Localized Laser Sintering of Metal Nanoparticle Inks Printed with Aerosol Jet® Technology for Flexible Electronics

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Abstract—Direct-write methods, such as the Aerosol Jet® technology, have enabled fabrication of flexible multifunctional 3-D devices by printing electronic circuits on thermoplastic and thermoset polymer materials. Conductive traces printed by additive manufacturing typically start in the form of liquid metal nanoparticle inks. To produce functional circuits, the printed metal nanoparticle ink material must be postprocessed to form conductive metal by sintering at elevated temperature. Metal nanoparticles are widely used in conductive inks because they can be sintered at relatively low temperatures compared with the melting temperature of bulk metal. This is desirable for fabricating circuits on low-cost plastic substrates. To minimize thermal damage to the plastic, while effectively sintering the metal nanoparticle inks, we describe a laser sintering process that generates a localized heat-affected zone (HAZ) when scanning over a printed feature. For sintering metal nanoparticles that are reactive to oxygen, an inert or reducing gas shroud is applied around the laser spot to shield the HAZ from oxygen. With the shroud gas-shielded laser, oxygen-sensitive nanoparticles, such as those made of copper and nickel, can be successfully sintered in open air. With very short heating time and small HAZ, the localized peak sintering temperature can be substantially higher than that of damage threshold for the underlying substrate, for effective metallization of nanoparticle inks. Here, we demonstrate capabilities for producing conductive tracks of silver, copper, and copper–nickel alloys on flexible films as well as fabricating functional thermocouples and strain gauge sensors, with printed metal nanoparticle inks sintered by shroud-gas-shielded laser.

Keywords—Printed electronics, laser sintering, metal nanoparticle ink

INTRODUCTION

To fabricate electronic circuits on flexible substrates of complex shapes, the approach of printing metal nanoparticle inks directly onto substrate followed by a postprocess metallization step has become increasingly popular for low-cost manufacturing [1]. With the Aerosol Jet® direct-write technology, the “ink” is deposited in a form of high-speed collimated jet of aerosol droplets through an aerodynamic focusing nozzle with sheath gas. Microscale high-aspect-ratio features of various materials can be conformally printed onto substrates of complex geometries. This makes the Aerosol Jet® technology attractive to numerous applications, such as printed electronics, printed sensors, to mention a few [2-4]. Its capability of noncontact conformal printing of metal nanoparticle inks and nonconductive polymer materials can be used to create electronic circuits in a variety of novel form-factors, for fabricating multifunctional 3-D devices.

But metal nanoparticle inks typically contain organic stabilizers (dispersants for preventing nanoparticle agglomeration in liquid solvent) and they do not become conductive with drying alone. The organic components must be removed and electrical contacts must be established between metal nanoparticles before useful conductivity can be achieved. The organic component removal and nanoparticle contact enhancement can be effectively accomplished at an elevated temperature, where polymers are eliminated by thermal decomposition–vaporization and the nanoparticles are fused via interparticle atomic diffusion.

Sintering metal nanoparticle inks has recently become an intensive research subject because of the growing interest in direct metallization with printed electronics, to replace the multistep, much more complicated lithographic processes used in traditional electronics production. Many sintering techniques have been developed with various levels of success. The simplest and most commonly used method is to heat the entire printed parts in a thermal oven. Depending on the ink formulation and nanoparticle size, the temperature for oven sintering is in the range from 120°C to 250°C, much lower than the corresponding bulk metal melting point. The melting point of nanoparticles is lowered by virtue of thermodynamic size effect associated with their large surface energy (known as “melting point depression”) [5]. When heated in an oven, many low-cost polymeric substrates with \( T_g \) close to the sintering temperature would suffer extensive thermal damage. Moreover, sintering in an oven with restricted temperature often takes hours. Such an extended heating makes oven sintering of oxygen-sensitive materials (e.g., copper and nickel) impractical under the ambient atmosphere. Copper nanoparticle inks are attractive for printed electronics because of its superior conductivity and low cost of raw materials. Although using oven sintering in vacuum or inert/reducing gas environment can mitigate the copper oxidation problem, it also eliminates its low cost advantage because expensive high-temperature plastic substrates must be used. Among several alternative techniques, rapid localized laser sintering offers the most desirable attributes, such as a small spot size for minimizing heat-affected zone (HAZ), while delivering adequate heating in a short duration, to enable sintering on temperature-sensitive substrates and to prevent extensive oxidation of oxygen-sensitive metals.
Promising results of laser sintering of metal nanoparticle inks have been reported by many authors, mostly with ink layers of thickness below one micron (i.e., <1,000 nm) [6-11]. Unlike inkjet printing which operates with larger droplets of low viscosity inks, the Aerosol Jet® printed lines can have a much higher aspect ratio (with layer thickness typically of several microns as printed in a single pass) because of the effective in-flight solvent removal with microdroplets of appropriately formulated inks [12]. For the same area of line cross-section, which determines the line conductance, the Aerosol Jet® printed lines can be much narrower, enabling production of higher density electronic circuitry. Sintering high-aspect-ratio lines can pose technical challenges with respect to crack formation [9] and material delamination (because of high pressure gas pocket formation) [11].

In this work, we present a shroud-gas-shielded laser sintering process of metal nanoparticle inks for producing conductive tracks of silver, copper, and copper–nickel alloys on flexible films, thermocouples, and strain gauges printed with the Aerosol Jet® direct-write technology. Challenges related to robust processing and scaling to production are also discussed.

**Methods**

As is typical with printed electronics, metal nanoparticle (NP) inks are first deposited on a substrate by a printing process, and then sintered at an elevated temperature. In the present work, the Aerosol Jet® direct-write technology is used for printing, and then a high-power laser beam is used for localized sintering as it moves at a variable speed along the same path as that for printing. By adjusting the laser power and scan speed, the local heating temperature and duration can be effectively controlled. To avoid thermal damage to temperature-sensitive substrate, it is important to restrict the heating duration to a time scale of milliseconds such that the metallization is accomplished before the thermal diffusion front penetrates too deeply into the substrate. A shroud-gas shield around the laser HAZ inhibits oxidation of sensitive metal NP inks, such as Cu, Ni, and Cu–Ni alloys [13].

**Aerosol Jet® System**

The Aerosol Jet® material deposition system consists of an atomizer, a deposition head, a mist transport-conditioning channel between atomizer and deposition head, and a substrate holding stage with adequately accurate motion control as well as a mist flow switching device (Fig. 1). The atomizer generates a mist of microdroplets of functional ink containing metal nanoparticles, which are then deposited onto the substrate in a form of high-speed collimated mist jet through an aerodynamic focusing nozzle with sheath gas. With a standoff of 1-5 mm between the nozzle and substrate, noncontact printing of various patterns on substrates of complex geometry is enabled with CAD-driven motion. Although the printed feature size can be as fine as 10 μm, the features printed in this work are on the order of 100 μm such that the laser irradiation spot of 60 μm can easily fit within the ink pattern, to avoid direct laser irradiation of the substrate material causing thermal damage.

Samples shown in this work consist of lines typically with a width over 100 μm and height about 3 μm (or with a cross-sectional area of more than 300 μm²), printed with a deposition nozzle of 300-μm diameter at printing speed of 10 mm/s. So, depending on the pattern size, each sample usually takes a few minutes to print. In general, the mass output of Aerosol Jet® printer depends on the size of deposition nozzle with a mist flow rate adjusted for the desired printing feature size and ink formulation. For example, with the 300-μm diameter nozzle, the (solid) mass output is typically ~2 mg/min for the copper ink but can go up to 5 mg/min with the silver ink used in this work (depending on the mist flow rate adjusted for desired feature size based on ink wetting property on the substrate). For a given mass output, the printing speed is determined by the electronic design requirement, such as line cross-section area for electrical conductance. With the constantan ink, the mist flow rate was adjusted to a mass output around 0.7 mg/min for printing required quality of strain gauge patterns. In this case, traces were overprinted three times to obtain a cross-section area equivalent to that printed with ~2 mg/min in a single pass.

**B. Shroud-Gas-Shielded Laser Sintering System**

As a standard option, a high-power fiber-coupled diode laser (JDSU 2486-L4) is conveniently mounted next to the Aerosol Jet® deposition head. In-situ postprocessing the printed features is done with the same motion-controlled stage. Having 60-μm aperture with the mean wavelength 830 nm and a continuous-wave output power of maximum 2W (but the actual power delivered via fiber to the irradiation spot is typically between 100-700 mW), this multimode diode laser is used for the present work with samples sintered in a laser power range between 300 and 600 mW at a scan speed between 5 and 20 mm/s. For inks with nanoparticles of silver and gold, laser sintering can be carried out in the ambient atmosphere without oxidation.
degradation because of high free energies of their oxides. Despite its high conductivity and oxidation resistance, silver is costly and does not have great mechanical strength. Silver is also known to be prone to electromigration that can cause failure of circuit functionality and is not easy to solder on. Copper, on the other hand, is intrinsically less susceptible to electromigration and relatively low cost because of its abundant availability. Copper is also known to have excellent conductivity, good mechanical strength, and easy for soldering. But copper tends to be oxidized when sintering at elevated temperature in ambient atmosphere.

To minimize oxidation during sintering, a reducing HydroStar® H5N gas (a mixture of nitrogen with 5.5% hydrogen commonly used as shielding gas for manual welding applications) is introduced locally through a nozzle as a shroud in the form of an impinging jet around the laser irradiation spot. A schematic configuration of the H5N gas nozzle with laser beam along its centerline is shown in Fig. 2, along with the H5N gas streamlines computed using the OpenFOAM® CFD package indicating that H5N (red) is effectively shielding the laser heating zone at the stagnation point without significant diffusive penetration of ambient air (blue) with diffusion layer (white) in between.

The computational model is based on a realistic set of process parameters, with an $h = 10$ mm gap between the nozzle exit and substrate, substrate moving in the x-direction at 10 mm/s speed, at an H5N gas flow rate of $Q = 2,700$ ccm ($= 4.5 \times 10^{-3}$ m$^3$/s) through a $2R = 5$-mm diameter nozzle. The average gas jet velocity is 2.55 m/s with peak value at 3.20 m/s, which leads to the jet Reynolds number around 850 indicating that results from the laminar flow model with the compressible flow solver “rhoPimpleFoam” (as used here) are valid. The streamline plot in Fig. 2 shows a reasonably symmetric laminar gas flow wraps around the laser beam along the centerline when flowing through the nozzle orifice impinging onto the moving substrate, despite the asymmetric location of the flow inlet and substrate motion. Our shroud gas process recipe came from the principles that the gas jet velocity is much greater than the substrate moving speed to prevent ambient air from entraining into the laser heating zone. The diameter of the shroud gas jet is sufficiently large to prevent ambient gas diffusion into the laser heating zone. With 2,700 ccm gas flow through a 5-mm nozzle, the jet velocity is 2.55 m/s, indeed much greater than 0.01 m/s substrate moving speed. If we use the value of $4R(\pi h D/Q)^{1/2}$ for an estimate of the penetration thickness $\delta$ of ambient gas from the edge of shroud gas jet flow [14], we have a penetration thickness of about $\delta = 1.18$ mm (or $\delta/R = 0.473$) with a diffusion coefficient of $D = 2 \times 10^{-5}$ m$^2$/s and time $t = (10$ mm$)/(2.55$ m/s) = 3.9 ms. Thus, a 5-mm diameter nozzle (with 2.5 mm radial distance from centerline to jet edge) is reasonable for a gas flow rate of 2,700 ccm to prevent significant amount of ambient gas diffusion into the laser heating zone.

C. Metal NP Ink Materials

The metal NP inks can be obtained from multiple commercial suppliers, e.g., silver NP ink from PV Nanocell, copper NP ink from Intrinsiq, constantan NP ink from Applied Nanotech Inc. (ANI), etc. The inks used for fabricating samples in this work were all printed using the standard
pneumatic atomizer that came with the Aerosol Jet® system with equipped virtual impactor for adjusting the mist flow rate to the deposition nozzle.

Table I shows that Ag has the best electrical conductivity, but does not offer good mechanical strength. The mechanical strength of Cu and Ni are much better than Ag, with electrical conductivity of Cu very close to that of Ag. On the other hand, Cu and Ni have good solderability that is usually lacking with Ag, and they are less susceptible to electromigration than Ag. The large temperature coefficient of resistance (TCR) of Ni combining with its high resistivity makes Ni a good material for making thermistors. The exceptionally low magnitude of the TCR of constantan (a Cu55Ni45 alloy) makes it attractive for many sensor applications when the signal sensitivity to temperature variation is undesirable. The large magnitude of Seebeck coefficient of constantan also makes it attractive for making thermocouples and applications in energy harvesting. Although Au has good electrical conductivity and large yield strength, it is cost-prohibitive in most applications. The silver polymer thick film (Ag PTF, which has Ag flakes imbedded in an elastomer) ink offers very high elongation that is attractive for flexible circuit applications, but it also has a much lower electrical conductivity compared with most of the metal NP inks.

It should be noted that the “sintering T” in thermal oven given in Table I only serves as a convenient reference value, which usually depends on the NP size as well as the dispersant type and solvents of a particular ink and can vary in a wide range.

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity (µΩ cm)</th>
<th>TCR (K⁻¹)</th>
<th>Yield strength (MPa)</th>
<th>Elongation (%)</th>
<th>Seebeck coeff. (µV/K)</th>
<th>Sintering T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver (Ag)</td>
<td>1.6</td>
<td>3.8E⁻³</td>
<td>55</td>
<td>35</td>
<td>6.5</td>
<td>120</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>2.4</td>
<td>3.4E⁻³</td>
<td>205</td>
<td>45</td>
<td>6.5</td>
<td>200</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>1.7</td>
<td>3.9E⁻³</td>
<td>117</td>
<td>40</td>
<td>6.5</td>
<td>220</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>7.0</td>
<td>5.8E⁻³</td>
<td>140-350</td>
<td>40</td>
<td>−15</td>
<td>350</td>
</tr>
<tr>
<td>Cu55Ni45</td>
<td>49.0</td>
<td>−7.4E⁻⁵</td>
<td>140</td>
<td>45</td>
<td>−35</td>
<td>400</td>
</tr>
<tr>
<td>Ag PTF</td>
<td>1,000</td>
<td></td>
<td></td>
<td>100+</td>
<td></td>
<td>170</td>
</tr>
</tbody>
</table>

Fig. 3. (a) Aerosol Jet® printed serpentine of silver NP ink on medical grade silicone elastomer under tension; (b) Localized laser sintering of printed silver ink; (c) Sintered silver serpentine tracks survived (uncontrolled) crumple test; (d) Resistance over the 150 mm long track remains consistently around 9 Ω up to 10% elongation by pressing a hemisphere to stretch the elastomer.
range. For example, the value “120” for silver NP ink actually came from that of PV Nanocell specifically used in this work (with NP diameters about 80 nm); there are many other silver NP inks often requiring higher oven sintering temperature (e.g., 150°C or even higher) for adequate conductivity, adhesion, etc.

RESULTS

The primary advantage of laser sintering are to enable printing electronic circuits on temperature sensitive substrates which would be susceptible to thermal damage when sintered in a thermal oven. Even with substrate materials that can withstand high temperature, the mismatch of thermal expansion behavior can cause printed traces to crack and delaminate when sintered in an oven for extended durations. Using localized laser irradiation, we have successfully sintered metal NP ink on an acrylic plastic (Tg ~ 100°C) and PET polymer film (Tg ~ 80°C). These materials would warp in a thermal oven at temperature approaching their Tg values. To avoid cracking caused by extensive thermal expansion of a substrate, we show the possibility of using a localized laser sintering to fabricate conductive silver tracks on flexible medical grade silicone elastomer. With the inert and/or reducing shroud gas of HydroStar H5N shielding around the localized laser heating zone, successful sintering of copper and nickel inks for fabricating thermocouples and strain gauges are also demonstrated.

A. Silver NP Ink on Silicone Elastomer

To sinter silver NP ink on temperature-sensitive materials (such as acrylic glass, PET film, etc.) without serious thermal damage to the substrate, the localized heating process needs to be carefully controlled. The key for success is to have sufficiently high laser power for effective sintering of the metal NP ink quickly within a short irradiation duration such that the thermal diffusion front cannot penetrate too deeply into the substrate before the laser irradiation is moved away. The same principle can be applied to sintering the metal NP ink on flexible substrates of elastomers, such as silicone. Although silicone can withstand higher temperature, its extensive thermal expansion tends to result in cracking and delamination of printed metal NP tracks that usually shrink during sintering at an elevated temperature. With localized laser sintering, the silicone thermal expansion can be limited in a small heat-affected zone, so the printed conductive tracks can be fabricated without cracking and delamination due to otherwise extensive thermal expansion of the substrate.

To demonstrate such an advantage of laser sintering, flexible conductive tracks consisting of silver ink serpentines are printed and sintered with localized laser irradiation on a medical grade silicone elastomer substrate. As shown in Fig. 3, those conductive tracks can remain conductive through crumple and stretch tests up to 10% elongation. In this case, the conductive tracks of ~200 μm wide and ~4 μm high were printed with a (solid) mass output of ~5 mg/min. With measured 9 Ω resistance over a 150 mm track of ~750 μm² cross-section area, we can derive a resistivity of 4.5 μΩ cm which is about three times that of bulk silver (i.e., 1.6 μΩ cm).

B. Thermocouples Printed with Copper and Copper–Nickel Alloy NP Inks

The large magnitude of the difference in Seebeck coefficient between copper and copper–nickel alloys (in Table I) indicates that they are good for making thermocouples. But copper and nickel are both prone to oxidation, especially at an elevated temperature during sintering. With the protection of shroud H5N gas around the laser heating zone, we can adequately sinter copper and nickel as well as their alloys without serious oxidation. The laser sintering process is then used to fabricate
thermocouples using copper and copper–nickel alloy inks as shown in Fig. 4. The response curves of those thermocouples show their reasonable functionality and that of the printed copper-constantan thermocouple is comparable to the commercial type T thermocouple.

C. Strain Gauges Printed with Constantan NP Ink

With its low temperature coefficient of resistance and high strain sensitivity (or gauge factor) as well as relatively high resistivity and elongation capability, constantan (Cu55Ni45) has become the popular choice of material for strain gauge applications. Using localized laser sintering with H5N gas shroud, the Aerosol Jet® printed Wheatstone bridge circuits of constantan on a Kapton film (Fig. 5) are shown to be fully functional for strain gauge applications. There is no signal degradation during a cyclic bending test on a 60-mm diameter pipe with a 0.3% strain over more than 10,000 cycles.

**DISCUSSIONS**

With the promising proof-of-concept results of laser sintering of Aerosol Jet® printed high aspect-ratio tracks of metal nanoparticle inks are demonstrated here [15], in-depth investigations of aspects relevant to reliable production of flexible electronic circuits are required to optimize this technology. For example, the high-power fiber-coupled diode laser has been used here only because of its availability in our laboratory; other types of lasers with different wavelengths and spot sizes can be acquired from different vendors for investigations of effects of laser wavelength and relative spot size on laser sintering outcomes. The HydroStar® HSN (with hydrogen as the reducing component) gas used for shielding the laser heating zone is shown to be effective for preventing oxidation of copper and nickel NPs during sintering, but a simpler inert shroud gas, such as pure nitrogen, might be just as effective, which should be explored in future work.

![Wheatstone Bridge Circuit](image)

**Fig. 5.** Aerosol Jet® printed Wheatstone bridge circuit with constantan ink on 0.005” Kapton film, sintered with localized laser irradiation with shroud H5N gas.
Moreover, it is also important to investigate the related adhesion and formation mechanisms of those apparent bubbles. Apparent bubble formation in sintered metal nanoparticles ink is undesirable for mechanical and electrical robustness of printed electronics. Although the nature and formation mechanisms of those apparent bubbles are likely to become subjects for future investigation. The nature and formation mechanisms of those apparent bubbles are likely to become subjects for future investigation.

CONCLUDING REMARKS

Successful laser sintering of Aerosol Jet® printed high aspect-ratio tracks of metal nanoparticle inks is demonstrated here for fabricating flexible electronic circuits on temperature sensitive substrates. For metal inks susceptible to oxidation (e.g., copper and nickel) at elevated temperature during sintering, a shroud gas of H5N shielding the localized heating zone is shown to be effective for preventing oxidation. This shroud-gas-shielded laser sintering process enables us to produce functional thermocouples with copper and copper–nickel alloy inks and strain gauges with a constantan nanoparticle ink [15]. Further work on process development with systematic characterization of laser sintering outcome is underway. Our goal is to develop an automated laser sintering system with a close-loop feedback control to bring this enabling and effective sintering method from laboratory proof-of-concept research to industrial production.

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