AIP | Applied Physics Letters

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Citation: Appl. Phys. Lett. **90**, 081905 (2007); doi: 10.1063/1.2645078
View online: http://dx.doi.org/10.1063/1.2645078
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v90/i8
Published by the American Institute of Physics.

Electrohydrodynamic printing of silver nanoparticles by using a focused nanocolloid jet

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(Received 8 November 2006; accepted 16 January 2007; published online 21 February 2007)

As a direct write technology, the electrohydrodynamic printing of silver nanoparticles by using a focused nanocolloid jet is introduced. In this letter, two categorized types of examples of two-dimensional patterning were printed by using the electrohydrodynamic printing method. A spiral-type inductor was printed to demonstrate the feasibility of the electrohydrodynamic printing as a fabrication process. The printed spiral inductor produced 9.45 μH and exhibited approximately five times larger resistivity (9.5 $\mu\Omega$ cm) than that of bulk silver after the sintering process. Then, complex geometries having square- and round-shape patterns were also printed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2645078]

Direct write technologies are the most recent approaches to form fine patterns whose linewidths range from meso- to nanoscales.[1] The term direct write refers to any technique or process capable of depositing, dispensing, or processing different types of materials over various surfaces following a preset pattern or layout. With a direct write approach, patterns or structures can be obtained directly without the use of variable fabrication processes, masks, and liquid for etching. Direct write technologies, therefore, are the low cost, high speed, noncontact, and environmental friendly processes.[2] As one of the direct write technologies, electrohydrodynamic printing can be used to obtain microlines onto a substrate.[3] Electrohydrodynamic printing is a pattern method that uses a fine jet generated at the apex of a liquid cone in the cone-jet mode of electrospray.[3] The fine jet consists of solid nanoparticles, liquid, and surfactants and called the nanocolloid jet. After the jet impinges on a substrate, the nanoparticles remain on the substrate. Generally, the jet generated in the cone-jet mode breaks into a spray of droplets before the jet contacts the substrate. Thus, the breakup process should be controlled for its proper application according to the desired linewidth of the pattern in electrohydrodynamic printing.[4–6]

Deposition of nanoparticles by electrohydrodynamic printing offers some advantages in fine patterning. Because the diameter of the nozzle (>100 μm) used is much larger than that of ink-jet printing (about 20 μm), blockages are prevented and the high viscous colloid containing solid particles can be easily processed. Additionally, electrohydrodynamic printing directly creates patterns onto the surface of a substrate without lithography and does not require expensive equipments, while a laser-guided direct writing method or dip-pen nanolithography method requires a laser or atomic force microscope equipment, respectively.

The phenomena of cone-jet mode of electrospray have been extensively studied, for example, charge versus droplet size,[7] scaling laws,[8–10] and jet stability.[11] Recently, researchers have proposed printing technologies using the jet of cone-jet mode in electrospray.[3,12–15] They tried to make one-dimensional patterns by deposition of ceramic,[3,12,13] latex,[3,14] and silver[15] particle suspensions.

In this letter, we introduce two categorized types of examples of two-dimensional patterning. A spiral-type inductor was patterned to demonstrate the feasibility of the electrohydrodynamic printing as a fabrication process since it is used in electric circuits as filters, oscillators, low-power converters, and magnetic field generators. Then, complex geometries having round corners were also patterned. The silver nanocolloid, which consists of 20% silver nanoparticles and about 80% ethylene glycol in weight with very small amounts of surfactants to prevent agglomeration between silver nanoparticles, was used. The geometric diameter of the silver nanoparticles was below 20 nm. Metal nanoparticles were employed because of their remarkable lower melting temperature than that of the bulk material.[16]

The electrohydrodynamic printing system used in this study consisted of a nozzle, electrodes, power supply, and *X-Y* stage, as shown in Fig. 1. A stainless steel nozzle (inner diameter: 180 μm, outer diameter: 320 μm) was used to produce a jet containing silver nanoparticles, which were uniformly supplied to the nozzle by a syringe pump (kds-100, KD Scientific Inc.). The nozzle was also used as anodes as well as a guide ring (inner diameter: 3.2 mm, outer diameter: 5.2 mm), which was located 0.03 mm below the nozzle. A pin-type electrode (400 nm in diameter) located 3.8 mm below the nozzle was used as the ground electrode to focus

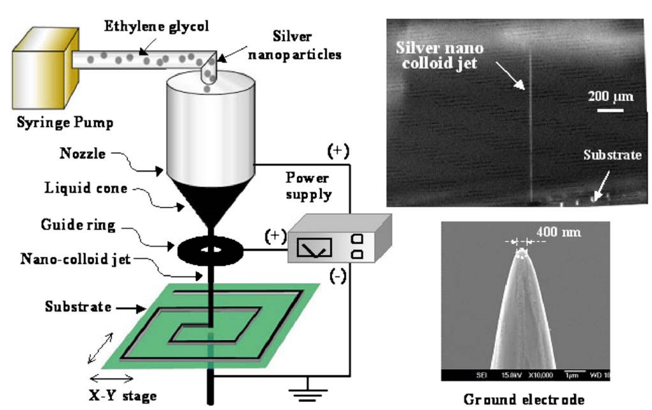

FIG. 1. (Color online) Schematic of the electrohydrodynamic printing.

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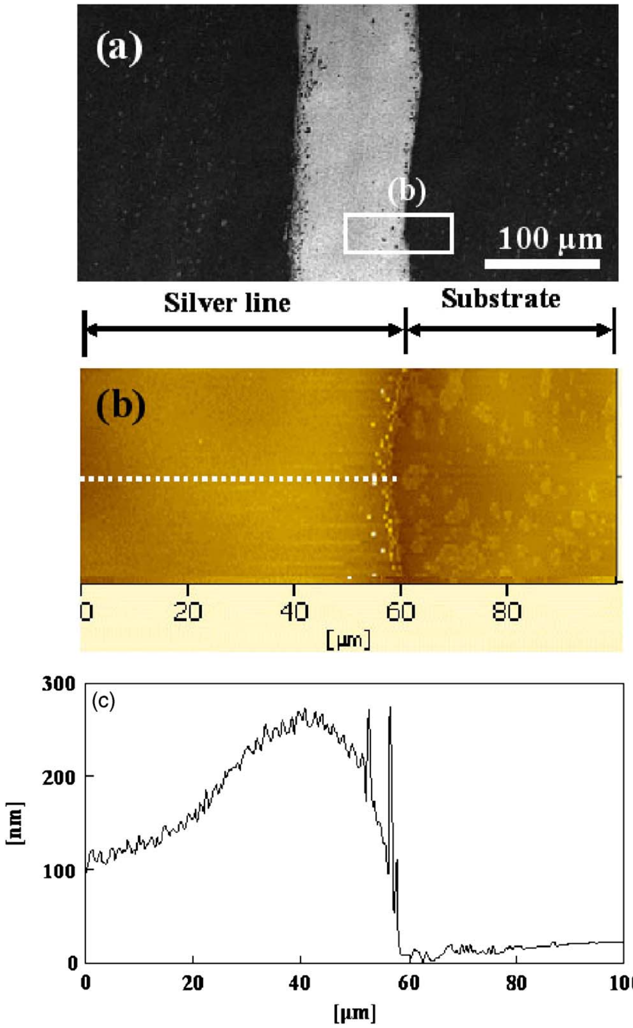

FIG. 2. (Color online) (a) Photo and (b) scanned images and (c) roughness profile of a silver line.

the jet onto the substrate, which was located 1.08 mm below the guide ring.

The micron-sized jets formed by the cone-jet mode are very difficult to stabilize.[3] To obtain a stable jet, the growth rate of the jet should be decreased by applying high axial electric fields, which are imposed by the potential difference between the nozzle and the ground electrode. However, increasing the potential difference between the electrodes could not only increase the axial components of the electric fields but also increase the radial components of the electric fields. Increasing the radial components might amplify the growth rate of the jet. The pin-type ground electrode with a 400 nm diameter used in this study effectively increased the axial electric fields but did not greatly change the radial electric fields, so the jet breakup was reduced.[4] Additionally, the guide ring with an inner hole reduced the chaotic motion of the jet and prevented the jet from digressing from the centerline.[4,17] Figure 1 shows that a stable and coherent jet of 10 μm in diameter was obtained when 5 kV was applied both to the nozzle and the guide ring. The jet having silver nanoparticles reached the substrate without converting into a spray. The flow rate was 2 μl/min. Although our printing method used a nozzle (180 μm) much larger than an ink-jet nozzle (about 20 μm), it allowed the generation of a micron-sized jet. Figure 1 also shows that the moving stage system

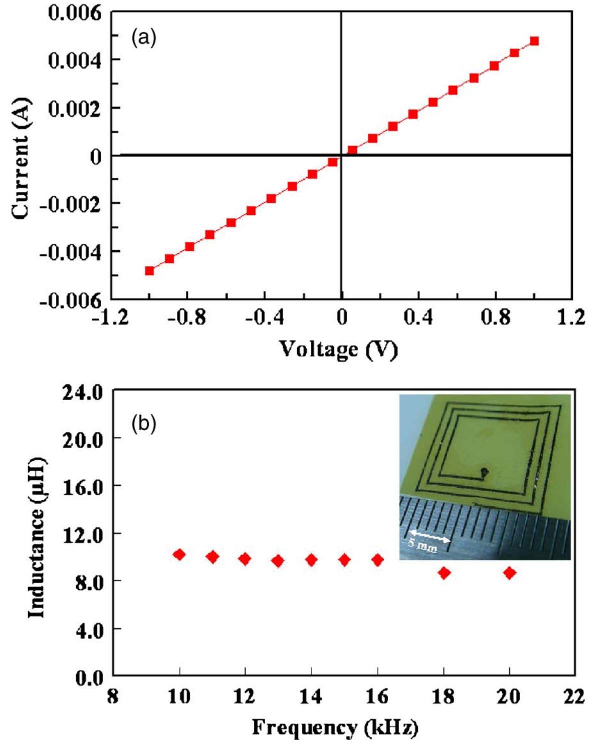

FIG. 3. (Color online) (a) *I*-*V* curve and (b) inductance of spiral-type inductor (inset) obtained by electrohydrodynamic printing of silver nanoparticles.

consisted of an *X*-*Y* linear motor stage (LPP LM1, DCT Inc.) and a programmable motion controller (motion controller, Parker Inc.), which communicates directly with a personal computer. Such a system can control the motion of a substrate so that nanoparticles can be deposited according to the patterns designed.

Once the focused silver nanocolloid jet was generated by the cone-jet mode of electrospray, a set of lines was printed onto the substrate when the stage was moved at 10 mm/s. After obtaining the printed lines, the lines were sintered by heating them at 230 °C, 1 atm, for 1 h at a constant heating rate of 2 °C/min. Figure 2(a) shows a magnified photo of the line printed onto the polyimide substrate after the sintering process. The magnified photo was obtained by using a laser scanning microscope (LSM 5 Pascal, Carl Zeiss). The applied voltage and flow rate were 5 kV and 1 μl/min, respectively. The average linewidth was about 100 μm. Figure 2(b) shows the image of the rectangular part of Fig. 2(a), which was scanned by using an atomic force microscope (SPA 400, Seiko). Figure 2(c) shows the thickness profile of the dash line in Fig. 2(b). The average line thickness was about 180 nm. It is interesting to note that the thickness was the lowest near the center of the line. This phenomenon is similar to the formation of a coffee-ring splash or donut structure, which has been a well-known problem in ink-jet printing.[18]

Next, a spiral-type inductor designed by using a computer-aided design was fabricated onto a polyimide substrate. The applied voltage and flow rate were 5 kV and 2 μl/min, respectively. The specific electrical resistivity ρ of the inductor was calculated by the formula $\rho = RA/l$, where R is the electrical resistance of the line, l is the length of the line, and A is the cross section area of the line. The resistances were calculated from an *I*-*V* curve measured by an *I*-*V* meter (4145B, HP). To calculate the cross section area

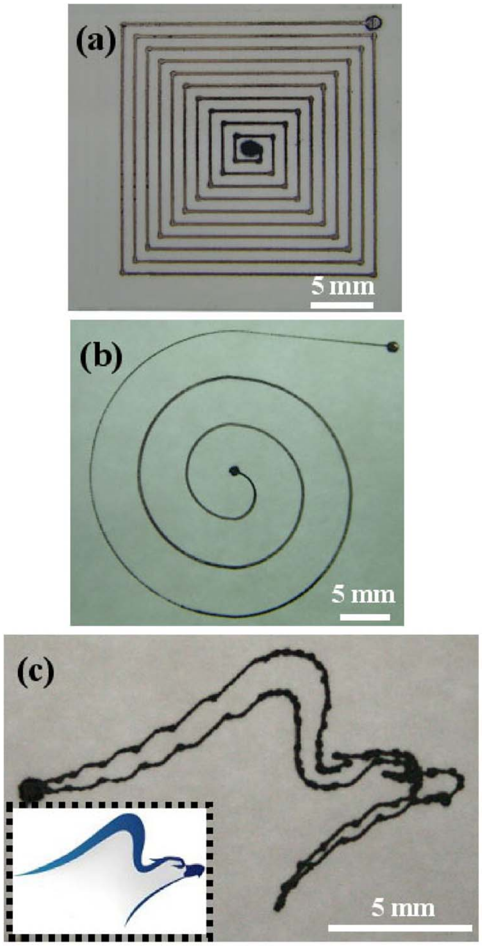

FIG. 4. (Color online) (a) Square-shape pattern, (b) round-shape pattern, and (c) one of the logos of Yonsei University formed by electrohydrodynamic printing of silver nanoparticles.

$(A=wt)$, the linewidth (w) and thickness (t) were measured by a laser scanning microscope and an atomic force microscope, respectively. Figure 3(a) shows that *I*-*V* characteristics of the spiral inductor showed a linear Ohmic behavior. The dc resistance of the spiral inductor calculated from the slope of the line [Fig. 3(a)] was about 200 Ω. The resistivities were approximately 9.5 $\mu\Omega$ cm, which was about five times higher than that (1.6 $\mu\Omega$ cm) of bulk silver. The inset of Fig. 3(b) shows that the inductor had a radius of 7 mm and average linewidth of 200 μm, line spacing of 1 mm, total length of 143 mm, and three turns. The average thickness of the inductor lines was about 320 nm. Figure 3(b) gives the plot of the inductance frequency variation of the inductor. The inductance for various frequencies was measured by an *RCL* meter (PM6304, Fluke). The inductances were about 10.2 μH at 10 kHz and 8.6 μH at 18 kHz, and the average inductance was about 9.45 μH in the range of frequency measured.

Finally, various complex two-dimensional patterns were printed onto a photo paper. Figure 4 shows a square-shape pattern (a), round-shape pattern (b), and one of the logos of Yonsei University (c) formed by silver nanoparticles. The square- and round-shape patterns were printed when the flow rate and applied voltage were 2 μl/min and 5 kV, respectively. The average linewidths were about 250 μm. A more complicated pattern [Fig. 4(c)] was obtained when the flow rate and applied voltage were 1 μl/min and 5 kV, respectively. The image located at the left side in Fig. 4(c) is an original picture of the eagle pattern. The average linewidth was about 130 μm.

This letter demonstrated the possible use of the silver nanocolloid jet generated in the cone-jet mode of electrospray to fabricate functional two-dimensional patterns of silver nanoparticles. Patterns of 100–300 nm in thickness were obtained when the nozzle passed once onto a substrate. Although the jet generated had a thin diameter of 10 μm, the patterns had larger widths than the diameter of the jet. In the future, we plan to reduce the variation of the pattern widths.

The authors thank Sung-Ho Park (Samsung Electro-Mechanics Company) and Eun-Soo Hwang and Jeong-Hun Seo (MEMS Laboratory in Yonsei University) for helpful discussions.

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