J Mater Sci: Mater Electron (2009) 20:1154–1157
DOI 10.1007/s10854-008-9843-6

# Freeform fabrication of metallic patterns by unforced electrohydrodynamic jet printing of organic silver ink

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Received: 18 November 2008 / Accepted: 22 December 2008 / Published online: 9 January 2009

**Abstract** Electrohydrodynamic jet printing (EHJP) technology was demonstrated by fabricating metallic patterns, using a commercialized silver metallo-organic ink. The electrospray was operated in a full voltage-controlled form but without the auxiliary assistance of gas pressure. The freeform deposition of basic structures of patterns was demonstrated, for the first time, by using the unforced electrospray. After heat treatment at 250 °C, an energy-dispersive X-ray spectrum confirmed that the main composition was silver in the patterns. Scanning electron microscope analysis revealed that dense packed silver crystallites were present in the fabricated patterns. An electrical resistivity of $4.34 \times 10^{-8}$ Ωm, close to the theoretical resistivity of bulk silver, was obtained in the 100 µm-width printed tracks.

## 1 Introduction

Recently, electrohydrodynamic jet printing (EHJP) technology has demonstrated a capability in direct printing fine features including dots, tracks, and complicated 3D structures. Consequently this has been rapidly developed for application such as solid freeform, biosensors and flexible printed electronic industry [1–5]. In this jet-printing process, a conductive liquid fed by a capillary is subjected to an electrical field. When the electrical field increases to overcome the surface tension of the liquid, then an electrically-driven jet will be emitted, which subsequently disintegrates into droplets [6]. By guiding the droplets onto the desired position on the substrate, a fine pattern of functional materials can be directly formed without a selective masking and then etching processes. By using this EHJP approach, it is possible to directly print a pattern without the assistance of expensive lithography or complicated wet-chemical processing.

Nowadays manufacturing within the electronic industry is highly demanding requiring smart fabrication of metallization and conductive micro-interconnects. For printing metallic patterns, lots of research work has been made on investigating two types of conductive materials, (1) the inks, based on the metal nanoparticle suspension [7–11] and (2) the organo-metallic compounds [12–16]. Of these two inks, the metallo-organic ink has received special interest in direct printing for its true-solution property, where the metal salt is fully dissolved in the solvent. This property is desirable for the EHJP technology as it can effectively reduce the sediment and clogging issues arising from nanoparticles in the suspension. Additionally, a low process temperature for thermal decomposition (normally below 300 °C) is required with the metallo-organic compounds, instead of the high temperature associated with sintering nanoparticles. These features make the organic inks quite favorable for printing.

In this article, we report on the application of electrohydrodynamic jet printing using a commercialized metallo-organic ink. Freeform deposition was performed in a full voltage-controlled fashion and regular printed structures were produced on Si substrate. After low-temperature thermal decomposition the printed tracks were found to have good conductivity of the order of $10^7$/Ωm in magnitude. Our preliminary results demonstrate the feasibility of the EHJP approach in flexible low-cost printing applications for the electronic manufacturing industry.

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## 2 Experimental details

The configuration of the unforced electrospray experiment for the deposition is shown schematically in Fig. 1, similar to the setup previously reported [17, 18]. Via a fast voltage switch (DEI PVX4130) high negative voltage relative to the nozzle was applied to an aluminum plate electrode, positioned perpendicular to the nozzle. The Al electrode was fixed to a movable stage, which was controlled by a computer. A Si substrate was placed on top of the Al electrode for the deposition. The spray distance between the nozzle tip and the substrate was set to 125 µm. The power supply used is a 2 kV high-voltage source (F.u.G. Electronik) and the 4 µm spray nozzles used for experiment were purchased from PicoTip. The commercialized organic silver ink was obtained from InkTec Elec., South Korea. The physical properties of the ink are listed as in Table 1.

The morphology and the chemical composition of the printed patterns were investigated by a scanning electron microscope (SEM, FEI Inspect F) and an energy-dispersive X-ray spectrometer (EDX, Oxford INCA x-act), respectively. The topography of the patterns was measured by an atomic force microscope (AFM, NTEGRA NT-MDT). The electrical resistance of the printed tracks was characterized by a four-point probe measurement.

## 3 Results and discussion

Figure 2 shows two arrays of dots of organic silver ink created on a Si substrate. For each deposition a pulse voltage of 750 V with a 500 ms duration was used. The diameter of the dots created is 135 ± 4 µm and the inter-dot separation in each column is 200 µm. After curing at 250 °C, no obvious change in the size was observed in all the dots. However, the color of the deposition is changed from originally black in (a) to shiny in (b). It implies that metallic bonding occurred, which is in line with our EDX results analyzed later in this report.

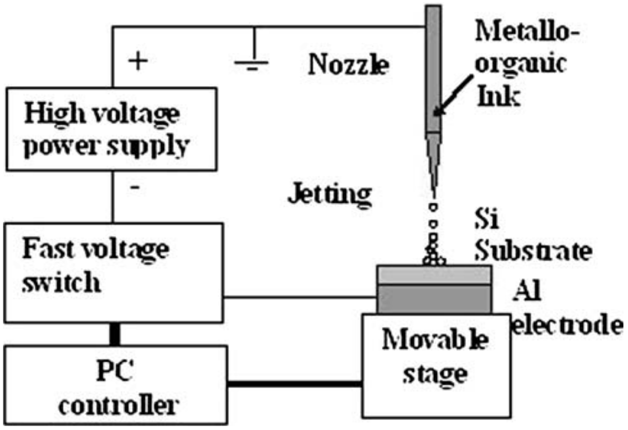


**Fig.1** Configuration of an unforced electrospray system to produce metallic patterns

**Table 1** Physical properties of the ink used in the experiment

| Organic silver ink | Silver content | Surface tension | Viscosity |
|---|---|---|---|
| TEC-IJ-020 | 20 wt.% | 30–32 dyne/cm | 9–15 cps |

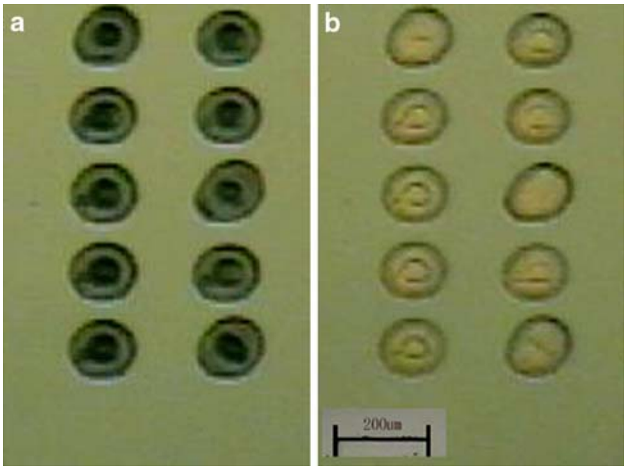


**Fig.2** Optical images of the printed ink dots on Si substrate, **a** before and **b** after curing at 250 °C for 30 min

Figure 3 shows an AFM image of a cured ink dot created on an Si substrate. The fabricated dot is a round shape with a diameter of 135 µm and the height of the dot was measured to be 250–300 nm. The topography of the dot shows a non-uniform surface structure. The depression in the center and the ridge nearby was formed due to Marangoni convection, which causes a material outward

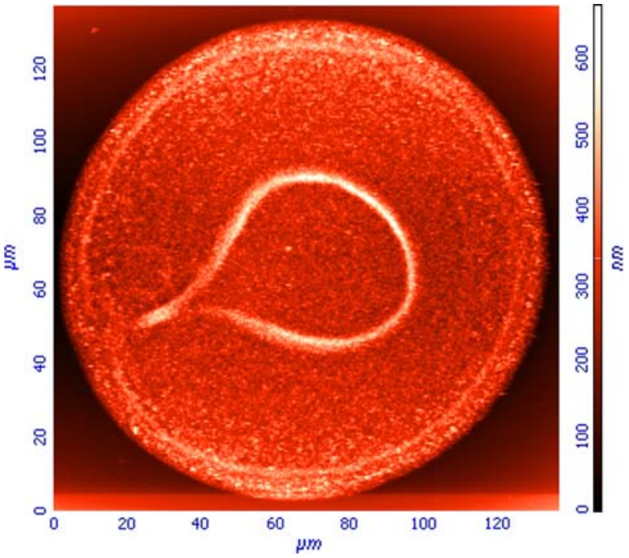
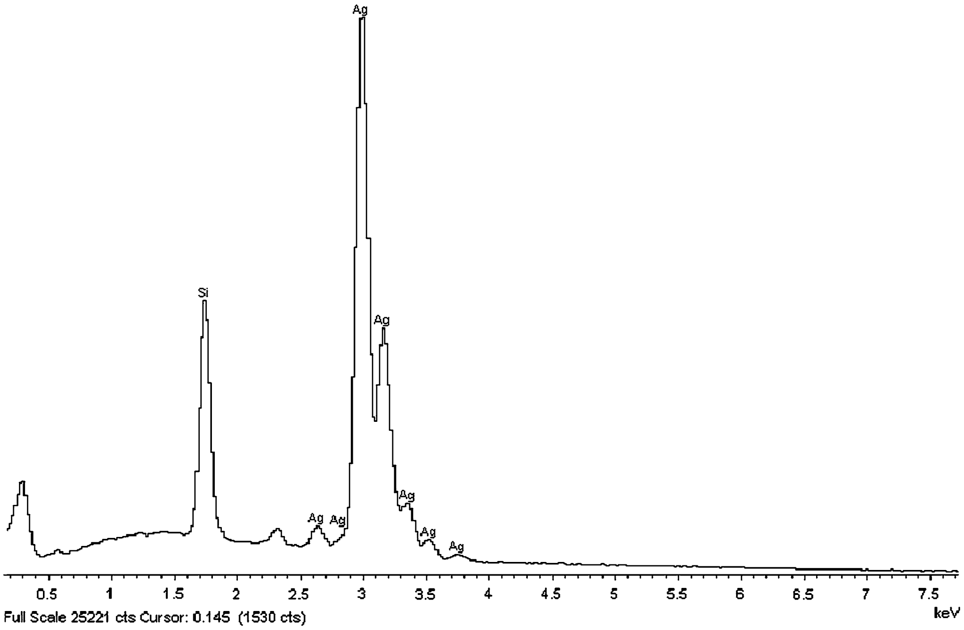


**Fig.3** AFM topography of a deposited dot pattern after heat treatment

**Fig.4** Energy-dispersive X-ray spectrum of cured ink pattern

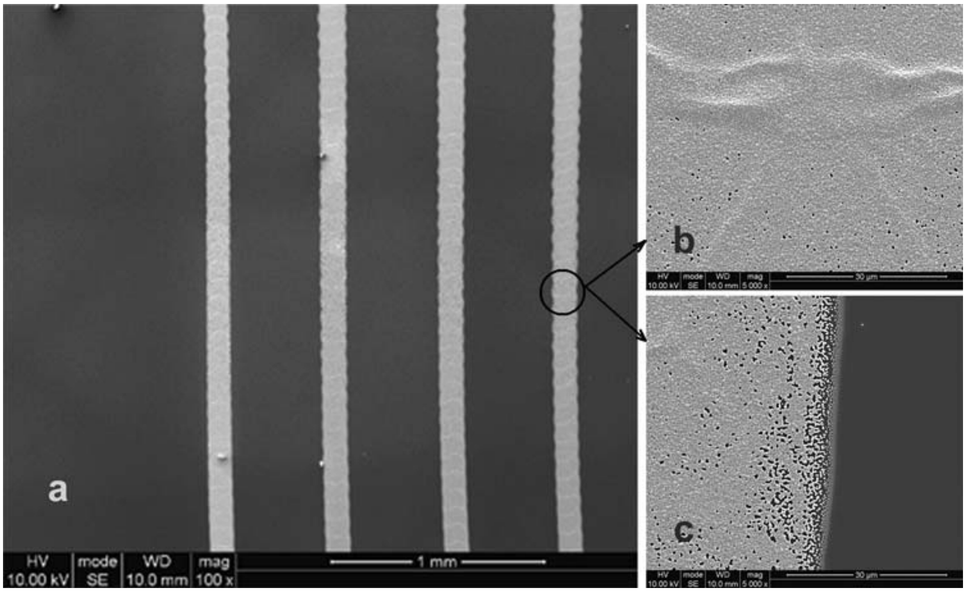


flowing [19]. This feature is commonly observed in the dried printing patterns [20].

Figure 4 shows the chemical elements measured from the surface of the ink pattern after the curing. The EDX spectrum shows significantly strong Ag and Si peaks. The additional signal of Si element is arising from the substrate. The detected composition confirms that metallic silver has been formed after the heat treatment at 250 °C.

Figure 5a shows the morphology of the printed tracks after curing. The tracks were formed by continuously moving the silicon substrate using the PC-controlled translation stage. A pulsed voltage of 560 V with 100 ms duration at a frequency of 1 Hz was provided by the fast voltage switch. Meanwhile, during the spraying process the substrate driven by the motor was scanned over a distance of 4.5 mm at a speed of ~80 μm/s. The SEM image in b and c show the microstructure in the center and near the edge part of the printed stripe on a 5,000× magnification. The SEM image reveals that the surface in the center of the stripes consists of densely packed crystallites and the bump arising from the overlap of the deposited dots is visible. Some porosity observed comes from the gaseous byproducts in the ink decomposition during curing. After the gas leaves the system, a metallic silver film with a good electrical conductivity is developed. However, the porosity will inevitably increase the resistivity. Compared with the

**Fig.5** An SEM image of silver tracks printed on Si substrate. For each track in **a** the total length is 4.5 mm and the width is 120 μm, on which the resistivity is measurable. **b** and **c** show the surface morphology of the center and edge of the stripe, respectively, at a high magnification of ×5,000



central part, the edge of the stripes possesses more porosity. This additional feature can be attributed to the repulsion interaction from the surface charges of the droplets during the spray. The smaller satellite droplets are forced to the edge of the jet and, accordingly, were more widely dispersed.

A mean electrical resistance value of $\sim 9.05\ \Omega$ was measured by using four-point probe measurement for the printed tracks with a length $l = 4.5$ mm on the silicon substrate. The linewidth and the average thickness of the tracks were measured to be around $w = 108\ \mu\text{m}$ and $t = \sim 200$ nm, respectively, by SEM and AFM. From this derived cross-sectional area for the tracks the electrical resistivity is obtained by the formula $\rho = RA/l$, which gives approximately $4.34 \times 10^{-8}\ \Omega\text{m}$. This value corresponds to 2.7 times of the theoretical value of bulk silver ($1.6 \times 10^{-8}\ \Omega\text{m}$), showing a good conductivity.

## 4 Conclusions

Electrospray technology in its unforced form has, for the first time, been applied for the printing of silver metallo-organic inks. The freeform deposition of basic structures, e.g., dots and stripes, was successfully demonstrated. Dense packed silver crystallites were formed in the fabricated patterns after curing. The resistivity obtained in the printing stripes was close to the theoretical value of bulk silver. This good conductivity is consistent with our EDX results, showing that metallic silver has been developed after heat treatment.

**Acknowledgments** This work is supported by the Engineering and Physical Sciences Research Council (EPSRC, UK), grant no.: EP/E03330X/1.

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