Detailed balance limit efficiency of silicon intermediate band solar cells*

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The detailed balance method is used to study the potential of the intermediate band solar cell (IBSC), which can improve the efficiency of the Si-based solar cell with a bandgap between 1.1 eV to 1.7 eV. It shows that a crystalline silicon solar cell with an intermediate band located at 0.36 eV below the conduction band or above the valence band can reach a limiting efficiency of 54% at the maximum light concentration, improving greatly than 40.7% of the Shockley–Queisser limit for the single junction Si solar cell. The simulation also shows that the limiting efficiency of the silicon-based solar cell increases as the bandgap increases from 1.1 eV to 1.7 eV, and the amorphous Si solar cell with a bandgap of 1.7 eV exhibits a radiative limiting efficiency of 62.47%, having a better potential.

Keywords: intermediate band, silicon solar cell, concentrated light, detailed balance principle

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1. Introduction

The silicon solar cell, the most commonly used solar cell, can now reach a world-record efficiency of 25% (monocrystalline silicon, in one sun condition).[1] Different novel concepts and structures, such as hot-electron[2] and nanostructured[3] solar cells, have been proposed to pursue higher efficiency. Among them, the intermediate bandgap solar cell (IBSC),[4−7] in which an intermediate band (IB) is placed in the traditional forbidden bandgap, can extend the absorption spectrum and then increase the current without a decrease of the output voltage. The pioneering IBSC model was established by Luque in 1997[4] and was also studied by Green in 2001.[5] The IBSC theory proposed by Luque shows a maximum efficiency of 63.2%[4] for a cell of gap 1.95 eV with the IB level located at 0.71 eV below the conduction band (CB) or above the valence band (VB) according to the detailed balance principle. Recently, Luque has evaluated the efficiency potential of an IBSC based on thin-film chalcopyrite materials,[6] and Ley[7] has studied the thermodynamic efficiency of an IBSC with low threshold Auger generation. However, the potential limiting efficiency of the silicon-based intermediate solar cell, which has the advantages of cheap cost and a mature production level,[8,9] has been seldom systematically studied. In this paper, the ideal limiting efficiency of a silicon-based solar cell with a bandgap between 1.12 eV and 1.7 eV is calculated using the detailed balance principle[10] and neglecting the contribution of nonradiative recombination.

2. Model and calculation

Figure 1 shows the band diagram of the IBSC. As the figure shows, an intermediate energy band usually formed by several means (diluted alloy, quantum dot superlattices, impurities, etc,[11−14]) is placed in the forbidden bandgap of a conventional two-band solar cell material, which can introduce additional absorption of lower-energy infrared photons. The common absorption of photons by the electron transitions between the valence and the conduction bands still exists, which corresponds to the $G_{\rm cv}$ process in Fig. 1. Moreover, two other absorption mechanisms, the absorptions with transitions between the valence and the intermediate bands (process $G_{\rm vi}$) and between the intermediate and the conduction bands (process $G_{\rm ic}$), also take place. As a result, the IBSC can absorb more

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photons and thus the conversion efficiency increases.

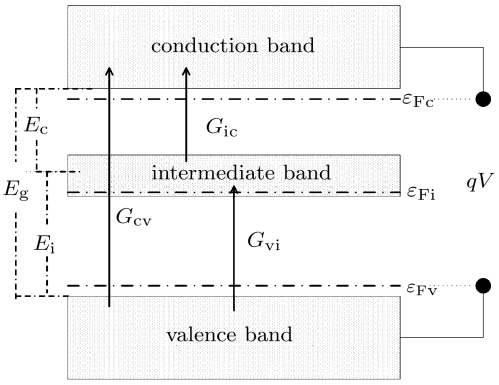


Fig. 1. Band diagram of a solar cell with an intermediate band.

Different models have been used to calculate the efficiency of solar cells.[4,14–17] The Shockley and Queisser (SQ) model,[10] which is based on the detailed balance principle, is considered to be the most reasonable and useful model dealing with the energy conversion process of the solar cells. So in our calculations, the SQ model is adopted to obtain the ideal efficiency of the ISBC.

In our work, the following assumptions are used. The notations are illustrated in Fig. 1.

i) We assume that $E_{\rm i}$ is the second largest bandgap, so that $E_{\rm g} > E_{\rm i} > E_{\rm c}$.

ii) The cell is thick enough to assure the full absorption of all possible photons.

iii) The nonradiative transitions between any two of the three bands are forbidden, so only direct recombination mechanisms exist in the process.

iv) The carrier mobility is infinite and the Ohmic contact resistance is negligible, so that all electrical energy can be exported to the external terminal.

v) The absorption by the transition between any two of the three energy bands has its priority dependent on the photon energy, i.e., photons with energy $E > E_{\rm g}$ can only be absorbed by the $G_{\rm cv}$ process corresponding to the biggest band gap $E_{\rm g}$, while photons with energy $E_{\rm g} > E > E_{\rm i}$ can only be absorbed by the $G_{\rm vi}$ process corresponding to bandgap $E_{\rm i}$, and photons with energy $E_{\rm i} > E > E_{\rm c}$ can only be absorbed by the $G_{\rm ic}$ process corresponding to bandgap $E_{\rm c}$.

vi) The intermediate band does not contribute to the electrical current, so no carrier can be extracted from the intermediate band. In addition the current is related to the splitting of the quasi-Fermi levels ($\varepsilon_{\rm Fc}$, $\varepsilon_{\rm Fi}$ and $\varepsilon_{\rm Fv}$) shown in Fig. 1 and consequently to the cell voltage.

vii) The sun is a blackbody at a temperature of $T_{\rm s} = 6000$ K, while the cell is a blackbody at a temperature of $T_{\rm c} = 300$ K. The environment is at the temperature of $T_{\rm a} = T_{\rm c} = 300$ K.

According to the assumptions above, the energy exchange between the solar cell and the sun can be obtained. As we know, the sun and the solar cell form an equilibrium system. Thus, the absorption energy by the cell from the sun is equal to the radiative energy from the cell to the sun due to the detailed balance principle.

We define $N(E_1, E_2, T, \mu)$ as the flux of photons leaving an object of temperature T,

$$N(E_1, E_2, T, \mu) = \frac{2}{h^3c^2}\int_{E_1}^{E_2} E^2 \Big/ \left[\exp\left(\frac{E-\mu}{k_BT}\right) - 1\right] {\rm d}E, \quad (1)$$

where μ is the chemical potential, $k_{\rm B}$ is the Boltzmann constant, h is the Planck constant and c is the speed of light. Then the output current of a simple two-energy-band solar cell can be described by

$$\begin{aligned} I_{\rm out} &= q \cdot A \cdot \{[F_{\rm s} \cdot N(E_{\rm l}, E_{\rm h}, 0, T_{\rm s}) \\ &\quad - F_{\rm s} \cdot N(E_{\rm l}, E_{\rm h}, 0, T_{\rm a})] - [F_{\rm c} \cdot N(E_{\rm l}, E_{\rm h}, \mu, T_{\rm c}) \\ &\quad - F_{\rm c} \cdot N(E_{\rm l}, E_{\rm h}, 0, T_{\rm a})]\} \\ &= q \cdot A \cdot [F_{\rm s} \cdot N(E_{\rm l}, E_{\rm h}, 0, T_{\rm s}) \\ &\quad + (F_{\rm c} - F_{\rm s}) \cdot N(E_{\rm l}, E_{\rm h}, 0, T_{\rm c}) \\ &\quad - F_{\rm c} \cdot N(E_{\rm l}, E_{\rm h}, \mu, T_{\rm c})], \end{aligned} \quad (2)$$

where q is the charge of an electron and F is a geometrical factor that depends on the solid angle subtended by the radiative object and the angle of the incidence at the receiving object.[10] In reality, F is giving by $F = F_{\rm s} = 2.18 \times 10^{-5}$ under the one sun condition and $F = \pi$ if we use an ideal concentrator (46050 suns). If we consider the cell as a radiative object, then the geometrical factor F is given by $F = F_{\rm c} = \pi$. The $E_{\rm l}$ is the lower photon energy and $E_{\rm h}$ is the higher photon energy. The A is the area of the cell and in our work A is equal to 1 m^2. The $F_{\rm s} \cdot N(E_{\rm l}, E_{\rm h}, 0, T_{\rm s}) - F_{\rm s} \cdot N(E_{\rm l}, E_{\rm h}, 0, T_{\rm a})$ is the net inflow photon density due to the absorption, while $F_{\rm c} \cdot N(E_{\rm l}, E_{\rm h}, \mu, T_{\rm c}) - F_{\rm c} \cdot N(E_{\rm l}, E_{\rm h}, 0, T_{\rm a})$ is the net outflow photon density due to the radiation.

Let us consider the ideal focusing situation, in which an ideal concentrator is used. Then $F_{\rm c} = F_{\rm s} = \pi$ and the output current of the IBSC can be rewritten as

$$I_{\rm out} = q \cdot A \cdot F_{\rm s} \cdot [N(E_{\rm g}, +\infty, 0, T_{\rm s})$$

$$- N(E_{\rm g}, +\infty, \mu_{\rm cv}, T_{\rm c})] + [N(E_{\rm i}, E_{\rm g}, 0, T_{\rm s}) - N(E_{\rm i}, E_{\rm g}, \mu_{\rm vi}, T_{\rm c})], \quad (3)$$

where $\mu_{\rm cv}$, $\mu_{\rm vi}$ and $\mu_{\rm ic}$ are the differences of the quasi-Fermi level given by

$$\mu_{\rm cv} = \varepsilon_{\rm Fc} - \varepsilon_{\rm Fv}, \quad (4a)$$

$$\mu_{\rm vi} = \varepsilon_{\rm Fi} - \varepsilon_{\rm Fv}, \quad (4b)$$

$$\mu_{\rm ic} = \varepsilon_{\rm Fc} - \varepsilon_{\rm Fi}, \quad (4c)$$

$$\mu_{\rm vi} + \mu_{\rm ic} = \mu_{\rm cv}. \quad (4d)$$

The model is similar to the one used by Luque to calculate the best efficiency of an ideal IBSC with an ideal concentrator.[4] We also have

$$q \cdot V = \mu_{\rm cv}, \quad (4e)$$

where V is the output voltage.

In consideration of assumption vi), no current can be extracted from the intermediate band, we have

$$N(E_{\rm i}, E_{\rm g}, 0, T_{\rm s}) - N(E_{\rm i}, E_{\rm g}, \mu_{\rm vi}, T_{\rm c}) = N(E_{\rm c}, E_{\rm i}, 0, T_{\rm s}) - N(E_{\rm c}, E_{\rm i}, \mu_{\rm ic}, T_{\rm c}). \quad (5)$$

Then the efficiency can be described as

$$\eta = \frac{VI}{\text{sun power}} = \frac{VI}{F_{\rm s}\sigma T^4}, \quad (6)$$

where σ is the Stefan–Boltzmann constant and equals $5.67 \times 10^{-8}\ \mathrm{W \cdot m^{-2} \cdot k^{-4}}$.

3. Results and discussion

Solving the equations above, the highest efficiency of the crystalline silicon intermediate solar cell is obtained when $E_{\rm i} = 0.76$ eV. Figure 2 plots the limiting efficiency of the crystalline silicon IBSC as a function of the position of the IB.

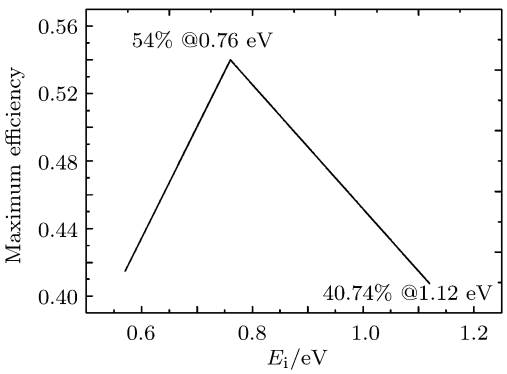


Fig. 2. Efficiency limit of a crystalline silicon IBSC as a function of the position of the intermediate energy level.

The efficiency limit reaches a maximum of 54% at $E_{\rm i} = 0.76$ eV, which is much higher than the efficiency of a single-junction-crystalline Si solar cell at the maximum light concentration. It shows great potential to increase the energy conversion efficiency. The curve shows good linear dependence when $E_{\rm i} < 0.76$ eV and $E_{\rm i} > 0.76$ eV. It could be explained by the formulas if we take derivative of the efficiency with respect to $E_{\rm i}$. The crystalline silicon intermediate band solar cells will degenerate into a common silicon solar cell if we choose $E_{\rm i} = 1.12$ eV. In this condition, the simulation shows a maximum efficiency of 40.74%, which is pretty close to the result of the former work by Henry.[18] The result shows good consistency, which verifies our model implicitly. The corresponding calculated optimum location of the IB level of 0.36 eV below the CB or above the VB is close to the position mentioned in the reference,[4] which is given as a rule of thumb to be about one third of the host semiconductor bandgap below the CB or above the VB.

Figure 3 shows the efficiency–voltage curve for the crystalline silicon IBSC when $E_{\rm i} = 0.76$ eV. As the voltage increases, the radiated flux of the photon generated by the direct recombination mechanism increases according the blackbody radiation theory. While the input flux of photon is not changed. When the voltage is small, the radiated flux of photon is negligible, the output current is almost unchanged, so the efficiency–voltage curve shows good linear dependence. When the voltage keeps increasing until the radiated photon flux is comparable to the absorption photon flux, the output current falls quickly and the efficiency drops. Figure 3 shows that the maximum efficiency of the crystalline silicon IBSC with $E_{\rm i}$ of 0.76 eV corresponds to the optimum output voltage of 1.05 eV.

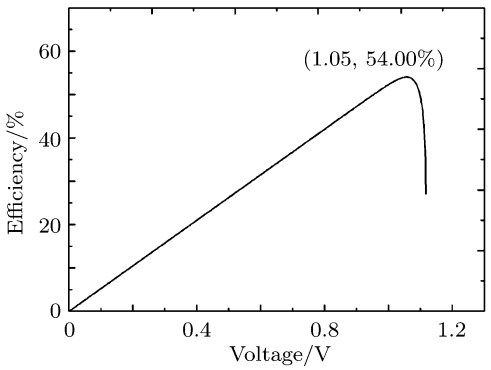


Fig. 3. Efficiency–voltage curve for crystalline silicon IBSC obtained in the simulation when $E_{\rm i} = 0.76$ eV.

In the following part, the potential limiting efficiency of other silicon-based IBSCs, such as micro-

crystalline Si and amorphous Si IBSCs, will be discussed. The bandgaps of these materials are supposed to vary between 1.12 eV and 1.7 eV (although due to the quantum size effect, the bandgap of the nanocrystalline Si may be expended to 2.0 eV and above, which is not considered here). To simplify the question, the energy band diagram of the amorphous silicon is considered to be similar to that of the crystalline silicon only with a larger bandgap, neglecting the effect of interface states and other expanding states inducing by the dangling bonds. However, the actual thin-film amorphous silicon material is characterized by a high density of defects introducing nonradiative recombination. The purpose of this part is to investigate whether, in this case, it is possible that the introduction of an IB can give beneficial results.

Figure 4 shows the efficiency of the Si-based IBSC as well as that of traditional two-band single junction solar cells with different host material bandgaps. For the conventional two-band solar cells, the optimum energy bandgap is about 1.1 eV.[10] It depends on the balance between carriers' production and emission. In the range of 1.12 eV$< E_{\rm g} <$ 1.7 eV, the efficiency decreases with the increase of the bandgap. However, for the IBSC, the trend is totally different. The difference of the efficiency trend is due to the absorption and recombination mechanism. As described by Eqs. (1) and (3), according to the blackbody radiation theory and the detailed balance principle, the energy of direct recombination is closely related to electron potential energy $q\mu_{\rm vi}$, which is only part of the output voltage. For the Si-based IBSC, the radiated energy keeps at a smaller value and increases much slower than the absorption energy. Therefore, unlike the two-band solar cells, the peak efficiency of the IBSC (63.2%)[4] is delayed due to the slowly increasing radiated energy until $E_{\rm g} = 1.95$ eV.[4]

In summary, as shown in Fig. 4, when $E_{\rm g}$ (1.12 eV$< E_{\rm g} <$ 1.7 eV) of the host material increases, the efficiency of the two-band solar cell drops, while the efficiency of the IBSC increases. The difference is more obvious for the host material with larger $E_{\rm g}$. At $E_{\rm g} = 1.7$ eV, a conventional amorphous Si band gap, the IBSC could increase its efficiency to 62.43%, while the conventional solar cell has only a maximal theoretical efficiency of 34%. Although the complex energy band induced by the long-range disorder of the atoms and the interface states is simplifed, the remarkable efficiency improvement margin still shows that the IB is a potential method to increase the performance of an amorphous Si solar cell.

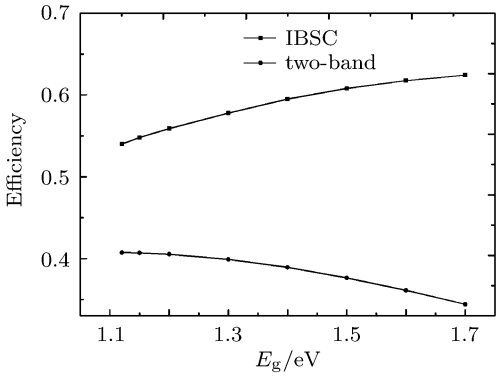


Fig. 4. Efficiency–$E_{\rm g}$ curves for Si-based IBSC and conventional two-band single junction solar cells with the bandgap of host materials varying from 1.12 eV to 1.7 eV at a full concentration condition.

4. Conclusion

By introducing one intermediate band into the forbidden bandgap of the semiconductor material, the limiting efficiency of silicon-based solar cells is investigated in this paper. The calculation is based on the blackbody approximation and the detailed balance principle under the fully concentrated sun light (46050 suns) condition. The limiting efficiency (54%) of the crystalline silicon IBSC is obtained with the optimal intermediate band located at 0.36 eV above the VB or below the CB, improving greatly than 40.7% of the Shockley–Queisser limit for the single junction Si solar cell. The simulation also shows that the limiting efficiency of the silicon-based solar cell increases with the host material bandgap in the range of 1.1 eV to 1.7 eV, and the amorphous Si solar cell with the bandgap of 1.7 eV exhibits a radiative limiting efficiency of 62.47%, having a better potential.

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