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ปีการศึกษา 2554

COMPARISON BETWEEN ELECTROPLATING AND ELECTROLESS PLATING METHOD WITH INKJET PRINTING FOR CONDUCTIVE LINE PATTERNING

Miss Wanida Tunyong

A Thesis Submitted in Partial Fulfillment of the Requirements

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วนิดา ตันยั่ง : การเปรียบเทียบระหว่างวิธีอิเล็กโตรเพลทติ้งและวิธีอิเล็กโตรเลสเพลทติ้งร่วมกับการพิมพ์แบบอิงค์เจ็ทเพื่อสร้างเส้นนำไฟฟ้า (Comparison Between Electroplating and Electroless Plating Method with Inkjet Printing for Conductive Line Patterning) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.สุรเทพ เขียวหอม, 55 หน้า.

งานวิจัยนี้ใช้เทคนิคการสร้างเส้นนำไฟฟ้าด้วยวิธีการพิมพ์หมึกเงินเพื่อเป็นสื่อนำไฟฟ้าร่วมกับวิธีอิเล็กโตรเพลทติ้งและวิธีอิเล็กโตรเลสเพลทติ้ง โดยจะเริ่มพิมพ์หมึกนำไฟฟ้าที่มีอนุภาคนาโนของเงินที่ความเข้มข้น 15% 25% และ 35% ด้วยเครื่องพิมพ์แบบอิงค์เจ็ทบนผิวของโพลีเอทิลีนเทอพาทาเลท (PET) แล้วนำไปซินเทอริ่งด้วยวิธีการอบที่อุณหภูมิ 150 องศาเซลเซียส เพื่อศึกษาผลของความเข้มข้นในหมึกนำไฟฟ้าก่อนและหลังขั้นตอนการซินเทอริ่งที่เหมาะสมสำหรับการเป็นสื่อนำไฟฟ้า จากนั้นนำแผ่นฟิล์มที่ได้ไป ทำการอิเล็กโตรเพลทติ้งและอิเล็กโตรเลสเพลทติ้งทองแดงที่ด้านบนของเส้นเงินนำไฟฟ้า โดยศึกษาความต่างศักย์ไฟฟ้าและเวลาในการทำเพลทติ้งในแต่ละวิธี เพื่อศึกษาสภาพความต้านทานไฟฟ้า ลักษณะโครงสร้าง ลักษณะพื้นผิวและโครงสร้างผลึก รวมทั้งศึกษาการยึดเกาะระหว่างโลหะและพื้นผิวและค่าความลึกต่อความกว้าง (aspect ratio)ของเส้นนำไฟฟ้าอีกด้วย โดยเครื่องมือที่ใช้ในงานการศึกษานี้ คือ เครื่องวัดค่าความต้านทานไฟฟ้าแบบโพรบสองเข็ม(two-point probe) กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด(SEM) เครื่องวิเคราะห์การเลี้ยวเบนของรังสีเอกซ์ (XRD) และกล้องจุลทรรศน์แรงอะตอม (AFM)

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต

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WANIDA TUNYONG: COMPARISON BETWEEN ELECTROPLATING AND ELECTROLESS PLATING WITH INKJET PRINTING FOE CONDUCTIVE LINE. ADVISOR: ASST. PROF. SOORATHEP KHEAWHOM, Ph.D., 55 pp.

In this thesis, the conductive lines were fabricated by combination of inkjet printing with electroplating and electroless plating method. The conductive lines of silver nanoparticles ink were written by drop-on-demand piezo electric. Then, heat treatment at 150°C was performed. Electroplating was carried out to form a copper layer on top of the silver pattern previously printed. We investigated the effects of metal content in silver nanoparticles ink, and determined the optimal metal loading with appropriate electrical resistivity and surface roughness to be used as seed layer. Moreover, the effect of voltage and plating time applied in electroplating process, and the effect of plating time applied in electroless plating at pH 7 were also studied. The conductive lines fabricated were characterized by a two-point probe, scanning electron microscope with energy dispersive x-ray microanalyzer, x-ray diffractrometer (XRD) and atomic force microscopy (AFM) to confirm the electrical resistivity, microstructure, crystal structure, shape, surface property, adhesion between metal and substrate and aspect ratio.

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LIST OF ABBREVIATIONS

Ag	Silver
Cu	Copper
SEM	Scanning electron microscope
AFM	Atomic force microscope
XRD	X-ray diffraction Analysis

CHAPTER I

INTRODUCTION

1.1 General introduction

The Printing technologies are promising technologies to fabricate low-cost flexible electronic devices. Recently, most conventional printing methods have been applied in the production of inexpensive electronics, such as radio frequency identification (RFID) tags, organic light emitting diodes (OLEDs), batteries and sensors and many more products. Inkjet printing is one of the patterning technique are widely used due to the simple process and alternative designs.

A typical application involves the ink-jet printing of conductive line, for example, by using inks based on organic silver or copper precursors. The precursor is reduced to the corresponding metal via a post-printing sintering step. In most cases, the ink is a dispersion of metal nanoparticles, usually silver [18]. A sintering step is necessary to provide the large grain size and brightness. The use of nanoparticles reduces the sintering temperature due to their high surface to volume ratio.

Currently, the most commonly used conductive ink is silver ink that used most frequently on account of their high electrical conductivity and chemical stability. The silver ink is printed as silver nanoparticles, and the pattern printed is then sintered at a low temperature to avoid degradation of the substrate [15]. However, the silver nanoparticles inks are expensive. A copper nanoparticles is a desirable alternative but, it is not usually used due to its tendency to oxidize in ambient condition, resulting in poor conductivity. Consequently, a more complex printing, reduction and sintering process would be needed [13, 19]. Therefore, a combination technique of inkjet printing to prepare “seed” layer on flexible substrate defining a pattern for electroless plating or electroplating which the application of metallic coatings to metallic or other conductive surfaces by electrochemical processes.

Metal plating on polymer substrate is particularly interesting because it directly relates to high conductivity, ordinary process, and transparent device application. The process is regulated by controlling a variety of parameters, including the voltage and amperage, temperature, residence times, and the composition of bath solutions.

In this research, we investigate the techniques to increase the conductivity of pattern. The effects of metal content of silver nanoparticles ink where printed at room temperature on PET substrate are investigated. We also study the surface roughness, morphology and electrical properties of the electroplated of copper depend on the processing variables, such as applied voltage and plating time. This process is used to improve the conductivity of the pattern. However, the electroplating process is too complicated to be used in industrial. The electroless plating have been developed [8, 9, 10]. It enables large scale deposition of copper on flexible substrate with complex patterns. The copper electroless plating solution consists of DMAB as a reducing agent for copper metallization, and EDTA as complexing agent [11].

The depositing lines fabricated after plating process were characterized by a two point probe, scanning electron microscope with energy dispersive x-ray-microanalyzer, x-ray diffractrometer (XRD) and atomic force microscopy (AFM) to confirm the resistivity, microstructure, crystal structure, shape and surface property.

1.1 Objectives of the research

1.2.1 To fabricate the conductive line patterned by inkjet printing and electroplating.

1.2.2 To fabricate the conductive line patterned by inkjet printing and electroless plating.

1.2 Scopes of the research

The research has been scoped as follows :

1.3.1 Epson t6o is the printer used in printing procedure

1.3.2 The substrate is resin coated polyethylene terephthalate (PET).

1.3.3 The conductive ink is silver nanoparticles at 15%, 25% and 35% of silver loading (commercial grade).

1.3.4 To print the desired pattern by inkjet printing method: two point- probe.

1.3.5 Study of the relation between silver loading (%) and resistivity of printed film.

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1.3.11 Eletroless copper plating evaluate as a function of immersed time.

1.3.12 Examine the aspect ratio and peel strength of deposited copper layer.

1.3.13 Characterize the printed pattern and deposited copper layer by a two-point probe, scanning electron microscope with energy dispersive x-ray microanalyzer, x-ray diffractrometer (XRD), and atomic force microscopy (AFM) to analyze the resistivity, microstructure, morphology, and crystal structure.

CHAPTER II

THEORY

2.1 Introduction to printed electronic

According to the printed electronics technology, innovation in printed electronics is occurring alongside wider developments in organic and thin-film electronics.

The biggest potential lies in organic or combined organic/inorganic structures because they often promise the lowest costs, allied to the fastest printing technology. Inkjet is also a most popular choice because of its flexible and simple process. Besides the obvious applications of flexible electronics in flat panel displays, flexible circuits are also promising for use in such applications as radio frequency identification (RFID) tags, low cost sensors, and other disposable electronic devices.

Printed electronics creates electrically functional devices by utilizing of traditional printing processes and broad range of substrates. So far the most common substrates are polymer films, ceramics, glass and silicon. Printing of functional devices on paper is also possible. In contrast to the terms organic electronics, printed electronics can utilize any solution-based material, including organic semiconductors, metallic conductors, nanoparticles, nanotubes etc [16].

In other words, printed electronic devices comprise solution-processable electronic materials deposited with a printing method. Printing processes include processes well known from the graphics art industry such as screen printing, flexography, gravure, offset lithography and inkjet. With printed electronics functional electronic or optical inks are used to print active or passive devices, such as transistors or resistors. Examples of printed electronics components include e.g. electrodes comprising printed metal particle ink, carbon ink or conductive polymers or diodes and transistors comprising printed organic semiconductor and dielectric layer.

Compared to conventional microelectronics, printed electronics is characterized by simpler and more cost-efficient fabrication of both high and low volume products. It enables roll-to roll fabrication and the processes employed to manufacture printed electronics also are more flexible, enabling shorter production runs. Very small series, customized or even unique products are possible through a digital printing process. Another advantage is its processing at low temperatures. The substrate is a solution which is printable and coatable enabling also flexible products. The additive processes might prove to be more environmentally friendly. Despite its many benefits, to date the performance of printed electronics in terms of the actual function and performance is reduced compared to that of conventional electronics. It is therefore believed that printed electronics will complement, rather than compete with silicon based electronics.

Printed electronics is expected to be useful for applications for low performance but also low-cost electronics. The applications will be also new electronics products for traditionally non-electronic applications such as smart labels, decorative and animated posters, and active clothing. They are also targeting large area products, flexible products, non-flat shaped products such as flexible displays and sensor walls.

2.2 Inkjet printing technology

The attraction of printing technology for the fabrication of electronics mainly results from the possibility to prepare stacks of microstructure layers in a much more simple and cost effective way compared to conventional electronics. Beside this, also the possibility to implement new or improved functionalities plays a role. The selection of used printing methods is determined by requirements concerning printed layers, by properties of printed materials as well as economic and technical considerations in terms of printed products.

Printing technologies divide between sheet-based and roll-to-roll-based approaches. Sheet-based techniques, such as inkjet and screen printing are best for low-volume, high-precision work. Gravure, offset and flexographic printing are more common for high-volume production. While offset and flexographic printing are mainly used for inorganic and organic conductors (the latter also for dielectrics), gravure printing is especially suitable for quality-sensitive layers like organic semiconductors and semiconductor/dielectric interfaces in transistors, due to high layer quality. In connection with high resolution, is also suitable for inorganic and organic conductors. Organic field-effect transistors and integrated circuits can be prepared completely by means of mass-printing methods.

Inkjets are flexible and versatile, and can be set up with relatively low effort. Inkjets are probably the most commonly used method. However, inkjets offer lower resolution. It is well suited for low-viscosity, soluble materials like organic semiconductors. With high-viscosity materials, like organic dielectrics, and dispersed particles, like inorganic metal inks, difficulties due to nozzle clogging occur. Because ink is deposited via droplets, thickness and dispersion homogeneity is reduced. Simultaneously using many nozzles and pre-structuring the substrate allows improvements in productivity and resolution, respectively. However, in the latter case non-printing methods must be employed for the actual patterning step. Inkjet printing is preferable for organic semiconductors in organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs), but also OFETs completely prepared by this method have been demonstrated. Front-planes and backplanes of OLED-displays, integrated circuits, organic photovoltaic cells (OPVCs) and other devices can be prepared with inkjets.

Screen printing is appropriate for fabricating electrics and electronics on industrial scales due to its ability to produce thick layers from paste-like materials. This method can produce conducting lines from inorganic materials, but also insulating and passivating layers, whereby layer thickness is more important than high resolution. Its 50 m^2/h throughput and 100 μm resolution are similar to inkjets. This versatile and comparatively simple method is used mainly for conductive and dielectric layers.

2.2.1 Conductive ink

Conductive inks are typically made of metallic particles such as silver or copper flakes in a retaining matrix, or carbon flakes/particles in a retaining matrix. Carbon is typically 2 magnitudes less conductive compared to metals but cheaper. Traditionally, the matrix was a ceramic such as glass frit, but now increasingly it is a polymer.

The retaining matrix is not conductive or weakly conductive once printed the matrix needs to be reduced so that conductance through the material occurs by conductive particles in contact with each other, which is done by curing. Curing can be performed by UV or temperature. For example, ceramic mixtures need high cure temperatures, such as 650 degrees Celsius for several minutes. This results in the need for a tough and expensive substrate. PTF mixtures have lower cure requirements such as 150 degrees Celsius and can therefore use cheaper substrates such as PET. However, curing temperatures depend on the ink formulation; some dry quickly at room temperature which is sufficient for some applications, such as the RFID tag antennas ink formulations mean that curing is just one factor in the final bulk conductivity of the printed ink.

Carbon based inks, which are only weak conductors, have typically been used for EMI/RF shielding, such as on monitor screens and speakers. Metallic based inks are commonly used for membrane switches and circuits, and now increasingly for RFID tag antennas. In the case of RFID, the conductivity of metal particle inks is typically more than sufficient so curing can be done at relatively low temperatures for a few seconds using a heated press is sufficient. Other applications include the use of conductive ink for connections on smart blister packs, which record when a pill is popped (because a circuit is broken), and for tamper evidence packs which work on a similar principle. As another example, tens of millions of printed battery testers have been sold, based on a conductive ink.

2.2.2 Substrate

Printed electronics allows the use of flexible substrates, which lowers production costs and allows fabrication of mechanically flexible circuits, mass printing methods nearly exclusively use flexible foil and paper. Polyethylene terephthalate (PET) is a common choice, due to its low cost and higher temperature stability. Other important substrate criteria are low roughness, high porosity and suitable wettability, which can be tuned pre-treatment [12, 17] such as coated resin and plasma treatment.

Porosity: The measurement of the porosity-related characteristics of a material. These characteristics include pore size, volume, distribution and density.

Wettability: The contact angle of the conductive ink with each substrate was determined using the First Ten Angstroms Dynamical Contact Angle Tensiometer. The tensiometer works by dispensing a single drop of a chosen liquid from a syringe onto a strip of the sample substrate. The camera takes a picture of this sessile drop and the image is analyzed by computer software. A low contact angle indicates high wettability.

Roughness: The roughness of the substrate was determined using AFM or SEM. The substrate should be low roughness, however the adhesive were poor between conductive ink and substrate.

2.2.3 Drop on demand printing

The principle of inkjet printing, printhead used to create small particle ink and eject by nozzle on desired position. There are two type of inkjet system

1. Continuous ink jet system, This technique of printing to be ejected at any time. *Ink toner* particles are charged by the Charge electrode for the ink to be forced to move. After that, Deflection plate to deal with deviations on the substrate in the desired position

2. Drop on demand system, utilizes the piezo electric effect to eject accurate and consistent quantities of fluids. This technique of technologies creates only the ink drops that are "demanded" to print the message and consists of a series of ink chambers with shared channel walls. Voltage is applied to the piezo material, changing its shape which in turn forces the ink out through a micro-orifice. Piezo technology can produce up to 20,000 drops per second and gives very high print resolution.

2.2.4 Applications

There are many applications in printed electronics that move from the lab to production.

- Radio frequency identification (RFID) tags and antennas.

- Organic light emitting diodes (OLEDs)
- Thin film photovoltaics (PV)
- Printed batteries
- Sensors
- greeting card and toys

2.3 Electroplating Process

Electroplating is a plating process in which metal ions in a solution are moved by an electric field to coated an electrode. The process uses electrical current to reduce cat ions of a desired material from a solution and coat a conductive object with a thin layer of the material, such as a metal. Electroplating is primarily used for depositing a layer of material to bestow a desired to a surface that otherwise lacks that property. Another application uses electroplating to build up thickness on undersized parts.

The process used in electroplating is called electrode position. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be placed on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A power supply supplies a direct current to the anode, oxidizing the metal atoms that comprise it and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, vis-a-vis the current flowing through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode.

The anode and cathode in the electroplating cell are both connected to an external supply of direct current a battery or, more commonly, a rectifier. The anode is connected to the positive terminal of the supply, and the cathode is connected to the negative terminal. When the external power supply is switched on, the metal at the anode is oxidized from the zero valence state to form cations with a positive charge. These cations associate with the anions in the solution. The cations are reduced at the cathode to deposit in the metallic, zero valence state. For example, in an acid solution, copper is oxidized at the anode to Cu^{2+} by losing two electrons. The Cu^{2+} associates with the anion SO_4^{2-} in the solution to form copper sulfate.

At the cathode, the Cu^{2+} is reduced to metallic copper by gaining two electrons. The result is the effective transfer of copper from the anode source to a plate covering the cathode.

Figure 2.1 is a scheme of the electroplating of copper in the aqueous solution of copper sulfate ($CuSO_4$). This process of coating copper deposition on cathode site, when the anode is made of the copper material, which is dissolved into the solution of copper sulfate in form of the metal ions, traveling through the solution and depositing on

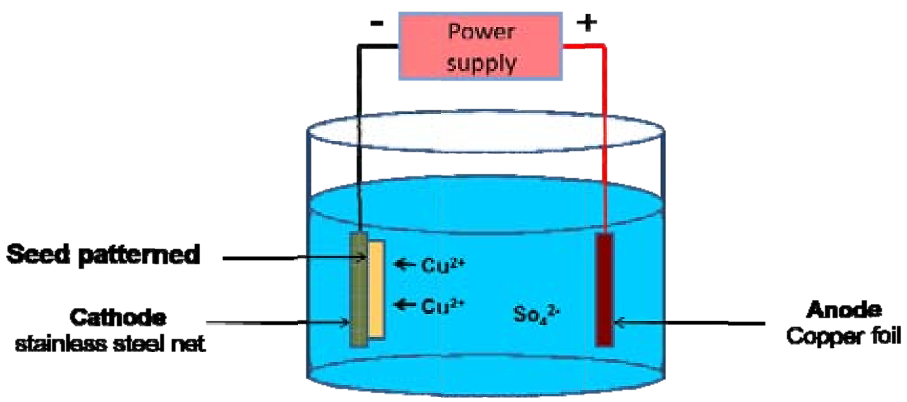


Figure 2.1 A scheme of the copper electroplating

the cathode surface. Positively charged copper ion moves towards the negative cathode and when it reaches the cathode surface it accepts two electrons, converts to the copper atom and deposits on the cathodes surface

2.4 Electroless plating Process

Electroless plating [20] of metal is an important industrial technique for depositing a metal on desired substrate. Electroless deposition is a catalytic electrochemical process through which a metal ion in solution is reduced to its metallic state, on a catalytic surface, by a reducing agent. The reductant acts as an electron donor, so no external power supply is necessary in order to reduce the metal ions. This last point means that the process can occur on nonconductive surfaces, as well as on metals and semiconductors. A schematic of the electroless deposition reaction can be seen in Figure 2, where the reducing agent goes from its reduced (red) to its oxidized (ox) form, providing the electrons needed to reduce the metal ion (M^{n+}) to its metallic state (M). The process is initially catalyzed by the substrate (S).

In many cases, metal nanoparticles are used to start the reaction. As the plating proceeds, the deposited metal can also be autocatalytic for the deposition process, as seen in the lower part of Figure 2. This metallization method was first studied

A wide range of applications has been found for electroless plating, including the preparation of chip interconnects and other devices in electronics, and batteries. It is used to produce thermic and electric conductors, as well as anticorrosion and decorative coatings. More recently, electroless deposition has been used in the metallization of carbon nanotubes and the formation of metal nanoparticles and nanowires.

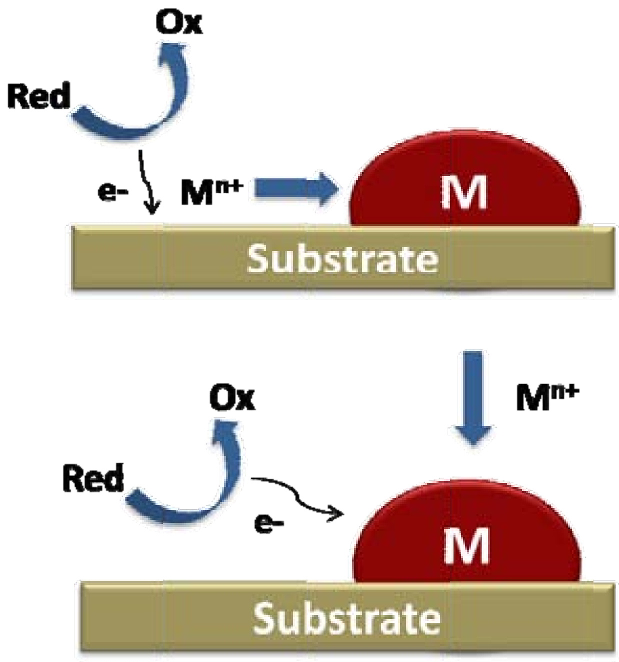


Figure 2.2 A scheme of the electroless plating (up : surface catalyzed, and down: autocatalytic)

A wide range of applications has been found for electroless plating, including the preparation of chip interconnects and other devices in electronics, and batteries. It is used to produce thermal and electric conductors, as well as anticorrosion and decorative coatings. More recently, electroless deposition has been used in the metallization of carbon nanotubes and the formation of metal nanoparticles and nanowires.

There are several advantages to using electroless deposition methods over other metallization processes such as physical and chemical vapor deposition or electro deposition techniques; it is a low cost technique which produces high quality films and can be easily incorporated into large scale processes, while not requiring excessively high temperatures of operation. Electroless plating is also a highly selective process, which plates well on complex-shaped substrates and nonconductive surfaces, such as glass, ceramics and polymers.

Electroless plating baths have very complex chemistry; other than the source of the metal ions and the reducing agent, they also include complexing agents and additives, which can be stabilizers or inhibitors. The complexing agents can act as buffers and prevent precipitation of the metal as hydroxides or other salts, as well as allowing some control over the stability of the bath and rate of reaction.

Several common reducing agents have been used in electroless plating baths such as formaldehyde, diamethylamine borane (DMAB), borohydride, hypophosphite and hydrazine. Formaldehyde is widely used as the reductant. They show high deposition rate, long electrolyte stability and film electrical properties and mechanical characteristics. However, formaldehyde has volatility, toxicity and requires a very high pH value. A hypophosphite is very stable based on plating bath, does not give dangerous fumes and can be used at lower pH. However, adding of nickel ions must exist in hypophosphite-based bath that used to co-deposit onto the copper film. Because the copper deposited cannot catalyze the oxidation of hypophosphite. This adding is decreasing film conductivity.

In most cases, to overcome the degradation effects caused by the high pH used, which leads to the poor adhesion of copper to the substrate. We propose the use of a low-pH electrolyte that does not hinder film adhesion during deposition and decreases the number of steps required. One of the reducing agents that functions at lower pH levels is dimethylamine borane (DMAB). It was stated that the copper obtained was of superior quality, having a higher conductivity and low roughness compared to the film deposited with hypophosphite

Physical properties of the metal deposits produced through electroless plating, such as resistivity, thickness, morphology, purity, adherence or ductility, depend on many factors, other than simply the identity of the metal being deposited. Bath composition, temperature, reaction rate and the catalytic substrate are amongst the variables that can influence the characteristics of the deposits, which often also include the co-production of hydrogen during the process. The plating rate and its efficiency have generally been found to be dependent on a number of factors, such as the nature of the catalytic surface, pH, temperature and bath composition, with the initial stages of the process being critical. [1]

A major benefit of this approach over electroplating is that power sources and plating baths are not needed, reducing the cost of production. The technique can also plate diverse shapes and types of surface. The downside is that the plating process is usually slower and cannot create such thick plates of metal.

CHAPTER III

LITERATURE REVIEWS

Printing techniques such as inkjet printing, gravure printing and screen printing are advantages in electronic field because of their cost reduction and wide range in electronic device. Inkjet printing technology is most interesting due to the ease of production, flexibility, low cost, and carries out without complicated process. There are many importance keys of inkjet printing for example, conductive ink, flexible substrate, and sintering method which necessary used to reduce the metallic particles on substrate.

The conductive ink is using metal nanoparticles dispersed in capping molecule which protect the agglomeration and oxidization of metal nanoparticles. A metallic silver nanoparticle is almost use in printed electronic field due to its chemical stability and low sintering temperature.

Many researches are investigated an alternate method to fabricated the Ag conductive line or film by inkjet printing such as Jolke P. et al. [2] determine the conductive silver tracks on a polyimide substrate are prepared by using microwave radiation to sinter silver nanoparticles printed on the substrate. Ag nanoparticles disperse in tetradecane that contain 57.8 wt% of silver nanoparticles. The diameter of nanoparticles ranging from 5 to 10 nm. After sintered time for 60 min at 220°C, the diameter grow to 500 nm by melting of particle after the decomposition of organic binder. The surface topography, thickness, and cross-sectional areas of the inkjet printing silver tracks were measured by an optical profilometer. This method shortens the necessary sintering time. The resistivity of the tracks as calculated from the resistance and cross-sectional area of a line is 3.0 $\times 10^{-7}$ Ωm which 5% of the value of bulk silver. The surface topography, thickness, and cross-sectional areas of the printed silver tracks were measured by an optical profilometer.

The Ag nanoparticles ink can be sintered at fairly low temperature, however it is high cost metal more than copper. Thus Seonhee J. et al. [3] investigate the alternated conductive ink. The Cu nanoparticles were printed on polyimide (PI) film as dog-bone patterns. Cu nanoparticles with 5 nm on average diameter were dispersed into non-polar solvent at 39% weight. The printed patterns were sintered at 250°C for 80 min under flows of nitrogen (N_2) and formic acid. The grain size of the film reached 500 nm upon grain growth and a crack-free Cu film was obtained after sintering. Some pores were occurring between grains due to volume shrinking from the use of nanoparticles ink during sintering. The resistance was 0.88 Ω on average. The size and shape of Cu, surface, microstructure, and resistance of printed patterns were analyzed by transmission electron microscopy (TEM), optical-microscopy, field emission scanning electron microscopy (FE-SEM), and digital multimeter, respectively.

Yong-Sung G. et al. [4] study the inkjet printing of copper (Cu) conductive ink on polyimide (PI) film to form Cu conductive patterns and determine the correlation between Cu ink based on Cu complex and flexible substrate. 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 and optimized plasma treatment parameters. 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 (H_2) atmosphere at 200 °C. The formed Cu conductive lines were analyzed by an optical microscope (OM), a field emission scanning electron microscope- (FE-SEM), an X-ray diffractometer (XRD), a non-contact 3D Profiler, and a four-point probe to confirm the shape, microstructure, crystal structure of conductive lines, and electrical-conductivity. The continuous lines having pure Cu phase and well-sintered microstructure were successfully formed on PI substrate modified by oxygen plasma treatment and the correlation between Cu ink and substrate surface property was determined.

Yasushi K. et al. [5] study novel materials and a metallization technique for the printed electronics were studied. Insulator inks and conductive inks were investigated. For the conductive ink, the nano-sized copper particles were used as metallic sources. These particles were prepared from a copper complex by a laser irradiation process in the liquid phase. Nano-sized copper particles were consisted of a thin copper oxide layer and a metal copper core wrapped by the layer. The conductive ink showed good ink-jettability. In order to metalize the printed trace of the conductive ink on a substrate, the atomic hydrogen treatment was carried out. Atomic hydrogen was generated on a heated tungsten wire and carried on the substrate. The temperature of the substrate was up to 60 °C during the treatment. After the treatment, the conductivity of a copper trace was 3 $\mu\Omega$ cm. It was considered that printed wiring boards can be easily fabricated by employing the above materials.

Hak-Sung K. et al. [6] study an intense pulsed light (IPL) from a xenon flash-lamp was used to sinter copper nanoparticles ink printed on low temperature polymer substrates at room temperature in ambient condition. The Cu particles of 5 nm diameter uniformly dispersed in a mix solvent of ethylene glycol and 2-methoxyethanol. The IPL can sinter the copper nanoparticles ink without damaging the polymer substrates in extremely short time (2 ms). The microstructure of the sintered copper film was investigated using X-ray powder diffraction (XRD), optical microscopy, scanning electron microscopy (SEM), X-ray microtomography, and atomic force microscopy

(AFM). The sintered copper film has a grainy structure with neck-like junctions. The resulting resistivity was 5 μΩ.cm of electrical resistivity. The IPL sintering technique allows copper nanoparticles to be used in inkjet printing on low-temperature substrates such as polymers in ambient conditions.

The inkjet printed film obtained from copper nanoparticles ink present good conductivity nevertheless, the damage of substrate and the high sintered temperature would be found. This problem was solved by addition another method as electroplating or electroless plating process to create copper film.

The electroplating were describe by Chang-Min L. et al. [7] research the flexible copper clad laminates(FCCLs) were fabricated using the electroplating process and the combined effect of the current density and plating time on their surface morphology, texture, hardness, electrical resistivity and folding behavior was evaluated. To achieve Cu layers with similar thicknesses, the current density was varied in the range of 0.2–3 A/dm^2 and the plating time was controlled in the range of 0.5–7.5 hr. to compensate for the variation of the current density. The surface morphology, hardness, and folding behavior were characterized by atomic force microscopy, and folding endurance test, respectively. The X-ray diffraction patterns indicated that the Cu phase was formed without any secondary phases; however, the preferred orientation changed from (220) to (111) as the current density increased over 1 A/dm^2. In addition, it was observed that the root-mean-square and hardness values decreased when the current density increased and the plating time decreased simultaneously. The electrical resistivity was as low as 21 nΩ.m.

Electroless plating of metal are very common and widespread in many industries for metalizing insulators (e.g., plastics, glass) and objects with geometries that are difficult to coat by electroplating. It should be note that the surface roughness, microstructure, morphology, and resultant mechanical and electrical properties of the electroless copper plating depend on the composition of electroless solution, reducing agent, substrate, bath temperature and pH

Farid H. et al. [10] study the electroless copper plating step by changing the complexing agent from tartarate or ethylenediaminetetraacetic (EDTA) baths used in through hole plating (THP) of printed circuit boards (PCBs). The effect of bath operating conditions (temperature, pH and agitation) and bath additives (pyridine, cytosine, thiourea, benzotriazole (BT) and 2-mercaptobenzothiozole (2MBT)) on plating rate, bath stability, morphology and etching rate of the coating has been studied. It has been 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 mg/(cm^2.h) in the tartarate bath at 30 °C and from 5.4 to 10.5 mg/(cm^2·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.

Xueping G. et al. [8] investigated the electroless copper plating on PET fabrics using hypophosphite as reducing agent. A continuous copper deposition could be obtained as the nickel ion concentration and temperature were more than 0.0030 M and 65°C, respectively. The deposition rate increased obviously with the increase of temperature, pH and nickel ion concentration. Potassium ferrocyanide ($K_4Fe(CN)_6$) was used to improve the properties of the copper deposits which reduce the deposition rate, make the deposits become more compact and change color of deposited from dark-brown to copper-bright, which led to lower surface resistance of copper-coated fabrics. The copper deposit had an intensified (111) plane orientation with the addition of $K_4Fe(CN)_6$ to the plating bath. The conductive fabrics could be prepared at the optimum condition with 0.0038M nickel ions and 2 ppm of $K_4Fe(CN)_6$.

Yinxiang L. [9] investigate the copper thin film on silane modified poly(ethylene-terephthalate) (PET) substrate was fabricated by ultrasonic-assisted electroless copper deposition to develop the adhesion between metal film and polymer substrate by chemical bonds with thiols. The composition and morphology of copper plating PET films with 75 μm thickness were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. The electroless bath composed of $CuCl_2.2H_2O$, H_3BO_3, $EDTANa_2.2H_2O$, and reducing agent as DMAB, and condition bath was operated at pH 7 and 50ºC for 2 h with and without ultrasonic assisted. Peel adhesion strength, as high as 16.7 N/cm, was achieved for the planting copper layer to the modified PET substrate with ultrasonic-assisted deposition; however, a relative low value as 11.9 N/cm was obtained for the sample without ultrasonic vibration by the same measurement. The electrical-conductivity of Cu film was changed from 7.9×10^4 to 2.1×10^5 S/cm by using ultrasonic technique. Ultrasonic operation has the significant merits of fast deposition

CHAPTER IV

EXPERIMENT

This chapter describes experimental system procedure used in this work which can be divided into three parts. All material in this work is shown in section 4.1. Details of printed electronic pattern are given in section 4.2. Finally, surface characterized by various techniques are explain in section 4.3.

4.1 Materials

The chemical and material lists are as follows.

- Resin coated Polyethyleneterephthalate
- Silver nanoparticle ink
- Electroplating solution (commercial grade)
- Copper(II)chloride dehydrate ($CuCl_2.2H_2O$), (99%, Rankem)
- Boric acid (H_3BO_3), (99.7%, Rankem)
- Ethylenediaminetetraacetic acid disodium salt dehydrate ($EDTANa_2.2H_2O$),(99.5%, Rankem)
- Dimethylamine borane (DMAB), (97%, Sigma-aldrich)
- Sodium hydroxide (NaOH), (99.5%, Lobal Chemie)
- Hydrochloric acid (HCl), (37%, Qrec)
- Deionized water

4.2 Methodology

The Flow chart of the entire experimental procedure is shown in Figure 4.1.

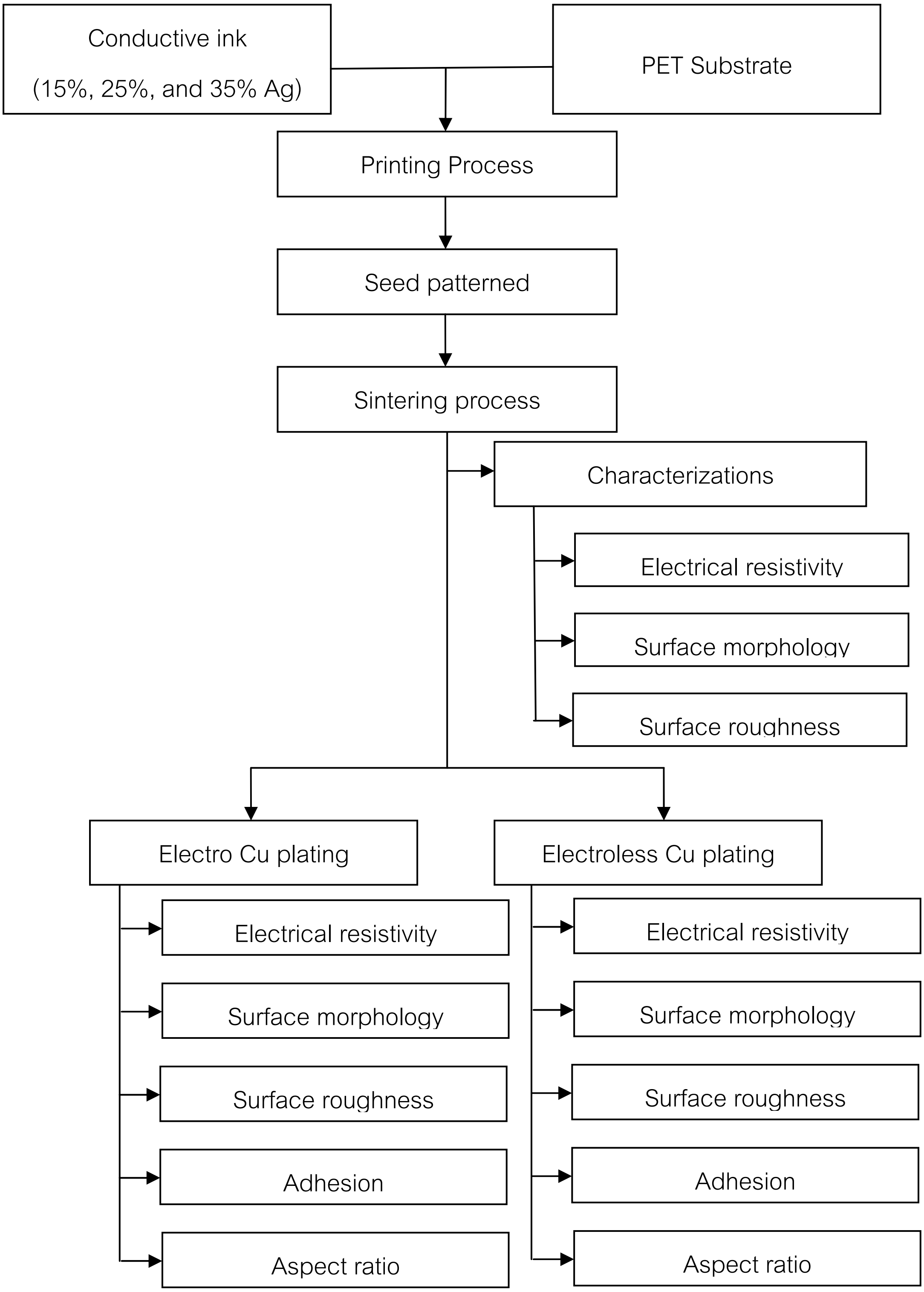


Figure 4.1 Schematic diagram of experimental procedure.

4.3 Procedures

4.3.1 Seed layer patterning procedure

The silver nanoparticles ink which 68.2 nm of diameter and dispersed in ethyleneglycal was printed by Epson Stylus Photo T60 Office inkjet printing on polymer substrate to patterned seed layer. The printer set up consisted of a drop-on-demand piezoelectric inkjet nozzle. The typical droplet size from such cartridges is 5 pl. The diameters of the ejected droplets were about 30 μm. The silver ink was printed on polyethyleneterephthalate (PET) used as substrate material. The pattern was designed for measurement of resistance that seen in fig 4.2. Three metal contents composed of 15%, 25% and 35% within the inks were used. The ink was injected into the reservoir of the cartridges and ejected as consecutive drops from nozzle of the head when a driving force was applied. These drops fell onto the substrate. The pattern were printed on PET substrate at room temperature then sintered in a furnace under flows of air atmosphere at 150^{o}C for 30 min. Finally, seed pattern or printed layer can be obtained. There are continues lines and uniform surface morphology.

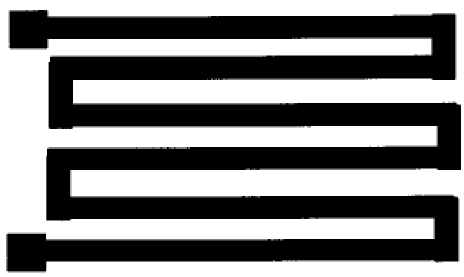


Figure 4.2 Pattern of inkjet printing process

4.3.2 Electroplating method

In the electroplating process, Cu was deposited on seed patterning that define by inkjet printing process with 25%. The electrolyte consisted of $CuSO_4.5H_2O$, H_2SO_4, HCl and additives. The electrodes consisted of pure copper and stainless steel net with 12 cm × 12 cm surface area at anode and cathode site. The seed substrate was put into an electroplating solution. When the voltage supplying on the electrodes, copper was deposited on seed layer that consisted of 25% Ag at room temperature. The voltage was varies in the range of 0.5 to 1.2 V and plating time was controlled in the range of 5 to15 min. After that the samples were rinsed in distilled water and then dried at 70^{o}C for 15 min to remove residual solvents in oven, the copper layer formed in this process.

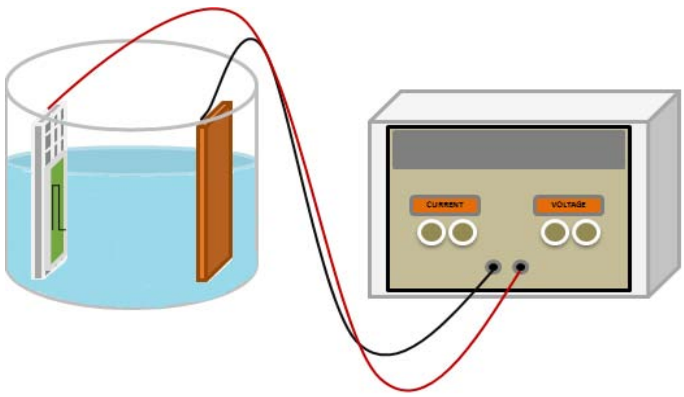


Figure 4.2 A scheme of electroplating

4.3.3 Electroless plating method

The printed film after sintering process were put into the solution which the composed of Copper(II) chloride ($CuCl_2.2H_2O$), boric acid (H_3BO_3), disodium- EDTA, dimethylamine borane (DMAB) and deionized water used to prepare the solutions. Plating was carried out at room temperature. The plating time was controlling in range of

60 to 120 min. The pH was adjusted using NaOH or HCl to require of pH value 7.0. After plating, the sample were carefully rinsed with deionized water, ethanol and dried in an oven at 50^{o}C for 1 h.

Table 4.1 Composition of electroless plating bath

Chemical	Concentration (g/L)
$CuCl_2.2H_2O$	9
H_3BO_3	6
$C_{10}H_{14}N_2Na_2O_8.2H_2O$(EDTANa$_2$.2H$_2$O)	18
$C_2H_{10}BN$(DMAB)	7

4.4 Characterization

The electrical resistivity of conductive layer was measured by a 2-point probe and the film thickness was measured using a stylus surface profiler of silver printed film and copper deposited layer. The microstructure was characterized by Scanning Electron-Microscopy and Energy Dispersive Spectrometry (SEM/EDX). The morphology and surface roughness of printed film was characterized using Atomic force microscopy (AFM). The crystal structure of the copper deposited in electroplating process was investigated using X-ray diffraction (XRD)

4.4.1 Electrical resistivity Measurement

The resistance of the samples was measured by two point probe and LCR meter at room temperature. At least three measurements were taken for each sample, and then the resistance value averaged. The thickness of seed and plating lines were examined by stylus surface profiler. The resistance in any sample is related to the dimensions of sample and electrical resistivity. Then the resistivity can be calculated by equation 4.1

$$\rho = \frac{Rt}{\left(L/W\right)} \tag{4.1}$$

Where

ρ	electrical resistivity
R	resistance
t	thickness
L	length
W	width

4.4.2 Scanning Electron Microscopy and Energy Dispersive Spectrometry (SEM/EDS)

Scanning Electron Microscope and Energy Dispersive X-Ray Spectrometer (SEM/EDS) can examine and analyze printed and plating layer at magnifications from 5X to 200,000X. Both the microstructure and morphology of surface are analyzed.

4.4.3 Atomic force microscopy (AFM)

The atomic force microscopy was used to characterized the surface morphology and roughness of printed line. The roughness value was obtained from the root mean-square of surface height measurements.

4.4.4 X-ray Diffraction (XRD) Analysis

The crystalline, structure and composition of samples before and after electroplating and electroless plating process were analyzed by XRD analysis. The X-ray diffraction patterns of the surface were carried out using an X-ray refractometer, SIEMENS D5000, with Cu K_{α} radiation, accurately measured in the 40° – 80° of 2 theta-angular region.

4.4.5 Adhesion analysis

An adhesion is provided by percent weight loss of copper deposited after ultrasonically washed in deionized water. All samples were measured weight before and after ultrasonically washed for 30 min.

4.4.6 Aspect ratio

The aspect ratio was defined as the ratio of thickness change to width change from seed line position of electroplating and electroless plating process. Average line thickness was determined by measuring the surface profile with a Dektak 150 Stylus Profiler at five locations for each sample. Measurement allow 3-D surface profile picture and can be used as characterization tools to measure film thicknesses. Average line width was determined by the semaphore program with scanning electron microscopy (SEM).

CHAPTER V

RESULTS AND DISCUSSION

This research consists of three parts. The first part concentrated on studying the effect of loading metal on inkjet printing process. The optimal electrical resistivity and surface roughness of printed line in part 1 was used to seed layer for experiment in part 2 and part 3. The second part focused on the optimal condition of copper electroplating method to patterning the conductive line on seed layer. Finally part, it concern about the optimal condition of electroless plating to form copper conductive line on seed layer. The characterization of conductive line from part 2 and 3 are similar. The best results of conductive line in part 2 and part 3 were compared and discussed to find the appropriate way to fabricate the conductive line.

5.1 Effect of silver loading on inkjet printing process

In order to study the effect of silver loading in conductive ink that was printed on PET substrate before sintering process. The surface microstructure and morphology of silver printed line was investigated by scanning electron microscope photographs (SEM) as seen in Fig 1. Figure 1(a) shows the surface of printed line on PET film before sintering step with 15% silver loading, 25% silver loading in fig 1(b) and 35% silver loading in fig 1(c). Each image shows the mixture of small and large grains of silver particle which partial necking between them and the average diameter of particle is about 70 nm. Some pores were observed between grains and the pore size was approximately 100, 140 and 200 nm on average with spherical shape in fig. 5.1(a), (b) and (c), respectively. This different pore size provide by the occurring of the particle agglomeration before printing step. The large containing of particles in conductive ink makes high percent agglomeration to form large grains size. This action has effect to the arrangement of particles such as 35% silver loading.

The SEM images in Fig. 5.1(d), 5.1(e) and 5.1(f) show the microstructure of silver nanoparticles after sintered step with 15%, 25% and 35% silver loading at 150^{o}C for 30 min. To compare with the conductive line before sintering step in Fig 5.1(a), 5.1(b) and 5.1(c), it's seen that the increasing of grain size, decreasing of pore size, and connecting between particles were increased after sintering process of all silver percent loading. The printed film with 35% Ag in Fig 5.1(f) has largest grain size and uniform surface without many pore that significantly improvement the resistivity of the printed pattern after sintering step. This result can be clearly confirmed in the electrical properties of conductive film related with their metal content, as seen in table 5.1

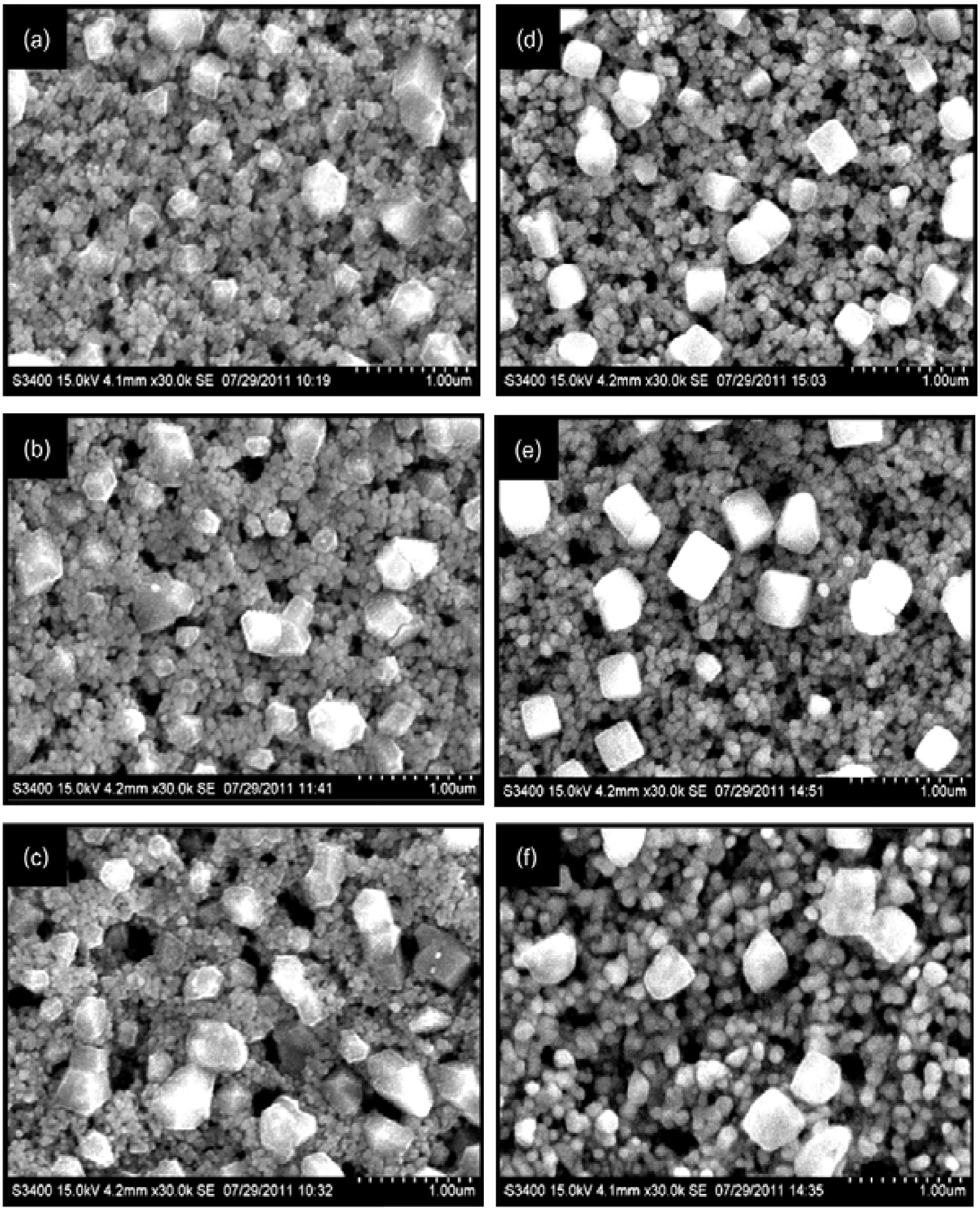


Figure 5.1. SEM image of printed film before sintering step: (a) 15%Ag, (b) 25%Ag, and (c) 35%Ag, and after sintering step: (d) 15%Ag, (e) 25%Ag and (f) 35%Ag

Table 5.1 Properties of printed pattern before and after sintering

Silver loading (%)	Resistivity (μΩ.cm)		Surface roughness(R_{rms})	
	Before	After	Before	After
15%	28.05	22.24	37.20	57.48
25%	21.32	16.52	50.44	60.63
35%	23.31	16.48	60.18	85.71

In table 5.1, The presented of root mean square (R_{rms}) and electrical resistivity (μΩ.cm) of printed films before and after sintering process evaluated by atomic force microscopy (AFM) and two point probe measurement. The change of R_{rms} was observed. There are increasing when, the silver content up to 25% and 35% both before and after sintered step. The R_{rms} of sintered film are higher than before sintered because of their grain size growth up during this process. The resistivity increased when silver content increased and sintering was appeared. The electrical resistivity depend on many variables such as surface roughness, particle size, morphology and the uniformly of printed film. To focus on the electrical resistivity value of conductive line with 25% and 35% silver loading before sintering step, the 35% silver loading obtained high resistivity more than 25% because the large pore that occurring on the line. This result is coincident with the SEM analysis. The printed silver line with 25% silver loading is provide a promising to deposited copper on printed silver line surface by electroplating and electroless plating method, cause their good in resistivity and appropriate surface roughness. Due to the rough surface exhibit the irregular intensity of electromagnetic field that causes the defect to rough area.

5.2 Study the electroplating method to fabricate the conductive line.

The printed line with 25% silver loading was used to prepare seed layer for deposited copper by electroplating method. This part investigate the optimal applied voltage and plating time to create low resistivity and suitable surface, including adhesion between connection surface and aspect ratio test of copper conductive line.

Table 5.2 Property of conductive lines after electro copper plating process.

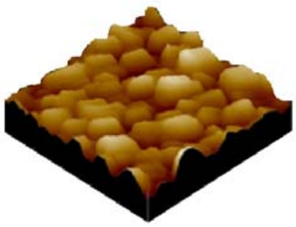
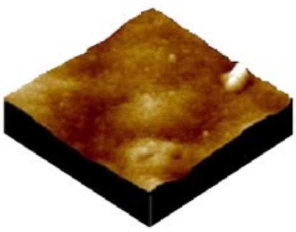
Sample	Voltage(V)	time(min)	AFM images	R_{rms}
1	0.5	10		182.49
2	0.8	10		122.38
3	1.0	10		66.89
4	1.2	10		28.91

Table 5.2 shows the AFM images and surface roughness (R_{rms}) of copper deposited on printed line at constant plating time and difference applied voltage. The AFM images show appearance grain size and morphology of copper deposited line in 3 dimensions. This result indicates that the surface roughness (R_{rms}) decreasing with increasing applied voltage. The R_{rms} value in range of 182.49 nm to 28.91 nm.

In addition, the electrical resistivity of copper deposited line as a function of applied voltage with constant plating time is shown in Fig. 5.2. The resistivity of deposited line was decrease with increasing of applied voltage. This result is likely to trend of surface roughness and do not fit the linear tend.

Copper line at 1.2 V is lowest roughness and resistivity but, the hydrogen bubbles were generated distribute over surface. This bubbles is a byproduct of that produced by the reduction of acid in electroplating solution at cathode side, therefore the conductive line at 1.0 v is the optimal voltage.

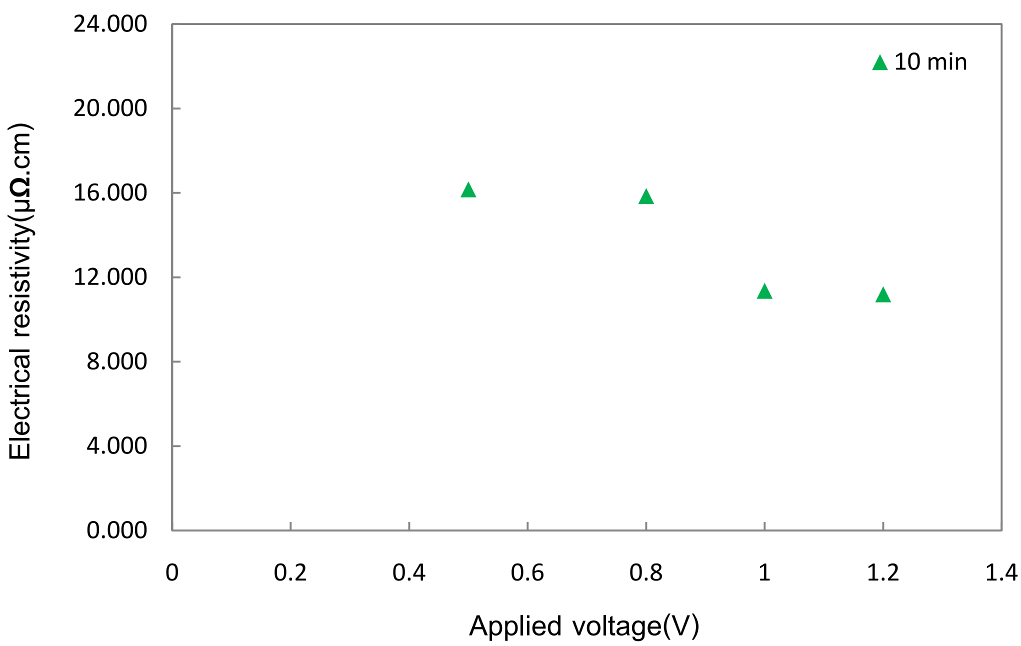
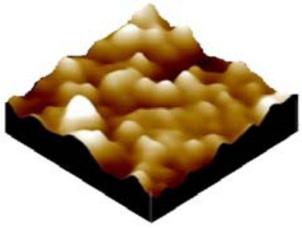
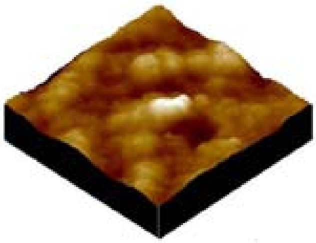


Figure 5.2. Electrical resistivity of conductive line after electro copper plating process as a function of applied voltage at constant plating time.

Table 5.3 Property of conductive lines after electro copper plating process.

Sample	Voltage(V)	time(min)	AFM images	R_{rms}
5	1.0	5		124.06
3	1.0	10		66.89
6	1.0	15		63.29

After the previous result, 1.0 V of applied voltage used to define the optimal plating time at 5, 10, and 15 min. The surface morphology and roughness of the copper conductive line with constant applied voltage and various plating time were observed by AFM profiles, as shown in table5.3. The AFM images clearly indicate that dense and uniformly surface after 10 min of plating time, and the grain size of copper relate with R_{rms} value. The R_{rms} was 124.06, 66.89 and 63.29 nm for 5, 10 and 15 min, respectively, revealing that its value decreased as the plating time decreased. This morphology of Cu deposited that analyzed by AFM present the same result with SEM images in Fig 5.3.

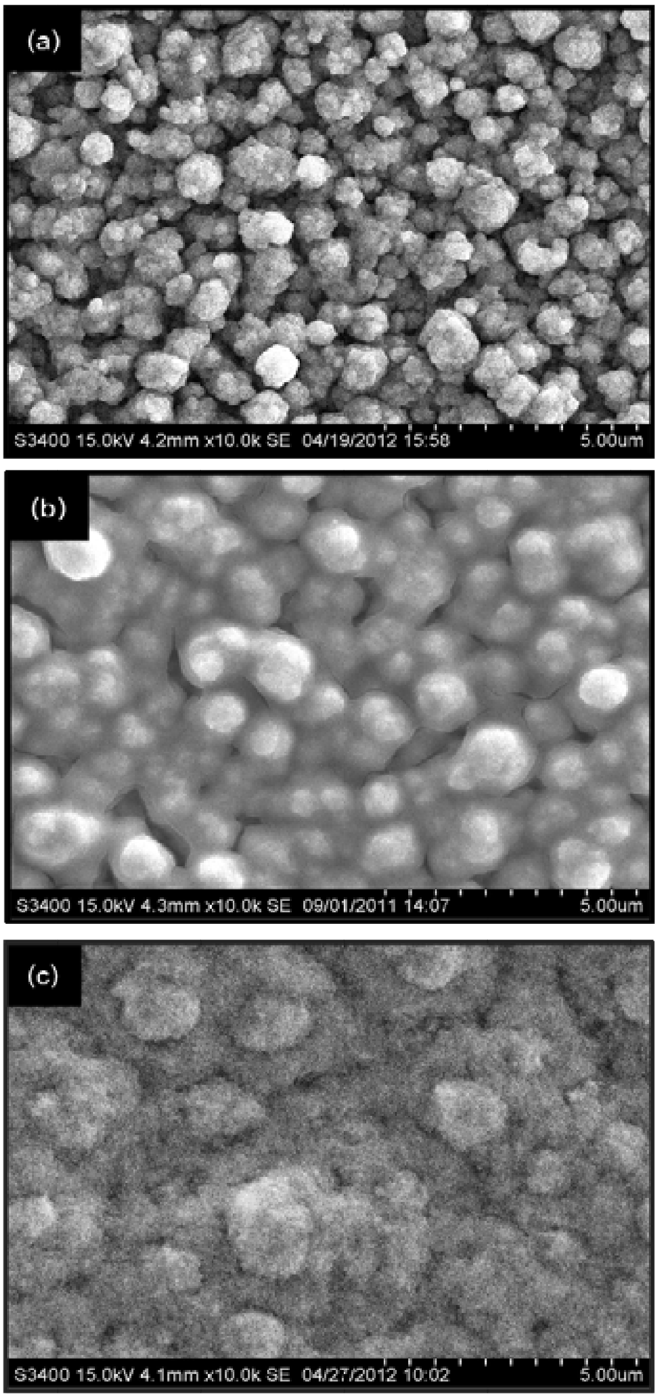


Figure 5.3 SEM image of Cu deposited by electroplating process at 1.0 V with different time: (a) 5 min, (b) 10 min and (c) 15 min.

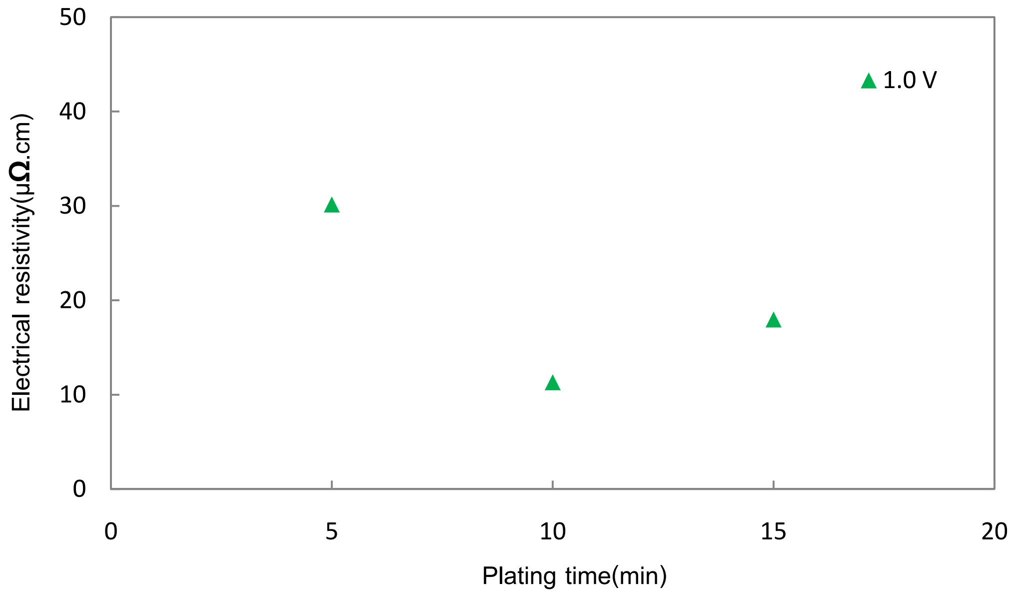


Figure 5.4. Electrical resistivity of conductive line after electro copper plating process as a function of plating time at constant voltage (1.0 V).

The images in Fig 5.3 show the surface morphology of copper deposited by electroplating process at 1.0 V and different time. It is obviously that the large grain and uniform surface as the plating time increased to 10 and 15 min .in Fig 5.4(b) and Fig 5.4 (c). In addition, the color of the Cu deposited had a bright Cu, it's usually indicated the good electrical properties.

The electrical resistivity of copper deposited as a function of plating time at constant voltage (1.0 V) as shown in Fig. 5.4. The electrical resistivity was 30.15, 11.33 and 17.97 μΩ.cm for 5, 10, and 15 min of plating time, respectively. The resistivity decreased with increasing of plating time to the minimum value as 11.33 μΩ.cm at 10 minute and raise to 17.97 μΩ.cm when plating time up to 15 min. Longer plating times does not reduce the resistivity because the deposited behavior of copper by plating process. The copper were deposited all surface of seed layer, both on top and sides as seen in Fig 5.5 (a) and (b). Figure 5.5(a) and (b) show the side-view images of conductive line after electroplating at 1.0 V and plating time for 10 and 15 min, respectively. Both of them show the layer of Ag and Cu but, the Cu in fig 5.5(b) were deposited on side of Ag too much and try to deposit under the Ag layer. This behavior is resulting in the low adhesion of metal and lead to the peel of conductive line.

Furthermore, the cross-section of conductive line after electroplating at various time as seen in fig 5.6 show the difference particle arrangement of copper, and the appearance of crack and void. The loose film was appeared that affect to the resistivity at 5 min of plating time. When the plating time increased to 10 and 15 min, the lines perform dense and necking between particles.

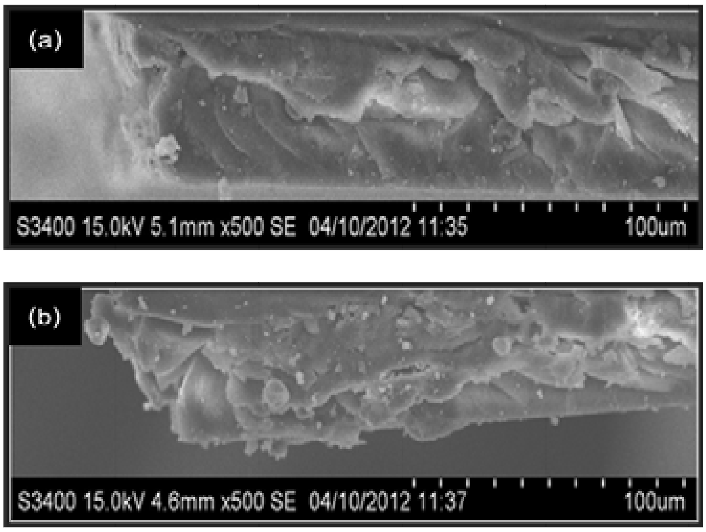


Figure 5.5. Side-view images of conductive line after electroplating at 1.0 V and different plating time: (a) 10 min and (b) 15 min.

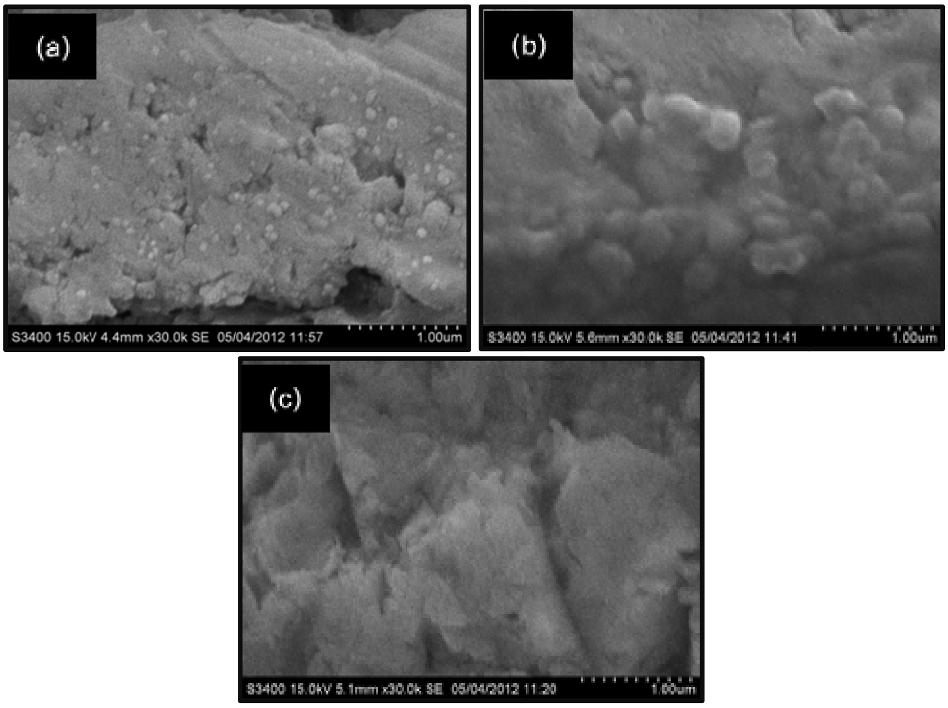


Figure 5.6. Cross-sectional images of conductive line after electroplating at 1.0 V and different plating time: (a) 5 min, (b) 10 min and (c) 15 min.

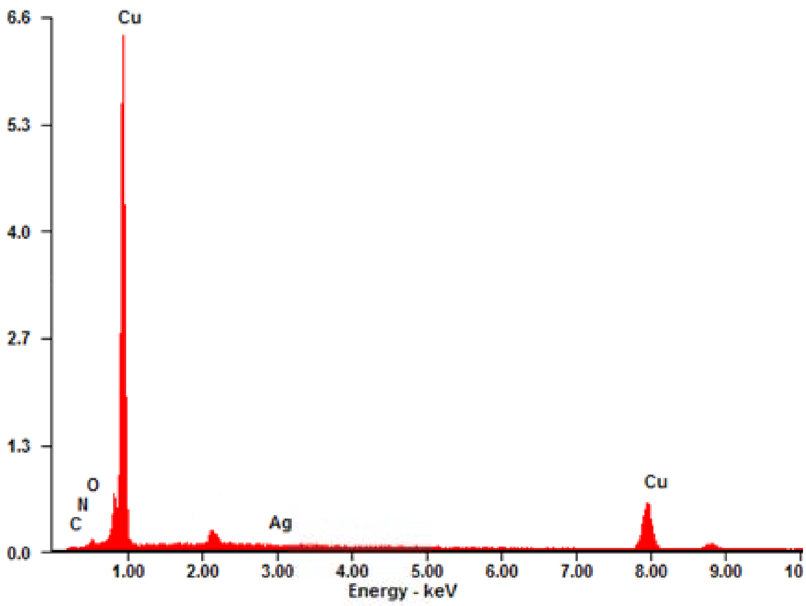


Figure 5.7. EDX spectra of conductive line after electroplating at 1.0 V and 10 min

The copper deposited was analyzed by Energy dispersive X-ray spectroscopy (EDX), Fig. 5.7 shown the typical of copper deposited on printed line at 1.0 V for 10 min. It indicates that the deposited is almost composed of Cu with a small of oxygen and carbon. The carbon and oxygen come from the contaminants of surface and air exposure, respectively

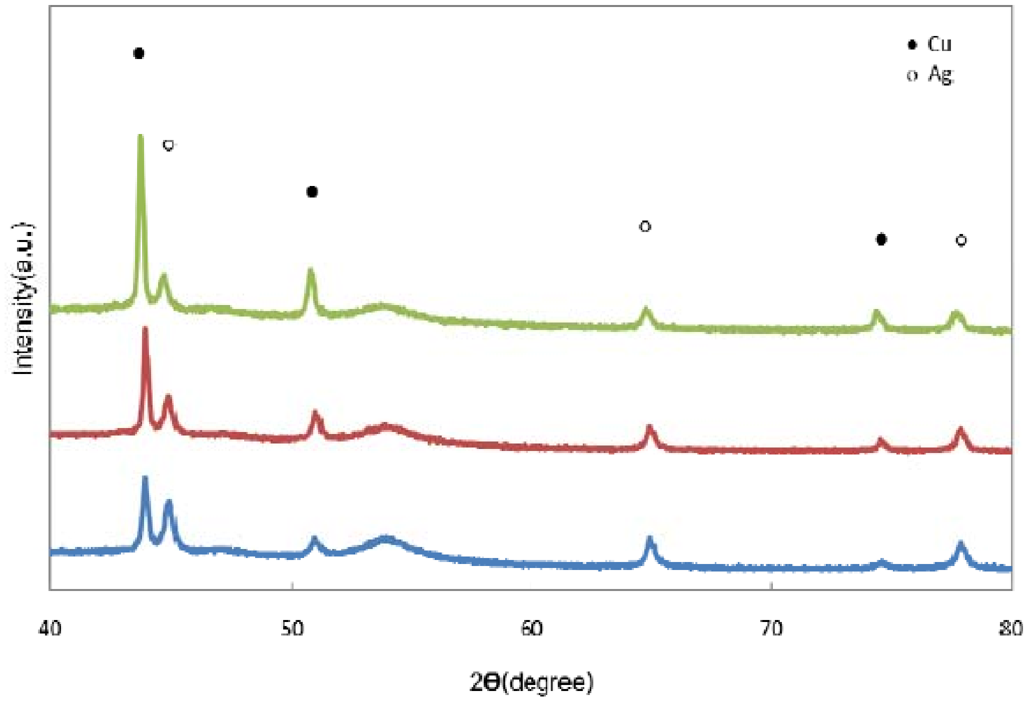


Figure 5.8. XRD spectra of conductive line after electroplating at 1.0 V and different time: (a) 5 min, (b) 10 min and (c) 15 min

To confirm the crystal phase at 1.0 V, crystal phase analysis was performed using X-ray diffraction (XRD). The XRD patterns for conductive line after electroplating with 1.0 V of applied voltage and different time (a) 5 min, (b) 10 min, and (c) 15 in Fig.5.8. Characteristic peaks are almost the same for these three curves. The peaks that appeared at 2θ = 43.2, 50.3, and 73.8 represent (111), (200), (220) and (311) plans of copper, respectively. The copper oxide phase was not detected in the deposits. The other peaks at 2θ = 44.8, 64.8 and 77.6 are characteristic peaks of Ag that obtained from seed layer. Comparing XRD patterns shown in Fig. 5.5(a), (b) and (c), the characteristic peak intensity with copper plans of conductive line is increased obviously with plating time. On the other hand, the characteristic peaks of Ag planes are decreased when plating time has increased.

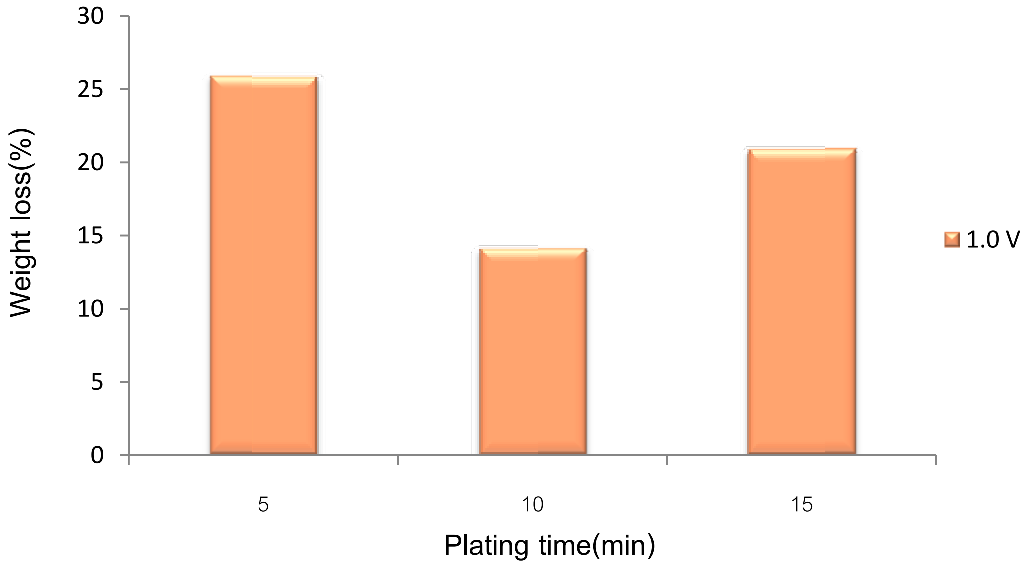


Figure 5.9. Percent weight loss of conductive line at 1.0 V after ultrasonic washing for 30 min as a function of plating time.

Percent weight loss of conductive line at 1.0 Vas a function of time after ultrasonic washing for 30 min as shown in Fig 5.9. This effect indicates that the adhesion between seed layer and copper deposited. The conductive line with 5 min shows the highest percent weight loss with 25.69% and reach to the minimum value 14.17% at 10 min while 15 min of plating time was obtained 20.93%. So, the conductive line with 10 min performs good adhesion in this process. These results relate with compact and dense of particle in conductive film in Fig 5.6.

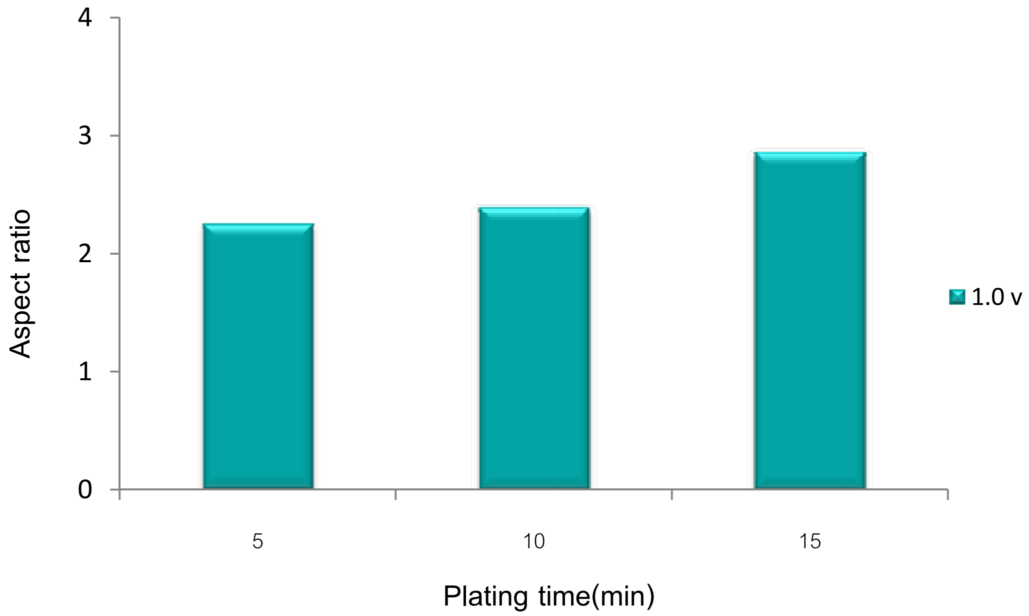


Figure 5.10. Aspect ratio of conductive line at 1.0 V as a function of plating time after electroplating process.

Measured line thickness to line width is an aspect ratio of conductive line after electro copper plating. Figure 5.10 shows plat of aspect ratio of conductive line with plating time (min). Aspect ratio gradually increased from 2.25 to 2.39, and 2.87 at 5, 10, and 15 min of plating time, respectively. The aspect ratios were obtained a small different value between its. Therefore, the copper deposited on depth direction more than width direction. This results indicate that a small of deviation from design dimension whereas the plating time does not effect to the aspect ratio of conductive line.

5.3 Study the electroless plating method to fabricate the conductive line.

In electroless copper plating bath, the pH and temperature would be control at value 7.0-7.12 and room temperature. The plating time was varying from 60 to 120 min for 5 point of time. After plating, all samples were characterized by two-point probe and stylus profiler to obtain the resistivity of conductive line as seen in Fig. 5.11. The electrical resistivity were decreasing with plating time increased except, 120 min of plating time. This result is confirmed by the SEM images of plating surface at various time in Fig 5.12(a) to 5.12(e). The copper was deposited on seed layer too fast when the time was increasing from 60 to 105 min that cause to the large grain size of copper. The reaction take place in longer time as 120 min, the reaction was slow. Then the Cu grain size in fig 5.11(e) is small and contributed.

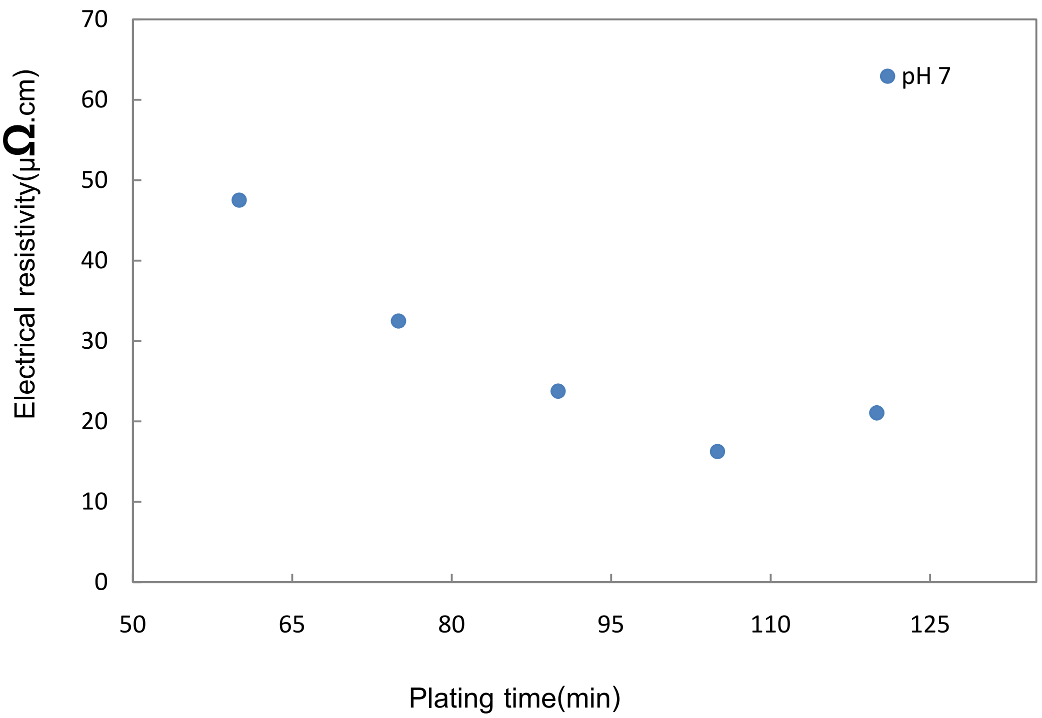


Figure 5.11. Electrical resistivity of conductive line as a function of plating time after electroless copper plating process

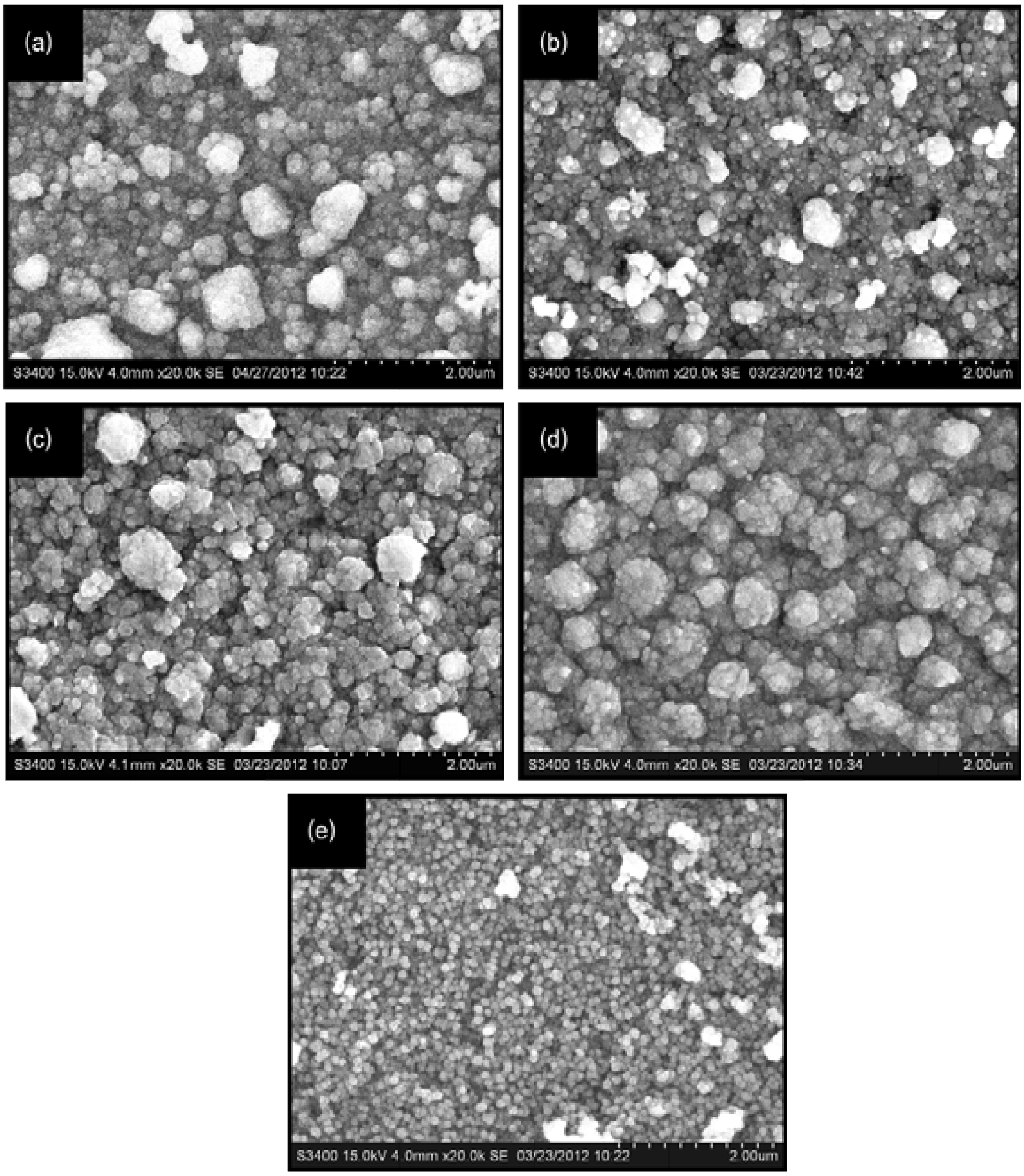


Figure 5.12. SEM images of conductive line after electroless plating at different plating time: (a) 60 min, (b) 75 min, (c) 90 min, (d) 105 min and (d) 120 min.

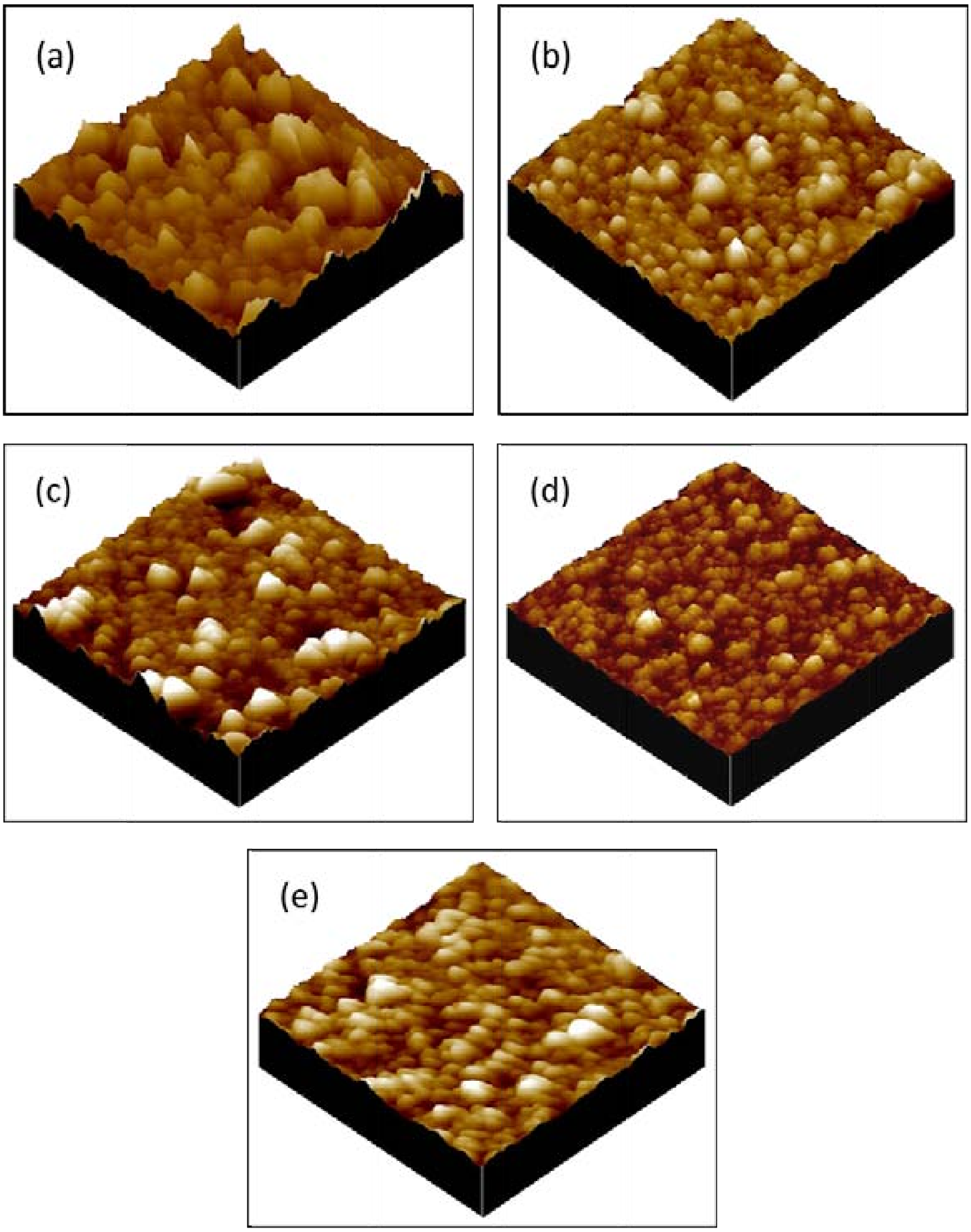


Figure 5.13. AFM images of conductive line after electroless plating at different plating time: (a) 60 min, (b) 75 min, (c) 90 min, (d) 105 min and (e) 120 min.

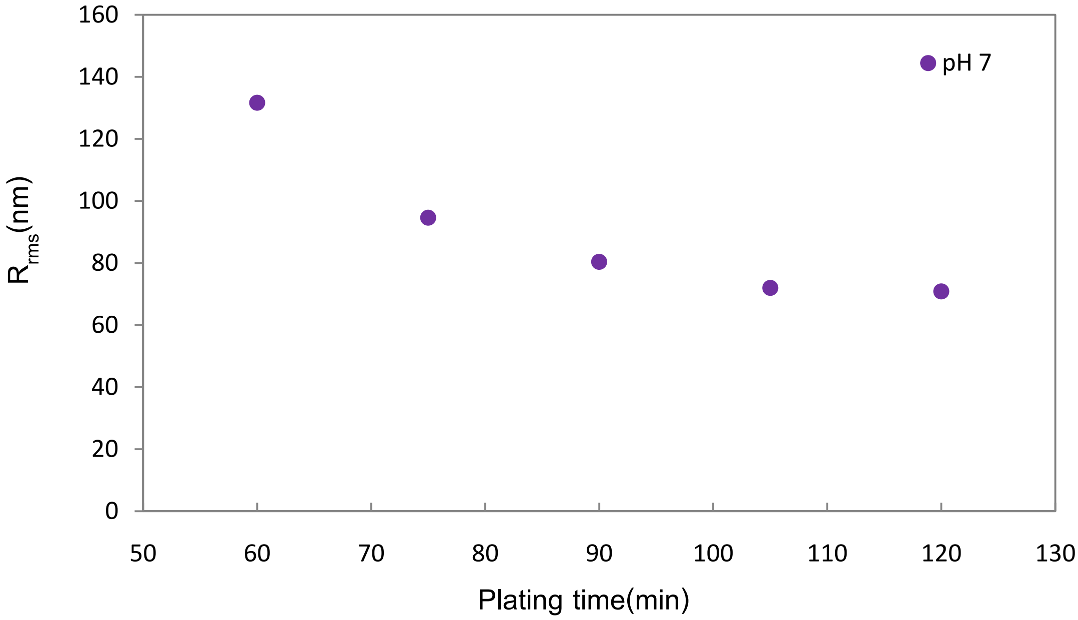


Figure 5.14. Surface roughness (R_{rms}) of conductive line as a function of plating time after electroless copper plating method.

The surface morphology of the conductive line after electroless plating was observed by the AFM, as shown in Fig 5.13. The surface morphology of copper deposited is also presented for comparison with plating time. The surface of Cu deposited at Fig 5.13(a) was performing clearly large grain size and so rough surface whereas more plating time. The surface of Cu deposited at the plating time more than 60 min indicated smooth, dense and wavy with uniform surface. The grain size was small and similar size, and its root-mean-square (R_{rms}) as a function of plating time presented in Fig 5.14.

The surface morphology in Fig.5.14.indicate that the relation between surface roughness (R_{rms}) of conductive line after electroless copper plating and plating time (min). These result shows the surface roughness of Cu deposited depend on the plating, revealing that its value decreased as the plating time increased.

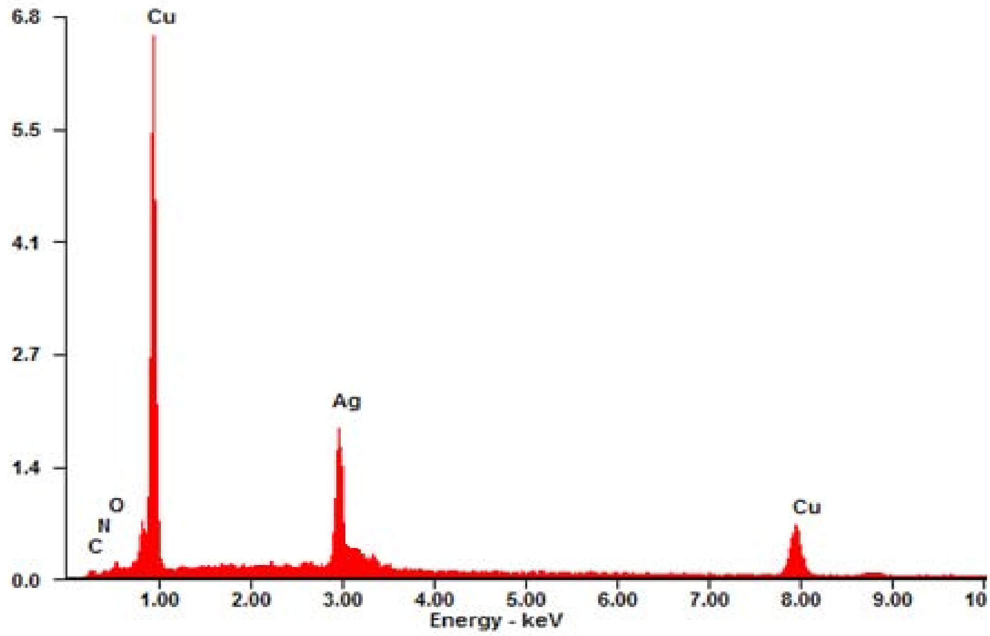


Figure 5.15. EDX spectra of conductive line after at 120 min after electroless plating

Figure 5.15.shows the typical EDX spectra of conductive line at 105 min of plating time after electroless plating process. It indicates that the copper deposited is composed of copper (Cu), silver (Ag) and a small of carbon (C) and oxygen (O). This result resemble to XRD analysis as seen in Fig 5.16. To confirm the crystal phase, crystal phase analysis was performed using X-ray diffraction (XRD). The characteristic peaks of pure copper phase that appeared at 43.2°, 50.4° and 74.1°, and other peaks are Ag phase from seed layer without significant oxide phase or other impurity phase. It is concluded that the C and O peaks come from the remnant solvent and air exposure, respectively. Therefore, there is no oxidation of the copper particle.

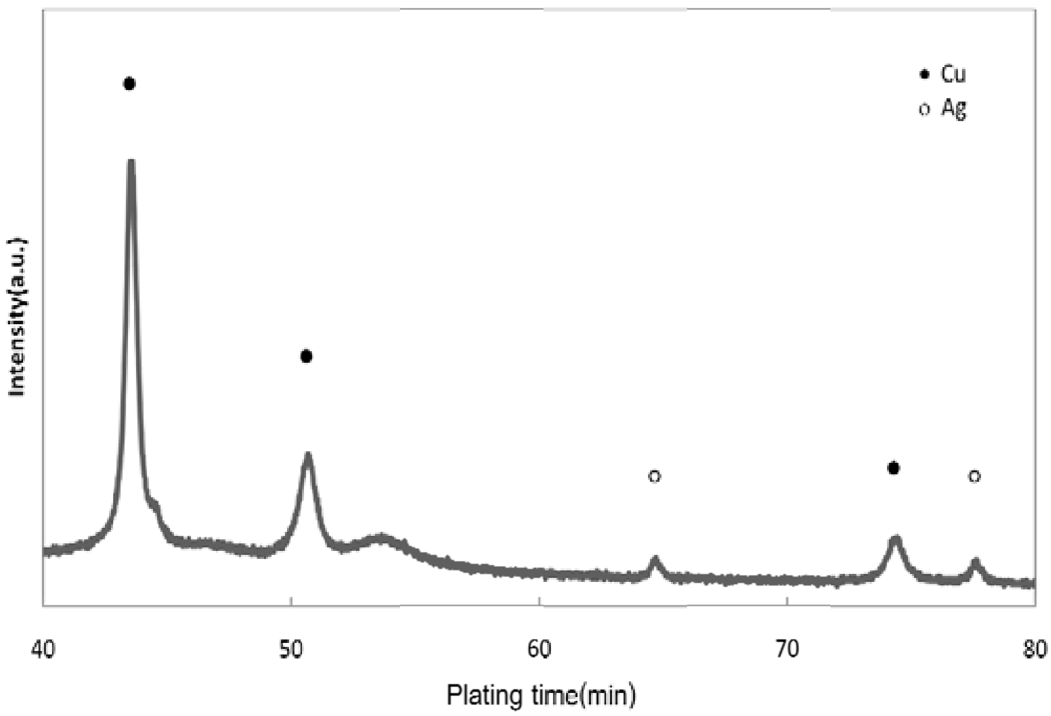


Figure 5.16 XRD spectra of conductive line at 120 min of plating time after electroless plating.

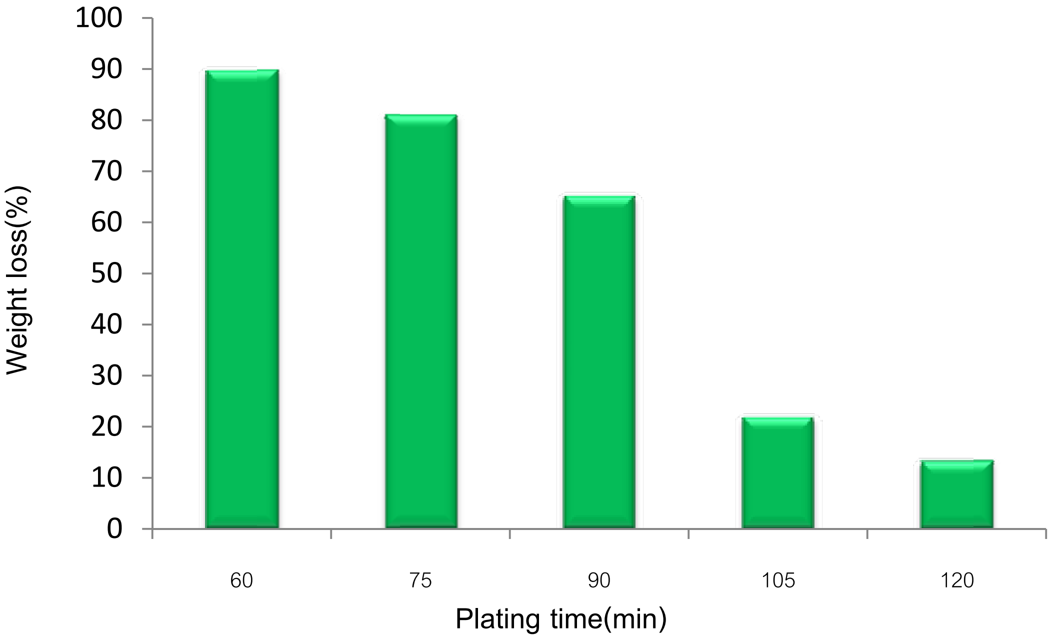


Figure 5.17. Percent weight loss of conductive line as a function of plating time

Percent weight loss of conductive line after electroless Cu plating as a function of plating time as seen in Fig 5.17. %weight loss was maximum value with 60 min of plating time and reach to minimum value at time equal to 120 min. It was implied to the adhesion of this conductive line. The small of percent weight loss obtained the good in adhesion value. Therefore, the adhesion be proportionate to the plating time.

Figure 5.18 shows the aspect ratio of conductive line after electroless Cu plating as a function of plating time. The aspect ratio is the difference of depth by the difference of width after electroless Cu plating. The line should be have the large of aspect ratio because the design of pattern was limited. In this case, the aspect ratio drop to value 0.93 at 90 min and raise to value 1.0 and 1.15 at 105, and 120 min, respectively. This behavior of metal depositing process influence at the long of plating time, and impact to the width more than the depth of conductive line.

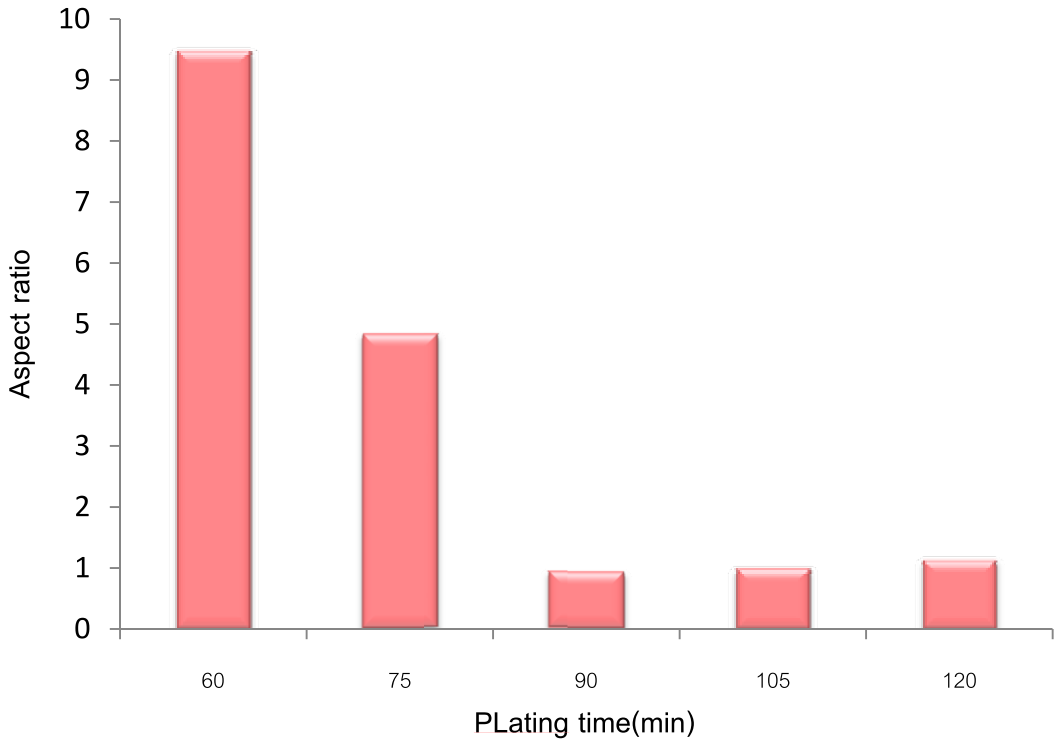


Figure 5.18. Aspect ratio of conductive line as a function of plating time

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

We have successfully combination of printed continuous silver lines by inkjet printing and deposited copper layer on printed pattern by electroplating and electroless plating method. In the printing method, the R_{rms} of printed line increased when silver content in the conductive ink and grain size increased. The electrical resistivity of printed line at different silver content be up to the particle size and partial necking between them, surface roughness, number and size of void that contributed on surface. The printed line was used as seed layer to improving the important properties such as electrical resistivity and adhesion between metal and substrate by copper electroplating and electroless plating method. The optimal resistivity and R_{rms} of printed silver film that was suitable for seed layer is 16.52 $\mu\Omega$.cm and 60.63 nm after sintering at 150^{o}C for 30 min with 25% silver content.

The conductive line was successfully fabricated by printing and electroplating method with a smooth and continuous line. 11.33 $\mu\Omega$.cm is the best resistivity of plating process at 1.0 V and 10 min of plating time with increasing of apply voltage and plating time, the surface more smooth and uniform. Furthermore, longer time does not reduce the electrical resistivity cause a peel of seed layer. The XRD confirms that the conductive layer patterned is almost copper and a small of silver. It seen like that EDX analyzed.

Investigate on the conductive line after printing and electroless copper plating were conducted to improve the electrical resistivity of this line. When the plating time was increased, the electrical resistivity, surface roughness, and adhesion of Cu deposited so increasing, and obtain the optimal resistivity as value 16.27 $\mu\Omega$.cm. Although the electrical resistivity is higher than electroplating method but, the adhesion exhibit better results. The XRD confirms that the conductive layer patterned is almost copper and a small of silver. It seen like that EDX analyzed.

6.2 Recommendations

1. The pattern would be another designed such as price tag and RFID pattern.
2. The electroless plating set the temperature to high temperature at any point to improve the electrical resistivity and adhesion of conductive line
3. The alternated substrate would be used: polyimide and paper.
4. The process of copper electroplating will design
5. The pH of electroless plating bath was varying to another value.

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