Fabrication of Conductive Patterns by Ink-Jet Prining of Copper Ink

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Abstract

We have studied ink-jet printing method for patterning of conductive line on flexible plastic substrates. Synthesized copper nano-particles of ~40 nm were used for the conductive ink and the printed patterns exhibit a smooth line whose line width is about 100 μm.

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 its low temperature process, direct writing, solution processability, and rapid prototyping.[1] Especially, ink-jet printing of conductive ink is an attractive alternative to photolithography[2,3] for direct patterning conductive lines owing to low-cost, low-waste, and simple process. Moreover, ink-jet printing of conductive ink is suitable for the production of the large-are flexible display, since this technology operates at low temperature and does not use corrosive solvent that are needed in etching procedure.

Metallic nano powder suspension is selected for conductive ink material among several candidates such as molten metals, conductive polymers, organo-metallic compounds, metal precursors, metallic nanoparticle suspensions and etc. In last decades, there are many interests for metallic nano powder suspension conductive ink.However most of the researches are focused on novel metals such as platinum, gold, and silver because of their high conductivity and stability in air. These novel metals are expensive, so that there are growing needs for alternatives that are inexpensive, highly conductive, and air stable.

In this work, we here developed a conductive ink which contains copper nano-particles and a processing method of conductive line patterning by ink-jet printing. For achieving the excellent conductivity, the metal particles should be mono-dispersed and nano-sized. 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 flow behavior, and surface tension of 20-70 mN/m.[4]. Finally, for the conductivity at low temperatures, sub-100 nm sized metal nano-particles dispersed at sufficient concentration are required.[5]

2. Results

2.1 Synthesis of copper powder

First of all, mono-disperse and nano-sized copper particles that are not oxidized at atmosphere is required to prepare copper nano powder suspended conductive ink. The printed conductive pattern should be annealed to generate conductive path by sintering of particles. So the size of particles should be reduced to nano scale because melting temperature of metal decrease drastically at nano scale due to increase of specific surface area.

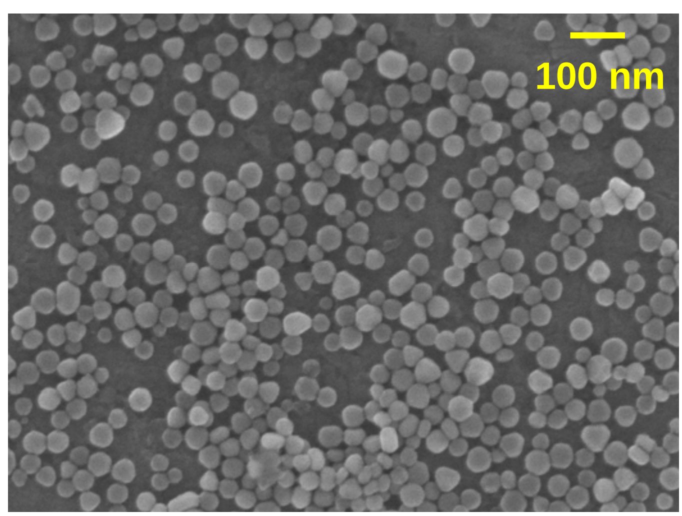

Figure 1. SEM image of copper nano particles of ~40nm diameter.

And the particles should be monodispere to increase packing density of printed particulate films. When the particles have monodisperse spherical shape, they could make a close packed structure.

Copper particles were prepared by polyol process. Capping molecule was dissolved in the DEG. Reducing agent was added to the solution and the solution was heated. The solution copper precursor in deionized water was injected to the heated DEG solution. After 1 hr of reaction the solution was cooled to room temperature and the particles were separated by centrifugation and then washed for 4 times. Figure 1 shows a resultant particles that are monodisperse and have mean diameter of 40~50nm.

In order to obtain highly conductive lines at lower temperature, it is necessary to use phase-pure crystalline metal nanoparticles (< 100 nm). However, copper is thermodynamically unstable at atmospheric condition and is easily oxidized into either Cu_2O or CuO, both of which are less conductive compared to copper. To solve this problem, Cu nanoparticles are coated with proper capping molecules which can prevent the Cu from excess surface oxidation in air and at the same time for agglomeration when dispersed in the ink.

Figure 3 shows XRD data of the synthesized copper particles depending upon storage conditions.

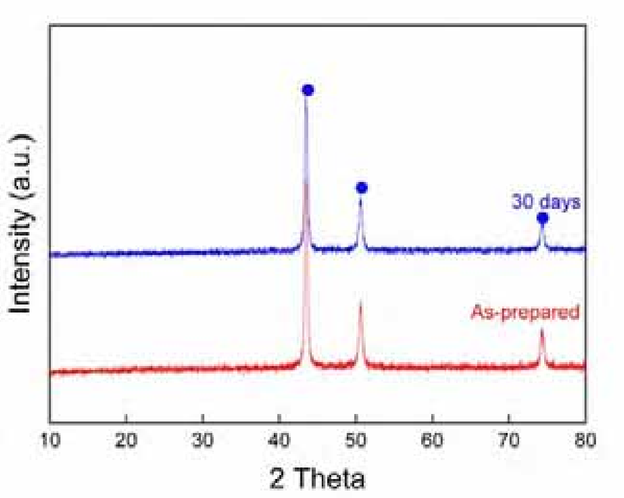

Figure 2 X-ray diffraction patterns for copper nanoparticles: (a) as-synthesized at 140 ^{o}C and (b) after exposure to atmospheric condition for 30 days

The obtained diffraction patterns for the as-synthesized particles are phase-pure crystalline copper characteristic peaks without any copper oxides as a secondary phase. The synthesized Cu particles exposed to ambient condition for 30 days exhibit the identical XRD patterns, suggesting that our copper nanoparticles are relatively stable against oxidation at least at X-ray detection level.

2.2 Properties of Conductive Copper Ink

Ink properties such as viscosity, surface tension, solid loading, wettability, and dispersion stability have great effect on the morphology of printed pattern. In general, printing with a high contact angle, high viscosity, and high tension ink produces smaller sized dot or line patterns as compared to the ink that has opposite properties. The ink was prepared by dispersing copper particles in a solvent mixture and dispersed by ball milling. Copper ink exhibits Newtonian rheological behavior. The viscosity of copper ink was about 5-10 mP·s and the surface tension was about 30-40 mN/m. These properties are the value in the satisfying the jetting condition as mentioned below[4].

The conductive path is generated when the conductive pattern is annealed. The conduction path between the particles is established by interparticle neck formation. The resistivity of annealed pattern is affected by two factors. One is copper particle's properties such as size and size distribution. The necking between particles is occurred at low temperature when size of particle is small. And size distribution affects the packing density. The other factor is dispersion stability of metal nanoparticle suspension. It also influences on the packing density. If dispersion density of ink is poor, there exist some coagulated particles and these coagulated particles hinder the particle neck formation.

To measure the conductivity of the ink, the prepared copper ink was coated on a slide glass. The coated film of copper ink was dried at temperature of 70℃ for 1hr, followed by heat-treatment in a vacuum annealing chamber (10^{-3} torr) at temperatures from 225℃ to 350℃, for 30min. Figure 3 shows resistivity variation as a function of annealing temperature. The conductivity increased with increasing temperature. Especially the heat-treatment above 300℃ makes the conductivity of the film become constant. After heat treatment at 300℃ for 1 hr, the resistivity of 9 μΩ·cm is exhibited, which is about eight times higher than that of bulk copper (1.7 μΩ·cm).

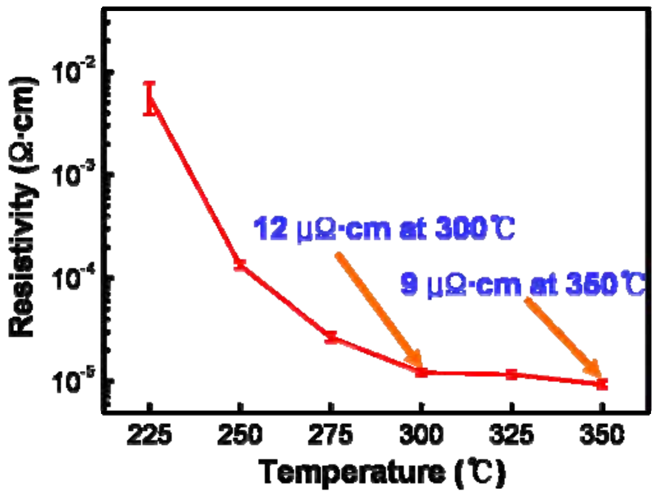

Figure 3. 4-point probe measurement of copper film conductivity

2.3 Ink-Jet Printing of Conductive Pattern with Copper Ink

The printer setup consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle with a 30μm orifice size. The print head was mounted onto a computer-controlled three-axis gantry system. Printing condition was optimized by varying applying voltages, lasting time, head frequency, and inter-spacing between droplets. 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 ejected droplet from nozzle has a diameter of about 50 μm and the velocity of 2-3 m/s. This single droplet makes about 100 - 110 μm sized dot after drying on the polyimide substrate.

Figure 4 shows array of single dots and Figure 5 shows continuous lines at a selected printing condition. Printing an ink droplet of 50 μm in diameter produced a dot with a size of 100 μm after drying. There individual separated dots merge together forming a continuous line as the placing distance between the droplets becomes closer. In the case of 80 μm droplet inter-spacing, the printed pattern forms smooth and continuous lines with line-width of 100 μm, whereas discontinuous irregular line patterns are obtained when drolet inter-spacing is larger than 110 μm because droplet distance is larger than the diameter of single droplet.

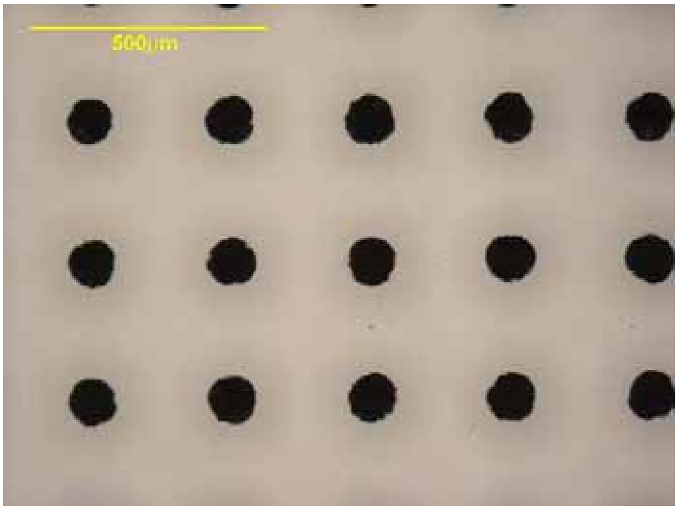

Figure 4. Printed dot by ink-jet printing (individual dot size is about 103 μm)

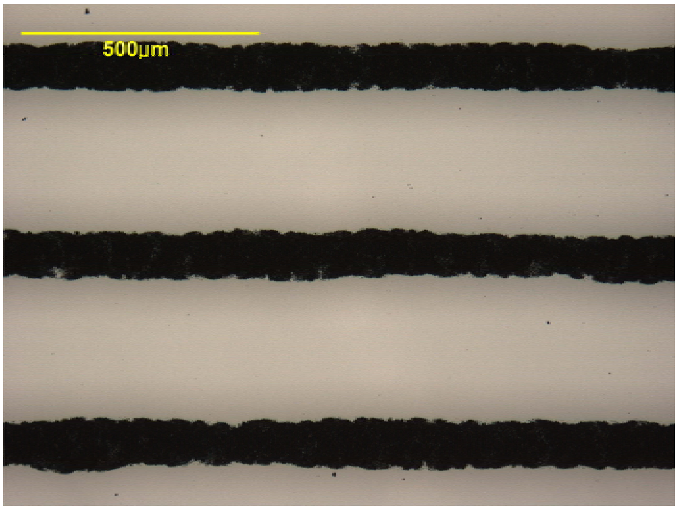

Figure 5. Printed line by ink-jet printing (line width is about 101 μm)

3. Conclusions

Recently much research efforts have been attempt to use ink-jet printing technology for a variety of the fields such as displays, electronics, etc. To achieve a technique by which the direct pattern is produced by ink-jet printing, copper nano particles and conductive ink containing copper nano particles are developed. The copper conductive ink was printed onto polyimide substrate. Continuous and smooth lines with line-width of 100 μm were formed when droplet distance was 80 μm. The resistivity of annealed film is 9 μΩ·cm after annealing at 300℃ for 1hr. This resistivity value is just about eight times larger than bulk copper's resistivity. 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.

4. Acknowledgements

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5. References

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