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Formation of Circuit Pattern on Liquid-Crystalline Polymer Film by Electroless Copper Plating

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Liquid-crystalline polymer (LCP) films were treated with N_2 plasma in order to improve adhesion with metal film. By N_2 plasma treatment, hydrophilic groups such as NH, COOH and OH were introduced into LCP film and the surface of the film was roughened slightly. After N_2 plasma treatment, a copper film was deposited on the LCP by electroless plating method. The circuit pattern of copper film with 0.5 mm (line) and 0.3 mm (space) intervals was fabricated on the LCP film.

Keywords: circuit pattern; electroless copper plating; liquid-crystalline polymer (LCP); plasma treatment

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INTRODUCTION

Recently electronic equipments have added more and more complicated functions and become smaller. So highly dense performance of electronic applications such as printed wiring boards and a flexible printed circuit boards have been demanded. Generally, polyimides and polycarbonates are used as suitable materials for electronic application's substrates.

Liquid-crystalline polymers (LCP) have an excellent combination of physical and chemical properties. The low dielectric constant and loss of the LCP are important for future flexible high-frequency applications. However, the LCP has poor adhesion with metal layers. In practical application, surface modification of LCP without changing bulk properties is demanded in order to improve adhesion. Various methods for polymer surface modification such as ion beam treatment, chemical etching, plasma treatment and graft copolymerization with functional monomers have been developed and applied to improve the adhesion property of the polymer substrates. For the metallization of LCP film, O_2 plasma treatment was used to modify the film surface [1,2].

Electroless plating is a simple and convenient method for metallization of polymer surface and has been widely used in the automotive and microelectronics industries [3]. Therefore, the adsorption of catalyst on polymer surface is very important in electroless plating process. Charbonnier *et al.* [4] have reported that the functional groups containing of nitrogen atom interacted firmly with palladium atom.

In this study, LCP films were treated with N_2 plasma in order to introduce the functional groups containing nitrogen atom into LCP surface. The fabrication of circuit pattern on LCP with copper film by electroless plating was examined.

EXPERIMENTAL

Materials

LCP film (Vecstar OC; 50 μm thickness) was supplied from Kuraray Co. Ltd. Vecstar OC is a co-polymer consisted of 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid. LCP films were cleaned by Soxhlet extraction with acetone before use. A catalyst solution containing $PdCl_2$/$SnCl_2$ (OPC-80 catalyst M), an accelerator solution containing sulfuric acid (OPC-500 accelerator MX-1), an electroless plating solution (OPC-750), and a glossy reagent (SF-M) were purchased from Okuno chemical industries Co. Ltd.

N_2 Plasma Treatment of the LCP Films

Plasma treatment of the films was performed in a bell-jar-type reaction chamber (SAMCO Model BP-1). LCP films were cut into pieces with 2 cm × 5 cm and fixed on a stainless steel sample holder placed between top and bottom electrodes. The distance between two electrodes was 3 cm. Reaction chamber was evacuated to 3 Pa and N_2 gas was then introduced over 100 Pa. After re-evacuation below 5 Pa, the pressure in the chamber was kept at 20 Pa by re-introduction of N_2 gas with a flow rate of 20 ml/min. Glow discharge was supplied by a high-frequency generator operating at 13.56 MHz with the radio-frequency (rf) power of 30–150 W.

Electroless Copper Plating on the Plasma-Treated LCP Films

Prior to electroless copper plating, plasma-treated LCP films were immersed in a catalyst solution at 23°C for 6 min and then immersed in an accelerator for 5 min. Electroless copper plating was performed in a plating bath at 5°C for 20 min. Copper film was deposited on the LCP film surface by following redox reaction.

$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu + 2HCOO^- + 2H_2O + H_2$$

Electroplating

After electroless copper plating, electroplating was performed in order to obtain thicker film of copper for the peel test. Plating bath consisted of 70 g/l of copper sulfate, 200 g/l of sulfuric acid, 100 mg/l of sodium chloride and 5 ml/l of a glossy reagent (SF-M). Electroplating was carried out at 25°C with current of 0.2 A and voltage of 0.5 V for 40 min. The total thickness of the copper film was about 20 μm.

Characterization

The 180° peel strength between LCP and copper films was measured with a Simadzu tensile tester (AG-1000D). The samples were cut into pieces with 10 mm width and peel strength measurement was carried out with a crosshead speed of 50 mm/min at room temperature. The contact angles of water and diiodomethane on the LCP surfaces were measured by the sessile drop method with contact angle measurement system (CA-X150; Kyowa Interface Science Co., Ltd.) under the 60% humidity at 20°C. The volume of the liquid drop was 0.2 μl. XPS was performed on an Ulvac-phi 5500 MT X-ray photoelectron spectrometer. The spectra were taken with a MgKα X-ray source exciting

radiation (1253.6 eV) at 15 kV, 200 W and an analyzer pass energy of 23.5 eV. The take off angle of electron from the sample was fixed at 45° relative to specimen surface. The relative atomic concentration of each element at the sample surface was estimated from peak areas using atomic sensitivity factors specified for the Ulvac-phi 5500 MT. A Hitachi S-800 scanning electron microscope (SEM) equipped with energy dispersion X-ray spectrometer and a Seiko Instruments SPI3700 atomic force microscope (AFM) were used to examine the surface topography of the deposited copper film and to observe the fracture surface of LCP/copper interface. The arithmetic mean of the surface roughness (R_a) was calculated from the roughness profile determined by AFM with a scanning length of 5 μm.

RESULTS AND DISCUSSION

XPS spectrum of untreated LCP film showed the carbon and oxygen peaks, corresponding to the chemical structure of LCP. After N_2 plasma treatment, the intensity of O1s peak increased and N1s peak appeared. This indicates that hydrophilic groups including oxygen and nitrogen atoms, such as NH_2, COOH and OH were introduced into LCP surfaces. XPS results and contact angle of water on LCP films soon after N_2 plasma treatment with various rf powers are summarized in Table 1. The N/O ratio for the plasma-treated LCP films increases with the increase of rf power. On the other hand, contact angles of water decreases with the increase of rf power. The hydrophilicity of the LCP film increased with introduction of functional groups by plasma treatment. In order to clarify the surface properties of LCP after plasma treatment, surface free energy (γ) is divided into dispersion (γ^d) and polar (γ^p) components with the contact angles of water and diiodomethane according to Owens' method [5]. The values of γ^d are almost equal. On the other hand, the γ^p increases markedly after

TABLE 1 XPS Results, Contact Angles of Water and Surface Free Energy of LCP Films Treated by Nitrogen Plasma with Various rf Powers

	Atomic concentration (%)			Contact angle	Surface free energy (mJ/m^2)		
Power (W)	C	O	N	(degree)	γ^d	γ^p	γ
untreated	84.4	15.6	γ	83.0	39.1	2.7	41.8
30	74.4	20.7	4.9	30.5	35.5	31.3	66.8
50	73.9	20.5	5.6	29.5	35.0	32.1	67.1
100	64.9	28.4	6.7	9.2	37.2	37.7	74.9
150	69.1	24.6	6.3	9.1	38.2	37.1	75.3

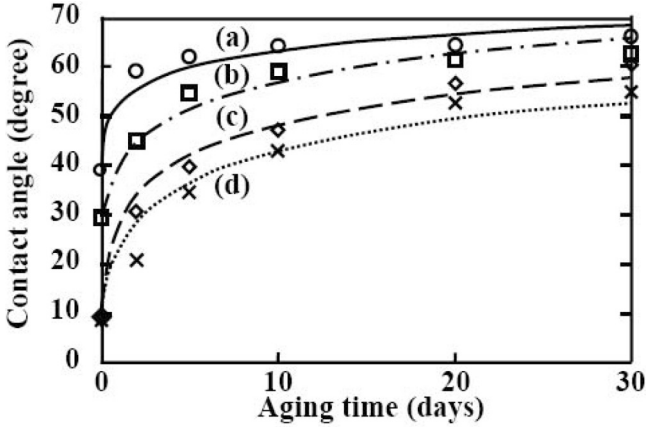

FIGURE 1 Change of contact angle of water on LCP films treated by nitrogen plasma with the rf powers of (a) 30 W, (b) 50 W, (c) 100 W, (d) 150 W.

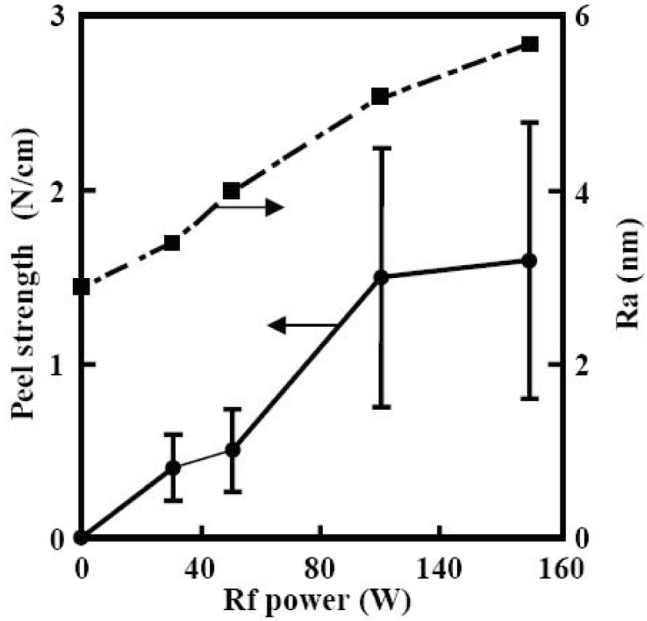

FIGURE 2 Peel strength (●) between copper and LCP films and Ra (■) of LCP as a function of rf power.

plasma treatment. Therefore, the increase of γ is attributed to introduction of polar groups into LCP surface.

Figure 1 shows the change of contact angles of LCP films treated by N_2 plasma with various rf power. The contact angles increase according to the aging time up to 10 days, and after that the values become stable. It is well known that the atmosphere is hydrophobic feature. The hydrophilic groups of LCP surface introduced by plasma treatment overturn and migrate into the film for stabilization [6–8]. Therefore, LCP surface became hydrophobic again.

The copper film was deposited even on the untreated LCP film by electroless plating, but the deposition occurred sparsely. On the other hand, uniform deposition was achieved on the plasma-treated LCP film. This explains the improvement of wettability of catalyst and electroless plating solutions against LCP film. Namely, palladium used as catalyst is adsorbed uniformly and forms N-Pd complex with the nitrogen atoms of the functional groups such as NH induced by N_2 plasma. N-Pd complex accelerates the redox reaction and copper film is deposited densely during electroless plating process. LCP surface

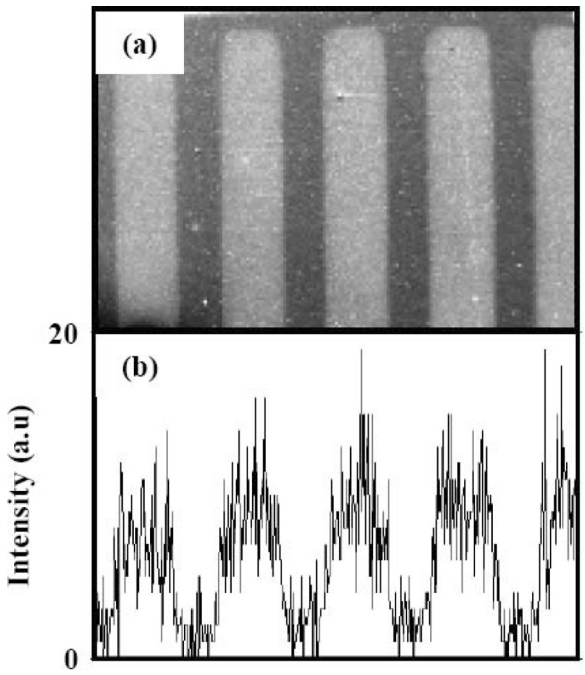

FIGURE 3 (a) SEM image and (b) X-ray microanalysis of circuit pattern formed on the LCP.

was roughened by etching after plasma treatment. Figure 2 shows Ra of LCP films and the 180° peel strength of adhesive joint between copper film and LCP film treated by plasma with various rf power. Ra increases with increase of rf power. The surface roughness of the film treated with 150 W plasma power is greater than those treated with the lower rf powers. Peel strength also increases with the increase of rf power. Roughened surface of the film is important in order to form the strong adhesion because mechanical interaction between LCP and copper film is achieved by penetration of deposited particles. The maximum peel strength (2.4 N/cm) was obtained when LCP was treated with rf power up to 100 W. After peeling, the fragments of LCP were attached to copper film and the cohesion failure of polymer was observed at LCP side. These results indicate that good adhesion performs at copper/LPC interface.

In order to fabricate the circuit pattern, LCP was plasma-treated with rf power at 100 W through the photo-mask. Figure 3 shows the SEM image of the film after electroless copper plating. The bright and dark areas are observed alternatively. Energy dispersion X-ray spectrum of the film indicates that the bright and dark areas are corresponding to copper layer and LCP substrate, respectively. The circuit pattern of copper film with 0.5 mm (line) and 0.3 mm (space) intervals is formed on the LCP film.

CONCLUSIONS

Effects of the N_2 plasma treatment on the adhesion between LCP and copper film were investigated. By plasma treatment, hydrophilic groups containing nitrogen and oxygen atoms were introduced onto the LCP surface. The hydrophilic groups enhanced wettability for plating solution. The uniform copper deposition was achieved on the LCP film by the electroless copper plating. The adhesion strength between copper and LCP increased with increase of rf power and reached to 2.4 N/cm in maximum. The circuit pattern of copper film with 0.5 mm (line) and 0.3 mm (space) intervals was formed on the LCP film by electroless copper plating after plasma treatment through photo-mask.

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