Efficiency limits of electronically-coupled upconverter and quantum ratchet solar cells using detailed balance

Emily Z. Zhang

Department of Physics, University of Ottawa, Ottawa, ON, Canada

Jacob J. Krich

Department of Physics, University of Ottawa, Ottawa, ON, Canada and School of Electrical Engineering and Computer Science, University of Ottawa, Ottawa, ON, Canada

The intermediate band solar cell (IBSC) and quantum ratchet solar cell (QRSC) have the potential to surpass the efficiency of standard single-junction solar cells by allowing sub-gap photon absorption through states deep inside the band gap. High efficiency IBSC and QRSC devices have not yet been achieved, however, since introducing mid-gap states also increases recombination, which can harm the device. We consider the electronically coupled upconverter (ECUC) solar cell and show that it can achieve the same efficiencies as the QRSC. Although they are equivalent in the detailed balance limit, the ECUC is less sensitive to nonradiative processes, which makes it a more practical implementation for IB devices. We perform a case study of crystalline-silicon based ECUC cells, focusing on hydrogenated amorphous silicon as the upconverter material and highlighting potential dopants for the ECUC. These results illustrate a new path for the development of IB-based devices.

I. INTRODUCTION

Shockley and Queisser used the detailed balance (DB) formalism to show that the efficiency of a solar cell made from a semiconductor with a single band gap can never exceed 31% under unconcentrated black-body sunlight [1]. Intermediate band (IB) materials – semiconductors with allowed electronic states deep in the gap, as shown in Figure 1a – enable solar cells to break this limit by absorbing sub-gap photons without harming the voltage of the cell [2]. In the radiative limit, the maximum efficiency of an intermediate band solar cell (IBSC) at one sun concentration is 47%, significantly exceeding the Shockley-Queisser limit [2]. Several intermediate band devices have been demonstrated, but high efficiencies have not been realized due to nonradiative recombination [3].

The quantum ratchet (QR) solar cell has been proposed as an improved implementation of the IBSC [4]. The intermediate band QR and conduction band QR implementations are shown in Figure 1b-c, respectively. The original idea of a IBQR solar cell is to increase the lifetime of the IB. In the case of the IBQR, carriers relax from the IB to a ratchet band (RB), which can suppress recombination to the valence band (VB). The ratchet also enables improved voltage matching between the subgap transitions and the band-to-band transitions [5-6]. The CBQR has the ratchet step above the conduction band edge, and an analogous valence band QR (not shown) has the ratchet step below the valence band edge. All three QR designs realize the voltage-matching improvements and can achieve detailed balance maximum efficiencies of 48.5% at one sun, greater than that of IBSCs. There have, however, been few QR experimental realizations and there are few suggestions for material systems [7].

In both IBSC and QRSC devices, the IB and QR regions are added to standard pn junctions in hopes of increasing current in the device, but if lifetimes are sufficiently short in the IB region, the IBSC or QRSC may even have lower current than the reference pn junction. Both IBSCs and QRSCs have an n-IB-p architecture, implying the holes created at the front of the cell must travel through the IB region to be collected. If hole lifetimes in the IB or QR regions are short, the nonradiative losses in the IB region will exceed the extra current generation, making efficiencies less than for the pn-diode solar cell alone [8-9].

The electronically-coupled upconverter (ECUC) is a less-studied architecture, which provides the potential to realize the same efficiency as a QRSC while being less sensitive to nonradiative processes [10-11]. As shown in Figure 1d, the ECUC has an n-p-IB architecture, with the IB region having a larger band gap than the standard semiconductor, unlike in the IBSC and QRSC where the large band gap $E_{CV}$ can be uniform through the device. As with IBSC and QRSC, the ECUC allows absorption of subgap photons, with the resulting carriers injected into the standard semiconductor. The minority carriers produced by absorption in the $pn$ junction never transit the IB region, so the current added from IB absorption can be obtained strictly as an addition, and low quality upconverter material cannot harm the cell as can occur in the IBSC/QRSC. However, the ECUC requires more complicated 2D contacts to avoid extracting current from the IB, with one possibility shown in Figure 2.

The detailed balance limiting efficiencies for the ECUC have not previously been calculated. In this work, we demonstrate that the QRSC and ECUC are mathematically equivalent in the DB limit, yet the ECUC may be a more practical implementation in actual devices. We show that, as with the QRSC, the ECUC configuration

* Current address: Department of Physics, University of Toronto, Toronto, ON, Canada
has the potential to exceed IBSC efficiencies at 1 sun. We perform a global optimization showing the maximum efficiencies possible as functions of \(E_{g1}\) and \(E_{g2}\) and also consider a case study of an ECUC based on crystalline silicon (c-Si), the most widely used and studied PV material. We show that there is potential to improve on c-Si solar cells using an ECUC.

II. DETAILED BALANCE MODEL

We use the well-known detailed balance formalism to model the ECUC and QRSC. We first show that in detailed balance, the ECUC and QRSC are mathematically equivalent, then we use this method to compute the limiting efficiencies for ECUC.

Detailed balance calculations assume all recombination is radiative, carriers have infinite mobility, and the cell is thick enough to assure full absorption of photons for each allowable transition. We further assume perfect photon selectivity, with each photon absorbed only by the highest-energy transition energetically permitted, to minimize thermalization losses; this condition is called non-overlapping absorptions and is not required for detailed balance [12, 13]. Since the carriers have infinite mobility,

\[
\mu_{CV} = qV_{ext},
\]

where \(q\) is the elementary charge, \(\mu_{CV}\) is the quasi-Fermi level difference between the electrons and holes, and \(V_{ext}\) is the external voltage. We take \(q = 1\).

Another key assumption is that there is one electron-hole pair generated/lost for each photon absorbed/emitted. Since all recombination events are assumed to be radiative, this assumption allows the current in the device to be written in terms of the photon fluxes \(\phi\) in and out of the device. These fluxes obey the modified Planck spectrum [14]

\[
\phi(E_{min,AB}, E_{max,AB}, T, \mu_{AB}) = \frac{2F}{h^3c^2} \int_{E_{min,AB}}^{E_{max,AB}} \frac{E^2dE}{e^{(E-\mu_{AB})/kT} - 1},
\]

where the process between bands \(A\) and \(B\) absorbs photons with energies between \(E_{min,AB}\) and \(E_{max,AB}\); \(T\) is the temperature, \(\mu_{AB}\) is the chemical potential difference between carriers in bands \(A\) and \(B\), \(h\) is Planck’s constant, \(c\) is the speed of light, \(k\) is Boltzmann’s constant, and \(F\) is the geometrical factor denoting the fraction of light incident on the cell. For the sun,

\[
F_{sun} = X \cdot \frac{\pi \left( \frac{\text{radius of sun}}{\text{distance between earth and sun}} \right)^2}{},
\]

where \(X\) is the solar concentration factor, and for emission from the cell,

\[
F_{cell} = \pi.
\]

In detailed balance, we have two photon sources: the sun and the cell. We can denote the photons absorbed from the sun in transitions between bands \(A, B\) by

\[
\dot{N}_{AB}^{\text{sun}} = \phi(E_{min,AB}, E_{max,AB}, T_s, 0),
\]

and the photons emitted by the cell in transitions between bands \(A, B\) by

\[
\dot{N}_{AB}^{\text{cell}} = \phi(E_{min,AB}, E_{max,AB}, T_a, \mu_{AB}),
\]

where \(T_s\) is the solar radiation temperature, which we take to be 6000 K and \(T_a\) is the ambient temperature, which we take to be 300 K. The current extracted from band \(A\) is the difference between absorbed and emitted photons involving band \(A\),

\[
J_A = \sum_B \pm \left( \dot{N}_{AB}^{\text{sun}} - \dot{N}_{AB}^{\text{cell}}(\mu_{AB}) \right),
\]

with the sign depending on whether the \(AB\) absorption process creates (+) or destroys (-) carriers in band \(A\).
For all of the devices, the total current is the net current extracted from either the CB or the VB, which are equal. For an ECUC, the total current is

$$J_{ECUC}^t = \dot{N}_{CV}^{sun} - \dot{N}_{CV}^{cell}(\mu_{CV}) + \dot{N}_{VI}^{sun} - \dot{N}_{VI}^{cell}(\mu_{VI}).$$

(8)

We also assume that no current is extracted from the intermediate band, so

$$J_{ECUC}^i = 0 = \dot{N}_{IV}^{sun} - \dot{N}_{IV}^{cell}(\mu_{IV}) - \dot{N}_{CI}^{sun} + \dot{N}_{CI}^{cell}(\mu_{CI}).$$

(9)

Note that the CI processes in Eq. 9 enter with the negative sign, as optical absorption from IB to CB removes an IB carrier. With equations [18,9] and the fact that

$$\mu_{CV} = \mu_{CI} + \mu_{IV},$$

(10)

we can solve for the chemical potentials and compute $J(V)$. These equations are of the same form as in the original IBSC calculation [2], but the ECUC has different band gaps in the different regions. Note that the $\mu_{CV}$ terms use $E_{g1}$ as their lower threshold.

For an IBQR, we assume the carriers in the IB and RB share a common quasi-Fermi level, so $\mu_{CI} = \mu_{CR}$ [4]. Then, the net current from the CB is

$$J_{CBQR}^t = \dot{N}_{CV}^{sun} - \dot{N}_{CV}^{cell}(\mu_{CV}) + \dot{N}_{CR}^{sun} - \dot{N}_{CR}^{cell}(\mu_{CR}),$$

(11)

and the net current in the IB is

$$J_{IBQR}^i = 0 = \dot{N}_{IV}^{sun} - \dot{N}_{IV}^{cell}(\mu_{CR}) - \dot{N}_{CR}^{sun} + \dot{N}_{CR}^{cell}(\mu_{CR}).$$

(12)

These equations for the ECUC and IBQR are equivalent. As shown in Figure 11, $E_{CI} + E_{IV} = E_{g2}$ for the ECUC. If we choose $E_{CV}$ for the IBQR to equal $E_{g1}$ for the ECUC then the first two terms in each of Eqs. 11 and 12 are equal to the equivalent terms in Eqs. 8 and 9. Further, if $E_{CR}$ for the IBQR equals $E_{CI}$ for the ECUC, and $E_{IV} + E_{CR}$ for the IBQR equals $E_{g2}$ for the ECUC, then the last two terms in each of those equations become equivalent. Therefore the ECUC equations are equal to the IBQR equations. Similarly, if $E_{IR} + E_{RI} = E_{g2}$ for the CBQR or $E_{IR} + E_{CI} = E_{g2}$ for the valence band QR (VBQR), then the equations also become equivalent to the ECUC. Since the equations for QR and ECUC are no different in detailed balance, the limiting efficiencies are also the same.

Figure 3 shows the maximum ECUC efficiencies at $X = 1$ and $X = 1/F_{sun} = 46200$, which is the maximum value. The peak efficiencies and band gaps for these cases are shown in Table I. The diagonal border at $E_{g1} = E_{g2}$ represents standard IB solar cells, and at one sun concentration (left), the detailed balance efficiency is highest at $E_{g1} \neq E_{g2}$. This result indicates that the ECUC has higher limiting efficiency than IBSC, similar to QR [4], spectrally-selective reflectors [15], and overlapping absorptions [12]. Therefore, the ECUC can exceed both the IBSC limit and the Shockley-Queisser limit. Figure 3 shows that there is a wide range of band gaps that can potentially achieve this goal.

At full concentration, the highest efficiency lies on $E_{g1} = E_{g2}$, so there is no gain from ECUC compared to a standard IBSC architecture. Both the ECUC and the IBSC significantly exceed the single junction efficiency limit, which has motivated interest in combining IBSC with concentrator systems [16,17].

### III. CASE STUDY: ECUC USING C-SI

In this section, we perform a case study of a potential ECUC using silicon as the front $pn$-diode material, since c-Si is an extremely well-understood material. Adding only an intermediate band to an $n$-IB-$p$ c-Si solar cell actually harms the efficiency of the cell, even in the detailed balance limit [12]. That failure occurs because silicon’s small band gap and the assumption of non-overlapping absorptions. Figure 3 however, shows that even with $E_{g1}$ equal to the band gap of c-Si, 1.12 eV, the ECUC allows considerable improvement over the Shockley-Queisser limit. First, we study the optimal range for $E_{g2}$ for an ECUC on silicon. Second, we consider an ECUC made of hydrogenated amorphous silicon (a-Si), which is a higher band-gap material frequently used for heterojunctions with c-Si. We perform a search...
for the best-suited $E_I$ for an a-Si upconverter on c-Si.

Figure 4 shows the maximum ECUC efficiency with $E_{g1} = 1.12$ eV as a function of $E_{g2}$ and $E_I$ at 1 sun concentration. The peak efficiencies and band gaps are shown in Table II. The optimal range of $E_{g2}$ lies approximately between 1.3 and 1.6 eV, with the maximum efficiency at $E_{g2} = 1.47$ eV, with $E_I$ near 0.9 eV. As $E_{g2}$ approaches $E_{g1}$, we recover the IBSC efficiency, which is lower than the Shockley-Queisser limit for a device with $E_g = 1.12$ eV. Note that when $E_{g2} > 1.3$ eV, the ECUC improves efficiencies for all values of $E_I$. For a large range of band gaps, it is possible to significantly exceed the SQ limit; therefore, there is potential for high efficiency silicon devices if an ECUC is added.

A promising upconverter material is amorphous silicon, since its band gap of $E_{g2} = 1.55$ eV falls in the high-efficiency range [18], and a-Si on c-Si devices are routinely made [19]. Figure 5 shows DB efficiency as a function of $E_I$ of a device using c-Si and an a-Si ECUC. All values of $E_I$ between $E_{g2} - E_{g1} = 0.43$ eV and $E_{g1} = 1.12$ eV give improved efficiencies over the bare c-Si cell. Doping of a-Si is more complicated than in crystalline semiconductors, as dopants can induce local coordination changes and dangling bonds, and the structures vary depending on deposition method [20]. The resulting $E_I$ for a dopant in a-Si can thus vary considerably depending on a-Si deposition and dopant precursor and pressure [20]. This variation could allow tuning of ECUC energy levels, which is not generally possible in crystalline semiconductor:dopant materials. To date, devices based on doped a-Si have generally desired shallow dopants, as in c-Si, so the most-studied dopants are those that produce relatively shallow states in the band gap, to give high conductivities. For an ECUC, optically active midgap states are desirable, which is the opposite of the standard case.

Figure 5 also shows estimated energetic positions for some common dopants in a-Si. The most studied dopants include boron and phosphorus as acceptors and donors, respectively, as in c-Si. Even when a-Si has tetrahedrally coordinated silicon, the bond angle distortions tend to make dopant energy levels lie deeper in the gap than in c-Si [25]. As an acceptor, B doping using $B_2H_6$ or BF$_3$ gives an electrical activation energy of $E_I = 0.88-0.91$ eV, with a higher concentration of active dopant states formed from the BF$_3$ precursor [24]. As a donor, P doping using PH$_3$ gives optical absorption in a band around $E_{g2} - E_I = 0.81$ eV [21]. As can be seen in Fig. 5, this energy level appears close to the middle of the band gap, which allows only minimal improvement in these detailed balance calculations. That dip in efficiency for $E_I \approx E_{g2}/2$ is an artifact of the non-overlapping absorption condition, as one of the subgap transitions becomes artificially depleted of photons when $E_I$ is close to mid-gap. Removing the non-overlapping absorption requirement, which is only a simplification for

![Figure 4. Maximum ECUC efficiency in detailed balance, with $E_{g1} = 1.12$ eV as a function of $E_{g2}$ and $E_I$ at 1 sun concentration. The detailed balance efficiency limit for $E_g = 1.12$ eV is shown with the white contour. Note that the data cutoff at the diagonal (black) occurs because the ECUC requires $E_I > E_{g2} - E_{g1}$ and $E_I < E_{g1}$.](image-url)

![Figure 5. Maximum ECUC efficiency vs. $E_I$ for c-Si ($E_{g1} = 1.12$ eV) and an a-Si upconverter ($E_{g2} = 1.55$ eV). The black dashed line shows the single-junction detailed balance efficiency with $E_g = 1.12$ eV. The potential dopants are labelled at their respective $E_I$. Doping with P is shown with the green dot (optical [21]) and a range of values with the yellow line (electrical activation [22]). Thermal activation energies for B are shown with stars, with red corresponding to doping with BF$_3$ [23] and purple to $B_2H_6$ [21]. The blue line shows the range of $E_I$ from thermal activation for alkali dopants, including Na, K, Rb, and Cs [24].](image-url)
IV. CONCLUSIONS

The ECUC has the potential to improve IB solar cell designs. Its maximum detailed balance efficiency is equal to that of a QRSC, and it may be easier to produce. Though DB calculations do not consider non-radiative processes, they give upper bounds on the efficiency of all photovoltaic devices. At low solar concentration, ECUC has a higher limiting efficiency than IBSC. This effect is realized in the c-Si case at one sun, where an IBSC with non-overlapping absorptions cannot improve on a standard single-gap solar cell, but an ECUC permits significantly improved efficiency. At high concentration, the DB efficiency limits of IBSC, ECUC, and QRSC are all the same, with a significant gain compared to a single junction device. Moving beyond DB, the ECUC architecture allows improved efficiency even with materials having significant nonradiative recombination. It is thus a promising architecture to pursue for near-term development of IB-based devices. The case of a-Si on c-Si provides a promising platform for developing an ECUC with the potential to significantly improve silicon-based solar cell efficiencies.

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