Novel electrohydrodynamic jet-printing of organic silver ink in unforced form

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Novel electrohydrodynamic atomization of metallo-organic silver ink in fully voltage-controlled form was investigated. During the spray, different atomization modes including pulsation and cone-jet were observed by a high-resolution CCD video microscope. By using an electrified-fluid-jet in either pulsed transient or steady mode, silver relics with ~200 μm diameters were successfully deposited on a Si substrate. Distinction in the morphology of the relics was revealed by SEM, which can be attributed to the varying jetting throughput at different voltages, and particularly in different modes. EDX analysis confirmed the main composition in all the relics after heat treatment was silver. The results demonstrated that pulsation and cone-jet are both effective modes in electrohydrodynamic jet (e-jet) printing.

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Electrohydrodynamic atomization (EHDA) has been extensively used in many applications such as ionization for analytical chemistry, electrospray deposition, micro/nano-sized particle fabrication, and nanoencapsulation for drug delivery etc [1-7]. Among them, electrospray (ES) deposition has been recently received special interest as a novel microfabrication method with a drop-on-demands (DOD) capability in printing fields and the liquid-typed materials can be directly deposited at a desired location or region without the need of expensive lithography [8-10]. In this electrohydrodynamic printing, a fluid jet driven by electric field is employed to create the fluid flow for a delivery, which is fundamentally different from the conventional ink-jet printing either by heating or applying physical pressure to force the fluid flow.

When a suitably high voltage is applied to a conducting liquid supplied in a capillary, the liquid meniscus will take a form of cone [11]. Further increasing the electric field on the surface of the liquid to overcome the surface tension, a microscopic jet will emerge from the tip of the liquid cone. Due to Rayleigh instability the jet breaks up into a spray, and fine droplets are ejected from the jet [12]. Consequently, by guiding the ejected droplets onto a desired place, and therefore achieving e-jet printing. Different atomization modes such as dripping, spindle, pulsating, cone-jet and multi-jets, can be induced by varying the voltage, and depend on the physical properties of the liquid, flow rate and nozzle diameter, *etc* [13]. Among them, pulsating and cone-jet modes were proposed to be used for controllable printing [9, 10]. By using micro-sized fine nozzles and controlling the jetting time, nES can operate at a low flow rate in a DOD fashion, which accordingly makes the delivery of tiny volumes possible [10, 14].

In this article, unforced e-jet printing is introduced as a flexible microfabrication approach. Direct deposition of commercialized metallo-organic ink using electrified-jets in different modes is investigated. Our results demonstrate the capability of the application of unforced e-jet printing in smart deposition.

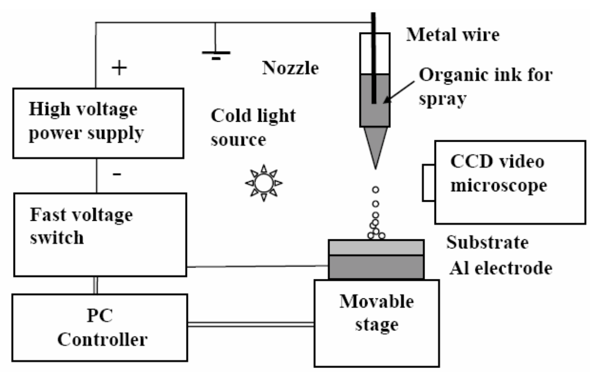

Fig. 1. Schematic configuration of the unforced e-jet printing rig.

Fig.1 illustrates the experimental configuration for unforced e-jet printing, similar to our setup before [15, 16]. The nozzle used for the deposition was produced by pulling borosilicate capillaries to form an outlet with a 16 μm exit. The ink for spraying was fed into the nozzle and a stainless steel wire was submerged into the ink solution; this wire was held at ground potential. A 2 kV high-voltage supply from F.u.G. Electronik was used. Via a fast voltage switch (PVX4130, DEI) the high voltage was applied to an aluminum electrode, on top of which a Si substrate for collection was attached. The aluminum electrode was fixed to a PC-controlled movable translation stage. The distance between the Si substrate and the nozzle was adjusted to 250μm. The shape of the liquid meniscus at the nozzle tip during the spray was monitored and recorded by an optical microscope coupled with a high-resolution CCD video camera (V500, Sony). For the microscope an infinity corrected objective lens (10×, Mitatoyu) on a variable zoom (12.5×, Thales Optem) was used, and a ~2μm resolution was obtained. For illumination a cold light source was used. The commercialized organic silver ink with 20 wt.% silver contents for spray was purchased from InkTec Elec., South Korea. The surface tension and viscosity of the ink were specified to be in the range of 30-32 dyne/cm and 9-15 cps, respectively. The morphology and the chemical composition of the deposited relics were examined by a scanning electron microscope (SEM, FEI Inspect F) and an energy-dispersive X-ray spectrometer (EDX, Oxford INCA x-act), respectively.

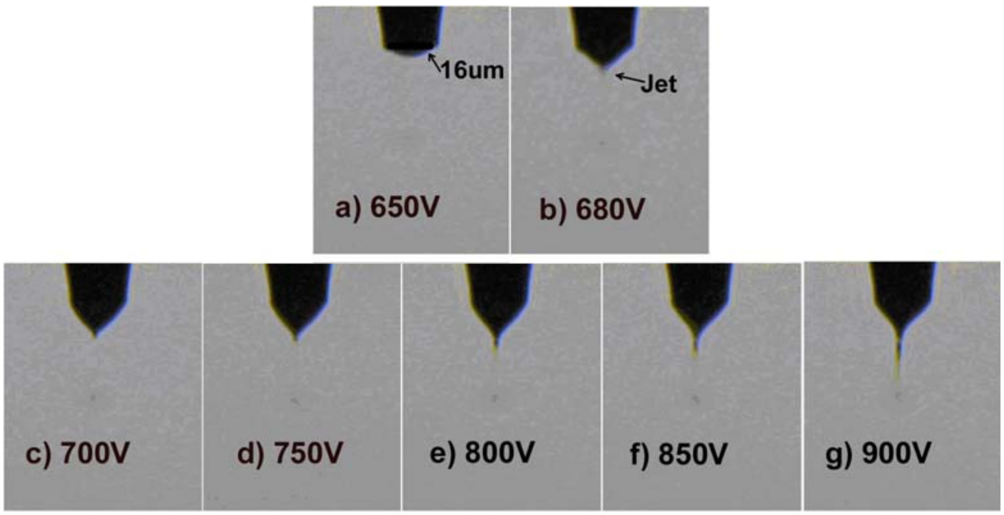

Fig. 2. Images captured by a high-resolution CCD video microscope, showing the shape of meniscus upon ejecting ink at different pulsed voltages. a) at 650 V and b) in pulsation mode at 680V. c-g) in cone-jet regime at the voltage ranged from 700V to 900V.

Fig. 2 shows the liquid meniscus shape upon ejection of ink at different pulsed voltages, captured by a high-resolution CCD video microscope. In all experiments the on-time of the pulsed voltages was 200 ms and a nozzle with 16 μm exit was used for the spray. Image of a) in Fig. 2 shows a spherical-cap-shaped meniscus formed at the nozzle tip at 650 V. When the voltage increases to 680V a faintly pulsating jet is visible, shown in image of b). This pulsating characteristic corresponds to an oscillating formation of quasi-steady jets as we observed before [10, 17]. Normally this pulsation mode occurs before the spray enters a cone-jet mode [15, 17]. Indeed, when the voltage increases to 700V the pulsation mode switches to a cone-jet mode, where a steady jet develops. Images of c)-g) were captured on the applied voltage ranged from 700V-900V, showing a typical Taylor cone shape and steady micro-sized jet. In the cone-jet regime the length of the jet appears to increase with the voltage due to enhanced electric-field stressing.

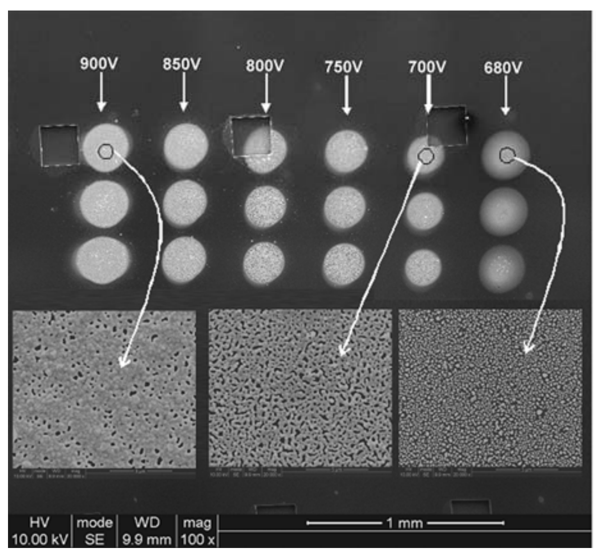

Fig. 3. Ink patterns created by using an e-jet induced at different pulsed voltages. A Si substrate, on which square marks with 200-μm size were pre-made for positioning, was used for collection. After deposition, patterns on the substrate were subsequently cured at 200 ℃ for 20 minutes to complete thermal decomposition of inks. Insets show central zone of the relics at a higher magnification of 20k×.

The scanning electron microscope (SEM) image in Fig.3 shows ink patterns created on a Si substrate, which were cured at 200°C immediately after deposition. The voltage applied ranges from 650V-900V with a 200 ms on-time. In each column three depositions were repeatedly performed at the same voltage with a ~300 μm separation. No patterns were created when a low voltage of 650V was applied. When voltages from 680V-900V were applied the relics with diameter in the range of 178-240 μm were created. Aside from the results created at 680V, it clearly shows that the size of relics created by steady jet increase with the voltage. At a low magnification of 100× dense surfaces were presented in the patterns created by the steady jet while the relics created by transient jet showed a 'halo' effect. At the higher magnification of 20k× the insets revealed a gradual evolution from interconnected structure to dense film in the relics created in cone-jet mode with an increase of voltage. In these relics a porous structure is visible with part of this porosity resulting from the releasing of the gaseous byproducts during the thermal decomposition of ink.

Particularly, the morphology of the relics created by the transient jet at 680V, revealed by SEM at a high magnification, is remarkably different from the others. Large amounts of sub-micron-sized clusters were 'individually' dispersed in the relics. This unique feature can be attributed to the relatively low throughput of the transient jet [17] and the greater electrostatic repulsion from the surface charges of the droplets induced in the EHDA [18, 19]. During jetting fine charged droplets were produced, yet were insufficient to fully cover the spray site. Meanwhile, rapid evaporation of the solvent in ink would be expected for the fine droplets during flight with the droplets also repelling each other due to their surface charge. Hence, the possibility for the agglomeration and coalescence of fine droplets is greatly reduced. Even after heat treatment on the substrate the relics still resemble a cross-section of spray plume with a core of primary isolated droplets in a shroud of satellites [20], i.e. a 'halo' feature.

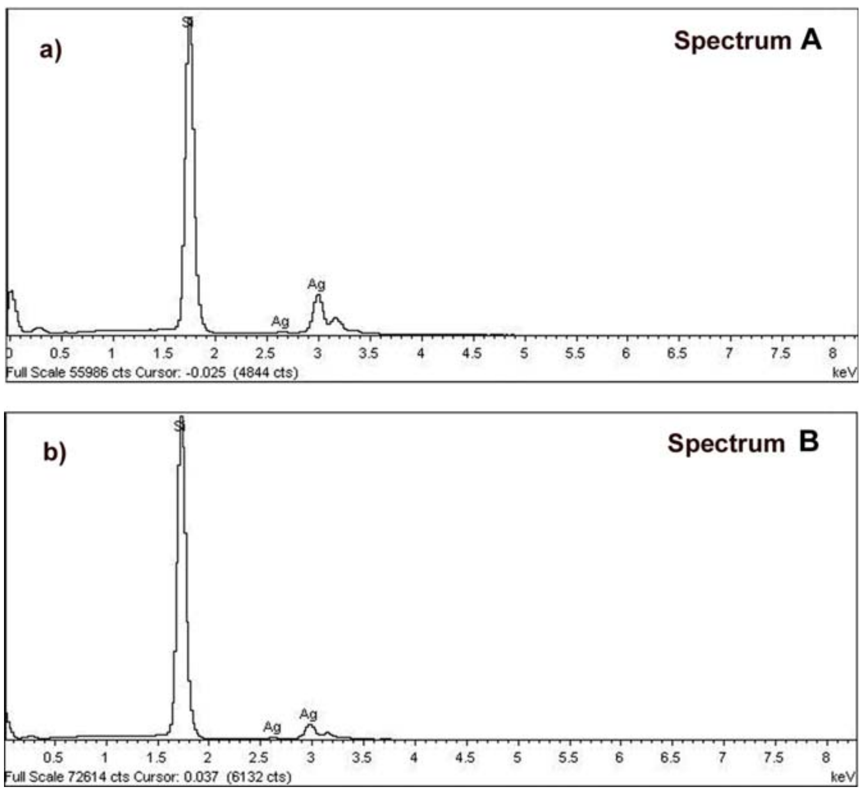

Fig. 4. Energy-dispersive X-ray (EDX) spectra of cured ink patterns. Spectrum a) created from the relic produced by steady jet at 700V and spectrum b) created by the transient jet at 680V.

Fig. 4 illustrates the chemical composition determined from the surface of the relics after curing. Here, the spectra from the relics created by the transient jet at 680V and steady jet at 700V were chosen for comparison. The EDX spectrum confirms that the main composition in both relics is silver. The additional signal of Si element comes from the substrate. No pronounced composition difference can be distinguished from the patterns created in two modes. The slight change of silver peak intensity in the spectra can be attributed to the different coverage of the two regimes. Very good conductivity, which is close to the theoretical value of bulk silver, was obtained in the printed tracks made by this method [16].

In brief, fully voltage-controlled e-jet printing of organic silver ink was demonstrated by using either transient or steady jetting. Comparable distinct morphology of the relics created was observed, associated with the different capability of the jetting throughput. EXD analysis confirmed that the main composition in all the produced relics was silver. Unforced e-jet printing, in either pulsation or cone-jet mode, has demonstrated a capability for smart deposition in a controllable fashion.

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