Investigation of Printing Properties on Paper Substrate

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In this article, the optimum printing parameters were found when using silver nanoparticle ink to print on Kodak 4-Star photo paper substrate. Fujifilm Dimatix 2831 was used as the inkjet printer. The printing parameters of interest included the number of printing layers, the drop spacing, and curing temperature of the ink. Analysis of Variance (ANOVA) analysis of the experimental data reveals sintering temperature to be significant (p < 0.05) to improve the conductivity. Pattern conductivity and surface roughness were used to identify the optimum printing parameters. The optimum printing parameters were found to be 15 μm drop spacing, two printing layers, and a sintering temperature of 90°C. The best conductivity measured under the above mentioned condition was found to be 5.56 × 10^16 Ω−1m−1. Further, the bending test indicated that the printed patterns were unaffected (in terms of conductivity) when flexed around a cylindrical support indicating excellent stability under stress. This study paves the way for developing mechanically robust flexible devices with excellent electrical properties for Internet of Things (IoT) applications.

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Abstract

Recent advancements in printed electronics has enabled the development of flexible devices and IoT products,1 antenna,2 sensors,3 solar cells,4 organic resistor,5 and organic transponder,6 to name a few. The field of flexible devices and wearables is growing fast primarily to fabricate devices without iterations in photolithographic mask design or etching methods.7 Inkjet printing can be performed using any type of conductive, resistive, and biological inks, with wide varieties of substrates including paper, PET film, textiles, fibers, etc. The electrical and mechanical properties of the printed samples depend on the type and quality of ink, as well as the surface characteristics of the substrate. Fujifilm’s commercially available Dimatix 2831 printer has been frequently used to print patterns on different substrates under various printing conditions.8 The paper based substrate has become popular to realize devices due to its versatile used and properties that include possibility of microwave frequency applications, reel-to-reel printing capability, low cost in nature, availability of hydrophobic or fire retardant type, low surface profile, multilayer printing options, and broad回首 printed media applications.9

In this context, the article reports on optimum printing parameters when using silver nanoparticle ink to print patterns on Kodak 4-Star photo paper substrate. The Compound Microscope, Scanning Electron Microscope (SEM), Optical Profilometer, meter and four point probe were used to inspect the samples for surface roughness and conductivity.

Experimental

Printing.—The printer used for this project was the Fujifilm’s Dimatix 2831 Inkjet Printer. The DMP printer offers drop-on-demand (DOD) piezoelectric ink-nozzles to ensure precision drop placement. It uses 10 μL drop-size cartridges (model: DMC-11610) for this experiment, which hold 1.5 mL of ink.

During filling of the cartridge, it is prescribed by manufacturer to avoid air, and keep the cartridge minimum 30 minutes in the idle state. It is recommended the cartridge be loaded in the printer carriage during this time, before giving the printing command. The ink used in this experiment was Ag Nanoparticle Inkjet 9104 Ink, purchased from Methode Electronics. The viscosity, density, and surface energy are as follows: 9 cps, 1.3 g/ml, 33 dynes/cm respectively.17 These ink properties ensure 25 mΩ/□ is the printing electrical resistance. The optimum fluid physical characteristics include a viscosity of 10–12 cps and a surface tension of 28–36 dynes/cm. Patterns sampled were first created using the ANSYS EM simulation software, and saved as a .dxf file, which then were converted to a bitmap file using the ACE3000 V7 software, and finally uploaded to the Dimatix program. Using the bitmap file uploader on the DMP, the resolution, drop spacing, layers, leader bar width, and reference point were set. A leader bar was used by printing a vertical line to the left of the pattern, to pre-jet nozzles and keep their drop velocity uniform.

To find the optimum printing technique, the drop spacing was varied from 5 μm to 20 μm. If the drop spacing is too close, it causes excess ink to form uneven lines in the print, resulting in poor print quality and conductivity. In contrast, too far of a drop spacing results in break connections in the droplets being ejected. Through a visual inspection, the optimum drop spacing resulting in uniform print lines was found to be 15 μm. The optimal printing parameters for this research are given in Table I.

Table I. Printing parameters investigated

| Parameter          | Values     |
|--------------------|------------|
| Drop spacing (μm)  | 5, 10, 15, 20 |
| Resolution (μm)    | 2, 5, 10    |
| Layers             | 1, 2, 3     |
| Leader bar width   | 2, 3, 4     |

Conditions investigated during this experiment are mentioned in Table I. The pattern conductivity and surface roughness were used to identify the optimum printing parameters. The optimum printing parameters were found to be 15 μm drop spacing, two printing layers, and a sintering temperature of 90°C. The best conductivity measured under the above mentioned condition was found to be 5.56 × 10^16 Ω−1m−1.
After waiting at least 30 minutes, the Drop Manager software was used to inspect the drop quality for the Ag nanoparticle ink. The key is to create uniform drops, falling with matching drop velocity, without a tail or any satellite drops lagging behind, to be formed in sequential jets. The DMP requires the jets chosen for printing to be sequential, and for this reason four sequential uniform drop-jets were chosen. To inspect the printed pattern, and to set the printing origin, the printer utilizes the Fiducial Camera, which has a resolution of 2.54 μm/pixel. Drop spacing is varied by adjusting the cartridge angle. The Fiducial Camera is also used to do a drop offset, consisting of a 10 mm line in the X direction and a single dot 1 mm next to the line.

Cleaning cycle is another important setting which helps to avoid jets clogging and ink settings. Cleaning cycle settings include three functions: purge, spit, and blot. After filling a new cartridge, it is important to run a cleaning cycle with purge, pushing air and debris out, clearing the nozzles. In this experiment, while printing, the group used a cleaning cycle consisting of blot, using a non-contact absorption pad, every 6 lines to maintain a clean print head. Once successfully printed, the samples were inspected using the DMP’s Fiducial Camera. A sample printed pattern is shown in Fig. 1.

### Sintering (Heat treatment).
Among various types of the sintering techniques, the most straightforward technique is thermal sintering. The experiment was conducted using Thermo Fisher Scientific’s digital hot plate (Model: HP88857100). Silver nanoparticles fuse together at much lower temperature than bulk Ag. If \( T_{\text{melt}} \) is the melting point of metal nanoparticles, \( T_{\text{bulk}} \) is the melting point of solid metal, \( \sigma \) is the characteristic parameter, and \( R \) is the radius of metal particles. Then, the relationship among these variables is given below:

\[
T_{\text{melt}}(R) = T_{\text{bulk}} \left( 1 - \frac{\sigma}{R} \right) \quad [1]
\]

Based on Equation 1 and the limitation of the paper substrate, the printed patterns were evaluated and compared with plain air drying.

### Resistivity measurements.
Electrical resistivity describes appropriate signal carrying capability of a conducting path. It depends not only upon the chemical properties of the silver nanoparticles, but also the geometry of the printed pattern: length (L), width (W), and thickness (t). Resistivity is given by:

\[
\rho = \frac{A}{L} = R \frac{W \times t}{L} \quad [2]
\]

To quantify the resistivity of the pattern, the resistance of the sample was measured using two-point probe (Fluke 87 V industrial multimeter) and the results verified with Jandel’s four-point probe. Then, thickness of the layer was measured using both Scanning Electron Microscope (Quanta 3D 200i) and Optical Profiling System (Veeco WYKO NT 1100). In total, five printed samples were tested at each condition and the reported resistivity is the average of the five samples.

### Flexibility test.
Mechanical reliability has been a primarily limiting factor toward realizing a vast array of flexible devices. To test the effect of bending, an earlier study conducted several bending tests, using the varied diameter of cylindrically shaped pattern, and deformed it using their hands. A similar approach was followed in this article and the resistivity was evaluated (as a function of bending) and compared with the resistivity of previously recorded non-bended results.

### Surface roughness measurement and surface characterization.
The sharpness of the edges, smoothness of the printing, and ink distribution were checked using the Fiducial Camera of DMP and CD microscope (Nikon MM-400). Surface roughness was measured using the Optical Profiling System. On the other hand, SEM (Quanta 3D 200i) was used to investigate the thickness of the layer and surface morphology.

### Results and Discussion

#### Sintering and resistivity results.
The resistivity of the printed pattern as a function of sintering temperature is shown in Table II. The resistivity of air dried patterns were exceptionally high due to the printed particles forming porous thin films over another porous paper substrate. The measured resistivity gradually decreased with increase in sintering temperature. The concentration of silver nanoparticle ink increases with an increase in the number of printed layers. Hence, the three layer printed pattern will have the highest conductivity. As inferred from Table II and Figure 3, the three layer printed pattern was found to have cracks after sintering which in turn reduces the conductivity. The optimal conductivity of the sample is obtained by investigating the drop spacing and sintering temperature.

A change of color of the printed pattern from yellowish-brown to tan was observed with increasing sintering temperature. Further, 15 μm drop spacing provided higher conductivity results than compared to 10 μm drop spacing. Firstly, to figure out an optimum drop spacing, this experiment considered many from 5 μm to 20 μm and the above table compared the data for 10 μm and 15 μm drop spacing respectively. Irrespective of the number of printed layers, the resistivity of the patterns plummeted after curing. Theoretically, the triple layer should have the highest conductivity. However, the double layer resistivity is lower compared to the triple layer at 120°C. Such an anomaly might be speculated due to the possibility miniscule cracks and discontinuities of ink explored further in this article. The resistivity versus temperature curve is given in Fig. 2.

Figure 2 shows the drastic fall of resistivity of printed samples for sintering temperatures above 60°C. The best conductivity was found for double layer printed samples cured at 90°C, (resistivity: \(1.8 \times 10^{-5} \Omega \cdot \text{cm}\), and conductivity: \(5.56 \times 10^{5} \Omega^{-1} \cdot \text{m}^{-1}\)). The resistivity values after 90°C were almost the same for all printing thicknesses. To analyze the significance of sintering temperature on pattern resistivity, one-way analysis of variance (ANOVA) analysis was pursued. The ANOVA results (Table III) indicate with a level of significance (\(\alpha = 0.05\)) that the sintering temperature is a significant factor affecting resistivity.
Table II. Resistivity results at different curing conditions and drop spacing.

| Sl. No. | Sintering Temperature (°C) | Cooling Period min | Resistivity $\times 10^{-4}$ Ω-cm |
|---------|-----------------------------|--------------------|-----------------------------------|
| 1       | air                         | 720                | 11800 2880 8300 1300 9580 970    |
| 2       | 60                          | 30                 | 84.87 26.32 37.1 19.8 29.9 7.86  |
| 3       | 75                          | 30                 | 21.71 6.8 3.6 5.4 3.24 2.62     |
| 4       | 90                          | 30                 | 1.13 0.283 0.54 0.18 0.262 0.262 |
| 5       | 120                         | 30                 | 0.47 0.189 0.18 0.18 0.262 0.262 |

Table III. ANOVA Analysis.

| Source            | SS        | DF | MS     | $F_0$ | $F_{critical}$ | P-Values |
|-------------------|-----------|----|--------|-------|---------------|----------|
| Sintering Temperature | 6.316E-06 | 3  | 2.1E-06 | 9.528 | 4.066 | p<0.05   |
| Error             | 1.768E-06 | 8  | 2.2E-07 |       |               |          |
| Total             | 8.084E-06 | 11 |        |       |               |          |

Surface characterization.—Imaging the corner side of the printed patterns was a priority as these are the most failure prone areas after printing. Figure 3 presents CD microscopy images of three different layers of printed samples. Images were taken at 10x magnification. Figs. 3a and 3b shows the single layer printed pattern cured at open air and 90°C respectively. A lot of pinholes, as well as non-continuous printed lines can be seen before curing. After curing at 90°C, the edge quality improved and brought ink more closer. Yet, the pattern contained many holes. The size of the hole of the substrates overtime may increase, decreasing the conductivity and eventually deteriorating the performances of the devices. Figs. 3c and 3d shows the images for double layer printed pattern. A significant improvement in printing quality has been observed: sharp edges, uniform ink depositions, fewer holes, and increased bonding with the substrate.

A closer observation of the image reveals coffee stain effects, particularly after curing. This effect can be controlled by decreasing the voltage of the droplets further in the cartridge settings.

For the three layer printed pattern (Fig. 3e) which is air cured, there are relatively no holes, ink is distributed evenly. But, there seems to be some satellite spots, which were not present for the single and double layer prints. When cured to 90°C and above, miniscule cracks appeared to form. At 120°C, there were even more cracks present (Fig. 3f). The probable cause is speculated to be that the increased amount of silver nanoparticles, as well as the associated impurities disintegrate at higher sintering temperatures. However, for single or double layers of printed patterns, such cracks or fatigue were absent.

Figure 4 shows the thickness of the double layer printed samples cured at 90°C for 30 minutes using 15 drop spacing. The thickness of the double layer printed pattern was found to be 1.8 μm. Table IV

Table IV. Layer thickness of the printed patterns.

| Layer | Single | Double | Triple |
|-------|--------|--------|--------|
| Thickness, (μm) | 0.944 | 1.8    | 2.62   |

Figure 3. CD microscopy images to observe ink deposition, holes, crack, and coffee ring effect at 10X magnification level. The printed samples are: (a) single layer, air cure, (b) single layer, cured at 90°C, (c) double layer, air cure, (d) double layer, cured at 90°C, (e) triple layer, air cure, and (f) triple layer, cured at 120°C.
Figure 4. Thickness of double layer printed samples using SEM.

shows the thickness of single, double, and triple layer printed patterns cured at 90°C. As expected, the thickness increased with an increase in layer thickness.

The 2D surface topographies of printed samples with different layer thickness cured at 90°C is shown in Figure 5. These graphs were obtained using the Veeco software associated with the Optical Profiler. The average roughness values of the different printed samples were calculated using MATLAB. Table V shows the surface roughness values as a function of the number of layers of printed pattern. This table indicates that the increasing of the number of layers of printed pattern increased the average surface roughness, but not proportionally.

Table V. Average roughness of 3 different printed layer samples.

| Layer | Single | Double | Triple |
|-------|--------|--------|--------|
| Roughness, (nm) | 289 | 328 | 356 |

SEM micrographs of the surface of the different printed layers is shown in Figure 6. Figures 6a, 6b, and 6c are the SEM pictures of the single layer, double layer, and triple layers of printed patterns respectively, cured at 90°C for 30 minutes. The number density of holes seems to decrease gradually from Figs. 6a to 6c.

Due to the cracking and pinhole issues in triple and single layer printing patterns observed earlier, we had chosen to focus on double-layer pattern for further analysis. The double layer pattern seems to deliver the best printing results of this particular substrate. It also cuts down one-third of the cost of printing (ink, cartridge, cleaning pad, drop watcher pads, etc.) related to material consumption compared to three layer printed pattern. According to the Figs. 6d, 6e, and 6f, a smooth surface morphology is observed for the double layer printed patterns at different sintering temperatures. The silver nanoparticles appeared to have fused together which helped boost up the conductivity upon sintering at different temperatures.

Mechanically induced electrical degradation is a primary concern for flexible devices. For each sample, five bending tests were sequentially performed: (a) flexed around 18 mm cylindrical shaped pattern, (b) 12 mm cylindrical pattern, and (c) three random diameter stress tests using human hand. The number of bend cycles were limited to 10. Fig. 7a and Fig. 7b shows the bending test. After repeated bending tests, the resistivity was measured using four-point probe method. The maximum deviation found in resistivity of the samples after repeating bending was about ±0.5%. No cracks were observed with naked eye and hence further imaging was not carried out. The thickness of the paper substrate is 0.254 mm. The results from the bending tests indicate the robustness of the printed patterns.

Conclusions

In this article, the electrical property and surface morphology of different layers of ink-jet printed patterns on paper substrate were investigated as a function of sintering temperature. ANOVA analysis indicated that the sintering temperature is a significant factor affecting conductivity of the samples. Among the three printed layers, the double layer printed pattern (cured at 90°C for 30 minutes)
Figure 6. SEM pictures for microstructural variations on the pattern surface as a function of number of printed layers and sintering temperature. The effect of amount of layer printed and cured at 90°C for a (a) single layer, (b) double layer, and (c) triple layer sample. Surface morphology of double layer printed pattern sintered at (d) 60°C, (e) 90°C, and (f) 120°C.

Figure 7. Bending test using (a) cylindrical shape structure and (b) hand. exhibited superior conductivity (conductivity: $5.56 \times 10^6 \, \Omega^{-1} \, \text{m}^{-1}$) along with a smooth morphology. Repeated bending tests did not change the electrical resistivity significantly indicating the durability of the double layer printed pattern. The results from this investigation will enable the development of a wide variety of paper based devices for IoT applications.

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