Materials Letters 132 (2014) 302–306

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Nickel and copper conductive patterns fabricated by reactive inkjet printing combined with electroless plating

Dmitrii I. Petukhov [a,b,*], Marina N. Kirikova [a], Alexander A. Bessonov [a], Marc J.A. Bailey [a]

[a] Nokia Research Center, Skolkovo, Moscow region, Russia
[b] Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia

A R T I C L E I N F O

Article history:
Received 15 May 2014
Accepted 17 June 2014
Available online 24 June 2014

Keywords:
Reactive inkjet printing
Copper electroless plating
Nickel electroless plating
Flexible electronics
Polymer metallization

A B S T R A C T

A simple, low-cost and easy scale-up technique for fabrication of conductive interconnects for flexible electronic devices is presented. A thin seed layer of nickel or copper was formed on the surface of PEN substrate via reactive inkjet printing of metal salt and reducing agent instead of traditional seed layers such as palladium nanoparticles and palladium or silver salts. For deposition of a uniform metal coating a polymer substrate patterned with the seed layer was immersed in an electroless plating bath. The electrical resistivity of deposited nickel–phosphorus and copper layers was $3.8 \pm 0.2\ \mathrm{m\Omega \cdot cm}$ and $29 \pm 2\ \mathrm{\mu\Omega \cdot cm}$, respectively. The obtained structures possess excellent adhesion to polymeric substrates and reveal only slight decrease of conductivity after 20,000 bending cycles.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In recent years flexible devices have aroused considerable attention both in industry and in academia due to their vast potential for new applications. Nowadays various approaches exist for the fabrication of flexible displays [1], supercapacitors [2] and batteries [3], transistors [4,5] and sensors [4,6–9]. Along with the main functional components, conductive metal interconnects capable of withstanding repeated mechanical deformations are essential for continuous functioning and a long lifespan of the whole device. It should be noted that conventional photolithographic approaches of metal patterning have poor compatibility with flexible substrates and require multiple steps and expensive facilities. In contrast to photolithography, inkjet printing avoid complex procedures and can be utilized using inexpensive and compact equipment [10].

Currently, the most common approaches for fabrication of conductive structures on the flexible substrates are based on printing methods using silver nanoparticle inks which typically require a sintering step. Xenon flash light [11,12], plasma [13] and low-temperature thermal sintering [14] are usually applied in order to avoid destroying of plastic substrates. Silver nanoparticle inks provide excellent conductivity, but the cost of these inks is quite high, that goes up the total cost of production method. A possible way to make the printing process affordable for mass production is to apply non-noble metal nanoparticle inks, such as copper [15] or nickel [16]. However, non-noble metals nanoparticles tend to rapidly oxidize in ambient conditions. Solving of oxidation problem requires covering of copper nanoparticles with protective carbon [17] or surfactant layer [18], or preparation of Cu–Ag core–shell nanoparticles [19], which complicate the nanoparticles preparation process. Also the post-treatment annealing in inert or reducing atmosphere can solve oxidation problem [20].

The alternative approach for preparation of conductive structures is so called reactive inkjet printing (RIP), which consists in printing of metal salt solution on the substrate followed by printing of reducing agent or, in another variation, printing of a mixture of metal salt and reducing agent with subsequent treatment to accomplish the metal reduction [21–24]. Since no particles are presented in the initial solutions, RIP could also help to overcome the frequent problem of conventional inkjet printing—the nozzle clogging. This technique was successfully used for deposition of nickel [21], copper [21,22] and silver [23,24] conductive structures on a number of substrates including glass, paper and porous polymers. In the case of inert polymer substrates the additional pretreatment of polymer is often required to improve the adhesion between the substrate and metal layer. However one limitation of reactive inkjet printing is that the deposition of metal traces with sufficient conductivity for extended use requires the repetition of a large number of printing cycles (more than 100); this is difficult to match with inkjet printing techniques, even when using highly concentrated solutions [21]. In another variation of RIP methodology, a relatively fast fabrication of stable copper and nickel metal interconnects on the polymeric substrates is possible via inkjet printing of a seed layer followed by

* Corresponding author at: Department of Chemistry, Lomonosov Moscow State University, 119991 Leninskie Hills 1-3, Moscow, Russia. Tel.: +7 495 9395248.
E-mail addresses: di.petukhov@gmail.com, petukhov@inorg.chem.msu.ru (D.I. Petukhov).

http://dx.doi.org/10.1016/j.matlet.2014.06.109
0167-577X/© 2014 Elsevier B.V. All rights reserved.

electroless plating. This approach was successfully applied for fabrication of copper and nickel–phosphorus coating on plastic substrates, where palladium [25,26] and silver [27] salts as well as palladium nanoparticles [28] were used as a seed layer.

In this work we suggest a simple, fast and low-cost method for fabrication of nickel–phosphorus layer on the polyethylene naphthalate (PEN) substrate via electroless plating using a nickel thin film as a seed layer. The seed layer was deposited by means of successive printing of metal salt and reducing agent solution. Finally, the PEN substrate with activated pattern was immersed in the electroless plating bath for fabrication of Ni–P compact layer. This two-step technique allows fabricating conductive interconnections at relatively low temperatures (below 60–70 °C) and without exposing the substrate to aggressive media. To demonstrate the generality of the method we also applied the same technique for deposition of copper structures on a polymeric substrate. The nickel and copper conductive structures are highly flexible, possess excellent adhesion to a polymeric substrate and retain their conductivity during cycled mechanical deformations.

2. Experimental

The thin films of nickel or copper used as a seed layer were prepared by means of reactive inkjet printing. First, the pattern was printed with the water solution of metal salt, 0.05 M $NiSO_4$ or 0.05 M $CuSO_4$, accordingly, then the solution containing 0.05 M $NaBH_4$ and 0.017 M NaOH was used as a reducing agent for printing on the top of first layer. The inkjet printing was performed using a Fujifilm Dimatix DMP-2831 Printer equipped with 16 jet printheads (10 pL drops), the substrate temperature was 45 °C. The 50 µm PEN film (Teonex® Q65FA) was used as a substrate. Before printing the PEN substrate was treated by oxygen plasma at low pressure for 2.5 min (40 kHz, 100 W). The Ni–P electroless plating bath with pH = 5.2 contained 0.09 M $NiSO_4$, 0.12 M CH_3COONa and 0.24 M NaH_2PO_2 [29]. The electroless plating of Ni–P layer was performed by immersing of the printed sample into the Ni–P bath at 60 °C for 5 min. The copper electroless plating bath with pH = 13.3 contained 0.03 M $CuSO_4$, 0.08 M Na_2EDTA, 0.02 M $NaBH_4$ and 4.4 M NH_3 [30]. The deposition was performed at 45 °C for 5 min. After deposition the samples were rinsed with deionized water and dried at ambient conditions. The preparation scheme is represented in Fig. 1. The thickness of obtained metal structures was determined by optical profilometry (microXAM100, KLA Tencor). The crystal structure of samples was characterized by X-ray diffraction (Rigaku D/MAX-2500V/PC). Microstructure characterization was performed using scanning electron microscopy (SEM, Leo Supra 50VP). The resistance measurements were made according to 2-point probe method. To evaluate the adhesion of the plated Ni–P film, a simple tape test was performed. Mecmesin Multitest system was used for realization of 3-point cyclic bending tests at the bending radius of 8 mm, while the relative resistance change (R/R_0) was recorded by 2-point probe measurements after every 500 cycles.

3. Results and discussion

Thin layers of nickel and copper particles were formed on the PEN substrate by reactive inkjet printing and then used as a seed layer for following electroless plating of Ni–P or copper conductive patterns, respectively, as it is shown in Fig. 1. The optical micrograph of the structure printed with 0.05 M $NiSO_4$ solution (Fig. 1) demonstrates a good wettability of polymer substrate. To form a seed layer, the reducing solution (0.05 M $NaBH_4$ + 0.017 M NaOH) was deposited on the substrate at the same position after drying out of the first printed layer. The optical micrograph of nickel seed layer formed by 3 printing cycles of metal salt and 3 printed cycles of reducing agent is also shown in Fig. 1. In contrast to the chosen inks with low concentrations of metal salt and reducing agent, the inks with high concentrations lead to the formation of a seed layer with poor adhesion. The subsequent electroless plating step is unable to form a compact metal layer due to the washing off of the seed layer from the substrate in the plating bath. This poor adhesion of the seed layer can be explained due to the formation of metal nanoparticles in the printed drops. According to SEM (Fig. 2a) and EDX analysis the formed seed layer consists of a thin Ni layer. However this layer does not demonstrate electrical conductivity, perhaps due to the fact that the Ni film appears to be thin and not continuous with plenty of cracks and voids.

In order to increase the thickness of the layer and thus enhance the conductivity, further Ni deposition over the seed layer can be performed in two ways, either by electroplating or electroless plating. The electroplating technique is unsuitable for further metal build up in this case due to the weak conductivity of the obtained nickel seed layer. So electroless plating deposition of nickel–phosphorous film from acidic solution was used for the following metal deposition atop the seed layer (Fig. 1). A SEM cross-section (Fig. 2b) revealed the Ni–P layer thickness of 1.20 ± 0.10 µm, that is in a good accordance with the value measured by optical profilometry—1.25 ± 0.20 µm (Fig. 2d). The

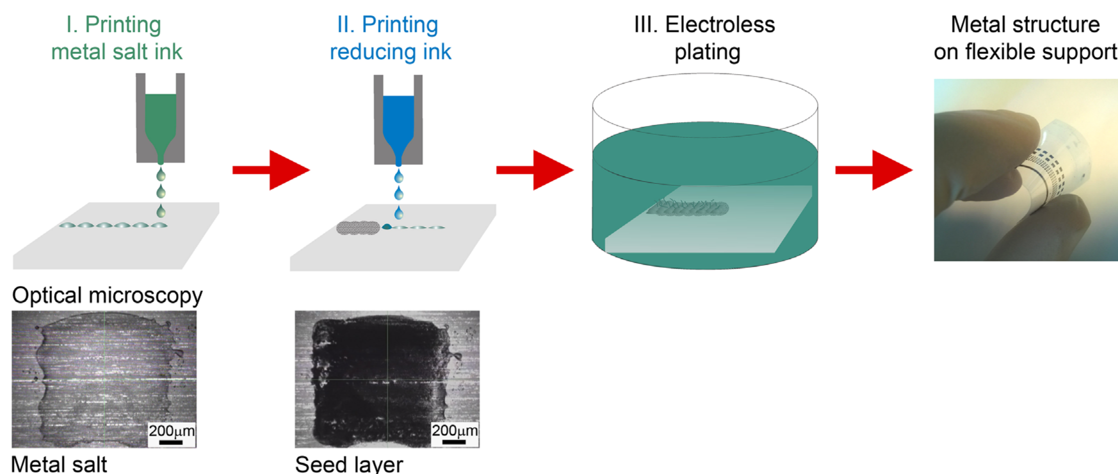

Fig. 1. Experimental scheme of nickel–phosphorous and copper conductive patterns manufacturing: deposition of seed layer (I–II) followed by electroless plating (III). Underlying optical micrographs represent printed nickel sulphate solution and nickel sulphate overprinted with reducing agent solution. Final conductive pattern on PEN is shown on photographic image.

Download English Version:

https://daneshyari.com/en/article/1643957

Download Persian Version:

https://daneshyari.com/article/1643957

Daneshyari.com