Parametric Study of Copper Zinc Tin Sulfide Thin Films by Convective Deposition Method

Mr. Thanawat Anantamongkolchai

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การศึกษาปัจจัยของฟิล์มบางคอปเปอร์ซิงค์ทินซัลไฟด์โดยวิธีการคอนเวคทีฟดีโพสิชัน

นายธนวัฒน์ อนันตมงคลชัย

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ปีการศึกษา 2561

Thesis Title	Parametric Study of Copper Zinc Tin Sulfide Thin Films by Convective Deposition Method
By	Mr. Thanawat Anantamongkolchai
Field of Study	Chemical Engineering
Thesis Advisor	Dr. Paravee Vas-Umnuay, Ph.D.
Thesis Co Advisor	Assistant Professor Dr. Sojiphong Chatraphorn, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Engineering

.... Dean of the Faculty of Engineering
(Associate Professor Dr. Supot Teachavorasinskun,
D.Eng.)

THESIS COMMITTEE

.... Chairman
(Associate Professor Dr. Varong Pavarajarn, Ph.D.)

.... Thesis Advisor
(Dr. Paravee Vas-Umnuay, Ph.D.)

.... Thesis Co-Advisor
(Assistant Professor Dr. Sojiphong Chatraphorn, Ph.D.)

.... Examiner
(Dr. Chalida Klaysom, Ph.D.)

.... External Examiner
(Tanyakorn Muangnapoh, Ph.D.)

ธนวัฒน์ อนันตมงคลชัย : การศึกษาปัจจัยของฟิล์มบางคอปเปอร์ซิงค์ทินซัลไฟด์โดยวิธีการคอนเวคทีฟดีโพสิชัน. (Parametric Study of Copper Zinc Tin Sulfide Thin Films by Convective Deposition Method) อ.ที่ปรึกษาหลัก : อ. ดร.ปารวี วาศน์อำนวย, อ.ที่ปรึกษาร่วม : ผศ. ดร.โศจิพงศ์ ฉัตราภรณ์

ในทุกวันนี้พลังงานส่วนใหญ่นั้นถูกผลิตมาจากพลังงานฟอสซิลที่ซึ่งทำให้เกิดก๊าซเรือนกระจกปริมาณมาก ดังนั้นนักวิจัยมากมายจึงเซาะหาพลังงานทางเลือกที่เป็นพลังงานสะอาดและเป็นพลังงานทดแทนที่สามารถหมุนเวียนมาใช้ได้อีก หนึ่งในตัวเลือกที่โดดเด่นสำหรับพลังงานทางเลือกคือ พลังงานแสงอาทิตย์ โดยพลังงานแสงอาทิตย์สามารถเปลี่ยนเป็นพลังงานไฟฟ้าได้โดยตรงด้วยเซลล์แสงอาทิตย์ ในทุกวันนี้เซลล์แสงอาทิตย์แบบฟิล์มชนิดคอปเปอร์ซิงค์ทินซัลไฟด์เป็นที่น่าสนใจในวงกว้างเนื่องจากมีช่องว่างระหว่างแถบพลังงานในช่วง 1.4-1.6 อิเล็กตรอนโวลต์ ที่ความสอดคล้องกับสเปกตรัมของแสงอาทิตย์และประสิทธิภาพในการรับแสงอาทิตย์ อย่างไรก็ตามเดิมทีกระบวนการผลิตเซลล์แสงอาทิตย์แบบฟิล์มชนิดคอปเปอร์ซิงค์ทินซัลไฟด์มีความซับซ้อนสำหรับการเคลือบฟิล์มรวมถึงชั้นคอปเปอร์ซิงค์ทินซัลไฟด์ที่เป็นชั้นรับแสง ดังนั้นงานนี้จึงมีเป้าหมายที่จะใช้วิธีการแบบใช้สารละลายด้วยวิธีการคอนเวคทีฟเดพโพสิชั่นสำหรับกระบวนการเคลือบชั้นรับแสงเนื่องจากการดำเนินการที่ง่ายและมีค่าใช้จ่ายที่ต่ำ ดังนั้นงานนี้จึงเลือกมุ่งเน้นที่จะศึกษาตัวแปรต่างที่ส่งผลกระทบต่อลักษณะของฟิล์มทางกายภาพ อาทิเช่น ความเร็วในการเคลือบ, ชนิดของตัวทำละลาย (2-เมททอกซีเอทานอล และน้ำ) และสัดส่วนของตัวทำละลาย โดยในส่วนของผลการทดลองที่ได้จะพบว่าที่ความเร็วในการเคลือบที่สูงจะส่งผลให้เกรนมีขนาดเล็กในฟิล์มคอปเปอร์ซิงค์ทินซัลไฟด์ ยิ่งไปกว่านั้นฟิล์มคอปเปอร์ซิงค์ทินซัลไฟด์ที่ตัวทำละลายน้ำเป็นองค์ประกอบในปริมาณมากจะให้ฟิล์มมีลักษณะที่แน่นกว่า ในทางตรงกันข้ามฟิล์มคอปเปอร์ซิงค์ทินซัลไฟด์ที่ตัวทำละลาย 2-เมททอกซีเอทานอลเป็นองค์ประกอบในปริมาณมากจะให้ฟิล์มมีลักษณะที่รูพรุนที่มากกว่า โดยฟิล์มที่เป็นที่เหมาะสมสำหรับการนำไปทำเซลล์แสงอาทิตย์นั้นต้องเป็นฟิล์มที่แน่นกว่าที่ซึ่งจะสอดคล้องกับผลของประสิทธิภาพ แล้วลักษณะฟิล์มที่ต้องการนั้นยังสามารถทำได้ภายใต้วิธีและเงื่อนไขที่ปฏิบัติของวิธีการคอนเวคทีฟเวคทีฟดีโพสิชั่น นอกเหนือจากนี้แล้ววิธีการคอนเวคทีฟเวคทีฟดีโพสิชั่นสามารถเคลือบฟิล์มบางสำหรับใช้ในหลายรูปแบบการใช้งาน

สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2561

ลายมือชื่อนิสิต ....
ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

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Nowadays, most of the energy production is from fossil fuel-resources, which is a major source of greenhouse gases. Therefore, several researchers have been looking for the alternative energy that is clean and renewable energy. One of the outstanding alternatives is to utilize solar energy for conversion into electricity. Recently, CZTS (*copper* zinc tin sulfide, Cu_2ZnSnS_4) thin film solar cells have received numerous interest because of its decent energy band gap of about 1.4 – 1.6 eV, which matches with the solar spectrum, and its high absorption coefficient. Nevertheless, the manufacture of CZTS solar cells has used sophisticated methods for fabrication including CZTS which is an absorber layer. Therefore, this work was aimed to use the solution-based convective deposition method for fabrication of CZTS thin films due to its simplicity and low-cost yet effective. The focus of this work was to investigate the effects of various deposition parameters including deposition speed, types of solvent (2-methoxyethanol and deionized water) and fraction of solvents on the physical properties of CZTS films. According to the experimental results, higher deposition speed led to small grains of CZTS in the films. Moreover, CZTS film prepared from a solvent with higher fraction of deionized water resulted in a compact film. On the contrary, the film prepared from a solvent with pure 2-methoxyethanol resulted in porous film. This desired compact CZTS film was proved to show a better performance (higher efficiency) of CZTS solar cell. As a consequence, it could be confirmed that a desired morphology of CZTS thin films could be obtained under a controlled deposition condition. Furthermore, convective deposition can be a potential method for fabrication of thin films for various applications.

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Student's Signature ....
Advisor's Signature ....
Co-advisor's Signature ....

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Chapter 1

INTRODUCTION

Nowadays, energy consumption issues are one of the important problems in almost every country due to the dramatically increasing energy demand. Fossil fuels majorly provide more than 80% of the energy that the world's population use today [1]. However, fossil energy production is a major source of greenhouse gases, which causes acid rain, air pollution and global warming. Moreover, fossil fuels will be gradually depleted in the near future. Therefore, many researchers have been looking for the alternative energy that is clean and renewable. Renewable energy for example ocean energy, biomass energy, geothermal energy, hydrogen energy and solar energy can be compensated in a short time by nature after use and these energies are clean. One of the outstanding choices of renewable energy is solar energy because it is abundant and free for conversion of energy [1].

In terms of energy conversion, solar cells are electrical devices that convert sunlight energy directly into electrical energy by the photovoltaic phenomenon. Solar cell was invented nearly 200 years ago, and it has still been developing continuously. By classification, solar cells can be categorized into three generations. The first one is crystalline silicon solar cells, which include single crystalline silicon solar cells and polycrystalline silicon solar cells. These have notable efficiency and high stability. On the other hand, crystalline silicon solar cells have a high weight and cost because the production uses plenty of energy for melting pure silicon. Furthermore, the process produces greenhouse gases emissions. The second generation is thin film solar cells, such as amorphous silicon solar cells and compound. Amorphous silicon solar cells are made from silicon, boron and phosphorus in the gas phase reaction and the formation of thin film is deposited on the glass, plastic or metal sheet [2]. While compound semiconductors solar cells such as copper indium gallium diselenide solar cells (CIGS, $CuIn_xGa_{(1-x)}Se_2$), cadmium telluride solar cells (CdTe) and copper zinc tin sulphur solar cells (CZTS, Cu_2ZnSnS_4) are high in efficiency. The third generation is organic photovoltaic solar cells that use organic compound as an absorber layer and charge transporting layer. This type is consisted of inexpensive materials and easy for processing. However, some of the organic photovoltaic solar cells are low in efficiency and the stability lasts a short lifetime.

Among thin film solar cells in the second generation, CIGS thin film solar cells has the highest efficiency, which consists of I-III-VI_2 compound semiconductor material with a chemical formula of $CuIn_{(1-x)}Ga_x Se_2$. Although CIGS thin film solar cells have high efficiency and good stability, indium (In) and gallium (Ga) are rare, resulting in costly elements. In addition, the complex vacuum based and expensive process are one of the drawbacks for commercialization. Conversely, Cu_2ZnSnS_4 (CZTS) have been considered as a noticeable candidate for photovoltaic applications because of its nontoxic composition and its low-cost and earth-abundant elements [3].

CZTS is a p-type quaternary semiconductor with a direct band gap and a high absorption coefficient $>10^4$ cm^{-1} in the visible region. Moreover, CZTS has a suitable energy band gap of 1.4-1.6 eV which is very close to the optimum value as an absorber layer in thin film solar cells [4]. In general, CZTS thin films can be fabricated on either flexible or rigid substrates by various gas-phase and solution-based methods, for example sputtering, thermal evaporation, spray pyrolysis, electrochemical deposition, chemical bath deposition and spin coating. However, most of the gas-phase techniques require expensive and sophisticated equipment with intense operating conditions, for example, under vacuum atmosphere and very high temperature environment. Therefore, the processes require high cleanliness and high energy input. On the other hand, most of the solution-based techniques require a lot of precursor solution utilization and time for deposition.

For this reason, convective deposition, which is a solution-based method, can be the alternative approach to solve aforementioned problems, because this method is carried out under ambient condition and requires simple equipment. In addition, this method takes less time-consuming and inexpensive apparatus for fabrication. Principally, convective deposition has been used to fabricate a monolayer film from colloidal or nanoparticles. The equipment of this method shown in figure 1.1 (a) consists of a deposition blade of about 10 µm above the substrate and the translation stage at the bottom. A microliter of precursor solution is injected between the deposition blade and substrate and then the substrate on the stage is pulled in the horizontal axis with a controllable speed. A meniscus of the solution occurs between a substrate and a blade at a certain speed forming a thin film of solution on the substrate [5]. During deposition, two physical processes occur simultaneously. First is the coffee ring effect, where a pattern is left by a puddle of particle-laden liquid. The convective flow to the edge is generated by the evaporation losses and left only aggregated thin film on the substrate, as shown in figure 1.1 (b). Secondly, the cheerio effect occurs which is the capillary attraction between particles on the liquid interface that are drawn to each other and forming into a close packed structure, as a result of the minimization of energy [6]. The parameters such as deposition speed, volume of precursor solution, concentration of solution, etc., affect to the physical processes and properties of thin films. Furthermore, this process is proper for a large scale by using only few volume of precursor.

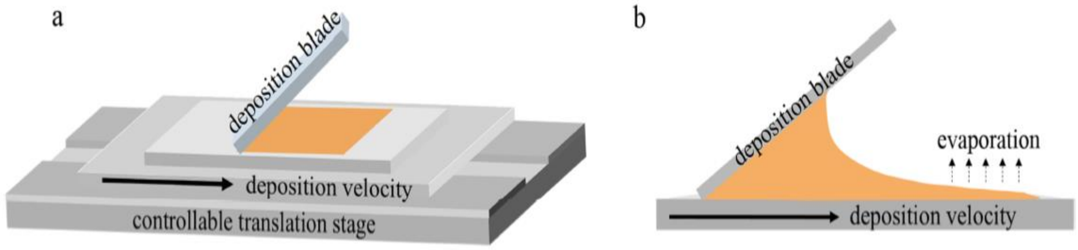

Figure 1.1 The illustrative representation of (a) experimental setup and (b) convective deposition technique for fabricating thin films [5].

1.1 Objectives

To investigate the effects of following parameters; deposition speed, types of solvents, fractions of solvents on physical properties of CZTS films and performance of CZTS solar cells.

1.2 Scopes of work

1.2.1 Prepare the precursor solution for the deposition of CZTS thin film by convective deposition technique. The solution contains Cu, Zn, Sn and S precursors with controlled concentrations and dissolved in a solvent such that the obtained CZTS thin films have a corresponding theoretical stoichiometric ratio of Cu:Zn:Sn:S of 2:1:1:4. The solution is stirred for 30 min at 50 ^{o}C until it is well mixed. The as-prepared solution of 20 μL is deposited on Mo-coated substrate (soda-lime glass) by convective deposition method at room temperature.

1.2.2 The fraction of solvents (2-methoxyethanol: deionized water) and the types of solvents used for the precursor solution are investigated. The ratio of 2-methoxyethanol: deionized water is varied from 100:0, 70:30 and 30:70. This parameter also affects the morphology, grain size and porosity of the film.

1.2.3 The deposition speed is varied from 500 μm/s to 1250 μm/s by using 100:0 of 2-methoxyethanol: deionized water as a solvent. This operating parameter strongly affects the morphology, porosity of the films and the film thickness.

1.2.4 Characterize the synthesized CZTS the films on Mo substrate and the CZTS solar cells by the following instruments;

1.2.4.1 X-Ray Diffraction (XRD): To examine phase formation of CZTS films.

1.2.4.2 Scanning Electron Microscope (SEM): To examine the surface and cross-sectional morphology of CZTS films.

1.2.4.3 Energy dispersive X-ray spectroscopy (EDS): To determine the chemical composition and stoichiometric of the CZTS films.

1.2.4.4 UV-VIS spectrophotometer: To evaluate the optical property in terms of the band gap.

1.2.4.5 Solar Simulator: To measure power conversion efficiency (PCE), fill factor (FF), open circuit voltage (V_{oc}) and short-circuit current density (J_{SC}).

Chapter 2
LITERATURE REVIEWS

Since most of the energy production is from fossil fuel-resources, which are a major source of greenhouse gases, therefore there have been a great deal of attempts to research for the alternative energy that is clean and renewable. One of the outstanding alternatives is to utilize solar energy for conversion into electricity. Consequently, we need to have something that can convert solar energy into electricity. This invention that can solve aforementioned problem is called “solar cell”.

2.1 Solar cell

A solar cell is an electronic device that can straightly convert solar energy into electricity. A current and a voltage to generate electric power are produced by a sunlight or an artificial light. This phenomenon requires an absorber material in solar cell devices, which can absorb energy from photons to release electrons and holes and generate an external circuit, as shown in figure 2.1. Many materials are potential for use as the absorber for photovoltaic energy conversion; however, in practice most of photovoltaic energy conversions use semiconductor materials as a p-n junction.

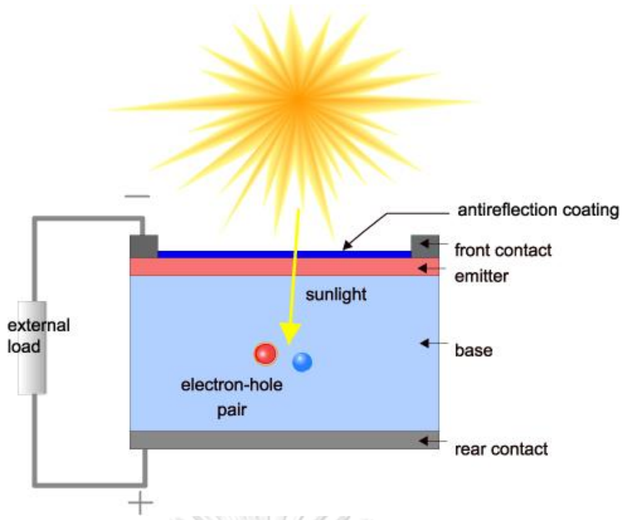

Figure 2.1 Schematic diagram of the cross section structure of a solar cell [7].

2.2 Solar cell generations

Solar cell was invented nearly 200 years ago, and it has still been developed continuously up to present. So far many types of solar cells have been emerged and developed. Solar cells can be made from only one single layer of absorb layer (single-junction) or many layers (multi-junctions) due to more advantages of higher absorption and better charge separation mechanism. By classification of solar cells, they can be classified into three generations as follows.

The first generation is crystalline silicon solar cells that composed of single crystalline silicon solar cells and polycrystalline silicon solar cells. These are currently the most efficient and have high stability. These technologies have been manufactured into a commercial product in the market today. However, crystalline silicon solar cells are high in weight and cost because the production process requires a plenty of energy for melting pure silicon which emits lots of greenhouse gases. Furthermore, their efficiencies have been stable for so long and the attempt to increase the efficiency is likely difficult.

The second generation is thin film solar cells with nano- to micrometers in thickness, such as amorphous silicon solar cells and compound semiconductors. The manufacturing process of thin film solar cells uses less materials and lower cost. Amorphous silicon solar cells are made of silicon, boron and phosphorus in the gas form as thin film for coating on the glass, plastic or metal sheet [2]. Compound semiconductors solar cell such as copper indium gallium selenide solar cells (CIGS, $CuIn_xGa_{(1-x)}Se_2$), cadmium telluride solar cells (CdTe) and copper zinc tin sulphur solar cells (CZTS, Cu_2ZnSnS_4) are also high in efficiency and have still been developed until now.

The third generation is organic photovoltaic solar cells that are based on organic compounds and conductive polymers. The production process of this type is inexpensive and easy, so many researchers have also been investigating on developing in terms of efficiency, stability and cost [2].

2.3 P-N junction

P-n junction is the interface between two types of semiconductor materials, p-type and n-type materials in which p-type material has an excess of holes and n-type material has an excess of electrons. When two semiconductor materials are contacted, electrons diffuse from n-side across to combine with holes in p-side. Moreover, filling a hole makes negative ion and abandons a positive ion on the n-side, as shown in figure 2.2. The depletion region and electrical field are present and they inhibit other electrons from n region to migrate during to attraction by the positive ions in n region and repelling by the negative ions in the p region. This is called “non-bias” or “equilibrium of junction”. For forward bias, the two semiconductors are applied voltage to overcome the coulomb barrier in depletion region hence the electrons can migrate to p-side.

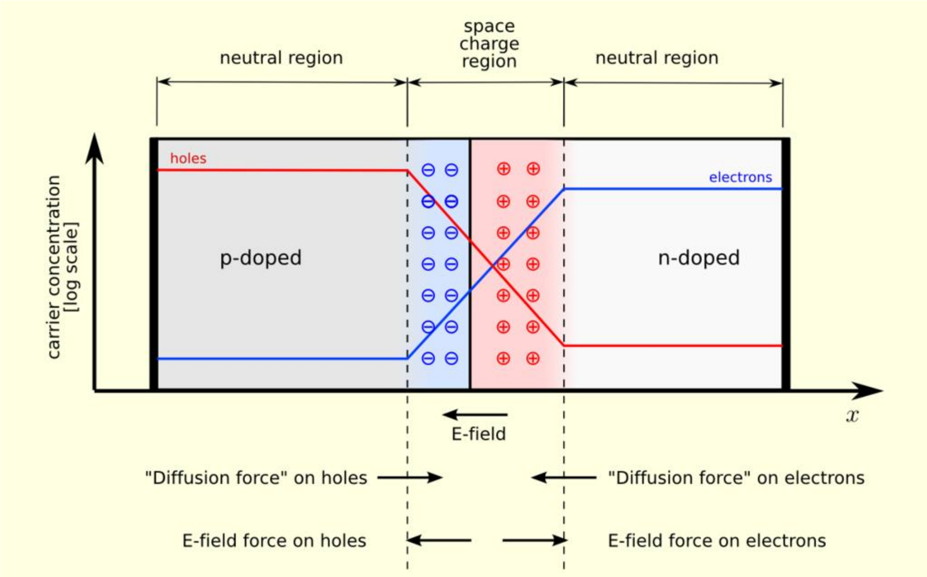

Figure 2-2 A p-n junction in the thermal equilibrium with zero-bias applied [8].

2.4 Thin film solar cells (TFSCs)

Thin film solar cells have been of well-known types of solar cells since 1970s. They are made by depositing thin film of about 5 to 50 µm thick on a rigid or flexible substrate. Therefore, this type of solar cell uses very little raw materials, which can save cost and energy in the manufacturing process.

In thin film solar cell structure, it consists of various different layers of materials which have different roles, such as transparent conducting oxide (TCO), window layer (n-type material), absorber layer (p-type material) and metal back contact layer, as shown in figure 2.3. In general, molybdenum (Mo) is used as the metal back contact layer which is deposited on soda-lime glass as a substrate. A p-type material with a band gap of about 1.1-1.5 eV is used as the absorber layer which harvests the sunlight energy and also identify the type of thin film solar cell, while CdS which is an n-type material is commonly used as a buffer layer to form a p-n junction. Each of these layers can be fabricated by many method for example physical vapour deposition (PVD), chemical vapour deposition

(CVD), molecular beam deposition (MBD), chemical bath deposition (CBD) and RF sputtering etc. Moreover, each layer has different physical and chemical properties such as crystal structure, microstructure, work function, diffusion coefficient, etc.[3]. Most transparent conducting oxides such as ZnO: In, SnO_2, In_2O_3: Sn, In_2O_3: Ga and Cd_2SnO_4 are n-type semiconductor, good electrical conductivity and high transparency [3]. The conductivity of a transparent conducting oxide relies on the carrier concentration and mobility that can be increased by improving crystalline properties to obtain a high performance TCO.

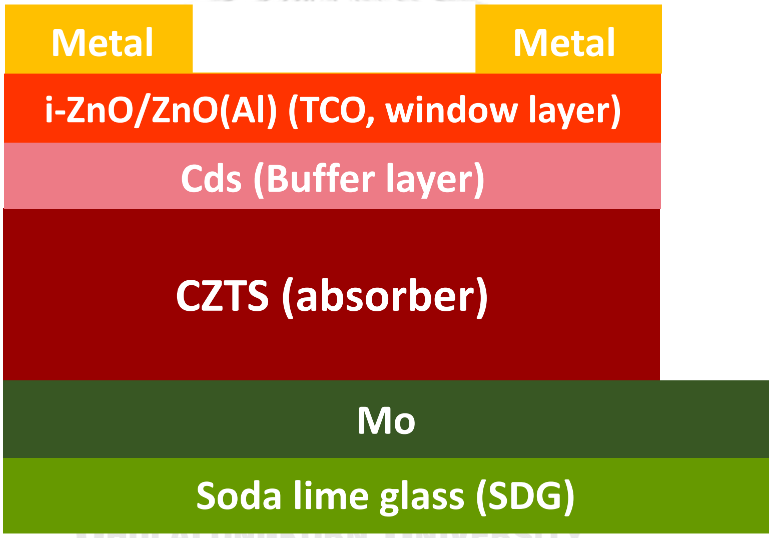

Figure 2.2 Cross-section structure of CZTS thin film solar cells.

In addition to the component of the thin film solar cells, the functional process of conversion solar energy to electrical energy in thin film solar cell is also important. The process is compose of the following steps:

1. When the electron gains enough energy from photon energy, the minimum energy that the electron can be break free is call the “band gap (E_g)” of a semiconductor.

2. The free electrons are generated and make empty space genearate a “hole” by removal of excited electrons to the conduction band (E_c). Hole is like an electron, but it is a positively charged electron.
3. The electrons from p-type side and the holes from n-type side are diffused to the depletion region. Furthermore, the minority carriers (electrons and holes) are separated by the influence of the internal electric field at P-N junction, as shown in figure 2.2.
4. The negatively charged electrons are collected around the n-type semiconductor. The positively charged electrons are collected around the p-type semiconductor for taking electrons. The current is generated when thin film solar cells is connected to the external circuit.

So far, CIGS thin film solar cells is one of the best thin film solar cell technologies which offer the highest efficiency of more than 20%. CIGS is a I-III-VI_2 compound semiconductor material with a chemical formula of $CuIn_{(1-x)}Ga_xSe_2$ that CIGS have a proper bandgap from 1.01-1.68 eV for photovoltaic application. Although CIGS thin film solar cells have high efficiency and good stability, indium (In) and gallium (Ga) are rare elements, therefore the costs of raw materials are increasing continuously. In addition, the complex vacuum based and expensive fabrication process have always been a drawback for commercialization. For this reason, Cu_2ZnSnS_4 (CZTS) has been considered as a noticeable candidate for photovoltaic applications because of its non-toxic composition and its low-cost and earth-abundant elements [3].

2.5 Copper zinc tin sulfide thin film solar cells (CZTS solar cells)

CZTS, a p-type quaternary semiconductor, is used as an absorber layer and it has a direct band gap with high absorption coefficient in visible region (>10^4 cm^{-1}). Moreover, CZTS has suitable energy band gap of about 1.4-1.6 eV which is very close to the optimum value for absorber layer in a thin film solar cell. CZTS is permeated with expectation that replaces CIGS absorber because it is composed of abundant, non-toxic and inexpensive elements [4]. Although CZTS thin films solar cells have low efficiency in the present, it is still widely studied and developed for commercial photovoltaic cell. In general, CZTS thin films can be fabricated on substrates by various gas-phase and solution-based methods, for example sputtering, thermal evaporation, spray pyrolysis, electrochemical deposition chemical bath deposition and spin coating. However, most of the gas-phase techniques require expensive and sophisticated equipment with intense operating conditions, for example under vacuum atmosphere. Therefore in this research work, the deposition of CZTS thin films was focused mainly on the solution-based process. In order to deposit the precursor solution by solution-based deposition process, the CZTS precursor solution must be prepared via a sol-gel process.

2.6 The sol-gel process

The sol-gel process began as early as the mid-1800s by studies about silica gels process. In a period from the late 1800s to 1920s, a lot of literature results from the research were published; however, the investigation of physical and chemical principles of sol-gel process were very little and has not been clearly understood. In 1950s and 1960s, novel ceramic oxide synthesis such as Al, Ti, Zr, etc. was used since the traditional method could not make this ceramic. Later, the sol-gel process has still been studied and developed until now.

The sol-gel process starts from making a sol. Sols are dispersion of colloidal particles, with diameters of 1-100 nm, in a liquid solvent. Sols can be synthesized at room temperature or high temperature. A gel is rigid network with pores and polymeric chains in which the average length is longer than a micrometer. A gel formation will happen during the hydrolysis and condensation reactions. Some sol-gel processes do not add water in the reaction that are called “Non-hydrolytic sol-gel (NHSG) processes”.

In the sol-gel process, the precursors are a colloid that is composed of metal or metalloid element encompassed by ligands. Ligands are an alkane lose one hydrogen (alkyl) or an alcohol lose one hydrogen in hydroxyl position (alkoxy), such as methyl ($^{\bullet}CH_3$), n-propyl ($^{\bullet}CH_3CH_2CH_3$), tert-butyl ($^{\bullet}C(CH_3)_3$), methoxy ($^{\bullet}OCH_3$), iso-butoxy ($^{\bullet}OCH_2CH(CH_3)_2$), n-butoxy ($^{\bullet}O(CH_2)_3CH_3$), etc. The metals and ligands can be formed to metal alkoxides which are matalorganic compounds. Metal alkoxides react easily with water; therefore, they are favored precursors. Hydrolysis reaction is substituted reaction that hydroxyl ion attach to the metal atom, as in the following reaction:

$$M(OR)_4 + H_2O \rightarrow HO\text{-}M(OR)_3 + ROH \qquad \text{(Eq. 2.1)}$$

R	represents a proton or other ligand
ROH	represents an alcohol
M	represents a metal

Some reactions occur by partially hydrolyzing inorganic precursors, as shown in equation 2.1 or some reactions are a completed hydrolysis reaction, as shown in the equation 2.2, depending on the amount of water and catalyst in the reaction.

$$M(OR)_4 + 4H_2O \rightarrow M(OH)_4 + 4ROH \qquad \text{(Eq. 2.2)}$$

Afterwards, two hydrolyzed molecules can link together with a condensation reaction, as in the following reaction:

$(OR)_3M\text{-}OH + HO\text{-}M(OR)_3 \rightarrow (OR)_3M\text{-}O\text{-}M(OR)_3 + H_2O$ (Eq. 2.3)

or

$(OR)_3M\text{-}OR + HO\text{-}M(OR)_3 \rightarrow (OR)_3M\text{-}O\text{-}M(OR)_3 + ROH$ (Eq. 2.4)

By principal definition, the condensation reaction releases a small molecule, such as water or alcohol. The reaction can continuously build larger and larger polymer as oxide networks by the polymerization.

For Non-hydrolytic sol-gel processes, the reaction starts from metal halides that reacts with secondary or tertiary ethers as the oxygen donor, leading to the formation of an inorganic oxide compound. Firstly, alkyl in ether compound is substituted by a metal halide and the reaction releases alkyl halide, as shown in equation 2.5. Moreover, metal alkoxides react with metal halide and becomes oxide or sulfide networks of metal halides.

$RCh\text{-}R + X_nM\text{-}X \rightarrow X_nM\text{-}Ch\text{-}R + R\text{-}X$ (Eq. 2.5)

and

$X_nM\text{-}Ch\text{-}R + X_nM\text{-}X \rightarrow X_nM\text{-}Ch\text{-}MX_n$ (Eq. 2.6)

Ch represents a chalcogenide (O, S)

X represents a halide

2.7 Synthesis of CZTS compound

In this thesis, the sol-gel process has both conventional sol-gel processes and non-hydrolytic sol-gel processes depending on solvent. For example, non-hydrolytic sol-gel processes in this thesis is using 2-methoxyethanol as solvent, as shown in the following equations:

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

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

$$SnCl_2 \longrightarrow Sn^{4+} + 4Cl^-$$

$$CH_4N_2S \longrightarrow S^{2-} + H^+ + NH_2\text{-}C{=}NH$$

The reaction of metal chlorides with ligand (2-methoxyethanol) produces metal alkoxides, as shown in following equation:

$$MCl_2{\cdot}2H_2O \xrightarrow[\text{Heat}]{C_3H_8O_2} M^+ + 2Cl^- + 2H_2O + C_3H_8O_2 \longrightarrow M\text{-}OC_3H_8O + 2HCl \qquad \text{(Eq. 2.7)}$$

The following equation shows a dissociated reaction of thiourea in 2-methoxyethanol solvent.

$$CH_4N_2S \xrightarrow{C_3H_8O_2} S^{2-} + H^+ + NH_2\text{-}C{=}NH + C_3H_8O_2 \qquad \text{(Eq. 2.8)}$$

The final solution from to CZTS compound are occurred, as in the following reaction:

$$XM1\text{-}OC_3H_8O + XM2\text{-}OC_3H_8O + XM3\text{-}OC_3H_8O + 4S^{2-} + 2H^+ \longrightarrow S\text{-}M1\text{-}\ddot{O}\text{-}C_3H_8O +$$

$$S\text{-}M3\text{-}\ddot{O}\text{-}C_3H_8O + S\text{-}M3\text{-}\ddot{O}\text{-}C_3H_8O \xrightarrow[\text{Heat}]{560\ ^{o}C} Cu_2ZnSnS_4 \qquad \text{(Eq. 2.9)}$$

2.8 Synthesis of CZTS thin film

Copper zinc tin sulfide (CZTS) films can be fabricated on either flexible or rigid substrate by vacuum and non-vacuum processes. However, most of the gas-phase techniques such as sputtering and thermal evaporation require expensive and sophisticated equipment with intense operating conditions, for example under vacuum atmosphere. Byungha Shin et al (2013) [9] used sputtering method for fabrication of CZTS film that the result shows the big grains of CZTS film on Mo, as shown in figure 2.4. On the other hand, non-vacuum techniques such as spin-coating, spray pyrolysis, electrodeposition, chemical bath deposition and convective deposition require inexpensive and simple equipment. From these reasons, solution-based methods are studied and developed many research groups, for example Jing Wang et al (2014) [10], Singh, Manjeet et al (2015) [11], Na Kyoung Youn et al (2015) [12] and Mostafa Boshta et al (2016) [13]. In some solution-based methods reported in previous research, the chemical composition of sulfur was found to be lower than the stoichiometric of CZTS owing to the high vapor pressure of sulfur but the stoichiometric composition of sulfur is little lower than ideal stoichiometric composition. From the aforementioned, advantages of non-vacuum processes are presented in following literature review so this thesis focuses on solution-based techniques, such as spray pyrolysis deposition, doctor blading, spin coating and convective deposition.

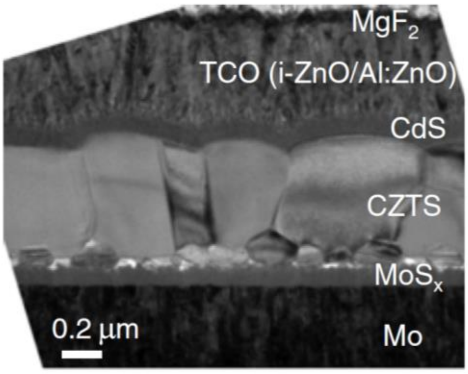

Figure 2.3 Cross-section of CZTS thin film solar cells showing big grain size of CZTS fabricated by sputtering method [9].

Non-vacuum processes

1. Spray pyrolysis deposition (SPD)

Spray pyrolysis deposition (SPD) is one of the techniques for deposition of thin film by spraying precursor on heated substrate. Generally, this process is popular for deposition of metal oxides. Furthermore, the technique is used for coating various layers in thin film solar cells production process, such as indium tin oxide (ITO) layer, Cds layer, absorber layer (CZTS), etc. Spray pyrolysis deposition (SPD) has many advantages such as a high deposition rate, a good adhesion, a high film quality, a simple method and inexpensive equipment. Besides, SPD is the method that can be easily scaled up. Mostafa Boshta et al (2016) [13] has used spray pyrolysis deposition (SPD) and the result of this research gives very smooth surface and compact film without any crack, as shown in figure 2.5 [13].

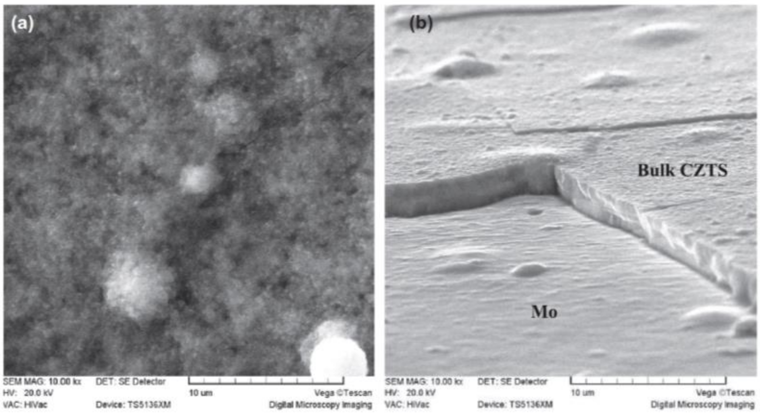

Figure 2.4 (a) Top-view SEM micrograph of the CZTS films grown on PI flexible substrates (b) SEM micrograph of the border between CZTS film and Mo/PI substrate [13].

2. Dip-coating

Dip-coating is a very simple method for film deposition. In this deposition process, the substrate is generally withdrawn in vertical direction from the fluid sol bath at a speed under controlled temperature and atmospheric condition. Meanwhile, the solvent is removed by gravitational draining and solvent evaporation and the condensation reactions occur as well. Finally, the result from all of the process becomes a solid film. This method has many advantage for example less equipment and less expensive. Nevertheless, the main advantage that is different from chemical vapor deposition and sputtering method is the modification microstructure of the thin film. G. Rajesh et al (2013) [14] has been successfully deposited CZTS thin film by simple dip coating method. From the results, the films are smooth, compact and dense film including to suitable for thin film solar cells, as shown in figure 2.6.

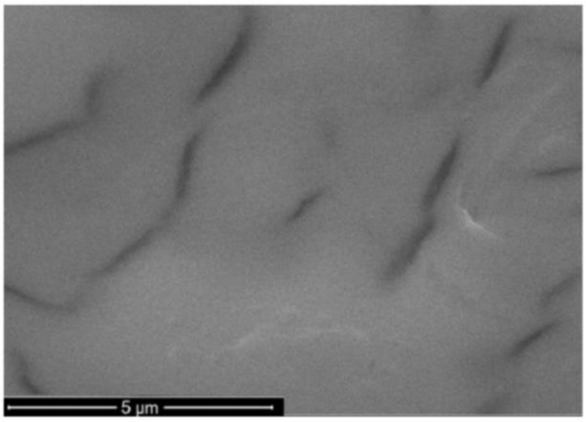

Figure 2.5 (a) Top-view SEM micrograph shows that the surface morphology of the dip-coated film is smooth, and the film is compact and dense in nature [14]

3. Doctor-blade

Doctor-blade coating is the fabrication film of small or large scale on rigid or flexible substrates. Doctor-blade method is used extensively in various process. For lab scale process, the blade is moved over a flat substrate. On the other hand, the blade is fixed over the substrate moving for the large scale, as shown in figure 2.7. In the process, the film thickness is controlled by gap length from the blade to the substrate. For example, Chen Qin-Miao et al. (2012) prepared CZTS films for low-cost solar cell by doctor-blade. The band gap of doctor-bladed CZTS thin film is around 1.41 eV and this film is used for absorber layer of CZTS thin film solar cell. The solar cell for this paper is composed of fluorine-doped tin oxide glass/TiO_2/In_2S_3/Cu_2ZnSnS_4/Mo which this is superstrate structure. The power conversion efficiency of CZTS solar cell by doctor-blade method is 0.55%.

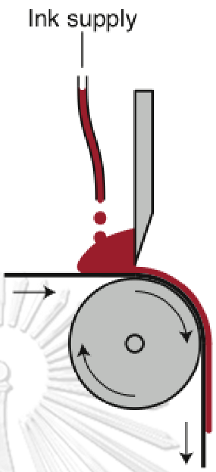

Figure 2.6 The schematic illustration shows the principle of doctor blading for large scale [15].

4. Spin coating

Spin coating is a common method for coating the thin films on substrate. This method is fast and simple; moreover, spin coating can produce very smooth and uniform film. An apparatus of spin coating is a spin coater. For common process, the precursor is dropped on the substrate that is contacted on the spin coater. Then spin coater rotates at high speed in order to spread the precursor by centrifugal force. Finally, the thin film is dried by airflow or baking, as shown in figure 2.8. Generally, the density and thickness of film depends on the speed of spinning and the viscosity of the precursor.

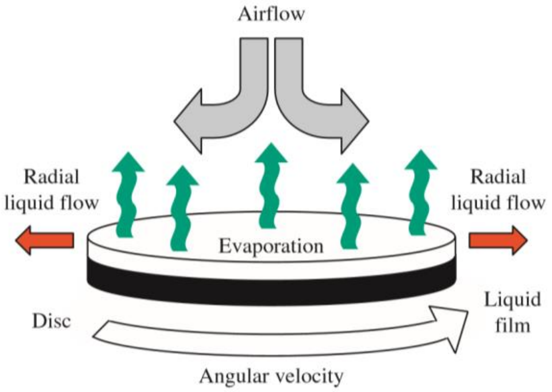

Figure 2.7 The Schematic illustration shows operation of the spin coating [16].

Due to aforementioned advantages, it is not surprising that many researchers pay attention to this method for coating absorber of thin film solar cell. For example, Manjeet et al (2015) [11] used spin coated method for depositing CZTS solution on Mo substrates. The efficiency of CZTS thin film solar cells are about 0.75 ± 0.43% to 2.03 ± 0.40% depending on the thickness of CZTS film. At same time, G.L. Agawan et al (2015) produced fine quality CZTS thin film solar cell and this thin film solar cell was prepared by non-toxic. The CZTS film of this solar cell is compact and dense, as shown in figure 2.9. The CZTS films were coated on the Mo substrates and annealed at 575 °C. The solar cell for this paper is composed of SLG/Mo/CZTS/CdS/i-ZnO/AZO/Al grid. The solar cell showed power conversion efficiency of 3.01% [17].

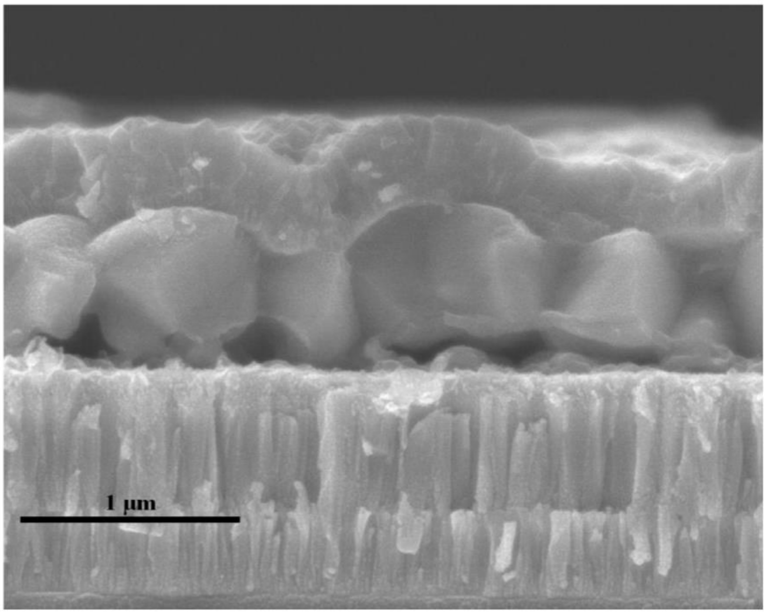

Figure 2.8 The cross-sectional FE-SEM image of a 3.01% CZTS solar cell [17].

5. Convective deposition

Convective deposition is one of the non-vacuum processes that is novel and noticeable. Moreover, this method takes less time-consuming, less precursor and inexpensive apparatus for fabrication. Moreover, convective deposition method can demolish limitation in other non-vacuum processes, such as production scale for spin coating and using a lot of precursor for dip coating and spin coating, etc. Therefore, this thesis pay attention to convective deposition method for fabricating CZTS thin films. In part of theory, these was explained in more information in section 2.9.

From aforementioned research, they show that non-vacuum processes show a similar performance compared to the vacuum processes. Furthermore, these require simple equipment and takes less time-consuming for fabrication. Table 2.1 summarizes the efficiencies obtained from the vacuum and non-vacuum processes

In addition to thin film deposition method, solvent is a factor that affects the morphology of CZTS films. Wei Wang et al (2013) [18] reported the world record of CZTSe solar cells with efficiency of 12.6% by using hydrazine as the solvent. Nevertheless, hydrazine can be explosive, very toxic and carcinogenic. From this reason, many research have studied the effect of solvent or non-toxic solvent. The lowest toxic solvent of CZTS is the ethanol-water that has efficiency of 5.29% by pre-annealing temperature at 350 °C [19]. Moreover, some researches use non-toxic 2-methoxyethanol for preparing precursor solution of CZTS. Manjeet et al. (2015) [11] use 2-methoxyethanol as solvent of CZTS that results in 2.03 ± 0.40% efficient CZTS solar cell. Although the efficiency of CZTS thin film solar cells that use non-toxic solvent are lower than that obtained from hydrazine solvent, non-toxic solvent can be adjusted for the better efficiency.

Table 2-1 Selection of CZTS solar cell devices with power conversion efficiency.

Process	Researcher	Method	Annealing temperature (ºC)	Efficiency (%)	Year	Addition	Ref.
Vacuum	Tsukasa Washio	Chemical vapor deposition	520-560	6.03	2012		[20]
	Tara P.Dhakal	Sputtering	525	6.2	2013	Without anti-reflection	[21]
	Jonathan J. Scragg	Sputtering	560	7.9	2013	Using TiN for back contact interface	[7]
	Byungha Shin	Thermal evaporation	570	8.4	2013		[9]
	Myeng G. Gang	Sputtering	580	5.1	2015		[22]
Non-vacuum	Lian Guo	Electrodeposition	550-590	7.3	2012		[23]
	EP Subramaniam	Chemical bath deposition	350	1.34	2014	FTO substrate	[24]
	Na Kyoung Youn	Spin coating	525	1.74	2015		[12]
	M. Singh	Spin coating	250	2.03	2015	Non-toxic	[11]
	G.L. Agawane	Spin coating	575	3.01	2015		[17]

2.9 Convective deposition method

Convective deposition method can be an alternative approach to solve aforementioned issues, because this method is carried out under ambient condition and requires simple equipment. In addition, this method takes less time-consuming and inexpensive apparatus for fabrication. Furthermore, this process is proper for large scale by using few volume of precursor for fabrication. Principally, convective deposition has been used to fabricate a monolayer film from colloidal or nanoparticles [5]. The equipment consists of a deposition blade of about 10 μm above the substrate and the translation stage at the bottom. A microliter of precursor solution is injected between the deposition blade and substrate and then the substrate on the stage is pulled in the horizontal axis with a controllable speed. A meniscus of the solution occurs between a substrate and a blade at a certain speed forming a thin film of solution on the substrate [5]. This method comprises two dominated regimes of the film deposition for explanation about thickness in terms of the deposition speed, which can be explained in figure 2.10 [22]. The first regime is evaporation regime which occurs at low speed condition. At low speed deposition, two physical processes occur simultaneously. First is the coffee ring effect, where a pattern is left by a puddle of particle-laden liquid. The convective flow to the edge is generated by the evaporation losses and left only aggregated thin film on the substrate. Secondly, the cheerio effect occurs which is the capillary attraction between particles on the liquid interface that are drawn to each other and forming into a close packed structure, as a result of the minimization of energy [6]. As a consequence, the film thickness increases with decreasing deposition speed. The second regime is called “Landau-Levich regime” that matches with all this thesis experiment. This regime is found at high speed deposition of more than 500 μm/s. For this regime, the solution film is dragged out by viscous forces and the solvent evaporates later in the process [22]. In terms of the effect of high deposition speed on film thickness, more particles in the bulk precursor solution are dragged along the convective line towards the settled particles due to a higher drag force, as shown in figure 2.11. As a result, thicker CZTS layer is obtained owing to more dragged particles. Besides the deposition speed of convective deposition method, there are also other parameters which affect the physical and chemical properties of thin film, for example volume of precursor solution, concentration of solution, and etc. The obtained thin films are expected to have different morphologies (e.g. compact films and porous films) and structures depending mainly on the deposition conditions.

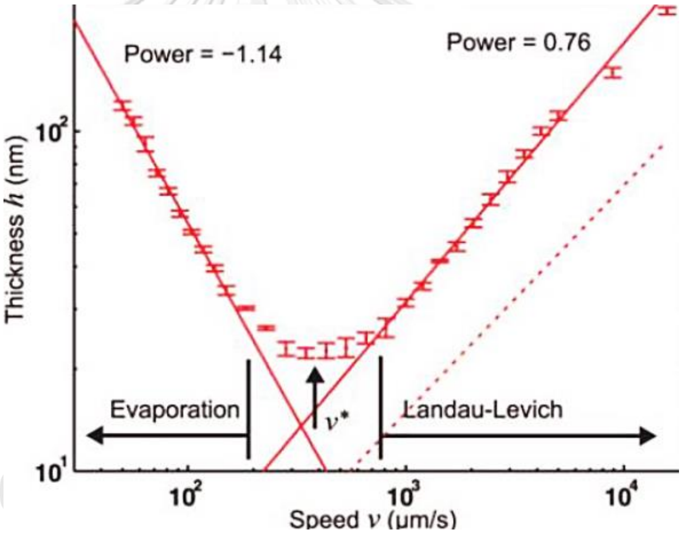

Figure 2.9 The film thickness as a function of deposition speed at two regimes [22].

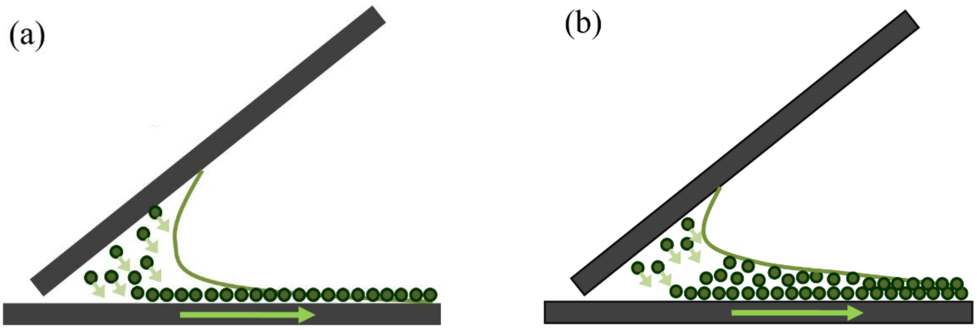

Figure 2.10 Comparison of film formation by convective deposition method in high speed regime at (a) a higher deposition speed (b) a lower deposition speed.

2.10 Porous CZTS thin film solar cells

In general, many thin film materials deposited by various solution-based deposition techniques are compact and uniform. However, in some deposition conditions the morphology of the films could be in a porous form which could be attributed to the operating conditions. For morphology-controlled deposition of CZTS thin films in particular, Si-nae Park et al. (2015) [25] compared the spin-coated CZTS film with the sputtered CZTS film in term of morphology, size of grains and device efficiency. Spin-coated CZTS thin films show porous and rough surface thin film; moreover, the films contain many nanopores. The nanoporous morphology is occurred by the removal of thiourea and metal chlorides at different rates during pre-annealing process. The nanograins size of spin-coated films which were sulfurizated at 540 °C resulted in tiny nanograins below 100 nm, while the film sulfurizated at 570 °C resulted in larger sizes of about 300-500 nm, as shown in figure 2.12. On the other hand, sputtered CZTS thin film shows a dense thin film with large grains above 1 μm, as shown in figure 2.12. As a results, nanoporous CZTS solar cells sulfurized at 540 °C show cell efficiency of 5.02%, which is superior to sputtered CZTS solar cell and nanoporous solar cells sulfurized at 570 °C [25]. Moreover, Pendcheng Dai et al (2012) [26] also prepared CZTS thin films in porous structure, as shown in figure 2.13. They revealed that the obtained porous morphology of the films have low reflectivity which can be a good light absorber. They applied the porous CZTS thin film as a p-type material in dye-sensitized solar cells (DSSCs) instead of platinum. DSSCs that use porous CZTS thin film increased the efficiency of 7% compared to the traditional DSSCs [26].

According to previous studies, it can be seen that various different morphologies of CZTS thin films have a strong influence on the performance in many applications. Therefore, the operating conditions associated with the convective deposition method is of importance in this study.

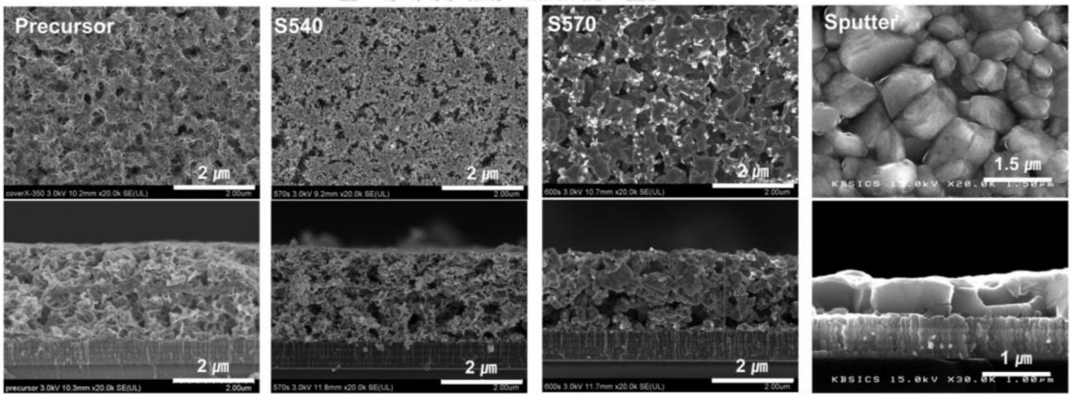

Figure 2.11 Surface and cross-sectional SEM images of solution-processed precursor film, CZTS films sulfurized at 540 and 570 °C, and CZTS films prepared from sputtering process, respectively [25].

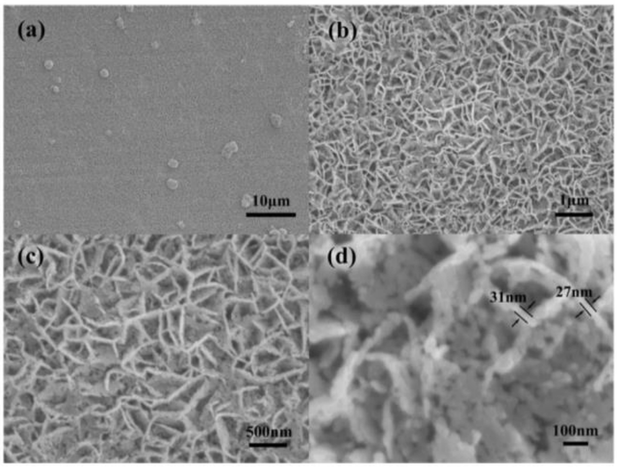

Figure 2.12 SEM images of the porous CZTS thin film at different magnifications [26].

2.11 Effect of deposition parameters on morphology of CZTS thin film

2.11.1 Deposition method

From figure 2.12, Si-nae Park et al (2015) showed CZTS films that were prepared from different deposition methods, i.e. spin coating and sputtering. The spin-coated CZTS films have porous and rough surface morphology, as shown in figure 2.12. Many nanopores occurred as a result of removal of thiourea or metal chlorides at different rates during high temperature pre-annealing and annealing process. On the other hand, the sputtered CZTS film shows a dense film structure with large grains above 1 μm.

2.11.2. Type of solvent used for CZTS precursor

One of the important factors that affect morphology of thin films is the type of solvent used to dissolve precursors. V Gohel et al. (2017) [27] showed the effect of type of solvent for fabrication the CZTS thin films on FTO glass by spin coating method. In this research, they used Dimethyl sulfoxide (DMSO), Isopropyl alcohol (IPA), Ethylene glycol (EG) and Propylene glycol (PG) as solvents of CZTS sol-gel. The obtained surface morphologies of thin films prepared from the different solvents are shown in figure 2.14.

According to the figures, different solvents make particles form into various shapes and sizes of nanoparticles, such as roped shape with minor void by using DMSO, DNA type connected with void by using IPA, flower shape with some agglomerated nanoparticles by using EG, and dense film by using PG, etc. [27]. From this study, the CZTS thin film using PG as a solvent is the best condition for thin film solar cells and has power conversion efficiency of 3.02% [27].

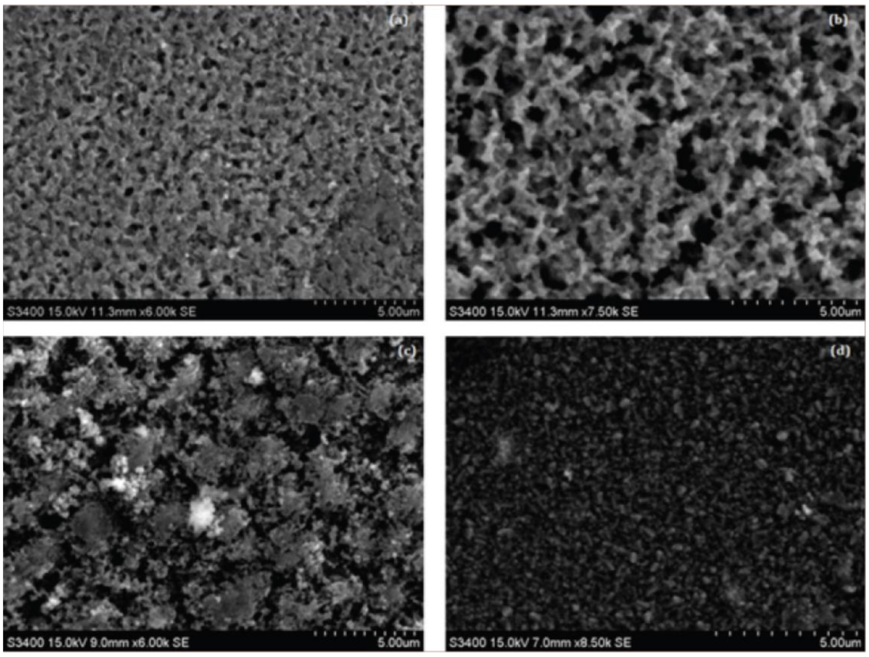

Figure 2.13 SEM micrographs of CZTS films deposited on FTO glass substrates prepared using different solvents (a) Dimethyl sulfoxide (b) Isopropyl alcohol (c) Ethylene glycol and (d) Propylene glycol [27].

2.11.3. Deposition speed for convective deposition technique

Deposition speed strongly affects the film thickness, which were studied by Maël Le Berre et al. (2009) [22] and previously described. They found two regimes of deposition speed which affects the variation in film thickness. Moreover, they also showed the relationship of thickness (h) and deposition speed (v) of both regimes to be $h \propto V^{\propto}$ with $\propto$ = -1.1 and 0.76 for low speed and high speed regimes, respectively.

2.11.4. Annealing temperature

Many researches have pointed out that annealing temperature significantly affects morphology, crystallinity, gran size and porosity of CZTS thin film, which consequently affects, the power conversion efficiency. For example, G.L. Agawane et al (2015) [17] fabricated CZTS thin films on Mo coated SLGs by spin coating and used three different annealing temperature 525, 550 and 575 °C under H_2S gas atmosphere. This work studied the effect of annealing temperature on the morphological, structural, chemical, compositional, optical and photovoltaic properties of the CZTS thin films. From XRD results in figure 2.15, the as-deposited thin film has low peak intensity than annealed films, which show crystallinity increase during annealing. For CZTS annealed at 575 °C the secondary phase at 32.02° of SnS_2 was observed. In figure 2.16, the plane and cross-sectional FE-SEM images of as-deposited, annealed at 525, 550 and 575 °C show the morphology of thin films that significantly improved with the increase of annealing temperature. Moreover, the thickness of the film slightly decreases by the evaporation of organic solvent when the annealing temperature increases. In figure 2.16 (d), the large and sharp tretragonal CZTS thin film is shown which correspond to XRD result.

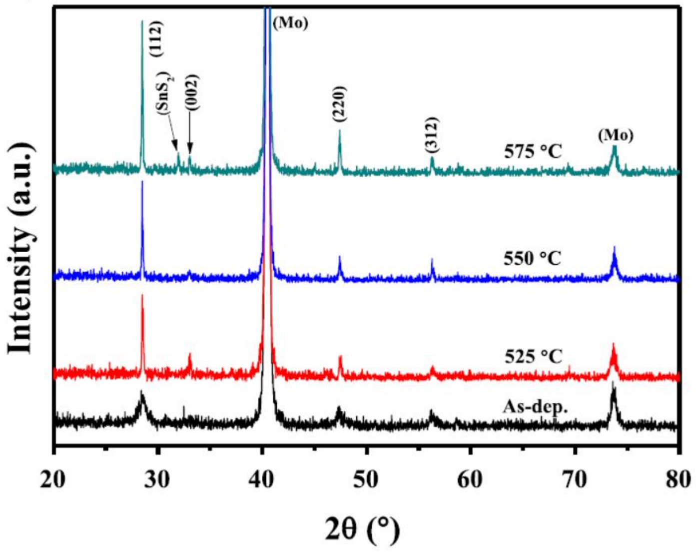

Figure 2.14 XRD results of CZTS thin film as-deposited, annealed at 525, 550 and 575 °C [17].

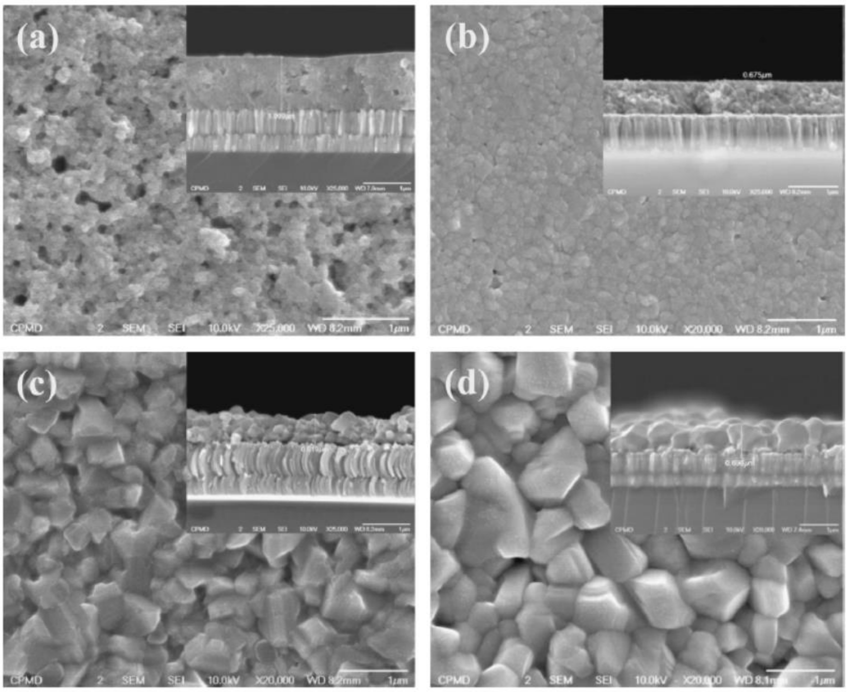

Figure 2.15 FE-SEM micrographs of CZTS films deposited on Mo (a) as-deposited (b) annealed at 525 (c) 550 and (d) 575 °C [17].

Chapter 3

PROCEDURES

3.1 Preparation of CZTS precursor solution

3.1.1 Materials

1. Copper (II) chloride ($CuCl_2·2H_2O$) from Ajax Finechem Pty Ltd.
2. Zinc (II) chloride ($ZnCl_2$) from Ajax Finechem Pty Ltd.
3. Tin (II) chloride ($SnCl_2·2H_2O$) from Ajax Finechem Pty Ltd.
4. Thiourea ($SC(NH_2)_2$) was from HiMedia Laboratories
5. 2-methoxyethanol
6. Deionized water
7. Triethanolamine (TEA)

3.1.2 Synthesis of CZTS precursor

All chemicals for preparation of CZTS precursor solution were of analytical grade and were purchased from Ajax Finechem Pty Ltd. except for thiourea ($SC(NH_2)_2$) from HiMedia Laboratories. The method for preparation of CZTS precursor is described as follows. Firstly, zinc (II) chloride 0.005 mol is added into 6-20 ml of 2-methoxyethanol as solvent. Similarly, tin (II) chloride 0.005 mol is added into 0-14 ml of DI water as solvent. The solutions are stirred and heated at 50 °C for 5 minutes on the hot plate. After that the two solutions are mixed together. Next, 0.01 mol of copper (II) chloride ($CuCl_2·2H_2O$) and 0.04 mol of thiourea ($SC(NH_2)_2$) are added into the mixed solution prepared earlier. Finally, triethanolamine (TEA) as a stabilizer of about 10 drops are dropped into the solution and is stirred at 50 °C for 30 minutes. For the high fraction of DIW as solvent, the solution was removed large particle by syringe filter at 0.45 μm of pore size.

3.2 Fabrication of CZTS thin films on molybdenum (Mo) coated glass

3.2.1 Experimental apparatus

1. DC magnetron sputtering

This apparatus operates under Argon atmosphere at 6x10^{-3} mbar with the DC sputtering power of 550 Watts and the 99.99% pure Mo is used as a sputtering target with the distance from the substrate holder about 7 centimeters.

2. Convective deposition

The convective deposition has been used to fabricate a monolayer film from colloidal or nanoparticles. The equipment consists of a deposition blade above the substrate and the translation stage at the bottom. 20 microliter of precursor solution is injected between the deposition blade and substrate and then the substrate on the stage is pulled in the horizontal axis with a controllable speed.

3. RF magnetron sputtering

This apparatus operates under Argon atmosphere at 6x10^{-3} mbar with the sputtering power of 80 Watts and 220 watt for i-ZnO and ZnO (Al) layers, respectively.

3.2.2 Experimental procedures

1. Substrate cleaning

- Soak the 3×3 cm^2 soda lime glasses in the dish washing detergent for 24 hours.
- Rub the SLGs with a wet soapy cellulose sponge.
- Put the SLGs in ultrasonic bath with a mixture of micro-90 and DI water at 60 °C for 1 hour.
- Put the SLGs in ultrasonic bath with DI water for 15 minutes.
- Soak the SLGs in chromic acid (H_2CrO_4) for 1 hour.
- Put the SLGs in ultrasonic bath with DI water for 15 minutes.

- Blow dry the SLGs with nitrogen gas 99.999%.

- Keep the SLGs in a dry and clean cabinet.

2. Deposit Mo film on the SLGs using the 99.99% pure of Mo target by DC magnetron sputtering under Argon atmosphere at 6×10^{-3} mbar for 11 minutes.

3. Deposit the precursor solution of CZTS on Mo coated substrates at varying speeds of 500-1250 μm/s by convective deposition.

4. Dry the coated film on a hotplate at 200 ºC for 5 minutes to remove the solvent from the film.

5. The coating and drying process is repeated for 6 -15 times.

6. Anneal the film in a nitrogen atmosphere at 550 ºC for 30 minutes.

7. Deposit CdS thin film on CZTS layer by chemical bath deposition (CBD) at 65 ºC for 15 minutes.

8. Deposit i-ZnO layer on the film obtained from step 7 by RF magnetron sputtering by using the ZnO ceramic (2-inch in diameter) target under Argon atmosphere at 6×10^{-3} mbar with the sputtering power of 80 Watt for 11 minutes. Then, the samples were also deposited with ZnO (Al) window layer by the RF magnetron sputtering power of 220 watt for 17 minutes.

9. Deposit Al grids by thermal evaporation through a shadow mask at the base pressure of 5.0×10^{-6}-1.0×10^{-5} mbar.

3.3 Analytical instruments

3.3.1 Viscometer

The CZTS solutions as prepared for convective deposition are measured the viscosity in order to explain the thickness of CZTS thin film by Viscometer (Brookfield RVDV-II+PRO).

3.3.2 X-Ray Diffraction (XRD)

Crystal structure and phase formation of the CZTS thin films is analyzed by X-Ray Diffraction (XRD; Bruker AXS, model D8 advance). The XRD analysis is operated at 5°/min of scan speed with 40 kV operating voltage and 30 mA current that uses a Cukα radiation source.

3.4.3 Scanning Electron Microscope (SEM)

The morphology and structure of CZTS films deposited on Mo substrates is investigated under various deposition parameters *via* FE-SEM with EDS (Hitachi SU8230). Moreover, cross-sectional images are obtained from SEM to identify the thickness of CZTS film.

3.4.4 Energy dispersive X-ray spectroscopy (EDS)

The chemical composition of the CZTS films is determined by Energy dispersive X-ray spectroscopy (Hitachi SU8230).

3.4.5 UV-VIS spectrophotometer

A UV–Vis Spectrophotometer (Shimadzu UV-2600) is used for the measurement of the optical property in term of band gap of the films in the wavelength ranging from 400 to 1100 nm.

3.4.6 Solar Simulator

Power conversion efficiency (PCE) and fill factor (FF) are measured by using current–voltage (J-V) measurement system under AM 1.5 and 0.1 Watt/cm^2 irradiance at 25°C that consists of the xenon light source (Yamashita Denso model YSS-80A), the DC power supply and a voltage source/current measurement unit (Keithley model 237).

3.4.7 ImageJ software

The porosity of films was measured by ImageJ software. The threshold and analyze mode were used for finding porous area and calculating percent area, respectively. The results were presented in percent area of porous area.

Chapter 4

Results and discussion

4.1 Synthesis of CZTS thin films

4.1.1 The elemental and chemical composition of CZTS thin film

The chemical composition of CZTS film has been intensively studied because the composition can be adjusted to be near the ideal stoichiometry for certain applications. In this study, the stoichiometric composition of CZTS film was detected by EDS. Table 4.1 shows the atomic percentage of Cu:Zn:Sn:S in CZTS films that were prepared using different solvents. From the results, all of the films prepared from different fractions of solvents revealed that the elemental compositions were rather close to 2:1:1:4. However, sulfur compositions were slightly deficient due to high temperature in the annealing process. The film which was prepared using 2-methoxyethanol 30: DIW 70 as the solvent contained a pronounced deficit of sulfur. This behavior could be attributed to the fact that when using this fraction of solvent, metal precursors could not be completely dissolved in the solvent, therefore prior to the deposition, the precursor solution needed to be filtered. For this reason, some of the sulfur component could be lost during that stage. It could also be observed that the composition of CZTS film using 2-methoxyethanol 70: DIW 30 as the solvent has the chemical composition closest to the ideal stoichiometric value of 2:1:1:4.

Solvents	Cu	Zn	Sn	S	total
2-methox 100: DIW 0	24.89	13.42	9.30	52.39	100
2-methox 70: DIW 30	22.46	13.74	14.16	49.64	100
2-methox 30: DIW 70	34.29	20.72	14.69	30.31	100

Table 4.1 Atomic percentages of CZTS thin films synthesized by different solvents.

4.1.2 The morphology and structure of CZTS films

4.1.2.1 Effect of the fraction of solvents and types of solvents

1. Film thickness

- The effect of particle formation

In many previous studies, researches on the CZTS synthesis by other solution-based processes have reported the effect of solvents on the formation of CZTS compound that resulted in different morphologies and sizes of CZTS nanoparticles in the film. In this work using convective deposition method, the effect of types of solvents were also investigated. Figure 4.1 presents obviously different CZTS morphologies of CZTS thin films which were prepared by various solvents. It can be observed that the films deposited from different fractions of solvents resulted in different morphologies and porosity in the films, which could significantly be attributed to the nature of solvents. The film prepared from 2-methoxyethanol 30: DIW 70 as solvent is compact, as shown in figure 4.1 (c), as the mixture of solvents with higher fraction of water can bring particles closer together during deposition process because the structure of particles are aggregated particles. Furthermore, the films obtained from this condition have lower thickness than those obtained from the solvents with higher fractions of 2-methoxyethanol at any deposition speeds, as shown in table 4.2. On the other hand, the CZTS film of 2-methoxyethanol 100: DIW 0 and 2-methoxyethanol 70: DIW 30 were in gauze structure so the particles could not aggregate with each other effectively, as shown in figure 4.1 (a-b), respectively. As a result, the CZTS films that were prepared from high fraction of 2-methoxyethanol provided higher thickness. The result of thickness in this study corresponds in all of the deposition speeds, as shown in table 4.2. It was noted that the film thickness in this study was evaluated from cross-sectional SEM images of the obtained films deposited for 6 times by convective deposition method.

Solvents	Avg. thickness Speed 500 μm/s	Avg. thickness Speed 750 μm/s	Avg. thickness Speed 1000 μm/s	Avg. thickness Speed 1250 μm/s
2-methox 100: DIW 0	579 nm	710 nm	829 nm	1175 nm
2-methox 70: DIW 30	286 nm	382 nm	695 nm	751 nm
2-methox 30: DIW 70	213 nm	307 nm	349 nm	428 nm

Table 4.2 The thicknesses of samples were fabricated using different solvents and deposition.

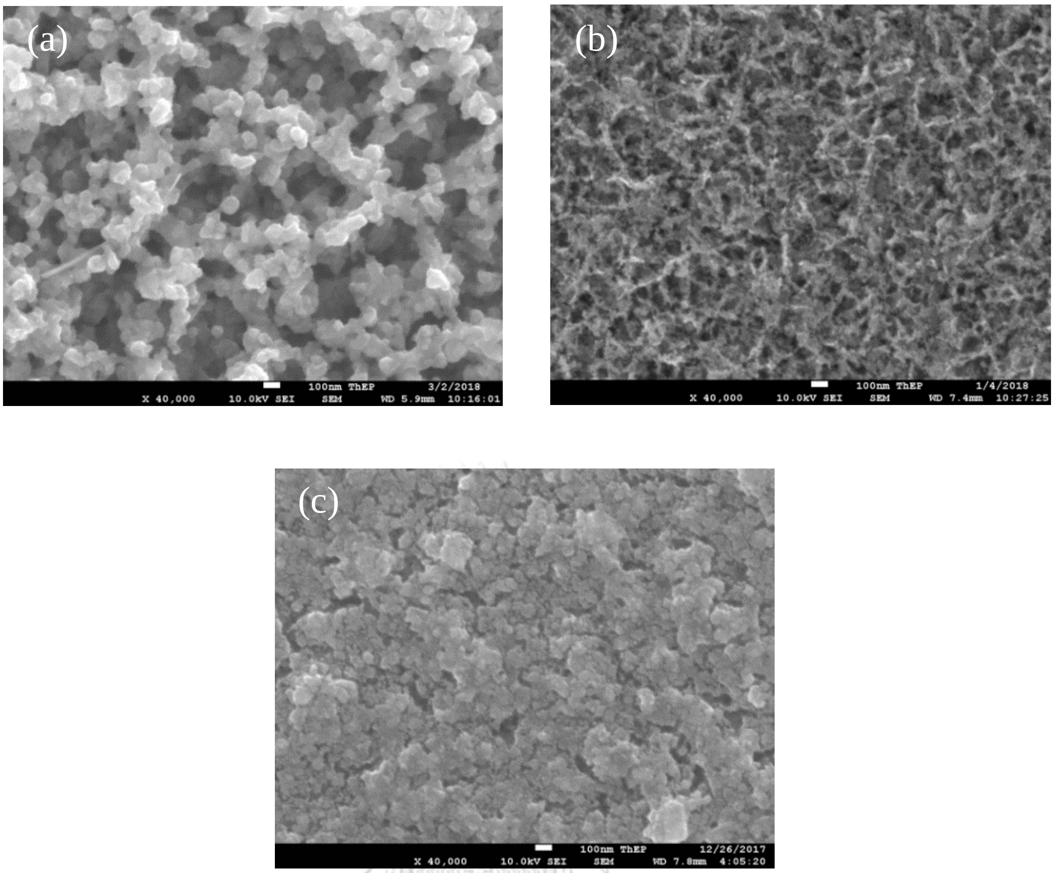

Figure 4.1 Comparison of the 6 layers annealed CZTS thin film prepared using deposition speed at 1250 µm/s with different fractions of solvents (a) 2-methoxyethanol 100: DIW 0, (b) 2-methoxyethanol 70: DIW 30, and (c) 2-methoxyethanol 30: DIW 70 on Mo substrate.

- Effect on viscosity of solution

To investigate the effect of different fractions of solvents in another aspect, the viscosity of the resulting solution prepared from different fractions were measured using the viscometer, as shown in table 4.3. The CZTS solutions were mixed and heated at 50 ˚C which were used for deposition. The viscosity of the solvent prepared from 2-methoxyethanol 100: DIW 0 as the solvent is greater than that prepared from 2-methoxyethanol 30: DIW 70 as the solvent. This result also corresponded to the observation from the experiment prior to the deposition. It can be confirmed that effect of the solvents resulted in variation in viscosity of the solution which could lead to variation in nanoparticle formation and morphology of the films. Moreover, the viscosity also affected the thickness of CZTS films since the deposition speed range studied in this thesis is in Landau-Levich regime that correspond to the Newton's Law of Viscosity. The relationship of viscosity and thickness is explained in the following.

Solvents	Viscosity (cP)
2-methox 100: DIW 0	1.8 ± 0.2
2-methox 30: DIW 70	1.4 ± 0.2

Table 4.3 The viscosity of CZTS solutions in various solvents were fabricated on the Mo substrate.

From the results in table 4.2, a higher deposition speed resulting in thicker CZTS films was a result of the viscosity of the solution. Firstly, the viscosity is the physical property that defines the flow resistance of fluid. The viscosity is the constant of fluid that is the proportionality of shear stress and the velocity, as shown in equation 4.1. From the equation, the viscosity corresponds to shear stress so the solution that has the high viscosity has also high shear stress during blade moving. The shear stress is the quantity of force per area that can change the fluid shape with the force direction. Since in the convective deposition process the meniscus of the high viscosity fluid of 2-methoxyethanol 100: DIW 0 was stretched along the surface on the blade direction rather than the low viscosity 2-methoxyethanol 30: DIW 70 due to higher shear stress of fluid, as shown in figure 2.11. On the other hand, the low viscosity fluid that was used for convective deposition is accumulated against the blade during blade moving. Since the low viscosity of fluid slightly affected the shear stress and slightly changed the fluid shape when compare to pure 2-methoxyethanol as solvent. Therefore, the high viscosity fluid created the thicker film due to high shear stress that made the quantity of CZTS against the blade decreased. Conversely, the solution on the substrate was increased due to stretching of solution against the blade. In the conclusion, the viscosity also very less affected the thickness of CZTS films when compares to the effect of deposition speed that was explained in the next part.

Newton's Law of Viscosity

$$\tau = \mu \frac{du}{dy} \qquad \text{(Eq. 4. 1)}$$

μ = Dynamic viscosity (Pas)

τ = Shear stress = F/A (N/m^2)

$\frac{du}{dy}$ = Rate of shear deformation (m^2/s)

2. The porosity of films

As previously seen in figure 4.1, the solvents used in the sol-gel process had an effect on the formation of gauze structure and porosity in the films. Since types of solvent influence on size and structure, composition, rate of condensation, rate of evaporation and capillary pressure of the precursor solution used for convective deposition method, this is the reason why this factor strongly caused the porosity in CZTS thin film. Previously, many researches had extensively described about the formation of porous CZTS films that were mainly caused from the annealing process at high temperature, in which different elements decomposed at different rates. Nonetheless, the results obtained in this work have shown differently. When the CZTS films were deposited on Mo substrate for 1 layer using 2-methoxyethanol 100: DIW 0 as the solvent at different deposition speeds ranging from 500-1250 μm/s, the surface morphology of the films before annealing were characterized by SEM. As shown in figure 4.2 (a-d), all the films deposited at any speed exhibit the porous structure which had emerged prior to the annealing process. Therefore, the formation of porosity in CZTS films by convective deposition method was likely affected by the type of solvents used that correspond to figure 4.3. The TEM figure 4.3 (a) shows the connected particle and gauze structure of irregular shaped CZTS particle during as solution by using 2-methoxyethanol 100: DIW 0 as the solvent that highly ensure the cause of porous of film from gauze structure apart from the annealing process at high temperature. Moreover, the CZTS particles that were prepared by using 2-methoxyethanol 30: DIW 70 as the solvent are circular shape and small size, as shown in figure 4.3 (b). This particle have tendency to close pack and form to be compact film.

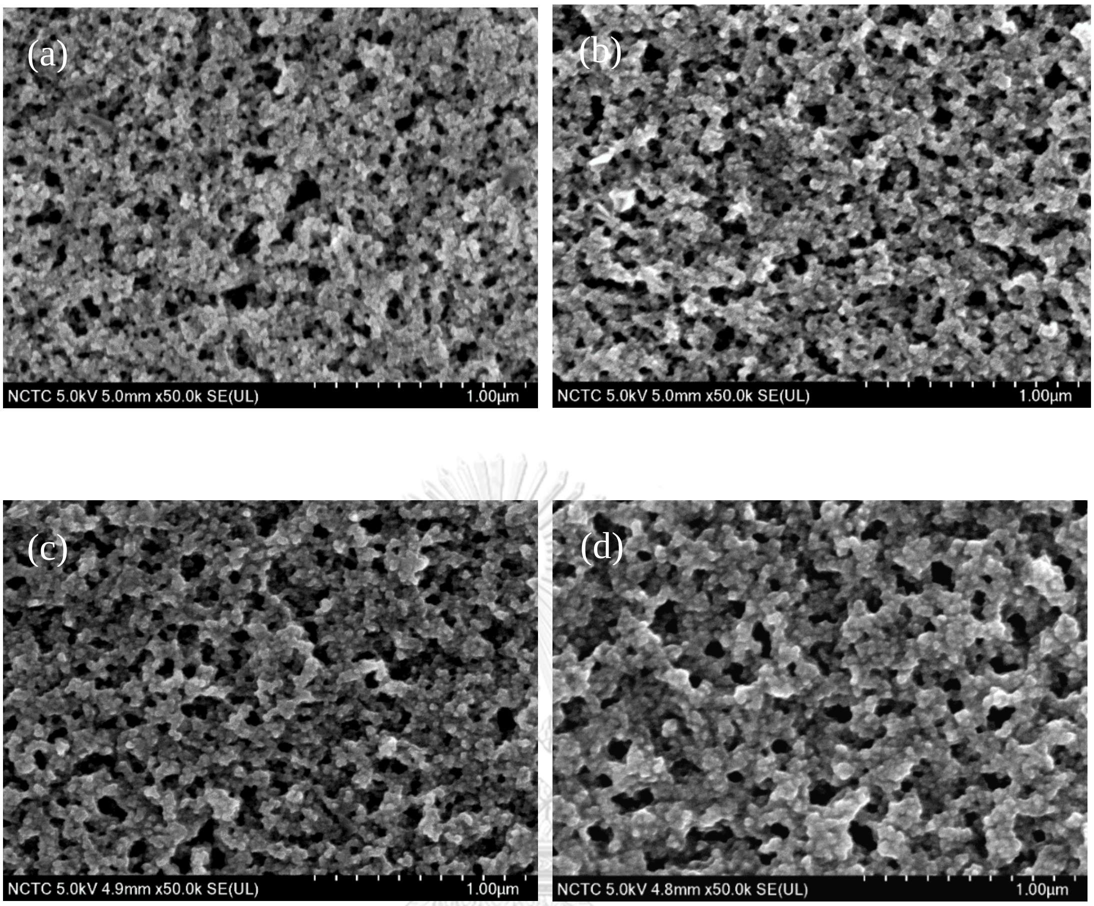

Figure 4.2 SEM micrographs of CZTS thin films deposited for 1 layer at deposition speed of (a) 500, (b) 750, (c) 1000 and (d) 1250 μm/s on Mo substrates after baking at 200 °C for 5 minutes.

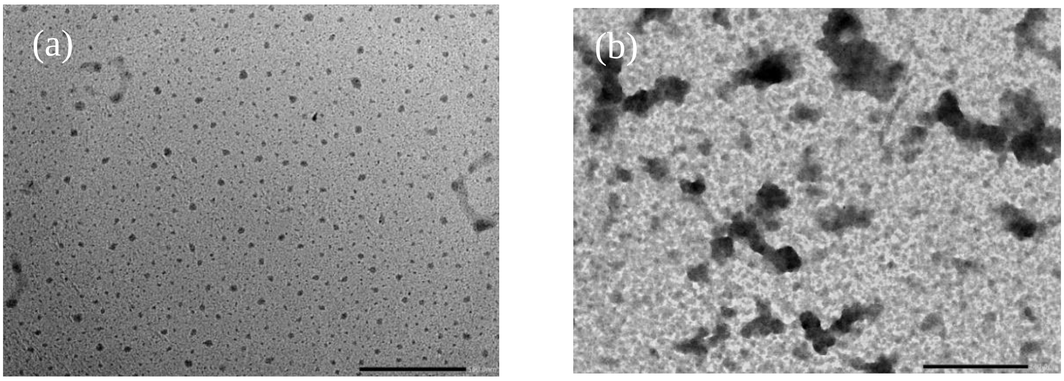

Figure 4.3 (a) and (b) TEM micrographs of CZTS solution prepared 2-methoxyethanol 100: DIW 0 as solvent after baking at 100 ˚C for 5 minutes.

- The effect of chemical structure

According to the obtained results, the morphology of CZTS film prepared from 2-methoxyethanol 30: DIW 70 as the solvent consisted of bulky and compact particles because large amount of DI water has a high tendency to occur a complete hydrolysis reaction, as shown in equation 2.2. Afterwards, the metal hydroxide product from equation 2.2 can readily react together at hydroxide position in the polymerization reaction owing to much hydroxide position in each molecule of metal hydroxide. As a result, the polymers have larger size and the monomer can connect closer to decrease porosity of CZTS thin film. In contrast, the morphology of CZTS film prepared from 2-methoxyethanol 70: DIW 30 consisted of smaller sizes of particles as a result of decreasing amount of DI water as the solvent that influence to hydrolysis reaction. The behavior is also similar to the reaction of using 2-methoxyethanol 100: DIW 0 as the solvent. In this case, the reaction occurs which follows equation 2.7-2.9. The particles are smaller than the particles of 2-methoxyethanol 30: DIW 70 as solvent, because in polymerization the monomer cannot connect in many directions like polymer of 2-methoxyethanol 30: DIW 70 as solvent, as shown in figure 4.2.

- The effect of boiling point of solvent

The films prepared from high fraction of DIW at any speed were smooth and compact, as shown in figure 4.1(c). Whereas, the films prepared from higher fraction of 2-methoxyethanol consist of voids. This is significantly attributed to the type of solvent, where 2-methoxyethanol has a higher solvent boiling point compared to DIW. Therefore, during the deposition by convective deposition method, the as-prepared solution with 2-methoxyethanol tends to evaporate slower than DIW, leaving a remaining solution above the monolayer of CZTS film. Moreover, the evaporation rates of different solvents are not equal. As a result, there is more room for particles within the remaining volume of solution above the monolayer of CZTS to relocate until they are settled and locked to each other by capillary force on the surface. Thus, a larger volume of remaining solution above the monolayer could result in a porous film. Conversely, the sol-gel precursor that has higher DIW fraction of solvent results in a denser film. This is attributed to a lower volume (less space) above the monolayer of CZTS, as a consequence of a higher evaporation rate; therefore, particles tend to draw to each other more compactly.

4.1.2.2 The effect of the deposition speed

1. Film thickness

From the aforementioned, the Newton's Law of viscosity equation is a relationship of the viscosity, shear stress and velocity, as shown in equation 4.1. The equation has been used for understanding the effect of the deposition speed on the thickness of the films in the Landau-Levich regime, where the high velocity of deposition results in increasing shear stress. In addition, shear stress also affects the thickness of the film, in which higher shear stress results in thicker film, as previously explained in the section of the effect of the fraction of solvents and types of solvent on film thickness. Since, the shear stress can be interpreted as the flux of x-momentum in the positive y direction and the flux means flow per unit area. In order to determine the thickness of CZTS films, cross-sectional images were obtained from SEM to determine the thickness of CZTS film that was deposited 6 times by convective deposition method. According to table 4.2, film thickness vs. deposition speed from different fractions of solvents (2-methoxyethanol 30: DIW 70, 2-methoxyethanol 70: DIW 30 and 2-methoxyethanol 100: DIW 0) could be plotted as shown in figure 4.4-4.6, respectively. From the results, thicker films were obtained at higher deposition speed. Furthermore, all of the graphs demonstrate a linear trend in log scale graphs. Therefore, in order to obtain the desired film thickness of CZTS deposited by convective deposition method, deposition speed could be predicted to apply for deposition from the tendency shown on the graphs.

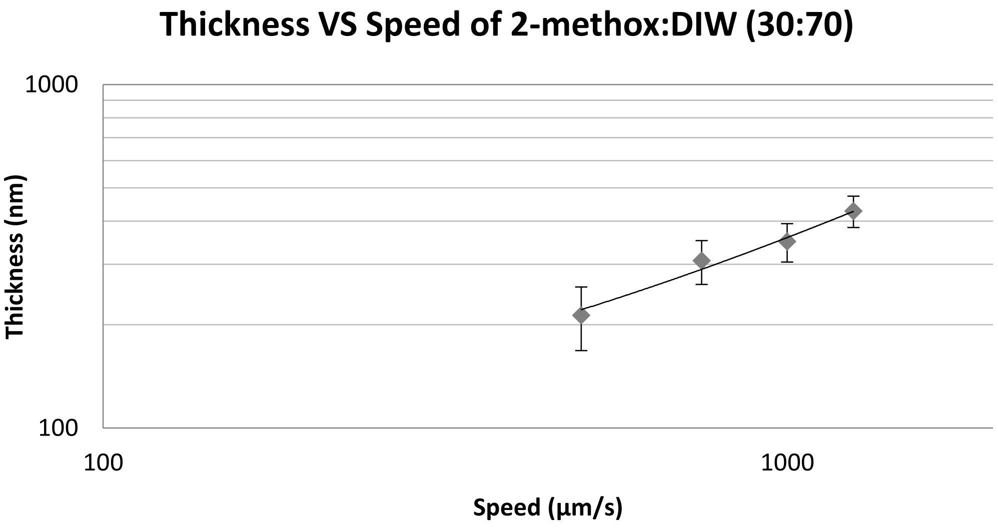

Figure 4.4 Relationship of CZTS film thickness and deposition speed (prepared from 2-methoxyethanol 30: DIW 70 as solvent).

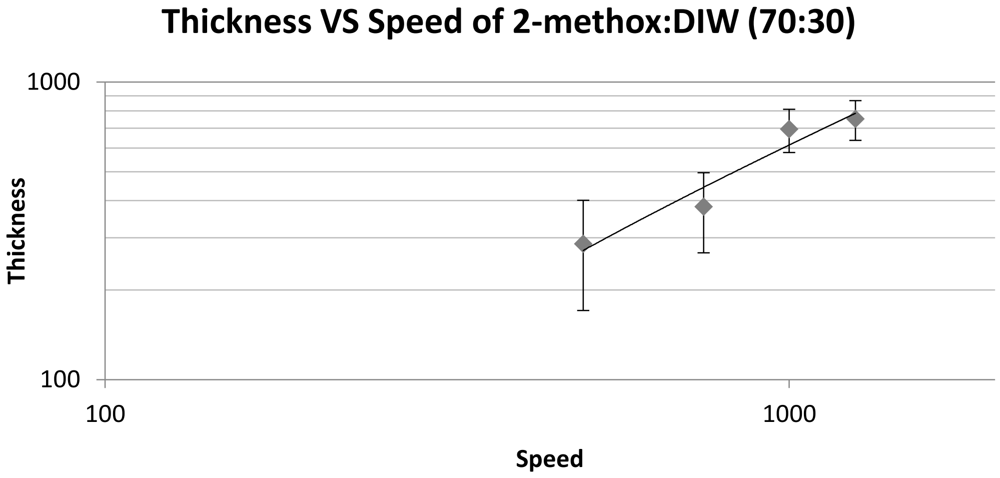

Figure 4.5 Relationship of CZTS film thickness and deposition speed (prepared from 2-methoxyethanol 70: DIW 30 as solvent).

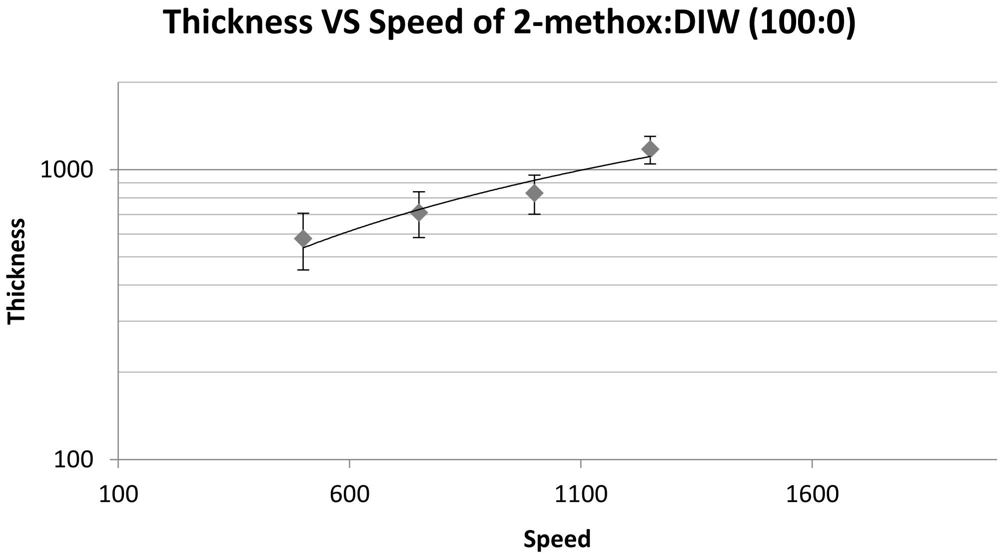

Figure 4.6 Relationship of CZTS film thickness and deposition speed (prepared from 2-methoxyethanol 100: DIW 0 as solvent).

2. The porosity of films

For some of the solution-based deposition methods e.g. spin coating, dip coating and convective deposition, evaporation is one of the important factors that induces the porous formation in the film. Film formation deposited by convective deposition method, in particular, was believed to be affected by deposition speed. As the substrate is pulled away from the blade, particles from the bulk solution move toward the edge to form a film. Therefore, at low deposition speed particles have more time to draw to each other to form a compact film before evaporation of the solvent occurs. Figure 4.7 (a-d) demonstrate surface morphologies of CZTS films prepared from 2-methoxyethanol 100: DIW 0 as the solvent at various deposition speeds ranging from 500-1250 µm/s. It can be seen that figure 4.7(c-d), which are the films deposited at lower deposition speeds, While those in figure 4.7(a-b), deposited at higher deposition speeds, present porous structure on the surface. Moreover, it could be observed that particle size of the film prepared at lower deposition speed was bigger than those prepared at higher speed. It could be because of the fact that particles had more time for continuous growth of CZTS particle during film depositing. In order to evaluate the porosity formation of the films obtained from different deposition speeds, the porous area from SEM micrographs present in figure 4.7 (a-d) was measured and compared with the total area. Therefore, the porosity was reported in percentage, as shown in table 4.4. From the table 4.4, the percentage of the porosity increases with increasing deposition speed, as expected.

For the CZTS films prepared from other different fractions of solvents, i.e. 2-methoxyethanol 70: DIW 30 and 2-methoxyethanol 30: DIW 70, the results are represented in figure 4.8 (a)-(d) and figure 4.9 (a)-(d), respectively. It can be clearly seen that different morphologies were obtained as a result of variation in deposition speed. As shown in figure 4.8(a-d), the morphologies of films are in gauze structure and particles are smaller than CZTS thin film prepared by using 2-methoxyethanol 100: DIW 0 as the solvent.

Moreover, the film was more compact when the deposition speed was decreased, which shows a similar trend. Similarly, the morphologies of CZTS films prepared by using 2-methoxyethanol 30: DIW 70 as the solvent, shown in figure 4.9 (a-d), also show a similar trend where compact film was obtained at lower deposition speed. More pinholes were observed from the film deposited at higher speed. In conclusion, any fraction of solvents used for CZTS film deposition in this thesis correspond to the relationship of the porosity of CZTS films and deposition speed. In terms of applying CZTS film as an absorber layer in thin film solar cell, compact film and large particles are preferred. For this reason, in the next step, CZTS films were prepared using very low deposition speed, outside the range studied previously, in order to attain the compact film and large particle that is proper for solar cell application.

Percent of the porous area at speed 500 μm/s	Percent of the porous area at speed 750 μm/s	Percent of the porous area at speed 1000 μm/s	Percent of the porous area at speed 1250 μm/s
14.988	25.623	34.347	44.236

Table 4.4 The percent of the porous area of CZTS film of 2-metthox: DIW (100: 0) as solvent at deposition speed 1250, 1000, 750 and 500 μm/s

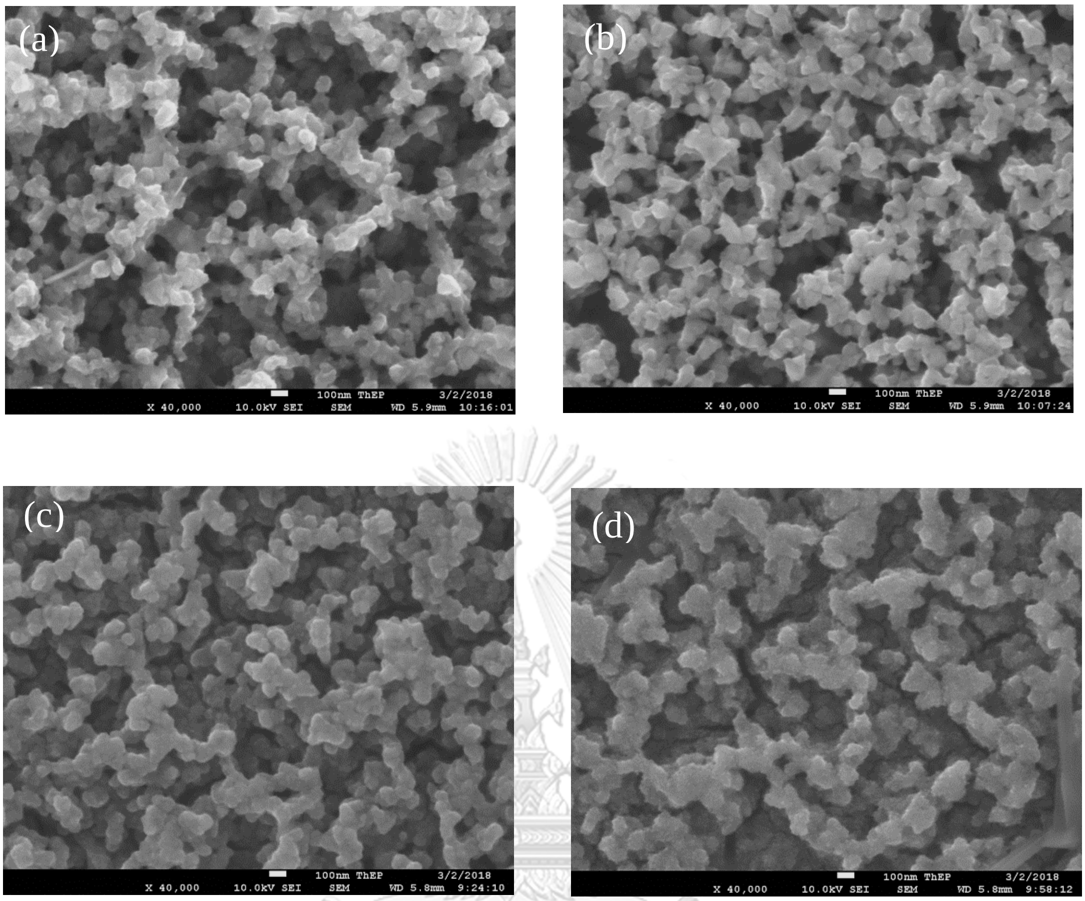

Figure 4.7 (a)-(d) SEM micrographs of 6 layers annealed CZTS films deposited on Mo substrates prepared by using 2-methoxyethanol 100: DIW 0 as the solvent at different deposition speeds as follows; (a) 1250 µm/s, (b) 1000 µm/s, (d) 750 µm/s and (d) 500 µm/s.

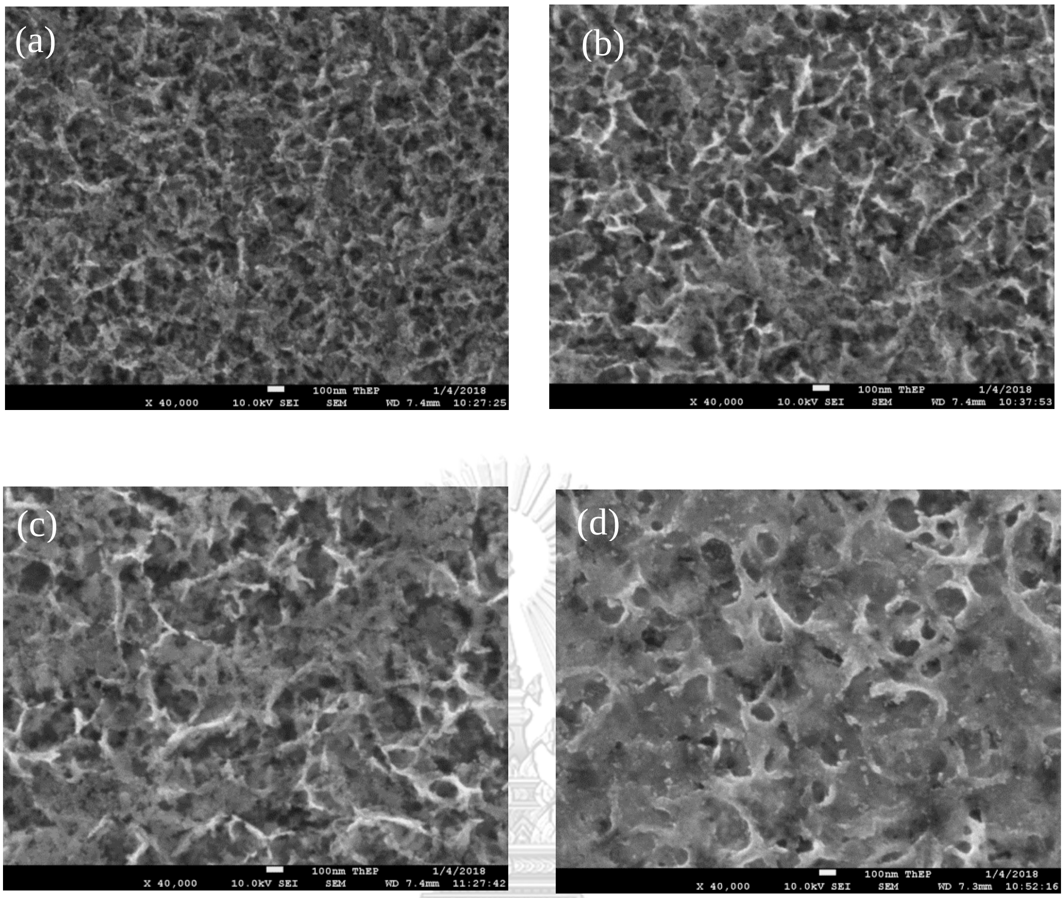

Figure 4.8 (a)-(d) SEM micrographs of 6 layers annealed CZTS films deposited on Mo substrates prepared by using 2-methoxyethanol 70: DIW 30 as the solvent at different deposition speeds as follows; (a) 1250 μm/s, (b) 1000 μm/s, (d) 750 μm/s and (d) 500 μm/s.

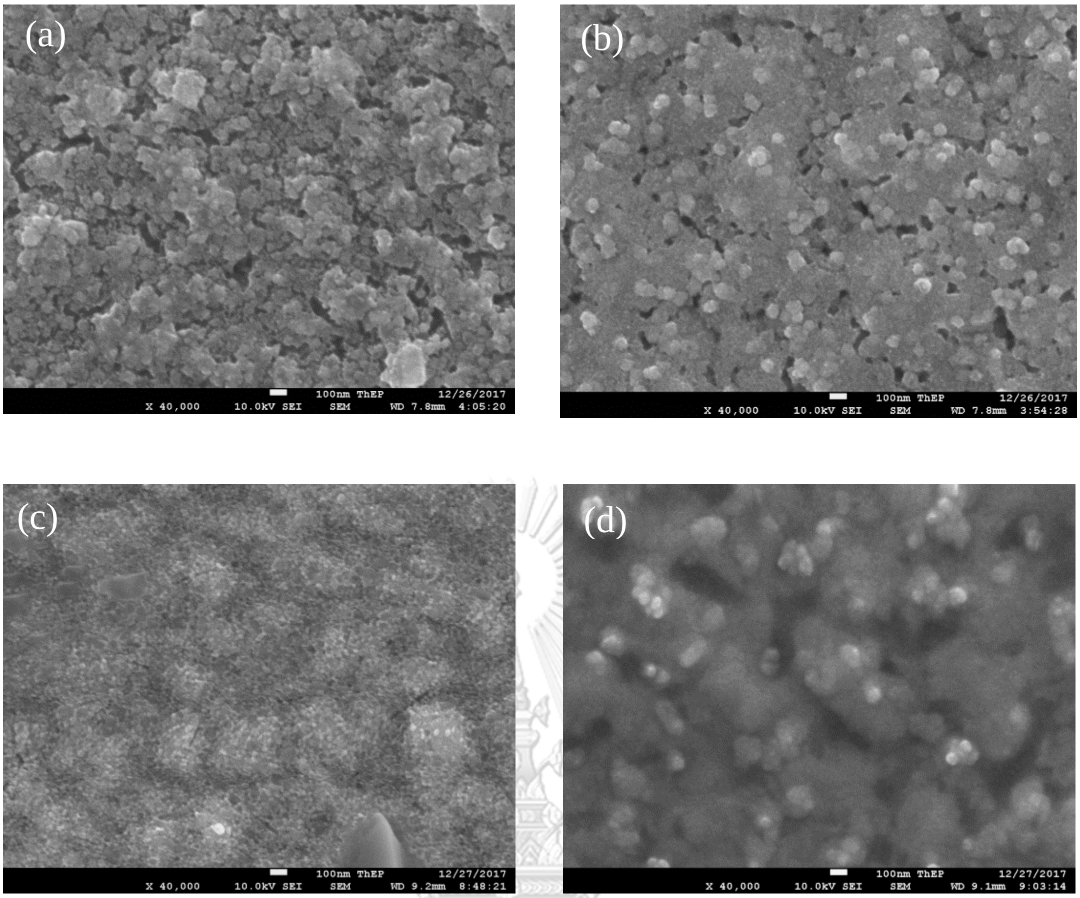

Figure 4.9 (a)-(d) SEM micrographs of 6 layers annealed CZTS films deposited on Mo substrates prepared by using 2-methoxyethanol 70: DIW 30 as the solvent at different deposition speeds as follows; (a) 1250 μm/s, (b) 1000 μm/s, (d) 750 μm/s and (d) 500 μm/s.

According to the obtained results, the low deposition speed provided the compact film and large particles, therefore low deposition speeds at 50 and 100 μm/s were used for preparation of CZTS films for 1 layer (by using 2-methoxyethanol 100: DIW 0 as the solvent). SEM micrographs of as-deposited CZTS films (before annealing) were used to characterize the film morphology, as shown in figure 4.10. As a result, both CZTS films prepared at 50 and 100 μm/s were more compact when compared with the CZTS films prepared at high speed, which were previously reported in figure 4.1. Based on the obtained results, the film prepared at deposition speed of 100 μm/s was more compact than that prepared at 50 μm/s. Thus, CZTS film prepared at 100 μm/s will be used for solar cell assembly in the next section.

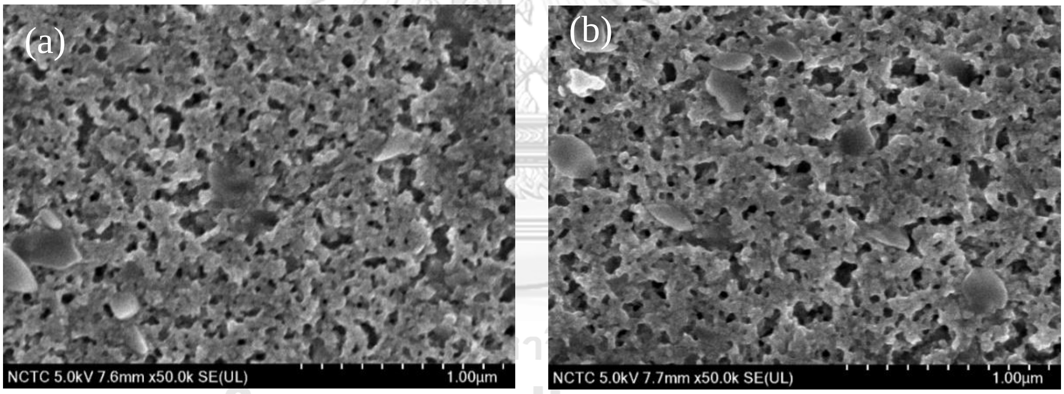

Figure 4.10 SEM micrographs of 1 layers of as-deposited CZTS films deposited on Mo substrates prepared by using 2-methoxyethanol 100: DIW 0 as the solvent at deposition speed of (a) 50 μm/s and (b) 100 μm/s.

4.1.3 The crystal structure and phase formation of the CZTS thin films

The crystal structure of CZTS films prepared by convective deposition method using different types of solvents was investigated by XRD and the results are shown in Fig. 4.11. The kesterite structure of CZTS was detected in these synthesized samples, which were obtained from different solvent fractions of 2-methoxyethanol: deionized water (DIW) as follows: 100:0, 70:30 and 30:70. The diffraction peaks occurring at 2θ = 28.449°, 32.970°, 47.314° and 56.117° are assigned to (112), (200), (220) and (200) planes of kesterite structure of CZTS (JCPDS 26-0575), respectively. In addition, other peaks at 2θ = 28.449°, and 56.117° could be assigned to (002) and (312) of wurtzite structure, respectively. Accordingly, the peaks at 2θ = 40.212° and 73.541° correspond to the diffraction of (110) and (211) planes of Mo. It can be observed that CZTS films deposited on Mo substrates, as shown in Figs. 4.11 (b-d), exhibit slightly higher crystallinity than that deposited on glass substrate, as shown in Fig. 4.11 (a). This could be attributed to a well lattice matching of CZTS with Mo, compared to CZTS and glass substrate. Moreover, CZTS films prepared using various fractions of solvents do not show much difference in the intensity.

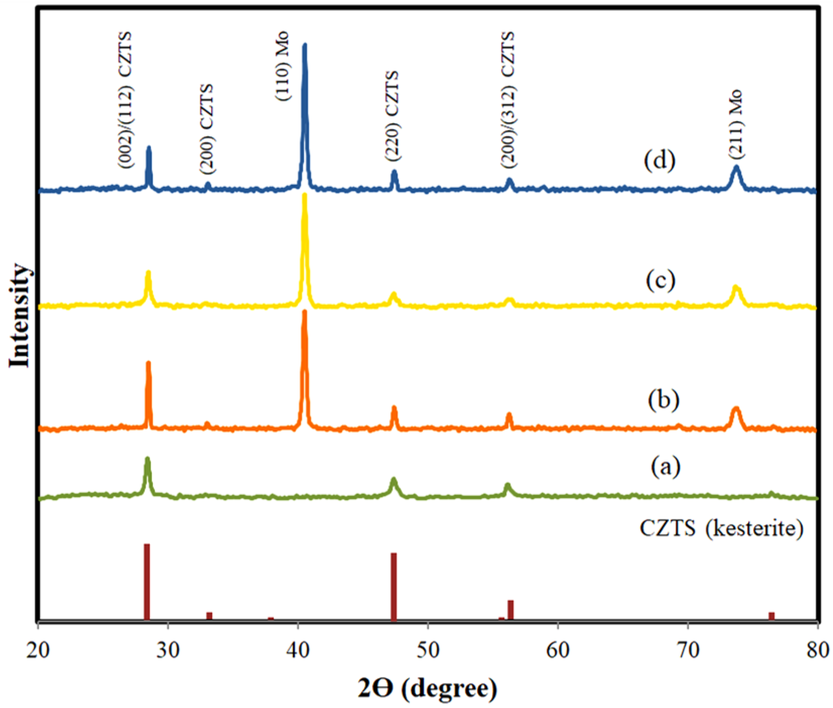

Figure 4.11 XRD pattern of the CZTS prepared using different fractions of solvents (a) 2-methoxyethanol 100: DIW 0 on glass slide, (b) 2-methoxyethanol 100: DIW 0 on Mo substrate, (c) 2-methoxyethanol 70: DIW 30 on Mo substrate, and (d) 2-methoxyethanol 30: DIW 70 on Mo substrate.

4.1.4 The UV-vis absorption spectrum and energy band gap of CZTS film

From figure 4.12, the CZTS thin films that were prepared by different solvent fraction between 2-methoxyethanol and DI water at 100:0, 70:30, 50:50 and 30:70 were measured reflectivity by UV–Vis Spectrophotometer (Shimadzu UV-2600). Moreover, the reflectivity of CZTS films were compared with the reflectivity of Mo substrate in order to show ability of spectra absorption of CZTS thin films. The Mo substrate's reflectivity is higher than 50% in the wavelength range from 200 to 1400 nm whereas the CZTS thin films reflectivity is below 20%, which shows a strong light-trapping effect, as shown in figure 4.12. This reveals that CZTS film prepared by convective deposition method is suitable to be used as the absorber layer in thin film solar cells.

In Figure 4.13, the percent reflectivity of the CZTS thin films that were prepared by using 2-methoxyethanol 100: DIW 0 and 2-methoxyethanol 30: DIW 70 as the solvent were exhibited in wavelength (nm) versus percent reflectivity graph. The percentage of reflectivity of 2-methoxyethanol 30: DIW 70 CZTS thin film is obviously higher than CZTS thin film 2-methoxyethanol 100: DIW 0 in the range from 200 to 700 nm that are in the visible light spectrum. These mean CZTS film prepared from using 2-methoxyethanol 100: DIW 0 as the solvent had a little higher absorbance ability than that prepared from 2-methoxyethanol 30: DIW 70 as the solvent. In contrast, the reflectivity of the CZTS film prepared from 2-methoxyethanol 100: DIW 0 is higher than that from 2-methoxyethanol 30: DIW 70 in the short range of light spectra. Although, the reflectivity of the 2-methoxyethanol 100: DIW 0 CZTS thin film is lower than the 2-methoxyethanol 30: DIW 70 CZTS thin film in range 840 to 1160 nm, this wavelength range was not determined for applying in solar cell process. As a result, the 2-methoxyethanol 100: DIW 0 CZTS thin film can absorb the spectrum in sunlight better than the 2-methoxyethanol 30: DIW 70 CZTS thin film so the CZTS thin film 2-methoxyethanol 100: DIW 0 is proper for solar cell application in optical side. Not only CZTS thin films for solar application had to regard about optical property, but also these had to consider about the morphology and electrical property.

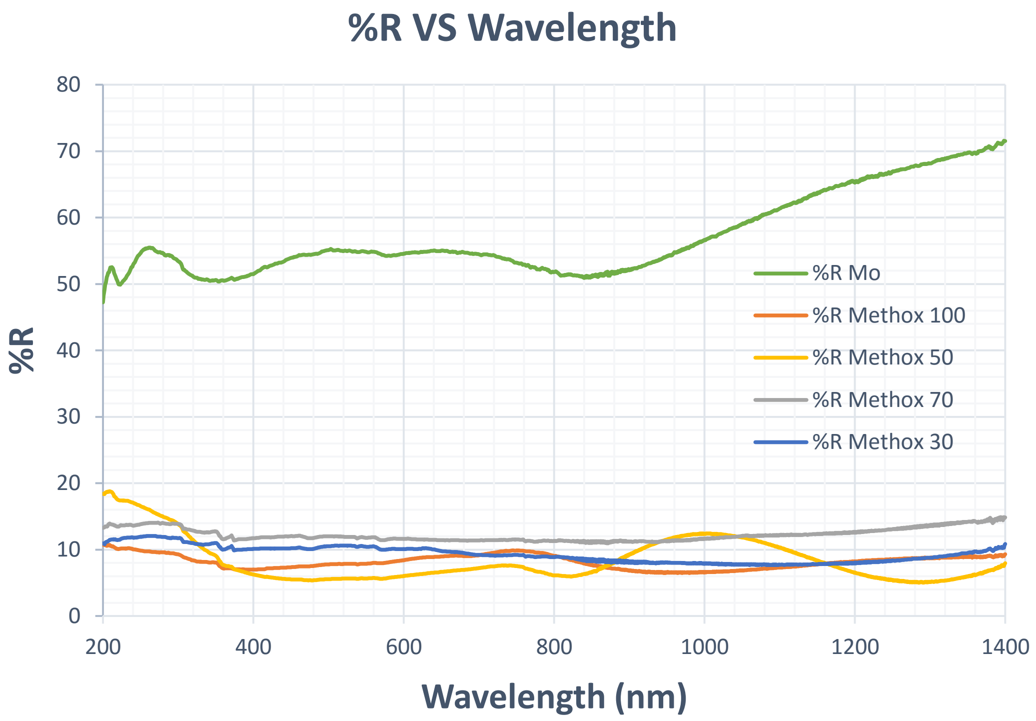

Figure 4.12 Reflectivity of CZTS thin films on Mo substrate prepared from using 2-methoxyethanol 100: DIW 0, 2-methoxyethanol 70: DIW 30, 2-methoxyethanol 50: DIW 50 and 2-methoxyethanol 30: DIW 70 as the solvent, and compared to the bare Mo substrate.

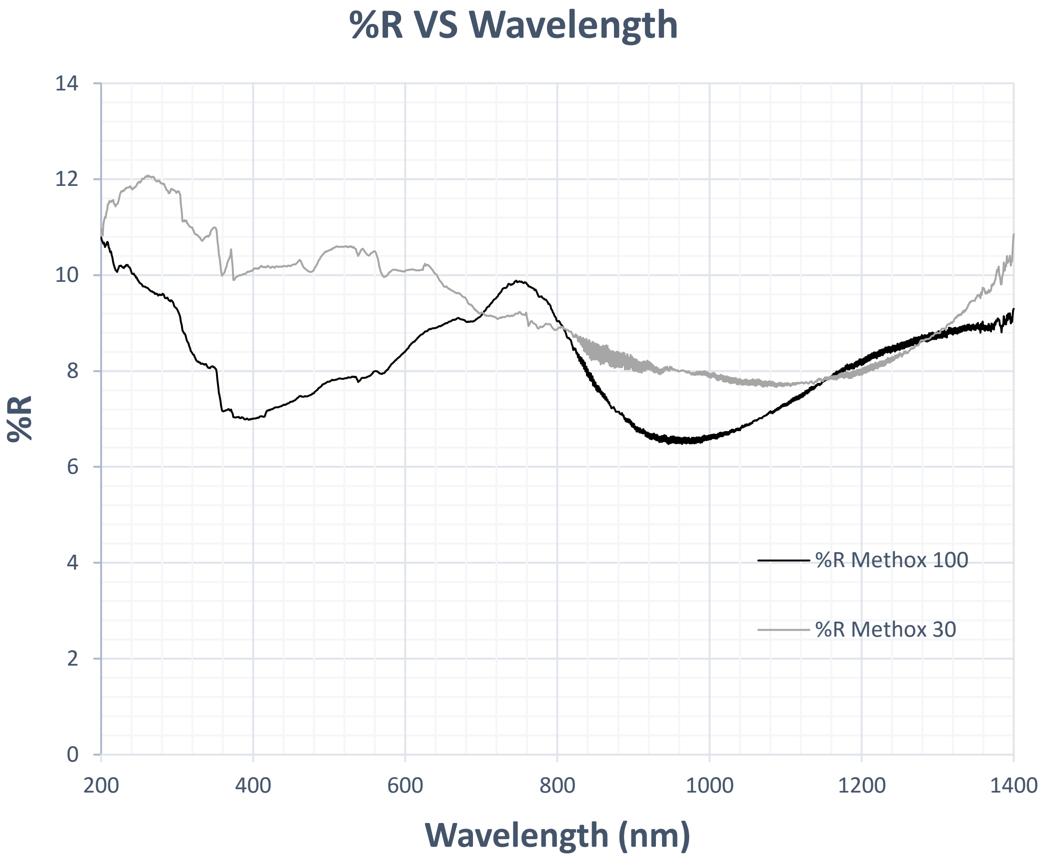

Figure 4.13 Reflectivity of porous and compact CZTS thin films prepared by using 2-methoxyethanol 100: DIW 0 2-methoxyethanol 30: DIW 70 as the solvent on Mo substrates.

In the part of optical transitions, the energy band gap was derived from using equation 4.2, as shown below.

$$(\alpha h\gamma)^2 = A(h\gamma - E_g) \qquad \text{(Eq. 4.2)}$$

The optical band gap of CZTS film prepared from pure 2-methoxyethanol as the solvent was derived by extrapolating the linear equation in $(\alpha h\gamma)^2$ versus $h\gamma$ graph, as shown in figure 4.14. The optical band gap energy exhibited 1.42 ± 0.2 eV for CZTS thin film. The band gap value from this calculation is similar to the band gap value obtained from other reports.

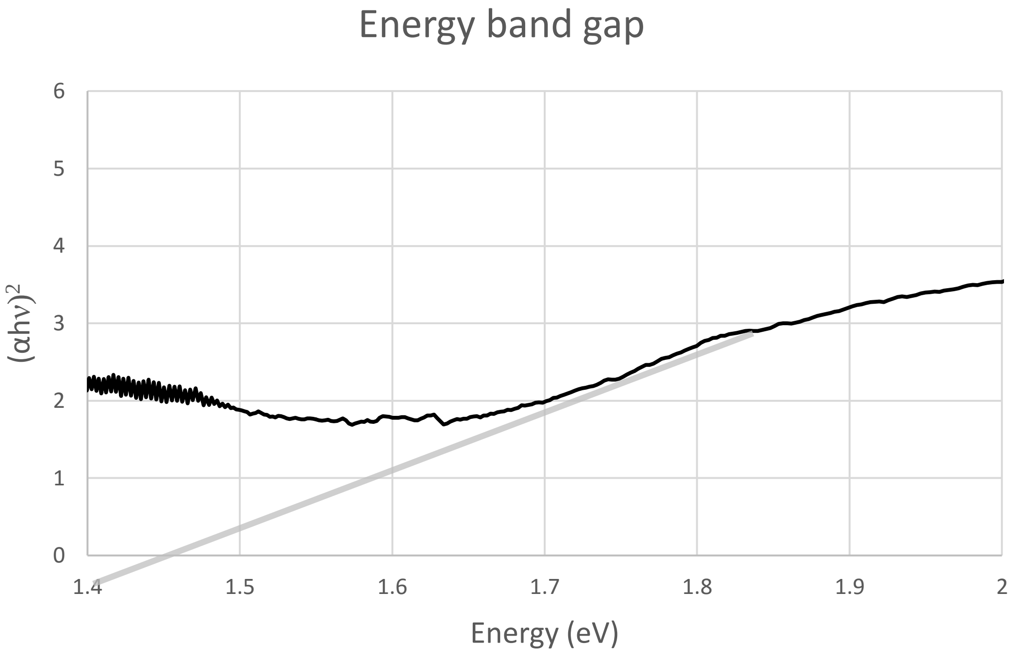

Figure 4.14 Band gap of CZTS thin film prepared by using 2-methoxyethanol 100: DIW 0 as the solvent on Mo substrate.

4.2 CZTS thin film solar cells

4.2.1 The electrical performance of CZTS thin film solar cells

CZTS solar cell is one of notable thin film solar cells since the material for producing is abundant, durable and non-toxic. On the other hand, CZTS thin films solar cell is no commercial solar cell its efficiency. Furthermore, the sophisticated equipment is used for deposited many thin films. Consequently, this thesis pay attention for the deposited method by using convective deposition method in order to deposit the CZTS thin films. As a result, the high DIW fraction of the solvent and deposition at low speed condition provide compact and big grains in the CZTS film. Consequently, this condition was used for preparation of the absorber layer in solar cell application. As aforementioned, CZTS thin film solar cells compose of many layers, for instance transparent conducting oxide (TCO), window layer (n-type material), absorber layer (p-type material) and metal back contact layer, as shown in figure 2.3. Each layer was deposited by various methods including equipment as follows;

1. Cleaning the SLG by 8 steps, as described in section 3.2.2
2. Depositing Mo on the cleaned SLG by DC magnetron sputtering
3. Depositing CZTS thin film by convective deposition

   This layer was paid attention and deeply studied in order to generate the effective CZTS solar cell.

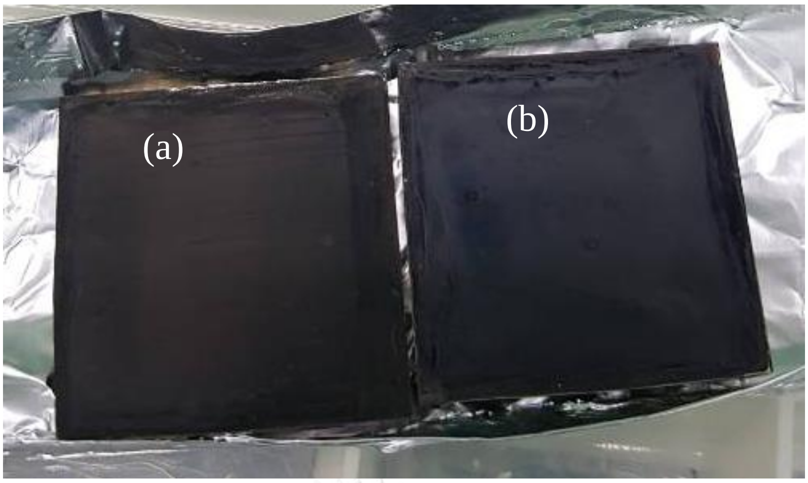

Figure 4.15 6 layers CZTS thin films deposited on Mo substrates by convective deposition by using (a) 2-methoxyethanol: DIW 100:0 at deposition speed 1106 μm/s and (b) 2-methoxyethanol: DIW 30:70 at deposition speed 3333 μm/s.

4. Depositing CdS thin film by chemical deposition

In order to generate CZTS solar cell, the Cds layer is used as n-type for P-N junction forming in CZTS thin film solar cell.

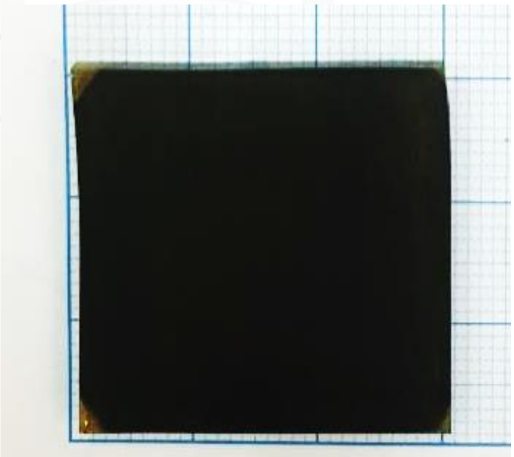

Figure 4.16 CdS thin film deposited on CZTS thin film by chemical bath deposition.

5. Depositing i-Zno thin film by RF sputtering

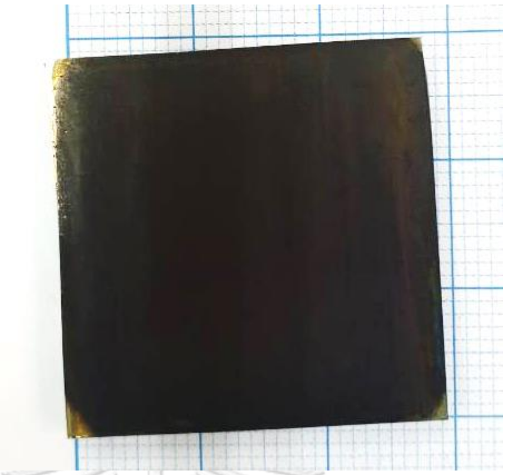

Figure 4.17 i-ZnO thin film deposited on the film obtained in figure 4.16 by RF sputtering.

6. Depositing ZnO (Al) thin film by sputtering

The ZnO (Al) thin film has function as n-type semiconductor.

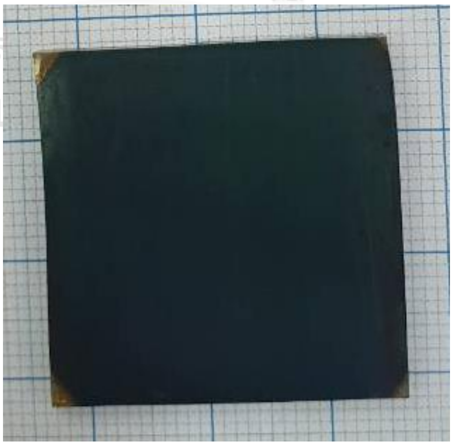

Figure 4.18 ZnO (Al) thin film deposited on the film obtained in figure 4.17 by DC magnetron sputtering.

7. Depositing Al grid by thermal evaporation

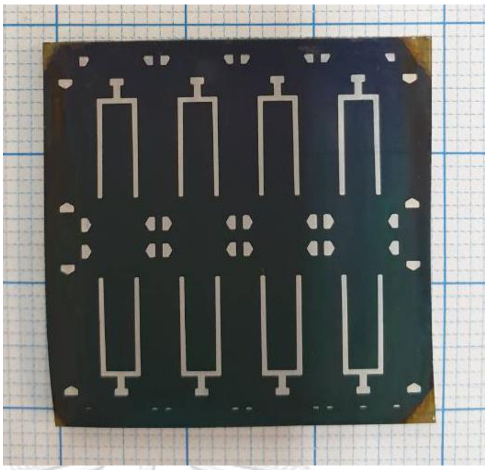

Figure 4.19 The full cell.

Following all above steps, the CSTZ thin film solar cells were slit in order to divide as a cell, as shown in figure 4.20. Next, the completed CZTS thin film solar cells were measured the efficiency by solar simulator. The solar simulator can measure short-circuit current density (J_{sc}), fill factor (FF), series resistance, shunt resistance, open-circuit voltage (V_{oc}) and power conversion efficiency (PCE) of solar cell. The results were shown in figure 4.21-4.24 and table 4.5. The figure 4.21-4.24 shows current-voltage (I-V) curves of CZTS solar cells at various condition. From the result 1, 2 and 3 in table 4.5, these are conditions that researcher expected the thickness of CZTS thin film about 1000 nm by varying speed deposition. The results shows the no efficiency for result 1 and 3. Furthermore, result 2 shows low power conversion efficiency that the efficiency was calculated from open-circuit voltage, short-circuit current density and fill factor. From the result 1, 2 and 3, the result 3 show power conversion efficiency so researcher chose to study 2-methox: DIW (70:30) as solvent by varying deposition speed in condition 4 and 5. In the result 4, researcher decreased the deposition speed from result 2 that researcher expected higher efficiency from result 2. Conversely, the result is unsatisfactory because the efficiency decrease from the result 2. Decreasing of the efficiency in result 4 causes of the decreasing of absorber layer thickness. Moreover, the result 5 for increasing deposition speed condition shows the efficiency that is alike result 2. Therefore, all of results make researcher paid attention on the deposition speed of absorber layer because deposition speed strongly affects to film morphology. Moreover, the thickness is one of the important factor to attain high efficiency thin film solar cell due to the life-time of electrons. From aforementioned, researcher considered the thickness and morphology in order to generate the CZTS thin film solar cell in condition 6. The result 6 presents outstanding efficiency from the others including V_{oc} and J_{sc}. As a results, J_{sc} has high value from the others because the electrons goodly transport in the compact film that attain from very slow deposition speed and high fraction of DIW as solvent. Therefore, researcher chose to used very slow deposition speed apart from studied deposition speed and used 2-methox: DIW (30:70) as solvent in condition 6 since researcher expect compact and smooth absorber film, as shown in figure 4.10.

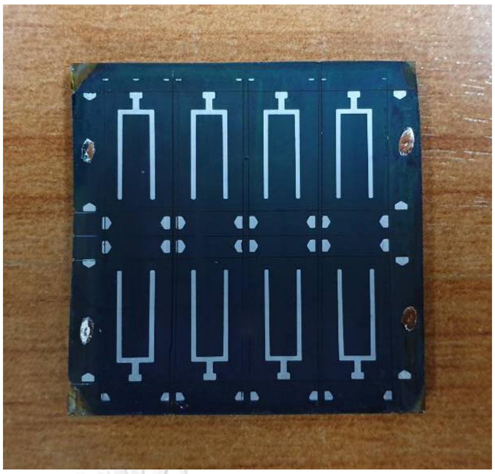

Figure 4.20 Al grid deposited on the film obtained in figure 4.19 by thermal evaporation and the completed cell.

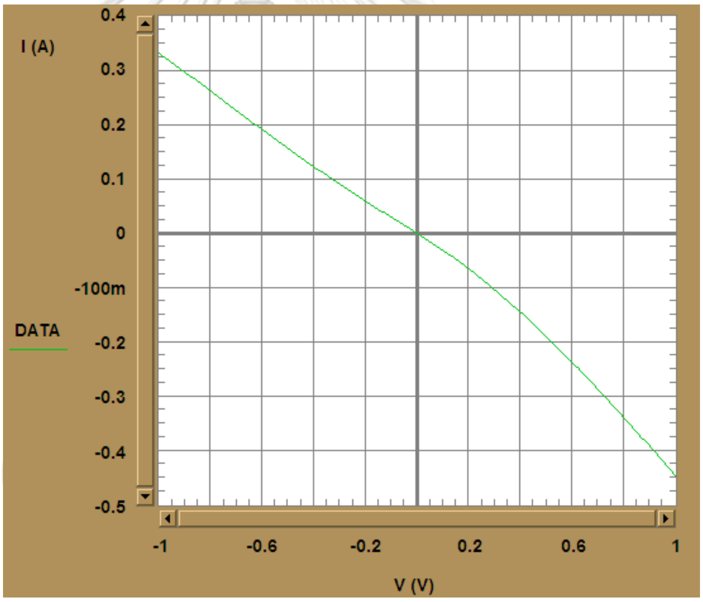

Figure 4.21 I-V curves of CZTS thin film solar cell devices by using 2-methox: DIW (70:30) as solvent 6 Layers at deposition speed 1563 μm/s.

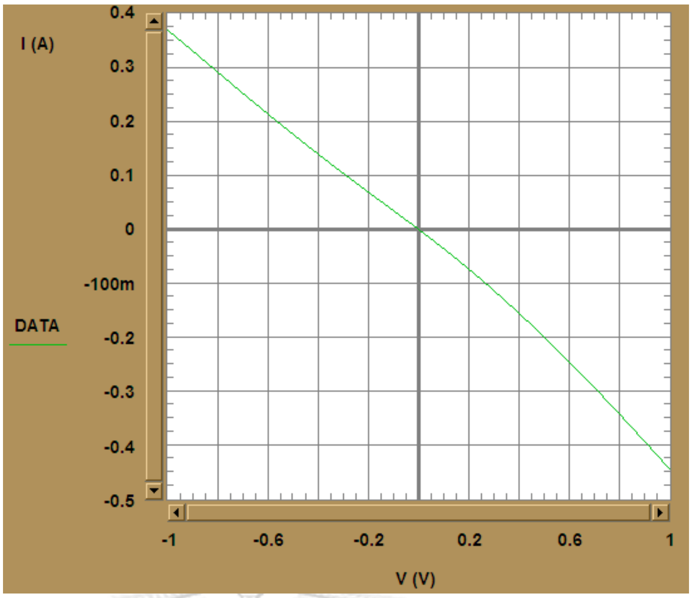

Figure 4.22 I-V curves of CZTS thin film solar cell devices by using 2-methox: DIW (70:30) as solvent 6 Layers at deposition speed 100 μm/s.

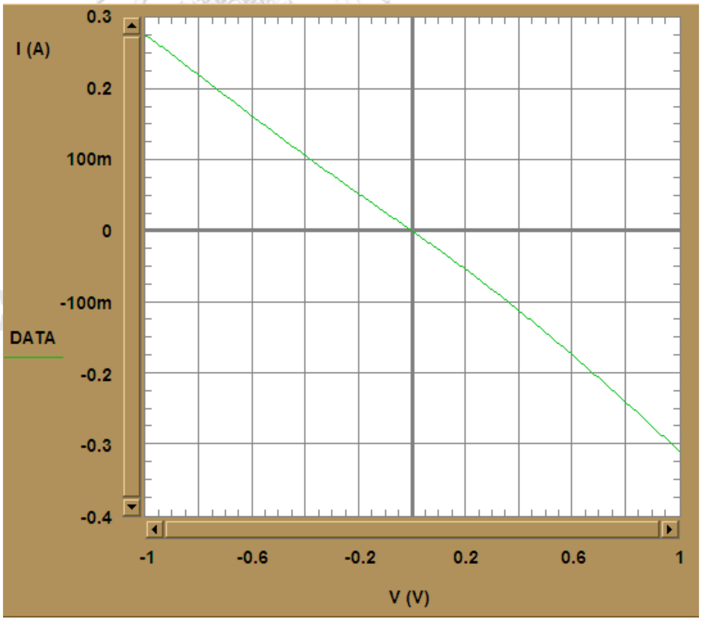

Figure 4.23 I-V curves of CZTS thin film solar cell devices by using 2-methox: DIW (70:30) as solvent 6 Layers at deposition speed 2292 μm/s.

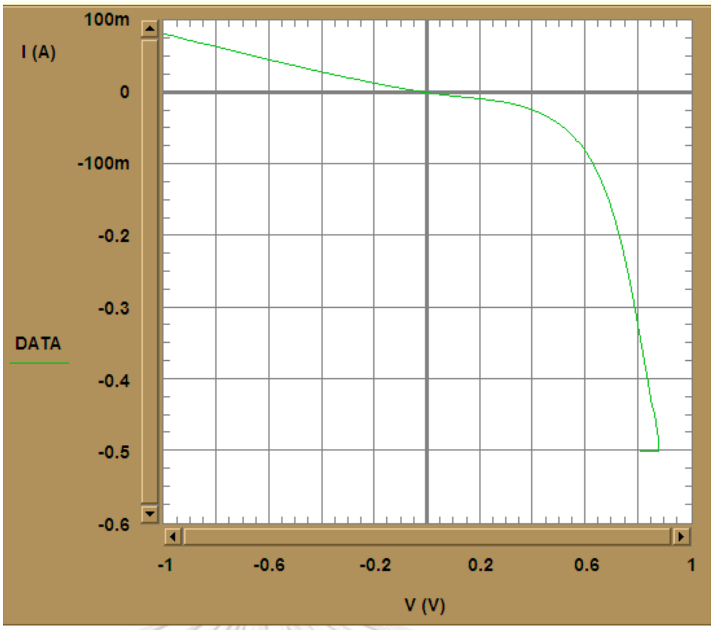

Figure 4.24 I-V curves of CZTS thin film solar cell devices by using 2-methox: DIW (30:70) as solvent 10 Layers at deposition speed 100 μm/s.

Table 4.5 CZTS solar cell parameters from I-V measurement

Conditions	Voc (mV)	Jsc (mA/cm^2)	FF (%)	Efficiency (%)	Absorber morphology
1) 2-methox :DIW (100:0) Layers at deposition speed 1106 μm/s	N/A	N/A	N/A	N/A	High porosity film
2) 2-methox :DIW (70:30) 6 Layers at deposition speed 1563 μm/s	0.1976	14.38 x 10^{-3}	0.8753	2.487 x 10^{-6}	Low porosity film
3) 2-methox :DIW (30:0) 6 Layers at deposition speed 3333 μm/s	N/A	N/A	N/A	N/A	Low porosity film
4) 2-methox :DIW (70:30) 6 Layers at deposition speed 1000 μm/s	0.0394	8.663 x 10^{-3}	0.2731 x 10^{-3}	10.65 x 10^{-9}	Low porosity film
5) 2-methox :DIW (70:30) 6 Layers at deposition speed 2292 μm/s	0.1184	8.663 x 10^{-3}	0.8564	0.879 x 10^{-6}	Low porosity film
6) 2-methox :DIW (30:70) 10 Layers at deposition speed 100 μm/s	1.192	0.1358	0.6899	0.112 x 10^{-3}	Compact film

From figure 4.25, the cross-section of some condition of CZTS thin film solar cells were shown. The CZTS thin film solar cell that used 2-methox: DIW (30:70) as solvent have obviously smooth than the other. In figure 4.25 (c), the smooth of top CZTS thin film solar cell cause of the flatness of absorber layer. On the other hand, figure 4.25 (d) show the rough top CZTS thin film solar cell that also cause of the roughness of CZTS film. All of SEM micrographs unclearly separate each a layer except for Mo layer.

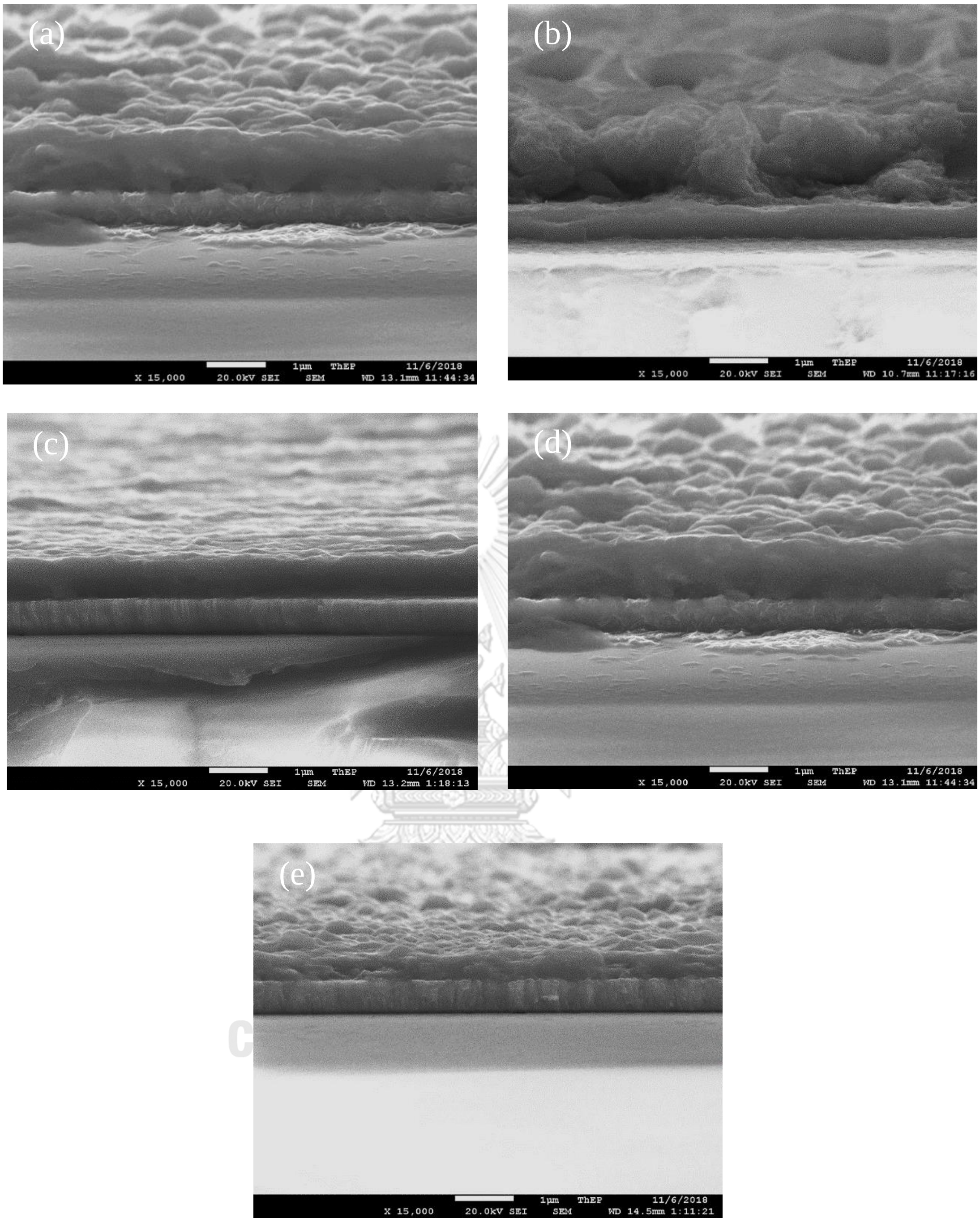
(a)
1μm ThEP 11/6/2018
X 15,000 20.0kV SEI SEM WD 13.1mm 11:44:34
(b)
1μm ThEP 11/6/2018
X 15,000 20.0kV SEI SEM WD 10.7mm 11:17:16
(c)
1μm ThEP 11/6/2018
X 15,000 20.0kV SEI SEM WD 13.2mm 1:18:13
(d)
1μm ThEP 11/6/2018
X 15,000 20.0kV SEI SEM WD 13.1mm 11:44:34
(e)
1μm ThEP 11/6/2018
X 15,000 20.0kV SEI SEM WD 14.5mm 1:11:21

Figure 4.25 (a)-(e) SEM micrographs of cross-section of CZTS thin film solar cells by using various solvents and deposition speed as follows; 2-methoxyethanol 100: DIW 0 as the solvent at different deposition speeds as follows; (a) 2-methoxyethanol 100: DIW 0 as the solvent at deposition speeds 1563 µm/s 6 layers, (b) 2-methoxyethanol 70: DIW 30 as the solvent at deposition speeds 2292 µm/s 6 layers, (c) 2-methoxyethanol 30: DIW 70 as the solvent at deposition speeds 1250 µm/s 12 layers, (d) 2-methoxyethanol 100: DIW 0 as the solvent at deposition speeds 1250 µm/s 9 layers and (e) 2-methoxyethanol 30: DIW 70 as the solvent at deposition speeds 100 µm/s 10 layers.

Chapter 5

Conclusion

Firstly, copper zinc thin sulphide (Cu_2ZnSnS_4: CZTS) thin films were synthesized on Mo substrates by convective deposition method that attain the especial film. The morphology of film is small particles and high porosity. In this work, the effect of deposition speed, types and fraction of solvent were strongly investigated. The optimized condition was used for deposition of CZTS thin film as absorber layer.

5.1 Conclusion

5.1.1 The properties of the CZTS thin film

1. All of CZTS thin films have near stoichiometric ratios theoretical ratios of CZTS.
2. The type of solvents affect to morphology of CZTS particles and formation of film that also affect to the thickness and porosity of film. The high fraction of 2-methoxyethanol as solvent provide higher porosity and thicker film.
3. The type of solvent affect to the viscosity of solution that affect to the thickness of film corresponding to Newton's Law of Viscosity. The high fraction of 2-methoxyethanol as solvent provide higher viscosity of solution.
4. The type of solvent affect to the sol-gel process that high fraction of DIW as solvent has a high tendency to occur a complete hydrolysis reaction. Moreover, the complete hydrolysis reaction makes larger CZTS particles.

5. The deposition strongly affect to the thickness of CZTS thin film. For studied deposition speed range, the thick film were obtained at high deposition speed corresponding to Newton’s Law of Viscosity.
6. The deposition speed affect to morphology of CZTS thin film. At the high deposition speed, the CZTS film has high porosity and slightly smaller particles. Conversely, the compact film and slightly larger particles obtained at low deposition speed. Moreover, the high deposition speed makes thicker film.
7. All of CZTS film at various solvent are explicit kesterite structure CZTS that is suitable for photovoltaic application.
8. The 2-methoxyethanol 100: DIW 0 CZTS thin film can absorb the spectrum in sunlight better than the 2-methoxyethanol 30: DIW 70 CZTS thin film so the CZTS thin film 2-methoxyethanol 100: DIW 0 is proper for solar cell application in optical side.
9. The energy band gap of CZTS film is range 1.4-1.5 eV that is nearly theoretical value.

5.1.2 The electrical performance of CZTS thin film solar cells

1. The CZTS thin film as prepared by low deposition speed provide compact film and slightly big particle that is proper for photovoltaic application. These film also provide higher power conversion efficiency.

2. The absorber film as prepared by very low deposition is outstanding about power conversion efficiency and performance.

3. The high fraction of DIW as solvent CZTS thin film solar cell obviously provide higher efficiency than high fraction of 2-methoxyethanol.

From this thesis, the convective deposition method can use for fabricating CZTS film as absorber layer for solar application. Moreover, the factors that were studied in this thesis can be used for high quality CZTS layer. Nevertheless, the thickness of each layers of thin films in CZTS thin film solar cell should be optimized in order to obtain proper thickness and higher efficiency CZTS thin film solar cell.

5.2 Recommendations for future work

1. Investigate more information about very deposition speed of CZTS fabrication by convective deposition in order to obtain the optimized condition.
2. Optimize the thickness of all layers especially absorber layer in order to provide good electron transportation.
3. Optimize the concentration of CZTS solution in order to obtain suitable condition for photovoltaic application.

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VITA

NAME	Thanawat Anantamongkolchai
DATE OF BIRTH	8 September 1993
PLACE OF BIRTH	Bangkok
INSTITUTIONS ATTENDED	Chemical Technology, Chulalongkorn University in Bachelor of Science (Chemical Engineering)
HOME ADDRESS	106/12 Wutthakat Rd., Chomtong, Bangkok 10150
PUBLICATION	Thanawat Anantamongkolchai, "Parametric Study of Copper Zinc Tin Sulfide Thin Films by Convective Deposition Method", Proceedings of The Pure and Applied Chemistry International Conference 2018 (PACCON 2018), Thailand