Improvement of Adhesion for Layer-to-Layer Connection for Built-up Printed Circuit Boards

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It appears possible to improve adhesion of copper printed circuits to insulating layers on resin substrates. This study confirmed that adhesion can be improved by retarding the rate of electroless copper deposition through addition of potassium thiocyanate.

The density of printed circuit boards has increased with miniaturization of the electronic devices.[1-3] The build-up method has been found useful for the fabrication of high-density printed circuit boards. It is a new manufacturing process implemented by stacking the insulation and conductive layers sequentially on the core circuit boards, as illustrated in Fig. 1. This process requires several technologies, such as selection of insulation resin, formation of via-holes and preparation of fine patterns. The adhesion strength between copper wiring and insulation layers is critical for connection reliability.[4,5]

Adhesion strength is mainly governed by etching of the insulation layer. In practice, adhesion strength of 0.8 to 1.0 kgf/cm is required between the insulation layer and the deposited copper. High adhesion, however, is not consistently obtained. Accordingly, improvement of adhesion strength between the insulation layer and deposited copper was the objective of this study.

Experimental Procedure

Two types of resin substrate were used in this study: liquid photoimageable dielectric[a], which is coated about 50 μm thick on the epoxy resin (LPD) and unclad epoxy resin. The unclad epoxy resin was obtained by cupric chloride etching, using the copper-laminated substrate, which thus had a roughened surface. LPD resin was treated with a desmear solution to get fine etched holes. Both resins were then treated with a palladium catalyst, followed by 0.5 μm of electroless copper plating, and finally copper electroplating. Adhesion strength was measured after 30 μm of copper electroplating.

The experimental procedure is shown in Table 1. The basic bath composition and operating conditions of the electroless copper plating are shown in Table 2. The fracture mode after peeling of the deposited copper from the resin substrate was examined by a scanning electron microscope (SEM). As shown in Fig. 2, the plated copper films were cut into 1-cm strips and the adhesion strength measured, using an Instron tester at cross-head-speed of 30 mm/min.

[a] ILD-300, JSR Co.

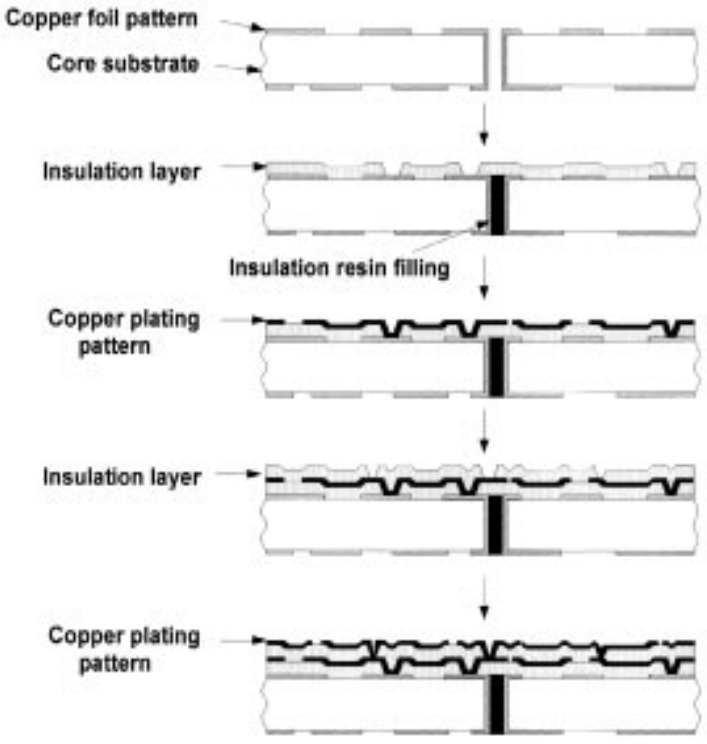

Fig. 1—Preparation of built-up printed circuit boards.

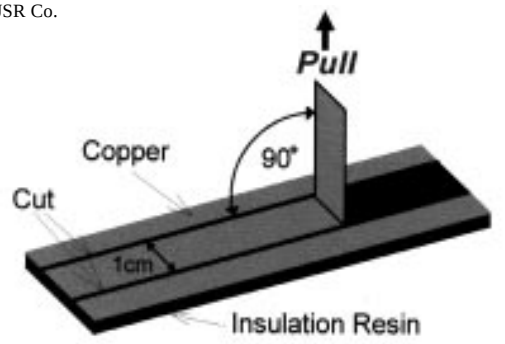

Fig. 2—Peeling test evaluation.

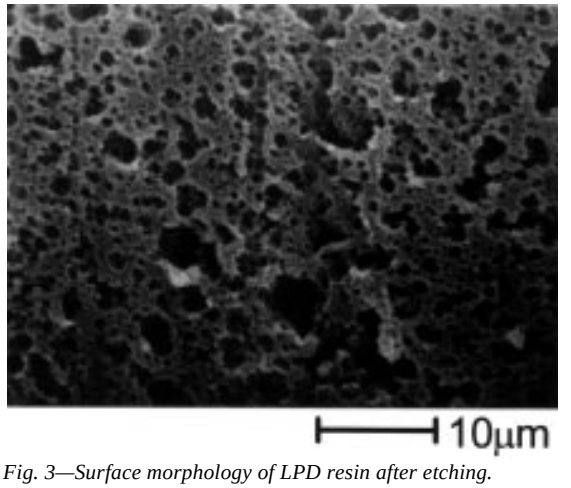

Fig. 3—Surface morphology of LPD resin after etching.

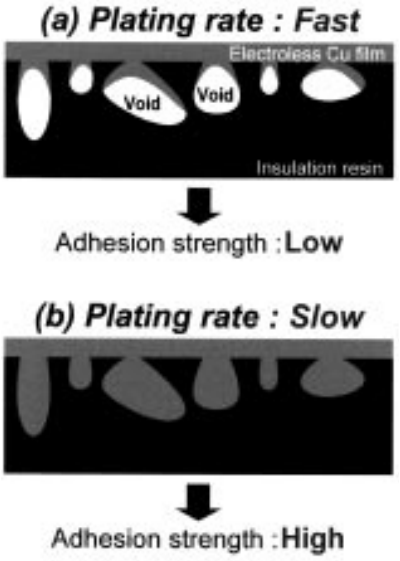

Fig. 4—Schematic model of cross sectional views of electroless Cu plating: (a) with fast plating rate; (b) with slow plating rate.

Results and Discussion

Pretreatment conditions, such as swelling, desmear and plating may affect the adhesion strength between copper and the insulation resin. Among these factors, the desmear and plating conditions are the focus of this study.

Influence of the Desmear Treatment

LPD resin was etched with a desmear solution for 15 to 30 min at 80 °C to get fine etched holes. The surface morphologies after etching are shown in Fig. 3. Fine holes ranging from 1 to 4 μm were distributed on the etched surface. The high adhesion strength between the deposited copper and the resin may therefore be obtained because of an anchor effect. The adhesion strength after electroplating showed only 0.2 to 0.5 kgf/cm, however, which is too low to be applicable to fabrication of copper circuits on the resin.

Adhesion Improvement by Plating Rate Control

These results suggested that high adhesion strength could not be obtained even under optimum etching conditions. This is because auto-catalytic deposition occurs continuously at the upper portions of the etched holes. Thus, most of the copper ions are consumed before reaching the bottom area of the holes; consequently, the bottom portions of the holes are not plated, preventing effective anchoring. The model can be illustrated by the cross sectional views of deposition films on the etched area, as shown in Fig. 4. If the reaction rate of electroless plating can be retarded, copper ions may penetrate the small etched holes, gradually filling them with copper. In this case, efficient anchor effect may be achieved after electroplating and good adhesion strength can be obtained (Fig.4-b).

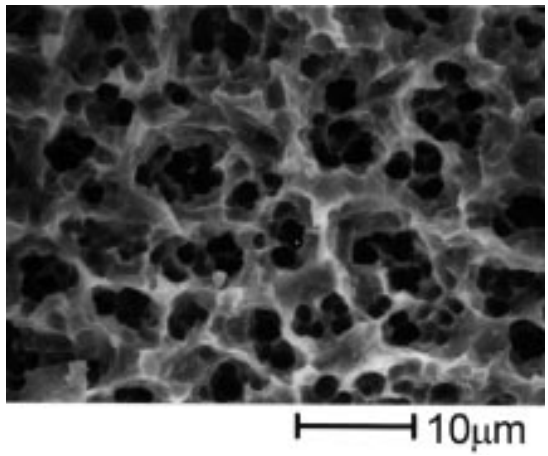

Fig. 5—Surface morphology of epoxy resin after removal of copper.

Based on this assumption, various kinds of additives with catalytic poisoning effect are evaluated for retardation of the reaction rate for electroless copper plating.[6] To avoid the size effect of the etched holes from desmear treatment, unclad resin was used for evaluation of the adhesion improvement. The surface morphologies of unclad resin obtained from copper laminated substrate are shown in Fig. 5. The holes are essentially about 2 to 5 μm in diameter; however, they seem larger because of agglomeration in the vicinity of the resin surface.

The results are shown in Fig. 6. Electroless copper reaction started on the palladium nucleus at the early stages. Within a

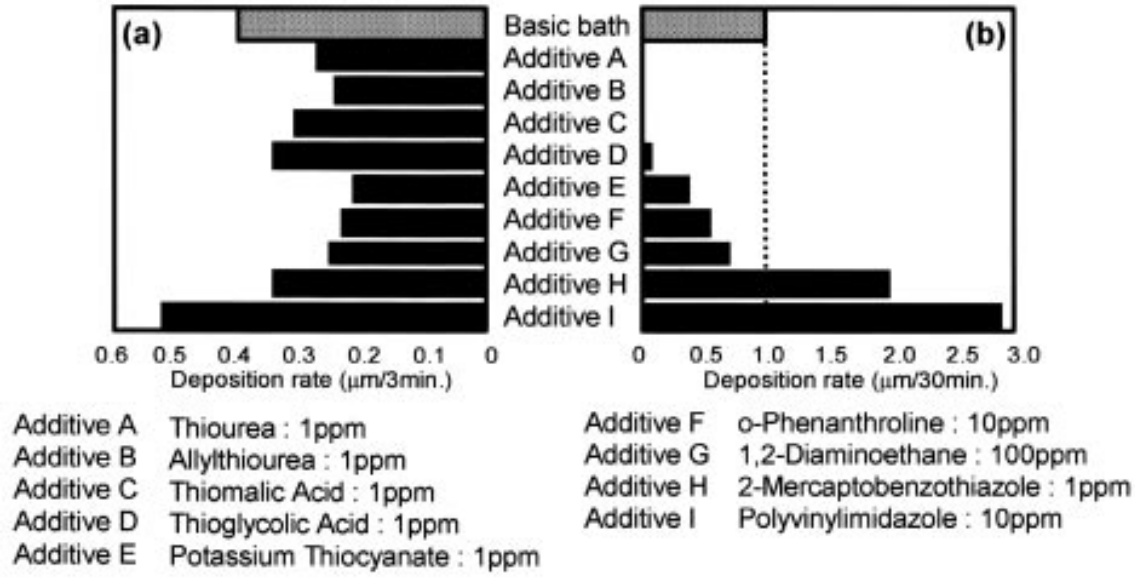

Fig. 6—Effects of various additives on electroless copper plating rate: (a) on palladium catalytic nuclei; (b) on copper.

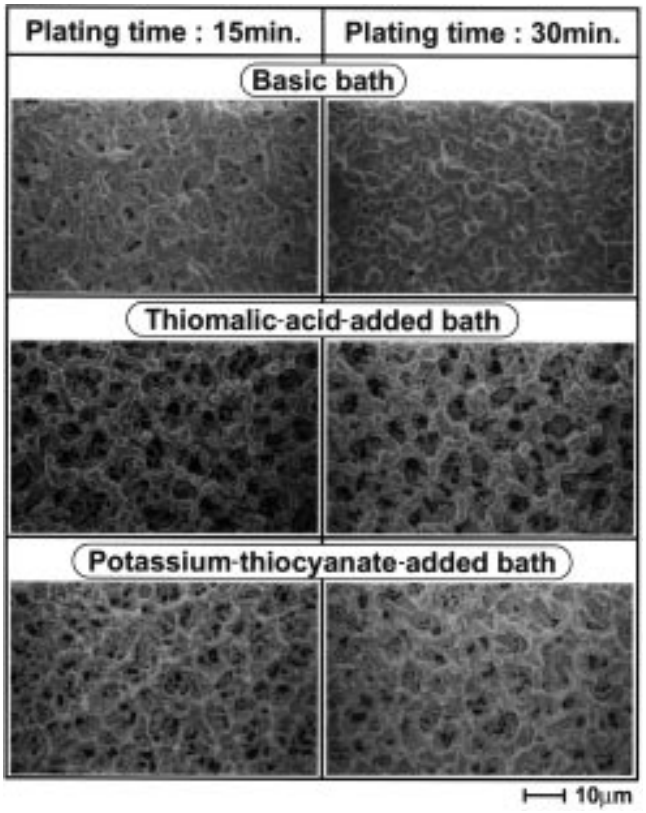

Fig. 7—Surface morphologies of electroless copper on epoxy resin.

few min, the copper deposition covered the palladium catalysts, then continued on top of the deposited copper. Here, the differences of deposition rate with copper substrate and the palladium-treated epoxy resin were evaluated. The deposition rate for the first 3 min was measured and was regarded as the deposition rate on the palladium adsorbed resin because copper covered within a few min.

Table 1
Experimental Procedure

Swelling: 80 °C
▼
Etching: 80 °C
▼
Neutralization: 45 °C, 5 min
▼
Conditioning: 45 °C, 5 min
▼
Predipping: 25 °C, 2 min
▽
Catalyzing: 25 °C, 5 min
▼
Accelerating: 25 °C, 5 min
(5% H_2SO_4)
▼
Electroless Cu plating
▼
Cu electroplating

LPD resin

Epoxy resin
(etched out Cu foil)

▼ with rinsing ▽ without rinsing

Process compounds supplied by Shipley Co.

Table 2
Basic Bath Composition & Operating Conditions For Electroless Cu Plating

$CuSO_4 \cdot 5H_2O$	0.03 M
EDTA_4H	0.24 M
2,2_-bipyridine	10 ppm
Polyethylene glycol 1000	100 ppm
Temp	60 °C
pH	12.5
Agitation	air

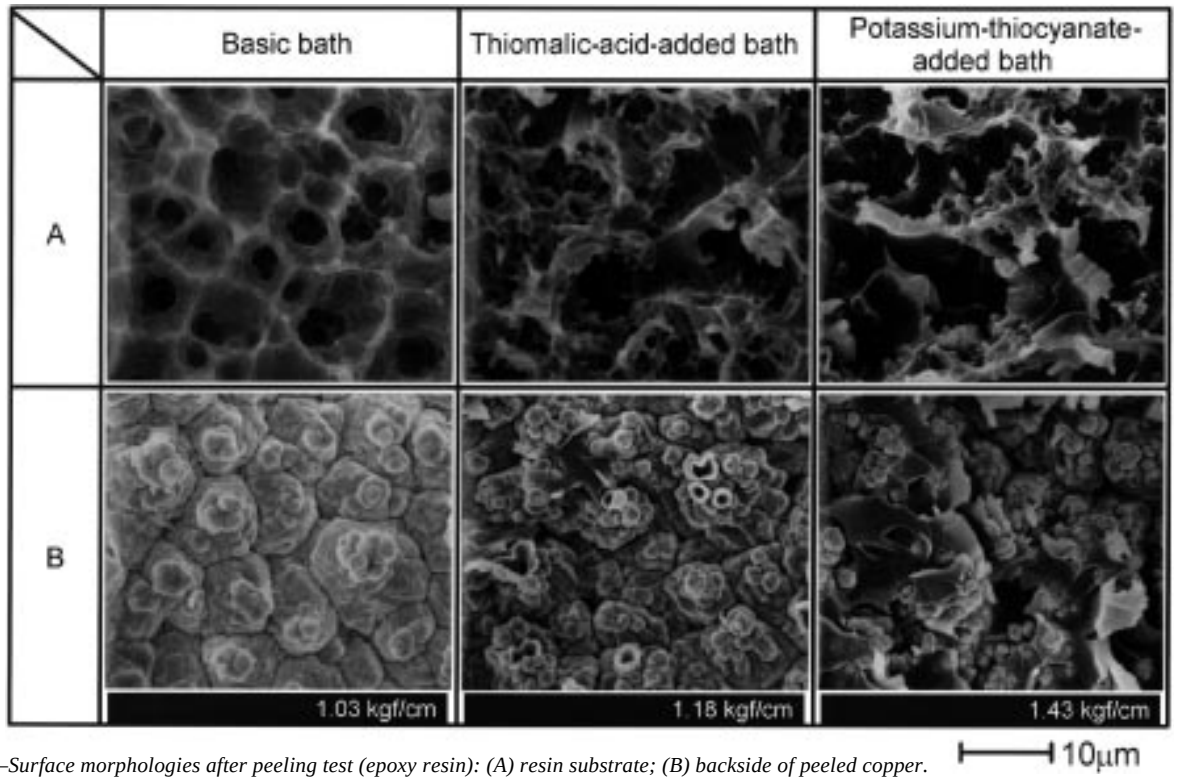

Fig. 8—Surface morphologies after peeling test (epoxy resin): (A) resin substrate; (B) backside of peeled copper.

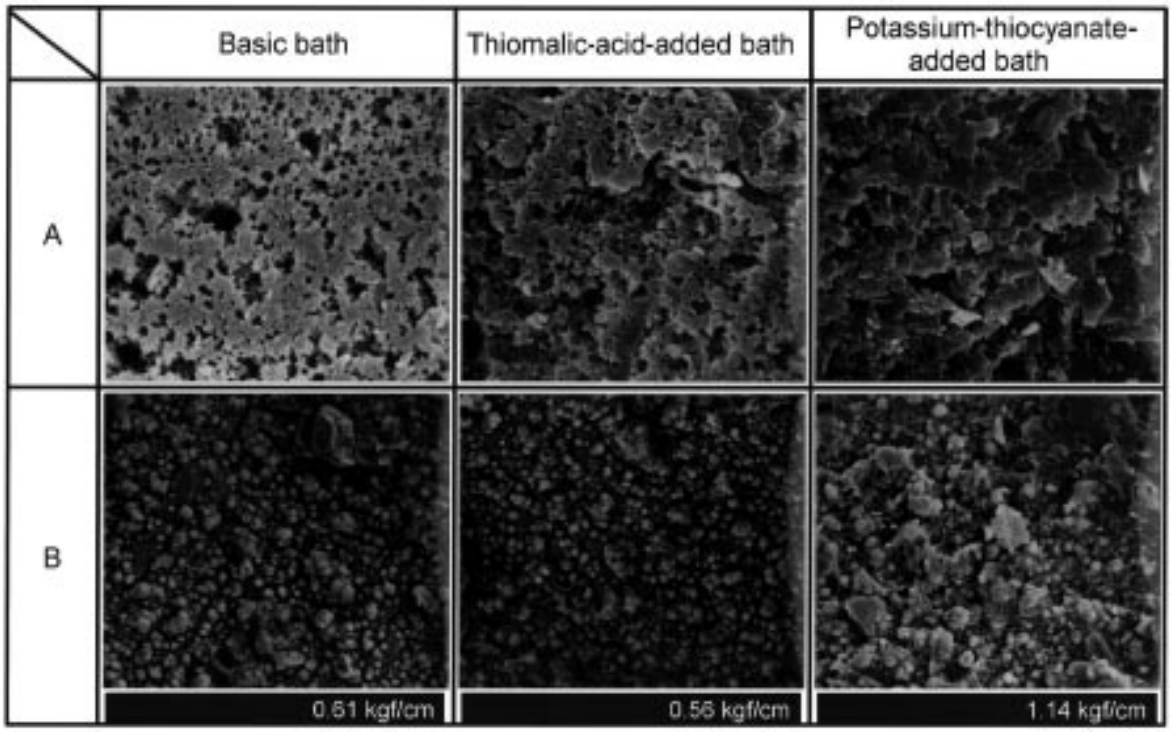

Fig. 9—Surface morphologies after peeling test (LPD resin): (A) resin substrate; (B) backside of peeled copper.

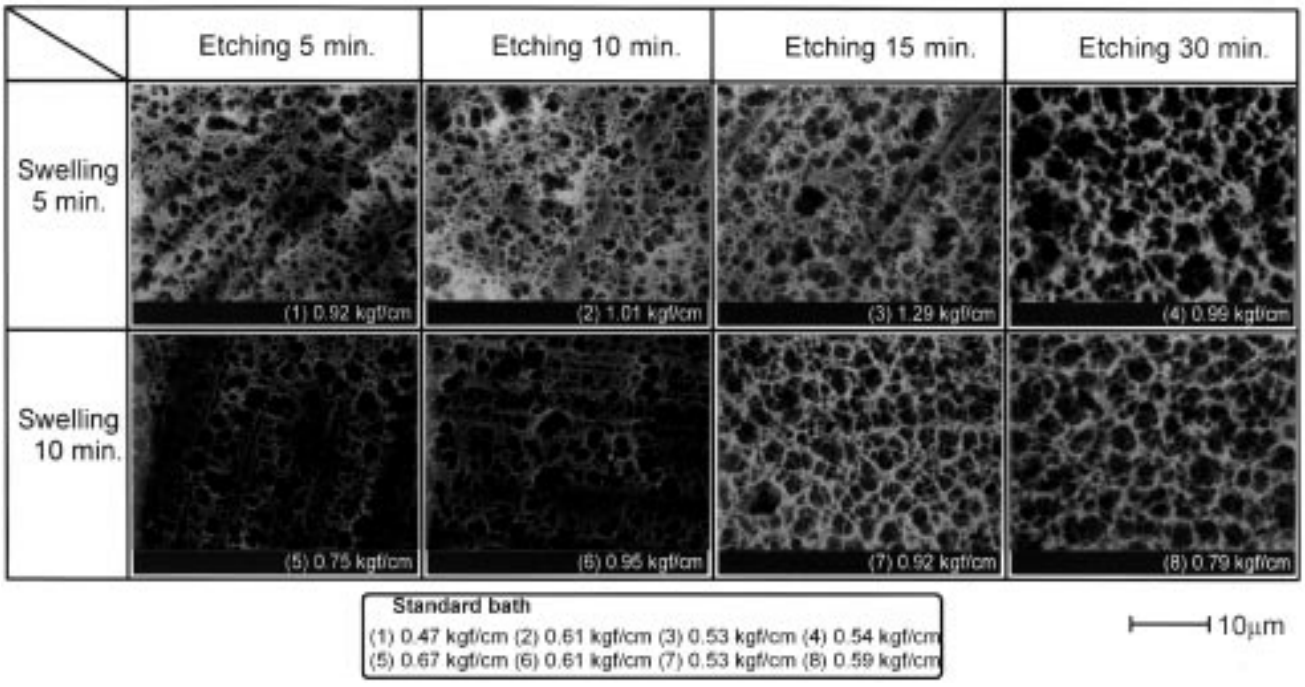

Fig. 10—Surface morphologies of resin after etching (potassium thiocyanate bath).

The reaction-inhibiting thio-compound additives were found to have little effect on the deposition rate on the palladium-adsorbed resin. On the other hand, the reaction rate on the copper substrate was retarded by the addition of thio-compounds because they tend to be adsorbed on the copper surface and act as a catalytic poisoner for the autocatalytic reaction. Once copper was deposited on the palladium-adsorbed resin, the plating reaction stopped. Consequently, copper ions could reach and be deposited at the bottom of the holes, leading to a successful anchor effect. Based on these results, thiomalic acid and potassium thiocyanate were selected as additives.

Influence of Surface Coverage on the Resin by Additive Agents

The surfaces of the etched holes were covered within 15 min of plating time with a standard bath. On the other hand, the surface was not completely covered even after 15 min with the thio-compound addition bath because the plating rate was slower and the reaction reached the bottom of the holes. In the

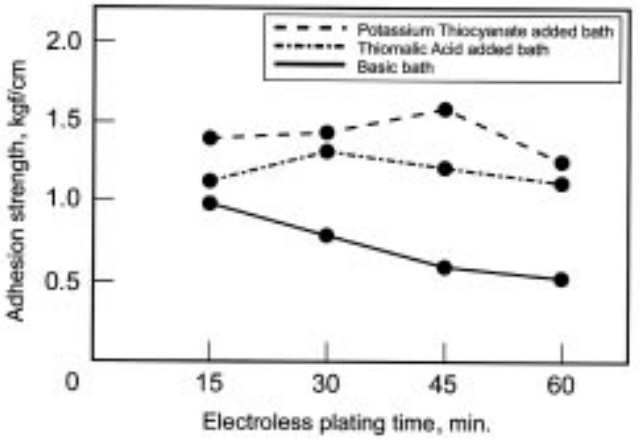

Fig. 11—Influence of electroless copper plating time on adhesion strength (epoxy resin).

latter case, therefore, plating was extended to 30 min. The surface morphologies after the electroless copper plating are shown in Fig. 7.

The adhesion strength was compared using the basic bath, the thiomalic-acid-added bath and the potassium-thiocyanate-added bath. Resin surfaces and peeled copper foils were observed by SEM after the measurement of adhesion strength. The results are shown in Fig. 8. Adhesion strength is obtained in the following order: 1.03 kgf/cm from the basic bath, 1.18 kgf/cm from the thiomalic-acid-added bath and 1.43 kgf/cm from the potassium-thiocyanate-added bath. The adhesion strength obtained from the thiomalic-acid-added bath was almost the same as from the basic bath. This was because copper was deposited only on the palladium-adsorbed resin and the deposition reaction stopped when copper completely covered the surface of the resin. Accordingly, the etched holes were not filled with copper, voids were created after electroplating and the adhesion strength did not increase.

For the potassium-thiocyanate-added bath, copper ions apparently reached the bottom of the etched holes and led to an anchor effect between resin and copper. Because the plating rate was retarded on the copper surface, the deposition reaction could occur at the bottom of the holes, allowing sufficient adhesion. Fragments of resin were found adhering on the copper side, plus fragments of copper on the resin side after the peeling test.

Adhesion strength was also evaluated on LPD resin. The results are shown in Fig. 9. Adhesion strength was 0.61 kgf/cm from the basic bath, 0.56 kgf/cm for the thiomalic-acid-added bath, and significantly higher (1.14 kgf/cm) for the potassium-thiocyanate-added bath. As expected, torn fragments of resin were found on the peeled copper in the case of the potassium-thiocyanate-added bath.

Influence of Etching Treatment Time

The etched holes become large with prolonged etching. The influence of the etched hole size for the adhesion strength was therefore evaluated. The results are shown in Fig. 10. The adhesion strength did not increase with etching time because the resin was overetched.

Influence of Electroless Copper Plating Time

The relationship between adhesion strength and electroless copper plating time was examined using unclad epoxy resin. Adhesion strength was affected by the plating time. As shown in Fig. 11, adhesion strength reached its highest value after approximately 15 min and decreased with increased plating time. The reason is that hydrogen and water are occluded in the deposits with increasing time, degrading the anchor effect between the resin and deposited copper.

In the case of LPD resin, the adhesion strength decreased significantly with increased plating time. This was because the resin was degraded in the bath with a pH above 12 and high temperature.

Summary

Adhesion strength between the insulation layer and the conductive layer was investigated, using LPD resin and unclad resin. It is confirmed that the adhesion strength can be improved by reducing the electroless copper deposition rate. Addition of potassium thiocyanate as a catalytic poisoner was effective in retarding the plating rate. Adhesion strengths of 1.14 kgf/cm on LPD resin and 1.43 kgf/cm on unclad resin were obtained.

Editor's note: Manuscript received, April 1999; revision received, June 1999.

References

1. Y. Tsukada, Y. Maeda & K. Yamanaka, *Proc. IEPS/ISHM 2nd Int'l Conf. & Exhibition on Multichip Modules*, 252 (1993).
2. Y. Tsukada, S. Tsuchida & Y. Mashimoto, *Proc. 7th IMC*, 252 (1991).
3. Y. Uno, Y. Takahashi, S. Ozawa, K. Nakakuki, Y. Iguchi, T. Kanamori & Y. Kasuya, *Proc. IMC*, **WB1-4, 61, (April 1994).**
4. H. Honma & T. Fujinami, *JIPC (Japan)*, **6**, 209 (1991).
5. T. Fujinami, K. Kou & H. Honma, *J. Japan Inst. Electronics Packaging (Japan)*, **1**, 66 (1998).
6. T. Fujinami & H. Honma, *J. Surf. Fin. Soc. (Japan)*, **43**, 595 (1992).

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