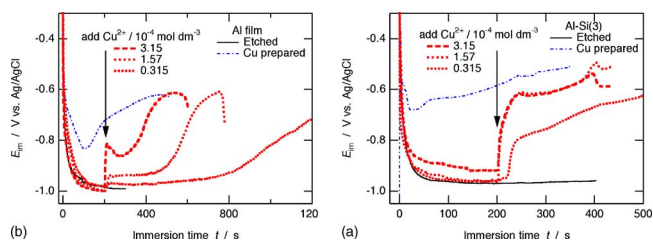


Figure 5. (Color online) Changes in immersion potential of (a) an Al film and (b) an Al-Si(3) film in $6.6 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution. CuSO_4 was added at 200 s to be 0.315 , 1.57 or $3.15 \times 10^{-4} \text{ mol dm}^{-3}$.

of $1.57 \times 10^{-4} \text{ mol dm}^{-3} \text{ Cu}^{2+}$ ions resulted in a potential shift in the noble direction with a long delay time (~ 300 s). This result indicates that deposition of Cu on an Al film does not occur efficiently compared with that on an Al-Si(3) alloy film. A comparison of E_{im} traces of Al-Si(3) in Fig. 3c and Fig. 5a shows that a shift in E_{im} in the noble direction occurred immediately after addition of Cu^{2+} in the latter, whereas the potential shift occurred after a few tenths of seconds in the former, in which Cu^{2+} ions were already contained. Furthermore, the delay time became shorter for the Al-Si alloy with increase in Si concentration. This means that Cu deposition is promoted by the existence of Si. For example, enrichment of Si on an alloy surface during etching may prevent growth of Al hydroxide on the surface and thus maintain rapid electron transfer to Cu^{2+} ions.

SEM images of Al-Si alloy films after double zincate process.— Figure 6 shows SEM images of Al and Al-Si(3) alloy films after double zincate pretreatment following etching in H_2SO_4 solution for comparison with the effect of Cu pretreatment. For both specimens, Zn was deposited in particulate form during the first and second zincate processes. As previously reported,¹⁷ such deposition is not only unsuitable for the following plating process but also a cause of damage to the films due to continuous dissolution beneath the Zn deposits.

Figure 7 shows SEM images of the Al film and Al-Si alloy films after the double zincate process following Cu pretreatment. For the Al film [Fig. 7a and b] and Al-Si(1) alloy film [Fig. 7c and d], Zn was deposited in particulate form in both the first and second zincate

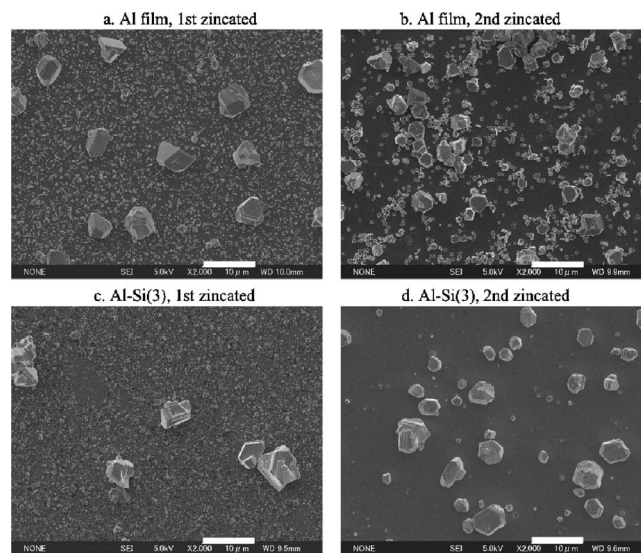


Figure 6. FESEM images of (a,b) an Al film and (c,d) Al-Si(3) films pretreated in 50 wt % H_2SO_4 solution after (a,c) the first zincate process and (b,d) the second zincate process.

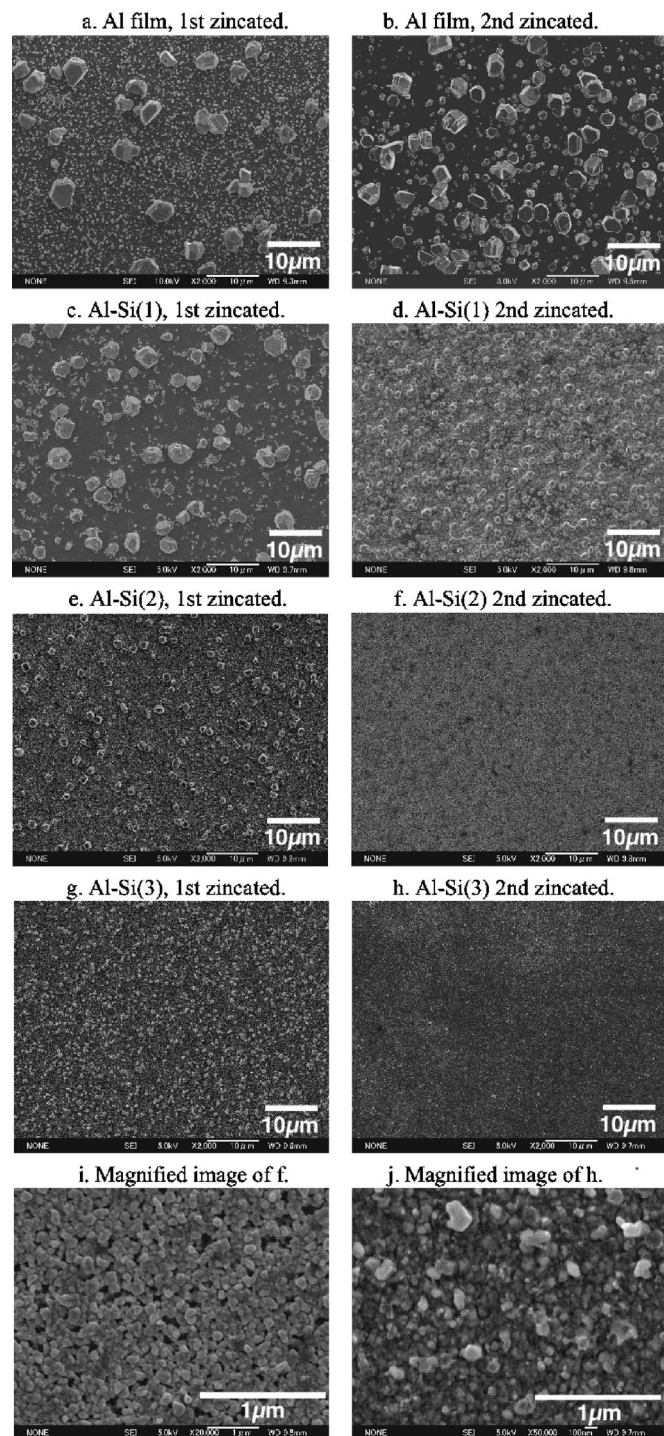


Figure 7. FE-SEM images of (a,b) an Al film and (c,d) Al-Si(1), (e,f) Al-Si(2) and (g,h) Al-Si(3) alloy films after (a,c,e,g) the first zincate process and (b,d,f,h) the second zincate process following Cu preparation. (i,j) Magnified FE-SEM images of (f) Al-Si(2) and (h) Al-Si(3) films after the second zincate process.

processes. On the other hand, Al-Si(2) [Fig. 7e and f] and Al-Si(3) [Fig. 7g and h] alloy films showed fine Zn deposits, particularly in the second zincate process. This was confirmed by magnified images of Al-Si(3) alloy surface shown in Figs. 7i and j. Such a surface covered with uniform and fine Zn deposits is suitable for the following plating process. Furthermore, a comparison of Zn-stripped surfaces of the Al film and Al-Si(3) alloy film after the second zincate process shown in Fig. 8 indicates that the surface of the Al-Si(3)

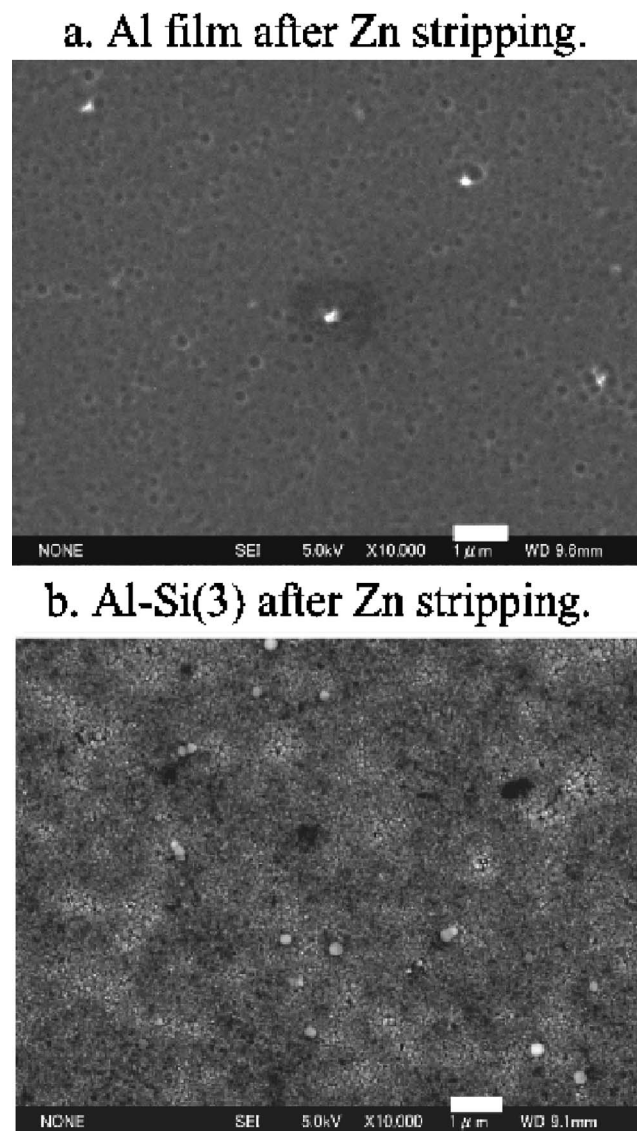


Figure 8. FESEM images of (a) an Al film and (b) an Al-Si(3) film after Zn stripping in 50 vol % HNO₃ solution after the first zincate process.

substrate beneath Zn deposition did not show dissolution pits which were observed on the Al-film substrate due to continuous alkaline dissolution.

Immersion potential during zincate process.—Figure 9 shows changes in E_{im} of various specimens during the first and second zincate processes measured for specimens etched in H₂SO₄ solution or Cu pretreated. The results for the Al film etched in H₂SO₄ solution [Fig. 9a] were almost the same as the results for a nonetched Al film previously reported.¹⁷ Transition of E_{im} during the double zincate process was explained by the mixed potential of Al dissolution (anode) and Zn deposition (cathode).⁶ Changes in anode and cathode areas during the zincate process resulted in a temporary potential shift in the less-noble direction followed by a steady state potential near the Zn reference electrode when most of the surface was covered with Zn deposition. In the case of an Al film [Fig. 9a and b], the continuance of potential shift in the less-noble direction for a few tenths of seconds in the first and second zincate processes indicates continuous dissolution of the Al substrate,¹⁷ even if the Al film specimen was subjected to Cu pretreatment. Al-Si alloy films etched in H₂SO₄ solution [Fig. 9c, e and g] also show continuance in potential shift of E_{im} in both the first and second zincate processes,

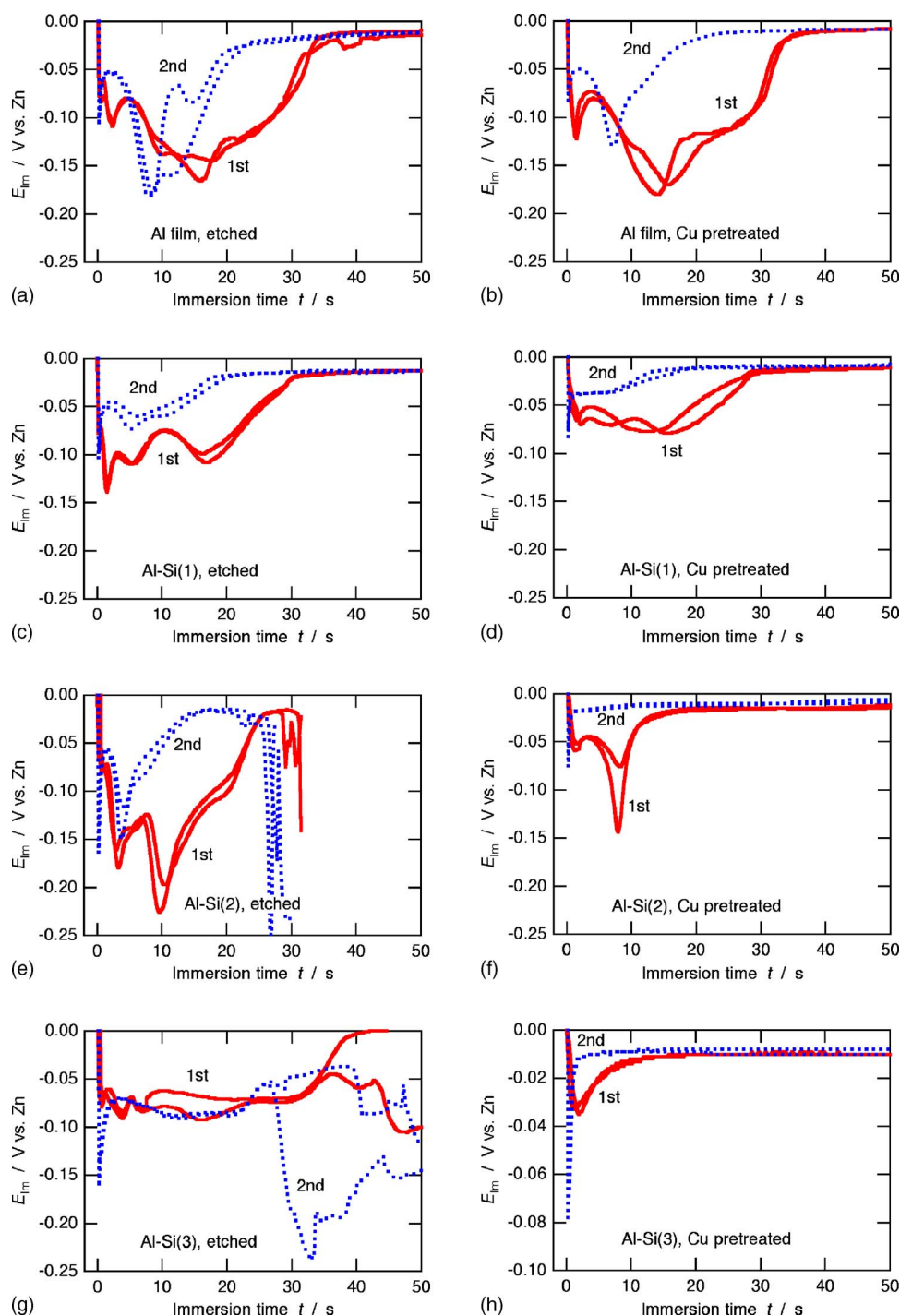


Figure 9. (Color online) Changes in immersion potential of (a,b) an Al film and (c,d) Al-Si(1), (e,f) Al-Si(2), and (g,h) Al-Si(3) alloy films during the first and second zincate pretreatments. Specimens were etched in (a,c,e,g) $6.6 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and (b,d,f,h) $6.6 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 3.15 \times 10^{-4} \text{ mol dm}^{-3} \text{ CuSO}_4$ solutions. Data of second zincate process were obtained for the specimen prepared by the first zincate process for 10 s followed by Zn stripping for 30 s.

although their potential range and behavior are different. This confirms that Al in Al-Si alloy films dissolved continuously during the first and second zincate processes. Unstable behavior of E_{imm} after ~ 25 s of immersion found for the Al-Si(2) alloy film was caused by dissolution out of the film in zincate solution [Fig. 9e]. Low-reproducible behavior of E_{imm} was also found in the Al-Si(3) alloy film after ~ 30 s [Fig. 9g]. It is possible that excess dissolution caused uncertain electric connection of the thin alloy film beneath Zn deposits. When Al-Si alloy films were subjected to Cu pretreatment, the transition of E_{imm} changed considerably depending on the concentration of Si in the alloy films. For Al-Si(2) [Fig. 9f] and Al-Si(3) [Fig. 9h] alloy films, the potential shift ceased within 20 s in the first zincate process and within a few seconds in the second zincate process, while duration of the less-noble potential shift for

the Al-Si(1) alloy film was almost unchanged [Fig. 9d]. These results indicate that the substitution reaction of Al dissolution and Zn deposition is almost terminated within a short time on Al-Si alloys containing more Si with Cu pretreated. Such rapid reaction in the second zincate process means that Zn deposition occurs at a high density on the surface and Zn deposits cover the surface immediately. Such dense and rapid Zn deposition is clearly provided by the nucleation ability of Cu deposits.

Cu is a noble metal and retains its metallic state in an alkaline zincate solution. This enables Cu deposits on Al-Si alloys to act as efficient charge transfer sites for Zn deposition even if their deposit size is very small. The high surface density of Zn deposits shown in Fig. 7i and j confirms the high surface density of Cu deposition. Therefore, Cu deposits survive the first zincate process and Zn strip-

ping process and retain their nucleation ability in the second zincate process. Improvement in the zincate process caused by Cu deposition occurs only on Al–Si alloys, and there seems to be a threshold concentration of Si for effective Cu deposition. In the case of the Al–Si alloy, eutectic Si is formed in α -Al at an Si concentration higher than 1.65 atom %.¹⁸ Even if such a clear structure is not formed in a magnetron sputter-deposited Al–Si alloy film, such eutectic Si may form and act as nucleation sites of Cu deposition. Details of such Cu deposition on Al–Si alloys are still under investigation.

In the present study, drastic improvement in zincate property due to deposition of a small amount of Cu was confirmed. Similar improvement in zincate or plating properties due to small amounts of alloying elements is already used in the manufacturing process. For example, 2000 or 4000 series Al alloys contain small amounts of Zn and Cu, which are added to improve zincate and plating properties.^{6,19,20} Even very low alloying compositions in Al-4N have strong effects on the metal deposition property, although details are not shown in this paper. Since the Al surface is usually covered with oxide or hydroxide film and thus electrochemical activity is low, addition of other electrochemically active elements to the surface greatly affects the electrochemical property of Al as a whole. In other words, activity of the Al surface can be controlled by adding a small amount of other elements to the surface.

Conclusion

Effects of etching of Al–Si alloy films in H_2SO_4 solution containing Cu^{2+} ions on double zincate pretreatment was investigated. The etching process dramatically improved uniformity of Zn deposition and suppressed Al dissolution in the double zincate process. This effect was presumed to be due to the following mechanism. (1) A small amount of Cu deposited on the Al–Si alloy during the etching process due to substitution reaction of Al dissolution. Uniform and dispersed Cu deposition is achieved in etching solution containing a low concentration of Cu^{2+} ions. (2) Cu deposits act as nucleation sites for Zn deposition in the zincate process, resulting in the formation of a thin, dense and fine Zn deposition layer suitable for the following plating process. Ability of Cu deposits for Zn nucleation is effective not only in the first zincate process but also in the

second zincate process. (3) The effect of Cu deposition becomes obvious with increase in Si concentration in the alloy films in the range from 1.0 to 2.56 atom %.

Acknowledgment

The authors express their appreciation to Professor Hiroki Habazaki (Graduate School of Engineering, Hokkaido University) who kindly provided us with magnetron sputter-deposited aluminum alloy films.

Hokkaido University assisted in meeting the publication costs of this article.

References

1. J. W. Golby and J. K. Dennis, *Surf. Technol.*, **12**, 141 (1981).
2. G. O. Mallory, *Plat. Surf. Finish.*, **72**, 86 (1985).
3. S. Wernick, R. Pinner, and P. G. Sheasby, *The Surface Finishing Treatment and Finishing of Aluminium and its Alloys*, p. 1023, Finishing Pub. Ltd., Teddington, UK (1987).
4. E. Stoyanova and D. Stoychev, *J. Appl. Electrochem.*, **27**, 685 (1997).
5. K. Tashiro, K. Chiba, Y. Hukuda, H. Nakao, and H. Homma, *J. Surf. Finish. Soc. Jpn.*, **45**, 720 (1995).
6. K. Azumi, M. Seo, and Leonard Nanis, *J. Surf. Finish. Soc. Jpn.*, **47**, 529 (1996).
7. J. I. Han and S. J. Hong, *Jpn. J. Appl. Phys., Part 1*, **36**, 2091 (1997).
8. H. Honma, H. Watanabe, and T. Kobayashi, *J. Electrochem. Soc.*, **141**, 1791 (1994).
9. H. Honma and H. Watanabe, *J. Electrochem. Soc.*, **144**, 471 (1997).
10. A. J. G. Strandjord, S. Popelar, and C. Jauernig, *Microelectron. Reliab.*, **42**, 265 (2002).
11. K. Azumi, Y. Koyama, and S. Kawashima, *J. Surf. Finish. Soc. Jpn.*, **54**, 422 (2003).
12. J. F. Rohan, P. A. Murphy, and J. Barrett, *J. Electrochem. Soc.*, **152**, C32 (2005).
13. L. Nanis, *Plat. Surf. Finish.*, **92**, 27 (2005).
14. F. J. Monteiro and M. A. Barbosa, *Surf. Coat. Technol.*, **35**, 321 (1988).
15. K. Azumi, T. Yugiri, T. Kurihara, M. Seo, H. Habazaki, and S. Fujimoto, *J. Electrochem. Soc.*, **150**, C461 (2003).
16. H. Yanagimoto, K. Akamatsu, S. Deki, and K. Gotoh, *J. Electrochem. Soc.*, **150**, C260 (2003).
17. K. Azumi, T. Yugiri, M. Seo, and S. Fujimoto, *J. Electrochem. Soc.*, **148**, C433 (2001).
18. M. Warmuzek, in *Atlas of Microfractographs*, Chap. 1, ASM International, Materials Park, OH (2004).
19. K. Azumi, Y. Fujishige, M. Seo, L. Nanis, H. Nakao, and Y. Tashiro, *J. Surf. Finish. Soc. Jpn.*, **47**, 802 (1996).
20. K. Azumi, Y. Fujishige, M. Seo, I. Saeki, L. Nanis, H. Nakao, and Y. Tashiro, *J. Surf. Finish. Soc. Jpn.*, **48**, 1019 (1997).