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PROPERTIES OF LOW TEMPERATURE VACUUM ANNEALED CZTS THIN FILMS DEPOSITED ON POLYMER SUBSTRATE

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Structural, compositional, morphological and electrical characterizations of the vacuum annealed Cu_2ZnSnS_4 (CZTS) thin films were carried out in this study. The films were annealed at the low temperature (200 ^oC) for a long time (1- 3 hours) without excessive sulphur ambient to investigate the possibility of (i) low temperature process and (ii) eluding the post deposition sulphurization process, respectively. The change in the microstructure with subsequent recrystallization and grain growth was observed in annealed thin films. The crystallite grain size, lattice constant, microstrain and dislocation densities of the films are quite different for the different films as observed from XRD analysis. The films are found in Zn poor and Cu rich and the ratio of Cu/(Zn+Sn) show that the films are very poor stoichiometric. The lowest resistivity 30.6 Ω-cm with mobility 6.8 cm^2/V-sec and highest resistivity 97.2 Ω-cm with mobility 5.4 cm^2/V-sec was observed for as-deposited and annealed CZTS thin films, respectively.

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1. Introduction

Cu_2ZnSnS_4 (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, direct band gap and high absorption coefficient (>10^4 cm^{-1}) [1-8]. It is using abundant, cheaper and nontoxic constituent elements compared to the existing CIGS and CdTe materials [9,10]. The CZTS thin film can be regarded as an alternative to $CuInS_2$ (CIS) and $CuInGaSe_2$ (CIGS) materials, in which the extremely expensive and resource limited indium is replaced by cheap and abundant zinc (Zn) and tin (Sn). At the same time, different secondary phases like ZnS, Cu_2SnS_3, and others are very easily formed during CZTS thin film preparation, and large compositional non-uniformity is present, it is very difficult to grow pure CZTS. Despite this fact, the best solar cells based on CZTS have already shown efficiencies of almost 10 % [11]. However, without understanding the basic physical and electrical properties of CZTS thin films, it will be impossible to make a breakthrough similar to CIGS solar cells that show efficiencies of over 20 % [12].

CZTS thin film has been prepared by various methods, including sputtering, evaporation, electro deposition, spray pyrolysis, and sol gel techniques [9, 13-15]. With the advantages of low deposition temperature, simple processing, high growth rate, low-cost equipment and suitability for large areas deposition, magnetron sputtering is one of the most promising deposition techniques. At first, Ito and Nakazawa published the sputtering technology for CZTS deposition in 1988 [16]. The CZTS thin films prepared by RF magnetron co-sputtering followed by sulfurization at 580°C resulted in a device efficiency of up to 6.77% [13].

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A single-step reactive sputtering process in sulphur ambient to incorporate the sulphur during the deposition was also developed [17]. Post deposition annealing using sulphur vapour is used to enhance the grain size and texture of CZTS films [18]. However, the use of H_2S gas or sulphur vapour for post deposition sulfurization is still an issue for the CZTS thin films prepared by sputtering technique.

In this work, we report on the properties of CZTS thin films prepared by sputtering from a single ceramic CZTS disc target at room temperature on the molybdenum (Mo) coated polymer substrate. The prepared films were then annealed long-time (1-3hrs) in the vacuum ambient at 200 ^oC to understand the effect of low annealing temperature without sulphur ambient. The change in compositional homogenization, phase formation, grain growth, and electrical properties with the low temperature process possibility are reported in this study.

2. Experimental Works

The polymer substrates were prepared to deposit CZTS thin films by cleaning in ultra-sonic-bath, degreased by ethanol-acetone-ethanol and deionized water about 10 minutes, respectively. The Mo thin films of around 1μm have been sputtered on the polymer substrate at 100 ^oC. Then, CZTS thin films of around 800 nm thick are deposited by sputtering technique from a single Cu, Zn, Sn and S source target with the stoichiometric compositional ratio at a room temperature. Since most of the polymer substrate is not stable at the high temperature, therefore, the prepared samples were annealed at 200 ^oC in a high vacuum, 50 mTorr ambient for different time, from 1hr to 3hrs. The samples were kept in the deposition chamber until the temperature cooled down to room temperature.

3. Result and discussions

XRD measurements were performed to confirm the crystallinity and phase composition of the CZTS thin films. Fig.1 demonstrates the XRD pattern of CZTS thin films prepared at various annealing durations with annealing temperature of 200 °C. It has been seen that although the XRD peak intensities are not too high, yet they are strongly dependent on the annealing duration. From XRD patterns, the as-deposited CZTS thin films showed amorphous nature, while the poly-crystalline nature is observed for the films annealed in the vacuum ambient for different durations. In particular, the films annealed in the vacuum ambient showed kesterite structure with major diffraction peaks towards (112), (220), and (312) directions (JCPDS card: 26–0575). The maximum peak intensity is observed for the film annealed for 1 hr. However, the peak intensity is distinctly decreased when the annealing duration is further increased to 3 hrs. It was reported that during the high-temperature annealing process without deliberate addition of SnS and S, the evaporation of SnS and S from the CZTS easily happened [19-21]. Therefore, we speculate that the deterioration of the XRD peak may be due to the loss of Sn and S atoms from the CZTS thin film after annealing in the vacuum for a long period. The same phenomena was also observed for high temperature annealing with various annealing time durations [22].
The mean crystallite sizes (D) of the films are also calculated using Scherrer formula [23].

$$D_{hkl} = 0.9\lambda/(\beta\cos\theta) \quad (1)$$

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

However, there may have a large number of grains in the polycrystalline films with various relative positions, and orientations which lead to the lattice misfit. In general, the lattice misfit depends on the growing conditions and post deposition processes of the films. This lattice misfit can be studied by the term ‘microstrain’. The microstrain (ε) is calculated from the following relation [24].

$$\varepsilon = (\beta/4)\tan\theta \quad (2)$$

where, ε is for microstrain, θ and β have their usual significances. Moreover, it is well known that dislocation is another matter of concern involved with the growth mechanism of thin films [25]. Dislocation gives information about the imperfection of crystal structure associated with the mis-registry of the lattice in one part of the crystal with respect to other parts. The dislocation density of thin films is calculated by the Williamson and Smallman's relation [26].

$$\delta = n / D^2 \quad (3)$$

where, n is a factor, which almost equals to unity for minimum dislocation density and D is the grain size. All of the results found from the above equations are presented in Table 1. The crystallite grain size, lattice constant, microstrain and dislocation densities of the films are quite different as observed from XRD analysis.

From the XRD spectra it is revealed that the full width at half-maxima (FWHM) corresponding to (1 1 2) peak dramatically varied among the samples. The highest crystallite size is found to be around 32 nm for the film annealed for 2 hrs. However, the values of dislocation densities changed similarly as crystallite size. The highest dislocation density of 5.49×10^{11} cm^{-2} and microstrain of 7.7×10^{-3} are observed for the sample annealed for 1hr indicating the highest lattice mismatch and dislocation in this film structure [23]. The dislocations and microstrains were reduced for the film annealed for 2 hrs and further increase for the film annealed for 3hrs. These phenomena indicate that the strains are released for a certain limit of annealing and constrained again for over annealing time.

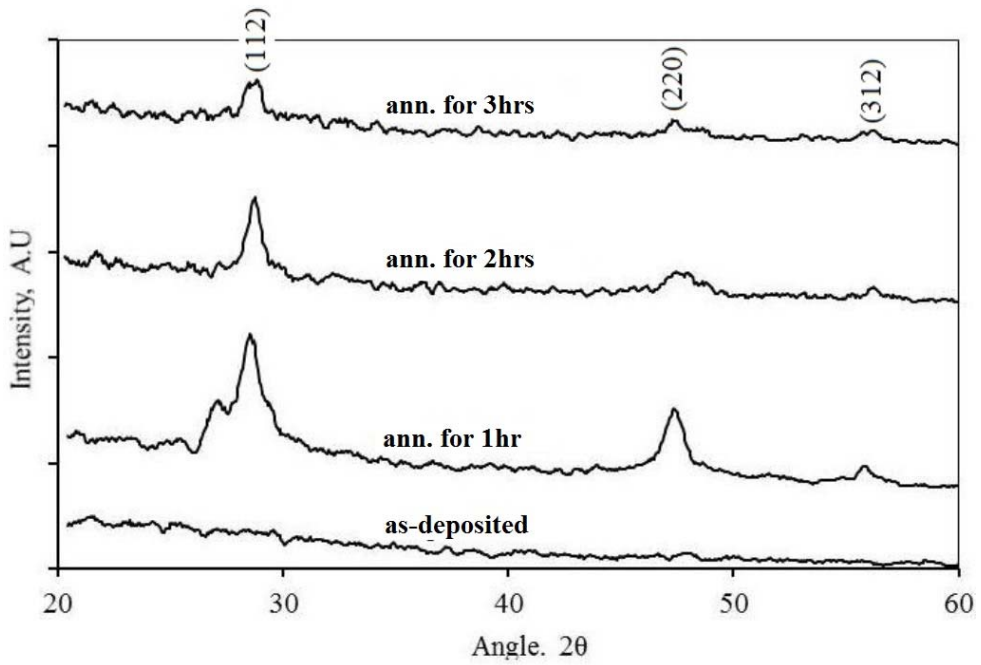

Fig.1 XRD graph for as-deposited and low temperature vacuum annealed CZTS films

Table 1 Calculated structural parameters from the XRD pattern corresponding to the dominant (1 1 2) peak of as-deposited and annealed CZTS thin films

Sample ID	Annealing time	2θ (◦)	FWHM (◦)	Crystallite size (nm)	Microstrain x 10^{-3}	Dislocation density x 10^{11} cm^{-2}
TS301A	As-deposited	-	-	-	-	-
TS301B	1 hr	28.45	0.45	18.21	7.7	5.49
TS301C	2 hrs	28.61	0.25	32.25	4.3	3.10
TS301D	3 hrs	28.22	0.40	20.71	6.7	4.83

The morphological analysis has been done by SEM and images of as-deposited and annealed CZTS thin films are depicted in Fig. 2. The as-deposited CZTS thin films showed non uniform distribution of agglomerated small particles with well-defined boundaries. The regular change of grain sizes with morphological differences between the surface layer and the deep layer are observed in annealed CZTS thin films. The annealed CZTS thin film with 1 hr. showed compact non-flat and highly rough grains, whereas the films annealed for 2 hrs and 3 hrs showed well defined crystallites with compact and less rough and without any voids on the surface. The films annealed for 2 hrs and 3 hrs in the vacuum are densely packed with compact faceted grain structure, having small grain sizes of about 0.1 μm. The small grain size may adversely affect the photovoltaic properties of the solar cell as the recombination rate of the photo-generated carrier is increased by small grain size [27].

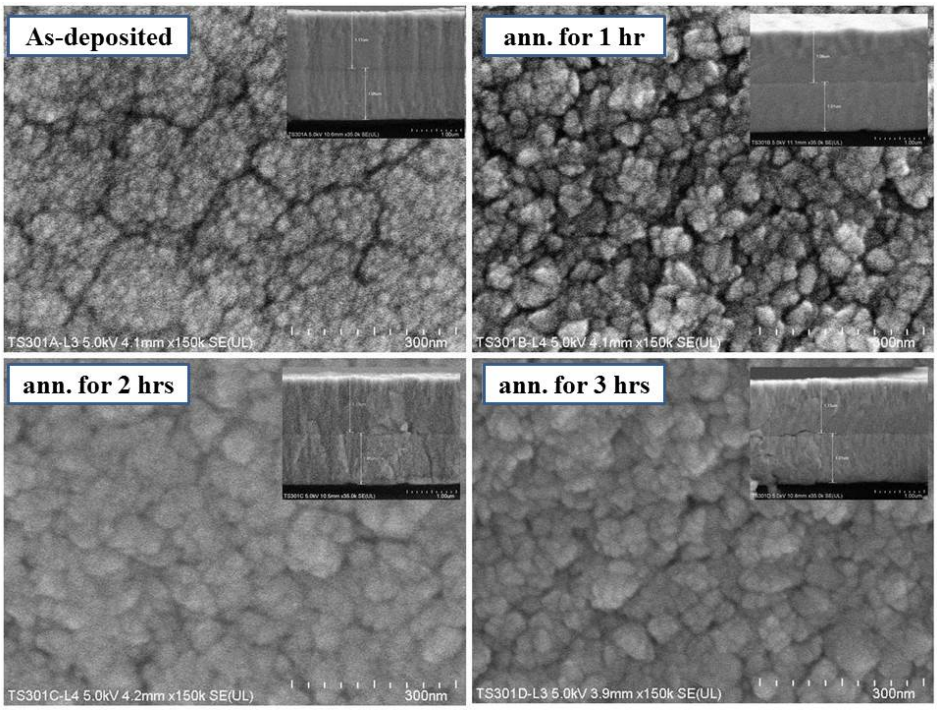

Fig.2 SEM images for as-deposited and low temperature vacuum annealed CZTS films (inset- cross-section of Mo/CZTS stacks)

Stoichiometric and compositional analysis of the films was performed by EDX which is presented in Figure 3. The EDX results are summarized in Table 2. All films were obtained as Cu rich and Zn-deficient, although the Zn/Sn ratio is always over 1. The atomic ratios of metals are decreased with the annealing time while the sulphur atomic ratio increases. However, the S/metal ratio is less than 1.0 in the films, indicating that sulphur is not sufficiently present on the films. The highest S is seen for the sample TS301C which is annealed for 2 hrs. From EDS studies; it is seen that the CZTS thin film deposited using sputtering technique from a single CZTS target have a poor stoichiometric composition. This indicates that vacuum annealing without sulphur ambient

cannot effectively improve the stoichiometric property of the CZTS film. It has been reported that the CZTS solar cells fabricated with Cu poor and Zn rich composition has shown high conversion efficiencies [28]. This investigation suggests that sulfurization process is needed for the S and Zn rich, Cu poor composition and for the good stoichiometric CZTS thin films even though it is prepared from a single compound target with stoichiometric composition. Chen et al. also approached the same suggestion, who theoretically studied the defect properties of CZTS using the first-principle calculations [7].

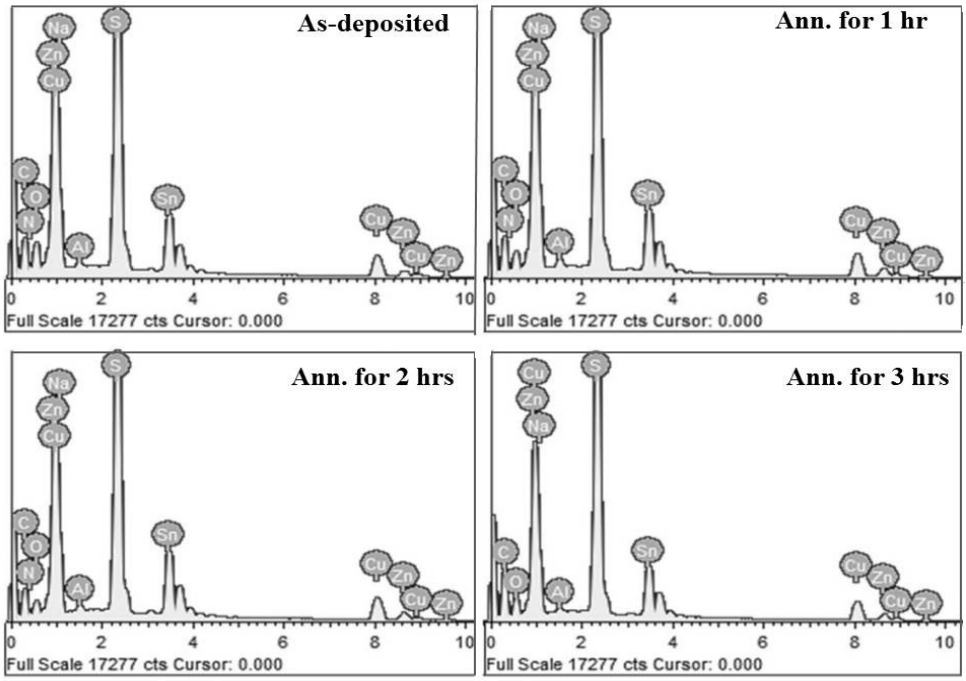

Fig.3 EDX graph for as-deposited and low temperature vacuum annealed CZTS films

Table 2 Composition of the low temperature vacuum annealed CZTS films

Sample ID	Chemical composition (at%)				Ratio of composition		
	Cu	Zn	Sn	S	Cu/(Zn+Sn)	Zn/Sn	S/Metal
As-deposited	16.17	5.66	5.35	22.46	1.47	1.06	0.83
Ann. for 1 hr	15.62	5.85	5.64	23.04	1.36	1.06	0.85
Ann. for 2 hrs	14.78	6.41	5.49	26.44	1.24	1.17	0.99
Ann. for 3 hrs	10.20	3.90	3.41	14.93	1.39	1.14	0.85

The electrical properties of the CZTS films were investigated at room temperature by Hall Effect measurements with an integrated resistivity/Hall measurement system (ECOPIA 3000). In this case, the magnetic field was applied perpendicularly to the surface of the sample, and the magnitude and polarity of this were alternated periodically, while a direct current was passed across the sample using one diagonal pair of the four gold electrodes connected to a current source. Then, by a frequency response analyzer (HMS-5000), alternating Hall voltage induced synchronously with the ac magnetic field was detected using the other pair of electrodes. The detection limit of the Hall voltage has significantly improved by following this method. The magnitude of the magnetic field and the current source was 0.55 T at the maximum and 50 μA, respectively. The carrier concentration, mobility, resistivity and hall coefficients were deduced from this study. The measured mobility, resistivity and hall coefficients are presented in Table 3.

Table 3 Electrical properties low temperature vacuum annealed CZTS films

Sample ID	Mobility (cm^2/V-s)	Resistivity [$x10^{-1}$] (Ω-cm)	Carrier concentration [$x10^{17}$] (cm^{-3})
As-deposited	6.83	36.0	71.7
Ann. for 1 hr	3.38	88.5	2.08
Ann. for 2 hr	5.36	97.2	1.13
Ann. for 3 hr	6.04	82.8	1.27

The as-deposited film (TS301A) showed the lowest resistivity and highest mobility among all the films. This might have occurred due to the highest metal ratio on this film as found in EDX analysis. The dependency of the mobility and resistivity on Cu/(Zn+Sn) ratios are shown in Fig. 4. It was commonly observed that the Cu and Zn antisite defect was the main cause for the p-type conductivity of CZTS thin films, which partly explains why CZTS thin films must be Cu-poor and Zn-rich to fabricate CZTS solar cells successfully [7]. In contrast with Fig.4, it has been seen that the resistivity reduces with the increase of Cu/(Zn+Sn) ratio. The similar behavior of the CZTS thin film resistivity was also reported [29].The lowest mobility is found for the sample TS301B which is annealed for 1 hr. in the vacuum ambient, but further increases of annealing time, the mobility started to increase.

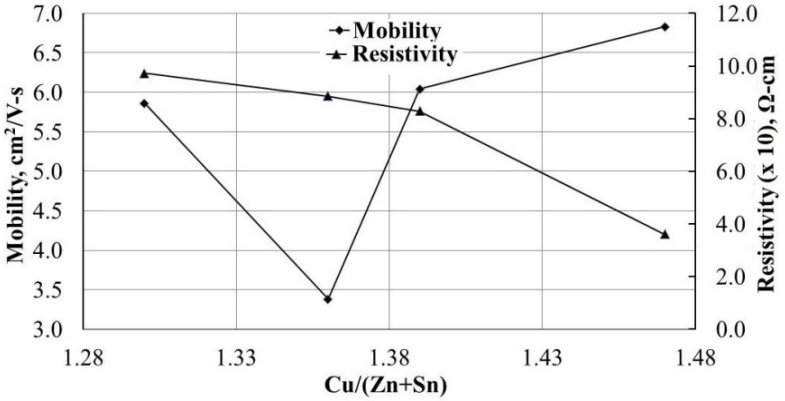

Fig.4 The change of mobility and resistivity vacuum annealed CZTS thin films with Cu/(Zn+Sn) ratio

4. Conclusion

The structural and electrical properties of the as-deposited and low temperature vacuum annealed films were studied by XRD, SEM, EDX, and Hall Effect Measurement. From the XRD analysis, it has been seen that although the annealing temperature is very low, but it has an effect on the structural properties of the film. The crystallite grain size, lattice constant, microstrain and dislocation densities of the films were regularly changed with the annealing time. From the SEM images, very small sized grains (0.1μm) were observed. The films were found as Cu rich and Zn poor and the ratio of Cu/(Zn+Sn) indicated very poor stoichiometry of the films. The S/Metal ratio was increased by annealing, and the highest ratio (0.99) has been observed for 2 hrs annealing. The resistivity of the films were decreased with the increase of Cu/(Zn+Sn) ratio. The lowest resistivity 30.6 Ω-cm with mobility 6.8 cm^2/V-sec was found for as-deposited films and the highest resistivity 97.2 Ω-cm with mobility 5.4 cm^2/V-sec was found for 2 hrs annealed CZTS thin films. However, this study suggested that to find a good stoichiometric CZTS thin film with the S and Zn rich, and Cu poor composition, sulfurization process is needed, even though it is prepared from a single compound target with stoichiometric composition. Further study for the CZTS film properties and corresponding photovoltaic response is presently under investigation and will be reported.

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