Ink-Jet Printing of Silver Conductive Patterns for Flexible Electronics

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Abstract

We have developed a conductive ink applicable to ink-jet printing to fabricate conductive lines on flexible substrates. Nano-sized silver particles having ~ 20nm diameter was used for the direct metal printing. Silver conductive ink was printed on polymer substrates such as polyimide (PI), polyethylene naphthalate (PEN), and polyethylene terephthalate (PET) for the application to flexible electronics. The printing conditions of pulse frequency, pulse amplitude, xy-stage moving velocity and substrate temperature were optimized to achieve smooth conductive track with high resolution. After heat-treatment at temperature of about 100 ~ 300℃ for 30 min, the printed silver patterns exhibit metal-like appearance and conductivity. The influence of the printing conditions on the microstructure and conductivity of the conductive track was investigated.

Introduction

Ink-jet printing technique of functional materials is of interest in a variety of fields including displays, electronics, optics and sensors 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. Low temperature processing is also very useful for the fabrication of flexible display devices. Flexible displays or flexible electronics have to use a flexible plastic substrate and most of the materials composing a device are organic materials.[2] For this reason, ink-jet printing technique is considered to be candidate process.

In this work, we here developed a conductive ink which contains silver nano-particles and a processing method of conductive line patterning by ink-jet printing. For the excellent 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-mode ink-jet device, the ink should have viscosity of 0.5-40 mP-s, Newtonian behaviour, and surface tension of 20-70 mN/m.[3] Finally, for the conductivity at low temperatures, sub-100nm sized metal nano-particles dispersed at sufficient concentration are required.[4]

We studied a method of patterning the conductive line on flexible plastic substrate by ink-jet printing of nano-sized silver ink. Silver nano-particles which have the size of about 20nm was synthesized by polyol process.[5] Polyimide (PI) was used as flexible plastic substrates. We investigated the microstructural features, as well as quality of the patterned dot and line, conductivity variation as a function of heat treatment temperature.

Experimental

The Ag nano particles were synthesized in our laboratory by well-known polyol method. Silver nitrate (99.9%, Aldrich) used as a precursor of Ag 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. Finally we obtained Ag nano particles whose size was 21.4 ± 3.5 nm.

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

The Ag conductive ink was printed by an ink-jet printer onto polyimide substrates. The printer set up consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle manufactured from Microfab Technologies, Inc. (Plano, TX) with a 50-µm orifice. 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 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.

The surface morphology of the Ag films and the microstructure of the printed dot and line were observed by SEM (JEOL-6500F, JEOL). The conductivity of silver films was measured by 4-point probe (Chang Min Co., Ltd., CMT-SR200N).

Results

Properties of Conductive Silver Ink

Figure 1 shows SEM image of the synthesized silver nano-particles with size of about 20nm. The particles were dispersed in a 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 a coffee-ring shape of printed patterns. Dispersion stability of the prepared conductive silver inks was excellent. Inks exhibit Newtonian rheological behaviour. The viscosity of silver ink was 10-20 mP-s and the surface tension was about 30-40 mN/m.

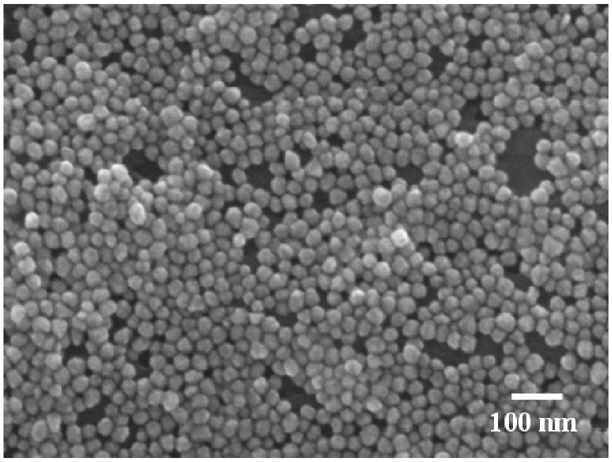

Figure 1. SEM image of silver nano-particles of ~20nm diameter.

The prepared silver ink was coated on a slide glass to measure the conductivity of the ink. The silver ink coated on glass was dried at temperature of 70°C for 1hr, followed by heat-treatment on a hot-plate at temperatures from 100°C to 300°C, for 30min. 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 Ag bulk resistivity (Figure 2). High conductivity at low heat-treatment temperature can be explained from microstructural observation of the Ag films heat-treated at varying temperatures.

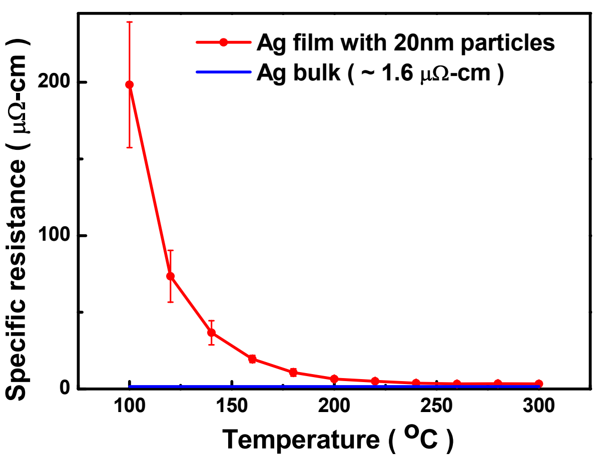

Figure 2. 4-point probe measurement of silver film conductivity according to heat-treatment temperature.

The microstructure of the Ag films heat-treated at temperature from 100°C to 300°C was presented in Figure 3. 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 are 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.

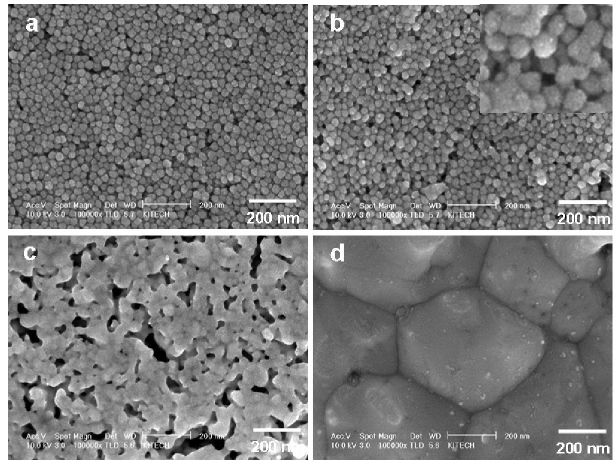

Figure 3. SEM images for the Ag nano particle films as a function of heat-treatment temperatures: the films heat-treated at (a) 100°C, (b) 140°C, (c) 200°C, and (d) 300°C.

Bulk Ag has a high melting point (T_m) of 960°C and the sintering temperature (T_s) is also high, but, if the Ag particle size is reduced to nanoscale, the melting point and the sintering point can be significantly lowered.[6]

Ink-Jet Printing of Silver Conductive Patterns

Silver conductive inks are printed on flexible plastic films using a piezoelectric DOD ink-jet printing device. As the flexible plastic substrate, polyimide film was used. Substrate temperature varied from 25°C, 50°C, to 75°C. The ejected droplet from nozzle has a diameter of about 60 μm, a volume of about 110 pl and the velocity of 1 - 2 m/s. This single droplet makes about 180 μm sized dot at room temperature and the size of the printed single dot is reduced to about 110 μm with increasing pre-heating substrate temperature. After the removal of solvents, the coffee-ring shaped dots were observed. However, the increases in silver particles loading and pre-heated substrate temperature have eliminated coffee-ring effect of deposited dot. Figure 4 shows SEM image of the deposited dots which were printed at room temperature with ink of 20 wt% silver particles (Figure 4(a)) and at 75°C with ink of 25 wt% silver particles (Figure 4(b)). At the elevated temperature of substrate, drying time of deposited dots became shorten and the deposited dot did not spread much, finally dot size decreases and coffee-ring effect is reduced due to a limited migration of the particles toward air/liquid/substrate triple phase boundary.

Patterning of the conductive lines was achieved by adjustment of spacing between the printed dots, controlling resolutions of image. Printing condition of 100 μm dot inter-spacing makes a smooth continuous line with line width of about 150 μm at room temperature. Dot spacing of more than 100 μm makes partially discrete line while printing with less than 100 μm increases line width with decreasing dot inter-spacing distance.

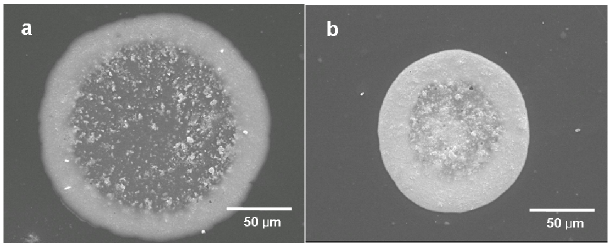

Figure 4. SEM image of the printed single silver dot: (a) ~ 180 μm printed with the ink of 20 wt% at 25 °C and (b) ~ 110 μm printed with the ink of 25 wt% at 75 °C.

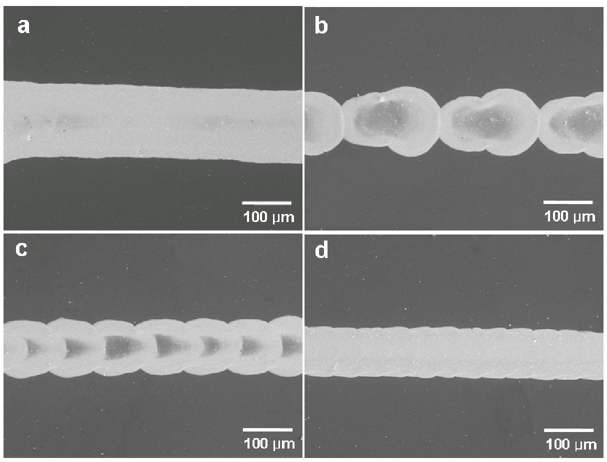

Figure 5. SEM images of the printed silver patterns on polyimide film at a frequency of (a) 200 Hz and of (b)/(c)/(d) 0.5 Hz: Printed dot spacing is (a) 100 μm, (b) 100 μm, (c) 90 μm, and (d) 50 um.

Figure 6. Various patterns ink-jet printed using Ag nano-particle on polymeric substrates.

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 [Figure 5 (a)] shows smooth line, while the printed line at 0.5 Hz, which is very low frequency compare to 200 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 exhibits continuous smooth, but wide line, although the substrate heating makes it dry fast. However the printing at a very low frequency of 0.5 Hz produces continuous line by overlaying the dried dots due to sufficient time for dot available to dry prior to 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.

Figure 6 shows various conductive patterns printed on flexible polymeric substrates including polyimide (PI), polyethylene naphthalate (PEN), and polyethylene terephthalate (PET).

Summary

Recently much research efforts have been attempt to use ink-jet printing technology for a variety of the fields such as displays, electronics, etc. 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 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 become 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.

Acknowledgements

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Author Biography

Dongjo Kim received his BS in school of advanced materials science and engineering from Yonsei University and is now PhD candidate in same affiliation. His work has focused on the development of materials for ink-jet printing and functional materials for ink-jet printing, especially conductive ink.