

The Effect of Laser Sintering Process Parameters on Cu Nanoparticle Ink in Room Conditions

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ABSTRACT

Copper is an interesting material for printed electronics inks because, for example, of its good conductivity and lower raw material price compared to silver. However, post-processing Cu inks is challenging because of non-conductive copper oxide. In this work, inkjet-printed Cu nanoparticle structures were sintered on a polyimide substrate with a continuous-wave 808-nm diode laser. Laser sintering was tested by varying the sintering parameters (optical power and scanning velocity), and the electrical resistance of the samples was measured. A minimum sheet resistance of approx. 90 mΩ/□ was obtained. All tests were run in room conditions. Sintered structures were then analyzed from SEM images. Results showed that laser sintering produces good repeatability, that a scanning velocity increment positively affects the process window, and that multiple sintering cycles do not increase conductivity.

Keywords: Nanoparticles; Electrical Properties; Laser Processing; Microstructure; Sintering; Thin Films

1. Introduction

In the past decade, printed electronics has come under extensive research, and not only printing technologies but also increasingly material development and post processing methods. Furthermore, printed electronics has found applications, for example, in electric paper, RFID tags, and various sensors [1,2]. In addition to contactless performance, inkjet printing, a most agile printing method, harbours possibilities for wide-ranging customization and is thus keenly studied by several research groups around the world [3-5].

Various materials, including conductive, dielectric, and semi-conductive materials, are available as suitable candidates for inkjet printing. A common conductive ink contains metal (e.g., silver, gold, nickel, or copper) nanoparticles surrounded by a thin dispersive material (commonly some polymer) and diluted in one or several solvents. In post-processing, called sintering, solvent and dispersants are removed, and a conductive path is formed across the metal particles by applying heat to the ink structure, usually by oven sintering [6,7]. Silver has been used most frequently because of its low resistivity and simple handling in post processing. However, recently,

copper, a less expensive raw material, has been generating interest but has also been posing post-processing challenges because of non-conductive copper oxide. An Ag ink can be sintered in an oven, but a Cu ink needs an inert atmosphere or an alternative approach to sintering. Laser sintering of screen-printed copper paste in nitrogen atmosphere has been demonstrated in a few studies so far [8,9].

In a non-inert atmosphere, nano Cu must be sintered in a very short time. Therefore, Cu ink can be sintered in ambient conditions using the following two techniques: pulsed light [10,11] and laser sintering [12]. In laser sintering, a laser beam scans the ink structure with either the beam or the substrate platform moving. Two laser types, continuous-wave and pulsed lasers, have been successfully used to sinter Ag nanoparticle ink. [13] The advantages of laser sintering over traditional oven sintering are speedy process and possibility to sinter locally. In this study, we discuss on sintering of inkjet-printed Cu nanoparticle ink on a polyimide substrate with an 808-nm continuous-wave diode laser. Tests were run in ambient room conditions instead of an inert atmosphere, different scanning velocities and laser powers were compared, and the repeatability of the process was assessed.

2. Experiments

2.1. Materials and Sample Fabrication

In this test, we used Applied Nanotech, Inc. Cu-IJ70 ink and 50- μm -thick Kapton HN polyimide film [14]. In addition to copper nanoparticles, the ink contained a complex combination of organic solvents, including aliphatic acetate and derivatized glycol ether, combined with a dispersion agent to create an electrostatic repulsion layer on nanoparticles to control agglomeration. According to the manufacturer, the particle size was 50 - 70 nm and the solid content 30 wt%. Polyimide film was chosen because it can withstand laser-irradiation-induced heat stress and thus rapid heating of the copper layer.

Our printing equipment was an inkjet material deposition system (iTj XY MDS2.0) and a drop-on-demand printhead (Dimatix Spectra SE-128) with 128 nozzles creating approx. 30 picoliter droplets. The drop diameter on a 70°C substrate was about 100 μm . For surface treatment before printing, the substrate was cleaned with isopropanol.

The printed structures were simple straight conductors (example can be seen **Figure 1(b)**) with measurement pads at both ends. The conductors were of length 40 mm and the squares 1 mm \times 1 mm; after printing, the conductors were, on average, of width 300 μm . We used print file of 800 dpi resolution.

2.2. Laser Equipment

We studied laser sintering in ambient room conditions

instead of an inert (e.g., nitrogen) atmosphere. The laser used was an 808-nm continuous-wave semiconductor laser HLU35C10x2-808-CB by LissotschenkoMikrooptik (LIMO) with its output power adjustable up to 35 W. The spectral width of the beam was 2.5 nm and the peak wavelength 808.6 nm. A spherical lens with a focal length of 125 mm was used. However, the lens was finally placed 127 mm over the sintering platform for the beam to be slightly off-focus to even out its intensity. The laser spot for sintering was ca. 1.1 mm \times 0.4 mm and placed so that the beam's longer edge was parallel to the sintering direction (x-axis). Based on our experiments, this placement provided ideal sintering results.

The laser diode was installed in a static frame, and the substrate was moved under the laser with a motorized XY-table. An area was sintered by sweeping the substrate under the beam at a steady pace along the horizontal axis and then moving it along the vertical axis in 0.3-mm increments (hatch) after each sweep (**Figure 1**). The speed of the XY-table was adjustable and a critical variable in our study, the other being the output power of the laser.

2.3. Structural Analysis

The surface of the laser-sintered structures was analyzed with a scanning electron microscope (SEM). Pictures were taken of the top surface and of sample cross-sections. A Zeiss Ultra-55 FE-SEM (field-emission scanning electron microscope) was used for surface SEM pictures. Conductor cross-sections were made using an FEI Helios

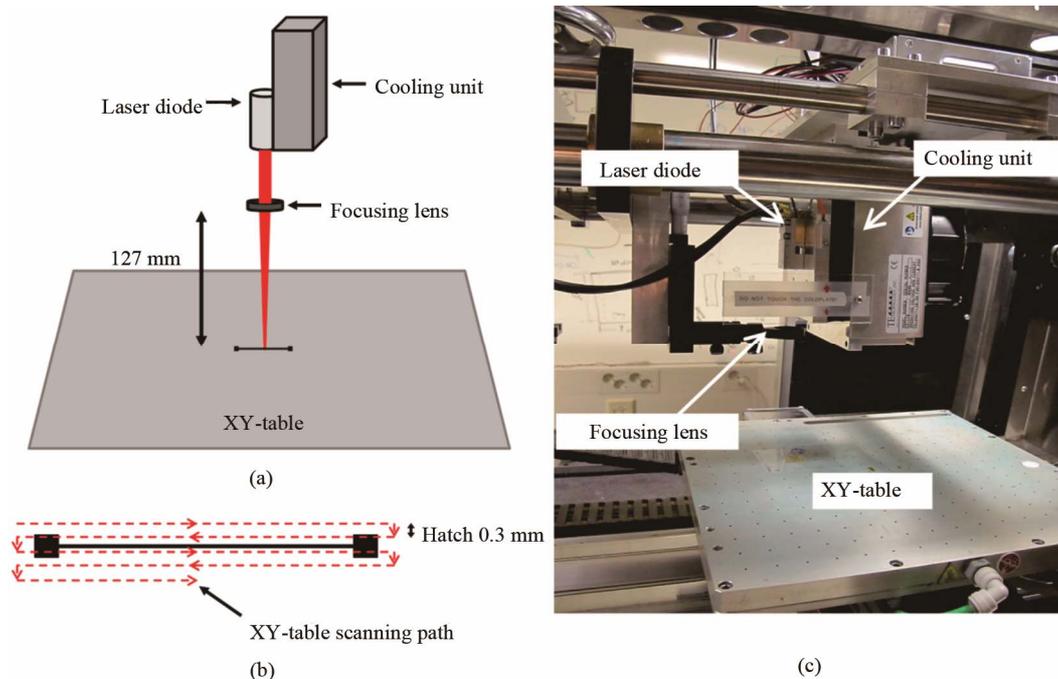


Figure 1. (a) and (c) Laser sintering process setup, and (b) scanning process sequence with 0.3 mm hatch.

Nanolab 600 dualbeam system. A thin layer of platinum ($\sim 0.5 \mu\text{m}$) was first deposited on the surface as a protective layer with a focused ion beam (FIB). A rough cross-section was then cut from the bulk material using the FIB's cross-section tool. The cross section surface was then polished with the FIB using a smaller current (*i.e.*, a small beam size). Then images of the cross section surfaces were taken with the Helios 600 dual-beam system SEM.

3. Results and Discussion

Sintered samples were electrically measured with a multimeter with values obtained at an accuracy of 0.1 ohms, which is below 1% of the average resistance value. **Figure 2** shows the resistance of Cu conductors after sintering as a function of the laser's optical power. Four different (50 mm/s, 100 mm/s, 200 mm/s, and 400 mm/s) xy-plate scanning velocities were used. The graphs show that the resistance dropped steeply as the laser's optical power was increased. After that the resistance stabilized at constant minimum, in this case, below 12Ω , *i.e.*, $90 \text{ m}\Omega/\square$. When the optical power was further increased, the copper conductor and the polyimide substrate film under it burned in each case. However, at 400 mm/s velocity this point did not occur because we did not wish to run our laser at close to its maximum power. In the figure, burning is shown as a rapid increment in resistance.

Comparing the graphs of different plate velocities, we

can observe that the higher the velocity of the XY-plate, the smaller the effect of a constant increment in optical power. This indicates that the power window for good conductivity was wider at high velocities. For example, the window was two times larger at 100 mm/s and at least five times larger at 400 mm/s than at 50 mm/s. High velocities not only shorten the production time but also benefit us when sintering uneven or three-dimensional surfaces, where a fixed laser's beam focus and thus its optical power vary depending on surface topography. Therefore, at high velocities the process is more tolerant of surface roughness.

The level of sintering copper ink was studied with SEM analysis. **Figure 3** shows three sintering stages. **Figures 3(a)-(c)** are cross-sectional images and **Figures 3(d)-(f)** are the corresponding images of surfaces. These SEM images are of samples sintered at 50 mm/s velocity and chosen from different points of the resistance-optical power graph such that the first is unsintered, the second sintered at 2.62 W optical power, and the third at 7.95 W. The first does not conduct, the second has a resistance of 53.7Ω , and the third has a stable minimum resistance of about $11 - 12 \Omega$. In the images, the Cu layer is about $1 \mu\text{m}$ thick.

The pictures show a difference in structural density in different cases. The unsintered sample (**Figure 3(a)**) is structurally very porous, but it forms markedly dense and solid, *i.e.*, larger grain size, as laser power is increased and conductivity enhances. The SEM images of samples

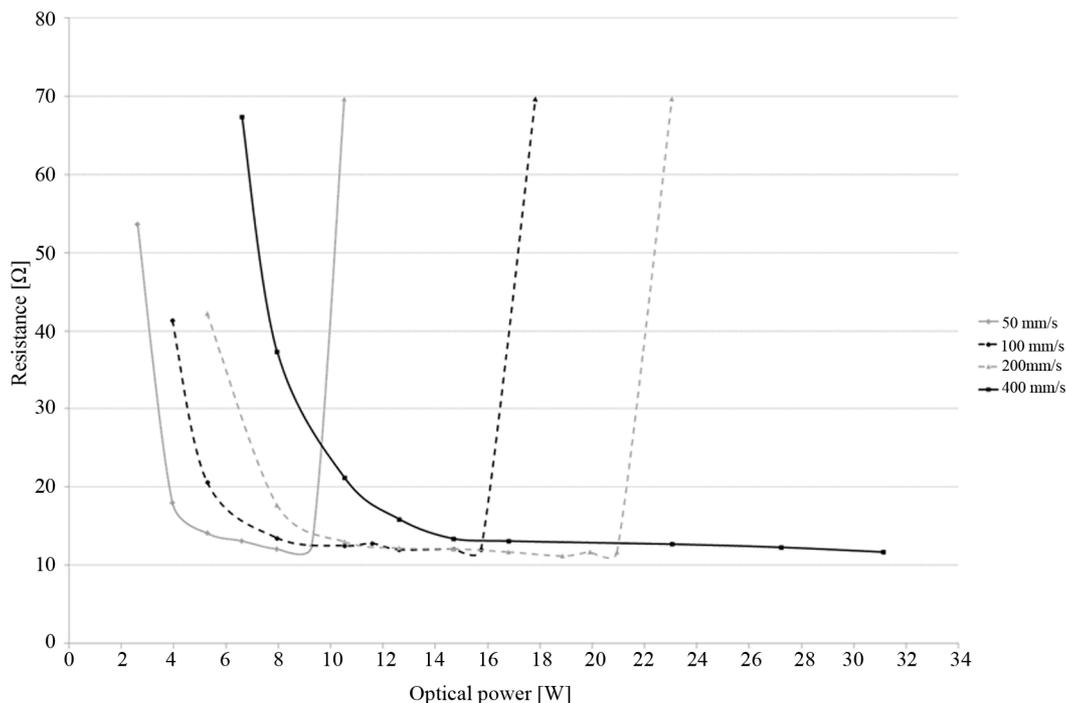


Figure 2. The resistance of laser sintered samples as a function of the optical power of the laser diode. Four (50 mm/s, 100, mm/s, 200 mm/s, 400 mm/s) scanning velocities were used.

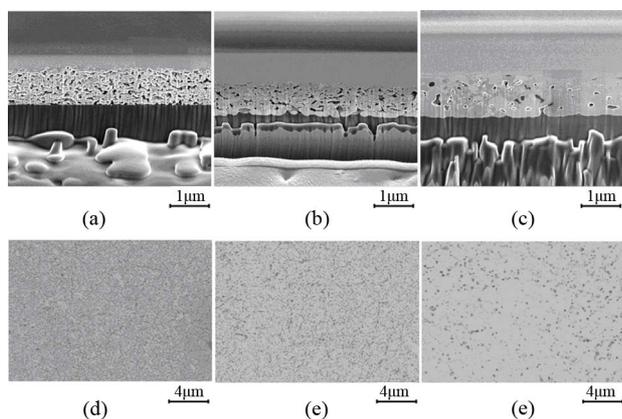


Figure 3. (a)-(c) cross-section and (d)-(f) surface SEM images from laser sintered Cu conductors. Sintering parameters were: for (a) and (d) speed: 50 mm/s, optical power: 0 W; for (b) and (e) speed: 50 mm/s, optical power: 2.62 W; for (c) and (f) speed: 50 mm/s.

sintered at 400 mm/s velocity showed just similar behavior. Interestingly, at every stage the Cu nanoparticle structure looks very homogenous through its whole thickness. Previous studies on oven and Argon plasma sintered silver nanoparticles have shown that the process proceeds from the upper surface of the structure towards the bottom interface between silver and substrate material [6,15]. These results indicate that the conductor structure forms differently in oven and laser sintering.

Repeatability analysis of the sintering process was made. Laser sintering parameters were: XY-table velocity: 200 mm/s, laser diode optical power: 4.5 W. **Table 1** shows results obtained when sintering several traces with constant laser sintering parameters. Measurement uncertainty explains most of the variation in the resistance results, though some other process parameters, such as printing quality, played a part.

In addition, we wanted to examine if repetitive laser irradiation cycles at constant optical power and speed could increase conductivity. The idea was to find out if we can achieve equal conductivity by sintering multiple times with a lower laser power than we obtained with higher power values. The tests were made with 100 mm/s and 200 mm/s velocities. However, conductor resistances remained the same regardless of the number of sintering cycles at the same constant optical power and speed.

4. Conclusion

Copper nanoparticle ink was inkjet-printed on polyimide substrate film. After that, the ink was sintered with an 808-nm continuous-wave diode laser in ambient room conditions. Several laser optical power values were used with four different scanning velocities. A sheet resistance of about $90 \text{ m}\Omega/\square$ was achieved. More importantly, increasing the scanning velocity seemed to widen the la-

Table 1. Laser sintering repeatability results with fixed parameters. Velocity 200 mm/s and optical power 4.5 W.

	Value	95% CI
N	11	
Resistance [Ω]	11.08	(10.77, 11.39)
Standard deviation [Ω]	0.439	(0.30, 0.80)

ser's power window for good conductivity, indicating that high velocities may reduce the effect of process variations, such as the altitude variance of surface. The study also shows that laser sintering has good repeatability and that multiple sintering cycles at constant optical power and velocity do not increase conductivity.

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