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Low Cost and Sol-Gel Processed Earth Abundant Cu_2ZnSnS_4 Thin Film as an Absorber Layer for Solar Cell: Annealing without Sulfurization

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Abstract: A low cost technique has been introduced to fabricate the absorber layer of a solar cell. Copper Zinc Tin Sulfide (Cu_2ZnSnS_4 or CZTS) thin film have been deposited on soda lime glass substrates by a spin coater and annealed in air with different temperature varied from 300-500° C. The effect of annealing temperature on structural, optical, electrical, morphological and compositional properties has been studied. The XRD study depicts that sharpness of the peak increases with annealing temperature. The major peaks are observed at 28.74º, 47.7º and 56.6º with (112), (220) and (312) plane. Optical studies show relatively high absorption co-efficient from 10^4-10^5 cm^{-1}. The band gap energy (E_g) varies from 1.42 to 1.49 eV for CZTS thin film. Hall measurements show p type conductivity. Further, SEM analysis revealed the surface texture of CZTS film. The EDX measurement for CZTS thin films confirms the formation of CZTS which is Cu rich and Zn poor.

Keywords: CZTS, Spin coating, annealing, band gap energy, absorption coefficient, absorber layer.

1 Introduction

Cadmium telluride (CdTe), copper indium selenide (CIS), and copper indium gallium selenide (CIGS) [1-3] have attracted considerable interests in the past few decades in the field of Absorber layer of thin film solar cell after ternary semiconductors evolved widely since 1980[4-5]. Due to the toxicity [6,7] of Cadmium(Cd) and Selenide(Se) and less availability of Indium(In), Gallium(Ga) and Tellurium(Te) in earth crust, it becomes a necessity to search nontoxic, ecofriendly and element abundant light absorber materials. Quaternary compounds, such as Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) have been viewed as one of the most promising photovoltaic materials upon this background. CZTS possess near-optimum direct band gap energy of 1.4~1.6 eV and large absorption coefficient of greater than 10^4 cm^{-1} with p type conductivity[8]. In addition, Zn and Sn are nontoxic and earth-abundant (Cu: 50 ppm, Zn: 75 ppm, Sn: 2.2 ppm, S: 260 ppm) compared to the elements of In and Ga. Thus CZTS is one of the best choices to be employed in the absorption layer and also possess theoretical limit of power conversion efficiency of 32.2% [9-11].

First CZTS thin film solar cell was reported in 1988 by I to and Nakazawa [12]. In 1996, Ito and Nakazawa [13] studied the effects of using an ethanol and water mixture as a solvent and near stoichiometric CZTS films were obtained up to 360 ºC. Power conversion efficiency (PCE) of CZTS based solar cell was increased to 6.7% in 2008[14] and then to 9.6% in 2010 with the improvement of Sulfurization technique [15]. In 2011, Jiang et al. [16] tested a nitrogen atmosphere for heat treatment instead of hydrogen sulfide gas. In 2012, CZTS based solar cell with PCE of 10.1% was fabricated by Barkhouse et al. by using a hybrid solution-particle slurry method [17]. Todorov et al. reported the PCE of 11.1% at 38th IEEE PVSC conference in 2013[18]. In the same year, Rajeshmon et al. reported an efficiency of 1.85% on spray pyrolysed CZTS/In2S3 solar cell [19]. The Japanese thin-film solar company Solar Frontier, IBM and Tokyo Ohka Kogyo (TOK) jointly announced their record setting CZTSSe solar cell capable of converting 12.6% of solar energy to electricity in 2013[20].

Numerous CZTS thin film preparation methods have been reported including sol-gel spin coating [21] such as pulse laser deposition [22], thermal deposition [23], spray pyrolysis [24] , sputtering [25], thermal evaporation[26], chemical vapor deposition[27] and electro-deposition [28]

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etc. High temperature and high vacuum processes are more suitable to obtain high efficiency solar cell with some drawbacks such as expensive precursor, complicated apparatus and techniques. Hence, non-vacuum processes like the sol-gel method is mostly preferred for simple technique, low-cost, eco-friendly and large scale film preparation. Researchers around the world is trying to improve the performances of CZTS thin film with the variation of deposition method, annealing temperature [29-30], sulfurization temperature[31], concentration of precursor[32], pH value and other process parameters. CZTS films require sulfurization to fill up the loss of S during annealing process which makes the process expensive. The effect of morphology, grain size, stoichiometric ratios, pin holes and degree of roughness etc. plays a vital role on the performance of solar cell [29]. In this study, CZTS thin film is deposited on SLG using simple and low cost sol gel method. The CZTS thin film is annealed in air without sulfurization to follow a low cost method. Structural, optical, electrical and morphological properties have been studied for varying annealing temperature from 300 to 500° C.

2 Experimentation

2.1 Materials

Zinc Chloride ($ZnCl_2.2H_2O$), Cupric Chloride ($CuCl_2.2H_2O$), Stannic Chloride ($SnCl_2.2H_2O$) and Thiourea ($SC(NH_2)_2$) is used as the precursor for CZTS. 2 Methoxyethanol is used as solvent. Precursor concentration was maintained as 2M, 1M, 1M and 7M respectively for $ZnCl_2.2H_2O$, $CuCl_2.2H_2O$, $SnCl_2.2H_2O$ and $SC(NH_2)_2$. Monoethanolamine (MEA) acts as a complexing agent.

2.2 Methods

The soda lime glass (SLG) substrates were rubbed by detergent and washed by DI water. Then it was cleaned with methanol, ethanol and DI water in ultrasonic bath successively. Precursors are dissolved in 2 Methoxyethanol. A few drops of MEA is added. The solution was stirred at 55-60 ºC for 30 minutes by magnetic stirrer to get yellow homogeneous solution. The precursor solution is filtered if needed and deposited on soda lime glass (SLG) substrates by spin-coating (SPS SPIN 150) with 2500 rpm for 30s at room temperature. Synthesized films were preheated at 200 °C for 5 min after each coating. Then it is dried and cooled naturally. This procedure was repeated three to five times to increase the thickness. So samples with 3 layers was prepared and annealed at different temperature as 300º, 350º, 400º, 450º and 500º C for 30 minutes and named as 300_3, 350_3, 400_3, 450_3, 500_3 respectively. Similarly, samples with 5 layers were named as 300_5, 350_5, 400_5, 450_5, 500_5 with temperature variance.

2.3 Characterization

The structural study was performed by X-ray diffractometer (GBC, ƐMMA) of the sol-gel-derived CZTS thin film. The X-ray diffractometer with Cu-Kα radiation and wavelength of 1.5406 Å was operated at 35kV and 28mA. UV-visible spectrophotometer (UH4150, Hitachi) is used to study optical transmittance and absorbance in the visible wavelength. The electrical properties of the CZTS thin films was measured by a Hall Effect measurement system (HT55T3, Ecopia) employing the Van der Pauw technique. And thickness of the film was measured with a Surface Profilometer (Dektak, Bruker). An EDX (EDAX, AMETEK) attached with Scanning Electron Microscope (Zeiss, EVO 18) is used to study compositional information and surface morphology of CZTS thin film.

3 Results and Discussion

3.1 Structural Properties

The XRD patterns of CZTS thin film deposited from sol gel spin coating are shown in Fig.1 and Fig.2. Fig.1 shows the XRD patterns with 3 layers for temperature varied from 300º -500º c. And Fig.2 shows the XRD Patterns for 5 layers with same temperature variance. The thickness of 3 and 5 layers film is 1.61 and 2.53 µm respectively.

Both Figure 1 and Figure 2 depict that sharpness of the peak increases with annealing temperature. Sharpness of the peak indicates good crystallinity for CZTS films. It also can be observed that films with 5 layers (Fig.2) shows more peak than films with 3 layers (Fig.1). The major peaks are observed at 28.74º, 47.7º and 56.6º with (112), (220) and (312) plane [29-30]. Including the most preferred orientation observed with (112) plane at 28.74º, all the characteristics peaks indicate tetragonal body centered polycrystalline kesterite CZTS according to JCPDS-26-0575. This lattice structure is the most stable. However, lattice parameters of some secondary phase i.e. SnS, tetragonal Cu_2SnS_3 and cubic ZnS is almost identical to CZTS film [30]. A properly controlled concentration of precursor solution with perfectly performed annealing process is the key to fabricate CZTS film without secondary phase.

In Figure1 there is no visible change in peak sharpness for (112) plane. In Figure 2, peak sharpness increases with increasing annealing temperature from 300 ° to 500° C for (112),(220) and (312) plane due to crystalline nature[29]. Sharper peak and smaller FWHM value indicates better crystallinity and larger grain size. The conversion efficiency of CZTS photovoltaic cell is directly related to the grain size. The larger grain size affects the minority carrier diffusion length to increase. Moreover, it maximizes the inherent potential of polycrystalline solar cell [33].

The crystallite size (D) can be estimated from the Debye-Scherrer Formulae [34].

$$D = \frac{0.9\lambda}{\beta Cos\theta} \qquad (1)$$

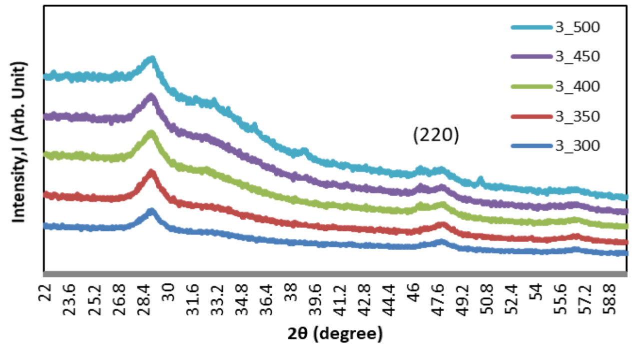


Fig.1: XRD patterns for CZTS for 3 layers.

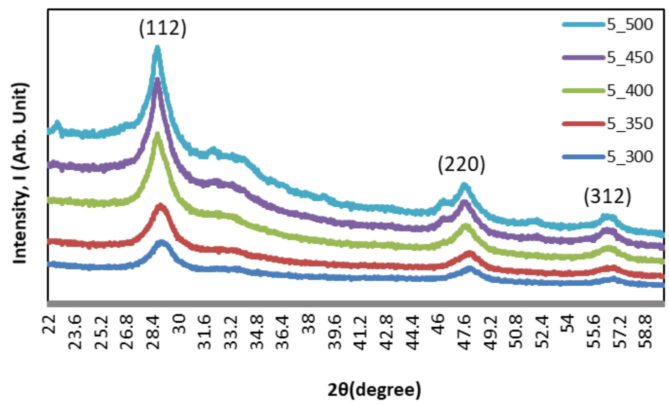


Fig. 2: XRD patterns for CZTS for 5 layers.

Where λ is X-ray wavelength (0.15406 nm), β is the line width at full width at half maximum (FWHM) of the diffraction peak at 2θ and θ is the Bragg Diffraction angle.

3.2 Optical Properties

The absorption coefficients spectra versus photon energy (hν) for CZTS film annealed at different temperature have been shown in Fig.3. The nature of absorption of the film has been determined by using classical Tauc equation [35] for absorption coefficient

$$\alpha=\frac{A(h\nu-E_g)^n}{h\nu} \qquad (2)$$

here, n is an index and n=1/2 for allowed direct transition and n=2 for allowed indirect transition. The absorption coefficient is found to be in the range of ~$10^4 cm^{-1}$ which is Comparable to previous reports [10]. As an absorber layer, CZTS is very promising for its strong absorption over broad solar spectrum. The optical band gap energy, E_g of direct transition is measured by Tauc plot shown in Figure 4 (a),(b) and (c). And estimated values of band gap for samples at different temperature are listed in Table 1. From Table1, it can be observed that band gap energy for all samples is in good agreement with the theoretical values [10]. So it can be predicted that it will behave as a perfect absorber for photovoltaic solar cell application. It is also observed that band gap tends to decrease with increasing annealing temperature. The change in homogeneity and crystallinity with temperature might be the reason for this change. [30,36].

Refractive index (**n**), static dielectric constant (ε_0) and high frequency dielectric constant (ε_∞) is also listed in Table1 which is consistent with previous reports [37]. For semiconducting materials, the refractive index (**n**) and dielectric constant (ε) plays a vital role in electrical and optical properties which is required for solar cell applications. These properties of semiconductor hetero-junctions are also important for designing some nano-electronic and optoelectronic devices. The refractive index (n) is calculated from Moss relation [38]

$$E_g n^4 = k \qquad (3)$$

Here k is a constant with a value of 108eV. Both the high and static frequency dielectric constant is measured for CZTS film. High frequency dielectric constant (ε_∞) is measured as

$$\varepsilon_\infty = n^2 \qquad (4)$$

Where n is refractive index. Static dielectric constant (ε_0) is calculated as

$$\varepsilon_0 = 18.52 - 3.08E_g \qquad (5)$$

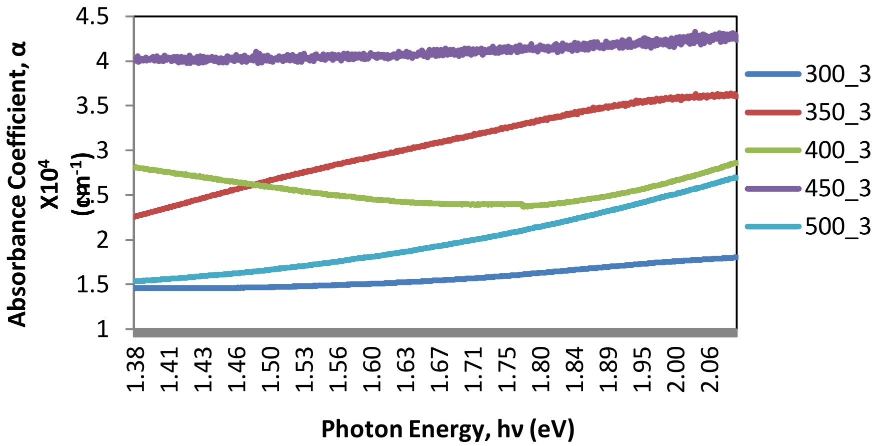
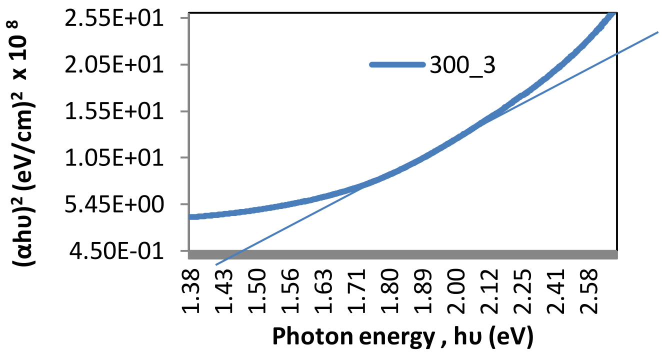
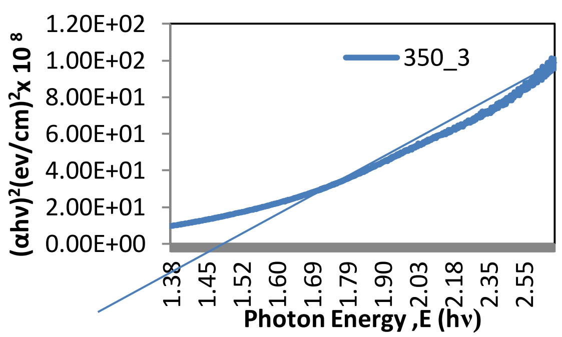


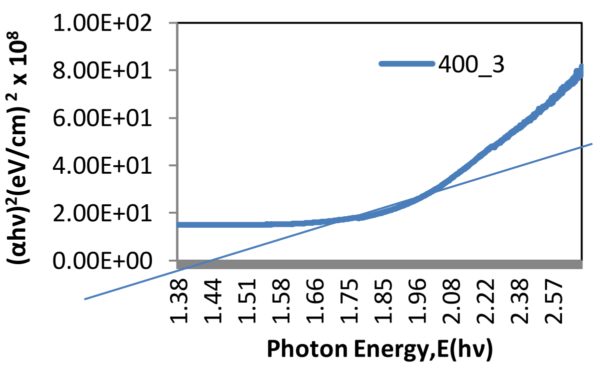
Fig.3: Absorption coefficient (α) spectra of CZTS thin films.



(a)



(b)



(c)

Fig. 4: Tauc plot of the CZTS film annealed at (a) 300º, (b)350º and (c) 400ºc.

Table1: Band gap energy (E_g), Refractive index (n), static dielectric constant(ε_0) and high frequency dielectic (ε_∞) constant.

sample	Band gap Energy (eV) E_g	Refractive index, **n**	Optical Static dielectric constant ε_0	Optical high frequency dielectric constant ε_∞
300_3	1.49	2.91	13.93	8.46
350_3	1.46	2.93	14.02	8.58
400_3	1.46	2.93	14.02	8.58
450_3	1.44	2.94	14.08	8.64
500_3	1.42	2.95	14.15	8.70

3.4 Electrical properties: Hall Effect Measurement

Hall effect measurement is a reliable instrument to investigate the electronic properties of semiconductor and compound semiconductors. The hall coefficient, R_H provides the information of a semiconductor as n or p-type as it lies on positive values. For CZTS film, hall measurements show p type conductivity. Hall measurement values of prepared CZTS film are shown in Table 2.

From Table2, it is revealed that the mobility increases and Carrier concentration decreases with an increase ofannealing temperature. Generally carrier electrons are generated by the increase of charge carriers. Then mobility of the ion is induced. When mobility increases, there is a decrease in carrier concentration [29, 39]. The highest mobility, μ is found for the sample annealed at 500° C.

It can be noted that mobility may also decreases with the increase of film thickness. So thickness of the film, mobility, carrier concentration etc. can be attributed for the improvement of the crystallinity of CZTS thin film. The less structural defects and larger crystal grain volume can result in better crystallinity of the thin film [29].

3.5 Morphological Properties

Figure 5 (a), (b),(c),(d),(e) respectively shows the SEM image of CZTS thin films annealed at 300-500ºc. It can be observed that the surface has not covered the substrate uniformly and roughness increases with temperature [29].

And with the increasing temperature, the layer of the film became thinner and cracks are seen in fig 4(d) and 4(e). This has occurred due to film contraction by the evaporation of volatile matter in CZTS at higher temperature [40]. Mali et al. [36] obtained this type of non-uniform distribution of the agglomerated particles annealed at 100ºc. This growth technique is explained on the basis of nucleation growth mechanism by Shinde et al. [30]. At the beginning all the metal ions of Zn^{2+}, Cu^{+} and Sn^{4+} come closer to create cationic nuclei on glass substrate. S^{2-} ions are adsorbed over this to form CZTS molecule.

confirms the formation of CZTS. It is evident that the films are Cu rich and Zinc poor. Cu is a lighter mass element with higher flow speed than higher mass elements. It leads to enrich of Cu in CZTS film [41]. Zn and S is also lighter elements but they are volatile. This is the reason of CZTS films to be Zn and S deficient. This composition of Cu rich and Zn poor condition is suitable for single phase growth of CZTS films reported by Chen *et al.*[42-43]. However, in 2010, Torodov et al. [15] reported CZTS thin film with the highest conversion efficiency with opposite compositional requirements i.e Zn rich and Cu poor. Park et al. [40] also reported same compositions of sol gel processed CZTS without sulfurization in 2013.

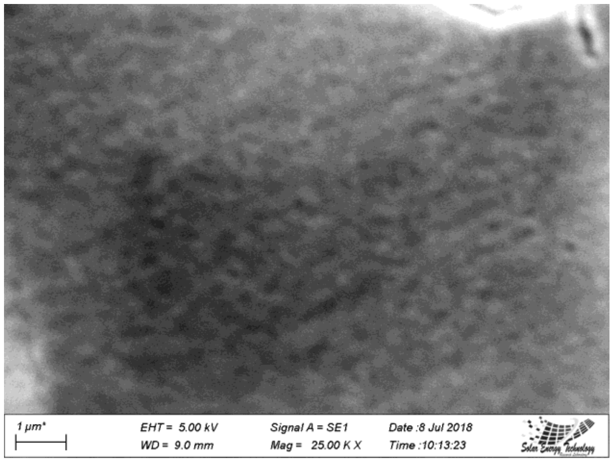
By this successive aggregation more CZTS molecules are created on each other which is called coalescence. Crystal growth takes places by continuous coalescence of CZTS molecule

The EDX measurement for CZTS thin films in Figure 5(f)

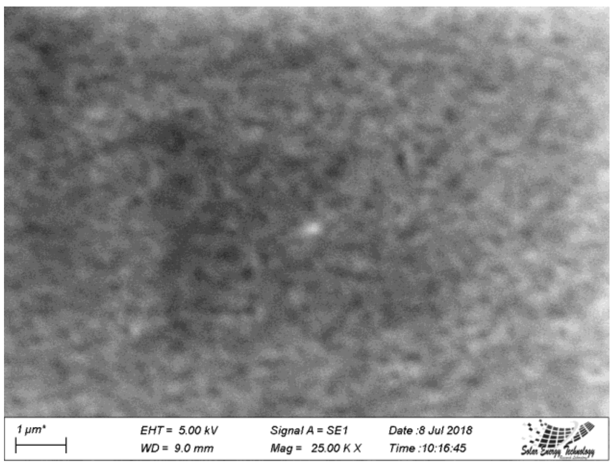
Table2: Hall measurement values of CZTS thin films annealed at different temperature.

Sample	Carrier concentration, N_b /cm^3	Hall mobility, μ cm^2/Vs	Hall Coefficient, R_H cm^3/C
300_3	5.828e13	4.3e1	+
350_3	9.783e12	6.2e1	+
400_3	4.806e11	1.4e2	+
450_3	3.699e11	2.1e2	+
500_3	3.285e11	3.9e2	+

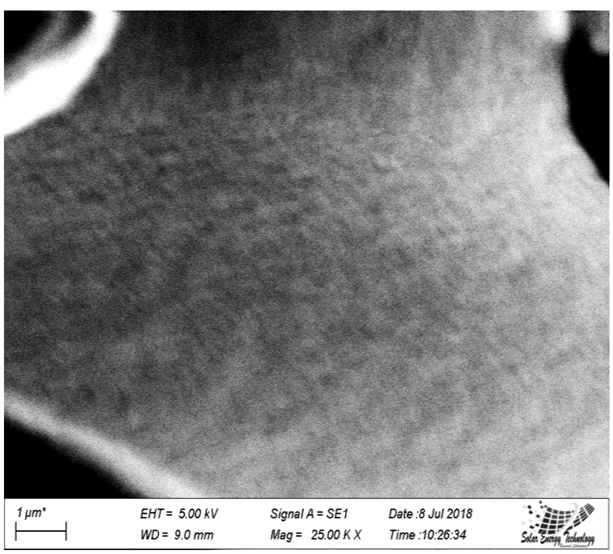
.


1 µm*
EHT = 5.00 kV
WD = 9.0 mm
Signal A = SE1
Mag = 25.00 K X
Date :8 Jul 2018
Time :10:13:23

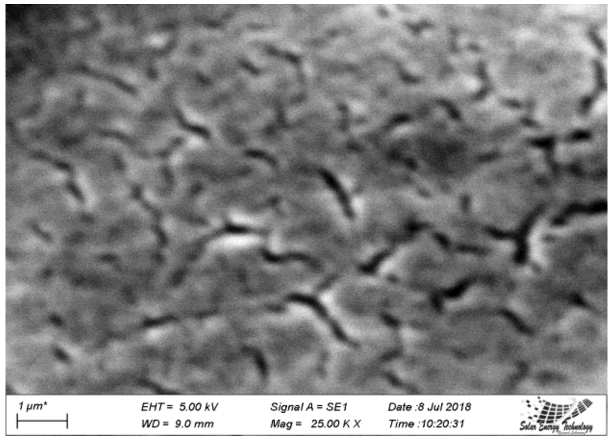
(a)


1 µm*
EHT = 5.00 kV
WD = 9.0 mm
Signal A = SE1
Mag = 25.00 K X
Date :8 Jul 2018
Time :10:16:45

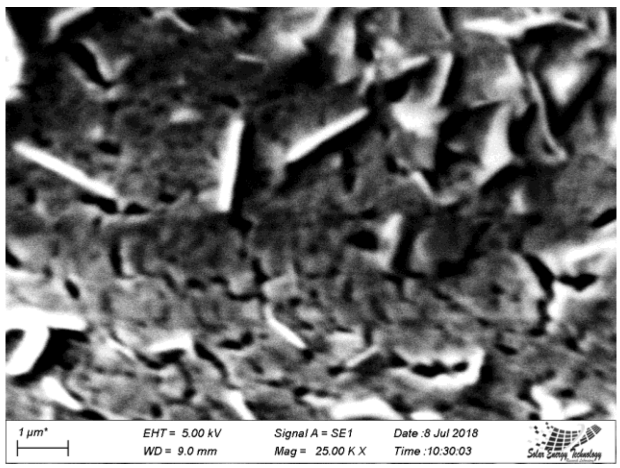
(b)


1 µm*
EHT = 5.00 kV
WD = 9.0 mm
Signal A = SE1
Mag = 25.00 K X
Date :8 Jul 2018
Time :10:26:34

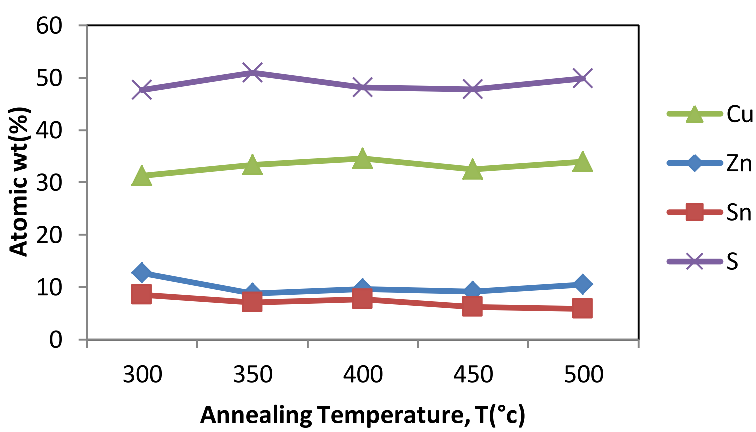
(c)



(d)



(e)



(f)

Fig. 5: SEM images of CZTS thin film at (a) 300º, (b) 350º, (c) 400º, (d) 450º and (e) 500º C temperature, (f) Atomic weight t(%) of CZTS films as the function of annealing temperature.

4 Conclusions

Quaternary CZTS thin film has been deposited on SLG by a simple non vacuum sol-gel spin coating process. The experimentation was performed under ambient temperature. Moreover, the material used for the deposition process is earth abundant and non-toxic as it is performed without sulfurization. So the introduced technique is both eco-friendly and low cost. The samples were air annealed at different temperature varied from 300-500° C and structural, optical, electrical and morphological properties have been investigated. XRD pattern shows perfect kesterite structure of CZTS where sharper peaks were observed with increasing temperature. Consequently, sharper peaks indicate better crystallinity of CZTS thin films. The absorption coefficient is found to be in the range of ~$10^4 cm^{-1}$ and band gap energy, E_g varies from 1.42-1.49 eV which are perfectly comparable with previous reports.

Hall effect studies revealed p-type semiconducting nature of CZTS thin film. In addition, Hall mobility(μ) increases with the increase of annealing temperature and the value of mobility is highest for sample annealed at 500°C. EDX analysis shows that synthesized films are Cu rich and Zn poor with sufficient S. However, the amount of Sn is quiet less than expected. The observed property of CZTS thin film implies that it can be used for fabrication of absorber layer of the photovoltaic cell. And it also suggests further improvements needed in CZTS thin film for fabrication of a complete solar cell for low cost energy.

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