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คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2560

# SYNTHESIS OF $Cu_2ZnSnS_4$ FOR THIN FILM SOLAR CELLS PREPARED BY SOLUTION-BASED PROCESSES

Miss Napaporn Khothong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
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| Thesis Title | SYNTHESIS OF $Cu_2ZnSnS_4$ FOR THIN FILM SOLAR CELLS PREPARED BY SOLUTION-BASED PROCESSES |
| By | Miss Napaporn Khothong |
| Field of Study | Chemical Engineering |
| Thesis Advisor | Paravee Vas-Umnuay, Ph.D. |

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Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.................................................................Dean of the Faculty of Engineering

(Associate Professor Supot Teachavorasinskun, Ph.D.)

THESIS COMMITTEE

.................................................................Chairman

(Associate Professor Seeroong Prichanont, Ph.D.)

.................................................................Thesis Advisor

(Paravee Vas-Umnuay, Ph.D.)

.................................................................Examiner

(Assistant Professor Apinan Soottitantawat, Ph.D.)

.................................................................External Examiner

(Pisist Kumnorkaew, Ph.D.)

นภาพร คอทอง : การสังเคราะห์ฟิล์มบางคอปเปอร์ซิงค์ทินซัลไฟด์สำหรับโซลาร์เซลล์ชนิดฟิล์มบางในสภาวะของเหลว (SYNTHESIS OF Cu$_2$ZnSnS$_4$ FOR THIN FILM SOLAR CELLS PREPARED BY SOLUTION-BASED PROCESSES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร.ปารวี วาศน์อำนวย, 60 หน้า.

การสังเคราะห์ฟิล์มบางคอปเปอร์ซิงค์ทินซัลไฟด์ด้วยวิธีการเคลือบแบบนำพาที่ใช้ความเร็วในการเคลือบที่ต่างกัน โดยสารตั้งต้นที่ใช้เป็นโซลเจลของสารละลาย 2-เมทอกซี่เอทานอลกับเมทอลคลอไรด์และไทโอยูเรีย ฟิล์มที่ถูกเคลือบจะถูกนำไปอบที่อุณหภูมิ 340 ถึง 550 องศาเซลเซียส ภายใต้บรรยากาศของไนโตรเจนเพื่อให้ได้ฟิล์มบางคอปเปอร์ซิงค์ทินซัลไฟด์ที่มีคุณภาพสูง โดยองค์ประกอบ ลักษณะทางสัณฐาน วัฏภาค และสมบัติทางแสงของคอปเปอร์ซิงค์ทินซัลไฟด์ถูกวิเคราะห์ด้วยอุปกรณ์วิเคราะห์ธาตุเชิงพลังงาน จุลทรรศน์อิเล็กตรอนแบบส่องกราด เครื่องวิเคราะห์การเลี้ยวเบนรังสีเอกซ์ เครื่องรามานสเปกโตรมิเตอร์ และเครื่องอัลตราไวโอเลต-วิสิเบิล สเปคโทรโฟโตมิเตอร์ตามลำดับ ฟิล์มบางที่สังเคราะห์ได้นั้นอยู่ในวัฏภาคของเคสเทอไรท์ และมีค่าแถบช่องว่างพลังงานประมาณ 1.4 ถึง 1.5 อิเล็กตรอนโวลต์ อีกทั้งฟิล์มบางคอปเปอร์ซิงค์ทินซัลไฟด์ที่สังเคราะห์ได้นั้นยังนำมาประยุกต์ใช้เป็นชั้นส่งผ่านโฮล์ของเซลล์แสงอาทิตย์ชนิดสารอินทรีย์ ถึงแม้ว่าประสิทธิภาพการแปลงพลังงานของอุปกรณ์เซลล์แสงอาทิตย์ชนิดสารอินทรีย์ที่มีฟิล์มบางคอปเปอร์ซิงค์ทินซัลไฟด์เป็นชั้นส่งผ่านโฮล์จะมีค่าน้อยแต่มีความเสถียรกว่าอุปกรณ์เซลล์แสงอาทิตย์ชนิดสารอินทรีย์แบบทั่วไปที่ใช้โพลี(3,4-เอทิลีนไดออกซี่ไทโอฟีน) โพลีสไตรีนซัลโฟเนตเป็นชั้นส่งผ่านโฮล์

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สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ........................................
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NAPAPORN KHOTHONG: SYNTHESIS OF $Cu_2ZnSnS_4$ FOR THIN FILM SOLAR CELLS PREPARED BY SOLUTION-BASED PROCESSES. ADVISOR: PARAVEE VAS-UMNUAY, Ph.D., 60 pp.

Copper zinc thin sulphide ($Cu_2ZnSnS_4$: CZTS) thin films were synthesized via convective deposition method at various deposit speeds based on sol-gel precursor of 2-methoxyethanol solution with metal chlorides and thiourea. The deposited films were annealed at 340 to 550ºC under $N_2$ atmosphere to yield high quality CZTS films. The compositions, morphology, phase, and optical properties of the CZTS films were characterized by Energy dispersive X-ray analysis (EDX), Scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, and UV-Vis spectrophotometer, respectively. The formation films exhibited in kesterite structure and the band gap was about 1.4-1.5 eV. The CZTS films also applied as a hole transporting layer of organic photovoltaics solar cells. Although the power conversion efficiency of the OPV device with CZTS film is less value, but it is more stable than ordinary OPV device with PEDOT:PSS as a hole transporting layer.

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

# INTRODUCTION

Energy is an important factor that meets the basic needs of people, businesses and industries. Nowadays, fossil fuel is the main source of energy but it is not enough for the number of population which is rapidly increased, causing the price of energy to be higher; so we need to consider the use of energy from fossil fuel more efficiently as much as possible. With the crisis, it is necessary to look for greener sources of energy as alternatives to replace the fossil fuels. Renewable energy such as hydropower energy, solar energy, biomass energy, wind energy and geothermal energy are inexhaustible and have less impact on the environment. Among various renewable energy sources, solar energy is one of the most interesting alternatives because it is free, clean, inexhaustible resource and suitable for meeting the energy demands. Solar energy can be utilized by direct transformation into thermal energy such as solar water distillation system or indirectly in the form of electricity.

Solar cell is a device that converts the energy of sunlight directly into electricity. Solar cell technologies are divided into three generations. The first generation solar cells are made from crystalline silicon. The advantages of this solar cell technology are their good performance and high stability, but have a high weight, higher cost and they are more risk to lose some of their efficiency at higher temperatures. The second generation solar cells are thin film solar cells which are based on amorphous silicon and nanocrystalline. Although thin film solar cells have lower efficiency, they are less expensive and have a lower weight than crystalline silicon because of using a lot less material. The third generation of solar cells technology uses organic material or small molecules for light absorption and electrical charge transport. This technology are low cost, simple and use materials that are readily available. The disadvantages of this solar cell generation are low efficiency and low stability compared to non-organic solar cells [1].

$CuIn_xGa_{1-x}Se_2$ (copper indium gallium diselenide: CIGS) has been reported to be a promising absorber layer materials for thin film solar cells with high efficiency, but indium (In) and gallium (Ga) are rare and extremely expensive. So low-cost production of CIGS is impossible. $Cu_2ZnSnS_4$ (copper zinc tin sulphide: CZTS) emerged as an alternative to CIGS thin film solar cells which replace indium and gallium atoms by zinc (Zn) and tin (Sn) atoms. CZTS thin films are made of copper (CU), zinc (Zn), tin (Sn) and sulphur (S) which are low cost materials, earth abundant elements and environment friendly compositions [2].

CZTS is a p-type semiconductor which has a direct band gap energy of 1.5 eV and a relatively high absorption coefficient ($10^4$ $cm^{-1}$). Because of the excellent properties, CZTS is a promising candidate for low cost absorber layer in thin film solar cells. CZTS films can be synthesized by vacuum and non-vacuum based techniques, such as sputtering, thermal evaporation, spray pyrolysis, pulsed laser deposition, sol-gel, spray pyrolysis, electrochemical deposition, and successive ionic layer adsorption and reaction (SILAR) technique [3]. Although CZTS thin films deposited by vacuum based techniques have high efficiency (8.4% best in 2011 [4]) and can be easily controlled of the reactants composition [3], these techniques are energy intensive, requiring high vacuum and temperatures that indirectly increase the effective cost. In contrast, non-vacuum techniques are simple processes, low cost, consume less energy, high-throughput production, and scalable synthetic routes. Spin-coating, for example, is one of the non-vacuum approaches so regarding the advantages of non-vacuum approaches, these methods are promising for manufacturing the CZTS thin film solar cells.

While spin coating technique is considerably simple, rapid and requires inexpensive equipment, but one of the problems of this technique is that significant amount of solution can be lost during the fabrication. To solve this problem, an alternative coating technique called rapid convective deposition was used to deposit solution of thin films. By rapid convective deposition method, very little amount of the solution, approximately 5–30 μL, was used to cover one square inch thin film. In addition, the convective deposition method is desirable to control the overall surface morphology and uniform particle layers due to its scalability.

Recalling the previous work, CZTS thin films have been prepared using toxic solvent i.e. hydrazine-based solvent. While hydrazine-based solution simplifies the deposition of high quality CZTS thin films solar cells with low-cost and high-throughput, but it has a drawback of using hydrazine as a solvent. If hydrazine is used in a large amount, it can be explosive, hepatotoxic, and carcinogenic [5]. Moreover, after the CZTS thin films were deposited on the substrate, the heat treatment as a post deposition is required to obtain good crystallinity and grain growth, and to control optical and electrical properties of CZTS films that affect the photovoltaic performance of CZTS thin film solar cells. Generally, heat treatment of the CZTS thin films is sulphurization by using hydrogen sulphide ($H_2S$) as precursor, but $H_2S$ is toxic. Hence, another approach of heat treatment will be involved i.e. annealing under inert atmosphere of nitrogen ($N_2$) or argon (Ar). As CZTS thin films are p-type material, they have been employed in conjunction with n-type materials, such as CdS and [6,6]-phenyl C61-butyric acid methylester (PCBM), to fabricate pn-junction solar cells.

The organic photovoltaic (OPV) solar cell is based on an active layer which is a composite of a p-type light-harvesting polymer and n-type intrinsic semiconductors. Fig. 1.1 shows the basic device configuration of an OPV cell. The active layer is deposited on top of an organic hole transport layer (HTL) which enables the collection of positive charge carriers. The photovoltaic active layer of the OPV cell is between anode and cathode electrodes which is composed of the electron donor and acceptor materials. In addition, the main advantage of organic materials is the ability to produce photovoltaic devices using solution phase techniques which could lead to a very cheap and high-throughput manufacturing.

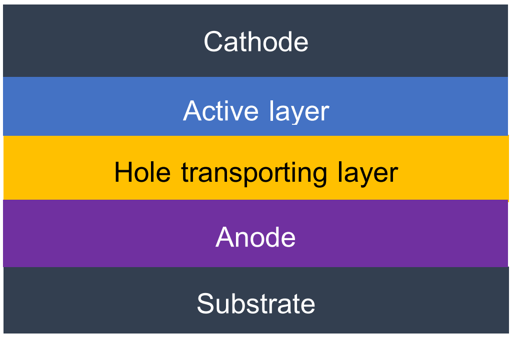


Figure: 1.1 The basic device configuration of an OPV cell

In this research, the CZTS thin films were fabricated by non-vacuum method; rapid convective deposition technique, due to its simple construction, ecological safety, and low temperature operation that indirectly decreases the effective cost. In addition, the CZTS precursor solution was prepared by using non-toxic chemicals of metal chloride, thiourea, and 2-methoxyethanol as precursors and solvent, respectively. The obtained films were annealed under $N_2$ atmosphere to yield high quality CZTS films. Moreover, the synthetic CZTS sol-gel was assembled with organic photovoltaic solar cells as a hole transporting layer. The aim of addition of the inorganic material into OPV solar cells to form an organic–inorganic hybrid solar cell was anticipated to improve the performance of OPV, due to the additional advantages such as the enhanced charge transport characteristics.

## 1.1 Objective

1.1.1 To synthesize CZTS compound for thin film solar cells in liquid phase by rapid convective deposition method.

1.1.2 To investigate the effect of process parameters on size, composition, morphology, phase, optical properties and find appropriate operating conditions suitable for solar cell device.

1.1.3 To fabricate the solar cell devices and to observe the grain size, morphology and uniformity which are correlated to structural and optical properties and solar cell performance.

## 1.2 Scopes of work

1.2.1 Synthesis of CZTS thin films in liquid phase by rapid convective deposition method. The synthesized CZTS thin films should have kesterite structure and stoichiometric of Cu:Zn:Sn:S corresponds with the theoretical value of 2:1:1:4. The optical band gap of the synthesized CZTS is about 1.5 eV which is optimal for photovoltaic applications. Moreover, CZTS thin film solar cells were fabricated by using the synthesized CZTS thin films as a hole transporting layer for organic photovoltaic solar cells. To obtain kesterite structure and stoichiometric value of the CZTS thin films, these parameters were studied as follows;

- Deposition rate of convective deposition method; this parameter affects the morphology and thickness of films that was varied from 500 to 1500 μm/s.
- Annealing temperature; this parameter affects the structure, grain size, optical and electrical properties of films which was varied at 340°C, 440°C and 550°C.

Then, the suitable conditions were used in fabricating the solar cell devices.

1.2.2 Fabrication of organic photovoltaic (OPV) solar cell devices with a layer of CZTS thin film which layers were deposited by rapid convective deposition method. The OPV solar cell devices were fabricated in a cell structure of FTO glass/ CZTS/PDCTBT:$PC_{70}BM/TiO_x$ /Al grid as shown in Fig. 1.2, in which the appropriate deposition rate to deposit CZTS thin films was investigated. The OPV solar cell devices were characterized by using a solar simulator in which the current voltage (I-V) characteristics were recorded under illumination conditions.

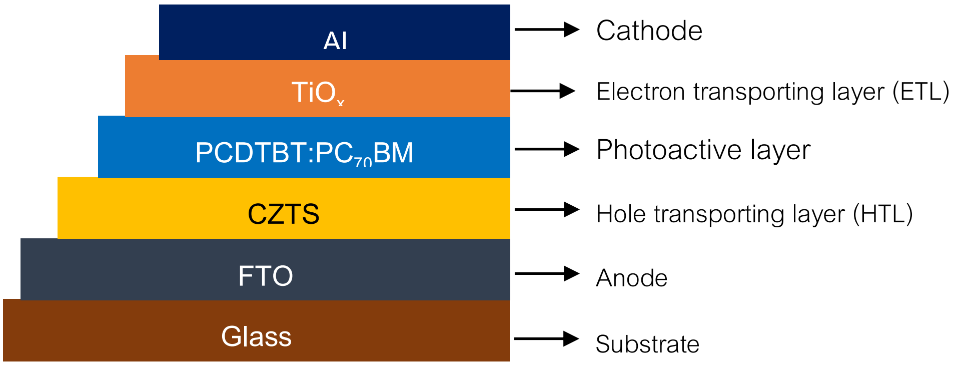


Figure: 1.2 The configuration of photovoltaic devices with a layer of CZTS thin film as HTL

1.2.3 Characterization of the synthesized CZTS thin films and the organic photovoltaic solar cell devices with a layer of CZTS thin film by following instruments;

- X-Ray Diffraction (XRD): Analyze the phase formation of the films.
- Raman spectroscopy: Confirm the phase formation of the films.
- Scanning Electron Microscope (SEM): Examine the surface and cross-sectional morphology of the films.
- Energy dispersive X-ray spectroscopy (EDS): Determine the chemical composition of the films.
- UV-VIS spectrophotometer: Estimate the band gap and the absorbance.
- Solar Simulator: Measure the power conversion efficiency (PCE), fill factor (FF), open circuit voltage ($V_{oc}$) and current density-voltage (J-V) curves.
- External quantum energy (EQE) spectra: Measure the external quantum energy.

# CHAPTER 2

# FUNDAMENTAL THEORY AND LITERATURE REVIEWS

In the last decades, using of energy has become a critical concern because of rapidly increase in energy demand. Furthermore, it is necessary to search for greener sources of energy because environmental issues of energy resources like global warming are important. Renewable energy sources such as hydropower, solar, biomass, wind and geothermal energy are favorable $CO_2$ free alternative, clean and inexhaustible resource [6]. Among all the renewable energy sources, solar energy is one of the most interesting alternatives because of abundance, free and clean. Photovoltaic devices are an electrical device which converts solar radiation directly into electrical energy, which is so called solar cells.

## 2.1 Solar cell

Generally, thin film solar cells are composed of a p-type semiconductor and an n-type semiconductor which convert solar energy into electrical energy. The basic processes behind the photovoltaic effect are [7]:

1. Generation of the charge carriers due to the absorption of photons in the materials which form a junction.
2. Separation of the photo-generated charge carriers in the junction.
3. Collection of the photo-generated charge carriers at the terminals of the junction.

When sun light hits the solar cell, two types of electrons which are negatively and positively charged electrons, are produced in the semiconductors. The negatively charged electrons are collected around the n-type semiconductor while positively charged electrons are collected around the p-type semiconductor. When electric devices are connected, electric current will flow between the two electrodes.

### 2.1.1 Solar cell generations [8]

In the recent years, solar cells are usually divided into three main generations. The first generation solar cells comprise of single crystal solar cells and multi crystal solar cells. These are the oldest and the mostly common used technology type due to high efficiencies. They are produced on wafers in which each wafer can supply the power of about 2-3 watt. Solar modules, which consist of many cells, are used to increase the power. Two types of the first generation of solar cells are different by their crystallization levels; single crystal solar cell and multicrystal solar cell. For the first type, the whole wafer has only one crystal, therefore the efficiency is usually higher than the second type.

The second generation of solar cells are thin film solar cells which are based on amorphous silicon (a-Si) and nanocrystalline (cadmium telluride/cadmium sulfide (CdTe/CdS), copper indium gallium selenide (CIGS), and copper zinc tin sulphide (CZTS)). For this generation, their efficiencies are less than that of the first generation, but their costs are cheaper and have a lower weight than the first generation.

The third generation of solar cells are organic-based solar cells, for example dye sensitized solar cells, polymer solar cells, and perovskite solar cells. These are the novel technologies which are promising but not commercially proven. Solar cells in this generation are being made from a variety of new materials besides silicon, including nanotubes, silicon wires, organic dyes, and conductive plastics. Although this technology is low cost, simple and use materials that are readily available, they still have low efficiency and low stability compared to non-organic solar cells.

## 2.2 Thin film solar cells (TFSCs)

In the present, energy conversion by using solar cells haven’t reached the world’s energy consumption since the electricity from solar cells is more expensive than energy from conventional sources. Therefore, there is further research necessary to increase the efficiency of solar cells and to make them cheaper. The thin film solar cell is one approach to this. Thin film solar cells have a thickness of only a few micrometers, which means that less material is used so that it can save energy and cost. In addition, the thin film solar cells are possible to adjust the band gap in some materials i.e. CIGS ($CuInGaS(e)_2$) by varying the composition. For this reason, the solar spectrum can be converted much better and a higher efficiency can be reached because the theoretical efficiencies depend strongly on the band gap [2].

### 2.2.1 Device structure

Despite the differences of several semiconductor materials, various thin film solar cells have a similar device structure. Since the thin film solar cells are very thin and to protect the back side, they have to be deposited on a substrate which is usually glasses. On the substrate, some kind of back contact is needed. The requirements for a back contact are a good conductivity, a good work function and stability against corrosion, and oxidation. On top of the back contact follows by the absorber layer which is the most important part of a solar cell. In this layer, photo-induced charge generation can occur via the absorption of incident solar light. Various methods are possible to deposit the material, including vacuum and non-vacuum methods, e.g. co-evaporation, sputtering, chemical vapor deposition (CVD), spray pyrolysis, successive ionic layer adsorption and reaction (SILAR) technique. The optimum thickness for the absorber is about 2–4 μm.

On the absorber is deposited with a buffer layer which can have several functions, for example improving the lattice matching between the absorber and the n-doped layer on the top. The buffer layer is capped by the n-layer. This forms a complete p-n-junction. At the same time, to collect the charge carriers without optical loss previous to arrival of incident light at the absorber, a transparent conducting oxide (TCO) is the most common materials, called window layer. The name for this layer results from the transmissibility for visible light. For further improvement, an anti-reflection coating is used to increase the amount of incoming light. Fig. 2.1 shows a cross section of a basic (a) CIGS and (b) CZTS solar cell as described above.

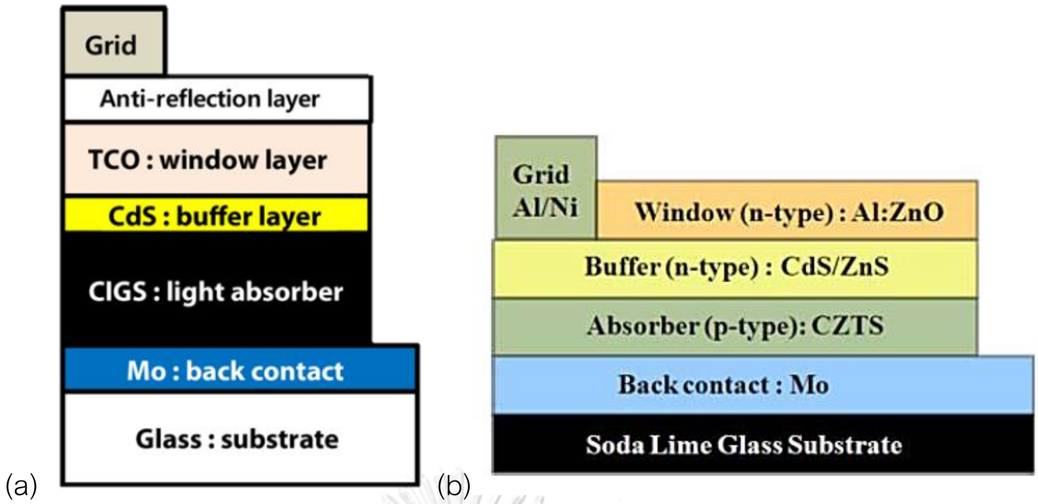


Figure: 2.1 a cross section of a basic (a) CIGS and (b) CZTS solar cell [3, 9]

### 2.2.2 Materials

Photovoltaic materials for thin film solar cells are inorganic semiconductors, which form suitable junctions with other materials and reveal a photovoltaic effect when exposed to light. An important condition of material for the thin film solar cells is a large absorption coefficient that all light should be absorbed in only a few micrometers. Moreover, the band gap should be in the range of 1–1.6 eV with a high solar optical absorption to provide the theoretical opportunity to reach sufficient efficiencies. Due to the high optical absorption, the optimal thickness of an absorber in the solar cell is of the order of the inverse of the optical absorption coefficient and thus it must be a thin film [10].

On the basis of silicon, two-component materials, which are attractive for the thin film solar cells that one deduce at first the III–V– semiconductors (e.g. GaAs) and II–VI– semiconductors (e.g. CdTe). In addition, compound semiconductor can be formed by substituting in the latter one half of the group-II element with a group-I and one half with a group-III element. Besides, a compound of quaternaries semiconductor can form a host of suitable photovoltaic materials that is replacing the Indium by Gallium to modify the band gap of CIGS ($CuInGaS_2$/$CuInGaSe_2$). Various substitutions are possible, for example substituting half of the group-III element with a group-II element and another half with a group-IV element. For CIGS, substituting In/Ga with Zn and Sn, this leads to CZTS ($Cu_2ZnSnS_4$).

However, the solar cell materials cannot be all of thinkable compounds since lots of conditions have to be fulfilled, like availability, producibility in industrial scale, ecological safety and costs. The examples of an interesting semiconductor to the thin film solar cells are amorphous silicon (a-Si), cadmium telluride (CdTe) and copper indium (gallium) sulfide or selenide (CIGS). At present, CIGS is a thin film material that is used in industrial with the highest efficiency. The process of CIGS is cheaper and less material consuming than for silicon. Nevertheless, the availability of materials for CIGS thin film solar cells could become the big problems, especially indium will run low within the next years. By problems of the CIGS thin film solar cell materials, the research for further materials has to be done and one approach is the material CZTS.

### 2.2.2 Copper zinc tin sulphide (CZTS)

For the recent years, copper zinc tin sulphide ($Cu_2ZnSnS_4$: CZTS) thin film solar cells have been developed to be a promising absorber layer materials for thin film solar cells. It is $I_1$–II–IV–$VI_4$ quaternary semiconductor compound which replaces indium and gallium atoms of CIGS chalcopyrite ternary compound by zinc (Zn) and tin (Sn) atoms. The highest power efficiency that has been achieved to date for CZTS is 9.2% (Hiroi et al 2013) [14]. This compound semiconductor is made of copper (Cu), zinc (Zn), tin (Sn) and Sulphur (S), which are low cost, abundant elements and environmental friendly in the used amounts.

CZTS is a p-type semiconductor with a direct band gap of approximately 1.4 - 1.5 eV. It is suitable for thin film solar cells because of its high absorption coefficient of more than $10^4$ $cm^{-1}$ in visible wavelength region. Since CZTS is derived from the CIGS structure, CZTS has some similar properties to CIGS. CZTS has two principal crystal structures known as stannite type and kesterite type. The two structures are different in arrangements of Cu and Zn atoms. However, CZTS material usually appears in kesterite phase because it is thermodynamically more stable compared to stannite type [3].

To fabricate CZTS thin films, there are many methods to prepare such as sputtering, pulsed laser deposition (PLD), thermal evaporation, electrodeposition, nanocrystal (NCs)-based fabrication method, sol–gel, spin-coating, spray pyrolysis, and chemical bath deposition (CBD).

#### 2.2.2.1 Spin-coating method [11]

Spin coating is one of the most common methods for applying uniform thin films to substrate. Due to its ability to fast and simple method, it can produce very uniform films from a few nanometers to a few microns in thickness. Parameters during process such as final rotational speed, acceleration, and fume exhaust contribute to how the properties of coated films are defined. An apparatus used for spin coating is called a spin coater.

A typical process of spin coating involves four steps. First, depositing an excess amount of a solution is placed onto the center of substrate. Second, the substrate is rotated at high speed in order to spread the fluid by centrifugal force, and eventually off the edge of the substrate. Then, airflow dries the majority of the solvent leaving a thin film of solution on the surface. Finally, the film fully dries to just leave the molecules on the surface. Fig. 2.2 shows scheme of the spin coating process.

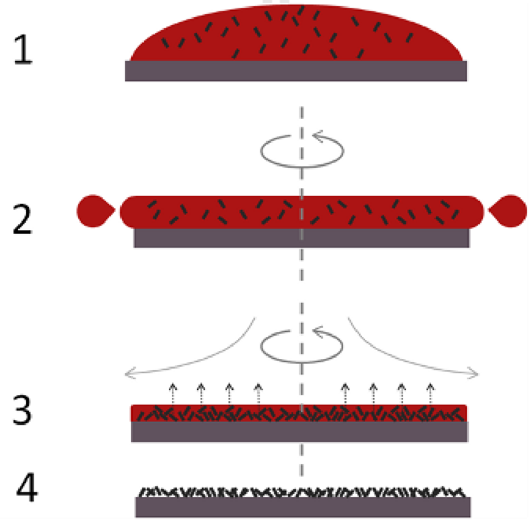


Figure: 2.2 Scheme of the Spin Coating process [11]

The rotation of the substrate at high speed causes the centripetal force combined with the surface tension of the solution which pulls the liquid coating into a fully covering. During this time, the solvent evaporates to leave the particle of material on the substrate in the uniform covering.

The range of spin speeds is important as it affects the thicknesses of films. In general, spin coating can easily produce uniform films from about 1000 rpm upwards. In most case, the film quality is attend which it can be achieved by decreasing the speed to around 500 or 600 rpm. For spin coating duration, the widely spin-coating usually rotates substrate until film is dry, so the duration will depend on the boiling point and vapor pressure of the solvent, and also on the ambient conditions that the spin coating is performed.

#### 2.2.2.2 Rapid convective deposition method [12, 13]

Rapid convective deposition method is one of the methods for the deposition of uniform particle layers on substrate. This method can deposit into various morphologies including submonolayers, monolayers, and multilayers of particles. The convective deposition method utilizes a pair of phenomena which are evaporation and capillary-driven particle assembly. The evaporation-driven flow is similarity with the “coffee ring effect” which draws particles to the edge of a droplet suspension. During the process, capillary force also plays a role to particles which causes particles lock into close-packed structures to minimize the energy, that similarity with the “cheerio effect”.

Fig. 2.3 shows the equipment of rapid convective deposition method. This process uses the horizontal deposition of small droplet which a suspension is injected between the deposition blade and substrate and also held by the capillary force at this place. Then the substrate is moved by a linear motor. When the substrate is transferred, the meniscus stretched into thin film across the substrate. Due to the capillary force, particles assemble into close-packed structures at the crystal front. The crystals are grown into monolayer or multilayer depend on the height of the meniscus at the crystal front. Monolayer crystals are formed when the height of the meniscus is less than the particle diameter whereas the higher crystal height to particle diameter contribute to multilayer crystal growth.

In short, due to the advantages of convective deposition method that are rapid, well-ordered, and can be scaled for large-area production, this process is applied to deposit microspheres in many fields, such as biomedical device technologies and fabricating organic solar cells.

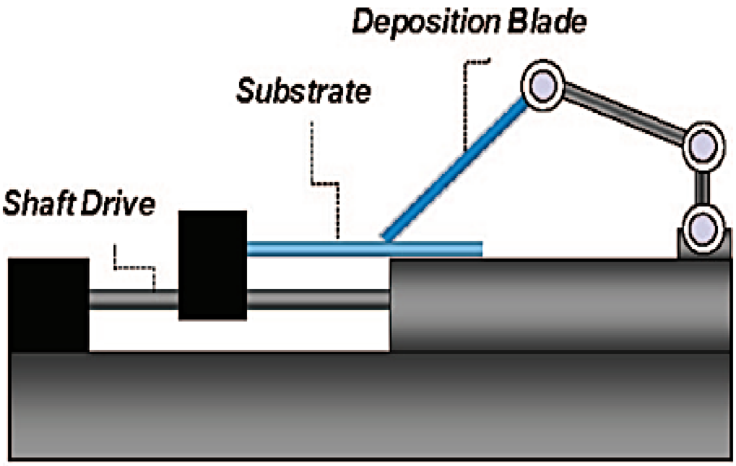


Figure: 2.3 Scheme of controlled rapid deposition [13]

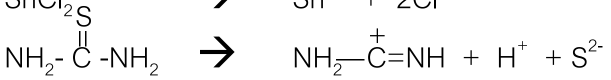
2.2.2.3 CZTS solution

The CZTS solution is prepared by using sol-gel process. The sol-gel process is a chemical solution process which commonly involves the use of metal alkoxides. The formation of metal oxide entails connecting the metal center with oxo (M-O-M) or hydroxo (M-OH-M) bridges in the precursor solution through hydrolysis and condensation polymerization reactions to give gel [14] . Park, et al. [15] synthesized the CZTS sol-gel in which 2-methoxyethanol was used as a solvent and thiourea was utilized to form M-S and/or M-S-M complexes with metal precursors and successfully made a Cu-poor and Zn-rich CZTS film based on spin coating of the sol–gel solution. Subramaniam et al. [16] prepared the CZTS by sol-gel process using $Cu(NO_3)_2$, $Zn(NO_3)_2$, $SnCl_2$ and thiourea as precursors which were dissolved in methanol. They proposed the possible reaction mechanism for the formation of CZTS as follows

$$Cu(NO_3)_2 \rightarrow Cu^{2+} + 2NO_3^-$$

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^-$$

$$SnCl_2 \rightarrow Sn^{2+} + 2Cl^-$$

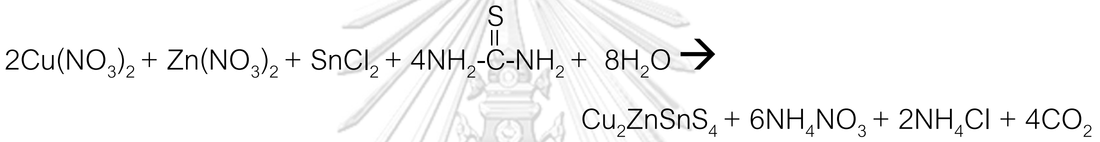


$$NH_2\text{-}\overset{S}{\overset{\|}{C}}\text{-}NH_2 \rightarrow NH_2\text{—}\overset{+}{C}{=}NH + H^+ + S^{2-}$$

The overall ionic reaction is

$$2Cu^{2+} + Zn^{2+} + Sn^{2+} + 4S^{2-} \rightarrow Cu_2ZnSnS_4$$

The thiourea complexes interact with metal ions in precursor solution via sulphur atom, therefore the CZTS formation is according to the equation



$$2Cu(NO_3)_2 + Zn(NO_3)_2 + SnCl_2 + 4NH_2\text{-}\overset{S}{\overset{\|}{C}}\text{-}NH_2 + 8H_2O \rightarrow Cu_2ZnSnS_4 + 6NH_4NO_3 + 2NH_4Cl + 4CO_2$$

### 2.3 Organic photovoltaic solar cells

An organic photovoltaic (OPV) solar cell is one of solar cells that aim to provide an earth-abundant and low energy production photovoltaic solution. Comparing with first and second generation solar technologies, this technology has the theoretical potential to provide electricity at a lower cost. Moreover, organic semiconductors have very high absorption coefficients, which permit very thin films to be used while still absorbing a sufficient portion of the solar spectrum [17]. Currently, the OPV solar cell technology has been developed its power conversion efficiency to be realized as commercial solar cell. Consequently, to achieve the high efficiency OPV solar cell, it depends on many factors such as material design and the parameters through the fabrication process [18].

#### 2.3.1 Device structure and OPV solar cells principle [19]

A regular OPV device consists of one or several photoactive materials sandwiched between two electrodes. Fig. 2.4 shows a typical bilayer organic photovoltaic device.

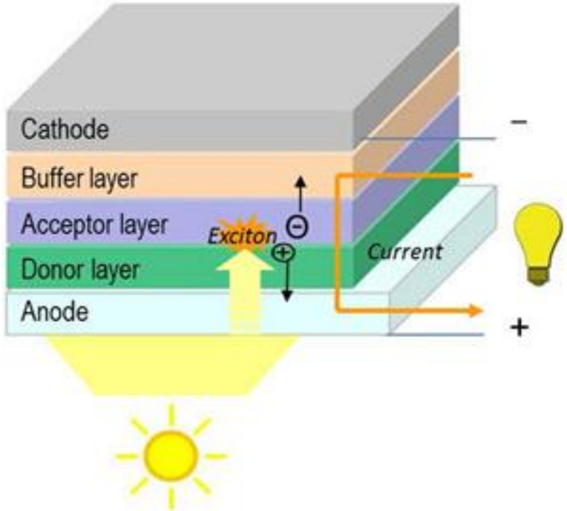


Figure: 2.4 Structure of a bilayer organic photovoltaic device [19]

OPV solar cell converts light into electricity, by converting a flux of photons into a flux of charged particles (a current). This conversion process is made possible by the combination of several types of materials. For a bilayer OPV cell, in the photoactive layers which composed of donor and acceptor semiconducting organic materials, sunlight is absorbed to generate photocurrents. The acceptor material withdraws electrons and mainly transports electrons while the donor material donates electrons and mainly transports holes. The photoactive materials collect photons from sunlight to form excitons (electron-hole pair), in which electrons are excited from the valence band into the conduction band. Because of the concentration gradient, the excitons diffuse to the interfaces of the donor/acceptor (exciton diffusion) on the LUMO (lowest unoccupied molecular orbital) level of the acceptor and holes on the HOMO (highest occupied molecular orbital) level of the donor, and separate into free holes (positive charge carriers) and electrons (negative charge carriers) which also called charge separation. When the holes and electrons move to the corresponding electrodes by following either donor or acceptor phase (charge extraction), they generate a photovoltaic as showed in Fig. 2.5 [19].

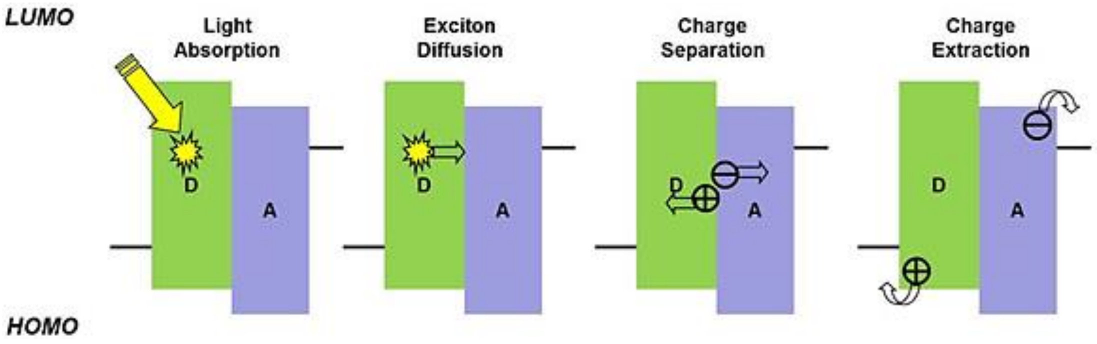


Figure: 2.5 Functional mechanism of a bilayer organic photovoltaic (D = donor, A = acceptor)

### 2.3.2 Hole Transport layer (HTL)

To increase the efficiency of organic photovoltaic solar cell, charge transport layers are usually comprised in OPV devices. The charge transport layers that are hole transport layer (HTL) and electron transport layer (ETL) can increases the efficiency of OPV device since they have much higher charge transporting properties compared with the active materials. The charges that reach the interfaces with the HTL or ETL can quickly move away from the active layer. This is an efficient way to avoid charge recombination (charges that recombine cannot be collected). Because hole transport layer has low electron mobility and low electron affinity, therefore in this layer electrons are blocked and cannot flow through while holes can flow through to the anode. On the other hand, electron transport layer do the opposite of HTL behavior, in which it blocks hole to flow through to the cathode.

In most of OPV devices, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is used as hole transport material (HTM) because of its high electrical conductivity and facile solution-processing. In addition, PEDOT:PSS has a proper work function which matches with many polymer donors to form good ohmic contact at the anode/active layer interface [20]. Nevertheless, the OPV devices with PEDOT:PSS as HTM rapidly degrade and have poor lifetime because PEDOT:PSS is acidity and highly hygroscopic material which can cause electrode corrosion and can retain a large fraction of water in OPV devices. Hence, the efficiency and stability of OPV devices can be improved by replacing PEDOT:PSS with a more stable hole transport materials. The replaced hole transport materials must be easily synthesized, soluble in a variety of solvents, have excellent electron blocking and hole transporting properties [21].

### 2.4 Literature review

The literature reviews are separated in 2 parts; 1) Synthesis of CZTS thin films and 2) The Fabrication of organic photovoltaic solar cell devices with a layer of CZTS thin film.

#### 2.7.1 Synthesis of CZTS thin films

Copper zinc tin sulphide (CZTS) films can be synthesized by both vacuum and non-vacuum processes. To fabricate thin film solar cells more cost-effectively, a solution process is desirable. Non-vacuum techniques are low cost in production, for example spray pyrolysis, electrodeposition, spin-coating, successive ionic layer adsorption and reaction, and chemical bath deposition. Among these methods, Agawane et al (2013)[22], N.K. Youn et al (2015) [23], Prabeesh, et al 2016 [24], Yeh et al (2016) [3] used the spin-coating method due to its advantages. In addition, the elemental components can be mixed on a molecular level in a precursor colloidal solution, which called sol-gel, by the solution-based processes. Sol-gel is composed of polycondensation of nanoparticles, then thin films with better crystallinity which can be obtained under a lower annealing temperature and reliable composition transfer from gel to thin films due to deposition at room temperature.

W. Wang et al (2013) [25] reported that a world record of a solar cell $Cu_2ZnSn(S,Se)_4$ (CZTSSe) with efficiency of 12.6% was achieved by using a hydrazine-based solvent. But, hydrazine is used in large amounts, it can be explosive, hepatotoxic, carcinogenic and it is unstable compound that requires extreme caution for handling. Thus, several research groups have studied relatively safe non-vacuum methods for the synthesis of CZTS thin film. Different types of precursor solution were introduced by selecting suitable solvents. To select a solvent, there are requirements for selecting that solvent should be good solubility to metal and sulfur sources, non-toxicity, and small molecular weight. Besides, solvents, which have very high vapor pressure, may rapidly dry that obstructing the deposition apparatus or creating defects in the layer. In contrast, solvents with low vapor pressure may require heating during the drying step. In some cases heating of solvents with too low vapor pressure may reduce viscosity and induce surface tension that can cause layer non-uniformity. K. Tanaka et al (2007) [26], H. Park, et al (2011) [15] and Z. Su, et al (2014) [27] prepared CZTS thin films by using 2-methoxyethanol as a solvent, which ethanol-based solution, and their thin films could work as solar cell absorber layers. Ethanol-based solution is an alternative solvent which are non-toxic, environmentally friendly, and stable chemical. Moreover, ethanol-based solution processing has potential for application in high-quality semiconductor films at relatively low fabrication temperatures.

However, organic-based solutions unavoidably contain residual amounts of carbon, nitrogen, and oxygen which are difficult to completely remove from CZTS thin films and could degrade the quality of the films. To minimize the amount of carbon residual in CZTS thin films, S-N Park et al (2013) [28] chose precursors for CZTS as metal chlorides, such as copper, zinc, and tin chlorides. For a source of sulphur, they used thiourea, which also used to stabilize the CZTS precursor solutions. By using metal chlorides and thiourea as the precursor solutions enabled them to synthesis the CZTS thin films without forming a carbon interlayer. In addition, an excess amount of thiourea in the precursor solution was used to avoid the formation of secondary phases and sulphur loss during post-annealing process, resulting in a homogeneous growth of CZTS films with the aid of formation of metal-S or metal-S-metal complexes.

Moreover, many research reported that the properties of the CZTS thin films should be influenced by the chemical composition of the CZTS thin films. K. Tanaka et al (2011) [29] reported that the Cu-poor, Zn-rich CZTS thin films generally show higher p-type conductivity and conversion efficiency than Cu rich, Zn-poor ones because more Cu vacancies form in Cu-poor thin films which produces shallow acceptors in the CZTS layer while the substitution of Cu at Zn sites is suppressed in Zn-rich thin films which produces relatively deep acceptors. So, it shows that high efficiencies solar cells were obtained using Cu-poor, Zn-rich CZTS absorber layers. Therefore, it is critical to control the chemical composition of the CZTS absorber layer to produce high efficiency CZTS solar cells.

Furthermore, the pre-annealing and annealing temperature were also an important factor in controlling the morphology, chemical composition, crystalline structure, and photovoltaic properties of the CZTS thin films. S-N Park et al (2013) [28]reported that, the pre-annealing temperature, which might be attributed to the different thermal degradation temperatures of the thiourea and metal chlorides in the CZTS precursor solutions, at higher temperature is appropriate for controlling the defect states in CZTS absorbers. S. K. Swami et al (2013) [29] fabricated CZTS thin films by spin coating method and using metal chloride, thiourea and 2-methoxyethanol as precursors and solvent, respectively. CZTS thin films were heated at 200°C for 5 min and dense films were annealed for half an hour. In addition, K. Tanaka, et al (2008) [30] revealed that as the annealing temperature was increased, the average particle size was also increased. By improving grain size of the film will enhance the photovoltaic properties by reducing the carrier recombination. Many voids are appeared when the film is annealed at too high temperature, so these large voids in absorber layer would result in lower conversion efficiency.

### 2.7.2 The Fabrication of organic photovoltaic solar cell devices with a layer of CZTS thin film

Organic-inorganic hybrid solar cells combine organic and inorganic nanoparticles, with the purpose of incorporating the advantages of both material groups. C.W. Tang et al (1989) [31] reported that the most common inorganic–organic interface is comprised of a conductive electrode and an organic hole (electron) transporting layer, often denoted as the HTL (ETL). At such interfaces, the magnitude of the barrier for charge injection depends on the energy level alignment between the Fermi level of the electrode and the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of the transport layer. To choose the materials to be an electron donor or accept for organic-inorganic hybrid solar cells, HOMO ad LUMO of the materials are considered. By the LUMO of the donor is higher than the LUMO of the acceptor, and the HOMO of the donor is higher than the homo of the acceptor which is a condition where charge separation might be possible.

CZTS has been applied to be a hole transport material for organic solar cells. Q. Wu et al (2015) [32] studied the effect of CZTS as a HTM for $CH_3NH_3PbI_3$ perovskite solar cells (PSCs) by comparing the power conversion efficiency (PCE) and the optical properties of the common PSCs which used spiro-MeOTAD HTM and CZTS HTM. The results showed that the best PCE of PSC devices with CZTS as HTM at the optimized conditions is 12.75%. The CZTS HTM can improve the light absorption of PSCs in visible wavelength region which lead to the increase of short-circuit current ($J_{sc}$). Moreover, CZTS HTM enhances the interfacial contact between the active layer and Au electrode so the electron and hole are prohibited to recombine. According to this study, not only CZTS can be a light absorber but can also be an effective and low cost inorganic hole transport material.

In conclusion, the inorganic materials can provide further advantages especially their stability to the OPV devices, while still maintaining low cost process ability. Adding inorganic materials to OPV devices could promote in overcoming one of the major defect of the technology.

# CHAPTER 3

# EXPERIMENTAL

## 3.1 Chemicals

### 3.1.1 CZTS precursor solution

All chemicals for preparation of CZTS precursor solution were of analytical grade and were used without further purification. Copper (II) chloride ($CuCl_2 \cdot 2H_2O$), zinc (II) chloride ($ZnCl_2$), and tin (II) chloride ($SnCl_2 \cdot 2H_2O$), were purchased from Ajax Finechem Pty Ltd. Thiourea ($SC(NH_2)_2$) was purchased from HiMedia Laboratories, 2-methoxyethanol and triethanolamine (TEA) were used as solvent and stabilizer, respectively.

### 3.1.2 An organic photovoltaic solar cell devices with a layer of CZTS thin film

CZTS sol-gel was used as a hole transporting layer and $TiO_x$ sol-gel was used as an electron transporting layer. For the photoactive layer using a solution of the p- and n-type components;Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and [6,6] phenyl $C_{70}$-butyric acid methyl ester (PCBM), which were dissolved in 1,2-dichlorobenzene solution and were stirred at 70°C for 1 hour. Aluminum (Al) will be used as a cathode.

## 3.2 Experimental apparatus

Fig. 3.1 shows rapid convective deposition equipment. It uses the horizontal deposition of a small droplet which a solution is injected between the deposition blade and substrate. Then, the substrate is moved by a linear motor with deposition speeds that will be adjusted [13].

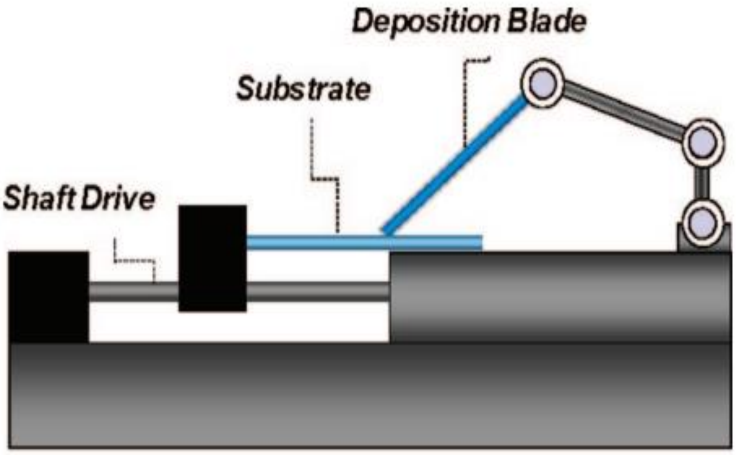


Figure: 3.1 Scheme of controlled rapid deposition [13]

### 3.3 Experimental procedures

#### 3.3.1 Synthesis of CZTS thin films

1. CZTS precursor solution was prepared by dissolving all of precursors in stoichiometric ratios that were varied in a solution of 2-methoxyethanol and TEA. Then, the solution was stirred and heated at 50°C for 30 minutes.

2. Glass substrates were cleaned by using ultrasonic cleaner with mild soap water, acetone and ethanol consecutively for 15 min each, and dried with free flow of nitrogen gas.

3. The CZTS precursor solution was fabricated on glass substrates by using the convective deposition method at deposition rates that were varied and volume of 30 μL. Then, the CZTS films were dried at 200°C for 10 min. This step was repeated 4 times to achieve required film thickness.

4. The as-deposited films were annealed in nitrogen atmosphere at different temperatures; 340, 440 and 550°C.

### 3.3.2 The Fabrication of organic photovoltaic solar cell devices with a layer of CZTS thin film

The organic photovoltaic devices with a layer of CZTS thin film were fabricated on 2.5 x 2.5 $cm^2$ fluorine-doped tin oxide (FTO) substrate with the following device configuration; FTO glass/ /CZTS/PDCTBT:$PC_{70}BM/TiO_x$ /Al grid, that show in Fig. 3.2.

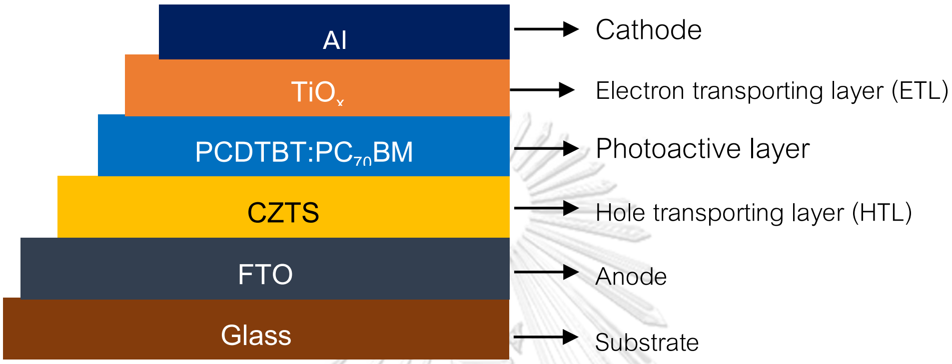


Figure: 3.2 The configuration of photovoltaic devices with a layer of CZTS thin film as HTL

1. The fluorine-doped tin oxide (FTO) glass substrates were cleaned in detergent and isopropanol alcohol by using an ultrasonic cleaner at 60°C for 15 min each, and dried with free flow of nitrogen gas. Then, the substrates were improved their hydrophobicity by oxygen plasma for 2 min.

2. The 15 μL of CZTS sol-gel was deposited on top of the FTO glass substrates at adjustable deposition rates by using convective deposition method. Then, the CZTS thin film was dried in air for 10 min at 200°C and was annealed at suitable temperature.

3. The photoactive layer was fabricated on the CZTS layer at a deposition rate and volume of 750 μm/s and 10 μL by convective deposition method.

4. $TiO_x$ thin film of $TiO_x$ sol–gel was deposited on top of the photoactive layer by convective deposition method at deposit speed and volume of 1250 μm/s and 10 μL, respectively. Then, the film was dried at 80°C in air for 20 min.

5. The solar cell devices were completed by deposition of a cathode, aluminum (Al), via thermal evaporation process.

## 3.4 Analytical instruments

The synthesized CZTS thin films and the fabricated organic photovoltaic solar cell devices with a layer of CZTS thin film were characterized to determine size, composition, morphology, phase, and optical and electrical properties by analytical instruments that were shown below.

### 3.4.1 X-Ray Diffraction (XRD)

Phase formation of the CZTS thin films were analyzed by X-Ray Diffraction (XRD; Bruker AXS, model D8 advance). XRD analysis was performed at 5°/min of scan speed with 40 kV operating voltage and 30 mA current and by using a Cukα radiation source. The X-ray diffraction patterns were collected by 2θ scan mode from 20 to 80º.

### 3.4.2 Raman spectroscopy

Phase formation of the CZTS thin films were confirmed by using Raman spectroscopy (NTEGRA spectra). Raman spectra of the thin films were obtained with a 473 nm laser.

### 3.4.3 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM; FE-SEM with EDS (Hitachi SU8230)) was used to observe the surface and cross-section morphology of the CZTS thin films.

### 3.4.4 Energy dispersive X-ray spectroscopy (EDS)

The chemical composition of the films were determined through Energy dispersive X-ray spectroscopy (EDS; FE-SEM with EDS (Hitachi SU8230)).

### 3.4.5 UV-VIS spectrophotometer

A UV–vis Spectrophotometer (Shimadzu UV-2600) was used to measure the absorption coefficient and band gap in the wave length range 400 to 1100 nm.

### 3.4.6 Solar Simulator

Power conversion efficiency (PCE), fill factor (FF), open circuit voltage ($V_{oc}$) and photocurrent density-voltage (J-V) curves were measured by solar simulator (model SN 258, ABET). The intensity of the simulated solar was 100 mW $cm^{-2}$ and density-voltage (J-V) curves were recorded under illumination condition.

### 3.4.7 External quantum energy (EQE) spectra

EQE efficiency were measured by EQE spectra. The measurement was done in air using an ORIEL Intelligent Quantum Efficiency (IQE) 200TM Measurement system established with the tunable light source.

All of the analytical instruments were utilized at NSTDA Characterization and Testing Service Center (NCTC).

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Synthesis of copper zinc tin sulphide (CZTS) thin films

The principle factors of high-efficiency solar cells are stoichiometry, crystalline quality and optical properties of photovoltaic materials. Consequently, the optimal conditions of synthetic materials should be investigated.

For this reason, in order to obtain high efficiency of solar cells, the synthesized CZTS thin films need to be well matched with the theoretical ratio of its stoichiometry, high crystallinity of kesterite phase, and corresponding band gap. Therefore, the effects of deposition speed and annealing temperature were investigated in this work to obtain the targeted conditions. CZTS thin films were deposited by convective deposition method with various deposition speed as follows; 500, 750, 1000, 1250 and 1500 μm/s for 4 times and annealed at different temperatures from 340 to 550°C.

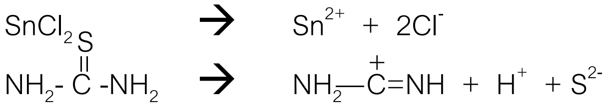
### 4.1.1 Composition of copper zinc tin sulphide (CZTS) thin films

CZTS solution is prepared by using 2-methoxyethanol as a solvent and metal chlorides and thiourea as precursors. Recalling to the study [16], the proposed reaction mechanism which describes the formation of CZTS is as below

$$CuCl_2 \rightarrow Cu^{2+} + 2Cl^-$$

$$ZnCl_2 \rightarrow Zn^{2+} + 2Cl^-$$

$$SnCl_2 \rightarrow Sn^{2+} + 2Cl^-$$



$$NH_2-\overset{\overset{S}{\|}}{C}-NH_2 \rightarrow NH_2—\overset{+}{C}=NH + H^+ + S^{2-}$$

The overall reaction is

$$2CuCl_2 + ZnCl_2 + SnCl_2 + 4SC(NH_2)_2 + 8H_2O \rightarrow Cu_2ZnSnS_4 + 8NH_4Cl + 4CO_2$$

According to the theoretical stoichiometry of CZTS thin films which is 2 : 1 : 1 : 4 (Cu : Zn : Sn : S), good quality of formation CZTS films should have the compositions similar to the theoretical value. The chemical compositions of the CZTS thin films which were annealed at various temperatures were determined by Energy dispersive X-ray spectroscopy (EDS) and are presented in table 4.1. From the analysis, most stoichiometric ratios of CZTS thin film samples were approximately close to the theoretical ratio especially the samples which were annealed at 340ºC. It is known that the best condition for working CZTS photovoltaic device should be in Cu-poor and Zn-rich conditions [29]. Since Cu-poor conditions improve more Cu vacancies form consequently resulting in shallow acceptors of CZTS film, while the replacement of Cu at Zn sites is suppressed at Zn-rich conditions which result in rather deep acceptor. Moreover, Cu-poor and Zn-rich conditions of CZTS films can avoid the formation of secondary phases [29] . According to the EDS measurements, the Cu-poor condition can be determined from the ratio of Cu/(Zn + Sn) and the Zn-rich condition can be determined from the ratio of (Zn/Sn). At the deposition speed of 500 µm/s and at various annealing temperatures, none of the samples shows Cu-poor and Zn-rich condition. The same trends were also observed in the samples prepared at the deposition speed of 1000 and 1500 µm/s at various annealing temperatures. However, the samples prepared at the deposition speeds of 750 and 1250 µm/s at annealing temperature of 340ºC show the Cu-poor and Zn-rich condition of CZTS, which is required for achieving high quality of CZTS. It can be explained that at low annealing temperature, the composition of each component are still under control. According to the proposed reaction described in Section 2.2.2.3, the precursors react under chemical reaction by using sol-gel process in which the synthesized CZTS does not associate with the deposit speed of convective deposition so the compositions of CZTS films should remain the same at all deposition speeds. As seen from the EDS measurement, the CZTS films consist of different compositions because the CZTS sol-gel was not immediately used prior to deposit, consequently the precursors further reacted when time passed. Therefore, the compositions of CZTS films are rather different with respect to the time that the sol-gel was used. While the annealing temperature plays a major role in the compositions of the CZTS films. At higher annealing temperature, it has a strong influence on the thermal stability of metal chlorides and thiourea, resulting in a deficient sulfur element Fig. 4.1 shows the Cu/(Zn+Sn) and Zn/Sn compositions of the CZTS film samples which were deposited at deposition speed of 750 μm/s at different annealing temperatures. The result shows a significant increase in Cu/(Zn+Sn) and a slight increase in Zn/Sn ratios, but S/(metal) ratio is dramatically decreased with increasing annealing temperature. It could be explained that different metal chlorides have different thermal stabilities, therefore each metal precursor is eliminated from the films through annealing process at different temperatures. However, sulfur is likely to have the least thermal stability since the S/(metal) ratio becomes decreased dramatically at high annealing temperature.

Table: 4.1 Composition of CZTS films deposited at different deposit speeds and annealing temperatures determined by EDS analysis.

| Sample | **Atomic %** | | | | **Atomic ratio** | | |
|---|---|---|---|---|---|---|---|
| (speed-temp.) | Cu | Zn | Sn | S | Cu/(Zn+Sn) | Zn/Sn | S/metal |
| 500-340 | 35.35 | 11.82 | 13.34 | 39.49 | 1.40 | 0.89 | 0.65 |
| 500-440 | 37.89 | 11.69 | 10.61 | 39.82 | 1.70 | 1.10 | 0.66 |
| 500-550 | 26.93 | 11.50 | 15.59 | 45.97 | 0.99 | 0.74 | 0.85 |
| 750-340 | 28.21 | 15.29 | 13.26 | 43.25 | 0.99 | 1.15 | 0.76 |
| 750-440 | 41.96 | 12.49 | 10.09 | 35.47 | 1.86 | 1.24 | 0.55 |
| 750-550 | 41.89 | 7.66 | 13.64 | 36.81 | 1.97 | 0.56 | 0.58 |
| 1000-340 | 32.62 | 14.88 | 12.56 | 39.94 | 1.19 | 1.18 | 0.66 |
| 1000-440 | 36.55 | 13.86 | 10.04 | 39.56 | 1.53 | 1.38 | 0.65 |
| 1000-550 | 32.10 | 9.20 | 16.13 | 42.58 | 1.27 | 0.57 | 0.74 |
| 1250-340 | 26.56 | 17.35 | 12.32 | 43.77 | 0.90 | 1.41 | 0.78 |
| 1250-440 | 34.40 | 14.42 | 9.72 | 41.45 | 1.42 | 1.48 | 0.71 |
| 1250-550 | 38.54 | 9.66 | 13.60 | 38.20 | 1.66 | 0.71 | 0.62 |
| 1500-340 | 31.55 | 13.35 | 12.04 | 43.06 | 1.24 | 1.11 | 0.76 |
| 1500-440 | 35.65 | 17.20 | 10.10 | 37.05 | 1.31 | 1.70 | 0.59 |
| 1500-550 | 29.71 | 10.04 | 14.25 | 45.99 | 1.22 | 0.70 | 0.85 |

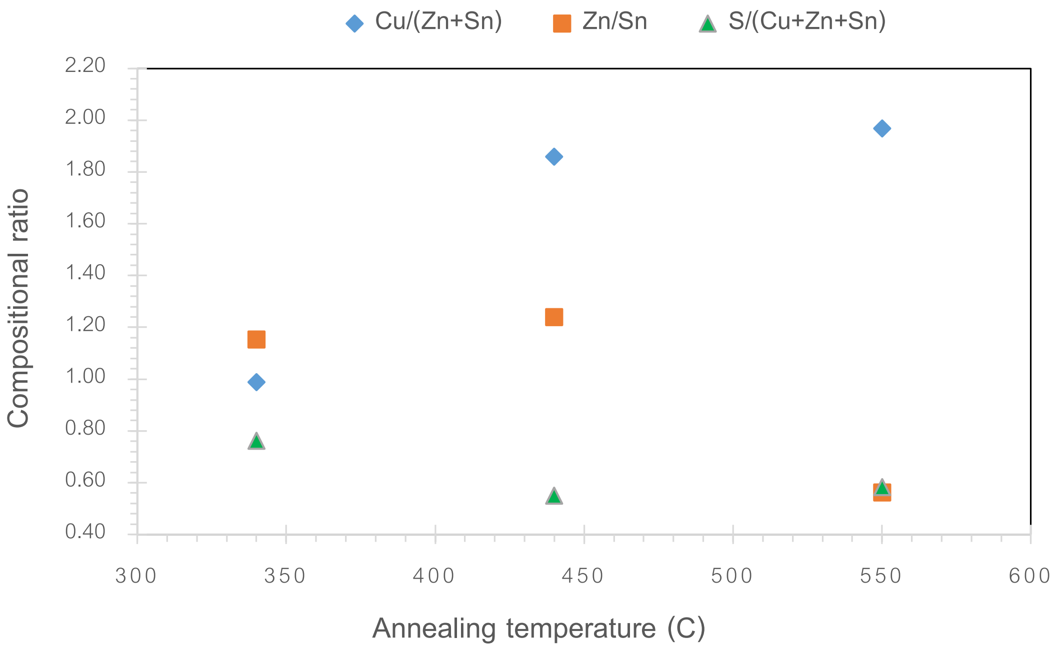


**Figure: 4.1** Cu/(Zn+Sn) and Zn/Sn compositions of CZTS film samples which were deposited at deposition speed of 750 μm/s at various annealing temperatures.

### 4.1.2 Morphology and structure of copper zinc tin sulphide (CZTS) thin films

Copper zinc tin sulphide (CZTS) sol-gel was deposited on the substrates to form CZTS thin films by convective deposition method. By this method, the effect of the deposition speed was investigated at 500, 750, 1000, 1250 and 1500 μm/s. To study the effect of deposition speed on the morphology of CZTS thin films, the scanning electron microscopy (SEM) was used to characterize the surface morphologies of the films at various deposition speed as shown in Fig. 4.2 to Fig. 4.4. At the same annealing temperature, particle sizes of the CZTS films which were deposited at low deposition speed are large and films contain some voids between particles. On the other hand, when the CZTS sol-gel was deposited on the substrates at higher deposition speed, the particle sizes become small and grain boundary is decreased which affect the optical properties of CZTS films. Moreover, films form in multilayer, resulting in nonuniform film thickness. As seen in Fig. 4.5, thickness of the films which was annealed at 340 °C slightly increase from 425 nm to 660 nm when the deposition speed increases from 750 to 1500 μm/s. During the deposition of films, the solvent is evaporating from the gel. The solvent is replaced by air which brings about major changes to the network structure. At lower speed, the solvent slowly evaporates in which the particles start to agglomerate to increase in the particle sizes. Meanwhile, at higher speed, the particles have no time to agglomerate due to the quickly evaporation rate of the solvent. Moreover, thickness of the films also increase with the increase in annealing temperature, as seen in Fig. 4.6. It can be explained that higher deposition speed results in a higher drag force because the substrate surface represents a no-slip boundary condition. For this reason, the substrate drags the film as well as draw the particles in the bulk solution along the convective line towards the moving film and form a close-packed structure as a result of capillary force. As a consequence, those particles stack up on the substrate as a multilayer of the film. However, if the deposition speed is higher than the optimal deposition speed to form a close-packed film structure, the films would form in multilayer instead of forming as a monolayer. On the other hand, if the deposition speed is lower than the optimal deposition speed, it would have voids in the films which affect the efficiency of the films. Meanwhile, the annealing temperature also plays a major role in the film formation. If the annealing temperature is increased, more voids in the film are observed in SEM micrographs, as compared in Fig. 4.2 to Fig. 4.4. This is attributed to the low thermal stability of the precursors where metal chlorides can be eliminate at temperature of 300-500°C and below 300°C for thiourea [28]. So at higher annealing temperature, the precursors were gradually lost which creates more voids within the films as seen in SEM images at 550 °C in Fig. 4.4.

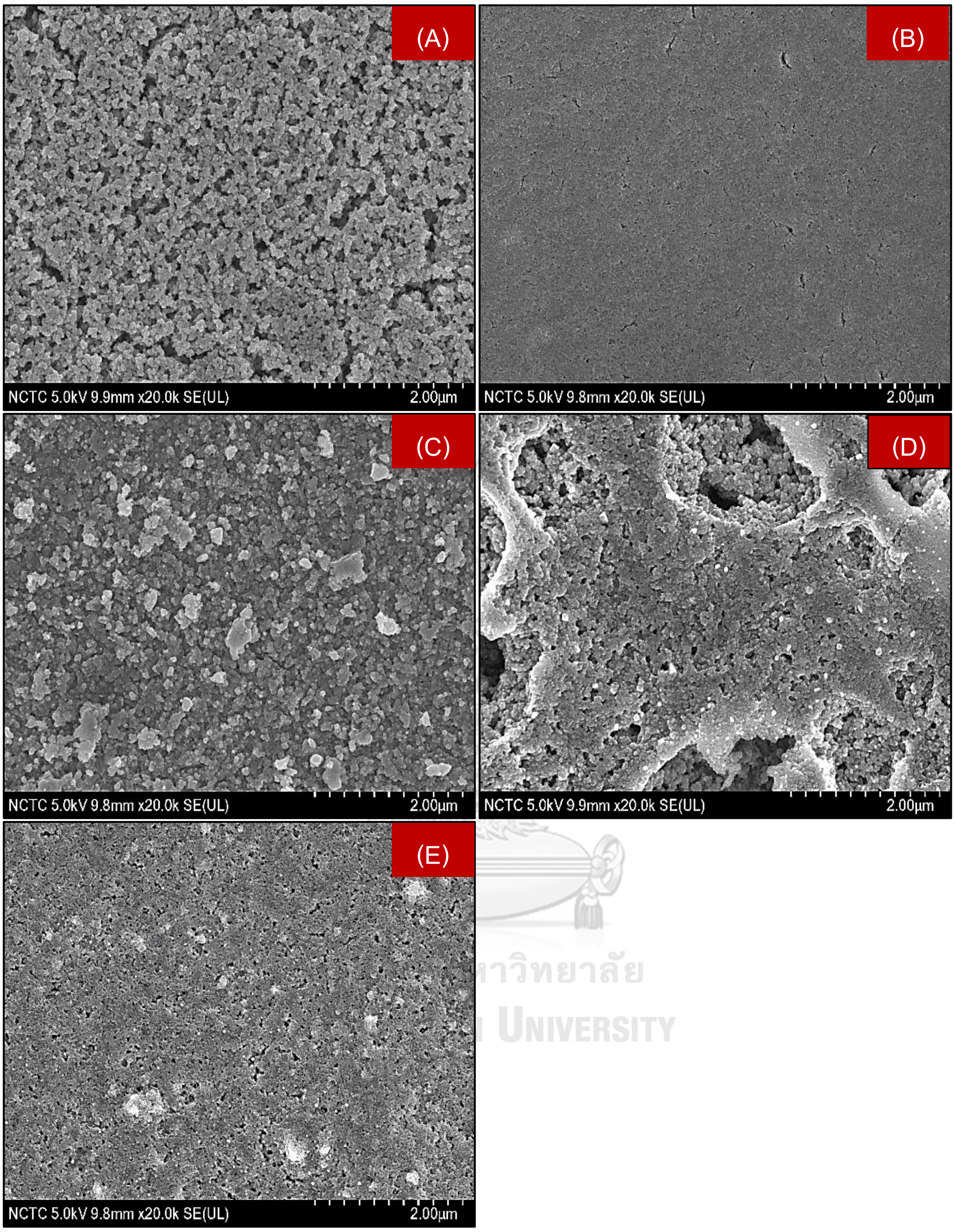


Figure: 4.2 SEM images of CZTS thin films annealed at 340°C and deposit rates of (A) 500 μm/s, (B) 750 μm/s, (B) 1000 μm/s, (D) 1250 μm/s and (E) 1500 μm/s.

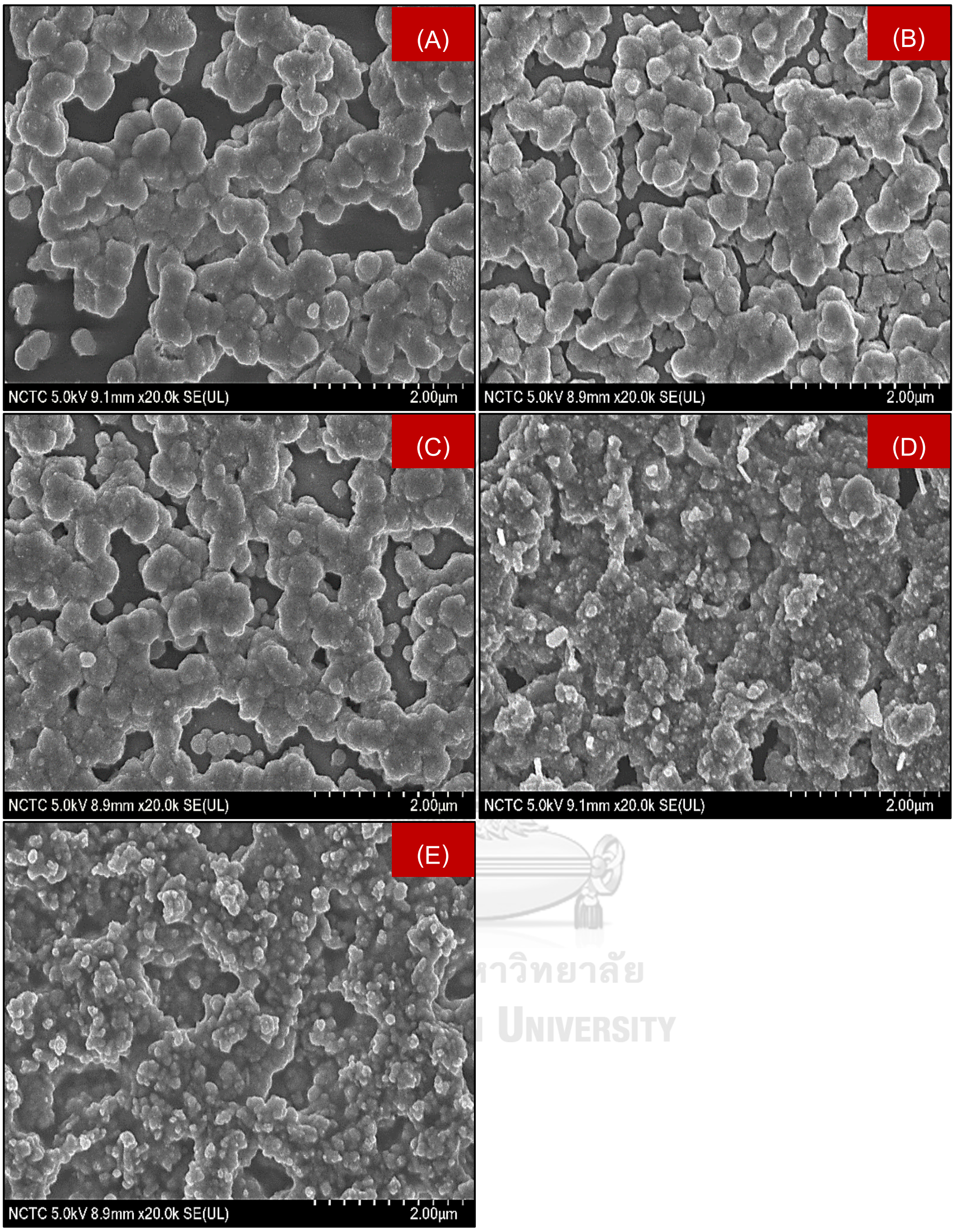


Figure: 4.3 SEM images of CZTS thin films annealed at 440°C and deposit rates of (A) 500 μm/s, (B) 750 μm/s, (B) 1000 μm/s, (D) 1250 μm/s and (E) 1500 μm/s.

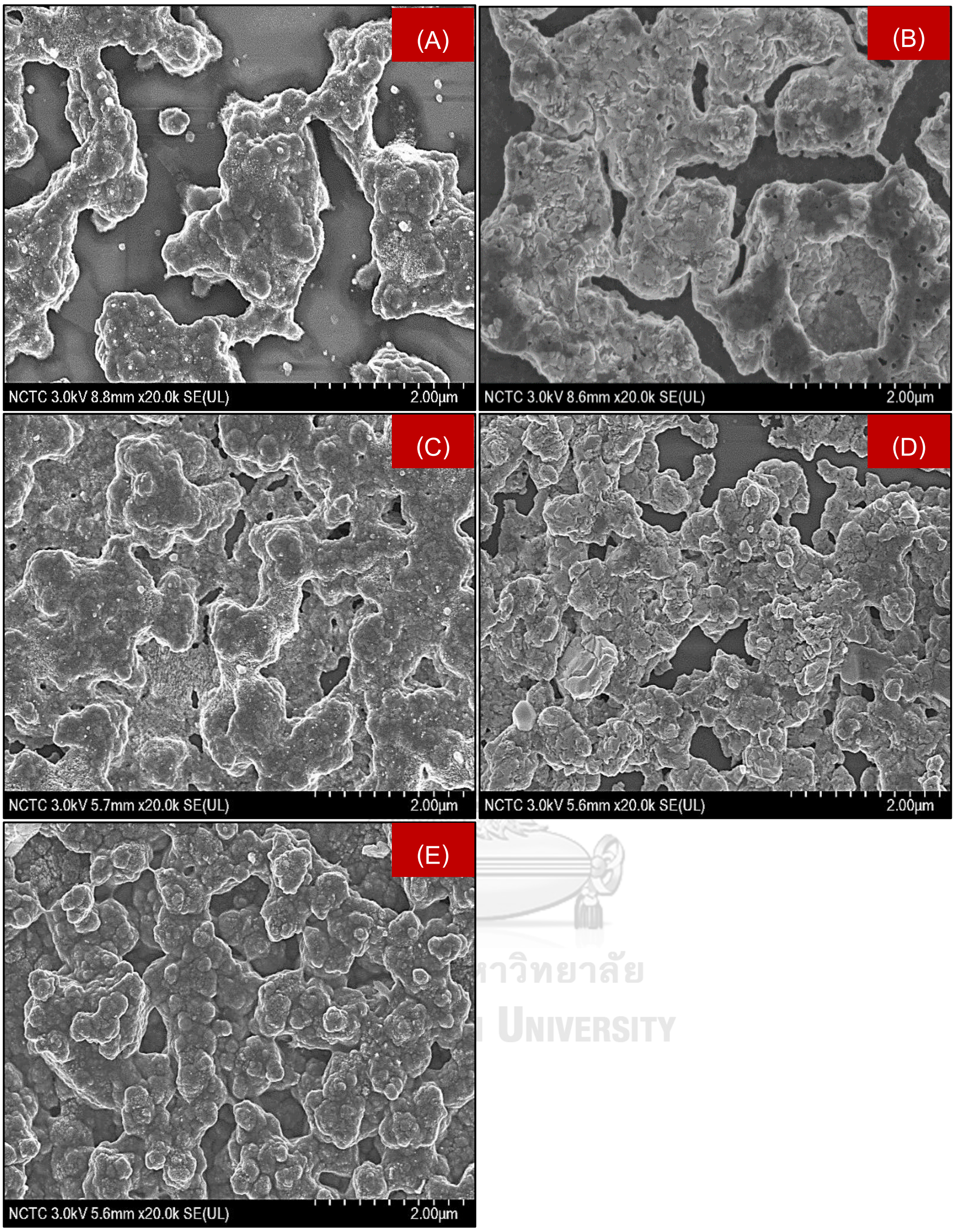


Figure: 4.4 SEM images of CZTS thin films annealed at 550°C and deposit rates of (A) 500 µm/s, (B) 750 µm/s, (B) 1000 µm/s, (D) 1250 µm/s and (E) 1500 µm/s.

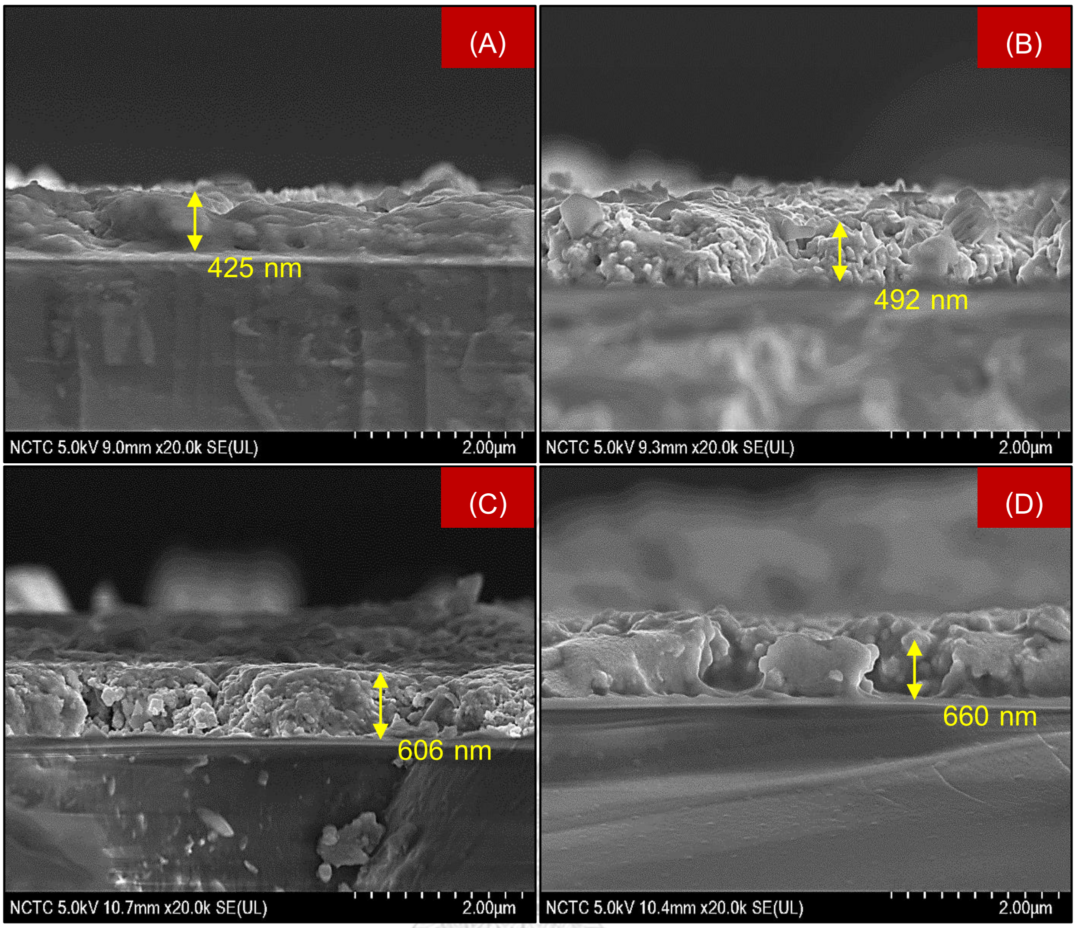


Figure: 4.5 Cross-sectional images of CZTS thin films annealed at 340°C and deposit rates of (A) 750 µm/s, (B) 1000 µm/s, (B) 1250 µm/s and (D) 1500 µm/s.

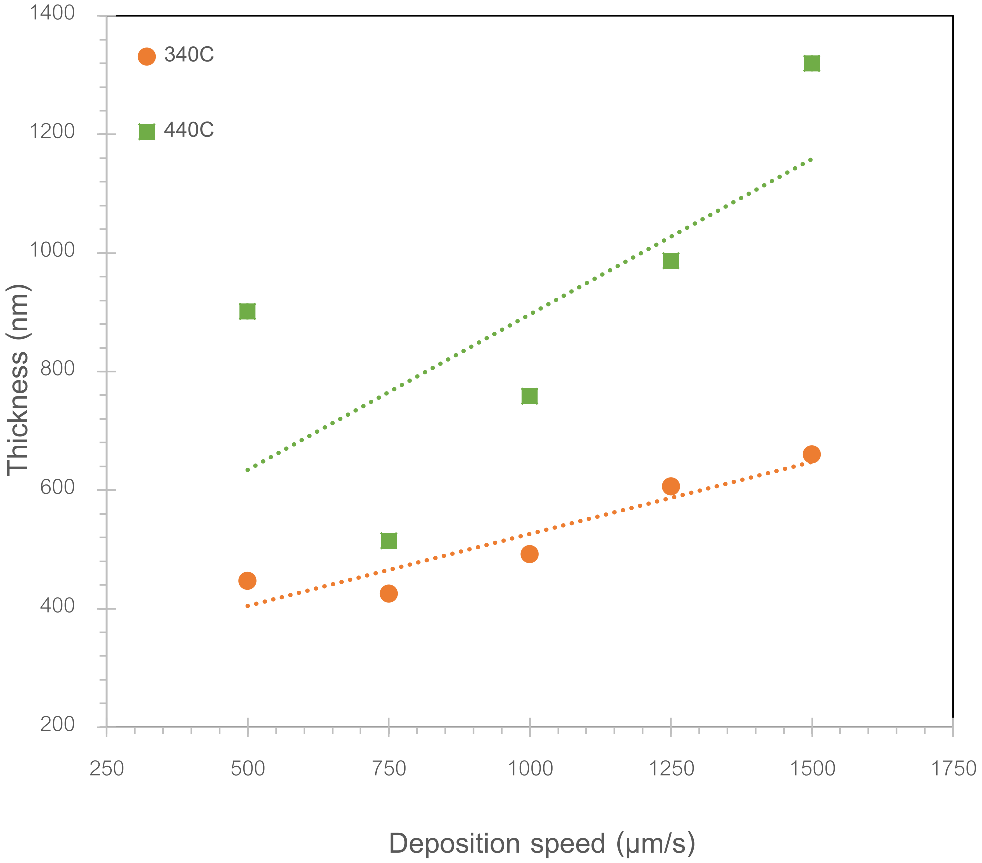


Figure: 4.6 Comparing the thickness of CZTS thin films between anneal temperature at 340°C and 440°C

The effect of annealing temperature on the structure of the CZTS films was investigated by X-Ray Diffraction (XRD). Fig. 4.7 shows the XRD patterns of CZTS films annealed in nitrogen atmosphere at 440°C and deposit speeds of 750 and 1000 μm/s. As seen in the XRD patterns, the films which were annealed at the same temperature show the same XRD patterns. Thus the crystallinity and phase of CZTS do not depend on the deposit speed of convective deposition. Fig. 4.8 shows the XRD patterns of CZTS films annealed in nitrogen atmosphere at various temperatures. At the same deposit rate, the film annealed at 340°C exhibits amorphous phase while the XRD peak of the films annealed at 440°C and 550 °C become sharper and stronger. The XRD peaks of annealed films exhibit major peaks at 28.8°, 32.9°, 47.3°, 56.1°, 69.2° and 76.4° that correspond to (112), (200), (220), (312), (008) and (332) planes of the kesterite CZTS (JCPDS no. 26-

0575). In addition, the phase of CZTS films was also confirmed by Raman spectroscopy to analyze XRD patterns from secondary phases i.e. zinc sulphide (ZnS) and copper tin sulphide (CTS). Fig. 4.9 shows the Raman peaks of annealed films at 340°C and 550°C which appear differently at various annealing temperatures. According to Raman peaks, when the annealing temperature increase, the main peaks of kesterite CZTS phase appear more intense which is due to the enhanced crystallinity of the films at higher temperatures. The Raman peaks appear at 287, 337, 350 and 370 cm$^{-1}$ which confirm the existence of kesterite structure [33] and the Raman peaks of secondary phases do not appear. Consequently, XRD and Raman results justify the good quality of synthesis CZTS thin films.

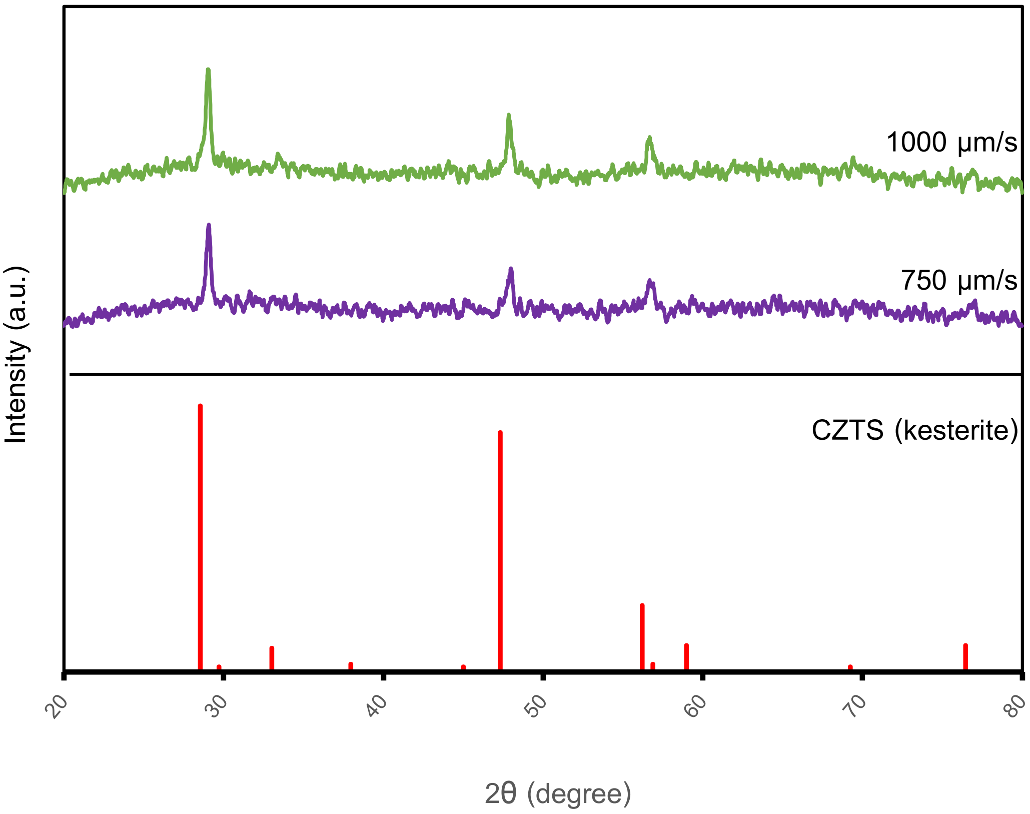


Figure: 4.7 XRD patterns of CZTS annealed films in nitrogen atmosphere at 440°C.

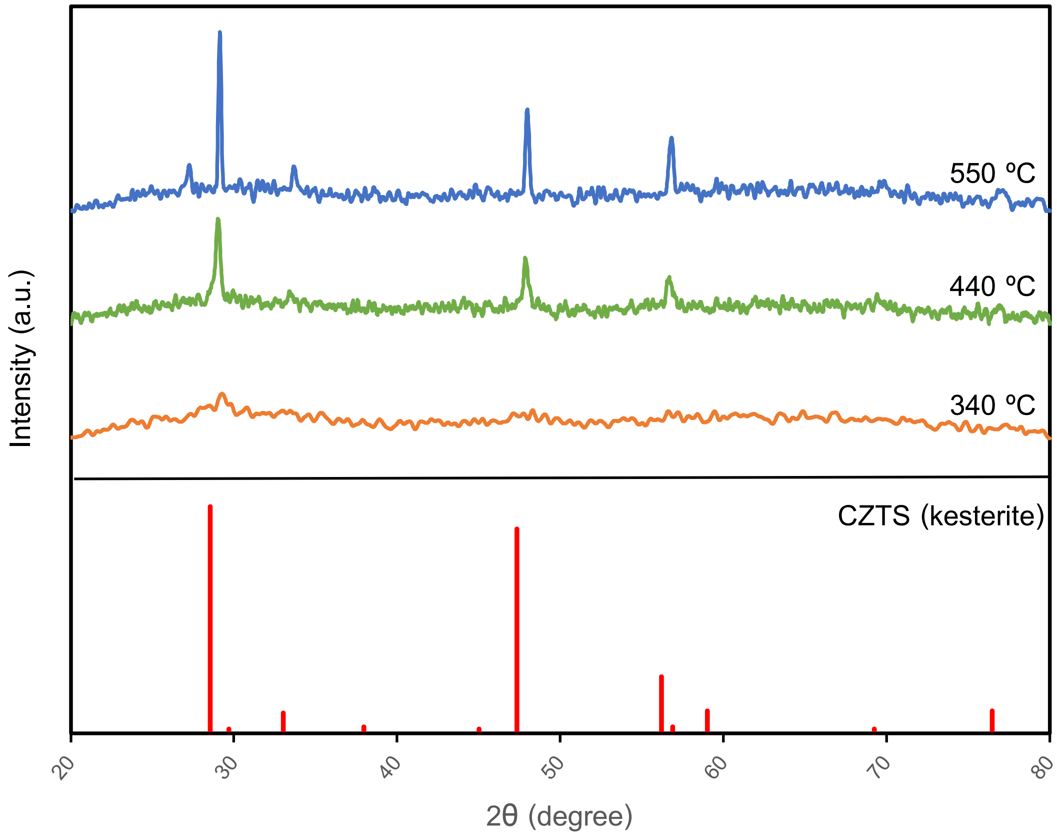


Figure: 4.8 XRD patterns of CZTS annealed films in nitrogen atmosphere at various annealing temperatures.

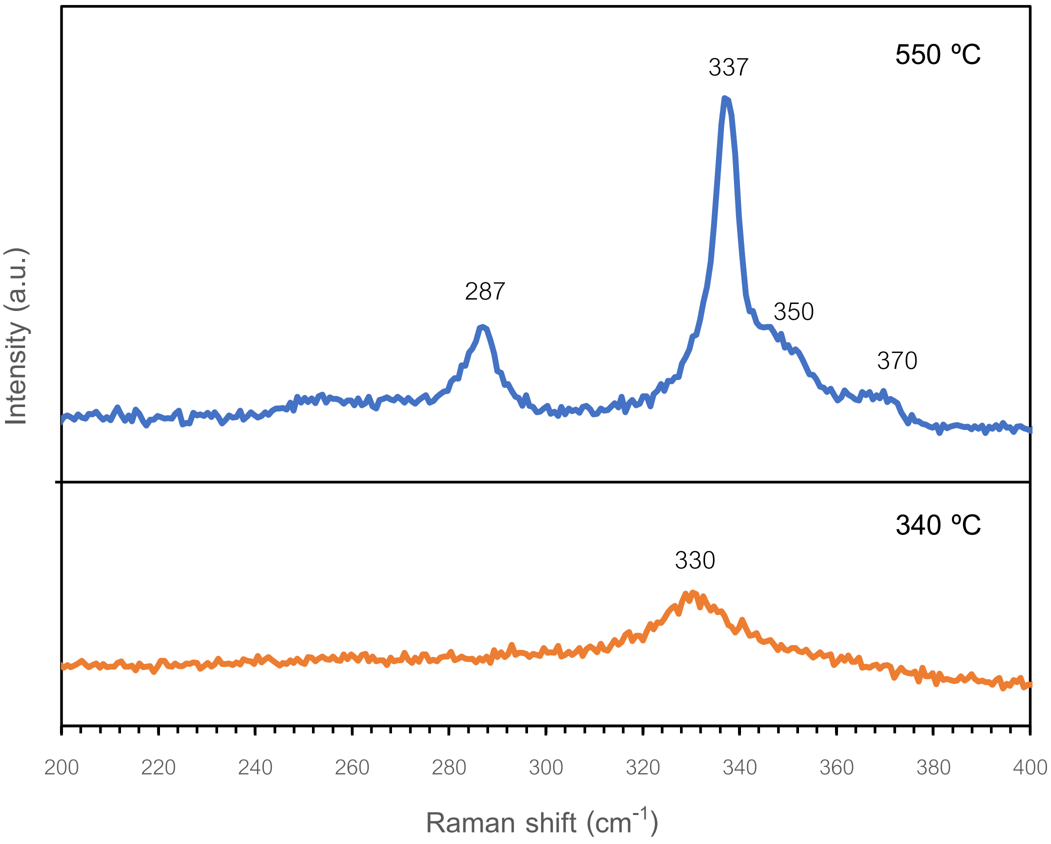


Figure: 4.9 Raman spectrum of the annealed films at different temperatures.

### 4.1.3 Energy band gap

Recalling the previous work, the band gap energy has been influenced by the variation in grain size and stoichiometry of the films [24, 34-38], which mainly depends on the deposition speed of convective deposition and annealing temperature. Band gap energies of the CZTS films were determined by extrapolating the linear region of $\alpha h\nu^2$ versus photon energy ($h\nu$) curve to the intercept of the photon energy axis of CZTS films deposited at different deposition speeds and annealing temperatures as shown in the Fig. 4.10 to Fig. 4.12 and the band gap values are summarized in Table 4.2. The results present the band gap energies decrease as the deposition speed increase. This variation is attributed to the change in morphology and composition of the films deposited at different conditions. CZTS films which were fabricated at higher deposition speed than the optimal deposition speed consist of small particles, therefore increasing the grain boundaries and forming as a multilayer as seen in the Fig. 4.2 and Fig. 4.3. These small particle sizes of the film deposited at high deposition speed influence on the optical properties due to the discontinuous path way of the moving electrons within the layer. Moreover, the film thickness also increases at the high deposition speed so the electrons take a long time to travel through the layer which may cause the recombination of electron and hole. On the other hand, if the deposition speed is lower than the optimal deposition speed, CZTS contains some voids within the film which affects the transporting of the charge inside the films. Meanwhile, the composition also plays a role in band gap energy of CZTS films. Babu et al. studied about CZTSe which has a function of the composition of Cu/(Zn+Sn) which is similar to CZTS. They reported that the band gap of CZTSe shifts to higher energies as Cu/(Zn+Sn) decreases [29] which refer to Cu-poor and Zn-rich conditions of CZTS films. Moreover, the energy band gap increases when the S content is decreased at higher annealing temperature [34]. As seen in Fig. 4.12, the band gap of CZTS annealed films at 550ºC shifts to higher energies when the Cu/(Zn+Sn) ratio and the S content decreases due to the influence of thermal degradation of precursors. However, at low annealing temperature, the compositions of each component are still under control by the deposition speed.

The synthesized CZTS films were investigated the effect of deposition speed of convective deposition and the annealing temperature on the composition, morphology, structure and energy band gap. According to the results, the optimal condition for the deposition of CZTS thin film to be applied on the organic photovoltaic solar cell devices as a hole transporting layer was obtained at the annealing temperature at 440ºC and the deposition speed under 1000 μm/s. Although the stoichiometry of films which were annealed at 340ºC were approximately close to the theoretical ratio, the films were still amorphous phase. On the other hand, the 550ºC annealed temperature extremely affects the loss of precursor contents, especially sulphur which create more voids within the films.

The films which have a lot of voids are not appropriate to be used as a transporting layer. Also the higher deposit speed of the CZTS films more than 1000 µm/s, the approximate thickness of films are more than 200 nm which are unsuitable to be a hole transporting layer. Therefore, the annealing temperature at 440°C and deposit speed of under 1000 µm/s are the suitable conditions to apply with the organic photovoltaic devices. Although the composition of the films at these conditions is slightly off the stoichiometric ratio of CZTS, the concentration of precursors can be adjusted to achieve the stoichiometric ratio. However, the detailed analysis is beyond the scope of this study.

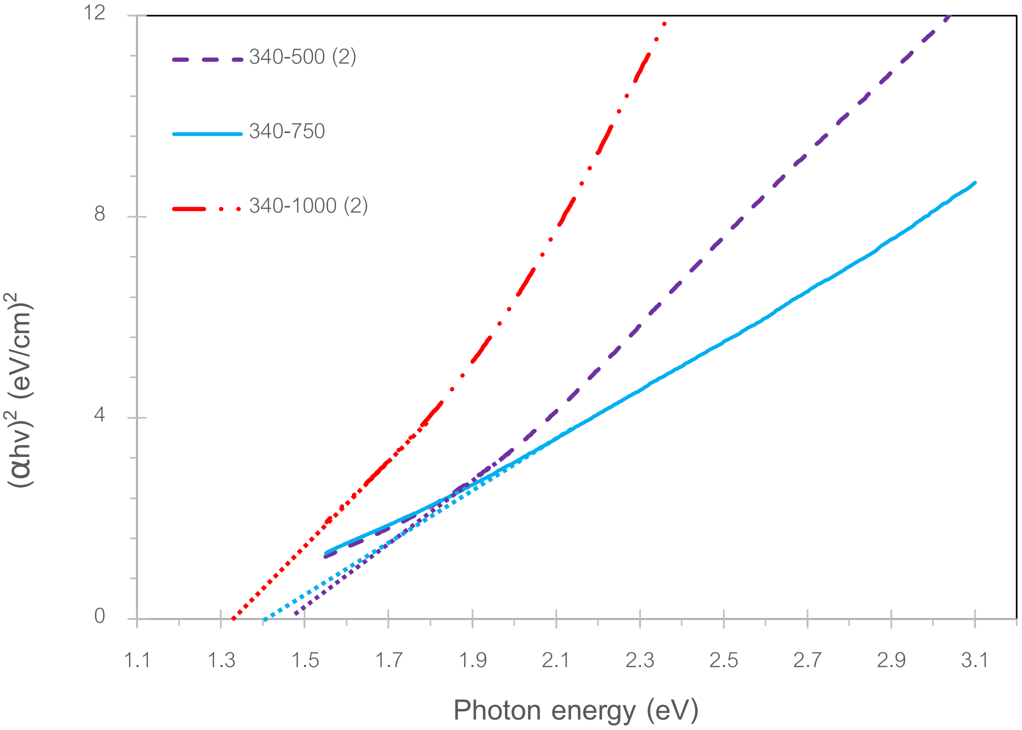
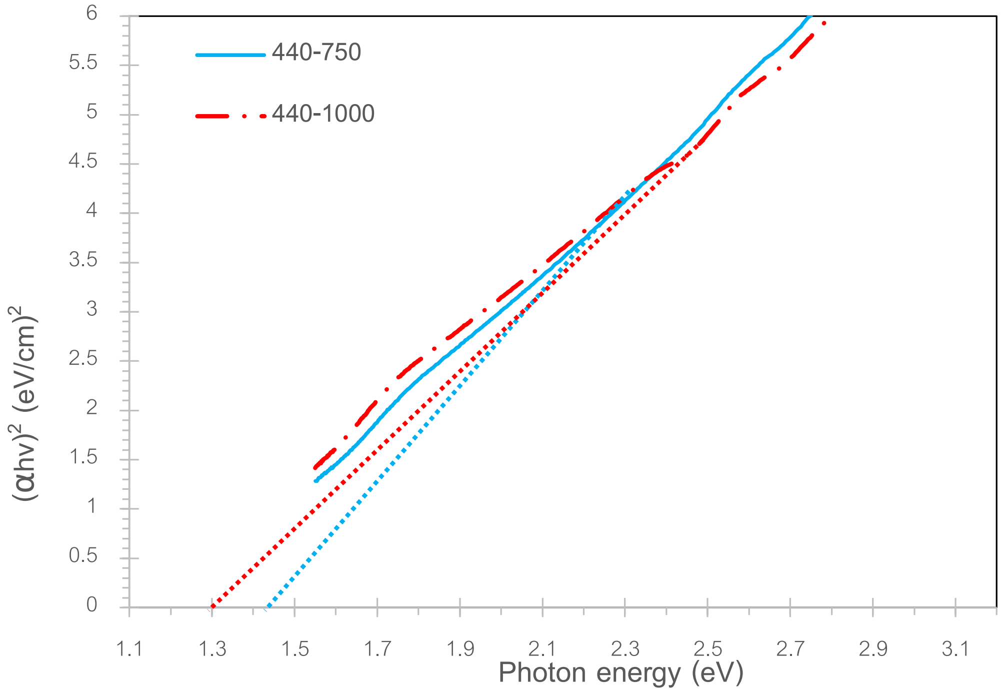


**Figure: 4.10** $(\alpha h\nu)^2$ as a function of photon energy for the annealed CZTS films at 340°C and deposit rate of 500,750, and 1000 µm/s.



. **Figure: 4.11** $(\alpha h\nu)^2$ as a function of photon energy for the annealed CZTS films at 440ºC and deposit rate of 750 and 1000 µm/s.

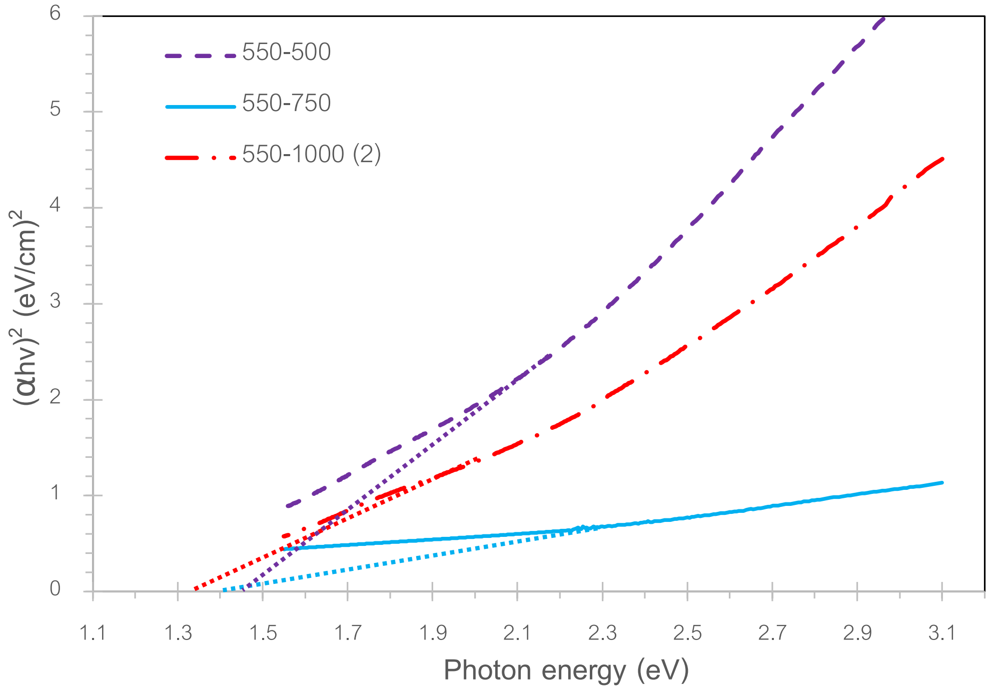


Figure: 4.12 $(\alpha h\nu)^2$ as a function of photon energy for the annealed CZTS films at 550°C and deposit rate of 500,750, and 1000 μm/s.

Table: 4.2 Band gap energy ($E_g$) of CZTS films deposited at different deposit speeds and annealing temperatures.

| Sample | | Band gap (eV) |
|---|---|---|
| Annealing temperature(°C) | Deposition speed (μm/s) | |
| 340 | 500 | 1.48 ± 0.05 |
| | 750 | 1.40 ± 0.02 |
| | 1000 | 1.33 ± 0.03 |
| 440 | 750 | 1.44 ± 0.05 |
| | 1000 | 1.30 ± 0.05 |
| 550 | 500 | 1.47 ± 0.05 |
| | 750 | 1.41 ± 0.02 |
| | 1000 | 1.35 ± 0.05 |

### 4.2 An organic photovoltaic solar cell devices with a layer of CZTS thin film

Generally, an organic photovoltaic (OPV) solar cell structure is composed of an active layer between electrodes. To increase the efficiency of OPV solar cell, a hole transporting layer and an electron transporting layer are added before and after the active layer, respectively. For hole transporting layer, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is commonly used as hole transporting material (HTM) but it still has several drawbacks that brings about OPV degradation. PEDOT:PSS is an organic material which has a low stability due to its highly hygroscopic which could affect the conductivity when present in the present of moisture [21]. Besides, PEDOT:PSS is acidic to electrode which causes the corrosion of electrode and can induce water into the OPV device. Therefore, the alternative like inorganic materials have become interesting to be used as HTMs because of their high chemical stability, high hole mobility, simple and low-cost synthesis process and easy storage [32]. Since there are several advantages of inorganic materials, Cu-based materials can be used as a hole transporting material due to its high conductivity and stability. In this study, $Cu_2ZnSnS_4$ (copper zinc tin sulphide: CZTS) thin films were applied as HTM in OPV solar cells. The OPV devices with a layer of CZTS thin film were fabricated by the following device configuration; FTO glass/ /CZTS/PDCTBT:$PC_{70}BM/TiO_x$ /Al grid, as shows in Fig. 4.13. Moreover, CZTS films were deposited at various deposition speeds of 100, 250, 500, 750 and 1000 µm/s which will be represented as CZTS-100, CZTS-250, CZTS-500, CZTS-750, and CZTS-1000, respectively, in this dissertation. The effect of CZTS HTM on the optical properties of OPV devices was investigated.

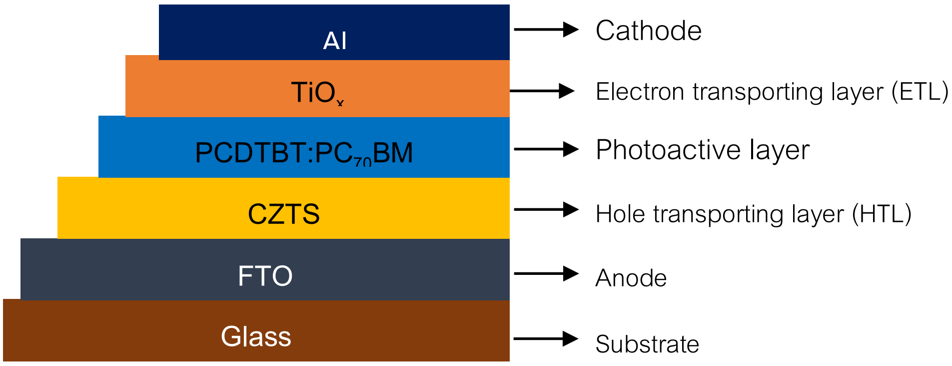


Figure: 4.13 The configuration of photovoltaic devices with a layer of CZTS thin film as HTL

Current density-voltage (J-V) curves of OPV devices with a CZTS layer deposited at various deposition speeds compared to the reference cell with PEDOT:PSS layer as a HTM were measured under illumination of a solar simulator in air are shown in Fig. 4.14. The photovoltaic parameters including open-circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$), fill factor (FF), and power conversion efficiency (PCE) of OPV devices are also shown in Table 4.3. The J-V curves of OPV devices with CZTS as HTM show a rather low $V_{oc}$ and $J_{sc}$. Among CZTS films deposited at different deposition speeds, the deposit speed of 500 µm/s gives the best performance device. The PCE of OPV device with CZTS-500 is 0.63% which was calculated from $V_{oc}$ of 0.45 V, $J_{sc}$ of 3.56 mA/cm2, and fill factor of 39.13%. At lower or higher deposition speeds than 500 µm/s, the PCEs become lower which could be related to the morphology of CZTS films. According to the effect of different deposition speeds on the morphology of CZTS films described previously, the higher deposition speed than the optimal deposition speed leads to form a multilayer of the film in which the film thickness is nonuniform throughout the whole surface of the substrate, therefore it is unsuitable to perform as a hole transporting layer. Besides, particle sizes and grain boundaries were decreased, resulting in a short path length for hole transportation and making it more difficult to travel to the next layer. This behavior directly affects $J_{sc}$. In contrast, the lower deposition speed than the optimal deposition speed brought about voids in the films which affected the electrical properties of the films.

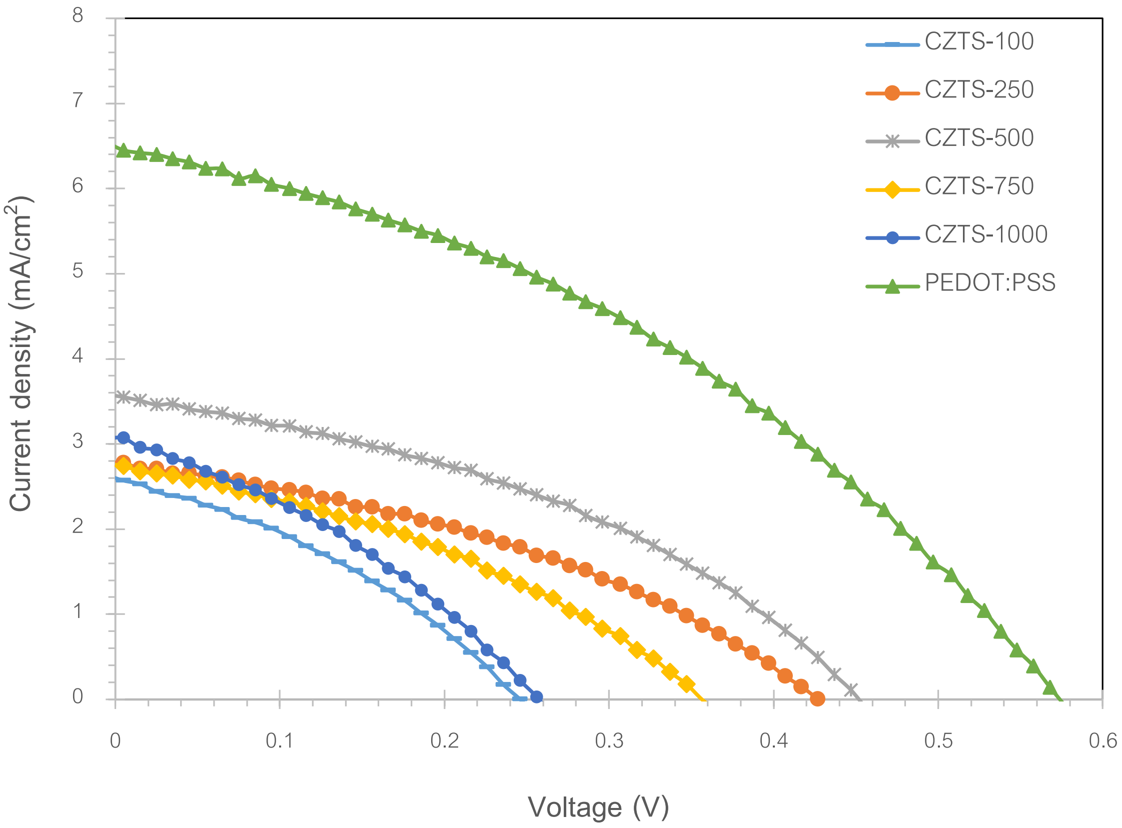


Figure: 4.14 J-V curves of OPV devices with CZTS or PEDOT:PSS as HTMs

Table: 4.3 The performance of OPV devices with difference HTMs.

| Hole Transporting Material (HTM) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF. (%) | PCE (%) |
|---|---|---|---|---|
| CZTS - 100 | 0.25 | 2.60 | 34.41 | 0.22 |
| CZTS - 250 | 0.43 | 2.79 | 37.30 | 0.44 |
| CZTS - 500 | 0.45 | 3.56 | 39.13 | 0.63 |
| CZTS - 750 | 0.36 | 2.76 | 36.27 | 0.36 |
| CZTS - 1000 | 0.26 | 3.08 | 33.68 | 0.27 |
| PEDOT:PSS | 0.57 | 6.49 | 37.46 | 1.39 |

Although the CZTS-500 film shows the best efficiency for OPV device, the PCE is still less than the reference OPV device with PEDOT:PSS as HTM. In general, the optimized thickness of PEDOT:PSS layer used in OPV device is less than 150 nm, but the CZTS-500 layer in this study is more than 150 nm, which could be one of the reasons of low PCE. Moreover, from the summary of the devices performances shown in Table 4.3, the results show that the higher $J_{sc}$ value of PEDOT:PSS than that of CZTS HTM conform to the UV-vis spectra. The comparison of UV-vis absorption of OPV devices with PEDOT:PSS and CZTS-500 as HTMs are shown in Fig. 4.15. The result shows that CZTS film can absorb photon slightly less than PEDOT:PSS in the visible wavelength region but the difference is not significant. This indicates that in terms of the optical property, CZTS can replace PEDOT:PSS for using as HTM for OPV devices. Moreover, it is also obvious in EQE spectra as shown in the Fig. 4.16 that EQE curve in visible wavelength region of OPV device with CZTS HTM is almost exactly the same to the curve of OPV device with PEDOT:PSS HTM, indicating that CZTS has an ability to transport hole in OPV devices un a similar manner to PEDOT:PSS.

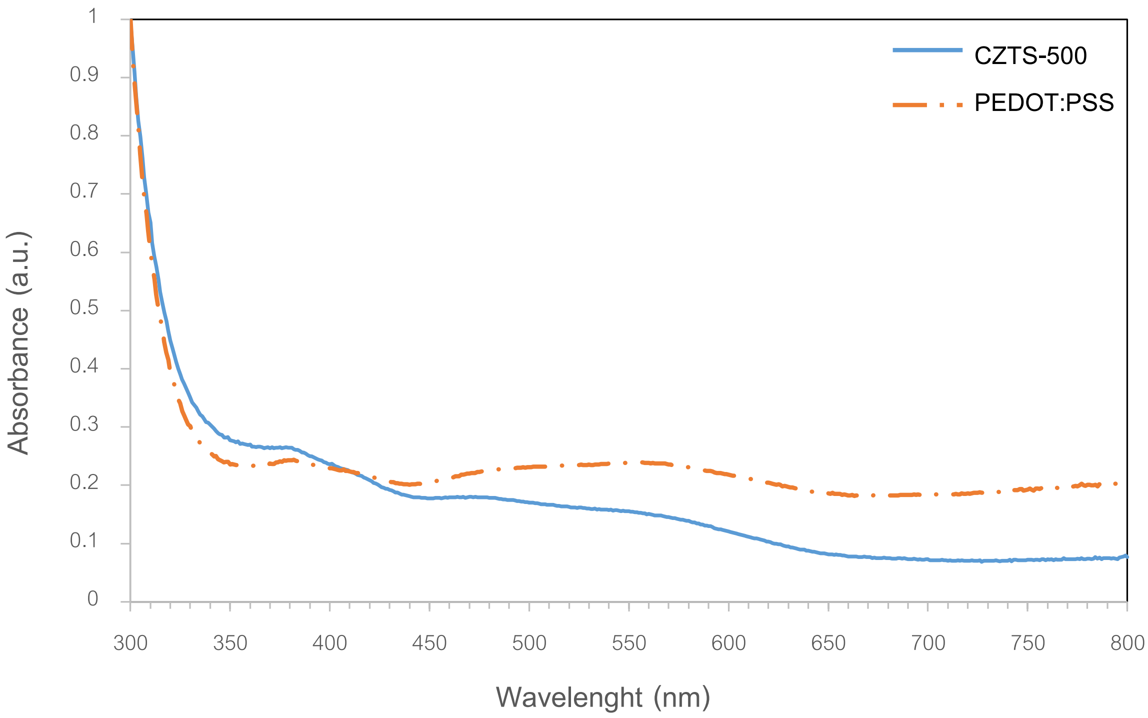


**Figure: 4.15** UV-vis absorption of the best FTO/HTM/PCDTBT:$PC_{70}BM/TiO_x$/Al OPV devices with different HTMs.

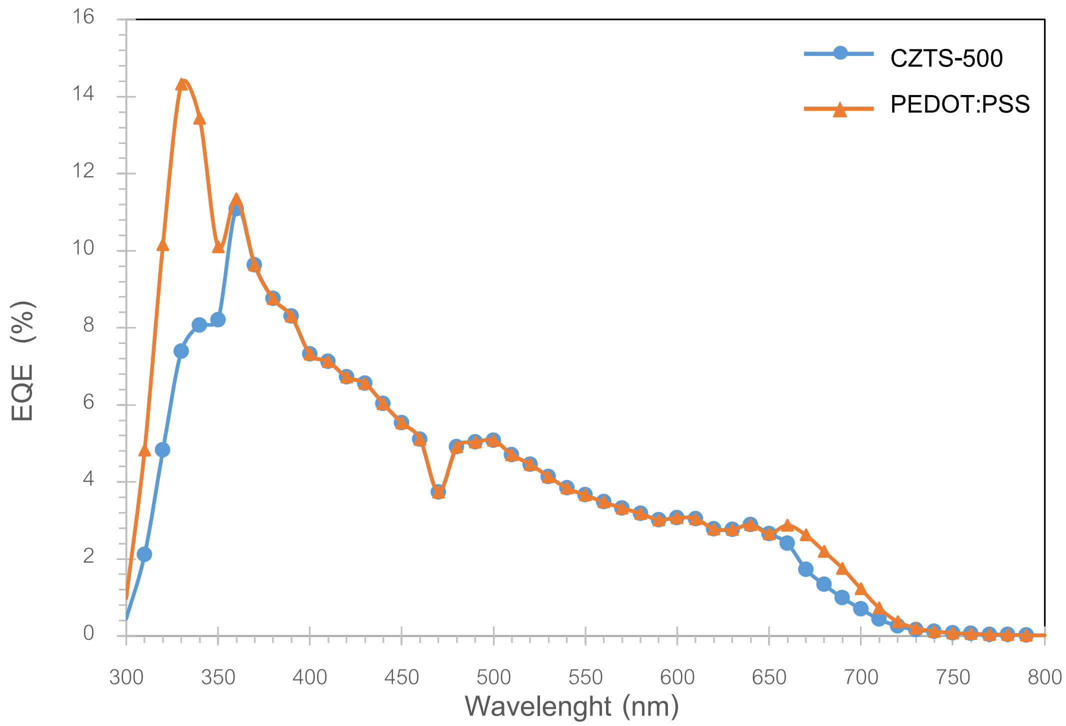


Figure: 4.16 External Quantum efficiency curves of OPV devices with different in HTMs.

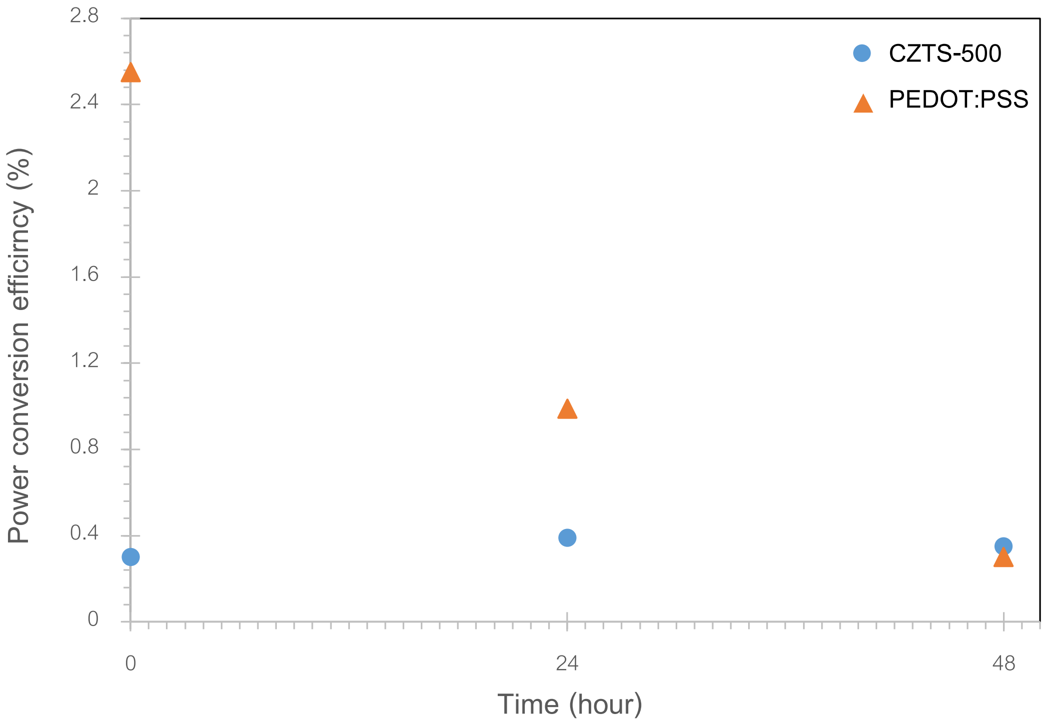


Figure: 4.17 Comparing the stability of OPV devices with different HTMs.

Because of the hygroscopic and acidic nature of PEDOT:PSS, the tendency to moisture absorption from the surrounding into the layer could significantly corrode the electrodes and consequently degrade the PCEs [39] . As seen in Fig. 4.17, it shows the stability of OPV devices over time. The device with CZTS HTM could be stabilized over the 48 hours during the measurement period, that with PEDOT:PSS HTM was dramatically degraded due to its characteristic nature as previously mentioned. Consequently, these results indicate that CZTS is capable of transporting holes together with maintaining high stability of the device, compared to the widely used PEDOT:PSS.

# CHAPTER 5

# CONCLUSION

Copper zinc thin sulphide ($Cu_2ZnSnS_4$: CZTS) thin films were successfully synthesized via convective deposition method. The films deposited at various deposition speeds were annealed under $N_2$ atmosphere to achieve high quality CZTS films. In this work, the effects of process parameters on composition, morphology, phase, and optical properties were investigated. The optimal condition was obtained and used for fabrication of the CZTS films as hole transporting layer of organic photovoltaic solar cell.

## 5.1 Summary of the results

### 5.1.1 The properties of the synthesized CZTS thin films

1. Under controlled parameters for the deposition CZTS thin films exhibit a kesterite structure. Most of the stoichiometric ratios of CZTS are approximately close to the theoretical ratio and the band gap energies of CZTS films are about 1.4-1.5 eV.
2. At higher deposition speed, the morphology of CZTS films is smooth and fully cover the substrate. Moreover, particle sizes are uniform throughout the whole surface of the film. In contrast, at lower deposition speed, the morphology of CZTS films showed the discontinuous films.
3. At the same annealing temperature, deposition at different speeds do not affect the crystallinity and phase of CZTS films.
4. High annealing temperature influences on thermal degradation of precursors which play a major role to compositions of the CZTS films.
5. The CZTS films obtained from the deposition speed in the range of 500-1000 μm/s are annealed at 440ºC, which are the optimal conditions for 4 times

deposited layer is suitable for using as hole transporting layer of OPV device, in term of the structure, morphology, compositions and band gap.

According to the results, the deposition of CZTS thin films via convective deposition method is highly effective for the device fabrication, because the obtained films are smooth, uniform in particle sizes and covering the whole surface of the substrate. In addition, this method is low cost and can be scaled for large-area production.

### 5.1.2 The organic photovoltaic solar cells with CZTS thin films as a hole transporting layer

1. The best power conversion efficiency of the OPV device with CZTS as a hole transporting layer is 0.63%, obtained from the film deposition speed of 500 μm/s.
2. Although the power conversion efficiency of the OPV device with CZTS as a hole transporting layer is still less than that with PEDOT:PSS as hole transporting layer, the device with CZTS demonstrates a higher stability than that with PEDOT:PSS. This factor is one of the most important factors for a long-term stable solar cell.

## 5.2 Conclusion

Convective deposition method is an efficient solution-based process to prepare CZTS thin films. The effects of deposition speed and annealing temperature were investigated in terms of compositions, morphology, phase, and optical properties of the films. The obtained CZTS films have a good morphology, high crystallinity and well-match optical band gap to the theoretical value, which is suitable as a hole transporting layer for OPV devices. Even though the OPV device with CZTS film as hole transporting layer has a lower efficiency than the reference-OPV device on this work, the OPV device with CZTS film does show a high stability which is one of the most important factors for the solar cell devices.

### 5.3 Recommendations for the future work

The synthesized CZTS films still have some drawbacks when using as a hole transporting material. The CZTS films can be improved by following ways;

1. Prepare the precursors into nanoparticle instead using sol-gel precursors. The form of nanoparticle precursor is easy to use and storage, and easier to control the film characteristics.
2. Dope the CZTS precursors with other metal oxide since the metal oxide may promote CZTS performance.

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# APPENDIX

# VITA

Ms.Napaporn Khothong was born on November 3, 1992, in Chiang Mai, Thailand. In 2015, she graduated from Chemical Technology, Chulalongkorn University in Bachelor of Science (Chemical Engineering). After that, she enrolled in the Department of Chemical Engineering, Chulalongkorn Uiversity, as a master's degree student.