# Influence an Oxide Layer Thickness on Resistivity of Cu Conductive Film and Ink-jet Printing of Cu Nanoparticle Ink

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## Abstract

*We have developed the synthesis method to reduce the surface oxide layer in Cu nanoparticle, which is based on controlling the molecular weight of capping polymer. In addition, we demonstrated how the variation of oxide layer thickness influences the resistivity of conductive Cu film.*

## 1. Introduction

Development of convenient and low-cost processing techniques to fabricate conductive lines has received more attention in recent years. 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] Currently, mainly noble metals such as gold and silver are being exploited, despite their costliness. In this regard, copper is a good alternative material as it is highly conductive and much more economical than Au and Ag. However, when Cu nanoparticles are synthesized using chemical reduction process, the formation of oxide layer onto Cu surface layer is inevitable, because the CuO is a thermodynamically stable phase in ambient atmosphere.[2] In the fabrication of conductive electrode using a metal ink containing Cu nanoparticle, the formation of surface oxide layer which is an insulating material must be prevented.

## 2. Experimental

Copper nanoparticles of 35 - 60 nm size were synthesized in ambient atmosphere by the polyol method. Capping molecules (Mw = 10,000, 29,000, and 40,000 g/mol, Sigma-Aldrich), acting as a capping molecule to prohibit a formation of oxide layer, was dissolved in diethyleneglycol (DEG, 99%, Sigma-Aldrich). Reducing agent was added to the DEG solution and the solution was heated to reaction temperatures. The aqueous solution of copper (II) sulfate pentahydrate (98%, Sigma-Aldrich) was then injected into the hot reaction medium via a syringe pump. After 1 h of reaction, the solution was cooled to room temperature and the particles were separated by centrifugation and then washed with methanol.

Conductive ink incorporating the synthesized Cu nanoparticle was prepared using a mixed solvent. The copper nanoparticles were dispersed in the premixed solvent, followed by ball milling for 12 hrs. The formulated ink was filtered through 5-μm nylon mesh prior to use. The solid loading of ink was 20 weight %. The Cu conductive ink was printed by an ink-jet printer onto the glass substrate or polyimide substrate (Kapton, Dupont). The printer set up consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle manufactured by Microfab Technologies, Inc. (Plano, TX) and the diameter of the nozzle was 30 m. Uniform ejection of the droplets was performed by applying a 25 V impulse lasting 10 s at a frequency of 400 Hz. The diameter and velocity of the ejected droplets were about 50 ㎛ and 3 m/s, respectively. Then, the ink-jet printed Cu nanoparticulate films were heat-treated to form interparticular connections for electrical conductivity.

## 3. Results and discussion

It is shown in Fig. 1 that the thickness of a surface oxide layer onto Cu nanoparticle decreases with increasing the molecular weight of capping polymer. A surface oxide layer is formed by the reaction between Cu and oxygen atom originated from $O_2$ or $H_2O$. It is believed that the oxide layer is formed during the synthesis, when the nanoparticles are synthesized in the reaction medium in which $O_2$ or $H_2O$ are dissolved. Copper ions dissolved in reacting medium are bonded with capping polymer prior to the nucleation and growth process,[3] which disturbs the chemical reaction between Cu ion and oxygen atom.

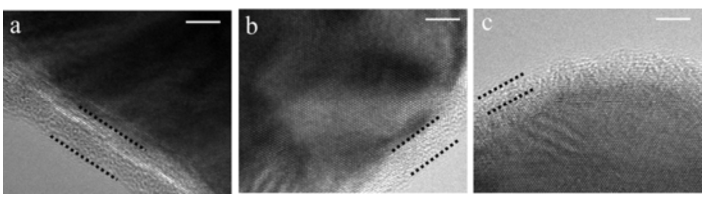


**Fig. 1. HRTEM image of Cu nanoparticles synthesized using capping molecules with different molecular weights: (a) 10,000 g/mol, (b) 29,000 g/mol, and (c) 40,000 g/mol. The dot line indicates the border of oxide layer. The oxide layer thickness of Cu nanoparticle is approximately 3.1 nm, 2.5 nm, and 1.6 nm, respectively. The synthetic conditions other than capping polymer are identical. Scale bar = 5 nm.**

For investigating an influence of oxide layer thickness on Cu conductive film, we have studied conductivity of heat-treated Cu film as a function of heat-treatment temperature, which is depicted in Fig. 2. The resistivity of heat-treated Cu film decreases with increasing the heat-treatment temperature. It is observed that the resistivity of Cu film prepared using higher molecular weight capping polymer is lower than that of film using lower molecular weight capping polymer. Before the heat-treatment, the Cu nanoparticles were individually located in film, without formation of conductive path. As the heat-treatment temperature increases, the coalescence between particles occurs and the complete sintering between particles was accomplished, producing a long-range conductive path. However, the capping molecules act as obstacles against a sintering process, because a sintering process is governed by a diffusion process and the capping molecule interrupts a migration of Cu atom into a neck area between adjacent Cu nanoparticles. Thus, during a heat-treatment procedure, the adsorbed capping molecules have to be partially removed. To confirm an influence of molecular weight on the thermal-decomposition temperature of capping molecules, we performed the thermal gravimetric analysis, which is shown in Fig. 3. The weight loss around 100 °C and 250 °C is attributed to a thermal-decomposition of adsorbed DEG and the capping molecule, respectively. It is observed that the capping molecules are thermally decomposed around 250 °C, regardless of molecular weights of the capping molecules

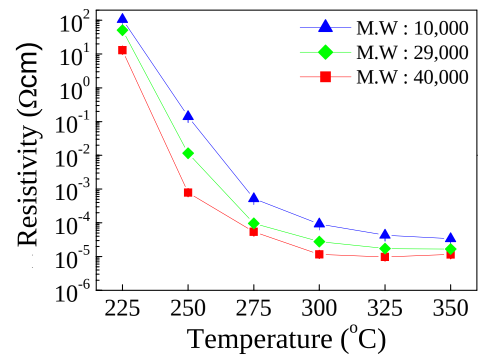


**Fig. 2. The resistivity variation of Cu conductive film as a function of heat-treatment temperature. The Cu films were heat-treated for 90 min under vacuum atmosphere of $10^{-3}$ torr.**

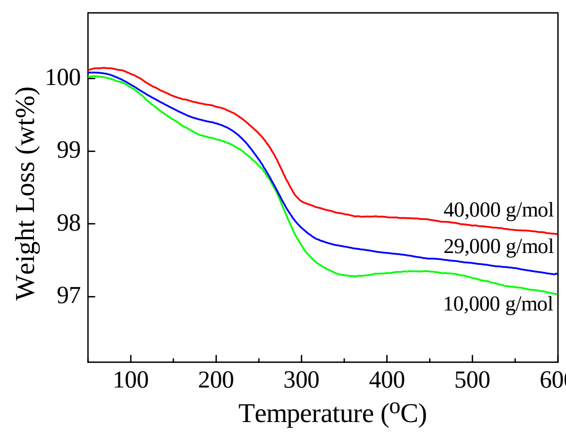


**Fig. 3. TG analysis of Cu nanoparticles synthesized using different molecular weight of the capping molecules**

It has been generally recognized that the sintering process occurs around the temperature which is 80% of melting point. Thus, because the melting point of CuO is higher than that of Cu (the melting point of CuO and Cu is 1330 °C and 1083 °C), the more junctions between particles are formed at the same temperature in the Cu film prepared from particles with a higher molecular weight of capping polymer, lowering the resistivity of conductive film. To investigate this different neck growth behavior as a function of oxide layer thickness, we analyzed the microstructure of Cu films, which is confirmed in Fig 4a. The microstructure of Cu film prepared from Cu nanoparticle with less surface oxide layer is denser than that of Cu film with more surface oxide layer. However, from Figure 4b, it is observed that the size of as-synthesized particle prior to beginning of sintering process increases with increasing the molecular weight of the capping molecules. The sintering temperature decreases dramatically, as the particles size decreases below 100 nm. This means that the oxide layer thickness play a dominant role to determine the resistivity of Cu film, overcoming the opposite trend due to the particle size effect.

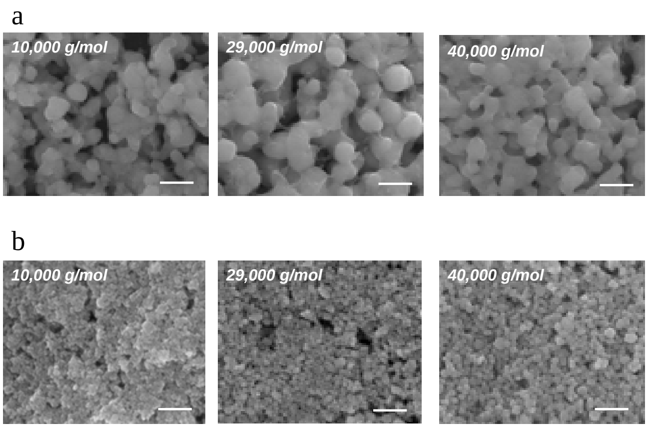


**Fig. 4. SEM image of Cu film (a) heat-treated at 325 °C and (b) not heat-treated. Scale bar = 500 nm.**

Fig. 5 shows complex conductive patterns printed on flexible polyimide substrate using Cu nanoparticle-based ink with molecular weight of 40,000 g/mol. Solvent evaporation from the printed single ink droplet produced a spherical dot pattern of ~120 ㎛ in diameter. The line pattern was generated by narrowing the dot-to-dot distance. The separated dots started to merge together at a distance of 80 ㎛, whereas the printing at the condition of 60 ㎛ resulted in the continuous line with ~130 ㎛ linewidth and a relatively smooth edge definition.

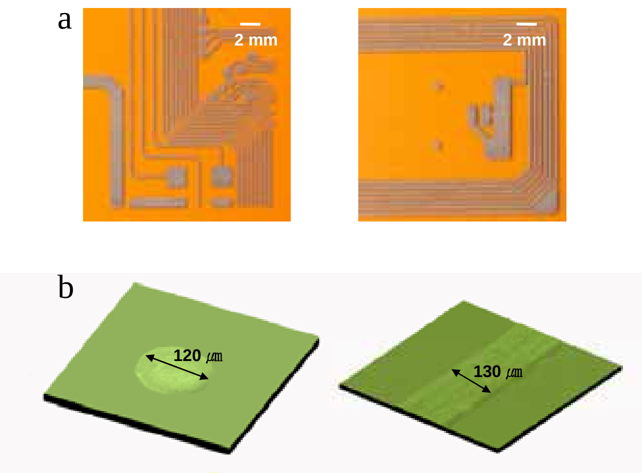


**Fig. 5. (a) Cu conductive patterns ink-jet printed on polyimide substrate using Cu nanoparticls with minimized oxide layer, (b) a confocal image of the single ink droplet after drying, and (c) the printed line.**

## 4. Summary

We have developed the way to control a thickness of oxide layer onto Cu nanoparticle surface by varying a molecular weight of capping molecules. It was demonstrated that capping molecule of a higher molecular weight is beneficial to reduce oxide layer thickness, which in turn improves the conductivity of printed Cu pattern by increasing connectivity between Cu nanoparticles. In addition, we fabricated the highly conductive and complicated pattern on flexible plastic substrate using Cu nanoparticle with minimal oxide layer thickness.

## 5. Acknowledgements

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