



Nitrogen-Annealed Copper Complex Synthesized Using CuO for Application to Conductive Cu Films

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A Cu(II) formate complex was synthesized by reacting low-cost Cu(II) oxide (CuO) with formic acid. The formate was mixed with α -terpineol to prepare a paste, which was stencil printed onto glass slides and thermally annealed under nitrogen at 400 °C to fabricate conductive Cu films. The Cu(II) formate decomposed and was transformed into pure Cu particles, which were sintered during annealing. A porous Cu film was obtained because of necking between the Cu particles, and the Cu film annealed for 2 h exhibited an excellent electrical resistivity of $2.13 \times 10^{-5} \Omega \cdot \text{cm}$.

Keywords: CuO, Organometallic Compound, Cu Complex, Conductive Paste, Cu Film, Electrical Resistivity.

1. INTRODUCTION

Conductive pastes are essential for the simple and low-cost processes used to prepare conductive lines or electrodes in electronic packaging.^{1–16} Although direct printing and sintering processes using conductive paste can be limited in application in terms of the implementation of high-resolution patterning, such simple processes can be substituted for many steps in photolithography. In addition, conductive pastes are representative materials for the roll-to-roll process used to develop flexible electronic modules and are also useful for large-area applications.^{8–10} In summary, conductive pastes are increasingly important in the additive processes used to form conductive lines or electrodes.

Although conductive pastes can be fabricated using metal particles and organometallic compounds as fillers, organometallic-based pastes have been more widely studied because the processing advantages and resulting electrical conductivity, achieved through the formation of fine conductive particles during annealing and subsequent sintering, are superior to those achieved through particle sintering in metal-particle-based pastes.^{11–14}

Noble metals such as Ag have conventionally been used as a source metal for producing conductive pastes because of their antioxidative properties.^{1–10} Although the Ag surface is oxidized, the electrical connection can be maintained between the particles because the oxide layer is electrically conductive.³ However, declining production costs in diverse electronic modules has led to a persistent

demand for inexpensive assembly materials. Cu is the preferred substitute for the more expensive Ag because Cu shows a high bulk conductivity similar to that of Ag.^{16–25} However, Cu-based pastes are highly susceptible to oxidation in air, especially during annealing.^{26–28}

According to previous reports, using Cu-based pastes to prepare highly conductive films requires annealing under a reducing atmosphere. Yabuki et al. have reported the effects of atmospheric conditions on the electrical conductivity of thermally annealed Cu nanoparticle paste.²⁰ The resistivity of a film annealed at 300 °C under nitrogen (N₂) was extremely high ($4.1 \times 10^3 \Omega \cdot \text{cm}$), whereas that of a film annealed under a 5% H₂-Ar mixed gas was reduced to only 8.8×10^{-2} – $1.4 \times 10^{-5} \Omega \cdot \text{cm}$. Nevertheless, the annealing process in N₂ is still required because of advantages such as simplified facility and management, reduced processing cost, and non-explosion. Because organometallic compounds can be converted into highly conductive films without using a reductive gas, such compounds can be used in environments whose atmosphere is inert.^{11–13, 29} Joo et al. developed a procedure for synthesizing a paste containing a Cu(II) formate (Cu(COOH)₂) complex from Cu(I) oxide (Cu₂O) and investigated the thermal and laser annealing characteristics of the paste under N₂.^{12, 13} A pure Cu film was formed by annealing Cu(II) formate at 275 °C, and the electrical conductivity of the film was measured on the order of $10^{-5} \Omega \cdot \text{cm}$.

As an extension of their research, therefore, we used low-cost Cu(II) oxide (CuO) powder to synthesize a Cu(II) formate complex paste, prepared films from the paste, thermally annealed the films under N₂, and analyzed the

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microstructure and electrical conductivity of the annealed films.

2. EXPERIMENTAL DETAILS

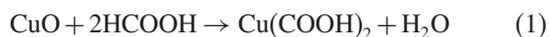
Cu(II) formate complexes were synthesized by adding either 10 or 20 g of CuO powder (99.1%, KG ETS) to 200 mL of formic acid (HCOOH, 99%, Samchun Chemicals). The mixtures were stirred using a magnetic bar at room temperature for 1 h. The color of the solutions changed from red to sky blue while the Cu complexes formed. The residual formic acid in the suspensions was neutralized with by washing the suspensions with ethanol (99.9%, Duksan Chemical Co.), and centrifuging them at 7000 rpm for 5 min 5 times each. The products were then separated and dried under vacuum at room temperature for 24 h.

The Cu-complex pastes were prepared by mixing 75 wt% Cu complex and 25 wt% α -terpineol (C₁₀H₁₈O, p-menth-1-en-8-ol, 98.5%, Samchun Chemicals). The pastes were stencil printed onto glass slides, which were inserted into a tube furnace where they were heated at 25 °C min⁻¹ and annealed for 2 h at a specific temperature under N₂ (5 N). The temperature was directly measured in the atmosphere around the specimen. The specimens were cooled for 1 h and then removed from the furnace to prevent Cu oxidation during the high-temperature annealing. The sintered films were ~100 μ m thick. The electrical resistivity of the films was measured using a 4-point probe (FPP-RS 8, Dasol Engineering), and the average resistivity was calculated based on five films prepared under the identical conditions.

The phases of the synthesized powders and annealed pastes were determined by X-ray diffraction (XRD, X'PERT PRO-MPD, PANalytical). The size and morphology of the various particles and the surface images of the sintered films were analyzed using field-emission scanning electron microscopy (FE-SEM, JSM-7500F, JEOL).

3. RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns for the complexes synthesized with either 10 or 20 g of CuO. Most of the peaks were indexed to Cu(II) formate, and none of the peaks was indexed to pure Cu, unlike the results previously reported for the complex synthesized using Cu₂O powder.^{12,13} The formation of Cu(II) formate can be expressed as follows:^{12,13}



In addition, the XRD pattern for the complex synthesized with 20 g of CuO showed a main peak closely indexed to CuO, indicating that some unreacted CuO powder remained in the complex because of the surplus amount of CuO compared with the amount of formic acid.

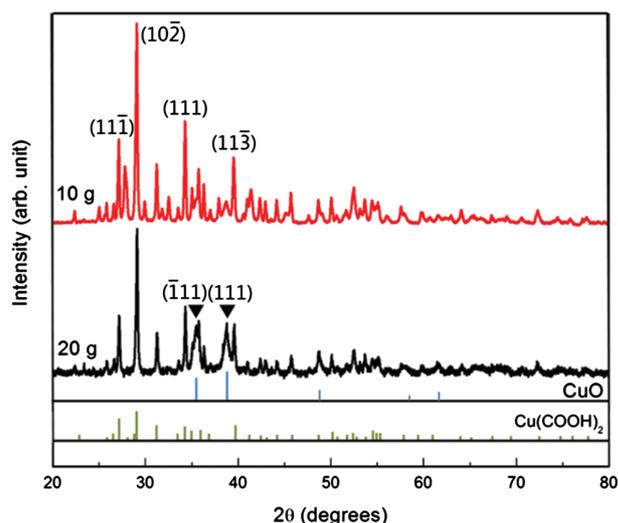


Fig. 1. XRD patterns for complexes synthesized with (a) 10 and (b) 20 g of CuO.

Hence, using only 10 g of CuO was optimal for obtaining a pure Cu complex powder because CuO cannot be reduced to Cu during annealing under N₂.

The SEM images showing the morphology of the initial CuO particles and the morphological evolution of the particles synthesized using 10 g of CuO for 10, 20, 40, 50, and 60 min are presented in Figure 2. The initial CuO

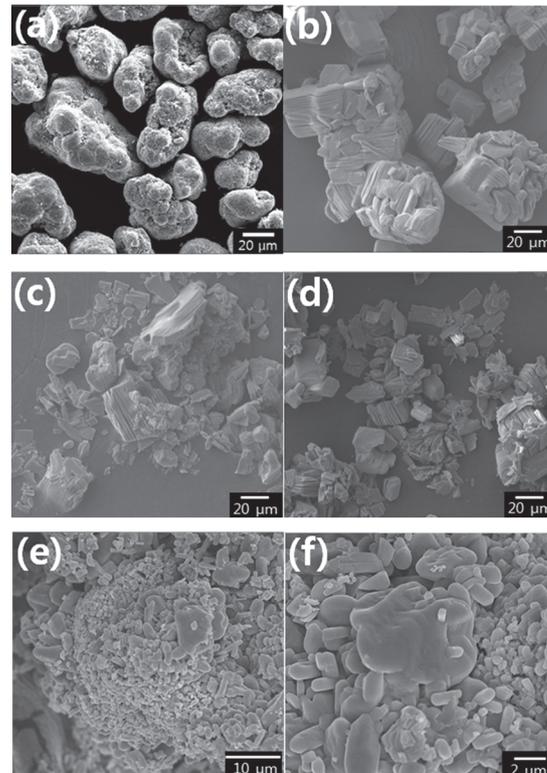


Fig. 2. SEM images showing (a) morphology of initial CuO particles and morphological evolution of particles synthesized using 10 g of CuO for (b) 10, (c) 20, (d) 40, (e) 50, and (f) 60 min.

particles were irregularly aggregated, were several tens of micrometers in diameter, and had dirty surfaces, as shown in Figure 2(a), because they were prepared using a chemical process that employed wastewater. The Cu(II) formate complex particles synthesized for 10 min abruptly transformed into clean and wrinkled aggregated crystals (Fig. 2(b)), which became smaller with increasing synthesis time up to 40 min. The surfaces of the aggregated crystals increasingly resembled flower stamens with increasing synthesis time after 40 min. Hence, the overall formation of the stamen-like crystals could be interpreted as the synthesis of pure Cu(II) formate.

Films of the printed pastes were then annealed under N_2 at either 350 or 400 °C to determine the optimal annealing temperature for converting the formate into pure Cu. Figure 3 presents the XRD patterns for the films prepared using 20, 10, and 10 g of CuO and annealed at 350 and 400 °C for 2 h, respectively. The pattern for the film synthesized from 20 g of CuO and annealed at 350 °C still showed peaks indexed to Cu(II) formate as well as peaks indexed to both pure Cu and Cu_2O . The pattern for the film synthesized using only 10 g of CuO and annealed at the identical temperature, however, did not show any peaks indexed to Cu(II) formate and only showed peaks indexed to pure Cu and Cu_2O . These results indicate that the remaining unreacted CuO in the suspension had transformed into Cu(II) formate during annealing, whereas the formate formed during the synthesis had transformed into pure Cu and Cu_2O . The pattern for the film synthesized using only 10 g of CuO and annealed at 400 °C only showed peaks indexed to pure Cu. These results suggest that annealing the films at 350 °C induced the formation of Cu_2O from the formate according to the following reaction:

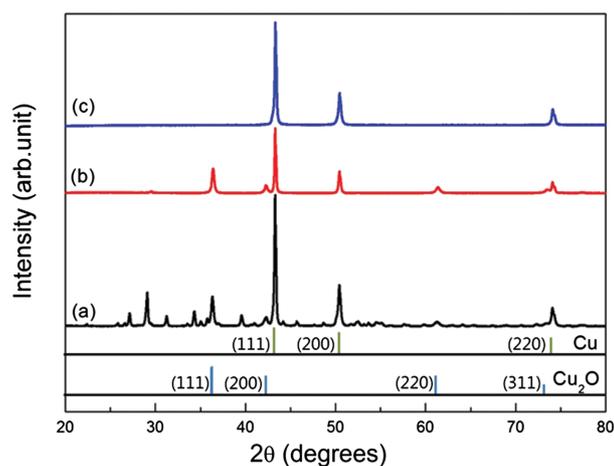
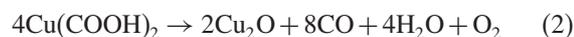


Fig. 3. XRD patterns for films annealed under N_2 for 2 h: (a) film synthesized using 20 g of CuO and annealed at 350 °C, (b) film synthesized using 10 g of CuO and annealed at 350 °C, and (c) film synthesized using 10 g of CuO and annealed at 400 °C.

The detection of pure Cu at the same temperature also indicates that another simultaneous reaction such as³⁰



induced the formation of Cu in the films annealed at 350 °C. However, the results also suggest that all the Cu(II) formate in the film annealed at 400 °C was transformed into pure Cu only through the reaction given by Eq. (3).

Figure 4 presents the surface SEM images of the films prepared using the Cu complex paste containing 10 g of CuO and annealed under N_2 at 400 °C for either 60 or 120 min. Compared with the Cu(II) formate particles shown in Figure 2(f), the particles in the film annealed for 60 min (Fig. 4(a)) were characterized by entirely different sizes and shapes. The particles in the annealed film were more uniform and polygonal and were smaller, on the order of only several micrometers in diameter, than the particles shown in Figure 2(f), suggesting that the annealed particles were pure Cu. In addition, the sintering slightly connected the Cu particles, as shown in Figure 4(a). Because the boiling point of α -terpineol is 217 °C, the α -terpineol would have evaporated through the voids between the particles. The particles in the film annealed for 120 min (Fig. 4(b)) showed a more sintered microstructure, resulting in significantly enhanced connections between the Cu particles in the film. However, the sintered film was still porous because it also contained voids.

Figure 5 shows the average electrical resistivity and standard deviation of the films prepared by annealing the

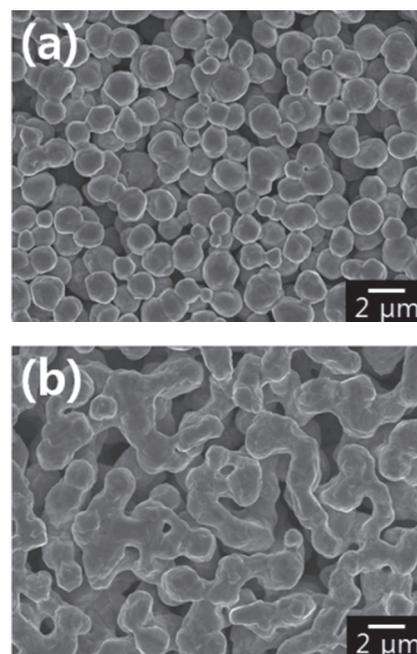


Fig. 4. Surface SEM images of films prepared using Cu complex paste containing 10 g of CuO and annealed under N_2 at 400 °C for (a) 60 and (b) 120 min.

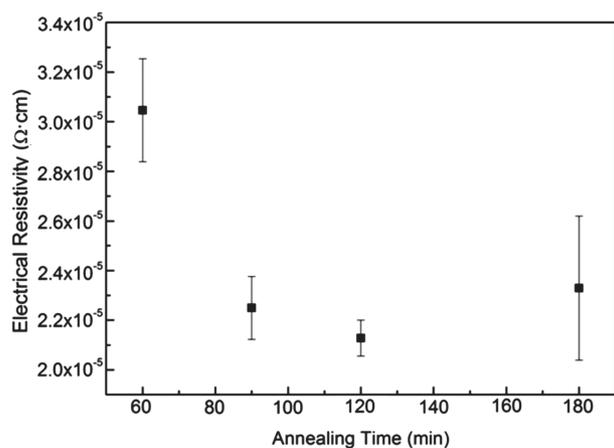


Fig. 5. Electrical resistivity of films prepared using Cu complex paste containing 10 g of CuO and annealed under N₂ at 400 °C for 60–180 min.

Cu complex paste under N₂ at 400 °C for 60–180 min. The resistivity, on the order of 10⁻⁵ Ω·cm, decreased with increasing annealing time up to 120 min. In particular, the resistivity of the film annealed for 120 min reached a minimum of 2.13 × 10⁻⁵ Ω·cm and was the most stable; the microstructure of the same film revealed more connectivity between the Cu particles. However, the resistivity increased with marked deviation when the film was annealed longer than 120 min, suggesting that annealing times longer than 120 min are more likely to oxidize the Cu film than to improve the microstructure, thereby increasing the resistivity.

4. CONCLUSIONS

A Cu(COOH)₂ complex was synthesized by reacting low-cost CuO with formic acid in the proper stoichiometric ratio. The CuO abruptly transformed into clean and wrinkled aggregated crystals, which became smaller with increasing synthesis time up to 40 min, and the surfaces of the aggregated Cu(II) formate complex crystals increasingly resembled flower stamens with increasing synthesis time after 40 min. A Cu complex paste was prepared by mixing the Cu(COOH)₂ with α-terpineol. The Cu(COOH)₂ in the printed paste decomposed and was transformed into pure Cu particles, which were sintered during annealing under N₂ at 400 °C forming a porous Cu film. The sintered film annealed for 1 h exhibited excellent electrical resistivity, on the order of 10⁻⁵ Ω·cm. The film annealed for 2 h showed the optimal resistivity of 2.13 × 10⁻⁵ Ω·cm. Annealing the films at 350 °C produced Cu₂O via a simultaneous side reaction in addition to pure Cu.

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