UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF VANADYL TETRABUTYLTETRAKIS (DIMETHYLAMINO) PHTHALOCYANINE (VTP) THIN FILMS BY DIFFERENT DEPOSITION TECHNIQUES

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ABSTRACT

Organic electronic devices have been gradually making their way into the commercial sector to replace inorganic electronic gadgets. The need to increase the performance of organic semiconductor materials has prompted large number of researchers to look for new ones. Metal phthalocyanines (MPcs) have gotten a lot of attention because of its appealing features, such as cost efficiency, eco-friendly organic material, and thermal and chemical resilience. In present studies, effects on different deposition techniques (i.e., spin coating and thermal evaporation) for vanadyl 3,10,17,24-tetra-tert-butyl-1,8,15,22-tetrakis(dimethylamino)-29H,31H-phthalocyanine (VTP) have been carried out.

The initial phase of the study is to deposit the VTP thin films to determine its structural, morphological and optical properties. Raman spectroscopy and X-Ray diffraction (XRD) has been utilized to investigate the structural properties of the deposited thin films. The FESEM images have been obtained for both spin-coated and thermal deposited VTP films to investigate their surface topography, while AFM imaging has been carried out to determine the surface morphological structures. UV-Visible spectroscopy (UV-Vis) has been used to study the optical properties for both thin films. The novelty of this work is mainly from the comparative study of VTP thin films deposition to unveiling the potential application of the VTP based semiconductor devices.

Keywords : VTP, Spin coating, Thermal deposition

ABSTRAK

Peranti elektronik organik telah secara beransur-ansur membuat jalan mereka ke sektor komersial untuk menggantikan alat elektronik bukan organik. Keperluan untuk meningkatkan prestasi bahan semikonduktor organik telah mendorong sebilangan besar penyelidik untuk mencari yang baru. Logam phthalocyanines (MPcs) telah mendapat banyak perhatian kerana ciri-cirinya yang menarik, seperti kecekapan kos, bahan organik mesra alam, dan ketahanan haba dan kimia. Dalam kajian sekarang, kesan ke atas teknik pemendapan yang berbeza (iaitu, salutan putaran dan penyejatan haba) untuk vanadyl 3,10,17,24-tetra-tert-butyl-1,8,15,22-tetrakis(dimethylamino)-29H,31H-phthalocyanine (VTP) telah dijalankan.

Fasa awal kajian ini adalah untuk mendepositkan filem nipis VTP untuk menentukan sifat struktur, morfologi dan optiknya. Raman spectroscopy dan X-Ray diffraction (XRD) telah digunakan untuk menyiasat sifat-sifat struktur filem nipis yang didepositkan. Imej FESEM telah diperolehi untuk kedua-dua filem VTP bersalut berputar dan haba untuk menyiasat topografi permukaan mereka, manakala pengimejan AFM telah dijalankan untuk menentukan struktur morfologi permukaan. Spekskopi UV-Visible (UV-Vis) telah digunakan untuk mengkaji sifat optik untuk kedua-dua filem nipis. Kebaharuan kerja ini adalah terutamanya dari kajian perbandingan pemendapan filem nipis VTP untuk melancarkan potensi penggunaan peranti semikonduktor berasaskan VTP.

Kata Kunci: VTP, Lapisan berputar, Pemendapan terma

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LIST OF ABBREVIATIONS

MPcs	:	Metal phthalocyanines
OFET	:	Organic field effect transistors
Pcs	:	Phthalocynanines
VTP	:	Vanadyl Tetrabutyltetrakis (dimethylamino) Phthalocyanine
OLED	:	Organic Light Emitting Diode
$PC_{71}BM$	:	Fullerene C70
IPA	:	2-propanol
DMSO	:	Dimethyl Sulfoxide
XRD	:	X-Ray Diffraction
AFM	:	Atomic Force Microscopy
FESEM	:	Field Emission Scanning Electron Microscope
EDS	:	Energy dispersive X-Ray Spectroscopy
UV-VIS	:	Ultraviolet-Visible Spectroscopy
FWHM	:	Full Width at Half Maximum

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

Organic electronics is a diverse field of modern electronics. It incorporates the synthesis of organic polymer/molecules, as well as the preparation and manufacture of electronic devices, to merge research in the domains of physics and chemistry. Organic materials are often made up of carbon that resembles the molecules found in living organisms. Heeger, Shirakawa, and MacDiarmid discovered polyacetylene, a highly conductive polymer, in 1977 (Bredas et al., 2002). Organic electronics applications were still missing a decade later. Growing interest in organic conductive materials was recognized in the engineering and applied physics sectors until the mid-1980s, resulting in the emergence of a new technology with a new market, namely polymer or plastic electronics (Zhou et al., 2014).

Until now, such devices have been shown to be inferior in terms of performance and durability when compared to normal silicon-based electronic devices. According to the Organic Electronics Market Research Report 2018, global organic electronics demand is expected to be one of the fastest growing markets worth billions of dollars by 2027, owing to environmental benefits, better resource utilization, and, most importantly, lower costs when compared to conventional inorganic electronics.

Metal phthalocyanines (MPcs) are a type of organic substances that has attracted a lot of attention as a molecular material because of its unique optical and electrical properties (Torre et al., 2007; Rossi et al., 2016). MPcs have been investigated extensively as active materials for electronic devices such as sensors, organic field effect transistors (OFETs), organic solar cells (OPVs), and optical switching and limiting devices throughout the last few decades. In general, phthalocynanines (Pcs) are made up of a tetrameric diiminoisoindoline conjugated macrocyle that is nitrogen-linked. Due to the chelate of metal with two covalent and two coordination bonds, the MPc is a highly stable substance that can be used as dyes, pigments, and active materials in organic electronic devices (Dahlen, 1939; Li et al., 2008; Yuen et al., 2012). Most MPcs are quite inexpensive and easy to obtain in large-scale production from major chemical producers due to the synthesis method. MPcs has become a popular material for a wide range of commercial applications because of these appealing characteristics, with extensive research facilities examining its potential in a variety of device applications.

The quest for a novel material is crucial to the organic devices market's future growth. In this study, properties such as structural, morphological, energy band gap and optical of VTP thin films deposited by spin coating and thermal evaporation are studied. The properties of VTP thin films deposited by spin coating and thermal evaporation are compared as to be applied for potential future application such as organic field effect transistor (OFET), optical and humidity sensor (Roslan, 2020)

1.2 PROBLEM STATEMENTS

As mentioned earlier, the capabilities of the material, VTP in semiconductor sector is widely expanded. A thorough study on investigating the VTP thin films-based semiconductor device (i.e. OFET, photodetector and humidity sensor) by using spin coating method have been previously reported (Roslan, Abdullah, Halizan, et al., 2018) . It was claimed that spin coating method is beneficial as it only requires a small amount of solution and easy to control the thickness of thin film within a nanoscale range, thus provide a low-cost method (Roslan, Abdullah, Halizan, et al., 2018). However, spin coating shows amorphous behavior which limit their competition to be applied in semiconductor devices (Roslan, Abdullah, Majid, et al., 2018). Hence, to circumvent this drawback, another deposition method, called thermal evaporation method is studied and the properties is compared with the spin coated thin films. On top of that, there are no studies that have been conducted in determining the properties of VTP thin films deposited by thermal evaporation.

1.3 PROJECT OBJECTIVES

This present study is carried out to determine the properties VTP thin films deposited through different deposition methods, that is spin coating and thermal evaporation method. The results are compared by their structural, morphological, and optical properties. The specific aim of this study are as follows:

a) To deposit the VTP material in two different deposition methods, i.e., spin coating and thermal evaporation method.
b) To characterize the structural, morphological, and optical properties of VTP thin films obtained from both depositions.
c) To compare the VTP thin film properties of two different depositions

1.4 THESIS FRAMEWORK

Chapter 1 brief about the background study on organic semiconductor materials, especially the MPcs derivatives and highlight about the main material used in this study which is the Vanadyl Tetrabutyltetrakis(dimethylamino) Phthalocyanine, (VTP). Next, this chapter also describe about the objectives and scope of work in this study which are then are done one by one in order according to the objectives and scope of work mentioned earlier. **Chapter 2** will be focused in elaborating general knowledge with the material and technique used in this study especially the VTP) Chapter 2 will be the literature review chapter for this study. Continue to **Chapter 3**, the materials employed throughout this thesis are detailed in this chapter, as are the thin film depositions and a brief discussion of thin film characterization methods. This chapter also covers the measurement methodologies for each instrument. For **Chapter 4,** will be the chapter that explain about the result of the studies. This chapter is bound together to achieve the objectives of this study. In this chapter, a comparative study will be discussed, mainly about different deposition techniques for VTP thin films. Finally, the overall conclusion and future research for this study will be discussed and presented in **Chapter 5.**

CHAPTER 2

LITERATURE REVIEW

2.1 PHTHALOCYANINE

Phthalocyanine or its abbreviation is (H_2Pc) is a complex organic compound which is originally found in the year of 1907. On that year, a blue compound which is called now as phthalocyanide have been first synthesized. A group of swiss researches claimed that they discovered three compounds known as Copper Phthalocyanine, Copper Naphthalocyanide, and Copper Octamethyl phthalocyanine complexes in the year of 1927. This discovery creates the idea of Phthalocyanine stability, but futher studies were not carried on. On the other hand, at Scottish Dyes of Grangermounth, Scotland Iron Phthalocyanine has been discovered while Sir Patrick Linstead found the chemical and structural properties of the compound. In 1928, Phthalocyanine was well used especially in industry such as dyes stuffs, paints, colors for metal surfaces, fabric and plastics. Phthalocyanine also popular in organic solar cell and application in optoelectronic devices. Moreover, Phthalocyanine has 4 types which is Nickel Phthalocyanine, Iron phthalocyanine which have been mention earlier, Cobalt Phthalocyanine and Copper Phthalocyanine. There are many derivatives of Phthalocyanine which make this compound unique. This can be produced by the Hydrogen (H_2) is substitute with functional group such as halogen, hydroxyl, amino, alkyl, thiol, and alkoxyl.

For its physical properties, Phthalocyanine is well known for its thermal efficiency which is thermally stable. This organic compound cannot be melted but can be sublimed temperature more than 500 °C under inert gas for example nitrogen or carbon dioxide. With these unique characteristics, it is well used in industry that require excessive heat and thus this organic compound is a good choice. In addition, the pigments in the organic compound can absorb light around 600-700 nm which produce blue or greenish in color. As the absorption occur, this phenomenon emits wavelength and as the wavelength occur, the pigments can change colour from blue to green and colorless. As Phthalocyanine is insoluble in most aqueous solution, Phthalocyanine can always be obtained in powder form.

As for its chemical and optical properties, as mentioned earlier, Phthalocyanine is insoluble in most aqueous solution, therefore it has low solubility in organic compound. Its low solubility makes it difficult to obtain polymeric material in high molecular weight. Therefore, as the research goes on, the scientist founds out that phthalocyanine can dissolve easily in sulfuric acid due to protonation of the nitrogen atom bridging the phyrole rings. Hence, tetramino derivatives such as Dimethyl Sulfoxide are used as it has the ability of solubility in solvent hence makes Phthalocyanine soluble and in aqueous solution. On the other hand, Phthalocyanine are good for its optical properties because this organic compound has high symmetry, planarity, has electron delocalization and also exist in several crystalline form.

2.1.1 METAL PHTHALOCYANINE

Metal phthalocyanines (M-Pcs) are a class of tiny macrocyclic conjugated compounds composed of a ligand and a core metal atom (shown by a M) that covalently bonded to create a coordinated complex, as illustrated in Figure 2.1. Metal phthalocyanines have historically been used as dyes and pigments nonetheless, these organic semiconductors have generated considerable interest due to their potential for use as novel functional materials and incorporation into active layers in electrical devices made of organic materials. They are employed in a variety of diverse applications, including as gas sensors and data storage, Organic Light Emitting Diode (OLED), and Organic thin film transistors.

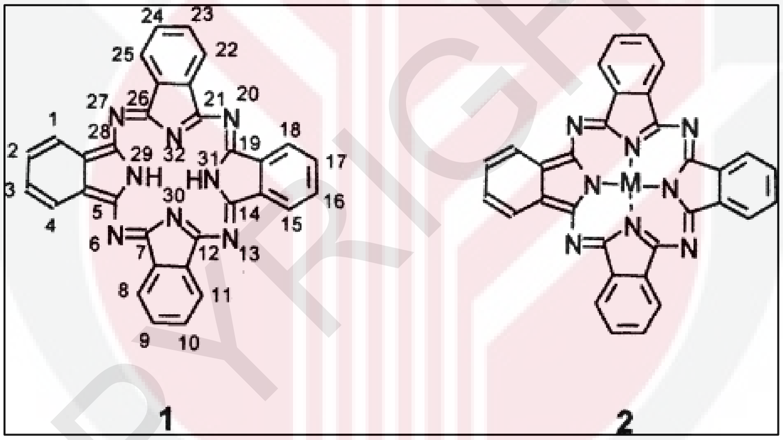

Figure 2.1: Molecular structure of metal Phthalocyanine

The two hydrogen atoms in the molecule's core have been replaced with metals from every group of the periodic table to generate the metal phthalocyanines group of chemicals. Additionally, one to sixteen of the peripheral hydrogen atoms in the phthalocyanine molecule's four benzene rings have been replaced with halogen atoms and a variety of chemical and inorganic groups, resulting in substituted phthalocyanines.(Liu & Zhu, 2001).

2.2 VANADIUM (V) AND VANADYL (V^{4+})

In 1801 in Mexico, Andrés Manuel del Ro discovered vanadium compounds while investigating a new lead-bearing mineral dubbed "brown lead." Though he initially believed its properties were due to the presence of a new element, he was subsequently convinced that the element was just chromium by French chemist Hippolyte Victor Collet-Descotils. Then, in 1830, Nils Gabriel Sefström synthesized vanadium chlorides, establishing the existence of a new element. He named it "vanadium" after Vanads, the Scandinavian goddess of beauty and fertility (Freyja). The name is derived from the variety of hues present in vanadium compounds. Due to the vanadium component in Del Rio's lead mineral, it was eventually termed vanadinite. Henry Enfield Roscoe discovered the element in 1867.

Vanadium is naturally occurring in around 65 minerals and fossil fuel sources. It is manufactured in China and Russia from slag from steel smelters. Other countries manufacture it directly from magnetite, heavy oil flue dust, or as a byproduct of uranium mining. It is primarily used to manufacture specialty steel alloys, such as high-speed tool steels and some aluminums alloys. Vanadium pentoxide, the most important commercial vanadium chemical, is employed as a catalyst in the manufacturing of sulfuric acid. Energy storage with vanadium redox batteries may be a significant application in the future.

Vanadium is a chemical element with the atomic number 23 and the symbol V. It is a malleable, hard, silvery-grey transition metal. Vanadium occurs in two isotropic forms, have an atomic weight of 50.94, density 6.11 g/cm3 (18.1°C), melting point 1910 ± 10°C, and boiling point 3420°C (Assem & Oskarsson, 2015). With the boiling point that high, Vanadium is well known as electrically conductive and thermally insulating. This is why, it become the main material in Vanadyl Tetrabutyltetrakis (Dimethylamino) Phthalocyanine (VTP) and suitable for becoming one of the organic semiconductors. Although the elemental metal occurs infrequently in nature, once isolated artificially, the creation of an oxide layer (passivation) protects the free metal from further oxidation.

Vanadium ions are present in high concentrations in a few organisms, presumably as a poison. Vanadium oxide and a few additional salts are somewhat poisonous. Vanadium is utilized by some life forms, particularly those found in the water, as an active center for enzymes, such as the vanadium bromoperoxidase found in some ocean algae. Vanadium is a member of the periodic system's group Vb and is a member of the first transition series. It predominantly forms compounds with an oxidation state of +3, +4, or +5. Vanadium is most stable in the +4 oxidation state, where it forms the oxovanadium (+4) ion (vanadyl; VO2+) (Assem & Oskarsson, 2015) which is then are used to produce the main material which is the Vanadyl Tetrabutyltetrakis (dimethylamino) Phthalocyanine, (VTP).

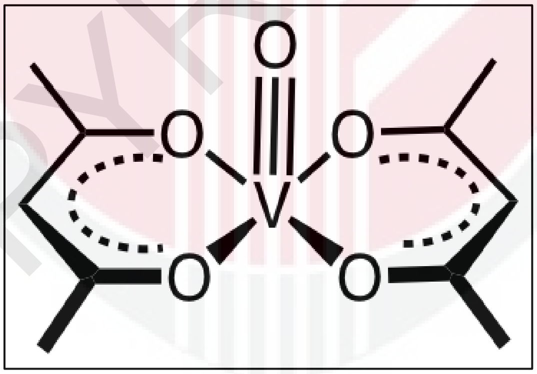

Figure 2.2: molecular structure of Vanadium

2.2.1 VANADYL 2, 9, 16, 23-TETRAPHENOXY-29H, 31H PHTHALOCYANINE (VOP_CP_HO)

M-Pcs are phthalocyanine (Pc) derivatives. Two hydrogen atoms in the phthalocyanine's core can be replaced by various metal ions to generate M-. In other words, phthalocyanine can serve as a host for metal ions contained in its hollow at the centre (Li, et al., 2008). By substituting hydrogen atoms for the hydrogen atoms in the vanadyl ion, VO2+, the substance is referred to as vanadyl. Figure 2.3 illustrates phthalocyanine, VOPc, and the molecular structure of VOP_CP_HO.

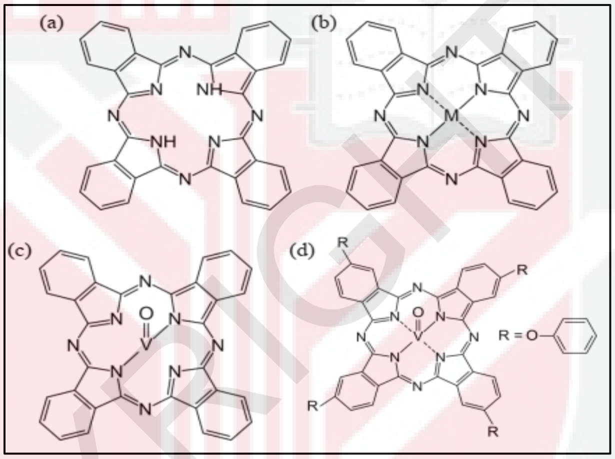

Figure 2.3: molecular structure of a) phthalocyanine b) VOPc c)VOPCPHO.

Vanadyl phthalocyanine has been shown to have excellent thermal and chemical stability (Qiu et al., 2005; Wang et al., 2007), good hole conductance (Kolotovska, Friedrich, Zahn, & Salvan, 2006), and an ultrafast optical response (Kolotovska, Friedrich, Zahn, & Salvan, 2006). Additionally, VOPc is a non-toxic material that is quite affordable to manufacture. According to reports, the VOPc thin film generates an absorption spectrum range between 300 and 1000 nanometers with two discrete absorption bands. A sharp and elevated A band of absorption having a peak at approximately 350nm is referred to as the Soret band or B-band. The Q-band is a wider absorption band with maxima near 660nm and 730nm. (Maruno et al., 1993). Due to the green's low absorption capacity VOPc thin film has a bright and sharp green colour in the wavelength range (490 nm-560 nm). Since, VOPc has a comparable absorption spectrum to PTCDA, it was previously considered that the coupling of VOPc and PTCDA should encompass the entire visible spectrum of solar radiation. According to the literature, VOPc has a LUMO between 4.2 and 4.7 eV and a LUMO between 4.2 and 4.7 eV.

At 5.6 eV-5.8 eV, HOMO has a band gap of around 0.9 eV-1.6 eV (Bamsey et al., 2011) This narrow band gap permits relatively high frequencies to be used. Probability of electrons in the HOMO energy level being excited to the LUMO energy level to occur. A strong diffraction pattern demonstrates the crystallization of a VOPc thin film. The peak at 2θ is approximately 7.3° to 7.5°, indicating that the VOPc molecules are parallel to the substrate with an interstack gap of 1.17nm-1.20 nanometers (Kolotovska, et al., 2006; Y.-l. Pan, et al., 1998a; Wang, et al., 2007). Wang et al. discovered that the VOPc deposited had a mobility of up to 1.5 cm^2/Vs on a para-sexiphenyl layer that is arranged (p-6P). They asserted that the VOPc is nonplanar. Compounds with a greater mobility than planar VOPc are possible. Nevertheless, no discussion appeal for the remarkable performance of VOPc which has been attributed to its crystal packing structure (Li, et al., 2008; Wang, et al., 2007).

2.2.2 VANADYL TETRABUTYLTETRAKIS (DIMETHYLAMINO) PHTHALO CYANINE (VTP)

Another less known organic compound, vanadium derivative or VTP, has been researched before with an emphasis on its optical and structural properties (Ahmad Makinudin & Supangat, 2016). When compared to VOPcPhO, the numerous extended ligands present in VTP have an effect on optical, morphological, and structural properties, electrical properties of organic semiconductor devices, as well as their performance. This is due to the improvement in charge delocalization, which improves the charge transport of organic devices based on VTP. The molecular architectures of VTP and VOPcPhO are depicted in Figure 2.4, with VTP having extended ligands at the perimeter that can improve the devices' sensitivity and charge transport. VTP's excellent solubility in the majority of organic solvents enables a simple solution process technique via spin coating, hence lowering the cost of manufacturing. The VTP and its derivative (VoPcPhO) differ in the number of substituents in the phthalocyanine macro-ring. VTP attract interest due to the insertion of specific attachments to the macro-ring site, which will result in considerable variations in its stability and photo absorption spectrum, as well as potential applications in optoelectronics.(Roslan, et al., 2018).

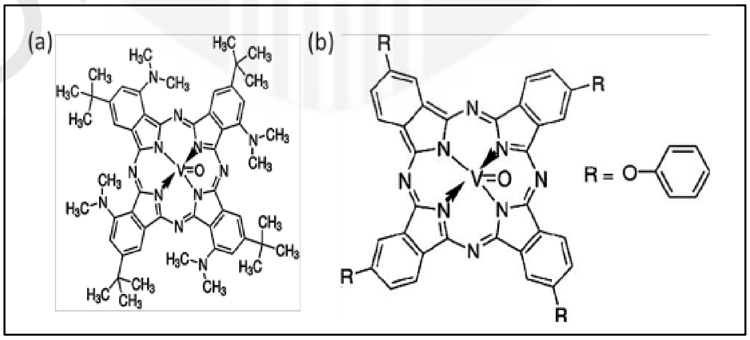

Figure 2.4: Molecular structures of a) VTP and b) VOPcPhO

As mentioned earlier, VTP was capable not just for being a good organic semiconductor but also as excellent active layer in Vertical Organic Field Effect (VOFET). This is because, VTP can be classified as a p-type organic semiconductor which can be fully used in active cells. Moreover, VTP is one of the derivatives of phthalocyanine which also act as hole injection or transport layer, because of the p-type material (Roslan, Abdullah, Halizan, et al., 2018). The electrical properties of VTP as an Active Organic Channel can be shown by the previous study, which the study concluded that The HOMO and LUMO energies of VTP were determined to be -5.10 and -3.90 eV, respectively. VOFETs have been manufactured utilizing VTP as the channel organic semiconductor, and the electrical operating performance is highly dependent on the channel thickness. The best VOFET performance was found using a 66.4 nm VTP layer with a maximum output current density of 37 mA/cm^2. This demonstrates that VOFETs created with VTP can be fabricated with higher output current and turn-on voltage using a straightforward and low-cost device preparation technique known as solution-processed fabrication (Roslan, Abdullah, Halizan, et al., 2018).

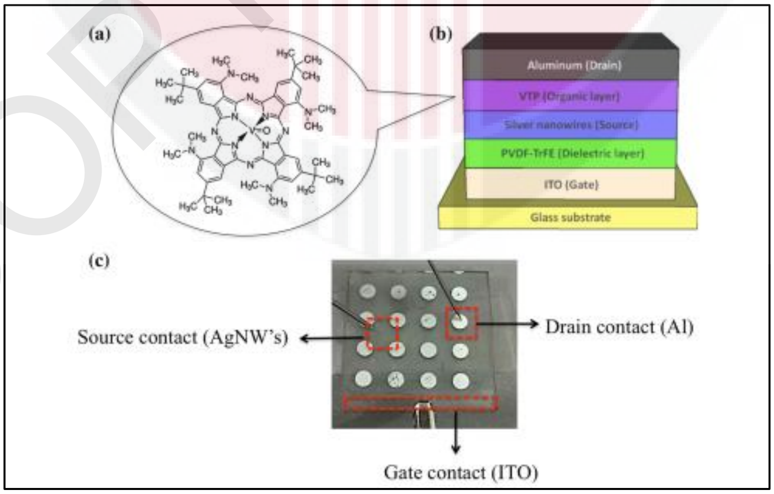

Figure 2.5: (a) Molecular structure of VTP. (b) Cross-sectional view of ITO/PVDF-TrFE/AgNWs/VTP/Al VOFET. (c) Image of the VOFET device

Recent study shows that VTP also proved to be a highly responsive organic photodetector. VTP is chosen because of the unique characteristics which VTP can be a donor material which have a special absorption property. In the study, the VTP were combined with a material called $PC_{71}BM$ which as acceptor material. This can be continuously explained as VTP has relatively good holes transport properties, while $PC_{71}BM$ has good electron transport ability, making them to be donor and acceptor components, respectively. Foremost, both of organic materials, VTP and $PC_{71}BM$, have good solubility in most organic solvent especially chloroform, which endows to facile solution process-able techniques. It was found that the combinations of the material have photoresponsivity of 2.30×10^{-1} A/W and fast response time of 350 ms, which is considerably practical for light sensing application (Roslan,et al., 2018). This can conclude that VTP is capable becoming an organic photodetector due to the sensing performances as a donor material.

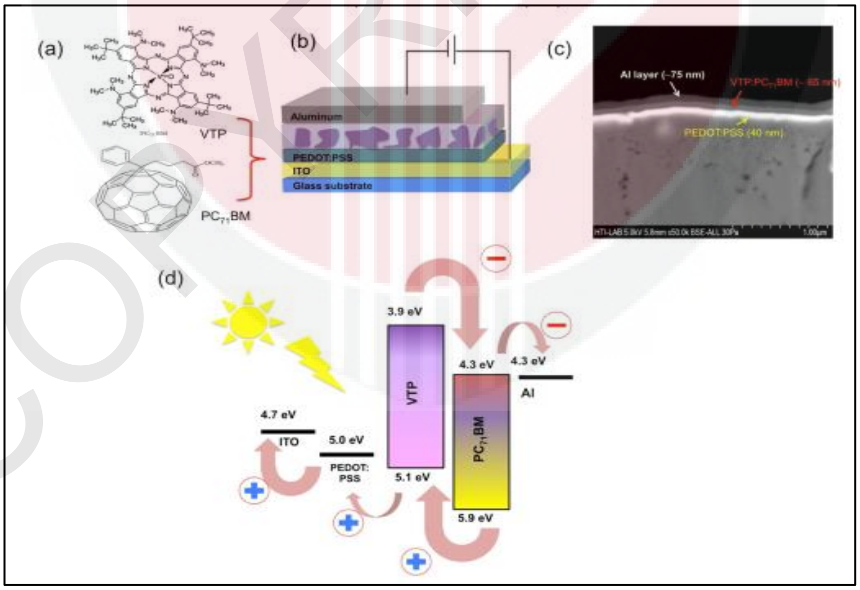

Figure 2.6: The molecular structure of VTP [7] and PC71BM [8], (b) a schematic diagram of photodetector, (c) cross section image of as-prepared sample and (d) energy diagram for ITO/PEDOT:PSS/VTP:PC71BM/Al organic photodetector

2.3 THIN FILM DEPOSITIONS METHODS

Deposition technology is unquestionably critical for the development of devices such as computers, as all microelectronic solid-state devices are built on material structures generated through thin-film deposition. Electronic engineers have consistently requested higher-quality and more sophisticated films for solid-state devices, necessitating significant advancements in deposition technology. Manufacturers of equipment have made significant strides toward meeting the requirements for improved and more economical deposition systems, as well as in-situ process monitors and controllers for measuring film properties. Another significant cause for deposition technology's rapid expansion is the increased understanding of the physics and chemistry of films, surfaces, interfaces, and microstructures enabled by extraordinary advances in analytical instrumentation during the last two decades.

There are many of deposition processes available to produce materials. Because this research deals with thin-film deposition methods for generating layers with a thickness of a few nanometers to around ten micrometers, the process of classifying the technologies is simplified by restricting the number of technologies considered. Essentially, thin-film deposition technologies fall into two categories: those that are entirely physical, such as evaporative methods, and those that are entirely chemical, such as gas- and liquid-phase chemical processes. Numerous operations using glow discharges and reactive sputtering incorporate both physical and chemical reactions; these overlapping processes are referred to as physical-chemical methods.

2.3.1 SPIN COATING METHOD

Spin coating is firstly introduced in 1958, where Emilia et.al developed the first spin coating model. The model that has been patented then evolved became even more specific and complicated models. Spin coating is one of depositions methods for creating thin films in the microelectronics industry. Definition of spin coating is basically a methods which solution or material is spread evenly over a surface of a substrate using centripetal force at high speed which is around 3000 RPM using a machine called spin coater or spinner. The thickness of the thin film that are required can be achieved by using these methods. The desired thickness can be obtain by following the equations below, which show the parameters that will affect the thickness (Chakraborty, 2010) :

$$\boxed{h = \left(1 - \frac{\rho_A}{\rho_{A0}}\right) \cdot \left(\frac{3\eta \cdot m}{2\rho_{A0}\omega^2}\right)^{1/3}} \qquad \textbf{(1)}$$

Where:

h = Thickness

ρ_A = Density of the volatile liquid

η = viscosity of solution

m = rate of evaporations

ω = angular speed

From the equation (1) , we can conclude that the higher the angular speed of the spin coater, thicker the thin film will be. Spin coating consist of several stages, such as fluid dispense, spin – up, stable fluid outflow, spin off and evaporation. These stages need to be followed to obtain high quality thin film (Chakraborty, 2010) The repeatability during spin coating is also one of the most important factors in spin coating. By doing so, we can measure different thickness varying different angular speed of the spin. In the industry, spin coating is occasionally used for several important technology which are used nowadays, such as in producing flat screen display, photoresist for patterning wafers in microcircuit productions and many more. Hence, this deposition methods are one of the easiest ways and low cost that can be practice to obtain thin film.

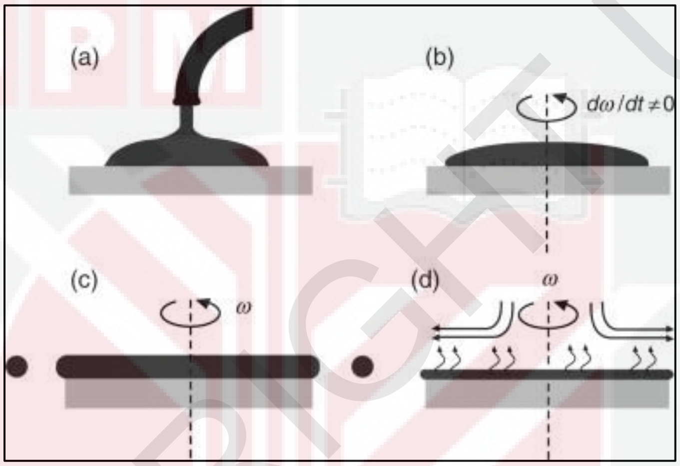

Figure 2.7: The four basic stages of spin coating: (a) deposition, (b) acceleration, c) flow domination, and (d) evaporation. ω is spin speed
(Taken from (Kerdcharoen & Wongchoosuk, 2013)

2.3.2 THERMAL EVAPORATION METHOD

Vacuum Thermal Evaporation is one of the most common techniques in thermal evaporation depositions method. Vacuum thermal evaporation technique is the vaporization of a material in vacuum by heating the material usually in high temperature which in vacuum, the vapor particles of the material will be moving and directly attached to the surface of the target object (substrate). After reaching the substrate, the vapor again will change to a solid state by condensing back. The object to be coated is referred to as substrate can be any wide variety of things such as semiconductor wafers, solar cells, optical components and much more. In here, glass slides have been utilized as the glass substrates and the material to be evaporated is VTP.

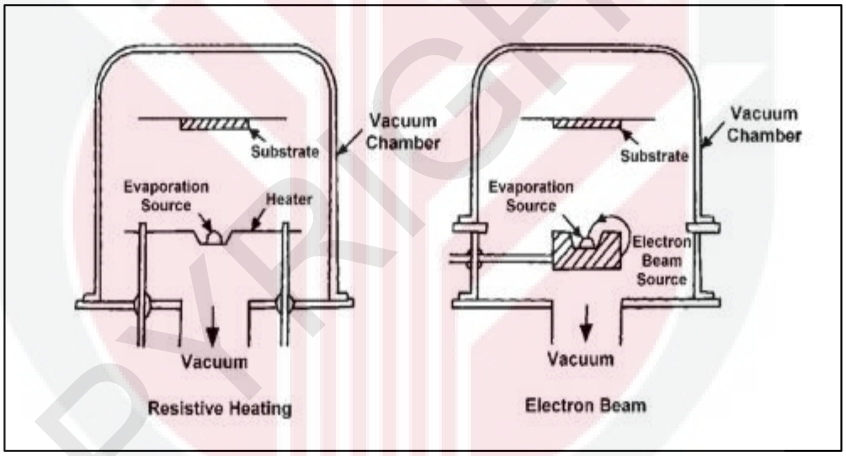

Figure 2.8: Vacuum Thermal Evaporation Process

There are commonly two types of thermal evaporation process which is resistive heating and electron beam heating. Figure 2.8 shows the schematic diagram of both processes. The most common process is by resistive heating. The material is evaporated by resistively heat the filament or boat, which is usually made with a high thermal sustainability such as tungsten. The filament will attach to crucible, where the material usually in powder are placed. The filament then heated with a high temperature in a vacuum chamber below 1.3 x 10^{-4} Pa (1 x 10^{-6} torr). The vapor then will rise above this bottom source, and the substate are held usually inverted in appropriate fixtures at the top of the chamber. The surfaces intended to be coated, thus facing down toward the heated source material to receive the coating. Another common process is by using electron beam or commonly known as E-Beam Evaporation. The main source in this system is the E-beam gun, where a small and very hot filaments boiled off electrons which are then accelerated by high voltage, forming an electron beam with considerable energy. This process is much more advance and involve dangerous high voltage usually 10,000 Volts.

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

In this chapter, the process involving the preparation of VTP thin film is explained and the characterizations performed to analyze the VTP thin films are presented. The steps in preparing the substrate, materials and both deposition process (spin coating and thermal evaporation) are discussed in detail. Structural characterizations techniques involving Raman spectroscopy and X-Ray diffraction (XRD) had been described. Morphological characterizations including Field Emission Scanning Microscopy (FESEM) and Atomic Force Microscopy (AFM) had been outlined in detail. Also, the optical characterizations using UV-Visible spectroscopy (UV-Vis) is presented.

3.2 SUBSTRATE PREPARATION

Microscope glass slides have been purchased and used for spin coating and thermal evaporation methods. Prior deposition of the material, the glass slides have been cut into fixed dimensions of 1.5 cm x 2.0 as shown in Fig. 3.1 (a). To ensure a precise measurement, glass cutter is used to perform the cutting process (refer Fig. 3.1 (b)). Following that, the cleaning process have been done to get rid of any contamination, e.g., dirt, grease and oil that can potentially lead to ineffectiveness of thin film adhesion. The substrates were cleaned thoroughly by subsequently sonicated them for 15 minutes into ethanol, iso-propanol (IPA), acetone and de-ionized water. Finally, the substrates were kept in a petri dish for drying process.

Figure 3.1 (a): Fixed size glass substrate after being cut

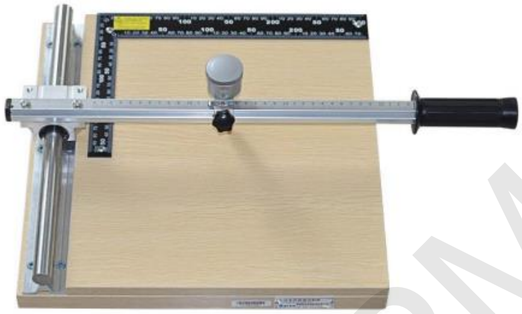

Figure 3.1 (b): System used for substrate cutting

3.3 EXPERIMENTAL PREPARATION

Two types of depositions have been carried out in this work, that is spin coating and thermal evaporation method. These depositions methods are important to obtain the thin film hence find the structural, morphological and optical of the VTP through various characterization methods. These methods required its own preparations and procedure to ensure we get the most accurate results during the experiment is held. Figure 3.2 (a) and (b) presents the flow chart of spin coating and thermal evaporation, respectively.

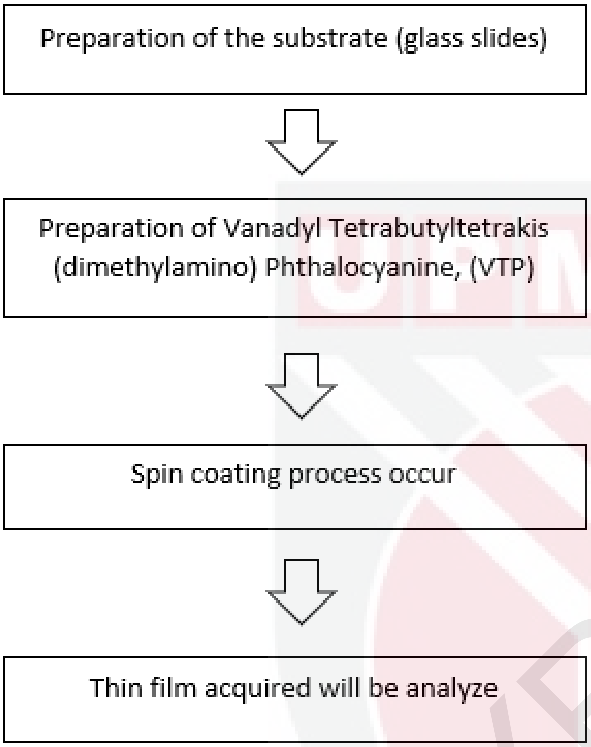

Figure 3.2 (a): Spin coating methods flow chart

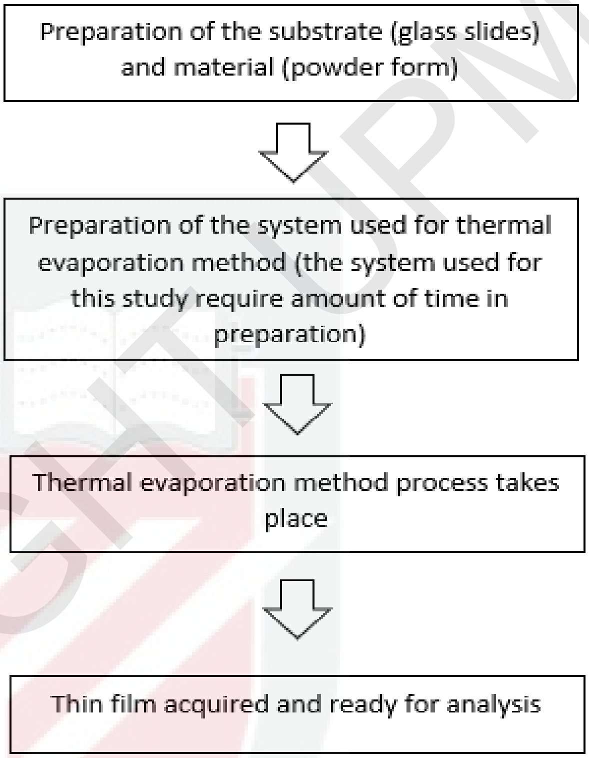

Figure 3.2 (b): Thermal evaporation method flow chart

3.3.1 SPIN COATING METHODOLOGY

Spin coating is one of the easiest and suitable ways to obtain the material thin films. It requires a small amount of solution and easy to control the thickness of thin film within a nanoscale range (Roslan, 2020). First, 10 mg of VTP was dissolved in 1 ml of dimethyl sulfoxide (DMSO) to form 10 mg/ml concentration. The solution was stirred overnight. A thin film sample was prepared by a simple spin coating technique at spin rate of 500 rpm. The spin coated film was annealed at 70 ℃ for 30 minutes. The whole procedure were done in the fume hood as DMSO was being used. The thin films were then ready to be analyzed.

Figure 3.3 (a): Spin coater machine used for this study

Figure 3.3 (b): Weighing scale machine used for this study

3.3.2 THERMAL EVAPORATION METHODOLOGY

Thermal evaporation technique is the second deposition method used in this work. An Auto Edward 306 deposition system has been utilized to evaporate the VTP thin film. 10 mg of VTP powder has been added on a tungsten boat before being placed inside of the deposition chamber. The pressure inside the chamber has been set at 1 x 10^{-6} Mbar prior to the depositing process. The vacuum chamber was then sealed by the bell jar to ensure a vacuum condition. The electric current was increased slowly to heat the tungsten boat. For thermal evaporation method, sputtering is frequently preferred over thermal evaporation in industrial applications due to its superior step coverage, wider material selection (including dielectrics), and often faster deposition rates (up to a few hundred nm/min) while still forming dense films with an acceptable adhesion quality (Luttge, 2011). For this study, the sputtering generates ions from an inert atmosphere and accelerates them toward the glass substrate on the masker. This subsequently enters the plasma phase and forms a coating on the substrate called the thin film. By thermal evaporation method, the thin film produced can be controlled through various parameters such as bias, pressure, and substrate temperature. These control techniques provide improved reproducibility, device optimization, and the adaptation of material properties. However, due to lack of time performed during the experiment, there are none parameters followed for this study as the system used itself has its limit. Hence, the only variable that was recorded was the voltage taken for the VTP thin film appeared on the glass substrate.

Figure 3.4 (a): Masker used for thermal evaporation technique

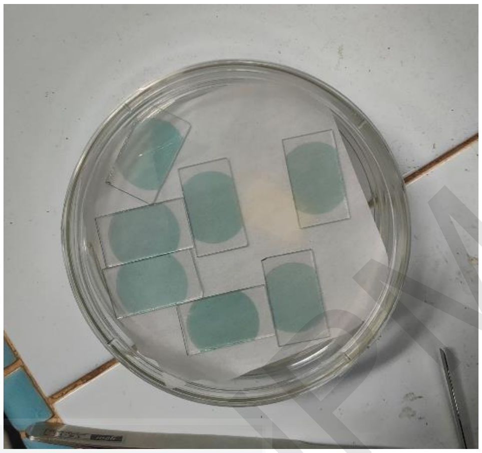

Figure 3.4 (b): VTP thin film on the substrate (glass slides)

3.4 STRUCTURAL CHARACTERIZATION

3.4.1 RAMAN SPECTROSCOPY

Raman Spectroscopy was named after the scientist C.V Raman who discovered the Raman effect in organic liquid in the year 1928 with his partners K.S Khrishanan. The founding wins them Nobel Prize Physics in the year of 1930. The discovery of Raman scattering was continued by a scientist named Franco Rasetti which found the Raman effect in gasses in the year of 1929.

Raman spectroscopy is well known used for finding the structural fingerprint of molecules which is how the molecules can be determined. Raman spectroscopy also used to determine the vibrational modes of molecules while finding the rotational of the molecules as well. the working principle or Raman spectroscopy is based on Raman scattering. Basically, Raman scattering detects the inelastic scattering of photons. The shift of the energy because of the laser light interacts with the molecular vibrations, phonons or other excitations show the vibrational modes in the system. Based through the working principle, the Vanadyl Tetrabutyltetrakis (dimethylamino) Phthalocyanine, (VTP) is heat up with a light usually a monochromatic light which is laser beam.

The illuminated site is collected with a lens and sent through a monochromator. Raman spectroscopy is used for this study with the collaboration of atomic force microscopy (AFM) and scanning electron microscopy (SEM) to compare and analyze the morphological and topological images of the VTP. The Raman instrument used for this study is Renishaw Raman-SPM/AFM (Refer figure 3.5) that is located at University of Malaya, Faculty of Science in Physics department.

Figure 3.5: Example of Renishaw Raman-SPM/AFM combined systems used (Extracted from: https://www.renishaw.com/en/raman-spm-afm-combined-systems--6638)

3.4.2 X-RAY DIFFRACTION

XRD relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. Crystalline refers to the degree of structural order and regularity in molecular arrangements of a material.(Shrivastava, 2018) .A primary use of the technique is the identification of compound based on their diffraction pattern. Effect that occurs when an incident beam of monochromatic X-rays interacts with a target material is scattering of X-rays form atoms within the target material. In materials with regular structure, the scattered X-rays undergo constructive and destructive interference. This is the process of diffraction. The diffraction of X-rays by crystals is described by Bragg’s law:

$$n\lambda=2d\sin\theta \qquad (2)$$

Where:

λ = Wavelength of the X-ray

d = Spacing of the crystal layers (Path difference)

θ = Incident angle (the angle between incident ray and the scatter plane).

n = integer

The diffraction occurs from plane set as angle θ is the diffraction angle with respect to incident radiation. The distribution of electron in the unit cell will determine the intensities of diffraction. Hence for this study, XRD is used for determined the crystallinity of the VTP between the deposition methods used.

3.5 MORPHOLOGICAL CHARACTERIZATION

3.5.1 ATOMIC FORCE MICROSCOPY (AFM)

Atomic force microscopy also known as AFM is known as one of the scanning probe microscopy types which enable scientist to detect information of the molecule by enhancing the resolutions of the device, more than 1000 times. AFM works as a stylus gauge which need to feel or touch the material but not literally. Basically, the mechanical probe or we called as the "stylus" moved up and down over a surface. the surface is moved in x-y pattern along the stylus. A part of the AFM known as the cantilever which has a sharp tip at its end is used to scan the material surface. The forces between the material and the cantilever tip create a deflection according to the Hooke’s Law.

$$F_s = -kx. \tag{3}$$

Where:

F = Spring force

K = Spring constantds

X = Spring stretch or compression

AFM is used for this research is based on the three of the AFM abilities which is AFM can be used to measure the force between the probe and the sample, find the topographic imaging and manipulation. In force measurements, the force between the probe and VTP can be used for force spectroscopy which can use to measure the mechanical properties of the VTP such as the material stiffness (Young Modulus). The reaction from the forces can be used to find the three-dimensional image (topographic) of the VTP at high resolution and manipulation, the forces between the tip and material can also used to manipulate the VTP in a controlled way. Hence, in this study, AFM was used to determine the surface roughness and morphology of VTP through different depositions methods.

Figure 3.6: The Alpha 300 RA confocal Raman-AFM microscope system *(GmbH, 2022)*

3.5.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPE (FESEM)

Field emission scanning electron microscopy (FE-SEM) is a sophisticated technique for capturing images of the microstructures of materials. FE-SEM is typically performed in a vacuum environment due to the tendency of gas molecules to disturb the electron beam and the secondary and backscattered electrons used for imaging. The advantages of using FESEM is that it has the ability to examine contamination spots in small areas using electron accelerating voltages that are well-matched to energy dispersive X-Ray Spectroscopy (EDS). EDS detects x-rays emitted by the sample during electron beam bombardment in order to determine the elemental composition of the volume being analyzed. This means that high quality and low voltage images can be obtained using FESEM. Moreover, by using FESEM, on this study, the material morphological can be analyze much more hence better results can be obtain when comparing the morphology of Vanadyl Tetrabutyltetrakis (dimethylamino) Phthalocyanine, (VTP) in different depositions methods. Figure 3.7 shows the example of morphology of material when using FESEM. The detailed of the images allowed to determined the thickness and the pore volume of the material.

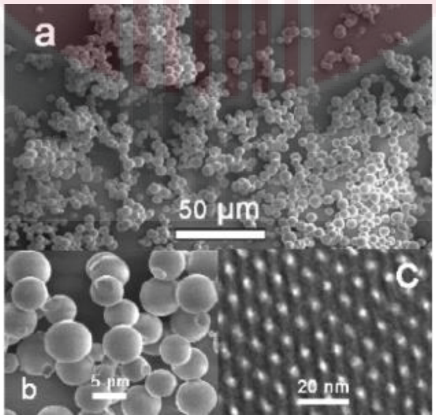

Figure 3.7: Example of FESEM images of mesoporous silica SBA-16 (Jin et al., 2007)

3.6 OPTICAL CHARACTERIZATION

3.6.1 ULTRAVIOLET-VISIBLE SPECTROSCOPY (UV-VIS)

Electromagnetic radiations can interact with matter in a variety of ways. The term ‘spectroscopy' refers to the study of the interaction between electromagnetic radiations of varying energies and matter, in which each interaction reveals some property of the matter being studied. A spectrophotometer is a device that determines the amount of light falling within a specified wavelength range as it passes through a medium. The fundamental concept behind this spectrometer is that as light propagates through a material, it interacts with the molecules contained within, resulting in light absorption, transmission, and reflection. These interactions occur when electromagnetic (light) photons are absorbed by molecules and are sufficiently energetic to promote the outer electrons from the HOMO to the LUMO levels of the material, thereby causing electronic transitions. UV-VIS spectroscopy data may be shown as a function of wavelength as an absorbance, optical density, or transmittance graph. However, the data is frequently presented in the form of a graph with absorbance on the vertical y axis and wavelength on the horizontal x axis.

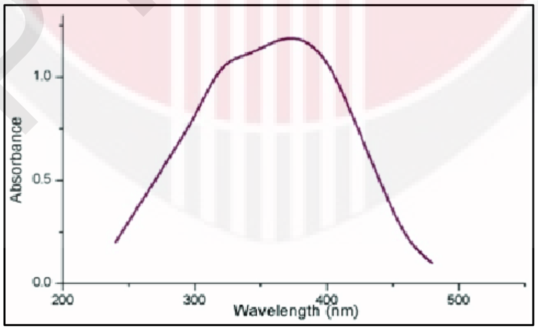

Figure 3.8: Example of UV-VIS graph (Shubha et al., 2017)

From the Figure 3.8, the graph highlighted the spectrum of absorption spectrum of the material. For this study, the similar graph will be used to determined the Vanadyl Tetrabutyltetrakis (dimethylamino) Phthalocyanine, (VTP) absorption spectrum in different depositions methods. The absorption spectrum is important because it can determine the molar absorptivity in which is useful in comparing the spectra of several substances and calculating the relative strength of their light-absorbing functions (chromophores).

$$\textbf{Molar Absorptivity, } \varepsilon = A / c\,l \qquad \textbf{(4)}$$

Where;
A= absorbance
c = sample concentration in moles/liter
l = length of light path through the sample in cm.

The chromophore is the component of a molecule that imparts its color. The chromophore is a portion of the molecule in which the energy difference between two distinct molecular orbitals is within the visible spectrum range. Thus, visible light incident on the chromophore can be absorbed by excited electrons. When the molecule is exposed to light, it undergoes a conformational shift. In addition, as VTP is a metal complex, which contain coordination complex with ligands, the targeted results will be the that VTP have conjugated Pi-system in which have best stability for its properties. Figure 3.9 (a) shows the type of UV-VIS spectrometer used in this study which is the Perkin-Elmer Lambda 750 UV-VIS-NIR spectrometer and figure 3.9 (b) shows that the UV-VIS spectroscopy used has two substrate holder which is a) the reference holder which act as baseline calibration and b) the sample holder, which holds the substrate with the material thin film on top.

Figure 3.9 (a): UV/visible/NIR spectrophotometer Perkin Elmer model Lambda 750

Figure 3.9 (b): reference and sample holders of the spectrophotometer

CHAPTER 4

RESULTS AND DISCUSSION

4.1 STRUCTURAL CHARACTERIZATION

4.1.1 RAMAN SPECTROSCOPY

Raman characterization was analyzed with 514 nm wavelength of laser source using Renishaw system. Raman spectroscopy is utilized to investigate the structural properties of the VTP thin film in different deposition methods by analyzing the shifting of the vibrational modes (CIT). Because this value is directly connected to energy, Raman shifts are commonly expressed in wavenumbers, which have units of inverse length. In the Raman spectrum, the following expression (5) can be used to convert between spectral wavelength and wavenumbers of shift.

$$\Delta\tilde{\nu} = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1}\right) \qquad \textbf{(5)}$$

Where:

$\Delta\tilde{\nu}$ = Raman Shift

λ_0 = Wavenumber

λ_1 = Raman spectrum wavelength

Raman shifts from the micro-Raman spectra can characterize the vibration and absorption of functional group of VTP thin film by following the IR spectrum table which contain the IR spectrum frequency range. The peak seen in the micro-Raman spectra can be elaborated about the functional group behavior which helps in characterized VTP.

Figure 4.1 shows the micro-Raman spectra of VTP thin film via spin coating deposition method and VTP thin film via thermal evaporation method. The Raman spectra was combined for easy comparisons of the Raman shifts and phase for both Raman spectra.

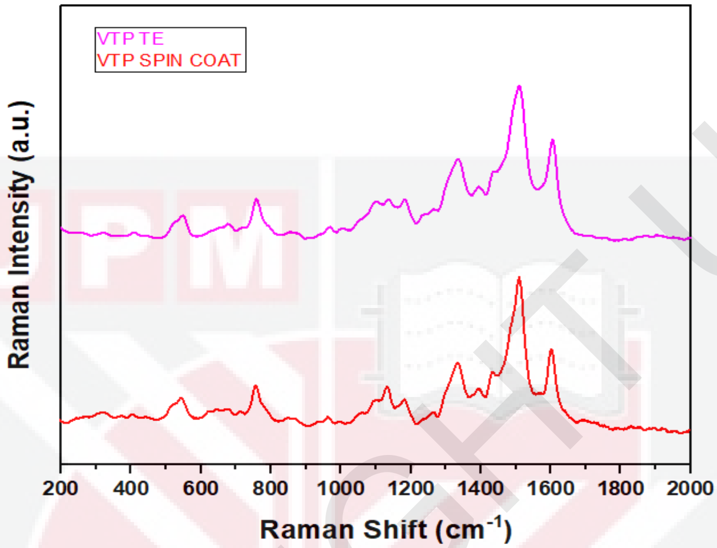

Figure 4.1: Raman spectra of VTP thin film for spin coating and thermal evaporation method

Based on the Raman spectra in Figure 4.1, it can be observed that the for the VTP thin film for spin coating method, the strongest peak is at 1610 cm^{-1} can be described to C=C stretching of the VTP molecule. Followed by the the highest strong peak at 1514 cm^{-1} which attributed to the vibration of stretching nitrogen bridging atoms. The medium peak at 1435 cm^{-1} allocated to isoindole stretching vibrations (Roslan, 2020), while the band at 1340 cm^{-1} linked with to C-H bending. The band located at 1188 cm^{-1} and 1138 cm^{-1} being referred to the ring vibration and ring deformation, respectively.

For Raman spectra VTP thin film for thermal evaporation method, the strongest peak is located at 1607 cm^{-1} where, the double bond carbon atom (C=C) is stretching same as for spin coating at 1610 cm $^{-1}$. Next, the highest peak in the Raman spectra at 1511 cm^{-1} band define to the strong nitrogen oxygen pair bond (N-O) stretching. Then, for the band located at 1436 cm^{-1} based on spin coating method, the isoindole stretching vibrations take place (Roslan, 2020) while the band at 1338 cm^{-1} attributed to medium C=C stretching. As for the band located at 1184 and 1136, assuming the same molecular character as spin coating method, as the band assign for the ring vibration and ring deformation, as well. Except for some bands that shifted to lower wavenumbers, the Raman spectra bands for VTP thin film by both of the deposition's methods almost identical, namely at 545, 1097, 1188, 1138, 1340, 1514, and 1603 cm^{-1}. This clarifies that even with different depositions methods, the VTP itself acts as a presiding material, which signifies that the VTP on both depositions methods seems insignificant. However, when carefully examined, there is a slight difference in term of intensity of those peaks. The peaks from VTP by thermal deposition sample showed higher intensity than the spin-coated sample. This would suggest the better crystallinity of the VTP by thermal evaporation and amorphous nature of the VTP by spin-coated.

VTP spin-coated	VTP thermal evaporated	Approximate assignment of vibrations
545	**542**	Ring deformation
757	**757**	Ring deformation
1097	**1098**	C-O stretching
1138	**1138**	Ring deformation
1188	**1184**	Ring deformation
1340	**1336**	Medium C=C stretching
1435	**1435**	Isoindole stretching
1514	**1511**	N-O stretching
1610	**1607**	Strong C=C stretching

Table 4.1: Raman shifts of VTP thin film between two depositions method

4.1.2 X-RAY DIFFRACTION (XRD)

XRD was used to characterize the crystalline phase of VTP thin film. Data that can be extracted instead of finding the crystallinity is Full Width at Half Maximum (FWHM), d-Spacing, HKL and crystallinity percentage. The use of FWHM is to characterize the VTP thin film qualities and attributes of surface integrity. FWHM can be obtain by using the Scherrer equation (also known as Debey-Sherrer equation) which tells that he presence of sub-micron particles/crystallites broadens the Powder X-ray diffraction peaks hence, the relationship between FWHM and the crystallite size can be related by expression (6) (Dorset, 1998)

$$\mathbf{FWHM} = \frac{\boldsymbol{k\lambda}}{\boldsymbol{LCOs\theta}} \qquad \textbf{(6)}$$

Where:

L = particle size

θ = Peak positions (2θ / 2) in radian

λ = wavelength of the X-ray used for diffraction

The value of FWHM can also be obtained by using the OriginPro Software as the software can automatically calculate the value and tabulated the data in the software. Next, the d-spacing can be defined as the distance between the atoms' planes that produce diffraction peaks. The importance of determine the d-spacing is because each crystalline solid has a distinctive pattern that can be used as a "fingerprint" for XRD identification (Latha, 2017). In order to find the d-spacing, the expression of the d-spacing is based on on one the popular equation in solid state, the Bragg equation. Bragg equation can be used by following expression (7)

$$n \times \text{wavelength} = 2d\sin(\text{theta}) \quad (7)$$

where;

n = the integral number of wavelengths

d = the interplanar spacing between the atoms in the crystal

Moreover, the Miller indices (hkl) data can also be extracted from the XRD spectra as well. (hkl) is used to determined the lattice plane of the atom in VTP thin film with the unit cell. There are several rules in order to get the miller indices of a XRD data. The rules follow as below:

1. Determine the intercepts of the face along the crystallographic axes
2. Take the reciprocals
3. Clear fractions
4. Reduce the lowest terms

From the instructions above, the Miller indices for VTP thin film can also be obtained form the Origin Pro software. Noted that the smaller the miller indices, the more parallel to the plane is to the axis while the larger the Miller indices, the more perpendicular a plane to the axis. (Upali, n.d.). Last but not least, the crystallinity percentage of VTP thin film can be extracted from the XRD. The percentage can be calculated through XRD deconvolution method, where the amorphous and crystalline contributions to the diffractions is separated. The ratio of the integrated area of all crystalline peaks to the total integrated area beneath the XRD peaks can be also used to determine crystallinity. (Khalifa, 2018).

Figure 4.2 (b) shows the XRD spectra of VTP thin film via spin coat and thermal evaporation method and the XRD spectra for XRD in powder form.

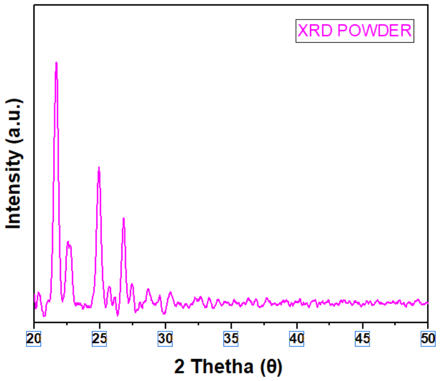

Figure 4.2 (a): XRD spectra of VTP powder

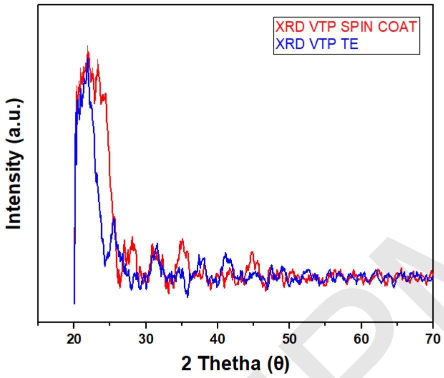

Figure 4.2 (b): XRD spectra of spin coating and thermal evaporation method

From the figure 4.2 (b) , the XRD spectra for spin coating and thermal evaporation method look exactly the same. The XRD spectra of spin coat shows there are seven major peaks exist on the XRD spectra with the highest peak at 24.10789 (2θ). As for the thermal evaporation method, there are 5 major peaks recorded with the highest peak is at 25.57327 (2θ). From the data above, thermal evaporation method has the highest peak which means that the method has the highest intensity compared to spin coating method. The highest peak of intensity for spin coating method also is located at lattices (-1,2,1) while for the thermal evaporation method, the highest peak is located at lattice (-2,0,2). The corresponding lattice planes is shown in figures 4.3 below.

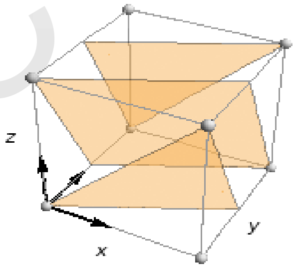

Figure 4.3 (a): lattice planes for spin coating method at highest peak

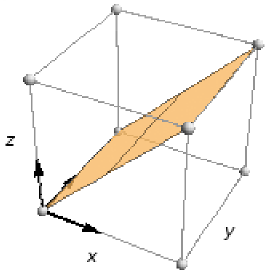

Figure 4.3 (b): lattice planes for thermal evaporation method at highest peak

As for the crystallinity percentage for both of the deposition's method of VTP thin film, the calculation is based on the expressions (8).

$$\textbf{Crystallinity (\%)} = \frac{Ic}{(Ic+Ia)}\textbf{x100} \qquad \textbf{(8)}$$

After calculated using expression (3), the crystallinity percentage of VTP thin film via thermal evaporation method are higher than the spin coating method, which was thermal evaporation had the crystallinity percentage value of 24.85 % better than spin coating method which has the crystallinity percentage value of 18.30 %. The data proofed that VTP thin film deposited via thermal evaporation method is the best compared to spin coating method. This can be confirmed by the data with other characteristics that are mention in this chapter. The AFM and FESEM images show that the surface roughness of VTP thin film deposited via thermal evaporation method tends to have better roughness and the surface morphology supported the claimed as well. However, the peak that can be seen for both depositions claimed to be amorphous crystallinity. This is because, according to the XRD spectra, the XRD pattern are not normal compared to other XRD as when cleaved or split, they create fragments with uneven, frequently curved surfaces; and when exposed to x-rays, they exhibit poorly defined patterns.(*Crystalline and {Amorphous} {Solids}*, 2021) . The XRD pattern for both of the deposition's methods are different from XRD spectra obtained from VTP powder. Based on figure 4.2 (a), notice that the peak rises from different point where for spin coat and thermal evaporate methods, the peak rises at the starting point of the XRD spectra while for the VTP powder, the XRD pattern peaks at some point in the XRD spectra. This proven more that the peak in figure 4.2 (b) can be from amorphous part of the thin film. The data of the comparisons between the two depositions method then are tabulated in table 4.2

VTP Thin Film (Spin Coating Method)

Peak	Peak Positions (2θ)	FWHM	d-Spacing (Å)	H,K,L	Crystallity percentage (%)
1	20.15978	0.05235	3.296	(2,1,0)	**18.303**
2	20.3129	0.18627	3.272	(0,2,0)	
3	20.54351	0.33798	3.235	(-2,1,1)	
4	20.89009	0.66796	3.182	(-2,1,1)	
5	21.65918	1.16836	3.071	(-2,1,1)	
6	23.30785	0.52918	2.856	(2,0,1)	
7	24.10789	2.01791	2.763	(-1,2,1)	
8	22.57989	1.0359	2.947	(2,0,1)	

VTP Thin Film (Thermal Deposition Method)

Peak	Peak Positions (2θ)	FWHM	d-Spacing (Å)	H,K,L	Crystallity percentage (%)
1	20.32352	0.40196	3.270	(0,2,0)	**24.85**
2	20.74917	0.70508	3.204	(-2,1,1)	
3	21.58593	1.36466	3.081	(-2,1,1)	
4	22.67827	1.88746	2.934	(2,0,1)	
5	25.57327	1.46156	2.607	(-2,0,2)	

Table 4.2: Comparisons data between the two deposition's method.

4.2 MORPHOLOGICAL CHARACTERIZATION

4.2.1 ATOMIC FORCE MICROSCOPY

The VTP thin film are characterized via AFM with the size of 3000 x 3000 nm scan rate to analyze the surface morphology and roughness. The AFM images of VTP thin film by both type of depositions method was acquired through tapping mode, which is one of the modes in AFM. The images produced then processed by the Nanoscope Analysis version 1.7 data visualization and analysis tool software. Figure 4.4 (a) shows the 2D image while Figure 4.4 (b) shows the 3D AFM image of VTP thin film through spin coating deposition method.

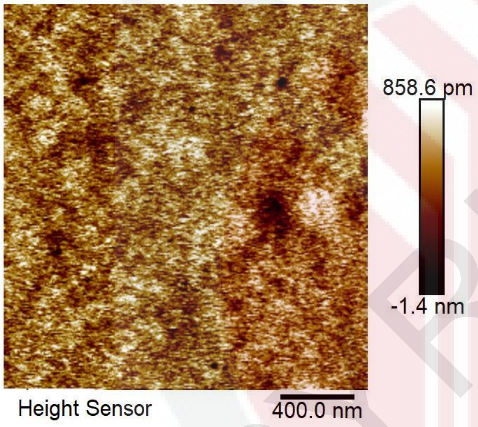

Figure 4.3 (a): 2D images of VTP thin film by spin coating deposition method.

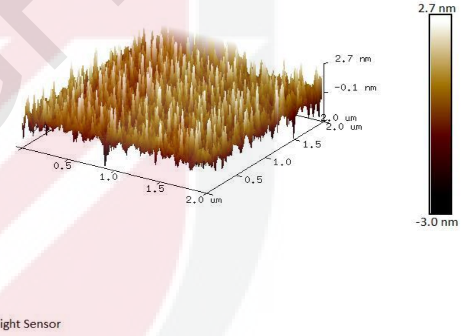

Figure 4.3 (b): 3D images of VTP thin film in spin coating deposition method.

Based on previous research, the AFM images of VTP thin films through spin coating deposition method shows non uniform and rough surfaces with peak presence in the images (Roslan, 2020). The AFM images results for this study are also coherent with the previous study, which the images show that the surface morphology of the VTP thin film acquired also have rough spike surface and non-linear surface which mean that the surface is not uniformly rough, there are certain part on the image are rough and some part that are smooth. The surface of the material has slightly pored which strongly supported the non-uniform theory. This can also be proven by looking at the 3D image of the VTP thin film in Figure 4.4. The image shows that the 3D images enhanced the spike looked surface of the VTP thin film. Based on the data acquired through Nanoscape Analysis software, the software indicates that the RMS roughness value of the VTP thin film was ~1.07 nm which is coherent from the previous study showed that the RMS roughness value of VTP thin film with spin coating method at rate of 2000 RPM was ~ 0.33 nm (Roslan, 2020). The data also shared the highest peak of the VTP thin film which counted as R_q of the data are valued ~0.190 µm. Through the RMS roughness and the surface morphology, the thin film of VTP by spin coating method are suitable as an organic semiconductor as the film topography suggest that the VTP thin film are potential in the usage of humidity sensing (Aziz et al., 2010). The AFM data of the thin film by spin coating method are then tabulated in Table 4.3

Results Properties	**Results**
Image R_q	0.00107 µm
Image R_a	0.257 nm
Image R_{max}	0.190 µm
Roughness R_{max}	0.190 µm
Peak Count	1240
Z Range	0.190 µm

Table 4.3: AFM data for spin coating method

Next, the AFM image for VTP thin film by thermal evaporation method are highlighted in Figure 4.5. Figure 4.5 (a) shows the 2D image, while in Figure 4.5 (b) shows the 3D image of VTP thin film via thermal deposition method.

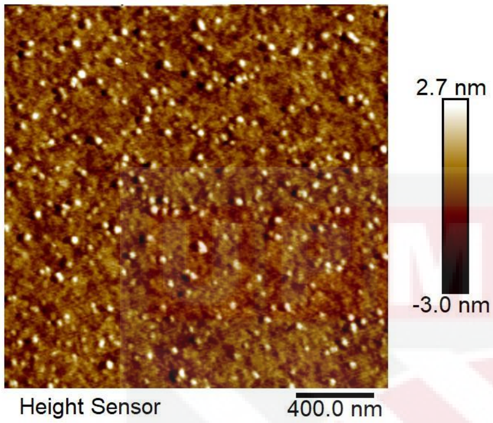

Figure 4.4 (a): 2D image of VTP thin film via thermal depositon method

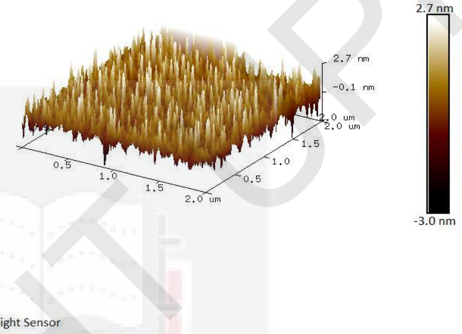

Figure 4.4 (b): 3D image of VTP thin film via thermal evaporation method

It reveals that the morphology of VTP evaporated are much more complex compared to spin coated VTP. The 2D images shows that the surface morphology of the material is grainy like surface, and pores were begin to presence. The surface morphology also shows that the surface roughness of the material is much more uniform compared to spin coating method. Table 5 presents the RMS roughness for the thin film valued ~ 0.00224 µm which support the theory earlier. The increase of the roughness are due to the presence of the pores which began to shape based on the images. The increase of RMS value also can be explained by the enhancement of nucleation and coalescence of grains (Henry et al., 2019). The exist of the grainy textured on the surface is also due to the thermal process. The uniform distribution of the grain seen on the surface of the film is due to the increasing temperature due to the thermal evaporation process. The increasing temperature can distribute the grain homogenously on the substrate (Henry et al., 2019) and can be observed by the crystallite of the thin film from the XRD analysis. The 3D image of the film revealed many sharp spikes formed compared to the spike formed in spin coat thin film. The spike observed the roughness of the material on the film after being heated with high temperature. The differences of height in spike also strongly follows the theory which based on the data in Table 4.4, the maximum Z range of the film is ~ 0.392 µm, which were much higher than spin coat method.

Results Properties	**Results**
Image R_q	0.00224 µm
Image R_a	0.500 nm
Image R_{max}	0.392 µm
Roughness R_{max}	0.392 µm
Peak Count	644
Z Range	0.392 µm

Table 4.4: AFM data for thermal evaporation method.

4.2.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPE (FESEM)

To further confirm the surface morphology of both thin films, Figure 4.5 (a) and (b) reveals the FESEM images for VTP thin film in low and high magnifications, respectively.

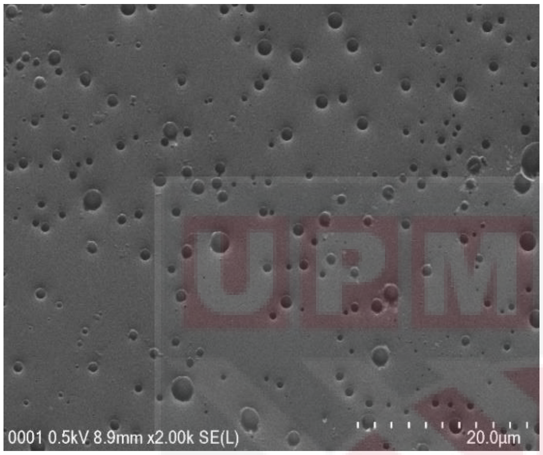

Figure 4.5 (a): FESEM image of VTP thin film via spin coat in 2.00 k magnification

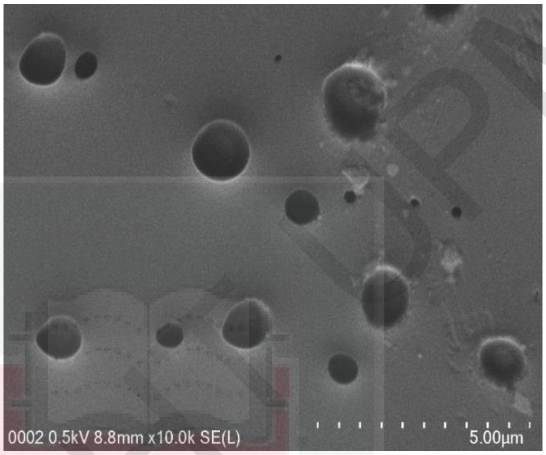

Figure 4.5 (b): FESEM image of VTP thin film via spin coat in 10.0 k magnification

The images show the surface morphology of the thin film after deposit via spin coating has non uniformly pores formed on the surface. The pores are spread unevenly across the substrate even though the material is evenly spread on the substrate. The average size pores assuming from the value above is around ~1.35 µm. The average value of the pores diameter makes VTP falls in macroporous type of porous material which is pores diameter *d* > 50 nm. The diameter of the pores explains the characteristics of the VTP itself. As mention earlier, VTP is a material which is good in sustaining in high temperature conditions which is proven based on the pores formed because the porous condition have presence of voids of controllable dimensions at the atomic, molecular and nanometer scale (Aquino & Maschmeyer, 2009)

The FESEM images present by VTP thermal evaporated results is varied from spin coating method. This is because the spin coating process depends on the RPM of the spin coating and the centripetal force. While, the thermal evaporation rate is determined by the vapor pressure of the source material at the evaporation temperature (Lévy, 2016)). As explained earlier, VTP is in aqueous solution when spin coating while VTP is in powder form when evaporate in the thermal system. The differences of the methods and material form influenced the variations of the resulting images. Based on the AFM, the images show the rough texture surfaces which is way rougher compared to spin coating. Figure 4.7 (b) and figure 4.7 (c) shows the average particle size of the VTP thin film using 2.00 k and 10.00 k magnification.

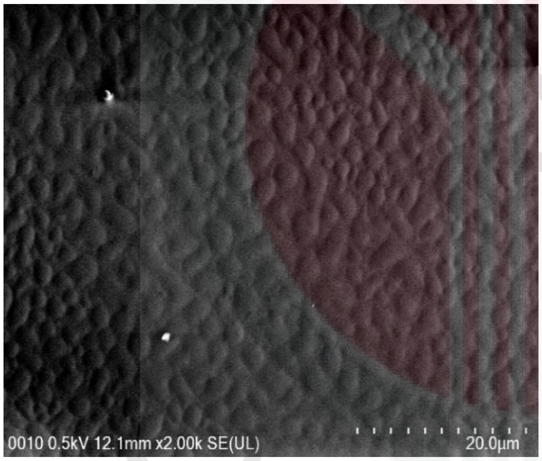

Figure 4.6 (a): FESEM image of VTP thin film via thermal evaporation in 2.00 k magnification

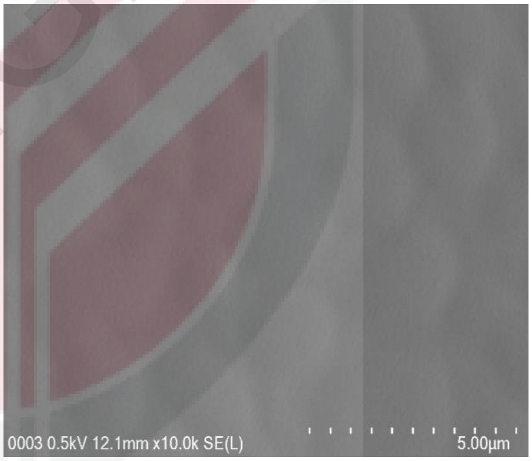

Figure 4.6 (b): FESEM image of VTP thin film via thermal evaporation in 10.00 k magnification

The particle size varies from (2.0 µm to 4.0 µm) which average of 3.00 µm. The image shows that the surface morphology of the thin film is almost uniformly round and oval shaped across the thin film. The surface is round grainy which makes the rough texture. This is relevant to the AFM results and XRD results as the thin film is much more crystalline compared to the spin coating method. Furthermore, as the temperature increases because of the increasing current during evaporation, a change in the current density from low to high values leads to a switch in the pore growth mechanism from being crystallographically oriented to current-line oriented VTP molecule that can be seen in figure 4.6 (a) (Langa et al., 2009). As Kim et al. reported that the conductivity of the material increased due to the increased of tight and dense grain growth (Kim et al., 2014). Hence, thermal evaporation is a good alternative for VTP thin film depositions method.

4.3 OPTICAL CHARACTERIZATION

4.3.1 ULTRAVIOLET-VISIBLE SPECTROSCOPY (UV-VIS)

Optical characterization is carried out to determine the energy band gap for different deposition methods. VTP thin film is targeted as a good semiconductor, which means that VTP thin film will have small band gap. There are two bands involved to find the band gap which is the Q- band and B-band region. B band is attributed to second π- π * transitions of macrocyclic ring of Metal Phthalocyanine (transition from ground state to second excited state) and Q band is due to first π- π * transitions of macrocyclic ring (transition from ground state to first excited state). These two bands are important to determine the band gap of a material. According to (Gandhi, 2020), B- band is correspond to the fundamental absorption band that can be utilized to determine the material's band gap. The value of the energy band gap can be calculated through the absorption spectra of the UV-VIS. According to (Schaf et al.,), by projecting a line on a dominating peak towards a corrected absorption base line, the optical energy band gap can be estimated from UV–VIS absorption spectra. Next, the wavelength value at the intersection of both lines is used to obtain the value of the optical energy band gap using the expression (9).

$$\mathrm{Eg} = \frac{1241}{\lambda} eV \qquad \textbf{(9)}$$

Figure 4.10 shows the comparisons of UV-VIS spectra of VTP thin film deposited via thermal evaporation at (0°C) and deposited via spin coating at 500 RPM.

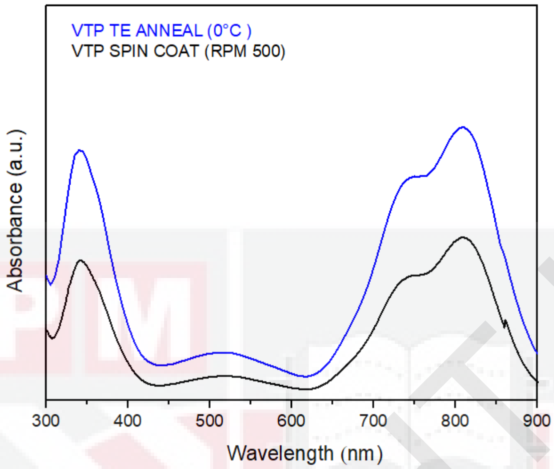

Figure 4.7: Comparisons of two different UV-VIS spectra

The reasons for choosing the UV-VIS spectrum of VTP thin film at RPM 500 is because VTP thin film that are deposited at RPM 500 has the highest absorbance compared to the other RPM. From the figure, the VTP thin film via thermal depositions method has the strongest absorbance for B-band region with 2.908 (a.u) at 340 nm wavelength, same goes for Q-band region, VTP thin film via thermal evaporation also has the strongest absorbance for Q-band region compared to spin coating method with 3.358 (a.u) at 810 nm wavelength. Same goes for this thin film, the energy band gap can be calculated through expression (1). The the intersection of both lines found to be at 890 nm wavelength which correspons to optical energy band gap of 1.37 eV. The optical energy band gap is similar or slightly different is due to the material that are used for the thin film is still the same which is the VTP. There are no booster or other material that can increase the band gap added in the thin film. However, from the comparisons also, it can concludes that the lowest RPM at 500 RPM which has the strongest absorbance compared to the other RPM have lower absorbance compared to the lowest annealing at (0°C) hence, with annealing, VTP thin film have the highest absorption by thermal evaporation method. In addition, VTP thin film via thermal evaporation method is a better use for organic semiconductor as according to the UV-VIS spectra, the absorption intensity of VTP thin film deposited by thermal evaporation is the highest compared to the spin coating method. The high absorbance value can be used in future study about the optical capabilities of VTP thin film as semiconductor.

CHAPTER 5

CONCLUSION

5.1 CONCLUSION

Organic electronic devices are experiencing a surge in popularity in the contemporary market. Having said that, the desire to discover a novel organic material that ensure the advancement of organic electronic applications and the enhancement of device performance is evident. This study is focused toward achieving this goal.

Initially, investigation of the VTP thin film deposited in different deposition methods are discussed in Chapter 4. The structural properties of both thin films have been studied via Raman spectroscopy and XRD. From XRD, the crystallinity percentage of VTP evaporated is higher compared to the spin coating with the value of 6.55 % difference. As for Raman spectra, no distinctive Raman shifts were observed for both of thin films. However, there is slightly difference in terms of peak intensity, in which the VTP evaporated showed more intense Raman shift than the VTP spin coated. This suggested that a better crystallinity formed by VTP evaporated. In addition, AFM and FESEM have been conducted to further analyze the morphology study of VTP thin films for both methods. AFM characterizations revealed that the RMS value of VTP evaporated is the higher compared to VTP spin-coated with the value of 2.24 nm. The morphology study was then further confirmed by FESEM, in which the surface of VTP evaporated has round grainy texture which makes the rough texture. In comparison, the surface morphology of VTP spin-coated consisted of porous surface which might reduce the conductivity of the material. Finally, UV-VIS spectroscopy has been utilized to measure the energy band gap for both deposition methods. It revealed that there is no major difference of the energy band gap value for both deposition methods, showing that, the energy band gap value does not give any effect on deposition methods. The comparative study of VTP thin films properties deposited by spin coating and thermal evaporation method has therefore been successfully performed.

5.2 FUTURE WORKS

This study opens many opportunities for all the scientists especially the ones who focus on organic semiconductor. The results of this study can be elaborate and continue for future works in order to get better innovation and creation in the future. Some ideas that can be studied based on the results from this study is:

1. The utilization of VTP thin film deposited by thermal evaporation method in fabrication of VOFET. Study the characterization and optimization of the thin film used in the VOFET itself.
2. Electrochemical etching toward VTP membrane using VTP thin film deposited by thermal evaporation method. The study of the behavior of cation and anion during etching.
3. The usage of VTP thin film deposited by thermal evaporation method in humidity sensor. Study the film which will enhance the humidity sensor functions and study the film morphology as well.

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