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POTENTIOSTATIC AND PULSED ELECTRODEPOSITION OF ZINC SELENIDE THIN FILMS

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By

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

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Chairman: Professor Zulkarnain Zainal, PhD

Faculty: Science

Zinc selenide attracts a lot of attention due to its wide potential applications in photovoltaic and optoelectronic devices, photodiodes, superionic conductors and sensors. Among all the techniques to synthesize ZnSe, electrodeposition is the simplest and the most cost-effective as well as it enables low temperature growth. However, in the previous work the influence of electrodeposition parameters in producing stoichiometric ZnSe and the effect on the photocurrent and optical properties were not studied in detail. In this work, ZnSe films were electrodeposited to produce stoichiometric films on ITO and their structural, optical and photoeelctrochemical properties were studied. The effect of varying selenium concentrations on the stoichiometric and optical properties of the films was also investigated.

The deposition potential range for synthesizing zinc selenide films was determined using cyclic voltammetry. Film produced was characterized using X-ray Diffractometry

(XRD) to determine the crystal structural, Linear Sweep Photovoltammetry Test (LSPV) to evaluate the photosensitivity to light, Scanning Electron Microscopy (SEM) to examine on the film morphology and High Surface Profiler to determine the film thickness. Optical band gap and the transition type of the films were determined using data obtained from UV-Vis Spectrophotometer. The electronic properties of ZnSe thin films were investigated by photoluminescence (PL) technique.

Potentiostatic eletrodeposition was carried out at different deposition potential, selenious acid concentrations, deposition time, bath temperatures and annealing temperatures. The XRD pattern showed that both as-deposited and annealed ZnSe films obtained from the increases deposition potential from -1.0 V to -0.6 V were polycrystalline with cubic phase for all selenious acid concentrations from 4 mM to 10 mM. Increasing deposition time from 1 hour to 3 hours and bath temperature from 27 °C to 80 °C, however, favors the growth of selenium rich films. Zinc selenide forms better deposit in acidic condition with optimum pH of 2.00.

Pulse electrodeposition was carried out by varying the cathodic pulse potential and duty cycles of 30 %, 50 %, 70 % and 90 %. The photocurrent response of the deposit increases with increasing duty cycles. However, the deposits showed poor photocurrent compared to samples deposited by potentiostatic technique.

The ZnSe films preparative parameters of both techniques were optimized based on their photosensitivity and stoichiometry of the films. All films exhibit good photoresponse towards white light with p-type semiconducting character in photoelectrochemical test. Calcination at temperature above 200 °C reduced the selenium content and improved the stoichiometry of the films. The film showed direct optical transition with the band gap of 2.65 eV.

The photoluminescence studies the fundamental electronic properties of ZnSe. Stoichiometric ZnSe films with different thicknesses were illuminated at different excitation wavelengths. Emission peak became more intense and narrow as the films excited to higher excitation wavelength. The ZnSe emission spectra obtained at a wavelength range is associated to the blue region which makes it suitable for fabrication of light emitting devices operating in the blue-green light and short-wavelength devices.

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

PENGELEKTROENAPAN POTENTIOSTATIK DAN DENYUT FILEM NIPIS ZINK SELENIDA

Oleh

NG SOOK MEY

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Zink selenida menarik perhatian ramai disebabkan oleh kepelbagaian potensi aplikasi dalam peranti fotovoltan dan optoelektronik, fotodiod, superionik konduktor dan penderia. Antara semua kaedah sintesis ZnSe, kaedah pengelektroenapan merupakan kaedah yang paling mudah, kos efektif dan boleh dilakukan pada suhu rendah. Walaubagaimanapun, di dalam kajian terdahulu, pengaruh parameter elektroenapan dalam penghasilan stoikiometri ZnSe serta kesan fotoelektrokimia dan optik tidak dikaji secara terperinci. Dalam kajian ini, ZnSe telah dielektroenap di atas ITO dan ciri struktur hablur, optic dan fotoeletrokimia dikaji. Selain itu, kesan perubahan kepekatan selenida terhadap stoikiometri dan sifat optik filem juga diselidiki.

Julat keupayaan pengelektroenapan filem ZnSe ditentukan dengan kitaran voltammetri. Filem yang dihasilkan dianalisis dengan peralatan Pembelauan Sinar-X (XRD) untuk menentukan struktur enapan. Ujian fotoeletrokimia (LSPV) dilakukan untuk menilai

fotosensitiviti filem terhadap cahaya. Mikroskopi Pengimbasan Elektron (SEM) untuk kajian morfologi filem dan *surface profiler* untuk menentukan ketebalan filem. Luang optik dan jenis peralihan zink selenida ditentukan melalui data yang diperolehi daripada spektrofotometer ultralembayung dan nampak (UV-Vis). Sifat-sifat elektronik filem nipis ZnSe telah disiasat dengan teknik fotoluminesen (PL).

Elektroenapan potentiostatik telah dijalankan pada pelbagai keupayaan, kepekatan asid selenida, masa, suhu larutan dan suhu pemanasan. XRD memaparkan kesemua filem ZnSe diperolehi melalui pengenapan dan penyeduhlindapan pada keupayaan antara -1.0 V sehingga -0.60 V adalah polihablur berfasa kuibik. Kepekatan asid selenida yang digunakan adalah 4 mM – 10 mM. Penambahan masa pengenapan daripada 1 jam kepada 3 jam dan suhu larutan daripada 27 °C hingga 80 °C menggalakkan pertumbuhan filem yang kaya selenida. Zink selenida tumbuh lebih baik dalam keadaan berasid dan mencapai optima pada pH 2.00.

Denyut elektroenapan dijalankan dengan menpelbagaikan keupayaan denyut pada katod dan kitaran kerja 30%, 50%, 70% dan 90%. Tindakan fotoarus enapan bertambah dengan pertambahan kitaran kerja. Walaubagaimanapun, enapan menunjukkan fotoarus rendah berbanding sampel-sampel dienapkan oleh teknik keupayaanstatik.

Parameter penyediaan filem ZnSe dengan kedua-dua teknik telah dioptimumkan berdasar fotosensitiviti dan stoikiometri filem. Semua filem menunjukkan fotoaktiviti yang baik terhadap cahaya putih dengan ciri semikonduktor jenis-p di dalam ujian fotoelektrokimia. Pemanasan pada suhu melebihi 200 °C telah menurunkan kandungan selenida dan meningkatkan stoikiometri filem. Filem menunjukkan jurang tenaga peralihan terus dengan nilai 2.65 eV.

Fotoluminesen menguji sifat asas elektronik ZnSe. Filem ZnSe dengan stoikiometri tetapi ketebalan yang berbeza telah disinarkan cahaya dengan panjang gelombang pengujaan berbeza. Puncak tenaga pemancaran lebih tertumpu apabila filem diuja pada panjang gelombang yang lebih panjang. Spektra pemancaran ZnSe yang dienapkan dalam kajian berada pada julat panjang gelombang rantau biru. Ini menjadikannya sesuai untuk digunakan di dalam peranti yang beroperasi dalam cahaya biru-hijau dan peralatan gelombang pendek.

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I certify that a Thesis Examination Committee has met on 13th June 2013 to conduct the final examination of Ng Sook Mey on her thesis entitled “Potentiostatic and Pulsed electrodeposition of Zinc Selenide Thin Film” in accordance with the Universities and University College Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the students be awarded the Master of Science.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

NG SOOK MEY

Date: 13th June 2013

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2θ	Two thetha
CV	Cyclic voltammetry
eV	Electron volt
FESEM	Field Emission Scanning Electron Microscopy
PEC	Photoelectrochemical
SEM	Scanning Electron Microscopy
UV-VIS	Ultraviolet-Visible

CHAPTER 1

INTRODUCTION

1.1 History background of semiconductor electrodes

The great evolution of thin film in the last few centuries is due to its variety of application as semiconductor electrodes. The semiconductor electrodes have been used in a variety of applications including liquid junction solar cells, photolytic splitting of water, semiconductor processing and sensor technology. Due to the concern over depletion of global fossil fuels, photoelectrochemical cell have developed intensively as solar energy conversion to electricity and chemical fuels.

The use of semiconductor as an electrode in photoelectrochemical cell was first introduced by Becquerel in 1839. He discovered the illuminated silver chloride electrode immersed in different pH electrolytes exhibited some photovoltaic effect. However, his findings were mainly for academic purposes and obtained considerable attention only after 1970s. Researchers had proven the possibility of using semiconductor such as titanium dioxide (TiO_2) in converting solar energy to chemical or electrical energy by decomposing water under sunlight to produce hydrogen and oxygen. Due to its non-polluting, renewable energy resources and flexibility with respect to conventional fuel alternatives, this finding had attracted researchers around the world to involve in semiconductor- electrolyte interface research.

Although TiO_2 semiconductor is stable against photocorrosion, it has poor delivery efficiency due to its wide band gap of 3.20 eV. Thus, sulfides and selenides semiconductor with optimum band gap are more efficient and gained intense interest in synthesizing semiconductor. Many efforts had been directed to generation of optoelectronic devices based on wide band gap semiconductors. Zinc selenide, ZnSe thin film have a wide band gap of 2.70 eV and capable in emitting light in the blue-green region which gained much interest in light emitting diode.

1.2 Semiconductor energy conversion

The development of semiconductor materials for solar energy conversion devices has been conducted throughout the world in order to exploit the abundance solar radiation. In many applications, the photovoltaic cell technology is ideal as it requires no or very little maintenance and lubrication. Semiconductor electrodes or thin films used in photovoltaic cell has photoelectric effect due to the generation of positive (holes) and negative (electrons) charge carriers in a solid state when the surface is illuminated with light of appropriate energy.

The photon strike is captured by semiconductor and caused transition of electron from valence band to conduction band. The wavelength of the light used should be equal or greater than the semiconductor energy band gap, E_g to enable transition process to occur. The valence electron captured sufficient energy will jump into conduction band resulting in electron-hole pair (e^-h^+) formation. However, the electron in e^-h^+ pair often recombine very quickly with the captured light degraded to heat or emission of photon.

In wide band gap semiconductor, the formation of e^-h^+ pair requires high energy light source such as ultra-violet light to excite valence electron to conduction band. The e^-h^+

pair formed will hardly recombine back and this resulting in higher energy conversion. Thus, wide band gap semiconductor is useful in making short-wavelength devices.

However, for short band gap semiconductor, the valence electrons can be excited easily to conduction band using low energy light. The e^-h^+ pair formed often recombine easily due to the short band gap separation. This recombination process leads to most energy is not converted and lost to heat. Therefore, to utilize the electricity generation, the e^-h^+ pair must be separated to minimize recombination process. This value of separation is determined by the band gap energy, E_g of the film.

1.3 Thin Films

Thin films are solid material build up as thin layer on a solid substrate or support using physical or chemical methods. This thin material layers have a thickness ranging from fractions of nanometer to several micrometers. The quality of the thin films produced depends on several factors such as method of deposition, the substrate materials, the substrate temperature, the rate deposition and the background pressure.

Thin films have grown dramatically in the last few years due to its wide usage and application mostly as optoelectronic devices. The popularity of thin film leads to the needs and approaches for their preparation methods and characterizations to expand significantly. Thin films synthesized using II-VI semiconductors have wide band gap energy and can be utilized in a variety optoelectronic application such as solar cells, semiconductors, photoconductors, photodiodes and light emitting diodes.

1.3.1 Thin Films Preparation

Good quality thin film can be prepared by physical or chemical techniques. Several physical techniques such as molecular-beam epitaxy, vacuum evaporation, sputtering, spray pyrolysis, pulsed laser deposition and chemical vapour deposition have been employed for the deposition of ZnSe thin film.

However, due to the physical technique requires expensive and complex experimental set-up, chemical techniques showed more favourable features. Chemical techniques such as chemical vapor deposition, electrodeposition, Langmuir- Blodgett technique, photochemical deposition (Kumaresan *et al*., 2002) and chemical bath deposition (CBD) are some of the techniques used widely by researchers around the world.

In chemical technique, thin films are formed by deposition of elements from aqueous solution which requires simple experimental set-up, inexpensive and easily scalable. Electrodeposition technique is one of the most widely accepted chemical techniques for its economical and efficient growth of thin films from aqueous solution.

1.3.2 Thin film growth process

Thin film produced from the deposition process involves three simple growth steps. These three growth steps consisting of nucleation process, surface diffusion controlled growth of nuclei and adherence onto the substrate to give continuous film. The initial step in deposition is the charged or uncharged species from bath deposition accumulates at the interface between semiconductor surface and electrolyte. This species at this interface will be transported to the substrate medium by diffusion process. The species will condensed onto the substrate surface forming solid deposits. The deposits will form a film through nucleation and growth process.

1.4 Zinc Selenide

Zinc selenide is a well-known II-VI semiconductor with a solid brownish appearance. It has wide band gap energy of 2.70 eV which associates to blue-green light region. Due to the many production of red and orange light emitting diode, many efforts are currently directed to a new generation photodiodes based on wide band gap semiconductors. Although normally zinc selenide is an n-type semiconductor, the electrodeposited zinc selenide present p-type semiconductor as inferred in photoelectrochemical response. The photoconductivity type of zinc selenide depends on the electrolyte composition whether it consist excess of zinc or selenium.

Electrodeposition of zinc selenide is studied in comparison to cadmium chalcogenides thin film. The deposition of zinc selenide is difficult due to the wide difference in the reduction potential of zinc and selenium ions. However, stoichiometric films can be produced by using suitable deposition potential and electrolyte compositions. Various promising applications of zinc selenide in optoelectronic devices (Gudage *et al*., 2009; Samantilleke *et al*., 2001; Matsuura *et al*., 1991), photodiodes, light emitting diodes and thin film solar cells as window material (Gavrushek *et al*., 2003)

In many of the review, in order to obtain a Zn/Se ratio close to 1 in the film, the deposition bath should contain high concentration of zinc (II) ion and a very low concentration selenious acid.

1.5 Semiconductor theory

Semiconductors are materials with properties of conductors and insulators. The properties of semiconductor and their difference between metal and insulator can be understood by examining their electronic structure. The energy band is obtained from the motion of a single electron in the crystal lattice and it is assumed that there is no interaction between the electrons and lattice points. This condition is called the zero potential energy. However, in real crystal, the electrons interact with the periodic potential field created by orderly arranged ions in the lattice. The electronic waves lead to formation of energy gaps in the band called band gaps (Figure 1).

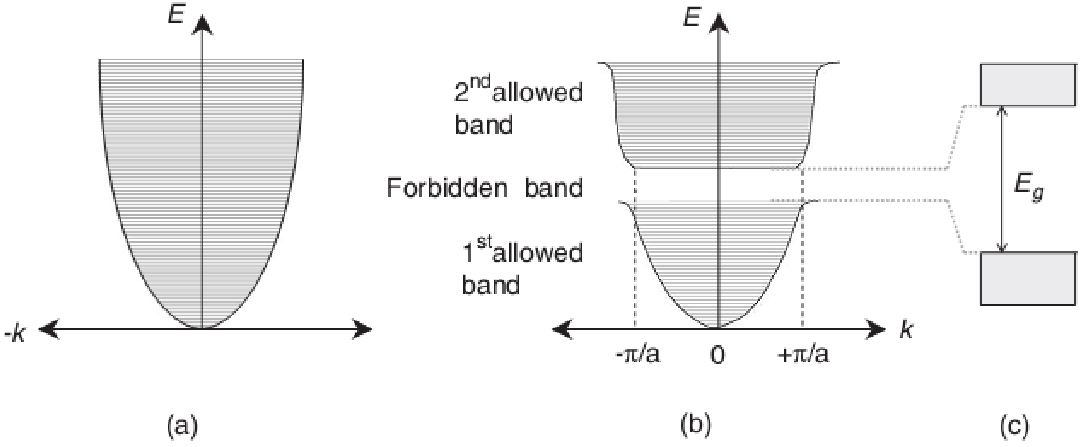

Figure 1: (a) Parabolic plot of energy, E vs. wave vector, k for free electron at zero potential energy where electron can acquire any value of energy. (b) The formation of forbidden band with lower hashed area is called valence band and the upper hashed area is conduction band. (c) The band model structure of solid. (McHale, 2011)

Electrons are filled in the atomic and molecular orbital (valence band) and the vacant anti-bonding orbital (conduction band) forming continuous bands. If the valence band and conduction band are partially or fully filled, the material is classified as metal. If the valence band is completely filled and the conduction band is empty, the material has properties either an insulator or semiconductor depending on its band gap energy, Eg value as shown in Figure 2.

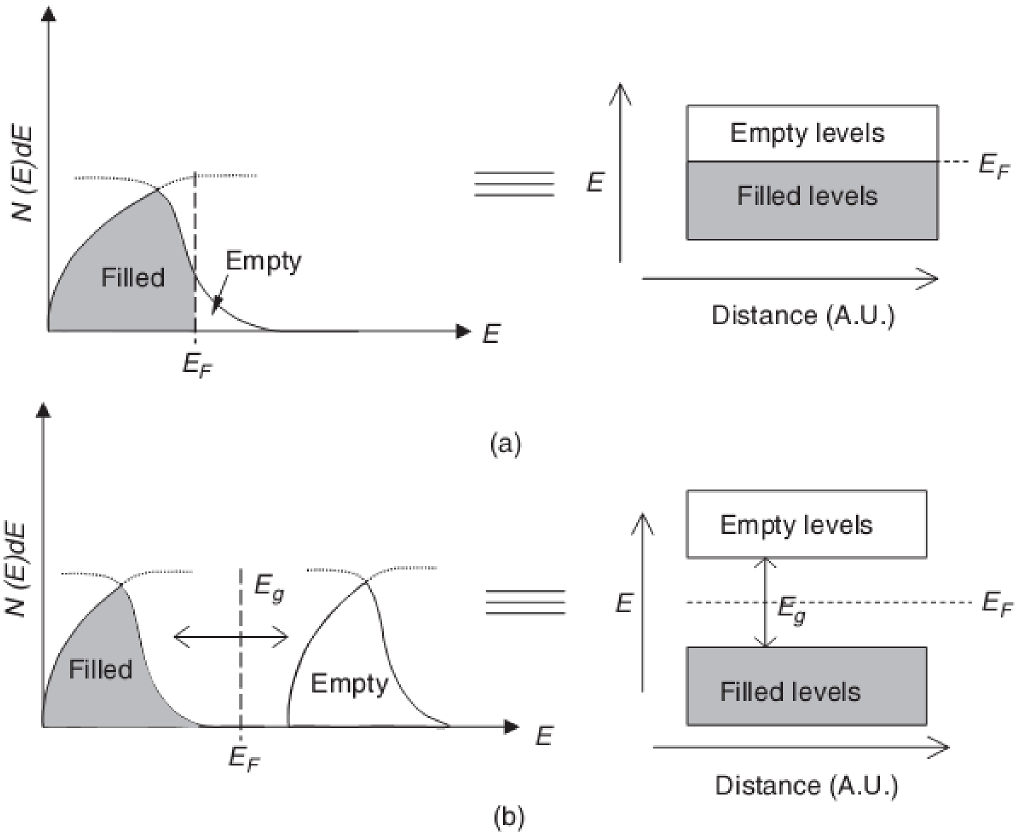

Figure 2: Band structure of (a) metal and (b) semiconductor. Right-hand side diagrams are plot of number of valence electrons vs. energy level. Left-hand side illustrations are the energy band gap difference between metal and semiconductor. (McHale, 2011)

1.6 Direct and Indirect Band Gap

Semiconductor optical transition can be classified into two types, namely direct and indirect transition as shown in Figure 3. Direct gap is the maximum energy of valence band and minimum energy of conduction band occurs at the same wave vector, k = 0 at the same crystal momentum. When illuminated, the electrons from valence band can be directly transited into conduction band which aligned directly above valence band. Examples of direct gap semiconductors are GaAs, InP, and InGaAs.

An indirect gap is the maximum energy of valence band and minimum energy of conduction band occurs at different wave vector, k = 0 at the same crystal momentum. Si, Ge, and AlAs are few of indirect gap semiconductors. An indirect transition involves the change in momentum for electron. The electrons in valence band can absorb a photon only if the phonon participates in the process. Therefore, indirect materials have weak interaction with light.

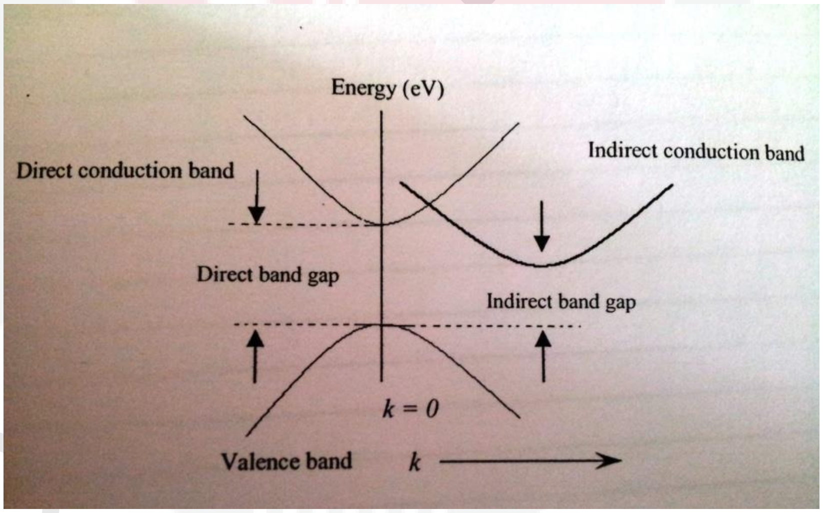

Figure 3: Variation of energy for direct and indirect semiconductors at crystal momentum.

The mobility of electrons in the conduction band and holes in the valence band imparts conductivity to the semiconductor crystal. At high temperature, valence electrons gain sufficient energy and are delocalized to the conduction band forming holes in the valence band. Electron-hole pairs are formed and this type of semiconductor is called an ‘intrinsic’ semiconductor. However, if there are other foreign atoms present in the electron-hole pairs, the semiconductor is called ‘extrinsic’ semiconductor. The foreign atoms are introduced into the crystal by a process called doping and present as a donor or acceptor atoms in the band gap region.

If a crystal is doped with a donor atom, the donor states are created in the band gap. This donor state or atom located beneath the conduction band where the electrons are ionized and promoted easily into the conduction band even at room temperature. Thus, the density of electrons in conduction band is increased compared with density of holes in the valence band. This conductivity is attributed to conduction band electrons (majority carriers) and this material is called an n-type semiconductor as shown in Figure 4(a).

In contrast, if the crystal is doped with impurity atoms, the acceptor states are created above the valence band. Thus, the electrons are promoted from the valence band easily leaving holes behind. The overall density of holes in valence band is greater than the density of electrons in conduction band. Therefore, this conductivity is attributed to minority carriers (holes) and is referred as p-type semiconductor as shown in Figure 4(b).

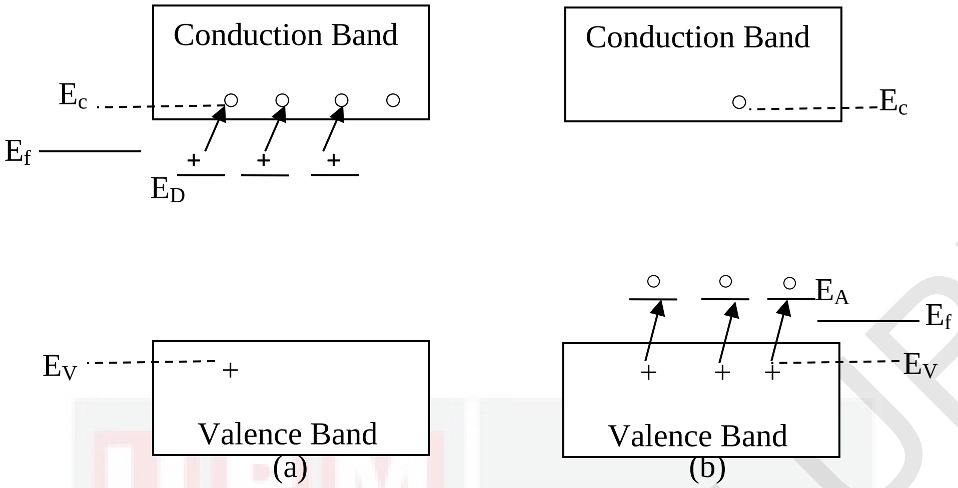

Figure 4: Two dimensional representation of (a) n-type semiconductor (b) p-type semiconductor. Note the shift in position of Fermi level (E_f) due to doping. (Handbook of Luminescent Semiconductor Materials by Leah Bergman, Jeanne L. McHale, CRC Press Set 7 2011)

1.7 Electrodeposition

Electrodeposition is one of the oldest techniques used to synthesize cheap and productive thin films. This technique is an electrochemical liquid phase thin film or powder preparation method process which electric current is passed across an electrolyte and substances is deposited at one of the electrode. In a standard three electrodes electrochemical cell, the reference electrode is used to control the working electrode and the corresponding potential or current can be measured. Though the ZnSe has been largely explored in bulk and thin film state, there is less research work in the case of synthesizing stoichiometric ZnSe thin films and the photosensitivity properties. In this research, we report the electrodeposition of ZnSe thin films from aqueous solution containing $ZnSO_4$ and Na_2SeO_3 and study the influence of various growth conditions on the film.

1.8 Problem Statements

Thin films have been synthesized using physical and chemical techniques. Both techniques able to produce good quality thin films for various applications. However, physical techniques were found to be rather expensive and require complex experimental set-up as compared to chemical techniques. Electrochemical method offers easy preparation steps and inexpensive set-up which makes it a more preferable approach to synthesize thin films. Various metal chalcogenide thin films have been synthesized using potentiostatic and pulsed electrodeposition techniques. These methods allow deposition parameters to be easily controlled thereby enable the control of film growth. However these techniques have not been well studied for the deposition of zinc selenide thin films. For long deposition period, potentiostatic electrodeposition is a more practical method compared to pulsed. The pulsed method requires longer synthesis time due to the time off in every duty cycles. Furthermore, the increasing interest in fabrication of blue-green light or photodiodes has enhanced the interest in zinc-based thin films.

1.9 Objectives

The objectives of this study are:

1. To deposit ZnSe thin films through potentiostatic electrodeposition and pulsed electrodeposition technique and to investigate the effect of various parameters.
2. To determine the crystal structure, surface morphology and elemental composition of thin films.
3. To investigate the photosensitivity and optical properties of the films.
4. To estimate the crystallite size and thickness of the films.
5. To determine the photoluminescence properties of the films.

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