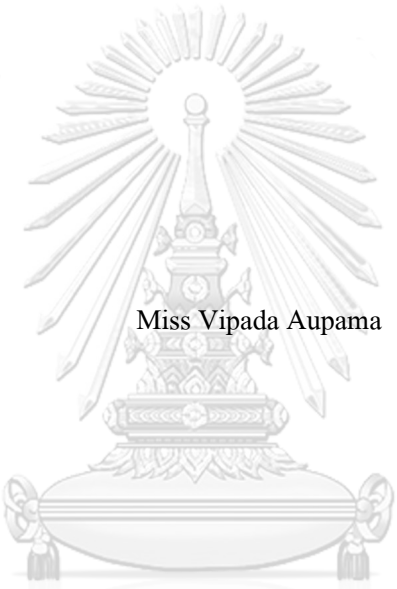
# Development of graphite-based conductive patterns by copper electroless plating and electroplating techniques

Miss Vipada Aupama





A Thesis Submitted in Partial Fulfillment of the Requirements
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# การพัฒนาเส้นลายนำไฟฟ้าฐานคาร์บอนโดยการเคลือบทองแดงด้วยเทคนิคการชุบแบบไม่ใช้ไฟฟ้าและการชุบแบบใช้ไฟฟ้า

น.ส.วิพาดา อุปมา



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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วิพาดา อุปมา : การพัฒนาเส้นลายนำไฟฟ้าฐานคาร์บอนโดยการเคลือบทองแดงด้วยเทคนิคการชุบแบบไม่ใช้ไฟฟ้าและการชุบแบบใช้ไฟฟ้า. ( Development of graphite-based conductive patterns by copper electroless plating and electroplating techniques) อ.ที่ปรึกษาหลัก : รศ. ดร.สุรเทพ เขียวหอม

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาปัจจัยที่มีผลต่อการขึ้นรูปเส้นลายนำไฟฟ้าคาร์บอนและการเพิ่มประสิทธิภาพการนำไฟฟ้าของเส้นลายด้วยวิธีการพิมพ์สกรีนและการใช้เทคนิคการชุบโลหะแบบใช้ไฟฟ้าและไม่ใช้ไฟฟ้าซึ่งการศึกษาจะแบ่งออกเป็น 2 ส่วนคือ การหาสัดส่วนที่เหมะสมในการเตรียมหมึกคาร์บอนระหว่างแกรไฟต์และโพลิไวนิลลิดีนฟลูออไรด์โดยในการเตรียมหมึกคาร์บอนจะใช้สัดส่วนของแกรไฟต์และโพลิไวนิลลิดีนฟลูออไรด์ที่แตกต่างกันคือ 2:0.1, 2:0.2, และ 2:0.3จากนั้นทำการวิเคราะห์และจากการคำนวณค่าปริมาณความต้านทานของเส้นลายนำไฟฟ้าที่สัดสัดส่วนของแกรไฟต์และโพลิไวนิลลิดีนฟลูออไรด์เท่ากับ 2:0.2 จะมีค่าปริมาณความต้านทานของเส้นลายนำไฟฟ้าต่ำสุดคือ 0.0122 โอห์มเมตร เมื่อเทียบกับสัดส่วนสัดส่วนของแกรไฟต์และโพลิไวนิลลิดีนฟลูออไรด์ 2:0.1 และ 2:0.3 ส่วนการศึกษาปัจจัยที่มีผลต่อการเพิ่มประสิทธิภาพการนำไฟฟ้าของเส้นลายด้วยเทคนิคการชุบโลหะแบบไม่ใช้ไฟฟ้าพบว่าที่อัตราส่วนระหว่างคอปเปอร์(II)ซัลเฟตและฟอร์มาลดีไฮด์เท่ากับ 1:2 จะทำให้อนุภาคของโลหะคอปเปอร์กระจายตัวได้ดีกว่าอัตราส่วนระหว่างคอปเปอร์(II)ซัลเฟตและฟอร์มาลดีไฮด์ 1:1 และ 2:1 และในส่วนของการใช้เทคนิคการชุบโลหะแบบใช้ไฟฟ้าพบว่าที่ความเข้มข้นของอิเล็กโทรไลต์ 0.5 โมลาร์จะต้องใช้ความต่างศักย์ไฟฟ้าเท่ากับ 8.5 โวลต์ ในขณะที่ความเข้มข้นของอิเล็กโทรไลต์ 1โมลาร์ ใช้ความต่างศักย์ไฟฟ้าแค่ 5 โวลต์ เพื่อรักษากระแสไฟฟ้าเคมีให้คงที่ 10 มิลลิแอมป์ โดยที่ชั้นของทองแดงมีความหนาเท่ากันเมื่อระยะเวลาที่ใช้ในกระบวนการเท่ากัน สำหรับเวลาที่แตกต่างกันที่ใช้ในกระบวนการชุบโลหะแบบใช้ไฟฟ้า 5, 10, และ 15 นาที พบว่าทิศทางการการโตของชั้นทองแดงจะตั้งฉากกับผิวหน้าของแกรไฟต์โดยที่เวลา 15 นาทีเส้นลายนำไฟฟ้าจะให้ค่าปริมาณความต้านไฟฟ้าลดลงถึง 0.8906 ไมโครโอห์มเมตร

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| สาขาวิชา | วิศวกรรมเคมี | ลายมือชื่อนิสิต ..... |
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KEYWORD: conductive ink/screen-printing copper/electroless plating/electroplating

Vipada Aupama : Development of graphite-based conductive patterns by copper electroless plating and electroplating techniques. Advisor: Assoc. Prof. SOORATHEP KHEAWHOM, Ph.D.

The screen-printing technique has been widely applied in electronic manufacturing field. In this work, graphite is used for fabricating conductive patterns by screen-printing technique. Moreover, enhance the performance of electrical conductivity by electroless plating and electroplating techniques. The study was separated into two parts. Firstly, optimize the mass ratio between graphite and polyvinylidene fluoride (PVDF). In prepared ink from varied mass ratio; 2.0:0.1, 2:0.2, and 2:0.3 respectively. Volume resistivity analysis of conductive patterns, it was found that the mass ratio between graphite and PVDF of 2: 0.2 provided the lowest volume resistivity of 0.0122 $\Omega$-m. In other cases, the mass ratio between graphite and PVDF of 2:0.1 and 2:0.3 provided volume resistivity of 0.8693 and 0.6445 $\Omega$-m, respectively. Secondly, this part of to study focuses on the factors affecting to improve conductivity efficiency by using electroless plating and electroplating techniques. Electroless plating was found concentration ratios between copper (II)sulfate($CuSO_4$) and formaldehyde(HCOH) of 1:2 provided the dispersion of spherical small copper better than concentration ratios between $CuSO_4$ and HCOH of 1:1 and 2:1, respectively. Electroplating was found the concentration of electrolytes unaffected to the copper layer at the constant current rate for the process also when the duration of electroplating increase in the copper layer of the pattern increased, within 15 min after electroplating the volume resistivity of conductive patterns reduced to 0.8906 $\mu\Omega$-m.



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Vipada Aupama

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# Chapter 1

# Introduction

## 1.1Background

Electronic manufacturing processes have used conventional photolithography techniques (Developing Etching Stripping, DES) to produce conductive patterns. However, these techniques are time-consuming, expensive, and highly complicated. Moreover, releases a significant amount of chemical waste that affects environments and require high waste treatment costs [1]. Therefore, the alternative printing technique on flexible polymer substrate (e.g., polyethylene terephthalate (PET), polyimide (PI)) has been investigated for producing the conductive patterns because it is relatively simple, cost-effective and environmentally friendly[2-4]. Presently, there are many printing techniques for producing conductive patterns such as ink-jet printing, spray-coating, stamp-transfer printing, and roll to roll printing. Screen-printing is one of the most simple and cost-effective techniques[5].

Commonly, gold (Au) and silver (Ag) have been the most used metals in the fabrication of metal-based inks due to the fact that they are highly conductive but very expensive[6, 7]. Moreover, some other metal-based inks can oxidize easily which cause decreasing performance of electrical conduction[1]. Therefore, conductive carbon materials such as graphite, graphene, or carbon black have been used in the manufacture of inks and coatings, e.g., printed electronic applications including printed circuit board (PCB)[8], light-emitting diodes (LEDs)[9], flexible displays[10] and current collecting grids[11].

Carbon inks have been widely studied in the field of conductive filler due to its outstanding stability, flexibility, and low cost[12, 13]. Although, the physical properties of carbon inks are advantageous, the electrical conductivity of carbon is inferior when compared with metal-based inks. For that reason, in order to achieve an excellent balance between cost and electrical performance. In this work carbon is chosen as conductive ink for making conductive patterns. After that, the patterns are coated metal to increase the efficiency of electrical conductivity by electroless

plating[14]and electroplating techniques[15]. Furthermore, copper (Cu) is considered the best metal material for producing conductive patterns because of its low cost, high electrical conductivity, and excellent property of electromigration[16, 17].

Electroless plating of copper is a copper coating technique. The small particles of copper are attached to the carbon surface by the chemical reaction between copper ions and formaldehyde. Electroplating of copper used to increase copper density and conductivity of conductive pattern. This technique applies electrical current to transfer and deposit copper ions onto the conductive surface.

This study focuses on the factors affecting the fabrication of carbon-based conductive patterns coated with copper. In the preparation of carbon inks, graphite powder and polyvinylidene fluoride(PVDF) polymer[18] are mixed together. After that, the screen-printing techniques are used for making carbon conductive patterns. The conductive patterns are then coated with copper to improves conductivity efficiency by using electroless plating and electroplating techniques.

**1.2 Objective**

1. To optimize mass ratio between graphite and polyvinylidene fluoride (PVDF) and operating condition for screen-printing technique of graphite conductive patterns.
2. To investigate the effects of concentration ratios between copper (II)sulfate($CuSO_4$) and formaldehyde(HCOH) in solution for electroless plating.
3. To investigate the effects of electroplating duration and concentration of electrolytes for electroplating technique.



**1.3 Scope**

Conductive pattern film from Graphite-Copper composite is fabricated by using the screen-printing technique for screen carbon conductive ink on polyimide (PI) substrates. After that, plating copper on the carbon conductive patterns by electroless and electroplating technique. The scope of this research is as follows:

1. The particle size of graphite powder is lower than 20μm for prepared carbon conductive ink.

2. Polyvinylidene fluoride binder for carbon conductive ink was varied from %weight 5,10 and 15.

3. Electroless copper plating is using copper (II)sulfate, potassium sodium tartrate tetrahydrate, sodium hydroxide, and formaldehyde.

4. Electroplating was performed using 0.5 and 1 M copper (II)sulfate as electrolyte.

5. Electroplating was performed by applying 10mA with vary electroplating duration 5,10, and 15 min.

**1.4 Research plan**

| No. | Activities | Period | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2020 | | | | | | | | | |
| | | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec |
| 1 | Literature review about conductive film, screen-printing, electroless and electroplating technique. | | | | | | | | | | |
| 2 | Experiment design | | | | | | | | | | |
| 3 | Study the effect ratio between carbon and binder for screen-printing technique. | | | | | | | | | | |
| 4 | Study the effect of Graphite-Cu composite on conductive patterns. | | | | | | | | | | |
| 5 | Write thesis and prepare for publication | | | | | | | | | | |

# Chapter 2

# Theory and Literature reviews

## 2.1 Carbon conductive ink

Carbon conductive inks are composed of carbon particles(such as graphite, graphene, or carbon black ), polymer binders, and other additives (for the dispersion, printing and adhesion tasks). graphite is a layered planer structure, typically tens of micro in length and is conductive primarily along its planes[19]. Within the polyvinylidene fluoride (PVDF) binder have a functionalized modifier containing a fluorine functional group can improve the compatibility and miscibility between the layers of graphite and PVDF to complimentary interaction bond with other layers[18].

## 2.2 Screen-Printing Process

Screen printing technique is printing inks onto various hardy or flexible substrates, and the entire procedure is simple, multipurpose, and low-priced. The screen printing is a push-through process using a porous material as the stencil, which means that during the printing process the inks pass through the stencil and are deposited onto the substrate. The printable inks can pass into the designed pattern zones because these areas are open and allowed the ink can through it and the other zones of the pattern are blocked off by hardened materials.



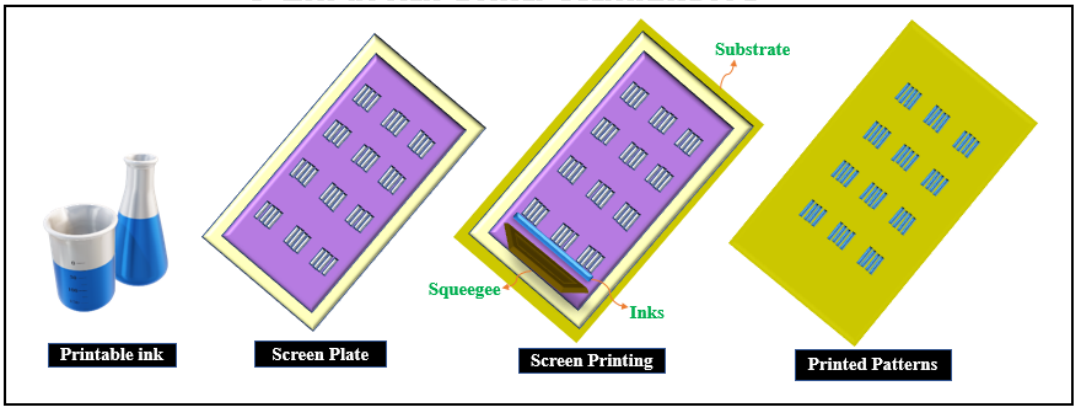


Figure 1 Schematic of the manufacturing process of screen printing

As shown in Figure.1, the screen plate is placed on top and the inks put on it until all the mesh openings are filled by ink. Then use a squeegee to move the mesh down to the substrate and pushes the squeegee onto the back of the screen. In the mesh openings, the inks are pumped by a capillary effect or squeezed onto the substrate in a manageable amount. When the squeegee moves forward, the tension on the back of the screen will decrease, making a mesh out of the substrate, leaving the inks upon the substrate surface. Then we can obtain the designed patterns on the substrate, which can be used in the next stage. The inks go through four stages in the printing process: filling, contact, adhesion, and release[11, 13, 20].

**2.3 Electroless copper plating**

Electroless copper is employed in the manufacture of printed circuit boards its purpose to make copper metal coating on carbon patterns to increase conductivity of the patterns. Typical electroless copper bath formulations will contain the following ingredients:

- Copper salts ($CuSO_4$)
- Reducing agent (formaldehyde)
- Alkaline hydroxide (NaOH)
- Chelating agent (EDTA, Rochelle salts, etc.)
- Stabilizers, brighteners, etc.
- Wetting agents (optional)



The formaldehyde and the hydroxide ions provide the reducing force essential for the deposition of metal copper. The deposition reaction must be initiated on the surface of the workplace to be plated. The main electroless plating reaction can be postulated to be:

$$Cu^{2+} + 2HCHO + 4OH^- \longrightarrow Cu^0 + 2HCOO^- + 2H_2O + H_2$$

The reaction as written is only autocatalytic with respect to copper metal in the presence of an activated surface or when hydrogen is being generated.

## 2.4 Electroplate copper

Electroplating is a process that create a metal coating on a solid substrate through the reduction of cations of that metal by means of a direct electric current. The part to be coated acts as the cathode (negative electrode) of an electrolytic cell; the electrolyte is a solution of a salt of the metal to be coated. In this study using copper (II) sulfate electrolyte. which provides a high concentration of copper (II) ions $Cu^{2+}$ and sulfate ions $SO_4^{2-}$ to carry the current during the electrolysis process. There are tiny concentrations of hydrogen ions $H^+$ and hydroxide ions ($OH^-$) from the self-ionization of water itself, but these can be ignored in this experiment.

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$$

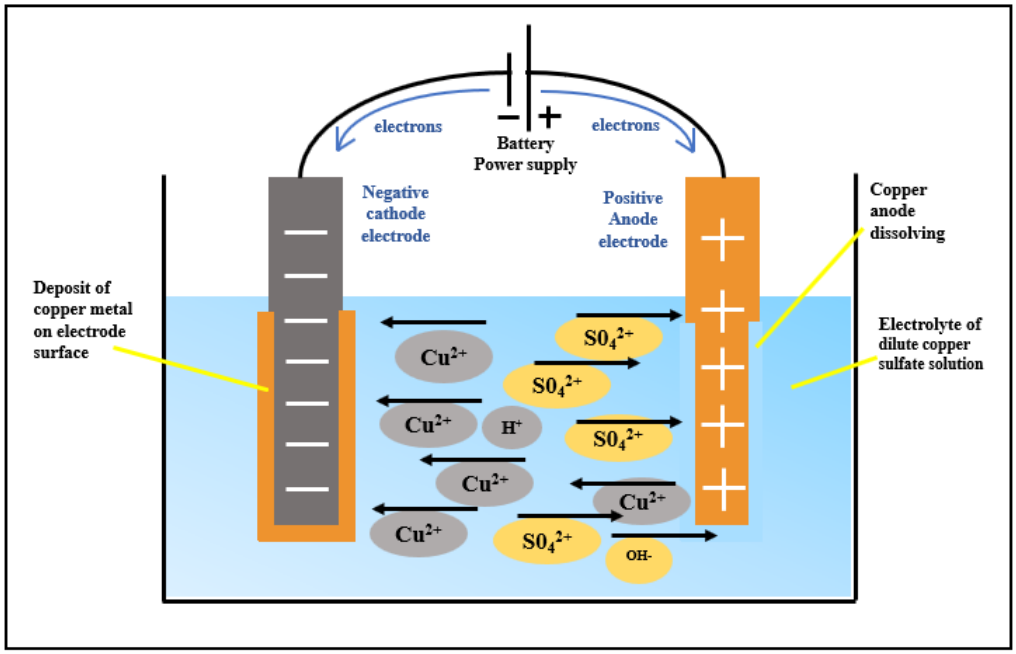


Figure 2 Schematic of Electroplate copper process

- The negative cathode reaction with copper or carbon electrodes

  -The negative cathode electrode attracts $Cu^{2+}$ ions (from copper sulfate) and $H^+$ ions (from water).

  -Only the copper ion is discharged, being reduced to copper metal.

-The less reactive a metal, the more readily its ion is reduced on the electrode surface.

A reduction electrode reaction at the negative cathode

$$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$$

- The positive anode reaction with a copper electrode

-The negative sulfate ions $SO_4^{2-}$ (from copper sulfate) or the traces of hydroxide ions $OH^{-}$ (from water) are attracted to the positive electrode.

-But both the sulfate ion and hydroxide ion are too stable and nothing happens to them because the copper anode is preferentially oxidized to discharge Cu2+ copper ions into the electrolyte solution.

An oxidation electrode reaction at the positive anode

$$Cu(s) \longrightarrow Cu^{2}+(aq) + 2e^{-}$$

**2.5 Characterizations**



2.5.1 Scanning electron microscope (SEM)

The Scanning electron microscope (SEM) is used to study the surface of the sample, where electrons are scattered on the surface of the object. The image has magnification 20-800,000 times. Moreover, energy dispersive x-ray spectrometer (EDS) can study the types, quantities, and dispersions of elemental elements of materials or impurities on the surface. The study material can be analyzed by analysis displays the type and quantity of elements. Also, map and line scan. The data can be it is used to improve and develop research work in the production process, analysis of the damage, Industrial problem solving, and quality control of materials.

2.5.2 Viscosity properties

The viscosity properties are used to study specific rheological characteristics, e.g., viscosity, surface tension, etc. Mostly, conductive inks require properties as shown in Table1.

| Printing technique | Viscosity (Pa s) | Surface tension (mN/M) |
|---|---|---|
| Screen-printing | 0.5-5 | 38-47 |
| Flexography | 0.01-0.5 | 14-23 |
| Inkjet printing | 0.001-0.1 | 15-25 |

Table 1 rheological properties for printing formulations (inks/pastes)[21].

The conductive inks cannot be described within the linear theory of viscoelasticity (Newtonian fluid) because the behavior of inks are non-Newtonian. Some type of conductive ink have behavior as Shear thickening flow or some are Bingham plastic flow. It depends on factors of inks such as components, solvent, and all additive.

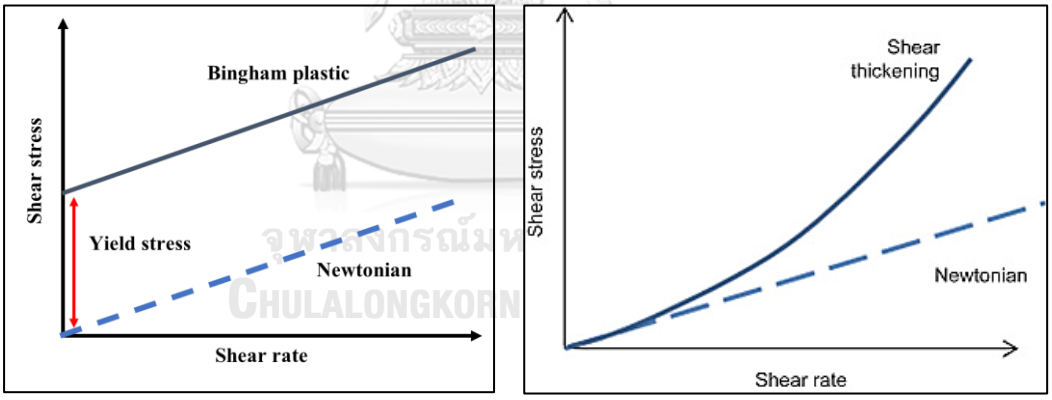


Figure 3 Bingham plastic behavior(left) and Shear thickening behavior(right)

2.5.3 Four-Point Probe

However, in practice, Resistance to high accuracy is quite difficult. Due to many effects such as machine temperature, measurement and installation of measuring instruments. This presents the measurement of resistance by the Four-point probe method which is standard of resistance measurement of semiconductor materials. By a pair of measuring needles provide current into the test specimen. Another pair of meters is used to measure the voltage from the work piece. This

method with this feature can avoid the effect of the resistance of the wires to measure and the voltage cross the point, Therefore, the calculated resistance more accurate.

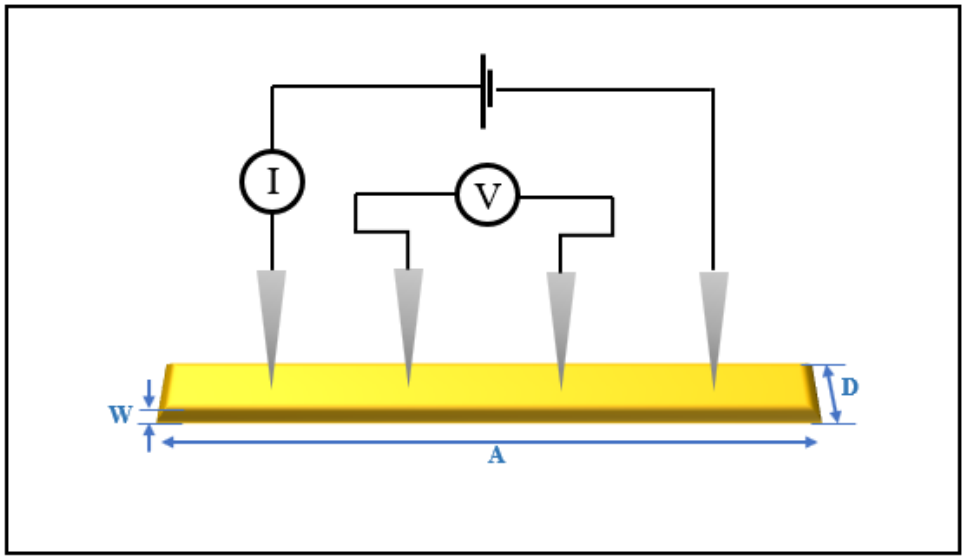


Figure 4 Schematic of Arrangement of a 4-point probe on a rectangular sample

The Measurement electrical resistance of materials in the case the shape of the rectangular area is A and length is L follow equation

$$\rho = RAL \quad \text{(E.1)}$$

When ρ is the volume resistivity

A is area (width x thickness)

L is the length of the pattern

A slope of voltage and current curve shows average resistance the surface patterns from Ohms law as equation

$$R = VI \quad \text{(E.2)}$$

When R is the resistance

I is the current

V is the voltage

The volume resistivity with uniform of μΩ.m is calculated with the electrical resistivity that resistance of a conductor with shape of the rectangular area is A and length is L.

$$\rho = RAL \qquad \text{(E.3)}$$

When is $\rho$ the volume resistivity (μΩ.m)

A is area (width x thickness) (m2)

L is the length of the pattern (m)

A slope of voltage and current curve shows average resistance the surface patterns from Ohms law as equation (E.2)

$$V = RI \qquad \text{(E.4)}$$

When R is the resistance (Ω)

I is the current (A)

V is the voltage (V)

From carbon conductive pattern provide four conductive line in sample. Therefore, the use 4-point probe for measure resistance of copper film pattern. The measurement will divide four time including 4-line, 3-line, 2-line and 1-line respectively that formulate overall resistance four equations.



$$Rn = RE + rn \qquad \text{(E.5)}$$

When $Rn$ is overall resistance with $n$ lines (Ω)

$RE$ is external resistance (Ω)

$r$ is internal resistance (Ω)

$n$ is a number of conductive lines

From 4-line:

$$R_4 = RE + r_4 \qquad \text{(E.6)}$$

From 3-line:

$$R_3 = RE+r_3 \qquad \text{(E.7)}$$

From 2-line:

$$R_2=RE+r_2 \qquad \text{(E.8)}$$

From 1-line:

$$R_1=RE+r \qquad \text{(E.9)}$$

**2.6 Literature reviews**

Phillips et al. (ref) prepare carbon conductive patterns on polyethylene terephthalate (PET) substrate by screen printing techniques. Carbon inks were prepared by graphite, carbon black, and vinyl polymer and used three roll mill machine for making carbon ink. At a higher total carbon loading ink of 29.4% by mass, optimal conductivity was 0.029 Ω•cm and achieved at graphite to carbon black ratio of 2.6 to 1.

Liu et al. (ref) synthesis graphene from graphite by a fluid-based method, two kinds of powders were prepared. Then, used graphene from synthesis to prepare inks for making conductive pattern, graphene powders, and carbon black and the polymer solution were mixed at weight ratio of 0.04 : 3: 17. At the inks with graphene powders and carbon black fraction of 15 % in the total conductive fillers exhibit printability down to lines of 90 μm in width and printed pattern electrical conductivity of 2.15×104 S/m at 7 μm thickness along with outstanding mechanical properties.

Zhao et al.(ref) develop an effective strategy for the fabrication of graphene nanoplatelets(GNPs)/Copper(Cu) composites through the two-step procedure involving the precoating of copper nanoparticles on GNPs by an electroless plating method followed by consolidation of GNP@Cu powders into bulk composites by spark plasma sintering (SPS) technique. from the experiment, the mechanical behavior of GNP/Cu composites was investigated by tensile tests. representative stress–strain relationship of Cu reference and GNP/Cu composites, It was the addition of a small amount of GNPs significantly increased the tensile properties of GNP/Cu composites. With only 1.3 wt.% (4.7 vol.%) GNPs, the tensile strength increased by 107% from 234 to 485 MPa, and the Young's modulus increased by 21% from 85 to103 GPa.



Li et al. (ref) study the properties of graphite nanosheets/polyvinylidene fluoride (PVDF) composite by a coupling agent. In the part of electrical conductivity when the GNs increase the electrical conductivity of composite material increases. Then, the PVDF-based composite material gradually changes from an insulator to a conductor.

An et al. (ref) presented a synthesis of the G-Cu composite thin film by dispersion electroplating of the composite. The electrochemically exfoliated multilayer graphene was introduced into an

electroplating solution by applying 10V for 5 min, and the weight fraction of graphene in the composite was approximately 1.9 wt%. The Young's modulus and shear modulus of the G-Cu composite were 123 and 51 GPa, which are 1.25 times greater and 1.22 times greater, respectively, than that of the pure Cu. The electrical resistivity of the G-Cu composite was 2.11 μΩ-cm, which is approximate to that of pure Cu~1.89 μΩ-cm.





# Chapter 3

# Experiments

### 3.1 Materials

Graphite powder(particle size < 20μm, ALDRICH Chemistry), polyvinylidene fluoride(PVDF, ALDRICH Chemistry ), AR Grade of N-methyl pyrrolidone(NMP, ALDRICH Chemistry), copper (II)sulfate($CuSO_4$, KEMUS), potassium sodium tartrate tetrahydrate ($KNaC_4H_4C_6 \cdot 4H_2O$, KEMAUS), sodium hydroxide pellets 98% (NaOH, LOBACHEMIE PVT.LTD), formaldehyde solution 37% extra pure(HCOH,)and polyimide(PI) substrates was used.

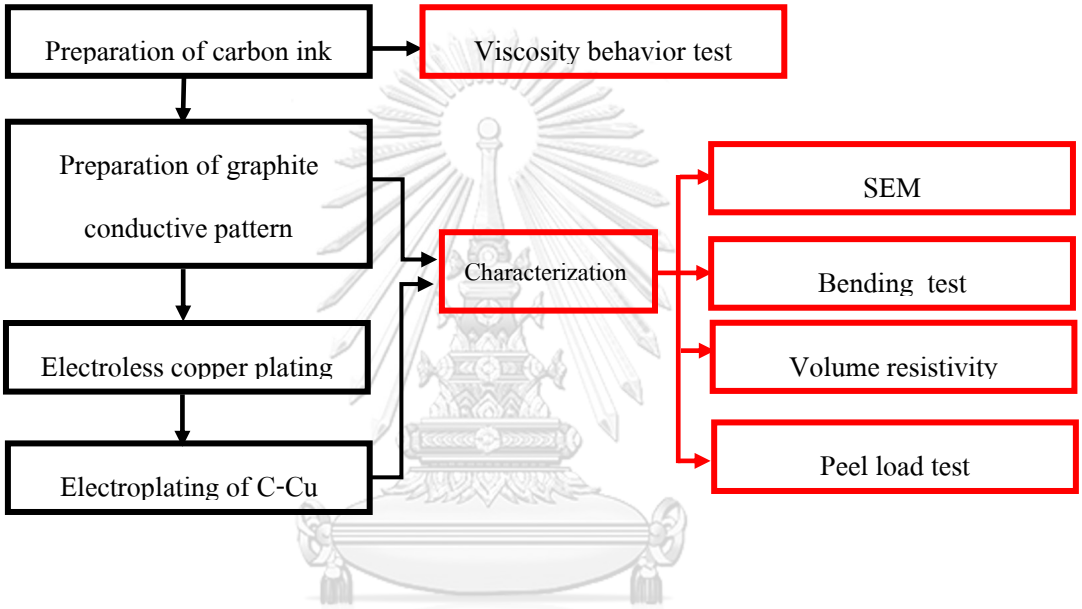


Figure 5 Schematic of experiments



### 3.2 Methodology

3.2.1 Preparation of carbon ink

Graphite powder 2 g combined with 4 g of 5,10, and 15% weight of PVDF. Then, mix them together by using a planetary ball milling machine with four 100 ml zirconia jars, 250 rpm in the speed of revolution, and 500 rpm in the speed of autorotation for 1 hr. Then, using screen printer machine to printing conductive patterns.

3.2.2 Preparation of carbon conductive pattern

Printing was carried out on a screen printer machine using a polyester mesh with 120 threads per cm at a printing speed of 50 mm/s. The carbon patterns printed for conductivity measurement on Polyamide (PI) substrate. Then, the wet printed carbon patterns were processed dried at 60$^{o}$C for 30 min.

3.2.3 Electroless copper plating

The copper solution for electroless plating was prepared by mixing compounds composed of 0.26 g/L $CuSO_4$, 4.1 g/L $KNaC_4H_4C_6 \cdot 4H_2O$,1.8 g/L NaOH and 3.5 mL/L HCOH in deionized water 100 ml. For the solution keep control pH value approximately 11-12 by NaOH and/or $H_2SO_4$. Then, Dip the carbon patterns in the solution bath 40 min.

| $CuSO_4$(g/L*) | HCOH(mL/L) | Ratio of $CuSO_4$:HCOH | |
|---|---|---|---|
| 0.26 | 3.5 | 1 | 1 |
| 0.26 | 7.0 | 1 | 2 |
| 0.52 | 3.5 | 2 | 1 |

*In 100 ml of solution

3.2.4 Electroplating of C-Cu composite

The electrolyte for electroplating was prepared at various $CuSO_4$ concentrations 0.5and 2 M for 300 ml. Then, applied 10mA electrical supply to the process at various operation times are 5, 10, and 15 min.

**3.3 Characterization**

3.3.1 Rheological properties

The Rheological properties of carbon ink were investigated by using a 25 mm diameter parallel plate rheometer (model AR-G2 manufactured by TA instruments). The experiment of rheological properties divided into two parts. First part is the steady state part (time-independent). This part investigates the behavior of conductive inks including shear stress and shear rate. Second

part is the dynamic part (time dependent). The method of measurement includes various functions e.g. frequency sweep mode, strain sweep, and temperature sweep.

3.3.2 Morphologies of conductive patterns

Scanning Electron microscope (SEM) instrument will be used to observe the morphologies of surface and cross-sections of the conductive patterns before and after plating copper on the carbon conductive patterns by electroless and electroplating techniques

3.3.3 Volume resistivity

The volume resistivity of the conductive patterns was measured by using Four-point-probe method for measurements that were carried out to determine the total resistance of the four lines. Each line was carefully scratched off. Then, the new resistivity value was determined. Under the assumption that each line array is a parallel resistor network, this method allowed measuring the average resistance of each cut line.

3.3.4 Bending strength

Bending strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The stresses induced due to the flexural load are a combination of compressive and tensile stresses, this effect is explained in figure 5.[22]

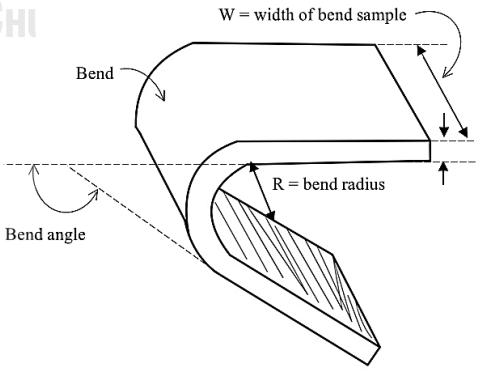


Figure6. Bend test specimen

3.3.5 Peel load

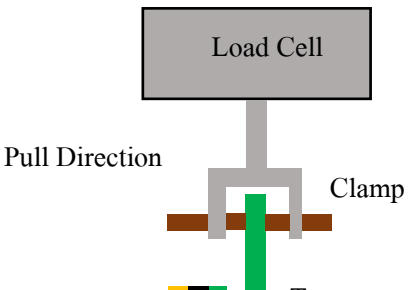

Figure 7. Schematic of the peel test setup

The peel test was performed on an Instron with a 10 N load cell. During the test, one end of the conductive pattern was fixed to the instrument. Scotch tape was strongly pressed on the conductive patterns, ensuring that there were no air bubbles between the tape and the pattern. The free end of the tape was attached to the moveable end of the instrument. The tape was peeled at an angle of 180° from the film at a speed of 100 μm/s.



## Chapter 5

## Results and Discussions

### 5.1 Graphite-Ink viscosity behavior

The viscosity of graphite-ink was investigated by using a parallel plate rheometer. The viscosity at the different shear rates from stead-state flow step test was measured, as shown for all ink in Figure 8. It can be seen all of inks performance of shear-thinning behavior[1, 3, 23], the viscosity of 15%wtPVDF higher than 10%wtPVDF and 5%wtPVDF respectively and viscosity of all of the ink decreasing as shear rate was increased. Such a result would imply that the amount of PVDF binder has an effect on the viscosity of inks because when the PVDF binder was increased interaction between particle-particle was increased. Figure 9 shows the relationship between shear stress and shear rate for all of ink varying %weight of PVDF were 5,10 and 15 it found the trend of inks, the graphite-inks initial to flow after the applied stress exceeds a certain critical value, called is yield stress. The yield stress for the graphite-inks with varying %weight of PVDF were acquired based on a simple Bingham model, when increased %weight of PVDF the yield stress of ink was increased[23].

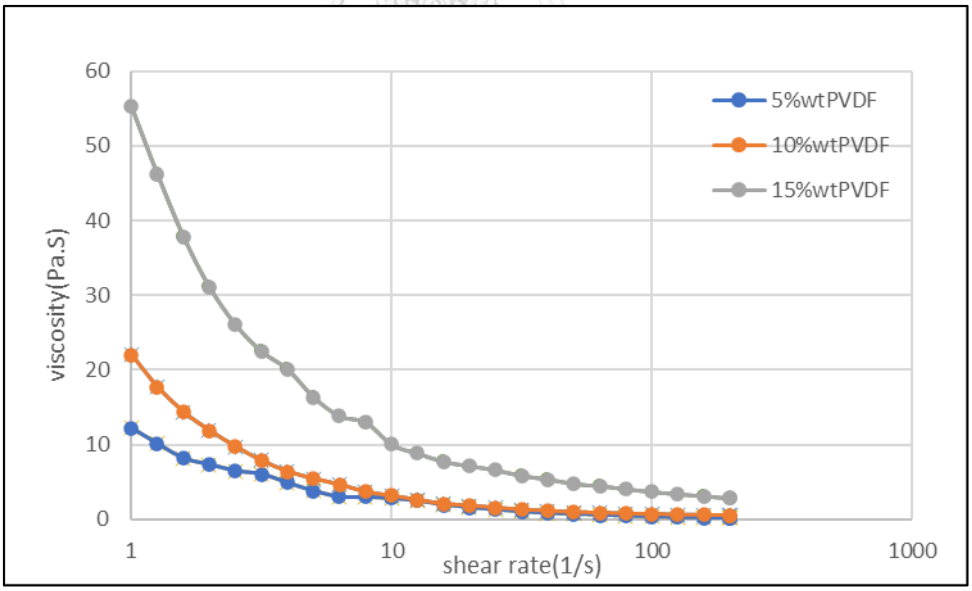


Figure 8. Viscosity as function of shear rate for the ink with varying %weight of PVDF

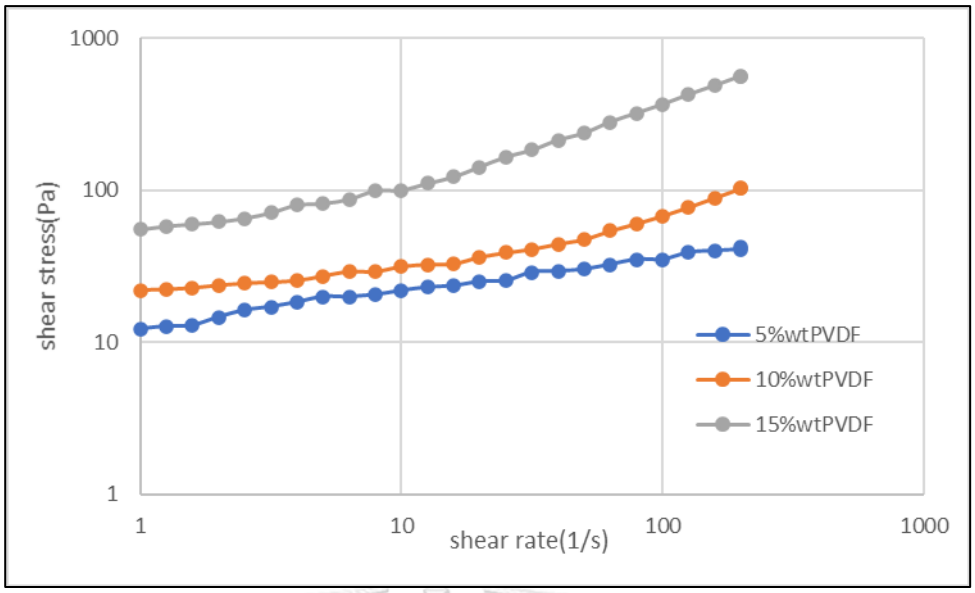


Figure 9. Shear stress as function of shear rate for the ink with varying %weight of PVDF

In the experiment, graphite inks mixed by using a planetary ball milling machine with four 100 ml zirconia jars, 250 rpm in the speed of revolution, and 500 rpm in the speed of autorotation for 1 hr. From figure 3. the particle size of graphite inks after used ball mill to mix them by used Laser particle size distribution analyzer (PSD). such the result as the particle size of all inks was not changed that mean ball mill machine force was unaffected to a particle size of graphite inks, the cause of the particle size did not change due to in the mixing step the composition of inks: Graphite as material, PVDF as a binder, and NMP as solvent, both compounds of PVDF and NMP could adsorb the force from ball mill machine as prevent direct force between the ball and the graphite particle was affected to the effect of particle size of graphite.

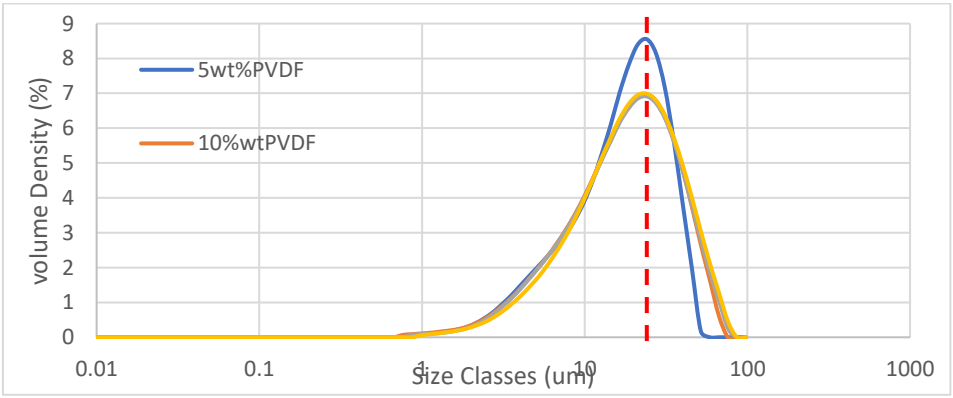


Figure 10. Sizes distribution of graphite after mixed with PVDF by ball mill machine

**5.2 Graphite conductive patterns**

After screen-printing process, the conductive patterns were observed by Scanning Electron microscope (SEM) as shown in Figure3.(a-c). The surface of patterns of 15%PVDF smooth than 10%PVDF and 5%PVDF due to graphite has a shape as a layer flake so when added binder to graphite ink, the graphite layers would be connected with each other and achieving dense microstructure of patterns when added increases amount of binder. The cross-section of patterns as shown in figure Figure3. (D-f) found that at 15% PVDF binder was cover on the surface of graphite layers and fill the gaps between the layers but in this case, the binder could decrease the performance of conductivity patterns[15].

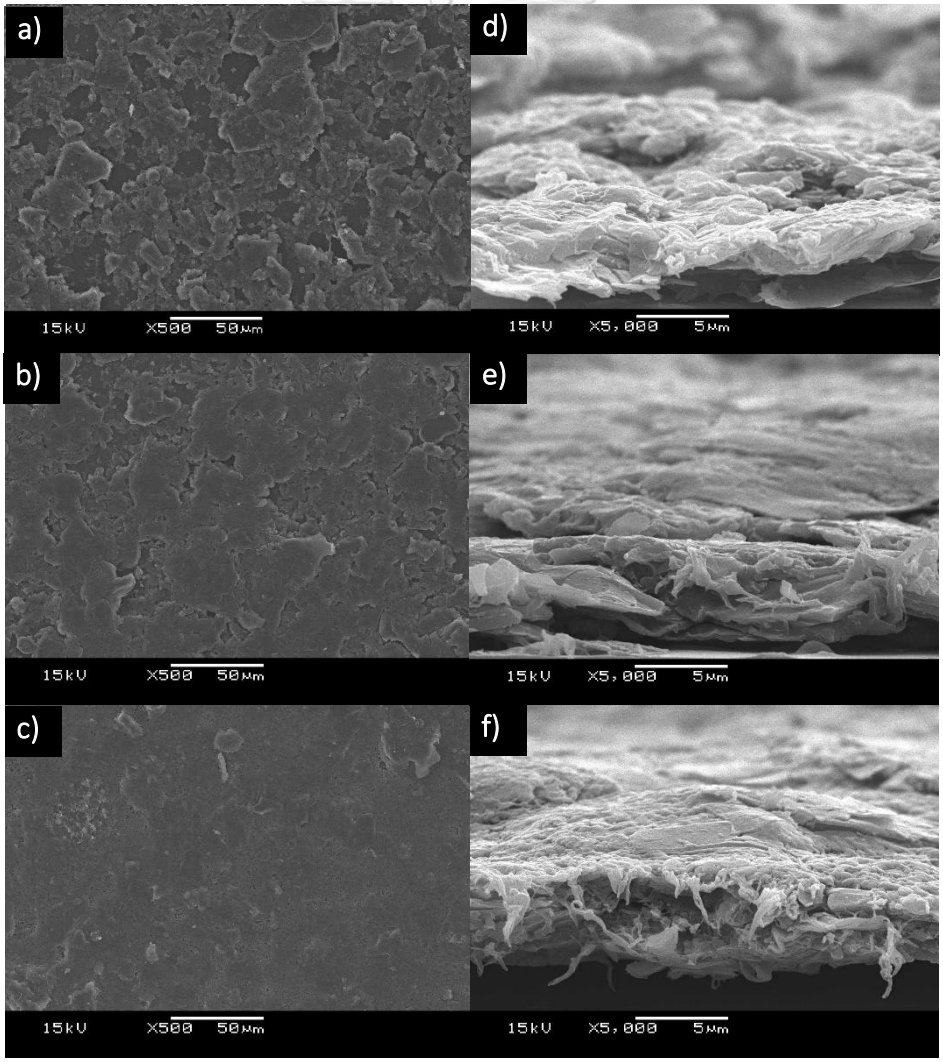


Figure 11. SEM images of graphite-based of conductive patterns at various percentage of binder: a,d) 5%wt PVDF, b,e) 10%wtPVDF, and c,f) 15%wtPVDF

In part of the volume resistivity test of conductive patterns, it was found that the mass ratio between graphite and polyvinylidene fluoride (PVDF); 2: 0.2 or 10% weight PVDF has the lowest volume resistivity as 2.6083 x $10^{-2}$ Ω.cm, compared with the mass ratio between graphite and polyvinylidene fluoride (PVDF); 2 : 0.1 or 5%weight PVDF has a volume resistivity as 0.8693Ω.cm and the mass ratio between graphite and polyvinylidene fluoride (PVDF); 2: 0.3 or 15% PVDF has a volume resistivity as 0.6445Ω.cm, as show in Fiqure12. Which at 5% weight PVDF, the volume resistivity was higher than 10 and 15% weight PVDF because the graphite layers would be connected with each other not well and the gap between the graphite layers was effect to the electron's pathway, due to the current density was largest near the surface of pattern and decrease exponentially with greater depths in the patterns[24] . So that if patterns has a gap around the surface of the pattern. The volume resistivity of the patterns from gap was dominated effected than binder in the pattern. resulting in the volume resistivity was higher. So that when increased binder ratio the graphite structure was dense an effect to higher electrical conductivity. However, at 15%weight PVDF the volume resistivity was increased due to binder instead of helping to connect the graphite layers, it becomes inhibit electron pathway It cannot be moved, resulting in a higher volume resistivity (ref). Also from figure12, the width of conductive patterns was not significant to the volume resistivity of patterns due to the range of patterns width was narrow than to compare with another width. Therefore, the optimal mass ratio between graphite and polyvinylidene fluoride (PVDF) of conductive ink for producing graphite conductive patterns were 2: 0.2 or 10%weight PVDF.

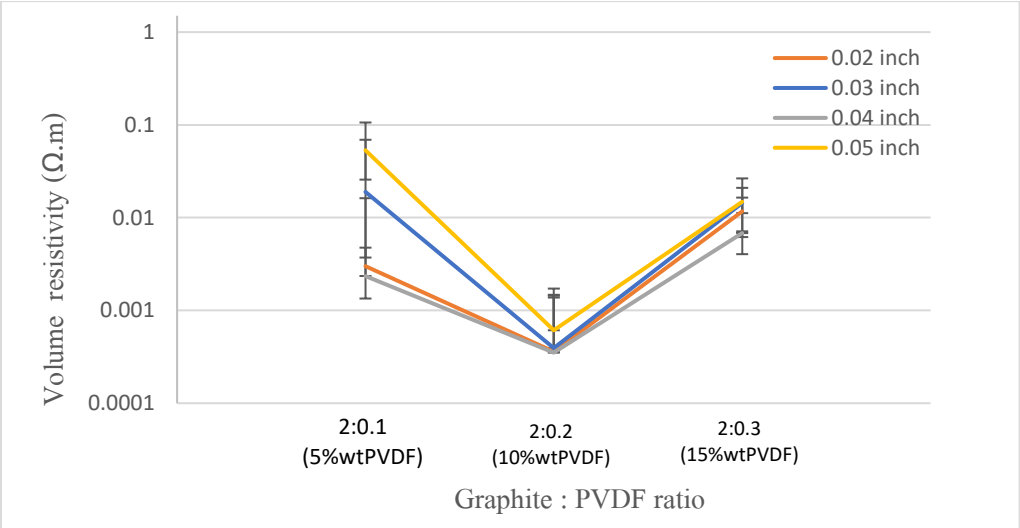


Figure 12. Volume resistivity as a function of Graphite and PVDF ratio

**5.3 Electroless plating**

After optimizing the mass ratio between graphite and polyvinylidene fluoride (PVDF) of conductive ink for printed conductive patterns, the next step of the experiment was to coat the copper on the surface of graphite conductive patterns to increase the electrical conductivity. Which in this step has two parts, the first part was copper coated on the surface of graphite patterns by electroless plating technique. In this step, the concentration ratios between copper (II)sulfate($CuSO_4$) and formaldehyde(HCHO) in the solution for electroless plating were varied, $CuSO_4$: Formaldehyde; 1:1, 2:1 and 1:2 respectively and the reaction of this technique followed by equation: $Cu^{2+} + 2HCHO + 4OH^- \longrightarrow Cu0 + 2HCOO^- + 2H_2O + H_2$. From figure 6. copper particles were observed on the graphite surface. As ratio $CuSO_4$: Formaldehyde; 1:2, dispersion of copper was better than ratio $CuSO_4$: Formaldehyde; 1:1 and 2:1. If the concentration of reducing agent increase, the electrons in the solution released from reducing agent also increase and the reducing agent power of the bath increase. Therefore, the electroless rate of the process was increase. However, if the reducing agent is present in excess the stability of the bath deteriorates and it even decomposes, so that the reduced neutral metal atoms decreases, which makes the electroless rate decrease [25]. From EDS as figure 13. could be confirmed the copper particle has a dispersion very well in ratio $CuSO_4$: Formaldehyde; 1:2

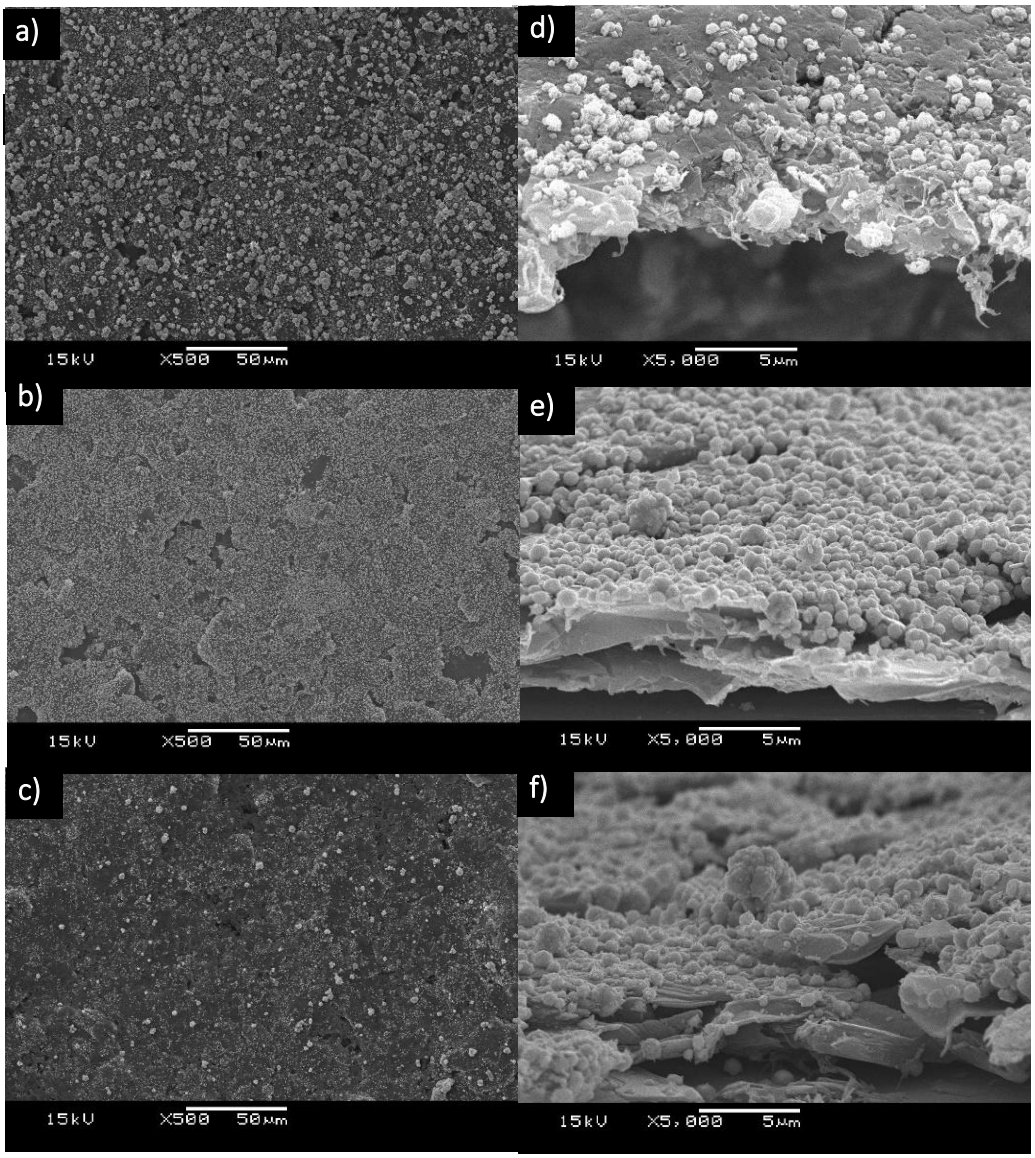


Figure 13. SEM images of conductive patterns after copper coated by electroless plating at various ratio between Copper (II)sulfate and Formaldehyde in solution for electroless plating; a,d) 1:1, b,e) 1:2, and c,f) 2:1

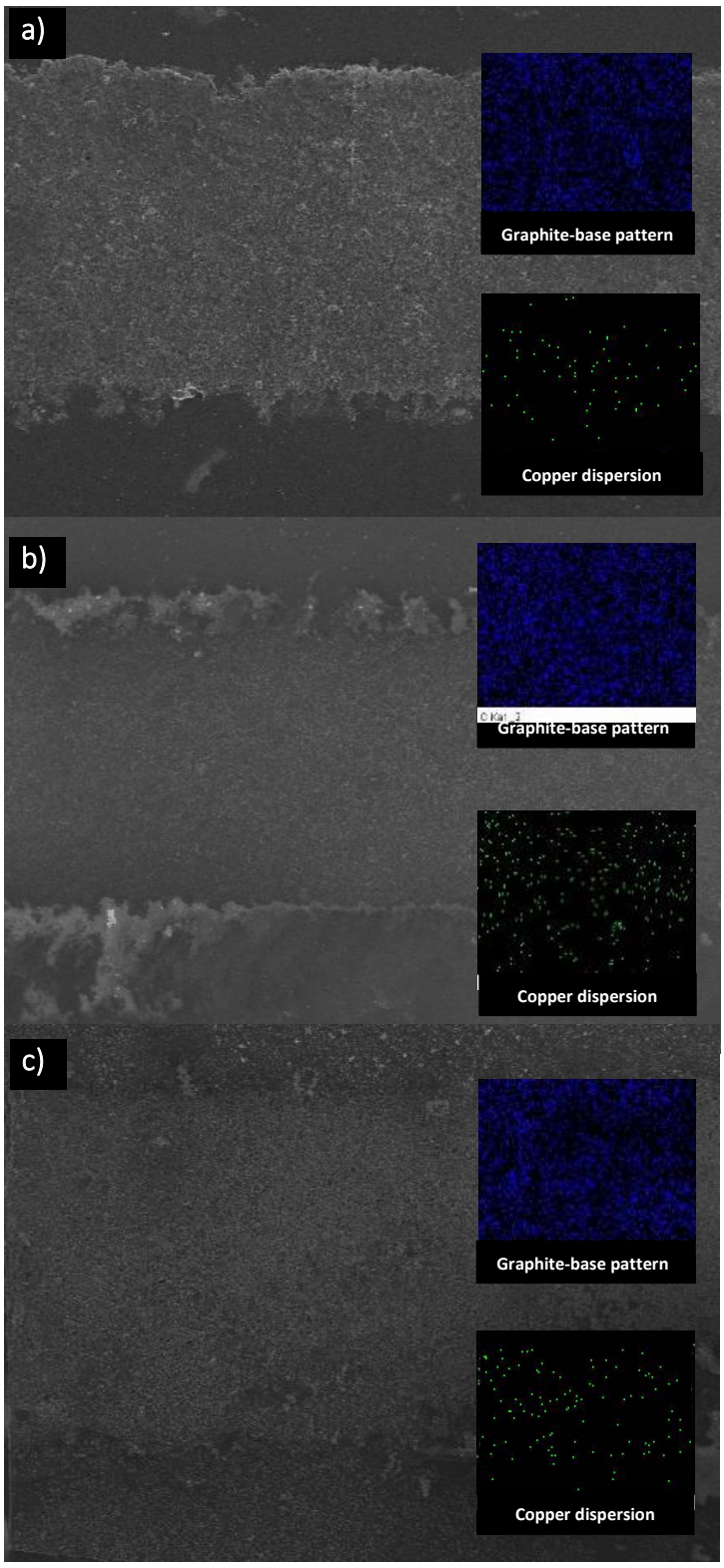


Figure 14. EDS images of conductive patterns after copper coated by electroless plating at various ratio between Copper (II)sulfate and Formaldehyde in solution for electroless plating; a) 1:1, b) 1:2, and c) 2:1

**5.4 Electroplating**

Electroplating was the last step for the experiment, in this step electroplating was performed by various 0.5 and 1 M copper (II)sulfate as an electrolyte and applying 10mA constant with vary electroplating duration 5,10, and 15 min. The effects of electroplating concentration of electrolytes for electroplating technique The effects of electroplating concentration of electrolytes for electroplating technique, was found at 0.5 M copper (II)sulfate as an electrolyte the voltage need increase to 8.5 V for keep the 10 mA was constant. While 1 M copper (II)sulfate as an electrolyte was to apply voltage 5.5 V for keep the 10 mA was constant. For suitable condition of conductive patterns was used 1 M copper (II)sulfate as an electrolyte was good condition because in 0.5 M electrolyte the voltage was 8.5 V to generate heat temperature to patterns as effect to the patterns could be melt From the figure 8. the effects of electroplating duration for electroplating technique could be observed, when increasing the duration time of the process the thickness of copper must be larger and the result to the volume resistivity of conductive patterns was lowered as show in table 2.



| **Duration time (min)** | **Average thickness of copper(μm±SE)** | **Volume resistivity (μΩ.m±SE)** |
|---|---|---|
| **5** | 4.923( ±0.0580) | 727.624( ±2.1280) |
| **10** | 7.189( ±0.0789 ) | 10.800( ±5.7029 ) |
| **15** | 7.884( ±0.0479) | 0.208( ±0.0527) |

Table 2. Relative of electroplating duration time with average thickness of copper and Volume resistivity

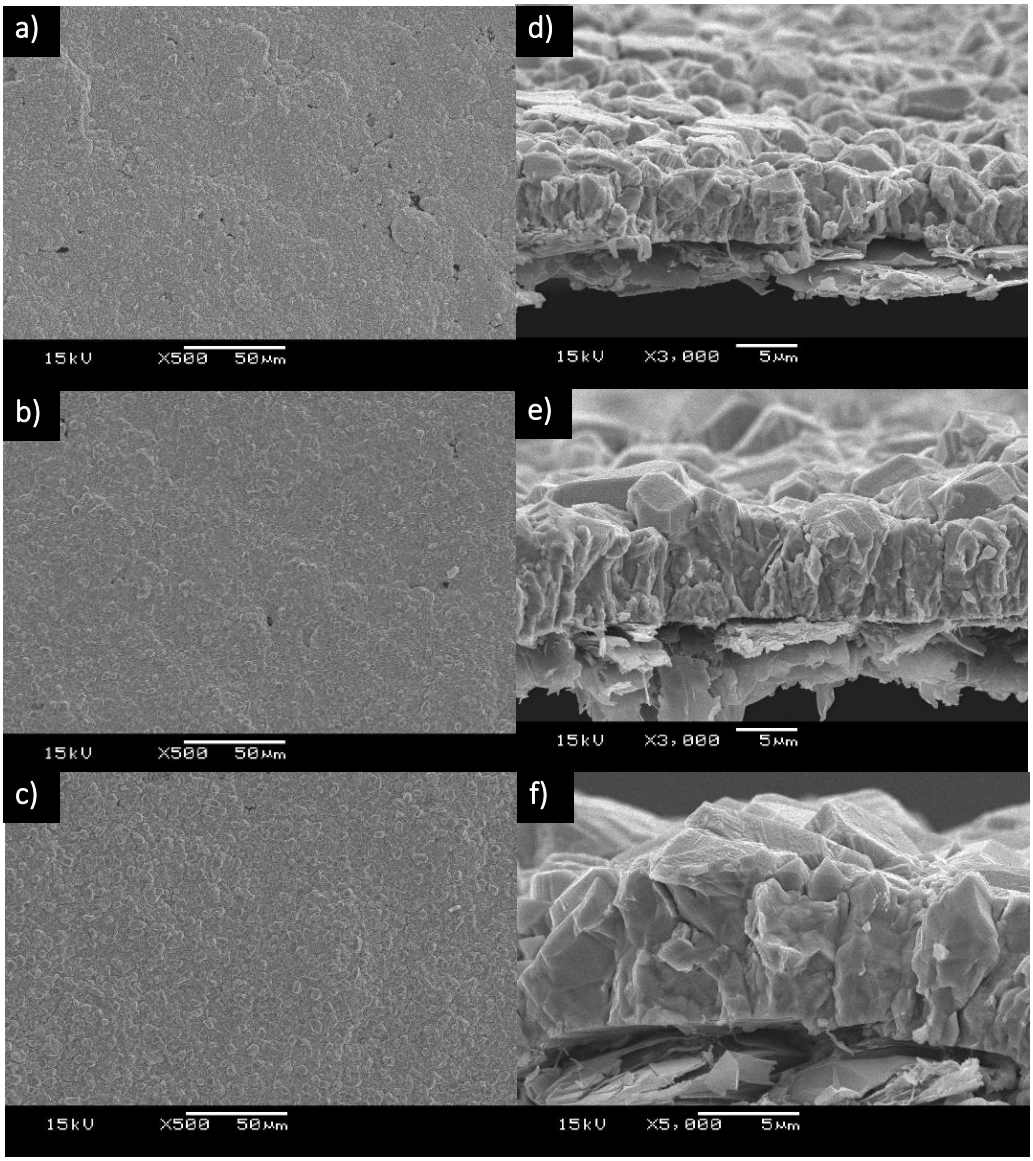


Figure 15. SEM images of conductive patterns at various duration for electroplating technique: a,d) 5 min, b,e) 10 min, and c,f) 15min

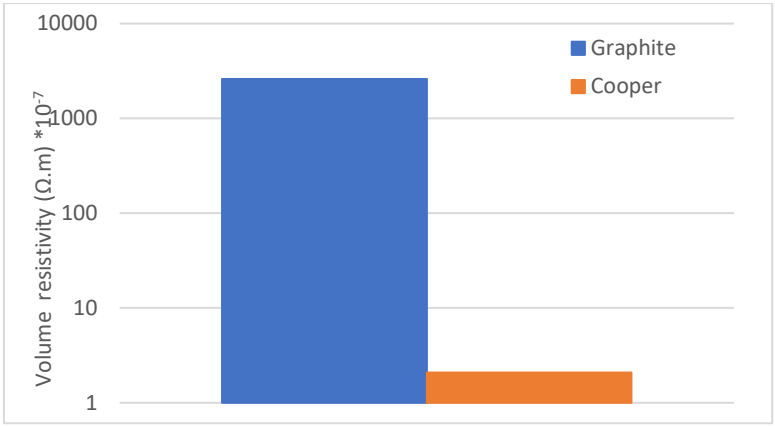


Figure 16. Volume resistivities of graphite patterns: copper coated and without copper coated

**5.5 Mechanical properties of patterns**

The mechanical integrity of conductive patterns was tested with peel and bending. The peel test was performed on an Instron with a 10 N load cell. During the test, one end of the patterns was fixed to the instrument. Scotch tape was firmly pressed on the conductive patterns, ensuring that there were no air bubbles between the tape and conductive patterns. The free end of the tape was attached to the moveable end of the instrument. The tape was peeled at an angle of 180° from the film at a speed of 100 μm/s. The load cell measured the force required to peel the tape.

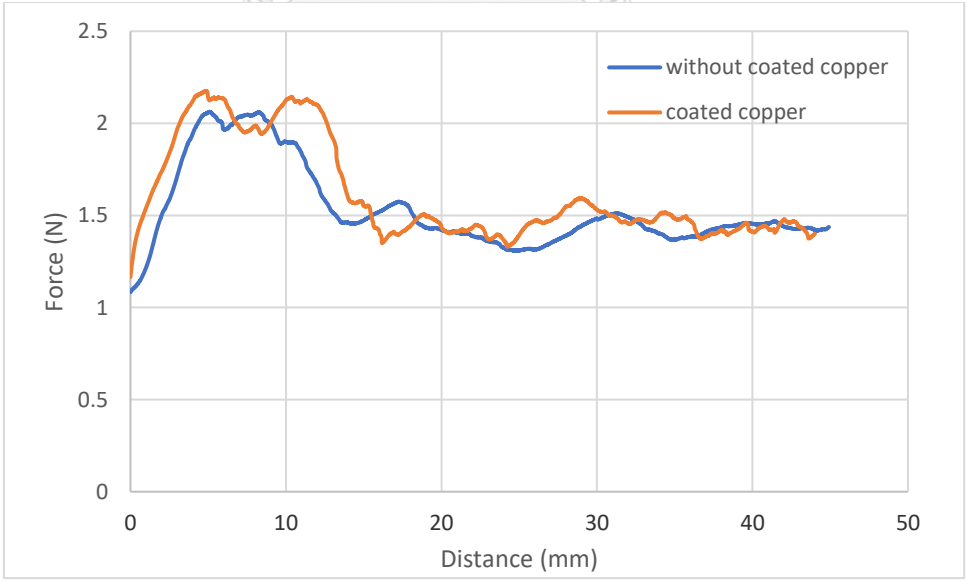


Figure 17. Typical peel force recorded by the load cell during test of conductive patterns: copper coated and without copper coated

In a conventional tape test, an adhesive tape is pressed on the film and removed with a constant motion. The amount of material removed from the substrate provides qualitative information about the adhesion strength of the substrate as shown in Fiqure10. compared with graphite conductive patterns and graphite conductive coated copper, the result showed adhesion strength between conductive patterns and substrate were not changed when coated copper on conductive patterns. The bending test was applied 4-point probe to measured conductivity of patterns while the patterns was bended. From the fiqure18. shown volume resistivity as function of conductive patterns were bended. The bending test was applied 4-point probe to measure the conductivity of patterns while the patterns were bent. From the fiqure11. shown volume resistivity as a function of conductive patterns were bent, as the result shows conductive patterns coated copper.

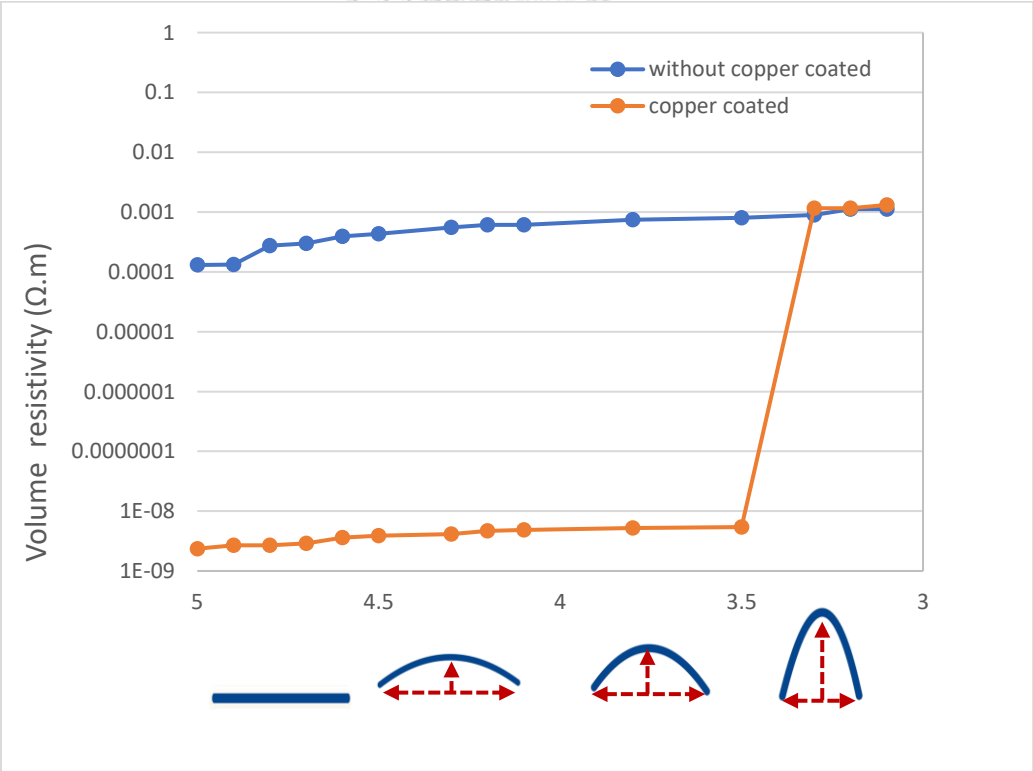


Figure 18. Typical peel force recorded by the load cell during test of conductive patterns: copper coated and without copper coated

# Chapter 6

# Conclusion

## 6.1 Conclusion

The screen printing graphite-based conductive patterns and copper coated on the patterns by electroless plating and electroplating techniques to enhance performance electrical conductivity of conductive patterns. According to studies, the optimal mass ratio between graphite and polyvinylidene fluoride (PVDF) of conductive ink for producing graphite conductive patterns were 2: 0.2 or 10%weight PVDF gives the volume resistivity as 2.6083 x $10^{-2}$ Ω.cm. In part for increase the conductivity. For increase conductivity of patterns we used two techniques for coating copper on the conductive patterns; first technique, electroless plating is use for coating copper by reaction between copper (II)sulfate($CuSO_4$) and formaldehyde(HCOH) in this techniques small particles of copper are attached to the carbon surface at ratio of copper (II)sulfate($CuSO_4$) and formaldehyde(HCOH) as 1:2 can give dispersion of small particles very well. Second technique, electroplating is use for dense the structure of copper Second technique, electroplating is used for dense the structure of copper in this technique have a many factor as affected to conductive patterns, in this work we focus on electroplating duration and concentration of electrolytes for electroplating technique as from study when duration of electroplating increase the thickness of copper on graphite base is thicken and effect to electrical conductivity of patterns is increasing. However, the mechanical properties of patterns such as bending strength are decreasing because coppers are brittleness. In part of electrical performance after coated copper volume resistivity of the patterns are 0.8906 μΩ-m. In the future, graphite-copper conductive patterns can be developed and apply to the circuit board manufacturing industry.

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# VITA

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# APPENDIX

A1 Volume resistivity

The volume resistivity of copper film pattern with μΩ.m is calculated with the electrical resistivity that resistance of a conductor with shape of the rectangular area is A and length is L.

$$\rho = RAL \quad \text{(A.1)}$$

When is $\rho$ the volume resistivity (μΩ.m)

A is area (width x thickness) (m2)

L is the length of the pattern (m)

From Ohms law as equation

$$R = VI \quad \text{(A.2)}$$

When R is the resistance (Ω)

I is the current (A)

V is the voltage (V)



From copper film pattern provide four conductive line in sample. Therefore the use 4-point probe for measure resistance of copper film pattern. The measurement will divide four time including 4-line, 3-line, 2-line and 1-line respectively that formulate overall resistance four equations.

$$Rn = RE + rn \quad \text{(A.3)}$$

When $Rn$ is overall resistance with $n$ lines (Ω)

$RE$ is external resistance (Ω)

$r$ is internal resistance (Ω)

From 4-line:

$$R_4 = RE + r_4 \quad \text{(A.4)}$$

From 3-line:

$$R_3 = RE + r_3 \quad \text{(A.5)}$$

From 2-line:

$$R_2 = RE + r_2 \quad \text{(A.6)}$$

From 1-line:

$$R_1 = RE + r \quad \text{(A.7)}$$