Preparation of Cu nanoparticles by a pulsed wire evaporation process for conductive ink applications

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Abstract. In the present study, Cu colloidal nanoparticles and nanopowders were successfully synthesized by a pulsed wire evaporation process. Cu-based nano-inks were prepared by mixing Cu nanoparticles with acrylic resin and solvent. Cu nanoparticles with a particle size of < 20 nm were uniformly dispersed in ethylene glycol. The Cu nanopowders were successfully coated with an organic solvent composed of a hydrocarbon compound. This organic coating effectively inhibited the oxidation of Cu nanopowders. In addition, the stability of dispersion of Cu nanoparticles in the inks was improved by a ball-milling process. The electrical conductivity of the prepared Cu nano-inks was 10–28 $\mu\text{S cm}^{-1}$ for 20–40 wt% of Cu.

Keywords. Cu; nanoparticles; nanopowders; electrical conductivity.

1. Introduction

Rapid development of the information technology industry is closely related to the improvement of the functionality of electronic materials. In recent years, advances in printing technology have improved the performance of electronic materials and reduced the manufacturing costs. In the applications of metal inks, the requirements regarding their properties are varied. The oxidation, dispersion stability, lifetime, viscosity and surface tension are the most important properties of metal inks; in addition, the curing temperature must be reduced for the application on a variety of substrates [1–6].

In the printing and electronic industries, pastes and inks are mainly produced using noble metals such as gold and silver, because they have low resistivity, low oxidation and high reliability [7–10]. However, their high cost limits their applications. Thus, research on relatively low-cost materials such as Cu, Ni, Sn, Zn and Bi, where the replacement of noble metals is being actively investigated, is very intense. Among these materials, Cu is a good alternative material because it is highly conductive and is also significantly cheaper than noble metals. However, Cu is easily oxidized in air into oxides such as Cu_2O and CuO , because the oxide phases are thermodynamically more stable than pure Cu. Additionally, the oxide layer covering the Cu conductive film acts as a highly resistive material that reduces the pattern of conductivity and increases the sintering temperature of the pattern. Thus, it is necessary to ensure the oxidative stability order to develop a highly conductive Cu pattern [11–15]. Many studies have

been carried out, including research on metal-surface coatings, use of alloy powders and core-shell composite powders [16–18].

Owing to the growing development of nanotechnology in recent decades, metal materials are being progressively replaced by their corresponding metal nanoparticles to maximize and to optimize their properties. Furthermore, electronic instruments are highly miniaturized; therefore, the demand for nanosized particles is increasing. However, to use them in soft disc applications, low-temperature sintering is required. Cu nanoparticles have been synthesized through different methods such as radiation, thermal decomposition, sonochemical reduction, chemical reduction, gas evaporation, aqueous solution reduction and microemulsion techniques [18–23]. However, these methods often use toxic chemicals and are generally time-consuming. The pulsed wire evaporation process could be used to overcome these problems.

The typical method for the preparation of Cu nano-inks involves the following steps. (i) Cu nanoparticles are added to a mixture of solvents or of resin and solvent; (ii) the resulting mixture is ultrasonically stirred at room temperature for 0.5–1 h and (iii) finally, the nano-inks are obtained by filtering the mixture using a nylon mesh [24].

In this study, Cu nanoparticles were prepared by the pulsed wire evaporation process, and oxidation-resistant Cu nanoparticles were developed by using an organic solvent in a simple coating process. Finally, Cu-based nano-inks were prepared and characterized.

Figure 1. TEM photos of Cu colloidal nanoparticles in (a) ethanol and (b) ethylene glycol.

2. Experimental

2.1 Preparation of Cu colloidal nanoparticles

Anode and cathode electrodes were placed in ethanol or toluene solvent. Cu wires with a diameter of 0.15 mm were automatically fixed to a continuous wire-feed supply device. When the wires were installed between the electrodes, electrical energy with a high voltage and high electric current was applied. As a result, the wire was heated, melted and evaporated. Finally, the Cu colloidal nanoparticles were obtained by condensation through a peripheral cooling gas or liquid.

2.2 Preparation of Cu nanopowders

Cu wires with a diameter of 0.15 mm were continuously supplied into the chamber under a nitrogen atmosphere through a wire-feeding system. A high voltage was used to charge the condenser with a controlled triggering through the spark routed to the high-voltage electrode. The Cu wires were converted to nanosized powders by evaporation and condensation. Forced gas was circulated using a blower, and the nanopowder was collected in the filter through a trap and a cyclone classifier. The collected powders were stabilized through a passivation process.

2.3 Surface modification of Cu nanopowders

The pure Cu nanopowders were placed within the vacuum chamber. An organic solvent (hexane or toluene) was heated to its boiling point and the vapour was allowed to flow into the vacuum chamber. The Cu nanopowder samples were rotated in the vacuum chamber to ensure that the coating was uniform. An organic coating with $-CH$ group was successfully formed on the Cu nanopowders.

2.4 Preparation of Cu nano-inks

The Cu nanoparticles were added in a mixture of acrylic resin and solvent. Then, they were dispersed by an ultrasonic treatment to obtain 10–40 wt% Cu nano-inks.

2.5 Characterization

The dispersion characteristics of the Cu colloidal nanoparticles were assessed using transmission electron microscopy (TEM, JEOL, JSM-6330F). The morphology of the nanoparticles was examined using scanning electron microscopy (SEM, JEOL, JXA840A).

The melting temperature of the Cu colloids was measured by differential scanning calorimetry (DSC, NETZSCH, 204 F1) at a heating rate of $5^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere.

The formation of oxide on the Cu surface was investigated by using X-ray diffraction (XRD, Rint-2000, Rigaku). The phase of the oxide was determined using X-ray photoelectron spectroscopy (XPS, VG Scientific ESCA LAB MK-II).

The viscosity of the Cu-inks was measured using an Anton Paar rolling ball AMVn viscometer. The surface tension of the Cu-inks was determined using a KRÜSS K8551 tensiometer (ring method). The electrical conductivities of the Cu-inks were measured using an electrical conductivity meter (EZTECH, AZ-8361).

3. Results and discussion

3.1 Preparation of Cu colloidal nanoparticles

Cu colloidal nanoparticles were prepared using the pulsed wire evaporation process. The dispersion characteristics of the Cu colloidal nanoparticles were assessed using TEM, and the results are shown in figure 1. As shown in figure 1, the

Figure 2. Thermal analysis of Cu colloidal nanoparticles.

particle size was <20 nm when ethanol and ethylene glycol were used as solvents. When ethanol was used, the Cu colloidal nanoparticles were agglomerated, whereas smaller

and non-aggregated Cu colloidal nanoparticles were produced when ethylene glycol was used. The results indicate that the dispersion of Cu colloidal nanoparticles in ethanol and ethylene glycol is different. The results can be explained as follows. Ethanol is a symmetric molecule, while ethylene glycol is asymmetric. Thus, the dipole moment of ethylene glycol is higher than that of ethanol. Additionally, many free electrons exist on the Cu surface. Then, Cu colloidal particles strongly combine with ethylene glycol molecules and uniformly disperse in ethylene glycol [25,26].

Thermal properties of the Cu colloidal nanoparticles were measured by DSC and the result is displayed in figure 2. As shown in figure 2, an endothermic peak appeared which shows melting point of the Cu colloidal nanoparticles. The onset-point, peak-point and end-point were 358, 362 and 368°C, respectively. Melting point of the Cu colloidal nanoparticle-based material decreased by about 30% when compared to that of the bulk material. At macroscopic length scales, melting temperature of the materials is size-independent. In contrast, melting temperature of the nanosized materials decreases significantly with decreasing particle size.

(a) $K = 2.1$

(b) $K=2.9$

(c) $K=3.6$

Figure 3. SEM photos of Cu nanopowders with various K values.

Figure 4. Morphologies of Cu nanopowders according to preparation processes: (a) in Ar, (b) in distilled water and (c) in ethylene glycol.

Figure 5. SEM–EDS results of Cu nanopowders prepared in (a) distilled water and (b) ethylene glycol.

The melting temperature of the nanosized particles can be calculated using the Gibbs–Thomson equation:

$$T_M = T_{MB} \left(1 - \frac{4\sigma_{sl}}{H_f \rho_s d} \right), \quad (1)$$

Figure 6. (a) TEM and (b) XPS results of Cu nanoparticles.

Figure 7. TEM photos of Cu nanoparticles coated with (a) *n*-hexane and (b) toluene.

where T_{MB} is the bulk melting temperature, σ_{sl} the solid–liquid interface energy, H_f the bulk heat of fusion, ρ_s density of the solid and d the particle diameter.

Equation (1) shows that the melting temperature decreases according to the exponential function when the particle size decreases below 50 nm [27].

3.2 Preparation of Cu nanopowders

Average particle size of the Cu powders was measured by means of nitrogen isothermal adsorption experiments. The average particle size was calculated by the following equation:

$$D = \frac{6}{\rho \times S} \quad (2)$$

where D is the average particle size, ρ the density of Cu and S the measured specific surface area.

Figure 3 shows SEM images of the Cu nanopowders with various superheating factor (K) values. When the K values

Figure 8. XRD patterns of Cu nanoparticles coated with (a) *n*-hexane and (b) toluene.

were 2.1, 2.9 and 3.6, the average particle sizes were 140, 110 and 80 nm, respectively. Different particle sizes with various modes were observed at lower K values (2.1 and 2.9), whereas the particle size was uniform when the K value increased to 3.6 [28].

Figure 4 shows SEM images of the Cu nanopowders according to the manufacturing process. When the Cu nanopowders were prepared under an Ar atmosphere, the particle size was about 300 nm and aggregation or combination with each other was observed, as shown in figure 4a. When the Cu nanopowders were prepared using distilled water or ethylene glycol, the particle size was <100 nm, as shown in figure 4b and c. This is because the explosion and condensation rates in liquid were higher than those observed under an Ar atmosphere; thus, the particle growth was inhibited. Additionally, the aggregation between the particles was hindered, which results in improved dispersion of the powders [29,30].

Figure 5 shows the SEM–EDS results of Cu nanopowders prepared in both distilled water and ethylene glycol. When the Cu nanopowders were prepared in distilled water, the elemental analysis results indicated that only oxygen and Cu were detected, and the oxygen content was about 20 wt%. However, when the Cu nanopowders were prepared in ethylene glycol, a large amount of carbon was detected (from carbon in the ethylene glycol) and the oxygen content was about 4 wt%. This oxygen content was five times lower than that for Cu nanopowders prepared in distilled water. Thus, the use of ethylene glycol as a solvent is an important additional factor to control the oxidation of Cu nanopowders.

The Cu nanopowders were easily oxidized in air. Therefore, investigation of the oxidation of nanopowders is very important. The surface characteristics of Cu nanopowders were investigated by TEM, and the result is shown in figure 6a. The TEM result showed the formation of ~5-nm-thick

Figure 9. SEM micrographs of Cu nanopowders (a) before and (b) after the dispersion improving process.

Figure 10. SEM micrographs of ink prepared by Cu nanopowders (a) before and (b) after ball-milling.

Table 1. Viscosity, surface tension and electrical conductivity of Cu nano-inks.

Cu content (wt%)	Viscosity (cP)	Surface tension (dyne cm ⁻¹)	Conductivity (μS cm ⁻¹)
10	25.5	31.3	3.53
20	67.40	30.2	10.14
40	52.00	—	28.18

amorphous oxide film. This can be attributed to the fact that the passivation was carried out to improve the stability after powder production. The phase of the oxide film formed at the powder surfaces was analysed using XPS, and the results are shown in figure 6b. The broad peaks of CuO were observed at 946 and 966 eV. From these results, it can be confirmed that the film formed at the Cu powder surfaces comprised CuO [31–33].

To prepare the Cu-based ink and improve the characteristics of its distribution, the oxidation at the powder surfaces must be minimized. In this study, the surface coating on the Cu nanopowder surfaces was carried out using an organic solvent composed of a hydrocarbon (C–H) compound. Figure 7 shows the TEM micrographs of the Cu nanopowder surfaces coated with *n*-hexane and toluene. As shown in figure 7, the oxide film was not observed on the nanopowder surface. The oxide formation was also investigated using XRD, and the results are shown in figure 8. The oxide peak was absent, as shown in figure 8. These results confirm that a surface coating based on a hydrocarbon compound can effectively prevent the oxidation of Cu nanopowders.

3.3 Preparation of Cu-based nano-ink

Figure 9 shows SEM micrographs of the Cu powders before and after the dispersion-improving process. The Cu particles prepared under an Ar atmosphere were aggregated, as shown in figure 9a. Thus, the treatment of release of Cu condensation is needed before the preparation of ink. A low-energy ball-milling process in the liquid can disperse the aggregated Cu particles, as shown in figure 9b [34].

Figure 10 shows the SEM micrographs of ink prepared from Cu powders under an Ar atmosphere. Figure 10a shows the ink prepared from the untreated Cu particles; the condensation between the powders remained after the preparation of the ink. Figure 10b shows the ink prepared using the Cu particles that were treated by ball-milling in the liquid; on the contrary, the Cu particles were uniformly dispersed [35].

Table 1 shows the viscosity, surface tension and electrical conductivity of the Cu-based nano-inks. When the Cu content was increased, the viscosity of the inks increased first and then decreased; the surface tension did not vary significantly; and the electrical conductivity increased significantly [36].

4. Conclusions

Cu colloidal nanoparticles and nanopowders were successfully prepared using a pulsed wire evaporation process. The Cu colloidal nanoparticles produced with a particle size below 20 nm were uniformly dispersed in ethylene glycol. The melting point of Cu nanoparticle-based material decreased by about 30% compared to that of the bulk material. The TEM results showed that a ~5-nm-thick amorphous oxide film was present on the Cu nanopowder surfaces; these correspond to CuO, as confirmed by XPS. A hydrocarbon coating on the Cu nanopowder surfaces was obtained using an organic solvent, which effectively improved the oxidative stability of these nanopowders. When the inks were prepared from aggregated Cu nanopowders synthesized under an Ar atmosphere, the dispersion characteristics of the Cu nanoparticles were improved by a ball-milling process. The electrical conductivity of Cu nano-inks produced was 10–28 μS cm⁻¹ for 20–40 wt% of Cu.

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