**UNIVERSITI PUTRA MALAYSIA**

# PREPARATION OF TIN SELENIDE THIN FILM SEMICONDUCTOR BY ELECTROCHEMICAL DEPOSITION AND ELECTROSELENISATION

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**FSAS 2000 10**

# PREPARATION OF TIN SELENIDE THIN FILM SEMICONDUCTOR BY ELECTROCHEMICAL DEPOSITION AND ELECTROSELENISATION

By

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**Thesis Submitted in Fulfilment of the Requirements for the**
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**Chairman:** **Associate Professor Zulkarnain Zainal, Ph.D.**

**Faculty:** **Science and Environmental Studies**

Electrochemical preparation of tin selenide thin film semiconductor for photoelectrochemical cells (PECs) was studied. The film has been potentiostatically deposited on tin substrate at room temperature from aqueous solution containing $SnCl_2$ and $Na_2SeO_3$. The effect of the electrodeposition potentials and bath electrolytes concentrations proportion were investigated to determine the optimum condition for electrodeposition. The structure, morphology and the photosensitivity of the electrosynthesised samples were studied by using X-ray diffraction, scanning electron microscopy (SEM) and linear sweep voltammetry techniques. The bandgap energy and type of optical transition were determined from optical absorbance data. The X-ray diffraction analysis confirmed the formation of polycrystalline SnSe on the tin substrate. Scanning electron microscopy reaffirmed the existence of a crystalline deposit with different grain size and shape. The films prepared in this study showed a *p*-type semiconductor behaviour with very good photosensitivity. The optical absorbance is in the visible light range and the bandgap energy ($E_g$) is 1.0 eV. The tin selenide thin film semiconductor was also deposited alternately, through electroselenisation technique on ITO-glass, from aqueous $SnCl_2$ and $Na_2SeO_3$ solutions in separate baths. The film showed very good photosensitivity, a *p*-type semiconductor behaviour and energy gap of 0.95 eV, but the XRD analysis cannot confirm the existence of tin selenide due to the very thin layer of the deposit.

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

# PENYEDIAAN LAPISAN NIPIS SEMIKONDUKTOR TIMAH SULFIDA MELALUI PENGENAPAN ELEKTROKIMIA DAN ELEKTROSELENISASI

**Oleh**

**ALI JIMALE ALI**

**September 2000**

**Pengerusi:** **Profesor Madya Zulkarnain Zainal, Ph.D.**

**Fakulti:** **Sains dan Pengajian Alam Sekitar**

Penyediaan filem nipis semikonduktor timah selenida secara elektrokimia untuk sel fotoelektrokimia (PECs) telah dikaji. Filem tersebut telah dienapkan pada keupayaan tetap di atas substrat timah pada suhu bilik daripada larutan akueous yang mengandungi $SnCl_2$ dan $Na_2SeO_3$. Kesan nisbah keupayaan elektroenapan dan kepekatan larutan elektrolit telah dikaji bagi menentukan keadaan optimum peng elektroenapan. Struktur, morfologi dan fotosensitiviti sampel yang dielektrosintesis telah dianalisis dengan menggunakan teknik pembelauan sinar-X, mikroskop pengimbasan elektron (SEM) dan voltammetri pengimbasan linear. Nilai luang tenaga dan jenis peralihan optik telah ditentukan daripada data serapan optik. Analisis pembelauan sinar-X membuktikan terdapat pembentukan polihablur SnSe di atas substrat timah. Mikroskopi pengimbasan elektron telah mengesahkan sekali lagi kewujudan hablur enapan dengan saiz butiran dan bentuknya yang berbeza. Filem yang disediakan dalam kajian ini menunjukkan sifat semikonduktor jenis-p,

bukan sahaja mempunyai fotosensitiviti yang sangat baik, tetapi juga serapan optik dalam julat cahaya nampak serta nilai luang tenaganya ($E_g$) 1.0 eV. Filem nipis semikonduktor juga telah disediakan melalui teknik elektroselenisasi di atas kaca-ITO daripada larutan akueous $SnCl_2$ dan $Na_2SeO_3$ secara berasingan. Filem tersebut menunjukkan fotosensitiviti yang baik, sifat semikonduktor jenis-p dan nilai luang tenaganya 0.95 eV, tetapi analisis XRD tidak dapat membuktikan kewujudan timah selenida kerana filem yang diperolehi terlalu nipis.

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| | |
|---|---|
| PECs | Photoelectrochemical Cells |
| $E_g$ | Energygap |
| ITO | Indium Tin Oxide |
| PEC | Photoelectrochemistry |
| LPD | Liquid Phase Deposition |
| VPD | Vapour Phase Deposition |
| DMF | Dimethyl formamide |
| DMSO | Dimethyl sulfoxide |
| CV | Cyclic Voltammetry |
| VB | Valence Band |
| CB | Conduction Band |
| EHP | Electron Hole Pair |
| EDTA | Ethylenediaminetetraacetic Acid |
| PTFE | Polytetrafluoroethylene |
| LSV | Linear Sweep Voltammetry |
| SEM | Scanning Electron Microscopy |
| EDAX | Energy Dispersive Analysis of X-ray |
| XRD | X-ray Diffraction |
| JCPDS | Joint Committee of Powder Diffraction Standard |
| μPDSM | micro Powder Diffraction Search/Match |

# CHAPTER 1

# INTRODUCTION

In order to sustain the present standard of life and development, reliable and save supply of electrical energy is vital. The electrical energy currently in use mainly comes from fossil fuels and nuclear reactor, but there is future uncertainty due to the limited resources of fossil fuels coupled by the increasing energy demand. The deep concern on the short and long term safety of nuclear reactors also adds to the energy problem. Thus, the renewable energy sources may play a significant role in sustainable energy supply in the future. This is due to the minor impact the renewable energy sources are expected to have on the environment and their great technological potential.

Among the renewable energy sources such as hydropower, wind energy and biomass, the solar energy is the most attractive and promising alternative energy source for the future, especially for the highly populated and ever growing societies in the tropical regions.

In order to exploit the solar energy, development of semiconductor materials for the solar energy conversion devices (photovoltaic cells) are essential.

Efforts are being made through out the world to produce new semiconductors as well as developing the existing ones.

The photovoltaic cells technology seems ideal as it requires no or very little maintenance and lubricants. Unlike the current electricity generators, it also involves no rotating parts. Furthermore, one of its versions (photoelectrochemical cells, PECs) enable us to convert the day time solar radiation energy and meantime store it as a chemical energy, so we can use it when we need (Yuri, 1990).

The PECs are more preferable than the solid-state photovoltaic solar cells since the latter are manufactured from highly pure and perfectly crystalline materials and the p-n-junctions in the photovoltaic cells are obtained by using sophisticated and costly technology. In the former, use is made of an interface which forms on mere by dipping the semiconductor into an electrolyte solution and do not call for creation of a p-n-junction (Yuri, 1990). Thus, to realise a significant utilisation and storage of solar energy, efforts should be made in developing a quality semiconductor materials for the PECs.

The semiconductors also have other important applications such as catalyst of photo-degradation process of the industrial effluents in the waste water. Figure 1.1 shows some of the various applications of the semiconductor materials. The disclosure of their diversified applications, in the past few decades, make them a subject of research interest in different fields.

This research is a part of the efforts to develop tin based semiconductors for PECs. Success made on tin based semiconductor materials will contribute the value added of the Malaysian minerals as tin is one of the local mineral resources.

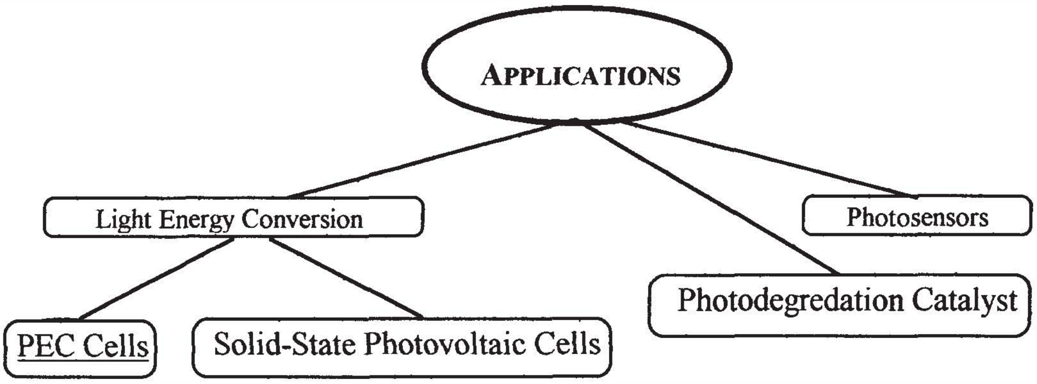

Figure 1.1: Different Applications of the Semiconductor Thin Films

Two important factors that should be considered in producing semiconductor material for solar cells are bandgap energy ($E_g$) matching with the solar spectrum (Figure 1.2) and the competitiveness of production cost (Zainal *et al.*, 1996).

The highest efficiency of the white light energy conversion is expected from solar cells device made from semiconductors with bandgap energy around 1.4 eV, as this kind of semiconductors can absorb all the bands in the visible region of the spectrum ($380 \leq \lambda \leq 750$ nm), thus the white light of solar radiation (Figure 1.2).

Bandgap energy ($E_g$) is the quantity of energy required to agitate the semiconductor electrons in the upper valence band so that they can participate in electricity conduction process. In other words, it is the quantum energy required to overcome the barrier between the valence and conduction bands. The barrier cannot be too small as recombination of electrons and holes may prevail and in turn reduce the efficiency (Zainal *et al.*, 1996). The bandgap energy of the semiconductor cannot be too high (more than 2.5 eV) as this kind of materials can only absorb a small portion of the visible light and waste the energy into heat (Figure 1.2).

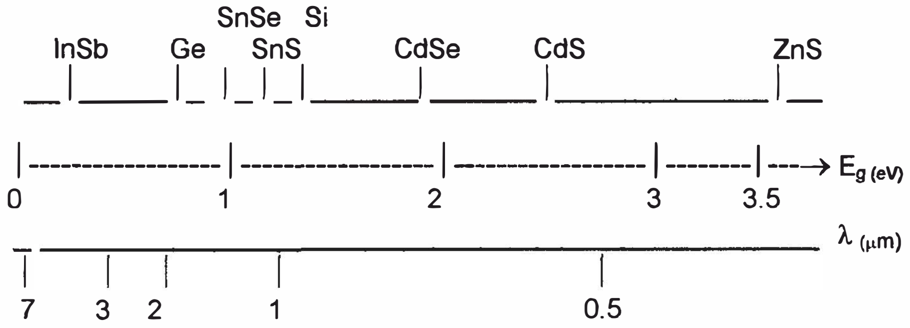

Figure 1.2: Bandgap Energy ($E_g$) of Some Common Semiconductors Relative to the Optical Spectrum (Ben, 1995).

## Semiconductor

A semiconductor, as indicated by the name, has a conduction property between an insulator and a metal. Its conduction property varies with heating and illumination, depending on the forbidden energy gap which separates the valence band (upper filled state) and conduction band (lower empty state), Figure 1.3.

Therefore in the semiconductor, the electrons which upon excitation by light had gone into the conduction band (CB) and the holes (missing electrons left behind in the valence band, VB) have a comparatively long life time, upto recombination, sufficient for them to participate in the electrochemical reaction at the semiconductor-electrode/electrolyte interface (Yuri, 1990).

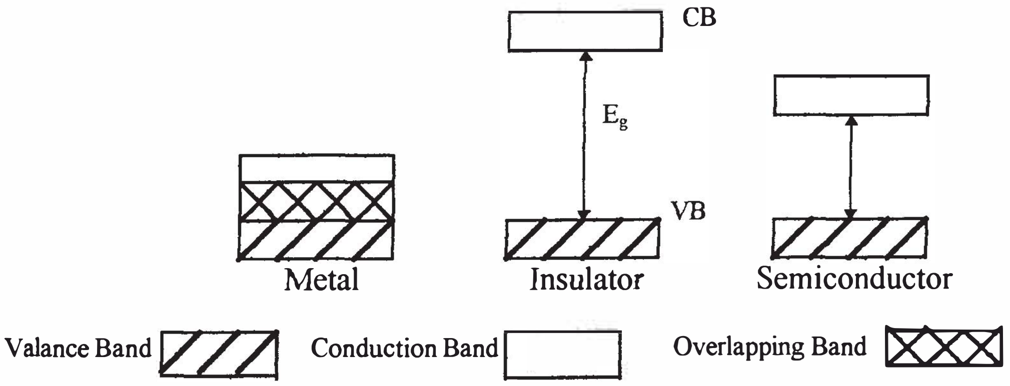

Figure 1.3: The Energy gap ($E_g$) Difference Between the Metal, Insulator and Semiconductor

An important distinction between a metal and semiconductor has been noted by Kavanos, 1990. In a metal, the orbitals are normally so closely packed that when an electron is promoted from a low-lying to higher-lying orbital, the electron almost instantaneously decays back to the lower state. In a semiconductor, the electron does not "relax" so rapidly since it must pass over a wider bandgap. This property make the semiconductor special and more appropriate for certain applications. Each semiconductor is characterised by a bandgap energy, $E_g$. Semiconductor can absorb photons having energy, $h\nu > E_g$ . The energy of each absorbed photon is consumed by raising an electron from the valence-band up to the conduction band and creating an electron and hole pair (EHP). Each photon having $h\nu$ greater than the $E_g$ (up to several $E_g$ ) is capable of generating an EHP, also known as charge carriers. Photons with $h\nu < E_g$ are basically not absorbed by the semiconductor and cannot generate

EHP. This fact and spectral distribution of radiation lead to the conclusion that the carriers-generation rate per unit area is a function of $E_g$ of the semiconductor (Hu and White, 1983).

Semiconductors can be divided into two groups, pure and doped. The pure semiconductors are those with their conductivity and $E_g$ determined by their inherent property. The doped are those with their conductivity and $E_g$ influenced by introducing traces of impurity atoms. By doping a pure semiconductor, the amount of energy required to induce conduction in the semiconductor is greatly reduced. The doped semiconductors can be subdivided into *p*-type (positive) and *n*-type (negative) according to their electrochemical behaviour. They would manifest anodic or cathodic photocurrent depending on their majority carrier current flow (Yuri, 1990). An *n*-type semiconductor would show anodic photocurrent as it contains electrons as its majority carriers while a *p*-type shows cathodic photocurrent flow as it contains holes as its majority carriers. Thus, the *p*-type induces reduction on the electrolyte species at the semiconductor-electrolyte interface while *n*-type induces oxidation, when they are deployed as photoelectrodes in the PECs.

**Direct and Indirect Semiconductors**

Beside the *p* and *n*-type, the semiconductor can also be direct or indirect transition material, depending on its electronic transfer between VB and CB. In its conduction band, the semiconductor has a low laying energy level (minimum, *m*)