Chapter 4

STUDIES ON CUINS$_2$ THIN FILMS PREPARED USING CHEMICAL SPRAY PYROLYSIS TECHNIQUE

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STUDIES ON CUIN\textsubscript{S\textsubscript{2}} THIN FILMS PREPARED USING CHEMICAL SPRAY PYROLYSIS TECHNIQUE

4.1 Introduction

Two of the principal requirements for a thin film solar cell material for terrestrial applications are high optical absorption as well as quantum efficiency and low fabrication costs. Several promising materials are currently being investigated in various research laboratories to improve optical/electrical properties and to reduce process cost. CuIn\textsubscript{S\textsubscript{2}} is one such material. Even though cell efficiency may not be as high as with competitive materials like Silicon, CdTe and CuInSe\textsubscript{2}, a very low processing cost and eco friendly nature would allow it to be a good candidate.

Chemical Spray pyrolysis (CSP) deposition, one of the chemical techniques suitable for preparation of thin films, has been applied to deposit a wide variety of thin films. It involves spraying a solution, usually aqueous, containing soluble salts of constituents of the desired compound onto a heated substrate. It is quite suitable for depositing large area thin films using simple apparatus with good reproducibility. Major shortcoming of this technique is that some times it may make films with voids.

CSP was developed in the early 1960s by Hill and Chamberlin and preparation of thin films of certain inorganic sulfides and selenides using this technique was first reported by Chamberlin and Skarman in 1966 [1]. At present, this method is used for preparation of ternary compounds and their quartenary and quinary alloys. Spray pyrolysis of CuIn\textsubscript{S\textsubscript{2}} and other I-III-VI\textsubscript{2} compounds has been reported by Pamplin et al. in 1979 [2]. Electrical and structural properties of CuIn\textsubscript{S\textsubscript{2}} thin films prepared using spray pyrolysis has been reported by Gorska et al. [3]. Hernandez et al. reported structural, kinetic and optical properties of spray pyrolysed CuIn\textsubscript{S\textsubscript{2}} films [4]. Again in a
very recent paper, Marsillac et al. reported the post-annealing treatment of spray-deposited CuInS$_2$ films [5]. An attempt to evaluate the content of chlorine, oxygen, carbon and nitrogen impurities in sprayed films was made by Krunks et al.[6].

One of the major problems with preparation of ternary chalcopyrites like CuInS$_2$ is the control of stoichiometry, i.e., control of the excess copper content and of the copper-to-indium and metal to chalcogen ratios. Interestingly in CSP technique, ratios of the constituent elements can be easily varied by controlling their concentration in the spray solution. In the present investigation, we varied the copper-to-indium and metal to chalcogen ratio in a wide range, at different growth temperatures. By means of detailed analysis of these films, we obtained further information about film resistivity and photosensitivity as a function of the composition in the solution. This information is helpful when designing solar cells made using this material. This chapter describes preparation and characterization of CuInS$_2$ films prepared using CSP.

4.2 Experimental Details

Experimental set-up for the deposition is schematically shown in Fig.4.1. Cleaned glass slides were placed on a thick iron block (15x9x1cm$^3$), which can be heated to the required temperature with a controlled heater. Temperature of substrate holder was measured using a digital thermometer (Thermins, series 4000) and temperature control was achieved using a variable transformer. Spray head and heater with substrate are kept inside a chamber provided with an exhaust fan for removing gaseous by-products and vapor of the solvent (here water). During spray, temperature of substrate was kept constant with an accuracy of ±5$^\circ$C. Pressure of carrier gas was noted using a manometer and was kept at 90±0.5 cm. of Hg. Spray rate was 15ml/min., and distance between spray head and the substrates was ~15cm. In order to get uniform
composition and thickness, spray head was moved to either side manually with uniform speed.

CuInS$_2$ thin films were deposited over glass substrates from aqueous solutions of cupric chloride (CuCl$_2.2\frac{1}{2}$H$_2$O), indium tri chloride (InCl$_3$), and thiourea (CS(NH$_2$)$_2$) using compressed air as the carrier gas. Thiourea was chosen as the source of sulfur ions in spray solution because it avoids precipitation of metallic sulfides and hydroxides since it forms complexes with copper and indium ions easily [7]. Aqueous solutions of these salts were prepared in distilled water, and Cu/In ratio and S/Cu ratio in spray solutions were varied. Substrates were kept at different temperatures in order to study its effects on the deposited films.

We varied deposition temperature from 200°C to 400°C, Cu/In ratio from 0.5 to 1.5 and S/Cu ratio from 4 to 8. Even though deposition and characterization of CuInS$_2$ thin films using spray pyrolysis was reported previously by several groups [8-10], such wide variation in composition of spray solution has not been reported yet. Structural, electrical, optical and composition analysis of all these films were done. Photosensitivity of these films were measured and obtained conditions for depositing films with good photoresponse (87%). To the best of our knowledge, such study has not been conducted for CuInS$_2$ thin films prepared from solutions with wide compositional variations. Each of these cases will be discussed in the following sections.
Fig. 4.1 Experimental set up for spray pyrolysis system
4.3 Variation of Cu/In at 400°C, keeping S/Cu = 4

Cu/In ratio in the solution was varied by adding appropriate amounts of indium chloride with respect to a fixed concentration of copper in the form of CuCl$_2$·$\frac{1}{2}$H$_2$O. At first, Cu/In molar ratio in spray solution was varied as 0.9, 1 & 1.1. It was already reported that because of loss of chalcogen during pyrolysis process, the amount of sulfur relative to copper in the spray solution should be at least double that required theoretically for stoichiometry [11]. Hence to compensate the loss of sulfur during spraying, S/Cu molar ratio was fixed at 4. The samples are named A, B, & C respectively. Composition of the spray solution was:

- CuCl$_2$·$\frac{1}{2}$H$_2$O – 0.025M; 100ml
- CS(NH$_2$)$_2$ -0.1M; 100ml
- InCl$_3$ – 0.0277M (for sample A), 0.025M (sample B), & 0.022M(sample C); 100ml

In all cases, pH of solution was kept at 3. The deposition temperature was 400°C. Glass slides (37.5mm×12.5mm×1.25mm) cleaned as described in section 5.2.1 were placed on the substrate holder and were heated to the required temperature. These were kept in that stabilized temperature for one hour and then solution was sprayed at a rate of 15ml/min. After completion of spray, the samples were kept at the same temperature for $\frac{1}{2}$ hour and were then allowed to cool at a rate of 3°C/min.

CuInS$_2$ is formed by pyrolytic decomposition of sprayed droplets on the surface of the heated substrates. Films obtained were extremely adherent to the substrates and were homogeneous in appearance. In order to characterize these films, structural, optical and electrical studies were carried out.
4.3.1 X-ray diffraction

X-ray diffraction patterns of the films are shown in Fig.4.2. They show good crystallinity with preferred orientation along (112) direction. Peak intensity is maximum for sample A, but the peak is sharper for sample B. For sample C (Cu/In = 1.1), peak height is very much less than that obtained for sample A.

Grain size was calculated from the (112) peak using Scherrer's formula and is tabulated in Table 4.1. Among the three samples, sample B has the largest grain size.

Fig.4.2 X-ray diffraction pattern of samples A, B & C
### Table-4.1. Grain size of samples A, B & C

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (nm)</td>
<td>23</td>
<td>30</td>
<td>16</td>
</tr>
</tbody>
</table>

#### 4.3.2 Optical properties

Figure 4.3 shows the transmission (T) as a function of wavelength for samples A, B & C. Transmission decreases sharply after a particular wavelength and onset of the decrease represents the fundamental absorption edge [12]. It was observed that this onset shifted slightly towards lower wavelength side as Cu/In ratio in the spray solution increased.

To calculate value of the bandgap, a graph with \((a\theta h\nu)^2\) against \(h\nu\) was plotted for region near and above the fundamental absorption edge (Figure 4.4). Extrapolated intercept on \(h\nu\) axis gave value of the bandgap. From the graph, band gaps obtained for samples A & C are 1.42 eV. For sample B, band gap is 1.4 eV. Band gap of sprayed films is expected to be lower than that of single crystal as a result of appearance of an exponential or nearly exponential absorption tail, due to the formation of density of states tail at band edge [8].
Fig. 4.3 Transmission spectra of samples A, B, & C
4.3.3 Scanning Electron Micrograph

SEM micrographs of the films indicated polycrystalline nature with well-defined circular grains and are shown in Fig.4.5. Among these samples, sample B has better crystalline nature as is evident from XRD as well.
Fig. 4.5 SEM of samples A, B, & C
4.3.4 Electrical properties

Resistivity, carrier concentrations and mobility of the films were determined using Hall measurement and results are tabulated in Table-4.2. All these films were found to be p-type. Resistivity of these films varies with variation in Cu/In ratio. Sample B (Cu/In =1) had the lowest resistivity (1.21Ω cm). Sample A and C had almost equal resistivity (70 & 60Ω cm. respectively).

Table-4.2 Hall measurement results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity (ρ) Ω cm</th>
<th>Mobility (μ) cm²/Vs</th>
<th>Carrier density (cm⁻³)</th>
<th>Type of carriers</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>70</td>
<td>4.73</td>
<td>1.88×10¹⁶</td>
<td>holes</td>
</tr>
<tr>
<td>B</td>
<td>1.21</td>
<td>2.24</td>
<td>2.29×10¹⁸</td>
<td>holes</td>
</tr>
<tr>
<td>C</td>
<td>60</td>
<td>103</td>
<td>1×10¹⁵</td>
<td>holes</td>
</tr>
</tbody>
</table>

4.3.5 Photosensitivity

Photosensitivity (S) was determined from measured values of resistance of the film in darkness and under an illumination of 40mW/cm², as described in section 3.7.4. Values obtained for samples A, B, & C are 13.8%, 14.2%, and 27.8% respectively. Here sample C was found to be better in photosensitivity.

4.3.6 XPS Analysis

Atomic concentration percentage (at.%) of different elements present in these samples was compared using XPS depth profile. In all the cases, Cu/In ratio in film was found to be greater than that in spray solution. Also, these samples are found to be deficient in sulfur. Table-4.3 gives approximate atomic concentration % of different elements present in the sample. Results of XPS analysis of sample B prepared at a lower temperature of 250°C are also included in the table.
Table-4.3 Atomic percentage from XPS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu %</th>
<th>In %</th>
<th>S %</th>
<th>O %</th>
<th>Cu/In</th>
<th>(Cu+In)/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>44</td>
<td>24</td>
<td>27</td>
<td>5</td>
<td>1.83</td>
<td>2.51</td>
</tr>
<tr>
<td>B</td>
<td>44</td>
<td>24</td>
<td>28</td>
<td>4</td>
<td>1.83</td>
<td>2.42</td>
</tr>
<tr>
<td>C</td>
<td>40</td>
<td>25</td>
<td>31</td>
<td>4</td>
<td>1.6</td>
<td>2.09</td>
</tr>
<tr>
<td>B(L.T)</td>
<td>35</td>
<td>28</td>
<td>35</td>
<td>2</td>
<td>1.25</td>
<td>1.8</td>
</tr>
</tbody>
</table>

From Table 4.3, it is evident that for the sample prepared at low temperature, at.% of S and Cu/In ratio is better. Depth profile of atomic concentration of sample B is shown in Fig.4.6. All the elements are almost uniformly present throughout the thickness of the sample.

Even though air was used as the carrier gas for spraying, only 2-5% of oxygen is present in these films, and for the sample prepared at low temperature, at.% of oxygen is only 2%.

Binding energy values obtained for different elements are in conformity with earlier reported values. XPS depth profile showing binding energy of one of these samples (sample B) is shown in Fig. 4.7. There is one peak corresponding to oxygen at the surface. This peak situated at binding energy of 531.75eV can be attributed to elemental oxygen due to surface contamination [10]. After etching, this contribution decreases strongly, which confirms that this is due to surface contamination itself.

Peaks corresponding to all elements are very slightly shifted as the analysis proceeds from the surface to the substrate. This is due to the influence of the substrate
as it is possible that all these elements may slightly diffuse into the glass substrate during deposition.

From above analysis, it is found that high substrate temperature does not favor better stoichiometry of CuInS₂ films. In order to optimize growth temperature, sample B was prepared at different temperatures.

### 4.4 Variation of deposition temperature

CuInS₂ films were prepared using CSP over glass substrates heated to different temperatures ranging from 200 °C to 400 °C, keeping composition of the spray solution same as that used for the preparation of sample B. i.e., using the solution in which Cu/In = 1, and S/Cu = 4. At 200 °C, the films formed were not uniform and had several pinholes and adhesion was very poor. Films prepared at higher temperatures (like 380°C and 400 °C) appeared thinner than those prepared at lower temperatures. Characterization of all these films was done using different techniques and these are described below

#### 4.4.1 XRD

As growth temperature increases, crystallinity of the films improves as indicated in Fig. 4.8. Good crystallinity was achieved between 350 °C and 400 °C. Preferred orientation of the crystallites is along the (112) plane. Peak corresponding to (220) plane is visible only for samples prepared above 300 °C. Grain size of these samples is listed in Table-4.4. From which, it is clear that grain size increases with deposition temperature.
Fig. 4.6 At.% vs. sputter time graph of sample B

Fig. 4.7 XPS depth profile of sample B
Fig. 4.8 XRD of samples prepared at different deposition temperatures

Table 4.4

Grain size of samples prepared at different deposition temperatures

<table>
<thead>
<tr>
<th>Deposition temperature</th>
<th>300°C</th>
<th>350°C</th>
<th>380°C</th>
<th>400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (nm)</td>
<td>22</td>
<td>48</td>
<td>38</td>
<td>30</td>
</tr>
</tbody>
</table>
4.4.2 Optical properties

Fig. 4.9 presents typical transmittance spectra obtained for CuInS$_2$ films deposited at different substrate temperatures. The spectra show that the transmission is around 55%-65% for these films in the 1000-2500 nm wavelength range. For samples prepared at 200°C and 250°C, there is only a single slope in the region 250nm - 1000nm, whereas, curves for samples prepared at temperatures above 350°C have two distinct slopes. For the sample prepared at 300°C, second slope is just beginning to appear while this is more prominent for the sample prepared at 380°C. Occurrence of two distinct slopes in the absorption edge suggests the presence of impurity phases in the sample [11]. However no such impurity phase could be detected using XRD.
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To determine the energy gap, \((\alpha \cdot h \cdot v)^2\) vs. \(h \cdot v\) graph was drawn for all these films and is represented in Fig.4.10. Variation of the band gap with growth temperature is shown in Fig.4.11. Except for the sample prepared at 200°C, band gap value lies in between 1.39 eV and 1.43 eV. In addition to the direct transition at 1.43 eV, films prepared at 380°C show a second transition at about 1.27 eV, which matches with optical gap of Cu\textsubscript{x}S. In the case of samples prepared at 400°C, second transition is at 1.17 eV. However, these Cu\textsubscript{x}S impurity phases could not be detected from XRD spectra. This indicates that these phases may be present in traces, which could not be detected using XRD.

![Graph](image)

*Fig.4.10 \((\alpha \cdot h \cdot v)^2\) vs. \(h \cdot v\) plot for the samples*
4.4.2 Electrical properties

Electrical properties of these films were studied using Hall effect measurements and the results are represented in Table- 4.5. Variation of electrical resistivity and mobility with deposition temperature is indicated in Fig. 4.12. Type of carriers was "holes" in all these cases. When deposition temperature is increased from 300°C to 380°C, electrical resistivity of films decreases. This is obviously caused by increase in grain size due to recrystallization processes. For sample prepared at 300°C, grain size was 22nm, and it increased to 48nm & 38nm respectively for samples prepared at 350°C & 380°C. For the sample prepared at 400°C, grain size was 30nm.
Table 4.5

Electrical properties of samples prepared at different deposition temperatures

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Resistivity Ω-cm</th>
<th>Mobility cm²/Vs</th>
<th>Carrier density (cm⁻³)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>1.21</td>
<td>0.285</td>
<td>1.81x10¹⁹</td>
<td>holes</td>
</tr>
<tr>
<td>300</td>
<td>34.9</td>
<td>7.19</td>
<td>2.49x10¹⁶</td>
<td>holes</td>
</tr>
<tr>
<td>350</td>
<td>3.04</td>
<td>4.06</td>
<td>5.05x10¹⁷</td>
<td>holes</td>
</tr>
<tr>
<td>380</td>
<td>0.219</td>
<td>6.5</td>
<td>4.38x10¹⁸</td>
<td>holes</td>
</tr>
<tr>
<td>400</td>
<td>1.21</td>
<td>2.24</td>
<td>2.29x10¹⁸</td>
<td>holes</td>
</tr>
</tbody>
</table>

Fig. 4.12 Variation in resistivity and mobility with growth temperature
4.4.3 Photosensitivity

Change in photosensitivity of these films with deposition temperature is illustrated in Fig.4.13. It follows that photosensitivity is maximum for the samples prepared at 300°C, and for samples prepared at temperatures above 350°C, photosensitivity is very low. Photosensitivity is an important criterion that should be given due importance while fabricating cells using these films. Hence although crystallinity was better for the samples prepared at higher temperatures, growth temperature for further preparations was fixed at 300°C.

![Fig.4.13. Photosensitivity of samples prepared at different deposition temperatures](image-url)
4.5 Variation of (Cu+In)/S ratio, keeping Cu/In = 1

CuInS$_2$ films were prepared by maintaining Cu/In ratio in the spray solution as 1 and by increasing S/Cu ratio from 2 to 8 in steps of one (i.e., (Cu+In)/S ratio from 1 to 0.25). Molarity of copper chloride and indium chloride solutions was fixed at 0.025M, and the molarity of thiourea alone was varied. An equal volume (100ml) of these three solutions was mixed together and was sprayed onto heated glass substrates kept at 300$^\circ$C.

4.5.1 XRD

Fig.4.14 shows the XRD spectra of these samples. As S/Cu ratio is increased, X-ray diffraction pattern indicated deterioration of crystallinity of the films. Grain size decreases from 33nm to 20nm as S/Cu ratio increases from 2 to 4. Grain size is still smaller and could not be evaluated for samples with S/ Cu ratio 5 & 6.

4.5.2 Optical properties

Transmission spectra of samples with different S/Cu ratio are represented in Fig.4.15. Here also, all these samples have transmission around 55%-65% in 1000 to 2500nm wavelength region, except the sample for which S/Cu =2. In this case, transmission is only around 10%.

Figure 4.16 shows the plots of ($\alpha$hv)$^2$ vs. hv and band gap values obtained are in the range 1.40-1.47 eV. For the samples prepared from solution containing S/Cu = 2, band gap is 1.51 eV. In addition to this, there is another absorption edge at 0.87 eV for this sample, which may be due to the presence of Cu$_x$S impurity phases in the sample.
Fig. 4.14 XRD of samples prepared with different S/Cu ratio
4.5.2 Electrical properties

Sheet resistance of the samples was measured at room temperature using Keithley I-V measurement system and the values obtained are depicted in Table-4.6. Silver electrodes were painted on the surface of the film keeping a distance of 5mm between the electrodes.

<table>
<thead>
<tr>
<th>S/Cu ratio in the spray solution</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheet resistance KΩ/□</td>
<td>13.6</td>
<td>2.2</td>
<td>143.5</td>
<td>39.8</td>
<td>80</td>
</tr>
</tbody>
</table>

Conductivity type of samples was determined using hot probe method. Samples prepared from solutions with S/Cu ratio 2 and 3 showed n-type conductivity and other samples showed p-type conductivity. This clearly indicates that excess of sulfur is not present in these two samples. But as sulfur concentration increases in solution, samples are converted into p-type.
Fig. 4.15 Transmission spectrum of samples prepared with different S/Cu ratio
Fig. 4.16 $(\alpha h v)^2$ vs. $h v$ plot for samples with different S/Cu ratio
4.5.4 Photosensitivity measurement

Photosensitivity of these samples is shown in Fig. 4.17. It decreases with increase in the S/Cu ratio and is maximum for samples prepared using the sulfur deficient solution containing S/Cu ratio = 2. Among the other samples the one prepared from a solution containing S/Cu ratio 4 is the best.

![Graph showing variation in photosensitivity with S/Cu ratio](image)

Fig. 4.17 Variation in photosensitivity with S/Cu variation in the spray Solution

4.6 Variation in Cu/In at 300°C, keeping S/Cu = 4

Another set of CuInS$_2$ films were prepared by varying Cu/In ratio in the spray solution, in a wide range. This time, the deposition temperature is 300°C, S/Cu ratio was 4 and the Cu/In ratio was varied from 0.5 to 1.5. Again these samples were characterized as in the earlier cases.
4.6.1 XRD

XRD pattern of samples prepared from different Cu/In ratios in solutions were compared and XRD spectra of some of these samples are represented in Fig.4.18. As Cu/In ratio increases in the spray solution, samples improve in crystallinity as indicated by the sharpness and intensity of the peaks. Also, an increase in grain size was observed with increase in Cu/In ratio and this is given in Table-4.7.

Fig.4.18 XRD pattern of samples with different Cu/In ratio
Table-4.7
Grain size of samples prepared from solution with different Cu/In ratio

<table>
<thead>
<tr>
<th>Cu/In ratio in solution</th>
<th>0.8</th>
<th>1.0</th>
<th>1.1</th>
<th>1.2</th>
<th>1.3</th>
<th>1.4</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (nm)</td>
<td>4.2</td>
<td>15</td>
<td>22</td>
<td>43</td>
<td>58</td>
<td>51</td>
<td>51</td>
</tr>
</tbody>
</table>

4.6.2 Optical properties

Optical band gap of these films was determined from the plot of \((\alpha \times h\nu)^2\) versus photon energy, and is represented in Fig.4.19. Extrapolation of the linear portion to the \(h\nu\)-axis gives value of energy gap, which falls in the range between 1.3 to 1.52 eV. For the sample prepared from Cu/In =1.2 solution, there are two slopes in the absorption edge region of which the first one corresponding to an energy transition at 1.47eV. The second one corresponding to a transition at 1.22eV, matches with the optical band gap of Cu₄S. Similar effect was observed by Tiwari et al. also for CuInS₂ films prepared with 50% excess copper [11].

For the sample prepared from a solution containing Cu/In =1.3, the band gap value is 1.3 eV, which is less than that of the other samples. However, an energy band gap of 1.3 has been reported earlier for sprayed films [2]. They attributed this to poor crystallinity. Variation in band gap with different Cu/In ratio in the solution is depicted in Fig.4.20. As Cu/In ratio in the solution increases, band gap gradually decreases. A possible cause for this effect may be carrier degeneracy in CuInS₂ due to the defects in the crystalline lattice [7]. It has been reported that copper and indium vacancies (\(V_{Cu}\) and \(V_{In}\)), interstitial sulfur(Sᵢ) and substitutional copper in indium sites (\(Cu_{In}\)) can introduce shallow accepter levels [13]. In the case of samples with high value for Cu/In ratio, probable defect may be Cu₄In. Bandgap of the film prepared from a solution with
Cu/In ratio 0.5 (1.52eV) is close to 1.55eV, which is the reported value for bulk crystalline CuInS$_2$. For films prepared from solution with Cu/In ratio 0.5 (In-rich solution), probable defects are $V_{Cu}$ and $V_{S}$ [14]. It is reasonable to assume that the $Cu_{in}$ and $V_{In}$ defect densities may increase when Cu/In increases, so that the material may become p-type degenerate. From thickness measurement, it was found that as Cu/In ratio increases, thickness decreases.

![Fig. 4.19 Optical absorption of films deposited from solutions with different Cu/In ratio.](image)
4.20 Variation in band gap with different Cu/In ratio in the spray solution

4.6.3 Thickness

Thickness of some of these films was measured using stylus profilometer. Thickness measurement was carried at three different regions in the film and the average of the consistent values were taken as the approximate thickness of the sample. Fig. 4.21 shows typical profile of the measurement done on a sample prepared using the solution with Cu/In ratio 0.5. Here the thickness is 0.77μm. For both the samples prepared using solutions with Cu/In ratio 1.0 and 1.7, thickness was found to be 0.46μm.

4.6.4 Electrical properties

Sheet resistance of all samples was measured using Keithley I-V measurement system. There is drastic decrease in the resistance value from 3009MΩ to 486 Ω, on
Fig. 4.21. Profile of thickness measurement
increasing the Cu/In ratio in the spray solution from 0.5 to 1.7. On increasing the copper concentration, copper impurity levels may increase and the extent of compensation provided by the indium donor levels decrease, leading to the lower dark resistance. Variation in sheet resistance of the samples with different Cu/In ratio (0.5 to 1.7) in the spray solution is shown in Fig.4.22. Raja Ram et al. observed an improvement in conductivity of films with increase in Cu/In ratio in the starting solution from 0.96 to 1.2 [8].

![Image of graph showing variation in sheet resistance of the samples with Cu/In ratio in the spray solution]

**Fig.4.22. Variation in sheet resistance of the samples with Cu/In ratio in the spray solution**

The type of conductivity of these samples was determined using hot-probe method. All the samples showed p-type conductivity irrespective of the Cu/In ratio in the spray solution. This indicated that carrier type is very much sensitive to S/Cu ratio (or sulfur to metal ratio).
4.6.5 Photosensitivity

Photosensitivity measurements of these samples (Fig.4.23) revealed that it is maximum for the sample prepared from the solution in which the Cu/In ratio is 0.5. Photosensitivity decreases gradually with increase in the Cu/In ratio up to 0.9, and thereafter it decreases rapidly to very low values as Cu/In value increased up to 1.2. Samples having still higher Cu/In ratio turn to be very poor in photosensitivity.

![Fig.4.23 Photosensitivity of samples with different Cu/In ratio in the solution](image)

4.6.6 XPS

XPS spectra of these films prepared from solutions with four different Cu/In ratios (i.e., Cu/In = 0.5, 1.0, 1.5 & 1.7) were taken. At. conc.% of Cu, In, S and O in these films are tabulated in Table- 4.8. Fig.4.24 illustrates the Cu/In ratio in the film as a function of Cu/In ratio in the solution.
Fig. 4.24 Cu/In ratio in the film as a function of Cu/In ratio in the solution

Table-4.8
At. % from XPS analysis

<table>
<thead>
<tr>
<th>Cu/In ratio in the spray solution</th>
<th>Cu%</th>
<th>In%</th>
<th>S</th>
<th>O</th>
<th>Cu/In in the film</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>34</td>
<td>33</td>
<td>26</td>
<td>7</td>
<td>1.03</td>
</tr>
<tr>
<td>1.0*</td>
<td>42</td>
<td>24</td>
<td>29</td>
<td>3</td>
<td>1.8</td>
</tr>
<tr>
<td>1.5</td>
<td>52</td>
<td>18</td>
<td>27</td>
<td>3</td>
<td>2.8</td>
</tr>
<tr>
<td>1.7**</td>
<td>50</td>
<td>17</td>
<td>27</td>
<td>3</td>
<td>2.9</td>
</tr>
</tbody>
</table>

* 2% Cl was detected in this sample
** 3% Na was detected
Fig. 4.25 XPS depth profile of sample prepared from the solution with Cu/In ratio 0.5
Fig. 4.26 At. conc. % vs. sputter time graph of sample prepared from solution with Cu/In ratio 0.5
Cu/In ratio in the film increases with increase in Cu/In ratio in the solution. Also, the ratio in the film is nearly double the ratio in the spray solution. Cu/In ratio in the film is 1 when the ratio in the solution is 0.5. XPS depth profile of binding energy and the spectrum showing the at.% versus sputter time graph for this sample are shown in figures 4.25 & 4.26. No change was observed in the binding energy and the values obtained are exactly the same as those obtained for the earlier samples.

As seen from above analysis, Cu/In ratio in the film is nearly 1 when the Cu/In ratio in the spray solution is 0.5. Here S/Cu ratio was 4 and surely there is some S deficiency in the sample. In order to improve the S content in the film and to study its effect on the photosensitivity, in the next stage, S/Cu ratio in the film was again varied keeping Cu/In ratio as 0.5.

**4.7 Variation in S/Cu ratio, keeping Cu/In = 0.5**

Molarity of copper chloride and indium chloride was fixed at 0.0125M & 0.025M respectively and the molarity of thiourea solution was varied to get different S/Cu ratios (from 4-8) in the initial spray solution. 300ml solution was sprayed at a time onto heated glass substrates kept at a temperature of 300°C at a spray rate of 15ml/min. These samples were also analyzed as in the previous cases.

**4.7.1 XRD**

XRD analysis of these samples revealed that they lack crystallinity. Fig.4.27 represents XRD spectrum of some of these samples. As S/Cu ratio increases, amorphous nature of films also increases.
4.7.2 Optical properties

Optical transmission of these films was recorded at room temperature and the curves for wavelength range of 450 nm to 2500 nm are shown in Fig.4.28. As in earlier cases, transmittance is constant for wavelengths higher than 1000 nm and then it decreases sharply in lower wavelength regions.

Fig.4.27 XRD of samples with Cu/In ratio 0.5 and different S/Cu ratio
Bandgap values were calculated from the \((\alpha \theta v)^2\) vs. \(h\nu\) graph (Fig. 4.29). The values obtained were 1.55 eV, 1.50 eV, 1.51 eV, 1.51 eV & 1.54 eV for S/Cu ratio 4, 5, 6, 7 & 8 respectively. An additional absorption edge at 1.76 eV was observed for the sample prepared from the solution containing S/Cu ratio 8, which closely matches with the direct band gap of Cu_xS with \(x = 2\).

*Fig. 4.28* Transmission spectra of samples with different S/Cu ratio, keeping Cu/In = 0.5
Fig. 4.29 Absorption spectrum of samples with Cu/In ratio 0.5 and different S/Cu ratio

4.7.3 Electrical properties

Sheet resistance of samples with different S/Cu ratio is represented in Fig. 4.30. It is found that as the S/Cu ratio increases, there is gradual increase in the sheet resistance of these samples. Conductivity type of these samples was tested using hot probe method and was found to be p-type for S/Cu ratios from 4 to 8.
Fig. 4.30 Variation in sheet resistance of samples with Cu/In ratio 0.5 and different S/Cu ratio

We could not conduct Hall measurement with most of these high resistive samples. It is to be noted that efforts of Hwang et al. to measure the mobility of rf sputtered CuInS$_2$ films were also unsuccessful [15]. However, we could measure the carrier concentration and mobility values for the sample prepared from the solution with S/Cu = 5. The resistivity, carrier concentration and mobility values for this film are, 254Ω-cm, 1.21×10$^{15}$ and 20.3 respectively.

4.7.4 XPS

XPS depth profile of four samples prepared from solutions containing S/Cu ratio 4, 5, 6 & 8 were recorded and chemical composition of the films was analyzed. Approximate at.% of different elements in these samples are listed in Table-4.9.
Table-4.9

At.conc.% from XPS Analysis

<table>
<thead>
<tr>
<th>S/Cu ratio in solution</th>
<th>Cu%</th>
<th>In%</th>
<th>S%</th>
<th>O%</th>
<th>Cu/In ratio in the film</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>34</td>
<td>33</td>
<td>26</td>
<td>7</td>
<td>1.03</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>31</td>
<td>31</td>
<td>3</td>
<td>1.12</td>
</tr>
<tr>
<td>6</td>
<td>38</td>
<td>29</td>
<td>29</td>
<td>4</td>
<td>1.31</td>
</tr>
<tr>
<td>8</td>
<td>24</td>
<td>37</td>
<td>39</td>
<td>0</td>
<td>0.65</td>
</tr>
</tbody>
</table>

As the S/Cu ratio is increased from 4 to 5, there is slight increase in the atomic concentration of S from 26% to 31%. When the S/Cu ratio is 8, at.% of S has increased to 39%, however, for this sample, Cu/In ratio in the film is only 0.65. Atomic conc.% versus sputter time graph for the samples prepared from solutions with S/Cu ratio 5 and 8 are shown in Fig.4.31 & 4.32 respectively.

There was no change in the binding energy values of different elements in these samples. XPS depth profile showing the binding energy values of different elements for the sample prepared from the sulfur rich solution (S/Cu = 8) is shown in Fig.4.33.
Fig. 4.31 Atomic conc.% versus sputter time graph of sample prepared from solution with S/Cu ratio 5
Fig. 4.32 Atomic conc. % versus sputter time graph of sample prepared from solution with S/Cu ratio 8.

Fig. 4.33 XPS depth profile of sample prepared from solution with S/Cu ratio 8.
4.7.4 Photosensitivity

Photosensitivity of these samples is shown in Fig. 4.34. It increases with increase in S/Cu ratio, reaches high values for S/Cu = 5 & 6 and then decreases with increase in S/Cu ratio. Photosensitivity is maximum for samples prepared using the solution containing S/Cu ratio = 5.

![Graph showing Photosensitivity vs S/Cu ratio]

Fig. 4.34 Photosensitivity of samples prepared from solution with different S/Cu ratio

4.8 Conclusion

In conclusion, spray pyrolysis deposition of thin films of CuInS$_2$ was successful. CuInS$_2$ films were prepared by varying the deposition temperature, Cu/In ratio and S/Cu ratio in the spray solution. Structural, electrical and optical characterizations of all these films were done and results are represented in Table 4.10. Photosensitivity measurements of these films were also conducted and the best photosensitivity was observed for a film prepared from the solution containing Cu/In ratio 0.5 and S/Cu ratio 5 and this sample was selected as the absorber layer for fabricating junction with CdS.
Table 4.10

Summary of properties of different samples prepared

I. Variation of Cu/In at 400°C, keeping S/Cu = 4

<table>
<thead>
<tr>
<th>Cu/In</th>
<th>XRD</th>
<th>Grain size (nm)</th>
<th>Energy Band gap (eV)</th>
<th>Photo sensitivity %</th>
<th>Electrical property</th>
<th>XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>p (Ω·cm)</td>
<td>µ (cm²/Vs)</td>
</tr>
<tr>
<td>0.9</td>
<td>Good crystallinity with preferred orientation along (112) plane</td>
<td>23</td>
<td>1.42</td>
<td>13.8</td>
<td>70</td>
<td>4.73</td>
</tr>
<tr>
<td>1.0</td>
<td>30</td>
<td>1.40</td>
<td>14.2</td>
<td>1.21</td>
<td>2.24</td>
<td>44</td>
</tr>
<tr>
<td>1.1</td>
<td>16</td>
<td>1.42</td>
<td>27.8</td>
<td>60</td>
<td>103</td>
<td>40</td>
</tr>
</tbody>
</table>
### I. Variation of deposition temperature (Cu/In - 1.0, S/Cu - 4)

<table>
<thead>
<tr>
<th>Deposition Temp.</th>
<th>XRD</th>
<th>Grain size (nm)</th>
<th>Energy Band gap (eV)</th>
<th>Photo Sensitivity %</th>
<th>Electrical property</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td></td>
<td>-</td>
<td>1.46</td>
<td>43</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>250°C</td>
<td></td>
<td>-</td>
<td>1.41</td>
<td>38</td>
<td>1.21</td>
<td>0.285</td>
</tr>
<tr>
<td>300°C</td>
<td>22</td>
<td>1.41</td>
<td>45</td>
<td></td>
<td>34.9</td>
<td>7.19</td>
</tr>
<tr>
<td>350°C</td>
<td>48</td>
<td>1.39</td>
<td>13</td>
<td></td>
<td>3.04</td>
<td>4.06</td>
</tr>
<tr>
<td>380°C</td>
<td>38</td>
<td>1.43</td>
<td>12.3</td>
<td></td>
<td>0.219</td>
<td>6.5</td>
</tr>
<tr>
<td>400°C</td>
<td>30</td>
<td>1.42</td>
<td>14.2</td>
<td></td>
<td>1.21</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Crystallinity were better of films Prep. At 350°C, but photosensitivity was higher for samples prepared at 300°C. Hence deposition temp was fixed at 300°C.

### III. Variation of (Cu+In)/S, keeping Cu/In = 1

<table>
<thead>
<tr>
<th>S/Cu</th>
<th>XRD</th>
<th>Grain size (nm)</th>
<th>Energy Band gap (eV)</th>
<th>Photo sensitivity %</th>
<th>Sheet resistance (KΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>33</td>
<td>1.51</td>
<td>18.05</td>
<td>13.6</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>25</td>
<td>1.45</td>
<td>1.06</td>
<td>2.2</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>20</td>
<td>1.42</td>
<td>4.49</td>
<td>143.5</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>-</td>
<td>1.43</td>
<td>3.55</td>
<td>39.8</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>-</td>
<td>1.47</td>
<td>1.14</td>
<td>80</td>
</tr>
</tbody>
</table>
### IV. Variation in Cu/In at 300°C keeping S/In = 4

<table>
<thead>
<tr>
<th>Cu/In</th>
<th>XRD</th>
<th>Grain size (nm)</th>
<th>Energy Band gap (eV)</th>
<th>Sheet resistance (Ohms)</th>
<th>Photo-sensitivity %</th>
<th>Cu%</th>
<th>In%</th>
<th>S%</th>
<th>Cu/In</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>XRD Pattern</td>
<td>-</td>
<td>1.52</td>
<td>3009M</td>
<td>71</td>
<td>34</td>
<td>33</td>
<td>26</td>
<td>1.03</td>
</tr>
<tr>
<td>0.6</td>
<td>Improved With</td>
<td>-</td>
<td>1.50</td>
<td>1118M</td>
<td>62</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>Increase In Cu/In ratio</td>
<td>4.2</td>
<td>1.44</td>
<td>459M</td>
<td>57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td></td>
<td>14</td>
<td>1.47</td>
<td>50M</td>
<td>53</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td></td>
<td>15</td>
<td>1.42</td>
<td>5.86M</td>
<td>18</td>
<td>42</td>
<td>24</td>
<td>29</td>
<td>1.8</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>22</td>
<td>1.41</td>
<td>1.4M</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td></td>
<td>43</td>
<td>1.47</td>
<td>5.73K</td>
<td>1.57</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td></td>
<td>58</td>
<td>1.30</td>
<td>1.99K</td>
<td>2.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td></td>
<td>51</td>
<td>1.43</td>
<td>901</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td></td>
<td>51</td>
<td>1.42</td>
<td>345</td>
<td>2.0</td>
<td>52</td>
<td>18</td>
<td>27</td>
<td>2.8</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td>486</td>
<td>1.75</td>
<td>50</td>
<td>17</td>
<td>27</td>
<td>27</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>1.7</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
V. Variation in S/Cu ratio, keeping Cu/In = 0.5

<table>
<thead>
<tr>
<th>S/Cu</th>
<th>XRD</th>
<th>Energy Band gap (eV)</th>
<th>Sheet resistance (Ohms)</th>
<th>Photo Sensitivity %</th>
<th>Cu%</th>
<th>In%</th>
<th>S%</th>
<th>Cu/In</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Crystallinity is not good</td>
<td>1.55</td>
<td>4444M</td>
<td>50</td>
<td>34</td>
<td>33</td>
<td>26</td>
<td>1.03</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>1.50</td>
<td>3.49M</td>
<td>87</td>
<td>35</td>
<td>31</td>
<td>31</td>
<td>1.12</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>1.51</td>
<td>3500M</td>
<td>86</td>
<td>38</td>
<td>29</td>
<td>29</td>
<td>1.31</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>1.51</td>
<td>4523M</td>
<td>59</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
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<td>8</td>
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<td>1.54</td>
<td>4377M</td>
<td>53</td>
<td>24</td>
<td>37</td>
<td>39</td>
<td>0.65</td>
</tr>
</tbody>
</table>
References


