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Synthesis and characterization of spin coated CZTS Thin films for solar cell applications

Abubakar A Sifawa* and Anas Shehu

Department of Physics, Sokoto State University Sokoto, Nigeria

***Corresponding author's email:**

aasifawa13@gmail.com

In recent time, the stoichiometric kesterite Cu_2ZnSnS_4 (CZTS) have been successfully synthesized on a clean soda lime glass substrates by spin coating technique. The structural, morphological and optical properties of the prepared sample have been studied via; X-ray Diffraction (XRD), Raman Spectrum, Field Emission Scanning Electron Microscope (FE-SEM), Energy Dispersive Spectrometer (EDS) and UV-Visible Spectroscopy respectively. The XRD pattern showed single phase of kesterite structure with dominant peak at (113) plane. The FE-SEM analysis revealed the texture structure for kesterite CZTS thin film. The optical band gap was found to be 1.50 eV matched well with bulk CZTS which is suitable for an absorber layer in thin films solar cell applications.

Keywords: CZTS, X-ray diffraction, Spin Coating technique, Band gap, Texture structure.

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1. Introduction

Cu_2ZnSnS_4 (CZTS) a promising semiconductor for low cost thin film solar cells has emerged due to its considerable environmental friendly, earth abundant nature with excellent and physical properties such as high absorption coefficient in the visible region (>10^4 cm^{-1}) and an energy band gap 1.5 eV which is very close to the optimum value for the absorber layer of thin film solar cells and low thermal conductivity [1], [2]. It derived from the CIGS structure by the isoelectronic substitution of two In (or one In and one Ga) atoms by one Zn and one Sn atom. As a consequence, CZTS has some similar properties as CIGS. The availability of Cu, Zn, Sn and S in the earth's crust are ~ 50, 75, 2.2 and 260 ppm respectively and the availability of In is only ~ 0.049 ppm [3], and all the constituents of CZTS are composed of only non-toxic and abundant elements in the earth's crust unlike CIGS (or other materials such as CdTe). The price and availability of indium in CIGS and tellurium in CdTe, as well as toxicity of cadmium have shorten their commercial quantity thus, became a necessity to search for alternative thin film solar absorber materials. Intrinsic point defects in CZTS make its conductivity p-type. Crystal structure of CZTS can allow some deviation from stoichiometry [4] making its deposition process easier. Also, grain boundaries in CZTS thin films are favourable to enhance the minority carrier collection [5]. The power conversion efficiency of CZTS is still considerably lower than CIGS and CdTe, with laboratory cell records of 11.0 % for CZTS and 12.6 % for CZTSSe as of 2019 [6]. There have been some of the reported CZTS film deposition techniques by both physical and chemical vapour deposition methods such as atom beam sputtering, thermal evaporation, sputtering and sequential evaporation, co-evaporation, multi-stage evaporation, pulsed laser deposition and sol-gel processing [7], [8], chemical bath methods [9], spray pyrolysis [10], [11] and spin coating methods [12] etc. Among these methods, spin-coating is a versatile and low cost, the techniques were very attractive with simple construction and large scale deposition of different semiconductors thin films.

In this work, we explore a simple approach based on the preparation of CZTS thin film using the highly stable nontoxic precursor solution by spin coating technique on soda lime glass substrate. By this low-price procedure the CZTS absorber material can be prepared easily, which may be useful for solar cell applications. The physical properties such as structure, phase evolution, morphology and stoichiometry composition were also studied.

2. Experimental

2.1 Sample Preparation

In the present work, soda lime glass were used as substrates. The substrates were cleaned. Firstly by degreasing of the surface to eliminate any organic residuals using trichlorethylin. Secondly by dipping in an ultrasonic acetone bath for 20 minutes to remove the residuals of trichlorethylin, and then rinsed with deionized water and drying by purging in nitrogen gas. CZTS precursors were prepared by using the mixture of cupric chloride (2M), zinc Chloride (1M), stannic chloride (1M) and thiourea (8M) and few drops of monoethanolamine (MEA), as precursor materials to deposit CZTS films on a suitably cleaned soda lime glass substrate. A clear yellow sol-gel was formed after being stirred at 50°C for 30 minutes and filtered and sealed for Spin coating deposition. Spin coating was employed to deposit the CZTS precursor on soda lime glass substrate at 3000 rpm for 30 s. Then the wet films were baked at 100°C for 10 minutes and cool it. The process were repeated 4 times to obtain a suitable thickness of CZTS. Compressed CZTS film annealed at 320°C for 30 minutes. The samples were allowed to cool to room temperature and then taken out for the characterization.

3. Results and Discussions

3.1 Structural Properties of as-deposited CZTS thin films

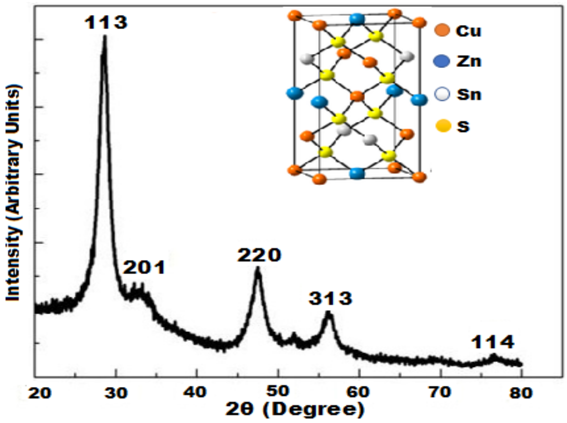

Fig.1. XRD of as-deposited CZTS thin film

XRD measurements were done on CZTS films as shown in the Fig. 1. Five broad peaks were observed corresponding to (113), (201), (220), (313) and (114), respectively indicating that these films were polycrystalline structure with no other secondary phase/impurities present. The dominant peak is (113), showing that, the crystallites in the film have preferential orientation in (113) direction, and closely matched the standard data (JCPDS card No. 26-0576). The XRD peaks were indexed using JADE software (Jade 5.0). (SRMIST, Research Institute India).

The mean crystallite grain size (D) of CZTS thin film can be calculated by the Scherrer formula,

$$D = \frac{0.9\times\lambda}{\beta\times\cos\theta} \quad (1)$$

where, λ is the wavelength of the radiation (0.15406 nm), β is the full width at half maximum of the film diffraction peak at 2θ in radians and θ is the Bragg's diffraction angle. The film thickness of as deposited CZTS was determined by using the standard procedure [13] and it was found to be 1.52 µm.

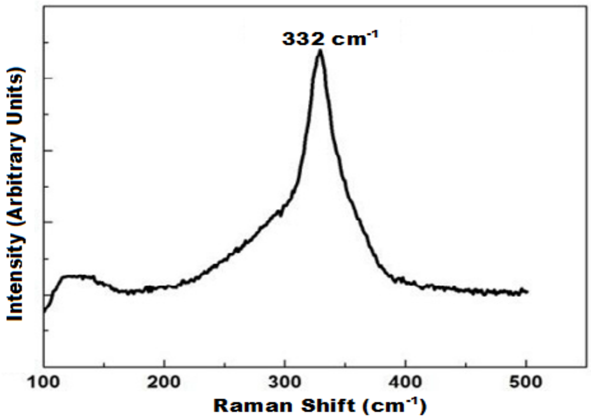

Fig.2. Raman spectrum of as-deposited CZTS thin film

To further confirm the phase formation obtained from XRD, Raman analysis were conducted as shown in the Fig. 2. Raman spectroscopy have recently been used by a number of researchers around the globe to investigate the phase purity of material. The Raman analysis of as-deposited CZTS thin film were studied. The peak positions in the collected spectra that gives information about the corresponding phase, was observed at (332 cm^{-1}), which indicate that, it is of single phase with no any other sulphide compounds present. Hence, both XRD and Raman studies confirmed the formation of good quality polycrystalline CZTS film.

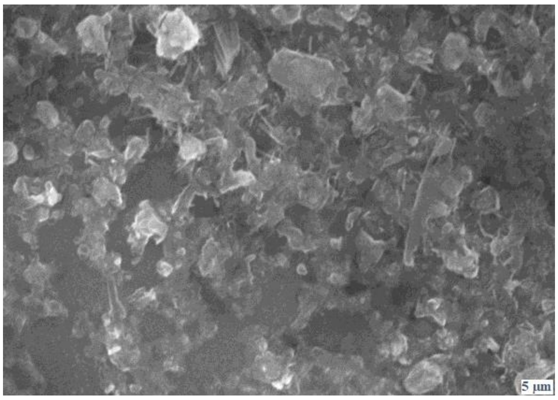

Fig.3. FE-SEM Image of as-deposited CZTS thin film

Fig. 3 show the surface morphology of as-deposited CZTS thin film sample. FE-SEM images indicate clearly that, the texture structure was formed for the as-deposited CZTS thin films. EDS in Table 1 confirmed the purity of the sample by detecting only copper, zinc, tin and selenium elements which is in good agreement with XRD analysis (Fig. 1)

Table 1: Elemental composition of as-deposited CZTS thin film

Element	**Atomic %**	**Weight %**
Cu	23.14	18.76
Zn	11.66	9. 74
Sn	11.28	17. 11
S	35.93	36. 6

3.2 Optical properties of as-deposited CZTS thin film

The uncertainty of crystal structure and basic composition of various candidate of solar cells, leads to the research difficulties of optical, material and electrical properties, such as width of energy band, density of states, doping behaviour, and transport properties. The optical properties of polycrystalline CZTS thin film was studied by optical transmittance spectrum on glass substrate at room temperature to obtain the absorption coefficient and the band-gap energy as shown in the Fig. 4.

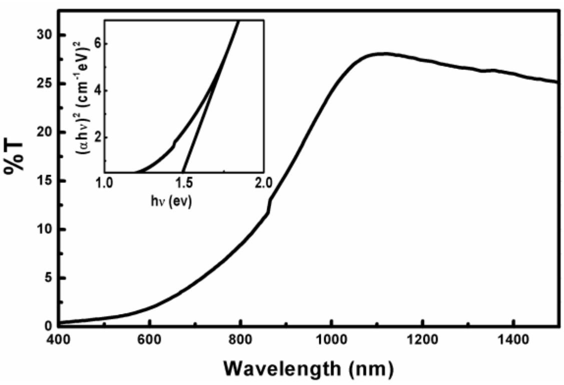

Fig.4. Transmittance of as-deposited CZTS thin film (Band gap estimation)

The absorption coefficient of the as-deposited CZTS thin film is larger than ~10^4 cm^{-1} in the visible region. The optical band gap energy was obtained using the following equation [14].

$$(\alpha hv) = A(hv - E_g)^n \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where α is the optical absorption coefficient, A is a constant that depends on the transition probability, E_g is the optical band gab and n = ½ for direct transition. The band gap were obtained by extrapolating the straight-line of the plot $(\alpha h\nu)^2$ versus photon energy (h*v*). Therefore, the estimated optical band gap of spin coated CZTS thin film on suitably cleaned soda lime glass substrate is 1.5 eV which is in good agreement and well suited for solar cell applications [15].

3.3 Electrical properties of as-deposited CZTS thin film

The electrical properties of the CZTS thin films have been measured using Vander Pauw measurements which indicates that as-deposited CZTS thin film exhibits a p-type conductivity with resistivity ~0.014 Ω-cm, carrier concentration ~7.9×10^{18} cm^{-3} and hall mobility ~5.44 cm^2 V^{-1} s^{-1} at room temperature matching well with the studied carried out by [16].

4. Conclusion

Cu_2ZnSnS_4 (CZTS) thin film have been successfully deposited by spin coating technique. The film shows a single CZTS phase with good crystallinity and preferential orientation in (113) plane. FE-SEM image shows clearly, the texture structure were formed. The EDS reveals that as-deposited CZTS thin film composed of only copper, zinc, tin and selenium element. Optical study confirmed the film has an optical band-gap of 1.5 eV comparable with the light spectrum. The study on Electrical properties indicates that as-deposited CZTS thin film exhibits a p-type conductivity with resistivity ~0.014 Ω-cm, carrier concentration ~7.9×10^{18} cm^{-3} and hall mobility ~5.44 cm^2 V^{-1} s^{-1} at room temperature. The results shows that the fabrication process of CZTS compound which is of low cost, and nontoxic could be easily prepared by this technology for the solar cell applications. All the characterization were conducted at (SRMIST, Research Institute India).

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Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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