**High Adhesion Plating on Smooth Resin Surfaces Using a High-power UV Lamp**

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**Abstract**

The increasing sophistication of information in society and the impending ‘Internet of Things’ will require smaller and higher-performance electronic devices, and faster also signal transmission. Particularly printed circuit board materials, such as cyclo-olefin polymers (COP) and liquid-crystal polymers (LCP), have been drawn attention for their low dielectric properties. Circuitry formation on these materials need plating treatment. Plating techniques on surface-modification using UV irradiation have been reported, but irradiation times of approximately 5 and 10 min, respectively, to achieve sufficient adhesion strength. However, these long treatment times present a challenge to productivity. To address this problem, we performed experiments using an improved, high-power UV lamp, with the aim of reducing the time required for surface modification treatment. We achieved significant reductions in UV-irradiation processing time, achieving an adhesion strength comparable to that obtained by a conventional method by irradiating COP plates for 45 seconds and LCP plates for 75 seconds.

**Keywords:** COP, LCP, Electroless Plating, UV Irradiation, High Power UV Lamp

1. **Introduction**

The increasing sophistication of information in society and the impending ‘Internet of Things’ have increased the need for smaller and higher-performance electronic devices. These trends necessitate the additional challenge of faster signal transmission speeds. To respond to this demand, manufacturers are looking for materials with lower dielectric constants, lower dielectric loss, and more stable dielectric properties to use in the printed circuit boards mounted inside electronic components. Insulating resins possessing these properties, such as cyclo-olefin polymers (COP) and liquid-crystal polymers (LCP), have drawn attention in recent years.[1]

In order to form circuitry on the surfaces of these insulating resins, one must ensure that the electroless plating layer is sufficiently adhered to the resin surface. Techniques used to ensure this include chemical etching and laser-light irradiation. Roughening of the insulating resin allows minute irregularities to form in its surface in which the electroless plating metal is deposited. The plating layer thus adheres strongly to the insulating resin surface as a result of anchor effects.[2–4]

However, interface roughness interferes with signal transmission, with greater impediments at higher frequencies. The “skin effect” causes the transmission signal to concentrate at the surface of the circuit board, and this occurs more strongly at higher transmission frequencies. Conduction loss thus increases with increasing surface roughness; this feature of insulating resins is well known.[6, 7]

We have previously experimented with irradiating a smooth resin surface with ultraviolet (UV) light in an atmosphere as a way to ensure that the electroless plating layer adheres to the resin surface while maintaining the smoothness of the interface between the two.[5–9] In this method, resin is irradiated with UV light from a low-pressure mercury lamp with emission wavelengths of 185 and 254 nm. We observed that COP and LCP require irradiation times of approximately 5 and 10 min, respectively, for them to achieve appropriate adhesion strength.[10] However, such long UV irradiation times present a great obstacle to productivity. Thus, reducing the irradiation time in
demanded for resin surface modification.

In this study, we tested a new process for the surface modification maintaining smooth surface using UV irradiation to ensure adhesion of the electroless-plating layer, with reductant of the UV irradiation time.

2. Experimental

2.1 Test substrates

The test substrates used in the experiments were 50 × 50-mm sections of COP film (thickness 188 μm; Zeonor-Film® ZF-16, Zeon Corporation) and LCP film (thickness 25 μm; Vecstar® CT-Z, Kuraray Co., Ltd.).

2.2 UV treatment procedure

Atmospheric UV treatment was carried out using either a high-power UV irradiation device (KOV1-75H/I, Koto Electric Co., Ltd.) or a miniature UV surface treatment device equipped with a conventional low-pressure mercury lamp (KOL1-300S, Koto Electric Co., Ltd.), each having emission wavelengths of 254 and 185 nm. Surface modification was performed with these two devices at 290 mm and 30 mm, respectively, from the surface of the test substrates.

Before the experiments, the devices were measured to have outputs of 16.1 and 6.5 mW/cm², respectively, at a wavelength of 185 nm when measured using a UV intensity meter (C8026 UV power meter, Hamamatsu Photonics K.K.).

Table 1 compares the arc lengths and output powers of the high-power UV lamp and low-pressure mercury lamp used in this study. The former has an output power ten times that of the latter (3,000 vs. 300 W). The electrodes are closer together in the high-power UV lamp, giving it a narrower inner volume, which increases mercury vapor pressure when lit and the amount of UV light emitted from it. However, the increased vapor pressure is accompanied by increased temperature. To reduce the effects of lamp heat on the samples during treatment, we placed them around ten times further away from the high-power UV lamp than from the low-pressure mercury lamp.

Table 2 Experimental process.

| Process                          | Temperature | Time     |
|----------------------------------|-------------|----------|
| UV irradiation                   |             | 5-60 sec.|
| ↓                                |             |          |
| Alkaline degreasing              | 65°C        | 2 min    |
| ↓Rinsing                         |             |          |
| Conditioning                      | 45°C        | 2 min    |
| ↓Rinsing                         |             |          |
| Catalyzing                       | 45°C        | 2 min    |
| ↓Rinsing                         |             |          |
| Accelerating                     | 45°C        |          |
| ↓Rinsing                         |             |          |
| E.L. Cu-Ni-P Plating             | 45°C        | 5 min    |
| ↓Rinsing                         |             |          |
| Heat treatment                   | 120°C       | 60 min   |
| ↓                                |             |          |
| Cu electro plating               | 25°C        | 45 min   |
| ↓Rinsing                         |             |          |
| Heat treatment                   | 120°C       | 60 min   |

Table 3 Composition of the electroless Cu-Ni-P plating bath.

| Electroless Cu-Ni-P plating bath |
|-----------------------------------|
| CuSO₄ · 5H₂O                      | 0.032 mol/L |
| NiSO₄ · 6H₂O                      | 0.0024 mol/L|
| C₆H₇Na₃O₇ · 2H₂O                 | 0.052 mol/L |
| NaH₂PO₂ · H₂O                    | 0.270 mol/L |
| H₃BO₃                            | 0.500 mol/L |
| Additive                          | 1.0 g/L     |
| Temperature                       | 45°C        |
| pH                                | 9.0         |
2.4 Observation of surface properties
Wettability and spreadability were observed using a contact angle measuring device (Simage Entry 3, Excimer Inc.) to check the effects of the UV modification treatment on the resin. In addition, a Fourier-transform infrared spectrometer (FT-IR) was used to obtain data on surface functional groups before and after UV treatment (AXIS-Ultra DLD, Jasco Corporation). Infrared absorption spectra were measured using attenuated total reflection (ATR) with a diamond prism.

2.5 Measurements of surface roughness
The surface roughness of the resins under each UV irradiation condition was measured using a scanning probe microscope (SPM) set in atomic-force-microscopy (AFM) mode (SPI4000 E-sweep, Seiko Instruments Inc.).

3. Results & Discussion
3.1 Contact angle tests
Figures 1 and 2 show images taken during water contact angle tests for substrates irradiated with UV for various lengths of time using the high power UV lamp. From a value of 97.9° for the untreated state, the COP substrates exhibited decreasing water contact angle with increasing UV irradiation time, down to 20° in the 60 s condition. The LCP substrates exhibited a similar fall with increasing UV irradiation time, from a water contact angle of 60.7° in the untreated state. Treatment with the high-power UV lamp achieved similar values to conventional treatment with the low-pressure mercury lamp: 24.1° for COP samples irradiated for 5 min, and 37.5° for LCP samples irradiated for 10 min. Our observations of decreasing contact angle with longer UV irradiation time for both COP and LCP substrates indicate the UV irradiation generated polar groups on the materials’ surfaces, improving their wettability.

3.2 Adhesion strength measurements
The COP samples were treated with the high-power UV lamp for eight different irradiation times: 5, 10, 30, 45, 60, 75, 105, and 120 s. Film deposition was incomplete for irra-
Radiation times of 5 and 10 s; complete film formation was observed for irradiation times of 30 s and higher. Adhesion strength measurements were performed on samples exhibiting complete film formation (i.e., irradiation times of 30, 45, 60, 75, 105, and 120 s). Adhesion strength was measured at 0.74 kN/m for the 45 s sample.

The LCP samples were treated with the high-power UV lamp for eight different irradiation times: 5, 10, 30, 45, 60, 75, 105, 120, 135, 150, 165, and 180 s. Adhesion strength was measured at 0.55 kN/m for the 55 s sample. Decreased adhesion strength was observed with extended irradiation times for both the COP and LCP samples. This trend is because excessive UV irradiation embrittles the modified surface layer, significantly decreasing adhesion strength.

We also tested both materials following irradiation with the low-pressure mercury lamp, under the optimum conditions. However, only extremely low adhesion was obtained in this case using the high-power UV lamp.

Films did form using the conventional technique, but they were very thin and had extremely low adhesion. The results are shown in Figs. 3 and 4. The COP substrates treated with the low-pressure mercury lamp reached their peak plating adhesion strength in the 5 min irradiation condition: 0.79 kN/m. The LCP substrates reached their peak value in the 10 min irradiation condition: 0.65 kN/m. These data demonstrate that a high-power UV lamp can reduce the UV irradiation time required for surface modification treatment to 1/5 that required by the conventional low-pressure mercury lamp, while achieving similar performance in terms of plating adhesion strength.[2]

3.3 Effects of UV irradiation conditions on surface properties

Figures 5–8 show the IR spectra measured using FT-IR (ATR) to observe the surface properties of the COP and LCP samples after UV irradiation performed for various times. The COP and LCP samples measured were UV-irradiated for six different times: 0, 5, 15, 30, 45, and 60 s.
Sharp absorption peaks were observed at 1,450 and 2,850–2,950 cm\(^{-1}\) for the COP specimens, due to olefin at the material’s surface. Following UV irradiation, a sharp absorption peak was detected at 1,700 cm\(^{-1}\) and a broad absorption peak was detected at 3,300 cm\(^{-1}\), which were both increasingly pronounced at longer irradiation times. These peaks are due to carboxyl (C=O) and hydroxyl (O-H) groups, respectively, which contribute to the surface’s hydrophilicity. We believe the findings above indicate that the UV radiation conferred hydrophilic functional groups to the surface of the treated COP samples, increasing their hydrophilicity. Similar peaks were observed in the spectra of specimens treated with the high-power UV lamp for 45 s and those treated with the conventional low-pressure mercury lamp for 5 min. In LCP, the change in peak by FT-IR in both high power UV lamps and low presser UV lamp could not be confirmed.

### 3.4 Measurements of surface roughness

Figures 9 and 10 show images of surface roughness analysis for the COP and LCP samples, respectively. For the COP specimens, the average surface roughness (Ra) was 0.41 nm before treatment (Fig. 9(a)), 0.45 nm following treatment with the high-power UV lamp (Fig. 9(b)), and 0.48 nm following treatment with the low-pressure mercury lamp (Fig. 9(c)).

The LCP specimens had respective Ra values of 49.90 nm (Fig. 10(a)), 50.95 nm (Fig. 10(b)), and 50.31 nm (Fig. 10(c)). We can see that, although treatment has changed the roughness of the resin surfaces, the resulting roughness values are much smaller than the micrometer-order values caused by normal roughening treatments. Roughness values for samples treated with the high-power UV lamp and those treated with the low-pressure mercury lamp were similar.

### 3.5 Comparison of UV irradiation devices

Table 4 compares the irradiation intensities at emission wavelengths for the high-power UV lamp and the low-pressure mercury lamp.

Table 4  Comparison of UV irradiation intensities.

| Mercury lamp             | Irradiation distance (mm) | Irradiation intensity (mW/cm\(^2\)) |
|-------------------------|---------------------------|-------------------------------------|
| High power UV lamp      | 290                       | 6.5 130 116                         |
| Low pressure mercury lamp | 30                        | 6.5 64 2                           |

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Fig. 7  FT-IR measurements for LCP specimens treated with a high-power UV lamp for various irradiation times.

Fig. 8  FT-IR measurements for LCP specimens treated with a low-pressure mercury lamp for various irradiation times.

Fig. 9  AFM analysis images of surface roughness for COP specimens before and after UV irradiation: (a) untreated, (b) high-power UV lamp, and (c) low-pressure mercury lamp.

Fig. 10  AFM analysis images of surface roughness for LCP specimens before and after UV irradiation: (a) untreated, (b) high-power UV lamp, and (c) low-pressure mercury lamp.
wavelengths of 351, 254, and 185 nm of the high-power UV lamp and low-pressure mercury lamp used in this study. The 351 nm wavelength is not involved in the surface modification mechanism, but is generated as a result of the design of the lamps. We list irradiation intensity values at 351 nm for comparison.

Light of a wavelength of 185 nm is considered to contribute most greatly to surface modification in resins. Thus, we configured the experimental set-up such that both lamps would emit 185 nm light at an irradiation intensity of 6.5 mW/cm². Nonetheless, the irradiation intensity was far higher for the high-power UV lamp, even when placed ten times further away from samples than the conventional low-pressure mercury lamp. The reduction in required UV irradiation time observed for the high-power UV lamp is due to the significant increase in UV irradiation intensity at wavelengths of 254 and 185 nm.

4. Conclusions

Our investigation of electroless plating on smooth resin surfaces using a high-power UV lamp found the following.

Using the high-power UV lamp to improve surface modification treatment of COP and LCP resins were obtained adhesion strengths of 0.74 kN/m for COP resin irradiated for 45 s, and 0.55 kN/m for LCP resin irradiated for 75 s.

These values were comparable to corresponding adhesion strengths obtained after 5 and 10 min of conventional treatment using a conventional low-pressure mercury lamp. Use of the high-power UV lamp allowed for a significant reduction in UV irradiation time.

In addition, FT-IR measurements revealed samples treated with the high-power UV lamp achieved similar surface properties to samples treated with the low-pressure mercury lamp while requiring shorter processing time. The new process achieved similar surface smoothness to that achieved by the low-pressure mercury lamp. Based on the findings above, we conclude that employing a high-power UV lamp significantly reduces UV irradiation time, and can be improved productivity of the circuitry formation by UV treatment process.

References

[1] Saiwai Shobo, “Introduction to Liquid Crystals,” p. 1, 1992.

[2] M. Sugimoto and H. Honma, “Adhesion Mechanism of Plating on Surface Reformed Resin by UV Irradiation,” Journal of the Surface Finishing Society of Japan, Vol. 59, No. 5, pp. 294–298, 2008.

[3] Y. Tsukuda, “New Movement of Multi Chip Model,” Journal of Japan Institute of Electronics Packaging, Vol. 11, No. 5, pp. 306–310, 1996.

[4] Y. Takasaki, “Build-Up Multilayer Board with Full Additive Technology,” Journal of Japan Institute of Electronics Packaging, Vol. 11, No. 7, pp. 472–474.

[5] S. Wakabayashi, “Fine-wiring Packages and the Expansion of Substrate Technology,” Scientific Lectures and Conference Proceedings from the 16th Conference on Electronics Packaging Technology, pp. 17–18, 2002.

[6] M. Watanabe, Y. Iimori, K. Matsui, M. Sugimoto, and H. Honma, “Surface Modification of Liquid Crystal Polymers Using UV Irradiation,” Journal of Japan Institute of Electronics Packaging, Vol. 10, No. 2, pp. 152–156, 2008.

[7] K. Baba, N. Nishimura, M. Watanabe, and H. Honma, “Metallizing on Cyclo Olefin Polymer Film Using UV Irradiation as a Surface Modification,” Journal of Japan Institute of Electronics Packaging, Vol. 13, No. 6, pp. 447–452, 2010.

[8] M. Watanabe, K. Matsui, M. Sugimoto, and H. Honma, “Smooth Circuit Formation on Cycloolefin Polymers,” Journal of Japan Institute of Electronics Packaging, Vol. 10, No. 3, pp. 229–233, 2007.

[9] M. Watanabe, M. Sugimoto, and H. Honma, “Metallization on Smooth Resin Substrate,” Journal of the Surface Finishing Society of Japan, Vol. 58, No. 12, pp. 774–778, 2007.

[10] T. Sugiyama, Y. Iimori, M. Watanabe, and H. Honma, “Surface Metallization on High-Temperature Liquid-Crystal-Polymer Film by UV Irradiation Process,” J. Electrochem. Soc., Vol. 156, No. 9, pp. 360–363, 2009.

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