Ink-Jet Printing of Conductive Silver Inks for Flexible Display Devices

Dongjo Kim, Jungho Park, Sunho Jeong, and Jooho Moon

School of Advanced Materials Science and Engineering,

Yonsei University, Seoul 120-749, Korea

Tel. +82-2-2123-2855, jmoon@yonsei.ac.kr

Abstract

We have studied ink-jet printing method for patterning conductive line on flexible plastic substrates. Synthesized silver nano-particles of ~20nm were used for the conductive ink and the printed patterns exhibit a smooth line whose linewidth is below 100 µm. This ink-jet printing technique can be applied to flexible displays and electronics.

1. 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 of 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 patterned dot and line, conductivity variation as a heat treatment temperature.

2. Experimental

The Ag nano particles used 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 is 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 30-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 at 25°C and 40% relative humidity.

The uniform ejection of the droplets was performed by applying ~ 35 V impulse lasting ~ 20 μs at a frequency of 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 was observed by SEM (JEOL-6500F, JEOL) and the microstructure of printed dot and line after drying was investigated by confocal laser scanning microscopy (LSM 5 Pascal, Carl Zeiss). The conductivity of silver films was measured by 4-point probe (Chang Min Co., Ltd., CMT-SR200N).

3. Results

3.1 Properties of Conductive Silver Ink

Figure 1 shows SEM image of synthesized silver nano-particles with size of about 20nm. The particles were dispersed in a solvent by ball-milling and ultra-sonication. Solid loading of silver powder varies from 10wt% to 30wt%. 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.

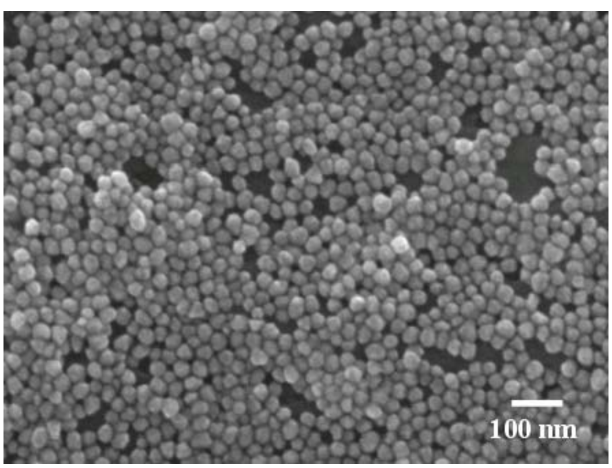

Figure 1 SEM image of silver nano-particles of ~20nm diameter.

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℃ for 1hr, followed by heat-treatment on a hot-plate at temperatures from 100℃ to 300℃, for 30min. The conductivity increased with increasing temperature. Especially the heat-treatment above 200℃ makes the conductivity become constant and the resistivity of Ag films was 2 – 3 times of Ag bulk resistivity (Figure 2). This result of conductivity appearance at low heat-treatment temperature was explained from microstructures of Ag films at each heat-treatment temperatures.

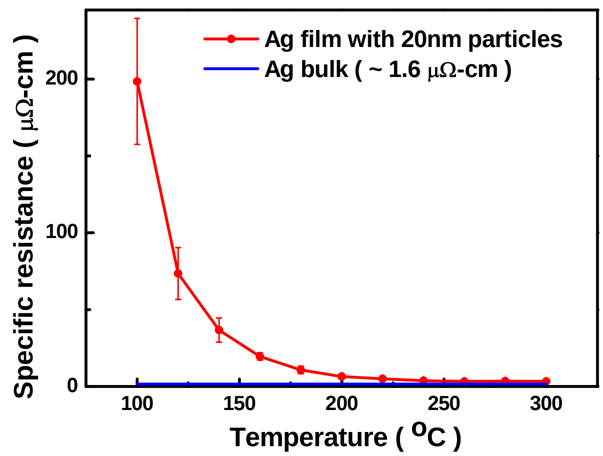

Figure 2 4-point probe measurement of silver film conductivity according to heat-treatment temperature.

The microstructure of Ag films heat-treated at temperature from 100 ℃ to 300 ℃ was presented as a function of temperature in Figure 3. The film heat-treated at 100 ℃ showed no significant difference in particle shape and size compared with as-synthesized particles. The particles which are sintered between each particle are observed at 140 ℃. There is necking rather than complete melting and these sintered particles are not observed at below 140 ℃. Films heat-treated at 200 ℃ show a dramatic change of particle shape from discrete and spherical particles to continuous and sintered particles. Furthermore, particle size gradually increased to form a grain structure at 300 ℃.

Bulk Ag has a high melting point (T_m) of 960 ℃ 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].

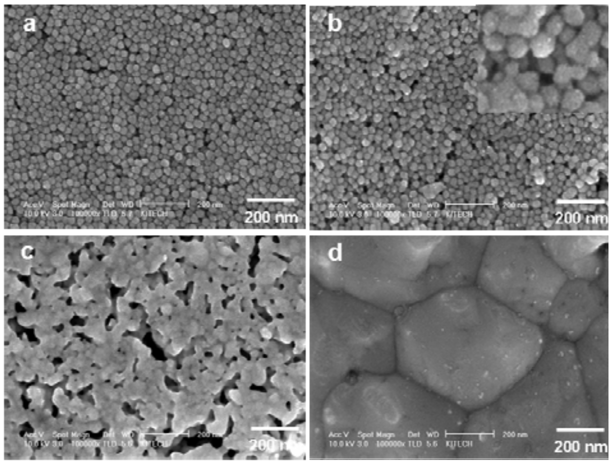

Figure 3 SEM images for the Ag nano particle films as a function of heat-treatment temperatures: the films heat-treated at (a) 100 ℃, (b) 140 ℃, (c) 200 ℃, and (d) 300 ℃.

3.2 Ink-Jet Printing of Silver Conductive Patterns

Silver conductive inks are printed on flexible plastic films using a piezoelectric DOD ink-jet printing device. The ejected droplet from nozzle has a diameter of about 50 μm and the velocity of 2-3 m/s. This single droplet makes about 85-90 μm sized dot, after the removal of solvents and coffee-ring shaped dots were observed. However, the use of the mixed solvent have reduced coffee-ring effect of deposited dot by increasing silver particles loading and increasing amount of co-solvent (Figure 4).

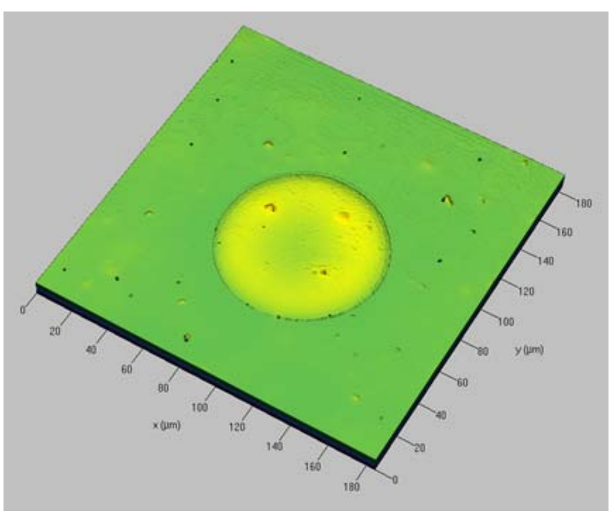

Figure 4 Confocal microscopy image of the printed silver dot (Dot size is ~85 μm).

Patterning of the conductive lines was achieved by adjustment of spacing between the printed dots, controlling resolutions of image. Printing condition of 50 μm dot inter-spacing makes a smooth and a continuous line with line width of about 90 μm. Dot spacing of more than 50 μm makes partially discrete line and that of less than 50 μm increases line width (Figure 5). Figure 6 shows various conductive patterns printed on flexible polymeric substrates including polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and polyimide (PI).

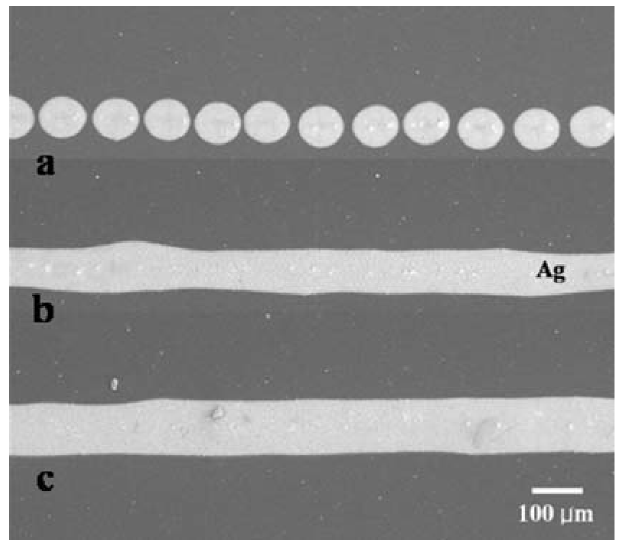

Figure 5 SEM images of the printed silver patterns on polyimide film: Printed dot spacing is (a) 100 μm, (b) 50 μm, and (c) 25 μm. Dot spacing of 50 μm makes a continuous silver line with ~ 90 μm width.

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

4. 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 by ink-jet printing. This offers the potential of replacing photolithography which has the several complex processing steps.

We also examined the conductivity of silver ink at various temperatures. It is observed that the printed line become highly conductive at low temperature, below 200 ℃. 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.

5. Acknowledgements

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6. References

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