

**Preface**

The mass consumption of fossil fuels, which are getting depleted and also causing pollution, has led to the development of new sources of energy called 'Photovoltaic'. Conversion of sunlight directly into electricity using photovoltaic technique of suitable materials is the most elegant energy conversion process. Solar cell technology had undergone enormous development during the last three decades, initially in providing electrical power for spacecraft, and more recently, for terrestrial applications. Cheap but low-grade solar energy may be converted to other forms of higher-grade energy through one of several methods, such as photothermal, photochemical, photoelectrochemical, photobiochemical and photovoltaic. Among these, the cleanest, most direct and efficient mode of conversion to electrical power is photovoltaic (PV) using solar cell devices.

The most widely used solar cells are based on the Silicon technology. However, there are many drawbacks for this, leading to considerable cost escalation. Hence with the idea of fabricating cheaper solar cells, thin film technology has emerged. Among the candidates for thin film solar cells, CuInSe₂ is known to be the ideal one as the absorber layer. CuInSe₂-based solar cells require less semiconductor material and are potentially lighter and thinner than Silicon Solar Cells. No evidence for long or short term device degradation was observed (as in a-Si solar cells) in the case of CuInSe₂ based solar cells. Thin film solar cells, made from Copper Indium Gallium Diselenide (CIGS) absorbers, exhibited great promise in achieving high conversion efficiencies (approaching 20%) and these devices were fabricated using co-evaporation techniques. CuInSe₂ has now entered into the market and the efficiency of CuInSe₂ module has reached 13.4%.

The key issues in the field of CuInSe₂ solar cells are developing simpler techniques for CuInSe₂ preparation, reduction of thickness of absorber layer and replacement of CdS with non-toxic buffer layer. The present work was focusing on these issues.

In this work, sub-micrometre thick CuInSe₂ films were prepared using two different techniques. In the first case, chemical bath deposited Selenium was used and
in the second case, vacuum evaporated Se was used for selenization. These methods are simpler than co-evaporation technique, which is known to be the most suitable one for CuInSe₂ preparation. The films were optimized by varying the composition over a wide range to find optimum properties for device fabrication. Typical absorber layer thickness of today’s solar cell ranges from 2-3μm. Thinning of the absorber layer is one of the challenges to reduce the processing time and material usage, particularly of Indium. Here we made an attempt to fabricate solar cell with absorber layer of thickness <1μm. Here In₂S₃ was used as the buffer layer, replacing toxic CdS.

CHAPTER 1 gives general introduction to photovoltaics with a sketch of three generations of developments in the field of solar cells. Working principle of a p-n junction and brief discussion on the materials for photovoltaics is included in this chapter. An exhaustive review on CuInSe₂ thin films is also included here.

CHAPTER 2 specifies the theory as well as experimental setup used for the sample preparation. Details of the characterization techniques used in the present work are also given in this chapter.

CHAPTER 3 focusses on preparation and characterization of CuInSe₂ thin films from chemical bath deposited Selenium. CuInSe₂ films were deposited using two techniques, viz. stacked elemental layer technique and thermal diffusion of Cu into In₂Se₃. Structural, compositional, optical and electrical characterizations of the films were carried out with the help of X-Ray Diffraction (XRD), Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Analysis (EDAX), resistivity, photosensitivity, optical absorption and transmission. Surface analysis was done using Atomic Force Microscopy (AFM). Comparison between the two methods was performed and best samples were selected for trial on device fabrication. Even though the films prepared using the two techniques showed similar variation in crystallinity, grain size and band gap with Cu to In ratio, the photosensitivity was found to be higher for those samples prepared using thermal diffusion of Cu into In₂Se₃. Hence this was considered to be suitable for solar cell applications. The films had good crystallinity with sphalerite structure as confirmed from XRD and Raman studies. Information on stoichiometry of the samples was obtained from EDAX
measurements. These CuInSe₂ films were free from voids and pinholes. Defect analysis was also performed using photoluminescence and temperature dependant conductivity studies.

The main advantage of this technique was that, highly toxic Se vapor or H₂Se gas could be completely avoided. An attempt to device fabrication was also made using vacuum evaporated CdS as buffer layer. But photovoltaic effect could not be observed at the junction. Even though this preparation technique was eco-friendly, it had the disadvantage that, thickness of Se layer was only 0.25μm. The problems with this lower thickness are reduced absorption of incoming photons and also increased back surface recombination. As techniques like light trapping and back reflectors were not employed in this configuration, slightly increased thickness (0.5-1μm) should be used. In this technique, the overall absorber layer thickness was lower for getting considerable absorption of the photons. Unfortunately the thickness of the absorber layer could not be increased further so as to increase the absorption.

A modified technique of vacuum evaporation was introduced in

CHAPTER 4, in which CuInSe₂ thin films were prepared using sequential elemental evaporation. In this technique Cu, In and Se were evaporated at moderately low substrate temperatures as an alternative to higher temperature deposition and co-evaporation. This method is simpler and more economically viable than co-evaporation. Moreover control of stoichiometry could easily be achieved. Composition was widely varied to find the suitability in device fabrication. For this, Cu and Se were varied, one at a time, keeping the others constant. Both p- and n-type films could be prepared using this technique. From the structural characterization using XRD and Raman scattering, structure of CuInSe₂ prepared using this method, was identified as “chalcopyrite” which is the most suitable and favourable structure for solar cells. In the earlier method of preparing CuInSe₂ (using chemical bath deposited Se), we could obtain only “sphalerite” structure. The grain size varied from 35 nm to 63 nm in these samples. However this grain size was still lower than the reported values, obtained through other techniques. This lead to increase in the number of grain boundaries which, in some cases, has beneficial effects on CuInSe₂ devices. Interestingly, the crystallinity of these samples was better than that of earlier
samples prepared using chemical bath deposited Se. Again grain size was three times larger than that of the samples prepared using CBD Se.

Band gap varied from 0.93 to 0.99 eV in the samples with variation in elemental concentrations. AFM analysis of the sample showed that geometry of the sample changed from spherical to pyramidal on going from In-rich to Cu-rich. Resistivity varied in the range of 0.002 Ωcm to 7916 Ωcm and hence highly conductive or highly resistive samples could be selected for device fabrication. Sample with resistivity of 0.08 Ωcm can be used as conductive bottom layer and sample with resistivity of 7916 Ωcm can be used as the resistive top layer of device. Photosensitivity of the highly resistive sample was 7.7. Highly stoichiometric film could also be prepared without using ultra high vacuum which is still a major challenge for many researchers working in ternary chalcopyrites. Typical concentration of the stoichiometric sample was Cu: 24.92%, In: 24.98% and Se 50.10%.

CHAPTER 5 describes the attempt for device fabrication using optimized samples. For this In$_2$S$_3$ prepared by Chemical Spray Pyrolysis was used as the buffer layer. This is a new buffer layer for CuInSe$_2$. CuInSe$_2$ layer (absorber) had a double layer structure with a highly conductive ($p^+$) bottom layer and a resistive ($p$) top layer. Total layer thickness was 0.85μm. Here the bottom layer acted as an “electron reflector”, thereby reducing back surface recombination. The junction characteristics were studied by varying thickness, In/S ratio and post deposition treatments of In$_2$S$_3$. We could observe only a feeble photovoltaic effect which may be improved by varying further parameters. As a trial of reduction of the absorber layer thickness and replacement of CdS, which remain as a challenge in the development of CuInSe$_2$ solar cells, in the present study, these two factors were taken into account. In$_2$S$_3$ seems to be a good buffer layer instead of CdS for CuInSe$_2$ solar cells.

CHAPTER 6 is the summary of the entire work. Important points are also included and the future scope of the work is added.