Faculty of Manufacturing Engineering

MORPHOLOGICAL CHARACTERIZATION OF TRANSITION METAL TERNARY MoSSe CHALCOGENIDE THIN FILMS BY ELECTROCHEMICAL ROUTE

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in fulfilment of the requirement for the degree of Master of Manufacturing Engineering (Advanced Material and Processing)

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DECLARATION

I declare that this thesis entitled "Morphological Characterization of Transition Metal Ternary MoSSe Chalcogenide Thin Films by Electrochemical Route" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature	:	…………………………..
Name	:	…………………………..
Date	:	…………………………..

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Manufacturing Engineering (Advanced Materials and Processing).

Signature : ……………………………………

Name : ……………………………………

Date : …………………………………….

DEDICATION

My beloved father, Nik Ramli Bin Nik Hassan

My loving mother, Norasinah Binti Talib

My friends.

ABSTRACT

Through the performance of the PEC systems in power conversation, it may be possible to build affordable photovoltaic panels. The main reason is to find the right alternative material for the conversion of solar energy. Molybdenum chalcogenide can be used for photovoltaic conversion in thin films as ternary materials for solar cells. This research will focus primarily on using electrodeposition technique to investigate transition molybdenum chalcogenide. Electrodeposition method is one of the methods that belongs to chemical route. This method able to synthesis the thin films at lower cost. Besides, it able to produce the thin films in a large scale which make it attractive for industry. Ternary molybdenum chalcogenide MoSSe was chosen as a material in this study. MoSSe thin films was synthesis through electrodeposition method at various deposition time. Moreover, the thin films are characterizing for its morphological and compositional properties by using SEM and EDX. In addition, the optical properties of the thin films also were observed to study the suitability of the materials for the used in photoelectrochemical cell. Ternary molybdenum chalcogenide of Molybdenum sulphoselenide MoSSe was prepared and ITO glass substrates was used as a substrate. MoSSe were deposited on the ITO glass substrates at different deposition time which are 10 minutes, 20 minutes, and 30 minutes and at the temperature of 40 ℃. The cyclic voltammetry process was taking places to ensure the potential value for the deposition process takes place. Then, the electrodeposition process was proceeding with the selected potential from the cyclic voltammetry. Then, the thin films were examined for its morphological, compositional and its optical properties. It was observed that the potential of the deposition process is at -1.0 V through the cyclic voltammetry process. Thus, the electrodeposition process was occurred at -1.0 V. The scanning electron micrograph reveal that the surface of the films tends to grow as the deposition time increase. In addition, the MoSSe thin films have been proved to be successfully deposited on the substrates as all the elements of Mo, S and Se from the composition analysis. Moreover, from the Mott-scottky plots, it shows that the flat band potential is decreasing upon an increasing of the thickness of the films. The results obtained reveals the suitability of MoSSe as solar cell alternative materials.

ABSTRAK

Ia ada kemungkinan untuk membina panel fotovoltaik yang berpatutan melalui prestasi system selfotoelektrokimia dalam mengubah kuasa. Tujuan utama adalah untuk mencari bahan alternative yang sesuai untuk penukaran tenaga suria. Molibdenum chacogenide dapat digunakan sebagai penukaran fotovoltaik dalam filem nipis sebahagi bahan terner untuk sel suria. Penyelidikan ini akan memfokuskan pada penggunaan teknik elektrodeposisi untuk menyiasati transisi molibdenum chalcogenide. Teknik elektrodeposisi adalah salah satu teknik yang tergolong dalam kumpulan kimia. Selain itu, ia dapat menghasilkan filem nipis dalam kuantiti yang besar yang menjadikannya tarikan daripada sektor industry. Molibdenum kalkogenida ternary MoSSe dipilih sebagai bahan dalam kajian ini. Filem nipis MoSSe disintesis melalui kaedah electrodeposisi pada pelbagai masa pemendapan. Selain itu, filem nipis dikaji melalui sifat moofologi dan komposisinya dengan menggunakan imbasan mikroskop electron dan xray penyebaran udara. Tambahan pula, sifat optic film nipis juga dikaji untuk menyeldidik kesesusaian bahan untuk digunakan dalam sel fotoelektrokimia. Molibdenum kalkogenida ternary sulphoselenide MoSSe telah disediakan dan substrat kaca ITO telah digunakan sebagai substrat. MoSSe didepositkan pada kaca ITO pada waktu pemendapan yang berbeza iaitu 10 minit, 20 minit dan 30 minit pada suhu 40 ℃. Proses kitaran voltammetri berlaku untuk memastikan nilai potensi untuk proses pemendapan berlaku. Kemudian, proses elektrodeposisi ditersukan dengan potensi yang dipilih dari kitaran voltammetri. Seterusnya, filme nipis diperiksa untuk sifat morfologi, komposisi dan optiknya.Daripada studi, ia telah terlihat bahawa potensi proses pemendapan adalah pada -1.0V yang didapat daripada proses kitaran voltammetri. Imbasan mikrograf electron menunjukkan bahawa permukaan filem cenderung tumbuh seiring pertambahan waktu pemendapan. Selain itu, filem nipis MoSSe telah Berjaya didepositkan pada substrat kerana kesemua elemen Mo, S, dan Se dapat dilihat dari Analisa komposisi. Selain itu, dari plot Mott-Schottky, inin menujukkan bahawa potensi jalur rata semaki berkurang dengan peningkatan ketebalan filem. Hasil yang diperoleh menunjukkan kesesuaian MoSSe sebagai bahan alernatif sel suria.

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LIST OF ABBREVIATIONS & SYMBOLS

Ag/AgCl	-	Silver or Silver Chlroide
CV	-	Cyclic Voltammetry
E_g	-	Bandgap
eV	-	Electron volt
HCL	-	Hydrochloric acid
ITO	-	Indium-tin-oxide
Mo	-	Molybdenum
MoSSe	-	Molybdenum sulphoselenide
PEC	-	Photoelectrochemical cell
PV	-	Photovoltaic
PVD	-	Physical Vapour DEposition
S	-	Sulphur
Se	-	Selenium
SEM	-	Scanning Electron Microscope
TW	-	Terawatts

UV-Vis	-	Ultraviolet-visible
V_{FB}	-	Flatband Potential

CHAPTER 1

INTRODUCTION

1.1 Background

The primary source of energy such as fossil fuels are gradually reduce even the energy demand is increasing globally. Since there is an increasing amount of energy demand, the renewable energy sources should be generated(Ajayan *et al.*, 2020). AL-Rousan (2018) states that renewable energy sources are more environmentally friendly and sustainable when compare with fossil fuels. Renewable energy comprises various forms like solar energy and wind energy.

The upper atmosphere of earth gets almost 174,000 terawatts (TW) of energy from the sun and 94,800 TW are accessible on surface of earth after losses which can be used for consumption of energy. Currently, world demand for energy is expected around 18 TW, a small fraction from energy generated on the surface of the earth. When 2030, to keep the current standard of living, world-wide the demand for energy is projected to rise around 30% (Munshi *et al.*, 2018). Thus, solar cells is considered the highly promising ways to meet global energy needs, as solar energy is the cheapest, cleanest, safest, and most available energy supply for the future renewable and sustainable energy technologies. Solar energy received can converted into electricity through high efficiency of solar cells to fulfill the energy demand for future worldwide. For the large-scale power generation, thin film photovoltaic has becoming a possible choice (Shelke *et al.*, 2017).

In recent decades, semiconductors have achieved great interest due to their exclusive optical, electrical and also catalytic properties making them the highly appropriate materials that can be used for thin films transistor, sensor, photodetectors and photovoltaic (Hernandez-Perez *et al.*, 2020). Besides, it also can be in many optoelectronic applications likes photoelectrochemical (PEC) solar cells due to wide direct optical band gaps with great optical and electrical properties that made it suitable for the optoelectronic device production (Patil *et al.*, 2019). Furthermore, there is a developing enthusiasm for multinary metal chalcogenide because of the search for new thin band gap semiconductors and the possibility to adjust the properties for optical and electrical across a wide-ranging range (Bagade and Bhosale, 2019).

The simple type of solar cell is photoelectrochemical cell (PEC) where a solid-liquid junction can be used to convert energy. Besides, PEC cells are favorable device as it is affordable and easy to manufacture. Developing inexpensive photovoltaic panels could be possible by increasing the efficiency of the PEC devices in power conservation (Patil *et al.*, 2019). Lately metal sulphide and metal selenide have got huge consideration for the used in photoelectrochemical cells. This is because sulfur and selenium can be used to get a narrow band gap as these two materials have greater lying p-band energy levels (Sivula and Van De Krol, 2016). The current interest is to find suitable alternate materials for solar energy conversion. Thus, this research will mainly focus on the investigation of transition thin film Molybdenum chalcogenides MoX_2 by using electrochemical route. The Molybdenum chalcogenide is one of the compound semiconductor materials. With the use of these Molybdenum chalcogenide in thin films form will be used for photovoltaic conversion since MoX_2 ternary material can be used as solar cell material.

1.2 Problem Statement

The most important and desirable alternatives of receive electricity is the conversion of solar energy through photovoltaic process. The currently available solar cell are quite costly as it is produced from highly pure and perfectly crystalline materials and P-N junction is gained by using the most sophisticated technology (Aloney *et al.*, 2009). Thin film solar cells, however, are currently represent the greatest interesting scheme for solar cell development and solar cell research (Mane *et al.*, 2015). Currently, silicon solar cells of thin films are the most significant materials utilized in photovoltaic applications. Unfortunately, the inherent indirect of the bandgap and low absorption of Si coefficient need a dense wafer to soak up sunlight, which makes it expensive compare to conventional fuels power production. Therefore, an alternative photovoltaic material and cost-effective are urgently needed and actively investigated (Liang *et al*., 2020). Moreover, in the field of photovoltaics, the new challenge is to generate solar energy at a cheaper cost while upholding the environmental standards (Beraich *et al.*, 2019). Therefore, to overcome these limitations, a new material which is ternary metal molybdenum chalcogenide specifically MoSSe will be proposed with lower cost but have a better conversion efficiency to replace the Si for this study. A higher coefficient of absorption together with direct values of the bandgap that are small make them as the best candidates as absorber materials in thin films solar cells since a thin layer of this kind of material is adequate for satisfactory performance for the device (Manivannan and Victoria, 2018).

Several methods have been used recently for the synthesis of thin films. Hydrothermal and chemical vapour deposition have been widely used to synthesis the thin films. Unfortunately, the deposition needs an additional step in order to get the good dispersion of the films on the substrates (Poongodi *et al.*, 2017).Besides, physical vapour deposition methods can produce a high quality films but it is hard to scale up (Liu *et al.*, 2012). Moreover, this PVD methods are not suitable to deposit a more than one materials at a single times as the process are more complex that cause it to be more expensive (Sensing *et al.*, 2020). Therefore, the development of a low cost and large scale up methods like electrodepositions is achieving a great interest (Liu *et al.*, 2012). Electrodeposition is a very favourable method for producing semiconductor thin films, and more precisely, it is also ideal for ternary compounds. In terms of ease of implementation and monitoring of the deposit reactions, it is conducted at low temperature, therefore able to remove some constraints associated with the substrates. It also provides excellent reproducibility, outstanding performance and the ability to deposit large area at a cheaper price where it makes the electrodeposition extremely attractive for industrial applications (Beraich *et al.*, 2019).

1.3 Research objectives

The main objectives of this study are

i. To synthesize MoSSe thin films by using electrodeposition method at various deposition time
ii. To characterize the thin films for their morphological and compositional properties using Scanning electron microscope (SEM) and energy dispersive X-ray (EDX)
iii. To evaluate the optical properties of the semiconductor parameters of thin films to decide the suitability as photoelectrochemical or solar cell by using Mott-Shottky.

1.4 Scope of work

This project was focus on the synthesis of transition metal chalcogenide especially Molybdenum sulphoselenide, MoSSe thin films by using potentiostat on indium-tin-oxide

(ITO)-coated conducting glass substrates. The thin films are synthesized under conditions which the deposition time are ranging from 10 minutes to 30 minutes with an interval of 10 minutes. The thin films then were characterized and investigate the effect of all the parameters on the properties of the thin films for the used in photoelectrochemical (PEC) / solar cell. The characterization are made for thickness, and surface morphology and compositional of the films by using, SEM and EDX analysis, respectively. Besides, other analysis include the optical and semiconductor studies by using Mott-Schottky to study the suitability of the materials used for PEC or solar cells.

CHAPTER 2

LITERITURE REVIEW

2.1 Introduction

In this chapter, it will cover all the literature review about the previous research and analysis that have been conducted especially in semiconductor thin films and transition metal chalcogenide. The main materials that were used in this study is ternary metal chalcogenide MoSSe. The technique that were used is electrodeposition. In this chapter, the technique, the characterization, properties, and microstructural analysis were discussed based on the previous research.

2.2 Solar Energy

Solar energy is plentiful free and do not pollute making it as one of the most attractive options available for renewable (Zhang *et al.*, 2020). As stated by Qu *et al.* (2020), solar energy is the biggest type for renewable energy and has played a big part in the energy supply sector, accounting for around 21percent of renewable energy in 2018 (Qu *et al.*, 2020). Solar energy is likely to replace fossil fuel to meet human demand for energy, which facilitates access to dependable and comprehensive energy supplies (Qu *et al.*, 2019).

The energy radiated from the sun reaching the earth's surface is estimated to be 10,000 times higher when compared to current consumption of global for one year (Pessoa *et al.*, 2015). Thus, some countries have increased their dependence on solar energy. Based on the figure 2.1, it shows the total amount of solar energy consumed in worldwide in million tonnes oil equivalent(AL-Rousan *et al.*, 2018). From the figure2.1, the total amount of solar energy consumed from 2000 to 2016 in worldwide increased exponentially and in 2016 the maximum amount of solar energy consumed was observed and the total solar energy capacity in Megawatt is shown in figure 2.2 .

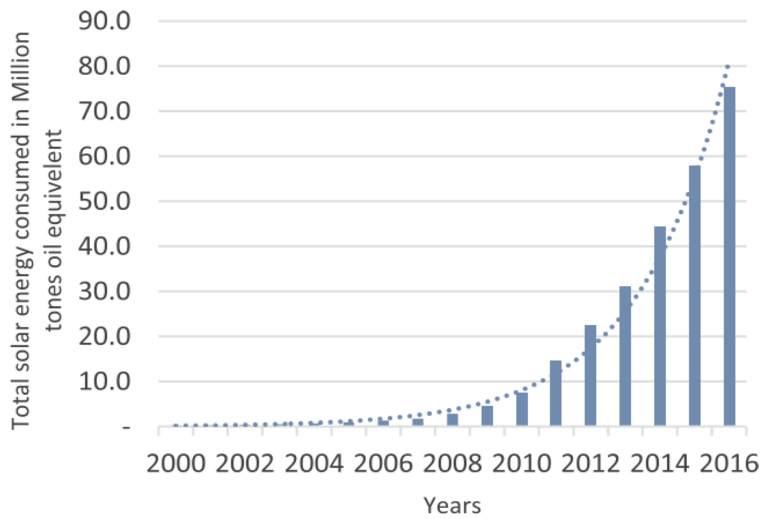

Figure 2.1 The consumption of solar in Million tonnes (AL-Rousan et al., 2018)

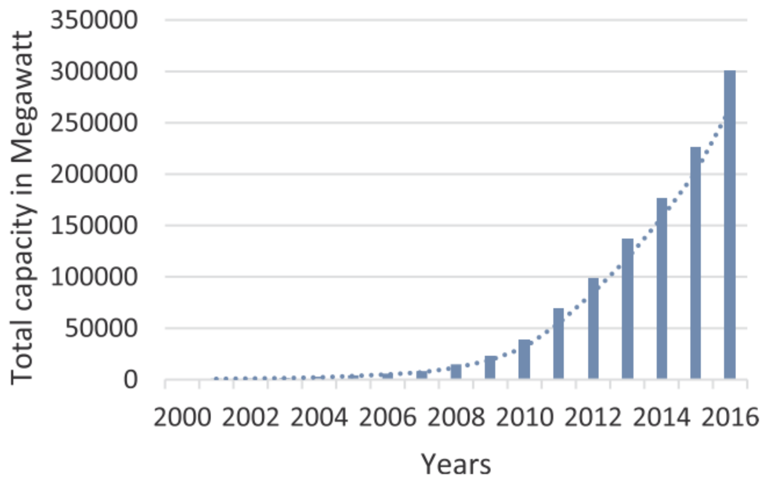

Figure 2. 2 Overall capacity of solar energy in Megawatt (AL-Rousan, Isa and Desa, 2018)

Solar cell able to convert solar power directly to electricity power has attracted tremendous research attention due to the possibility to partially compensate in part for non-renewable fossil fuels (Liang *et al.*, 2020). There are many techniques that can be utilized to change the solar energy to chemical or even electrical energy which are photovoltaics, PEC and also artificial photosynthesis as shown in figure 2.3 (Pessoa *et al.*, 2015). Currently, solar energy of full spectrum has attracted widespread attention as it has the possibility to improve solar energy conversion. (Qu *et al.*, 2019)

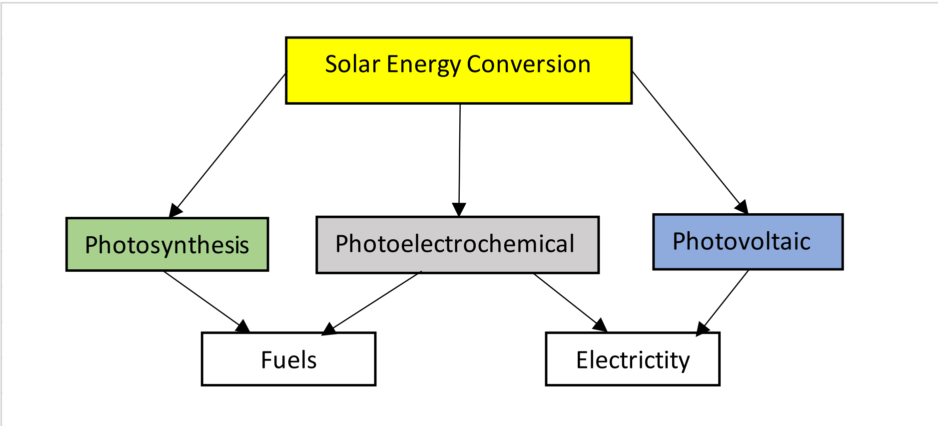

Figure 2.3 Methods of solar energy change into fossil fuels (Pessoa et al., 2015).

2.2.1 Advantages of Solar Energy

The available solar energy is about 10,000 times that of the world's annual energy requirements (Patil *et al.*, 2019). Solar energy is a completely new energy among these renewable energies, where it is secure, clean, and also can be reproduce as well as an environmentally friendly energy source (Mane *et al.*, 2014). Besides that, solar energy also freely available, abundant and carbon free which able to make it environment-friendly (Patil *et al.*, 2019). In addition, the important benefits of solar energy are that it can be utilized effortlessly by both home and business user as it does not need a massive set-up. Besides, solar energy not only benefits individual owner but also benefits the environment (Siddiqui *et al.*, 2017).

2.3 Photoelectrochemical / Photovoltaic system

Photoelectrochemical (PEC) devices let the photocatalytic solar conversion to electricity as well as chemical energy (Pessoa *et al.*, 2015).According to Chaudhary *et al.* (2004), PEC with an active semiconductor junction of electrolytes are considered an effective solar energy harvester. Pessoa et al. (2015) states that the PEC converts light energy into electricity in a two-electrode cell where a material with maximum absorption of solar energy is essentially used on the photo-electrode to produce electrical energy. Thus, development of materials with potential for PEC utilization has gained considerable attention within the scientific and industrial communities

Full light absorption, load separation and transport as well as chemical reactions on the surface are the mains requirements for highly efficient energy conversion (Choi *et al.*, 2015). Besides, a key component in a photoelectrochemical solar cell is the semiconductive material. It absorbs photons from incidents and creates electron-hole pairs (Patil *et al.,* 2019). Ahmed and Dincer (2019) states that the photoelectrochemical reaction is based in the use of an electrode with a bandgap between the valence band gap and the conduction band. The reaction takes places under illumination of light with the support of photons where the photons energy is greater than the energy gap between semiconductor bands.

Photoelectrodes are required under many conditions for use in photoelectrochemical cells (Choi *et al.*, 2018). For ideal semiconductor for this kind of works, the band gap should be in range of 1.0 to 2.0 eV (Chaudhary *et al.*, 2004). This is due to the gap that is small where it is easier to encourage an electron to move from one band to the other. This will