Topographical Observation of Tin Precipitation for Pulse Plating by Using SEM & AFM

Hideyuki Kanematsu*, Nobumitsu Hirai**, Toshihiro Tanaka** & Takeo Oki*** (*Suzuka National College of Technology, **Osaka University, ***Nagoya University)

Pulse plating has been well known for homogeneous, dense and fine precipitation. In this study, we observed the precipitation process for pulse plating topographically, by using Atomic Force Microscopy (AFM) as well as SEM. Even though AFM is not always recognized as a suitable measure for the precipitation phenomenon in aqueous solution, we applied AFM to the qualitative observation. Different potential sequences for pulse plating were applied to sulfate solution for tin plating. In situ precipitation behavior was observed as well as the static one by AFM and the results were compared with those by SEM.

For more information, contact:

Prof. Hideyuki Kanematsu, Dr. Eng., MIMF Dept. MS & E., Suzuka National College of Technology Shiroko-cho, Suzuka, Mie, 510-0294, Japan Voice/Fax: +81-593-68-1849 E-mail: kanemats@mse.suzuka-ct.ac.jp

INTRODUCTION

Nano technology is an important development in this new 21st century where different nanoscale processes in various industrial fields may produce a second industrial revolution⁽¹⁾. Atomic Force Microscope (AFM) is a type of Scanning Probe Microscope $(SPM)^{(2), (3)}$ that is available for surface observation with high three-dimensional resolution and a promising nano-technology for surface observation on a nano-scale⁽⁴⁾⁻⁽¹¹⁾. The electroplating process can be refined by close examination on a nano-scale and from that perspective, the application of AFM to the study of electrodeposition processes may facilitate the exploration of another new world⁽¹²⁾. Therefore, we investigated the applicability of AFM to the electrodeposition processes of pulse plating.

Pulse plating has generally high exchange current densities and has been used for silver plating showing dendrite growth, smooth electrodeposition of tin and zinc, and other processes⁽¹³⁾. Recently, the application has been expanded to various other fields such as partial plating, the formation of micropatterns and multilayers that require accuracy and reliability. Generally speaking, the high overpotential makes deposited films denser and more uniform, since the nucleation rate becomes higher than the growth rate. Therefore, pulse plating facilitates has denser and more uniform deposits than other electroplating processes⁽¹⁴⁾⁻⁽¹⁶⁾. In this series of experiments, we carried out constant voltage pulse plating with different pulse widths, plating times and bath compositions, than observed the static surface deposition conditions by scanning electron microscope (SEM). In addition, we observed the dynamic in situ deposition processes by AFM and discussed the applicability of AFM to the surface observation based on a comparison between AFM and SEM.

EXPERIMENTAL

Iron foil measuring 0.1m in thickness $(3.94 \times 10^{-3} \text{ in})$ was used as a substrate. Each 10 x 10 mm (0.394in x 0.394in) specimen was cut from the same mother sheet. The lead wire was attached to one side of each specimen electrically and the surface was coated with insulative organic compound. The other non-coated side was used as working electrode.

A tin sulfide bath was chosen for this series of investigation. The bath was composed of sulfuric acid (15g) and tin sulfide (5g-15g) in 300 ml aqueous solution. Polyethylene glycol



Fig.1 Schematic diagram of experimental appratus

(molecular weight:2000) was added to solutions as the occasion demands. Firstly, cyclic voltammograms were measured by the apparatus shown in Fig.1. Specimens were used as working electrodes, silver/silver chloride electrodes as reference electrode and helical platinum wire as counter electrodes. All these three electrodes were connected to a potentiostat (Hokuto Denko, HA-303) and the potentials were scanned at a constant rate (10mv/sec) with the combination of a function generator (Hokuto Denko, HB-111) and the



Fig.2 Pulse schemes used in this experiment.

experiment from the perspective of potential combinations, as shown in Fig.2.

specimens, using an apparatus similar to that described above. In this case, a pulse generator (Hokuto HB-211) was used instead of a function generator (Fig.1). Fig.2 shows the pulse potential schemes used in this experiment. Rest potentials were measured and these were used as a start potential. Then the potentials were imposed to a certain anodic limit potential, kept there for a very short time then immediately imposed to a certain cathodic potential. After the potential was kept there, then it was imposed to the same anodic value again and this procedure was repeated. Five ms, 500ms, and 5000ms were chosen as the pulse width. Five patterns were used in this

Pico-SPM).

observed.

Electrodeposition



Fig.3 Schematic experimental set-up of the EC-AFM equipment.

The EC-AFM cell was filled with the tin sulfide-sulfuric acid solution working electrode. described above, and a series of potential pulses was applied to the iron electrode (W.E). All images could be observed during a series of pulse plating and the capture rate was 112s per an AFM image. The AFM observation area was 10 micrometers x 10 micrometers (3.94 x 10⁻⁴ in. x 3.94×10^4 in.). And the AFM images were compared with SEM images in corresponding cases.

potentiostat. The currents and potentials were read out to a data logger (Hioki 8420) and currentpotential curves were made on a personal computer by an software application (Origin ver.7J). Then several potential applied pulses were to

conditions

characterized and analyzed by a Scanning

Electron Microscope (SEM, Hitachi S-4300)

and an Electrochemical Atomic Force

Microscope (EC-AFM, Molecular Imaging,

specimens with electrodeposition by pulse

plating were prepared in advance then

electrodeposition by application of pulse

potentials was observed in situ by EC-AFM.

The apparatus is shown in Fig.3. The surface

of the pure iron foil used in this experiment was first polished, degreased by acetone and

then the foil was assembled in the cell as the

multiple

SEM

For

А

were

of

observations.

series

Cyclic voltammograms



-04 -02

potential (v)

Fig.6 Cyclic voltammogram of a pure iron foil in tin sulfide (15g) - sulfuric acid bath.

-06



Fig.5 Cyclic voltammogram of a pure iron foil in tin suflide (10g) - sulfuric acid bath.

Figs.4, 5 and 6 shows the cyclic voltammograms of iron foils in tin sulfide-sulfuric acid baths with different tin sulfide concentrations. For Fig.4, the bath contained 5g tin sulfide and the cathodic peak was observed at about -0.7V, corresponding to the tin precipitation. Another peak at about -1.2V represented the current increase for hydrogen evolution. Fig.5 and Fig.6 correspond to the results obtained with 10g and 15g tin sulfide baths, respectively. When the concentration of tin sulfate increased, the cyclic voltammograms in cathodic polarization became monotonous, which indicates the increase in tin deposition. The hydrogen evolution

continuously followed the tin deposition. Based on these findings, we fixed the composition corresponding to Fig.4 as the experimental solution in the following investigation.

SEM observations

0

-10 -08

SEM Fig.7 shows photographs when pulse pattern 4 was applied to the specimen in tin sulfides (5g) - sulfuric acid bath without PEG. Fig.7-(a) shows the photo when the pulse width was 500ms, while that was 5000ms in Fig.7-(b). When the pulse width was 500ms, the precipitated particles







were relatively fine. However, particles became very large, when the pulse width was 5000ms. When the pulse width increased, the growth rate of nuclei is much larger than the formation rate of nuclei. Therefore, the nuclei formed on the surface of specimen could grow sufficiently when the pulse width was longer. Fig.8 shows the SEM photographs of the specimens obtained when pulse pattern 4 was applied in a tin sulfide

(5g) – sulfuric acid bath with PEG. Fig.8-(a) shows that when the pulse width was 500ms. Compared with Fig.7-(a), the precipitation was homogenous and the surface was fully covered with precipitation particles, while some places remained precipitation free in Fig.7-(a), even though the pulses pattern was quite the same. The precipitated particles were not so small. However, we can presume that the growth of nuclei was relatively held down and the formation rate of nuclei was large. All of them can be attributed to the addition of PEG. Fig.8-(b) shows the SEM photo when the pulse width was 5000ms. When the pulse width was very long, the precipitated particles were relatively small and the surface was completely covered with precipitated particles. All of these results suggest that a surfactant like PEG inhibits the growth of nuclei and accelerates the formation of nuclei.

In situ observation by EC-AFM



Fig.9 In situ EC-AFM photos for the specimens in tin sulfide (5g) - sulfuric acid bath without PEG (pulse pattern 1).

Precipitation behaviors for pulse plating were observed by EC-AFM. Fig.9 shows in situ photo by AFM when pulse pattern 1 was applied to a specimen in tin sulfide (5g) – sulfuric acid bath without PEG. The pulse width in the case was 5ms. In Fig.9-(a), the pretty large nuclei were observed and after 112 seconds, the precipitated particles were too large to be observed by EC-AFM. This can be attributed to that the applied potential amplitude was too large. Very similar results were obtained when the pulse width were 500ms and 5000ms. The large overpotential allowed nuclei to grow sufficiently.

Therefore, we applied another potential pulse to the specimen in the same bath where the potential amplitude became smaller as shown in Fig.2-(b). In this case, the nuclei grew too rapidly and EC-AFM cantilever could not follow the rapid change in the surface, regardless of the potential width chosen.

Fig.10 shows in situ photos obtained with EC-AFM, when pulse pattern 3 was applied to specimens in tin sulfide (5g) – sulfuric acid bath without PEG. In this pulse pattern, the anodic current was almost the same as the cathodic current. The pulse width in Fig.10 was 500ms. This







Fig.11 In situ EC-AFM photographs of the specimens in tin sulfide (5g) - sulfuric acid bath without PEG (pulse pattern 4, pulse width:5ms)



Fig.12 In situ EC-AFM photographs of the specimens in tin sulfide (5g) - sulfuric acid bath without PEG (pulse pattern 4, pulse width: 500ms)

indicates that no change occurred and the surface condition remained the same, even though the time passed. As described above, the anodic current and cathodic one were quite the same. In cathodic polarization, precipitation occurs, while dissolution occurs at the anodic polarization. Precipitation and dissolution occurred to the same extent in this case. Therefore, there was no change occurring on the surfaces. When the pulse widths were 5ms and 5000ms, the same tendencies were observed.

Figs.11, 12 and 13 show SEM photographs when pulse pattern 4 was applied to the specimens in tin sulfide (5g) – sulfuric acid bath. In Fig.11, the pulse width was 5ms and the shortest in the series of experiment. Fig11-(a) was the initial condition and the next photo reflected the another surface condition after 112 seconds. Even though Fig.11-(b), (c) are almost quite the same as the initial condition, a very large precipitation is shown in Fig.11-(d). Since the precipitation was too great, a good photo could not be obtained. From the results of SEM observation shown in Fig.7 and 8, the precipitation particles were expected to have been tiny. However, the results were different, as shown in Fig.11. Fig.14 shows in situ AFM observation when precipitation occurred by direct cathodic polarization. Fig.1-(b) shows the very early stage of a large precipitation, and in Fig.14-(c),

> a large precipitation similar to that in Fig.11-(d) occurred. These results suggest that the same phenomenon also occurred in pulse plating with a very short pulse width. This can be attributed to the reference electrode in the EC-AFM cell not being able to follow the very short pulse response, since the salt bridge became very long in the special cell. Fig.12 shows the in situ AFM observations when the pulse width was 500ms in the same bath. From Fig.12-(a) to (c), there was no significant precipitation found, and a tiny precipitation occurred in Fig.12-(d). Finally, a large precipitation was observed in Fig.12-



Fig.13 In situ EC-AFM photographs of the specimens in tin sulfide (5g) - sulfuric acid bath without PEG (pulse pattern 4, pulse width: 5000ms).



Fig.14 In situ EC-AFM photographs of the specimens in tin sulfide (5g) - sulfuric acid bath without PEG (direct cathodic polarization).

(e). This indicates that the nuclei growth was slow. The reason can be attributed to the short pulse width. The growth could be inhibited to some extent, since the anodic dissolution process occurred alternatively in an appropriate cycle. Fig.13 shows in situ AFM observations when the pulse width increased(5000ms). In Fig.13-(b), the

tiny precipitation was already observed and in Fig.13-(c), the very large precipitation prevented an appropriate photo from being taken. From that perspective, the growth rate of the nuclei was much larger than that in Fig.12.

Fig.15 shows the in situ AFM photographs when pattern 5 was applied to the specimens when PEG was added to the same bath in the case of Figs.11-14. Since PEG was added to the bath, the potential of the specimens changed to some extent. Therefore, the pulse pattern was changed so that the same currents could flow both in anodic and cathodic polarizations. In Fig.15, the pulse width was 500ms. From Fig.15-(a) to (f), we could observe that several tiny nuclei were formed in the scan area and that they grew gradually, compared to those in Fig.12. It indicates that the addition of the surfactant, PEG,



Fig.15 In situ EC-AFM photographs of the specimens in tin sulfide (5g) - sulfuric acid bath with PEG. (pulse pattern 5, pulse width: 500ms).

increased the active points for precipitations and that the growth of nuclei was held down with the combination of PEG and pulse plating. The growth of nuclei was accelerated with the increase of pulse width, but the extent of acceleration was decreased by the addition of PEG.

All of these in situ AFM observations were compared with SEM photographs. We confirmed that AFM could be utilized for direct in situ observation during electrodeposition processes like

plating. The number of nuclei was not great in our study, even though the scan area was relatively large for the size of nuclei. This can be attributed to formation of nuclei under the probe being generally very hard. However, AFM could be applied to the qualitative dynamic observation for electrodeposition. AFM, one of SPMs, can be used for characterization on a nanoscopic scale. Therefore, we will try to apply the current technique to a much earlier stage of precipitation in the near future.

CONCLUSIONS

Different potential sequences for pulse plating were applied to iron specimens in tin sulfide – sulfuric acid bath for tin plating, and in situ precipitation behavior was observed and compared the static results observed by SEM. The following results were obtained.

- (1) The growth of the precipitated nuclei tended to be suppressed with the decrease of pulse width.
- (2) When surfactant was added to the bath, the number of nuclei formed was increased and the formation of fine particles was increased.
- (3) Both results in (1) and (2) were confirmed by SEM as well as EC-AFM.
- (4) In comparison with SEM observation, AFM could be utilized for in situ dynamic observation of electrodeposition.

REFERENCES

- (1) Web page for CEHMICAL INDUSTRY VISION 2020, technology partnership : http://www.chemicalvision2020.org/index.html
- (2) A.A.Gewirth & B.K.Niece, *Chem.Rev.*, **97**, 1129(1997)
- (3) K.Itaya, Prog. Surf. Sci., 58, 121(1998)
- (4) N.Hirai, H.Tanaka & S.Hara, *Appl. Surf.Sci.*, **130-132**, 506(1998)
- (5) N.Hirai, V.Ruxandra, T.Tagawa & S.Hara, *Hyoumenkagaku (Surface Science)*, **20**, 228(1999)
- (6) N.Hirai, H.Sano & S.Hara, *Electrochemistry*, **67**, 1120(1999)
- (7) N.Hirai, K.Watanabe, A.Shiraki & S.Hara, J.Vac.Sci. & Technol. B, 18, 7(2000)
- (8) N.Hirai, H.Okada & S.Hara, *ISIJ Inter.*, **40**, 702(2000)
- (9) N.Hirai & S.Hara, Youyuuen Oyobi Kouonkagaku (Moten Salts & High Temperature Chemistry), 43, 7(2000)
- (10) Y.Yamaguchi, M.Shiota, Y.Nakayama, N.Hirai & S.Hara, J.Power Sources, 85, 22(2000)
- (11) Y.Yamaguchi, M.Shiota, Y.Nakayama, N.Hirai & S.Hara, J.Power Sources, 93, 104(2001)
- (12) N.Hirai, Materia Japan, 40, 808(2001)
- (13) T.Oki et al., *Hyoumensyorikougaku (Surface Finishing Engineering)*, ed. by SFSJ (Surface Finishing Society of Japan), published by Hikkan Kougyou Co. 2000
- (14) E.J.Taylor, J.J.Sun B.Hammack, C.Davidson & M.Inman, *Plating & Suface Finishing*, **89**(May), 88(2002)
- (15) J.J.Sun, L.E.Gebhart, M.Inman & E.J.Taylor, *Plating & Surface Finishing*, **89**(May), 94(2002)
- (16) M.Aroyo & N.Tzonev, *Plating & Surface Finishing*, **89** (July), 48(2002)