Laser Direct-Write of Metallic Nanoparticle Inks

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The combination of nanoparticle inks with laser direct-write allows the laser printing of fine electrically-conductive patterns on substrates requiring extremely low processing temperatures (< 250 ºC). Silver lines with widths under 20 microns and thicknesses under one micron have been laser printed (using a 355 nm laser direct-write system) on polyimide substrates. These features are equivalent to those seen in typical vapor deposited and lithographically patterned thin films. Electrical resistivities of these lines in the range of 5-10 times bulk silver have been demonstrated. The low processing temperature of the nanoparticle inks also allows the laser-curing of printed silver lines without damage to the sensitive substrate. A cw 532 nm laser was used to cure as-deposited silver lines with a resistivity similar to that achieved in oven-curing. This approach is ideally suited for the prototyping and short production runs of interconnects for flexible electronics, RFID antennas and OLED displays. This work will show how these nanoparticle inks are processed using laser direct-write, and will discuss the structure and electrical properties of these printed lines on polyimide substrates.

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1. Introduction

The growing importance of flexible electronics has driven the development of alternative manufacturing methods such as direct-write and its component technologies such as inkjet. Subtractive techniques such as etching and lithography usually involve multiple steps and are more costly, time-consuming and less environmentally-friendly. Direct-write techniques provide a maskless low-cost and single-step method to produce a precise pattern with fine features on a flexible substrate. Inkjet provides many of these advantages and has progressed beyond its initial graphical printing purpose and is now being used to print electronic devices [1,2], filters [3] and displays [4,5,6]. Much of the critical technology surrounding inkjet is unpublished owing to its huge market potential. Nevertheless, inkjet has been used to print electronics materials such as gold down to linewidths of 8 µm [7] on silicon and silver dots down to 5 µm diameter and lines of 10 µm width on glass [8]. By using properly dispersed nanoparticles and a suitable solvent, a sufficiently low viscosity ink can be developed to minimize clogging in the inkjet nozzle. A consequence of the low viscosity is that the solids content is usually low implying multiple passes are required to build up the pattern thickness.

Alternatively, laser direct-write (LDW) of rheological materials [9] can be used with a wider range of ink viscosities with the only stipulation that the ink layer absorbs sufficient laser energy and remains adherent to a support long enough to allow the laser transfer. Laser direct-write has been successfully demonstrated for the transfer of metallic pastes [10], various electronics passive components [11] and other electronics materials [12,13]. The lack of a specially-formulated ink requirement can often mean that commercially available materials can be tried immediately without much preparation. Combining this versatility with the other advantages of a laser such as micro-machining, small spot resolution and high scanning speed (with a galvo), laser direct-write is a good candidate for direct printing of functional materials on organic temperature-sensitive substrates.

Inkjet printing of metallic nanoparticle solutions directly onto organic substrates such as polyimide has been reported [14,15]. A gold line as narrow as 8 µm was achieved by laser curing with a 4 µm diameter focal spot [15], but no electrical resistivity measurements were made. By combining laser curing with substrate heating, resistivities of 3-4 times higher than bulk were measured for 70-80 µm wide gold lines. However due to rapid heating of the printed line, some delamination of the gold film was observed. In addition, cooling of the inkjet nozzle was recommended to prevent clogging due to heat transfer from the heated stage. In all these works, the initial as-deposited linewidth is > 100 µm and the smaller laser curing spot must be scanned across the line. In our work, the deposited metal (Ag) linewidth is slightly smaller than the focal spot of the curing laser thus allowing curing in a single laser pass. It will be shown that the larger laser spot size allows a more uniform intensity profile across the linewidth resulting in a more uniform height profile after curing. In addition, our laser direct-write process is able to print a higher viscosity ink which minimizes any thermocapillary flow of the ink due to a higher solvent content.

Inkjet printing of either silver nanoparticle ink [16] or silver nitrate precursor [17] onto polyimide substrates has also been reported. The printed linewidths were greater than 100 µm and the measured resistivities were at least an order of magnitude above that of bulk silver. Porosity of the line cross-section was observed in both results.

The printing of higher viscosity inks such as those employed in the screen-print industry has been reported. Laser direct-write has been used to deposit commercial thick-film silver inks onto alumina substrates [18]. The linewidths achieved were below 20 µm although the lines had to be oven-fired at high temperature.

The dynamics of droplet behavior once it reaches the receiving substrate is an area which affects both inkjet and laser direct-write. The "coffee stain effect" [4] is a differential evaporation phenomenon which results in a dual-peaked height profile. Various techniques such as substrate heating and "crossed" laser beams [14,19,20] have been successful in removing this effect.

In this work, two silver nanoparticle inks of different viscosities and composition are laser transferred onto narrow lines on polyimide (Kapton) substrates. They will then be post-processed by either oven or laser curing and their electrical performance and morphology compared. It will be shown that silver lines with resistivities less than 10 X bulk can be achieved and that line morphology can be improved significantly (from the dual-peaked profile) with laser curing.

2. Procedure

The laser direct-write system used in this work has been described previously [10]. Briefly, our laser direct-write system consists of the laser transfer of volume elements ('voxels') of material from a target substrate placed in close proximity to a receiving substrate. A secondary laser may also be used to post-process the deposited material on the receiving substrate.

The transfer laser is a tripled $Nd:YVO_4$ laser operating at 355 nm with pulse energies of a few hundred µJ at kHz repetition rates. The laser pulses are controlled in amplitude and time by an acousto-optic modulator (AOM). These laser pulses are directed through a 20X objective which focuses the beam into a focal spot size of ~ 16 µm diameter (as measured on polyimide). An in-line CCD camera provides direct viewing of the receiving substrate (referred simply as the 'substrate') and the actual laser transfer from the target substrate (hereinafter referred as the "ribbon"). Typical laser energies used for laser transfer are ~ 50 nJ (30 ns FWHM) as measured on an Ophir PD10 energy meter after the objective resulting in a fluence of 200 mJ/cm^2. The substrate is held by a vacuum chuck on top of a computer-controlled X-Y stage pair.

The target substrate or ribbon is a 50 mm x 75 mm glass microscope slide which can be secured by a vacuum frame holder and is placed to within a few microns gap from a receiving substrate. The silver nanoink is applied to the ribbon and then carefully placed with the ink layer side facing the substrate. The laser spot is focused onto this ink layer and a series of lines is laser transferred without removing the ribbon until visual inspection of the lines is required. This approach was used to minimize any disturbance to previously deposited lines and to minimize ribbon residue on the sample. The laser and stage movement conditions are then varied to give optimal transfer.

The silver nanoinks used in this work, ink 1 (Cabot) and ink 2 (PChem) have a solvent vehicle and an aqueous-based one respectively. Inks 1 and 2 have a silver solids content of ~ 20 and ~ 50 wt% respectively. Both inks have nanoparticle sizes below 100 nm which are important in lowering their melting and sintering temperatures. Ink 1 has a much lower viscosity (~ 14 cP) than that of ink 2 (>10,000 cP estimated) and the effect on the laser transferred lines will become apparent in the results. Another consequence of the 2 different vehicles used is that evaporation rates of the 2 inks (and hence the ribbon) are much different. Ink 2 has only a 10-15 minute ribbon lifetime whereas ink 1 can extend to > 30 minutes. Laser transfers of paste- and ink-like material are best when the ribbon retains a "damp" appearance.

Lines were laser transferred with a single pass using the two inks on 178 µm-thick Kapton HN substrates for general characterization, on Si for scanning electron microscopy (SEM) and across Au pads (deposited by e-beam) on Kapton for electrical measurements. The Kapton HN substrates used were general purpose all-polyimide films (maximum operating temperature ~ 400 °C) and were not pre-treated by any special techniques other than general laboratory solvents nor were they micro-machined or textured with any pockets or trenches. After transfer, the samples were either placed in an oven for final curing or remain on the stage for laser curing. Typical oven cure conditions for inks 1 and 2 were 250 ºC (40 minutes) and 120 ºC (7 minutes) respectively.

After relatively good-quality lines were obtained with oven curing, single-pass laser curing of as-deposited lines on Kapton were performed with a cw green laser operating at 532 nm. This laser beam was first sent through a ~ 1.2 mm diameter iris to select the central Gaussian intensity profile and then directed through the same 20X objective as that used by the transfer laser and focused onto a ~ 30 µm diameter spot as measured on Kapton. Typical laser powers measured after the objective ranged from 30 to 95 mW (damage threshold) resulting in intensities from 4 to 13 kW/cm^2 on the sample.

Some parameters that were used to judge the quality of the transferred line were the thickness and width uniformity, the line edge sharpness, the total amount of debris, the presence of any porosity and electrical conductivity. The materials properties, the laser transfer conditions and post-processing conditions all play important roles in affecting the final quality of the deposited lines. Characterization of these lines were performed with optical microscopy, contact profilometry, SEM and 4-probe measurements across Au pads.

3. Results and Discussion

Optical micrographs of oven-cured LDW lines on Kapton using nanoink 1 are shown in Fig. 1. The field of view in a) is ~ 434 µm. As seen in a)-c), relatively uniform linewidths of 20 µm were obtained. Surprisingly, with the same spot size and transfer conditions, a narrower linewidth of 11 µm was attained on one occasion as seen in d). This behavior could be indicative of transfer occurring in the jetting regime [21]. Some of the filamentation seen

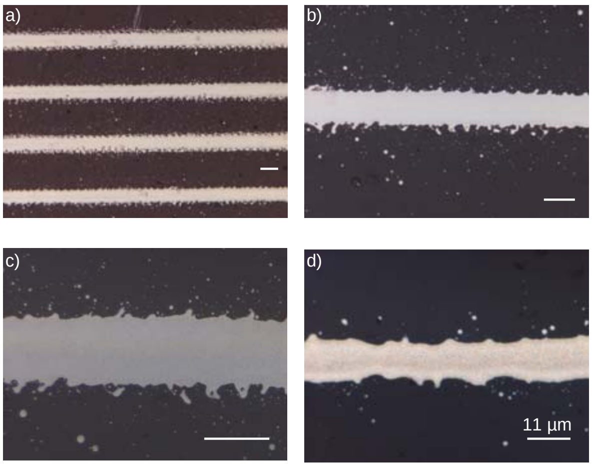

Fig. 1 Micrographs of LDW Ag lines on Kapton using nanoink 1. The horizontal bar represents 20 µm unless otherwise noted. Background color variations are due to image processing artifacts.

at the line edges and the surrounding 'droplet' debris could be caused by the low viscosity of the ink material and/or the wetting behavior of the Kapton surface with this ink. Optical micrographs of oven-cured LDW lines on Kapton using nanoink 2 are shown in Fig. 2. This ink material is

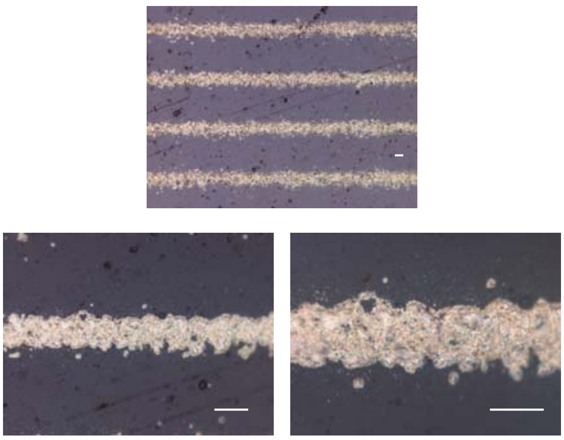

Fig. 2 Micrographs of LDW Ag lines on Kapton using nanoink 2. The horizontal bar represents 19 µm. Background color variations are due to image processing artifacts.

more viscous and less homogeneous than ink 1 resulting in a transferred line with a less uniform appearance. Nevertheless, linewidths near 19 µm were achieved with this material.

In order to examine the nanoparticles density, size and distribution within the transferred lines, a deposited line can be fractured somewhere across its width and SEM performed on its cross-section. Because polyimide does not fracture easily, silver lines were laser transferred onto Si substrates under the same conditions used for Kapton and then oven-cured. As shown in Fig. 3, there is better particle necking and a resulting smoother film for nanoink 1 than that observed for 2.

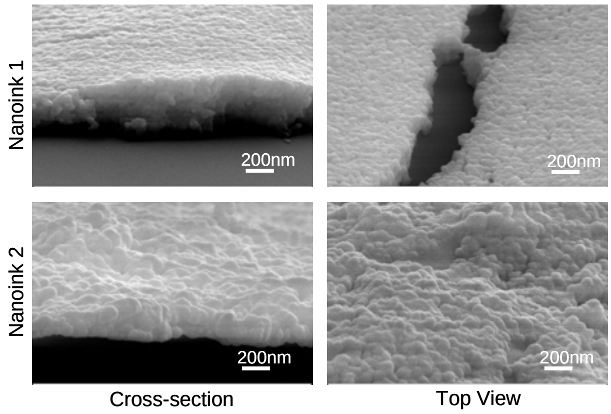

Fig. 3 SEM's of fracture cross-sections of LDW lines on silicon substrate using nanoinks 1 and 2.

Electrical characterization was next performed by laser writing ~450 µm long Ag lines across Au contact pads on 178 µm-thick Kapton. Figs. 4 and 5 show micrographs of oven-cured lines transferred with nanoinks 1 and 2 respectively and their resulting height profiles. Nanoink 1 shows overall better height uniformity than that of 2 which is consistent with the optical and scanning electron micrographs. Both height profiles display the two-peak behavior which reflects the 'coffee-stain' effect as discussed earlier in the introduction. Heating the substrate prior to deposition has been shown to minimize this effect [14,19], however in our case, heat from the substrate would change the rheology and transfer properties of the ink due to its close contact to the ribbon.

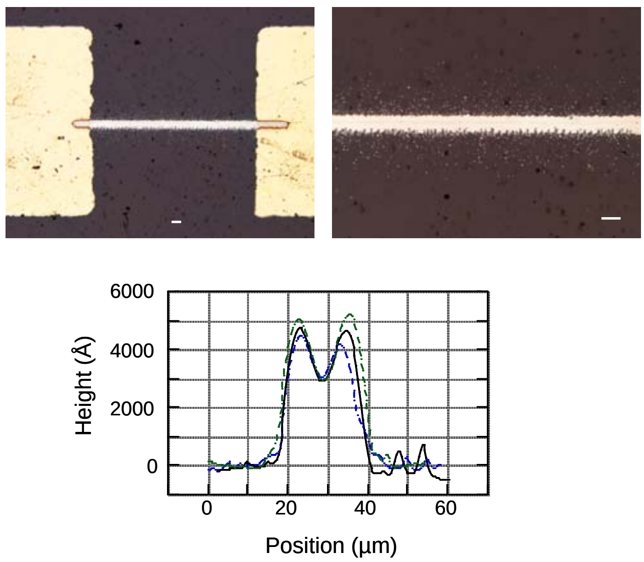

Fig. 4 Photographs of LDW Ag line (nanoink 1) across Au pads on Kapton. The white horizontal bar represents 21µm. The distance between the pads is ~ 470 µm long. A profilometer scan across 3 different sections of the line is shown – the solid black line is a scan made across the middle of the line.

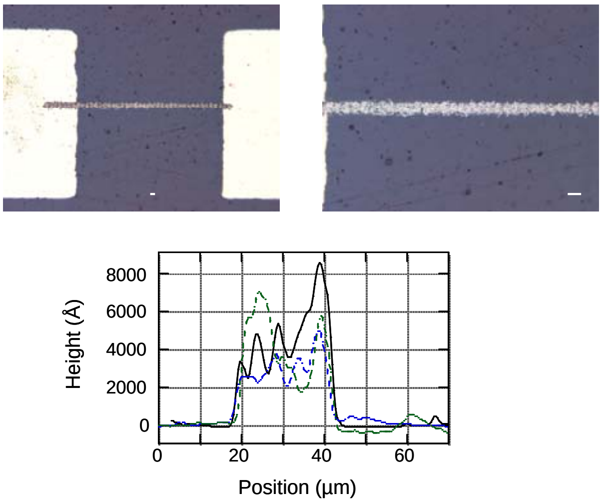

Fig. 5 Photographs of LDW Ag line (nanoink 2) across Au pads on Kapton. The horizontal bar represents 16 µm. The distance between the pads is ~ 450 µm long. A profilometer scan across 3 different sections of the line is shown – the solid black line represents the middle of the line.

The resistance of the lines was measured using a four-probe measurement and the results are summarized in the figures. The measurements were performed soon after thermal processing to minimize degradation under ambient atmosphere. The calculated resistivities compare well with those of bulk and are consistent with the very good 'necking' behavior of the nanoparticles seen in the SEM's. Because of the low processing temperature of these nanoinks, laser radiation should be able to provide enough thermal energy to cure these inks without damaging the substrate. Fig. 6 shows a micrograph and a height profile of a laser-cured LDW line on Kapton using nanoink 1. The curing laser provided ~86 mW of power at 532 nm and was focused to a 30 µm diameter spot. The intensity at the focus was ~ 12 kW/cm^2 and the line was cured in a single pass at 0.1 mm/s. Note that the wider laser spot compared to the width of the transferred line (~ 20 µm) may minimize any "coffee-stain effect" due to less variation of the laser intensity profile across the width of the line. No pre-drying steps were necessary before laser curing as the solvent in nanoink 1 was sufficiently stable after transfer. In addition, no "micro-cracking" was observed in the line due to rapid vaporization of the wet ink during laser curing. The low line thicknesses allow rapid thermal diffusion of the laser energy and provide a more uniform curing of the entire line cross-section.

No sign of damage to the underlying substrate is apparent. There is slightly more debris in this transfer than that seen in Fig. 1 but the height profile is smoother and single-peaked as compared to that found in oven-curing. Fig. 7 shows the measured resistivities of various lines laser-cured under different laser powers. The best resistivity achieved was close to 5 X Ag, which is slightly better than the oven-cured sample but is within the range of experimental error. It is possible that a more rapid delivery of laser energy into a concentrated area can result in a higher local temperature than that encountered in the slower oven cure, thereby resulting in even better sintering (or even melting) of the nanoparticles. Unlike oven curing, laser curing allows the thermal processing of intermediate deposited layers *in-situ* without any disturbance of the sample.

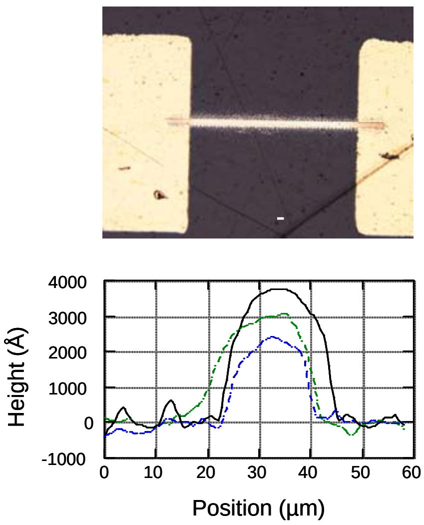

Fig. 6 Photograph of laser-cured Ag line using nanoink 1. The horizontal bar represents 18 µm. A profilometer height profile shows 3 different scans across the line with the solid black line representing the center.

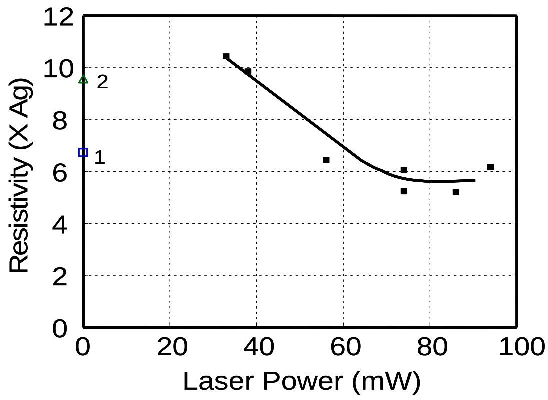

Fig. 7 Measured resistivity of LDW Ag lines of nanoink 1 vs. curing laser power. Oven-cured resistivities are shown for nanoinks 1 and 2 for comparison. Nanoink 1 was cured at 250 °C for 40 minutes, while ink 2 was cured at 120 °C, 7 minutes. The solid line is only a visual guide.

4. Conclusions

Narrow silver lines with widths of < 20 µm and heights of ~ 0.5 µm have been laser transferred onto polyimide substrates. Their electrical resistivities are below 10X bulk silver using either oven or laser curing. No damage to the underlying polyimide substrate was observed. Excellent particle necking is seen in the line cross-sections which is consistent with good electrical conductivity. Curing of as-deposited lines with a cw laser resulted in a smoother line height profile than that observed in oven-curing.

Laser direct-write combined with oven or laser curing has been used to print narrow conducting lines onto a temperature-sensitive substrate (polyimide). Its ability to print both a low and high viscosity ink demonstrates its versatility as a direct-write technique for flexible electronics. With further optimization of transfer parameters and improved understanding of ink and substrate surface behavior, even narrower and more conductive metallic lines should be achievable.

Acknowledgments

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