การศึกษาผลและกลไกของปัจจัยที่ถูกควบคุมโดยอุตสาหกรรมต่อกระบวนการชุบนิกเกิล/ทองแบบไม่ใช้ไฟฟ้า

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ปีการศึกษา 2559

THE STUDY OF EFFECTS AND MECHANISMS OF INDUSTRIAL CONTROLLED FACTORS ON ELECTROLESS NICKEL IMMERSION GOLD (ENIG) PLATING PROCESS

Miss Suphitsara Pattarakiatikun

A Thesis Submitted in Partial Fulfillment of the Requirements
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ศุภิสรา ภัทรเกียรติคุณ : การศึกษาผลและกลไกของปัจจัยที่ถูกควบคุมโดยอุตสาหกรรมต่อกระบวนการชุบนิกเกิล/ทองแบบไม่ใช้ไฟฟ้า (THE STUDY OF EFFECTS AND MECHANISMS OF INDUSTRIAL CONTROLLED FACTORS ON ELECTROLESS NICKEL IMMERSION GOLD (ENIG) PLATING PROCESS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. อนงค์นาฏ สมหวังธนโรจน์, 151 หน้า.

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาผลและกลไกของปัจจัยที่ถูกควบคุมโดยอุตสาหกรรมต่อกระบวนการชุบนิกเกิล/ทองแบบไม่ใช้ไฟฟ้า ซึ่งประกอบด้วยขั้นตอนการเตรียมผิวซับสเตรต และสภาวะที่ใช้ในการชุบนิกเกิล/ทองแบบไม่ใช้ไฟฟ้า ผลการวิเคราะห์ความหนาของชั้นฟิล์มนิกเกิล และทองโดยเครื่องมือวิเคราะห์หาปริมาณธาตุองค์ประกอบในสารตัวอย่าง โดยการวัดปริมาณรังสีเอ็กซ์ฟูออเรสเซนต์ (XRF) พบว่าการเพิ่มความเข้มข้นของสารตั้งต้น สารคีเลต ความเป็นเบสในช่วงที่ควบคุมของสารละลาย อุณหภูมิ และการลดปริมาณออกไซด์บนผิวซับสเตรตส่งผลให้ความหนาของชั้นฟิล์มนิกเกิล และทองเพิ่มมากขึ้น ซึ่งปริมาณฟอสฟอรัสบนผิวของฟิล์มนิกเกิลส่งผลให้ความหนาของทองลดลงเช่นกัน สำหรับอัตราส่วนของโลหะผสมนิกเกิลถูกวัดปริมาณโดยเทคนิคการวิเคราะห์ธาตุด้วยรังสีเอ็กซ์ (EDX) โดยอัตราส่วนนิกเกิลจะมากขึ้นเมื่อเพิ่มความเข้มข้นของเกลือนิกเกิล เพิ่มความเป็นเบสในสารละลายที่ใช้ในการชุบนิกเกิลแบบไม่ใช้ไฟฟ้า หรือเพิ่มอุณหภูมิ แต่การเพิ่มอุณหภูมิมากกว่า 90 องศาเซลเซียสจะส่งผลให้สารละลายนิกเกิลสลายตัว นอกจากนี้การลดความเข้มข้นของตัวรีดิวซ์สามารถทำให้อัตราส่วนนิกเกิลในโลหะผสมเพิ่มมากขึ้น สิ่งที่ส่งผลต่อความขรุขระ และลักษณะของพื้นผิวนิกเกิล ซึ่งวัดโดย SEM และสไตลัส ประกอบด้วย พื้นผิวของซับสเตรต ฟองแก๊สที่เกิดขึ้นจากปฏิกิริยา ซึ่งส่งผลต่อการไหลของสารละลายที่ใช้ในการชุบโลหะ และการกวนสาร ในกรณีของความขรุขระฟิล์มทองจะขึ้นอยู่กับความขรุขระของผิวนิกเกิล การชุบทองที่หนาเกินไปจะส่งผลให้การยึดติดระหว่างฟิล์มทองบนผิวนิกเกิลลดลง ตัวแปรที่ไวต่อการเปลี่ยนแปลงสำหรับการชุบนิกเกิลแบบไม่ใช้ไฟฟ้า คือ สารผลิตภัณฑ์พลอยได้จากปฏิกิริยา และ pH ของสารละลายชุบนิกเกิล สำหรับการชุบทอง คือ pH ของสารละลายชุบทอง

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

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SUPHITSARA PATTARAKIATIKUN: THE STUDY OF EFFECTS AND MECHANISMS OF INDUSTRIAL CONTROLLED FACTORS ON ELECTROLESS NICKEL IMMERSION GOLD (ENIG) PLATING PROCESS. ADVISOR: ASSOC. PROF. ANONGNAT SOMWANGTHANAROJ, Ph.D., 151 pp.

This research aimed to study the effects of the factors and mechanisms which were controlled by the industry on the electroless nickel immersion gold (ENIG) process including pretreatment step and condition used in ENIG. The thickness analysis of nickel and gold layers by X-ray fluorescence spectrometry (XRF) found that increasing the concentration of precursors, chelating agents, the alkalinity in the controlled range, temperature, and decreasing of oxides on the surface of the substrate resulting in a thick layer of nickel and gold. Also the phosphorus on the nickel substrate caused the thinner layer of gold. For the Ni/P alloy, the nickel composition ratio measured by energy dispersive X-ray spectrometer (EDX) would be greater due to increasing of nickel salt, alkalinity in the EN plating solution or temperature. However, increasing the temperature more than 90 °C caused decomposition of EN plating solution. Moreover, the decreasing of reducing agent resulted in increasing of nickel composition ratio of nickel alloy. The factors affected the roughness and morphology of the nickel surface measured by scanning electron microscopy (SEM) and stylus containing the morphology of the substrate, the gas bubbles generated by the plating reaction which affected the flow of the plating solution and agitation. In the case of gold roughness was based on the nickel surface roughness. The too thick gold plating layer resulted in the dropping of the adhesion between gold layer and nickel surface. The sensitive parameters of EN plating were by-product of plating reaction and pH of EN solution. For IM plating, the sensitive parameter was pH of IM plating solution.

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

Introduction

1.1 Introduction

In the electronics field, flexible printed circuit boards (FPCBs) are ubiquitous in electronics applications including smart phone, flexible mouse, LCD television, laptop, and camera. Since the prominent features of FPCBs are flexibility, thinness and freedom of design, they are suitable for electronic devices that have a decreasing tendency of size. Polymers and copper are the raw materials for the FPCBs production. However, the conductive surface of FPCBs produced from copper is easy to be oxidized and damaged by solder. Therefore, surface finishing is required.[1]

Surface finishing is the surface treatment process of product to improve its properties by coating the copper surface to prevent the oxidation reaction. There are many kinds of surface finishes for FPCBs and each kind of them has different characteristics and is suitable for specific applications. Electroless nickel immersion gold or ENIG is also one of them.

ENIG is the surface finishing technique consisting of two processes, electroless nickel plating and immersion gold plating, which provide nickel and gold layers in two-dimensional nanostructure also known as nano film.[2] These processes involve electrochemical reaction. Namely, the metal ions in the aqueous solution receive the electrons and then deposit on the substrate without any supplied electric current. The resultant of this technique is a nickel alloy layer covered by a very thin gold layer on the substrate as shown in Figure 1.1. For the purpose of FPCBs surface finishing, ENIG is applied on copper surface. Nickel alloy protects copper during soldering process and behaves like a barrier between copper and gold to prevent migration between them. Moreover, gold protects nickel from oxidization and provides low contact resistance.

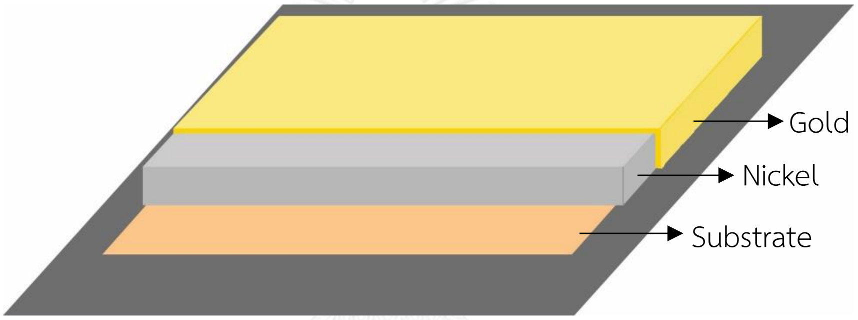


Figure 1.1 Structure of nickel and gold layer on substrate by ENIG process

ENIG process is the primary choice for electronics production in Mektec Manufacturing Corporation (Thailand) Ltd. (MMCT). For this reason, it is necessary to study ENIG process to figure out the functions of controlled parameters and the considerable factors which affect the outputs of the product from production line. Unlike electrolyte plating, the deposition rate, roughness, film topography of ENIG film and composition of nickel alloy depend on the concentration of reactants [3], composition of substance, and deposition condition. Accordingly, the production process should be carefully controlled in order to achieve the desired properties and quality assurance of the product.

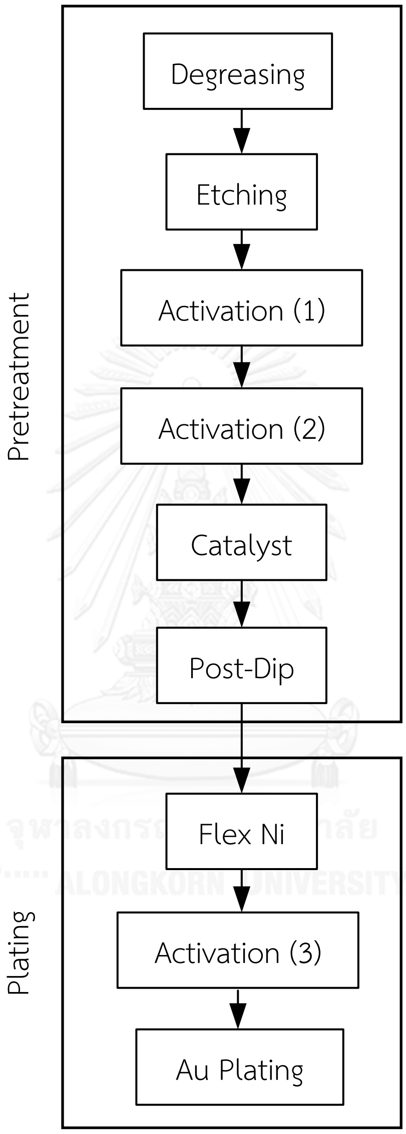


Figure 1.2 Block flow diagram of ENIG process

This research focuses on studying controlled chemicals and parameters of the ENIG plating production line in MMCT which consists of chemicals concentration, pH, temperature and specific gravity of chemicals in pretreatment and plating bath. The process of surface finishing by ENIG could be divided into two parts which are pretreatment section and plating section. As shown in Figure 1.2, the pretreatment section contains degreasing, etching, activation (1, 2, and 3) for cleaning and removing oxide, catalyst plating and removing catalyst from the unwanted area in post-dipping process. While, the plating section contains nickel plating and gold plating. Effects of the process parameters on the appearance and quality of the nickel and gold plating are concerned. The most sensitive parameters which affect nickel and gold thickness and plating mechanism are recognized by collecting thickness data in MMCT production line as well as reviewing the related articles to formulate predicted trend line and explanation of the plating mechanism. After finished identifying the most sensitive parameters, the lab experiments were conducted to confirm the results from the prior step and its reproducibility as well as to investigate the effects of other parameters which are not measured yet. The details of analytical methods are in table 1.1. Our research team expects that this study based on real data from the production line and the laboratory experimental data will be helpful for MMCT to improve the performance of the electronics product prepared by ENIG process.

Table 1.1 Analysis method in ENIG

Outputs	Analysis methods	Indications
Nickel Alloy	SEM-EDX	Nickel alloy topography Amount of phosphorus in nickel alloy
	XRF*	Nickel alloy thickness
	Peeling test	Adhesion of nickel alloy on copper
	Stylus	Nickel alloy roughness
Gold	SEM	Gold topography
	XRF*	Gold thickness
	Peeling test	Adhesion of gold on nickel

* Required the ENIG plating standard from MMCT

1.2 Objectives

1.2.1 To study the effects of chemicals and pH which are controlled by industry on the final thickness of nickel and gold layers

1.2.2 To study the plating mechanism and plating rate of nickel and gold layers by varying the chemicals and pH

1.3 Scopes of research

1.3.1 The baths in the electroless nickel immersion gold (ENIG) in the production line of MMCT which are degreasing bath, etching bath, activation 1-3 baths, catalyst bath, post-dipping bath, electroless nickel plating bath and immersion gold bath are investigated.

1.3.2 Surface properties include nickel thickness, the amount of phosphorus in nickel alloy, gold thickness, surface topography and surface roughness.

1.4 Procedure of research

1.4.1 Extract knowledge from literature

1.4.2 Analyze data from the production line to find the sensitive variables

1.4.3 Set up lab-scale ENIG plating process experiment and measure input parameters, controlled output parameters and other output parameters

1.4.4 Compare the result between the lab-scale experiment and the production line as well as assay other parameters that affect the outputs

1.5 Outline of this thesis

1.5.1 Chapter 1: Introduction

In this chapter, statements, objectives and scopes of this research are described. The basic knowledge of ENIG production and product appearance are explicated. The procedure and outline of this research are summarized.

1.5.2 Chapter 2: Theory and literature reviews

The roles of each step of the ENIG process are clarified by the theory and literature from the published researches. The steps include all pretreatment procedures, electroless nickel plating and immersion gold plating. In the pretreatment section, the principles and chemical reactions are considered. For the plating section, the effects of the concentration of reactants and pH which are the controlled parameters in actual process are the main issue. Out of this, some of other input parameters which are concerned by the published research are included.

1.5.3 Chapter 3: Information access from the actual production

The input and output parameters are collected in the actual process and analyzed the effect of each parameter on the plated layer thickness by the statistical program, JMP7. The most sensitive parameters from each plating bath are found.

1.5.4 Chapter 4: Experiments

The experiments are designed by the results in published articles as explained in chapter 2 and data analysis in chapter 3 for checking the results from chapter 3. The experiments are divided into 2 parts, i.e., the electroless nickel plating and immersion gold plating. The concerned parameters are concentration of the reactants, pH of solution, and the effect of characters of nickel substrate on the immersion gold plating.

1.5.5 Chapter 5: Results and discussion

The results are divided into 2 parts: electroless nickel plating and immersion gold plating. The results are analyzed by the analytical methods, as shown in Table 1.1 and then compared to the published researches as mentioned in chapter 2 and data analysis from chapter 3.

1.5.6 Chapter 6: Trouble shooting

The results that show the problems are discussed in this chapter. The effects of the experimental method and conditions are concerned.

1.5.7 Chapter 7: Conclusions and recommendations

In this chapter, the overall of this research is concluded. The recommendation for controlling the ENIG process are also mentioned.

CHAPTER 2

Theory and literature reviews

Electroless nickel immersion gold (ENIG) is one of the surface treatment technique which provides the electroless nickel (EN) film that is covered by immersion gold (IG) film on the surface of substrate. The films are produced as nanofilm by plating process which is a thermodynamically bottom-up approach. The process is started by nucleation of metal ion on the surface of different materials and then growing into film.[2] However, the reactions require clean environment and clean substrate to prevent unrequired impurities which affect the process. Aforementioned, the production of ENIG includes two sections, pretreatment section for preparing clean substrate and plating section to deposit nickel and gold layers, as shown in Figure 2.1.

2.1 Pretreatment section

The pretreatment section in ENIG process contains 7 steps starting from degreasing to post-dipping. Activation (3) which is the step after nickel plating is also a pretreatment process. The purposes of this section are for cleaning the substrate, removing oxide and preparing substrate for the plating section.

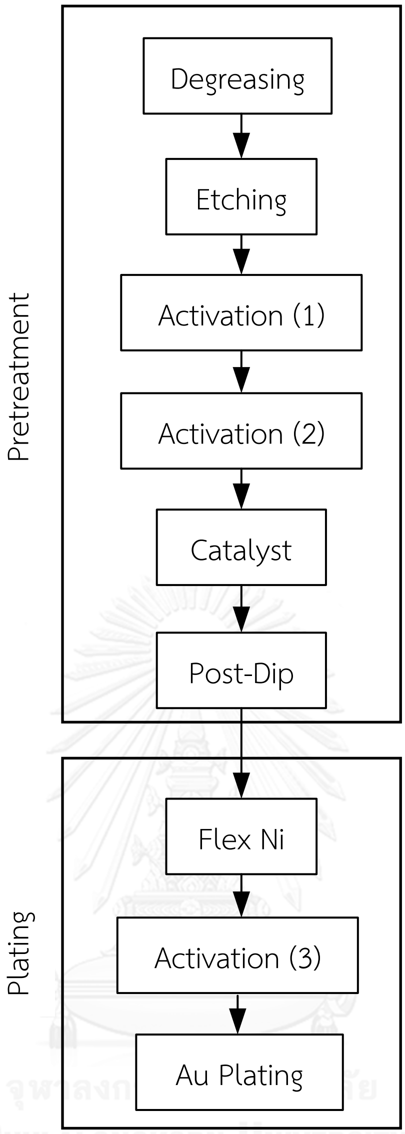


Figure 2.1 Block flow diagram of ENIG process

2.1.1 Degreasing

The main chemical used is inorganic base which is used as cleaning[4] and sanitizing agent for removing proteins, oils, fats, and greases on the surface of substrate. Proteins are dissolved in this inorganic base. Other proteins such as bacteria, yeast and fungi are also inactivated.[5, 6] Oils, fats and greases are removed by saponification reaction, as displayed in reaction 2.1.[7] Another chemical is surfactant which prevents the redisposition of dissolved substances.

$$triglyceride\ + inorganic\ base \rightarrow glycerol + soap\ (ester) \tag{2.1}$$

2.1.2 Soft etching

This step is a soft etching step due to usage of dilute etching chemicals such as inorganic salt which is oxidizing agent and inorganic acid. The surface of substrate is etched to remove oxides and increase the surface roughness for providing good adhesion of nickel film on substrate. The reason why the dilute inorganic acid only reacting with copper oxide will be described in section 2.1.3. The reaction in this bath is as follows [8, 9]:

$$Cu\ + inorganic\ salt \rightarrow Cu^{2+} + other\ productS \tag{2.2}$$

$$Cu_2O + dilute\ inorganic\ acid \rightarrow Cu + Cu^{2+} + other\ product + 2H_2O \tag{2.3}$$

$$CuO + dilute\ inorganic\ acid \rightarrow Cu^{2+} + other\ product + 2H_2O \tag{2.4}$$

2.1.3 Activation (1)

The chemical in this bath is a pure dilute inorganic acid. The oxides and smuts remaining on the substrate are removed in order to ensure that there is no chemicals and impurities on the substrate. The reaction is the same as reaction 2.3 and 2.4. The standard potential of this inorganic acid could be 0, +0.2, +0.17 and -0.93 V[8] depending on the reactants and products. Therefore, the total potential of reaction equations with this inorganic acid at room temperature calculated by equation 2.8 are negative (-0.337, -0.137, -0.167 and -1.267 V), Thus the reaction with copper is not occurred by any oxidant. Furthermore, dilute inorganic acid is non-oxidizing agent but the concentrated inorganic acid is and it requires high temperature to evoke one of the oxidation of inorganic acid reaction with the new value of the reduction potential. Nevertheless, the ionic charge of copper in the reaction 2.3 is changed from 1+ into 2+ and 1+ into 0. The one of copper ion is reduced and the other one is oxidized, so this redox reaction is occurred by the reduction and the oxidation reaction of the 2 copper ions and the total potential of reaction equations is 0.362 V. However, the reaction 2.4 is ionic reaction, so it can be occurred.

$$Cu_2O + dilute\ inorganic\ acid \rightarrow Cu + Cu^{2+} + other\ product + 2H_2O \tag{2.3}$$

$$CuO + dilute\ inorganic\ acid \rightarrow Cu^{2+} + other\ product + 2H_2O \tag{2.4}$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow\ Cu_{(s)} \qquad E^0 = +0.337\,V \tag{2.5}$$

$$Cu^{2+}_{(aq)} + e^- \rightarrow\ Cu^{+}_{(aq)} \qquad E^0 = +0.159\,V \tag{2.6}$$

$$Cu^{+}_{(aq)} + e^- \rightarrow\ Cu_{(s)} \qquad E^0 = +0.521\,V \tag{2.7}$$

$$E^0_{cell} = E^0_{cathode} -\ E^0_{anode} \tag{2.8}$$

2.1.4 Activation (2)

This step is a preparation for catalyst deposition step. The impurities and other chemicals are washed by the solvent similar to that using in the catalyst batch, so the impurity, water and other chemicals would not contaminate in the catalyst batch.

2.1.5 Catalyst plating

For preparing the nickel deposition reaction, the metal catalyst is deposited on the surface of copper substrate first. The reaction of this process is a galvanic displacement of surface of substrate by catalyst, as shown in reaction 2.10.[10] The change of the weight of plating would be slow after the metal covered all the substrate. Temperature slightly affects the rate of catalyst plating. Its function is to initiate the nickel deposition reaction by adsorption of hydrogen atom from reducing agent.[11] For plating catalyst on the substrate, just islands of it is fine[12], as shown in Figure 2.2. The evidence is shown in Figure 2.3 that the EN is deposited on the daub of catalyst plating before the deposition on the clear substrate. The details of the mechanism will be discussed in 2.2.1.1 on the topic of EN plating mechanism.

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E^0 = +0.337\,V \tag{2.5}$$

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)} \qquad E^0 \geq +0.337\,V \tag{2.9}$$

$$Cu + \frac{2}{n}M^{n+} \rightarrow Cu^{2+} + \frac{2}{n}M \tag{2.10}$$

M = Catalyst

n = Catalyst oxidation number

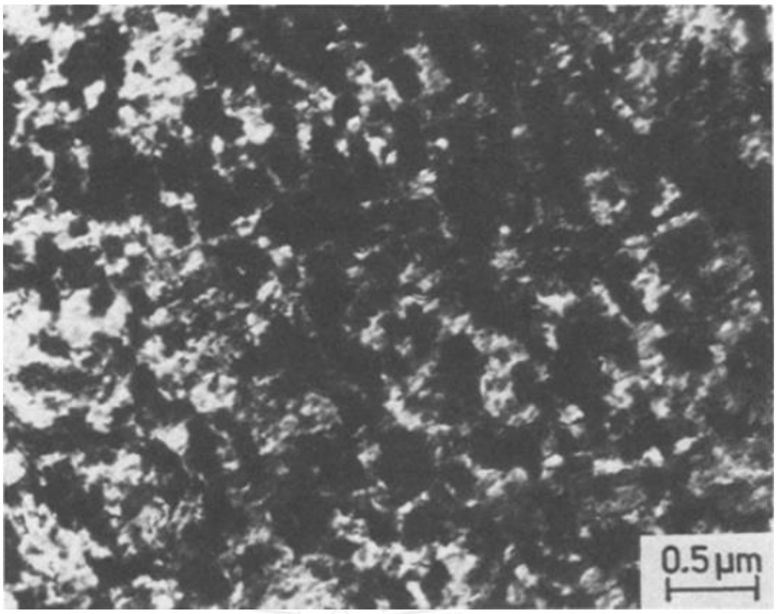


Figure 2.2 Catalyst (black) plated on copper substrate (light).[12]

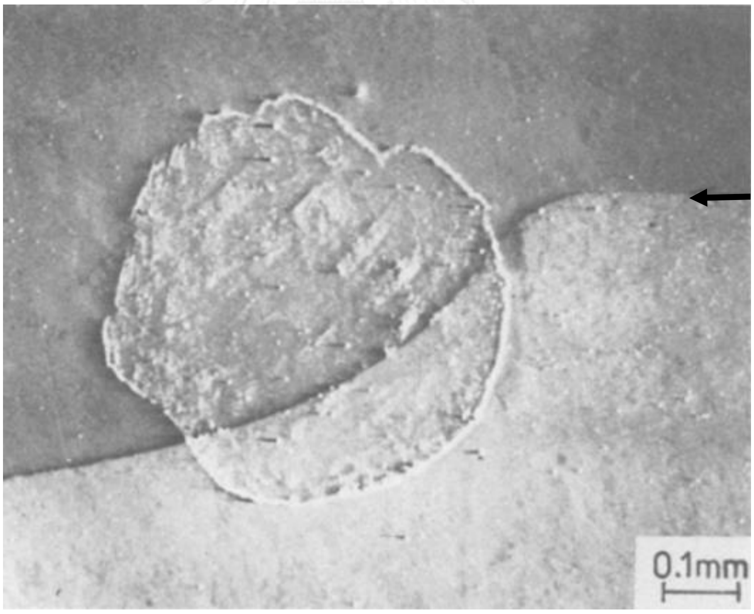


Figure 2.3 The daub of catalyst (center), copper substrate (above arrow) and electroless nickel plating (under arrow).[12]

2.1.6 Post-dipping

The main chemicals in this bath are diamine and organic acid as the chelating agent or complexing agent as shown in previous published works[11, 13, 14]. Since the standard reduction potential of the catalyst is highly positive value, there are not many substances which can receive electron from the catalyst. Hence, there is no etching or redox reaction in this bath. To eliminate the catalyst on the needless area, the chelating agent is necessary. The complex around the remained catalyst ions and very small particles on that area are established and then desorbed from the surface. This step allows the neatly electroless nickel plating that is not an exceptional plating area.

2.1.7 Activation (3)

The chemical in this bath is a dilute inorganic acid and its role is similar to that in Activation (2) bath. However, this bath is placed after EN plating bath so the substrate which is cleaned in this bath is nickel. The rust of nickel, nickel (II) oxide and nickel (III) oxide, is removed in this bath. Nickel (II) oxide is eliminated by ionic reaction with the inorganic acid as shown in reaction 2.13. To dispose nickel (III) oxide, the reaction 2.14 shows that Ni^{3+} is changed into Ni^{2+} by receiving the electron from O^{2-} which is converted into O and then the reaction 2.13 occurred that Ni^{2+} reacts with the inorganic acid.[15] The dissolution rate of all nickel oxide depends on the acid concentration and the nickel (II) oxide seems to be removed easier than nickel (III) oxide.[16] In addition, nickel also reacts with the inorganic acid. Since it is a dilute acid, the reductant is hydrogen, thus the reaction 2.15 is the result from the reaction 2.11 and 2.12.

$$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)} \qquad E^0 = -0.25\,V \tag{2.11}$$

$$2H^{+}_{(aq)} + 2e^- \rightarrow H_{2(s)} \qquad E^0 = 0\,V \tag{2.12}$$

$$NiO + inorganic\ acid \rightarrow Ni^{2+}_{(aq)} + other\ product + H_2O \tag{2.13}$$

$$2Ni_2O_3 \rightarrow 4NiO + O_2 \tag{2.14}$$

$$Ni + 2H^+ \rightarrow Ni^{2+}_{(aq)} + H_2 \tag{2.15}$$

2.2 Plating section

In this section, metal films are created on the substrate. To grow the film, the nucleation and growth process of metals require 6 deposition steps of reactants, as shown in Figure 2.4. Growth species, which can be either metal ion or complex metal ion, are diffused from the bulk and then adsorb on the surface of substrate. In the adsorption step, if the length between species and surface is more than adsorption length, the species desorb. After adsorption, the species receive electrons to be atoms and then diffuse to the surface. When the atoms find the surface which matches their energy, they change into crystal structures. Then, the by-products desorb and diffuse from the substrate. This process, the adsorption and surface reaction are the important steps. After the reaction occurs, the thickness of diffusion layer will be thicker as shown in Figure 2.5. Figure 2.6 shows that the concentration of reactant affects the growth rate and what will be the rate determining step (RDS). If the concentration is low, diffusion is RDS. On the other hand, surface reaction is RDS. For ENIG process, the concentrations of reactant is low. To have better adsorption, the chelating agent or complexing agent is required. The details of the chelating agent will be discussed in 2.2.1.2.[2]

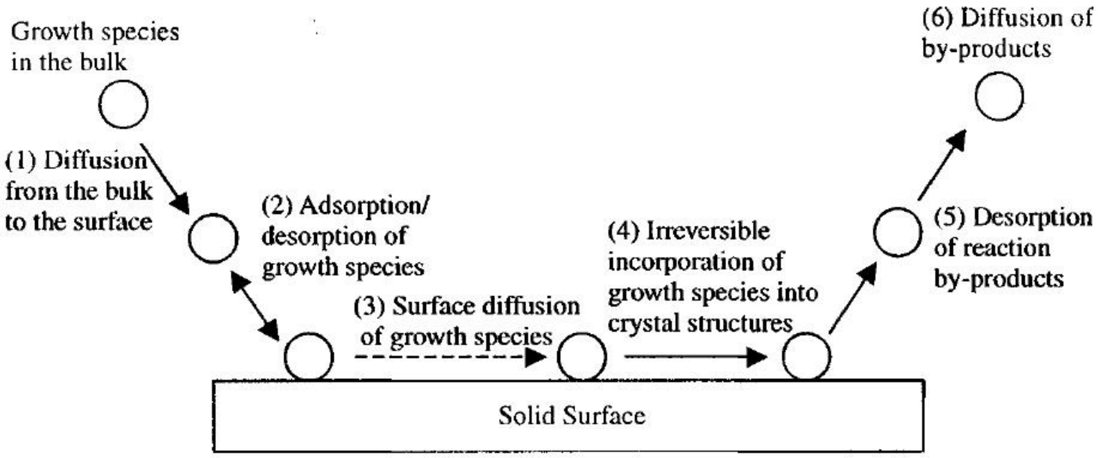


Figure 2.4 The deposition steps of metal ion on the substrate[2]

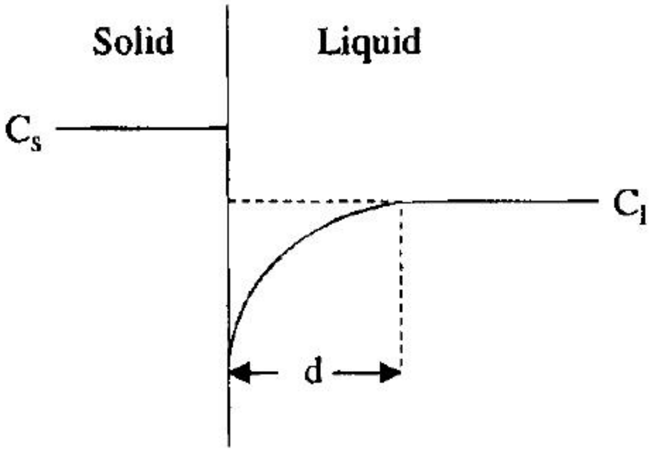


Figure 2.5 The concentration gradient of reactant[2]

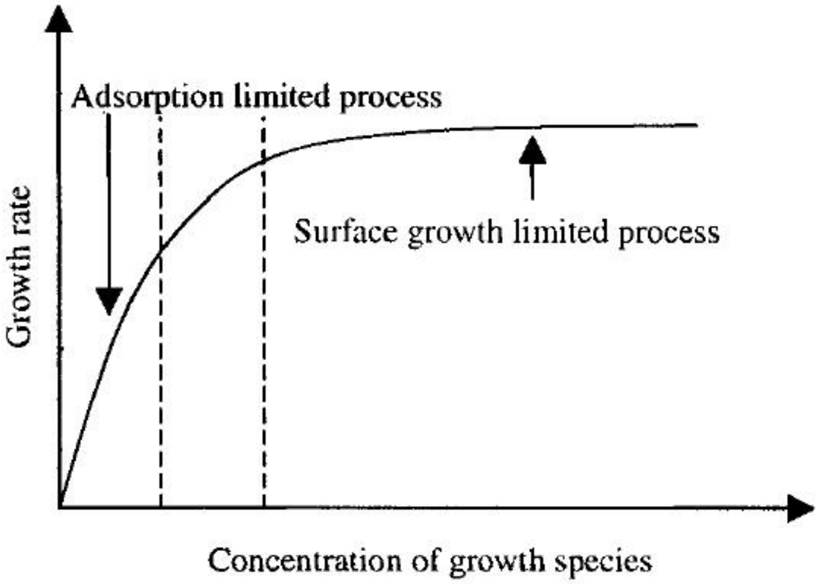


Figure 2.6 Relation between growth rate and reactant concentration.[2]

2.2.1 Electroless nickel (EN) plating

A layer of nickel-phosphorus alloy is formed on the copper surface after finishing this step. The necessary components for EN plating are a source of nickel ion, a reducing agent, complexing agents, stabilizers or inhibitors and energy. For acid bath (pH = 4 - 6), the operation temperature should be controlled near 90 °C.[17] The proportion of chemicals content and pH of solution affects the plating rate, crystallinity (phosphorus content) and surface roughness of Ni-P alloy. There are 4 mechanisms for EN plating. However, there are only 2 mechanisms; oxidation of atomic hydrogen and hydride transfer, which are widely investigated.

2.2.1.1 Mechanisms of electroless nickel plating

Oxidation of atomic hydrogen mechanism

This mechanism was proposed by Brenner and Riddell.[17] The reaction between reducing agent which has phosphorus contented and water generated atomic hydrogens which were adsorbed on catalyst (H_{ad}). The catalyst can be other metals which had the hydrogen adsorption ability in which nickel was including.

$$reducing\ agent + H_2O \rightarrow productA + 2H_{ad} \tag{2.16}$$

Then, nickel ion which was adsorbed on the catalyst surface was reduced by the adsorbed atomic hydrogen. Meanwhile, some of atomic hydrogens were recombined into hydrogen gas.

$$Ni^{2+} + 2H_{ad} \rightarrow (Ni^{2+} + 2H^+ + 2e) \rightarrow Ni^0 + 2H^+ \tag{2.17}$$

$$2H_{ad} \rightarrow (H + H) \rightarrow H_2 \tag{2.18}$$

Gutzeit[18] who agreed with oxidation of atomic hydrogen mechanism, had developed the phosphorus plating mechanism.

$$reducing\ agent \xrightarrow{cat} productB + 2H \tag{2.19}$$

$$productB + H_2O \ \rightarrow productC + H^+ \tag{2.20}$$

$$reducing\ agent + H \rightarrow P + OH^- + H_2O \tag{2.21}$$

Nevertheless, this mechanism does not clarify why the hydrogen gas always occurs at the same time with nickel deposition and there is always less than 50 percent of the utilization of stoichiometric for the reducing agent.

Hydride transfer mechanism (Hersch[19] and then modified by Lukes[20])

For this mechanism, the reducing agent was assumed to donate hydride ions (H^-) which reduced the nickel ion. In addition, there were reaction that hydride reacted with proton and water. The mechanism was divided into two parts, in acid and alkaline solution.

In acid solution:

$$2reducing\ agent + 2H_2O \xrightarrow{cat} 2productA + 2H^+ + 2H^- \tag{2.22}$$

$$H^+ + H^- \rightarrow H_2 \tag{2.23}$$

In alkaline solution:

$$2reducing\ agent + 6OH^- \xrightarrow{cat} 2productA + 2H_2O + 2H^- \tag{2.24}$$

$$H_2O + H^- \rightarrow H_2 + OH^- \tag{2.25}$$

The nickel ion was reduced by hydride ion as follow:

$$Ni^{2+} + 2H^- \rightarrow (Ni^{2+} + 2H + 2e) \rightarrow Ni^0 + H_2 \tag{2.26}$$

Moreover, if the hydride ion was bonded with the phosphorus formerly, the equation 2.23 could be clarified. This mechanism also accounted the decrease of nickel and hydrogen in which the oxidation of atomic hydrogen mechanism could not explain.[21]

$$reducing\ agent + 2H^{+} + H^{-} \rightarrow 2H_2O + \frac{1}{2}H_2 + P \qquad (2.27)$$

<u>Electrochemical mechanism</u> (Brenner and Riddell, and modified by others)[17]

$$Ni^{2+}_{(aq)} + 2e^{-} \rightarrow Ni_{(s)} \qquad E^{0} = -0.25\ V \qquad (2.11)$$

$$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)} \qquad E^{0} = 0\ V \qquad (2.12)$$

$$reducing\ agent + 2H^{+} + e^{-} \rightarrow P + 2H_2O \qquad E^{0} = +0.50\ V \qquad (2.28)$$

$$reducing\ agent + H_2O \rightarrow productA + 2H^{+} + 2e^{-} \qquad E^{0} = +0.50\ V \qquad (2.29)$$

The equations above show that, the hydrogen gas can be generated during nickel deposition. However, it contradicts the previous study which reported that nickel concentration was the zero order variable in rate of reaction in the acid bath, so this mechanism is not applied to references.

The coordination of hydroxyl ions with hexaquonickel ion mechanism (Cavallotti and Salvago)[22]

According to this mechanism, it related to the nickel complex of hydroxyl ion and water molecule which is supported by calorimetric studies on EN.[23] However, there are some contradictions. The reaction 2.32 shows that $NiOH^+$ must be adsorbed on the catalyst and reacted with reducing agent, then the product is nickel solid. Then the reaction 2.34 can be activated. After phosphorus plating, the surface will be full with $NiOH^+$ again. If this sequence goes on, the product would be the lamellar structure in which it does not happen. Hence, this mechanism is not widely used.

$$H_2O \rightarrow 2H^+ + 2OH^- \tag{2.30}$$

$$Ni(OH)_{2(aq)} + reducing\ agent \rightarrow Ni(OH)^+_{ads} + productA + H \tag{2.31}$$

$$Ni(OH)^+_{ads} + reducing\ agent \rightarrow Ni^0 + productA + H \tag{2.32}$$

$$H + H \rightarrow H_2 \tag{2.33}$$

$$Ni_{cat} + reducing\ agent \rightarrow P + Ni(OH)^+_{ads} + OH^- \tag{2.34}$$

$$Ni(OH)^+_{ads} + H_2O \rightarrow Ni(OH)_{2(aq)} + H \tag{2.35}$$

2.2.1.2 The effects of input parameters on nickel plating characteristic

Nickel concentration[11]

In acid bath (pH = 4 - 6), the nickel concentration is beyond 0.085 M (5 g/L), the rate of deposition was independent or slightly dependent on nickel concentration.[24] The variable that was most affected by nickel concentration is the amount of phosphorus content in EN plating, as shown in Figure 2.7. The increase of nickel concentration decrease phosphorus content but it did not change when the nickel concentration was beyond 0.1 M (5.8 g/L). However, in alkaline bath, type of chelating agents could affect the result, for example in citrate bath, the concentration of nickel slightly affected the deposition rate and the rate was increased obviously in the pyrophosphate bath. The result of nickel concentration variation in pyrophosphate bath is shown in Figure 2.8.

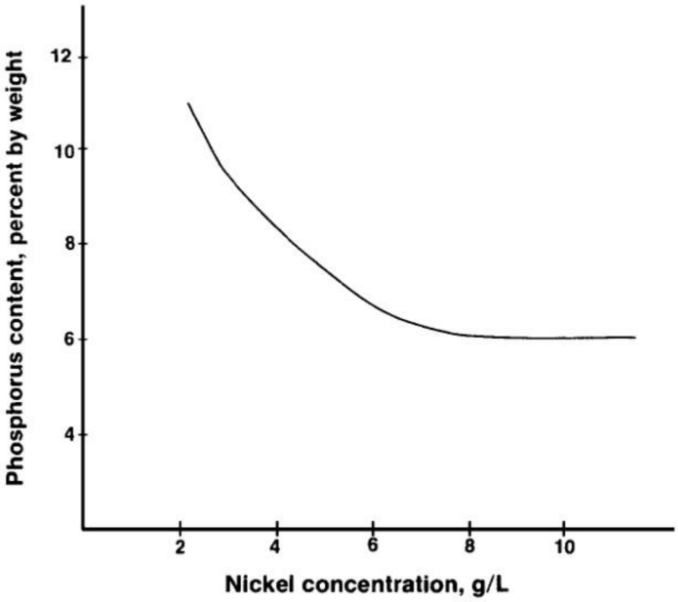


Figure 2.7 Effect of nickel concentration on phosphorus content in acid bath[25]

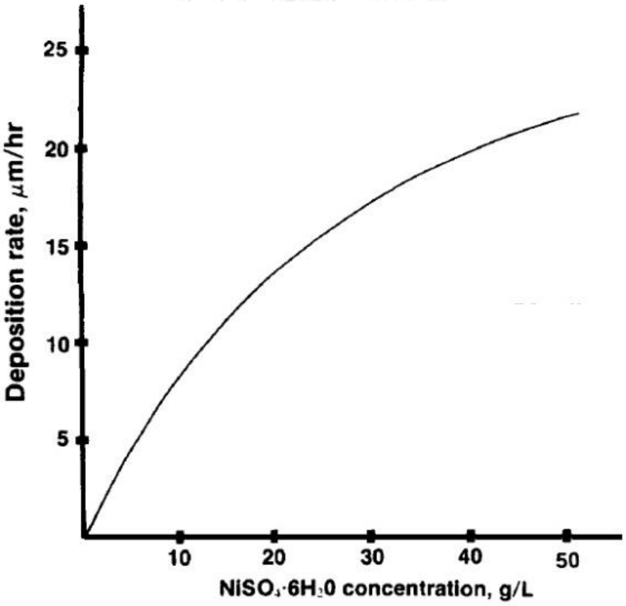


Figure 2.8 Effect of nickel concentration on deposition rate in alkaline pyrophosphate bath[25]

Table 2.1 The conditions used in the results in Figure 2.8

Parameters	Amount
Nickel conc.	vary
Reducing agent conc.	25 g/L
pH	10 – 10.5
Chelating agents	Pyrophosphate
Temperature	74 °C
Deposition time	1 hr

Reducing agent concentration[11]

The rate of nickel and phosphorus deposition was changed by changing reducing agent concentration as the first order reaction for the deposition rate of nickel in acid bath and second order reaction for rate of phosphorus deposition[26] which increasing of reducing agent and proton incurred more of phosphorus deposition, as shown in Figure 2.9. However, in alkaline bath, the order of rate of deposition also depended on types of chelating agent. Increasing reducing agent made an increase of rate deposition, as shown in Figure 2.10 but it decreases the stability of plating bath.

$$\frac{dp}{dt} = K[reducing\ agent]^{1.91}[H^+]^{0.25} \tag{2.36}$$

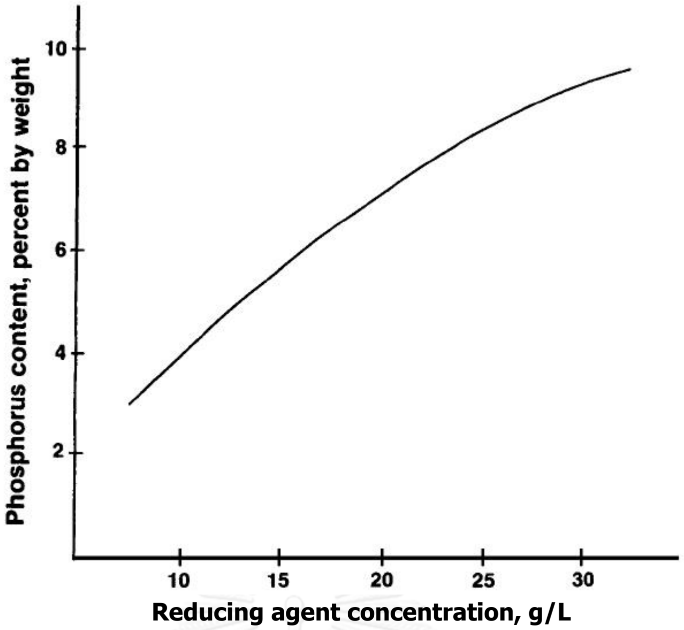


Figure 2.9 Effect of reducing agent concentration (g/L) on phosphorus content in acid bath[25]

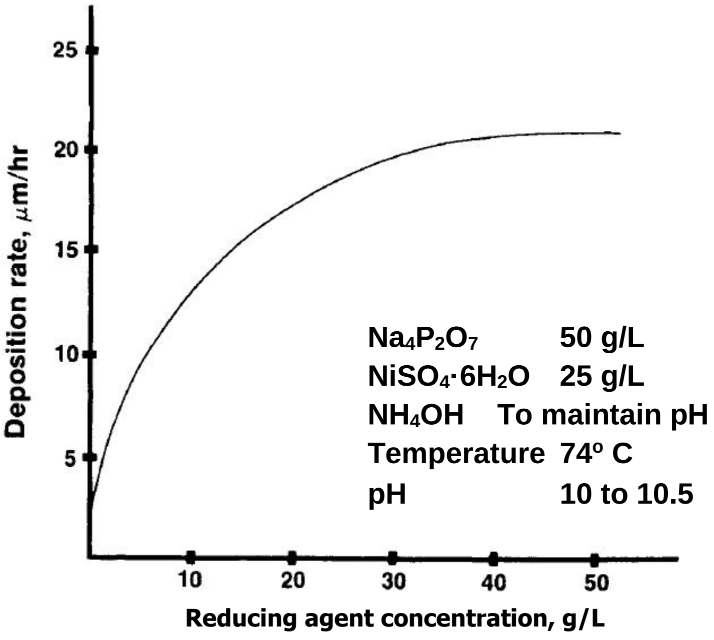


Figure 2.10 Effect of reducing agent concentration on deposition rate in alkaline pyrophosphate bath[11]

Table 2.2 The conditions used in the results in Figure 2.10

Parameters	Amount
Nickel conc.	25 g/L
Reducing agent conc.	vary
pH	10 – 10.5
Chelating agents	Pyrophosphate
Temperature	74 °C
Deposition time	1 hr

pH of EN plating solution[11]

When nickel ion was deposited, protons were evoked and then pH decreased. Therefore, the deposition rate decreased at lower pH due to increasing by-product, protons. Furthermore, pH of nickel plating solution affected the phosphorus content and roughness in nickel layer. As mentioned, the proton was also considered in phosphorus deposition rate. The lower pH resulted in increasing the amount of phosphorus deposition. Yoon and coworkers [27] proved that pH affected the nodule size of nickel. High pH caused large nodule of nickel, so the roughness of nickel decreased by increasing pH. Although lower pH caused low deposition rate, it increased the solubility of another by-product, phosphorus acid which should be considered for optimum pH. The effects of pH on the deposited phosphorus content, deposition rate, and RMS are demonstrated in Figure 2.11 and 2.12.

$$\frac{dNi^0}{dt} = K\frac{[reducing\ agent]}{[H^+]^b} \tag{2.37}$$

b = Order of the reaction

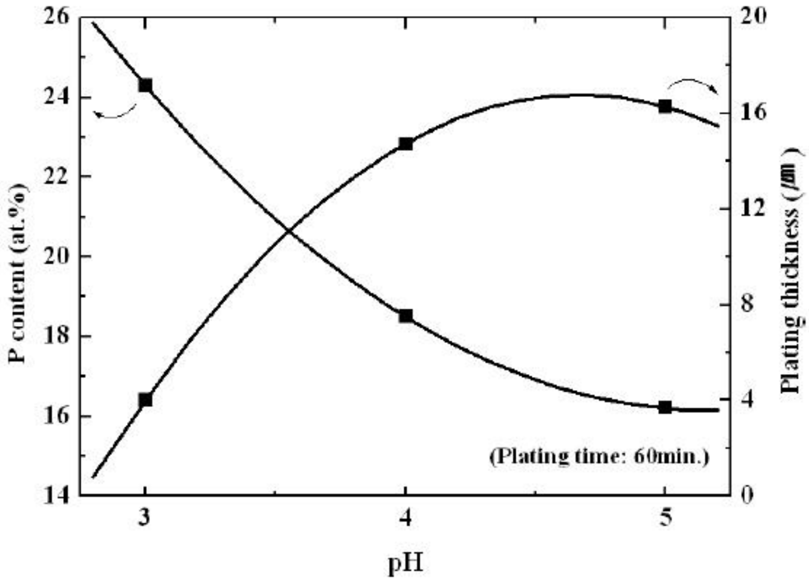


Figure 2.11 Effect of pH on phosphorus content and deposition rate[27]

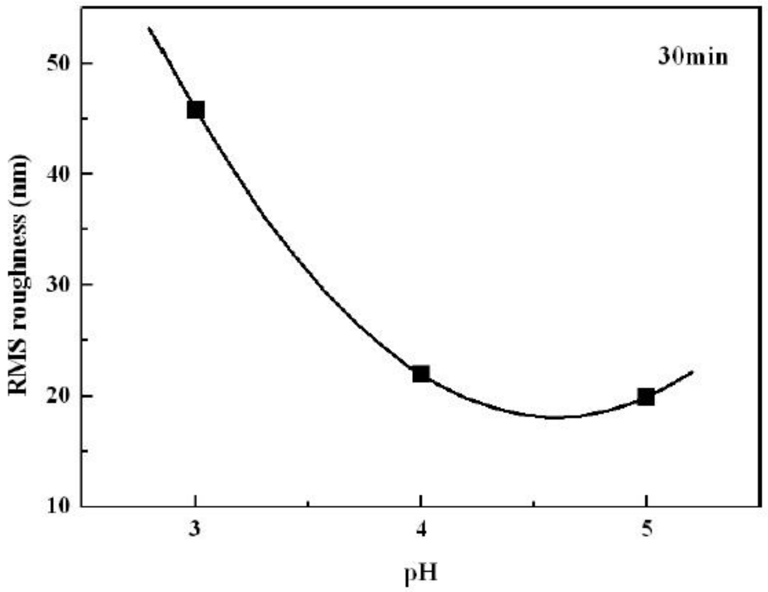


Figure 2.12 Effect of pH on RMS roughness of nickel surface[27]

Molar ratio of nickel ion to reducing agent[11]

The molar ratio of nickel ion to reducing agent should be considered. The recommended range was 0.30 - 0.45. Figure 2.13 shows that the deposition rate of nickel alloy at high pH was faster than that at low pH by varying nickel ion. At very low molar ratio between 0.20 - 0.25, the trend of deposition rate was opposite. Namely, the deposition rate at low pH was faster than that at high pH. The result of this opposite trend resulted from a very low concentration of nickel. However, too high level of nickel ion made the decrease of deposition rate because of lacking of reducing agent. At slow deposition rate, it gave high roughness and dull nickel plating. On the other hand, fast deposition rate gave smooth surface and bright nickel plating.[28]

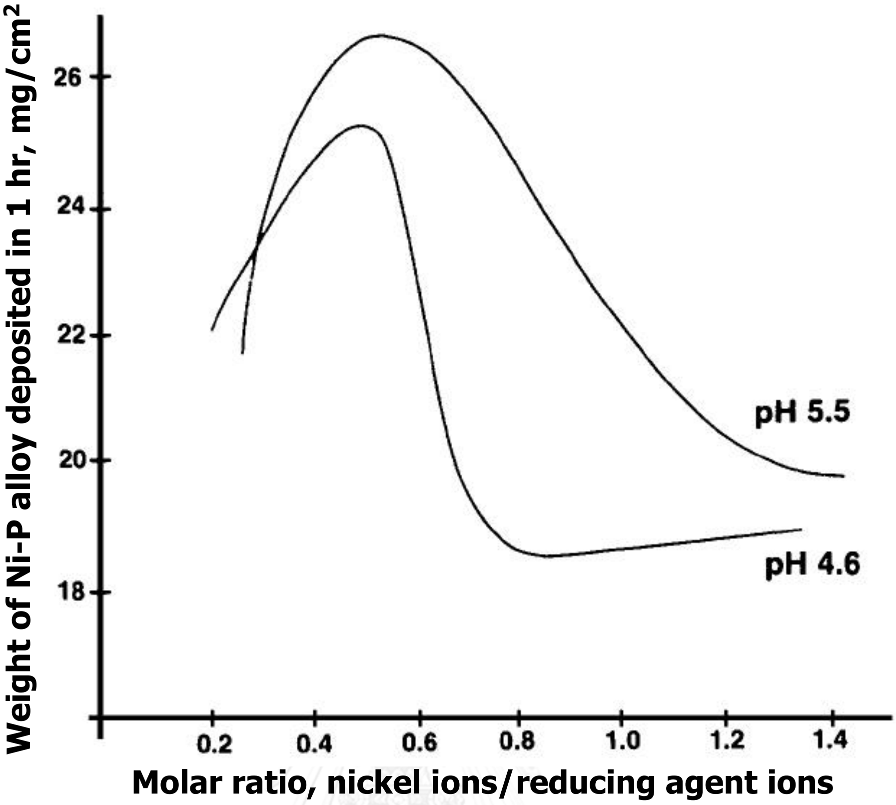


Figure 2.13 Effect of molar ratio of nickel ions and reducing agent ion on deposition rate[29]

<u>By-product from the reducing agent</u>[11]

Phosphorus acid and nickel-reducing agent compound are the by-products of nickel-phosphorus alloy plating reaction that accumulate in plating solution. Their solubility are low at high temperature. Adding alcohol helped solubility of by-product. To help nickel-reducing agent compound dissolved, the effective methods which prevents its precipitation are plating at low pH solution and adding hydroxyl carboxylic acids such as lactic and hydroxyacetic acids. These chemicals take the role as the chelating agents that prevent the precipitation at low concentration of nickel-reducing agent compound. For the well calculated bath which is used in production, there is the parameter that casually calculates the amount of by-products, MTO parameter. There was previous work that studied the effect of MTO parameter on the stability of plating bath.[30] Figure 2.14 shows that the pH and the stability constant of plating bath was decreased by the generated by-product.

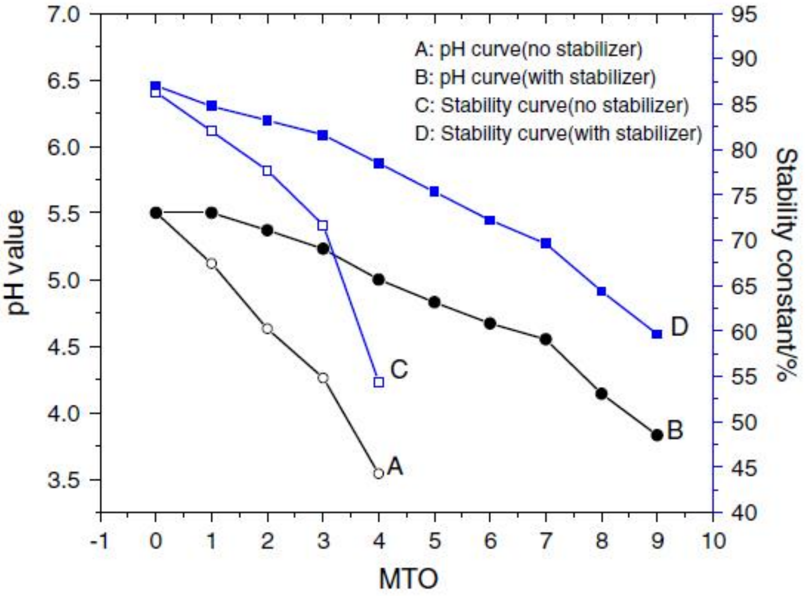


Figure 2.14 Effect of MTO on pH (A) without/(B) with pH stabilizer and stability of bath (C) without/(D) with pH stabilizer[30]

Note: MTO parameter = Variable measures how a substance is added as a number of times (MTO) of default.

$$\%stability\ constant = \frac{weight\ of\ Nickel\ deposite\ (g)}{(C_{nickel1}V_{1-}C_{nickel2}V_2) \times MW_{nickel}} \times 100 \qquad (2.38)$$

Temperature[11]

The suitable operating temperature was between 85 – 90 °C. High temperature helped nickel plating rate and reduced phosphorus deposition rate. However, operating at high temperature led to the possibility for the solution to be decomposed quickly.

Chelating agent[11]

The chemicals which can serve as chelating agent or complexing agent are organic acids or their salt, pyrophosphate anion (for alkaline EN solution) and ammonium ion. Other roles of these chemicals are being buffer, preventing the precipitation of nickel salt and decreasing the free nickel ion. The most important role of chelating agent is being complex of metal ion to increase adsorption rate.[31] Some of properties of metal complex will be different by different types of complex such as, color, reduction potential and solubility. The type of chelating agent can be divided by the amount of functional groups such as, carboxyl and amine in the chain which are called monodentate, bidentate, tridentate etc. There are two ways to attach the metal, attaching as a chain and creating the chelate rings as shown in Figure 2.15. The coordinate atoms are N and O in which N atom seemed to be more stable than O atom with high stability constant (pK) and made low deposition rate. The stable ring size was five and six ring size.[21] The chelating agent which could create more than seven ring size would prefer to attach two metal ion rather create ring. Table 2.3 shows some of the chelating agent types which are used in EN bath. Moreover, each type of chelating agent gives the highest deposition rate, as shown in Figure 2.16. The amount of phosphorus was also affected by the type of chelating agent, as shown in Figure 2.17. The O coordinating atom tended to provide high phosphorus contented opposite the N coordination.[21]

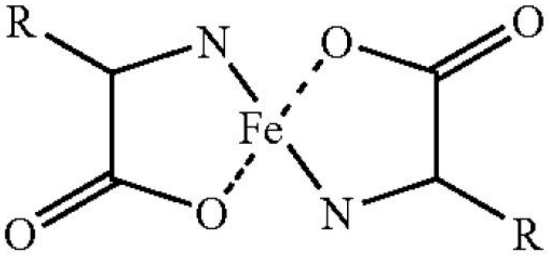


Figure 2.15 Two chelating agent rings with 5 ring size.[32]

$$NiL_3{}^{2-3n} \overset{k_1}{\leftrightarrow} NiL_2{}^{2-2n} + L^{-n} \tag{2.39}$$

$$NiL_2{}^{2-2n} \overset{k_2}{\leftrightarrow} NiL_2{}^{2-n} + L^{-n} \tag{2.40}$$

$$NiL^{2-n} \overset{k_3}{\leftrightarrow} Ni^{2+} + L^{-n} \tag{2.41}$$

$$K_m = k_1 k_2 \dots k_m = \frac{[Ni^{2+}][L^{-n}]^m}{\left[NiL_m{}^{2-mn}\right]} \tag{2.42}$$

$$K_{NiL} = \frac{1}{K_m} = Stability\ constant \tag{2.43}$$

L = Chelating agent

n = Ionization number of chelating agent

m = Amount of chelating agent attachment (monodentate = 6, bidentate = 3 …)

Table 2.3 The chelating agents regularly used in EN bath[11]

Anion	No. of chelate ring	Ring size	pK
Monodentate			
Acetate	0	-	1.5
Succinate	0	-	2.2
Bidentate			
Aminoacetate	1	5	6.1
Ethylenediamine	1	5	13.5
Malonate	1	6	4.2
Pyrophosphate	1	6	5.3
Tridentate			
Malate	2	5,6	3.4
Quadridentate			
Citrate	2	5,6	6.9

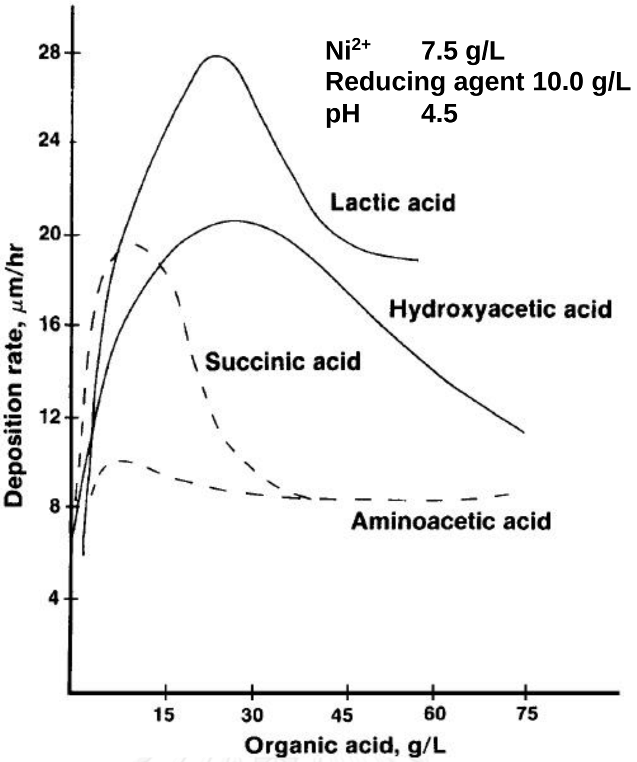


Figure 2.16 Effect of complexing agent concentration on deposition rate of nickel[33]

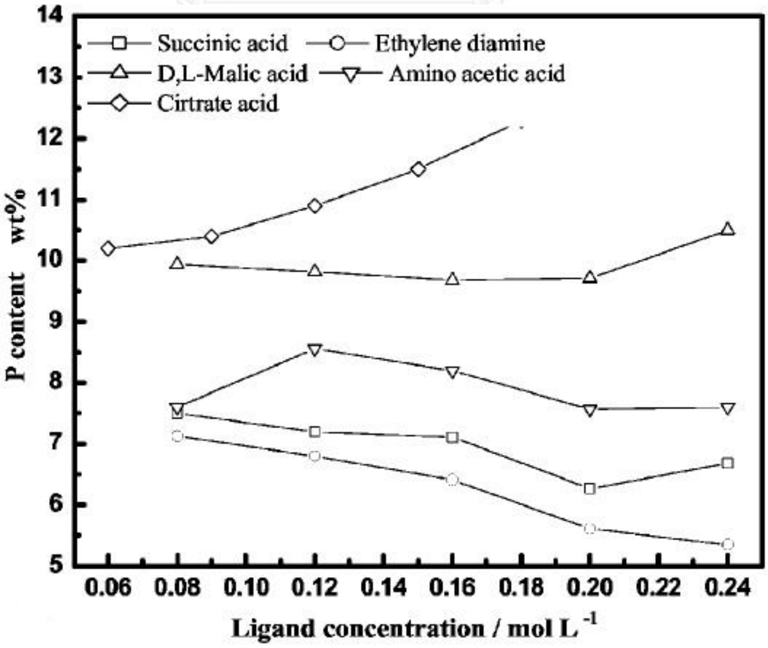


Figure 2.17 Effect of complexing agent concentration on deposition rate of nickel[21]

Stabilizer (catalytic inhibitor)[11]

The stabilizer is the additive which prevents the hydrogenation and dehydrogenation reaction. It can be divided into four classes.

1. Compounds of group VI elements such as, S, Se and Te.
2. Compounds containing oxygen such as AsO2-, IO3- and MoO42-
3. Heavy metal cations
4. Unsaturated organic acids

Class 1 and 2 are strong adsorption stabilizers on catalyst that can reduce amount of reactant adsorption on catalyst, especially thiourea from class 1 which could cause microporosity and sulfur deposition. They also helped reducing the amount of phosphorus plating, so they were adapted for the nickel with low phosphorus alloy plating.

Class 3 of the stabilizer are working on the metal colloidal particles. The cations on the particle repel other particles due to their charge on the surface to prevent the sedimentation of metal and decomposition of the plating bath. For the same composition of plating bath, the product from the plating bath that stabilizer is class 3 tends to have phosphorus content more than class 1 and 2.

Class 4 also adsorbs on the catalyst but it receives the hydrogen from the catalyst to change itself into saturated organic acid which it will not be the stabilizer anymore or other isomer which still has the ability as stabilizer.

Agitation

The agitation is required for electroless nickel plating to disrupt the diffusion layer at the surface. Most of previous works used gas bubbles to agitate and the most effective gas for increasing stability of the plating bath is oxygen gas.[11] Lack of agitation can cause the gas pit or streaking of the deposit. However, the proper agitation is need. The transition region of mixing was the best for agitation due to prevention of sedimentation and there was no disturb diffusion and adsorption of the ions.[34]

2.2.2 Immersion gold plating

The gold layer could be formed on Ni-P surface for protecting nickel from oxidization reaction. The proportion of chemical content and pH of gold solution is affects the gold plating rate which affects the quality of product and invariability of film thickness. The reaction of this process is galvanic displacement of surface of substrate by gold, as shown in reaction 2.45.[31]

$$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)} \qquad E^0 = -0.25\,V \tag{2.11}$$

$$Au^{+}_{(aq)} + e^- \rightarrow Au_{(s)} \qquad E^0 = +1.692\,V \tag{2.44}$$

$$Ni + 2Au^{+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Au_{(s)} \tag{2.45}$$

2.2.2.1 The effects of input parameters on immersion gold plating characteristic

Plating time

From Figure 2.18, the deposition rate can be divided into 3 periods. At the first period (t = 0 – t1) or initial period, the deposition rate increased very fast. Then the deposition rate gradually decreased at the second period (t1 - t2). At the third period (longer than t2), the deposition rate decreased slowly. Liu and coworkers[31] claimed that gold layer was rather closed to the nickel surface. Because the duty of gold plating is to prevent the nickel substrate from oxidization, the porousness of gold plating should be small. In reaction 2.45, one nickel ion was removed and then two ions of gold deposited. The atom of gold is larger than the atom of nickel so there must be some pinholes on the gold layer[35] and the deposition rate was not equal to zero because the holes on gold layer allowed nickel to dissolve (Figure 2.19). Thus, the reaction did not stop and the nickel substrate was continuously dissolved after time passed by. The corrosion of nickel also affected the adhesion of the gold film to the substrate and the shear strength while soldering on gold surface.[36] To have less pinholes, the slow deposition rate was required so that the atom had longer time to diffuse and find the suitable spot to deposit.[2] Moreover, the pinhole could cause black spot (nickel oxide) on gold layer after process.[37] Therefore, the plating time should be suitable that the gold layer covers all nickel surface and the nickel is not immoderately corrodded due to the porosity of gold layer.

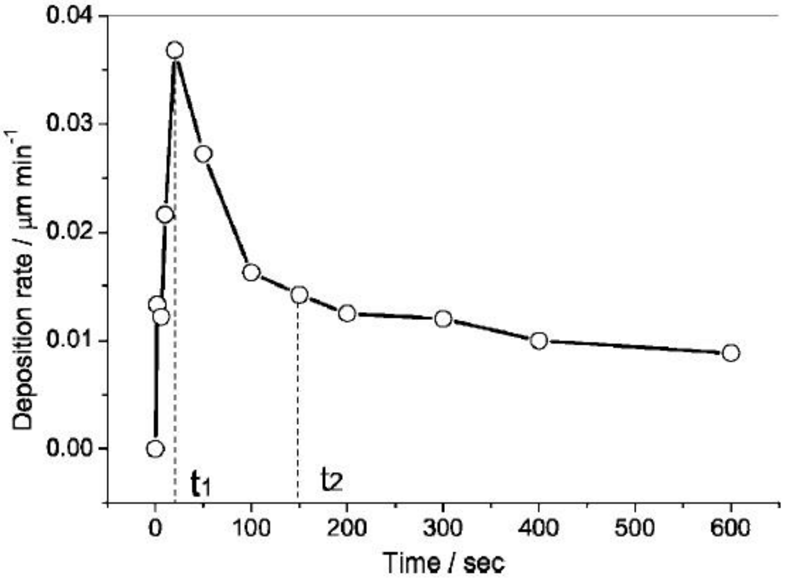


Figure 2.18 Deposition period of immersion gold plating[31]

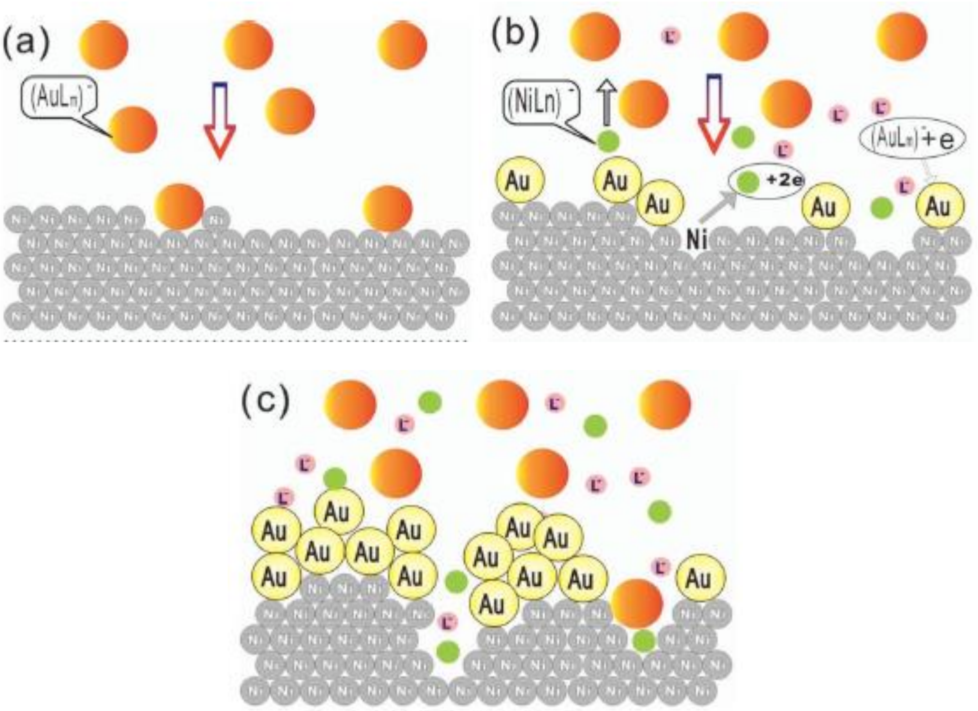


Figure 2.19 Simulation of gold plating at (a) initial, (b) plating and (c) finishing period[31]

Gold concentration[31]

Increasing gold concentration in gold plating solution affected the deposition rate of gold as increasing reactant in reaction 2.45 and Figure 2.20. Figure 2.21 shows that increasing gold concentration had an effect on the time that potential used to get to the plateau state. The time of getting to the plateau state tended to decrease after increasing the gold concentration which means the rate of surface reaction is increased. When the concentration exceeded 2.0 g/L, the deposition rate became slightly increasing, so the variation range was between 1.0 – 2.0 g/L considering the desired deposition rate.

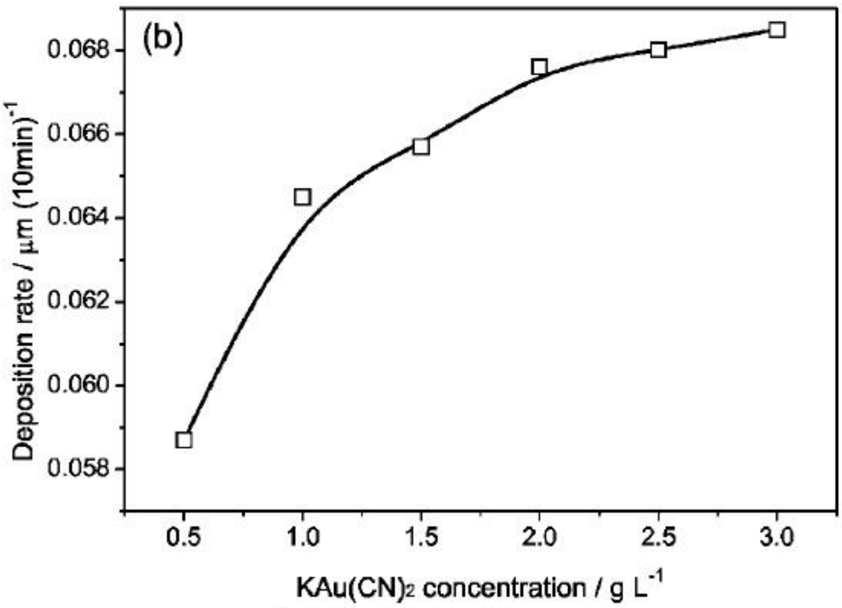


Figure 2.20 Effect of gold concentration on gold deposition rate[31]

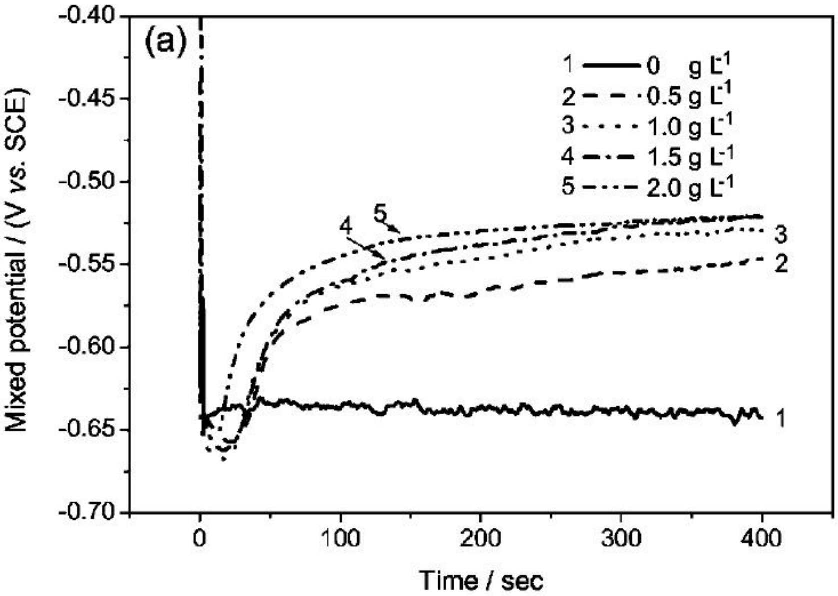


Figure 2.21 The mixed potential of gold concentration variation[31]

pH of IG plaing solution[31]

The increase of pH or decrease of concentration of proton affected the equilibrium of chelating agents in solution since they are in the form of organic acid and salt. When the pH of solution increased, the equilibrium shifted towards the side with higher concentration of organic salt ion. The large amount of salt ion caused the ternary complexes on gold ion. Liu and coworkers reported that salt ion had stronger adsorption property that affected the deposition rate, than both binary complexes, as shown in Figure 2.22 and 2.23. The mixed potential result showed that the peaks of potential were more negative after increasing pH which means that the adsorption rate increased. In addition, increasing adsorption meaned increasing the metal ion surface, so the surface reaction also increased, resulting in decrease of time for getting the plateau state. For the result by Liu and coworkers, the suitable pH range was 6.0 - 7.0 due to give the high deposition rate with less nickel substrate damaged.

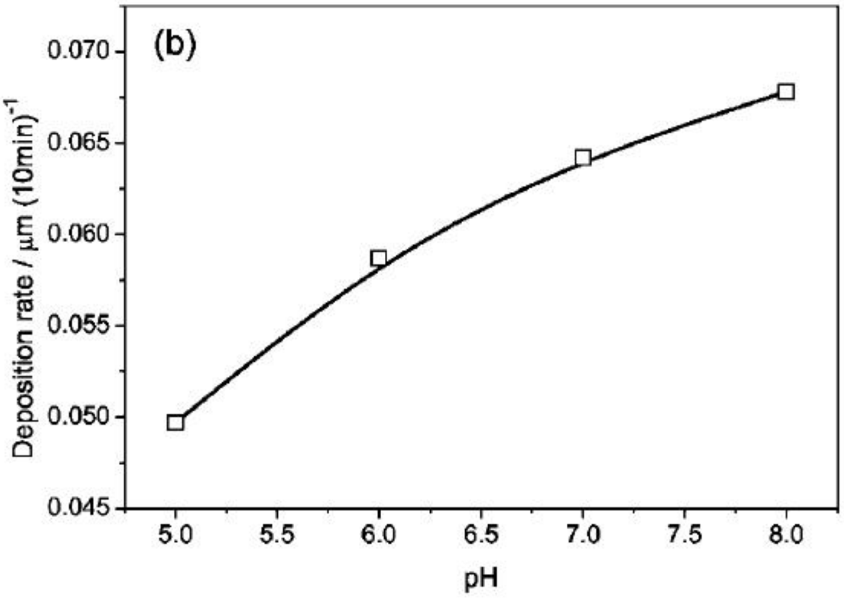


Figure 2.22 Effect of pH on deposition rate of gold[31]

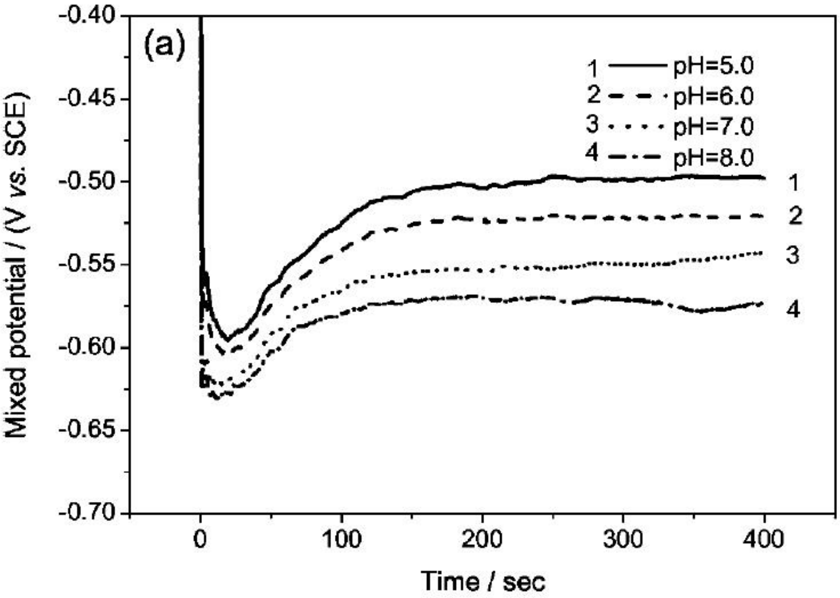


Figure 2.23 The mixed potential of pH variation[31]

Chelating agent

As mentioned in 2.2.1.2 in the topic of chelating agent and 2.2.2.1 in the topic of pH, the chelating agent helped improving the adsorption rate and gave one peak of the highest deposition rate, as shown in Figure 2.24. The amount of chelating agent or organic salt ion (at constant pH) affected the type of complex on the gold ion. Increasing organic salt ion would create more ternary complexes on the metal ion which has stronger adsorption than binary complexes. Figure 2.25 shows the effect of concentration of chelating agent on the mixed potential. Increasing amount of chelating agent caused faster adsorption rate which is similar to the result of pH variation in 2.2.2.1 in the topic of pH. However, the surface reaction was not in the same trend as 2.2.2.1 in the topic of pH. Too much chelating agent redounded the decrease of surface reaction.

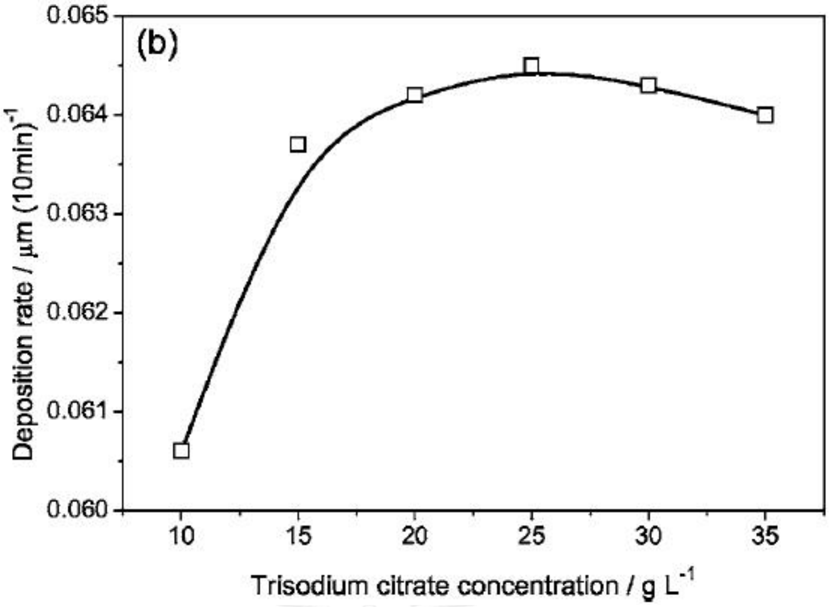


Figure 2.24 Effect of the chelating agent on deposition rate of gold[31]

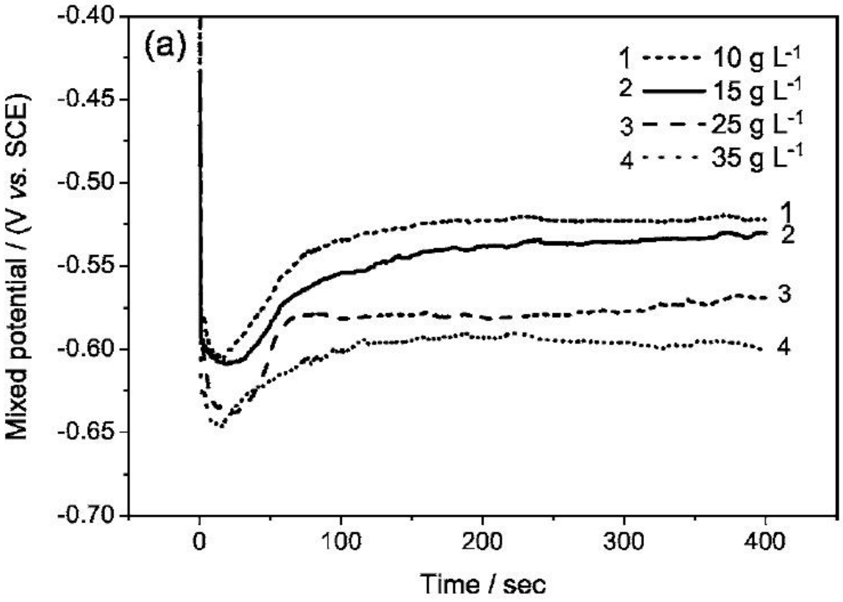


Figure 2.25 The mixed potential when the concentration of chelating agent was varied[31]

Temperature

The deposition rate of gold linearly increased with increasing of the operation temperature because the nickel atom was replaced by gold atoms and exchanged ligands with gold in which the reaction was endothermic reaction, as shown in reaction 2.48 and Figure 2.26. However, the thicker of gold film meant more corrosion of nickel that affected the adhesion of gold layer on nickel surface.[36] From the Figure 2.27, the temperature range 70 - 90 °C slightly affected the adsorption rate and time to get plateau state, so the factor which indicated the optimal temperature was thickness of gold and also the oxidation rate of nickel. Figure 2.24 shows that the optimal temperature in this previous study were 75 - 85 °C which resulted 0.048 – 0.065 μm of gold film.

$$Ni + 2Au(CN)_{2(aq)}^{-} \rightarrow Ni(CN)_{4(aq)}^{2-} + 2Au_{(s)} \quad \Delta H = +116.8\ {}^{kJ}/_{mol} \qquad (2.48)$$

$$\Delta H^0_{f,Au(CN)_2{}^-} = 242.3\ {}^{kJ}/_{mol}$$

$$\Delta H^0_{f,Ni(CN)_4{}^{2-}} = 367.8\ {}^{kJ}/_{mol}$$

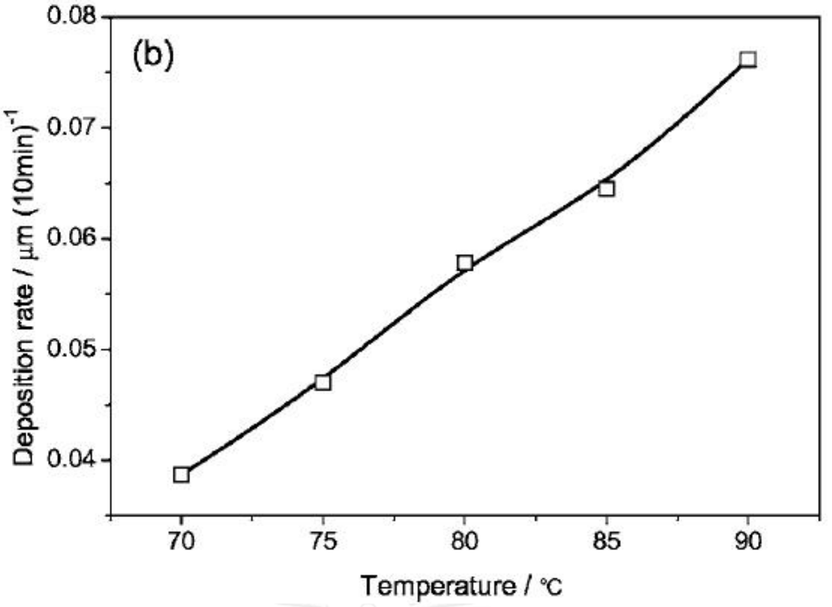


Figure 2.26 Effect of the temperature on deposition rate of gold[31]

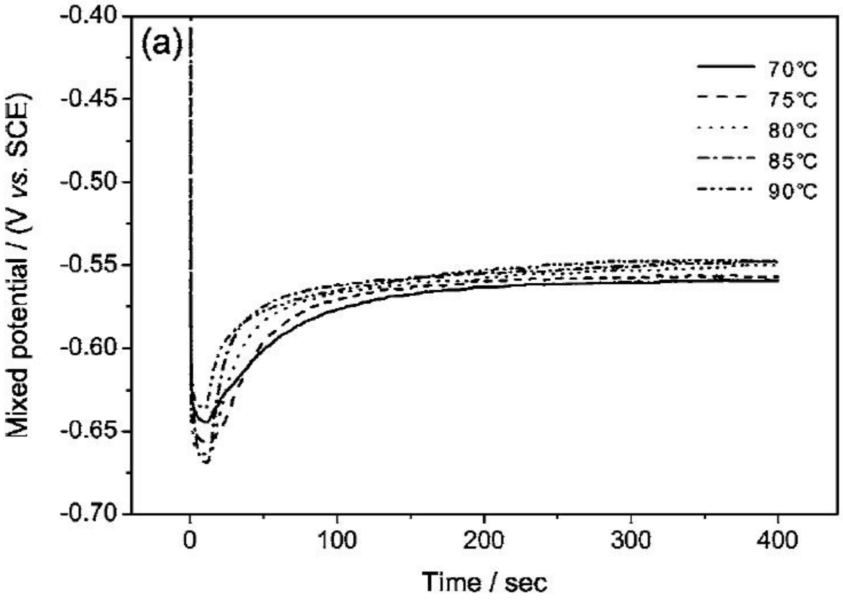


Figure 2.27 The mixed potential of the temperature variation[31]

The rate of gold deposition

The study by Won and coworker[37] was about the deposition rate of the immersion gold plating. Figure 2.28a shows that gold atom less deposited in the pit of surface so the nickel atom at the pit diffused and corroded, as shown in Figure 2.28b. In the Figure 2.28c and 2.28d, the low reactivity provided the neat layer of IG plating and regular corrosion of nickel. The low deposition rate provide time for atoms to diffuse on the surface of the substrate[2], so the low reactivity provided more uniform gold layer than the high reactivity.

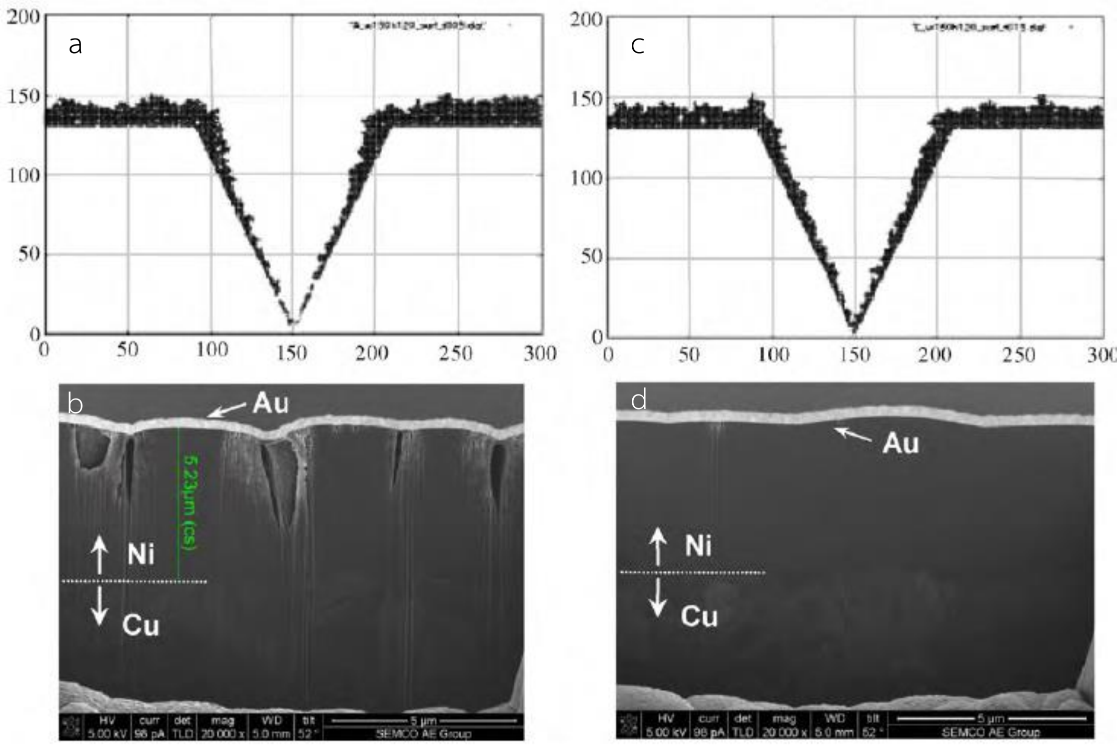


Figure 2.28 The gold layer growth with (a) high reactivity by simulation and (b) cross-sectional SEM image and (c) low reactivity by simulation and (d) cross-sectional SEM image[37]

CHAPTER 3

Information Access from the Actual Production

From the real electroless nickel immersion gold (ENIG) production in Mektec Manufacturing Corporation (Thailand) Ltd. (MMCT), the data of chemicals and the output were collected from 9 October 2015 – 20 November 2015 which contains 15,673 data. The output data contented nickel thickness and gold thickness which were affected by all input parameters, so all data were analyzed and simulated by JMP7. The result was divided into two parts, the effect of input parameters on EN and the effect of input parameters on IG, based on the average value of the other input parameters except the varied one. However, the concentration of all reactants and by-products were not collected as frequent as other data, so JMP7 could not analyze all input parameters in the same time. After simulated sets of input parameters, all of them which are sensible in each turn were picked and simulated simultaneously. The details of all parameters are shown in table 3.1. The model which was used for analysis was full factorial design with random effect.

Table 3.1 The input and output parameters which were collected in actual process

	Categories	Unit
Electroless nickel (EN)		
Input parameters		
Degreasing bath	- Specific gravity	-
Etching bath	- Removed copper thickness	µm
Activation (1) bath	- Specific gravity	-
Activation (2) bath	- Specific gravity	-
Catalyst bath	- Catalyst concentration	ppm
	- Solvent concentration	mL/L
	- Additive concentration	%
	- Copper impurity	ppm
Post-Dipping bath	- Post-Dipping concentration	%
Flex nickel plating bath	- pH	-
	- Nickel concentration	g/L
	- Reducing agent concentration	g/L
	- By-product concentration	g/L
	- Impurity	ppm
Activation (3) bath	- Specific gravity	-

Output parameters		
Nickel	- Nickel thickness	μm
Immersion gold (IG)		
Input parameters		
H_2SO_4 activation (3) bath	- Specific gravity	-
Au plating bath	- Specific gravity	Baume
	- pH	-
	- Gold concentration	g/L
	- Conductive salt	g/L
	- Nickel impurity	ppm
	- Copper impurity	ppm
	- Iron impurity	ppm
	- Lead impurity	ppm
	- Zinc impurity	ppm
Output parameters		
Gold	- Gold thickness	μm

3.1 The effect of input parameters on electroless nickel plating

After sorting out the input parameters which might affect the nickel thickness by grouping them and simulating, the remaining input parameters included thickness or copper etching rate, specific gravity of activation (1) bath, nickel concentration, reducing agent concentration, pH of nickel plating solution, by-product concentration, specific gravity of activation (3) bath and copper thickness, as shown in Figure 3.1 - 3.8. The graphs showed the trend of input parameters variation (black line), the confidence interval of data (blue dash line) and the sensitive indicator as the triangle shape. From the result, the copper thickness slightly affect the nickel plating rate with high error. The increase of reactants concentration and pH rendered the nickel deposition rate. On the other hand, the deposition rate of nickel was decreased by increasing of by-product and etching in activation (3) bath. The most sensitive parameter in nickel plating bath was by-product concentration and the second one was pH of nickel plating solution. The other important parameters were copper etching rate and specific gravity of activation (1) bath. Since the process of etching (etching bath and activation (1) bath) had an effect on the nickel thickness, it was possible that the deposition rate of nickel was affected by the roughness of substrate or the oxide on substrate or both of them. The interaction profile of this simulation is shown in Appendix A.

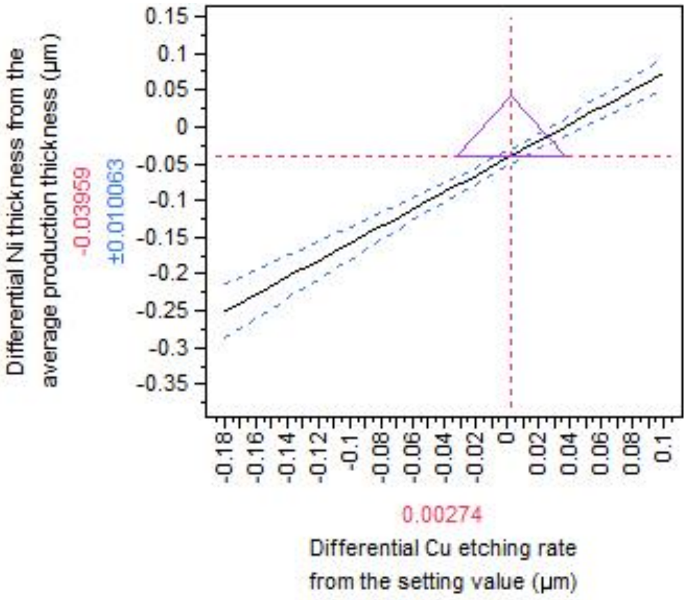


Figure 3.1 The effect of copper etching rate on nickel thickness

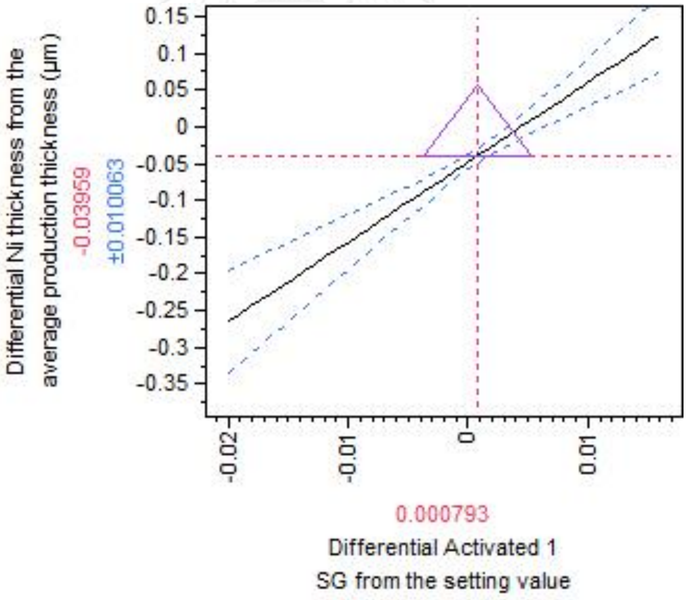


Figure 3.2 The effect of activation (1) bath on nickel thickness

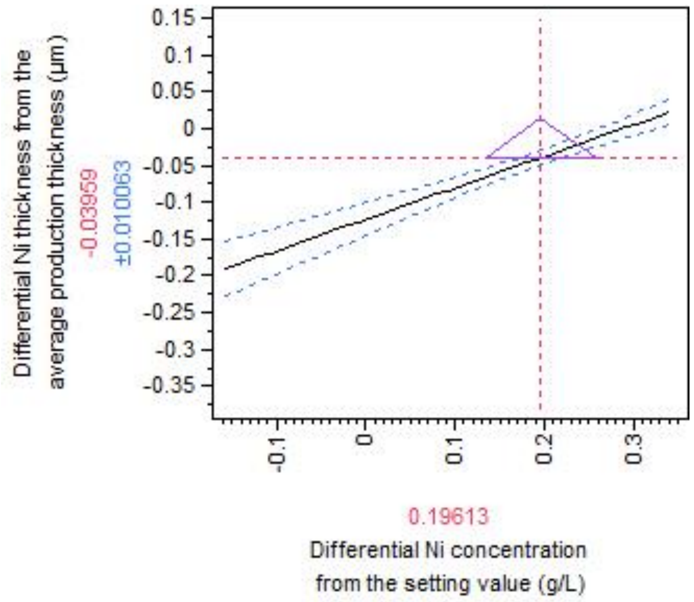


Figure 3.3 The effect of nickel concentration on nickel thickness

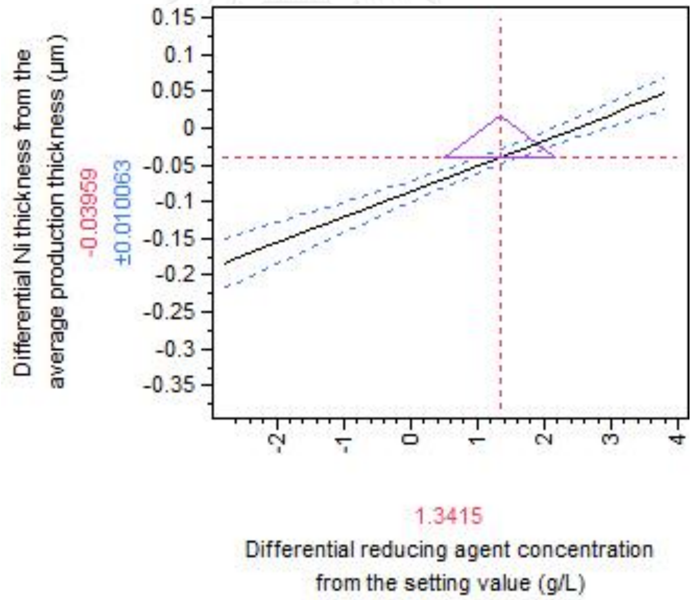


Figure 3.4 The effect of reducing agent concentration on nickel thickness

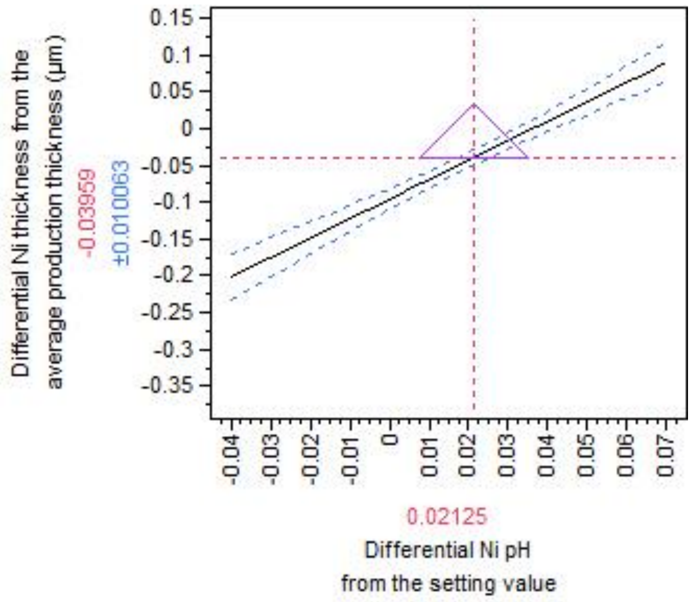


Figure 3.5 The effect of pH of nickel plating solution on nickel thickness

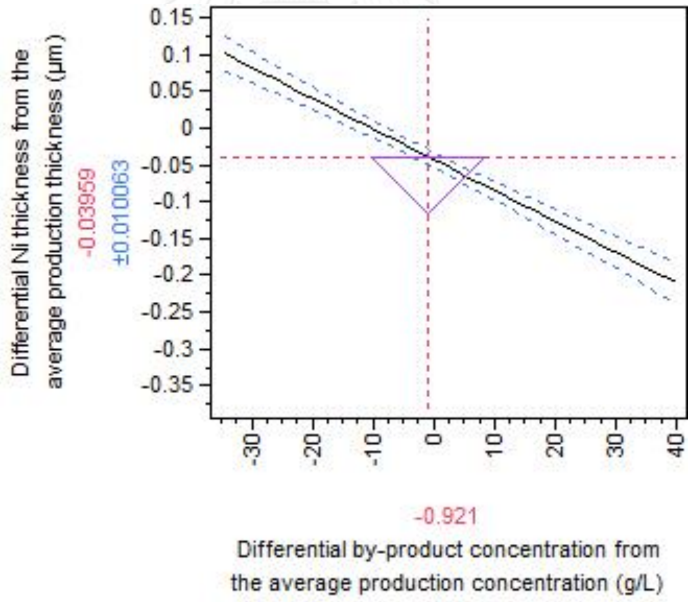


Figure 3.6 The effect of by-product concentration on nickel thickness

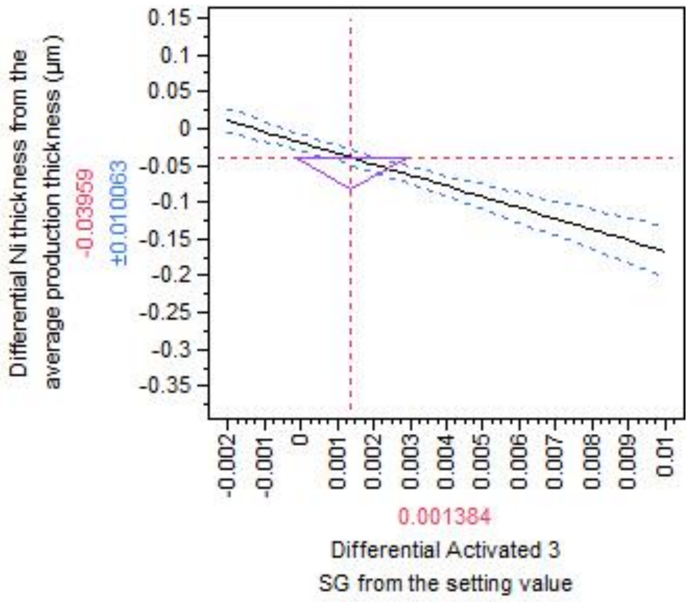


Figure 3.7 The effect of activation (3) bath on nickel thickness

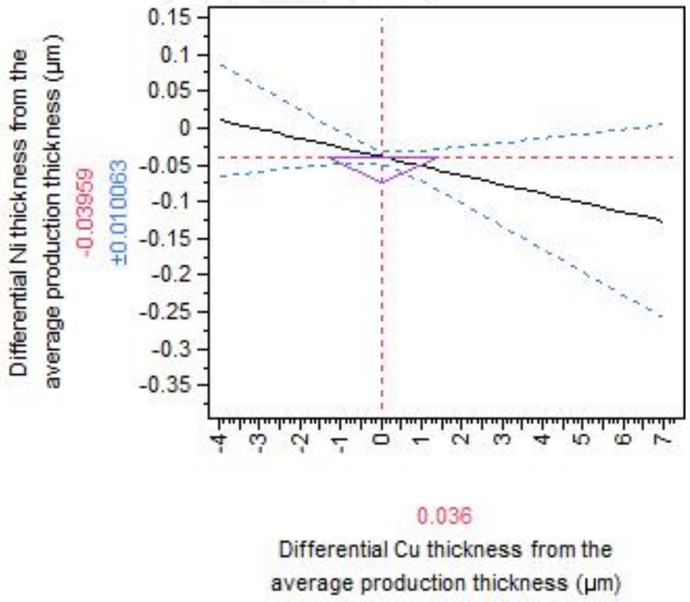


Figure 3.8 The effect of copper thickness on nickel thickness

Table 3.2 The summary of the effect of input parameters on EN plating thickness

	The effect on nickel thickness when increase the input parameters	Range of data
Pretreatment bath		
Cu etching rate (μm)	Increase	-0.2 – 0.2
SG of activation(1)	Increase	-0.05 – 0.05
SG of activation(3)	Decrease	-0.02 – 0.02
EN plating bath		
pH	Increase	-0.2 – 0.2
Nickel concentration (g/L)	Increase	-0.5 – 0.5
Reducing agent concentration (g/L)	Increase	-5 – 5
By-product concentration (g/L)	Decrease	-103 – 46
Checking variable		
Cu thickness (μm)	Decrease	-5 - 2

3.2 The effect of input parameters on immersion gold

Same as EN plating, the frequency of data collecting was not the same for all input parameters, so only some of them could be simulated. The procedure for choosing the input parameters was the same as topic 3.1. The selected input parameters were specific gravity of activation (3) bath, gold concentration, pH and specific gravity of gold plating solution, conductive salt concentration, nickel impurity concentration and nickel thickness, as shown in Figure 3.9 - 3.15. From the result, the deposition rate of gold plating was increased by increasing gold concentration and pH of gold solution but counter-trend of deposition rate was affected by increasing the by-product. The increase of specific gravity of gold plating solution which is an indicator for measuring the amount of chelating agents and volume of plating solution caused the increase of gold deposition rate. Wherewith adding the chelating agents or the vaporization of the plating solution made the specific gravity increasing, the concentration of chemicals in plating bath were accrued. The most sensitive parameter in gold plating bath was pH of gold plating solution. On the other hand, the least sensitive input parameters were the conductive salt concentration which was the brightening chemical in the previous study.[38] The other important parameter was nickel thickness which is the substrate. The reaction 2.45 shows that the reaction rate only depends on the gold concentration. The surface area of substrate should not affect the deposition rate. Moreover, the trend of specific gravity of activation (3) bath variation seemed to not making sense. The roles of this bath are to etch the nickel substrate and eliminate the nickel oxide, so the rate of reaction should be increased by increasing concentration of sulfuric acid. Then the roughness of nickel should be increased and the nickel oxide should be less remaining or eliminated more than at low concentration of acid in activation (3) bath. The interaction profile of this simulation is shown in Appendix A.

$$Ni + 2Au^{+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Au_{(s)} \tag{2.45}$$

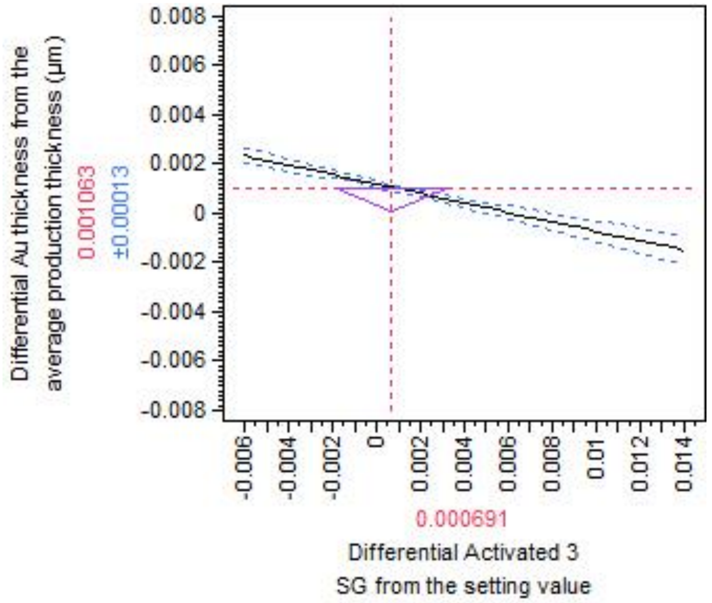


Figure 3.9 The effect of sulfuric acid in activation (3) bath on gold thickness

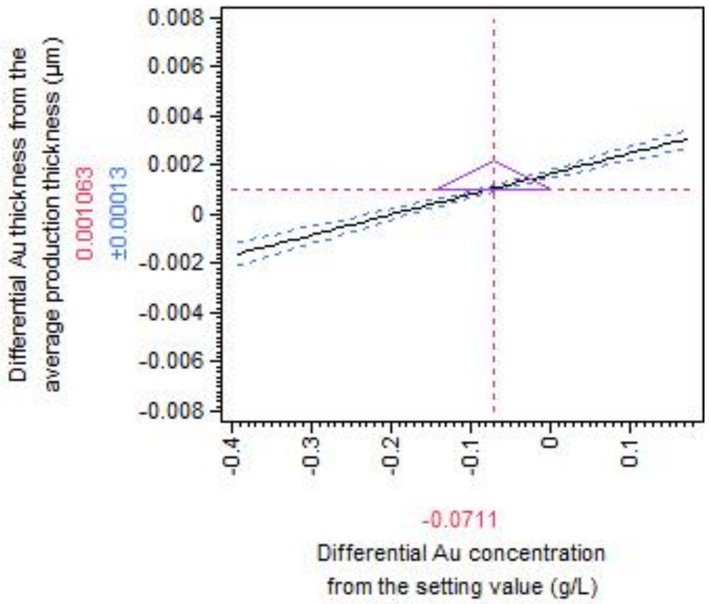


Figure 3.10 The effect of gold concentration on gold thickness

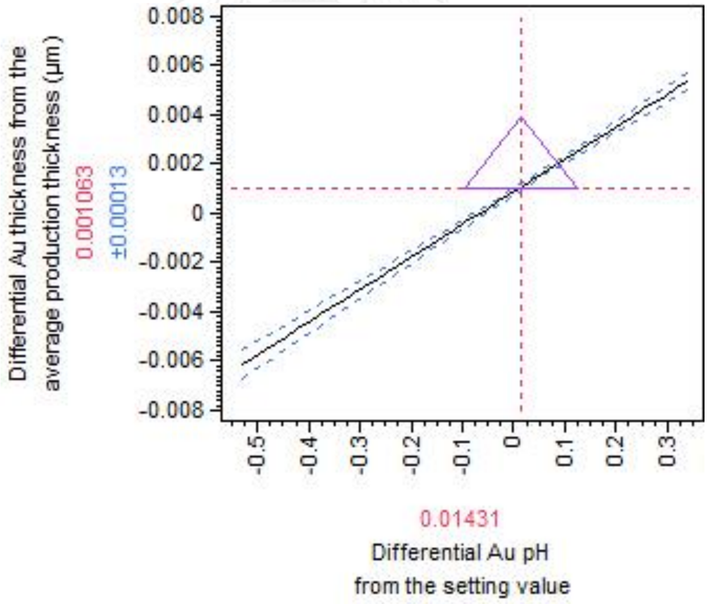


Figure 3.11 The effect of pH of gold solution on gold thickness

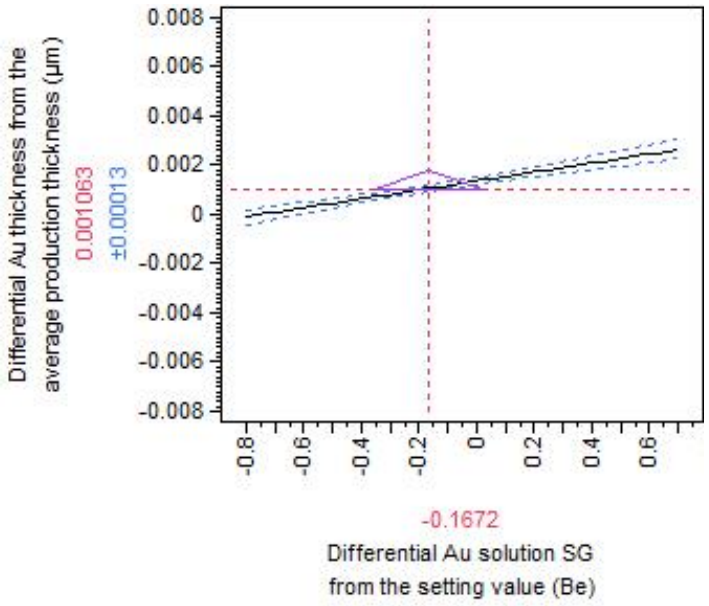


Figure 3.12 The effect of specific gravity of gold solution on gold thickness

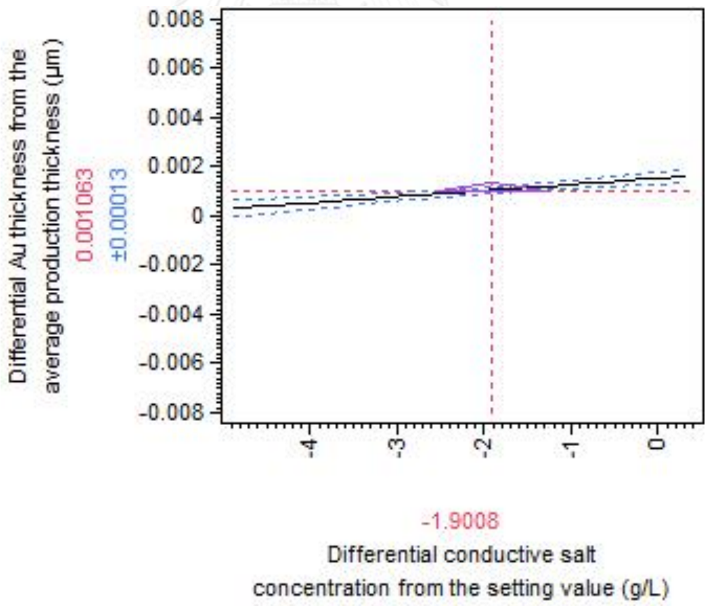


Figure 3.13 The effect of conductive concentration on gold thickness

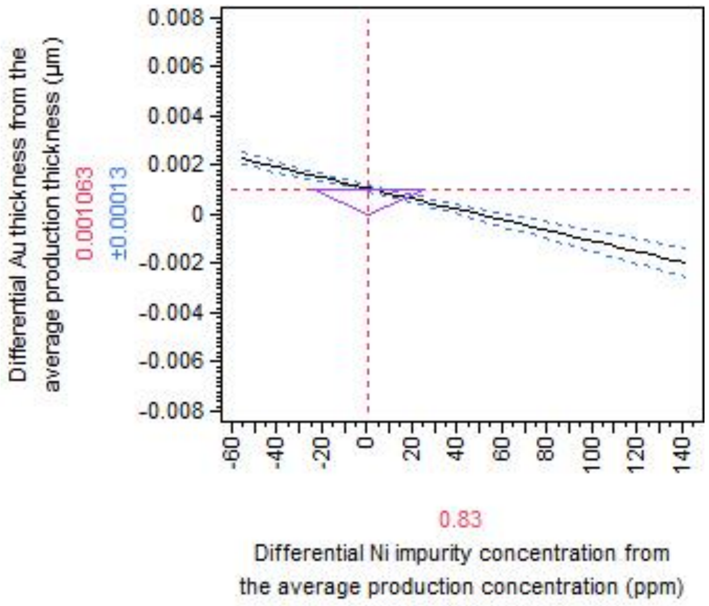


Figure 3.14 The effect of nickel impurity in gold solution on gold thickness

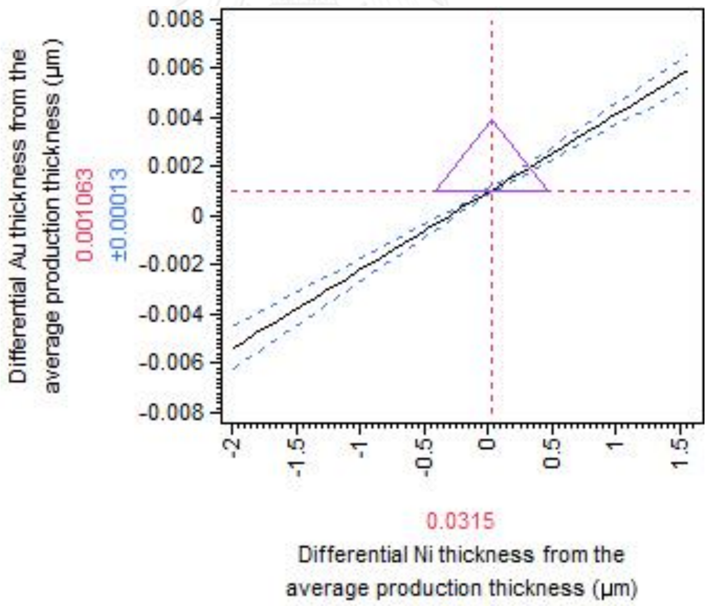


Figure 3.15 The effect of nickel thickness on gold thickness

Table 3.3 The summary of the effect of input parameters on IG plating thickness

	The effect on nickel thickness when increase the input parameters	Range of data
Pretreatment bath		
SG of activation(3)	Decrease	-0.02 – 0.02
EN plating bath		
Gold concentration (g/L)	Increase	-0.2 – 0.3
pH	Increase	-0.3 – 0.3
SG of gold solution (^{o}Be)	Increase	-1.3 – 3.7
Conductive salt concentration (g/L)	Non effect	-2 - 2
Ni impurity (ppm)	Decrease	-130 - 46
Checking variable		
Cu thickness (μm)	Increase	-1 – 0.9

3.3 Summary of the simulation

The trends of input parameters in the plating bath could be obtained by comparing the theories and previous studies except for the nickel concentration in which the deposition rate should be independent or affected slightly. Since there were strange trend and result, it was possible that there were some of other input parameters or these input parameters were the relative parameters, thereby the experiments for checking are required. The more discussion would be carried on in chapter 5.

CHAPTER 4

Experiments

After the simulation of the data from real electroless nickel immersion gold (ENIG) production, the experiments was carried on to compare the results. First, to check the reliability of the simulation the input parameters which are reactants and conditions in plating bath were carried on. Then, the experiment for checking the effect of the pretreatment bath and the thickness of substrate from the simulation on the deposition rate was designed to assay the real input parameters that affected the deposition rate of electroless nickel (EN) and immersion gold (IG).

4.1 Chemicals and materials

There were four sets of the chemicals, including pretreatment, nickel plating, gold plating and other chemicals. The substrates and plating solutions were prepared from Mektec Manufacturing Corporation (Thailand) Ltd. (MMCT) except for the pure chemicals. The catalyst plating solution series and EN plating solution series were from Okuno Chemical Industries co., Ltd. The gold plating solution and IM-Gold FG series were from Japan Pure Chemical co., Ltd. The details of chemicals used were in Table 4.1.

Table 4.1 All materials and chemicals used in this study

Materials	Components	Annotation
Substrates		
Copper sheet	Copper 100%	Through degreasing, etching and activation (1) process.
Nickel sheet	Nickel ~ 86.77% Phosphorus ~ 13.23%	The EN plating
Pretreatment		
Catalyst solution	Catalyst salt Solvent Additive	
Electroless nickel		
Nickel Solution	Nickel salt Inhibitor	
Reducing agent solution	Reducing agent Chelating agent	
Solvent	Solvent for by-product Surface active agent	

Immersion gold		
Gold plating solution	Gold salt Set of chelating agents Conductive salt	Ready to use for plating
IM-Gold FG Replenisher	Gold salt Set of chelating agents	Ready to add for gold replenishment
IM-Gold FG Conductive Salt Replenisher	Additive Set of chelating agents	Mixed powder
IM-Gold FG Density Adjusting Salt	Set of chelating agents	Mixed powder
$K[Au(CN)_2]$		
Sodium citrate		
Ammonium chloride		
Other		
Inorganic acid		
Inorganic base		
Acetone		

Adhesive tape

4.2 Experiments

4.2.1 Electroless nickel plating

From the simulation, the input parameters which needed to be checked were nickel concentration, reducing agent concentration and pH. If these input parameters gave the same results as the simulation, the result of simulation of other input parameters would be reliable and the input parameters were chosen correctly to simulate.

The copper sheet substrate which was passed through some of pretreatment processes was marked by adhesive tape (3M) into dimensions of 1 x 1 cm. Then, it was washed by acetone to remove glue from the adhesive tape, dust and greases which might stain on the plating area. The procedure of this experiment was shown in Figure 4.1. The composition and conditions of solution were varied, as shown in Table 4.2. The temperature of solution and deposition time for plating were the same as the production line. The volume of plating solution was 200 mL and non-shaking dipping method was performed, which is different from the agitation in plating solution in the real production of MMCT. The concentration of nickel and reducing agent were controlled by nickel solution and reducing agent solution, respectively. The pH of nickel solution was adjusted by adding inorganic acid to lower it or adding inorganic base to raise it. Table 4.3 shows the analysis method for these experiment.

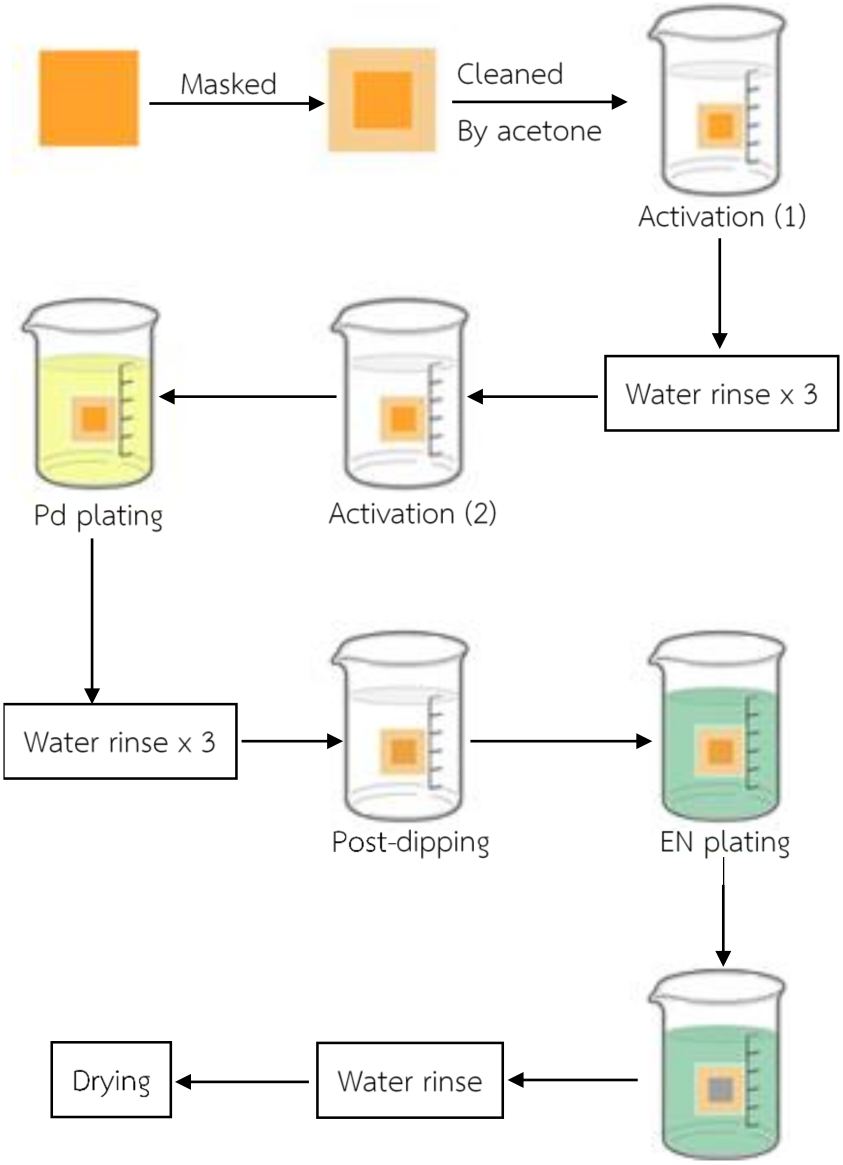


Figure 4.1 Electroless nickel plating procedure

Table 4.2 Electroless nickel plating lab setting differential from the setting value

Parameters	Ni concentration (g/L)	Reducing agent concentration (g/L)	pH
Setting Value	0.0	0.0	0.0
- Shaking			
- Non shaking			
- Without catalyst			
- Half catalyst			
Ni conc variation	-0.5	0.0	0.0
	0.5	0.0	0.0
Reducing agent conc variation	0.0	-5.0	0.0
	0.0	5.0	0.0
pH variation	0.0	0.0	-1.60
	0.0	0.0	-0.20
	0.0	0.0	0.20
	0.0	0.0	2.90

Table 4.3 The methods for analyzing the electroless nickel plating

Analysis methods	Indications
SEM-EDX	Nickel alloy topography
	Amount of phosphorus in nickel alloy
XRF*	Nickel alloy thickness
Peeling test	Adhesion of nickel alloy on copper
Stylus	Nickel alloy roughness

* Required the ENIG plating standard from MMCT

4.2.2 Immersion gold plating

From the simulation, the input parameters which needed to be checked were gold concentration, density of solution and pH. The substrate in this experiment was controlled. It was the EN plated substrate which was plated in the MMCT production line. The EN sheet substrate was marked by adhesive tape (3M) into dimensions of 1 x 1 cm. Then, it was washed by acetone to remove glue from the adhesive tape, dust and greases which might stain on the plating area. The procedure of this experiment was shown in Figure 4.2. The composition and conditions of solution were varied, as shown in Table 4.4. The temperature of solution and deposition time for plating were the same as the production line. The volume of plating solution was 200 mL without agitation. Chemicals which were used in this experiment were prepared by MMCT. To adjust the values of input parameters, the gold solution for replenishment and the density adjusting salt were used. To lower the concentration of gold and density of solution, the conductive salt was important to keep its concentration constant. The pH of gold solution was adjusted by adding organic acid which is one of the chelating agent to lower it or adding inorganic base to raise it. Table 4.5 shows the analysis method for these experiment. Unlike the nickel alloy, there was no need to measure the roughness of gold surface because the roughness of gold surface was changed slightly from nickel substrate roughness in nanoscale which required the precise analytical equipment. It could be assumed that the roughness was the same as the substrate due to the very thin layer of gold.[31]

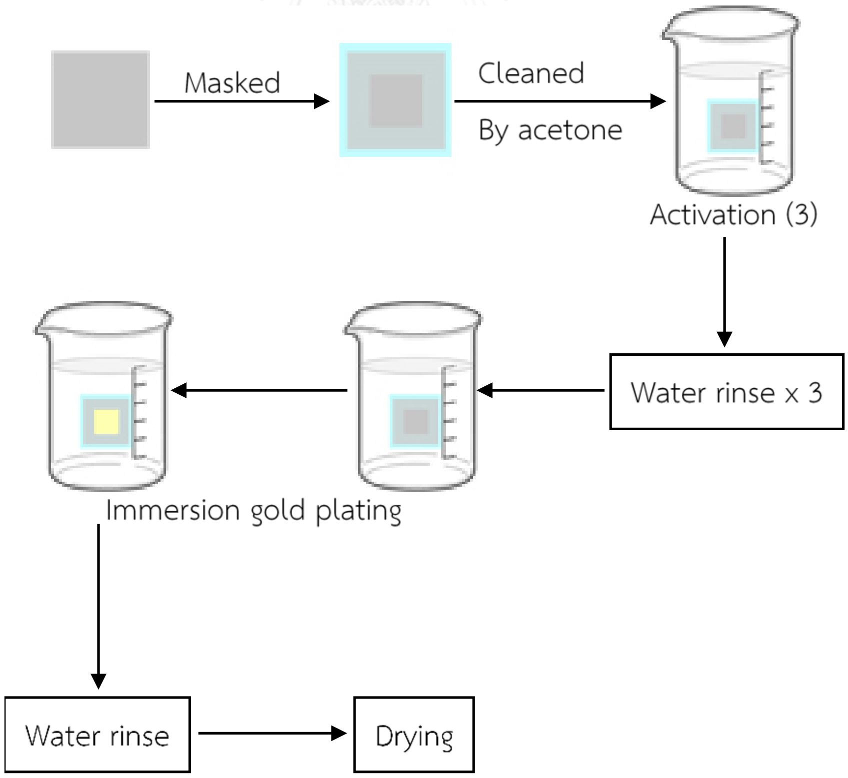


Figure 4.2 Immersion gold plating procedure

Table 4.4 Immersion gold plating lab setting

Parameters	Au concentration (g/L)	Density (^{o}Be)	pH
Setting Value	0.0	0.0	0.0
Au conc variation	-0.1	0.0	0.0
	0.2	0.0	0.0
	0.4	0.0	0.0
Density variation	0.0	-1.3	0.0
	0.0	1.3	0.0
	0.0	2.1	0.0
pH variation	0.0	0.0	-0.30
	0.0	0.0	-0.15
	0.0	0.0	0.15
	0.0	0.0	0.30

Table 4.5 The methods for analyzing the immersion gold plating

Analysis methods	Indications
SEM	Gold topography
XRF*	Gold thickness
Peeling test	Adhesion of gold on nickel alloy

* Required the ENIG plating standard from MMCT

4.2.3 Checking other effects on plating

4.2.3.1 Examining between the gold simulation results and the experiment

Since the composition of chemicals in gold plating solution was not explicit, it needed the reference that had the certain composition of chemicals in solution to compare. This experiment was replicated the previous study[31] by using the same substrate as the experiment 4.2.2 to test the accuracy of the experiment 4.2.2. The chemical used were potassium gold cyanide, sodium citrate and ammonium chloride as the chelating agents and hydrochloric acid and sodium hydroxide for adjusting pH. The procedure of this experiment is shown in Figure 4.2 and the variation detail in Table 4.6. The volume of plating solution was 200 mL without agitation. The plating time was 10 minute. The analysis methods were the same as the experiment 4.2.2 (Table 4.5).

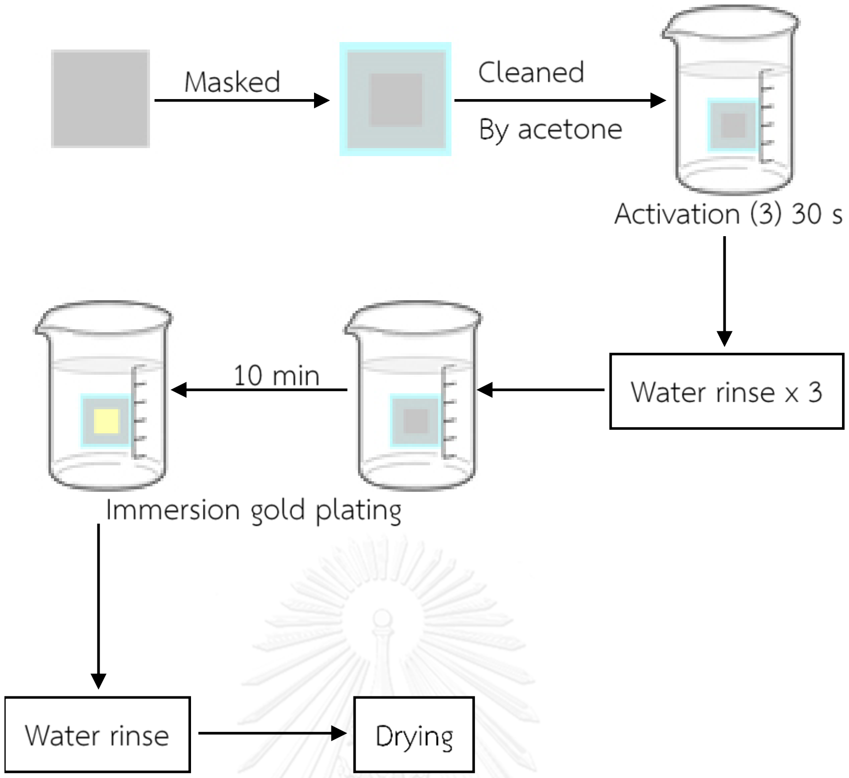


Figure 4.3 Immersion gold plating procedure for the previous study imitation

Table 4.6 Immersion gold plating lab using Liu and other conditions[31]

Parameters	Au concentration (g/L)	Sodium citrate (g/L)	Ammonium chloride (g/L)	pH
Setting Value	1.0	25	40	7.0
Au conc variation	0.5	25	40	7.0
	1.5	25	40	7.0
Sodium citrate variation	1.0	10.0	40	7.0
	1.0	20.0	40	7.0
	1.0	30.0	40	7.0
pH variation	1.0	25	40	5.0
	1.0	25	40	6.0

4.2.3.2 Testing the effect of characteristics of nickel substrate on gold plating thickness

From previous studies, there is a variable which involves the nucleation and growth mechanism, the roughness of substrate. Moreover, adulterated things such as protein, greases and oxide could affect the deposition of metal. Then, this experiment was carried on to test the effect of the thickness and roughness of nickel and the phosphorus content in nickel alloy on the gold deposition rate. The details of substrates used in this experiment are shown in Table 4.7. All the substrates were plated simultaneously in the setting condition of immersion gold solution from MMCT.

Figure 4.4 shows the plating procedure. The temperature of solution and deposition time for plating were the same as the production line. The volume of plating solution was 200 mL without agitation.

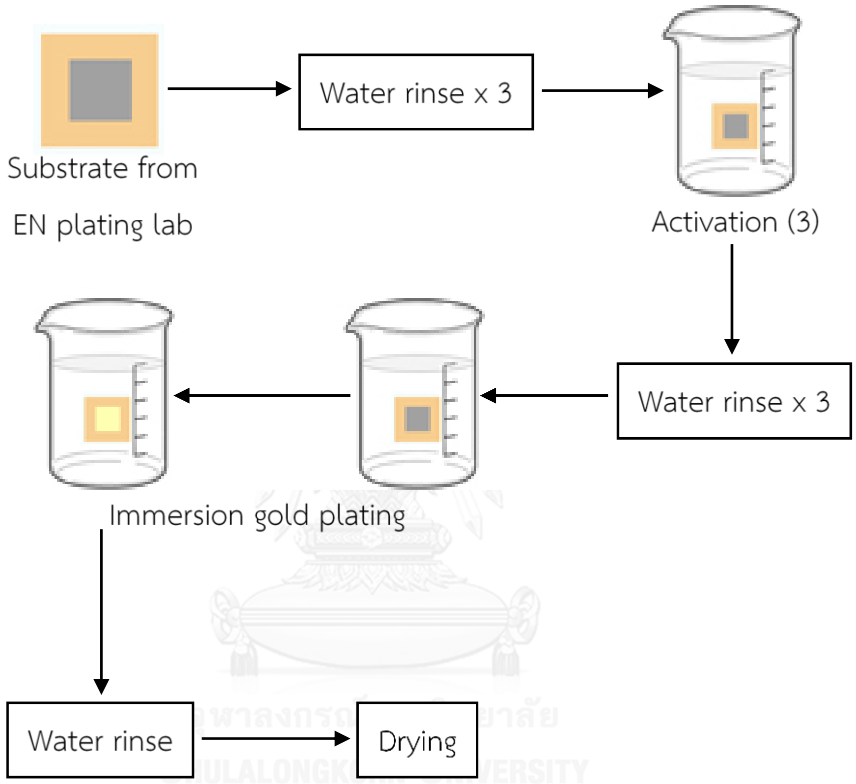


Figure 4.4 Immersion gold plating procedure for the experiment 4.2.3.2

Table 4.7 The characteristics of nickel alloy substrate

Ni thickness (μm)	RMS roughness (nm)	%Phosphorus
0.283 ± 0.0244	787.21	14.06 ± 0.137
2.112 ± 0.0403	1130.0	9.00 ± 0.072
3.354 ± 0.1857	967.02	12.10 ± 0.191
4.998 ± 0.0287	711.89	9.11 ± 0.305

CHAPTER 5

Results and Discussion

In this chapter, it contained three parts including electroless nickel plating experiment, immersion gold experiment, and influence of other effects on the immersion gold plating. The thickness of the alloy and metal, amount of phosphorus on the nickel surface, roughness and peeling test were investigated. The results of the experiments were shown in graphs comparing with the published study and the simulations from the data in Chapter 3. The simulation was performed under the same condition as that in experiments in which the by-products were excluded. All of the plating experiments passed the peeling test which could be concluded that the copper and nickel substrates were clean enough[11] and the thickness of gold was not too thick[36].

5.1 The results of electroless nickel (EN) plating experiment

5.1.1 The effect of plating catalyst on the nickel thickness

No catalyst plating

As shown in Figure 5.1, there was no nickel plating on the copper substrate without the presence of catalyst, which is agreeable with the reaction mechanism. The reaction 2.22 and 2.26 show that the catalyst which can be nickel or other metals is required for adsorbing the halide to activate the nickel plating reaction.

$$2reducing\ agent + 2H_2O \xrightarrow{cat} 2productA + 2H^+ + 2H^- \quad (2.22)$$

$$Ni^{2+} + 2H^- \rightarrow (Ni^{2+} + 2H + 2e) \rightarrow Ni^0 + H_2 \quad (2.26)$$

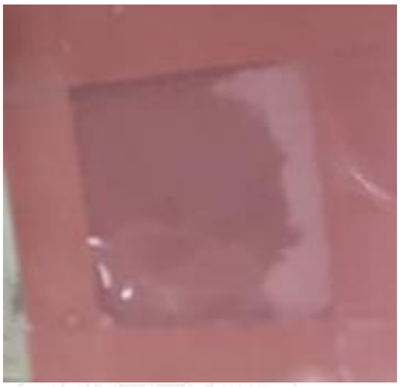


Figure 5.1 The copper substrate without catalyst after dipping in EN plating solution for the same deposition time as the actual production

Half plating catalyst

The half coated catalyst on copper substrate was showed in Figure 5.2(a) in which the catalyst coated area is in the box. After that, the half catalyst coated substrate was dipped in EN plating solution. Firstly, the nickel was deposited on the catalyst area (the black area in Figure 5.2(b)). After that the remaining area was plated by nickel (Figure 5.2(c)). The difference of nickel average thickness between the catalyst area and non-catalyst area was about 0.4 μm after dipping for the same deposition time as that in the actual process. In Table 5.1, the profile of the nickel thickness showed that on the area without catalyst nickel did not deposit at first from the edge of the plated nickel layer on the catalyst area because the thickness of nickel next to the catalyst area (shading cell) was the thinnest. It is possible that the nickel ion received electrons from the nickel on the catalyst area. When the deposition rate was slower by consuming of reactants, the atom had time to diffuse on the surface to find the area which matched its energy[2], including the area without catalyst.

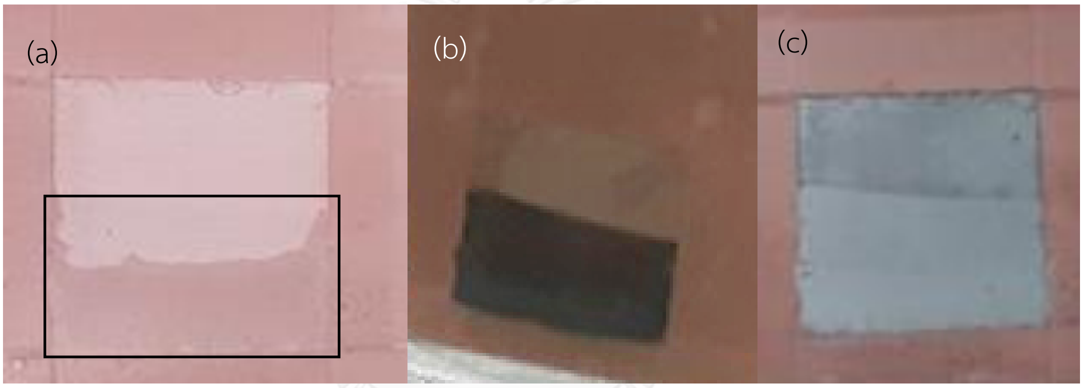
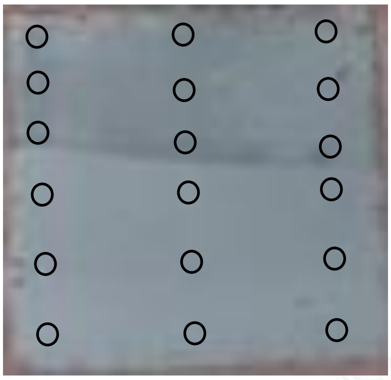


Figure 5.2 (a) The half plating catalyst on substrate (in the box) then the substrate was dipped in nickel solution for (b) 60 s and (c) the same deposition time as the actual production

Table 5.1 The profile of the nickel thickness on the substrate with half plating catalyst

The measured points	Nickel thickness profile (μm)		
	2.232	2.156	2.284
	2.113	2.310	2.265
	1.679	2.063	2.103
	2.448	2.734	2.453
	2.408	2.453	2.344
	2.539	2.703	2.687

5.1.2 The effect of nickel concentration on the thickness, amount of phosphorus on surface and roughness of nickel plating

The effect of nickel concentration on the nickel thickness

The result of this experiment is shown in Figure 5.3 and the condition is shown in Table 5.2. The simulation result supported the previous study done by Gutzeit[18] who reported that concentration of nickel ion did not affect or slightly affected the deposition rate of EN plating when the concentration of nickel ion was higher than 0.02 M (1.17 g/L). Since the result from the previous study was EN plating in alkaline pyrophosphate bath, it was the exception that the trend of variation of nickel ion concentration was not the zero order reaction. Furthermore, the plating time of the previous study was longer than those of simulation and lab experiment, so the nickel thickness was thicker than those using Mektec’s plating condition even though the temperature used was lower. The experimental result was superimposed the simulation result except at low nickel ion concentration. There were three possibilities which can be explained this result.

The first possibility was from the papers of C. Baldwin and T. Such.[24] They described that the plating reaction of EN was zero order with respect to the nickel ion concentration when the concentration equal to or higher than 0.085 M (5 g/L). The nickel ion concentration at the lowest limit of the experiment was less than 5 g/L, so the order of reaction when the differential concentration from the setting value between -0.5 – 0.0 g/L was not a zero order reaction.

The second possibility was due to the other components in the nickel solution such as stabilizer or inhibitor, which did not involve the reaction directly. Since the nickel solution used in this experiment was prepared by adding some unknown components, lowering the nickel ion concentration means that these components became low. Perhaps they exceeded the lowest limit of the concentration that should be in plating solution, so the trends of lab experiment and simulation did not overlap.

The last possibility was the different solution preparation method. The solution used in the EN plating production was always prepared at the setting control. The low nickel concentration of nickel ion could be occurred by consuming of nickel ion after the reaction completed, so the concentration of other chemicals which did not involve the reaction directly such as chelating agent and stabilizer is the same as that in the setting control. However, high nickel ion concentration could be occurred only by adding nickel solution into the EN plating solution; therefore, other chemicals in the bath increased too. Therefore, low concentration of nickel did not overlap the simulation due to different preparation method. On the other hand, the preparation of EN plating solution at the setting value and at high nickel concentration was the same as actual production, so the results of lab experiment and simulation overlapped.

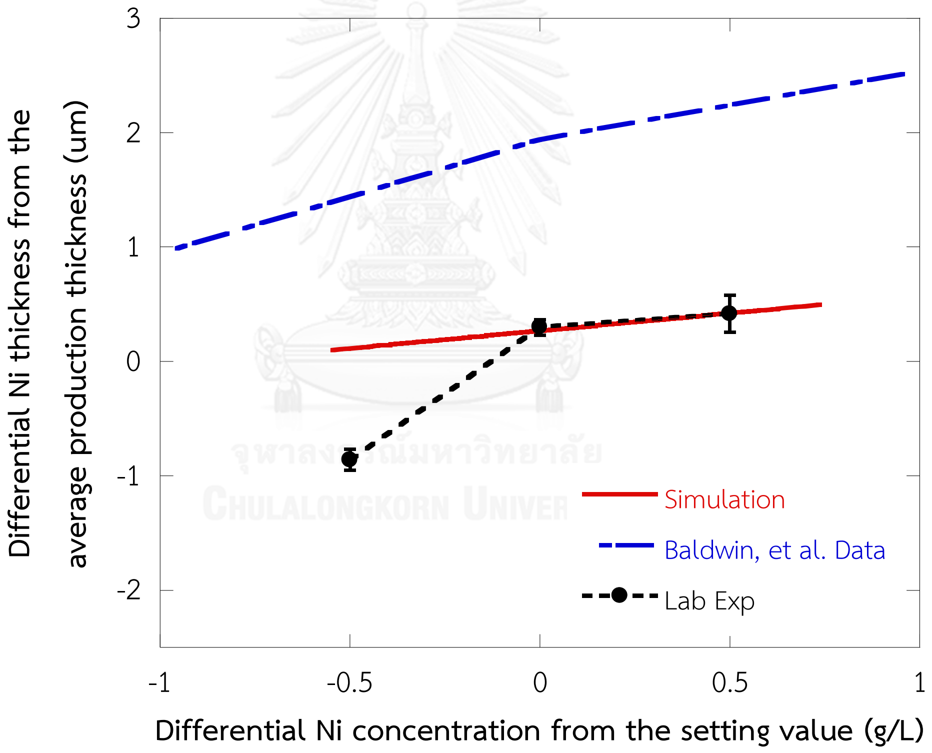


Figure 5.3 The comparison of the effect of nickel concentration on the nickel thickness between the previous study[25], simulation and lab experiment

Table 5.2 The conditions used in the results in Figure 5.3

	Baldwin, et al.[25]	Differential value from setting value	
		Simulation	Lab experiment
Nickel conc.			
Reducing agent conc.	25 g/L	0.0 g/L	0.0 g/L
pH	10 – 10.5	0.0	0.0
Chelating agents	Pyrophosphate	Unknown	Unknown
Temperature	74 °C	Same as the actual production	
Deposition time	1 hr	Same as the actual production	

The effect of nickel concentration on the amount of phosphorus on plating surface

From the previous study, there was a range of the concentration of nickel ion that affected the amount of phosphorus in nickel alloy. Exceeding this range, the amount of phosphorus remained constant or slightly changed.[11] In addition, increasing the nickel ion concentration increased surface reaction.[31] In Figure 5.4, increasing the nickel concentration increased nickel deposition but the phosphorus deposition rate was constant. As a result, the amount of nickel deposition on the substrate was increased by increasing the rate of nickel plating reaction, so the amount of phosphorus deposition was decreased. Figure 5.3 shows that the plating reaction rate was slow obviously at -0.5 g/L of differential nickel ion concentration from the setting value. Due to constant rate of phosphorus deposition, the phosphorus content on the nickel alloy surface, which was plated by -0.5 g/L of differential nickel ion concentration from the setting value, was explicitly more than the nickel alloy which was plated at 0.0 and 0.5 g/L of differential nickel ion concentration from the setting value. To compare the result from the previous study in which the amount of phosphorus on the nickel alloy surface was constant at more than 5.8 g/L of nickel ion concentration[11], the slope of the result of 0.0 and 0.5 g/L of differential nickel ion concentration from the setting value was similar to that of the previous study. Thus, the amount of phosphorus could be reduced when the concentration of nickel was greater than 0.5 g/L of differential nickel ion concentration from the setting value.

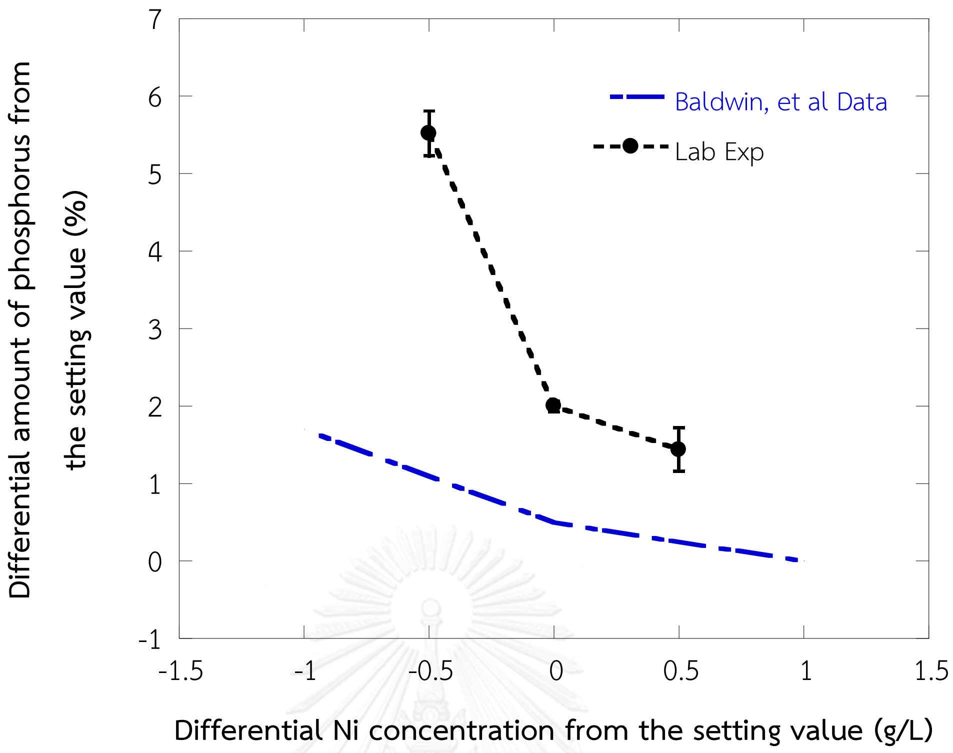


Figure 5.4 The comparison of the effect of nickel concentration on the phosphorus content between the previous study[25] and lab experiment

Table 5.3 The conditions used in the results in Figure 5.4

	Baldwin, et al.[25]	Lab experiment in differential value from setting value
Nickel conc.		
Reducing agent conc.	Unknown	0.0 g/L
pH	Acid	0.0
Chelating agents	Unknown	Unknown
Temperature	Unknown	Same as the actual production
Deposition time	Unknown	Same as the actual production

The effect of nickel concentration on the roughness of nickel alloy

The result in Figure 5.5 agreed with those of Yoon and coworkers.[27] When the plating rate was fast, the roughness of the plated surface decreased due to the increase of the thickness of plating and the increase of diffusion layer in which the growth process was more favored than the nucleation process.[2] Hence, the roughness decreased when the plating rate was fast. See more discussion in the topic 5.1.5.

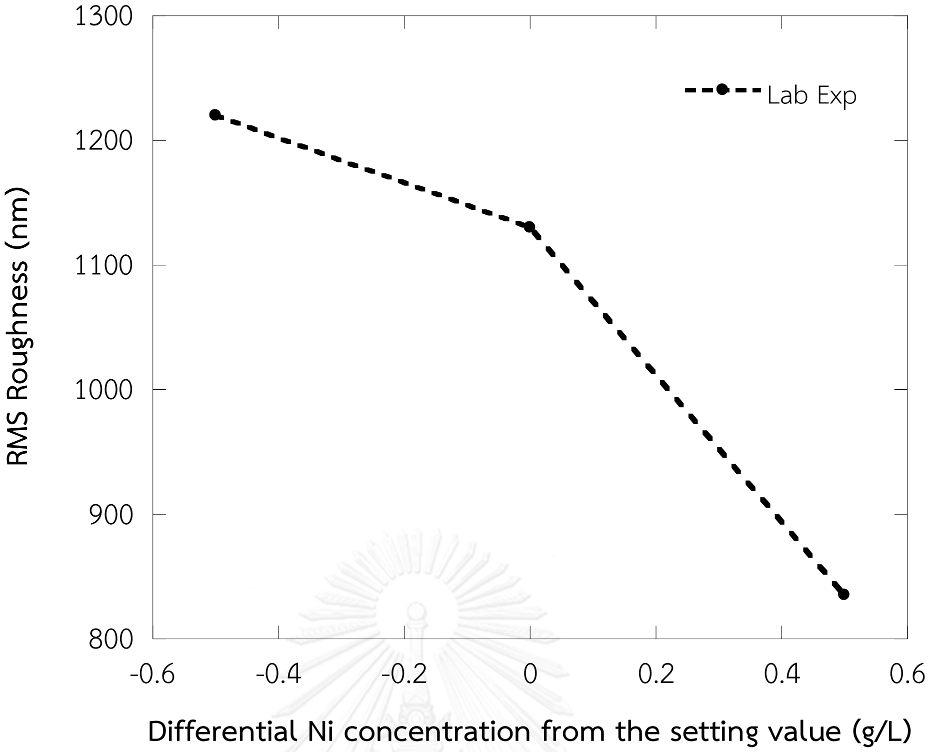


Figure 5.5 The effect of nickel concentration on the roughness of the nickel alloy surface

5.1.3 The effect of reducing agent concentration on the thickness, amount of phosphorus on surface and roughness of nickel plating

<u>The effect of reducing agent concentration on the nickel thickness</u>

From the simulation result in section 3.1, the slope of the nickel thickness to reducing agent concentration variation was slightly steeper than the slope of nickel thickness to nickel ion concentration variation, implying that the reducing agent concentration was more sensitive than the nickel ion concentration. The previous studies by Lee[26] proposed that the nickel plating rate was a first order dependence on the reducing agent concentration in acid bath, which is in an agreement with the results from lab experiment and the simulation, as shown in reaction 2.39. Same as in the alkaline bath, the nickel plating rate depended on the reducing agent concentration as well but there was no specific reaction order. Figure 5.6 shows that the nickel thickness from the previous study was thicker than that from the lab experimental and the simulation result because of long plating time and high pH despite of low temperature. The lab experimental result was rather overlapped with the simulation result in which the nickel thickness of lab result was a bit lower than that from the simulation result at the low concentration of the reducing agent, which shows the same trend as the nickel ion concentration variation. However, from the MSDS, reducing agent solution contained various chelating agents with no traces of stabilizer or inhibitor. The change of the reducing agent concentration from the setting value also changed the concentration of chelating agents. There was the possibility that the amount of chelating agents in EN plating solution at low concentration of reducing agent was less than that in the simulation because the preparation of solution was different. At low concentration of reducing agent, the simulation result based on the reducing agent consumed after plating reaction but the experiment deliberately prepared it, so the amount of chelating agents should not be the same amount. On the other hand, the preparation of the EN plating solution in the lab experiment was the same as the actual production in which the reducing agent solution had to be increased, so the lab experiment result overlapped with the simulation result.

$$\frac{dNi^0}{dt} = K\frac{[reducing\ agent]}{[H^+]^b} \tag{2.37}$$

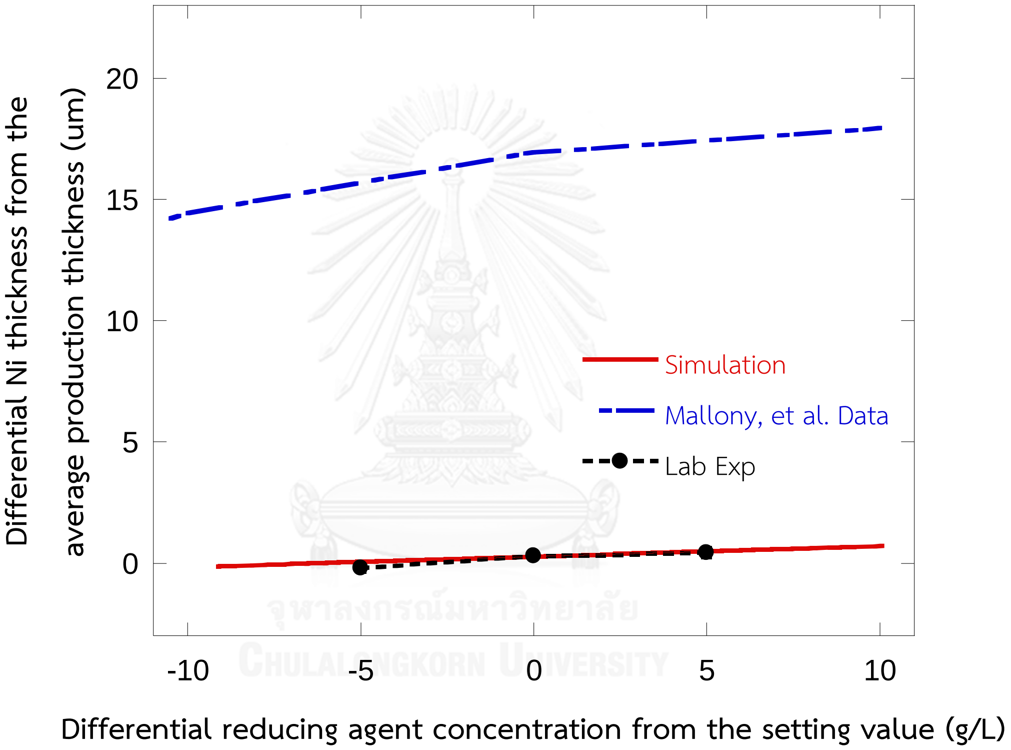


Figure 5.6 The comparison of the effect of reducing agent concentration on the nickel thickness between the previous study[11], simulation and lab experiment

Table 5.4 The conditions used in the results in Figure 5.6

	Mallony, et al.[11]	Differential value from setting value	
		Simulation	Lab experiment
Nickel conc.	25 g/L	0.0 g/L	0.0 g/L
Reducing agent conc.			
pH	10 – 10.5	0.0	0.0
Chelating agents	Pyrophosphate	Unknown	Unknown
Temperature	74 °C	Same as the actual production	
Deposition time	1 hr	Same as the actual production	

The effect of reducing agent concentration on the amount of phosphorus on plating surface

According to the result from Lee[26] the phosphorus deposition rate depended on the reducing agent concentration as the second order in the reaction, as shown in reaction 2.36. Baldwin et al.[24] (Figure 5.7) presented that the amount of phosphorus in nickel alloy was increased by increasing reducing agent concentration but it did not seem to be second order reaction because the short range variation. However, the amount of phosphorus in nickel alloy maintained at about 9% in lab experiment result. It was possible that the chelating agents in the reducing agent solution affected the deposition rate of the phosphorus. There were some chelating agents such as amino acetic acid, succinic acid, and ethylene diamine that caused the decrease of phosphorus deposition rate.[21] Therefore, the constant phosphorus deposition rate would be affected by 2 opposite effects; the increase of reducing agent concentration, fastening phosphorus deposition rate, and the increase of the chelating agent concentration decreasing phosphorus deposition rate.

$$\frac{dp}{dt} = K[reducing\ agent]^{1.91}[H^{+}]^{0.25} \tag{2.36}$$

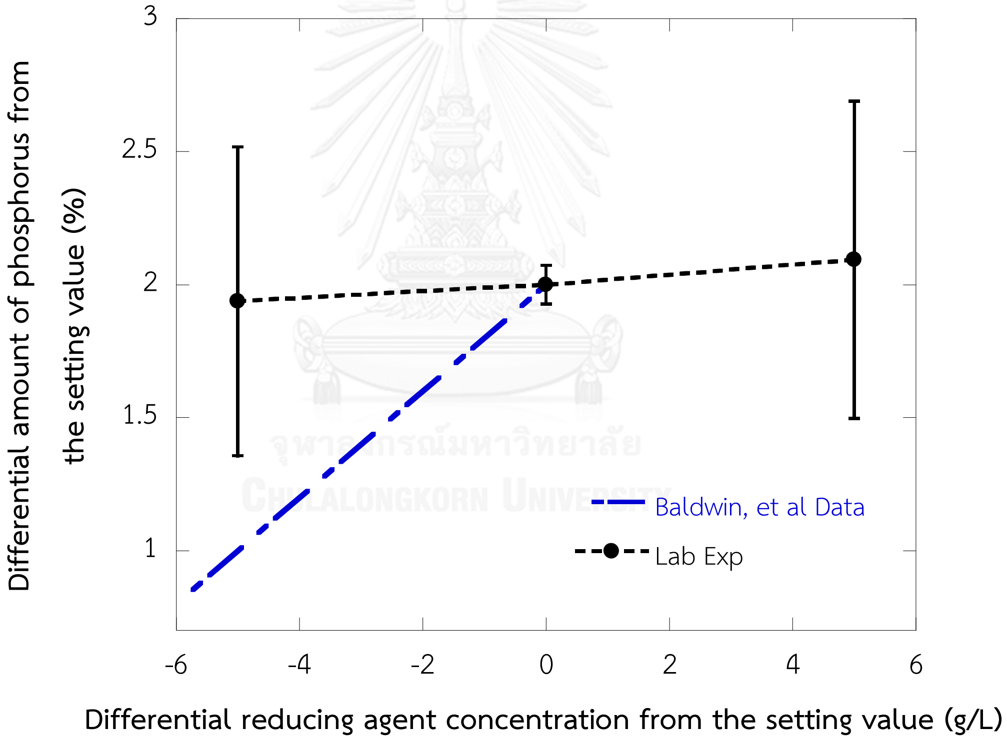


Figure 5.7 The comparison of the effect of reducing agent concentration on the phosphorus contented between the previous study[25] and lab experiment

Table 5.5 The conditions used in the results in Figure 5.7

	Baldwin, et al.[25]	Lab experiment in differential value from setting value
Nickel conc.	Unknown	0.0 g/L
Reducing agent conc.		
pH	Acid	0.0
Chelating agents	Unknown	Unknown
Temperature	Unknown	Same as the actual production
Deposition time	Unknown	Same as the actual production

The effect of reducing agent concentration on the roughness of nickel alloy

Figure 5.8 shows that the maximum roughness of nickel surface occurred at setting value of the reducing agent concentration. See more discussion in topic 5.1.5.

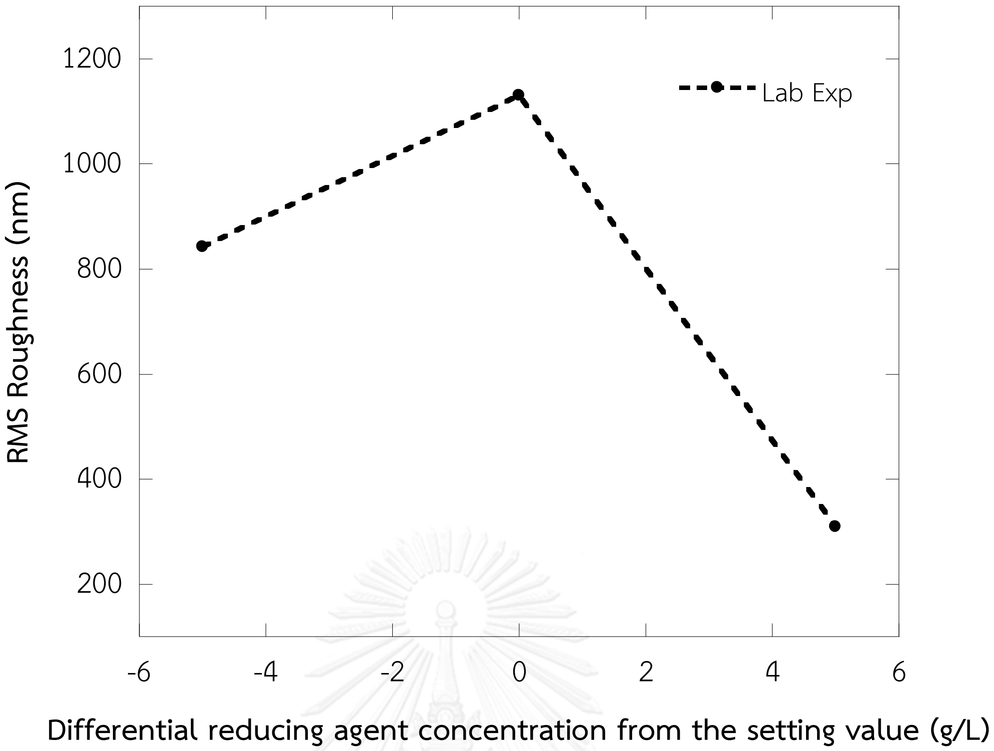


Figure 5.8 The effect of reducing agent concentration on the roughness of the nickel alloy surface

5.1.4 The effect of pH of EN plating solution on the thickness, amount of phosphorus on surface and roughness of nickel plating

The effect of pH of EN plating solution on the nickel thickness

Many previous work studied the effect of pH of EN plating solution on the nickel thickness. In Figure 5.9, the oldest published study was gathered by Mallony and coworkers[11]. The chemicals used by Yoon et al.[27] were purchased from Okuno

Chemical Industries Co., Ltd which are the same source as MMCT and it was also guaranteed that these chemicals provided the nickel plating with same amount of phosphorus content as the chemicals MMCT used but different additives for making the product flexible. The plating time from Mallony et al. was equal to the plating time which Yoon et al. used but the deposition rate of nickel was faster than the result from Yoon and other. Figure 5.10 shows that hydroxyacetic acid or glycolic acid were less stable than the succinic acid and the types with N coordinate which was used for maintaining the amount of phosphorus in nickel alloy. Therefore, the deposition rate of nickel in glycolic acid bath was faster than the study by Yoon et al. The deposition rates of simulation and lab experiment result were slower than Mallony et al. due to the short plating time and different type of chelating agent. At controlled values, the experiment result overlapped well with the simulation result because of the same condition and preparation. The high concentration of proton or at low pH rendered deposition rate of nickel, as shown in reaction 2.37[11]. However, the deposition rate of nickel at 2.9 of differential pH from the setting value was lower than that at 0.2 of differential pH from the setting value because of low nickel ion to reducing agent ratio, as shown in Figure 2.13. At 2.9 of differential pH from the setting value, the deposition rate of nickel was decreased due to the fast deposition rate at the start and no agitation which caused wider diffusion layer due to the fast consuming of reactants, so the adsorption rate of reactants were decreased.

$$\frac{dNi^0}{dt} = K\frac{[reducing\ agent]}{[H^+]^b} \tag{2.37}$$

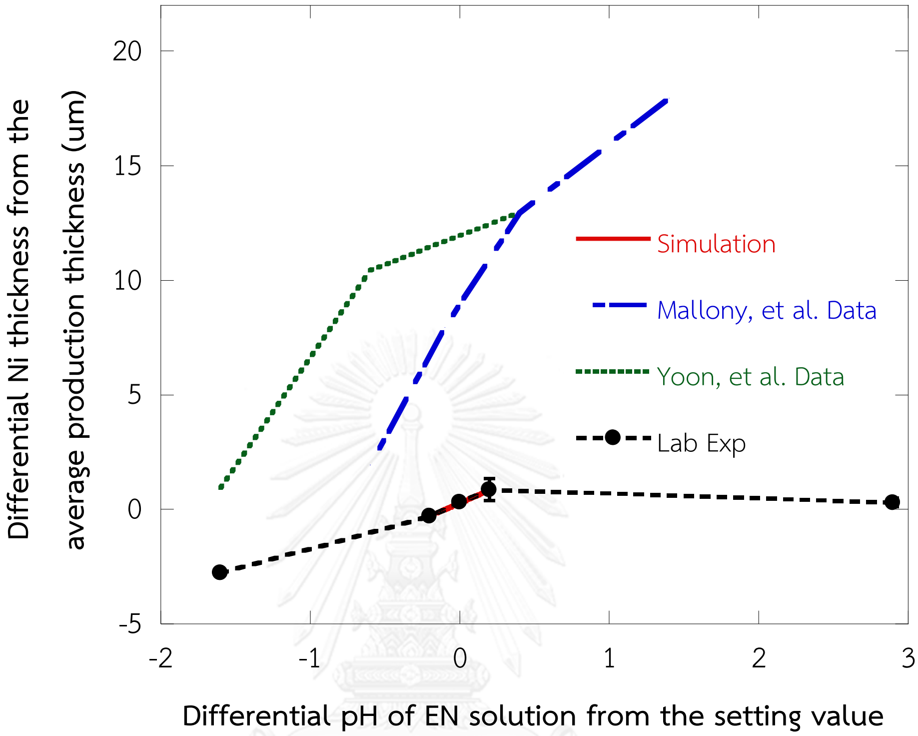


Figure 5.9 The comparison of the effect of pH of EN plating solution on the nickel thickness between the previous studies[11, 27], simulation and lab experiment

Table 5.6 The conditions used in the results in Figure 5.9

	Mallony, et al.[11]	Yoon, et al.[27]	Differential value from setting value	
			Simulation	Lab experiment
Nickel conc.	6 g/L	Unknown	0.0 g/L	0.0 g/L
Reducing agent conc.	25 g/L	Unknown	0.0 g/L	0.0 g/L
pH				
Chelating agents	Glycolic acid	Unknown	Unknown	Unknown
Temperature	87 °C	90 ± 1 °C	Same as the actual production	
Deposition time	1 hr	20 min	Same as the actual production	

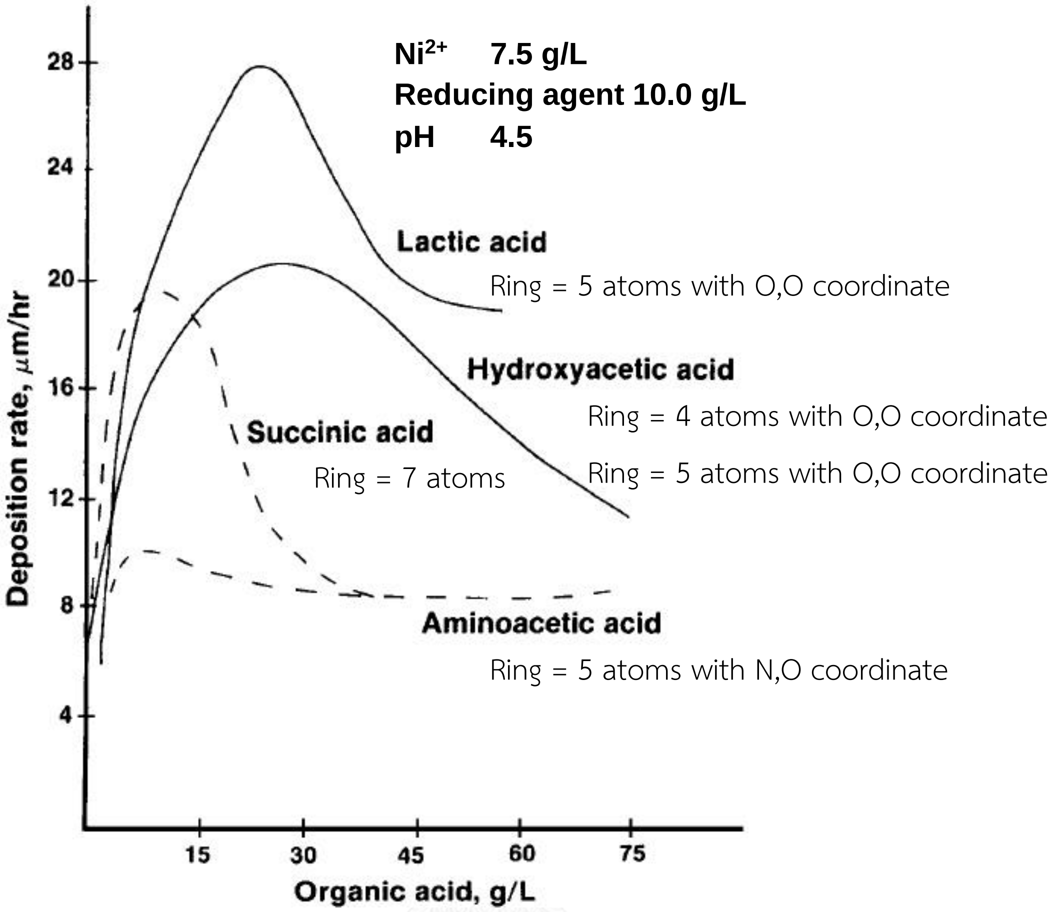


Figure 5.10 Effect of complexing agent concentration on deposition rate of nickel[11, 21]

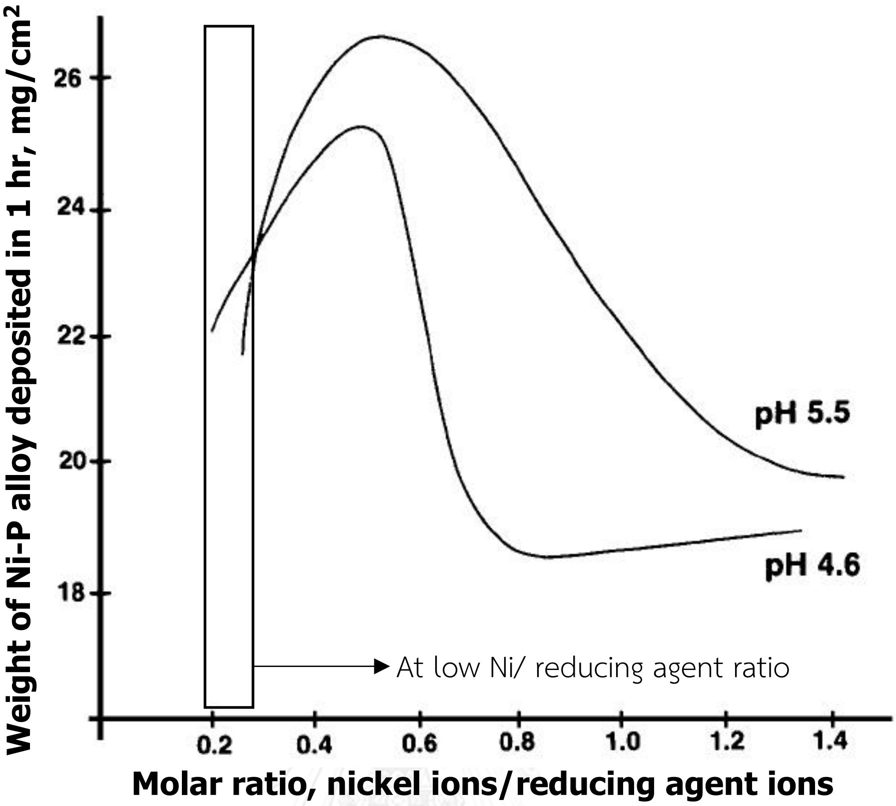


Figure 2.13 Effect of molar ratio of nickel ions and reducing agent ions on deposition rate[11]

<u>The effect of pH of EN plating solution on the amount of phosphorus on plating surface</u>

According to the previous studies, decreasing proton or increasing pH gave low phosphorus content in nickel alloy. Different types of chelating agent, stabilizers and composition of reactants also gave different phosphorus deposition rates [11, 27, 30], so the trends were alike but the amount of phosphorus were different. From the lab experiment result, the trend was in agreement with the previous studies and the reaction 2.36.[26] However, the phosphorus deposition rate at 2.9 of differential pH from the setting value was faster than those at the controlled range (-0.2 - +0.2 of differential pH from the setting value). To combine the result with Figure 5.9, the deposition rate of nickel at 2.9 of differential pH from the setting value was slower than that at 0.2 of differential pH from the setting value which was able to conclude that there was a wide diffusion layer formed. The reducing agent ion which was more intense than nickel ion would have thinner diffusion layer due to the driving force of mass transfer, so the amount of deposited phosphorus could be higher than that at the controlled range.

$$\frac{dp}{dt} = K[reducing\ agent]^{1.91}[H^+]^{0.25} \tag{2.36}$$

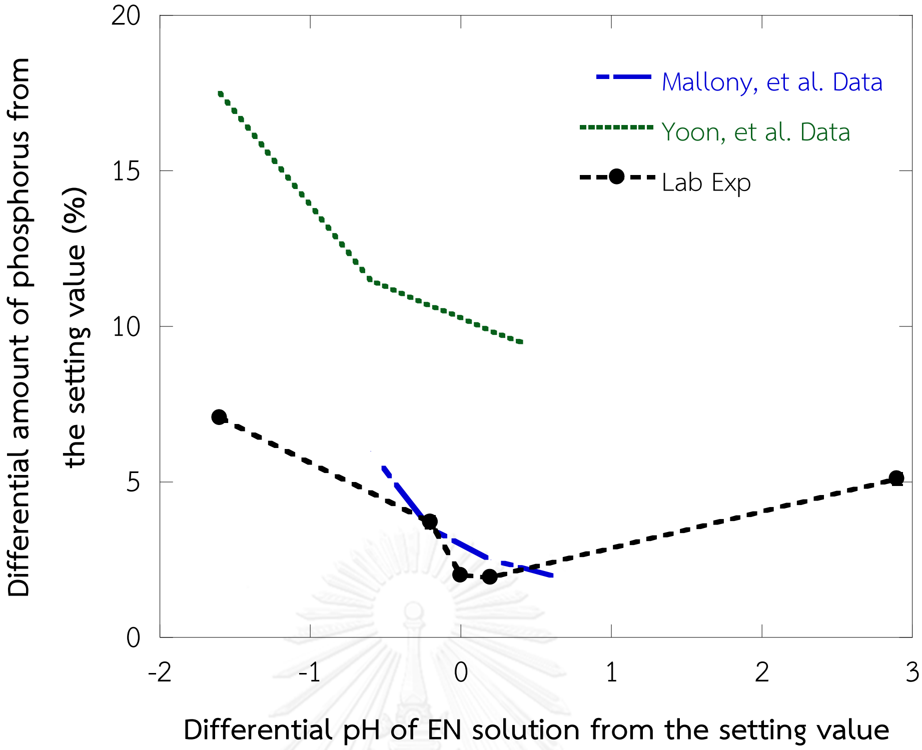


Figure 5.11 The comparison of the effect of pH of EN plating solution on the phosphorus content between the previous studies[11, 27], simulation and lab experiment

Table 5.7 The conditions used in the results in Figure 5.11

	Mallony, et al.[11]	Yoon, et al.[27]	Lab experiment in differential value from setting value
Nickel conc.	Unknown	Unknown	0.0 g/L
Reducing agent conc.	Unknown	Unknown	0.0 g/L
pH			
Chelating agents	Unknown	Unknown	Unknown
Temperature	Unknown	90 ± 1 °C	Same as the actual production
Deposition time	Unknown	1 hr	Same as the actual production

<u>The effect of pH of EN plating solution on the roughness of nickel alloy</u>

As same as the reducing agent variation, Figure 5.12 shows that the maximum roughness of nickel surface occurred at setting value of pH (pH 4.6) and the trend was not the same as Yoon and others[27]. They said that the nodule size increased and the number of nodule decreased at higher pH because of the wide diffusion layer at higher pH, so there was no nucleation at the low concentration of reactants but the growth continued to occur.[2] Therefore, the nodule size increased, the number of nodule decreased and the roughness was lower at higher pH. At differential pH +2.9, the RMS roughness of nickel alloy surface was similar to that at the setting pH. From the effect of pH on nickel thickness and amount of phosphorus content as mentioned above, the results showed that the thickness of nickel at differential pH +2.9 was thinner than that at differential pH +0.2 and the amount of phosphorus on the nickel surface was more than that at the controlled pH (differential pH ±0.2). The mechanism of nickel plating at differential pH +2.9 would be fast at the beginning of the reaction and then slow down due to the diffusion layer which resulted the thinner nickel thickness than that at differential pH +0.2 and higher phosphorus content due to less nickel ion concentration at the end of plating time. Also the result in section 5.1.2, the low concentration of nickel ion caused the high RMS roughness of the nickel alloy surface. Therefore, the RMS roughness at differential pH +2.9 was increased due to the slow deposition rate of nickel. See more discussion in section 5.1.5.

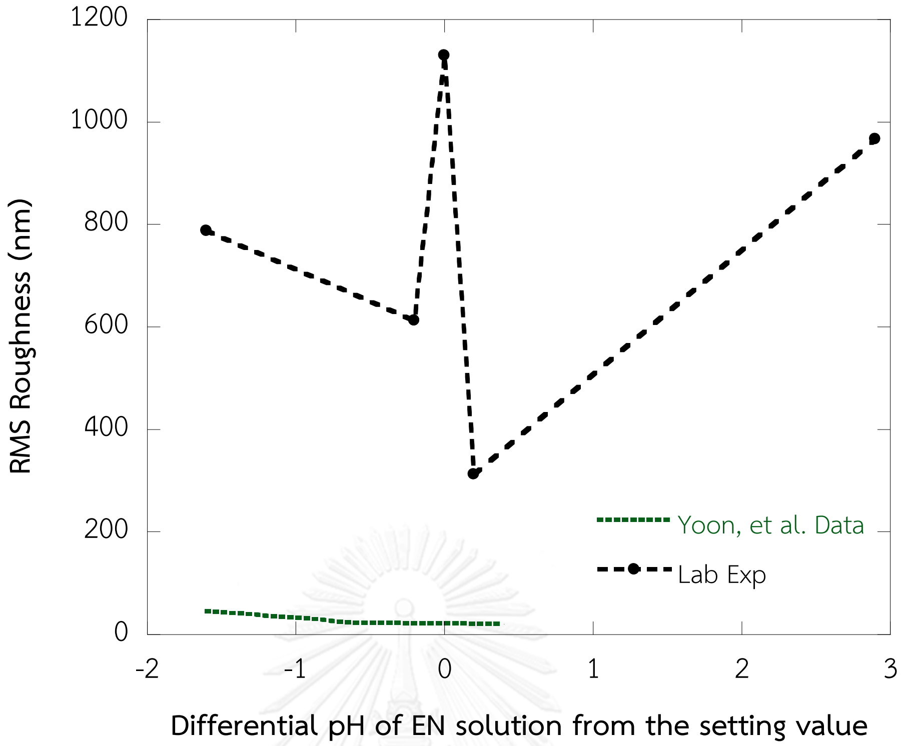
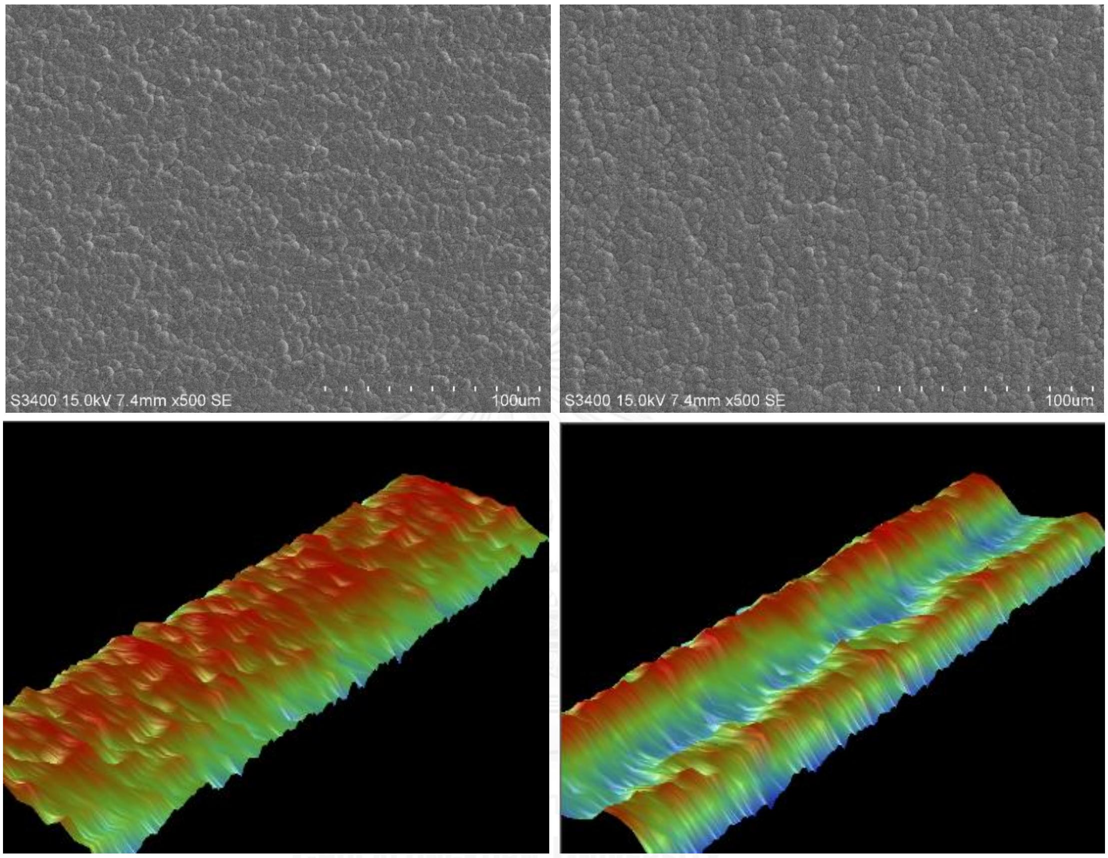


Figure 5.12 The comparison of the effect of pH of EN plating solution on the roughness of the nickel alloy surface between the previous study[27] and lab experiment

5.1.5 The effect of agitation on the characteristics of nickel plating

All the lab experiments performed without agitation (shaking) gave the same topographic pattern of the nickel surface, as shown in Figure 5.13 Right. There were the straight lines crossed the surface. Figure 5.13 Left shows the topographic pattern of the nickel surface resulted from the agitation of EN plating solution. The surface topographic pattern looked like flakes with nodules. There were some straight lines crossed the surface but they were less than that in the non-shaking one. Probably, it was because the hydrogen gas generated after the plating reaction took place, as shown in Figure 5.14. When the hydrogen gas flew up, it caused the flow of the EN plating solution too, so the straight lines could be the flow pattern in the EN plating bath. Therefore, the pattern of the surface was changed by flow pattern in the plating bath and it slightly affected the roughness of the plating product too. The surface roughness in topic 5.1.3 and 5.1.4 were not in an agreement with that in the theory and previous studies owing to the flow in the plating bath. However, the rate of nickel deposition in topic 5.1.2 at low nickel ion concentration (-0.5 g/L of differential nickel ion concentration from the setting value) made the obviously slow reaction, so the diffusion layer was thin and less hydrogen gas was generated. The surface pattern in Figure 5.15 was not a complete straight line as that in Figure 5.13 Right but it was also not the same as that in Figure 5.13 Left. Thus, the flow in this bath was too slow due to the slow rate of hydrogen gas generation and they were too slow to mess up the roughness which was caused by the reaction rate.

The nickel plating with agitation and without agitation was performed under the same condition. The results in Table 5.8 show that nickel plating with agitation had thicker thickness, higher phosphorus content, and more variance than nickel plating without agitation. It proved that there was a diffusion layer after the beginning of the plating reaction, so the deposition rate was faster when the EN plating solution was mixed during the reaction. However, there was no shaking machine to do this experiment, so jolting was performed by reckoning time and shaking. The mixing rate would not be the stable rate in this experiment, so it affected the variance of the thickness and phosphorus content.



With agitation (shaking) Without agitation

Figure 5.13 The topographic photo of nickel surface from shaking and non-shaking EN plating solution (x500 for top and 20 nm sample size for bottom)

* See the details of the 3D profile in Appendix B

Figure 5.14 Hydrogen gas on the mask of the substrate

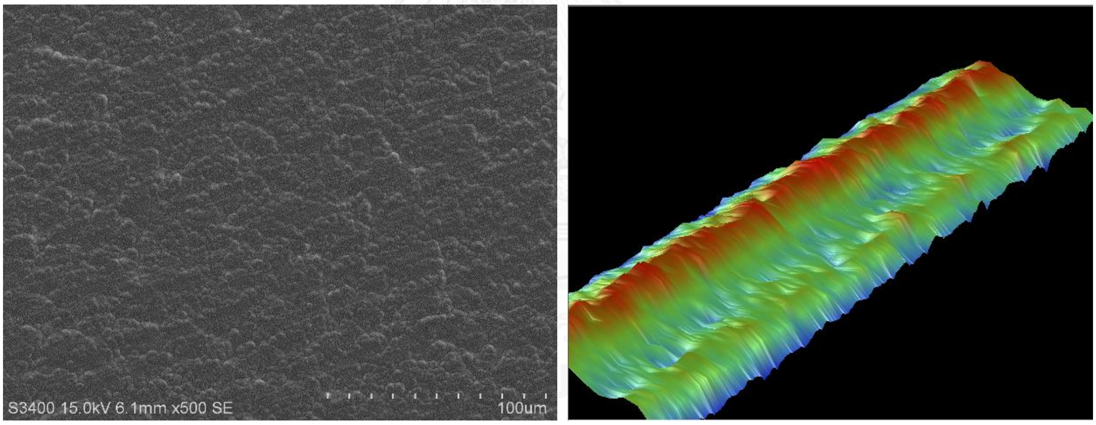


Figure 5.15 The topographic photo of nickel surface resulted from -0.5 g/L of differential nickel ion concentration from the setting value x500 (left) and 20 nm sample size (right)

Table 5.8 The conditions used in the results in Figure 5.14 and other results

	Differential value from setting value	
	Shaking	Non-shaking
Nickel conc.	0.0 g/L	0.0 g/L
Reducing agent conc.	0.0 g/L	0.0 g/L
pH	0.0	0.0
Chelating agents	Unknown	Unknown
Temperature	Same as the actual production	
Deposition time	Same as the actual production	
Nickel Thickness	0.513 ± 0.2234 μm	0.300 ± 0.0669 μm
Phosphorus	2.13 ± 0.331 %	2.00 ± 0.072 %
Roughness		
- R_a	887.52 nm	952.89 nm
- R_{RMS}	1.13 μm	1.13 μm
- R_t	5.67 μm	5.73 μm

R_a = Arithmetic average roughness

R_{RMS} = Root mean square roughness

R_t = Maximum height of the profile

5.2 The results of immersion gold (IG) plating experiment

The substrate used in this experiment was EN plating from MMCT. As the result from SEM-EDX, the composition of nickel and phosphorus in nickel alloy surface deviated ± 3.55 %.

5.2.1 The effect of gold ion concentration on the gold thickness

As the result in Figure 5.16, all of the results showed that increasing gold concentration increased gold deposition rate by increasing the surface reaction. The lab experiment result did not overlap the simulation result and each point of the result had wide variance. However, at the setting value (differential Au concentration from the setting value = 0 g/L) which was the initial setting parameters of IG plating solution from the production provided the average result close to the simulation trend. Moreover, the results from Liu and coworker[31] and the imitation whose plating condition was the same as Liu and coworkers' study gave similar slope but the thickness was about 2 times difference. The difference between those two results were the nickel substrate used. The imitation of the study by Liu and coworkers used the EN substrate that was plated by MMCT production. More of the discussion would be carried on in section 5.2.4.

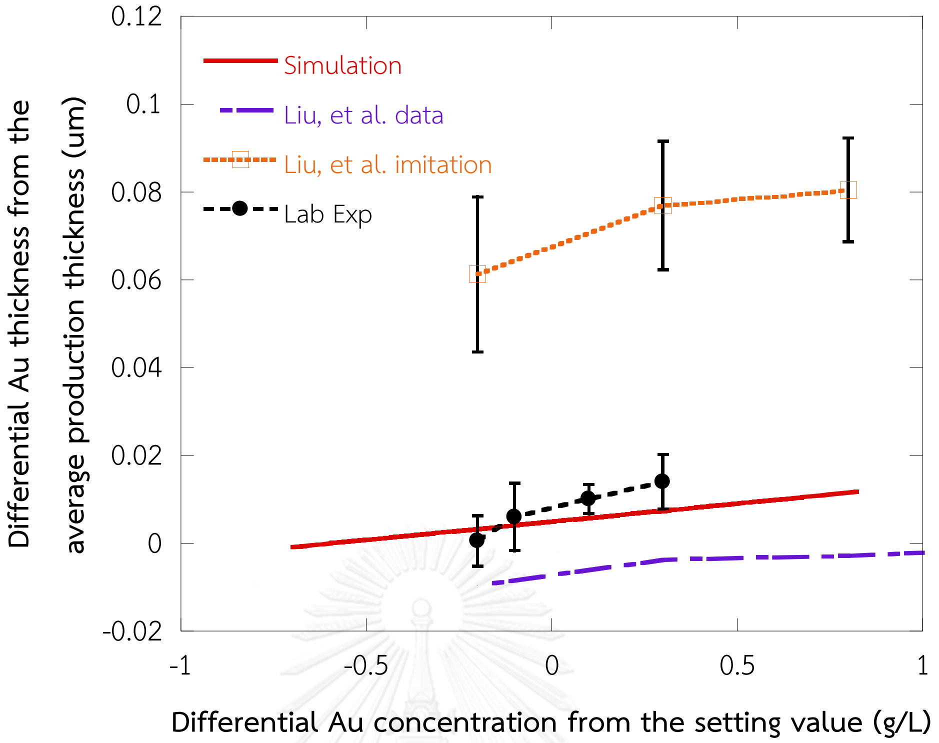


Figure 5.16 The comparison of the effect of gold concentration on the gold thickness between Liu et al.[31], the repeat from Liu et al., simulation, and lab experiment

Table 5.9 The conditions used in the results in Figure 5.16

	Liu, et al. and the imitation[31]	Differential value of simulation and lab experiment
Gold conc.		
pH	7.0	0
Chelating agents	Trisodium citrate 25 g/L NH_4Cl 40 g/L	Set of chelating agents* (0 °Be)
Temperature	85 ± 1 °C	Same as the actual production
Deposition time	10 min	Same as the actual production

* Controlled by density

5.2.2 The effect of specific gravity on the gold thickness

In the actual IG plating production, the density of the IG plating solution could impart that:

- The amount of chelating agent in the IG plating bath because it cannot be measured directly.
- The volume of the IG plating solution which could vaporize during process.

In this experiment, the density of the IG plating solution is a relative parameter based on the amount of chelating agent. The previous studies showed that each type of chelating agent provided one maximum deposition rate.[11, 31] From the lab experiment and simulation result, the deposition rate kept increasing by increasing the adsorption rate when the concentration of chelating agents increased in the controlled range, so it might not meet the maximum point yet, as shown in Figure 5.17. Same as in section 5.2.1, at the setting value (differential SG of IG solution from the setting value = 0 ^{o}Be) the initial setting parameters of IG plating solution from the production provided the average result nearby the simulation trend. However, the result at the low density was much lower than the simulation result. It might be because the trend of chelating agents' variation was not a linear trend[11, 31] and the amount of chelating agent below the differential SG of IG solution from the setting value -1 ^{o}Be was not at the range of the chelating agents concentration that slightly affected the plating thickness. After adding the chelating agents, the salt form of chelating agents increased due to constant pH. Then, the salt form of chelating agent attached to the complex of the metal ion as the ligand. If the amount of salt form was high enough, it provided the ternary complex which gave better adsorption.[31]

Same as in section 5.2.1, the result from the study by Liu and others provided thinner gold thickness than the imitation[31]. The slopes were similar to each other, as shown in Figure 5.18. The only difference between these two set was the nickel substrate used. More discussion would be carried out in section 5.2.4.

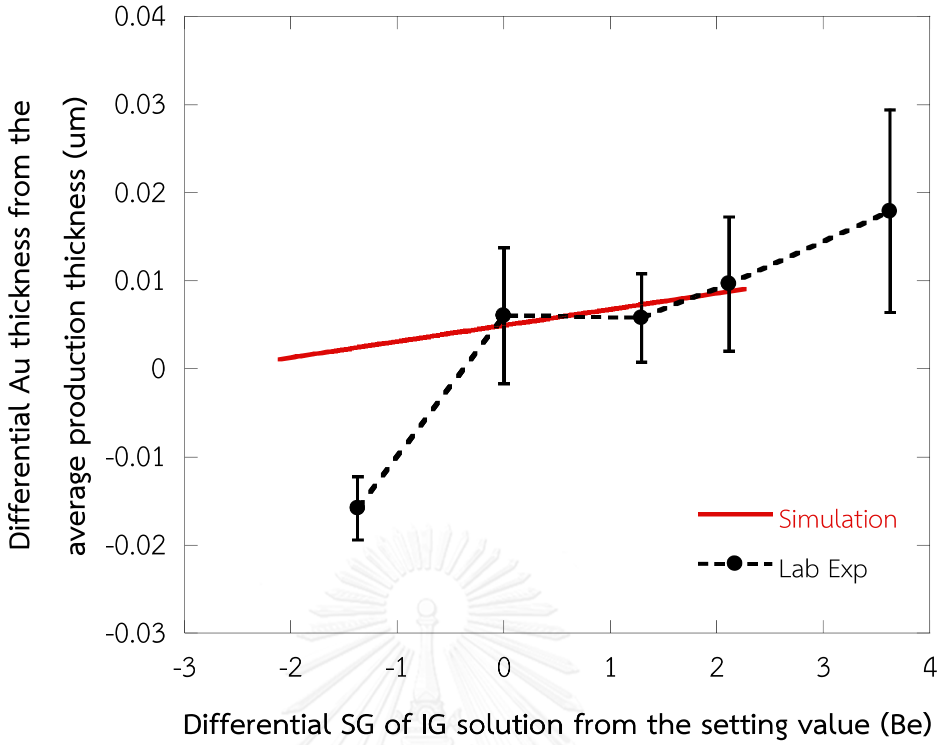


Figure 5.17 The comparison of the effect of specific gravity on the gold thickness between the simulation and lab experiment

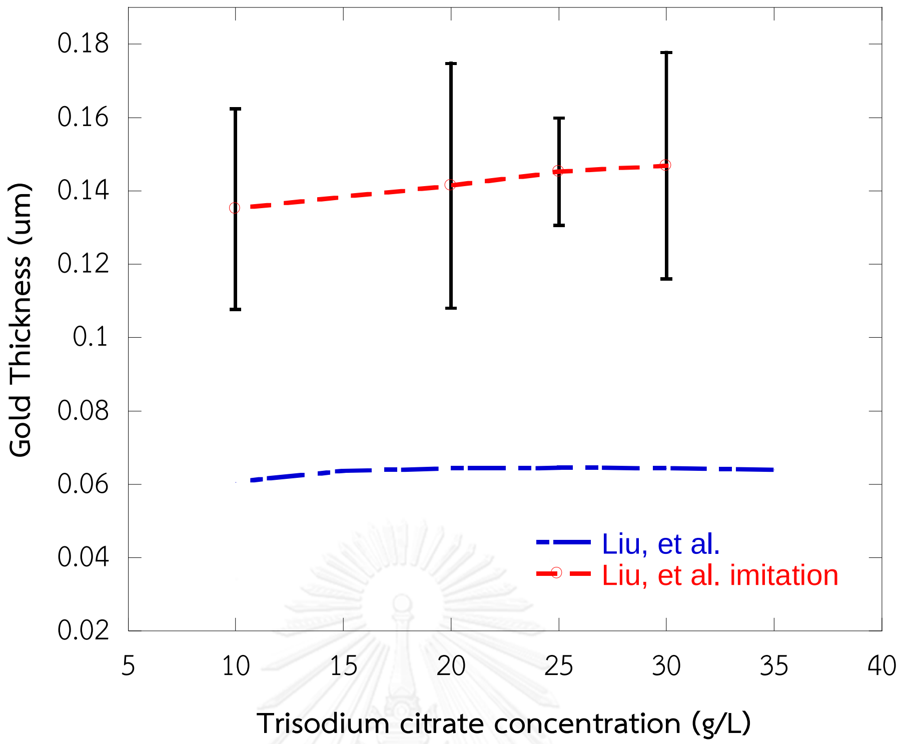


Figure 5.18 The comparison of the effect of trisodium citrate concentration on the gold thickness between the previous study and the imitation[31]

Table 5.10 The conditions used in the setup in Figure 5.17 and 5.18

	Liu, et al. and the imitation[31]	Differential value of simulation and lab experiment
Gold conc.	1 g/L	0 g/L
pH	7.0	0
Chelating agents	Trisodium citrate	Set of chelating agents*
	NH_4Cl 40 g/L	
Temperature	85 ± 1 °C	Same as the actual production
Deposition time	10 min	Same as the actual production

* Controlled by density

5.2.3 The effect of pH of IG plating solution on the gold thickness

The previous study and the imitation gave similar result in which the thickness in imitation result was thicker than the previous study result as shown in the section 5.2.1 and 5.2.2. However, the slope between at pH 5 and pH 6 was higher than the previous study result. The more discussion about this would be carried out section 5.2.4. In Figure 5.21, the lab experiment result could be divided into two types, at lower than setting value (differential pH of IG solution from the setting value < 0) and at higher than setting value (differential pH of IG solution from the setting value > 0). At the setting value (pH 5.7) the initial setting parameters of IG plating solution from the production provided the result matching with the simulation trend.

For the result at higher than setting value (differential pH of IG solution from the setting value > 0), the pH in this part was adjusted by inorganic base, so there was only one effect occurred. After adding inorganic base, the equilibrium of acid- base of the chelating agents shifted to the salt form which could provide the complex with the metal ion. Same as in section 5.2.2, if the salt form of the chelating agents was high enough, it provide the ternary complex which gave good adsorption and fast deposition rate. The summary of the mechanism is shown in Figure 5.19.

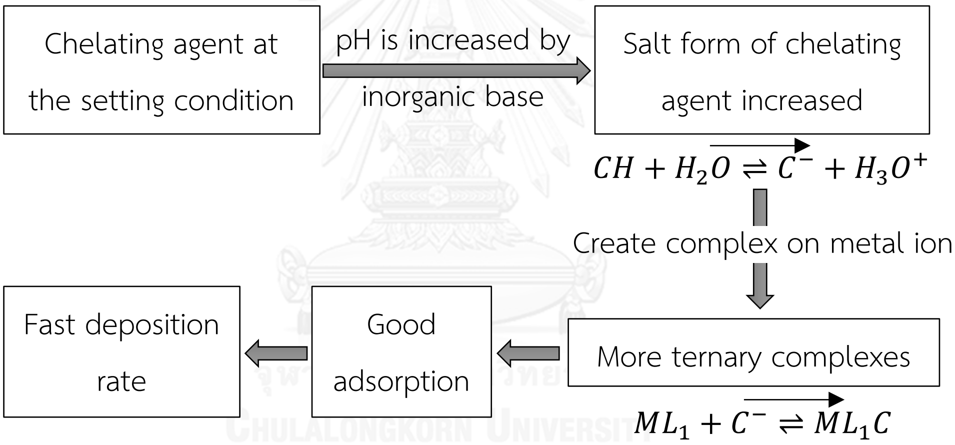


Figure 5.19 The chelating mechanism after increasing pH by inorganic base

For the result at lower than setting value (differential pH of IG solution from the setting value < 0). pH in this part was adjusted by the organic acid which has the property of chelating agent, so there were two effects occurred. When the pH of IG plating solution decreased, the salt form of chelating agents decreased, so the amount of ion to form ligand decreased. Then the ternary complex of metal decreased too.

As a result, the adsorption rate was slow and then the deposition rate was poorer than that at setting pH. However, pH was adjusted by the organic acid, so the amount of chelating agents was increased and then the adsorption rate and deposition rate were faster than those at setting pH. That is why there were two slopes in Figure 5.21. The simulation result in chapter 3 shows that the pH of IG plating solution was the sensitive parameter, so the pH of the IG plating solution affected the gold thickness more than the amount of chelating agents in which the result showed that adding the organic acid to decrease the pH gave thinner thickness of gold. The summary of this part is in Figure 5.20.

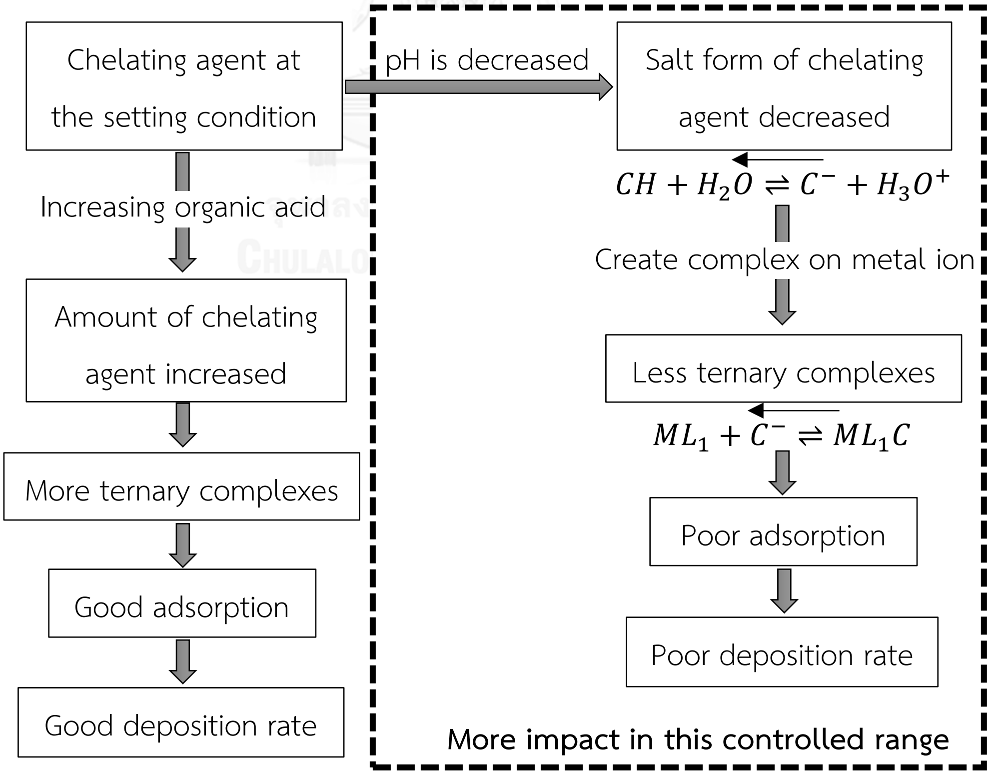


Figure 5.20 The chelating mechanism after decreasing pH by organic acid

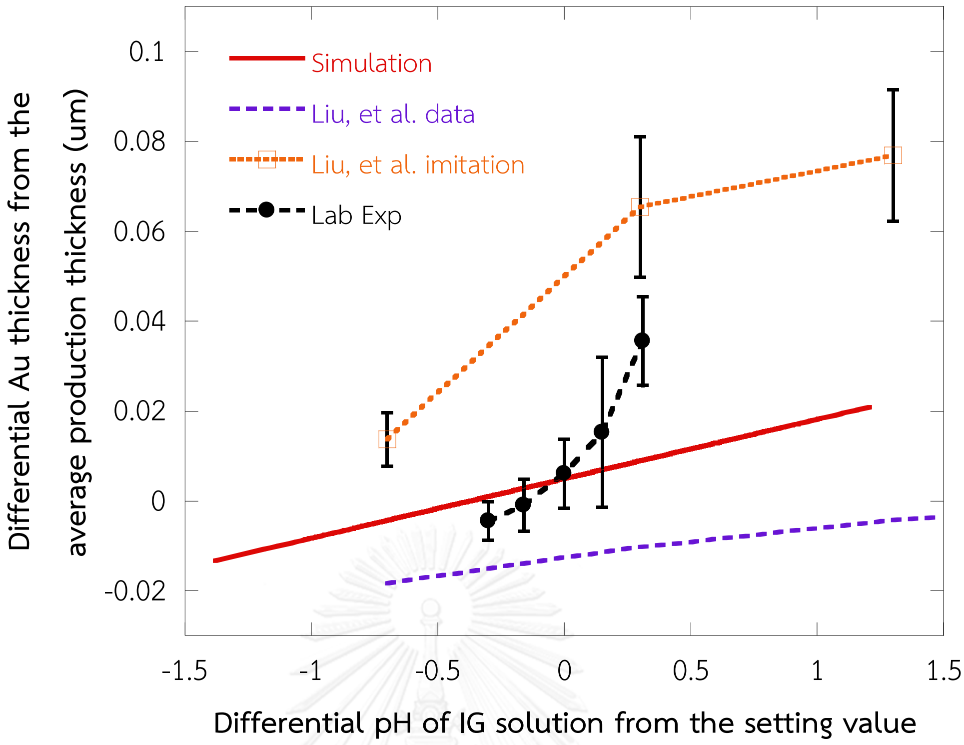


Figure 5.21 The comparison of the effect of pH of IG plating solution on the gold thickness between the previous study[31], the imitation, simulation and lab experiment

Table 5.11 The conditions used in the results in Figure 5.21

	Liu, et al. and the imitation[31]	Differential value of simulation and lab experiment
Gold conc.	1 g/L	0 g/L
pH	(adjusted by HCl and NaOH)	(adjusted by organic acid and inorganic base)
Chelating agents	Trisodium citrate 25 g/L NH_4Cl 40 g/L	Set of chelating agents* (0 ^{o}Be)
Temperature	85 ± 1 ^{o}C	Same as the actual production
Deposition time	10 min	Same as the actual production

* Controlled by density

5.2.4 The effect of other parameters on the gold thickness

Since the substrate used in this experiment was combined by three effects, the statistical analysis was required to separate each effect. In this study JMP7 was used as the statistical analysis program to analyze the effect of nickel thickness, RMS roughness and phosphorus content on the gold thickness, as shown in Figure 5.22 – 5.24. As a result of the experiment, there was only a slight effect of nickel thickness and RMS roughness on the gold thickness which opposed the simulation result in which the thickness of nickel affected the thickness of gold sensitively. Only the amount of phosphorus in nickel alloy affected the thickness of gold, so the result of the simulation slightly distorted by lacking of the amount of phosphorus in nickel alloy as a variable. The other parameters such as copper etching rate and specific gravity of activation (1) and (3) solution would be relative parameters which measured the oxide on copper substrate which would react with the catalyst ion afterwards. If catalyst was not plated dispersedly, the thickness of nickel would uneven as shown in the result in section 5.1.1.

By comparing results of the study done by Liu et al.[31] and the imitation of Liu's work, the result showed that the slopes were similar but the gold thickness of the imitation experiment was about 2 times higher than the original one. The difference between these two results may be caused by the amount of phosphorus in the nickel alloy substrate because of the different compositions and conditions of EN plating bath. The composition and condition used by Liu et al.[31] are shown in Table 5.12. Also the comparison between the simulation results and lab experiment results, the comparison result mentioned above did not overlap each other and had high deviation. Those result would be affected by the amount of phosphorus on the substrate surface which had the composition of nickel and phosphorus in nickel alloy surface deviated by ± 3.55 %.

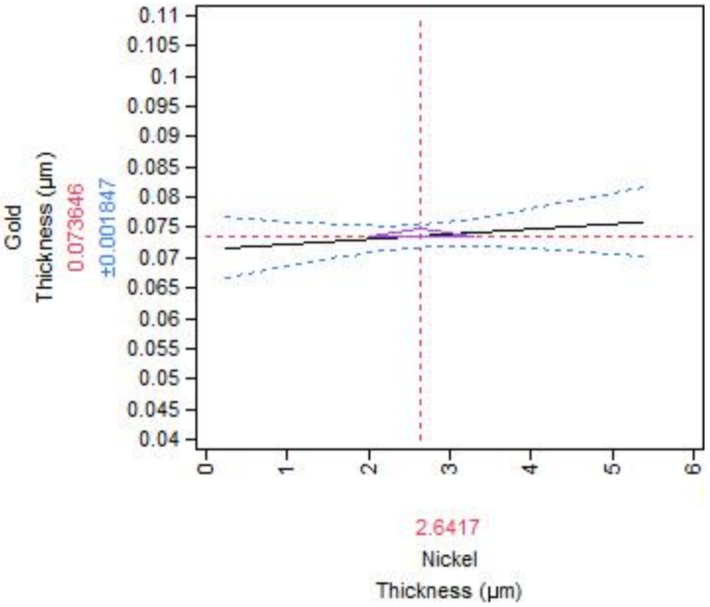


Figure 5.22 The effect of nickel thickness on the gold thickness

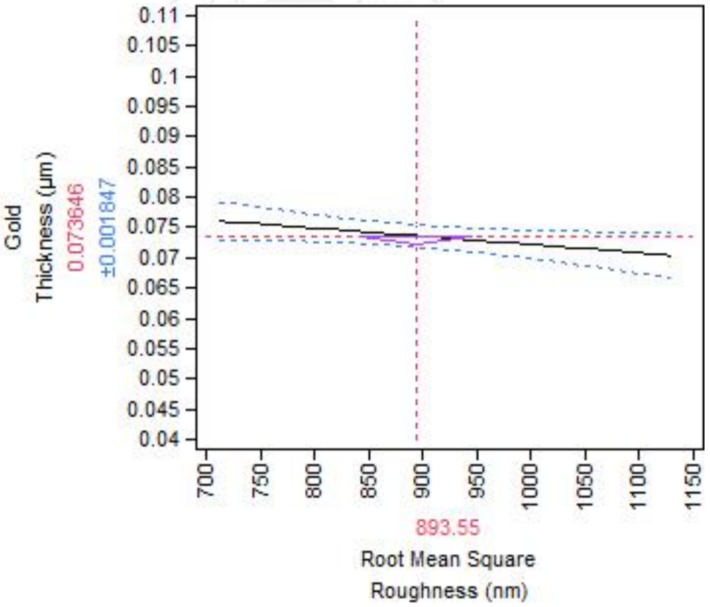


Figure 5.23 The effect of RMS roughness on the gold thickness

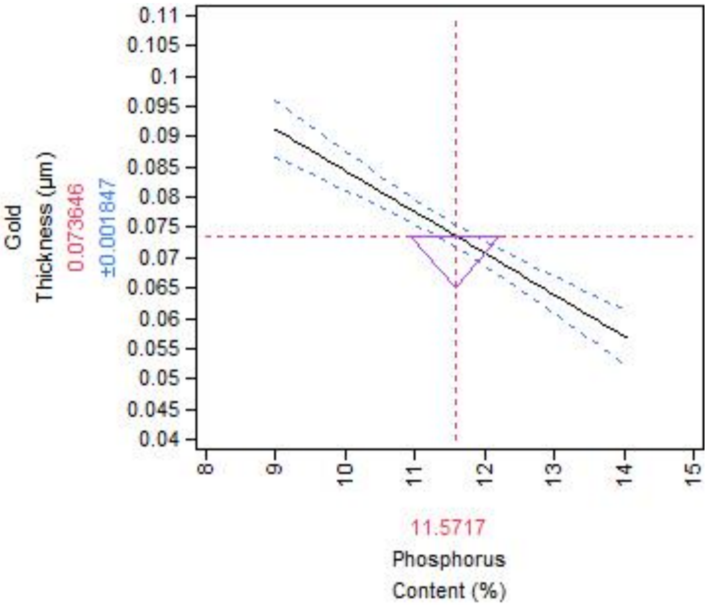


Figure 5.24 The effect of phosphorus content in nickel substrate on the gold thickness

Table 5.12 Bath composition and conditions for EN plating by Liu and other[31]

	Amount	Unit
$NiSO_4 \cdot 6H_2O$	27	g/L
$NaH_2PO_2 \cdot H_2O$	29	g/L
Lactic acid	25	mL/L
Malic acid	12	mL/L
pH	5.0 ± 0.2	
Temperature	88 ± 1	°C
Deposition time	10	min
Agitation	Without	

CHAPTER 6

Trouble shooting

6.1 Skip plating and uneven plating

6.1.1 No catalyst plating

From the discussion in topic 5.1.1, the reaction 2.24 could not occurred if there was no catalyst on the substrate, so the reaction 2.28 did not take place because of no reactant which is the product from reaction 2.24. The result was in Figure 5.1.

$$2H_2PO_2{}^- + 2H_2O \xrightarrow{cat} 2H_2PO_3{}^- + 2H^+ + 2H^- \tag{2.24}$$

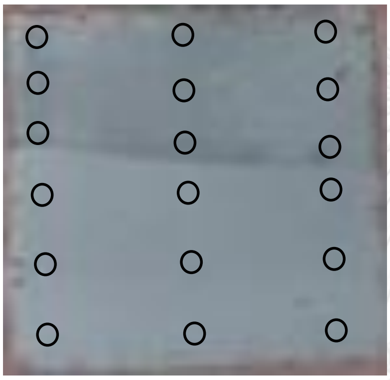
$$Ni^{2+} + 2H^- \rightarrow (Ni^{2+} + 2H + 2e) \rightarrow Ni^0 + H_2 \tag{2.28}$$

To prevent non-catalyst plating, the pretreatment steps before catalyst plating step which are cleaning and removing the oxide should be concerned. The catalyst plating reaction could not be occurred on the oxide surface.

6.1.2 The catalyst was not dispersedly plated

This incident could be occurred by the island oxide on the copper surface, so the cleaning bath and the condition of the copper substrate packaging should be concerned. If the non-catalyst area was large, it would cause the uneven plating, as shown in Table 5.1. To prevent this incident, the pretreatment steps before catalyst plating step should be concerned for the same reason that as in section 6.1.1.

Table 5.1 The profile of the nickel thickness on the substrate with half plating catalyst

The measured points	Nickel thickness profile (μm)		
	2.232	2.156	2.284
	2.113	2.310	2.265
	1.679	2.063	2.103
	2.448	2.734	2.453
	2.408	2.453	2.344
	2.539	2.703	2.687

6.1.3 Metallic contamination

In this experiment, the method of hanging the substrate was using something to grip the substrate. First, the wood peg was used, as shown in Figure 6.1. However, peg had the iron part. The displacement reaction occurred when the iron part touched the electroless nickel (EN) plating solution, as shown in reaction 6.1. The nickel plated on the iron part and some of iron ion dissolved. Then, the iron ion was reduced by the reducing agent into the sediment, reaction 6.4. Moreover, the displacement reaction might be faster than the electroless plating reaction, so the skip plating and uneven plating occurred, as shown in Figure 6.2. After the incident, double clip which was coated by nail polish was used.

$$Fe + Ni^{2+} \rightarrow Ni + Fe^{2+} \qquad (6.1)$$

$$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)} \qquad E^0 = -0.44\,V \qquad (6.2)$$

$$\begin{aligned} &reducing\ agent + H_2O \\ &\qquad \rightarrow productA + 2H^+ + 2e^- \end{aligned} \qquad E^0 = +0.50\,V \qquad (6.3)$$

$$Fe^{2+}_{(aq)} + reducing\ agent + H_2O \rightarrow Fe_{(s)} + productA + 2H^+ \qquad (6.4)$$

Figure 6.1 The wood peg which was used to grip the substrate

Figure 6.2 The uneven plating (a, b) and skip plating (c) defect from iron contamination

Figure 6.3 The double clip (left) and double clip coated by nail polish (right)

6.2 Patterns of the surface

6.2.1 Poor agitation

In this experiment, the agitation was performed by reckoning time and then shaking the beaker of plating solution. The EN plating solution would not be well-mixed due to slow shaking and irregular force. The topography of the sample surface size 1 x 1 cm^2 was measured randomly. As shown in Figure 6.4, there were two layouts of surface which may be affected by the poor mixing. Figure 6.4 right shows the uncertain size of nodules in which nodules growth was widespread differently from those in Figure 6.4 left which has the uniform size of nodule. To have the uniform nodule size, the concentration of the reactants near the substrate should be homogeneous which would provide the same process, nucleation or growth, so the good agitation is required. From the previous study[34], the best agitation should be in the transition region.

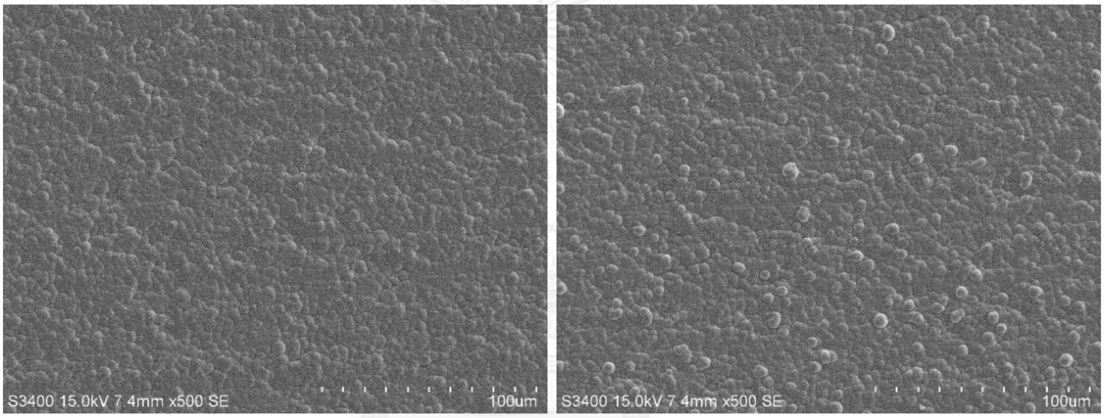


Figure 6.4 The two layouts of the EN plated surface

6.2.2 Lack of agitation

As discussed in section 5.1.5, the straight line pattern might be caused by the flow created by the hydrogen gas. Shaking the EN plating solution removed the hydrogen gas which attached on the mask of the substrate, as shown in Figure 5.14. If there was no agitation, the hydrogen gas would agglomerate and then flew up which caused flow pattern, as shown in Figure 6.5.

Figure 5.14 Hydrogen gas on the mask of the substrate

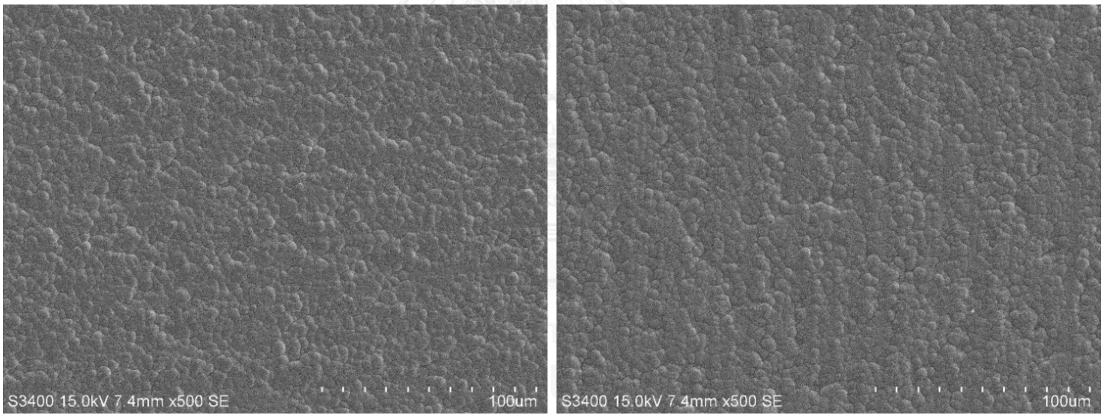


Figure 6.5 The topographic x500 of nickel surface resulted from shaking (left) and non-shaking (right) EN plating solution

6.2.3 Substrate pattern

In Figure 6.6 left, the copper substrate looked like discontinuous layers. This pattern was forwarded to the EN plating surface pattern, as shown in Figure 6.6 right. Moreover, the pattern of immersion gold (IG) plating surface was the same as the nickel substrate pattern[31], as shown in Figure 6.7. Therefore, to control the plating pattern, the surface pattern should be controlled too.

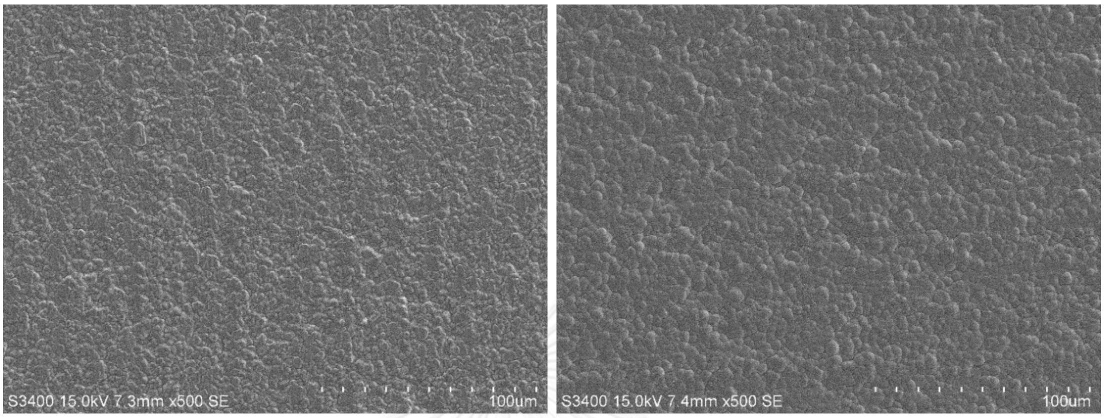


Figure 6.6 The topographic x500 of copper substrate (left) and nickel surface resulted from shaking EN plating solution (right)

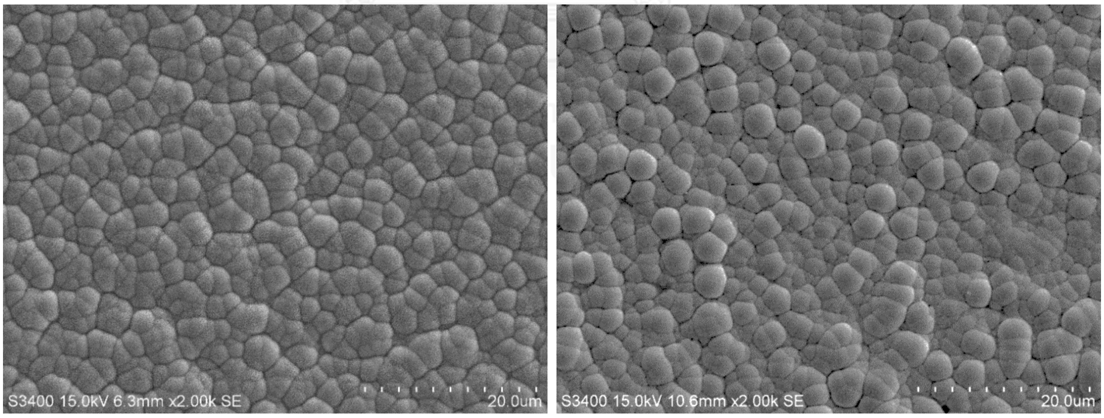


Figure 6.7 The topographic x2.00k of nickel substrate (left) and IG plating surface (right)

6.3 Thickness

The environment was one factor that should be concerned. The clean environment was required for preventing the interference of plating. As shown in Figure 6.8, the dust in environment caused thiner EN plating thickness than the normal one. Dust which is attached on the substrate and the equipment as well as contaminate the plating solution would be concerned. There were two possibilities which would happen.

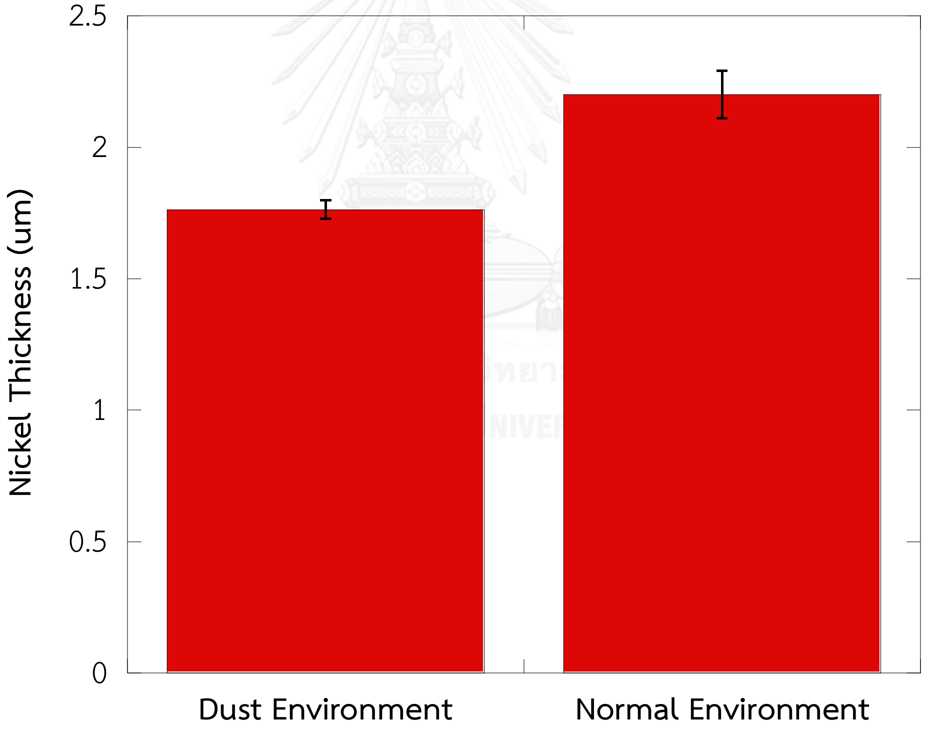


Figure 6.8 The comparison between plating process in dust environment and normal environment

The first possibility was the interference of diffusion on the surface step. Figure 2.4 shows that there are six steps of the deposition of metal ion. The third step, surface diffusion is the step that the atom of metal diffused on the surface to find the matching spot to deposit. The spot could be whatever spot in the same sheet or the surface of object which was attached on the surface. If there was atoms of nickel deposition on the impurity, they could be the catalyst for the other layer of EN plating on that impurity. So, the thickness could be decreased by more consuming of the reactants and the stability of plating bath would be decreased too.

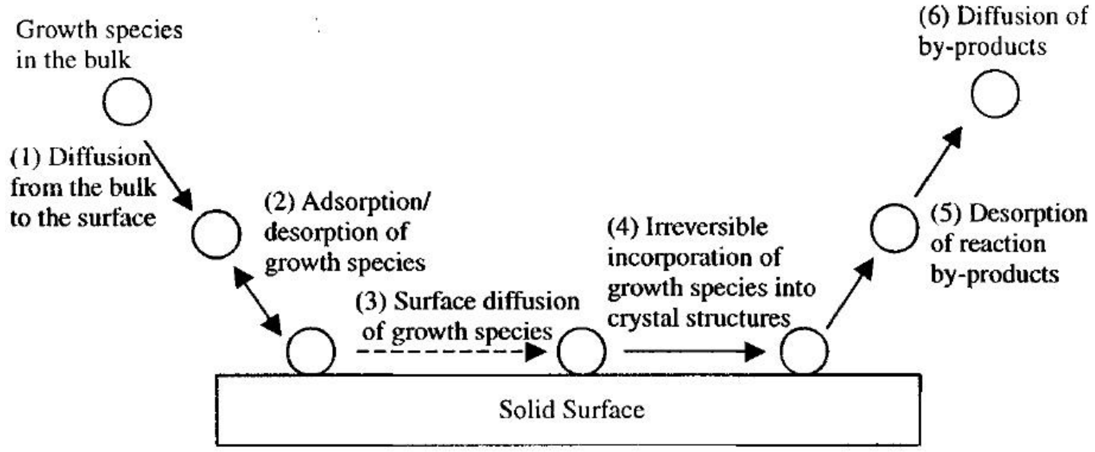


Figure 2.4 The deposition steps of metal ion on the substrate[2]

The last possibility was the pit on the plating surface.[35] This incident would be occurred by the dust attached on the surface and then flew off in duration of plating reaction. Moreover, if the dust was organic substance, the pit could be occurred not only the incident mentioned above but also after the heat treatment too. These case was really important for the IG plating because it was one of the incident which was the cause of black pad or the nickel oxide on the gold surface, as shown in Figure 6.9.

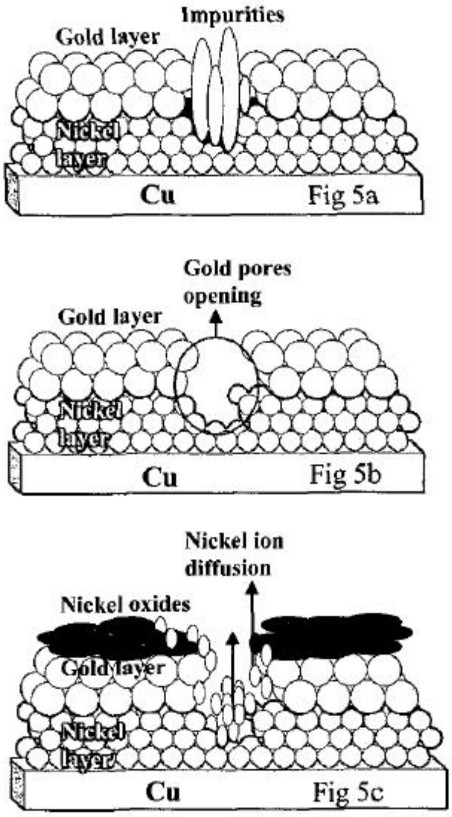


Figure 6.9 The incident that the impurities attached the surface of substrate or unfinished plating surface[35]

CHAPTER 7

Conclusions and Recommendations

7.1 Conclusions

In this study, the considered parameters were the controlled parameters in the actual production such as the reactants concentration, pH of plating solution, the by-product concentration and other controlled parameters of the pretreatment. The result was analyzed by the JMP7.

7.1.1 Electroless nickel (EN) plating

The most sensitive parameter in EN plating process which was analyzed by JMP7 was the by-product concentration. The second sensitive parameter was the pH of EN plating solution. The other important parameters were the parameters which controlled the etching process and the activation (1) process which were the process for removing the oxide on the substrate. The operating temperature should not exceed 90 ^{o}C to prevent the decomposition of plating solution. These parameters were important for the nickel thickness. However, the other output which should be considered was the phosphorus content in nickel alloy. The amount of phosphorus was affected by the chemicals in the EN plating bath. Moreover, the agitation was the other parameter that should be concerned for the uniform pattern of product. The transition region of agitation was the best for giving maximum nickel thickness and preventing the precipitation of nickel. The summary effects of input parameters on the EN plating product were in Table 7.1.

Table 7.1 The summary of the effects of the increased input parameters on the EN plating product

	Ni thickness	%P contented	Roughness
Ni concentration	Increase	Decrease	Decrease
$H_2PO_2^-$ concentration	Increase	Increase	Max at setting
By-product concentration	Increase	-	-
pH	Increase	Decrease	Max at setting
Temperature	Increase	-	-
Agitation	Increase	Increase	Less than non-agitation
Copper etching rate*	Increase	-	-
Activation (1)*	Increase	-	-

* Relative parameters which are the measurement the oxide on the substrate

7.1.2 Immersion gold (IG) plating

The most sensitive parameter in IG plating process analyzed by JMP7 was the pH of IG plating solution. In addition, the other parameter affecting the gold thickness and the actual production that has not been collected was the amount of phosphorus in nickel alloy. Since the IG plating reaction was the endothermic reaction, high temperature was required to proceed the reaction. However, too fast deposition rate caused the non-uniformity of gold deposition. The roughness of IG plating was the same as the nickel substrate due to the very thin layer of gold. The summary effects of input parameters on the IG plating product are in Table 7.2. Too thick of gold thickness affected the adhesion of gold film on the nickel substrate due to the corrosion of nickel surface under the gold film.

Table 7.2 The summary of the effects of the increased input parameters on the IG plating product

	Au thickness
Au concentration	Increase
pH	Increase
Temperature	Increase
%P on nickel substrate	Decrease

7.2 Recommendations

The environment of production

To control the thickness of plating, the clean environment was required. It was not only for the thickness of plating, but also preventing the defects such as the pit on the surface and black pad on the gold surface.

7.2.1 Electroless nickel (EN) plating

The controlled range

The controlled range which was applied in the actual production was appropriate for the required specification of EN plating such as the thickness of nickel and amount of phosphorus in nickel alloy. If the controlled range of input chemicals was narrow, the range of other parameters should be narrow too especially the by-product concentration, so the MTO parameter should be decreased which may cause higher cost of production. The interaction profile of the effect of input parameters on the nickel thickness is shown in A.1 of Appendix A.

Metallic contamination

Considering the basket used in the actual production, the core of basket was iron which is covered by the plastic. The basket should be checked whether the plastic was cracked to prevent iron contaminated in the EN plating solution.

Agitation

As mentioned above, the suitable agitation was in a transition region to prevent the precipitation of nickel. However, the turbulent region affected the diffusion and adsorption step, so the thickness would be thinner than that at transition region.[34]

Amount of oxide on surface

To control the nickel thickness, the amount of oxide affected the surface reaction area by reducing the active area of catalyst plating. The amount of oxide on the substrate surface should be measured to keep the homogeneous reaction which resulted the uniform catalyst on the substrate surface. The uniform catalyst influenced the uniform thickness of nickel. The measurement should be carried on as soon as possible after the activation (2) step to make sure the mount of oxide remained on the surface before catalyst plating.

7.2.2 Immersion gold (IG) plating

The controlled range

Same as in section 7.2.1, the controlled range which was applied in the actual production was appropriate for the required specification of IG plating. Faster deposition rate affected the uniformity of gold layer. The interaction profile of the effect of input parameters on the gold thickness is shown in A.2 of Appendix A.

The amount of oxide and phosphorus on surface

To control the gold thickness, the amount of oxide and phosphorus affected the surface reaction area by reducing the active area of IG plating. The amount of oxide and phosphorus on the substrate surface should be measured to keep the homogeneous reaction which resulted in the uniform and maximum thickness of gold. To have the exact result of the amount of oxide on nickel, the measurement should be carried on as soon as possible after the activation (3) step.

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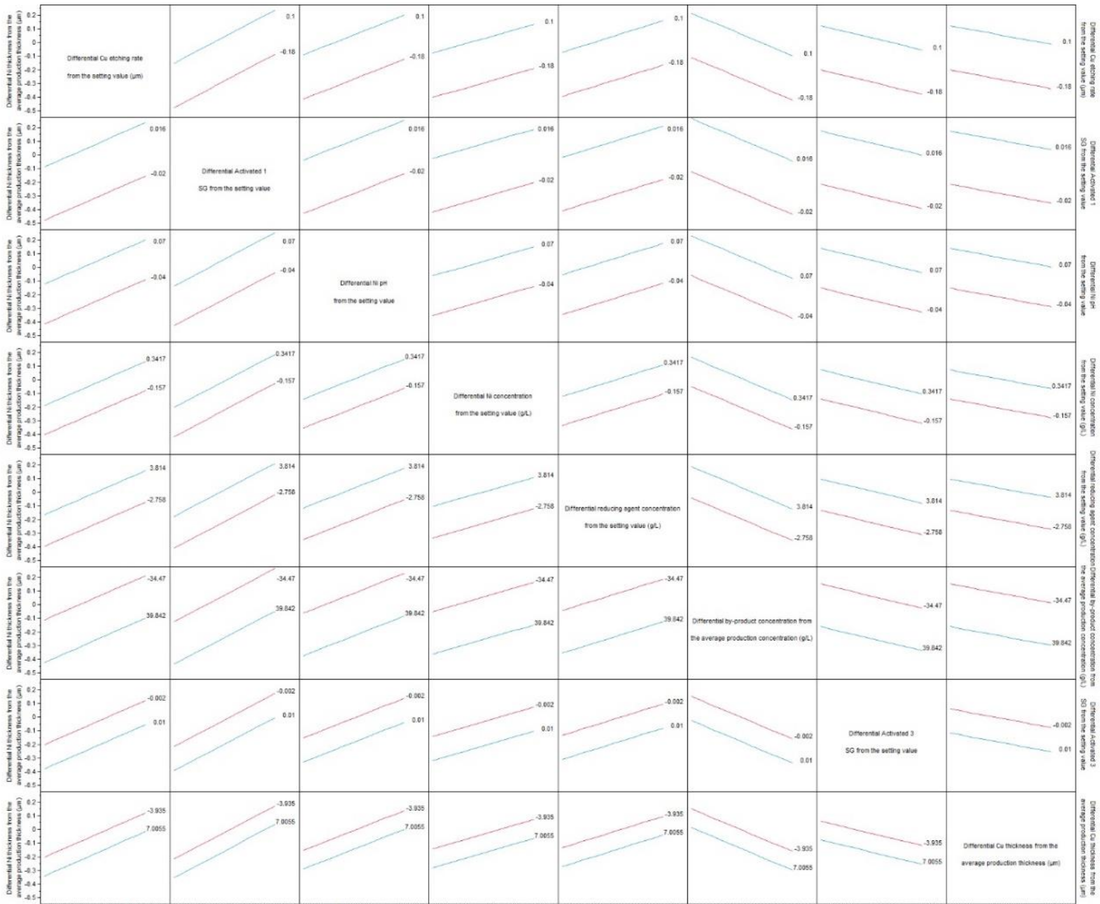
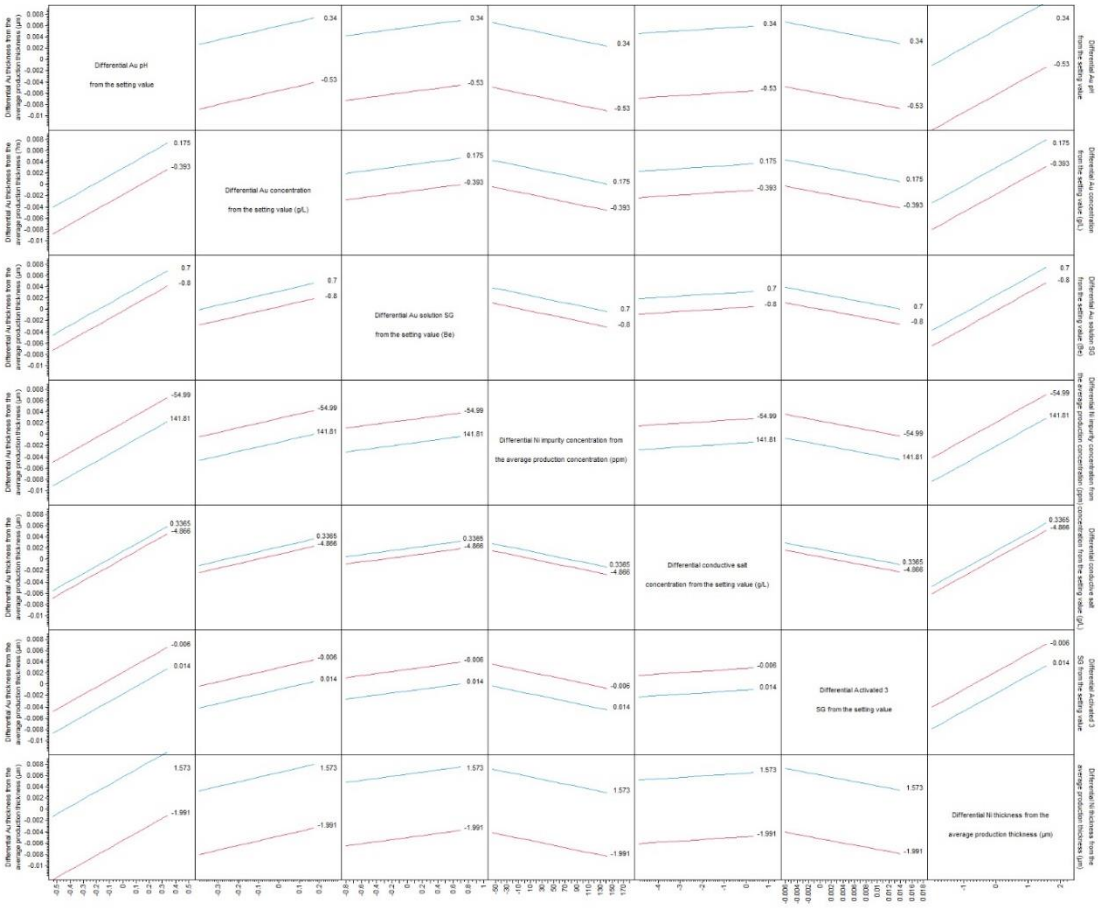
APPENDIX A

The interaction profile from collecting data simulation

A.1 The interaction profile of electroless nickel simulation



A.2 The interaction profile of immersion gold simulation

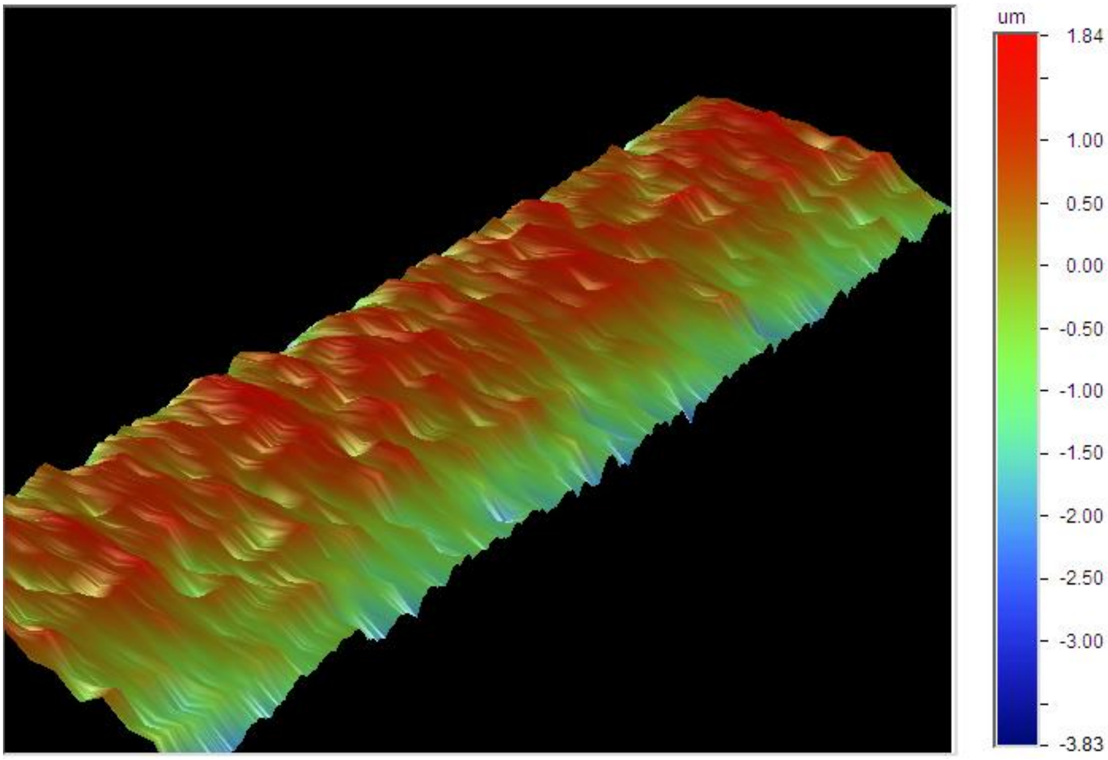


APPENDIX B

The 3D Profile of the EN plating result

B.1 The 3D profile of the electroless nickel (EN) plating

B.1.1 The profile of EN plating with agitation



The sampling size = 20 nm

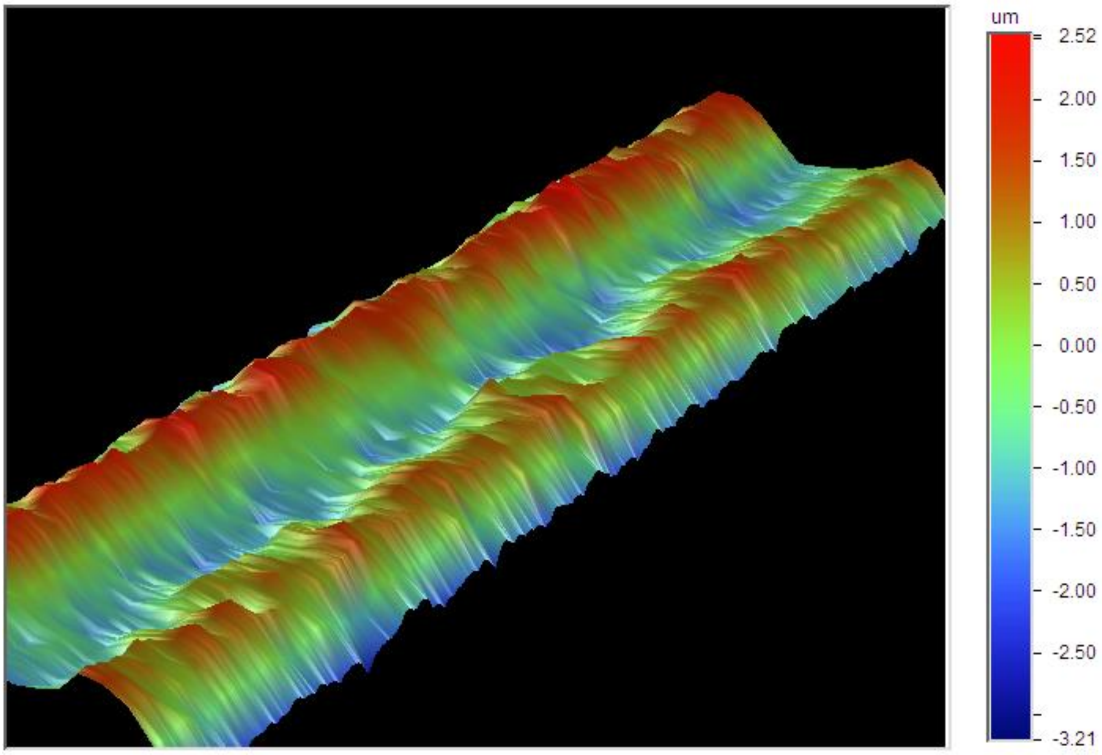
<u>Roughness</u>

Arithmetic average roughness = 887.52 nm

Root mean squared roughness = 1.13 μm

Maximum height of the profile = 5.67 μm

B.1.2 The profile of EN plating without agitation



The sampling size = 20 nm

<u>Roughness</u>

Arithmetic average roughness = 952.89 nm

Root mean squared roughness = 1.13 μm

Maximum height of the profile = 5.73 μm

VITA

Ms. Suphitsara Pattarakiatikun was born on July 21, 1990 in Bangkok, Thailand. She graduated from Sai Nam Peung School, Bangkok as high school in 2009 and had Bachelor’s degree in chemical engineering from Faculty of Engineering, Chulalongkorn University in 2014. In the same year of receiving Bachelor’s degree, she did a masters in chemical engineering at Faculty of Engineering, Chulalongkorn University. During her graduate study, she exhibited her poster presentation in the title of “Effect of pH on Gold Thickness in Electroless Nickel Immersion Gold (ENIG)” in The 7th Research Symposium on Petrochemical and Materials Technology and The 22nd PPC Symposium on Petroleum, Petrochemicals, and Polymers (PETROMAT and PPC Symposium 2016) on May 24th, 2016 in Bangkok, Thailand.