Direct Metallization Using Surface Modification of Thermosetting Polyphenylene Ether Resin Laminate

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熱硬化型 PPE樹脂の表面改質を利用するダイレクトプレーティング

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Introduction

The electronics industry is constantly researching 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 superior properties, such as low dielectric constant, high glass transition temperature, and low water absorption¹⁾.

In this paper, a new method for formation of a copper thin film on a thermosetting allylated PPE (A-PPE) resin laminate through surface modification with chromic acid mixture of the laminate followed by adsorption and reduction of copper ions was investigated.

Experimental

The aromatic poly-phenylene ether (A-PPE) resin laminate (Asahi Chemical Industry Ltd.) was used¹⁾. Test samples of the A-PPE resin laminate were dipped in 3M CrO₃/4M H₂SO₄ mixture at 50°C, thoroughly rinsed, and then dried.

Carboxylation of surface of the A-PPE laminate were confirmed by FTIR and XPS spectrometer. FTIR ATR spectra were obtained on a Nicolet Magna 750 FTIR spectrometer equipped with a Nic-Plan microscope (Spectra-Tech Inc.) using an ATR objective (zinc selenide). XPS spectra were obtained on an ULVAC-PHI ESCA system 5400 MC.

The carboxylated samples were dipped in 0.05M

CuSO₄ solution for 5 min to adsorb the copper ions. After rinsing, the test samples adsorbed copper ions were dipped in NaBH₄ solution for 5 min, producing a conductive through reduction of the copper ion to form a copper thin film. The surface conductivity of the test samples was measured using multimeter. The adsorbed copper ion was dissolved in 5% HNO₃ solution and measured by atomic absorption spectrometry.

Results and discussion

Fig. 1 shows the FTIR ATR spectra of A-PPE resin laminates untreated and treated with 3M CrO₃/4M H₂SO₄ at 50°C. According to these spectra, skeletal structure of A-PPE resin appeared at 1602, 1420, 1376, 1304, and 1181 cm⁻¹, respectively²⁾. The triallyl-1,3,5-triajino-2,4,6-trione for setting and cross-linking agent appeared at 1677, 1448, and 1303 cm⁻¹, respectively³⁾. The intensity of the peak due to the skeletal structure

Fig. 1 FTIR ATR spectra of thermosetting PPE resin surface modified with 3M CrO₃/4M H₂SO₄ at 50°C.
○ Poly (2,6-dimethyl-1,4-phenylene ether)
● Triallyl-1,3,6-triajino-2,4,6-trione

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Fig. 2 XPS (C 1s) spectra of thermosetting PPE resin surface modified with 3M CrO_3 /4M H_2SO_4 at 50°C for 30 min.

Numerals: Peak area ratio (at.%)

of A-PPE resin decreased with the CrO_3 / H_2SO_4 treatment, and new peaks assigned to carboxyl group appeared from 1700 to 1620 cm^{-1} regions.

Fig. 2 shows the C 1s XPS core level spectra for the A-PPE resin laminates treated with 3M CrO_3 /4M H_2SO_4 at 50°C for 30 min. The CrO_3 / H_2SO_4 treatment makes the increase of the C-O component, the C=O component, and the COO component, and simultaneously makes the C-H and/or C-C component decrease. The COO concentration increases from 3% to 30%, and the C=O from 0% to 7%. A decrease of the C-H and/or C-C component concentration increase from 83% to 46% means that there is degradation of aromatic rings in the A-PPE resin by the CrO_3 / H_2SO_4 treatment. From the C 1s core level spectra, we conclude that the CrO_3 / H_2SO_4 treatment leads to the predominant formation of the COO component as an oxygen functionality, and also the degradation of aromatic rings in the A-PPE resin laminates.

The A-PPE resin laminates were dipped in 3M CrO_3 /4M H_2SO_4 solutions at 50°C for 30 min, and then dipped in 0.05M copper sulfate solution for 3 min to adsorb the copper ions. After rinsing, the samples were treated with 5% HNO_3 solution to dissolve copper ions, and the concentration of copper ions was determined by atomic absorption spectrometry. The results are shown in Fig. 3. The amount of adsorbed copper ions increases as an exponential function with increasing CrO_3 and H_2SO_4 concentration, and was 350 nmol/cm^2 on the sample treated with 3M CrO_3 /4M H_2SO_4 solution. Using the copper lattice constant, 0.362 nm, the thickness of the copper

Fig. 3 Amount of adsorbed copper ions on thermosetting PPE resin surface modified with CrO_3 / H_2SO_4 at 50°C for 30 min.

thin film formed after the reduction process was estimated to be 26 nm.

The test samples adsorbed copper ions were reduced with NaBH_4 solutions for 5 min. The maximum value of the conductivity of the test samples was 6 $\text{nS}/\square$ at 0.004M NaBH_4 , and the surface appeared to be bright metallic copper. However, the conductivity value obtained was inconsistent with the expected value from the adsorbed copper ions on the A-PPE resin surface⁴⁾. Thus the discrepancy in the conductivity comes from surface cracks, which reaching glass-fiber cloth of the laminate.

Conclusion

A new conducting method for an A-PPE resin laminate was proposed in this paper. The carboxy group, as a cation exchange group, was introduced onto the A-PPE resin laminate surface through the CrO_3 / H_2SO_4 treatment. The amount of adsorbed copper ions increased with increasing CrO_3 and H_2SO_4 concentration, and was 350 nmol/cm^2 on the sample treated with 3M CrO_3 /4M H_2SO_4 solution at 50°C for 30 min. The maximum value of the conductivity of the test samples was 6 $\text{nS}/\square$ at 0.004M NaBH_4 , and the surface appeared to be bright metallic copper.

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