

# Inkjet Printing and Sintering of Nano Copper Ink

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## Abstract

*An alternative low cost replacement for silver and gold conductive inks is of great interest to the printed electronics industry. Nano particle copper inks and silver coated nano copper inks are some of the alternative materials being tested for use, especially in applications where low temperature flexible substrates are favored. Although the inkjetability of nano copper ink influence on print quality has been reported, information regarding the relationship between ink film thickness and energy required for sintering by intensive pulse light is not yet understood. In this study, an inkjettable nano copper ink was printed on PET (PolyEthyleneTerephthalate) and glass and the samples were sintered using bursts of high intensity pulsed light. The amount of energy applied determined the degree of sintering among particles. The greater the number of sintered nanoparticles, the higher is the conductivity of the printed traces. A comparison of energy levels required for sintering on glass and PET in relationship to ink film thickness is reported and the thermal contribution of the substrate to the processing energy requirements of this ink is revealed.*

## Introduction

Inkjet printing is an attractive printing technology for the deposition of functional inks, due to its advantages of low-cost, ability to print fine lines and thin layers, and due to the wide range of available materials available for printing by this method. Although the inkjet printing of silver and gold is already being practiced, their high costs have limited their use, especially in low cost flexible electronic applications. As a result, low cost alternative materials are of interest. The use of conductive organic polymers, organo-metallic compounds, metal precursors and metal-based nano inks have all been reported, with different print methods being employed for their deposition. Although conductive polymers meet the requirements in terms of being used in soluble deposition printing, their low conductivity and instability to the air are significant shortcomings.<sup>1</sup> Metal precursor and organo-metallic compounds require a heat treatment for reduction, which leaves residual organic matter in the fabricated film that may adversely affect the product performance.<sup>2</sup> For metal-based nano inks, the requirement for low-temperature, in-situ sintering of the inks is an issue.<sup>3</sup> Kim et al.<sup>4</sup> sintered Ag nano ink at 200 °C for 30 min. in a thermal oven and found that the conductivity was changed based on the sintering temperature and size of the nano Ag particles applied. Ko et al.<sup>5</sup> used a localized sintering technique to sinter nano Au particles on polyimide films, but found that the sintering technology used was not useful over a large area.

To address the high throughput needs for R2R processing and desire for a low cost alternative to Ag and Au inks, the use of intensive pulsed light (IPL) generated from a Xenon lamp source, to sinter nano copper ink particles under ambient conditions, was examined.<sup>6</sup> IPL delivers a quick burst of intense near UV energy

to the printed surface. The intensity of energy, duration of the pulse and distance from the printed surface can all be varied to alter the amount of energy applied. Due to the short time interval (milliseconds) of the light pulses, the nano particles can be sintered without damage to the underlying substrate layer. This makes it appropriate for use with PET film and paper for flexible printed electronic applications. For copper based inks, conductivity is achieved through either the conversion of CuO nano particles to Cu, or vaporization of a protective coating layer applied to the Cu nanoparticles to prevent oxidation prior to sintering. Though the mechanism for conversion of these inks from the non-conductive to the conductive state is understood, until now, the relationship between ink film thickness and amount of irradiated energy required for sintering has not yet been examined.

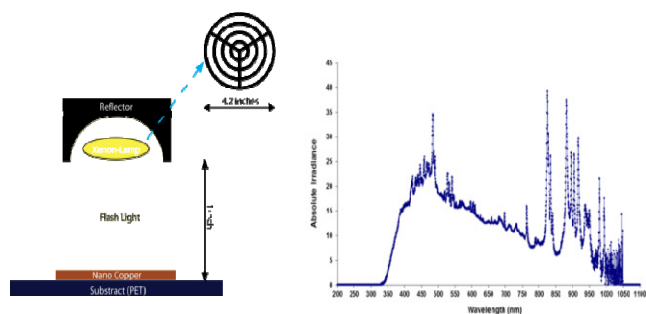
In the present work, the inkjet printability, print quality and electrical properties of a new commercially available nano particle copper ink was studied on PET and glass before and after sintering. The inks were printed using a Dimatix DMP-2800 inkjet printer. Sintering was performed using a Xenon Sinteron 2000 unit. The amount of energy applied was controlled by varying the applied voltage, duration of pulse and number of pulses. The extent of particle sintering was examined under high magnification with a scanning electron microscope (SEM).

## Experiment

A commercial nano copper ink, CI-002, (Intrinsiq Materials, UK) containing 45 nm diameter of particles (10 % Wt.) was used to print multiple 1 cm × 0.5 cm rectangular samples. The samples were printed at different drop spacing intervals (10, 20 and 30 μm) using a Dimatix DMP 2800 inkjet printer (Fujifilm, CA). Prior to printing the inks were characterized by measuring the surface tension and rheological properties with a FTA 200 (First Ten Angstroms, Inc., VA) dynamic contact angle measuring device and RA 2000 dynamic stress rheometer (TA Instruments, DE), respectively. The surface energy of the ink was determined at room temperature using the Owens-Wendt Model<sup>7</sup> with high purity water and methylene iodide as test fluids. Since the jetting performance of an inkjet ink strongly depends on its dimensionless Z-number, this value was calculated from viscosity, surface tension, density and drop diameter (nozzle orifice) measurements.<sup>8</sup>

Viscosity measurements were performed at a fixed shear rate of 10 s<sup>-1</sup>, which was determined to be in the second linear plateau region of the steady flow curve obtained for this ink. Surface tension was measured by the pendant drop method. Prior to printing, the ink was placed into an ultrasonic bath for one hour to ensure homogeneity and degassing of the ink. The ink was then injected into a 10pL cartridge and loaded into the DMP, where it was allowed to equilibrate for 30 minutes. The waveform and temperature range of cartridge (from 28 to 70 °C), were then adjusted by observing the ink jetting behavior and the drop

formation of the ink through a drop watcher camera until satisfactory jetting was achieved (no satellite drops or puddling at the nozzle). Two substrates were printed – a 127  $\mu\text{m}$  PET film Melinex ST505 (DuPont Teijin Films, Delaware) and a 614  $\mu\text{m}$  glass film (Alkaline Earth Boro-Aluminosilicate type). After printing, the samples were immediately sintered (Sinteron 2000, Xenon Corporation, MA). The least amount of energy required to obtain the lowest electrical resistance without damage to the ink film or substrate was determined by inspecting each sample after sintering and measuring its electrical resistance using a 4 point probe. The IPL system consisted of a 15 cm diameter xenon spiral Type B lamp<sup>9</sup>, power supply, capacitors, lamp flash control panel and air cooling system, as illustrated in Figure 1a. The spiral lamp irradiated over a wide wavelength spectrum in the range from 330 nm to 1,050 nm as shown in Figure 1b.



**Figure 1.** Schematic of intensive pulsed light sintering system (left), spectral distribution of the Xenon lamp at 3600 V - 15 Hz setup (right).

Using equation 1, the electrical energy per pulse was calculated,

$$\frac{\{C \times (V)^2\}}{2} = \text{Electrical Energy / pulse} \quad (1)$$

where C and V refer to capacitance and voltage applied to the system, respectively. The pulse energy was varied from 5175 to 10909 J, while the capacitance and pulse duration was fixed at 115 F and 500  $\mu\text{s}$ , respectively. During printing of the samples, it was observed that the ink did not wet the PET film well, resulting in incomplete coverage and poor uniformity of the ink film. To improve wetting, the film was treated with UV/Ozone (Jelight Inc., CA) for up to 275 sec. The UV/Ozone treatment raised the surface energy of the film promoting better wetting, which improved the quality of the printed ink film.

As a first step, after printing each sample received a single pulse flash, after which the sheet resistance was measured using a 4 point probe sensing mode (Keithley multimeter model 2400, OH). If the sample was non-conductive, the IPL treatment procedure was repeated. Based on the results, changes were made to the increase the pulse energy by adjusting the lamp voltage in order to minimize the number of pulses required. Once the number of pulses and voltage required to obtain the lowest resistance for each sample was determined, on average, 3 samples for each substrate were treated and 3 resistance measurements per sample taken. The quality of the printed pattern was analyzed using an ImageXpert, Inc. image analyzer. Next, the surface of sintered

samples was examined under a scanning electron microscope and Wyko white light interferometry microscope. Adhesion tests were performed using a Friction / Peel Tester Model 225 (Thwing Albert instrument company, PA), equipped with a diamond tip attached to a sled containing a 1 kg weight, which was dragged across the surface of the samples at 0.1 cm/s.

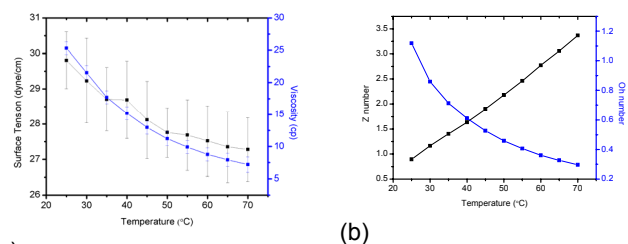
## Result and Discussion

In order to predict the inkjetability of the nano copper ink on the Dimatix DOD inkjet printer, the Z number was calculated according to Eq (2). This number is the reciprocal of the Ohnesorge number

$$Z = \frac{Re}{We} = (d\rho\sigma)^{\frac{1}{2}} \frac{1}{\eta} = Oh^{-1} \quad (\text{Ohnesorge number}) \quad (2)$$

where  $\eta$ ,  $\rho$ , and  $\sigma$  are the viscosity, density, and surface tension of the liquid, respectively, and  $d$  is the diameter of the nozzle aperture (21.5  $\mu\text{m}$ ). The Z number is important, because it predicts the drop formation quality through an inkjet nozzle.

As a first step to calculate the Z and Oh numbers, the change in surface tension and viscosity of the ink with temperature was measured. As shown in Figure 2a, the temperature of the ink was increased from 25  $^{\circ}\text{C}$  (room temperature) to 70  $^{\circ}\text{C}$  (maximum attainable cartridge temperature adjustment). The properties of the ink were measured at elevated temperature because it was determined that elevated temperatures were needed for good jetting. The change in Z number and Oh number with change in surface tension and viscosity are shown in Figure 2a,b. As a consequence of heating, both the surface tension and viscosity of the ink decreased, which consequently resulted in the lowering of the Z number. According to Reis,<sup>8</sup> et al., for best jetting the Z number should fall between 1 and 10. As shown in Figure 2b, the Z number does not meet this criterion at 25  $^{\circ}\text{C}$ , but this criterion is met at any temperature above 27  $^{\circ}\text{C}$ . However, in practice, it was found that a minimum cartridge temperature of 34  $^{\circ}\text{C}$  at an applied voltage of 40 V was needed to jet the ink. Under these conditions, a drop speed of 2 m/s is accomplished with good jetting characteristics.



**Figure 2.** Change in surface tension and viscosity (a), Z number and Oh number (b).

Although the 34  $^{\circ}\text{C}$  temperature was higher than what was expected to be needed for good jetting, at this temperature, the Z number (1.35), does fall within the theoretical Z number range for good jetting. In general, for good jetting the kinetic energy applied to the drop needs to be higher than the surface tension energy of the liquid and the viscous dissipation of the liquid for drop ejection to occur. This means that a high surface tension and viscosity ink will require more kinetic energy, to expel it from the cartridge.

Based on this reasoning, the ink did not jet well at room temperature due to its viscosity and surface tension being higher than the kinetic energy that could be generated by the waveform. Practically, the measured viscosity of 28.3 cp at room temperature was much higher than the 1 ~ 12 cp range recommended by Dimatix. Increasing the cartridge temperature reduced the surface tension and viscosity low enough for the kinetic energy to be sufficient to promote jetting. However jetting is not the only characteristic that needs to be controlled, drop speed is also important. If the drop speed is too slow, the ink volume delivered to the substrate could be too low, leading to incomplete coverage or an insufficient ink film thickness to meet the desired electrical property requirements. Furthermore, a slow drop speed often results in the misdirection of the ink droplets as they travel towards the substrate. Thus, to obtain good print quality, the cartridge temperature and drop speed must be properly adjusted. Drop speed is adjusted by altering the firing voltage. Drop volume is adjusted by altering the waveform. For this ink, the best jetting and print quality was accomplished at a drop speed of 4 m/s and cartridge temperature of 47 °C. Using this set-up, a 1 cm by 0.5 cm pattern, was printed at three different drop spacings (10 μm (2540 dpi), 20 μm (1270 dpi) and 30 μm (847 dpi)) to obtain ink films of different thicknesses. The waveform used and picture of the jetting evolution are displayed in Figure 3.

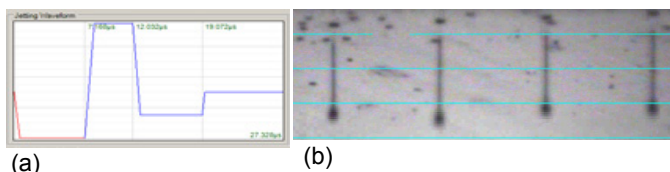


Figure 3. The waveform (a) and ink ejection for nano copper ink (b).

The initial deposition of the ink onto the PET film did not result in good ink wetting or ink adhesion. On the other hand, the ink printed well on the glass. The differences in results can be explained by the differences in the surface energies. As shown in Table 2, the surface energy of the glass, 63.7 dyne/cm, is much higher than the PET film, 43.8 dyne/cm.

Table 2. Surface Energy Values of Substrates

Unit: dyne/cm

Name	Surface Tension	Surface Energy	Dispersive	
Nano Cu	29.8 ±1.2	-	-	-
PET	-	43.8	2.3	41.8
UV/Ozone treated PET (275 sec)	-	62.7	46.2	16.5
Glass	-	63.7	47.4	16.4

To alleviate the problem, the surface energy of the PET was increased to 62.7 dyne/cm by application of a UV/Ozone treatment. The change in surface energy of the film with UV/Ozone exposure time is shown in Figure 4. The surface energy of the film greatly increased after 100 s of exposure. Before

treatment, the ink film was rough and beaded ink drops are observed. After treatment, the ink film was smooth.

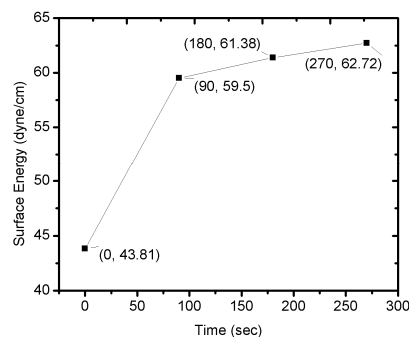


Figure 4. Influence of UV/Ozone treatment on PET with time

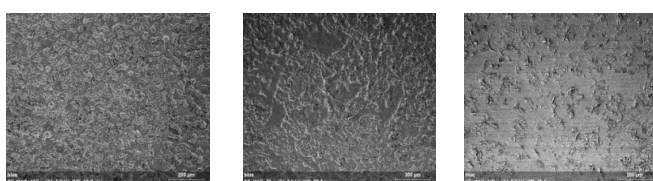
Application of the UV/Ozone treatment for 275 seconds increased the surface energy from 43.8 to 62.7 dyne/cm. The treatment especially affected the dispersive energy component of the surface energy value (Table 2). This is in agreement with Ton-That et al.<sup>12</sup> who reported that the π bonding of phenyl groups in the PET is broken by absorbing UV energy absorbed, which leads to an increase in the number of ester groups at the surface. The greater the exposure time, the greater the number of ester groups through which the oxidation readily takes place, resulting in larger grains at the surface of the treated PET than that of untreated PET. The grain size is proportional to roughness. Therefore, exposure of the film to UV/Ozone roughens the surface of the film, which for a hydrophilic substrate raises the surface energy in accordance with the Young-Laplace equation.<sup>13,14</sup> The increase in PET film surface energy improved the print quality of the nano copper ink.

The experimental design followed for sintering the substrates is shown in Table 3. The energy applied was altered by changing the voltage of the lamp and time of printed sample exposure. As shown, the total energy applied was varied from 5175 to 10909 J. The optimized total electrical energies for the samples printed at 10, 20 and 30 μm drop spacings were 10909 J, 5455 J and 5175 J, respectively. Under these conditions, the lowest resistance obtained was 1.4 ±0.2 Ω/□. Since sample No.1 was printed with a drop spacing of 10 μm, it had the highest ink film thickness (595 nm) prior to exposure to the xenon lamp. So this was the sample used to approximate the needed conditions for sintering the other samples (No. 5 and 9) of thinner ink film thicknesses (110 and 62 nm, respectively). Likewise, the sintering condition for sample No. 9 printed at a drop spacing of 30 μm was used to estimate the energy required for sintering the No.6 printed sample with a drop spacing of 20 μm drop. The amount of energy applied for sample No. 1 and 5 caused damage to the No. 7 and 8 samples. The influence of IPL energy on the morphology of the inks can be seen from the SEM images shown in Figure 5. Since the energy intensity of the spiral lamp decreases as the sample is away from the center of the lamp, the influence of lamp energy on particle sintering could be obtained.

**Table 3. The Experimental Design followed for Altering the Amount of Energy applied to the Nano Copper printed PET Film.**

Sample No.	Drop Spacing ( $\mu\text{m}$ )	Pulse Width ( $\mu\text{s}$ )	Capacitance ( $\mu\text{F}$ )	Applied Voltage (V)	Applied times (sec)	Distance (inch)	Total Electrical Energy (J)	Resistance ( $\Omega/\square$ )
1	10	500	115	3080	10	1	10909	1.4 $\pm$ 0.2
2	10	500	115	3080	5	1	5455	Not dried
3	10	500	115	3000	5	1	5175	Not dried
4	20	500	115	3080	10	1	10909	105M*
5	20	500	115	3080	5	1	5454.6	6.18 $\pm$ 0.42
6	20	500	115	3000	5	1	5175	47k $\pm$ 6K
7	30	500	115	3080	10	1	10909	105M*
8	30	500	115	3080	5	1	5455	105M*
9	30	500	115	3000	5	1	5175	20.0 $\pm$ 0.3

\* Greater than the measurable impedance of the instrument used.



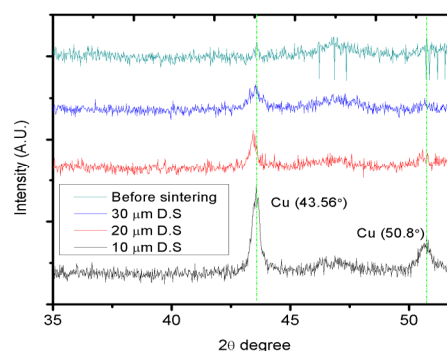
a). Applied energy: 5454 J Resistance: 6.18  $\Omega/\square$   
 (b). Applied energy: 4800 J Resistance: 7.2  $\Omega/\square$   
 (c). Applied energy: 3709 J Resistance: >105  $\text{M}\Omega/\square$   
**Figure 5. SEM micrographs of sintered samples (Magnification  $\times$  100).**

There was a space of 2.54 cm between each position of (a), (b) and (c) where (a) is the center of the lamp. From the SEM pictures, it is clear that as the energy applied increased, fewer individual nano particles are present as a result of particle sintering.

Figure 6 shows the XRD pattern for the copper ink before and after sintering the samples printed with different drop spacing. The sintered XRD pattern shows two characteristic peaks at 43.56 and 50.80°. The peaks verify the presence of the face-centered cubic (FCC) copper phase without any oxidation or other impurity phases being present after IPL sintering. The increase in Cu peaks with decrease in drop spacing indicates the amount of coalescence of Cu increased. Comparison of the surface roughness of the sintered and un-sintered samples indicates that the roughnesses of the printed ink films were affected by this result. The average of measured roughness (Ra) of the unsintered film printed at the 10  $\mu\text{m}$  drop spacing was 11.49 nm and 4089, 84.0, 20.6 nm for the sintered samples at the 10, 20 and 30  $\mu\text{m}$  drop spacings, respectively.

Since the surface roughness of base film (PET) is less than 10 nm (as reported by the manufacturer), the vacuum oven dried ink film was also very smooth. However, after sintering, the roughness dramatically increased due to the movement and cohesion of the nano Cu particles and burn off of carrier solvent within the ink and other ink components.

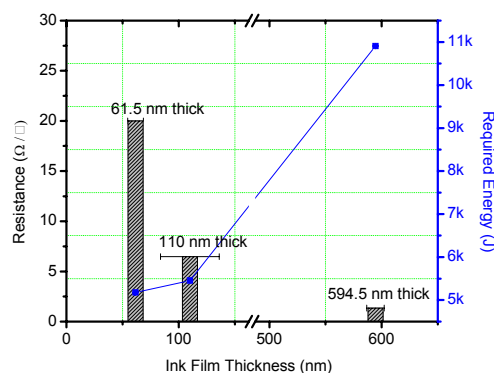
Figure 7 shows the relationship between ink film thickness and sintering energy requirements. The relationship between sintering energy and resistance is also shown. The energy required



**Figure 6. XRD patterns of copper nano copper ink sintered using light intensity of 10909 J on the sample printed at 10  $\mu\text{m}$  drop spaced interval.**

for sintering is proportional to the ink film thickness while the resistance is inversely related to the ink film thickness. Resistance decreased with ink film thickness as a result of more nano copper particle-to-particle contact in the printed ink film.

In addition to determining the influence of ink film thickness on sintering energy requirements, the influences of the substrate thermal properties on sintering energy requirements were also



**Figure 7. Relation between average ink film thickness and required energy for sintering nano copper ink on PET**

determined by comparing the energy required to sinter the nano copper ink on a transparent 614  $\mu\text{m}$  thick glass and 127  $\mu\text{m}$  thick PET. Since the glass had a similar surface energy to that of the UV/Ozone treatment PET, it did not have to be treated before printing. Both substrates were printed at a drop spacing of 20  $\mu\text{m}$ . Application of 5455 joules (Sample 5 in Table 2) of energy was insufficient to sinter the particles on glass. Instead, significantly more energy (about 10 times higher) was needed. This application of higher energy resulted in a resistance of  $68.9 \pm 9.5 \Omega/\square$ , but unfortunately, the adhesion of the copper ink on the glass was poor.

The reason for this finding can be explained as follows: Suppose an IPL with  $1 \text{ J/cm}^2$  is irradiated onto a 10  $\mu\text{m}$  thick nano copper ink film printed over 127  $\mu\text{m}$  thick PET film and 614  $\mu\text{m}$  thick glass film. Assume further that all of the light energy is absorbed into both layers without scattering and reflection. Then, based on these assumptions, the increase in temperature for all the materials can be estimated by use of the lumped mass method as follows<sup>3</sup>,

$$\Delta T = \frac{E}{\rho C_p V} = \frac{E}{\rho C_p A t} = \frac{\text{Energy Density}}{\rho C_p t} \quad (3)$$

where  $\rho$ ,  $C_p$ ,  $A$  and  $t$  are the density, the heat capacity, area and the ink film thickness, respectively.

Using the thermal properties of the materials provided in Table 4, sintering produces an increase in the copper, PET and glass film temperatures to 297, 43.5 and 8.9  $^{\circ}\text{C}$ , respectively. Since the PET and glass are both poor thermal conductors, as shown in Table 4, the copper plays an important role in the adhesion between the substrates by melting the substrate at the ink interface. For the glass, there was only 8.9  $^{\circ}\text{C}$  increase in temperature, which is about 5 times lower than that of the PET. This temperature difference explains the poor adhesion of the copper to glass in comparison to the PET.

## Conclusion

In order to sinter the nano copper ink printed onto a PET film under ambient conditions, an Intensive Pulsed Light (IPL) treatment was applied. The effect of inkjetting conditions and sintering, without preheating, was studied. The relationship between ink film thickness and required energy for sintering the amount of bridging present increased with the amount of energy applied. Overexposure of the samples to the Xenon lamp resulted in damage to the printed samples and loss in electrical properties. The influence of the thermal conductivity properties of the substrate on sintering energy requirements for the nano copper ink was also determined by use of the lumped mass method.

**Table 4.** Thermal Properties of Materials<sup>15,16</sup>

Material	Thermal conductivity (W/mK)	Heat capacity (J/g/K)	Density (g/cm <sup>3</sup> )	Melting temperature ( $^{\circ}\text{C}$ )
Copper	170	0.386	8.71	1084
Polyethylene terephthalate (PET)	0.14	1.3	1.39	255
Glass	0.01	0.768	2.38	No data

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