[Technical Paper]

Formation of Fine Circuit Patterns on Cyclo Olefin Polymer Film

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Abstract

In recent years, with the miniaturization of electric devices, the demand for flexible printed circuits (FPCs) using polyimide has increased, because of its excellent heat resistance and size stability. Polyimide also has good flexibility and surface smoothness. However, polyimide absorbs moisture readily and is highly permeable to gas. In contrast, Cyclo Olefin Polymer (COP) has low moisture absorption, excellent size stability and excellent high frequency electrical properties. Therefore, COP is attractive as a substrate for FPCs. However, it is difficult to form a metal film using electroless plating on the COP with conventional processes. We could form a copper film with high adhesion strength while maintaining a smooth resin surface by modifying the surface using UV irradiation. Surface modification by UV irradiation was effective to achieve good adhesion (about 1.0 kN/m) between the COP resin and the deposited metal without roughening the COP surface. The interface electric conductivity of the printed circuit on COP produced by this method indicated a value of approximately 80% up to around 30 GHz.

Keywords: Electroless Plating, UV Irradiation, Metalizing Process, Resin Modification

1. Introduction

High frequency bands in the GHz region are used in the telecommunication field, and wavelengths in the millimeter region are used for the prevention of car collisions, high-speed wireless LAN systems, and so on. In these frequency bands, the substrata materials should have excellent electrical characteristics, such as low dielectric constants and low dielectric dissipation factors ($\tan\delta$). Amongst various resins, Polytetrafluoroethylene (PTFE) is one of the candidates for use as a substrate. However, it is difficult to form a metal film using electroless plating on PTFE.[1] A surface-roughening step is essential to obtain good adhesion between the deposited metal and the PTFE substrate. However, the roughness of the resin surface is not suitable for obtaining finer and denser circuit patterns, which require higher speed propagation and higher frequency characteristics. Therefore Cyclo Olefin Polymer (COP) has attracted attention because COP resin has electrical characteristics equal to PTFE, and COP resin also has excellent low absorptive capacity. Moreover, COP resin is used for electrical equipment that demands trans-

parency because COP resin has a high transparency. We have confirmed that a metal film can be formed with high adhesion strength while maintaining a smooth resin surface using UV irradiation of the COP. In this study, the adhesion strength after surface modification with UV irradiation was evaluated. The interface electrical conductivity ratio of the electric circuit made by this process was also analyzed.

2. Experimental Details

The samples used in this experiment consisted of COP film (Zenor Film ZF-16, thickness 188 μm , Zeon Co. Ltd.) cut into 50 mm $\times$ 50 mm pieces. The equipment used for surface modification was UV irradiation equipment (KOGAQ-500ULS, KOTO Co. Ltd.) fitted with a low pressure Hg lamp. The low pressure Hg lamp has wavelengths of 184.9 nm and 253.7 nm, and was placed at a distance of 15–30 mm from the sample. Each sample was irradiated for 1–10 minutes. Table 1 shows the plating process used in this experiment. Conventional conditioning and catalyzing treatments were performed after the UV surface modification, and electroless plating was deposited, followed by the copper electroplating. Moreover, the comb-like pattern circuits were formed by a subtractive method and electro-

Table 1 Process of metal plating on COP resin.

Process

Electroless plating solution bath

CuSO ₄ ·5H ₂ O	0.032 mol dm ⁻³
NiSO ₄ ·6H ₂ O	0.0024 mol dm ⁻³
C ₆ H ₅ Na ₃ O ₇ ·2H ₂ O	0.052 mol dm ⁻³
NaH ₂ PO ₂ ·H ₂ O	0.27 mol dm ⁻³
H ₃ BO ₃	0.50 mol dm ⁻³
Polyethylene glycol (Mw: 1000)	1.0 g dm ⁻³
Temperature	45°C
pH	9.0

Electro plating solution bath

CuSO ₄ ·5H ₂ O	50 g/dm ³
H ₂ SO ₄	200 g/dm ³
NaCl	80 mg/dm ³
Toplucina SF-M	5 ml/dm ³
Temperature	25°C ± 2
pH	0.1~

chemical migration was performed.[2] (The electrochemical migration test conditions are shown in Table 4.) The chemical changes in the resin surface were measured using a fourier transform-infrared spectroscope (FT-IR: Shimadzu FTIR-ATR). Surface morphologies were observed with a scanning electron microscope (JEOL, JSV-5300LV), a transmission electron microscope (FEI Tecnai G2 F20), and an atomic force microscope (AFM: Shimadzu, SPM-950J3). The surface chemical structures were observed using an X-ray photoelectron spectroscopic analysis (XPS: AXIS-ULTRA DLD, Shimadzu Co., Ltd), inductively coupled plasma (ICP: ICPE-9000, Shimadzu Co., Ltd), and water-drop contact-angle meters. The samples for the ICP measurement were each subjected to catalyzing followed by dipping in enchants (nitric acid: hydrochloric acid: pure water = 1:1:1). The amount of carbon in the alkaline solution that was used to treat the COP resin (15 cm²) after UV irradiation was measured using total organic carbon (TOC: TNC-6000, Toray Engineering Co., Ltd.). For the measurement of adhesion strength between the modified COP resin and the deposited metal, the deposited metal films (10 mm in width) were peeled at a speed of 50 mm/min. from the COP resin vertically using an instron tester (Shimadzu EZ-test). The interface electric conductivity of the circuit made by this process was measured with a MIC-type dielectric substance resonator.[3] This analysis was performed by Prof. Kobayashi at Saitama University.

3. Results and Discussion

The chemical changes on the resin surface after the UV irradiations were measured using FTIR-ATR and XPS. As shown in Figure 1, adsorption peaks from carbonyl groups (C=O) and hydroxyl groups (-OH) appeared after UV irradiation.

Fig. 1 FTIR spectrum of COP before and after surface modification. (a) original COP surface. (b) UV irradiation for 5 min. (c) alkaline treatment after UV irradiation.

diation. On the other hand, the heights of the peaks based on the C-H groups of the resin surface were decreased following the UV irradiation. This shows that hydrophilic carbonyl and hydroxyl groups were formed by the UV light irradiation and the wettability was somewhat improved.[4, 5] Figure 2 shows the C 1s spectra of the COP surface, before and after the UV irradiation. On the original COP surface, the C 1s spectrum consisted simply of the component resulting from a carbon bond (C-C). On the other hand, after UV irradiation of the COP surface, a new component due to a carbonyl group (C=O) appears in addition to a decrease of the component due to the hydrocarbon bond. Furthermore, an increase of the carboxyl group was confirmed because the OH group and C=O were detected by FT-IR and XPS. From these results, it appears that carboxyl groups were created on the COP surface by the UV irradiation.[6, 7]

Figure 3 shows the relation of each water contact angle after the UV irradiation and alkaline treatment. The water contact angle decreased with a UV irradiation time of five minutes and then maintained the same level for times up to 10 minutes. However, the contact angle increased with the alkaline treatment because the excessively modified

Fig. 2 XPS result on the COP surface before and after the UV irradiation: A) Original COP surface, B) after UV irradiation for 5 min.

Fig. 3 Water contact angle after the processing of the UV irradiation and alkaline treatment.

COP resin was dissolved by the treatment, though part of the modified COP resin remained after the alkaline treatment.

Table 2 shows the result of the surface-roughness measured using AFM. The surface of the COP resin before treatment was very smooth. After UV irradiation, the roughness of the COP resin surface rose slightly because UV has the energy to disintegrate the COP resin surface. The main chain of the COP molecules at the resin surface was broken by the polar radicals generated with the UV irradiation. The nano-level roughness on the surface was produced by the ensuing alkaline treatment dissolving the low-molecular-weight components. After processing the COP resin with the alkaline solution, the TOC measurement showed that the amount of carbon was five times higher than before the UV treatment. The nano-level roughness contributed to the adhesion by fostering an anchoring effect between the resin and the electrically conductive layer.

Table 3 shows the amount of catalyst adsorbed on the COP film with and without UV irradiation measured using ICP. The amount of Pd adsorption before UV irradiation was $0.36 \mu\text{g}/\text{cm}^2$, and the adsorption of Pd increased ten-fold after UV irradiation ($3.8 \mu\text{g}/\text{cm}^2$). Apparently, an electroless deposition reaction occurred after the UV irradiation because enough Pd was adsorbed to initiate the reaction.

Figure 4 shows the relationship between the UV irradiation time and the adhesion strength between the COP

Table 2 Surface roughness of COP resin in each condition by AFM. (a) original COP. (b) UV irradiation for 5 min. (c) alkaline treatment after UV irradiation.

	(a)	(b)	(c)
Ra	0.83 nm	1.82 nm	3.16 nm
Rz	4.89 nm	8.59 nm	18.19 nm

Table 3 Amount of Pd adsorption in each condition by ICP.

	Without UV treatment	After UV irradiation (5 min.)
Amount of Pd adsorption ($\mu\text{g}/\text{cm}^2$)	0.36	3.8

resin and the metal, shown in Table 1. When the UV exposure time is less than one minute the UV modification of the resin was not enough to achieve good adhesion. A UV irradiation time of about 5 minutes was optimal. The adhesion strength decreased above five minutes of UV irradiation due to resin deterioration.

Cross-sectional observations using TEM and EDX are shown in Figures 5 and 6. Figure 5 shows the images after electroless plating and Figure 6 shows the images after electro plating. In Figure 5, the right side of the figure shows the COP film layer and the left side shows the conductive layer of electroless plated film. A mixed resin-metal layer of 50–90 nanometres was confirmed for the UV irradiation. Notably, the Pd ions were slightly deeper into the inner modified area compared with other ions, as shown in Figure 6. From the TEM images and element mapping

results, the modified layer and the COP film were closely interwoven at the interface of the COP film and conductive layer. It can be concluded that the conductive layer penetrated into the modified layer that controlled at a nano-level roughness and contributed significantly to the superior adhesion.

Figures 7 show circuits with a comb-like pattern produced using a subtracting method and a semi-additive method, respectively. Fine patterns with 25 μm line widths without debris or tails were obtained using UV irradiation followed by metal plating. The interface electrical conductivity that was produced with this method was also evaluated. Table 4 shows the results of the migration test. From these results, it can be seen that migration was not recognized even 1000 hours after applying the cover layer due to the flatness of the COP resin. Preparation of fine circuit patterns without residuals can be achieved using UV irradiation.

Fig.4 The dependence of UV irradiation time and adhesion strength between the COP resin and the metal produced by Table 1.

Fig.5 TEM images of the cross sectional observation between COP resin and electroless plating metal film. A) Metal layer B) resin-metal mixed layer C) COP resin.

Fig. 6 EDX images of cross section element mapping of COP resin and electro plating metal.

Fig. 7 SEM images of circuit patterns of subtracting method a). And circuit patterns of semi-additive method b).

Table 4 Results of migration test. (85%, 80 °C)

Applied voltage	Line width	Endurance time
10 V	L/S = 75/75 μm	1000 hour over
	L/S = 50/50 μm	1000 hour over
25 V	L/S = 75/75 μm	1000 hour over
	L/S = 50/50 μm	1000 hour over

Fig. 8 Interface electric conductivity between resin and conductive layer of substrate made by this process.

Moreover, the printed circuits made using this process showed an interface electric conductivity of about 80% in the 30 GHz area as shown in Figure 8. Conventionally, good adhesion between the resin and the deposition metal has been created by forming mechanical micro holes on the resin surface through chemical etching. Therefore, the treated resin surface becomes rough and it causes transmission losses after preparation of the printed circuit. Whereas, the printed circuits formed with this process demonstrated excellent interface electric conductivity due to the maintenance of a smooth interface between the COP resin and the conductor.[3]

4. Conclusions

Excellent adhesion strength was obtained from the UV irradiation processing between the smooth COP resin and

a deposited metal.

- (1) Wettability was shown on the surface of the COP resin after UV irradiation. Moreover, a significant amount of catalysts were adsorbed onto the COP resin treated with UV irradiation.
- (2) The printed circuit could be formed on the smooth COP resin using the UV irradiation method.
- (3) This technique is suitable for circuits that need good high-frequency properties because the circuit produced by this process showed an excellent interface electrical conductivity.

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