# Detailed-Balance-Limit Efficiencies of Solar Cells with Intermediate Bands and Carrier Multiplication 

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#### Abstract

Detailed-balance-limit efficiencies of solar cells with intermediate bands and carrier multiplication have been calculated. We assumed a single intermediate energy level and carrier multiplication up to the second order. The calculations have been conducted carefully filtering the conditions where carrier multiplication occurs according to the quantitative relation among spectrally segmented solar photon fluxes to be distributed to the transitions in the multilevel systems to determine the total photocurrent generated in the devices. The highest efficiency calculated in our work reaches 67\% under the full solar concentration. The efficiency can further increase by incorporating more intermediate levels, higher-order carrier multiplication, and thermal or tunneling carrier escape.


## 1. Introduction

Solar-cell efficiencies can be increased by utilizing intermediate bands (IBs) [1-3] and carrier multiplication (CM) [4-6] relative to those for the conventional non photonic up/down-conversion systems. Detailed-balance-limit efficiencies $[7,8]$ were previously calculated for each of cells with IBs $[9,10]$ and CM [11,12]. In the present work, we have calculated, for the first time to the best of our knowledge, detailed-balance-limit efficiencies for the case combining the IB and CM effects, as an ultimate class of photovoltaic device.

## 2. Theory and Calculations

The basic assumptions and calculation scheme we adopted in this work followed those in Ref. 7 and 8. To treat IB and CM at the same time, we have specifically established a computational algorithm for the resulted current according to the transition energies related with the integrated photocurrent generated in each solar-spectrum section, as follows. We define $E g_{I}, E g_{2}$ and $\Delta E_{C I}$ as the photovoltaic semiconductor's bandgap energy, transition energy from the valance band to IB, and the secondary transition energy ( $=E g_{1}-E g_{2}$ ), respectively, and A-E as the photon fluxes in the spectral regions divided by $E g_{1}, E g_{2}, 2 E g_{2}$ and $\Delta E_{C I}$, in the high-to-low-energy order (Fig. 1). The resulted photocurrent generation in the device, $J_{p h}$, is:
Case 1: $E g_{1}>2 E g_{2}>\Delta E_{C I}>E g_{2}$ :

1. $\mathrm{D}>2 \mathrm{~B}+\mathrm{C}->J_{p h}=\mathrm{eB}+\mathrm{eC}$ (no CM)
2. $\mathrm{D}<2 \mathrm{~B}+\mathrm{C}(\mathrm{w} / \mathrm{CM})$
$2-1 . \mathrm{D}+2 \mathrm{~B}>\mathrm{C} \rightarrow J_{p h}=2 / 3 \mathrm{eB}+2 / 3 \mathrm{eC}+1 / 3 \mathrm{eD}$ (partial
CM)
$2-2 . \mathrm{D}+2 \mathrm{~B}<\mathrm{C}->J_{p h}=\mathrm{eB}+1 / 2 \mathrm{eC}+1 / 2 \mathrm{eD}$ (full CM)
Case 2: $E g_{1}>\Delta E_{C I}>2 E g_{2}>E g_{2}$ :
3. $\mathrm{B}<\mathrm{C}+\mathrm{D}->J_{p h}=\mathrm{eB}$ (no CM)
4. $\mathrm{B}>\mathrm{C}+\mathrm{D}->J_{p h}=2 / 3 \mathrm{eB}+1 / 3 \mathrm{eC}+1 / 3 \mathrm{eD}$ (partial CM$)$

Case 3: $2 E g_{2}>E g_{1}>E g_{2}>\Delta E_{C I}$ :

1. $\mathrm{C}>\mathrm{D}->J_{p h}=1 / 2 \mathrm{eC}+1 / 2 \mathrm{eD}$ (no CM)
2. $\mathrm{C}<\mathrm{D}->J_{p h}=\mathrm{eC}$ (no CM)

The basic concept of this algorithm is to count the number of photons in each energy region and account which of first or second excitation is rate-limiting to determine the total number of generated free carriers. Air Mass 1.5 Global solar spectrum (AM1.5G) was used as the incident photon flux for the cases of 1 -sun irradiation intensity. Air Mass 1.5 Direct solar spectrum (AM1.5D) was used for the concentration cases considering only direct incidence of the sunlight, not scattered photons, as appropriate for optical concentrators.


Fig. 1 Schematic for the photocurrent segmentation out of the solar spectrum related with the transition energies, drawn for Case 1 superposed to the AM1.5G, 1 sun spectrum as an example. CB and VB denote the conduction and valence band edges, respectively.

## 3. Results and Discussion

We first of all would like to note that our test calculation for the case without IB or CM resulted in a $31 \%$ effi-
ciency at 1 sun, thus verifying the consistency with the results in Ref. 7 and 8. Fig. 2 shows the calculated efficiencies with varied $E g_{1}$ and $E g_{2}$ for the cases with both IB and CM, and with IB but without CM, under AM1.5G, 1 sun. CM is seen to slightly add to the IB-only cases for conditions. Note that the efficiency curves for the IB +CM cases merge into those for IB-only for the energy-level alignments where CM does not work, as sorted in the calculation algorithm in the previous section. The symmetry in the efficiency curves centered at the points $E g_{2}=1 / 2 E g_{1}$ is simply understood as the swapping of the first and second excitation energies.


Fig. 2 Calculated solar-cell efficiencies with varied $E g_{1}$ and $E g_{2}$ for the cases with both IB and CM, and with IB but without CM, under AM1.5G, 1 sun.

Fig. 3 shows the calculated solar-cell efficiencies with varied $E g_{1}$ and $E g_{2}$ for the cases with both IB and CM, and with IB but without CM, under AM1.5D, 46000 suns (i.e., the full solar concentration). It is seen that the highest solar energy-conversion efficiency among the conditions we calculated for reaches $67 \%$ by the combination of IBs and CM, somewhat meaningfully higher than those for the IB-only cases. Importantly, it should be noted that we assumed solely a single IB level in a cell, and carrier multiplication only of the second order in this work. Inclusion of higher numbers of IBs as well as higher-order harmonics in CM would further increase the efficiency limit. In addition, if the carriers or excitons at IBs were able to "escape" to the conduction bands by the mechanism of thermal excitation or tunneling (under a certain bias) for the cases where the band offset between the conduction band and IB is relatively small, this transition would require no photon absorption to save the sunlight partially instead to distribute to another excitation and thus adds the efficiencies, while we solidly assumed that any transition requires a corresponding or higher-energy photon in this work.


Fig. 3 Calculated solar-cell efficiencies with varied $E g_{1}$ and $E g_{2}$ for the cases with both IB and CM, and with IB but without CM, under AM1.5D, full solar concentration (46000 suns).

## 4. Conclusions

We calculated the detailed-balance-limit efficiencies for the solar cells co-equipped with IB transitions and CM for the purpose to theoretically test an ultimate version of photovoltaic device, accounting for the photon-absorption balance among the spectral energy regions to be distributed for the multiple transitions to determine the total photocurrent generation. The highest efficiency among the conditions we calculated for reaches $67 \%$. Utilization of more IBs, high-er-order CM, and/or thermal or tunneling escape would increase the efficiencies even further.

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