In situ observation of bubble traces in nickel electrodeposition

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Abstract

The birth, growth, and separation of bubbles are microscopically observed in the electrodeposition of nickel in a nickel sulfamate bath. Bubbles repeatedly nucleate and grow at the same locations on the electrode used in the electrodeposition. The bubbles disturb ion transportation to the electrode surface for a long duration, causing the formation of holes, because electrodeposition only occurs outside the areas where bubbles are generated. Scanning electron microscopy (SEM) observation revealed that the surface texture of the bubble traces is smoother than that of the other areas and that there are many cracks and fragments in the bubble traces, which cause local changes in the characteristics of the electrodeposited film.

Key words: electrodeposition, nickel sulfamate, bubble trace, in situ observation

1. INTRODUCTION

In the electrodeposition process used in electroplating and electroforming, bubbles are continuously generated on both positive and negative electrode surfaces. Generally, hydrogen and oxygen gases are produced on the negative and positive electrodes, respectively. Bubbles grow when there is oversaturation of hydrogen or oxygen molecules in the liquid solution. The nucleation of the bubbles occurs on the electrode surface. The size of the bubbles increases by the accumulation of gas molecules. Finally, the bubbles are detached from the surface when the buoyancy force becomes larger than the surface adhesive force\(^1\)-\(^5\)). This process has the beneficial effects of promoting the transport of ions to the electrodes and heat diffusion by stirring the liquid near the electrodes\(^6\), \(^7\)). However, in most cases, the bubbles adversely affect the quality of the electrodeposited film.

The generation of gases is one of the reasons for the change in the electrodeposition conditions during the process. For example, if oxygen gas is generated in the Ni electrodeposition process, it is difficult to maintain stable conditions because the pH of the electrolytic solution gradually changes and the current efficiency is decreased. Also, some researchers have reported that the absorption of hydrogen in the film leads to disorder in the crystalline lattice, which results in internal stress in the film\(^8\), \(^9\)).

In particular, in the electroforming process, the effect of bubble traces should be completely eliminated from products to realize high replication accuracy. In high-precision electroforming, Ni is a commonly used material and it takes several days for a layer of Ni with a thickness of several millimeters to be deposited\(^10\), \(^11\)). Even micrometer-size bubbles degrade the replication accuracy by producing minute holes in the electrodeposited product. When bubbles are attached for a long time, Ni is not deposited and holes are formed in the areas of attachment, leading to serious deformation\(^12\), \(^13\)). For this reason, various methods, such as the bubble stirring method and the reduced pressure method, have been introduced to completely remove minute bubbles from the deposited surface.

To realize a stable electrodeposition process, it is important to understand the mechanism of bubble evolution on the electrodes. In this study, we observe bubbles during electrodeposition with 10 \(\mu\)m spatial resolution. We constructed an in situ observation device by introducing a microscopic optical system into the setup used for electrodeposition. Ni electrodeposition was performed at room temperature of approximately 25\(^\circ\)C, the temperature used in high precision electroforming\(^12\). As reported in this paper, we successfully observed the birth, growth and separation of bubbles in detail.

2. EXPERIMENTAL SETUP

In this study, bubble traces in the Ni electroforming process are observed. The electrodeposition conditions are given in Table 1.

| Electrolyte | 2.8 mol/L nickel sulfamate solution |
|-------------|-----------------------------------|
| Temperature | 25\(^\circ\)C                        |
| Anode       | nickel plate                      |
| Pressure    | 1.0 atm, 0.1 atm                  |
| Current Density | 4.0 mA/cm\(^2\), 12.0 mA/cm\(^2\) |

In our experimental setup, electrodeposition is performed inside a transparent chamber in which it is possible to reduce the pressure. Ni electrodeposition on the electrodes can be directly observed through the transparent wall. Fig. 1 shows
a schematic drawing of the experimental setup. The distance between the positive and negative electrodes is 100 mm. The surface of the negative electrode on which Ni is deposited faces the wall. The gap between the wall and this electrode is 5 mm.

The negative electrode is prepared by depositing a Ni film on a glass surface by electron beam vaporization. The root-mean-square (RMS) roughness of the deposited Ni surface is 0.5 nm. The initial surface should be flatter than the electrodeposited surface because electrodeposited films grown on rough surfaces are different from those grown on smooth surfaces.

In this study, electrodeposition is performed at two current densities. At a current density of 0.4 mA/cm$^2$, the current efficiency of Ni deposition is 94% and the deposition rate is 4.4 $\mu$m/h. At a current density of 1.2 mA/cm$^2$, the current efficiency and deposition rate are 90% and 13.0 $\mu$m/h, respectively. The nickel sulfamate bath is not stirred in the experiments. Under the electrodeposition conditions in Table 1, hydrogen generation is observed when the cathode potential is -0.320 V vs SHE or lower, at which the current density on the cathode is 3.3 $\mu$A/cm$^2$. The hydrogen overvoltage, defined as the difference from the theoretical potential where hydrogen generation can be observed, is 0.03 V.

The microscopic optical system consists of a CMOS camera and lenses. Two types of lenses can be selected. One is a macro lens giving a wide field of view. The other one is a high-power lens for microscopic imaging with a spatial resolution of 10 $\mu$m. This system uses aberration-corrected lenses with a long focal distance of 32 mm and a high numerical aperture (NA) of 0.17. The electrodeposited surface is obliquely illuminated with a light-emitting diode (LED) light source.

Generally, the electromagnetic field at the edge area is complicated in electrodeposition. Therefore, in this study, the observation area is the center of the electrode. We confirmed that the deviation of the current density in the observation area is within approximately 10%.

3. WIDE-FIELD-OF-VIEW OBSERVATION OF BUBBLES AND BUBBLE TRACES DURING ELECTRODEPOSITION

Firstly, the growth process of bubbles was observed with a low-magnification imaging system. Nickel was electrodeposited at a current density of 4.0 mA/cm$^2$ for 72 h, during which images were captured at 10 min intervals. Figs. 2 (a), (b), and (c) show the images captured in situ after 10 min, 24 h, and 72 h of electrodeposition, respectively. Fig. 2 (d) shows an image of the same area of the electrodeposited film after the completion of electrodeposition. In Figs. 2 (b) and (c), the positions of many bubbles are similar. Furthermore, as shown in Fig. 2 (d), the holes in the electrodeposited film are produced at similar locations where bubbles were attached during electrodeposition.

Fig. 3 shows close-up views of one of the bubble traces in Fig. 2. These images clarify the process of separation of bubbles from the surface. The bubbles are detached by the buoyancy force. The typical diameter of a bubble when it is detached from the surface is 1-2 mm. The bubbles do not separate suddenly; before separation, the bubbles move up slightly, as shown in Figs. 3 (a) and (b), and then are detached from the surface as shown in Fig. 3 (c). In
Fig. 3 (c), small bubbles are generated around the dark area indicating the bubble trace. Then, the bubbles coalesce into a single bubble and the coalesced bubble continues to grow in the same area as shown in Fig. 3 (d). By repeating this process, bubbles are generated continuously at the same locations during electrodeposition. Some holes are elongated such as the one in Fig. 3. The slight upward motion of the bubble before separation is the reason for the elongated shape.

Fig. 3 Magnified images of a bubble trace on the negative electrode in Fig. 3 during electrodeposition. The interval between images (a) and (b), (b) and (c), and (c) and (d) are 5 h, 1 h, and 4 h, respectively.

In many cases, bubble traces retain bubbles and the size and depth of the bubble traces increase during electrodeposition. In some cases, bubble generation stops on the bubble traces during electrodeposition. Then, the electrodeposition restarts on the surfaces of bubble traces. The series of images in Fig. 4 shows shots of an area where a hole was previously formed by the generation of bubbles. No bubble appears after the bubble in Fig. 4 (a) was removed. Here, the experiment was performed at a current density of 4.0 mA/cm² under atmospheric pressure. The bubble trace appears as a dark area immediately after the bubble has been detached. The mirrored surface appears to be dark because of the oblique illumination, in contrast to the rough surface of the other area. The area of the bubble trace is no longer dark 1 h after the bubble has detached as shown in Fig. 4 (b). The hole corresponding to the bubble trace has almost disappeared after 30 h.

Next, we focus on an elongated bubble trace and investigate the relation between the time of the bubble on the surface, which is calculated from the movie, and the depth profile of the bubble trace. The depth profile is estimated by multiplying the time on the surface by the deposition rate. The depth profile of the target bubble trace is also measured by a laser scanning confocal microscope. Figure 5 shows an image of the target bubble trace. Figure 6 shows a comparison between the estimated and the measured depth profiles, which indicates that the two profiles are in good agreement.

Fig. 4 Images focusing on a bubble trace. In these images, the bubble trace disappears.

Fig. 4 Comparison of estimated and measured depth profiles of a bubble trace.

4. MICROSCOPIC OBSERVATION OF BEHAVIOR OF BUBBLES

An in situ microscopic observation is carried out to analyze the generation process of bubbles around the bubble traces in further detail. In this observation, the number of bubbles is intentionally increased by adjusting the electrodeposition conditions to clearly observe the birth of bubbles in the microscopic view. The current density is set to 12.0 mA/cm² and the electrodeposition is performed under a reduced pressure at 0.1 atm.

Fig. 7 shows eight shots of bubble motion taken at intervals of 0.033 s. Many more bubbles can be observed around the vertically elongated bubble trace on the right of the images than on the planar surface on the left. This is clearly displayed in the motion video (included in the on-line journal). Moreover, most of the bubbles are generated from a
few specific areas indicated by the circles in Frame 1. In particular, the solid circles correspond to the edges of the bubble trace in the images. This is because the more complex shape of an edge makes it a more suitable location for the nucleation of bubbles or because small bubbles sometimes remain in the complex structure of the edges when they separate from the surface and then continue to grow by the absorption of dissolved gas molecules.

Fig. 7 Images from a motion video of a bubble trace taken at intervals of 0.033 s. Bubbles are consecutively generated from the circled areas in Frame 1. The solid circles correspond to the edges of the bubble trace in the images.

Fig. 8 comprises a series of images showing the motion of another bubble trace at intervals of 0.25 s. In this series, a bubble flows upward from outside the field of view (Frames 1, 2) and then adheres to the hole formed by bubbles (Frame 3). This phenomenon indicates that bubble traces exert a strong adhesive force on bubbles owing to their complex shape. The transportation of bubbles from other areas is another reason for the enlargement of bubble traces.

Fig. 8 Images of a bubble around a bubble trace taken at intervals of 0.2 s. The bubble indicated with an arrow flows upward and adheres to the electrodeposited surface.

5. SEM OBSERVATION OF MORPHOLOGY OF BUBBLE TRACES

The difference in the surface characteristics between the bubble trace and the normal deposition area was investigated by scanning electron microscopy (SEM). Fig. 9 (a) shows a SEM image of a typical bubble trace. Figs. 9 (b) and (d) show images of the surface texture in areas A and B indicated in Fig. 9 (a), respectively. Fig. 9 (c) shows an image of the area outside the bubble trace. The images clearly indicate that electrodeposition occurred in the bubble trace, although almost the entire area inside the bubble trace is smoother than outside it. Some mechanism yet to be clarified leads to the smooth electrodeposition along the surface of bubbles.

Cracks can be observed on the surface of the bubble trace, as shown in Fig. 9 (d). This is considered to be due to tensile stress. The characteristics of the electrodeposited Ni in the bubble trace are different.
from those in the normal deposition area because of the insufficient transportation of nickel ions or concentration of hydrogen. In the previous section, we reported that the holes corresponding to bubble traces decrease in size during electrodeposition after bubbles on them are removed. However, the deterioration of mechanical properties occurs in these areas even if the holes are observed to disappear. Cracks that appear in products during electroforming degrade the replication accuracy owing to local changes in the stress distribution. The bubble traces have complex structures such as the rough surface in the lower part of Fig. 9 (b) or the cracks shown in Fig. 9 (d). Around these structures, bubbles grow continuously because bubble nucleation occurs preferentially.

6. CONCLUSION

In this study, we successfully captured several images showing the birth, growth, and separation of bubbles during electrodeposition with high spatial resolution. Using SEM, we also observed the surface morphology of the electrodeposited film at a hole formed by bubble attachment. Our results led to the following findings on bubble creation:

1. Bubbles are attached on the surface for a long duration because they are repeatedly generated at the same location. Ni is only electrodeposited outside the areas where bubbles are attached. This phenomenon is the main reason for the formation of holes in electrodeposited products.

2. In situ observation of the bubbles clearly indicates that the depth of the bubble trace is quantitatively determined by the time of the bubble on the surface.

3. SEM observation indicates that the surface morphology of the electrodeposited film at the holes is completely different from that in other areas. The roughness in almost the entire area inside the holes is less than that in other areas. Cracks appear on the surface in the areas of the holes.

There have been many studies investigating the relationship between electrodeposition conditions and the properties of electrodeposited products. In situ observation is a visual method enabling the complicated phenomena in the evolution of bubbles to be intuitively understood. The results of this study indicate that bubbles are repeatedly generated and then grow at the same locations. Moreover, the electrodeposition conditions under the bubbles are clearly different from those elsewhere. This reduces the homogeneity of electrodeposited films. We believe that these findings on bubbles will help to realize a stable electrodeposition process for advanced electroplating and electroforming.

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