Fabrication of Electrical Circuit Using Palladium Colloid

Toshihiko Oguchi and Keiki Suganami, Morimura Chemicals Ltd., Kanagawa, Japan

Abstract

A precise electrically conductive circuit was fabricated on a plastic film substrate with an electroless Cu-plating layer that was formed on a metal colloid printed pattern. The printed pattern was formed with the inks that contain the mixture of silver colloid and palladium colloid. The degree of catalytic activity of the printed pattern upon the electroless Cu-plating was enhanced by the addition of an extremely small amount of palladium colloid into the metal colloid ink; plating speed was increased by the three times on the metal colloid pattern that was formed with the inks containing only 1 wt% of mixed metal colloids. The Electronic circuit formation and its practical performance were confirmed for the circuit fabricated by both PIJ (Cu-plating on ink jet pattern) and PFS (Cu-plating on filled and squeezed pattern) processes.

Introduction

Recently, printing technologies such as silkscreen printing, electrophotography, and ink jet printing, etc., is regarded as the most promising technologies for the fabrication of precise electrically conductive circuits. These technologies are expected to realize an on-demand, simple, rapid, and low cost, circuit fabrication in near future.

In the previous paper at NIP 19, the authors reported on the utilization of silver colloid ink jet ink for the fabrication of electrical circuit on various substrates. In NIP 20, the authors introduced new fabrication processes, namely, PIJ (Plating on Ink Jet pattern) and PFS (Plating on Filled and Squeeze pattern) processes. The electrical circuits for practical use that have a line width of less than 5 μm, reliable conductivity and durability for practical use were realized with these new fabrication processes. The difficulty in these processes, however, is that they need a long time for the electroless Cu-plating process to obtain enough conductivity for an electrical circuit.

In this report, the inks containing a palladium salt or a palladium colloid was used to enhance the catalytic activity for the Cu-plating processes. Consequently, the plating speed increased remarkably especially when an extremely small amount of palladium colloid was added to the silver colloid ink. It was confirmed that the reliable electrical circuits on various film substrates were obtained easily in both PIJ and PFS methods. More precise results on this topic will be mentioned below.

Experimental

Metal Colloids

As a silver colloid, an aqueous dispersion of silver particles having an average particle size of 20 μm was used. As a palladium colloid, an aqueous dispersion of palladium particles having an average particle size of 10 μm was used. These colloids are obtained by deposition of metal particles from aqueous solutions which are containing the respective metal ions. The obtained colloids are well dispersed in water with a protective layer that is formed on the metal particle surface.

Preparation of Metal Colloid I-J Inks

Ink jet inks were prepared by the addition of various surfactants into the metal colloid aqueous dispersion. The surfactants were selected to adjust the surface tension and viscosity, and to stabilize the dispersion. The typical values of the physico-chemical properties of the inkjet ink containing metal colloids mentioned below are shown in Table 1. The basic values such as viscosity and surface tension are nearly the same as those of typical pigment dispersed ink jet ink. Various circuit patterns could be obtained without changing the operation parameter for the ink jet printer. The formulations of metal colloid inks used in this experiment are shown in Table 2. They consist of one silver colloid ink, one palladium chloride ink, three palladium colloid inks, and seven mixed inks containing the silver colloid and palladium colloid.

Table 1: Properties of Metal Colloid Ink

	Metal Colloid Ink	Pigment I-J Ink
Viscosity (mPa•s)	3.6	2.0 to 5.0
Surface tension (dyne/cm)	3.2	30 to 40
Solid content %	15	15 to 20
PH	11.0	7 to 9
Conductivity (μs/cm)	1,300	500 to 3000

Table 2: Metal Colloid Inks for PIJ and PFS Processes

Item No.	Af Colloid conc.	Pd Colloid conc.
1	15.0 wt%	0
2	$PdCl_2$ solution conc. 1.0 wt%	
3	0	1.0 vwt%
4	0	0.5 wt%
5	0	0.1 w%
6	15.0 wt%	0.5 wt%
7	15.0 wt%	0.1 w%
8	15.0 wt%	0.01 wt%
9	15.0 wt%	0.001 wt%
10	0.970 wt%	0.030 wt%
11	0.485 wt%	0.015 wt%
12	0.097 wt%	0.003 wt%

Substrates

A polyester film substrate (thickness: 50 μm) having a micro-porous styrene-acrylic polymer layer linings (thickness: 30 μm) on both sides was used as the substrate for the circuit pattern formation in the PIJ process.

A polyester film substrate (thickness: 100 μm) having a UV light absorbing layer (thickness: 10 μm) was used as the substrate for the circuit pattern formation in the PFS process.

Formation of Conductive Circuit with PIJ and PFS Method

The flow charts of the formation of the conductive circuit by the PIJ and PFS methods are shown in Fig. 2 and Fig. 3, respectively. In the PIJ circuit, patterns are printed with the metal colloid inks by using a thermal type ink jet printer that has a printing resolution of 4800 dpi (horizontal) × 2400 dpi (vertical). In the PFS circuit, patterns were prepared in the following two steps; 1) a grooved pattern (line width: 10 μm, line depth: 10 μm) was engraved on the substrate surface by the laser abrasion with 355 nm UV laser, 2) the groove was filled with the metal colloid inks, the excessive part of which was squeezed from the substrate surface. The patterns formed by both methods were baked at 150ºC for 15 min and dipped into an electroless Cu-plating bath to form a conductive copper layer onto the metal colloid pattern.

Evaluation of Catalytic Activity of Metal Colloids for Cu-Plating Layer Formation

To evaluate the degree of catalytic activity of the metal colloids for the formation of Cu-plating layer, a test pattern shown in Fig. 1 was used. The ink jet-printed test patterns on the polyester film substrate were prepared by the procedure mentioned below with the various ink jet inks listed in Table 2. After baking, obtained pattern was dipped into an electroless Cu-plating bath that was maintained at 40ºC. After the lapse of a prescribed time, the test pattern was taken out from the bath, and the resistance between the terminals A and B was measured. The degree of the catalytic activity was evaluated from relationship between the resistance and the plating time.

Figure1. Test pattern prepared by ink jet printing

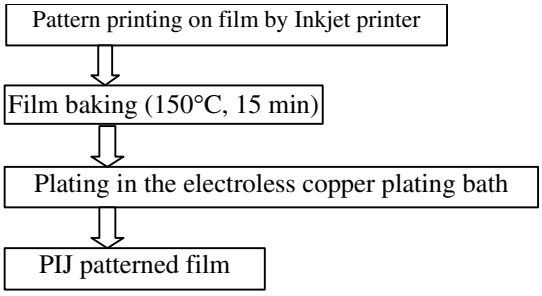

Figure 2. Preparation of conductive circuit by PIJ process

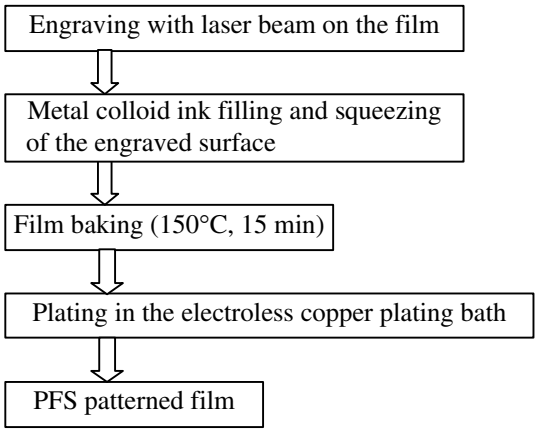

Figure 3. Preparation of conductive circuit by PFS process

Results and Discussion

Catalytic Activity of Palladium Ion or Palladium Colloid in Cu-Plating Process

Stable Cu-plating layers were obtained on the test pattern formed with inks #3, #4 and #5 which contained palladium colloid. However, the Cu-plating layer was not formed on the test pattern with an ink #2 in which, instead of palladium colloid, palladium chloride was contained. It was thus confirmed that the metallic palladium is essential to obtain an effective catalyst for the Cu-plating.

Figure 4 shows the decrease of the electric resistance between the terminals A and B in the test pattern with the increase of the Cu-plating time. The decrease of the resistance is attributed to the formation of the Cu-plating layer on the metal colloid pattern. The palladium colloid pattern was formed with the inks #3, #4 and #5 containing palladium of different concentrations. Assuming that the decrease rate of the resistance is correlated to the increase rate of Cu-plating layer thickness, the formation of Cu-plating layer on the palladium colloid patterns seems not so rapid as the formation of Cu-plating layer on the silver colloid pattern which was formed with an ink #1. The palladium colloid, however, is acting as a more effective catalyst than that of the silver colloid for the formation of Cu-plating layer, because the concentration of metal colloid in the inks #3, #4 and #5 is much lower than that of silver colloid ink #1; in the case of Cu-plating layer on the palladium colloid pattern formed of the ink #5, which contain only 0.1 wt% of palladium colloid, the decrease rate of the resistance is comparable to the case with the ink #1 which contained 15% silver colloid. It is interesting that, at the beginning stage of Cu-plating, the decrease rate of the resistance is nearly the same on the palladium colloid pattern formed with the inks #3, #4 and #5.

It is Also remarkable that, at the beginning of Cu-plating, the pattern formed with the ink containing only 0.1 wt% palladium realize the same plating speed with the ink containing 15 wt% silver colloid. As a result, the palladium colloid can be regarded as an effective catalyst for the formation of Cu-plating layer.

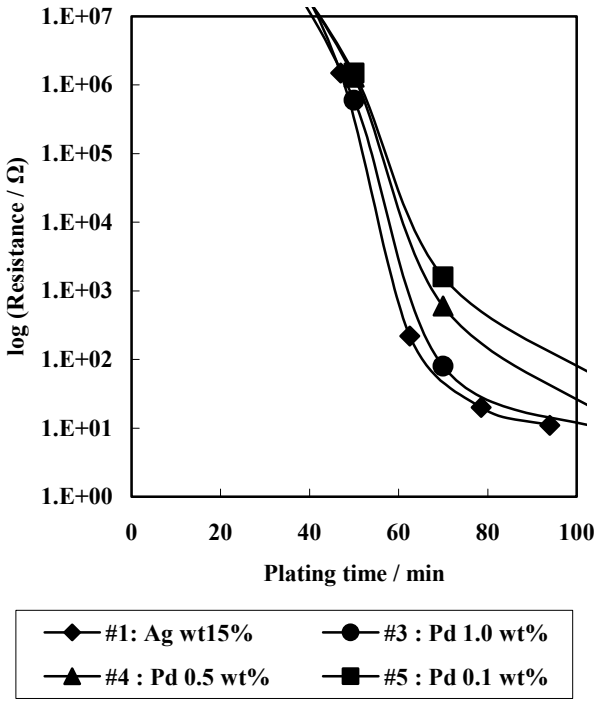

Figure 4. Electroless Cu plating characteristics of IJ pattern prepared with inks containing Pd colloid

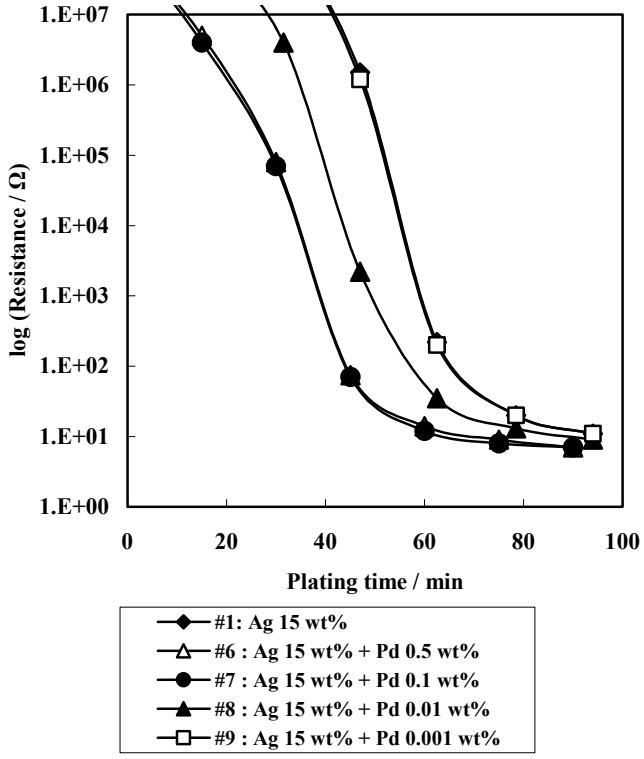

Figure 5. Electroless Cu plating characteristics of IJ pattern prepared with inks containing mixture of Pd and Ag colloids

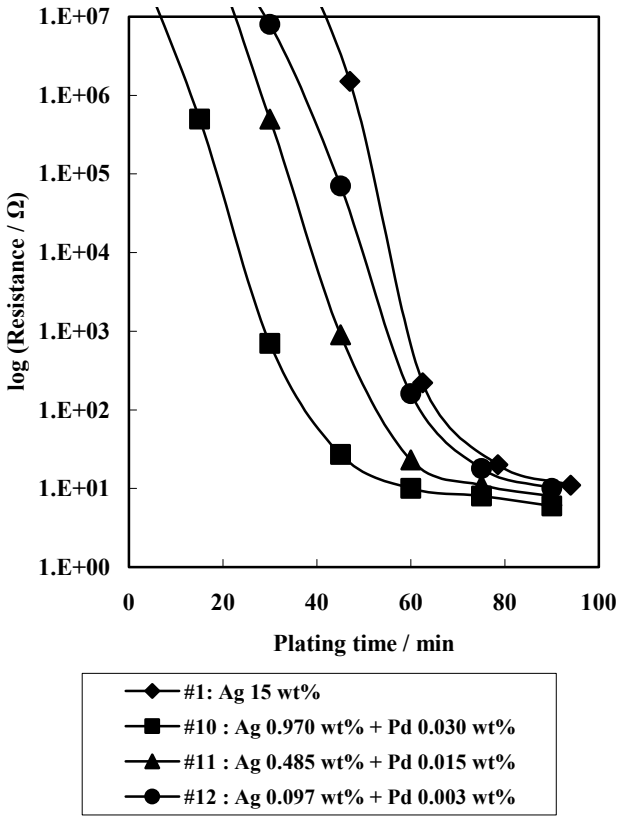

Figure 6. Electroless Cu-plating characteristics on IJ pattern formed with inks containing mixture of Pd and Ag colloid

Catalytic Activity of Palladium Colloid and Silver Colloid Mixture in Cu-Plating Process

The inks #6, #7 and #8 were prepared by the addition of 0.001 wt% to 1.0 wt% palladium colloid into the silver colloid ink which is containing 15 wt% silver colloid. The color of the printed pattern changed from yellow to black with the increase of the added amount of palladium colloid into the silver colloid ink. Even in the case of the ink #8 that contains only 0.01 wt% of palladium colloid in it, the color change was clearly visible with naked eye.

Figure 5 shows the decrease of electric resistance between the terminals A and B in the test pattern with increase the Cu-plating time. The test patterns were formed with the inks #1, #6, #7, #8 and #9 respectively. The Cu-plating time necessary for attaining the resistance of 1 M was shortened with the increase of the added amount of palladium colloid in the inks. In the case of the inks #6 and #7, the needed Cu-plating time to attain the resistance of 1 M can be shortened to 1/3 of the case with the ink #1. The difference of the metal colloid composition in the two inks #7 and #1 is the presence or absence of 0.1 wt% palladium colloid. The result suggests that the catalytic activity is extremely increased by the presence of an extremely small amount of palladium colloid.

Figure 6 shows the similar characteristics of resistance decrease as Fig. 5. However, these characteristics were obtained by the Cu-plating layer with the inks #1, #10, #11, and #12 which inks have

different metal colloid compositions from those of the inks used in Fig. 5 in the sense that 1) the weight ratio of palladium/silver colloid was increased to 3/97 and maintained constant, and 2) the total amount of mixed metal colloids in the inks are less than 1.0 wt%. In the case of Cu-plating layer that was formed with the ink #10, the Cu-plating time needed to attain the resistance of 1 MΩ is shortened to less than 1/3 of the time needed to attain the same resistance with the ink #1. It is interesting that the Cu-plating speed obtained with the ink #10 which contains only 1.0 wt% metal colloids is higher than that obtained with the ink #7 in Fig. 5 which contained 15.1 wt% metal colloids. The results suggest that the ratio of palladium colloid to silver colloid is an important factor to obtain the strong catalytic activity for the Cu-plating.

Fabrication of Conductive Circuit by PFS Method

Figure 7 shows a Cu-plating checked pattern (groove line width: 10 μm, groove line depth: 10 μm, gap between the lines: 300 μm) formed by the PFS process where the polyester film with the lining of the 355 nm UV light absorbing layer was used as the substrate. The ink #10 was used to fill the grooves. After baking the ink-filled pattern, the substrate was dipped into the electroless Cu-plaiting bath for 15 minutes to obtain the conductive circuit.

The obtained Cu-plating layer had a thickness of 5 to 6 μm and showed a specific resistivity of 3×10^{-6} Ω-cm. The transparency of this film was 85% under the visible light and the excellent durability was obtained.

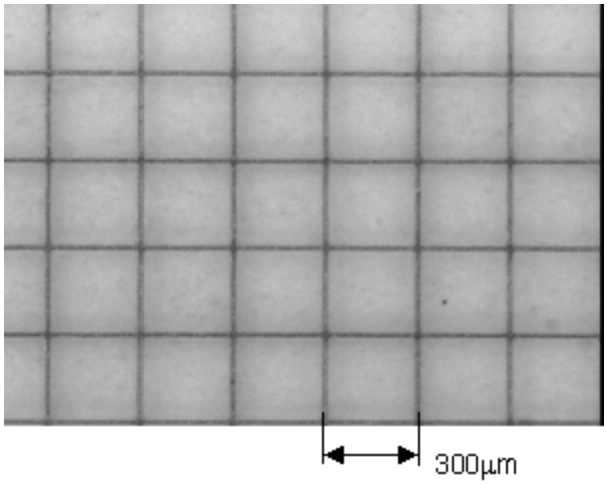

Figure 7. Transparent electromagnetic wave shield film prepared by PFS method using Ag/Pd mixed colloid ink

Conclusion

The precise electrical circuit was fabricated on the film substrate by both PIJ (Cu-plating on ink jet pattern) and PFS (Cu-plating on filled and squeezed pattern) processes. The Cu-plating layer was formed on the metal colloid circuit pattern that was printed with the inks containing a mixture of the silver colloid and palladium colloid. It was confirmed that the metal colloid pattern functions as an effective catalyst for the electroless Cu-plating. A plating speed of thee times was obtained by using the silver colloid containing an extremely small amount of palladium colloid. With the addition of 0.03 wt% palladium colloid, the strongest catalytic activity was observed for the ink containing 0.97 wt% silver colloid. Electronic circuit formation and its practical performance are confirmed for the circuit fabricated by both PIJ (Cu-plating on ink jet pattern) and PFS (Cu-plating on filled and squeezed pattern) processes.

References

1. P. H. Kydd and D. L. Richard, Proceedings of IS & T's NIP 14, p.222 (1998)
2. Toshihiko Oguchi and Keiki Suganami, Japan Patent Disclosure 2002-134878
3. Toshikatsu Kobayashi, J. Japan Soc. Colour Material, 75, 66 (2002)
4. T. Oguchi, K. Suganami, T. Nanke, and T. Kobayashi, Proceedings of IS & T's NIP 19, p.656 (2003)
5. Ming-Huan Yang, Wanda W. W. Chiu, Kevin Cheng, and Jane Chang, Proceedings of IS & T's NIP 20, p.256 (2004)
6. Wanda W. W. Chiu, Ming-Huan Yang, Kevin Cheng, and Chieh-Yi Hung, Proceedings of IS & T's NIP 20, p.261 (2004)

Author Biography

Toshihiko Oguchi joined Morimura chemicals Ltd. in April 2000. He is responsible for new product development and application research. Previously at R & D center in Toshiba Corporation his work has primary focused on the development of liquid and dry toners for electro-photography and perpendicularly recording magnetic media. He is a chief member of ISJ's Technical Committee part III meeting (The technical committee of toner-based material). He received his BS from Tokyo Metropolitan University in 1967 and Dr. of Engineering from Tokyo Institute of Technology in 1988.