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Impact of thermal treatment parameter on the properties of Cu_2ZnSnS_4 solar absorber layer

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Abstract

In this present study Cu_2ZnSnS_4 (CZTS) thin films were grown by Chemical Bath Deposition (CBD) method at optimized parameters. These as grown CZTS films were annealed at 300^0C for different time 1 hr, 2 hr, 3 hr. These films were characterized by scanning electron microscope (SEM), UV-VIS Spectrophotometer, I-V measurement for study of surface morphology, optical and electrical properties respectively. The SEM analysis revealed that surface modification takes place as the annealing time increases. The optical study shows high absorption in visible region and as annealing time increase red shift in energy band gap occurred. The current-voltage characteristics of the specimen indicated that conductivity of film increases with increased annealing time. Thus, annealing time has prominent impact on surface modification which changes optoelectronic properties of CZTS thin film and results shows that film annealed at 300^0C for 3 hr gives high absorption and better conductivity for CZTS thin films. Copyright © 2018 VBRI Press.

Keywords: Thin films, annealing, surface modification, optical properties, electric properties.

Introduction

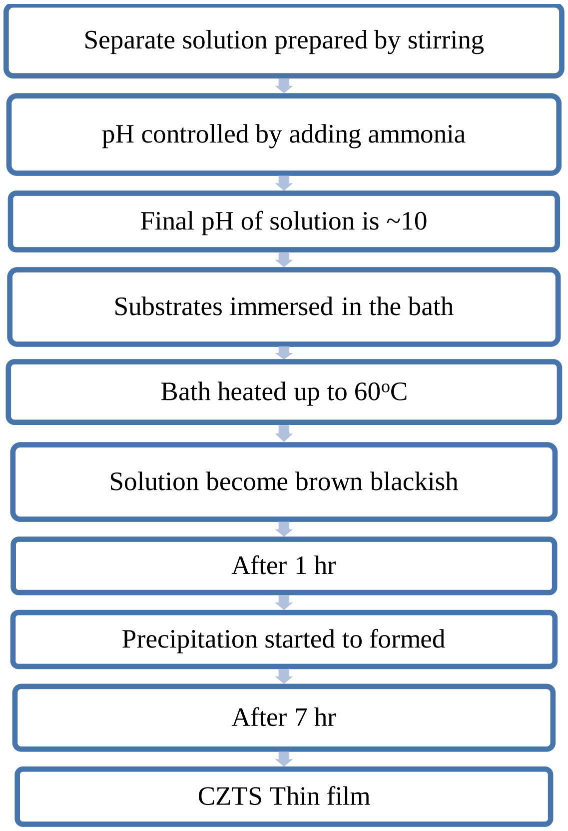
In order to find the suitable alternate of conventional energy resources there are several renewable energy resources are under consideration from last decades. Solar energy in the form of electricity by using photovoltaic is most approachable solution. Thin film solar cells are in the category of recent generation solar cells and compound semiconductor thin film solar cells are good candidate among them. Although for the purpose of commercialization, chalcopyrite solar cells achieved the efficiencies of 20.3% [**1**] and 17.3% [**2**] respectively, but there are some shortcomings of these cells such as limited supply of element In, Ga and toxic element such as Cd.

Copper-Zinc-Tin-Sulphide (CZTS) is an interesting alternative of Chalcopyrite CIGS and CdTe based solar cells due to its analogy with chalcopyrite solar cells and required set of properties with p-type conductivity, direct band gap of ~1.5 eV and absorption coefficient of -10^4 cm^{-1} [**3**]. All elements of CZTS i.e. Cu, Zn, Sn and S are abundant in the crust of the earth and are relatively cheap and non-toxic [**4-5**]. According to Shockley-Queisser limit theoretical conversion efficiency are expected 32.2% for CZTS solar cells [**6**]. Recently efficiency have increased above 10% for CZTS [**7**], but method used in this work is hydrazine based which is unstable, toxic and require extra caution in working, so more work is required for making CZTS solar cells commercially available.

Recently several successful attempts have been reported by various mentioned vacuum based methods such as DC and RF magnetron sputtering [**8**], co-evaporation [**9**], pulsed laser deposition [**10**], thermal and electron-beam evaporation [**11-12**], screen printing [**13**], chemical vapor deposition [**14**], spray pyrolysis [**15**], sol-gel spin-coated deposition [**16**], electrodeposition [**17-18**], but there are some issues related to these techniques. Vacuum based technique requires sophisticated, expensive equipments, limited area deposition and high temperature deposition condition which reduce the simplicity of deposition process. So, researchers in this field are trying to develop a simple method which can be used commercially. Chemical Bath Deposition method is simple and economical method. In our earlier work we reported the optimization of parameter for chemical bath deposition (CBD) method [**19**].

It was reported that the efficiency of polycrystalline thin film solar cell has dependence on morphology and grain size of the absorber layer and surface/interface of the thin film which can be modified by post deposition treatments like thermal annealing which increase the efficiency of thin film solar cell [**20**]. In case of thermal annealing time is an important parameter and optimization of annealing parameter is required for best results.

Considering this aspect in this present work we study the annealing time effect on CZTS thin films for solar cell performance. Therefore, annealed CZTS thin films were characterized by different characterization tools for the study of annealing time effect on the properties of thin films. Results and conclusion of this work give important data for enhancement in the appropriate properties of CZTS film for further use of film as an absorber layer.



Schematic diagram of deposition method is shown in **Fig. 1**. During the deposition of CZTS thin film following reactions take place.

Experimental

Materials

Chemical bath was prepared by Sigma Aldrich, India analytical reagent grade (AR) chemicals of 99.9% purity. Copper Chloride dehydrate ($CuCl_2.H_20$), Zinc Chloride ($ZnCl_2$), Tin Chloride pentahydrate ($SnCl_4.5\ H_2O$) and Thiourea (NH_2CSNH_2) were used as precursor chemicals for Cu^{2+}, Zn^{2+}, Sn^{2+} and S^{2-} ions. Chemical concentrations were taken as 0.1 M $CuCl_2$, 0.05$ZnCl_2$, 0.05 $SnCl_4$, 0.5 NH_2CSNH_2 in equal volume ratio and EDTA was taken as complexing agent. Soda Lime Glass (SLG) was used as substrates which were previously cleaned by detergent then ultrasonically cleaned by Acetone, Methanol and De-ionized (DI) water and dried in air.

Material synthesis

Details of deposition method and parameters are reported in our earlier work [**19**], while steps of CZTS thin film deposition are following:

(1) Dissociation of Sulfur ions
(2) Formation of metal complex
(3) Replacement of complex ion by sulfur

$$CuSo_4+4H_2O+4NH_3 \longrightarrow 2[Cu(NH_3)_4]^{+2}+4OH^-+2H_2SO_4$$

$$ZnSO_4+4H_2O+4NH_3 \longrightarrow 2[Zn(NH_3)_4]^{+2}+4OH^-+2H_2SO_4$$

$$SnSO_4+4H_2O+4NH_3 \longrightarrow 2[Sn(NH_3)_4]^{+2}+4OH^-+2H_2SO_4$$

$$2[Cu(NH_3)_4]^{+2}+[Zn(NH_3)_4]^{+2}+[Sn(NH_3)_4]^{+2}+4S^{-2} \longrightarrow Cu_2ZnSnS_4+12NH_3$$

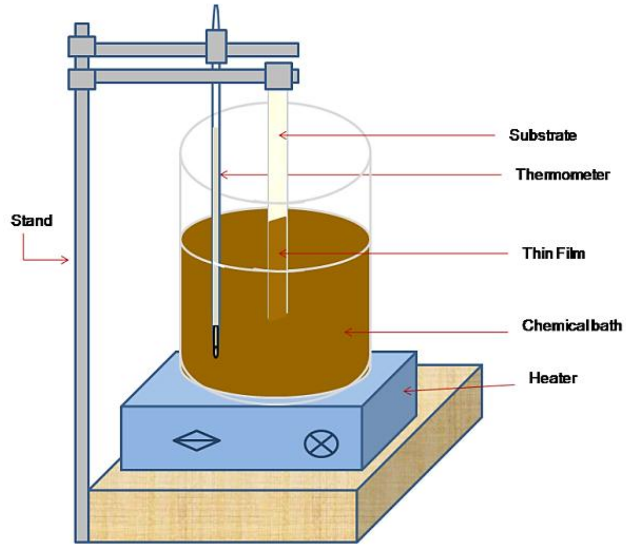


Fig. 1 Schematic diagram of Chemical Bath Deposition (CBD) method.

After the deposition, as grown CZTS thin films were annealed in tubular furnace in air at 300°C and annealing time was taken 1hr, 2hr and 3hr. Annealed films were cooled naturally as abrupt quenching of temperature could result in cracks or defects generation. Further as deposited and annealed thin films were labeled as S_1, S_2, S_3 and S_4.

Characterizations

The surface morphological study was carried out using scanning electron microscope (SEM) JEOL JSM model 6360. The optical absorption spectra were recorded using UV–VIS Spectrophotometer (HITACHI U-2900) within the wavelength range of 300-800 nm. I-V characteristic studied using Lab equipped Keithely, model SMU-2400 computer interface set up unit.

Results and discussion

Surface morphological analysis

The surface morphology of CZTS films were studied by SEM image. Fig. 2(a) shows surface morphology of annealed film at 300°C for 1 hr depicts the snow flacks like structure which could work as a nucleation center as after annealing crystallization started to occur. SEM image of thin film annealed for 2 hr [**Fig. 2(b)**] reveal that grain growth takes place after annealing and surface was covered by compact unevenly distributed grains. **Fig. 2(c)** shows surface morphology of annealed CZTS film for 3 hr and indicates that grain size increased with increased annealing time.

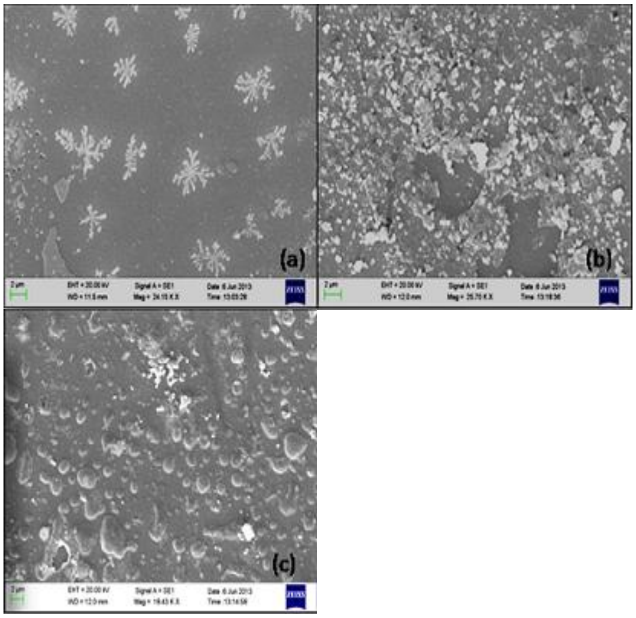


Fig. 2 SEM images of annealed film at 300^{o}C (a) for 1hr (b) for 2 hr (c) for 3 hr in air.

This analysis shows that surface modification takes place as annealing time increases results in growth of grains with fewer boundaries which is essential for reduction of charge carrier recombination, but after certain time uneven growth voids and cracks could be seen. It gives very important parameter in aspect of effect of annealing time on CZTS thin films.

Optical absorption study

The absorption spectra and energy band gap of the material can be deduced by the optical absorption spectroscopy. The optical absorption of CZTS films was studied in the wavelength range 280 nm to 1100 nm. **Fig. 3(A)**, represents the optical absorbance spectra of CZTS films i.e. variation of absorbance (a. u.) with respect to wavelength (λ) which shows that CZTS film have high absorbance in visible region (380-600 nm), suggesting its applicability for an absorber layer. Optical absorption was found to be increased with increasing annealing time. Further optical data were analyzed by using Tauc relation [**21**] which gives the absorption coefficient α by following formula for semiconductor material.

$$\alpha = \frac{A(h\upsilon - Eg)^n}{h\upsilon} \quad (1)$$

where, α is absorption coefficient, A is constant, hν is incident photon energy, E_g is energy band gap i.e. separation between bottom of conduction band and top of the valance band, n is constant which depends on the nature of transition i.e. n=1/2 for allowed direct transition, n=2 for allowed indirect transition. Plot of $(\alpha h\upsilon)^2$ (by taking n=1/2) vs hυ is a straight line which show it is a direct band gap material.

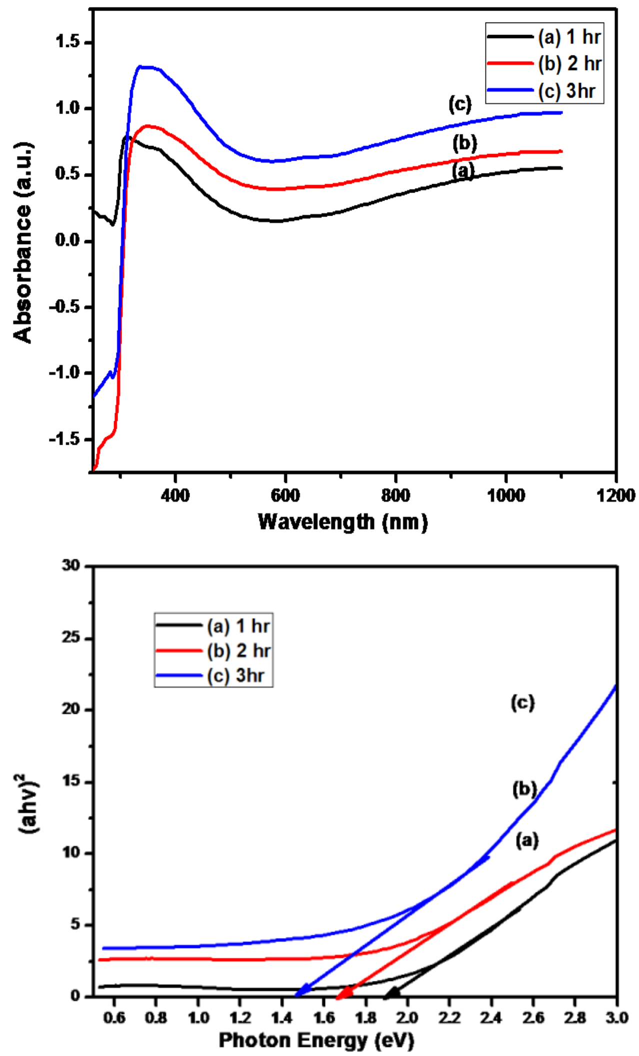


Fig. 3 (A) Variation of absorption (a.u.) with wavelength (nm) of (a) Annealed CZTS film for 1 hr (b) annealed film for 2 hr (c) annealed film for 3 hr film in air at 300^{o}C. (B) The plots of $(\alpha h\upsilon)^2$ vs hυ of (a) annealed CZTS film for 1 hr (b) annealed film for 2 hr (c) annealed film for 3 hr in air at 300^{o}C

Extrapolation of Tauc plot to zero absorption coefficient (α=0) give energy band gap values. **Fig. 3(B)** shows that band gap energy decrease with increase in annealing time and results for as-grown and annealed CZTS films were summarized in **Table 1**. Calculated energy band gap values are nearly equal to theoretical values of optimized band gap of solar energy spectrum [**22-23**].

Table 1: Energy Band Gap values for annealed CZTS thin film.

Sr. No.	Sample	Band Gap (eV)
1	Annealed CZTS for 1 Hr	1.9
3.	Annealed CZTS for 2 Hr	1.7
4.	Annealed CZTS for 3Hr	1.5

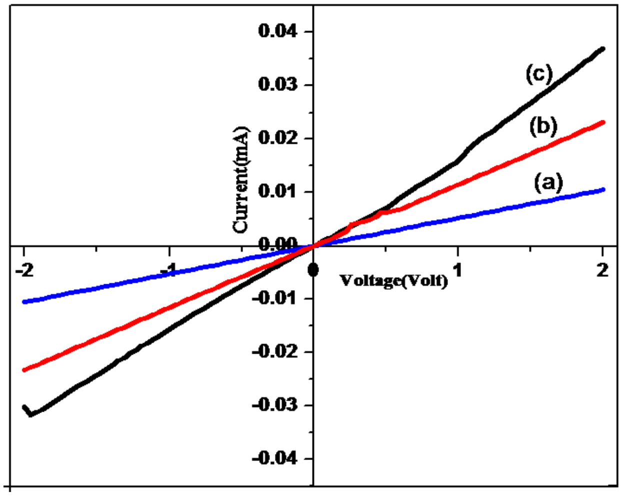


Fig. 4. I–V characteristics of annealed film at 300^{o}C (a) for 1hr (b) for 2 hr (c) for 3 hr in air.

Electrical analysis

For detecting the photosensitivity of CZTS absorber layer the Schottky diode was constructed by metal contact on top of CZTS samples and I-V measurement was obtained under the illumination intensity of 60 mW/cm^2. **Fig. 4** shows the current –voltage characteristics curve for annealed CZTS absorber layer for different time. As annealing time increases value of current increase which shows that recombination is decreasing as annealing time is increasing.

This gives an important parameter for increasing the efficiency of absorber layer. It is concluded that as annealing temperature increases band gap decreases and short circuit current increases, which is accordance with previously drawn results by H.J. Hovel [**24**].

Conclusion

We were successfully synthesized CZTS thin film absorber layer by low cost Chemical Bath Deposition (CBD) method with a most economical approach. For improving the properties of as grown film annealing was performed for different time. Annealed thin films were characterized by different characterization tools. CZTS film shows larger grain as annealing temperature increase and found direct optical transition with band gap energy of 1.5 eV. Also concluded as annealing time increases value of current increase which shows that recombination is decreasing as annealing time is increasing.

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Author’s contributions

Conceived the plan: IBV,MCS,SKS; Performed the expeirments: IBV; Data analysis: IBV& MCS; Wrote the paper: IBV. Authors have no competing financial interests.

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