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Increasing efficiency in intermediate band solar cells with overlapping absorptions

Akshay Krishna[1,2,3] **and Jacob J Krich**[1,4]

[1] Department of Physics, University of Ottawa, Ottawa, ON, Canada
[2] Department of Electrical Engineering, Princeton University, Princeton, NJ, USA
[3] Department of Physics, Indian Institute of Technology Madras, Chennai, India
[4] School of Electrical Engineering and Computer Science, University of Ottawa, Ottawa, ON, Canada

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Abstract

Intermediate band (IB) materials are promising candidates for realizing high efficiency solar cells. In IB photovoltaics, photons are absorbed in one of three possible electronic transitions—valence to conduction band, valence to intermediate band, or intermediate to conduction band. With fully concentrated sunlight, when the band gaps have been chosen appropriately, the highest efficiency IB solar cells require that these three absorptions be non-overlapping, so absorbed photons of fixed energy contribute to only one transition. The realistic case of overlapping absorptions, where the transitions compete for photons, is generally considered to be a source of loss. We show that overlapping absorptions can in fact lead to significant improvements in IB solar cell efficiencies, especially for IB that are near the middle of the band gap. At low to moderate concentration, the highest efficiency requires overlapping absorptions. We use the detailed-balance method and indicate how much overlap of the absorptions is required to achieve efficiency improvements, comparing with some known cases. These results substantially broaden the set of materials that can be suitable for high-efficiency IB solar cells.

Keywords: intermediate band solar cells, detailed balance, photovoltaics

(Some figures may appear in colour only in the online journal)

1. Introduction

The intermediate band solar cell (IBSC) has the potential to break the Shockley–Queisser efficiency limit for single-junction solar cells [1, 2]. Shockley and Queisser derived the most important thermodynamic efficiency limits of single-junction solar cells, proving that such cells cannot exceed 31% efficiency with unconcentrated black-body sunlight and 40.7% efficiency with fully concentrated sunlight [2]. The goal of breaking those limits has motivated the development of many high efficiency solar cell concepts, including multi-junction and hot-carrier solar cells, multiple exciton generation, and up- and down-conversion [3]. Multijunction solar cells have already broken the Shockley–Queisser limits [4], but their persistently high price and demanding material growth make it desirable to find other routes to high efficiency.

In an IBSC, an intermediate band (IB) material is placed between standard n- and p-type regions, as shown in figure 1. In the IB region, there is a set of allowed electronic levels at energy E_i between the valence band (VB) and conduction band (CB). High energy photons can be absorbed by VB–CB transitions throughout the device, while the IB allows sub-gap photons to be absorbed in VB–IB and IB–CB transitions. Two sub-gap photons can thus create an additional electron-hole pair, which can be collected at a voltage that is limited by the large band gap E_g. This additional current at high voltage increases the efficiency, allowing detailed balance efficiency limits of 46.8%, 63.2% under 1-Sun and full-concentration, respectively, each about 50% (relative) higher than for a single-junction solar cell [5]. Since IB materials do not exist in nature, the first problem is engineering appropriate systems with the correct band gaps. There has been considerable success in creating IB materials and demonstrating the IB effect in them [6], but the materials considered to date are hampered by excessive non-radiative recombination [6, 7]. Modified IB structures that have potential to overcome some of these problems have been proposed but not yet implemented [8, 9]. In this paper, we widen the scope of attractive IB materials by showing that the set of IB band energies that

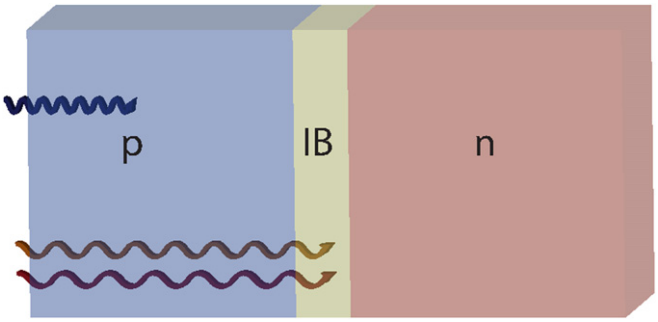

Figure 1. Schematic of the architecture of an IBSC, showing the IB region sandwiched between the p- and n-type regions. High energy photons are absorbed in the normal semiconductor region and subgap photons are absorbed in the IB region.

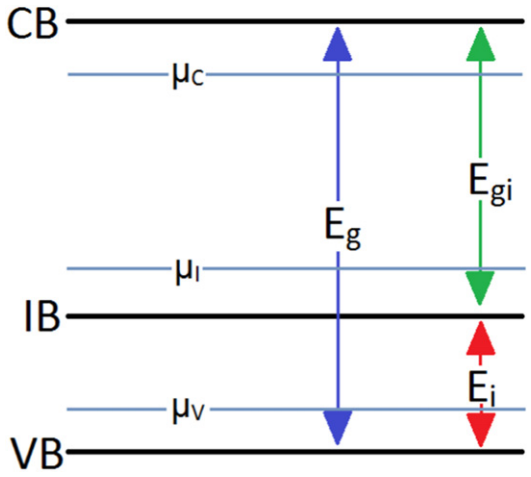

Figure 2. Schematic of energy levels in the IB region, showing the conduction band (CB), valence band (VB) and intermediate band (IB), along with the corresponding quasi-Fermi levels μ_C, μ_V and μ_I.

can make highly-efficient IBSC's is substantially broader than in previous predictions.

A high-efficiency IBSC requires that the currents be matched between the VB–IB and IB–CB transitions, since no current is extracted from the IB. For example, at full concentration of sunlight, the most efficient IBSC has a bandgap of 1.97 eV with an IB 0.72 eV away from either band, producing sub-gap transitions of 0.72 and 1.25 eV [1]. Since the solar spectrum has nearly the same flux of photons between 0.72 and 1.25 eV as it has between 1.25 and 1.97 eV, these transitions are current matched and the optimal efficiency is achieved by having no overlapping absorptions. For example, maximum efficiency requires that photons of energy 1.5 eV must only be absorbed in the higher-energy sub-gap transition.

Currently known IB materials do not have the ideal band energies [6, 10–12]. In many cases, theoretical efficiencies can be increased when realistic overlapping absorptions are considered, which can restore current matching. Overlapping absorptions have generally been considered to be a source of loss [13, 14], but their effect depends strongly on the band gaps considered. A similar observation was made for the case of silicon in [15]. In this paper, we show the efficiency gains that can be achieved by allowing overlapping absorptions in IBSC. We show that at 1-Sun concentration, overlapping absorptions can improve the efficiency of all IBSC with $0.5 < E_g < 2.7$ eV. With fully concentrated light, we show that the optimal efficiency at fixed E_g is attained with non-overlapping absorptions, but in systems with E_i near $E_g/2$, overlapping absorptions can significantly improve efficiency. We thus demonstrate that overlapping absorptions can give increases in both the peak attainable efficiencies (e.g., the peak efficiency at 1-Sun increases from 46.8% to 48.5%) and, possibly more importantly, that IB's near the middle of the gap can be highly efficient.

2. Non-overlapping absorptions

Luque and Martí used the detailed balance formalism to calculate the efficiency of an ideal IBSC, indicated in figure 2, as a function of E_g and IB energy E_i [1]. In these detailed balance calculations, the only recombination is radiative, carrier mobilities are infinite, and the cell is thick enough to absorb all photons above the threshold energy of the lowest transition. Since each absorbed photon is assumed to produce a single electron-hole pair, the current of the device can be determined entirely by considering the difference between the photon fluxes into and out of the cell [2]. It is common to assume, as we do, that the solar spectrum is that of an ideal black body at $T_{Sun} = 6000$ K, and the cell is at an ambient temperature $T_{cell} = 300$ K.

A key additional assumption of Luque and Martí is that of non-overlapping absorption—at a given photon energy, only one of the three possible transitions is excited. The three transitions are described by absorptivities α_{CV}, α_{CI} and α_{IV}. For simplicity, we assume these transitions to be step functions of equal height, as in figure 3(a), and choose units of length so all of these absorptivities peak at 1.

Figure 4 shows the detailed-balance maximum efficiencies as a function of E_g and E_i for solar concentrations X of 1, 100, and 46 260 (which is fully concentrated), using the Luque–Martí method. The peak efficiencies and band gaps in these cases are shown in table 1.

An IBSC achieves its greatest benefit when there is a current match between the VB–IB and IB–CB transitions. In other words, the photon flux integrated between E_i and E_{gi} must equal that between E_{gi} and E_g. This condition occurs when E_i is approximately equal to $E_g/3$. Note that the detailed balance calculations at fixed E_g are symmetric when sending E_i to $E_g - E_i$, as is clear from figure 4. In the discussion below, we assume $E_i < E_g/2$ for specificity, and the other case follows symmetrically.

For a fixed value of E_g, one can see that as E_i increases from 0, the efficiency increases from its single-junction value, peaks, and then drops rapidly back to the single junction value as E_i approaches $E_g/2$. This drop occurs becausse as E_i approaches $E_g/2$ from below, E_{gi} approaches $E_g/2$ from

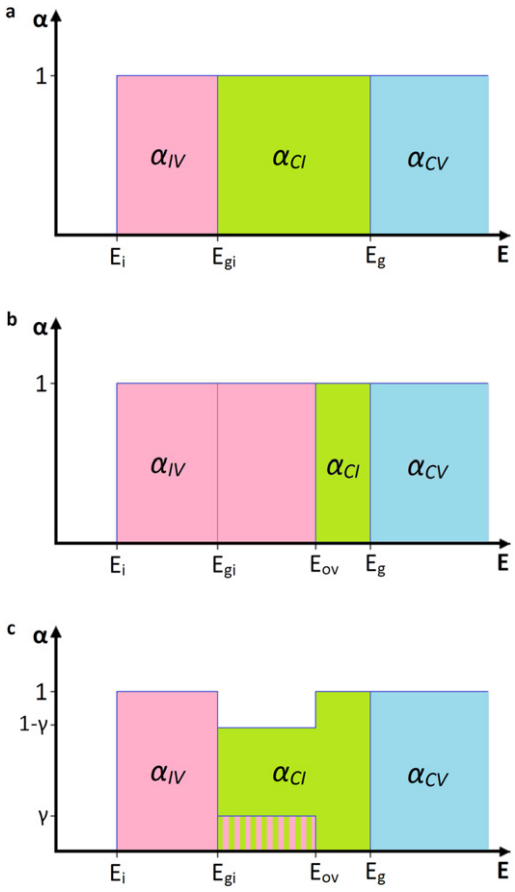

Figure 3. (a) Non-overlapping absorptivities of the three optical transitions from valence to intermediate band, α_{IV}, intermediate to conduction band, α_{CI}, and valence to conduction band, α_{CV}, as assumed by Luque and Martí [1]. (b) Perfectly overlapping absorption, in which all photons energetic enough to cause an IB–CB transition, up to a threshold E_{ov}, are actually absorbed by a VB–IB process. (c) Imperfectly overlapping absorption, in which a fraction γ of all photons with energies such that $E_{gi} < E < E_{ov}$ is absorbed in the VB–IB transition, and the rest are absorbed by the IB–CB transition. The non-overlapping case is $\gamma = 0$, and $\gamma = 1$ is the perfectly overlapping absorption case.

above, and the VB–IB transition, which absorbs from E_i to E_{gi}, is starved of photons. This unphysical result can be removed by considering overlapping absorptions.

3. Overlapping absorptions

Counterintuitively, overlapping absorptions can improve IBSC efficiencies. Luque and Martí included the assumption of non-overlapping absorptions because they were looking for the highest efficiency solar cell. As they suggested, it is best to choose materials where the VB–IB and IB–CB transitions do not compete for photons while at the same time remaining current matched to each other. However, when E_i is close to the center of the band gap, the non-overlapping assumption become highly non-optimal, as the VB–IB transition becomes starved of photons and the system is far from current matched. It is clear, and has been pointed out previously [15, 16], that it is desirable to have the two transitions share photons when E_i is near $E_g/2$. We show the improvement that can be obtained by allowing such overlaps. In particular, for unconcentrated sunlight and fixed band gap $0.5 < E_g < 2.7$ eV, it is possible to make a higher efficiency IBSC using overlapping absorptions than it is without, as shown in figure 5. For higher concentration, overlapping absorptions give an improvement for a smaller range of E_g; at full concentration, the optimal efficiency for fixed E_g is not improved with overlapping absorptions. But even at full concentration, when E_i is near $E_g/2$, overlapping absorptions are essential to achieving high efficiency IBSC.

The set of possible overlapping absorptions must be parameterized to be studied. Continuing with the case where $E_i < E_g/2$ (i.e., $E_{gi} > E_i$), the VB–IB transition can only absorb photons with energy greater than E_i and the IB–CB transition can only absorb photons with energy greater than E_{gi}, as is clear from figure 2. Accordingly, photons with $E_i < E < E_{gi}$ can only be absorbed by the VB–IB transition. Photons with $E > E_{gi}$ can, in principle, be absorbed by either transition. Following [15], we specify the competition for those photons with the parameter $\gamma(E) = \alpha_{IV}(E)/[\alpha_{IV}(E) + \alpha_{CI}(E)]$, and recall that we assume $\alpha_{IV} + \alpha_{CI} = 1$ for all $E_i < E < E_g$. The usual case of non-overlapping absorptions is $\gamma(E) = 0$ for $E_{gi} < E < E_g$, but any function $0 \leqslant \gamma(E) \leqslant 1$ for $E_{gi} < E < E_g$ describes a possible overlapping absorption condition.

There are many possible functions $\gamma(E)$, but the most important design criterion is the contribution of overlapping absorptions to current matching. Let the absorption current density energetically available to the CB–IB transition be $J_{CI}^{abs} = e\int_{E_{gi}}^{E_g} I(E)/E$, where $I(E)$ is the incident solar intensity. We can define J_{IV}^{abs} similarly for the the VB–IB transition from E_i to E_{gi}. Then consider the fraction of photons 'stolen' by the VB–IB transition, $f = e\int_{E_{gi}}^{E_g} \gamma(E)I(E)/(EJ_{CI}^{abs})$. If non-overlapping absorptions give $J_{IV}^{abs} = KJ_{CI}^{abs}$ for some constant $K < 1$, then current matching can be achieved by setting $f = (1 - K)/2$. Note that f approaches $1/2$ as $J_{IV}^{abs} \to 0$, which occurs as E_i reaches the middle of the gap. In that case, the two transitions must evenly share the photons from $E_i = E_{gi}$ to E_g.

All efficiencies are calculated using the detailed balance formalism as clearly and carefully derived in [13, 17]. Reference [13] shows that overlapping absorptions give rise to a new form of bulk loss in IBSC's. A radiative recombination event between the CB and IB can produce a photon with energy $E > E_{gi}$ that is reabsorbed by the lower-energy VB–IB transition, where the electron rapidly thermalizes to E_i. These losses increase with the size of the system, so the thickness W of the IB region must be optimized to balance the absorption against the losses. Note that there is no bulk loss term when $\gamma(E)$ exclusively takes the values 0 and 1, as there are no energies where the transitions compete for photons. We assume that photons with energy greater than E_g are fully absorbed in the standard semiconductor before reaching the IB region. Therefore, any overlap of absorptions with the VB–CB transition is irrelevant, and we also set the effective

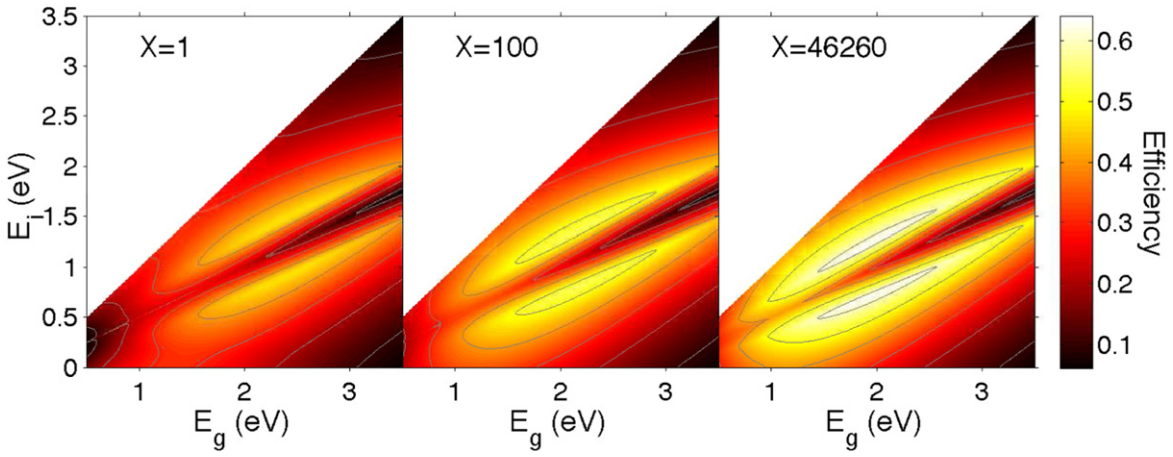

Figure 4. Detailed balance efficiencies as a function of band gap E_g and intermediate band position E_i with non-overlapping absorptions. (Left) 1-Sun concentration, (middle) 100 suns, (right) fully concentrated sunlight. Contours mark every 10%.

Table 1. Maximum detailed balance efficiencies and the band gaps that produce them for IBSC's with non-overlapping ($\gamma = 0$) and perfectly overlapping ($\gamma = 1$) absorptions at a range of concentration factors X. For the $\gamma = 1$ results, the E_{ov} of the maximum efficiency is also given. Note that in the case of full concentration, non-overlapping absorptions are optimal, so $E_{ov} = E_{gi}$.

γ	X	η (%)	E_g (eV)	E_i (eV)	E_{ov} (eV)
0	1	46.76	2.41	0.92	—
0	100	53.58	2.17	0.81	—
0	46 200	63.16	1.97	0.72	—
1	1	48.47	2.11	0.95	1.43
1	100	54.53	2.04	0.84	1.34
1	46 200	63.16	1.97	0.72	1.25

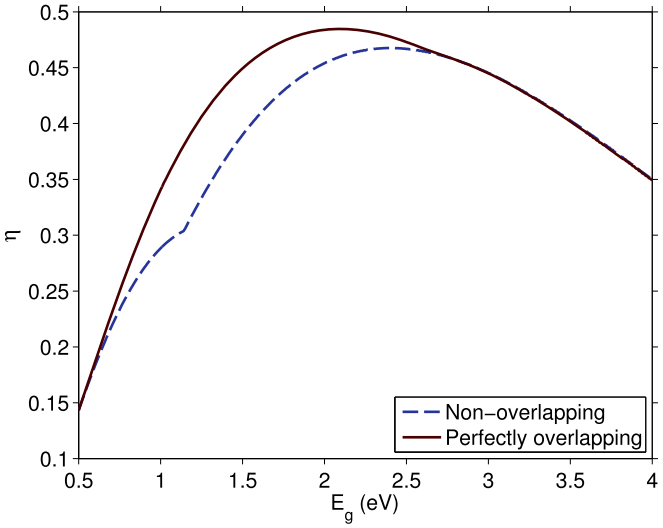

Figure 5. Maximum IB efficiencies with and without overlapping absorptions without concentration. Note that the kink in the non-overlapping curve is a real effect. For $E_g < 1.13$ eV, the no-overlap IBSC is always less efficient than a single junction cell, meaning that the trivial value of $E_i = 0$ (equivalent to a single junction cell) has the highest efficiency. For $E_g > 1.13$ eV, an intermediate band is superior. Overlapping absorptions can improve efficiencies for all $0.5 < E_g < 2.7$ eV.

width of the material to be infinite for $E > E_g$. For $E_i < E < E_g$, W is the width of the IB region. These losses are especially significant with unconcentrated sunlight, where radiative recombination substantially reduces the operating voltage. Such effects are beyond the simple current-matching picture and are included in all of the calculated results.

We begin by considering $\gamma(E)$ as a simple step function, which takes the value 1 for $E < E_{ov}$ and 0 for $E_{ov} < E < E_g$, as shown in figure 3(b). Such a $\gamma(E)$ is an approximation to a physical case where $\alpha_{CI}(E)$ begins much smaller than $\alpha_{IV}(E)$ and rapidly increases to exceed $\alpha_{IV}(E)$ at E_{ov}. In this approximation, only the VB–IB transition absorbs photons all the way up to E_{ov}, even though some of these photons could, energetically, be absorbed by the IB–CB transition. We refer to this case, where $\gamma(E)$ is 1 up to E_{ov} and 0 above E_{ov} as 'perfectly overlapping'. Optimizing over E_{ov} allows any value of f to be attained.

We first consider the case of perfectly overlapping absorptions and show the increases in IBSC efficiency that can be found by appropriate choice of E_{ov}, for fixed E_g, E_i. We then consider the more realistic case that $\gamma(E)$ is not precisely equal to 0 or 1. We show that even for realistically achievable values of $\gamma(E)$, it is possible to achieve increased efficiency with overlapping absorptions.

3.1. Perfectly overlapping absorptions

In the case of perfectly overlapping absorptions, where $\alpha_{CI}(E) = 0$ for $E < E_{ov}$, there are two extra benefits in addition to allowing better current matching between the transitions. First, the bulk loss term from overlapping absorptions is eliminated, both increasing efficiency and decreasing computational complexity, as W no longer needs to be optimized. Second, in the detailed balance method, the electron populations in the VB, IB, and CB are each described by Fermi distributions with temperature T_{cell} and independent quasi-Fermi levels, μ_V, μ_I, and μ_C, respectively, indicated in figure 2. The voltage of the device is equal to μ_{CV}, which must equal $\mu_{CI} + \mu_{IV}$, where $\mu_{XY} \equiv \mu_X - \mu_Y$. Ordinarily, the quasi-Fermi level splitting μ_{CI} cannot be larger than E_{gi}. But when $\gamma(E) = 1$, μ_{CI} becomes limited by $E_g - E_{ov}$ rather

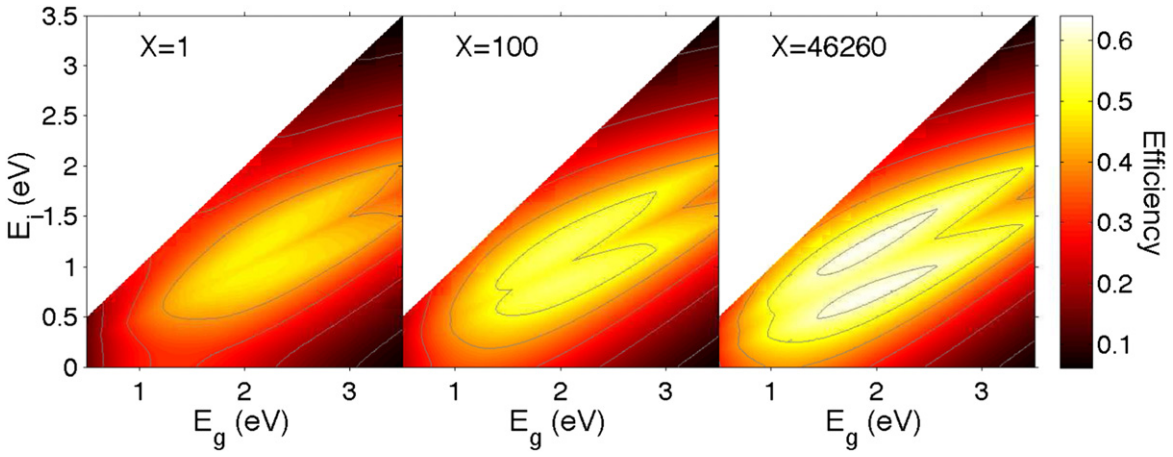

Figure 6. Detailed balance efficiencies with perfectly overlapping absorptions ($\gamma = 1$ and optimal choice of E_{ov}).

than $E_g - E_i$, allowing larger voltages out of the system. We discuss this effect further below.

Figure 6 shows optimized efficiencies in the perfectly overlapping case, where all points have been optimized over E_{ov}. The maximum efficiency for fully concentrated sunlight in this case is still limited by the Luque–Marti value of 63.16%. But with unconcentrated sunlight, we find an improvement in peak efficiency from 46.8% to 48.5%, as given in table 1, which also shows an improvement in the peak efficiency at 100-suns concentration. The same improvement in maximum 1-Sun efficiency has been seen in IB systems with spectrally-selective reflectors [18] and ratchet bands [19]. All three of these methods share in common the effect that they allow the IB to behave electrically as though it has $E_i + E_{gi} = E_g$ but with effective optical cutoffs where $E_i + E_{gi} > E_g$.

Figure 6 further shows that the high efficiency regions are much larger than in the non-overlapping case of figure 4. The unphysical valley of low efficiency along $E_g = E_i/2$, seen in figure 4, becomes much shallower. The improvement overlapping absorptions can allow is summarized in figure 7, which shows the broad region in design space where overlapping absorptions can give an improvement in efficiency, including improvements over 30% absolute.

However, setting $\gamma = 1$ exactly is a physically unattainable ideal. It is impossible to engineer an IB system in which one transition is completely suppressed in favour of another over a range of photon energies. We therefore explore the effects of imperfect overlap.

3.2. Imperfectly overlapping absorptions

We now consider that $\gamma(E)$ is still given by a step function, but its peak value is less than 1, giving partial overlap for $E_{gi} < E < E_{ov}$. We again consider piecewise constant absorption coefficients, as in figure 3(c). The total absorption coefficient $\alpha_{CI} + \alpha_{IV} + \alpha_{CV}$ is still set to be 1 for all $E > E_i$, for convenience. Since $0 < \gamma < 1$ requires optimizing over both E_{ov} and W, we do not present results at all values of E_g, as in figure 6. We instead look more closely at two cases of strong relevance for IBSC, $E_g = 1.12$ eV and $E_g = 1.424$ eV, representing the cases of silicon and GaAs.

For silicon under 1-Sun illumination with non-overlapping absorptions, IBSC's cannot improve the efficiency over a single-junction design for any value of E_i [15], as shown in figure 8, where the single-junction efficiency is 30.2%. When $\gamma = 1$, however, the maximum efficiency can reach 37.5% with $E_i = E_g/2$; even for more realistic values of $\gamma < 1$, the IBSC can still improve over the single-junction limit, showing that overlapping absorptions can produce effective silicon IBSC's, even at 1-Sun.

Similar efficiency improvements can be found from overlapping absorptions in GaAs, as shown in the right panel of figure 8. At 1-Sun, the optimal GaAs IBSC has an efficiency of 43.8% with overlap and 37% without overlap.

Note that as concentration increases, the efficiency increase becomes less sensitive to the value of γ. At $X = 100$, overlapping absorptions give both an increase in the maximum achievable efficiency (from 47.1% to 50.5% for GaAs) and efficiencies that are not strongly sensitive to γ. At full concentration, overlaps do not give a significant improvement in peak efficiency, but they all show a large improvement when E_i is near the middle of the gap. With fully concentrated light, the operating voltage is generally very close to the band gap, and any $\gamma(E)$ that obeys $f = (1 - K)/2$ will give approximately the same efficiency, as can be seen from the small dependence of the efficiency η on γ in figure 8. At lower concentrations, the shape of $\gamma(E)$ is more significant, as the details of the bulk loss term become important in addition to the current matching[5].

Many materials exhibit large values of γ. For example, in the case of an IB material made from Si doped with high concentrations of sulfur, the sulfur state can appear at

[5] Note that [15] also considers overlapping absorptions for silicon with $E_{ov} = E_g$ and optimizing over γ but finds no improvement at 1-Sun. They neglect the bulk loss term from overlapping absorptions (and the accompanying optimization over W) by arguing that light trapping in thin devices can make the absorption large and the loss small. In fact, light trapping also effectively increases the loss term, so it must be kept. We also believe that [15] has an additional typo in its equation (6). These differences and the different form of $\gamma(E)$ produce some discrepancies between their results and ours.

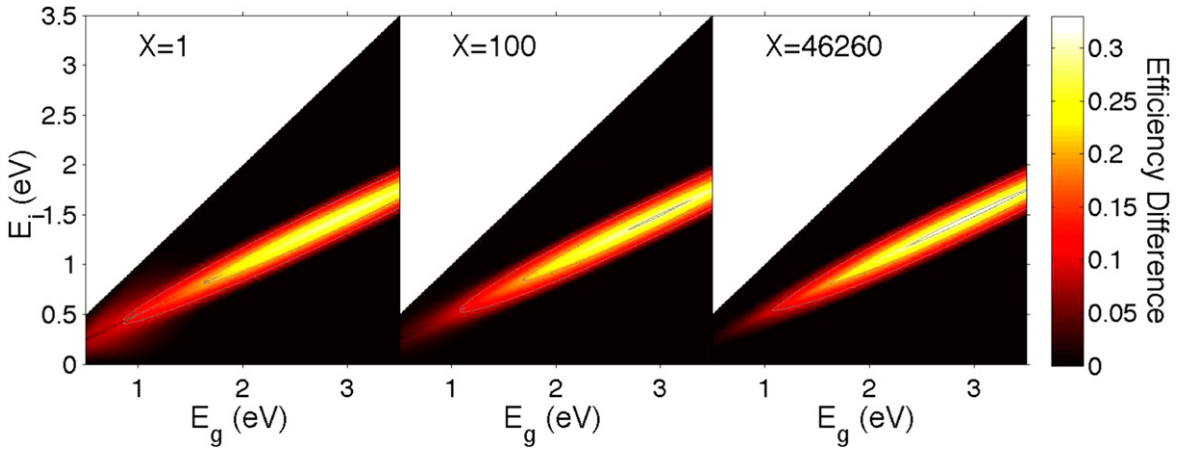

Figure 7. Difference between the non-overlapping and overlapping detailed balance efficiency limits of figures 4 and 6. For E_i near the middle of the band gap, overlapping absorptions can produce absolute efficiency increases of over 30%. In the black regions, non-overlapping absorptions are optimal.

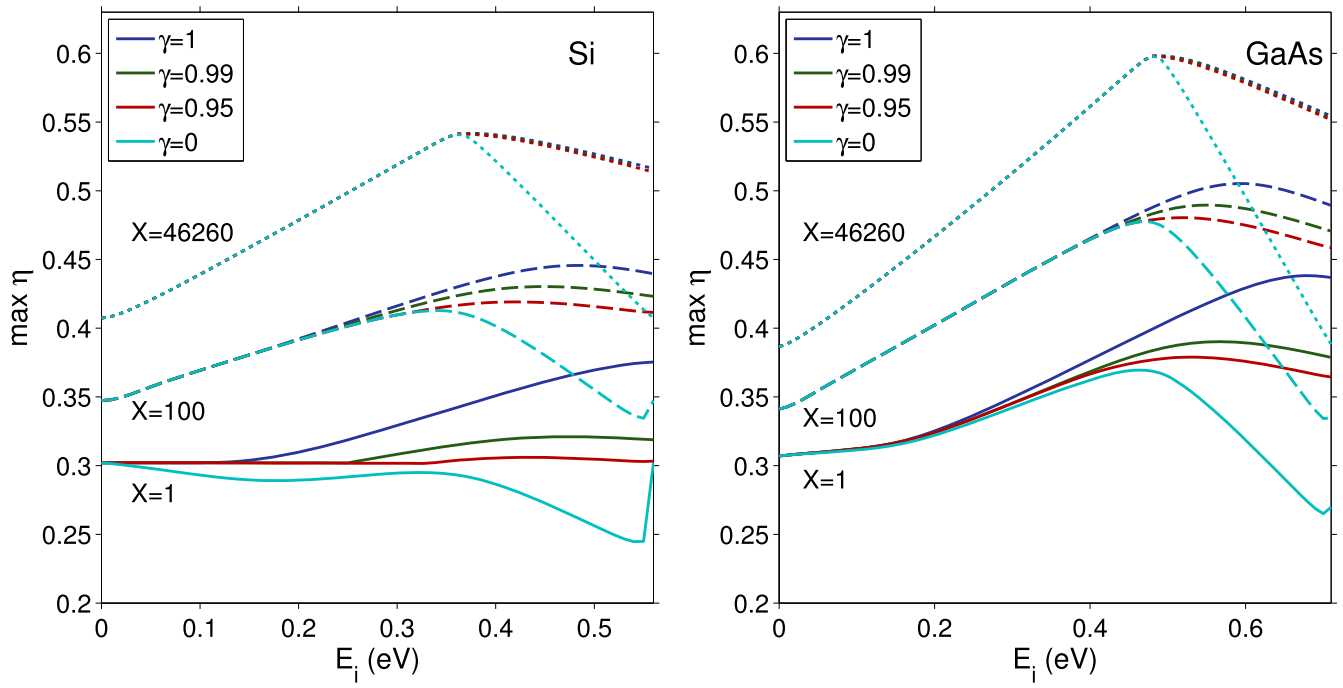

Figure 8. Maximum efficiencies for silicon ($E_g = 1.12$ eV, left) and GaAs ($E_g = 1.424$ eV, right) for four values of the overlap strength γ and three concentration values. Overlapping absorptions allow significant improvements over the non-overlapping ($\gamma = 0$) case, especially at lower concentration. In all cases, overlapping absorptions are helpful when E_i is near $E_g/2$. At lower concentrations, the absolute efficiency maximum over all E_i is substantially increased by optimal overlapping absorptions. For $\gamma > 0$, results are optimized over E_{ov} and for $0 < \gamma < 1$, results are optimized over W, too.

approximately 0.3 eV below the CB edge [20, 21], and α_{CI} can be 3-20 times larger than α_{IV} in the energy range where both are allowed [22, 23], corresponding to γ between 0.75 and 0.95; this absorptivity discrepancy has been considered to be a disadvantage for the Si:S system, but it may in fact be superior to the non-overlapping case. Similarly, the Zn double-acceptor in silicon (located 580 meV above the VB edge) has γ between 0.67 and 0.995 [24, 25]. In general, when one of the optical transitions is allowed and the other is forbidden, a large γ can result, which can be beneficial for mid-gap IBSC. Such a condition often occurs in quantum dot and quantum well based IBSC [6, 26].

Real material absorptivities depend on the occupation levels of each band, but detailed balance calculations are generally performed with all α_{XY} being constant. However, when μ_{CI} exceeds E_{gi}, there is a population inversion and the cell produces net stimulated emission at all energies $E < \mu_{CI}$ where $\alpha_{CI}(E)$ is nonzero [27]. This stimulated emission usually limits μ_{CI} to be less than E_{gi}. In the case of perfectly overlapping absorptions, no stimulated emission is produced until $\mu_{CI} > E_g - E_{ov}$, which allows a larger voltage to be

produced. Modeling this effect for $\gamma < 1$ requires allowing $\alpha_{CI}(E)$ to depend explicitly on μ_C and μ_I, as is done in a general cell analysis [27]. When $\gamma = 1 - \epsilon$ for some small ϵ, it should still be possible to find $\mu_{CI} > E_{gi}$, but such results are impossible in the standard detailed balance formalism, as in [13]. We performed a general cell analysis to include these effects and found no significant change in the maximum efficiencies achievable, though considerably larger W was often required. Since the results are nearly the same as in the simpler detailed balance calculations, we do not include the general cell analysis here.

4. Conclusion

Despite the longstanding belief that overlapping absorptions are a problem for IB solar cells, we show that overlapping absorptions are in fact essential to realizing the highest efficiency IBSC's at low to moderate solar concentration. Even though overlapping absorptions introduce a new bulk loss mechanism into IB devices, they can still be beneficial due to improved current matching. At high concentration, the exact shape of the overlapping absorptions does not matter—the only important parameter is the fraction of higher-energy photons absorbed by the lower-energy transition. At lower concentrations, the detailed form of the overlapping absorptions is important to determine the efficiency. We consider idealized step-function shaped absorption profiles, but real material absorption profiles should have similar properties. The possible improvement from overlapping absorptions, summarized in figure 7, is substantial and shows that IBSC's can be effectively produced from a wider range of IB materials than previously appreciated.

Acknowledgments

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