

## Cu-based ink-jet printable inks for highly conductive patterns at lower temperature

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### Abstract

*The metal films ink-jetted using the conductive ink based on a mixture of copper and silver nanoparticles were investigated. The porosity and resistivity of films were minimized by adjusting the mixing ratio of Cu and Ag nanoparticles. We demonstrated that the printed tracks with good conductivity could be obtained at sufficiently lower annealing temperatures where plastic substrates could be used.*

### 1. Introduction

Ink jet printing technology based on the use of metal nanoparticles with high electronic conductivity has been considered as a promising alternative to traditional lithography technology [1-5]. Among conductive metals such as gold and silver, copper with high conductivity and inexpensiveness is a good material for the application in the conductive tracks. However, when Cu nanoparticle is synthesized using chemical reduction process, the formation of oxide layer on the Cu surface is inevitable, because CuO is a thermodynamically stable phase in ambient atmosphere. The presence of surface oxide increases the annealing temperature due to its higher melting point ( $T_m$ ) and reduces the electrical conductivity. For example, bulk CuO has a higher melting point ( $T_m = 1330^\circ\text{C}$ ) and much higher resistivity ( $5.1 \times 10^7 \mu\Omega\cdot\text{cm}$ ) than copper ( $T_m = 1083^\circ\text{C}$ , resistivity  $= 1.72 \mu\Omega\cdot\text{cm}$ ). In other words, this surface oxide layer brings about further reduction in the film conductivity when annealed at temperature where the use of plastic substrate is allowed.

In order to develop higher conductive patterns at lower annealing temperatures, we try to improve the packing density of the metal particulate film by adding silver nanoparticles with a specified size with respect to the size of copper nanoparticles. Silver particles effectively fill the inter-particle pores between Cu nanoparticles, thereby the denser and

higher conductive patterns are obtained.

In this paper, we demonstrate conductive patterns with a reasonably high conductivity which were annealed at  $175^\circ\text{C}$  on transparent flexible substrate. The film conductivity improves due to enhanced particle packing density when small silver nanoparticles are mixed in that effectively fill the inter-particle pores between Cu nanoparticles. It should be noted here that silver nanoparticles were selected because they are easily synthesized with good size controllability. Any metal nanoparticles that meet physical dimension requirements as well as have high conductivity and low melting point would be usable. The microstructure and conductivity evolution of granular films as a function of the mixing ratio between Cu and Ag were investigated. We fabricated complex conductive tracks on a transparent substrate by ink-jet printing.

### 2. Experimental

The copper with the size of  $65 \pm 3\text{nm}$  and silver nanoparticles of  $21 \pm 2\text{nm}$  were synthesized in our laboratory by polyol method [6-7]. They were mixed at varying volume ratios from Cu:Ag = 2:1 to 4:1. The metal particles were dispersed in a mixed solvent of methanol, 2-methoxy ethanol, and ethylene glycol. The solid loading of all inks was 20 wt%. The formulated inks were milled by a planetary milling machine for 60 min, followed by filtration through a  $5 \mu\text{m}$  nylon mesh. The prepared conductive inks were printed with an ink-jet printer on a PES (thickness  $\sim 0.125\text{ mm}$ ) substrate. The printer set-up consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle manufactured by Microfab Technologies, Inc. (Plano, TX) with a nozzle diameter of  $30 \mu\text{m}$ . Uniform ejection of the droplets was achieved by applying a 35 V pulse lasting  $10 \mu\text{s}$  at a frequency of 1000 Hz. The diameter and velocity of the ejected droplets were

about 36  $\mu\text{m}$  and 3 m/s, respectively. The ink-jet printed films were annealed at various temperatures ranging from 150°C to 325°C for 90 min under vacuum condition ( $10^{-3}$  Torr) to form inter-particle connections for developing electrical conductivity.

### 3. Results and discussion

Figure 1 shows the SEM images of the synthesized copper and silver nanoparticles. The mean sizes of copper nanoparticles and silver nanoparticles are about 65 nm and 21 nm, respectively. We confirmed the existence of the surface CuO layer with a thickness of 2-3 nm by XPS and HR-TEM [8]. This surface oxide layer on the copper nanoparticle is expected to increase the annealing temperature and to reduce the conductivity of the film.

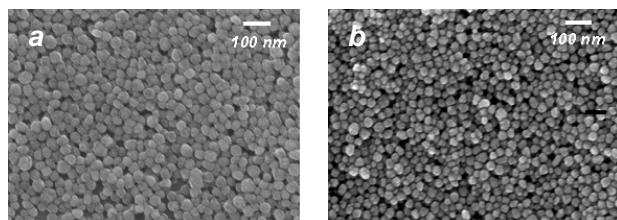


Fig. 1. (a) SEM image of copper nanoparticles which have the mean size of  $65 \pm 3$  nm. (b) SEM image of silver nanoparticles which have the mean size of  $21 \pm 2$  nm.

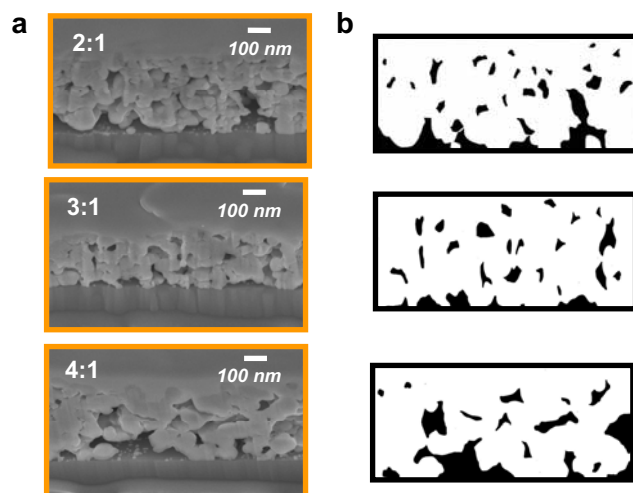


Fig. 2. (a) SEM images showing the cross-section of the printed films as a function of the Cu/Ag mixing ratio. The films were annealed at 200°C for 90 min under vacuum ( $10^{-3}$  Torr). (b) the binary image showing the metal and pore structures as a function of the Cu/Ag mixing ratio.

In order to develop higher conductive patterns at lower annealing temperatures, we try to improve the packing density of the Cu particulate film by adding silver nanoparticles with a specified size. The size of silver particles is selected in order to fit into the inter-particle pores between the Cu nanoparticles in the particulate film. We prepared the conductive films depending upon the mixing ratio of copper and silver nanoparticles. Figure 2 shows the cross-sectional images of these films annealed at 200°C. As determined by image analysis, when the volume ratio of the Cu particles to the smaller Ag particles varies from 4 through 3 to 2, the annealed density of the corresponding film is  $79\% \pm 1.5$ ,  $86\% \pm 1.7$ , and  $82\% \pm 2.1$ .

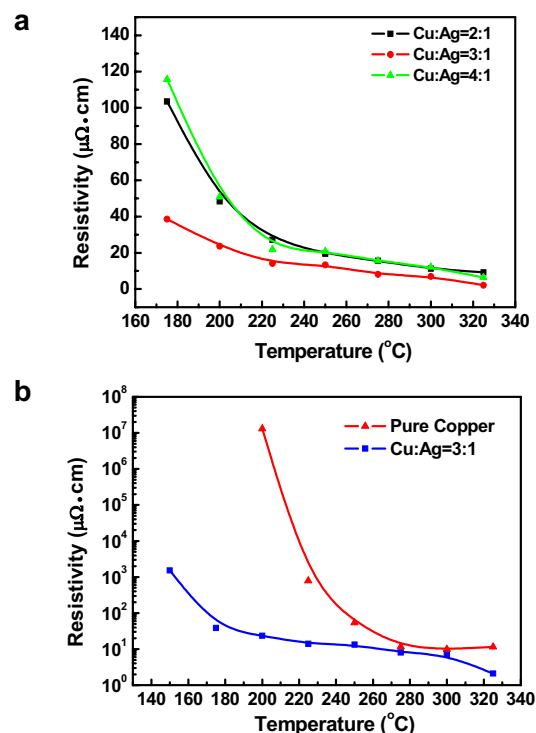
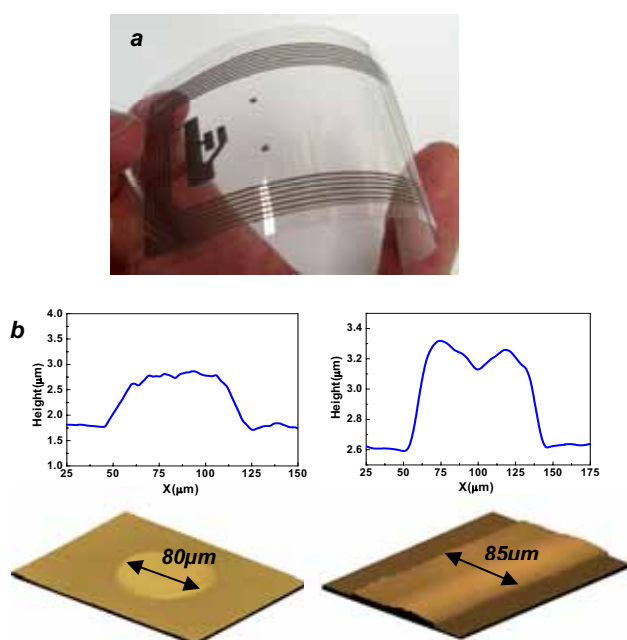


Fig. 3. (a) The resistivity variation as a function of annealing temperature for the mixed metal films with various Cu/Ag mixing ratios. (b) The variation in resistivity of pure Cu film and Cu-Ag mixed film as a function of annealing temperature.

Addition of small Ag particles with specific particle size and mixing ratio with respect to the larger Cu particles effectively maximizes the packing density by filling the interstices. The enhancement in the packing density means that there are more inter-particle contact areas, which enables the granular film to develop a denser nanoparticulate film structure when

annealed, resulting in better conductivity. To verify the effect of the density improvement, we measured the film resistivity as a function of the mixing ratio as shown in Fig. 3a. The film conductivity for all samples increases with increasing annealing temperature. The film composition of 3Cu1Ag exhibited the lowest electrical resistivity ( $23.6 \pm 2.5 \mu\Omega \cdot \text{cm}$  when annealed at  $200^\circ\text{C}$ ) compared to 2Cu1Ag ( $48.3 \pm 0.9 \mu\Omega \cdot \text{cm}$ ) and 4Cu1Ag ( $50.8 \pm 1.2 \mu\Omega \cdot \text{cm}$ ). The observed resistivity also matches well with the annealed density variation of the corresponding films. The effect of particle mixing becomes more evident when comparing the resistivity of the metal film composed only of Cu nanoparticles (Fig. 3b). There was significant improvement in the film conductivity ( $23.60 \mu\Omega \cdot \text{cm}$  when annealed at  $200^\circ\text{C}$ ) when annealed between  $150$  and  $250^\circ\text{C}$  as compared to that of the pure copper film ( $1.294 \times 10^7 \mu\Omega \cdot \text{cm}$ ).



**Figure 4. (a) Ink-jet printed complex conductive patterns on flexible and transparent PES substrates. The ink contains a mixture of Cu and Ag nanoparticles at a ratio of Cu:Ag = 3:1. (b) The cross-sectional profiles and the confocal laser scanning images of a single ink droplet after drying and a single printed line.**

To demonstrate the applicability of the mixed metal based conductive ink (Cu:Ag = 3:1) from which high conductive tracks form by annealing at low temperature,

we direct-wrote complex patterns on transparent plastic substrates. Figure 4 shows conductive patterns printed on flexible polyethersulphone (PES) substrate. Solvent evaporation from the printed single ink droplet produces a spherical dot pattern of diameter  $\sim 80 \mu\text{m}$ . The line pattern is generated by reducing the dot-to-dot distance. The separated dots begin to merge together at a distance of  $100 \mu\text{m}$ , and printing at an inter-dot distance of  $90 \mu\text{m}$  results in a continuous line with a  $\sim 85 \mu\text{m}$  line-width and relatively smooth edge definition. The conductive features exhibited relatively low electrical resistivity of  $38.6 \mu\Omega \cdot \text{cm}$  after annealing at  $175^\circ\text{C}$  for 90 min and  $23.6 \mu\Omega \cdot \text{cm}$  (10 times higher than theoretical resistivity) at  $200^\circ\text{C}$ .

#### 4. Summary

We have developed ink-jet printable ink containing Cu and Ag nanoparticles of different sizes, which can be used to form highly conductive tracks on a flexible substrate after annealing at low temperature. Addition of small Ag particles significantly improves the particle packing density by filling the pores between the larger Cu particles, which in turn facilitates faster sintering kinetics and better conductivity at lower temperatures. The particle size and volume ratio of the Ag particles with respect to the larger Cu particles should be well-controlled to achieve maximum packing density in the bimodal particle system, which is in good agreement with theoretical considerations based on the Furnas random packing model. The maximum annealed density of the film was determined to be 86% when Ag with a mean size of 20 nm was added to Cu with a mean size of 65 nm at the ratio of Cu:Ag = 3:1. The film resistivity reached  $23.6 \mu\Omega \cdot \text{cm}$  when annealed at  $200^\circ\text{C}$ . Importantly, this mixed metal-based conductive ink allows us to directly write conductive features on transparent plastic substrates, suggesting the potential of creating plastic electronics for applications such as radio frequency identification (RFID) tags and thin-film transistor (TFT) circuits in a simple and economic manner.

#### 5. References

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