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Full Length Article

Fabrication of conductive copper patterns using reactive inkjet printing followed by two-step electroless plating

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ABSTRACT

A simple and low-cost process for fabricating conductive copper patterns on flexible polyimide substrates was demonstrated. Copper catalyst patterns were first produced on polyimide substrates using reactive inkjet printing of Cu (II)-bearing ink and reducing ink, and then the conductive copper patterns were generated after a two-step electroless plating procedure. The copper layers were characterized by optical microscope, SEM, XRD and EDS. Homogeneously distributed copper nanoclusters were found in the catalyst patterns. A thin copper layer with uniform particle size was formed after first-step electroless plating, and a thick copper layer of about 14.3 μm with closely packed structure and fine crystallinity was produced after second-step electroless plating. This resulting copper layer had good solderability, reliable adhesion strength and a low resistivity of 5.68 $\mu\Omega$ cm without any sintering process.

1. Introduction

Conductive patterns are essential and vital features for electronic and optoelectronic devices, such as RFID tags, thin film transistors, and light emitting devices. They are usually fabricated by photolithography which is a time-consuming multi-step process and requires expensive facilities. In addition, the photolithography generates large amounts of hazardous waste which is environmentally detrimental. Therefore, a better alternative to the photolithographic procedure is needed. In recent years, inkjet printing technology has attracted great interest as a means of non-contact deposition mode [1–4]. Being a novel patterning technique, the inkjet printing possesses many advantages compared to the photolithography, such as low cost for manufacturing large-area patterns by using cheap and compact equipment [5], and applicability to various substrates [6–10].

The inkjet printing technology for conductive patterns is commonly conducted with inks that are made of metal nanoparticles [10–12] or based on metal-organic decomposition [13–15]. An additional step of sintering, which is usually done in oven or on a hot plate, is required after inkjet printing to obtain metallic patterns with desired electrical conductivity. However, the sintering process with high temperature and long-time duration is considered as a challenge when inkjet printing is carried out on flexible polymeric substrates [16]. Furthermore, conductive copper inks, a low-cost replacement for silver inks, have to be sintered in inert or reducing atmosphere or with sophisticated equipment to prevent the oxidation of metallic copper [17–20]. Besides, protective shells are also developed to ensure a high air stability and chemical inertness for synthesized copper nanoparticles [21,22].

An alternative means to produce conductive patterns is reactive inkjet printing which prints two particle-free inks on substrate to form the metallic patterns based on a simple chemical reaction [23,24]. This method allows materials to be produced *in situ* at low temperature and can largely avoid nozzle-clogging problems caused by agglomeration of nanoparticle-based conductive inks. However, multiple printing passes must be performed for building a thick layer to improve the conductivity of the metallized patterns.

Another approach for producing conductive pattern is to print metal seeds or precursors on substrate and then immerse the substrate with activated pattern into an electroless plating bath. In this approach, the printed seeds or precursors will act as a catalyst for subsequent electroless plating, and highly conductive features can be achieved from the thick metal layer based on the control of plating time without the requirement of high sintering temperature. Various inks containing palladium [25] or silver [26] salts as well as palladium [27] or silver [28] nanoparticles were inkjet printed as a seed layer, and considerable conductivity of deposited copper

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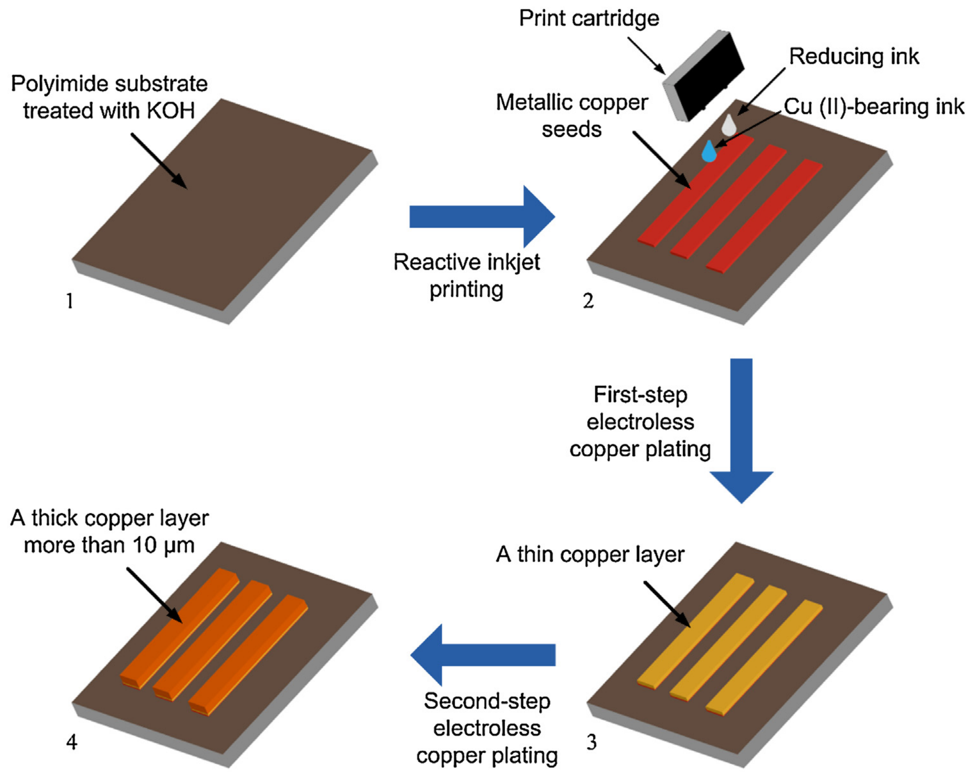

Fig. 1. Schematic of fabricating conductive copper layers on polyimide (PI) substrates. PI is treated with KOH solution to improve the wettability of inks on it (step 1), and then the Cu (II)-bearing ink and the reducing ink are inkjet-printed simultaneously to obtain the metallic copper seeds (step 2). A thin copper layer grow during the first-step electroless copper plating (step 3), and a thick layer more than 10 μm can be obtained after the second-step electroless copper plating (step 4).

Table 1
Main constituents of the two electroless plating baths.

Constituents	$CuSO_4{\cdot}5H_2O$	NaOH	37% HCHO	$C_4H_4KNaO_6{\cdot}4H_2O$	Na_2EDTA	TEA
The first-step bath	0.032 M	0.300 M	12 mL/L	0.085 M	0.005 M	–
The second-step bath	0.060 M	0.180 M	18 mL/L	–	0.010 M	0.180 M

layer was obtained. In addition, copper particles [29] were also used as a seed layer prepared by means of reactive inkjet printing. This method was simple, fast and low-cost although the conductivity of copper structure was still low.

In this study, a convenient and low-cost approach to realize conductive copper patterns via a combination of reactive inkjet printing and two-step electroless plating is presented. Metallic copper seeds, which were produced on substrate via the simultaneous printing of Cu (II)-bearing ink and reducing ink, were chosen to replace noble metal seeds such as palladium or silver to act as a catalyst for the electroless plating. Without the demand of many printing passes and any sintering process, this approach can produce highly conductive copper patterns from thick copper layer.

2. Experimental

2.1. Ink preparation and inkjet printing

The chemicals utilized in this work were all analytical reagents. $CuSO_4{\cdot}5H_2O$ was dissolved in deionized water and kept stirring along with the mixture of ethylene glycol and 2-propanol, to produce Cu (II)-bearing ink with the concentration of 0.3 M. The addition of these organic solvents was to tailor the ink's viscosity and surface tension which finally maintained at 2.5 mPa s (measured with a NDJ-5S viscometer, Shanghai Fangrui Instrument Co., Ltd) and 35 mN/m (measured with a BZY-1 surface tensiometer, Shanghai Fangrui Instrument Co., Ltd) at 30 °C, respectively. For the preparation of the reducing ink, 0.01 M NaOH was firstly dissolved in deionized water, and then 0.6 M sodium borohydride ($NaBH_4$) was added to the NaOH solution. Subsequently, ethylene glycol and 2-propanol were incorporated into the solution to adjust the viscosity and surface tension to be 3.0 mPa s and 30 mN m^{-1} at 30 °C, respectively.

Polyimide (PI, Dongguan Fangyuan Electronic Insulation Co., Ltd., China) was used as substrate with the thickness of 175 μm. A schematic representation of fabricating conductive copper pattern on PI substrate is shown in Fig. 1. In order to improve the wettability of the ink and ensure adequate adhesion strength between the resulting layer and the substrate, the PI substrate was treated with KOH solution of 2 M at 60 °C for 5 min and then rinsed with deionized water, and finally dried in air at room temperature (step 1 in Fig. 1).

The printing was performed by a modified Epson ME35 piezoelectric inkjet printer equipped with several cartridges. The Cu (II)-bearing ink and the reducing ink were firstly loaded into different cartridges that are usually applied for cyan, magenta, yellow and black graphic inks after passing through a 0.45 μm filter. Then these two inks were driven to be jetted out from their own nozzles on the substrate in the same printing route similar to the printing of a color image (step 2 in Fig. 1). Finally, the two inks reacted to form copper