Chapter 9

SUMMARY AND CONCLUSIONS

Semiconducting thin films of chalcopyrite group are currently under intensive investigation for highly efficient solar energy conversion. The chalcopyrite semiconductor $CuInS_2$, is one of the most promising optical absorbers for efficient solar cells due to its optimum band gap (1.5 eV), which is matching well with solar spectrum. Moreover, constituents of this compound are abundant and have low toxicity. Lot of work is also going on for the effective replacement of CdS, using other buffer layers having wider band gap than that of CdS. This not only avoids toxic cadmium but also improves light transmission in the blue region. In_2S_3 is one such material.

We characterized both these materials ($CuInS_2$ and In_2S_3) prepared using CSP technique under different sample preparation temperatures and molar concentration ratios. CSP is a simple and low cost technique, which is well suited for deposition of large area films. Moreover, composition and doping profile of the thin film can be easily varied by varying molar concentration of the respective salt in the spray solutions used in this technique. This prompted us to select this technique for the deposition of these two films in the present work.

First, indium sulfide thin films were prepared using chloride based precursor solutions. The films showed β-In_2S_3 phase with preferential orientation along (220) plane. Band gap was found to be 2.67 eV for In/S ratio 2/3. XPS analysis of the samples revealed presence of oxygen as surface contamination on the surface, for all the samples. We could get good control over the stoichiometry of the films by varying the substrate temperature or In/S ratio in the film. The sample having In/S ratio 1.2/8 showed maximum photosensitivity ($\Delta I/I_D$ = 949.97), but it was highly resistive. On increasing the indium concentration resistivity as well as photosensitivity of the samples decreased. These two parameters of a semiconductor are important

factors for the fabrication of efficient solar cells. High resistance of the films will increase the series resistance and reduce the fill factor of the cell. Thus we must have a compromise between these two parameters for solar cell applications. In the present work thick indium sulfide films (4 μm) were prepared by spraying 1000 ml of the solution.   Presence of chlorine also resulted in the increase of resistivity of the samples. In order to avoid this, we prepared indium sulfide films using nitrate based precursor solutions.

Interestingly for indium sulfide thin films, prepared using nitrate precursor solution, only the In/S ratio 2/3 showed good crystallinity with band gap 2.66 eV. But chloride samples showed better crystallinity on increasing sulfur concentration. We could get better control over stoichiometry while using nitrate solution. Moreover concentration of sulfur in the sample could be made even greater than 60% by increasing sulfur concentration in spray solution. Depth analysis of the sample using XPS indicated formation of In_2O_3 phase for sample having In/S ratio 2/4 which had maximum electrical resistivity and photosensitivity. But there was considerable decrease in the photosensitivity ($<10^2$) when compared to chloride-based samples. Another important point is that, unlike chloride-based samples, nitrate based one showed considerable increase in conductivity on increasing the sulfur concentration (2/6 to 2/8). In general, nitrate based samples were found to be more conducting, compared to chloride samples. As photosensitivity and crystallinity of the samples were not as good as chloride samples, chloride samples might be better as buffer layer for fabricating solar cells. But thickness of both samples could be increased upto ~ 4 μm in CSP technique.

We prepared and characterized $CuInS_2$ films also using two types of precursor solutions- nitrate and chloride. But in this case the major difficulty was that in a single spray, we could not increase the total volume of the solution sprayed beyond 375 ml as the samples got damaged. This corresponds to 0.6 μm thickness of the sample.

Samples showed better crystallinity on increasing Cu/In ratio while band gap reduced. Electrical conductivity enhanced with Cu/In ratio in both cases. Cu-poor (In-rich) samples were found to be n-type. For nitrate-based samples Cu/In ratio followed faithfully the variation of molarity ratio of the solution better than that of chloride based ones. The atomic ratio was almost equal to that in the solution. Photosensitivity was slightly better for chloride samples. But the difference was small for Cu rich samples. Defect levels were identified using temperature dependent conductivity measurements and composition analysis. The shallow levels that were found in Cu rich samples, might be contributing to the high conductivity of these samples. Better crystallinity, stoichiometry, conductivity and photosensitivity of nitrate-based samples gave a feeling that these samples might be better for solar cells in the case of $CuInS_2$ samples.

We adopted 'multiple spray technique' to increase the thickness of $CuInS_2$ films because spraying large volume of the solution in a single stretch resulted in development of pin holes in the sample. Using this technique we prepared samples having thickness >1 μm. Greater Cu/In ratio resulted in better crystallite size and the band gap reduced from 1.49 eV to 1.3 eV. Depth analysis of the sample indicated absence of oxygen in the bulk of the sample even after multiple sprays. But Na was present throughout the depth of the sample, which might have diffused from the glass substrate. Cu/In ratio in the film was slightly less than that taken in the solution. Activation energies of defects of the sample were obtained using temperature dependent electrical conductivity measurements. Two distinct slopes corresponding to activation energies 390 meV (increases resistivity) and 196 meV (In_i or In_{Cu}) were obtained for sample having Cu/In ratio 0.5. Vacancy of copper, generated a level having activation energy 90 meV with the sample having Cu/In ratio 1. Here also we could find a shallow level for Cu/In ratio 1.5 contributing to its high conductivity.

In this work we fabricated solar cell having structure $ITO/CuInS_2/In_2S_3/metal$ electrode and illumination was given from the substrate side. This structure was adopted, as we could not prepare junction in the real superstrate structure. Thin In_2S_3 layer was damaged while spraying $CuInS_2$ over it. But even when we prepared it in superstrate structure by using thick In_2S_3 layer, we found that the superstrate structure was not having any junction effect. Effect of atomic concentration as well as thicknesses of both absorber and buffer layers on the characteristics of the cell was studied. It was found that these two are very important factors affecting performance of the cell. Performance of the cell was improved when it was kept at the preparation temperature itself for 1 hour after deposition. The best cell parameters obtained were $V_{oc} = 529$ mV, $J_{sc} = 3.62$ mA/cm^2, FF = 29.88% and $\eta = 0.57$%. XPS results indicated diffusion of copper from the $CuInS_2$ layer to the In_2S_3 layer, which might be one of the reasons for the low value of short circuit current. Also oxygen was detected throughout the depth of the cell leading to the increase of the series resistance. Efficiency of the cell increased to 2.65% when a thin layer (50 Å) of indium was deposited on the top of In_2S_3 layer followed by annealing at 100°C for 30 minutes. Thermal diffusion of indium at the top might have helped in the formation of a layer of In_2S_3 free of Cu at the top of the cell. Also it might be reducing the sheet resistance near the electrode. Aluminium deposited using vacuum evaporation was used as electrode in all these cases.

After the completion of works on single layer, $CuInS_2$ was sprayed in two steps (multiple spray) to increase thickness of the absorber layer without increasing thickness of In_2S_3 layer. The cell fabricated in this way had better efficiency of 5.87%. Concentration of Cu decreased towards CIS/In_2S_3 interface as evident from XPS analysis. Also there was no oxygen in the bulk of the cell, reducing the series resistance of the cell. Thick absorber layer should increase light absorption in the layer and hence the number of photogenerated carriers.

Maximum efficiency of 9.5% was obtained when the In_2S_3 layer was fabricated in two layers. This layer was thicker than the other cases. One could observe a layer of In_2S_3 free of Cu at the top of the cell. Diffusion of copper might have created Cu deficiency at the surface of the CIS layer probably making the CIS layer more photosensitive. Here also there was no oxygen in the bulk of the sample. Another interesting point was that deposition of silver at the top of In_2S_3 as top electrode could improve the crystallinity of In_2S_3 layer. Series resistance of the cell was reduced to 0.83 Ω and this value was found to be much less than that of the other cases. Cell parameters obtained were V_{oc} = 588 mV, J_{sc} = 48.2 mA/cm^2, FF = 33.5% and η = 9.5%. To the best of our knowledge this is the maximum efficiency obtained for a CIS/In_2S_3 cell fabricated using CSP technique to deposit both the absorber and buffer layers. Moreover, we could effectively replace CdS using In_2S_3 as buffer layer.

Future Scopes

We could not prevent diffusion of copper from CIS layer to In_2S_3 layer because of the high temperature at which spraying has to be done. Hence we must adjust the thickness of CIS and In_2S_3 layers so as to compensate for diffusion. Fine adjustments in the atomic concentrations of both layers may also result in better efficiency of the cell. Reduction in the fill factor of the cell is another serious problem to be investigated. This could be achieved by reducing the series resistance of the cell. Doping the buffer layer (ie, In_2S_3) using Ag, In or Sn may reduce series resistance of the cell, increasing fill factor and thus efficiency. We characterized $CuInS_2$ and In_2S_3 films prepared using nitrate based precursor solutions, and effect of using these films for fabrication of the cell could also be investigated. Thickness and atomic concentrations of these layers also should be optimized by varying these two parameters in very fine steps for further improvement of cell properties. But this sort of fine-tuning of atomic concentration may not be possible through the adjustment of ratio of molar concentration of spray solution. Instead, we may have to use thermal

diffusion of very thin layer of the required material (Cu or In) deposited using vacuum evaporation. But after knowing the correct required concentration, this can be probably achieved through repeated adjustment of molar concentration in spray solution.