Impact of Annealing Temperature on the Phase of CZTS with the Variation in Surface Morphological Changes and Extraction of Optical Bandgap

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Abstract. Quaternary CZTS (Cu\textsubscript{2}ZnSnS\textsubscript{4}) is an emerging alternative semiconductor material for solar cell technologies due to its earth abundance, low cost and non-toxic nature. In addition, CZTS has a direct band gap of ~1.5 eV which is the optimal value for converting the maximum amount of energy from the solar spectrum into electricity. The aim of the present study is to investigate the impacts of annealing temperature on the phase formation and morphological behavior of CZTS and material optical characteristics. X-ray Diffraction (XRD) reveals the single phase of kesterite CZTS that has been grown from the material precursors. Scanning electron microscope (SEM) shows the variation of morphological changes of CZTS with respect to annealing temperature. UV-Vis analysis confirms the optical band gap of 1.5 eV in the visible region which is suitable for photovoltaic applications.

Keywords: X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Ultraviolet-Visible absorption Spectroscopy (UV-Vis), Kesterite CZTS, Optical Bandgap

Introduction

Copper zinc tin sulfide (Cu\textsubscript{2}ZnSnS\textsubscript{4} called CZTS) emerged as an alternative material which is abundant, environmentally benign, and inexpensive with a high absorption coefficient (10\textsuperscript{4} cm\textsuperscript{-1}) with the suitable optical energy bandgap of 1.5eV which minimizes the quantity of material used in devices for thin film semiconductor solar cells [1]. These
advantages of CZTS make it a possible substitute of other thin film solar cells such as CdTe, CdSe, InP or GaAs which are having variety of concerns such as low abundance and high cost [2]. The quaternary kesterite CZTS, a competitive candidate for photovoltaic (PV) semiconductor material has its own challenge at its initial synthesis process because of simultaneous presence of secondary phases during its formation. The presence of secondary phases predicted to be the barriers for carriers, limits the exciton movement by formulating traps at interfacial layers that decreases the performance of PV cell which is not good for the prospective CZTS solar cell application [3-5]. Therefore the elimination of ternary Cu$_3$SnS$_4$ is a challenging task without affecting the objective phase CZTS in an ambient condition. So it is utmost important to remove these secondary phases from the kesterite CZTS material which could harm the optoelectronic properties such as optical energy band gap that characterizes the transition process of electrons within visible-near infrared region for PV applications [8]. To avoid secondary phases various study have been reported about the widely used post annealing process to get proper CZTS phase in both vacuum and non-vacuum deposition technique[2]. Post annealing process plays an intensive major role to enhance the crystallinity as well the single kesterite phase of CZTS. But the secondary phases are also the inevitable during the annealing ambient condition and have the close tendency to temperature changes. Weber et al. have reported that the copper sulfides and zinc sulfides are formed due to the CZTS phase decomposes at temperatures above 350 °C [6]. Morphological evidence like nano flower shaped two dimensional secondary phases of Cu$_3$SnS$_4$ has been reported by Yang et al which is difficult to exclude from the objective CZTS phase [7]. So it needs to suppress the undesired secondary phase formation near to the quaternary CZTS semiconductor with the ramping up annealing temperature but with a careful and controlled manner. The degree of temperature variation in the ambient condition has proportionate effect for the elimination of secondary phases. This study explores that the kesterite CZTS could be grown in single phase with the impact of annealing temperature with the evidence of no secondary phase formation; which could enhance the performance of the cell. A generalized photovoltaic device structure of CZTS is shown in Fig 1.

![Figure 1. Generalized photovoltaic device structure of CZTS](image-url)
Experimental Details

Synthesis of CZTS material

The proposed work delivers an alternative route for removal of secondary phases by the impact of annealing temperatures that are synthesized by the compatible non-toxic and low cost subsequent solution process which adds a beneficiary progress in the current state of art technology for single phase kesterite CZTS (Cu$_2$ZnSnS$_4$). A schematic representation of CZTS (Cu$_2$ZnSnS$_4$) preparation is shown in Figure 2. The solution is prepared using Cu, Zn, Sn precursors and Sulphur content solutions. The final solution is subjected for stirring with ethanol for 30 minutes at room temperature. The collected product then annealed at three different temperatures (i.e. 350 °C, 375 °C, 400 °C) which is performed by a tubular furnace at working pressure of 0.05 milibar with argon as carrier gas for 1 hour.

![Diagram of CZTS synthesis](image)

Figure 2. Synthesis of single phase of kesterite CZTS (Cu$_2$ZnSnS$_4$) semiconductor material

Characterization techniques

Phase analysis has been characterized by X-ray-diffraction (XRD) technique with CuKα radiation (λ=0.15406nm) by using Rgakujapan/Ultima-IV model X-ray diffractometer. Surface morphologies have been studied by using scanning electron microscopy (JEOLJSM-6084LV) resolution: 3.0nm (ACC V 30 Kv, working distance 8mm). Optical
properties were investigated by studying the absorbance spectra recorded by UV-Vis-NIR spectrophotometer (Shimadzu/model 3600).

Results and Discussion

XRD (X-ray-Diffraction) analysis

The annealed CZTS at 350 °C, in argon atmosphere at working pressure of 0.05 milibar for 1 hour has been characterized by XRD and is shown in Figure 3(a). The peaks have been analyzed using Joint Committee on Power Diffraction Standards data (JCPDS 26-0575). The result displays the spectra from 2θ = 20 - 70° in which strong peaks of CZTS at 29.02°, 33.01°, 47.45°, 56.83°, 69.40° corresponds to the tetragonal CZTS crystal planes (112), (200), (220), (312), (008).

![Figure 3. Powder XRD patterns of annealed CZTS (Cu2ZnSnS4) semiconductor material at (a) 350 °C, (b) 375 °C and (c) 400 °C annealing temperatures](image)

In association with the main CZTS characteristics peaks, secondary phases Sn S2 at 33.02°, SnS at 45.80° (JCPDS-83-1707), SnS at 37.27°, 39.81°, 51.8°, 56.36°, 58.39° (212), (2012), (2018), (3212), (406) are also observed. Though the increased in annealing temperature to 375°C keeping the duration of period constant resulted partial elimination of secondary phases, but still presence of a few secondary phases in CZTS is reflected from the XRD pattern as shown in Fig 3(b). However, complete elimination of secondary phases are observed in CZTs when it is annealed at 400 °C (Fig 3(c)). The peaks 29.04°, 33.50°, 47.97°, 56.75°, 69.42°
correspond to the planes (1 1 2), (0 0 2), (2 2 0), (3 1 2), and (0 0 8) infer to a single phase of kesterite CZTS structure. Peak broadening in the XRD of CZTS as a result of annealing temperatures from 350 °C to 400 °C reveals decrease in crystalline size. The formation of single phase CZTS with increased annealing temperature could be attributed to the diffusion of binary sulfides to maintain appropriate distance for improved density [9]. A negligibly shifts of XRD peak of CZTS annealed at 400 °C towards the right side might be due to the compressive stress and the pronounced antisite defect complexes presence inside the CZTS material with a low level Cu/Zn disorder [10].

**SEM (scanning electron microscope) analysis**

![SEM image of CZTS (Cu₂ZnSnS₄) annealed at 350 °C full of Nano flower like structure](image)

Figure 4. SEM image of CZTS (Cu₂ZnSnS₄) annealed at 350 °C full of Nano flower like structure

SEM micrographs of CZTS at different annealing temperature are shown in the Figure 4 - 6. It is observed from the SEM images (Fig.4) that the formation of flower like nanostructures might be due to the presence of predominant secondary phase Cu₃SnS₄ along with CZTS annealed at 350 °C [7]. The observed less flower like structures in the SEM micrograph (Fig.5) of CZTS annealed at 375 °C might be due to the partial elimination of secondary phases Cu₃SnS₄ along with other phase such as SnS and/or SnS₂ which has been observed in XRD [7]. Disappearance of flower like structures is seen when the CZTS is annealed at 400 °C as shown in SEM micrograph (Fig.6) suggesting complete removal of secondary phases supported by XRD result.
Figure 5. SEM image of CZTS (Cu$_2$ZnSnS$_4$) annealed at 375 °C with less Nano flower like structure and formation of less amount of euhedral blocky shaped structure.

Figure 6. SEM image of CZTS (Cu$_2$ZnSnS$_4$) annealed at 400 °C Nano flower structure completely disappears and all structures are changed to crystalline euhedral blocky shaped structure.

**UV-Vis Absorption Spectroscopy**

Due to the influence of particle composition at high annealing temperature the bandgap changes from 1.37 eV to 1.45 eV with CZTS morphology from, which further provides evidence that the annealing temperature strongly affect the CZTS properties [1]. Absorption spectrum of CZTS (Cu$_2$ZnSnS$_4$) annealed at 400 °C is measured using UV-Vis NIR range. The absorption spectrum appears from 300 nm to 1000 nm at room
temperature. Since the optical absorption coefficient is related to the optical energy band gap $E_g$ near the absorption edge that could be determined by the Tauc’s formula [1]:

$$
\alpha = \frac{A(h\nu-E_g)^n}{h\nu}
$$

(1)

where, $A$ is an energy-independent constant, $h$ is the Planck’s constant, $\nu$ is frequency, and $n$ is an index that characterizes the transition process and is theoretically equal to 2 and $\frac{1}{2}$ for indirect and direct allowed transitions for indirect band gap and direct bandgap semiconductors, respectively.

Figure 7. UV-vis absorption spectra of single phase kesterite CZTS annealed at 400 °C with good crystallinity without any secondary phases

Extrapolation of the straight line to zero absorption coefficient ($\alpha = 0$) allows estimation of $E_g$. The band gap of single phase kesterite CZTS annealed at 400 °C are estimated to be around 1.52 eV by extrapolating the linear region of curve to intercept of photon energy as shown in the inset of the Figure 7. The straight line fit that yields $E_g = 1.5$ eV for the exponent $n=2$ in Tauc’s formula reveals that the prepared single phase kesterite CZTS is a direct bandgap semiconductor [1].

**Conclusion**

The quaternary CZTS ($\text{Cu}_2\text{ZnSnS}_4$) compound semiconductor material powder has been synthesized at room temperature by solution method taking copper, zinc chloride, Tin and Thiourea at a required molar concentration ratio ($\text{Cu}$: $\text{Zn}$: $\text{Sn}$: $\text{S}$). XRD characterization resembled with JCPDS number (26-0575) confirmed the kesterite phase of CZTS ($\text{Cu}_2\text{ZnSnS}_4$). Our method of increased annealing temperature has
significant positive impact on removal of secondary phases and achieved single phase kesterite CZTS at annealing temperature 400 °C. The surface morphology of CZTS material attributed to subjective changes with good crystallinity. In conclusion we have demonstrated a low cost promising state of art to yield single phase kesterite CZTS (Cu₂ZnSnS₄).

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