Cu₂ZnSnSe₄ Solar Cell by Co-Sputtering with CdS and ZnCdS Hetero-Junction Companion and Its Effects Near to Hetero-interface: A Better Power Source for Micro and Nano Robotic System

D. Sivasamy^{1*}, M. Dev Anand², V. Krishnama Naidu³

¹Department of ECE, Jawaharlal Nehru Technological University, Hyderabad - 85, Andhra Pradesh, India

²Department of Mechanical Engineering, Noorul Islam Centre for Higher Education, Kanyakumari District, Tamil Nadu, India

³Department of ECE, GRIET, Hyderabad, Andhra Pradesh, India

***Corresponding author: E-Mail: sivasamy.d@gmail.com**

ABSTRACT

In this report, copper zinc tin selenide Cu₂ZnSnSe₄ (CZTSe) solar cell photo conversion efficiency of 4% and 2.2% were achieved by co-sputtered CZT precursor followed by selenization process without any carrier gas flow and with the aid of chemical bath deposited cadmium sulfide (CdS) and zinc cadmium sulfide (ZnCdS) hetero-junction companion and its effects related to Se, Sn, Cu elemental loss near to the CdS/ZnCdS and ZnCdS/CZTSe hetero-interface then CdS/ZnCdS and ZnCdS/CZTSe solar cell performance is preliminarily presented and discussed. Especially this work frames a good baseline for obtaining CZTSe absorber without any carrier gas flow during the selenization process and ZnCdS hetero-junction companion consisting of very less cadmium content alternative to the cadmium rich CdS buffer layer for earth-abundant CZTSe solar cells. The present grain based discrete CZTSe p-n junction solar cell device is very useful as a power energy source for micro and nano robot system.

KEY WORDS: Thin film, co-sputtering, CZTSe solar cell, CdS, ZnCdS, RTP selenization, Micro robot, Nano robot system.

1. INTRODUCTION

Solar cells based on CdTe and Cu(In, Ga) (S/Se)₂ (CIGS) thin film absorber layer have demonstrated major improvements over recent years and are currently experiencing considerable large scale development and production. Recently many frontier research groups dedicated on CIGS solar cell development and their effort lights the laboratory scale photo conversion efficiency reported from 19% to 20 % and the recent world record photo conversion efficiency of 20.8 % was reported by ZSW. Recently there is an increased interest on the fabrication of CuZnSn (S/Se/SSe) solar cell because of the earth abundant elements participation. In both CIGS and CZTS solar cell case chemical bath deposited CdS hetero-junction partner plays an important role such as (a) absorber layer protection from the plasma damage during the deposition of ZnO and Al: ZnO deposition by sputtering, (b) protect the absorber layer from the environment, (c) an appropriate CdS/(CIGS/CZTS) junction formation with specific barrier height (d) ultra-low cost and low temperature processing (e) superior photo conversion efficiency was reported by many research groups (Ramanathan, 2003; Contreras, 2005; Philip Jackson, 2007; Repins, 2008; Ito, 1988). In recent years CZT(S, Se/SSe) solar cell by vacuum and non-vacuum based research and development rapidly increasing because of its cost effectiveness and easily tunable band gap from 0.9 eV to 1.5 eV by fine tuning the elements especially Se to S (Ennaoui, 2009; Schubert, 2011; Shimada, 2007; Qijie Guo, 2012; Liu, 2010). In particular CZTSe solar cells was widely reported by using reactive sputtering method (Hiroaki Matsushita, 2000) selenization by H₂Se gas or selenization by rapid thermal process at high temperatures with controlled carrier gas flow during the selenization or sulfurization process. The present work emphasis the CZTSe thin film absorber layer fabrication by using co-sputtered CZT precursor and RTP selenization without any harmful carrier gas flow and fabrication of ZnCdS hetero-junction companion by chemical bath deposition method and its effectiveness on the CZTSe solar cell device fabrication.

2. EXPERIMENTAL

Molybdenum (Mo) thin film layer of 1.2 μm were deposited on soda-lime glass substrate by sputtering method and the fabricated Mo/glass substrates were ultrasonically cleaned by ethanol, acetone and water to remove the residues which results the suitable adhesion and MoSe₂ quasi ohmic layer formation during the CZTSe thin film absorber layer fabrication. CZTSe thin film absorber layer were fabricated on Mo substrate by co-sputtered CZT precursor followed by RTP selenization at the selenium growth rate of 23 ÅS⁻¹. The RTP selenization temperature of 500 °C and the duration of selenization process of 10-20 min were optimized from the several attempts made on the fabrication of suitable CZTSe thin film absorber layer fabrication which particular optimized condition utilized for all our CZTSe absorber layer fabrication. ZnCdS hetero-junction companion were fabricated on the CZTSe absorber layer (ZnCdS/CZTSe) by chemical bath deposition (CBD) method to make an appropriate hetero-junction. The aqueous methanol and ammonical base bath comprising of zinc sulfate (ZnSO₄), cadmium sulfate (CdSO₄), thiourea (CS(NH₂)₂) in the ratio of 2:(0.1):4 at the bath temperature of 70-75°C were employed for the fabrication of

ZnCdS layer on top of the CZTSe thin film absorber layer. The fabricated CZTSe absorber layer and ZnCdS fabricated on CZTSe layer were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and Raman spectroscopy measurements to investigate its structural, surface morphology, elemental and optical properties. The high resistive intrinsic zinc oxide (i-ZnO) and transparent conducting aluminum doped zinc oxide (Al:ZnO) layer of thickness 50nm and 450nm were fabricated on ZnCdS/CZTSe structure by widely utilized predetermined sputtering conditions. Finally Al grid pattern of thickness 1 μ m were fabricated to finalize the CZTSe solar cell structure by using mechanical shadow mask with the aid of electron beam evaporation at the controlled growth rate of 5 $\text{\AA}\text{s}^{-1}$.

Proposed Micro and Nano Robot Experimental Model: Usually nano and micro robot system action is vibration, rotation, translation and other combination of these mechanical actions. In this work we proposed a new model for rotation and vibration and translational motion of micro and nano robot simple system for various applications. In this model there are three stages of robot device fabrication; (a) Internal discrete Copper (Cu) metal nano wire grain arrangement, (b) ultra-thin polymer encapsulation layer covering, (c) top micro (or) nano continuous magnet layer fabrication. Taking positive and negative output from discrete Cu metal grains and giving power from CZTSe micro (or) nano cells. Then this nano and micro robotic rotational and vibration assembly started to work.

3. RESULTS AND DISCUSSION

Structural and Surface Micromorphology: The XRD analysis of the fabricated CZTSe thin film absorber layer were carried out to find the possible structural disorders and residual peak related to the impurity incorporation during the RTP selenization without any carrier gas. Figure.1, shows the XRD pattern of the fabricated CZTSe absorber at the scan rate of 0.025° per min at room temperature. The observed XRD pattern of the fabricated CZTSe absorber showed an major intense growth direction of (112) plane at 2 θ value of 27.125° and other two minor diffraction peak at 2 θ value of 45.139° and 53.40° related to the growth direction of (204) and (312) planes. The Mo substrate major and minor diffraction peak position at 2 θ values of (110) and (211) plane respectively. The observed CZTSe crystal growth direction are in good agreement with the reported literatures (Olekseyuk, 2002; Lian Guo, 2014; Ahn, 2010). XRD pattern of the ZnCdS/CZTSe (Figure.2), layers showed that there is no significant change on the bottom CZTSe diffraction peaks and two new peaks arrived at the 2 θ value of 34.44° and 36.27° which corresponds to the diffraction from the ZnCdS layer.

Figure.1. The XRD pattern of CZTSe thin film absorber layer fabricated by co-sputtering of CZT precursor on ~ 1 μ m Mo coated soda-lime glass substrate followed by the RTP selenization of 500°C for 10 min without any carrier gas flow

Figure.2. The XRD pattern of chemical bath deposited ZnCdS layer on CZTSe absorber layer

Surface micromorphology of the fabricated CZTSe absorber (Figure.3), showed a porous morphology with many pinholes and the SEM cross-section of the fabricated CZTSe absorber exhibited the thickness of around 1.5 – 1.8 μ m and the cross-view SEM of the total CZTSe device (Al:ZnO/ZnO/ZnCdS/CZTSe/Mo) displayed in the figure. 4. The surface morphology of the ZnCdS/CZTSe structure showed a pinhole free sphere like agglomerated granular surface morphology and the total CZTSe layer covered by ZnCdS layer which confirms the micro level uniform deposition and was shown in the figure.5, which is one of the important prerequisite to fabricate the high uniformity CZTSe solar cell devices. Number of small crystallites combined together and formed one spherical granules and an average size of each sphere like granules in the range of 0.5-0.7 μ m.

Figure.3. SEM top surface view of the fabricated CZTSe absorber layer

Figure.4. SEM cross section of the fabricated Al:ZnO/ZnO/ZnCdS/CZTSe/Mo/Glass structure

Figure.5. SEM top surface view of the ZnCdS/CZTSe layers

Elemental Analysis: Stoichiometry of the CZTSe absorber layer and ZnCdS/CZTSe layers were investigated by EDX analysis. Table.1, represents the elemental composition of the (a) CZTSe absorber layer, (b) ZnCdS/CZTSe layers and (c) ZnCdS only (CZTSe omitted). EDX analysis of the fabricated CZTSe absorber layer showed the Zn/Sn ratio of 2.06 and Cu/(Zn+Sn) ratio of 0.635 which showed the copper poor and zinc rich compound formation. The zinc rich CZTSe formation is one of the important essential requirement to attain the high efficiency CZTSe solar cell and were widely reported by many research groups. EDX analysis of the total ZnCdS/CZTSe layers showed the Zn presence excessively (76.91 atomic %), cadmium and sulfur presented only 2.24 and 1.32 atomic (atm) %. Copper and tin reduced half from the CZTSe absorber composition after the fabrication of ZnCdS layer. The major noteworthy influence of the ZnCdS formation on CZTSe absorber was the dramatic loss of Se from 49.84 atm% (CZTSe absorber) to 6.5 atm%. From the EDX survey of the CZTSe absorber and ZnCdS/CZTSe layers results the heavy elemental loss occurred in our fabricated CZTSe bulk material after the fabrication of the ZnCdS buffer layer on the CZTSe absorber which can play a vital role in the CZTSe solar cell device properties. Figure.6, displays the possible pictorial representation of the Cu, Sn and Se elemental loss near to the ZnCdS/CZTSe interface and SCR region in CZTSe bulk.

Figure.6. Pictorial representation of the Se, Sn, Cu elemental loss near to hetero-interface and SCR region due to the fabrication of n-type ZnCdS layer on the CZTSe absorber layer

Table.1. Elemental Composition

Elements	Cu (atm %)	Zn (atm %)	Sn (atm %)	Se (atm %)	Cd (atm %)	S (atm %)
(a) CZTSe layer	19.48	20.65	10.02	49.84	--	--
(b) ZnCdS/CZTSe layer	8.46	76.91	4.58	6.50	2.24	1.32
(c) ZnCdS layer	--	95.73	--	--	2.61	1.65

Raman Spectra Analysis: Raman spectroscopy is very useful tool to get the detailed information related to the possible presence of ZnSe, Cu_xSe, SnSe₂, Cu₂SnSe₃, CZTSe formation in the fabricated CZTSe thin film absorber layer. Raman spectra were recorded in the wavenumber range of 100-500cm⁻¹ to obtain the detailed information corresponds to the CZTSe absorber and ZnCdS/CZTSe layers. Figure.7, shows the Raman spectra of (a) CZTSe absorber layer and (b) ZnCdS/CZTSe layers. The major intensity Raman peak of CZTSe absorber layer occurred at 192.23 cm⁻¹ and other minor intensity peak observed at 233.4 cm⁻¹ which corresponds to the CZTSe compound. Another subsidiary peak identified at the wavenumber of 168.4 cm⁻¹ which evidences the formation of MoSe₂ and

there was no other notable peaks were observed. Raman spectra of ZnCdS/CZTSe layers showed the newly arrived intense broad ZnCdS peak at the wavenumber of 300.27 cm^{-1} and the bottom CZTSe layer showed a major and one minor intensity peaks resembled the above said separate CZTSe thin film absorber layer Raman shift. Another CZTSe minor intensity peak at the wave number of 233.4 cm^{-1} was merged sequentially with ZnCdS peak.

Figure.7. Raman spectra of (a) CZTSe absorber layer and (b) ZnCdS/CZTSe layers

Figure.8. Current-voltage characteristics of the fabricated ZnCdS/CZTSe solar cell device

Figure.9. A new proposed Nano robot engine design with nano (or) micro isolated grain CZTSe solar cell power source

Electrical Properties: Figure.8, shows the I-V graph of the n-type ZnCdS thin film assisted CZTSe solar cell device. The solar cell efficiencies were measured and recorded using a Keithley 4300 source meter under 100 mW/cm^2 irradiation (Oriel® Sol3A™, 450-W solar simulator equipped with an AM 1.5-G filter; Oriel Instruments, Irvine, CA, USA). The best CZTSe solar cell showed the efficiency of 2.3% under the optimized chemical bath deposited ZnCdS layer. The open circuit voltage (V_{oc}) was 273 mV and the short circuit current density (J_{sc}) was 20.1 mA/cm^2 . The series (R_s) and shunt (R_{sh}) resistances are $12.55\text{ }\Omega\text{cm}^2$ and $82.97\text{ }\Omega\text{cm}^2$ and the fill factor (FF) is 40.3%. The relatively low R_{sh} , V_{oc} and FF can be attributed to the Cu, Sn and Se elemental loss and morphological disorders after the fabrication of ZnCdS buffer layer on CZTSe absorber layer.

Proposed Micro and Nano Robot Power Source Application: CZTSe solar cells has individual grain stacked device structure (ie) device p-n junction is not continuous and just nano and micro grains joined and form p-n junction. So it is very easy to isolate micro and nano level devices using simple mechanical scribing (or) solution based etching method. This micro and nano level solar cell device is very useful for generating micro and nano power efficiency which can easily charge and operate micro and nano robot system.

4. CONCLUSION

Elemental precursors of Zn, Sn, Cu were co-sputtered and RTP selenized at 500°C to obtain the device quality CZTSe thin film absorber layer and there was no carrier gas flow during the RTP selenization. The XRD pattern of the fabricated CZTSe absorber showed a kesterite structure with no secondary phase formation. The SEM top-view of the CZTSe absorber layer showed a porous surface micro morphology with many permeable pinholes. EDX analysis of the CZTSe absorber layer showed a zinc rich and copper poor stoichiometry. The XRD pattern of the ZnCdS/CZTSe layers showed no significant change on the CZTSe absorber layer peaks and two new diffraction peaks were identified which originated by ZnCdS layer. The EDX analysis of ZnCdS/CZTSe layers showed a heavy elemental loss of Se, Sn and Cu which might be happened near to ZnCdS/CZTSe interface and space charge region (SCR) which leads the lower V_{oc} , R_{sh} and FF. The photo-conversion efficiency of 2.2% was achieved by the fabricated CZTSe solar cell device with the n-type ZnCdS hetero-junction partner. Improvement of CZTSe solar cell needs the further investigations related to the suitable modification of less or non-toxic n-type layer and its major influence near to the hetero-interface and SCR region which all are in line. Micro and nano robotic system operating power source application of CZTSe isolated grain based natural device structure proposed and its possibilities explained within our explanation limitation.

REFERENCES

- Ahn S, Jung S, Gwak J, Cho A, Shin K, Yoon K, Park D, Cheong H, Yun JH, Determination of band gap energy (Eg) of $\text{Cu}_2\text{ZnSnSe}_4$ thin films, on the discrepancies of reported band gap values, *Appl. Phys. Lett.*, 97, 2010.
- Contreras MA, Ramanathan K, AbuShama J, Hasoon F, Young DL, Egaas B, Noufi R, Diode characteristics in state of the art $\text{ZnO}/\text{CdS}/\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ solar cells, *Prog. Photovolt. Res. Appl.*, 13 (3), 2005, 209-216.
- Ennaoui A, Lux-Steiner M, Weber A, Abou-Ras D, Ko'tschau I, Schock H.W, Schurr R, Ho'lzling A, Jost S, Hock R, Vos T, Schulze J, Kirbs A, $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cells from electroplated precursors, novel low-cost perspective, *Thin Solid Films*, 517, 2009, 2511-2514.
- Hiroaki Matsushita, Takashi Maeda, Akinori Katsui, Takeo Takizawa, Thermal analysis and synthesis from the melts of Cu-based quaternary compounds Cu-III-IV-VI_4 and $\text{Cu}_2\text{-II-IV-VI}_4$ (II = Zn, Cd; III = Ga, In; IV = Ge, Sn; VI = Se), *Journal of Crystal Growth*, 208, 2000, 416-422.
- Hironori Katagiri, Kazuo Jimbo, Win Shwe Maw, Koichiro Oishi, Makoto Yamazaki, Hideaki Araki, Akiko Takeuchi, Development of CZTS-based thin film solar cells, *Thin Solid Films*, 517, 2009, 2455-2460.
- Ito K, Nakazawa T, Electrical and optical properties of stannite-type quaternary semiconductor thin films, *Jpn. J. Appl. Phys.*, 27, 1988, 2094-2097.
- Lian Guo, Yu Zhu, Oki Gunawan, Tayfun Gokmen, Vaughn R Deline, Shafaat Ahmed, Lubomyr T, Romankiw and Hariklia Deligianni, Electro deposited $\text{Cu}_2\text{ZnSnSe}_4$ thin film solar cell with 7% power conversion efficiency, *Prog. Photo volt: Res. Appl.*, 22, 2014, 58-68.
- Liu F, Li Y, Zhang K, Wang B, Yan C, Lai Y, Zhnag Z, Lie J, Lu Y, Insitu growth of $\text{Cu}_2\text{ZnSnS}_4$ thin films by reactive magnetron-sputtering, *Sol. Energy Mater. Sol. Cells*, 94 (12), 2010, 2431-2434.
- Moriya K, Fabrication of $\text{Cu}_2\text{ZnSnS}_4$ Thin-Film Solar Cell Prepared by Pulsed Laser Deposition, *Jpn. J. Appl. Phys.*, 46 (9A), 2007, 5780.
- Olekseyuk ID, Gulay LD, Dydechak IV, Piskach LV, Parasyuk OV, Marchuk OV, Single crystal preparation and crystal structure of the $\text{Cu}_2\text{Zn}/\text{Cd}$, Hg/SnSe_4 compounds, *Journal of Alloys and Compounds*, 340, 2002, 141-145.
- Philip Jackson, Dimitrios Hariskos, Erwin Lotter, Stefan Paetel, Roland Wuerz, Richard Menner, Wiltraud Wischmann and Michael Powalla, New world record efficiency for $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ thin-film solar cells beyond 20%, *Prog. Photovolt: Res. Appl.*, 19, 2011, 894-897.
- Philip Jackson, Roland Wurz, Uwe Rau, Julian Mattheis, Matthias Kurth, Thomas Schlotzer, Gerhard Bilger and Jurgen H, Werner, High Quality Baseline for High Efficiency, $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ Solar Cells, *Prog. Photovolt. Res. Appl.*, 15, 2007, 507-519.
- Qijie Guo, Grayson M Ford, Wei-Chang Yang, Charles J. Hages, Hugh W Hillhouse, Rakesh Agrawal, Enhancing the performance of CZTS solar cells with Ge alloying, *Sol. Energy Mater. Sol. Cells*, 105, 2012, 132-136.
- Ramanathan K, Contreras MA, Perkins CL, Asher S, Hasoon FS, Keane J, Young D, Romero M, Metzger W, Noufi R, Ward J, Duda A, Properties of 19.2% efficiency $\text{ZnO}/\text{CdS}/\text{CuInGaSe}_2$ thin-film solar cells, *Prog. Photo volt. Res. Appl.*, 11 (4), 2003, 225-230.
- Repins I, Contreras M, Romero M, Yan Y, Metzger W, Li J, Johnston S, Egaas B, DeHart C, Scharf J, McCandless BE, Noufi R, Characterization of 19.9% efficient CIGS absorbers, *IEEE Photo voltaics Specialists Conference Record*, 33, 2008.
- Repins I, Contreras MA, Egaas B, DeHart C, Scharf J, Perkins CL, To B, Noufi R, 19.9% efficient $\text{ZnO}/\text{CdS}/\text{CuInGaSe}_2$ solar cell with 81.2% fill factor, *Prog. Photo volt. Res. Appl.*, 16 (3), 2008, 235-239.
- Schubert B, Marsen B, Cinque S, Unold T, Klenk R, Schorr S, Schock H, $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cells by fast co-evaporation, *Prog. Photo volt. Res. Appl.*, 19, 2011, 93-96.
- Shimada T, Abstract book of The 2007 International Symposium on Organic and Inorganic Electronic Materials and Related Nanotechnologies, 2007, 162.