Synthesis of CZTS solar cell absorber material by chemical spray pyrolysis method

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***Abstract**:*

Thin films of Cu_2ZnSnS_4 (CZTS) is one of the most promising semiconductor materials for absorption layer in thin film solar cells because of its suitable optical band gap, cost-effective and eco-friendly nature. CZTS thin films were successfully deposited on soda lime glass substrates using spray pyrolysis and the effect of variation of substrate temperature on the structural and optoelectronic properties was investigated. The depositions were carried out on substrate temperature at 400^0C. The structural, optical, morphological and elemental composition of the deposited films were characterized by X- ray diffraction (XRD), UV-visible spectroscopy, Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive analysis of X-ray(EDAX). The powder X-Ray diffraction of the deposited thin films showed that the crystallinity was improved with increasing substrate temperature and it has a polycrystalline nature with (112), (220) and (312) phases. Optical band gap of the films had been studied using UV–Vis spectrometer and was found to be 1.95 eV which is close to the ideal band gap for highest theoretical conversion efficiency of solar cell

Keywords

Cu_2ZnSnS_4; Thin films; Spray pyrolysis; Substrate temperature; Solar cells

1. Introduction

The absorber $CuInS_2$ chalcopyrite semiconductors have proved to be successful candidates for photovoltaic (PV) applications. These cells exploit expensive and scarce elements like indium, which affect large scale production. In order to achieve the goal of cost-effective photovoltaic cell, it is necessary to search new materials like $Cu_2ZnSnSe_4$, Cu_2ZnSnS_4 and other quaternaries of these chalcopyrite-like semiconductors, which is obtained by replacing half of the indium atoms in chalcopyrite $CuInS_2$ with zinc and the other half with tin. The elements zinc and tin in these compound semiconductors are relatively costeffective and found in abundance compared to indium. Cu_2ZnSnS_4 (CZTS) thin film is one of the most promising materials for absorption layer in thin film solar cells because of the suitable band-gap energy of 1.9 eV, the large absorption coefficient over 10^4cm. Various techniques including both physical and chemical methods have been employed to prepare CZTS thin films. The physical methods including thermal evaporation [8], RF sputtering [9], pulsed laser deposition [10], atomic layer deposition [11] and these methods require expensive high vacuum systems for the deposition. The non-vacuum based chemical methods are chemical bath deposition [12], spray pyrolysis [13][18], chemical precipitation [14], sol-gel and solvothermal method [15-16]. Among these, spray pyrolysis is the most popular deposition method because simple, low cost, minimal waste product, ability to coat large surface area and easy to include in an industrial production line [17].

2. Experimental

2.1 Sample preparation

Thin films of CZTS were deposited on to the glass substrate using Spray pyrolysis technique. Glass substrates were cleaned by sonication for 15 min each in soap solution followed by dilute HCl and finally with double distilled water. After the cleaning process, the substrates were dried completely in air and placed on the plate to start the deposition process. The thin layers of CZTS are prepared from the precursor solution containing Copper chloride dehydrate (0.01M),Zinc acetate dehydrate (0.005M), Tin chloride dihydrate (0.005M) and thiourea (0.04M). The solution was kept for stirring for about 30 min to dissolvethe particles completely in order to obtain a clear solution. The obtained clear solution was used for the deposition of nanostructured CZTS thin films at a temperature of about 400°C and distance between the spray nozzles to the substrates was around 20-28cm.

2.2 Characterization Tools

The deposited CZTS thin films were characterized by powder X-ray diffraction (XRD, Rigaku) equipped with a Cu Kα -1.5406 Å radiation.To study the optical properties, UV-Visible spectroscopy using Perkin Elmer (Model Lambda 35) has been used to analyze. The surface morphology and the element composition of the obtained films were determined by Field Emission scanning electron microscope FESEM with EDAX.

3 RESULTS AND DISCUSSION

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3.1 Structural Analysis

The X-ray diffraction patterns of the CZTS films synthesized at various substrate temperatures are shown in Fig.1. The peaks located at 28.6, 47.1 and 56.4 corresponding to the (112), (220) and (312) orientation of CZTS could be attributed for the characteristic of kesterite (tetragonal system) structure [JCPDS card No: 26-0575]. The crystallinity of CZTS thin films was improved with increasing the substrate temperature.

The average crystallite size of the deposited film is calculated using the Debye Scherrer formula,

$$D = K\lambda/(\beta\cos\theta) \quad (1)$$

Where K is the Scherrer constant (K = 0.89), λ denotes the wavelength of used radiation Cu-Kα (λ = 1.5406 Å), β is the full width at half maximum of the diffraction peaks and θ is the Bragg's angle.Crystallite size of the films calculated using Scherrer formula. The crystallite size is 30 nm.

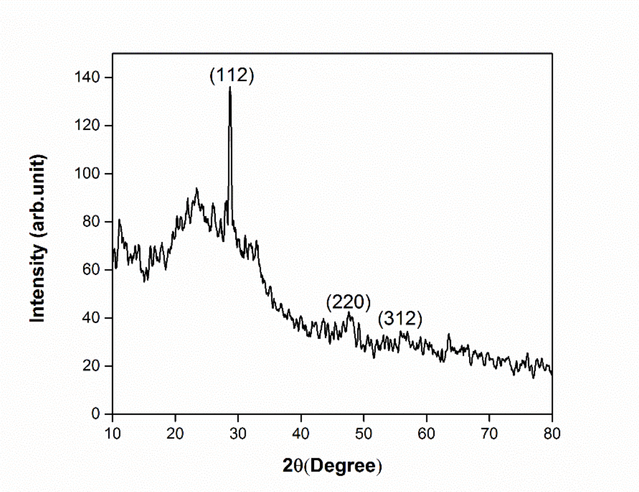

Fig. 1. XRD pattern of CZTS thin films

3.2 Optical Properties

The optical properties of the spray-deposited CZTS nanostructured thin films are studied by UV-Visible spectroscopy. Optical transmittance and absorption spectrum for the CZTS thin film on the glass substrate are measured in the range of 300-1100 nm. Fig.2 gives the transmittance spectrum of the deposited film. From the transmittance spectrum it is evident that the deposited film is having 50-60% transmittance in visible and near IR region. Absorption spectrum of ZnS thin films that are shown in Fig.3 clearly indicate that the material is having low absorption in the entire visible and near IR region.

The optical band gap is calculated using the formula,

$$\alpha h\nu = A[h\nu - E_g]^n \quad (2)$$

where α is the absorption coefficient, A is a constant, Eg is the band gap energy and n = ½ for direct allowed transitions. The band gap energy can be determined by extrapolating straight of the plot (α hν)^{2}verses hν that are shown in Fig.4. The band gap of the deposited nanostructured ZnS thin film is found to be 1.9 eV, having the wide direct band gap energy is suitable for electronic device applications.

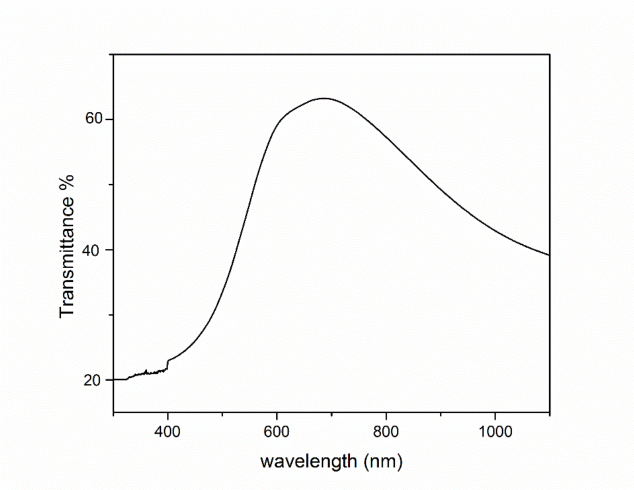

Fig.2. Transmittance spectrum

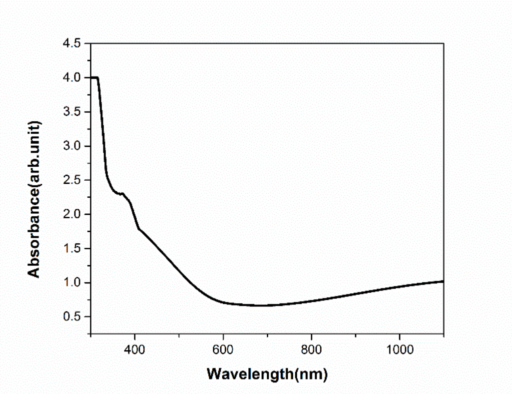

Fig.3. Absorption spectrum

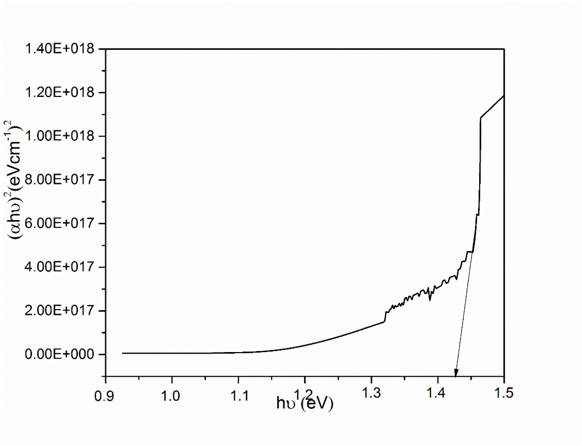

Fig.4. Tauc plot of the CZTS thin film

3.3 Field Emission Scanning Electron microscope

The surface morphology of the sample prepared at 400˚C temperature is studied using field emission scanning electron microscope (FESEM) are shown in Fig.5. From the images it is clear that the film is coated uniformly and there are no apparent cracks on the surface of the deposited film. The surface morphology of the deposited CZTS nanostructured thin films is composed of a large number of uniform sphere like particles.

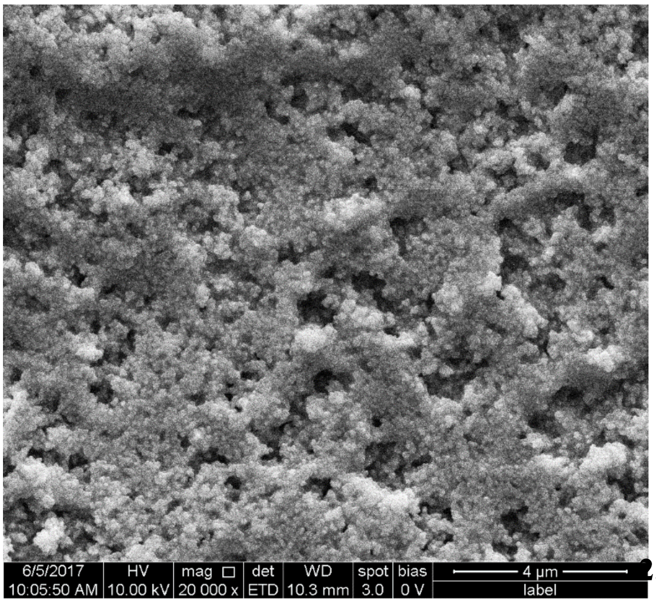

Fig.5. SEM image of the CZTS thin film

3.4. EDAX

Elemental composition of the deposited CZTS nano structured thin film is studied using EDS analysis and the equivalent pattern is shown in Fig. 6. EDS pattern clearly indicate that ZnS thin film consists of Cu, Zn, Sn, S and a small amount of the O atom. The presence of O element in the deposited film is due to the open aperture deposition and high temperature. The elemental percentage which are present in the prepared films are listed in the table

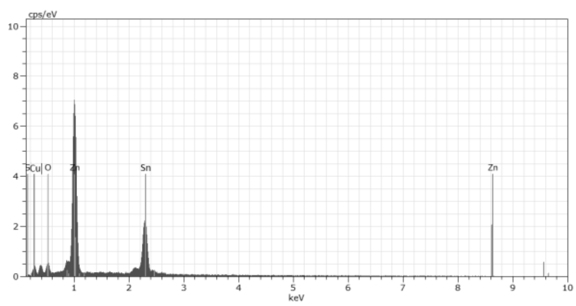

Fig.6. EDS pattern of CZTS thin films

El	C norm(wt.%)	Atom(at%)
Zn	24.01	24.25
S	22.05	23.62
Sn	20.0	22.02
Cu	28.22	17.98
O	5.72	12.13
Total	100	100

Conclusion

In this study CZTS thin films were successfully deposited on glass substrates by chemical spray pyrolysis technique**.** Copper chloride dihydrate, Zinc acetate dihydrate, Tin chloride dihydrate ,Thiourea used as a precursors. The X-ray diffractions spectra (XRD) indicate that all the films obtained are polycrystalline with a Kestrite structure with a preferred orientation along the 112, 220 and 312 direction. The crystallite size of the material is 30 nm. The band gap is determined for the CZTS thin film using uv-visible spectrometer. The band gap for the material is 1.90 eV. This CZTS thin films have good band gap energy and so this is good material to used as a photovoltaic cell. The CZTS solar cell energy conversion efficiency could be increased in the future.

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