UNIVERSITI PUTRA MALAYSIA

ELECTROCHEMICAL PREPARATION AND CHARACTERIZATION OF POLY(3-HEXYLTHIOPHENE)-CADMIUM SULFIDE HYBRID SEMICONDUCTOR FILMS

ING YAH CHZEH

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ELECTROCHEMICAL PREPARATION AND CHARACTERIZATION OF POLY(3-HEXYLTHIOPHENE)-CADMIUM SULFIDE HYBRID SEMICONDUCTOR FILMS

By

ING YAH CHZEH

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

November 2014

Dedicated to my beloved parents, sister and brothers for their love and support

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

ELECTROCHEMICAL PREPARATION AND CHARACTERIZATION OF POLY(3-HEXYLTHIOPHENE)-CADMIUM SULFIDE HYBRID SEMICONDUCTOR FILMS

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November 2014

Chairman : Professor Zulkarnain Bin Zainal, PhD

Faculty : Science

Cadmium sulphide (CdS) is an interesting II-VI semiconductor with medium band gap (~2.4 eV) which can absorb visible light. In this study semiconducting CdS thin films were prepared using potentiostatic electrodeposition and pulse electrodeposition techniques on indium doped tin oxide (ITO)-coated glass substrate at room temperature. CdS thin films were deposited onto ITO coated glass from deposition bath containing 0.01 M $CdSO_4$and 0.35 M $Na_2S_2O_3$ and pH was adjusted to 3 using sulphuric acid. A three electrode-cell system was used where Ag/AgCl | 3 M NaCl as the reference electrode, platinum wire as the counter electrode and ITO-coated glass as the working electrode. Cyclic voltammetry was used to determine the suitable range of deposition potential and the potential range obtained was between –0.75 V to –1.00 V. CdS thin films were deposited by applying various deposition potentials.

XRD patterns showed that the as-deposited CdS thin films were polycrystalline with hexagonal structure with hkl planes corresponding to (100), (002), (101), (102), (103), and (110) reflections. The band gap energy of samples prepared by both techniques was found to be within the range of 2.40 – 2.42 eV with direct transition. Photoelectrochemical (PEC) properties of CdS films were measured, using linear sweep photovoltammetry by intermittently illuminating the samples immersed in 0.01 M $Na_2S_2O_3$with a 300 W halogen lamp. Photocurrent was observed to be more apparent at anodic potential region. Thus, CdS is an n-type semiconductor. XRD and PEC results showed good quality film was obtained at deposition potential of –0.90 V. Cadmium sulfide thin films prepared by the pulse electrodeposition technique exhibit desirable optical properties as semiconductor material and better photoresponse compared with the films deposited by normal potentiostatic electrodeposition technique.

Poly(3-hexylthiophene) thin films were deposited electrochemically onto ITO coated glass in a two-electrode cell, ITO coated glass was used as working electrode and platinum wire as the counter electrodefrom bath comprised of 0.05 M 3-hexylthiophene monomer and 0.10 M tetrabutylammonium tetrafluoroborate (TBATFB) in acetonitrile at deposition potential of 5 V. The effect of solution aging

time on homogeneity of electrodeposited P3HT thin films was studied. A smooth adhered film was obtained using solution aged for 5 days. FTIR showed characteristic bands of 2, 5-disubstituted-3-alkylthiophene. Photocurrent were observed at the cathodic direction indicated that P3HT film deposited in this study is p-type semiconductor. The band gap energy of the prepared P3HT is 1.8 eV with indirect transition.

Organic-inorganic hybrid films based on P3HT and CdS was fabricated by using electrochemical deposition method, a layer of CdS was pulse electrodeposited on P3HT film which was first deposited on ITO. Cyclic voltammetry of P3HT in bath containing supporting electrolytes showed that P3HT is stable in aqueous solution under applied potential and suitable to be used as base layer for cathodic electrodeposition of CdS. The optical properties were analyzed and the band gap energy was found to be 2.07 eV between that of P3HT films (1.8 eV) and CdS (2.4eV) with indirect transition. The photoelectrochemical properties were recorded in the form of current density-voltage curves showed CdS/P3HT presents a higher photocurrent response than that of pure P3HT and absorbs radiation in a wider region.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENYEDIAAN FILEM SEMIKONDUKTOR HIBRID POLI(3-HEKSILTIOFENA)-KADMIUM SULFIDA SECARA ELEKTROKIMA DAN PENCIRIANNYA

Oleh

ING YAH CHZEH

November 2014

Pengerusi : ProfesorZulkarnain Bin Zainal, PhD

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Kadmium sulfida (CdS) merupakan semikonduktor kumpulan II-VI yang menarik dengan tenaga luang jalur serdahana ~2.4 eV yang berkeupayaan untuk meyerap cahaya tampak. Dalam kajian ini, filem nipis semikonduktor CdS telah disediakan dengan menggunakan teknik pengelektroenapan potentiostatik dan pengelektroenapan denyutan atas kaca bersadur timah oksida terdop indium daripada larutan enapan yang mengandungi 0.01 M $CdSO_4$ dan 0.35 M $Na_2S_2O_3$, pH dilaraskan kepada 3 dengan menggunakan asid sulfurik. Sistem sel tiga elektrod digunakan dengan Ag/AgCl | 3 M NaCl sebagai elektrod rujukan, wayar platinum sebagai elektrod kaunter dan kaca bersadur ITO sebagai elektrod kerjanya. Kitar voltametri digunakan untuk menentukan julat keupayaan pengenapan yang sesuai dan lingkungan keupayaan yang diperolehi ialah di antara –0.75 V hingga –1.00 V. Kadmium sulfide telah dienapkan pada beberapa keupayaan enapan yang berbeza.

Keputusan pembelauan sinar-X (XRD) menunjukkan bahawa filem nipis CdS yang terenap bersifat polihablur dengan struktur heksagonal dan mempunyai hkl yang bersepadan dengan refleksi daripada satah (100), (002), (101), (102), (103), and (110) dalam struktur heksagonal. Tenaga luang jalur bagi sampel yang dienapkan dengan menggunakan kedua-dua teknik adalah didapati dalam julat 2.40 – 2.42 eV dengan peralihan langsung. Sifat fotoelektrokimia (PEC) bagi filem nipis CdS telah dinilai dengan menggunakan pengimbasan fotovoltametri linear dengan menyinarkan sampel yang direndam dalam larutan 0.01 M $Na_2S_2O_3$ secara bersela menggunakan lampu halogen 300 W. Arus foto diperhatikan lebih ketara di bahagian anodik. Maka, CdS merupakan semikonduktor jenis–n. Kedua-dua keputusan XRD dan PEC telah menunjukkan bahawa filem yang berkualiti diperolehi pada keupayaan enapan –0.90 V. Filem nipis CdS yang disediakan dengan teknik pengelektroenapan denyutan mempunyai sifat optikal yang diingini sebagai semikonduktor and respon foto yang lebih baik berbanding dengan filem yang dienapkan dengan teknik pengelektroenapan potentiostatik.

Filem nipis poli(3-heksiltiofena) (P3HT) telah dienapkan secara elektokimia atas kaca bersadur ITO dalam sel dua elektrod dengan ITO sebagai elektrod kerja dan wayar platinum sebagai elektrod perantaraan daripada larutan asetonitril yang

mengandungi 0.05 M monomer 3-heksiltiofenadan 0.10 M tetrabutilamonium tetrafloroborat(TBATFB) pada keupayaanenapan 5 V. Kesan masa penuaan larutan enapan pada kehomogenan filem nipis P3HT terenap telah dikaji. Filem terlekat yang rata telah diperolehi menggunakan larutan yang talah dituakan selama 5 hari. Keputusan spektroskopi infra merah transformasi fourier(FTIR) menunjukkan kehadiran kumpulan berfungsi 2, 5-terganti-3-alkiltiofena. Arus foto diperhatikan pada arah katodik menunjukkan bahawa filem P3HT terenap dalam kajian ini merupakan semikonduktor jenis–p. Tenaga luang jalur P3HT tersebut adalah 1.8 eV dengan peralihan tidak langsung.

Filem hibrid organic-inorganik berdasarkan P3HT dan CdS telah disediakan dengan menggunakan kaedah pengenapan elektrokimia, satu lapisan CdS dienapkan secara enapan denyutan atas P3HT yang terdahulu dienapkan atas ITO. Kitar voltametri dijalankan pada P3HT dalam larutan mengandungi elektrolit sokongan dan keputusannya menujukkan bahawa P3HT adalah stabil dalam larutan akueus tersebut pada keupayaan yang diaplikasikan dan oleh itu P3HT adalah sesuai digunakan sebagai lapisan dasar untuk pengenapan katodik CdS. Sifat optikal filem dinilai dan didapati bahawa tenaga luang jalur adalah bernilai 2.07 eV berada di antara nilai tenaga luang jalur filem P3HT (1.8 eV) dan filem CdS (2.4 eV) dengan peralihan langsung. Sifat fotoelektrokimia telah direkodkan dan graf ketumpatan arus-voltan menunjukkan bahawa CdS/P3HT mempersembahkan arus foto yang lebih tinggi daripada arus foto filem P3HT dan ia menyerap radiasi dalam lingkungan yang lebih luas.

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I certify that an Examination Committee has met on 19 November 2014 to conduct the final examination of Ing Yah Chzeh on her PhD thesis entitled "Electrochemical Preparation and Characterization of Poly(3-Hexylthiophene)-Cadmium Sulfide Hybrid Semiconductor Films" in accordance with the 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 Doctor of philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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This is to confirm that:

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_____
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_____
Name of Member of Supervisory Committee: Wan Mahmood Mat Yunus, PhD

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
CV	Cyclic Voltammetry
eV	Electron Volt
EDX	Energy Dispersive X-rays
E_g	Band Gap Energy
e^-	Electron
FTIR	Fourier Transform Infrared Spectroscopy
h^+	Hole
ICDD	International Centre for Diffraction Data
ITO	Indium Tin Oxide
P3HT	Poly(3-hexylthiophene)
PEC	Photoelectrochemical
PL	Photoluminescence
SEM	Scanning Electron Microscopy
UV-vis	Ultraviolet-visible
V_{cd}	Cadmium vancancies
V_s	Sulphur vacancies
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

At present, world primary energy relies heavily on non-renewable energy sources especially fossil fuels such as coal, oil (petroleum) and natural gas. Today, fossil fuels still dominate the world energy consumption, with a market share of 87% (BP Statistical Review of World Energy June 2012). The majority of the world's electricity is currently produced via fossil fuels. The main problem with fossil fuels is the damage that they do to the environment when they are burned. Burning fossil fuels impacts the environment through the production of greenhouse gases. Greenhouse gases including carbon dioxide, water vapour, methane and nitrous oxides together they trap the sun's heat in the earth's atmosphere to cause the greenhouse effect. Greenhouse gas effect is thought to be responsible for acid rain, global warming and related changes in the Earth's climate.

Another most talked problem with fossil fuels is they are finite resource and will run out shortly with heavy consumption. There has been an enormous increase in the global demand for this non-renewable energy in recent years as a result of industrial development and population growth. This extremely uneven energy consumption will eventually causes the coming of energy crisis. In 2011, the violent events of the Arab Spring shook energy markets and cause the oil price to increase globally because of the high dependence on Middle Eastern oil. Beside economy and political instability, energy crisis drives man to shift to the use of nuclear power which led to another major crisis – the nuclear crisis. Nuclear waste can remain radioactive for thousands of years. The nuclear industry has a shameful safety record. There is always the risk of a meltdown or explosion. The Chernobyl disaster was a nuclear accident that occurred on 26th April 1986 at the Chernobyl Nuclear Power Plant in Ukraine. An explosion and fire released large quantities of radioactive particles into the atmosphere, which spread over much of Western USSR and Europe. The fallout from Chernobyl can still be detected in our atmosphere. In 2011, another large nuclear disaster following a major earthquake, a 15-metre tsunami disabled the power supply and cooling of three Fukushima Daiichi reactors, causing a nuclear accident on 11 March 2011 --the Fukushima Daiichi nuclear disaster.

It is therefore a necessity to find a new source of energy. Energy derived from natural processes (e.g. sunlight and wind) that are replenished at a faster rate than they are consumed. Solar, wind, geothermal, hydro, and some forms of biomass are common sources of renewable energy which are continually replenished.

1.1 Solar cells

A solar cell is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect (will be discussed later). The most common seen device is probably calculators with solar cells -- devices that never need batteries and in some cases, don't even have an off button. As long as there's enough light, they seem to work forever.

Over the years solar power has been viewed by many people as the ideal energy source. The hope for a "solar revolution" has been floating around for decades. The idea that one day we will all use free electricity from the sun. This is a seductive promise, because on a bright, sunny day, the sun's rays give off approximately 1,000 watts of energy per square meter of the planet's surface. If we could collect all of that energy, we could easily power our homes and offices for free.

Solar power uses the energy of the sun as source with a great advantage which is no emissions like burning fossil fuels. Solar energy is promising because the Earth receives more energy from the Sun in an hour than is necessary for all humanity within a year (Wong *et al.*, 2010). And this can be done easily by using solar cells to turn the sun light directly into electricity. Solar cells are long lasting sources of energy which can be used almost anywhere. Solar cells provide cost effective solutions to energy problems in places where there is no main electricity. Solar cells are also totally silent and non-polluting. As they have no moving parts they require little maintenance and have a long lifetime. Compared to other renewable sources they also possess many advantages; wind and water power rely on turbines which are noisy, expensive and liable to breaking down.

1.1.1 Photovoltaic cells

A solar cell is also called a photovoltaic cell. That is because the method of harvesting of energy from sunlight and its conversion into electricity is called photovoltaics, which as the name implies, 'photo' means light and 'voltaic' means 'electricity'.

Photovoltaics possess three key properties which make it unique. (i) It directly generates electricity, without the need of generators. (ii) It is a flexible technology that supplies electrical power in form of portable modules in the milliwatt scale up to entire power plants with peak capacities in the multiple megawatt regime; and (iii) it is the only renewable energy which can be customized, i.e., handled by individuals (Hadziioannou and Malliaras, 2007).

Photovoltaic cells are made of special materials called semiconductors. Figure 1.1 shows a simple diagram of a conventional photovoltaic device. It is made of an n-type and a p-type semiconductor, where the charge of the mobile carriers is negative (electrons) or positive (holes), respectively.

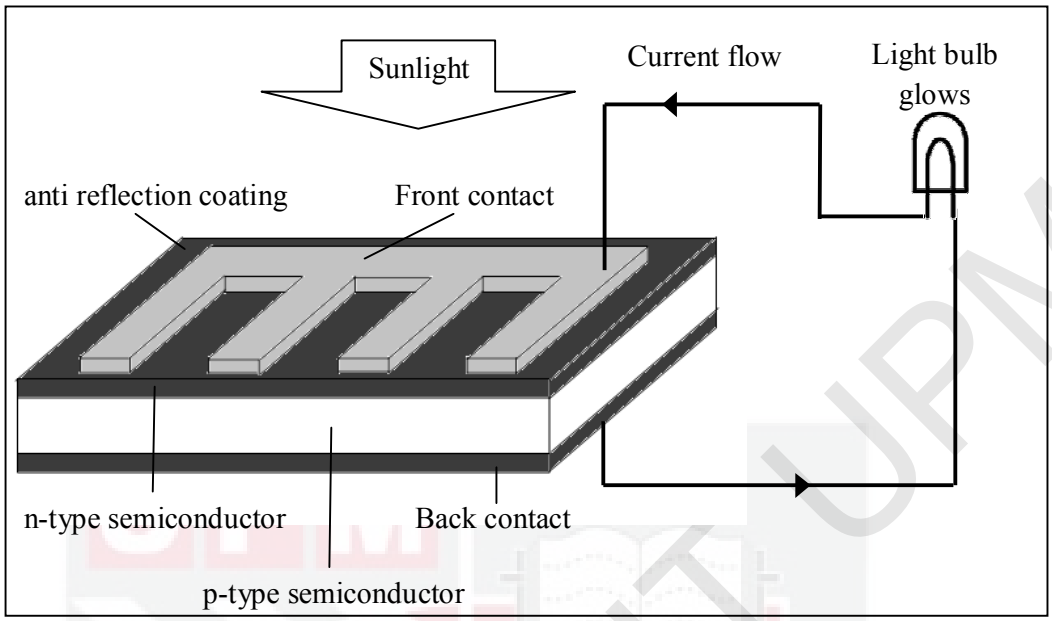

Figure 1.1: Schematic diagram of a photovoltaic cell generates electricity when illuminated by sunlight (Source: How do solar cells work? http://www.brighthub.com/environment/renewable-energy/articles/7470.aspx).

Basically, when the cells are exposed to light, a certain portion of the light struck on the cell is being absorbed within the semiconductor material. This means that the energy of the absorbed light is transferred to the semiconductor. The energy knocks electrons loose, allowing them to flow freely induces electron-hole pairs generation in semiconductors. Spontaneous electron and hole transfer across the junction upon contacting the two materials resulting electric field. The electric field helps to collect the photogenerated carriers producing a net photocurrent (Grätzel, 2007).

1.1.2 Photoelectrochemical cells

Photoelectrochemical cells or PECs are solar cells which generate electrical energy from light, including visible light. Some photoelectrochemical cells simply produce electrical energy, while others produce hydrogen in a process similar to the electrolysis of water. Photoelectrochemical cells are often referred to photocurrent-generated devices having photosensitizer molecules in contact with electrolytes, which distinguished them from solid state solar cells (do not contain liquid). In PEC cell semiconductor photoelectrode, an electrolyte, and counter electrode are the three basic constituents. These conversion cells have such potential advantages as, a) easy method of fabrication, b) no problem of lattice mismatch, c) no need for antireflection coatings, d) with proper choice of an electrolyte redox couple, the Fermi level of an electrolyte could be adjusted to a desired level etc, over the conventional devices. In theory, there are three options for the arrangement of photo-electrodes in the assembly of PECs (Tryk *et al.*, 2000):

- photo-anode made of a n-type semiconductor and a cathode made of metal;

- photo-anode made of a n-type semiconductor and a photo-cathode made of a p-type semiconductor;
- photo-cathode made of a p-type semiconductor and an anode made of metal.

According to the principle of PECs, the two photo-electrodes are optical function, required to obtain maximal absorption of solar energy, and catalytic function, required for other reactions such as water decomposition.

Consequently, the development of high-efficiency photoelectrodes that satisfy the requirements entails processing of the materials in order to achieve optimized properties in terms of performance characteristics, including high efficiency of solar energy conversion, durability in aquatic environments, and low cost.

Figure 1.2 presents a schematic diagram of a PEC prepared by two electrodes: a semiconductor film on a substrate (the photoelectrode) connected through an external meter to a second electrode (the counter electrode).

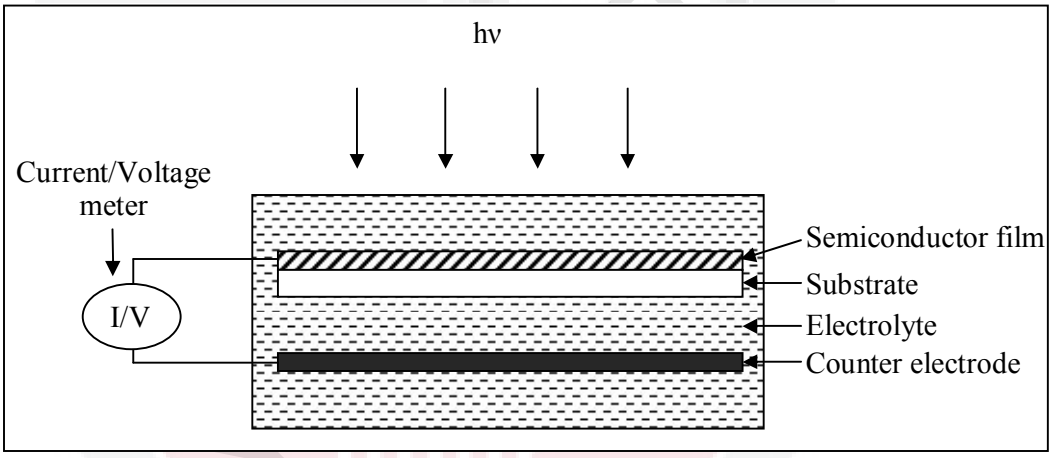

Figure 1.2: Schematic diagram of side view of a PEC cell (Hodes, 2003).

Both electrodes are immersed in an electrolyte containing suitable redox couples, and the semiconductor film is exposed to illumination. A light (hν) with photon energy higher than the band gap (E_g) of semiconductor is used for illumination, light absorbed by semiconductor induced the generation of electron-hole pairs. The holes flow to the semiconductor/electrolyte junction and take part in the oxidizing of some species in the electrolyte. While, electrons flow to the counter electrode through external circuit and reduce some electrolyte species (Hodes, 2003).

1.2 Semiconductor

Semiconductor is composed of two words 'semi' and 'conductor', and as its name implies, it is a material which has electrical conductivity between that of a conductor and an insulator. Metals contain a band that is partly empty and partly filled regardless of temperature. Therefore they have very high conductivity. Semiconductors usually have E_g in the range of 1 eV – 4 eV (Rajeshwar, 2007). The

lower most band is called the valence band which is almost fully occupied in an insulator or semiconductor (Figure 1.3). The uppermost, almost unoccupied band is called the conduction band because only when electrons are excited to the conduction band can current flow in these materials. In general, these bands are separated by a forbidden region or band gap energy (E_g). The electrical and optical properties of the solid are strongly influenced by the size of the band gap. The difference between semiconductors and insulators is the magnitude of the band gap energy (E_g) between the filled and vacant bands. The forbidden band gap between the valence band and conduction band is larger in an insulator, so that fewer electrons are found there and the electrical conductivity is lower. Because one of the main mechanisms for electrons to be excited to the conduction band is due to thermal energy, the conductivity of semiconductors is strongly dependent on the temperature of the material (Bard and Faulkner, 2001).

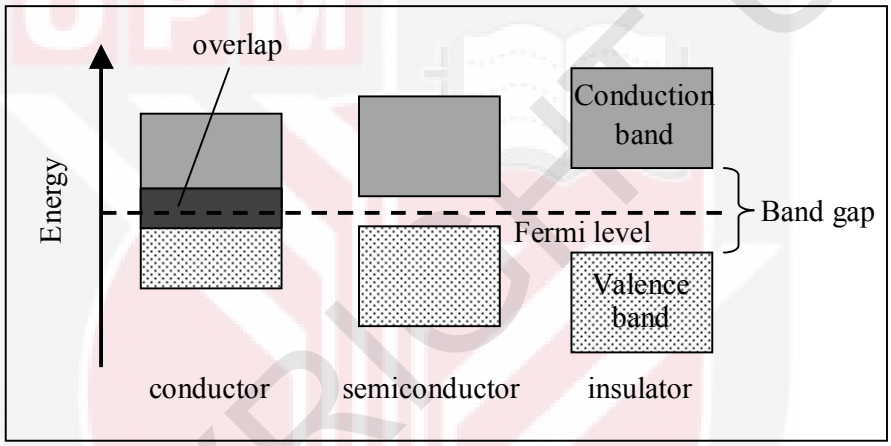

Figure 1.3: Simplified diagram of the electronic band structure of metals, semiconductors, and insulators.

One of the most important components in the assembly of photoelectrochemical cell is the semiconductor photoelectrode. As the charge transfer rate across the semiconductor/ electrolyte junction and generation of the short circuit current *Isc* (as the current flowing through the external circuit when the load resistance and the voltage across are zero) and open circuit voltage V_{oc} (as the load resistance is infinity, and current is zero in the external circuit) in PEC cell are directly related to both the properties of a semiconductor and an electrolyte, the performance and effectiveness of a photoelectrochemical cell device mainly depend upon them. Hence, the choice of the semiconductor involved is very crucial.

1.2.1 Types of semiconductors

There are two types of semiconductor, (a) intrinsic semiconductor and (b) extrinsic semiconductor. An intrinsic semiconductor is chemically very pure material which possesses poor conductivity. It carries equal number of negative and positive charge carriers. Extrinsic semiconductors are improved version of intrinsic semiconductors.

Small amount of impurities are added by doping process to alter the electrical properties and to improve the conductivity of the semiconductor. Doping process creates two groups of semiconductors: (i) negative charge semiconductor or n-type; electrons are major carriers and holes are minor carriers and (ii) positive charge semiconductor or p-type; holes are major carriers and electrons are minor carriers.
In doping semiconductors, impurities are introduced into crystal structure of a stoichiometry semiconductor to alter its conductivity. In n-type semiconductors, the electron energy levels are near the top of band gap, causes easy excitation into the conduction band (Figure 1.4). In p-type semiconductors, extra holes lie in band gap allow excitation of valence band electrons leaving mobile holes in valence band (Singh, 2009).

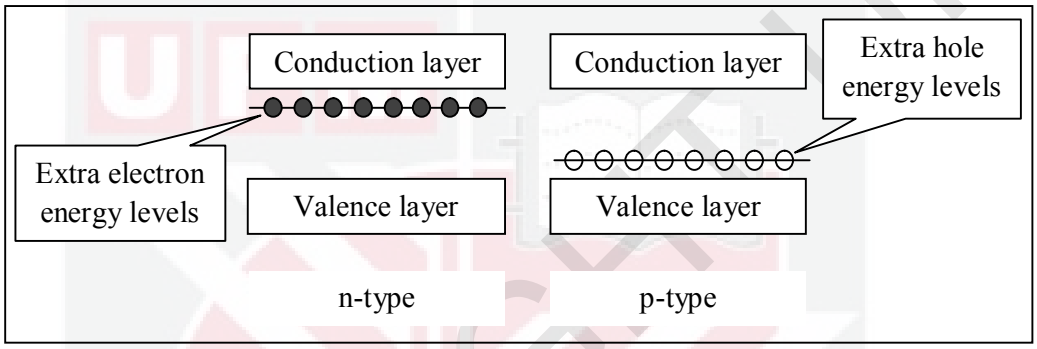

Figure 1.4: n-type and p-type semiconductors (Singh, 2009)

Various semiconducting materials have been used in the fabrication of solar cells with varying efficiencies and have varying costs. Semiconductors presently used for photovoltaic solar cells include monocrystalline silicon, polycrystalline silicon, armophous silicon that are cut into wafers from bulk materials. Till now, silicon remains the most popular material for solar cell. High cost single-crystal silicon can be replaced by polycrystalline silicon in manufacturing of high performance solar cells. However, in order to be useful as a semiconductor material in solar cells, polycrystalline silicon must be refined to a purity of 99.9999% (six nines) which costs many millions in the manufacturing process. As a result, researchers continuously found and developed low-cost alternatives such as nanocrystalline TiO_2 (Lee *et al.*, 2001; Dozzi and Selli, 2013; Tsai *et al.*, 2014), other metal oxides like ZnO (Gal *et* al., 2000; Thambidurai *et* al., 2013; Yao, *et al*., 2014), chalcogenide materials (Sato *et al*., 2005; Jones *et al*., 2009; Gao *et al*., 2014) and conducting polymers (Venkatesan *et al*., 2014).

1.3 p-n junction

Solar cells are often fabricated from a range of inorganic and organic p-n junction. A junction between a p-type and an n-type semiconductor is important in many semiconductor devices. A p-n junction is achieved by combining together p-type and n-type semiconductors closely. Both p-type and n-type semiconductors are conductive but the junction between them is non-conductive, the non-conductive

layer is known as the 'depletion zone' (Figure 1.5). Assume that there are only holes in the p-region and electrons in the n-region, because of the density gradient across the junction, electrons will diffuse through the junction to the left, and holes to the right. These mobile electrical charge carriers (electrons in n-type and holes in p-type) attract and eliminate each other in recombination process. As a result, the acceptor ions near the junction in the p-region and the donor ions near the junction in the n-side are left unneutralized. An electrical field is generated across the junction directed from the n-region to the p-region (Chattopadhyay, 2006; Achuthan and Bhat, 2007).

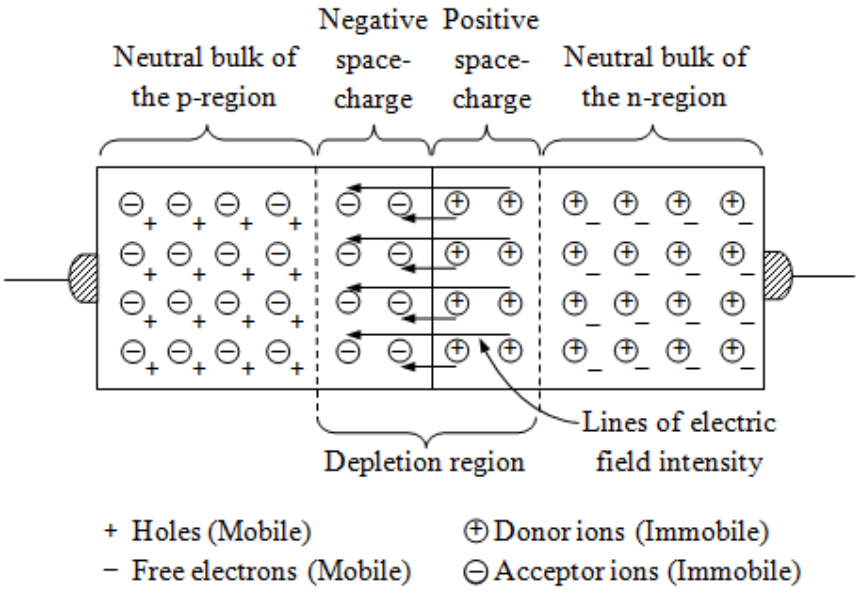

Figure 1.5: Schematic diagram of a p-n junction showing mobile and immobile charges (Chattopadhyay, 2006).

1.4 CdS thin films

Thin chalcogenide films are of particular interest for the fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensors etc. Materials of II-IV class semiconductors and related compounds are among the leading candidates of the new generation photovoltaic solar cells. Chalcogenides of cadmium were proven to be efficient absorbers of electromagnetic radiation due to their high absorption coefficient with an allowed direct type of transitions, nearly matching band gaps with the visible region of the electromagnetic spectrum and high photosensitivity over a considerable range of photon energy (Sharma *et al.*, 2004). Intensive studies have been carried out on the preparation of polycrystalline CdS thin films because of its usefulness in fabrication of various solid-state devices. CdS is an n-type semiconductor with optical band gap of 2.42 eV which can absorb visible light, thus it is an ideal material widely used in thin film solar cells with p-type semiconductors to form heterojunctions (Lee *et al.*, 1999; Johnson 2000; Duffy *et al.*, 2002; Sharma *et al.*, 2003). In these devices, light penetrates the CdS layer and is

absorbed in the p-type semiconductor close to the pn junction (Ximello-Quiebras *et al.* 2004).

1.5 Poly(3-hexylthiophene) thin films

Extensive research in the field of conducting polymers started in year 1977 when the simplest conjugated polymer, polyacetylene was demonstrated that it can be made electrically conductive through a chemical doping reaction which involves partial reduction or oxidation (n-type or p-type doping) of its spatially extended π-bonding system (Chiang *et al.*, 1978). This discovery induced intensive research in this field especially related to the synthesis, doping, spectroscopic, photo-physical, structural and electrical characterization of systems such as polyacetylene, polypyrrole, polyaniline, polythiophene, polyparaphenylene and their copolymers, composites or blends, etc (Singh *et al.*, 2006).

Thin films based on these π-conjugated conducting polymers have been studied intensively due to their promising electrical and optical characteristics. They are gaining more attention among researchers for widespread applications in optoelectronic devices, electroactive organic compounds are being investigated in photovoltaic (PV) solar cell technologies (Coakley and McGehee, 2003; Li *et al.*, 2005; Wang *et al.*, 2007), and in light emitting diodes (LEDs) (Na *et al.*, 2009; Valadares *et al.*, 2009) and field effect transistors (FETs) (Dimitrakopoulos and Malenfant, 2002; Gburek and Wagner, 2010).

Among all conjugated polymers, polythiophene is one of a range of conducting polymer which has been the subject of considerable recent interest because of their good environment stability and easy modification of the properties by designing the synthesis parameters. However, this useful polythiophenes are infusible and insoluble in common organic solvents. Insertion of long alkyl side chains at the monomer 3 position increase solubility of the polymer (Sandstedt *et al.*, 1995).

Alkyl-substituted polymers especially poly(3-alkylthiophene) are very attractive because of their high solubility in common organic solvent (Nakao *et al.*, 2008). This solution processible polythiophene derivatives, poly(3-hexylthiophene) (P3HT) have been studied extensively because of its excellent optical, electrical properties and chemical stability (Pang *et al.*, 2007).

1.6 Significance of study

This project is carried out to prove that a bilayer p-n junction solar cell can be solely fabricated by using electrodeposition method. The potential contributions are (i) to reduce the manufacturing cost of solar cell materials as electrodeposition uses relatively lower concentration of starting materials and are carried out at room temperature and room pressure, (ii) to prove that by combining organic and inorganic semiconducting materials in solar cell will improve the photoefficiency of solar cell. Therefore it is absolutely necessary to carry out this project to promote the application of electrodeposition method in preparation of solar cell materials.

1.7 Problem statement

Global demand for solar cell materials has increased due to its cleanliness in converting solar energy into electricity. However, preparation of the materials and fabrication of devices are usually costly. Electrochemical preparation methods are relatively cheaper as compared to other physical methods especially in this study, the hybrid films are deposited at room temperature which further lowered the processing cost. In this study, CdS thin film was deposited by using two different electrochemical techniques which are potentiostatic and pulse electrodeposition. Very few reports on pulse electrodeposition of CdS were made by researchers. If so, post-deposition heat treatment was applied to obtain hexagonal phase CdS which is a more stable as compared to cubic phase. In this study, by using the deposition bath used by Fatas *et al.* (1987), it is possible to obtain hexagonal phase CdS film at room temperature and does not require a post-deposition thermal annealing treatment. In order to fabricate hybrid CdS/P3HT electrochemically, deposition of CdS has to be conducted at room temperature to avoid the possibility of corrosion of P3HT films in high temperature bath. Also, post-deposition annealing can cause the decomposition of P3HT as organic compounds are usually having lower thermal stability than inorganic compounds.

Low efficiency of single layer organic solar cell is also a problem that was being addressed of solar devices fabricated. To remedy this situation, an inorganic CdS layer was deposited onto P3HT thin film in this study. The hybrid CdS/P3HT solar cell gathers advantages from both inorganic and organic materials.

Transparent conducting indium doped tin oxide (ITO) substrate is very useful in solar cell devices but there are no studies reported in the literature related to deposition of P3HT on ITO substrate because P3HT film has very poor adherence on ITO glass at low depositing potentials. Thus, attempts have been made in this study to electrodeposit P3HT film on ITO glass at higher depositing potential. There are many reported studies on solar cells based on the hybrid of P3HT and inorganic compound. However, there were none of them using electrochemical deposition for both layers. Since electrodeposition is very promising technique in preparing film, it is reasonable to prepare a hybrid film using only electrochemical method.

1.8 Objectives

The objectives of this study are:

1. To electrodeposit CdS thin films using potentiostatic electrodeposition and pulse electrodeposition onto ITO-coated glass substrates.
2. To electrodeposit P3HT thin films onto ITO-coated glass substrates.
3. To prepare CdS/P3HT hybrid films using electrodeposition onto ITO-coated glass substrates.
4. To determine the crystal structure, surface roughness, surface morphology and elemental composition of the films.
5. To evaluate the photoelectrochemical and optical properties of the films.

1.9 Scope of study

This study centred its scope on development of a bilayer CdS/P3HT p-n junction by using electrodeposition method for solar cell application. Two electrochemical techniques namely potentiostatic electrodeposition and pulse electrodeposition will be used to deposit CdS onto ITO. Phase purity, photoelectrochemical properties and surface morphology of the films by using both techniques will be compared to assist selection of the more suitable technique to prepare CdS for solar cell application. Then, attention will be turned to electrodeposit P3HT on ITO. Based on the P3HT on ITO, the final step will be to elecrodeposit CdS onto P3HT through electrodeposition technique. The work documented here focuses on using current and voltage analysis to study photoelectrochemical properties of CdS, P3HT and hybrid CdS/P3HT hybrid films.

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