



Cu₂ZnSnS₄ SOLAR CELL ABSORBER LAYER FOR OPTIMIZED GRAIN GROWTH

R.Malathi, S.Sakthivel, N.Adhilajahan, T.Shalini

Thin Film Physics and Nano Science Laboratory

PG and Research department of Physics

Rajah Serfoji Govt.College (Autonomous), Thanjavur, Tamilnadu, INDIA.

Affiliated to Bharathidasan University, Tiruchirappalli.

Abstract

Kesterite solar cells appear to be the most promising for thin film solar cell. The thin films of Cu₂ZnSnS₄ (CZTS) have been successfully deposited on ordinary glass substrates by blade coating technique. Kesterite solar cell was fabricated using the REMI simulator, in which different CZTS absorber layer. CZTS films were prepared by blade coating of a solution by dissolving of Copper chloride, Zinc chloride, Tin chloride dihydrate and Thiourea in Ethanol with distilled water. The X-ray diffraction studies showed the formation of kesterite phase with the peaks corresponding to (002), (112), (105) and (224). These studies are investigated by surface morphology, structure analysis, optical properties and thickness measurement. Therefore CZTS show better power conversion efficiency which is applicable for kesterite solar cells.

Keywords: CZTS thin films, Kesterite, Blade coating, Solar cell

INTRODUCTION

Cu₂ZnSnS₄ (CZTS) is one of the most promising absorber layer materials for low-cost thin film solar cells due to its semiconductor properties such as P- type conductivity [1], direct band gap and high absorption coefficient, as well as the earth abundant and nontoxic constituent element [2]. This factor together led to a quick development in the CZTS based thin film PV research in last few years, which is evident from the rise of record power conversion efficiency to 12.6% [3] in very short span. The major challenge in the fabrication of CZTS based solar cell is the deposition of defects- free, stoichiometric CZTS film without allowing other parasitic secondary phases to form [4].

Further, it is equally important to achieve such a film using the deposition process, which is cost-effective and commercially scalable for sustainable thin film PV technology [4]. Kesterite have a tetragonal crystal structure, with copper, zinc and tin ions occupying specific sites in the crystal lattice. But copper zinc

has almost identical ionic radii, and both have tetrahedral coordination, so it's all too easy for them to swap places, upsetting the electronic properties of the material [5].

Numerous research articles about kesterite appeared during the last 5-10 years an overview of the rapid development of the kesterite solar cells can be found in a recent review by Todorov. The solution based chemical synthesis is a potential thin- film deposition technique meets these criteria. Interestingly CZTS is one of the rare materials for which the record efficiency is achieved using chemical deposition.

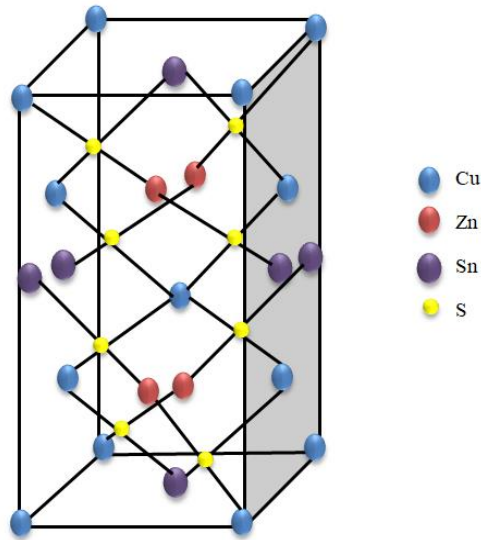


Figure1. Structure of Copper Zinc Tin Sulfide

The main component of the solar cell is CZTS, a semiconductor material having a suitable band gap, which harvest the solar light and convert directly into usable electricity. Kesterite solar cells, based on the prototypical absorber $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), are cheap, nontoxic, and chemically stable, thus rendering them promising, based-Si photovoltaic technologies. Hence the study on low- temperature deposition of CZTS using suitable chemical synthesis becomes particularly significant.

Many groups have employed wet chemical methods for CZTS thin film deposition such as spray pyrolysis [6], Sol-gel [7], Spin coating [8], Successive Ionic Layer Adsorption and Reaction (SILAR) [9], dip coating [10], Blade coating [11]. In this work we report CZTS thin film preparation by blade coating technique on glass substrate.

Kesterite structure

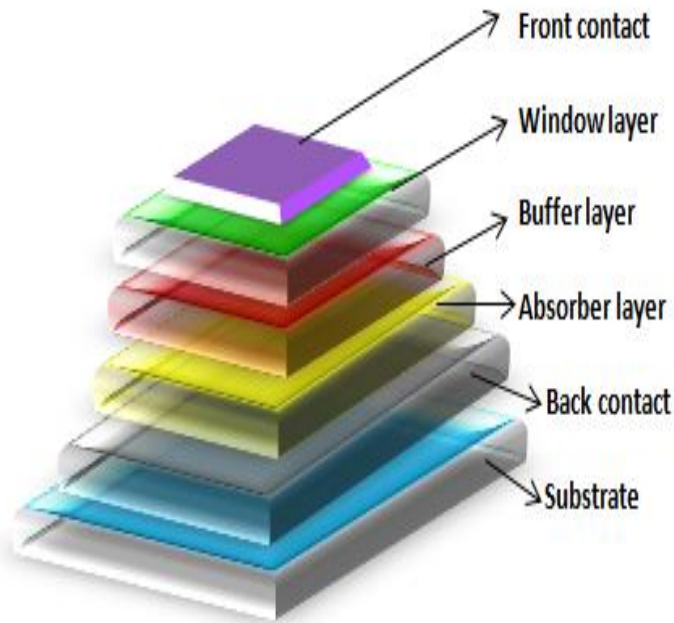


Figure 2 schematic diagram of kesterite structure

EXPERIMENTAL METHOD

Synthesis

The dissertation comprises of synthesis and characterization of CZTS film prepared by blade coating technique. The present work aimed to prepare CZTS film kesterite solar cell by blade coating method for different concentrations.

$\text{Cu}_2\text{ZnSnS}_4$ thin films were deposited by blade coating technique. To take cupric chloride or Copper chloride (2M), Zinc chloride (1M), Tin chloride dihydrate (1M), and Thiourea (8M). These materials are dissolved in Ethanol with distilled water in the ratio 70:30%. Clear yellow solution was formed after being stirred at 50°C for 40 minutes. The solution was coated in glass substrate with blade coating technique. The samples were annealed in 70°C for 5 minutes. Finally the samples were 24 hours at room temperature. The film thickness was calculated. The fabrication process of CZTS film by blade coating technique is shown by flow chart.

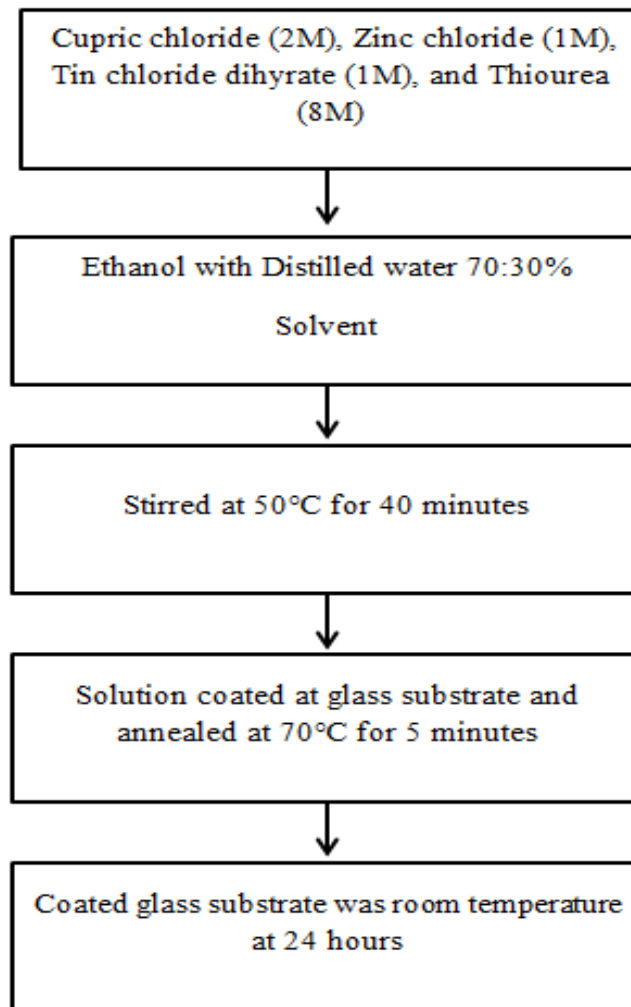


Figure 3 Flow chart of experimental process

Fabrication

The glass substrates were cleaned with distilled water and allow to heat until it evaporates. Then the glass substrates are cleaned with acetone. The precursor solution was coated the glass substrate. Dip the glass rod in the solution. Now take the glass substrates and drop the precursor solution drop wise nearby drop on the substrate with help of glass rod till spread the precursor solution. Screen the solution on the glass plate using blade. The three concentrations give better coating of CZTS thin film kesterite solar cell. Each glass plate weight is measured before and after coating.

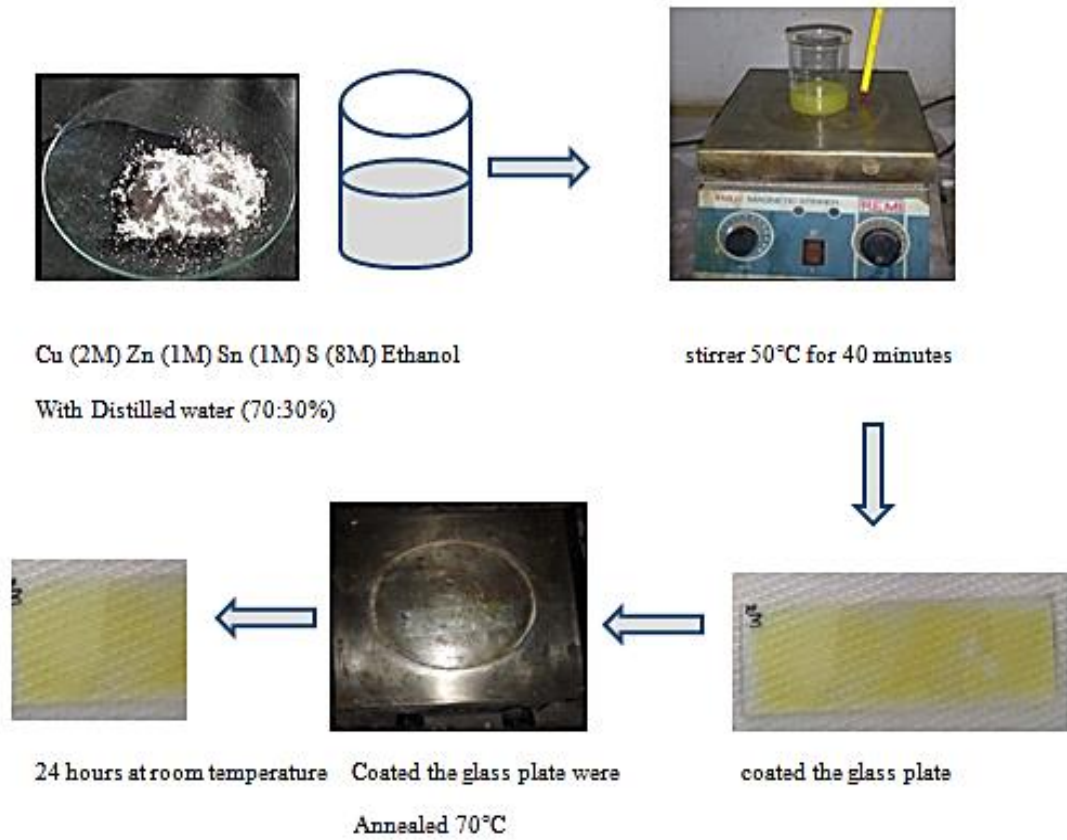


Figure 4 Present process works

Result and discussion

UV-Vis spectrometer

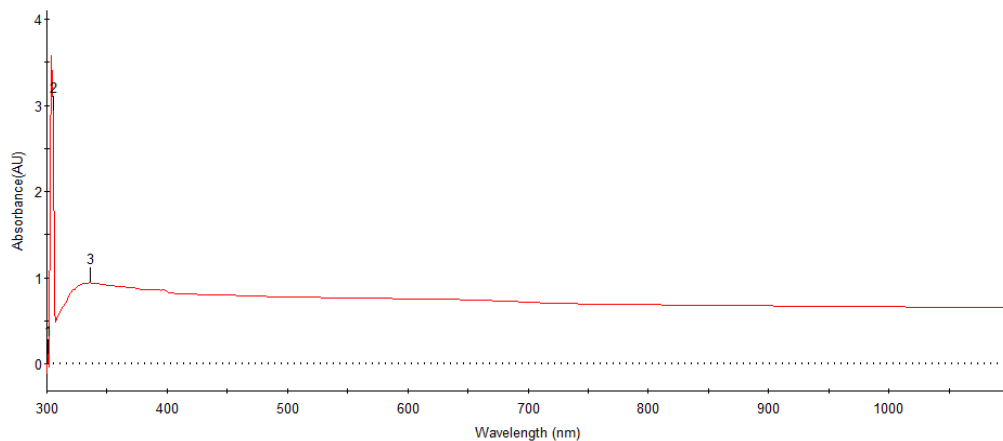


Figure 5(a) Optical absorbance of CZTS kesterite layer of solar cell

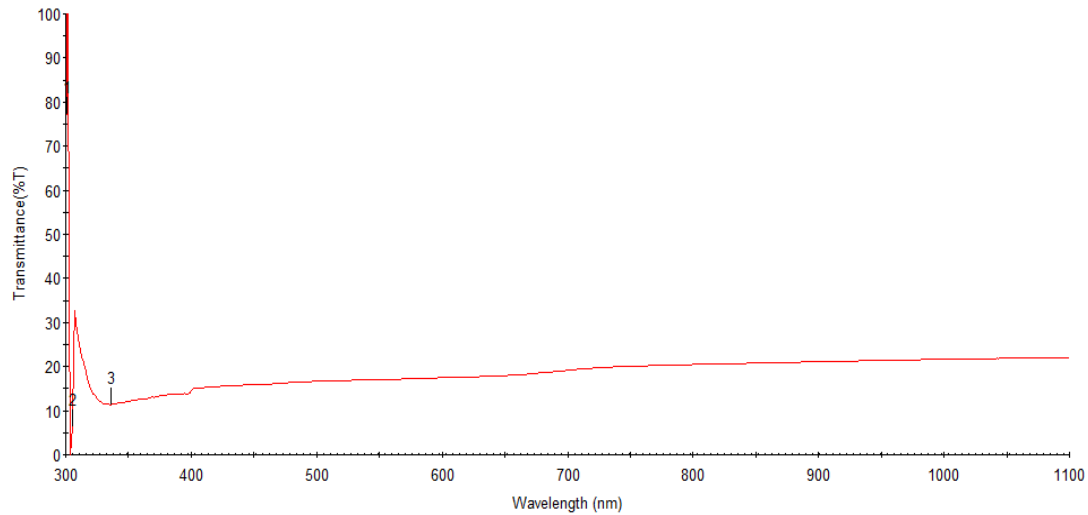


Figure 5(b) Optical transmittance of CZTS kesterite layer of solar cell

The optical properties have been studied by using UV-Visible spectrometer. The figure 5(a) and 5(b) are shown as an absorbance and transmittance measurements range 200-800 nm. However, this film has low absorption and high transmittance within the region of the spectrum.

The band gap energy can be calculated of CZTS thin film kesterite layer of solar cell is 3.96eV respectively.

X- Ray Diffraction analysis

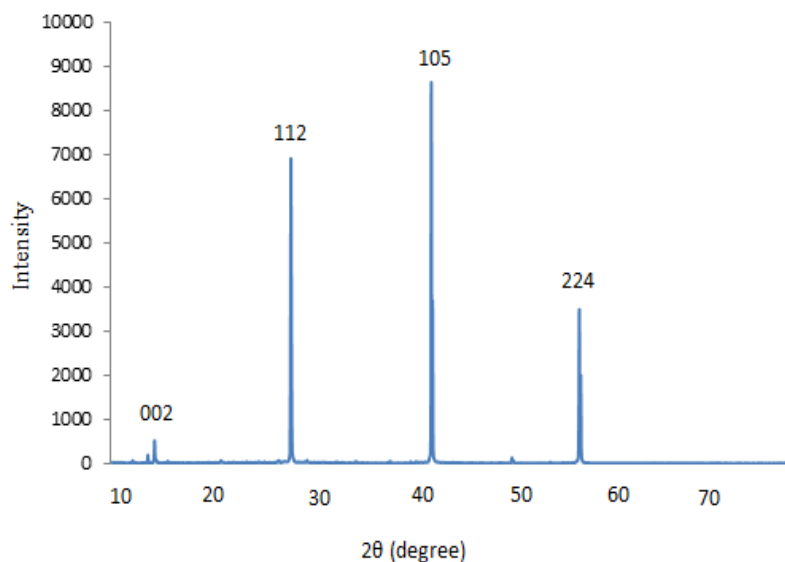


Figure 6 X-ray diffractogram spectrum of CZTS thin film

The X-ray diffraction figure 6 shows the CZTS thin film kesterite layer annealed at 300°C. The structural properties of the CZTS coated thin film has been studied using X-ray diffraction (XRD) analysis. Which is carried out by using a $\text{CuK}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiated

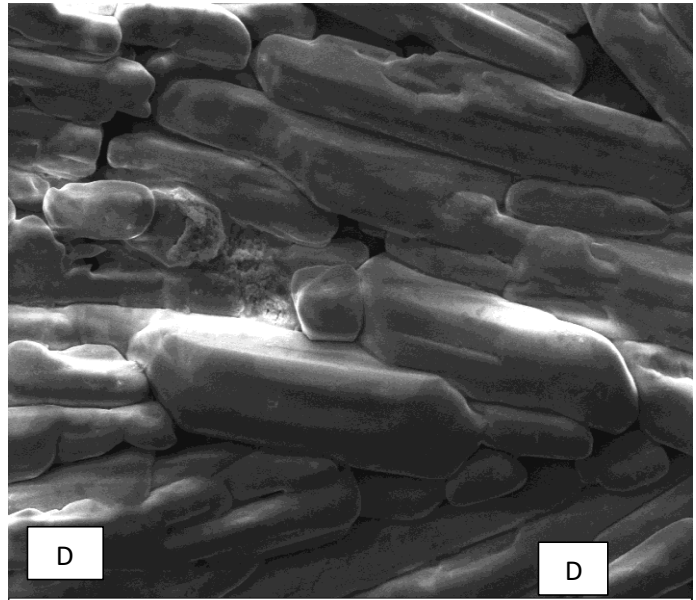
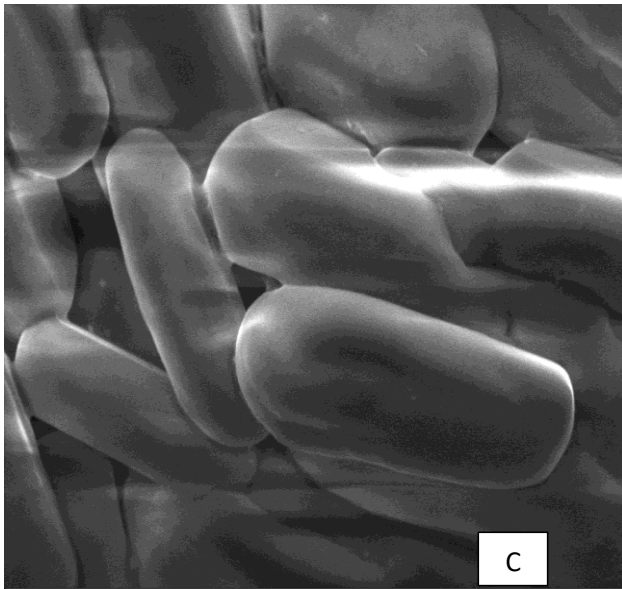
from 10° to 60° of 2θ . The obtained X-ray diffraction patterns of CZTS thin film sample were compared with JCPDS file number [JCPDS 96-900-4751]. The X- ray diffraction peaks of 2 theta.14.4105°, 28.4840°, 42.9978°, 58.1821° are compared. The peaks corresponding to the planes are (002), (112), (105) and (224). The average grain size is 36.0186 nm.

Scanning Electron Microscopy Analysis

A

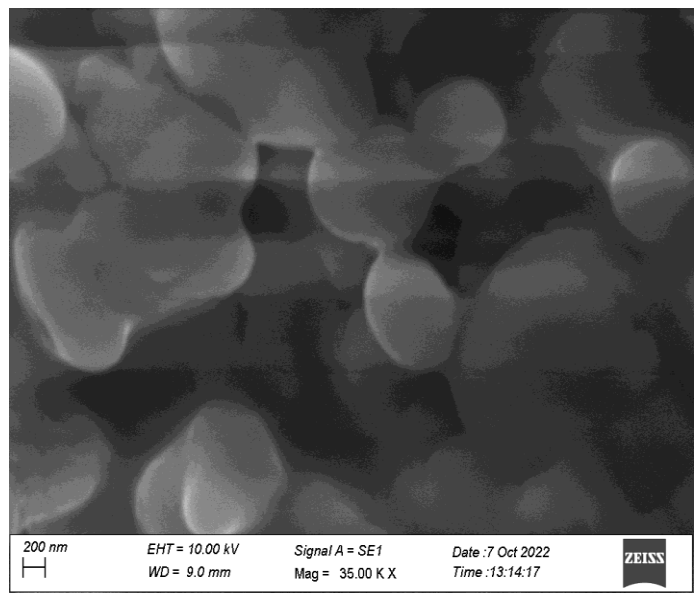
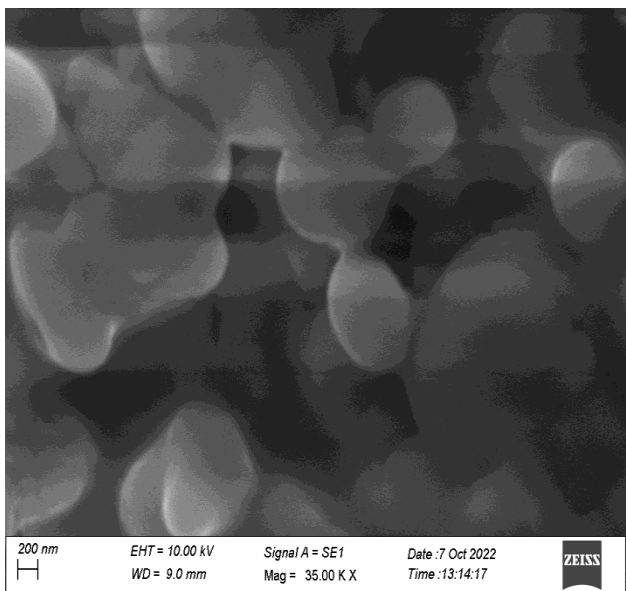
B

Figure 7 Scanning Electron Microscopic Image of CZTS samples



C | 2 μ m | EHT = 10.00 kV | Signal A = SE1 | Date :7 Oct 2022 | ZEISS
WD = 9.0 mm | Mag = 10.00 K X | Time :13:09:21

D | 10 μ m | EHT = 10.00 kV | Signal A = SE1 | Date :7 Oct 2022 | ZEISS
WD = 9.0 mm | Mag = 2.50 K X | Time :13:09:57



200 nm | EHT = 10.00 kV | Signal A = SE1 | Date :7 Oct 2022 | ZEISS
WD = 9.0 mm | Mag = 35.00 K X | Time :13:14:17

200 nm | EHT = 10.00 kV | Signal A = SE1 | Date :7 Oct 2022 | ZEISS
WD = 9.0 mm | Mag = 35.00 K X | Time :13:14:17

The SEM morphological image of CZTS was shown in figure 7 revealed that the film annealed at 300°C. The sample CZTS characterized by the presence of grains of the order 2µm, 10 µm, 200nm. The higher temperature annealed at 300°C presence of irregular shape of grains are presents in the entire sample surface. SEM image is in capsule structures.

Energy Dispersive X-ray Spectroscopy Analyses

The EDX results shown in Table 1 confirm proper elemental composition in the blade coated film.

Element	Atomic %
Cu	10.95
Zn	1.31
Sn	0.99
S	11.56

Table 1 Elemental composition of the blade coated CZTS films

Fourier Transform Infrared Spectroscopy

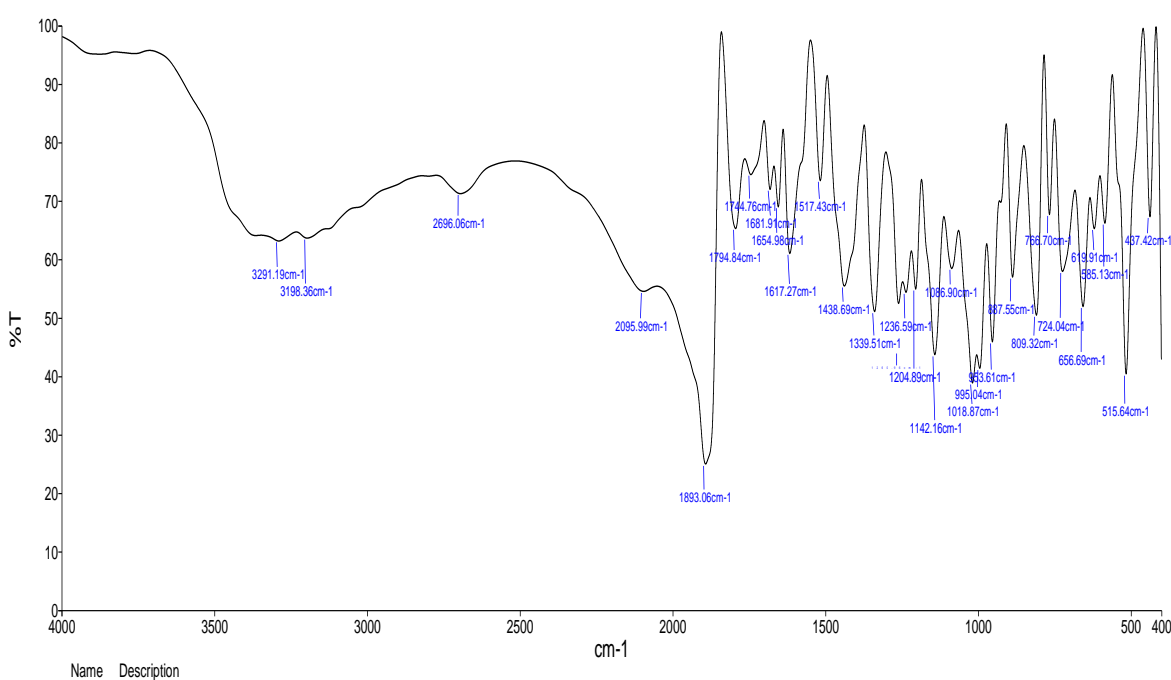


Figure 8 FTIR spectrum of CZTS layer for kesterite solar cell

Figure 8 shown in FTIR spectrum of CZTS kesterite layer of solar cell. The weak peak 1893.06cm^{-1} was indicated C-H bending of aromatic compound. 3291.19cm^{-1} are absorbed stretching C-H group in alkyne. 1794.84cm^{-1} , 1681.91cm^{-1} and 1654.98cm^{-1} peaks were absorbed stretching C=O groups in acid halide, conjugated aldehyde and conjugated ketone. 2095.99cm^{-1} peak are absorbed stretching N=C=N group in carbodiimide. 1617.27cm^{-1} peak are absorbed stretching C=C group in conjugated alkene. 1517.43cm^{-1} peak are absorbed stretching N-O group in nitro compound. 1236.59cm^{-1} , 1204.89cm^{-1} 1142.16cm^{-1} and 1086.90cm^{-1} peaks were absorbed stretching in C-O groups in alkyl aryl ether, vinyl ether, aliphatic ether and secondary alcohol. 1339.51cm^{-1} peak are absorbed stretching S=O group in sulfate. The medium peak is 766.70cm^{-1} absorbed C=C bending in alkene. 995.04cm^{-1} strong peak are absorbed C=C bending of alkene. 809.32cm^{-1} and 585.13cm^{-1} peak were absorbed stretching C-Cl and C-I groups in halo compound. Finally 656.69cm^{-1} peak are absorbed stretching C-Br group in halo compound.

Fluorescence spectroscopy

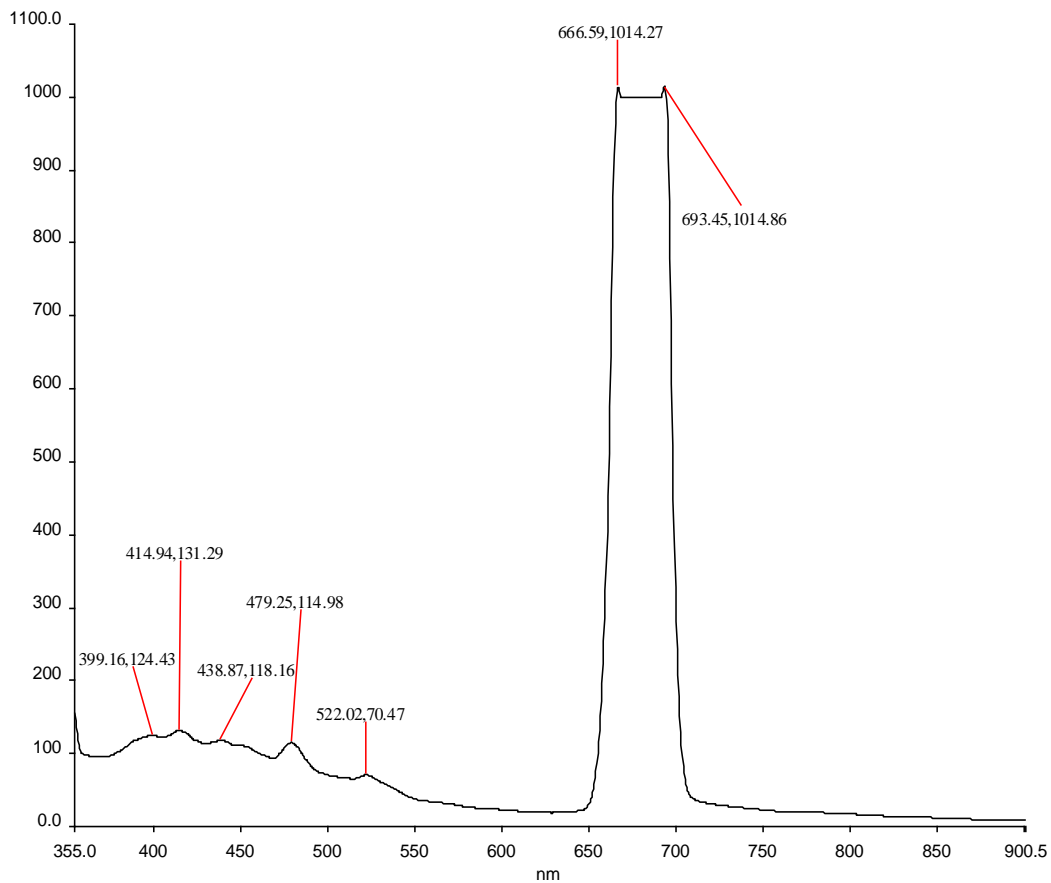


Figure 9 Fluorescence emission spectra of CZTS with excitation wavelength

The fluorescence spectroscopy was shown in figure 9 after excitation by photons the electron-holes recombine at various pressures. The recombination is closely related to the electronic structures and crystal structure. The curve shows seven peaks presented. The emission peaks are around 124.43 nm, 131.29 nm, 118.16 nm, 114.98 nm, 70.47 nm, 1014.27 nm and 1014.86 nm. The peak at 124.43 nm can be ascribed as self-dropped excitons localized on the kesterite layer and the peak at 1014.86 nm is associated with oxygen vacancies.

Photoluminescence

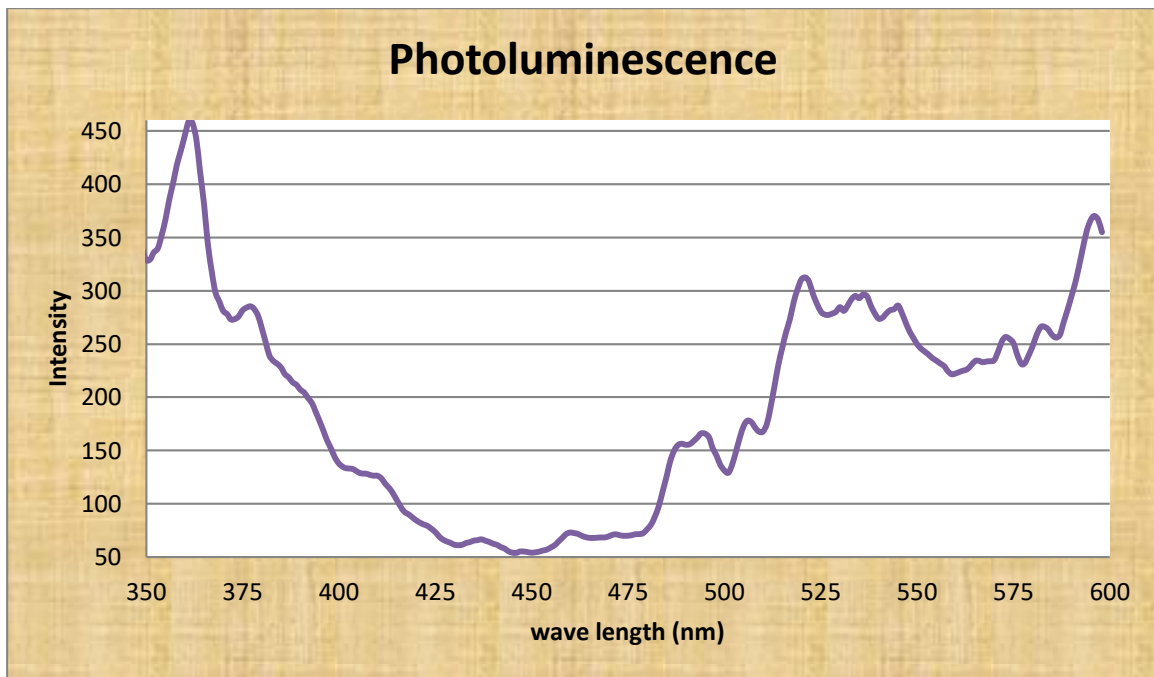


Figure 10 photoluminescence spectrum of CZTS layer

The photoluminescence was shown in figure 10. Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. The excitation energy and intensity are chosen to probe different regions and excitation concentrations in to the sample. The curve shows nine peaks are presented. The peaks are 360nm, 373nm, 491nm, 504nm, 518nm, 541nm, 571nm, 581nm, and 594nm.

Thickness measurement

Film thickness can be used in surface profilometer instrument. Surface profilometer is a contact measurement technique in which a diamond- tipped styles is used to measure surface topography as it moves across the surface of a specimen. It is common to use to profilometer to measure film thickness and surface texture.

The average thickness is 28.59 μ m.

Conclusion

CZTS kesterite layer of solar cell were deposited on to cleaned glass substrate from aqueous solution using blade coating technique. This technique is simple, economic and offers a possibility for suitable area depositions. A thin is well adherent and shows a good stability. Prepared film was characterized by using FTIR, UV, Fluorescence spectroscopy, XRD, Photoluminescence and thickness measurement. The film thickness is 28.59 μ m can be obtained. FTIR spectrum of CZTS kesterite layer of solar cell studies shows the vibrations of the C-N group are appeared. The vibrations of C-Br group are appeared. The O-H alcohol groups are appeared and fourteenth strong peaks were appeared. XRD pattern confirms polycrystalline nature of the CZTS kesterite layer of solar cell with different grain sizes. XRD average grain size is 36.0186 nm. The highest intensity peak is 693.45 nm. The fluorescence spectroscopy peaks of CZTS thin film for kesterite solar cell absorber layer. The wavelength cut-off is 335nm. The highest intensity peak is 360 nm. The photoluminescence spectrum peaks of CZTS thin film kesterite solar cell absorber layer.

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