공학석사 학위논문

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신동훈의 석사 학위논문을 인준함

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위 원 장 **Jan Lagerwall (인)**

부위원장 박 원 철 (인)

위 원 김 연 상 (인)

Abstract

A Self-reducible and Alcohol Soluble Copper Based Metal Organic Decomposition Ink for Printed Electronics

Dong-Hun Shin

Program in Nano science and Technology

The Graduate School

Seoul National University

In this master thesis, we report a new method for synthesis of a self-reducible (thermally reducible without a reducing atmosphere) and alcohol-soluble copper-based metal-organic decomposition (MOD) ink for printed electronics. Alcohol-solvent-based conductive inks are necessary for commercial printing

processes, offset and reverse offset process, because these methods usually use polydimethylsiloxane (PDMS) as a blanket material. We selected copper (II) formate as a precursor and alkanolamine (2-amino-2-methyl-1-propanol) as a ligand to make an alcohol-solvent-based conductive ink and to assist in the reduction reaction of copper (II) formate. In addition, a co-complexing agent (octylamine) and a sintering helper (hexanoic acid) were introduced to improve the metallic copper film. The specific resistivity of in this study's ink after heat treatment at 350 °C is 9.46 μΩ·cm, which is 5.5 times higher than the specific resistivity of bulk copper. A simple stamping transfer using PDMS as a stamping mold was conducted to demonstrate the potential of our ink for commercial printing processes.

Keyword **:** conductive ink, metal organic decomposition ink, alkanolamine, copper formate

Student Number **:** 2011-23986

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1. Introduction

1.1. Motivation

Simplicity is an important attribute of printed electronics techniques, and for this reason such techniques are regarded as promising candidates to replace other methods commonly adopted in the fabrication of conductive lines or electrodes in electronic devices.[1, 2] The printing method involves only two steps, printing inks on the substrates and sintering, which allows the manufacturing of electronic devices more cost-efficient. On the other hand, the conventional photolithography method takes multiple steps to obtain conductive patterns on substrates, including deposition, masking, lithography, and etching processes. These steps are complicated and need expensive equipment, which makes the final products expensive.[3, 4] Therefore, if the printed electronics techniques can replace traditional photolithography, it will have a significant impact on the consumer electronics market. However, there are several issues that must be resolved before the printed electronics techniques can be applied commercially. One important issue is the development of appropriate conductive inks.

Currently, silver-based inks are most commonly used for printed electronics,[1, 4] mainly because they have the lowest resistivity among all materials (1.59 μΩ·cm) and a high redox potential, which enables them to be handled more easily and to be stable in air. However, silver also has two drawbacks, its low electromigration resistance[5] and high cost.[1] Electromigration is a diffusion of ions in conductor. This phenomenon occurs when conducting electron's momentum is transferred to metal atom in conductor. Actually, if the metal have a homogeneous crystalline structure this phenomenon is not occurred because conducting electrons will not collide with metal atoms. However in real situation, there are many lattice defects in metal and metal atoms continuously vibrate and move due to thermal energy. Thus in real situation, electrons collide with these metal atoms and it causes diffusion of metal atoms in conductor. This phenomenon could be a serious problem in microelectronic devices because in microelectronic devices, size of electrodes and conducting lines are very small and high direct current densities are usually used. And silver's high cost can also be a critical problem, because it removes the main advantage of the printed electronics technique (low-cost products). In this respect, copper has gained significant research interest in the printed electronics field, not only because it is a low-cost material but also because it possesses

excellent electronic properties, such as a low resistivity (1.72 μΩ·cm, similar to silver) and higher electromigration resistance.[6] Several methods for synthesis of copper-nanoparticle-based inks for printed electronics have been published.[6-10] However, because of the low oxidation resistivity of copper, these inks inevitably contain copper oxides and yield low-quality films.[4]

To overcome this problem of easy oxidation, copper-based metal-organic decomposition (MOD) inks are also being researched.[11-14] MOD inks consist of metal-organic compounds, solvents, and some additives. These types of inks have their copper source in a monovalent or divalent state in the metal-organic compounds, so there are no possibilities for similar problems such as the formation of un-desired copper oxide or precipitation of the metal source to occur. Despite their strengths as conductive inks, there have been limited studies on copper-based MOD inks, and these inks have two shortcomings that make them hard to apply commercially. First, most of them require a reducing atmosphere (e.g., hydrogen gas or formic gas). This requirement should be avoided for the industrial production of printed electronics, due to safety and cost issues. Second, these inks are not generally based on alcohol solvents. As far as mass production is concerned, the inks should work well for commercial printing processes, especially reverse offset printing, which is regarded as a

suitable technique for mass production with a high resolution.[15] Since such printing processes commonly use polydimethylsiloxane (PDMS) as a blanket,[16] inks that have good compatibility with PDMS should be selected carefully. Alcohol-solvent-based conductive inks might be good candidates for the commercial printing processes, offset and reverse offset process, because unlike nonpolar solvents, alcohol solvents do not lead to damage on PDMS (swelling).[17] In this regard, it is necessary to develop alcohol-soluble and self-reducible copper MOD inks for commercialization of printed electronics.

Herein, we report a self-reducible and alcohol-soluble copper MOD ink. To synthesize the ink, copper (II) formate is chosen as the starting material because it can be thermally decomposed to metallic copper and no residuals remain after calcination. Furthermore, to make copper (II) formate soluble in alcohols and to lower its decomposition temperature, we used an alkanolamine called 2-amino-2-methyl-1-propanol (AMP) as a ligand for copper (II) for-mate. In addition, to achieve an even better copper film after heat treatment of the MOD ink, we introduced octyl-amine and hexanoic acid to the MOD ink as a co-complexing agent and a sintering helper, respectively and these additions are based on the several examples of solventless nanoparticles synthesis. To the best of our knowledge, this is the first introduction of the concept of solventless

nanoparticle synthesis to improve the performance of MOD ink. The specific resistivity of the heat-treated MOD ink was measured as a function of temperature, and a simple stamping transfer using PDMS as a stamping mold is briefly discussed.

1.2. Background Information

A. printing methods

a) Inkjet Printing

Inkjet printing method creates lines or images by propelling droplets of ink onto substrates. This printing method has been developed extensively and now it can fabricate lines or images with a high resolution. This method has several advantages. First, the process is very simple thus can fabricate cost-efficient products. Second, it creates patterns by propelling droplets of ink onto where we want to pattern, so there is little loss of materials compared to other printing methods such as gravure, offset, and reverse offset printing. However, because inkjet printing creates patterns sequentially from beginning to end, its' printing speed is too low. Therefore it is not suitable method for mass production.

. b) Screen Printing

Screen Printing is another printing method that creates image by passing pastes through the patterns of mesh. Its advantage is that there is little loss of materials as like an inkjet printing. However, printing materials have to have high viscosity to be used as source of screen printing so inks could not be used for screen printing. The highest resolution of screen printing is about 20 μm.

c) Gravure printing.

Gravure printing uses cylinder and patterns are engraved onto this cylinder. Ink is firstly spread out onto cylinder and then ink on convex part of cylinder is removed by scraping. Remaining ink on concave part of cylinder is then transferred to a substrate. This method is now widely used for commercial printing of magazine, book, etc. Because gravure printing is a continuous process, mass production is possible.

c) Offset printing.

Offset printing basically consists of three rotating cylinder. These are a plate cylinder (metal plate attached to it), a blanket cylinder which is capped by a thin rubber, and an impression cylinder which presses a substrate against the blanket cylinder. The plate cylinder is consist of hydrophilic part and hydrophobic part and hydrophobic part is printing areas. In the first step, the plate cylinder contacts with wet roller so non-printing area are covered by

water. After that, ink is coated onto hydrophobic part of the plate cylinder. This ink is then transferred onto blanket cylinder and transferred again onto a substrate. This printing method is commonly used in printing industry but its resolution is a little bit lower than gravure printing.

d) Reverse offset printing.

High resolution and sophisticate patterns can be fabricated with reverse offset printing method. Thus it is now regarded as a suitable printing method for printed electronics. In the reverse offset printing, soft blanket roll (silicon rubber) is coated with ink and then it is rolled on a glass cliché with electrode patterns (pick up process). This process removes unnecessary ink. Then remaining ink on blanket roll is transferred onto substrate. The reason of reverse offsets high resolution is related to its pick up process. As can be seen figure 1, when ink is removed by glass cliché there are tiny bubbles are generated and these bubbles facilitate separation of ink.[37]

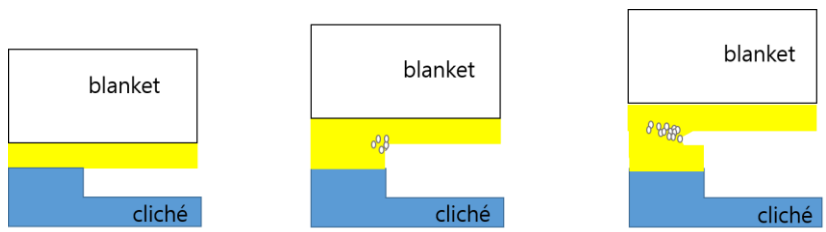

Figure 1. Pick up process of reverse offset.

B. Type of Conductive Ink

There are two types of conductive ink. One is a nanoparticles based ink and the other is a metal-organic decomposition ink. Nanoparticles based ink is a suspension of conductive metal nanoparticles. To synthesize suspension of metal nanoparticles for conductive ink wet chemistry is usually adopted because this methods can provide well size controlled nanoparticles compared to other methods. When synthesizing nanoparticles by wet chemistry, capping ligand or surface ligand molecules are introduced to control particles growth and these ligands also act as a stabilizer for nanoparticles so stable suspension of nanoparticles is subsequently obtained after the reaction. High metal concentration is one of the main advantages of nanoparticles based ink. But there are possibility of precipitation and agglomeration of nanoparticles, so nanoparticles based ink's stability is very low. One good way to prevent precipitation and agglomeration of nanoparticles is introducing long alkyl chain ligand or polymer. But these molecules have higher boiling point so if they are introduced to conductive ink to prevent precipitation of metal source, higher cuing temperature is needed which is undesirable situation for printed electronics. In the case of metal-organic decomposition ink, metal-organic salt is dissolved in suitable solvents. Metal-organic decomposition ink is very stable

which means there is no possibility of precipitation of metal source. However metal concentration is very low compared to nanoparticles ink because each metal ions have organic ligand. Most reported metal-organic ink is silver based. The reason is that silver has higher redox potential. Most of silver organic salt can be reduced to metallic silver by just heating them. However, in the case of copper, suitable organic ligand have to be introduced with serious consideration due to its low redox potential. This is the reason why copper based metal organic decomposition inks are rare.

C. Surface Ligand (capping agent)

Surface ligand have to be introduced when synthesizing inorganic nanoparticles in the solution phase synthesis. They have several roles. Firstly, they control the thermodynamic and kinetic factors of growth step of nanoparticles. Secondly, they prevent coagulation between nanoparticles and thus give better size controlled nanoparticles during synthesis reaction and make nanoparticles to be stable suspension after synthesis. Electrostatic stabilization or steric stabilization and sometimes combination of these two factors are the reason for surface ligands' stabilization ability against aggregation between nanoparticles. Surface ligand is introduced to make uniform sized nanoparticles or shape controlled nanoparticles. In the case of

shape controlled nanoparticles, well-shaped nanoparticles can be obtained by carefully controlling kinetic and thermodynamic factors in reaction system. Until now, a large number of wet chemical methods to obtain desired shape of nanoparticles were reported and most of these methods indispensably need introducing organic or inorganic surface ligands. The use of capping agent to engineer the final morphology of nanoparticles is regarded as thermodynamic approach. The reason is that by introducing a proper surface ligand, interfacial free energies of crystallographic facets of nanoparticles can be controlled due to preferential binding property of surface ligands on specific facets of nanoparticles which means controlling relative growth rate of each facet is possible thus shape of nanoparticles can be manipulated. In the case of uniform sized nanoparticles, or spherical shape or non-shaped nanoparticles, surface ligands favor all crystalline facet of nanoparticles so nanoparticles grow into a spherical-like shape because this shape has lowest surface energy. This means that surface ligand might not have critical effects on thermodynamic factors of synthesis condition. They might more related with kinetic factors of synthesis condition. In this case, ligands are usually bulky with a small anchor group. When synthesizing these type of nanoparticles, ligand should have dynamics which means ligand should attach and detach on the surface of seed or

nanoparticles periodically to give a chance to meet between inorganic atoms and seed or nanoparticles. How dynamics ligand has in the synthesis condition is the important factor. If they have little dynamic, particles' growth rate will be decreased. This mild growth rate usually render better control of the size of the nanoparticles. For these reasons choosing proper ligands for synthesis of inorganic nanoparticles is very important factors.

2. Experimental Section

2.1. Chemicals and Materials

Copper (II) formate tetrahydrate (98%) was obtained from Alfa Aesar. Methyl alcohol (99.8%), Toluene (99.8%) isopropyl alcohol (99.8%), benzyl alcohol (99%), ethanolamine (99%) and diethanolamine (99%) were obtained from Samchun. 2-Amino-2-methyl-1-propanol (AMP, 95%), tert-butyl alcohol (≥ 99%), octylamine (99%), amino-2-propanol (93%), oleic acid (technical grade) were obtained from Aldrich. Hexanoic acid (98%) and diisopropanolamine (98%) were obtained from Junsei. All reagents were used as received without further purification.

2.2. Synthesis of Copper (II) Formate Based Metal Organic Compounds

Copper (II) formate-AMP complexes based ink (Cuf-AMP Ink) was synthesized as follows. First, 30 ml methyl alcohol and 260 mmol AMP (complexing agent) were added into a 250 ml flask and magnetically stirred for 30 min. Then, 130 mmol of copper (II) formate tetrahydrate powder was

introduced to the mixture. (The molar ratio of copper (II) formate to the complexing agents was fixed to 1:2). An instant color change to transparent blue occurred as soon as the copper (II) formate tetrahydrate was added. This solution was stirred for 1 h to ensure complete formation of the copper (II) formate-AMP complexes. The resulting solution was then dried to extract the methyl alcohol and water by a rotary evaporator under reduced pressure at 50 ^{o}C, after which vacuum drying was carried out for 8 h at the same temperature. Finally, high-viscosity liquid of dark blue color was obtained and this high-viscosity liquid is called the copper (II) formate-AMP complexes (Cuf-AMPc). To form Cuf-AMP ink, 3 g of this high-viscosity liquid was dissolved into 1.29 g of isopropyl alcohol by sonication and vortexing. Modified ink from Cuf-AMP ink (Cuf-AMP-O ink) was synthesized in the same manner as the Cuf-AMP ink, except a mixture of 130 mmol AMP and 130 mmol octylamine was added instead of 260 mmol AMP. Sintering-promoted copper MOD ink (Cuf-AMP-O-H ink) was prepared by adding 40 μL of hexanoic acid to 4.29 g of Cuf-AMP-O ink.

2.3. Preparation of Conductive Copper Films.

To prepare the conductive copper films, 200 μL of ink was dropped onto a 1.5 cm x 1.5 cm glass substrate and was spread out on the entire substrate using a pipet tip. This ink-coated glass substrate was baked at a temperature range from 200 ℃ to 350 ℃ for 30 min under a nitrogen (99.99%) atmosphere.

2.4. Stamping Transfer Test.

Cuf-AMP-O-H ink was spin-coated on a PDMS substrate at 1200 rpm for 120 sec and dried for 10 min under vacuum. This spin-coated Cuf-AMP-O-H ink on the PDMS stamp was transferred onto an ultraviolet ozone (UVO)-treated glass substrate (the glass was exposed to UVO for 20 min). This transferred Cuf-AMP-O-H ink on glass substrate was heat treated at 300 ^{o}C for 30 min under nitrogen atmosphere.

2.5. Characterization

The sheet resistivity was measured using a 4-point probe (CMT-SERIES, CHANG MIN), and the thickness of the point where we measured the sheet

resistivity was measured by a surface profiler (Alpha-Step IQ, KLA Tencor) before the specific resistivity was calculated. This step was repeated more than 5 times, and average values are reported in this paper. The surface morphology of the films was characterized by scanning electron microscopy (SEM; Hitachi S-4800). For thermal gravimetric analysis (TGA), a TGA/DSC 1 star system (Mettler Toledo) was used with a heating rate of 10 ℃ /min under a nitrogen (99.9999%) atmosphere. X-ray diffraction (XRD) patterns were obtained on a New D8 Advance diffractometer (Bruker) in the reflection geometry using Cu Kα radiation (1.5406 Å). Elemental analyses were performed using a ThermoFinnigan Flash1112 (CE Instrument, Italy). The surfaces of the copper films after heat treatment of ink were investigated by X-ray photoelectron spectroscopy (SIGMA PROBE, ThermoVG, U.K.).

3. Results and Discussion

In this study, the copper-based MOD ink is prepared by complexing copper (II) formate with AMP and octylamine then dissolving them into an alcohol solvent. A small amount of fatty acid (hexanoic acid) was also introduced to produce a well-sintered copper film after heat treatment. To elucidate the exact calcination and sintering mechanisms and to achieve the best performance in the final results, the following experiments were conducted carefully. First, the role of the alkanolamine (especially 2-amino-2-methyl-1-propanol) is examined and discussed. Second, the co-complexing agent (octylamine) and sintering helper (hexanoic acid) are introduced to produce a better metallic copper film. Third, the resistivity of the copper films sintered at various temperatures and a simple experiment demonstrating the potential use of our MOD ink for commercial printing processes are presented.

3.1. The roles of 2-amino-2-methyl-1-propanol (AMP)

Copper formate is a promising material for copper MOD inks because it can be thermally reduced to metallic copper without a reducing atmosphere and because it leaves no by-products after thermal decomposition. However, copper formate itself is not a suitable copper source for conductive inks because it is not soluble in most organic solvents. Thus, to employ copper (II) formate as copper precursor in a conductive ink, it must be modified to be soluble in an appropriate solvent. For this purpose, Akihiro Yabuki et al. suggested a way to change its solubility.[14] They introduced alkylamines to copper (II) formate to generate copper (II) formate-alkylamine complexes, and because of the alkyl groups of these complexes' ligands, copper (II) formate exhibited good solubility in toluene. Although their method could allow copper (II) formate to be employed as a copper source for conductive ink, it is not suitable for reverse offset printing or other commercial printing methods that use PDMS as a blanket material, since introducing an alkylamine only allows nonpolar-solvent-based inks. To overcome this limitation, we introduced AMP (a kind of alkanolamine) to copper (II) formate and successfully synthesized an alcohol-solvent-based copper MOD ink. In this study, the AMP has two roles. First, it

helps copper (II) formate to freely dissolve in the alcohol solvent, and second, it lowers the decomposition temperature of copper (II) formate by acting as a mild reducing agent.

A photograph of Cuf-AMPc (the molar ratio between copper (II) formate and AMP is 1:2) dissolved in various alcohols and a nonpolar solvent (toluene) is shown in Figure 2. Ethyl alcohol, isopropyl alcohol, tert-butyl alcohol, and benzyl alcohol were introduced as solvents to confirm the good solubility of these complexes in alcohols. The complexes could not dissolve in the nonpolar solvent (toluene), but they were completely dissolved in these alcohols (as can be seen in Figure 2), and no precipitation or separation layer was observed even after storage for two months. This result confirms that the method presented here can provide excellent solubility of copper (II) formate in alcohols. The reason for the good alcohol solubility is probably related to the hydroxyl group on the alkanolamine. We hypothesize that only the amino group of AMP seems to coordinate with the copper (II) formate, and the oxygen in the hydroxyl group does not participate in the coordination, because the complexes' color is the same as that of copper (II) formate-alkylamine complexes.[18] Consequently, the uncoordinated hydroxyl group and alkane backbone of the ligands help

copper (II) formate to freely dissolve in alcohols, according to the aphorism "like dissolves like."

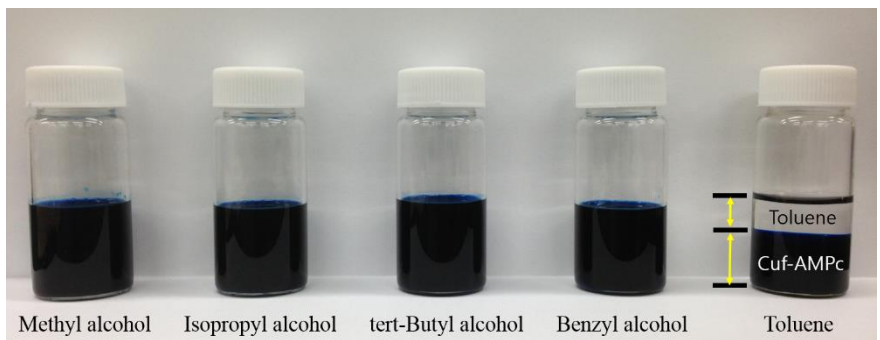

Figure 2. Photograph of Cuf-AMPc dissolved in various alcohols and in toluene. In the latter case, phase separation between an upper toluene-rich phase and a lower Cuf-AMPc phase takes place.

In addition to the first role of AMP discussed above, it also acts as a mild reducing agent to lower the thermal decomposition temperature of copper (II) formate. The TGA data clearly demonstrate this second role of AMP (Figure 3). In Figure 3a (TGA curve of commercial copper (II) formate tetrahydrate), two-step weight loss was observed. The first weight loss started from near 50 ^{o}C and finished at 114 ^{o}C and occurred because of the evaporation of H_2O and the phase transformation of copper (II) formate tetrahydrate into orthorhombic anhydrous copper (II) formate.[18] The second weight loss started from around 188 ^{o}C and ended near 240 ^{o}C and was caused by the decomposition of anhydrous copper (II) formate into metallic copper.[18, 19] However, in the case of Cuf-AMPc, one-step weight loss was observed that started near 125 ^{o}C and ended near 190 ^{o}C (Figure 3b). The difference between the complete decomposition temperatures of commercial copper (II) formate tetrahydrate and the Cuf-AMPc is approximately 50 ^{o}C (Figure 3). This difference indicates that AMP can effectively assist in the reduction of copper (II) formate.

In addition to the TGA analysis, XRD analysis was conducted after heat treatment of the copper (II) formate-AMP complexes at 175 ^{o}C for 30 min under a nitrogen atmosphere, to identify whether the Cuf-AMPc were completely reduced to metallic copper. The XRD pattern in Figure 4 shows that

only metallic copper existed, and no other undesired substances (Cu2O or CuO) were detected after the heat treatment of the copper (II) formate-AMP complexes.

This mild reducing ability of the AMP may be related to the properties of the alkanolamine. Alkanolamines are subject to oxidative degradation under heating conditions by dioxygen or oxidants.[19-21] Since the thermal treatment of MOD ink in this study is performed under an inert atmosphere, the partial pressure of dioxygen during calcination is negligible. Thus, the oxidative degradation of alkanolamine by dioxygen is not considered in this study. On the other hand, in the absence of dioxygen, metal ions with a proper redox potential can directly oxidize alkanolamine and consequentially become reduced.[19] This situation matches well with the thermal treatment of MOD ink, because the main factors required for oxidative degradation of alkanolamine by metal ions, namely, the presence of metal ions and alkanolamines, a high temperature, and the absence of dioxygen, are fulfilled. Therefore, it is possible that some AMPs are directly oxidized by copper ions and donate electrons to them during the heating of Cuf-AMPc, and this reaction would promote the reduction of copper (II) formate, lowering the decomposition temperature.

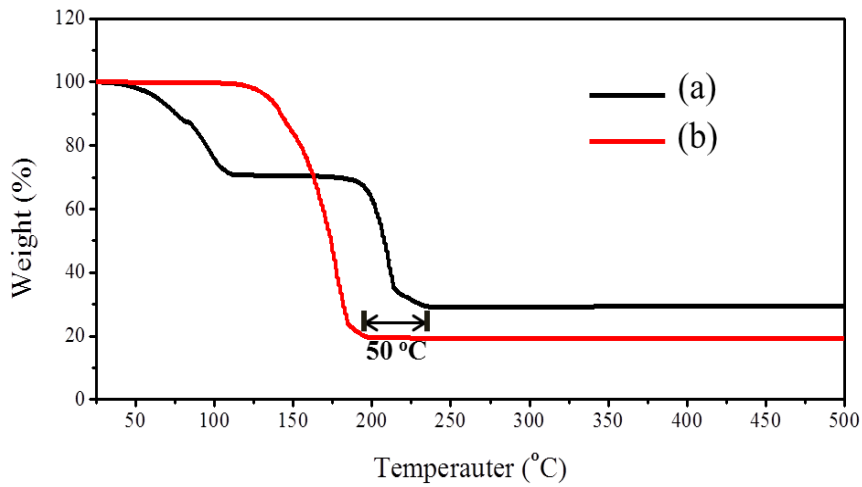

Figure 3. Thermo gravimetric analysis of (a) commercial copper (II) formate tetrahydrate and (b) Cuf-AMPc.

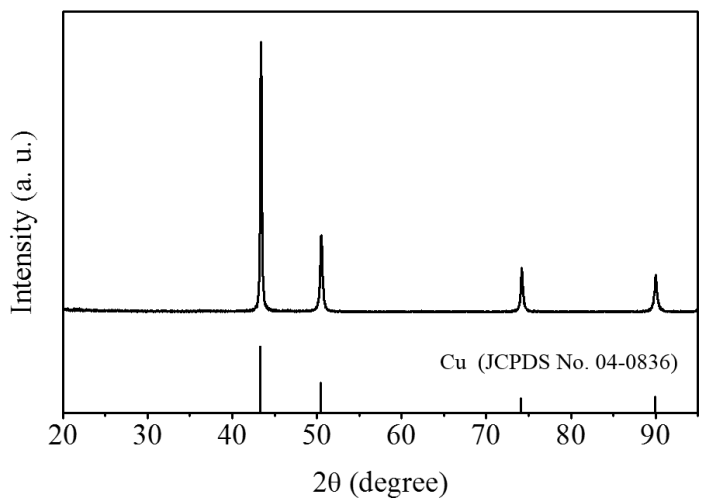

Figure 4. XRD pattern of copper film after heat treatment of Cuf-AMPc at 175 ^{o}C for 30 min under a nitrogen atmosphere.

We tried several alkanolamines to synthesize a suitable MOD ink, including ethanolamine (MEA), amino-2-propanol (A2P), diethanolamine (DEA), diisopropanolamine (DIPA), and 2-amino-2-methyl-1-propanol (AMP) and their skeletal structure are shown in figure 5. The synthetic procedures for copper (II) formate-alkanolamine complexes with different alkanolamine compounds were similar to the procedure for the Cuf-AMP ink described in the experimental section, except for the synthesis of the ethanolamine complex. Since copper (II) formate-ethanolamine complexes cannot be synthesized using the procedure for Cuf-AMP ink, we just dissolved copper (II) formate tetrahydrate in ethanolamine (the molar ratio between copper (II) formate and ethanolamine is also 1:2). Table 1 shows the elemental analysis data for several copper (II) formate-alkanolamine complexes calcined at 300 ^{o}C for 30 min (primary alkanolamines MEA and A2P, sec-ondary alkanolamines are DEA and DIPA, and the sterically hindered alkanolamine is AMP). The elemental analysis data in Table 1 indicate that after the heat treatment, copper (II) formate complexes with primary and secondary alkanolamines contain a large amount of residuals, whereas the amount of residuals for the copper (II) formate complex with the sterically hindered alkanolamine (AMP) is extremely low.

The existence of organic residuals in the film is detrimental to the conductivity, because they could inhibit the physical contact between metals in the film. Therefore, chemical compounds that leave small amounts of residuals after the heat treatment should be the best choice for MOD inks. In this respect, among the alkanolamines that were examined in this research, AMP is the most appropriate compound for MOD ink.

The reason for AMP's low residual generation after heat treatment is related to its structural characteristics. Copper (II) formate has to be heated under an inert atmosphere to induce the reduction reaction, and during that reaction, one copper (II) formate molecule generates 2 carbon dioxide molecules. The reduction reaction of copper (II) formate proceeds as follows:[22]

$$Cu(HCOO)_2 \rightarrow Cu + 2\ CO_2 + H_2 \qquad (1)$$

Alkanolamine is also known to undergo carbamate polymerization in the presence of carbon dioxide at high temperature.[23, 24] When copper formate is thermally reduced to metallic copper, these two main factors necessary for carbamate polymerization of alkanolamine are fulfilled. Thus, the production of high-molecular-weight degradation by-products from some alkanolamines that have not participated in the reduction reaction during the calcination of Cuf-

AMPc is possible. If this occurs, some organic species will remain in the copper film rather than evaporating because of their high boiling point, and these remaining organic by-products will interrupt the metallic contact between the copper metals, resulting in a lower electrical conductivity of the copper film. Therefore, it is axiomatic that among several alkanolamines, a substance that does not undergo severe carbamate polymerization should be carefully selected as a complexing agent for MOD inks. AMP is a sterically hindered primary amine (the amino group is attached to tertiary carbon atom).[25] Owing to the steric hindrance near the α-carbon bound to the amino group, formation of stable carbamate ions is inhibited, so carbamate polymerization of AMP is restricted compared to that of other primary and secondary alkanolamines.[23-25] Therefore, one can expect that AMP will leave a smaller amount of carbon residuals than other alkanolamines after the calcination of copper (II) formate-alkanolamine complexes, and this fact is supported by the elemental analysis data shown in Table 1. For this reason, we choose AMP as the copper source for the MOD ink to produce a better metallic copper film.

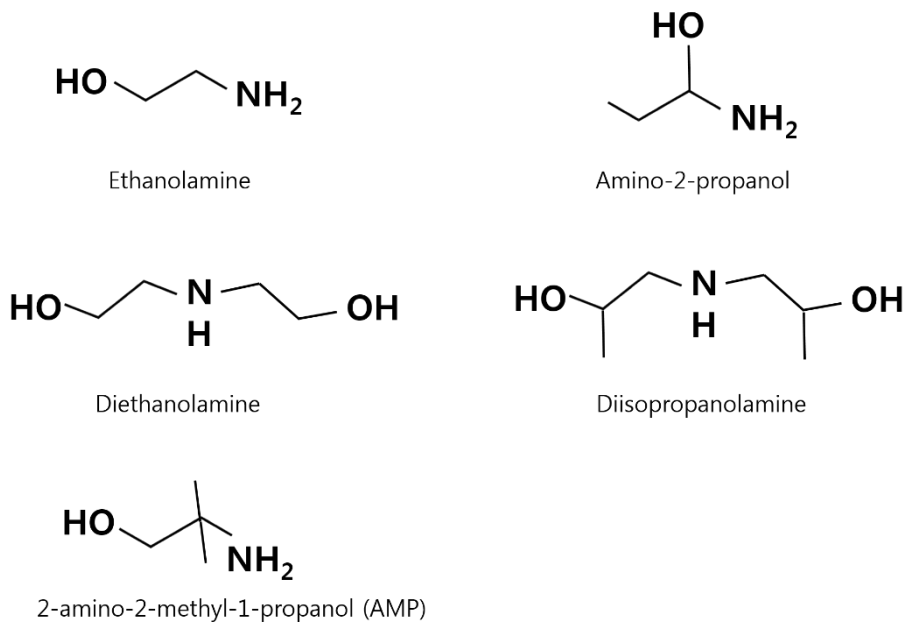

Figure 5. Skeletal structure of several alkanolamines.

Table 1. Elemental analysis of various copper formate-alkanolamine complexes calcined at 300 ºC for 30min under a nitrogen atmosphere.

Sample	Carbon (wt%)	Hydrogen (wt%)	Nitrogen (wt%)	Totals (wt%)
Cuf-MEA	4.4238	0.4645	1.5474	6.4357
Cuf-A2P	2.4482	0.2349	0.6652	3.3483
Cuf-DEA	22.2529	3.0485	6.1482	31.4496
Cuf-DIPA	1.3158	0.1329	0.2197	1.6683
Cuf-AMP	0.3608	0.0469	0.0849	0.4925

Cuf: copper formate. MEA: ethanolamine. A2P: amino-2-propanol. DEA: diethanolamine. DIPA: diisopropanolamine. AMP: 2-amino-2-methyl-1-propanol

3.2. Effects of introducing co-complexing agent: Octylamine

Figure 6a shows the SEM image of the metallic copper films that were produced by calcination of Cuf-AMP ink at 300 ℃ for 30 min under a nitrogen atmosphere. In the calcined Cuf-AMP ink, microsized particles were generated with many void spaces. These phenomena led to a reduction in the physical contact between the copper particles, resulting in bad conductivity of the metallic copper films. To obtain uniformly coated metallic films with good conductivities on the substrates, modification of Cuf-AMP ink was conducted. For this, octylamine was introduced as a co-complexing agent. We introduced equal moles of AMP and octylamine to copper (II) formate and this ink is called Cuf-AMP-O ink (the molar ratio of copper (II) formate to the complexing agents in Cuf-AMP-O ink is also fixed to 1:2 as like the Cuf-AMP ink). The calcined Cuf-AMP-O ink (Figure 6b) has little void space with smaller particles and they were packed more densely than those in the Cuf-AMP ink. Thus better physical contact between copper particles were obtained compared to the film obtained from the Cuf-AMP ink. Furthermore, as can be seen in Figure 7, Cuf-AMP-O ink also has good solubility in alcohols and can

be changed to metallic copper completely at 175 ℃ (Figure 8). These results demonstrate that employment of octylamine as a co-complexing agent can enhance the quality of the MOD ink without changing the roles of the alkanolamine such as providing alcohol solubility and assisting the reduction.

The use of MOD inks can be considered to be similar to the solventless particle synthesis method, because they both generate particles *in situ* in the absence of solvent, since the decomposition of ink starts near 125 ^{o}C so that there was no solvent (isopropyl alcohol) during formation of metallic film. In solventless particle synthesis, shape- and size-controlled nanoparticles can be synthesized if the metal-organic precursors have proper ligands. For example, Kang et al. synthesized copper, iron oxide, and silver nanoparticles without solvent by just heating metal oleate under low pressure.[26, 27] Recently, our group reported a one-step synthesis method for ferrite/carbon hybrid nanosheets, which is another example of solventless particle synthesis, because uniform iron oxide or manga-nese-ferrite nanocubes are generated first on the solid templates (without solvent) before carbonization of their surfactant layers at 400 ^{o}C.[28] From these examples, it can be anticipated that the shape- and size-controlled particles can be synthesized even in the absence of solvent if the

metal precursors have appropriate ligands that can control the particle growth. Therefore, we introduced this concept to our MOD ink process.

When only AMP used, the interparticle collisions between copper particles and diffusion of reduced copper ions into copper particles are not interrupted, because AMP is not a good organic compound for controlling particle growth. In this situation, small particles and reduced copper ions tend to attach and grow on certain bigger particles to achieve a minimum surface energy. As a result, copper particles are not homogenously generated throughout the entire substrate layer, and the formation of many void spaces subsequently occurred. To solve this problem, octylamine was employed as a co-complexing agent based on the concept of solventless nanoparticle synthesis. Alkylamines are commonly used in nanoparticle synthesis to control the size and shape of nanoparticles.[29] Although organic compounds with long alkyl chains show better size- and morphology-control abilities,[30] their boiling points are generally high, so if they are introduced to MOD ink as ligands, a higher curing temperature will be required. With that in mind, we choose octylamine as a co-complexing agent because its boiling point is relatively low, at 179 ^{o}C (similar to that of AMP, 165 ^{o}C), and it has comparatively good size-control ability.[14]

Then, the quality of the resulting copper films was improved compared to that obtained with only AMP as a ligand.

Moreover, by introducing co-compexing agent, wetting property of complexes in this study on substrate seems to can be tuned. Figure 9 shows photographs of Cuf-AMP ink and Cuf-AMP-O ink after heat treatment. Cuf-AMP ink underwent a severe shrinkage (figure 9a) but Cuf-AMP-O did not (figure 9b) and this phenomenon is considered to be caused by wetting property between complexes and substrate. Since we used isopropyl alcohol as a solvent, only high-viscosity liquid (complexes) remain before temperature reach to ink's decomposition temperature. This high-viscosity complexes lose their viscosity steeply as temperature increased. When they lose their viscosity and become more fluid, wetting property between complexes and substrate is raised as a new issue. In this report, this problem is not investigated but we believe that by changing co-complexing agent from octylamine to other suitable organic species, wetting property of complexes could be tuned so thus more improved metallic film could be obtained.

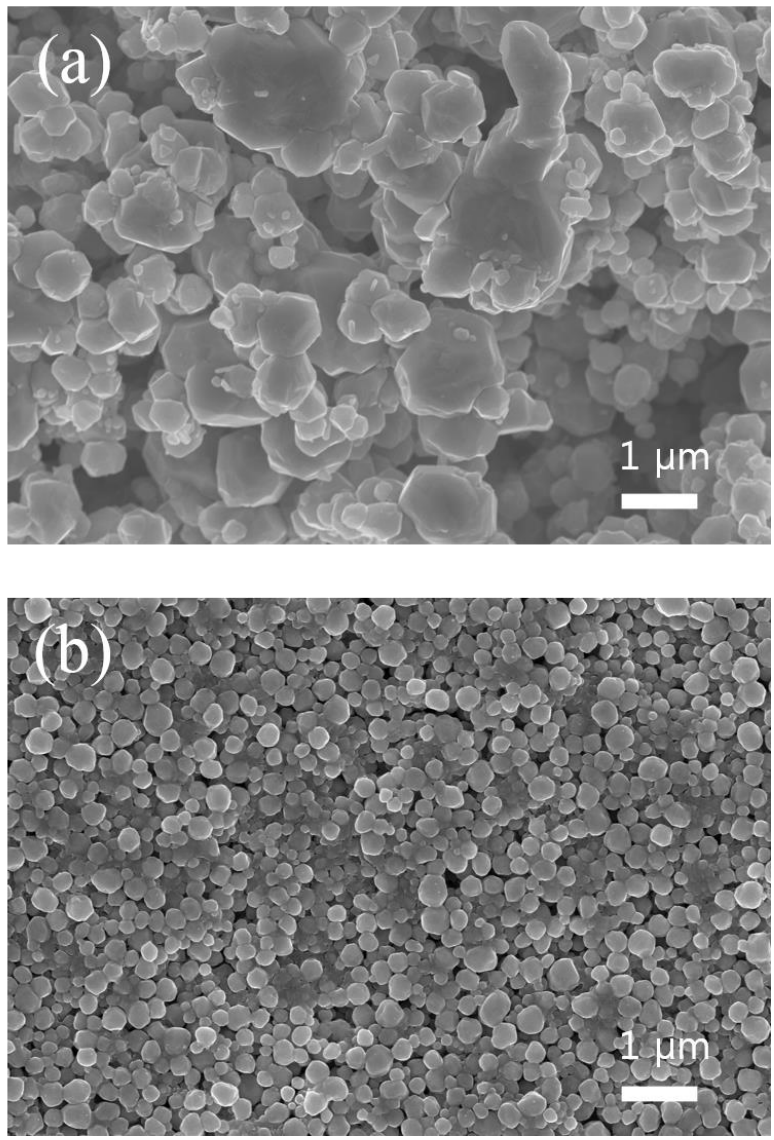

Figure 6. SEM images of (a) Cuf-AMP ink and (b) Cuf-AMP-O ink after heat treatment at 300 ºC for 30 min under a nitrogen atmosphere.

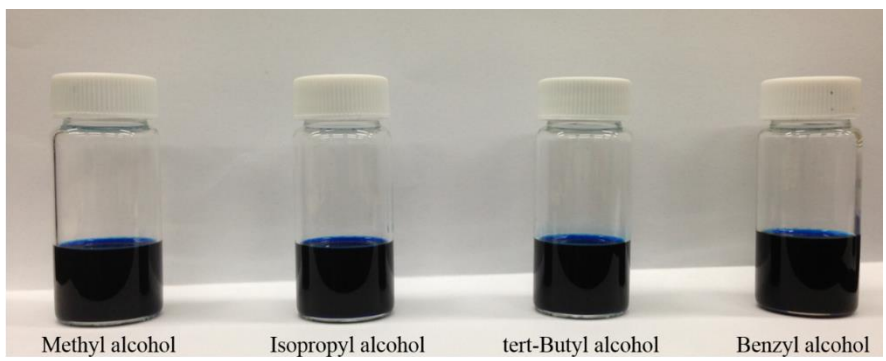

Figure 7. Photograph of copper (II) formate-AMP, octylamine complexes dissolved in various alcohols (Cuf-AMP-O ink)

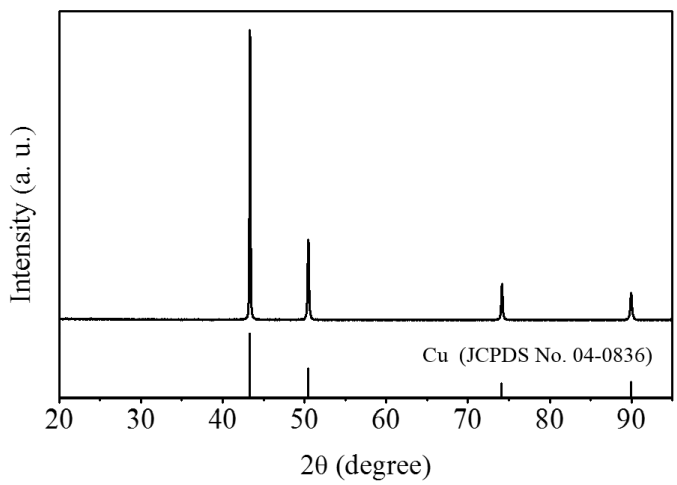

Figure 8. XRD pattern of copper film (Cuf-AMP-O ink) after heat treatment at 175 ºC.

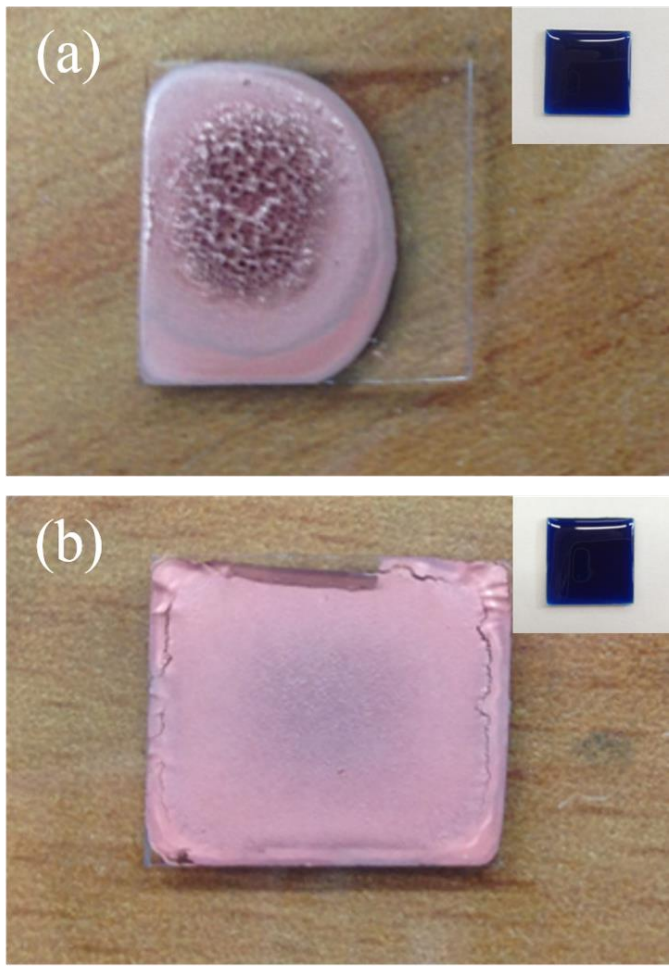

Figure 9. Photographs of (a) Cuf-AMP ink and (b) Cuf-AMP-O ink after heat treatment at 300 ℃ for 30 min under a nitrogen atmosphere. The inset shows the sample before thermal treatment. The pink color may be related to light scattering at the rough surface.

3.3. Addition of carboxylic acid to promote sintering

Even though the particles in calcined Cuf-AMP-O ink are densely packed, so good metallic contacts are attained, the film is still not sufficient for use as electrodes or interconnect conductive lines for printed electronics because their spherical shape inevitably involves small contact areas. Therefore, to achieve better performance of the printed metallic copper film, the copper particles should be fused into continuous networks.[1] In other words, the copper particles have to be sintered. It is well known that a decrease in the size of metal nanoparticles results in a decrease in their melting point compared to that of their bulk counterpart,[31] so to obtain a well sintered copper metallic film at a relatively low temperature, the size of the generated copper nanoparticles should be sufficiently small. However, the copper particles of the Cuf-AMP-O inks are too large to be sintered at 300 ºC (Figure 6b), so the particle size must be decreased to expedite sintering. With the purpose of decreasing the copper nanoparticle size to promote sintering, a fatty acid was introduced. Fatty acids are among the most widely used chemical compounds for size and shape control of nanoparticles in solution-phase synthesis.[32] Furthermore, from several previous reports, it seems that fatty acids can also perform their size-

and shape-controlling roles even in the absence of solvents.[33-36] Since our MOD ink method can be regarded as a solventless particle synthesis, as mentioned above, we anticipated that introducing a fatty acid to Cuf-AMP-O ink will reduce the size of particles and thus lower their sintering temperature.

In this work, two kinds of fatty acids, hexanoic acid and oleic acid, were tested to promote sintering. Their skeletal structure are shown in figure 10. For these tests, 40 μL of fatty acid was added to 4.29 g of Cuf-AMP-O ink which was then coated onto glass substrates and baked at 300 ºC for 30 min under a nitrogen atmosphere. Figure 11a is a SEM image of Cuf-AMP-O ink with hexanoic acid (Cuf-AMP-O-H ink), and Figure 11b is a SEM image of Cuf-AMP-O ink with oleic acid (Cuf-AMP-O-O ink) after heat treatment. The copper film from Cuf-AMP-O-H ink is completely sintered and very well fused to form conduction networks of metallic copper. This result well demonstrates that addition of fatty acid in MOD ink could effectively facilitate the sintering of copper nanoparticles However, in the Cuf-AMP-O-O ink, the nanoparticles were not sintered even though large numbers of small nanoparticles were generated. This difference can be explained on the basis of their boiling points (205.8 ºC for hexanoic acid and 360 ºC for oleic acid). Since sintering occurs when after all organic species are removed and thus the formation of necks

between particle, effective removal of organic species is a prerequisite to achieving better sintering of the particles.[1] The temperature of 300 °C should be high enough to remove the hexanoic acid layer (the boiling point of hexanoic acid is 205.8 °C) on the surface of the copper nanoparticles, but insufficient for the removal of the oleic acid layer (the boiling point of oleic acid is 360 °C). The specific resistivity of copper films obtained from Cuf-AMP-O ink and Cuf-AMP-O-H ink were 16 μΩ·cm and 12.79 μΩ·cm, respectively after heat treatment of them at 300 °C for 30 min. Cuf-AMP-O-H ink showed better performance than Cuf-AMP-O ink. This improvement was resulted from sintering effect of metallic copper nanoparticles in the film. However, the resistivity of film obtained from Cuf-AMP-O-O was very high (its sheet resistivity was on the order of mega ohms per square). Its high resistivity must have come from the existence of oleic acid in film. From this observation, we selected hexanoic acid as an additional additive to trigger sintering of the copper nanoparticles, since it could effectively induce sintering of the generated copper nanoparticles,

Sometimes, XRD analysis is unsuitable for identifying the existence on oxide layer on metal particles, because the oxide layer can exist in an amorphous form. Therefore, we also conducted X-ray photoelectron spectroscopy (XPS)

analysis of the surfaces of copper films that were annealed at 300 ^{o}C for 30 min under a nitrogen atmosphere to confirm whether copper oxide really exists on the copper film. Figures 12a and 12b are the peak-fitted Cu 2$p_{3/2}$ spectra of the copper films formed from Cuf-AMP-O ink and Cuf-AMP-O-H ink, respectively. Interestingly, only one peak centered at 932.27 eV was observed for Cuf-AMP-O-H ink (932.31 eV in the case of Cuf-AMP-O ink), and this value is assigned to Cu.[7] These XPS data show that our MOD ink produces only pure metallic copper, so it is a good candidate material for printed electronics.

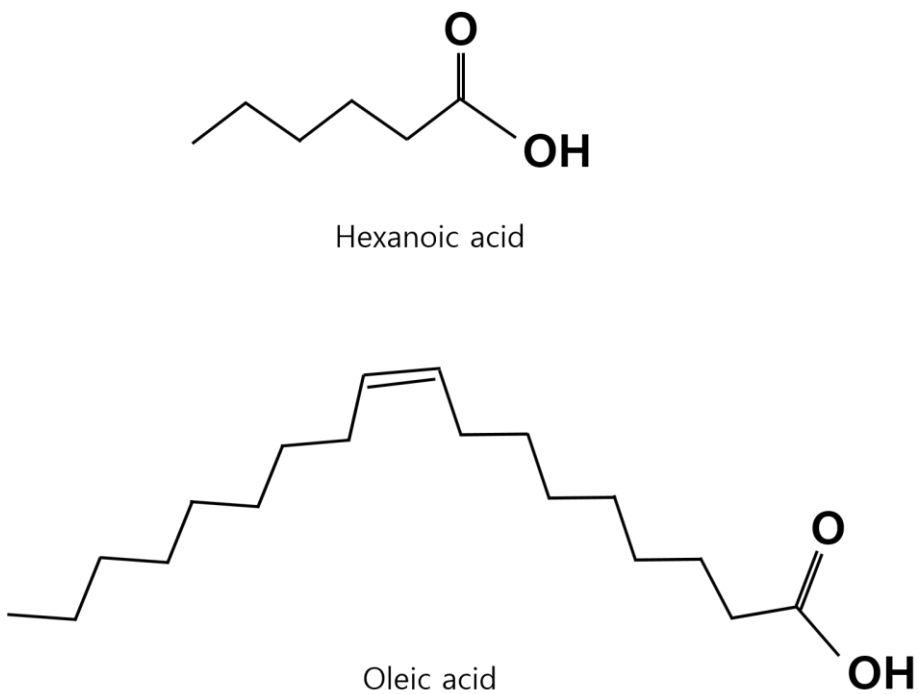

Figure 10. Skeleton structures of hexanoic acid and Oleic acid.

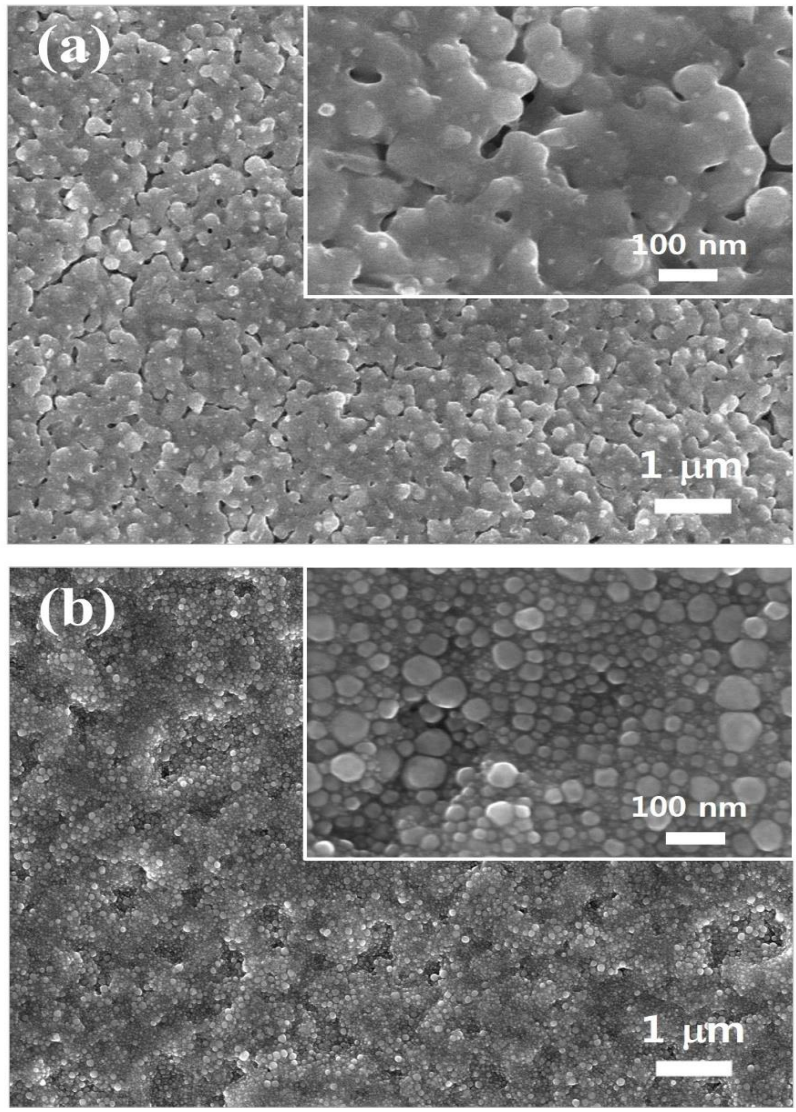

Figure 11. SEM images of calcined Cuf-AMP-O inks with sintering helpers. (a) Addition of hexanoic acid and (b) addition of oleic acid. The insets show high-magnification views.

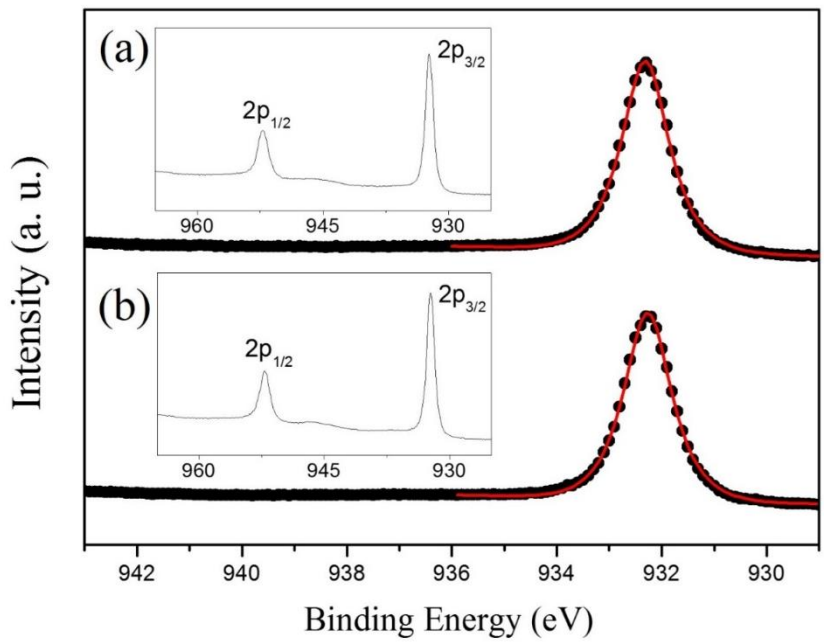

Figure 12. XPS Cu 2p spectra of (a) Cuf-AMP-O ink and (b) Cuf-AMP-O-H ink after heat treatment at 300 ℃ for 30 min. The insets are the Cu 2p doublet spectra.

3.4. Resistivity of copper films at various temperatures

Measurement of the specific resistivity was conducted to identify the performance of the MOD ink. The obtained specific resistances of the Cuf-AMP-O-H ink were 23.4 μΩ·cm, 18.7 μΩ·cm, 12.79 μΩ·cm, and 9.46 μΩ·cm for heat treatment at 200 ºC, 250 ºC, 300 ºC, 350 ºC, respectively. It should be pointed out that although the specific resistivity of the Cuf-AMP-O-H ink was a little bit higher than other previously reported data, [11-13] the heat treatment of our MOD ink was conducted under an inert atmosphere, unlike in other previous reports where a reducing atmosphere was commonly introduced to enhance the reduction of the copper-based MOD ink. The specific resistivity obtained for heating at 350 ºC is 9.46 μΩ·cm, which is just 5.5 times higher than the specific resistivity of bulk copper (1.72 μΩ·cm). Furthermore, the specific resistivity obtained after heat treatment at a relatively low temperature (200 ºC) is 23.4 μΩ·cm and this value implies that our ink can be used in flexible printed electronics when polyethersulphone or polyimide is used as substrate.

The obtained results are plotted in Figure 13 as a function of heating temperature, and their surface morphologies (SEM images) are also presented.

As can be seen in Figure 13, as the curing temperature increases, better conductivity of the copper film is obtained, and the SEM images show that more sintering of the copper nanoparticles occurs. From this result, we confirm that in addition to removing organic residuals from the copper film, promoting the sintering of the copper nanoparticles is another important factor for obtaining good conductivity.

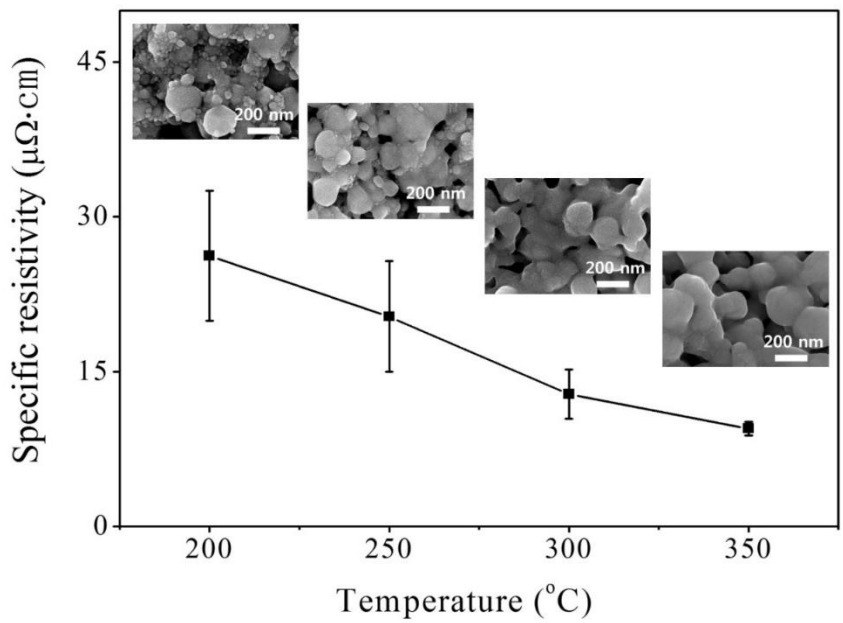

Figure 13. Specific resistivity of the film obtained after heating Cuf-AMP-O-H ink for 30 min under a nitrogen atmosphere as a function of heating temperature. The inset SEM images show the surface morphologies of the corresponding copper films.

3.5. Simple Stamping Transfer Test.

To show the potential of our MOD ink for reverse offset printing, we carried out a simple stamping transfer test using PDMS as a stamping mold. The result is shown in Figure 14. Although some residues remained on the PDMS stamp after transfer (these residues appeared in the pores after sintering; see Figure 14b), Cuf-AMP-O-H ink can be transferred fairly well from the PDMS stamp onto the glass substrate. This indicates that the MOD ink developed in this study is a good candidate for reverse offset printing. Furthermore, it is worth noting that we used the Cuf-AMP-O-H ink without solvent modification or ink formulation for printing. Therefore, if a professional printing technique and ink formulation are combined with our ink, we are certain that the quality of imprinted copper film will be improved.

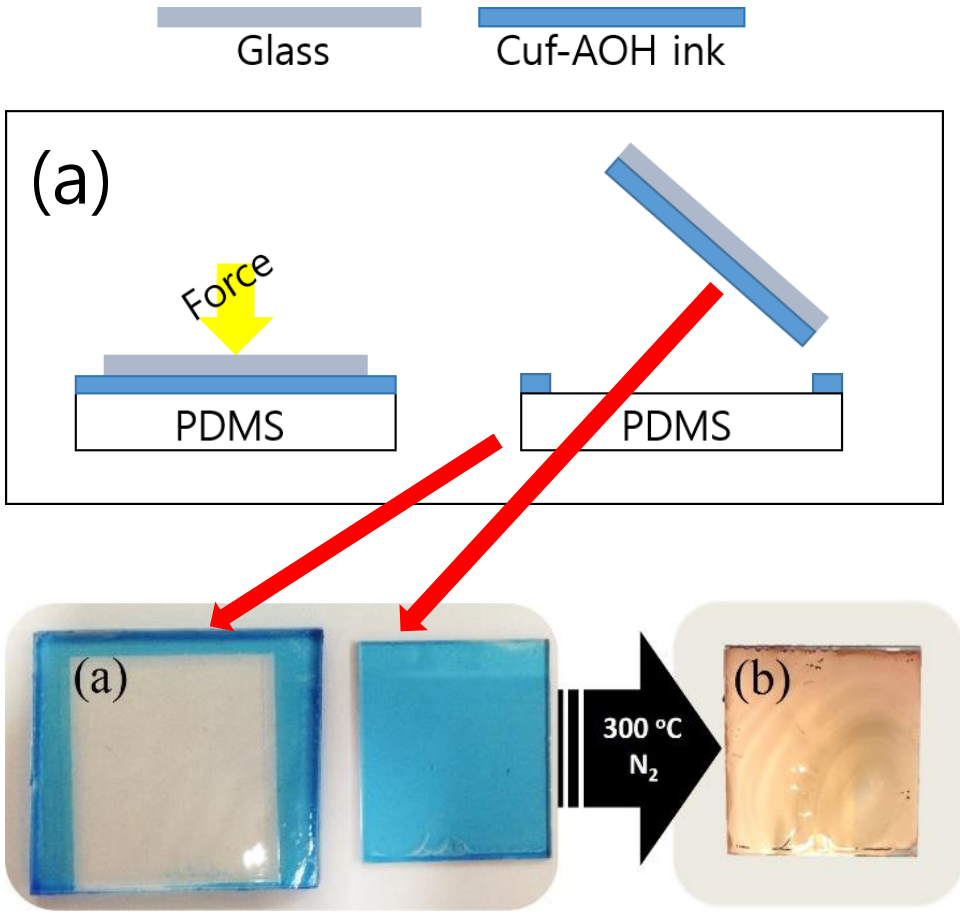

Figure 14. (a) Schematic illustration of stamping-transfer process (b) Stamping-transferred CuF-AMP-O-H layer on the UVO-treated glass. (c) Copper film from transferred CuF-AMP-O-H ink in (b).

6. Conclusion

In summary, an alcohol-soluble and thermally reducible (without a reducing atmosphere) copper-based MOD ink has been synthesized. Alcohol-solvent-based conductive inks are necessary for commercial printing processes because these methods usually use PDMS as a blanket material. We choose copper (II) formate as a precursor because of its good potential for use as a conductive ink (it is thermally decomposed to metallic copper with volatile residuals). Then, an alkanolamine called AMP was exploited as a complexing agent to provide solubility of copper (II) formate in alcohol solvents and to reduce the decomposition temperature of copper (II) formate. In addition, for the purpose of obtaining a well-sintered metallic copper film after heat treatment, octylamine and hexanoic acid were introduced to our system as a co-complexing agent and sintering helper, respectively. Their introduction on the MOD ink was came from the several examples of the solventless nanoparticle synthesis. We believe that this approach can be extended to other MOD inks and will therefore be a positive influence on the field of solution-process-based electronic devices. The MOD ink developed in this study has fair resistivity even at after heat treatment at a relatively low temperature (23.4 μΩ·cm when it

was calcined at 200 ºC), and the resistivity achieved at 350 ºC is 9.46 μΩ·cm, which is just 5.5 times higher than the specific resistivity of bulk copper. This result implies that MOD ink can be applied to various types of printed electronics such as flexible displays, transistors, and antennas. Furthermore, to show the potential of our MOD for commercial printing processes such as offset or reverse offset printing method, a stamping transfer test using PDMS as a stamping mold was conducted, and a good result was obtained. Based on this result, we are certain that if a professional printing technique is applied to our MOD ink, it could be useful in commercial printed electronics. Finally, the use of this ink is strongly related to solution-process-based electronic devices, and further applications such as thin-film transistors, organic thin-film transistors, etc., are now under our investigation.

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요 약 (국문초록)

본 학위 논문 에서는 알코올 솔밴트에 용해가 용이하며 환원제 없이 열분해 만으로도 금속 구리로 환원이 가능한 구리 유기 전구체를 합성하여 전도성 잉크를 만들었다. 구리 (II) 포르메이트를 시작 물질로 하여 알카놀 아민 중에 하나인 2-amino-2-mehtyl-1-propanol (AMP) 을 리간드로 도입하였다. AMP 는 카퍼 (II) 포르메이트를 알코올에 녹게 만들어 주며 또한 카퍼 (II) 포르메이트의 열분해 온도를 낮추어 주는 역할을 수행한다. 이것에 더하여 옥틸 아민과 헥사노익 에시드를 첨가하여 소성후 생성되는 카퍼 전도성 막의 성능을 향상 시켰다. 이것의 메커니즘에 대해서는 무용매 무기 입자 합성법을 이용하여 설명하였다. 비저항 값은 350 ºC 에서 소성 하였을 경우 9.46 μΩ·cm 로써 이는 카퍼 자체의 고유값 보다 5.5 배 높은 값이다. 본 학위 논문의 잉크가 리버스 오프셋에 적용이 가능한 것을 확인하기 위해 간단한 스탬핑-트랜스퍼 실험을 수행하여 본 잉크의 실제 응용 가능성을 보였다.

Keyword : 전도성 잉크, 알카놀 아민, 카퍼 포르메이트, 유기 금속 열분해 잉크

Student Number : 2011-23986

감사의 글

2 년동안 저를 지도해 주시고 방향을 제시해 주신 저의 지도교수님 박원철 교수님께 감사를 드립니다. 또한 공동지도 교수님이신 김연상 교수님께도 감사의 말씀을 드립니다. I also appreciate to professor Jan Lagerwall for his valuable advice about my research and kind consideration about me.

융합과학기술대학원에 처음 입학을 결정할 당시 많은 고민이 있었습니다. 하지만 지금 2 년의 시간을 돌이켜 보니 이 곳에서 정말 많은 것을 얻었다는 것을 느낍니다. 자신의 실험실 구성원에 갇혀 있지 않고 다른 실험실 학생들과 오피스를 공유하게 하여 타 분야와의 교류가 많게 만든 융대원의 시스템 덕분에 연구에 대한 시야를 넓힐 수 있었던 점이 가장 큰 혜택인 것 같다고 느끼고 있습니다. 이런 환경을 조성해 주신 융합과학기술대학원의 나노융합전공 교수님들께 감사의 말씀을 드립니다.

항상 실험하느라 밤을 지새우며 같이 고생한 경모, 실험이나 생활에 있어서 많이 도움을 주고 항상 같이 놀아 준 윤석이, 나를 이곳으로 오게 만든 룸메이트 영엽, 그리고 월요일 술친구 영춘에게도 고맙다는 말을 전합니다. 대학원 생활은 힘들고 재미가 없다고 들

하는데 이 친구들이 있어서 2 년동안 너무 즐거웠고 웃을 일이 많았습니다. 꼭 미래에 다시 모여서 연구 할 수 있는 기회가 오기를 희망합니다.

같이 카퍼 과제를 하면서 1 년 반 동안 함께 고생한 상훈이, 실험실 생활과 연구를 도와주신 승희 누나 그리고 항상 밤에 오피스에 계셔서 외로움을 느끼지 않게 해주시고 실험에 대해 많은 도움을 주신 승현이 형님께도 감사의 말을 드립니다.

항상 저를 응원해 주시는 동범이 형과 민욱이 형 그리고 미국에서 고생하고 있는 인영이 에게도 고마운 마음을 전합니다. 모든 것이 뜻하는 대로 이루어 지기를 기도합니다.

끝으로, 제가 공부할 수 있게 지원과 응원을 해주시는 아버지, 어머니, 누나에게 가장 감사합니다. 항상 건강하시고 행복 하셨으면 합니다. 더욱 성실히 노력하며 살아 부끄럽지 않은 아들이 되겠습니다.

신동훈 드림.