Enhancing Cu_2ZnSnS_4 Solar Cell Efficiency through Antimony Substitution for Tin: A SCAPS-1D Simulation Study

Sushmita Chaudhari, and Kannan P. K.

***Abstract*— SCAPS-1D, a one-dimensional solar cell simulator, provides a valuable tool for predicting device performance based on layer-by-layer material properties. Copper Zinc Tin Sulfide (CZTS) has emerged as a promising absorber material due to its exceptional light absorption coefficient and the abundance and non-toxic nature of its constituent elements. This study leverages SCAPS-1D to investigate the working mechanism of CZTS-based solar cells. We simulate a Mo/CZTS/CdS/ZnO device structure under AM 1.5 spectrum illumination and 300 K temperature, analyzing the impact of individual layer thickness on photovoltaic performance. Further, a comparative analysis explores the influence of various n-type materials. In addition, the introduction of antimony (Sb) doping into CZTS leads to a significant change in efficiency of the cell. The efficiency of Sb-doping CZTS attained 21.90%, while there was a great improvement by 3% via reduced recombination losses and enhanced photocurrent. This work gives an insight into the possibility of Sb doping for the improvement in the performance of thin-film solar cells.**

Link to graphical and video abstracts, and to code: https://latamt.ieeer9.org/index.php/transactions/article/view/9125

***Index Terms*— Photovoltaic cell, SCAPS-1D, CZTS, CdS, ZnO, Thin film.**

I. Introduction

THE increasing demand for clean and sustainable energy sources has driven significant research into renewable energy technologies. Among these, solar photovoltaics (PV) hold immense promise due to their ability to convert sunlight directly into electricity. Theoretically, only a small fraction of the Earth's surface covered with efficient solar cells could meet global energy demands. While solar PV accounted for roughly 8.3% of global electricity generation in 2024 [1], further efficiency improvements can significantly reduce production costs and make solar a viable alternative to fossil fuel-based power generation. Common thin film solar cell absorber materials are CdTe, ZnSe, Sb_2S_3, ZnTe and CZTS [2-9]. Among all Copper Zinc Tin Sulfide (CZTS, Cu_2ZnSnS_4) has emerged as a promising candidate for second-generation thin-film solar cells. Its high absorption coefficient, earth-abundant and non-toxic constituents, and direct bandgap make it an attractive substitute for currently used CdTe/CdSe-based thin-film solar cells. However, the maximum reported efficiencies for CZTS solar cells is around is around 10% and 12.6% for a CZTS and CZTSSe based solar cell solar cell [10-12] remain lower than those achieved with CIGS (Copper Indium Gallium Selenide) technology and theoretical predictions for CZTS.

Several deposition methods, both vacuum-based (sputtering [13], E-beam evaporation [14-15] etc.) and non-vacuum-based (dip coating [16-18], spin coating [19], electrodeposition [20-23], chemical bath deposition [24], combination technique of electrodeposition followed with chemical bath deposition [25] etc.), can be used to fabricate CZTS absorber layers. However, the performance of a solar cell depends not only on the absorber material but also on the other constituent layers, such as the buffer layer, window layer, and electrical contacts. These elements influence factors like band structure at heterojunctions and overall device functionality. In addition, there are several disadvantages of experimental methods such as cost inefficient, time inefficient etc. Optimizing parameters using experimental approach is very challenging and sometimes leading to inconsistent results. Secondly, reproducibility in various environmental or experimental conditions is also a biggest challenge. Hence in this study simulation is preferred as an invaluable tool instead of experimental approach before moving to experimental validity.

Researchers often use the SCAPS 1D simulation tool for optimize thin film solar cell performance. It facilitates the study of the effect of different parameters for example layer thickness, doping concentration etc. on the performance of device characteristics like QE, FF, Voc and Jsc. This make SCAPS 1D an important tool in solar cell design and optimization strategies. Specifically, researchers have been working to optimize second generation thin film solar cell using SCAPS 1D, including ZnTe based solar cell [7-8], CdTe based solar cell [2-3], ZnSe based solar cell [4] and CZTS based solar cell [9]. In case of CZTS various dopants have been reported with the view to minimizing the defects in Cu_2ZnSnS_4 (CZTS) and thereby improve the photocurrent of solar cells. Of these, antimony (Sb) has received much interest because of its ability to replace tin (Sn) within the CZTS crystal structure. This substitution also results in the formation, of an intermediate band about 0.5 eV below the valence band [26]. The existence of this intermediate band

The associate editor coordinating the review of this manuscript and approving it for publication was Diego Rivelino Espinoza-Trejo (*Corresponding author: Sushmita Chaudhari*).

Sushmita Chaudhari gratefully acknowledge MITS Gwalior for providing funding through the IRS scheme 2021 for this project and Marc Burgelman from Gents University in Belgium's department of electronics and information systems for generously providing the software free of cost.

Sushmita Chaudhari is with Department of Computer Science and Engineering, Brainware University Barasat, Kolkata-700125, West Bengal India (e-mail: sushmita.chaudhari@gmail.com).

Kannan P. K. is with Department of Physics, PSG Institute of Technology and Applied Research Coimbatore-641062, Tamil Nadu, India (e-mail: kannan@psgitech.ac.in).

TABLE V
MATERIALS PARAMETERS USED IN CASE OF SB DOPED CZTS

Parameters	*Sb doped CZTS*	*CdS*	*ZnO*
Thickness (μm)	2	0.05	0.08
Bandgap (eV)	1.14	2.4	3.3
Electron Affinity χ	4.35	4.5	4.6
Dielectric permittivity ε	13.6	10	9.0
CB density of state	2.2E18	2.2E18	2.2E18
VB density of state	1.8E19	1.8E19	1.8E19
Electron thermal velocity	1.0E7	1.0E7	1.0E7
Hole thermal velocity	1.0E7	1.0E7	1.0E7
Electron mobility	1.0E2	1.0E2	1.0E2
Hole mobility	2.5E1	2.5E1	2.5E1
Donor density	1.0E1	1.0E18	1.0E18
Acceptor density	1.0E17	0	1.0E1

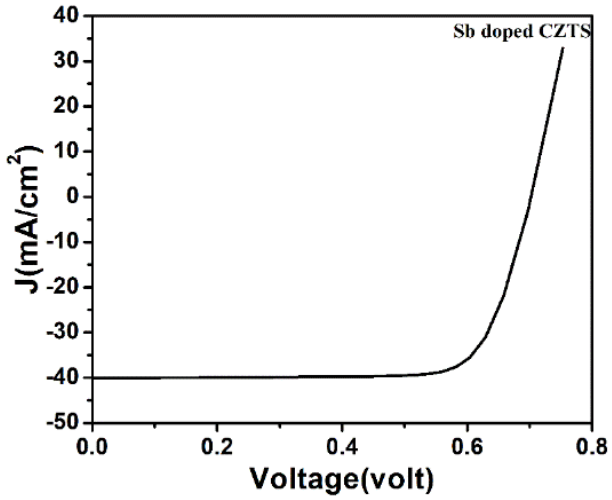

Fig. 9. J-V curve of Mo/Sb-CZTS/CdS/ZnO cell.

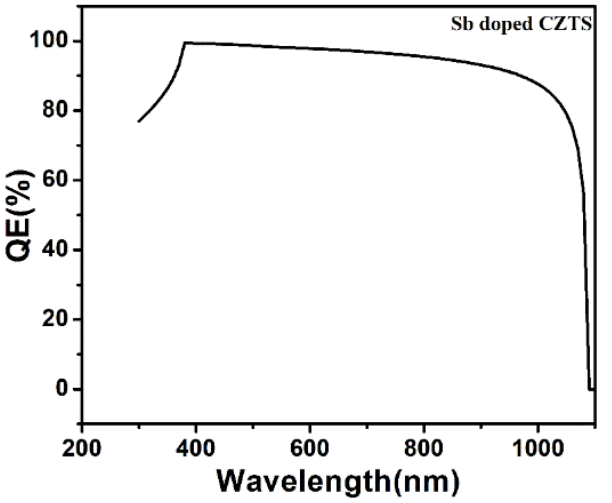

Fig. 10. Quantum Efficiency (QE) versus wavelength of Mo/Sb-CZTS/CdS/ZnO cell.

above 10% up to a wavelength of 1000 nm, as opposed to the 830 nm limit observed for the undoped device (Fig. 3). This signifies a significant improvement in light utilization by the Sb-doped CZTS solar cell. By effectively harvesting a broader range of light within the solar spectrum, Sb doping has the potential to contribute to the observed enhancement in overall device efficiency. Fig. 11 illustrates the simulated band

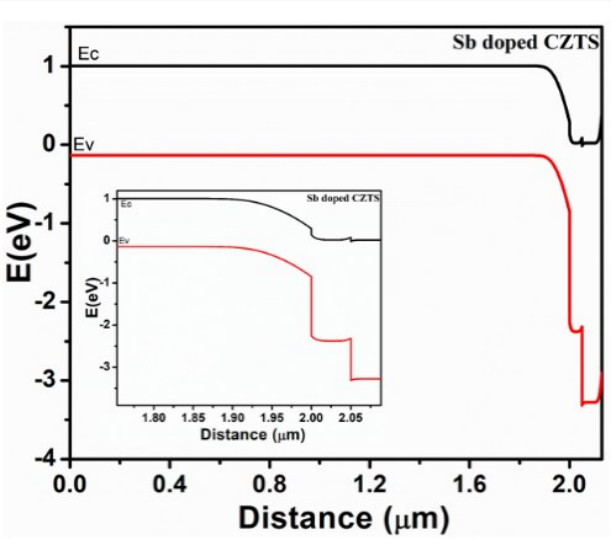

Fig. 11. Band alignment of Mo/Sb-CZTS/CdS/ZnO solar cell.

alignment for the Mo/Sb-CZTS/CdS/ZnO solar cell. The band alignment at the critical CZTS/CdS interface, which forms the heterojunction, appears largely unaffected by the Sb doping within the CZTS layer.

IV. CONCLUSION

This study employed numerical simulations to comprehensively investigate the device parameters of Mo/CZTS/CdS/ZnO thin-film solar cells. The simulations revealed that various parameters, including the thickness of the CZTS, CdS, and ZnO layers and impact of different buffer layer materials, significantly impact cell performance. The study additionally investigated the effects of Sb cation substitution within the CZTS structure. The results demonstrated a notable improvement in solar cell efficiency with Sb doping, suggesting this approach as a viable strategy for further efficiency enhancements. These findings hold significant potential for the development of next-generation high-efficiency solar cells. In the future, experimental studies of Sb doped CZTS solar cells are proposed for validation based on the SCAPS 1D simulation findings which suggest the improved efficiency of the cell. It includes synthesis of Sb doped CZTS material using non-vacuum techniques followed by the characterization to confirm the formation of Sb-doped CZTS material. Further, fabrication of Sb doped CZTS device is proposed to assess the Jsc, Voc, FF and efficiency of the cell under AM 1.5G condition. Formation of intermediate band above Valence band Maxima will be validated by the first-principles DFT calculations. Simulation results will be compared with experimental results to confirm the practical implementation of Sb-CZTS based solar cell.

REFERENCES

[1] Élodie de l'Épine and Ignacio Landivar, "2024 PV Trends: Global growth and challenges," PV Magazine International, Nov. 12, 2024. [Online]. Available: https://www.pv-magazine.com/2024/11/12/2024-pv-trends-global-growth-and-challenges.

[2] S. H. Zyoud et al., "Effect of Absorber (Acceptor) and Buffer (Donor) Layers Thickness on Mo/CdTe/CdS/ITO Thin Film Solar Cell Performance: SCAPS-1D Simulation Aspect," I.RE.MO.S., vol. 14 (1), pp. 10-17, Aprl 2021. doi:https://doi.org/10.15866/iremos.v14i1.19953

[3] S. H. Zyoud et al., "Numerical Modelling Analysis for Carrier Concentration Level Optimization of CdTe Heterojunction Thin Film–Based Solar Cell with Different Non–Toxic Metal Chalcogenide Buffer Layers Replacements: Using SCAPS–1D Software," Crystals, vol. 11 (12), pp. 1454, Dec 2021. https://doi.org/10.3390/cryst11121454https://doi.org/10.3390/cryst11121454

[4] S. H. Zyoud et al., "Simulation and Numerical Investigation of the Effect of Temperature and Defect on ZnTe/ZnSe/ZnO Thin-Film Photovoltaic Solar Cell Performance Efficiency," IREA, vol. 11, pp. 1-10 Jan 2023. https://doi.org/10.15866/irea.v11i1.20839

[5] M. S. Aljuboori et al., ''Enhancing Photoconversion Efficiency by Optimization of Electron/Hole Transport Interlayers in Antimony Sulfide Solar Cell using SCAPS-1D Simulation,'' JSESD, vol. 13 (1), pp. 97-113 Jun 2024. https://doi.org/10.51646/jsesd.v13i1.175

[6] Mubarak H. O. et al., "Simulation Analysis for the Efficiency Enhancement of Sb_2S_3 Solar Cell Using SCAPS-1D," CMMS, vol. 23 (4), pp. 19-29 2023. https://doi.org/10.7494/cmms.2023.4.0817

[7] S. H. Zyoud et al., "Numerical Simulation for Optimization of ZnTe-Based Thin-Film Heterojunction Solar Cells with Different Metal Chalcogenide Buffer Layers Replacements: SCAPS-1D Simulation Program," I.RE.MO.S., Vol. 14 (2), pp. 79-88 Aprl 2021. https://doi.org/10.15866/iremos.v14i2.19954

[8] S. H. Zyoud et al., "Investigating the impact of temperature and interlayer defects on the efficiency of Mo/ZnTe/ZnSe/SnO_2 heterojunction thin-film solar cells: A SCAPS-1D simulation study," I.RE.MO.S., vol. 16(3), pp. 120-128 June 2023. https://doi.org/10.15866/iremos.v16i3.22739

[9] S. H. Zyoud et al., "Numerical Modeling of High Conversion Efficiency FTO/ZnO/CdS/CZTS/MO Thin Film-Based Solar Cells: Using SCAPS-1D Software," Crystals, vol. 11, pp. 1468 (1-21) Nov 2021. https://doi.org/10.3390/cryst11121468

[10] Xin Cui et al., "Cd-Free Cu_2ZnSnS_4 solar cell with an efficiency greater than 10% enabled by Al_2O_3 passivation layers," Energy Environ. Sci., vol. 12, pp. 2751-2764 July 2019. https://doi.org/10.1039/C9EE01726G

[11] Wei Wang et al., "Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency," Adv Energy Mater., vol. 4(7), pp. 1301465 (1-5) Nov 2013. https://doi.org/10.1002/aenm.201301465

[12] H.-Q. Xiao et al., "Boosting the efficiency of solution-based CZTSSe solar cells by supercritical carbon dioxide treatment," Green Chem., vol. 22, pp. 3597-3607 May 2020. https://doi.org/10.1039/D0GC01355B

[13] S. Zhuk et al., "Critical review on sputter-deposited Cu_2ZnSnS_4 (CZTS) based thin-film photovoltaic technology focusing on device architecture and absorber quality on the solar cells performance," Sol. Energy Mater. Sol. Cells, vol. 171, pp. 239-252 Nov 2017. https://doi.org/10.1016/j.solmat.2017.05.064.

[14] Kannan P. K. et al., "Detailed investigations on influence of precursor stacking and sulfurization for Cu_2ZnSnS_4 film formation," Thin Solid Films, vol. 649, pp. 81-88 Mar 2018. https://doi.org/10.1016/j.tsf.2018.01.038.

[15] Kannan P. K. et al., "Effect of anionic substitution of S by Se in CZTSSe films prepared from electron beam evaporation," Mater. Today Proc., vol. 21 (4), pp. 1787-1792 2020. https://doi.org/10.1016/j.matpr.2020.01.232.

[16] S. Chaudhari et al., "Investigation of optimum annealing parameters for formation of dip-coated Cu_2ZnSnS_4 thin film," Thin Solid Films, vol. 612, pp. 456-462 Aug 2016. https://doi.org/10.1016/j.tsf.2016.06.046.

[17] S. Chaudhari et al., "Influence of stabilizing agent on dip coating of Cu_2ZnSnS_4 thin film," Thin Solid Films, vol. 636, pp. 144-149 Aug 2017. https://doi.org/10.1016/j.tsf.2017.05.045.

[18] S. Chaudhari et al., "Formulation of selenium-rich $Cu_2ZnSn(S_xSe_{1-x})_4$ film through non-vacuum dip coating technique," J. Mater. Sci.: Mater. Electron., vol. 32, pp. 19102-19109 July 2021. https://doi.org/10.1007/s10854-021-06427-y.

[19] K. Madhuri et al., "Investigations on treatments on CIGS formation using spin-coated CIG precursor," J. Mater. Sci.: Mater. Electron., vol. 32, pp. 1521-1527 Jan 2021. https://doi.org/10.1007/s10854-020-04921-3.

[20] S. Chaudhari et al., "Pulsed electrodeposition of Cu_2ZnSnS_4 absorber layer precursor for photovoltaic application," Thin Solid Films, vol. 600, pp. 169-174 Feb 2016. https://doi.org/10.1016/j.tsf.2016.01.021.

[21] S. H. Zyoud et al., "Influence of the redox couple concentration and activity of a NaOH/Na_2S/S electrolyte on the performance of CdS thin-film photoelectrochemical cells," Chem. Eng. J., vol. 10, pp. 100864 (1-9) Dec 2024. https://doi.org/10.1016/j.cscee.2024.100864.

[22] A. Zyoud et al., "Enhanced PEC characteristics of pre-annealed CuS film electrodes by metalloporphyrin/polymer matrices," Solar Energy Mater. Solar Cells, vol. 144, pp. 429-437 Jan 2016. https://doi.org/10.1016/j.solmat.2015.09.034.

[23] A. Zyoud et al., "High PEC conversion efficiencies from CuSe film electrodes modified with metalloporphyrin/polyethylene matrices," Electrochimica Acta, vol. 174, pp. 472-479 Aug 2015. https://doi.org/10.1016/j.electacta.2015.05.125.

[24] H. Sabri et al., "Enhancement of CdSe film electrode PEC characteristics by metalloporphyrin/polysiloxane matrices," Electrochimica Acta, vol. 136, pp. 138-145, Aug 2014. https://doi.org/10.1016/j.electacta.2014.05.071.

[25] A. Zyoud et al., "Enhanced PEC characteristics for CdSe polycrystalline film electrodes prepared by combined electrochemical/chemical bath depositions," J. Electroanal. Chem., vol. 774, pp. 7-13, Aug 2016. https://doi.org/10.1016/j.jelechem.2016.04.048.

[26] Xiaoli Zhang, Miaomiao Han, Zhi Zeng and Yuhua Duan, "The role of Sb in solar cell material Cu_2ZnSnS_4," J. Mater. Chem A, vol. 5, pp. 6606-6612 Mar 2017. https://doi.org/10.1039/C7TA01090G

[27] Kannan P.K. and Mariappan Anandkumar, "A theoretical investigation to boost the efficiency of CZTS solar cells using SCAPS-1D," Optik, vol. 288, pp. 171214 Oct 2023. https://doi.org/10.1016/j.ijleo.2023.171214.

[28] S. Siebentritt, "Why are kesterite solar cells not 20% efficient?," Thin Solid Films, vol 535, pp. 1-4 May 2013. https://doi.org/10.1016/j.tsf.2012.12.089

[29] Touria Ouslimane, Lhoussayne Et-taya, Lahoucine Elmaimouni, Abdellah Benami, "Impact of absorber layer thickness, defect density, and operating temperature on the performance of $MAPbI_3$ solar cells based on ZnO electron transporting material," Heliyon, vol. 7, pp. e06379 (1-6) Mar 2021. https://doi.org/10.1016/j.heliyon.2021.e06379

[30] Maykel Courel, J A Andrade-Arvizu and O Vigil-Galán, "The role of buffer/kesterite interface recombination and minority carrier lifetime on kesterite thin film solar cells, " Mater. Res. Express vol. 3 pp. 095501 (1-15) Sep 2016. https://doi.org/ 10.1088/2053-1591/3/9/095501

Sushmita Chaudhari is an Assistant Professor in Computer Science and Engineering department Brainware University Barasat, Kolkata India. She received her Ph.D. degree from Indian Institute of Technology Hyderabad. Her research interests include fabrication of semiconductor materials and its characterization. Additionally, Simulation and prediction of photovoltaic cell performance based on its layer by layer properties using SCAPS 1D.

Kannan P. K. is a renowned professor and researcher working in the field of Materials Science and Engineering. He received his PhD from the Indian Institute of Technology Hyderabad. At present, he works as an Assistant Professor (Senior Grade) in the Department of Physics at PSG Institute of Technology and Applied Research, Coimbatore, India. Dr. Kannan's research interest includes photovoltaic materials, high entropy oxides, perovskite etc.