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Synthesis and Characterization of Copper-Zinc-Tin-Sulfide (CZTS) Thin Film Absorber Layer for Solar Cell Application

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Abstract: Copper zinc tin sulfide (CZTS) thin film was synthesized on soda lime glass substrate by using spin coating method. The synthesized CZTS thin film showed maximum absorption coefficient of 0.193×10^4 cm^{-1} and maximum extinction coefficient of 0.011. The direct optical band gap, Urbach energy and steepness parameter of the synthesized CZTS thin film were 1.52 eV, 0.52 eV and 0.05 respectively. The CZTS thin film was found to be polycrystalline tetragonal in nature. The scanning electron microscopy (SEM) revealed that the texture structure was formed for the CZTS thin film.

Key words: CZTS, absorber layer, solar cell, spin coating deposition.

1. Introduction

A significant contribution will have to be made for world energy supplies by photovoltaic (PV) solar electric technology when feasible and proficient PV power products can be fabricated in large volumes at minimum cost. PV cost can be minimized by the use of thin-film technologies in which thin layers of photoactive materials are deposited on large-area substrates. The semiconductive absorber materials like copper–indium–gallium–selenide (CIGS) and cadmium telluride (CdTe) are two dominant candidates used for thin film solar cell technology. In the mentioned technologies, cadmium (Cd) and selenium (Se) are toxic whereas indium (In), gallium (Ga) and tellurium (Te) are not exorbitant in earth, which are the matter of conscious. Nevertheless, the non-toxicity and abundance of the elemental composition of copper-zinc-tin-sulfide (CZTS) makes it a very fascinating alternative of $Cu(In,Ga)Se_2$ (CIGS) and CdTe solar cells which suffer from the deficiency and toxicity of the elements. CZTS is reported to have a band gap of about 1.5 eV and an absorption coefficient of about 10^4 Cm^{-1} which makes it highly attractive as a solar cell material [1-3]. The CZTS absorber layers are prepared by various formation methods, such as thermal evaporation [4, 5], e-beam evaporation with a post sulfurization [6], sputtering [7-9], pulsed laser [10], electrochemical deposition [11-13] and spin coating methods [14].

Dhakal et al. [15] in 2014 synthesized CZTS thin films by sputtering method and obtained a band gap of nearly about 1.5 eV with solar cell efficiency of 6.2%.

Su et al. [16] showed in his article published in 2015 that the sol-gel prepared CZTS shows band gap of about 1.4 eV and cell efficiency of 9%.

In 2013 Swami et al. [17] published an article on showing the deposition of CZTS thin film by spin

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coating method getting a band gap of 1.5 eV and optical absorption coefficient of 10^4 cm^{-1}.

In 2015 Zhang et al. [18] showed the preparation of CZTS thin films via spin coating method.

In 2016 Yeh et al. [19] demonstrated the deposition of CZTS thin films by spin coating method. They showed the variation of optical band gap of CZTS with Cu/(Zn+Sn) ratio where the band gap ranges from about 1.7 eV to about 1.4 eV and also obtained the cell conversion efficiency of 1.13%.

In this study, we prepared CZTS thin film by using spin coating method. The structural, surface morphological and optical properties were determined.

2. Experimental

2.1 Preparation of CZTS Thin Film

Soda lime glass (SLG) was used as substrate. The SLG substrate was cleaned in an ultrasonic acetone bath for 20 min, and then rinsed with deionized water. Copper (II) chloride dihydrate (1.9 M), Zinc (II) chloride (1.17 M), Tin (II) chloride dihydrate (1 M), and Thiourea (3 M) were dissolved in deionized water having 40 vol.% ethanol. The solutions were stirred at 58 °C for 25 min and then coated on the SLG substrate at a speed of 2,000 revolution per minute (rpm) for 2 minutes. Then, the film was annealed at 280 °C for 30 min. The spin-coating and synthesizing processes were repeated 3 times to get favorable thickness of CZTS thin film.

2.2 Chacterization of CZTS Thin Film

The optical properties of the CZTS thin film were studied with the help of Ultraviolet-Visible Spectroscopy (UV-1601, UV-Vis spectrophotometer (Shimadzu Corporation, Japan) at Pilot Plant and Process Development Center (PP & PDC), BCSIR, Dhaka. The structural property of the thin film was studied using X-ray Diffractometer (BRUKER D8 XRD system with Cu-K_α radiation using the wavelength of 1.5406Å, operated at 40 kV and 40 mA, at PP & PDC, BCSIR, Dhaka. The surface morphological study of the formed film was performed by using Scanning Electron Microscopy (Analytical Scanning Electron Microscope, Model: JEOL JSM-6490LA, at IPD, BCSIR, Dhaka).

3. Experimental Results

3.1 Surface Property

Fig. 1 shows the surface morphology of the deposited CZTS thin film. It is seen that the texture structure is formed for this film.

3.2 Structural Property

The following Fig. 2 shows the X-Ray Diffraction (XRD) pattern of CZTS thin film.

The CZTS thin film is found to be polycrystalline in nature. The CZTS thin film shows the (112), (220) and (312) planes corresponding to 2θ values of about 28.437°, 47.302° and 56.094° respectively. This result is almost congruent with the previous studies [17-21]. This ensures that the polycrystalline tetragonal structure, that is CZTS, is formed.

3.3 Thickness

The thickness of the deposited CZTS thin film is found to be 6.2 μm.

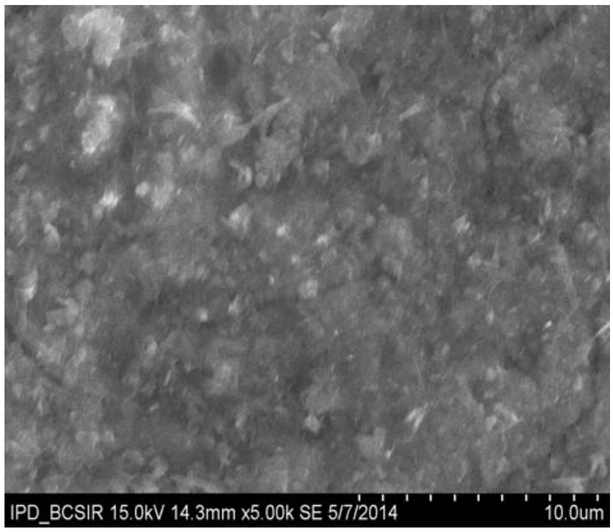

Fig. 1 SEM image of CZTS thin film.

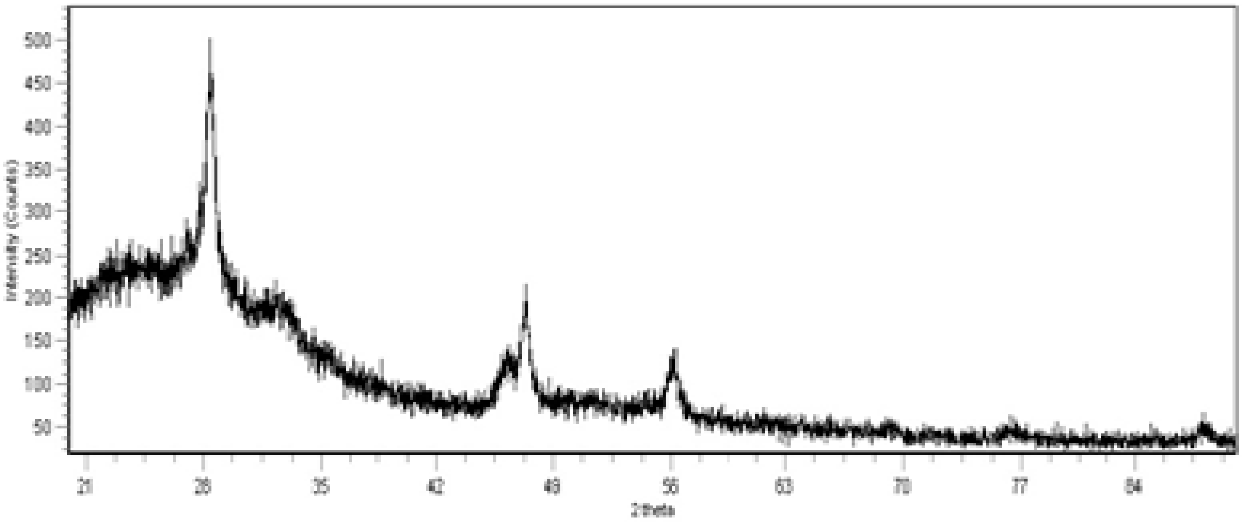

Fig. 2 X-ray diffraction pattern of CZTS thin film.

3.4 Optical Property

Fig. 3 represents the dependency of absorbance on wavelength (400-1,100 nm) for the CZTS thin film. The term absorption refers to the physical process of absorbing light, whereas, absorbance is a mathematical quantity which is often defined as,

$$A_\lambda = -\log_{10}(I_1/I_0) \quad (1)$$

where I_1 is the intensity of radiation (light) that has passed through the material (transmitted radiation), and I_0 is the intensity incident radiation.

Absorptance refers to the ratio of the absorbed radiation by a surface to that incident upon it. Total absorptance indicates absorptance measured over all wavelengths.

It is seen that the maximum absorbance is 0.5197 for the thin film in the visible region (400-700 nm) of the spectrum. The corresponding absorptance is 0.6978 and this means that the deposited CZTS thin film absorbs maximum 69.78% light of the incident radiation in the visible region of spectrum. In the infrared region of the spectrum, CZTS shows maximum absorbance of 0.4427 and the corresponding absorptance of 0.6392. This means that a maximum of 63.92% of the incident light is absorbed by CZTS thin film in the infrared region. The absorbance decreases with increase in wavelength in both the regions.

Fig. 4 represents the variation of transmittance, T

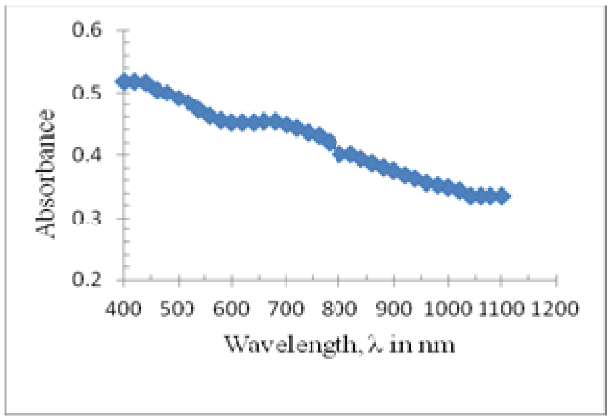

Fig. 3 Absorbance versus wavelength graph of CZTS thin film.

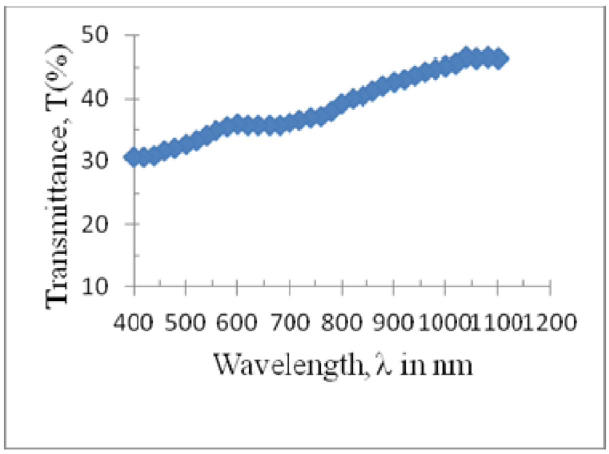

Fig. 4 Transmittance versus wavelength graph of CZTS thin film.

(%) with wavelength λ (nm) in the wavelength range 400-1,100 nm for the deposited CZTS thin film. Transmittance is the fraction of incident light (electromagnetic radiation) at a specified wavelength that transmits through a sample.

From Fig. 4, it is seen that the transmittance is low in the visible region and it increases with increase in wavelength from visible to infrared region.

Fig. 5 shows the relationship of absorption coefficient (α) of the prepared CZTS thin film with photon energy. The absorption coefficient indicates the distance into a material that can be penetrated by light of a definite wavelength prior to the absorption. The low absorption coefficient means the poor absorption and if the material is thin enough, it will appear transparent to that wavelength. The absorption coefficient depends on the material and also on the wavelength of the incident light. The absorption coefficient, α was calculated using the following formula [20, 21]

$$2.303A = \alpha d$$

$$\text{So, } \alpha = 2.303A/d \quad (2)$$

where, A is the absorbance and d is the thickness of the thin film.

The maximum value of absorption coefficient of the CZTS thin film is 0.193×10^4 cm^{-1}. This result is compatible with the previous result [1-3, 20, 21].

It is seen that the absorption coefficient is dependent on photon energy and it increases with increase in photon energy.

The extinction coefficient, K, can be calculated using the relation [20, 21],

$$K = \alpha\lambda/4\pi \quad (3)$$

where, λ is the wavelength and α is the absorption coefficient.

Extinction coefficient implies how strongly the absorption of light at a particular wavelength occurs in a material.

Fig. 6 demonstrates the variation of extinction coefficient with photon energy.

It is found that the extinction coefficient depends on photon energy and it decreases with increase in photon energy. The maximum value of extinction coefficient is 0.011. This behavior of extinction coefficient was shown by the previous studies [20, 21].

The band gap of the CZTS film was obtained using the relation [20, 21]

$$\alpha h\nu = B(h\nu - E_{opt})^n \quad (4)$$

where, $h\nu$ is the incident photon energy, h Planck constant, ν the frequency of incident radiation, B an energy independent constant, E_{opt} the optical band gap and n is an index depending on the type of optical transition caused by photon absorption. The index n equals ½ and 2 for allowed direct and indirect transitions respectively. Since CZTS is a direct band gap material, we used $n = 0.5$, i.e.,

$$\alpha h\nu = B(h\nu - E_{opt})^{0.5} \quad (5)$$

so,

$$(\alpha h\nu)^2 = B^2(h\nu - E_{opt}) \quad (6)$$

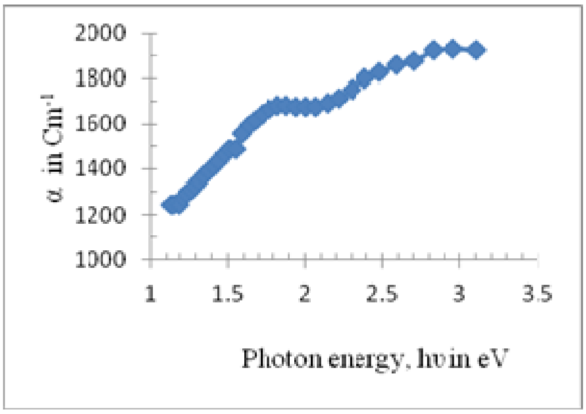

Fig. 5 Absorption coefficient (α) versus photon energy (hυ) graph of CZTS thin film.

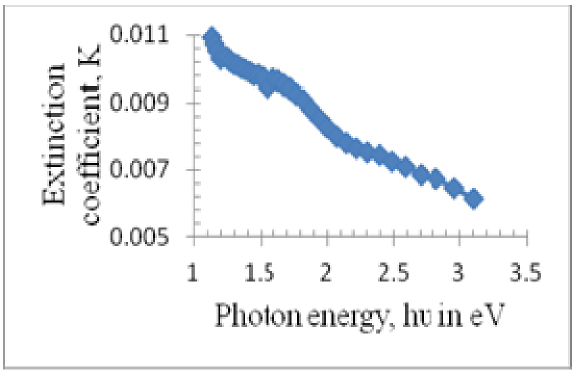

Fig. 6 Extinction coefficient (K) versus photon energy (hυ) graph of CZTS thin film.

Fig. 7 shows the variation of $(\alpha h\upsilon)^2$ with photon Energy, hυ of the CZTS thin film.

Extrapolating the straight line portion of the curve in energy axis gives the value of band gap energy as shown in Fig. 7.

The direct optical band gap of the prepared CZTS thin film is 1.52 eV, which is almost verified by the previous studies [1-3, 20, 21]. Band gap is very important for solar energy absorption. The photon only having energy equal or greater than the band gap energy of the film may excite an electron from the valence band to conduction band and then is absorbed in the film.

The urbach energy of the CZTS thin film was calculated using the formula [20, 21].

$$\alpha = \alpha_0 \exp(E/E_U) \quad (7)$$

where, α_0 is a constant, E is the photon energy hυ and E_U is the Urbach energy. Thus, the plots of lnα vs. hν will be linear whose slope gives the inverse of Urbach energy (E_U).

Urbach energy represents the crystalline quality of a material. It is mentionable that the low urbach energy indicates the better crystalline structure.

The lnα vs. hν plot for the CZTS thin film is shown in Fig. 8.

The inverse of slope of lnα versus hν graph is the urbach energy which is found to be 1.923 eV. It is observed that the urbach energy has an increasing trend with photon energy [20, 21].

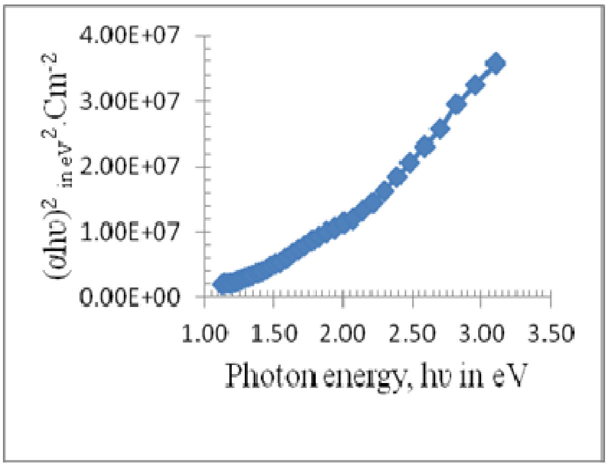

Fig. 7 $(\alpha h\upsilon)^2$ versus hν graph of CZTS thin film.

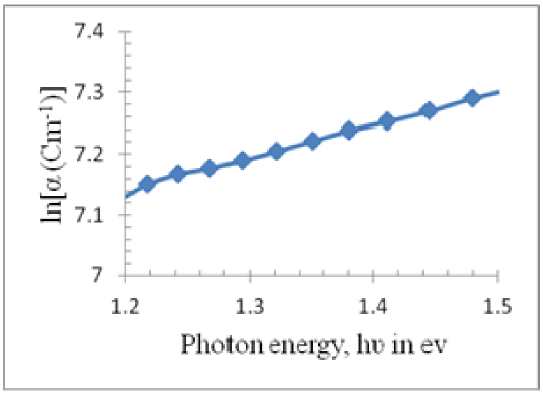

Fig. 8 lnα versus hν graph of CZTS thin film.

The steepness parameter, σ, measures the widenning of the optical absorption edge due to electron-phonon or exciton-phonon interactions, which can be calculated by the equation [22],

$$\sigma = kT/E_U \quad (8)$$

where, k is the Boltzmann constant, T is the absolute temperature and E_U is the Urbach energy. The value of σ is calculated by taking T as room temperature 298 K. The steepness parameter of the synthesized CZTS thin film is found to be 0.019.

4. Conclusions

Since CZTS thin film is used as an absorber layer in solar cell so its absorbance needs to be high as far as possible. The synthesized CZTS thin film has the maximum value of absorption coefficient of 0.193×10^4 cm^{-1}. In this respect the deposited CZTS thin film may be used as an absorber layer for solar cell applications. The band gap is one of the focused properties of the absorber layer. The optical band gap of the synthesized CZTS thin film is found to be 1.52 eV which is comparable to the solar energy spectrum. So the prepared CZTS thin films have the possibility of using as the efficient absorber layer in solar cell and this film can be prepared by spin coating technique.

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