

Single- / multiple- junction(s) and graded bandgap solar cell

5.1 Introduction

Much emphasis is currently being placed on cost-effective and efficient energy conversion using photovoltaic technology. After the available CdTe and CIGS-based commercial solar cells, the $\text{Cu}_2\text{ZnSn}(\text{S}/\text{Se})_4$ (CZTS) has been regarded as a more pronounced candidate for its relative earth abundance and non-toxic elements. Although the efficiency of single junction CZTS is currently 13.8% (P. Chen et al., 2023), it is significantly lower than the 22.1% for CdTe (Green et al., 2018) and 23.35% for CIGS (Chantana et al., 2020) solar cells due to a variety of factors such as high voltage deficit due to Cu_{Zn} antisite defects (Nisika et al., 2020), Sn-related deep energy level defects, grain interior defects, and so on (G. Lim et al., 2023). Recently, it is claimed that the Cu-Zn disorder in different planes is more detrimental as it elongates the Sn-S/Se bond length and, hence, downshifts the conduction band, decreasing the band gap and reducing the optical absorption (Zhu et al., 2024). Several methods have been used to improve CZTSSe-based thin film solar cells, including cation substitution (Ag, Li for Cu, Cd for Zn, and Ge for Sn) to reduce Cu and Sn-related defects, (ii) using passivation layers at the front and back interface, and (iii) alkali metal doping to passivate grain boundary defects. Moreover, further solutions, such as graded bandgap absorbers along multiple junction absorbers, have considerably attempted to enhance efficiency. Guo et al. recently established a 12.25% efficient bandgap graded $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cell and explained its significance for efficient carrier collection and light harvesting (Guo et al., 2022). This study applies the simple sol-gel technique while annealing the device to make Cd-graded CZTSSe and achieve a decent-quality absorber. Inspired by this, we hope that graded junctions will be suitable for fabricating a solar cell.

As stated in Chapter 1, CHTS and its alloys provide an equal chance for flexible photovoltaic applications as CZTS due to their substantial absorption coefficient of 10^4 cm^{-1} and acceptable bandgap of 0.8 eV to 1.33 eV. Consider the similar potential of CHTS, which we explored in our work for its photovoltaic response. The first photovoltaic response of an $\text{Al}:\text{ZnO}/\text{ZnO}/\text{CdS}/\text{Cu}_2\text{HgSnS}_4/\text{back contact}$ heterostructure-based thin film solar cell is investigated using drift-diffusion modelling. The impact of various physical factors such as absorber defect density, minority carrier lifetime, and so on is examined. Then, to ensure the lowest transmission loss, we proposed a tandem junction device with $\text{Cu}_2\text{HgSnS}_4$ as the top cell and its Se counterpart $\text{Cu}_2\text{HgSnSe}_4$ as the bottom cell. Finally, we investigate the CHTS absorber material as an alternate graded bandgap solar cell material, with $\text{Cu}_2\text{HgSnS}_4$ at one end, producing a junction with the CdS buffer layer, and CHTSe on the other, with the S percentage believed to drop from CHTS to CHTSe while enriching Se on the other.

5.2 Device Modelling and Simulation

The schematic of CdS (n-type)/CHTS (p-type) heterojunction solar cell structure is shown in Figure 5.1 (a). We considered Molybdenum (Mo) as the back contact, ZnO as the window layer, CdS as the buffer layer, and Al-doped ZnO top layer as the transparent conducting oxide layer, acting as the front contact. Here, a p-type CHTS layer is an active absorber, and a wide bandgap n-type CdS is the buffer layer, allowing the larger solar spectrum to reach the absorber with a proper band alignment with other corresponding layers in the device. All the desired material parameters are listed in Table 5.1. Most of the material's properties are considered from the previous study, as discussed in Chapter 1.

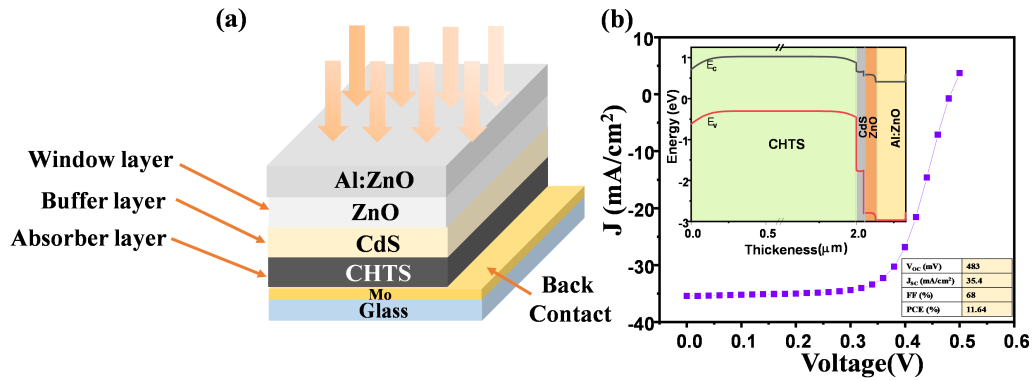


Figure 5.1. (a) Schematic diagram of the “Al:ZnO/ZnO/CdS/CHTS/back contact”, single-junction solar cell. (b) Estimated I-V characteristics of CHTS-based solar cells using SCAPS-1d software with an inset showing band alignments of different interfaces.

Table 5.1. Material properties considered in this work to simulate the single-junction solar cell.

Parameters	CHTS	CdS	i-ZnO	Al:ZnO
Thickness (μm)	2	0.05	0.08	0.2
Electron Affinity (eV)	4.3	4.5 (Simya et al., 2015)	4.6(Kanevce et al., 2015)	4.6 (Kanevce et al., 2015)
Bandgap (eV)	1.33 [*]	2.42 (Simya et al., 2015)(Kanevce et al., 2015)	3.37 (Kanevce et al., 2015)	3.37 (Kanevce et al., 2015)
Dielectric permittivity	10.6 [*]	9 (Simya et al., 2015)(Kanevce et al., 2015)	9(Simya et al., 2015) (Kanevce et al., 2015)	9(Simya et al., 2015) (Kanevce et al., 2015)
CB effective density of states (cm ⁻³)	2.20×10 ¹⁸	1.80×10 ¹⁹ (Morales-Acevedo, 2006)(Courel et al., 2016)	2.20×10 ¹⁸ (Wenhao Zhao et al., 2012)	2.20×10 ¹⁸ (Courel et al., 2016)
VB effective density of states (cm ⁻³)	1.80×10 ¹⁹	2.40×10 ¹⁸ (Morales-Acevedo, 2006)(Courel et al., 2016)	1.80×10 ¹⁹ (Wenhao Zhao et al., 2012)	1.80×10 ¹⁹ (Courel et al., 2016)

Thermal velocity of electron (cm/s)	1×10^7	1×10^7 (Kanevce et al., 2015)	1×10^7 (Kanevce et al., 2015)	1×10^7 (Courel et al., 2016)
Thermal velocity of hole(cm/s)	1×10^7	1×10^7 (Kanevce et al., 2015)	1×10^7 (Kanevce et al., 2015)	1×10^7 (Kanevce et al., 2015)
Electron Mobility (cm^2/Vs)	100	160 (Gupta & Dixit, 2018)	150 (Gupta & Dixit, 2018)	150 (Gupta & Dixit, 2018)
Hole Mobility (cm^2/Vs)	35	50 (Courel et al., 2016)	25 (Courel et al., 2016)	25 (Courel et al., 2016)
Donor concentration	0	10^{17}	10^{17}	10^{20}
Acceptor concentration	1.00×10^{16}	0	0	0
Absorption Coefficient	File *	SCAPS	SCAPS	SCAPS
Radiative recombination coefficient	1.04×10^{-10}	1.04×10^{-10} (Gupta & Dixit, 2018)	1.04×10^{-10} (Gupta & Dixit, 2018)	
Electron effective mass	$2.5 \times 10^{-1} m_0$ *	$2.5 \times 10^{-1} m_0$ (Courel et al., 2016)	$2.75 \times 10^{-1} m_0$ (Courel et al., 2016)	$2.75 \times 10^{-1} m_0$ (Courel et al., 2016)
Hole effective mass	$9.10 \times 10^{-1} m_0$ *	$7 \times 10^{-1} m_0$ (Courel et al., 2016)	$5.90 \times 10^{-1} m_0$ (Courel et al., 2016)	$5.90 \times 10^{-1} m_0$ (Courel et al., 2016)
Capture cross section hole (cm^2)	1.0×10^{-15}	1.00×10^{-13} (Courel et al., 2016)	1.00×10^{-15} (Courel et al., 2016)	1.00×10^{-15} (Courel et al., 2016)
Capture cross section electron (cm^2)	1.00×10^{-15}	1.00×10^{-15} (Gupta & Dixit, 2018)	1.00×10^{-15} (Gupta & Dixit, 2018)	1.00×10^{-15} (Gupta & Dixit, 2018)
Minority carrier lifetime (ns)	1.00×10^2			
Interface recombination speed (cm/s)	10^4			
Defect-type at CHTS	Donor			
Defect type at CHTS/CdS interface	Neutral			

*computed in this work

The simulation is performed using the one-dimensional numerical simulator SCAPS (Hartiti et al., 2017), which works on solving the coupled Poisson and continuity equations numerically for both electrons and holes for the defined boundary conditions at interfaces and contacts. The absorber CHTS layer is susceptible to both acceptor and donor defects. However, it is intrinsically p-type due to the low formation energy of acceptor defects. In the present work, within the bulk CHTS, donor impurities are considered to ensure that it would not affect the minority carrier lifetime yet compensate acceptor concentration and hence affect the space charge region. The donor defects are considered at a 0.6 eV above valence band in the absorber CHTS and the CHTS/CdS heterointerface to ascertain the device's deep defects. Mo is considered the back contact with 5 eV work function together with $10^5 \text{ cm}^{-3} \text{ s}^{-1}$ and $10^7 \text{ cm}^{-3} \text{ s}^{-1}$ as the electron and hole surface recombination speeds, respectively. Thermionic emission is considered for the majority charge carriers. The interband recombination is considered in bulk along with radiative recombination with a recombination coefficient equal to $1.04 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (Simya et al., 2015). However, Auger recombination is ignored because it contributes only at high carrier concentrations (Goetzberger et al., 2014) (“Solar Cells—Operating Principles, Technology and System Applications,” 1982). The electron and hole capture cross-section are considered to be the same, $\sim 10^{-15} \text{ cm}^2$, and thermal velocity is suggested to be 10^7 cm s^{-1} for both carriers. The interface

recombination speed is assumed at $\sim 10^4 \text{ cm s}^{-1}$ for the CHTS/CdS interface. The considered minority carrier lifetime in bulk is $\sim 10 \text{ ns}$, as the comparable value is reported for a similar $\text{Cu}_2\text{ZnSnS}_4$ absorber system (Courel et al., 2016).

5.3 Single junction Device Analysis

We simulated a single junction solar cell device, Figure 5.1 (a), with a CHTS absorber using standard material parameters, as listed in Table 5.1. The computed current-voltage plot is shown in Figure 5.1 (b), with the inset showing the energy band diagram indicating band alignment at different interfaces for the considered solar cell. The band alignment study becomes essential to understand the contribution of the spike- and cliff- like structure at the interface because of the type-1 and type-2 heterostructures. In the present work, we optimized the device parameter on the absorber and at the interface to avoid the hindrance in photoelectron flow due to the significant spike at the interface and proper band alignment for the single-junction solar cell. The said solar cell's optimal efficiency is $\sim 11.6\%$ with 0.483 V open-circuit voltage, and the device performance parameters are shown in the bottom inset of Figure 5.1 (b).

5.3.1 Role of absorber CHTS layer thickness on photovoltaic response

We varied the CHTS absorber layer thickness to understand its impact on photovoltaic response. The open-circuit voltage (V_{oc}) slightly increases with increasing thickness, Figure 5.2 (a). It is attributed to the enhanced majority charge carriers in the absorber. In contrast, there is a significant increase in J_{sc} with increasing absorber thickness, Figure 5.2 (a), which is attributed to the increased photogenerated charge carriers in relatively thicker absorber layers. The collective results showed a rise in efficiency, as shown in Figure 5.2 (b). The photovoltaic efficiency is comparatively less sensitive to absorber thickness after a critical thickness of $\sim 2 \mu\text{m}$. The fill factor increases significantly with increasing thickness and reaches up to 67% for a $4 \mu\text{m}$ thick CHTS absorber layer. It is in accordance with Beer-Lambert's law $I = I_0 e^{-\alpha x}$, i.e., the intensity decreases with increasing thickness. The external quantum efficiency (EQE) versus wavelength curve is also shown in Figure 5.2 (c) for the different CHTS absorber thicknesses, showing the efficient absorption in the 400-800 nm visible range. Thus, increasing absorber layer thickness increases the photovoltaic response, yet higher thickness beyond a critical thickness will also result in unwanted carrier recombination and thus, may degrade the photovoltaic response. Therefore, the other parameter, i.e., minority carrier lifetime, is also essential in conjunction with absorber thickness, and a trade-off will be required to achieve the optimal device performance. The impact of minority carrier lifetime and thickness on photovoltaic efficiency is summarized in Figure 5.2 (d). The contours show the variation of thickness against these parameters. We notice that even for the low minority carrier lifetime, photovoltaic efficiency remains very low and independent of absorber thickness. It is attributed to the less contribution of photogenerated carriers at the p-type quasi-neutral region because most of the electron-hole pairs cannot reach the depletion region and recombine in the quasi-neutral zone.

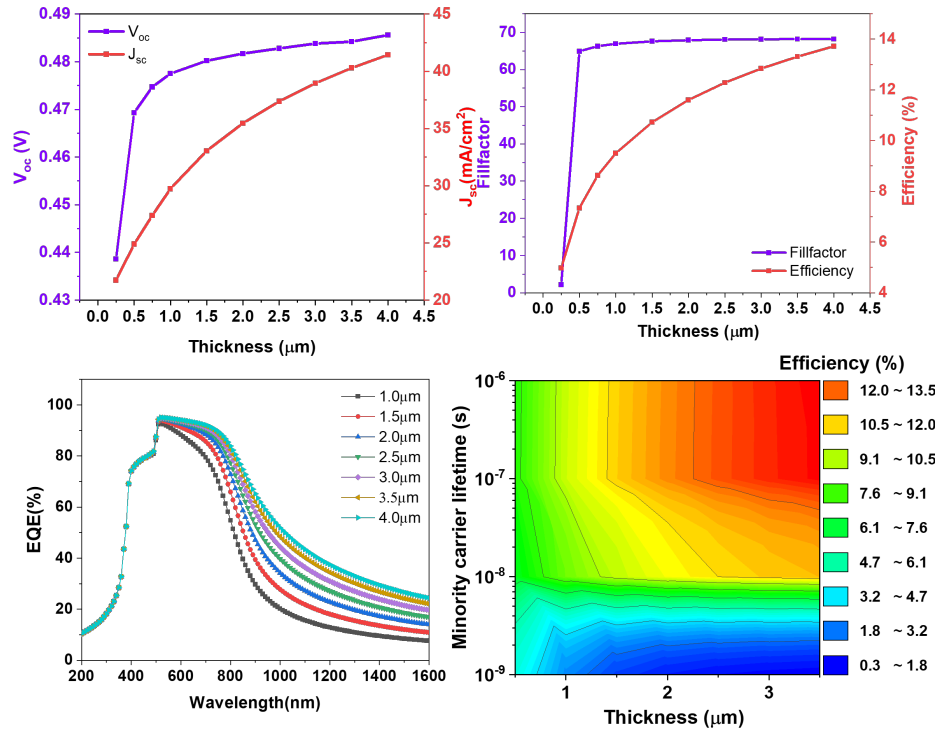


Figure 5.2 (a) Variation of open circuit voltage and short circuit current with absorber thickness. (b) Variation of fill factor and efficiency with absorber thickness (c) External quantum efficiency with different wavelengths at different thicknesses of absorber (d) Contour curve CHTS efficiency as a function of CHTS width and minority carrier lifetime considering interface recombination speed of $10^4 \text{ cm}^2 \text{ s}^{-1}$.

5.3.2 Role of absorber CHTS layer doping concentration on solar cell

An n⁺-p junction is formed between n-type CdS and intrinsic p-type CHTS layers. The carrier concentration in the n-type CdS buffer layer is fixed at 10^{17} cm^{-3} to ensure a relatively higher doping level and varies in the CHTS absorber layer from 10^{12} cm^{-3} to 10^{17} cm^{-3} . The impact of carrier concentration on open-circuit voltage, short-circuit current, efficiency, and fill factor are plotted in Figure 5.3. The short-circuit current density increases sharply in the range of 10^{14} cm^{-3} to 10^{15} cm^{-3} carrier concentration and decreases with any further increase in carrier concentration. This trend is evident because an increase in the concentration of holes on the absorber will reflect as photogenerated carriers. However, passing a specific limit of concentration will reduce the junction's depletion width; hence, reduced photogenerated carriers or J_{sc} . A similar trend is observed for V_{oc} , Figure 5.3 (a), and a peak in $V_{oc} \sim 0.5 \text{ V}$ is noticed at $\sim 5 \times 10^{15} \text{ cm}^{-3}$ hole concentration. The efficiency and fill factor also showed similar variation, Figure 5.3 (b), and a maximum of 12% efficiency is observed at around 10^{16} cm^{-3} concentration.

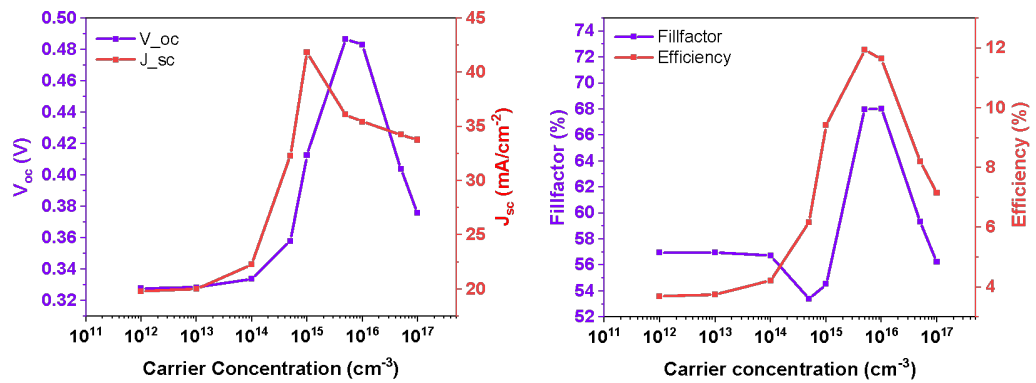


Figure 5.3 (a) Open-circuit voltage and short-circuit current and (b) fill factor and efficiency against CHTS hole carrier concentration.

5.3.3 Role of defect concentration at absorber CHTS and CHTS/CdS interface

The formation energy of acceptor defects is low for the CHTS absorber, similar to that of the CZTS system, making it intrinsically p-type absorber material. Considering a single donor deep defect, 0.6 eV below the conduction band edge in the CHTS absorber and taking neutral impurities in the CHTS/CdS interface, we varied defect concentration from 10^{14} to 10^{17} cm^{-3} absorber while 10^8 to 10^{16} cm^{-3} in CHTS/CdS interface. The defect concentration in the CHTS controls the minority carrier lifetime, while defects in the interface control the carrier recombination speed. In Figure 5.4 (a), the effect of the donor defect on V_{oc} and J_{sc} in CHTS is shown, where up to a particular concentration, V_{oc} and J_{sc} are nearly constant. The efficiency and fill factor variations also showed the same trend, Figure 5.4 (b). The efficiency and fill factor are almost insensitive to moderate 10^{16} cm^{-3} defect concentrations. The constant efficiency is probably due to the less photogenerated carrier scattering from defects in bulk CHTS. The sharp decrease at and above 10^{16} cm^{-3} is because of the compensation of holes by the donor defect in the bulk. Further, CHTS/CdS interface defect degrades the open-circuit voltage, Figure 5.5 (a); therefore, efficiency, Figure 5.5 (b), decreases drastically and seems more responsible for its poor performance. Thus, lowering the CHTS/CdS interface defect is essential to achieve higher photovoltaic efficiency.

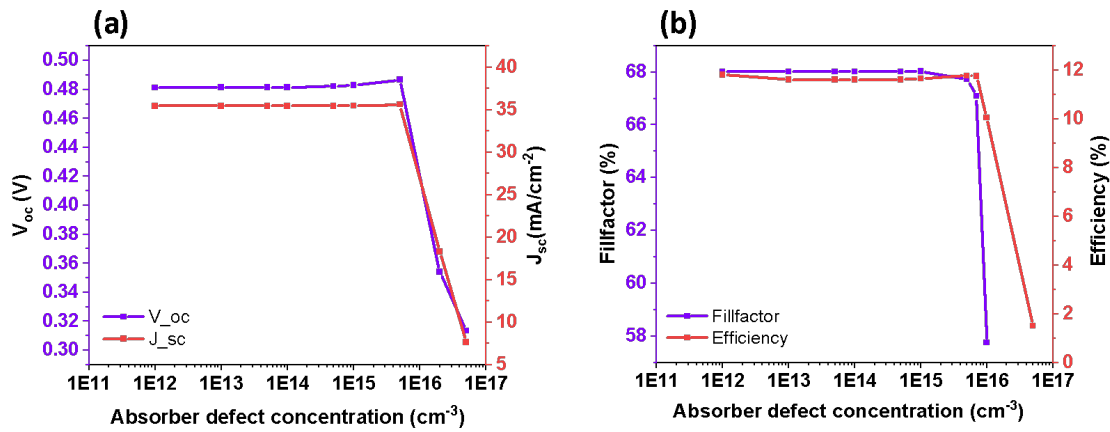


Figure 5.4 Role of deep defect (a) open-circuit voltage and short circuit current and (b) Fill factor and efficiency as a function of absorber defect concentration.

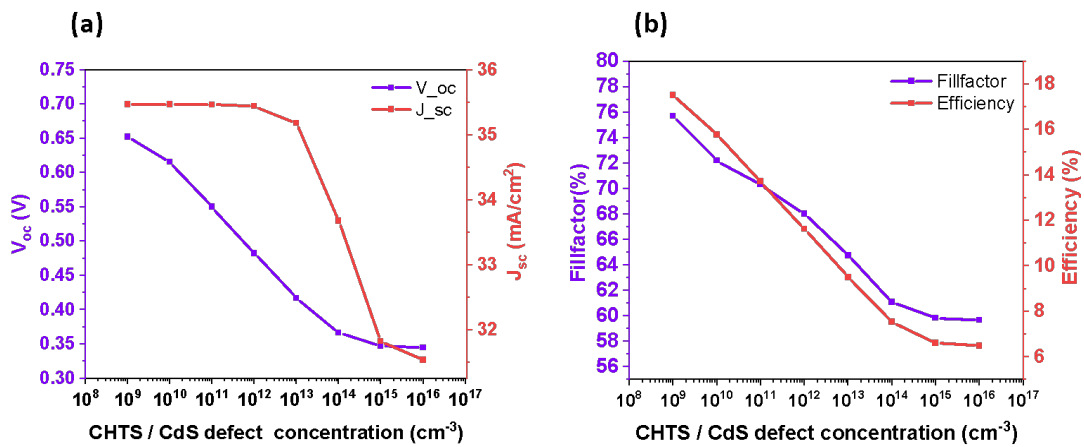


Figure 5.5 CHTS/CdS interface defect (a) variation of open-circuit voltage and short circuit current with defect concentration at interface (b) variation on fill factor and efficiency with defect concentration at interface.

The performance of a solar cell depends not only on the number of photogenerated carriers but also on the minority carrier lifetime of the absorber and the interface recombination speed of carriers. If the minority carrier lifetime is low, recombining electron and hole pairs at the p-type quasi-neutral region is possible before reaching the depletion region. The effect of minority carrier lifetime in CHTS bulk on photovoltaic response with different interface recombination speeds is presented as a contour plot, shown in Figure 5.6 (a). On varying the minority carrier lifetime from 10^{-9} s to 10^{-6} s, we found higher efficiency for a higher lifetime with commonly used interface recombination speed 10^3 to 10^4 cm s^{-1} , Figure 5.6 (a). At a higher lifetime, the carriers can reach the diffusion region from the quasi-neutral part of the device without recombining in between. V_{oc} also exhibits a similar trend over a range of minority carrier lifetime and interface recombination speed, as shown in Figure 5.6 (b). It also confirms that as the lifetime of minority carriers increases, the value of dark current in the solar cell decreases, allowing open-circuit voltage to increase by the relation;

$$V_{oc} = \frac{kT}{q} \ln(1 + J_{ph}/J_0) \quad (5.1)$$

Here J_{ph} and J_0 are the photocurrent and dark current densities, respectively.

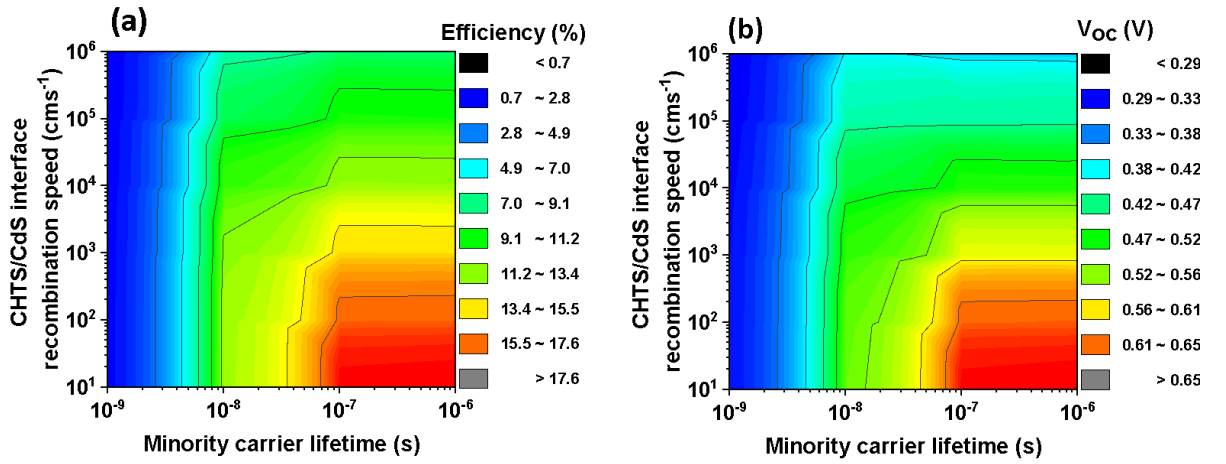


Figure 5.6 Contour plot of the (a) Efficiency and (b) open-circuit voltage as a function of the interface recombination speed and minority carrier lifetime.

5.3.4 Role of the buffer layer

The band alignment in a heterojunction solar cell plays a crucial role in its response and is mainly contributed by the buffer layer. CdS is used for this purpose in a CZTS solar cell as it has robust transmission on blue wavelength. Below 590 nm, photons get absorbed through CdS as it has a bandgap of around 2.4 eV and covers 24% of the spectrum. To know the effect of thickness and carrier concentration of buffer layer on the photovoltaic response, these are varied simultaneously and plotted in Figure 5.7 (b). The graph shows that the efficiency increases significantly with the increasing carrier concentration, independent of the CdS layer thickness. The trap states in the interface also provide a recombination site for the photogenerated carriers. These exist due to the difference in the absorber and buffer layer's crystal structure, lattice mismatch, i.e., lattice constant causing stress in the interface, different work functions, and electron affinity. The type of interface formed between CdS and CHTS, characterized by the respective conduction bands, is also important. The difference in electron affinities of the absorber and buffer layers defines the conduction band offset. If the conduction band of the absorber is lower than that of the buffer layer, then a spike is formed at the interface, which is known as Type-1 heterostructure. On the contrary, if the conduction band of the absorber is higher than

that of the buffer, then the cliff is formed at the interface, and the heterostructure is known as Type-2 heterostructure. The electron transport is hindered in Type-1 heterostructure due to a spike at the interface, causing recombination at the interface, leading to the lower open-circuit voltage. On the other hand, for Type-2 structure, the low difference between the absorber and the buffer layer's conduction band results in the lower open-circuit voltage, whereas the smooth transport of electrons results in the enhanced short-circuit current (Gansukh et al., 2020). The band alignment at the heterostructure interface is shown in Figure 5.7 (a) for different electron affinity values of the buffer layer, indicating the onset of spikes and cliffs at the interface. Further, we computed the photovoltaic response, i.e., efficiency, open-circuit voltage, and short-circuit current for different electron affinities of the buffer layer and interface recombination speed, and results are summarized in Figure 5.8.

The effect of a spike on the V_{oc} is clear from Figure 5.8 (b), suggesting that at lower electron affinity, V_{oc} is high for at and below 10^4 cm s^{-1} interface recombination speed; while J_{sc} value in Figure 5.8 (c) remains unaffected from this. At this optimal speed of 10^4 cm s^{-1} , the variation in open circuit voltage and efficiency along with J_{sc} and FF is also shown in Figure 5.9, indicating the suitability of buffer layer material's electron affinity in the range of 4.1 eV to 4.4 eV.

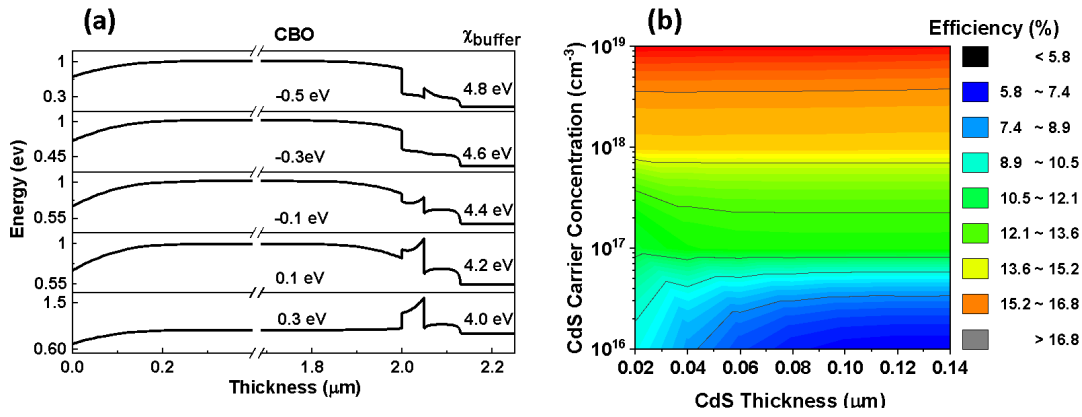


Figure 5.7 (a) Band alignment and conduction band offset with variation in electron affinity of buffer layer (CdS) and (b) efficiency as a function of CdS thickness and CdS carrier concentration.

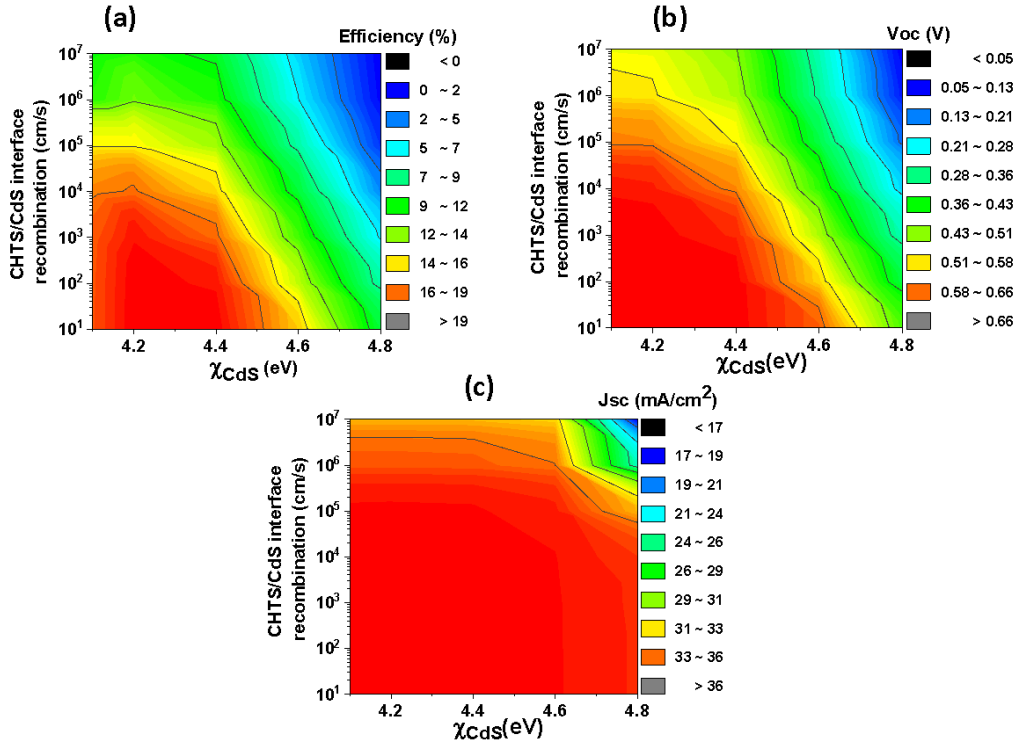


Figure 5.8 Effect of different interface recombination speed with electron affinity of buffer layer on (a) efficiency (b) open circuit voltage and (c) short circuit current.

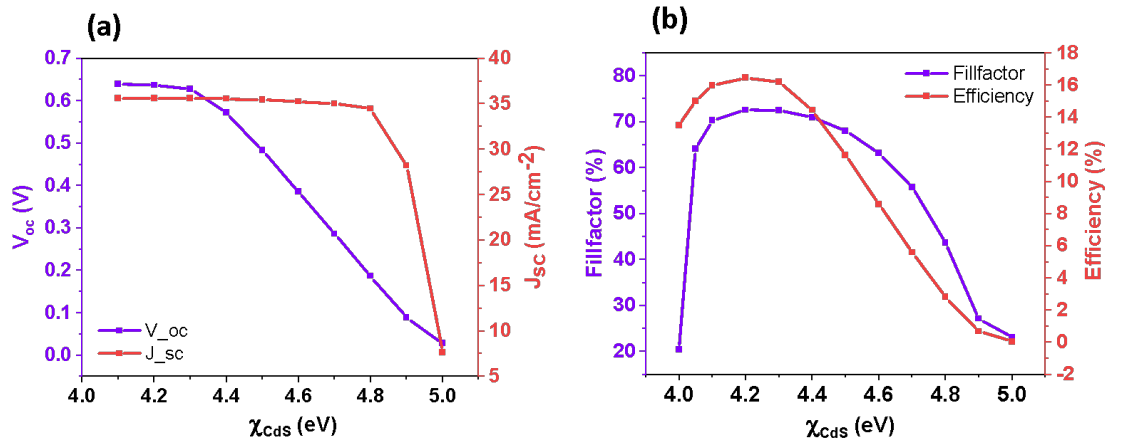


Figure 5.9 Impact of CdS electron affinity on (a) open-circuit voltage and short circuit current (b) fill factor and efficiency.

5.3.5 Role of back contact metal

A higher work function material is preferred to ensure an Ohmic contact with the CHTS material. The most commonly used back contact material is Molybdenum (Mo) for CIGS solar cells and CZTS solar cells due to its excellent adhesion with the absorber material and suitable work function. CHTS is a new absorber material, and to understand the effect of back contact work function, we varied it from 4.4 to 5.5 eV and computed the change in photovoltaic response. The observed variations are summarized in Figure 5.10. We observed that the photovoltaic response becomes constant after a particular work function value, i.e., 5 eV. Therefore, a higher work function metal may show the enhanced photovoltaic response for CHTS-based solar cells.

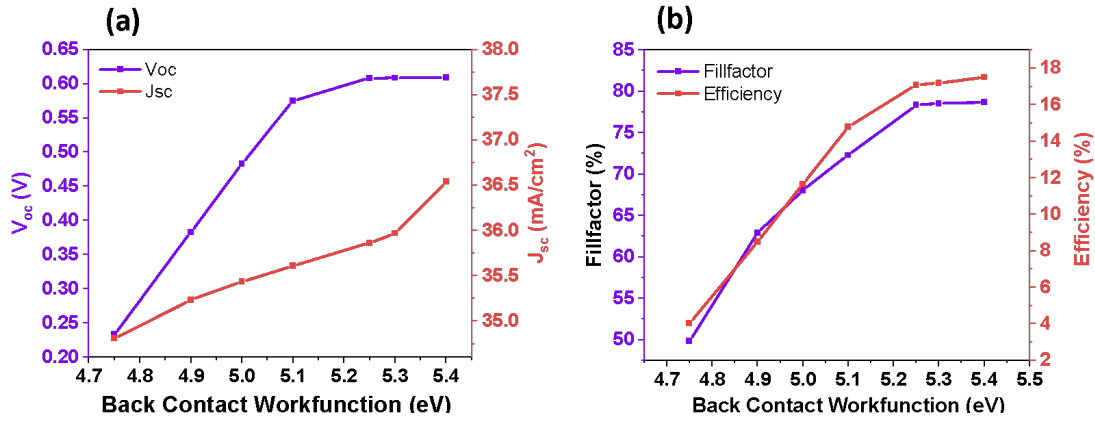


Figure 5.10 Impact of back contact work function effect on (a) open circuit voltage and short circuit current and (b) fill factor and efficiency.

Hence, the computed material parameters are used to model AZO/ZnO/CdS/CHTS/Mo heterojunction-based single-junction. The results suggest that about 2 μm CHTS thickness will show the optimal photovoltaic response. Further, a more realistic 100 ns lifetime of minority carriers is used with 10^4 cm/s recombination speed to simulate the practical CdS/CHTS interface, thus exhibiting 11.64% efficiency (Kukreti et al., 2021a). Interface engineering can improve this response, i.e., enhancing the minority carrier lifetime and reducing the recombination speed to $\sim 10^3$ cm/s. However, there remains a possibility of mitigating transmission loss by using tandem stacking of solar cell along with a bandgap grading-based absorber, which is investigated in the next section.

5.4 Modelling Approach for Tandem Junction and Graded Bandgap Device

5.4.1 Tandem Structure

Monolithic tandem and bandgap-graded solar cells are numerically simulated using SCAPS-1D software (M. Burgelman et al., 2000). For preparing 2 terminal tandem solar cells, top and bottom sub-cells are designed separately. The higher bandgap material CHTS (1.33 eV) is selected for the top cell, with Al:ZnO/ZnO/CdS/Cu₂HgSnS₄ cell configuration. The structure for the bottom cell is Al:ZnO/ZnO/CdS/Cu₂HgSnSe₄. Al:ZnO is taken as the window layer in the top cell, which acts as the recombination layer for the bottom cell. The bulk defects are managed in mid-gap states to provide bulk recombination. General interface defects are assumed at the absorber and buffer layer to capture the interface recombination. The sub-cells are connected serially, and in principle, the top cell filters out the spectrum, and the bottom cell utilizes the remaining spectrum. For our simulation, we considered an optically active and electronically inactive pseudo-top absorber in the bottom cell to filter out the spectrum. The device parameters considered for the different layer materials are summarized in Table 5.2.

Table 5.2. The different layer materials' optoelectronic parameters, used in the initial device simulation (Kukreti et al., 2021b; Kukreti, Ramawat, et al., 2023)

Properties	CHTS	CHTSe	Graded Absorber Variation	CdS	ZnO	Al:ZnO
Bandgap (eV)	1.33	0.81	Parabolic	2.42	3.37	3.37
Electron Affinity (eV)	4.3	0.81	Linear	4.5	4.6	4.6

Relative Dielectric Permittivity	10.6	16.05	Parabolic	9	9	9
Effective Density of States at Conduction Band (N_c) (cm^{-3})	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}
Effective Density of States at Valence Band (N_v) (cm^{-3})	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}
Electron Thermal Velocity (cm/s)	2.03×10^7	3.31×10^7	Parabolic	10^7	10^7	10^7
Hole Thermal Velocity (cm/s)	1.22×10^7	1.22×10^7	1.22×10^7	10^7	10^7	10^7
Hole Mobility (cm^2/Vs)	35	35	35	1.5×10^2	1.5×10^2	1.5×10^2
Electron Mobility (cm^2/Vs)	100	100	100	2.5×10^1	2.5×10^1	2.5×10^1
Acceptor Concentration (cm^{-3})	10^{16}	10^{16}	10^{16}	0	0	0
Donor Concentration (cm^{-3})	0	0	0	10^{17}	10^{20}	10^{20}

5.4.2 Graded Structure

The device configuration, i.e., Al:ZnO/ZnO/CdS/Cu₂HgSn(S_{1-x}Se_x)₄/Mo is considered for the graded bandgap solar cell. In this structure Al:ZnO and ZnO act as the window structure while CdS is the buffer layer and Molybdenum is the back contact in the device. Further, we changed the selenium composition exponentially for the absorber layer with respect to the position as the following function (H. Li & Zhang, 2020):

$$Se (\%) = \frac{\sinh\left(\frac{d-t}{L}\right)}{\sinh\left(\frac{d}{L}\right)} \quad (5.2)$$

Where d and L are the thickness of the absorber, the position with respect to back contact, and L is the characteristic length. The characteristic length is defined as the distance where the concentration of selenium reduces to 33%. The composition of selenium was kept higher at the back contact, and the content of sulfur was kept higher near the buffer region so that the top side of a cell with higher S content retained a high bandgap and the bottom side with a large Se content retained the low bandgap. It is termed as positive grading for the absorber layer. The electronic and optical properties for alloys with 0.25, 0.50, 0.75, and 1.00 selenium mole fractions were

calculated using density functional theory in our previous study (Kukreti, Ramawat, et al., 2023). However, in this study, we have considered that alloy composition varies continuously with the position in absorber layer. The properties of alloys, namely bandgap (E_g), relative dielectric permittivity (ϵ), and electron thermal velocity (v_{th}) with intermittent Selenium mole fraction (x), are found by fitting the previous data. For electron affinity, data was adapted from values of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ and fitted using linear fitting. The fitted equations are as follows:

$$E_g(x) = 0.395 x^2 - 0.881 x + 1.307 \quad (5.3)$$

$$\chi(x) = -0.2 x + 4.3 \quad (5.4)$$

$$\epsilon(x) = -6.29 x^2 + 11.34 x + 10.85 \quad (5.5)$$

$$V_{th} = (9.5 x^2 + 3.34 x + 2.04) \times 10^7 \quad (5.6)$$

For electrons and holes, the quasi-drift terms are $-q\mu_e n \nabla \chi$ and $-q\mu_p p (\nabla \chi + \nabla E_g)$. While the quasi-diffusion terms are written as $-q\mu_e \nabla \ln N_c$ and $-q\mu_p p \nabla \ln N_v$. From Einstein's relation, we get $-q\mu_e n (\nabla \chi + kT \nabla \ln N_c)$ for electrons and $-q\mu_p p (\nabla \chi + \nabla E_g - kT \nabla \ln N_v)$ for holes. We see that $\nabla \chi \gg kT \nabla \ln N_c$ and also $\nabla \chi + \nabla E_g \gg kT \nabla \ln N_v$ (Topic et al., 1998). So, in the present study, only the effect of quasi drift field in the bulk region was considered, and effect of the quasi-diffusion term was not considered; thus effective density of states at the conduction band and valence band were kept constant. Absorption coefficients are taken to the square root of the bandgap model. In $Cu_2HgSn(S_{1-x}Se_x)_4$ alloy, the effective mass of the hole did not change much, so properties relevant to the mass of the hole were kept uniform. In a graded bandgap device, the electrons will experience extra drift in the bulk region due to the gradient in the conduction band, and this occurs due to changes in the electron affinity of materials. The equation governing the electron transport is given (D. Zhang et al., 2021);

$$J_e = -q\mu_e n \frac{dE_c}{dx} \quad (5.7)$$

$$E = -\left(\frac{1}{q}\right) \times \frac{d\chi}{dx} = \frac{1}{q} \times \left(\frac{dE_c}{dx}\right) \quad (5.8)$$

Similarly, the holes will experience extra drift in the bulk region due to a gradient in the valence band, and this occurs due to a change in the bandgap of the material, the equations are;

$$J_p = q\mu_p p \frac{dE_v}{dx} \quad (5.9)$$

$$E = \left(\frac{1}{q}\right) \times \frac{dE_v}{dx} \quad (5.10)$$

Where, E is electric field strength, χ is electron affinity, and q is the charge on electron. E_c and E_v represent the conduction and valence band edge energy at position x . The electron (hole) current density and mobility are denoted by J_e (J_p) and μ_e (μ_p), respectively.

5.5 Result and Discussions

5.5.1 Tandem Configuration

We considered a 2T device with the Cu_2HgSnS_4 ($E_g \sim 1.33$ eV) as the top cell active layer and $Cu_2HgSnSe_4$ ($E_g \sim 0.8$ eV) as the bottom one for our two-junction tandem device, which absorb the corresponding wavelength from the solar spectrum as shown in schematically in Figure 5.11. The current matching is fixed through thickness optimization. At the same time, the degenerately doped ($\sim 10^{20} \text{ cm}^{-3}$) AZnO layer is placed between two cells to play the role of recombination layer and connect both cells in series. The high doping facilitates the tunnelling by providing a less depletion width and is decided by the following function;

$$l_{dep} = \left[2\epsilon \frac{(\phi_0 - V)}{q} \frac{N_A + N_D}{N_A N_D} \right]^{\frac{1}{2}} \quad (5.11)$$

Where ϵ , N_A , N_D , denotes the permittivity, ionized acceptor, and donor concentration of the material while ϕ_0 and V shows the built-in voltage and applied bias. The tunnelling junction behaves as a resistor for a slight forward bias and any reverse bias condition. However, after a particular forward bias, the thermionic emission dominates, and no longer tunnelling of the carrier is allowed. Therefore, the photocurrent in the device should be lower than the peak tunnelling current in the junction. The peak tunnelling current J_p is given by (A Arefin et al., 2016);

$$J_p \propto \exp \left[-\frac{E_g^{\frac{3}{2}}}{\sqrt{N^*}} \right] \quad (5.12)$$

Where E_g is the bandgap of the tunnelling junction layer and $N^* = \frac{N_A + N_D}{N_A N_D}$, denotes effective doping concentration.

A good lattice and current matching under maximum power point are required to achieve the best multijunction device performance properly. For that, appropriate tunnelling junctions become crucial for these devices. It should be transparent to a high wavelength that must be absorbed in the bottom cell and provide low electrical resistance to the device. Tunnelling junctions are made by introducing a recombination layer between two cells, which not only prevents the direct connection of the top cell p-type layer to the bottom cell n-type layer to form an opposite p-n junction in the cell but also directly tunnels the carrier to lead recombination of majority carriers and avoid any charge accumulation in bulk of the device. As shown schematically in Figure 5.11 (a) of stacked two sub-cells, the band alignment allows an electron (hole) coming from the bottom(top) sub-cell to recombine at AZnO/Cu₂HgSnS₄ interface junction. Thus, the overall layers alignment supports the minority carrier extraction at the end terminals of the device.

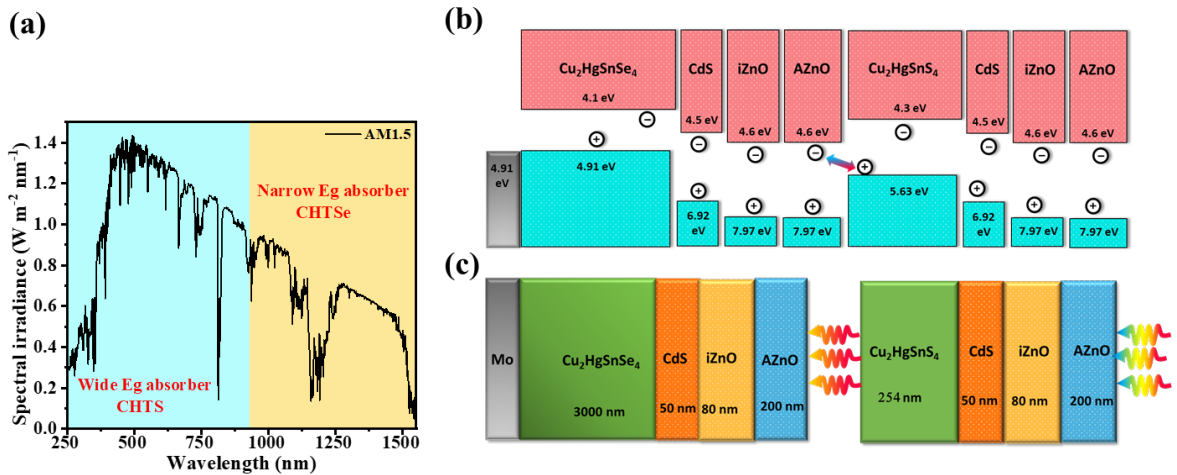


Figure 5.11 (a) Spectrum covered via two wide and narrow bandgap absorbers (b) Energy offsets of different layers of top and bottom sub-cells (c) Tandem solar cell schematic and thickness of different layers. Al-doped ZnO (Al:ZnO) acts as the tunneling junction between the top and bottom sub-cells.

As discussed in the previous modelling sub-section, the top cell is simulated first with AM 1.5 spectrum. Then, to allow the residual spectrum (except absorbed in top absorber layer), a pseudo-top cell of the same thickness is considered over the bottom cell ZnO layer. In this

bottom cell simulation, the pseudo top cell $\text{Cu}_2\text{HgSnS}_4$ layer is considered highly n-type doped to ensure that it is electronically inactive, and only bottom cell absorber $\text{Cu}_2\text{HgSnSe}_4$ is active for the photogenerated carriers by absorbing $h\nu > 0.8$ eV for this cell. The simulation procedure is adopted to provide the actual two-junction tandem cell performance with 2 terminal devices.

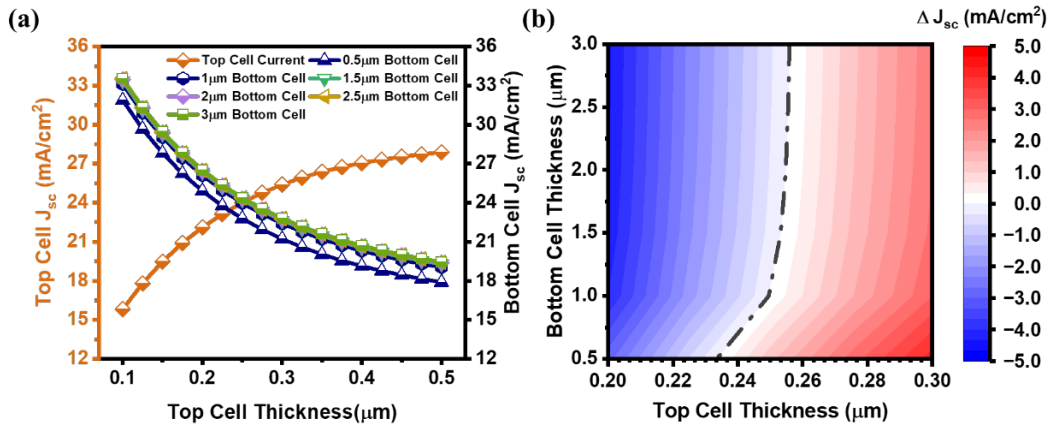


Figure 5.12 (a) Variation of J_{sc} of sub-cells due to increment in thickness of top sub-cell plotted against current from bottom sub-cells of varied thickness. The intersection of two curves is the current matching condition (b) ΔJ_{sc} refers to a difference in current from top and bottom sub-cells. The dashed line shows the current matching condition. The current from the bottom cell is limited; hence, the top cell thickness cannot be increased more than 0.25 μm to satisfy the current matching condition.

The sum of the voltage generated by both individual cells can be the maximum possible voltage from the double junction device, while the maximum current can be one of the cell currents, whichever have a large value generated by the two cells. The current contribution also varies as the constituent cells are of dissimilar bandgap in the device. To get the matched current density across the device, we consider the point of intersection in the top, and bottom cell current with varying thicknesses, Figure 5.12 (a). The current contribution from the bottom absorber layer as a function of thickness shows a plateau at around 22 mA cm^{-2} . So, it is not beneficial to increase the thickness of top absorber layer to achieve the current matching condition. In the contour plot, Figure 5.12 (b), we have plotted the difference of current from both the cells as a function of their thickness. Despite an increase in bottom absorber from 0.5 to 3 μm , the suitable top absorber layer has just varied from 0.23 μm to around 0.25 μm . The efficiency of tandem solar cell does not increase much with thickness because of saturation in J_{sc} . We cannot utilize the top absorber layer to its optimum limit because of this associated limitation of the bottom absorber layer. The efficiency of tandem solar cell might increase by utilizing a thicker top absorber layer. However, the inability to current matching in such higher thickness of top absorber, it is not possible. Finally, on analyzing the top and bottom cell current densities, an optimal tandem device top cell with $\text{Cu}_2\text{HgSnS}_4$ active layer should be of smaller thickness ~ 0.25 μm , whereas the bottom cell having $\text{Cu}_2\text{HgSnSe}_4$ absorber thickness can be varied from 1 to 3 μm . The optimal thicknesses of the top and bottom solar cells, satisfying the current matching constraint, are considered and the results are summarized in Figure 5.13. The current-voltage (I-V) characteristics are shown in Figure 5.13 (a) for tandem cell configuration together with the single junction top and bottom cells with a maximum of 0.8 V as open circuit voltage and ~ 24 mA cm^{-2} short circuit current density. The variation of solar cell parameters such as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), efficiency, and fill factor against the thickness of the bottom cell is shown in Figure 5.13 (b), showing no significant change for the tandem cell performance. For instance, at 2 μm bottom cell thickness, a maximum of 16.87% efficiency is achieved with this device configuration, which remains almost constant till 3 μm . Further, the external quantum efficiency for both top and bottom cells is shown in Figure 5.13 (c), showing the contribution of each over the different wavelengths of the solar spectrum.

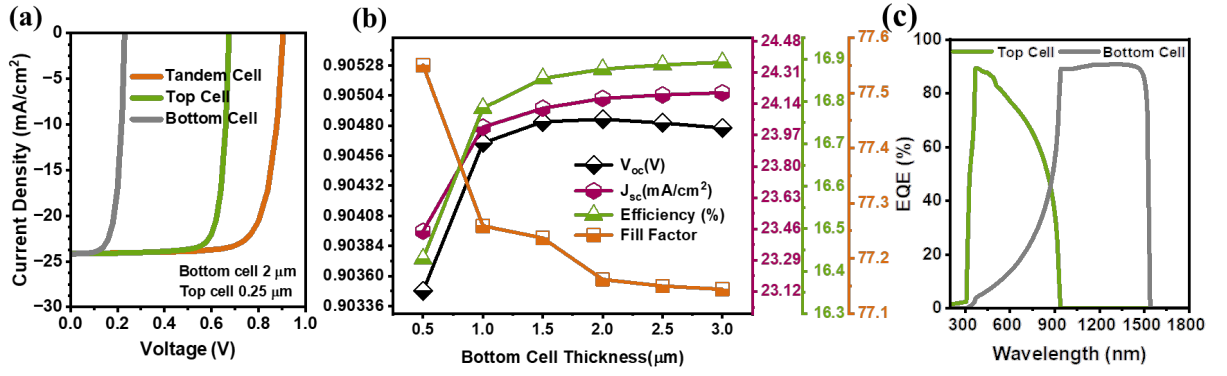


Figure 5.13 (a) I-V curve of tandem solar cell in current matched condition (b) Performance of tandem solar cell with different thickness of bottom absorber layer (c) External quantum efficiency of top and bottom sub-cell covering spectrum in range 250 nm to 1500 nm.

5.5.2. Graded Configuration

Usually, a positive bandgap grading, where the back contact has a relatively lower bandgap compared to the absorber/CdS junction side, is preferred for better photo conversion efficiency (X. Li et al., 2022). However, it brings an additional electric field opposite to the built-in electric field due to the different S/Se content in the absorber. This additional field remains weaker in magnitude compared to the strong built-in field in the junction, giving a good output. In contrast, in negative bandgap grading, where back contact has a larger bandgap and absorber/CdS junction has lower, provides reduced V_{oc} and efficiency due to the decrease in bandgap belonging to the junction side and hence not advantageous (J. Xu et al., 2018).

A suitable grading function needs to be chosen for device simulation, which can replicate the bandgap grading pattern and should also be achievable experimentally using various diffusion processes. Considering the same, the exponential grading is considered for the device simulation. For this, a crucial parameter defined as characteristic length (CL) is optimized so that the absorber gives us maximum output or efficiency. It signifies how fast/slow the bandgap decreases towards the back contact. We create a gradient in absorber valence and conduction band by introducing this grading such that photogenerated electrons and holes follow the descended path from CHTSe to CHTS and vice versa, respectively, as explained schematically in Figure 5.14. The transmission loss of higher wavelength can also be minimized through the lower bandgap region contributed by higher Se concentration at the bottom or back contact, simultaneously in this graded absorber.

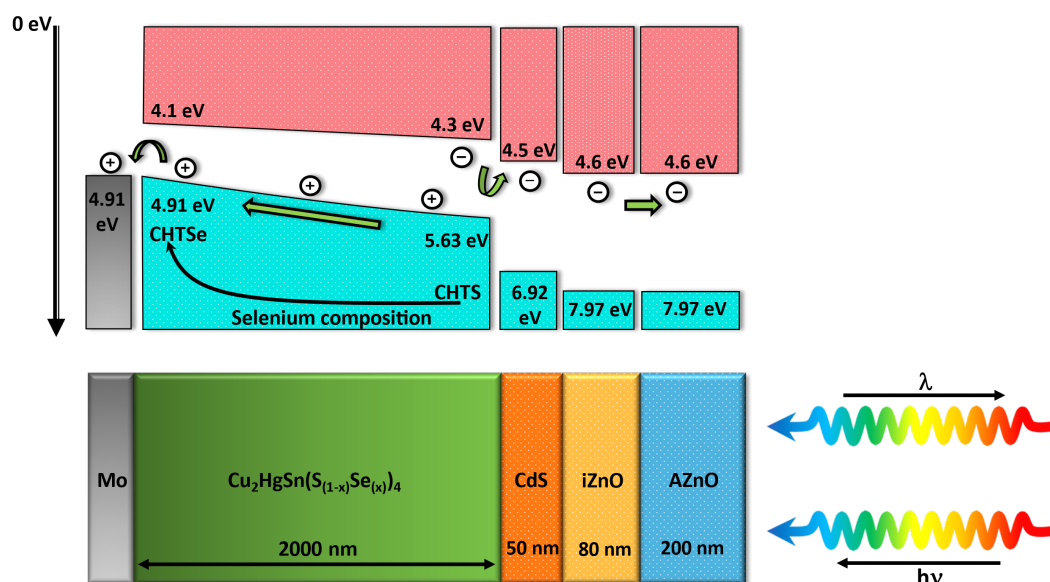


Figure 5.14 Energy offsets of graded solar cell. Selenium ratio is higher near the Mo back contact which causes curvature in Valence and Conduction band. At bottom thickness profile of different layers in graded solar cell with illumination from Al:ZnO side.

5.5.2. 1 Significance of grading pattern

To visualize the grading function, we plotted the ratio of selenium change with absorber thickness for different characteristic lengths in Figure 5.15 (a). Starting from back contact ($t = 0$ nm), a lowering in selenium concentration with respect to the absorber's thickness is visible, which completely diminished at $t = 2000$ nm. The reducing selenium content is to be considered as reducing the percentage of selenium-rich alloy with an increasing share of sulfur-rich alloy. This type of grading is easier to achieve than the double-grading V structure (Cui et al., 2022)(Sun et al., 2019). In this grading structure, light first interacts with the highest bandgap alloy and then with materials with decreasing bandgap. To select the proper CL, we scanned the cell performance for a range of CL shown in Figure 5.15 (b). We observed that the low-value of CL device performs better. Thus, the required criterion to achieve higher efficiency is achieving a steep gradient in bandgap or higher content of sulfur rich alloy in the absorber layer. It is attributed to the fact that S-dominated regions have large bandgaps which correspond to the lower wavelength, say 300 to 900 nm region, contributing most to the solar spectrum. On the other side, the Se-dominated area provides more quantum yield for higher wavelength parts, contributing less to the solar spectrum. Thereby the device performs the best when having less Se-dominated region. As CL increases, the grading pattern approaches the linear trend, and the device becomes comparatively less sensitive for the lower wavelength spectrum. We considered 2 μm thick absorber for the study because our intention is to present a comparative study of single junction, double junction and graded bandgap solar cell and for all the devices same thickness is taken.

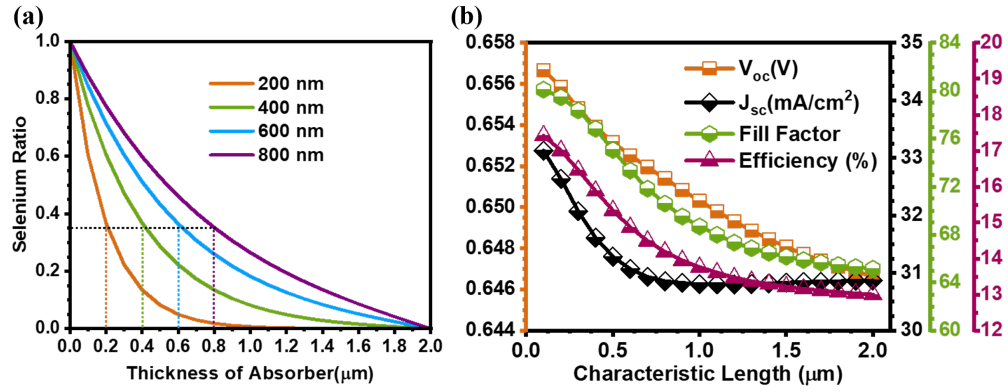


Figure 5.15 (a) The graph shows the ratio of Selenium changes in the absorber layer for different characteristic lengths. Characteristic length is the distance in absorber where the ratio of Selenium in the alloy is 33% and is marked by dotted line. A higher characteristic length indicates a slow rate of Selenium variation in the absorber layer (b) Performance of graded solar cells for the varied characteristic length.

5.5.2.2 Significance of Positive Grading

As the composition is varied with respect to distance, it is always expected that the electronic property like conduction and valence band edges also modifies accordingly. The flux of photoinduced carrier and its dynamics is also modified along with the electric field. It also changes on the bulk of the absorber layer. By adopting a positive bandgap-graded solar cell, we examined the carrier generation and recombination profile in the absorber material at different characteristic length (CL) values in Figure 5.16 (a). We note that the photocarrier generation rate on lower CL is $\sim 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$. It increases with increasing CL value, reaching $10^{22} \text{ cm}^{-3} \text{ s}^{-1}$ in the back contact side for CL = 200 nm, it confirms the enhanced electronic contribution due to the low bandgap selenium-rich region. A significant increase in Shockley-Read-Hall (SRH) recombination is also noticed in solar cells wherein the value of CL in absorber layer is high. This recombination rate also reaches closer to the generation rate at the back contact for large CL value, as noticed $\sim 2 \times 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$ for 800 nm CL, while for a lower 200 nm CL value, it remains $1.5 \times 10^{20} \text{ cm}^{-3} \text{ s}^{-1}$. It makes the large-value CL grading less suitable for better photoconversion efficiency. As discussed earlier, an additional but opposite field developed in these devices is also observed, and the values increase up to $15 \times 10^3 \text{ V cm}^{-1}$ in regions with higher Se concentration than the region near the junction. However, the strength of the junction field is significant enough ($> 20 \times 10^3 \text{ V cm}^{-1}$) to separate the photogenerated carriers and move them across the depletion region [see Figure 5.16(b)]. The field near the back contact decreases with increasing CL and is attributed to the lower slope in bandgap grading, resulting from less descent in band edges. This reduced opposite field does not seem advantageous because of the lower generation profile in large CL grading. Therefore, we considered 200 nm CL grading in bandgap for further device optimization. Additionally, to quantify the gain of a grading-based device over the pure $\text{Cu}_2\text{HgSnS}_4$ -based absorber, we computed the performance of two solar cells, one with a graded absorber layer and the other with homogenous $\text{Cu}_2\text{HgSnS}_4$ absorber layer with identical 2 μm thickness. We found gain in every metric like efficiency, V_{oc} , and fill factor. All metrics' values increase from 10% to 17%, 0.48 V to 0.66 V, and 63% to 79%, respectively, as shown in Figure 5.16 (c). This augmented outcome can also be justified via Figure 5.16 (a), where we see the generation rate is modified substantially in the 200 nm CL case by utilizing the low energy spectrum at the nearby region of the back contact where the Se effect comes into the picture while for pure generation rate is relatively lower because of the loss of the low energy spectra.

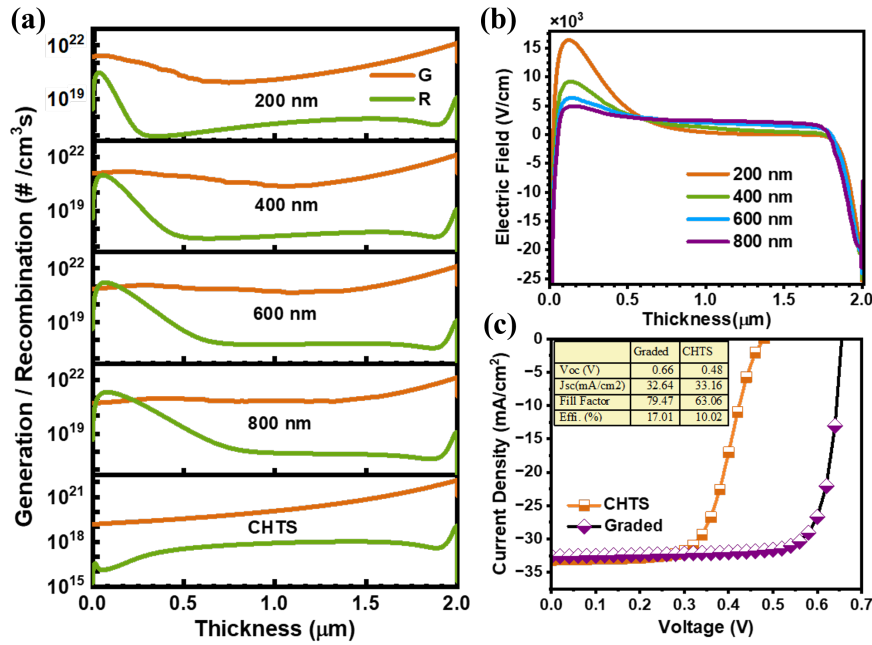


Figure 5.16 (a) Generation and recombination profile in the graded bandgap absorber while varying CL value 200 to 800 (top to bottom) and for pure Cu₂HgSnS₄ absorber (b) Electric field in bulk of graded absorber layer for different characteristic length (c) I-V plot comparing graded and without graded device and device parameters are tabulated in inset.

5.5.2.3. Doping and Defect Density Effect

On considering the 200 nm CL and fixing 10^{14} cm⁻³ bulk defect density, we further probed the performance parameters of the solar cell by varying the acceptor concentration on the bulk and defect concentration on the bulk and interface as well which is most crucial to better understand the realistic defect mediated performance degradation in the device. As expected, on increasing the acceptors in the absorber, the J_{SC} increases up to 41 mA cm⁻² at 3×10^{14} cm⁻³ doping. Further increase in doping results in diminishing because acceptor doping approaches the CdS carrier concentration. It narrows the depletion region; hence, the absorber contributes less photogenerated carrier to the device. With this, CHTS/CdS interface geometry is also affected, and at the higher doping side, it results in the form of cliff-like geometry, which pushes the V_{OC} down after reaching a maximum of 0.68 V at 10^{15} cm⁻³ [see Figure 5.17 (a)]. The device shows an almost stable fill factor up until 10^{15} cm⁻³ doping, which indicates that this region could provide a good working point for the solar cell. The maximum conversion efficiency of ~18.1% can be observed at around 2×10^{15} cm⁻³ when the maximum power point voltage and current also become stable due to the saturated fill factor [Figure 5.17 (b)].

The device is examined for its output by scanning over a range from 10^{12} to 10^{17} cm⁻³ bulk defect density [see Figure 5.17 (c)]. Till 10^{15} cm⁻³ defect concentration, it shows stability with no degradation in efficiency with fixed maximum power point. However, above this carrier concentration, all the device metrics are affected adversely due to the loss of photogenerated carrier in SRH recombination. The sensitivity of the interface quality is reflected in Figure 5.17 (b), which indicates that as the opposite carrier or donor appears more in the interface, it plays the role of recombination centre by providing trapping sites and degrades the device efficiency from 20.5% to 12%. The overview of the simultaneous variation in bulk and interface defects is shown in the contour form in Figure 5.17 (e). This signifies that the device can perform best around the 10^{15} cm⁻³ bulk defect density region. In addition, the influence of interface recombination (IR) rate on the efficiency, even for the large lifetime of carrier in bulk becomes dominant, as can be visualized in Figure 5.17 (f). Even for the large carrier lifetime, say 100 ns or larger, the device does not perform well if the recombination rate is higher than 10^5 cm s⁻¹.

Therefore, an interface with fewer defects or a low recombination rate is also essential for graded devices.

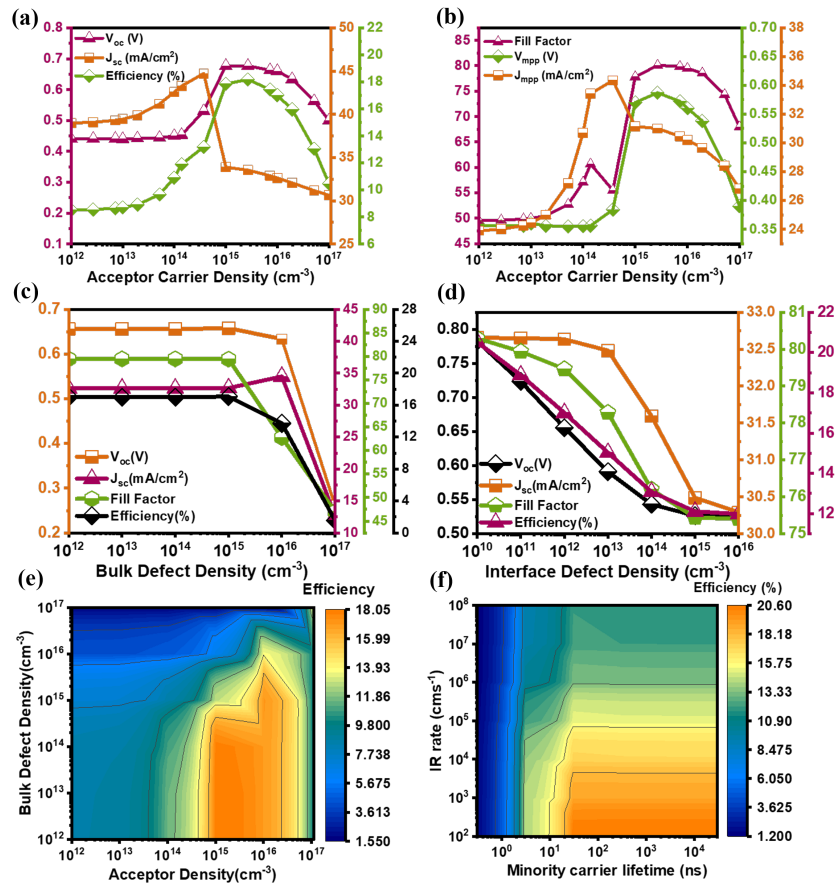


Figure 5.17 (a) Performance of graded solar cell with increased shallow acceptor density throughout the absorber layer (b) Voltage at maximum power point V_{mpp} , Current at maximum power point J_{mpp} and Fill factor variation with increased shallow acceptor density (c) Performance of solar cell with variation in single donor deep bulk defect density (d) Performance of solar cell with varied neutral defect density in CHTS/CdS interface (e) A contour plot showing variation in efficiency of solar cell as effect of bulk defect density and shallow acceptor density (f) The effect in efficiency on simultaneous variation in minority carrier lifetime and interface recombination rate.

5.5.2.4. Hetero-interface band geometry effect

The role of the heterointerface between absorber and buffer is also essential to understand, which actually originates due to the conduction band offset (CBO) and creates multiple geometries like spike and cliff in the CHTS/CdS interface. Majorly, this heterointerface governs the charge separation in the middle of the device, which is further collected through both terminals. Usually, the spike-kind barrier serves high open circuit voltage, while cliff-type geometry increases the J_{sc} (Gansukh et al., 2020; Yan et al., 2014). Therefore, band alignment examination becomes equally important and can be realized by varying electron affinity. Here, we varied the electron affinity of pure CHTS from 4.2 eV to 4.8 eV, Figure 5.18, and considered CdS electron affinity at a constant value of 4.5 eV. Initially, the cliff and negative CBO are formed with a lower-lying conduction band of CdS compared to CHTS, which renders higher J_{sc} but low V_{oc} , Figure 5.18(a) and (b). The corresponding electric field variation is shown in Figure 5.18(c), for different electron affinity values against device thickness. As the affinity value increases and spike formation starts after 4.4 eV and increases CBO value to 0.3 eV, a significant potential difference between two band edges contributes large V_{oc} to the device accompanying lower J_{sc} .

Figure 5.18 (b). This positive CBO value of 0.3 eV seems suitable for better efficiency as the performance increased from 17.01% to 22% for the same set of other parameters, Figure 5.18 (b). The higher performance with 0.3 eV CBO also looks consistent in the literature where the

CdS/CZTSSe heterostructure-based bandgap graded cell has claimed the best efficiency in the range of 0 to 0.4 eV CBO value (Haight et al., 2011). Further, an increase in this value may hinder electrons from crossing the barrier, and an abrupt decrease may result in the current. The detailed discussion can be accessed through reported article (Kukreti, Sapkota, et al., 2023).

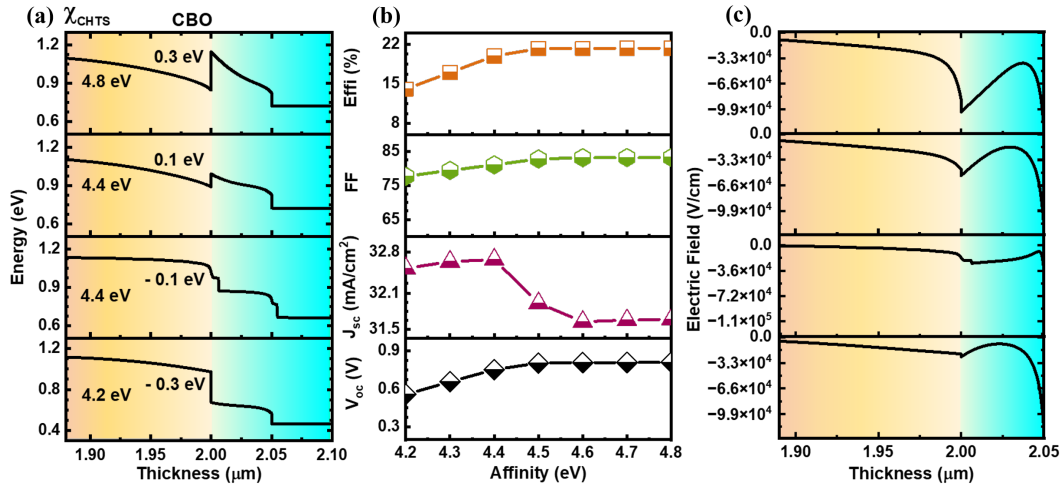
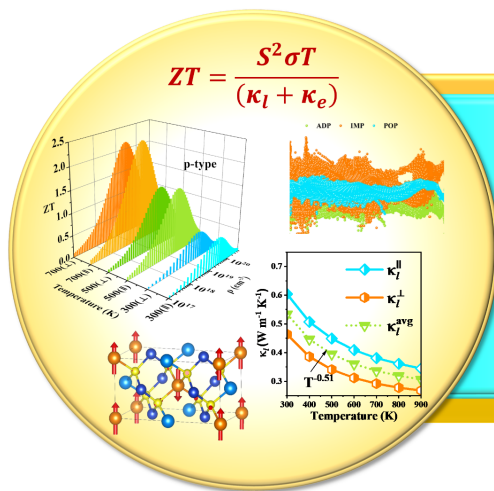


Figure 5.18 (a) Conduction band offset when electron affinity of alloy rich in sulfur is increased. Increased electron affinity results in spike-like feature and positive conduction band offset (b) Performance of graded solar cell with increased electron affinity of sulfur-rich alloy (c) Electric field near CHTSSe/CdS layer. The spike-like feature enhances the junction potential.

5.6. Conclusion:

We demonstrated $\text{Cu}_2\text{HgSn}(\text{S}/\text{Se})_4$ active layer-based single junction, tandem junction, and graded bandgap solar cells and highlighted vital performance parameters. We find that the efficiency of a single junction device is 11.9%, that of a tandem device is 16.87%, and that of graded bandgap absorbers is above 20%. This study uncovers the importance of the different grading patterns, which may help experimentalists to materialize an efficient device. The optimized characteristic length ($\text{CL} = 200 \text{ nm}$) performs well in these kinds of solar cells. The lower CL value-based absorber results in higher carrier generation with less recombination. The studies further emphasized that the graded bandgap device can perform better for $< 10^{15} \text{ cm}^{-3}$ bulk donor defect concentration with minimum defect density at the interface. A proper band alignment with 0 to 0.3 eV CBO can further push up the device output. Even with the only $2 \mu\text{m}$ absorber graded bandgap device, it can provide us $\sim 22\%$ maximum efficiency. Thus, our findings would be material-specific and provide a benchmark for developing and understanding the other graded bandgap absorber-based solar cells, which may be a better alternative to tandem solar cell structures.



$\text{Cu}_2\text{HgSnS}_4$: Phonon Dynamics & Thermoelectrics

- ✓ Hg-harnessed low thermal conduction
- ✓ ADP, IMP, POP scattering
- ✓ Intermediate temperature thermoelectric