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# Printing Contractive Silver Conductive Inks Using Interface Interactions to Overcome Dewetting

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**ABSTRACT** Surface energy incompatibility between ink and substrate is a significant obstacle for inkjet printing of electronic components, causing printed lines to dewet and break apart. In this paper, it was demonstrated that smooth, continuous silver lines could be printed via control of ink-substrate interactions, despite the tendency of the ink to dewet from the substrate. The silver lines were printed using drop-on-demand inkjet printing of silver nanoparticle ink onto non-crosslinked SU-8 coated polyethylene terephthalate (PET). The lines were subsequently heated to control dewetting and cause contraction from 60 $\mu$m to 14 $\mu$m. The SU-8 film underneath the silver line was dissolved and redistributed to form a ridged concave structure that prevented the lines from bulging and breaking apart. Additionally, photonic sintering was used to achieve low resistivity of 0.06 $\mu\Omega$m for the narrow printed lines.

**INDEX TERMS** Ink-substrate interaction, printed electronics, silver nanoparticles, narrow conductive lines.

## I. INTRODUCTION

Printed conductive lines serve as wires in printed electronics, and as such, they are one of the most fundamental components in fully printed electronics. They are also components of printed devices themselves, such as the electrodes in an organic thin film transistor. Improved resolution for these lines is critical for improving the performance of printed electronic devices by increasing device density [1]. There is a significant amount of research being done to investigate the usage of inkjet printing to form narrow lines by varying parameters such as drop spacing, solvent composition, and ink [1], [2] or by using methods such as reverse offset or gravure [3], [4]. Meanwhile, there is some research being done on the interactions between the ink and the substrate, but the primary focus is on self-assembled monolayer structures and not direct physical or chemical interactions [5], [6]. Utilizing an active ink-substrate combination opens up a wide range of possibilities for processing and performance enhancements. For example, Xu *et al.* [7] reported that printed PEDOT:PSS dissolved a polyvinyl alcohol (PVA) coating on PET in order to pin line edges in place and prevent dewetting.

Additionally, in our previous work, silver lines were inkjet printed onto a film of non-crosslinked SU-8 coated on polyethylene terephthalate (PET), which is soluble in the silver ink. These lines were shown to narrow and contract upon heat treatment, resulting in extremely narrow, high aspect ratio lines [8]. This phenomenon is due to the solvent in the ink dissolving the small non-crosslinked SU-8 molecules. Upon heating, the solvent evaporates which causes the dissolved SU-8 to migrate from the center of the printed line to the edges due to the coffee ring effect. This forms a concave well in the SU-8 bordered by raised ridges, which acts as a confining structure to constrain the ink. As the solvent evaporates, the surface energy changes and the ink dewets and contracts into a narrow line. Heating also serves to increase the solubility of the SU-8 in the ink and decrease the viscosity of the overall solution. Increased solubility allows more of the SU-8 to be dissolved in the ink, and decreased viscosity allows more SU-8 to be redistributed to the edges of the lines [8].

This work further explores the contraction phenomenon with different ink formulations in order to further investigate the effects of the ink-substrate interactions. The water based inks used in this work had substantially different surface energy than the substrate, causing the ink to dewet upon printing. Frequently, plasma treatment is used to overcome this problem by raising the surface energy of the substrate. Plasma treatment forms dangling bonds and free radicals on the surface of the substrate which allow the ink to wet the surface and form stable printed lines [9]. However, plasma treatments are sensitive to processing parameters and it is difficult to achieve a uniform surface energy for a large area substrate [9]. Additionally, when plasma treatment was used on the non-crosslinked SU-8 interlayer, it damaged the interlayer and caused the surface to wrinkle and deform upon heating. As such, plasma treatment is unsuitable for use with non-crosslinked SU-8.

As an alternative to plasma treatment, this work investigates the usage of ink-substrate interactions to contract printed lines to achieve narrow linewidth while simultaneously overcoming the surface energy incompatibility between ink and substrate.

## II. EXPERIMENTAL METHODS

To prepare the inkjet-printed samples, a 300 μm wet thickness film of non-crosslinked MicroChem SU-8 2002 photoresist was coated onto a PET substrate via doctor blade at 2.5 mm/s. The coated PET was then soft baked at 90 °C in order to evaporate the solvent from the SU-8 coating. This served to planarize the PET forming a smooth surface for inkjet printing, as well as providing a soluble interlayer for the contraction of the silver lines.

A Dimatix DMP 5005 inkjet printer was then used to print the silver ink onto the substrate in single drop wide, 2 mm long lines using a drop spacing of 20 μm. Immediately following printing, the substrate was placed onto a hot plate for 15 minutes in order to contract the lines. The sample was exposed to UV light for 30 seconds in order to crosslink the SU-8, then the printed silver lines were sintered using either thermal treatment at 140 °C for 10 minutes or with photonic sintering using a Xenon Sinteron 2020 photonic sintering system.

Novacentrix Metalon JS-A191 silver ink was used for this study, and is comprised of 40% silver nanoparticles (30-50 nm) with ethylene glycol (10-15%) and water (balance) as the primary solvents. This silver ink was unable to form stable printed lines on the non-crosslinked SU-8 interlayer and it quickly dewetted due to the surface energy incompatibility [10]. Different ink formulations with ethanol added to the stock JS-A191 ink were investigated in this work. Ethanol was chosen to lower the surface energy of the ink to improve stability, as well as to increase the solubility of SU-8 in the ink.

## III. RESULTS AND DISCUSSION

### A. INK FORMULATION BY ADDITION OF ETHANOL

When the JS-A191 silver ink was printed on non-crosslinked SU-8, continuous lines were initially formed but they broke apart at room temperature within a few minutes. With the post-printing heat treatment at 60 °C, many of the lines were continuous and the linewidth contracted from 60 μm to 20 μm, but 28 out of 60 lines were still broken and unusable due to the large difference in surface energy between ink and substrate. In order to lower the surface energy of the ink and increase the interaction between ink and substrate, JS-A191 silver ink was formulated by addition of ethanol.

To evaluate and determine the amount of ethanol to be added to the JS-A191 silver ink, several lines were printed on non-crosslinked SU-8 with three different concentrations: no ethanol (tested previously), 25% v/v ethanol, and 50% v/v ethanol. The printed lines were then heat treated immediately after printing. The resulting printed lines were evaluated for resistivity and morphology (linewidth, discontinuities, dewetting).

The resistivity of the printed silver lines heat treated at 60 °C and sintered at 140 °C for different ethanol concentrations is shown in Figure 1. For the silver lines with no ethanol, a resistivity of 0.3 μΩ m was obtained. It is clear that increasing ethanol concentrations significantly increased the resistivity of the printed silver lines. This may be caused by the ethanol affecting unknown additives in the commercial ink which interferes with thermal sintering, preventing the silver nanoparticles from forming a dense, conductive line.

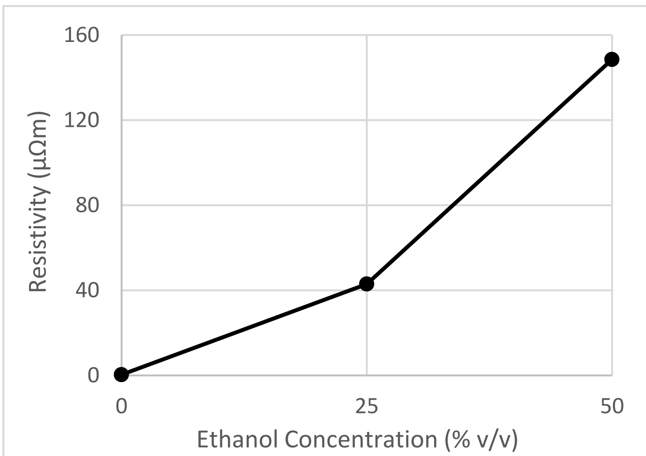


**FIGURE 1. Resistivity of inkjet printed lines at different ethanol concentrations after heat treatment at 60 °C and thermal sintering at 140 °C.**

As mentioned previously, 28 out of 60 lines printed with no ethanol added to the ink dewetted and broke apart following the heat treatment and sintering, resulting in unusable lines. At 25% ethanol, the failure rate decreased to 10 out of 60, and the measured line width was 17 μm. The 50% ethanol inks had the best morphology, with extremely narrow 14 μm lines and a failure rate of only 3 out of 60. As printed, the lines were 60 μm, so each of the lines showed significant linewidth reduction following the post printing heat treatment. Figure 2 shows the printed lines for each of the different ethanol concentrations tested. With no ethanol added, the lines were discontinuous and not smooth, which

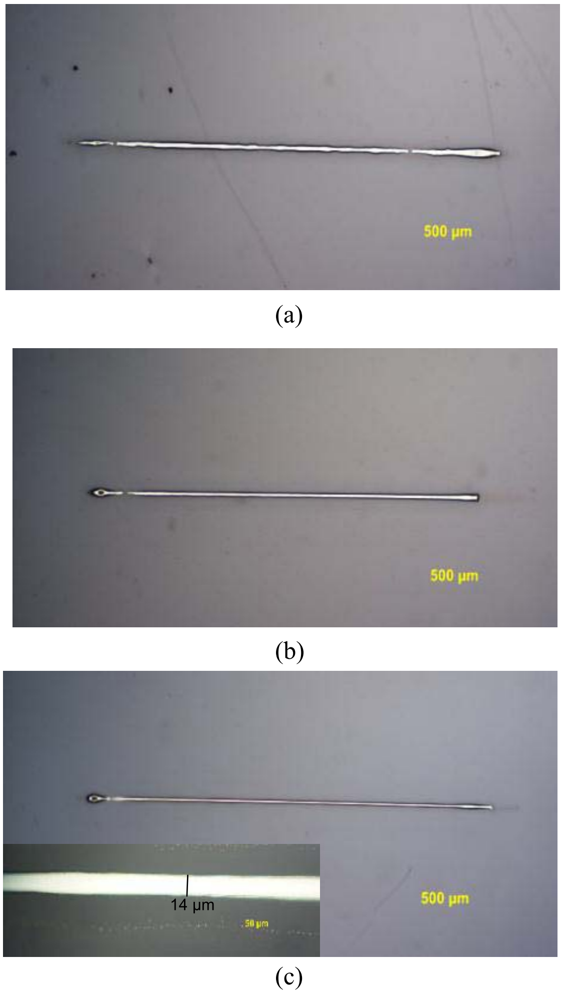


**FIGURE 2.** **Morphology of inkjet printed lines at different ethanol concentrations after heat treatment at 60 °C and thermal sintering at 140 °C with A) 0% ethanol, B) 25% ethanol, and C) 50% ethanol.**

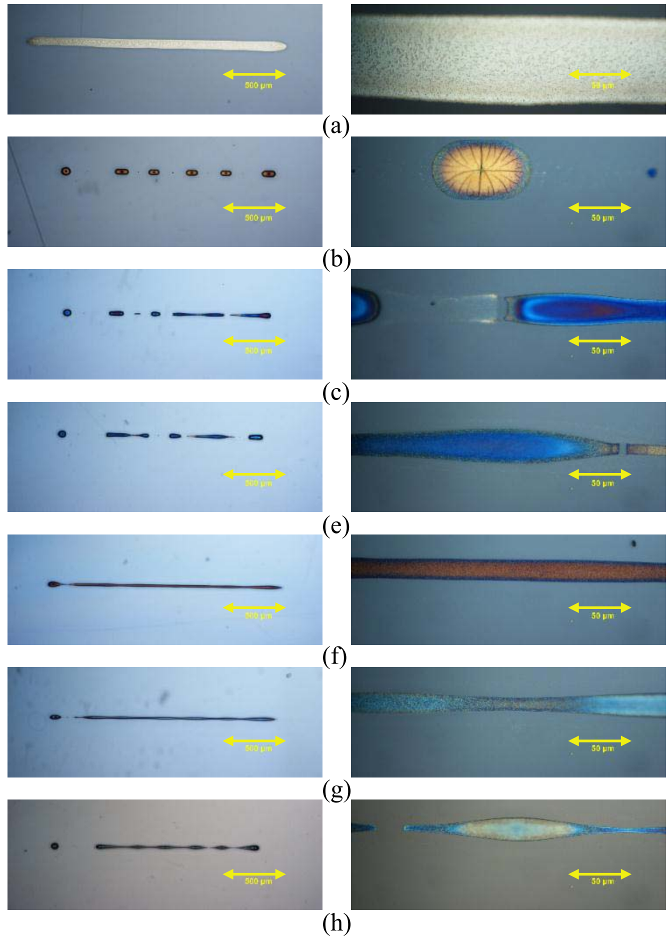


**FIGURE 3.** **Inkjet printed silver lines heat treated at different temperatures: a) reference b) as printed, c) heated at 50 °C, d) 55 °C, e) 60 °C, f) 65 °C, and g) 70 °C, and shown at two different magnifications. After heat treatment, the SU-8 interlayer of each sample was crosslinked by exposure to UV light, then the samples were heat treated again at 140 °C in order to hard bake the SU-8 and sinter the silver nanoparticles.**

is not fit for use in printed electronics. The lines printed with 25% ethanol inks have much smoother edges, but still show some signs of discontinuities. At 50% ethanol, discontinuities were rare and the lines became much finer compared to the other tests.

Although the addition of ethanol did not make the printed lines fully stable at room temperature, it did increase their stability enough that they did not dewet significantly before the post printing heat treatment. Without added ethanol, the lines began to dewet and form discontinuities immediately after printing, resulting in high failure rates. Alternative sintering methods can be used to increase conductivity, so the 50% ethanol ink was selected as the best candidate for further investigation due to the significantly improved morphology and low failure rate.

### *B. EFFECT OF TEMPERATURE FOR POSTPRINTING HEAT TREATMENT*

From Fig. 3b, it can be seen that the inkjet printed lines left at room temperature without any heat treatment prior to sintering had completely dewetted into individual droplets. Despite the addition of 50% ethanol which lowered the surface energy of the ink, the lines were not fully stable at room temperature. In contrast, the heat treated lines were much more stable. The lines heat treated at lower temperatures (50 and 55 °C) showed some wavy edges and discontinuities indicative of dewetting, but the discontinuities were much smaller than for the untreated lines. At 60 °C in Fig. 3e, the lines were almost perfectly smooth with no discontinuities, and the line width contracted from 60 µm as printed to 14 µm after heat treatment. Above 60 °C in Fig. 3f and 3g, the lines became unstable and formed bulged lines because the dewetting was too rapid and severe. At the optimal temperature of 60 °C, there was sufficient contraction in order to constrain the lines to prevent the formation of discontinuities, but the dewetting was not severe enough to cause instability and breakages in the printed silver lines.

Also shown is a reference line printed with unmodified JS-A191 ink on crosslinked SU-8 with a 50W plasma treatment for 30 seconds, as an example of typical inkjet printing processes. Although this line is stable at room temperature, it is much wider than the heat treated lines printed on non-crosslinked SU-8 at almost 100 μm.

### C. PROPOSED MECHANISM FOR PREVENTION OF DEWETTING

From these results it can be seen that the dewetting of unstable lines was controlled with a post-printing heat treatment which simultaneously reduced linewidth to improve resolution and prevented the formation of discontinuities. With uncontrolled dewetting at room temperature, the lines formed into round droplets in order to decrease the total interfacial surface energy from the surface energy incompatibility. This involved expansion in the transverse direction as well as contraction in the longitudinal direction, which formed discontinuities as illustrated in Fig. 4b. When the dewetting was controlled with the heat treatment process at 60 °C, the solvent interaction with the SU-8 formed a confining structure that prevented the expansion in the transverse direction, as shown in Fig. 4c. The controlled dewetting resulted in contraction in the transverse direction and expansion in the vertical direction. If the ink cannot expand in the transverse direction, the ink is also prevented from contracting in the lateral direction. This ultimately prevented the formation of discontinuities. As such, it was possible to print stable, narrow lines by controlled dewetting, despite the ink and substrate having incompatible surface energies. This process is shown visually in the illustration Fig. 4.

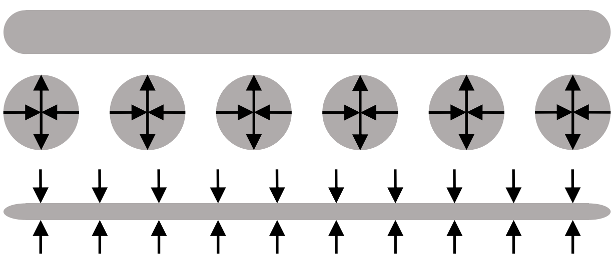


**FIGURE 4.** Schematic diagram showing proposed mechanism of ink flow during dewetting. A) Shows lines immediately after printing, B) shows ink flow during uncontrolled dewetting, C) shows ink flow during controlled dewetting where the lines contract.

### D. CROSS SECTION OF LINES

A focused ion beam was used to cross section a contracted silver line printed with 50% ethanol formulated ink in order to investigate the morphology further. SEM was used at a 45° incident angle in order to image the sample. From figure 5, it can be seen that the silver ink sinks into the substrate and the edges of the SU-8 overlap with the silver line. This shows the confining structure formed by the SU-8 interlayer that prevents the silver ink from breaking apart and dewetting. Additionally, this is beneficial for printed organic thin film transistors and other stacked geometry devices, as it results in a flatter surface, reducing the required thickness of subsequent layers to prevent short circuiting of the device and improving device performance [11], [12]. Because the lines are embedded into the substrate, they may also have improved adhesion and mechanical durability. This is particularly useful for flexible electronics.

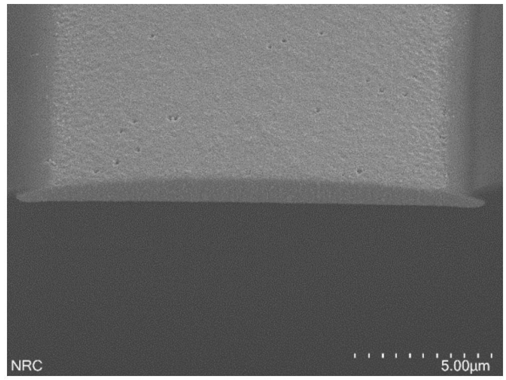


**FIGURE 5.** SEM micrograph of a cross section of 50% ethanol modified ink printed onto non-crosslinked SU-8 following contraction process.

The silver embedded lines may also be effective in preventing electrochemical migration, which poses a significant problem in many applications like printed sensors and organic thin film transistors [13]. The sides of the line are surrounded by SU-8, so growth of silver dendrites may be impeded by this phenomenon.

### E. OPTIMIZATION OF CONDUCTIVITY

From Section III-A, thermal sintering of the contracted lines using ethanol formulated inks resulted in an extremely high resistivity of 148.5 μΩ m, compared to 0.30 μΩ m for the contracted lines without ethanol modification. In order to overcome this, photonic sintering was used as an alternative method of sintering the ink while avoiding damage to the PET substrate that would result from higher temperature thermal sintering [14]. Thermal sintering forms porous, low density networks of silver nanoparticles via Ostwald ripening, which have low conductivity [15]. In contrast, photonic sintering uses short pulses of high energy, broad spectrum white light which are absorbed by the dark silver ink rather than the transparent PET substrate. This causes the silver to rapidly melt and sinter into a dense, conductive film [15]. The heating characteristics of the photonic sintering process can be modified by changing the pulse duration, the delay between pulses, the number of pulses, and the voltage applied to the xenon lamp, which in turn affects the final microstructure and conductivity of the silver.

In order to improve the conductivity of the contracted lines with ethanol formulated silver ink, the parameters for photonic sintering were varied according to Table 1. The delay time and applied voltage were fixed at 500 ms and 2200 V respectively, and the total sintering energy was adjusted by varying the pulse duration and count. Energy per pulse was determined by the pulse duration, and total applied energy was modulated by varying the number of

**TABLE 1.** Parameters for photonic sintering.

| Parameter | Values |
|---|---|
| Pulse Duration (μs) | 600, 900 |
| Pulse Count | 20, 40, 60, 80 |
| Delay (ms) | 500 |
| Applied Voltage (V) | 2200 |

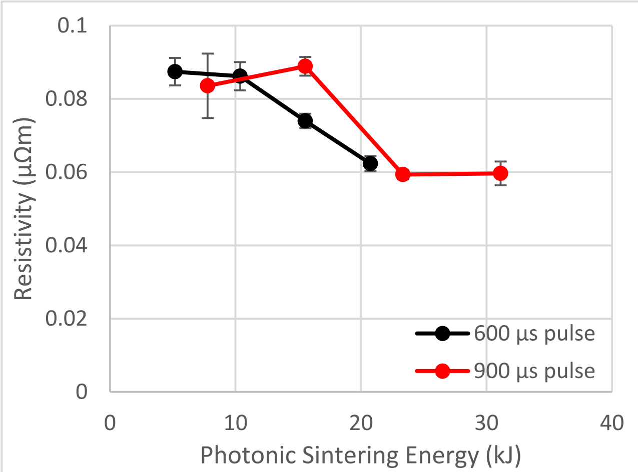


**FIGURE 6.** Summary graph of results from photonic sintering experiment showing resistivity as a function of photonic sintering energy applied to silver lines. Each point represents a different pulse count.

pulses. The resulting conductivity of the contracted lines is shown in figure 6.

With photonic sintering, the resistivity decreased drastically compared to using thermal sintering. At the lowest energy of 5 kJ, photonic sintering already resulted in a resistivity that was 0.06% that of the thermal sintered lines. The resistivity seemed to plateau around 23 kJ, where further photonic sintering no longer yielded any benefit. The final resistivity of 0.06 μΩ m is only 3.8 times that of bulk silver, which is sufficient for printed electronics applications.

## IV. CONCLUSION

It was shown that silver lines could be contracted from 60 μm to 14 μm despite a surface energy incompatibility which would otherwise cause the line to break up and dewet. The interaction between the ink and the non-crosslinked SU-8 interlayer enabled the formation of a concave confining structure to control the dewetting of the ink and prevent the formation of discontinuities. This interaction between the ink and substrate enabled printing narrow lines with otherwise incompatible systems, without requiring substrate modification through plasma treatment. Low resistivity of the lines was also achieved by using photonic sintering in lieu of thermal sintering.

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