EtaOpt – a program for calculating limiting efficiency and optimum bandgap structure for multi-bandgap solar cells and TPV cells

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ABSTRACT: The detailed balance limit of efficiency has been widely used to estimate the potential of new solar cell concepts. Although in principle the calculation is simple, the results obtained by various authors are hard to compare because they are based on different assumptions. To discuss the differences, a review of the basic idea and the procedure of the calculation is described and assumptions, approximations and numerical techniques commonly used in this method are evaluated. The influence of the total internal reflection is highlighted. In order to verify and to be able to modify the calculations a very flexible object oriented program based on Wolfram Research's Mathematica - etaOpt - has been developed. The results obtained by this program are compared to calculations performed by different authors. Last but not least some example applications are given, where etaOpt was used to calculate optimal bandgap structures. For the purpose of enabling the reader to calculate the limiting efficiency of his own applications etaOpt is available for free at http://www.ise.fhg.de/english/fields/field2/mb5/index.html.
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1. INTRODUCTION

To estimate the potential of new cell concepts for photovoltaic (PV) as well as for thermophotovoltaic (TPV) applications the limiting efficiency based on thermodynamics has often been calculated in the past.

A widely spread approach is the "detailed balance limit of efficiency of p-n-junctions...", which was first presented by W. Shockley and H.J. Queisser in 1961 [1]. This method takes into account only the radiative recombination, because this is the only fundamental limiting process, and in addition an one-diode characteristic of the p-n-junction. All other losses such as optical, thermal and resistive losses are strongly influenced by the particular cell design, material and technology and therefore not considered.

The detailed balance limit was picked up by different authors and applied to very different applications, like multi-junction cells [2,3], and TPV applications [4,5]. However the calculations are not based on the same assumptions.

A short review is given to understand the differences of the simulation procedure thereby highlighting assumptions and approximations and their influence. To verify the accuracy of the newly programmed etaOpt a comparison between calculations of different authors and etaOpt is presented. Selected examples point out the capability of etaOpt to calculate limiting efficiency for a huge variety of set-ups. In the appendix the program structure is outlined.

2. SIMULATION PROCEDURE

The efficiency for a solar cell with a particular current-voltage dependence j(V) is given by

$$h = \frac{P_{cell}/A}{P_{in}/A} = \frac{V_{mpp}\, j_{mpp}}{P_{in}/A}. \qquad (1)$$

Where P_{cell}/A is the power of the cell per area, P_{in}/A is the power of the spectral irradiance per area, V_{mpp} (j_{mpp}) is the voltage (current density) of the cell at the maximum power point (mpp). The calculation can be devided into three parts:

1) *Calculate the generation current* j_g (also known as short-circuit current j_{sc}) by integrating the spectrum.
2) *Determine the recombination current* j_r. In our case only radiative recombination is assumed.
3) *Compute the maximum power* of the cell by establishing a current voltage dependency and considering current-matching.

2.1 Model assumptions

For each single-junction in the cell following assumptions are made:

- Photons with an energy greater than the bandgap will be absorbed. Photons with smaller energies will be transmitted.
- Each absorbed photon generates k_{EQE} electrons. k_{EQE} is usually set to 100 %.
- Radiative recombination is the only loss mechanism in the junction.
- The junction behaves according to the 1-diode model.
- Carrier mobility approaches infinity, so no additional ohmic losses are present.
- In monolithic junctions current-matching is achieved by assuming semi-transparent top cells.

All other losses such as optical, thermal and resistive losses are strongly influenced by the particular cell design, material and technology. To account for these losses either semi-empirical models - which can be easily implemented into etaOpt - or rigorous modelling including all relevant physical effects are necessary.

2.2 Generation current

The generation current density j_g can be calculated by multiplying the number of incident photons N_{photon} with the number of generated electrons per photon k_{EQE} and the elementary charge q

$$j_g = k_{EQE}\, qN_{photon} \qquad (2)$$

This has to be done at all energy intervals of the spectrum I(λ)

$$j_g = k_{EQE}\frac{q}{hc}\int_0^{l_g} l\, I(l)\, dl \qquad (3)$$

where c is the speed of light, h Planck's constant, I(λ) the power density of the spectrum per wavelength, λ_g the bandgap of the junction in wavelengths ($\lambda_g = hc/E_g$) and k_{EQE} is the number of electrons generated per photon.

The integration of "λI(λ)" is well defined for analytic spectra like a blackbody spectrum. However, for tabulated spectra like AM1.5d there are two plausible methods:

1) I(λ) is a step function, recommended by ASTM [6]
2) I(λ) is a linear interpolated function, popular and obvious method
3) Linear interpolation of λI(λ) at the sampling points of I(λ), often used, "quick and dirty" method.

Method 3 can result in errors up to 10 %abs depending on the integration range and therefore is not recommended. The average difference between method 1 and 2 is 0.04 %abs but can result in up to 0.2 %abs deviation in the efficiency (e.g.: AM1.5d: 1900 – 2400 nm). EtaOpt can use either method. In this paper for comparison reasons the first method was used.

For a stack of junctions one has to consider, that each junction k only sees a part of the spectrum. Namely the short wavelength range will be cut off at the minimum bandgap λ_{min} of the above lying junctions i (numbering starts at the illuminated side). In this case we have to modify equation (3):

$$j_{g,k} = k_{EQE,k}\frac{q}{hc}\int_{l_{g,k}}^{l_{\min}} l\, I(l)\, dl,\ l_{\min} = Min\left(l_{g,i}\right) for\ i<k \qquad (4)$$

Since monolithic multi-junctions are series connected, they must have the same current. This means that the junction with the lowest current limits the whole stack. To avoid this situation current matching of each junction can be achieved by semi-transparent top cells.

To determine the highest possible current in the stack etaOpt uses a special algorithm. At the beginning the optimum current is assumed. This is equal to the current generated by a single-junction with the same spectral sensitivity as the multi-junction cell devided by the number of junctions. In a second step it is verified for each junction that the above lying junctions provide enough "spare energy" to be transfered to junctions below. In the case of not enough "spare energy" the possible current would lower the current of the whole stack.

2.3 Recombination current

As sole recombination mechanism radiative recombination is assumed. This occurs in each junction due to the radiation equilibrium of the cell with its environment. The derived expression for the recombination current j_{rad} is:

$$j_{rad} = \frac{2pq}{h^3c^2}\left(n_o^2 + n_u^2\right)\int_{E_g}^{\infty} E^2\,\frac{1}{\exp\left(\frac{E-qV}{kT}\right)-1}\,dE \qquad (5)$$

$n_{o/u}$	*Meaning*
0	No escaping rays on this surface; equal to ideal mirror
1	Interface to air; only rays within a cone $\sin\theta < 1/n_{material}$ can escape
$n_{material}$	No optical interface, no TIR, all photons can escape

Table I: Impact of the refractive index over and under the junction on the escaping rays (also see figure 1).

For a brief derivation see [7]. V is the applied voltage, n_o (n_u) is the refraction index of the medium over (under) the junction. The factor $\left(n_o^2 + n_u^2\right)$ represents the influence of total internal reflection (TIR) of the escaping rays as visualised in figure 1. Table I summarises the effect of particular values of $n_{o/u}$.

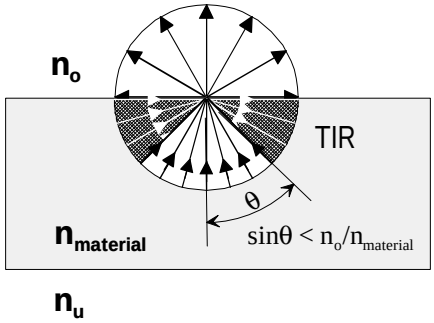

Figure 1: The sketch illustrates the escape of light in dependence of n_o and n_u. The rays in the shaded area are captured by total internal reflection (TIR).

Looking for the limit one can assume that the cell is designed with a minimum of radiative losses. This is reflected by assuming air on the one side and a mirror on the other side ($n_o = 1$, $n_u = 0$). All calculations presented in this paper were performed with this setting, unless indicated otherwise. Figure 2 shows the influence of different values for n_o and n_u. Notable is the change of optimal bandgap.

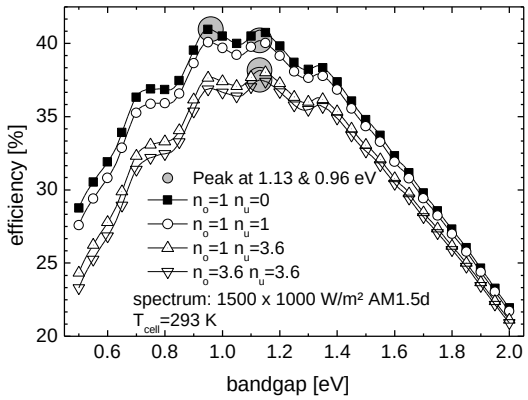

Figure 2: Influence of n_o and n_u demonstrated on a single-junction at T=293 K, 1500 x 1000 W/m² AM1.5d.

To calculate the maximum power later on, one needs an analytic solution of equation (5). The integral in equation (5) can be solved, if the "-1" in the denominator is neglected, which is equivalent to the Boltzmann approximation

$$j_{rad} = j_w\, e^{\frac{E_g - qV}{kT}}$$
$$j_w = \frac{2pq\left(n_o^2 + n_u^2\right)}{h^3c^2}kT\left[E_g^2 + 2kTE_g + 2(kT)^2\right] \qquad (6)$$

One has to keep in mind, that this approximation is only valid for $E - qV >> kT$. For a reasonable value of $qV = 0.8\,E_g$ and a temperature of around 300 K the underestimation of the integral by the approximation is less than 2 % for $E_g > 0.4$ eV.

For the term j_w of the radiative current a further approximation has been used frequently to simplify calculations [2]:

$$j_{w'} = \frac{2pq\left(n_o^2 + n_u^2\right)}{h^3 c^2} kTE_g^2 \qquad (7)$$

This leads to an overestimation of j_w of 2 – 10 % in the range 2 - 0.5 eV and 300 – 400 K. Therefore, especially at low bandgaps, high temperatures and low concentration, where the influence of j_r is strong, the results obtained with this simplification should be treated with care.

2.4 Current voltage dependence & maximum power

To determine the maximum electrical power, the one-diode equation is used.

$$j(V) = j_g\left(I(l), E_g\right) - j_0\left(e^{qV/kT} - 1\right)$$
$$j_o = j_w e^{\frac{E_g}{kT}} \qquad (8)$$

In addition etaOpt offers the possibility to add any other j(V) dependence e.g. semi-empirical functions for j_o as assumed by [8].

Building the inverse function leads to

$$V(j) = \frac{kT}{q}\log\left(\frac{j_g - j}{j_0} - 1\right). \qquad (9)$$

Since the current of each junction i of a stack k is equal, the power of the stack is

$$P_k(j_k) = j_k \sum_i V(j_{k,i}). \qquad (10)$$

One can calculate the maximum power P_{mpp} for each stack according to

$$\frac{dP_k(j_k)}{dj_k} \overset{!}{=} 0 \Rightarrow P_{mpp,k}. \qquad (11)$$

The total maximum power of the cell then is given by summing up the power of the stacks

$$P_{cell} = \sum_k P_{mpp,k}, \qquad (12)$$

hence we can calculate the cell efficiency using the starting equation (1).

3. DISCUSSION

In order to derive more realistic efficiency limits several attempts have been made in the past:

a) reducing the EQE [5]
b) using semi-empirical values for j_0 [8]

Although these attempts are comprehensible and entitled they can not lead to more realistic efficiencies. In order to predict more realistic efficiencies one has to go into the details of the particular cell design with its individual significant loss mechanisms, which might not only decrease the efficiency limit but also shift the optimal bandgap combination systematically. Therefore, values obtained by the detailed balance method for optimal bandgap combinations should not be taken as exact. They rather give ranges where the optimum should lie and above all ranges where it could not lie.

3.1 Examples from different authors

Description	*Author*	*EtaOpt*
Single-junction 1 x AM1.5d [3]	32.5 (1.13)	32.7 (1.13)
Triple-junction 46200 x AM1.5d [3]	67.0 (1.84/1.16/0.69)	67.3 (1.84/1.16/0.69)
Single-junc. for TPV blackbody @ 2500 K [4]	35.3 (0.46)	35.4 (0.45)

Table II: Efficiency limit and optimal bandgap combination η [%] (opt. E_g [eV])?for different applications compared to calculations made by etaOpt.

Table II shows efficiencies calculated by different authors for different applications and compares it to the corresponding calculation performed with etaOpt.

It is obvious that etaOpt is able to calculate very different set-ups with sufficient accuracy. The small deviations are results of numerical treatments.

3.2 Indication of all parameters

It is taken for granted that all parameters of a calculation are given. Unfortunately the detailed balance limit is very sensitive to the parameter input. For example increasing the cell temperature of a single-junction not only lowers the absolute value of the efficiency but also changes the optimum bandgap from 1.14 eV to 0.96 eV (figure 3).

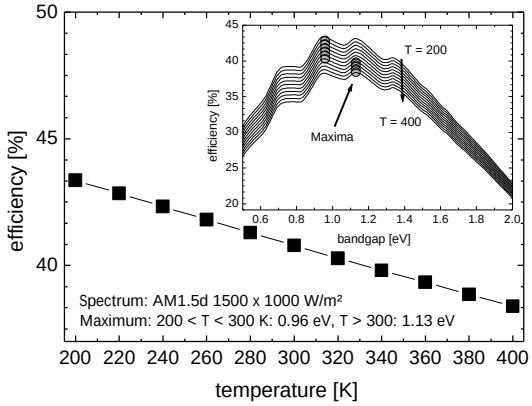

Figure 3: Temperature dependence of a single-junction under 1000 x 1500 W/m² AM1.5d. The optimum bandgap is shifted from 0.96 eV to 1.14 eV at 300 K while increasing the temperature.

A similar behavior for varying the concentration is shown in figure 4. If the power of the irradition is increased, at 1000 suns the optimum bandgap changes from 1.14 eV to 0.94 eV.

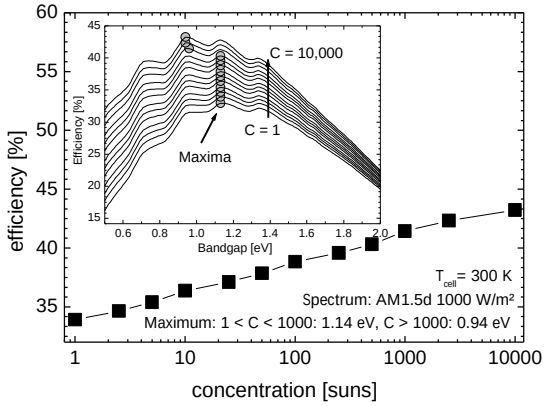

Figure 4: Concentration dependence of a single-junction with a cell temperature of 298 K under AM1.5d. The optimum bandgap changes from 1.14 eV to 0.96 eV while increasing the concentration.

4. EXAMPLES CALCULATED WITH ETAOPT

In the following some examples are given where etaOpt has been used to estimate optimal bandgap combinations for different set-ups. To obtain further details the reader is referred to the given references.

4.1 Triple-junctions

The simplest way to boost cell efficiency is to take two developed concepts, a monolithic tandem cell and a GaSb single-junction. Assuming a cell temperature of 315 K and an irradiation of 500 x 767 W/m² AM1.5d the efficiency limit can be enhanced by 10 % reaching 59 %. For further details see [9].

4.2 Quattro-junction based on GaAs and GaSb

To simplify the development of a four-junction cell it has been suggested to build a mechanical stack of two monolithic tandem cells each based on the familiar material GaAs and GaSb for top and bottom tandem respectively [10]. The optimum bandgap combination range reaching an efficiency limit of about 60 % is depicted in figure 5.

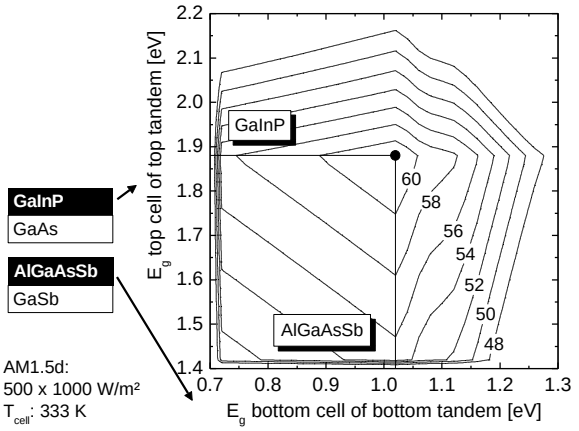

Figure 5: Example of two mechnically stacked monolithic tandem cells at T=333 K and 500 x 1000 W/m² AM1.5d calculated with etaOpt.

To optimise this approach one can adjust *both* bandgaps of the bottom tandem cell [11]. The top tandem cell is still based on GaInP/GaAs. For an irradiation of 500 x 1000 W/m² AM1.5d and a cell temperature of 333 K an optimum bandgap of 0.96 eV and 0.5 eV was found for the bottom tandem. This could increase the total cell efficiency by further 11 % reaching 71 % in total.

5. CONCLUSION

Reviewing the detailed balance method for calculating limiting efficiencies, aspects of approximations and numerical integration were emphasised.

For bandgaps smaller than 0.4 eV the approximations used for calculating the radiative current result in a significant underestimation. This is especially important at low concentrations and high temperatures.

A flexible program etaOpt has been developed to calculate limiting efficiencies for many different applications. To enable the reader to calculate the limiting efficiency of his own applications this program is available for free at
http://www.ise.fhg.de/english/fields/field2/mb5/index.html.

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6. APPENDIX - DESCRIPTION OF ETAOPT

EtaOpt is a package for Mathematica ≥ 4.0 and therefore available on almost all operating systems. It is programmed object oriented which leads to a very flexible and easy way to implement new structures. All of the above discussed approaches like the different approximations, TIR for all thinkable combinations of mechanical and monolithically stacked junctions can be realised. Figure 6 shows a simple example code for calculating a monolithic tandem stack:

```
eta = etaOpt.new[name -> "Monolithic tandem cell",
  item -> mechStack.new[item -> {
    monoStack.new[item -> {
      oneDiodeJunction.new[name -> "top",
          temperature -> 298],
      oneDiodeJunction.new[name -> "bottom",
          temperature -> 298]
     }]
  }],
  spectrum -> spectrum.new[
    name -> "AM15d/am15d.dat",
    powerOfOneSun -> 1000,
    concentration -> 100
  ],
  bandgapRange->{{1.0, 1.9, 0.02},{0.4, 1.4, 0.02}}
]

eta.calcAll[];
eta.export[subset -> {y, x}];
```

Figure 6: Example code of etaOpt for calculating a monolithic tandem cell at T=298 K under 100 x 1000 W/m² AM1.5d

The first block creates an simulation objects with the desired object and their properties like cell temperature, type of spectrum. In the second block the calculation is started and the data exported.

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