Effect of annealing atmosphere and temperature on the properties of the sol-gel spin coated Cu_2ZnSnS_4 (CZTS) thin films

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***Abstract**:*

Cu_2ZnSnS_4 (CZTS) is emerging as a promising material for thin film solar cell applications. The reason behind its popularity is the requirement of low-cost and easily available materials, low band gap (1.4-1.6 eV) and high absorption coefficient of CZTS. In the present study, CZTS thin films are prepared using a low cost sol-gel spin coating method. Thin films of CZTS are generally annealed under the H_2S + N_2 atmosphere. The handling of H_2S is its self a challenge and it is not an environment friendly route. Hence, to move towards the environment friendly preparation of CZTS thin film, the thin films are annealed under open air, vacuum and argon atmosphere. The effect of annealing atmosphere on the optical, structural and morphological properties of CZTS thin films is observed. Further, to optimize the properties of CZTS thin films, the annealing temperature is also varied from 400-600ºC. In addition, the solar cell is fabricated using the optimum condition. More than 3 % of power conversion efficiency is achieved by solar cell. For film characterization X- ray diffraction, scanning electron microscope are used for structural and morphological analysis, respectively. The optical properties are studied using. The solar cell performance is measured using Keithley 2400 solar simulator.

Keywords

CZTS, sol-gel spin coating, annealing atmosphere, annealing temperature

1. Introduction

As the world's population is increasing, the requirement of energy is also increasing. Solar energy is huge source of increasing which can be use freely. Solar cell is thing that can convert the solar energy into electrical energy. Nowadays, CIGS (copper indium gallium diselenide) and CdTe (cadmium telluride) are used. These material based solar cells have achieved more than 20% efficiency on laboratory scale [1]. However, due to toxicity of Cd and Se and availability issues of In and Te, the production of the PV devices based on these absorber layer is limited [2]. So, a low cost easily available, non-toxic and less manufacturing time absorber layer is required. Recently, a new absorber layer is come in picture and get the attention of researchers and it is Cu_2ZnSnS_4 (CZTS). It is the low cost, less toxic and earth abundant absorber layer. Moreover, CZTS has band gap between 1.4-1.6 eV (closed to theoretically calculated optimum band gap 1.45 eV) and high absorption coefficient nearly 10^5 cm^{-1} in visible spectrum [3]. Theoretically, the conversion efficiency of solar cell with CZTS is 32%. However, actual reported efficiency by CZTS based solar cell is 12.7% attributed to low open circuit voltage (V_{OC}) and fill factor. Hence, there is wide opportunity for improvement [4].

So far, numerous methods for CZTS thin films synthesis have been reported, such as thermal deposition [5], electro deposition [6], pulse laser deposition [7], sol-gel method [8] and spray pyrolysis [6], etc. chemical solution-based deposition methods have several advantages, mainly low temperatures and cheap manufacturing equipment. Among the solution-based deposition methods, the sol-gel is one of the most simple and low cost process [9].

In present study, CZTS thin film is prepared using sol-gel spin coating. The effect of annealing atmosphere and temperature on the CZTS film is studied in detail. The annealing atmosphere is varied as open air, vacuum and argon instead of toxic H_2S atmosphere or sulphur vapour. The annealing temperature is varied as 400ºC, 500ºC, 550ºC and 600ºC. The optical, structural and morphological analysis of CZTS thin film are also carried. Additionally, the unique solar cell fabrication structure is implemented. The solar cell fabricated as FTO/i-ZnO/Al:ZnO/CdS/CZTS/ CuS/Carbon. The J-V characteristics of solar cell is also measured.

2. Material and methods

2.1. Materials

Copper acetate, zinc acetate, tin chloride, and thiourea were used as the source of different elements (Cu, Zn, Sn and S). Propylene glycol was used as solvent. All the chemicals were purchased from S. D. Fine Chemicals, India. The fluorine doped tin oxide glass substrate was purchased from Sigma Aldrich. All the chemicals were used as it obtained.

2.2. Methods

2.2.1. Sample preparation

The precursors were added into propylene glycol and stirred for 60 min at 50˚C temperature. A few drops of MEA were added as stabilizer. A clear yellowish solution is acquired after completion of process. In present study, to get dissolve copper acetate into solution, more amount of thiourea was added than its stoichiometric requirement.

2.2.2. Thin film preparation

Thin film was prepared using sol-gel spin coating method. The prepared solution was deposited on substrate by rotating at high spin speed. Further, it is dried at 250ºC temperature to get crystalline thin film. This procedure was repeated for certain time to get proper thickness of thin film. Further, it is annealed at specific temperature. Numerous researchers have reported H_2S annealing or annealing under sulphur vapour or with sulphur powder [5, 10, 11]. However, H_2S handling in quite difficult and use of H_2S, sulphur vapour and sulphur powder are not environment friendly. Hence, in present study, to move on environment friendly rout for annealing the annealing atmosphere was varied as open air, vacuum and Argon (Ar). Moreover, it is frequently reported that annealing temperature may affect the crystallinity of thin film. Hence to study the effect of annealing temperature the temperature was varied as 400ºC, 500ºC, 550ºC and 600ºC.

2.2.3. Device fabrication

The FTO substrate (20 mm X 20 mm X 2 mm) was etched with Zn powder and 2 M HCl diluted in water, then cleaned with DI water first, then sonicated with acetone for 10 mins, further it was rinsed in double distilled water and finally dried under vacuum oven at 60ºC. Initially i-ZnO was prepared by spray coating method (0.2M solution of Zinc acetate in IPA). Consequently, Al-doped ZnO was prepared by spray coating. Further, CdS was coated by spin coating method (0.1M solution of Cadmium acetate and thiourea in propylene glycol). Then certain layers of CZTS was prepared by spin coating method according to required thickness. Subsequently, CuS was prepared by spray coating (0.1M solution of copper chloride and thiourea in IPA). Finally, the carbon was used as back contact.

2.2.4. Characterization

The structural properties were determined by XRD using D/Max 2200 system with CuKa radiation (CuKa = 1.5418Å). Films morphology were analysed using scanning electron microscope using S3400, Hitachi international limited. The band gap was estimated from tauc plot ($(\alpha h\upsilon)^2$ vs $h\upsilon$), by extrapolating straight line portion $(\alpha h\upsilon)^2$ to x-axis ($h\upsilon$) regime (where α is absorbance coefficient and $h\upsilon$ is photo energy) using UV-Vis (HACH-DR 6000/2 UV spectrometer) within the range of 300 nm to 1100 nm at room temperature. The J-V characteristics of solar cell were recorded using Keithley 2400 under AM 1.5G illumination at 100 mW/cm^2. A xenon lamp was used as source of light.

3. Result and discussion

3.1. Effect of annealing atmosphere

When CZTS thin film was annealed in open air, degradation in thin film was observed. The film became greyish instead of dark blackish. The surface morphology showed cracks in SEM image. The XRD pattern also exhibited a very small peaks with high polycrystallinity. The film annealed under vacuum demonstrated better stability and single phase (confirmed by XRD analysis) CZTS thin film. The surface morphology also improved and well dispersed nanoparticles were observed. The best result were achieved by film prepared under argon atmosphere. A single phase CZTS thin film was confirmed by XRD analysis with high intensity, which suggest better crystallinity. The SEM images also shown dense and uniform thin film.

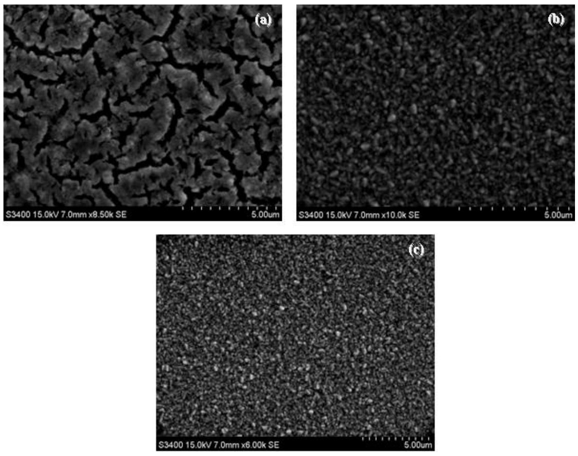

Figure 1 Surface morphology of thin film annealed under (a) open air, (b) Vacuum and (c) Argon atmosphere

The optical analysis of thin film prepared under vacuum and Ar atmosphere was in total agreement with XRD analysis. Both films demonstrated the peaks assigned to (112), (200), (204) and (312) planes of CZTS were present in the whole diffraction patterns. These peaks are assigned to the kesterite phase (according to the card JCPDS 26-0575) [12–14]. However, both films were marginally polycrystalline. 1.53 eV and 1.51 eV band gap was observed for thin film prepared under vacuum and under Ar atmosphere, respectively, which is very close to frequently reported (1.5 eV) for CZTS thin film [15–17].

International Journal of Research
Available at https://edupediapublications.org/journals

e-ISSN: 2348-6848
p-ISSN: 2348-795X
Volume 04 Issue 13
October 2017

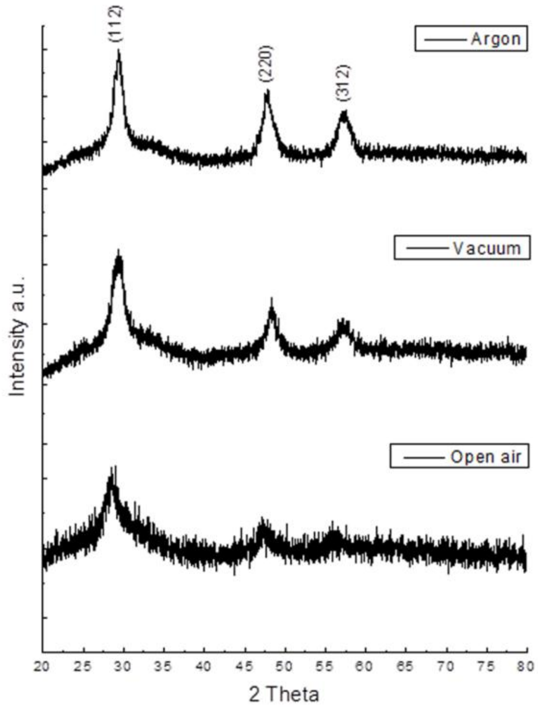

Figure 2 XRD analysis of CZTS thin films annealed under different atmosphere.

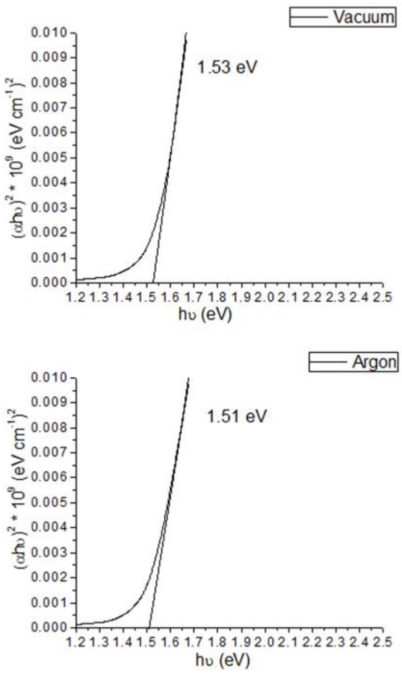

Figure 3 Tuac's plot $(\alpha h\upsilon)^2$ vs $(h\upsilon)$ plot for thin film annealed under different atmosphere.

3.2. Effect of annealing Temperature

After getting good results with Argon atmosphere, the temperature variation is carried out under Ar atmosphere only. The effect of annealing temperature is determined by optical, structural and morphological analysis [19]. The band gap obtained by film annealed at 400ºC, 500ºC, 550ºC and 600ºC are shown in Fig. 5. It is observed that at lower temperature (400ºC) the band gap is enlarged (1.66 eV). However, upon increasing temperature the band gap is reduced to 1.51 and 1.5 eV. Further increment in temperature (600ºC) attributed film degradation. The band gap enlargement can be revealed by XRD analysis (Fig. 6). The lower annealing temperature attributed secondary phase of ZnS, whereas at higher temperature didn't exhibited any secondary phase. In present study, it is observed that there isn't much difference in result of film deposited at 500ºC and 550ºC. Hence, to reduce the operation cost of getting more temperature (550ºC), the 500ºC temperature is considered as optimum one. The SEM images (Fig. 7) also shown dense and uniform thin film at higher temperature.

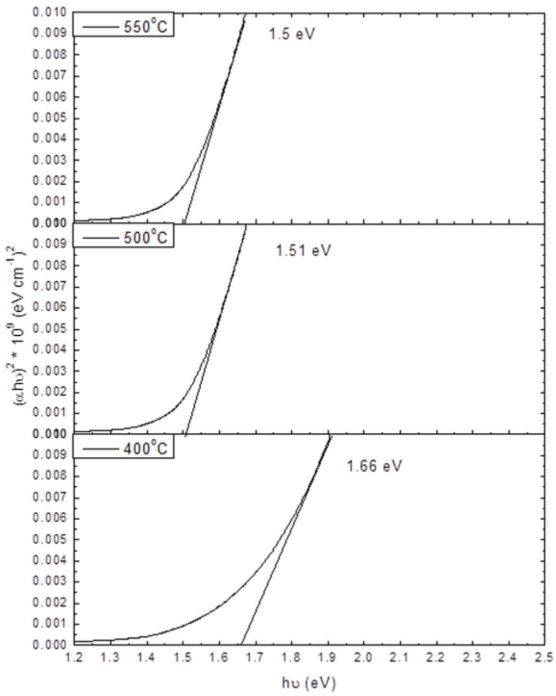

Figure 4 Tauc's plot $(\alpha h\upsilon)^2$ vs $(h\upsilon)$ for CZTS thin films annealed at different temperature.

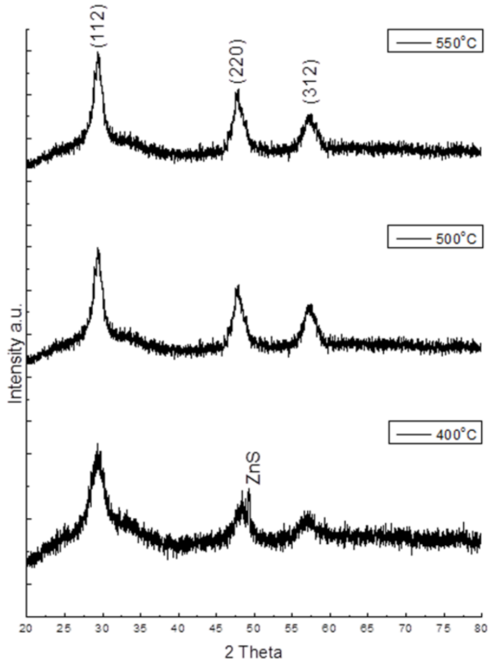

Figure 5 XRD analysis of CZTS thin films annealed at different temperature under Argon atmosphere.

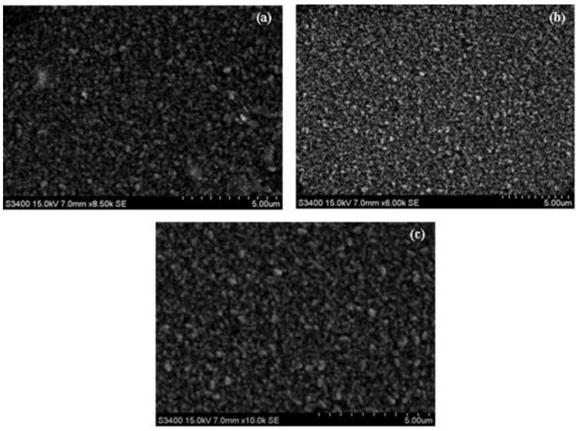

Figure 6 SEM images of CZTS thin films annealed at (a) 400ºC, (b) 500ºC and (c) 550ºC.

3.3. Solar cell application

Fig. 8 depicts the current density – voltage (J–V) characteristic of a solar cell for an active area of 0.31 cm^2 prepared from the CZTS absorber layer annealed at 500ºC. From Fig. 8 it can be seen; a short circuit current density (J_{sc}) of 15.6 mA/cm^2, open-circuit voltage (V_{oc}) of 450 mV, fill factor (FF) of 43% and power conversion efficiency (PCE) (η) of 3.02% under simulated AM 1.5 illumination.

Table 1 Solar cell performance results

	Spin coated CZTS
V_{OC} (mV)	450
J_{SC} (mA/cm^2)	15.6
Fill factor (%)	43
Efficiency (%)	3.02

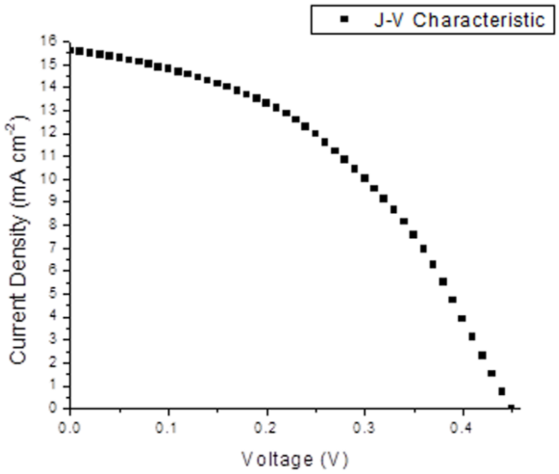

Figure 7 J-V characteristics of solar cell fabricated using optimum condition

4. Conclusion

CZTS thin films are successfully deposited by sol-gel spin coating technique. The effect of annealing temperature and annealing atmosphere on the optical, structural and morphological properties of CZTS thin film are investigated. In open air annealing, film is degraded. In vacuum annealing, a single phase thin film with some agglomerated nano particles is achieved. However, superior results are achieved with thin film prepared under Argon atmosphere owing to increment in intensity in XRD analysis (suggest better crystallinity) and band gap 1.51 eV (close to 1.5 eV, frequently reported). Furthermore, the solar cell is fabricated successfully. A novel solar cell fabrication (inverted) is introduced. The solar cell is fabricated as FTO/i-ZnO/Al:ZnO/CdS/CZTS/CuS/carbon. 3.02% of PCE is achieved successfully, which quite promising.

5. Acknowledgements

The authors would like to acknowledge the sophisticated instrumentation center and Department of Chemical Engineering of S.V. National Institute of Technology, surat.

6. References

[i] Ghorpade, U., Suryawanshi, M., Shin, S.W., Gurav, K., Patil, P., Pawar, S., Hong, C.W., Kim, J.H. and Kolekar, S., "Towards environmentally benign approaches for the synthesis of CZTSSe nanocrystals by a hot injection method: a status review", *Chemical Communications*, *50*(77), 2014, pp.11258-11273.

[ii] Ali, N., Hussain, A., Ahmed, R., Wang, M.K., Zhao, C., Haq, B.U. and Fu, Y.Q., "Advances in nanostructured thin film materials for solar cell applications", *Renewable and Sustainable Energy Reviews*, *59*, 2016, pp.726-737.

[iii] Patel, S. B., Gohel, J. V., "Recent developments in Cu_2ZnSnS_4 (CZTS) preparation, optimization and its application in solar cell development and photocatalytic applications", *Material Research Forum LLC*, 2017.

[iv] Vanalakar, S.A., Agawane, G.L., Shin, S.W., Suryawanshi, M.P., Gurav, K.V., Jeon, K.S., Patil, P.S., Jeong, C.W., Kim, J.Y. and Kim, J.H., "A review on pulsed laser deposited CZTS thin films for solar cell applications", *Journal of Alloys and Compounds*, *619*, 2015, pp.109-121.

[v] Sripan, C., Madhavan, V.E., Viswanath, A.K. and Ganesan, R., "Sulfurization and annealing effects on thermally evaporated CZTS films", *Materials Letters*, *189*, 2017, pp.110-113.

[vi] Patil, S.J., Lokhande, V.C., Lee, D.W. and Lokhande, C.D., "Electrochemical impedance analysis of spray deposited CZTS thin film: Effect of Se introduction", *Optical Materials*, *58*, 2016, pp.418-425.

[vii] Cazzaniga, A., Crovetto, A., Yan, C., Sun, K., Hao, X., Estelrich, J.R., Canulescu, S., Stamate, E., Pryds, N., Hansen, O. and Schou, J., "Ultra-thin Cu_2ZnSnS_4 solar cell by pulsed laser deposition", *Solar Energy Materials and Solar Cells*, *166*, 2017, pp.91-99.

[viii] Liu, R., Tan, M., Zhang, X., Chen, J., Song, S. and Zhang, W., "Impact of sol–gel precursor treatment with preheating temperature on properties of Cu_2ZnSnS_4 thin film and its photovoltaic solar cell", *Journal of Alloys and Compounds*, 655, 2016, pp.124-129.

[ix] Lanjewar, M. and Gohel, J.V., "Enhanced performance of Ag-doped ZnO and pure ZnO thin films DSSCs prepared by sol-gel spin coating", *Inorganic and Nano-Metal Chemistry*, *47*(7), 2017, pp.1090-1096.

[x] Khalkar, A., Lim, K.S., Yu, S.M., Kim, J.H. and Yoo, J.B., "Sulfurization approach using sulfur vapor, graphite box and H_2S gas atmospheres for co-sputtered Cu_2ZnSnS_4 thin film", In *proceedings 40th IEEE Photovoltaic Specialist Conference (PVSC), 2014*, pp. 0390-0394.

[xi] Cai, C.H., Wei, S.Y., Huang, W.C., Hsu, C.H., Ho, W.H. and Lai, C.H., "Efficiency enhancement of $Cu_2ZnSn(S, Se)_4$ solar cells by S-modified surface layer", *Solar Energy Materials and Solar Cells*, *162*, 2017, pp.21-29.

[xii] Riha, S.C., Parkinson, B.A. and Prieto, A.L., "Solution-based synthesis and characterization of Cu_2ZnSnS_4 nanocrystals", *Journal of the American Chemical Society*, *131*(34), 2009, pp.12054-12055.

[xiii] Guo, Q., Hillhouse, H.W. and Agrawal, R., "Synthesis of Cu_2ZnSnS_4 nanocrystal ink and its use for solar cells", *Journal of the American Chemical Society*, *131*(33), 2009, pp.11672-11673.

[xiv] Mali, S.S., Shinde, P.S., Betty, C.A., Bhosale, P.N., Oh, Y.W. and Patil, P.S., "Synthesis and characterization of Cu_2ZnSnS_4 thin films by SILAR method", *Journal of Physics and Chemistry of Solids*, *73*(6), 2012, pp.735-740.

[xv] Rajeshmon, V.G., Menon, M.R., Kartha, C.S. and Vijayakumar, K.P., "Effect of copper concentration and spray rate on the properties Cu_2ZnSnS_4 thin films deposited using spray pyrolysis", *Journal of Analytical and Applied Pyrolysis*, *110*, 2014, pp.448-454.

[xvi] Thiruvenkadam, S., Jovina, D. and Rajesh, A.L., "The influence of deposition temperature in the photovoltaic properties of spray deposited CZTS thin films", *Solar Energy*, *106*, 2014, pp.166-170.

[xvii] Courel, M., Andrade-Arvizu, J.A., Guillén-Cervantes, A., Nicolás-Marín, M.M., Pulgarín-Agudelo, F.A. and Vigil-Galán, O., "Optimization of physical properties of spray-deposited Cu_2ZnSnS_4 thin films for solar cell applications", *Materials & Design*, *114*, 2017, pp.515-520.