Deposition of nano-structured multilayer coatings of Cu₂ZnSnS₄ (CZTS) thin films by vacuum thermal evaporation method

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Abstract. The three step deposition of binary sulfides in the order CuS/ZnS/SnS thin films are prepared on Molybdenum (Mo) substrate by thermal evaporation method in order to obtain kesterite Cu₂ZnSnS₄ (CZTS) thin films. The CZTS thin films were annealed 500°C for one hour. The Phase studies and chemical compositions were investigated to obtain CZTS thin films using X-ray Diffractometer and Scanning Electron Microscopy (SEM). The optimized CZTS thin films show good optical properties and Electrical Properties. CZTS thin film was found to have a direct energy band gap of 1.5eV. Surface morphology studies have been studied using Atomic Force Microscopy (AFM) and SEM. It is reported that the good quality films were achieved with order of stacking CuS/ZnS/SnS precursor layers in this paper. Further, it has been observed that the crystalline size of CZTS has been improved after the sulfurization.

Keywords: CZTS, Thin film Photovoltaics (PV’s), Thermal evaporation studies, Surface morphological studies.

1. Introduction

Resources such as fossil fuels are limited and it is evident from the current studies that these fuels will probably be drained over the coming generations. Hazardous impact on the environment is mainly due to the increased consumption of such fuels globally. Thus, the requirement for a feasible design, environmentally pleasant and low price solar cells has been attracting considerable attention. Numerous renewable energy devices such as thin film
Photovoltaics have been introduced in the market. Cadmium telluride (CdTe) and Copper Indium Gallium Selenide (CIGS) are the most popular materials used in solar cells of second generation.

However, the toxicity and scarcity of cadmium and indium respectively, have motivated research in the direction of developing auxiliary light absorbers which are made from rich earth materials.

Quaternary compound Cu$_2$ZnSnS$_4$ (CZTS) semiconductor material has developed as one of the highly suitable candidates for this purpose and has engrossed considerable interest in recent times since it has an optimum direct bandgap energy of ~1.5 eV and a greater coefficient of absorption($>10^4$ cm$^{-1}$). Further, all the constituents in CZTS are earth abundant materials and are having very low toxicity [1]. CZTS thin films can be fabricated by using several physical methods like co-evaporation, sputtering and pulsed laser deposition whereas methods like microwave, sol–gel, electro-deposition, hydrothermal, hot injection, and precipitation constitutes the chemical methods.

There are issues to be resolved in the chemical methods even though they offer reduced wastage of raw materials with small investment of resources. The major issues with the chemical methods are multiple uniform coating, and cracks.

Therefore, thermal evaporation method is adopted in order to overcome the above mentioned issues. The advantages of using thermal evaporation method are highly crystalline which also provides control over deposition rate and property control features of structural as well as morphological types. Thin film deposition over large area can prove evaporation of thermal type to be a cost-effective procedure. In this research work, CZTS film is deposited on Mo coated glass substrates using CuS, ZnS and SnS as the precursors followed by sulfurization under H$_2$S. All possible orders of stacking order and their individual characterization have been investigated and the results are presented here.

In this research paper, compositional, structural and optical properties of CZTS-based solar cells prepared by simultaneous evaporation of Cu, Zn, and Sn individual elements layer-by-layer on a DC sputtered Mo coated SLG glass substrate are reported.

2. Experimental

2.1 Materials

Copper Sulfide (99.8%), Zinc Sulfide (35%) and Tin Sulfide (99%) were supplied by Sigma Aldrich Pvt. Ltd, India.

2.2 Methods

Mo-coated soda lime glass (SLG) substrate was chosen as a contact for CZTS absorber. The sequential growth of binary sulphides of CuS, ZnS, and SnS elements were thermally evaporated on 1 μm thickness of DC sputtered Mo coated soda-lime glass substrates. The annealing was carried out for binary sulphides at various temperatures in a vacuum furnace. CuS thin film deposited on Mo coated SLG substrate which was annealed at 500°C for 1 hour, ZnS thin film at the temperature of 400°C for 1 hour and SnS thin film used temperature of 500°C for annealing for 1 hour. In this experiment, Mo deposited time was ~3 minutes using DC sputtering in order to obtain 1 μm thickness. The crystallinity fluctuates expressively as the conditions of growth changes viz. deposition rate, gas flow and pressure inside the chamber. The working pressure of 2.7×10$^{-3}$ mbar was maintained in the vacuum chamber during deposition at the rate of 1.5 Å/s. The precursor pellets were placed in Mo evaporation boat. The obtained thickness of CuS, ZnS and SnS are 150 nm, 200 nm and 150 nm respectively. Further, to improve the crystallinity of the CZTS thin film, sulphurization was done by placing thiourea (CH$_2$N$_2$S) pellets in Mo boat and then thermally evaporating it.

3. Results and Discussion
The structural properties of the as-deposited thin films were carried out using X-ray Diffractometer (XRD, Bruker D2 Phaser with CuKα radiation, λ=1.5406 Å). XRD analysis for the each individual phase of CZTS i.e Copper Sulfide (CuS), Tin Sulfide (SnS), Zinc Sulfide (ZnS) and CZTS (Cu2ZnSnS4) were studied in detailed. The studies on the roughness, morphology and formation of grain were carried out using atomic force microscope (AFM).

### 3.1 X-ray Diffractometer

#### 3.11 CuS Phase:

The sharp peaks represent the formation of polycrystalline structure of CuS thin film. The experimental data indicates the presence of strong peaks at 28.66° and 30.33° indexed to [102] and [103] planes of CuS respectively, whereas the peak at 40.3° corresponds to Molybdenum [110] plane. The AFM image of binary sulfide of CuS thin film at the scan size of 5µm*5µm is depicted in figure 2. It can be visible that spherical CuS particles are well dispersed throughout Mo SLG substrates. The average surface roughness of CuS thin films obtained from AFM image is 18.2085 nm. Figure 1 shows XRD graph of the binary sulfide of CuS thin film deposited on Mo coated SLG substrate which was annealed at 500°C for 1 hour.

![Figure 1: XRD graph of CuS (500°C)](image1)

![Figure 2: AFM image of CuS (500°C)](image2)
The crystallite size profile of the CuS films is calculated from the Scherrer Formula as mentioned below:

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad [1]$$

Where D is crystallite size, B is Full Width Half Maximum (FWHM), \(\theta\) is the diffraction angle and \(\lambda\) is the wavelength of X-ray source. A peak was found at 23 nm which depicted the average size of the calculated crystallite using the FWHM of [102].

Figure 3 shows the SEM images of CuS deposited film. The CuS crystals can be clearly observed. The various sizes of the crystals were measured and are shown in the figure 3.

3.12 ZnS phase:

Figure 4 shows XRD patterns of the binary sulfide of ZnS thin film on Mo coated SLG substrate which was annealed later at 400°C for 1 hour. From the XRD pattern, the strong peaks are observed at 28.76°, 48.08°, 51.38° and 73.79° indexed to [111], [220], [311] and [400] planes of ZnS (JCPDS card No. 5-0566) indicating the poly-crystallinity nature of the ZnS film, whereas the peak at 40.3° corresponds to Molybdenum [110] plane.
Figure 4: XRD graph of ZnS (400°C)

Figure 5: AFM image of ZnS (400°C)

Figure 5 shows AFM image of binary sulfide of annealed (at 400°C) ZnS thin film at the scan size of 5µm*5µm. It can be observed that spherical ZnS particles are well dispersed throughout Mo SLG substrates. The average surface roughness of ZnS thin films obtained from AFM are found to be 6.523nm.

Table 1 shows the crystallite size of different planes of ZnS phase which was calculated by using equation [1].

Table 1: Crystallite size profile of different ZnS planes.

| Sl. No. | Planes | Crystallite size, D (nm) |
|---------|--------|-------------------------|
| 1.      | [1 1 1] | 10                      |
| 2.      | [2 2 0] | 12                      |
| 3.      | [3 1 1] | 13                      |
3.13 SnS phase:

To further investigate the phase structure of SnS layer, XRD measurements were done. Fig. 6 shows the XRD spectra of the binary sulfide of SnS thin film deposited on DC sputtered Mo coated SLG substrate which was later annealed at 500°C for 1 hour. The strong peak at 31.89° indexed to [111] of SnS (JCPDS card no: 65-3812) indicates the presence of polycrystalline structure of the SnS thin film, whereas the peak at 40.3° corresponds to Molybdenum [110] plane.

Figure 6: XRD graph of SnS (500°C)

Figure 7 shows AFM image of as-deposited binary sulfide of SnS thin film at the scan size of 5µm*5µm which was annealed at 500°C. From the AFM image, it can be observed that the SnS particles are well dispersed throughout Mo SLG substrates. The average surface roughness of SnS thin films obtained from AFM image is 13.079 nm. The crystallite size of SnS plane is measured by using equation [1], as depicted in table 2.
The figure 8 shows scanning electron microscope (SEM) image of the as-deposited SnS thin film. Large densely packed grains are clearly observed from the SEM image.
3.14 CZTS phase:

Figure 9 shows XRD graphs of the CZTS thin film deposited on DC sputtered Mo coated substrate (SLG) which was annealed at 500°C for 1 hour. The sharp peaks obtained at 27.948°, 28.7°, 38.39°, 46.34°, 51.47°, 53.45° are attributed to [100], [002], [102], [110], [103] and [112] planes respectively. XRD pattern at 31.8995° corresponds to SnS [111] plane whereas XRD pattern at 40.3° corresponds to Molybdenum [110] plane. It can be emphasized that the crystallinity of CZTS thin film increases after sulfurization, as shown in figure 10. Figure 11 shows AFM image of CZTS thin film after sulphurization at the scan size of 5µm*5µm. AFM measurements of the as-deposited CZTS film on DC sputtered Mo SLG substrate shows that spherical CZTS particles are well dispersed throughout the substrate. At higher temperature i.e. after annealing at 500°C the CZTS particles tries to agglomerate with each other and thus starts forming spherical hills. The average surface roughness of CZTS thin films obtained from AFM is found to be 34.338 nm.

![Figure 9: XRD graph of CZTS (annealed at 500°C) before sulfurization](image1)

![Figure 10: XRD graph of CZTS (500°C) after Sulfurization.](image2)
Figure 11: AFM image of CZTS.

Figure 12: SEM images of CZTS (before sulphurization)
Figure 13: SEM images of CZTS (after sulphurization)

Figure 12 and 13 shows the SEM images of CZTS before and after sulphurization respectively. The CZTS crystals can be clearly observed in the figure 12. The size of the crystals were measured and shown in the figure 12. Figure 13 depicts the sulphur layer that has formed on the top of the CZTS surface. This helps in passivating the CZTS layer.

Table 3 reveals crystalline size of CZTS planes before sulphurization. Crystallite sizes were calculated for various planes using the Scherrer Formula (equation [1]).

| Sl. No. | Planes  | Crystallite size, D (nm) |
|---------|---------|------------------------|
| 1.      | [0 0 2]  | 24                     |
| 2.      | [1 1 1]  | 24                     |
| 3.      | [1 0 3]  | 70                     |
| 4.      | [1 1 2]  | 67                     |

Table 4 reveals the different crystallite size profile of the various planes of the CZTS thin film. By comparing Table 3 with Table 4, it can be observed that the crystallite sizes of the planes increases after sulphurization. Note that the crystallite sizes of the different planes are calculated using the Scherrer Formula (equation [1]).

| Sl. No. | Planes  | Crystallite size, D (nm) |
|---------|---------|------------------------|
| 1.      | [1 0 0]  | 54                     |
| 2.      | [0 0 2]  | 31                     |
| 3.      | [1 1 1]  | 65                     |
| 4.      | [1 0 2]  | 75                     |
| 5.      | [1 1 0]  | 42                     |
| 6.      | [1 0 3]  | 89                     |
| 7.      | [1 1 2]  | 141                    |
3.2 Optical characterization of CZTS

The optical band gap of the absorber CZTS is evaluated from the measured transmission spectra using UV-VIS SPECTROSCOPY. Absorption coefficient ($\alpha$) can be depicted in a common form as a function of energy incident as photon as mentioned below:

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

Where $A$ is a constant, $E_g$ is band gap, and $n$ is a number related to the electron transition process. The $n$ value is around 1/2 for direct allowed and 1/3 for forbidden transitions respectively.

The absorption coefficient $\alpha$, and its determination method was described in reference [8].

According to the standard thin-film procedure, $\alpha$ satisfies the relation, $\alpha = (h\nu - E_g)$ if it is direct allowed transition between the two bands i.e., conduction and valence bands. Thus, the plot of $\alpha h\nu$ versus $\nu$ yields a straight line with energy intercept of $E_g$ [9].

The direct optical band gap of CZTS before and after sulphurization was approximated by plotting the curve of $(\alpha h\nu)^2$ vs. Energy as shown in Figure 14 and 15, respectively. The curve inclines to form a straight line in the energy region of high photons whose optical band-gap is given by the X-axis intercept. It can be observed that the band gap is improved with respect to the sulfurization. It clearly emphasized the direct band gap of CZTS after sulphurization was found to be 1.5042 eV whereas the direct band gap before sulphurization was 1.6077 eV. It has been reported that CZTS nano-crystals of band gap $\sim$ 1.51 eV are able to contribute quantum confinement [10]. This value is much lower than those reported earlier 1.56 eV [11].

![Figure 14: Band gap of CZTS before sulphurization](image)

**Figure 14:** Band gap of CZTS before sulphurization
4. Conclusion

An feasible synthesis method is efficaciously used to fabricate a phase pure Cu2ZnSnS4 (CZTS) absorber layer using thermal evaporation method. It was observed that crystallinity of CZTS thin films was improved after sulfurization. The optimised CZTS thin films showed tremendous optical and electrical properties and it can be used in Photovoltaics. The binary sulphide phase was analysed using XRD and AFM and reported the valuable infromation. In addition, bandgaps of CZTS corresponding to different thicknesses were calculated. Transmission measurements and band gap energy of the CZTS film confirm its applicability to solar cells. Therefore, it can be determined that the various considerations are essential (thickness, annealing temperature, atmosphere) to develop the control of phase, composition and accordingly the productivity of solar cells.

By adopting thermal evaporation technique conferred above, it may be possible to achieve large area CZTS thin film photovoltaics with a comparatively low cost.

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