CHARACTERIZATION OF SnₓSeᵧ-ZnO:Al P-N JUNCTION FOR SOLAR CELL APPLICATIONS

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A thesis submitted in partial fulfillment of the requirement for the award of the Degree of Master of Science (Electronics and Instrumentation) in the School of Pure and Applied Sciences of Kenyatta University

October, 2011
DECLARATION

This thesis is my original work and has not been presented for the award of a degree or any other award in any University

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DEDICATION

This thesis is dedicated to my dear sons Joe and Ben; always let the sky be the limit.
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### ABBREVIATIONS, SYMBOLS AND ACRONYMS

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<th>Description</th>
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<tbody>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>AMO</td>
<td>Air mass zero</td>
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<tr>
<td>CPV</td>
<td>Cyclic photovoltametry</td>
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<tr>
<td>CuO</td>
<td>Copper Oxide</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>Copper I Oxide</td>
</tr>
<tr>
<td>CdTe</td>
<td>Cadmium Telluride</td>
</tr>
<tr>
<td>C-V</td>
<td>Capacitance versus voltage</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>CZTS</td>
<td>Copper Zinc Tin Sulphide</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>E&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Conduction band</td>
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<tr>
<td>E&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Band gap energy</td>
</tr>
<tr>
<td>E&lt;sub&gt;v&lt;/sub&gt;</td>
<td>Valence band</td>
</tr>
<tr>
<td>EHP</td>
<td>Electron-hole pair</td>
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<tr>
<td>EF</td>
<td>Fermi level</td>
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<tr>
<td>FF</td>
<td>Fill factor</td>
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<tr>
<td>Ge</td>
<td>Germanium</td>
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<tr>
<td>GaAs</td>
<td>Gallium Arsenide</td>
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<tr>
<td>HEP</td>
<td>Hydro electric power</td>
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<tr>
<td>I&lt;sub&gt;D&lt;/sub&gt;</td>
<td>Diode current</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
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<tr>
<td>I-V</td>
<td>Current versus voltage</td>
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<tr>
<td>Abbreviation</td>
<td>Definition</td>
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</tr>
<tr>
<td>$I_o$</td>
<td>Dark saturated current</td>
</tr>
<tr>
<td>$I_{sc}$</td>
<td>Short circuit current</td>
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<tr>
<td>LED</td>
<td>Light emitting diode.</td>
</tr>
<tr>
<td>LVD</td>
<td>Liquid vapour deposition</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal organic chemical vapour deposition</td>
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<tr>
<td>PDT</td>
<td>Post deposition treatment</td>
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<tr>
<td>PEC</td>
<td>Photo electrochemical</td>
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<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>PVD</td>
<td>Physical vapour deposition</td>
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<tr>
<td>Sn$_x$Se$_y$</td>
<td>Tin Selenide</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conducting oxide</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>$V_a$</td>
<td>Applied voltage</td>
</tr>
<tr>
<td>$V_{bi}$</td>
<td>Built in voltage</td>
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<tr>
<td>$V_{ref}$</td>
<td>Reference voltage</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open circuit voltage</td>
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<tr>
<td>ZnO: Al</td>
<td>Zinc oxide doped with aluminium</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Conversion efficiency</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Sheet resistivity</td>
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ABSTRACT

Thin film semiconductors of Sn_xSe_y and aluminum doped ZnO are potential candidates for the development of future generation improved efficiency and low cost solar cell devices. This is due to their high absorption co-efficient and good optical properties in the visible region of the solar spectrum. Optical characterization of the two thin films under varied composition and deposition conditions was done by optimizing them for an improved solar cell. Deposition of both Sn_xSe_y and ZnO:Al thin films on glass substrate was done by evaporation technique using an Edward Auto 306 RF/DC Magnetron deposition chamber. Synthesized specific ratios of p-material i.e. tin (Sn) and selenium (Se) metal samples were both mixed together and evaporated under these conditions: Temperature of 500K, current of 3.5A, and a pressure of 3.5x10^{-5} millibars. For aluminium (Al) and zinc (Zn) samples, they were similarly mixed together in specific ratios under the same conditions. However this n-material had an additional oxygen gas flow rate of 20sccm/min let into the chamber so as to form ZnO:Al thin films. Transmittance and reflectance data in the range 300nm-2500nm was obtained using UV-VIS NIR Spectrophotometer Solid State 3700 DUV for all the samples that were prepared. A solar cell was then fabricated and characterized from the optimized thin films. The resulting optical measurements were analyzed using scout software to determine optical constants for thin film solar cell. The band gap energy of optimized SnSe thin film was found to be 1.18±0.05 eV. For the optimized 4% doped ZnO:Al thin film, the band gap energy was found to be 3.28±0.05 eV. Electrical measurements of the thin films was done by four point probe method in which measurements were obtained using Keithley 2400 Source Meter interfaced with a computer using LabView program. The sheet resistivity at room temperature of unannealed and 150^0C annealed SnSe thin films was 26.98±0.05 Ωcm and 18.25±0.05 Ωcm respectively. For ZnO:Al thin films, the sheet resistivity was 24.42±0.05 Ωcm for unannealed film and 20.38±0.05 Ωcm for the 150^0C annealed film. XRF and XRD analysis of the thin films were done by use of MiniPal 2 spectrometer and PW 3040/60 X’Pert diffractometer respectively. XRF analysis of the thin films gave their respective elemental composition and XRD analysis of the thin films showed that as-deposited SnSe thin films were amorphous in nature whereas ZnO:Al thin films were crystalline. The solar cell had an open circuit voltage (V_{oc}) of 0.59V, short circuit current (I_{sc}) of 1.06mA/cm^2, fill factor (FF) of 0.65 and conversion efficiency of 0.41% as calculated from current density-voltage (J-V) values obtained by the solar simulator.
CHAPTER 1
INTRODUCTION

1.1 Background to the study
One of the most promising technologies for the future is the thin film technology by use of materials with good photoelectrical properties in visible, infra-red and ultra–violet regions of the solar spectrum for solar cell applications. Compounds that have been used to fabricate thin film semiconductors for solar cell applications include Si, Al, GaAs, CuInSe2 CuO, CdTe among others. Tin selenide and aluminum doped zinc oxide would provide a wide range of potential in solar cell applications. Solar cells are useful for both space and terrestrial applications and furnish the long-duration power supply for satellites. Solar cells convert sunlight to electricity and can provide a nearly permanent power at low operating cost; and is virtually non-polluting. A solar cell uses solar energy that is inexhaustible, and is cheaply fabricated to produce power both for domestic and commercial purposes. On comparison with other energy sources such as hydroelectric power and geothermal plants, it’s relatively easy and cost effective to install and use the solar cells (Markvat, 1998). This power generation is very reliable with the operation and maintenance costs being very low. Furthermore its installation does not need transmission lines.

Solar cells fabricated using tin metal such as tin-zinc, tin-antimony, tin-cadmium and copper-tin alloys are stable and their operation lifetime is long (Ohring, 1992). Optical characteristics of these materials used such as direct energy band gap and high absorption co-efficient makes them more promising materials for application in photovoltaic cells. SnSe is a group 1V-VI semiconductor thin film having a wide range of applications due to its high absorption co-
efficient and suitability for optoelectronic applications. This is because of having a direct band gap energy of 1.21 eV and so can absorb light energy from the high energy end of the solar spectrum. It also has a superior optical transmission in the range of 0.5-20μm capable of improving conductivity and increasing current flow in a P-N junction (Bindu et al., 2004). ZnO:Al is a transparent conducting oxide semiconductor suitable for application in photovoltaic cells. This is due to its high absorption coefficient in the visible regions of the solar spectrum and low-cost of production. It is also a direct band gap energy material having non toxic constituent materials that are abundantly available on the earth. It equally has good electrical and structural properties with very little degradation (Zhao et al., 2002).

1.2 Problem statement and justification

Various semiconductors have been studied to fabricate thin film semiconductors for the solar cell applications. Conventional energy sources such as crude oil and fossil fuel have negative effects on the environment mainly due to pollution. These effects have necessitated the development of alternative energy sources such as solar energy. Although silicon based technology has been extensively used in solar cells, it is very expensive. Hence there is need to develop alternative materials for solar cell applications with low cost of production. This research studies the characterization of SnₓSeᵧ and ZnO:Al thin film materials as a P-N junction in solar cells by varying the deposition parameters and composition of the thin films; due to their low production cost and direct optical energy band gap.
1.3 Objectives

1.3.1 Main objective
To optically and electrically characterize thin films of tin selenide (Sn$_x$Se$_y$) and aluminum doped zinc oxide (ZnO:Al) for solar cell applications.

1.3.2 Specific objectives
(i) To deposit (Sn$_x$Se$_y$) and ZnO: Al thin films by evaporation and reactive evaporation respectively.
(ii) To optically characterize Sn$_x$Se$_y$ and ZnO:Al thin films.
(iii) To electrically characterize Sn$_x$Se$_y$ and ZnO:Al thin films using four point probe method.
(iv) To fabricate and characterize Sn$_x$Se$_y$-ZnO:Al P-N junction solar cell.

1.4 Rationale of the study
Solar cells are useful for both space and terrestrial applications. Solar cells furnish the long duration power supply for satellites. For our country Kenya, it can no longer meet the country’s energy demands from its hydroelectric power and geothermal plants. This is due to the expanding population and unpredictable rainfall patterns. Additionally, use of fossil and nuclear fuels results in environmental degradation during procurement, consumption, and waste disposal. In order to bridge this gap there is need to invest in alternative energy sources. Hence solar energy is being exploited as an alternative source of energy. On the other hand, even though resistivity of thin film solar cells as functions of target composition and evaporation conditions have been presented before, clarification on the composition of some thin films has not been done. This has prompted the need to search for improved materials for solar cell applications. Tin selenide (Sn$_x$Se$_y$) and aluminum doped zinc oxide
(ZnO: Al) semiconductor have an important role in solar cell devices. This is because of their unique properties such as direct and narrow band gap and high absorption co-efficient. Their composition and properties will also be investigated in this study under varied deposition conditions.
CHAPTER 2

LITERATURE REVIEW

2.1 Thin film materials for solar cell
Photovoltaic effect is the field of technology and research related to the application of solar cells in generating electricity. It was first recognized in 1839 by a French Physicist called Becquerel. In 1883, Charles Fritts coated semiconductor selenium with a thin layer of gold to form a P-N junction of a solar cell which had about 1% efficient. Many researchers have conducted research on various materials of thin films for solar applications. Among them includes CuInSe$_2$/ZnO, ZnO/In$_2$Se$_3$, Cu(InGa)Se$_2$, CuO/ZnO:Al and many more (Sheng et al., 2006). These researches are basically aimed at improving the efficiency of solar cells, developing better fabrication technologies and coming up with new and better solar cell materials.

2.2 Classification of solar cells
Solar cells are classified into three generations which indicates the order of which each is important. First generation cells consist of large area, high quality and single junction devices. They involve high energy and labour inputs which prevent any significant progress in reducing production costs. The second generation materials were developed to address energy requirement and solar cells production cost. Techniques such as solution deposition, vapour deposition, electroplating and use of Ultrasonic Nozzles have advantages since they reduce high temperature processing. Successful second generation materials include cadmium telluride (CdTe), copper indium gallium selenide, amorphous and micromophous silicon (Hirshman et al., 2008). Third generation technology enhances the poor electrical performance of second generation technology and maintains low production costs. Modern
researches target high conversion efficiency of 30-60% while retaining low costs; and one attempt to achieve higher efficiencies is the use of thermal generation by UV light to enhance voltage collection, and concentration of incident spectrum (Green, 2002). The main strategies used to reduce the photovoltaic electricity cost are increasing the efficiency and decreasing the cost of solar cells per generated unit of power.

2.3 Related works done
The modern junction semiconductor solar cell was patented by Russell Ohl in 1946 (Chapin et al., 1954). ZnO:Al was deposited on surfaces of SnO$_2$:F substrate and the degradation extent was monitored and its function as a back reflector studied (Zhao et al., 2002). Samples that had been coated with ZnO:Al had little degradation and had very good solar cell properties. Tang et al. (2000) studied doped films of ZnO and found that they exhibited transmittance in visible spectra region, high reflectance in IR region and good conductivity. Optical, electrical and structural properties of the doped thin films heavily depended on deposition parameters. Tin based solar cells were studied and found to exhibit good properties while its alloys showed high efficiency solar cell materials. Some of the alloys had a direct band gap and high absorption co-efficient compared to silicon and gallium arsenide (Toshiyuki et al., 1991). Highest efficiency solar cell of ZnO and thin Cd was prepared at 14.1% (Mitchell et al., 1991).

Jaeyoung and Yongsug (2000) studied selective electrodeposition of ZnO on to Cu$_2$O. The co-deposition of cuprous oxide and zinc oxide on indium tin oxide (ITO) substrate was executed by two different electrochemical methods and formation mechanism of ZnO on to Cu$_2$O investigated. The optical properties depended on deposition parameters while the electrical properties and interfaces of Cu$_2$O/ZnO/ITO P-N depended on chemical deposition
method. Its I-V characteristics were studied and found to have smaller turn on voltage than barrier potential, because of interface defects (Zhang et al., 2004).

Shadia et al. (2009) prepared highly transparent conducting ZnO:Al thin films by the spray pyrolysis technique on glass substrates at a substrate temperature of 450°C. Electrical properties of the films was investigated at room temperature before and after annealing in nitrogen atmosphere by recording and analyzing the I–V measurements. The resistivity was found to be 133 Ωcm for the undoped ZnO films, but 90 Ωcm for the Al-doped films before annealing and 84Ωcm after annealing. Optical properties were investigated by measuring the transmittance curves that were used to find the optical band gap energy. The band gap energy was found to be 3.27 eV for the undoped ZnO films and 3.18 eV for the Al-doped ZnO films after annealing. The electro-optical properties of the films had improved with Al doping and annealing in nitrogen atmosphere.

Hirahara et al. (2006) reported the preparation and characterization results of Cu$_2$ZnSnS$_4$ (CZTS) based solar cells. CZTS absorber was obtained by sulfurization of dc magnetron sputtered Zn/Sn/Cu layers. The solar cell had the following structure: CZTS/CdS/i-ZnO/ZnO:Al/Al grid. The solar cell showed an open-circuit voltage of 345 mV, a short-circuit current density of 4.42 mA/cm$^2$, a fill factor of 44.29 % and an efficiency of 0.68% under irradiation at AM 1.5 and 100 mW /cm$^2$.

Pathinettam et al. (2000) prepared a polycrystalline thin film of SnSe by vacuum deposition at a substrate temperature of 423K. Illumination in the thin film of SnSe was found to increase with photosensitivity. Influence of substrate temperature on growth of SnSe thin film prepared by evaporation was studied by Hema et al. (2007). The electrical resistivity varied from 3.0-8.1 Ωcm$^{-1}$ in the thickness range of 150-300 nm. Sharma et al. (2007) prepared and
characterized nanocrystalline SeSn (n-SnSe) thin film by thermal evaporation of the material in the presence of argon carrier gas. The band gap value increased to \((2.18 \pm 0.01)\) eV as compared to the bulk value of \((1.68 \pm 0.01)\) eV.

\(\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{Sn}((\text{Se}_{1-y}\text{S}_y))_4\) monograin powders with different \(x\) and \(y\) values were prepared from binary compounds in the liquid phase of flux material in evacuated quartz ampoules. All the materials had uniform composition and p-type conductivity. Photoluminescence (PL) spectra (10 K) of the as grown \(\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{Sn}((\text{Se}_{1-y}\text{S}_y))_4\) monograin powders showed one PL band with peak position around 0.85 eV which shifted linearly to the lower energy side with increasing cadmium content. \(\text{Cu}_2\text{ZnSnS}_4\) material showed asymmetrical photoluminescence band at 1.31 eV attributed to band-to-tail recombination. Photoluminescence (PL) is the process in which a thin film absorbs photons and then re-radiates them again. Raman spectra (which occurs due to the measurement of wavelength and intensity of inelastically scattered light from a molecule) of \(\text{Cu}_2\text{ZnSnS}_4\) showed an intensive peak at 338 cm\(^{-1}\) and additional peaks at 287 cm\(^{-1}\) and 368 cm\(^{-1}\). The best solar cell that was based on the \(\text{Cu}_2\text{Zn}_{0.8}\text{Cd}_{0.2}\text{SnSe}_4\) had open circuit voltage 422 mV, short circuit current of 12 mA/cm\(^2\) and fill factor of 44% (Altosaar et al., 2007).

In the band gap study of Se-Te-Sn thin films ternary glasses, Vibhav et al. (2007) deposited thin films on glass substrate employing flash evaporation technique. Amorphous nature of the films was confirmed by their XRD patterns. Optical band gap of these thin films was determined with the help of absorption spectra of the films of different concentration of Sn in the Se-Te-Sn glassy matrix. It was observed that band gap decreases with the increase of Sn concentration in the system. This variation in the band gap is explained on the basis of change in structure of the system in the introduction of Sn in Se-Te-Sn glassy system.
Mariappan *et al.* (2010) deposited tin selenide (SnSe) thin films using chemical spray pyrolysis on non-conducting glass substrates at different temperatures ranging from 250-400 °C. The composition, surface morphology, structural, optical and electrical properties of deposited films were studied using energy dispersive analysis by X-rays (EDAX), scanning electron microscopy (SEM), X-ray diffraction (XRD), UV-Vis spectrometry and four probe techniques. SEM studies reveal that the SnSe films exhibited uniformly distributed grains over the entire surface of the substrate. The optical band gap of SnSe thin films evaluated using transmittance and reflectance data showed a direct band gap of the 1.08 eV and the value is in conformity with 1.1 eV reported earlier for SnSe thin films (Jeewan *et al.*, 2005). The electrical resistivity shows that the films are semiconducting and the resistivity is found to be minimum at optimized substrate temperature.

A promising future technology is the use of thin film photovoltaic cells as effective absorbers. Major attention has been paid to the copper indium chalcogenide materials such as CuInSe$_2$, Cu(InGa)Se$_2$, and CuIn(SnSe)$_2$. This is because they allow tailoring of the energy band gap to enhance device performance (Madelung *et al.*, 1992). It is also evident that the properties of thin films are dependent on the deposition techniques and conditions. Hence, the challenge of increasing the photovoltaic efficiency has a lot of interest academically and economically. This study aims to deposit Sn$_x$Se$_y$ and ZnO:Al thin films under varied deposition conditions, optimize the best conditions in depositing thin films and fabricate an improved solar cell device.
CHAPTER 3
THEORETICAL CONSIDERATIONS

3.1 Thin-Film Cell Structure

A typical thin-film device does not have a metal grid for the top electrical contact. Instead, it uses a thin layer of a transparent conducting oxide, such as tin oxide which is highly transparent and conduct electricity very well. A separate antireflection coating might top off the device, unless the transparent conducting oxide serves that function in the cell. Polycrystalline thin-film cells are made of many tiny crystalline grains of semiconductor materials. The materials used in these polycrystalline thin-film cells have properties that are different from those of wafer-based crystalline silicon (c-Si), hence creating an electric field at an interface between two different semiconductor materials. The type of interface is referred to as heterojunction. The typical polycrystalline thin film cell has a very thin (less than 0.1 micron) layer on top called the "window" layer. The window layer's role is to absorb light energy from only the high-energy end of the spectrum. It must be thin enough and have a wide enough bandgap (2.8 eV or more) to let all available light through the interface (heterojunction) to the absorbing layer. The absorbing layer under the window, usually doped p-type must have a high absorptivity for high current and a suitable band gap to provide a good voltage. An "ohmic contact" is used to provide a good electrical connection to the substrate.

3.2 The P-N junction

A solar cell is a large-area semiconductor p-n junction. A piece of n-type material is brought into contact with a piece of p-type material and diffusion of electrons from the region of high
electron concentration (the n-type side of the junction), into the region of low electron concentration (p-type side of the junction) occurs. When the electrons diffuse across the p-n junction, they recombine with holes on the p-type side. This diffusion of carriers does not happen indefinitely however, because of the electric field which is created by the imbalance of charge immediately either side of the junction which this diffusion creates. Electrons from donor atoms on the n-type side of the junction crosses into the p-type side, leaving an excess of positive charge on the n-type side of the junction. At the same time, these electrons are filling in holes on the p-type side of the junction, making an excess of negative charge on the p-type side of the junction. The imbalance of charge across the p-n junction sets up an electric field which opposes further diffusion of charge carriers across the junction. This region where electrons have diffused across the junction is called the depletion region because it no longer contains any mobile charge carriers. The electric field set up across the p-n junction creates a diode, allowing current to flow in only one direction across the junction. Figure 3.1 below shows an equivalent circuit of a solar cell.

Figure 3.1: Equivalent circuit diagram for a solar cell, showing photocurrent (I_L), diode current (I_D), series resistance (R_S), shunt resistance (R_sh), and a load (R_L) (Mitchell et al., 1991).
3.3 P-N junction I-V Characteristics

In equilibrium, a P-N junction with no external inputs represents an equilibrium between carrier generation, recombination, diffusion and drift in the presence of the electric field in the depletion region. Flow of current is proportional to $e^{(V_a/V_{ref})}$ due to the exponential decay of carriers into the majority carrier bands. Current flow is dominated by minority carriers flowing across the junction and becoming majority. Figure 3.2 below shows generation of electron-hole pair on absorption of a photon (O’Leary et al., 1997).

![Figure 3.2: Band diagram of a p-n homojunction solar cell, illustrating generation of an E-H hole pair by absorption of a photon.](image)

3.4 Thin film deposition techniques

Deposition techniques for thin films broadly fall in five categories: Physical vapour deposition (PVD), Chemical vapour deposition (CVD), Oxidation, Spin coating and Plating. In PVD technique, films are formed by atoms that are directly transported from source to the substrate through gas phase and they include sputtering, evaporation (Thermal evaporation and E-Beam evaporation) and Reactive PVD. On the other hand, in CVD technique, films are formed by chemical reaction on the surface of the substrate and they include Low-Pressure
CVD (LPCVD), Plasma-Enhanced CVD (PECVD), Atmosphere-Pressure CVD (APCVD) and Metal-Organic CVD (MOCVD). Evaporation and sputtering are the two main techniques employed in physical vapour deposition. In this study, due to its advantages such as proper control on the film chemical composition, high deposition rate and low substrate heating during film deposition, evaporation technique has been adopted.

### 3.4.1 Vacuum Evaporation Technique

Vacuum evaporation is a widely used PVD technique. It is where materials from a thermal vaporization source reaches the substrate with little or no collision with gas molecules in the space between the source and substrate. The gaseous atoms are transported to the substrate surface in reduced pressure environment (Ohring, 1992). The vacuum environment during evaporation provides the ability to reduce gaseous contamination in the deposition system to a low level. This technique is generally done using thermally heated sources such as tungsten wire coils or by high energy electron beam heating of the source material itself. Generally, the substrates are mounted at an appreciable distance away from the evaporation source to reduce radiant heating of the substrate by the vaporization source. Figure 3.3 below depicts a schematic diagram of vacuum evaporation system (Hema et al., 2007).

![Schematic diagram of vacuum evaporation system](image)

**Figure 3.3:** Schematic diagram of vacuum evaporation system
3.4.2 Other Deposition Techniques

3.4.2.1 Sputtering Deposition Technique

Sputtering is a physical vapour deposition (PVD) technique whereby bombarding particles incident on a target collide with surface atoms thus dislodging them from the lattice through a transfer of energy (Ohring, 1992). The displaced lattice atoms as well as the bombarding particles (projectile) then undergo collisions with other lattice atoms, dislodging them and a chain reaction of collision ensues. Atoms with sufficient energy required to overcome the surface potential called the surface binding energy \( U_0 \) will escape (Matsunarmi et al., 1980). There is a minimum projectile kinetic energy needed to induce sputtering called threshold energy \( E_{th} \) and is given by Bohdansky (1984) as:

\[
E_{th} = \frac{U_o}{\beta(1 - \beta)} \text{ for } \frac{M_1}{M_2} \leq 0.3
\]

(3.1)

where \( M_1 \) is projectile mass, \( M_2 \) is mean molecular mass per atom of a target and \( \beta \) is maximum fractional energy transfer possible in a head-on collision given by:

\[
\beta = \frac{4M_1M_2}{(M_1 + M_2)^2}
\]

(3.2)

and for \( \frac{M_1}{M_2} > 0.3 \), \( E_{th} = 8U_0 \left( \frac{M_1}{M_2} \right)^{\frac{1}{2}} \)

(3.3)

Sputtering processes are wide and varied. They can be divided up into four categories; DC, RF, magnetron and reactive. There are also important variants within each category for example DC bias and even hybrids between categories (Almen and Bruce, 1961).
3.4.2.2 Arc Vapour Deposition Technique

Arc vapour deposition uses a high current, low-voltage arc to vaporize a cathodic electrode (cathodic arc) or anodic electrode (anodic arc) and deposit the vaporized material on a substrate. The vapourized material is highly ionized and usually the substrate is biased so as to accelerate the ions to the substrate surface.

3.4.2.3 Ion Plating Technique

Ion plating utilizes concurrent or periodic bombardment of the depositing film by atomic-sized energetic particles, to modify and control the properties of the depositing film. In ion plating the energy, flux and mass of the bombarding species along with the ratio of bombarding particles to depositing particles are important processing variables.

3.4.2.4 Chemical Vapour Deposition Technique

Thermal chemical vapour deposition is the deposition of atoms or molecules by the high temperature reduction or decomposition of a chemical vapour precursor species which contains the material to be deposited. Reduction is normally accomplished by hydrogen at an elevated temperature. Decomposition is accomplished by thermal activation. The deposited material may react with other gaseous species in the system to give compounds (e.g. oxides, nitrides). CVD technique has numerous other names and adjectives associated with it such as Vapour Phase Epitaxy (VPE) when CVD is used to deposit single crystal films, Metal-organic CVD (MOCVD) when the precursor gas is a metal-organic species, Plasma Enhanced CVD (PECVD) when a plasma is used to induce or enhance decomposition and reaction, and Low Pressure CVD (LPCVD) when the pressure is less than ambient.
3.5 Optical characterization

3.5.1 Optical behaviour in thin films

When light is emitted from or absorbed in a thin film semiconductor, both momentum and energy are conserved. In direct band gap semiconductor thin films, the carrier transitions between valence and conduction bands occur without change in momentum of the two states involved. The emission of light occurs by an electron moving from the minimum conduction band level to maximum valence band energy level. However in indirect band gap semiconductor, the transition occurs with a change in momentum that is mainly accommodated by excitation of lattice heating and vibrations. This makes direct electron-hole recombination with photon emission unlikely.

3.5.2 Optical reflectance

Reflectance is the percentage measure of ratio of intensity of incident light to that of reflected light. In the spectrophotometer, incident light of known wavelength and intensity is shone onto the surface of thin film and the intensity of reflected light measured. The two intensities are compared by reference called reflectance (R) as given in equation 3.4 below;

\[
\text{Reflectance (R)} = \frac{I_R}{I_o} \times 100
\]  

(3.4)

where: \(I_R\) and \(I_o\) are intensities of the reflected and incident beams respectively.

3.5.3 Optical transmission

Photons of selected wavelengths and beam intensity \(I_o\) (photons/cm\(^2\)-s) are directed at the film. Those with energies greater than band gap (\(E_g\)) are absorbed while those with energies less than \(E_g\) are transmitted. This is because photons with energy less than band gap do not
excite electrons in the valence band to higher states, hence transmitted. The comparison between intensities of incident ($I_o$) and transmitted ($I_t$) photons is given by transmittance. Transmittance is given by equation 3.5 below.

$$\text{Transmittance}(T) = \frac{I_t}{I_o} \times 100$$

(3.5)

### 3.5.4 Absorption of light

Absorption takes place when a photon of energy more than the band gap excites an electron from lower to higher energy state. When light falls on a thin film, it is absorbed when passing through a medium from one point to another. Absorption is expressed by absorption coefficient ($\alpha$) which is relative rate of decrease in light intensity along the propagation path. For incident photon of intensity $I_o$, intensity of photon transmitted ($I_t$) through the film of thickness $l$ and absorption coefficient $\alpha$ are given by;

$$I_t = I_o e^{-\alpha l}$$

(3.6)

$$\alpha = \frac{1}{l} \ln \left( \frac{I_o}{I_t} \right) \ (cm^{-1})$$

(3.7)

Amount of absorption depends on photon wavelength, thickness of film and properties of the film. Absorption coefficient is zero or very small for photon energies below band gap and well above phonon energies. As photon energy is increased above band gap ($E_g$), absorption coefficient ($\alpha$) increases rapidly to values larger than $10^4 \ cm^{-1}$. This makes the film to become opaque for photon energies higher than band gap unless thickness is very small (Yu and Cardona, 1996). Absorption coefficient is related to frequency ($\omega$) and extinction coefficient ($k$) by equation 3.8 below;
3.5.5 Refractive Index

Refractive index is related to wave vector (k) as follows:

\[ k = \frac{\bar{n}\omega}{c} \]  

(3.9)

Where n(\omega) is refractive index. Refractive index is also related to dispersion and absorption of radiation by medium.

\[ \bar{n}\omega = n + ik \]  

(3.10)

Dielectric function is directly related to material properties and is connected to refractive index as follows.

\[ \varepsilon = \varepsilon_1 + i\varepsilon_2 = n^2 = (n + ik)^2 \]  

(3.11)

\[ \varepsilon_1 = n^2 - k^2 \]  

(3.12)

\[ \varepsilon_2 = 2nk \]  

(3.13)

Where \( \varepsilon_1 \) and \( \varepsilon_2 \) are respectively real part and imaginary part of dielectric function (\( \varepsilon \))

3.5.6 Physical models

OJL (O’Leary et al. 1997) model has been employed to describe inter band transition in amorphous materials; while drude model has been used to account for the movement of free electrons. OJL inter band model give expressions for the density of states for the optical transition from the valence band to conduction band. Parabolic bands are assumed with tail states exponentially decaying into the band gap as shown in figure 3.4 below.
The original parameters of OJL density of states model are energy, $E_v$ and $E_c$, and the ‘damping constants’ of the valence and conduction bands, $\gamma_v$ and $\gamma_c$ respectively. Also included are the masses of the valence and conduction bands, $m_v$ and $m_c$.

The expressions

$$E_{m,v} = E_v - \frac{1}{2} \gamma_v$$

(3.14)

and

$$E_{m,c} = E_c + \frac{1}{2} \gamma_c$$

(3.15)

denote the mobility edges of the valence and conduction bands respectively. The mobility gap, $E_o$, in the OJL is therefore given by:

$$E_c + \frac{1}{2} \gamma_c - \left[ E_v - \frac{1}{2} \gamma_v \right] = E_o$$

(3.16)
The band gap energy, $E_g$, is the difference between $E_c$ and $E_v$ values, i.e. the band gap in the case of no disorder, which is realized when both $E_v$ and $E_c$ are zero. This band gap energy is different from the mobility band gap which depends on the values of the disorder parameters $E_v$ and $E_c$. The band gap energy is calculated by scout 98 programme which converts the wave numbers to energy (eV) by dividing it with a constant (8065).

### 3.6 Thin Film Resistivity Measurement

#### 3.6.1 Four Point Probe method

Four point probe set up usually consists of four equally spaced tungsten metal tips with finite radius. Each tip is supported by springs on the other end to minimize sample damage during probing. The four metal tips are part of an auto-mechanical stage which travels up and down during measurements (Masato et al., 1993). A high impedance current source is used to supply current through the outer two probes and a voltmeter used to measure the voltage across the inner two probes as shown in figure 3.5. These values of sourced current and measured voltage are used to determine the sample resistivity. Typical probe spacing $S$ is about 1 mm.

#### 3.6.2 Thin Film Sample

Considering a thin film with a square geometry as in figure 3.5, for a very thin layer (thickness, $t \ll$ probe spacing, $S$), current rings instead of spheres are got (Brown & Jakeman, 1996).
Figure 3.5 Probe tips on film sample surface with square geometry (Brown & Jakeman, 1996).

Therefore, the area,

\[ A = 2\pi t \quad \text{where } t \text{ is the film thickness} \tag{3.17} \]

\[ R_s = \int_{x_1}^{x_2} \rho \frac{dx}{2\pi t} \tag{3.18} \]

\[ = \int_{S}^{2S} \frac{\rho}{2\pi t} \frac{dx}{x} \text{ where } S \text{ is the probe spacing} \tag{3.19} \]

\[ = \frac{\rho}{2\pi t} \ln \left( x \right) \bigg|_{S}^{2S} \tag{3.20} \]

\[ = \frac{\rho}{2\pi t} \ln 2 \tag{3.21} \]

Consequently, for \( R = \frac{V}{2I} \), the sheet resistivity of the thin film sheet is given by:

\[ \rho_s = \frac{\pi t}{\ln 2} \left( \frac{V}{I} \right) \tag{3.22} \]
It is noted that equation 3.22 is independent of the probe spacing $S$. Furthermore, this latter expression is frequently used for characterization semiconductor layers, such as a diffused N+ region in a p-type substrate. In general, sheet resistivity can be expressed as:

$$\rho_s = K \frac{V}{I}$$  \hspace{1cm} (3.23)

where the factor $K$ is a geometric factor. In the case of a semi-infinite thin sheet, $K = 4.532$, which is just $\pi/\ln2$ from the derivation. The factor $K$ will be different for non-ideal samples. So the sheet resistance and sheet resistivity can be simply expressed as below in equations 3.24 and 3.25, respectively.

$$R_s = 4.532\left(\frac{V}{I}\right)$$  \hspace{1cm} (3.24)

$$\rho_s = 4.532r\left(\frac{V}{I}\right)$$  \hspace{1cm} (3.25)

### 3.7 Structural and elemental characterization

#### 3.7.1 X-Ray diffraction (XRD)

X-rays are electromagnetic radiation with typical photon energies in the range of 100eV-120keV. For diffraction applications, only short wavelength x-rays (hard x-rays) in the range of a few angstroms to 0.1 angstrom (1-120 keV) are used. Because the wavelength of x-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms in a wide range of materials. In XRD measurements, x-rays falling on thin films cause electrons around the atoms to oscillate with the same frequency as incident beam. Due to the arrangement pattern of atoms in the films, the diffracted waves which are in
phase hence undergo constructive interference while those out of phase undergo destructive interference. X-Ray diffraction (XRD) technique reveals the crystallinity or the amorphous nature of the thin films. It measures the average spacing between layers of atoms and determines the orientation of a single crystal or the structure of the thin films.

3.7.2 X-Ray fluorescence (XRF)

The technique is non-destructive, multi-elemental, fast and cost effective. High energy photons (X-rays) displace inner shell electrons. Outer shell electrons then fall into the vacancy left by the displaced electron. In doing so, they emit light (fluoresce) equivalent to the energy difference between the two states. Since each element has electrons with more or less unique energy levels, the wavelength of light emitted is characteristic of the element and the intensity of light emitted is proportional to the elements concentration. There are two types of XRF spectrometers: wavelength dispersive and energy dispersive. Wavelength dispersive system uses a diffraction crystal to focus specific wavelengths onto a detector. Energy dispersive spectrometer focuses all the emitted X-rays onto an energy analyzing detector. While this is faster and less expensive, wavelength dispersive spectrometers are more sensitive and have higher resolution. For this reason, a wavelength dispersive system was applied in this research work.
CHAPTER 4
MATERIALS AND METHODS

4.1 Preparation and deposition of Sn\textsubscript{x}Se\textsubscript{y} thin films
This research employed the use of evaporation techniques to deposit the thin films. The thin films were produced in Edwards 306 vacuum coater. The chamber was vacuum cleaned to remove any dust debris and the wall covered with a foil to avoid coating it. Ordinary glass slide measuring 38mm by 26mm by 1mm was used as substrate for preparing Sn\textsubscript{x}Se\textsubscript{y}. The substrate was thoroughly cleaned using distilled water and ethanol and allowed to completely dry. Tin (99.0%) purity and selenium (99.5%) purity samples were synthesized in specific ratios by mass ranging from 0.2 to 1.2 before using them to deposit the thin films. This was done by putting the samples together in a silica tube and heated to melt resulting in a homogenous compound, then allowed to cool. The compound was ground in a porcelain motor, and placed in an evaporator boat in a vacuum chamber and heat thermally supplied to the boat at a current of 3.5A. A substrate was mounted to the substrate holder by clips and the shutter directly overhead was removed to allow deposition on the substrate. Deposition temperature of the thin films was controlled by varying time and current to the heater as they were key variables that influenced the evaporation rate and deposition of the thin film.

4.2 Preparation and deposition of ZnO:Al thin films
Zinc and aluminum were mixed at predetermined specified ratios and then heated in closed glass tube until they melted to form a compound. Glass substrate was properly cleaned to remove stains on them using distilled water and ethanol and allowed to completely dry. The substrate was then mounted on a rotating substrate holder and the chamber covered tightly and pumped down to 3.0×10\textsuperscript{-5} millibars. The compound was placed in a boat and current of
3.5A supplied to the heater to evaporate it. The shutter was removed to allow deposition on glass substrate in the presence of oxygen which was let into the chamber. Oxygen flow rate, total pressures used and different ratios of zinc and aluminium used were used to optimize and obtain a thin film layer of ZnO:Al.

4.3 Optical characterization of thin films

The optical properties of the thin films were determined by use of the spectro 3700 optical spectrum analyzer. Properties such as reflectance, transmittance and absorption coefficient were determined in the spectral range 200-2500nm. The first reference measurements were determined with no sample between the lamp and the detector as shown in the figure 4.1 below.

![Schematic diagram for the optical transmission measurements](image)

**Figure 4.1:** Schematic diagram for the optical transmission measurements

The photons of selected wavelengths (380-1700 nm) and beam intensity, \(I_0\) (Photons/cm\(^2\)-s) were directed at the film of thickness \(l\) and their relative transmissions observed. Photons with energies greater than band gap energy were absorbed while those with energies less than band gap energy were transmitted. This gave accurate measurements of band gap energy. The
type of band gap (either direct or indirect) can be identified using the absorption coefficient values from the equation:

\[ h\nu \alpha = A(h\nu - E_g)^m \]  

(4.1)

where: \( E_g \) is the material band gap, \( A \) is the energy dependant constant.

Absorption coefficient, \( \alpha \), of the thin films defines the amount of light absorbed by the films and the inverse of the absorption coefficient, \( \alpha^{-1} \), is the average distance traveled by a photon before it gets absorbed. The amount of absorption depends on wavelengths, thickness and properties of the film as previously shown in equations 3.6 and 3.7 respectively. A beam of monochromatic light of sufficient energy, known frequency and intensity was directed on to the film. Much of the beam is absorbed as a small fraction of incident light is transmitted. Intensity of the reflected and transmitted light was measured by the automatic peak detector.

4.4 Electrical characterization of thin films

The electrical properties were determined by use of four point probe method (Agumba, 2010) to get the sheet resistivity of the two thin films. This method is per the Van der Pauw set up (Pathinettam, P. 2000). Measurements were made through four contact terminals at each corner of the thin film labeled counter clockwise. Readings were collected by use of keithley 2400 source meter. With a symmetrical square geometry adopted, the Sn\(_x\)Se\(_y\) and Zn0:Al thin films were displayed as shown in figure 4.2 below.
Figure 4.2: Schematic diagram for the electrical measurements of thin films

L₁ and L₂ refer to the length of the thin film. The measurements taken were \( V_{12} \) and \( I_{34} \), \( V_{34} \) and \( I_{12} \), \( V_{23} \) and \( I_{14} \), \( V_{14} \) and \( I_{23} \) from which the sheet resistivity was computed using equation 4.2 below. The resistance of the thin film sheet is given by:

\[
R_s = \frac{\pi}{\ln 2} F(Q) \frac{V_{43} + V_{23}}{2l} \left[ \frac{\Omega}{\text{square}} \right]
\]  

(4.2)

where: \( F \) and \( Q \) are the symmetry and correction factors respectively. For \( V_{23} \leq V_{43} \),

\[
Q = \frac{V_{23}}{V_{43}}
\]

and vice versa. \( F \) is a function of \( Q \) and is valid for \( Q \) less than 10. It is expressed in the form:

\[
F = 1 - 0.34657 \left[ \frac{Q-1}{Q+1} \right]^2 - 0.09236 \left[ \frac{Q-1}{Q+1} \right]^4
\]  

(4.3)

where: \( \frac{V_{43} + V_{23}}{2l} \) is the average resistance as a function of target compositions and evaporating conditions of the thin films. Average resistance was obtained from the slope of
the average resistance curves using linear regression. The specific resistivity was determined from the thin film thickness and sheet resistance using the expression.

\[ \rho_s = R_s t 10^{-1} \mu \Omega \text{cm} \]  

(4.4)

where: \( t \) is the film thickness

**4.5 Fabrication of SnSe-ZnO:Al heterojunction**

The heterojunction solar cell with glass/ZnO:Al/SnSe/Ag was fabricated in stages. The N-type layer of transparent conducting ZnO:Al film was deposited first onto a glass substrate at a temperature of 500K and pressure of 3.0x10^{-5} mbar by reactive evaporation technique. Then a P-type layer of SnSe was deposited onto ZnO:Al on the same substrate at the same temperature. Digital thermometer attached to the backside of molybdenum boat was used to measure 500K deposition temperature. Fabrication was completed by deposition of silver back contact on SnSe film. The thin film obtained was SnSe-ZnO:Al which formed the P-N heterojunction.

**4.6 Diode characteristics of thin film solar cell**

The diode characteristics of SnSe-ZnO:Al P-N junction were determined by a solar cell simulator. When under forward bias, the junction potential barrier is reduced resulting to increase in current through the thin film. Reverse bias increases the junction potential. This generates small current, \( I_0 \) (dark saturation current). Since \( I_0 \) is smaller than current under forward bias, the junction behaves as a diode. Below is a typical I-V curve of a P-N junction.
Figure 4.3: Schematic diagram of I-V characteristics of a P-N junction

The p-n junction I-V characteristics are given by Shockley equation below.

\[ I = I_0 \left( \exp \left( \frac{qV}{kT} \right) - 1 \right) \]  

(4.5)

where: \( I \) is current, \( I_0 \) is dark saturation current, \( V \) is voltage, \( K \) is Boltzmann’s constant \((8.62 \times 10^{-3} \text{eV/k})\), \( q \) is electron charge and \( T \) is absolute temperature (273K). Figure 4.4 below represents measurement set-up of diode characteristics.

Figure 4.4: Measurement set-up of diode characteristics
Under short circuit conditions, the largest current was achieved. Short circuit current ($I_{sc}$) is given by:

$$I_{sc} = I(V=0) = I_L$$

and open circuit voltage, $V_{oc}$ (when $I=0$) is given by:

$$V_{oc} = \frac{AkT}{q} \ln \left[ \frac{I_L}{I_0} + 1 \right] \quad (4.6)$$

From maximum power input, fill factor (FF) was calculated. Fill factor measurements quality of the cell through squareness of current voltage and is given by:

$$FF = \frac{V_{max} I_{max}}{V_{oc} I_{sc}} \quad (4.7)$$

With total radiation ($P_{in}$) incident on thin film solar cell from the solar simulator, then the conversion efficiency ($\eta$) was calculated as shown.

$$\eta = \frac{V_{max} I_{max}}{P_{in}} = \frac{V_{oc} I_{sc} FF}{P_{in}} \quad (4.8)$$
CHAPTER 5

RESULTS AND DISCUSSION

5.1 Optical properties of Sn$_x$Se$_y$

Optical properties of the thin films were analyzed by drawing transmittance and reflectance data against wavelength as obtained from the experimental results. Figure 5.1 below shows the transmittance spectra of Sn$_x$Se$_y$ experimental data.

5.1.1 Transmittance data against wavelength

Figure 5.1: Graph of transmittance spectra of Sn$_x$Se$_y$ thin films varied by mass ratios
From the spectral data in figure 5.1 above, variation of transmittance against wavelength for Sn$_x$Se$_y$ lies between 65-80% in the visible range. It is observed that transmittance increases with the increase of wavelength of incident photon. Within the visible range, at wavelengths above 700 nm, transmittance decreases slightly due to increased optical scattering caused by rough surface morphology of the thin films. The maximum and minimum points formed at wavelengths above 800nm are due to constructive and destructive interference of the light waves.

**5.1.2 Reflectance data against wavelength**

Figure 5.2 below shows reflectance spectra of thin films prepared at different Sn:Se ratios.

![Reflectance Spectra](image)

**Figure 5.2:** Graph of reflectance spectra of Sn$_x$Se$_y$ thin films varied by mass ratios
The thin films reflectance is low and lies between 0-45% in the visible region. Low reflectivity shows that the thin films are good absorbers of light energy that generates more electron-hole pairs.

5.1.3 Simulated and Experimental graphs

The experimental and simulated data were plotted against wavelength for the different samples doped. The simulated curves fitted perfectly in to the experimental curves as shown in figures 5.3 (i)-(vi) below. The data was used to calculate the band gap energies and thickness of the thin films.

Figure 5.3(i): Simulated and experimental graph for Sn:Se [1:1.0]
Figure 5.3(ii): Simulated and experimental graph for Sn:Se [1:0.8]

Figure 5.3(iii): Simulated and experimental graph for Sn:Se [1:0.6]
Figure 5.3(iv): Simulated and experimental graph for Sn:Se [1:0.4]

Figure 5.3(v): Simulated and experimental graph for Sn:Se [1:0.2]
Figure 5.3(vi): Simulated and experimental graph for Sn:Se [1:1.2]

5.1.4 Optical band gap energies

Table 5.1 below shows the optical band gap energy for different ratios of Sn:Se thin film samples. The band gap energy values were obtained by the scout 98 programme that was used in simulation. The optical band gap energy lies between 1.18-1.75±0.05 eV with the Sn:Se ratio of 1:1.0 having the lowest band gap energy. The thickness of the thin films was found to lie between 49.5-69.5±0.5nm as calculated by the scout 98 programme. The absorption is from the top of the valence band to the bottom of the conduction band. Generally the thin films exhibit direct optical energy band gap. Obtained values are in good agreement with the band gap value range of 1.18-1.85±0.05 eV as reported by Kumar et al. 2010.
Table 5.1: $\text{Sn}_x\text{Se}_y$ variation by mass ratio and calculated band gap energy values

<table>
<thead>
<tr>
<th>Sn:Se mass ratio</th>
<th>Optical band gap $[\pm0.05 \text{ (eV)}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.2</td>
<td>1.75</td>
</tr>
<tr>
<td>1:0.4</td>
<td>1.42</td>
</tr>
<tr>
<td>1:0.6</td>
<td>1.36</td>
</tr>
<tr>
<td>1:0.8</td>
<td>1.25</td>
</tr>
<tr>
<td>1:1.0</td>
<td>1.18</td>
</tr>
</tbody>
</table>

From the results, a graph of optical band gap energy versus Sn:Se sample ratios was drawn. The variation in graph shows that the optimum Sn:Se thin film ratio value is that of 1:1.0 since it had the lowest energy band gap value of 1.18±0.05 eV as shown in the figure 5.4 below.

Figure 5.4: Graph of variation of optical band gap energy with different Sn:Se ratios
5.1.5 Refractive index

The refractive index of the Sn$_x$Se$_y$ samples was plotted against wavelength as shown below.

![Graph of refractive index (n) as a function of wavelength](image)

**Figure 5.5:** Graph of refractive index (n) as a function of wavelength

The above graph shows that the refractive indices of the thin films decreases or remains constant as the wavelength increases. This must be related to the complex reflectance behaviour on the surface of the deposited thin films. This is attributed to spectroscopic ellipsometry theory; which defines the ability to report real refractive index of thin films over a wide range of wavelength values.

5.2 Optical properties of ZnO:Al

Optical analysis of ZnO:Al thin films had transmittance and reflectance data plotted as a function of wavelength. The graphs are shown below in figures 5.6 and 5.7 for transmittance and reflectance data respectively.
Figure 5.6: Graph of transmittance spectra of aluminium doped zinc oxide thin films

In figure 5.6 above, transmittance percentage is high ranging between 65%-90% in the IR, VR, and UV regions for the ZnO:Al thin films. From the spectral data, transmittance increases sharply to maximum and then remains constant for all the doped samples as the wavelength of incident photon energy increases. This is because there is no optical absorption that is taking place because photon energies are smaller than band gap of the thin films which results in lower absorption hence higher transmittance. The 5% aluminium doped sample had a slightly lower transmittance than the other samples which may be attributed to increased optical scattering caused by the thin film surface morphology.
Figure 5.7: Graph of reflectance spectra of aluminium doped zinc oxide thin films

Reflectance spectra is low and lie in the range of 10-45% in the ultra violet, visible range of the solar spectrum and the infra red region. The maximum and minimum points formed are due to interband transitions where electrons from filled states at the top of valence band are excited and jump to empty states in the conduction band. These points are attained within energy range which corresponds with the energy band gap of the thin films. This interband transition causing maximum and minimum points at wavelength of 600nm and above is due to fundamental absorption of photons.

5.2.1 Simulated and Experimental graphs

Experimental and simulated data were plotted against wavelength for the different samples doped. The simulated curves fitted perfectly in to the experimental curves as shown in figure
5.8 (i)-(v) below. From the graphs, the optical band gap energies and thickness of the films were calculated using the scout 98 programme.

**Figure 5.8(i):** Simulated and experimental graph for 2% aluminium doped ZnO

**Figure 5.8(ii):** Simulated and experimental graph for 3% aluminium doped ZnO
Figure 5.8(iii): Simulated and experimental graph for 4% aluminium doped ZnO

Figure 5.8(iv): Simulated and experimental graph for 5% aluminium doped ZnO
Figure 5.8(v): Simulated and experimental graph for 6% aluminium doped ZnO

5.2.2 Optical band gap energies

Table 5.2 below shows the optical band gap energy with doping percentages of ZnO:Al. The optical band gap energy lies between 3.28-4.20±0.05 eV and the film thickness varied between 48.3-52.6±0.5 nm. Both were calculated by scout 98 programme used in simulation.

Table 5.2: ZnO doped with aluminium and calculated band gap energy values

<table>
<thead>
<tr>
<th>Doping of ZnO with Aluminium (%)</th>
<th>Band gap energy [±0.05 (eV)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>4.20</td>
</tr>
<tr>
<td>3.0</td>
<td>3.55</td>
</tr>
<tr>
<td>4.0</td>
<td>3.28</td>
</tr>
<tr>
<td>5.0</td>
<td>3.48</td>
</tr>
<tr>
<td>6.0</td>
<td>3.98</td>
</tr>
</tbody>
</table>
The graph in figure 5.9 below shows the variation of optical band gap energy with doping concentration.

![Graph of variation of band gap energy with doping concentration](image)

**Figure 5.9:** Graph of variation of band gap energy with doping concentration

Decrease in band gap energy can be attributed to creation of new donor levels in the forbidden zone; and a shift in the fermi level causing a change in the band structure of the films. Creation of new donor level makes the electrons to jump from the maximum valence band to minimum conduction band because of being a direct band gap material (Shadia *et al.*, 2009). The band gap energy trend shows that ZnO:Al samples is optimized at a 4% doping concentration which has the lowest band gap energy of 3.28 ±0.05 eV.
5.2.3 Optimized deposition parameters of Sn$_x$Se$_y$ and ZnO:Al thin films

Table 5.3 below depicts the optimized deposition parameters for the varied sample ratios of Sn$_x$Se$_y$ and different doped concentrations of ZnO:Al thin films.

**Table 5.3:** Optimized deposition parameters for Sn$_x$Se$_y$ and ZnO:Al thin films

<table>
<thead>
<tr>
<th></th>
<th>Sn$_x$Se$_y$</th>
<th>ZnO:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimized ratio of x:y</td>
<td>1:1.0</td>
<td></td>
</tr>
<tr>
<td>Deposition pressure</td>
<td>3.5x10^{-5} mb</td>
<td>3.5x10^{-5} mb</td>
</tr>
<tr>
<td>Evaporation temperature</td>
<td>500.0 K</td>
<td>500.0 K</td>
</tr>
<tr>
<td>Deposition current</td>
<td>3.5 A</td>
<td>3.5 A</td>
</tr>
<tr>
<td>Oxygen flow rate</td>
<td></td>
<td>20 scc/min</td>
</tr>
<tr>
<td>Doping concentration</td>
<td></td>
<td>4.0%</td>
</tr>
<tr>
<td>Deposition pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evaporation temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deposition current</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.3 Electrical characterization of SnSe and ZnO:Al thin films

5.3.1 SnSe thin film

The sheet resistivity measurements were done by four point probe system that was interfaced to a computer and Keithley 2400 source meter using Lab View programme. The sheet resistivity values were measured for the optimized Sn:Se thin film sample ratio of 1:1. The
Sheet resistivity for unannealed thin film of thickness of 49.5 nm was 26.98±0.05 Ωcm and for 150°C annealed thin film was 18.25±0.05 Ωcm. This low resistivity is due to high carrier mobility and carrier concentration associated with the films. Optimized deposition conditions such as pressure, temperature and current may also have contributed to low resistivity by changing the thin film surface physically hence affecting its binding properties (Sharma et al., 2007).

The film that was annealed at 150°C at a rate of 5°C/min for 30 minutes had a lower resistance value compared to the unannealed thin film. This indicates that annealing promotes incipient fusion of small crystallites and thereby reduces the grain boundaries, which are known to act as recombination centres for minority carriers and trapping centres for majority carriers. This physical change on the surface of the thin films affected the binding properties of SnSe and finally changes the resistivity of the SnSe thin films. The observed electrical low resistivity is explained based on hopping conduction mechanism (Jiaping et al., 2002).

### 5.3.2 ZnO:Al thin film

The thin films at room temperature were found to have sheet resistivity 24.42±0.05 Ωcm for unannealed film and 20.38±0.05 Ωcm for the 150°C annealed film. Doping and deposition parameters such as pressure, temperature, current and oxygen flow rate influenced the resistivity of the films. The mobility and carrier concentration of ZnO:Al are both associated with Al³⁺ ions substituting Zn²⁺ ions at that site hence creating an extra free charge carrier. From the optimized film of aluminium 4% dopant, the many dopant atoms introduced replaces the Zn²⁺ ions resulting in increased charge carriers, hence high conductivity (Mudjat et al., 2008). Low resistivity obtained from aluminium doped ZnO thin film is also associated with the difference in Hall mobility that measures the average carrier density in a grain.
After annealing at 150°C for 30 minutes at a rate of 5°C/min, the films exhibited lower resistivity. This may be interpreted that besides the effect of annealing on enhancing the grain growth and narrowing the grain boundaries, annealing helps to move the Al atoms from the grain boundaries to be effectively incorporated into the crystal lattice. The result is an increase in the number of free charge carriers and then a decrease in the resistivity. Annealing also results in large reduction of ZnO:Al thin film sheet resistance because of oxygen desorption from the surface pores and grain boundaries, resulting in creation of vacant sites which will act as donor states. The fact that the effect of annealing is strong is due to the low substrate temperature of 150°C used. (Shadia J. et al., 2009). These thin films with low resistivity are obtained by evaporating zinc doped with aluminium and in the process introducing oxygen gas during the deposition procedure.

5.4 Structural and elemental characterization of SnSe and ZnO:Al thin films

5.4.1 X-ray fluorescence (XRF) of thin films

X-Ray Fluorescence (XRF) is a technique that is used to measure the percentage of metals within metal alloys and thin films. The schematic diagrams below shows the XRF results of the thin films which analyses the presence of heavy materials. The analysis was carried out to ascertain the elemental composition of the thin films. The analysis is peak-based where elemental intensities of thin films are calculated and respective spectral background obtained.
Figure 5.10: XRF spectral graph of as-deposited optimized ZnO:Al thin film

Figure 5.11: XRF spectral graph of annealed optimized ZnO:Al thin film at 150°C
The yellow coloured spectrum shows the composition of the elements present in the thin films at $K_{\alpha}$, $K_{\beta}$, $L_{\alpha}$, and $L_{\beta}$ lines. The bottom line represents the background radiation which shows the radiations detected by the XRF machine but are not present in the thin film samples. These radiations may have originated from the machine itself, or/and the room in.
which the measurements were taken. The highest colourless peak represents the detector escape which is a spectrum for detector peak (Rhodium) element that the machine is made of. XRF results shows that the elemental composition for both as-deposited and annealed films remain the same. The results confirm the existence of the thin films as the only elements present.

5.4.2 X-ray diffraction (XRD) of thin films

XRD measures the diffraction of the x-ray beam from different sections of a compound. This measurement is then used to characterize the crystallinity of a compound at an atomic level, since all compounds diffract the beam differently. XRD measurements show the crystallinity or amorphous nature of the thin films and their crystal structure. Figure 5.14 below shows XRD pattern of ZnO:Al.

5.4.2.1 ZnO:Al thin film (as-deposited)

![Graph of XRD pattern of 4% Al-doped ZnO thin film](image)

**Figure 5.14:** Graph of XRD pattern of 4% Al-doped ZnO thin film
The XRD patterns of all the Al-doped ZnO films show the presence of a sharp peak indicating that the films are highly oriented as shown in figure 5.14. The XRD patterns of the films reveal a crystalline hexagonal structure with the main diffraction peak located at angle $2\theta = 30.6^\circ$. This implies that aluminum has stronger growth of grains which are effectively incorporated into the crystal lattice by filling in the zinc vacant sites hence replacing zinc in the hexagonal crystal lattice (Afify et al., 2005). Peak intensity of the XRD diffraction reflections is determined by the crystalline grain size, structure and axis orientation. These results are in agreement with those of Mudjat et al. (2008). XRD analysis reveals that the film exhibit only the (002) peak, indicating that they have preferred orientation, implying a c-axis growth perpendicular to the substrate surface. The dominant (002) peak becomes sharper, indicating the well-established c-axis orientation of hexagonal structure of ZnO:Al thin films.

### 5.4.2.2 SnSe thin film (as-deposited)

The background of the diffraction pattern indicates the presence of a significant content of amorphous phase of the thin films. The orthorhombic structure of these amorphous films, as determined by X-ray diffraction, consists of randomly packed atoms with two-fold coordinated tin atoms mixed with two-fold coordinated selenium atoms. The peaks present in the annealed film also show the formation of orthorhombic structure of the SnSe thin films.
Figure 5.15: Graph of XRD pattern of as-deposited optimized SnSe thin film

Figure 5.16: Graph of XRD pattern of annealed optimized SnSe thin film at 150°C
Annealing improves the thin films from amorphous to crystalline nature having sharp peaks; but does not induce any compositional changes in the thin films (Zainal, Z. et al., 2003).

5.5 Fabrication and characterization of SnSe-ZnO:Al heterojunction

The heterojunction solar cell with glass/ZnO:Al/SnSe/Ag was fabricated in stages. The N-type layer of thin transparent conducting ZnO:Al film was deposited onto a glass substrate and a thin film of SnSe deposited onto ZnO:Al on the same substrate to form P-type layer. Fabrication was completed by deposition of silver as back contact on SnSe film to form the solar cell.

![Diagram of heterojunction solar cell]

**Figure 5.17:** Schematic diagram of fabricated ZnO:Al/SnSe/Ag P-N heterojunction solar cell

A solar cell simulator fitted with dichroic reflector was used to extract data that was used to plot the current-voltage characteristics. From the I-V characteristic, the open circuit voltage and short circuit current values were obtained. Figure 5.18 below shows the I-V characteristic of the fabricated P-N junction solar cell.
Figure 5.18: Simulated I-V characteristic of the fabricated SnSe-ZnO:Al P-N heterojunction solar cell

Open circuit voltage ($V_{OC}$) occurs when there is no current passing through the cell, $V$ (at $I=0) = V_{OC}$. The short circuit current ($I_{SC}$) corresponds to the short circuit condition when the impedance is low and is calculated when the voltage equals zero. $I$ (at $V=0) = I_{SC}$. $I_{SC}$ occurs at the beginning of the forward-bias sweep and is the maximum current value in the power quadrant.

The I-V characteristic from the solar cell simulator gave the following results for the fabricated solar cell of an area 4cm$^2$. The open circuit voltage, $V_{OC}$ was 0.59V and short circuit current, $I_{SC}$ was 1.06mA/cm$^2$. The value of short circuit current is generally low the due to presence of impurities during deposition process, electron-hole recombination and resistance of the back silver contact making the solar cell to have a slightly higher resistance to current.
Fill factor (FF) which essentially measures the quality of the solar cell through squareness of current-voltage was obtained by comparing the maximum power to the theoretical power (P_T) that would be output at both the open circuit voltage and short circuit current together. Its value was found to be 0.65.

Using the solar simulator’s radiation incident power of 100W on the fabricated solar cell, the conversion efficiency (η) which is the ratio of the electrical power output P_{out} compared to the solar power input, P_{in}, into the solar cell was obtained to be 0.41%.

The values obtained conforms with the results of Afify et al. (2005) which found the characteristics of Se/ZnO:Al/n-Si solar cell to have open circuit voltage (V_{oc}) of 0.58V; short circuit current (I_{sc}) of 5.47mA/cm^2 and fill factor (FF) of 0.68V.
CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Successful deposition of thin films of Sn$_x$Se$_y$ and ZnO:Al was done by thermal evaporation and reactive thermal evaporation techniques respectively. The reflectance and transmittance data showed aluminium-doped ZnO films have high transmittance above 65% and low reflectance below 45% within the visible range, infra red and ultraviolet regions. For Sn$_x$Se$_y$ films, transmittance was above 40% and reflectance below 45% within the visible range.

The optical properties investigated indicated that doping of ZnO with aluminium, and tin with selenium reduces the band gap of the thin films. SnSe thin had a low band gap energy of 1.18±0.05 eV that makes it a good absorber of photons of different wavelengths and ZnO:Al had a band gap energy of 3.28±0.05 eV that makes it a good transmitter by allowing photons to pass through. The structural properties of the thin films as revealed by XRD pattern showed that as-deposited SnSe films are amorphous while ZnO:Al are crystalline in nature.

Post-deposition annealing is important in improving the thin films electrical properties. Both SnSe and ZnO:Al had low resistivity values of 18.25±0.05 Ωcm and 20.38±0.05 Ωcm respectively. Annealing at 150°C changes chemical nature of the thin films surfaces by enhancing stronger growth of grains in SnSe thin films and making aluminium atoms to be effectively incorporated into the ZnO lattice. This improved the thin films conductivity by lowering their resistivity in the solar cell.
This research study found that the fabricated solar cell, SnSe-ZnO:Al/Ag, had a short circuit current of 1.06mA/cm², open circuit voltage of 0.59V, fill factor of 0.65 and an efficiency of 0.41%.

6.2 Recommendations

Further research is recommended by use of Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) which have high resolution for the thin films analysis. This is due to the small de Broglie wavelength of the electrons that allows very fine details of the thin films to be examined. Future research should also consider application of anti reflector on top of n-material in order to trap more light and generate more electron-hole pairs hence increase short circuit current in the solar cell. The vacuum chamber should also be re-designed in order to control the films thickness. These recommendations will improve solar cell conversion efficiency.
REFERENCES


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Shadia, J., Naseem, M. and Riyad, N. (2009). Electrical and Optical properties of ZnO:Al thin films prepared by pyrolysis technique. Faculty of Science; Physics department, University of Jordan; Ammam, **11942**, Jordan, 212-422.


APPENDICES

Appendix I: Photograph of Edwards Auto 306 vacuum coater

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Appendix III: Photograph of the Designed and Fabricated Sheet Resistivity Measurement system

Appendix IV: Photograph of MiniPal 2 XRF Spectrometer
Appendix V: Photograph of PW 3040/60 X’Pert XRD diffractometer
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