http://dx.doi.org/10.5012/bkcs.2014.35.1.147

Copper Electrode Material using Copper Formate-Bicarbonate Complex for Printed Electronics

Jaeeun Hwang, Sinhee Kim, Kevin Ray Ayag, and Hongdoo Kim*

*Department of Advanced Materials Engineering for Information & Electronics, Kyung Hee University, Gyeonggi-do 446-701, Korea. *E-mail: hdkim@khu.ac.kr*
Received September 9, 2013, Accepted October 19, 2013

Copper ink has been prepared by mixing copper(II) formate and 2-ethyl-1-hexylammonium bicarbonate (EHABC) to overcome some weak points such as aggregation and degradation of copper nano-type ink. Ink was coated on glass substrate and calcined at 110 ºC to 150 ºC to generate electrically conductive copper film under two different atmospheres such as nitrogen gas and gaseous mixture of formic acid and methanol. The lowest resistivity of 1.88 μΩ·cm of copper film was obtained at 150 ºC in gaseous formic acid condition. The long-term resistivity shows to increase from 1.88 μΩ·cm to 2.61 μΩ·cm after one month.

Key Words : Copper electrode material, Copper formate complex, Printed electronics

Introduction

Nowadays, there is a growing interest in printed electronics which can be attributed to its lower production cost, large scale application, and feasibility to flexible substrates.[1] Success to this manufacturing technique depends on raw materials, printing machines, and easy process. Among various materials for printed electronics, high conductive materials such as silver and copper have been utilized in the fabrication of electronic components such as circuit boards, memory cards, RFID, sensors, and solar cells. The selection of proper conductive material is a very important factor and can affect the efficiency and life span of the device. Conductive electrode or pad can be prepared from various forms; metallic nanoparticles,[2-4] conductive polymers,[5] and organo-metallic compounds.[6,7] In the case of nanoparticles, they may be easily aggregated when re-dispersed in solvents. Furthermore, they are usually synthesized in smaller scale, need a particular storage condition, and are more expensive.[8] Conductive polymers have also a pitfall such as low conductivity and easy degradation. These disadvantages may be overcome by organo-metallic compounds.

Although silver, as nanoparticles or organo-metallic precursor, has been widely utilized in the industrial production of conductive inks due to its high electrical conductivity and resistance to oxidation,[9] an alternative to silver has been looked for because of some drawbacks. Aside from its high market price, it also has an electrochemical migration tendency which can lead to short circuit failure.[10,11] Copper can be a potential replacement for silver. It is cheaper, resistant to electrochemical migration, and its conductivity is comparable to that of silver. Nevertheless, one major drawback of copper is its easy oxidation in air. Many previous studies have already addressed this issue, especially for copper nano-particles. Oxidation can be prevented by avoiding copper to be in contact with oxygen by adding various capping agents in the formulation of the inks.[12-15] Moreover, different reduction methods were also adapted such as laser sintering[16-18] and calcination in nitrogen,[19] hydrogen,[20,21] and formic acid[7] atmospheres.

In this study, conductive inks were prepared by forming complexes of copper(II) formate and 2-ethyl-1-hexylammonium bicarbonate (EHABC). The effects of annealing temperature and environment were investigated by heating the ink at different temperatures under nitrogen gas or gaseous mixture of formic acid and methanol. The stability and resistant to oxidation of the inks and the generated copper films during a storage period were also observed.

Experimental

Copper(II) formate was prepared by precipitation from the reaction of formic acid with copper carbonate.[22] The reagents were used as received. 100 mL aqueous solution of 1.25 M sodium carbonate (anhydrous, 99.0%, Duksan) was slowly added to 100 mL aqueous solution of 1.25 M copper sulfate pentahydrate (99.0%, S.P.C. GR Reagent) with constant stirring. The solid product, copper hydroxylcarbonate, was washed with deionized (DI) water, filtered, and dried in vacuum oven at 45 ºC for 6 h. 48 grams of the synthesized copper hydroxylcarbonate was then added to 500 mL of 30% aqueous solution of formic acid (Duksan) with stirring. After ceasing the evolution of carbon dioxide, the resulting solution was kept inside a refrigerator for 2 h. Finally, the blue precipitate of copper formate was washed with ethanol twice and dried in vacuum oven at 65 ºC for 48 h. The synthesis may be summarized as follows:

$$2\ CuSO_4 + 2\ Na_2CO_3 + H_2O \rightarrow Cu_2(OH)_2CO_3 + 2\ Na_2SO_4 + CO_2 \uparrow \quad (1)$$

$$Cu_2(OH)_2CO_3 + 4\ HCOOH \rightarrow 2\ Cu(HCOO)_2 + 2\ CO_2 \uparrow + 3\ H_2O \quad (2)$$

2-Ethyl-1-hexylammonium bicarbonate (EHABC, CH_3-

$(CH_2)_3CH(C_2H_5)CH_2NH_3^+HOCOO^-$) was prepared by mixing equal moles of carbon dioxide (dry ice), 2-ethyl-1-hexylamine (EHA) (98%, Sigma-Aldrich) and DI water in a closed vessel. EHABC was added to copper(II) formate anhydrate with stirring at 35 °C for 30 min. The unreacted or excess amount of EHABC was removed by means of vacuum aspiration to increase the copper content of the ink. The thermal properties of the inks and copper formate anhydrate were analyzed by thermal gravimetric analysis (TGA, TA instrument, Q50). Approximately, 2 mg of sample was put in a platinum pan and was heated from 30 °C to 300 °C at a rate of 10 °C/min under nitrogen.

Copper ink was coated on glass substrate and calcined at 110 to 150 °C under N_2 gas and/or gaseous mixture of formic acid and methanol. The volume ratio of formic acid to methanol was 3. The electrical conductivity of the copper film was measured using four-point probe (MS Tech) and Keithley 2400 Source Meter. To calculate the volume resistivity, cross-sectional thickness of copper film was determined using an optical microscope (Olympus BX51). The surface topology and quality of the copper film were examined by scanning electron microscope (SEM, Hitachi S-4800) and X-ray diffractometer (XRD, Bruker D8 Advance).

Results and Discussion

Unlike other copper salts such as copper nitrate, copper oxalate, copper chloride, copper acetate and copper sulfate, copper(II) formate can be readily reduced to metallic copper (Eq. 3) when it is heated to decomposition at 230 °C as illustrated in Figure 1(a).

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

The reaction between copper(II) formate anhydrate and EHABC gives a deep blue-colored complex. This is due to the coordination complex formed between the copper ions and the ligand EHABC. The mole ratio of ligand to metal for a complete reaction is 2 as shown in Eq. (4).

$$Cu(HCOO)_2 + 2EHABC \rightarrow Cu(HCOO)_2(EHABC)_2 \quad (4)$$

$$Cu(HCOO)_2(EHABC)_2 \rightarrow Cu + 2\,EHA + x\,CO + y\,CO_2 + z\,H_2 + m\,H_2O \quad (5)$$

Meanwhile, as shown in Eq. (5), the prepared copper complex is decomposed to metallic copper, 2-ethyl-1-hexylamine, carbon monoxide, carbon dioxide, hydrogen, and water upon thermal degradation. As depicted in the TGA results in Figure 1(b), the decomposition temperature of copper formate is reduced by about 80 °C when it is coordinated with EHABC. This coordination may weaken the bonding between Cu and oxygen of formate resulting in lowering the decomposition temperature. For copper ink formulation, EHABC ligand decreases the decomposition temperature of the ink to as low as 150 °C but the proper amount of solvent or EHABC should be determined. Too much excess of it does not only makes the ink less viscous but also lowers the copper content of the ink itself. It is ideal

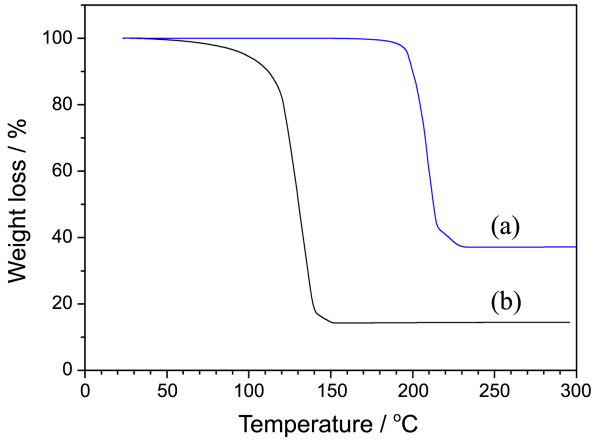

Figure 1. TGA of (a) copper(II) formate and (b) copper ink in nitrogen gas.

to have a conductive ink with metal content as high as possible for better deposition on the substrate. Considering the copper content and the annealing temperature in the formation of copper films, copper ink was prepared with the mole ratio of copper formate to EHABC of 1:2.5 in further works to determine the properties of the conductive film. In this composition, the ink contained 14.4 wt % copper as indicated in Figure 1(b).

Figure 2 shows the electrical resistivity of copper films calcined at 110 °C to 150 °C under N_2 gas and/or mixture of formic acid and methyl alcohol. It was noticed that films were formed faster and resistivity decreased gradually at higher temperature. In comparison, films calcined at 150 °C had resistivities 10 times lower than those generated at lowest temperatures in both annealing conditions. As shown in Fig. 1(b), 150 °C is also the decomposition temperature of the prepared ink. It was also observed that conductive films started to form at 110 °C under N_2 gas (Fig. 2(a)) and at 120 °C under the gaseous mixture of formic acid and methanol (Fig. 2(b)).

In addition, copper films formed under the mixture of formic acid and methanol have higher conductivity than

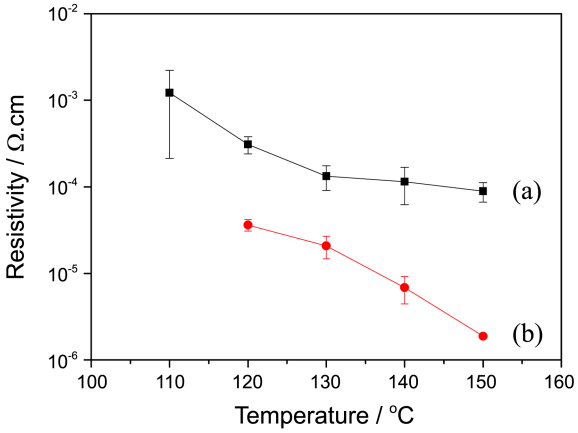

Figure 2. Resistivity of copper film by calcination temperatures in (a) nitrogen gas and (b) the mixture gases of formic acid and methyl alcohol.

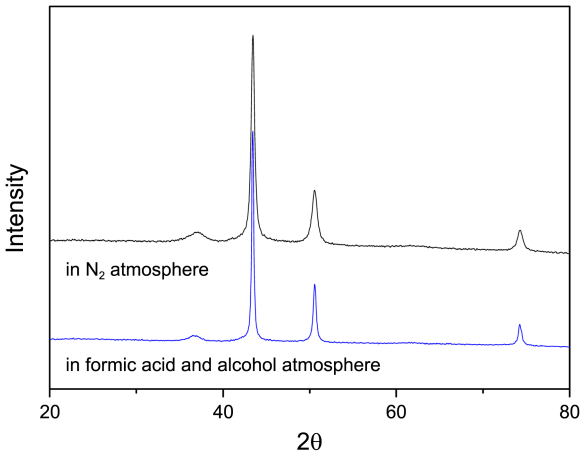

Figure 3. XRD pattern of calcinated copper film at 150 °C for 1 min in two different atmospheres.

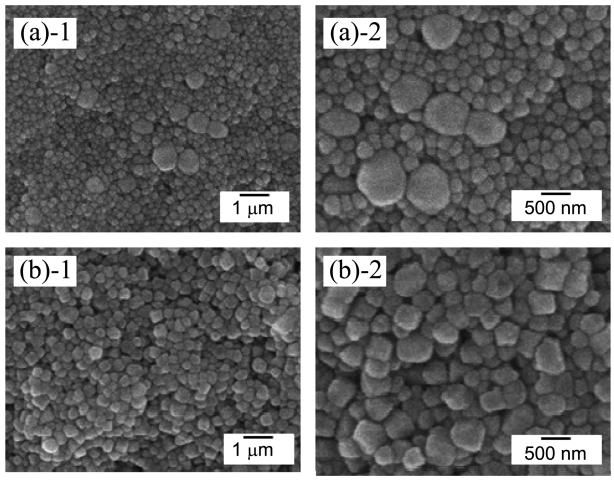

Figure 4. SEM images of the surface of copper film after calcination within 1 min at 150 °C in gaseous of N_2 (a) or mixture of formic acid and methyl alcohol (b).

those films generated under N_2 gas. The lowest resistivity obtained under N_2 is 89.1 μΩ·cm while it is 1.88 μΩ·cm under gaseous mixture of formic acid and methanol, which is almost similar to the resistivity of bulk copper, 1.68 μΩ·cm. N_2 gas does not efficiently block and prevent the oxygen from having contact with copper resulting to higher resistivity. Although formic acid is an effective reducing agent, it causes stains on the surface of copper film, thus methanol is added in this case.[22]

The XRD results of the copper films calcined at 150 °C under both atmospheres are illustrated in Figure 3. The first three peaks, from right, represent Cu (200), Cu (110), and Cu (111), respectively. The leftmost peak of Cu_2O (111) indicates the presence of copper oxide on the surface of the film.

Considering the relative peak intensity, Cu_2O (111)/Cu (111), the amount of copper oxide was negligible. Copper films formed under N_2 atmosphere had stronger and broader Cu_2O (111) peak explaining their higher resistivity compared to those prepared under formic acid and alcohol atmosphere. Cuprous oxide is a semi-conductor and therefore, its existence degrades the electrical conductivity of the metal.

Further explanations regarding the difference in resistivity between the two annealing conditions can be deduced from the SEM images of the surface of copper films after calcination at 150 °C shown in Figure 4. Under the N_2 gas atmosphere, the average particle size of copper is approximately 200 nm but some particles are as large as 1 μm (Fig. 4(a)). On the other hand, films generated under the gaseous mixture of formic acid and methanol are denser, have no pores, and are consist of bigger and uniform copper particles with sizes averaging to 500 nm (Fig. 4(b)). Porosity due to the uneven particle size distribution can greatly affect and reduce the conductivity of the films. Boundaries between the small and large particles may cause defects in the crystal lattice, building up pores leading to the decrease in the electrical and thermal conductivity of the material. Therefore, copper films should have minimal porosity containing large particles with uniform size distribution for optimum electrical conductivity.

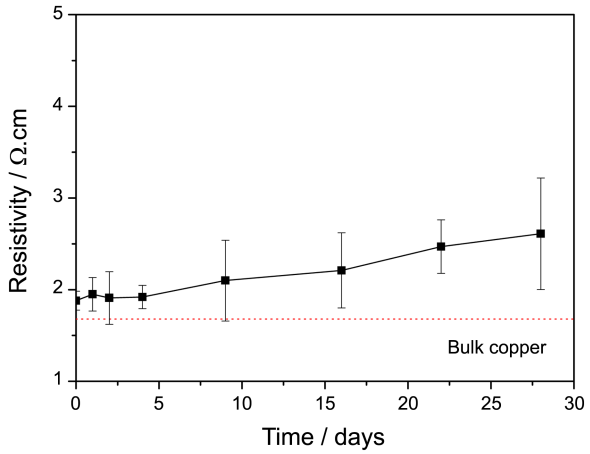

Figure 5. Resistivity change of formed copper film at 150 °C in a gaseous mixture of formic acid and methyl alcohol.

Changes in electrical resistivity with respect to time after calcination were also investigated. Film calcined at 150 °C under the gaseous mixture of formic acid and methanol was kept under ambient temperature and pressure. Figure 5 shows the resistivity of the film measured during one month storage period. It can be noticed that there is no drastic increase in resistivity, from 1.88 μΩ·cm to 2.61 μΩ·cm, within the specified time-frame. From this observation, the generated copper film from the copper-bicarbonate complex is relatively stable in air. This may be due to the fact that 2-ethyl-1-hexylamine of the ligand part has a boiling point of 169 °C. It stays on the surface and acts as a capping agent protecting the film from interacting with oxygen.

Conclusion

Conductive inks containing 14.4 wt % copper which decomposed at 150 °C were synthesized from the complexes of copper(II) formate and EHABC. The inks were found to be stable in air for a few months. Copper films were formed

on glass substrate at different temperatures by calcination of the inks under N_2 gas and/or gaseous mixture of formic acid and methanol to prevent oxidation. Results show that the resistivity of the films decreases as the annealing temperature increases. It is also revealed that copper films generated under the gaseous mixture of formic acid and methanol have lower resistivity than those produced under N_2 environment. The lowest resistivity is 1.88 μΩ·cm, comparable to that of bulk copper, 1.68 μΩ·cm. Furthermore, under the gaseous mixture of formic acid and methanol, the size of copper particles are not only larger, with an average of 500 nm, but are also uniformly distributed. This can be accounted for the lower resistivity of the films which is also supported by the XRD results showing the less amount of copper oxide formed. It has been also found that the generated films are stable for at least one month in ambient condition with a small increase in resistivity, from 1.88 μΩ·cm to 2.61 μΩ·cm.

Acknowledgments. This research was supported by the Basic Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology, Korea (grant number # 20120895).

References

1. Leenen, M. A. M.; Arning, V.; Thiem, H.; Steiger, J.; Anselmann, R. In *Printable Electronics: Flexibility for the Future*; Section Title: Electric Phenomena; 2009; pp 17-34.
2. Kim, N.; Hwang, S.; Kim, E.; Han, K. N. *Jpn. J. Appl. Phys.* **2010**, 5, Pt. 2, 05EA04/1-05EA04/4.
3. Magdassi, S.; Grouchko, M.; Berezin, O.; Kamyshny, A. *ACS Nano* **2010**, *4*, 1943-1948.
4. Kobayashi, Y.; Shirochi, T.; Yasuda, Y.; Morita, T. *Solid State Sci.* **2011**, *3*, 553-558.
5. Tchoudakov, R.; Breuer, O.; Narkis, M.; Siegmann, A. *Polym. Eng. Sci.* **1996**, *10*, 1336-1346.
6. Yabuki, A.; Arriffin, N.; Yanase, M. *Thin Solid Films* **2011**, *19*, 6530-6533.
7. Kim, S. J.; Lee, J.; Choi, Y.; Yeon, D.; Byun, Y. *Thin Solid Films* **2012**, *7*, 2731-2734.
8. Tang, X.; Yang, Z.; Wang, W. *Colloids Surf., A* **2010**, *1-3*, 99-104.
9. Kim, D.; Moon, J. *Electrochem. Solid-State Lett.* **2005**, *11*, J30-J33.
10. Lin, J. C.; Chan, J. Y. *Mater. Chem. Phys.* **1996**, *3*, 256-265.
11. Zuo, R.; Li, L.; Gui, Z. *Ceram. Int.* **2000**, *6*, 673-676.
12. Dang, T. M. D.; Le, T. T. T.; Fribourg-Blanc, E.; Dang, M. C. *Adv. Nat. Sci.: Nanosci. Nanotechnol.* **2011**, *1*, 015009/1-015009/6.
13. Lee, Y.; Choi, J.; Lee, K. J.; Stott, N. E.; Kim, D. *Nanotechnology* **2008**, *41*, 415604/1-415604/7.
14. Mott, D.; Galkowski, J.; Wang, L.; Luo, J.; Zhong, C. *Langmuir* **2007**, *10*, 5740-5745.
15. Wu, S.; Chen, D. *J. Colloid Interface Sci.* **2004**, *1*, 165-169.
16. Joo, M.; Lee, B.; Jeong, S.; Lee, M. *Thin Solid Films* **2012**, *7*, 2878-2883.
17. Kim, H.; Dhage, S. R.; Shim, D.; Hahn, H. T. *Appl. Phys. A: Mater. Sci. Process* **2009**, *4*, 791-798.
18. Yung, K. C.; Plura, T. S. *Appl. Phys. A: Mater. Sci. Process* **2010**, *2*, 393-397.
19. Kang, J. S.; Kim, H. S.; Ryu, J.; Thomas Hahn, H.; Jang, S.; Joung, J. W. *J. Mater. Sci.: Mater. Electron.* **2010**, *11*, 1213-1220.
20. Lee, B.; Kim, Y.; Yang, S.; Jeong, I.; Moon, J. *Current Applied Physics* **2009**, *2*, Supplement, e157-e160.
21. Kim, I.; Kim, J. *J. Appl. Phys.* **2010**, *10*, 102807/1-102807/5.
22. Okada, K.; Kay, M. I.; Cromer, D. T.; Almodovar, I. *J. Chem. Phys.* **1966**, *4*, 1648-1653.