Stretchable Copper Wires based on Reduction of Active Metallic Nanoparticles and Electroplating

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Abstract—Herein we proposed a novel technique in fabricating stretchable copper conductive circuits combining galvanic replacement with Zn-based active paste and electroplating process on elastomeric substrates. The conductive patterns exhibited excellent electrical conductivity and stretchability. An active precursor paste composed of zinc nanoparticles and thermal-curable polyurethane resin were used, which was aimed to render the formation of copper layer as the conductive materials by a galvanic replacement reaction. Additionally, electroplating process was employed, with which the as-formed copper layer can be further thickened to improve the electrical conductivity. With this method, a maximal longitudinal tensile elongation of 38.4% was achieved for the wires with negligible conductivity loss. In summary, the flexible copper-based conductive circuits with excellent performances were produced in a cost-effective way. This technology will be a promising candidate for future stretchable electronic applications.

Keywords—stretchable circuits; copper; galvanic replacement; electroplating

I. INTRODUCTION

Flexible and stretchable wiring have attracted increasing interest in recent decades for the application of flexible and stretchable devices [1], including flexible energy storage and conversion ones [2], flexible displays [3], skin-like pressure sensors[4] and so on [5-6]. Efforts towards fabricating stretchable electronics have originated from wiring metal foils on rubbery substrates [4] and gradually expanded to the printed conductive composite materials etc. [2, 5-6]. A lot of conductive materials have been investigated, such as conductive polymers [7-9], graphene films [10-11], carbon nanotube paste composites [9, 12], metal nanowires [11-12], nanoparticles, and flakes and so on. [13]. A conventional strategy is to encapsulate these conductive wires or sheets into the elastic substrates and to ensure percolation networks, so that the wires or sheets could contact with each other during stretching [14], providing excellent electric conductivity. However, there are still many limitations for these materials, such as low conductivity, poor stretchability and increased resistance with applied strain.

As an effective alternative strategy, serpentine structures of bulk metals with plane layout or wavy shape have been fabricated as interconnects for stretchable electronic devices [15-17], where the designed metal structures could maintain bulk property under tensile stress such as negligible changes of resistance during repeated stretching. However, this strategy always requires relatively complicated processes like photolithography [18-19], vacuum evaporation [20-21] and sputtering [22], etc. Besides, the ever-reported wiring metals are often Au and Ag, which are too expensive for broad applications. Additionally, those metal wires attached to the substrate may delaminate under repeated mechanical loadings, and the interface between the elastomeric substrates and rigid metal layers tends to fatigue more easily than conventional circuits [6, 23].

Recently, many efforts have been devoted to develop technologies on fabricating copper (Cu) conductive circuits with printing methods because Cu is much cheaper than silver (Ag) and gold (Au), which have been most considered in academic studies for printed electronics [24-27]. However, the intrinsic oxidation problem of Cu under ambient conditions remains the main obstacle which deteriorates the conductivity of Cu wires. In this regard, low temperature sintering techniques, such as flash light sintering [28-30], laser sintering [31] and microwave sintering technology [32], have been employed. Even so, sophisticated equipment is needed and the processing cost is high.

In this paper, we reported a novel fabrication process of stretchable copper conductive circuits based on reduction of active zinc nanoparticles and a subsequent copper electroplating process. An active precursor paste composed of zinc (Zn) nanoparticles and polyurethane resin were adopted as the seed ink, which could be screen printed on the elastomeric polyurethane film substrate to form serpentine patterns. With a subsequent Cu deposition process based on the galvanic replacement reaction between Zn and Cu$^{2+}$, we could obtain the Cu conductive layer capping on the Zn paste patterns. The electrical conductivity of the Cu circuits was further improved with Cu electroplating by thickening the Cu surface layer. As the polyurethane resin was tenacious and combined well with both the Cu layer and the substrate, the strain could be buffered by this layer when the Cu circuits were stretched. In this approach, A maximal elongation of about 40% was achieved with little conductivity loss for the patterned Cu wires, and the as-prepared Cu patterns could maintain a conductivity of $1.8 \times 10^4 \Omega \cdot \text{cm}$ after 2000 cycles of stretching and adhered well to the substrate.
II. EXPERIMENTS AND METHODS

A. Preparation of Zn-based active paste, printed circuits and Cu²⁺ containing solution

The Zn-based active paste was composed of Zn nanoparticles (200nm in size, Beijing Dk Nano technology Co., Ltd), thermal-curable polyurethane resin (DESMODUR BL 4265 SN, Bayer Materials Science), toughener (MX154, Dalian Liangsheng Trading Co., Ltd), curing agent (glycerol, Sinopharm Chemical Reagent Co., Ltd) and catalyst (dibutyltin dilaurate, CR, SCR). In order to prepare the active paste, firstly 65 wt% of Zn powder is mixed with polyurethane resin (27 wt%), toughener (5 wt%) and curing agent (3 wt%). Then, a small amount (0.5 wt% over the total weight of the above mixture) of catalyst was added into the above mixture followed by mixing in a planetary mixer at 80 rpm for 10 min to form the homogeneous Zn-based paste. Subsequently, the as-prepared Zn-based paste was screen printed onto a polyurethane elastomeric substrates (maximal tensile ductility: 450%, SHEEDOM TPU DUS605-CER) with designated patterns (with line width down to 200 μm). Finally, the patterned elastomeric films were heated in a vacuum oven at 120 °C for 30 min to cure the Zn-based paste.

During the preparation of Cu²⁺ containing solution, 60g CuSO₄ (AR, Aladdin) was dissolved in 140 g deionized water (totally 200 g). Then, 60 mg poly (ethylene glycol) (PEG), (MW: 4000, AR, Aladdin) was added into the solution to act as stabilizer and 1M H₂SO₄ solution was used to adjust the pH value of the solution to 1.5.

B. Galvanic replacement deposition and electro-plating of Cu conductive layer

The galvanic replacement deposition was performed by immersing the sample into a Cu²⁺ aqueous solution for 30 min to obtain reduced Cu (termed r-Cu) covered wires. Then, the as-obtained samples were washed with deionized water for several times to remove the impurities and desiccated in a vacuum oven at 60 °C for 30 min before copper electroplating. During the electroplating process, the r-Cu conductive patterns was employed as cathode and the phosphor copper plate as anode with an applied current density of 10 mA/cm² for 20 min to thicken the copper layers and increase the conductivity for conductive circuits. Finally, the electroplated Cu (termed as e-Cu) conductive films were washed with deionized water for several times and dried in a vacuum oven at 60 °C for 30 min. The main components of the electroplating solution are listed in Table 1.

<table>
<thead>
<tr>
<th>Components</th>
<th>Content</th>
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<tbody>
<tr>
<td>CuSO₄</td>
<td>1.25 mol/L</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.6 mol/L</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.4 mol/L</td>
</tr>
<tr>
<td>Brightener (BASF 910)</td>
<td>2.6 mL/L</td>
</tr>
<tr>
<td>PEG4000</td>
<td>0.1 mmol/L</td>
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III. CHARACTERIZATIONS

A metallographic microscope (Olympus GX 51) was employed to analyze the surfaces and cross sections of the patterns in each step. The stretching tests were performed to characterize the stretchability and reliability performance of the circuit samples depending on the variation in sheet resistance measured by the four-point-probe method (LorestaGP T610, Mitsubishi Chemical Analytech Co. Ltd.). The scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) analysis was conducted on an FEI Nova NanoSEM450 electron microscope.

![Fig. 1](image-url)

*Fig. 1* a) photographic image of printed Zn pattern; b) photographic image of the sample after galvanic replacement deposition of Cu; c) photographic image of the sample after electroplating; d) SEM-EDS mapping image of the cross section views of the conductive circuit after copper electroplating.
IV. RESULTS AND DISCUSSION

A. Pattern design, schematic and microstructures

Generally, both the selection of materials and the design of pattern structure should be seriously considered. In this paper, polyurethane resin substrate with a reversible strain of 450% was used as the elastomeric matrix, and polyurethane resin was selected to fabricate active paste with Zn powder where toughener (5 wt%) was added which could act as buffer agents to enhance the elasticity of the conductive circuits. On the other hand, serpentine structure was selected as stretchable interconnects based on the advantages of higher tensile performance over straight line-based structure. Therefore, conductive circuits prepared combining the two above optimized design are expected to exhibit excellent tensile properties.

A brief schematic for fabricating highly conductive circuits is presented in Fig. 1 a) to c). The Zn-based paste was screen printed onto PU films to form bottom circuits with designed serpentine structures. Then, r-Cu was in situ reduced from Cu$^{2+}$ via galvanic replacement reaction with Zn and capped on Zn particles in a reaction bath. Finally, electroplating process was employed to strengthen the conductivity of the patterned wires. The cross sectional view was given in Fig. 1 d) for the final highly conductive wires, from which we can observe that the Zn nanoparticles was mainly covered with r-Cu and thick e-Cu layers (about 20 μm in thickness) which guaranteed a high conductivity and surface smoothness.

B. The influence of pH value of Cu$^{2+}$ containing solution

During the galvanic replacement reaction, the formation of r-Cu layer could be described by the following chemical equation:

\[ \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \quad (1) \]

which is a catalyst-free and simple spontaneous galvanic reaction between Zn seeds and the target metal Cu$^{2+}$ ions. Fig. 2 shows the top view of the r-Cu layer. Fig. 2a) is the original Zn layer on the surface of elastomeric substrates. When the patterned films were immersed in the initial CuSO$_4$ solution with the pH value of 2.5 for 30 min, little r-Cu could be observed (Fig. 2b). When the pH value of Cu$^{2+}$ containing solution reduced from 2.5 to 2.0, 1.8, 1.6 and 1.5 respectively, more r-Cu was deposited and more uniformly capped on the Zn layer, as indicated from Fig. 2b) to 2f). However, the r-Cu layer became sparsely distributed from Fig. 2f) to Fig. 2i) when the pH value further decreased from 1.5 to 1.4, 1.2 and 1.0, due to the fact that the Zn particles might be oxidized by the presence of too much H$^+$ before it reacted with Cu$^{2+}$. Therefore, the pH value of Cu$^{2+}$ containing solution was tailored to 1.5 for galvanic replacement reaction throughout all subsequent processes. Apart from the analysis of optical microscopic images, sheet resistance measurements were further taken on each corresponding sample, the results of which agreed well with that of the former as illustrated in Fig. 3.

![Fig. 2 Optical microscopic images of original Zn paste (a) and r-Cu reduced from Cu$^{2+}$ containing solution with a pH value of 2.5 (b), 2.0 (c), 1.8 (d), 1.6 (e), 1.5 (f), 1.4 (g), 1.2 (h), and 1.0 (i). All scale bars are 5 μm.](image1)

![Fig. 3 The surface resistivity of r-Cu layer versus pH value of Cu$^{2+}$ containing solution (30±2 μm in thickness for all conductive circuit layers).](image2)

C. Tape peeling test

The tape peeling test was conducted to evaluate the adhesion between e-Cu layer and the PU substrates, as depicted in Fig. 4. From Fig. 4, we could observe that the designed circuits with semicircular line (200 μm in width) still remained intact after tape peeling, and no exfoliation was found on the tape. This result demonstrated that the circuits prepared in the present work had a strong bonding strength between e-Cu with PU substrates. This may be attributed to the robustness of the continuous e-Cu layer and the strength enhancement from the mechanical interlocking effect of the rough interface between the e-Cu layer with the polyurethane resin.
D. Stretchability tests

To assess the stretchability of the patterned wires, longitudinal stretching tests were performed on the patterned films (70 mm in length and 10 mm in width) as shown in Fig. 5, which indicated a maximal tensile rate of 38.4% (from 26 mm (as marked in Fig. 5a) to 36 mm (as marked in Fig. 5b)) with little conductivity loss. When the drawing force further increased, the whole circuits would peel off from the substrate due to the deformation stress which had already surpassed the adhesion strength between e-Cu with substrates. To be noted, no crack was found even when the circuits were separated from the substrates.

In order to further evaluate the reliability performance of wires, the samples were stretched with a constant elongation of 20% for 2000 cycles as shown in Fig. 6. We can observe that the resistance of patterned-circuits maintained almost invariable during the first 200 cycles, which might because that the micro-cracks were just initiated and hadn’t damaged the consistency of conductive copper layers within these cycles. When the stretching cycles increased, the micro-cracks propagated and formed larger cracks, and thus resulting in a conductivity loss of 72% for the patterned circuits within 1000 cycles. With the gradual growth of cracks, the conductivity loss became severe and finally resulted in the failure of the copper layers after 2000 cycles (as shown in the insert image of Fig. 6).

V. CONCLUSION

In summary, a convenient and cost-effective technology was proposed to fabricate flexible and elastomeric circuits with designed patterns, which was based on the galvanic replacement reaction between the Zn-based active paste with Cu²⁺ and the electroplating processes. Tensile tests demonstrated that a maximal elongation of 38% could be achieved for the patterned circuits with excellent conductivity. To be noted, the Zn-based active paste developed here was cheap and compatible with conventional printing techniques. It
is reasonable to believe that other active paste (such as Fe and Ni) and conductive layers (Ag or Au) can be used for fabricating a wide range of highly conductive and flexible electronic circuits.

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