

เส้นลายนําไฟฟ้าบนแผ่นพอลิเมอร์แบบยืดหยุ่นซึ่งสร้างด้วยวิธีการพิมพ์อิงค์เจ็ท  
ของสารละลายเกลือของโลหะ

นางสาวกมลรัตน์ ฝอยทอง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต  
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี  
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย  
ปีการศึกษา 2554  
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)  
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CONDUCTIVE LINES ON FLEXIBLE POLYMER SUBSTRATES FABRICATED BY  
INKJET PRINTING OF METAL SALTS SOLUTION

Miss Kamolrat Foithong

A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2011

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Thesis Title	CONDUCTIVE LINES ON FLEXIBLE POLYMER SUBSTRATES FABRICATED BY INKJET PRINTING OF METAL SALTS SOLUTION
By	Miss Kamolrat Foithong
Field of Study	Chemical Engineering
Thesis Advisor	Assistant Professor Soorathep Kheawhom, Ph.D.

---

Accepted by the Faculty of Engineering, Chulalongkorn University in  
Partial Fulfillment of the Requirements for the Master's Degree

..... Dean of the Faculty of Engineering  
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

..... Chairman  
(Professor Piyasan Prasertdam, Dr.Ing.)

..... Thesis Advisor  
(Assistant Professor Soorathep Kheawhom, Ph.D.)

..... Examiner  
(Assistant Professor Anongnat Somwangthanoj, Ph.D.)

..... External Examiner  
(Assistant Professor Prakorn Ramakul, Ph.D.)

กมลรัตน์ ฝอยทอง : เส้นลายนำไฟฟ้าบนแผ่นพอลิเมอร์แบบยืดหยุ่นซึ่งสร้างด้วยวิธีการพิมพ์อิงค์เจ็ทของสารละลายเกลือของโลหะ. (CONDUCTIVE LINES ON FLEXIBLE POLYMER SUBSTRATES FABRICATED BY INKJET PRINTING OF METAL SALTS SOLUTION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร.สุรเทพ เขียวหอม, 66 หน้า.

ในปัจจุบันอิเล็กทรอนิกส์โดยการพิมพ์ได้รับความสนใจอย่างมากเนื่องจากเป็นกระบวนการที่ง่ายในการทำเส้นลายนำไฟฟ้าบนแผ่นรองรับที่หลากหลาย ในงานวิจัยนี้จึงเลือกใช้สารละลายเกลือของโลหะเป็นหมึกนำไฟฟ้าเพราะสามารถหลีกเลี่ยงปัญหาการเกิดรูพรุนและความไม่สม่ำเสมอของพื้นผิวเส้นลายนำไฟฟ้าได้ นอกจากนี้ยังศึกษาถึงวิธีการทำเส้นลายนำไฟฟ้าของโลหะซึ่งประกอบไปด้วยการพิมพ์อิงค์เจ็ทแบบทำให้เกิดปฏิกิริยา การอบพร้อมการเกิดปฏิกิริยาและการชุบโลหะทองแดงแบบไม่ใช้ไฟฟ้า

ในกระบวนการพิมพ์แบบทำให้เกิดปฏิกิริยาเส้นลายนำของโลหะเงินถูกสังเคราะห์โดยการพิมพ์ตัวรีดิวซ์และสารละลายซิลเวอร์ในเทรตตามลำดับ โดยสภาพด้านทานไฟฟ้าต่ำสุดของเงินได้จากการพิมพ์สารละลายซิลเวอร์ในเทรตความเข้มข้น 5 ไมลาร์ จำนวน 15 รอบการพิมพ์มีค่าเท่ากับ  $4.62 \times 10^{-4}$  โอห์ม-เซนติเมตร หรืออีกวิธีหนึ่งในการเตรียมเส้นลายนำไฟฟ้าที่ต่อเนื่องและเรียบจากกระบวนการอบพร้อมการเกิดปฏิกิริยาของไอของกรดฟอร์มิคและไอของเอทิลีนไกลคอล ค่าสภาพด้านทานไฟฟ้าของเส้นลายนำเงินที่ได้จากการอบในไอของกรดฟอร์มิคที่อุณหภูมิ 150 องศาเซลเซียส เวลา 120 นาที มีค่าเท่ากับ  $1.86 \times 10^{-4}$  โอห์ม-เซนติเมตร และค่าสภาพด้านทานไฟฟ้าของเส้นลายนำเงินที่ได้จากการอบในไอของเอทิลีนไกลคอล ที่อุณหภูมิ 250 องศาเซลเซียส เวลา 30 นาที มีค่าเท่ากับ  $1.20 \times 10^{-4}$  โอห์ม-เซนติเมตร เมื่อทำการเปรียบเทียบกับกระบวนการพิมพ์แบบทำให้เกิดปฏิกิริยาพบว่ากระบวนการอบพร้อมการเกิดปฏิกิริยาจะให้เส้นลายนำที่ต่อเนื่องและเรียบมากกว่าซึ่งเป็นผลให้สภาพความต้านทานไฟฟ้ามีค่าต่ำกว่า นอกจากนี้เส้นลายนำของทองแดงสามารถเตรียมจากวิธีการชุบโลหะทองแดงแบบไม่ใช้ไฟฟ้าบนเส้นลายนำเงินที่อุณหภูมิห้อง โดยค่าความต้านทานไฟฟ้าของเส้นลายนำทองแดงที่ผ่านกระบวนการชุบนาน 15 นาที มีค่าเท่ากับ  $1.92 \times 10^{-5}$  โอห์ม-เซนติเมตร

ภาควิชา.....วิศวกรรมเคมี..... ลายมือชื่อนิสิต.....  
 สาขาวิชา.....วิศวกรรมเคมี..... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก.....  
 ปีการศึกษา.....2554.....

## 5370394421 : MAJOR CHEMICAL ENGINEERING

KEYWORDS : INKJET PRINTING / METAL SALTS SOLUTION / CONDUCTIVE LINE /  
POLYMER SUBSTRATES

KAMOLRAT FOITHONG : CONDUCTIVE LINES ON FLEXIBLE POLYMER  
SUBSTRATES FABRICATED BY INKJET PRINTING OF METAL SALTS  
SOLUTION. ADVISOR : ASST. PROF. SOORATHEP KHEAWHOM, Ph.D., 66  
pp.

Recently, printed electronics has attracted lots of attentions because it is a simple process of making a desired conductive pattern on various substrates. In this research, the metal salt was selected as conductive ink because problems of porosity and non-uniform surface on conductive printed pattern can be avoided. The methods to fabricate metal conductive patterns including reactive inkjet printing, reactive sintering and electroless copper plating were investigated.

In reactive inkjet printing, the silver line was synthesized by sequentially printing reducing agent and silver nitrate solution. The lowest resistivity of silver line obtained by using 5 M of silver nitrate solution and 15 printing cycles was  $4.62 \times 10^{-4} \Omega \text{ cm}$ . Alternatively, continuous and smooth patterns of silver lines were fabricated by the reactive sintering process of formic acid vapor and ethylene glycol vapor. The resistivity of the silver line obtained by formic acid vapor reduction at  $150^\circ\text{C}$  for 120 min was  $1.86 \times 10^{-4} \Omega \text{ cm}$ . The resistivity of the silver line obtained by ethylene glycol vapor reduction at  $250^\circ\text{C}$  for 30 min was  $1.20 \times 10^{-4} \Omega \text{ cm}$ . As compared to reactive inkjet printing, the reactive sintering process gives more smooth and continuous pattern resulting in lower resistivity. Additionally, the copper line was prepared by electroless copper plating on silver seed layer at room temperature. The resistivity of copper line obtained by electroless plating for 15 min was  $1.92 \times 10^{-5} \Omega \text{ cm}$ .

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

Field of Study : ..Chemical Engineering..... Advisor's Signature .....

Academic Year : ..2011.....

## ACKNOWLEDGEMENTS

The author wishes to express her sincere gratitude and appreciation to her adviser, Assistant Professor Soorathep Kheawhom for his valuable suggestion, and useful discussion throughout this research. The author would also be grateful to Professor Piyasan Prasertdam as the chairman and Assistant Professor Anongnat Somwangthanaroj and Assistant Professor Sirirat Wacharawichanant as the members of thesis committee.

Moreover, financial and analytical equipment support for this thesis study from Mektec Manufacturing Corporation (Thailand) Ltd. was grateful acknowledged.

Eventually, special thank all members of Life Cycle Engineering Research Laboratory (LCE) in Chulalongkorn University for their assistance along the course of the study.

Finally, the author would like to thank her parents (Mr. Thummasak Foithong and Ms. Siriporn Foithong) for their eternal care, endless supports and understandings in my life throughout the course of education

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# CHAPTER I

## INTRODUCTION

### 1.1 BACKGROUND AND MOTIVATION

In the electronics industry, the fabrication of conductive lines is vital. Conventional manufacturing processes for electronic devices use thin-film deposition and lithography techniques to fabricate micro-patterns. However, thin-film deposition techniques, which include physical and chemical vapor deposition, are expensive, very complicated, and inefficient. For these reason, the development of convenient, fast processing, and low-temperature processing techniques to fabricate conductive lines has attracted a lot of attention in recent years. Inkjet printing technology is considered as a promising alternative to conventional processes for the reason that it has many advantages, such as low cost, eco-friendship, and simple process, over the common patterning process [1].

Inkjet printing requires low viscosity liquid phase materials that were used as inks in inkjet printing process. Inks were printed through a nozzle and form to conductive line after heat treatment process. There are three kinds of conductive inks have been adopted for this technique. The first is to use suspensions of metallic nanoparticles, which have sintering temperatures to make metal continuous lines and the temperature due to the small size of metal particles. The second way is to use solutions of metallo–organic precursors, which can be converted to metal at low temperatures. The third way is to use solutions of metal ion compound, such as silver nitrate solution, copper sulfate solution which can be converted to metal at high temperatures. Metals nanoparticles based inks are the most commonly used materials

such as silver and copper, because of their low resistivity and reasonable prices. There are several methods proposed for preparing metal nanoparticle suspensions, including chemical and physical methods. In synthesis of silver nanoparticles by the chemical reduction method, stabilizing agents such as poly(N-vinyl-2-pyrrolidone), thiosalicylic acid, 1-Nonanethiol etc., are usually needed to be added as the protecting agent [2, 3]. However, the formation of pores that caused by the decomposition of the protecting agent during thermal treatment can decrease the conductivity of the printed pattern. Additionally, the printable inks containing nanoparticles is to overcome the strong agglomeration of the particles in dispersion medium and causes the system to change to the one with fewer but larger particles that effect on the property of conductive pattern. The lager particles would be normally caused of nozzle clogging [4]. The particles of printed patterns from nano-particle suspension are accumulated at the edge and depleted at the center, showing a so-called "coffee ring effect". This coffee ring effect make non-uniform surface structure of printed lines patterns that cause to also decrease of conductivity value. The use of organo-metal compounds or metal precursor requires additional heat-treatment for reduction to metallic species, and the conductive films fabricated by this method also contains relatively large amount of organic residues which may adversely affect the conductivity [1, 5].

To solve these problems, metal salts solution are used as conductive ink to avoided formation of porosity and non-uniform surface structure on printed lines patterns. In this study, inkjet printing of metal salts solution is fabricated metal conductive patterns on polymer flexible substrate and combines with various methods: reactive inkjet printing, reactive sintering and electroless copper plating.



## 1.2 OBJECTIVES OF THE RESEARCH

- 1.2.1. To investigate a method to fabricate silver conductive lines on flexible polymer substrates by silver salt inkjet printing combined with reactive inkjet printing and reactive sintering.
- 1.2.2. To investigate a method to fabricate copper conductive lines on flexible polymer substrates by metal salts solution inkjet printing combined with reactive sintering and electroless copper plating.

## 1.3 SCOPE OF THE RESEARCH

- 1.3.1 Commercially inkjet printer (Epson Stylus Photo T60) is used in metal salts solution inkjet printing process at room temperature.
- 1.3.2 The desire pattern to printed conductive line is two-point probe pattern.
- 1.3.3 Silver nitrate, copper-amine complex and Palladium ion solutions are used as metal salt solutions in this study.
- 1.3.4 Flexible substrates are used in this experiment as shown below:
  - 1.3.4.1 Polyethylene terephthalate (PET) substrate is coated with resin (75  $\mu\text{m}$  thickness)
  - 1.3.4.2 Polyimide (PI) substrate (25  $\mu\text{m}$  thickness) is modified the surface property by oxygen plasma treatment (Plasma cleaning system, SAMCO, PC-1100) with working power and oxygen flow rate at 200 watt and 40 sccm, respectively.
- 1.3.5 In reactive inkjet printing, silver nitrate solution and 1 M of L-ascorbic acid are used as a conductive ink and a reducing agent, respectively. PET film is used as polymer substrate in this experiment. In addition, the influence of

parameters on silver conductive printed lines patterns are investigated from the lists below:

1.3.5.1 Effect of  $\text{AgNO}_3$  concentration in range of 5 to 10 M

1.3.5.2 Effect of printing cycle of L-ascorbic acid and silver nitrate solution in range of 5 to 15 cycles

1.3.6 In metal salts inkjet printing with reactive sintering process, silver and copper salt solutions are used in this process. Then, they are multilayer printed on polymer substrate. The printed patterns are sintered with various methods. Additionally, the influence of parameters on conductive printed lines pattern are investigated from the list below:

1.3.6.1 Reactive sintering under vapor of formic acid at  $150^\circ\text{C}$ : to study the effect of sintering time in range of 30 to 120 min, respectively.

1.3.6.2 Ethylene glycol vapor reduction at  $250^\circ\text{C}$ : to study the effect of sintering time in range of 15 to 60 min, respectively.

1.3.6.3 Sintering under  $\text{H}_2$  atmosphere at  $200^\circ\text{C}$  for 1 h.

1.3.7 In electroless copper plating process, Ag printed lines and palladium printed lines are used as seed layers. The influences of plating times on deposited copper plating in range of 15 to 60 min are investigated.

#### 1.4 EXPECTED BENEFITS

Available techniques to fabricate metal conductive lines patterns from inkjet printing of metal salts solution.

## CHAPTER II

### THEORY

#### 2.1 PRINTED ELECTRONICS

Printed electronics is a set of printing methods used to create electrical devices on various substrates. Printing typically uses common printing equipment or other low-cost equipment suitable for defining patterns on material, such as screen printing, flexography, gravure, offset lithography and inkjet. Electrically functional electronic or optical inks are deposited on the substrate, creating active or passive devices, such as thin film transistors or resistors. Printed electronics is expected to facilitate widespread, very low-cost, low-performance electronics for applications such as flexible displays, smart labels, decorative and animated posters, and active clothing that do not require high performance.

The term printed electronics is related to organic electronics or plastic electronics, in which one or more inks are composed of carbon-based compounds. These other terms refer to the ink material, which can be deposited by solution-based, vacuum-based or some other method. Printed electronics, in contrast, specifies the process, and can utilize any solution-based material, including organic semiconductors, inorganic semiconductors, metallic conductors, nanoparticles, nanotubes, etc.

For the preparation of printed electronics nearly all industrial printing methods are employed. Similar to conventional printing, printed electronics applies ink layers one a top another, so that the coherent development of printing methods and ink materials is the field's essential tasks.

The most important benefit of printing is low-cost volume fabrication. The lower cost enables use in more applications. An example is RFID-systems, which enable contactless identification in trade and transport. In some domains, such as light-emitting diodes printing does not impact performance. Printing on flexible substrates allows electronics to be placed on curved surfaces, for example, putting solar cells on vehicle roofs. More typically, conventional semiconductors justify their much higher costs by providing much higher performance.

## 2.2 INKJET PRINTING TECHNOLOGY

Inkjet technology has become a household word through its presence on the consumer desktop as a low cost, reliable, relatively quick and convenient method of printing digital files. Although inkjet technology has been around since the 1950s in speciality printing, the impact of the technology in a wide range of industrial applications is only now becoming clear.

In theory, inkjet technology is simple - a printhead ejects a pattern of tiny drops of ink onto a substrate without actually touching it. Dots using different coloured inks are combined together to create photo-quality images.

In practice however, successful implementation of the technology is very complex. The dots that are ejected are smaller than the diameter of a human hair (70 microns), and they need to be positioned very precisely to achieve resolutions as fine as 1440x1440 dots per inch (dpi). This precision requires multi-disciplinary skills; a combination of careful design, implementation and operation across physics, fluid mechanics, chemistry and engineering.

Inkjet technology is increasingly viewed as more than just a printing or marking technique. It can also be used to apply coatings, to deposit precise amounts of materials, and even to build micro- or macro-structures. The benefits of inkjet technology

are significant and include the reduction of manufacturing costs, provision of higher quality output, conversion of processes from analogue to digital, reduction in inventory, printing onto very large, very small, fragile or non-flat substrates, reduction of waste, mass customisation, faster prototyping and the implementation of just-in-time manufacture.

The introduction of industrial inkjet technology into manufacturing environments has the potential to make a revolutionary step-change to existing capabilities with huge commercial benefits

### **2.2.1 Industrial inkjet printing**

Industrial inkjet printing essentially means using inkjet technology as a printing or deposition process in manufacturing or on production lines - a similar principle to the inkjet printer on your desktop but very different in scale. While all inkjet technologies can fundamentally be described as the digitally controlled ejection of drops of fluid from a printhead onto a substrate, this is accomplished in a variety of ways

Industrial inkjet printing systems, and the industrial inkjet printheads they are based on, are broadly classified as either continuous (CIJ) or drop on demand (DOD), with variants within each classification. As the name implies, continuous inkjet technology ejects drops continuously from the printhead. These drops are then either directed to the substrate as printing drops or to a collector for recirculation and re-use. Drop on demand technology ejects drops from the printhead only when required.

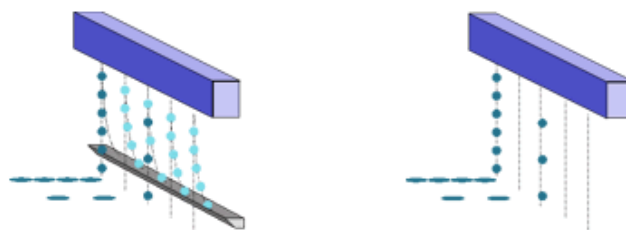


Figure 2.1 Types of industrial inkjet printheads: a) continuous inkjet (CIJ) and b) Drop on demand inkjet (DOD)

### 2.2.2 Drop on demand inkjet printing

Drop on demand (DOD) is a broad classification of inkjet printing technology where drops are ejected from the printhead only when required. In general, the drops are formed by the creation of a pressure pulse within the printhead. The particular method used to generate this pressure pulse creates the primary subcategories within DOD, namely thermal and piezo.

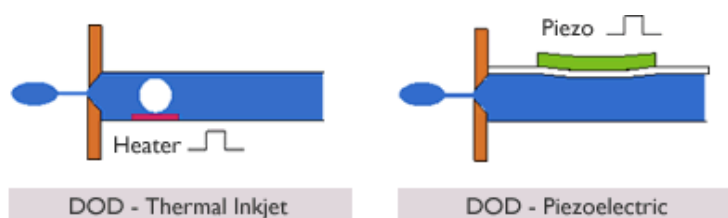


Figure 2.2 DOD thermal inkjet and DOD piezoelectric inkjet

Thermal inkjet technology (TIJ) is most used in consumer desktop printers but is also making some inroads into industrial inkjet applications. In this technology, drops are formed by rapidly heating a resistive element in a small chamber containing the ink. The temperature of the resistive element rises to 350-400°C, causing a thin film of ink above the heater to vaporise into a rapidly expanding bubble, causing a pressure pulse that forces a drop of ink through the nozzle. Ejection of the drop leaves a void in the

chamber, which is then filled by replacement fluid in preparation for creation of the next drop.

The advantages of thermal inkjet technology include the potential for very small drop sizes and high nozzle density. High nozzle density leads to compact devices, lower printhead costs and the potential for high native print resolution. The disadvantages of the technology are primarily related to limitations of the fluids which can be used. Not only does the fluid have to contain a material that can be vaporised (usually meaning an aqueous or part-aqueous solution) but must withstand the effects of ultra high temperatures. With a poorly designed fluid, these high temperatures can cause a hard coating to form on the resistive element (coking) which then reduces its efficiency and ultimately the life of the printhead. Also, the high temperature can damage the functionality of the fluid due to the high temperatures reached (as is the case with certain biological fluids and polymers).

Piezoelectric (piezo) drop on demand inkjet technology is currently used for most existing and emerging industrial inkjet applications. In this technology, a piezoelectric crystal (usually lead zirconium titanate) undergoes distortion when an electric field is applied. This distortion is used to create a pressure pulse in the ink chamber, which causes a drop to be ejected from the nozzle. There are many variations of piezo inkjet architectures including tube, edge, face, moving wall and piston, which use different configurations of the piezo crystal and the nozzle.

The advantages of piezo inkjet technology include the ability to jet a very wide variety of fluids in a highly controllable manner and the good reliability and long life of the printheads. The main disadvantage is the relatively high cost for the printheads, which limits the applicability of this technology in low cost applications.

## 2.3 FLEXIBLE POLYMER SUBSTRATE

Printed electronics allows the use of flexible substrates, which lowers production costs and allows fabrication of mechanically flexible circuits. While inkjet and screen printing typically imprint rigid substrates like glass and silicon, mass-printing methods nearly exclusively use flexible foil and paper. Poly(ethylene terephthalate)-foil (PET) is a common choice, due to its low cost and higher temperature stability. Poly(ethylene naphthalate)- (PEN) and poly(imide)-foil (PI) are alternatives. Paper's low costs and manifold applications make it an attractive substrate, however, its high roughness and large absorbency make it problematic for electronics.

Other important substrate criteria are low roughness and suitable wettability, which can be tuned pre-treatment (coating, corona). In contrast to conventional printing, high absorbency is usually disadvantageous.

### 2.3.1 Polyethylene terephthalate (PET)

Polyethylene terephthalate (sometimes written poly(ethylene terephthalate)), commonly abbreviated PET, PETE, or the obsolete PETP or PET-P, is a thermoplastic polymer resin of the polyester family and is used in synthetic fibers; beverage, food and other liquid containers; thermoforming applications; and engineering resins often in combination with glass fiber.

PET consists of polymerized units of the monomer ethylene terephthalate, with repeating  $C_{10}H_8O_4$  units. PET is commonly recycled, and has the number "1" as its recycling symbol



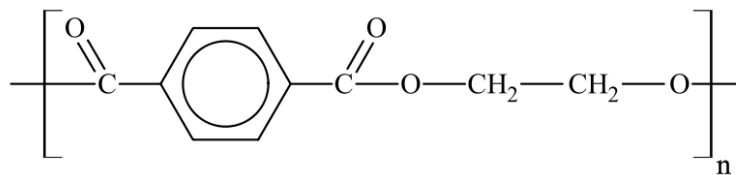


Figure 2.3 Structure formula of polyethylene terephthalate

### 2.3.2 Polyimide (PI)

Polyimide (sometimes abbreviated PI) is a polymer of imide monomers. The structure of imide is as shown in figure 3.4. Polyimides have been in mass production since 1955.

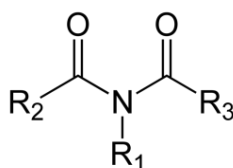


Figure 2.4 Structure formula of imide monomer

Thermosetting polyimides are known for thermal stability, good chemical resistance, excellent mechanical properties, and characteristic orange/yellow color. Polyimides compounded with graphite or glass fiber reinforcements have flexural strengths of up to 50,000 p.s.i. (345 MPa) and flexural moduli of 3 million p.s.i. (20,684 MPa). Thermoset polyimides exhibit very low creep and high tensile strength. These properties are maintained during continuous use to temperatures of 450 °F (232 °C) and for short excursions, as high as 900 °F (482 °C). Molded polyimide parts and laminates have very good heat resistance. Normal operating temperatures for such parts and laminates range from cryogenic to those exceeding 500 °F (260 °C). Polyimides are also inherently resistant to flame combustion and do not usually need to be mixed with flame

retardants. Most carry a UL rating of VTM-0. Polyimide laminates have a flexural strength half life at 480 °F (249 °C) of 400 hours.

The polyimide materials are lightweight, flexible, resistant to heat and chemicals. Therefore, they are used in the electronics industry for flexible cables, as an insulating film on magnet wire and for medical tubing. For example, in a laptop computer, the cable that connects the main logic board to the display (which must flex every time the laptop is opened or closed) is often a polyimide base with copper conductors. Examples of polyimide films include Apical, Kapton, UPILEX, VTEC PI, Norton TH and Kaptrex.

The semiconductor industry uses polyimide as a high-temperature adhesive; it is also used as a mechanical stress buffer. Some polyimide can be used like a photoresist; both "positive" and "negative" types of photoresist-like polyimide exist in the market.

An additional use of polyimide resin is as an insulating and passivation layer in the manufacture of digital semiconductor and MEMS chips. The polyimide layers have good mechanical elongation and tensile strength, which also helps the adhesion between the polyimide layers or between polyimide layer and deposited metal layer. The minimum interaction between the gold film and the polyimide film, coupled with high temperature stability of the polyimide film, results in a system that provides reliable insulation when subjected to various types of environmental stresses.

Polyimide powder can be used to produce parts and shapes by sintering technologies (hot compression moulding, direct forming, and isostatic pressing). Because of their high mechanical stability even at elevated temperatures they are used as bushings, bearings, sockets or constructive parts in demanding applications. To improve tribological properties compounds with solid lubricants like graphite, PTFE or molybdenum sulfide are common. Polyimide parts and shapes include P84 NT, VTEC PI, Meldin, Vespel and Plavis.

In coal-fired power plants, waste incinerators or cement plants, polyimide fibres are used in hot gas filtration. A polyimide needle felt separates dust and particulate matter from the exhaust gas. The IKAROS solar sailing spacecraft uses polyimide resin sails to operate without rocket engines. Polyimide film in the form of Kapton can be used as a diaphragm in loudspeaker tweeters.

## 2.4 REDOX REACTION (OXIDATION-REDUCTION REACTION)

Redox reactions or oxidation-reduction reactions refer to all chemical reactions in which atoms have their oxidation state changed. Fundamentally, redox reactions are a family of reactions that are concerned with the transfer of electrons between species. The term comes from the two concepts of reduction and oxidation. It can be explained in simple terms: Oxidation is the loss of electrons or an increase in oxidation state by a molecule, atom, or ion. Reduction is the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.

Like acid-base reactions, redox reactions are a matched set, that is, there cannot be an oxidation reaction without a reduction reaction happening simultaneously. The oxidation alone and the reduction alone are each called a half-reaction, because two half-reactions always occur together to form a whole reaction. When writing half-reactions, the gained or lost electrons are typically included explicitly in order that the half-reaction be balanced with respect to electric charge.

Though sufficient for many purposes, these descriptions are not precisely correct. Oxidation and reduction properly refer to a change in oxidation state — the actual transfer of electrons may never occur. Thus, oxidation is better defined as an increase in oxidation state, and reduction as a decrease in oxidation state. In practice, the transfer of electrons will always cause a change in oxidation state, but there are many reactions that are classed as "redox" even though no electron transfer occurs

(such as those involving covalent bonds). Non-redox reactions which do not involve changes in formal charge are known as metathesis reactions.

#### 2.4.1 Oxidizing agent

An oxidizing agent (also called an oxidant, oxidizer or oxidiser) can be defined as a substance that removes electrons from another reactant in a redox chemical reaction. The oxidizing agent is "reduced" by taking electrons onto itself and the reactant is "oxidized" by having its electrons taken away.

Common oxidizing agents : Oxygen ( $O_2$ ), Ozone ( $O_3$ ), Hydrogen peroxide ( $H_2O_2$ ) and other inorganic peroxides, Fluorine ( $F_2$ ), chlorine ( $Cl_2$ ), and other halogens, Nitric acid ( $HNO_3$ ) and nitrate compounds, Sulfuric acid ( $H_2SO_4$ ), Persulfuric acids ( $H_2SO_5$  and  $H_2S_2O_8$ ), Chlorite, chlorate, perchlorate, and other analogous halogen compounds, Hypochlorite and other hypohalite compounds, including household bleach ( $NaClO$ ) Hexavalent chromium compounds such as chromic and dichromic acids and chromium trioxide, pyridinium chlorochromate (PCC), and chromate/dichromate compounds, Permanganate compounds, Sodium perborate, Nitrous oxide ( $N_2O$ ), Silver oxide ( $Ag_2O$ ) Osmium tetroxide ( $OsO_4$ ) and Tollens' reagent

#### 2.4.2 Reducing agent

A reducing agent (also called a reductant or reducer) is the element or compound in a reduction-oxidation (redox) reaction that donates an electron to another species; however, since the reducer loses an electron we say it is "oxidized". This means that there must be an "oxidizer"; because if any chemical is an electron donor (reducer), another must be an electron recipient (oxidizer). Thus reducers are "oxidized" and oxidizers are "reduced".

Strong reducing agents easily lose (or donate) electrons. An atom with a relatively large atomic radius tends to be a better reductant. In such species, the

distance from the nucleus to the valence electrons is so long that these electrons are not strongly attracted. These elements tend to be strong reducing agents. Good reducing agents tend to consist of atoms with a low electronegativity, the ability of an atom or molecule to attract bonding electrons, and species with relatively small ionization energies serve as good reducing agents too. "The measure of a material to oxidize or lose electrons is known as its oxidation potential. The table below shows a few reduction potentials that could easily be changed to oxidation potential by simply reversing the sign. Reducing agents can be ranked by increasing strength by ranking their oxidation potentials. The reducing agent is stronger when it has a more positive oxidation potential and weaker when it has a negative oxidation potential.

**Table 2.1** Reduction potential of the indicated reducing agent at 25 °C

Oxidizing agent	Reducing agent	Reduction potential (V)
$\text{Al}^{3+} + 3\text{e}^{-}$	Al	-1.66
$2\text{H}_2\text{O}_{(l)} + 2\text{e}^{-}$	$\text{H}_{2(g)} + 2\text{OH}^{-}$	-0.83
$\text{Fe}^{2+} + 2\text{e}^{-}$	Fe	-0.44
$2\text{H}^{+} + \text{e}^{-}$	$\text{H}_2$	0.00
$\text{Sn}^{4+} + 2\text{e}^{-}$	$\text{Sn}^{2+}$	+0.15
$\text{Cu}^{2+} + \text{e}^{-}$	$\text{Cu}^{+}$	+0.16
$\text{Ag}^{+} + \text{e}^{-}$	Ag	+0.80
$\text{Br}_2 + 2\text{e}^{-}$	$2\text{Br}^{-}$	+1.07
$\text{Cl}_2 + 2\text{e}^{-}$	$2\text{Cl}^{-}$	+1.36
$\text{MnO}_4^{-} + 8\text{H}^{+} + 5\text{e}^{-}$	$\text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.49

Common reducing agents : Lithium aluminium hydride ( $\text{LiAlH}_4$ ), Nascent (atomic), hydrogen, Sodium amalgam, Sodium borohydride ( $\text{NaBH}_4$ ), Compounds containing the  $\text{Sn}^{2+}$  ion, such as tin(II) chloride, Sulfite compounds, Hydrazine (Wolff-

Kishner reduction), Zinc-mercury amalgam (Zn(Hg)) (Clemmensen reduction), Diisobutylaluminum hydride (DIBAH), Lindlar catalyst, Oxalic acid ( $C_2H_2O_4$ ), Formic acid (HCOOH), Ascorbic acid ( $C_6H_8O_6$ ), Phosphites, hypophosphites, and phosphorous acid, Dithiothreitol (DTT) – used in biochemistry labs to avoid S-S bonds, Compounds containing the  $Fe^{2+}$  ion, such as iron(II) sulfate

## 2.5 SINTERING PROCESS

Sintering is a method used to create objects from powders. It is based on atomic diffusion. Diffusion occurs in any material above absolute zero, but it occurs much faster at higher temperatures. In most sintering processes, the powdered material is held in a mold and then heated to a temperature below the melting point. The atoms in the powder particles diffuse across the boundaries of the particles, fusing the particles together and creating one solid piece. Because the sintering temperature does not have to reach the melting point of the material, sintering is often chosen as the shaping process for materials with extremely high melting-points such as tungsten and molybdenum.

Sintering is effective when the process reduces the porosity and enhances properties such as strength, electrical conductivity, translucency and thermal conductivity; yet, in other cases, it may be useful to increase its strength but keep its gas absorbcency constant as in filters or catalysts. During the firing process, atomic diffusion drives powder surface elimination in different stages, starting from the formation of necks between powders to final elimination of small pores at the end of the process.

The driving force for densification is the change in free energy from the decrease in surface area and lowering of the surface free energy by the replacement of solid-vapor interfaces. It forms new but lower-energy solid-solid interfaces with a total

decrease in free energy occurring on sintering 1-micrometre particles a 1 cal/g decrease. On a microscopic scale, material transfer is affected by the change in pressure and differences in free energy across the curved surface. If the size of the particle is small (or if the radius of curvature is large), these effects become very large in magnitude. The change in energy is much higher when the radius of curvature is less than a few micrometres, which is one of the main reasons why much ceramic technology is based on the use of fine-particle materials.

For properties such as strength and conductivity, the bond area in relation to the particle size is the determining factor. The variables that can be controlled for any given material are the temperature and the initial grain size, because the vapor pressure depends upon temperature. Through time, the particle radius and the vapor pressure are proportional to  $(p_0)^{2/3}$  and to  $(p_0)^{1/3}$ , respectively.

The source of power for solid-state processes is the change in free or chemical potential energy between the neck and the surface of the particle. This energy creates a transfer of material through the fastest means possible; if transfer were to take place from the particle volume or the grain boundary between particles, then there would be particle reduction and pore destruction. The pore elimination occurs faster for a trial with many pores of uniform size and higher porosity where the boundary diffusion distance is smaller. For the latter portions of the process, boundary and lattice diffusion from the boundary become important.

Control of temperature is very important to the sintering process, since grain-boundary diffusion and volume diffusion rely heavily upon temperature, the size and distribution of particles of the material, the materials composition, and often the sintering environment to be controlled

## 2.6 ELECTROLESS PLATING

Electroless plating, also known as chemical or auto-catalytic plating, is a non-galvanic type of plating method that involves several simultaneous reactions in an aqueous solution, which occur without the use of external electrical power. The reaction is accomplished when hydrogen is released by a reducing agent, normally sodium hypophosphite (Note: the hydrogen leaves as a hydride ion), and oxidized thus producing a negative charge on the surface of the part. The most common electroless plating method is electroless nickel plating, although silver, gold and copper layers can also be applied in this manner, as in the technique of Angel gilding.



## CHAPTER III

### LITERATURE REVIEWS

To conducting the experimental, the literature surveys on the subject of inkjet printing technology in electronic device, methodology to fabricate metal conductive line and the improvement of flexible polymer substrate have been revised. Some typical references are reviewed and summarized as shown below.

Ink-jet printing of metal nanoparticles is an attractive method for direct patterning conductive metal lines owing to low-cost, low-waste, and simple process. While most of the researches here focused on novel metals such as gold and silver, Bong K.P. et al. [1] have developed a conductive ink containing copper nanoparticles as an alternative that is inexpensive conductive material. Copper particles with a size of 40–50 nm were synthesized by polyol process, from which the well-dispersed conductive ink with low viscosity was prepared. We have successfully demonstrated a direct writing of the conductive lines using Cu conductive ink. The ink-jet printed copper patterns exhibited metal-like appearance and became highly conductive upon heat treatments. The resistivity of the film reached to  $17.2 \mu\Omega \text{ cm}$  at  $325 \text{ }^\circ\text{C}$  for 1 h in vacuum.

The main problem in preparing stable and printable inks containing nanoparticles for inkjet printing is to overcome the strong agglomeration of the particles in dispersion medium. A. Kosmala et al. [4] studied the silver particles with diameter around 50 nm were produced by a simple wet chemistry method. Stable aqueous printable inks were formulated by using the combination of a triblock copolymer and

high intensity focused ultrasound (HIFU). Various factors that affect the ink stability, such as, copolymer content and time of HIFU treatment, were investigated. The ink containing 5 wt% silver has a viscosity of about 2 mPa s and surface tension  $30 \text{ mN m}^{-1}$  at 25 °C, which meet inkjet printer requirements. Such inks have been successfully printed on Al<sub>2</sub>O<sub>3</sub> ceramics and low-temperature co-fired ceramics (LTCC) and the printed films. The silver printed patterns of multilayer inkjet printing was fire together at 350 °C after 60 layers deposition and fire after the deposition of 20 layers showed a low resistivity values of 40  $\mu\Omega$  cm and 20 $\mu\Omega$  cm, respectively.

Akihiro Y. et al. [6] used copper nanoparticles with a mean diameter of 20 nm to prepare electrical conductive films at low temperature. After dispersal in an organic solvent, the copper nanoparticle pastes were coated onto a glass substrate, which was then annealed under various conditions to investigate the effects of various atmospheric conditions, such as air, nitrogen gas or hydrogen gas, as well as different annealing temperatures. Two-step annealing, which first involves oxidation in air followed by reduction, is effective in the preparation of high electrical conductive copper nanoparticle films. The copper nanoparticle films that were calcined in air for 1 h and then hydrogen gas for 1 h at a low temperature of 200 °C showed a low resistivity of 20  $\mu\Omega$  cm.

Seonhee J. et al. [7] used copper nanoparticles (NPs) to fabricate the Cu conductive printed pattern by inkjet printing. Then, the printed patterns were sintered at 250 °C under N<sub>2</sub> atmosphere and reducing by formic acid. The size of NPs covered by organic capping molecules was 5 nm on average. A crack-free Cu film was obtained after sintering. The grain size of the film reached 500 nm upon grain growth. However,

only agglomeration of NPs was observed at the bottom of the film. The resistance was  $0.88 \Omega$  on average and the patterns were electrically tested by light-emitting diodes.

Chien L. et al. [8] fabricated the conductive patterns on a flexible polyimide film by using Ag nanoplate ink of 10 wt% solid content by inkjet printing and baking at a low temperature of  $100^\circ\text{C}$ . Sintering on these printed nanoplates at a low temperature ( $100^\circ\text{C}$ ) led to the formation of connections between nanoplates. A four-point probe measurement indicated that the resistivity of the line obtained by printing nanoplates is  $26.3 \mu\Omega \text{ cm}$  and this is lower than that of the line obtained by printing spherical nanoparticles,  $43 \mu\Omega \text{ cm}$ .

J.T.Wu et al. [9] reported using ethylene glycol vapor reduction approach to fabricate conductive silver tracks directly from silver nitrate solution by ink-jet printing. The silver nitrate precursor can be reduced in ethylene glycol vapor to form silver at low temperatures. X-ray diffraction, thermogravimetric analysis, and energy dispersive spectrometric analysis results indicate that the silver nitrate has been converted to silver completely. Using a high concentration silver nitrate solution, continuous silver conductive lines with a resistivity of  $73.14 \mu\Omega \text{ cm}$  have been produced, which is relatively close to the resistivity of bulk silver.

S.M. Bidoki et al. [10] studied, ink-jet printing techniques were used to directly deposit metallic conductive patterns to produce wiring boards, antennas, electrodes and so forth. In these methods, aqueous solutions of metal salt and reducing agent were ink-jet printed consecutively onto the substrate, where an immediate chemical reduction transformed the metal cations into very fine metallic particles. The best performing reducing agent for ink-jet metal deposition was found to be ascorbic acid at neutral pH. Using this chemistry, nanosized silver patterns, composed of particles in the size range

10–200 nm, were successfully formed using a standard office ink-jet thermal-head printer. Deposited layers of silver with high electrical conductance up to  $1.89 \times 10^5 \text{ S m}^{-1}$  and sheet resistance up to  $0.5 \text{ } \Omega/\square$  were printed whilst higher conductivities might be expected using more appropriate devices.

Y.S. Goo et al. [11] conducted ink-jet printing of copper (Cu) conductive ink on polyimide (PI) film to form Cu conductive patterns. First, the oxygen plasma treatment was performed to modify the surface property of the PI film, and contact angles were measured to confirm the change of its surface property. Thus, we confirmed the decrease of contact angles to saturation contact angle was about  $33^\circ$  with optimized plasma treatment times for 3s. Then Cu conductive lines were formed on unmodified and modified PI films using ink-jet printing, and the printed lines were reduced and sintered by thermal treatment in hydrogen ( $\text{H}_2$ ) atmosphere at  $200^\circ\text{C}$  for 1 h. The electrical resistivity of copper conductive printed lines was  $62.26 \text{ } \mu\Omega \text{ cm}$ . The continuous lines having pure Cu phase and well-sintered microstructure were successfully formed on PI substrate modified by oxygen plasma treatment.

To optimized and controlled factors affecting on electroless copper plating process, Farid H. et al. [12] firstly studied effect of different electroless copper baths from tartarate and EDTA complexing compounds on printed circuit boards. The effect of bath operating conditions (temperature, pH and agitation) and bath additives that consisted of pyridine, cytosine, thiourea, benzotriazole (BT) and 2-mercaptobenzothiozole (2MBT) on plating rate, bath stability, morphology and etching rate of the coating has been studied. The results of this experimental, found that all the organic additives studied except thiourea not only stabilize electroless copper baths but also enhance the plating rate from 1.1 to 1.8  $\text{mg}/(\text{cm}^2\text{h})$  in the tartarate bath at  $30^\circ\text{C}$

and from 5.4 to 10.5 mg/(cm<sup>2</sup> h) in the EDTA bath at 50 °C. Mild air agitation increases the bath stability 20 times that of bath without aeration. The additives were found to modify the crystal structure with the production of small grain size, dense, tightly adherent and etching resistant copper deposit.

The developed the patterned of copper tracks on flexible polyimide film was studied by Stephan B. et al. [13] The workflow comprises inkjet printing of an aqueous palladium(II) solution on to surface treated polyimide film by wet chemical method, followed by reduction with sodium borohydride to metallic palladium and selective copper deposition on the printed pattern by electroless copper plating at 25°C for up to 60 min. The resistivity of copper plated lines is about 0.33 – 0.40  $\mu\Omega$  cm.

Chun C. et al. [14] studied novel methodology for preparation of palladium (Pd) nanoparticles reduced by vinyl acetate (VAc) oligomers. The noble metal nanoparticles reduced and stabilized by vinyl acetate oligomer showed their well dispersion in the aqueous solution without surfactant and reductant in the mixture. These Pd nanoparticles can be used as activator to replace the traditional Pd/Sn colloid for electroless metal deposition. Based on these results, the coverage of Cu layer completely on substrate was achieved after 30 min deposition at 75 °C. The ink based on VAc/Pd colloids was successfully inkjet printing onto a FR-4 plate. The formed metallic palladium patterns were subjected to electroless copper plating, yielding well-defined copper lines. The copper film had electrical resistivity of about 7.37  $\mu\Omega$  cm a factor of only 4.29 times higher than the bulk copper. This process provides a clean, easy and low-cost method for preparation of high resolution Cu patterning.

## CHAPTER IV

### EXPERIMENTAL DETAILS

This chapter describes the research methodology to fabricate metal conductive lines in four steps. Firstly step is Preparation of metal salts solution. Second step is preparation of flexible polymer substrates. Next step is inkjet printing process combined with various methods and the last step is characterization of metal conductive lines.

Additionally, all of materials, equipments and instruments are used in this experiment to be given explanation in this chapter.

#### 4.1 MATERIALS

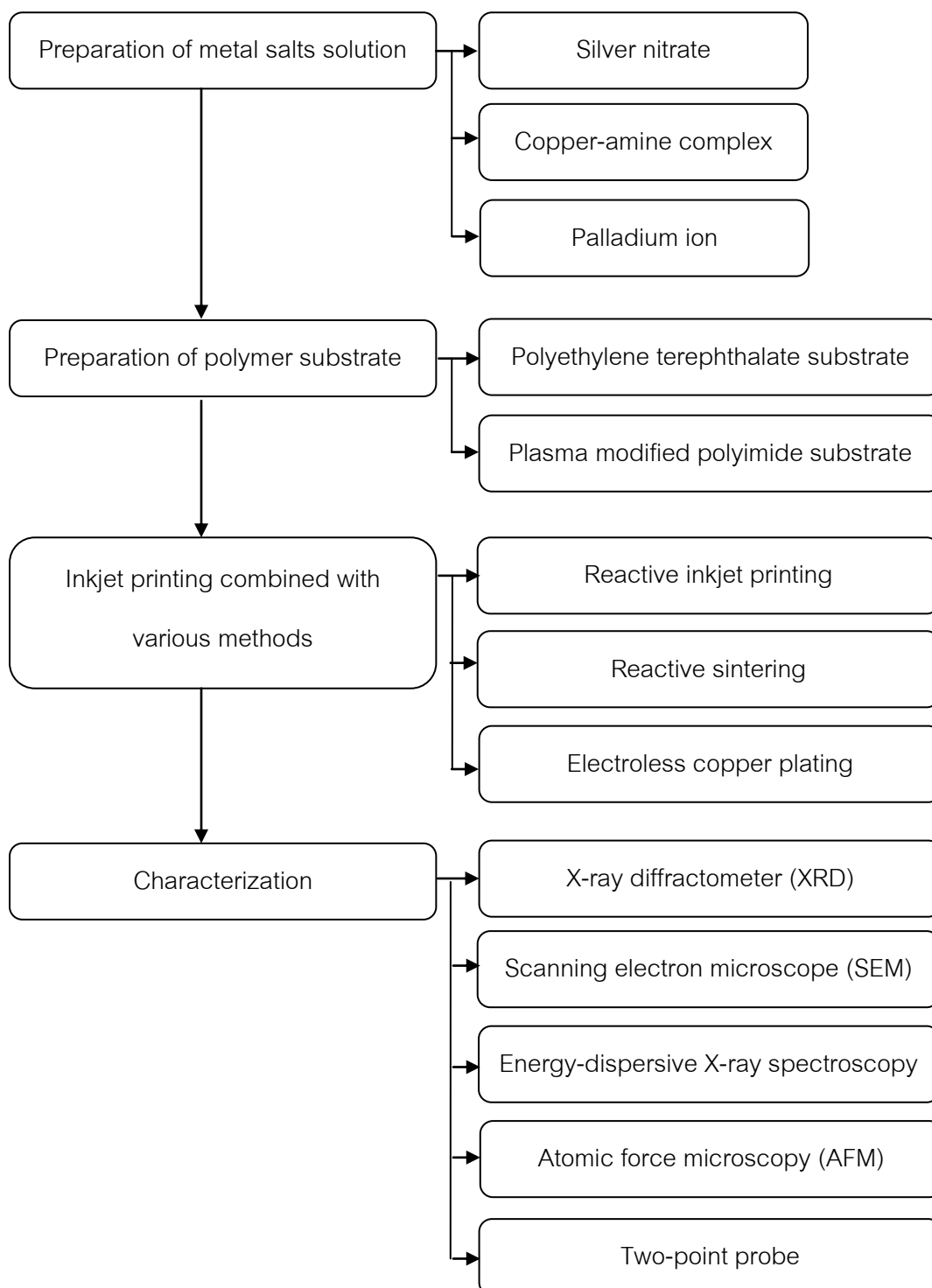
The list of chemical material was used in this experimental as shown below:

**Table 4.1** List of chemical material

Material	Molecular Formula	Company
Silver nitrate	AgNO <sub>3</sub>	S D Fine-Chem
0.13 mm thick of Copper foil	Cu	Ajax Finechem
25% Ammonia solution	NH <sub>4</sub> OH	QRëC™
85% Formic acid	HCOOH	QRëC™
Palladium (II) Chloride	PdCl <sub>2</sub>	Sigma Aldrich
Ammonium Chloride	NH <sub>4</sub> Cl	Ajax Finechem
L-Ascorbic acid	C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	Ajax Finechem
Ethylene Glycol	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	QRëC™
Copper (II) sulphate	CuSO <sub>4</sub> .5H <sub>2</sub> O	Ajax Finechem
Ethylenediaminetetraacetic acid	EDTA	Sigma Aldrich
Sodium Hydroxide	NaOH	RANKEM
Sodium Borohydride	NaBH <sub>4</sub>	RANKEM

## 4.2 EXPERIMENTAL METHODOLOGY

Figure 4.1 Schematic of experimental methodology



### 4.3 PREPARATION OF METAL SALTS SOLUTION (CONDUCTIVE INK)

Silver nitrate, copper-amine complex and palladium ion were used as source of silver, copper and palladium, respectively that were conducted to fabricate metal conductive lines. The methods to prepare metal salt solutions are shown below:

#### 4.3.1 Silver Nitrate Solution

5 M of silver nitrate was prepared by dissolving 8.5 g of silver nitrate in 10 ml of de-ionized water in a beaker and then stirring the solution for 20 min. To study the effect of silver nitrate concentrations, it is prepared in similar procedure with different concentrations between 5 and 10 M.

#### 4.3.2 Copper-Amine Complex Solution

The copper-amine complex ink was synthesized by the direct electrochemical reaction. Bulk Cu plates were used as cathode and anode electrodes in the electrolytic cell. The electrolyte solution consisted of 25 wt% ammonia solution as a complexing agent and 0.04 M of formic acid as an ionization agent in de-ionized water.

First, electrolyte solution was prepared from 10 ml of Formic acid solution and 200 ml of ammonia solution. Bulk Cu electrodes were dipped in an electrolyte solution. Then, the electrodes were connected to an electric power supply (GPS-S Series, GW Instek) of 25 DC Voltages. The solution was stirred. The system was controlled temperature system below 25°C and continued reaction for 2 hours. The experimental set up is shown schematically in Figure 4.2.



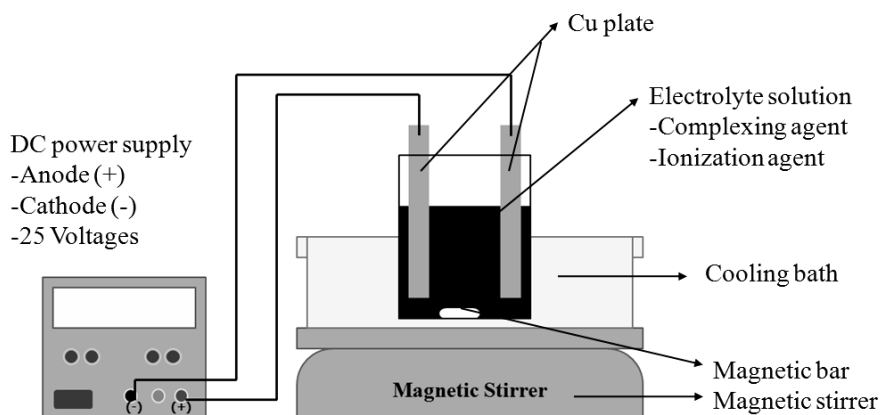


Figure 4.2 Experimental setup of the synthesis copper ion complex ink.

#### 4.3.3 Palladium Ion Solution

Palladium salts was prepared from mixing of 40 mg palladium (II) chloride (Pd (II) Cl, Sigma Aldrich) and 40 mg ammonium chloride in water. The solution was stirred for 1 h. Palladium ion ink was obtained to inkjet printing process

### 4.4 PREPARATION OF POLYMER FLEXIBLE SUBSTRATE

#### 4.4.1 Polyethylene Terephthalate (PET) Substrate

PET substrate (75  $\mu\text{m}$  thickness) was cut in dimension 7 cm  $\times$  10 cm and cleaned with delicate task wipers (KIMTECH) to remove contaminate on surface of substrate before using in inkjet printing process.

#### 4.4.2 Oxygen Plasma Treatment of Polyimide Film

In order to improve the surface roughness and hydrophilicity of polyimide film, the film was treated by oxygen plasma treatment in plasma dry cleaning system (SAMCO, PC-1100).

First, the polyimide film was cut in dimension 7 cm × 10 cm and cleaned with de-ionized water and acetone to remove particles and organic contaminates on the surface. After cleaning, PI film was placed in a chamber and set operating condition with a back pressure of 15 Pa and working power at 200 W. After vacuum process, 40 sccm of pure oxygen gas flow rate was fed in to a chamber. The oxygen plasma treatment of polyimide film was carried out in range of 1 to 10 s.

#### 4.5 INKJET PRINTING

All printing experiment was carried out with a commercially available multi-color drop-on-demand ink-jet printer (Epson Stylus Photo T60) with a resolution of 5760 x 1440 dpi. This printer has a piezoelectric head with 90 nozzles configuration in each color, and each droplet volume is approximately 1.5 pL. The metal salts solution was poured into the ink cartridge and printed as a two point probe pattern as shown in figure 4.3. This pattern was used for measurement of resistance.

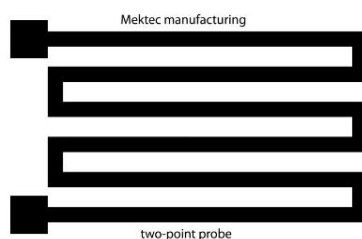


Figure 4.3 Two point probe printed line pattern

#### 4.6 REACTIVE INKJET PRINTING

In this experiment, silver nitrate solution with different concentration and 1 M of L- Ascorbic acid were used as a conductive ink and a reducing agent, respectively. Reducing agent and silver nitrate solution were sequentially printed onto a PET substrate at room temperature.

Printing cycle started by firstly printing reducing agent on PET substrate at room temperature and then drying printed pattern at room temperature for 5 – 10 min. The pattern printed was then overprinted by silver nitrate solution. The same printing cycle procedure was repeated several times to obtain a multi-layer conductive pattern. After that, the printed pattern was baked at 150°C for 30 min. The effect of printing cycle was studied in 5, 10 and 15 cycles.

## 4.7 REACTIVE SINTERING

### 4.7.1 Reactive Sintering of Formic Acid Vapor Reduction

7 M of silver nitrate solution with 5 printing cycle on PET substrate was used. The pattern printed was placed on hotplate (C-MAG HS 7, IKAMAG®) inside a glass disk with formic acid and heated to 150 °C. The pattern printed was held at this temperature for 30, 60, 90 and 120 min to convert to a conductive silver line. It was then naturally cooled down to room temperature inside the glass dish. The experimental setup is shown schematically in figure 4.4. Additionally, the effect of reactive sintering time on silver conductive lines was investigated.

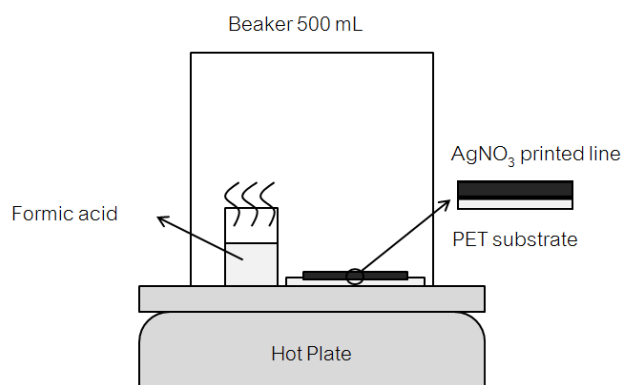


Figure 4.4 Experimental setup of reactive sintering under formic acid vapor

#### 4.7.2 Reactive Sintering of Ethylene Glycol Vapor Reduction

The pattern printed by using 5 printing cycle of 7 M of silver nitrate on treated PI film was used. It was heated to setting temperature at 250°C with ethylene glycol vapor inside a glass disk and held at this temperature to convert silver ions to a silver conductive pattern. The experimental setup of ethylene glycol vapor reduction is shown in figure 4.5. Additionally, the effect of sintering time on silver pattern was studied in range of 15 to 60 min.

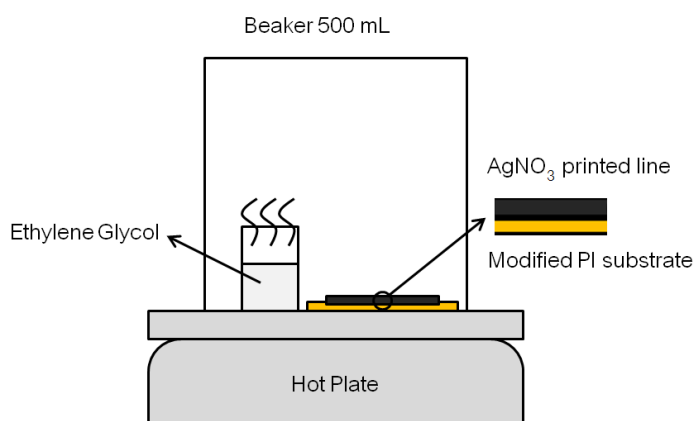


Figure 4.5 Experimental setup of reactive sintering under ethylene glycol vapor

#### 4.7.3 Reactive Sintering under H<sub>2</sub> Atmosphere

The patterns printed by using 10 printing cycle of copper salt solution were sintered under H<sub>2</sub> atmosphere in tube furnace with 100 ml/min of H<sub>2</sub> gas flow rate and heating rate 10°C/min. The sintering condition was carried out at 200°C for 1 h.

## 4.8 ELECTROLESS COPPER PLATING

The silver seed layer was prepared by 5 printing cycle of silver nitrate solution and then reactive sintering with formic acid vapor at 150°C for 120 min.

The palladium seed layer was prepared by 5 printing cycle of palladium ion solution and then reduction with NaBH<sub>4</sub> bath for 5 min.

The electroless copper bath was prepared by dissolving 0.87 M of sodium hydroxide (NaOH), 0.17 M of ethylenediamine tetraacetic acid (EDTA) and 0.10 M of copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) in DI water, adding 0.4 ml of 37% aqueous formaldehyde (HCOH). The pH values were adjusted to 12.4 – 12.5 by dropwise addition of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) or concentrated sodium hydroxide (NaOH) in the electroless baths. The seed layer of printed pattern on PET film was immersed in electroless bath at the condition of temperature 25°C and deposition time between 15 to 60 min. In addition, the electroless bath was operated in ultrasonic cleaning system for freshly solution of electroless copper bath.

## 4.9 CHARACTERIZATIONS

### 4.9.1 Characterization of Polyimide Film Modification

The Polyimide film before and after modified surface property was investigated wettability by contact angle analyzer (CAM, Melles Griot) at room temperature. The DI water droplet of 5 µl was dropped on the PI film by a micro-syringe. The contact angles and droplet images of DI droplet on polyimide film were then recorded from 1 to 360 s.

### 4.9.2 Characterization of Metal Conductive Lines

The element of metal conductive lines was measured by Energy Dispersive Spectrometer (EDS). The metal conductive lines on substrate were characterized by X-

ray diffraction (XRD) and scanning electron microscope (SEM) to confirm the crystal structure and morphology, respectively. The roughness copper deposited pattern was characterized by Atomic Force Microscopy (AFM). Finally, the resistivity of metal patterns was measured by two-point probe at room temperature.

## CHAPTER V

### RESULTS AND DISCUSSIONS

#### 5.1 INK PROPERTY

Silver nitrate solution, copper–amine complex solution and palladium ion solution were used as the metal salt solution in inkjet printing process. The properties of solutions are shown in table 5.1.

Table 5.1 The properties of metal salt solution

Metal salt solution	Concentration (Molar)	Viscosity (cP)
AgNO <sub>3</sub>	5	3.43
	7	3.79
	10	4.46
Copper-amine complex	0.47	2.12
Palladium ion	0.01	2.97

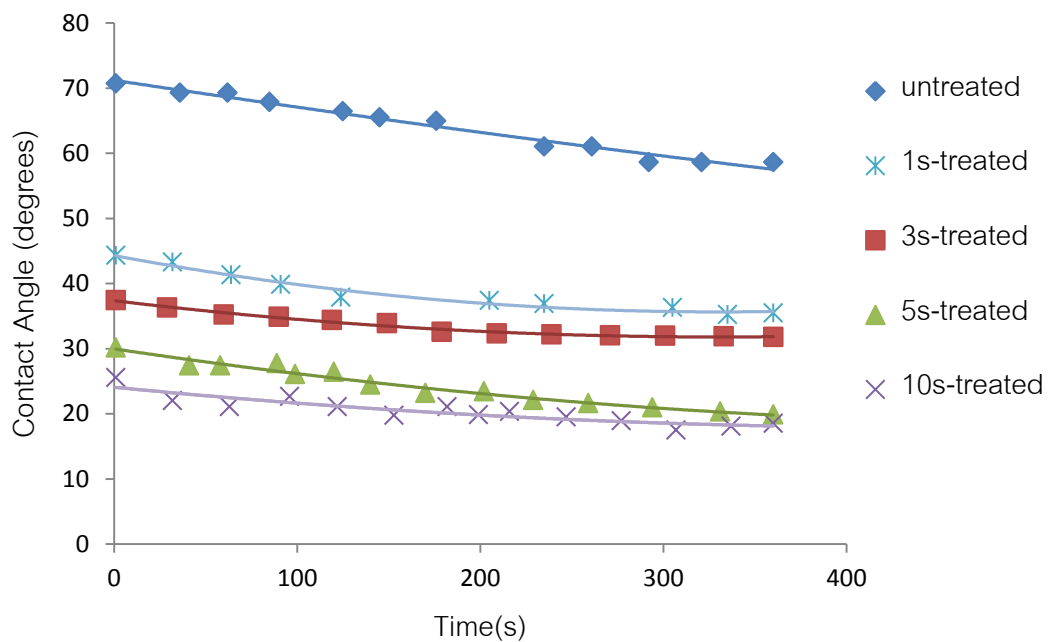
From the table 5.1, the viscosity of metal salts solutions ranged from 2.12 to 4.46 cP, which are suitable for use in conventional office inkjet printer [9].

#### 5.2 MODIFICATION OF POLYIMIDE SUBSTRATE

In this study, polyimide film was used as polymer substrate in reactive sintering process at high temperature because of its thermal property of polyimide film. However, polyimide film has a hydrophobic surface due to its low surface energy. When water based ink is printed onto a polyimide film surface, each ink droplet has a high contact

angle due to problem of surface wettability. It resulted in the difficulty to make continuous line and uniform shape.

The oxygen plasma treatment was used to enhance the surface property of polyimide film from hydrophobic to hydrophilic. To confirm the change of surface property, the contact angles of droplet DI water on untreated and treated polyimide films were measured.

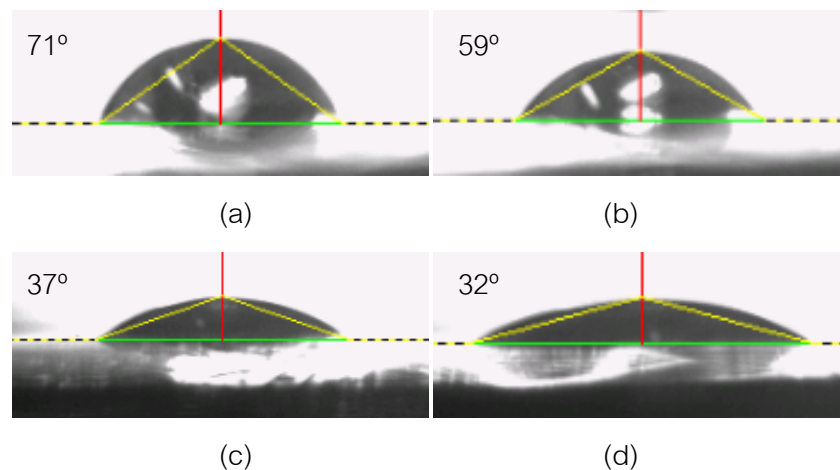


**Figure 5.1** The contact angle graph of the DI water droplet on the polyimide films at different oxygen plasma treatment times.

Figure 5.1 shows the contact angle of the DI water droplet on the polyimide substrate before and after modified by oxygen plasma treatment with various time. It was observed that the contact angles were decreased by increasing the oxygen plasma treatment time, and the contact angles were saturated after a specific time. The value of the contact angle for a bare polyimide film was about  $59^\circ$  and decreases to  $35^\circ$ ,  $32^\circ$ ,  $20^\circ$ , and  $19^\circ$  after oxygen plasma treatment time for 1 s, 3 s, 5 s and 10 s, respectively.



In the case of the polyimide film treated for 3 s, the contact angle value is suitable for inkjet printing [11, 15].



**Figure 5.2** Image of DI water droplet on polyimide substrate: (a) 1 s after dropped on the untreated film, (b) 360 s after dropped on the untreated film, (c) 1 s after dropped on the treated film, and (d) 360 s after dropped on the treated film. The treated films were modified by oxygen plasma treatment at a power of 200 W for 3 s.

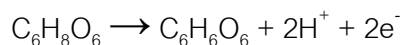
Additionally, figure 5.2 shows the snapshot image of DI water droplet on untreated and oxygen plasma treated polyimide film for 3 s. The contact angle was decreased after dropped DI water for 360 s in both case. But, the contact angle on treated polyimide film was significantly decreased compared to the untreated one.

The decrement of contact angle was also observed. The surface property of the polyimide film changes from hydrophobic to hydrophilic. It could be explained that the surface energy of the polyimide film was decreased by increasing oxygen concentration or oxygen plasma treatment time and changes in the chemical bonds of the polyimide film introducing polar groups such as -OH, -COOH, and -C=O [16].

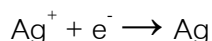
### 5.3 PREPARATION OF SILVER CONDUCTIVE LINES BY REACTIVE INKJET PRINTING

In reactive inkjet printing process, the silver conductive line was prepared from sequentially print reducing agent and salt on PET substrate. The silver nitrate solution was selected as silver salt because of its high water solubility, stability and reasonable price. L-ascorbic acid was used as reducing agent in this experiment.

In printing cycle step, when 1 M of L-ascorbic acid solution was firstly printed on PET substrate, the print-out was seen as white line pattern. Then, overprinted of 5 M of silver nitrate solution on top of previously printed area, the dark grey line pattern was observed on the printed out film. It indicated that metal formation occurred on the printed line as a consequence of the redox reaction between reducing agent and silver salt solution and leaving a metallic layer on the surface of substrate. The oxidation reaction of L-ascorbic acid is represented by the equation:



The released electrons are utilized to reduce silver ions as shown in the equation:



To prepare the silver conductive line, the silver particle content and thickness of silver printed pattern was be studied by repeating the number of printing cycle and changing of silver nitrate concentration.

### 5.3.1 Effect of Printing Cycle on Silver Pattern

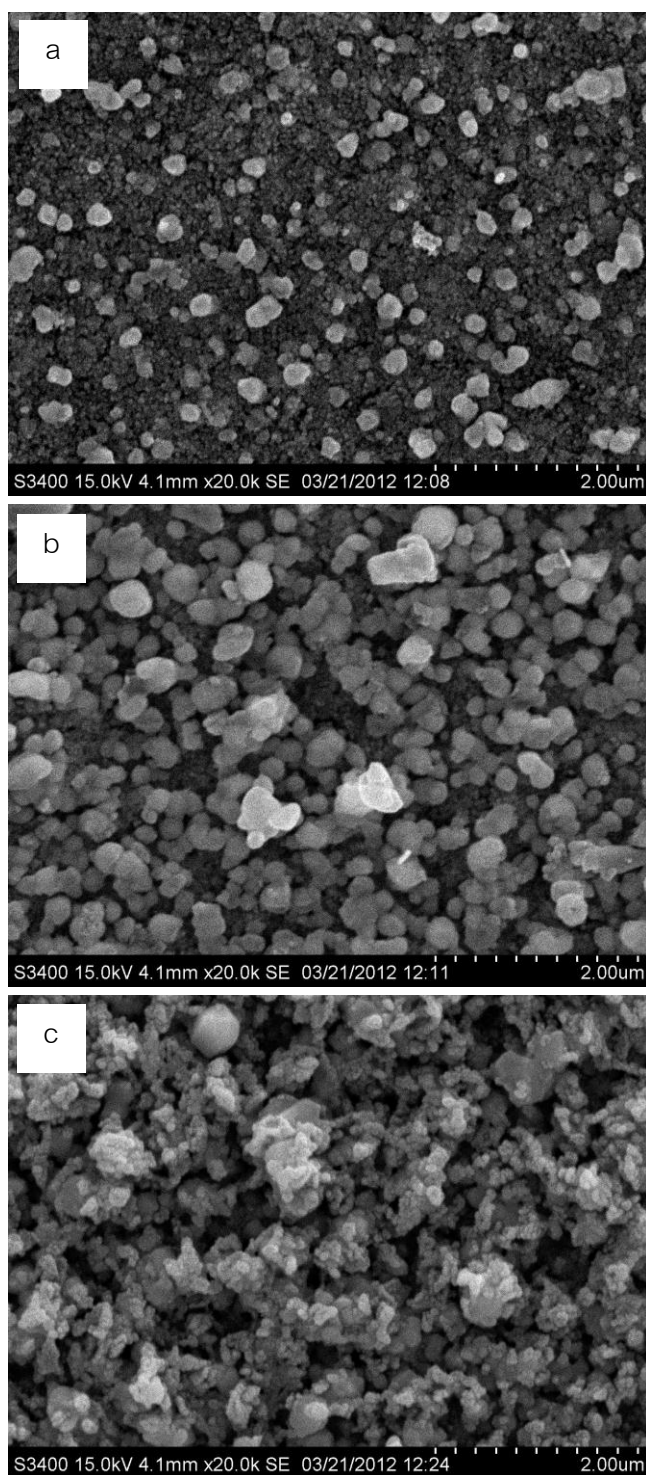


Figure 5.3 SEM images of morphology of silver printed pattern obtained by reactive inkjet printing of ascorbic acid and 5 M of silver nitrate solution: (a) 5 cycles, (b) 10 cycles, and (c) 15 cycles.

The effect of the number of printing cycle on silver printed pattern was carried out at 5, 10 and 15 cycles as shown in figure 5.3. From SEM images, it could be seen that the reactive inkjet printing process was able to produce silver nanoparticles on the substrate. Many spherical particles of approximately 100-300 nm, 100-400 nm and 100-500 nm were observed on the surface of silver printed pattern obtained by 5, 10 and 15 cycles, respectively. Non-contiguous pattern was observed in figure 5.3a. The pattern became contiguous and thick by increasing printing cycle as observed in figure 5.3b and c. The contiguous pattern and large particle sizes were noticed while increase the number of printing cycle that caused by silver particle occurrence and growth of small particles.

EDS and XRD diffraction analysis were used to verify silver form on the surface of printed pattern as shown in figure 5.4 and 5.5.

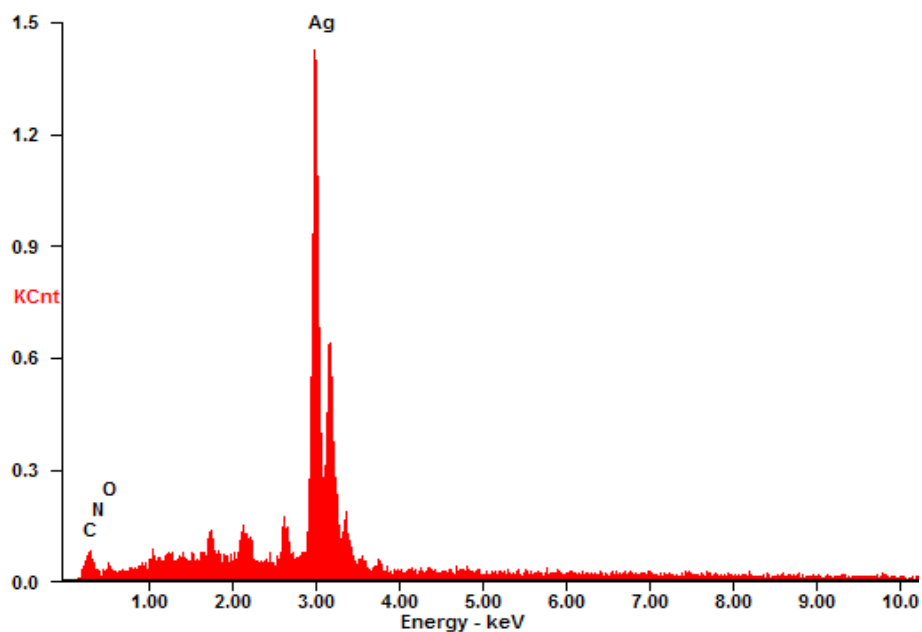
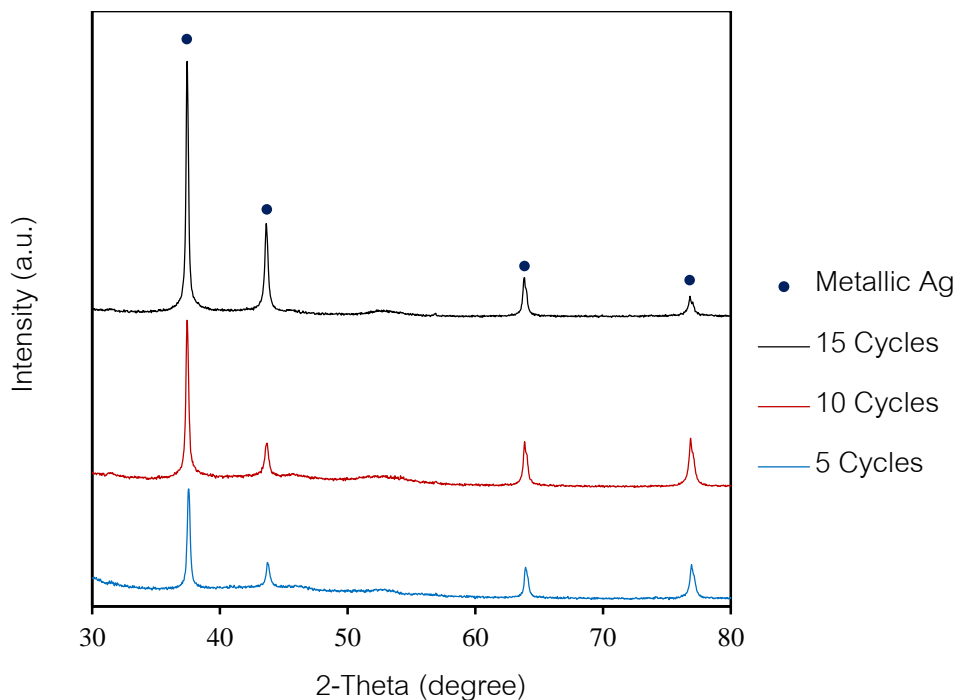


Figure 5.4 EDS pattern of silver printed pattern obtained by 15 cycles of reactive inkjet printing of L-ascorbic acid and 5 M of silver nitrate solution.



**Figure 5.5** XRD diffraction patterns of silver printed patterns obtained by reactive inkjet printing of L-ascorbic acid and 5 M of silver nitrate solution by 5, 10, and 15 printing cycles.

The EDS and XRD analysis confirm that the printed pattern is silver. The XRD patterns show the peak characteristic of metallic silver that consisted of one strong peak located at  $37.42^\circ$  and three weak peaks located at  $43.68^\circ$ ,  $63.87^\circ$ , and  $76.80^\circ$ . They were detected and attributed to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) diffraction planes of the face-centered cubic structure, respectively.

The effect of printing cycle on electrical resistivity is shown in figure 5.6. The printed pattern obtained by 5 cycles of reactive inkjet printing showed high electrical resistivity. The printed patterns obtained by 10, and 15 cycles showed decrease of electrical resistivity values as  $35.31 \times 10^{-4} \Omega \text{ cm}$ , and  $4.62 \times 10^{-4} \Omega \text{ cm}$ , respectively. The lowest resistivity was showing in the silver printed patterns obtained by 15 cycles of reactive inkjet printing. The increasing of the number of printing cycles was result on

decrease electrical resistivity due to increase of particles content and formation to the contiguous pattern. However, the number of printing cycle was limited by alignment of repeating printing process.

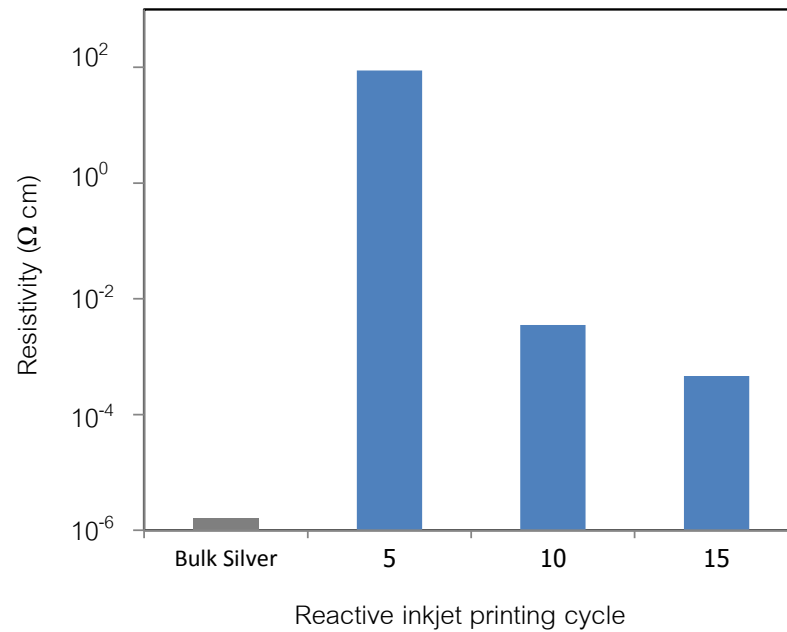


Figure 5.6 Effect of the number of printing cycle on electrical resistivity of silver printed patterns

### 5.3.2 Effect of Silver Nitrate Concentration on Silver Pattern

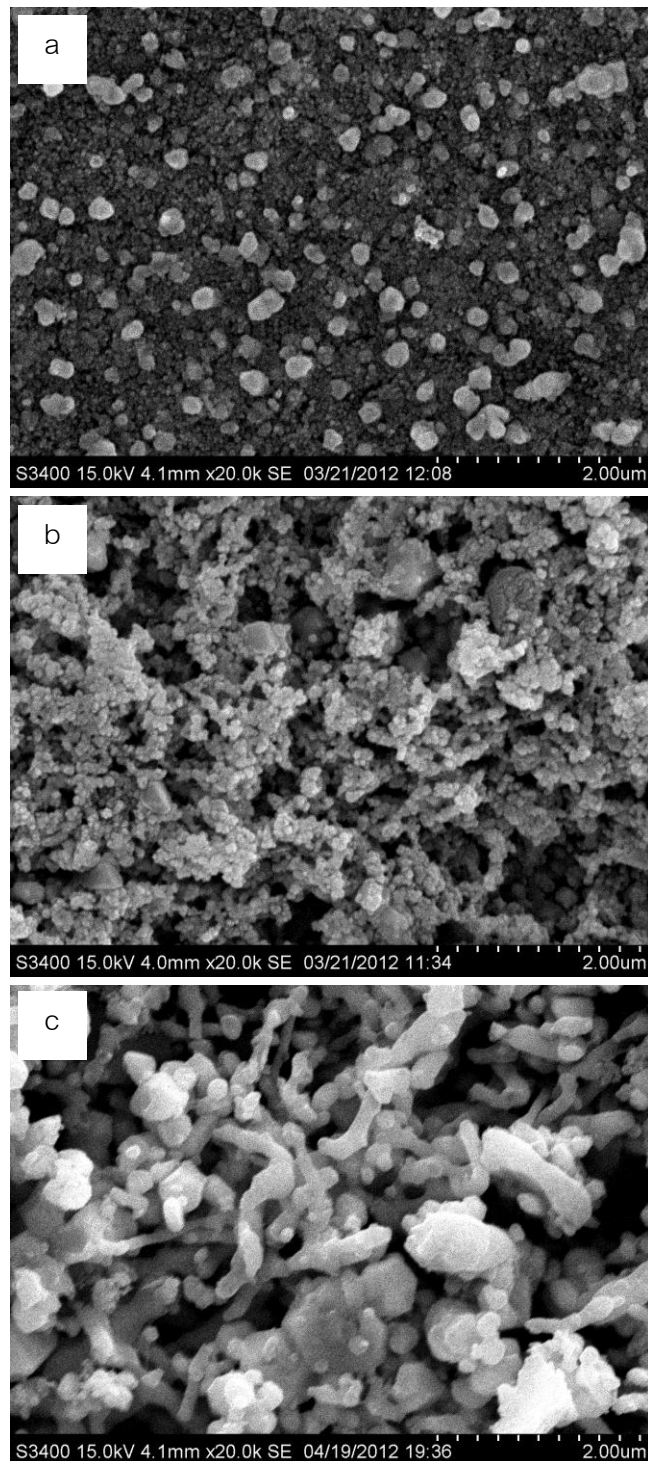
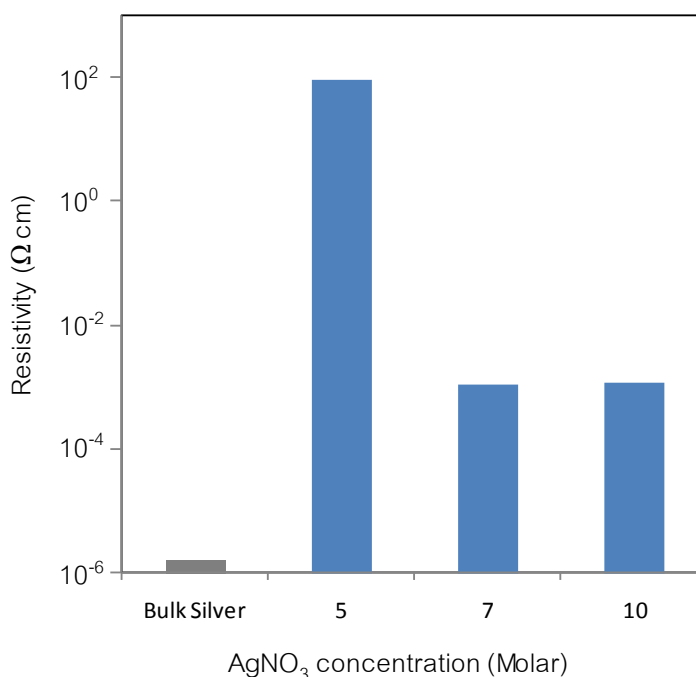


Figure 5.7 SEM image of morphology of silver printed pattern obtained by 5 cycles of reactive inkjet printing of L-ascorbic acid and silver nitrate solution of (a) 5 M, (b) 7 M, and (c) 10 M.

The morphology images of silver printed patterns on PET substrate using 5, 7, and 10 M silver nitrate solutions prepared by repeated five times of reactive inkjet printing are shown in figure 5.7. For 5 M solution (figure 5.7a), continuous pattern could not be formed due to the low concentration. The silver particles could be form to contiguous pattern by increasing the silver nitrate concentration to 7 M and 10 M. In figure 5.7b, the spherical particles with particle size as 200-400 nm were observed. The spherical and long particles of approximately 200–500 nm were observed in figure 5.7c. It could be seen that increase in silver nitrate concentration increase the metal content and size of particle.



**Figure 5.8** Effect of silver nitrate concentration on electrical resistivity of silver printed patterns obtained by 5 cycles of reactive inkjet printing.

Figure 5.8 shows electrical resistivity of silver printed pattern obtained by reactive inkjet printing using silver nitrate concentration of 5 M, 7 M, and 10 M solution. They are  $8.77 \times 10^{-1} \Omega \text{ cm}$ ,  $10.67 \times 10^{-4} \Omega \text{ cm}$ , and  $12.03 \times 10^{-4} \Omega \text{ cm}$ , respectively. With the



increase of concentration from 7 M to 10 M solution, the resistivity of the printed pattern gradually decreases due to the clearance gaps between the particles on the surface of printed pattern of 10 M solution. When using the high concentration of silver nitrate solution as result in the silver particles content in printed pattern increase but it also increase porosity on printed pattern due to the large size of particle.

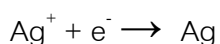
#### 5.4 PREPARATION OF SILVER PATTERN BY REACTIVE SINTERING

The reactive sintering is consisting of reactive and sintering process. In the reactive process, the metal ion is reduced to metal particle by reducing agent and then the metal particle is interconnected between particle and form to the contiguous pattern by heat treatment in sintering process.

In this experiment, 7 M of silver nitrate solution was printed five times on polymer substrate. After that, the printed pattern was conducted to reactive sintering process

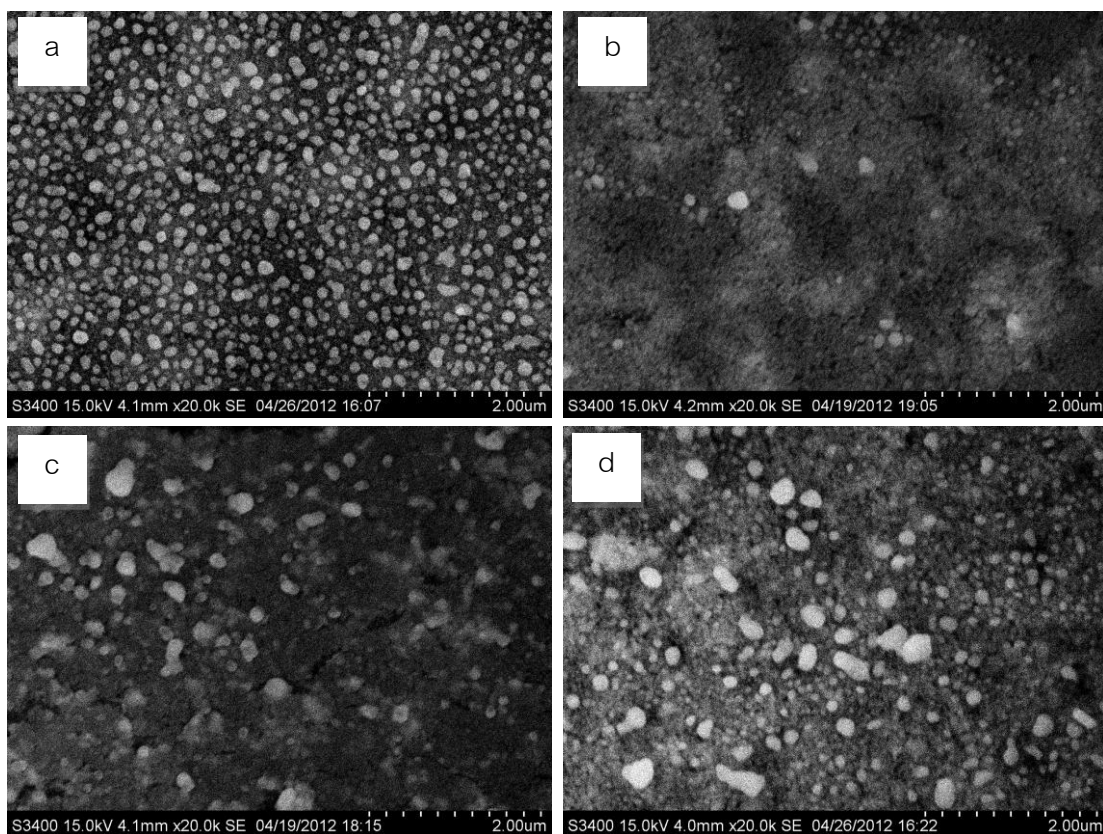
##### 5.4.1 Reactive Sintering of Formic Acid Vapor Reduction

Formic acid vapor was used as reducing agent in this process. The influence of reactive sintering time on silver pattern obtained by formic acid vapor reduction was investigated. The oxidation reaction of formic acid and the reduction reaction of silver ions are represented by equation, respectively.



The morphology images of silver pattern obtained by reactive sintering with formic acid vapor reduction at 150°C for 30, 60, 90, and 120 min are shown in figure 5.9. The spherical particle of approximately 100-200 nm was observed on the surface of

silver pattern obtained by reactive sintering for 30 min (figure 5.9a). The printed pattern showed an indented surface and the silver particles could not form continuous pattern due to short reactive sintering time. Then, the silver particles start to coalesce into film when reactive sintering for 60 min (figure 5.9b). After reactive sintering time for 90 and 120 min, silver particles could be clearly seen on the surface and the printed pattern form to contiguous pattern.



**Figure 5.9** SEM images of morphology of silver pattern obtained by reactive sintering with formic acid vapor at 150°C for (a) 30 min, (b) 60 min, (c) 90 min, and (d) 120 min.

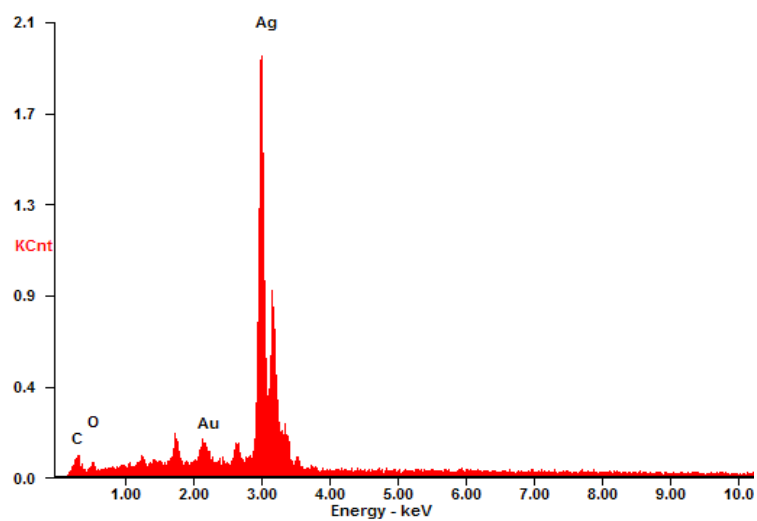


Figure 5.10 EDS pattern of silver printed pattern obtained by reactive sintering with formic acid vapor at 150°C for 120 min.

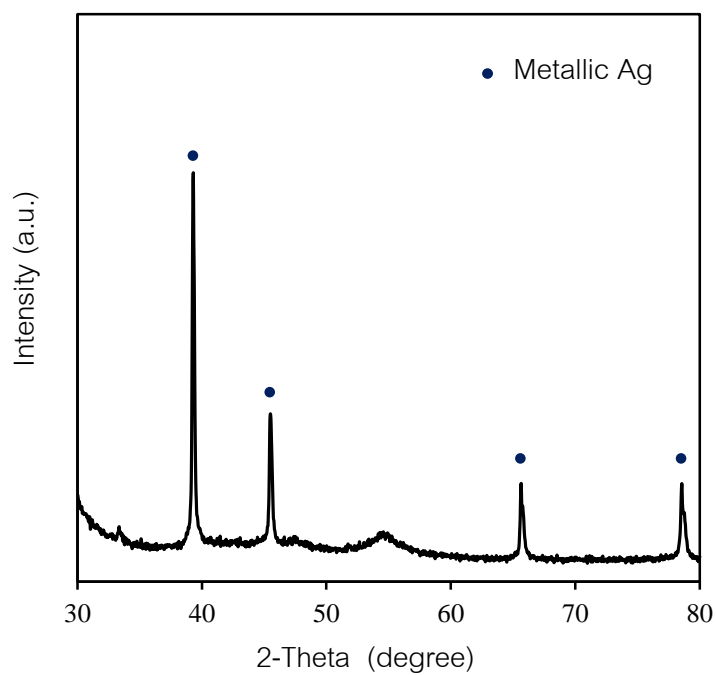
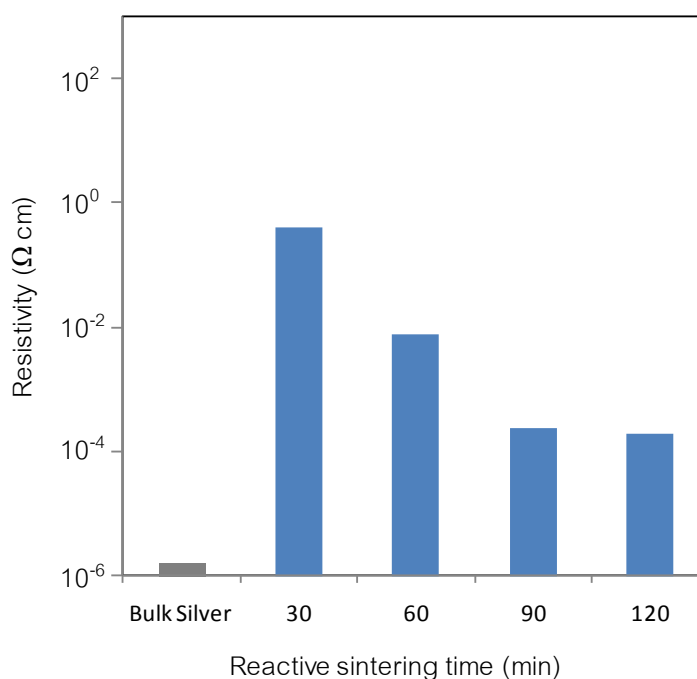


Figure 5.11 XRD pattern of silver printed pattern obtained by reactive sintering with formic acid vapor at 150°C for 120 min.

Figure 5.10 and 5.11 show the EDS and XRD diffraction patterns of silver pattern obtained prepared by formic acid vapor reduction at 150°C for 120 min. The strong peak of silver was shown from the EDS pattern. In addition, the peaks of XRD diffraction pattern located at 39.31°, 45.46°, 65.62°, and 78.53° that were detected to the peaks of metallic silver. They were confirmed that silver nitrate solution was reduced to a silver particle by formic acid vapor at 150°C



**Figure 5.12** Effect of reactive sintering time on electrical resistivity of silver patterns obtained by formic acid vapor reduction at 150°C

The electrical resistivity variations of silver pattern as a function of reactive sintering time are exhibited in figure 5.12. The resistivity decreases with increasing reactive sintering time. The silver pattern obtained by reactive sintering for 30 min showed high electrical resistivity. The printed patterns obtained by reactive sintering for

60 and 90 min showed decrease of electrical resistivity values as  $76.27 \times 10^{-4} \Omega \text{ cm}$ , and  $2.29 \times 10^{-4} \Omega \text{ cm}$ , respectively. The minimal value of electrical resistivity was  $1.86 \times 10^{-4} \Omega \text{ cm}$  by reactive sintering time for 120 min. Therefore, the reactive sintering by formic acid vapor reduction at  $150^\circ\text{C}$  for 120 min is optimum condition to reduce silver ions to silver particles and then sintering of silver particles to contiguous pattern.

#### 5.4.2 Reactive Sintering of Ethylene Glycol Vapor Reduction

The ethylene glycol vapor was used as a reducing agent to prepare silver conductive pattern from silver nitrate solution printed pattern on polyimide substrate at  $250^\circ\text{C}$  for 15, 30, 45, and 60 min.

The reactive sintering steps can be explained. The ethylene glycol is evaporated to ethylene glycol vapor at  $197^\circ\text{C}$ . Silver nitrate solution melts at  $212^\circ\text{C}$  and form a smooth liquid surface. Ethylene glycol vapor can reduce liquid silver nitrate to silver particle. It can be seen the silver nitrate printed pattern change to light silver color on printed pattern.

The effect of reactive sintering time on morphology of silver pattern obtained by ethylene glycol vapor reduction at  $250^\circ\text{C}$  is shown in figure 5.13. The silver particles were observed on printed pattern after sintering for 15 min (figure 5.13a). These result suggest that the particles occur and growth rapidly. However, the particles could not form to contiguous pattern due to short sintering time. The silver particles coalesced in to the smooth and contiguous pattern after sintering for 30 min as shown in figure 5.13b. With increasing the reactive sintering time to 45 and 60 min, the silver particles were significant coarsening pattern due to the grain growth that resulting on the formation of clearance gab and porosity on silver pattern.

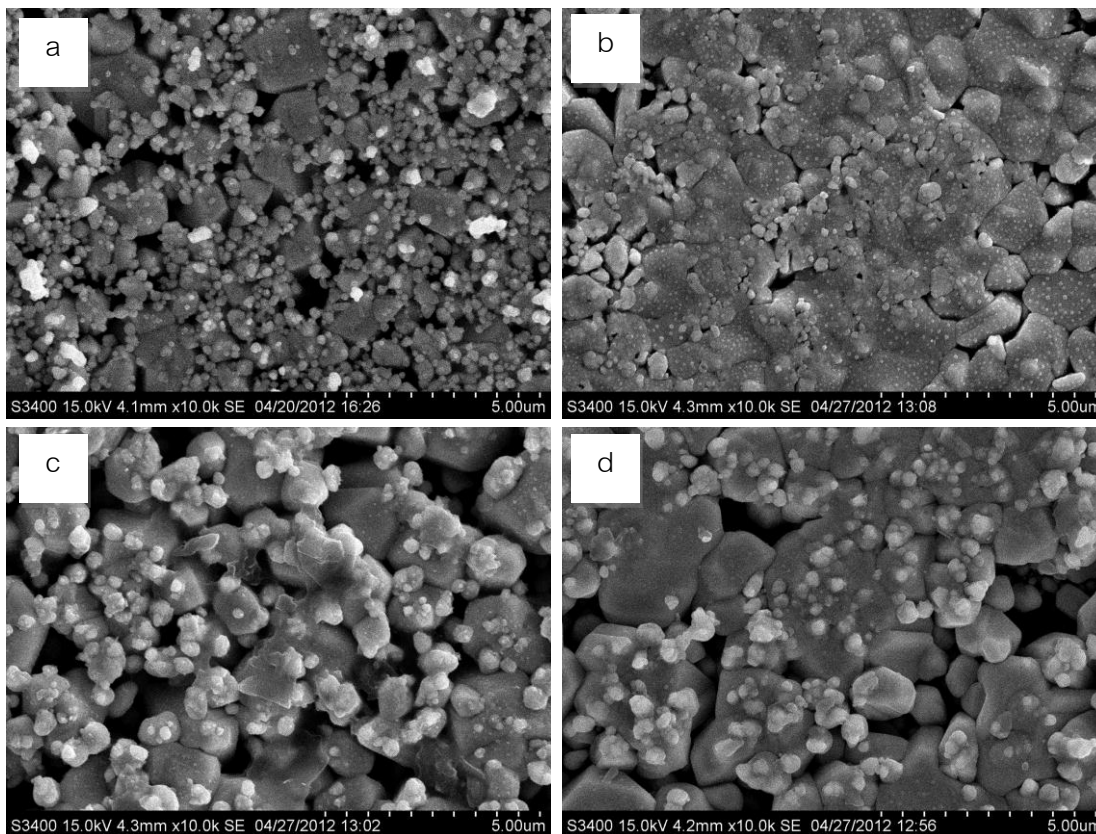


Figure 5.13 SEM images of morphology of silver printed pattern obtained by reactive sintering with ethylene glycol vapor at 250°C for (a) 15 min, (b) 30 min, (c) 45 min, and (d) 60 min.

Figure 5.14 and 5.15 show the EDS and XRD diffraction patterns of silver printed pattern obtained by ethylene glycol vapor reduction at 250°C for 30 min. The peak of silver is shown in the EDS pattern. In addition, the XRD diffraction pattern shows the peak characteristic of metallic silver at 38.06°, 44.26°, 64.37°, and 77.29°. They were detected to the face-centered cubic structure indicating that the silver is well crystallized. These results suggest that the silver ions were reduced by ethylene glycol vapor to silver particles.

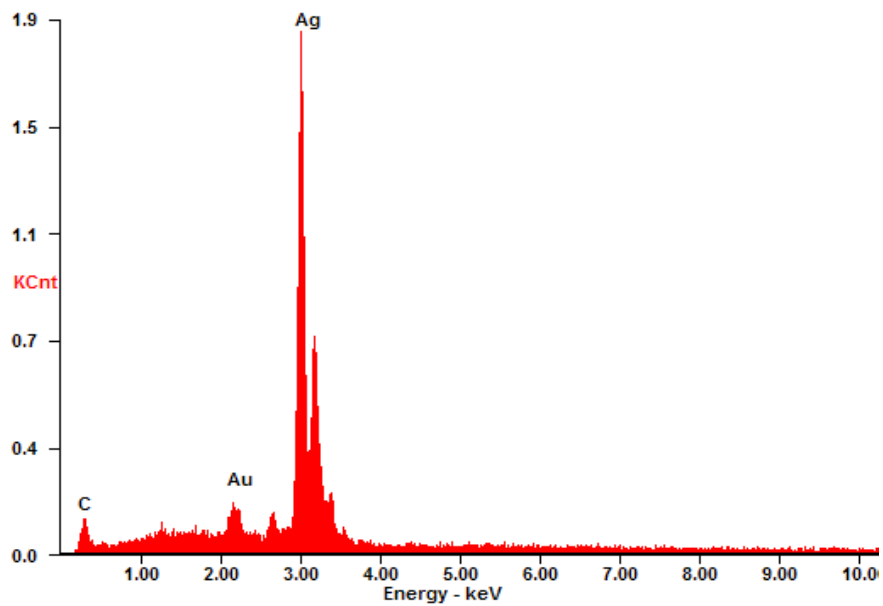


Figure 5.14 EDS pattern of silver printed pattern obtained by reactive sintering with ethylene glycol vapor at 250°C for 30 min.

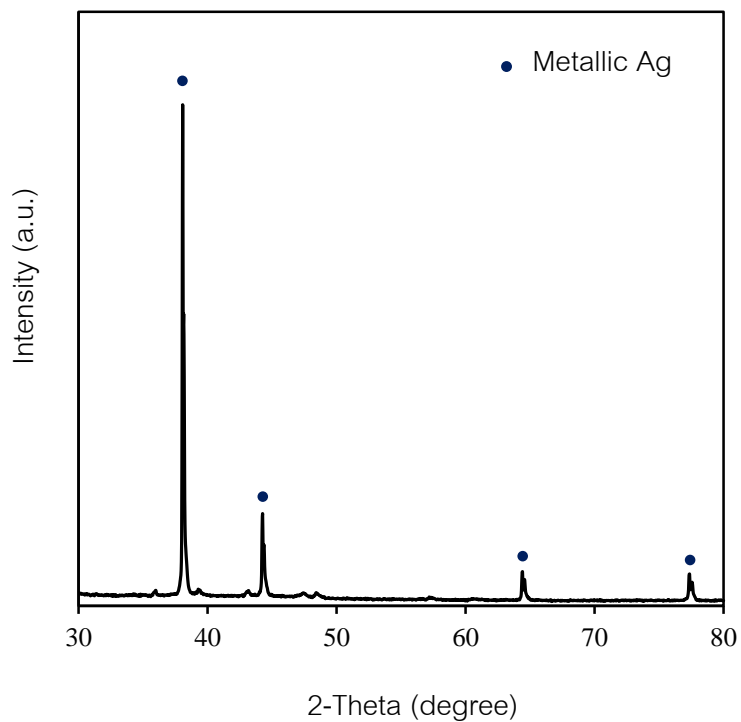
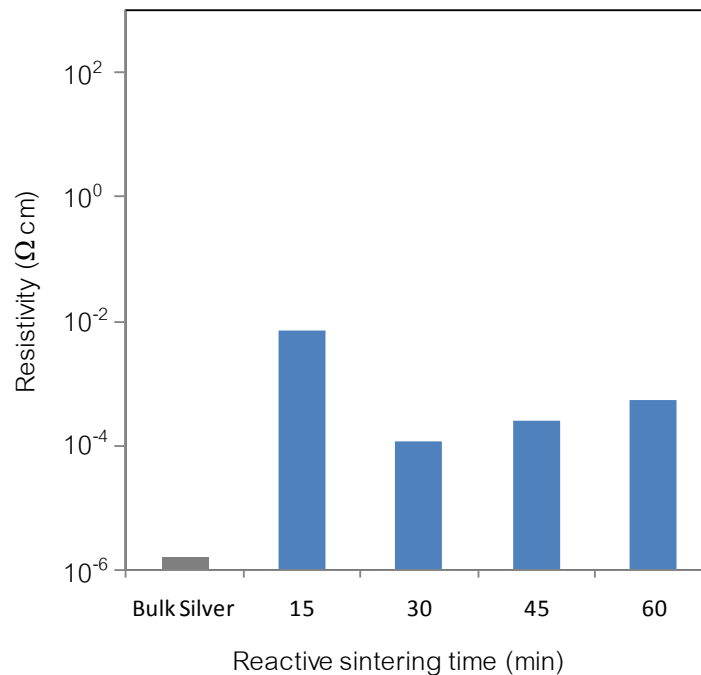


Figure 5.15 XRD pattern of silver printed pattern obtained by reactive sintering with ethylene glycol vapor at 250°C for 30 min.



**Figure 5.16** Effect of reactive sintering time on electrical resistivity of silver patterns obtained by glycol vapor reduction at 250°C

The effect of reactive sintering time on the electrical resistivity is shown in figure 5.16. The resistivity of silver printed pattern obtained by reactive sintering time for 15 min was  $7.12 \times 10^{-3} \Omega$  cm. The resistivity decreased to  $1.20 \times 10^{-4} \Omega$  cm by increasing reactive sintering time for 30 min. Next, the resistivity gradually increased to  $2.61 \times 10^{-4} \Omega$  cm and  $5.57 \times 10^{-4} \Omega$  cm by increasing reactive sintering time for 45 and 60 min, respectively. It could be explain that the resistance produced by particle contact is largely dependent on the contact resistance of particles. Therefore, the contact resistant between particles determined the electrical of the films [6]. In figure 5.15c and d, the clearance gabs and porous were observed, its cause be increasing the resistivity value of printed pattern.



Hence, the reactive sintering with ethylene glycol vapor at 250°C for 30 min is the optimum condition to reduce silver nitrate printed pattern.

### 5.5 PREPARATION OF COPPER LINES BY REACTIVE SINTERING

The preparation of copper line by reactive sintering process of copper salt printed pattern on polymer substrate was studied. The copper-amine complex was used as a copper salt solution. The solution was printed 10 times on polymer substrate. Then the printed pattern conducted to reactive sintering process of 3 methods that consist of formic acid vapor reduction at 150 °C for 90 min, ethylene glycol vapor reduction at 250 °C for 30 min and H<sub>2</sub> atmosphere at 200 °C for 60 min.

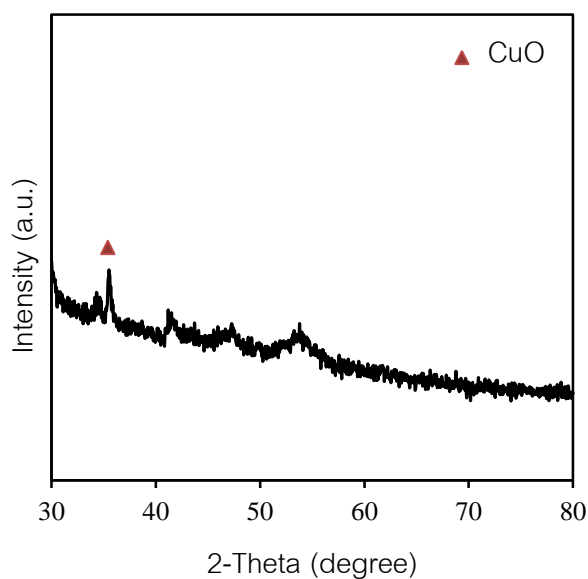


Figure 5.17 XRD diffraction pattern of copper pattern obtained by reactive sintering of formic acid vapor reduction at 150°C for 120 min

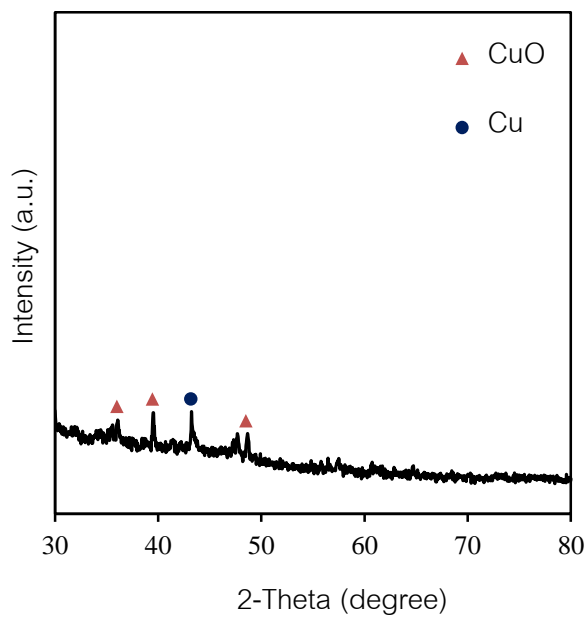


Figure 5.18 XRD diffraction pattern of copper pattern obtained by reactive sintering of ethylene glycol vapor reduction at 250°C for 30 min.

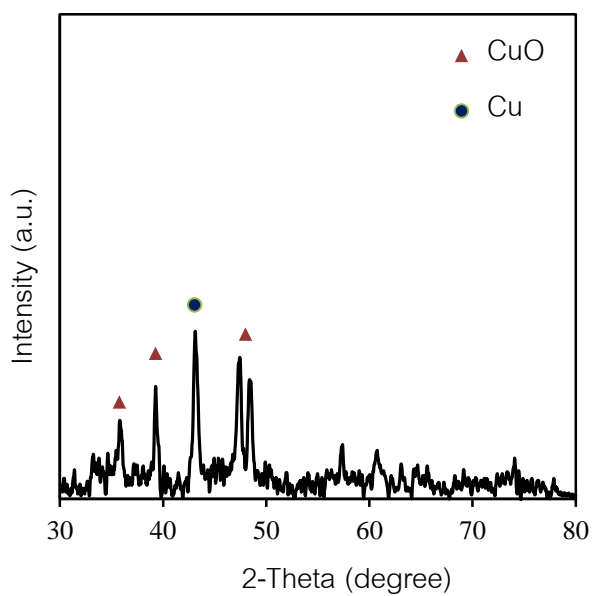


Figure 5.19 XRD diffraction pattern of copper printed pattern obtained by reactive sintering in H<sub>2</sub> atmosphere at 200°C for 60 min

Figure 5.17-5.19 show XRD diffraction pattern of copper line obtained by reactive sintering with formic acid vapor, ethylene glycol vapor and hydrogen atmosphere, respectively. The peaks of copper and copper oxide as secondary phase were exposed in the XRD patterns of copper printed patterns from figure 5.17-5.19. These results indicated that after the reactive sintering process, some of copper particles were oxidized by excess oxygen in atmosphere. Then, the particles were rapidly converted to copper oxide and formed in the printed pattern. Moreover, the non-contiguous patterns of copper lines after reactive sintering process was exhibited that caused by the small percentage of copper content in the solution. It was significant reason of easily transform copper particle to copper oxide.

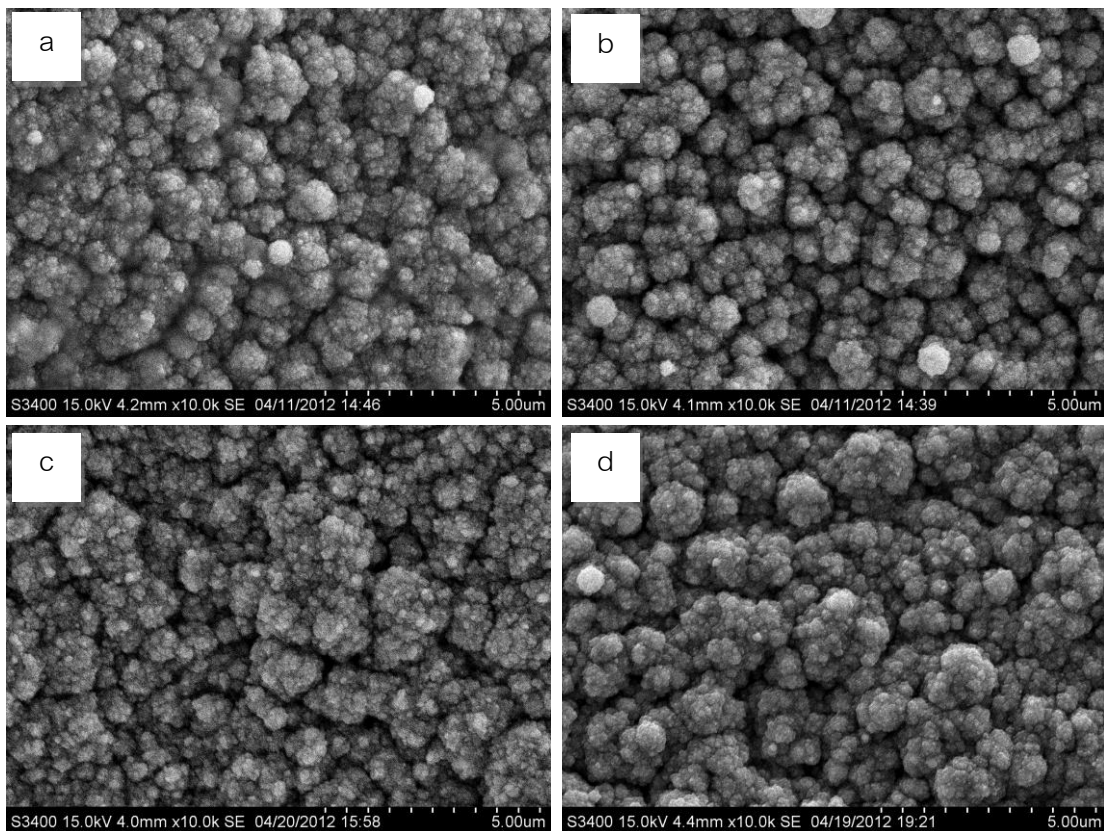
## 5.6 ELECTROLESS COPPER PLATING

The electroless plating, also known as autocatalytic plating, is a surface treatment technique exploiting the autocatalytic redox reaction between a metal salt and a reductant in the same solution to form metal coating on a catalytic surface in the absent of external current flow. Electroless copper plating is a very effective surface metallization method for the uniform deposition of copper ions on the surface of the substrate.

In this study, the silver printed pattern obtained by reactive sintering with formic acid vapor reduction at 150°C for 60 min and palladium printed pattern were used as catalytic seed layer.

### 5.6.1 Electroless Copper Plating on Silver Printed Pattern

The effect of electroless copper plating time on copper deposited lines pattern using silver as seed layer was investigated by SEM and AFM images. Additionally, the XRD diffraction pattern was used to confirm the copper deposition on the surface of silver seed layer.



**Figure 5.20** SEM images of copper deposited pattern obtained by electroless copper plating on silver seed layer for (a) 15 min, (b) 30 min, (c) 45 min, and (d) 60 min.

Figure 5.20 shows the morphology of copper deposited pattern on silver seed layer at different plating time. Many spherical of copper particles approximately grain sizes of 500-1000 nm were observed on copper deposited lines obtained by electroless copper plating for 15 and 30 min. The grain sizes of copper particles were increased to

1000-1500 nm for longer plating time of 45 and 60 min. It indicated that the grain size increased by increasing plating time. Additionally, the seed layer coverage seemed to be complete after 15 min deposition. This result can be ascribed to the deposition rate of electroless copper was fast by used the silver printed pattern as catalytic seed layer.

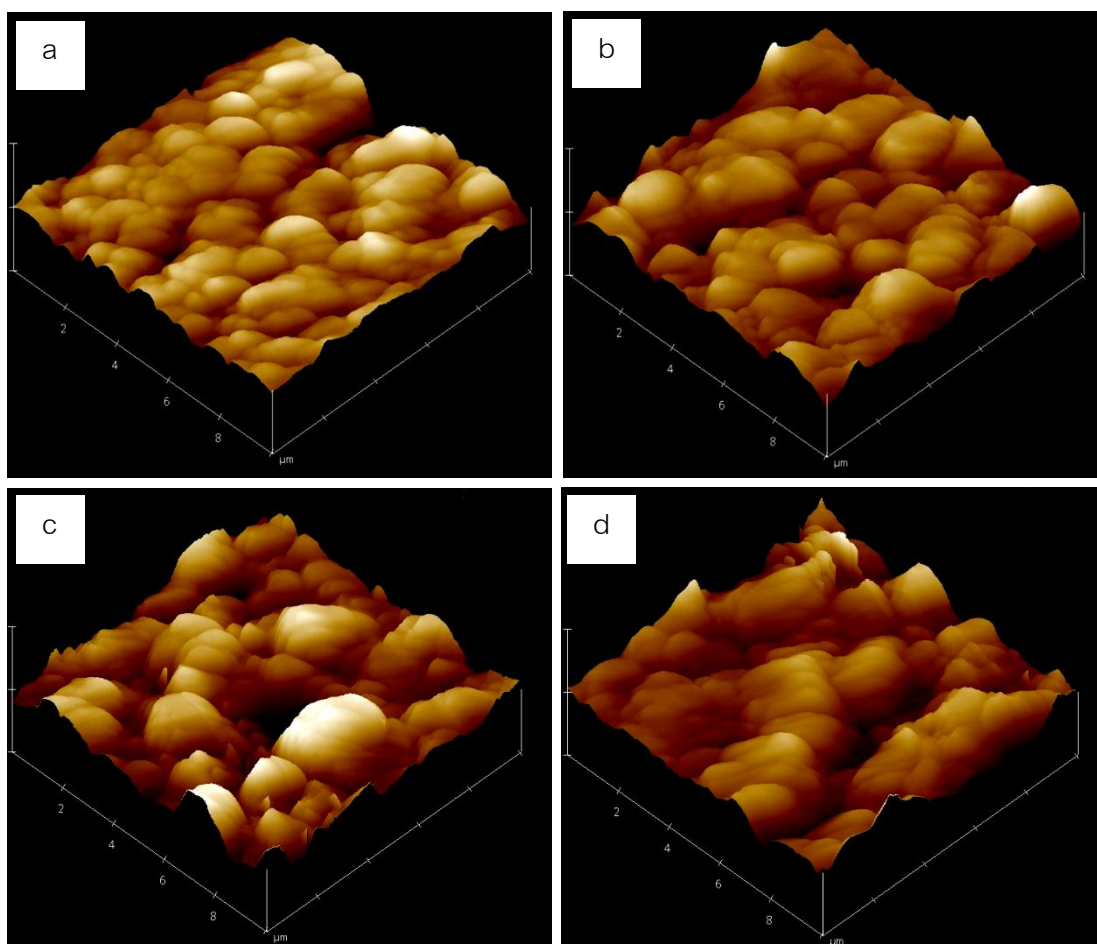
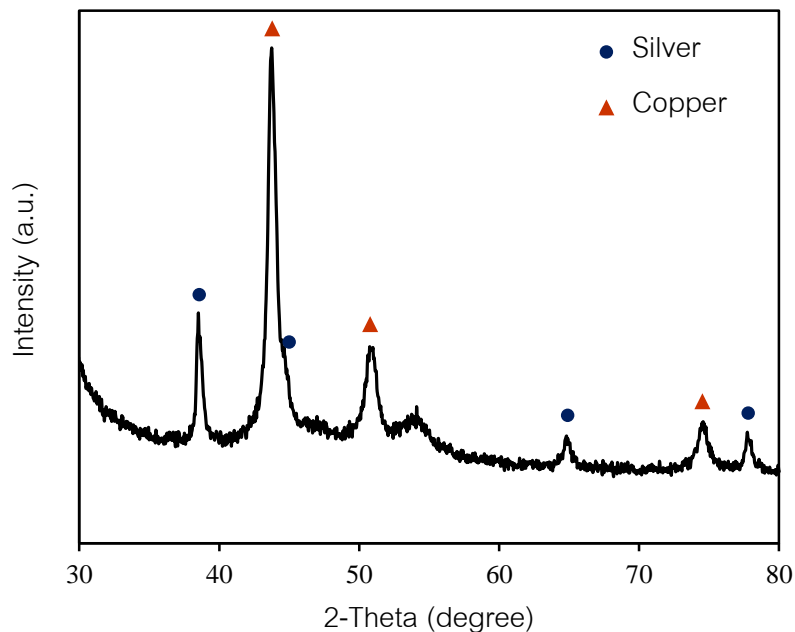


Figure 5.21 AFM images of copper pattern obtained by electroless copper plating on silver seed layer for (a) 15 min, (b) 30 min, (c) 45 min, and (d) 60 min.

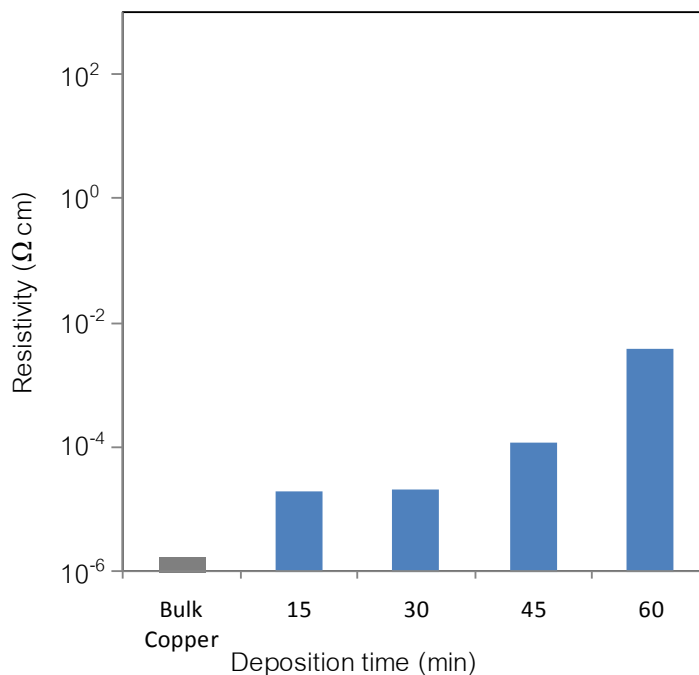
Figure 5.21 shows 3D image of surface roughness of copper deposited pattern prepared from electroless copper plating at different electroless plating time. The root mean square roughness ( $R_q$ ) of copper deposited lines was reported of 92.59 nm,

106.60 nm, 146.81 nm, and 121.27 nm at electroless plating time for 15 min, 30 min, 45 min, and 60 min, respectively. These results indicated that the copper deposited pattern obtained by electroless copper plating for 15 min was a smooth and uniform surface.



**Figure 5.22** XRD pattern of copper pattern obtained by electroless copper plating on silver seed layer at room temperature for 15 min.

Figure 5.22 shows the XRD diffraction of copper pattern prepared by electroless copper plating on silver seed for 15 min. The XRD pattern shows the strong peaks of copper particle at  $43.8^\circ$ ,  $50.8^\circ$  and  $74.5^\circ$  without copper oxides as secondary phase. In addition, the weak peaks of silver particle at  $38.2^\circ$ ,  $43.9^\circ$ ,  $64.4^\circ$  and  $77.3^\circ$  are shown in the XRD pattern because the silver line was used as catalytic seed layer.



**Figure 5.23** Effect of plating time on electrical resistivity of copper pattern obtained by electroless copper plating on silver seed layer.

The effect of electroless plating time on electrical resistivity of copper deposited pattern is shown in figure 5.21. The electrical resistivity of copper deposited pattern produced by electroless copper plating at room temperature for 15, 30, 45 and 60 min are  $0.19 \times 10^{-4} \Omega \text{ cm}$ ,  $0.21 \times 10^{-4} \Omega \text{ cm}$ ,  $1.19 \times 10^{-4} \Omega \text{ cm}$ , and  $36.67 \times 10^{-4} \Omega \text{ cm}$ , respectively. In this study, the lowest resistivity of copper pattern was  $0.19 \times 10^{-4} \Omega \text{ cm}$ , which is about 11.5 times of the resistivity of bulk copper ( $1.67 \times 10^{-6} \Omega \text{ cm}$ ).

### 5.6.2 Electroless Copper Plating on Palladium Printed Pattern

The palladium ion was printed five times on PET substrate. Then, it was dried and reduced by 0.1 M of  $\text{NaBH}_4$ . The palladium printed pattern was used as catalytic seed layers for electroless copper plating for 20, 40, and 60 min.

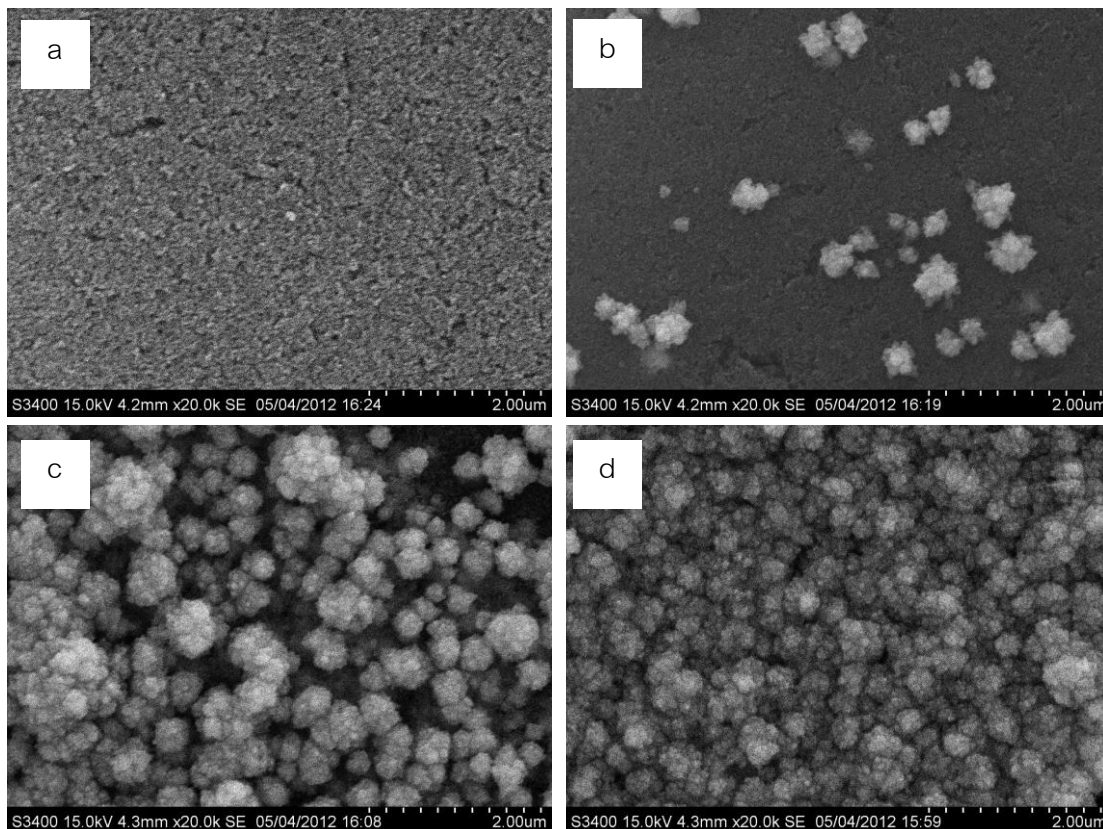
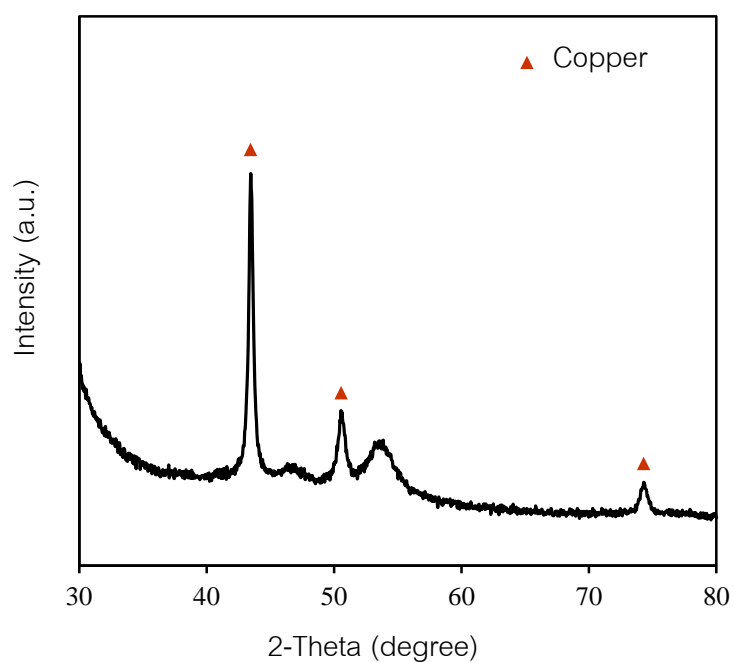


Figure 5.24 SEM images of (a) blank substrate; and copper pattern obtained by electroless copper pattern on palladium seed layer for (b) 20 min, (c) 40 min and (d) 60 min

Figure 5.24a shows the SEM image of bare substrate. The surface morphology images of copper patterns deposited at room temperature for 20 min, 40 min, and 60 min, respectively, are displayed in figure 5.24 b, c and d. In figure 5.24 b, it was seen that copper was initial deposited on the substrate surface. Figure 5.24 c and d show the images of surface morphology of copper patterns for longer plating time. It indicated that the deposition increase with the reaction time and a layer of film was formed on the substrate. However, the substrate was not covered completely by copper plating time for 60 min.





**Figure 5.25** XRD pattern of copper pattern obtained by electroless copper plating on palladium seed layer at room temperature for 60 min.

Figure 5.25 shows XRD patterns of copper deposition activated by palladium seed layer at room temperature for 60 min. The peaks of copper located at  $43.4^\circ$ ,  $50.5^\circ$  and  $74.3^\circ$  that were indicated the phase pure of metallic copper without copper oxides. The peaks of palladium and PET substrate are shown at  $46.0^\circ$  and  $52.9^\circ$ , respectively.

## CHAPTER VI

### CONCLUSIONS

#### 6.1 CONCLUSIONS

In this study, polyimide film surfaces were successfully modified to be more hydrophilic by oxygen plasma treatment. The enhancement of wettability was confirmed by decrease in the contact angles of the DI water droplet from 59° to 32° after the oxygen plasma treatment for 3 sec. The improvement in wettability of polyimide films can be explained by changes in the chemical bonds of polar groups on the polyimide film surfaces such as -OH, -COOH, and -C=O.

The reactive inkjet printing process could be synthesis silver conductive line by using silver nitrate as the silver precursor and L-ascorbic acid as the reducing agent. The effect of printing cycle and silver nitrate concentration on silver printed patterns was studied. The silver contiguous pattern was synthesized on the PET substrate by increasing the number of printing cycle. The resistivity of the silver line obtained by 15 printing cycles of 5 M silver nitrate solution was  $4.62 \times 10^{-4} \Omega \text{ cm}$  and this is lower than the silver line obtained by 10 and 5 cycles. Additionally, the silver nitrate concentration affected on the size of silver particle and particle content of the printed pattern. The large particles and contiguous pattern were observed when increasing the concentration of silver nitrate solution. The silver pattern obtained by 5 M solution and 5 printing cycle was shown non-contiguous and no conductivity value. The silver patterns became contiguous and thick by using 7 M and 10 M solution. The resistivity of the silver patterns obtained by using 7 M solution was  $10.67 \times 10^{-4} \Omega \text{ cm}$ . The resistivity was gradually increased in the silver printed pattern produced by using 10 M solution because of the formation of porosity on the printed

pattern. So, reactive inkjet printing using low concentration of silver nitrate with high number of printing cycles yields a smooth pattern with low resistivity.

The reactive sintering by using formic acid vapor reduction could be successfully synthesized silver pattern at low temperature of 150°C on PET substrate. The silver nitrate printed pattern was completely reduced and formed contiguous and smooth pattern of silver metal after sintering time in range of 90 to 120 min. The electrical resistivity decreased with increasing reactive sintering time and shown minimal value as  $1.86 \times 10^{-4} \Omega \text{ cm}$  after sintering for 120 min. Additionally, silver conductive pattern was synthesized on PI substrate by reactive sintering in ethylene glycol vapor at 250°C for 15 to 60 min. The silver nitrate printed pattern was rapidly reduced and converted to silver particle after short sintering time. The contiguous and smooth pattern of silver was observed after sintering for 30 min that was shown the lowest resistivity of  $1.20 \times 10^{-4} \Omega \text{ cm}$ . The electrical resistivity of silver patterns slightly increased after sintering for 45 and 60 min due to the formation of clearance gap between the grains.

**Table 6.1** The electrical resistivity of silver patterns was synthesized from reactive inkjet printing and reactive sintering.

Sample	Methodology	Resistivity ( $\Omega \text{ cm}$ )
Silver	Reactive inkjet printing of $\text{AgNO}_3$ 7 M, 5 cycles	$10.67 \times 10^{-4}$
Silver	Reactive sintering with formic acid vapor at 150°C for 120 min	$1.86 \times 10^{-4}$
Silver	Reactive sintering with ethylene glycol vapor at 250°C for 30 min	$1.20 \times 10^{-4}$

Table 6.1 shows the electrical resistivity of silver patterns obtained by reactive inkjet printing and reactive sintering. In a comparison, the resistivity of the silver pattern obtained by reactive sintering is lower than the silver pattern obtained by reactive inkjet printing.

Thus, the reactive sintering process gives more smooth and contiguous pattern resulting in lower resistivity.

The reactive sintering of copper salt solution on polymer substrate by using formic acid vapor at 150°C, ethylene glycol vapor at 250°C, and H<sub>2</sub> atmosphere at 200°C were found to be a promising method to fabricate copper conductive line. The copper amine complex solution was selected as copper salts solution that was synthesized by electrolytic method. After reactive sintering process, the copper and copper oxide phases were exposed in line patterns. The copper line was shown no conductivity value. The main difficulty in all reactive sintering of copper salt solution was that copper oxidation occurred after the reactive sintering process. To ensure that copper metal production was the main outcome, it would be necessary to control copper oxide formation and this would add technical complexity to the process such as a nitrogen atmosphere would be required. Additionally, the copper content in the copper salt solution should be increased in order to make contiguous line patterns of copper.

The copper conductive line patterns on PET substrate have been successfully fabricated by electroless copper plating at room temperature. The electroless copper plating on silver seed layer was shown contiguous and smooth copper deposited line. The resistivity of copper deposited line after 15 min electroless plating time was  $1.92 \times 10^{-5}$ , which is relatively close to the resistivity of bulk copper ( $1.67 \times 10^{-6} \Omega \text{ cm}$ ). In contrast, the electroless copper plating on palladium layer at room temperature for 60 min, the copper particle deposited on palladium printed line but it was not completely covered on the substrate and the copper deposited line was shown no conductivity value.

## 6.2 RECOMMENDATIONS

The effect of temperature in reactive sintering of silver nitrate would be study to find the optimum temperature that produce low resistance silver conductive line.

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## VITA

Miss Kamolrat Foithong was born on July 20, 1987 in Bangkok, Thailand. She graduated high school from Bangpakok Wittayakom school in 2005 and received the bachelor degree of engineering in chemical engineering at King Mongkut's University of Technology Thonburi. After graduation, she immediately pursues her graduate study for a master degree in chemical engineering at Chulalongkorn university.