Analytical evaluation of the efficiency and open circuit voltage limit in a-Si:H based solar cells

Bas Vet and Miro Zeman

Abstract—**The open circuit voltage of hydrogenated amorphous silicon solar cells is a topic that is not fully understood. In this article we use analytical tools to derive a closed form expression for the recombination through valence band tail states. The expression is used to determine the limit of the open circuit voltage and conversion efficiency of a-Si:H solar cells. The performance limit of a-Si:H solar cells based on the recombination rate through valence band tail states amounts to $19.5\ \% \pm 0.1\ \%$. Using the analytical approach the relation between the band gap and the performance limit is determined. The performance has an optimum at a band gap of about $1.5\ eV$. The performance limit is determined for different absorption schemes. For the case where all light is absorbed independent of the absorber layer thickness, the efficiency limit decreases with the absorber layer thickness. For more realistic systems the efficiency increases with the thickness of the absorber layer but stabilizes at about $500\ nm$.**

Index Terms—**Hydrogenated Amorphous Silicon, Solar Cells, Performance Limit, Open Circuit Voltage, Simulations.**

I. Introduction

THE last 30 years a lot of research effort has been invested in developing hydrogenated amorphous silicon (a-Si:H) based solar cells. This type of second generation solar cells has a large potential to answer the global demand for cheap solar energy. Today, amorphous silicon solar cells are emerging in solar cell market, as a growing number of companies set up production lines for a-Si:H solar cells.

In order to further decrease the cost of solar electricity, research is dedicated to improving the conversion efficiency of a-Si:H solar cells. Many researchers study advanced light trapping techniques that can improve the short circuit current of the solar cells [1]. Another approach is to improve the open circuit voltage (V_{oc}) of the solar cells.

However, despite many theoretical [2], [3], experimental [4] and simulation [5], [6] studies, a firm theoretical understanding of the V_{oc} still lacks.

Our attention is focused on theoretical analysis of the V_{oc} in a-Si:H solar cells. Our opinion is that a theoretical understanding of the limits of the device performance is a prerequisite for thorough design and optimization of a-Si:H solar cells.

The works of Tiedje [2] and Lagos et Al. [3] relate the performance of a-Si:H solar cells to recombination through band tail states. They both consider the "lumped circuit" limit[1]. Tiedje uses non-equilibrium steady-state statistics [7] to derive expressions for recombination rate as a function of the electron and hole quasi-Fermi levels. These equations introduce an empirical integration constant and can be solved numerically using this constant. For the case where the recombination rate through conduction band tails is negligible, an approximate solution for the quasi-Fermi level splitting is obtained, which is used to determine the performance limit. The calculated efficiency limit amounts to $16\ \%$ [2].

Lagos et al. provide a general theoretical framework called "electron-hole kinetics", which deals with an arbitrary distribution of states within the band gap. For a material with symmetric conduction and valence band tails, they derive an equation for the current density as a function of the voltage. However, this equations can only be solved numerically, resulting in a efficiency limit of $12\ \%$ [3].

To our best knowledge, no attempt has been made to find an analytical solution for the recombination rate through band tail states as function of the splitting of the quasi-Fermi levels since Tiedje and Lagos.

In this article, we derive analytical closed form expressions of the recombination for an a-Si:H material in which the density of states within the bandgap is characterized only by an exponentially decaying valence band tail. Although this material is not representative for a-Si:H, the calculations still serve as an upper limit, since introducing the conduction band tail and defect states certainly leads to a reduction of the device performance [2]. With the expressions the 'lumped circuit' efficiency limit for a-Si:H solar cells is calculated and expressed as a function of band gap and characteristic tail width. Device simulations support the recombination rate results obtained with the expressions and the calculated values for efficiency and V_{oc}.

II. Analysis

In this article we investigate the intrinsic performance limit of solar cells based on an a-Si:H absorber layer. To that end a lumped circuit model is considered that neglects spatial dependence and allows for instantaneous extraction of generated charge carriers, see Fig. 1. The absorber layer is a semiconducting material with an exponentially decaying valence band tail.

The objective is to find a closed form expression for the band tail recombination as a function of the splitting of the quasi-Fermi levels for holes and electrons respectively.

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[1] The lumped circuit model neglects the spatial dependence and considers only uniform penetration of radiation in the device. Also the generated charge carriers are instantly available for extraction.

[2] Based on an short-circuit current of $181\ Am^{-2}$

[3] Based on an empirical short-circuit current of $150\ Am^{-2}$

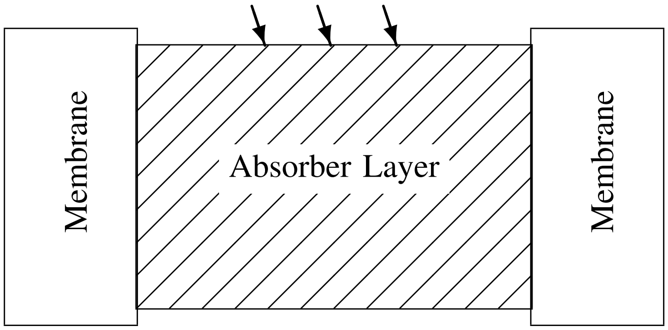

Fig. 1. The lumped circuit device: no spatial dependence is taken into account and charge carriers are instantly available for extraction

In the approach described in this article, the first step is to find an expression for the density of holes trapped in valence band tail states. From this expression the recombination rate through valence band tail states can readily be obtained. The next step is to determine the ratio of free electrons and free holes from the equation of charge neutrality. Finally, using this ratio, the recombination rate can be expressed in terms of the splitting of the quasi-Fermi levels of electrons and holes, which is related to the external voltage.

The total density of trapped holes can be expressed using the theory described by [7]:

$$p_t = \int_{E_{\mathrm{VB}}}^{E_{\mathrm{CB}}} N_D(E) f^+(E) dE \quad (1)$$

$$= \int_{E_{\mathrm{VB}}}^{E_{\mathrm{CB}}} \frac{N_D(E)(C_p^0 p + e_n^0(E))}{C_n^+ n + e_n^0(E) + C_p^0 p + e_p^+(E)} dE \quad (2)$$

Here p_t is the density of trapped holes, $N_D(E)$ denotes the energy distribution of donor-like valence band tail states, $f^+(E)$ is the occupation function of these states which is determined using the principle of detailed balance, C_p^0 and C_n^+ are the capture-rate coefficients for holes and electrons respectively and e_n^0 and e_p^+ are the emission-rate coefficients for holes and electrons respectively.

In Eq. 2 e_n^0 can safely be neglected in both the nominator and denominator [7]. Therefore, using exponentially decaying valence band tail states $N_D(E) = N_{\mathrm{D0}} e^{\frac{E_{\mathrm{VB}}-E}{E_{\mathrm{VBT}}}}$ and $e_p^+(E) = C_p^0 N_{\mathrm{VB}} e^{\frac{E_{\mathrm{VB}}-E}{kT}}$ [8], we obtain:

$$p_t = C_p^0 p \int_{E_{\mathrm{VB}}}^{E_{\mathrm{CB}}} \frac{N_{\mathrm{D0}} e^{\frac{E_{\mathrm{VB}}-E}{E_{\mathrm{VBT}}}}}{C_n^+ n + C_p^0 p + C_p^0 N_{\mathrm{VB}} e^{\frac{E_{\mathrm{VB}}-E}{kT}}} dE \quad (3)$$

here N_{D0} is the density of donor-like valence band tail states at the mobility edge, N_{VB} is the effective density of states in the valence band and E_{VBT} denotes the characteristic tail energy.

When looking at the denominator, energy regions can be distinguished. In the first region the term $C_n^+ n + C_p^0 p$ dominates and in the second region $C_p^0 N_{\mathrm{VB}} e^{\frac{E_{\mathrm{VB}}-E}{kT}}$ is dominant.

The cutoff energy (E_{cut}) that separates these regions is determined by:

$$C_p^0 N_{\mathrm{VB}} e^{\frac{E_{\mathrm{VB}}-E}{kT}} = C_n^+ n + C_p^0 p \Rightarrow$$
$$E_{\mathrm{cut}} = E_{\mathrm{VB}} - kT \ln \frac{C_n^+ n + C_p^0 p}{C_p^0 N_{\mathrm{VB}}} \quad (4)$$

Using the two regions we can now approximate (3) to:

$$p_t = C_p^0 p \int_{E_{\mathrm{VB}}}^{E_{\mathrm{cut}}} \frac{N_{\mathrm{D0}} e^{\frac{E_{\mathrm{VB}}-E}{E_{\mathrm{VBT}}}}}{C_p^0 N_{\mathrm{VB}} e^{\frac{E_{\mathrm{VB}}-E}{kT}}} dE + C_p^0 p \int_{E_{\mathrm{cut}}}^{E_{\mathrm{CB}}} \frac{N_{\mathrm{D0}} e^{\frac{E_{\mathrm{VB}}-E}{E_{\mathrm{VBT}}}}}{C_n^+ n + C_p^0 p} dE \quad (5)$$

which after some algebra results in:

$$p_t = Ap \left[\frac{C_n^+ n + C_p^0 p}{C_p^0 N_{\mathrm{VB}}} \right]^{\frac{(kT - E_{\mathrm{VBT}})}{E_{\mathrm{VBT}}}} - Ap \frac{kT}{E_{\mathrm{VBT}}} \quad (6)$$

with

$$A = \frac{C_p^0 N_{\mathrm{D0}}}{C_p^0 N_{\mathrm{VB}}} \frac{{E_{\mathrm{VBT}}}^2}{E_{\mathrm{VBT}} - kT} \quad (7)$$

As long as $E_{\mathrm{VBT}} > kT$ the last term of Eqn. 6 can be neglected. Further, the material under consideration has no conduction band tails, so that none of the electrons are trapped. Therefore the density of free electrons is much larger than the density of free holes and density of holes can be neglected in Eqn. 6. Device simulations show that in a-Si:H solar cells the density of electrons in the absorber layer of the device is generally two orders higher than the density of holes.

$$p_t = Ap \left[\frac{C_n^+ n}{C_p^0 N_{\mathrm{VB}}} \right]^{\frac{(kT - E_{\mathrm{VBT}})}{E_{\mathrm{VBT}}}} \quad (8)$$

Equation 8 gives an expression for the density of holes in the valence band tail. The recombination rate through valence band tail states is a function of the trapped holes and can now be expressed as[4]:

$$R_{\mathrm{VB}} = p_t n C_n^+ \quad (9)$$
$$= A C_n^+ p n \left[\frac{C_n^+ \frac{n}{p} p}{C_p^0 N_{\mathrm{VB}}} \right]^{\frac{(kT - E_{\mathrm{VBT}})}{E_{\mathrm{VBT}}}} \quad (10)$$

The above equation shows that the recombination rate through valence band tail states depends both on the absolute density of free electrons and holes and on the ratio of free electrons and holes. The first factor can be expressed in terms of the quasi-Fermi level splitting. The latter factor, in turn, varies as a function of the quasi-Fermi level splitting.

The quasi-Fermi level splitting is related to the external voltage, since the same quasi-Fermi level splitting can be obtained by injection of charge carriers when applying an external voltage and by generation of charge carriers by illumination.

The key to expressing the recombination rate as a function of the external voltage lies in finding the relation between the

[4] e_n^0 is negligible, as discussed earlier

ratio of electrons and holes and the external voltage. This can be done by using the equation of charge neutrality:

$$p + p_t = n + n_t \tag{11}$$

which leads to[5]:

$$\frac{n}{p} = \frac{p_t}{p} + 1 \tag{12}$$

$$= A\left[\frac{C_n^+ \frac{n}{p} p}{C_p^0 N_{\rm VB}}\right]^{\frac{(kT - E_{\rm VBT})}{E_{\rm VBT}}} + 1 \tag{13}$$

Since the number of trapped holes is several orders higher than the number of free holes the last term can be neglected.

By rewriting the expression for the external voltage and isolating the fraction $\frac{n}{p}$:

$$pn = N_{\rm VB} N_{\rm CB} e^{\frac{qV - E_g}{kT}} \tag{14}$$

$$p^2 = \frac{p}{n} N_{\rm VB} N_{\rm CB} e^{\frac{qV - E_g}{kT}} \tag{15}$$

we find:

$$\frac{n}{p} = A^{\frac{2E_{\rm VBT}}{3E_{\rm VBT} - kT}} \left[\left(\frac{C_n^+}{C_p^0}\right)^2 \frac{N_{\rm CB}}{N_{\rm VB}} e^{\frac{qV - E_g}{kT}}\right]^{\frac{kT - E_{\rm VBT}}{3E_{\rm VBT} - kT}} \tag{16}$$

Combining equations 10, 14 and 16 results in an exponential expression for the recombination as a function of the external voltage:

$$R_{\rm VB} = R_{\rm VB0} e^{\frac{qV}{E_{\rm RVB}}} \tag{17}$$

where the $R_{\rm VB0}$ is:

$$R_{\rm VB0} = \left(A e^{\frac{-E_g}{kT}}\right)^{\frac{2E_{\rm VBT}}{3E_{\rm VBT} - kT}} N_{\rm CB} N_{\rm VB} C_n^+ \times \left[\left(\frac{C_n^+}{C_p^0}\right)^2 \frac{N_{\rm CB}}{N_{\rm VB}}\right]^{\frac{kT - E_{\rm VBT}}{3E_{\rm VBT} - kT}} \tag{18}$$

and characteristic recombination energy $E_{\rm RVB}$ is:

$$E_{\rm RVB} = \frac{kT\left(3E_{\rm VBT} - kT\right)}{2E_{\rm VBT}} \tag{19}$$

III. V_{oc} AND η LIMIT

The previous section arrived at a fairly simple exponential expression for the recombination rate as a function of the external voltage. This section investigates how the expression can be applied to study the limit of the V_{oc} and η of a-Si:H solar cells. To arrive at a current-voltage characteristic the relation between generation rate (G), recombination rate (R) and external current (J_{ext}) is used:

$$J_{ext} = J_{rec} - J_{gen} = \int_0^d q\left(R - G\right) dx \tag{20}$$

where d is the thickness of the absorber layer.

To determine the generation rate, first the absorbed photon flux density is calculated by adopting the method used by Shockley and Queisser [9]. They assume a step-wise quantum efficiency, i.e. all photons with energy larger than the band gap are absorbed. Unlike Shockley and Queisser[6], we use the AM1.5 spectrum as the irradiation source. Since uniform generation is assumed, the generation rate is obtained from the absorbed part of the photon flux density by dividing by the thickness.

To investigate the accuracy of the expression for the recombination rate, simulations are carried out with the device simulation software ASA [10].

The performance limit of a lumped circuit solar cell having an a-Si:H absorber layer is evaluated using the following material parameters: the effective density of valence band and conduction band states $N_{\rm VB} = N_{\rm CB} = 1 \times 10^{26}\ m^{-3}$, the density of valence band tail states at the mobility edge $N_{D0} = 5 \times 10^{27}\ m^{-3} eV^{-1}$, the valence band tail state capture rate coefficients for holes and electrons $C_p^0 = C_n^+ = 5 \times 10^{-16}\ m^3 s^{-1}$, the characteristic valence band tail energy $E_{\rm VBT} = 4.5 \times 10^{-2}\ eV$, the mobility gap $E_g = 1.73\ eV$ and the thickness of the absorber layer $d = 300\ nm$.

The external parameters of the lumped circuit solar cell have been simulated and calculated. The short circuit current is calculated from the generation multiplied by the elementary charge and the thickness[7]. The open circuit voltage is calculated by solving the voltage from Eqn. 20 for $J_{ext} = 0$:

$$J_{ext} = 0 \Rightarrow J_{rec} = J_{gen} \tag{21}$$

The voltage and current at maximum power point, V_{mpp} and J_{mpp}, are found from the optimum of:

$$V \times J_{ext} \tag{22}$$

The fill factor is calculated from the formula:

$$FF = \frac{V_{mpp} J_{mpp}}{V_{oc} J_{sc}} \tag{23}$$

The efficiency is determined by:

$$\eta = \frac{V_{mpp} J_{mpp}}{P_{in}} \tag{24}$$

with $P_{in} = 1000\ Wm^{-2}$.

The calculated external parameters are: a short-circuit current density of $J_{sc} = 2.18 \times 10^2\ Am^{-2}$, a open-circuit voltage of $V_{oc} = 1.033\ V$, a fill factor of $FF = 0.867$ and a conversion efficiency of $\eta = 19.5\ \%$. The diode ideality factor amounts to: $n = \frac{E_{\rm RVB}}{kT} = 1.21$

The simulation resulted in the following external parameters: $J_{sc} = 2.18 \times 10^2\ Am^{-2}$, $V_{oc} = 1.038\ V$, $FF = 0.868$, $\eta = 19.6\ \%$ and the simulated ideality factor is $n = 1.21$.

Despite the numerical sensitivity [8], the results of both methods correspond accurately for this set of material parameters.

[5]While keeping in mind that n_t can be neglected, since no conduction band tail states are considered

[6]Shockley and Queisser use a black-body irradiation source at a temperature of 6000K

[7]The generation is uniform

[8]the numerical and simulated results are especially sensitive to the product of the Boltzmann constant and the temperature (the kT factor)

IV. RESULTS

The analytical results provide tools for determining the performance limit of a lumped circuit solar cell based on a material with a exponentially decaying valence band tail. Although a-Si:H solar cells does not fall in this category, the analysis can still function as a upper limit for the performance of a-Si:H solar cells.

In addition, since most recombination in the bulk of the intrinsic layer takes place through the valence band tail states [2], the mathematical results give insight in the relative influence of the material parameters on the total recombination in the bulk.

In this section the effect of changing the band gap, the characteristic tail energy and the thickness of the device on the performance limit are discussed.

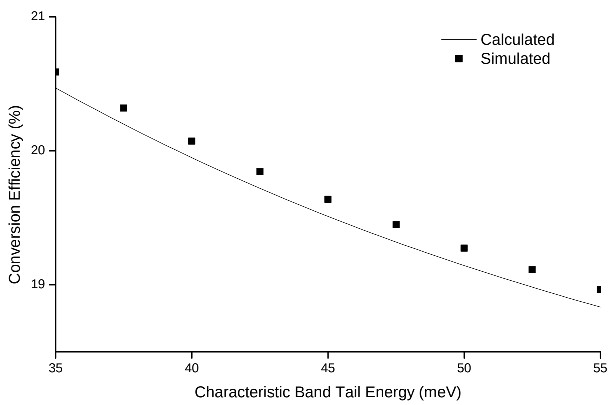

Fig. 2. The calculated and simulated plot of the conversion efficiency as a function of the characteristic valence band tail energy

Figure 2 illustrates the relation between the lumped circuit solar cell performance and the characteristic tail energy of the absorber layer. The calculated and simulated data have a mismatch of less than 1% and show the same trend, the solar cell performance decreases as the band tail becomes wider. A larger characteristic valence band tail energy stands for more band tail states, resulting in a larger total recombination rate.

Figure 3 depicts the relation between the band gap and the conversion efficiency for different values of the characteristic tail energy. The graphs show an optimum at around $E_g = 1.5\ eV$. Near the optimum the conversion efficiency limit remains high, but below $E_g = 1.4\ eV$ and above $E_g = 1.7\ eV$ the performance decreases steeply.

The optimal band gap deviates from the $1.1\ eV$ found by Shockley and Queisser. This is because for narrower band gaps the V_{oc} is restricted too much by the band tail recombination, which results in inefficient energy conversion. The calculated open circuit voltage for a band-gap of $1.1\ eV$ amounts to only $0.35\ V$, where for bulk crystalline solar cells the open circuit voltage can theoretically be as high as $0.73\ V$.

The graphs of figure 3 show that the optimal band gap does not shift much when changing the characteristic band tail energy from $0.035\ eV$ to $0.055\ eV$.

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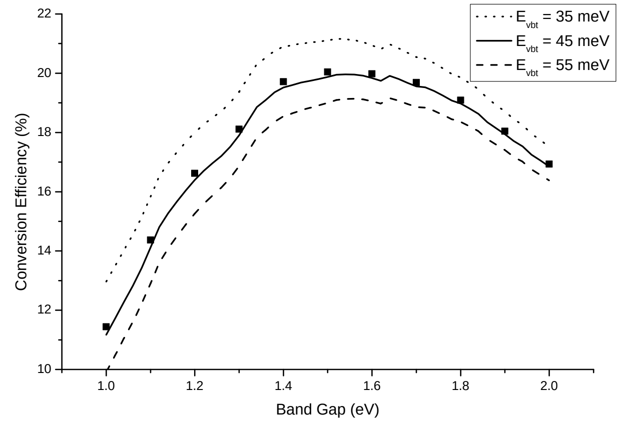

Fig. 3. The calculated (lines) and simulated (squares) plot of the conversion efficiency as a function of the band gap for different values of the characteristic valence band tail energy

V. ABSORPTION SCHEME

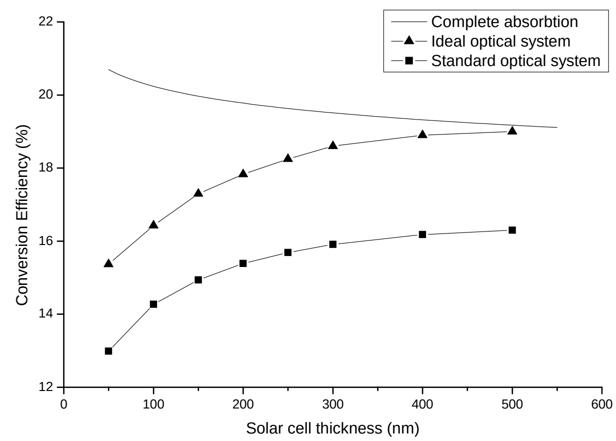

Fig. 4. The calculated conversion efficiency as a function of the thickness of the solar cell device for 3 optical systems.

In figure 4 the conversion efficiency limit is plotted against the thickness of the device[9]. Interestingly the performance shows a inverse proportional relation with the thickness. For a thickness of $50\ nm$ the conversion efficiency rises over $21\ \%$. The thin devices act as a concentrator, because all photons from the same part of the AM1.5 photon flux density are absorbed within a thinner a layer. This increases the generation rate, allowing for higher open circuit voltages.

The implication of this observation on a-Si:H solar cell design is that light designing light trapping techniques have two benefits. They enhance the absorption in the absorber layer, leading to a larger short circuit current. On top of that they allow for a reduction of the thickness of the device. Which

[9]Keeping in mind that the device retains a stepwise quantum efficiency, i.e. all the photons with energy more than the band gap are absorbed uniformly within the layer.

has the advantages of allowing a higher V_{oc}, reduction of costs and more stable solar cells.

The calculated performances depart from the assumption of a stepwise quantum efficiency. A more realistic generation rate can be obtained from optical simulations with ASA. The simulations calculated the absorption of an ideal glass - a-Si:H - back-reflector structure using measured refractive index data for the a-Si:H layer. Both the front and the back interfaces scatter the light uniformly and have a haze value of 1[10]. The back-reflector has an optimized complex refractive index of $n = 0.01 + 3.0i$, which is comparable to the refractive index of silver.

For a thickness of 300 nm the resulting short circuit current amounts to $204.4\ Am^{-2}$. Figure 4 also plots the calculated performance limit of the solar cells based on the short circuit current obtained by simulations as a function of the thickness of the device. The performance decreases for lower thickness because the optical system does not absorb all the light, resulting in a lower short-circuit current.

For a thickness larger than 500 nm the line in figure 4 of the ideal optical system converges to the line of complete absorption. This means that almost all of the incident photon flux is absorbed within the absorber layer for an ideal optical system with an absorber layer thickness of more than 500 nm

Finally an optical system has been simulated that approaches the current design of a-Si:H solar cells. This system consists of glass - TCO - p-layer at the front and n-layer-TCO-Ag-layer at the back of the absorber layer. The optical losses introduced by this system lead to a short circuit current of $178\ Am^{-2}$ for a absorber layer thickness of 300 nm. Figure 4 plots the calculated performance limit for the thickness series using this optical system.

The plot shows that the performance also stabilizes at a thickness of about 500 nm. In this case the light is also almost totally absorbed, however, a part of it is absorbed in the p-layer and the n-layer and does not contribute to the current through the device. The performance difference between this absorption scheme and the previous one is almost completely attributed to the difference in the short circuit current, although the open circuit voltage as a result is also decreased by $0.03\ V$.

VI. Conclusion

This article presents a novel analytical procedure for deriving the performance limit of a lumped circuit device based on a material with a valence band tail.

With the obtained expression the efficiency limit for a-Si:H solar cells using the lumped circuit model is calculated and it amounts to approximately 19.6 %. Simulations validate this result and show a mismatch of less than 1 % with the calculations

The analytical results are applied to investigate the effect of varying the band gap, the characteristic valence band tail energy and the device thickness on the solar cell performance limit. A decreasing trend for increasing characteristic band tail energy is found. The performance limit shows an optimum at a band gap of 1.5 eV.

The efficiency limit decreases with thickness for the assumption that all light is absorbed. For a more realistic optical system the efficiency limit increases with thickness but stabilizes at about 500 nm

[10] i.e. all incident light is scattered

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