Detailed balance model for intermediate band solar cells with photon conservation

Chien-chung Lin,* Wei-Ling Liu, and Ching-Yu Shih

Institute of Photonic Systems, College of Photonics, National Chiao-Tung University, No. 301, Gaofa 3rd Road, Gueiren District, Tainan City, 71150, Taiwan
**chienchunglin@faculty.nctu.edu.tw*

Abstract: We developed a comprehensive detailed balance model of intermediate band solar cell (IBSC). The key feature of our model is based on the conservation of photons in solar spectrum. Together with parametric analysis of carrier partition, we calculated the power conversion efficiency and found an enhancement of 1.5 times in wide band gap material IBSC (such as GaN). On the other hand, this model can also explain the inferior performance of GaAs-based IBSC through the degradation of open-circuit voltages, which can be attributed to the strong non-radiative recombination and the increased photo-generated carriers. The resulting maximum efficiency is complied with the classical Shockley-Queisser limit, and should be considered for the future IBSC design.

OCIS codes: (040.5350) Photovoltaic; (350.6050) Solar energy; (250.5590) Quantum-well, -wire and -dot devices.

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1. Introduction

The intermediate band solar cells (IBSCs) have attracted great attentions due to the possibility of exceeding the Shockley-Queisser (SQ) limit [1]. From the analysis by Luque et al. [2], the ideal efficiency can be as high as 62%. Since its introduction in 1997, there have been many efforts, including theoretical and experimental works, to explore this idea. In many cases,

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quantum dot (QD) solar cells were proposed as the possible candidate for IBSC implementation [3–5]. However, so far, the expected superior performance of IBSC has not been realized in a practical manner. In most cases, the demonstrated power conversion efficiencies were either inferior or at most equivalent to their single junction counterparts. Several explanations or modifications have been addressed: separation of quasi-Fermi level (QFL) [6], absorption between intermediate band [7], occupation rate of IB [8], and low threshold Auger generation [9] etc. Most of the analysis put emphasis on how to quantify and theorize the quasi-Fermi level separation and how to apply the drift-diffusion model of current-voltage relationship. But we think it is more intuitive to parametrically analyze the partition of the involved carriers between different energy band transitions. We can assume certain percentage of carriers for the intermediate band absorption and others are for direct band gap absorption. By this way, we can avoid the tedious work of quasi-Fermi level calculation. Another often-overlooked facts are: it takes two photons for intermediate band absorption to generate an electron hole pair [2]; and the photon flux density has to follow the general blackbody radiation rule and should be conserved. To include all these thoughts, we need to re-formulate the detailed balance model. In this work, we developed a concise, but realistic detailed balance model which should be useful for device designer and could shed some lights on the physical mechanism of IBSCs. At the end, we also apply our model and compare the degradation of open-circuit voltage (V_{oc}) of different research groups. The comparison demonstrates the validity of our model and the potential of using this model for IBSC device analysis and design.

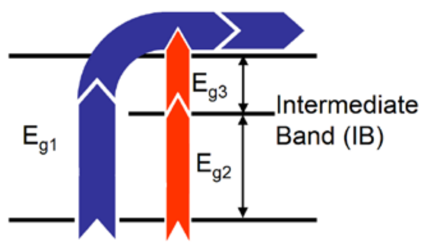

Fig. 1. Schematic diagram of an IBSC.

2. Intermediate band and photon quanta conservation

Figure 1 shows the schematic energy band diagram of an IBSC. The E_{g1} is the largest energy band gap and usually is the band gap of the host semiconductor material. E_{g2} and E_{g3} represent the separation of intermediate band to valence band and conduction band, respectively, and they can be introduced by quantum dots, superlattices, or impurities [2]. With the assumption of infinitesimal width of intermediate band, it is conceivable that $E_{g1} = E_{g2} + E_{g3}$. From Fig. 1, we can artificially assert that there are two portions of electrons/holes involved in the photovoltaic action: one is from E_{g1} transition (denoted as "direct transition"), and the other is from E_{g2} and E_{g3}, i.e. the intermediate band transition (IB). The combination of photo-generated carriers of these two transitions will flow into metal contact and become photovoltaic currents. The ratio or the partition between these two transitions (Direct vs. IB) was usually determined by quasi-Fermi level [2]. In this paper, instead of calculating possible QFL separation or contemplating if QFL should be constant along the solar cell junction, we reverse this sequence and use parametric assignment of carrier partition as the inputs. The resulting calculation is based on how many carriers involve in the direct transition and the intermediate band transition respectively. We believe this should greatly simplify the calculation meanwhile it still provides useful information for the device designers.

There is one critical point, though, not very clearly clarify in the past. It is the conservation of the total number of incident photons from the sun, which is described best in a blackbody radiation form [2] shown below:

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$$N(\varepsilon_1, \varepsilon_2, T, \mu) = \frac{2}{h^3 c^2} \int_{\varepsilon_1}^{\varepsilon_2} \frac{\varepsilon^2 d\varepsilon}{e^{(\varepsilon - \mu)/kT} - 1}, \quad (1)$$

where N is the flux of photon at any given unit time interval, ε_1 and ε_2 are the beginning and ending of photon energy, T is the temperature and μ is zero for photon distribution. In an ideal case, this photon flux N should be conserved at any time frame, and it puts an upper limit of the photon numbers that a solar cell can possibly receive. With this thought in mind, Fig. 2 illustrates the concept of our model and the comparison to the original one. The original IBSC concept [2] emphasized the enhanced absorption due to intermediate band, and each band independently owns a group of photons as shown in Fig. 2(a). In our modified model in Fig. 2(b), we consider the partition of photo-generated carriers first, and group them into different photonic transitions, in which the total combination has to be constant. If we refer to Fig. 1, the IBSC absorption can be divided into 4 different photonic energy regimes: above E_{g1}, between E_{g2} and E_{g1}, between E_{g2} and E_{g3} and below E_{g3} (we assume E_{g3} is smaller than E_{g2}). Different mini-band transitions possess their own photon populations, which correspond to carriers involved in detailed balance model, as shown in the areas of A1~A3 of Fig. 2(c). In

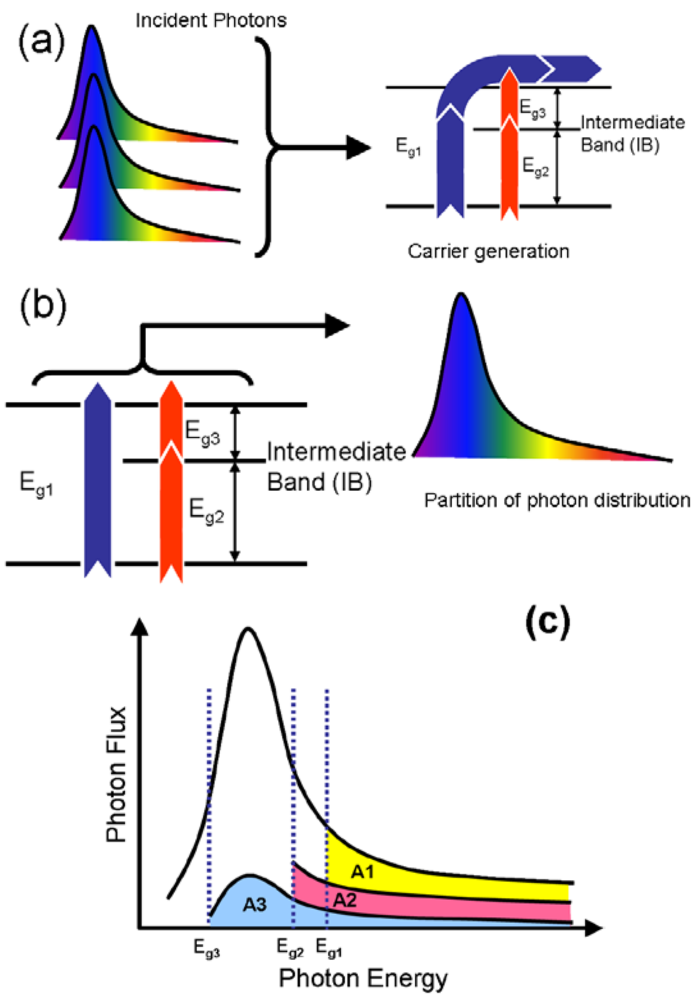

Fig. 2. Illustration of the photon-conserved detailed balance model: (a) The original concept of IBSC; (b) The concept of photo-generated carriers assignment and photon partition; (c) The concept of photon quanta conservation of blackbody radiation

our model of IBSC, each transition can be treated as if they are in the single band gap situation, and the spectral line shapes in Fig. 2(c) are determined by the original blackbody radiation and the individual band gap. Each transition in this case, is proportionally scaled down by the criteria of photon conservation addressed in the next paragraphs. Between these transitions, the total number of photons involved should follow Eq. (1), since the number of photons at certain wavelength is not infinite. Therefore, we can set up general guidelines of our model as follows:

2.1. General detailed balanced model

In the detailed balance model, the theoretical numbers of carriers for an individual energy band (or transition) is equal to the blackbody radiation photonic fluxes as in Eq. (1). The short-circuit current of a solar cell under ideal condition can then be directly related to the above expression by [1]:

$$\begin{aligned} I_{sh} &= q \times (\text{photons from the sun - photons emitted by cell}) \\ &\cong q \times (\text{\# of photons from the sun}) \\ &= A \times \int_E^{\infty} \frac{\varepsilon^2 d\varepsilon}{\exp(\varepsilon / kT_s) - 1}, \end{aligned} \tag{2}$$

where A is a constant combining electron charge, and the speed of light. The open-circuit voltage can also be calculated as [1]:

$$V_{oc} = \frac{kT_c}{q} \ln\left(f \int_{E_g}^{\infty} \frac{\varepsilon^2 d\varepsilon}{\exp(\varepsilon / kT_s) - 1} \Big/ \int_{E_g}^{\infty} \frac{\varepsilon^2 d\varepsilon}{\exp(\varepsilon / kT_c) - 1} \right), \tag{3}$$

where f is a composite constant consisting of the ratio of radiative recombination rate to overall recombination rate, subtended angle, and the absorption probability of incident photons, etc. [1]. T_c and T_s are the temperatures of solar cell and the sun, respectively.

2.2. Assignment of percentage of involved carriers

Our photon-carrier relationship is in the reverse direction compared to the original IBSC theory: we assign certain percentages of carriers to direct transition and others are for indirect (intermediate band) transition. These photo-generated carriers then can be directly one-to-one mapped into photon distributions that belong to different transitions. Different energy bands can carry their own photon distributions. For transition of E_{gi} (i = 1, 2, 3):

$$N_i(E_{gi}, \infty, T_s, 0) = C_i N(E_{gi}, \infty, T_s, 0) = \frac{2C_i}{h^3 c^2} \int_{E_{gi}}^{\infty} \frac{\varepsilon^2 d\varepsilon}{e^{\varepsilon/kT_s} - 1}, \tag{4}$$

where C_i (i = 1, 2, 3) is the corresponding portions of involved carriers for each band, and needs to be determined in our model.

2.3. Conservation of photons

Since the absorption events of a IBSC happen in such an infinitesimal time interval that the overall consumed photon population should be the same group in all three transitions, and thus it needs to be conserved. When the incident photon's energy is higher than the direct transition (E_{g1}), all of them are absorbed and the total number of photon flux has to be the same as the general blackbody radiation formula (i.e. Eq. (1)); thus the following deduction must hold:

$$\begin{aligned} &\sum_i N_i(E_{g1}, \infty, T_s, 0) = N(E_{g1}, \infty, T_s, 0) \\ &\Rightarrow \left[\sum_i C_i \right] N(E_{g1}, \infty, T_s, 0) = N(E_{g1}, \infty, T_s, 0) \Rightarrow \sum_i C_i = 1. \end{aligned} \tag{5}$$

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By comparing the two sides in Eq. (5), we find that the summation of C_i has to be one to satisfy the requirement of photon conservation at every wavelength.

2.4. Electronic isolation of IB

Since we assume the electronic isolation of IB, and we do not consider the re-emission or re-absorption issues, it is conceivable that the number of absorbed photons from valence band to IB shall equal to the number of elevated photons from IB to conduction band. So implementing this requirement, we have

$$C_2 N(E_{g2},\infty,T_s,0) = C_3 N(E_{g3},\infty,T_s,0). \quad (6)$$

This guideline is the same as the original IBSC theory [2]. From Eqs. (5) and (6), when we parametrically assign a certain numerical number (<1) to one of the C_i coefficients, and the other two can be solved accordingly.

2.5. Modified efficiency of IB transition

Finally, the introduction of IB will cause the change of the original single band gap power conversion expression. Following the same notation in Shockley and Queisser paper [1], we can write down the corresponding ultimate efficiency as:

$$u(x_g) = \left[C_1 x_{g1} \int_{x_{g1}}^{\infty} \frac{x^2 dx}{(e^x - 1)} + C_3 x_{g3} \int_{x_{g3}}^{\infty} \frac{x^2 dx}{(e^x - 1)} \right] \Big/ \int_0^{\infty} \frac{x^3 dx}{(e^x - 1)}. \quad (7)$$

Similar to previous single gap version, x_{gi} (i = 1, 2, 3) represents the different normalized energy transition in the IBSC, and it equals E_{gi}/kT_s (i = 1, 2, 3), T_s is the temperature of the sun . Once these five guidelines are set, it is possible for us to solve C_i, and calculate the PCE and open-circuit voltages under the constant photon flux assumption.

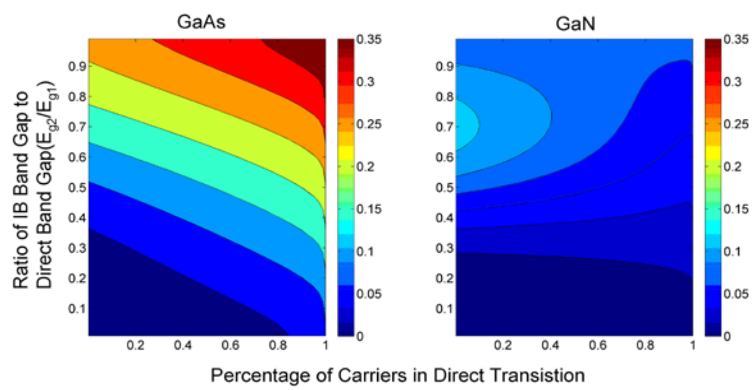

Fig. 3. The PCE of GaAs and GaN system, using partition of carriers and IB band gap size as variables. The highest x axis value is 1, which means 100%.

3. Results and discussion

We first start with the popular material systems. Figure 3 shows the PCE of GaAs and GaN IBSC with percentage of direct transition carriers and normalized IB band gaps (divided by host material's E_g) as two parameters. We can observe that IBSC design is not favorable in GaAs system, since the maximum efficiency happens at direct transition point. However, in the GaN system, the enhancement of IB is much more pronounced. The single band gap ultimate efficiency is 8.4%, but the introduction of intermediate band can boost the efficiency to 12.7%, which equals an increase of 1.5 times.

If we look into GaAs material system more closely, the calculation results in Fig. 3 agree with most of the experimental cases: the IBSC is worse than the single gap device. To probe further, we can analyze the device I-V characteristics. From published data, the change in V_{oc} is usually responsible for the degradation of the PCE [3–5,10–12]. Using Eq. (3), we can approximately calculate the possible V_{oc} in the proposed detailed balance model if ideal diode operation is assumed. The published works with EQE and V_{oc} can be used for comparison to our model. The EQE is generally the quantum yield of generated electrons vs. incident photons. So the area underneath the EQE curves multiplied by the solar spectral photon flux density can be regarded as the number of carrier actually involved in the energy transition. Similar argument has been explored in [11].

Figure 4 shows our calculation against the measured V_{oc} of GaAs based quantum dot solar cells [5,11,12]. The percentages of carriers for E_{g1} transition can be obtained by comparing reference EQE to that of a QD device. By varying the f factor, we can see that the V_{oc} data can be closely fitted to certain values of the f factor. Also the data points from the same group can be fitted with the same f factor (except for one data point, whose device performance is deteriorated due to emitter layer degradation [11]). Since the f factor is a conglomerate of several coefficients [1], which differs from device to device, we can only conclude that it did distinguish between different groups. The main reason of V_{oc} degradation can be the strong non-radiative recombination which often happens in quantum dot structures and thus lower the f factor significantly through the inclusion of the ratio between radiative and non-radiative recombination coefficients in its own definition. The other important factor we would like to point out is that the V_{oc} degradation is unavoidable even from the most ideal detailed balance model with ideal diode characteristics [1]. The reason resides in Eq. (3), when the amount of available photo-generated carriers increases due to intermediate band absorption, the ratio of the integrals within the natural logarithm mathematically will drop. The resulting V_{oc}/V_g will decrease accordingly.

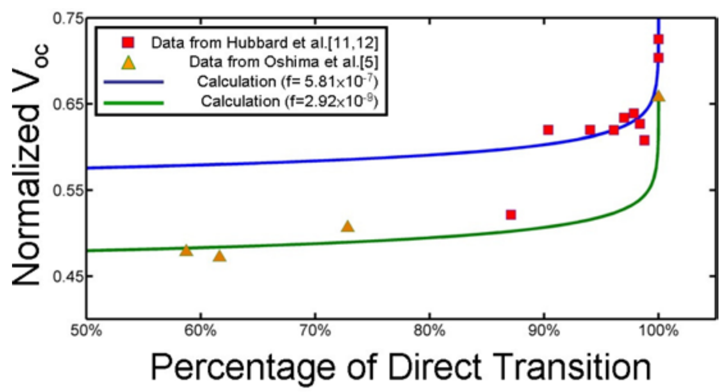

Fig. 4. Normalized V_{oc} versus percentage of direct transition through E_{g1}, and the data points are from [5,11,12]. Calculation based on our model can be fitted well with different values of factor f.

This model can provide a good, but not precise estimate of the IBSC problem, since we did not consider other important factors in this model, such as voltage-dependent non-radiative recombination, re-emission and re-absorption between transitions, the non-standard ideality factor, saturation of quantum dots, etc. However, the trend is clear and the degradation of V_{oc} can be improved by regulating the above-mentioned factors.

4. Conclusion

We developed a concise model with photon conservation criteria. The calculation revealed the enhancement of IB can be strong with wide band gap material such as GaN, and limited in smaller band gap material like GaAs. Meanwhile, it is also illustrative to use this model to calculate the degradation of open-circuit voltage, which can be a good tool to further improve the performance of IBSCs.

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