Photovoltaic conversion of solar energy appears to be one of the most promising ways of meeting the increasing energy demands of the future when conventional energy sources are being depleted. 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 frontrunner among the class of materials that can convert sunlight directly into electrical energy. Currently, a wide range of semiconductors are explored for their potential use in photovoltaic applications. General criteria determining the choice of a particular semiconductor are efficiency, cost, availability and toxicity of the raw material along with environmental conditions (e.g., terrestrial or space applications and duration of sunshine). 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 among 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. Furthermore, the constituents of these compounds should be non-toxic. Nowadays lot of research is going on for the replacement of the CdS buffer layer. Among the various materials with wide bandgap investigated (Zn(OS), Zn(OH,S), ZnO, ZnS, ZnSe, In$_2$S$_3$, In(OH)$_3$, In(OH,S)$_3$ [29,30]) the best performance was achieved using the CdS buffer material. This is contrary to the performance gain expected for wider band gap materials due to lower light absorption. This underline the fact that alternate buffer layers are not yet optimized to capture its full potential.
Indium sulfide ($\text{In}_2\text{S}_3$) is a rare case of ordered crystalline material with large number of vacancies and has proved its potential as a Cd-free buffer layer. Owing to tetragonal sites formed by the incompletely coordinated sulfur atoms, indium sulfide can serve as a host for a number of metal ions. Doping $\text{In}_2\text{S}_3$ produces materials with exceptional optical, electrical, and magnetic properties that can be adjusted by the concentration of the guest ion.

In the present work, structural, optical and electrical properties of indium sulfide are tuned by specific and controlled doping. Silver, tin, copper and chlorine were used as the doping elements. $\text{In}_2\text{S}_3$ thin films for the present study were prepared using a simple and low cost “Chemical Spray Pyrolysis (CSP)” technique. This technique is adaptable for large-area deposition of thin films in any required shape and facilitates easiness of doping and/or variation of atomic ratio. It involves spraying a solution, usually aqueous, containing soluble salts of the constituents of the desired compound onto a heated substrate. Doping process was optimized for different doping concentrations. On optimizing doping conditions, we tuned the structural, optical and electrical properties of indium sulfide thin films making them perform as an ideal buffer layer. This thesis is divided into seven chapters. A brief description of each chapter is given below.

**CHAPTER 1** is a general introduction to buffer layer in thin film photovoltaics. It briefs about the importance of thin films in solar cells and the role of buffer layer. Further it continues with discussion on present hurdles of thin film photovoltaics, toxicity of cadmium and Cd-free buffer layers. The chapter concludes by discussing the factors limiting the efficiency of solar cell and thoughts to overcome it.

**CHAPTER 2** presents an exhaustive review on indium sulfide, the material under study. This chapter provides a thorough insight on the studies done so far in this material.
CHAPTER 3 presents the anomalous behavior of silver doped indium sulfide thin films. It was observed that silver got diffused into In$_2$S$_3$ films at room temperature itself without any post deposition treatments. These samples were characterized using different techniques. Depth profile using X-ray Photoelectron Spectroscopy clearly showed diffusion of silver into In$_2$S$_3$ layer without any annealing. X-ray analysis revealed significant enhancement in crystallinity and grain size up to an optimum percentage of doping concentration. This optimum value showed dependence on thickness and atomic ratio of indium and sulfur in the film. Sample having optimum doping was found to be more photosensitive and low resistive when compared with pristine sample. Impact of post annealing on the optimum doping was also studied; results proved that optimum value of silver decreased on enhancing the diffusivity by thermal assistance and excess silver retraced to the surface of the films on annealing. Thus silver diffused indium sulfide surpassed pristine sample for crystallinity and photosensitivity.

CHAPTER 4 deals with the studies on tin doped indium sulfide thin films. The motive behind this was to reduce resistivity of the films. Effect of both in-situ and ex-situ doping were analyzed. Ex-situ doping was done through thermal diffusion which was realized by annealing Sn/In$_2$S$_3$ bilayer films. In-situ doping was done by introducing Sn into the Spray solution using SnCl$_4$.5H$_2$O. Interestingly, it was noted that by ex-situ doping, the conductivity of the sample enhanced by five orders without affecting any of the physical properties, such as crystallinity or band gap. Analysis also showed that higher doping percentage resulted in samples with lower crystallinity and negative photosensitivity. However, in-situ doping resulted in amorphous films. Conductivity of the samples increased for with low doping concentrations and at higher doping concentration conductivity decreased. Oxygen incorporation was also found to be very high with in-situ doped samples and resulted in widening of the optical bandgap. These films were highly photosensitive even when it exhibited very wide bandgap. These observations proved that tin incorporation modified the band
gap and electrical properties of the In$_2$S$_3$: Sn films favorably over wider ranges making it highly suitable for different optoelectronic applications.

**CHAPTER 5** describes copper doping in indium sulfide thin films. Doping was achieved through thermal diffusion by annealing bi layer films having structure Cu/In$_2$S$_3$. XRD analysis revealed formation of CuInS$_2$ in addition to tetragonal $\beta$-In$_2$S$_3$ phase at high doping concentration. Optical absorption edge of these films showed a shift towards longer wavelength due to the presence of CuInS$_2$. Electrical measurements indicated a considerable reduction in the sheet resistance of the sample. Hot probe measurements showed that Cu diffused samples resulted in p-type conductivity. Photoactive 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.

Role of chlorine in indium sulfide films, prepared by chemical spray pyrolysis method employing indium chloride precursor solution is discussed in **CHAPTER 6**. The role of incorporated Cl in the films prepared using chemical methods was not revealed. Hence, in order to find the part played by chlorine atoms, it was purposefully doped. Chlorine was omitted in the pristine films by replacing the precursor solution of indium chloride by indium nitrate. Films prepared from indium nitrate precursor solutions were amorphous. Chlorine was found to be instrumental in imparting crystallinity to films. Controlled doping of chlorine resulted in micro/nano structures. Chlorine also initiated defect level absorption. Photosensitivity of chloride based samples could be increased by introducing chlorine. Persistent photoconductivity was also observed for doped films. This study proved the implicit role played by chlorine in giving highly crystalline films with specific optical and electrical properties.

**CHAPTER 7** is a summary of the entire work. The important points are highlighted. The chapter ends with future scope of the present work.