INVESTIGATIONS ON Cu_2ZnSnS_4THIN FILMS AS ABSORBER LAYER IN THIN FILM HETEROJUNCTION SOLAR CELLS

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Abstract: Cu_2ZnSnS_4 films have been successfully deposited by spray pyrolysis technique onto soda-lime glass substrate by two stage process. In the first stage, ZnS films are deposited by spray pyrolysis technique onto soda-lime glass substrates at substrate temperature (T_s) 713 K. Later, Copper Tin Sulphide (Cu_2SnS_3) films deposited onto heated ZnS films at substrate temperature (T_s) 643 K. The substrate temperature could be maintained to an accuracy of ± 5 K using a digital temperature controller. Finally, for achieving Cu_2ZnSnS_4 films, ZnS/Cu_2SnS_3 films were annealed in sulphur ambiance at a temperature 763K in the two-zone tubular quartz furnace. X-ray diffraction studies revealed that films are single phase and polycrystalline in nature with kesterite structure. The lattice parameters are found to be a= 0.543 nm and c= 1.086 nm. The optical band gap of as deposited film is found to be 1.44 eV, which is close to optimum band gap (1.5eV) for highest theoretical conversion efficiency. The average optical absorption coefficient is found to be 10^4 cm^{-1}. The films are found to be p-type in nature.

Keywords: Cu_2ZnSnS_4, Kesterite , Thin films, Solar cell absorber, Spray pyrolysis.

Introduction: It is apt to say that, the standard of living and quality of life directly depends on the energy resources of a country. Over the past few decades, the demand for affordable electric power is increasing due to rapid increase in population, a surge in urbanization. Unfortunately, the energy resources are low and it is highly essential either to develop new energy resources or to improve the available energy resources to meet the ever increasing demand for electric power. At present, the average energy consumption of the power is to the tune of 10 TW and it is expected that this requirement grows to around 30 TW by 2050 [1]. Presently, we are getting energy predominantly from thermal energy, nuclear energy, hydro energy etc. However, these sources of energy are expected to deplete in the next few decades. Hence, there is a need to search for alternative energy sources, which are user friendly and importantly, pollution free. Solar energy is one such attractive option for a tropical country like India. Solar cells made up of single crystal Si and multi-crystalline Si solar cell modules are commercially available but are highly expensive. Thin film solar cells based on CdTe, $CuInGaSe_2$ (CIGS), a-Si are relatively less expensive and are commercialized. Among these, $CuInGaSe_2$ (CIGS) based thin film solar cells have exhibited a record efficiency of 22.6 % at the laboratory level [2] and CdTe exhibited an efficiency of 16.7 % [3]. However, CIGS did not yield the expected cost reduction since it contains expensive and scarce elements (In, Ga) where as CdTe is toxic. In this context, Cu_2ZnSnS_4 (CZTS) is emerging as an alternative solar cell absorber layer to CIGS due to its eco- friendly and abundant elements. In addition, the other salient properties of CZTS namely direct band gap of 1.45 eV [2], high optical absorption coefficient (10^4 cm^{-1}), kesterite structure and p- type electrical conductivity. In 2011, Shin et al. [4] reported CZTS based solar cells with a maximum conversion efficiency of 8.4 %. In 1988, Ito and Nakazawa [5] for the first time reported CZTS based solar cell which exhibited an open circuit voltage (V_{oc}) of 165 mV under AM 1.5 illumination. Various groups have grown CZTS thin films using techniques like sputtering [6], thermal evaporation [4, 7], co-evaporation [10], sol-gel [9] and spray pyrolysis [10-12]. Among these, spray pyrolysis is a versatile and low cost approach for the growth of CZTS films.

Experimental: CZTS films have been successfully deposited by spray pyrolysis technique onto soda-lime glass substrates by two stage process. In the first stage, ZnS films were deposited by spray pyrolysis technique onto soda-lime glass substrates at substrate temperature (T_s) of 713 K with aqueous solution containing zinc acetate and thiourea. Subsequently, Copper Tin Sulphide (Cu_2SnS_3),a ternary compound semiconductor film grown onto ZnS films at a substrate temperature (T_s) of 643 K. Cu_2SnS_3 (CTS) films were deposited with aqueous solution containing cupric chloride, stannic chloride and thiourea with the concentrations in the range 0.01M to 0.03M. Excess thiourea was taken to compensate for the loss of sulphur during pyrolysis. The pH of the solution was around 3.3. In the present depositions, compressed air was used as the carrier gas and the spray rate was maintained 15 ml/min. The substrate temperature could be maintained to an accuracy of ± 5 K using a digital temperature controller. Finally, for achieving Cu_2ZnSnS_4 absorber layer, ZnS and Cu_2SnS_3 films were annealed in sulphur ambiance at a temperature of 763 K in the two-zone tubular quartz furnace.

Results and discussion: The CZTS films developed by two stage process are extremely adherent and uniform in nature.

Structural properties: The XRD pattern of spray deposited CTS films is shown in Figure 1. From XRD pattern, the films were found to be polycrystalline in nature with grains oriented along (112), (220)/(204) and (312)/(116) directions of tetragonal structure. The lattice parameters deduced from d-spacing were found to be a = 0.541 nm and c = 1.082 nm. These values are in good agreement with reported data [13]. In general, CTS films exhibit different phases like cubic (89-2877), tetragonal (89-4714), monoclinic (04-010-5719) and triclinic (27-0198), the respective 2θ values are 28.45°, 25.54°, 28.41° and 28.40°. However, the differences in 2θ values of these structures are very small (< 0.15°).

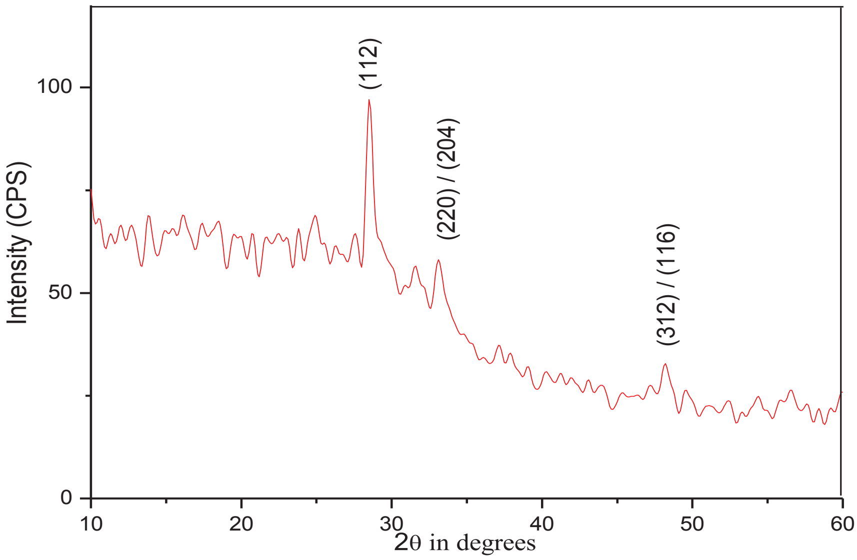

Figure1. XRD pattern of spray deposited CTS film

The micro-Raman spectrum of spray deposited CTS films indicates modes at 219, 286, 331 and 339 cm^{-1} is shown in Figure 2. The intense modes at 331, 339 cm^{-1} are attributed to tetragonal CTS phase [13, 14]. The mode corresponding to 286 cm^{-1} is attributed to monoclinic CTS phase. The low intense mode at 219 cm^{-1} is attributed to SnS_2 / Cu_3SnS_4. However, the peaks corresponding to SnS_2 / Cu_3SnS_4 were not observed in XRD pattern. XRD analysis of the deposited films confirmed the presence of tetragonal CTS phase.

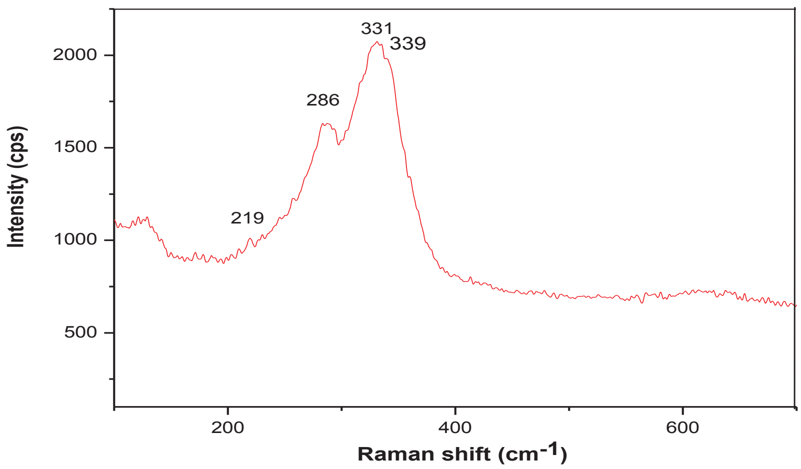

Figure 2.Micro-Raman spectra of spray deposited CTS film

From XRD studies, ZnS films were found to be polycrystalline in nature with grains oriented along (111) and (220) cubic structure. The lattice parameters are found to be a = b = c = 0.542 nm.

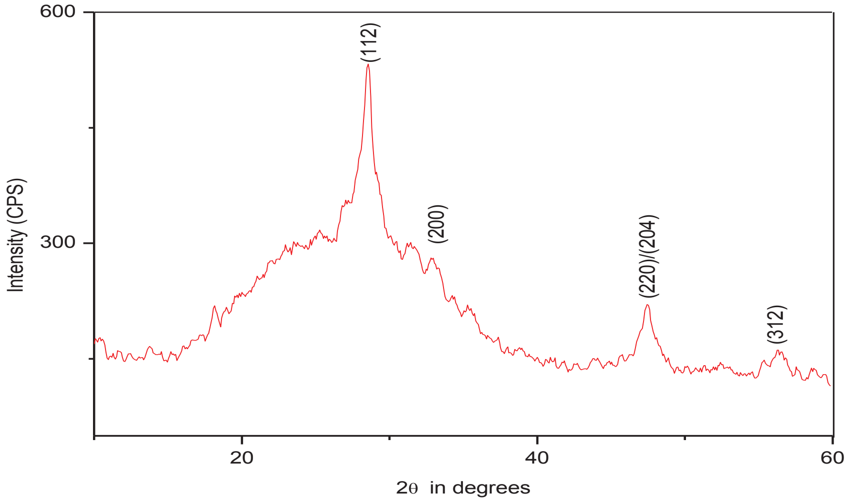

Figure 3. XRD pattern of CZTS film

The XRD pattern of CZTS films is shown in Figure 3. The XRD pattern of annealed CZTS films were found to be polycrystalline in nature oriented along (112) directions of kesterite structure. The films were seems to be single phase, since no peak corresponding to any secondary phases. The lattice parameters were found to be a = 0.543 nm and c = 1.086 nm, which are in good agreement with reported values [10, 11].

Optical properties: Figure 4shows the spectral transmittance (T) as a function of wavelength of ZnS film. The optical absorption coefficient (α) of these films is calculated using the simple relation [15]

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{t}$$

where 'T' is the spectral transmittance, 't' is thickness of film.

For direct optical transition between the parabolic bands, the dependence of optical absorption (α) on photon energy (hν) is given by the equation [15]

$$(\alpha h\nu) = A\,(h\nu - E_g)^{1/2}$$

where A is constant

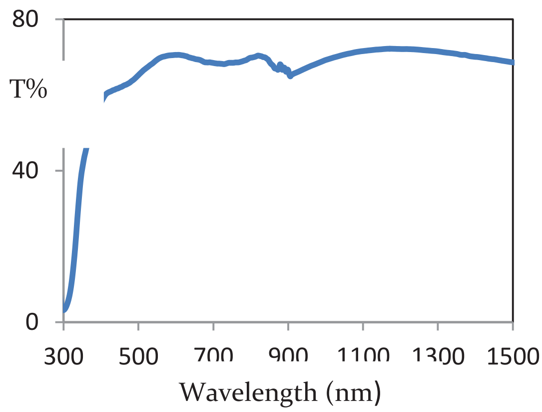

Figure 4. Spectral t ... posited ZnS film

The linear fit indicates that the optical transition is direct in nature. The band gap of the films is obtained by extrapolating the linear portion of plot onto hν-axis. The intercept on hν-axis gives band gap (E_g). The band gap of ZnS films was found to be 3.68 eV. The uncertainty in the determination of the band gap is ±0.02 eV. The band gap of C_2SnS_3 films was found to be 1.1 eV [14] and Cu_2ZnSnS_4 films was found to be 1.44 eV [11].

Conclusions: Single phase Cu_2ZnSnS_4 thin films were successfully deposited by chemical spray pyrolysis method. XRD pattern revealed that the films are polycrystalline in nature with Kesterite structure. The lattice parameters were found to be a = 0.543 nm and c = 1.086 nm. The optical band gap of the films was found to be 1.44 eV. The films were found to be p-type in nature.

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