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Formate-Free Metal-Organic Decomposition Inks of Copper Particles and Self-Reductive Copper Complex for the Fabrication of Conductive Copper Films

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Abstract: Metal-organic decomposition (MOD) inks have been developed for printed electronics applications. Cu-based MOD inks prevent the oxidation of the metal during storage, as the Cu is already present in an oxidized form (i.e. a salt). However, usually hazardous formates such as Cu (II) formate have to be used as the copper salt in order to ensure thermal decomposition and self-reduction of the metal salt at moderate temperatures (less than 150 °C). In this study, a formate-free hybrid ink containing copper particles and a Cu/1-amino-2-propanol (AmIP)/acetate complex was developed for the fabrication of conductive copper films on flexible polymer substrates at low sintering temperatures. A hybrid ink with a weight ratio of 3:1copper particles to MOD ink produced a conductive copper film with close-packed copper particles and a low resistance of $7.3\times10^{-5}\Omega$ cm after sintering at a temperature of 180 °C for 60 min under a N_2 gas flow. Good oxidation resistance of the copper films was observed after exposure to air at 23 °C for two months.

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1. INTRODUCTION

Copper-based conductive inks are of great interest for printed electronics, due to their high conductivity, low cost, and reduced electro-migration effect. Usually, two main types of ink are used, metal nanoparticle-based inks and metal-organic decomposition (MOD) inks [1, 2]. A major challenge for copper-based inks is the very rapid oxidation rate in air, during storage and sintering (essential for obtaining conductive percolation paths). To avoid the oxidation of copper in the sintering process, a reducing gas, such as hydrogen, is typically introduced to supress the oxidation during the sintering process, and the reduction temperature should be higher than 230 ºC when hydrogen is used in order to achive the enhanced reducing aibility [3, 4].

MOD copper inks enable us to overcome the oxidation of copper during storage, since the metal is already present in its oxidized form (i.e. Cu (II) salt). In most cases, Cu (II) formate is used in the MOD inks from the benefit of formate: low thermal decomposition of Cu (II) formate at moderate temperatures (less than 150 °C) and the self-reduction reaction ability of the Cu (II) salt by the formate [5-13]. However, there are stains and corrosion problems caused by formic acid vapor as strong acid during the sintering process. Thus, alternative MOD inks based on copper carboxylate have been developed from the view point of being formate free to achieve adequately conductive copper films, although the sintering temperatures are relatively high (above 250 °C) [14]. Another issue in MOD copper inks is the low Cu content (typically 20wt %) in the ink compared to the Cu nanoparticle-based ink (more than 40 wt %). In order to ensure a sufficiently high copper content, the effectiveness of hybrid MOD ink with copper particles has been demonstrated for fabricating conductive copper films (~ 9×10^{-4} Ω cm) at 100 °C [15]. Previously, we have demonstrated that 1-amino-2-propanol (AmIP) has reduction abilities in a copper nanoparticle-based ink [16]. Hence, AmIP is expected to be appropriate for replacing formate in MOD inks due to the self-reduction reaction ability of the Cu (II) salt [16].

In this study, we present a formate-free hybrid MOD ink containing copper particles and Cu (II)/AmIP/acetate complex for the fabrication of conductive copper films on flexible polymer substrates. The Cu particles are inter-connected via the thermal decomposition of the complex at low temperatures between 120 and 140 °C, compared to the case (above 250 °C) of Cu (II) acetate. As a result, the hybrid ink produced a conductive copper film with a low resistance

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of ~ 7 × 10^{-5} Ω cm after sintering at a temperature of 180 °C under a N_2 gas flow without reducing gas such as hydrogen and formic acid.

2. MATERIAL AND METHODS

Polyimide (PI) films with a thickness of 50 μm and high thermal resistance were used as flexible substrates for the Cu films. All the chemicals were used as received without further purification. 1-amino-2-propanol (AmIP, 98%), ethylene glycol (99.5%), and methanol (99.5%) were purchased from Wako Chemicals, Japan. Copper particles (1~5 μm) were purchased from Kojundo Chemical Laboratory Co., Ltd, Japan. A Cu (II)/AmIP/acetate complex was prepared by mixing Cu (II) acetate (3g) and AmIP (2.6mL) in a mixed solvent of methanol (7mL) and ethylene glycol (0.67 mL) at ice bath. The resultant solution was stirred for 2 h. The free acetic acid and the residual methanol were removed by drying under vacuum for 1 h at 50 °C and then for 3 h at room temperature under vacuum, resulting in a MOD ink. To ensure a high copper content, a hybrid MOD ink was prepared by stirring the MOD ink with copper particles (1~5 μm) in mortar under air for about 30 min until they turn into paste. Before the mixing the copper particles with the MOD ink, where the copper particles were immersed in N,N-diethyl hydroxylamine, and then copper particles were washed with AmIP, toluene, and hexane. The prolonged de-solvent process for the hybrid MOD ink under high vacuum should be avoided due to the risk of elimination of ethylene glycol from the ink, resulting in the aggregation of copper particles. In this case, a few drops of ethylene glycol(~10 μL) into the MOD ink could produce paste-like hybrid MOD ink by re-dispersion of copper particles.

We prepared hybrid MOD inks with different weight ratios of copper particles to Cu:MOD ink = 3:1 (0.3:0.1 g) , 2:1 (0.27:0.13 g), 1:1(0.2:0.2 g), and 1:2 (0.13:0.27 g). The hybrid MOD ink was deposited into wiring gutter on a polyimide film using a doctor blade method. The resulting Cu films were then sintered at various temperatures for 60 min in an electric furnace (FT-6000, FuLL-TECH, and Osaka, Japan) under a N_2 gas flow of 1.1 L/min. The thickness of each Cu film after heating (~80μm) was determined using a surface roughness measurement tool (SJ 310, Mitutoyo, Japan). The electrical resistivity of the Cu conductive films was analyzed using a four-point probe instrument (Loresta AX MCP-T370, Mitsubishi Chemical Analytech Co., Japan) from the measured values of the sheet resistance and the thickness of Cu film.

Field-emission scanning electron microscopy (FE-SEM; JSM-6700, JEOL, Japan) images were collected at an acceleration voltage of 5.0 kV. X-ray diffraction (XRD) patterns were obtained using a diffractometer (D2 Phaser, Bruker, Germany) with a Cu-K_α radiation source (λ = 1.5406 Å). Thermo-gravimetric analysis (TGA) was performed using a TG analyser (Thermo plus EVO, Rigaku, Japan) at a heating rate of 10 °C/min under a nitrogen flow.

3. RESULTS AND DISCUSSION

FT-IR spectrum of Cu (II)/AmIP/acetate complex is shown in Figure **1a**. The O-H stretching and N-H stretching bands were observed 3255 and 3067 cm^{-1} for the complex, respectively, which are originated from the AmIP ligands in the complex. In addition, the symmetric and antisymmetric carboxylate stretch modes (1405 and 1560 cm^{-1}) were also observed in the complex, indicating that the complex also includes the coordination of acetate to the Cu (II). The thermogravimetric analysis of the Cu (II)/AmIP/acetate complex under a nitrogen flow is shown in Figure **1b**. The total content of Cu in the complex was estimated approximately to be 22 ± 3.5 wt% from the weight loss in the TG curve, which is close to the theoretical value (19.3 wt %) of Cu (II)/AmIP/acetate complex with a molar ratio of 1:2:2[Cu (II):AmIP:acetate]. This estimation is based on the fact that the weight loss in the TG curve is attributed to the decomposition/ volatilization of ligands in the complex. That is, the residue at high temperature (~400 °C) can be regarded as copper. From the FT-IR and TG-DTA data, it is likely that the copper complex

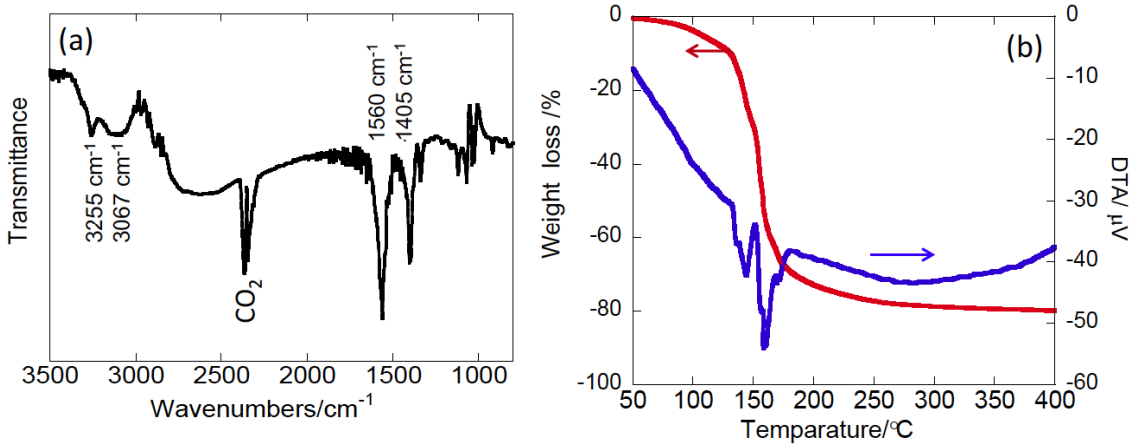

Figure 1: (**a**). FT-IR spectrum of Cu(II)-AmIP-acetate complex with a molar ratio of 1:2:2 (Cu(II):AmIP:acetate). (**b**) TG-DTA curves of the Cu(II)-AmIP-acetate complex at a heating rate of 10 °C/min under a N_2 flow.

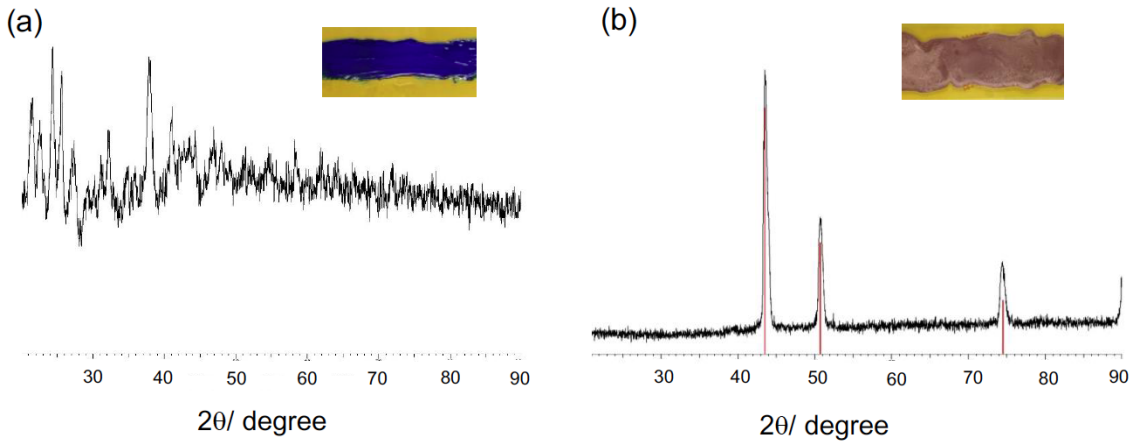

Figure 2: XRD pattern of (**a**) MOD ink with Cu(II)-AmIP-acetate complex with a molar ratio of 1:2:2 (Cu(II):AmIP:acetate) and (**b**) copper film achieved after calcination of the MOD ink at 150 °C for 30 min. The insets are photographs of the MOD ink (**a**) and the copper film on a polyimide substrate (**b**).

prepared in this study is Cu (II)/AmIP/acetate complex (1:2:2).

It should be noted that the thermal decomposition of the Cu(II)/AmIP/acetate complex occurred at low temperatures between 120 and 140 °C in the TG curves, which is much lower than that (>250 °C) of Cu(II) acetate complex [17]. It has been reported that the coordination of amine to Cu(II) reduces the thermal decomposition temperature [8, 9]. The reduction of thermal decomposition temperature of the Cu (II)-AmIP-Ac complex is attributed to the coordination of AmIP to Cu (II).

The XRD analysis of MOD ink containing the Cu (II)/AmIP/acetate complex showed no diffraction peaks of metallic copper before the heating, while the thermal decomposition of MOD ink by the heating of 150 °C for 30 min under a N_2 gas produced metallic Cu, which was identified by its diffraction peak (Figure **2**). There was no observation of the oxidation of copper in the Cu film. Thus, we found the MOD ink containing Cu (II)/AmIP/acetate complex could produce Cu film at 150 °C due to the reducing ability of AmIP. However, it was difficult to obtain a uniform Cu film from the MOD ink owing to the formation of many cracks and the in homogeneity. The resultant Cu film showed high resistivity value with more than 10^6 Ω cm.

In order to ensure a sufficiently high copper content, hybrid MOD inks were prepared by mixing of metallic Cu nanoparticles and the MOD ink. The pure copper particles-based film without the MOD ink showed high resistivity value of more than 10^6 Ω cm even after the heating of 180 °C for 60 min under a N_2 gas flow. In contrast, the electrical resistivity of Cu film after the heating of 180 °C from the hybrid MOD ink dramatically decreased. The resistivity values were of the order of 10^{-4}~10^{-5} Ω cm, depending on the weight ratio of the Cu particles to the hybrid MOD ink in the range examined here. The resistivity values were 8.1 × 10^{-5}±1.3×10^{-5}, 7.3 × 10^{-5}±1.8×10^{-5}, 7.6× 10^{-5}±0.5× 10^{-5}, 15 × 10^{-5}±4.5×10^{-5}, and 24 × 10^{-5}± 6.5×10^{-5}Ω cm for weight ratios of 4:1, 3:1, 2:1, 1:1, and 1:2 Cu particles to MOD ink, respectively (Figure **3**). The Cu film with lowest electrical resistivity was obtained from the hybrid MOD ink with a 3:1 ratio of Cu particles to MOD ink [hybrid MOD ink (3:1)]. The SEM images of the Cu film obtained from the hybrid MOD ink (3:1) showed close-packed Cu particles on the surface of the calcined film at the the heating temperature of 180 °C for 60 min under a N_2 gas flow (Figure **4**). By adding the MOD ink into Cu particles, the packing density of Cu particles and the electric connection were significantly improved, resulting in the low electrical resistivity of Cu film.

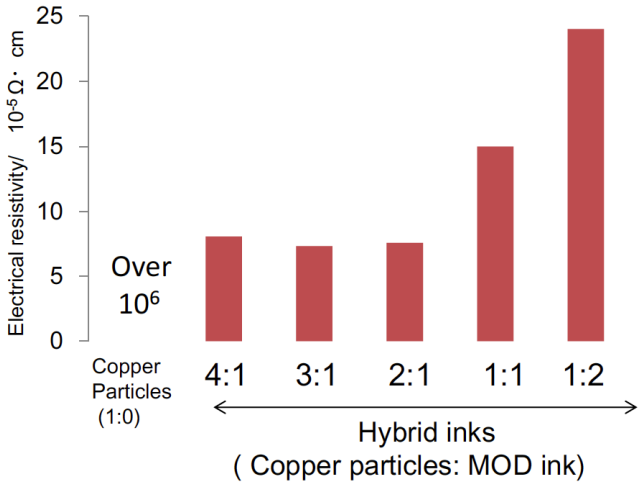

Figure 3: Electrical resistivity of Cu films after thermal sintering of the hybrid MOD inks with different weight ratios of copper particles to MOD ink at 180 °C for 60 min under a flow of N_2.

Figure **5a** shows the electrical resistance of the Cu films prepared from hybrid MOD ink (3:1) sintered at different temperatures between 120 and 250 °C for 60 min under a N_2 gas flow. The electrical resistivity of the Cu films dramatically decreased between 120 and 150 °C, which is consistent with the thermal decomposition temperature of Cu (II)-AmIP-acetate complex (as shown in Figure **1b**). The electrical

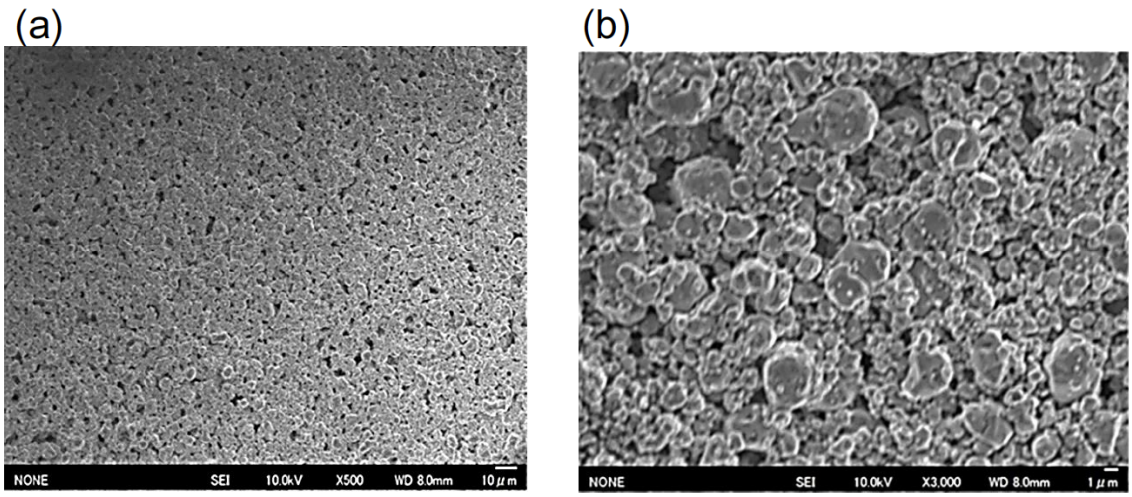

Figure 4: FE-SEM images of a Cu film made from a hybrid MOD ink with a weight ratio of 3:1 (copper particles:MOD ink) on a polyimide film after sintering at 180 °C for 60 min under N_2 flow.

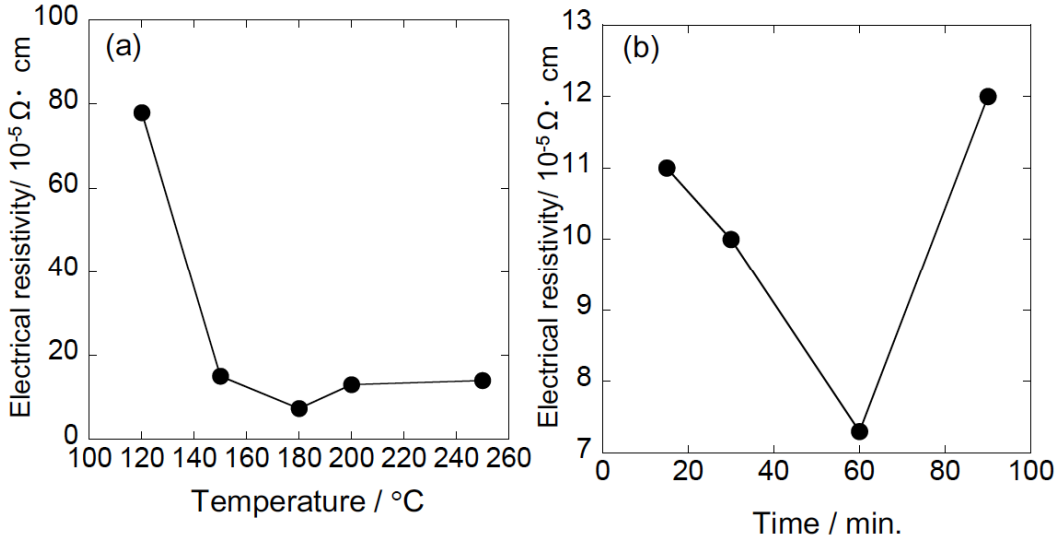

Figure 5: Electrical resistivity of Cu films (prepared from a hybrid MOD ink with a weight ratio of 3:1, copper particles:MOD ink) on polyimide films as a function of (**a**) sintering temperature (60 min sintering time), and (**b**) sintering time (180 °C sintering temperature).

resistivity values decreased further above 120 °C ($78\times10^{-5}\pm15\times10^{-5}$, $15\times10^{-5}\pm4.5\times10^{-5}$, and$7.3\times10^{-5}\pm1.8\times10^{-5}$ Ω cm at 120, 150, and 180 °C, respectively), and they slightly increased as the heating temperature increased from 180 to 250 °C ($7.3\times10^{-5}\pm1.8\times10^{-5}$, $13\times10^{-5}\pm3.5\times10^{-5}$, and $14\times10^{-5}\pm2.5\times10^{-5}$Ω cm at 180, 200, and 250 °C, respectively). The sintering temperature to obtain the Cu film with the lowest electrical resistivity from the hybrid MOD ink (3:1) is 180 °C. The electrical resistivity of the Cu films depended on the sintering time, as shown in Figure **5b** for the hybrid MOD ink (3:1) sintered at 180 °C. It shold be emphasized that a low electrical resistivity of 11×10^{-5} Ω cm was achieved at even a short heating time of 15 min, and that the minimum value of 7.3×10^{-5} Ω cm was obtained after heating for 60 min. Longer times above 60 min resulted in an increase in the resistivity, which might be due to the oxidation of copper.

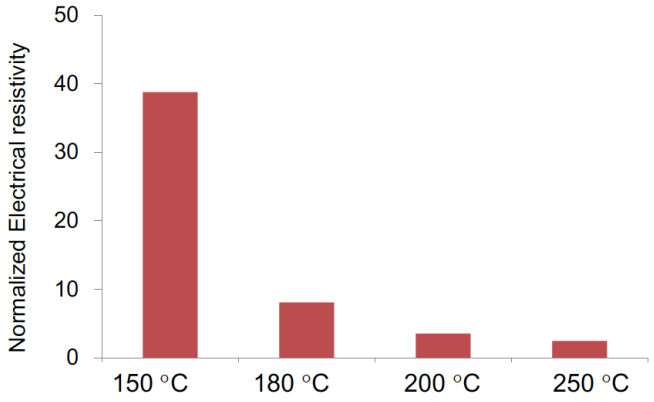

Figure 6: Normalized electrical resistance of Cu films (prepared from a hybrid MOD ink with a weight ratio of 3:1, copper particles:MOD ink)sintered at different temperatures after exposure to air and humidity (30 ± 5%) at 23 °C for two months. The reference resistance was the initial value before this ageing test.

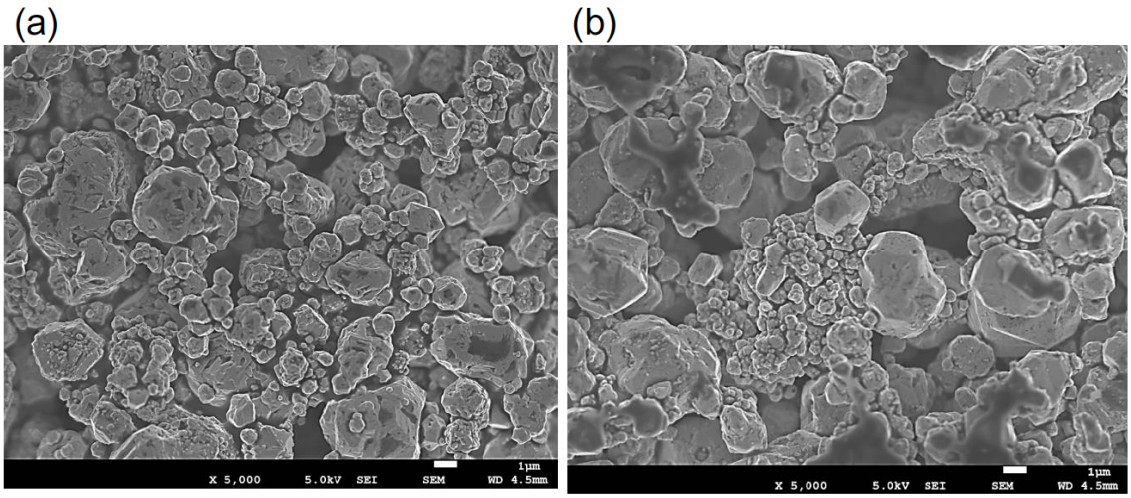

Figure 7: FE-SEM images of a Cu film (prepared from a hybrid MOD ink with a weight ratio of 3:1, copper particles:MOD ink) on a polyimide film after sintering at (**a**)150 °C and (**b**) 200 °C for 60 min under N_2 flow.

In the present study, we also examined the long-term stability of Cu films after two months under an air atmosphere at 23 °C, which were prepared from the hybrid MOD ink (3:1) (Figure **6**). The long-term stability of the Cu film strongly depended on the sintering temperatures of Cu films. The increase of Cu film resistance after two months was observed for the Cu film obtained from the sintering temperature of 150 °C, but it became smaller for the Cu film heated at higher temperatures of more than 180 °C. A low film resistance of 10^{-4} Ω cm was kept even after exposure to air for two months at the sintering temperatures of more than 180 °C. It should be noted that the electrical resistivity value of Cu film obtained from the sintering temperature of 150 °C (15×10^{-5} Ω cm) was almost identical to that (13×10^{-5} Ω cm) at 200 °C after the preparation, but the long-term stability of Cu film prepared at 200 °C was much higher than that at 150 °C.

The SEM images showed the Cu (II)-AmIP-acetate complexes are decomposed to form Cu nanoparticles less than 1 μm, and they are randomly stacked together with large Cu particles, as shown in Figure **7b**. Moreover, the continuous Cu films clearly exist on the surface of large Cu particles. The small Cu nanoparticles from thermal decomposition of Cu (II)-AmIP-acetate complexes connect the large Cu particles together to improve the electrical resistivity and the long-term stability.

4. CONCLUSIONS

Highly conductive copper films were achieved at low sintering temperatures using a hybrid MOD ink containing copper particles and Cu (II)-AmIP-Ac complex. For the first time, high quality copper films could be formed from such inks without requiring formate or a reducing gas as the AmIP successfully reduced the Cu (II) complex at low temperatures between 120 and 140 °C. The conductive copper film consisted of close-packed copper particles with a low resistance of 7.3×10^{-5}Ω cm after sintering at 180 °C for 60 min under a N_2 gas flow. Removing formate from the processing would make the use of hybrid MOD inks safer and simpler for fabricating printed electronic devices.

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