Synthesis and characterization of CZTS thin films from compound target deposited by RF sputtering method

S Abdullahi1*, M Momoh1, AU Moreh1, AM Bayawa2 and A Saidu1
1Department of Physics, Usmanu Danfodiyo University, Sokoto, Nigeria.
2Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, Sokoto, Nigeria.
*E-mail: abdullahi.sanusi@udusok.edu.ng

Abstract. A potential way to improve the quality of Copper-Zinc-Tin-Sulfide (Cu2ZnSnS4(CZTS)) absorber thin film by one step process of Radio Frequency (rf) sputtering using a single compound target is proposed for thin film solar cells. Structural and Optical characterizations were carried out using X-ray Diffractometer, Raman spectrophotometer and UV-VIS spectrophotometer. The X-ray diffraction analysis showed hkl planes of (002), (110), (112) and (212). Raman results confirmed the existence of secondary phases of SnS, Cu2xS and CTS. The optical absorption coefficient of the thin film was found to be greater than 10^4 cm^{-1} indicating a direct band gap nature of the samples. The optical band energy was calculated and found to be in the range of 1.51 eV to 2.4 eV. The band gap energy obtained is more appropriate for photovoltaic applications.

Keywords: Film thickness, annealing temperature, rf sputtering, compound target, XRD, absorption coefficient

1. Introduction

Copper-Zinc-Tin-Sulfide (CZTS) made entirely from abundant materials, has attracted a great interest due to its potential applications in sustainable thin-film solar cell devices. It is a p-type semiconductor with a favorable band gap (~ 1.5 eV) and a high absorption coefficient (>10^4 cm^{-1}) [1] which minimizes the quantity of material used in devices. In other words, a thin layer of this material can absorb a greater number of photons from solar radiation and can therefore be used as an absorber layer for solar cell. A variety of deposition techniques were
employed for the deposition of CZTS. These techniques include but not limited to thermal and electron-beam evaporation [2], co-evaporation [3], direct current (DC) and radio frequency (RF) magnetron sputtering [4-7], hybrid sputtering [8], sol-gel spin-coated deposition, and electro deposition (co-electroplating) [9-10], chemical bath deposition [11], One temperature method [12] and SILAR [13]. Sputtering is one of the most viable methods for depositing thin films. It has the advantage over other vacuum deposition techniques of being simple as all the deposition parameters can be controlled [14-17]. So far, most of the reported CZTS thin film depositions are in the order of 1000 nm or more in terms of the film thickness. Annealing of thin films on the other hand is known to improve the properties of thin films [18-20]. Reports of depositions below 1000 nm thick and annealing at 450 °C or below for CZTS thin films are scarce. For this purpose, CZTS thin films of 550 nm thickness were deposited on corning glass substrates by radio frequency (rf) sputtering technique. The influence of annealing temperature on the thin films was investigated.

2. Experimental Procedures

2.1 Preparation and annealing of the CZTS thin films

CZTS thin films were grown by rf sputtering technique on bare corning glass 7059. The substrates were pre-cleaned with acetone and ethanol followed by rinsing with deionized water and drying in flowing nitrogen (N₂) of 99.99% purity. The sputtering chamber was evacuated to 10⁻⁴ Pa. A pre-sputtering was carried out for 1 minute. The Zn-rich target is a single disk composed of CZTS of 4N purity at ratios of 1.1:1.8:0.9:1.0 (AJA International) having a diameter of about 2 cm and a thickness of about 0.25 cm. The target/substrate distance was maintained at 7 cm while the rf power was kept constant at 75 W. To ensure uniform deposition, the substrate was rotated at 35 rpm throughout the deposition period. After the deposition of the 550 nm thick thin films, the samples were rinsed with deionized water, dried in flowing nitrogen and then heated under nitrogen atmosphere for 30 min at 250, 350 and 450 °C in a tubular furnace, while the dwelling period was maintained at 60 min. The samples were then allowed to naturally cool to room temperature. Out of the four samples deposited, three were annealed and the fourth sample was reserved as the reference or as-deposited sample.
2.2 Characterization

The crystalline properties of the films were analyzed by high-resolution X-ray diffraction (XRD – SIEMENS Diffractometer D5000) operated at 40 kV and 30 mA. Raman scattering spectroscopy (Reinshawinvia Raman Microscope) with an Olympus microscope equipped with a 100X magnification lens and in the backscattering configuration. The excitation source was a green Argon ion laser operating at 532 nm and 220 mW output powers. The morphology of the films was inspected by Field Emission Scanning Electron Microscope (FE-SEM, Model: JBM-7000F, Japan). The optical properties were analyzed by spectrophotometer (AVANTES AVASPEC-2048 UV-VIS-NIR) operated in the wavelength range of 180-1100 nm at room temperature.

3. Results and Discussion

3.1 X-ray diffraction

The stacked XRD diffractograms of all the samples are displayed in Figure 1. The spectra of the samples appeared polycrystalline which may be attributed to the film thickness and the nature of the substrate. Some of the samples exhibited kesterite structure with diffraction peaks at various angles. The as-deposited sample shows diffraction peaks at $2\theta = 15.94^\circ$, $26.82^\circ$ and $34.46^\circ$ corresponding to (002), (110) and (212) according to ICSD 01-075-412. Diffraction peaks observed at $2\theta = 30.66^\circ$ and $43.86^\circ$ for the sample annealed at 250 $^\circ$C indicates the existence of secondary phases of SnS$_2$ and Cu$_2$SnS$_2$. The presence of a single peak at $2\theta = 43.78^\circ$ for the sample annealed at 350 $^\circ$C also indicates the presence of Cu$_2$SnS$_2$.

After annealing at 450 $^\circ$C, diffracting planes of (110), (112) and (212) at $2\theta = 26.32$, 28.5 and $33.82^\circ$ were observed.
Figure 1. X-ray diffraction patterns of the as-deposited sample and the samples annealed at 250, 350 and 450 °C.

Table 1 gives the structural parameters for the thin films of CZTS. The parameters in the table are the diffraction peak (hkl), lattice parameters (a and c), full width at half maximum (FWHM), grain size (D), dislocation density (δ) and micro strain (εm). The hkl plane of (110) observed for the as-deposited sample is also reported elsewhere [15, 21]. The hkl plane shifted to higher angle at the annealing temperature of 250 °C. The annealing temperature of 350°C and 450 °C resulted in the emergence of the hkl planes of (112) and (212) of the kesterite CZTS phase. The standard value for a as given by the Joint Committee on Powder Diffraction Standards (JCPDS) is 0.5421 nm along the (002) plane. The value obtained for the as-deposited samples is very close to that obtained in the literature [21-22]. Annealing the samples at 250 °C did not produce much change in the lattice parameter ‘a’. The lattice parameter ‘a’ obtained for the sample is very close to those obtained by researchers [23-25]. Lattice parameter ‘a’ for the samples annealed at 350 and 450 °C are within the reported range by other researchers [26-28].

The standard lattice parameter c for CZTS is 1.0848 nm as referenced in the JCPDS. A low value of 0.88 has been determined for the as-deposited sample. Annealing the sample at 250
°C led to the decrease in the value of $c$ compared to the as-deposited sample. Increasing the annealing temperature to 350 °C further changed the value of $c$.

At the annealing temperature of 450 °C, the sample deviated from the standard value of $c$ which might be associated with high concentration of ions which lowers ionic radii as reported [29]. Variations of $c$ observed in all the samples might also be connected to nano-grained materials whose crystallites were under strain. Such strain creates local deviation of lattice constants from its bulk value which is size dependent [30]. Changes in the values of $c$ more especially indicates that the crystallites are experiencing compression in the $c$ direction implying that defects can cause changes in the lattice constant. Variations in the lattice parameters $a$ and $c$ are also observed elsewhere [29-30]. The values reported here are close to those obtained in previous studies [22, 31].

The FWHM (obtained from x-ray software calculations) for the as-deposited sample is 0.6927. The value of FWHM decreased to 0.1732 when the sample is annealed at 250 °C. As the annealing temperature is increased to 350 °C, the FWHM stood at 0.6927. At the annealing temperature of 450 °C, the FWHM is 0.2598. A decrease in the FWHM has been observed for the sample annealed at 450 °C compared to the sample annealed at 350 °C. The FWHM obtained is very close to that reported elsewhere [30, 32-33].

The grain size was estimated from the full width at half maximum (FWHM) of the (112) peak using Scherrer’s formula [21, 34]

$$D = \frac{0.94}{\beta \cos \theta}$$

where $\lambda$ is the wavelength of the X-ray used, $\beta$ is the FWHM and $\theta$ is the Bragg’s angle

The crystallite size (Table 1) observed for the as-deposited sample is 13.45 and 59.81nm for the sample annealed at 250 °C. The crystallite size for the sample annealed at 350 °C is lower than that of 250 °C which however increased for higher temperature which is similar to those previously reported [34-35]. As the annealing temperature is increased to 450 °C, the crystallite size increased if compared with the samples annealed at 350 °C. Increase or
decrease in the grain size reflects either the increase or decrease in the concentration of lattice imperfections due to the change in the internal micro-strain within the films.

The as-deposited sample has the highest dislocation density \((\delta)\) of \(5.53 \times 10^{-15} \text{lines/m}^2\). Annealing temperature of 250 °C resulted in the decrease of the dislocation density. An increase in the dislocation density has also been observed for the sample annealed at 350 °C if compared with the sample annealed at 250 °C. At the annealing temperature of 450 °C, the dislocation density decreased if compared with the sample annealed at 350 °C. The dislocation density reported here is very close to earlier reports [33, 35].

The micro strain \((\varepsilon_m)\) of the as-deposited sample is determined to be 0.16. At the annealing temperature of 250 °C, the micro strain decreases if compared with the as-deposited sample. At the annealing temperature of 350 °C, the micro strain increases if compared with the sample annealed at 250 °C. Micro strain from sample annealed at is 450 °C is 0.06. Micro strain of the sample annealed at 450 °C reduced when compared with the sample annealed at 350 °C. The change in the value of the micro-strain because of the increase in annealing temperature may be due to the movement of interstitial sulfur atoms from inside the crystallites to the grain boundary, which leads to a reduction in the concentration of lattice imperfections.

**Table 1.** Observed structural parameters of CZTS thin films

| Annealing temp. (°C) | Thickness (nm) | hkl | \(a\) (nm) | C (nm) | FWHM (β) | \(D\) (nm) | \(\delta\) (× \(10^{-15}\) lines/m²) | \(\varepsilon_m\) |
|----------------------|----------------|-----|-----------|--------|----------|-----------|---------------------------------|-------------|
| As-deposited         | 550            | 110 | 0.550     | 0.88   | 0.6927   | 13.45     | 5.53                            | 0.16        |
| 250                  | 550            | 114 | 0.530     | 1.06   | 0.1732   | 59.81     | 0.28                            | 0.04        |
| 350                  | 550            | 212 | 0.550     | 1.00   | 0.6927   | 27.53     | 1.32                            | 0.08        |
| 450                  | 550            | 112 | 0.530     | 1.06   | 0.2598   | 36.70     | 0.74                            | 0.06        |
3.2 Raman characterization

The phase purity and composition of the samples was analyzed by Raman spectroscopy. Figure 2 shows the measured Raman spectra for the as-deposited sample and the samples annealed at 250, 350 and 450 °C under nitrogen atmosphere. The spectra show several peaks characteristics of vibrational modes of CZTS and some of its secondary phases. The as-deposited sample showed a strong peak at 297 cm\(^{-1}\) which is a phase of CTS [36]. Annealing at 250 °C resulted in the disappearance of the peak at 297 cm\(^{-1}\) and appearance of CZTS peak at 288 cm\(^{-1}\). There are no visible CZTS peaks observed for the sample annealed at 350 °C. A low CZTS peak at 337 cm\(^{-1}\) has been observed for the sample annealed at 450 °C. This peak corresponds to the A\(_1\) mode associated with S-cation (322 to 377 cm\(^{-1}\)). There are some arm shoulder peaks for all the samples. These shoulder peaks are related to defects [37].

![Raman spectra](image)

**Figure 2.** Raman spectra of the as-deposited sample and the samples annealed at 250, 350 and 450 °C.

3.3 SEM characterization

Figure 3 (a, b, c and d) exhibits the micrographs of the CZTS thin films magnified at x30,000. Figure 3a is for the as-deposited sample which shows grains sizes with spherical shaped
nanoparticles with uniform distribution. The direct contact of Cu and Zn may be responsible for this [38]. Fig. 3b (sample annealed at 250 °C) shows a cloudy surface in which some of the cloudy structures are brighter than others. The annealing temperature of 250 °C has transformed the spherical shaped nanoparticles of the as-deposited sample to a cloudy surface seen in Figure 3b.

Figure 3c (sample annealed at 350 °C) shows granular particles covering the entire surface of the substrate. The needle-like structures seen in Figure 3c may be attributed to the presence of CuO in the film. These CuO needles are formed after annealing. The increase in the annealing temperature has transformed the cloudy surface of the sample annealed at 250 °C to the needle-like structures. The surface of Figure 3d (sample annealed at 450 °C) is marked by void less compacted structure. There are many transformations observed when the annealing temperature has been increased from 350 to 450 °C. The surface of the sample annealed at 350 °C changed from void less structure to a surface with granular particles seen in Fig. 3d.

Figure 3. SEM micrographs of the as-deposited sample (a) and the samples annealed at 250 (b), 350 (c) and 450 °C (d)
3.4 Optical characterization

(a) Transmittance

Figure 4 presents the transmittance spectra of the as-deposited and annealed CZTS thin films taken at room temperature. With average transmittance of 0.0092%, the as-deposited sample is practically opaque. It is observed that this film exhibits low transmittance, indicating that the film grew with a high density of native defects (vacancies, interstitial and antisites). The sample annealed at 250 °C is having an average transmittance of 2.25%. The annealing temperature may be responsible for the increase in transmittance if compared with the as-deposited sample. Low transmittance indicates high absorption [39]. The scattering of the incident light on the surface of the films affects the film transmittance by reflecting the incoming light and thus reducing the transmittance. This explains the difference in transmittance of the CZTS films [21, 25, 40]. The average transmittance of the sample annealed at 350 °C stands at 13.40%. The increase in the annealing temperature to 350 °C has resulted in the increase in transmittance for this sample. Transmittance spectra of thin film of CZTS thin film annealed at 450 °C is also shown in Fig 4. The spectra show that the sample is practically opaque having an average transmittance of 1.02 %. There is a decrease in the transmittance if this sample is compared with sample annealed at 350 °C of the same thickness. This decrease is attributed to the increase in the annealing temperature. The absorption edge observed for the samples annealed 250 °C and 350 °C ranges from 380 nm to 480 nm.
Figure 4. Transmittance spectra of the as-deposited sample and the samples annealed at 250, 350 and 450 °C.

(b) Energy band gap

The optical energy band gap can be calculated as follows [15]:

\[(\alpha \nu)^n = A(\nu - E_g)\]  

where \( h \) is Planck’s constant; \( \nu \) is the frequency of the incident photon; \( E_g \) is the optical band gap; \( A \) is a constant; and \( n \) is an index characterizing the type of optical transition. For a direct allowed transition such as that of CZTS, \( n \) is equal to 2. For direct band gap materials, the optical energy gap is determined by extrapolating the straight-line segment of the \((\alpha \nu)^2\) versus \( \nu \) plot to the \( \nu \)-axis.

Figure 5a, b, c and d show the optical band gap of the as-deposited sample and the samples annealed at 250, 350 and 450 °C respectively. The band gap of the as-deposited (Figure 5a) sample is determined to be 1.4 eV which is very close to the standard. This band gap has been reported [21]. The band gap of sample annealed at 250 °C has also been exhibited in Figure 5b. This sample shows a deviation (2.5 eV) from the standard (1.5 eV) in the value of band gap compared with the bulk CZTS.

The increase in the band gap is attributed to the presence of CTS and ZnS in the samples as
confirmed by XRD and Raman. The increase may also be attributed to the presence of a quantum confinement in band structure due to size or strain effect [41]. Furthermore, a decrease in sulfur or variation of composition may also be responsible for the deviation [42]. The shift in the value of the band gap because of annealing has also been reported [43].

The sample annealed at 350 °C is having an average band gap of 1.4 eV. The increase in the annealing temperature from 250 °C to 350 °C improved the band gap of the sample. In general, the distortion of the band gap from the standard is related to structural defects such as lattice strain [24]. The band gap of the sample annealed at 450 °C (1.5eV) is close to the value reported in the literature [23, 44]. The annealing temperature of 450 °C led to the improvement of the band gap of the sample annealed at 350 °C.

![Figure 5. (αhv)² versus Photon energy (eV) for the as-deposited sample and the samples annealed at 250, 350 and 450 °C.](image-url)
(c) **Absorption coefficient** ($\alpha$)

Based on the transmittance ($T$) and reflectance ($R$) data, the absorption coefficient can be determined near the band edge [15, 23]:

$$\alpha = \frac{1}{t} \ln \left[ \frac{(1-R)^2}{T} \right]$$  \hspace{1cm} (3)

where $\alpha$ is the absorption coefficient; $R$ is the reflectance; $T$ is the transmittance; and $t$ is the thickness of the film.

The absorption coefficient determines how strongly the specific wavelength of light is absorbed in the material. Figure 6 shows the absorption coefficient ($\alpha$) versus wavelength for as-deposited CZTS thin films. All the samples showed absorption coefficient greater than $10^4$ cm$^{-1}$ in the visible and near infrared spectral range showing that even the as-deposited sample have the property of absorbing photons. The absorption coefficient determines how strongly the specific wavelength of light is absorbed in the material [45]. The average absorption coefficient for the as-deposited sample is $3.50 \times 10^4$ cm$^{-1}$. The value obtained is in good agreement with that obtained [33, 46]. The absorption coefficient of the sample annealed at $250^\circ$C is also of the order of $10^4$ cm$^{-1}$, which supports direct band gap nature of the material. The absorption coefficient has slightly decreased if compared with that of the as-deposited sample. The absorption coefficient for this sample is $3.21 \times 10^4$ cm$^{-1}$. From Figure 6, it is evident that the film annealed at $350^\circ$C is having high absorption coefficient. According to the Hopfield quasi-cubic model for copper-containing compounds, this complex near-edge spectrum is determined by the p–d hybridization of the valence band of the compound [12]. The absorption coefficient ($\alpha$) for this sample is $3.55 \times 10^4$ cm$^{-1}$. The annealing temperature has led to the increase in the value of $\alpha$ if compared with the sample annealed at $250^\circ$C. The optical absorption coefficient of the CZTS thin film annealed at $450^\circ$C was also greater than $10^4$ cm$^{-1}$ in the visible region indicating a direct band gap characteristic of the thin film.
Figure 6. Absorption coefficient versus wavelength for as-deposited sample and the samples annealed at 250, 350 and 450 °C.

Conclusion
CZTS thin films have been deposited by rf sputtering technique from compound target. The annealing temperature was varied from 250 to 450 °C. The structural and optical properties of the samples were investigated. From XRD and RAMAN analysis, some of the samples exhibited the expected secondary phases of ZnS and CTS, while some showed the kesterite structure in preferred orientation of (002), (110), (112) and (212) respectively. The XRD spectra of all the samples appeared amorphous but that did not affect the magnitude of the absorption coefficient if compared with the literature. This shows that even though the film thickness is less than 700 nm and the annealing temperature is less than 500 °C, the absorption coefficient is similar to what is obtained in the literature. The band gap of some of the samples is within the range suggested for absorber layer of a solar cell. The absorption coefficient was greater than $1 \times 10^4 cm^{-1}$. Further investigations are necessary to control the emergence of secondary phases in CZTS thin films.

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