CHAPTER 5

FABRICATION OF CdS/SnS AND Cd\textsubscript{1-x}Zn\textsubscript{x}S/SnS SOLAR CELL DEVICE STRUCTURES AND THEIR CHARACTERIZATION FOR PHOTOVOLTAIC APPLICATIONS

5.1 INTRODUCTION

SnS has attracted considerable attention due to its application in photovoltaic devices (Ichimura et al 2000, Hua et al 2005). SnS has band gap of 1.1 to 1.5 eV, therefore, it can be used as an absorption layer for solar cells with CdS, CdZnS and ZnS window layers. SnS is a non-toxic material which is abundant in nature. From the physical data of SnS, it can be used as a promising material for photovoltaic application and it is very cheap for the mass production (Patil et al 1971, Hardee et al 1977, Matsumoto et al 1984, Engelken et al 1987, Sharon et al 1988, Parenteau et al 1990, Hua et al 2005). In the present investigation SnS absorption layers have been prepared using ECD technique, which is the cheapest method among the other techniques to deposit large area thin films. This method has the advantages like producing uniform films and electroplating applications.

Noguchi et al (1994) has deposited the SnS absorption layer by vacuum evaporation and fabricated CdS/SnS structure and studied the photovoltaic properties. Ristov et al (2001) has reported the photovoltaic cell prepared by using the chemically deposited SnS with different window layers.
like CdO, Cd$_2$SnO$_4$ and SnO$_2$:F and studied the photovoltaic behavior. Ramakrishna Reddy et al (2004) reported 1.3% efficiency for CdS/SnS structure prepared using spray pyrolysis. It is noted that so far there is no report on the SnS based heterojunction solar cells fabricated using ECD technique.

The lattice constant of SnS is close to that of II-VI compounds, CdS and CdZnS, so the resulting heterojunction has minimum lattice mismatch thereby minimizing the interface problem (Yamaguchi et al 1996). The band energy of Cd$_{1-x}$Zn$_x$S can be controlled in the range from 2.42 eV (CdS) to 3.6 eV (ZnS) by changing the x value in the alloy composition. CdS and CdZnS with SnS become a subject of considerable interest due to the possibility of using these materials as window layers in the heterojunction solar cells (Agnihotri et al 1979).

The replacement of CdS with the higher band gap ternary CdZnS alloy has also led to an increase in the short circuit current and open circuit voltage in the solar cell (Chu et al 1991). In the present work the n-type window layers were deposited using photochemical deposition method (PCD).

The deposition of SnS by pulsed electrochemical deposition and fabrication of CdS/SnS and CdZnS/SnS solar cells, are discussed elaborately in this chapter. CdS and CdZnS window layers were deposited by photochemical deposition (PCD) method. The surface property and the compositional details were studied using scanning electron microscopy (SEM) and Auger electron spectroscopy (AES), respectively. The fabricated p-SnS/n-CdS and p-SnS/n-CdZnS solar cells were characterized under the illuminating condition 100 mW/cm$^2$ (AM1.5).
5.2 EXPERIMENTAL PROCEDURE FOR DEPOSITION

5.2.1 Cadmium sulphide and cadmium zinc sulphide deposition

CdS window layers were deposited on a well ultrasonically cleaned ITO coated glass plates by photochemical deposition technique. The deposition of CdS was carried out from an aqueous solution containing 2 mmol/l CdSO$_4$ and 100 mmol/l Na$_2$S$_2$O$_3$. The details are presented in chapter 2. CdZnS window layers were also deposited by the similar process, for depositing Cd$_{1-x}$Zn$_x$S alloys the chemicals such as CdSO$_4$, ZnSO$_4$ and Na$_2$S$_2$O$_3$ were used. The molar ratios of the chemicals were adjusted to obtain the desired alloy composition. The reaction mechanism of CdS and CdZnS formation has been elaborately discussed in chapters 2 and 3. Figure 5.1 shows the (a) as deposited CdS, (b) 100$^\circ$C annealed CdS and (c) as deposited CdZnS layer on ITO substrate using PCD method.

![Figure 5.1](image)

**Figure 5.1** CdS and CdZnS thin films deposited for solar cell fabrication: (a) as deposited CdS, (b) 100$^\circ$C annealed CdS and (c) as deposited CdZnS layer
5.2.2 Tin sulphide deposition

Tin sulphide (SnS) absorbing layer was deposited by using electrochemical deposition (ECD) technique. ECD setup consists of three electrode cell, saturated calomel electrode (SCE) was used as a reference electrode, platinum sheet as the counter electrode (anode). CdS or CdZnS deposited on ITO coated glass sheet was used as a working electrode (cathode). The SnS deposition area was about 0.7 to 0.9 cm² remaining area was masked. An aqueous solution containing 30 mmol/l SnSO₄ and 100 mmol/l Na₂S₂O₃ (pH=2.7) was used for the deposition of SnS absorbing layer and the pH of the solution was not adjusted. The SnS layers were deposited on CdS and CdZnS layers for the fabrication of heterostructure solar cell structure.

SnS layers were deposited by using different applied potential. The potential applied is in the form of three step pulse and two step pulse. For fabricating solar cell structure the following three conditions were followed:

1. Condition A (Three step pulse – Negative to positive)
2. Condition B (Three step pulse – Positive to Negative)
3. Condition C (Two step pulse)

The detailed explanation for all the three conditions has been given in chapter 4. Figure 5.2 shows the current profile of the three step pulse applied for the SnS deposition (condition A) on various substrates ITO, ITO/CdS (as deposited) and ITO/CdS (annealed 100°C). In the case of SnS deposition on ITO substrate: when the first step potential \( V_1 = -1.0 \) V Vs. SCE is applied
Figure 5.2 Current profile during SnS deposition (condition A) under various substrate conditions.
for the deposition, there is a sudden increase in the current value for about 6 to 7 mA. This current gradually decreases even when the potential is constant for about 6 seconds, owing to the decrease of Sn\(^{2+}\) ions and S atoms near the substrate surface. The gradual decrease in current shows decrease in the deposition rate of SnS because the concentration of Sn\(^{2+}\) ions and S atoms near the substrate is not constant. In the second step there is no such increase or decrease in the current value, it is almost zero and during this step it is expected that the Sn\(^{2+}\) ions and S atoms approach the substrate surface, but do not participate in the deposition. When the third step potential \(V_3=0.0\) V Vs. SCE is applied, there is an increase in the current value in the positive direction to about 7 to 8 mA. This current is responsible for dissolving of unreacted metal ion or weakly bonded SnS layer near the film solution interface.

There was a difference in the current value when the CdS coated ITO substrate was used, which is due to the presence of the CdS layer. However there is no much difference in cyclic voltammogram measured for the CdS/ITO/Glass and ITO/Glass as the substrates. The potential used for SnS deposition on ITO substrate is used for the deposition of SnS layer in the fabrication of SnS/CdS or SnS/CdZnS solar cells. Especially for the CdS layer annealed at 100°C the positive current which is responsible for dissolving the unreacted Sn or weakly bonded SnS, is observed. The solar cell using 100°C annealed CdS layer shows improvement in the solar cell parameters which will be discussed in the photovoltaic characterization part.

### 5.3 FABRICATION OF \( p\)-SnS/\( n\)-CdS AND \( p\)-SnS/\( n\)-CdZnS STRUCTURES

The ITO coated glass sheets were used for the fabrication of the SnS/CdS heterostructure. The resistance of the ITO used is about
8 to 9 Ω/cm$^2$. The substrate size is about 2.5 cm x 1 cm, which is cleaned well using organic solvent alkyl benzene in the ultrasonic bath. The cleaned substrates were masked and CdS layer was deposited using photochemical deposition method. The CdS deposition area is about 1 cm$^2$ to 9 mm$^2$ and then the Glass/ITO/CdS structure was used as the substrate for SnS deposition. For SnS deposition the substrate is again remasked, so that the SnS layer deposits only on the CdS or CdZnS layer. All the depositions were carried out at room temperature.

The SnS layer was deposited using pulsed electrochemical deposition technique. Indium metal (purity 99.9%) was evaporated on the SnS as a contact electrode. The electrode size is 1 mm$^2$ and the distance between two electrodes is 1 mm. Finally Glass/ITO/CdS/SnS/In structure was fabricated. In the similar way Glass/ITO/CdZnS/SnS/In structure was also fabricated, the solar cells were also fabricated for different $x$ values in Cd$_{1-x}$Zn$_x$S alloys. The schematic representation of the fabricated solar cell structure is shown in Figure 5.3. The fabricated solar cell structures CdS/SnS and CdZnS/SnS are shown in Figures 5.4 and 5.5, respectively. The fabricated solar cell was characterized under 100 mW/cm$^2$ (AM 1.5) using the xenon lamp.

![Figure 5.3 Schematic representation of the fabricated solar cell structure](image-url)
5.4 RESULTS AND DISCUSSION
5.4.1 Thickness and surface morphology

The thickness of the CdS and CdZnS window layers are about 0.1 to 0.2 μm and the SnS layer deposited on CdS is about 2 μm. The thickness measured for CdS/SnS structure using step height method is shown in Figure 5.6. The surface of the SnS layer was analysed by using scanning electron microscopy (SEM). Figures 5.7 and 5.8 show the surface morphology of the SnS layer deposited using condition A on as deposited CdS and annealed CdS window layer (annealing condition: 100°C/N₂/1 hour). The SnS layer deposited on as deposited CdS shows bigger grain size and also the surface is rough. The as deposited CdS layer has some surface roughness...
which is also observed in the SnS growth. The SnS layer deposited on 100°C annealed CdS layer shows decrease in the grain size and the surface roughness is less compared to the SnS layer deposited on as deposited CdS. Annealing the CdS layer results in the improvement of SnS layer deposited on it, also the SnS films are more compact. Similarly, Figures 5.9 and 5.10 show the surface morphology of SnS layer deposited using condition B on as deposited CdS and 100°C annealed CdS layers, respectively. Figures 5.11 and 5.12 show the surface morphology of SnS layer deposited using condition C on as deposited CdS and 100°C annealed CdS layers, respectively.

![Graph](image_url)

**Figure 5.6** Thickness measured for the CdS/SnS structure using step height method
Figure 5.7  SEM micrograph of SnS layer deposited using condition A on as deposited CdS window layer

Figure 5.8  SEM micrograph of SnS layer deposited using condition A on 100°C annealed CdS window layer
Figure 5.9  SEM micrograph of SnS layer deposited using condition B on as deposited CdS window layer

Figure 5.10  SEM micrograph of SnS layer deposited using condition B on 100°C annealed CdS window layer
Figure 5.11  SEM micrograph of SnS layer deposited using condition C on as deposited CdS window layer

Figure 5.12  SEM micrograph of SnS layer deposited using condition C on 100°C annealed CdS window layer
5.4.2 Auger electron spectroscopy (AES) for compositional analysis of SnS

Figure 5.13 shows the AES spectrum for SnS absorbing layer deposited on CdZnS window layer. In addition to Sn and S, the presence of oxygen is also observed. The presence of oxygen is not only in the film surface but also present throughout the film, but compared to surface the oxygen present inside the film is less. The AES differential spectrum shows no cadmium peak, so it is very clear that the SnS layer has covered the window layer CdZnS completely. Standard SnS and SnO were used for calculating the atomic ratio of elemental Sn, S and O in the SnS film deposited on CdZnS layer. The atomic ratio was calculated as Sn = 1, S = 1.4 and O = 0.2, which shows SnS layer is rich in sulphur. In the present elemental calculation the presence of oxygen is considered as SnO.

![AES spectrum](image)

**Figure 5.13** AES spectrum for SnS layer deposited on CdZnS window layer
5.4.3 X-ray diffraction studies

The as deposited SnS layers deposited under different conditions were subjected to XRD studies for their structural properties. Figures 5.14, 5.15 and 5.16 show the XRD spectrum for the SnS layer deposited using condition A, condition B and condition C on as deposited and 100°C annealed CdS window layers, respectively. It is very clear that the deposited SnS layer is of orthorhombic structure and the obtained XRD data were compared with the JCPDS data. The XRD data for SnS deposited on as deposited and 100°C annealed CdS layer seem to be similar. The deposited SnS films are amorphous in nature. The peaks observed at 2θ values 32.1°, 39.3°, 44.2° and 45° degrees are attributed to (040), (131), (141) and (150) planes. The broad peak at about 2θ=26.8° corresponds to (021) plane. Since the layers were deposited on ITO coated glass sheet the ITO peaks were also observed.

Figure 5.14 X-ray diffraction pattern for SnS layer deposited using condition A
Figure 5.15  X-ray diffraction pattern for SnS layer deposited using condition B

Figure 5.16  X-ray diffraction pattern for SnS layer deposited using condition C
5.5 PHOTOVOLTAIC CHARACTERIZATION

5.5.1 Performance of n-CdS/p-SnS heterojunction solar cells

The solar cells were fabricated with CdS as a window layer, which was deposited by using PCD method. Two types of CdS window layers were used, one is the as deposited CdS and another is 100°C annealed CdS. The CdS annealing was carried out as follows: after depositing CdS layer the film was kept at 100°C in nitrogen atmosphere for about one hour, here the nitrogen is kept continuously flowing at the rate of 1.5 to 2 liters per minute.

The SnS layers were deposited using three deposition conditions: (1) In condition A the applied potential is $V_1 = -1.0$, $V_2 = -0.6$ and $V_3 = 0.0$ V Vs. SCE, where $V_1$, $V_2$, $V_3$ are applied for about 6, 10, 10 seconds, respectively. (2) In condition B the applied potential is $V_1 = 0.0$, $V_2 = -0.6$ and $V_3 = -1.0$ V Vs. SCE, where $V_1$, $V_2$, $V_3$ are applied for about 10, 10, 6 seconds, respectively. (3) In condition C the SnS deposition was carried out using two step pulse potential: $V_1 = -1.0$ V Vs. SCE for 6 seconds and $V_2 = 0.0$ V Vs. SCE for 10 seconds. The SnS layers were deposited for about 30 minutes in all the above three conditions. The rectification property of n-CdS/p-SnS heterojunction solar cell is shown in Figure 5.17. The fabricated solar cell shows rectifying property, but it has some leakage current also. The fabricated solar cells were subjected to photovoltaic characterization under AM1.5 condition.

I-V characteristic curves of CdS/SnS heterostructure fabricated using SnS layer deposited under condition A on as deposited and 100°C annealed CdS layers are shown in Figure 5.18. The performance of the fabricated solar cells was analyzed under 100mW/cm² (AM1.5). The cell fabricated on as deposited CdS layer shows open circuit voltage
(V_{oc}) = 117 mV, short circuit current density (I_{sc}) = 1.14 mA/cm^2, fill factor (FF) = 0.29 and efficiency (\eta) = 0.038%. The cell fabricated on 100°C annealed CdS window layer shows V_{oc} = 180 mV, I_{sc} = 1.31 mA/cm^2, FF = 0.30 and \eta = 0.072%.

I-V characteristic curves of CdS/SnS heterostructure fabricated using condition B for SnS deposition on as deposited and 100°C annealed CdS window layers are shown in Figure 5.19. The cell fabricated on as deposited CdS window layer shows V_{oc} = 270 mV, I_{sc} = 2.37 mA/cm^2, FF = 0.35 and \eta = 0.22%. The cell fabricated on 100°C annealed CdS window layer shows V_{oc}=210 mV, I_{sc} = 1.29 mA/cm^2, FF = 0.31 and \eta = 0.086%.

I-V characteristic curves of CdS/SnS heterostructure fabricated using condition C for SnS deposition on as deposited and 100°C annealed CdS window layers are shown in Figure 5.20. The cell fabricated on as deposited CdS window layer shows V_{oc} = 175 mV, I_{sc} = 1.09 mA/cm^2, FF = 0.33 and \eta = 0.064%. The cell fabricated on 100°C CdS window layer shows V_{oc} = 170 mV, I_{sc} = 3.3 mA/cm^2, FF = 0.37 and \eta = 0.2%.

The cell fabricated using condition B shows the maximum V_{oc} value but the efficiency is low because the observed current density is low compared to the other solar cells. The result obtained from the solar cell fabricated using annealed CdS window layer shows higher solar cell parameters than the cell fabricated using as deposited CdS window layer. The solar cell parameters for different SnS deposition condition on as deposited and 100°C annealed CdS under AM1.5 illuminating condition are tabulated in Tables 5.1 and 5.2.
Figure 5.17  Rectification property of CdS/SnS heterostructure solar cell

Figure 5.18  Photovoltaic behaviour of the heterostructure solar cell fabricated using condition A for SnS layer deposition
Figure 5.19  Photovoltaic behaviour of the heterostructure solar cell fabricated using condition B for SnS layer deposition

Figure 5.20  Photovoltaic behaviour of the heterostructure solar cell fabricated using condition C for SnS layer deposition
Table 5.1  
Solar cell parameters for different SnS deposition conditions on as deposited CdS under AM1.5 illuminating condition

<table>
<thead>
<tr>
<th>n-CdS/p-SnS</th>
<th>Condition A</th>
<th>Condition B</th>
<th>Condition C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{oc}$ (mV)</td>
<td>117</td>
<td>270</td>
<td>175</td>
</tr>
<tr>
<td>$I_{sc}$ (mA/cm$^2$)</td>
<td>1.14</td>
<td>2.36</td>
<td>1.09</td>
</tr>
<tr>
<td>FF</td>
<td>0.29</td>
<td>0.35</td>
<td>0.33</td>
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</tbody>
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Table 5.2  
Solar cell parameters for different SnS deposition conditions on 100°C annealed CdS under AM1.5 illuminating condition

<table>
<thead>
<tr>
<th>n-CdS/p-SnS</th>
<th>Condition A</th>
<th>Condition B</th>
<th>Condition C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{oc}$ (mV)</td>
<td>180</td>
<td>210</td>
<td>170</td>
</tr>
<tr>
<td>$I_{sc}$ (mA/cm$^2$)</td>
<td>1.31</td>
<td>1.29</td>
<td>3.3</td>
</tr>
<tr>
<td>FF</td>
<td>0.30</td>
<td>0.31</td>
<td>0.37</td>
</tr>
</tbody>
</table>
5.5.2 Performance of n-CdZnS/p-SnS heterojunction solar cells

The band gap of CdZnS can be varied from 2.42 to 3.6 eV by changing the alloy composition and change in the alloy composition leads to the change in lattice parameters. The change in band gap will be much favourable for the window layer application and change in lattice constants will solve the lattice mismatch problem. Considering these parameters the solar cells were fabricated using n-Cd$_{1-x}$Zn$_x$S as a window layer with different x values. The rectification property of the CdZnS/SnS structure is shown in Figure 5.21. The solar cell structure n-Cd$_{1-x}$Zn$_x$S/SnS was fabricated using x value 0.07 and SnS layer by using condition B. The I-V characteristics of the structure Cd$_{0.93}$Zn$_{0.07}$S/SnS under AM1.5 condition is shown in Figure 5.22. The photovoltaic parameters like $V_{oc} = 264$ mV and $I_{sc} = 3.91$ mA/cm$^2$, FF = 0.34 and $\eta = 0.35\%$ were obtained for the fabricated cell using Cd$_{0.93}$Zn$_{0.07}$S as window layer.

The cell fabricated with x value 0.13 shows $V_{oc} = 288$ mV, $I_{sc} = 9.1$ mA/cm$^2$, FF = 0.27 and $\eta = 0.71\%$. Current-voltage characteristics for the solar cell fabricated using x value 0.13 in Cd$_{1-x}$Zn$_x$S/SnS structure and the SnS layer deposited using condition B is shown in Figure 5.23. The I-V characteristics of Cd$_{0.81}$Zn$_{0.19}$S/SnS are shown in Figure 5.24. The solar cell fabricated with x value 0.19 shows $V_{oc} = 258$ mV, $I_{sc} = 3.4$ mA/cm$^2$, FF = 0.26 and $\eta = 0.23\%$. It is observed that using CdZnS as a window layer, the photovoltaic parameter values increase. In the present work the solar cell was fabricated using x = 0.07, 0.13 and 0.19 in Cd$_{1-x}$Zn$_x$S window layer among that x = 0.13 shows the highest solar cell parameter and the efficiency calculated is about 0.71\%.
The effect on solar cell parameters of 100°C annealed CdZnS layer was also studied using 13% zinc in the alloy composition. The cell parameters obtained for the SnS layer deposited using condition B show $V_{oc} = 72 \text{ mV}$, $I_{sc} = 1.289 \text{ mA/cm}^2$, FF = 0.24 and $\eta = 0.023\%$. In the case of SnS layer deposited using condition A, $V_{oc} = 280 \text{ mV}$, $I_{sc} = 4.82 \text{ mA/cm}^2$, FF = 0.34 and $\eta = 0.46 \%$ were obtained. The cell fabricated using 100°C annealed CdZnS window layer with SnS deposition using condition A shows maximum solar cell parameters.

![Figure 5.21 Rectification property of CdZnS/SnS heterostructure](image-url)
Figure 5.22  I-V characteristics of n-Cd$_{0.93}$Zn$_{0.07}$/p-SnS

Figure 5.23  I-V characteristics of n-Cd$_{0.87}$Zn$_{0.13}$/p-SnS
Figure 5.24  I-V characteristics of n-Cd$_{0.81}$Zn$_{0.19}$/p-SnS

Table 5.3  Cell parameters under AM1.5 illuminating condition for Cd$_{1-x}$Zn$_x$S/p-SnS structure with different x values and SnS layer deposited using condition B

<table>
<thead>
<tr>
<th>n-Cd$_{1-x}$Zn$_x$S/p-SnS</th>
<th>Condition B</th>
<th>V$_{oc}$ (mV)</th>
<th>I$_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
</tr>
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<tr>
<td>x=0.07</td>
<td>264</td>
<td>3.91</td>
<td>0.34</td>
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<tr>
<td>x=0.13</td>
<td>288</td>
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<td>0.27</td>
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<tr>
<td>x=0.19</td>
<td>258</td>
<td>3.40</td>
<td>0.26</td>
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</tr>
</tbody>
</table>
5.6 CONCLUSIONS

SnS/CdS and SnS/CdZnS solar cells were successfully fabricated using ECD and PCD techniques. The two techniques used in the present study have advantages like economic, easy to scale up and large area deposition. Both CdS/SnS and CdZnS/SnS heterostructures show good rectification property. The surface morphology of the SnS layer deposited on as deposited and 100°C annealed CdS window layers was analyzed. The SnS layer deposited on 100°C annealed CdS window layer shows better surface morphology. The AES measurement shows good surface coverage and no elemental peak corresponding to window layer was observed. The solar cell fabricated on the annealed CdS window layer shows improvement in the solar cell parameters. The SnS/CdS heterostructure fabricated using condition B shows maximum solar cell parameters. The CdZnS/SnS solar cells fabricated using 13% zinc concentration in CdZnS window layer shows maximum solar cell parameters. The solar cell fabricated using CdZnS window layer shows higher cell performance than the solar cell fabricated using CdS window layer. It is possible to obtain higher efficiencies using this structure in future by changing the deposition parameters.