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Effect of Carboxylic Acid on Sintering of Inkjet-Printed Copper Nanoparticulate Films

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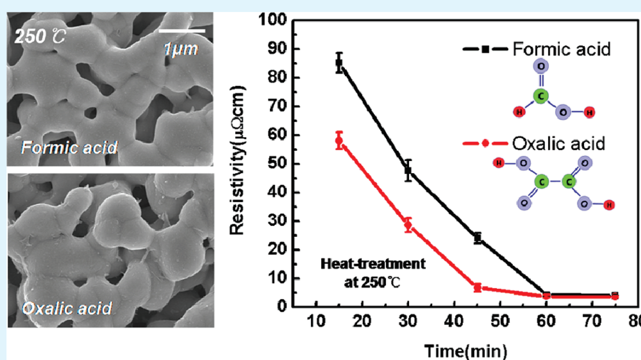
ABSTRACT: The reduction effect of various carboxylic acids on inkjet-printed copper film was investigated. Carboxylic acids were exposed to the film by nitrogen gas that was bubbled through the liquid acids during the annealing process. It was observed that in the case of saturated monocarboxylic acid (formic, acetic, propionic, butyric), the acids with shorter hydrocarbon chains perform better in reducing the surface copper oxides in the printed copper conductive film. The printed films exposed to formic acid vapor exhibited the lowest resistivity (3.10 and 2.30 $\mu\Omega$ cm when annealed at 200 and 250 °C, respectively). In addition, the oxalic acid more effectively reduces copper oxide than formic acid and its usage can shorten the annealing time for highly conductive printed copper film. This reductive annealing process allows fabrication of copper patterns with low resistivity, (3.82 $\mu\Omega$ cm annealed at 250 °C) comparable to the resistivity of bulk copper.



KEYWORDS: copper nanoparticles, inkjet printing, copper oxide reduction, carboxylic acid, conductivity

1. INTRODUCTION

Printed devices, which employ families of electrically functional printable materials to fabricate electronic devices, have facilitated widespread, low-cost electronics for a variety of applications, such as flexible displays, solar cells, and smart labels.[1−8] In contrast to the vacuum-based method, solution-based electronic materials including metal nanoparticles, conducting polymers, inorganic semiconductors and carbon nanotubes, are available for the fabrication of printed electronic devices at low cost.[9−11] For printed conductive features, silver nanoparticles are used most frequently on account of their high electrical conductivity and chemical stability.[12−14] However, the high cost of silver-based materials limits their use for commercialization of printed electronics.

Copper metal has been a focus of research as a main material as the electrical electrode because of its low price and high electrical conductivity, in addition to anti-ionic migration compared to Ag.[15−18] However, the thermodynamically favorable formation of copper oxide has been a serious impediment to using copper metal nanoparticles for conductive inks. Copper oxide reduces electrical conductivity and increases annealing temperatures to form conductive granular films because CuO has a higher melting point (T_m = 1330 °C) and much higher resistivity (5.1×10^7 $\mu\Omega\cdot$cm) than copper (T_m = 1083 °C, resistivity = 1.72 $\mu\Omega$ cm). In our previous work, we have shown that copper inks exhibit better conductivity in printed patterns as a result of controlled surface oxidation by adjusting the molecular weight of the capping agent covering the copper nanoparticles.[18] However, although it minimizes the copper oxide layer on copper nanoparticles, the presence of the oxide layer prevents development of a highly conductive copper film with resistivity comparable to bulk resistivity.

Recently Lee et al. and Kim et al. reported that printed copper patterns were cured under reductive atmosphere (nitrogen gas bubbled through formic acid), exhibiting low resistivity (3.6−4 $\mu\Omega\cdot$cm) at a relatively low annealing temperature (200 °C).[16,17] Their observation means that formic acid is a good reducing agent for copper oxide and annealing in a reductive atmosphere is an effective method of producing printed copper patterns with low resistivity. In the present study, we compared the reduction abilities of various carboxylic acids (formic, acetic, propionic, butyric, oxalic and citric acids). The printed copper films were exposed to the vapor of carboxylic acid carried by nitrogen gas as bubbled through liquid acids during the annealing process. It enables us to fabricate high conductive film (resistivity <10 $\mu\Omega$ cm) by annealing at sufficiently low temperature (200−250 °C) where the temperature-sensitive plastic substrate such as polyethersulphone (PES, T_g = 220 °C) and polyimide (PI, T_g = 310 °C) can be used. The electrical resistivities of the inkjet-printed copper films were measured as function of the

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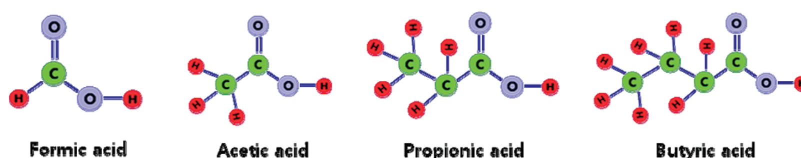


Figure 1. Structures of saturated monocarboxylic acids selected as reducing agents. The general formula of saturated monocarboxylic acid is R-COOH, where R is C_nH_{2n+1} (n = 0, 1, 2, 3).

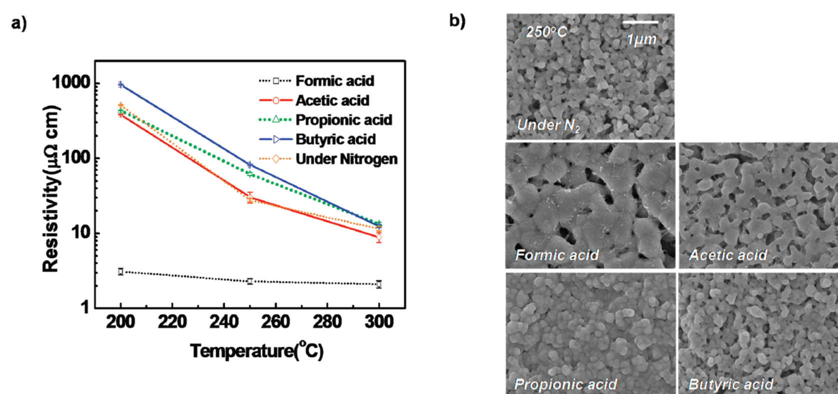


Figure 2. (a) Resistivity variation as a function of heat-treatment temperature for the printed copper films exposed to monocarboxylic acid (formic, acetic, propionic, and butyric acids) vapors; (b) corresponding SEM images showing microstructures of the copper films treated with monocarboxylic acid vapors at 250 °C.

annealing temperature and the type of carboxylic acid. In addition, the microstructures of the films were monitored by scanning electron microscopy (SEM). The surfaces of the copper films after heat-treatment with various carboxylic acids were investigated by X-ray photoelectron spectroscopy (XPS).

2. RESULTS AND DISCUSSION

2.1. Effect of Monocarboxylic Acid Vapor on Printed Copper Film. The starting copper nanoparticles (65 ± 3 nm) surrounded by a CuO layer of ~1.6 nm thickness were synthesized in ambient atmosphere by the polyol method and the conductive films were inkjet-printed, as previously reported.[18,19] The resistivity of the inkjet printed Cu nanoparticulate films heat-treated at 200 °C under vacuum nitrogen atmosphere was determined to be 513.0 $\mu\Omega$ cm. Even when the annealing temperature increased to 300 °C, the resistivity of the resulting printed films was about six times higher (11.5 $\mu\Omega$ cm) than bulk copper resistivity since copper nanoparticles were still insufficiently sintered. It was proved that the presence of the native oxide layer on the synthesized metal colloids hinders the sintering process, resulting in a decrease in the conductivity of the granular electrodes after thermal treatment.[19] This means that the native surface oxide layer of copper nanoparticles should be removed or reduced to copper metal to produce conductive tracks with low resistivity, comparable to copper bulk resistivity. As the first set of experiments, saturated monocarboxylic acids as shown Figure 1 were selected as reducing agents to reduce surface oxide to Cu in the printed films.

To compare the reducing capability of the saturated monocarboxylic acids (formic, acetic, propionic and butyric acids), we measured the resistivity as a function of heat-treatment temperature as shown in Figure 2a. The printed films exposed to formic acid vapor exhibited the lowest resistivity (3.10 and 2.30 $\mu\Omega$ cm when annealed at 200 and 250 °C, respectively) regardless of annealing temperature, which implies that the copper oxide is successfully reduced to metallic copper by formic acid. However, the films annealed under acetic, propionic, and butyric acids were relatively resistive without noticeable improvement in the conductivity. The resistivity of the films annealed under propionic and butyric acids even increased as compared to the one annealed under N_2. The influence of formic acid becomes more evident when comparing the microstructure of printed films (Figure 2b). The films treated with the acetic, propionic and butyric acids showed no significant microstructural change when compared with the film annealed under nitrogen gas. Although partial necking between copper nanoparticles was observed, there were still interspersed particles remaining in those films. In the film annealed at 250 °C under formic acid, however, large grains were observed, indicative of significant sintering of copper nanoparticles. These microstructural observations clearly demonstrate that the effective reduction of copper oxide to copper by formic acid facilitates the sintering of nanoparticles and consequently provides a continuous pathway for electronic conduction.

Surface chemical analysis was performed to elaborate the reduction effect by saturated monocarboxylic acids. The X-ray photoemission spectroscopy results for Cu $2p_{3/2}$ and O 1s of the copper films exposed to formic, acetic, propionic and butyric acid vapors during heat-treatment at 250 °C are shown in Figure 3. All the binding energies are readjusted with respect to C 1s (284.5 eV). The curve fitting deconvolutes the Cu 2p3/2 region into three peaks at 932.2, 933.8, and 935.1 eV. These peaks originate from metallic copper, copper atoms bonding with oxygen atom and copper atoms bonding with carboxylic acids, respectively. When the printed copper film is exposed to formic acid, the peak at 933.8 eV disappears. However, in the case of films treated with other monocarboxylic acids, the peak remains almost unchanged. On the other hand, the O 1s region deconvolutes

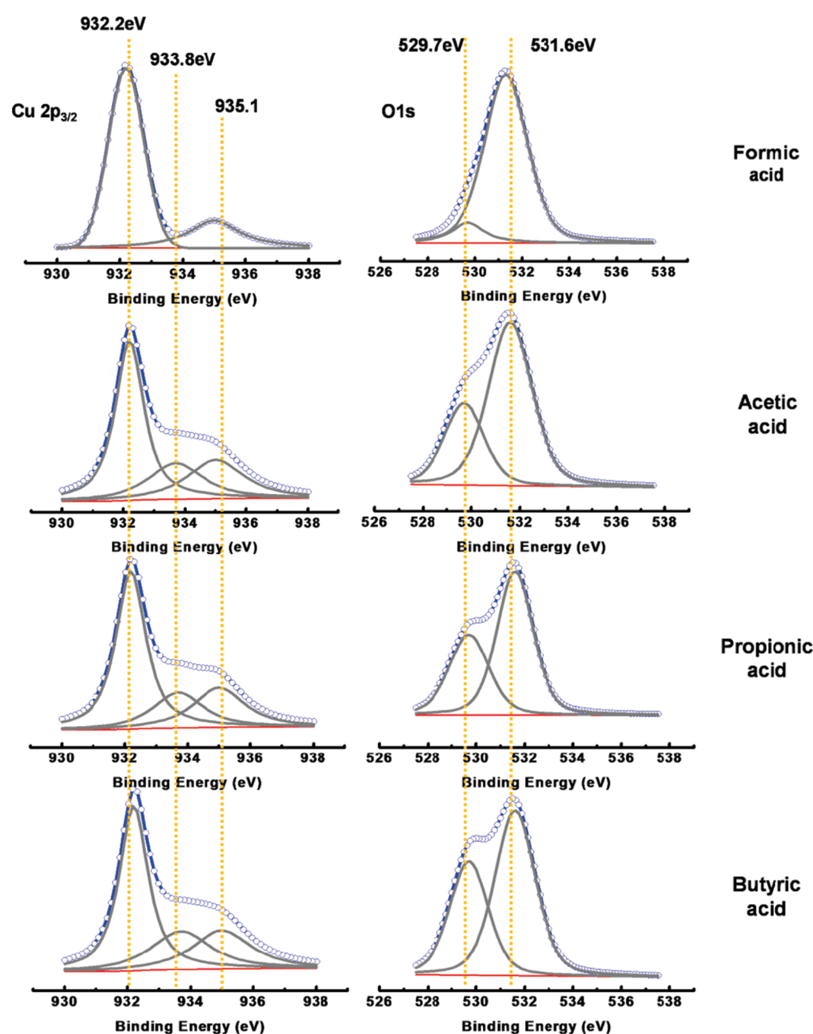
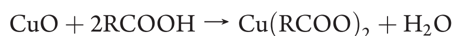


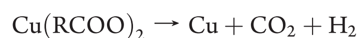
Figure 3. X-ray photoemission spectra (Cu $2p_{3/2}$, O 1s) of the copper films exposed to formic, acetic, propionic, and butyric acid vapors during heat-treatment at 250 °C for 1 h.

into two peaks at 529.7 and 531.6 eV. The first subpeak at 529.7 eV can originate from oxygen atom bonding with copper or the oxygen atom in the capping polymer (polyvinylpyrrolidone) chemisorbed on the surface of copper nanoparticles. However, since the films are annealed at 250 °C where the capping polymer is nearly decomposed,[19] the peak at 529.7 eV reflects the oxygen atom bonding with copper. When the formic acid vapor was introduced as the reducing agent, the peak intensity at 529.7 eV was very low. However, in the case of the monocarboxylic acids except for formic acid, the peak at 529.7 eV became evident and this indicates the presence of copper oxide. The second subpeak at 531.6 eV could be assigned to carboxyl oxygen atoms (O═C) that bond with copper atoms. The observation of this subpeak for all samples suggests that the copper film was well-exposed to carboxylic acids. XPS results clearly confirm that the surface copper oxide is reduced to copper metal more effectively when the copper film is annealed under formic acid vapor than other saturated monocarboxylic acids.

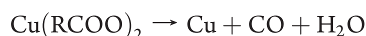
The surface copper oxide can be reduced to copper metal by saturated monocarboxylic acids (RCOOH where R = C_nH_{2n+1}) according to the following reactions[20]



$$CuO + 2RCOOH \rightarrow Cu(RCOO)_2 + H_2O$$



$$Cu(RCOO)_2 \rightarrow Cu + CO_2 + H_2$$



$$Cu(RCOO)_2 \rightarrow Cu + CO + H_2O$$

Formic acid effectively reduces copper oxide, while other saturated monocarboxylic acids have little or even an adverse influence on the conductivity. This difference in the reduction capability can be explained by a degree of acid dissociation. The acid should dissociate by releasing the proton prior to the interaction with CuO. The acid dissociation constant (pK_a) increases in the order of formic acid (pK_a = 3.75) > acetic acid (pK_a = 4.76) > propionic acid (pK_a = 4.86) > butyric acid (pK_a = 4.82). The same order is observed for the conductivity variation of the Cu films treated under the corresponding acid vapors in Figure 2a. Carboxylic acids with shorter hydrocarbon chains are easily dissociated to proton and carboxylate ion, but long non-polar hydrocarbon chains sterically hinder the dissociation. Therefore, the carboxylic acids with shorter hydrocarbon chains allow for more dissociated carboxylate ions (i.e., formate ions in the case of formic acid), which readily react with the surface CuO surrounding Cu to form copper carboxylates, which are then reduced to Cu.

2.2. Effect of Mono/di/tricarboxylic Acid Vapors on Printed Copper Film. We also investigated mono/di/tricarboxylic acids selected as a reducing agent as shown in Figure 4. The aqueous solutions of oxalic and citric acids at a concentration of 1.0 M were used because di- and tricarboxylic acids are solid at room temperature. Although formic acid was liquid, it was diluted to the same concentration to compare with oxalic and citric acids. Figure 5a shows the resistivity variation of the printed films exposed to formic, oxalic and citric acid vapors during heat-treatment. Copper films exposed to formic, oxalic, and citric acids exhibited resistivities of 4.40, 3.82, and 26.60 $\mu\Omega$ cm, respectively, when annealed at 250 °C. Both the films exposed to formic and oxalic acids had low resistivity similar to copper bulk resistivity, while citric acid containing three carboxylic groups did not significantly improve the conductivity. The microstructure of the films annealed under formic, oxalic and citric acids is shown in Figure 5b. The size of grains in the printed films (annealed at 250 °C) exposed to oxalic acid vapor ranged from 0.5 to 1.2 μm, which was similar to the grains in the film treated with formic acid. However, there were much smaller grains in the film annealed under citric acid. Smaller grain size indicates that the particles are not densified, probably due to less reduction of copper oxide by citric acid.

XPS results for Cu 2p3/2 and O 1s of copper films exposed to formic, oxalic and citric acid vapors during heat-treatment (250 °C) are shown in Figure 6. In the Cu 2p3/2 spectra, when the printed copper films were exposed to formic and oxalic acids, the peak at 933.8 eV originating from the copper atom bonding with the oxygen atom almost disappeared. However, in the case of films exposed to citric acid vapor, the peak at 933.8 eV had relatively high intensity. In addition, the peak at 529.7 eV in the O 1s spectra assigned to the oxygen atom bonding with Cu was almost invisible when the formic and oxalic acid vapors were introduced, while the peak had high intensity in the case of the film-exposed citric acid. This result indicates that the copper oxide is reduced to metallic copper when exposed to formic and oxalic acid vapors during heat-treatment.

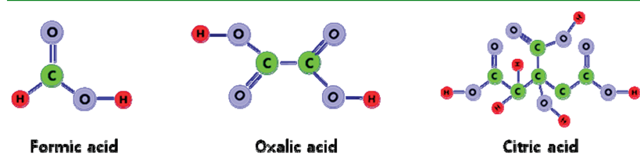
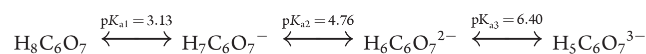


Figure 4. Structures of mono/di/tricarboxylic acids selected as reducing agents.

The CuO reduction abilities of oxalic acid and citric acid are also related to their dissociation constants because carboxylate anions have to react with copper cation in CuO to form copper carboxylate, which is further decomposed to CO/CO_2 and H_2O and Cu metal, like the CuO reduction by monocarboxylic acids. Therefore, in the case of oxalic acid, oxalate anion such as $HC_2O_4^-$, and $C_2O_4^{2-}$ have to react with copper cation in CuO to form copper oxalate (CuC_2O_4). Oxalic acids can exist in aqueous solution in three different forms namely, $H_2C_2O_4$, $HC_2O_4^-$, and $C_2O_4^{2-}$ depending upon the pH. The equilibria between these species can be depicted as

$$H_2C_2O_4 \overset{pK_{a1}=1.25}{\longleftrightarrow} HC_2O_4^- \overset{pK_{a2}=4.26}{\longleftrightarrow} C_2O_4^{2-}$$

The first dissociation constant (pK_{a1}) and the second dissociation constant (pK_{a2}) of the oxalic acid are 1.25 and 4.26, respectively. For 1.0 M oxalic acid solution, the pH value was measured to be 1.3. At this pH, the mole fraction of $H_2C_2O_4$, $HC_2O_4^-$, and $C_2O_4^{2-}$ species in 1.0 M oxalic acid solution is 0.47, 0.53, and 1×10^{-5}, respectively. This means that the predominant anion form is $HC_2O_4^-$, which can actively participate in the reaction of CuO reduction. Therefore, the reaction between $HC_2O_4^-$ and copper oxide is likely a dominant mechanism for CuO reduction by oxalic acid. Although $C_2O_4^{2-}$ can be involved in formation of copper oxalate, this anion cannot contribute greatly to copper oxide reduction because there is a small amount of $C_2O_4^{2-}$ in the 1.0 M oxalic acid solution. On the other hand, it was experimentally observed that citric acid as the reducing agent for copper oxide does not perform as compared to formic and oxalic acid. Citric acid containing three protons can exist in aqueous solution in four different forms, namely $H_8C_6O_7$, $H_7C_6O_7^-$, $C_6O_7H_6^{2-}$, and $H_5C_6O_7^{3-}$



$$H_8C_6O_7 \overset{pK_{a1}=3.13}{\longleftrightarrow} H_7C_6O_7^- \overset{pK_{a2}=4.76}{\longleftrightarrow} H_6C_6O_7^{2-} \overset{pK_{a3}=6.40}{\longleftrightarrow} H_5C_6O_7^{3-}$$

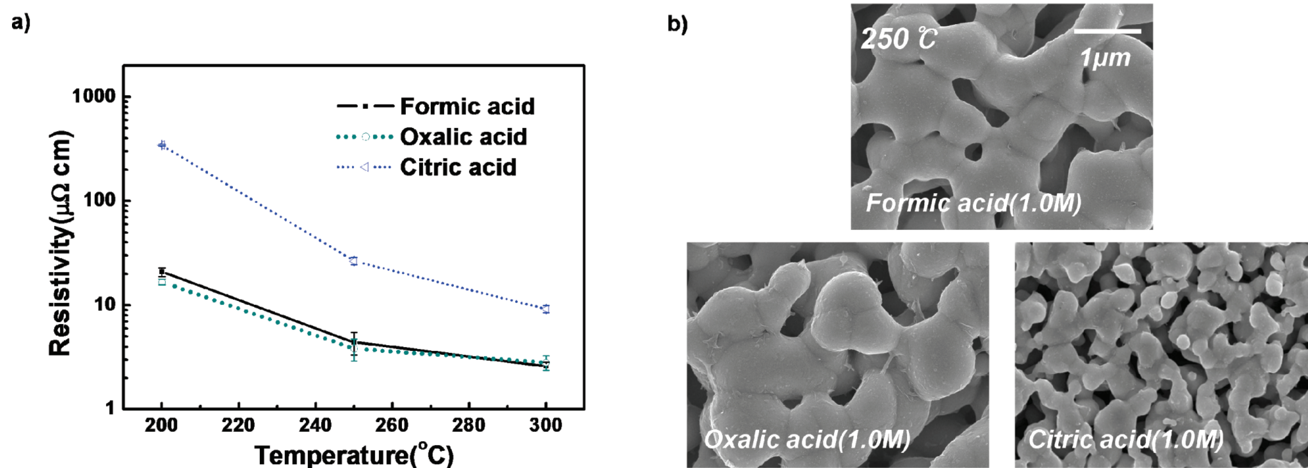


Figure 5. (a) Resistivity variation in the printed films exposed to formic, oxalic and citric acid vapors during heat-treatment; (b) corresponding SEM images showing microstructures of the copper films treated with formic, oxalic, and citric acid vapors at 250 °C.

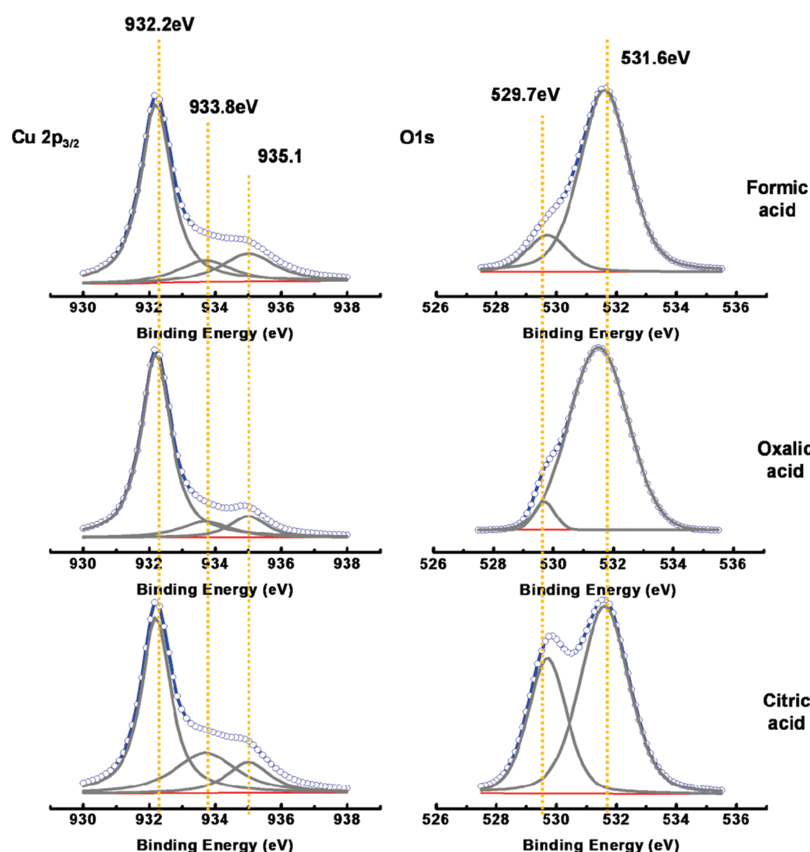


Figure 6. X-ray photoemission spectra (Cu $2p_{3/2}$, O 1s) of copper films exposed to formic, oxalic, and citric acid vapors during heat-treatment (250 °C).

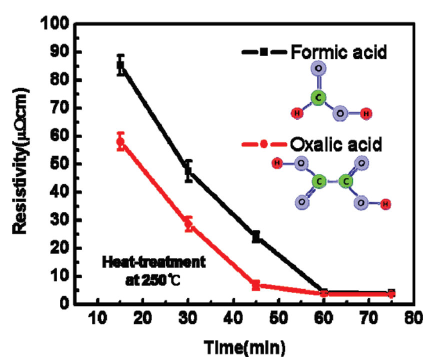


Figure 7. Resistivity variation of the films exposed to formic acid and oxalic acid as a function of time. The films were annealed at 250 °C and aqueous solutions at a concentration of 1.0 M are used.

For 1.0 M citric acid solution, the pH value was measured to be 1.58. $H_8C_6O_7$ species predominates over other aqeuous species at this pH, which cannot react with copper oxide. In other words, the citric acid is not dissociated enough for the CuO reduction.

To compare the reduction kinetics of oxalic acid and formic acid as reducing agents for copper oxide, isothermal reduction experiments at 250 °C were carried out. The resistivity variation of the films exposed to formic and oxalic acid is shown in the Figure 7. When the film was exposed to oxalic acid, the resistivity neared its minimum value within 45 min and then it remained unchanged. However, the resistivity of the film treated with formic acid neared its minimum value after annealing for over 60 min. This implies that oxalic acid shortens the sintering time of copper nanoparticles compared to formic acid.

3. CONCLUSIONS

We investigated the reduction effect of various carboxylic acids (formic, acetic, propionic, butyric, oxalic and citric acid) on inkjet-printed copper film. The printed copper films were exposed to vapors of carboxylic acids carried by nitrogen gas as bubbled through the carboxylic acids during the annealing process. It was observed that in the case of saturated monocarboxylic acids (formic, acetic, propionic, butyric), formic acid performed better in reduction of copper oxide in printed copper film than other acids. This difference in the reduction capability of mono carboxylic acids is due to a degree of dissociation. Formic acid with no hydrocarbon chains that is easily dissociated into proton and carboxylate ion provides abundant carboxylate ions, which readily react with surface CuO to form copper carboxylates and are then reduced into Cu. This effective reduction by formic acid facilitates the sintering of copper nanoparticles during heat-treatment and it allows us to fabricate copper patterns with low resistivity (2.30 $\mu\Omega$ cm annealed at 250 °C). In addition, we observed that oxalic acid is more effective as a faster reducing agent for copper oxide than formic acid. Usage of oxalic acid may shorten the annealing time (45 min) and allow fabrication of printed copper patterns with low resistivity (3.82 $\mu\Omega\cdot$cm annealed at 250 °C) comparable to bulk copper resistivity, suggesting potential for creating plastic printed electronics such as radio frequency identification (RFID) tags, microwave transmission line components, and thin-film transistor (TFT) circuits in a simple and economical manner.

4. EXPERIMENTAL SECTION

4.1. Preparation of Copper Conductive Films. Copper nanoparticles were synthesized in our laboratory by the polyol method, in which poly(N-vinylpyrrolidone) (M_w = 40 000 g mol^{-1}, Sigma-Aldrich)

was used as a capping material. The details of the particle synthesis procedure and the ink preparation were described in our previous work.[18,19] The synthesized copper nanoparticles were dispersed in a mixed solvent of methanol, 2-methoxy ethanol, and ethylene glycol. The formulated inks were ground by planetary milling for 60 min, followed by filtration through a 5 μm nylon mesh. The prepared conductive inks were printed with an inkjet printer on a glass (thickness ~0.125 mm) substrate. The thickness of the films was approximately 0.4 μm. The printer setup consisted of a drop-on-demand piezoelectric inkjet nozzle manufactured by Microfab Technologies, Inc. (Plano, TX) with a nozzle diameter of 30 μm. Uniform ejection of the droplets was achieved by applying a 35 V pulse lasting 10 μs at a frequency of 1000 Hz. The diameter and velocity of the ejected droplets were about 36 μm and 3 m/s, respectively.

4.2. Heat-treatment for the Copper Films under Reducing Vapors. A tubular furnace was used for annealing the printed Cu films under the reducing atmosphere at temperatures ranging from 200 to 300 °C for 60 min. The various carboxylic acids were introduced as reducing agents during the annealing. The carboxylic acids including formic, acetic, propionic, butyric, oxalic, and citric acids were tested. The carboxylic acid vapors were produced by blowing N_2 gas through the liquid acids kept at 25 °C. For oxalic and citric acids, which are in a solid state at room temperature, aqueous solutions at a concentration of 1.0 M were used. The flow rate of the carrier gas was controlled to 200 cc min^{-1}.

4.3. Characterization. The sheet resistivities of the conductive films were measured as a function of the annealing temperatures and the type of reducing agents by a 4-point probe (CMT-SR200N, Chang Min Co., Ltd.), and the film thickness was measured using a surface profiler (AS500, KLA-Tencor Co.). All the resistivity data reported in this work consists of averaged values from more than five measurements to improve accuracy. The microstructures of the films were analyzed by high resolution SEM (JSM-6700F, JEOL). The surfaces of the copper films after heat-treatment were investigated by XPS (PHI 5800 ESCA System, Physical Electronics).

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