Anticorrosive, Uniform Au Coating by Electroplating Using Emulsion of Dense CO_2 in Electroplating Solution

Masato Sone[1*], Kazuhisa Fujii[2], Takabumi Nagai[2], Byung-Hoon Woo[1], Akinobu Shibata[1], Chiemi Ishiyama[1], and Yakichi Higo[1]
[1]Precision and Intelligence Laboratory, Tokyo Institute of Technology, Japan
[2]Daikin Environmental Laboratory, Ltd.,3 Banchi, Miyukigaoka, Tsukuba, Ibaraki 305-0841, Japan
*Correspondence: msone@pi.titech.ac.jp

ABSTRACT: In this paper, we conducted Au plating by novel emulsion electroplating method using a supercritical carbon dioxide (sc-CO_2) as a solvent and characterized the plated Au film. The plated Au film of 300 nm thickness by our method did not have any pinholes, which come from hydrogen babbles produced by the electrolysis of water, while that by conventional method had many pinholes. The formation of pinholes could be prevented by H_2 dissolution in CO_2. Moreover, we conducted the corrosion test which the plated Au films were immersed in 2N H_2SO_4 solution for 2 weeks. The plated Au Films by our method were not corroded in the strong acidic atmosphere, while those by conventional method were heavily corroded.

1 INTRODUCTION

Gold plating offers good corrosion resistance and good solderability and is often used in electronics, to provide a corrosion-resistant electrically conductive layer on copper typically in electrical connectors and printed circuit boards[1]. However, gold plated film thinner than 500 nm has pin-holes that were voids formed from the hydrogen bubbles produced by the electrolysis of water. These voids cause fatal corrosion of the plated film.

Recently, we have proposed a novel electroplating method, which is a hybrid of supercritical fluid and electroplating technology[2-10]. Sc-CO_2 has excellent characteristics of intermolecular interaction control due to the changeability of its density and its ability to convey materials to a nano scale area because of its high density and high diffusivity. In this technology, electroplating reactions are carried out in emulsion of supercritical carbon dioxide (CO_2) and electroplating solution with surfactants. The plated film by this method did not have any pinholes, which come from hydrogen babbles produced by the electrolysis of water. Compared to electroplating from the solution only, higher quality nickel films have been prepared by this method, which have higher uniformity, smaller grain size (11.1nm), and significantly higher Vickers hardness. Moreover, the current efficiency and electric resistance value were measured as a function of CO_2 volume fraction in the emulsion with three kinds of surfactants. These results show that dense CO_2 beyond critical point of CO_2 is effective to form emulsion for the electroplating reaction.

This character of this novel electroplating method is applicable to plating of novel metal, especially gold, because pinholes are fatal for novel metal plating. The aim of this work is to clarify the structural or anticorrosive features of Au coating by electroplating using emulsion of dense CO_2 in electroplating solution.

2 Experimental details

2.1 Materials

Carbon dioxide with a minimum purity of 99.99% was purchased from Nippon tansan Co. Ltd. In our experiments, we employed a nonionic surfactant polyoxyethylene lauryl ether ($C_{12}H_{25}(OCH_2CH_2)_{15}OH$, CAS No.9002-92-0) supplied by Toshin Yuka Kogyo. The Au electroplating was conducted with Au cyanide solutions purchased from Okuno Chemical Industries Co. Ltd. The substrate was SUS304 covered by strike Ni electroplating for 30sec. Before a reaction, the substrate was washed with acetone and rinsed in deionized water. The cleaned sample was degreased by dipping successively in a 10 wt. % NaOH and a 10 wt. % HCl and rinsed in deionized water. The sample was rinsed in deionized water. This pretreatment was applied to all SUS304 steel substrates regardless of the condition of the electroplating reaction.

2.2 Experimental apparatus

A high-pressure experimental apparatus (Japan Spectra Company) for electroplating is shown in Fig.1. The temperature variation of each run was observed to be less than 1.0 K. The maximum working temperature and the maximum pressure were 424 K and 50 MPa, respectively. The reaction cell that had a volume of 50 ml was a stainless steel 316 vessel in a temperature-controlled air bath with a magnetic agitator. An agitation was performed using a cross-magnetic stirrer bar. The substrate was attached using stainless wires to the reactor.

A typical electroplating reaction was performed in a constantly agitated ternary system of dense CO_2, the electroplating solution and a surfactant. The electroless Au plating solution and the surfactant were both put in a high-pressure cell. Liquid CO_2 was introduced to the high-pressure cell using a HPLC pump and pressurized to a predetermined pressure. The ternary system was then constantly agitated at a speed of 500 rev./min under 333K, and the electroplating reaction started at the same time as the agitate beginning.

We discuss the properties of the plated film by our method in comparison with properties of a plated film fabricated by a conventional method of electroplating. The experimental conditions of conventional method were performed at 333 K, atmospheric pressure, and used the plating solution of the same chemical composition as the novel electroless method.

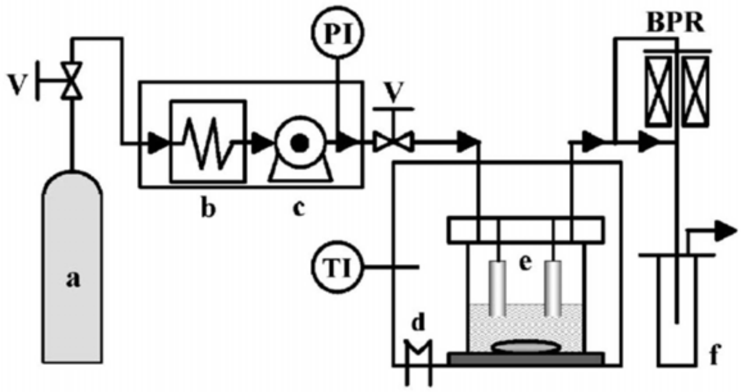

Figure 1. Experimental apparatus used for batch reaction in the electroplating experiments beyond the critical point of CO_2; (a) CO_2 cylinder; (b) cooler; (c) high pressure pump; (d) temperature controlled air bath; (e) reactor with magnetic stirrer; and (f) trap; BPR: back-pressure regulator; PI: pressure indicator; TI: temperature indicator; V: valves.

2.3 Analysis

The characteristics of the nickel films obtained using our method was analyzed on the basis of optical microscopic images. The optical microscopic images were obtained using a KEYENCE Violet Laser Microscope VK-9500 and Digital HF Microscope VH-8000. Pore size of the nickel plated film was measured using the software Digitizer Version 1.0.

3 RESULTS AND DISCUSSION

3.1 Surface features

Au Electroplating was done at a current density of 0.25 A/dm^2 at a temperature of 333 K and a pressure of 10 MPa in a constantly agitated ternary system of sc-CO_2 (15 ml), and the Au electroplating solution (30ml) and the surfactant (0.5 wt% to the electroplating solution). After 60 and 120 seconds of plating, we obtained a thickness of 150 and 300 nm, respectively. Optical microscopic images of these four samples were almost same and showed very beautiful surfaces. Figure 2 shows SEM images of the plated Au film (film thickness 300nm) plated by conventional plating method and by our method. On the view points of micrometer level, the surface of the plated Au film used in our method is clearly smoother than of the films prepared using the electroplating solution only at atmospheric pressure as shown in figure 2. Especially, the surface of Au electroplated by conventional method shows grain-like morphology. This difference of surface morphology is suggested to come from the crystal growth of electroplated Au. Moreover, it is notable that any pinholes are not observed in the both surfaces in figure 2. Usually, pinhole is known to be fatal problem for Au electroplating and the film thickness of 300nm is too thin to hinder the generation of pinhole, which come from hydrogen babbles produced by the electrolysis of water. Thus, pinhole may be too small to observe in this scale because the film thickness is 300nm. The surface can be too rough to find pin hole.

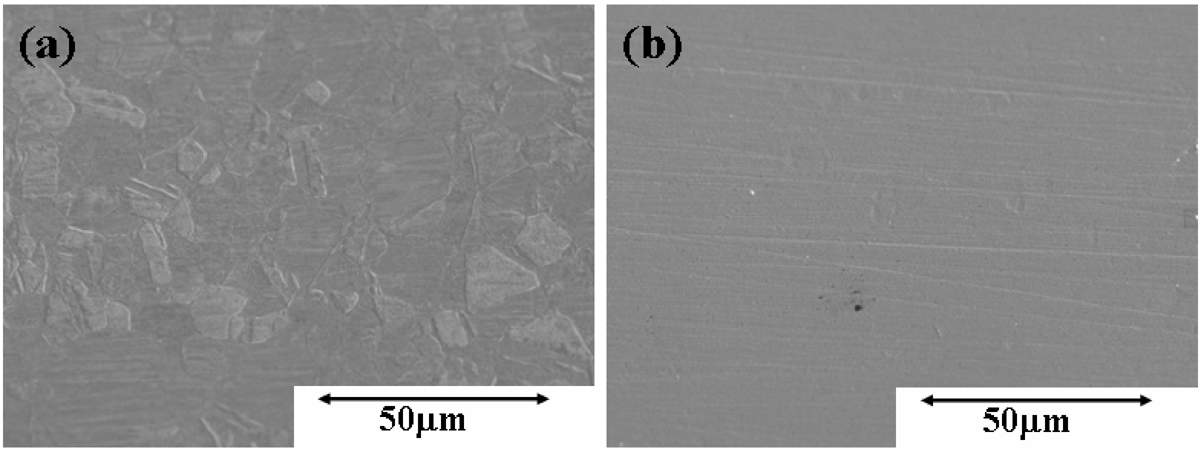

Figure 2. SEM images of Au films plated by conventional Au electroplating (a) and emulsion plating with supercritical CO_2(b)

3.2 Anticorrosive features of Au coating by electroplating using emulsion of dense CO_2 in electroplating solution

In order to clarify anticorrosive features of Au coating by electroplating using emulsion of dense CO_2 in electroplating solution, we conducted the anticorrosive test that the plated Au films (film thickness; 150 and 300nm) by conventional electroplating method and our method were immersed in 2N sulfuric acid solution for 2 weeks. Figure 3 shows the electroplated Au films by conventional electroplating method and our method after immersion 2N sulfuric acid solution. Figures 3(a) and (b) show that Au films (film thickness; 150nm) both by conventional electroplating method and our method were corroded and especially many corroded points are observed. This result means that the corrosion occurred from the point of pinholes and the area of the corroded points increased to about 100 nm with increase of immersion time. Moreover, 150 nm is too small thickness for plated Au film to show anticorrosive feature. When we compare the surface features of figure 3(a) and (b), the number of the corroded points in figure 3(a) is larger than that in figure 3(b). This implies that the plated Au film by our method did have smaller number of pinholes than that by conventional method.

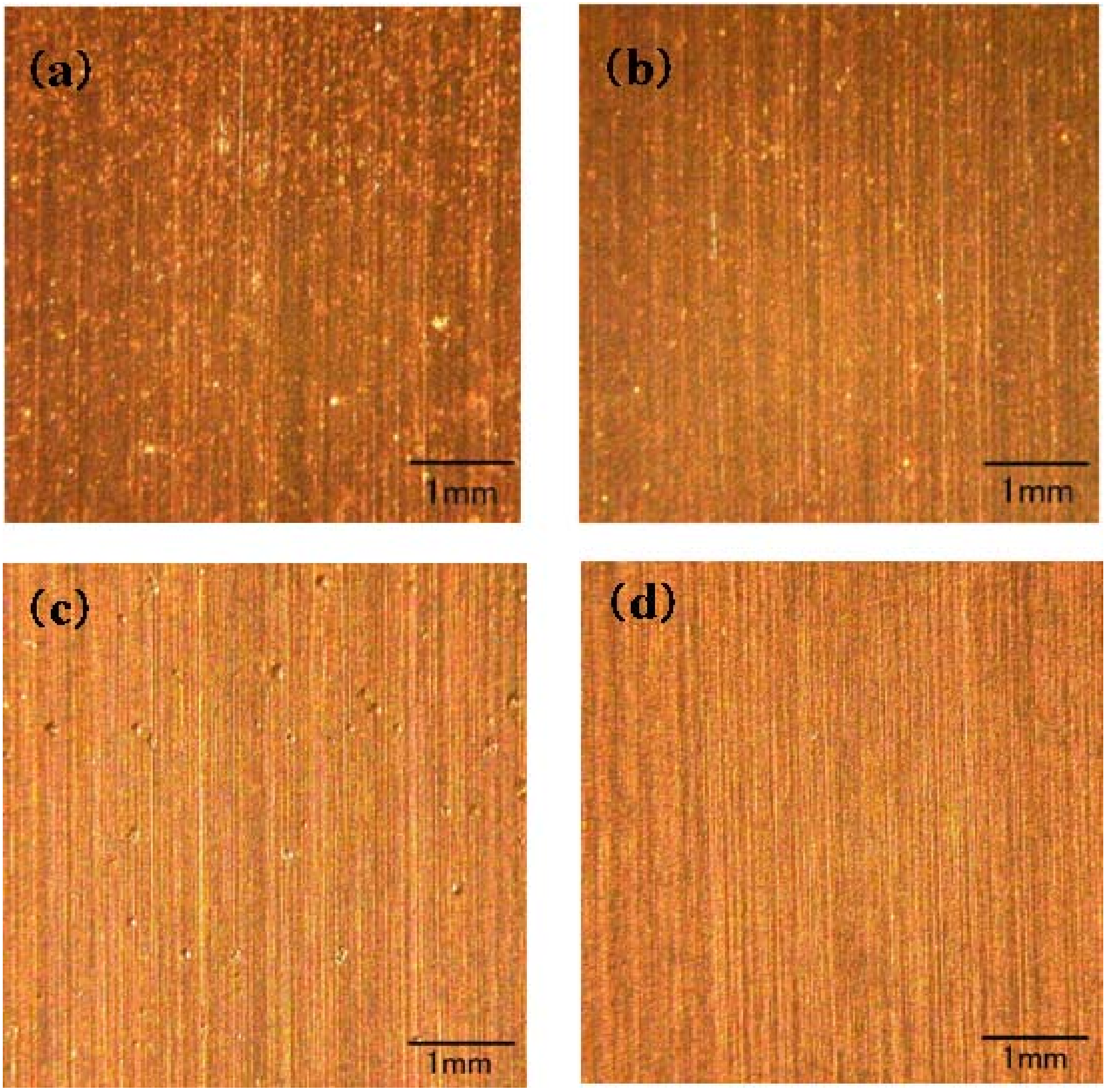

Figure 3. Optical microscopic images of Au films plated by conventional Au electroplating (a), (c) and emulsion plating with supercritical CO_2 (b), (d) after immersion in 2N sulfuric acid solution for 2 weeks. (a) and (b); film thickness of 150 nm, (c) and (d); film thickness of 300 nm.

On the other hand, figures 3(c) and (d) show great difference of surface between our method and conventional method. Both figures were obtained on the plated Au with 300 nm film thickness. Figure 3(c) shows smaller number of corroded points as compared with the surface with 150 nm thickness. While figure 3(d) shows no corroded point on the Au surface. This result means that our novel plating method can give pinholeless Au film with the thickness more than 300 nm, though the conventional Au plating is impossible to give the same surface of Au.

In our previous study about Ni electroplating, high pressure electroplating did not give good results because the buoyancy of the hydrogen bubbles produced by the electrolysis of water in the high pressure system becomes smaller than that at atmospheric pressure[5]. Hence, the larger bubbles prevent the metal from covering the plate. It is interesting to note that the pinholes did not appear in the Au film plated using our method although the high pressure conditions used during electroplating are not good for the uniformity. Since sc-CO_2 and hydrogen are miscible. The hydrogen bubbles produced by the electrolysis of water could dissolve in the sc-CO_2 parts of the emulsion and therefore the pinholes would not appear in the plated film using our method.

Au plating is one of the most important techniques for recent advanced technology, for example advanced electronics, fuel cell technology and MEMS. It is widely accepted that a problem of pinhole generation, which leads corrosion, has been fatal. This is because pinhole becomes the origin point of the corroded part to lead electrochemically corrosion reaction by ionization potential between Au and substrate metal. This study shows that Au electroplating method in emulsion of CO_2 in electroplating solution can give pinholeless Au film with thickness of 300 nm. This thickness is smaller than limit of Au film without pinhole by conventional electroplating film.

4 CONCLUSION

Au electroplating reactions were carried out in an emulsion of sc-CO_2 and an Au electroplating solution with surfactant. The plated Au film of 300 nm thickness by our method did not have any pinholes, which come from hydrogen babbles produced by the electrolysis of water, while that by conventional method had many pinholes. The formation of pinholes could be prevented by H_2 dissolution in CO_2. Moreover, we conducted the corrosion test which the plated Au films were immersed in 2N H_2SO_4 solution for 2 weeks. The plated Au Films by our method were not corroded in the strong acidic atmosphere, while those by conventional method were heavily corroded. Thus, electroplating method in emulsion of supercritical CO_2 is a powerful tool for making thin, finer metal structure and has a possibility to open era to new fabrication technology.

REFERENCES

[1] Reid, F.H., Goldie, W., (Editor), “Gold Plating Technology” *Electrochemical Publication* **1987**.

[2] Yoshida, H., Sone, M., Mizushima, A., Abe, K., Tao, X.T., Ichihara, S., Miyada, S., *Chem.lett.* vol. 11, **2002**, pp1086.

[3] Yoshida, H., Sone, M., Mizushima, A., Yan, H., Wakabayashi, H., Abe, K., Tao, X.T., Ichihara, S., Miyada, S., *Surf. Coat. Tech.* , vol.173(2-3), 2003, pp285.

[4] Yan, H., Sone, M., Sato, N., Ichihara, S., Miyata, S., Surf.Coat.Tech., vol.182, **2004**, pp.329.

[5] Yoshida, H., Sone, M., Wakabayashi, H., Yan, H., Abe, K., Tao, X-T., Mizushima, A.,

Ichihara, S., Miyata, S., Thin Solid Films, vol. 446, **2004**, pp194.
[6] Yan, H., Sone, M., Mizushima, A., Nagai, T., S.Ichihara, S.Miyata, *Surf. Coat. Tech*., vol. 187/1, **2004,** pp86.
[7] Wakabayashi, H., Sato, N., Sone, M., Takada,Y., Yan, H., Abe, K., Mizumoto, S.Ichihara, K., S.Ichihara, S.Miyata, *Surf. Coat. Tech.*, vol.190/2-3, **2005**, pp200.
[8] Mizushima, A., Mizushima, A., Yan, H., Nagai, T., S.Ichihara, S.Miyata, *Surf. Coat. Tech.*, vol.194/1, **2005**, 149-156
[9] Uchiyama, H., Sone, M., Ishiyama, C., Endo, T., Hatsuzawa, T., Higo, Y., *J. Electrochem. Soc.*, vol.154 (7), **2007**, ppE91-E94.
[10] Woo, B.H., Sone, M., Shibata, A., Ishiyama, C., Masuda, K., Yamagata, M., Endo, T.,Hatsuzawa, T., Higo, Y., *Surf. Coat. Tech.*, vol.202,**2008**,pp.3921.