Chapter 3

Fabrication of TCO/CuInS$_2$/In$_2$S$_3$/Ag heterojunction solar cells using single and double layer structure for the absorber layer

3.1 Introduction

The superstrate configuration of CuInS$_2$ (i.e., TCO/TiO$_2$/In$_2$S$_3$/CuInS$_2$/Ag) does not work up to our expectation, as explained in detail in last chapter. Hence trials were also conducted to fabricate solar cells without using TiO$_2$ thin films and followed TCO/In$_2$S$_3$/CuInS$_2$/Ag configuration with light from TCO side. Thickness of In$_2$S$_3$ was kept as low as possible to ensure that maximum light is transmitted to the CuInS$_2$ absorber layer. As we are depositing CuInS$_2$ layer over thin In$_2$S$_3$ layer it gets peeled off. On increasing buffer layer thickness, junction is formed between CuInS$_2$ and In$_2$S$_3$, but it shows feeble light activity. This is because light is not reaching up to the absorber due to the absorption in thick In$_2$S$_3$. It is to be specifically noted that here the entire device fabrication was done using automated spray pyrolysis machine having facilities to control precisely the spray parameters like spray rate, substrate temperature and spray head movement [1]. Still a working device with TCO/In$_2$S$_3$/CuInS$_2$/Ag configuration could not be fabricated. Similar observations were also made by John et al. while fabricating CuInS$_2$/In$_2$S$_3$ heterojunction using manual spray technique; this may be due to specialty of spray technique [2]. Devices are hence fabricated hereafter with TCO/CuInS$_2$/In$_2$S$_3$/Ag structure and it shows photo activity. This structure is used for further studies in this chapter.
3.2 ITO/CuInS$_2$/In$_2$S$_3$/Ag solar cell fabrication and characterization

A schematic diagram of the fabricated device is shown in Figure 3.1(a). ITO films coated glass (sheet resistance ~ 12 $\Omega/\square$, Geomatec, Japan; deposited employing sputtering) was used as the substrate in this work. Over ITO, CuInS$_2$ absorber and In$_2$S$_3$ buffer layer were spray deposited using the optimized spray conditions as explained in chapter 2. Finally, for top contact, silver is vacuum evaporated over the cell structure. Silver is a good choice for top electrode in CuInS$_2$/In$_2$S$_3$ heterojunction solar cells as it improves the crystallinity of In$_2$S$_3$ thin films [3]. Dark and illuminated J-V characteristics of the heterojunctions were recorded using source measure unit (NI PXI-1033). For illumination purpose ‘Class AAA’ solar simulator (PET, model SS50AAA) was used.

![Figure 3.1(a) Schematic diagram of the fabricated device (b) Top view of the device.](image)

3.2.1 Effect of CuInS$_2$ absorber layer thickness on solar cell performance

Absorber layer in a solar cell absorbs sunlight and converts the electromagnetic energy of sunlight to the energy of electron hole pairs. Hence
thickness of the absorber layer is crucial parameter that can influence the overall performance of the device. The absorber layer should possess enough thickness to absorb maximum amount of light. At the same time, thickness of the absorber should be comparable with minority carrier diffusion length to ensure effective charge carrier collection [4, 5]. Hence there should be an optimum thickness for the absorber layer. In this study absorber layer thickness was varied simply by adjusting the spray volume of the precursor solution. Buffer layer thickness (~ 300 nm) was kept constant for all trials. Top contact silver was deposited as an array of 9 electrodes, each having area of 0.03 cm² and thickness of 50 nm (Figure 3.1(b)) for all devices, which were isolated by curving around each electrode, using doctor-blade. Five samples were prepared for each thickness of the absorber layer (i.e. total of 45 cells were considered for each thickness in this study). The photovoltaic (PV) parameters like $V_{oc}$, $J_{sc}$, fill factor and efficiency were measured for each sample. Average value, (along with upper and lower limit values) of these parameters for each thickness of the absorber is tabulated in Table 3.1.

<table>
<thead>
<tr>
<th>Spray volume(ml)</th>
<th>Thickness of CuInS₂ (nm)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>Fill factor (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>150±10</td>
<td>408±30</td>
<td>6.52±1.98</td>
<td>37±4</td>
<td>1.02±0.28</td>
</tr>
<tr>
<td>60</td>
<td>210±14</td>
<td>448±26</td>
<td>9.74±0.89</td>
<td>42±2</td>
<td>1.84±0.30</td>
</tr>
<tr>
<td><strong>72</strong></td>
<td><strong>320±18</strong></td>
<td><strong>481±11</strong></td>
<td><strong>11.13±1</strong></td>
<td><strong>44±3</strong></td>
<td><strong>2.33±0.26</strong></td>
</tr>
<tr>
<td>84</td>
<td>370±20</td>
<td>467±17</td>
<td>7.66±1.64</td>
<td>45±5</td>
<td>1.61±0.25</td>
</tr>
<tr>
<td>96</td>
<td>440±25</td>
<td>393±50</td>
<td>6.45±1</td>
<td>31±6</td>
<td>0.78±0.31</td>
</tr>
</tbody>
</table>

Table 3.1 Performance parameters of the device with different absorber layer thickness.

As absorber layer thickness increases from ~ 150 nm to 320 nm, an overall improvement in performance parameters can be observed. Average values of $V_{oc}$ improves from 408 to 481 mV, $J_{sc}$ improves from 6.52 to 11.13 mA/cm², fill factor improves from 37 to 44 % and efficiency improves from...
1.02 to 2.33%. But for devices with thickness of absorber layer above ~ 320 nm, the PV parameters start decreasing. In our case, light reaches the junction through absorber side and hence more absorption will be naturally near ITO-absorber interface. If thickness of the absorber was very high (above 320 nm), light generated carriers far away from the junction will find it difficult to reach the junction due to losses because of recombination and/or other losses. This may be the reason for poor functioning of the devices with absorber layer thickness above 320 nm. Best efficiency range (2.33 ± 0.26 %) was observed for device with an absorber layer thickness of 320 ± 18 nm. Out of the measurements from 45 cells (five different trials) of this configuration, 25 cells (55 % of total cells) exhibited this efficiency range.

3.2.2 Effect of buffer layer thickness on solar cell performance

In CuInS$_2$/In$_2$S$_3$ heterojunction, diffusion of Cu from CuInS$_2$ to In$_2$S$_3$ buffer layer was an easy process due to the high mobility of Cu ions [6, 7]. As a result of this diffusion, a portion of In$_2$S$_3$ buffer layer, near to CuInS$_2$ layer, gets converted to CuInS$_2$. Hence, if the buffer layer thickness is too low, Cu diffusion becomes significant reaching top of the buffer layer and the device gets shorted. For higher thickness of the resistive buffer layer (~ $10^3$ Ω.cm), series resistance of the device increases which adversely affect the current obtained from the device [8, 9]. Hence there should be an optimum thickness of buffer layer for better performance of CuInS$_2$/In$_2$S$_3$ heterojunction. In the next step, In$_2$S$_3$ buffer layer thickness was varied above and below 300 nm by adjusting the spray volume of the precursor solution. Here absorber layer thickness was kept constant around 320 nm, which is fixed from the above studies. Five samples were prepared for each thickness of the buffer layer. Average value (along with upper and lower limit values) of PV parameters for each thickness of the buffer layer is tabulated in Table 3.2.
Fabrication of TCO/CuInS\textsubscript{2}/In\textsubscript{2}S\textsubscript{3}/Ag Heterojunction Solar Cells……

<table>
<thead>
<tr>
<th>Spray volume (ml)</th>
<th>Thickness of In\textsubscript{2}S\textsubscript{3} (nm)</th>
<th>V\textsubscript{oc} (mV)</th>
<th>J\textsubscript{sc} (mA/cm\textsuperscript{2})</th>
<th>Fill factor (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>230±15</td>
<td>413±39</td>
<td>8.76±0.99</td>
<td>38±4</td>
<td>1.46±0.23</td>
</tr>
<tr>
<td>24</td>
<td>300±10</td>
<td>481±11</td>
<td>11.13±1</td>
<td>44±3</td>
<td>2.33±0.26</td>
</tr>
<tr>
<td>32</td>
<td>410±25</td>
<td>498±8</td>
<td>7.83±1.16</td>
<td>40±2</td>
<td>1.58±0.31</td>
</tr>
</tbody>
</table>

Table 3.2 Performance parameters of the device with different buffer layer thickness.

By varying buffer layer thickness above or below 300 nm, there is no improvement in the efficiency of the device. At lower thickness (~ 230 nm) of the buffer layer, Cu diffusion may be prominent which can reduce the PV parameters. At higher thickness, due to the resistive nature of In\textsubscript{2}S\textsubscript{3} buffer layer, series resistance of the device increases [8]. As a result, the average value of current decreases from 11.13 to 7.83 mA/cm\textsuperscript{2}.

One can conclude from the studies that the absorber layer thickness should be ~ 320 nm and buffer layer thickness should be ~ 300 nm for the better performance of ITO/CuInS\textsubscript{2}/In\textsubscript{2}S\textsubscript{3}/Ag heterojunction solar cells. The best device under this study has V\textsubscript{oc} = 478 mV, J\textsubscript{sc} = 12.13 mA/cm\textsuperscript{2}. Fill factor and efficiency are 45 % and 2.59 % respectively. The illuminated J-V characteristics of the best device fabricated is shown in Figure 3.2.
Figure. 3.2 J-V characteristics of ITO/CuInS₂/In₂S₃/Ag solar cell.

3.2.3 XPS depth profile analysis of the device

XPS depth profile analysis of the fabricated solar cell was carried out to determine chemical state of elements across the thickness of the cell. Here argon ion sputtering was employed for layer by layer etching of the solar cell. The information collected from each layer is represented as series of peaks corresponding to binding energies of valence electrons of each element; one such graph is denoted as an ‘etching cycle’ in Figure 3.3. The lowest value/beginning of Y-axis represents the surface of the solar cell (In₂S₃ portion) and top represents the substrate.
In order to collect information about the chemical states of copper, indium, sulfur and oxygen across the thickness of the device, 250 cycles of Ar ion sputtering was done. Binding energy (B.E) peaks at 932 eV (2p_{3/2}) and 952 eV (2p_{1/2}) correspond to that of copper [10]. Presence of indium is confirmed by the B.E peaks at 445.2 eV (3d_{5/2}) and at 454 eV (3d_{3/2}). B.E peak at 162.32 eV corresponds to S 2p_{3/2} [11]. Presence of oxygen is also observed inside the device. B.E of oxygen at the surface of the sample was 534 eV and that in the sample was 531 eV. This shift in B.E of oxygen is due to the substitution of sulfur in the surface of the device by oxygen to form sulfate [2]. This process can be inferred by the decrease in peak height of sulfur and increase in peak height of oxygen at the surface of the device.

Lower portion of the graph (beginning of Y-axis) represents In_{2}S_{3} portion. For device fabrication thicker (~ 300 nm) In_{2}S_{3} was used. XPS analysis shows that pure In_{2}S_{3} was present only for one etching cycle of the device. From the second etching cycle onwards, binding energy peaks
correspond to Cu was observed in In$_2$S$_3$ buffer layer, which indicates the diffusion of Cu from CuInS$_2$ absorber layer to In$_2$S$_3$. Cu has high diffusion coefficient [12], moreover, the device fabrication is at a temperature of 350 °C i.e., the circumstances are favoring diffusion of Cu from CuInS$_2$. As result of this Cu diffusion, some portion of the In$_2$S$_3$ buffer layer converted to CuInS$_2$, which reduces the effective buffer layer thickness in the cell structure. Even the device may get shorted for lower buffer layer thicknesses. Hence Cu diffusion is observed to be a major deterioration factor that limits the performance of CuInS$_2$/In$_2$S$_3$ heterojunction solar cells.

3.2.4 Cross sectional SEM of the device

The cross sectional SEM of one of the sample in the efficiency range 2.33 ± 0.26 % is shown in Figure 3.4. SEM analysis was performed without coating the top Ag electrodes.

![Image of Cross sectional SEM](image)

Figure. 3.4 Cross sectional SEM image of ITO/CuInS$_2$/In$_2$S$_3$/Ag solar cell.

Individual layers in the cell structure are well distinguished from the SEM image. As discussed in section 3.2.1 and 3.2.2, the expected thicknesses of absorber and buffer layer were ~ 320 nm and 300 nm respectively. XPS depth profile analyses of the device clearly indicate Cu diffusion from absorber to buffer layer, which can convert some portion of In$_2$S$_3$ to CuInS$_2$. Cross sectional SEM measurement of the device shows that, after all inter diffusion
processes in the cell structure, thicknesses of CuInS$_2$ absorber layer and In$_2$S$_3$ buffer layer were ~ 400 nm and ~ 200 nm respectively.

### 3.2.5 Fabrication of large area (2.5 x 2 cm$^2$) device

In order to prove the capability of CSP for the fabrication of large area solar cell, CuInS$_2$ absorber and In$_2$S$_3$ buffer layers were deposited in sequence over an ITO coated glass substrate having 3 x 3 cm$^2$ area. The deposition parameters for CuInS$_2$ and In$_2$S$_3$ were kept same as that of best cell obtained in an area of 0.03 cm$^2$. Over this structure silver back contact was deposited in an area of 2.5 x 2 cm$^2$ by vacuum evaporation. External connections are made possible using copper wires. Silver paste was used for fixing this wire at a corner of the silver electrode. Outdoor measurements (carried out in sunlight intensity of 50m W/cm$^2$) showed short circuit current of 10.15 mA and $V_{oc}$ of 416 mV (Figure.3.5) [13].

![Figure 3.5 Outdoor measurements of ITO/CuInS$_2$/In$_2$S$_3$/Ag solar cells with an active area of 5cm$^2$ to study the performance of the device under direct sunlight.](image)

The indoor measurement of the device was also recorded using class AAA solar simulator. The device showed $V_{oc}$ of 432 mV and $J_{sc}$ of 6.33 mA/cm$^2$. Fill factor and efficiency were 34 % and 0.94 % respectively [13].
Chapter 3

The performance parameters are low for large area devices when comparing with small area device (area = 0.03 cm²) having same spray deposition parameters for individual layers. This is because in large area cells, the external connection from the solar cell is taken from a corner of the silver electrode. This will increase the series resistance of the device and adversely affects all PV parameters [14]. The PV parameters of the device were also monitored for 100 days. Table 3.3 shows the variation in PV parameters with time. It is to be noted that the cell was kept in ordinary atmosphere without any protective coatings [13].

<table>
<thead>
<tr>
<th>Days</th>
<th>(V_{oc}) (mV)</th>
<th>(J_{sc}) (mA/cm²)</th>
<th>Fill factor (%)</th>
<th>Efficiency (%)</th>
<th>(R_s) (Ω cm²)</th>
<th>(R_{sh}) (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>432</td>
<td>6.33</td>
<td>34</td>
<td>0.94</td>
<td>34</td>
<td>125</td>
</tr>
<tr>
<td>20</td>
<td>395</td>
<td>5.95</td>
<td>32</td>
<td>0.75</td>
<td>37</td>
<td>125</td>
</tr>
<tr>
<td>40</td>
<td>386</td>
<td>5.50</td>
<td>33</td>
<td>0.71</td>
<td>53</td>
<td>166</td>
</tr>
<tr>
<td>60</td>
<td>372</td>
<td>5.28</td>
<td>32</td>
<td>0.63</td>
<td>50</td>
<td>143</td>
</tr>
<tr>
<td>80</td>
<td>350</td>
<td>4.9</td>
<td>32</td>
<td>0.54</td>
<td>50</td>
<td>119</td>
</tr>
<tr>
<td>100</td>
<td>301</td>
<td>4.19</td>
<td>26</td>
<td>0.33</td>
<td>63</td>
<td>76</td>
</tr>
</tbody>
</table>

Table 3.3 Photovoltaic parameters of the large area device with time.

Even after 100 days, the device works with an efficiency of 0.33 %, which was 0.94 % for freshly prepared device. After 100 days, \(V_{oc}\) of the device decreased to 301 mV from 432 mV and \(J_{sc}\) decreased to 4.19 mA/cm² from 6.33 mA/cm² [13]. The percentage decreases in \(V_{oc}\), \(J_{sc}\), fill factor and efficiency were 30.3 %, 33.8 %, 23.5 % and 64.9 % respectively. The decrease in PV parameters with time can explain on the basis of series (\(R_s\)) and shunt resistances (\(R_{sh}\)). With ageing, silver top electrode can be diffused to \(\text{In}_2\text{S}_3\) buffer layer as a result the contact resistance (series resistance) of the device
increased drastically from 34 to 63 $\Omega \cdot \text{cm}^2$ after 100 days [15]. On the other hand shunt resistance decreases from 125 to 76 $\Omega \cdot \text{cm}^2$. As the device was kept in open atmosphere, there was a possibility of getting impurities in to the cell, which can promote the recombination of light generated carriers [16]. It should be noted that the device maintains almost same fill factor (~33%) up to 80 days, which indicates the quality of the device.

3.2.6 Fabrication of ‘all sprayed’ solar cells

Sputtered ITO back contact in the device structure was replaced with FTO films (thickness = 300 nm, sheet resistance = 20 $\Omega/\square$, transparency of 75% in the visible region) prepared through spray pyrolysis, in our own lab. Thus by spray depositing the buffer, absorber, and back contact, we were able to fabricate an ‘all sprayed’ solar cell. A schematic diagram of the fabricated device is shown in Figure 3.6.

![Figure 3.6](image)

Figure 3.6 (a) Schematic diagram of all sprayed CuInS$_2$/In$_2$S$_3$ solar cell
(b) Top view of the device.
For CuInS$_2$ deposition over FTO, Cu: In: S ratio was 1.4: 1: 5 and spray rate was fixed at 4 ml/min. It was observed that, at 350 °C (optimized temperature for CuInS$_2$ deposition over ITO surface) adhesion of CuInS$_2$ over FTO was very poor. Hence initially the substrate temperature was reduced to 275 °C for improving the adhesion of CuInS$_2$ over FTO and the thickness of this layer was ~ 100 nm. After this, substrate temperature was set at 350 °C for further deposition of CuInS$_2$. In$_2$S$_3$ buffer layer was then spray deposited over CuInS$_2$ and the spray parameters were kept same as discussed in section 2.5. The optimized thicknesses for CuInS$_2$ absorber layer and In$_2$S$_3$ buffer layer for this configuration was ~ 500 nm and ~ 200 nm respectively. Finally silver electrodes are deposited by vacuum evaporation over this cell structure for top contact. Nine silver electrodes each having an area of 0.03 cm$^2$ and thickness of 50 nm were deposited (Figure 3.6 (b)). The best device in this study shows a $V_{oc}$ of 457 mV and $J_{sc}$ of 5.45 mA/cm$^2$. The fill factor and efficiency are 38 % and 0.94 % respectively [17]. Dark and illuminated J-V characteristics of the device are shown in Figure 3.7. On comparing with best cell fabricated on ITO back contacts (section 3.2.2), the percentage decreases in $J_{sc}$, $V_{oc}$ and fill factor for the ‘all sprayed’ solar cells are 55 %, 4.4 % and 15.5 % respectively. Higher value of sheet resistance (20 Ω/□) and low transparency (75 %) for FTO back contacts when comparing with ITO back contacts (sheet resistance of 12 Ω/□ and transparency of above 85 %) adversely affected the carrier generation and collection of all sprayed solar cells. As a result $J_{sc}$ value is very much affected and device exhibits 63.7 % decrease in efficiency. If we can reduce the sheet resistance of FTO films, better device parameters that are equivalent to device with ITO back contacts can be achieved.
3.2.7 Effect of Al₂O₃ inter layer on the performance of CuInS₂/In₂S₃ solar cell

It was reported that the presence of an ultra-thin Al₂O₃ insulator coating in the cell structure can decrease the Cu diffusion in CuInS₂ based solar cell. This insulator coating decreases the interface recombination rate. The origin of beneficial effect of these coatings is still under discussion [18]. For the present work also Cu diffusion was observed from CuInS₂ absorber layer to In₂S₃ buffer layer (Figure 3.3). In order to control this Cu diffusion, ultra-thin (2 nm) insulator coating of Al₂O₃ was deposited using atomic layer deposition (ALD) as an interlayer in between CuInS₂ and In₂S₃ in the optimized cell configuration. Hence the device structure for the present study is ITO/CuInS₂/Al₂O₃/In₂S₃/Ag.

XPS depth profile analysis of the solar cell with Al₂O₃ inter layer is shown in Figure 3.8. On comparing with device without Al₂O₃ inter layer (Figure 3.3), the binding energy peaks corresponding to Cu in In₂S₃ portion is...
very much reduced in devices with Al₂O₃ inter layer. Hence the copper diffusion to In₂S₃ buffer layer is very much controlled on introducing an Al₂O₃ inter layer. The J-V characteristics of the devices with and without this Al₂O₃ inter layer is shown in Figure 3.9.

Figure. 3.8 XPS depth profile analysis of CuInS₂/In₂S₃ heterojunction with Al₂O₃ inter layer. Presence of peaks corresponding to B.E of Al₂O₃ layer at middle of the cell (depth-wise) is clearly visible.

Figure. 3.9 Illuminated J-V characteristics of the CuInS₂/In₂S₃ heterojunction with and without Al₂O₃ inter layer.
For device with Al₂O₃ inter layer $V_{oc}$ increases only by a small value (to 484 mV from 473 mV) and fill factor improves from 44 % to 50 %. This is due to the increase in shunt resistance of the device from 151 $\Omega \cdot \text{cm}^2$ to 250 $\Omega \cdot \text{cm}^2$, which reduces the recombination rate of light generated carriers [19, 20]. But due to the presence of Al₂O₃ insulator layer, $J_{sc}$ value decreased to 8.34 mA/cm² from 10.16 mA/cm². In effect, the efficiency values for both configurations are almost same (i.e., 2.1 % and 2 %). The PV parameters for the two configurations are tabulated in Table 3.4.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$R_s$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$R_{sh}$ ($\Omega \cdot \text{cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without Al₂O₃</td>
<td>473</td>
<td>10.16</td>
<td>44</td>
<td>2.1</td>
<td>14</td>
<td>151</td>
</tr>
<tr>
<td>With Al₂O₃</td>
<td>484</td>
<td>8.34</td>
<td>50</td>
<td>2</td>
<td>10</td>
<td>250</td>
</tr>
</tbody>
</table>

Table. 3.4 PV parameters of device with and without Al₂O₃ inter layer.

3.3 Double layered CuInS₂ for ITO/CuInS₂/In₂S₃/Ag solar cells.

On introducing an ultra-thin insulator interlayer of Al₂O₃ in the cell structure, Cu diffusion to In₂S₃ buffer layer was reduced and the device showed significant improvement in fill factor. Al₂O₃ inter layer for the device was prepared using atomic layer deposition (ALD). By combining CSP and ALD for cell fabrication, the overall deposition process becomes sophisticated and not cost effective. Hence we thought of utilizing CSP technique itself to deposit a resistive CuInS₂ layer in the cell structure instead of Al₂O₃ insulator layer. Resistivity of CuInS₂ layer can be manipulated by reducing Cu/In ratio in the precursor solution [17, 21-23]. The resistive, “Cu-poor” CuInS₂ inter layer can accommodate the diffused Cu ions from the absorber layer. As a
result, Cu diffusion to In\textsubscript{2}S\textsubscript{3} is very much controlled and there is a probability for the existence of “Cu-free” In\textsubscript{2}S\textsubscript{3} buffer layer in the cell structure. Also, by introducing this resistive inter layer near CuInS\textsubscript{2}/In\textsubscript{2}S\textsubscript{3} junction, probability of recombination of light generated carriers are reduced appreciably and the device can have a better value of shunt resistance (R\textsubscript{sh}). For solar cell fabrication, the spray deposition conditions (on ITO layer) for CuInS\textsubscript{2} absorber and In\textsubscript{2}S\textsubscript{3} buffer layer were kept same as discussed in section 3.2. The only difference is that we are introducing a resistive CuInS\textsubscript{2} inter layer with Cu: In: S ratio 0.6: 1: 5 [17]. Thickness of this resistive layer was varied as 40 nm, 80 nm, 110 nm and 140 nm to find the optimum thickness for the device. Here also five samples were prepared for each thickness of the inter layer. Thickness of CuInS\textsubscript{2} and In\textsubscript{2}S\textsubscript{3} layers are 320 nm and 300 nm respectively for all samples. The photovoltaic parameters like V\textsubscript{oc}, J\textsubscript{sc}, fill factor and efficiency were monitored for each trial. Average value, (along with upper and lower limit values) of these parameters for each thickness of the inter layer is tabulated in Table 3.5.

<table>
<thead>
<tr>
<th>Thickness of CuInS\textsubscript{2} inter layer (\textsim nm)</th>
<th>V\textsubscript{oc} (mV)</th>
<th>J\textsubscript{sc} (mA/cm\textsuperscript{2})</th>
<th>Fill factor (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>475\pm22</td>
<td>9.64\pm1.48</td>
<td>50\pm9</td>
<td>1.98\pm0.29</td>
</tr>
<tr>
<td>80</td>
<td>492\pm12</td>
<td>8.8\pm0.45</td>
<td>53\pm4</td>
<td>2.34\pm0.21</td>
</tr>
<tr>
<td>110</td>
<td>477\pm27</td>
<td>7.87\pm1.85</td>
<td>46\pm4</td>
<td>1.81\pm0.45</td>
</tr>
<tr>
<td>140</td>
<td>384\pm48</td>
<td>7.65\pm1.33</td>
<td>44\pm9</td>
<td>1.32\pm0.37</td>
</tr>
</tbody>
</table>

Table. 3.5 PV parameters of ITO/CuInS\textsubscript{2}/In\textsubscript{2}S\textsubscript{3}/Ag solar cells with different thickness of the CuInS\textsubscript{2} inter layer.

Studies show that the device exhibits better PV responses when fabricated with an interlayer thickness of \textsim 80 nm. Best efficiency was in the
range 2.34 \pm 0.21 \% for these devices. Out of the measurements from 45 cells of this configuration, 30 exhibited this efficiency range. As the thickness of the inter layer increases, the effective thickness of the absorber layer also increases. Since the illumination is from substrate side, enough light may not be reaching the junction. This may be a reason for the decrease in PV parameters for higher thickness (above 80 nm) of the inter layer. Average value of efficiency decreases from 2.34 \% to 1.32 \% as inter layer thickness increases from 80 nm to 140 nm. The best device under this study has a $V_{oc}$ of 495 mV and $J_{sc}$ of 9.07 mA/cm$^2$. Fill factor and efficiency were 57 \% and 2.55 \% respectively. Illuminated J-V characteristics of the device is shown in Figure 3.10. On comparing with the best device without resistive CuInS$_2$ inter layer, present configuration exhibits improvements in $V_{oc}$ (from 478 mV to 495 mV) and fill factor (from 45 \% to 57 \%). This is attributed to the reduced recombination rate of light generated carriers due to the presence of resistive CuInS$_2$ inter layer in the cell structure. At the same time resistive nature of the inter layer decreases the $J_{sc}$ obtained from the device (from 12.13 mA/cm$^2$ to 9.07 mA/cm$^2$). In effect, the efficiency values for both configurations are almost same (i.e., 2.59 \% and 2.55 \% for devices without and with resistive inter layer)
Figure 3.10 Illuminated J-V characteristics of ITO/CuInS$_2$/In$_2$S$_3$/Ag solar cells with 80 nm thick CuInS$_2$ inter layer.

3.3.1 XPS analysis of the device

XPS depth profile analysis of the device with the optimum thickness of inter layer (~ 80 nm) is shown in Figure 3.11. Intensity of binding energy peaks corresponding to copper is very much reduced in In$_2$S$_3$, when comparing with that of device without this resistive inter layer (see Figure 3.3). Hence copper diffusion from the absorber to buffer layer was very much in control for the device with resistive inter layer. Moreover, oxygen was absent inside the device which is also favorable for the device [11]. XPS depth profile analysis of Cu in ITO/CuInS$_2$/Al$_2$O$_3$/In$_2$S$_3$/Ag cell structure (see Figure 3.8) also has similar trends as observed in Figure 3.11.
3.11 XPS depth profile analysis of ITO/CuInS$_2$/In$_2$S$_3$/Ag solar cells with CuInS$_2$ inter layer. There is ‘no’ oxygen inside the cell.

### 3.3.2 Cross sectional SEM of the device

Cross sectional view of CuInS$_2$/In$_2$S$_3$ solar cell fabricated with the resistive CuInS$_2$ inter layer is shown in Figure 3.12. The component layers of the cell structure i.e., CuInS$_2$ absorber layer, CuInS$_2$ inter layer and a “Cu-free” In$_2$S$_3$ layer are well distinguished from the SEM image and layers are almost free from voids. A compact grain structure having columnar growth is observed for both CuInS$_2$ and In$_2$S$_3$ layers. As discussed in section 3.3, the deposited thicknesses of CuInS$_2$ absorber layer, CuInS$_2$ inter layer and In$_2$S$_3$ buffer layers were 320 nm, 80 nm, 300 nm respectively. But SEM measurements shows that, after all inter diffusion processes in cell structure, thickness of CuInS$_2$ absorber layer, CuInS$_2$ inter layer and In$_2$S$_3$ buffer layer were ~ 300 nm, ~ 200 nm and ~ 150 nm respectively. It should be noted that, due to Cu diffusion there are significant increase in thickness of CuInS$_2$ inter layer and decrease in thickness of In$_2$S$_3$ buffer layer from the expected values.
Figure. 3.12 Cross sectional image of ITO/CuInS$_2$/In$_2$S$_3$/Ag solar cells with CuInS$_2$ inter layer.

3.4 Conclusions

CuInS$_2$/In$_2$S$_3$ heterojunction solar cells were fabricated using ITO as back contact and Ag as front contact having the structure ITO/CuInS$_2$/In$_2$S$_3$/Ag. Thicknesses of CuInS$_2$ absorber and In$_2$S$_3$ buffer layer are optimized for the better performance of this device. The best cell fabricated using the optimized conditions has $V_{oc} = 478$ mV, $J_{sc} = 12.13$ mA/cm$^2$, fill factor = 45 % and efficiency = 2.59 %. In order to explore the potential of spray deposition for large area coatings, solar cell having an active area of 2.5 x 2 cm$^2$ was fabricated using this optimized configuration. Performance of this device was monitored up to 100 days and we observed that the device was working even after 100 days without any protective coatings. The cell was kept in open air condition and minimum damage of the device was observed from 20 days onwards. In next step, ITO back contacts are replaced with sprayed FTO to realize a cost effective “all sprayed” solar cells and the device shows
an efficiency of 0.94%. XPS depth profile analysis of the device revealed the diffusion of Cu from CuInS$_2$ absorber to In$_2$S$_3$ buffer layer, which can deteriorates the device performance. An ultra-thin insulator coating of Al$_2$O$_3$ deposited employing ALD was used as interlayer in the cell structure and we observed that Cu diffusion to In$_2$S$_3$ buffer layer was very much reduced in this case. The device exhibited an improvement in $V_{oc}$ and fill factor; but $J_{sc}$ decreased. In effect there was no improvement in efficiency for these structures. As Al$_2$O$_3$ deposition using ALD was sophisticated and not cost effective, we employed spray pyrolysis itself to deposit a resistive CuInS$_2$ inter layer in the cell structure. Copper diffusion to In$_2$S$_3$ was reduced on introducing this inter layer. Although the device exhibits repeatability, in this case also, there is not much improvement in efficiency.
References


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Chapter 4

Extremely thin absorber layer solar cells using mixed phases of CuInS$_2$ and Cu$_2$S in absorber layer

4.1 Introduction

In ‘Extremely Thin Absorber (ETA)’ solar cells, absorber layer thickness is reduced to few hundreds of nanometer to overcome the efficiency limits due to low mobility values and defects in solar cells based on thicker absorber layer. As thickness of absorber layer is reduced, light absorption in the absorber layer also decreases. Light absorption in the absorber can be improved either by introducing defect levels or by creating multiple band gaps in the absorber layer. In the present work, a ‘multiple band gap’ absorber was made possible by incorporating both CuInS$_2$ ($E_g = 1.45$ eV) and Cu$_2$S ($E_g = 1.80$ eV) in a single film employing simple, versatile and cost effective CSP technique (section 4.2.3). For the present case, two conduction bands at different energy levels are available in the same absorber material which can promote multiple photon absorption and this result in improvement of carrier collection in the device.

CuInS$_2$ and Cu$_2$S are important chalcogenide compounds for using as absorber layer in thin film solar cells. The interest lies mainly because of eco-friendly nature and earth abundance of their elements. Simple production techniques for cell fabrication are also available for these materials. Moreover, their electrical and optical properties are highly suitable as an absorber layer in solar cells [1-4]. CuInS$_2$ films deposited using various technique show high absorption coefficient ($\sim 10^5$ cm$^{-1}$) and optimum band gap ($\sim 1.5$ eV) for PV conversion [5-7]. Theoretically its conversion efficiency is 28.5 %, which is the highest value when comparing with other chalcopyrites [4]. Cu$_2$S is also a