



Full Length Article

Deposition of pure Cu films on glass substrates by decomposition of Cu complex pastes at 250 °C and additional Cu plating

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ABSTRACT

Pure Cu film strongly adherent to glass substrates was deposited by printing $\text{Cu}(\text{COOH})_2$ -containing paste and decomposing it at 250 °C in nitrogen atmosphere. The complete transformation of $\text{Cu}(\text{COOH})_2$ into Cu required 30 min and generated a low sheet resistance of 0.167 Ω/sq (volume resistivity: 15.0 $\mu\Omega\text{-cm}$). Maximum adhesion between the Cu film and substrate was attained at the Cu complexes: α -terpineol mixing ratio of 6:4 by weight. The spike-shaped microstructure at the Cu/glass interface was determined to be the main cause for the outstanding adhesion properties. The resistance further decreased to 0.084 Ω/sq by increasing the thickness and modifying the surface of the Cu film via electroless Cu plating.

1. Introduction

Although the formation of a Cu film on a glass or ceramic substrate is considered a basic technology in substrate-related industries [1–5], its progress has been slow. Because pure Cu cannot directly adhere onto substrates, pre-depositing an adhesion layer, such as Cr, Ti, or TiW, is usually required [5–8]. This method is normally implemented using expensive vacuum deposition and patterning techniques involving lithography and etching [1,2,5–8]. Moreover, these techniques generate large amounts of polluting metals, which have to be properly discarded. Adopting a paste containing Cu particles as a patternable base material could eliminate the expensive processes. However, glass frits, which deteriorate the electrical properties of the final sintered film, should also be added to the paste to ensure proper adhesion with the substrate during heat sintering under an inert atmosphere [3,4]. Moreover, because of the high sintering temperature in the 600–720 °C range, Cu particles can be easily oxidized by trace oxygen even under a nitrogen atmosphere [9,10]. Therefore, highly conductive pastes co-containing Ag particles and glass frits have been commercialized for use on ceramic substrates [11]. However, application methods of Cu-based conductive pastes are highly required, because while the electrical conductivities of Cu and Ag are similar [3,4,12–18], the cost of Cu is approximately 1/100 that of Ag. If the low-temperature sintering of pure Cu could be achieved without using glass frits, the pattern-printing/sintering process to form films presenting excellent conductivity on glass substrates and relatively low transition temperatures would be possible.

Pioneering research on the low-temperature formation of pure Cu films on glass substrates via the thermal decomposition of Cu-based pastes has been previously conducted by Yabuki et al., who used pastes containing copper-amine complexes and decomposed them at 140 °C under a nitrogen atmosphere [14,15]. Although excellent electrical resistivities in the 5.0×10^{-6} to 2.0×10^{-5} $\Omega\text{-cm}$ range were obtained, the adhesion properties between the pure Cu films and glass substrates, considered crucial for industrial applications, have not been reported. Adhesion properties were nonetheless speculated to be unsatisfactory, because some cross-sectional microstructures at the Cu film/glass substrate interfaces indicated that Cu films separated from the glass substrates. On the other hand, Joo and Lee et al., reported the fabrication of pure Cu films on polyimide using a single paste formulation containing Cu complexes [16–18]. They observed a low resistivity of 8.2×10^{-6} $\Omega\text{-cm}$ and good adhesion properties after heating the sample at 250 °C for 30 min under a nitrogen atmosphere. Therefore, in this study, a sintering process at 250 °C using a Cu complex paste on a glass substrate was evaluated to concurrently achieve optimal adhesion properties and superior electrical conductivity. The relatively low processing temperature would be industrially advantageous for large-scale applications as it could reduce the interfacial stress induced by the mismatch in the coefficient of thermal expansion between metal films and glass substrates at the edges of specimens, suppress the oxidation of the formed Cu films, and reduce energy consumption.

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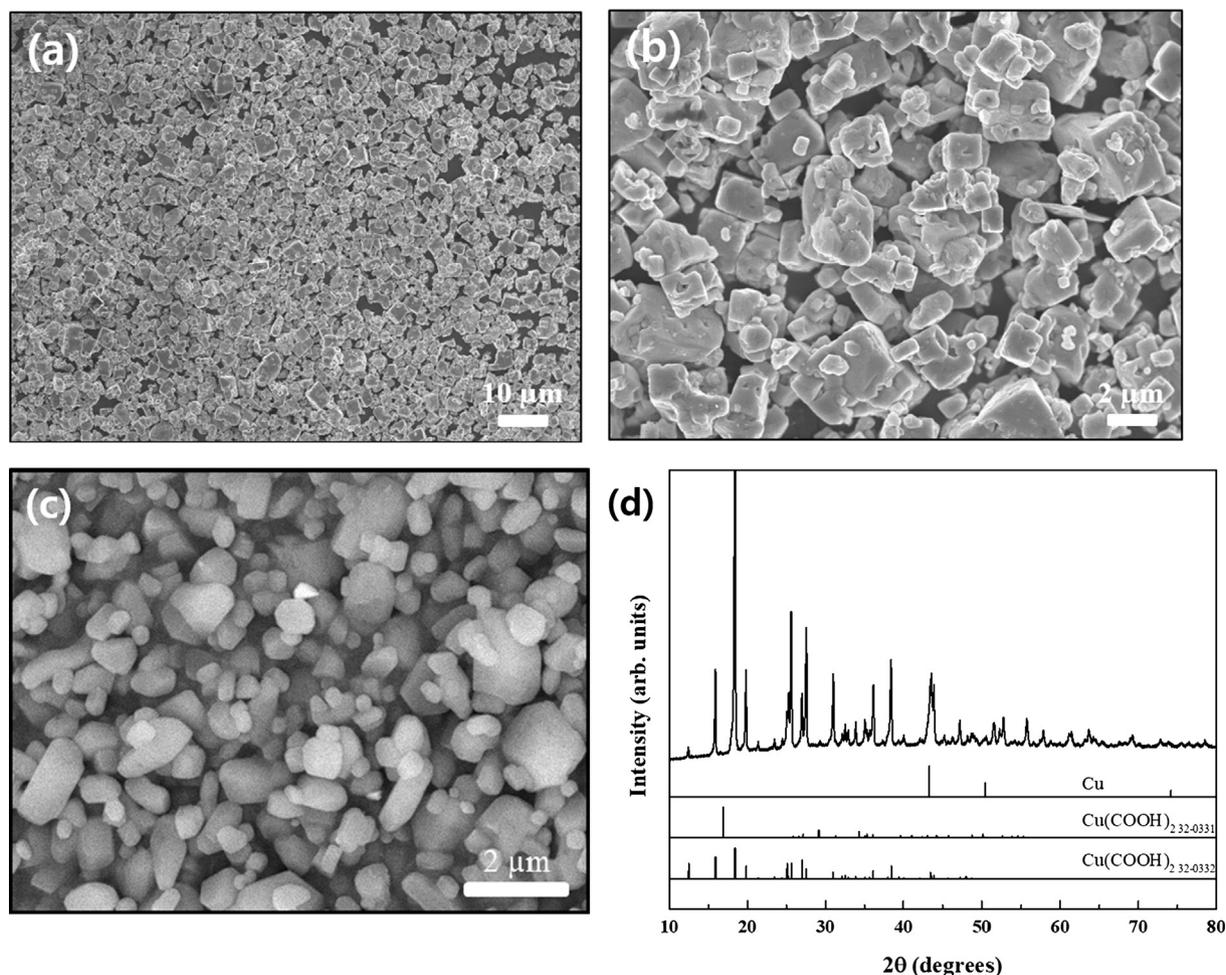


Fig. 1. (a) Low- and (b) high-magnification SEM images of used Cu_2O particles, (c) BSE image and (d) XRD spectra of Cu complex particles synthesized using a mechanochemical method for 5 h.

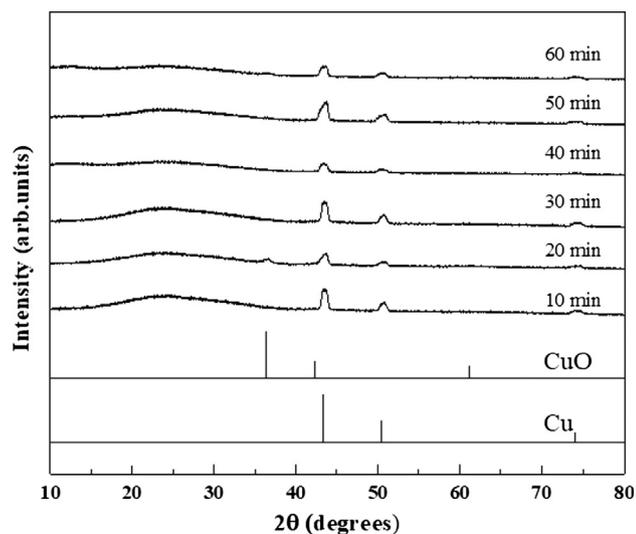


Fig. 2. (a) XRD spectra of films deposited by heating the Cu complexes and α -terpineol mixture with a weight ratio of 6:4 at 250 °C for different times under a nitrogen atmosphere.

2. Material and methods

Cu complexes were synthesized using a mechanochemical method. In brief, 23 g Cu_2O powder (95%, Daejung Chemical Industry Co., Ltd.),

103.5 mL formic acid (HCOOH, 85%, OCI), and 86.3 mL zirconia balls (1 mm in diameter) were added to a 500 mL zirconia jar. The contents were subsequently subjected to intense mechanical collisions at 300 rpm for 5 h using a planetary mill. The resultant slurry was separated by filtration, which was followed by five washes with ethanol (95%, Samchun Pure Chemical Co., Ltd.). Afterward, the filtered sludge was dried under vacuum at 50 °C for 2 h. The paste containing Cu complexes was prepared by mixing specific weight ratios of Cu complexes and α -terpineol (98.5%, Samchun Pure Chemical Co., Ltd.) using a spatula. The paste was then screen-printed on a $10 \times 10 \text{ mm}^2$ area of a soda-lime silica glass (71.5% SiO_2 -14.5% Na_2O -9.5% CaO , microscopic slides, Heinz Herenz) substrate, followed by heating at 250 °C at a rate of 10 °C/min in a tube furnace under a nitrogen atmosphere to decompose the Cu complexes and form a pure Cu film. To deposit an additional Cu coating on the already formed Cu films, electroless Cu plating was also conducted using a plating solution prepared by mixing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99%, Duksan Pure Chemicals Co., Ltd.), ethylenediaminetetraacetic acid tetrapotassium ($\text{C}_{10}\text{H}_{12}\text{K}_4\text{N}_2\text{O}_8$, 98.5%, Daejung Chemical Industry Co., Ltd.), 2,2'-bipyridine ($\text{C}_{10}\text{H}_8\text{N}_2$, 99%, Junsei Chemical Co., Ltd.), polyethylene glycol (M_w : 1000, 98.5%, Samchun Pure Chemical Co., Ltd.), formaldehyde (HCHO, 99.5%, Daejung Chemical Industry Co., Ltd.), and deionized water. Plating was performed for 3 min at pH 12.5 and 60 °C.

The microstructures of the synthesized Cu complex particles and final films were examined by scanning electron microscopy (SEM, SU8010, JEOL Ltd.), and the crystal structures were analyzed by X-ray diffraction (XRD, DE/D8 Advance, Bruker). The depth profiles of

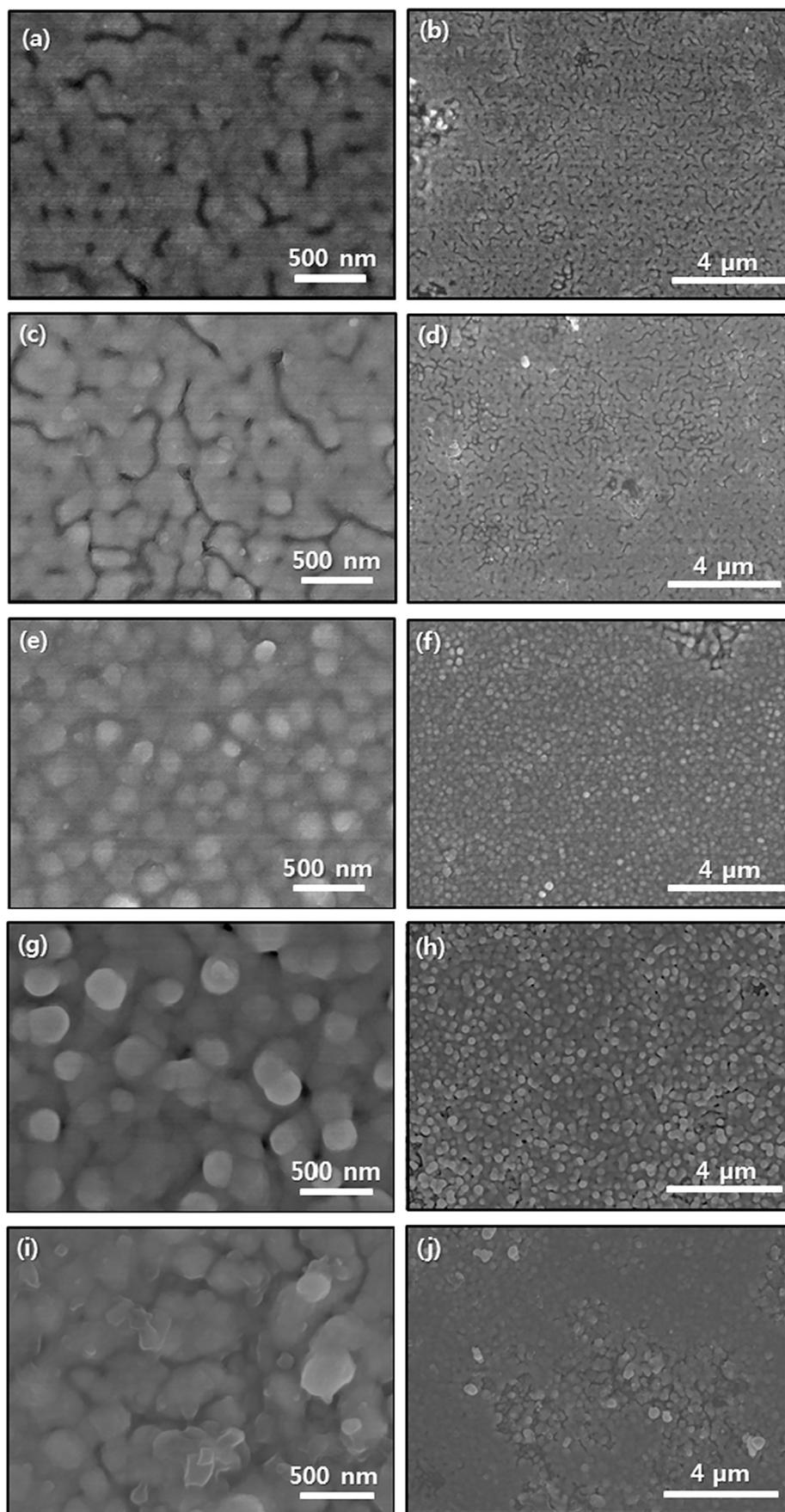


Fig. 3. SEM images of films deposited using the Cu complex paste heated for (a) and (b) 10 min, (c) and (d) 20 min, (e) and (f) 30 min, (g) and (h) 40 min, and (i) and (j) 50 min at 250 °C under a nitrogen atmosphere.

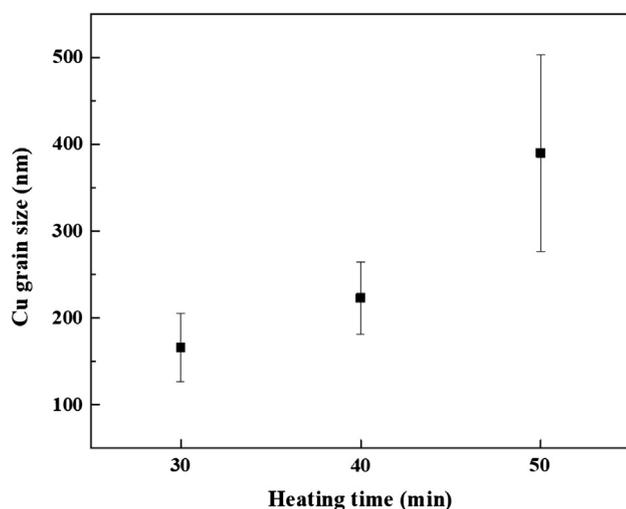
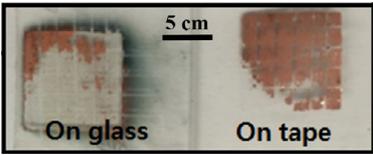


Fig. 4. Grain size of films deposited by heating the Cu complex paste at 250 °C for 30–50 min under a nitrogen atmosphere.

Table 1

Adhesion properties of pure Cu films formed on glass after heating Cu complexes and α -terpineol mixtures with different weight ratios at 250 °C for 30 min under a nitrogen atmosphere.

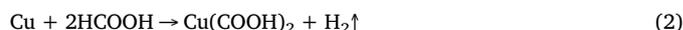
Cu complex: α -terpineol weight ratios	Images after adhesion test	Adhesion grade (ASTM class)
5:5		0B
6:4		5B
7:3		4B
8:2		0B

elements at the Cu film/glass interface were examined using Auger electron spectroscopy (AES, PHI-700, ULVAC-PHI). The adhesion properties were evaluated by inspecting the Cu films deposited on glass after removing them using adhesive tape, as specified by the American Society for Testing and Materials (ASTM) standard D3359 [19]. Finally, the sheet resistance of the formed films was measured using a four-point probe connected to a source meter (2400, Keithley Instruments).

3. Results and discussion

Fig. 1 presents the SEM images of the used Cu_2O particles, the backscatter electron (BSE) image, and XRD patterns of the Cu complex

particles synthesized using the mechanochemical method described above for 5 h. Although the average size of Cu_2O particles was measured to be 6.43 μm from the SEM images, particles of irregular shapes were observed, and their size distribution was wide, ranging from several hundreds of nanometers to several micrometers. The average particle size of the sky-blue Cu complex particles was 550 nm (standard deviation: 276 nm), but the particles were irregular in both shapes and sizes. In addition, small amounts of pure Cu phase and balanced Cu $(\text{COOH})_2$ phase were detected, while no Cu_2O was present (Fig. 1(b)). The formation of pure Cu could be described as a sequential reaction using the following equations [16–18]:



Unlike the first reaction step in Eq. (1), H_2 gas was generated during the second reaction step in Eq. (2) through the reaction between Cu formed in the first reaction and formic acid. An increase in pressure in the sealed jar because of H_2 formation could hinder reaction (2), thus preserving the Cu formed in the first reaction [17].

The XRD spectra of films heated for different periods at 250 °C under a nitrogen atmosphere using a Cu complexes: α -terpineol weight ratio of 6:4 are presented in Fig. 2. Cu phases could be indexed after 10 min of heat treatment, and the intensities of the peaks generally increased as the heating time increased. Only minor evidence for the presence of the CuO phase could be detected, even after 60 min of heating. These results indicated that the decomposition reaction of Cu $(\text{COOH})_2$ from the Cu complexes at 250 °C proceeded as follows [17]:



The surface SEM images of the films in Fig. 2 are presented in Fig. 3. The finely wrinkled surface microstructures of the films heated for 10 or 20 min and their relatively low Cu peak intensities implied that the decomposition reaction in Eq. (3) did not reach completion. However, for the films heated for 30 min, a microstructure of repetitive grains was observed, while the Cu peak intensities increased tremendously. Hence, the grains were determined to consist of Cu. Subsequently, the grain size progressively increased when the heating time increased beyond 30 min, as shown in Fig. 4. However, the sintered Cu films did not exhibit dense structures, even after 60 min of heating. In fact, the upper portions of the formed Cu films could easily be removed by dusting while applying little external force. It was surmised that the outgassing of CO_2 and H_2 from Eq. (3) would increasingly hinder sintering between Cu grains as the sintering region was close to the surfaces of the films, therefore resulting in the formation of a fragile upper structure.

The adhesion properties of pure Cu films deposited on glass substrates by heating mixtures of Cu complexes and α -terpineol with different weight ratios at 250 °C for 30 min are summarized in Table 1. Adhesion tests were performed after removing the Cu particles that were not attached to the glass substrate. Approximately half of each Cu film was dusted off because of this removal. At the Cu complexes: α -terpineol ratio of 5:5, the Cu film presenting a cross-cut area significantly greater than 65% was detached and transferred onto the surface of the adhesive tape. However, the adhesion properties dramatically changed when the Cu complexes: α -terpineol ratio was 6:4, where the edges of the cuts of the Cu film on glass remained completely smooth and none of the lattice squares was detached. This implied that the adhesion between the Cu film and glass substrate was the most optimal. The adhesion properties subsequently deteriorated again when the Cu complexes: α -terpineol ratio increased to 7:3. For these samples, less than 5% detachment of small flakes of the Cu film was observed at the intersections of the cuts. Finally, the adhesion properties were completely eliminated when the Cu complexes: α -terpineol ratio was increased up to 8:2. These results indicated that the Cu complexes: α -terpineol mixing ratio tremendously affected the adhesion properties. When the α -terpineol content exceeded a certain optimal value, a

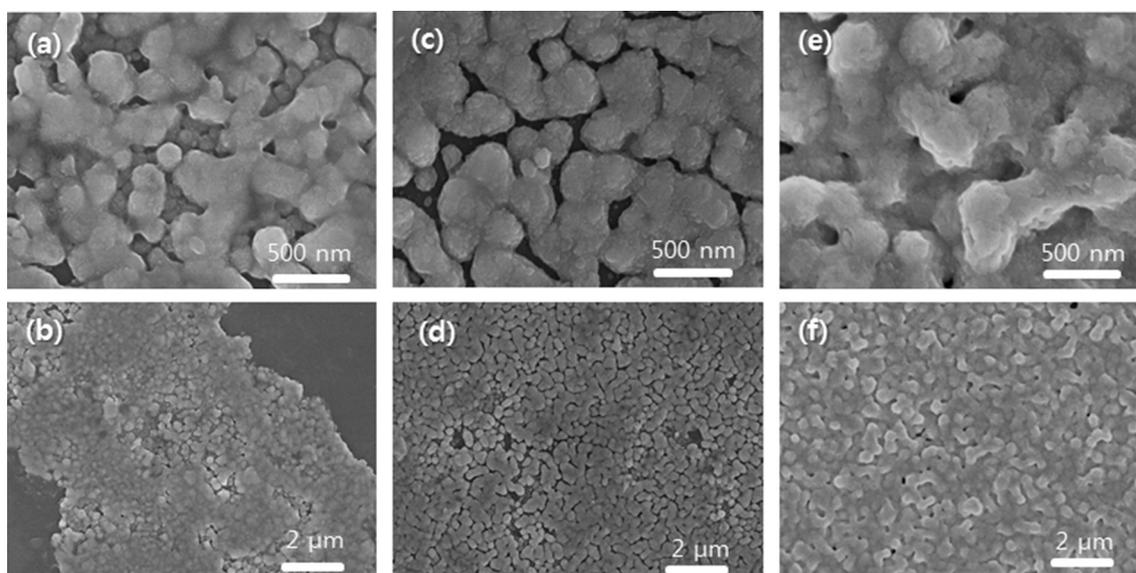


Fig. 5. Surface SEM images of Cu films deposited on glass by heating mixtures of Cu complexes and α -terpineol with weight ratios of: (a) and (b) 6:4, (c) and (d) 7:3, and (e) and (f) 8:2, at 250 °C for 30 min under a nitrogen atmosphere.

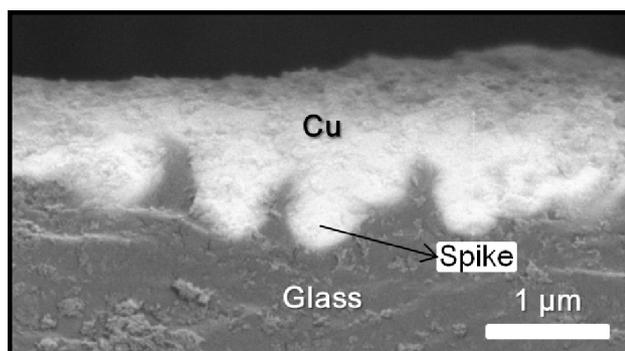


Fig. 6. Cross-sectional BSE image of sample in Fig. 5(a).

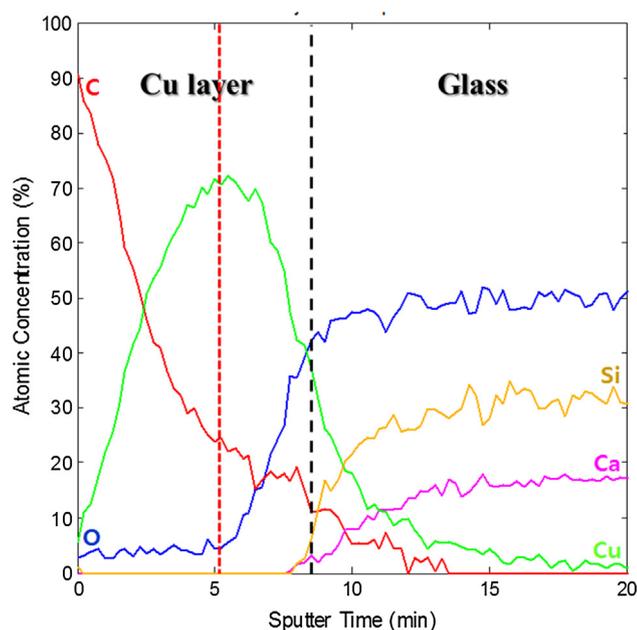


Fig. 7. AES depth profiles of sample in Fig. 5(a).

sparse configuration of Cu atoms and grains on the glass surface was observed. In addition, excessive evaporation of α -terpineol during heating occurred, which induced low adhesion between the Cu film and substrate. By contrast, concentrations of Cu complexes exceeding the optimum level might interrupt the outgassing behavior of H_2 during decomposition due to a decrease in the number of open pores, and could, thus, result in the upward displacement of the nano-sized Cu particles formed near the glass surface. This extrusion seemed to occur even in the region close to the glass surface as the Cu complex content increased, and resulted in significant changes in the adhesion properties, as shown in Table 1.

The surface SEM images of the Cu films deposited on glass substrates by heating mixtures of Cu complexes and α -terpineol with different weight ratios at 250 °C for 30 min are displayed in Fig. 5. As discussed above, the density of the Cu films slightly increased as the Cu complexes: α -terpineol weight ratio increased. Therefore, a denser microstructure lowered the adhesion grade between the Cu films and glass substrates because of the reaction mechanisms, which included the effects of the outgassing behavior of H_2 .

The cross-sectional BSE image of the pure Cu film in Fig. 5(a), which was deposited using the Cu complexes: α -terpineol weight ratio of 6:4, is presented in Fig. 6. At the Cu film/glass interface, the Cu film deposited onto the glass surface was spike-shaped, and presented an irregular size and round tips. Moreover, the density of the Cu grains along the deposition direction gradually decreased. The formation of the spike-shaped interface might be interpreted as the result of the chemical reaction between the as-reduced Cu which presented an excess reaction potential and soda-lime silica glass. It has previously been reported that the reaction between Cu and O atoms generates chemical bonds in diverse systems [20]. The formation of the spike-shaped morphology can be explained by a local electrochemical phenomenon that is associated with the redox reactions between Cu and O atoms in amorphous grains. The active Cu atoms, which were reduced from $Cu(COOH)_2$, could be easily oxidized, and the generated Cu ions could rapidly migrate along grain boundaries or easier migration paths such as a nanoporous structure [21]. This phenomenon might be the reasonable cause for both the locally fast diffusion of Cu ions and resultant uneven interface. From the AES results in Fig. 7, a mixing region of Cu and O atoms (between the dashed lines), where the Cu profile rapidly decreased and the O profile abruptly increased, was observed. These findings implied that Cu diffused and formed chemical bonds with O atoms. Since the formation of the spike-shaped interface became hard to observe when

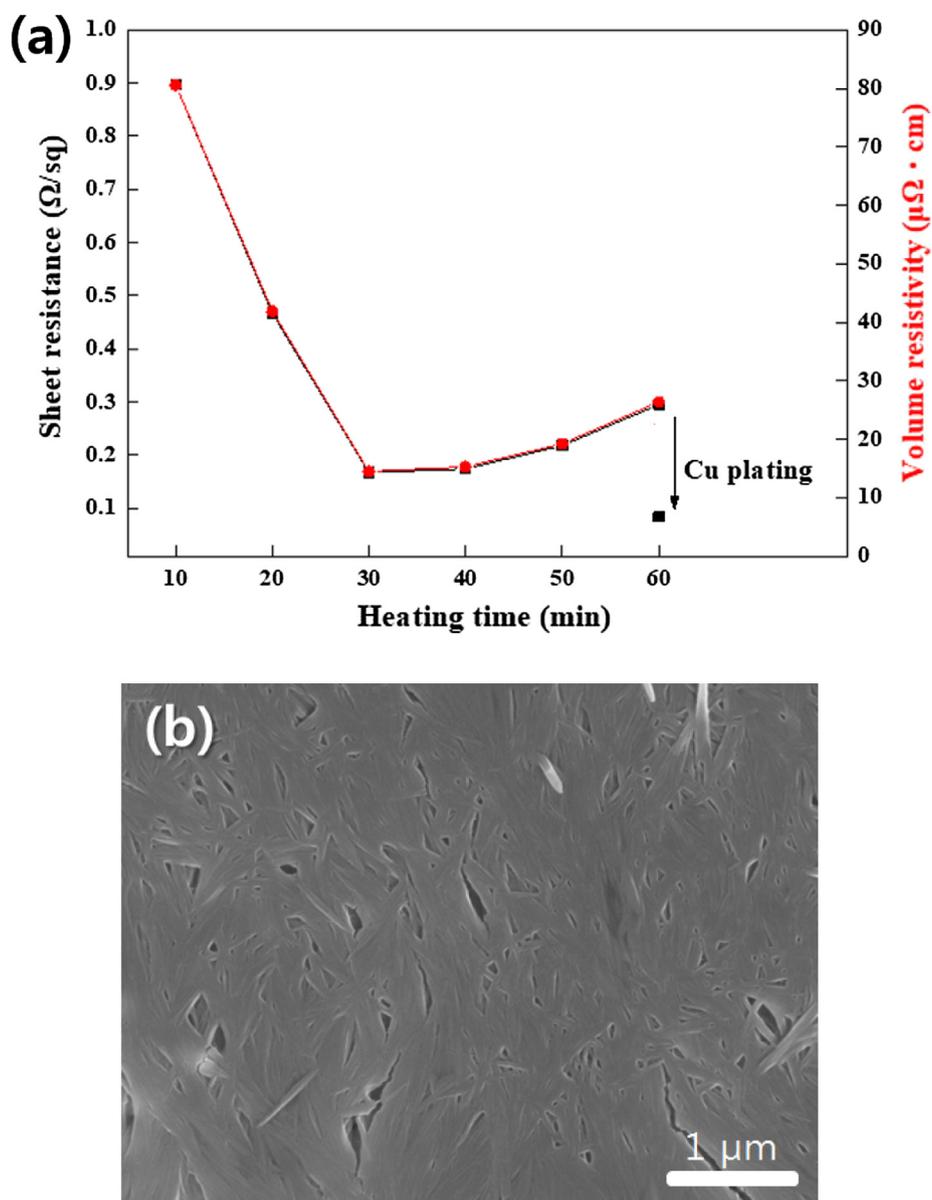


Fig. 8. (a) Sheet resistance of films deposited on glass by heating mixtures of Cu complexes and α -terpineol with the weight ratio of 6:4 at 250 °C for different times under a nitrogen atmosphere and (b) surface SEM image after electroless Cu plating on the Cu film deposited for 60 min. Note that the resistance decreased to 0.084 Ω/sq after plating.

the Cu complexes: α -terpineol weight ratio changed, the interface was considered to be a deciding factor for the adhesion properties of the pure Cu film deposited on glass.

The sheet resistances of Cu films deposited on glass substrates by heating the Cu complexes and α -terpineol mixture with the weight ratio of 6:4 at 250 °C for different periods of time are illustrated in Fig. 8(a). For the films heated for 10 and 20 min, the decomposition of Cu(COOH)₂ was incomplete, and the sheet resistance values were abnormally high. However, the resistance rapidly decreased upon increasing the heating time to 30 min. The minimum sheet resistance of 0.167 Ω/sq (volume resistivity of 15.0 $\mu\Omega \cdot \text{cm}$) was obtained at the heating time of 30 min, which, from the above discussion, was considered to be the time required for the complete transformation of Cu(COOH)₂ into pure Cu. The resistance gradually increased when the heating time increased to 60 min, although the number of grain boundaries per unit length decreased, as observed in Fig. 4. The increase in Cu grain size as the heating time increased should contribute to a decrease in electrical resistance. Considering the XRD results in Fig. 2, the increase in the

resistance could be attributed to the minor surface oxidation of the pure Cu films. While the minor surface oxidation of the film could not be clearly observed as an XRD peak, it might significantly affect the surface resistance value.

The surface SEM image after electroless Cu plating on the Cu film heat-treated for 60 min is presented in Fig. 8(b). Although defects presenting irregular shapes existed on the surface of the Cu film, the surface microstructure became smooth and dense compared to the uneven one observed in Figs. 3 and 5. Because electroless plating was conducted after removing the Cu particles that were unattached to glass, the total thickness of the Cu film increased to approximately 900 nm, which was slightly more than double the thickness before plating. Because of the plating, the resistance decreased from 0.296 to 0.084 Ω/sq , which was close to the resistance values of common pure Cu films.

4. Conclusions

In this study, we fabricated pure Cu films strongly adhered, according to ASTM class 5B, on glass substrates by printing a paste containing Cu(COOH)₂ and inducing its decomposition at 250 °C under a nitrogen atmosphere. To achieve full conversion of Cu(COOH)₂ into pure Cu, 30 min of heat treatment at 250 °C were required, where the additional heating time gradually increased the sheet resistance of the pure Cu film. The mixing ratio of Cu complexes:α-terpineol was a crucial factor governing the adhesion properties between the Cu films and glass substrates, which were found to be the most optimal at the 6:4 wt ratio. A spike-shaped microstructure at the Cu/glass interface was determined to be the main cause for the outstanding adhesion properties of the pure Cu films on glass. Although the sheet resistance was relatively high immediately after heating, because of the non-dense and loose upper region of the resulting Cu film, it decreased to 0.084 Ω/sq, which was close to the resistance of common pure Cu films after electroless Cu plating. The aforementioned adhesion properties of pure Cu films on glass and the thickness enhancement and improvement of electrical properties by additional Cu plating confirmed the feasibility of the proposed low-temperature and low-cost process for the formation of Cu conductors or electrode patterns on glass substrates.

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