Solar cells efficiency enhancement using multilevel selective energy contacts (SECs)

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Abstract
High-energy incoming photons can be absorbed and concluded to generate Hot Carriers. In normal solar cells, these carriers are scattered by electron–electron and electron-lattice mechanisms and rapidly lose extra energy and approach to conduction band energy edge. This event plus other loss mechanisms cause that the efficiency of the solar cells to be limited to 33% theoretically. If one makes the possibility for carriers that can be extracted rapidly, before scattering and releasing extra energy to the lattice, the efficiency of solar cells is enhanced considerably. This type of solar cell is named hot carrier solar cells (HCSCs). To this end and improvement the conversion efficiency, multilevel energy selective contacts (ESCs) as a new concept and new mechanism in solar cells are used. In the other words, several appropriate energy levels as carrier extraction contacts in the conduction band are introduced. Here, we use multilevel ESCs, and based on our simulation it is shown that the maximum efficiency of 75% is achievable for low bandgap materials. For a typical material such as Si, the maximum efficiency is increased to 60% using ten ESCs.

Keywords Hot carrier solar cells · Energy selective contacts · Efficiency · Detailed balance model · Entropy

1 Introduction
In a conventional solar cell, thermalization losses of photo-generated carriers are an important issue that decreases conversion efficiency. Thermalization refers to carriers that have excess energy higher than the bandgap of absorber materials. The absorbed
carriers emit energy as phonon to reach the band edge and waste their energies as heat (Green 2006). The effect of this phenomenon can be seen in the decrement of power conversion efficiency. So if these carriers can be extracted rapidly, the efficiency will be increased and overcome the Shockley-Queisser limit (Shockley and Queisser 1961). Shockley and Queisser showed that the maximum efficiency for single-junction solar cells is 40.7% that can be obtained for materials with a bandgap of 1.12 eV (Shockley and Queisser 1961). Also, in a new method, this limitation was approved for solar cells (Henry 1980). There are some ways to overcome this limitation such as introducing impurity levels (Keevers and Green 1994; Azzouzi and Tazibt 2013; Green 2001), multi-junction, Multiple Exciton Generation (MEG) (Beard 2011), and hot carrier extraction before wasting their energies (Ross and Nozik 1982). Intermediate Band Solar Cells (IBSCs) increase the efficiency using the absorption of the low energy photons in two or more steps (upconversion), in addition to the valence band to conduction band transitions in traditional solar cells (Luque and Marti 1997; Luque 2010; Marti and Luque 2012). The multi-junction method splits the spectrum into several spectra and light is absorbed with well-matched absorbers such as tandem solar cells (Hadipour, B.de Boer, P. W. Blom. 2008). Another method is the hot carrier extracting related to high-energy photons. It is an important issue to take a method to decrease dissipation time and extract the carriers immediately before their completely thermalize. If the thermalizing time assumed 1 ns, it has been revealed that the power conversion efficiency is higher than the efficiency related to the single-junction solar cells. With increasing of this time, the efficiency can be increased too. For extraction of hot carriers, Energy Selective Contacts (ESCs) are purposed. ESCs are double barrier resonant tunneling diodes consisting of Si quantum dots embedded in SiO2 matrices (Shrestha et al. 2010).

In this paper, we introduce a new model to extract the hot carriers based on multiple ESCs implanted on the valance and conduction band. Figure 1 shows the schematic diagram of the proposed model. The width of each ESC has been assumed to be zero and their intervals are Δε.

**Fig. 1** Schematic diagram of multiple energy selective contacts
2 Effect of thermalization time on hot carrier solar cells

To analyze a hot carrier solar cell we make two assumptions: (i) an absorber with a bandgap that generates carriers with photoexcitation. (ii) Multiple Selective Energy Contacts (ESCs) implanted on the conduction band and valance band at each specific energy level that can extract hot carriers to metal electrodes (Shrestha et al. 2010). Moreover, enough time requires for hot carriers to reach the electrodes. This time is called the thermalization time and here we assumed a finite thermalization time.

2.1 Detailed Balance model for particles and energy fluxes

To calculate the conversion efficiency of an HCSC, a detailed balance model for particles, energy fluxes, and entropy generation are considered. The output current \((I_{out})\) accounted for the difference between absorbed and emitted photon fluxes.

\[
I_{out} = I_{abs} - I_{em}
\]

where, \(\varepsilon_{cv} = \varepsilon_{cv} - \varepsilon_{cv}^{0}\) is the difference between energy levels in the conduction and valance bands. \(T_h\) is the hot carrier temperature and \(I_{cell}\) is the emitted photon flux from the cell that is calculated from Plank’s law (Green 2006).

\[
I_{cell} = \frac{2\pi}{h^3c^2} \left[ \exp \left( \frac{-\varepsilon}{K_BT_h} \right) - 1 \right]
\]

where, \(h\) denotes the Planck constant, \(C\) is the velocity of light; \(KB\) is the Boltzmann constant and \(\mu_{cv}\) is the chemical potential. Energy flux extracted from the cell is the balance of the absorbed energy, \(U_{abs}\), and dissipated energy created by emitted energy, \(U_{em}\), and thermalized energy, \(U_{th}\), respectively (Takeda et al. 2009; Takeda and Motohiro 2013).

\[
U_{abs} = \int_{\varepsilon_{cv}}^{\infty} \varepsilon I_{cell}(\varepsilon, 0, T_{sun}) d\varepsilon
\]

\[
U_{em} = \int_{\varepsilon_{cv}}^{\infty} \varepsilon I_{cell}(\varepsilon, \mu_{cv}, T_h) d\varepsilon
\]

\[
U_{th} = 3K_B n (T_h - T_{RT}) d/\tau_{th}
\]

In Eq. (6) \(d\) denotes the thickness of the absorber and its value is assumed to be 500 nm (Takeda and Motohiro 2013), \(\tau_{th}\) is the thermalization time, \(T_{RT}\) is the room temperature and \(n\) is the carrier density that accounted from Eq. (7).
In Eq. (7), $m^*$ is the effective mass of electrons in the conduction band and the valance band. For numerical simulation $m^*$ is 0.01$m_0$ ($m_0$ is the electron rest mass). The energy extracted from the absorber by one carrier is equal to the ratio of $\Delta \varepsilon$ and $I_{\text{out}}/q$, which is the difference between the ESC levels for electrons and holes ($\Delta \varepsilon$).

$$
\Delta \varepsilon = \Delta U / (I_{\text{out}}/q)
$$

For extracting hot carriers in $T_h$ to electrodes at temperature $T_{RT}$, entropy should be generated [1, 15], and the output power could be calculated from:

$$
P_{\text{out}} = \Delta U - T_{RT} \Delta S
$$

In Eq. (9), $T_{RT} \Delta S$ can be written as:

$$
T_{RT} \Delta S = (\Delta U - (I_{\text{out}}/q)\mu_{cv})T_{RT}/T_h
$$

And finally, the conversion efficiency ($\eta$) is written as:

$$
\eta = P_{\text{out}}/\int_0^\infty \varepsilon I_{\text{sun}}(\varepsilon)d\varepsilon
$$

2.2 Effect of thermalization on efficiency

Figure 2 shows the efficiency versus bandgap of the absorber in various thermalization times. The S-Q model for a single junction is shown in the black curve. Maximum efficiency of 40.7% is achievable for the material with a bandgap of 1.12 eV. Increasing the
thermalization time to 1 ns shifts the maximum efficiency to the bandgap of 0.55 eV which the efficiency is about 70% for this condition. With a thermalization time of 100 ns, the maximum efficiency reaches 82% for a bandgap of 0.5 eV.

Figure 3a shows efficiency versus bandgap in various thermalization temperatures ($T_H$). When $T_H$ is 600 K, efficiency reaches to upper than the S-Q limit (48%) and when $T_H$ is 3600 the efficiency is maximum. Figure 3b Shows that in $T_H$ = 3600 K, the efficiency is constant, and increasing the $T_H$ more than this point has no effect on the efficiency of the cell.

3 Multilevel energy selective contacts (ESCs)

Figure 1 shows multilevel energy selective contacts for extracting hot carriers from different energy levels in conduction and valance bands. The width of ESCs is narrow to reduce the entropy generation in extracting hot carrier to cold electrodes (Shrestha et al. 2010). For evaluating the performance of this type of hot carrier solar cells the Detailed Balance model is generalized and the output current density is written as:

$$J_{out} = q \sum_{i=1}^{n} \left[ N(\epsilon_1, \epsilon_h, 0, T_S) - N(\epsilon_1, \epsilon_h, \mu_i, T_C) \right] + N(\epsilon_h, \infty, 0, T_S) - N(\epsilon_h, \infty, \mu_h, T_C)$$

(12)

$$\epsilon_i = \epsilon_c + 2(i - 1)\delta\epsilon, \ldots, \epsilon_h = \epsilon_c + 2i\delta\epsilon$$

In Eq. (12) $n$ is the number of implanted ESCs and $N$ is the particle flux and comes from plank’s law (Green 2006).

$$N(\epsilon_i, \epsilon_h, \mu, T) = \frac{2\pi}{h^3C^2} \int_{\epsilon_i}^{\epsilon_h} \frac{e^2d\epsilon}{\exp[(\epsilon - \mu)/kT] - 1}$$

(13)

The chemical potential of each ESC according to the difference between ESCs can be written as:

![Fig. 3 Efficiency versus a bandgap in different thermalization temperatures b thermalization temperatures](image-url)
\[ \mu_i = (\varepsilon_e + (i-1)\delta\varepsilon) - (\varepsilon_h - (i-1)\delta\varepsilon) \] (14)

\[ \mu_h = (\varepsilon_e + i\delta\varepsilon) - (\varepsilon_h - i\delta\varepsilon) \] (15)

\( \delta\varepsilon \) is the interval of ESCs in the valance and conduction bands. The output voltage from each ESC can be written as a function of the location of ESCs in valance and conduction bands:

\[ V_{\text{out}}(i) = (\varepsilon_{cv} + 2i\delta\varepsilon) \left( 1 - \frac{T_c}{T_s} \right) \] (16)

where, \( T_c \) and \( T_s \) are the cell and sun temperatures, respectively. The total output power is the sum of generated powers from each ESCs and power conversion efficiency is the ratio of output power to input power. Input power can be calculated from \( p_{\text{in}} = \sigma T_s^4 \), where \( \sigma \) is the Stephan-Boltzmann constant and is equal to \( 5.67 \times 10^{-8} \text{W.m}^{-2}.\text{k}^{-4} \) (Blevin and Brown 1971).

\[ p_{\text{out}} = \sum_{i=1}^{n} J_{\text{out}}(i) \times V_{\text{out}}(i) \] (17)

\[ \eta = \frac{p_{\text{out}}}{p_{\text{in}}} \] (18)

For evaluating the effect of the location of each ESC on the efficiency of the cell, the number of ESCs is considered as one, two, three, four, five, and ten. So the efficiency variations were plotted versus the location of ESCs. In the case of one ESC, the efficiency cannot increase and becomes lower than the S-Q limit (40.7\%). This is due to that ESC is implanted in the edge of conduction and valance bands and swept to the upper energies in these bands. Location of ESC denotes the new bandgap for the absorber and new output voltage in sweeping is obtained while the current is decreased. For each level, while the output voltage is increased, the output current of the absorber decreases, and finally, the decrement of current prominent and the output power decreases. When we use one ESC (since a new bandgap for absorber is created) the S-Q limit reaches to lower value of bandgap as shown in Fig. 4a. In other words, when we use a low bandgap absorber, we expect that efficiency should be low, while by using ESC, efficiency reaches a maximum limit of S-Q. Another result from this achievement is removing the restriction for choosing the appropriate material to reach the high efficient solar cells.

Figure 4b shows the efficiency contour for two ESCs that are implanted symmetrically on the conduction and valance band. The dark region for materials with a bandgap of 0.7 eV to 0.9 eV and ESCs interval at 0.5 eV shows that the efficiency breaks the S-Q limit and is increased to 55\%. In this case, the first ESC is implanted in the edge of the conduction and valance band and the second ESC with an interval of \( \delta\varepsilon \) is upper than the first one and the extracted voltage from the absorber is more than one case. This idea enhances the power conversion efficiency, because, the output voltage is enhanced. This event comes back to electron extraction from high energy in conduction band and hole in valance band. So, the total current is constant, but the electric potential is enhanced. This is the physics behind this method. Figure 5 shows efficiency contour plots for three, four, five, and ten
ESCs which are implanted symmetrically on the conduction and valance bands. In Fig. 5) the dark region indicates that maximum efficiency is about 63% for materials with band gaps between 0.4 and 0.8 eV and location of ESCs around 0.4 eV.a

To achieve higher efficiency, we use ten ESCs implanted on the conduction and valance bands symmetrically with $\delta e$ intervals. Figure 5d shows that for materials with a bandgap

![Figure 4](image1.png) Efficiency versus the location of ESC in a one ESC and b two ESCs

![Figure 5](image2.png) Efficiency versus the location of ESCs in a three cases b four cases c five cases d ten cases
between 0 eV and 0.5 eV and interval of ESCs around 0.2 eV, the maximum efficiency is obtained as 75%. In this way, we decrease the thermalization of hot carriers by extracting them using the two, three, four, five, and ten ESCs. Using this method maximum efficiency is achievable for low bandgap materials too because high electric potential can be provided. In typical semiconductors, low bandgap materials create low output voltage but high output current and we need to have an optimum bandgap to reach the maximum efficiencies. This condition causes a restriction for choosing the best material for achieving high efficiencies. In our proposed model we can use zero bandgap materials (such as graphene) with ten ESCs while we have high power conversion efficiency.

Figure 6a shows the effect of the number of ESCs on efficiency that it is promoted to 75% using ten ESCs. In this case, we use one, two, three, four, five, and ten ESCs on the conduction and valance bands. The efficiency increases in all cases except one ESC case. This is due to sweeping the location of ESC in upper energies which increases the effective bandgap of the material. The larger bandgap has a larger open-circuit voltage but lower output current, and the current degrade the efficiency. When the number of ESCs is more than one, the S-Q limit is broken and efficiency will reach 55%, 63%, 67%, 70%, and 75% for two, three, four, five, and ten ESCs respectively.

Figure 6b shows the efficiency versus the location of ESCs in a typical material like Si that indicates if we use more than one ESC we can achieve high efficiency and breaks the Shockley-Queiser limit for single-junction solar cells based on Si. In this type of solar cell, the efficiency increases and reaches 60% if ten ESCs are used.

4 Conclusions

In this work, ultra-high efficiency solar cells using minimizing the thermalization energy was illustrated. To this end, multiple Energy Selective Contacts were used to allow the rapid collection of the hot carriers to contacts. Due to the fast carrier extraction process, we illustrated that the conversion efficiency of single-junction solar cells can be increased. We calculated the precise position of ESCs in the energy domain. Our simulated results

![Fig. 6](image-url) Efficiency versus Intervals ESCs in one, two, three, four, five, and ten ESCs implanted on the conduction and valance band symmetrically a different material b typical material (Si)
showed that the efficiency of Si-based solar cells can be increased from 40.7% in classical case to 60% with applying ESCs by using ten ESCs.

References

Azzouzi, G., Tazibt, W.: Improving silicon solar cell efficiency by using the impurity photovoltaic effect. Energy Procedia 41, 40–49 (2013)

Beard, M.C.: Multiple exciton generation in semiconductor quantum dots. J. Phys. Chem. Lett. 2(11), 1282–1288 (2011)

Blevin, W.R., Brown, W.J.: A precise measurement of the Stefan-Boltzmann constant. Metrologia 7(1), 15 (1971)

Green, M.A.: Multiple bands and impurity photovoltaic solar cells: general theory and comparison to tandem cells. Prog. Photovolt. Res. Appl. 9, 137–144 (2001)

Green, M.A.: Third Generation Photovoltaic: Advanced Solar Energy Conversion, vol. 12. Springer, Berlin (2006)

Hadipour, A., de Boer, B., Blom, P.W.: Organic tandem and multi-junction solar cells. Adv. Funct. Mater. 18(2), 169–181 (2008)

Henry, C.H.: Limiting efficiencies of ideal single and multiple energy gap terrestrial solar cells. J. Appl. Phys. 51(8), 4494–4500 (1980)

Keevers, M.J., Green, M.A.: Efficiency improvements of silicon solar cells by the impurity photovoltaic effect. J. Appl. Phys. 75(8), 4022–4031 (1994)

Luque, A., Martí, A.: Increasing the efficiency of ideal solar cells by photon induced transitions at intermediate levels. Phys. Rev. Lett. 78(26), 5014 (1997)

Luque, A., Martí, A.: The intermediate band solar cell: progress toward the realization of an attractive concept. Adv. Mater. 22(2), 160–174 (2010)

Marti, A., Luque, A., Stanley, C.: Understanding intermediate-band solar cells. Nat. Photonics 6(3), 146–152 (2012)

Ross, R.T., Nozik, A.: Efficiency of hot carrier solar energy converters. J. Appl. Phys. 53(5), 3813–3818 (1982)

Shockley, W., Queisser, H.J.: Detailed balance limit of efficiency of p-n junction solar cells. J. Appl. Phys. 32(3), 510–519 (1961)

Shrestha, S.K., Alberti, P., Conibeer, G.J.: Energy selective contacts for hot carrier solar cells. Sol. Energy Mater. Sol. Cells 94(9), 1546–1550 (2010)

Takeda, Y., Ito, T., Motohiro, T., König, D., Shrestha, S., Conibeer, G.: Hot carrier solar cells operating under practical conditions. J. Appl. Phys. 105(7), 074905 (2009)

Takeda, Y., Motohiro, T.: Intermediate band-assisted hot carrier solar cells using indirect bandgap absorbers. Prog. Photovoltaics Res. Appl. 21(6), 1308–1318 (2013)

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