Direct Metallization Using Sulfonation of Thermosetting Polyphenylene Ether Resin Laminate

By H. Nawafune, T. Kanai, S. Mizumoto & M. Seita

A new, direct metallization method of a thermosetting allylated poly-2,6-dimethyl-1,4-phenylene ether (A-PPE) resin for manufacture of printed wiring boards is proposed. The A-PPE resin surface was roughened by the potassium permanganate/sodium hydroxide mixed solution treatment. The sulfo group, as a cation exchange group, was introduced onto the A-PPE resin surface via sulfuric acid treatment. The amount of adsorbed copper ions increased with increasing sulfuric acid concentration, and was 1000 nmol/cm^2 for the sample treated with 18 M sulfuric acid at 70 °C for five min. The thickness of the thin copper film formed after the reduction process was estimated to be 71 nm. The test samples permit direct electroplating of copper at a current density of 2 A/dm^2.

Recently, much importance has been attached to the problem of environmental pollution. The use of electroless copper plating becomes increasingly difficult because of the use of harmful formaldehyde and the problems associated with waste treatment of chelating agents in spent solutions. The electroless plating processes are known for a conductive film, such as palladium colloid, conductive polymer, or graphite for direct plating to a circuit board.[1]

The electronics industry is constantly searching for organic materials with low dielectric constant and high glass transition temperature for printed wiring boards. Thermoplastic poly-2,6-dimethyl-1,4-phenylene ether (PPE) was chemically modified into thermosetting allylated PPE without sacrificing its superior properties, such as low dielectric constant, high glass transition temperature, and low water absorption.[2]

In this paper, a new method for the formation of a thin copper film on a thermosetting allylated PPE(A-PPE) resin laminate through surface modification by sulfonation, followed by adsorption and reduction of copper ion will be reported.

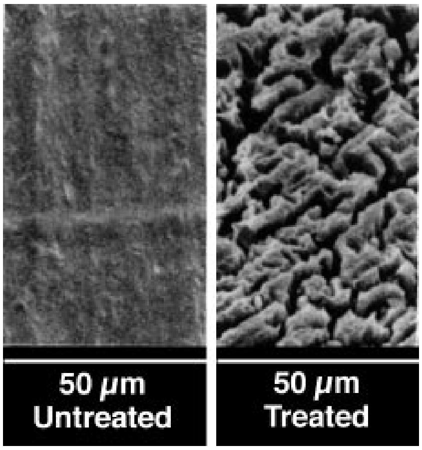


Fig. 1—Surface morphology of untreated (left) and treated (right) A-PPE resin laminate roughened with 0.3 M potassium permanganate/6 M sodium hydroxide solution at 100 °C for 2 hr.

Experimental Procedure

Chemical Roughing & Sulfonation of the A-PPE Resin Surface

The allylated poly-phenylene ether(A-PPE) resin laminate, which has the following structural formula, was used.[2] The A-PPE resin surface was roughened with alkaline permanganate etchant. Each sample of the A-PPE resin laminate was immersed in 10 to 18 M sulfuric acid at a temperature of 40 to 70 °C, thoroughly rinsed, then dried. The degree of sulfonation on the A-PPE laminate surface was determined with an FTIR spectrometer equipped with a microscope, using an ATR objective (diamond). ATR spectra in the 2000 to 700 cm^{-1} range were obtained by co-adding 100 scans at 4 cm^{-1} resolution with a narrow bandpass HgCdTe (MCT) detector.

Adsorption, Reduction Treatment of Copper Ion & Peel Strength

Each sample of the sulfonated A-PPE resin laminate was immersed in 0.05 M copper sulfate solution for 5 min to adsorb the copper ions. After rinsing, the copper-ion-adsorbed samples were immersed in sodium borohydride (NaBH$_4$) solution for 10 min, to reduce the copper ions to a thin copper film on the laminate surface. The surface conductivity of the reduced copper film was measured with a digital multimeter.

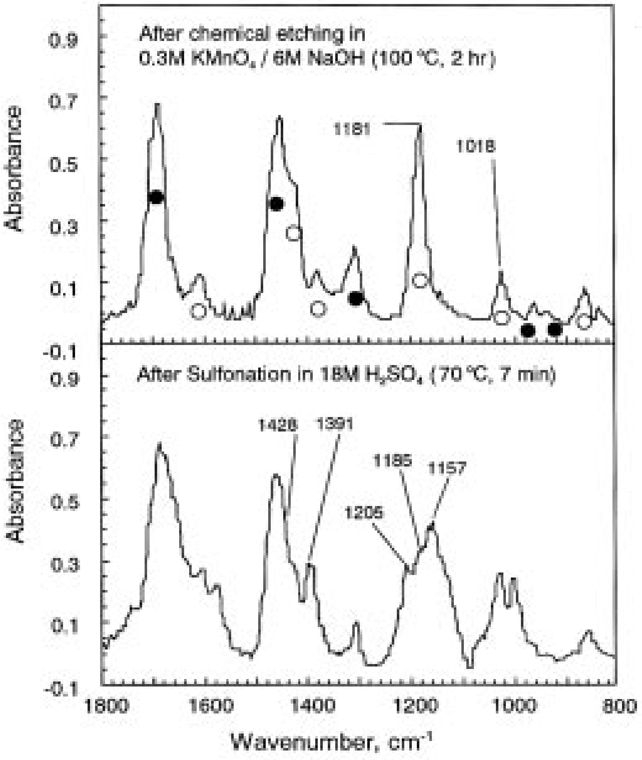


Fig. 2—FTIR ATR spectra of thermosetting A-PPE resin laminate surface: (○) A-PPE; (●) Triallyl-1,3,5-triamino-2,4,6-trione.

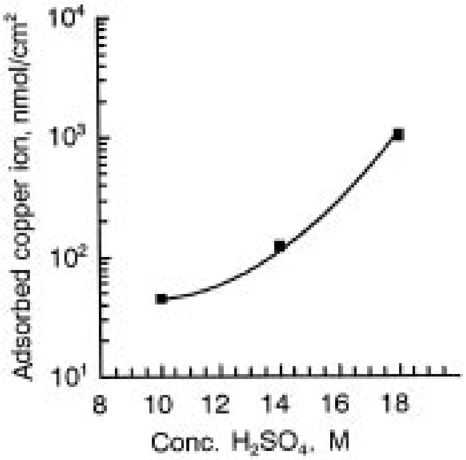


Fig. 3—Change in amount of adsorbed copper ions with sulfuric acid treatment at 70 °C for 5 min.

The adsorbed copper ion on A-PPE resin laminate was extracted from the laminate with 5-percent nitric acid solution to determine its content by atomic absorption spectrometer. Each copper film sample (size 30 x 100 x 2 mm) was used as a cathode for electroplating. Two plain copper sheets were used as anodes. Electroplating of copper was carried out galvanostatically (cathode current density 2 A/dm^2) in an electrolyte containing 0.25 M copper sulfate, 2 M sulfuric acid and proprietary additives with air agitation, until the deposited copper films grew to 25 µm. Their peel strength was determined by the 90° peeling test.

Results & Discussion

Chemical roughening and sulfonation of the A-PPE resin surface (Fig. 1) shows the surface morphology of A-PPE resin laminate roughened with 0.3 M potassium permanganate/6M sodium hydroxide solution at 100 °C for 20 min. Figure 2 shows the FTIR ATR spectra of A-PPE resin laminates treated and untreated with 18 M sulfuric acid at 70 °C for seven min. According to these spectra, the structure of A-PPE resin appeared at 1602, 1420, 1376, 1304, and 1181 cm^{-1}, respectively.[3] Infrared absorption for the triallyl-1,3,5-triamino-2,4,6-trione, a setting and cross-linking agent, appeared at 1677, 1448, and 1303 cm^{-1}.[4] The O-C-O mode of the asymmetric and symmetric stretching appeared at 1184 and 1018 cm^{-1}, respectively. The intensity of these peaks decreased remarkably with the sulfuric acid treatment, and new peaks appeared at 1428 and 1157 cm.$^{-1}$ These peaks were assigned to the R-O-SO_3H mode of the asymmetric and symmetric stretching bands. It is therefore obvious that the sulfo group, as a cation exchange group, was introduced onto the A-PPE resin laminate surface through sulfuric acid treatment.

Adsorption, Reduction Treatment of Copper Ion & Peel Strength

The A-PPE resin laminates were immersed in sulfuric acid solutions at 70 °C for five min, then immersed in 0.05 M copper sulfate solution for five min to adsorb the copper ions. After rinsing, the samples were used to determine the copper ion adsorption by dissolving them with 5-percent nitric acid and to determine the ion concentration by atomic absorption spectrometer. The results are shown in Fig. 3. The amount of adsorbed copper increases exponentially with increased sulfuric acid concentration. A 1000 nmol/cm^2 Cu^{+2} adsorption was observed when the surface was treated with 18 M sulfuric acid. Using the copper lattice constant, 0.362nm, the thickness of the thin copper film formed after the reduction process was estimated to be 71 nm.

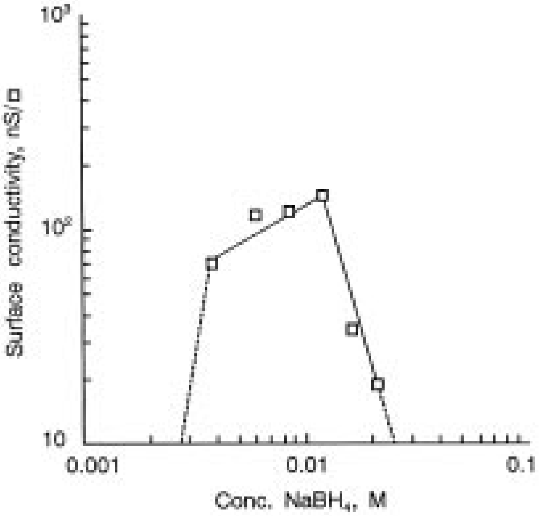


Fig. 4—Relation between concentration of sodium borohydride and conductivity of A-PPE surface treated by reducing process at 25 °C for 10 min.

Samples with adsorbed copper ions were treated with sodium borohydride solution for five min to reduce copper. Figure 4 shows the results of the surface conductivity. The maximum value of the conductivity was 150nS/sq when samples were treated with 0.01 M sodium borohydride. The surface appearance of these samples was bright metallic copper. All test samples were subjected to pull tests from direct electroplating of copper at cathode current density of 2 A/dm^2.

Figure 5 shows the relation between peel strength and sulfonation time. The value of the peel strength decreases with increasing sulfonation time. It was found that 0.6 kgf/cm was required when the surface was treated with 18 M sulfuric acid at 70 °C for five min. The peel strength decreases with excessive sulfonation time because of dissolution of the roughened resin surface.

The processes mentioned above, that is, the introduction of an ion exchange group to a plastic substrate, adsorption of metal ions, and the conversion of adsorbed ions to metals,

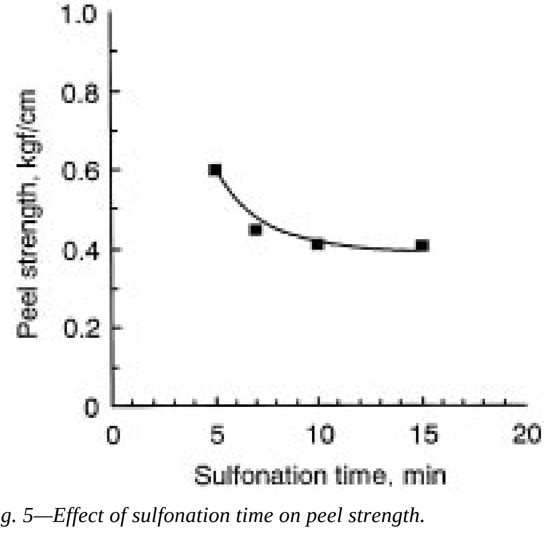


Fig. 5—Effect of sulfonation time on peel strength.

metal oxides or metal sulfides, would also be useful for the metallization of plastics, preparation of semiconductor materials and metallic clusters.

Summary

A new method for forming a conductive film on an A-PPE resin laminate was proposed in this paper. The sulfo group, as a cation exchange group, was introduced on the A-PPE resin laminate surface through sulfuric acid treatment. The amount of adsorbed copper ions increased with increasing sulfuric acid concentration, and at a rate of 1000 nmol/cm^2 of surface with 18 M sulfuric acid at 70 °C for five min treatment.

The sample gave maximum conductivity of 150 nS/sq was obtained when the Cu^{+2}-adsorbed surface was treated with 0.01 M sodium borohydride. The appearance of the reduced resin surface was bright metallic copper. All test samples permitted direct electroplating of copper at a current density of 2 A/dm^2.

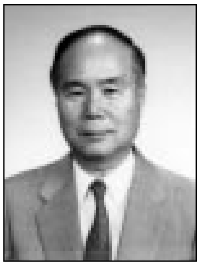
The value of the peel strength decreases with increasing sulfonation time. Peel strength of 0.6 kgf/cm was obtained when the resin surface was treated with 18 M sulfuric acid at 70 °C for five min.

Editor's note: *Manuscript received, September 1997.*

References

1. Karl H. Dietz, *Plat. and Surf. Fin.*, **82**, 60 (June 1995).
2. T. Arai, H. Oda & T. Katayose, *Electronic Circuit & Packaging Technology*, **9**, 429 (1994).
3. C.J. Pouchert, *The Aldrich Library of FT-IR Spectra*, **2**, 1209 (1985).
4. C.J. Pouchert, *ibid.*, **1**, 813 (1985).

Nawafune



Mizumoto

Seita

About the Authors

Drs. Hidemi Nawafune and Shozo Mizumoto are associate professor and professor of Applied Chemistry, respectively, at Konan University, Japan. Their research interests include electrolytic and electroless plating and related fields.

Toshinobu Kanai received BS and MS degrees in chemistry at Konan University.

Masaru Seita is employed in R&D by LeaRonal Japan Inc., 296-4, Yoshino-cho, Ohmiya-shi, Saitama, Japan. He is in charge of research and development of new products for printed circuit board manufacturing.*

** To whom correspondence should be addressed.*