# Direct Metallization on Surface-Modified Polyimide Resin

By M. Seita, M. Kusaka, H. Nawafune and S. Mizumoto

**A new method was investigated for formation of a thin copper film on a polyimide resin, through sulfonation of the resin surface, followed by adsorption and reduction of copper ions.**

Polyimide is a generic name for a group of thermally stable resins that contain imide rings. This resin can be represented by a reaction product of oxydianiline and pyromellitic anhydride. Because of its excellent thermal stability, mechanical strength, electrical characteristics, and low flammability,[1] polyimide resin is widely used in electronic miniaturization, and multilayer circuit board applications. Polyimide resin becomes indispensable for flexible printed circuits (FPC), tab automated bonding (TAB) film carriers, and dielectric for multilayer applications.

The conventional FPC is made of three layers,[2] namely, copper foil, epoxy or acrylic adhesive, and base film (polyester, polyimide or others). For FPC in particular, with high thermal stability and flexibility, polyimide is almost exclusively used to satisfy the adhesive thermal treatment conditions and flexibility requirement.[3] The adhesive resin in the laminate tends to absorb chloride ion, however, during the circuit formation processes. This contamination can deteriorate the insulation resistance and promote copper migration after the circuit is formed.

Very thin copper film is vacuum deposited onto the polyimide film without the use of adhesive.[4-6] In addition to the lamination and vacuum deposition, an available alternate is electroless copper deposition on polyimide resin.[7,8] The latter method is still not in practical use, however, because the copper film made by this method lacks sufficient peel strength as a result of a strong alkaline attack on the polyimide surface during the plating process. In this paper, a new method for direct metallization on surface modified polyimide resin will be reported.

## Experimental Procedure

### Sulfonation of a Polyimide Resin

The polyimide laminate used was Toray-Dupont film 100-H. The structural formula of this resin is shown in Fig. 1. Test samples of the polyimide laminate were dipped in 0 to 30 % fuming sulfuric acid at 15 to 40 °C for a specified time, rinsed thoroughly, then dried. The degree of sulfonation was determined with a spectrophotometer equipped with a Nic-plan microscope, using an ATR Reflector (Zinc Selenide). ATR spectra in the 2000 to 700 $cm^{-1}$ were obtained by co-adding scans at 4 $cm^{-1}$ resolution, with a narrow band-pass HgCdTe (MCT) detector.

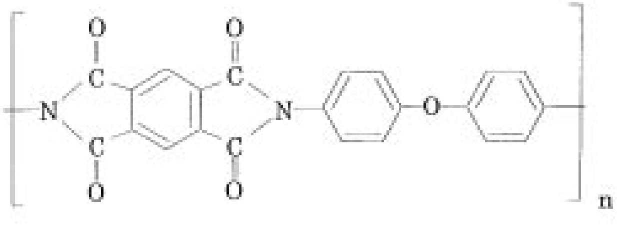

Fig. 1—Skeletal structure of polyimide resin.

### Adsorption and Reduction Treatment of Copper Ions

The sulfonated test samples were dipped in 0.5 M copper sulfate solution for three min to adsorb the copper ions. After a thorough water rinse, the samples were dipped in 0.001 to 0.01 M sodium tetrahydroborate solution for two min, to convert copper ion to metallic copper and form a thin, conductive copper film.

The surface conductivity of the test sample was measured with a digital multimeter. The amount of copper ion adsorbed on the sulfonated polyimide was determined by eluting the copper ion from the sulfonated surface (2 x 2 cm) with 5-percent nitric acid, and by measuring the copper ion ineluent by Zeeman atomic absorption spectrometry.

## Results and Discussion

### Sulfonation of Polyimide Resin

Figure 2 shows FTIR ATR spectra of a polyimide laminate surface treated and untreated with fuming sulfuric acid (30% $SO_3$, 25 °C) for 30 sec. In the spectrum of the untreated polyimide laminate, imide ring and benzene ring stretching bands appeared at 1774 to 1704 $cm^{-1}$ and 1597 to 1496 $cm^{-1}$, respectively. C-H out-of-plane bending bands also appeared at 881 $cm^{-1}$. The ether ʋ-C-O mode of the symmetric and asymmetric stretching bands appeared at 1235 and at 1110 to 1080 $cm^{-1}$, respectively. The intensity of these peaks decreased after the fuming sulfuric acid treatment. A new peak

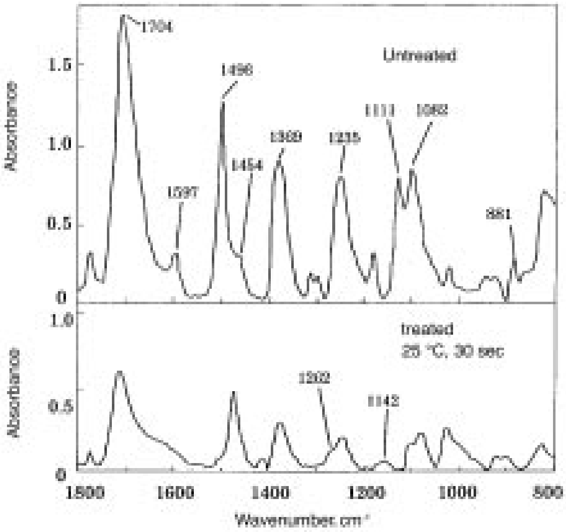

Fig. 2—FTIR ATR spectra of polyimide resin surface treated with fuming sulfuric acid (30% $SO_3$). 1600-1500 $cm^{-1}$, benzene ring stretching; 881 $cm^{-1}$, C-H out of plane; 1235 and 1110-1080 $cm^{-1}$, ethers ʋ-C-O bending; 1262 and 1142 $cm^{-1}$, sulfo group ($[H_3O]^+[RSO_3]^-$).

attributed to a sulfonyl group appeared at 1262 and 1142 cm$^{-1}$. In general, the sulfonyl group shows the $SO_2$ symmetric and asymmetric stretching bands in the 1350 cm$^{-1}$ and 1160 cm$^{-1}$ regions. Inspection of the FTIR for the sulfonated surface (Fig. 2) revealed that these peaks were shifted toward lower frequencies. This peak shift is an indication of the presence of the hydrated species of sulfonic acid ($[H_3O]^+[RSO_3]^-$). It is obvious, therefore, that the sulfonyl group, as a cation exchange group, was introduced onto the polyimide surface. The structural formula for polyimide resin consists of phenyl, imide and ether groups. Considering the strong electrophilic reaction of sulfonation, the benzene ring having an ether linkage is the most likely site for sulfonation.

### Adsorption and Reduction Treatment of Copper Ions

Figure 3 shows the effect of free $SO_3$ concentration in fuming sulfuric acid on the amount of adsorbed copper ions and, as a result, sulfonyl group introduction on the polyimide surface. The amount of adsorbed copper ions increased with the increase of free $SO_3$ concentration, then leveling off when Cu(II) ions reached 1129 nmol/cm$^2$. Two sulfonic groups are needed to adsorb one Cu(II) ion. Using the copper lattice constant of 0.362 nm, the thickness of the average copper thin film after the reduction process was estimated to be about 80 nm. Figure 4 shows the effect of treatment temperature on the amount of copper ion adsorption, which increased with the increase of treatment temperature. In this study, it was found that the polyimide laminate was severely attacked when treatment temperature exceeded 40 °C. Figure 5 shows the effect of treatment time on the amount of adsorbed copper ions and sulfonic groups on a polyimide laminate surface. The amount of adsorbed copper ions increased with increase of treatment time, reaching saturation at 45 sec. Longer exposure (60 sec) in fuming sulfuric acid resulted in surface attack.

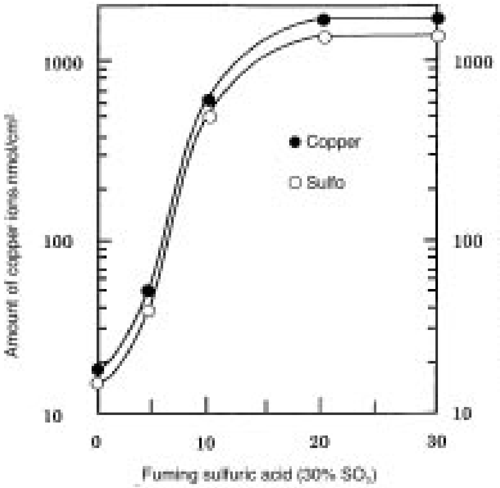

*Fig. 3—Effect of free $SO_3$ concentration on amount of adsorbed copper ions and sulfo groups on polyimide resin surface. Conditions: Fuming sulfuric acid, 30 sec, 25 °C; $CuSO_4$, 0.5 M, 3 min, 25 °C.*

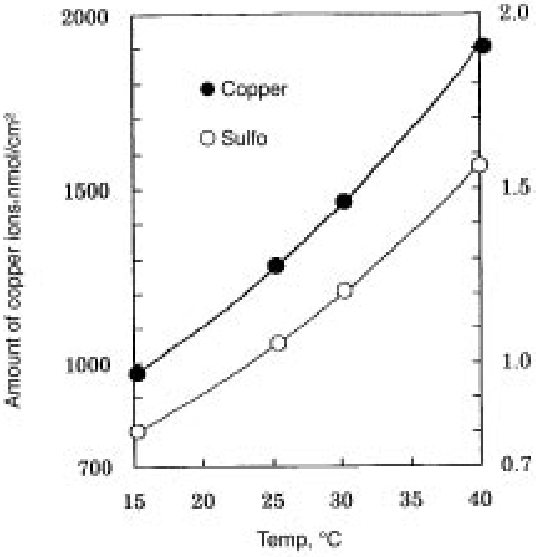

*Fig. 4—Effect of treatment temperature on amount of adsorbed copper ions and sulfo groups on polyimide resin surface. Conditions: Fuming sulfuric acid, 30 sec, 25 °C; $CuSO_4$, 0.5 M, 3 min, 25 °C.*

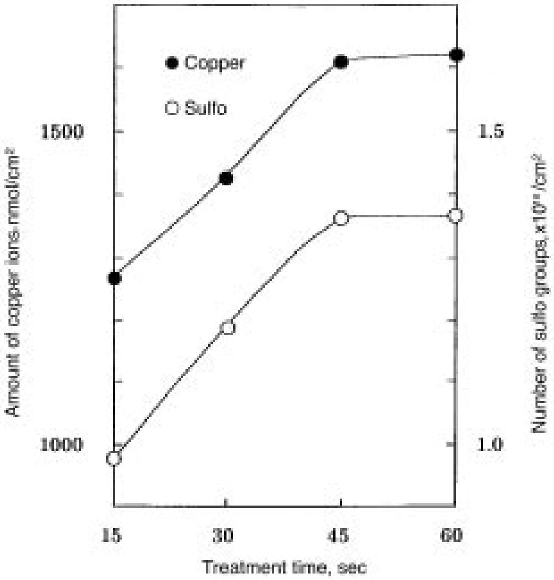

*Fig. 5—Effect of treatment time on amount of adsorbed copper ions and sulfo groups on polyimide resin surface. Conditions: Fuming sulfuric acid, 30 sec, 25 °C; $CuSO_4$, 0.5 M, 3 min, 25 °C.*

Figure 6 shows the relationship of surface conductivity and sodium tetrahydroborate reduction condition. The maximum conductivity obtained was 0.0083 S/sq (120 Ω/sq) at 0.007 M sodium tetrahydroborate concentration and, under this condition, it gave a bright metallic copper appearance. When the concentration of sodium tetrahydroborate exceeded 0.02 M, the reduction resulted in detachment of reduced copper deposits from the polyimide surface. The surface conductivity of copper thin film is much higher than that of other direct metallization systems, so that a coating of copper can be plated on the film directly.

Figure 7 shows that X-ray diffraction patterns for copper and polyimide were observed at 43°, 50.0° and at 23.9° and 26.7°, respectively. A weak diffraction for $Cu_2O$ was observed at 36.3°. It is concluded, therefore, that a minute amount of $Cu_2O$ was codeposited with the copper.

### Summary

A new method for polyimide laminate preparation is proposed. The sulfonic group, as a cationic exchange group, was introduced onto the polyimide laminate surface through fuming sulfuric acid treatment. The amount of adsorbed copper ions increased with increase of fuming $SO_3$ concentration; 1129 nmol/cm$^2$ exchange equivalent was obtained

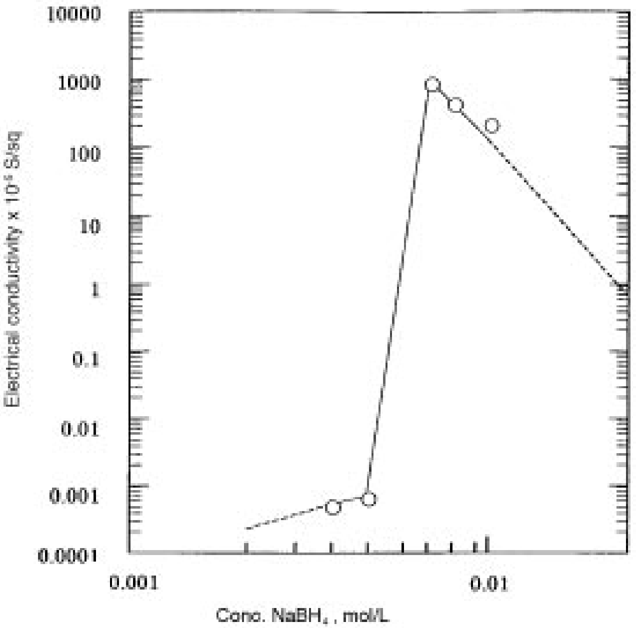

*Fig. 6—Relation between concentration of $NaBH_4$ and electrical conductivity of polyimide resin surface after reducing treatment. Conditions: Fuming sulfuric acid, 30 sec, 25 °C; $CuSO_4$, 0.5 M, 3 min, 25 °C; $NaBH_4$ (0.001-0.01 M), 2 min, 25 °C.*

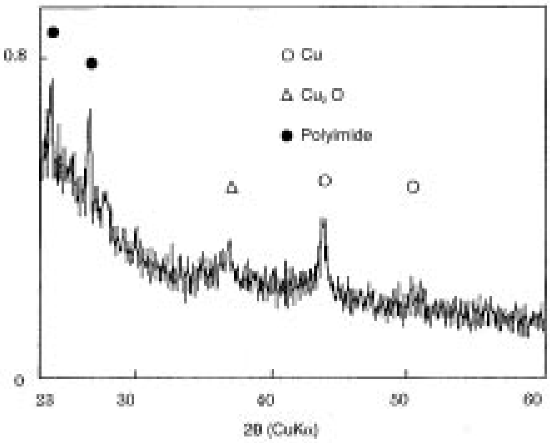

*Fig. 7—X-ray diffraction pattern of deposit on polyimide resin.*

when the sample was treated with fuming sulfuric acid (30% $SO_3$) at 25 °C for 30 sec. The thickness of the thin copper film formed after the reduction process was estimated to be about 80 nm. The surface conductivity of the sample was 0.0083 S/sq (120 Ω/sq). The new direct metallization technology can be applied to the manufacture of copper-film-coated polyimide substrate without adhesive. This process will provide high reliability because no adhesive layer exists between the polyimide and the copper. Further development of this process can extend its application beyond FPC and TAB as well.

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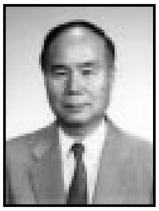

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