

## FABRICATION OF p-Cu<sub>2</sub>ZnSnS<sub>4</sub> AND n-CdZnS CHALCOGENIDE LAYER BY CBD METHOD FOR Cu<sub>2</sub>ZnSnS<sub>4</sub> SOLAR CELL APPLICATION

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Copper zinc tin sulfide Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) solar cell thin film p-type absorber layer was fabricated using chemical bath deposition method at bath temperature 80 °C. The structural property of our fabricated p-CZTS thin film absorber layer was investigated by X-ray diffraction (XRD) method. The elemental composition of our fabricated p-CZTS layer was investigated by EDAX analysis. Then a 50 nm n-type Cadmium zinc sulfide (n-CdZnS) chalcogenide layer was fabricated on top of p-CZTS thin film absorber layer. The top view and cross-sectional view of p-CZTS/n-CdZnS layer was examined by using Scanning electron microscopy (SEM) analysis. The investigated results are presented and discussed in the present research article.

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**Keywords:** Copper zinc tin sulfide, CZTS solar cells, n-CdZnS chalcogenide layer, XRD, SEM, EDAX

### 1. Introduction

Thin film homo and hetero-junction solar cells were vastly investigated for low-cost manufacturing and renewable energy sources. Predominantly, Cu(In,Ga)Se<sub>2</sub> (CIGS) thin film hetero-junction solar cells are being importantly addressed [1-9] for present market opening. Further possibilities of Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> (CZTSSe) solar cells being issued more recently for further reduction of manufacturing cost by the use of earth abundant materials. Fundamentally, fabrication of the quaternary thin film solar cells depends on the base basic platform technologies. Thin film solar cells mostly fabricated with the help of both vacuum methods and chemical bath method. Each method has its own merit and demerit points. For the fabrication of thin film solar cells, there are several methods available such as vacuum-based, electro-chemical based and complex chemical solution-based depositions [10-15]. Examples for vacuum methods: RF sputtering, DC sputtering, co-evaporation, e-beam, PVD, CVD, MOCVD, Rapid thermal processing and many other existing vacuum methods are available in the present market. Examples for chemical methods: chemical bath deposition, SILAR method, ion exchange process, doctor blade method, electro deposition, electro less deposition, paste coating method, spray coating method etc., Among these methods chemical bath deposition (CBD) method is also a relatively simple and cost effective method. In the present work we utilized a well known CBD method for the fabrication of p-CZTS layer and n-CdZnS layers. These high quality layers are very important to fabricate cost effective CZTS solar cells.

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## 2. Experimental

Copper zinc tin sulfide  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) solar cell thin film p-type absorber layer was fabricated using chemical bath deposition (CBD) method. Chemical bath temperature was maintained at  $80^\circ\text{C}$  so that the reaction was very fast. Bath temperature was maintained constant throughout whole experiment to avoid any unbalanced reactive products. An appropriate amount (500 ml) of deionized water and tartaric acid ( $\text{HOOC}(\text{CHOH})_2\text{COOH}$ ) mixture 5 : 0.6 was taken in to a double wall glass bath and the ammonium citrate ( $\text{HOC}(\text{CO}_2\text{NH}_4)(\text{CH}_2\text{CO}_2\text{NH}_4)_2$ ) of 0.045 M was added to the above chemical solution. The whole solution mixture reaction was stirred until the whole salt mixture was dissolved and the final solution becomes transparent. After wards the copper sulfate of 0.023 M was added to the above mixture. The ammonium citrate was added to the above solution and this served as a copper ion complex agent. This complex agent sequesters the metal ions and resupplies the attracted metal ions in a slow rate so that the reaction was in a steady state. Further zinc sulfate and tin sulfate of 0.005 M and 0.015 M which appropriate mixture ratio were mixed with the above chemical reaction and finally the reaction mixture was completed with the sulfur source sodium thiosulfate and sodium sulfide 0.03-0.04 M. Then a Molybdenum (Mo) metal coated glass substrate was inserted inside this chemical bath and the experiment was continued over 1 hour to get reasonable thick p-CZTS thin film absorber layer. The fabricated p-CZTS particle thin film layer was investigated by XRD, SEM and EDX analysis to confirm the structural, surface and composition. Next stage a 50 nm n-CdZnS layer formed on p-CZTS layer using CBD method.  $\text{CdSO}_4$  (0.007 M),  $\text{ZnSO}_4$  (0.01 M), Ammonia water and sulfur source Thiourea (1.1 M) was used to fabricate n-CdZnS tin film. Afterwards a SEM top view was measured to find the surface quality of n-CdZnS layer. The investigated results are presented and discussed in detail.

## 3. Results and discussion

Fig. 1 showed the X-ray diffraction pattern of chemical bath deposited p-CZTS thin film absorber layer. The investigated XRD pattern showed very high intensity diffracted peaks which indicated that the fabricated p-CZTS thin film absorber layer have very high crystalline quality. The observed XRD peak angle  $2\theta = 30.517, 31.033, 37.787, 40.500, 49.704$  and  $73.704^\circ$  respectively. The multiple XRD peaks showed the fabricated p-CZTS have polycrystalline nature. The maximum XRD intensity peak observed at  $2\theta = 40.500$  and all other solder peaks have very small intensity than major peak.

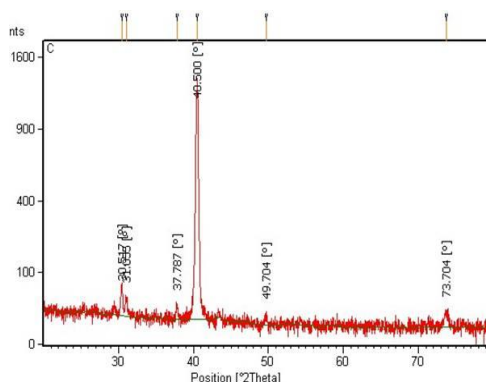
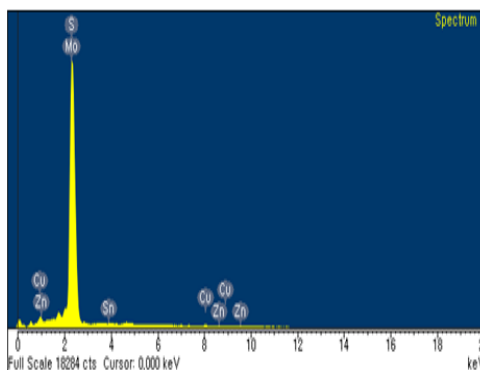


Fig. 1. X-ray diffraction pattern of chemical bath deposited p-CZTS thin film absorber layer.

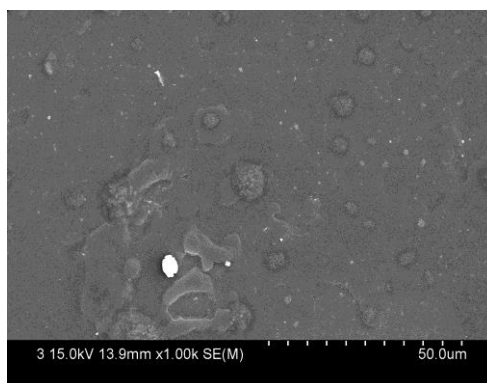
Fig. 2 showed the Energy dispersive analysis of X-rays (EDX) spectrum of our fabricated p-CZTS thin film absorber layer. The investigated EDX spectrum shows all elements (ie) Cu, Zn, Sn and S elements presented. The observed elemental composition atomic percentage was S (8.92%), Cu (1.54%), Zn (0.64%), Mo (88.57%) and Sn (0.33%) respectively. Here the substrate

elemental peak was more dominant because the fabricated p-CZTS thin film layer is less than  $1\mu\text{m}$  so that X-ray can easily penetrate CZTS layer. Sulfur rich CZTS is very important because much sulfur can go out during other solar cell layer fabrication the sample usually subjected for more than  $200\text{ }^{\circ}\text{C}$  processing temperature. Our fabricated CBD-CZTS EDX spectra showed sulfur atomic percentage rich S (8.92 %) which is 7 times higher than Cu element atomic percentage. So our fabricated p-CZTS thin film absorber layer is more suitable for solar cell fabrication directly.



*Fig. 2. EDX analysis of chemical bath deposited p-CZTS thin film absorber layer.*

Fig. 3 showed the top surface SEM view of our fabricated Glass/Mo/p-CZTS/n-CdZnS layer. In the top surface SEM view one can clearly see smoothly formed n-CdZnS layer with very little surface defects. This smooth surface morphology is very important to fabricate good quality solar cell device.



*Fig. 3. The SEM top surface view of our fabricated Glass/Mo/p-CZTS/n-CdZnS layer.*

Fig. 4 showed the Scanning electron microscopy (SEM) image of Glass/Mo/p-CZTS/n-CdZnS layer. The observed SEM cross-view showed very clear cut-off p-CZTS layer formation and each layer (ie) Glass, Molybdenum, p-CZTS and n-CdZnS layer formed very clearly without any diffusion.

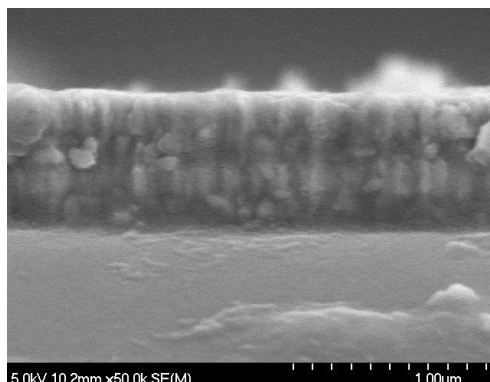


Fig. 4. Scanning electron microscopy (SEM) image of Glass/Mo/p-CZTS/n-CdZnS layer.

#### 4. Conclusions

A p-CZTS thin film absorber layer was fabricated on well cleaned Molybdenum coated soda lime glass substrate using a cost effective CBD method. The fabricated p-CZTS layer showed very high crystallinity and was confirmed by XRD. The investigated EDX result on CBD deposited p-CZTS layer showed very high sulfur elemental atomic percentage than other elements which is more important to fabricate good quality CZTS solar cells.

An n-CdZnS layer was fabricated on top of p-CZTS layer using CBD method. The SEM cross-section image of our fabricated Glass/Mo/p-CZTS/n-CdZnS showed very clear stack layer formation with our any material diffusion. The SEM top surface view of n-CdZnS layer fabricated on glass/Mo/p-CZTS showed very smooth surface morphology and very less porous nature only observed. This smooth surface morphology and very clear layer by layer stack without any layer diffusion is very important to fabricate good quality thin film multilayer solar cells. The present investigated chemical bath deposited p-CZTS/n-CdZnS layers results are very useful to fabricate high efficiency CZTS solar cells within a low cost.

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