ABSTRACT

Earth abundant, low cost, highly efficient photovoltaic material Cu$_2$ZnSnS$_4$ (CZTS) quantum dots have been synthesized by simple chemical precipitation technique. The X-ray diffraction pattern of CZTS quantum dots exhibit broad peaks which reveals that the synthesized particles have very small crystallite size and is found to be 9.1nm. The structural analysis and phase purity of quaternary material CZTS quantum dots have been studied by Raman spectroscopy. In the Raman spectra of CZTS quantum dots, A maximum intensity peak observed at 332cm$^{-1}$ and this corresponds to the vibrational $A_1$ symmetry mode of kesterite CZTS. The raman spectra did not show any evidence for the presence of secondary phases. The FESEM images shows that the constituents particles of CZTS have agglomerated and also the particles are small in size and spherical in shape. The HRTEM image showed lattice fringes corresponding to the kesterite phase of CZTS and the average crystallite size has been calculated using the HRTEM image and it was found to be 8.3nm. The elemental distribution in the CZTS quantum dots was carried out using STEM elemental mapping and the images show the uniform distribution of all the four elements Cu, Zn, Sn & S.

The stoichiometry and the oxidation states of CZTS quantum dots has been carried out using X-ray photoelectron spectroscopy (XPS). The core level XPS spectra of Cu 2p, Zn 2p, Sn 3d and S 2p confirms the presence of the constituent elements Cu, Zn, Sn and S in the synthesized CZTS. The formation of CZTS quantum dots has also been confirmed by photoluminescence (PL) spectroscopy. The optical band gap is found to be shifted to the higher energy side and it shows the presence of quantum confinement effect. Growth mechanism of CZTS spherical quantum dots has
also been studied. The study shows that, copper sulfide nuclei forms, and serves as the starting point for the nucleation and growth of CZTS quantum dots.

Nanocrystalline CZTS thin films with tunable nanostructures have been synthesised by sol-gel dip coating method without using any toxic chemicals, catalyst, capping agent and surfactants. The prepared CZTS thin films is found to exhibit different nanostructures depending on annealing time. When the prepared films were annealed for 1 hr at 250°C CZTS nanospheres were formed. When the annealing time was increased to 2 hrs at 250°C nano sphere got transformed to nano cubes, and as the time was further increased to 3 hrs at 250°C CZTS nano rods have been formed. The X-ray diffraction patterns of the CZTS nanospheres, nanocubes and nanorods based films reveal the formation of kesterite structure CZTS. The XRD pattern of CZTS nanorods shows sharp, high intensity and well defined peak which shows that the small size grains have started to grow with increasing annealing time. The Raman spectra of CZTS nanospheres, nanocubes and nanorods based thin films are found to have a peak at 331 cm$^{-1}$ which corresponds to the vibrational A1 mode of CZTS. This peak appears to be shifted to lower wave number. This shift to the lower wavenumber is probably due to the gradient in strain in nanostructures. It is observed that in the raman spectra there is no evidence for additional peaks corresponding to impurity phases such as, SnS, and Cu$_2$S.

The FESEM image of 1 hour annealed CZTS thin film reveals that the particles of CZTS have agglomerated and has led to the formation of particles in spherical shape. When the annealing time is increased to 2 hours CZTS nanospheres change to nanocubes and on further increasing the annealing time to 3 hrs results in the formation of CZTS nanorods all over the surface. The HRTEM image of spherical CZTS nanocrystals
synthesized by 1 hour annealing shows the crystallite size of the spherical CZTS nanocrystals as ~11 nm. When the annealing time is increased from 1 hour to 2 hours, spherical nano crystals of CZTS transform to cube-like CZTS with crystallite size of ~16 nm. Rod-like CZTS nanocrystals with an average length of ~400 nm and diameter of ~50 nm are obtained when the annealing time is increased to 3 hours. The EDAX analysis of the samples reveals that the constituent elements Cu, Zn Sn and S are present in the samples. In the EDAX spectrum of the CZTS nanospheres based thin film, the excess chlorine confirms the presence of excess thiourea SnCl₂ complex. The elemental mapping image of the CZTS sphere, cubes and rods based films show uniform distribution of the elements along the whole surface of the films.

The Hall effect studies of the CZTS thin film composed of nanorods revealed that they exhibit the lowest resistivity which indicates the efficient charge transfer in the 1-D structure. The obtained optical band gap energy of CZTS thin film is in the range of 1.46-1.54 eV, which is quite close to the optimum theoretical value required for solar cell applications. The shape transformation of 1D Cu₂ZnSnS₄ (CZTS) nanorods from nanospheres and nanocubes has also been studied. From the study, it is understood that the excess Sn and Cl in the preliminary stage of the growth formed the molten flux for the growth of nanorods.

The electrical bistability of CZTS thin film based device is very prominent and Current-voltage characteristics showed two distinct paths for forward and reverse biased condition. In which a device exhibits two different states of electrical conductivities, at the same applied voltage. Conductive atomic force microscopy (c-AFM) analysis provides the spatial resolution of the electronic properties of the individual atom in CZTS film. The current –voltage characteristics of the CZTS thin film device clearly
shows two different states of electrical conductivities, at the same applied voltage.

CdS thin films have been prepared by successive ionic layer adsorption and reaction (SILAR) method. The X-ray diffraction pattern of CdS shows that hexagonal phase CdS has been formed. The EDAX analysis of CdS shows the presence of Cd and S in the sample. The optical properties of CdS have been studied using the absorbance spectra. The band gap energy of CdS films have been found to be 3.84eV. The structural and optical properties of prepared ZnO thin films has been studied. The X-ray diffraction pattern confirms the formation of hexagonal ZnO.

CZTS/CdS/ZnO thin film based solar cells have been fabricated with device configuration ITO/CZTS/CdS/ZnO/Al. The J-V characteristics of CZTS/CdS/ZnO solar cells fabricated using CZTS absorber layer annealed for different time have been studied. The Cu$_2$ZnSnS$_4$ thin film based solar cell fabricated using CZTS film annealed at 250°C for 1 hr exhibited a power conversion efficiency ($\eta$) of 2.18 % with short circuit current density ($J_{sc}$) of 5.64 mA/cm$^2$, open circuit voltage ($V_{oc}$) of 0.67 V and fill factor (FF) of 0.58. The power conversion efficiency ($\eta$) of solar cell fabricated using CZTS film annealed at 250°C for 2 hrs was 2.56% with short circuit current density ($J_{sc}$) of 6.38 mA/cm$^2$, open circuit voltage ($V_{oc}$) of 0.67 V and fill factor (FF) of 0.60. The power conversion efficiency ($\eta$) of CZTS thin film solar cell fabricated using a CZTS film annealed at 250°C for 3 hrs was 2.70 % with short circuit density ($J_{sc}$) of 6.67 mA/cm$^2$, open circuit voltage ($V_{oc}$) of 0.70 V and fill factor (FF) of 0.58.