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Relation	

Stable shape for copper film using low-temperature thermal decomposition of copper microparticles for printable electronics

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ABSTRACT

A paste of copper microparticles, formic acid, and octylamine were developed for the copper thick films with a stable shape and low electrical resistivity via low-temperature calcination. In this study, (1) Effect of cleaning the copper microparticle surface with formic acid, (2) Effect of calcination temperature, and (3) Effect that the addition of amine exerted on volume resistivity and on the shape of copper film are discussed. The volume resistivities of the thick copper film are measured using a 4-point probe method. The surface, thickness and shape of the cross section of copper film was observed by FE-SEM and optical microscope. The copper film obtained at 150 °C from the paste with optimal condition had a stable shape, uniform thickness of 43 μm, and low resistivity of 32.3 μΩ cm.

Keywords: Copper particle; Copper formate; Thermal decomposition; Printable electronics; Volume resistivity

1. Introduction

Ink-jet printing has attracted attention as a process that uses conventional photolithography to produce electronic devices [1], [2], [3], [4]. By comparison with conventional photolithographic techniques, ink-jet printing offers the significant advantage of reductions in time, cost, and waste produced during manufacturing. One notable application of this technology is the production of solar cell electrodes. Generally, silver paste is used to harvest solar energy. Silver has good electrical conductivity and is stable [5], [6], [7], [8]. To cut costs, however, copper is being considered as a candidate that can produce highly efficient solar energy at a low cost [9], [10], [11], [12]. Nevertheless, there are limitations. Copper is easily oxidized in air, and material limitations must be overcome for sintering at high temperatures or under air. For this reason, various methods have been proposed to manufacture copper films under low temperatures.

Kim et al. [13] have reported an ultra-high-speed flash white light (FWL) sintering method that utilizes poly (N-vinylpyrrolidone) functionalization of the copper nanoparticles. Other polymer substrates such as polyimide or polyethylene terephthalate possess thermal conductivity that is lower than that of silicon wafers. To overcome these limitations, those researchers used a multi-pulsed FWL sintering method. Yoshida et al. [14] introduced a new Cu-alloy paste composed of copper particles and low melting point alloy (LMPA) particles. When the LMPA particles melt, metal contact is formed with the Cu particles, which prevents oxidation. This Cu-alloy paste forms excellent electrical contact at the paste/ITO interface. This Cu-alloy paste has shown utility for use in solar cells that require low-temperature processes.

In our previous work [15], [16], it has succeeded in lowering the temperature by adding amines. The conductive film prepared from copper formate-amine complexes with various types of amines (dipropylamine, dibutylamine, diamylamine, dihexylamine, hexylamine, heptylamine, octylamine and nonylamine) were prepared and their electrical conductivity was evaluated. A thin film composed of a copper-octylamine complex with a volume resistivity of 9.6 μΩ cm and a thickness of 1 μm was manufactured under a nitrogen atmosphere at 140 °C [16]. However, the finger electrodes for solar cells require a width of less than 80 μm, a height of more than 32 μm, and an aspect ratio of more than 0.4. Those stipulations suggested the need for a thicker film that could maintain a freestanding edge under the sintering process.

In order to overcome the thin copper film, which was a limitation in previous research [16], we are attempted to find a condition for thickening the copper film and maintaining its shape. A thicker copper film with a stable shape are prepared by adding formic acid and amine to copper microparticles. To find the best condition of thick copper film, we suggest the cleaning method for surfaces of the copper microparticles which are first chemically cleaned using a formic acid-ethanol solution. Aspects such as the concentration of the formic acid, the calcination temperature, and the ratio of amine to formic acid are controlled to prepare a thick copper film that would provide both low resistivity and a stable shape.

2. Experimental

2.1 Materials

Copper microparticles approximately 1 μm in diameter (Rare Metallic Co., Ltd.) was the source of the paste. Formic acid (FA, 88%, Tokyo Chemical Industry Co., Ltd.) was used to clean the surface of the copper microparticles. Ethanol (EtOH, 99.5%, FUJIFILM Wako Pure Chemical Industries, Ltd.) was used as a solvent to control the formic acid concentration. n-Octylamine (OA, 98.0%, Tokyo Chemical Industry, bp=176 °C) was used as a complexing agent to bond the copper dissolved from the surface of the copper microparticles after being chemically cleaned with the FA-EtOH solution.

2.2 Preparation of copper films

Copper microparticles (0.4 g) were placed in a clean screw bottle, the cleaning solution (FA and EtOH mixture) was added to the copper microparticles in the bottle, and the solution was then stirred for 10 minutes. OA was then added with stirring for another 10 minutes. The screw bottle was centrifuged to separate the supernatant and precipitate. The precipitate was used as a paste. The film formation method involved the use of masking tape (width 9 mm, thickness 50 μm) pasted onto a glass substrate 15 mm in length with a width of 15 mm. The paste was formed via a squeegee method using a glass slide. Then, the paste was formed onto the substrate with a thickness of 50 μm. In order to prevent oxidation, the synthesized copper film was calcined under a nitrogen atmosphere using a bell jar type vacuum oven (BV-001, Shibata Scientific Co., Ltd.). During calcination, the temperature was raised from 20 °C by 5 °C/min for 30 minutes until a holding temperature of 120-170 °C was reached, followed by cooling. To observe the cross section of copper film, epoxy resin was added as a curing agent with a mass ratio = 5:3 with stirring for 5 minutes. This resin was then coated onto the copper film, which was then dried at 80 °C for 90 minutes.

2.3 Evaluation of copper microparticles and copper films

The electrical resistivity of film calcined under various conditions was measured using a 4-point probe (MCP-T600, Loresta-GP, Mitsubishi Kagaku) method. The thickness of the film was measured by examining a cross section to calculate its volume resistivity (Digital microscope, VH-2450, VHX-100F, KEYENECE). The morphologies of copper microparticles before and after cleaning, and the film surfaces were observed via field-emission scanning electron microscopy (FE-SEM) (JEOL JSM6340F) at an accelerated voltage of 20 kV. The crystallite structures of the copper microparticles before and after cleaning were identified via X-ray diffraction (XRD, RINT 2200 V, Rigaku) with Cu Kα radiation.

3. Results and discussion

3.1 Effect of cleaning the copper microparticle surface with formic acid

The effect of cleaning of copper microparticles surface on volume resistivity was investigated. During the fabrication process of the copper film, the surface cleaning of the copper microparticles helped obtain a high level of electrical conductivity, because the surface of the as-received copper microparticles was oxidized and covered with surfactant. FA was selected as the cleaning agent, since it performs a double role by promoting the formation of copper formate, as will be shown later. The copper microparticles were first immersed in formic acid for surface cleaning. Copper microparticles behave as a gel with high viscosity, which causes them to resist being uniformly coated onto a glass substrate. To improve the coating properties, a solvent was added to the FA solution. Several solvents were tested, which revealed that low-volume resistivity could be obtained using a highly hydrophilic solvent, although high-volume resistivity was obtained when using a lipophilic solvent such as ethylene glycol. Copper film with low-volume resistivity was obtained when using a hydrophilic solvent with a small molecular weight, an EtOH mixture.

The volume resistivity shown in Fig. 1 involved copper film prepared from copper microparticle paste immersed in an FA-EtOH mixture at 10 to 50 mol % of FA. After cleaning the surface of the copper microparticles, the ratio of added OA to FA was 1, and calcination was conducted at 150 °C for 30 minutes. At FA concentrations of 20 to 45 mol%, all copper films showed approximate levels of low-volume resistivity. Copper films prepared at a FA concentration of less than 25 mol%, as well as those prepared at more than 45 mol%, showed high-volume resistivity. The high resistivity of the films prepared at low FA concentrations was caused by insufficient cleaning of the surface of copper microparticles. The film prepared at high FA concentrations showed also high resistivity. The shape of the copper film was not uniform due to the high viscosity of the paste, resulting in that thinner portion of the film was brought about the high resistivity.

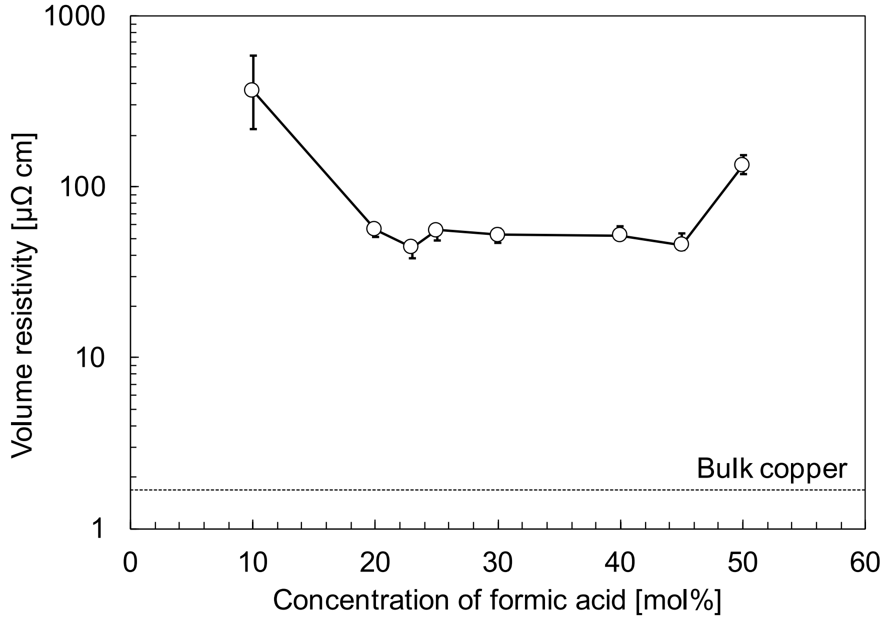

Fig. 1. The volume resistivity of the copper films prepared from paste using copper microparticles immersed in a FA-EtOH mixture with different concentrations of FA. The ratio of OA to FA is 1, and calcination was conducted at 150 °C for 30 minutes.

Copper particles were observed via SEM to confirm the change in the particle surface by cleaning. Fig. 2 shows the copper microparticles before (Fig. 2a) and after (Fig. 2b) cleaning with a FA-EtOH mixture of 50 mol% FA. The particle surface after cleaning became smoother than untreated particles, and the crystal face could clearly be observed. It is conceivable that the application of the FA not only removed the coating on the surface of the copper microparticles, but also dissolved the surface portions of the copper microparticles themselves that were easily dissolved, leaving only the crystal face that was more difficult to dissolve.

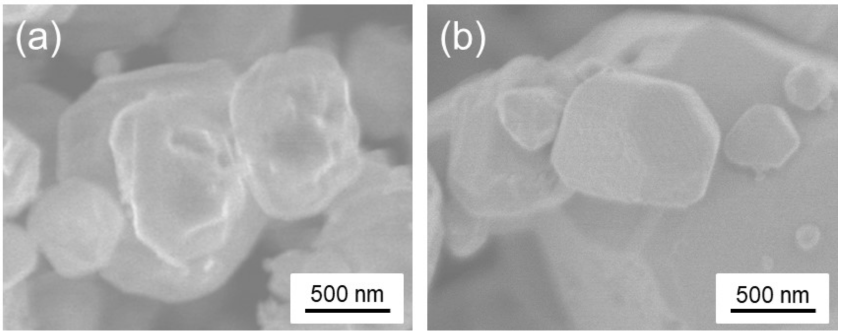

Fig. 2. SEM images of copper microparticles (a) before and (b) after cleaning by a FA-EtOH mixture made up of 50 mol% FA.

Fig. 3 shows the XRD patterns of the copper microparticles before (Fig. 3a) and after (Fig. 3b) cleaning with a FA-EtOH mixture of 50 mol% FA. The peaks of copper were observed in both copper microparticles before and after cleaning at 2θ=43.2˚, 50.3˚, and 73.9˚, which corresponded to miller indexes of (111), (200), and (220), respectively (JCPDS 01-070-3038). The surface of the copper microparticles became smooth by the cleaning with FA-EtOH mixture as shown in Fig. 2, however, it didn't affect the structural change of the copper microparticles.

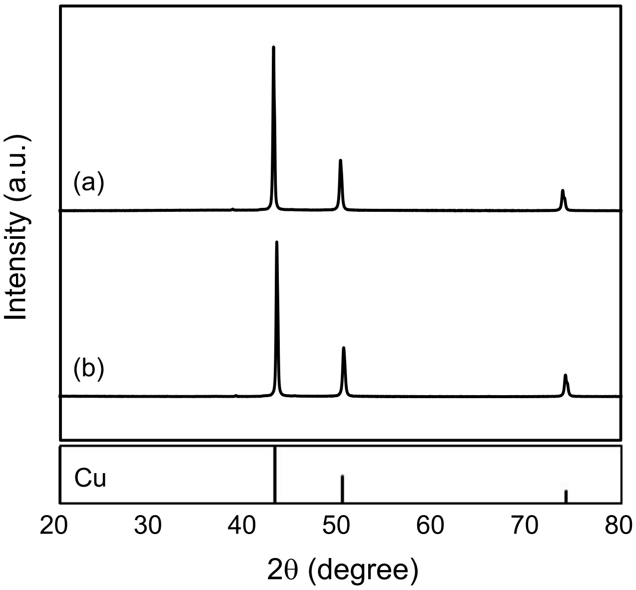

Fig. 3. XRD patterns of microparticles (a) before and (b) after cleaning by a FA-EtOH mixture made up of 50 mol% FA.

3.2 Effect of calcination temperature

The effect of calcination temperature was investigated, since the prepared paste consisted of brown copper microparticles and a blue solution, which may have been a copper formate-OA complex consisting of dissolved copper, formic acid, and OA, which will be explained later. As we have reported, the complex ink could be thermally decomposed at temperatures above 120 °C [15], [16]. The effect of the calcination temperature on the volume resistivity of the copper film was investigated by comparison with copper films calcined at temperatures ranging from 120 to 170 °C, as indicated in Fig. 4. The cleaning solution for copper microparticles was 23 mol% FA solution, and the ratio of OA to FA was 1. The volume resistivity of copper films showed a tendency to decrease at 120 to 150 °C. When the calcination temperatures were above 150 °C, the volume resistivity was increased, and the lowest rate of resistivity occurred at 150 °C. This seemed related to the boiling point of octylamine (bp=176 ºC). Below 150 °C, the value of the volume resistivity was influenced by the octylamine that remained on the surface. Such a low temperature could be insufficient to form the complex. On the other hand, at temperatures above 150 °C, the vaporization of octylamine disturbed the formation of a copper formate-amine complex.

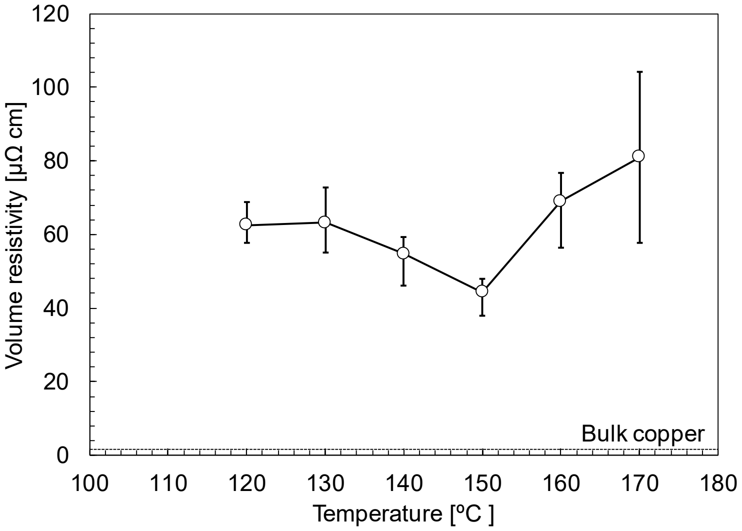

Fig. 4. The volume resistivity of copper film prepared at calcination temperatures from 120 to 170 °C. The cleaning solution of copper microparticles was 23 mol% FA solution. The ratio of OA to FA was 1.

3.3 Effect that the addition of amine exerted on volume resistivity and on the shape of copper film

The effect of the addition of OA on volume resistivity and shape of copper film was investigated. Copper film showed a lower level of volume resistivity at FA concentrations between 20 and 45 mol%, as shown in Fig. 1. Copper films prepared with 20 and 40 mol% FA solutions for the cleaning of copper microparticles were used. The volume resistivities of copper films prepared with molar ratios of OA to FA that ranged from 0.5 to 2 are shown in Fig. 5. The calcination temperature was 150 °C. The lowest values for volume resistivity, 32.3 μΩ cm, were found when a ratio of 1.2 (= OA/FA) was used for cleaning with a 20 mol% FA solution, and when a ratio of 1.2 (= OA/FA) was used for cleaning by 40 mol % FA solution. These were the results of the connection by copper nanoparticles generated from a copper formate-OA complex, as shown by the following equations.

$$Cu^{2+} + 2\ HCOO^{-} \rightarrow Cu(HCOO)_2 \qquad (1)$$

$$Cu(HCOO)_2 + 2C_8H_{17}NH_2 \rightarrow Cu(HCOO)_2(C_8H_{17}NH_2)_2 \qquad (2)$$

As Eqs. (1) and (2) show, a quantity of OA of 2 mol is needed for 2 mol of FA to form a complex at a complexing ratio of 1 (=2/2). In fact, the color of the cleaning solution should change to blue, which obviously indicates the formation of a complex. Excess OA is effective in forming the complex. Copper metal can be obtained from a reduction of copper formate by thermal decomposition.

$$Cu(HCOO)_2 \rightarrow Cu + 2CO_2 + H_2 \qquad (3)$$

The effect of amine complexes on thermal decomposition is a lowering of the decomposition temperature of prepared ink, as previously noted [15], [16].

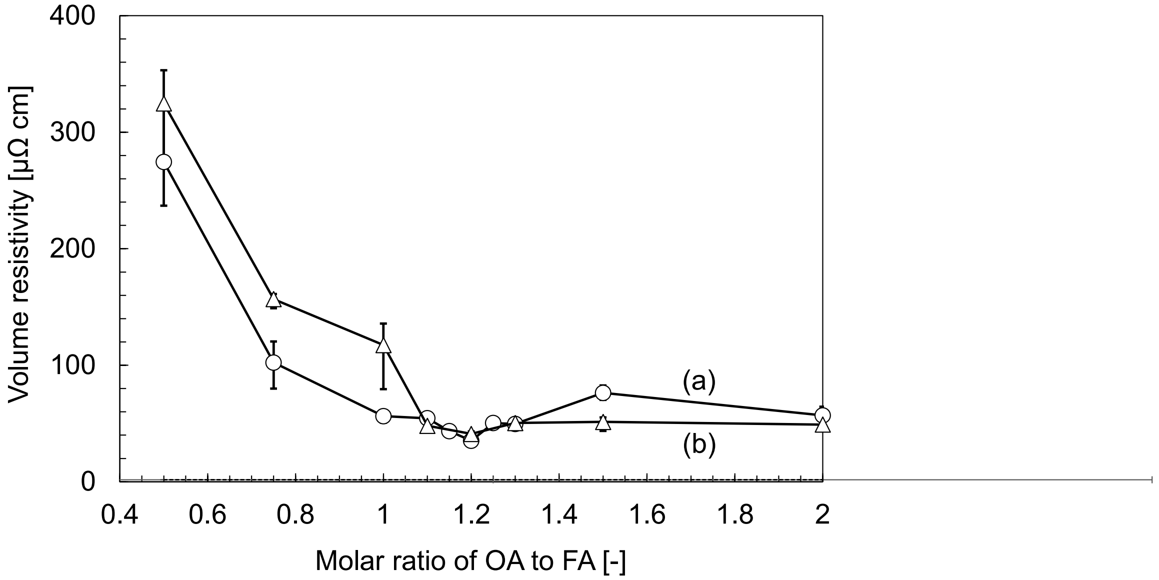

Fig. 5. The volume resistivities for copper films prepared with molar ratios of OA to FA that ranged from 0.5 to 2. FA concentrations for the cleaning of copper microparticles are (a) 20 mol% and (b) 40 mol%, and calcination was conducted at 150 °C for 30 minutes.

Fig. 6 shows the condition of the edges and the uniformity of the copper films prepared from pastes with various ratios of OA to FA: 0.5, 1.2 and 2.0. A 20 mol % FA solution was used to clean the copper surface. The calcination temperature was 150 °C. At an OA/FA ratio of 0.5 (Fig. 6a), the edges of the copper film were rough with an angle of approximately 45°. On the other hand, the copper film prepared with an OA/FA ratio of 1.2 (Fig. 6b) had edges that approximated a right angle, but with a slight overhanging edge as a result of how the paste flowed onto the top during calcination. The thickness was approximately 43 μm. The copper film prepared with an OA/FA ratio of 2 (Fig. 6c) showed a smooth surface comparable to film prepared with an OA/FA ratio of 1.2, but at this higher ratio the paste flowed during calcination and resulted in an edge angle of 45°. Thus, edge stability depended on the addition of OA during the formation of the copper formate and OA complex. As a result, the copper film prepared from the paste with an OA/FA ratio of 1.2 had both shape stability and low-volume resistivity.

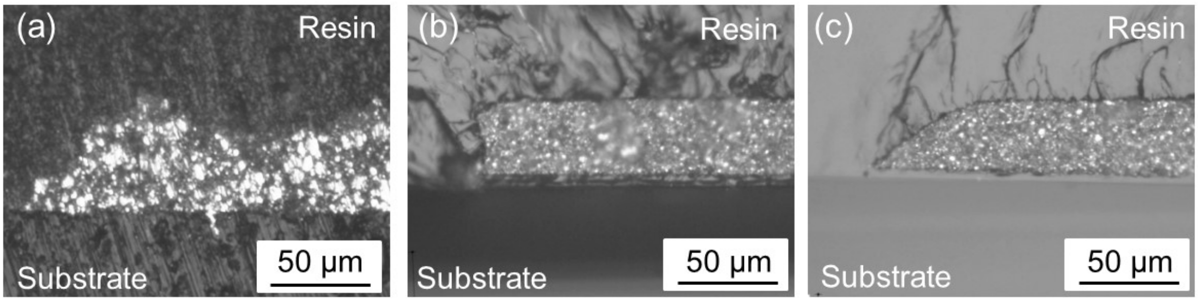

Fig. 6. The optical microscope images of the edges of the copper films prepared from copper microparticle pastes with various ratios of OA to FA: (a) 0.5, (b) 1.2, and (c) 2 at 150 °C for 30 minutes. The concentration of FA solution for cleaning was 20 mol%.

3.4 Mechanism of copper film with low resistivity and a stable shape

The mechanism responsible for the formation of copper films with both low resistivity and a stable shape was investigated. Fig. 7 shows the copper microparticles in copper films following calcination. Copper nanoparticles (100 nm) existed between the copper microparticles, and necking was observed between the copper microparticles and the copper nanoparticles. The nanoparticles were the same size as those prepared from a copper formate-OA complex [15], [16], and that is why the volume resistivity of the film prepared from the copper formate-amine complex rapidly decreased when the amine ratio was 1 or more, as shown in Fig. 5. Necking occurred between the copper microparticles and nanoparticles because OA was adsorbed onto the surfaces of the copper microparticles.

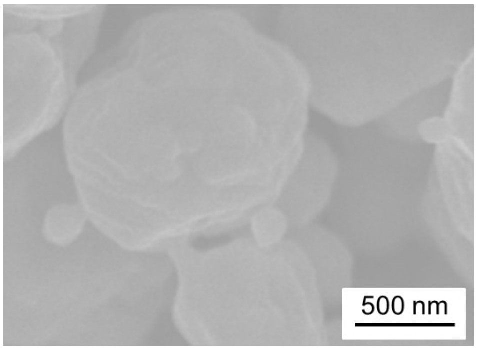

Fig. 7. SEM image of copper microparticles in copper films calcinated from the paste with microparticles cleaned with 20 mol% FA solution at 150 °C. The ratio of OA to FA was 1.2.

Fig. 8 features the simple schematics of the formation of copper film using copper microparticles. The formic acid that remained during the process of cleaning the surface of the copper microparticles and copper formate-amine complex is expressed by the light gray color shown in Fig. 8b. During the calcination process, the copper formate-amine complex produced copper nanoparticles, and the process of connection between copper microparticles and copper nanoparticles proceeded simultaneously. When the amount of amine was insufficient to generate a copper formate-amine complex, copper nanoparticles were not generated and the copper microparticles could not be connected, which caused instability in the shape of the copper film (Fig. 6a). When the amount of amine was in excess compared with the theoretical amount, the excess amine remained in the paste during calcination, and the copper microparticles were moved (Fig. 6c). Consequently, when the amine ratio reached 1.2, copper film with a stable shape and low-volume resistivity was generated without moving the paste.

The ratio was somewhat larger than the theoretical values that appear in Eqs. 1 and 2. This was caused by the adsorption of amine onto the copper microparticles that were cleaned by the formic acid. The thick copper film prepared via the method using microparticles was thicker than 32 μm with a stable shape, which suggests this film could be used as finger electrodes for solar cells. Based on this mechanism, high-quality copper patterns can be obtained even by simple treatment at a low temperature and for a short time.

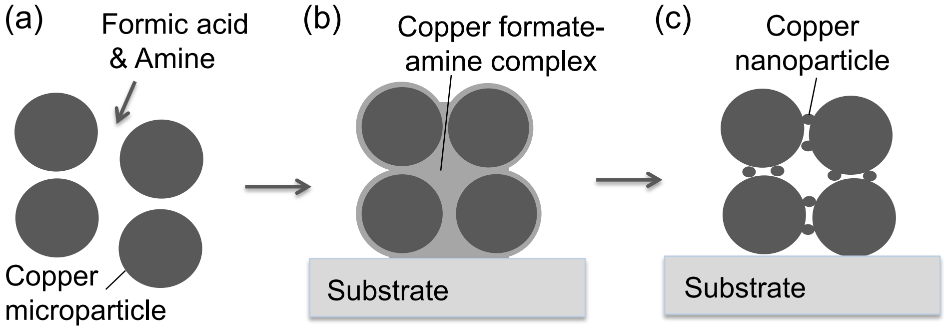

Fig. 8. The schematics of the formation of copper film from a paste using copper microparticles; (a) copper microparticles were mixed with formic acid and amine, (b) copper microparticles surface was cleaned and copper formate-amine complex was generated between copper microparticles, and (c) copper microparticles were connected with nanoparticles produced form the complex by calcination.

4. Conclusions

A paste of copper microparticles, formic acid and octylamine was developed to prepare thick copper film with a stable shape and low-volume resistivity via low-temperature calcination lower than 200 °C. The surfaces of the copper microparticles were chemically cleaned using a formic acid-ethanol solution. The copper dissolved by cleaning was converted to copper formate via the use of formic acid, which was followed by the formation of a copper formate-amine complex via the addition of amine. A formic acid-ethanol mixture of 20 to 45 mol% was a suitable solution for cleaning the surface of the copper microparticles. To obtain copper film with lower-volume resistivity, a calcination temperature of 150 °C proved optimal. The ratio of amine to formic acid was a key parameter in obtaining copper film with a stable shape. With a ratio of 1.2, copper film with a thickness of 43 μm, a stable shape, and low resistivity (32.3 μΩ cm) could be prepared. This method could be applied as finger electrodes for solar cells.

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