Chapter 7

Summary and Conclusions

The structural, optical and electrical properties of indium sulfide, an important material for optoelectronic and photovoltaic applications, are tuned by specific and controlled doping. This binary compound semiconductor is a promising candidate for many technological applications due to its stability, comparatively wider band gap and photoconductive behavior. It can be used as an effective nontoxic substitute for cadmium sulfide (CdS) in Cu(In,Ga)Se₂ based solar cells. Even though CdS is capable of forming efficient heterojunction, there is great interest in replacing CdS by a cadmium-free buffer, due to environmental reasons. Also performance gain is expected for wider band gap materials like indium sulfide due to lower light absorption. Thus indium sulfide buffer layers are to be optimized for an improved performance than CdS.

The present work is on engineering the properties of indium sulfide by doping so as to make it an ideal buffer layer for thin film solar cells. Silver, tin, copper and chlorine were used as the dopants. Interestingly, Cl is an unnoticed [but involuntary] dopant in most of the indium sulfide films prepared by chemical methods, where indium chloride is used.

In₂S₃ thin films were deposited on soda lime glass substrates using chemical spray pyrolysis (CSP) technique. Doping was achieved either by diffusion or by incorporating the dopant in the spray solution itself. For doping by diffusion, a two-stage process was adapted. As the first stage a thin layer of the metal was deposited over the In₂S₃ layer, using vacuum evaporation technique (pressure during evaporation was ~2x10⁻⁵ m bar). Silver diffusion occurred even at this stage. Second stage provided thermal assistance to diffusion by annealing the bilayer structure at a higher temperature. The latter technique was applied for doping Sn and Cu. In situ
doping of Sn and Cl was achieved by incorporating the dopant in the spray solution itself. Doping concentration was varied to achieve optimum performance.

Doping $\beta$-In$_2$S$_3$ thin films with Ag resulted in samples with enhanced crystallinity and grain size. From XPS depth profile of the sample, it could be seen that silver diffused throughout the depth even without annealing. It was also observed that there was an optimum amount of Ag, required for doping and further increase in doping concentration showed retracing effects. Electrical resistivity of the films decreased drastically from $1.2 \times 10^3 \ \Omega \text{cm}$ to $0.06 \ \Omega \text{cm}$ due to doping. Defect studies showed an increase in indium interstitials with doping which could be the major reason for low resistivity of the samples. It was observed that at low doping concentration, silver atoms were positioned in the ordered vacancy sites (activation energy $\sim 1.2 \ \text{eV}$). At still higher doping concentration, silver atoms were setting into indium sites creating an acceptor level (activation energy $\sim 0.6 \ \text{eV}$). On further increase in doping concentration, silver atoms got into interstitial positions commencing drastic decrease in resistivity. The most striking and interesting observation was that, photosensitivity of optimum doped $\beta$-In$_2$S$_3$ film was greater than the pristine sample, even when its resistivity was much lesser. Presence of the acceptor level might have helped the increase of photosensitivity of the film. Thus doping $\beta$-In$_2$S$_3$ film with optimum amount of silver modified the structural and electrical properties of the films favorably so that the Ag electrodes given to the ITO/CuInS$_2$/In$_2$S$_3$ cell structure itself acted as a doping agent for the In$_2$S$_3$ layer enhancing the cell efficiency.

Sn doping considerably enhanced the conductivity of the In$_2$S$_3$ samples. Effect of both ex-situ (by diffusion) and in-situ (incorporating in spray) doping was analyzed. Conductivity of the films enhanced by five orders on ex-situ doping, There was no impact on the physical properties like crystallinity or band gap. By ex-situ doping, we could limit the diffusion to surface layer so that during junction fabrication
for photovoltaic applications, we can have a low resistive n-type layer near the electrode while the highly resistive and photosensitive layer (pristine) remains near the junction. Carrier generation and collection can be promoted by such a structure, which is very useful for photovoltaic applications. However, it was also noted that high doping concentration resulted in samples with low crystallinity, negative photosensitivity and slight increase in band gap. Through in-situ doping of Sn, we could achieve a wider band gap and lower resistivity, which is very useful for buffer layer applications in solar cells. Low resistive buffer layer will decrease the series resistance of the cell and wider band gap will improve light transmission in the blue wavelength. Both factors facilitate in increasing the short circuit current of the photovoltaic cell. This was specifically observed for low percentage of doping. Higher band gap could be attributed to oxygen incorporation in the samples and lower resistance might be due to the donor action of tin. Samples having higher doping concentration of Sn exhibit wider band gap (up to 3.78 eV). Though the samples had very high band gap and resistivity, anomalously they exhibited very high photosensitivity \([> 10^4]\). Studies proved that the change in band structure with higher oxidation of the samples was responsible for this phenomenon. The results also proved that tin incorporation modified the band gap and electrical properties of the In\textsubscript{2}S\textsubscript{3} films favorably over wider ranges, making it suitable for different optoelectronic applications.

Copper was diffused into In\textsubscript{2}S\textsubscript{3} (n-type) by annealing bi layer films having structure Cu/In\textsubscript{2}S\textsubscript{3}. Through solid state reaction between copper and indium sulfide, the top layer could be converted into CuInS\textsubscript{2} (p type), so as to make a CuInS\textsubscript{2}/ In\textsubscript{2}S\textsubscript{3} bilayer p-n junction. XRD analysis revealed formation of CuInS\textsubscript{2} in addition to tetragonal \(\beta\)-In\textsubscript{2}S\textsubscript{3} phase. Optical absorption edge of these films showed a shift towards longer wavelength proving the presence of CuInS\textsubscript{2}. Sheet resistance of the sample also reduced considerably. Hot probe measurements proved that Cu diffused samples resulted in p-type nature. Cationic vacancies of the stoichiometric In\textsubscript{2}S\textsubscript{3} films,
grain boundaries and dangling bonds might have made the diffusion of copper much easier. Junction could be fabricated by controlling the diffusion of copper by adjusting the thickness of Cu and In$_2$S$_3$ layers at optimized temperature. This junction was found to be photoactive and hence could be used as a simple technique for the fabrication of solar cell.

Chlorine is an involuntary dopant in most of indium sulfide films prepared by chemical methods that use chloride based precursor solutions. However none of the earlier studies have revealed the role of Cl on the properties of the films. Hence, In$_2$S$_3$ films were purposefully doped to find the part played by chlorine as a dopant. Chlorine was found to be helpful in improving the crystallinity of the films. SEM and AFM proved that grain formation was initiated in clusters where the atomic concentration of Cl was high. Cluster concentration increased with doping concentration providing uniform grain formation at higher doping concentrations. Controlling the Cl doping concentration in metal rich indium sulfide films yielded micro/nano structures. Optical absorption studies proved the onset of defect level absorption with Cl doping. Interestingly samples exhibited persistence in photocurrent decay with Cl incorporation. In these samples, a defect level at 24 meV was detected by temperature dependent photoconductivity studies. Photosensitivity and resistivity of chloride based samples showed a direct correlation to the atomic concentration of chlorine.

Many of the results obtained over here could be explained from the perspective of “impurity photovoltaic effect (IPV)”, which is believed to be the future generation of photovoltaics that can take the efficiencies beyond the theoretical limits. Indeed through doping of In$_2$S$_3$, we could create levels in the band gap resulting in IPV. Defect analysis proved the formation of such intermediate levels by doping which contributed on molding the doped indium sulfide as an ideal buffer layer.
Future Scopes

Natural progression of present research would be its application in solar cell fabrication. Combining the goodness of different dopants by co-doping can be the direction of future research. Silver doping towards the junction and surface doping with tin could give better performance. The wide bandgap photosensitive material developed can be optimized for its potential application in see-through PV modules. Junction fabrication by Cu diffusion is a very simple cost effective way to achieve junction. The simplicity of the process is quite admirable and the junction fabrication by diffusion is quite similar to process adapted in silicon technology, renowned for its simplicity among the solar cell fabrication processes. This has opened up a new avenue of cell fabrication that has to be further optimized for optimal performance. Fine adjustments in the thickness of both layers and annealing temperatures may result in better efficiency of the cell. Chlorine doping using acid based compound has to be carried out to have a better understanding of electrical properties of nitrate based samples.