

# Efficiency enhancement of ideal photovoltaic solar cells by photonic excitations in multi-intermediate band structures

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We present an efficiency analysis of ideal photovoltaic solar cells based on multi-intermediate band structures. It is shown that the difference between the thermodynamic limit of photovoltaic conversion and the limit of efficiency of traditional bulk semiconductor solar cells can be gradually bridged if an optimum energy band structure is achieved. Efficiency enhancement originates from photonic excitations among multiple energy bands. Several possible ways to design the optimum energy band structures are proposed. © 2003 American Institute of Physics.

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The theoretical efficiency of ideal solar cells can be determined by a detailed balance approach based on the Shockley and Queisser (SQ) model.<sup>1</sup> The standard semiconductor *p-n* junction has a sunlight-to-electricity efficiency limit of about 33%,<sup>2</sup> while the thermodynamic limit is as high as 93%.<sup>3</sup> Several attempts using low-dimensional systems have been made to improve solar cell performance.<sup>4</sup> “Stacked” or tandem cells can improve the limiting efficiency to 66%<sup>5</sup> by using more than one cell to reduce energy loss. The multiple quantum well (MQW) solar cell, proposed by Barnham and Duggan,<sup>6</sup> is an alternative approach to achieving high photovoltaic conversion efficiency. The efficiency of solar cells can also be increased by introducing impurities.<sup>7</sup> This has motivated a theoretical model that considers the impurity energy level as intermediate within the semiconductor gap.<sup>8</sup> The limit of ideal efficiency in this system is predicted to be 63.1%. The enhancement in efficiency originates from a photon-induced transition at the intermediate level.

In this letter we consider the following questions: If the intermediate level is extended to a number of energy bands, what will happen due to excitation among the multiple band structure; and is it possible to design an optimum energy band structure to obtain a higher limit of efficiency? The efficiency of ideal solar cells with a multi-intermediate band structure (MIBS) will be analyzed based on the SQ model. It is shown that the efficiency is enhanced due to excitations among bands, which absorb additional lower energy photons. Optimum structures can be achieved in a number of ways.

The model solar cell here contains a negative-contact band (NB), a positive-contact band (PB), and the intermediate structure including *k* bands (*k* = 1, 2, 3, ...) (shown in Fig. 1). Each energy band except the PB has the lowest energy of  $\epsilon_i$  (*i* = 1, 2, ..., *k*, *k* + 1). Here, zero energy is set at the highest energy of the PB, labeled *i* = 0, i.e.,  $\epsilon_0 = 0$ . The NB can also

be considered a band, labeled *i* = *k* + 1 and  $\epsilon_{k+1} = \epsilon_G$ . According to the SQ model,<sup>1</sup> the photon-induced electrical current originates from the difference between the rates of photon absorption and the photon emission due to radiative recombination. In efficiency-limiting analysis of photovoltaic conversion, several ideal conditions similar to those in the intermediate-level model<sup>8</sup> are assumed: (1) All incident photons with energy equal to or greater than the band gap are absorbed, and they generate exactly one electron-hole pair. Photons with energy lower than the band gap are not absorbed. (2) The recombination of one electron and one hole will produce exactly one photon. Only interband radiative transitions are considered. Nonradiative transitions between any two bands are forbidden. In practice the problem of impurity photovoltaic solar cell or intermediate band semiconductor is the nonradiative recombination. (3) Carrier mobilities are infinite. Therefore the quasi-Fermi levels (QFLs) throughout the whole cell are constant. The *k* + 2 separated QFLs are assumed as  $\epsilon_{F_i}$  (*i* = 0, 1, ..., *k*, *k* + 1). The separation between the two QFLs is  $\mu_{i,j} = \epsilon_{F_j} - \epsilon_{F_i}$  (*i* < *j*). (4) Only electrons, not holes, can be extracted from the NB

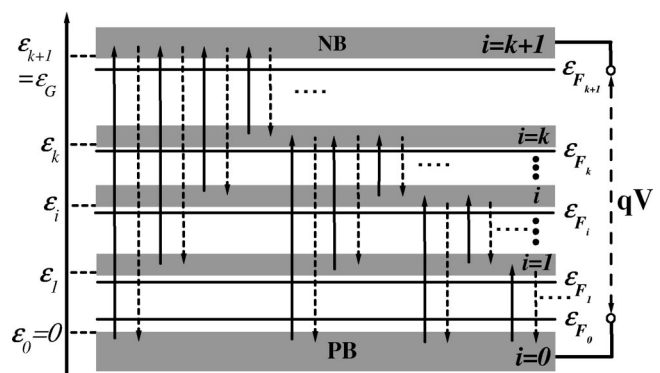


FIG. 1. Schematic of radiation transitions in the model solar cell with intermediate multiband structure.

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to form the external current. Furthermore, only holes, not electrons, can be extracted from the PB. No carrier can be extracted from the intermediate band structure. The light generated carriers are collected with 100% efficiency. (5) The radiation generated only escapes by the front area of illumination. No optical loss is assumed. (6) In order to use the solar energy monotonically, it is necessary to define a series of reasonable ranges of energy. Here we assume  $\epsilon_i < \epsilon_{i,i+1} < \epsilon_{i+1}$ , where  $\epsilon_{i,i+1} = \epsilon_{i+1} - \epsilon_i$ . For each energy range, only one absorption length is important. (7) The incident and emitted radiation is a blackbody and is isotropic, thus assuming the maximum concentration possible.

In thermodynamic equilibrium the absorption or emission of photons obeys the following distribution<sup>9</sup>

$$R(\epsilon_{\min}, \epsilon_{\max}, T, \mu) = \frac{2\pi}{h^3 c^2} \int_{\epsilon_{\min}}^{\epsilon_{\max}} \frac{\epsilon^2 d\epsilon}{e^{(\epsilon - \mu)/k_B T} - 1}, \quad (1)$$

where  $R$  is the absorption rate or the radiative emission rate for photons with energy above  $\epsilon_{\min}$ ;  $\epsilon_{\min}$  and  $\epsilon_{\max}$  are the photonic energies,  $\mu$  is the local chemical potential or QFL separation in the semiconductor,  $T$  is the temperature of the sun ( $T_s$ ) or a crystalline system ( $T_a$ ),  $k_B$  is the Boltzmann constant,  $c$  is the speed of light, and  $h$  is the Planck constant. The absorbed photons generate electron-hole pairs, whereas radiative recombination annihilates electron-hole pairs. The balance of electrons gives the current, which is delivered to the external load by the positive and negative contacts. Now we consider the current output in the multiband model solar cell. Looking at the negative-contact band [corresponding to the  $(k+1)$ th band], we have

$$I/q = [R(\epsilon_G, \infty, T_s, 0) - R(\epsilon_G, \infty, T_a, \mu_{o,k+1})] + \sum_{i=1}^{k(k \geq i)} [R(\epsilon_{i,k+1}, \epsilon_{i-1,k+1}, T_s, 0) - R(\epsilon_{i,k+1}, \epsilon_{i-1,k+1}, T_a, \mu_{i,k+1})], \quad (2)$$

where  $q$  is the charge of electrons,  $\epsilon_{i,j} = \epsilon_j - \epsilon_i$  ( $i < j$ ), and  $\mu_{i,j} = \epsilon_{Fj} - \epsilon_{Fi}$  ( $i < j$ ). Because no current is extracted from any intermediate band, for example, the  $i$ th band ( $i = 1, 2, 3, \dots, k$ ), we have

$$[R(\epsilon_i, \epsilon_{i,i+1}, T_s, 0) - R(\epsilon_i, \epsilon_{i,i+1}, T_a, \mu_{0,i})] + \sum_{j=1}^{i-1(i > 1)} [R(\epsilon_{j,i}, \epsilon_{j-1,i}, T_s, 0) - R(\epsilon_{j,i}, \epsilon_{j-1,i}, T_a, \mu_{j,i})] + \sum_{j=i+1}^{k+1} [R(\epsilon_{i,j}, \epsilon_{i-1,j}, T_a, \mu_{i,j}) - R(\epsilon_{i,j}, \epsilon_{i-1,j}, T_s, 0)] = 0. \quad (3)$$

For a given external voltage  $V$ , we have the QFL separation that satisfies

$$qV = \mu_{0,k+1} = \mu_{0,i} + \mu_{i,k+1}, \quad (4)$$

$$\mu_{i,j} = \mu_{i,k} + \mu_{k,j} \quad (i < k < j).$$

Therefore, the efficiency of the cell is given by

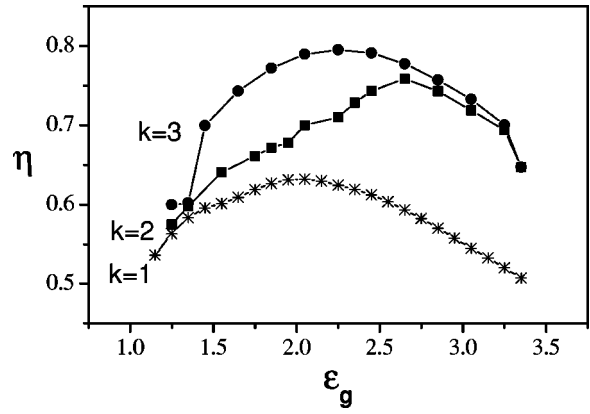


FIG. 2. Limiting efficiency for the solar cell with three different intermediate multiple band structures ( $k=1,2,3$ ) as a function of the band gap between the negative-contact and positive-contact bands  $\epsilon_G$ . The lines are a guide to the eye.

$$\eta = \frac{VI}{\sigma T_s^4}, \quad (5)$$

where  $P = \sigma T_s^4$  is the incident power and  $\sigma$  is the Stefan-Boltzmann constant. The efficiency limit can be obtained by finding the highest value of  $\eta$  at arbitrary combinations of  $\epsilon_G$  and  $\epsilon_i$  ( $i = 1, 2, \dots, k$ ) when the separation of QFLs satisfies Eqs. (3) and (4).

Different intermediate band structures give different efficiency limits. Figure 2 presents the limiting efficiency as the band gap between NB and PB ( $\epsilon_G$ ) is varied in three different intermediate band structures. Three aspects at least are very interesting. (1) The limit of efficiency has increased. It can also be seen from Table I that, if there is one intermediate band ( $k = 1$ ), the efficiency limit is 63%, i.e., the same as in Ref. 8. If there are two intermediate bands the limit efficiency increases to around 76%. If there are three intermediate bands, it increases further to 80%. It is likely that the efficiency limit approaches the thermodynamic limit if the optimum band structure can be achieved. Improvement of the efficiency limit comes from absorption of the additional lower energy photons [see Eq. (2)], which stimulates the excitation between bands in the multiband structure. (2) The same efficiency limit can be obtained in the cells with lower band gap  $\epsilon_G$  if we increase the number of levels in the MIBS. For example, Table I also gives the three band structures ( $k = 1, 2, 3$ ), which have an efficiency limit of around  $\eta \approx 65\%$ . (3) With band gap  $\epsilon_G$  fixed, as the number of bands in the intermediate structure increases, the efficiency limit

TABLE I. Efficiency limit  $\eta$  in several different band structures.  $k$  is the band number in the intermediate energy-band structure,  $\epsilon_G$  is the gap between the negative-contact and positive-contact bands,  $\epsilon_i$  ( $i = 1, 2, 3$ ) is the lowest energy of each intermediate band (shown in Fig. 1).

$k$	$\eta$ (%)	$\epsilon_G$ (eV)	$\epsilon_1$ (eV)	$\epsilon_2$ (eV)	$\epsilon_3$ (eV)
1	63	1.95	0.70	...	...
2	76	2.65	0.25	1.30	...
3	80	2.25	0.18	0.50	1.10
2	64	1.55	0.15	0.60	...
3	69	1.45	0.12	0.25	0.70

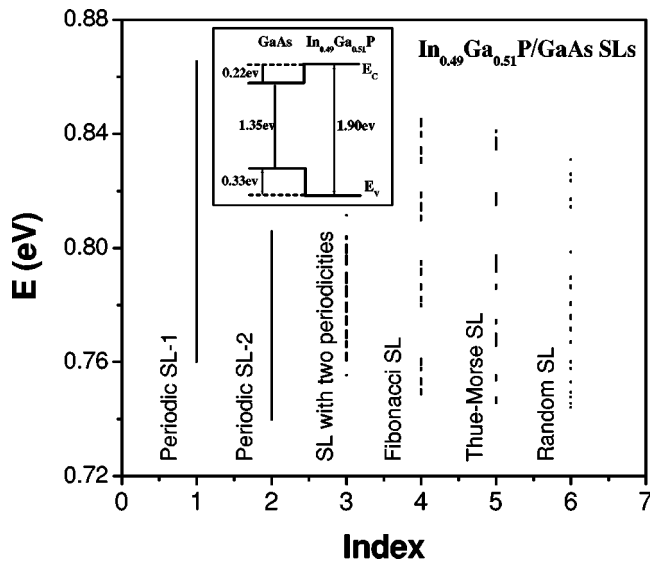


FIG. 3. Electronic miniband structures for the several periodic and aperiodic  $\text{In}_{0.49}\text{Ga}_{0.51}\text{P}/\text{GaAs}$  superlattices below the barrier. The origin of the energies is set at the center of the gap of well material GaAs. The index equal to 1–6 stands for the following structure: 1—periodic SL with  $N=21$ ,  $a=b=2.5$  nm; 2—periodic SL with  $N=21$ ,  $a=b=3.5$  nm; 3—SL with two parts: the first part with  $N=10$ ,  $a=b=2.5$  nm, and the second part with  $N=11$ ,  $a=b=3.5$  nm; 4—Fibonacci SL:  $N=21$ ,  $a=2.5$  nm,  $b=3.5$  nm; 5—Thue–Morse SL:  $N=16$ ,  $a=2.5$  nm,  $b=3.5$  nm; 6—one kind of random SL with  $N=21$ ,  $a=2.5$  nm,  $b=3.5$  nm, where  $N$  is the total number of layers,  $a$  and  $b$  are two thicknesses of the wells ( $a$  for block A and  $b$  for block B), and the thickness of each barrier of all SLs is the same as  $d=2.0$  nm. The inset is a schematic of the band-edge diagram of the  $\text{In}_{0.49}\text{Ga}_{0.51}\text{P}/\text{GaAs}$  interface (at room temperature).

definitely increases. For example, if  $\epsilon_G=1.85$  eV, the efficiency limit  $\eta\approx 62\%$  in a one-band MIBS,  $\eta\approx 67\%$  in a two-band MIBS, and  $\eta\approx 77\%$  in a three-band MIBS. It seems the gap between the limit of efficiency within the thermodynamic limit and that of the traditional single band gap solar cell can gradually be filled by this method. This property may make it possible to achieve a low-dimensional high-performance solar cell by designing an optimum band structure.

Now we consider the inverse problem of the energy band structure. There are certain features of these structures: the bands should be well separated by different values, and the spacing of bands should be nonuniform. Interestingly, aperiodic semiconductor superlattices or aperiodic semiconductor/insulator superlattices are suitable for this kind of solar cell because they produce these energy band structures. In the last decade, the notion of aperiodic order not only has stimulated much attention especially in one-dimensional (1D) systems,<sup>10,11</sup> but also has contributed potential technological applications.<sup>12</sup> A typical example in a 1D quasiperiodic system is a Fibonacci sequence, which can be obtained by repeated application of substitution rules  $A\rightarrow AB$  and  $B\rightarrow A$ . It has been proved that the energy spectrum of the Fibonacci chain is a singular continuous Cantor set.<sup>13</sup> Here we define the building block A, B as follows: each building block has the same barrier thickness ( $d$ ), but the thickness of the well is different ( $a$  for block A and  $b$  for block B). Then accord-

ing to the sequence chosen, arrange A and B to get an aperiodic superlattice. The theoretical electronic structure of aperiodic semiconductor superlattices can be obtained by using a two-band model based on a Dirac-like equation<sup>14,15</sup> and the transfer-matrix method.<sup>15</sup>

Figure 3 presents the allowed electronic subminibands below the barrier in several  $\text{In}_{0.49}\text{Ga}_{0.51}\text{P}/\text{GaAs}$  superlattices. The  $\text{In}_{0.49}\text{Ga}_{0.51}\text{P}/\text{GaAs}$  superlattice (SL) is chosen just as an example, since it is lattice matched.<sup>16</sup> The continuous miniband in the periodic superlattice has been split nonuniformly by the aperiodic order, like as in the Thue–Morse case (an intermediate case between periodicity and quasiperiodicity),<sup>17</sup> in the Fibonacci case (a quasiperiodic system), and even in the random case. That is to say, more gaps occur in the band structure, which originate from the loss of long-range quantum coherence of the electrons. The spacing of minibands of the superlattice depends on the material, the structural configuration and the thickness of the well and barrier layers.

In summary, based on the SQ model, the limit of efficiency of an ideal solar cell with multi-intermediate band structure was analyzed. The excitation model with multi-intermediate band structure reduces the design of a low-dimensional high-performance solar cell to the requirement for electronic band gap engineering. This approach could also be useful in other areas such as optoelectronics.

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