CHAPTER 11

CONCLUSIONS AND SCOPE FOR FUTURE WORK

11.1. INTRODUCTION

The group of materials belonging to III-V and II-VI compounds have been extensively studied because of their semiconducting nature. But an ever increasing demand and curiosity for new materials with different new properties, stimulated the search for ternary semiconductors, which are related to the former compounds.

The ternary chalcopyrites under two broad categories viz I-III-VI_2 and II-IV-V_2 can be regarded as the ternary analogous of the II-VI and III-V binary compounds. Many of these ternary chalcopyrite crystals have wide technological interest due to application in the area of visible and infrared light emitting devices, infrared detectors, optical parametric oscillators, upconverters and infrared generators.

$CuInS_2$ is one of the many ternary chalcopyrite compounds which has received considerable attention in solar energy conversion applications and as a potential material for optoelectronic devices. Reasons are its possessing of direct band gap and ease with which it can be made both n- and p-type conducting.

Author has undertaken its growth by chemical vapour transport (CVT) technique and studied its various properties accompanied by an application in the fabrication of photoelectrochemical solar cells. Here, a sincere attempt has been made to arrive at some important conclusions from the results of the present work and to find out the scope for the future work.

11.2. CONCLUSIONS

Growth of $CuInS_2$ chalcopyrite single crystals has been carried out by chemical vapour transport (CVT) technique using halogen iodine as the transporting agent. The reason for the choice falling on CVT from the vast growth techniques was to avoid two solid state phase transitions possessed by $CuInS_2$ at $980^{o}C$ and $1045^{o}C$ before melting at $1090^{o}C$. Due to these phase transitions, growth had to be done below the lowest phase transition temperature i.e. $980^{o}C$, to obtain crack free, strain free and large size good quality crystals.

The as-grown CVT crystals were completely characterised. Structural characterisation using X-ray diffraction confirmed its tetragonal structure with $c/a \simeq 2$. The crystals were found to be stoichiometrically perfect by

EDAX analysis. Thermal analysis of $CuInS_2$ by DTA and TGA in an open atmosphere upto 1000^oC showed an additional exothermic peak at 570^oC other than the standard peaks. The n-type conductivity of the crystals was verified by Hot probe method. While the semiconducting nature of the crystal was ascertained by high temperature four probe resistivity study. Surface microtopographic study by ordinary optical microscope suggested a layer growth mechanism.

The as-grown $CuInS_2$ crystals were highly resistive, making it unfeasible for any use. To reduce the resistivity for any possible application, the as-grown crystals were suitably doped. Doping was done with three different concentrations of cadmium under controlled condition. All the three cadmium doped samples were fully characterised.

The low temperature resistivity curves showed the semiconducting nature of the samples. The values of Seebeck coefficient and Hall coefficient were found to be negative indicating that all the crystals of cadmium doped $CuInS_2$ were n-type in nature and the majority charge carriers in them were electrons. The increase in carrier concentration with increase in cadmium content in $CuInS_2$ crystals and the fact that Seebeck coefficient became less negative corresponded to a trend towards the metallic side for the samples. This conclusion was further enhanced from the decrease of optical energy band gap values of the doped $CuInS_2$ with increasing cadmium content.

Thin films of $CuInS_2$ were grown by flash evaporation technique on glass slide and freshly cleaved NaCl crystal substrates. The films were grown at five different substrate temperatures, viz. 303 K, 373 K, 423 K, 473 K and 523 K. The X-ray diffraction studies of these thin films clearly indicated an increase in crystallinity of the films with increase in substrate temperature. All the films showed (112) plane to be highly significant in comparison to others, this fact clearly indicated that the $CuInS_2$ grain in the films at all substrate temperatures were possibly in an orientation of the (112) plane parallel to the film surface. The optical studies of $CuInS_2$ films clearly indicated that the the bandgap energy values increased with increase in the substrate temperature further supporting the increase in crystallinity of the films with increase in substrate temperature.

The d.c. resistance measurement as a function of temperature on all the five thin film samples deposited at different substrate temperatures confirmed the semiconducting nature of the thin films. The thermal activation energies calculated from the log R vs 1/T curves, showed that the activation energy increased with increase in the substrate temperature. This increase was similar to that of optical band gap energy, enhancing the earlier confirmation of increase in the crystallinity of the films with increase in substrate temperature. It was seen that the room temperature resistance values decreased with increase in substrate temperature, which was successfully explained using Petritz's model. The electron diffraction studies further augmented the above confirmation that the crystallinity of the films increased with substrate temperature.

Photoelectrochemical solar cells were fabricated using the as-grown $CuInS_2$ and cadmium doped $CuInS_2$ crystals as photoanodes with polysulfide electrolyte. Platinum grid was used as the counter electrode. Mott-Schottky plots were obtained for the as-grown $CuInS_2$ electrode / polysulfide electrolyte / counter electrode cells for different polysulfide electrolytes. From these plots location of valence and conduction band edges was estimated and most suitable electrolyte was determined. The electrolyte 3M Na_2S + 3M NaOH + 3 M S was concluded to be the most appropriate for $CuInS_2$

PEC solar cell. Photoresponse of cadmium doped $CuInS_2$/ - polysulfide electrolyte PEC cells using 3 M Na_2S + 3 M NaOH + 3M S as electrolyte showed that the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) increased with increasing intensity adhering to the theoretical expectation. Best photoresponse was found with the PEC cells fabricated with the lowest cadmium doped $CuInS_2$ crystals electrodes.

High pressure studies of CVT grown $CuInS_2$ single crystals were undertaken upto 8 GPa pressure. Thermoelectric power S and a.c. resistance R_w of the as-grown n- and p-type $CuInS_2$ crystals were measured as a function of pressure. The high pressure studies on the CVT grown $CuInS_2$ crystals concluded that there was a large concentration of intrinsic defects and the electrical transport was dominated by hopping process.

11.3. SCOPE FOR FUTURE WORK

The author has carried out the summarised work in line with the title and topic of the thesis. Lot more work can still be persuaded in the same direction, which was beyond the scope of the present thesis.

The growth mechanism of CVT grown $CuInS_2$ can further be studied in more detail by employing high resolution sophisticated techniques and equipments. The techniques like light profile microscopy, multiple beam interferometry, scanning tunnelling microscopy etc. can be used to extract lot more information and can throw more light on the growth mechanism.

Chemical vapour transport (CVT) technique yielded good quality large size crystals, but contamination by transporting agent cannot be ruled out. To avoid this disadvantage of transporting agent incorporation in the crystals some other methods should be thought of.

One can also study the effect of doping in detail by pursuing with more cadmium concentrations. It will also be worthwhile to try more materials as dopant for $CuInS_2$ and study there effect on the various physical properties. These different doped samples of $CuInS_2$ can be further used for PEC cell fabrication. Also many more combinations of polysulfide electrolyte can be used for optimising the PEC performance.

No efforts have been made in the direction of improving over all photoresponse of the PEC cells. Some of the standard processes being reported to have improved PEC performance in other samples can be adopted for $CuInS_2$ PEC's.

They are the following :

1. Trying different materials for providing ohmic contacts to the photoelectrodes used in the fabrication of the cell.
2. Surface treatments such as chemical etching, photoelectrochemical etching etc. to remove surface defects.
3. Minimising the absorption losses in the electrolyte.
4. Reducing the reflectivity of the semiconductor electrode surface.

All these can form best guideline to lead the future PEC investigations on the material.