เส้นลายนำไฟฟ้าโดยการสเปรย์ไพโรไลซิสของหมึกสารประกอบเชิงซ้อน คอปเปอร์เอมีน ที่รีดิวซ์ด้วยตัวเอง

นางสาวศิริพร เกศโพคะศิริ

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Conductive patterns by spray pyrolysis of

a self-reducing copper-amine complex ink

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A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

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ศิริพร เกศโพคะศิริ : เส้นลายนำไฟฟ้าโดยการสเปรย์ไพโรไลซิสของหมึกสารประกอบเชิงซ้อนคอปเปอร์เอมีน ที่รีดิวซ์ด้วยตัวเอง (Conductive patterns by spray pyrolysis ofa self-reducing copper-amine complex ink) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. สุรเทพ เขียวหอม, หน้า.

เส้นลายทองแดงนำไฟฟ้า เตรียมโดยวิธีการสเปรย์ไพโรไลซิสจากหมึกของสารประกอบเชิงซ้อนคอปเปอร์เอมีน บนแผ่นโพลีไอไมด์ ในสภาวะบรรยากาศไนโตรเจน หมึกของสารประกอบเชิงซ้อนเตรียมจาก คอปเปอร์ฟอร์เมต สารประกอบเอมีน และ ไอโซโพรพานอล งานวิจัยนี้ศึกษาผลกระทบของชนิดของเอมีน (ไดเอทานอลเอมีน, ไดบิวทิวเอมีน และ อ๊อกทิวเอมีน), สัดส่วนโดยโมลระหว่างคอปเปอร์ฟอร์เมตและเอมีน และ อัตราการสเปรย์หมึก ที่อุณหภูมิ 200 องศาเซลเซียส ระยะเวลาในการอบ 25 นาที ในสภาวะบรรยากาศไนโตรเจน 6 ลิตร/นาที จากผลการทดลองพบว่า ที่อัตราการสเปรย์หมึกลดลง อนุภาคของคอปเปอร์ในชั้นฟิล์มจะเชื่อมต่อกันได้ดีขึ้น ค่าความต้านทานไฟฟ้าจะลดลงอย่างมีนัยสำคัญ เมื่อลดสัดส่วนโดยโมลระหว่างคอปเปอร์ฟอร์เมตและเอมีนลง รวมทั้งการใช้ไดเอทานอลเอมีน เป็นลิแกนก็สามารถลดค่าความต้านทานไฟฟ้าลงได้ด้วยเช่นกัน ค่าความต้านทานไฟฟ้าที่ต่ำที่สุดของเส้นลายทองแดง คือ 2.691 ไมโครโอห์มเซนติเมตร ที่สัดส่วนโดยโมลระหว่างคอปเปอร์ฟอร์เมตและไดเอทานอลเอมีน เท่ากับ 1:0.12, อัตรากาสเปรย์หมึก 0.53 มิลลิลิตรต่อนาที, ที่อุณหภูมิ 200 องศาเซลเซียส ระยะเวลาในการอบ 25 นาที

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SIRIPORN KETPOKASIRI: Conductive patterns by spray pyrolysis ofa self-reducing copper-amine complex ink. ADVISOR: ASSOC. PROF. SOORATHEP KHEAWHOM, Ph.D., pp.

Copper conductive films were prepared by spray pyrolysis method using copper-amine complex ink. Copper-amine ink was prepared by mixing amine solution and copper (II) formate. 0.35 M of Copper (II) formate was mixed with blend amines (diethanolamine, octylamine and dibutylamine) and 4 ml of solvent. Copper-amine complex ink was coated on PI substrate by spray pyrolysis at N_2 atmosphere. The effect of types of amines and molar ratio of Cuf and amine were investigated at 200°C, 25 min. of annealing time under 6 LPM of N_2 atmosphere. Moreover, the effect of spraying rate was examined by varying 0.53, 0.67 and 0.8 ml/min. The volume resistivity depends on above effect. The volume resistivity was decreased when using Cuf-DEA without alkylamine and decreasing spraying rate. The lowest resistivity of 2.691 μΩ.cm was obtained at 200 °c using 1 Cuf : 0.12 DEA, 0.53 ml/min of spraying rate, 25 min of annealing time which is about 1.57 times higher than the resistivity of bulk copper. Moreover, the well sintered layer of the film was exhibited when decreasing spraying rate.

Department:	Chemical Engineering	Student's Signature	....
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Chapter 1

Introduction

1.1 Background

A conductive layer is an important component for all electrical devices. The photolithography/DES process has been used for the manufacture of conductive layer. However, this method is time consuming and expensive. Moreover, a large amount of chemical waste is generated from this process [1, 2].

A printing method has been investigated as an alternative technique for the fabrication of a conductive layer as it is simple, inexpensive, and environmental friendly. Many printing techniques have been developed such as ink-jet printing, stamp-transfer printing, roll to roll printing, screen-printing and spray-coating [1, 3]. Spray pyrolysis is considered as a promising alternative technique to deposit various different materials in thin film formed on various substrates [1].

Various materials, such as gold and silver, have been well developed for direct metallization owing to their superior conductivity and stability. Nevertheless, these metals are too expensive to be employed in large scale applications. Copper (Cu) is suitable as an alternative material because the cost is lower and electro migration is diminished [2, 4, 5].

Two types of metal based inks have been frequently reported as nanoparticle-based ink and metal organic decomposition (MOD) ink [6, 7]. Cu inks are synthesized using Cu nanoparticles (NPs). However, NPs can be oxidized in an ambient atmosphere and this drawback limits its wide use. Recently, various Cu complex inks have been extensively investigated since these complex inks are more resistant to oxidation than

Cu NPs and thermal decomposition below 200°C [4, 5]. However, the major problem of MOD inks is nozzle clogging [6].

Recently, preparation of conductive film deposited on glass and polyimide (PI) substrates using spray pyrolysis of copper-silver complex solution under a N_2 atmosphere was studied. The copper-silver complex solution was prepared by mixing copper (II) acetate monohydrate, silver oxide, ammonia solution and diethanolamine. Volume resistivity was decreased by using a higher spraying temperature, longer annealing time and adding silver. At spray pyrolysis temperature 200°C and annealing time 25 min. the conductive film with volume resistivity of 19 μΩ.cm, which is 11 times higher than the resistivity of bulk coper, could be fabricated using molar ratio of copper to silver 0.8:0.2 on glass substrates. The film deposited on the PI substrates exhibited resistivity 5 times higher than that deposited on the glass substrates [1].

In the present study, electrical conductivity copper film was prepared using spray pyrolysis of a self-reducing copper-amine complex ink under a N_2 atmosphere. In this work, copper (II) formate is used as a precursor due to its lower cost: silver is not used. The advantage of the formate counter ion is its low organic content of the complexes. Therefore, inks with high copper load can be prepared. Moreover, decomposition products are volatile and low decomposition temperature enables printing [7]. Ink containing copper (II) formate and various amines was coated onto a PI substrate. The deposition rate of particles was controlled by particle size. The effects of types of amine, spraying time and spray flow rate were investigated.

1.2 Objective

The objective of this work is to investigate the effects of the types of amine, spraying time, spraying rate and molar ratio of copper to amine used in spray pyrolysis. Decreasing void spaces and grain boundaries of copper conductive film depends on the particle size and deposition rate of particle. Particle sizes and deposition rate are controlled by the above mentioned effects.

1.3 Scope

Conductive film from copper-amine complex ink is fabricated using spray pyrolysis of self-reducing copper-amine complex ink which is composed of ions of copper (II) formate in amine. The scope of this research is as follows:

1.3.1 Copper (II) formate is synthesized by mixing copper (II) oxide with 85% of formic acid under atmosphere at room temperature.

1.3.2 Ink-mixed copper (II) formate and various types of amine as blended amines of dibutylamine or octylamine and diethanolamine are studied.

1.3.3 Spraying rate at 0.53, 0.67 and 0.8 ml/min is studied

1.3.4 The molar ratio of copper to amine is studied.

1.3.5 N_2 flow rate at 6 LPM is studied.

1.3.6 Spray pyrolysis temperature at 200°C is studied.

1.3.7 Annealing time at 25 min. is studied.

1.3.8 PI substrate is studied.

1.3.9 Types of solvent of copper amine complex ink as ethanol, toluene and isopropanol are studied.

1.4 Expected benefits

The optimal conditions for deposition, sintering and conductivity using spray pyrolysis are obtained. The particle sizes can be controlled. The gap between the particles and grain boundaries of copper conductive film will be reduced.

Chapter 2

Theory

2.1 Metal organic decomposition ink (MOD)

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MOD compounds are pure, synthetic, metal-organic compounds which decompose cleanly at a low temperature to precipitate the metal as the metallic element or the oxide, depending on the metal and the atmosphere. The molecular nature of the metal organic compound allows a relatively low temperature formation of the metals. Using this simple concept, the wiring of Au, Ag and Cu has been developed for printing applications.

[7]Cu based MOD ink generates copper metallic at low temperature under vacuum atmosphere. MOD inks have many advantages. They are chemically stable, easy to process in inkjet printing, and their preparation is very simple and feasible. They have the ability to undergo self-reduction and have a lower decomposition temperature (below 250 ºC)[8] as compared to the copper salt. Hence, Cu MOD ink has great potential for application in printing electronics.

2.2 Spray pyrolysis

Spray pyrolysis technique is a process in which a thin film is deposited by spraying a solution on a heated surface where the constituents react to form a chemical compound. Chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition[9]. The quality and properties of the films depend largely on the process parameters. The most important parameter is the substrate surface temperature. The higher the substrate temperature, the rougher and more porous are the films. If the temperatures are too low the films are cracked. Thermal decomposition also affects the crystallinity, texture, and other physical properties of the deposited films. A precursor solution is the other important spray parameter which affects the morphology and the properties of the deposited films. In addition, the film morphology and properties can be drastically changed by using various additives in the precursor solution[10].

[11] A general simplified scheme for spray pyrolysis deposition is shown in Fig. 1 where three processing steps can be viewed and analyzed:

1) Atomization of the precursor solution.

2) Aerosol transport of the droplet.

3) Decomposition of the precursor

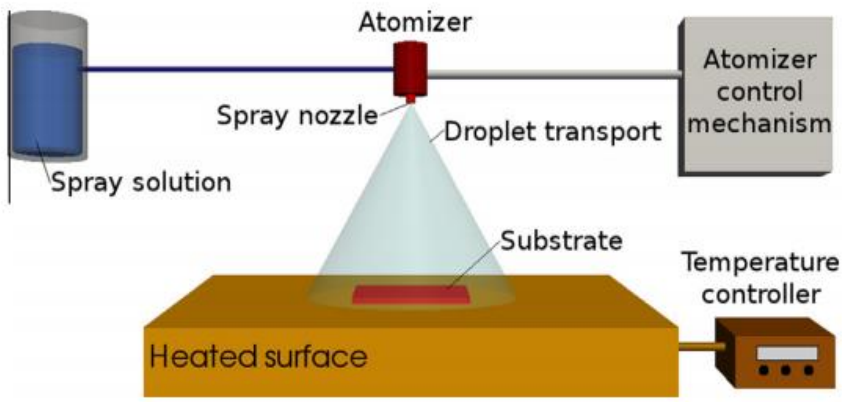

Figure 1 General schematic of a spray pyrolysis deposition process [11]

2.2.1 The deposition process

1) Atomization of the precursor solution.

The atomization procedure is the first step in the spray pyrolysis deposition system. The idea is to generate droplets from a spray solution and send them, with some initial velocity, towards the substrate surface.

2) Aerosol transport of the droplet.

The droplets are transported with the aim of as many droplets as possible reaching the surface in the aerosol form. The droplet size and ambient temperature depend on this process as following Fig. 2.

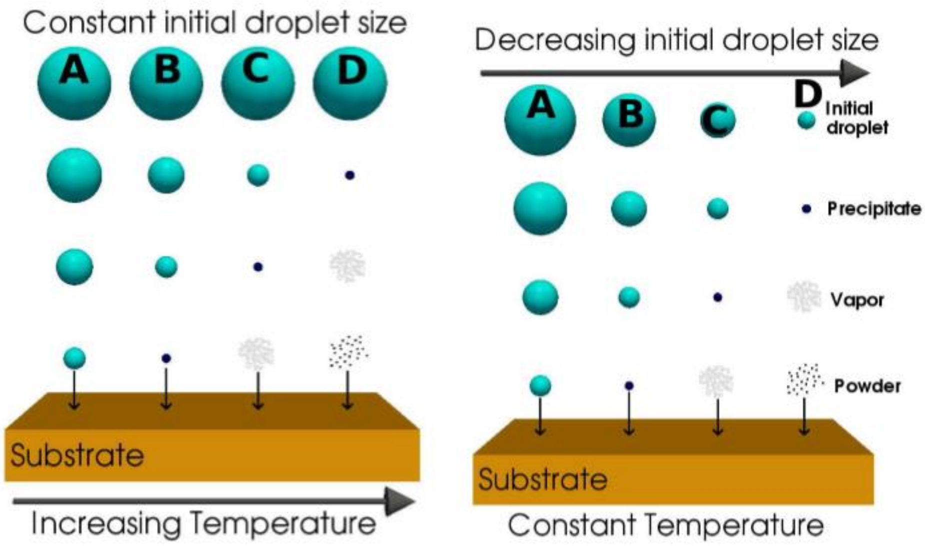

Figure 2 Spray pyrolysis droplets modifying as they are transported from the atomizing nozzle to the substrate. Whether the temperature or the initial droplet size is varied, there are four potential paths which the droplet can take as it moves towards the substrate (A-D)[11].

3) Decomposition of the precursor

In the lowest temperature, the droplet splashes onto the substrate and decomposes. At higher temperatures, the solvent evaporates completely during the flight of the droplet and dry precipitate hits the substrate where decomposition occurs. At even higher temperatures, the solvent also evaporates before the droplet reaches the substrate. Then, the solid precipitate melts and vaporizes without decomposition and the vapor diffuses to the substrate to undergo a chemical vapor deposition process. At the highest temperatures, the precursor vaporizes before it reaches the substrate.

Consequently, the solid particles are formed after the chemical reaction in the vapor phase[10].

2.3 Characterizations

2.3.1 X-ray diffraction (XRD)

X-ray diffraction is a characterization tool used in solid state chemistry and materials science. XRD is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).

Other applications include:

- characterization of crystalline materials
- identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- determination of unit cell dimensions
- measurement of sample purity

In this work, copper (II) formate and copper metal are analyzed.

[12]The XRD pattern of copper hydroxyformate [Cu(OH)HCOO], ICDD File 50-0663 can be observed at 13.088 and 26.284 (º). Peaks of anhydrous copper formate [$Cu(HCOO)_2$], ICDD File 32-0331 can be observed at 16.920, 29.154, and 34.360 (º). The XRD peaks of copper formate dihydrate [$Cu(HCOO)_2 \cdot 2H_2O$], ICDD File 16-0954 can also be observed at 18.178, 18.962, and 19.466 (º). While the XRD peaks of copper formate tetrahydrate [$Cu(HCOO)_2 \cdot 4H_2O$] using available information from the Cambridge Crystallographic Data Center, crystalline structure RefCode CUFOHY04 can be observed at 14.201, 15.482, and 19.558 (º).

[13]In Fig.3 below, three peaks at 2ϴ values of 43.297, 50.433, and 74.130 degree corresponding to (111), (200), and (220) planes of copper from the standard powder diffraction card of JCPDS, copper file No. 04–0836 are shown.

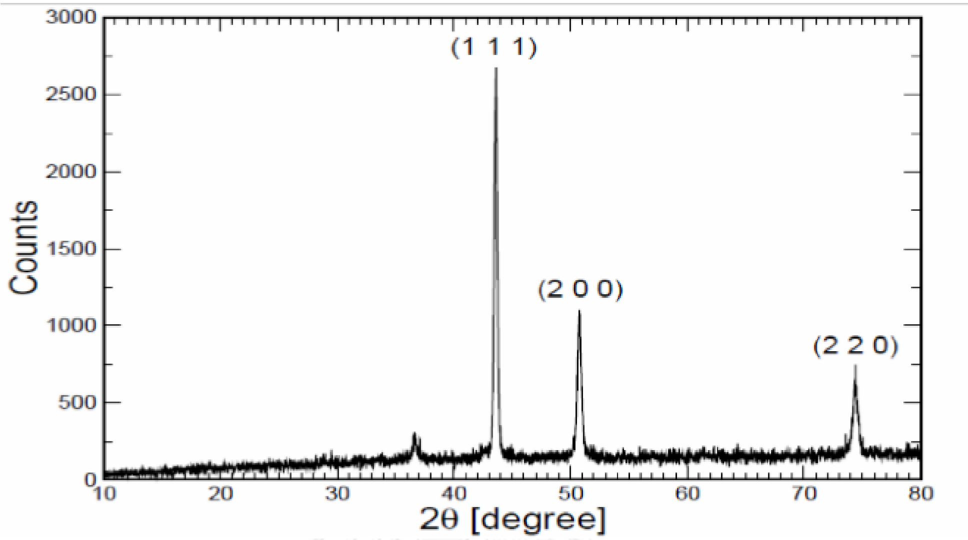

Figure 3 XRD patterns of copper nanoparticles[13]

2.3.2 4-point probe

A 4-point probe is a device to measure the resistivity of copper conductive pattern. The method employs a square pattern that contacts the probes. The two probes are used for adjusting the current along the material surface and the other two probes are used for measuring the voltage. A voltmeter measures the voltage across the inner two probes (See Fig. 4) to determine the sample resistivity. A slope of voltage and current curve shows average resistance between the surface patterns from Ohms law as equation (1) and the volume resistivity can be calculate following equation (2)

$$R = V / I \qquad \text{Eq. (1)}$$

When R is the resistance (Ω)

I is the current

V is the voltage

$$\rho = RA / L \qquad \text{Eq. (2)}$$

When ρ is the volume resistivity (Ω.cm) A is area (width x thickness)

L is the length of the pattern

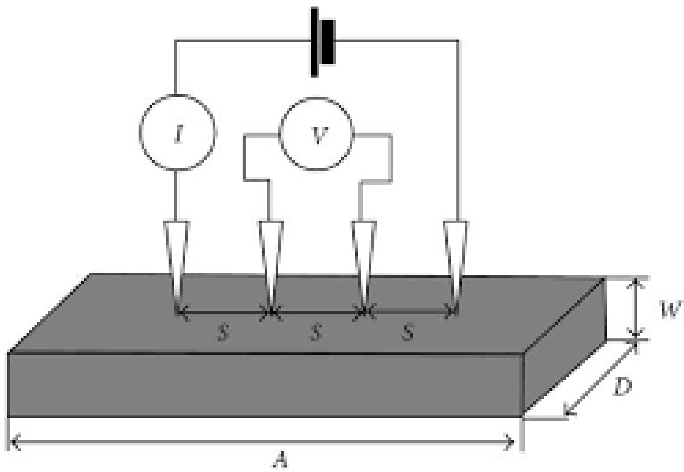

Figure 4 Arrangement of a 4-point probe on a rectangular sample

Chapter 3

Literature reviews

Yabuki et al.[14] studied the effect of types of amine on electrically conductive films calcined from a copper-amine complex ink. The copper amine complex inks were synthesized by adding copper (II) formate and various amines at molar ratio 1:2. Amine with various alkyl chain lengths were used as complexing agents. There were 4 types of primary amines (hexylamine, heptylamine, octylamine, and nonylamine) and 4 types of second amines (dipropylamine, dibutylamine, diamylamine, and dihexylamine). Ink-jet printing was used to make the conductive layer. Complex ink of copper (II) formate and blended amines of 80 mol% of octylamine and 20 mol% of dibutylamine produced lowest resistivity about 5.0×10^{-6} Ω.cm achieved by calcination at 140°C.

Conductive copper films, under an air atmosphere, were successfully expanded by using copper aminediol complexes and were synthesized by adding copper (II) formate and various aminediol at molar ratio 1:2. The ink was coated onto glass substrate at a constant temperature ranging from 160 to 180°C for 5 minutes under air atmosphere. Types of aminediol used were 3-dimethylamino-1,2-propanediol (DMAPD), 3-diethylamino-1,2-propanediol (DEAPD), 3-methylamino-1,2-propanediol (MAPD) and 3-amino-1,2-propanediol (APD). The copper aminediol complex inks from DEAPD provided minimum surface resistivity of 0.2 $\Omega.sq^{-1}$ at 180°C [2].

Lee et al. [5] presented copper complex ink made of copper formate, isopropyl alcohol, hexylamine and 2-amino-2-methyl-1-propanol by laser sintering. The ink was deposited on polyimide substrate by spin coating and scanning under N_2 atmosphere. Minimum resistivity of 1.70×10^{-5} Ω.cm was obtained.

J Hwang et al.[15] synthesized conductive inks by mixing copper (II) formate and 2-ethyl-1-hexylammonium bicarbonate. Ink was coated on glass substrate and calcined at 110^{o}C to 150^{o}C under two different atmospheres such as N_2 gas and gaseous mixture of formic acid and methanol. Results show that resistivity of the films decreases as the annealing temperature increases. It also revealed that copper films generated under the gaseous mixture have lower resistivity than those produced under N_2. The lowest resistivity of 1.88 μΩ.cm of copper film was obtained at 150°C in gaseous formic acid condition.

Shin et al.[16] synthesized self-reducing and alcohol soluble copper based metal organic decomposition (MOD) ink for spin coating technique on polydimethylsiloxane substrate. Copper (II) formate as a precursor and 2-amino-2-methyl-1-propanol as a ligand were selected to make an alcohol solvent based conductive ink and to assist in the reaction reduction 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 copper based MOD ink (Cuf-AMP-OH ink) after heating at 350oc is 9.46 μΩ.cm which is 5.5 times higher than the specific resistivity of bulk copper.

Farraj et al.[17] prepare conductive copper patterns on various flexible substrates by inkjet printing. Copper films were obtained from a metallic organic decomposition (MOD) ink composed of a copper salt complex and suitable low-viscosity solvents. The required layer thickness for current conduction was assessed by printing on PET and sintering at 150°C for 30 minutes in a vacuum oven while [7] MOD ink was synthesized from copper formate and 2-amino-2-methyl-1-propanol (Cuf-AMP), decomposes under nitrogen at 140°C.

Wen Xu and Tao Wang [8] studied blending two types of amines with different alkyl chain lengths as ligands could improve the conductivity of copper films, compared with using one of these amines alone. The activating effect and capping effect were dependent on the alkyl chain length. The alkyl chain length of amine increased, the activating effect declined, whereas the capping effect was enhanced. Blended amines as ligands to Cuf displayed the synergism of long chain and short chain amines, showing both strong activating effect in copper nucleation and good capping effect in particle growth. The lowest resistivity of 4.28 μΩ.cm of the films heated at 200 ºC for 40 min from Cuf-butyl-octyl was obtained. The molar ratio of Cuf and amines was fixed as 1:2 that the blend of 50 mol% octylamine and 50 mol% butylamine showed the best balance of the activating effect and the capping effect.

Li W et al.[18] fabricated copper conductive patterns using Cuf-AMP-Cu seed inks and their printing by screen printing method. Copper inks composed of copper-amino complexes and preset submicron copper seeds (0.17, 0.7 and 3.0 μm) which can increase the copper load of inks to achieve high performance thick and dense conductive patterns. The lowest electrical resistivity of 11.3 μΩ.cm is obtained though heat treatment at 140 ºC for 15 min when the size of copper seeds is about 0.7 μm and the ratio of Cuf-AMP complexes and copper seeds is 3:1.

Cho S et al.[19] prepare copper ion complex ink for air sinterable conductivity electrode using formate, alkanolamine groups and poly alcohols (EG, glycerol, DEG, TEG, and PEG 200). In particular, among various polyol solvents, glycerol was found to be the most suitable reduction assistant-material because of its relatively abundant hydroxyl groups, good evaporation properties, and environmental friendly solvents. The optimized properties of the sintered Cu electrode film made using 3 wt% gCu-ink showed a resistivity of 17μΩ.cm at 350 ºC under air sintering conditions.

Yonezawa et al.[20] prepared a copper ink consisting of a mixture of copper fine particles and copper (II) formate alkanolamine complexes including 1-amino-2-propanol (IPA), 2-amino-1-butanol (2AB), and 2-diethanolaminoethanol (DEAE). The inks were deposited on alumina substrates using a doctor blade and sintered in a tube furnace at 100 ºC under N_2 atmosphere. Thus, the lowest resistivity of copper film was determined to be 9 μΩ.cm using Cuf-IPA-Cu ink.

Chapter 4

Methodology

4.1 Materials

Copper (II) oxide (99.0%, Sigma Aldrich), ethanol (99.9%, QReC), formic acid (85.0%, QReC) were used to synthesize copper (II) formate (CuF). Alkanolamine including diethanolamine ($HN(CH_2CH_2OH)_2$, DEA, 98.5% purity), Alkylamine including dibutylamine ($((CH_3CH_2CH_2CH_2)_2NH$, DBA, 99% purity) and octylamine ($CH_3(CH_2)_7NH_2$, OA, 99% purity), Iso-propanol (QReC) and toluene (QReC) were used to prepare the copper ink. Polyimide (PI, Dupont Kapton 100HN 25 µm.) was used as substrates.

4.2 Methodologies

4.2.1 Preparation of copper (II) formate

Copper (II) formate was prepared by precipitation from the reaction of copper (II) oxide with formic acid. 20 g of copper (II) oxide powder was put into 200 ml of 85% formic acid and the mixture was vigorously stirring at room temperature in an ambient atmosphere for 1 h. As a result of the reaction, the color of the mixture changed from black to sky blue. The synthesized copper (II) formate was separated by filtering the mixture and washed with ethanol. The product was dried at 40^{o}C for 5 h.

Figure 5 Copper (II) formate

4.2.2 Preparation of copper-amine complexes ink and conductive pattern

Copper-amine ink was prepared by mixing amine solution and copper (II) formate. 0.35 M of Copper (II) formate was mixed with blend amines (diethanolamine, octylamine and dibutylamine) and 4 ml of solvent (toluene, ethanol and isopropanol). Copper-amine complex ink was coated on PI substrate by spray pyrolysis at N_2 atmosphere.

The effect of the spray pyrolysis on electrical conductivity was investigated at 200^{o}C, 25 min. of annealing time under N_2 atmosphere. The effect of spraying rate was examined by varying 0.53, 0.67 and 0.8 ml/min.

4.2.3 Characterization

The volume resistivity of the conductive films was measured by the van der Pauw method using 4-point probe (Keithley Instruments, 2182A digital nanovolmeter).

The morphologies of the surface of the conductive patterns were observed using scanning electron microscopy (SEM). The thickness of the film was observed from the cross-sectional image from Field emission scanning electron microscopy (FE-SEM; JEOL, JSM-7610F).

The crystalline structures were measured by X-ray diffractometer (XRD; Bruker, D2 PHASER). Samples were measured at 2θ from 30 to 80º. Moreover, thermal gravimetric differential thermal analyzer (TG/DTA; Perkin elmer Instruments, DIAMOND) was used to evaluate thermal decomposition behavior of the complex ink.

Chapter 5

Results and discuss

5.1 Basic chemical reaction

5.1.1 Chemical reaction and characterization of copper (II) formate

Copper (II) formate was prepared by mixing copper oxide with formic acid. The reaction of copper oxide with formic acid was occurred as follows equation. (1).

$$CuO + 2HCOOH \longrightarrow Cu(HCOO)_2 + H_2O \quad (1)$$

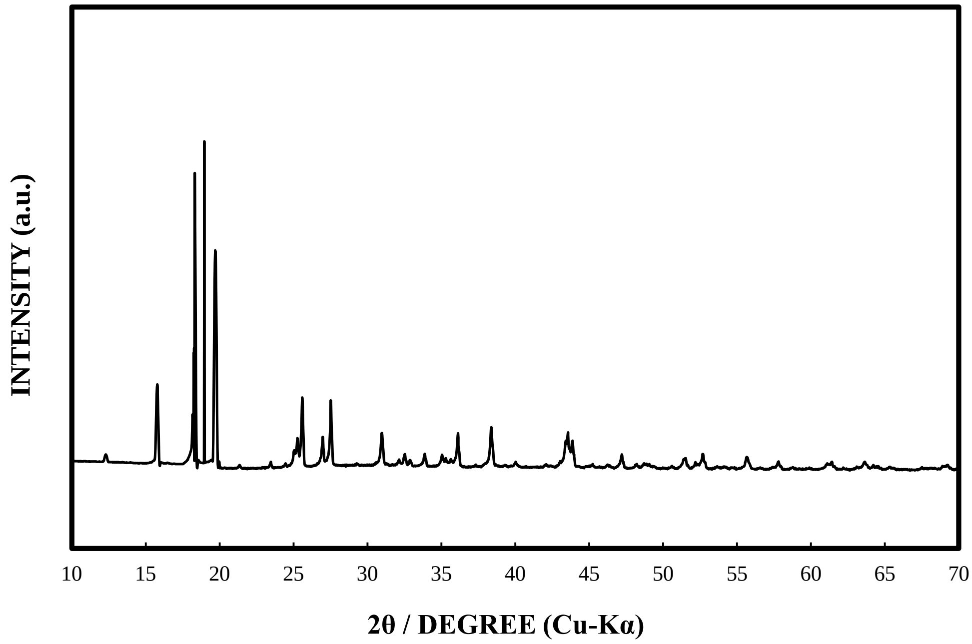

Figure 6 X-Ray diffraction pattern of copper (II) formate

Figure 6 shows representation XRD patterns recorded from 10 to 70 2θ degrees for copper (II) formate. The copper formate was detected, with the XRD pattern revealing peaks at 18.32, 18.96, and 19.72 (°). This result confirms that the reaction of copper (II) oxide and formic acid was completed at 25 °C for 1 h. The product contains copper (II) formate without copper (II) oxide.

5.1.2 Chemical reaction of copper-amine complexes inks

Copper-amine complexes inks were prepared by the mix of copper (II) formate, a solution of each amine (diethanolamine, octylamine and dibutylamine) and solvent (toluene, ethanol and isopropanol).

Complexes ink of copper (II) formate and alkanolamine (diethanolamine) were generated, as follows equation (2) [2].

$$Cu(HCOO)_2 + 2NR_2\text{-}R'(OH)_2 \longrightarrow Cu(HCOO)_2\,(NR_2\text{-}R'(OH)_2)_2 \quad (2)$$

While complexes ink of copper (II) formate and alkylamines (octylamine and dibutylamine) were generated, as follows equation (3) [8, 14].

$$Cu(HCOO)_2 + 2R\text{-}NH_2 \longrightarrow Cu(HCOO)_2\,(R\text{-}NH_2)_2 \quad (3)$$

Copper metal can be generated from a reduction in copper (II) formate by thermal decomposition as in the following equation (4) [2, 14].

$$Cu(HCOO)_2 \longrightarrow Cu + 2CO_2 + H_2 \quad (4)$$

Therefore, copper-amine complexes inks can reduce to copper metal as in the following equation (5) [2] and (6).

$$Cu(HCOO)_2\,(NR_2\text{-}R'(OH)_2)_2 \longrightarrow Cu + 2CO_2 + H_2 + 2NR_2\text{-}R'(OH)_2 \quad (5)$$

$$Cu(HCOO)_2\,(R\text{-}NH_2)_2 \longrightarrow Cu + 2CO_2 + H_2 + 2R\text{-}NH_2 \quad (6)$$

5.1.3 Thermal analysis of the complex ink

The decomposition of the copper-amine complexes were also confirmed using TG/DTA. In figure 7, a two-step weight loss is observed. The first weight loss starts from near 30°C and finishes at 100°C and occurs because of evaporation of isopropanol. The second weight loss starts from around 180°C decompose of copper complex into metallic copper.

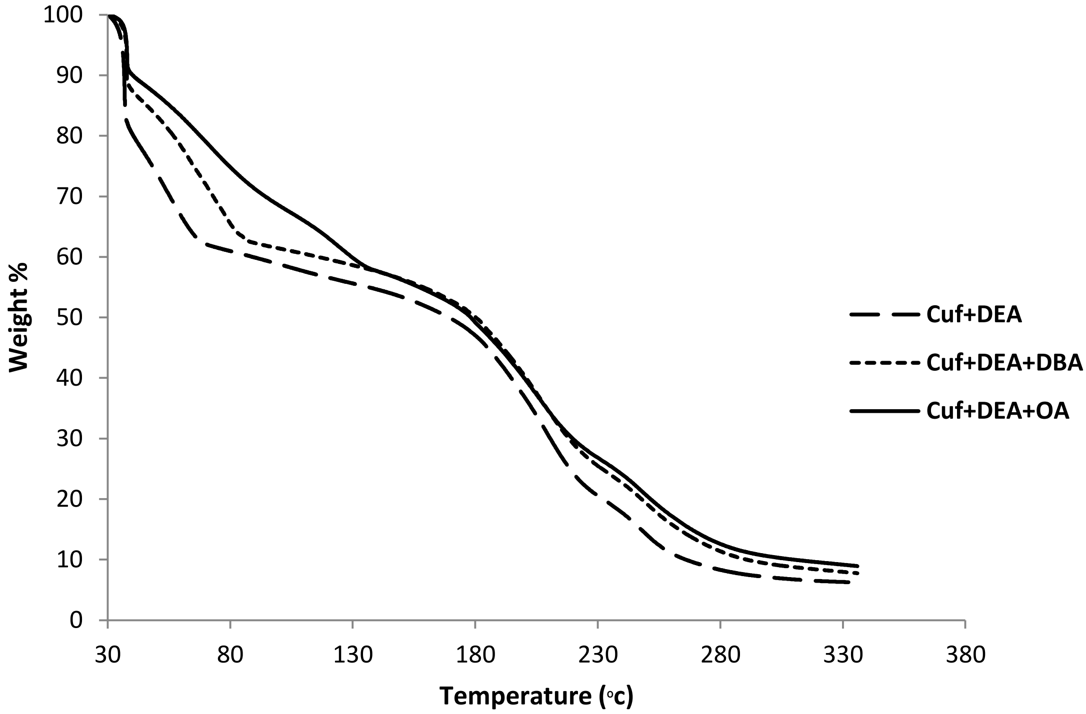

Figure 7 Thermal gravimetric and differential thermal analysis of Cuf-DEA, Cuf-DEA-DBA and Cuf-DEA-OA ink

5.2 Effect of types of solvent (toluene, ethanol and isopropanol)

This demonstration showed that each of amines can be dissolved in solvents of any kind. Copper-amine complexes inks were prepared by mixing Cuf with blend amines as 4 ml of DEA and 1 ml of alkylamine (DBA and OA) and solvent including toluene, ethanol and isopropanol. In all cases, DEA can't dissolve in toluene and alkylamine can't dissolve in ethanol. On the contrary, DEA and alkylamine can dissolve in isopropanol. Accordingly, isopropanol was used as the solvent for the next experiment.

5.3 Effect of types of amines

There are two types of amines were investigated including alkanolamine and alkylamine. Amines were selected to study the stability and resistance. Copper amine complexes ink was prepared using a 1:0.12 molar ratio of Cuf and DEA. Alkylamine was added using a 1:0.034 molar ratio of Cuf and alkylamine into the Cuf-DEA complex to make the ink. The conductive films were fabricated at 200 °C using 0.35 M of Cuf with spraying rate 0.8 ml/min, 25 min of an annealing time.

Figure 8 shows volume resistivity of copper film fabricated on PI substrates from different Cuf-amine complex ink. Types of amine affect volume resistivity of conductive films. Volume resistivity of the film from Cuf-DEA-DBA ink was significantly lower than the film fabricated using Cuf-DEA-OA ink. However, copper film from Cuf-DEA ink showed better performance compared with Cuf-DEA-DBA ink and Cuf-DEA-OA ink. The resistivity values were 10.25, 32.196 and 3.16 μΩ.cm for Cuf-DEA-DBA, Cuf-DEA-OA and Cuf-DEA ink, respectively.

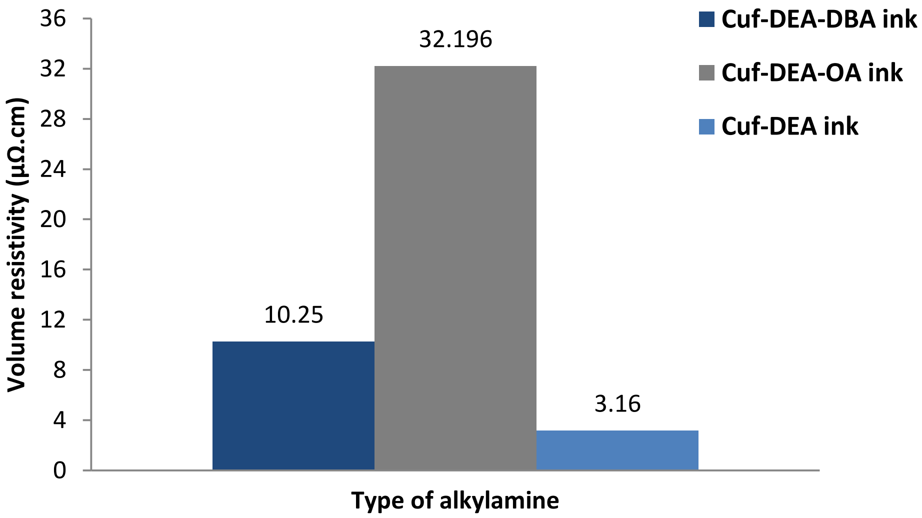

Figure 8 Volume resistivity of the film fabricated using Cuf-DEA-DBA, Cuf-DEA-OA ink and Cuf-DEA ink.

The XRD analysis of the conductive films fabricate using 1 Cuf : 0.034 alkylamine ink on PI substrates is shown in figure 9. For both alkylamine, peaks at 35.48°, 43.9°, 51.1°, 53.8° and 74.55° were observed, indicating that the obtained conductive film contained copper metallic and copper oxide. Likewise, peaks of the films fabricated using Cuf-DEA ink was contained copper metallic and copper oxide [21]. The three major 2θ peaks were 43.9°, 51.1° and 74.55°, which were copper metallic. The films fabricated from Cuf-DEA-alkylamine ink are more easily oxidized in air because alkylamine adsorbed onto the copper particles could not block the oxygen diffused from an air atmosphere. While the film fabricated using Cuf-DEA ink has OH-groups of DEA covered the copper particle and prevented oxygen under an air atmosphere [2].

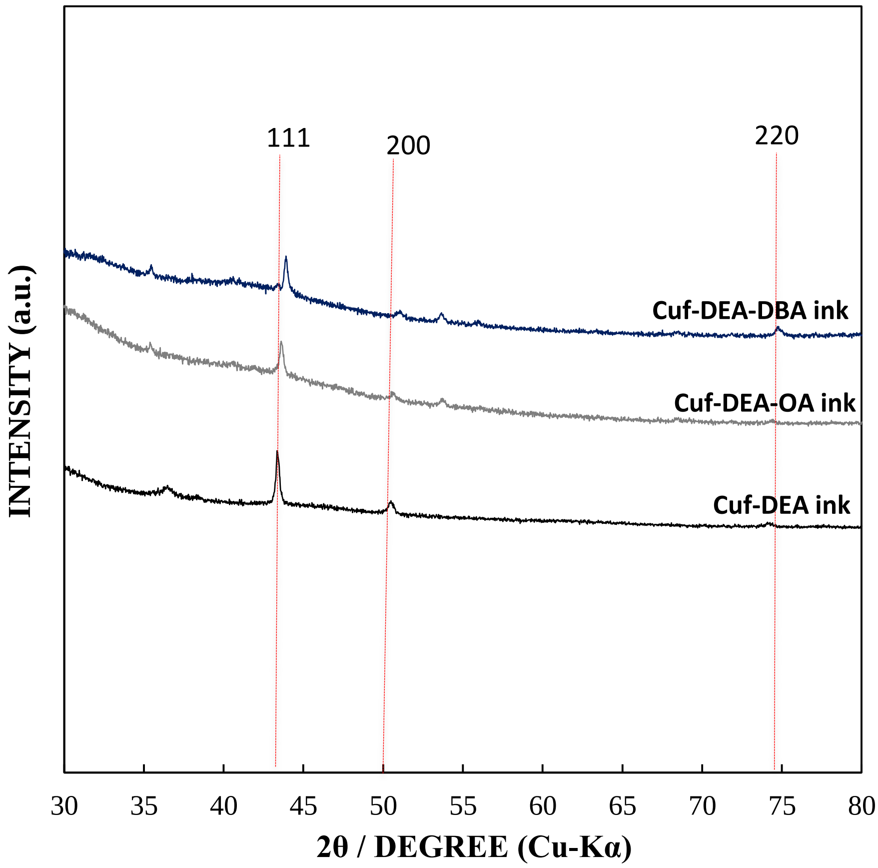

Figure 9 X-ray diffraction of copper film fabricated using Cuf-DEA-DBA ink, Cuf-DEA-OA ink and Cuf-DEA ink.

The morphology of copper films was analyzed using SEM images. Figure 10 reveal that SEM images of the films prepared from Cuf-DEA-DBA ink (fig. 10a), Cuf-DEA-OA ink (fig. 10b) and Cuf-DEA ink (fig. 10c). In all cases, the films composed of interconnected small copper particles with a few void spaces. Furthermore, the grain boundaries were still apparently noticeable. The conductive films derived from Cuf-DEA-DBA ink and Cuf-DEA-OA ink (fig. 10a and fig. 10b) consisted of small and lagre particles. While the film from Cuf-DEA ink (fig. 10c) consisted only large particles.

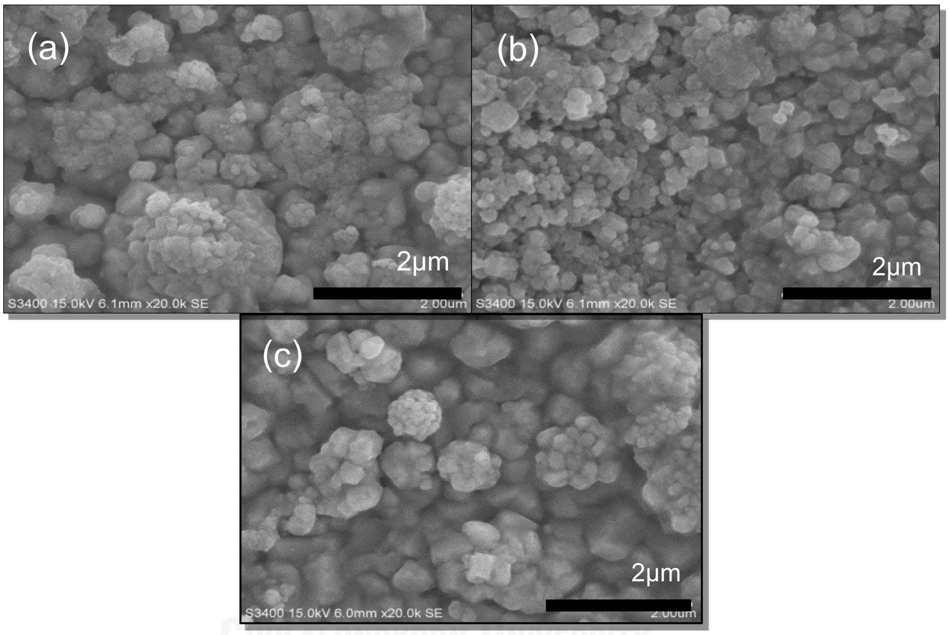

Figure 10 SEM images of copper films from different Cuf-amine complex inks fabricated at 200 ºC using 0.35 M of Cuf with spraying rate 0.8 ml/min, 25 min of an annealing time. (a) Cuf-DEA-DBA ink, (b) Cuf-DEA-OA ink and (c) Cuf-DEA ink

Figure 11 shows cross section images of the films was analyzed using FE-SEM images. In all cases, a layer with low sintering degree of copper particle was observed. The films derived from Cuf-DEA ink composed of larger particles. Consequently, the films from Cuf-DEA ink were thicker than the film fabricated using Cuf-DEA-DBA ink and Cuf-DEA-OA ink.

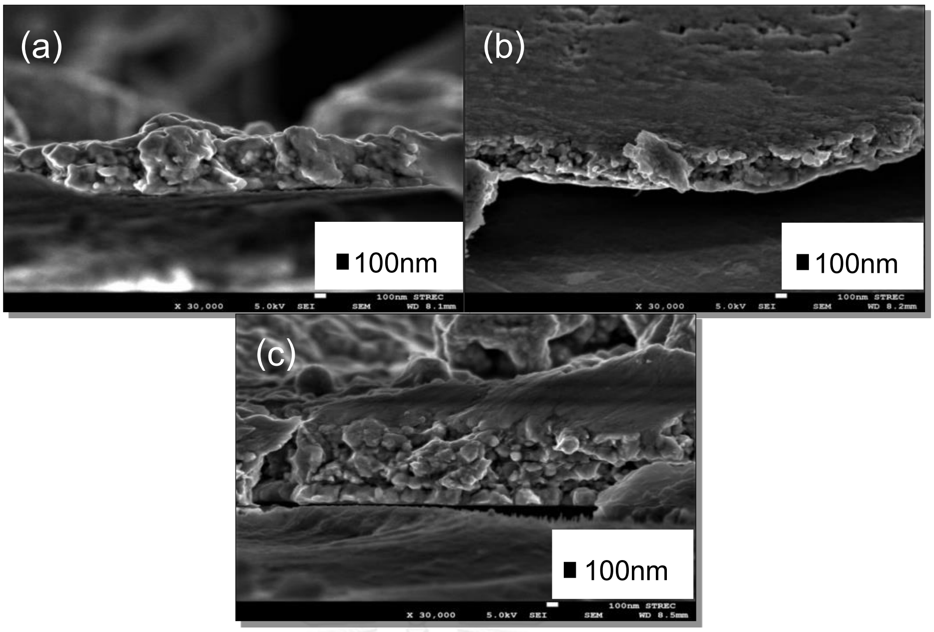

Figure 11 Cross section images of copper films from different Cuf-amine complex inks fabricated at 200 ºC using 0.35 M of Cuf with spraying rate 0.8 ml/min, 25 min of an annealing time. (a) Cuf-DEA-DBA ink, (b) Cuf-DEA-OA ink and (c) Cuf-DEA ink

5.4 Effect of molar ratio of Cuf and amine

Figure 12 displays the volume resistivity of the conductivity films fabricated using Cuf-DEA-DBA ink and Cuf-DEA-OA ink at 200 ºC, 0.35 M of Cuf with spraying rate 0.8 ml/min, 25 min of an annealing time using 1:0.017 and 1:0.034 molar ratio of Cuf to alkylamine. The molar ratio of Cuf to amine also affected volume resistivity of the conductive films. In all cases, volume resistivity of films dropped considerably with decreasing concentration of alkylamine. The resistivity of conductive films fabricated using Cuf-DEA-DBA ink was lower than the films fabricated using Cuf-DEA-OA ink.

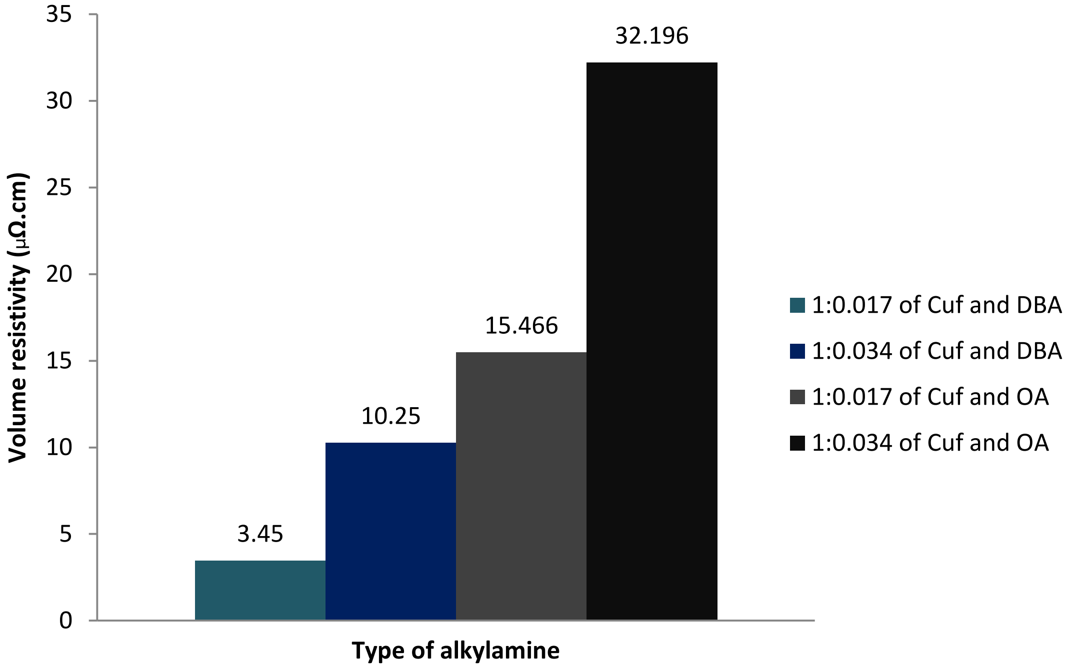

Figure 12 Volume resistivity of the film fabricated using different molar ratio of Cuf to DBA and Cuf to OA.

The XRD analysis of the conductive films fabricated using 1 Cuf : 0.017 DBA, 1 Cuf : 0.034 DBA, 1 Cuf : 0.017 OA and 1 Cuf : 0.034 OA ink is shown in figure 13. For the conductive films fabricated using 1 Cuf : 0.034 DBA and 1 Cuf : 0.034 OA, peaks at 35.48°, 43.9°, 51.1° and 74.55° were observed, indicating that the obtained conductive film contained copper metallic and copper oxide. On the contrary, the peaks of conductive films fabricated using 1 Cuf : 0.017 DBA were 43.9°, 51.1° and 74.55° which only copper metallic was present while the peaks of conductive films fabricated using 1 Cuf : 0.017 OA were not detected because it is amorphous.

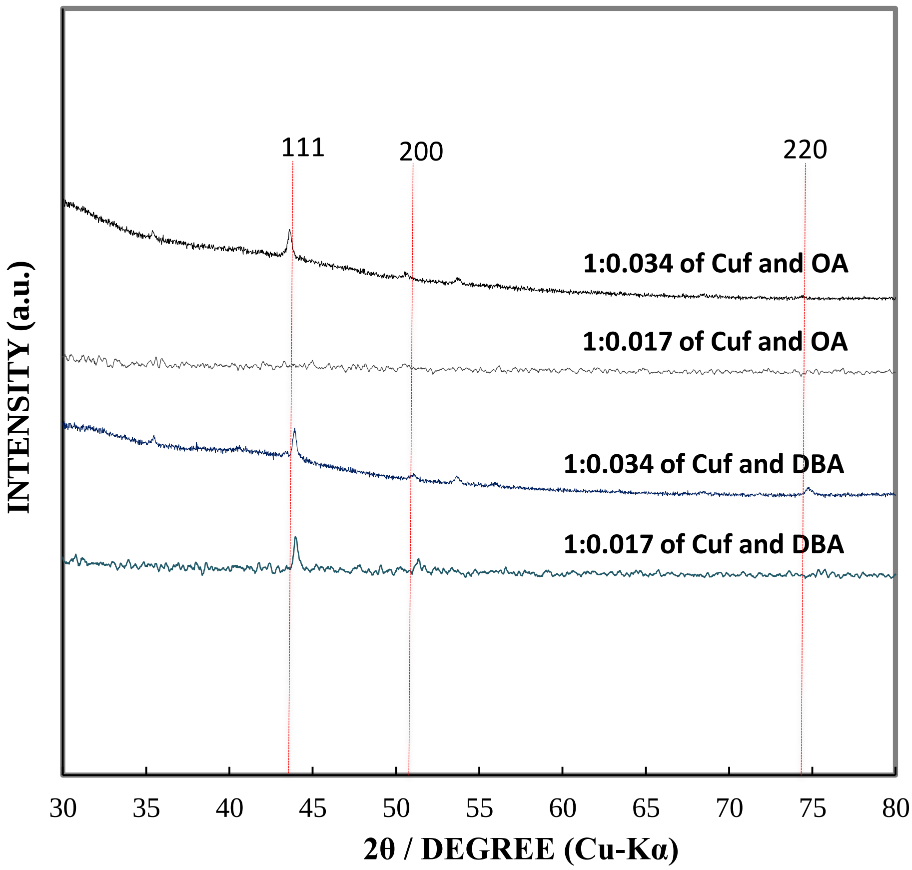

Figure 13 X-ray diffraction of copper film fabricated using different molar ratio of Cuf to DBA and Cuf to OA.

The SEM images of conductive films fabricated using different molar ratio of Cuf to DBA and Cuf to OA are shown in figure 14. In all cases, the films consisted of small particles piling in large particles. Obviously, surface of the conductive film fabricated derived from lower concentration of alkylamine (fig. 14b and fig. 14d) was smoother than the film fabricated using high concentration (fig. 14a and fig. 14c). The films that produced high concentration of alkylamine had lower number of grain boundaries, the size of void spaces increased. In contrast, using lower concentration, relatively smaller void spaces were generated, number of grain boundaries increased and porous decreased.

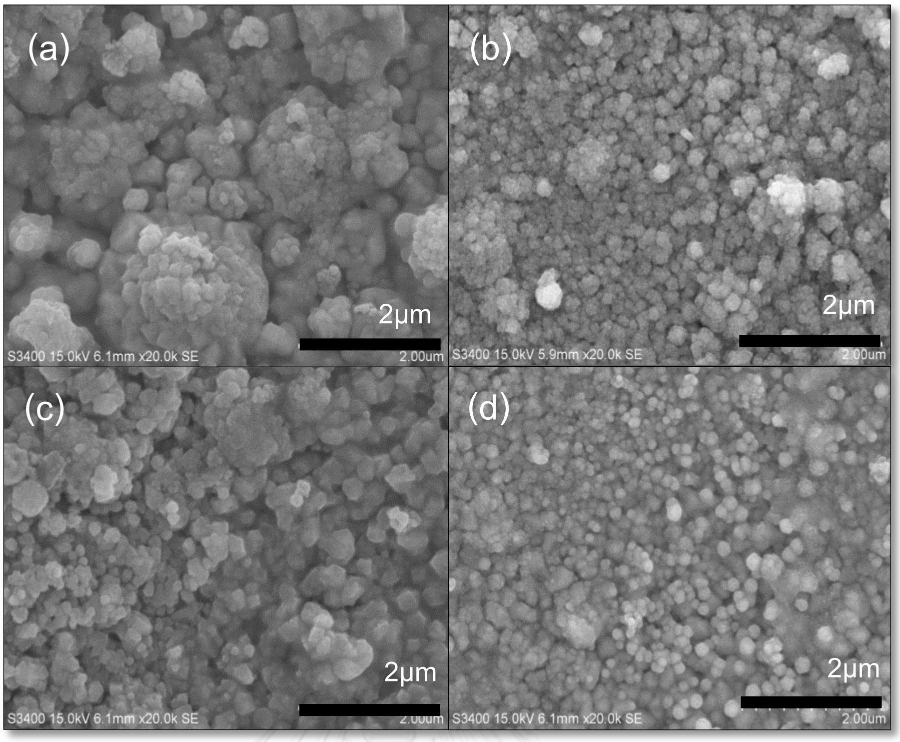

Figure 14 SEM images of copper films from different Cuf-amine complex inks fabricated at 200 ºC using 0.35 M of Cuf with spraying rate 0.8 ml/min, 25 min of an annealing time. (a) 1:0.034 of Cuf and DBA, (b) 1:0.017 of Cuf and DBA, (c) 1:0.034 of Cuf and OA and (d) 1:0.017 of Cuf and OA

Figure 15 shows cross section images of the films was analyzed using FE-SEM images. In all cases, low degree of sintering in the films was obtained. Cuf-DEA-DBA ink and Cuf-DEA-OA ink were taken as examples for complexes with a short alkyl chain and a long alkyl chain, respectively. Therefore, the films from Cuf-DEA-OA ink composed smaller particles compared with the film made from Cuf-DEA-DBA ink. Thickness of the films fabricated using Cuf-DEA-DBA ink was thicker than the films derived from Cuf-DEA-OA ink.

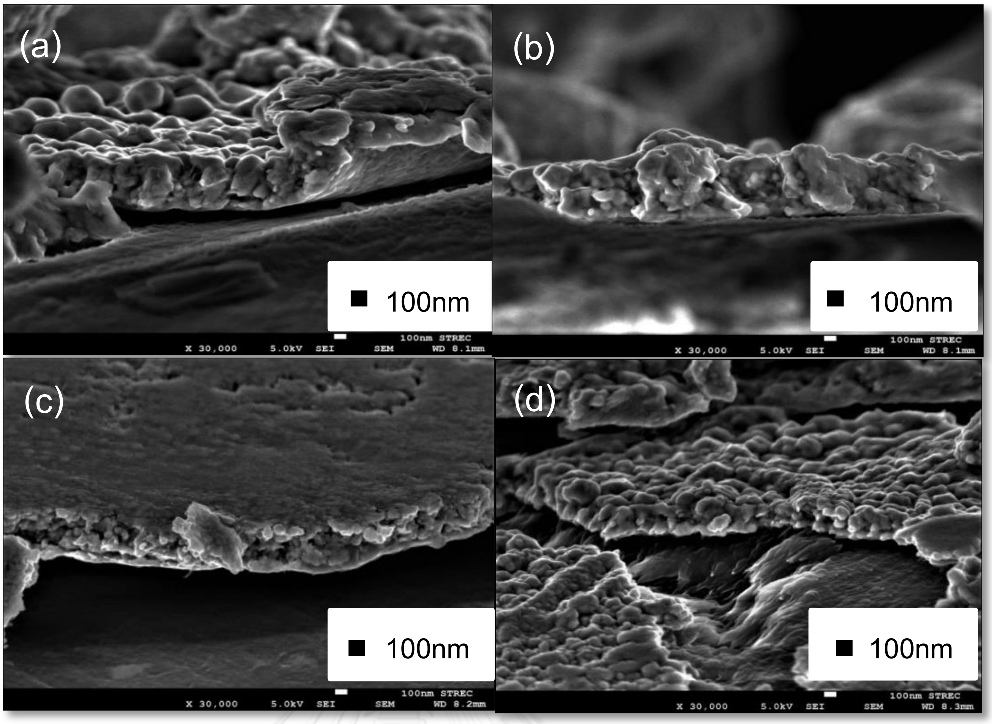

Figure 15 Cross section images of copper films from different Cuf-amine complex inks fabricated at 200 ºC using 0.35 M of Cuf with spraying rate 0.8 ml/min, 25 min of an annealing time. (a) 1:0.034 of Cuf and DBA, (b) 1:0.017 of Cuf and DBA, (c) 1:0.034 of Cuf and OA and (d) 1:0.017 of Cuf and OA

5.5 Effect of spraying rate

The volume resistivity of the film fabricated using Cuf-DEA ink, Cuf-DEA-DBA ink and Cuf-DEA-OA ink at 200 ºC, 0.35 M of Cuf with various spraying rate including 0.53, 0.67 and 0.8 ml/min on PI substrate is displayed in figure 16. The molar ratio of Cuf, DEA and alkylamine was fixed as 1:0.12:0.017. In all cases, the films fabricated using low spraying rate exhibited lower volume resistivity. Cuf-DEA inks showed the lowest volume resistivity of 2.691 μΩ.cm, which is only 1.57 times the resistivity of bulk copper. When we changed the spraying rate to 0.67 and 0.8 ml/min, the conductive films derived from Cuf-DEA ink still showed the best conductivity compared with other complexes inks.

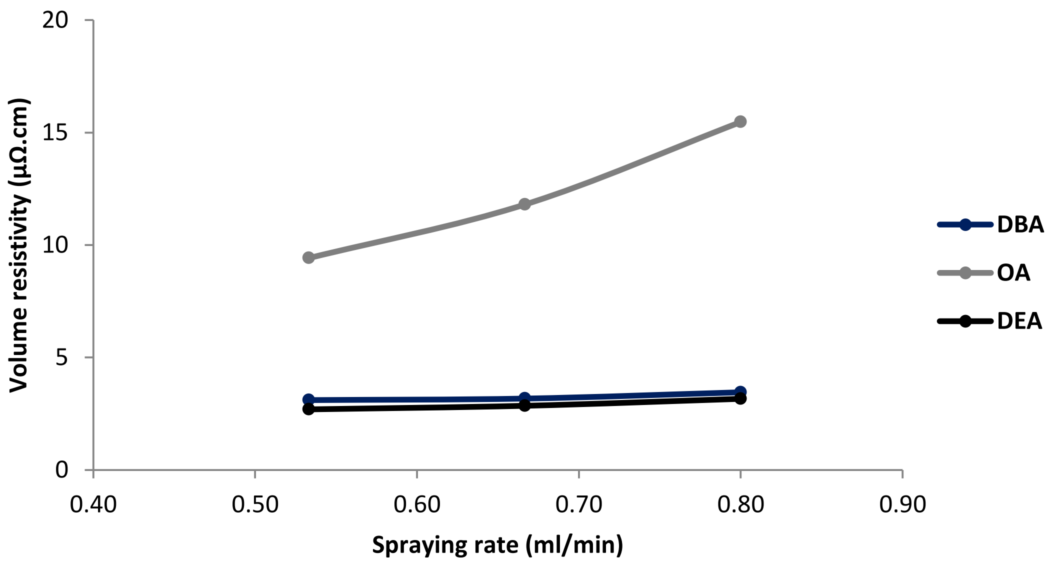

Figure 16 Volume resistivity of the film fabricated with spraying rate 0.53, 0.67 and 0.8 ml/min using Cuf-DEA, Cuf-DEA-DBA and Cuf-DEA-OA ink.

Figure 17 shows representative XRD patterns recorded from 30 to 80 2θ degree for the conductive films using copper amine complexes ink. The conductive films derived from Cuf-DEA ink peaks can be observed at 36.49º, 43.9º, 51.1º and 74.55º, indicating that the obtained conductive film contained copper metallic and copper oxide. XRD patterns of the film fabricated using Cuf-DEA-DBA ink revealing peaks at

43.9º, 51.1º and 74.55º as only copper metallic. And peaks of the films made using Cuf-DEA-OA ink was not detected because it is amorphous, except spraying rate at 0.53 ml/min was detected at 43.9º, 51.1º and 74.55º.

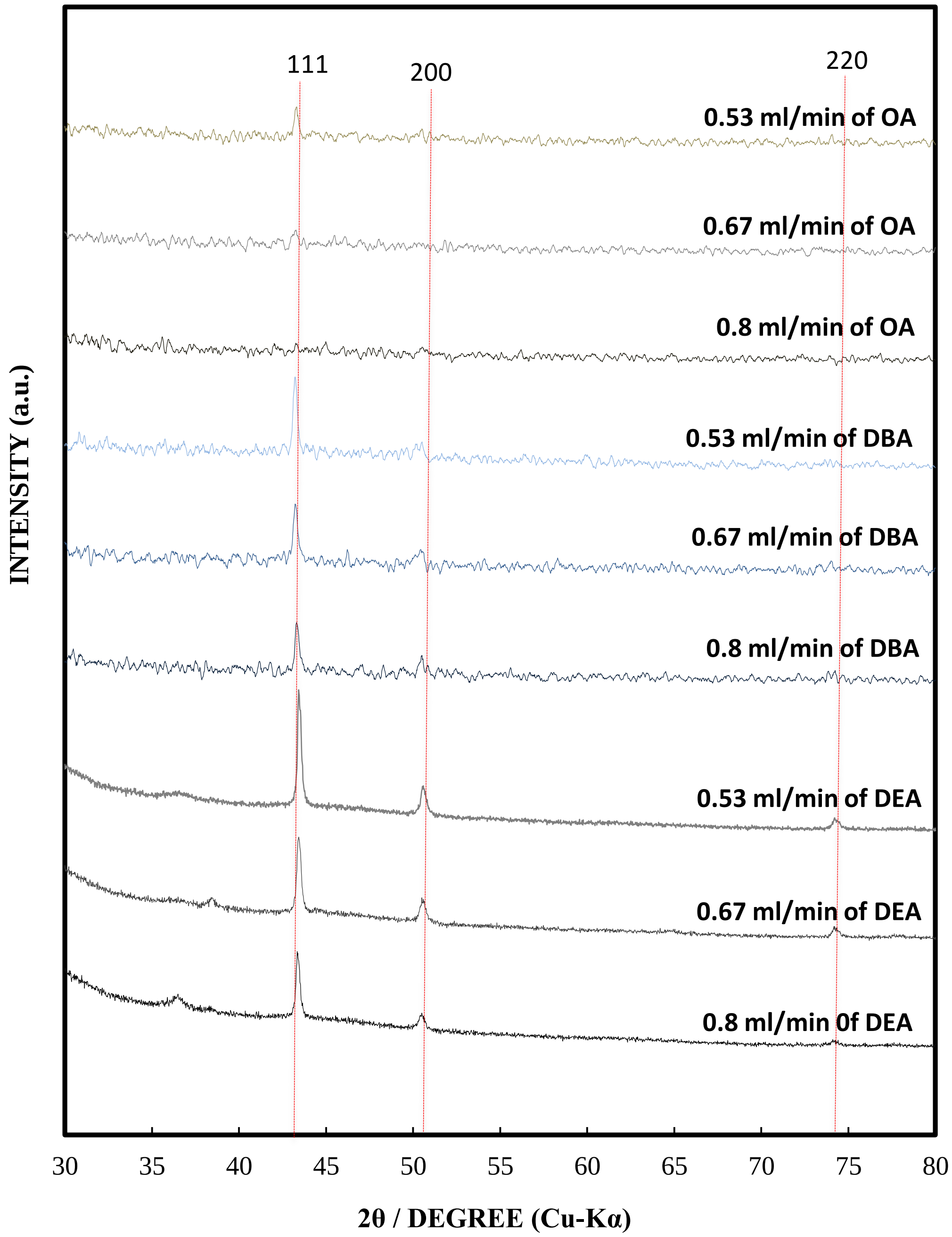

Figure 17 X-ray diffraction of copper film fabricated with spraying rate 0.53, 0.67 and 0.8 ml/min using Cuf-DEA, Cuf-DEA-DBA and Cuf-DEA-OA ink.

Figure 18, 19 and 20 show a typical SEM image of conductive film fabricated using copper amine complexes ink. In all cases, the films with high sintering degree were significantly increased by lowering the spraying rate. Thus, the films fabricated at 0.53 ml/min were smoother and denser than the films fabricated at higher spraying rate. Moreover, void spaces and grain boundaries of the films at lower spraying rate were decreased.

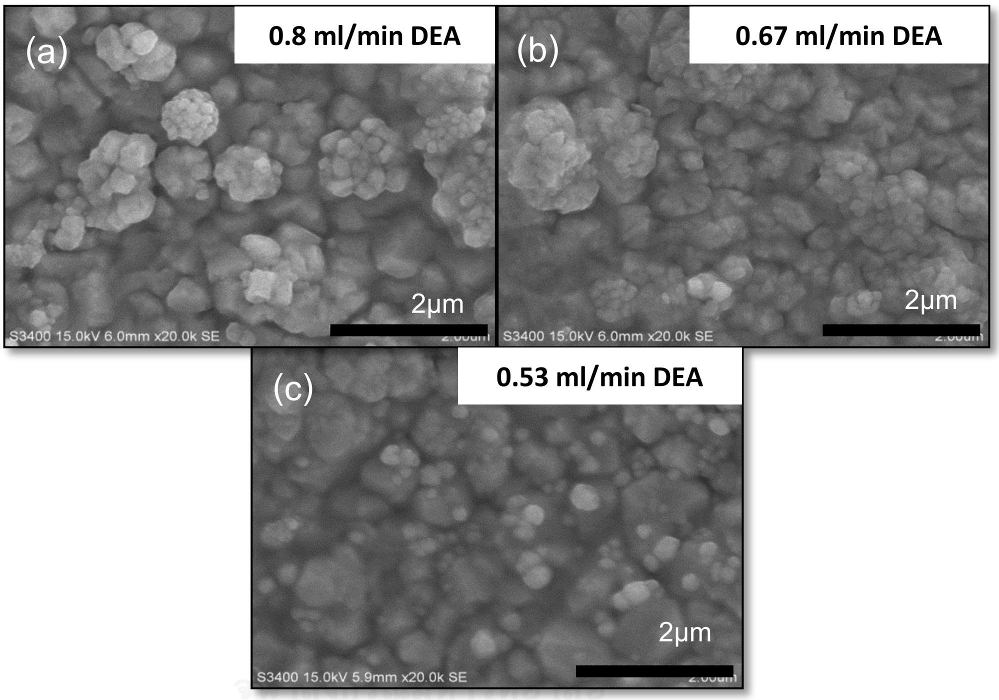

Figure 18 SEM images of copper films fabricated with spraying rate 0.53, 0.67 and 0.8 ml/min using Cuf-DEA ink.

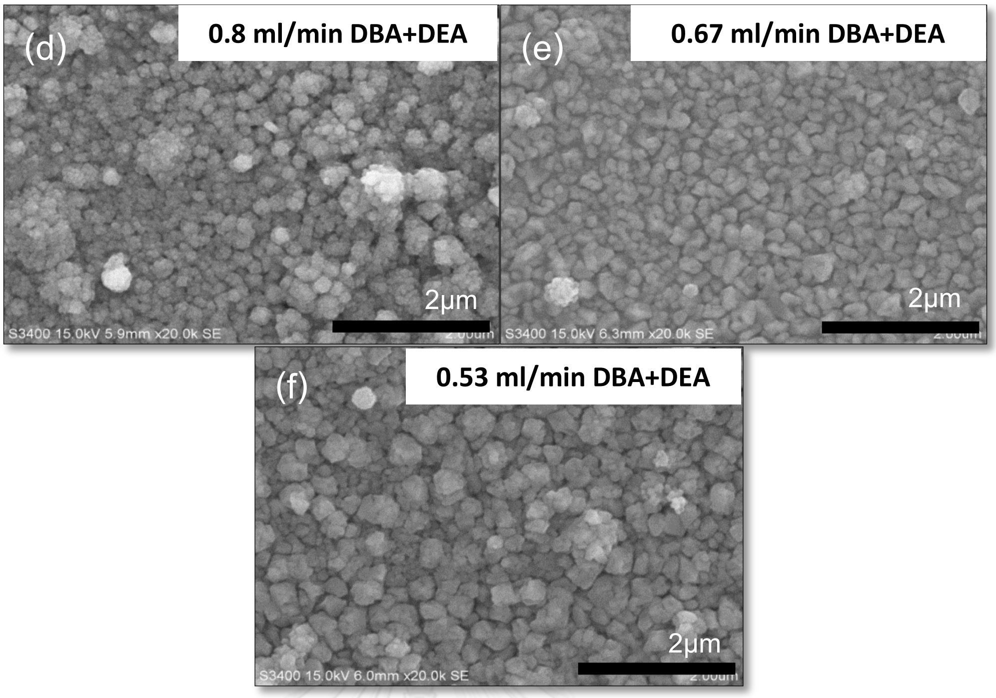

Figure 19 SEM images of copper films fabricated with spraying rate 0.53, 0.67 and 0.8 ml/min using Cuf-DEA-DBA ink.

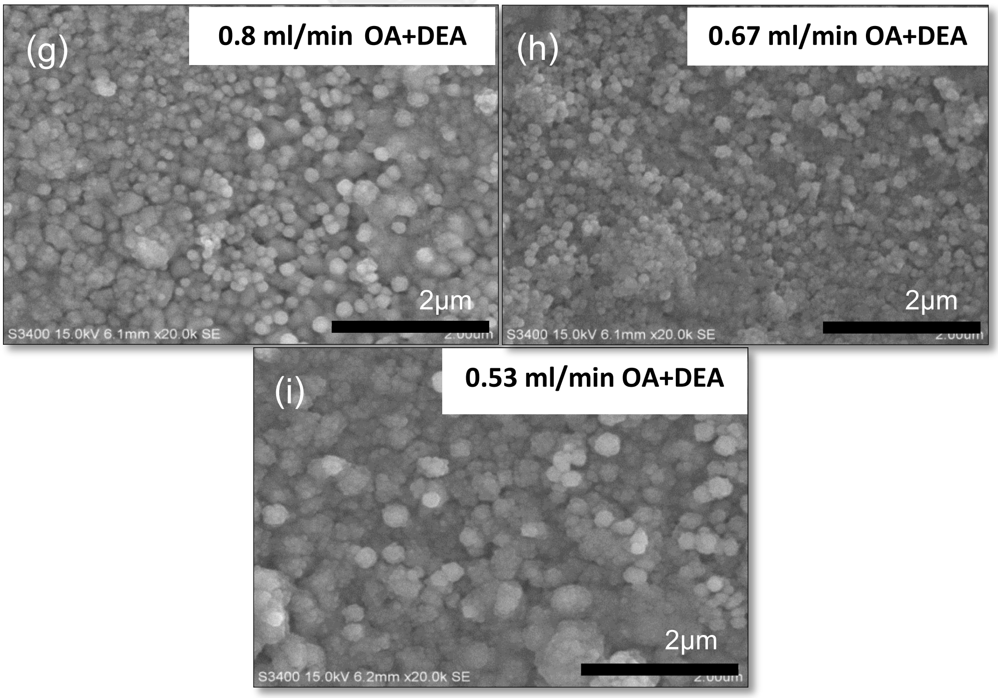

Figure 20 SEM images of copper films fabricated with spraying rate 0.53, 0.67 and 0.8 ml/min using Cuf-DEA-OA ink.

Figure 21, 22 and 23 show cross section images of the films was analyzed using FE-SEM images. In all cases, degree of sintering of the films fabricated using copper amine complexes ink was increased when decreasing spraying rate. Apparently, the lower spraying rate yielded a higher degree of sintering.

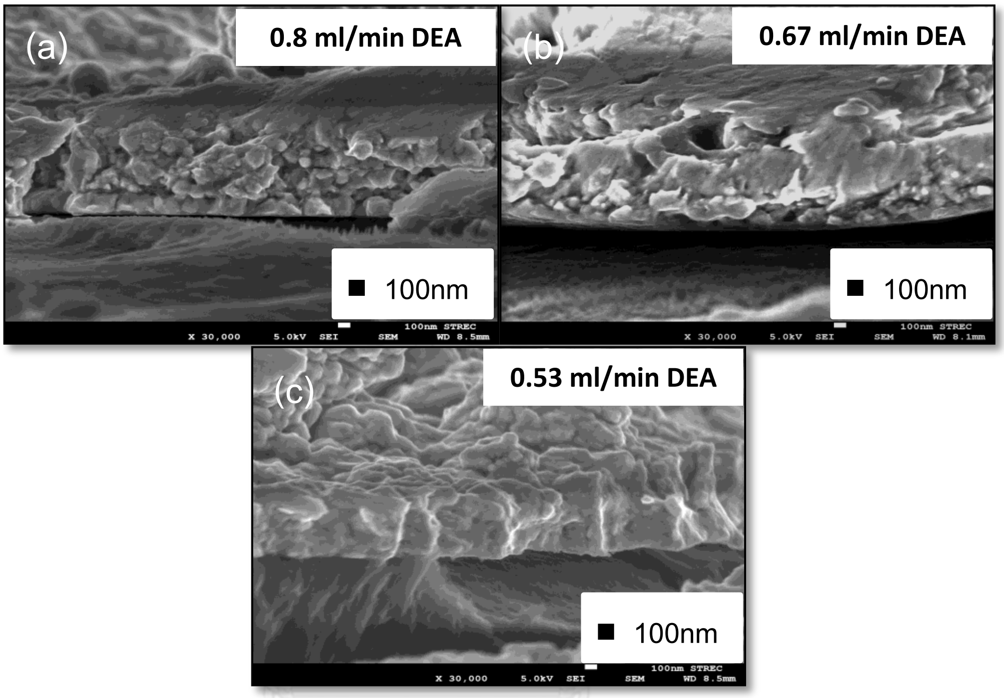

Figure 21 Cross section images of copper films fabricated with spraying rate 0.53, 0.67 and 0.8 ml/min using Cuf-DEA ink.

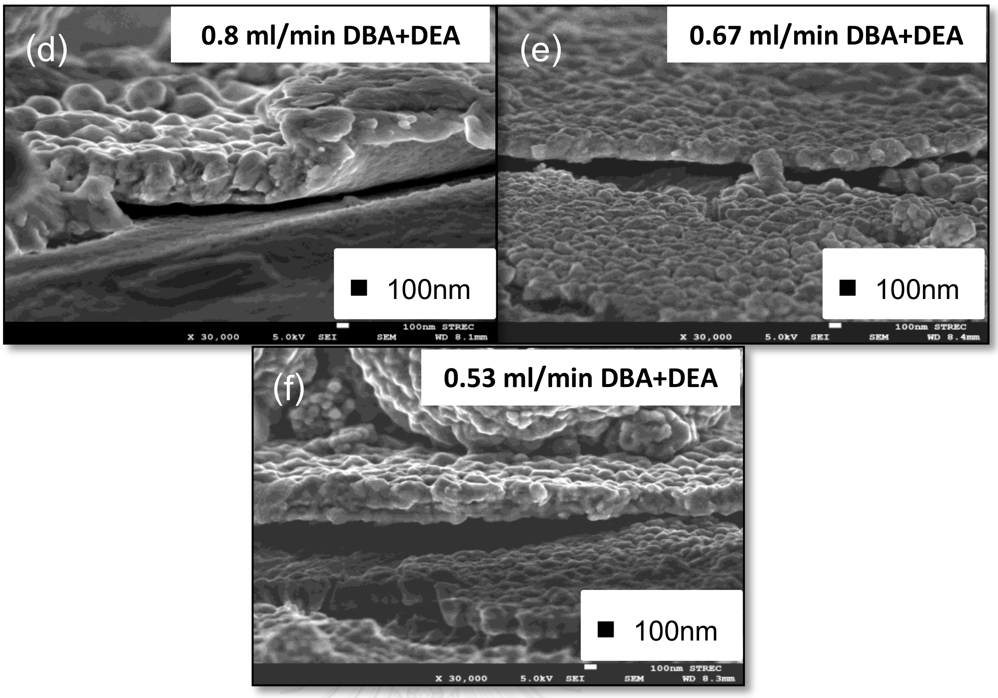

Figure 22 Cross section images of copper films fabricated with spraying rate 0.53, 0.67 and 0.8 ml/min using Cuf-DEA-DBA ink.

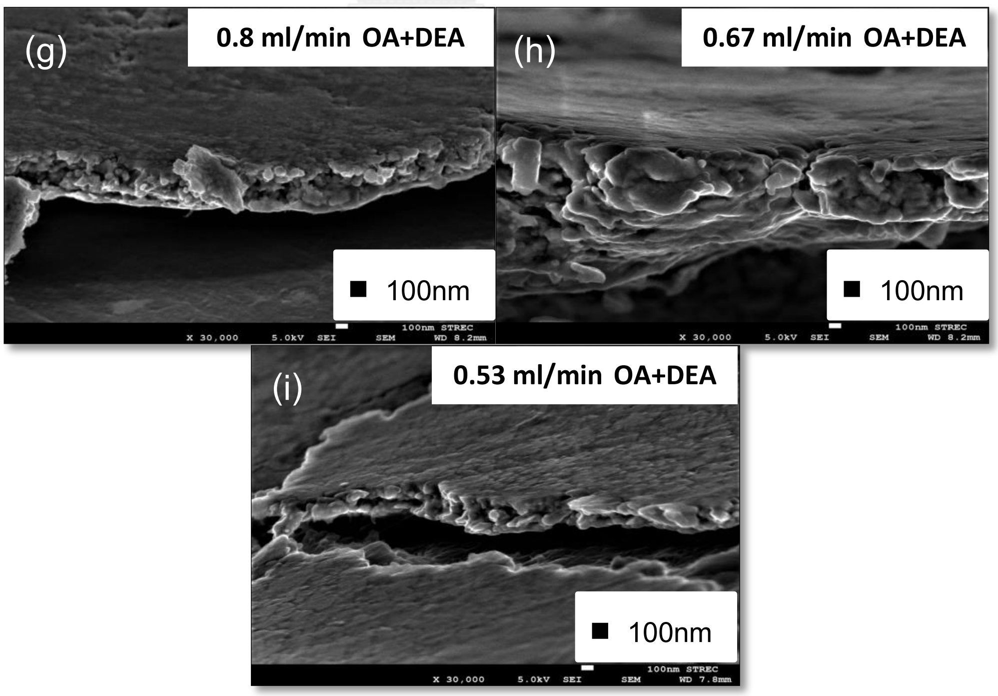

Figure 23 Cross section images of copper films fabricated with spraying rate 0.53, 0.67 and 0.8 ml/min using Cuf-DEA-OA ink.

Chapter 6

Conclusion

Fabrication of copper conductive films using spray pyrolysis of a copper amine complexes ink, mainly consisted of copper (II) formate (Cuf) and amine (Diethanolamine, Dibutylamine and Octylamine). The films fabricated using 0.35 M of Cuf at 200 °c, 25 min of annealing time with different of molar ratio of Cuf and alkylamine, at various spraying rate. The volume resistivity depend on types of amine, molar ratio of Cuf and alkylamine and spraying rate. The volume resistivity was decreased when using Cuf-DEA without alkylamine and decreasing spraying rate. The lowest resistivity of 2.691 μΩ.cm was obtained at 200 °c using 1 Cuf : 0.12 DEA, 0.53 ml/min of spraying rate, 25 min of annealing time which is about 1.57 times higher than the resistivity of bulk copper. Moreover, the well sintered layer of the film was exhibited when decreasing spraying rate. This technique has a great potentail in fabricating low cost electronic devices. Also, the study suggests the way to fabricated thin films with high degree of sintering using spray pyrolysis.

Recommendation

The spray pyrolysis method has been investigated as an alternative technique for the fabrication of a conductive layer as it is simple, inexpensive, and environmental friendly. In this work, we want to reduce volume resistivity which had many effect were investigated including types of amine, molar ratio of Cuf and amine and spraying rate. Fabrication of copper conductive films using spray pyrolysis is recommended that using low spraying rate and using Cuf-DEA without alkylamine. Further research is required to fabricate by screen printing using Cuf-DEA ink

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APPENDIX

VITA

Miss Siriporn Ketpokasiri was born on January 3, 1993 in Bangkok, Thailand. She received the Bachelor Degree of Chemical Engineering at Thammasat University in 2014. She continued her education in chemical engineering at Chulalongkorn University.