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FABRICATION OF ELECTRONIC DEVICES USING PLASMA-POLYMERIZED POLYPYRROLE

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เดชา ลาภส่งผล: การประดิษฐ์อุปกรณ์อิเล็กทรอนิกส์โดยใช้พลาสมา-พอลิเมอไรซ์พอลิพิร์โรล (FABRICATION OF ELECTRONIC DEVICES USING PLASMA-POLYMERIZED POLYPYRROLE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.บุญโชติ เผ่าสวัสดิ์ยรรยง, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร.วรวรรณ พันธุมนาวิน, 65 หน้า.

งานวิจัยนี้ได้ประดิษฐ์อุปกรณ์อิเล็กทรอนิกส์โดยใช้พลาสมา-พอลิเมอไรซ์พอลิพิร์โรล โดยได้ประดิษฐ์อุปกรณ์อิเล็กทรอนิกส์ 2 ชนิด คือ ไดโอดชอทท์กี้ และ piezoresistive strain sensor ในการสังเคราะห์พอลิพิร์โรลด้วยวิธีพลาสมา ได้ใช้ความต่างศักย์ไฟฟ้ากระแสสลับในช่วง 800-1400 โวลต์ และใช้เวลาในการสังเคราะห์ 30-90 นาที จากนั้นนำมาวิเคราะห์ด้วยเทคนิคสเปกโทรโฟโตเมทรี การวิเคราะห์หมู่ฟังก์ชันของโครงสร้างฟิล์มพอ พิร์โรลด้วยเทคนิคฟูเรียร์ทรานฟอร์มอินฟราเรดสเปกโทรสโคปี พบว่าพลาสมา-พอลิเมอไรซ์พอลิพิร์โรลมีหมู่ฟังก์ชันสอดคล้องกับสารละลายมอนอเมอร์ ในการวิเคราะห์สัณฐานวิทยาของฟิล์มพอลิพิร์โรลด้วยกล้องจุลทรรศน์แบบส่องกราด พบว่าฟิล์มพอลิ พิร์โรลมีลักษณะเรียบ เนื้อแน่น ไม่มีรูพรุน และมีความหนาอยู่ในช่วง 1.02 – 2.60 ไมโครเมตร โดยเมื่อนำไปประดิษฐ์เป็นไดโอดแบบชอทท์กี้พบว่า สภาวะที่เหมาะสมในการเตรียมฟิล์มเพื่อประดิษฐ์ไดโอดคือ สภาวะที่มีการโดปแบบอินสิทูด้วยไอโอดีน และใช้ความต่างศักย์ต่ำๆ ที่เวลาน้อยๆ ส่วนการประดิษฐ์ piezoresistive strain sensor ได้เตรียมฟิล์มพอลิพิร์โรลด้วยวิธีทางพลาสมา ลงบนแผ่นรองรับที่ทำจาก polymethyl methacrylate ซึ่งมีคุณสมบัติในการดัดโค้งและคืนรูปได้ โดยวัดคุณภาพของเซนเซอร์โดยวัดค่าเกจแฟคเตอร์ (gauge factor) ได้อยู่ในช่วง 18.69–59.65 โดยเซนเซอร์ที่เตรียมด้วยพอลิพิร์โรลที่ความต่างศักย์ 800 โวลต์ ที่เวลา 30 นาที ให้ค่าเกจแฟคเตอร์สูงที่สุด

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต...

ปีการศึกษา ……………2554……………......... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก…………

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DECHA LAPSONGPHOL: FABRICATION OF ELECTRONIC DEVICES USING PLASMA-POLYMERIZED POLYPYRROLE. ADVISOR: ASST. PROF. BOONCHOAT PAOSAWATYANYONG, Ph.D., CO-ADVISOR: ASST. PROF. WORAWAN BHANTUMNAVIN, Ph.D., 65 pp.

The Schottky barrier diodes and piezoresistive strain sensor were fabricated by using plasma polymerized polypyrrole. The polypyrrole was prepared by using plasma at AC voltage in the range of 800-1400 volt and reaction time for 30-90 min. The polypyrrole film was characterized by spectrophotometry and the functional groups of polypyrrole film were identified by Fourier transform infrared spectroscopy (FTIR). The FTIR confirmed that the polypyrrole was successfully obtained. The morphology of polypyrrole film was observed by Scanning electron microscopy (SEM) that shows dense, smooth, and uniform film. The thickness of polypyrrole films were in the range 1.02-2.60 μm. The suitable condition for Schottky barrier diode fabrication was *in-situ* doped by I_2 under low voltage and less reaction time. For the fabrication of piezoresistive strain sensor, polypyrrole film was prepared by plasma on polymethyl methacylate substrate. The product shows flexible property. Piezoresistivity is quantified by the gauge factor. The sensor was fabricated by polypyrrole at 800 volt for 30 min which led to the highest gauge factor.

Field of Study: Petrochemistry and polymer science Student's Signature ……………………......
Academic Year: ……….2011…………… Advisor's Signature …..............................
Co-advisor's Signature …………………

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LIST OF ABBREVIATIONS

A = Ammeter
ATR = Attenuated Total Reflection
cm = Centimeter
DC = Direct Current
EDS = Energy-dispersive X-ray spectroscopy
eV = electron volt
FTIR = Fourier Transform Infrared
HH = head-to-head
HT = head-to-tail
I = current
min = minute
mL = milliliter
mm^3 = cubic millimeter
mmol = millimole
nm = nanometer
OES = Optical Emission Spectroscopy
PPPPy = plasma polymerized polypyrrole
$PPPPy/I_2$ = iodine doped plasma polymerized polypyrrole
S = siemen
sccm = Standard Cubic Centimeters per Minute
SEM = Scanning Electron Microscope
TT = tail-to-tail
UV = Ultraviolet
V = voltage
W = watt
μm = micrometer

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

The polymer material is widely used due to excellent properties and variety of fields in general, the polymer dielectric properties. Thus it plays a role in the electronics industry, just as insulator. Conducting polymers have been studied intensively since the 1970s. The first conducting polymer was synthesized in doped polyacetylene by the group of Alan J. Heeger, Alan G. Macdiarmid, and Hideki Shirakawa [1]. Conducting polymer is an organic semiconductor with good properties such as light weight and flexibility. In a conducting polymer substance, polypyrrole (PPy) has received much attention due to its chemical stability, low oxidation potential, high conductivity, and atmospheric stability at room temperature [2,3]. PPy has been used for the wide variety of applications such as supercapacitors, biological sensors, batteries, and many more [4,5,6]. These polymers have been generally synthesized by two methods namely, electrochemical and chemical polymerization. However, both methods have considerable disadvantages. By the chemical technique, an insoluble powdered polymer is synthesized, which requires further purification for the removal of oxidants and surfactants [7]. With the electrochemical technique, a precise current density control is required to produce films, and the obtained films are rather fragile restricted [8].However PPy exhibits poor processability because of its insolubility in most common organic solvents. The direct fabrication of PPy into a thin film is a plausible solution of this problem.

Plasma polymerization is a technique that can polymerize monomer in the gas phase to fabricate film directly. This method therefore does not have processability problem. In addition plasma polymerization is an environmental friendly technique without necessity of using solvent in polymerization process.

This work presents the fabrication of two type electronic devices (Schottky barrier diode and Piezoresistive strain sensor), AC plasma polymerization technique was used for preparation of polypyrrole. Polypyrrole film was characterized by scanning electron microscope and attenuated total reflection fourier transforms infrared spectroscopy and electrical conductivity were also measured.

1.2 Objectives

This research is focused on the fabrication of Schottky barrier diode and Piezoresistive strain sensor by using AC plasma polymerization method and found the optimal conditions for prepared polypyrrole film by study the effects of process variables of voltage and reaction time on electrical properties of Schottky barrier diode and Piezoresistive strain sensor.

CHAPTER II

THEORY AND LITTERATURE REVIEW

2.1 Conducting polymer

2.1.1 Introduction to conducting polymers

Compare to metal, polymer material is the great features such as toughness, flexibility, strength and light weight that is why the polymer has been used extensively. In the past, polymer which had an electrical insulating property, had been used as an insulating conducting wire until 1973 That year Walatka, Labels, and Perlstein presented in their research that they discovered inorganic polymers which have high electrical conductivity and known as poly (sulfur nitride) $(SN)_x$ [9]. Conductive polymer's research was given more interest in 1997 because MacDiarmid, Heeger, and Shirakawa discovered how to increase the conductivity of polyacetylene[1,10]. The preparation of crystalline polyacetylene films and placed in the vapor of chlorine bromine and iodine, which can dramatically increase the electrical conductivity of polyacetylene. The electrical conductivity of the polyacetylene increases due to Electrons in the polymer chain was removed from the valence band by the halogen gas as oxidizing agent. The result is a hole in the polymer chain, giving Energy band gap decreases as the conductivity can be improved. Due to the research, MacDiarmid, Heeger, and Shirakawa received the Nobel Prize in Chemistry in 2000 [16]. Doping process of the research mentioned above was a p-doping. While another was in the process containing reducing the electron to the polymer chain was called the n-doping. Doping process enables the conductivity of the conductive polymer increased and can be more utilized in the electronic.

The conductive polymer is different from the general polymer because it must have π-conjugate electron system in the polymer main chain structure, conjugated electron system is the structure of the substance with a single bond between the double bond which makes the molecular chain with a system of connected p-orbital (see **Figure 2.1**), electrons in the conjugated electron system can be moveable inside the molecular chain of the polymer, and the conductivity of the conductive polymer is higher than common polymer.

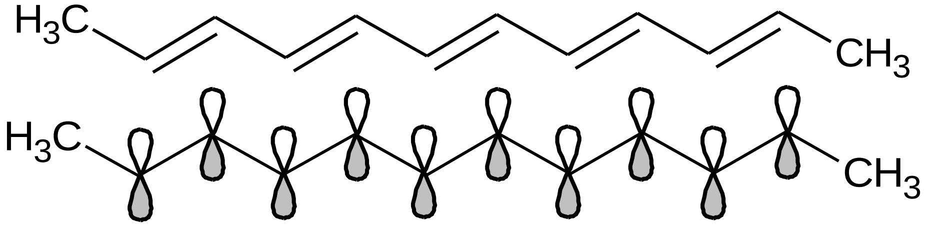


Figure 2.1 Conjugated structure of polyacethylene.

The conjugated polymers had a wide variety which can be classified into the different types and the classifying methods are discussed in the following sections.

2.1.2 Classification of conducting polymers

The simplest conjugated polymer is a polymer chain that consists of an alternating of double and single bonds. This conjugated polymer called polyacetylene, which is the most crystalline conjugated polymer that be used to study in the beginning. However, the instability of polyacetylene in the environment makes this polymer's usages limited. Therefore, the other types of conjugated polymers be interested in the study and synthesis. As the result of study about conjugated polymers, they are synthesized into many types as shown in **Figure 2.2**.

The conductive polymer has many varieties. It can be classified into two groups; non-carbon atoms structure and carbon atoms structure [11]. The example of non-carbon atoms structure is poly (sulfur nitride), and the conductive polymer containing carbon atoms is divided into three classes, including polyvinylenes, polyarylenes, and polyheterocyclic. First, polyvinylenes are the straight chain conjugated polymer, which has a substituent bonding to the polymer chain, such as polyacetylene. Properties of polyvinylenes are good thermal stabilities and high electrical conductivities [12], but the downside is the oxidation in the air happens easily. Secondly, polyarylenes or polyaromatics, which include the polymer chains that consist of the aromatic components, such as poly (p-phenylene), polyazulene, and poly (p-phenylene vinylene). Poly (p-phenylene) was the first non-acetylenic hydrocarbon polymer that showed the high conductivity on doping which was demonstrated in 1980 [13]. The last type of carbon polymer is polyheterocyclics, which are composed by heteroatom in the pentagonal rings. The example of polyheterocyclics consists of polypyrrole, polythiophene, and polyfuran [14]. Overview of the classification of the conductive polymer as shown in **Figure 2.3**.

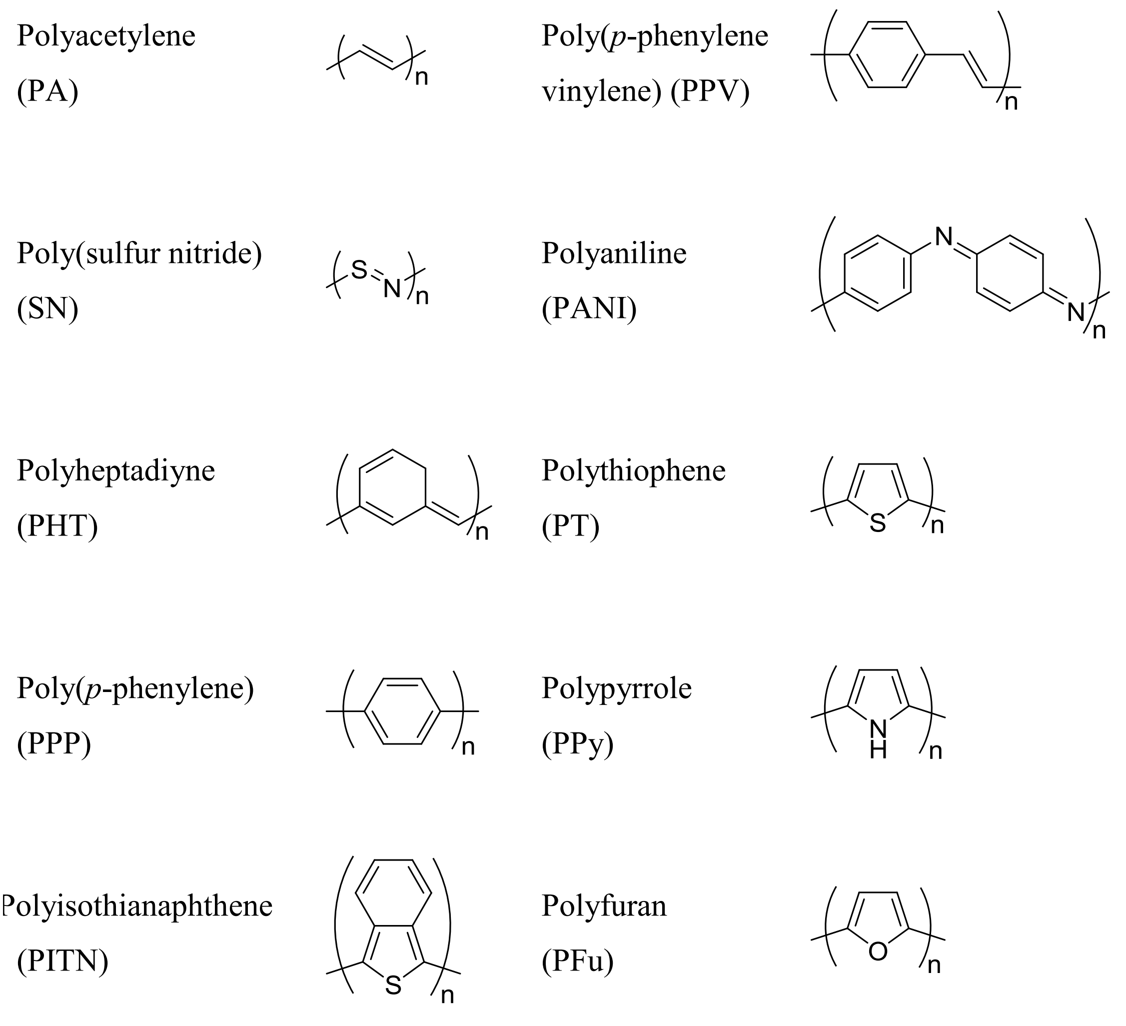


Figure 2.2 Molecular structures of some conjugated polymers.

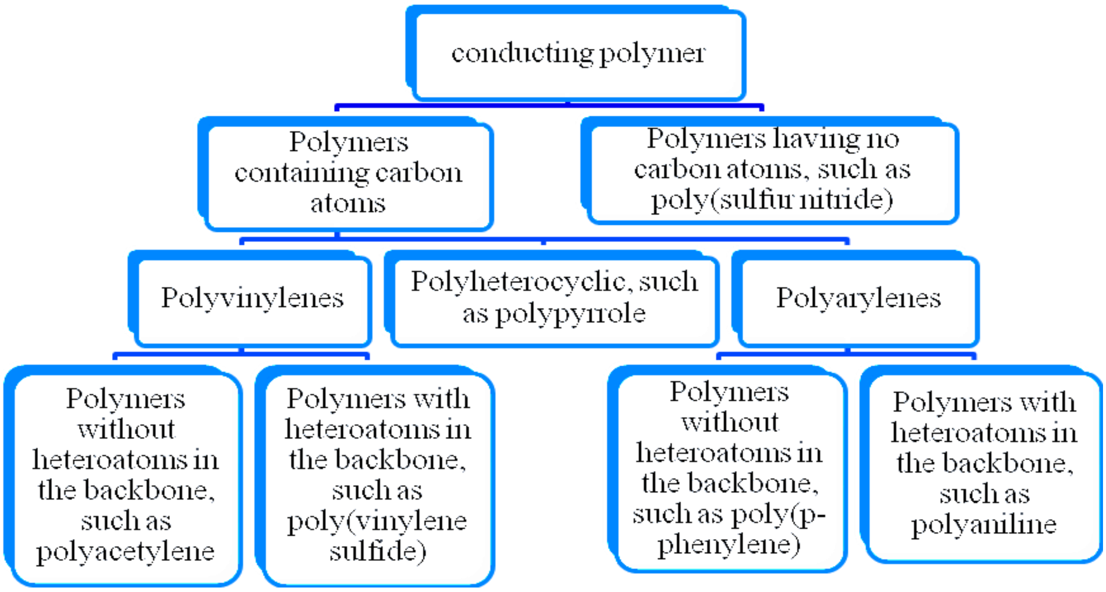


Figure 2.3 Classification of conducting polymers [11].

From the foregoing, it can be seen that the conductive polymer can be classified into several groups which have different advantages and disadvantages. However, the one thing that is interested for studying in electrically conducting polymer is a mechanism in the electrical conductivity of the conductive polymer, which is shown in the following sections.

2.1.3 Band theory and mechanism of conducting polymers

As mentioned above, the conductive polymer is classified into many types, but these polymers have the same structure that is a conjugated double bond structure. This structure allows electrons to move within the network of molecular chains, resulting in polymers with good electrical conductivity [15]. **Figure 2.4** shows the energy levels of materials with electrical properties in three types of insulators, semiconductors, and metal. Energy levels are comprised of the valence band or the highest occupied band (sourced from the highest occupied molecular orbital (HOMO) of a single polymer unit), which the electrons are in the valence band, While another band called the conduction band or the lowest unoccupied band (originating from the lowest unoccupied molecular orbital (LUMO) of a single polymer unit), Which is built on the lowest offered no electrons in the orbital. The distance between the valence bands to the conduction band is energy used to make the electrons jump from the valence band to the conduction band called the band gap energy or simply, band gap (E_g) [41].

As shown in **Figure 2.4**, insulating material has the large distance between the valence bands and the conduction band, so the current flows through the material of this type is very difficult. Semiconductor material conducts electricity better than insulating materials due to the energy level of valence band are close to conduction band over than the insulating material. Moreover, **Figure 2.4** shows the valence band and conduction band of metal is not only close to each other, but it is the overlap of energy levels. The overlap of this band was due to molecular orbital of the metal has a large number (typically 1022 for 1 cm^3 metal piece) and there are a lot of spaced orbital [41]. Such make the electrons of the metal rather have the freedom to move within the metal bonds, the metal can conduct electricity very well. The electrical conductivity of the material with different electrical properties is shown in **Figure 2.5.**

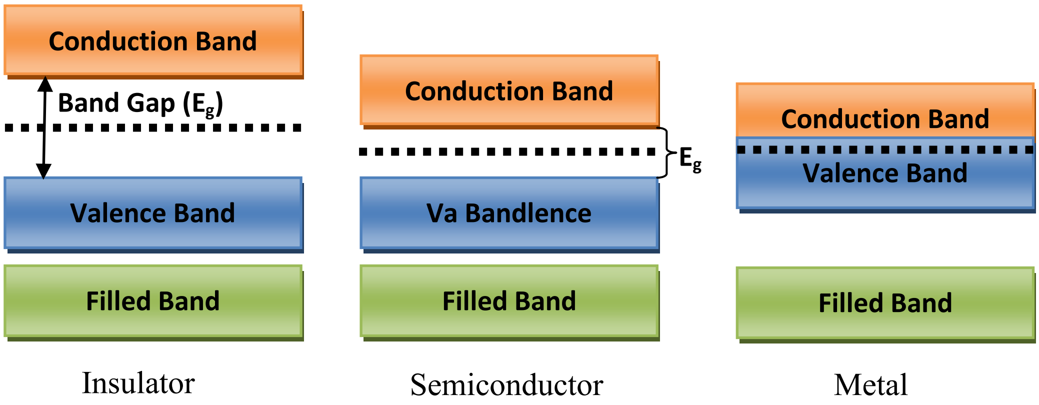


Figure 2.4 Energy band diagrams of materials.

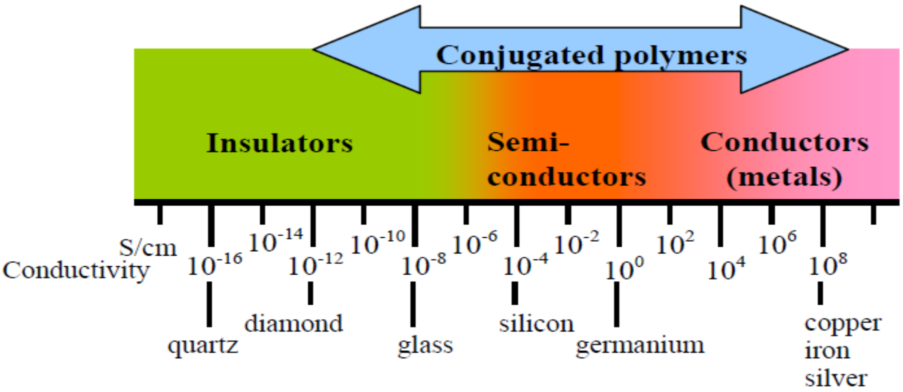


Figure 2.5 Conductivity of different materials [16].

The electrical conductivity of conjugated polymers is ranked to the insulating material. However, there is a method for enhancing the conjugated polymers' conductivity called doping. The mechanism of doping substances affects the conductivity of the polymer as shown in the following sections.

2.1.4 Effects of doping with conjugated polymer

The doping is the addition of impurities into the polymer in order to improve the conductivity of the polymer. There are many ways to dope conjugated polymer whether chemical or electrical doping. In the case of chemical doping, the principle is a doping substance reacts with the polymer chain by redox reaction. In addition, doping processes are divided into two types; p-type doping and n-type doping [24].

P-type doping is accomplished by using doping substance to extract electrons from the bonds of the conjugated polymer chain, or it can be described as doping substance to react oxidation with the polymer chain. The reaction of a p-type doping is presented in the equation below.

p-type

$$(\pi\text{-polymer})_n + 3/2\ ny\ (I_2) \longrightarrow [(\pi\text{-polymer})^{+y}\ (I_3^-)y]_n$$

N-type doping is doped by using doping substances to reduced with conjugated polymer chains, which received electrons into the chain. The equation has shown as below.

n-type

$$(\pi\text{-polymer})_n + [Na^+(\text{naphthalide})\cdot]_y \longrightarrow [(Na^+)_y((\pi\text{-polymer})^{-y}]_n + (\text{naphthalene})\cdot$$

Mechanism of the conjugated polymer's electrical conductivity, which is developed by doping process, is described by the following example of iodine doped with polypyrrole, which is known as p-type doping. This example describes the mechanism of doping in the polymer chain, which affects the electrical conductivity of polypyrrole. From **Figure 2.6**, iodine pulls electron from the chain of polypyrrole, and then spinless positive charge and free radical are formed on the polymer chain, both positive charge and free radical are called a positive polaron. Subsequently, the polymer chain rearranges by itself into the quinoid-like rings as shown in **Figure 2.6 b**. According to the occurrence of polaron due to the new energy band between the valence and conducting bands, the conduction of polymer is better. For the distribution of polarons, they are close to each other at a distance of only four pyrrole rings. It is the result of the effect of lattice distortion of the polypyrrole chain. In addition, the state of high level doping makes a new spinless defect that is much lower energy levels than the two-polarons, It is called bipolaron as shown in **Figure 2.6c.** It is possible that the bipolaron is formed by merging between two polarons. If polymer chains are highly doping, the value of bipolaron will increase continuously, in the polymer chains. Energy levels are arising from a lot of bipolarons that have induced themselves resulted in a continuous energy band between the valence band and conduction band. Then, the band gap decreases and the conductivity increases as close to the conductivity of the metal, as shown in **Figure 2.6**.

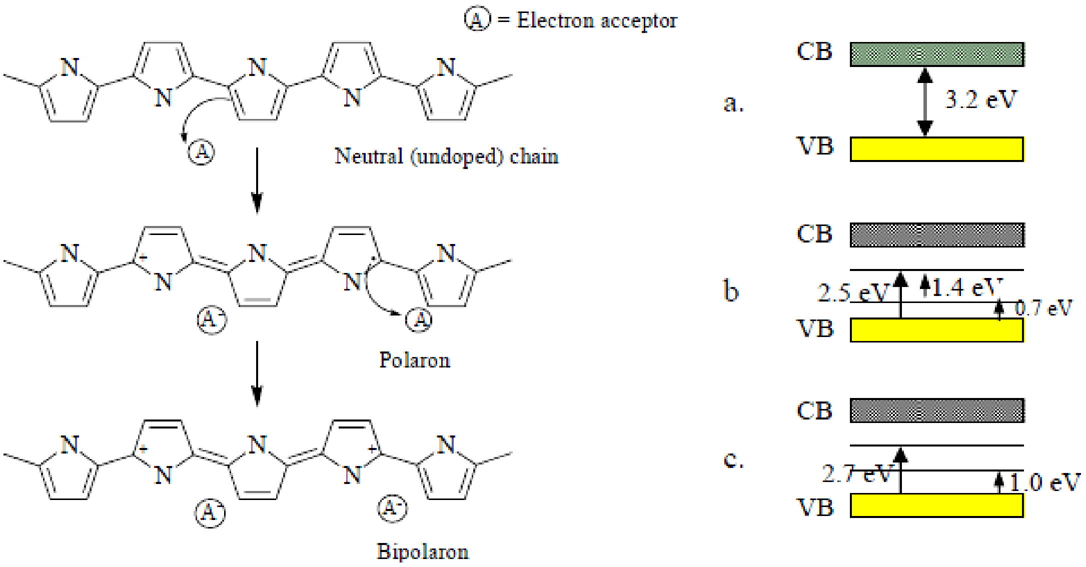


Figure 2.6 Neutral state, polaron and bipolaron structures for lightly and heavily doped polypyrrole, respectively, with their corresponding schematic band structures and the allowed electronic transitions [40].

2.1.5 Applications of conducting polymer [17]

The polymer materials have various features; moreover they can be used in many applications. The conjugated polymer is another dimension of polymer usage, because the generally polymer has dielectric properties but conjugated polymer is electrically conductive. It is also possible to modify the electrical conductivity from the range of insulating to the metal by different ways such as method of preparation, amount or type of doping substance, and the polymer type, etc.

The applications of conjugated polymers are divided into two major groups. The first is the conjugated polymers that are grouped in the electrical conductivity group. The second conjugated polymers group works on the electro activities as shown in **Table 2.1**.

Table 2.1 Applications of conducting polymers [17].

Group 1	Group 2
electrostatic materials	molecular electronics
conducting adhesives	electrical displays
electromagnetic shielding	chemical biochemical and thermal sensors
printed circuit boards	rechargeable batteries and solid electrolytes
artificial nerves	drug release systems
antistatic clothing	optical computers
piezoceramics	ion exchange membranes
active electronics (diodes transistors)	electromechanical actuators
aircraft structures	smart structures

2.2 Polypyrrole

Polypyrrole is a polyheterocyclic conjugated polymers. A structure of pyrrole is a pentagon and repeats as long chain. The first report on the chemical oxidation of pyrrole appeared in 1888. Later, in 1916 [18], the polypyrrole were prepared by chemical polymerization method using hydrogen peroxide to yield polymer that has a black conductive polymer called “pyrrole black”. Moreover, the synthesis of polypyrrole with electrochemical polymerization was reported in the first time in 1968. Furthermore variety of oxidizing agent was used in the preparation of the polymer. Since then, the preparation methods of polypyrrole with chemical polymerization and electrochemical polymerization [19, 22, 23] were commonly used in the preparation of polypyrrole.

Polypyrrole is one of the most studied conducting polymers because polypyrrole has a relatively high conductivity and environmental stability in the conducting state. Moreover, Polypyrrole can withstand many kinds of solvents. In addition, polypyrrole can be used in many ways, for examples transparent electrode in polymer light-emitting diodes, photoelectrochemical cells, metal coating, flexible plastic transistors, batteries, super capacitor and many more. In conclusion, polypyrrole become one of the most attentions because of its advantages.

2.2.1 Chemical polymerization of Pyrrole

Chemical polymerization is a common process used in the synthesis of polypyrrole. The synthesis of polypyrrole has been done by chemical oxidation of pyrrole monomers before the propagation of the chain reaction. There are variety of the oxidant, the widely used oxidant are ammonium persulfate, $(NH_4)_2S_2O_8$, and $FeCl_3$, although hydrogen peroxide and a range of transition metal salts (e.g., Fe^{3+}, Ce^{4+}, Cu^{2+}, Cr^{6+}, and Mn^{7+}) [19] have also been employed.

The mechanism of the reaction starts by oxidation reaction of the monomer to form a radical cation. Radical cation monomer can react by 2 ways base on the monomer. Firstly, “neutral monomer” is filled in the polymer chain by addition polymerization reaction; on the other hand, radical cation monomers reacted by coupling reaction followed deprotonation of intermediate will be utilized to generate the neutral dimer. Furthermore, active polymer will be produced by the reaction between dimer and radical cation monomers. The polymerization reaction can be continued [20]. The mechanism of the reaction has been shown in **Figure 2.7**.

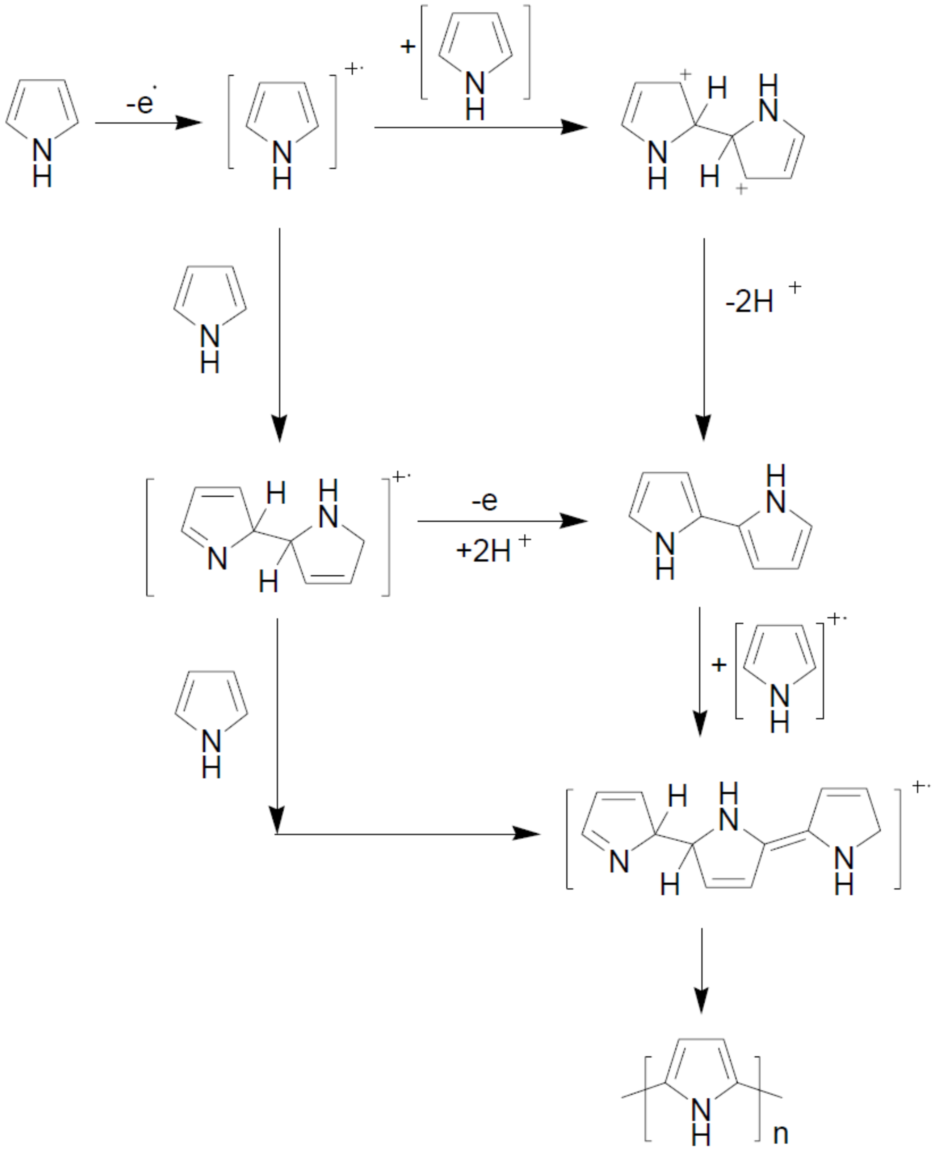


Figure 2.7 Mechanism of chemical polymerization of polypyrrole [20]

Factors affecting the synthesis of polypyrrole by chemical polymerization are many factors. The amount of oxidizing agent is the one that has a direct effect on the conductivity of the polypyrrole film, as in the case of synthetic polypyrrole using $FeCl_3$ as an oxidant. An [oxidant]/[pyrrole] molar ratio of ca. 2.3 is often used. PPy has come out with good electrical conductivity in the range of conductor, because polypyrrole has a positive charge in every three repeating units of pyrrole. Furthermore, there is research report on the effect of the solvent in the synthesis of polypyrrole with $FeCl_3$ as an oxidant. It has been found that the conductivity of PPy films prepared in water and alcohol (range from methanol to octanol) are more electrical conductivity than films prepared in other solvent as acetonitrile, tetrahydrofuran, chloroform, and benzene under the same condition of preparation [21].

The advantage of PPy films prepared by chemical synthesis is that it is easy to increase the scale of the synthesized and the product is to be powder, or colloids. Therefore, the PPy films prepared with this method can be deposited onto a substrate for both conductive and non conductive. However, limitation of this approach is required a solvent that can dissolve both pyrrole monomer and oxidant.

2.2.2 Electrochemical polymerization of Pyrrole

Electrochemical polymerization is the synthesis of polymers by electrochemical methods. The basic principle is the oxidation of the monomers at the anode and the reaction of synthetic polymers produced polymer deposition on the anode as a thin film. So, this process can be prepared in either aqueous or non aqueous solution. The mechanisms of electrode chemical polymerization of PPy have a lot to offer. One mechanism that has been widely accepted as the report of the Diaz et al. [24]

As with the synthesis of polymers in general are divided into three steps, ie initiation step, propagation step and termination step. The initiation step was the oxidation of pyrrole monomers at the anode and change monomers into the radical cation monomer, to be able to react dimerization via radical-radical coupling followed by removal of the two protons become a neutral dimer [25, 26]. Dimer is more easily oxidized than monomers because radical cation dimer is more stable than radical cation monomer. The reaction is similar to that previously mentioned repeatedly until the long chain of polypyrrole, as shown in **Figure 2.8** [23]. Finally, the polymer chains are positively charged pyrrole every 3-4 pyrrole units and anion of the electrolyte salt will act as a counterbalanced. During the growing film showed that the pH of the electrolyte solution decreases, which corresponds to the removal of α protons as in the proposed mechanism.

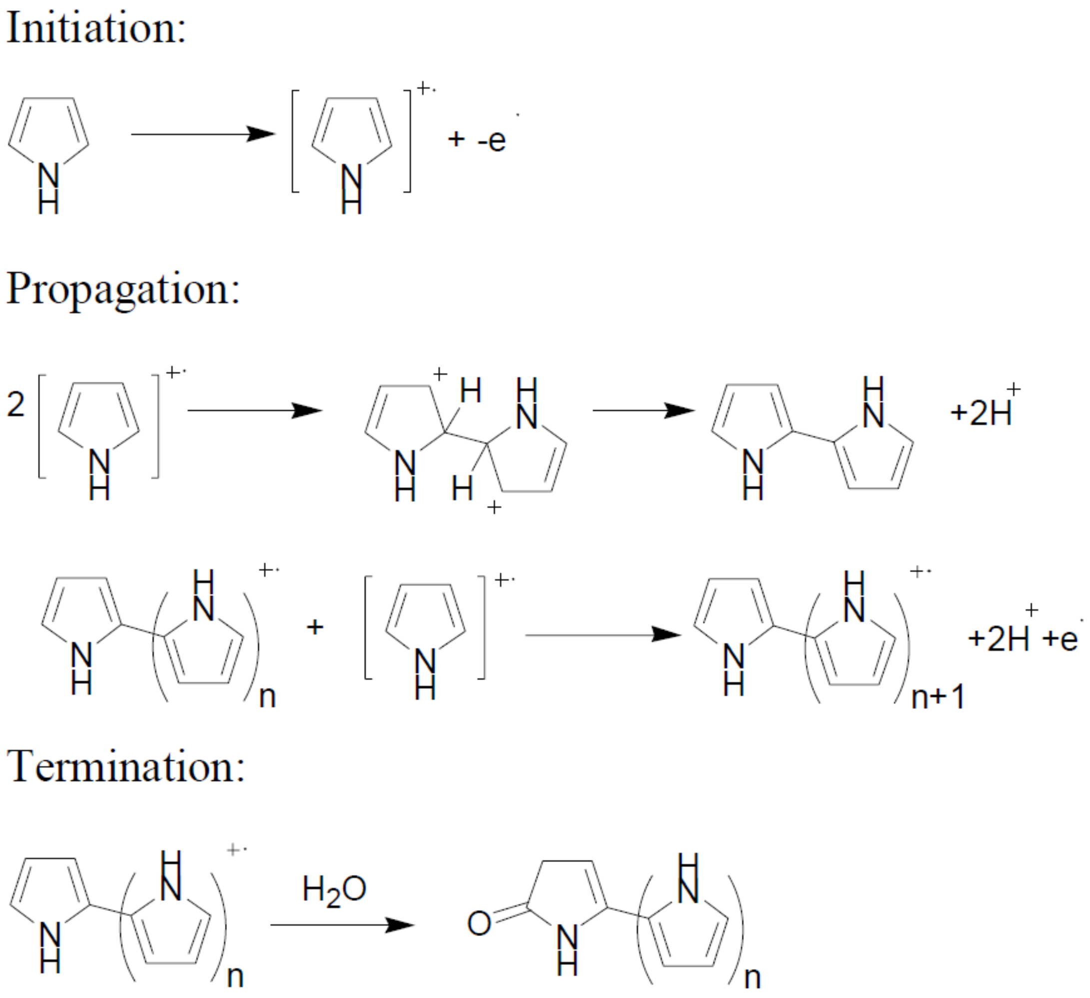


Figure 2.8 Mechanism of Electrochemical polymerization of polypyrrole [23].

Electrochemical polymerization is a technique which has gained popularity in the preparation of the thin film technique. The advantages of the method of electrochemical synthesis process are simple and fast to control of the reaction, and the synthesis can be done in both the presence of water and non water solvent. However, this technique can provide a thin film on the substrate electrode, which will conduct electricity only. It is a limitation of the polypyrrole films prepared by this technique.

Apart from these two methods have already mentioned, there are a lot of choices for the synthesis of polypyrrole. One of them is plasma polymerization, which is the appropriate way to prepare thin films as shown in the following sections.

2.3 Plasma

Plasma is the fourth state of matter. When heated solid to the melting temperature, it will changed to liquid and then will be gas and when the more heat will cause the plasma, which is an ionized gas [27]. The solid, liquid and gas containing a lot of atoms or molecules and the molecules or atoms are moving as one unit. On the other hand, Plasma contains a very large number of free electrons and ions induced the separation of ions and electrons. One of the properties change when the gas becomes plasma is electrical conductivity. In general, gas has properties as an insulator, but when it converted into plasma, the electrically conductive as well. Due to free electrons in the plasma can move freely. So, the plasma state is an electrically conducting medium.

Because plasma is a partially ionized gas so plasma is composed of free electrons, ions, radicals and photons with positive and negative charges are equal called the quasi-neutral. Quasi-neutral means are equal, both positive and negative ions in the plasma. So overall charge in the most of plasmas are neutral

Plasma can be divided into two main types: hot plasmas (near equilibrium plasmas) and cold plasmas (non-equilibrium plasmas). Hot plasmas are very high temperatures of the the plasma electrons and heavy particles, and high degrees of ionization (almost 100%). Examples of hot plasmas include electrical arcs, plasma jets of rocket engines, thermonuclear reaction generated plasmas, etc. In the case of the cold plasmas, temperature of electrons as high enough hot plasmas, but the temperature of the other particles was lower than the hot plasma case (charged and neutral molecular and atomic species) and low degrees of ionization (10^{-4} - 10%). The cold plasmas include low-pressure direct current (DC), Alternating current (AC), radio frequency (RF), microwave (MW) power, and discharges from fluorescent (neon) illuminating tubes and Corona discharges [28].

Plasma is used in four major themes: 1) surface reactions of polymers (plasma treatment); 2) plasma polymerization; 3) plasma-initiated polymerization; and 4) plasma reduction. The preparation of conductive polymers in this study, the plasma is used for reactive plasma polymerization.

2.3.1 Plasma polymerization

Plasma polymerization is an alternative in the preparation of thin polymer films (50nm-1µm). Plasma polymerization takes place in a low pressure and low temperature plasma that is produced by a glow discharge through an organic gas or vapor. Therefore, it is not necessary to use a solvent in the synthesis of the film. Plasma polymerization is a process that is environmentally friendly [40].

The first report of plasma polymerization is the preparing of polymer from oil vapor by using an atmospheric-pressure electrical discharge, as reported by scientists in the Netherlands in 1796 [29]. Later in the year 1860-1870s Berthelot have developed a plasma polymerization [29]. Berthelot has proposed method of preparation polyacetylene by arc synthesis. And in the plasma-induced methane conversion, Berthelot found that the output consists of acetylene, hydrogen and aromatic compounds such as benzene, styrene, biphenyl, and naphthalene, as well as plasma polymer was found. Also in the 1960s Jesch et al. have analyzed the structure of the plasma polymer and have been found that the structure of the plasma polymer with unsaturated bond (C=C, C≡C), the crosslink between the polymer chains, and the addition of oxygen in the air into the polymer chain [29]. As mention above, the structure of the plasma polymer is different from the conventional polymers. For even more understand of the plasma polymerization, the mechanism of the plasma polymerization has been studied extensively [28, 31]. The inclusions of these mechanisms are summarized in the following sections.

2.3.1.1 Mechanisms of Plasma Polymerization

The structure of the plasma polymer is different from the structure of a conventional polymer and therefore the study of the proposed mechanism of the plasma and polymerization can be divided into three mechanisms [32].

2.3.1.1.1Plasma-Induce Radical Chain-Growth Polymerization Mechanism

Plasma can be induced radical and radical may be form as radical fragments of monomers [33, 34], the radical-site at the polymers or monomer. The emergence of radical will be the beginning of the polymerization reaction, as the following equation.

$$\text{M} + \text{plasma} \rightarrow \text{fragments}\bullet$$

$$\text{fragment}\bullet + \text{M} \rightarrow \text{fragment-M}\bullet \text{ . . . . . } \rightarrow \text{fragment-M}\bullet + \text{M} \rightarrow \text{P}_n\bullet$$

Free radical recombination dominates the termination of chain growth or disproportionation or radical transfer or termination by initiator radicals.

$$2\ \text{P}_n^{\bullet} \rightarrow \text{P}_n\text{- P}_n$$

$$\text{P}_2^{\bullet} + \text{P}_1^{\bullet} \rightarrow \text{P}_1 + \text{P}_2$$

$$\text{P}_n^{\bullet} + \text{R} \rightarrow \text{P}_n + \text{R}^{\bullet}$$

$$\text{P}_n^{\bullet} + \text{fragment}^{\bullet} \rightarrow \text{P}_n\text{- fragment}$$

In addition, the plasma can produced C-radicals on the polymer chain by hydrogen abstraction or C-C bond scission, when exposed to the plasma, as the following equation:

$$\sim\text{CH}_2\text{-CH}_2\sim + \text{plasma} \rightarrow \sim\text{CH}_2\text{-CH}^{\bullet}\sim + 0.5\text{H}_2$$

$$\sim\text{CH}_2\text{-CH}_2\sim + \text{plasma} \rightarrow \sim\text{CH}_2^{\bullet} + {}^{\bullet}\text{CH}\sim$$

From the mechanism, plasma polymerization via radical polymerization show the fragment of monomer, the hydrogen abstraction and C-C bond scission. This will cause the polymer to have a branching structure and the crosslink polymer.

2.7.1.1.2 Ion-Molecule Reaction

Ion-molecule reaction is not a conventional monomer addition reaction as in the case of radical or ionic polymerization. But ion-molecule reaction is exchanging ions from one molecule to another molecule [35], such as equation.

$He^{+} + CH_4 \rightarrow C(H_{4-x})^{+} + xH + He^{0}$

However, ion-molecule products can be obtained with more molecular weights than the reactance as following equation.

2.3.1.1.3 Fragmentation Recombination

This mechanism of plasma polymerization is the most different from the chemical chain-growth polymerization reaction [36, 37]. The molecules of the monomers will be completely fragmentation. Then it occurred recombination to the polymer that contains the functional groups and different from the original, as equation.

$$\mathrm{ABCDEF + plasma \rightarrow A + B + CD + E + F}$$
$$\mathrm{n(A + B + CD + E + F) \rightarrow [FCABDE]_n}$$

One of the factors affecting the occurrence of the polymerization model is the energy of the plasma. If the plasma energy is high, the complete fragment of monomers will obtained. If the plasma has lower power, certain molecules may not break down and polymers structured is more likely conventional polymer.

Therefore, mechanism of plasma polymerization is different from the conventional polymerization. Thus, the polymer product has to be different. It is interesting to the chemical structure of the plasma polymer. Which has been studied and proposed the structure of the plasma polymer (see **Figure 2.9**). **Figure 2.9** shows the structure of the plasma-polymerized polyethylene compared with the conventional polyethylene. The structure of the plasma polymer has branching and crosslink between the polymer chains. While the structure of conventional polymer is straight chain. The different structure of the polymers effect to properties of polymer. Properties of the plasma polymer compared to the conventional polymer is more soluble stability, more mechanically tough, and more thermally stable.

Moreover, in the year 2003 Kumar and coworkers have synthesized polypyrrole by using RF plasma (13.56 MHz) at 0.2 torr of pressure and a current density 20 mA/cm^2. And from the infrared spectra analysis, the researcher proposes the chemical structure of plasma-polymerized polypyrrole films as shown in **Figure 2.9**[30-31].

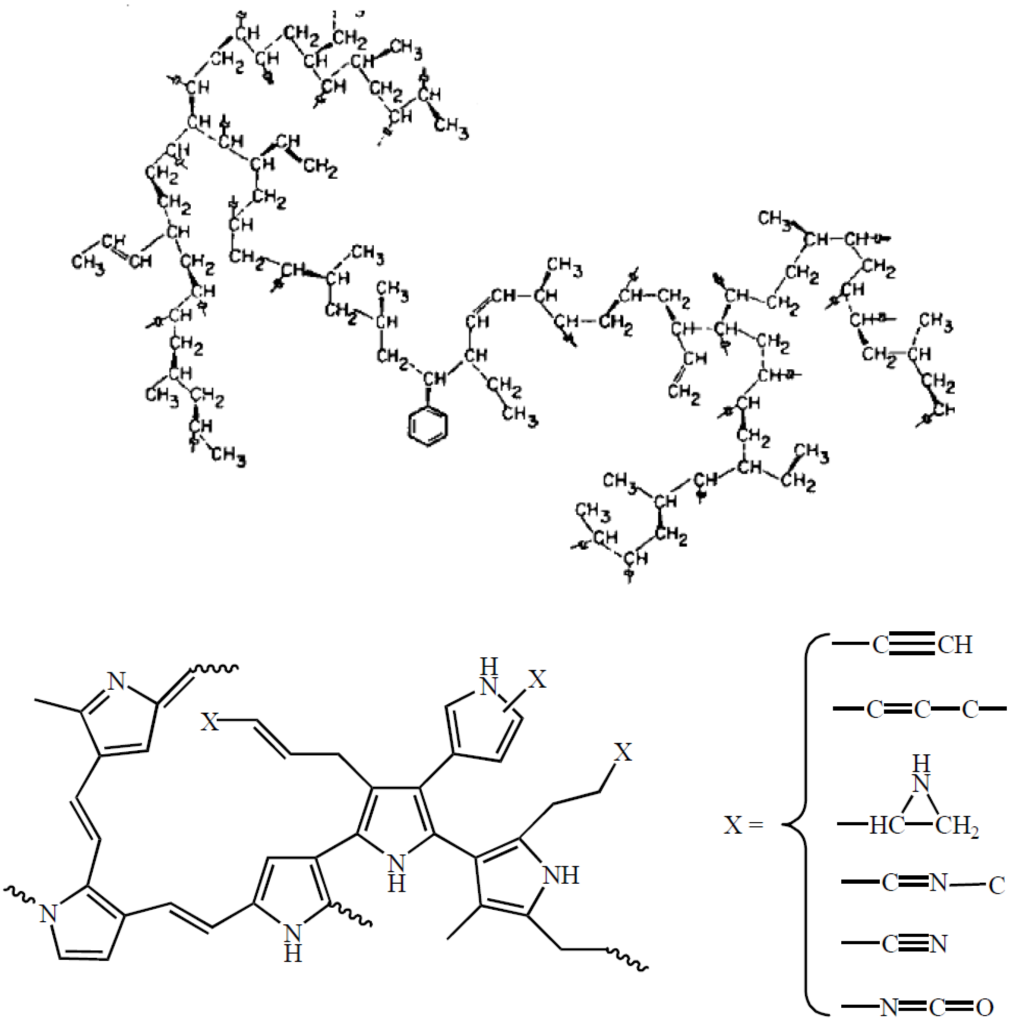


Figure 2.9 Proposed structures of plasma-polymerized polypyrrole [32].

In 2010 Paosawatyanyong and coworkers have prepared polypyrrole films using AC plasma polymerization and in situ doping with iodine [40]. The film is a dense and pin hole free. When increasing the synthesis voltage, the fragmentation of pyrrole ring was increased (see the C/N ratio) and the electrical conductivity of polypyrrole film was decreased too.

From mention above, it is evident that the polymer film prepared by using plasma polymerization. The product film is a dense and pin hole free. The chemical structure of product polymers are containing with branching and crosslinking and this structure are hindering the crystallinity arrangement of the polymer. In the case of the conductive polymer, when the crystallinity of the polymer decrease the conductivity of the polymer will decreases. Therefore, the structure of the conductive polymer with high conductivity is required low branching and crosslink. These can achieve by using plasma at low pressure and the decreased energy of the plasma used in the synthesis.

So plasma polymerization technique is an interesting alternative way to synthesized polymer for the fabrication of electronic device.

2.4 Diode

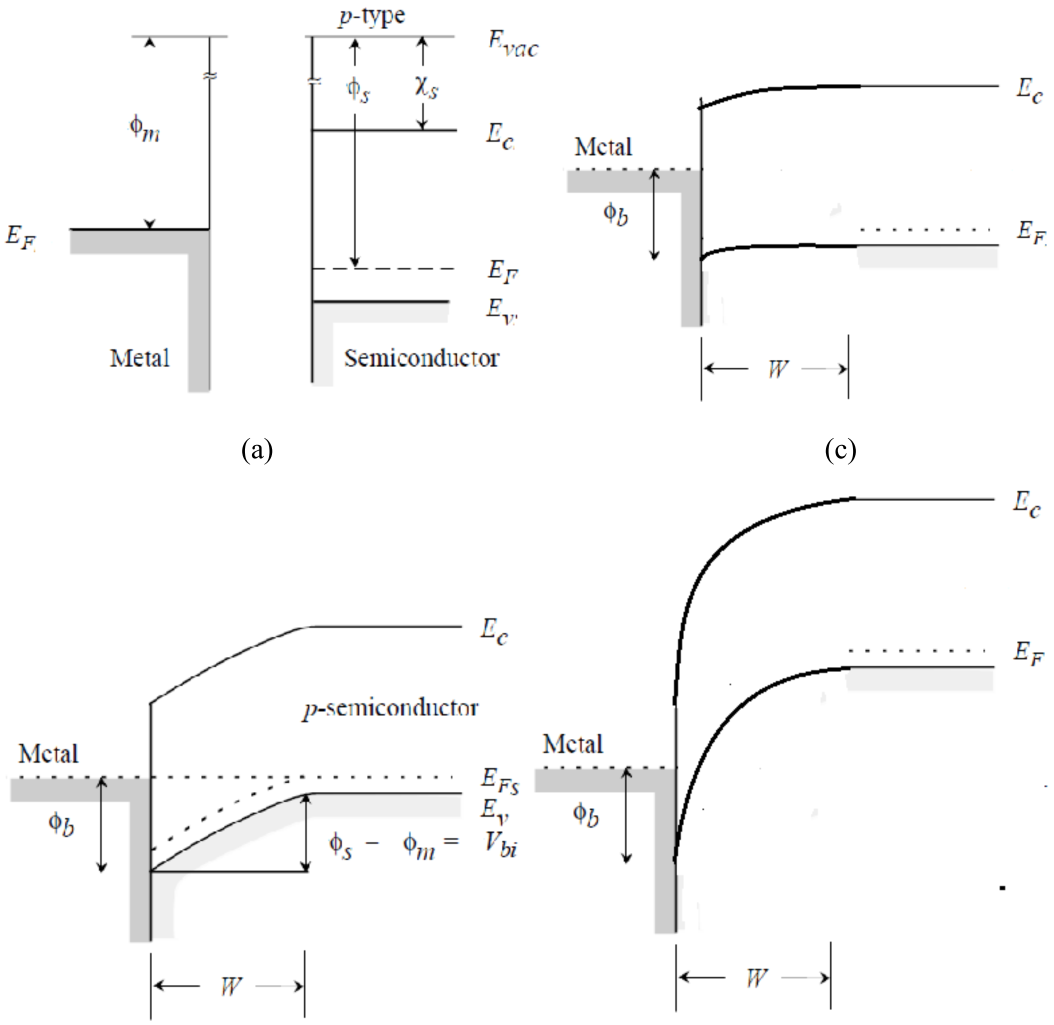
The diode is a two-terminal electronic device. Diodes are often used in the design and control the flow of electric current. It will allow electricity to flow in one direction and block the flow in the opposite direction. There are several types of diodes, each of them is suitable for various applications such as p-n junction diode is the general diode, Zener diode to control the voltage in the circuit, Power diode used in high voltage circuits [41].

In this study, to be fabricated Schottky barrier diode, a diode with a fast recovery time can be used in AC circuits.

2.4.1 Schottky barrier diode

Schottky barrier diode made from junction between the metal and the semiconductor with the different work function and the charge transfer has been occurred until the system equilibrium. Work function is the distance between the fermi level of metal or semiconductor to the vacuum level (fermi level is the level of energy of 50% chance to discover the electron) [41, 58]. The semiconductor-metal junction is divided into two categories, namely p-type and n-type. Details of both are to present follow.

For the p-type semiconductor, fermi level is close to the valence band rather than conduction band. From **Figure 2.10** fermi level of metal is higher than the fermi level of p-type semiconductor and when the metal contacts on p-type semiconductor under zero applied voltage. In this case work function of the semiconductor (ϕ_s) higher than the metal work function (ϕ_m). So the electrons from the metal are transferred to p-type semiconductor and cause negative charges near the interface. While the metal loses electron it will have a positive charge near the interface as well. The charged area is called the "depletion region" or "space charge region". From **Figure 2.10b** evident that the depletion region electric field causes a voltage V_{bi}. V_{bi} to resist the diffusion of charged at the interface of the p-type. semiconductor to the metal caused by the difference in work function (ϕ_s - ϕ_m) until to the equilibrium transfer charged will stop. And the V_{bi} be increased or decreased.

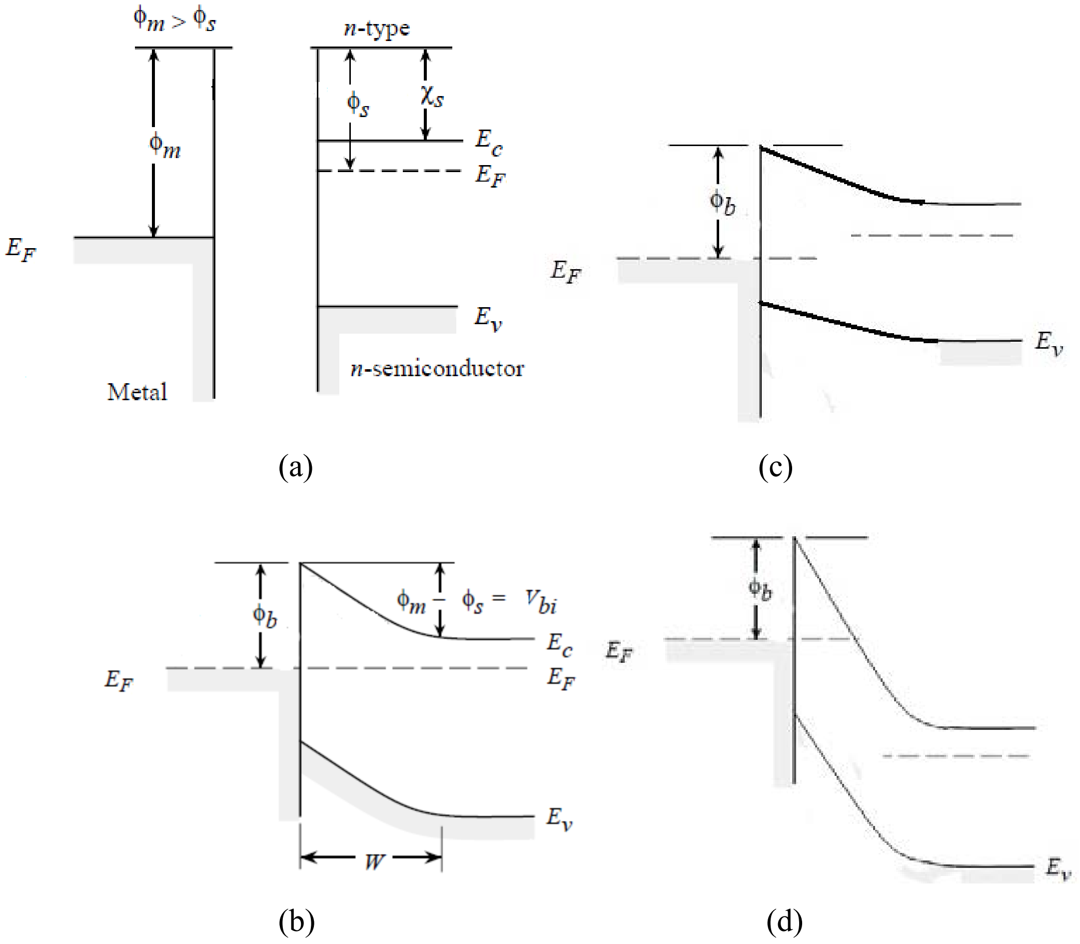


(a) (c)

(b) (d)

Figure 2.10 Schematic band diagram for metal to p-type semiconductor contact when $\phi_s > \phi_m$ showing band bending in the semiconductor (a) disconnected profile (b) zero bias (c) forward bias (d) reverse bias.

When applied voltage to the diode, with the forward or reverse bias voltage. Potential to inject electrons from semiconductor to the metal is the barrier height (ϕ_{Bp}) which is equivalent to $E_g - (\phi s - \chi)$. E_g is the band gap energy of semiconductor, is the electron affinity, which is measured from the vacuum level to the semiconductor's conduction band.



(a) (c)

(b) (d)

Figure 2.11 Schematic band diagram for metal to N-type semiconductor contact when $\phi_s < \phi_m$ showing band bending in the semiconductor. (a) disconnected profile (b) zero bias (c) forward bias (d) reverse bias.

The n-type semiconductor contact is different from p-type semiconductor. The fermi level of the n-type semiconductor is close to the conduction band as shown in **Figure 2.11**. When the n-type semiconductor contact with the metal, electrons from the n-type semiconductor will be transferred to the metal due to the work function of n-type semiconductor less than that of metal ($\phi_s < \phi_m$) cause the depletion region, as well as recent case. In addition, the barrier height of n-type semiconductor can be calculated from $\phi_m - \chi$

At zero applied voltage and equilibrium system, the depletion region of diode has a fixed width. If the applied voltage across the junction whole forward(V_f) or reverse(V_r) bias, Will result in the depletion region width of the semiconductor band will shift down or shift up, as shown in **Figure 2.10 (c, d)** of p-type semiconductor and **Figure 2.11 (c,d)** of n-type semiconductor, respectively

Figure 2.10 b, in equilibrium and zero applied voltage, the electrical current will not flow through. When applied forward bias voltage to metal-to-p-type junction (see **figure 2.10 c**), the barrier for p-region holes is decreased by the volume of bias voltage, and the current flow across the junction dramatically increased. When applied reverse bias voltage to metal-to-p-type junction (see **figure 2.10d**), the barrier is increased, the current flowing through difficulty.

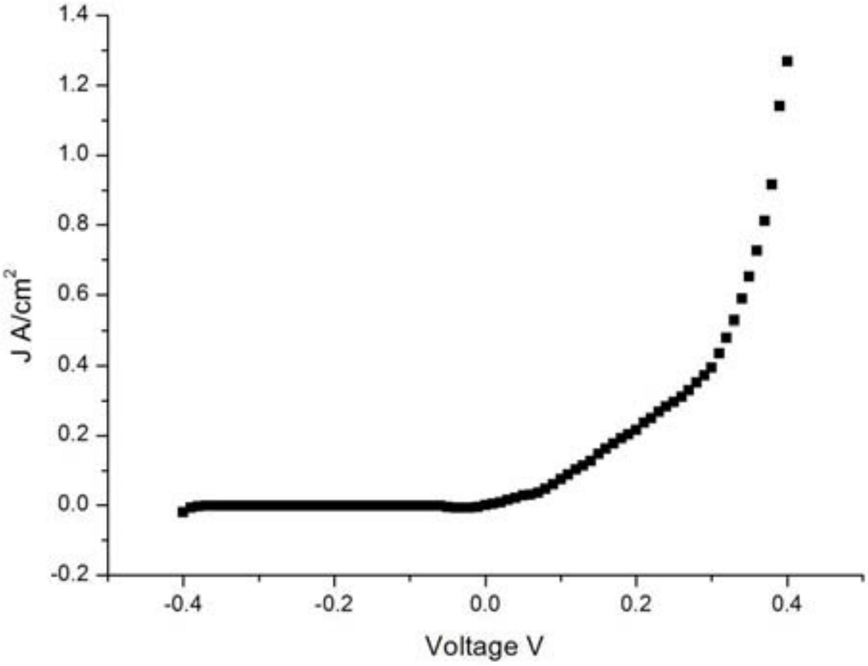


Figure 2.12. I-V characteristic of I_2 doped Plasma-polymerized polypyrrole Schottky diode preparation at 800V for 30 min

From the foregoing, when plot the relationship between the current flows through the diode with bias voltage. The I-V relationship has shown in **Figure 2.12**.

2.4.1.1 Schottky barrier diodes current-voltage equation

The forward current-voltage (I-V) characteristic of Schottky barrier diode compliance the thermionic emission theory as the following Shockley equation [41]

$$I = I_0[\exp(qV_J/kT)-1]$$

Where q is electronic charge, V_J the voltage applied across the diode, k is the Bolzmann constant, I_0 is saturation current, and T is absolute temperature

Moreover, most Schottky diodes show deviations from ideal behavior. It is calculated to describe deviation characteristic of Schottky diodes from above equation by an empirically determined dimensionless parameter called the ideality factor η as the following equation

$$I = I_0[\exp(q(V-IR_B)/ \eta kT)]$$

Factors affecting the deviation characteristic of Schottky diodes have been many factors include quantum mechanical tunneling of carriers though the junction, recombination of electrons and holes in the depletion region

The barrier height of a Schottky barrier diode is an important parameter. The calculation of Schottky barrier height can achieve by using a following equation

$$I_0 = A_eA^{**}T^2 \exp(-q\Phi_B/kT)$$

$$\phi\Phi_B = (kT/q)\ln(A_eA^{**}T^2/I_0)$$

Where A_e is the effective area of the diode, A^{**} is the effective Richardson's constant and ϕ_B is the barrier height of a Schottky barrier diode

There are a lot of reports about fabrication of Schottky barrier diode with polypyrrole. Most of them, Electrochemical polymerization is selected for the fabrication. The metal used to make the rectification contact with several types of Al Au In to be rectifying properties with the polypyrrole.

In 1995 Onganer and coworkers [43] prepare metallic polypyrrole film on a p-type Si substrate by an anodization process. The formed polymer/*p*-Si Schottky diode has been investigated. The polypyrrole polymer offers a well rectifying contact to the *p*-Si semiconductor. The I-V (barrier height $\Phi_B = 0.84$ eV) and C-V ($\Phi_B = 0.94$ eV) characteristics of the devices are improved with increasing Φ_B and decreasing the ideality factor ($n = 1.20$) subsequently a polymer melt processing step. These values of Φ_B, are larger than those of conventional Schottky barrier diodes. Moreover, this study shows that room temperature processing the high barrier metallic polypyrrole/*p*-Si structures.

In 1996 Bantikassegn and coworker prepared sandwich structure of polypyrrole (PPy) doped with small anions like ClO_4^- or large polymeric anions such as polystyrenesulphonate (PSS^-) forms a conducting organic solid. The I –V characteristics of the PSS^--doped device was symmetrical but non-ohmic, while that of the ClO_4^- -doped diode was rectifying.

In 1997 Singh and coworker [44] study the I –V characteristics of the junction between metal and different polymers viz. polypyrrole (PPY), poly (N-methyl pyrrole) [P(NMPY)] and copolymer poly(N-methyl pyrrole–pyrrole) [P(NMPY–PY)] having different compositions. Capacitance–voltage characteristics and Chot plots were used for confirm the formation of the junctions. The results have been explained on the basis of thermionic emission. The fabricating of device from the copolymer with 0.025 M pyrrole and 0.075 M (N-methyl pyrrole) can absolutely not be ruled out as better value of η.

In 1999 Nguyen and coworker [45] prepared electrochemically polymerized polypyrrole, using nickel phthalocyanine toluenesulfonate (NiPcTS), tetraethylammonium toluenesulfonate (TOS), or copper phthalocyanine toluenesulfonate (CuPcTS) as dopants.

The I-V characteristics of these junctions are nonlinear and asymmetrical. The junction parameters, as the ideality and the rectification ratio, are strongly affected by the dopant of the conducting polymer.

In 2000 Van and Potje-kamloth [46] fabricated a gold (Au) contact with polypyrrole (PPy) films doped with the copper phthalocyanine toluenesulfonate (CuPcTS) anion. The J –V characteristics of these junctions are asymmetrical and nonlinear. The junction parameters extracted from the J –V characteristics (the saturation current density, the rectification ratio and the ideality factor) and from the C–V characteristics (the built-in voltage and the charge carrier concentration) are strongly influenced by the thickness and by the preparation temperature of the PPy layer.

In 2001 Abthagir and Saraswathi [47] fabricated Schottky barriers of the type Au/polypyrrole/Al (or In). The rectification characteristics were obtained from the current–voltage and capacitance–voltage measurements at room temperature. The analysis of data using thermionic emission theory for calculated the junction parameters of reverse saturation current, ideality factor, rectification ratio, and barrier potential. As the result, the diode formed with Al metal presented better values for the ideality factor, rectification ratio, and breakdown voltage.

In 2002 Campos [48] was synthesized thin polypyrrole films doped with dodecylbenzene sulfonic acid and measured current density as function of voltage (J-V) and capacitance-voltage (C-V). The J –V characteristics of these junctions are asymmetrical and nonlinear. This diode shows methane sensor properties, which was explained by changes in the Schottky barrier height and in the carrier concentration of polypyrrole sample owing to methane exposure.

In 2007 Chan Yu King and coworkers [49] synthesize copolymer composed of pyrrole and 3-alkyl pyrroles. A strong linear depend on the alkyl chain length on the as-prepared copolymer physical properties is described via (a) DSC (for phase transition temperatures and enthalpy changes) and (b) UV-vis. A trend in the doping level of copolymers vs alkyl chain length is also evaluated, via IR, by taking the ratio of polaronic and bipolaronic band intensities. The copolymers are found to be soluble in organic solvents and their solutions can be cast onto glass substrates or metals resulting in thin films. But the copolymer cannot be used as the electroactive component for Schottky diode with high ideality factor.

In 2009 Shakoor and Rizvi [50] study electrical properties of Schottky barrier diode fabricated using Aluminum for Schottky contact and indium tin oxide for ohmic contact and containing polypyrrole doped with dodecylbenzene sulfonic acid in the presence and in the absence of a plasticizing agent hydroquinone. Various parameters, e.g. saturation current, ideality factor, built in voltage; carrier concentration and barrier height have been calculated and found to be affected by the presence of hydroquinone in the doped polymer. The electrical behavior of the systems was found to be in a good agreement with the thermionic emission model for the Schottky barrier devices. The interaction of the doped polypyrrole with hydroquinone was explained in terms of change in the barrier height and in the carrier concentration of the diodes.

From literatures, polypyrrole presented rectifying properties with several types of metal such as Au, In, Al. The contact of PPy/Al presented good properties of Schottky barrier diode as low ideality factor. The most of preparation technique is electrochemical polymerization. But less reports to prepared Schottky barrier diode with plasma polymerization. Therefore, we interested to fabricate Schottky barrier diode using plasma polymerization.

2.5 Piezoelectric Polymer

Piezoelectricity refers to the general from stress or strain on the piezoelectric material, and conversely to the mechanical deformation of the material in response to application of an electric signal.

Prior to 1940, the only single-crystal material was show piezoelectric properties including quartz, Rochelle salt (tetrahydrate of sodium potassium tartrate), ammonium dihydrogen phosphate, and tourmaline [51]. Later 1940s piezoelectric effects could acquire in polycrystalline ceramics. They were first subjected to electric field large enough to preferentially orient electric moments within polarized regions of the material. The process of subjecting a material to high electric fields to impart dipole orientation can be reversed under the influence of an electric field is said to be ferroelectric. The most common ceramic piezoelectric materials are barium titanate and mixtures of lead titanate and lead zirconate (PZT) [52]. Some natural materials such as bone, tendon, and wood also have piezoelectric property as well as synthetic polyaminoacids, have been summarized by Fukada and co-workers [53]. In general, the piezoelectric coefficients of these materials are too small to find application outside the system. The first report of organic piezoelectric polymer synthesize with large piezoelectric effects to be of commercial interest can be attributed to Kawai in 1969, who reported large response from drown and poled polyvinylidene fluoride (PVDF). Since then, contributions from laboratories around the world have led to more understanding of ferroelectricity in this polymer.

In addition to electrical properties of the piezoelectric polymer, the physical properties of the piezoelectric polymer are similar to the common polymer. They are obtained in large-area flexible sheets that present high strength and in major cases, high impact resistance. These properties are dissimilarity from those of single-crystal or ceramic piezoelectrics. Therefore, it rarely found the using of piezoelectric polymer to replace the ceramic piezoelectrics.

2.5.1 Piezoelectric coefficients

The electrical response out of piezoelectric leashed to a mechanical incentive can be explained in a diversity of coefficients that depend upon the amounts of measured and the seat of the electrodes relative to the mechanical strain or stress direction. Semicrystalline polymers are often leashed to mechanical orientation between processing resulted in anisotropic mechanical properties. Anisotropic mechanical property is the property of being directionally dependent. Therefore, the calculation of the coefficient can be calculated either x, y, z axis.

The mechanical variable can be each the strain applied, S, or the stress that results, T. Electrical response can be measured by the charge per unit area, D, displaced through a closed circuit between the two electrodes, or the electric field, E, generated across the polymer film under open circuit conditions. The “strain constants” are

$$e = (\partial D / \partial S)_E \qquad \text{and} \qquad h = (\partial E / \partial S)_D$$

The “stress constants” are

$$d = (\partial D / \partial T)_E \qquad \text{and} \qquad g = (\partial E / \partial T)_D$$

These piezoelectric constants are related the material’s mechanical and electrical properties such as permittivity ($\epsilon\epsilon_0$) and Youmg’s modulus (G) [54].

$$d_{ij} = \epsilon_0 \epsilon_i g_{ij} \quad \text{and} \quad e_{ij} = d_{ij} G_j$$

In polymer films case, the coefficient is the summarized of responses in the three axis. That is,

$$d_{sum} = d_x + d_y + d_z$$

Where d_x, d_y, d_z are piezoelectric constants of X, Y, Z axis respectively [54].

2.5.2 Piezoresistive strain sensor

The piezoelectric material has the potential to be fabricated the piezoresistive strain sensor. The material is resistant changes in to strain. The quality of the strain sensor can be measured from the resistance of sensor and gauge factor (GF). The gauge factor (GF) can be derived from Ohm's law and Hooke's law [42]:

$$\frac{\Delta R}{R_0} = GF \cdot \varepsilon$$

Where $\Delta R = R - R_0$, R_0 and R are the resistances at zero strain and at strain ε, respectively, and GF is the piezoresistive gauge factor.

There are some reports on the polypyrrole in the piezoelectric property. Methods to prepare the film that either electrochemical polymerization, chemical polymerization, and photopolymerization. The films synthesized by these techniques showed piezoelectric behavior.

In 2005 Dunne and coworkers [55] developed polypyrrole-coated polyurethane foam sensor was explained, as well as the development of a prototype sensing garment with sensors in several areas on the torso to measure breathing, shoulder movement, neck movement, and scapula pressure. The polypyrrole foam represents considerable promise as a sensor for medical and wearable applications. Furthermore, the foam's stability of response shows durability over time.

In 2007 Pini and coworkers [56] used method to grow a PPy/p-toluene sulfonic acid (PPy/pTSA) structure in the form of an IDE around a layer of ceramic fibers for application as active fiber composites (AFC) with polymeric electrodes.

Through-the-thickness electrodes are expected to enhance the overall actuation properties of the AFC by improving the contact angle between fibers and electrodes. The use of polymeric electrodes is prospective to ease up the fabrication process and make it more flexible. AFCs can be used both as sensors or actuators.

In 2009 Yamada and coworkers have expanded a new method for the growing of conductive polymer in 3D microstructures [57]. A Nafion sheet was utilized as the deposition substrate instead of a glass plate. The sheet substrate was actualized for photofabrication by using a low power of laser. This is probably due to the acceleration of the photopolymerization reaction based on the higher density of the reaction components and the improved nucleation process of the pyrrole polymeric products in the Nafion sheet. The polymerization area reported a high spatial selectivity and can be scanned in the XYZ axis by a piezo device.

In the same year Barnoss and coworkers synthesized polypyrrole via chemical polymerization from the vapor phase and investigated as a function of the pressure of various chemically inert gases as well as of the film thickness. They noted that the character of the piezoresistive response is a function of the pressure and the pressurization respond observed at films with thicknesses lower 70 nm. Therefore, thin PPy films appear better candidates for pressure sensors than thicker films.

The mentioned above reports displayed that polypyrrole films have piezoelectric property with various synthesized methods. Therefore, we would like to fabricate strain sensor by using plasma-polymerized polypyrrole and explore more into details.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

Analytical grade chemicals were utilized without further purification. Pyrrole monomer was acquired from SIGMA-ALDRICH. Iodine (dopant), acetone, and methanol were purchased from MERCK. Nitrogen gas was obtained from TIG.

3.2 Equipment

The attended devices were studied by the following technique.

3.2.1 Attenuated total reflection Fourier transforms spectroscopy (ATR-FTIR)

Nicolet iS10 FT-IR spectrometer was employed for investigates functional groups of polypyrrole films. The spectra were detected in the range of 750 - 4000 cm^{-1}.

3.2.2 Scanning electron microscope (SEM)

JEOL, JSM-6480LV scanning electron microscope was used for analyzed surface morphology and thickness of polypyrrole films. The film thickness was measured by cross sectional mode and each value was an average of three reading before reported.

3.2.3 Electric conductivity

Two-probe technique was used to measure the resistance of the electrical conductivity. HP 4140B pA meter / DC voltage source was used to measure the current (I) as a functional of the applied voltage (V) from -5 to 5 V, including Lab View program.

A Hewlett Packard pA meter model 4140B was used to measure the DC current-voltage characteristic of the Schottky diodes. A diagram of DC measurement setup is illustrated in **Figure 3.7**.

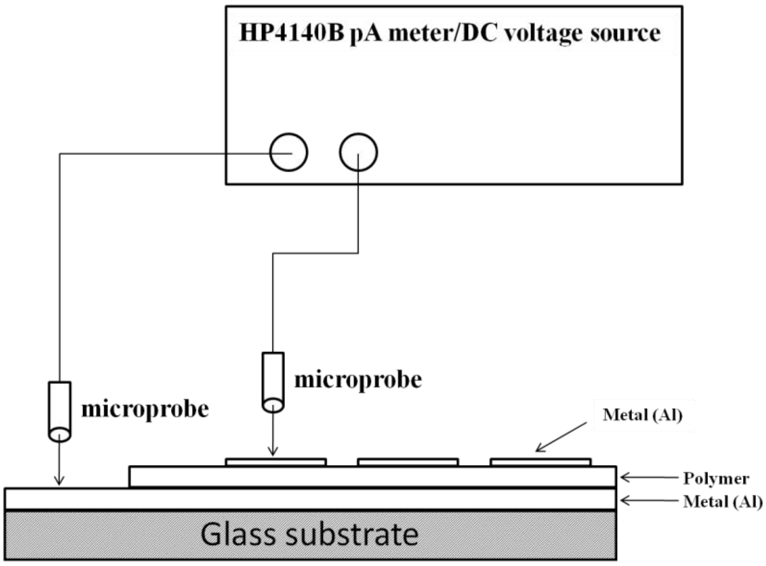


Figure 3.1 Schematic diagram of DC measurement setup.

3.3 Fabrication of Schottky barrier diodes

Generally, Schottky barrier diodes need to be ohmic contact and rectifying contact. In this research, Schottky barrier diodes were invented by the sandwich structure, the polypyrrole film between a rectifying contact on the top and ohmic contact (see **Figure 3.1**). The Schottky barrier diodes were fabricated by these following steps.

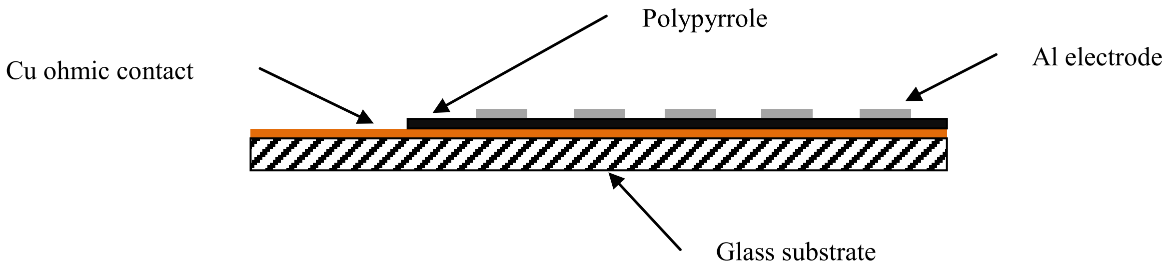


Figure 3.2 Drawing show cross-section view of one example of a plasma polymerized Schottky diode structure.

3.3.1 Preparation of glass substrates

The first step of Schottky barrier diode fabrication was prepared glass substrates. Glass substrate (1.5×2.5 cm^2) was washed by ultrasonic bath for 5 minutes with three types of solvents including acetone, methanol and deionized water. After that, substrate was cleaned and baked in the oven at 100 °C for 5 minutes. Later, the substrates can be stored in a desiccator for using.

3.3.2 Ohmic contact preparation (first layer)

Glass substrate was coated with a copper through the glass substrate to act as an ohmic contact of the Schottky barrier diode with a DC magnetron sputtering under a pressure of 6.0×10^{-5} torr power 27W for 15 minutes.

3.3.3 Plasma polymerization and iodine doped plasma polymerization of polypyrrole (second layer)

AC-plasma system (see **Figure 3.2**) was used for fabricated polypyrrole electronic devices. Then, they were characterized with the following equipment. Details of characterization as shown following topic.

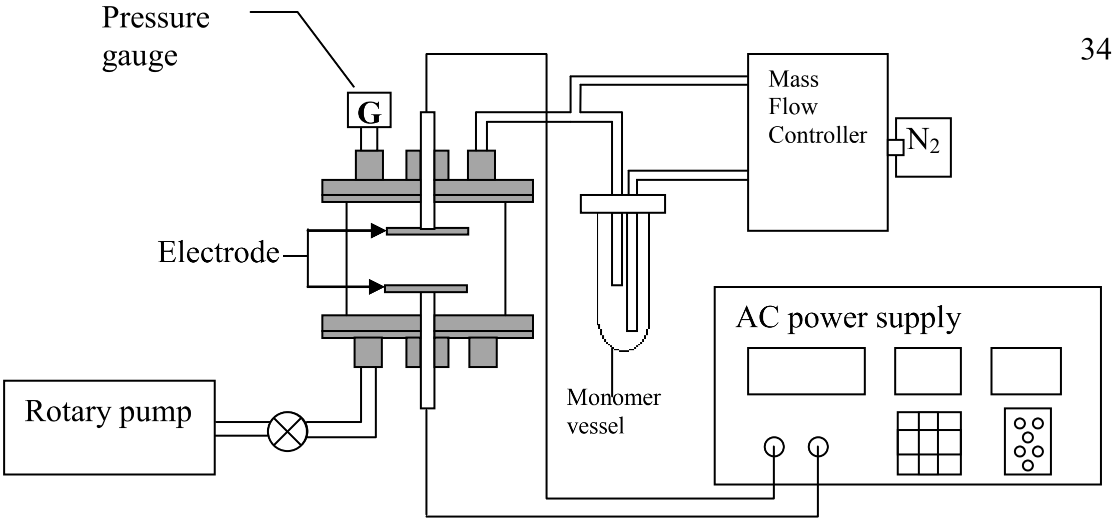


Figure 3.3 The simplifiled schematic diagram of the AC plasma system

All polypyrrole films were used in present research were prepared by the AC plasma system. The substrates with Ohmic contact were placed in the chamber (between electrodes) as shown in **Figure 3.2**.The system's pressure was decreased to 0.02 torr for setting the vacuum system. The nitrogen gas was fed with 5 sccm flow rate into the chamber. Then, plasma pre-treatment was used with 800V of voltage, 0.4 torr of pressure for 1 minute.

After the pre-treatment, Nitrogen gas was fed through the monomer vessel into the chamber, the gas bubbles through the monomer vessel and pyrrole monomer was brought into the chamber with nitrogen gas. Pyrrole monomer vapor and nitrogen gas within the chamber can be induced by an alternating current to generate plasma. Then, plasma polymerization was started the deposition onto the sample. This process was performed at various conditions; AC voltage inputs for glowing plasma discharge were 800, 1000, 1200 and 1400 V. The operating time was kept at 30, 60, and 90 minutes. The result is second layer of the Schottky barrier diode has been prepared.

In doping process, the iodine crystals in a small glass tube were placed into the chamber before the start of the pre-treatment with plasma.

3.3.4 Rectifying contact preparation (Third layer)

In this step, the metal top layer of the samples which acts as rectifying contact with PPPPy was prepared by metal films from metal evaporation technique, of metals at low pressure. Metal molecules were evaporated up to the surface of the sample, and formed metal films on the surface of the sample. This technique is particularly suitable for coating a metal on the polypyrrole film rather than using DC magnetron sputtering technique. Because the bombardment of metal molecules on a polymer film by using DC magnetron sputtering technique can damage the polymer films on the surface of the sample.

Kurt J. Lesker Company Aluminum pellets of 99.99% purity and 1/8" diameter was used to evaporate for making films with 3.75 x 10^{-6} torr of pressure. In the first stages of evaporation, the aluminum pellets are heated by the power supply of the electrodes 75A for 2 minutes. Then increasing the amount of electric current of the electrode until the aluminum film thickness is 200 nm.

3.4 Strain sensors fabrication

Strain sensor was prepared by the deposition of polypyrrole film on a flexible substrate. The resistance of the sample changed, when apply strain to the sample. The polypyrrole strain sensor fabrication process is shown as follows.

Prior to plasma polymerization process, the preparation of Polymethyl methacrylate (PMMA) substrate need to be carried out for the electrical conductivity test of the film with two copper electrodes on each end of the PMMA substrate. The DC magnetron sputtering operated at 0.005 torr, 27 W, and 10 minutes was used to coated copper electrodes with the size of 0.7×1.5 cm^2. For the PPPPy film fabrication process, nitrogen gas was used as a carrier gas to transport pyrrole monomer vapor from the monomer vessel into the chamber. The synthesis of PPPPy film was performed by using inputs voltage of 800, 1000, 1200 and 1400 V for 30 min.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Chapter overview

This research is divided into two parts as fabrication of Schottky barrier diodes and fabrication of piezoresistive strain sensor

Schottky barrier diodes are used as a sandwich structure with three layers films. The first layer is a Copper film prepared by DC magnetron sputtering technique, producing smooth Copper film on a glass substrate. The second layer of polypyrrole films were prepared by using the AC plasma polymerization producing a film of polymer on the Copper first layer by varied of input voltage 800,1000,1200,1400 V in the synthesis and the operating time was varied for 30, 60, 90 minutes. Finally, the third layer is the aluminum film, which was prepared by metal evaporation technique with using a shadow mask over the substrate so that a film with a spot diameter 1 mm.

The properties of the Schottky barrier diodes were divided into the polypyrrole film properties, and electrical properties of diodes. The two parts are reciprocity. In the beginning the plasma polymerized polypyrrole film was measured by ATR-FTIR spectroscopy to analyze the functional groups. The morphology and thickness of polypyrrole films were investigated by SEM. The properties of polypyrrole films would be summarized to determine with the electrical properties of the Schottky barrier diodes as shown by the IV characteristics. Then calculate the diode parameters such as saturation current I_0, ideality factor η, bulk resistance R_B, barrier height ϕ_B were measured.

The AC plasma polymerization technique can be used for production of piezoresistive strain sensor using PMMA films as substrates, which are flexible property. Before plasma polymerization, the electrodes can be prepared by DC magnetron sputtering technique to produce the electrodes by a gap of 1mm. Then the synthesis of poly-pyrrole film onto a space, result to a strain sensor. The results of the strain sensor were analyzed by measuring the resistance of the sensor. Then strain was applied to the sensor and measures the resistance to change. This is indicated by the gauge factor GF to determine the quality of the sensor.

4.2 Schottky barrier diodes

For the fabrication of Schottkybarrier diodes, the parameters of time and voltage on plasma polymerizationwere studied. The characterization of polypyrrole films and electrical properties of Schottky barrier diodes were discussed in details below.

4.2.1 Characterization of plasma-polymerized polypyrrole films (PPPPy)

4.2.1.1Functional groups and chemical characteristics

ATR FT-IR spectroscopic was operated on the AC plasma-polymerized polypyrrole films to analyze the significance functional groups of the film. For **Figure 4.1**, the spectra obtained from films synthesized at 800,1000,1200,1400 V of voltage and data are summarized in **Table 4.1**.

All of the spectra from plasma-polymerized polypyrrole exhibit same peaks. Each spectrum contains characteristic peaks of plasma-polymerized polypyrrole as found in the previous work [40]. A band is observed between 3500-3000 cm^{-1}, together with two overlapping peaks of N-H stretching of the pyrrole ring at 3400 cm^{-1}, and the C-H aromatic bonds at 3200 cm^{-1} band [40]. The absorption of aliphatic C-H bonds is found at 2938 cm^{-1}, due to partial fragmentation of the pyrrole ring. The N-H bending of amine and/or a C=C aromatic stretching at 1633 cm^{-1} was observed this peak is indicated a conjugated system contain corresponding to in the polypyrrole chain or the generated of aromatic cyclic structure. The new position at 2200 cm^{-1} maybe assigned to C≡N stretching and/or –N=C=O stretching. It is may be found that oxygen contains in the films, but does not consist on liquid pyrrole. In the chamber, oxygen and pyrrole coincidentally turn to plasma phase during polymerization with accordance to the result of other authors [40]. Whereas, if AC plasma system doesn’t have contaminated oxygen, this peaks may be consisted from fragmentation of some pyrrole rings.

Table 4.1 ATR FT-IR band assignments of plasma-polymerized polypyrrole compare to chemically-synthesized polypyrrole from previously reported [40].

Assignments	Wavenumber (cm^{-1})	
	Chemically synthesized polypyrrole [40]	Plasma-polymerized polypyrrole
N-H stretching	3400	3350
Aromatic C-H stretching	3145	3200
Aliphatic C-H stretching	2938	2935,2851
C≡N stretching, and/or –N=C=O stretching	2250	2200
N-H bending and/or aromatic C=C stretching	1633	1630
Aliphatic C-N stretching and/or aromatic N-H bending	1210,1020	-

Moreover, Peaks found in the spectrum of polymer are relatively broad band due to the amorphous structure of the plasma polymerized material with containing with branching and crosslinking. This caused by fragmentation of pyrrole rings in the high energy plasma process.

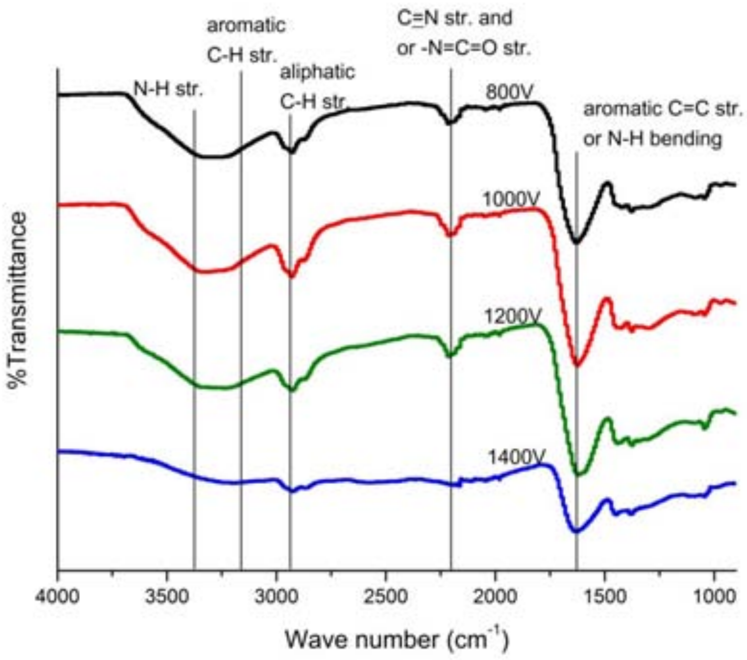
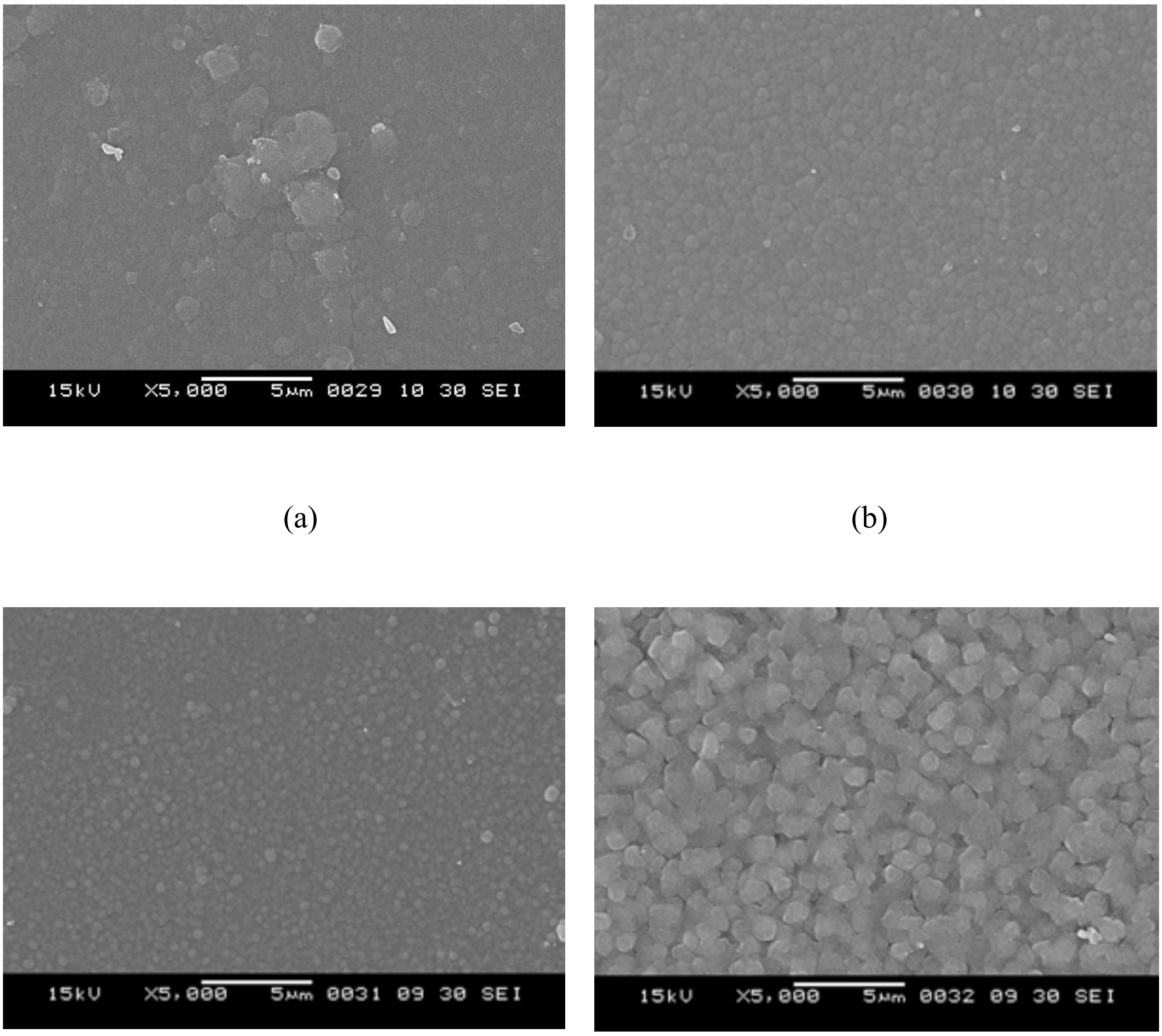


Figure 4.1 ATR-FTIR spectra of plasma-polymerized polypyrrole at different synthesized voltage (800, 1000, 1200, 1400V)

4.2.1.2 Films morphology

SEM analysis was used to investigate the morphology of plasma-polymerized polypyrrole films. SEM displayed in **Figure 4.2** Shows the surface of the plasma polymerized polypyrrole with various voltages. It represented that the polypyrrole films with small degree of grain became smooth at the voltage less than 1200 V. The film grain size was reduced when the voltage increases due to the synthetic polymer with the high power, a lot of the producing nucleide were generated and the number will be increased according to the used of energy. As a result, the grain size was reduced at high voltage. In case of 1400V, the film has a high roughness due to the very high deposition rate of the film. Cross section of the film is shown in **Figure 4.3** demonstrated that plasma-polymerized polypyrrole have dense and pinhole-free films under all applied voltages. In addition, film thickness increases with increasing of synthesis potential as shown in **Figure 4.4(a)** and the effect of reaction time on the thickness of the film was also shown. When reaction time increased, film thickness was increased as **Figure 4.4(b)**.

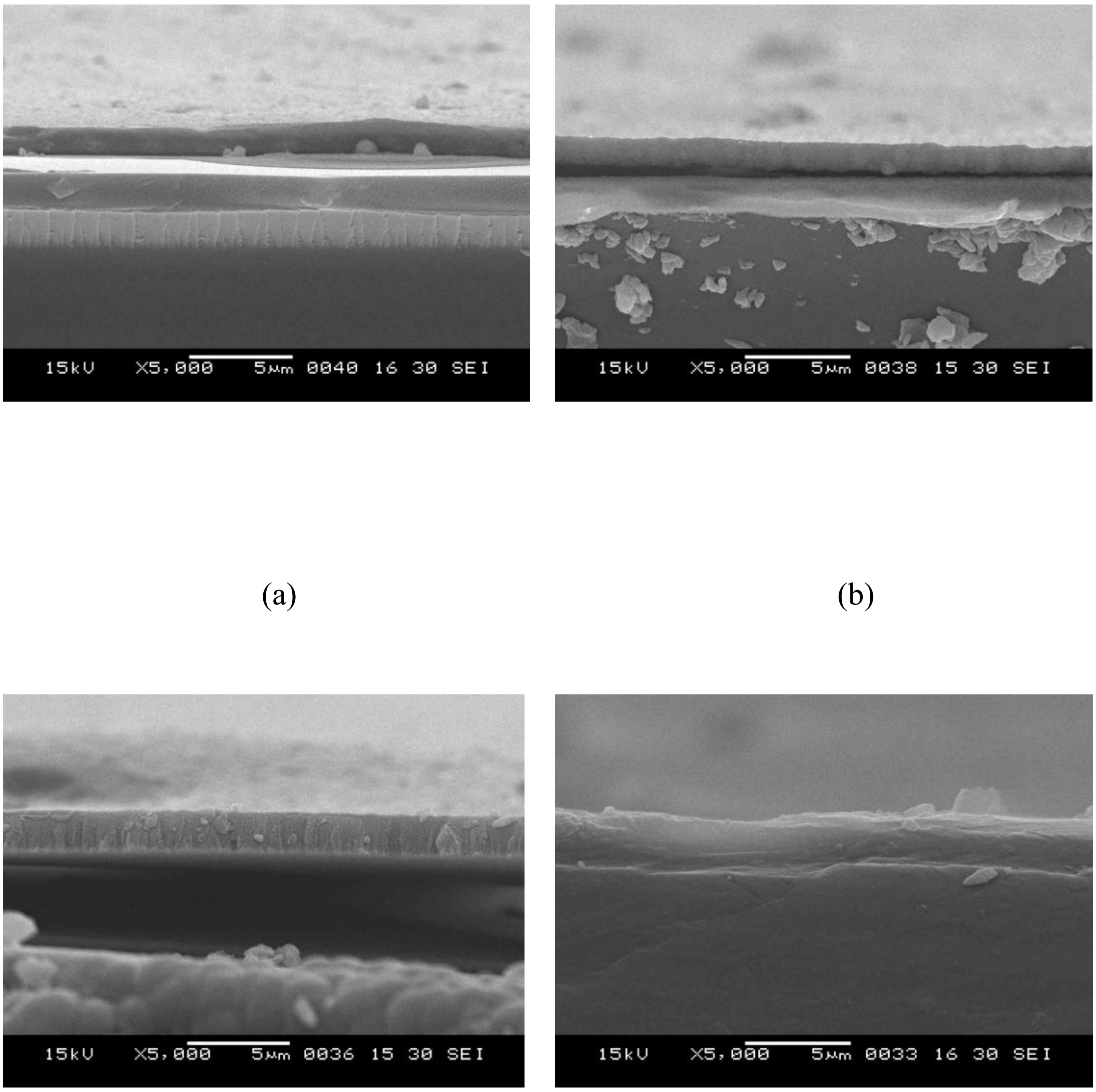
From these results, the increasing of voltage and reaction time resulted to high film thickness and the high voltage resulted to a lot of small grain and high quality of grain boundary. However, a lot of the grain boundary was negative in conductive action film. In addition, as rough film was obtained at 1400 V due to the high deposition rate, the polymer chain could not be arranged the structure on the surface. Moreover, ATR-FTIR spectra showed that the structure of plasma polymerized polypyrrole was different from conventional polypyrrole. The peak of aliphatic C-H stretching at 2938 cm^{-1}, 2200 cm^{-1} maybe assigned to C-H stretching and C≡N stretching and/or –N=C=O stretching, respectively. The literature reported carbon per nitrogen ratio (C/N ratio) of AC plasma polymerized polypyrrole value was 4.0-5.4[32]. It was found that, there is a discrepancy from the ideal of polypyrrole (C/N ratio = 4). This incident is typical of the plasma polymer synthesis, especially at high power. Therefore the plasma required lowest power for prepared smooth and low fragmentation of pyrrole ring.



(a) (b)

(c) (d)

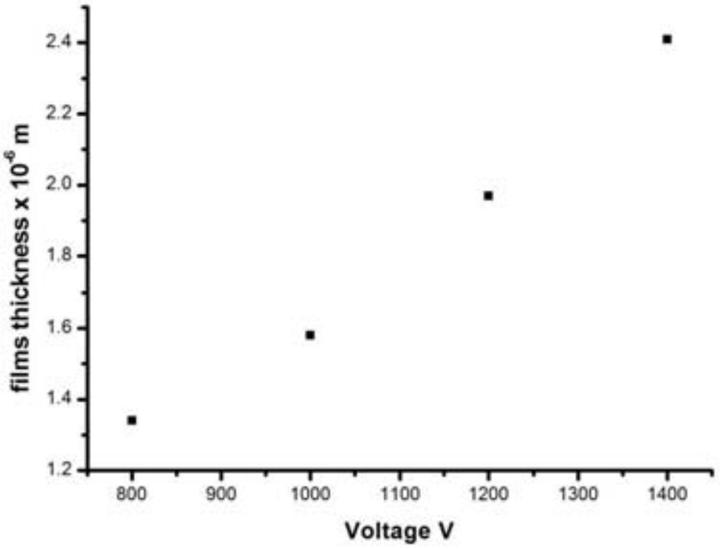
Figure 4.2 Morphology of plasma-polymerized polypyrrole films on the Copper coated glass substrates determined by scanning electron microscopic technique at 30 minutes and various voltages; (a) 800 V, (b) 1000 V, (c) 1200 V, (d) 1400 V



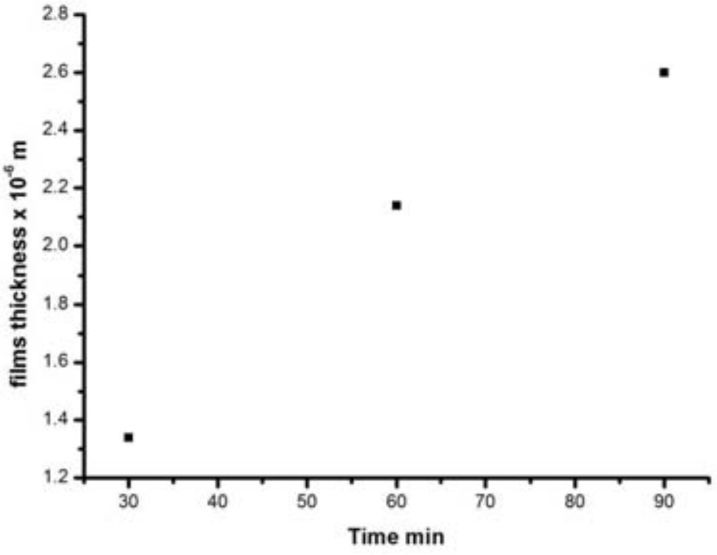
(a) (b)

(c) (d)

Figure 4.3 Cross-sectional analyses of plasma-polymerized polypyrrole films on the Copper coated glass substrate determined by scanning electron microscopic technique at 30 minute and various voltages; (a) 800 V, (b) 1000 V, (c) 1200 V, (d) 1400 V



(a)



Figrue 4.4 The PPPPy film thickness at (a) various AC voltages (b) reaction times.

4.2.2 Characterization of in situ Iodine doped plasma-polymerized polypyrrole films (PPPPy/I_2)

4.2.2.1Functional groups and chemical characteristics

Figure 4.5 shows the ATR-FTIR spectra of in situ iodine-doped plasma-polymerized polypyrrole by AC plasma polymerization at different AC voltages for 30 minute compared to undoped spectrum at 800V of voltage. Characteristic peak of PPPPy/I_2 spectra appear at the same position of undraped. However, spectra of iodine-doped plasma-polymerized polypyrrole were broader than undoped, indicating high amorphous. This may be due to iodine molecule is larger than that of nitrogen molecule resulting in high energy of collision and high pyrrole ring fragment, confirmed by C/N ratio. From previous work, the C/N ratio in the range of 5.5-7.3 indicates the loss of nitrogen atom increased. The peak at 1400 cm^{-1} as assigned to CH_2I and $CI=CH_2$ stretching of PPPPy/I_2 related to iodine in polymer chain.

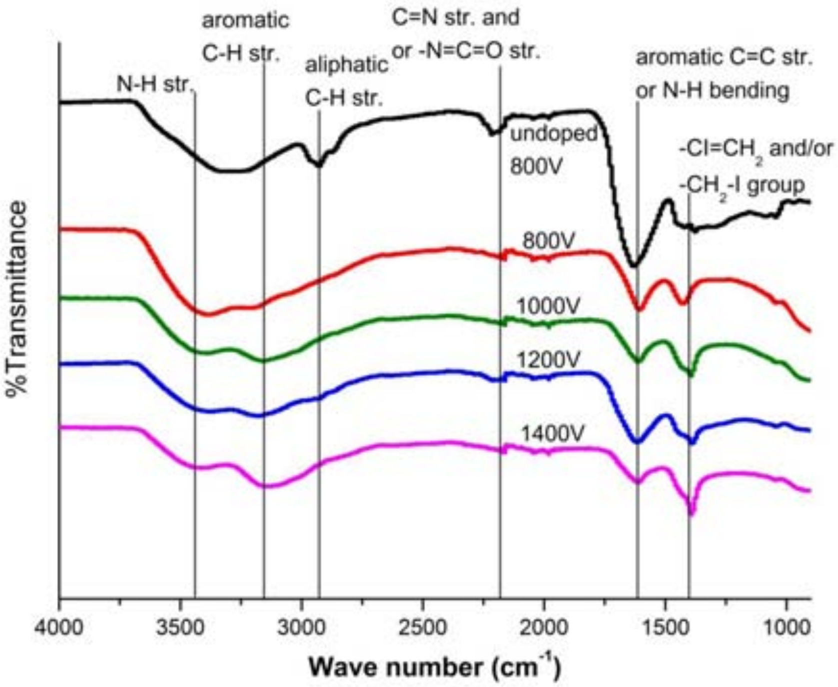


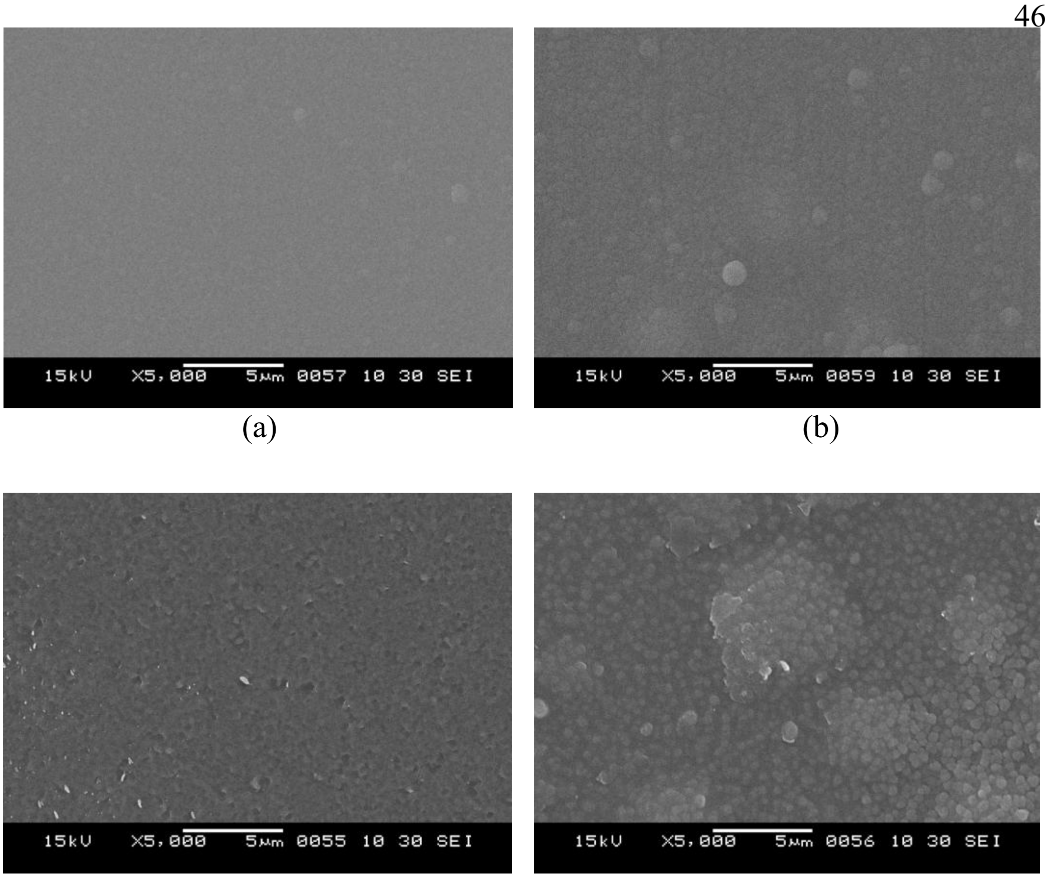
Figure 4.5 ATR-FTIR spectra of undoped at 800 V for 30 minute and in situ iodine-doped plasma-polymerized polypyrrole at different AC voltages at 30 minute reaction time.

4.2.2.2 Film morphology

Figure 4.6 the *in situ* iodine-doped plasma-polymerized polypyrrole films by AC plasma polymerization at various voltages and thickness of the films are provided in **Figure 4.7**. Surface of PPPPy/I_2 films was occupied is shown in **Figure 4.6** smoother than that films compared to those of the undoped polypyrrole films. This is consistent with the results as thickness of PPPPy/I_2 films (1.02-1.98 μm.) less than PPPPy films (1.34-2.41 μm). So, the deposition rate of PPPPy/I_2 is lower than undoped PPPPy, this may be caused by the absorption energy of iodine in the system. Therefore, the polymer chains have more time to arrange the structure on the surface, resulted to thin and smooth PPPPy/I_2 films.

The in situ iodine-doped plasma-polymerized polypyrrole films by AC-plasma polymerization at various voltages is shown in **Figure 4.6** and thickness of the films is provided in **Figure 4.7**. Surface of PPPPy/I_2 films were occupied smoother than that films compared to those of the undoped polypyrrole films. This result is relates with thickness of PPPPy/I_2 films (1.02-1.98 μm.) thinner than PPPPy films (1.34-2.41 μm). This noted that the deposition rate of PPPPy/I_2 was lower than that of undoped due to the absorption of energy. Therefore, the polymer chains have more time to arrange the structure on the surface, resulted to thin and smooth PPPPy/I_2 films.

In conclusion, the properties of PPPPy/I_2 films are also tending to PPPPy films. Thickness increases with increasing the voltage or the reaction time. However, PPPPy/I_2 films have a smooth surface rather than PPPPy films which is probably a result of iodine vapor to absorb the energy of the plasma, the rate of polymerization was reduced. The product film is smooth due to more time to arrange. Therefore, it is estimated that PPPPy/I_2 films are suitable for preparing a Schottky barrier diode.



(a) (b)

(c) (d)

Figure 4.6 Morphology of in situ iodine-doped plasma-polymerized polypyrrole films on the Copper coated glass substrate determined by scanning electron microscopic technique at 30 minute and various voltages; (a) 800 V, (b) 1000 V, (c) 1200 V, (d) 1400 V

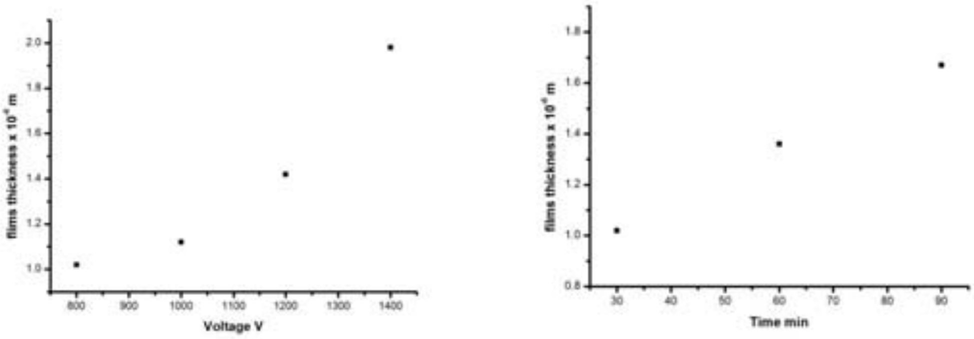


Figure 4.7 The PPPPy/I_2 films thickness at (a) various AC voltages (b) reaction times.

4.2.3 Copper/PPy Ohmic test

Before measured I-V characteristic the Ohmic contact between Cu and PPy must be confirmed by prepared sandwich structure sample as **Figure 4.8**

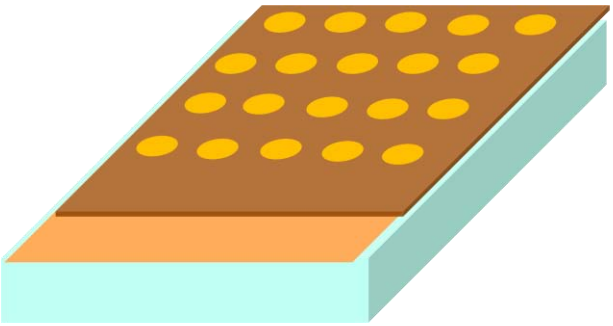


Figure 4.8 Ohmic test sample (Cu/PPPPy/Cu)

I-V curves of this sample presented good Ohmic contacts between Cu and PPPPy(**Figure 4.9**). However, some of samples present a little deviate from Ohmic property, presumably due to the presence of Copper oxide contaminate in the Copper films. However, this deviation has little effect when compared with the effects of PPPPy/Al junction. Therefore, Copper can be used for Ohmic contact with PPPPy films.

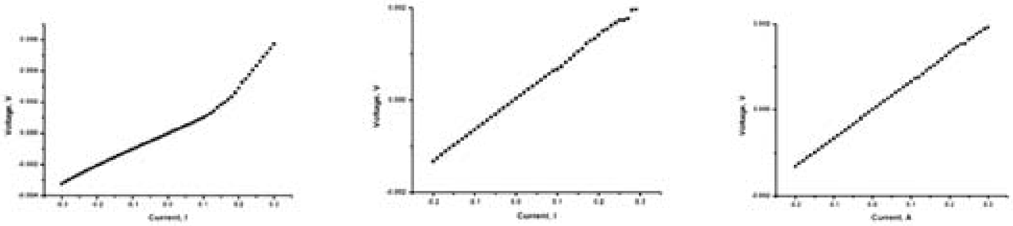


Figure 4.9 I-V curves of PPPPy/Cu for Ohmic test

4.2.4 I-V characteristic of Schottky barrier diode

The properties of Schottky barrier diode were affected by the size of Aluminum rectifying contact. Therefore, the size of the Aluminum films was studied to find the optimum size in the fabrication Schottky barrier diode by the point size of

3, 2, and 1 mm, respectively. The results obtained from the IV characteristic. It is seen that, when the aluminum dots is large, the IV curve was even more linear. Because these effects can be clearly seen, there is no need to calculate the parameters of the diode. Therefore, the Al dot size of 1mm was chosen to the fabrication of Schottky barrier diode.

The Schottky barrier diode has been prepared by the changing the voltage at 800, 1000, 1200, 1400V. I-V curves of the undoped polypyrrole at various voltages are shown in **Figure 4.1**. I-V curve of the state of 1400V shows is a straight line. This is in accordance with Ohm's Law, therefore, that there is a resistive behavior. The other graphs are non-linear, it is a graph of diode and the diode parameters are calculated for comparison with the PPPPy/I_2 Schottky barrier diode.

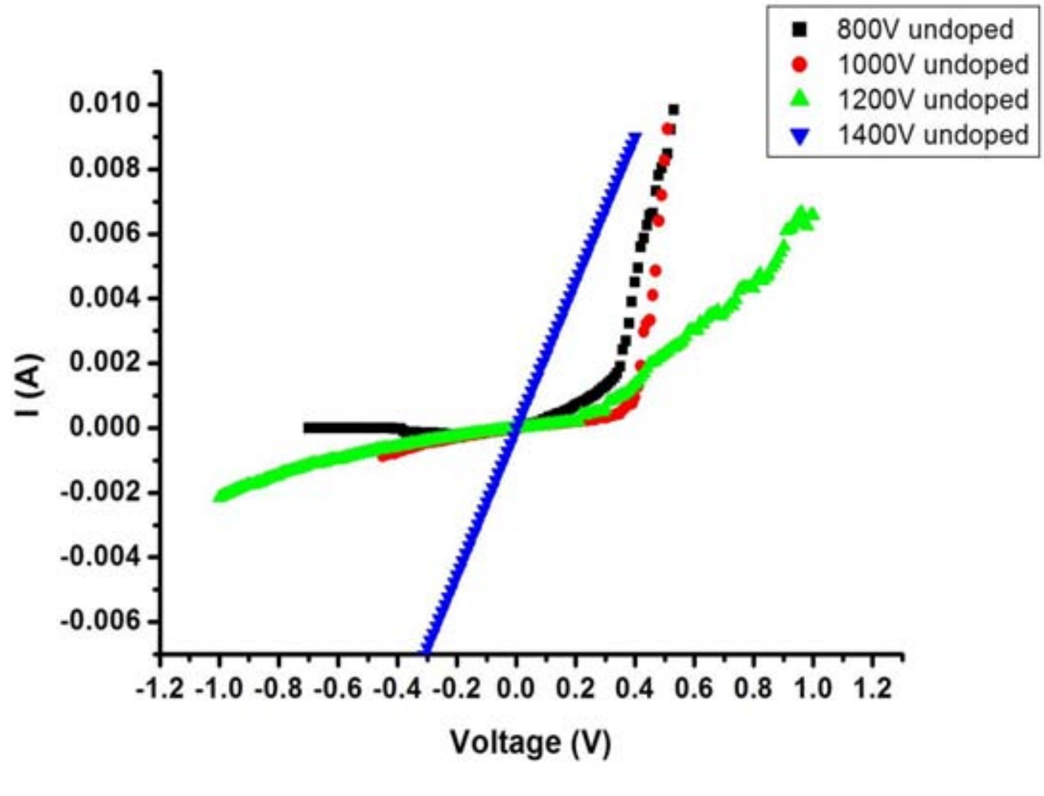


Figure 4.10 I-V characteristic of undoped plasma polymerized polypyrrole at various voltages

For the preparation of PPPPy/I_2 Schottky barrier diode, the diode shows rectifying properties were observed from the non linear IV characteristic. And the doped polypyrrole with iodine resulted to p-type semiconductor and the higher work function, which causes the Schottky phenomenon as well. In addition, parameter of the diode has been calculated to compare with undoped PPPPy diode.

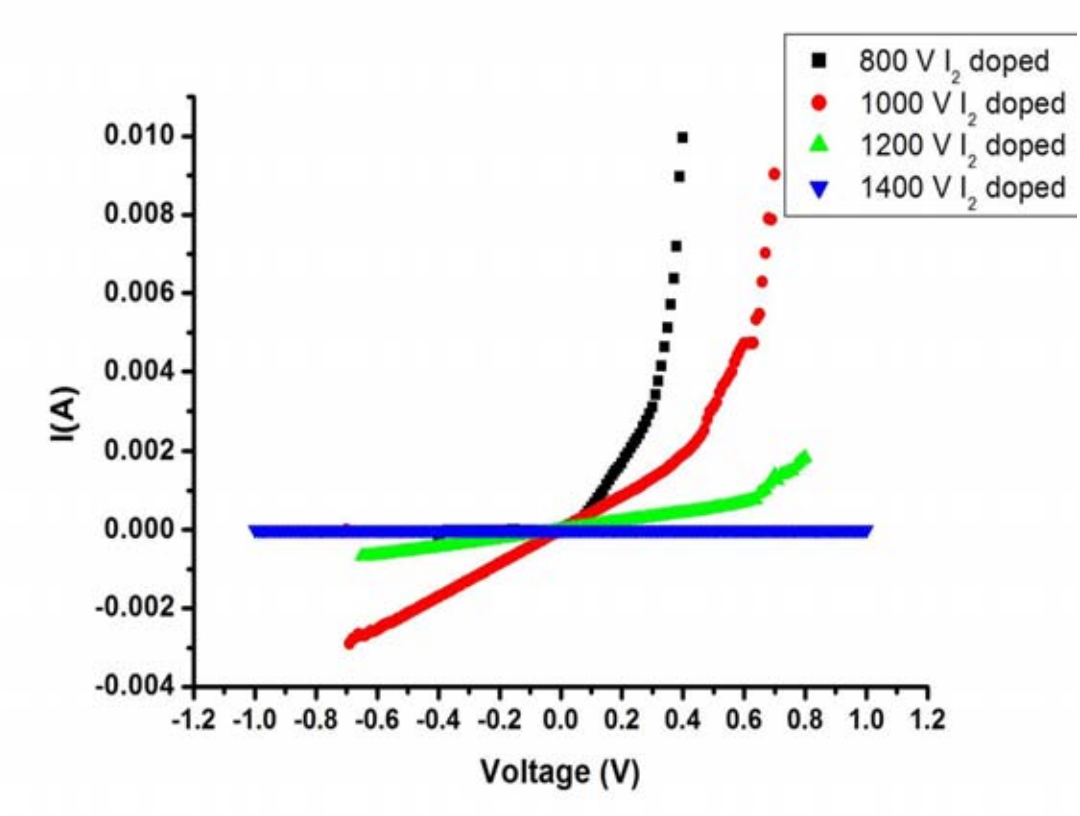


Figure 4.11 I-V curve of I_2 doped plasma polymerized polypyrrole at various voltages.

Each parameter of Schottky barrier diode has been calculated by using thermionic emission theory

$$I = I_0[\exp(qV_J/ \eta kT)]$$

$$I_0 = A_eA^{**}T^2 \exp(-q\Phi_B/kT)$$

If we take logarithm of the equation we get linear relation between log I and V with y-intercept equal to log I_0 and slope equal to q/ ηkT (**Figure 4.12**). The barrier height of Schottky barrier diode (Φ_B) can be calculate if known the value of effective

Richardson's constant (A**).For only thermionic emission theory, effective Richardson's constant of p-type Schottky diode can calculated from

$$A^{**} = 120 \cdot \left(\frac{m_{lh}^{*} + m_{hh}^{*}}{m_0}\right)$$

Where m_0 is free electron mass and m_{lh}^{*} and m_{hh}^{*} are the effective masses for light and heavy holes, respectively. We have unfortunately no reference to the effective Richardson's constant for PPPPy, but the value of Φ_B is not very sensitive to the variation of A** [45,58], therefore the value of A** can be approximation the theoretical values of A** based on thermionic emission theory with an effective mass of unity, that is 120 A/cm^2 K^2 [37,41-42]

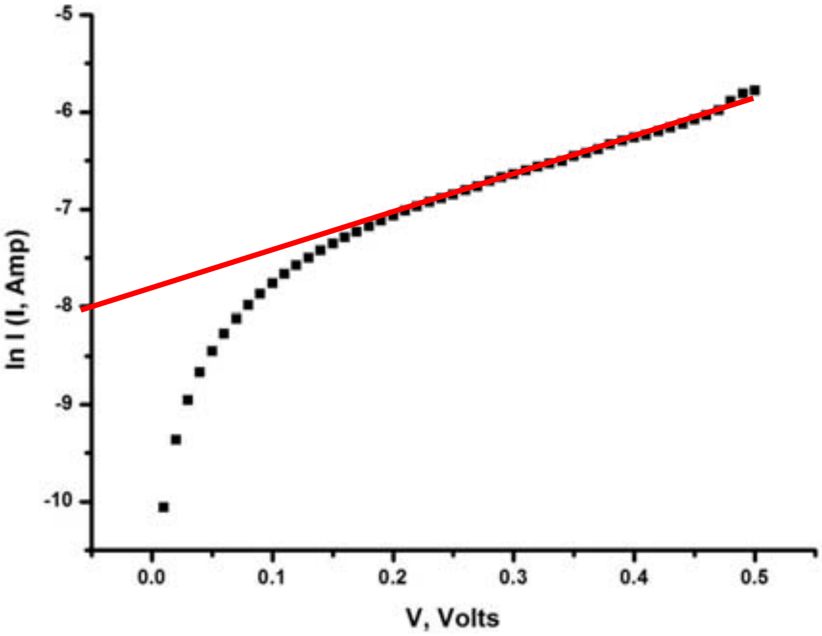


Figure 4.12 plot of ln(I) Vs voltage (V) of I_2 doped PPPPy 1000V 30 min

The results are shown in **table 4.2** and **table 4.3**. From the table, when increasing voltage ideality factor η resulted in the increasing of bulk resistance R_B significantly. Ideality factor is used for the thermionic emission model (η = 1). Consequently the diodes prepared by a low voltage, showed the properties closed to thermionic emission theory more than others. Bulk resistance is the resistance of the area outside the space charge region; the bulk resistance caused a voltage drop in the diode by increasing of the bulk resistance and resistance of the film. However, the increasing of voltage did not affect on the other parameters (barrier height and current density).

Table 4.2 Parameter of undoped PPPPy Schottky barrier diode at various AC voltage.

Synthesis voltage (V)	Undoped PPPPy			
	I_0,A	η	Θ_b,eV	R_B,Ω
800	3.38E-05	1.78	0.56	23.65
1000	1.99E-05	2.03	0.57	15.00
1200	0.0045	4.15	0.43	119.62
1400	-	-	-	-

Table 4.3 Parameter of *in situ* iodine-doped PPPPy Schottky barrier diode at various AC voltage.

Synthesis voltage (V)	Iodine doped PPPPy			
	I_0,A	η	Θ_b,eV	R_B,Ω
800	6.17E-05	1.77	0.54	12.13
1000	7.34E-05	2.04	0.54	16.52
1200	1.80E-05	1.87	0.58	166.39
1400	3.81E-05	2.42	0.56	181818.20

The effect of the reaction time to the Schottky barrier diode parameter as same as the synthesis voltage case. Therefore, the thickness of the film is one of the factors that are important to diode's ideality factor and bulk resistance

Table 4.4 Parameter of undoped PPPPy Schottky barrier diode at various reaction time.

Recation time (min)	undoped PPPPy			
	I_0,A	η	Θ_b,eV	$R_{B,}\Omega$
30	3.38E-05	1.78	0.56	23.65
60	3.02E-10	11.28	0.86	32673.29
90	8.04E-09	39.02	0.78	625000.00

Table 4.5 Parameter of *in situ* iodine-doped PPPPy Schottky barrier diode at various reaction time.

Recation time (min)	Iodine doped PPPPy			
	I_0,A	η	Θ_b,eV	$R_{B,}\Omega$
30	6.17E-05	1.77	0.54	12.13
60	7.34E-05	2.04	0.54	16.52
90	1.80E-05	1.87	0.58	166.39

When comparing the importance of Iodine doping and undoped polypyrrole to various parameters of the diode. In many conditions, the value of the ideality factor and bulk resistance and barrier heigth of PPPPy/I_2 diode is less than PPPPy diode iodine doping, because the charge in the bulk polymer and the electrical conductivity of the polymer is better than ever.

The results of the Schottky barrier diode can be concluded that, voltage and reaction time are affected the thickness, the morphology, and chemical structure of the film. When the fabrication to Schottky barrier diode, it will affect the electrical properties of diodes too. The conditions were suitable for preparing polymer must operate at low voltage and shot reaction time. This could be able to produce the diode close to the thermionic emission model and low bulk resistance and barrier height.

4.3 Piezoresistive strain sensor

Piezoresistive strain sensor is a device used for measuring the strain on the sensor. The most important property of the sensor required is flexible. In this research, the using a transparent PMMA as the substrate and plasma polymerized polypyrrole as piszoelectric material.

Strain sensor consists of an electrode at both ends. With a 1 mm gap in the middle, the poly-pyrrole films were prepared onto this gap. Prior to measurement of electrical properties we must studied properties of PPPPy films by ATR-FTIR and SEM techniques to see all the functions and characteristics of the film morphology and thickness of the film.

4.3.1 Functional groups analysis

As **Figure 4.13** Peaks on the spectra of PPPPy strain sensor is the same as the peak of the fabrication PPPPy diodes but there is a different position. It is the peak of the C-N stretching at around 1240 cm^{-1}.

4.3.2 Morphology of PPPPy films

Figure 4.14 shown surfaces of PPPPy films at various synthesis voltages as 800V, 1000V, 1200V, and 1400V. The film will be dense and pin-hole free and when considered the films synthesis at different voltages. Found that the trend of morphology of films versus voltage is the films will has small grain when voltage increased as same as the PPPPy Schottky barrier diode case.

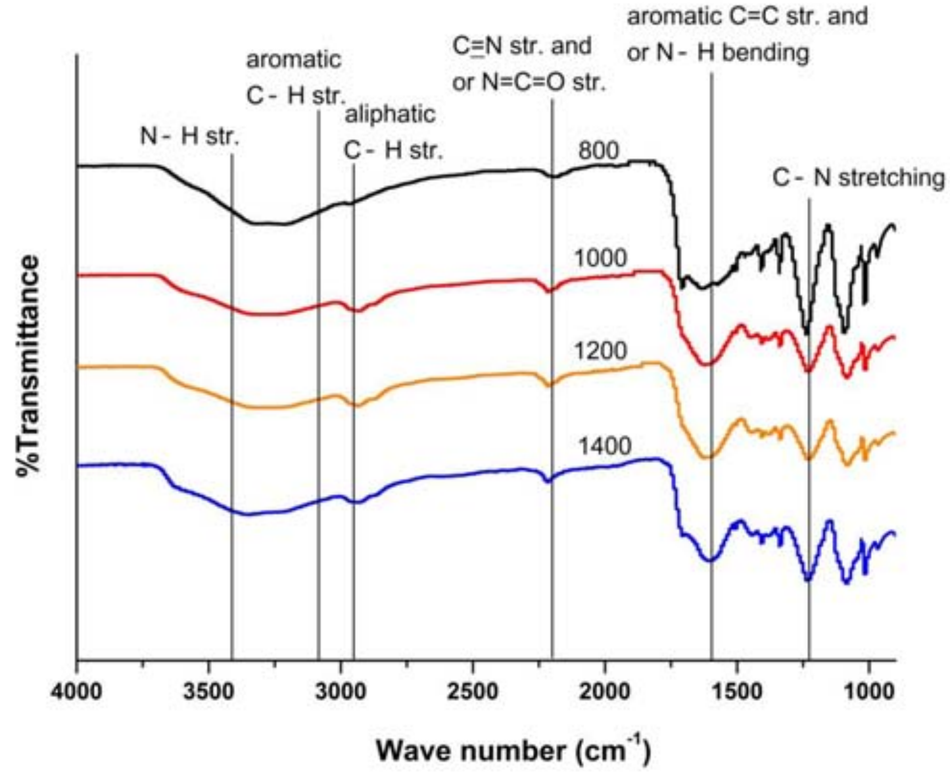
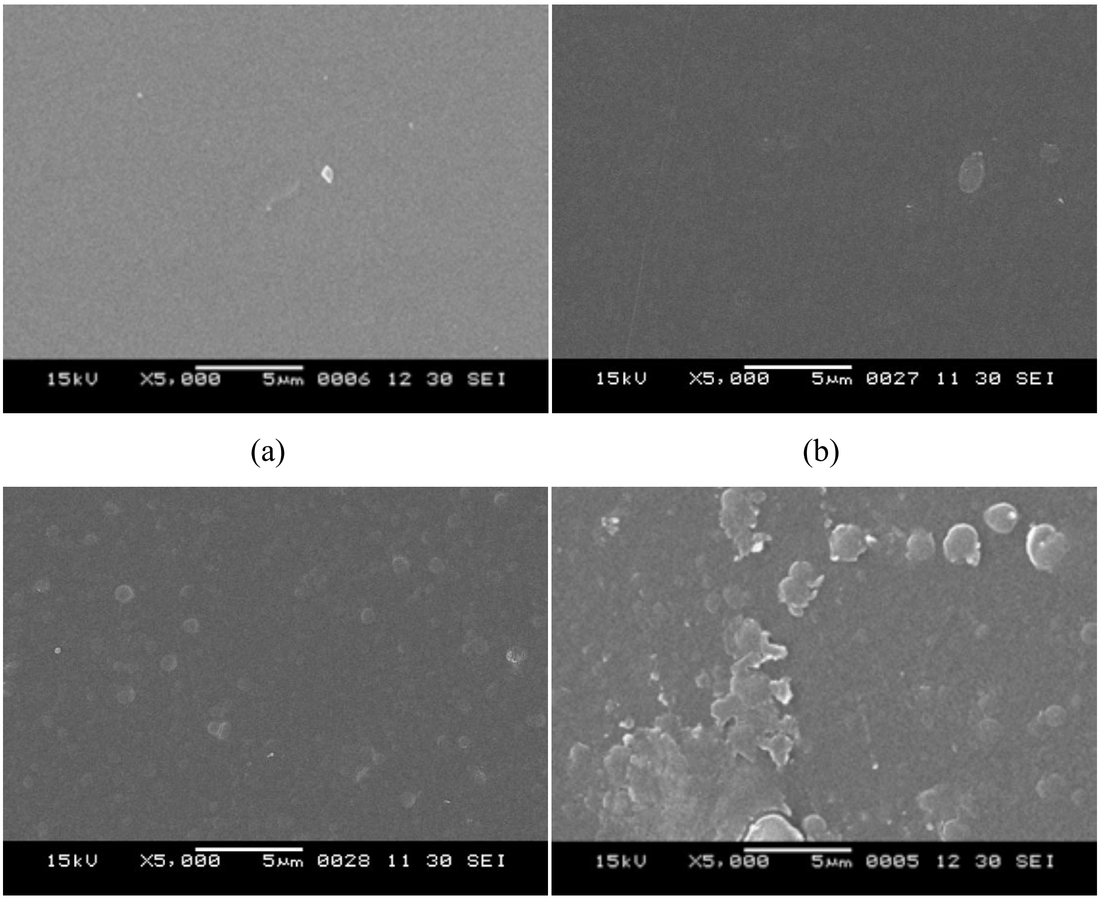


Figure 4.13 ATR-FTIR spectra of plasma-polymerized polypyrrole strain sensor at different synthesized voltage (800, 1000, 1200, 1400V)

The results of film characterization can conclude and that when we use a low voltage in the synthesis the film will be smoother and more crystalline.



(a) (b)

(c) (d)

Figure 4.14 Morphology of plasma-polymerized polypyrrole films on the PMMA substrates determined by scanning electron microscopic technique at 30 minutes and various voltages; (a) 800 V, (b) 1000 V, (c) 1200 V, (d) 1400 V

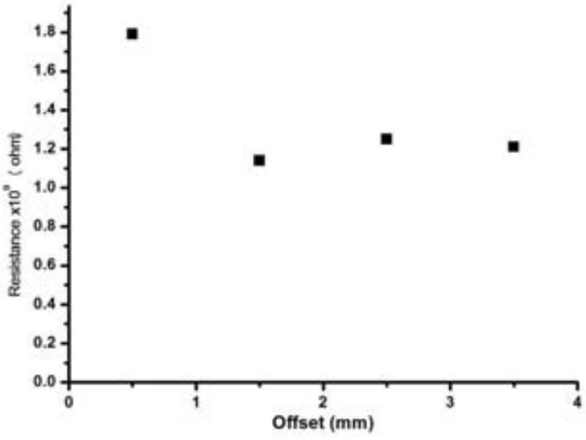


Figure 4.15 Change in resistance along examined offset distance.

4.3.3 Measurement setup

Before measured sample, we must find the point of fixation and select distance of the most change in resistance when revised strain. As **Figure 4.15** the most change in resistance distance is 0.5 mm from the center of PPPPy film

4.3.3.1Calculation of gauge factor (GF)

Gauge factor is the represents the quality of the strain sensor can be calculated from the equation by a plot of $\Delta R/R_0$ and ε then find the slope.

$$\frac{\Delta R}{R_0} = GF \cdot \varepsilon$$

Each parameter will be included in the summary **Table 4. 6**

The voltage is reduced to increase the value of gauge factor, because of morphology and the crystallinity of the films. The film amosphous polymer will have a void between the molecular chains. So when it was stretched to make the polymer chains are arranged along the force and when the crystal is increased, the conductivity can be improved. These events will take place in the polymer with low crystallinity including plasma polymerization, which was prepared at high voltage. The resistance of the polymer increased only slightly at the strain the gauge factor is less as well.

Table 4.6 Effect of voltage to plasma polymerization polypyrrole piezoresistive strain sensor

Voltage (V)	PPy film properties		Strain sensor properties	
	Thickness (μm)	Conductivity ($S \times 10^{-8}$/cm)	Resistance (GΩ)	GF
800	0.92	64.70	1.12	59.65
1000	1.15	51.26	1.13	39.70
1200	1.75	33.04	1.15	21.20
1400	2.22	24.94	1.20	18.69

CHAPTER V

CONCLUSIONS

The fabrication of schottky barrier diode was varied in the range of AC voltage at 800, 1000, 1200, and 1400V. The effect of AC plasma polymerization on chemical structure and polymer morphology were summarized. For ATR-FTIR spectra of plasma-polymerized polypyrrole, The bands were observed at 3500-3000 cm^{-1}, together with two overlapping peaks of N-H stretching of the pyrrole ring at 3400 cm^{-1}, and the C-H aromatic bonds were observed 3200 cm^{-1} band. The absorption band of aliphatic C-H bonds was found at 2938 $cm^{-1}$and the peak at 2200 cm^{-1} maybe assigned to C≡N stretching or –N=C=O stretching this was resulting from partial fragmentation of the pyrrole ring or may be found the oxygen contains in the films and the spectra of *in situ* iodine doping plasma-polymerized polypyrrole, the observed band is similar with PPPPy spectra except the peak of-CH_2I and / or-CI = CH_2 stretching at 1400 cm^{-1} This result indicates that the AC-plasma polymerization technique can be used in the preparation of polypyrrole onto a glass plate coated with copper. As well as, *in situ* iodine doping plasma-polymerized polypyrrole can be applied. The morphology of plasma-polymerized polypyrrole are smooth and pin hole free while the high voltage lead to a lot of small grain and high quality of grain boundary, resulting in a poor conductive film due to effects of space on the grain boundary. For PPPPy/I_2, the films were smoother and thinner as compared with the undoped due to the absorbtion of some energy of plasma by I_2 molecules, therefore, the reaction was retarted and the polymer chains had more time to arrange the structure on the surface resulting in the smooth films. Then, the films can be fabricated into schottky barrier diode and the synthetic voltage and reaction time affected to some parameter of the diode such as ideality factor, bulk resistance, and barrier height. The conditions were suitable for preparing polymer must operate at low voltage and shot reaction time. This could be able to produce the diode close to the thermionic emission model and low bulk resistance and barrier height.

Piezoresistive strain sensor was fabricated by deposition of plasma polymerization polypyrrole onto PMMA substrate and measured the change in resistance of sensor with applied strain. The strain sensor is quantified by the gauge factor (GF). The gauge factor of piezoresistance strain sensor is in the range of 58.65 – 18.69, the gauge factor values increases with the crystallinity of the film.

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