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ORIGINAL ARTICLE - THEORY, CHARACTERIZATION AND MODELING

Characterization of Copper Complex Paste: Manufacture of Thin Cu-Seed Films on Alumina Substrates

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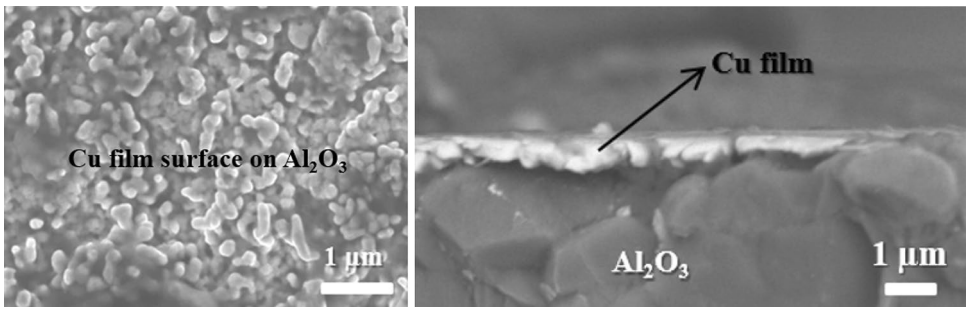
Abstract
The fabrication process of pure Cu films on an alumina substrate using a copper complex paste was evaluated. After vigorous milling for 7 h, copper complexes (copper(II) formate and pure Cu) with an average particle size of 312 nm were formed. A printed pattern was prepared with a paste containing the particles and a pure Cu film was formed by annealing at 250 °C for 30 min under nitrogen atmosphere. After removing the upper part of the film, a homogenous Cu film with a thickness of 424 nm was observed on the substrate. The film demonstrated excellent adhesion properties and had an low electrical resistivity of 4.38 μΩ cm. Hence, the film can be used as a seed for additional Cu plating.

Graphical Abstract



Keywords Thin copper film · Alumina substrate · Copper complex paste · Adhesion · Electrical resistivity

1 Introduction

The formation of conductive Cu films on an alumina substrate is considered to be one of fundamental technologies in electronic component industries [1–4]. However, traditional technologies for fabrication of films are still used today. For the formation of thick Cu films, a Cu foil can be directly bonded onto an alumina substrate using a CuO film; this is called direct bonded copper technology. In the case of thin pure Cu films, they cannot be directly adhered onto alumina. Hence, the pre-deposition of an adhesion layer, such as Cr, Ti, or TiW, is usually required [5–8]. This process normally requires expensive and inconvenient vacuum conditions. Moreover, the patterning of films usually involves complex processes such as lithography and etching [1, 2, 5–8]. These processes also require large amounts of Cu to be removed, which generates additional environmental problems. However, by using a paste containing Cu-based particles, it is possible to obtain a directly patternable material and eliminate the lithography and etching processes.

The composition of the Cu-based particles is usually chosen as alloy which has lower electrical conductivity than pure Cu due to severe oxidation of pure Cu during heat sintering in air [9–11]. Moreover, during this heat sintering process, glass frits, which exacerbate the electrical properties

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of the final sintered film, need to be added into the paste to obtain sufficient adhesion with the substrate [3, 4]. The high sintering temperature (usually exceeding 600 °C) also influences the oxidation properties of the particles and increases the overall process cost [4]. The study and development of Cu-based pastes are nevertheless justified based on the fact that Cu shows similar electrical conductivity [3, 4, 12–18] and outstandingly low material cost when compared with Ag. In addition, using a low processing temperature would be industrially advantageous in several ways: it reduces delamination failure and large interfacial stress (induced by the thermal expansion coefficient mismatch between Cu films and the substrate), it inhibits the oxidation of formed Cu films and lowers energy consumption. Yabuki et al. [14, 15] studied low-temperature formation of pure Cu films on a glass substrate by thermal decomposition under a nitrogen atmosphere using pastes containing copper–amine complexes. Although the electrical resistivity values were low, in the range of 2.0×10^{-5} to 5.0×10^{-6} Ω cm [14, 15], the adhesion properties of the pure Cu films, which is crucial for industrial applications, were not reported at all. Lee et al. [16–18] reported on the formation of pure Cu films on a polyimide film using a paste containing Cu complexes. They observed good adhesion properties after heating at 250 or 275 °C under a nitrogen atmosphere and a low resistivity value of 1.3×10^{-5} to 8.2×10^{-6} Ω cm [17, 18]. Hence, this study focuses on low-temperature fabrication of pure Cu films on an alumina substrate using a Cu complex paste.

2 Experimental

Copper complex particles were synthesized by a mechanochemical method: 23 g of copper(I) oxide (Cu_2O, 98.5%, Junsei), 103.5 mL of formic acid (HCOOH, 85.0%, OCI), and 86.3 mL of zirconia balls of 0.5 mm diameter were inserted into a alumina jar with a volume of 500 mL. The contents were mixed at a speed of 300 rpm for 1–7 h using a planetary mill (HPM501, HAJI Engineering and Global). The resulting slurry was filtered, washed with ethanol (C_2H_5OH, 95%, Samchun Pure Chemical), and dried in a vacuum chamber at 50 °C for 7 h. The paste for the formation of Cu films was prepared by mixing copper complex particles and α-terpineol (98.5%, Samchun Chemical) at a weight ratio of 6:4 using a spatula. The prepared paste was then screen-printed onto a 96.4 wt.% alumina substrate (Nikko Company, Al_2O_3–$2.02SiO_2$–$0.81MgO$–$0.27CaO$–$0.19ZrO_2$–$0.07Na_2O$–$0.02K_2O$–$0.01Fe_2O_3$–$0.01Bi$–$0.01Y$, thickness: 1 mm) covering an area of 10×10 mm^2 with a thickness of 100 μm. The substrate was heated at 250 °C at a heating rate of 10 °C/min in a tube furnace under a nitrogen atmosphere to decompose the copper(II) formate and form a pure Cu film.

The microstructures of the synthesized copper complex particles and sintered films were investigated using scanning electron microscopy (FE-SEM, JSM-6700F, JEOL Ltd.), and the phase identification was performed using X-ray diffraction (XRD, DE/D8 Advance, Bruker). The average size of particles was determined by direct measurement in the FE-SEM micrographs. The adhesion property was examined by inspection of the sintered film on the alumina after removal of an adhesive tape as specified by the American Society for Testing and Materials (ASTM) standard D3359 [19]. Sheet resistance of the sintered film was measured using a four-point probe linked to a source meter (2400, Keithley) and electrical resistivity was calculated from thickness of the films measured by SEM.

3 Results and Discussion

Figure 1 shows the SEM images of sky-blue copper complex particles obtained by milling with different times. After 1 h, irregular particles with angled shapes were observed. The irregularity in size significantly diminished after additional milling and the average particle size decreased after 7 h.

Figure 2 indicates the average particle size of copper complex particles as a function of milling time. The particle size is 861 nm with large deviation after 1 h and rapidly decreases by approximately half after 2 h. This size is maintained even after 3 h, with lower deviation, and remains stable up to 6 h. However, the size abruptly decreases to 312 nm after 7 h.

XRD patterns of copper complex powders as a function of milling time are displayed in Fig. 3. For all powders, pure Cu and copper(II) formate, i.e., $Cu(COOH)_2$ phases are indexed. These results indicate that changes in particle size do not influence the resultant phases for different milling times. However, the intensities of the main Cu (111) peaks at $2\theta = 43.3°$ increases as the milling times increase. XRD measurements show that following reaction (1) occurs during the milling process [16–18].

$$Cu_2O + 2HCOOH \rightarrow Cu(COOH)_2 + Cu + H_2O \quad (1)$$

Particles obtained after 7 h of milling were used to prepare a paste for a stencil printing process on an alumina substrate. Films were formed by annealing at 250 °C under nitrogen atmosphere for different times: 1, 10, and 30 min. SEM images of these films are shown in Fig. 4; because the obtained film was brittle due to gas-generating reactions, the images show the part of the film that remains on the substrate after delamination and removal of initial covering by air blowing. Nevertheless, the remaining film would be used as a seed for additional Cu plating. As shown in the sample annealed for 1 min (Fig. 4b), Cu was formed almost immediately and is visible as fine particles throughout the

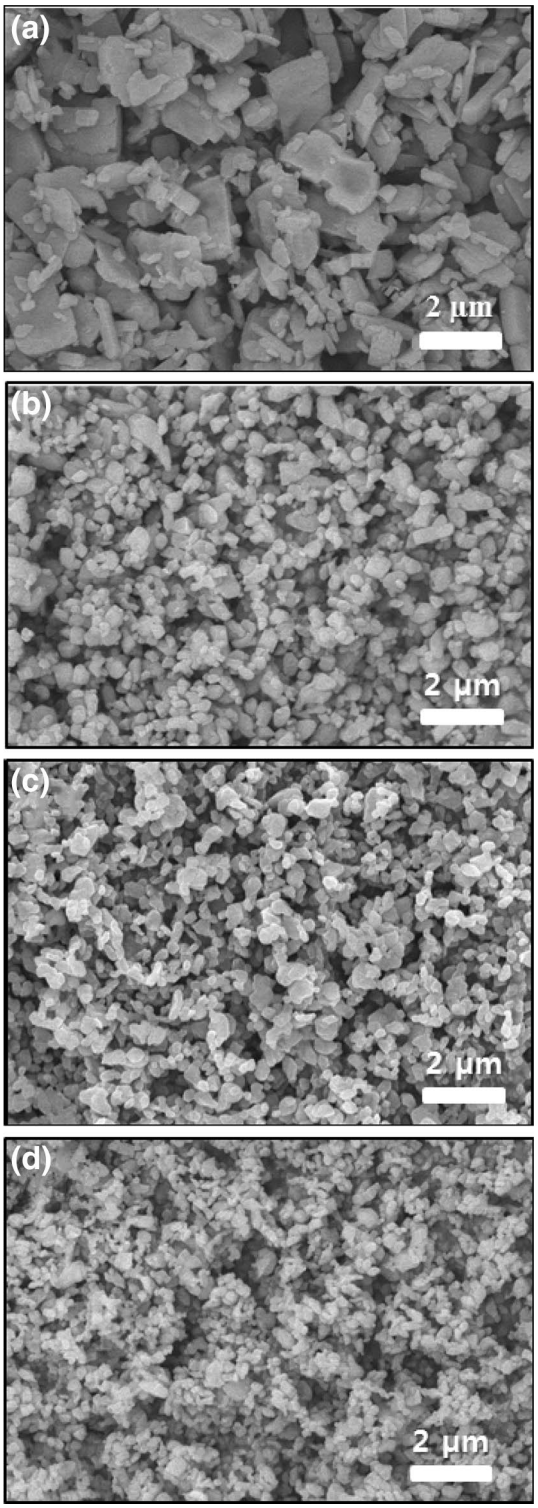

Fig. 1 SEM images of copper complex particles synthesized with different milling times: **a** 1, **b** 3, **c** 5, and **d** 7 h

alumina surface. After 10 min (Fig. 4c), the Cu particles grew into bigger ones, where a densification process (sintering) formed aggregated structures on the alumina surface.

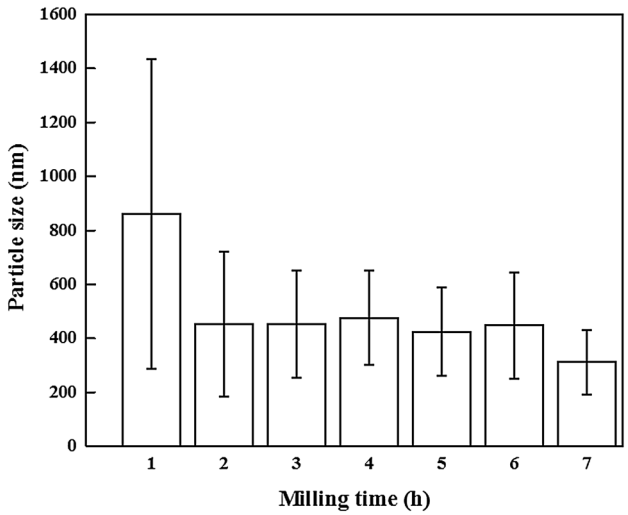

Fig. 2 Average particle size of copper complex particles synthesized with different milling times

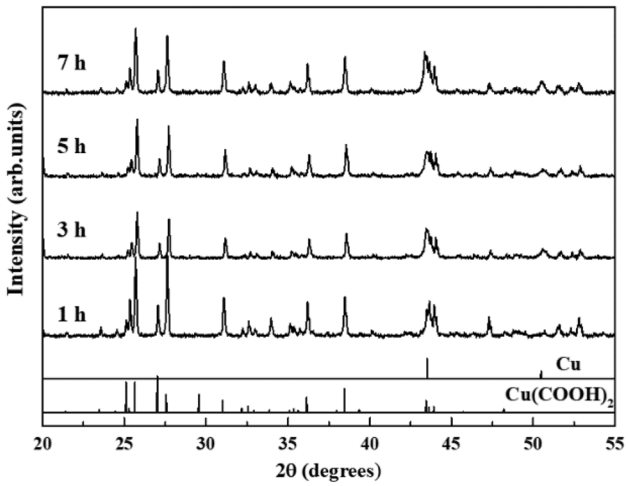

Fig. 3 XRD patterns of copper complex powders synthesized with different milling times

The electrical resistance of the so-formed film was tremendously high owing to its discontinuous structure. For longer annealing times, the surface was fully covered by a continuous Cu film which was formed through sintering between bigger Cu particles, modifying the initial morphology of the alumina surface (Fig. 4d). The results in Fig. 4 show that the amount of reduced Cu increases when the annealing time is longer. The reduction process that forms Cu from $Cu(COOH)_2$ consists of a two-step decomposition process, as shown by the following reactions [17].

$$Cu(COOH)_2 \rightarrow Cu(COOH) + CO_2 \uparrow + 1/2H_2 \uparrow \quad (2)$$

$$Cu(COOH) \rightarrow Cu + CO_2 \uparrow + 1/2H_2 \uparrow \quad (3)$$

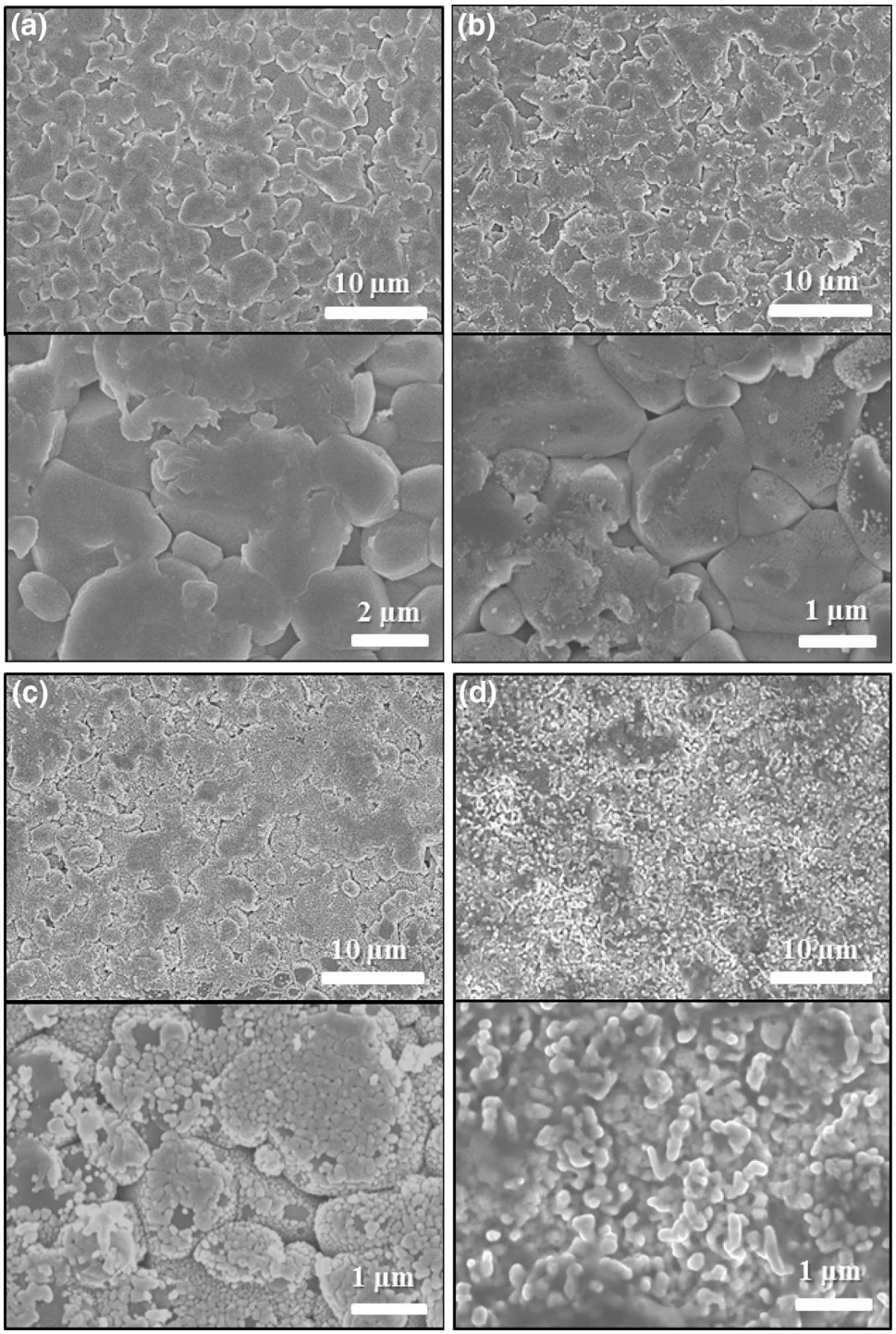

Fig. 4 SEM images of **a** initial surface of an alumina substrate and films annealed at 250 °C for different times after printing of the paste containing copper complex particles: **b** 1, **c** 10, and **d** 30 min

XRD results in Fig. 5a show that only pure Cu and alumina peaks were observed after annealing at 250 °C for 30 min. This confirms that the coating material in Fig. 4d is Cu. The alumina peaks can be detected because the remaining Cu film is thin. Therefore, it is expected that the formation and sustentation of the pure Cu by the pyrolysis of Cu(II) formate is possible even under attack by trace oxygen in the nitrogen atmosphere. Main cause of the sustentation may be in situ formation of an atmosphere envelope that protects from the oxygen, owing to the generation of carbon dioxide and hydrogen by Eqs. (2) and (3).

A cross-sectional SEM image of the Cu film is shown in Fig. 5b. The cross-sectional plane was formed by breaking off the substrate after making notch on the surface. Although the Cu film was thin (the thickness was 424 nm), the adhesion between the Cu film and alumina seems to be excellent

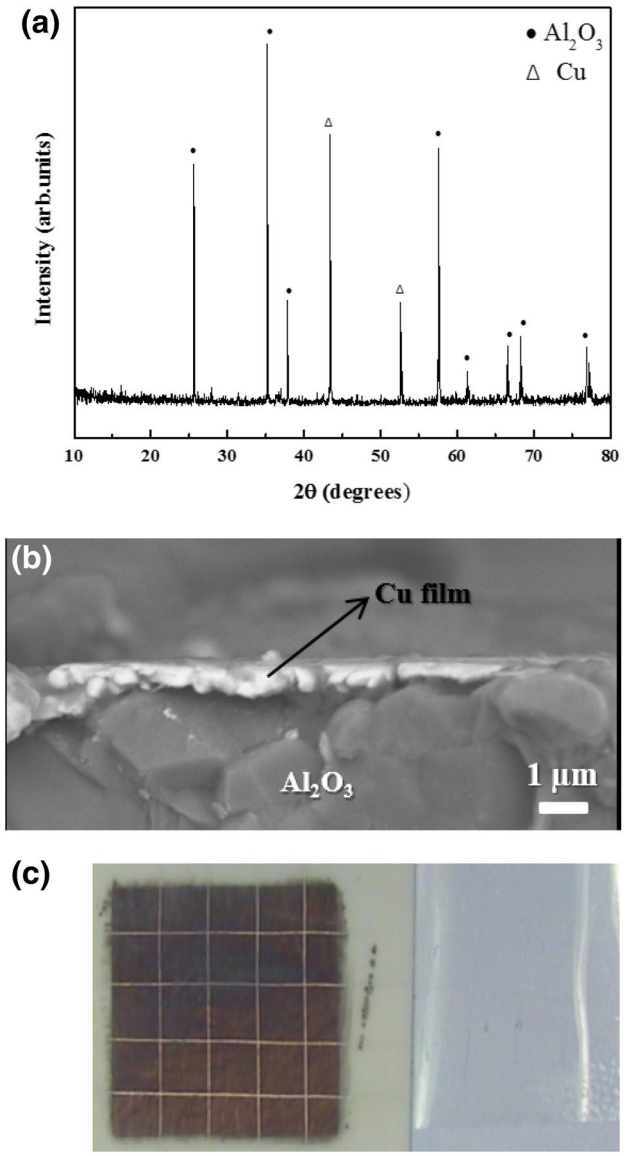

Fig. 5 **a** XRD patterns of the film on the alumina surface after annealing at 250 °C for 30 min. **b** A cross-sectional SEM image of the film and **c** an image indicating a tape test result

since no delamination was detected at the interface. The Cu film also seems to penetrate into the grainboundaries of alumina substrate. From the tape test of D3359, the edges of cuts of the Cu film on the alumina substrate remained completely smooth and none of squares of the lattice were detached; this implies that the adhesion between the Cu film and alumina was of the best grade (ASTM class 5B) [19]. The cause of the excellent adhesion might be the formation of Cu ions at the alumina surface, as represented by the following Eq. (4). Cu ions, which are formed together with CO during decomposition of formate compounds in acidic oxides such as alumina or zirconia [20], could react easily with the O in alumina and create chemical bonds.

$$Cu(COOH) \rightarrow Cu^{+} + CO \uparrow + OH^{-} \quad (4)$$

The electrical resistivity of the Cu film was measured as a low value of 4.38 (± 1.17) μΩ cm, which is just 2.5 times higher than that of pure Cu (1.76 μΩ cm). Based on previous reports [14–18], the electrical properties of the obtained Cu film also seem to be dependent on process parameters in the fabrication and thermal decomposition processes of Cu complex particles. An additional plating process might increase the thickness of a pure Cu layer in a dense structure and lower the resistivity so that it is closer to pure Cu.

4 Conclusions

A milling process was used to produce copper complex particles. Different milling times were studied. Both copper(II) formate and pure Cu were observed in all powder samples and the amount of pure Cu slightly increased with increasing milling time. After 1 h, irregular particles with angled shapes with an average size of 861 nm were obtained. Large particles among these irregular particles were transformed into smaller, more homogenous particles as the milling time was increased to 7 h. The average size of the particles obtained after 7 h was 311.8 nm. These particles were used as a filler to fabricate a paste, which was printed onto an alumina substrate and annealed at 250 °C under nitrogen atmosphere for different times. The upper part of the film was removed by delamination and air-blowing, and the remaining film can be used as a seed for additional Cu plating. SEM images show that Cu particles adhered to the alumina substrate even after annealing for 1 min. As the annealing time was increased, the Cu particles grew and sintering between the particles resulted in a pure Cu film fully covering the substrate. For an annealing time of 30 min, the thickness of the remaining Cu film was 424 nm and the adhesion between the film and alumina was excellent, corresponding to class 5B according to the tape test of ASTM D3359. Moreover, the Cu film also showed an outstanding electrical resistivity value of 4.38 μΩ cm, which is just 2.5 times higher than that of pure Cu.

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