



**UNIVERSITI PUTRA MALAYSIA**

***PREPARATION OF TIN SELENO TELLURIDE THIN FILMS BY  
POTENTIOSTATIC AND PULSE ELECTRODEPOSITON TECHNIQUES***

**CHIA CHEW PING**

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**PREPARATION OF TIN SELENO TELLURIDE THIN FILMS BY  
POTENTIOSTATIC AND PULSE ELECTRODEPOSITON TECHNIQUES**

By

**CHIA CHEW PING**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in  
Fulfilment of the Requirements for the Degree of Master of Science**

**April 2015**

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## DEDICATION

Dedicated to my beloved parents and Chee Siong for their love, support, understanding and encouragement.



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

## **PREPARATION OF TIN SELENO TELLURIDE THIN FILMS BY POTENTIOSTATIC AND PULSE ELECTRODEPOSITON TECHNIQUES**

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**CHIA CHEW PING**

**April 2015**

**Chairman: Professor Zulkarnain Zainal, PhD**  
**Faculty: Science**

Deposition of tin seleno telluride thin film on fluorine doped tin oxide (FTO) coated glass was successfully carried out by potentiostatic deposition and pulse electrodeposition methods. The deposition process was done in an acidic bath consisting of Sn-EDTA, Na<sub>2</sub>SeO<sub>3</sub> and TeO<sub>2</sub> solutions. Deposition potential was initially determined using cyclic voltammetry (CV), where the CV results indicated that the possible potential range for deposition of tin seleno telluride is between -0.35 V to -0.65 V.

In potentiostatic deposition, the effect of deposition potential, annealing temperature, deposition time, bath temperature and bath concentration were studied. Comparison was done based on the results obtained from photoelectrochemical test (PEC) and X-ray diffraction (XRD). It was found that tin seleno telluride thin film which was deposited for 40 minutes at -0.40 V in a deposition bath containing 0.010 M Sn-EDTA, 0.010 M Na<sub>2</sub>SeO<sub>3</sub> and 0.005 M TeO<sub>2</sub> at room temperature exhibited the highest photocurrent and has the good crystallinity. It was also observed that the tin seleno telluride thin film was produced when the sample was annealed at 250 °C.

Pulse electrodeposition was carried out for 40 minutes at a potential of -0.40 V vs Ag/AgCl in a solution containing 0.010 M Sn-EDTA, 0.010 M Na<sub>2</sub>SeO<sub>3</sub> and 0.005 M TeO<sub>2</sub>. The sample was annealed at 250 °C for 30 minutes. The effect of varying duty cycle was studied. PEC and XRD results showed that tin seleno telluride deposited at 50% duty cycle produced a thin film with high crystallinity and good photoresponse.

The photocurrent for the thin film deposited using both methods appeared at negative potentials region, revealing the fact that tin seleno telluride is a p-type semiconductor. The XRD results showed that tin seleno telluride (SnSe<sub>0.3</sub>Te<sub>0.7</sub>) is polycrystalline with strong cubic structure reflections at (002), (022), (222), (004) and (024) planes. Micrographs obtained from Scanning Electron Microscopy (SEM) showed that the thin film deposited using potentiostatic deposition appeared as non-uniform dendritic

crystals where as thin film deposited using pulse electrodeposition appeared as short, rod type loose aggregates at 10 to 50% duty cycle. The thin film obtained from pulse electrodeposition also has better surface coverage compared to the potentiostatic deposition.

Data obtained from Energy Dispersive Analysis of X-rays (EDX) revealed that the composition of Sn:Se:Te was 1:5.4:2.8 and 1:7.4:3.5 respectively for both potentiostatic and pulse electrodeposition. The crystallite size of tin seleno telluride obtained from pulse electrodeposition is larger than that from potentiostatic deposition. Optical studies showed that the thin film deposited using both deposition methods have a direct band gap transition with band gap value of 1.60 eV.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Sarjana Sains

## **PENYEDIAAN FILEM NIPIS TIMAH SELENIDA TELLURIDA DENGAN TEKNIK ELEKTROENAPAN POTENTIOSTATIK DAN DENYUTAN**

Oleh

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Pengelektroenapan filem nipis timah selenida tellurida pada kaca bersadur timah oksida terdop fluorin (FTO) berjaya dihasilkan dengan mengguna kaedah penganapan potentiostatik dan kaedah pengelektroenapan denyutan. Proses penganapan dijalankan di dalam larutan berasid yang terdiri daripada larutan Sn-EDTA,  $\text{Na}_2\text{SeO}_3$  dan  $\text{TeO}_2$ . Kitar voltametri dijalankan untuk menentukan julat keupayaan enapan, julat di antara  $-0.35$  V hingga  $-0.65$  V didapati berkemungkinan mengenyapkan timah selenida tellurida.

Parameter yang divariasikan termasuk keupayaan enapan, suhu pemanasan, masa penganapan, suhu larutan dan kepekatan elektrolit telah dikaji dalam kaedah penganapan potentiostatik. Kesan pembelauan sinar-X (XRD) dan fotoelektrokimia (PEC) telah dikaji. Enapan yang terhasil pada keupayaan  $-0.40$  V dalam larutan elektrolit  $0.010$  M Sn-EDTA,  $0.010$  M  $\text{Na}_2\text{SeO}_3$  dan  $0.005$  M  $\text{TeO}_2$  pada suhu bilik menunjukkan tindak balas foto yang tinggi dan sifat hablur yang lebih baik. Suhu penganapan timah selenida tellurida yang paling sesuai ialah pada suhu pemanasan  $250^\circ\text{C}$ .

Pengelektroenapan denyutan dilakukan selama 40 minit pada keupayaan  $-0.40$  V berbanding Ag/AgCl di dalam larutan yang mengandungi  $0.010$  M Sn-EDTA,  $0.010$  M  $\text{Na}_2\text{SeO}_3$  dan  $0.005$  M  $\text{TeO}_2$ . Sampel dipanaskan pada suhu  $250^\circ\text{C}$  selama 30 minit. Kesan kitar kerja telah dikaji. Keputusan fotoelektrokimia dan pembelauan sinar-X menunjukkan penganapan pada 50% kitar kerja menghasilkan filem nipis yang mempunyai sifat hablur dan tindak balas foto yang tinggi.

Tindak balas foto bagi sampel yang dienap melalui kedua-dua kaedah berlaku di keupayaan negatif, ini menunjukkan timah selenida tellurida ialah semikonduktor jenis-

p. Keputusan pembelauan sinar-X menunjukkan timah selenida tellurida ( $\text{SnSe}_{0.3}\text{Te}_{0.7}$ ) ialah polihabur dengan struktur kubus pada satah (002), (022), (222), (004) dan (024). Mikrograf yang diperolehi daripada mikroskopi pengimbasan elektron (SEM) menunjukkan timah selenida tellurida yang diapakan dengan menggunakan kaedah penganapan potentiostatik mempunyai morfologi dendritik yang tidak sekata, manakala sampel yang disediakan dengan menggunakan kaedah pengelektroenapan denyutan pada kitar kerja 10-50% menghasilkan sampel dengan morfologi kumpulan-kumpulan batang kecil yang bebas dan mempunyai permukaan liputan yang lebih baik.

Keputusan analisis penyerakan tenaga sinar-X (EDX) menunjukkan komposisi untuk Sn:Se:Te ialah 1:5.4:2.8 dan 1:7.4:3.5 bagi penganapan potentiostatik dan pengelektroenapan denyutan. Saiz habur lebih besar bagi sampel yang diapakan melalui kaedah pengelektroenapan denyutan berbanding dengan kaedah potentiostatik. Analisis optik bagi sampel daripada kedua-dua kaedah menunjukkan timah selenida tellurida merupakan semikonduktor peralihan jalur terus dengan nilai luang jalur 1.60 eV.



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I certify that an Thesis Examination Committee has met on (16 April 2015) to conduct the final examination of Chia Chew Pingon her thesis entitled “Preparation of Tin Seleno Telluride Thin Films by Potentiostatic and Pulse Electrodeposition Techniques” in accordance with Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Master of Science. Members of the Thesis Examination Committee were as follows:

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## LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
Ag/AgCl	Silver/ Silver chloride
EDTA	Ethylenediamine Tetraacetic Acid
EDX	Energy Dispersion X-ray
$E_g$	Band Gap Energy
FTO	Fluoride Tin Oxide
$h\nu$	Photon energy
ICDD	International Centre for Dffraction Data
JCPDS	Joint Committee of Powder Dffraction Standard
LSPV	Linear Sweep Photovoltammetry
PEC	Photoelectrochemical Test
SEM	Scanning Electron Microscopy
$T_{ON}$	Duration of Cathodic Pulse Potential
$T_{OFF}$	Duration of Zero Current Potential
XRD	X-ray Diffraction



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## CHAPTER 1

### INTRODUCTION

World energy consumption is targeted to rise by more than 50% and will keep increasing towards the year 2030. The main source of energy comes from oil, gas and coal. However, there is an emergence state of concern revolving around the crisis of energy source due to the unstable prices of oil and finishing stock, as well as environmental problems, which include the green house effect and global warming. Hence, renewable energy sources such as solar, wind, hydroelectric, hydrothermal and biomass energy becomes vital.

Solar cells are renewable energy source which converts energy from solar in light into electricity. It is clean, non-polluting and the solar source is readily abundant and free. The technology was first revealed by French physicist Antoine-Edmond Becquerel in 1839. Becquerel discovered the production of electrical current when metals immersed in solutions were exposed to sunlight. The current produced due to this phenomenon is known as photocurrent. Photocurrent generation involved electrochemical processes that are usually achieved by using a photoelectrochemical cell (PEC).

Solar energy based on PEC becomes important due to its photovoltaic and chemical energy conversion ability. Generally, a PEC consists of a semiconductor as the main component and a redox electrolyte. The performance of a PEC lies on the properties of the semiconductor being used; the semiconductor should have a high efficiency in absorbing visible light and possess long-term storage stability for conversion of sunlight to chemical or electrical energy.

Since 1950, semiconductor electrode based on silicon was discovered and its applications were investigated. Silicon is a semiconductor element, which has good stability as well as good physical and chemical properties. Silicon also has a good electronic performance, which makes it suitable for microelectronics, especially as solar energy material.

Apart from that, silicon is well performing in photoelectrochemical industry. However, the production of silicon material involves a high cost production process (Turmezei, 2004).

The worldwide demand for solar cell encourages an ongoing pursuit by concerned scientists to discover different varieties of semiconductor which is cheaper and more efficient. These include studies on the properties and applications of metal chalcogenide semiconductors.

## 1.1 Tin Chalcogenide Semiconductor

In this study, the primary attention is focused on tin chalcogenide. Tin chalcogenide semiconductor is made up of combination of tin with class VI element such as sulphide, selenide and telluride. Tin chalcogenide is a semiconductor which has interesting applications in photovoltaic energy conversion as well as in various optical and optoelectronic devices. It has also been widely used in sensors, lasers and thermoelectric cooling materials (Engelken *et al.*, 1987; Zweibel, 2000). These advantages have led to the studies of binary and ternary tin chalcogenide, such as SnS (Mariappan *et al.*, 2011), SnSe (Bicer and Sisman, 2011), SnTe (Sisman and Oz, 2011; Lukinskas, *et al.*, 2006), and SnSSe (Subramanian, *et al.*, 2003). Binary tin chalcogenide semiconductor such as tin selenide, tin telluride and tin sulphide which have band gap energy between 0.35 eV to 1.5 eV were efficient material for solar energy. They are used in memory switching devices (Rao *et al.*, 1988), light emitting diodes or laser diodes (Krause *et al.*, 1994), infrared photodetectors, thermoelectric devices (Furst *et al.*, 2002), halographic recording system (Lindgren *et al.*, 2002) and solar cells (Sharon and Basavaswaran, 1987). Ternary tin chalcogenide such as tin seleno telluride, is considered to have a high potential in optical recording, thermoelectric converters and infrared devices applications (Tearao *et al.*, 1989; Fan, *et al.*, 2006; Tritt and Subramanian 2006; Dresselhaus *et al.*, 2007). The presence of tellurium selenium material in ternary semiconductor was found to improve thermal stability and temperature (Partial, 2011) due to their semiconductivity and high photosensitivity properties. Materials that contained tellurium selenium are used in information optical recording (Bhargavafet *et al.*, 2010) as well as for solar energy conversion in photoelectrochemical and photovoltaic cell. For this research, the main interest and focus will be on ternary tin chalcogenide compound, tin seleno telluride.

## 1.2 Preparation of Tin Seleno Telluride Thin Film Semiconductor

Compared to bulk material, thin film semiconductor is more suitable to be used as solar energy material as interface interaction will improve with larger surface area. Methods that have been used to prepare thin film include chemical bath deposition, vacuum evaporation, chemical vapour deposition and electrodeposition.

Previous methods of preparing tin seleno telluride include solid state reaction, sputtering, solid solution quenching melting method and laser evaporation. However, these methods involved a more complicated process and expensive set up. The quenching melting method, for example, requires a higher temperature and produces samples in powder form. Chen *et al.*, (2012) reported that sample preparation was time consuming and required higher thermal heating before the samples were able to be coated at thin film form.

Electrodeposition is widely used to produce high quality thin film due to advantages over other method such as lower cost, large-scale production, minimum waste component, easy to adjust parameter and easy control of film properties (Michel *et al.*, 2003; Zainal *et al.*, 2005). In addition, the thickness, composition and uniformity of the produced film sample is also able to be controlled. Thin film photoelectrochemical



cell has more advantages including economic fabrication as well as easier formation of semiconductor and electrolyte junction.

Preparation of tin seleno telluride via electrodeposition has never been reported. Therefore, in this study, the electrodeposition method was chosen to fabricate the tin seleno telluride thin film. The photocurrent and band gap properties of the tin seleno telluride thin film prepared by electrodeposition method was also studied. In this study, potentiostatic and pulse electrodeposition were applied to prepare tin seleno telluride thin film by controlling and manipulating different parameters. The properties of tin seleno telluride prepared via both potentiostatic deposition and pulse electrodeposition technique is discussed.





### 1.3. Objectives

The objectives of this study are:

1. To prepared Tin Seleno Telluride thin films using potentiostatic deposition and pulse electrodeposition.
2. To optimize experimental parameters
  - To determine the potential range for potentiostatic deposition.
  - To evaluate the effect of varying deposition potentials, concentration of electrolyte, deposition time, bath temperature and annealing temperature on potentiostatically deposited tin seleno telluride.
  - To evaluate the effect of duty cycles on pulse electrodeposition of tin seleno telluride.
3. To characterise the deposited thin film
  - To determine crystalline structure, photocurrent, morphology and band gap of the deposited films.

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