Copper foil electrodeposition is operated at high current densities (30~80 A·dm⁻², 30~80 ASD), which is subject to the demand of printed circuit boards (PCBs) or packaging substrates of chips. Traditionally, copper electroplating additives can be divided into three categories, depending on their functions: 1–17 accelerators (or brighteners), suppressors (or inhibitors, suppressors type I), and levelers (or suppressors type II). These additives are commonly used for via and through hole filling process. 1,2,4–17 Typically, the current density operated for the filling process is lower than 2 ASD. 1,2,5–17 On the contrary, copper electrodeposition influenced by additives at extremely high current density was seldom discussed in previous studies.

The additives usually used in electrodeposited copper foil industry are gelatin 8,10 and hydroxyethyl cellulose (HEC), 20 which can be operated at high current densities (30~80 ASD), but we think outside the box to choose other additives in this work. In the copper filling plating process, most studies were focused on smoothening the surface and filling these vias by tuning formulation. We can imagine that a rough copper surface has a lot of submicro or nano-scaled vias. As a result, smoothening the copper surface is similar to filling these vias. In this work, the effects of the additives on the microstructure and surface roughness of copper foil deposited at high current densities are studied.

Not only the chemical parameters (i.e., additives), but also the physic parameters (i.e., forced convection) are discussed in this work. In copper electrodeposition, the convection-dependent adsorption (CDA) of additives 14,17 explained how forced convection influences the additives adsorption on copper surface, and correspondingly on the copper filling process. Moreover, it indirectly explained how to smoothen the rough copper surface. 14,17 A pilot copper plating bath used in this work was designed according to fluid dynamics simulation. The optimal fluid flow rate and the corresponding formula were consequently obtained and were used to fabricate a copper foil with low surface roughness, which will be employed to make a PCB for high frequency transmission. 1,22

Experimental

The pilot copper plating bath with water-jet function at the bath bottom was designed and set up according to computer simulation. A two-electrode system with an IrO₂/Ti plate and a Ti plate was employed as an anode and a cathode, respectively. The detailed dimensions of the copper plating bath were described in Fig. 1. The details of the simulation process of fluid dynamics were described in the supplemental material. The solution temperature was maintained at 30 °C (±0.5 °C). The virgin makeup solution (VMS) was composed of 0.88 M CuSO₄ and 0.54 M H₂SO₄. Chloride ions from NaCl and organic additives were extra added in the VMS. The organic additives used in this study contained polyethylene glycol (PEG) with a molecular weight of 20000 g·mole⁻¹ (Fluka) and a commercial accelerator (RAS with a molecule structure of R-S-C₆H₄-SO₃⁻). All the organic additives were dissolved in deionized (DI) water to make concentrated solutions first, and then added in the VMS. The copper patterns following the fluid streamline plated on the copper foil were produced in VMS with 16 ppm Cl⁻ and 200 ppm PEG. This copper plating formula was defined as the convection-sensitive formula which was used to validate the fluid dynamics simulation.

Because the surface roughness on the deposited side of the copper foil was mainly determined by the current density, fluid flow rate, and the components of the copper plating solution, it had to be analyzed to realize their contributions to the surface roughness. The surface
roughness was measured using a profile meter (SURFCOM 130A). Scanning electron microscope (SEM, JOEL 6010LA) was used to examine the microstructures of the cross-sections of these copper foils. The cross-sections of these copper foils were observed after a specific etching process. The etching solution formulated for the cross-sectional examination consisted of H₂SO₄, NaCl, and Na₂CrO₄. The etching time was 10 seconds followed by cleaning the samples using DI water, and then put the samples in the DI water with ultrasonic auxiliary for 15 minutes to make sure of no copper fragment residual.

Results and Discussion

The copper deposit with streamline patterns, as shown in Fig. 2, was produced with the convection-sensitive plating solution. The streamline copper patterns on the copper deposit highly fit the patterns obtained from computer simulation. In the pilot copper plating bath, one electrodeposition experiment was divided into five areas at five different flow rates. The five areas were located at the middle of the cathode, as shown in Fig. 2E. The fluid flow rate at each area was calculated by integrating 100 data points (a 10 × 10 matrix) within a 2 × 2 cm² area, as defined in Fig. 2F. The values of fluid flow rate within each area were 40.12 cm·s⁻¹, 37.62 cm·s⁻¹, 36.53 cm·s⁻¹, 29.57 cm·s⁻¹, and 20.41 cm·s⁻¹ (see Fig. 2F).

Copper foil was produced at high current densities (typically at 40~60 ASD). There were some concerning problems: (a) the organic additives lose their functions; (b) the limiting current density occurs, which may lead to voids formation in the copper deposit or powdery copper on the copper surface. Figure 3A shows the surface appearance of deposited side on the plated copper foils obtained in the VMS at the current densities from 10 to 60 ASD and the fluid flow rate from 20.41 to 40.12 m·s⁻¹. The surface roughness of the deposited side was mainly determined by the formulation of the copper solution. On the other hand, the surface roughness of the cathode side (i.e., copper surface contacting with the cathodic surface) was mainly determined by the surface morphology of the TiO₂/titanium cathode. The mass transfer rate of cupric ions was determined by forced convection in this system, so that weak forced convection easily led to limiting current density of copper electrodeposition. With increasing current density, the deposited copper appeared dark brown within the low convection areas, as shown in Fig. 3A. Most of these dark brown areas were powdery copper rather than a copper film, as shown in Fig. 3. SEM images and profile meter analyses of the plated copper foils obtained in VMS were also summarized in Fig. 3, indicating that the surface roughness increased rapidly when the current density was larger than 20 ASD. Powdery copper foils deposited at fluid flow rate of 20.41 and 29.57 cm·s⁻¹ at 40 ASD and at the fluid flow rate of 20.41, 29.57, 36.53, 37.62 cm·s⁻¹ at 60 ASD, which were marked by dashes as shown in Fig. 3. VMS formed a flat surface (Ra < 0.8 µm, Rz < 4.0 µm) at 10, 20, and 40 ASD and at fast fluid flow rate. However, it could not form a flat surface at 60 ASD, even if the fluid flow rate was very fast (i.e., 40.12 m·s⁻¹). When the mass transfer rate of cupric ions was slower than the electrochemical reduction rate of cupric ions within the diffusion boundary layer, the surface roughness of the copper deposit became rough, even rougher than that of cathodic surface. In this situation, if the overpotential of the cathode rose, protons would be reduced to hydrogen bubbles on the plated copper to form the powdery copper. The copper electrodeposition was stopped when the hydrogen bubbles occupied and blocked the mass transfer of cupric ions. Hydrogen bubbles resulted in a lot of pinholes on the copper deposit and the rough surface thereof.

Subsequently, chloride ions were added in the VMS to produce the copper foil. The surface roughness of the copper foil at the deposited side soared and the area of the powdery copper significantly increased as shown in Fig. 4. It is different from the result of the previous study that the copper deposit surface was atomic flat when chloride ions formed an adlayer on the copper surface and the adsorbed chloride ion can control the copper deposition orientation. On the other hand, chloride ion plays another role of reducing the activation energy of cupric ions reduction by cuprous chloride formation. Chloride ions accelerate copper electrodeposition, but they were not uniformly distributed on the copper surface. According to the mass transfer of chloride ion, only convection term is beneficial to the chloride ion transport forward to the cathodic surface during electroplating. The diffusion and the migration terms is negligible and negative effects, respectively, on the transport of chloride ion forward to the cathodic surface because chloride ion is not consumed at the cathode and, also, chloride ion bears a negative charge. As a result, non-uniform chloride ion distribution on the copper surface during electrodeposition was formed. Chloride ions preferred to selectively adsorb at convex area rather than concave area. Consequently, acceleration on copper ion reduction caused by chloride ions was not uniform on the copper surface. Hence, the plated copper surface was rough, even rougher than that of the cathodic surface, as shown in Figs. 4B, 4C. Not only the adsorption effect of chloride ion but also the formation of hydrogen bubbles roughened the copper surface and facilitated the powder deposition.

The plating results dramatically changed when chloride ions, PEG, and accelerator were simultaneously added in the VMS. The surface roughness of the deposited copper foils was very low, even at the high current density of 60 ASD. The photos of the surface appearance of the electroplated copper foil shown in Fig. 5 confirmed a mirror-like appearances (Ra < 0.3 µm, Rz < 2.0 µm) at a wide flow rate range, especially at 20 ASD. A mirror-like appearance was also observed at 60 ASD when the fluid flow rate was very fast (i.e., 40.12 cm·s⁻¹). However, only one fifth to two fifths part of the areas where the flow rate was faster showed the mirror-like appearance (Ra = 0.26 µm, Rz =

Figure 2. Streamline simulation of copper plating solution and experimental confirmation at the inlet flow rate (i.e., pumping the fluid into the pipe shown in Fig. 1) is (A, B) 0.24 m·s⁻¹ and (C, D) 1.20 m·s⁻¹. The five areas were located at the middle of the cathode (Fig. E). Each fluid flow rate was calculated by integrating 100 data points in a dimension of 2 × 2 cm² (Fig. F). The flow rates within the five areas are listed in Fig. (G). The data points were on the x-z plane and located at y = 0.10 cm and only the z direction flow rate is considered.
1.78 μm) (see Figs. 5A, 5B). In addition to that, the grain size become small when the corresponding roughness was low, and vice versa. The adsorbed amount of PEG depends on the distribution of chloride ions, \(^{14,27-29}\) therefore, the suppression effect of PEG on copper electrodeposition is more strong at the convex area because the PEG-Cl\(^{-}\) complex\(^ {30,31}\) prefers to adsorb there. On the other hand, accelerator occupied where chloride ion coverage is low, meaning that PEG-Cl complex coverage is correspondingly low at the concave area.\(^ {32}\) As a result, a flat surface, even a mirror-like surface, was formed, because the copper deposition at the concave area is accelerated.
Figure 4. Surface morphologies and microstructure analyses obtained in the VMS with chloride ions only at various fluid flow rates and current densities. (A) Digital photos. (B) Cross-sectional SEM images. (C) Profile meter analyses.

whereas the copper deposition at the convex area is suppressed. The essentials of the organic additives for the copper plating at high current densities (40–60 ASD) were (1) polymers with a high molecule weight (e.g., PEG with a molecule weight higher than 20000 g·mole⁻¹), and (2) molecular structures that are resistant to oxidative decomposition, particularly, if the anode is insoluble, such as ring-containing molecules (e.g., accelerator bearing a benzene-like structure). For example, 3-(2-nitrophenylthio)-1-propanesulfonic acid, sodium salt is a promising accelerator. The area of the powdery deposit shown in Fig. 5B was similar to that shown in Fig. 4B, which only Cl⁻ was added. It is speculated that the organic additives lost their functions when the operation current density approached the
Figure 5. Surface morphologies and microstructure analyses obtained in the VMS with chloride ions, PEG and accelerator at various fluid flow rates and current densities. (A) Digital photos. (B) Cross-sectional SEM images. (C) Profile meter analyses.

limiting current density of cupric ions. In the meantime, the cupric ion concentration within the diffusion boundary layer was very low and non-uniform, so the mass transfer of cupric ions and chloride ion depended on the current density and flow rate rather than the distribution of the organic additives. Consequently, when the current density is high, such as 60 ASD, the area of the powdery deposit is similar no matter what formula is employed (see Fig 3C, 4B, 5B).

Based on the results as mentioned above, the surface roughness of the plated copper foil is controllable for practical applications. The high surface profile (i.e., high surface roughness) copper foils are of-
ten used for high bonding strength between the copper foil with resin of a PCB, whereas the low surface profile (i.e., low surface roughness) copper foils are used to minimize the signal loss in conductor (i.e., skin effect)\(^{21,22,33,34}\) for high-frequency transmission application. The \(\text{Cl}^-\) -contained formula without an accelerator was suitable for fabricating the high bonding strength copper foil, whereas the \(\text{Cl}^- + \text{PEG} + \text{accelerator formula}\) was suitable for fabricating the high-frequency transmission copper foil. In traditional, there were two manufacture processes of the electrodeposited copper foil, including electroforming process and surface treatment process.\(^{35}\) In the electroforming process, various organic additives and chloride ion were added to the copper-sulfuric acid electrolyte to maintain the property of the copper foil. However, it was difficult to reduce the surface roughness of the deposited side at such high current density. As a result, surface modification process was alternatively employed to improve the surface property of copper foil, such as reducing surface roughness.\(^{35}\) In this work, from a mirror-like copper foil in one step process that integrates the electroforming process and the surface treatment process together was obtained by fluid flow rate simulation for the plating bath design and the plating formula thereof. The most important result is that the mirror-like copper foil was successfully produced when the current density reached to 60 ASD at fluid flow rate of 40.12 m \(\cdot s^{-1}\), as confirmed in Fig. 5.

### Conclusions

The streamline pattern of the copper plating solution was simulated and analyzed by computer simulation and practical plating results. The simulated results highly fit the real electrodeposition patterns in the copper plating bath with the convection-sensitive formula. The simulation can assist engineers to obtained accurate fluid flow rate and jet design in the copper plating bath for fabricating copper foil with various surface roughness. The limiting current density of cupric ions and the distribution of chloride ion facilitate the deposit with a rough surface. Only proper organic additives (i.e., formula) combining with a fast flow rate can deposit a smooth copper surface at such high current density (i.e., 60 ASD). However, the organic additives cannot effectively function when the operating current density is close to the limiting current density of cupric ions. Moreover, the grain size of the plated copper is smaller and smaller with decreasing the surface roughness and vice versa.

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