Additive Fine-Line Circuit Process through Catalyst Induced Copper Electroless Plating

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Abstract: To response the demand for fine line in electronic products, additive manufacturing process integrated printing techniques and deposited methods to reach fine line circuit, with the merits of reduced material wastage, low fabrication costs, and mass production advantage capability. Recently, we have developed additive process in fabricating circuit on flexible substrate through catalyst induced copper electroless deposition (ELD) method. The additive processes that integrated printing, activation, and metallization were applied to produce fine-line circuit with 5 \textmu m line width. The sample with ultraviolet (UV) activation shows better conductive property in comparison with the sample without activation after electroless deposited process. Accordingly, the results indicated that the reaction of catalyst induced electroless copper plating strongly depends on UV activation. The fine-line circuit exhibits a narrow line width circuit (around 5 \textmu m), lower resistance (6.2 \textmu \Omega cm), and mass production with low pollution in comparison with lithographic processes (with photoresist and acid pollution) with a high throughput system (R\textsuperscript{2}R system) for the applications of double side flexible printed circuit board (FPCB).

Key words: Additive process, fine-line circuit, gravure offset printing, electroless plating, catalyst.

1. Introduction

Reliable and fast processes for fabricating fine-line circuit have been of great interests for vital applications of electronic devices. Recently, increased attention on the additive processes has been paid for printed electronics (PE) technology, due to the corrosive chemicals and environment pollution in subtractive processes [1, 2]. However, fine-line and electrical conductivity are the critical requirements for additive processes in printed electronics technology because the performance and reliability of an electric device depend on the scale and conductivity of the pattern [3, 4]. For instance, Fujikura Company printed 30 \textmu m Ag conductive paste patterns on polyethylene telephthalate (PET) film with resistance of 40 \textmu \Omega cm by gravure offset printing technology [5]. The researchers in University of Minnesota printed 20 \textmu m conductive silver line with aspect ratios greater than 0.1 by aerosol jet printing method [6]. In addition, AIST (National Institute of Advanced Industrial Science and Technology in Japan) has used super-fine inkjet printing technology to fabricate \leq 1 \textmu m conductive line with silver nanoparticle ink [7]. To response the demand for additive processes in printed electronics, throughput is an important factor for printing electronic circuits of mass-production. Gravure offset printing is a particularly promising technique with several advantages, including process simplification, high throughput (~10\textsuperscript{2} m\textsuperscript{2}/s), high adaptability of the substrate over large area, and high printing resolution (offers micron-scale resolution). Here, we demonstrated high-performance printed fine conductive line, scaling to unprecedented levels via advanced additive processes to apply in double-side
flexible printed circuits boards. The excellent results were achieved through a combination of proper material, improved gravure off-set technology, suitable ultraviolet (UV) energy to induce catalyst and optimized metallization method. These results exhibited an important step in the development of fully additive process for large scale manufacturing fine-line circuit technology in double-side flexible printed circuit board (FPCB).

2. Materials and Methods

For the experimental part of the research, we had integrated printing, activation and metallization in additive processes and its key components (including transfer ink with precursor, gravure plate, printer and metallization solution) to print patterned circuits with minimum linewidth ~5 μm on a substrate surface through 3 main working steps of gravure off-set printing, UV activation, and copper electroless deposition (ELD). First, the thin seed layer of precursor pastes was printed on the substrate through gravure offset printing. Then, the pattern was activated by UV curing and dried with oven curing. Finally, the substrate with patterned precursor pastes was immersed in electroless plating bath to deposit a cooper conductive layer. The additive process of fabricating fine-line circuit manufacturing technology was shown in Fig. 1. In gravure offset printing processes, the Ag nanoparticle base precursor paste was synthesized by processes in Ref. [8] with functional high transferring rate. The engraved stainless plate was fabricated by ultra-fast laser technology for printing circuits. After laser engraving, the surface roughness of gravure plate was reduced by electro-polishing method. In activation, the sample was activated in UV irradiation with 362 nm wavelength. After activation, the sample was dried in oven on 150 °C for 30 min. After cuing treatment (UV and oven), the samples were immersed in electroless plating bath on 50 °C with pH 12.6 to metallize pattern circuit.

3. Results and Discussions

Here, we focused on additive fine-line circuit processes to improve the value and quality of flexible printed circuit board (FPC). Gravure off-set printing process can be divided into the blading, off and set processes. The ink filled the engraved gravure cell with doctor blade (blading process), picking up from the blanket roller (off process) and finally transferred onto the flexible substrate (set process). Fig. 2a showed the patterned circuit with ink (thin precursor paste layer) was printed on substrate surface through gravure offset printing processes. The image from optical microscope (OM) in Fig. 2b displayed that the minimum linewidth was around 3.4 μm without widening or smudging issues [9]. Therefore, the results indicated the fine-line pattern (< 5 μm) could

Fig. 1 Additive fine-line circuit process: (a)—Gravure offset printing, (b)—UV curing and (c)—electroless plating.
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Fig. 2  The patterned circuit printed on polyimide (PI) substrate through gravure offset printing processes.

Fig. 3  The sheet resistance of patterned circuit was activated by UV irradiation. The results were plating Cu for 5 min.

be transferred completely in gravure off-set printing processes. To realize the role of activation, activated treatments were mainly used to enhance conductive and adhesion properties of fine line circuit by increasing catalyst activation and decreasing solvent content by UV and oven curing processes. From an examination of Fig. 3, the copper deposited on the pattern surface with sheet resistance was around 3 Ω/□ as UV curing energy reached 20 W. However, the sheet resistance was too large to measure in the sample without UV activation. As the UV irradiated energy exceeded 20 W, sheet resistance was still around 3 Ω/□. Accordingly, the results indicated that precursor (catalyst) induced copper deposited reaction strongly depends on UV activation and the precursor (catalyst) on circuit surface was already induced when the irradiated energy approached 20 W.

In metalized processes, the samples were immersed in electroless plating bath after UV activation and oven curing. The relationship between plating time and condition of Cu deposited on precursor surface was revealed in Fig. 4. The thickness of Cu layer increased with the plating time and the resistance achieved 6.2 μΩ·cm when Cu layer thickness was around 2.5 μm (plating time: ~ 30 min). These results exhibited high conductivity and fine-line in comparison with silver paste material in Company Fujikura (40 μΩ·cm, 20 μm) [7]. Fig. 5 showed that double-side FPC with line width around 5 μm was fabricated by R²R printed processes. These results exhibited high resolution and

Fig. 4  Cu deposited on catalyst layer surface increased with plating time. The samples were exposure in 20 W UV irradiation.
good conductive characteristics in double-side flexible printed circuit boards, particularly in continuous roll to roll processes.

4. Conclusions

Additive process in fabricating fine-line circuit on flexible substrate has been demonstrated with a high throughput system (R²R system) for double-side FPC applications through catalyst induced copper electroless plating method. Despite the relatively complicated catalytic mechanism of electroless plating, additive process exhibits a narrow line width circuit (around 5 μm), lower resistance (6.2 μΩ·cm), and mass production with low pollution in comparison with lithographic processes (with photoresist and acid pollution).

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