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D.Y. LEE[1]
E.S. HWANG[1]
T.U. YU[2]
Y.J. KIM[1]
J. HWANG[1,✉]

Structuring of micro line conductor using electro-hydrodynamic printing of a silver nanoparticle suspension

[1] School of Mechanical Engineering, Yonsei University, Seoul, 120-749, Korea
[2] Manufacturing System Division, Korea Institute of Industrial Technology, 330-825, Korea

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ABSTRACT The generation of a fine pattern of metallic materials from suspensions is gaining significant interest because it is the key in the fabrications of displays and printed circuit boards. In our experiments, a silver nanoparticle suspension was first deposited onto a Kapton® polyimide film by using an electro-hydrodynamic printing system, including a guide ring and pin (nozzle)-to-pin (ground) electrodes. Then after thermal curing of the particles deposited, a conductor line as fine as 32 μm in width and 0.3 μm in thickness was obtained onto the film. The resistivity of the line was about 13 μΩ cm. The pin type ground electrode was helpful in the deposit of the silver nanoparticle suspension along a specific direction. The guide ring repressed the chaotic motion of the jet and prevented the jet from digressing from the centerline. With the electro-hydrodynamic printing method, a nozzle (inner diameter: 140 μm, outer diameter: 320 μm) much larger than an ink jet nozzle could be used.

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1 Introduction

The generation of a fine pattern of inorganic and metallic materials from precursor suspensions is the key in the fabrication of electronic and sensor devices as well as integrated power sources. Direct write technologies are the most recent and novel approaches of forming a fine pattern whose line width ranges from the meso to the nano scale [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. In a direct-write approach, patterns or structures can be obtained directly without the use of masks and without the use of liquid for etching. Direct write technologies, therefore, are low cost, high-speed, non-contact, and environmentally friendly processes [2].

As one of the direct write technologies, electro-hydrodynamic printing is a pattern method using the cone-jet mode of electrospray [3]. When a liquid is supplied to a nozzle and the interface between air and the liquid is charged to a sufficiently high electrical potential (∼ kV), the liquid meniscus takes the form of a stable cone, whose summit emits a microscopic jet. This is referred to as the cone-jet mode in electrospray.

Deposition of nanoparticles by the electro-hydrodynamic printing, where the suspension flows through a nozzle at a high voltage, offers some advantages in fine patterning. First, by suitably fixing the flow rate and applied voltage and by optimizing the physical properties of the liquid, one can apply electro-hydrodynamic printing to produce a narrow distribution (geometrical standard deviation ∼ 1.1) of fine droplets (40 nm ∼ 1.8 μm) [4]. Second, the diameter of the nozzle (above 100 μm) used can be larger than that (about 20 μm in diameter) of an ink-jet printing. The use of a larger nozzle prevents blockages and allows easier processing of a viscous suspension containing a high level (above 30 wt %) of solid particles. Despite the use of much larger nozzles, the droplet sizes generated are much finer.

Numerous studies have been attempted to establish the principles of the cone-jet mode of electrospray. De la Mora and Loscertales [5], Ganan-Calvo et al. [6], and Hartman et al. [7] showed that liquid properties (electrical conductivity, viscosity, surface tension, relative permittivity and density) and two process parameters (applied voltage and flow rate) play a crucial role in achieving the cone-jet mode of electrospray. They suggested equations for predicting the jet diameter or droplet size from the liquid properties and flow rate. Recently, Poon [3], Jayasinghe et al. [8] and Wang et al. [9] proposed printing technologies using the cone-jet mode of electrospray. They tried to make patterns by deposition of ceramic suspensions. However, few recent studies have investigated the structuring of a micro-sized line conductor using the cone-jet mode of the electrospray.

We first attempted to structure a line conductor by using the electro-hydrodynamic printing and thermal curing of silver nanoparticles deposited from a suspension, which consisted of 30% silver and about 70% toluene in weight with very small amounts of surfactants to prevent the agglomeration of silver nanoparticles. The average diameter of the nanoparticles lay between 3 and 7 nm. Metal nanoparticles were employed because of their remarkably

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✉ Fax: +82 2 312 2159, E-mail: hwangjh@yonsei.ac.kr

lower melting temperature than that of the bulk material. This low melting temperature of metal nanoparticles has received much theoretical attention. Buffat and Borel [10] showed that nanoparticles of Au, Pb and other metals have a melting-point depression of up to as much as 30% for particles of 2 ∼ 3 nm in diameter. This low melting temperature of metallic nanoparticles is due to the large ratio of surface atoms to inner atoms. This high portion of surface atoms drastically decreases the melting temperature, since smaller particles exhibit reduced interaction between the surface and the inner atoms [10].

2 Experimental setup and conditions

The experimental set up consisted of a liquid supply system, an electrical system, and a moving stage system. The liquid supply system included a syringe pump (minimum flow rate: 16.7 pl/min for 1 ml syringe) and a stainless steel nozzle (inner diameter: 140 µm, outer diameter: 320 µm). A silver nanoparticle suspension was injected downward from the nozzle. The moving stage system consisted of an *X*-*Y* moving stage and a digital control system, in which a programmable motion-controller that communicates directly with a PC controlled the motion of a substrate. The electrical system consisted of a high voltage power supply (∼ DC 15 kV) and three electrodes. The nozzle used for the liquid supply system was also used as anodes as well as a guide ring (inner diameter: 3.2 mm, outer diameter: 5.2 mm), which was located 0.26 mm below the nozzle. A point-like electrode (1 µm in diameter) located 3.1 mm below the nozzle was used as the ground electrode.

The guide ring in the experimental setup was used to restrain the chaotic motion of a jet. In the cone-jet mode of electrospray, the jet of solution will erupt from the surface of the cone and travel toward the nearest electrode of opposite polarity, or electrical ground. Although the details of charge motion in the jet are not well understood, it is believed that excess charge is essentially static with respect to the moving coordinate system of the jet [11]. This means that the jet can be thought of as a string of charge elements connected by a viscoelastic medium, with one end fixed at the point of origin and the other end free. The free end of the jet follows a chaotic path as it travels toward the grounded collection plate [11]. Melcher and Warren [12] suggested a ring electrode to suppress the jet's chaotic motion, and they obtained a millimeter-sized glycerol jet having steady flow. Poon [3] suggested a cylindrical wall electrode to form a steady flow of the jet generated from the liquid cone. Deitzel [13] demonstrated the feasibility of dampening the instability of a polymer fiber generated from the liquid cone by using several ring electrodes. Poon [3], Melcher and Warren [12], and Deitzel [13] applied ring electrodes to pin (nozzle)-to-plate (electrode) type electrospinning systems. In our research, however, a pin-to-plate type having a ring electrode was inadequate to focus the jet onto the point we wanted (refer to results and discussion). To obtain a micro-sized conductor line by using the cone-jet mode, we used the pin-to-pin type electrospray of having a guide ring electrode.

A substrate (30 mm width × 30 mm length × 0.1 mm thickness) made of Kapton® polyimide film was located 2.24 mm below the guide ring. The surface of the substrate was pretreated by RIE (reactive ion etching) process for 15 min. This process increased the surface roughness of the substrate, which was helpful for adhesion between the silver nanoparticle suspension and the surface of the Kapton® polyimide film. For the silver nanoparticles suspension described in the introduction, we were able to obtain the cone-jet mode for electro-hydrodynamic printing at various applied voltages when the liquid flow rate was fixed at 0.5 µl/min. One-dimensional patterns were printed by using the jet of the cone-jet mode on the polyimide film. After the silver lines were deposited on the substrate, the printed patterns were cured by heating at 220 °C for 20 minutes in a convection oven. Thicknesses of the patterned silver lines were measured by a confocal laser scanning microscope (LSM 5 Pascal, Carl Zeiss). The specific electrical resistivities, ϱ, of the printed lines were calculated by measuring the electrical resistance, R, the length, l, and the cross section, A, of the line, and by formula, $\varrho = RA/l$. The resistances of the silver lines were measured by I–V meter (4200 I–V characterization system, Keithley) for various voltages.

Experiments were first performed without using the guide ring. Then, experiments were carried out with the guide ring. All the experiments were conducted in a Class 100 (for particles larger than 0.5 µm) clean room. Numerical calculations were also conducted to expect the effects of the guide ring on electric field distributions. A commercial solver package (Maxwell 3D, version 5) based on the finite element method was used.

3 Results and discussion

We tried to print a line pattern by using the cone-jet mode of electrospray and also by using a point-like (pin) ground electrode. The latter method deposited charged nanoparticles along a specific direction. Figure 1 shows the pre-patterns before thermal curing, for both microdripping ($V \sim 3$ kV) and cone-jet modes ($V \sim 5$ kV), when the guide ring was not used. In both modes, the silver nanoparticle suspension was intermittently deposited along the direction to be printed, resulting in a dotted line pattern. A continuous line pattern could not be formed even in the cone-jet mode because of the chaotic motion of the jet generated from the liquid cone. As shown in Fig. 1, some of the patterns from the jet were shaped like a "hook" due to the chaotic motion of the jet. To remove this problem, we decided to use a guide ring electrode in the electro-hydrodynamic printing system.

Before the guide ring was installed, numerical calculations were carried out to predict the effects of the guide ring

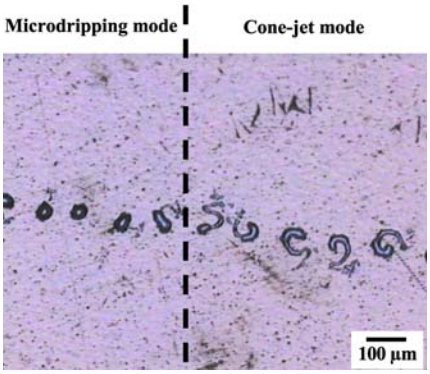

FIGURE 1 Magnified picture of patterns when a guide ring was not used

on electric field strengths. The Poisson's equation, $\nabla \bullet (\varepsilon_0 \varepsilon_r \nabla V) = -\varrho$ (ϱ: volume charge density, V: electric potential, ε_0: permittivity in vacuum, ε_r: relative permittivity), was solved. We assumed that the nozzle above the substrate was a stick (0.32 mm in diameter and 5 mm in length) having no inner space. Electric potentials at the pin, nozzle, and guide ring were 0 kV, 3 kV, 3 kV, respectively, which were used as boundary conditions. Figure 2a shows two-dimensional electric field distributions between the guide ring and the substrate. The electric field vector is defined as $\boldsymbol{E} = -\nabla V$. As shown in Fig. 2a, electric fields were concentrated inside the ring due to the electric potential applied to the ring electrode. Figure 2b shows electric fields along the A–B line in Fig. 2a for cases with and without the guide ring. When the ring electrode was not used, the electric field strength was reduced along the radial direction from the centerline, which might cause the charged jet to drift towards the radial direction. However, when the ring electrode was used, the radial motion of the charged jet might be suppressed since the high electric field near the ring electrode was directed toward the centerline. Moreover, the axial motion of the jet toward the pin electrode along the centerline was accelerated since the electric field at the centerline in the presence of the ring electrode was higher than that in the absence of the ring electrode. These calculations indicate that the ring electrode would repress the instability of the jet generated from the liquid cone.

Figure 3 shows the final patterns printed by the jet generated in the cone-jet mode with the guide ring. Figure 3a shows that the continuous line pattern that was obtained for $V \sim 5$ kV after using the ring electrode. Figure 3b shows the pattern after thermal curing. The line width and line thickness were 165 μm and 5 μm, respectively. When a higher voltage was applied ($V \sim 7$ kV), a much finer line pattern was obtained, as shown in Fig. 3c. The line width and line thickness were 32 μm and 0.3 μm, respectively. The resistivities of both printed lines in Figs.3b and 3c were approximately 13 μΩ cm, which was about eight times higher than that (1.6 μΩ cm) of bulk silver. Although a much larger nozzle (140 μm) than an ink jet nozzle (about 20 μm in

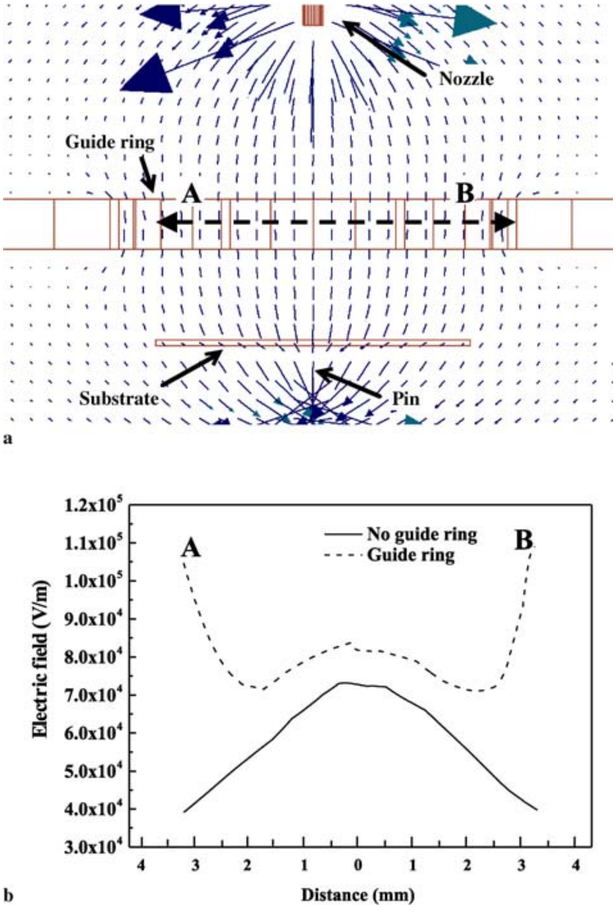

FIGURE 2 (**a**) 2D electric field distributions with the guide ring (**b**) Electric fields along *A–B line* with and without the guide ring

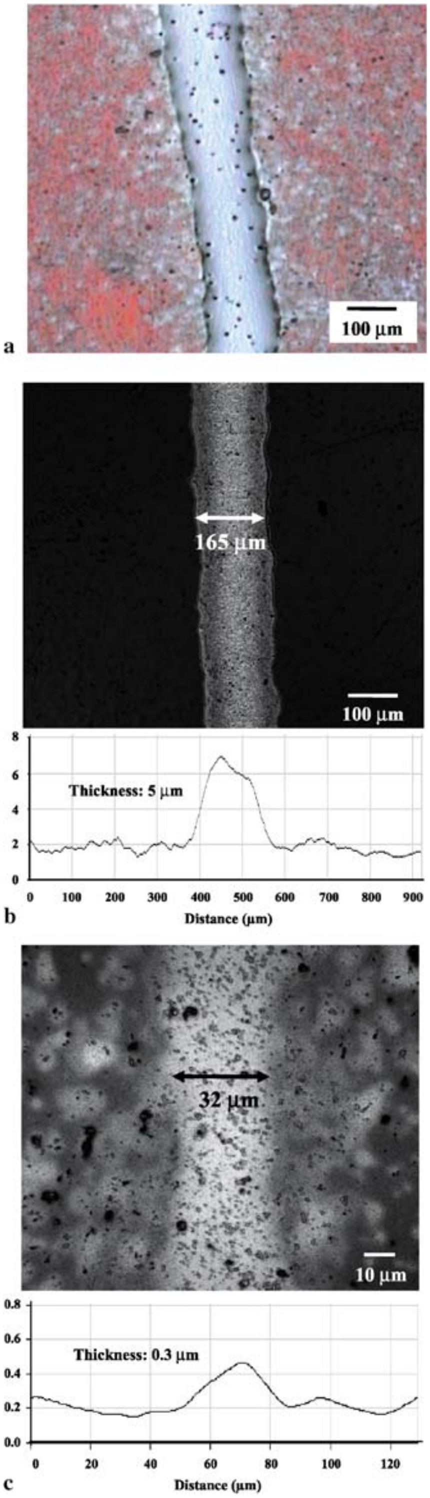

FIGURE 3 Geometries of silver lines after printed onto a Kapton® polyimide film (**a**) Before thermal curing ($V \sim 5$ kV), (**b**) After thermal curing ($V \sim 5$ kV), (**c**) After thermal curing ($V \sim 7$ kV)

diameter) was used, our printing method allowed structuring of metal lines of several hundreds and tens of micrometer in width onto a Kapton® polyimide film.

4 Conclusions

In our research, a silver nanoparticle suspension was first deposited onto a Kapton® polyimide film by using an electro-hydrodynamic printing system, including a guide ring and pin (nozzle)-to-pin (ground) electrodes. Then after thermal curing of the printed patterns, conductor lines as fine as $32 \sim 165\,\mu\mathrm{m}$ in width and $0.3 \sim 5\,\mu\mathrm{m}$ in thickness were obtained onto the film. The resistivity of the lines was about $13\,\mu\Omega\,\mathrm{cm}$. By using the pin type ground electrode, the silver nanoparticle suspension could be deposited along the specific direction. The guide ring repressed the chaotic motion of the jet and prevented the jet from digressing from the centerline. The electro-hydrodynamic printing method allowed us to use a much larger nozzle (inner diameter: $140\,\mu\mathrm{m}$, outer diameter: $320\,\mu\mathrm{m}$) than an ink jet nozzle. In the future, we plan to structure two-dimensional line patterns onto a Kapton® polyimide film by using this printing method and analyze the electrical performances of the patterns.

REFERENCES

1 A. Pique, D.B. Chrisey (Eds.), In: *Direct-Write Technologies for Rapid Prototyping Applications* (Academic Press, San Diego 2002)
2 D.B. Chrisey, Science **289**, 879 (2000)
3 H.F. Poon, Electrohydrodynamic Printing, Ph.D. Thesis, Department of Chemical Engineering, Princeton University (2002)
4 D.R. Chen, D.Y. Pui, S.L. Kaufman, J. Aerosol. Sci. **26**, 963 (1995)
5 J. Fernandez De La Mora, I.G. Loscertales, J. Fluid. Mech. **260**, 155 (1994)
6 A.M. Ganan-Calvo, Phys. Rev. Lett. **79**, 217 (1997)
7 R.P.A. Hartman, D.J. Brunner, D.M.A. Camelot, J.C.M. Marijinissen, B. Scarlett, J. Aerosol. Sci. **31**, 65 (2000)
8 S.N. Jayasinghe, M.J. Edirisinghe, T.D.A. Wilde, Mat. Res. Innovat. **6**, 92 (2002)
9 D.Z. Wang, S.N. Jayasinghe, M.J. Edirisinghe, J. Nanopart. Res. **7**, 301 (2005)
10 P. Buffat, J.P. Borel, Phys. Rev. A **13**, 2287 (1976)
11 D.H. Reneker, A.L. Yarin, H. Fong, S.J. Koombhongse, J. Appl. Phys. **87**, 4531 (2000)
12 J.R. Melcher, E.P. Warren, J. Fluid. Mech. **47**, 127 (1971)
13 J.M. Deitzel, J.D. Kleinmeyer, J.K. Hirvonen, N.C. Beck Tan, Polymer **42**, 8163 (2001)