Adhesion between Flat Copper Surfaces and Epoxy Insulation Resin without Roughening

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Key Words : Printed Circuit Boards, Inner Layer Copper, Sulfide Treatment, Adhesion Strength

Introduction

Adhesion between the copper conductor and laminating epoxy resin is very important in the production of multi layer printed circuit boards, and is done by forming roughened films on the copper surface by the formation of copper oxide with black oxide treatment and oxide reduction using DMAB or NaBH$_4$, the formation of dendric Cu-Ni-P films, or etching.

Conductor surface roughness causes a problem in high-speed signal propagation with electronic component miniaturization. It is suggested that the alternative is the formation of insulation layer on a flat copper surface without roughening.

Sulfide-treated rubber adheres strongly to a flat metal surface using triazine dithiole or its derivatives. We studied adhesion strength between flat copper and epoxy resin by forming sulfur codeposited copper films or sulfide films on the flat copper surface.

Experiments

Double-sided copper-laminated boards 50×100 mm were used as samples. Sulfur containing copper was deposited about 0.5 μm using an electroless copper plating bath with trace amounts of sulfide compound. After degreasing and soft etching, the sample was immersed in the electroless copper plating bath operated at 60°C and pH 1.5 with the following bath composition: 0.03 M CuSO$_4$, 0.24 M EDTA, 0.2 M HCHO, 10 ppm 2,2'-dipyridine, and 1-1000 ppm Na$_2$S (sodium sulfide). Sulfide or triazine dithiole films were also formed on the sample by dipping in the sodium sulfide or triazine dithiole solution.

Epoxy prepreg resin was coated and pressed on treated copper samples at 140°C for 20 min., then raised to 175°C for 100 min. at 30 kgf/cm$^2$. Adhesion strength was then measured by an instron tester. A solder float test was also conducted based on JIS, floating the prepreg-coated sample on the solder bath at 260°C and thermal resistance was determined from the onset time of blisters or peeling.

Results

Formation of sulfur codeposited copper

Copper films obtaining from electroless copper plating without or with the addition of sodium sulfide adhered to epoxy resin. Adhesion strength was about 0.4 kgf/cm for the additive-free bath and 1.2 kgf/cm for the 100 ppm sodium sulfide bath. Resin adhered to the copper side when laminated copper was torn from the resin layer.

Surface morphology did not change with increasing sulfur additives (Fig. 1). In the solder float test, thermal resistance increased with increasing amounts of sodium sulfide. According to JIS, thermal resistance must exceed 20 sec. We confirmed that the addition of sodium sulfide over 10 ppm to the electroless copper plating bath effectively improved adhesion strength between copper and epoxy resin.

The sulfur distribution in copper films from the sodium sulfide bath was measured by EPMA (Fig. 2). Sulfur was detected with increasing addition. Adhe-
Letters

<table>
<thead>
<tr>
<th>Additive-free</th>
<th>Sodium sulfide concentration</th>
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<td>SEM</td>
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<td>Solder float test (sec.)</td>
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Fig. 1  Effect of sodium sulfide concentration on surface morphology and adhesion strength.

Fig. 2  EPMA analysis for sulfur distribution at surface of deposited copper films.

Fig. 3  Interface between flat copper and epoxy resin.

Adhesion strength and thermal resistance improved with increasing sulfur content in deposited copper films.

Similar effects for improving adhesion strength and thermal resistance were confirmed by using other sulfur compounds such as thioglycolic acid and 2-mercaptobenzothiazole.

Improvement of other sulfur compound treatment

Sulfide films were also formed on the copper surface by dipping several sulfide solutions. Sodium sulfide showed the highest values in the solder float test. Treated copper surfaces turned darkish black and thermal resistance improved with increasing treatment time. Thermal resistance decreased in the treatment of high concentrations of sodium sulfide due to increased sulfide layer thickness.

Triazine dithiole treatment also similarly improved adhesion strength between copper and epoxy resin.

Adhesion mechanism

The adhesion strength was improved by forming sulfur-codeposited or sulfide films on the metal surface using various sulfur additives. Adhesion was improved by chemical bonding between epoxy groups in the epoxy resin and sulfur atoms in the sulfur-codeposited copper or sulfide films (Fig. 3).

Summary

Adhesion strength between flat copper and epoxy resin was studied by forming sulfur codeposited copper films or sulfide films on the flat copper surface, with the following results:

1. Copper films from an electroless copper plating bath with sodium sulfide strongly adhered to epoxy resin. Adhesion strength was particularly improved by adding over 100 ppm sodium sulfide to the plating bath.

2. The formation of sulfide films on the copper surface using sodium sulfide solution also effectively improved adhesion. Triazine dithiole treatment also showed a similar effect.

(Received August 19, 1998; Accepted October 2, 1998)

References

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