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นางสาวพชรพร กองสัมฤทธิ์

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THERMAL STABILITY OF THIOLATE SELF-ASSEMBLED MONOLAYERS

ON COPPER SURFACE

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พชรพร กองสัมฤทธิ์ : เสถียรภาพทางความร้อนของชั้นผิวแบบเรียงตัวชั้นเดียวของสาร กลุ่มทิโอเลตบนพื้นผิวทองแดง. (THERMAL STABILITY OF THIOLATE SELF-ASSEMBLED MONOLAYERS ON COPPER SURFACE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.สุรเทพ เขียวหอม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ. ดร.จูงใจ ปั้นประณต, 47 หน้า.

การสร้างการเรียงตัวชั้นเดียวของสารออแกโนทิออลเป็นวิธีการหนึ่งที่ดีเยี่ยมในการป้องกัน การกัดกร่อนซึ่งสามารถประยุกต์ใช้ได้ในหลายๆ งานด้วยกัน ในงานวิจัยนี้ศึกษาศึกษาเสถียรภาพ ทางความร้อนของสารกลุ่มทิโอเลตซึ่งเคลือบบนพื้นผิวทองแดง โดยศึกษาสารเคลือบสามชนิด ด้วยกัน ได้แก่ 1-octanethiol (OTT) 2-ethylhexanethiol (2-EHT) และ 2-phenylethanethiol (2-PET) ซึ่งสารเคมีทั้งสามชนิดมีองค์ประกอบทางเคมีเหมือนกัน แต่มีความแตกต่างกันทางลักษณะ ทางโครงสร้าง โดยจะใช้ contact angle SEM AFM FT-IR XPS และ potentiodynamic polarization เพื่อวิเคราะห์สมบัติความชอบน้ำ และความไม่ชอบน้ำ ลักษณะของพื้นผิว ความ ขรุขระ การสลายตัวของสารเคลือบ (SAMs) และความสามารถในการป้องกันการกัดกร่อน โดยใน ลำดับแรกจะหาสภาวะที่เหมาะสมในการเตรียมพื้นผิวด้วยออกซิเจนพลาสมา ผลการทดลองแสดง ให้เห็นว่าเวลาในการทำออกซิเจนพลาสมาที่เหมาะสมคือ 15 วินาที ออกซิเจนพลาสมาจะเพิ่ม ความขรุขระให้พื้นผิวทองแดงและเหนี่ยวนำให้เกิดสมบัติความชอบน้ำซึ่งเหมาะต่อการก่อตัวของ สารเคลือบบนพื้นผิวทองแดง จากนั้นผิวทองแดงซึ่งเคลือบด้วยสารเคลือบแต่ละชนิดข้างต้นจะถูก นำไปอบที่อุณหภูมิตั้งแต่ 25 ถึง 250 องศาเซลเซียส สารเคลือบ OTT จะสลายตัวที่อุณหภูมิ 80 องศาเซลเซียส ขณะที่สาร 2-EHT สลายตัวที่อุณหภูมิสูงกว่าคือ 140 องศาเซลเซียส ส่วนสาร 2-PET ไม่เกิดการสลายตัวที่อุณหภูมิต่ำกว่า 140 องศาเซลเซียส เนื่องจากโครงสร้างของ 2-PET ประกอบไปด้วย วงอะโรมาติกซึ่งมีความเสถียรมากกว่าหมู่ฟังก์ชันอื่นๆ ในโครงสร้างของสาร เคลือบ OTT และ 2-EHT ผลการทดลองยังแสดงให้เห็นถึงการช่วยเพิ่มเสถียรภาพทางความร้อน ของพันธะทิโอเลตด้วยวงอะโรมาติกในโมเลกุล 2-PET สารเคลือบทั้ง 3 ชนิดนี้จะสลายตัวอย่าง สมบูรณ์ที่อุณหภูมิ 250 องศาเซลเซียส โดยสรุปสารเคลือบ 2-PET มีความเหมาะสมที่สุดในด้าน เสถียรภาพทางความร้อน

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
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> PACHARAPORN KONGSUMRIT: THERMAL STABILITY OF THIOLATE SELF-ASSEMBLED MONOLAYERS ON COPPER SURFACE. ADVISOR: ASST. PROF. SOORATHEP KHEAWHOM, Ph.D., CO-ADVISOR: ASSOC. PROF. JOONGJAI PANPRANOT, Ph.D., 47 pp.

The formation of self-assembled monolayers (SAMs) of organothiol is one of the excellent methods for corrosion protection being able to be used in various applications. This work studies the thermal stability of thiolate SAMs coating on a copper surface. Three types of thiolate SAMs including 1-octanethiol (OTT), 2-ethylhexanethiol (2-EHT), and 2-phenylethanethiol (2-PET) are investigated. These chemicals are similar in terms of the chemical formula but different in chemical structure. Contact angle, SEM, AFM, FT-IR, XPS, and potentiodynamic polarization are used to analyze hydrophilic and hydrophobic features, morphology, roughness, decomposition of SAMs, and corrosion inhibition efficiency, respectively. Firstly, the optimum condition of oxygen plasma treatment is determined. The results show that the optimum time for the treatment is 15 s. The oxygen plasma increases roughness of the copper surface and induces the hydrophilic feature, which is suitable for SAMs to form on the copper surface. Thereafter, the copper surfaces coated by each SAMs are annealed at the temperature ranging from 25 to 250°C. The OTT is decomposed at the annealing temperature of 80°C while the 2-EHT is decomposed at the higher annealing temperature of 140°C. The 2-PET is not decomposed at annealing temperature below 140°C, because the 2-PET consists of aromatic rings that are more stable than other functional groups in OTT and 2-EHT structures. These results also refer to improvement of thiolate bond stability aided by aromatic ring in the 2-PET molecule. All SAMs are completely decomposed at the annealing temperature of 250°C. In conclusion, the 2-PET is the most favorable in terms of thermal stability.

Department : _____Chemical Engineering_____ Student's Signature_____

Field of Study : ___Chemical Engineering___ Advisor's Signature_____

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CHAPTER I

INTRODUCTION

1.1　Background

Copper is one of the most important metals generally used in industries such as microelectronics and chemical industries due to its excellent thermal and electrical conductivities, low cost and malleability. [1-4] However, one of the drawbacks of copper is that it is prone to oxidation and corrosion in air or in a humid ambient at low temperature resulting in degradation of its properties. [2, 3] Corrosion inhibition of copper can be achieved through the modification of its surface by forming self-assembled monolayers (SAMs) of organic inhibitors. The strong chemical interaction between sulphur atoms and the metallic surfaces leads to robust and easy preparation of chemisorbed organic films. The advantages of SAMs include simplicity of preparation, versatility, stability, reproducibility and the possibility of introducing different chemical functionalities with high level of order on a molecular dimension [2]. The SAMs of organic molecules are found to produce effective barriers to the penetration of corrosive chemicals to the copper surface and to limit the oxidation of copper metal [2]. The chemisorption of alkanethiols with long hydrocarbon chains provides densely packed SAMs on the surface. SAMs on copper surfaces have been found to be effective inhibitors for copper corrosion. Because of a high blocking effect of the films, the densely packed monolayers can be applicable for protective films on copper surface against corrosion.

The method to prepare organothiol SAMs on copper surface in this research involves two important steps. The first step involves the activation of copper surface through chemical reaction, UV radiation or plasma etching. Oxygen plasma etching is an interesting technique because it leaves no residues or hazardous wastes. The second step is to deposit monolayer film on copper surface by immersing the specimen in organothiol SAMs solution.

In addition, the organothiol self-assembled monolayers on copper surface are inhibition corrosive on copper surface in the microelectronics process but anyway it should be resistant at high temperature. Because of the microelectronics process is heat generate at copper. Therefore the thermal stability study of thiolate self-assembled monolayers coating on copper substrate is interesting. The thermal behavior of SAMs has been studied not only to understand the chemical interaction between the head group and the substrate, but also to consider the applications. To successfully incorporate these films into the production of low surface energy structures, it is necessary for the films to withstand the temperatures used in subsequent processing and packaging steps.

The aim of this research is to study thermal stability of thiolate self-assembled monolayers on copper surface. Moreover, the optimal condition of oxygen plasma dry cleaning system due to coated with thiolate self-assembled monolayers for protection copper surface from oxidation is determined. The thermal behavior of 1-octanethiol (OTT), 2-ethylhexanethiol (2-EHT) and 2-phenylethanethiol (2-PET) SAMs are studied.

1.2   Research objective

The objective of this research is to study the thermal stability of thiolate self-assembled monolayers coating on copper substrate.

1.3   Research scopes

1.3.1. Copper surface preparation, polishes with 240, 600, 1000, 1500 and 2000 grades, respectively of silicon carbide emery paper on rotating disk.

1.3.2. The electropolishing in a 59.5% phosphoric acid at 1.5 V DC for 15 minutes and copper is used as cathode and then rinses with 20% phosphoric acid solution.

1.3.3. The oxygen plasma dry cleaning system treatment (Model PC1100, Semiconductor and Materials Company, Kyoto, Japan) at 200 W under the

following conditions gas pressure 15 Pa, oxygen flow rate 40 sccm for various times 5, 10, 15 and 20 seconds, respective are used in this study.

1.3.4. The coating on copper surface with 0.01 M of 1-octanethiol, 2-ethylhexanethiol and 2-phenylethanethiol solutions in isopropanol for 2 hours at ambient atmospheric conditions.

1.3.5. The thermal stability study of thiolate (1-octanethiol, 2-ethylhexanethiol and 2-phenylethanethiol) self-assembled monolayers on copper surface at temperature range between 25°C and 250°C for 10 minutes. By the way annealing the passivating film at temperature range between 25°C and 250°C for 10 minutes after coating with thiolate (1-octanethiol, 2-ethylhexanethiol and 2-phenylethanethiol) self-assembled monolayers on copper surface.

1.3.6. To investigate hydrophobic or hydrophilic features of the sample substrates with contact angle meter (Model no. 2500702, Tantec Inc., Schaumburg, Germany). The contact angle of 5 µL deionized (DI) water that dropped on the sample substrates are measured under the ambient atmospheric conditions.

1.3.7. The passivating film are characterized by the scanning electron microscope analysis (SEM) JSM-5800 LV and atomic force microscope analysis (AFM) Nano scope IV with tapping mode Si-Probe.

1.3.8. The decompose temperature range of thiolate SAMs are measured by Fourier transform infrared spectrometry (FT-IR) and x-ray photoelectron spectroscopy (XPS).

1.3.9. The inhibition corrosion efficiency is measured by the potentiodynamic polarization studies. These are carried out in a three-electrode cell assembly at room temperature (25°C). The bare copper substrate or copper substrate with SAM is used as the working electrode. Platinum is used as the counter electrode and the reference is a silver-silver chloride (Ag/AgCl) electrode. The studies are made in the potential range of -1.0 to +1.4 V versus Ag/AgCl in 0.5 M NaCl solutions.

1.4   Expected benefit

1.4.1.   Insight on thermal stability and thermal decomposition mechanisms of thiolate self-assembled monolayers on copper surface are obtained.

1.4.2.   A coating with self-assembled monolayers can be applied in microelectronics devices for corrosion inhibition.

CHAPTER II

THEORY

2.1   Metal corrosion [5, 6]

Corrosion is the chemical reaction occurring between the oxygen molecules and the substances, called the oxidation reaction. Four components, occurring during the electrochemical corrosions, are (1) anode, (2) cathode, (3) electron path and (4) electrolyte. Anode and cathode are electrochemical cells in the chemical activity of the metal. Anode is the produced electrons whereas cathode is the consumed electrons. Theoretically, due to the difference of voltage between anodic and cathodic reactions, the electrons are flowing from the anodic sites to cathodic sites through the electron path. Electrolytes are the solutions that can conduct the electrical currents through the movement of ions.

In case of metal corrosion, metal was lost the electron (e^-) from the metallic atom; afterwards the metal atom was changed to be a positive ion or anode. The corrosion occurred during the exchange of electrons which can be called as "electrochemical corrosion", commonly used in the terms as "rusting" or cathode. Moisture or solution on surface is the electrolyte. Typically, types of damage are oxide(s) and/or salt(s) of the original substance. Not only metals can occur the corrosion but also the other materials, such as ceramics or polymers.

Even though the copper is the metallic surface within this study, the result of an increase in positive charge on the atom is undergoing oxidation reaction. Copper can be lost more than one electron which is the most common anodic reaction as below:

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

Where:

Cu   = metallic copper

Cu^{2+} = copper ion that carries a double negative charge

$2e^-$ = electron that remains in the metallic copper

2.2   Electropolishing [7]

Electrochemical is one alternative method for polishing the metallic surface aside from mechanical method. The electrochemical method is suitable to prepare the material surface which specially needs high quality, smooth, clean, high resistance for corrosion, and extra shine. This method is good application for the single-phase alloy such as stainless steel, aluminum, copper, magnesium, zirconium and titanium; on the other hand, the multi-phase alloy cannot apply this method because of the different electrolytic potentials between their individual phases.

Power supply, electropolishing bath, electrolytic cell (anode and cathode) and electrolyte are essential materials as shown in Fig. 2.1. The position of the anode is the particular specimen whereas the cathode is the consumed electrons. Cathode is commonly not able to react to the electrolyte, for instance, platinum, lead, copper. A proper cathode depends on the budgets and the usage purposes.
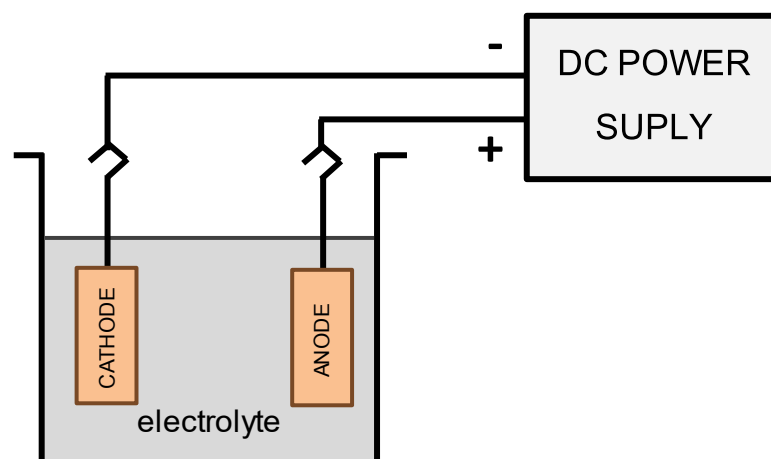

Figure 2.1 An electrolytic cell showing the materials and equipments for electropolishing method [8]

The electrolytes are usually a viscous acid such as a phosphoric acid (H_3PO_4), hyperchloric acid ($HClO_4$), sulphuric acid (H_2SO_4). Glycerol, butyl and urea can be

added to increase the viscosity; however, these substances are not used within this research. The electrolytic polishing is help to create the smooth surface because the anodic dissolution of the sample surface in the electrolytic cell.

The current density (A/cm^2) and voltage (V), the distance of the sample from the electrode, size ratio of cathode to anode, surface condition of the anode, polishing time, temperature of the electrolyte, agitation of the electrolyte, and concentration of the electrolyte are the controlling factors for a good quality of polishing process.

The advantages for electrolytic polishing can be listed as below

- No deformation and smeared surface layers

- Short time and good reproducibility; applies only when using a suitable recipe

- No or only little heat generation of the sample

- Possibility for subsequent etching with the same equipment

- Easy removal of deformation or smeared surface layer from mechanical grinding or polishing with a short electrolytic polish

2.3   Plasma

Plasma can be subdivided into two conditions; directional direct plasma and reactive ion etching plasma (RIE). The directional direct plasma condition is prepared by using only free radial reactivated on the sample surface. It consists of two electrical cells; powered and grounded electrodes. In common practice, the copper sample is placed at the grounded electrode, subsequently; the ion is migrating to the powered electrode after obtained the power supply. On the other hand, free radical is moving to the grounded electrode and reactivated the sample surface as illustrated in Fig. 2.2.

The reactive ion etching (RIE) plasma is using both free radical and ion bombardment to reactivate at the sample surface. The copper sample is attached to the

powered electrode. After supplied the current, the ion and free radical are moving to the powered electrode as shown in Fig. 2.3.
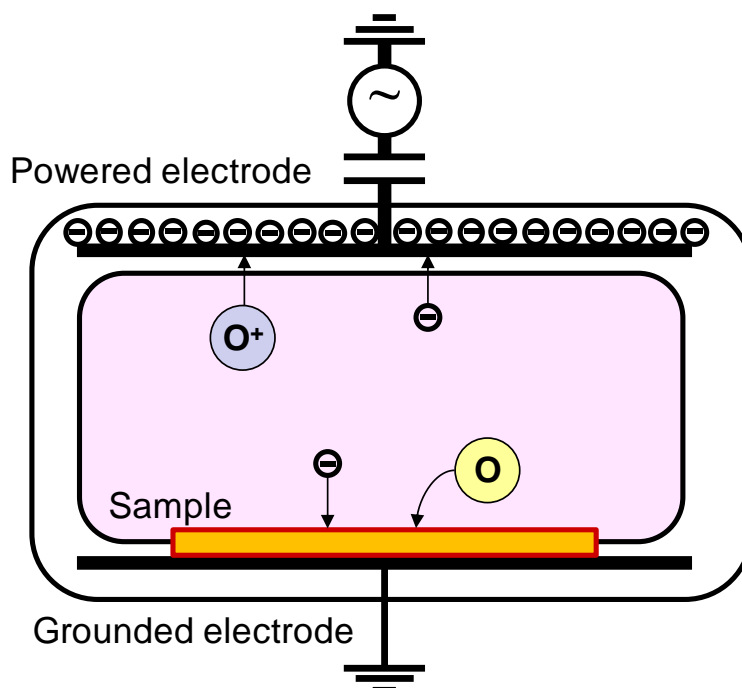
Figure 2.2 The directional direct plasma
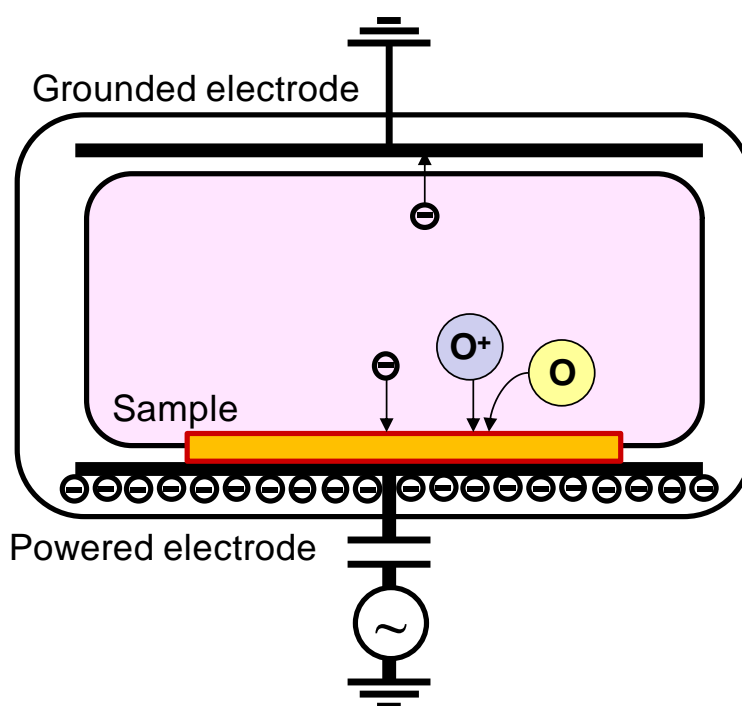
Figure 2.3 The reactive ion etching

2.4   Self-assembled monolayers coating on metallic surface [9]

The self assembled monolayers (SAMs) are the coating method on the metallic surface by organic inhibitor as a thin film layer. SAMs can be generally divided into two groups; head and tail as shown in Fig. 2.4.

Head group is a functional group which can be well formed to the surface of substrate and depends on the type of metal. Several functional groups, such as azoles group, amines group, amino acid group and thiol group, can be coated on the metallic surface in order to protect the metal corrosion. Tail group is the organic compound at the terminal end of head group.
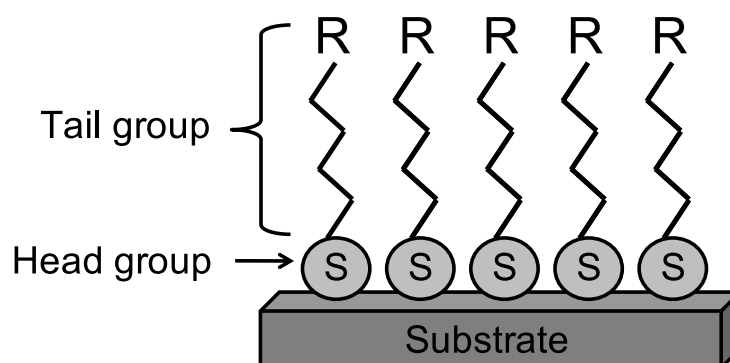
Figure 2.4 Self-assembled monolayers (SAMs) coating on metallic surface

In preparation of SAMs, SAMs can be prepared by various techniques, for instance, physical vapor deposition techniques, electrodeposition or electroless deposition in order to coat on the metal substrates. Alkanethiol SAMs were employed in this study and produced by an adsorption from the solution by immersing a substrate into a dilute solution of alkanethiol in ethanol, though many different solvents. In general, SAMs often form over 12 to 72 hours at room temperature; however, Alkanethiol SAMs can be formed within minutes. Nevertheless, SAMs can also be absorbed from the vapor phase.

2.5 Principle of analytical techniques

This topic mainly concerns about the principle techniques which were used to analyze copper surface as the following details.

2.5.1 Contact angle measurement [10]

Wettability is a measure of the tendency of a fluid to spread over a solid surface, and based on two major forces; cohesive and adhesive. The cohesive force is an intermolecular in the similar substance which causes a tendency in liquids to resist separation. On the other hand, the adhesive force is the attractive forces between two substances including mechanical and electrostatic forces.

When water is placed on a surface, it is in the equilibrium condition between cohesive and cohesive forces. If the adhesive forces (water and a surface) are stronger, they will pull water down causing the wetting surface. Alternatively, if the cohesive forces (water and water itself) are stronger, water will retain a spherical shape on the surface. However, if the adhesive forces are extremely larger than cohesive forces, water will not stick on the surface but will combine as droplet and roll on the top of surface.

Wettability can be quantified in terms of contact angle which is the angle between liquid and a material surface. The contact angle is used to classify the wettability as below Fig. 2.5 and Table 2.1.
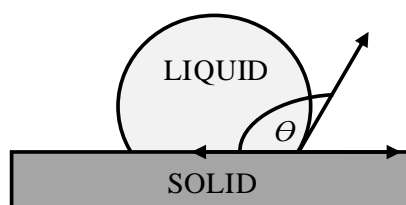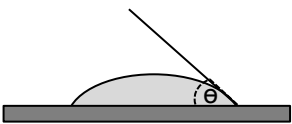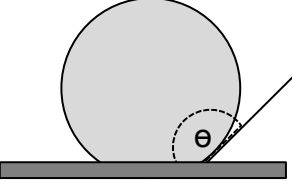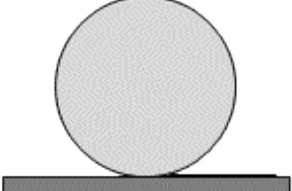
Figure 2.5 Contact angle at a solid surface liquid and gas interface

Table 2.1 Type of wettability based on contact angles for common water and a solid interfaces

Types	Contact angle (θ, deg)	Descriptions	Diagrams
Superhydrophilic	0	Completely water wet; adhesive force >> cohesive force, water spreads along a solid surface as thin film layer	
Hydrophilic	0 – 90	Water wet; water spreads on a solid surface as small drop	
Hydrophobic	90 – 150	Water droplet with small area touching to a solid surface	
Superhydrophobic	>150	Not wet; adhesive force << cohesive force, water can freely move on a solid surface	

2.5.2 Scanning electron microscopy [11]

Scanning Electron Microscope (SEM) instrument generated the electrons which are accelerated by an electric field and bypassed through the condenser lens to facilitate to be a beam. The size of beam can be adjustable which is depended on the sharpness and contrast. In case of more detailed study, the beam of electron needs to be finer size.

The SEMs is used to sweep a finely collimated beam of electrons across the surface of a specimen. Once the beam interacted with the material surface and emitted the electrons and photons which were detected and yielded the information of the surface topography with 10x nanometer magnification. SEM provides the 3D image information; therefore, it is used for detailed study on the morphology of material surface or biological samples such as tissues and cells.

2.5.3 Atomic force microscope [12]

Atomic force microscope (AFM) is used for checking surface morphology covering by thin film layer at the nanoscales. The AFM consists of a tiny probe (tip) attached to the cantilever which is able to bend to touch and scan the material surface as shown in Fig. 2.6. The principle of AFM is based on the interaction of atomic force between probe and surface material and consequently processes to be a surface morphological image.

Principally, possible imaging can be separated into static (contact) and dynamic (non-contact or tapping) modes. In contact mode, the probe is always dragged across the sample surface result in the resistive force paralleling to the movement along the surface. Consequently, the cantilever could be bended or twisted causing the erroneous measurement.

For the non-contact mode, the probe shortly contacts in perpendicular to the sample surface which is similar to finger tapping. Hence, there is no resistive force in vertical; therefore, the tapping mode is selected for this study. However, the oscillation of cantilever could provide the instable and imprecise measurement.

Additionally, the AFM is able to measure the insulator surface such as polymers, ceramics, and glass as well as biological molecules.
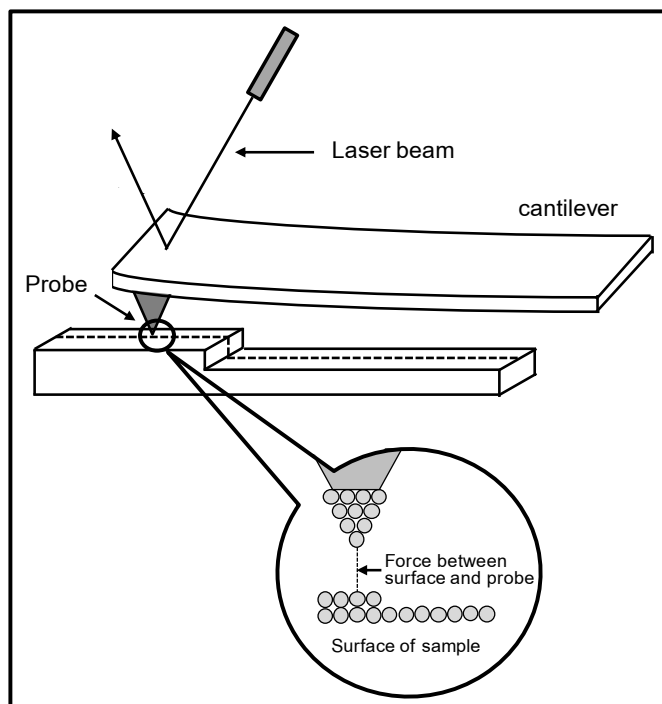
Figure 2.6 The atomic force microscope (AFM) using for nanoscale measurement [12]

2.5.4   Fourier transform infrared spectrometry [13]

Fourier Transform Infrared Spectrometry (FT-IR) is the tool for organic and inorganic analysis by infrared light stimulation at different wavelength. Each molecular structure has its own absorption in which different infrared wavelength. Based on this individual character, the functional groups, such as hydroxyl group (-OH), methyl group (-CH$_3$) or carbonyl group (-CO), can be differentiated. Nevertheless, this technique should incorporate with the spectrum compared with the reference spectrum same as fingerprint authentication.

This technique is also used to apply for the material and petrochemical industries such as the polymer type identification due to the cost effectiveness.

2.5.5   X-ray photoelectron spectroscopy [14]

X-ray photoelectron spectroscopy (XPS) is the measurement technique to quantify the composition, empirical formula, chemical state and electronic state of elements existing within a material. The analytical sample is bombarded by a beam of x-ray, while intensity and binding energy are being measured continuously at the nanoscale.

The XPS also provides chemical properties at the material surface such as type and number of elements, chemical structure, type of chemical bonding, and oxidation state, including the alteration of chemical surface after heating, chemical process, ionization, plasma process, and ultraviolet irradiation.

X-ray photoelectron spectroscopy is used to analyze many different types of materials both organic and inorganic such as metallic compounds, semiconductors, polymers, glass, ceramics, paintings, coatings, paper, ink, stick, cosmetics, teeth, bones.

2.5.6   Potentiodynamic polarization measurement [15, 16]

Potentiostat is an electric device used for generating the cyclic potentiodynamic polarization scan. The potentiostat comprises three electrical cells; working electrode (WE), counter electrode (CE) and reference electrode (RE) as shown in Fig. 2.7. The working electrode (corroding) is the sample material; the counter electrode is an inert material using platinum in this instrument, and the stable reference electrode using silver-silver chloride (Ag/AgCl).

The potentiostat requires a constant voltage from an external source between working and reference electrodes by continuously increasing voltage to electrode until reached the condition of anodic polarization. An increasing voltage can accelerate the oxidation reaction of electrode which conducts the corrosion.
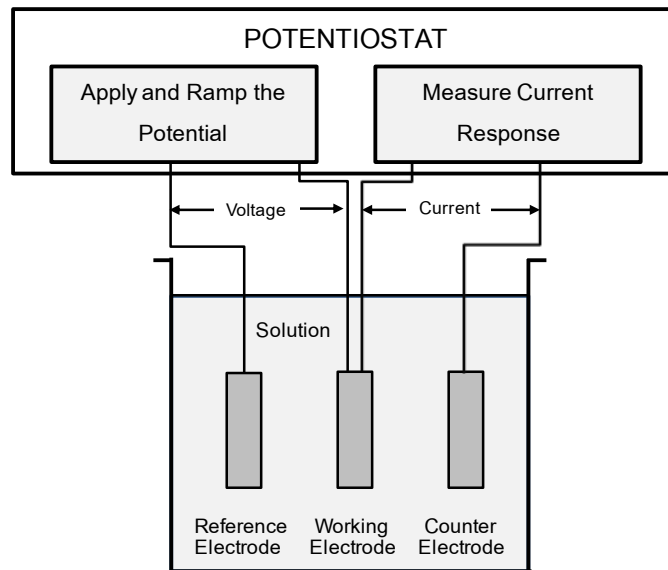
Figure 2.7 The potentiostat showing three electrodes [17]

The electrical current flowing from the working and counter electrodes is measured during the increasing voltage. A plotted graph illustrates a changing of electrical current compared with the potential as shown in Fig. 2.8. From the graph, the corrosion current density is the intersection point between anodic and cathodic polarizations.
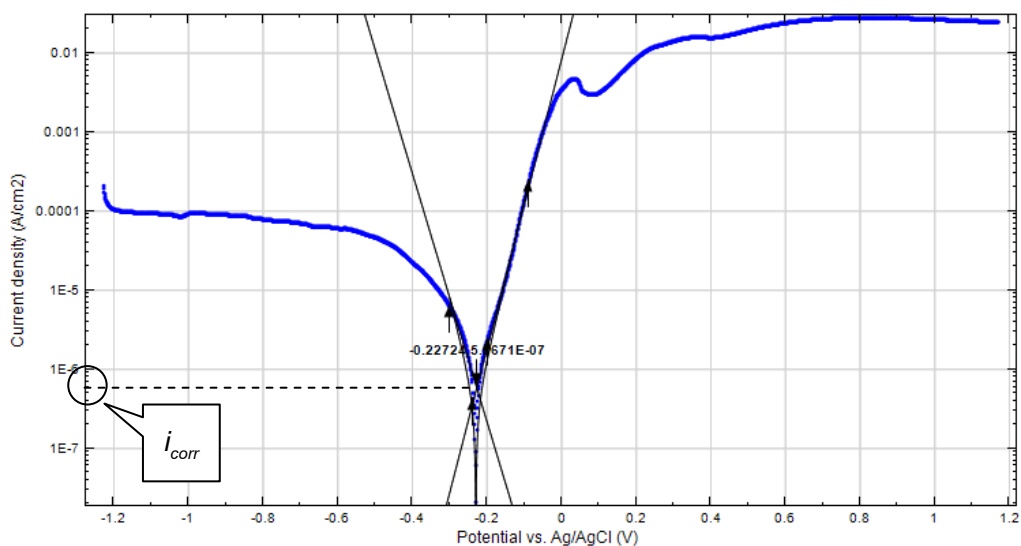
Figure 2.8 A plotted graph between current density and potential from potentiostat equipment showing the corrosion current densities at the intersection point

The corrosion inhibition efficiencies are calculated as the below equation.

$$IE(\%) = \frac{(i_{corr} - i'_{corr}) \times 100}{i_{corr}} \qquad (2.1)$$

Where:

IE = corrosion inhibitor efficiencies

i_{corr} = the corrosion current densities of the bare copper substrate

i'_{corr} = the corrosion current densities of the SAMs coated copper substrate

CHAPTER III
LITERATURE REVIEWS

Sinapi, F., et al. studied formation of n-organothiols such as n-dodecanethiol (DT), (3-mercaptopropyl)trimethoxysilane (MPTS) and 11-perfluorobutylundecanethiol (F_4H_{11}) self-assembled monolayers (SAMs) onto polycrystalline copper surfaces for protecting copper from oxidation. Starting from preparation surface substrate to Cu_{EtOH} by polished polycrystalline copper foils with silicon carbide papers followed by diamond pastes and colloidal silica then treated with UV-ozone for 15 minutes, immersed in an ethanolic sonication bath for 15 min, rinsed with absolute ethanol and blown dried in an argon stream. Finally, Cu_{EtOH} coupons were immersed in 10^{-2} M organothiols (DT, MPTS or F_4H_{11}) in ethanolic solutions for 2 h to allow for surfaces modification, rinsed with absolute ethanol for 3 minutes and dried under an argon flow. They are referred to as CuDT, CuMPTS and CuF_4H_{11}, respectively that investigated by contact angles measurements and X-ray photoelectron spectroscopy (XPS). The polarization and cyclic voltammetry curves were used to compare the inhibition efficiency of the three organic coatings. And atomic absorption spectrometry measurements (AAS) were carried out in domestic water and in 0.5 M NaCl solutions in order to evaluate and quantify the dissolution of copper electrodes before and after protection. Results showed evidences that, among the three organic compounds assessed, F_4H_{11} is the most suitable candidate to slow down the copper oxidation process [1].

Quan, Z., et al. studied the corrosion protection of self-assembled films derived from Schiff bases, including N-2-hydroxyphenyl-(3-methoxy-salicylidenimine) (V-bso), N-2-hydroxyphenyl-(salicylidenimine) (S-bso) and N,N'-o-phenylen-bis(salicylidenimine) (S-o-ph-S) on copper surfaces. And they studied the corrosion protection of these films were modified by 1-dodecanethiol (DT). Start from copper electrode were washed with double-distilled water, etched in a 7 M HNO_3 solution for 30 seconds, rinsed with double-distilled water rapidly followed by ethanol and then immersed in a 1 mM different adsorbate solutions (V-bso, S-bso or S-o-ph-S) in ethanol immediately for 30 min to form self-assembled films, rinsed with ethanol and double-distilled water. For these films were

modified by 1-dodecanethiol (DT) study, they modified copper electrodes by immersion of Schiff base covered electrodes in 1 mM 1-dodecanethiol solution for 30 minutes. After that they investigated by electrochemical techniques in an aqueous electrolyte (0.5 M NaCl). These studies suggest that the pure films of Schiff bases possess some unfilled defect sites. However, when the films were modified by 1-dodecanethiol, the quality and corrosion resistance of mixed films was improved markedly [18].

Y.S. Tan, et al. studied the corrosion inhibition efficiency of a series of substituted benzenethiol (BT) molecules, $X–C_6H_4–SH$ (where X = meta-NH_2, ortho-NH_2, para-NH_2, para-$NHCOCH_3$, para-F, para-CH_3 and para-$CH(CH_3)_2$) self-assembled monolayers (SAMs) have been prepared by adsorption from a solution onto a fresh copper surface. Strat from preparation copper substrate by etching with 7 M nitric acid (HNO_3) for 30 minutes and then rapidly rinsed with deionized water followed by pure ethanol. After that coated surface to the self-assembled films by immersed immediately in 5 mM different inhibitor solutions in absolute ethanol for an hour at room temperature, rinsed with ethanol and then dried with nitrogen. The nature of the surface films was examined using contact angle measurements, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) measurements and Ellipsometric measurements. The electrochemical measurements were performed in 0.5 M sulfuric acid solution and carried out at room temperature in air. The results of the corrosion inhibition efficiency indicated the substituted functional groups on BT are strongly influenced by the type and the position of the substituent on the benzene ring. The benzenethiol molecules without any substituent group on the ring are ineffective corrosion inhibitors. Moreover the chemical configuration is the key factor in determining the efficacy of the SAMs as barriers to electrochemically corrosive ions [19].

L. Carbonell, et al. studied the thermal stability of 1-decanethiol (C10) and benzenethiol (BT) Self-Assembled Monolayers (SAMs) on metallic and oxidized copper surfaces. Unpatterned electrodeposited (ECD) copper and oxidized copper layers were used in this study. The first step to preparation copper surface by immersion in 3.7% hydrochloric acid for 5 minutes followed by rinsed with deionized water. The oxidized

copper surfaces were prepared by immersion in hydrogen peroxide at 100 °C for 15 minutes. The clean copper and oxidized copper substrates were rinsed with deionized water followed by isopropyl alcohol immediately. The next step was coating with self-assembled monolayers by immersion in 10^{-3} M 1-decanethiol (C10) or 10^{-3} M benzenethiol (BT) solutions in isopropyl alcohol (IPA) for over 12 h at ambient temperature, rinsed with isopropyl alcohol and dried under nitrogen. The contact angle measurements and high resolution X-ray photoelectron spectroscopy (XPS) measurements were used to assess SAM quality and chemical analyses of the surfaces, respectively. The result showed high quality 1-decanethiol and benzenethiol self-assembled monolayers exhibit low thermal stabilities on clean copper surfaces with a maximum in decomposition occurring between 100 and 150 °C that investigated by thermal desorption spectrometry (TDS) measurements. The decomposition of SAMs follows different mechanisms. For the alkanethiol, a direct interaction between the alkyl group of the thiolate and the metallic copper surface is the dominant pathway for the C−S bond scission. The head group desorbs as oxidized sulfur and this is followed by desorption of the alkyl fragments of the chain adsorbed on the clean copper surface. In the case of benzenethiol, a simultaneous desorption of the head group as oxidized sulfur and the benzene group occurs. SAM formation on the oxidized copper surface results in complete removal and/or reduction of the CuO layer. Higher SAM surface coverage on the resulting Cu/Cu_2O surface is result from the enhanced surface roughness of the substrate. The decomposition mechanisms and thermal stabilities of the 1-decanethiol and benzenethiol self-assembled monolayers are dependent on the oxidation state of the underlying substrate and the chemical nature of the chain [20].

Myung M. Sung, et al. studied alkanethiols $(CH_3(CH_2)_{n-1}SH)$ based; hexadecanethiol (HDT), octanethiol (OTT), butanethiol (BTT) self-assembled monolayers (SAMs) on the clean copper surfaces. Starting from polished polycrystalline copper substrates with alumina powder (0.3 μm), rinsed with deionized water, and degreased ultrasonically in acetone. A chemical oxide was grown by placing the sample in a hydrogen peroxide solution at 100°C for 15 minutes. The oxide layer on the copper

surface was removed by etching with a 7 M HNO_3 solution for 1 minute. The sample was rinsed with deionized water, ethanol and then dried with nitrogen. The HNO_3 treatment has been shown to produce a metallic copper surface nearly free of carbon and oxygen. The clean copper sheets were transferred under a positive flow of nitrogen to a 2.5 mM solution of the alkanethiols (hexadecanethiol (HDT), octanethiol (OTT), butanethiol (BTT)) dissolved in deoxygenated ethanol for 3 hr. Monolayer deposition was carried out at room temperature. The samples were then ultrasonically washed in ethanol to remove excess reactants and dried with nitrogen. The quality of the monolayer was checked by water contact angle, which was 120° for HDT-coated Cu, 115° for OTT-coated Cu, and 105° for BTT-coated Cu. Immediately after the samples prepared, the SAMs-coated samples were placed into a temperature and humidity chamber. We can simultaneously control relative humidity and temperature. The samples were annealed at temperatures between 25 and 220 °C for 10 min. Relative humidity was kept fixed at 50%. X-ray photoelectron spectroscopy (XPS) was used to investigate monolayers desorption, that founds the monolayers are stable in air up to about 140 °C. Above 160 °C the monolayers begin to desorb through the oxidation reaction of the thiolate to sulfonate, with the alkyl chains remaining intact. Following this desorption step, the copper surface has begun to oxidize to CuO at about 180 °C [21].

Two years later, Myung M. Sung, et al. studied octanethiol ($CH_3(CH_2)_7SH$) based self-assembled monolayer on Cu(111) in ultra-high vacuum. Starting from polished Cu monocrystal with diamond paste and following alumina paste down to a 0.05 μm size then cleaned by repeated cycles of argon-ion sputtering. Octanethiol was introduced into the chamber through a variable leak valve and discharged from a nozzle located 3 cm above the substrate at room temperature. The quality of the octanethiolate monolayer on copper surface was checked by water contact angle, which was 115°. The x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), intergrated desorption mass spectrometry (IDMS) were used to investigated the octanethiolate monolayer decomposition. The monolayers are stable up to temperatures of about 480 K. Above 495 K the monolayers decompose via the γ-hydrogen elimination

mechanism to yield 1-octene in the gas phase. The thiolate head groups on the copper surface change to Cu_2S following the decomposition of hydrocarbon fragments in the monolayers at about 605 K [25].

Wuttichai Suthipongkiat studied optimum method for treatment copper surface before coating with 0.01 M octadecanthiol (ODT) solution in isopropanal for corrosion protection in heat exchanger such as polished surface with emery paper only, used oxygen plasma, immersed in piranha solution (sulfuric acid + hydrogen peroxide), immersed in nitric acid, immersed in hydrogen peroxide, immersed in hydrogen peroxide and following by nitric acid, immersed in hydrochloric acid, and immersed in phosphoric acid. The octadecanthiol film on copper surface was characterized by contact angle measurements, scanning electron microscope (SEM) and atomic force microscopic (AFM). Corrosion protection ability of octadecanthiol film was evaluated in 0.5 M sodium chloride (NaCl) aqueous solution using potentiodynamic polarization. The results showed the optimum condition of copper surface treatment which coated with octadecanthiol self-assembled monolayer for corrosion protection was oxygen plasma treatment at -400 mmHg from ambient pressure for 20 minutes [22].
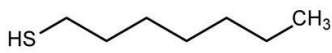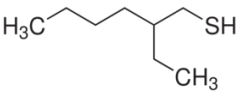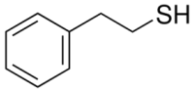
CHAPTER IV
EXPERIMENTAL

4.1 Materials and Chemicals

1. A commercial pure copper sheet (purity ≈ 99.9%) thickness 1 millimeter was used as a substrate.

2. Silicon carbide emery paper number 240, 600, 1000, 1500 and 2000 grades (3M Brand, China)

3. Aqueous solution of 99.5% isopropanol (IPA) (QRёCTM Brand, New Zealand)

4. Aqueous solution of 99.5% acetone (QRёCTM Brand, New Zealand)

5. 85% phosphoric acid (H_3PO_4) (QRёCTM Brand, New Zealand)

6. 1-octanethiol (OTT) with 99.4% chemical purity (Tokyo Chemical Industry Co., Ltd., Japan)

7. 2-ethylhexanethiol (2-EHT) with 97% chemical purity (Sigma-Aldrich Pte., Ltd., Singapore)

8. 2-phenylethanethiol (2-PET) with 99.5% chemical purity (Tokyo Chemical Industry Co., Ltd., Japan)

9. Sodium chloride (NaCl) (Loba Chemie Pvt. Ltd., India)

All chemicals used in this work were analytical grade.

Table 4.1 Structure of thiolate self-assembled monolayer in this experimental

Thiolate Self-Assembled Monolayer	Molecule Structure
1-octanethiol (OTT)	
2-ethylhexanethiol (2-EHT)	
2-phenylethanethiol (2PET)	

4.2   Preparation copper substrates

The copper substrates were polished with 240, 600, 1000, 1500 and 2000 grades, respectively of silicon carbide emery paper on rotating disk, rinsed with distilled water followed by acetone and then dried with nitrogen [3]. After that polishing in a 59.5% H_3PO_4 that called "elctropholishing" at 1.5 V DC for 15 minutes and copper was used as cathode, rinsed with 20% H_3PO_4 followed by distilled water and then dried with nitrogen [4, 8].

4.3   The optimum time for oxygen plasma treatment

To study the effect of oxygen plasma treatment time, the copper surface was activated by using the oxygen plasma dry cleaning system (Model PC1100, Semiconductor and Materials Company, Kyoto, Japan) at 200 W under the following conditions gas pressure 15 Pa oxygen flow rate 40 sccm. This study used the effect of treatment time at 5, 10, 15 and 20 seconds. The formation of OTT self-assembled monolayers was done by immersing the substrates in 0.01 M OTT solution in IPA for 2 hours [1] and rinsing with IPA. And then the substrates were dried with nitrogen.

4.4   Thermal stability of thiolate self-assembled monolayers on copper surface

The optimum condition of oxygen plasma treatment determined previously was used to activate the copper surface. The self-assembled monolayers were created by immersing the substrates treated in 0.01 M OTT or 2-EHT or 2-PET solution in IPA for 2 hours [1], rinsing with IPA and then drying with nitrogen. After that the substrates were annealed at temperature ranging between 25°C and 250°C for 10 minutes in order to study the thermal stability [21].

4.5 Analytical techniques

Techniques	Analytical and Measurement
The contact angle meter (Model no. 2500702, Tantec Inc., and Schaumburg, Germany)	• To analyze hydrophobic or hydrophilic features • The contact angle of 5 µL deionized (DI) water that dropped on the sample substrates were measured under the ambient atmospheric conditions
The scanning electron microscope analysis (SEM) (Model JSM-5800 LV)	• To analyze morphology of the surface
The atomic force microscope analysis (AFM) (Nano scope IV with tapping mode Si-Probe)	• To analyze roughness of the surface
The Fourier transforms infrared spectrometry (FT-IR) (Model Nicolet 6700, Serial no. AHR0700954, Becthai Company)	• To analyze the decomposition mechanism of self-assembled monolayers
The X-ray photoelectron spectroscopy (XPS) (Model MERLIN M25, AMICUS)	• To analyze the decomposition mechanism of self-assembled monolayers
The potentiostats/ Galvanostats (Model no. PGSTAT 302 N, Metrohm Autolab company)	• To analyze the corrosion inhibition efficient • This carried out in a three-electrode cell assembly at room temperature (25°C). • Working electrode: bare copper or copper with SAM • Counter electrode: platinum • Reference electrode: silver-silver chloride (Ag/AgCl) • The potential range: -1.0 to +1.4 V versus Ag/AgCl in 0.5 M NaCl solutions [13]

CHAPTER V

RESULTS AND DISCUSSIONS

5.1   The optimum time for oxygen plasma treatment

The optimum condition of oxygen plasma treatment before coating copper surface with 1-octanethiol (OTT) self-assembled monolayers (SAMs) is characterized by (1) hydrophobic or hydrophilic features of the sample substrates, (2) morphology, (3) roughness and (4) corrosion inhibition efficiencies.

Figure 5.1 shows the effects of oxygen plasma treatment time on water contact angle of the copper surface and the copper surface with OTT SAMs. Before deposition of SAMs, the water contact angle tends to decrease with increased treatment time, and reaches the minimum of 20.61° at 15 seconds. In comparison, after deposition of OTT SAMs, the reverse trend was observed.

The structure of OTT can be separated into two groups; head and tail. The head group has hydrophilic feature with low water contact angle while the tail group has hydrophobic feature with larger water contact angle. SAMs are created by the attachment of head group onto a substrate and then followed by a slow organization of tail group. Thus, the attachment of head group onto a substrate can be promoted by using a more hydrophilic substrate. Based on the Fig 5.1, the maximum contact angle of the copper surface with OTT SAMs is 117.17°. Hence, the optimum time for oxygen plasma treatment is 15 seconds.

Scanning electron microscope (SEM) was utilized to measure the morphology of the copper surface before and after deposition of SAMs at each treatment times of oxygen plasma as shown in Figs. 5.2 – 5.3. But these SEM images are not clearly defined the morphology of each surface. Thus, the atomic force microscope (AFM) was utilized to measure the morphology and roughness of the copper surface before and after deposition of SAMs at each treatment times of oxygen plasma as shown in Figs. 5.4 – 5.5 and the roughness values were illustrated in Table 5.1 and Fig. 5.6.

The roughness of the substrate tends to increase with increased treatment times, and reaches the maximum at 15 seconds. The SAMs coating on copper surface does not change the trend of roughness variation. Moreover, the hydrophilic surface with higher roughness has lower water contact angle than the hydrophilic surface with lower roughness. In opposition, the hydrophobic surface with higher roughness has larger water contact angle than the hydrophobic surface with lower roughness. The results agree with the lotus leaf effect [23]. These observations suggest that rough surface at 15 seconds treatment time renders the lowest contact angle value on a hydrophilic surface and highest contact angle value on a hydrophobic surface as show in Fig. 5.1.
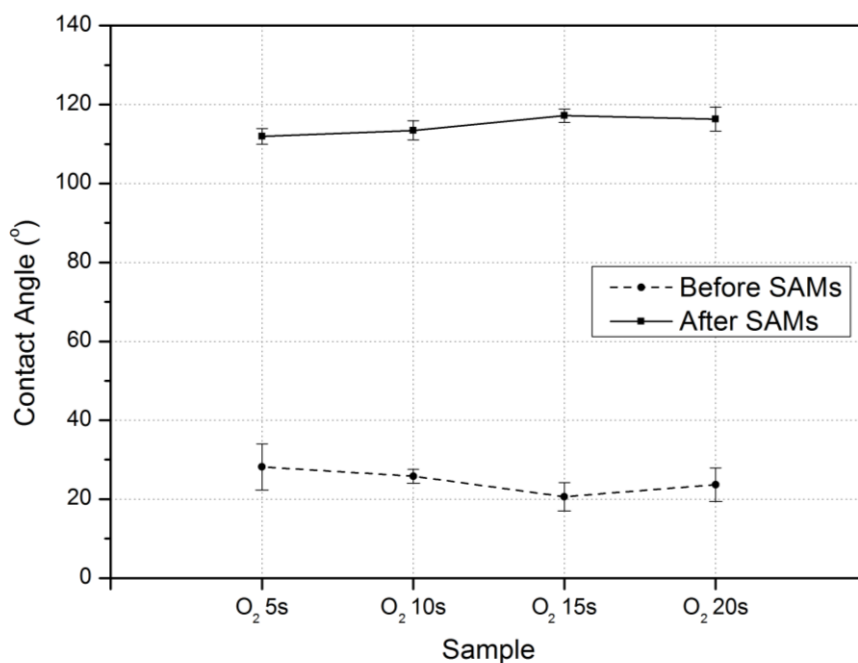

Figure 5.1 The effect of oxygen plasma treatment times on water contact angle of the copper surface

Figure 5.2 SEM images as a function of times of oxygen plasma treatment before coating with OTT SAMs on copper surface (a) 5 s, (b) 10 s, (c) 15 s and (d) 20 s

Figure 5.3 SEM images as a function of times of oxygen plasma treatment after coating with OTT SAMs on copper surface (a) 5 s, (b) 10 s, (c) 15 s and (d) 20 s
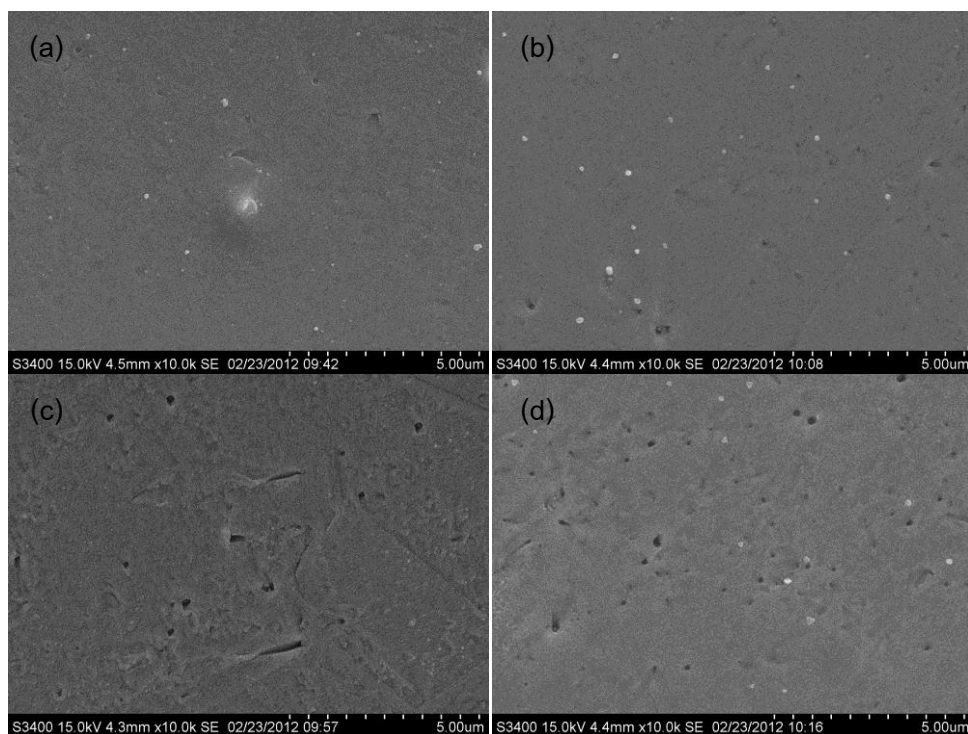
Figure 5.4 AFM images as a function of times of oxygen plasma treatment before coating with OTT SAMs on copper surface (a) 5 s, (b) 10 s, (c) 15 s and (d) 20 s
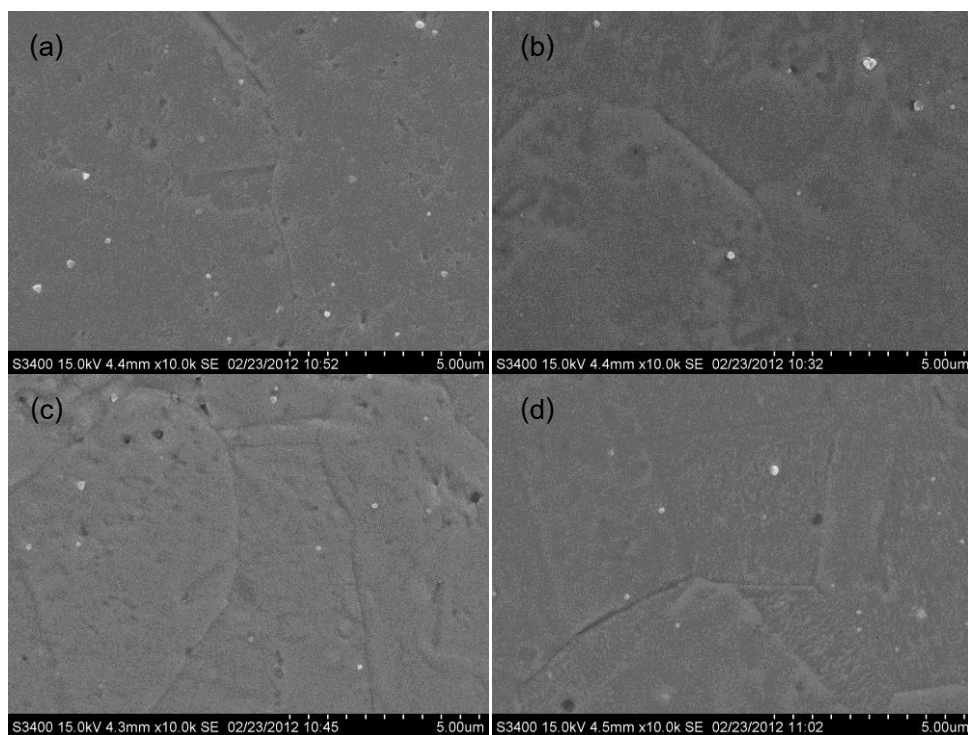

Figure 5.5 AFM images as a function of times of oxygen plasma treatment after coating with OTT SAMs on copper surface (a) 5 s, (b) 10 s, (c) 15 s and (d) 20 s
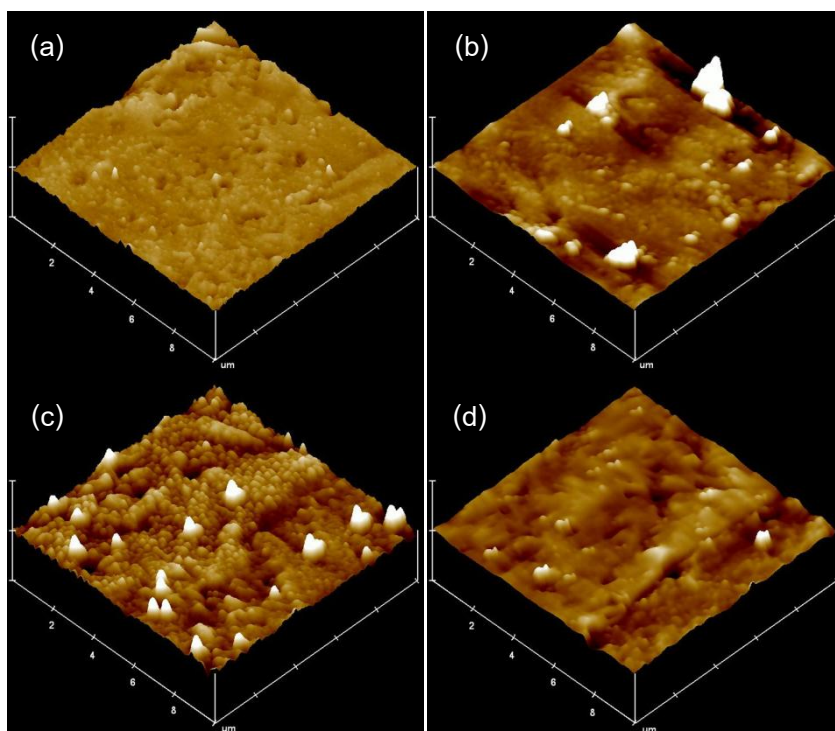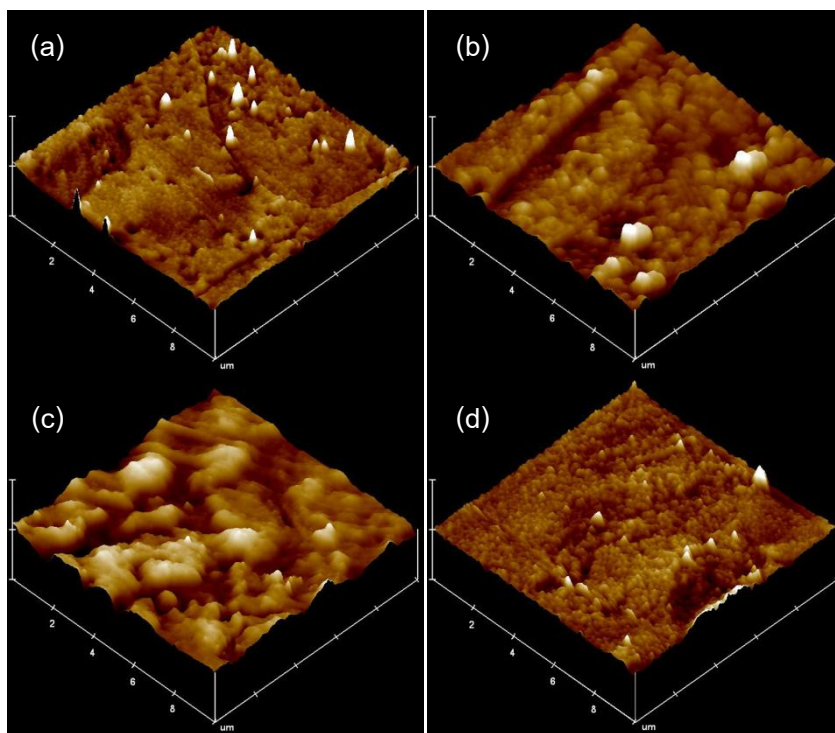
Table 5.1 Roughness values of the copper surface as a function of times of oxygen plasma treatment before and after coating with OTT SAMs on copper surface from AFM.

Sample	Roughness; Rms (nm)
O_2 plasma 5 s	7.337
O_2 plasma 10 s	12.405
O_2 plasma 15 s	15.639
O_2 plasma 20 s	8.844
O_2 plasma 5 s with OTT SAM	9.647
O_2 plasma 10 s with OTT SAM	13.296
O_2 plasma 15 s with OTT SAM	18.444
O_2 plasma 20 s with OTT SAM	9.149

The corrosion inhibition efficiencies, IE(%), of monolayers on copper surface obtained from potentiodynamic polarization studies as shown in Table 5.2 are calculated according to the following formula [2]:

$$\text{IE(\%)} = \frac{(i_{corr} - i'_{corr}) \times 100}{i_{corr}} \tag{5.1}$$

where i_{corr} and i'_{corr} are the corrosion current densities of the bare copper and the copper with SAM substrate, respectively.

The substrate with 15 seconds of oxygen plasma treatment yields OTT SAMs with highest corrosion protection at 88.81%. The IE(%) are in good agreement with the results on contact angle and roughness as shown in Fig. 5.6.

Table 5.2 The effects of oxygen plasma treatment times on corrosion inhibition efficiencies of the copper surface from potentiodynamic polarization studies

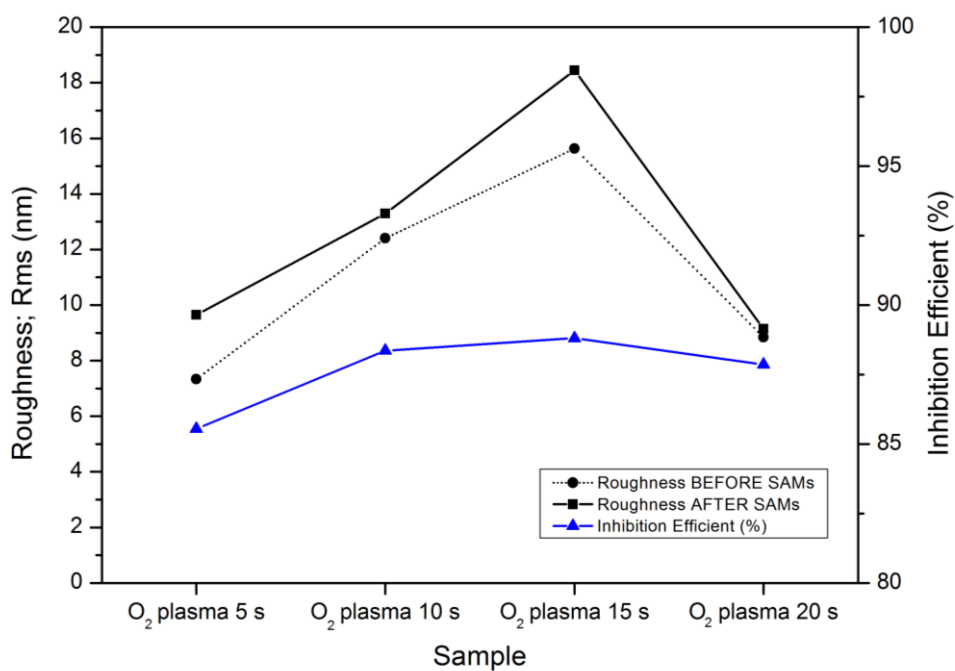| Sample	E_{corr} (V) vs. Ag/AgCl	i_{corr} (A/cm^2)	Inhibition Efficient (%)
Bare Cu	-0.234	3.25×10^{-6}	-
O$_2$ plasma 5 s	-0.242	4.70×10^{-7}	85.55
O$_2$ plasma 10 s	-0.210	3.79×10^{-7}	88.36
O$_2$ plasma 15 s	-0.239	3.64×10^{-7}	88.81
O$_2$ plasma 20 s	-0.189	3.95×10^{-7}	87.86

Figure 5.6 The effects of oxygen plasma treatment times on the roughness and corrosion inhibition efficiencies of the copper surface from AFM and potentiodynamic polarization studies, respectively

5.2   Thermal stability of thiolate self-assembled monolayers on copper surface

The thermal stability of thiolate self-assembled monolayers on copper surface is characterized by (1) hydrophobic or hydrophilic features of the sample substrates, (2) morphology, (3) roughness, (4) the Fourier transform infrared spectrometry (FT-IR), (5) the X-ray photoelectron spectroscopy (XPS), and (6) corrosion inhibition efficiencies. Three types of monolayers; 1-octanethiol (OTT), 2-ethylhexanethiol (2-EHT) and 2-phenylethanethiol (2-PET), are coated on copper surfaces. The thermal stability of each sample is study in the temperature ranging between 25ºC to 250ºC.

Figure 5.7 shows the effects of annealing temperature on water contact angle of copper surface coated with 2-EHT, OTT, and 2-PET SAMs. The water contact angles of all substrates tend to decrease with increased annealing temperature, and approach the minimum at 250°C. The results suggested that all SAMs are completely destroyed at this temperature. The water contact angles of the substrates with 2-EHT and OTT SAMs drastically decrease. In comparison, the water contact angle of the substrate with 2-PET SAMs exhibits a gradually decreasing. Thus, 2-PET SAMs is more stable than 2-EHT and OTT SAMs.

The morphologies of coated copper surfaces are measured by the SEM as shown in Fig. 5.8. The results show that the 2-EHT SAMs on copper surface is rough surface than OTT and 2-PET SAMs but is more clearly defined with the roughness by the AFM as shown in Fig. 5.9. Regarding to Fig. 5.7, the water contact angle of 2-EHT, OTT, and 2-PET coated on copper surface is 121.96º, 117.17º, and 104.83º at 25 ºC, which is related to the roughness of 18.842, 18.444, and 9.844 nanometers, respectively. The results agree with the lotus leaf effect [23].
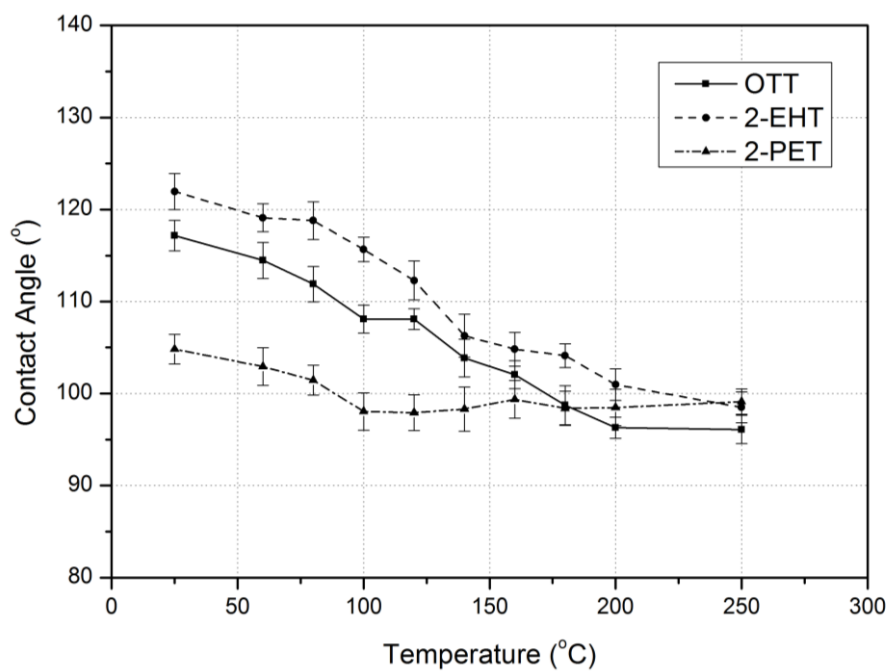
Figure 5.7 The effects of annealing temperature on water contact angle of copper surface coated with different SAMs
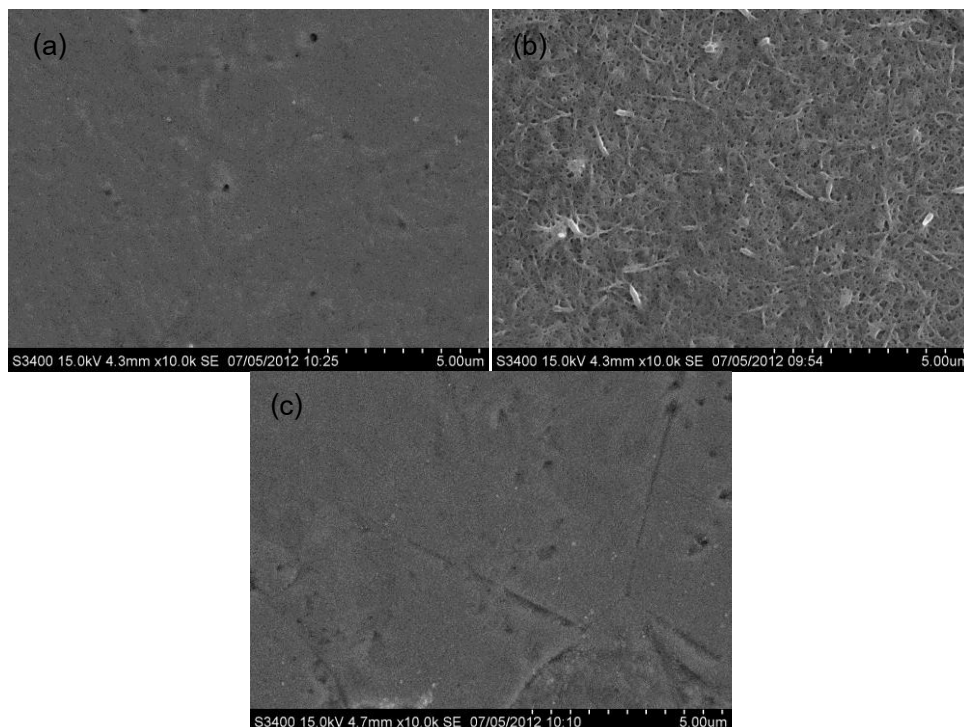

Figure 5.8 SEM images of SAMs on copper surfaces at 25ºC, (a) OTT, (b) 2-EHT and (c) 2-PET
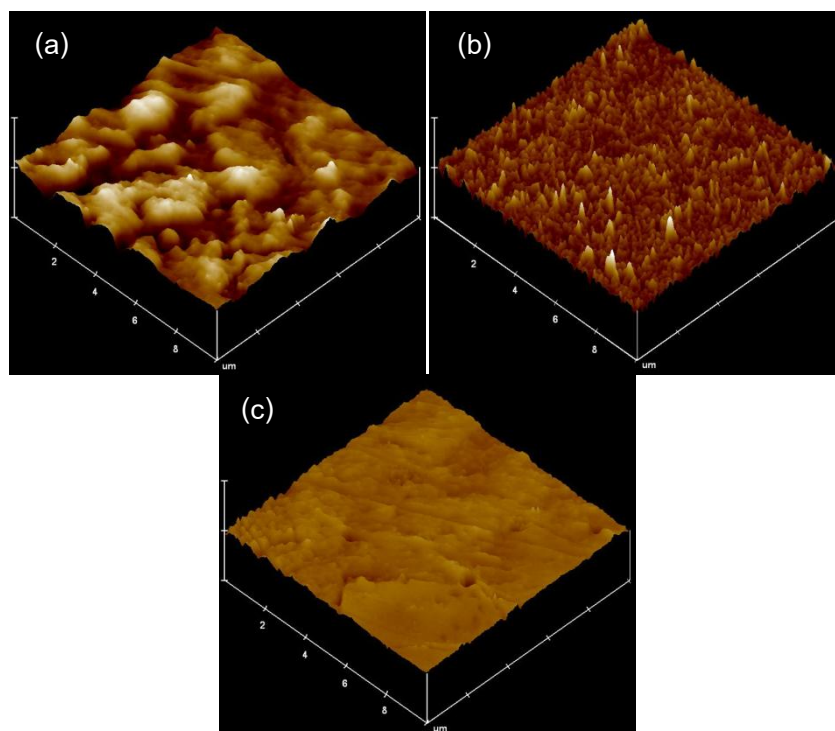
Figure 5.9 AFM images of SAMs on copper surface at 25ºC, (a) OTT, (b) 2-EHT and (c) 2-PET

Figure 5.10 shows FT-IR results of the substrates with OTT SAMs annealed at temperature ranging from 25ºC to 250ºC. The peaks at wavenumber 2962±10 cm^{-1} and wavenumber 2855±10 cm^{-1} are -CH$_3$ and -CH$_2$, respectively. Both of them are the major components of OTT structure. It can be inferred that the OTT is actually coated on the copper surface because of the presences of peaks of -CH$_3$ and -CH$_2$ at 25ºC. After annealing to 80°C, the peak of -CH$_3$ and -CH$_2$ tends to be decreased because of the decomposition of OTT.

Figure 5.10 FT-IR of OTT SAMs on copper surface annealed at various temperatures

The FT-IR of the substrates with 2-EHT SAMs annealed at temperature ranging from 25ºC to 250ºC are presented in Fig. 5.11. The peaks at wavenumber 2962 ± 10 cm^{-1} and wavenumber 2855 ± 10 cm^{-1} are -CH$_3$ and -CH$_2$, respectively, and both of them are the major components of 2-EHT structure. The amount of -CH$_3$ in 2-EHT is higher than that contains in OTT. Therefore, the absorbance of this peak in 2-EHT is higher than that contain in OTT. It can confirm that the 2-EHT is actually coated on the copper surface because of the presences of peaks of -CH$_3$ and -CH$_2$ at 25ºC. After annealing to 140°C, the peak of -CH$_3$ and -CH$_2$ tend to be decreased because of the decomposition of 2-EHT.
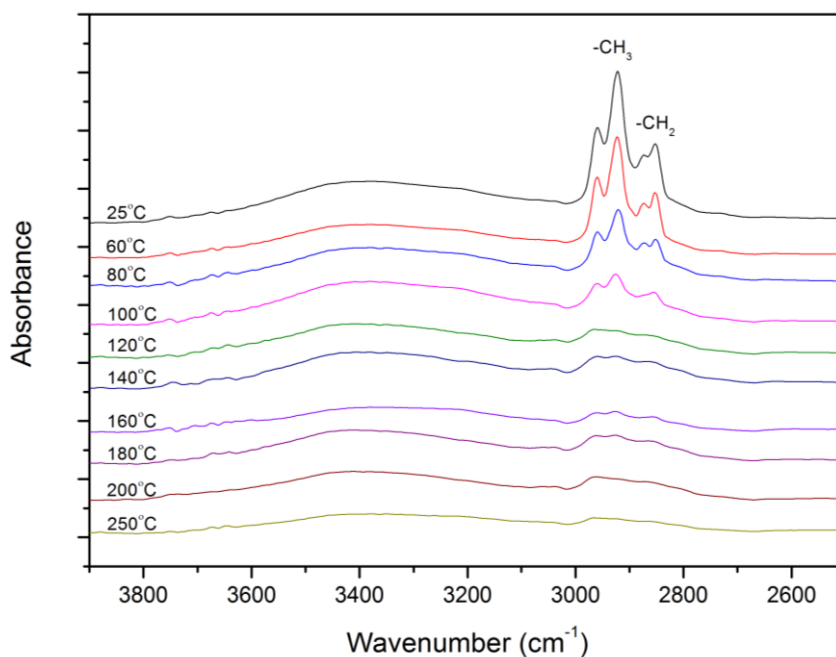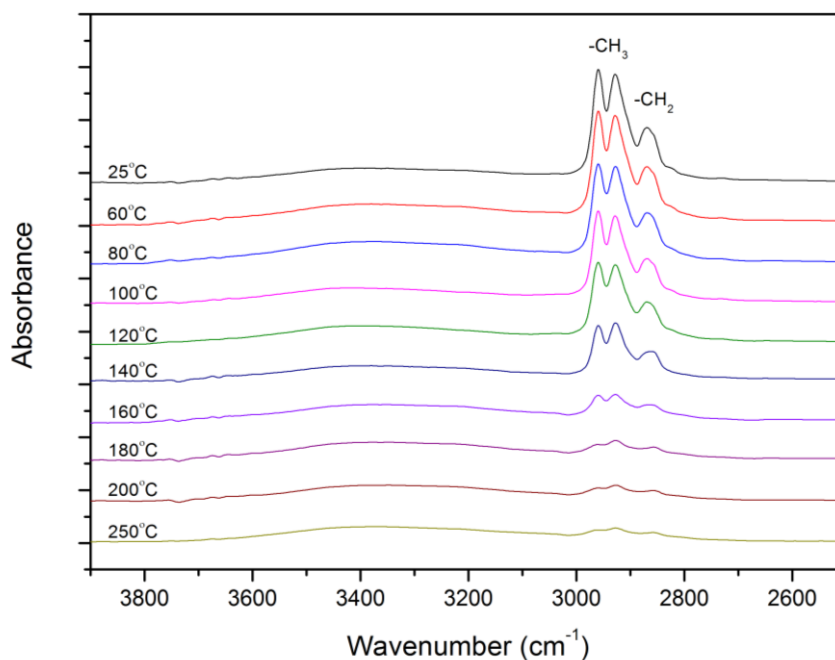
Figure 5.11 FT-IR of 2-EHT SAMs on copper surface annealed at various temperatures

The FT-IR of the substrates with 2-PET SAMs annealed at temperature ranging from 25°C to 250°C are presented in Fig.5.12. The 2-PET structure is not only composed of -CH_2, as in OTT and 2-EHT structures, but also composed of aromatic ring. The aromatic ring appears at wavenumber from 3200-3400 cm^{-1}. After annealing to 250°C, the peaks of -CH_2 and also aromatic ring can be observed from this measurement method. From this observation, 2-PET is not decomposed.

According to three different monolayers, OTT starts decomposing at the annealing temperature of 80°C while the 2-EHT is at the annealing temperature of 140°C. 2-EHT is interpreted to be more resistant to the higher temperature than OTT and the most resistant to the high temperature is 2-PET.
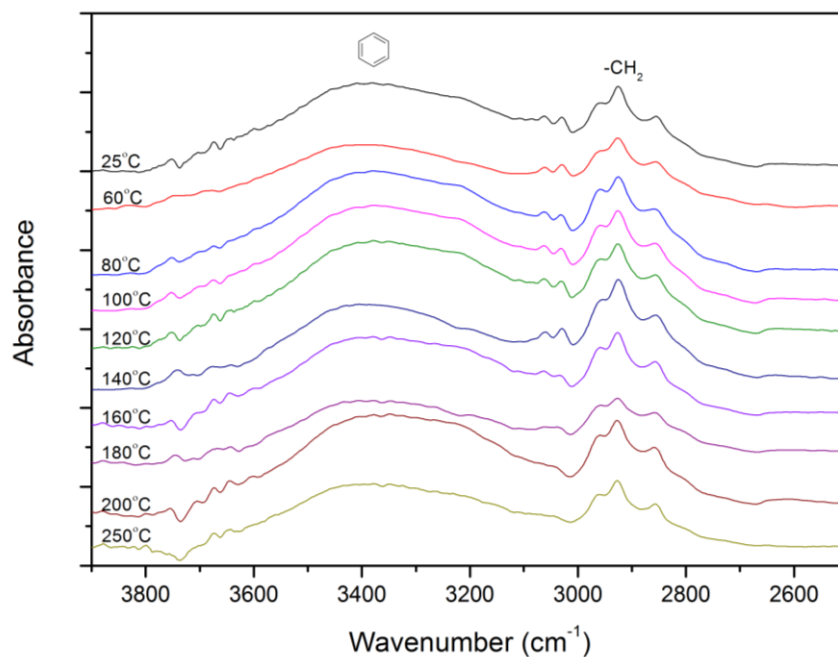
Figure 5.12 FT-IR of 2-PET SAMs on copper surface annealed at various temperatures

Regarding to the result of decomposed temperature by using FT-IR measurement, these temperatures of decomposition are studied in more detail by using the XPS measurement method. Three differences of monolayers; OTT, 2-EHT, and 2-PET, are also conducted by using 4 annealing temperatures; 60, 80, 140 and 250°C in Figs. 5.13 – 5.18. It is assumed that there is no discrepancy in FT-IR results at the annealing temperature of less than 60°C.

The XP survey spectra of the substrates with OTT SAMs annealed at various temperatures are shown in Fig. 5.13. Initially, the binding energy scale was calibrated to 284.3 eV for the main C(1s) peak. The intensity of C(1s) of OTT monolayers was decreasing through annealing temperatures, whereas the peak of O(1s) of OTT monolayers at the binding energy of 530 eV [24] increased due to the fact that the OTT monolayers reacted with oxygen and monolayers was decomposed.

Figure 5.13 XP survey spectra of OTT SAMs on copper surface annealed at various temperatures

The XP high resolution spectra of S(2p) regions of the substrates with OTT SAMs annealed at various temperatures are shown in Fig. 5.14. The S(2p) regions of OTT monolayers presences the binding energy of 162.9 eV at the annealing temperature of 60°C and considered to be the "thiolate bond" [25]. Consequently, the peak of S(2p) was shifted the binding energy to 161.7 eV at the annealing temperature of 80°C. At this position, the binding energy is interpreted to be a copper (I) sulfide (Cu_2S) [25] which is the same position until 140°C but less intensity. Nevertheless, the peak of S(2p) disappeared in the annealing temperature of 250°C. Thus, OTT layer started to decompose, the thiolate bond changed to a Cu_2S at 80°C and completely decomposed at 250°C.

Figure 5.14 XP high resolution spectra of S(2p) regions of OTT SAMs on copper surface annealed at various temperatures

The XP survey spectra of the substrates with 2-EHT SAMs annealed at various temperatures are shown in Fig. 5.15. Initially, the binding energy scale was calibrated to 284.3 eV for the main C(1s) peak. The intensity of C(1s) and O(1s) of 2-EHT monolayers showed the same trend as previous mention in OTT monolayers as shown in Fig. 5.13 due to the fact that the 2-EHT monolayers reacted with oxygen and monolayers was decomposed.

The XP high resolution spectra of S(2p) regions of the substrates with 2-EHT SAMs annealed at various temperatures are shown in Fig. 5.16. The intensity of thiolate bond of S(2p) of 2-EHT monolayers at 60°C is similar to the S(2p) peak at 80°C but its intensity is slightly descending at the annealing temperature of 140°C and totally missing at the temperature of 250°C. It suggested that the 2-EHT layer decomposed at the temperature of 140°C and totally decomposed at the 250°C.
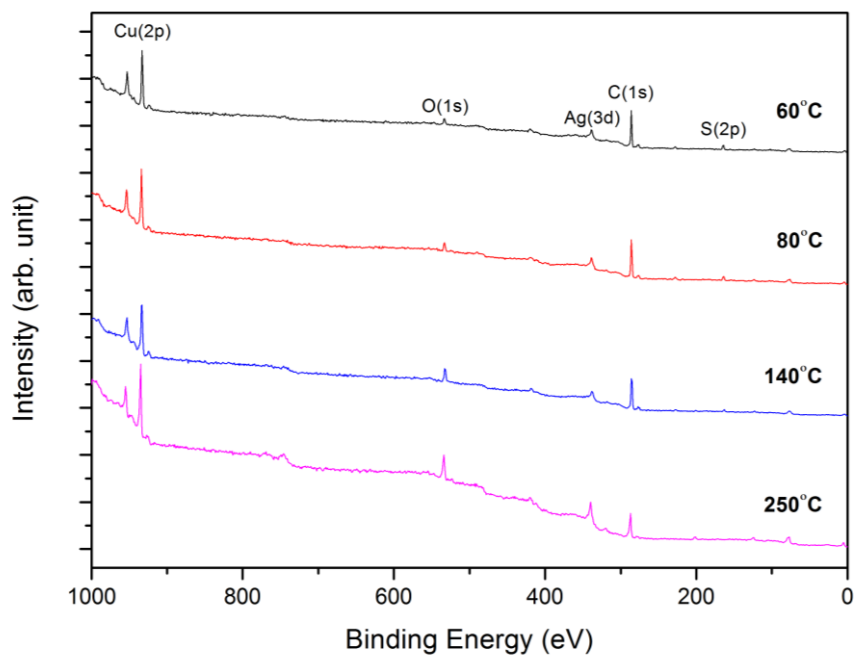
Figure 5.15 XP survey spectra of 2-EHT SAMs on copper surface annealed at various temperatures
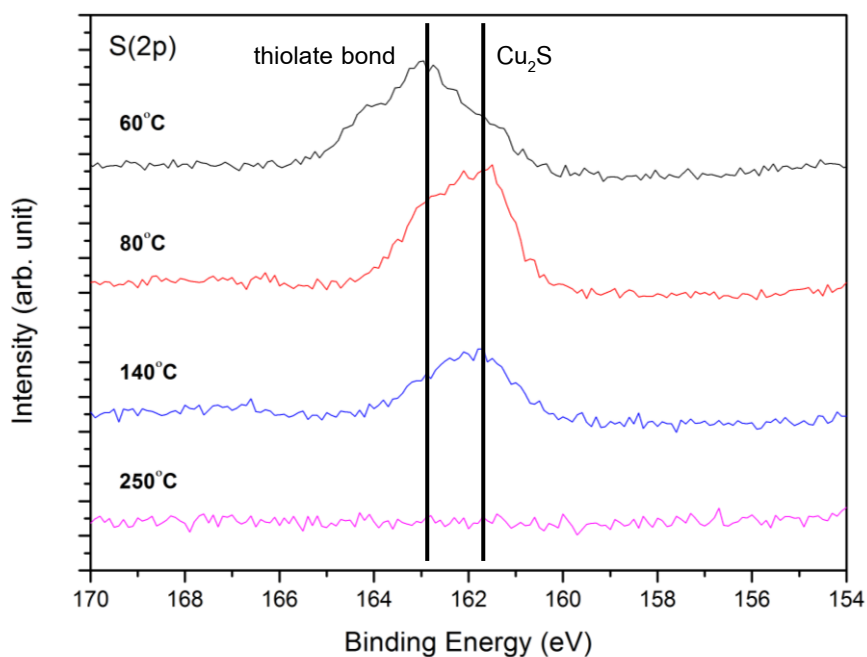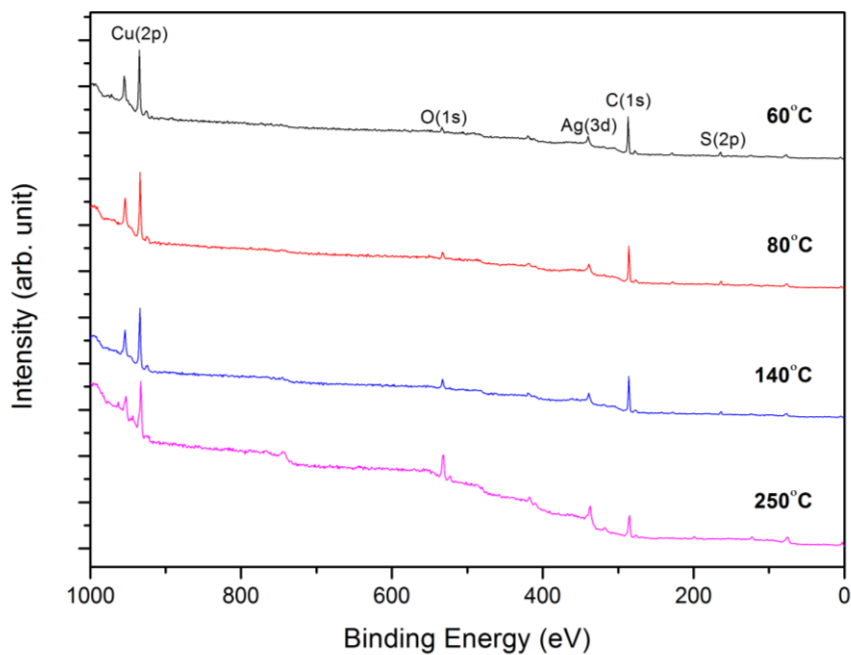

Figure 5.16 XP high resolution spectra of S(2p) regions of 2-EHT SAMs on copper surface annealed at various temperatures

Likewise, the XP survey spectra of the substrates with 2-PET SAMs annealed at various temperatures are shown in Fig. 5.17. Initially, the binding energy scale was calibrated to 284.3 eV for the main C(1s) peak. The intensity of C(1s) and O(1s) of 2-PET monolayers showed the same trend as previous mention in OTT and 2-EHT monolayers (Fig. 5.13 & Fig. 5.15) due to the fact that the 2-PET monolayers reacted with oxygen and monolayers was decomposed.

The XP high resolution spectra of S(2p) regions of the substrates with 2-PET SAMs annealed at various temperatures are shown in Fig. 5.18. In the XP high resolution spectra of S(2p) regions of 2-PET monolayers, it was not decomposed at annealing temperature below 140°C. According to the FT-IR and XPS results indicate that the structure of 2-PET is more stable than OTT and 2-EHT because 2-PET includes aromatic ring in the structure.
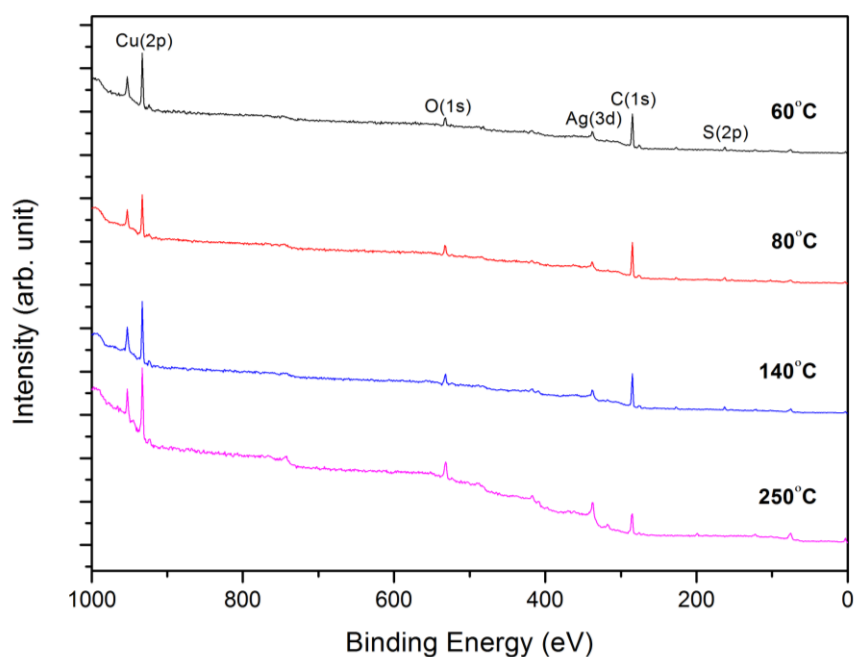
Figure 5.17 XP survey spectra of 2-PET SAMs on copper surface annealed at various temperatures
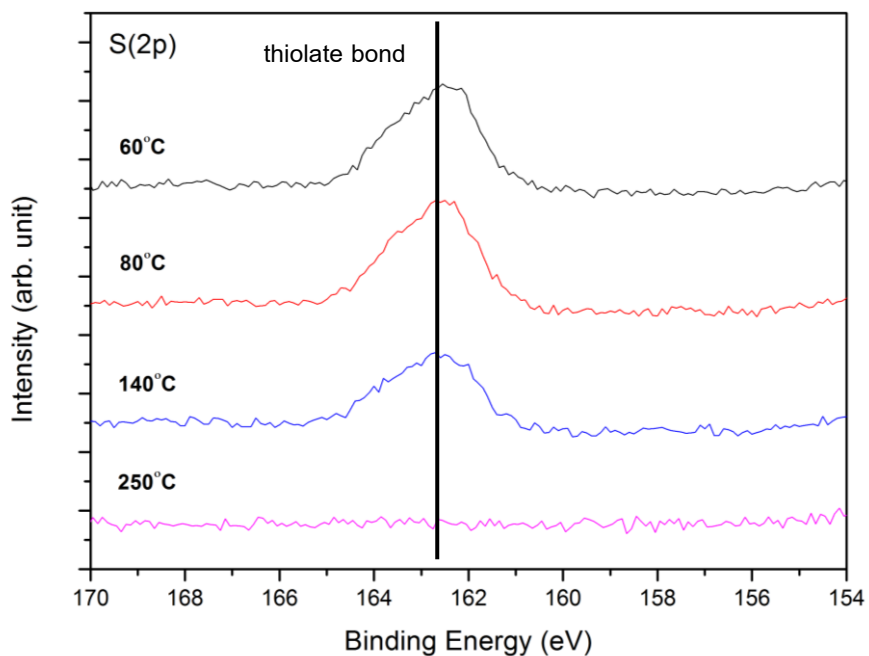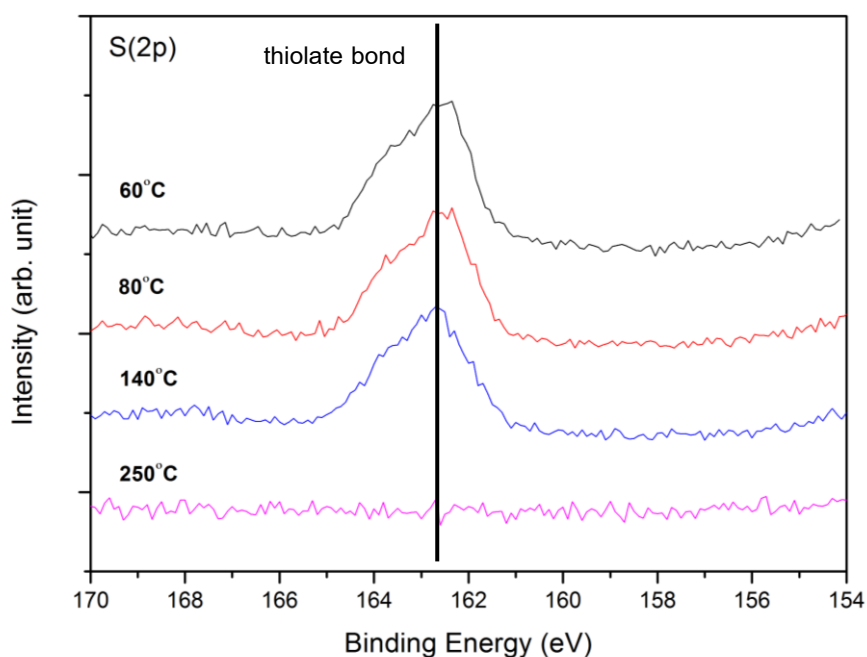
Figure 5.18 XP high resolution spectra of S(2p) regions of 2-PET SAMs on copper surface annealed at various temperatures

The corrosion inhibition efficiencies (%IE) of the substrates with OTT, 2-EHT and 2-PET SAMs annealed at various temperatures can be calculated based on formula 5.1 as shown in Table 5.3. The higher %IE means the ability to protect the surface from corrosion. For comparison three different monolayers coated on copper surface, the %IE starts from the high number and decreased though the annealing temperature within this study. The %IE of OTT drastically decreases at annealing temperature 80°C. The decomposition of OTT SAMs initiated at this temperature. The %IE of 2-EHT SAMs sharply decreases at annealing temperature 140°C. This refers to the initiation of the 2-EHT SAMs decomposition. At annealing temperature less than 140°C, the %IE of 2-PET SAMs is rather constant. This concludes that the 2-PET is not decomposed at annealing temperature below 140°C. These results are in good agreement with FT-IR and XPS results.

Table 5.3 Corrosion inhibition efficiencies of the SAMs on copper surfaces annealed at various temperatures from potentiodynamic polarization studies

Sample	E_{corr} (V) vs. Ag/AgCl	i_{corr} (A/cm^2)	Inhibition Efficient (%)
Bare Cu	-0.235	3.25×10^{-6}	-
OTT_25°C	-0.232	3.64×10^{-7}	88.81
OTT_80°C	-0.215	4.88×10^{-7}	84.99
OTT_140°C	-0.215	5.69×10^{-7}	82.51
OTT_250°C	-0.239	2.75×10^{-6}	15.56
2-EHT_25°C	-0.242	3.60×10^{-7}	88.95
2-EHT_80°C	-0.232	4.06×10^{-7}	87.52
2-EHT_140°C	-0.215	5.25×10^{-7}	83.86
2-EHT_250°C	-0.240	2.78×10^{-6}	14.60
2-PET_25°C	-0.238	3.29×10^{-7}	89.88
2-PET_80°C	-0.242	3.66×10^{-7}	88.74
2-PET_140°C	-0.232	3.83×10^{-7}	88.24
2-PET_250°C	-0.239	2.73×10^{-6}	16.10

CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Copper is commonly used to be the material in the industry, however, the copper is easier oxidation even expose in the air. In general, copper surface is coated by organothiol self-assembled monolayers (SAMs), especially the straight chain structure. In this study, 8-carbon atoms are selected for SAMs because of several varieties of structure but same chemical formula. Three different structural; (1) straight chain, (2) branched chain, and (3) aromatic rings, are named as 1-octanethiol (OTT), 2-ethylhexanethiol (2-EHT), and 2-phenylethanethiol (2-PET), respectively. Since, this research studies the thermal stability of three different SAMs on a copper surface. Oxygen plasma is the appropriate method for copper surface preparation prior to coating. The optimum time of oxygen plasma treatment for copper surface activation is 15 seconds. Thereafter, copper surfaces treated by oxygen plasma for 15 seconds are coated by OTT, 2-EHT, and 2-PET in order to study the thermal stability in each SAM at various different annealing temperatures. The OTT is quickly decomposed at the lowest annealing temperature of 80°C while the 2-EHT is decomposed at the higher annealing temperature of 140°C. The mechanism of OTT decomposition relates to the transformation of thiolate bound to Cu_2S. The 2-PET is decomposed at the temperature above 140°C, and it is totally decomposed at 250°C. In accordance with this experiment, it suggests that the aromatic rings structure in 2-PET is more stable than the other structures. These results indicate that the thermal stability of thiolate bond can be improved by aromatic ring in the 2-PET molecule. Hence, 2-PET SAMs is the most favorable in terms of thermal stability.

6.2 Recommendations

Due to the temperatures of 2-EHT and 2-PET were fairly large ranges in this study, it has been recommended to narrow down the temperature range in order to clarify more specific temperature.

REFERENCES

[1]   Sinapi, F., Lejeune, I., Delhalle, J., and Mekhalif, Z. Comparative Protective Abilities of Organothiols SAM Coatings Applied to Copper Dissolution in Aqueous Environments. <u>Electrochimica Acta</u> 52 (2007): 5182-5190.

[2]   Kumar, K. C., Raoa, B. V. A., Iqbal, M. Y., and Sreedhar B. Corrosion Protection of Copper by Self Assembled Monolayers. <u>Indian Journal of Chemical Technology</u> 16 (2009): 25-31.

[3]   Raoa, B. V. A., Iqbal, M. Y., and Sreedhar B. Electrochemical and Surface Analytical Studies of the Self-Assembled Monolayer of 5-Methoxy-2-(Octadecylthio)Benzimidazole in Corrosion Protection of Copper. <u>Electrochimica Acta</u> 55 (2010): 620-631.

[4]   Wang, P., Liang, C., Wu, B., Huang, N., and Li, J. Protection of Copper Corrosion by Modification of Dodecanethiol Self-Assembled Monolayers Prepared in Aqueous Micellar Solution. <u>Electrochimica Acta</u> 55 (2009): 878-883.

[5]   Wikipedia, the free encyclopedia. <u>Corrosion</u> [Online]. 2011. Available from: http://en.wikipedia.org/wiki/Corrosion [2012, September 20]

[6]   Corrosionist. <u>Fundamental of Corrosion Chemistry</u> [Online]. 1992 Available from: http://www.corrosionist.com/Corrosion_Fundamental.htm [2012, September 19]

[7]   Namurata Sathirachinda. <u>Electropolishing</u> [Online]. 2010 Available from: http://siamkaewkumsai.blogspot.com/2010/12/electropolishing.html [2012, September 18]

[8]   Petzow, G. <u>Metallographic Etching</u>. 2nd edition. United States of America: ASM International[®] Materials Park, 1999.

[9]   Wikipedia, the free encyclopedia. <u>Self-assembled monolayer</u> [Online]. 2011. Available from: http://en.wikipedia.org/wiki/Self-assembled_monolayer [2012, September 15]

[10]   Pakorn Thaipituk. <u>Wetting</u> [Online]. 2011 Available from: http://www.vcharkarn.com/varticle/43544 [2011, December 11]

[11] College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang. Scaning Eletron Microscopy (SEM) [Online]. 2009. Available from: http://www.nano.kmitl.ac.th/index.php?option=com_content&view=article&id= 218:scaning-eletron-microscopysem-&catid=23:2009-06-05-03-28- 18&Itemid=24 [2012, September 18]

[12] College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang. Atomic Force Microscope (AFM) [Online]. 2009. Available from: http://www.nano.kmitl.ac.th/index.php?option=com_content&view=article&id= 219:atomic-force-microscope-afm-&catid=23&Itemid=24 [2012, September 18]

[13] Faculty of Science Naresuan University. Fourier Transform Infrared Spectroscopy (FT-IR) [Online]. 2009. Available from: http://www.sci.nu.ac.th/slc/ tools.php?tool_I D=7 24 [2012, September 18]

[14] ThEP Center. X-ray Photoelectron Spectroscopy [Online]. 2010. Available from: http://www.thep-center.org/src/machine_xps.php [2012, September 18]

[15] Institute for Innovative Learning. Intergrated Electrochemistry [Online]. 2010. Available from: http://www.il.mahidol.ac.th/eng/index.php/e-media.html [2011, September 4]

[16] Wikipedia, the free encyclopedia. Potentiostat [Online]. 2010. Available from: http://en.wikipedia.org/wiki/Potentiostat [2011, September 4]

[17] JAMWiki. Cyclic Potentiodynamic Polarization Scans [Online]. 2008. Available from: http://www.argentumsolutions.com/wiki/en/Cyclic_Potentiodynamic_Polarizatio n_Scans [2011, September 4]

[18] Quan, Z., Chen, S., and Li, S. Protection of Copper Corrosion by Modification of Self-Assembled Films of Schiff Bases with Alkanethiol. Corrosion Science 43 (2001): 1071-1080.

[19] Tan, Y. S., Srinivasan, M. P., Pehkonen, S. O., and Chooi, Simon Y. M. Effects of Ring Substituents on the Protective Properties of Self-Assembled Benzenethiols on Copper. Corrosion Science 48 (2006): 840-862.

[20] Carbonell, L., Whelan, C. M., Kinsella, M., and Maex, K. A Thermal Stability Study of Alkane and Aromatic Thiolate Self-Assembled Monolayers on Copper Surfaces. Superlattices and Microstructures 36 (2004): 149-160.

[21] Yunsoo, K., Myung, M. S., Self-Assembled Monolayers of Alkanethiols on Clean Copper Surfaces. Bulletin of the Korean Chemical Society 22 (2001): 748-752.

[22] Wuttichai Suthipongkiat. Optimum Condition of Copper Surface Treatment for Octadecanethiol Self-Assembled Monolayer Coating for Corrosion Protection. Master's Thesis, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, 2011.

[23] Miwa, M., Nakajima, A., Fujishima, A., Hashimoto, K., and Watanabe, T. Effects of the Surface Roughness on Sliding Angles of Water Droplets on Superhydrophobic Surfaces. Langmuir 16 (2000): 5754-5760.

[24] Myung, M. S., Kiwhan, S., Chang, G. K., Sun, S. L., and Yunsoo, K. Self-Assembled Monolayers of Alkanethiols on Oxidized Copper Surfaces. The Journal of Physical Chemistry B 104 (2000): 2273-2277.

[25] Myung, M. S., Yun Sung, W., Sun, S. L., and Yunsoo, K. Thermal Decomposition of Octanethiolate Self-Assembled Monolayers on Cu(111) in UHV. Bulletin of the Korean Chemical Society 24 (2003): 610-612.

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Publications

Kongsumrit, P. and Kheawhom, S., Copper Surface Treatment for Octadecanethiol Self-Assembled Monolayers Coating. The 22th Annual National Conference of Thaksin University, Thai-ASEAN: Path of Collaboration, 23-26 May 2012 (Songkla, Thailand).