Deposition of quaternary Cu_2ZnSnS_4 (CZTS) thin film by chemical bath deposition method for solar cell application

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The quaternary p-type semiconducting material, Cu_2ZnSnS_4 (CZTS), has been investigated extensively in solar cell studies because of its nontoxic constituent materials, low cost, suitable band gap and high absorption coefficient (10^4 cm^{-1}). In this present work, the thin film of CZTS (kesterite) was successfully deposited over glass substrate using the chemical bath deposition (CBD) method. The structural properties of the synthesized material were studied using X-Ray Diffraction (XRD). Scanning Electron Microscope (SEM) was used to obtain surface morphological information. UV-Visible spectrophotometer was employed to study the optical characteristics of the samples. Raman spectroscopy was used to determine the presence of any secondary phase impurities.

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1. Introduction

In chalcogenide thin film solar cell, Cadmium telluride (CdTe) and Chalcopyrite (CIGS) have become successful absorber layers with efficiency 12.5% and 19.6% respectively [1]. As the constituents of these compounds are either toxic or not abundant, an alternate absorber layer material, CZTS is gaining importance in this solar cell technology. The band gap of CZTS quaternary compound semiconductor is between 1.4eV to 1.5eV [2] and absorption coefficient is 10^4 cm^{-1}. Hence, it is suitable for absorber layer material in thin film solar cell. The cost of solar cell using CZTS technology is also low. The reported maximum efficiency for kesterite CZTS solar cell is 8.4% [3] and for CZTSe solar cell is 12.6% [4]. To deposit the CZTS layer, many physical processes such as sputtering [15], Pulsed Laser Deposition [11] etc. and chemical processes such as Successive Ionization Layer Adsorption and Reaction [14], Chemical Bath Deposition, sol-gel sulfurization [18] etc. have been proposed. The physical methods require vacuum chambers, high temperature, large power supplies and specially designed equipment. In comparison to physical methods, chemical deposition methods are more convenient, simpler, and more reliable, require low temperature processes, are non-hazardous and cost effective.

Seol J. et. al. synthesized the thin film of CZTS by magnetron sputtering. The coefficient of absorption of the film was 10^4 cm^{-1} and the band gap was 1.51eV with 112 crystal plane [15]. Shyju TS et al. deposited CZTS/CZTSe by mechanosynthesis process at 673K substrate temperature and obtained p-type single phase CZTS film and observed that the bandgap increases with the increase in substrate temperature [17]. Tanaki K et al. prepared CZTS thin film by sulfurizing sol-gel deposited precursor and annealing at 500ºC. The composition of CZTS layer was almost stoichiometric and it had a band gap of 1.49eV [18]. Moriya K et al. prepared film of CZTS by pulsed laser deposition and obtained a nearly stoichiometric film. The X-ray diffraction peaks of this film were at 112, 220 and 312. The direct bandgap energy of the film, annealed at 500^0C was 1.5eV [11]. Shinde N.M. et al. synthesized large area thin films of CZTS by chemical synthesis and annealing at 673K. In this synthesis process, tetragonal structure polycrystalline film of CZTS was obtained, with a band gap of 1.5eV [17].

In CZTS deposition by SILAR method, the cations and anions are not distributed uniformly on the substrate and so it is difficult to control its composition. M. P. Suryawanshi et al. prepared a polycrystalline structure of CZTS film, deposited by modified SILAR method, with an efficiency of 3.81% of photo electro chemical solar cell [5] and J. Henry et al. obtained poly crystalline kesterite structure of CZTS film using SILAR method [6]. To overcome the limitations of SILAR method, an alternative method Chemical bath deposition (CBD) can be used. Using CBD method for CZTS deposition, C. Gao et al. obtained solar cell efficiency of 4.5% [7]. The lack of crystallinity of the deposited film using CBD method limits its efficiency. The CBD method is simple and suitable for making large area solar cells. The cost of production is also low for CBD method. Hence extensive research is required to produce good quality CZTS film by CBD method. In CBD method, the required film thickness and and its composition are obtained by controlling the solution parameters: i) temperature, ii) concentration, iii) pH and iv) complexing agents. There is a peeling-off problem from the substrate when the second layer is deposited, which can be solved by controlling the pH level of the precursor.

2. Experimental

The thin film of CZTS was deposited by CBD method at room temperature. The soda lime glass slide was used as substrate. Analytical reagent grade of (0.2M) $CuSO_4$, (0.1M) $ZnSO_4$, (0.2M) $SnCl_2$ and (0.4M) CH_4N_2S precursors were used as it is, for the preparation of chemical bath. The first step was cleaning the glass slides using distilled water and detergent. Then the glass slides were boiled for 30 minutes in chromic acid (0.5M), followed by washing with double distilled water. After that, it was immersed in an ultrasonic bath for 30 minutes. Finally, acetone solution was used to degrease the glass slides before deposition. A good quality of Cu_2ZnSnS_4 thin films were obtained by varying the preparative parameters like concentration of the precursors, stabilizing agent and dipping time. The organic solvent used in the chemical bath was methanol. Monoethanol amine (MEA 0.6ml) was used to increase the salt solubility and stabilize the solution. The clean glass slide was immersed in the chemical bath for 60 minutes to make thin film of CZTS. The film was annealed for one hour at 350ºC in air.

3. Results and analysis

3.1. XRD analysis

The XRD patterns of the thin film of CZTS on glass substrate is shown in Fig. 1. The analysis reveals that the crystallinity of films improves after annealing, which results in narrow and sharper diffraction peaks of the thin films of CZTS. The annealed thin films of CZTS are polycrystalline and confirm the kesterite tetragonal (I-42m) crystal structure as the observed ‘d' values match with the standard values in the JCPDS reference (PDF#26-0575) and other outlined values [20]. From the X-ray diffraction pattern, the lattice parameters for tetragonal structure are observed. In the XRD pattern, the peaks are not visible for the as-deposited film. In the pattern for the annealed film, the peak intensity increases as the crystallinity of the film improves. Three major peaks appeared in the X-ray pattern. The first peak appears at 2θ= 28.51°and can be attributed to (112). The second at 2θ= 47.56°, attributed to (220). The third at 2θ= 56.25attributed to (312) planes of CZTS. To calculate the average crystallite size of the Cu_2ZnSnS_4 thin film Debye Scherer formula [$D= K\lambda/ (\beta \cos \theta)$] was used. In Debye Scherer formula, D is the crystallite size, λ, the X-ray wavelength, θ, the Bragg diffraction angle and β, the full width at half maximum (FWHM). The calculated average crystallite was found to be 53 nm. From the Debye Scherer calculation it is evident that the obtained lattice constants (a =5.433 Å and c = 10.854 Å) were in good agreement with the reported lattice parameters of JCPDS No. 00/26/0575(a=5.427 Å and c = 10.848 Å). The thickness of the film was measured and found to be 1.4µm.

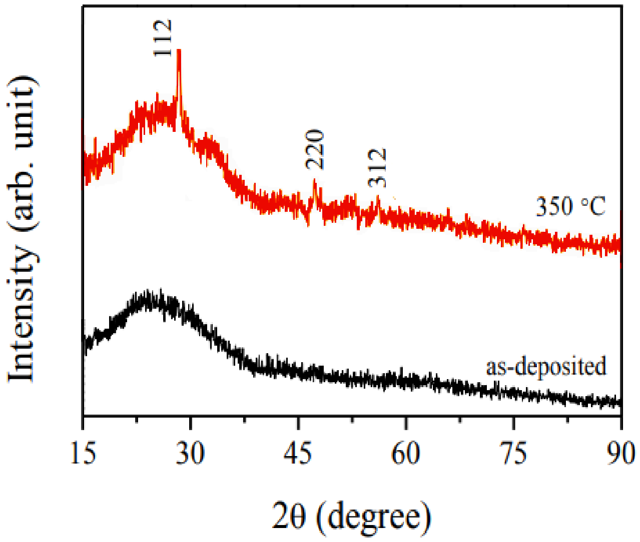

Fig. 1. XRD pattern for thin film of CZTS (color online)

3.2. Morphological studies

Scanning Electron Microscope (SEM) was used to study the morphological features of the thin film of CZTS fabricated through CBD method. The SEM micrographs of the as-deposited thin film is shown in Fig. 2a. It shows that the fabricated CZTS film over the glass substrate is covered fully and there are no cracks or holes. Figure 2(b) shows the formation of sub-micrometre crystallites over the surface in the sample after annealing, which is found with distinguished boundaries. Some holes that are present in some parts of the annealed CZTS film surface indicate the porosity and agglomerated particles. In the annealed CZTS film, as shown in Fig. 2a, the particles have a much larger size of 150nm.

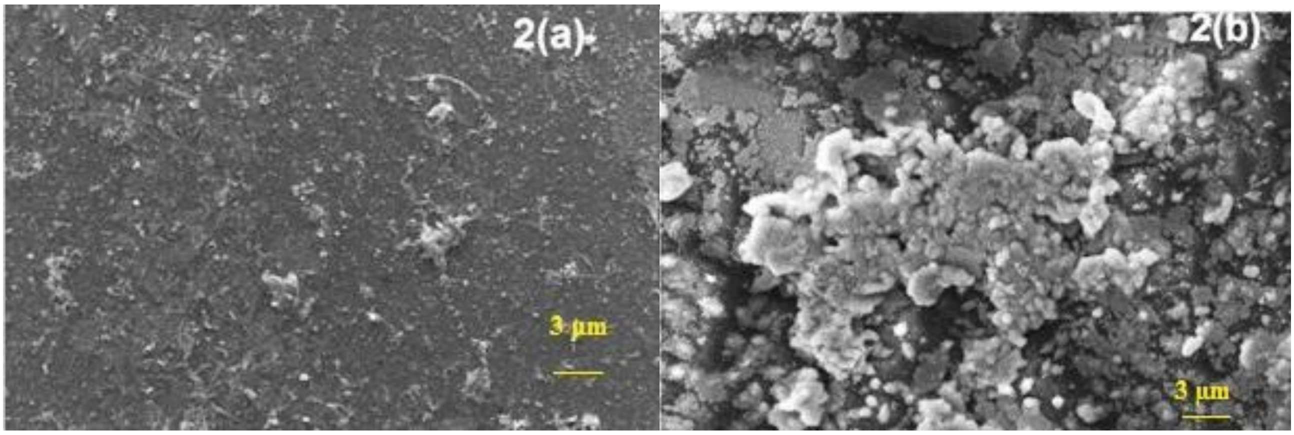

Fig. 2. SEM images for CZTS and annealed CZTS film (color online)

3.3. Optical properties

The absorption property of the CZTS film has been studied in this work. The UV-Visible absorption spectrum of the film is shown in Fig. 3. The absorption coefficient of CZTS is greater than $10^4 cm^{-1}$ in the visible region which is same as the value previously reported. The relation between absorbance and transmittance is given by,

$$A = \log [1/T] \quad (1)$$

or,

$$A = \log [I_o/I]) \quad (2)$$

Incident light is denoted by I_0 and transmitted light is denoted by I. The study of optical absorption of any particular material provides the information about the band structure of that material. For direct transition, the band gap (E_g) is related to absorption coefficient (α) by

$$\alpha h\nu = (h\nu - E_g)^{1/2}. \quad (3)$$

where Planck's constant is h, frequency of the incident light is ν and energy bandgap is E_g. To determine the band gap energy, Tauc's plot is used here in Fig. 4. where the photon energy(hν) is plotted along x-axis and $(\alpha h\nu)^2$ is plotted along y-axis. From the extrapolation to the x-axis, the direct bandgap of the annealed thin film of CZTS is found to be 1.69eV and the band gap for the as-deposited film is 1.6eV. This value is supports the previous reports [19]. The resulting bandgap value is suitable to the optimum bandgap essential for visible light absorption, and thus it is recommended that CZTS thin film may be used as the alternative candidate for visible light active photovoltaic applications. The optical absorption character of the material is an important property for making it a solar cell absorber. From Fig. 3 it is observed that the thin film of CZTS absorbs light with energy greater than 450 nm and provides the favourable basis of the photo absorption ability of the prepared CZTS film.

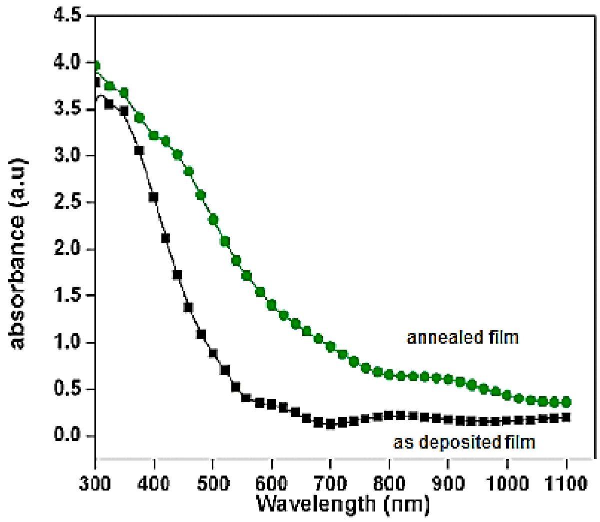

Fig. 3. Optical Absorption spectra for CZTS thin films (color online)

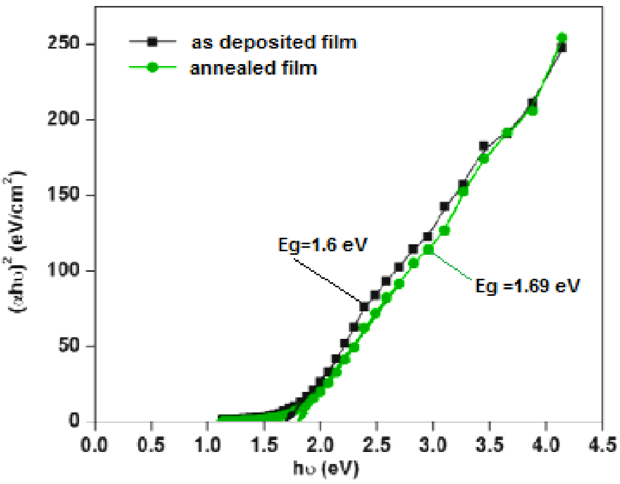

Fig. 4. Tauc's plot for CZTS thin films (color online)

3.4. Raman scattering

To find out the presence of any secondary phase in the CZTS film, the X-ray diffraction pattern is not sufficient because the lattice and other design parameters of cubic ZnS and tetragonal Cu_2SnS_3 are indistinguishable. To ensure that the thin film of CZTS contains only single phase and there are no secondary phases, Raman scattering has been used. The peaks in the Raman spectrum of CZTS film, as shown in Fig. 5, are compared with Lorentzian curves. There are two peaks one at 287.2 cm^{-1} and the other at 336.3 cm^{-1}. These two dominant peaks represent vibrational symmetry mode A of the film CZTS. The peak at 366.2 cm^{-1}represents symmetry mode B. The peaks for ZnS, if present, are to be at 350 cm^{-1} and 275 cm^{-1}. The peaks for Cu_2SnS_3, if present are to be at 304 cm^{-1} and 356 cm^{-1}. The peaks for Cu_2S, if present are to be at 476 cm^{-1}. Not all those peaks were noticed in the spectrum in Fig. 5. Thus, the spectrum suggests that there are no secondary phase impurities in the synthesized thin film of CZTS.

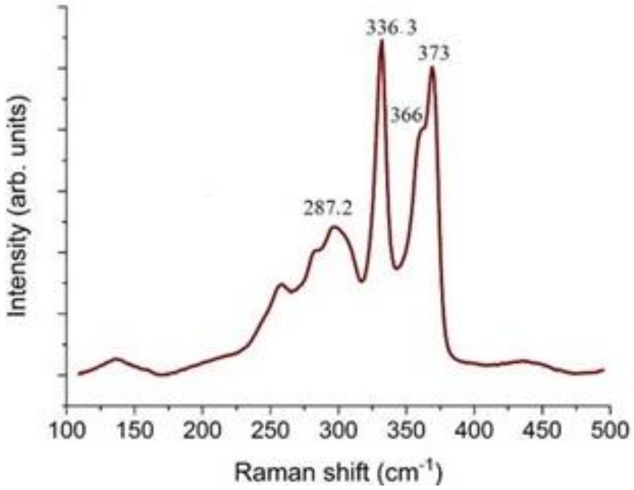

Fig. 5 Raman spectra for CZTS film (color online)

4. Conclusions

As per the above results, kesterite CZTS films without any secondary phase impurities can be deposited by CBD method. The analysis of XRD pattern of the film confirms that it consists of kesterite phase CZTS. The crystalline nature of the film has been increased by annealing at 350^0 C. The results have been compared with already reported work [20]. The morphology of the prepared CZTS films constituted of spherical structures, with average particle size of 150nm.The bandgap of annealed thin film of CZTS is 1.69 eV which is higher than as-deposited CZTS film. These results can greatly increase the photovoltaic efficiency of the CZTS thin film.

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