Influence of gamma radiation on structural, microstructural and optical properties of Cu$_2$ZnSnS$_4$ (CZTS) thin films prepared by thermal evaporation technique

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Abstract. Cu$_2$ZnSnS$_4$ (CZTS) thin films for three samples were prepared at the same deposition parameters by thermal evaporation method at a vacuum pressure of $6.0 \times 10^{-5}$ Torr and investigated using irradiation technique. The films deposited were irradiated with the gamma irradiation source (Cs-137) when activity = 1317.72 MBq, dose rate = 100.686 Gy/h for 300 and 600 Gy doses to study the influence of gamma irradiation on the structural, morphological and optical properties of the films. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) and UV–Vis were used to investigate the properties of the as-deposited and irradiated films. X-ray diffraction (XRD) studies of the as-deposited and irradiated thin films revealed a kesterite structure with tetragonal lattices at a preferred orientation along $2\theta = 28.55^\circ$. The intensity of the preferred peaks and the crystallite sizes showed a significant decrease with an increase in irradiation dose. Other microstructural parameters such as microstrain, dislocation density and the texture coefficient increase with the increase in irradiation dose. The field emission scanning electron microscopy (FESEM) images from the surface morphology investigation indicated that the as-deposited thin film was non-uniform and irradiated films became more compact and uniform with distinct grain size as the gamma radiation dose increases. Optical properties including band gap, absorption coefficient, transmittance and absorbance spectra for both as-deposited and irradiated films were also studied. It was found that the band gap for the as-deposited, 300 Gy and 600 Gy films were 1.48, 1.50 and 1.53 eV respectively. The absorption coefficient ($\alpha$) decreased from 7.1235 to $5.6056 \times 10^4$ cm$^{-1}$. The influence of irradiation dose used in this work has shown a positive influence on the structural, morphological and optical properties.

Keywords. Gamma irradiation; Cu$_2$ZnSnS$_4$ thin films; structural; microstructural, optical properties.

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1. Introduction

Photovoltaic (PV) technology is one of the alternative energy sources in which when solar radiation strikes the absorber layer of a solar cell, the incident radiation is directly converted into clean energy without burning fossil fuel and without any other by-products. This technology is sensitive to radiation with short wavelengths such as X-rays and $\gamma$-rays and widely served as power sources in the solar system [1]. Ionising radiations are abundantly available in the solar system for solar energy systems and other applications. As part of other applications, it plays a vital role in a deep understanding of the photovoltaic materials or devices made from them to study their behaviour when used in the radiation environment [2–4]. Radiation can induce damage in the devices making it essential for developing materials or devices that are radiation-resistant. High-energy radiation causes lattice defects in PV devices and these defects reduce the efficiency of the PV cells. The effects caused by radiation in the lattice periodicity increase the energy levels in the band gap and the additional energy levels change the physical properties of the solar cells especially the electrical property of the
material. This is due to the electron–hole pairs generated near the band gap of the materials [5,6]. Irradiation alters the physical, chemical and mechanical properties of PV materials or devices, and this might be either beneficial or detrimental. The effect depends on the dose of the radiation, the distance of the material from the radiation source and other parameters such as the thickness of the material [7]. The physical properties, such as the structural, microstructural, morphological, optical and electrical properties of the irradiated materials could be beneficial in tailoring the properties of the materials with a view to enhance the performance of various devices, thereby creating new materials with desirable properties [8–10].

Cu(InGa)Se2 (CIGS), CdTe and Cu2ZnSnS4 thin films show good performance as absorber layers in the solar cells. They are regarded as commercial alternatives to silicon solar cells [11,12]. Cu2ZnSnS4 stands for copper zinc tin sulphide (CZTS) thin films which have the most promising properties such as direct band gap, high absorption coefficient (>10^4 cm^−1) and band gap (1.4–1.5 eV) and highly desired as PV absorber materials [13]. It is made by replacing indium and gallium with zinc and tin with selenium in the Cu(InGa)Se2 thin films. This new semiconductor compound (Cu2ZnSnS4) is made of non-toxic, earth-abundant and cheap elements compared to indium and gallium making it a great area of research in thin-film solar cells [14–16]. However, it is essential to investigate the response of CZTS thin films in the radiation environment to ascertain if radiation exposure would cause modification of the physical properties or damage the film. Therefore, this work is aimed to study the influence of gamma radiation on the structural, morphological and optical properties of the CZTS thin films.

2. Experimental details

CZTS thin films were made by evaporating the metallic precursors and sulphurisation. The deposition of Zn, Sn and Cu metallic precursors respectively was done on glass substrates using an EDWARD FL 400 thermal evaporator at a substrate temperature of 150°C and vacuum pressure of 6.0×10^−5 Torr using molybdenum boats (11.5 cm). The stacked metallic precursor thin films in the order Zn/Sn/Cu were subjected to a reaction in sulphur vapour in a chamber at a given temperature of 500°C with a ramping rate of 25°C per minute. Sulphur vapour was allowed into the chamber using argon as the carrier gas and after 1 h, the temperature was dropped to 300°C. At room temperature, the source of sulphur vapour was disconnected and cooled to get Cu2ZnSnS4 compound. The irradiation of CZTS thin films was done in a chamber containing a gamma source of 137Cs radionuclide with an activity of 1317.72 MBq, half-life of 30.07 years and dose rate of 100.686 Gy/h. The films were labelled A2 and A3, then placed at 0.1 cm distance in a chamber with an irradiation dose of 300 and 600 Gy, exposing the samples to gamma radiation at room temperature while sample A1 (as-deposited) was not irradiated.

3. Results and discussion

3.1 Structural analysis

The full-scale X-ray diffraction (XRD) of CZTS thin films was carried out on the as-deposited and irradiated films using XRD PANalytical at 2θ = 25–60°, step size = 0.040° and counting times = 3.17 s/step. Figure 1 shows the little expanded peaks of the films which revealed about seven diffraction peaks of CZTS thin films.

The main diffraction peaks for the as-deposited and irradiated films occurred at 2θ = 28.55, 33.05, 47.31 and 56.22 representing 112, 020, 024 and 116 planes. These peaks indicate the presence of CZTS thin films which are in good agreement with the peaks phases formation when compared to the standard X-ray diffraction

![Figure 1. X-ray diffraction (XRD) spectra for the as-deposited and irradiated CZTS thin films.](image-url)
Table 1. Summary of the deposition parameters of the as-deposited and irradiated CZTS thin films.

<table>
<thead>
<tr>
<th>Metallic precursor and thickness (nm)</th>
<th>Deposition time (s)</th>
<th>Rate of evaporation A/S</th>
<th>Temp. of evaporation (°C)</th>
<th>Vacuum pressure of deposition (Torr)</th>
<th>Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (150)</td>
<td>590.0</td>
<td>2.3</td>
<td>240.00</td>
<td>6.0 × 10⁻⁵</td>
<td>2.0</td>
</tr>
<tr>
<td>Sn (150)</td>
<td>585.0</td>
<td>3.4</td>
<td>966.84</td>
<td>6.0 × 10⁻⁵</td>
<td>2.0</td>
</tr>
<tr>
<td>Cu (150)</td>
<td>305.0</td>
<td>4.5</td>
<td>998.73</td>
<td>6.0 × 10⁻⁵</td>
<td>2.0</td>
</tr>
</tbody>
</table>

data file (ICSD collection code 262388). The preferred peak (112) at 2θ = 28.55° confirmed the formation of CZTS thin films with a tetragonal-type structure (kesterite structure) for both as-deposited and irradiated thin films indicating that all the films are polycrystalline and are consistent with the JCPDS data file (JCPDS No. 26-0575). Both as-deposited and irradiated films show strong preferential crystal orientation along (112) but the intensity of the peaks decreased with an increase in radiation dose (300–600) Gy. This result reveals that there was enough radiation dose to cause disorder in the films and affect the crystallites size [17,18]. It is also observed that the irradiated films have a slight left shift causing an enlargement of the angle (29.0°–26.5°) of the XRD patterns when compared with the as-deposited film. The microstructural properties including grain size (D), microstrain (ε), dislocation density (δ) and texture coefficient (TC) of the films were determined. Grain size (D) of the films was calculated using Debye–Scherer’s equation:

\[ D = \frac{\kappa \lambda}{\beta \cos \theta}, \]  
\[ D = \frac{0.9 \lambda}{\beta \cos \theta}, \]  

where D is the grain size of the films, β is the full-width at half-maximum (FWHM), β is the Bragg diffraction angle, k is the shape factor and λ is the wavelength of the Cu-kα X-ray radiation used (1.5406 Å or 0.154 nm) [19].

Microstrain ε representing strain in parts per million is estimated using [20]

\[ \varepsilon = \frac{\beta \cos \theta}{4}, \]  

where β = FWHM.

Dislocation density which is another parameter that has great importance in material science was studied because its excessive increment can ruin the performance of the device and render the device useless. It was determined using the following equation:

\[ \delta = \frac{1}{D^2}. \]  

Table 1 shows the crystallinity properties of the films for the preferred plane. The crystalline size values of as-deposited and radiated Cu₂ZnSnS₄ thin films are found to decrease from 291.40 nm to 260.19 nm in the 112 planes. This indicates that the crystallisation of the films was slightly deteriorated, which might be due to the decrease in the peaks after irradiation. The decrease in the values of crystallite size with the increasing radiation dose is expected because radiation causes some defects which decrease the coherence length. The calculated microstrain (ε) values show a slight increase from 1.17 × 10⁻³ to 1.33 × 10⁻³ after irradiation. This change in the values suggests that the film is slightly strained which might be from the change in the constitution of the native imperfections [21]. But the dislocation density of the as-deposited and irradiated thin films significantly are found to increase from 1.13 × 10¹³ m⁻² to 1.48 × 10¹³ m⁻² with an increase in radiation dose.

3.2 Surface morphology analysis

The property of surface morphology is very essential for solar cells because of its effect on the interface among different film layers. In this research, the CZTS thin films were studied to estimate the influence of gamma radiation on the surface morphology of the films.

Figure 2 shows the micrographs of the as-deposited and irradiated CZTS thin films investigated using field emission scanning microscopy (FESEM) JEOL JSM - 7600F at 10,000× magnification. The micrograph of the as-deposited film shows large agglomerations and does not exhibit well-defined grains. After irradiation, the grain morphology is seen with distinct grain size for radiation doses of 300 and 600 Gy. The large agglomerations in the as-deposited films are a result of some intrinsic defects that are always formed during the deposition of CZTS thin films but upon gamma irradiation, the agglomerations and the number of defects in the irradiated films are seen to be less due to the recombination effect, causing improvement of the intrinsic defects [22,23].
3.3 Elemental composition analysis

The composition of the as-deposited and irradiated films of CZTS thin films was measured using energy-dispersive X-ray attached to the FESEM.

Figure 3 shows the field emission scanning electron microscopy-energy-dispersive X-ray (FESEM-EDX) spectra of all the elements with the characteristics of X-ray energies ranging from 1.0 to 8.0 keV. The FESEM-EDX spectrum analysis indicates the presence of copper, zinc, tin and sulphur in both as-deposited and irradiated films. However, as-deposited and 600 Gy-irradiated CZTS thin films show zinc-rich peak as the strongest peak whereas 300 Gy thin films show copper-rich peak as the strongest peak. Also, there is no evidence of any other element in the films which shows the absence of impurity from the glass substrate or other sources. This is in contrast to the work done by Isah et al. [24].

Table 3 shows the weight and atomic composition of the as-deposited and irradiated CZTS thin films. The as-deposited and 600 Gy-irradiated films revealed a poor percentage of copper indicating that the films are zinc-rich both in weight and atomic composition and corresponding to the results of the FESEM-EDX spectra in figure 3. The condition, where copper is less, leads to the formation of copper vacancies which in turn creates weak acceptors whereas the zinc-rich condition suppresses the copper substitution at zinc sites which increases strong acceptors in CZTS [25]. Therefore, copper-poor and zinc-rich Cu2ZnSnS4 films have higher p-type conductivity, resulting in high conversion efficiencies in solar cells [26].

3.4 Analysis of optical properties

Optical properties are very important for the fundamental understanding of solar cells. The behaviours of transmittance, optical band gaps and absorbance of CZTS thin films exposed to different doses of gamma irradiation were carried out using Avantes UV–Vis spectrophotometer (AVASPEC 2048) in the wavelength range of 400–900 nm.

3.4.1 Optical transmittance. The optical transmission spectra for all the films as a function of wavelength in the range (400–900) nm are shown in figure 4. It can be seen that the transmittance of the films increases as the radiation dose increases to 600 Gy. This behaviour correlates with our earlier observation of zinc-rich condition in films radiated with 600 Gy as discussed in the EDX result. However, the transmittances of both the as-deposited and radiated films increase as both wavelength and gamma irradiation dose increase.

3.4.2 Optical absorbance. Figure 5 shows the effect of gamma irradiation on the absorbance spectra of the films. The spectra decrease with increasing radiation dose and also with the wavelength in the visible region. The maximum optical absorbance for the as-deposited, 300 Gy- and 600 Gy-irradiated films in the visible regions (400–900 nm) of the spectrum are 3.5, 3.0 and
Figure 3. EDX Spectra for (a) as-deposited, (b) 300 Gy- and (c) 600 Gy-irradiated CZTS thin films.

Table 2. Some calculated crystallinity properties from XRD result for the preferred plane (112).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$2\theta$ (°)</th>
<th>hkl</th>
<th>d (Å)</th>
<th>D (nm)</th>
<th>$\varepsilon$ ($\times 10^{-3}$)</th>
<th>$\delta$ ($\times 10^{13}$ m$^{-2}$)</th>
<th>TC</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>28.44</td>
<td>1 1 2</td>
<td>3.1270</td>
<td>291.40</td>
<td>1.170</td>
<td>1.131</td>
<td>0.48</td>
<td>5.409</td>
<td>10.88</td>
<td>2.01</td>
</tr>
<tr>
<td>300 Gy</td>
<td>28.54</td>
<td>1 1 2</td>
<td>3.1282</td>
<td>260.19</td>
<td>1.332</td>
<td>1.477</td>
<td>0.35</td>
<td>5.400</td>
<td>10.91</td>
<td>2.02</td>
</tr>
<tr>
<td>600 Gy</td>
<td>28.54</td>
<td>1 1 2</td>
<td>3.1282</td>
<td>260.19</td>
<td>1.332</td>
<td>1.477</td>
<td>0.70</td>
<td>5.400</td>
<td>10.91</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Table 3. Elemental analysis of the as-deposited and irradiated CZTS thin films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SK</th>
<th>CuL</th>
<th>ZnL</th>
<th>SnL</th>
<th>CK</th>
<th>SK</th>
<th>CuL</th>
<th>ZnL</th>
<th>SnL</th>
<th>CK</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>17.06</td>
<td>9.91</td>
<td>46.97</td>
<td>26.04</td>
<td>–</td>
<td>32.72</td>
<td>9.59</td>
<td>44.20</td>
<td>13.49</td>
<td>–</td>
</tr>
<tr>
<td>300 Gy</td>
<td>5.41</td>
<td>43.41</td>
<td>35.10</td>
<td>16.08</td>
<td>–</td>
<td>11.10</td>
<td>43.67</td>
<td>36.33</td>
<td>8.91</td>
<td>–</td>
</tr>
<tr>
<td>600 Gy</td>
<td>14.92</td>
<td>5.87</td>
<td>47.83</td>
<td>37.25</td>
<td>–</td>
<td>30.79</td>
<td>5.28</td>
<td>48.43</td>
<td>20.77</td>
<td>–</td>
</tr>
</tbody>
</table>

K stands for K line and L stands for L line.

2.4 Au respectively. The trend of these values proves that optical absorbance spectra respond to the gamma radiation dose in this work [27].

3.4.3 Optical absorption coefficient. The value of the absorption coefficient can be calculated either using transmittance ($T$) or absorbance ($A$). In this work, the optical absorption coefficient value for the as-deposited and irradiated CZTS films is obtained from UV–Vis spectrometer at room temperature using the following relation:

$$\alpha = -\ln(T)/t,$$

where $\alpha$ is the absorption coefficient, $T$ is the average transmittance and $t$ is the film thickness [28].
3.4.4 Optical transmittance spectra for the as-deposited and irradiated CZTS thin films.

Figure 4.

3.4.5 Optical absorbance spectra for the as-deposited and irradiated CZTS thin films.

Figure 5.

The absorption coefficients were obtained as 7.1235, 6.0567 and $5.6056 \times 10^4$ cm$^{-1}$ for the as-deposited, 300 Gy- and 600 Gy-irradiated films respectively. These values show that the absorption coefficient of the as-deposited films is slightly affected by the radiation doses and this means that the absorption coefficient decreases linearly with an increase in gamma radiation dose. This trend indicates that the range of radiation dose used in this work has caused radiation hardness of the films [29].

3.4.4 Optical band gap. The optical band gap is one of the most significant optical parameters which is related to the electronic structure. The value of the band gap is estimated using Tauc relation.

$$\alpha h v = B (h v - E_g)^r,$$

where $h v$ is the photon energy, $\alpha$ is the absorption coefficient, $E_g$ is the optical band gap, $B$ is the Tauc parameter that depends on the transition probability and the index $r = \frac{1}{2}$ and 2 is for allowed direct and indirect transition energy gaps respectively which explains the optical transition between the valence and conduction bands [30].

Figure 6 shows the plot of $(\alpha h v)^2$ vs. photon energy ($h v$) for the as-deposited and irradiated CZTS thin films with the corresponding wavelength. The values of the energy band gap ($E_g$) were determined by extrapolating a portion of the curve at $(\alpha h v)^2 = 0$. The energy band gaps are 1.48 eV for the as-deposited and 1.50 and 1.53 eV after irradiation with 300, 600 Gy respectively. The linear nature of the plots indicates the existence of direct transition and it can be seen that the direct energy band gaps increase by increasing the exposure of radiation in the range (300–600) Gy. This increase is due to the excess energy which leads to the creation of localised energy states in the normally forbidden energy states. That is, whenever gamma radiation interacts with the thin film, induced defects will be formed and the density of the localised states increases, increasing the energy gap [31].

4. Conclusion

This work studied the response of different doses of gamma irradiation ($^{137}$Cs source) on the properties of CZTS thin films to ascertain the stability and suitability of the films in the radiation environment. XRD, FESEM, SEM-EDX and UV–Vis were used to investigate the properties of the as-deposited and irradiated films and we came to the following conclusions:

(a) The intensity of the peaks and the crystalline size of the films decreased with increasing doses of gamma irradiation.
(b) Microstrain, dislocation density and the texture coefficient increased after irradiation.
(c) The FESEM micrograph of the as-deposited film showed non-uniform grains and after irradiation, the grains became more uniform leading to partial healing of the intrinsic defects.
(d) Microstructural studies via FESEM-EDX showed the presence of all the elements in both as-deposited and radiated films but after irradiation, the 300 Gy film indicated Cu-poor and Zn-rich peaks and vice versa in 600 Gy film.
Figure 6. Optical band gap for (a) as-deposited, (b) 300 Gy- and (c) 600 Gy-irradiated CZTS thin films.

(e) Upon irradiation, optical parameters such as the optical band gap increased, the absorption coefficient decreased, the variation of transmittance increased and absorbance decreased. Hence CZTS thin film is stable within the range of irradiation doses used in this work.

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