Preface

There is an increasing demand for renewable energies due to the limited availability of fossil and nuclear fuels and due to growing environmental problems. Photovoltaic (PV) energy conversion has the potential to contribute significantly to the electrical energy generation in the future. Currently, the cost for photovoltaic systems is one of the main obstacles preventing production and application on a large scale. The photovoltaic research is now focused on the development of materials that will allow mass production without compromising on the conversion efficiencies. Among important selection criteria of PV material and in particular for thin films, are a suitable band gap, high absorption coefficient and reproducible deposition processes capable of large-volume and low cost production. The chalcopyrite semiconductor thin films such as Copper indium selenide and Copper indium sulphide are the materials that are being intensively investigated for lowering the cost of solar cells. Conversion efficiencies of 19 % have been reported for laboratory scale solar cell based on CuInSe₂ and its alloys.

The main objective of this thesis work is to optimise the growth conditions of materials suitable for the fabrication of solar cell, employing cost effective techniques. A typical heterojunction thin film solar cell consists of an absorber layer, buffer layer and transparent conducting contacts. The most appropriate techniques have been used for depositing these different layers, viz; chemical bath deposition for the window layer, flash evaporation and two-stage process for the absorber layer, and RF magnetron sputtering for the transparent conducting layer. Low cost experimental setups were fabricated for selenisation and sulphurisation experiments, and the magnetron gun for the RF sputtering was indigenously fabricated. The films thus grown were characterised using different tools. A powder X-ray diffractometer was used to analyse the crystalline nature of the films. The energy dispersive X-ray analysis (EDX) and scanning electron microscopy
(SEM) were used for evaluating the composition and morphology of the films. Optical properties were investigated using the UV-Vis-NIR spectrophotometer by recording the transmission/absorption spectra. The electrical properties were studied using the two probe and four probe electrical measurements. Nature of conductivity of the films was determined by thermoprobe and thermopower measurements. The deposition conditions and the process parameters were optimised based on these characterisations.

The results of the investigations are presented in 6 chapters. An overview of the developments in the field of photovoltaic is briefly presented in Chapter 1 with focus on the I-III-VI₂ based solar cells. The advantages of I-III-VI₂ group chalcopyrite thin film semiconductors over other solar cell materials are discussed. The device structure, performance and the defect chemistry of a solar cell is also presented in this section. The review gives an insight into the developments in the field of photovoltaic and references to the literature on chalcopyrite polycrystalline solar cells during the past decade.

Chapter 2 deals with the various deposition methods and characterisation tools employed in the present study. Different customised experimental setups were fabricated for thin film depositions.

Chemical bath deposition (CBD) was effectively utilised for the preparation of some II-VI group semiconductors as the buffer layers for solar cells and the results are summarised in Chapter 3. The chapter is divided into four parts and the relevant literature review is included in each part. Part A describes the preparation and characterisation of CdS thin films. The chemical bath deposited CdS films were uniform and was having a high carrier concentration of ~10¹⁷ carriers/cm³. The films showed a blue shift in the absorption edge (Eₚ) due to the nanocrystalline growth, which is advantageous for the application in solar cells to get higher conversion efficiency. The relatively low band gap of the CdS films limits the conversion efficiency of the solar cells. Higher band gap buffer layers are needed to enhance the response in short wavelength region. With this outlook a ternary derivate of CdS, ZnₓCd₁₋ₓS films were prepared by CBD.
The Zn incorporation into the CdS facilitates band gap engineering. It was observed that, though the band gap increased with Zn incorporation, the resistivity of the film also increases, which is undesirable for a window layer in the solar cell. In order to enhance the conductivity, indium was doped by adding InCl₃ in the chemical bath for the growth of ZnₓCd₁₋ₓS films. The results of the preparation and characterisation of ZnₓCd₁₋ₓS thin films and the effect of indium doping are presented in Part B of Chapter 3. Part C deals with the preparation and characterisation of a cadmium free, wide band gap ZnS buffer layer. ZnS thin films were prepared from two different host solutions of Zn. The reaction mechanism and the effect of pH on the electrical and optical properties of the CBD-ZnS are presented. The properties of CBD-ZnS are compared with the ZnS films prepared by electron beam evaporation. Part D describes a simple method to prepare ZnO thin films from the chemical bath deposited ZnS films by thermal oxidation. Poly crystalline ZnO films were obtained and the films were showing high resistivity.

Chapter 4 describes the preparation and characterisation of chalcopyrite absorber layers for solar cells. The chapter is divided into two parts, Part A discusses the preparation and characterisation of copper indium selenide and Part B deals with copper indium sulphide thin films. Chalcopyrite CuInSe₂ thin films were prepared by flash evaporation followed by the annealing in selenium vapour. The effect of selenisation on the electrical and optical properties of the films is investigated. CuInS₂ is a promising chalcopyrite material, which is expected to show superior efficiency than CuInSe₂ due to its ideal band gap. The ‘two stage process’; which is a simple, scalable and cost effective technique; was optimised for preparing single phase, p-type CuInS₂ thin films. The two-stage process involves the preparation of Cu-In alloy followed by the sulphurisation using H₂S gas. The dependence of processing parameters and the Cu/In ratios of the starting precursors on the electrical, optical and structural properties have been studied and are presented in Part B of Chapter 4.
Tin doped indium oxide (ITO) thin films are having numerous applications in opto-electronic devices and are widely used as the transparent conducting electrode in solar cells. ITO films have been deposited by RF magnetron sputtering at room temperature and the results are presented in Chapter 5. The effect of target to substrate spacing and the post deposition annealing in vacuum, on the structural, electrical and optical properties of the films are discussed. Poly crystalline films were obtained by the room temperature sputtering, which is advantageous for many device applications where flexible substrates are used. Highly conducting and transparent films were obtained by post deposition vacuum annealing. Chapter 6 is the concluding chapter, which highlights the major results and proposes the future steps for fabricating and improving the device performance using the techniques developed for the growth of various layers presented in the thesis.

*Part of the thesis has been published in the internationally referred journals.*


V. Effect of selenisation on the flash evaporated copper indium selenide thin films, Aldrin Antony and M.K. Jayaraj
(communicated)

VI. ZnO thin films prepared by the thermal oxidation of chemical bath deposited ZnS, Aldrin Antony and M.K. Jayaraj
(communicated)

Conference Proceedings


Other publications to which author has contributed,


