Preface

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The motivation behind this study is to investigate the effectiveness of low cost, earth abundant and high efficiency photovoltaic (PV) materials. Devices employing PV materials play a significant role in resolving the problems of energy shortage and environmental pollution. Silicon (Si) based solar cells have dominated the energy market but the high cost of the manufacturing process takes them beyond the reach of the common consumer.

One way of overcoming this problem is to find suitable replacements for Si. Thin film solar cells made up of chalcogenide semiconductor nanomaterials have the potential of reducing the cost of raw materials used in solar cells. Copper based chalcogenides such as $CuInS_2$ (CIS), (CIGS) $CuInGa(S,Se_2)$ and GaAs are promising light absorber materials. However, the lack of availability and extreme toxicity of the elements like indium (In) and gallium (Ga) are causes of concern. It is important to develop low cost, naturally abundant, non-toxic and environment friendly chalcogenide materials for photovoltaic applications. In recent years, chalcogenide based quaternary semiconductor such as Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) have attracted much attention, for potential application in thin film photovoltaic cells due to their optimum optical band gap (~1.5 eV). Also, the replacement of Zn with more earth abundant elements like Ni and Fe would provide a significant leap forward in the development of photovoltaic technology.

The present work is devoted to the synthesis of relatively new quaternary semiconductor materials, viz., Cu_2NiSnS_4 (CNTS) and Cu_2FeSnS_4 (CFTS) for photovoltaic applications. These semiconducting materials are considered as suitable alternatives for (CZTS/Se) because of their appropriate band gap value which is around 1.1-1.5 eV. In the present study, CNTS and CFTS solar cells have been fabricated through the spin coating technique. An attempt has been made to synthesize CNTS and CFTS nanoparticles by various methods using different precursor ratios. The synthesized nanoparticles have been characterized by different techniques and their utilization as potential absorbance layers in thin film solar cells investigated.

The thesis is organized into ten chapters. The brief outline of the thesis is as follows:

Chapter one deals with the importance of Nanomaterials in various fields and gives a brief introduction to photovoltaic technology and the generation wise development of solar cells. Several leading solar materials, their current status and the problems that arise are analyzed and the requirement for alternate solar absorber materials in the thin film industry discussed. Survey of literature related to the synthesis of Cu- based quaternary chalcogenide compounds by various methodologies and their potential applications are also deliberated in the chapter. The objective of the present work is briefly discussed at the end of the chapter.

Chapter two contains a general discussion of the various synthesis processes for the preparation of CNTS and CFTS nanoparticles with specific attention to the chemical precipitation and hydrothermal methods. Various characterization techniques, namely the X-ray diffraction (XRD), Raman spectroscopy, UV-Vis spectroscopy, Field emission scanning electron microscopy with energy dispersive spectroscopy (FE-SEM-EDAX), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), which have been employed in the present investigation are also briefly discussed. The thin film fabrication process and characterization are also presented in this chapter.

Chapter three deals with the synthesis of Cu_2NiSnS_4 nanoparticles by a facile chemical route method. The structural, morphological, optical and electrical characteristics of the synthesized nanoparticles have been analyzed. This chapter deals with the optimization of the CNTS composition concentration to overcome the problems by varying the concentration of the constituent elements.

Chapter four discusses the synthesis of $Cu_2Ni_xSn_{(1-x)}S_4$ (CNTS) nanoparticles of different compositions (x = 0, 0.2, 0.4, 0.6, 0.8 and 1M) by the facile chemical precipitation method. Analysis of the crystalline structure was done by X-ray diffraction, Raman spectroscopy and UV-Vis absorption spectra revealed that the nanoparticles have a strong absorption band in the visible region. The variation of the optical band gap with change in x in the above range is discussed. The electrochemical properties of CNTS nanoparticles were investigated by cyclic voltammetry at different scan rates and electrochemical impedance spectroscopy. The choice of the best CNTS composition for use as absorbance layer in solar cells is also deliberated in this chapter.

Chapter five presents the synthesis of $Cu_2Ni_xSn_{(1-x)}S_4$ (CNTS) nanoparticles of different compositions (x = 0, 0.2, 0.4, 0.6, 0.8 and 1 M) through the hydrothermal method. The structural, morphological, compositional and optical characteristics of the synthesized nanoparticles are elaborated in this chapter. The suitability of the $Cu_2Ni_xSn_{(1-x)}S_4$ nanoparticles with x = 0.8 with the appropriate optical band gap for application in thin film solar cells is discussed. This chapter also explains the investigation of the electrochemical properties of CNTS nanoparticles by cyclic voltammetry with different scan rates and electrochemical impedance spectroscopy to choose the suitable composition for use as absorbance layer in solar cells.

Chapter six clarifies the synthesis of Cu_2FeSnS_4 nanoparticles by the hydrothermal method. The analysis of the phase pure tetragonal structure by XRD and Raman spectroscopy is explained. The strong absorption band observed in the UV-Visible region and the electrochemical characteristics are also discussed in the chapter. The optimization of the CFTS composition concentration to overcome the drawbacks by increasing the concentration is discussed.

Chapter seven discusses the synthesis of $Cu_2Fe_xSn_{(1-x)}S_4$ (CFTS) nanoparticles of different compositions (x = 0, 0.2, 0.4, 0.6, 0.8 and 1 M) by the chemical precipitation method and the study of the structural, morphological, composition and optical properties of the synthesized nanoparticles by various characterization techniques such as XRD, Raman spectroscopy, FESEM-EDX and UV-Vis spectroscopy analysis. The determination of the phase and structure of the prepared nanoparticles by powder XRD and Raman spectroscopy is explained. It is shown that the $Cu_2Fe_{(x)}Sn_{(1-x)}S_4$ nanoparticles with x = 0.8 exhibit good crystalline phase and the optical band gap suitable for thin film solar cell application. The study of the electrochemical properties by cyclic voltammetry with different scan rates and electrochemical impedance spectroscopy for CFTS nanoparticles to facilitate the choice of the best composition for use as absorbance layer is discussed.

Chapter eight deals with studies on $Cu_2Fe_xSn_{(1-x)}S_4$ (CFTS) nanoparticles of different compositions (x = 0, 0.2, 0.4, 0.6, 0.8 and 1 M) synthesized by the hydrothermal method. The investigation of the structural properties confirming the highly crystalline tetragonal structure of the synthesized nanoparticles is discussed. It is shown that the CFTS nanoparticles with $x = 0.8$ exhibit the best crystalline structure. The use of cyclic voltammetry with different scan rates and impedance spectroscopy to study the electrochemical properties of the CFTS nanoparticles to choose the one best suitable for use as thin film absorbance layer is also discussed.

Chapter nine describes the fabrication of thin film solar cells using absorbance layers of CNTS and CFTS nanoparticles synthesized by the different methods detailed in the previous chapters. The fabrication of thin films based photovoltaic cells with structure FTO/ZnO/CdS/CNTS (and CFTS)/Ag and the study of their performance under simulated AM 1.5 illumination are discussed. The deposition of ZnO window layer and CdS buffer layer by spin coating and chemical bath deposition methods respectively to achieve the desired device architecture is discussed. The X- ray diffraction pattern of ZnO showing the hexagonal phase and the structural and optical properties of the prepared CdS thin films are detailed. The conversion of the synthesized $Cu_2Ni_xSn_{(1-x)}S_4$ (CNTS) and $Cu_2Fe_xSn_{(1-x)}S_4$ (CFTS) nanoparticles (with $x= 0.8$ concentration) into the ink form and the deposition of the obtained ink on a FTO substrate are explained. This chapter also gives the detailed results of the analysis of I-V characteristics of all the fabricated thin films. The optimization of the device fabrication parameters to get maximum power conversion efficiency (η) is also deliberated.

Chapter ten summarizes the results obtained in this work and discusses the scope for future work in thin film solar cells.