

Effect of annealing atmosphere on structural and optical properties of CZTS thin films prepared by spin-coating

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Abstract

Copper zinc tin sulfide (CZTS) thin films were deposited by spin coating procedure of a sol-gel prepared from the solution of copper (II)chloride, zinc acetate, tin (II) chloride and thiourea in 2-methoxyethanol followed by annealing under two different atmospheres viz. N₂ gas and Sulphur (S) powder at 530 °C for 5 minutes. The effect of different annealing atmosphere on the structural and optical properties of the CZTS thin films were investigated. The X-ray diffraction study showed higher intensity peaks for films annealed under N₂ gas ambient. SEM study revealed that the surfaces of the films in both cases are non-uniform. Films annealed in N₂ gas atmosphere showed better absorption coefficient (exceeding 10⁴ cm⁻¹ in the visible region) than the sulphurized ones. The optical band gap (E_g) of the films were found to be in the range of 1.46 - 1.53 eV.

Keywords: CZTS thin-film; Spin coating; X-ray diffraction; Scanning electron microscope; UV-visible spectrometry

Introduction

Emerging Cu₂ZnSnS₄ (CZTS) based solar cell has drawn the attention of the researchers due its earth-abundant low cost non-toxic raw materials and it is considered to be the best replacement of the conventional CIGS thin-film solar cell which has rare earth constituent Indium (In) and highly expensive Gallium (Ga) in its composition (Siebentritt, 2013). Copper zinc tin sulfide thin film plays the vital role of capturing sunlight and converting it into electricity. Structural, optical and electrical properties of this layer have a profound impact on the overall performance of the solar cell. To date, a list of deposition techniques has been applied to deposit this CZTS thin film. Among these, the high vacuum techniques used are pulse laser deposition (Agawane *et al.*, 2014), co-evaporation (Tanaka *et al.*, 2006), sputtering (Wang *et al.*, 2013; Zhou *et al.*, 2013). Non-vacuum process includes spray pyrolysis (Valdes *et al.*, 2014), electro-deposition (Li *et al.*, 2015), spin coating (Kahraman *et al.*, 2013), successive ionic layer adsorption and reaction (Suryawanshi *et al.*, 2014), and chemical bath deposition (Wangperawong *et al.*, 2011). Of these techniques, spin coating is frequently used to deposit CZTS absorber layer because of its simplicity for having less steps and also its ability to produce a uniform stable thin film (Kahraman *et al.*, 2013). The precursor solution used in majority of them is sol-gel. Sol-gel prepared spin coated thin-film also subjected

to annealing chamber for robust and physically stable film where it experiences different types of inert atmosphere such H₂S (Min *et al.*, 2009), N₂ gas (Jiang *et al.*, 2014; Jiang *et al.*, 2011) and S powder (Su *et al.*, 2014). But using H₂S gas in annealing chamber creates toxic hazard atmosphere (Min *et al.*, 2009).

In this study, CZTS absorber layer has been prepared through a sol-gel spin coating process followed by annealing in two different atmospheres (N₂ gas annealed and sulphurized) and the effect of these two different annealing conditions on their structural, morphological and optical properties were studied.

Materials and methods

Cu₂ZnSnS₄ thin films were deposited on soda lime glasses by spin-coating method. The chemicals used were copper (II) chloride (2.05 M) (VWR international, England, 99%), zinc acetate (1.13 M) (Scharlu, Spain, 99%), tin (II) chloride (0.75M) (Scharlu, Spain, 99%) and thiourea (16.28 M) (Merck, Germany, 99%) in 2-methoxyethanol (10 ml) (Merck, Germany, 98%). At first, the solutions of metal salt were mixed at room temperature. A magnetic stirrer bar was placed inside the beaker for uniform mixing. Then the solution temperature was gradually increased. When the temperature reached at 45°C, thiourea was added to the

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solution and after that the temperature was again increased and fixed at 60°C. Two drops (~5µL) of mono ethanol amine (MEA) was added to the solution as stabilizer. Then the solution was stirred for 90 minutes and gradually the colorless transparent solution turned into a transparent yellow sol-gel over time. Then it was aged for more than 18 hours at room temperature before being used in the spin coating process. A further stirring of the solution was done at 55°C for 20 minutes before spin coating. Spin coating was done in a two-step process. In the first step, the spin coating was performed at 600 rotations per minute (rpm) for 10 seconds. In the second step, the spin coating was done at 1800 rpm for 20 seconds. Then the films were dried at 250 °C but, the time duration used was different for each film sample. This whole coating process was repeated three times

for the films to obtain desirable thickness. To realize the effect of annealing atmosphere i.e., the effect of N₂ gas and S powder in annealing chamber, on structural and optical properties of sol-gel spin coated CZTS thin films, two sets of films were annealed at 530 °C (temperature ramp: 10° C per minute) for 5 minutes separately. Films were wrapped in aluminum foil with S powder inside for the annealing in S powder atmosphere. Films annealed in N₂ gas atmosphere were labeled as Sample 1, 2 and 3 with respect to their pre-annealing time of 60, 90 and 120 seconds respectively. Other films annealed in S powder at 530 °C for 5 minutes were labeled as Sample 4, 5 and 6 respectively with respect to their pre-annealing time of 60, 90 and 120 seconds respectively. Oven (Binder, USA) was used for the pre-annealing purpose. Table I illustrates the whole procedure in detail.

Table I. CZTS Deposition and process conditions used in this work

Chemicals	Pre-annealing temperature (°C)	Pre -annealing time (seconds)	Annealing conditions	Label
CuCl ₂ .2H ₂ O - 2.0545 M	250	60	In N ₂ gas at	Sample 1
Zn (CH ₃ COO) ₂ .2H ₂ O-1.13 M		90	530°C for 5	Sample 2
SnCl ₂ .2H ₂ O - 0.75 M		120	minutes	Sample 3
NH ₂ -CS -NH ₂ -16.28 M		60	at 530°C for 5	Sample 4
		90	minutes	Sample 5
		120		Sample 6

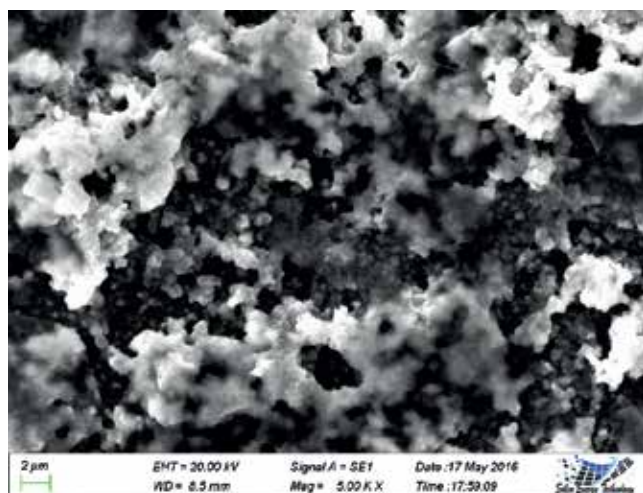


Fig. 1. SEM micrograph of N₂ gas annealed CZTS thin film

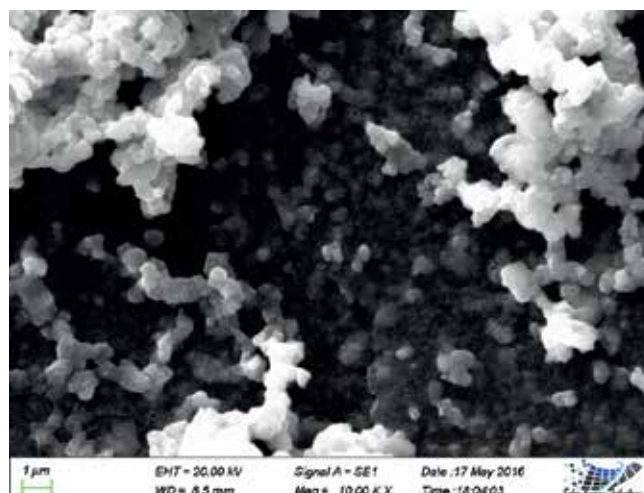


Fig. 2. SEM micrograph of sulfurized CZTS thin film

BRUKER D8 X-ray Diffractometer was used for the crystalline phase identification. The surface morphology of the as-deposited and annealed films was investigated by a 6490 JEOL JSM model scanning electron microscope (SEM). The optical parameters were estimated from data obtained using a UH4150 Spectrophotometer in the 300 – 900 nm wavelength range.

Results and discussion

Fig. 1 and Fig. 2 show the SEM micrograph of the surface of the N₂ gas annealed and sulphurized CZTS thin films respectively. Both the images confirm that the surface is coarse, large agglomeration of grains covered with clusters and consist few voids. This has occurred due to volume contraction arising from the evaporation of volatile products in CZTS precursor (Park *et al.*, 2013) (Suryawanshi *et al.*, 2014).

Fig. 3 and Fig. 4 show the EDAX spectrum of the N₂ gas annealed and sulphurized CZTS thin films respectively. Table II shows the atomic percentage of different elements present in the films under two different annealing conditions that closely matches the Cu₂ZnSnS₄(CZTS):: 2: 1: 1: 4 compositional ratios. It is evident from the table that in both

cases the films are Cu-rich and Zn-poor. But, sulphurization results in making the film even more Cu-rich and Zn-poor.

Normalized XRD pattern of all N₂ gas annealed film (Fig. 5) shows reflection peaks corresponding to the (112), (220), (312) planes of reflection. These are the characteristic peaks of the kesterite structure according to JCPDS no: 26-0575. Though the films were pre-annealed for 60, 90 and 120 seconds, all three XRD patterns were almost identical in their peak intensity. This suggests that the pre-annealing temperature did not affect the crystallinity of these three films. The normalized XRD pattern of the films labeled as ‘Sample 5’ and ‘Sample 6’ in Fig. 6 also show peaks corresponding to the (112), (220), (312) planes of reflection. These two films were pre-annealed for 90 and 120 seconds respectively. Film pre-annealed for 60 seconds at 250 °C (Sample 4) did not show any characteristic peak. There is only a broad peak around 25 degrees in the XRD pattern (Fig. 6). This confirms the poly crystalline nature of this film. For the other two films (Fig. 6) an increase in pre-annealing time results in increased magnitude of the CZTS characteristic peaks. From this we can say that the sulphurized films’ crystallinity improves with increasing pre-annealing time. The highest intensity of the characteristic peaks of the

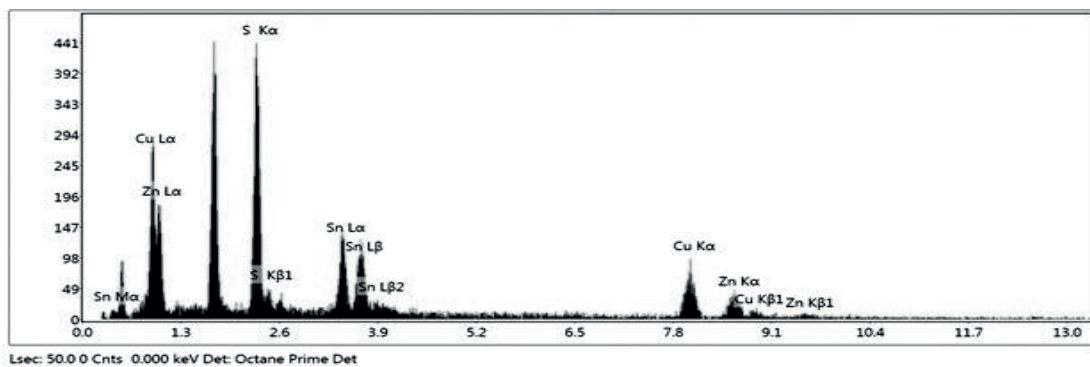


Fig. 3. EDAX spectrum of N₂ gas annealed film (Sample 2)

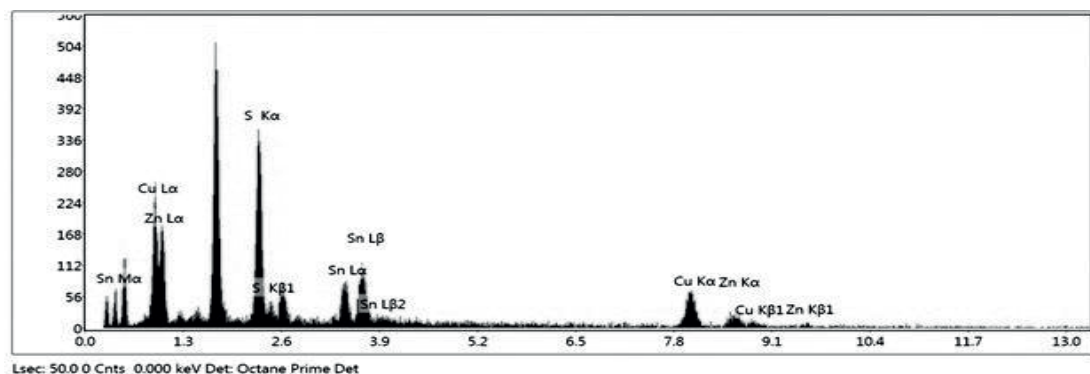


Fig. 4. EDAX spectrum of sulphurized film (Sample 5)

sulphurized film is less than that of any of the films that were annealed in presence of N_2 gas. From this it can be said that, CZTS films annealed in N_2 gas atmosphere has bigger crystallite size. Distinction between CZTS phase and secondary phases like Cu_xS , cubic ZnS and tetragonal Cu_2SnS_3 could not be made from the XRD pattern because of

the closeness of their peak intensity positions. Raman study should be carried out for this purpose.

CZTS is a very promising material for the absorber layer of a solar cell because of its strong absorption over a broad solar spectrum. The direct optical band gaps (E_g) of the CZTS

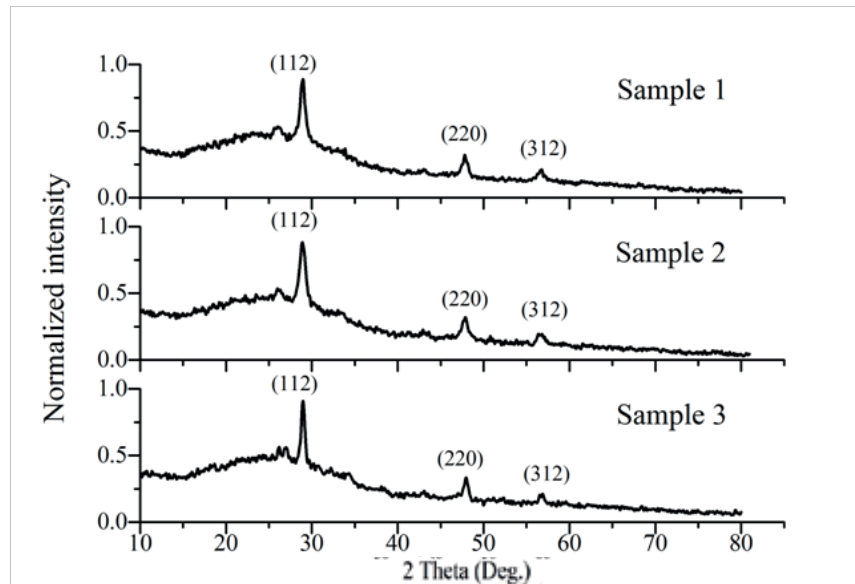


Fig. 5. XRD (vertically off-set) of N_2 gas annealed CZTS thin films

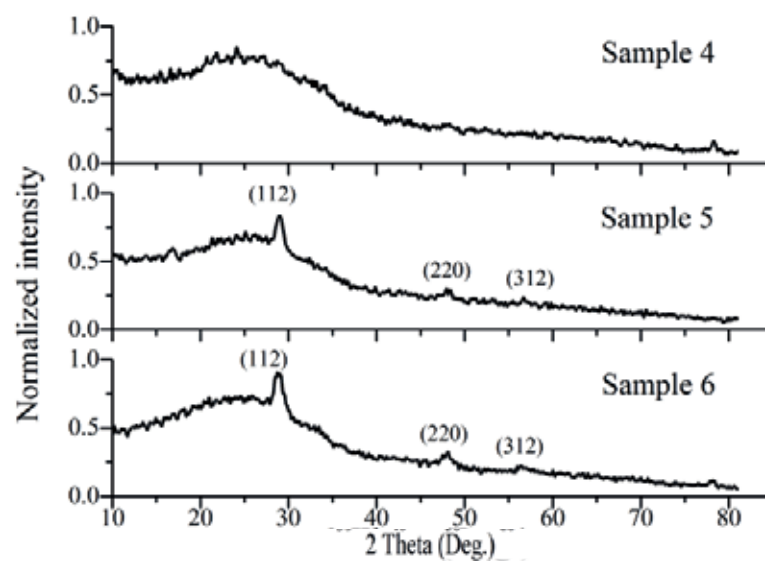


Fig. 6. XRD (vertically off-set) of sulphurized CZTS thin films

Table II. Elemental composition of the CZTS thin films from EDAX analysis

Element	Atomic Percentage (%)	
	N ₂ gas annealed films (pre-annealing time = 90 second)	Sulphurized films (pre-annealing time = 90 second)
Cu K	25.9	29.2
Zn K	16.9	13.5
Sn L	11.5	8.8
S K	45.7	48.5

thin films were determined from Tauc plot and found to be in the range of 1.46-1.53 eV (Fig. 7 and Fig. 8). Tauc plots were obtained from the absorbance spectra measured by the UV-vis spectrometry in the wavelength range of 300–900 nm.

The optical absorption coefficients calculated is shown in Figs. 9 and Fig. 10.

It is found to be greater than 10⁴ cm⁻¹ for ‘Sample 2’ and ‘Sample 3’ (Fig. 9). These optical parameters are well suited for the absorber layer of a solar cell.

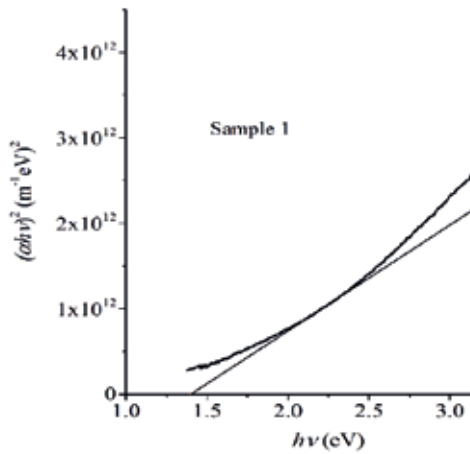


Fig. 7(a). Tauc plot-Sample 1

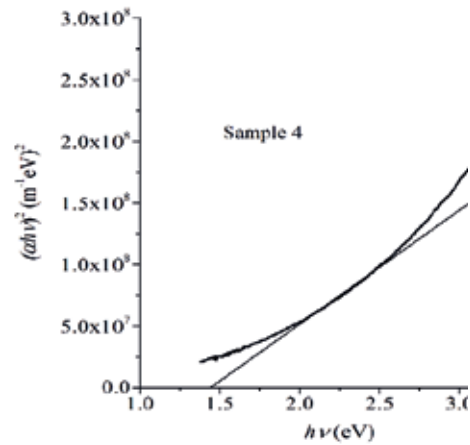


Fig. 8(a). Tauc plot-Sample 4

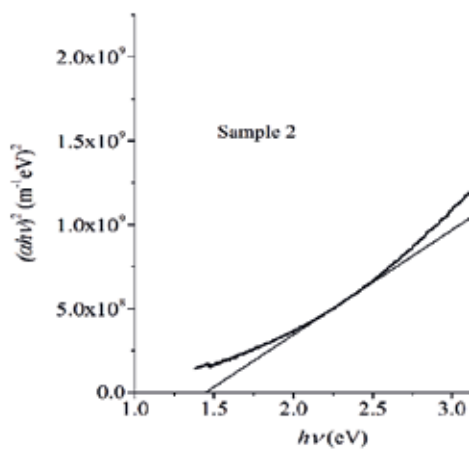


Fig. 7(b). Tauc plot-Sample 2

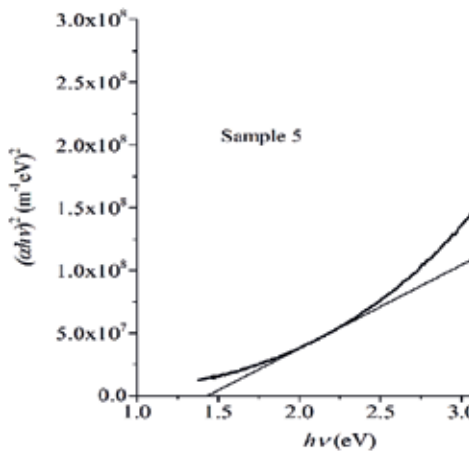


Fig. 8(b). Tauc plot-Sample 5

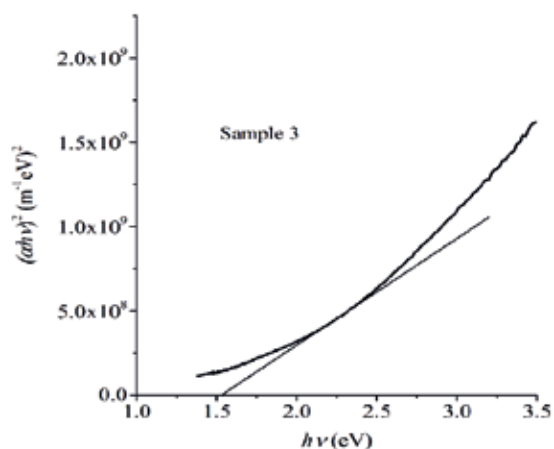


Fig. 7(c). Tauc plot-Sample 3

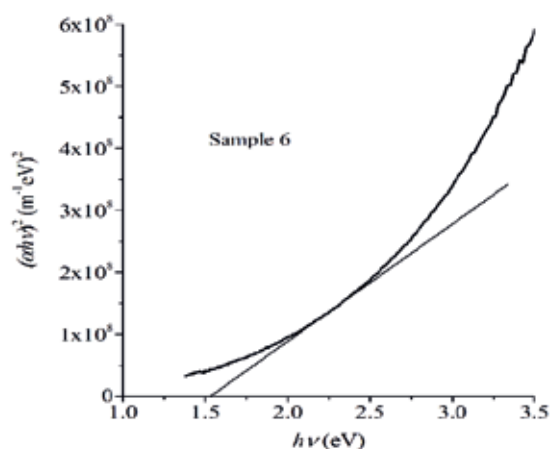
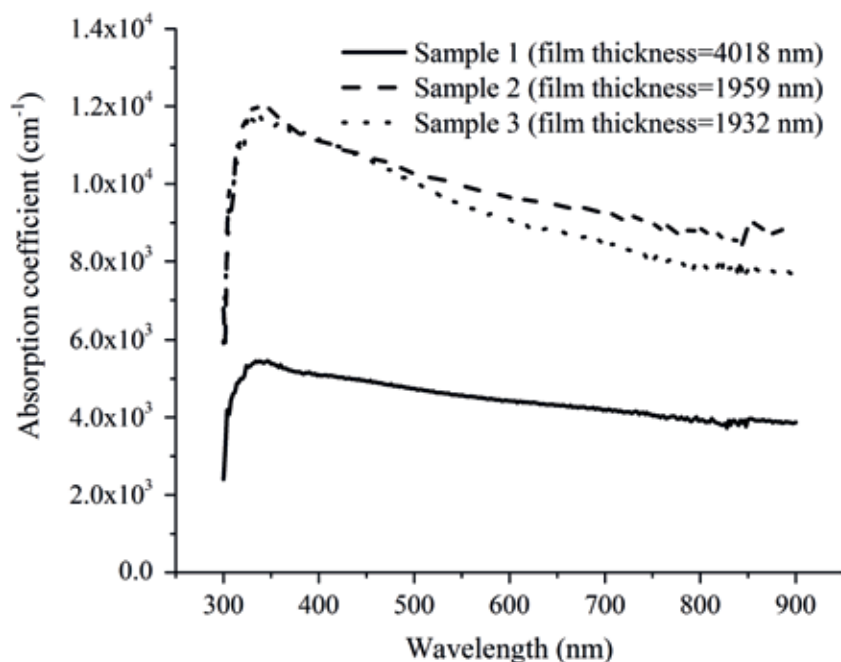


Fig. 8(c). Tauc plot-Sample 6

Fig. 9. Absorption coefficient vs wavelength graph of N_2 gas annealed CZTS thin films

Conclusion

CZTS thin film was successfully deposited by sol-gel spin coating method. Annealing under two condition viz. N_2 gas atmosphere and in S powder were performed. Our study revealed that sulphurized samples show better crystallinity with increasing pre-annealing temperature and the N_2 annealed samples' XRD pattern remained unaffected with the

variation of pre-annealing temperature. Overall, the samples annealed under N_2 gas atmosphere showed better crystalline property than the sulphurized ones. All the thin films possess high optical absorption coefficient and optical band gap near to that of the bulk CZTS. So, the film developed could be used as an absorber layer in thin-film solar cell.

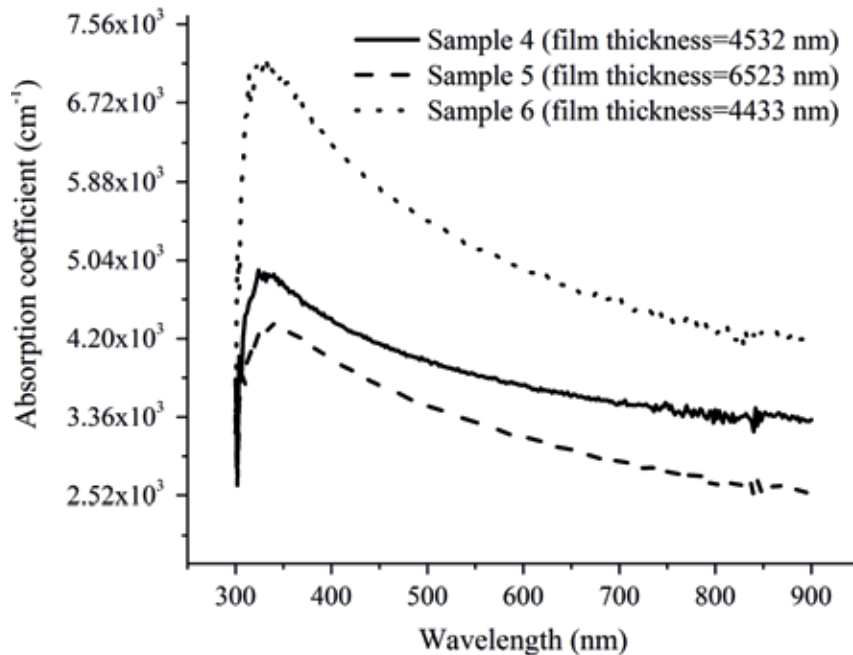


Fig. 10. Absorption coefficient vs wavelength graph of sulphurized CZTS thin films

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