

# SYNTHESIS OF COPPER NANOPARTICLES WITH VARIOUS SIZES TOWARDS IMPROVING THE ELECTRICAL CONDUCTIVITY OF COPPER FILMS AT LOW SINTERING TEMPERATURE

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**Abstract.** The synthesis of copper nanoparticles (CuNPs) by surfactant-assisted chemical reduction method was studied aiming to identify the content of PVP-surfactant corresponding to the size of copper particles. The crystallite size and phase of CuNPs were determined by X-ray diffraction (XRD) analysis while transmission and scanning electron microscopy (TEM and SEM) were used to characterize the size of copper particles. The copper films were fabricated by the doctor-blade technique on polyimide (PI) and Al<sub>2</sub>O<sub>3</sub> substrates. The effect of sintering temperature on conductive properties of the copper film was investigated. The electrical conductivity of copper films was measured by using the four-point probe method. The electrical resistivity of copper films achieved stable values at the low sintering temperature above 200 °C, and equal to about 0.22 mΩ.cm and 0.63 mΩ.cm for that of Al<sub>2</sub>O<sub>3</sub> and PI substrates, respectively.

*Keywords:* copper nanoparticles, low sintering temperature, chemical synthesis.

*Classification numbers:* 2.10.2, 2.8.1, 2.9.2.

## 1. INTRODUCTION

Nowadays, printed electronics (PE) on various substrates has attracted a great attention in both research and commercialization [1-2]. Screen printing and ink-jet are the alternative to photolithography method as a low cost, high quality, high efficiency method using nanomaterials. Noble metal nanomaterials such as silver and gold are commonly used for these methods [3] because of their excellent conductivity, stability, and sintering efficiency under conventional processing conditions. Due to the high cost of these noble metals, they are too expensive for mass-production. Accordingly, copper nanoparticles (CuNPs) have become a low-cost substitute for silver and gold. In comparison with noble nanometals, the synthesis of stable metallic CuNPs is a challenging assignment as they suffer from rapid oxidation in air or aqueous media [4]. The aggregation of CuNPs forms severely without using the proper protection

methods. Thus, the CuNPs have to be encapsulated to stabilize their nanometric size by surfactants.

In some researches, CuNPs with the particle sizes of below 150 nm was used as precursor material in the preparation of conductive copper paste that was applied to fabricate electrodes of solar cells and flexible boards [5]. In these applications, polyimide (PI) was utilized as substrates of flexible boards while aluminum oxide ( $\text{Al}_2\text{O}_3$ ) was used as negatively charged surface passivation layer in crystalline silicon solar cells which is next to electrode layer [6]. For instance, Hyun-Jun Hwang *et al.* used ultra-high speed flash white light sintering method of copper nanoparticles pastes on silicon substrates to fabricate copper electrodes for crystallite silicon solar cell at the room temperature, they achieved the resistivity of  $9.37 \mu\Omega\cdot\text{cm}$  [7]. Chaoliang Cheng *et al.* studied on the sintering process of copper nanoink on PI substrates and the obtained resistivity ranged from  $688 \mu\Omega\cdot\text{cm}$  to  $11 \mu\Omega\cdot\text{cm}$  when sintering temperature varied from  $200^\circ\text{C}$  to  $300^\circ\text{C}$  [8]. Yeon-Ho Son *et al.* had copper nanoparticles coated with 1-octanethiol to prevent oxidation. The copper nanoink printed on PI substrates and sintered by flash-light method showed excellent antioxidation behavior over two months and reached the resistivity of  $24 \mu\Omega\cdot\text{cm}$  [9].

In this research, CuNPs were synthesized with less than 100 nm particle size via a wet chemical reduction method. The effect of PVP as a surfactant on the crystallite size and the agglomeration of copper nanoparticles was also investigated. In addition, we have conducted the fabrication of conductive copper pastes as well as aimed at increasing the conductivity of copper nanoparticles. The effect of low sintering temperatures on the electrical resistivity of the copper films that sintered on  $\text{Al}_2\text{O}_3$  and PI substrates was investigated.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

Laboratory grade of chemical substances was used without any further purification. Copper (II) sulfate pentahydrate salt ( $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  - 99.0 %), ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ -99.7 %), Polyvinylpyrrolidone K-30 (PVP K-30), tert-butanol ( $(\text{CH}_3)_3\text{CHO}$  - 99.0 %) and lactic acid ( $\text{C}_3\text{H}_6\text{O}_3$  - 90.0 %) were purchased from Acros, India. Ethanol 99.97 % was obtained from Prolabo, France. Sodium borohydride ( $\text{NaBH}_4$ - 99 %, Sigma-Aldrich) was used as the main reducing agent. The 50- $\mu\text{m}$ -thick Kapton HN polyimide film was supplied by 3M company. Aluminum oxide ( $\text{Al}_2\text{O}_3$ ) substrate of Merck are 99,99 %.

### 2.2. Experimental details

#### 2.2.1. Synthesis of copper nanoparticles

In this study, CuNPs were synthesized by using the wet chemical reduction method with different amounts of PVP as a surfactant. These amounts used in correspondence to molar ratios of this surfactant to copper sulfate pentahydrate of 1:100, 1:50, 1:30 and 1:10. Firstly, various amounts of PVP was added to the  $\text{CuSO}_4$  solution in four different ratios under rapid stirring (800 rpm) at a temperature  $60^\circ\text{C}$  in a beaker for 20 minutes. After that, the solution of ascorbic acid was added to the mixed solution of  $\text{CuSO}_4$ /PVP with the molar ratio of 1:0.5. Then, the 0.4 M  $\text{NaBH}_4$  solution was added dropwise to the latter solution in that beaker at 313 K with magnetic rod stirring. The color of the mixture was changed from blue to brown, indicating the

precipitation of Cu nanoparticles. The copper nanoparticles were obtained by centrifugation 5000 rpm for 5 min and washed three times with ethanol.

### 2.2.2. Fabrication of copper nano pastes

To fabricate conductive copper paste, the solvent was prepared by mixing ethanol and tert-butanol. The solvent with the weight ratio of ethanol and tert-butanol is 1:2 and the weight ratio of copper nanoparticles and the solvent is 1:2. The synthesized CuNPs with less than 100 nm particle size were used as a precursor. The mixture of CuNPs and the solvent was dispersed by using ultrasonic waves in 20 minutes. Then, we added lactic acid to the latter solution with the weight ratio of lactic acid to copper nanoparticles of 1:10. Finally, the conductive paste was coated on Al<sub>2</sub>O<sub>3</sub> and PI substrate using doctor-blade method. The copper films were then sintered with the different sintering temperatures in argon atmosphere.

## 2.3. Characterization

The morphologies of copper nanoparticles and films were characterized by field emission scanning electron microscopy (FE-SEM, S4800 Hitachi) and transmission electron microscopy (TEM, JEM-14000). The crystallite phases of CuNPs were determined by X-ray diffraction (XRD) using the D8 Advance-Bruker with Cu K $\alpha$  radiation. Four-point probing is used for measuring electrical properties of conductive patterns. The electrical sheet resistances were examined by using the Kikusui PMC-18-2, 18V, 2A.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of PVP on the size of copper nanoparticles

Figure 1 presents the XRD patterns of the CuNPs synthesized using different amounts of PVP in copper sulfate solution. The obtained products are almost phase pure copper nanoparticles because there are no other diffraction peaks of impurities, such as CuO or Cu<sub>2</sub>O, except for those of Cu, which means the specimens were protected from oxidation during the synthesis process. When the content of PVP surfactant is increased, the copper nanopowders have a crystallite size of 35 nm, 30 nm, 26 nm and 21 nm corresponding to the PVP/Cu<sup>+2</sup> ratio of 1:100, 1:50, 1:30 and 1:10. Hence, PVP is added to minimize crystal growth. As the amount of PVP increases, it leads to the decrease of crystallite size of copper nanoparticles.

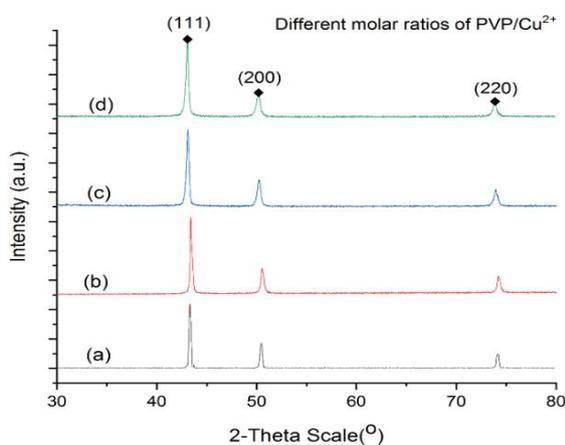


Figure 1. XRD patterns of the synthesized CuNPs with different amounts PVP in copper sulfate solution: (a) 1:100; (b) 1:50; (c) 1:30; (d) 1:10.

SEM images in Figure 2 (a), (b), (c) and (d) show that the synthesized CuNPs with the molar ratio of PVP/Cu<sup>+2</sup> of 1:50, 1:30, 1:10 have particle size reduction from about 400 nm to under 100 nm, respectively. It can be seen clearly that the crystallite agglomeration is reduced

due to the increase of PVP. The synthesized CuNPs are less than 100 nm in size using the PVP/Cu<sup>+2</sup> ratio of 1:10 that can be applied in electrical materials as originally proposed.

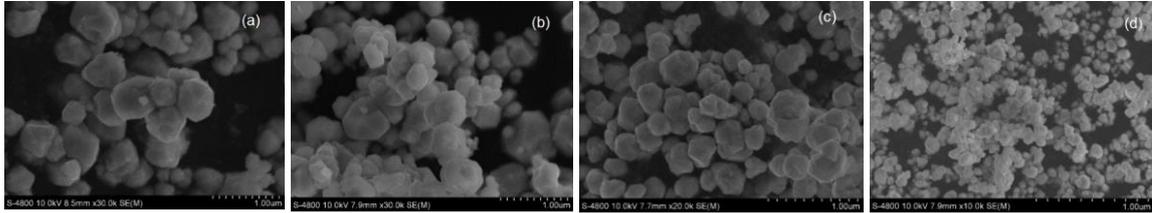


Figure 2. SEM images of copper nanopowders with the molar ratio of PVP/CuSO<sub>4</sub>.5H<sub>2</sub>O: (a) 1:100; (b) 1:50; (c) 1:30; (d) 1:10.

TEM analysis was carried out for observing nanoparticles with size smaller than 100 nm. Figure 3 illustrates TEM images of the CuNPs particles that were formed by the aggregation of the smaller spherical particles with the size of less than 20 nm.

### 3.2. Effect of sintering temperature on electrical conductivity of copper films

The electrical resistivity of the sintered copper films on PI and Al<sub>2</sub>O<sub>3</sub> substrates at various sintering temperatures are shown in Figure 4. When sintering temperature increases, the electrical resistivity of copper films decreases for both kinds of substrates. In particular, the electrical resistivity of copper film sintered on PI substrate reduces from  $7.14 \times 10^{-3} \Omega \cdot \text{cm}$  to  $3.62 \times 10^{-4} \Omega \cdot \text{cm}$  when temperature rises from 150 °C to 300 °C. With Al<sub>2</sub>O<sub>3</sub> substrate, the electrical resistivity of copper film decreases from  $7.25 \times 10^{-4} \Omega \cdot \text{cm}$  to  $6.0 \times 10^{-5} \Omega \cdot \text{cm}$  as temperature increases from 150 °C to 300 °C. The electrical resistivity of sintered copper film on Al<sub>2</sub>O<sub>3</sub> is smaller than that on PI substrates at the same sintering temperature. This can be explained by the fact that Al<sub>2</sub>O<sub>3</sub> material has a lower specific heat

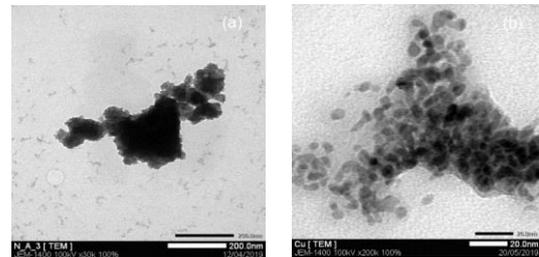


Figure 3. TEM image of copper powder at the molar ratio of PVP/Cu<sup>+2</sup> of 1:10 (a) low-magnification and (b) high-magnification.

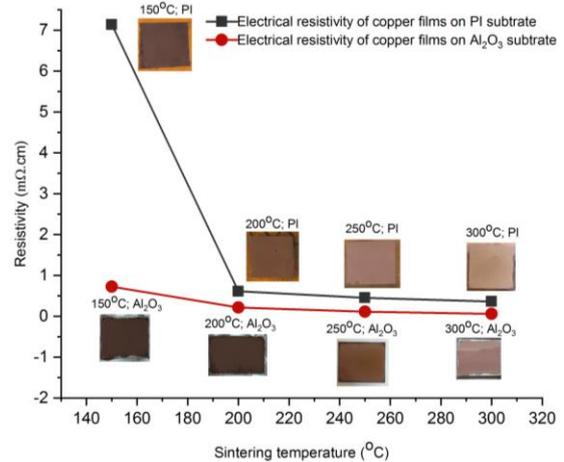


Figure 4. The electrical resistivity of the copper film on PI and Al<sub>2</sub>O<sub>3</sub> substrates at different sintering temperatures.

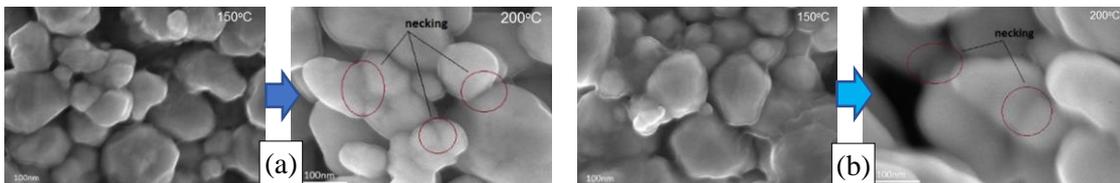


Figure 5. SEM images of copper films on PI (a) and Al<sub>2</sub>O<sub>3</sub> (b) substrates with different sintering temperatures.

capacity than PI material. It can be seen clearly that sintering temperature and substrate material have a great effect on the electrical resistivity of the copper film.

The resistivities of copper film on PI and Al<sub>2</sub>O<sub>3</sub> substrates decrease to less than 1 mΩ.cm at 200 °C. After a gradual decrease in the resistivity, they become almost constant above 200 °C (0.22 mΩ.cm for Al<sub>2</sub>O<sub>3</sub> substrate and 0.63 mΩ.cm for PI substrate). As the sintering temperatures increase above 200 °C, a conductive path between the particles are established by inter-particles neck formation. Figure 5 shows that the neckings in sintered copper films on PI and Al<sub>2</sub>O<sub>3</sub> substrates appear more densely when the sintering temperatures increases from 150 °C to 200 °C. Thus, the effect of sintering temperatures on nano-sized copper particles was shown in these experimental results, considering that the melting point of the bulk copper is 1083 °C

#### 4. CONCLUSIONS

In this paper, copper nanoparticles were successfully synthesized by a chemical reduction method. Experimental results show that it is possible to obtain samples with different sizes only by changing the PVP content. The copper nanoparticles have a crystallite size of 35 nm, 30 nm, 26 nm and 21 nm corresponding to the PVP/Cu<sup>2+</sup> ratio of 1:100, 1:50, 1:30 and 1:10. The smallest particle size is below 100 nm which is suitable for use as the base of a copper ink for applications of flexible boards and electrodes in a solar cell.

These experimental results clearly show a low sintering temperature effect for nano-sized copper particles. The sintering temperature increases from 150 °C to 300 °C, the electrical resistivity of copper films decreases from 7.14×10<sup>-3</sup> Ω.cm to 3.62×10<sup>-4</sup> Ω.cm and 7.25×10<sup>-4</sup> Ω.cm to 6.0×10<sup>-5</sup> Ω.cm correspondingly to PI and Al<sub>2</sub>O<sub>3</sub> substrates. The electrical resistivity of copper films achieves stable at the low sintering temperature above 200 °C, *i.e.* about 0.22 mΩ.cm and 0.63 mΩ.cm for that of Al<sub>2</sub>O<sub>3</sub> and PI substrates, respectively

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