Preface

Photovoltaic conversion of solar energy appears to be one of the most promising ways of meeting the increasing energy demands of the future in a time when conventional energy sources are being depleted. The present growing interest in photovoltaic conversion is a consequence of the concern to identify future sources of energy that will be inexpensive as well as ecofriendly.

Semiconductors have emerged as the most promising class of materials that can convert sunlight directly into electrical energy. Currently, a wide range of semiconductors is explored for their potential use in photovoltaic applications. The general criteria determining the choice of a particular semiconductor are efficiency and cost considerations, the environmental conditions (eg. terrestrial or space applications and duration of sunshine) and the availability and toxicity of the raw materials. Each material requires a particular solar cell device structure for optimum performance, and the choice is primarily determined by the available processing techniques and the photovoltaic properties that can be achieved under these conditions.

Lowering the cost of solar cell production is one of the most important intentions in photovoltaic research. To achieve this, thin film technology need to be developed with thin film materials having good photovoltaic properties and appropriate band gap that can be deposited uniformly over large areas. Recent developments in solar cell research proved that $CuInSe_2$ and its alloys and $CuInS_2$ are promising absorber layers for high efficiency solar cells. Recently efficiency upto 19.2% has been achieved with $ZnO/CdS/CuInGaSe_2$ (CIGS) cell structure.

$CuInS_2$ is particularly important because of band gap of 1.5 eV, which is close to the optimum value for photovoltaic conversion and controllable conversion type. Moreover, the constituents of this compound are non-toxic. Efficiency of the order of 13% was obtained for $TCO/CdS/CuInS_2/CuGaS_2$ cell structure. Nowadays lot of research is going on for the replacement of the buffer layer CdS by a Cd-free, wider band gap materials like $In_x(OH,S)_y$, ZnO, ZnSe, In_2Se_3 or In_2S_3. In_2S_3 films deposited using Atomic Layer Chemical Vapour Deposition (ALCVD) yielded an efficiency of 16.4% in CIGS based cells.

In the present work, we have prepared and characterized $CuInS_2$ and In_2S_3 thin films using the simple and low cost Chemical Spray Pyrolysis (CSP) technique. The technique is also suitable for large area film deposition. The films were optimized for different substrate temperatures and atomic concentrations. Making use of the optimized conditions for films with good photovoltaic activity, we could fabricate all sprayed $CuInS_2/In_2S_3$ having 9.5% efficiency, which is the first one of its kind to the best of our knowledge. The thesis is divided into nine chapters and a brief description of the contents of each chapter is described below.

CHAPTER 1 is a general introduction to photovoltaics. It begins with the description of the origin and use of solar energy along with detailed theory of *pn* junction. The factors affecting the efficiency of solar cell and the importance of thin film materials are also explained here. In the next section structure of the thin film solar cell with description of the requirements of different layers is given. This chapter is concluded with a discussion on different materials presently used for thin film solar cells.

CHAPTER 2 presents an exhaustive review on copper indium sulfide, indium sulfide and $CuInS_2$ based solar cells.

Preparation and characterization of indium sulfide thin films, using Chemical Spray Pyrolysis technique (CSP), is described in **CHAPTER 3.** Chloride based precursor solutions were used for sample preparation. CSP technique is essentially suitable for solar cell production, because of the possibility of large-area deposition of thin films in any required shape, easiness of doping and/or variation of atomic ratio and low cost/low tech nature of the technique. We prepared indium sulfide thin films systematically, at different substrate temperatures and by varying the In/S ratio in the spray solution. Structural, compositional, optical and electrical characterizations of the films were carried out using X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), EDAX, resistivity, photosensitivity, optical absorption and transmission. Surface analysis was done using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). We could optimize the composition of the spray solution to get good values of resistivity and photosensitivity. When this material is used as buffer layer in solar cells, these two parameters are important. In terms of crystallinity, photosensitivity and band gap the sample having In/S ratio 1.2/8 was selected for fabricating solar cells in this work.

CHAPTER 4 deals with the studies on indium sulfide thin films prepared using nitrate based precursor solutions. The motivation behind the replacement of the precursor solution was to remove chlorine, which caused the enhancement of electrical resistivity of In_2S_3 films. Another advantage was that indium nitrate could be pyrolysed at relatively low temperature. Interestingly the In/S ratio 2/3 only showed crystallinity. We could get better control over stoichiometry of the films by varying In/S ratio taken in the solution, using nitrate based precursor. But there was considerable decrease in the photosensitivity of the samples. Maximum photosensitivity was obtained for the sample having In/S ratio 2/4. Nitrate based samples were found to be more conducting compared to chloride based ones.

We used chloride and nitrate based precursor solutions for preparing $CuInS_2$ samples also. The details of preparation and characterization are given in **CHAPTER 5**. Films were prepared with different Cu/In ratio in the initial spray solution. The maximum thickness that could be achieved with single spray was 0. 6 μm and 375 ml of the solution was sprayed for this. Structural, compositional, electrical and optical characterizations of the films obtained were carried out. It was found that chemical composition of the solution controlled film resistivity and photoresponse.

Conductivity of the films was found to increase with increase in Cu/In ratio. Defect levels were identified using temperature dependent conductivity measurements.

We tried multiple spray pyrolysis technique to increase the thickness of $CuInS_2$ film. A systematic study on the samples prepared with different Cu/In ratio is presented in **CHAPTER 6**. Thickness of the samples could be increased to 1.17 μm by spraying 225 ml of the solution four times (total volume 900 ml). Thicker absorber layer was found to improve the performance of the cell (explained in chapter 8). Enhanced conductivity was obtained for samples having greater Cu/In ratio. Oxygen was absent in the bulk of the sample even after multiple spraying as revealed by XPS studies. EDAX measurements pointed out that Cu/In ratio was slightly less than that taken in the solution. Structural, optical and electrical characterizations of the films were also done.

CHAPTER 7 describes the fabrication of all sprayed $CuInS_2/In_2S_3$ solar cell. The effect of variation of the thickness and atomic concentration of the absorber ($CuInS_2$) and buffer layer (In_2S_3) are explained in this chapter. Performance of the cell improved by annealing in air or keeping it at the preparation temperature itself for 1 hour after spray. The effect of annealing on the characteristics of the cell depends on the thickness and atomic concentration of the layers.

Modifications made to improve the performance of the cell are described in **CHAPTER 8**. The thickness of the buffer layer was increased to compensate for copper diffusion from $CuInS_2$ to In_2S_3. Silver, used as the top electrode, was found to improve the crystallinity of the In_2S_3 layer and this is resulted in enhancement of efficiency to 9.5% for all sprayed $CuInS_2/In_2S_3$ solar cell.

CHAPTER 9 is a summary of the entire work. All the important points are highlighted. The chapter ends with future scope of the present work.