Theoretical analysis of CZTS/CZTSSe tandem solar cell

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Abstract

Kesterite Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$ has tunable band-gap values in the range 1 to 1.5 eV depending upon the Sulphur/Selenium stoichiometry. We analyze the proposed tandem configuration of kesterite absorber family using SCAPS-1D for device performance. Pure sulphide kesterite Cu$_2$ZnSnS$_4$ (CZTS) of bandgap 1.5 eV is utilized as top cell and a sulpho-selenide Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$ (CZTSSe) of band-gap 1.1 eV as the bottom cell stacked in a tandem configuration. We utilize the script file capability of SCAPS to simulate the effect of the presence of the top cell on the bottom cell; as the incident spectrum passes though the top cell, a portion of the incident spectrum is filtered out before it reaches the bottom cell. The condition of identical short circuit current ($J_{SC}$) in the two cells in the tandem is attained by device optimization. We observe that a conservative estimate of two-junction tandem configuration of CZTS could achieve a minimum efficiency of 15%. This study brings out the device configuration of thin film CZTS/CZTSSe multi-junction for enhancing the efficiency of earth abundant CZTS based solar cells.

Keywords  Multi-junction · SCAPS-1D · Simulation · Band-gap tuning · Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$

1 Introduction

Single junction solar cells with a constant band-gap absorbs only a portion of the incident solar spectrum. Their efficiency is mainly limited by the non-absorption and thermalization losses; this sets a limit to the maximum value on efficiency of 33% (Honsberg and Barnett 2005), known as the Shockley-Queisser limit (SQL). A host of new techniques are suggested to suppress these losses and overcome SQL (Honsberg and Barnett 2005). Light concentration, spectrum conversion (up/down conversion), multiple temperature, multi-absorption and multi-energy level, multi-junction (MJ) are some techniques for overcoming SQL (Vos 1980). Theoretical efficiency of photovoltaic is 33–68% by various techniques under 1.5 AM Global (1-Sun) illumination (Vos 1980). Among all these, only the multi-junction (also known as tandem solar cell architecture) has achieved practical efficiency of around ~45% way beyond SQL (Vos 1980). This technology however is expensive and...
has been used only for specialized applications, e.g., in artificial satellites and deep space probes. It’s impact will be immense if implemented in a low-cost manner. Current research efforts are focused on lowering the cost and thus increasing the cost competitiveness in implementation of multi-junction in low-cost earth-abundant material based thin film solar cells. Low-cost material and high efficiency device will impart higher Watt/$ parameter (Wadia et al. 2009). This compelled the research community to choose low-cost material like DSS, CZTS and implement high efficiency configuration such as MJ/tandem in them to come up with a high Watt/$ tag. DSSC/CIGS (Seyrling et al. 2009), CGS/CIGS (Nishiwaki et al. 2003), Perovskite/CZTS (Todorov et al. 2014) are some experimentally reported attempts for implementation of tandem configuration for terrestrial applications.

The chalcogenide Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$ (CZTSSe) is composed of earth abundant materials such that CZTSSe solar cells have the highest Watt/cost tag among all the solar cells with efficiency higher than 10% (Wadia et al. 2009). It is a derivative of CIGS where In and Ga are replaced with earth abundant Zn and Sn (with a fraction of S replaced by Se) and considered a replacement for CIGS as a possible alternate for large scale deployment of low cost photovoltaic. The complex defect physics of CZTS has limited its efficiency to 12.6% as of now (Wang et al. 2014). The CZTS$_{1-x}$Se$_x$ has a well reported band-gap tuning (by varying the ratio of S/Se) in the range of 1–1.5 eV (Chen et al. 2011; Kumar 2021a), given by:

$$E_g = xE_{gCZTS} + (1-x)E_{gCZTSe} - bx(1-x)$$

where, $E_{gCZTS}$ is 1.5 eV, and $E_{gCZTSe}$= 1 eV, b is the bowing factor (=0.1 eV) (Chen et al. 2011; Kumar 2021a). CZT(S$_x$Se$_{1-x}$)$_4$ band gap tuning is advantageous for effectively absorbing the solar spectrum. Mechanically stacked arrangement of two thin films, to share same incoming radiation can capture the solar radiation more effectively. We propose a MJ or tandem configuration of Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$ solar cell to enhance its efficiency. Section 2 provide details of the methodology and simulation package used in the computational analysis. Here, the physics of tandem configuration and logic of tandem script are described. Section 3 explains the proposed conditions to achieve optimal efficiency and also talks about the complete working of the tandem configuration.

2 Simulation

In tandem configuration, the stacks of different band-gap junctions are arranged one over other in a decreasing band-gap order to absorb incident spectrum efficiently. The ith cell in the multijunction stack will generate current equal to the number of photons absorbed in that energy range of $E_{g i}$ (band-gap of the ith cell) to $E_{g i+1}$ (band-gap of the i + 1th cell). Here, the absorption of light emitted by another solar cell is neglected. The net generated power, P will be given by the product of current and total voltage in the stack and is empirically given by:

$$P = \sum_{i=1}^{n} IV_i$$  \hspace{1cm} (1)

The current is limited by the lowest current producing cell in the stack i.e. the value of current flowing through each cell in the whole stack. The current flowing through each cell in such a tandem structure is same that’s why I is a constant in the Eq. 1. Thus, the important
requirement in these cells is the operation of each device at identical current; for this we need to adjust parameters including thicknesses of absorber layers and band-gaps of absorber layers. This configuration is such that the current values is same and the voltage is added up from each junction. Each cell should be adjusted to their maximum performances and then operated at a common current and individual voltages. The Cu2ZnSnS4 (1.5 eV) and Cu2ZnSn(S0.8Se3.2) (1.1 eV) are attached in tandem sharing the same incident light spectrum. The higher band gap at the top will absorb the high energy photons (i.e. lower wavelength part in the incident spectrum). The high wavelength part of spectrum (i.e., low energy photons) will be transmitted from the top (with a large band-gap absorber layer) cell. This transmitted part is the illumination for the bottom cell (with a low band-gap absorber layer). The current densities in the two cells is given by the spectrum absorbed by the respective absorbers and is given by:

\[ J_{\text{CZTS}} = q \int_{E_{\text{gCZTS}}}^{E_{\text{gAM1.5}}} \phi_{\text{AM1.5}}(\lambda) d\lambda \]

\[ J_{\text{CZTSSe}} = q \int_{E_{\text{gCZTSSe}}}^{E_{\text{gAM1.5}}} \phi_{\text{AM1.5}}(\lambda) d\lambda \]

where, \( \phi_{\text{AM1.5}} \) is the spectral photon flux. We performed theoretical analysis of the current generated by the two layers in tandem and the overall efficiency of such tandem structure by using SCAPS-1D (Solar cell capacitance simulator) (Adewoyin et al. 2017; Burgelman et al. 2000; Kumar 2021b,2021c; Kumar and Ranjan 2021,2020; Kumar and Thakur 2021,2019,2018a,2018b; Islam et al. 2021) version 3.3.02. We use script file for optimizing the spectrum absorbed in the different bandgap in the multijunction (Kim et al. 2017). The device is illuminated with AM1.5 single sun spectrum. In tandem configuration, identical current flows through the two cells; this current matching is done by varying thickness of the two cells. The J-V of tandem is obtained by a series connection of two cell using SCAPS script “tandem connection.script”. It calculates the transmitted spectrum from top cell and applies that spectrum to bottom cell as illumination. The absorption of the two cells is added to get the J-V of the tandem cell. We first benchmark the CZTS and CZTSSe devices individually (Leea et al. 2016). The rationale behind benchmarking the CZTSSe (Leea et al. 2016; Kumar and Thakur 2018c) and CZTS (Patel and Ray 2012) cells are reported in our earlier work. The CZTS solar cell and CZTSSe cell are simulated separately. Multivalent defect of charge state \{3+/2+, 2+/+, +/0\} in conduction band (CB) at \( E_0 = 1.40 \) eV and charge state \{0/−, −/2−, 2−/+ \} at valence band (VB) are used for the purpose. A defect density of \( 5 \times 10^{14} \) cm\(^{-3}\), capture cross section of \( 10^{-13} \) cm\(^2\), a recombination coefficient of \( 10^{-13} \) cm\(^{-3}\)s, an Auger recombination coefficient of \( 10^{-28} \) cm\(^6\)s, and an interface neutral defect density of \( 10^{12} \) cm\(^{-3}\) (taken at CZTS/CdS junction) were used for a realistic device simulation. The material parameters used here are detailed in Table 1 (Islam et al. 2021; Kumar and Thakur 2018a,2018b,2018c; Kumar and Ranjan 2020; Kim et al. 2017; Leea et al. 2016; Patel and Ray 2012; Hironiwa et al. 2014).
The schematic of the CZTS/CZT(S_xSe_1−x)4 tandem configuration is shown in Fig. 1a. Tandem cell comprise of Cu_2ZnSnS_4 as absorber layer with band-gap of 1.5 eV in the top cell and the Cu_2ZnSn(S_0.8Se_3.2) (where x = 0.2) as an absorber layer with a band-gap of 1.1 eV in the bottom cell. The cells are mechanically stacked one over other in series (with identical current) sharing the incident spectrum. The inter-connect between two cell is thought to be ohmic, optically transparent and conductive (Sameshima et al. 2011; Tung et al. 2011).

The J-V characteristics of individual cells is simulated in Fig. 1b. Individual cell configuration include absorber (Cu_2ZnSnS_4)/buffer (CdS) and absorber (Cu_2ZnSn(S_0.8Se_3.2)/buffer (CdS), respectively. Individual simulated power conversion efficiency (PCE) of CZTS solar cell is 8.37% and that of CZT(S_xSe_1−x)4 solar cell is 12.67%. A low band-gap absorber will absorb higher spectrum as compared to high band-gap absorber. Thus, bottom cell with low band-gap has higher J_SC and lower V_OC as compared to top cell. The wavelength ranges of absorption in CZTS and CZTSSe layer are simulated in quantum efficiency (QE) plots. The comparative QE plots are shown in Fig. 1c. It brings out higher wavelength range of absorption in CZTSe (low band-gap of 1.1 eV). It implies that the current J_SC will be higher in the bottom CZTSe layer. Figure 1d shows the rate of change of QE with wavelength (λ) in the range of 700–1200 nm. The steep dip in dQE/dλ shows the cutoff wavelength for the two absorbers. Radiation below the cutoff wavelengths are absorbed by the respective cells. The J-V curve shows an inherent challenge, i.e. the different J_SC values in CZTS and CZTSe solar cells. The proposed tandem will have more than one current source of different values and they are to be attached in series.

Current generating from the two cells must be equal for a tandem configuration. For this we have to adjust (and optimize) device parameters to achieve similar current in both the cell. The one practical solution to have identical short circuit current flowing in the circuit is by optimizing thicknesses of the two layers. Along with it, we have to take care

### Table 1 Material parameter of the different absorber as used in the simulation. (Islam et al. 2021; Kumar and Thakur 2018a, 2018b, 2018c; Kumar and Ranjan 2020; Kim et al. 2017; Leea et al. 2016; Patel and Ray 2012; Hironiwa et al. 2014)

| Parameter                                      | CZTS_xSe_1−x | CdS | ZnO |
|-----------------------------------------------|--------------|-----|-----|
| Thickness (nm)                                 | Variable     | Variable | 80  | 400 |
| Bandgap (eV)                                   | 1.1          | 1.5 | 2.4 | 3.3 |
| Electron affinity (eV)                         | 4.1          | 4.2 | 4.25| 4.5 |
| Dielectric permittivity                        | 10           | 7   | 9   | 9   |
| CB effective density of state N(C)(cm⁻³)        | 2.2 (×10¹⁵)  | 2.2 | 1.8 | 2.2 |
| VB effective density of state N(V)(cm⁻³)        | 1.8 (×10¹⁵)  | 1.8 | 2.4 | 1.8 |
| Electron thermal velocity(cm/s)                | 10⁷          | 10⁷ | 10⁷ | 10⁷ |
| Hole thermal velocity(cm/s)                    | 10⁷          | 10⁷ | 10⁷ | 10⁷ |
| Electron/hole mobility(cm²/Vs)                 | 40           | 75  | 80  | 30  |
| Donor/ Acceptor density, N_D /N_A (cm⁻³)       | 10¹⁵         | 10¹⁶| 10¹⁷| 10¹⁸|
| Absorption coefficient(cm⁻¹)(×10⁴)             | 5            | 5   | SCAPS value | SCAPS value |
of the spectrum absorption in the two absorbers. The top is optically present for bottom cell; as incident spectrum passes through the top cell first, the short wavelength portion of spectrum is filtered out before it reaches the bottom cell. Top layer therefore acts as the spectrum source for bottom cell such that the top cell is illuminated with the full solar spectrum, and the bottom cell is illuminated with the residual spectrum transmitted by the top cell. This condition is kept in calculation for attaining similar current values in the two cells. Current is limited by the cell producing the lowest current. Voltage generated in individual cell can be directly added as they are connected in series. Simulations are run for optimizing thicknesses with top cell illuminated with full spectrum and bottom cell illuminated with transmitted spectrum, to attain the condition of current matching $J_{SC}$ (short circuit current) in top Cu$_2$ZnSnS$_4$ cell and bottom Cu$_2$ZnSn(S$_{0.8}$Se$_{3.2}$) cell. Figure 2a shows the J-V of the bottom cell (in red line), top cell (in blue line) and of tandem connection (in black line) using ‘tandem connection.script’. Current of the bottom cell is higher than the top cell. The tandem J-V is shown in black color line (not plotted in the current mismatch region below 0.4 V) as shown in Fig. 2a. The $J_{SC}$ value in the top cell is 18.7 mA/cm$^2$, this is the current value at which tandem device is required to be operated. The bottom cell with lower band-gap has high current value; thus the bottom absorber thickness could be reduced to vary the current so as to match it with the top cell. Figure 2b shows the plot
of $J_{SC}$ dependence on thickness of bottom cell in the residual spectrum transmitted from top cell. Thickness corresponding to short circuit value in top cell is the optimal thickness ($t_b$) of the bottom absorber as can be seen in Fig. 2b (marked by dotted lines). At current matching condition, the optimum value of thickness for bottom layer (1.1 eV) is 0.148 micron and top layer (1.5 eV) thickness is 0.6 micron. The crucial issues in the tandem device design are the spectrum calculation of the two cell and the short circuit current $J_{SC}$ matching.

The final J-V at the current matched condition for the Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$ is shown in the Fig. 3. The tandem J-V shows the $J_{SC}$ of 18.7 mA/cm$^2$ and the voltage of the tandem is the linear sum of individual voltages in the two cells. When the condition of same current in the stack is met, the the corresponding tandem J-V curve (upto short circuit condition) is shown by black color line in Fig. 3. The cell parameters of $V_{OC}$, $FF$ and $J_{SC}$ in individual cells and the tandem stack are shown in Fig. 3. The optimized configuration of tandem cell device parameters are $V_{OC}$ of 1.21 V, $J_{SC}$ of 18.6 mA/cm$^2$, fillfactor of 66%, and PCE of 0.52

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**Fig. 2** a The J-V for the CZTS, CZTSSe and tandem solar cell configuration. The current is highly mismatched; SCAPS does not plot tandem J-V for the mismatched region. b Shows the dependence of short circuit current with the thickness of bottom cell

**Fig. 3** The final optimized J-V of the tandem cell. The individual J-V of the CZTS and CZTSSe is also shown, at optimum thickness for current matching condition
15.12%. This efficiency is higher than the best reported PCE of earth abundant chalcogenide photovoltaic device of 12.6%.

4 Conclusion

CZTS/Se material has tremendous potential among possible thin film solar cell materials suitable for MJ owing to its wide bandgap tuneability. Analysis of tandem or multi-junction for Kesterite family with composition formula of \((\text{CZTS}_x\text{Se}_{1-x})_4\), having bandgap pair (1.1 and 1.5 eV) is presented here. Simulated results show a high value of voltage 1.21 V (higher than the band-gap of one of the cells in tandem) and a high efficiency of 15.12%. Thickness of the absorber layer in two solar cells in tandem is optimized to obtain current matching condition. This work proposes a suitable tandem architecture which could realize high efficiency in thin film multi-junction Kesterite CZTS/CZTSSe solar cells. Our computational analysis shows that the experimental realization of tandem configuration could possibly be a cost-effective way to enhance the efficiency in CZTS/ CZTSSe based solar cells.

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Declarations

Conflict of interest Authors declare no competing conflict of interest.

References

Adewoyin, A.D., Olopade, M.A., Chendo, M.: Enhancement of the conversion efficiency of Cu2ZnSnS4 thin film solar cell through the optimization of some device parameters. Optik 133, 122–131 (2017)
Burgelman, M., Nollet, P., Degrave, S.: Modelling polycrystalline semiconductor solar cells. Thin Solid Films 361–362, 527–532 (2000)
Chen, S., Walsh, A., Yang, J., Gong, X.G., Sun, L., Yang, P., Chu, J., Wei, S.: Compositional dependence of structural and electronic properties of Cu2ZnSn(S, Se)4 alloys for thin film solar cells. Phys. Rev. B 83, 125201 (2011)
Hironiwa, D., Murata, M., Ashida, N., Tang, Z., Minemoto, T.: Simulation of optimum band-gap grading profile of Cu2ZnSn(S, Se)4 solar cells with different optical and defect properties. Jpn. J. Appl. Phys. 53, 071201 (2014)
Honsberg C. B., Barnett A. M.: Paths to ultra-high efficiency (>50% efficient) photovoltaic devices. In 20th European photovoltaic solar energy conference, 6 – 10 June 2005, Barcelona, Spain, 453–456 (2005)
Islam, M.T., Kumar, A., Thakur, A.K.: Defect density control using an intrinsic layer to enhance conversion efficiency in an optimized SnS solar cell. J. Elec. Mater. 50, 3603–3613 (2021)
Kim, K., Gwak, J., Ahn, S.K., Eo, Y., Park, J.H., Cho, J., Kang, M.G., Song, H., Yun, J.H.: Simulations of chalcopyrite/c-Si tandem cells using SCAPS-1D. Sol. Energy 145, 52–58 (2017)
Kumar, A.: Impact of selenium composition variation in CZTS solar cell. Optik 234, 166421 (2021)
Kumar, A.: Efficiency enhancement of CZTS solar cells using structural engineering. Superlattices Microstruct. 153, 106872 (2021)
Kumar, A.: Numerical modelling of ion-migration caused hysteresis in perovskite solar cells. Opt. Quant. Electron. 53, 166 (2021c)
Kumar, A., Ranjan, P.: Defects signature in Voc characterization of thin-film solar cells. Sol. Energy 220, 35–42 (2021)
Kumar, A., Thakur, A.D.: Design issues for optimum solar cell configuration. AIP Conf. Proc. 1953, 050022 (2018b). https://doi.org/10.1063/1.5032677
Kumar, A., Thakur, A.D.: Comprehensive loss modeling in Cu2ZnSnS4 solar cells. Curr. Appl. Phys. 19, 10 (2019)
Kumar, A., Ranjan, P.: Impact of light soaking on absorber and buffer layer in thin film solar cells. Appl. Phys. A 126, 397 (2020)
Kumar, A., Thakur, A.D.: Improvement of efficiency in CZTSSe solar cell by using back surface field. IOP Conf. Ser.: Mater. Sci. Eng. 360, 012027 (2018)
Kumar, A., Thakur, A.D.: Role of contact work function, back surface field, and conduction bandoffset in Cu2ZnSnS4 solar cell. Jpn. J. Appl. Phys. 57(S3), 08RC05 (2018)
Kumar, A., Thakur, A.D.: Impurity photovoltaic and split spectrum for efficiency gain in Cu2ZnSnS4 solar cell. Optik 238, 166783 (2021)
Lee, S., Price, K., Park, J.: Quantum efficiency modeling of thin film solar cells under biased conditions with a case study of CZTSSe solar cells. Thin Solid Films 619, 208–213 (2016)
Nishiwaki, S., Siebentritt, S., Walk, P., Ch. Lux-Steiner, M.: A stacked chalcopyrite thin-film tandem solar cell with 12 V open-circuit voltage. Prog. Photovolt: Res. Appl. 11, 243–248 (2003)
Patel, M., Ray, A.: Enhancement of output performance of Cu2ZnSnS4 thin film solar cells—a numerical simulation approach and comparison to experiments. Phys. B 407, 4391–4397 (2012)
Sameshima, T., Takenezawa, J., Hasumi, M., Koida, T., Kaneko, T., Karasawa, M., Kondo, M.: Multi junction solar cells stacked with transparent and conductive adhesive. Jpn. J. Appl. Phys. 50(5R), 052301 (2011)
Seyrling, S., Calnan, S., Bücheler, S., Hüpkes, J., Wenger, S., Brémaud, D., Zogg, H., Tiwari, A.N.: CuIn1−xGaxSe2 photovoltaic devices for tandem solar cell application. Thin Solid Films 517, 2411–2414 (2009)
Todorov, T., Gershon, T., Gunawan, O., Sturdevant, C., Guha, S.: Perovskite-kesterite monolithic tandem solar cells with high open-circuit voltage. Appl. Phys. Lett. 105, 173902 (2014)
Tung, V.C., Kim, J., Cote, L.J., Huang, J.: Sticky interconnect for solution-processed tandem solar cells. J. Am. Chem. Soc. 133, 9262–9265 (2011)
Vos, A.D.: Detailed balance limit of the efficiency of tandem solar cells. J. Phys. D: Appl. Phys. 13, 839 (1980)
Wadia, C., Paul Alivisatos, A., Kammen, D.M.: Materials availability expands the opportunity for large-scale photovoltaics deployment. Environ. Sci. Technol. 43(6), 2072–2077 (2009)
Wang, W., Winkler, M.T., Gunawan, O., Gokmen, T., Todorov, T.K., Zhu, Y., Mitzi, D.B.: Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency. Adv. Energy Mater. 4, 1301465 (2014)

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