Intense Pulsed Light Healing of Copper Nanoparticles Based Flexible Circuits

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Robin Jeong[1], Tyler Horton[1], Simon S. Park[1*]

[1] Department of Mechanical and Manufacturing Engineering,
University of Calgary, 2500 University Drive NW, Calgary, AB T2N 1N4, Canada

Abstract

Flexible electronics presents exciting advancements in flexible displays, physiological sensors, wearable devices, and photovoltaics. Additive deposition of conductive inks on flexible substrates presents opportunity for cost and time savings in manufacturing of flexible circuits. In this study, a printable hybrid conductive paste can be achieved by utilizing copper nanoparticles in a paste form that can be easily incorporated into existing printing technology. As these printed copper nanoparticles are initially non-conductive, intense pulsed light (IPL) irradiation is employed to quickly reduce oxides and sinter the nanoparticles. By reducing copper oxides to their metallic form and sintering the loose particles, conductivity in the printed track is achieved within milliseconds. However, these conductive circuits exhibit microcracks when subjected to cyclic bending. By utilizing additional IPL healing flashes after cyclic bending, the loss in electrical conductivity due to microcracks is recovered. Within this study, a composition of conductive ink as well as conceptualization of circuitry healing after 100 cycles of 1% bending strain is presented.

Keywords: Copper nanoparticles, cyclic bending, intense pulsed light sintering, flexible circuitry, IPL healing

1. Introduction

Conventional circuit manufacturing is achieved by lithographic processes on planar surfaces such as printed circuit board (PCB) manufacturing. The demand for electronics is projected to grow exponentially worldwide, stressing the modern PCB manufacturing [1]. PCB manufacturing entails removal of select copper (Cu) patterns to leave behind the desired conductive track through the usage of masks and hazardous etchant chemicals. To overcome these challenges, additive printing of conductive inks has been garnering interest. These conductive inks can provide a simple, fast, and highly customizable circuit printing solution.

In addition, printable conductive inks are applicable to a wide variety of surfaces including flexible substrates. To accommodate flexible substrates, the printed ink must be able to survive varying strains without major increases to its electrical resistance. This is due to metallic inks forming microcracks. Microcracks will sever the printed inks physical connections, destroying electron pathway and contributing to the overall resistance. Several complex methods have been utilized to overcome this issue. Li et al. [2] embedded rigid, 'islands,' onto a substrate and linked them with flexible bridges. The rigid islands were placed onto the substrate with a density proportionate to the substrates average strain profile. While this process worked effectively at preventing straining circuit damage, complexities make this process inefficient for large scale manufacturing.

As an alternative to creating re-enforced ink circuits, circuits may instead be healed after they suffer strain induced damages. Sintered metallic nanoparticles is one such structure that could be utilized for such a process.

Various methods exist to sinter metallic nanoparticles. Conventional thermal sintering requires large processing times. In addition, environments heated for extended periods of time can not only damage polymeric substrates but can also cause oxidation on the metallic nanoparticles. Although oxidation can be bypassed by using noble metals such as silver or gold-based nanoparticles [3], the use of these precious metals in circuitry is prohibitively expensive. Copper nanoparticles is an alternative to these precious metals while retaining electrical performance. However, copper nanoparticles are prone to oxidation. Fortunately, simple and fast methods for reducing copper oxides to metallic species has been achieved before.

Utilizing light-based sintering such as laser or intense pulsed light (IPL) irradiance allows for the use of thermally sensitive substrates. This is attributed to the localized heating of metallic particles thus protecting substrates with relatively low glass transition temperatures. In addition, copper oxides can be reduced with implementation of photo-thermally degrading binders [4]. IPL sintering is attractive due to the simplicity of its implementation. Instead of programming a laser's path and speed, a simple mask can be utilized to print and sinter. Although this method requires an additional masking step similar to photolithography, the re-useable mask and reduced ink consumption provide an economic advantage for IPL sintering. Flash via xenon-lamp is a popular form of flash irradiation where high current excites xenon gas, producing a broad-band white-light similar to sunlight (~350 to 1050 nm). Energy delivery can be further modified by extension of the pulsed light duration, repeat pulses, and sample distance (relative to focal distance of the reflectors where applicable).

The objective this study is to develop a method where printed conductive copper nanoparticle (CuNP) circuit regains electrical performance after undergoing cyclic bending strain. The usage of CuNPs provides the circuit with strong electrical performance while still retaining cost effectiveness relative to other conductive metals. IPL is utilized to quicky reduce oxides and sinter the printed tracks while protecting the polymeric substrate. Additive manufacturing of circuitry on flexible substrates is utilized using doctor-blade printing and IPL sintering. By printing flexible conductive tracks, advancements in displays, wearable electronics, and sensors can be achieved.

2. Methodology

The present section outlines experimental steps and parameters to develop a printed flexible Cu track. Paste composition, IPL regimes, cyclic loading parameters, and characterization steps are outlined (see Figure 1). These investigations will be utilized to produce an additively manufactured conductive track capable of recovering conductivity after multiple bending loads.

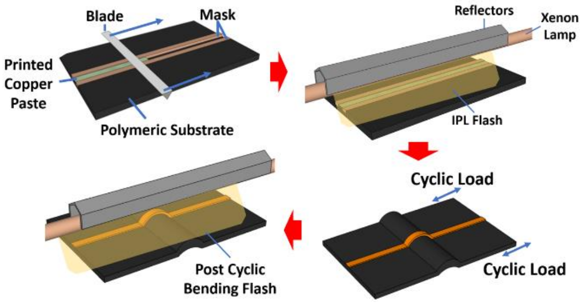

Fig. 1. Schematic detailing the printing, IPL sintering, cyclic-bending, and healing flashing steps.

2.1 Paste synthesis and printing

Copper pastes were prepared by 5 min vortex mixing of 2.16 g of 50 nm diameter CuNPs in 1.08 g of diethylene glycol (DEG, >99% liquid; Sigma Aldrich) and 0.08 g of polyvinylpyrrolidone (PVP; Sigma Aldrich). In a separate vial, 0.648g of $Cu(NO_3)_2$ (Sigma Aldrich) and 0.47 g of diethylene glycol butyl ether (DEGBE, 99%; Sigma Aldrich) were mixed. The CuNP and $Cu(NO_3)_2$ containing vials were sonicated individually for 30 mins after which the two vials were mixed, vortexed, and sonicated again. The resultant CuNP based ink was either immediately doctor bladed or stored in a freezer to minimize oxidation until doctor blading.

The synthesized paste was printed as 5 x 80 mm tracks by doctor blading using 50 µm thick polyimide tape masks on 127 µm polyimide film substrates. Printed tracks were dried for 50 mins under an IR lamp at 100^{o}C before sintering.

2.2 IPL flash sintering and Cyclic Bending

The as printed and dried tracks are not yet conductive and lack coherency. To create a conductive and mechanically coherent track, the loose copper nanoparticles must be sintered. Thus, to achieve sintering, the tracks were exposed to IPL irradiation. Xenon S-2300 dual-stage sintering system (2100V, 3 ms pulse on-time, 50mm from lamp) was utilized to provide a broadband flash and sinter the loose nanoparticles. The energy of this IPL regime was measured as 5.42 ± 0.25 J/cm^2 by a power meter (PM10-50C, Coherent). Sheet resistance was measured at various stages via the 4-probe method with a multimeter (34460A, Keysight). Track thickness and changes in surface morphology was observed with an optical profilometer (Zeta-20). The printed and sintered thickness was found to be 56.97 ± 2.77 µm prior to cyclic bending.

After post-print sintering and characterization, the tracks were subjected to cyclic bending using a tensile tester (ESM303, Mark-10). Equation 1 was used to calculate the required radius of curvature for 1% strain (ε_m) at a fixed substrate thickness of 127 µm (h). An important assumption was made where the thickness of the printed track was not considered in h. Based on the calculated radius of curvature of 6.35 mm, the required movement of the tensile tester jaws (dL) is calculated using Equation 2. Equation 2 was derived from previous work by Park et al. [5] and utilized with an initial jaw width of 30 mm (L). Thus, the required movement of the jaws was calculated as 16.96 mm to induce a bending strain of 1%. Sheet resistance and surface morphology was characterized after 100 cycles of bending. Following cyclic bending and damage characterization, the track was re-flashed to recover/heal lost conductivity. Finally, the effect of the re-flashing or healing flashes were characterized with final sheet resistance and surface morphology observations.

$$\varepsilon_m = \frac{h}{2r} \tag{1}$$

$$r = \frac{L}{2\pi\sqrt{\frac{dL}{L} - \frac{\pi^2 h^2}{12L^2}}} \tag{2}$$

The change in conductivity after cyclic bending and heal flashing was observed by calculating the percent difference in resistance relative to the initially sintered track. Heal flashing was performed twice with the same parameters as the initial sintering (2100V, 3 ms pulse on-time, 50mm from lamp). Second heal flashing was performed to further the healing process as preliminary studies showed the first flash ineffective. Based on the outlined methodology, a flexible paste-based circuit manufacturing process with healing capabilities is achieved as shown in Figure 2.

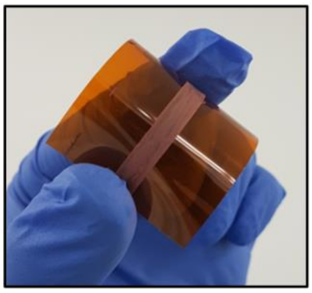

Fig. 2. Printed and sintered copper paste prior to cyclic bending.

3. Results and Discussion

Results of the methodology outlined in the previous section and the underlying mechanisms are presented in this section. This includes investigations in IPL regime, physical effects of sintering, cyclic bending and healing IPL irradiation. By optimizing the flash regime for inducing or recovering conductivity, a copper paste suitable for flexible substrates is achieved.

3.1 Initial resistivity and IPL sintering mechanisms

The effect of IPL irradiation on metallic nanoparticles is crucial for utilizing copper nanoparticle-based pastes. With a fixed focal length of 50 mm from the lamp (due to reflectors), a voltage of 2100V and irradiation time of 3 ms was finalized. This power setting provided sufficient conductivity and healing while maintaining a smooth and coherent track. Powers below or above this setting resulted in unsintered or severely ablated surfaces, respectively. It should be noted that higher power settings such as 2300V at 3 ms achieved lower initial sheet resistances than 2100V at 3ms. However, this power provided a rough copper track surface due to ablation and easily flaked-off.

Based on the average thickness and the 4-probe measured sheet resistance values (Ω/sq), the initial bulk resistance of the printed and flashed (2100V, 3 ms) conductive Cu tracks were $2.75\times10^{-2} \pm 8.26\times10^{-3}$ Ω*mm. This high resistance relative to conventional bulk copper (1.68×10^{-5} Ω*mm) is attributed to the sintered nanoparticle structure. Sintered structures contain internal voids and necks. Characteristics add to the overall impedance to electron pathway and this increases the total resistance. Conventional powder sintering utilizes high pressure pressing before sintering to aid in final density. However, incorporating a pressing stage drastically increases manufacturing time and can damage polymeric substrates.

To increase the sintered structures overall density without pressing, $Cu(NO_3)_2$ was added. $Cu(NO_3)_2$ when exposed to IPL irradiation was found to thermally degrade Cu oxides and seed the reduced Cu onto CuNP surfaces. In parallel action, PVP thermally degrades Cu oxide species, producing conductive metallic Cu [4]. By seeding and filling the voids between CuNPs, a smooth and dense Cu track can be achieved.

Additionally, utilizing IPL protects the polymeric substrate by an important phenomenon that allow sintering at relatively short times and low temperatures: the plasmonic effect. The plasmonic effect occurs when a metallic material is excited by incident light and plasmons are induced on its surface. Coherent oscillation of these electrons equilibrizes at a resonant frequency and causes an increase in absorption of incident irradiation and collapsing surface energies [6]. This allows sintering of copper particles at temperature ranges 250-300ºC, well below the typical 750ºC and above required in conventional sintering [4, 6, 7].

Thus, easily printed and scalable copper nanoparticle paste has been realized with IPL sintering. Oxide reduction, conductivity, and a coherent smooth surface is achieved at low temperatures and short irradiation times. This allows the present copper paste to be applied to a variety of surfaces including polymeric or flexible substrates.

3.2 Effect of Cyclic Bending

Polyimide film as a substrate can survive high temperatures while maintaining flexibility. This high-performance plastic is an ideal candidate for flexible circuits and has been utilized in a variety of studies [5, 7-10]. To achieve and conceptualize flexible circuitry, the printed and IPL sintered copper tracks on polyimide were subjected to cyclic loading. The track is expected to lose conductivity via induced microcracks, and the extent of this damage is investigated below.

After 100 cycles of cyclic bending bulk resistance increased from $2.75\times10^{-2} \pm 0.83\times10^{-2}$ Ω*mm initial to $1.88\times10^{-1} \pm 3.94\times10^{-2}$ Ω*mm (see Fig.3). This 580% increase in resistance is attributed to losses in electron pathway from microcracks and the thin film geometry [8, 11, 12]. Printed thin films tracks exhibit different mechanical properties than their bulk material counterparts. Although the geometrical differences are obvious, the effect this has on their mechanical properties is complex. Thin copper films have been found to exhibit higher yield and ultimate tensile stress relative to thicker copper films [9, 13, 14]. This is due to the thin films' dislocation motion restriction as well as limiting nucleation of new dislocations. However, limiting dislocations also reduces the overall ductility of the films. By limiting dislocation movement, the films are embrittled and experience failure at smaller elongations. In addition, sintered structures can exhibit low ductility due to their internal voids. Voids provide stress concentrations and can act as crack precursors [15]. $Cu(NO_3)_2$ was introduced to improve overall density by seeding Cu onto nanoparticle surfaces and filling voids. Despite these considerations, Fig. 3. shows significant increase in electrical resistivity after cyclic loading.

As expected, cyclic bending severely increased the resistivity of the printed and sintered track. This was attributed to a variety of factors inherent in printed and sintered nanoparticles. To recover conductivity, the tracks were treated with two more IPL flashes.

3.3 Effect of post-bending flash

The resultant increase in resistance from 100 cycles of 1% bending strain must be recovered. This was achieved with re-flashing at the same IPL flash parameters as initial sintering. These millisecond healing flashes allow the printed track to recover electrical performance with minimal processing. By investigating the extent and mechanisms in IPL healing, the copper track is made suitable for flexible applications.

To repair conductivity, the cyclic-bent Cu tracks were flashed again at the same IPL parameters, twice. Regardless, the bulk resistances decreased to $4.28\times10^{-2} \pm 1.49\times10^{-2}$ and $3.32\times10^{-2} \pm 0.72\times10^{-2}$ Ω*mm (see Figure 3.) after first and second healing flashes, respectively. This correlated to 55.33% and 20.29% increase from the initial resistance for first and second healing flashes, respectively. Although repair of microcracks was not directly observed due to the magnification limitations of the optical profilometer, other mechanisms have been previously found to explain the recovery of conductivity. The additional sintering of the overall copper track structure created new electron pathways. This phenomena was previously observed by Devaraj and Malhotra [11] where the regained electrical performance was attributed to new sintered connections rather than crack-repair. The increase in metallic copper is evident in the optical profilometer images of Figure 3. This is based on the deepening of the copper colour hue that was observed after being healing flashed twice [7].

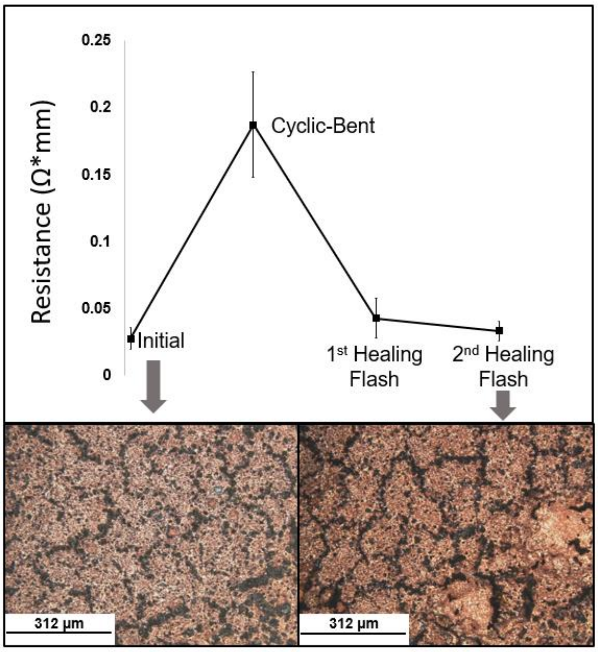

Fig. 3. Bulk resistance values of the sintered track at various stages of experimentation. Optical profilometer images show increased reduction of oxides.

Thus, the effect of IPL, cyclic-bending, $Cu(NO_3)_2$, and re-flashing has been presented. After a resistance increase of 580% from cyclic bending, overall resistance was recovered to a final 20.29% increase relative to the initial value. By combining IPL sintering, $Cu(NO_3)_2$, and re-flashing, a conductive flexible track capable of healing is achieved.

The assumption of using only the substrate thickness when calculating bending strain is an important limitation in the present study. For future studies, a bilayer model can be used to describe bending strain of a sintered copper electrode printed on flexible polyimide [10]. Other important factors do not present in this study include oxidation resistance and the lifetime effect of additional bending and healing stages. Future compositions can incorporate oxidation resistant species such as silver and self-healing agents such as indium in the paste synthesis. Nevertheless, the present study was able to achieve an additively printed copper electrode on a flexible substrate. By incorporating IPL healing with no additional equipment or material usage, a streamlined production of flexible circuitry is conceptualized.

4. Conclusions

The development of printable conductive tracks allows streamlined circuit manufacturing and application of flexible substrates. To demonstrate this, a copper-based paste capable of recovering electrical conductivity after cyclic bending was achieved. IPL sintering was utilized to induce and recover conductivity while protecting the polyimide substrate. $Cu(NO_3)_2$ was used to provide additional densification during IPL sintering. Post-bending heal flashing allowed further reduction of oxides and development of new CuNP connections. The present method is compatible with large scale lithography such as silk screen printing and provides a pathway in rapid conductive circuit production on flexible substrates.

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