Abstract

Photodetectors are widely used as image sensors, in optical communication, remote sensing etc. IR detectors find widespread applications in night vision cameras and medical diagnostics. In this thesis a new chalcopyrite material Cu_2SnS_3 has been studied for photodetector applications. Cu_2SnS_3 has a near IR band gap in the range of 0.93 to 1.5 eV which is optimum for solar light absorption and IR applications. It has a high absorption coefficient of 10^4 to 10^5 cm^{-1} thus suitable for harnessing the solar photons. Thus, Cu_2SnS_3 can be envisaged as a potential candidate for optical applications such as photodetectors, photovoltaics, light emitting diodes, photocatalysis and nonlinear optics.

The thesis deals with the preparation of Cu_2SnS_3 thin films and nanostructures by solution processable techniques. The electrical transport mechanism in Cu_2SnS_3 and Cu_2SnS_3/Al:ZnO heterojunction is studied. The band offsets at the Cu_2SnS_3/Al:ZnO and Cu_2SnS_3/ITO heterojunctions are determined using XPS. Finally, the visible and infrared photo response of the Cu_2SnS_3 thin films, nanostructures and inorganic organic hybrid systems have been investigated.

Chapter-1 gives the introduction to the topic of photodetection, the motivation behind the present work and about the material Cu_2SnS_3.

Chapter-2 describes the various synthesis techniques for making Cu_2SnS_3 films and nanostructures. Also, the characterization techniques for analyzing the Cu_2SnS_3 material and device fabrication for various optoelectronic applications have been presented.

Chapter-3 deals with the preparation of Cu_2SnS_3 films using a solution processible spin coating method and its characterization using several techniques. The various phase transformations and deposition temperature of the precursor solution was determined using TGA and DSC. The Cu-Sn-thiourea complex precursor was analysed using Fourier Transform Infrared Spectroscopy. The phase formation of the films was determined using X-ray diffraction. The vibrational modes of Cu_2SnS_3 were deduced using Raman spectroscopy. The structure and morphology of the films as well as the composition were determined from Scanning electron microscopy and Energy dispersive spectroscopy, respectively. The surface morphology of the films and roughness was determined using noncontact mode Atomic force microscopy. The thickness of the deposited films was measured using stylus profilometry. The absorption spectra of the films were obtained using UV-VIS-NIR spectrophotometer. The refractive index, extinction coefficient and relative permittivity were determined using spectroscopic ellipsometry. Electrical properties were measured using Hall effect studies.

Chapter-4 discusses the temperature dependent current voltage characteristics of the Cu_2SnS_3 films. The temperature dependent electrical properties of the drop casted Cu_2SnS_3 films were measured in the temperature range 140 K to 317 K. The log I versus √V plot showed two regions wherein the region at lower bias was due to electrode limited Schottky emission and the higher bias region was due to bulk limited Poole Frenkel emission. The ideality factor was calculated from the ln I versus V plot for different temperatures fitted with the thermionic emission model and was found to vary from 5.6 to 8.13. This large value was attributed to the presence of defects or amorphous layer at the Ag / Cu_2SnS_3 interface. From the Richardson's plot the Richardson's constant and the barrier height were calculated. Owing to the inhomogeneity in the barrier heights, the Richardson's constant and the barrier height were also calculated from the modified Richardson's plot. The temperature dependent current graphs showed two regions of different mechanisms. The log I versus 1000/T plot gave activation energies E_{a1} = 367.1 – 257.68 meV and E_{a2} = 38.42 - 42.45 meV. The log (I/T^2) versus 1000/T graph gave trap depths Φ_{o1} = 314.16 - 204.75 meV and Φ_{o2} = 7.43 - 11.16 meV. With increasing voltage, the activation energy E_{a1} and the trap depth Φ_{o1} decreased. From the ln ($IT^{1/2}$) versus $1/T^{1/4}$ graph, the low temperature region was attributed to variable range hopping mechanism and the high temperature region was attributed to thermionic emission.

Chapter-5 deals with the study of the band offsets at the Al:ZnO/Cu_2SnS_3 heterojunction interface using X-ray photoelectron spectroscopy. Al: ZnO/Cu_2SnS_3 semiconductor heterojunction was fabricated. The structural and optical properties of the semiconductor materials were studied. From the measurement of the core level energies and valence band maximum of the constituent elements, the valence band offset was calculated to be -1.1± 0.24 eV and the conduction band offset was 0.9± 0.34 eV. The band alignment at the heterojunction was found to be of type-I.

The variation of the current transport behavior as a function of temperature was studied for the heterojunction. The log *I* - log *V* plot exhibited three regions of different slopes showing linear ohmic behaviour and non-linear behaviour following the power law. There was a variation in the ideality factor and barrier height with temperature. The Richardson constant was calculated and its deviation from the theoretical value revealed the inhomogeneity of the barrier heights. Transport characteristics were modelled using the thermionic emission model. The Gaussian distribution of barrier heights was applied and from the modified Richardson plot the value of the Richardson constant was found to be 47.18 $Acm^{-2}K^{-2}$.

Chapter-6 deals with the study of band offsets at the Cu_2SnS_3 / In_2O_3: Sn interface using X-ray photoelectron spectroscopy. Cu_2SnS_3 thins films were ddeposited onto In_2O_3: Sn coated soda lime glass substrates by spin coating technique. The films were structurally characterized using X-Ray Diffraction and Atomic Force Microscopy. The morphology of the films was studied using Field

Emission Scanning Electron Microscopy. The optical properties of the films were determined using UV-Vis-NIR spectrophotometer. The electrical properties were measured using Hall effect measurements. The energy band offsets at the Cu_2SnS_3/In_2O_3: Sn interface were calculated using X-ray photoelectron spectroscopy. The valence band offset was found to be -3.4$\pm$0.24 eV. From the valence band offset value, the conduction band offset was calculated to be -1.95$\pm$0.34 eV. The energy band alignment indicates a type-III heterostructure formation.

Chapter-7 deals with the study of the visible and infrared photo response of Cu_2SnS_3 thin films. The Cu_2SnS_3 thin films were deposited using an economic, solution processible, spin coating technique. The films were found to possess a tetragonal crystal structure using X-ray diffraction. The film morphology and the particle size were determined using scanning electron microscopy. The various planes in the crystal were observed using transmission electron microscopy. The optimum band gap of 1.4 eV and a high absorption coefficient of 10^4 cm^{-1} corroborate its application as a photoactive material. The visible and infrared (IR) photo response was studied for various illumination intensities. The current increased by one order from a dark current of 0.31 μA to a current of 1.78 μA at 1.05 suns and 8.7 μA under 477.7 mW/cm^2 IR illumination intensity, at 3 V applied bias. The responsivity, sensitivity, external quantum efficiency and specific detectivity were found to be 10.93 mA/W, 5.74, 2.47% and 3.47×10^{10} Jones respectively at 1.05 suns and 16.32 mA/W, 27.16, 2.53% and 5.10×10^{10} Jones respectively at 477.7 mW/cm^2 IR illumination. The transient photo response was measured both for solar and IR illuminations.

Chapter-8 deals with the incorporation of Cu_2SnS_3 in visible and infrared photodetector applications. Various device structures such as Cu_2SnS_3 nanostructures and Cu_2SnS_3 nanostructures-P3HT-PCBM inorganic-organic hybrids were used. The visible and infrared photo response as well as the time dependent photo response was studied. The sensitivity, responsivity, external quantum efficiency and specific detectivity were measured.

Chapter- 9 presents the summary and the future work