Effect of 6 MeV electron Irradiation on Nano-Cu₂ZnSnS₄

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Effect of 6 MeV electron Irradiation on Nano-Cu₂ZnSnS₄

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Abstract

Microwave synthesized nano sized Cu₂ZnSnS₄ (CZTS) powder was irradiated with 6 MeV electrons, to investigate stability under radiation. The structural, optical, vibrational and morphological properties were explored using X-ray diffraction, UV-Visible spectroscopy, Raman spectroscopy and Scanning Electron Microscope (SEM). The irradiated sample shows significant change in properties when compared to the pristine sample. X ray peak broadening analysis has been used to estimate the crystallite size and lattice strain. Raman spectroscopy analysis confirms the transition of ordered kesterite to disordered kesterite phase after electron irradiation at electron fluence of $4 \times 10^{15} \text{ e}^-/\text{cm}^2$. CZTS nano-particles having hierarchical flower like morphology starts agglomerating after electron irradiation as observed from SEM images. The sample did not amorphize upto the highest fluence $4 \times 10^{15} \text{ e}^-/\text{cm}^2$ employed in this study.

Keywords: Cu₂ZnSnS₄, Electron Irradiation, XRD, UV, Raman spectroscopy, SEM.

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1 Introduction

All the spacecrafts and satellites use photovoltaic solar cell power in space as an energy source [1]. For many decades in conventional spacecrafts Si [2-5], multi junction solar cell [6-9] and GaAs/Ga are used [10-13] which provide high efficiency and are also quite robust to space environment. Researchers are trying to replace it with an alternate. Photovoltaic thin film solar cell array which offers high reliability, lower production cost, proven manufacturing and scalability of required power levels have been shown as useful for space mission [14]. The report from M. R. Reddy suggests that conventional solar cell can be replaceable with flexible thin film solar cell array of CIGS based solar cell which reduces not only mass but also lowers the cost by ~30% compared to the conventional space solar cell [15].

One of the most important necessities of space solar cell is the ability to withstand harsh space radiation environment. The energetic particles in space environments such as proton, electron, gamma etc. cause lattice damage in an active area of solar cell which degrades the performance of the solar cell used as a power sources in space satellite [10-16]. This puts a limit on the use of solar cell for longer duration. Therefore, the stability of material which is used for making the solar cell for space application is very important. A study by Jasenek et al., shows that CuInGaSe₂ (CIGS) solar cell can tolerate more than 10 times larger fluence of high energy electrons than any other solar cell [17]. This study was further strengthened by Karsten Otte et al., which reported that flexible CIGS thin film solar cells are superior to that of GaAs with respect to radiation hardness [18]. However, indium and gallium are rare earth metals, due to which cost of solar cell is high. Therefore, the necessity of alternative material to CIGS is needed which can stand harsh radiation environment.

Very recently Sauli et al., reported that after gamma irradiation the structural and optical properties of Cu₂ZnSnS₄ (abbreviated as CZTS hereafter) thin films improves, making them favourable in order to use them in outer space where gamma radiation is abundant [19]. In another study, Sugiyama et al. reported effect of electron and proton irradiation on CZTS solar cell. In their study they reported the effect of electron irradiation using constant energy of 2 MeV and the fluence was varied from $1 \times 10^{14} \text{ e}^-/\text{cm}^2$ to $2 \times 10^{17} \text{ e}^-/\text{cm}^2$, while for proton irradiation, the energy was kept 380 keV from a 400 KV ion implanter with fluence ranging from 1×10^{12} to $3 \times 10^{16} \text{ cm}^{-2}$. They claimed CZTS solar cell performance improves up to small amount for both electron and proton irradiations, which shows that CZTS solar cell tolerates electron and proton irradiation analogous to CIGS solar cell [20]. Similar study was also done by Suvanam et al., where thin films of Cu₂ZnSnS₄/Se₄ (CZTSSe) and CZTS were investigated after 3 MeV proton irradiation; it showed that CZTSSe and CZTS are high radiation hardened materials compared to CIGS solar cell [21]. In continuation with these studies, we have carried out an experimental study in which our objective was to explore the effect of 6 MeV electron irradiation on CZTS nano-flower like structures. Further we carried out detailed analysis using micro-Raman spectroscopy to investigate how the structure changes or modifies upon irradiation. There are no reports available on structural transition of CZTS due to electron irradiation. Earlier Parkin et. al. reported, how the presence of electron beam induces sulphur vacancies in monolayer of MoS₂ and Raman spectroscopy was used as non-destructive method to estimate defect concentration in MoS₂[22].

In our study we report 6 MeV electron irradiation induced changes on nano-crystalline CZTS (size ~14.4nm). The structural, vibrational, optical and morphological properties were studied using X- ray diffraction,

Raman spectroscopy, UV visible spectroscopy and Scanning Electron Microscope (SEM).

2 Materials and Methods

One step Microwave assisted synthesis method was used to synthesize the material as mentioned in previous reports[23-24] with a slight modification that instead of cyclic microwave irradiation, single step microwave irradiation was carried out. In a typical synthesis process, all the required precursors were taken in an appropriate concentration and exposed to microwaves for 10 min. After that, the precipitate was washed with ethanol, centrifuged and dried to get the final $\text{Cu}_2\text{ZnSnS}_4$ nano-powder. Indigenously developed Race-Track Microtron accelerator having 6 MeV energy electron beam with faraday cup attached to a counter (1count= 10^{11} electrons) was used [25] for irradiation. To determine crystal structure and crystallite size of the sample X-ray diffractometer D8 Advance BRUKER AXS was used with Cu $K\alpha$ ray of wavelength 1.54 Å. Optical absorption measurements were done using JASCO V 670, UV Visible spectrometer. For simplicity throughout the text we are representing pristine CZTS (without irradiation) sample as A1 and 6 MeV electron irradiated with fluence $1 \times 10^{15} \text{ e}^-/\text{cm}^2$, $2 \times 10^{15} \text{ e}^-/\text{cm}^2$, $3 \times 10^{15} \text{ e}^-/\text{cm}^2$ and $4 \times 10^{15} \text{ e}^-/\text{cm}^2$ as A2, A3, A4 and A5 respectively.

Laboratory based X-Ray Diffractometer is not sufficient to differentiate the two forms of CZTS crystal structures [26,27]. To identify various impurity phases, quantifying disorder and also to estimate the quality of crystallinity in this class of compounds Raman spectroscopy is particularly used. Renishaw Raman spectrometer was used in backscattering configuration at the excitation wavelength of 532 nm for Raman spectroscopy measurements. For Raman spectra analysis, Lorentzian function was used to fit Raman spectra to determine mode frequencies, area under the curve, FWHM and integrated intensity. Fitting was carried out with the minimum number of peaks which provides peak position, FWHM and integrated intensity. The same standard procedure is followed for the data for all electron irradiated samples.

3 Results and Discussion

Figure 1 shows X-ray diffraction pattern of pristine nano- $\text{Cu}_2\text{ZnSnS}_4$ (A1) and nano- $\text{Cu}_2\text{ZnSnS}_4$ irradiated at different electron fluences $1 \times 10^{15} \text{ e}^-/\text{cm}^2$ (A2), $2 \times 10^{15} \text{ e}^-/\text{cm}^2$ (A3), $3 \times 10^{15} \text{ e}^-/\text{cm}^2$ (A4) and $4 \times 10^{15} \text{ e}^-/\text{cm}^2$ (A5). The broad peaks occurring at 28.4° , 47.6° and 56.5° are indexed to (112), (220) and (312) planes which are signature peaks of kesterite phase CZTS and are very well matched with JCPDS card no. 26-0575. The X-ray diffraction (XRD) pattern does not show any extra peak in pristine nano- $\text{Cu}_2\text{ZnSnS}_4$ which in general suggests the absence of impurity phases. Further, it is observed after irradiation there is a decrease in peak intensities revealing that the crystallinity is decreasing with increase in electron fluence. Moreover, we can clearly observe that up to fluence of $3 \times 10^{15} \text{ e}^-/\text{cm}^2$ the XRD pattern remains same, but at a fluence of $4 \times 10^{15} \text{ e}^-/\text{cm}^2$ the intensity of peak at 56.5° for (312) plane completely vanished and new peaks appear at 57.9° and 62.9° . The new peaks may be attributed to the secondary phase formation or disorder arising due to the effect of electron irradiation. An important observation is that the sample did not amorphize up to the highest fluence applied. This indicates radiation stability of CZTS and is significant in the context of its application as a solar cell material in space. Voigt function was used to fit X-ray diffraction patterns. To calculate crystallite size and strain on $\text{Cu}_2\text{ZnSnS}_4$ we have used Williamson-Hall method. Total Peak broadening β_T is caused by crystallite

size broadening β_D and micro strain broadening β_ε of the crystallite.

$$\beta_T = \beta_D + \beta_\varepsilon \quad (1)$$

From Scherrer equation we know that,

$$\beta_D = \frac{K\lambda}{D \cos \theta} \quad (2)$$

Where θ is the diffraction angle, λ is the wavelength of X-ray (1.54 Å), D is the crystallite size and K (0.9) is shape factor.

Similarly, the X-ray diffraction peak broadening due to strain is given by,

$$\beta_\varepsilon = 4\varepsilon \tan \theta \quad (3)$$

where, β_ε is the broadening due to strain, ε is the micro strain and θ is the diffraction angle.

Putting equation (2) and (3) in (1) we get,

$$\beta_T = \frac{K\lambda}{D \cos \theta} + 4\varepsilon \tan \theta \quad (4)$$

Rearranging above equation we get

$$\beta_T \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \quad (5)$$

Equation 5 represents Uniform Deformation Model (UDM) where it was predicted strain is uniform in all crystallographic directions [28]. $\beta_T \cos \theta$ is plotted as a function of $4 \sin \theta$ for peaks of $\text{Cu}_2\text{ZnSnS}_4$. Strain (ε) is estimated from slope of the fit, and crystallite size D is estimated from the Y intercept of the fit.

Figure 2 represents Williamson-Hall Plot of (a) pristine $\text{Cu}_2\text{ZnSnS}_4$ and (b) $\text{Cu}_2\text{ZnSnS}_4$ sample irradiated with 6 MeV electron at $3 \times 10^{15} \text{ e}^-/\text{cm}^2$ electron fluence. The crystallite size of pristine $\text{Cu}_2\text{ZnSnS}_4$ is estimated to be 14.4 nm and upon irradiation the average crystallite sizes of A2, A3, A4 and A5 samples are obtained to be around 13.6 nm, 13.2 nm, 12.3 nm and 10.8 nm which is also represented in Figure 3. Here we can clearly see crystallite size decreases with electron fluence. Figure 4 shows strain due to electron irradiation on $\text{Cu}_2\text{ZnSnS}_4$. We can clearly see that change in strain on $\text{Cu}_2\text{ZnSnS}_4$ with electron irradiation is marginal. Figure 5 shows peak position as a function of electron fluence which clearly indicates there is no change in peak position due to electron fluence, whereas area under the curve (integrated intensity) is decreasing for (112), (220) and (312) planes with increase in electron fluence. Considering pristine sample intensity as 100 % for (112) peak intensity decreases to ~ 30%, for (220) peak intensity decreases to ~ 26% and for (312) it decreases to ~ 16% for the $4 \times 10^{15} \text{ e}^-/\text{cm}^2$ electron fluence as shown in Figure 6, indicating decrease in crystallinity as decrease in XRD peak intensity generally implies decrease in crystallinity [29]. Figure 7 shows UV absorption spectra of pristine and electron irradiated samples of $\text{Cu}_2\text{ZnSnS}_4$ and the corresponding Tauc's plot is shown in Figure 8. The band gap energy was calculated from the absorption spectra by extrapolating the linear portion of the graph of $(\alpha h\nu)^{1/2}$ as a function of $(h\nu)$ to the energy axis using Tauc's relation. The band gap of pristine sample i. e. A1 is 1.5 eV and for A2, A3, A4 and A5 band gap goes on increasing to 1.57 eV, 2.13 eV, 2.83 and

3.95 eV. Therefore, with increase in electron fluence, the band gap goes on increasing. Such a vast change in a band gap cannot be attributed to the change in particle size and we believe that this could be due to decrease in crystallinity of $\text{Cu}_2\text{ZnSnS}_4$ because of electron irradiation.

Figure 9 shows Raman spectra of CZTS for pristine and irradiated samples. Bands at 280 cm^{-1} and 331 cm^{-1} are the signature peaks of nano $\text{Cu}_2\text{ZnSnS}_4$ [30-32]. From figure 9 we can clearly observe that up to $2 \times 10^{15}\text{ e}^-/\text{cm}^2$ Raman mode frequencies of $\text{Cu}_2\text{ZnSnS}_4$ are stable, while for further irradiation at $4 \times 10^{15}\text{ e}^-/\text{cm}^2$ the relative intensity of band at 280 cm^{-1} increases compared to 331 cm^{-1} mode. Our earlier high temperature study on nano-CZTS indicated that beyond 550 K there is a considerable variation in relative intensities of 280 cm^{-1} mode and 331 cm^{-1} Raman mode frequencies indicating phase transition from ordered kesterite to disordered kesterite structure[33]. The transition that occurs at higher irradiation dose is exactly same as transition at high temperature. Figure 10 shows electron fluence dependence of Raman mode frequencies of nano-CZTS. Here, we see that Raman mode at 331 cm^{-1} is stable with increase in electron fluence, while Raman mode frequency of the 280 cm^{-1} mode decreases marginally with electron fluence. Electron irradiation dependent FWHM of Raman mode frequencies of nano-CZTS is plotted in Figure 11. It shows that the width of mode at 280 cm^{-1} increases with electron fluence, but width of 331 cm^{-1} is stable which shows irrespective of the electron fluence the strongest mode of CZTS is stable. Intensity ratio of mode at 280 cm^{-1} to mode at 331 cm^{-1} is plotted in Figure 12, which shows a clear increase beyond $4 \times 10^{15}\text{ e}^-/\text{cm}^2$, indicating a phase transition to a disordered kesterite phase.

The SEM images of CZTS before irradiation are shown in Figure 13(a); it consists of hierarchical flower like morphology having around $1\text{ }\mu\text{m}$ particle size clearly visible in magnified image fig 13(b). Figure 13(c) shows SEM images after different irradiation. We can clearly see for $1 \times 10^{15}\text{ e}^-/\text{cm}^2$ there is no change in morphology but beyond this, particles start agglomerating and become irregular. For $4 \times 10^{15}\text{ e}^-/\text{cm}^2$ irradiation fluence, the morphology is completely changed as shown in SEM image in Figure 13 (d).

4 Conclusions

In conclusion, the effect of electron irradiation on $\text{Cu}_2\text{ZnSnS}_4$ was investigated, to explore its radiation stability. The samples were characterized for their structural, optical, vibrational and morphological properties using X ray diffraction, UV visible spectroscopy, Raman spectroscopy and Scanning Electron Microscope (SEM). Results reveal phase transition from ordered kesterite to disordered kesterite for $4 \times 10^{15}\text{ e}^-/\text{cm}^2$ irradiation fluence. The XRD shows decrease in crystallite size from 14.4 nm to 10.8 nm with increase in electron irradiation. Also, crystallinity decreases with increase in electron irradiation. Bandgap of the material changed from 1.5 eV to 3.95 eV. Raman spectroscopic measurements confirm the structural phase transition beyond $3 \times 10^{15}\text{ e}^-/\text{cm}^2$. SEM study reveals the morphology of hierarchical flower $\text{Cu}_2\text{ZnSnS}_4$ start agglomerating with electron irradiation and it completely changes at $4 \times 10^{15}\text{ e}^-/\text{cm}^2$. The samples did not amorphize in the fluence range used and thus indicate radiation stability.

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Figure Captions

Fig 1. X-Ray Diffraction patterns of $\text{Cu}_2\text{ZnSnS}_4$ samples irradiated with 6 MeV electron at different irradiation fluences.

Fig 2. Williamson-Hall Plot of (a) pristine $\text{Cu}_2\text{ZnSnS}_4$ and (b) $\text{Cu}_2\text{ZnSnS}_4$ sample irradiated with 6 MeV electron at $3 \times 10^{15} \text{ e}^-/\text{cm}^2$ fluence.

Fig 3. Estimated crystallite size of $\text{Cu}_2\text{ZnSnS}_4$ samples using XRD at different irradiation fluences.

Fig 4. Strain on $\text{Cu}_2\text{ZnSnS}_4$ samples calculated using XRD patterns at different irradiation fluences.

Fig 5. Dependence of X-ray diffraction peak positions of $\text{Cu}_2\text{ZnSnS}_4$ samples for different electron irradiation fluences.

Fig 6. Dependence of intensity (area under the curve) of (112), (220) and (312) peaks of X-ray diffraction patterns of CZTS samples for different electron irradiation fluences.

Fig 7. UV absorption spectra of $\text{Cu}_2\text{ZnSnS}_4$ samples irradiated with 6 MeV electron at different fluences.

Fig 8. Tauc plot of $\text{Cu}_2\text{ZnSnS}_4$ samples irradiated with 6 MeV electron at different fluences. Estimated band gaps are shown in brackets.

Fig 9. Raman spectra of $\text{Cu}_2\text{ZnSnS}_4$ samples irradiated with 6 MeV electron at different fluences.

Fig 10. Electron irradiation fluence dependence of Raman mode frequencies of CZTS samples.

Fig 11. Dependence of FWHM of Raman modes of nano-CZTS on electron irradiation fluence.

Fig 12. Intensity ratio $I_{288 \text{ cm}^{-1}}/I_{331 \text{ cm}^{-1}}$ as a function of electron irradiation fluence.

Fig 13.(a) SEM image of pristine (A1) $\text{Cu}_2\text{ZnSnS}_4$. **(b)** pristine (A1) $\text{Cu}_2\text{ZnSnS}_4$ at magnified view

(c) SEM image of $\text{Cu}_2\text{ZnSnS}_4$ samples irradiated with 6 MeV electron at $1 \times 10^{15} \text{ electrons/cm}^2$ (A2), $2 \times 10^{15} \text{ electrons/cm}^2$ (A3), $3 \times 10^{15} \text{ electrons/cm}^2$ (A4) and $4 \times 10^{15} \text{ electrons/cm}^2$ (A5).

(d) SEM image of $\text{Cu}_2\text{ZnSnS}_4$ after irradiation $4 \times 10^{15} \text{ electrons/cm}^2$ (for $1 \mu\text{m}$ scale).

Fig 1.Kandare *et al*

Fig 2.(a) and (b)Kandare *et al*

Fig 3.Kandare *et al*

Fig 4.Kandare *et al*

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Fig 9.Kandare *et al*

Fig 10.Kandare *et al*

Fig 11.Kandare *et al*

Fig12.Kandare *et al*

Fig13. (a) and (b) Kandare *et al*

Fig13. (c) Kandare *et al*

Fig13. (d) Kandare *et al*

Figures

Figure 1

X-Ray Diffraction patterns of $\text{Cu}_2\text{ZnSnS}_4$ samples irradiated with 6 MeV electron at different irradiation fluences.

Figure 2

Williamson-Hall Plot of (a) pristine $\text{Cu}_2\text{ZnSnS}_4$ and (b) $\text{Cu}_2\text{ZnSnS}_4$ sample irradiated with 6 MeV electron at $3 \times 10^{15} \text{ e}^-/\text{cm}^2$ fluence.

Figure 3

Estimated crystallite size of $\text{Cu}_2\text{ZnSnS}_4$ samples using XRD at different irradiation fluences.

Figure 4

Strain on Cu₂ZnSnS₄ samples calculated using XRD patterns at different irradiation fluences.

Figure 5

Dependence of X-ray diffraction peak positions of Cu₂ZnSnS₄ samples for different electron irradiation fluences.

Figure 6

Dependence of intensity (area under the curve) of (112), (220) and (312) peaks of Xray diffraction patternsof CZTS samples for differentelectron irradiation fluencies.

Figure 7

UV absorption spectra of Cu₂ZnSnS₄samples irradiated with 6 MeV electron at different fluencies.

Figure 8

Tauc plot of Cu₂ZnSnS₄ samples irradiated with 6 MeV electron at different fluences. Estimated band gaps are shown in brackets.

Figure 9

Raman spectra of Cu₂ZnSnS₄ samples irradiated with 6 MeV electron at different fluences.

Figure 10

Electron irradiation fluence dependence of Raman mode frequencies of CZTS samples.

Figure 11

Dependence of FWHM of Raman modes of nano-CZTS on electron irradiation fluence.

Figure 12

Intensity ratio $I_{288 \text{ cm}^{-1}} / I_{331 \text{ cm}^{-1}}$ as a function of electron irradiation fluence.

Fig13. (a) and (b) Kandare *et al*

Fig13. (c) Kandare *et al*

Fig13. (d) Kandare *et al*

Figure 13

.(a) SEM image of pristine (A1)Cu₂ZnSnS₄ .(b) pristine (A1)Cu₂ZnSnS₄ at magnified view (c) SEM image of Cu₂ZnSnS₄ samples irradiated with 6 MeV electron at 1 x10¹⁵ electrons/cm² (A2), 2 x10¹⁵ electrons/cm² (A3), 3 x10¹⁵ electrons/cm² (A4) and 4 x10¹⁵ electrons/cm²(A5). (d) SEM image of Cu₂ZnSnS₄ after irradiation 4 x10¹⁵ electrons/cm² (for 1μm scale).

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