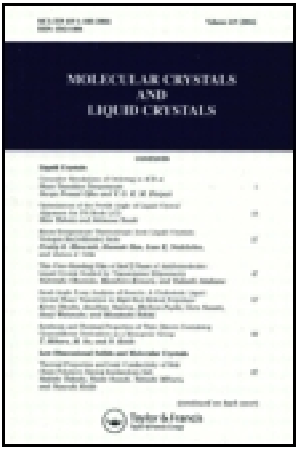

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Ink-Jet Printing of Silver Conductive Tracks on Flexible Substrates

Dongjo Kim [a] , Sunho Jeong [a] , Jooho Moon [a] & Kyungtae Kang [b]

[a] Department of Materials Science and Engineering, Yonsei University, Seoul, Korea

[b] Korea Institute of Industrial Technology, IbJang-myun, Chon An-si, Korea

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Dongjo Kim
Sunho Jeong
Jooho Moon
Department of Materials Science and Engineering, Yonsei University, Seoul, Korea

Kyungtae Kang
Korea Institute of Industrial Technology, IbJang-myun, Chon An-si, Korea

We have developed a conductive ink applicable to ink-jet printing to fabricate conductive lines on flexible substrates. Nano-sized silver particles with $\sim$*21 nm diameter were used for the direct metal printing. Silver conductive ink was printed on polymer substrates for the application to flexible electronics. The printing conditions of pulse amplitude, head frequency, xy-stage moving velocity and substrate temperature were optimized to achieve smooth conductive track with high resolution. After heat-treatment at temperature of 100* $\sim$ *300°C for 30 min, the printed silver patterns exhibit metal-like appearance and high conductivity. The influence of the printing conditions on the microstructure and conductivity of the conductive track was investigated.*

Keywords: conductive pattern; direct metal printing; ink-jet printing; silver nano particle

INTRODUCTION

Ink-jet printing technique of functional materials is of interest in a variety of fields including displays, electronics, optics and sensors

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Address correspondence to Prof. Jooho Moon, Department of Materials Science and Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749 Korea (ROK). E-mail: jmoon@yonsei.ac.kr

due to the capabilities of low cost solution-based process and direct writing at low temperature [1]. Especially, the patterning of conductive track by ink-jet printing method is attractive for replacing conventional processes such as screen printing and photolithography, because it can reduce processing cost and time enormously [2,3]. Low temperature processing is also very useful for the fabrication of flexible display devices, because flexible displays or electronics have to use a flexible plastic substrate and most of the materials required are organics [4]. In this respect, the ink-jet printing technique is considered to be candidate process.

We here developed a conductive ink which contains silver nano-particles and a processing method of conductive line generation by ink-jet printing. To formulate well-performing conductive ink, the metal particles should be mono-dispersed nano-particle. They must also be well dispersed in a solvent as an ink, meeting various requirements in the aspects of fluidic properties for stable jetting. Using our piezoelectric driven ink-jet device, the ink should have a viscosity of 0.5–40 mPa·s, Newtonian flow behavior, and surface tension of 20–70 mN/m [5]. In particular, the achievement of high conductivity at low temperatures requires sub-100 nm sized metal nano-particles dispersed at sufficiently high solid content [6–9].

We have studied a method of patterning the conductive line on flexible plastic substrate by ink-jet printing of nano-sized silver ink. Silver nano-particles that have the size of about 20 nm was synthesized by polyol process [10]. Polyimide (PI), polyethylene naphthalate (PEN), and polyethylene terephthalate (PET) were used as flexible plastic substrates. We have investigated the microstructural features, as well as the quality of the patterned dots and lines and the conductivity variation as a function of heat treatment temperatures.

EXPERIMENTAL

The silver nano particles were synthesized in our laboratory by the well-known polyol method [10]. Silver nitrate (99.9%, Aldrich) used as a precursor of silver nano particles was dissolved in polyol medium. This solution was stirred vigorously in a reactor with a reflux condenser, followed by heating and reaction. After the reaction completes, the solution was cooled to room temperature, and the silver particles were separated from liquid by centrifugation and repeatedly washed with ethanol. The resulting particles were dried at room temperature.

The synthesized silver nano particles were dispersed in our propriety solvent system by adding a dispersant. The solid loading of the ink was 10–30 wt%. The formulated ink was ball milled for 24 h, followed by filtration through a 5 μm nylon mesh.

The silver conductive ink was printed by an ink-jet printer onto various flexible polymeric substrates. The printer set up consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle manufactured from Microfab Technologies, Inc. (Plano, TX) and the diameter of orifice was 30 and 50 μm. With 30-μm orifice, it has some problem that is clogging of the nozzle on the heated substrate and it is a common affair when a particulate ink is printed with volatile solvents or printed on heated substrate. So, we used the nozzle with 50-μm orifice for investigation of substrate heating effect on patterned images. The print head was mounted onto a computer-controlled three-axis gantry system capable of movement accuracy of ± 5 μm. The gap between the nozzle and the surfaces was maintained at about 0.5 mm during printing. The uniform ejection of the droplets was performed by applying ~ 35 V impulse lasting ~ 20 μs at a frequency of 0.5–200 Hz. CCD camera equipped with a strobe-LED light was employed to watch individual droplet by which the physical properties of the droplets were analyzed. There is not much difference of applied pulse conditions for two different sized nozzles, but they ejected two different sized droplets.

The shape and size of the synthesized silver nano particles were observed using scanning electron microscopy (SEM, JSM-6500F, JEOL), transmission electron microscopy (TEM, JEM-2010, JEOL) and the particle size distribution was obtained by image analysis. The surface morphology of the silver films and the microstructure of the printed dot and line were observed by optical microscopy (Leica, DMLM) and SEM. The resistivity was calculated from sheet resistance which was measured by 4-point probe (Chang Min Co., Ltd., CMT-SR200N) and the thickness of the Ag films which was obtained by SEM observation.

RESULTS AND DISCUSSION

The SEM and TEM images of the synthesized silver nano-particles and their particle size distribution are exhibited in Figure 1. The size distribution of silver nano particles shows 21 ± 4 nm sized and monodisperse particles. The X-ray diffraction pattern of the synthesized silver nano particles, presented in Figure 2, shows the peaks characteristic of metallic silver and the synthesized silver powders exhibit good crystallinity.

The particles were dispersed in a propriety solvent by ball-milling and ultra-sonication. The mixture of main solvent and small amount of co-solvent was used as the solvent for inks to prevent from forming

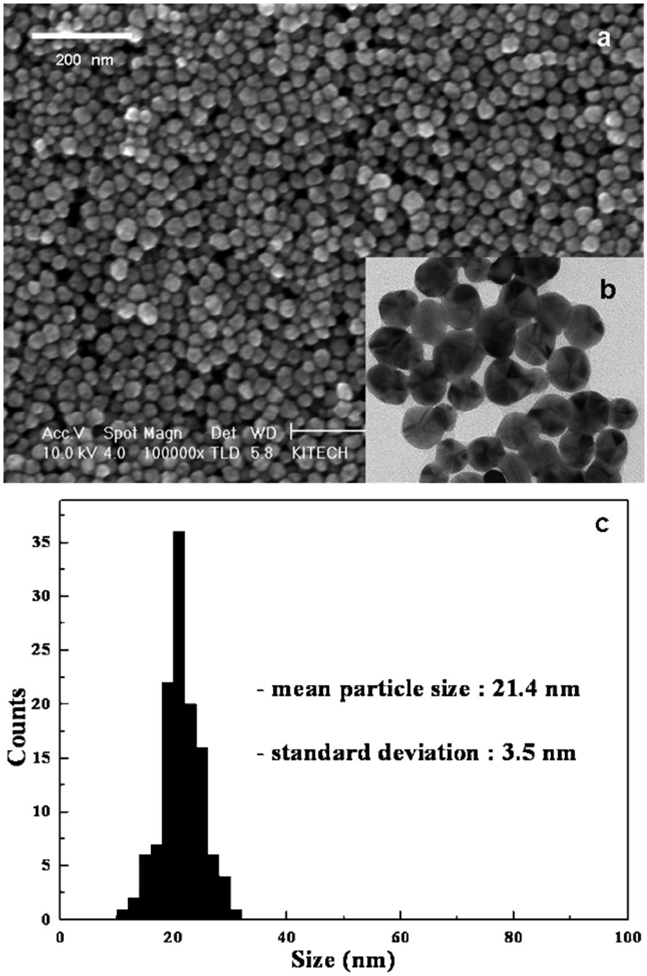

FIGURE 1 (a) SEM and (b) TEM images of the synthesized silver nano particles for conductive ink and (c) particle size distribution by image analysis.

a coffee-ring shape of printed patterns. Dispersion stability of the prepared conductive silver inks was excellent. Inks exhibit Newtonian rheological behavior. The viscosity of silver ink was about 10 mPa·s at shear rate of $50\,s^{-1}$ as measured by cone and plate viscometer and the surface tension of the ink was about 30 mN/m.

Various conductive patterns were printed successfully on flexible polymeric substrates including polyimide (PI), polyethylene naphthalate (PEN), and polyethylene terephthalate (PET). For our

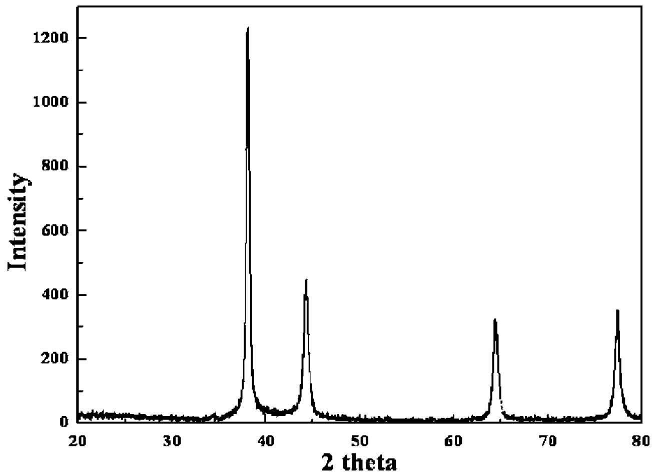

FIGURE 2 XRD diffraction patterns of the synthesized silver nano particles.

specific research on the ink-jet printed dots and lines and the conductivity variations of the printed films as a function of temperatures, heating up to 300°C, we used polyimide film as a substrate, because of its high thermal stability.

To obtain smooth conductive patterns with high resolution, the various printing conditions, including the inter-spacing distance between dots, the substrate temperature, the printing speed which is related with firing frequency and the composition of the prepared silver ink were adjusted. Figure 3 shows ink-jet printed lines with our particulate silver ink whose solid loading is 25 wt% on the polyimide substrate of 25°C. The orifice size of nozzle was 30 μm with 200 Hz printing frequency and the droplet ejected from the nozzle has a diameter of about 40 μm and the size of deposited drops was about 95 μm. When the inter-spacing distance exceeded the diameter of the deposited drops the printed pattern consisted of individual dots as in Figure 3(a). Reducing the distance between adjacent drops and overlapping led to regrouping of the drops on the substrate surface. In Figure 3(b), at an 80-μm distance the adjacent drops merged forming the larger and oval drops and partially continuous line was formed. Further reducing of the inter-spacing distance between the drops to 60 μm produced continuous and smooth lines with about 85-μm width (Fig. 3(c)) which is smaller size than the deposited single dots of 95-μm size because of merging between deposited dots. Reducing the inter-drop distance below 60 μm provided no further improvement in the line shape and rather led to increase in the line

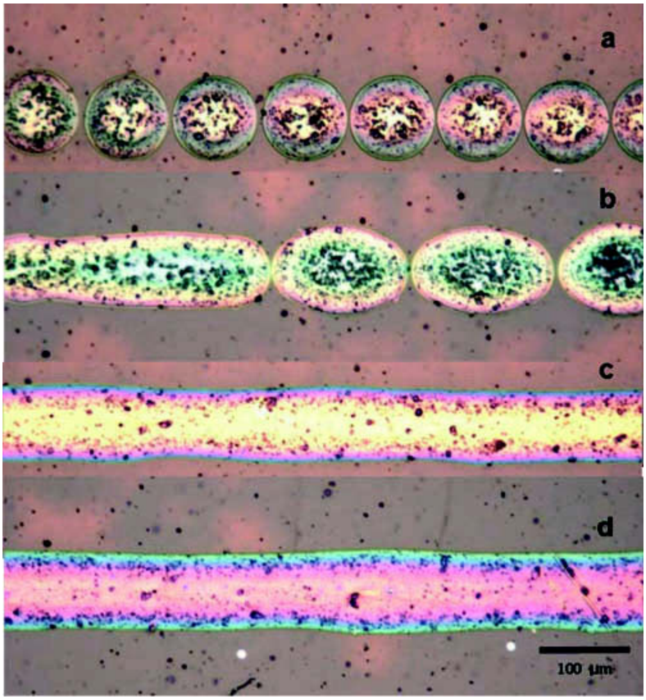

FIGURE 3 Optical microscopic images of the printed patterns using nanoparticle silver ink: inter-dot spacing of (a) 100 µm, (b) 80 µm, (c) 60 µm and (d) 50 µm.

width. For example, at a 50-µm distance the line width was 95 µm. The shape of the lines printed at lower substrate temperatures of 25°C suggests the merging of the individual printed drops prior to complete solvent evaporation. When substrate heated, however, the deposited dots and lines show some different deposit morphologies.

For the investigation of influence of the substrate temperature during printing on the shapes of dots and lines, substrate temperatures varied from 25°C, 50°C, to 75°C. The diameter of nozzle used was 50 µm and the ejected droplet from nozzle has the diameter of about 60 µm. This single droplet produced about 180 µm sized dot after drying when the substrate was maintained at room temperature. In contrast, the size of the printed single dot was reduced to about 110 µm with increasing pre-heating substrate temperatures. After the removal of solvents, the coffee-ring shaped dots (i.e., the segregation of the particle at the periphery of the dot pattern) were observed. However, the increases in both silver particles loading and pre-heated substrate temperature could reduce coffee-ring effect of the deposited dot. Figure 4 shows SEM image of the deposited dots which were printed at room temperature with the ink of 20 wt% silver particles (Fig. 4(a)) and printed at 75°C with the ink of 25 wt% silver particles (Fig. 4(b)). At the elevated temperature of the substrate, drying time of deposited dots became shorten and the deposited ink droplet did not spread much. Thus, the deposited dot size decreased and the particles do not have sufficient time to be transported to the edge of the droplet driven by outward solvent flow.

With the nozzle of 50 μm orifice, patterning of the conductive lines was also achieved by the adjustment of spacing between the printed dots except for larger deposited dot size and line width than that with 30 μm nozzle. Printing condition of 100 μm dot inter-spacing produced a smooth continuous line with the line width of about 150 μm at room temperature and dot spacing of more than 100 μm made partially discrete line while printing with less than 100 μm increased the line width with decreasing dot inter-spacing distance. This process of continuous line formation by merging of printed dots from reduction of inter-dot spacing was not different when substrate temperature elevated up to 50°C.

Figure 5 shows the ink-jet printed continuous lines at the condition of substrate temperature at 75°C. The conductive line printed at a frequency of 200 Hz (Fig. 5(a)) shows smooth line, while the printed line at 0.5 Hz exhibits a little different feature. When printing at frequency of 200 Hz, the deposited dots are merged with the previous dot deposited nearby that is partially dried. Final printed feature was continuous smooth, but wider line, although the substrate heating makes

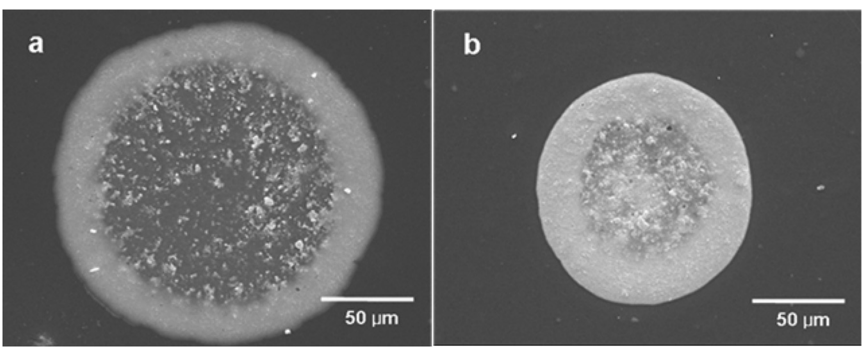

FIGURE 4 SEM images of the printed single silver dot: (a) ~180 μm printed with the ink of 20 wt% at 25°C and (b) ~110 μm printed with the ink of 25 wt% at 75°C.

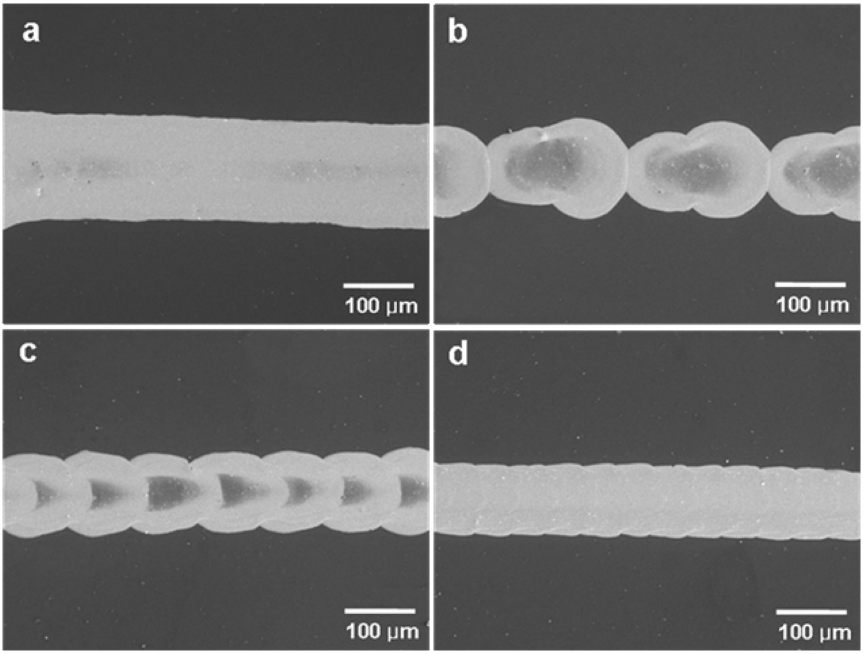

FIGURE 5 SEM images of the printed silver patterns on polyimide film at a frequency of (a) 200 Hz and (b)/(c)/(d) 0.5 Hz: Printed dot spacing is (a) 100 μm, (b) 100 μm, (c) 90 μm, and (d) 50 μm.

the ink dry fast. However the printing at a very low frequency of 0.5 Hz produced continuous line by overlaying the dried dots due to sufficient time available for the ink droplet to dry prior to the deposition of next ink droplet. By decreasing inter-spacing distance and overlaying droplets, it is possible to remedy the coffee-ring effect caused by previous droplets. This results in the formation of relatively uniform smooth line with improved resolution.

To investigate the conductivity of the ink as a function of heat-treatment temperature, the silver ink films were printed on a polyimide substrate. The silver ink printed films on polyimide was heat-treated on a hot-plate at temperatures from 100°C to 300°C, for 30 min. The conductivity increased with increasing temperature. Especially the heat-treatment above 200°C makes the conductivity become constant and the resistivity of Ag films was 2–3 times of silver bulk resistivity (Fig. 6). The heat-treatment temperature of 200°C is low enough to apply to direct metal patterning on polymeric films such as polyethersulfone (PES) and polyimde (PI) films for flexible

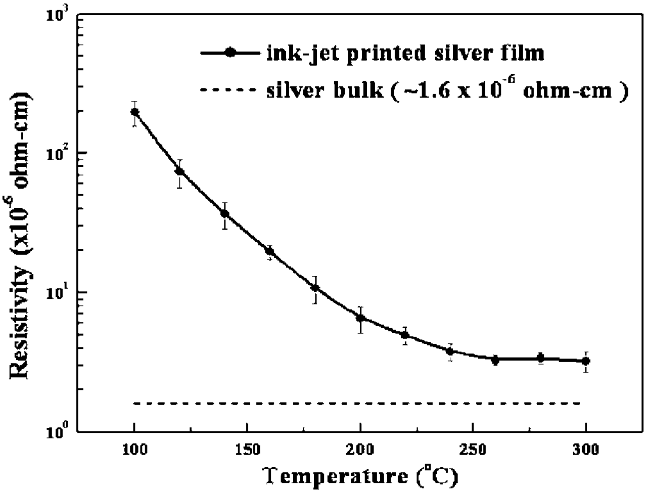

FIGURE 6 4-point probe measurement of silver film conductivity according to heat-treatment temperature.

electronics as a substrates [11]. High conductivity at low heat-treatment temperature can be explained from microstructural observation of the silver films heat-treated at varying temperatures.

The microstructure of the silver nano particle films heat-treated at temperature from 100°C to 300°C was presented in Figure 7. The film heat-treated at 100°C showed no significant difference in particle shape and size compared with the as-synthesized particles. The particles which were sintered between each particle are observed at 140°C. There occurs necking rather than complete melting and these sintered particles are not observed at below 140°C. The films heat-treated at 200°C show a dramatic change of particle shape from discrete and spherical particles to continuous and sintered particles. Furthermore, the particle size gradually increased to form a grain structure at 300°C. Bulk silver has a high melting point (T_m) of 960°C and the sintering temperature (T_s) is also high, but, if the silver particle size is reduced to nanoscale, the melting point and the sintering point can be significantly lowered [12].

CONCLUSIONS

We developed a conductive nano-silver ink and achieved a technique by which the defined pattern is produced by ink-jet printing. This offers the potential of replacing photolithography which has the

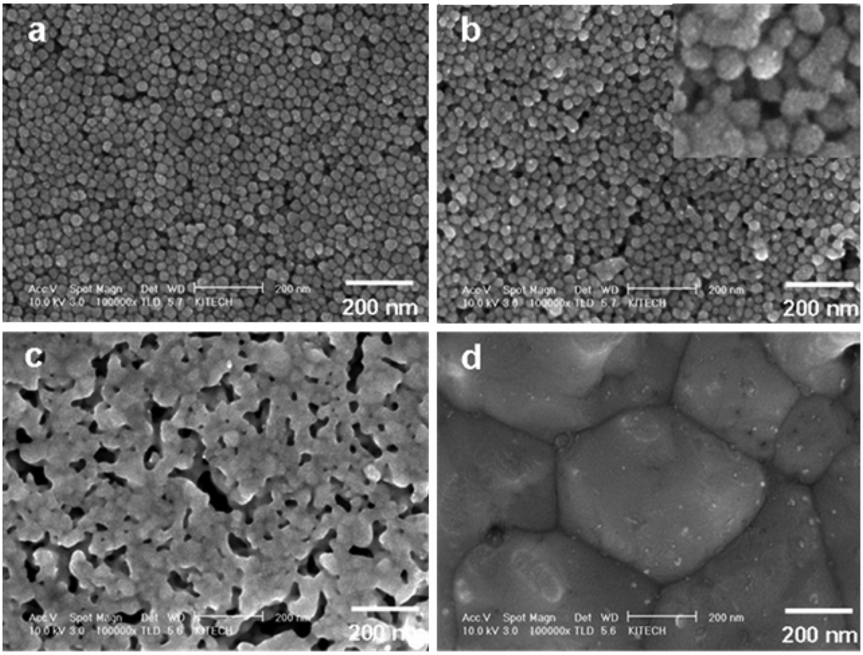

FIGURE 7 SEM images for the Ag nano particle films as a function of heat-treatment temperatures: the films heat-treated at (a) 100°C, (b) 140°C, (c) 200°C, and (d) 300°C.

several complex processing steps. We also examined the conductivity variation of silver nano particulate film as a function of heat-treatment temperatures. It is observed that the printed line becomes highly conductive at low temperature, below 200°C. This result shows that conductive pattern by ink-jet printing can be adapted to flexible display devices, such as organic light emitting devices (OLED) and organic thin film transistor (OTFT) for driving flexible LCD or OLED, which require low temperature processing.

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