

Characterization of Acid Copper Plating Solution for Via-Filling

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Abstract

The use of acid copper plating process for via-filling effectively forms interlayer connection in build-up PWBs with high-density interconnections. However, in the case of copper film deposited in a bath, which is greatly dependent on the effects of additives like via-filling technique, the drop in mechanical properties and the increase in stress in electro-deposits due to co-deposition of the additives are likely weaknesses. In view of such weaknesses, we concentrated our study on the mechanical properties of the copper films plated in two types of conformal acid copper plating baths that have been in use for some time and two types of acid copper plating baths for via-filling.

As a result, selection of suitable additives was confirmed to be of great importance for the acid copper plating bath for via-filling. The use of the additives that easily deposit with copper was likely to cause drop in mechanical properties of the film. On the other hand, the fact that the acid copper plating process for via-filling nevertheless deposits a film comparable to that out of the recognized conformal type acid copper plating bath in the use of the most suitable additives was confirmed.

Introduction

Build-up technique has been prevailing as a circuit formation method for PWBs used for electronic devices such as mobile phones, PCs, video cameras, and game consoles in recent years.^{1, 4} In the technique, very fine holes (through holes and blind via holes (hereafter called “via holes”) are drilled in laminates and they form interlayer connections when filled with metal deposits. For via holes, among those fine holes, the interlayer connections are formed by conformal plating and via-filling plating techniques. However, the conformal plating technique has difficulty in forming a structure for stacked type connection like via-on-via.

On the contrary, the via-filling plating technique, by which via holes are filled with metal, can completely fill the holes. Furthermore, as long as the metal surfaces in the holes are flat, yet another via holes may be stacked up on them after lamination. This characteristic makes the technique quite useful for downsizing PWBs and devices. As a consequence, demand for the via-filling plating technique that fills via holes for interlayer connection is increasing to replace the conformal plating technique that imposes limitation on further dense layout designing of PWBs.^{5, 11}

The conformal type plating bath is the so-called high-throw bath (the bath with a high throwing power that contains a low concentration of metal but a high concentration of sulfuric acid) and the reliability of the mechanical properties of the film out of the bath have already been established in the field of PWBs. On the other hand, the plating bath for via-filling generally is high in metal concentration and low in sulfuric acid concentration. In addition, it contains highly concentrated additives and uses the adsorption effect of the additives to ensure good filling performance.¹²⁻¹⁴ Thus, the plating bath for via-filling is greatly different from that for conformal plating in terms of bath composition and additives but there have been few reports on the mechanical properties of the film obtained by the bath.

Accordingly, we studied the mechanical properties of the copper films out of two types of acid copper plating solutions for conformal plating and two types for via-filling. As the former two types, Solution A intended for PWBs (Cu-Brite TH manufactured by Ebara-Udylite Co., Ltd.) and Solution B for HDI (Cu-Brite 21 manufactured by the same company) were used. As the latter two types, Solution C for LSI package substrate (Cu-Brite VF II manufactured by Ebara-Udylite Co., Ltd.) and Solution D prepared in reference to various reports¹⁵⁻¹⁸ were used.

Experimental

Tables 1 and 2 show the compositions and operating conditions of those baths used for our study. Table 3 shows the composition of Bath D. The mechanical properties of the films obtained by those solutions were assessed in the following manners: of 1) Measurement of X-ray diffraction (XRD) patterns, 2) Measurement of elongation and tensile strength, 3) Concentration analysis of impurities, 4) Measurement of stress, 5) Measurement of hardness, 6) Measurement of throwing power, 7) Thermal resistance test, and 8) Observation of surface condition after micro-etching with a scanning electron microscope (SEM).

Table 1 – Compositions and Operating Conditions of Conformal Type Plating Baths

CuSO ₄ ·5H ₂ O	75 g/L
H ₂ SO ₄	180 g/L
Cl ⁻	60 mg/L
Additives	Additive A*
	Additive B*
Cathode current density	0.75 & 3 A/dm ²
Temperature	25 °C
Agitation	Air

* Additives A, B, and C are commercially available products.

Table 2 – Compositions and Operating Conditions of Filling Type Plating Baths

CuSO ₄ ·5H ₂ O	200 g/L
H ₂ SO ₄	50 g/L
Cl ⁻	60 mg/L
Additives	Additive C*
	Additive D
Cathode current density	0.75 & 3 A/dm ²
Temperature	25 °C
Agitation	Air

Table 3 - Additive Composition of Bath D

PEG4000: Polyethylene glycol	50 mg/L
SPS: Bis-(sodium sulfopropyl)-disulfide	10 mg/L
JGB: Janus Green B	10 mg/L

Measurement of XRD Patterns

The XRD patterns were measured immediately after plating and after annealing (120°C for 1 hour) with the XRD-6100 (Shimadzu Corporation). Copper films of 24 µm were plated on copper-clad laminates (FR-4). They were plated in two levels of cathode current density, i.e., 0.75 A/dm², a rather low level for acid copper plating, and at a rather high cathode current density of 3 A/dm².

Measurement of Elongation and Tensile Strength

They were measured in the manner specified by the Japanese Industrial Standards (Z-2241, 1980). Specifically, 50-µm-thick films were plated on SUS plates in each bath. The films were annealed (120°C for 1 hour); cut into test pieces of a specific size, and then the properties were measured with a tensile tester (Autograph AGS-H 500N of Shimadzu Corporation). For plating, the cathode current density was conditioned in two ways, i.e., 0.75 and 3 A/dm².

Concentration Analysis of Impurities

The test pieces prepared for the measurement above were also used in obtaining the contents of organic impurities in them. For the elemental analysis of carbon and sulfur, high-frequency induction furnace method was used and for that of oxygen and nitrogen, inert gas fusion method.

Measurement of Stress

The stresses of the copper films were measured with a spiral stress tester (Yamamoto-MS Co., Ltd.). The 20-µm-thick films were plated at cathode current densities of 0.75 and 3 A/dm² and the difference in stress between the electro-deposited films was assessed.

Measurement of Hardness

The Vickers hardness around through hole corners was measured with a hardness tester (MVK-G2 of Akashi Co. Ltd.) immediately after plating and after annealing (120°C for 1 hour) with a weight of 10g and retention time of 15 seconds. Copper-clad laminates (FR-4), 1.6 mm in thickness and with through holes 1.0 mm in diameter, were used. Films 24 µm in thickness were plated at cathode current densities of 0.75 and 3 A/dm².

Measurement of Throwing Power and Thermal Resistance

The annealed (120°C for 1 hour) test pieces used for the hardness test above were again used for measuring the throwing power. They were also used to determine the chance of cracks around through holes after a thermal resistance test. Cracks were counted after the treatment with silicone oil which comprised 10 cycles of the following conditions: Dip in silicone oil of 260°C for 5 sec immediately followed by that of 25°C for 15 sec. Figure 1 shows the locations in which cracks were counted (a to f) and the calculation method of throwing power.

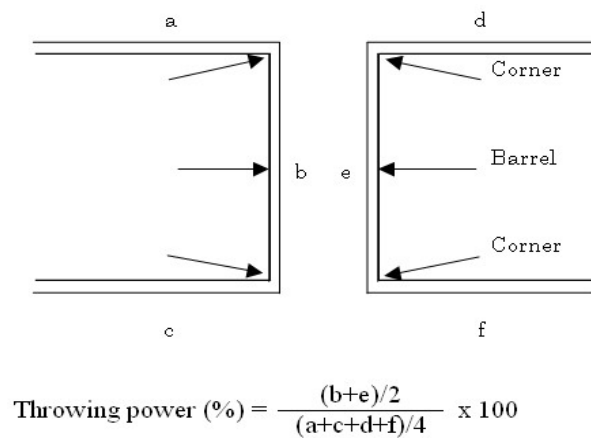


Figure 1 - Locations of Cracks and Calculation Method of Throwing Power

Observation of Surface Condition with SEM after Micro-etching

The copper surface of the annealed (120°C for 1 hour) test pieces used for the measurement of hardness were etched by 3 µm with an etchant composed of sodium peroxide (100 g/L) and sulfuric acid (100 g/L) and the surface condition was observed with a scanning electron microscope (JSM-5600 manufactured by JEOL, Ltd.)

Results and Discussion

XRD

Figure 2 shows the XRD patterns of the as-plated films and those after annealing (120°C for 1 hour). Immediately after plating at 0.75 A/dm², orientation (220) was dominant in all the films. However, orientations (111) and (200) were prevailing after annealing. On the other hand, in the case of 3 A/dm², the intensity of orientation (111) was as great in the films immediately after plating as those after annealing. Based on the supposition that the intensity of orientation (111) of pure copper according to JCPDS is 100, then copper has peaks at 46 and 20 for orientations (200) and (220), respectively. In general, the film deposited in the acid copper plating solution containing additives has orientations different from those of pure copper and consists of very fine crystals due to the effects of the additives. Presumably, when plated at a low cathode current density, the film has unique characteristics in terms of orientation reflecting the effects of the additives for they are sufficiently supplied to the surface of substrate. On the other hand, the additives may not demonstrate the effects when the cathode current density is high for copper ions preferentially reach the substrate before the additives do, resulting in the film which is similar to pure copper in terms of orientation even in the stage immediately after plating.

The shift in orientation towards the one similar to pure copper by annealing in both the cases was assumed to be due to recrystallization of the films. In other words, the metastable state of crystals immediately after plating seemed to have shifted towards the stable state as the crystal size of copper increased.

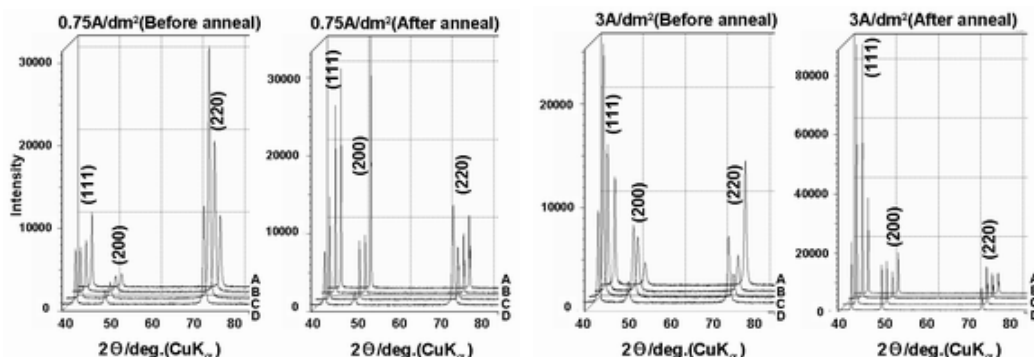


Figure 2 - XRD Patterns

Elongation and Tensile Strength

Figure 3 shows the results of measurement of elongation and tensile strength of the copper films after annealing (120 °C for 1 hour). The results indicate that the film deposited in Bath D is lower in elongation but higher in tensile strength in comparison with those out of the other baths. Considering the fact that the basic composition of Bath D is the same as that of Bath C, the drop in those mechanical properties may be attributed to the effects of the additives.

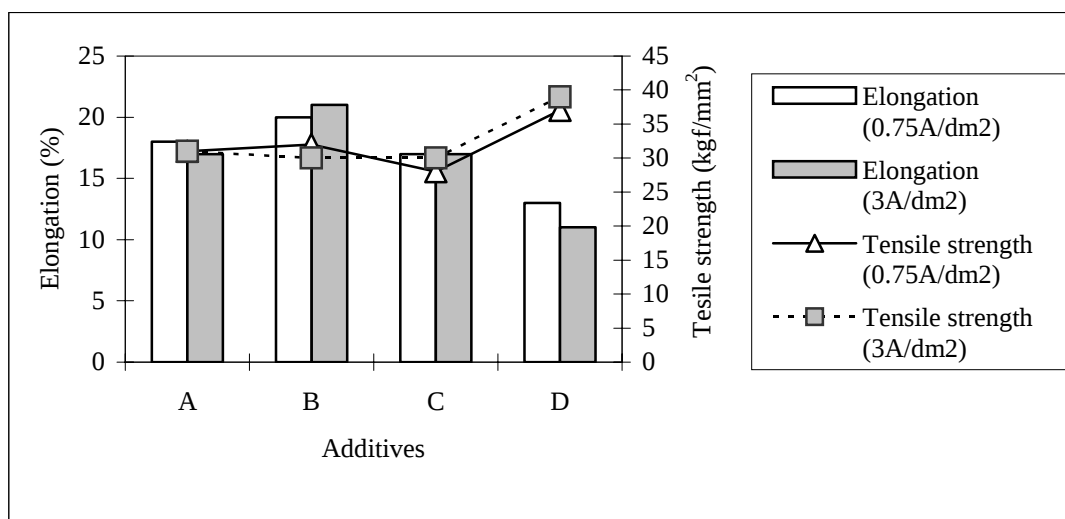


Figure 3 – Mechanical Properties

Content of Impurities

Table 4 shows the results of measurement of organic impurities contained in the films after annealing (120 °C for 1 hour). The measurement was performed to supplement the measurement of elongation and tensile strength. As a result, two tendencies were confirmed.

The first one is that the lower the cathode current density, the higher the co-deposition rate in every bath. The cause of this phenomenon seems, as was presumed based on the results of measurement of the XRD patterns, that copper is quite likely to co-deposit with the sufficient quantities of additives that have adsorbed on the surface of substrate when the cathode current density is low. On the other hand, at a high current density, copper deposition starts before the additives adsorb sufficiently on the substrate and thus co-deposition may not be great. It is assumed to be due to those phenomena that a low current density generally results in great effectiveness of the additives, great consumption rates of them, as well as great co-deposition rates.

Secondly, the quantity of impurities co-deposited in the film out of Bath D was confirmed to be greater than the other three. The drop in mechanical properties of the film out of Bath D is assumed to be attributable to the co-deposited impurities. Component JGB, which is the strongest adsorption property among them, seemed to be most likely to be taken in the film.

Table 4 – Impurities In The Films ($\times 10^{-3}$ mass %)

Bath	Base solution	A/dm ² ×min	C	S	O	N
A	75/180/60	0.75×200	1.5	< 0.3	5.8	0.6
A	75/180/60	3×50	1.4	< 0.3	4.7	0.6
B	75/180/60	0.75×200	1.5	< 0.3	4.5	0.6
B	75/180/60	3×50	1.2	< 0.3	4.6	0.6
C	200/50/60	0.75×200	1.2	< 0.3	6.3	0.6
C	200/50/60	3×50	1.2	< 0.3	4.7	0.5
D	200/50/60	0.75×200	8.5	0.6	7.8	0.8
D	200/50/60	3×50	6.3	0.7	6.6	1.0

Stress Measurement

Table 5 shows the values of stress in electro-deposits, 20 μm -thick, measured by spiral method. Tensile stress is shown as positive and compression stress as negative in the table. As a result, in the case of the two types of base solutions and Bath D, the tensile stress was greater for the current density of 3 A/dm² than for 0.75 A/dm². On the other hand, Baths A, B, and C showed the opposite results. Since the base solutions with no additives showed the same tendency as Bath D, it seems that the stress in electro-deposits is not necessarily depends on the co-deposition of the additives. Taking the results into consideration with those of Item 2) above, it may not be possible to determine the order of superiority between the films.

Table 5 – Stress In Electro-Deposits Measured By Spiral Method

(kg/mm ²)				(kg/mm ²)			
	No additives (75/180/60)	Bath A	Bath B		No additives (200/50/60)	Bath C	Bath D
0.75A/dm ²	1.5	12.1	18.7	0.75A/dm ²	1.38	2.46	-1.92
3A/dm ²	3.54	1.81	-0.28	3A/dm ²	2.28	-0.6	1.27

Hardness Measurement

Table 6 shows the results of measurement of Vickers hardness around the through hole corners, immediately after plating and after annealing (120 °C for 1 hour) for all the baths. Copper-clad laminates (FR-4), 1.6 mm in thickness and with through holes 1.0 mm in diameter, were used. All the films immediately after plating had great values, 150 Hv or more, but most of them dropped to the levels around 100 Hv after annealing. For the films out of Bath D, however, the hardness remained high even after annealing, being more than 150 Hv.

In consideration of the results of the XRD measurement above, which showed intense inclination toward orientation (111) after annealing, it can be concluded that there is no relationship between the type of orientation of the film and its hardness. However, a “no relationship found” may be caused by the selection of the measuring points. In other words, while the surface of substrate was observed by the XRD measurement, hardness was measured around the through hole corners. The corners are subjected to rather vigorous agitation compared to other locations. The great hardness of the films out of Bath D only after annealing may be attributed to the greater effect of agitation than the other baths. In other words, to the corners that were subjected to vigorous agitation, the additives were supplied in greater quantities than to the surface of substrate and this phenomenon may also explain the results.

Table 6 – Vickers Hardness

		(Hv)			
		Bath A	Bath B	Bath C	Bath D
0.75 A/dm ²	Before annealing	192	180	173	203
	After annealing	92	95	98	169
3 A/dm ²	Before annealing	201	183	182	221
	After annealing	106	102	109	179

Measurement of Throwing Power and Thermal Resistance Test

Table 7 shows the results of measurement of throwing power and crack ratio after the thermal resistance test. In the measurement of throwing power, good values of 80% or more were obtained for all the baths. However, with regard to cracks, a large number of them were found in the test pieces out of Bath D. The cause for the large number of them is assumed to be the great chance of co-deposition of the additives as well as the profile of deposits. As shown in Figure 4, in Bath D, one wall tended to have thick deposits while the opposite wall had thin deposits. Thus, the deposition profile in Bath D greatly depends on the condition of agitation and the thin deposits may be caused by constant exposure to the solution by which the suppression effect of the additives grew. In the area of thin deposits, the volume of co-deposited additives is assumed to be comparatively great to other areas. Therefore, it seems to have caused many cracks after the thermal resistance test in spite of the good throwing power of 80% or more Bath D (Figure 4) has, which is comparable to the other baths, according to the results of measurement based on the calculation method shown in Figure. 1.

Table 7 – Throwing Power and Crack Ratio Around Through Holes

		Bath A	Bath B	Bath C	Bath D
0.75 A/dm ²	Throwing power (%)	94.5	99.7	93.5	90.9
	Crack ratio (n/30)	0	0	0	17 (57%)
3 A/dm ²	Throwing power (%)	89.8	95.1	82.0	81.8
	Crack ratio (n/30)	0	0	0	30 (100%)

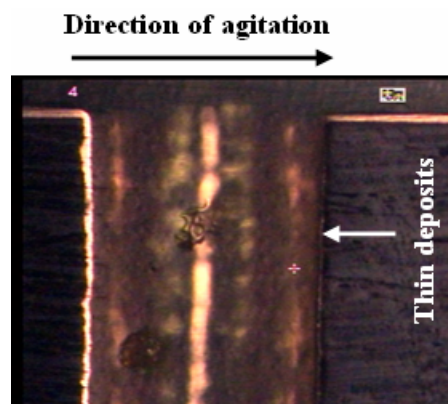
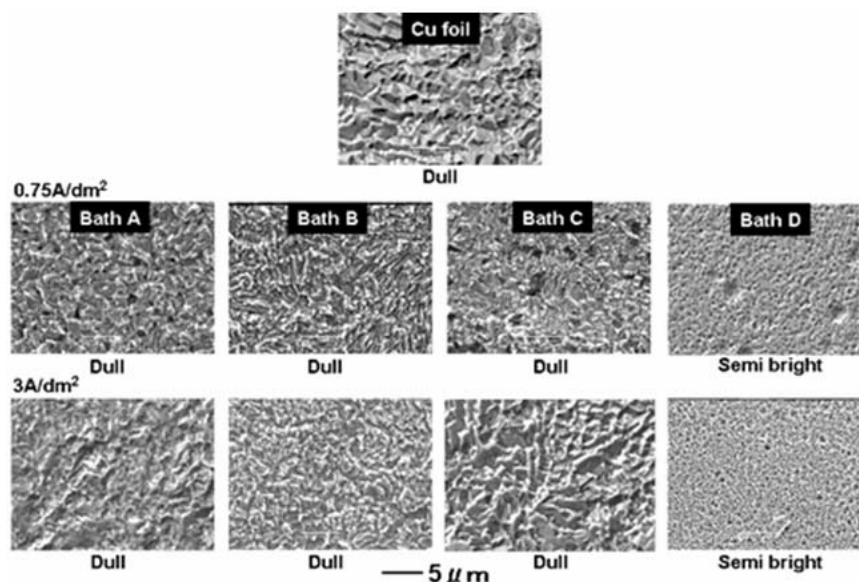
**Figure 4 – Cross-Sectional View of a Through Hole Plated in Bath D****SEM images of Surfaces after Micro-Etching**

Figure 5 shows the SEM images of 4 types of copper films after etching. The top image is the surface of a general copper foil treated in the same manner and shown for the purpose of comparison. The test pieces were plated in the respective baths and annealed (120 °C for 1 hour). As the etchant, a mixture of sodium peroxide (100 g/L) and sulfuric acid (100 g/L) was used. The films were etched by 3 μm . The flash etching process of the semi-additive technique, one of the build-up techniques, was simulated. In the process, the surface of copper circuits was etched by 1 to 3 μm . If the surface of copper lines remains to be bright even after the etching, sufficient unevenness may not be obtained in the roughening stage for the anchor effect that is essential for good adhesion with the resin in forming a build-up structure in the later stage. For that reason, the copper film is desirably mat after the etching of 1 to 3 μm , i.e., with unevenness of 1 to 2 μm in the surface. After the test, all the films except those out of Bath D had a mat appearance with a proper level of unevenness after the etching. The films deposited in Bath D, however, were semi-bright. Since etching depths, which were proven by the measurement of weight, were almost the same, the films out of Bath D are quite likely to have a weakness in terms of etching characteristic. As was seen in the results of the measurement of XRD patterns, all the films including those out of Bath D preferentially had orientation (111) after annealing. However, the etching characteristic may likely be affected more by the condition of co-deposition of the additives and the fine crystal structure than the orientation of the film.

**Figure 5 – SEM Images of the Films after Micro-Etching by 3 μm**

Conclusion

Most of the reports on the acid copper plating solution for via-filling in the past have dealt with the adsorption mechanism of additives, the via-filling mechanism, and the plating conditions. However, there has been little study on the characteristics of copper films out of acid copper plating solutions for via-filling. Therefore, we concentrated our research on the analysis of the films in various manners in comparison with those out of acid copper plating solutions for conformal plating. As a result, it was confirmed that the films out of Bath D were greatly different from those out of Baths A to C in connection with the characteristics. The following three items were considered to have influence over the characteristics of the copper films:

- Type of additive
- Bath composition
- Plating conditions

The above items were confirmed to have influences over the following:

- Orientation of film
- Change in mechanical properties by annealing
- Co-deposition of additives
- Dependence of deposition efficiency on agitation
- Etching characteristic of the film

The drop in mechanical properties of the film due to co-deposition of the additives was difficult to overcome even by annealing. Therefore, the selection of best-suited additives is essential in obtaining a film with desirable mechanical properties. It is especially important to pay careful attention to the bath composition in the use of acid copper plating solution for via-filling for which levelers with a strong adsorption effect, such as JGB, are required. In the future, we would like to study further not only the deposition characteristics of the solution like filling performance but also the characteristics of the film obtained.

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