Direct Metallization Using Ni-Co Alloy On Surface Modified Polyimide Film

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A simplified method has been examined for the formation of a thin Ni-Co alloy on polyimide film by sulfonation modification of its surface, followed by adsorption of Ni^{+2} and Co^{+2} ions and subsequent reduction with sodium tetrahydroborate. The sulfonic group, as a cation exchange group, was introduced onto the polyimide resin surface through 16 M H_2SO_4/0.05% H_2O_2/1 M $(CH_3CO)_2O$ mixed solution treatment. The amount of Ni^{+2} and Co^{+2} ions adsorbed increased with increase of sulfuric acid concentration. Adsorption of 1200 nmol/cm^2 of Ni^{+2} and 1000 nmol/cm^2 of Co^{+2} adsorption was observed when the surface was treated with 16 M sulfuric acid. The average thickness of Ni and Co alloy thin film after the reduction process was estimated to be about 150 nm. The maximum conductivity obtained was 0.042 S/sq(11.9Ω/sq) when the ions-adsorbed surface is treated with 0.007 M sodium tetrahydroborate and, under this condition, it gave a bright metallic Ni-Co alloy appearance. After reduction, each test sample permitted direct copper electroplating at cathode current density of 2 A/dm^2.

The conventional flexible printed circuit (FPC) board is made of three layers, namely, copper foil, epoxy or acrylic adhesive and base film (polyester, polyimide or others). This construction in particular requires high thermal stability and flexibility; therefore, polyimide is almost exclusively used for this application to satisfy the adhesive thermal treatment conditions and flexibility requirement.[1] 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.

It has been reported that copper film can be vacuum deposited onto the polyimide film without the use of adhesive.[2-4] In addition to the copper-clad laminate and vacuum deposition, another alternate available is direct electroless copper deposition on polyimide resin.[5-6] Accordingly, formation of a conductive thin film on a polyimide resin surface without the use of adhesive was examined. Direct metallization, using copper thin-film on surface-modified polyimide resin has been reported.[7] In this paper, a new method for direct metallization using Ni-Co alloy thin-film on surface-modified polyimide film is reported.

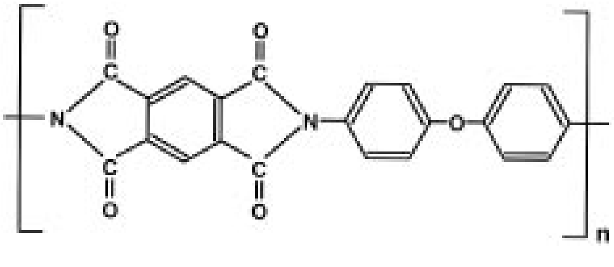

Fig. 1—Skeletal structure of polyimide resin.

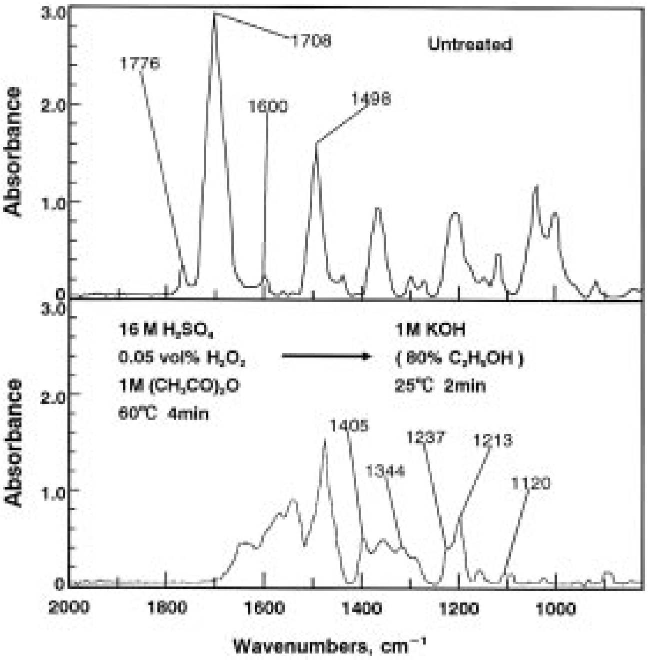

Fig. 2—FTIR ATR spectra of polyimide resin surface; peaks at wavenumbers 1776 and 1708 cm^{-1} indicate imide ring stretching; at 1597 and 1498 cm^{-1}, benzene ring stretching; peaks at 1344 and 1120 cm^{-1} indicate sulfo groups.

Experimental Procedure

Sulfonation of a Polyimide Resin

The polyimide laminate used was Toray-Dupont film 200-H. The structural formula of this resin is shown in Fig. 1. Each test sample of the polyimide laminate was dipped in 16 M H_2SO_4/0.05%H_2O_2/$(CH_3CO)_2O$ mixed solution at 60 °C for a specified length of time, then thoroughly rinsed. The test samples were then dipped in 0.2~3 M KOH/80% C_2H_5OH solution at 25 °C for 0.5~10 min, thoroughly rinsed, then dried. The degree of sulfonation was determined with a FTIR spectrophotometer equipped with a 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.

Adsorption & Reduction Treatment of Ni^{+2} & Co^{+2} Ions

The sulfonated test samples were dipped in 0.05 M nickel sulfate/0.05 M cobalt sulfate mixed solution for five min to adsorb the Ni^{+2} and Co^{+2} ions. The amount of these ions adsorbed on sulfonated polyimide was determined by eluting them from the sulfonated surface (2 × 2 cm) with 5-percent nitric acid, then measured them in the eluent by atomic absorption spectrometry. After thorough water rinse, each sample was dipped in 0.001 to 0.01 M sodium tetrahydroborate

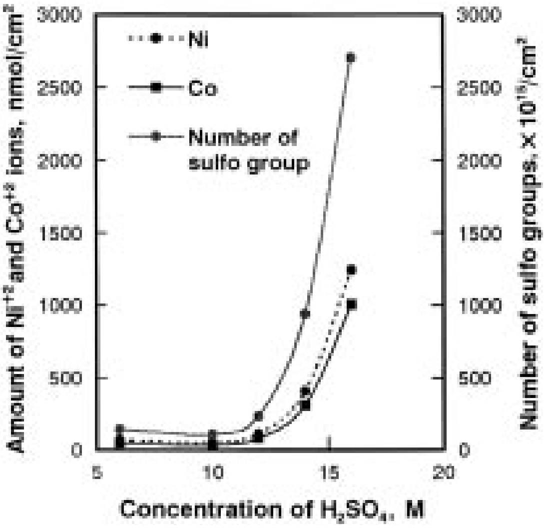

Fig. 3— Effect of sulfuric acid concentration on amount of adsorbed Ni^{+2} and Co^{+2} ions and sulfo groups on polyimide resin surface. Conditions: 6~16 M H_2SO_4/0.05 vol pct H_2O_2/$(CH_3CO)_2O$; 60 °C, 4 min; 1 M KOH (80% C_2H_5OH), 25 °C, 2 min; 0.025 M $NiSO_4$/0.025 M $CoSO_4$, 25 °C, 5 min.

solution for 30 min to convert the Ni and Co ions to metallic, conductive Ni-Co alloy thin film.

The surface conductivity of the test samples was measured with a digital multimeter. The composition of the Ni-Co alloy thin film was analyzed by X-ray diffraction.

Acid Copper Plating on Ni-Co Alloy Thin Film

Acid copper plating was carried out at 2 A/dm² for 60 min (25 µm thick) on the Ni-Co alloy thin film after activation by 10-percent sulfuric acid, thoroughly rinsed, then dried. The acid-copper-plated samples were then annealed at 120 °C for one hr. Each sample was cut to one-cm width and its peel strength measured with a tension tester.

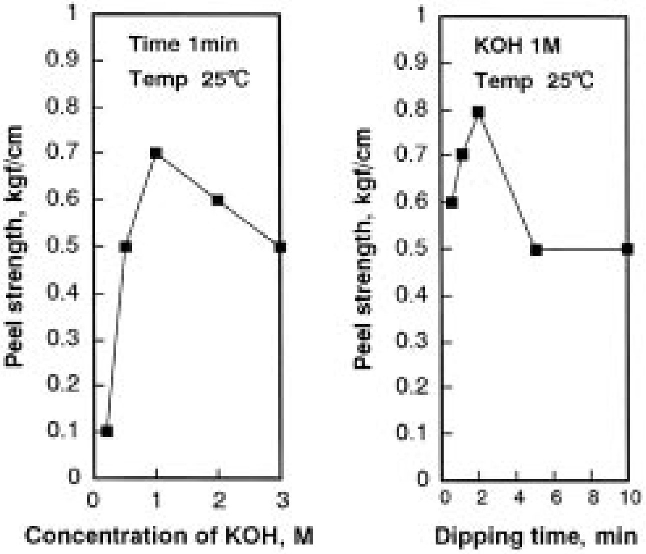

Fig. 5—Relation between etching condition and peel strength. Conditions: 16 M H_2SO_4/0.05 vol pct H_2O_2/$(CH_3CO)_2O$; 60 °C, 4 min; 0.2~3 M KOH (80% C_2H_5OH), 25 °C, 0.5~10 min; 0.025 M $NiSO_4$/0.025 M $CoSO_4$, 25 °C, 5 min; 0.007 M $NaBH_4$, 25 °C, 30 min; acid copper plating, 2 A/dm², 25 µm.

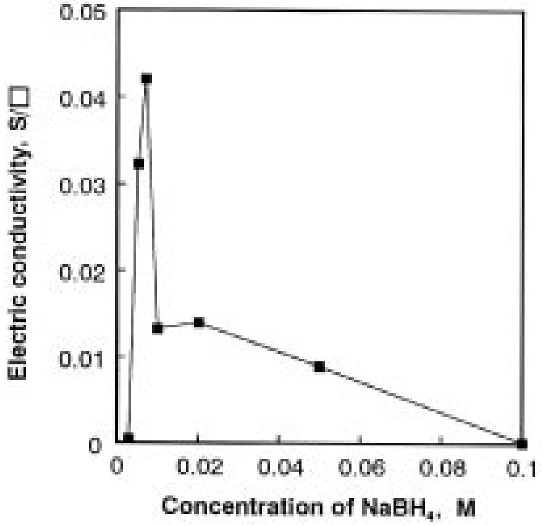

Fig. 4—Relation between concentration of $NaBH_4$ and electric conductivity of Ni-Co alloy thin film on polyimide resin. Conditions: 16 M H_2SO_4/0.05 vol pct H_2O_2/$(CH_3CO)_2O$; 60 °C, 4 min; 1 M KOH (80% C_2H_5OH), 25 °C, 2 min; 0.025 M $NiSO_4$/0.025 M $CoSO_4$, 25 °C, 5 min; 0.001~0.1 M $NaBH_4$, 25 °C, 30 min.

Results and Discussion

Sulfonation of Polyimide Resin

Figure 2 shows the FTIR ATR spectra of polyimide laminate surface untreated and treated with 16 M H_2SO_4/0.05% H_2O_2/$(CH_3CO)_2O$ mixed solution at 60 °C for four min. In the spectrum of 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 ν-C-O mode of the asymmetric and symmetric stretching appeared at 1235 and 1110 to 1080 cm^{-1}, respectively. The intensity of these peaks decreased after 16 M H_2SO_4/0.05%H_2O_2/$(CH_3CO)_2O$ mixed solution treatment. A new peak attribut-

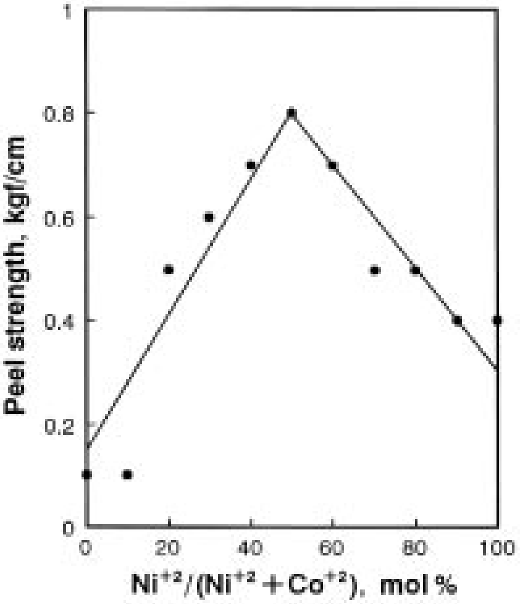

Fig. 6—Relation between peel strength and adsorbed Ni^{+2}/(Ni^{+2} + Co^{+2}) ratio in solution. Conditions: 16 M H_2SO_4/0.05 vol pct H_2O_2/$(CH_3CO)_2O$; 60 °C, 4 min; 1 M KOH (80% C_2H_5OH), 25 °C, 2 min; total ion conc. = 0.05 M, 25 °C, 5 min; 0.007 M $NaBH_4$, 25 °C, 30 min; acid copper plating, 2 A/dm², 25 µm.

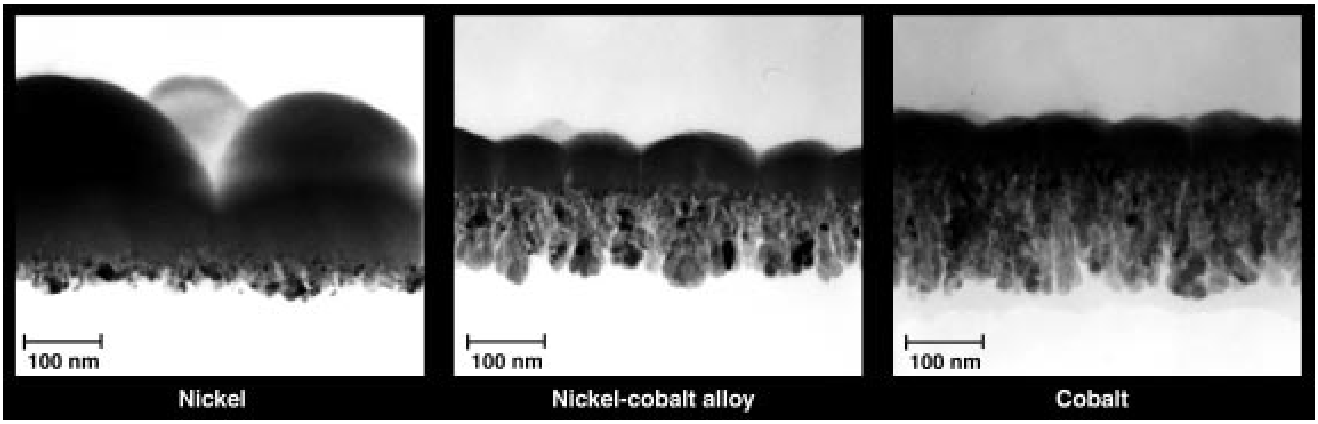

Fig. 7—TEM photographs of nickel, Ni-Co alloy, and cobalt deposits.

able to a sulfonyl ether group appeared at 1344 and 1120 cm^{-1}. It is obvious, therefore, that the sulfonic group, as a cation exchange group, was introduced onto the polyimide surface. The structural formula for polyimide resin consists of phenyl, imidyl 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 & Reduction Treatment of Ni^{+2} & Co^{+2} Ions

Figure 3 shows the effect of sulfuric acid concentration on the amount of adsorbed Ni^{+2} and Co^{+2} ions and sulfo groups on a polyimide resin surface. The amount of adsorbed Ni^{+2} and Co^{+2} ions increased with increase of sulfuric acid concentration. Adsorption of 1200 nmol/cm^2 Ni^{+2} and 1000 nmol/cm^2 Co^{+2} was observed when the surface was treated with 16 M sulfuric acid. Two sulfonic groups are needed to adsorb one Ni^{+2} or Co^{+2} ion. The average thickness of Ni and Co alloy thin film after the reduction process was estimated to be about 150 nm.

Figure 4 shows the relation between the concentration of $NaBH_4$ and the electric conductivity of Ni-Co alloy thin film on polyimide resin. Each sample of the polyimide laminate was dipped in 16 M H_2SO_4/0.05%H_2O_2/$(CH_3CO)_2$ mixed solution at 60 °C for four min, rinsed thoroughly, then neutralized with 1 M KOH/C_2H_5OH mixed solution at 25 °C for two min. The maximum conductivity obtained was 0.042 S/sq (11.9Ω/sq) when the ion-adsorbed surface was reduced with 0.007 M sodium tetrahydroborate and, under this condition, it showed a bright metallic Ni-Co alloy appearance. When the concentration of sodium tetrahydroborate exceeded 0.02 M, the reduction resulted in detachment of reduced Ni-Co deposits from the polyimide surface. The surface conductivity of Ni-Co thin film is much higher than that of other direct metallization systems, so that an electroplating of copper can be deposited on the film directly.

The relation between etching condition and peel strength is illustrated in Fig. 5. Samples were plated (25 µm) in an acid copper bath at 2 A/dm^2 after the formation of the Ni-Co thin film on the polyimide resin surface. Each test sample was cut to one-cm width and the 90° peel strength between Ni-Co alloy thin film and polyimide resin surface was measured at a crosshead speed of 5 mm/min with a tension tester.

The relation between the concentration of KOH in an etching solution and peel strength is shown in Fig. 5 (left). The maximum peel strength between the Ni-Co alloy thin film and the polyimide resin surface was 0.7 kg/cm at 1 M KOH. When the concentration of KOH exceeded 1 M, the peel strength decreased with the increase of KOH concentration in the etching solution. The relation between dipping time in 1 M KOH solution and peel strength was also shown in Fig. 5 (right). The maximum peel strength obtained was 0.8 kg/cm with 2 min treatment.

Figure 6 reveals the relation between adsorbed $Ni^{+2}/(Ni^{+2} + Co^{+2})$ ratio on the polyimide resin surface and peel strength. The Ni content in Ni-Co alloy deposits after reduction was directly proportional to the $Ni^{+2}/(Ni^{+2}+Co^{+2})$ ratio in nickel sulfate/cobalt sulfate mixed solution. The peel strength increased with an increase of the ratio in the mixed solution, a maximum peel strength obtained was 0.8 kg/cm at 50 percent molar ratio of $Ni^{+2}/(Ni^{+2}+Co^{+2})$. It is suggested that the grain structure of the Ni-Co alloy deposit changed to a finer grain when the cobalt ratio in the deposit increased to 50 percent molar ratio.

TEM photographs of nickel, nickel-cobalt (deposition ratio of Ni to Co = 1:1), and cobalt deposits are shown in Fig 7. Photographs for each of these deposits exhibited a double layer structure, namely a lower layer which was bound to the resin surface and an upper layer of minute crystal valleys. The adhesion of the deposits to the polyimide resin is dependent on the deposition morphology of the lower layer. The boundary between the nickel-cobalt alloy deposit and the polyimide resin surface exhibited a fine crystal morphology like driven stakes. It is assumed that the highest peel strength of the nickel-cobalt alloy deposit is a result of this unique driven stake crystal morphology.

Summary

A simplified method for a polyimide laminate preparation was proposed. The sulfonic group, as a cationic exchange group, was introduced onto the polyimide resin surface with 16 M H_2SO_4/0.05%H_2O_2/$(CH_3CO)_2$ mixed solution treatment. The amount of adsorbed Ni^{+2} and Co^{+2} ions increased with increase of sulfuric acid concentration, Ni^{+2} ions of about 1200 nmol/cm^2 and Co^{+2} ions of 1000 nmol/cm^2 exchange equivalent were obtained when the sample was treated with 16 M H_2SO_4/0.05%H_2O_2/$(CH_3CO)_2$ mixed solution at 60 °C for four min. The thickness of the Ni-Co alloy thin film formed after the reduction process was estimated to be about 150 nm. The conductivity of the sample was 0.042 S/sq

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