Formation of Precise Electrically-Conductive Circuit with Metal Colloid Ink

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Abstract

Precise electrically-conductive circuit were formed using silver colloid pattern on a plastic film by a PIJ (Plating on Ink Jet pattern) method or a PFS (Plating on Filled and Squeezed pattern) method. In the PIJ, method a copper plating layer was formed on a silver colloid pattern that was formed in advance with an ink jet printer. In the PFS method, a copper plating layer was formed on the silver colloid pattern which was obtained by filling the laser engraved groove with silver colloid particles. The layer thickness of the copper plating layer in this case was in a range of 5 to 10μm. The finest line width obtained was about 30 μm in the PIJ pattern and 5 μm in the PFS pattern. An electrical resistivity of smaller than $10^{-5}\Omega$cm was attained.

The adhesive strength of the copper layer onto the substrate surface was improved by adjusting the porosity of the film surface for ink jet printing or the depth of the groove on the laser engraved film surface.

Applications of these techniques to electronic components such as electric circuit boards, capacitors, inductors, electrodes, RFID antennas and electromagnetic wave shield films were discussed.

Introduction

Recently, screen printing, electrophotographic printing and ink jet printing have been used to form an precise electrically-conductive pattern by depositing metal particles onto an insulating substrate surface.[1,2]

Among the above three printing technologies, the ink jet printing technology which uses ink containing metal colloid particles is considered to be most promising because electrically-conductive circuit patterns are obtained directly based on a circuit design data from a computer.[2]

Concerning the metal colloid particle layer that is formed with an ink jet printer, however, there are fatal problems to be solved. First, high baking temperature is needed to obtain a solid metal conductivity. Second, it is difficult to obtain sufficient adhesive strength to the substrate surface. Third, it is difficult to obtain required electrical conductivity because the printing thickness obtained by an ink jet printer is smaller than 1 μm.

In this paper, a PIJ (Plating on Ink Jet pattern) method and a PFS (Plating on Filled and Squeezed pattern) method were investigated to obtain a precise-electrically conductive circuit. In both methods, an electroless copper plating layer is applied onto a silver colloid pattern formed by an ink jet printer or onto a silver colloid pattern which is obtained by filling the laser engraved grooves with silver colloid particles. The problems and solutions for practical applications of the obtained conductive circuit will be mentioned below.

Experimental

Preparation of Silver Colloid Ink

Silver colloid ink was prepared by dispersion of silver colloid particles having an average particle size of about 20 nm into water.[3,4] The silver colloid particles were deposited slowly from an aqueous solution of silver nitrate by addition of a reduction agent such as a tertiary amine. Obtained colloid particles were encapsulated with a hydrophilic block copolymer layer to prepare protected silver colloid particles. A dispersion stabilizing agent, surface tension adjusting agent, and organic solvents were added to the silver colloid dispersion having a particle concentration of 30 wt% to obtain the silver colloid ink.

Substrates

As a substrate for the PIJ method, a polyester (PET) film having porous layers that acts as an ink reservoir layer was used.

As a substrate for the PFS method, a polyimide (PI) film, polyethersulfone (PES) film or surface treated PET film all showing high absorption in 355 nm UV light was used.

Circuit Formation by PIJ Method

A commercial ink jet printer that can reproduce a precise pattern of 4800 dpi (horizontal) × 1200 dpi (vertical) was used to obtain an ink jet circuit pattern.

The printed film which has a circuit pattern layer of the silver colloid particles was baked in a 120°C oven for 15 minutes. The baked film was immersed for about 3 hrs in an electroless copper plating bath which was maintained at a temperature of 40°C to obtain a PIJ patterned film. The PIJ patterned film was washed with water, dried up and used as a sample for electrical evaluation.

Circuit Formation by PFS Method

Grooves having a line width of 10 to 15 μm and a depth of 1 to 10 μm were engraved on a PI, PES, or PET film surface by 355 nm laser beam irradiation. The silver colloid ink was applied to the engraved surface and squeezed by a urethane rubber squeezer to obtain a FS (Filled and Squeezed) patterned film. The film was baked in the 120°C oven for 15 minutes. After baking, the FS patterned film was immersed for about 3 hrs in the electroless copper plating bath which maintained at a temperature of 40°C for about 3 hrs to obtain a PFS patterned film. The PFS film was used as the sample for electrical evaluation.

Results and Discussion

Circuit by PIJ Method

Surface of Polyester Film for Ink Jet Printing

Figure 1 shows a SEM photograph of a film for ink jet printing (Peachcoat WE-110: Nisshinbo Industries, Inc.) which is a PET film having the porous layer on its surfaces. Innumerable pores having a pore size of smaller than 0.5 μm are seen on the film surface. The pores act as the silver colloid ink reservoirs and reduce the blur generation during the printed ink drying process.

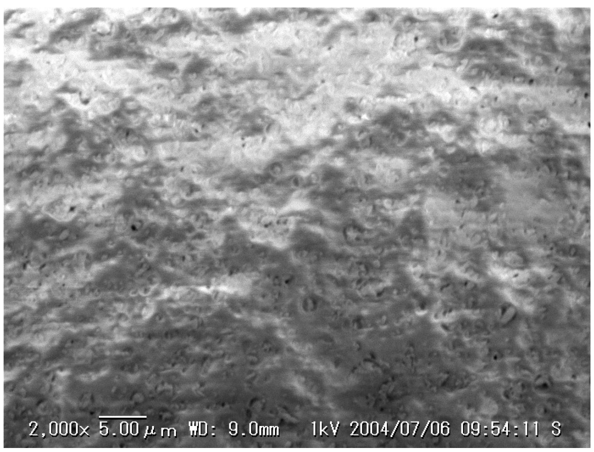


Figure 1. Surface of ink jet printing substrate

Cross Sectional Observation of PIJ Patterned Film

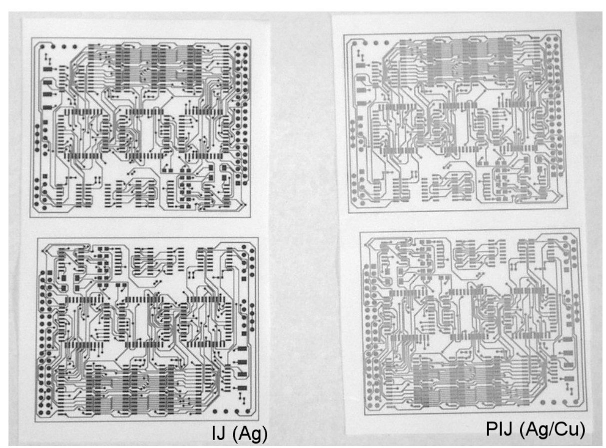
A cross-sectional view of the PIJ patterned film using the WE-110 substrate is shown in Fig. 2. The substrate consists of three layers, namely porous layer / polyester substrate / porous layer, their respective thickness being 30 μm / 50 μm / 30 μm. The PIJ layer is seen in the left half portion of the upper porous layer. The boundary between the copper deposited area and the non copper deposited area is clearly seen as a vertical line. The result suggests that the printed silver colloid ink penetrates the pores vertically and forms a colloid particle layer on the pore wall surface to make the IJ pattern. Figure 2 also shows that after the electroless copper plating process, the copper deposits on the silver colloid layer and fills the pores completely.

Typical Examples of PIJ Circuit Pattern

A typical example of circuit pattern formed by the PIJ method is shown in Fig. 3. Figure 3(a) shows an example of silver colloid ink jet pattern formed by a commercial ink jet printer. Figure 3(b) shows a PIJ pattern obtained by applying the electroless copper plating onto the ink jet pattern. The PIJ pattern shows that the area of copper deposition on the substrate surface is precisely restricted to the ink jet patterned area. As a result, the copper plating layer is regarded as an overwrite layer that reproduces the ink jet pattern with high fidelity.

When the physico-chemical properties of silver colloid ink and the feeding amount of the silver colloid ink onto the unit area of the substrate are adjust to the optimum, the finest line width obtained by the PIJ method was estimated about 30 μm. The thickness of the copper plating layer from 5 to 10 μm was required to obtain sufficient conductivity. The specific resistivitiy of the copper plating layer can be estimated to be at the same level as that of copper metal. The time required to obtain the above plating thickness was dependent on the plating condition.

Figure 2. Cross sectional view of PIJ patterned film



(a) ***(b)***

Figure 3. Typical example of IJ and PIJ patterned circuit

Application of PIJ Circuit

The PIJ pattern on both front side and back side of the substrate can be connected easily by a through hole in a connecting portion. During the ink jet circuit patterning from both sides of the substrate, the silver colloid ink penetrates the through hole, and the wall of the through hole is covered with the silver colloid layer. As a result, the ink jet circuit patterns of both sides are connected.

An LED unit was mounted on the PIJ pattern that was formed on the WA-110 substrate. The obtained module worked well as a warning signal generator.

An RFID device working at a frequency of 915 MHz was developed using the PIJ patterned PET film. The obtained device constituted an excellent component in a system.

Nevertheless, further improvements of the physico-chemical and mechanical properties of the substrate surface such as adhesive strength, heat resistance, ink absorbing capacity, etc., are essential to obtain a PIJ circuit for practical use.

A roll to roll process is suitable for the production of the PIJ circuit. The PIJ method will be applied in future to the print circuit board, electrode, RFID antenna, inductor, capacitor, connector, etc.

FS (Filled and Squeezed) Pattern on the Plastic Film

Figure 4a shows a typical FS pattern on a PES film. The pattern was obtained by filling and squeezing the silver colloid ink in the horizontal and vertical grooves that are engraved by 355 nm laser beam irradiation. A sharp edged check pattern consisting of lines having 15 μm line width is obtained. The interval between the lines is 300 μm. It was confirmed that, in the FS patterning technique, the line width smaller than 5 μm can be realized.

PFS Pattern on the Plastic Film

Figure 4b shows the PFS pattern in which the electroless copper plating layer was formed on the silver colloid FS pattern. The copper-plating area is precisely restricted to the silver colloid FS patterned area; the line width and the interval between the lines in the PFS pattern maintain the same value as those in the FS pattern.

Figure 5 shows the transmittance spectra of the PFS the film shown in Fig. 4b. The ratio of the copper deposition area to the non-deposition area is estimated to be 10.25%. The light transmittance of the film in the wavelength region from 400 nm to 700 nm maintained at a level of 80%. The film can be used as an excellent transparent conductive film because the PFS pattern of Fig. 5 is highly conductive.

Cross Sectional View of PFS Pattern

Figure 6 shows the cross sectional views of the grooved portion in Fig. 4. The samples for the observation were prepared by tore apart the patterned films along the horizontal groove.

Photograph A shows a cross sectional view of the groove wall along the horizontal groove axis. The groove wall is seen in an upper layer portion of the film. A large number of holes that were formed by the bubble are seen on the wall. The bubbles were created by the high temperature generated in the laser abrasion process. The intersection point of horizontal and vertical grooves in Fig. 4 is seen as a V shaped hole at the center of the upper layer. The depth of the groove is estimated to be about 5 μm.

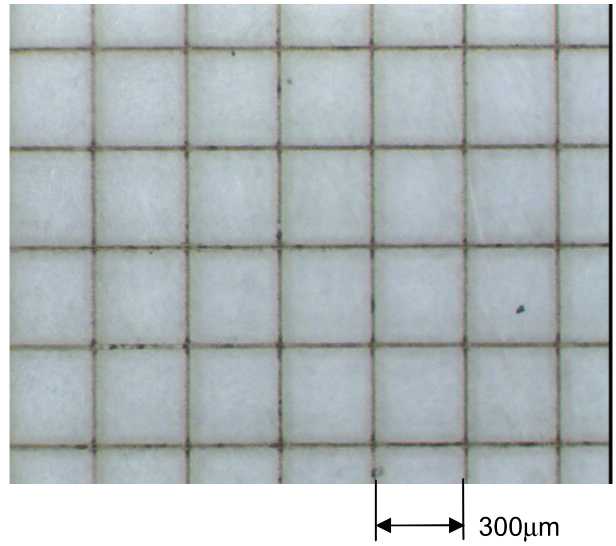


Figure 4a. FS pattern formed on PES film

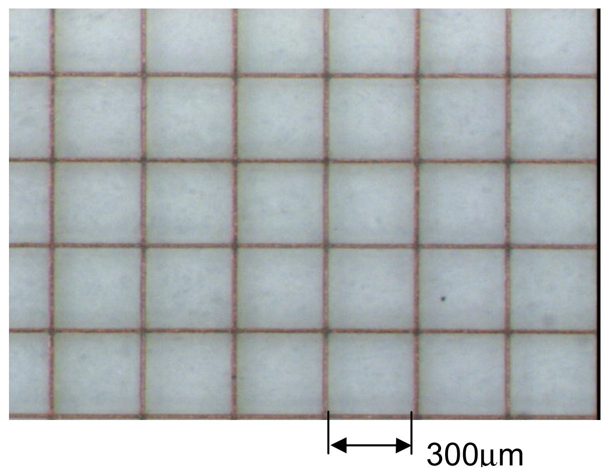


Figure 4b. PFS pattern formed on PES film

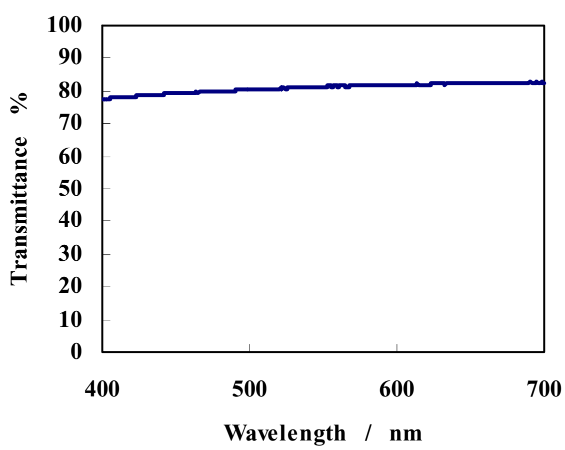


Figure 5. Transmittance of electromagnetic wave shield film

Photograph B shows the cross sectional view of the FS patterned groove wall along the horizontal groove. Numerous white spots in the upper layer represent the silver particles. The particles are filling the bubbles and forming island-like structures around the bubbles.

Photograph C shows the cross sectional view of the PFS pattern along the horizontal groove. Almost all of the silver particles and the plated copper in the horizontal groove are removed during the tearing process in the sample preparation. However the mixture of the silver colloid particles and plating copper that fill the full space of the vertical groove is seen at the V shaped groove in the center of the upper layer.

In the horizontal groove wall, a small amount of silver particles or plating copper is remaining in the bubble. The result suggests that the silver colloid ink and plating copper penetrate each bubble and fill the whole space of the bubble. The copper depositing in the bubble is acting as an anchor in the groove. As a result, the PFS pattern showed the excellent adhesive strength in cellulose tape peering tests.

As shown in Fig. 6C, the plated copper fills the groove space densely. Hence, the PFS pattern in Fig. 4b can be regarded as a copper wire mesh that is embedded in the PES film surface.

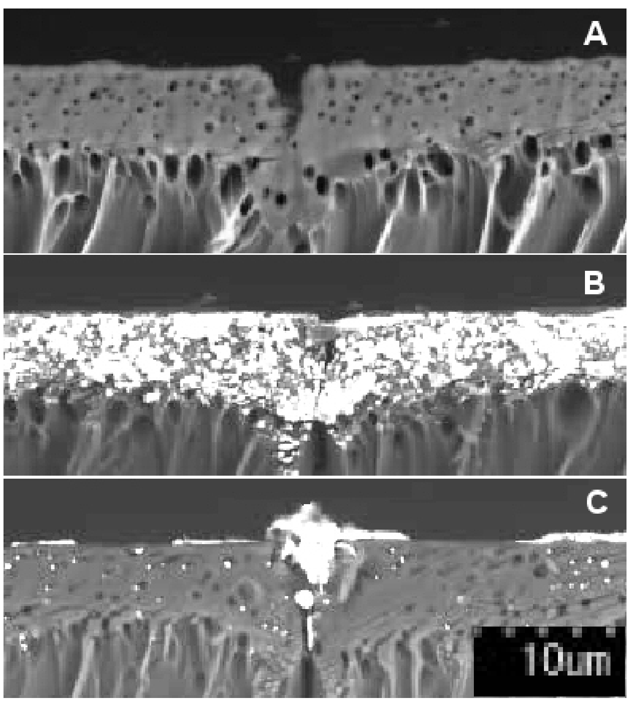


Figure 6. Cross sectional views of patterned film in PFS process

Application of PFS Circuit

The PFS pattern in Fig. 4b showed an excellent performance as a transparent electro-magnetic wave shield film.

Various type of films which show a strong adsorption for 355 nm laser beam are tested. By using a PET film which has a coated layer strongly absorbing 355 nm UV light, a laser engraving speed exceeding $0.1m^2$/min was confirmed in the pattern shown in Fig. 4.

The PFS method can be regarded as the most suitable process to obtain the precise conductive circuit pattern. The groove obtained by Nano-in-printing technique that realizes a groove width of smaller than 1 μm is also promising. By using those grooved patterns, a PSF circuit with the line width of smaller than 1 μm will be possible in the future.

The PFS method can also be applied to roll to roll process to produce a precise conductive circuit. In addition to the applications that are confirmed in the PIJ method, circuit formation for OLED devices and organic semiconductors seems to be a promising application field for the PFS method.

Conclusion

Two methods which form the precise electrically-conductive circuit on a plastic film using silver colloid particles were investigated. One is a PIJ (Plating on Ink Jet pattern) method for fabricating a copper plating circuit on the silver colloid pattern formed with an ink jet printer. The other is a PFS (Plating on Filled and Squeezed pattern) method for fabricating a copper plating circuit on the silver colloid pattern which is obtained from the laser engraved groove filled with silver colloid particles.

Finest line width obtained was about 30 μm in the PIJ circuit and 5 μm in the PFS circuit. Specific electrical resistivity of smaller than 10^{-5} Ω cm was obtained. Fatal practical problems to be solved for obtaining the precise conductive circuit were investigated.

Applications to electronic components such as electric circuit boards, capacitors, inductors, electrodes, RFID antennas and electromagnetic wave shield films were discussed.

References

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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.