Characteristics of High-Speed Copper Plating Films Using a Jet Flow Device

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Abstract: Since copper has excellent properties such as malleability and conductivity, it is widely used in the electronics field. Copper sulfate plating is expanding further in fields requiring thick deposits such as for heat dissipation boards and bumps for stress relaxation during semiconductor packaging. In this study, high-speed copper plating at 50 A/dm² or more was achieved using a jet flow device. In addition, as a result of comparison with the low current density film, the current density had little effect on electrical conductivity and film surface structure. On the other hand, it was confirmed that the etching rate of the high current density film was greatly increased as the crystallites on the film surface became smaller than low current density film. Increase in productivity is expected due to shorter plating time enabled by film deposition at high current density. Furthermore, the increase of etching rate is expected to contribute to the suppression of undercuts that occur when removing the seed layer during wiring and bump fabrication.

Key words: Electro copper plating, high current density, film characteristics, jet flow device.

1. Introduction

Recently, in the electronics field, copper having excellent characteristics such as malleability and conductivity has been used as rolled copper foil, electrolytic foil and plated film [1, 2]. Among them, the amount to use of copper sulfate plating is expanding to fields that require thickening such as heat dissipation boards, bumps for stress relaxation during semiconductor mounting, and so on. In order to improve productivity and for cost reduction, high speed electroplating using high current density has been desired [3, 4]. To achieve high speed plating, it is necessary to increase current density. However, there is a limited current density in the electrode reaction, and the metal ion concentration at the cathode electrode surface becomes zero in that area. Therefore, in exceeding the limited current density, abnormal deposition such as burnt and lumps was caused by insufficient supply of metal ions. The limited current density in electroplating reaction could be represented by the following scheme.

\[
i_L = zFD\frac{C_0}{\delta}
\]

(1)

\(i_L, z, F, D, C_0 \text{ and } \delta\) are the limited current density, the number of electrons in the reaction, the Faraday constant, the diffusion constant, the solution concentration and the thickness of the diffusion layer, respectively. Also, the thickness of the diffusion layer in the plating reaction is expressed by the following schemes.

\[
\delta = \delta_0 \left( \frac{D}{v} \right)^{1/3}
\]

(2)

\[
\delta_0 = 5 \left( \frac{vx}{U} \right)^{1/2}
\]

(3)

\(\delta_0, v, x \text{ and } U\) are the thickness of the boundary layer, the kinematic viscosity of the electrolyte, the distance from the electrode and the flow rate of the plating solution, respectively. From the above 3 schemes, the
increase of the limited current density can be realized by increasing the metal ion concentration and thinning the diffusion layer [5, 6]. However, the metal ion concentration is limited because there is the solubility in each substance. Therefore, to achieve high-speed plating, it is essential to make the diffusion layer thin. As shown in scheme 3, because the thickness of the diffusion layer could be made thin by increasing the stirring speed of the plating solution [7], in this study, we have achieved high-speed plating by using a jet flow device that can stir at high speed as shown in Fig. 1. By optimizing the equipment conditions, the production of the plating film with a shiny appearance was achieved at 50 A/dm² or higher. However, the current density which is generally performed at present, is about 3 to 5 A/dm², and there are very few reports of plating under a current density 20 times higher than the conventional method. Furthermore, in this paper, the characteristics of the plating film prepared under high current density were investigated.

2. Experimental

2.1 Preparation of Plating Film

Copper foil was used for the substrate, and the degreasing treatment with 50 g/dm³ NaOH and the activation treatment with 10 vol.% H₂SO₄ were performed as pre-treatment of electroplating. An insoluble anode coated with Pt on Ti was used as the anode electrode, and the plating solution was stirred at a flow rate of 2 L/min. The current density was plated at 40, 50, 60 A/dm² for high-speed plating, and 5 A/dm² as the conventional method using air agitation, and each target was plated to a thickness of 20 μm. Table 1 shows the composition of plating solution. Bis (3-sulfopropyl) disulfide (SPS), Janus Green B (JGB), and polyethylene glycol average molecular weight 20,000 (PEG) were added as additives [8, 9]. After plating, annealing was performed at 120 °C for 60 min in order to ignore the effects of self-annealing.

2.2 Evaluation of Physical Properties

The structure of the plating film was observed using a Field Emission Scanning Electron Microscope (JEOL Ltd. JSM-7000F; SEM), and the surface roughness was measured by a laser microscope (Olympus Co. Ltd. OLS4100), respectively. The crystal structure was analyzed using X-ray diffraction (Rigaku Co. Ltd. RINT-2200; XRD). The crystallite

![Fig. 1 Jetflow device.](image)

| Table 1 | Plating bath condition. |
|---------|-------------------------|
| CuSO₄·H₂O | 250 g/dm³ |
| H₂SO₄ | 50 g/dm³ |
| Cl | 50 mg/dm³ |
| SPS | 50 mg/dm³ |
| JGB | 30 mg/dm³ |
| PEG | 30 mg/dm³ |
size was calculated using the half width of the peaks, Scherrer’s equation and the Halder-Wagner method [10, 11]. In order to evaluate the etching characteristics, after soft etching for the purpose of removing the oxide film after annealing the amount of etching when immersed in persulfuric acid based etchant for 60 s was measured. For investigating the electrical conductivity of the film, the sheet resistance was measured using a resistivity meter (NPS, INC. Resistivity Processor MODEL Sigma-5).

3. Results & Discussion

3.1 Surface Structure of Plated Films and Crystal Orientation

The plating films prepared with the solutions shown in Table 1 produced shiny films with no abnormal precipitation such as burnt and lumps under any current density of 40 to 60 and 5 A/dm², respectively. Fig. 2 shows the image of surface structure and surface roughness (arithmetic mean estimation; Ra) of each film. It was confirmed that the influence of current density on the surface structure was very small, and a similar structure under any conditions. Also, the surface roughness was 20 nm for each film. It was confirmed that the plating film produced at high current density had the similar appearance and structure as those produced at low current density. Fig. 3 shows the crystal orientation at each current density. Cu films produced both high-speed plating and conventional method had (111) crystal plane of 60%. It was considered that a plating film with a high current density did not have a large effect on the crystal orientation. Furthermore, as for the high-speed plating, the current density from 40 to 60 A/dm², the (200) decreased but the (111) orientation tended to become stronger. However, since the change in orientation was slight, the influence on the physical properties of the plating film was considered to be small.

![Fig. 2 Surface morphology and surface roughness of each film.](image)

![Fig. 3 Crystal orientation of each film.](image)
3.2 Effect on Etching Characteristics

Fig. 4 shows the results of the etching characteristics evaluation. The films produced by high-speed plating showed approximately the same etching rate of 2.5 μm/min. On the other hand, the film produced by 5 A/dm² was 1.75 μm/min, and it was confirmed that etching rate of high-speed plating film was increased about 30%. The cross-sectional observation results and crystallite size of each film were shown in Figs. 5 and 6, respectively. From these results, although the crystallite size of each plating film varies greatly from 0.5 to 3.0 μm, the same crystal structure was obtained at any current density. However, it was confirmed that the crystallite size was strongly influenced by the current density.

The crystallite size of the films produced by high-speed plating was about 30 nm at each current density, whereas the low current density at 5 A/dm² was about 50 nm, so it has been confirmed that the crystallite size is significantly reduced by plating at a high current density. There is a difference of about 100
times between the apparent particle size and the crystallite size. This is considered to be due to the difference between the crystallite that can be regarded as a single crystal and the particles that are composed of them. Metallic crystals including plating films are composed of crystallites and particles, and it has been reported that the film characteristics were varied greatly depending on the size of these crystals [12, 13]. It was considered that the difference in the etching rate was caused by not particle size but crystallite size. The reason for the increase in the etching rate of the high-speed plating film is presumed that the surface area has increased due to the smaller crystallites.

Fig. 7 shows the surface structure after etching of the plating film. There was no significant difference between the high-speed plating and the low current density film, and the Ra values were equivalent. From these results, it was expected that the influence of the difference in etching rate was very small in the film form after the etching process.

3.3 Effects on Electrical Conductivity

Fig. 8 shows the relationship between current density and sheet resistance. Sheet resistance was from 0.95 to 0.98 mΩ/sq. in any condition. The sheet resistance of pure copper with a thickness of 20 μm was 0.86 mΩ/sq., and it was confirmed that these plating films in any condition were inferior to pure copper [13]. It had been reported that the conductivity of metal of the same composition was affected by the size of the crystals [14]. As discussed in Section 3.2, the crystal of each plating film has roughly the same particle size, but the crystallite size differed greatly. Since the sheet resistance value was almost the same, it was expected that the electrical conductivity was strongly influenced by not the particle size but the crystallite size of the plating film.

Furthermore, the film was compared with the plated by 50 A/dm² without annealing treatment. Since the sheet resistance value without annealing treatment was 1.4 mΩ/sq., it was confirmed that the sheet resistance value was reduced about 30% by annealing. The cross-sectional observation results of the without annealed film were shown in Fig. 9 and the crystal orientation by XRD was shown in Fig. 10, respectively. It was confirmed that the particle size of

| Current Density (A/dm²) | Sheet Resistance (mΩ/sq.) |
|-------------------------|---------------------------|
| 5 A/dm²                 | 1.2                       |
| 40 A/dm²                | 1.0                       |
| 50 A/dm²                | 0.9                       |
| 60 A/dm²                | 0.8                       |

Fig. 7 Observation of surface morphology after etching.

Fig. 8 Relationship between current density and sheet resistance.
the film without annealing was very small compared to that of the annealed film [15-17]. On the other hand, the effect on crystal orientation was small, showing strong orientation in (111) plane regardless of the presence or absence of annealing. Moreover, the crystallite size before annealing was about 10 nm. Therefore, it was confirmed that both the particle size and crystallite size were increased by annealing. When the effects of current density were compared, the crystallite size changed significantly, but the sheet resistance value was not affected. On the other hand, it was revealed that the crystallite size was affected by the presence or absence of annealing than the current density. From the above results, it was clarified that the sheet resistance value depends not on the crystallite size but on the particle size. Moreover, it has been reported that the increase of crystallite size by annealing is affected by co-deposited carbon, nitrogen and sulfur, which inhibit the growth [18, 19].

The crystallite size before annealing of the film prepared by 5 A/dm² was about 10 nm as in the case of 50 A/dm². On the other hand, as shown in Fig. 6, the crystallite size after annealing was smaller for 50 A/dm², and it was confirmed that the growth of crystallites due to annealing was suppressed. Therefore, it was suggested that the film produced by high-speed plating may contain more co-deposited impurities than that of low current density, however, the deterioration of electrical conductivity due to impurities was not confirmed.

4. Conclusion

High-speed copper plating at 50 A/dm² or more was achieved by using a jet flow device and optimizing plating condition. Furthermore, it was confirmed that the effect of the current density on the crystal orientation and electrical conductivity was small by comparing with the copper film plated at a low current density. On the other hand, it was confirmed that etching rate of high-speed plating film was increased.
about 30%, because the crystallite size was reduced by high current density. An increase of the etching rate can be advantageous. For example, when a pattern was formed by a subtractive method, the difference of the etching rate between the based electroless copper plating film and the electro copper plating film was reduced, so that the undercut occurs after etching can be suppressed [20, 21]. Based on the above results, it fully responded to the speeding up of electro copper plating that is currently required in the electronics field, and eliminated the concern of deterioration in physical properties due to high current density, which was rarely reported.

Therefore, this technology is expected to contribute to productivity improvement in the electronics field where film thickness is required.

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