THE LIMITING EFFICIENCY OF FOUR-BAND CELLS REVISITED

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***Abstract* — The limiting theoretical efficiency of four-band solar cells is revisited. In previous work, researchers have looked at the theoretical efficiency of four band cells where the smallest of the three sub-band gaps is closest to the valence band and the largest closest to the conduction band. In this work, limits are calculated also for other possible band configurations.**

In multi-band cells, photon selectivity can be assured by adjusting the band widths. The present work shows that previous authors have put too rigid constraints on the band structure to achieve spectral selectivity. Relieving these constraints gives a considerably higher limiting efficiency for cells with band width restriction than previously reported. The highest efficiency for four-band cells with band width restriction is found to be 69.4 %.

***Index Terms* — Multi band cells, theoretical efficiency, spectral selectivity**

I. INTRODUCTION

In a four-band solar cell, two intermediate bands (IBs) are found in the otherwise forbidden band gap of the cell material. The two IBs allow electrons to follow four different excitation routes from the valence band (VB) to the conduction band (CB), as shown in Fig. 1. This allows photons with energy lower than the band gap to contribute to the photo-excitation of electrons from the VB to the CB. In 2002, Brown et al. calculated two limiting efficiencies for four-band cells [1]. Both limits are found by assuming spectral selectivity, which implies that photons are assumed to excite electrons only over the largest band gap, or combinations of band gaps, allowed by energy conservation. Spectral selectivity is equivalent to having non-overlapping absorption coefficients. The first of the two limiting efficiencies is calculated without specifying the origin of the spectral selectivity. The absorption coefficient over the smallest sub-band gap is just assumed to go to zero when the photon energy reaches the energy of the second largest band gap. The absorption coefficient over the second smallest band gap is then assumed to go to zero when the photon energy reaches the third largest band gap, etc. (An exception to this is the absorption coefficient over E_2, this is discussed below.) With such assumptions, ref. [1] reports a limiting efficiency of 71.7 %.

In the second limit presented by Brown et al. [1], the spectral selectivity is achieved by restricting the width of the four bands. Excitation over one of the band gaps is then restricted upwards by the respective band gap energy plus the sum of the widths of the two adjacent bands. In the following, any cells analyzed with this constraint are referred to as bandwidth restricted cells.

In the present work, two types of adjustments are made to the existing theory to further investigate theoretical efficiencies of four-band solar cells. The first adjustment is related to the possible band gap configurations. Previous work has only considered band gap configurations with $E_1 \leq E_2 \leq E_3$. (Equivalent configurations with $E_3 \leq E_2 \leq E_1$ are then implicitly treated.) The present work also explores other possible configurations.

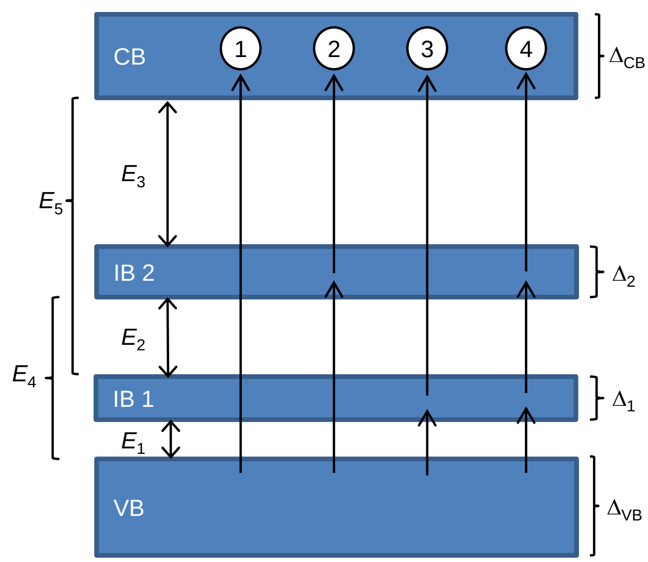

Fig. 1. In a four band cell there are four possible excitation routes from the VB to the CB.

The second adjustment relates to the fact that Brown et al. did not take into account the possibility of having energy intervals without photon absorption. For example: In the configuration shown in Fig. 1, absorption over the band gap E_1 will take place in the energy interval between E_1 and $E_1 + \Delta_{VB} + \Delta_1$. In ref. [1], the restriction $E_2 = E_1 + \Delta_{VB} + \Delta_1$ is then applied to the band structure. In the present work, energy intervals without photon absorption are allowed. That is, the restriction to E_2 becomes $E_2 \geq E_1 + \Delta_{VB} + \Delta_1$. Similar considerations also apply to the other band gaps in the cell.

This paper first gives a short recap of the detailed balance model applicable to four-band cells. Different types of band configurations are then discussed together with the various constraints and related to each of these configurations. Finally theoretical efficiencies are presented for the various band configurations.

II. Method and Investigated Cases

The mathematical model used in this work resembles the detailed balance models used by previous authors when treating multi-band cells [1]-[3]. As explained in the introduction, the novelty of the present work lies in the extended range of band configurations to which the detailed balance formalism has been applied. To recall, in the detailed balance theory for four-band cells the recombination rates over band gap n is given by

$$R_n = \frac{8\pi}{h^3c^2}\int_{E_L}^{E_H}\frac{E_\gamma^{\,2}\,\mathrm{d}E_\gamma}{\exp\left(\dfrac{E_\gamma - q\mu_n}{kT_C}\right)-1}, \qquad (1)$$

where h is Planck's constant, c the speed of light, k Boltzmann's constant, T_C the cell temperature and q the elementary charge. The cell temperature is set to 300 K. The integral is taken over the photon energy E_γ. μ_n is the quasi Fermi level split between the bands on each side of band gap n. E_L and E_H represents the lowest and highest, respectively, energy that the photons can have to be allowed to excite electrons over band gap n. E_L and E_H are discussed in detail below. In addition to the five band gaps indicated in Fig. 1, we also have the total band gap $E_6 = E_1 + \Delta_1 + E_2 + \Delta_2 + E_3$.

The excitation rate over band gap n is given by

$$G_n = \frac{8\pi}{h^3c^2}\int_{E_L}^{E_H}\frac{E_\gamma^{\,2}\,\mathrm{d}E_\gamma}{\exp\left(\dfrac{E_\gamma}{kT_S}\right)-1}, \qquad (2)$$

where T_S is the temperature of the sun, set to 6000 K.

In steady state, the rate of electrons entering each of the IBs must balance the rate of electrons leaving the same band. This gives rise to the equations

$$G_1 + R_2 + R_5 = R_1 + G_2 + G_5 \text{ and} \qquad (3)$$
$$G_2 + G_4 + R_3 = R_2 + R_4 + G_3\,. \qquad (4)$$

A third equation for particle conservation is found by noticing that the net rate of electrons excited to the CB has to equal the net number of holes excited to the VB. This gives

$$G_1 - R_1 + G_4 - R_4 = G_5 - R_5 + G_3 - R_3\,. \qquad (5)$$

As for single band gap cells and other types of solar cells the output voltage V of the cell is related to the split between the quasi-Fermi levels of the CB and the VB by

$$qV = \mu_6\,. \qquad (6)$$

Equations (3)-(6) are sufficient to determine the position of the quasi-Fermi levels of each of the bands. Solving this system of equations allows us to calculate the IV-curve of the cell and from that the cell power and efficiency.

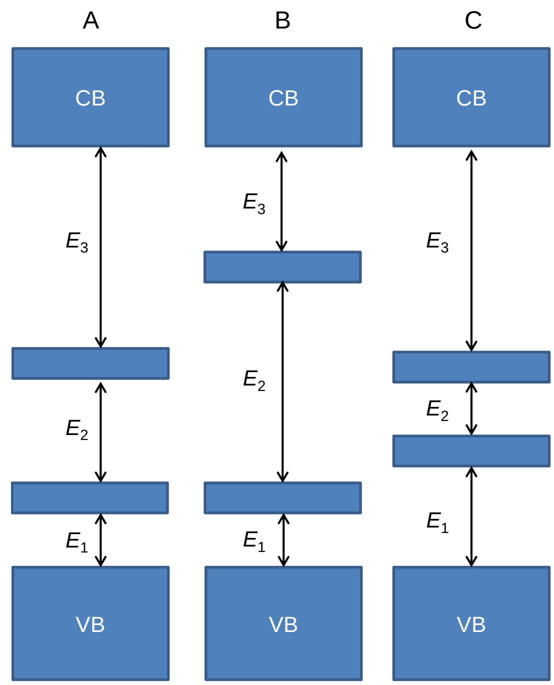

Fig. 2. Three classes of different band gap configurations treated in this work. A: $E_1 \le E_2 \le E_3$, B: $E_2 \le E_1 \le E_3$ and C: $E_1 \le E_3 \le E_2$. Type A and C can occur in two important variants, variant 1 with $E_3 < E_4$ and variant 2 with $E_3 > E_4$. Other variants are either impossible or have relatively low theoretical efficiency.

TABLE I

Integration Limits and Band Gap Restrictions for Cells with Restricted Band Widths

Band gap	E_L – Type A-1	E_L – Type A-2	E_L – Type B	E_L – Type C-1	E_L – Type C-2	E_H
E_1	E_1	E_1	E_1	$E_1 \ge E_2 + \Delta_1 + \Delta_2$	$E_1 \ge E_2 + \Delta_1 + \Delta_2$	$E_1 + \Delta_1 + \Delta_{VB}$
E_2	$E_2 \ge E_1 + \Delta_1 + \Delta_{VB}$	$E_2 \ge E_1 + \Delta_1 + \Delta_{VB}$	$E_2 \ge E_3 + \Delta_2 + \Delta_{CB}$	E_2	E_2	$E_2 + \Delta_1 + \Delta_2$
E_3	$E_3 \ge E_2 + \Delta_1 + \Delta_2$	$E_3 \ge E_4 + \Delta_2 + \Delta_{VB}$	$E_3 \ge E_1 + \Delta_1 + \Delta_{VB}$	$E_3 \ge E_1 + \Delta_1 + \Delta_{VB}$	$E_3 \ge E_4 + \Delta_2 + \Delta_{VB}$	$E_3 + \Delta_2 + \Delta_{CB}$
E_4	$E_4 \ge E_3 + \Delta_2 + \Delta_{CB}$	$E_4 \ge E_2 + \Delta_1 + \Delta_2$	$E_4 \ge E_2 + \Delta_1 + \Delta_2$	$E_4 \ge E_3 + \Delta_2 + \Delta_{CB}$	$E_4 \ge E_1 + \Delta_1 + \Delta_{VB}$	$E_4 + \Delta_2 + \Delta_{VB}$
E_5	$E_5 \ge E_4 + \Delta_2 + \Delta_{VB}$	$E_5 \ge E_3 + \Delta_2 + \Delta_{CB}$	$E_5 \ge E_4 + \Delta_2 + \Delta_{VB}$	$E_5 \ge E_4 + \Delta_2 + \Delta_{VB}$	$E_5 \ge E_3 + \Delta_2 + \Delta_{CB}$	$E_5 + \Delta_1 + \Delta_{CB}$
E_6	$E_L = E_6 \ge E_5 + \Delta_1 + \Delta_{CB}$ for all types					$E_6 + \Delta_{VB} + \Delta_{CB}$

TABLE II

OPTIMAL BAND GAPS, BAND WIDTHS AND LIMITING EFFICIENCY FOR UNRESTRICTED CELLS.

	A-1 (ref. [1])	A-2	B	C-1	C-2
Efficiency	71.7 %	68.7 %	70.4 %	70.3 %	71.0 %
E_1	0.53 eV	0.25 eV	0.45 eV	0.80 eV	0.56 eV
E_2	0.89 eV	0.70 eV	1.50 eV	0.70 eV	0.39 eV
E_3	1.02 eV	1.33 eV	0.86 eV	1.21 eV	1.27 eV
Δ_1	0.07 eV	0.05 eV	0.03 eV	0.08 eV	0.06 eV
Δ_2	0.05 eV	0.23 eV	0.45 eV	0.02 eV	0.11 eV

Fig. 2 shows three main types of band configurations that four-band solar cells might have. These are type A, where $E_1 \leq E_2 \leq E_3$, type B, where $E_2 \leq E_1 \leq E_3$ and type C, where $E_1 \leq E_3 \leq E_2$. Due to symmetry, $E_3 \leq E_2 \leq E_1$ is equivalent to type A, $E_2 \leq E_3 \leq E_1$ is equivalent to type B and $E_1 \leq E_3 \leq E_2$ is equivalent to type C when it comes to theoretical efficiency.

The integration limits in (1) are different for the different types of band configurations. The lower integration limits E_L are always equal to the band gap energy in question. For cases with band width restriction, the values of E_L have lower limits which are listed in Table I. Without band width restriction, the values of the upper integration limits are equal to the value of the band gap that follows next when going upwards in energy. The only exception is the upper integration limit for E_2., which cannot exceed $E_2 + \Delta_1 + \Delta_2$. With band width restriction the upper integration is equal to the energy of the band gap in question plus the width of the two adjacent bands. The value of the upper integration limits E_H for band width restricted cells are also shown in Table I.

Although we always have $E_1 + E_2 < E_2 + E_3$, it is possible to construct band configurations where $E_5 < E_4$ if $\Delta_1 > \Delta_2$. For unrestricted cases it turns out that such configurations are less efficient than those with $E_5 > E_4$. This work is therefore focusing on configurations with $E_5 > E_4$. For restricted cases, it is not possible to have configurations with $E_5 < E_4$. This is a result of the restrictions on the integration limits. $E_5 < E_4$ implies that $E_4 \geq E_5 + \Delta_{CB} + \Delta_1$, which, after substitution of $E_4 = E_1 + \Delta_1 + E_2$ and $E_5 = E_2 + \Delta_2 + E_3$, gives $E_1 \geq E_3 + \Delta_{CB} + \Delta_2$. The latter inequality cannot be fulfilled by any type of band configuration unless by some inverted configuration equivalent to a configuration with $E_5 > E_4$.

Configurations where $E_4 < E_3$ is possible for type A and C both for unrestricted and restricted band widths. In the following type A with $E_4 > E_3$ is denoted A-1 and type A with $E_4 < E_3$ is denoted A-2. A similar annotation is used for type C configurations as well. A-2 and C-2 requires a separate treatment. In Table I, the lower integration limits E_L as well as the restrictions on the band gaps for configurations with $E_4 < E_3$ are listed in the columns marked A-2 and C-2.

A computer algorithm is used to find the efficiency peaks for each type of band configuration. The algorithm starts with an initial set of band gaps and band widths that fit the restrictions to the configuration type in question. The independent parameters are then systematically varied to check whether or not there exists a combination of band gaps and band widths in the vicinity of the starting point that gives a higher efficiency. If a higher efficiency is found, the algorithm moves to the set of parameters that yields this higher efficiency and starts varying the parameters again. This procedure is repeated until no point with higher efficiency is found. Close to the efficiency peaks, the variation of the parameters in this optimization is set to 1 meV. The value of the band gaps presented in section III are rounded to the closest 10 meV.

III. RESULTS AND DISCUSSION

Maximum theoretical efficiencies for unrestricted cells are shown in Table II. The optimal band gaps and band widths are listed in the same table. The maximum value of 71.7 % found by Brown et al. [1] is still the highest theoretical efficiency

TABLE III

OPTIMAL BAND GAPS, BAND WIDTHS AND LIMITING EFFICIENCY FOR CELLS WITH RESTRICTED BAND WIDTHS.

	A-1 (ref. [1])	A-1 (this work)	A-2	B	C-1	C-2
Efficiency	59,0 %	60.0 %	57.1 %	69.4 %	61.0 %	61.3 %
E_1	0.45 eV	0.41 eV	0.41 eV	0.32 eV	1.14 eV	0.56 eV
E_2	0.92 eV	0.94 eV	0.55 eV	1.40 eV	0.93 eV	0.50 eV
E_3	0.92 eV	0.94 eV	1.51 eV	0.76 eV	1.50 eV	1.43 eV
Δ_{VB}	0.47 eV	0.53 eV	0.14 eV	0.44 eV	0.32 eV	0.31 eV
Δ_{CB}	0.45 eV	0.41 eV	0.41 eV	0.32 eV	0.44 eV	0.50 eV
Δ_1	0	0	0	0	0.04 eV	0
Δ_2	0	0	0.41 eV	0.32 eV	0.17 eV	0.06 eV

found for the four-band cell. For configurations of type B and C the highest efficiencies are 70.4 % and 71.0 %, respectively. The results show that efficiencies above 70 % can be found for band gap combinations very different from the optimal band configuration of type A-1. A visualization of the optimal band configurations for type A, B and C is found in Fig. 3. Variants of the A, B and C configurations with $E_5 < E_4$ have limiting efficiencies of 61.5 %, 64.3 % and 64.1 %, respectively. These are not listed in Table 2.

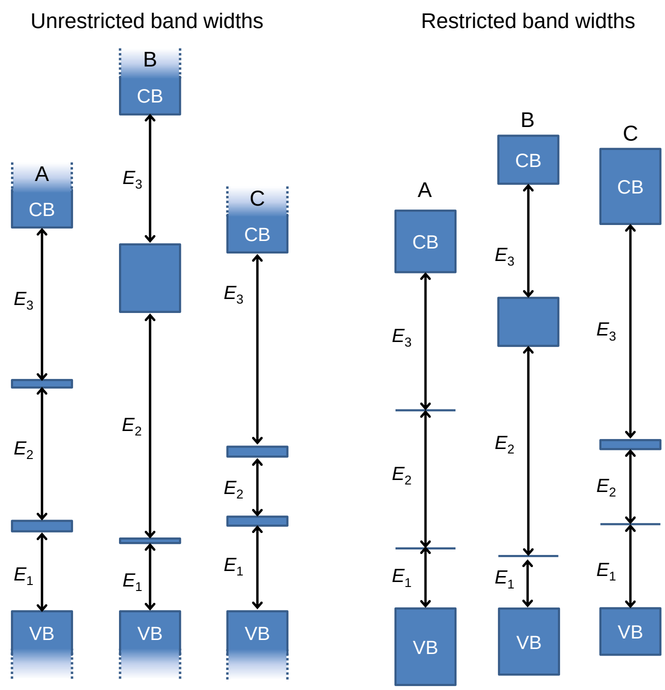

Fig. 3. In scale comparison of the band configurations giving the highest limiting efficiencies for type A, B and C configurations. The left half of the figure shows the best configurations for cells without band width restriction, while the right half shows the best configurations for band width restricted cells. The optimal configurations of type C are of the C-2 variant.

The limiting efficiency as well as the optimal band gaps and band widths for restricted cells are listed in Table III. The highest efficiency is found for a type B configuration, with a maximum efficiency of 69.4 %. This is significantly higher than the 59.0 % limit found in ref. [1]. The type B band configuration allows restricted calls to have a band structure resembling that of an optimal unrestricted cell. For type A-1, the optimal structure has $E_2 = E_3$ and $\Delta_1 = \Delta_2 = 0$. This prevents photo-excitation of electrons across E_2, resulting in lower efficiency than type B. In fact, this band configuration is on the border to type B. Therefore it is not surprising that a higher theoretical efficiency is found for type B. For type C-1, the band width restriction gives an optimal configuration with rather large band gaps, resulting in a limiting efficiency much lower than that of type B configurations. Type C-2 yields optimal band gaps with a rather small difference between E_2 and E_1, which also results in a relatively low efficiency.

Also the optimal band configurations for restricted cells are visualized in Fig. 3. Note that $E_4 < E_3$ for the best configurations of type C both with and without band width restriction

Note that the optimal band configuration of type A-1 found in this work also satisfies the restrictions put on the band configuration in ref. [1]. The limiting efficiency found in the present work is still a bit higher. This is probably due to the difficulties involved in identifying the optimal configurations of 7 variables combined with the number of restrictions limiting the possible values of these variables. Using the algorithm described above for peak identification there is a risk that unidentified efficiency peaks exist. An effort has been made to avoid this by starting the optimizing procedure with different sets of start configurations.

For the thee-band cell, or the intermediate band cell, the limiting efficiency is 63.2 % without band width restriction and 58.9 % with band width restriction [1]. The reduced efficiency with restriction is mainly due to high energy photons that are not absorbed. Now that the theoretical efficiency of four-band cells with band width restriction is found to be 69.4 % instead of 59.0 %, the ratio between the theoretical efficiency of restricted and unrestricted four-band cells is more in line with that of the intermediate band cell.

The number of possible types of band configurations increases with the number of bands. To identify the ultimate limiting efficiency of multiband cells, the different band configurations should be examined. So far, theoretical efficiencies have only been calculated for certain types of band configurations for cells with more than four bands [2].

IV. CONCLUSIONS

The theoretical efficiency of four-band cells has been investigated in greater detail than in earlier work. This involves examining various classes of band configurations as well as relieving some unnecessarily strict constraints imposed on the band structure of band width restricted cells.

Changing the band gap configuration does not change the maximum efficiency for cells without restrictions of the band widths. All of the three main types of band configurations have theoretical efficiencies above 70 %.

For cells with restricted band widths the efficiency limit is found to be 69.4 %. This is considerably higher than the 59.0 % limit reported earlier. The 69.4 % limit is found for a band configuration of type B with $E_1 = 0.32$ eV, $E_2 = 1.40$ eV, $E_3 = 0.76$ eV, $\Delta_1 = 0$, $\Delta_2 = 0.32$ eV, Δ_{VB} 0.44 eV and $\Delta_{CB} = 0.32$ eV. Band width restricted cells of type A and C have considerably lower limiting efficiencies of 60.0 % and 61.3 %, respectively.

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