PHOTOVOLTAIC STRUCTURES USING THERMALLY EVAPORATED TIN SULFIDE THIN FILMS

Bushra A. Hasan
University of Baghdad, College of Science, Department of Physics

ABSTRACT

A reasonable photoelectric conversion efficiency has been achieved in thin film polycrystalline CdS/SnS solar cell which consists of 100 to 300nm layer of polycrystalline SnS with small grain size formed at room temperature using thermal evaporation technique. Tin sulfide forms in two crystalline structures depending on preparing conditions used: orthorhombic, SnS(OR), and zinc-blende, SnS(ZB). The prepared films posses n-type electrical conductivity for low thickness convert to p-type electrical conductivity as thickness increases, have band gaps between 2.1 and 1.7 eV. The photovoltaic structure: CdS/SnS shows an open circuit voltage (V_{OC}) of 400 mV, a short circuit current density (J_{SC}) of 0.061 mA/cm\(^2\), fill factor of 0.812and conversion efficiency of 1.49% under 106mW/cm\(^2\) illumination intensity. We present an evaluation for improvement in the light generated current density when the two types of SnS absorber films are used. The results given above were obtained with SnS film of 0.3 \(\mu m\) in thickness.

Index Terms- Tin sulfide, Thin films, Photovoltaic materials, Thermal evaporation, Optical properties, Solar cell.

1. INTRODUCTION

We reported previously [1,2] that chemically deposited thin films of tin(II) sulfide are polymorphic: SnS(ZB), consisting of zinc blend and orthorhombic structures or only orthorhombic, SnS(OR). With p-type conductivity and optical band gaps (E_g) of 1.7 eV and 1.2 eV, respectively, the SnS (ZB) and SnS(OR) films are candidates as absorbers in solar cells. Photovoltaic structures of SnO\(_2\):F/CdS/SnS(ZB)–Ag paint, have shown open circuit voltage V_{OC}=380 mV, and short circuit current density J_{SC}=0.05 mA/cm\(^2\), and those with SnS(OR) in place of SnS(ZB) have shown V_{OC}=380 mV and J_{SC}=0.17 mA/cm\(^2\) [1,2]. Other groups [3,4] have reported the use of SnS thin films deposited by electrochemical or spray pyrolysis as absorber components in CdS/ SnS solar cells.
With the electrochemically deposited SnS thin layers of 2 µm thickness [3], the cells showed 
\( V_{OC} = 270 \text{ mV}, J_{SC} = 2.36 \text{ mA/cm}^2, \text{fill factor } FF = 0.35 \) and efficiency \( \eta = 0.2\% \), for an area of 0.01 cm\(^2\), using evaporated In contacts. For a similar structure using SnS (0.6 µm) films deposited by spray pyrolysis [4], \( V_{OC} = 260 \text{ mV}, J_{SC} = 9.6 \text{ mA/cm}^2, FF = 0.53 \) and efficiencies of 1.3%, for an area of 0.3 cm\(^2\) were reported. The relative abundance 2.2 ppm of tin on the earth’s crust, which contrasts with 0.05ppm of In has prompted other groups to investigate \( \text{Cu}_2\text{ZnSnS}_4 \) as a structurally related alternative absorber material to chalcopyrites for application in thin film solar cells [5,6]. Conversion efficiencies of 5.74% have been reported in solar cells of \( \text{CdS/Cu}_2\text{ZnSnS}_4 \) [5]. Thus, tin chalcogenides are worth investigating as suitable absorbers in solar cells. In the present work we deposited photovoltaic structures of \( \text{CdS/SnS} \) and investigated their characteristics. From the measured I–V characteristics, we analyzed the solar cell parameters. The effect of thickness of SnS absorber components on the I–V characteristics are investigated.

2. EXPERIMENTAL DETAILS

Source material, SnS was prepared by melting high purity elements (99.99%) Sn and S in an evacuated quartz tube at a temperature of 1173 K. Tin sulfide films with different thicknesses (100, 200 and 300nm) were deposited on corning 7059 microscopic glass substrate by thermal evaporation technique under high vacuum (10 \(^{-5}\) Torr) at room temperature. The distance between source and substrates, rate of deposition have been maintained as constant at 15 cm and 8 Å/s, respectively. The as-deposited thin films of SnS were characterized for structural properties. The composition of the films was estimated using atomic absorption spectroscopy (AAS). Optical Interference Fringes was used to measure film thickness and Fizeau fringes of equal thickness are obtained in an optical apparatus of the type, the film thickness (d) is given by:

\[
t = \frac{\lambda \Delta x}{2 x}
\]

Where \( \Delta x \) is the shift between interference fringes. \( \lambda \) is the (Na) wavelength (589.3nm) and \( x \) is the distance between interference fringes. The samples having almost thickness of about \( t \pm 10\text{nm} \).

The phase of the synthesized thin films was confirmed by X-ray diffraction analysis. Further, the crystallite size was calculated by Scherer formula and found to increase from 58 to 79 nm with increase of thickness. For thickness, \( t = 300\text{nm} \), the films showed orthorhombic OR phase with a strong (111) preferred orientation. The films deposited with thickness \(< 200\text{nm} \) deviated from stoichiometry and additional phases such as \( \text{Sn}_2\text{S}_3 \) was found to be present. \( \text{CdS} \) layer of 0.1 µm thickness were deposited on SnS thin films. Photovoltaic structures were completed by printing electrodes of Ag paint and by evaporated electrodes of Al. The evaporation was done in a vacuum of \( 2 \times 10^{-5} \text{ mTorr} \). The electrical measurements for (CdS/SnS) Heterojunction, includes current-voltage characteristic measurements in the dark and under illumination conditions as well as capacitance-voltage characteristic measurements.

The capacitance of the Heterojunction is measured as a function of the reverse bias voltage at the range (0-1.5) Volt with fixed frequency of 1 kHz using HP-R2C unit model 4274A and 4275A multi-frequency LRC meter. Capacitance voltage measurements can be manipulated to yield a number of parameters such as: type of the junction (abrupt or graded), built in voltage (\( V_{bi} \)), carrier concentration and the width of the junction (depletion layer). The charge-carrier density \( (N_d) \) and width of the depletion layer \( (w) \) for both devices are calculated by the following equations:
When \( A' \) the active area (0.1962cm\(^2\)). The current-voltage measurements in the dark were done for the (CdS/SnS) heterojunction using Keithley digital electrometer 616 and D.C. power supply. The bias voltage was varied in the range of (0 – 1.5) Volt in the case of forward and reverse bias. From plots of the relation between the forward current and bias voltage, the ideality factor (\( \beta \)) can be determined by the relation defined as:

\[
I_s = I_s \exp \left( \frac{qV}{\beta k_B T} \right)
\]

where \( I_s \) is the saturation current, and \( \beta \) is the ideality factor parameter related to the various physical properties of the heterojunction having a value between 1 and 2. We can calculate the width of the depletion region by:

\[
w = \sqrt{\frac{2\varepsilon_s \gamma_{bi} V}{qN_d}}
\]

Where \( \varepsilon_s \) is the semiconductor permittivity for the two semiconductor materials and it is given by:

\[
\varepsilon_s = \frac{\varepsilon_n \varepsilon_p}{\varepsilon_n + \varepsilon_p}
\]

I-V measurements were made for (n-CdS/p-SnS, n-CdS/p-SnS n-CdS/p-SnS) heterojunction when they were exposed to Halogen lamp light Philips (120W) with intensity 106 mW/cm\(^2\) using Keithley Digital Electrometer 616, voltmeter and D.C. power supply under reverse bias voltage which was in the range (0-1.5) Volt.

**3. RESULTS AND DISCUSSION**

The junction capacitance variations of the reverse bias of SnS/CdS heterojunction prepared with different thicknesses (100, 200 and 300) nm are plotted in Figs. 1 to 3. It is clear that the capacitance increase with the increase of reverse bias, this is due to increase in the depletion layer width, which lead to an increase in built in voltage values. On the other hand the capacitance increase with the increase of thickness. This behavior ascribes to the increase of carrier concentration as a result of reduce the potential barrier accompanies the crystalline structure enhancement which lead to increase the capacitance and reduction of width layer. The width of depletion layer \( w \) decreases from 3.873 to 0.843\( \mu \)m with the increase of \( t \) from 100 to 300nm. The linear dependence of \( C^2-V \) curves give an indication that the impurity profile near the junction is abrupt. Table. 1 illustrates the parameters measured in this work. It is obvious that built in voltage decreases from 1.1 eVto 0.49eVwith the increase of \( t \) from 100 to 300 nm, this can be explained as follows: it well known that \( I_s \) decreases exponentially with \( E_g \) according to the relations:

\[
I_s = A q N_s \left( \frac{1}{N_A} \frac{D_n}{\tau_n} + \frac{1}{N_D} \frac{D_p}{\tau_p} \right) \exp \left( \frac{-E_g}{kT} \right)
\]

and \( V_{OC} \) is related to saturation current according to the relation:

\[
V_{OC} \approx \frac{kT}{q} \ln \frac{I_L}{I_s},
\]

thus large \( E_g \) leads to large \( V_{OC} \), and reducing of \( E_g \) as result of thickness increment lead to reduces \( V_{OC} \), on the other hand it is know that the maximum \( V_{OC} \) is the built-in potential of the junction, and the maximum built-in potential is close to the energy gap. Thus reducing of energy gap lead to reducing the built-in potential which consequently reducing \( V_{OC} \) as seen in next section. The carrier concentration increase one order of magnitude with increase of thickness in mentioned range.
Fig. 1 Variation of $A^2/C^2$ versus reverse biasing voltage for SnS/CdS with $t=(100)$ nm when the
$f=10$ kHz

Fig. 2 Variation of $A^2/C^2$ versus reverse biasing voltage for CdS/ SnS with with $t=(200)$ nm when the
$f=10$ kHz

Fig. 3 Variation of $A^2/C^2$ versus reverse biasing voltage for CdS/ SnS with with $t=(300)$ nm when the
$f=10$ kHz.

Fig. 4 show the semi-log relation of forward dark current and the biasing voltage (0-0.2)Volt for (p-CdS /n-SnS, p-CdS /p-SnS heterojunction prepared with different thicknesses (100, 200 and 300) . It clear that there are two region the first the recombination current is dominated while the
tunneling current is dominated at the second region, hence it is obey the recombination-tunneling mechanism. The mechanism of transport current also estimated from the ideality factor $\beta$ which is determined from the reverse saturation current which represents the intercept of straight line of the current at zero biasing. The measurements $\beta$ are listed in Table.1. The ideality factor increases from 1.126 to 1.431 when $t$ increase from 100 to 300nm. This is expected because such increase of thickness vanishing the diffusion mechanism, where $\beta$ equal take lower value therefore $\beta$ take higher value at higher $t$.

![Fig. 4 I-V characteristics for CdS/ SnS heterojunction with different thicknesses under dark condition](image)

One of the important parameters of diode measurement is a current-voltage characteristic which explains the behavior of the resultant current with the applied forward and reverse bias voltages. Fig. 5 to 7 show I-V characteristics for (n-CdS /p-SnS, heterojunction prepared with different thicknesses (100, 200 and 300) nm at forward and reverse bias voltages. The significant feature of these figures is the non ohmic behavior, where current flow in the forward biasing, but very law current flows in reverse biasing.

In general, the forward dark current is generated due to the flow of majority carriers and the applied voltage injects majority carriers which lead to the decrease of the built-in potential, hence decreases the width of depletion layer. One can recognize two region in the foreword current. The low biasing voltage region where the current is generation recombination, here the generated carriers is greater than the intrinsic carriers $n_p>n_i^2$.

The high biasing voltage, the current attributed to tunneling effect. The reverse bias current also contains from two regions. In the first region of low voltages, where the generation current dominates, here the increase of the applied voltage, lead to increase the depletion width with in turn increases, while at the second high voltage region, the diffusion current dominates. Also we can observe from this figure that the value of the current increases with increasing of thickness of CdS /SnS /films which is attributed to structure enhancement that imply the domination of one phase (orthorhombic) rather than two phases in lower thickness as well as increase of grain size.

The relation between illumination current and voltage of the n-SnS/n-CdS, (p-SnS/n-CdS and p-SnS/n-CdS heterojunction prepared R.T with different thicknesses (100, 200 and 300) nm and presented in Figs. (5 to 7). The measurements were carried out under incident power density equal to (106) mW/cm². From these figures it is clear that the photocurrent increases with increasing of the bias voltage, also at forward biasing voltage the current rises nearly exponential with forward voltage until the slope becomes more gradual. This can be due to high level injection of carriers such that the
applied voltage is no longer totally developed across the depletion region. At the high reverse biasing break down can occur due to impact ionization or zener tunneling. These mechanisms can be separated by temperature dependence. The width of the depletion region increases with increasing of the applied reverse bias voltage. The reverse bias illumination current is a function of the generation and diffusion of carriers. It can be noticed for all samples that the illumination current increases when thickness increases from 100 to 300nm which is due to the decrease of energy gap with the increase of t as presented in research published previously[7] (see table .1), the illumination current of n-CdS /p-SnS thickness of 300nm reveals proceeding increment with the increase of thickness as a result of increase of grain size values. The short circuit current $I_{SC}$ is determined. It is proportional to the light intensity, if the circuit is open, an open circuit voltage $V_{OC}$ will be generated, theses two parameters are of considered as distinction feature for the solar cell. It is obvious that $V_{OC}$ increases with the increase of t, this due to the increase of grain size value with the increase of thickness.

**Fig. 5** I–V curve of photovoltaic structures CdS/SnS Illumination, 106 mW/cm$^2$ with t=100nm.

**Fig. 6** I–V curve of photovoltaic structures CdS/SnS Illumination, 106 mW/cm$^2$ with t=200nm
It is clear from table .3 that \( V_{oc} \) change in systematic sequence with the increase of thickness for the three binary junction CdS / n-SnS, CdS/ p-SnS and CdS/ p-SnS, i.e \( V_{oc} \) increases with increase of thickness. The increasing of \( V_{oc} \) is attributed to decreasing of electron affinity \( \chi \) between the SnS system and CdS layer. Anyway the high values \( V_{oc} \) and at thickness 300nm p-SnS/CdS indicates that this junction at this condition of preparation is the most suitable for solar cell fabrication. For photocurrent consideration which is equal to short circuit current \( I_{sc} \), the smaller band gap the better because more photons are collected.

It is well known that to obtain a large \( V_{oc} \) a large \( E_{g}^{opt} \) is required. One can notice that maximum \( E_{g}^{opt} \) value 1.6 eV corresponding the maximum \( V_{oc} \) value 400 mV; the maximum \( V_{oc} \) is the built in potential \( V_{bi} \) of the junction, and the maximum \( V_{bi} \) is close to the energy gap. On the other hand the voltage increases with \( E_{g}^{opt} \) by having a small saturation current, so to maximize the power there exists an optimum value of \( E_{g}^{opt} \). It is found that efficiency has abroad maximum in the \( E_{g}^{opt} \) range (0.8-1.4eV). The ideal efficiency increases primarily due to the increasing of \( V_{oc} \) while the photocurrent is increased linearly with the intensity .Solar cell consists from the deposition of CdS layer on SnS thin film with different thicknesses 300 nm at room temperature, when the area of solar cell is equal (0.1962cm\(^2\)). This junction appears as current – voltage characteristic shown in Fig. 8 at dark, and under illumination, at incident power \( P_{in} = 106 \text{ mW/cm}^2 \).

The I–V curves of the structure showed initially an open circuit voltage, \( V_{OC} \), of 140 mV, and very low values of short circuit current density, \( I_{SC} \), of 0.0008mA. However, When the thickness increases to 200nm the \( V_{OC} \) increases to 380 mV, and \( I_{SC} \) increases slowly to 0.0012mA indicating good matching between the to window layer and absorber due to disappearance of another phase i.e. \( S_2Sn_3 \). With further increase of thickness the structure showed: \( V_{OC}=400 \text{ mV}, I_{SC}=0.0018 \text{ mA and FF}=0.816 \) with SnS thickness of 300nm. We attempted to improve the \( I_{SC} \) by increasing the thickness of the absorber films in the cell. The series resistance for the cell area mentioned with the Ag contacts together suggest that \( t=300\text{nm} \) is the best thickness among the three to provide good
contact with the top layer of the photovoltaic structure. The CdS film is the “window” or n-type layer. The low band gap of CdS (2.4–2.5 eV) for example, limits the solar cell performance due to absorption losses in the short wavelength range, resulting in a reduced short circuit current $I_{sc}$. The previous published data also show that increasing the thickness of SnS absorber results in increased series resistance in the photovoltaic structure.

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>$V_{bi}$ (volt)</th>
<th>$N_D$ (cm$^{-3}$)</th>
<th>$w_D$(µm)</th>
<th>$\beta$</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.1</td>
<td>$1.77 \times 10^{18}$</td>
<td>3.873</td>
<td>1.126</td>
<td>0.0008</td>
<td>140</td>
</tr>
<tr>
<td>200</td>
<td>0.95</td>
<td>$2.35 \times 10^{18}$</td>
<td>1.145</td>
<td>1.248</td>
<td>0.0012</td>
<td>270</td>
</tr>
<tr>
<td>300</td>
<td>0.49</td>
<td>$1.77 \times 10^{19}$</td>
<td>0.843</td>
<td>1.431</td>
<td>0.0018</td>
<td>400</td>
</tr>
</tbody>
</table>

p-CdS/ SnS Heterojunction under Illumination with thickness of (300) nm

<table>
<thead>
<tr>
<th>$P_{in}$/A (mW/cm$^2$)</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (Volt)</th>
<th>$I_{max}$ (mA)</th>
<th>$V_{max}$ (Volt)</th>
<th>$P_{out}$/A (mW/cm$^2$)</th>
<th>F.F</th>
<th>$\eta$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>106</td>
<td>0.012</td>
<td>400</td>
<td>0.01</td>
<td>390</td>
<td>72.49</td>
<td>0.812</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Solar cell from thin films of SnS assumed to have a shorter lifetime that thicker one cell. To improve the efficiency of solar cell it is absolutely essential to gain some understanding of the relationship between the structure include the gain boundaries and the carrier transport process, in particular the carrier lifetime (diffusion length) that determine the solar cell characteristics and the recombination velocity at the grain boundaries. However the general non uniformity that is typical of...
the grain structure has the direct and complex effect on the carrier transport. Rather the efficiency of SnS solar cell has only recently come to light. It was reported previously [8] that very small crystal exhibit relatively favorable cell characteristics. The cell characteristics are the product of current, voltage and fill factor, the open circuit voltage $V_{OC}$ is directly related to the cell lifetime and is used as a guide to the overall cell characteristics. This is because the current is related to light trapping effect and cell film thickness. According to Warner et al., the reason why low thickness cell exhibits a high conversion efficiency regardless of its small size is because of very low recombination speed at its grain boundaries. The low recombination velocities originate from the small barrier height at the grain boundaries.

4. CONCLUSIONS

We have demonstrated the use of thermally deposited SnS thin films of three different optical band gaps and crystal structures in solar cells consisting of CdS/SnS. By increasing the thickness of SnS layer in the structure, $I_{SC}$ could be increased to 0.0018 mA, maintaining a $V_{OC}$ of 400 mV. Further work on optimization of preparing condition of the films may improve the cell characteristics.

REFERENCES