Proposal of simplified model for absorption coefficients in quantum dot array based intermediate band solar cell structure

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Abstract: We propose a simplified theoretical model to analyze the absorption coefficients in quantum dot intermediate band solar cell (QD-IBSC) structure. Our theoretical model, based on the multiband tight-binding Hamiltonian including the conduction, valence, and the intermediate band, can capture some essential features in the actual QD-IBSC such as the absorption path dependence of the absorption strength and the line shape of the absorption spectrum in spite of its simplicity. The main feature of this model is its ability to be applied to any QD-IBSC system regardless of the geometrical parameters (QDs shapes and spacing) or the base materials by changing the relevant coupling parameters. The proposed simplified should be of useful for the semi-quantitative understanding and modeling of QD-IBSC.

Keywords: quantum dot, solar cells, intermediate band, tight-binding model

Classification: Electronic materials, semiconductor materials

References

[1] A. Luque and A. Marti: Phys. Rev. Lett. 78 (1997) 5014. DOI:10.1103/PhysRevLett.78.5014
[2] K. Yu, W. Walukiewicz, J. Ager, III, D. Bour, R. Farshchi, O. Dubon, S. Li, I. Sharp and E. Haller: Appl. Phys. Lett. 88 (2006) 092110. DOI:10.1063/1.2181627
[3] C. Tablero: Sol. Energy Mater. Sol. Cells 90 (2006) 588. DOI:10.1016/j.solmat.2005.04.036
[4] P. Palacios, K. Sanchez, J. Conesa and P. Wahnon: Phys. Status Solidi A 203 (2006) 1395. DOI:10.1002/pssa.200566179
[5] F. Rahayu and Y. Darma: AIP Conf. Proc. 1454 (2012) 203. DOI:10.1063/1.4730721
[6] B. Lee and L. Wang: Appl. Phys. Lett. 96 (2010) 071903. DOI:10.1063/1.3298553
[7] T. Sogabe, Y. Shoji, M. Ohba, K. Yoshida, R. Tamaki, H.-F. Hong, C.-H. Wu, C.-T. Kuo, S. Tomic and Y. Okada: Scientific Reports 4 (2014) 4792. DOI:10.
1 Introduction

The efficiency of a single junction solar cell can be improved by introducing a way to better absorption of solar spectrum. It has been shown by Luque and Marti that by introducing an intermediate band (IB) inside the forbidden region of a regular semiconductor the absorption of two below band gap photons via the IB in two-step process becomes possible [1]. Many candidate material systems to implement such processes have been presented [2, 3, 4, 5, 6], followd by recently reported successful fabrication [7]. It has been shown that confined levels associated with quantum dots (QDs) are suitable to form at least one IB which is located in the forbidden energy gap of the QD material and is separated from the valence and conduction band of the barrier material with separated quasi Fermi level (QFL) from the conduction and valence band QFLs [8, 9]. Additional absorption of two sub-bandgap photons from VB to IB and then from the IB to CB which together add up to the induced current through the VB-CB transition. Accordingly, one IBSC exhibits three absorption coefficients $\alpha_{V1}$, $\alpha_{IC}$ and $\alpha_{CV}$ for the mentioned transitions, respectively. These coefficients dictate the probability of a photon being absorbed or emitted for each of the generation and radiative recombination processes in the detailed balance theory [10]. The shapes, values of those coefficients dependent to the frequency play the important role in the IBSC limiting efficiency which are being studied in several papers [8, 9, 11, 12]. For instance, one important hypothesis behind the ideal model of IBSC proposed by Luque and Marti [1] is to design a QDs array structure with a single metallic-like IB located in the optimal position inside the forbidden gap with a finite bandwidth. Therefore, it is of a great interest to analyze the changes in the amplitude and shape of absorption coefficients lines with respect to the QDs spacing, IB position and IB bandwidth because of their important roles on the limiting efficiency.

This paper presents a very useful multi-band tight-binding (TB) approach to estimate for each transition its related absorption coefficient which is applicable for any QD based material system and structure and give some insights into better
understanding phenomenology of photon absorption process of the QD-IBSCs. The proposed TB Hamiltonian in this work is very convenient to investigate the absorption coefficients compared with the calculations based on k-p theory method [8, 9, 13, 14] or other TB models based on the realistic shape of QDs due to its adjustability to different QD-IBSC designs. On the other hand, with some similarities to Ref. [11] where the IB related transitions wave numbers are restricted within a finite range, the CB and VB continuum dispersions in this work are considered with more discrete energy levels.

2 Model structure and theoretical method

Fig. 1(a) is the schematic illustration of the QD-IBSC structure analyzed in this work, where 1-dimensionally arranged QDs boxes with the QD center-center spacing $a_{\text{QD}}$ are assumed as the IB absorber medium. For the purpose of simplicity we simplified the model with some assumptions:

(i) QDs are placed with fictitious atoms chain with the distance between two adjacent dots $a_{\text{QD}}$, where the role of QDs width and shapes can be represented by hoping energies and the IB central position $\epsilon_1$.

(ii) To minimize the TB Hamiltonian dimension, the energy dispersions along $y-z$ directions are considered parabolic and they are represented in the diagonal elements of the general Hamiltonian.

(iii) Only $s$ and $p_x$ atomic orbital for the bulk semiconductor are used.

(iv) Only along the electric field (i.e., polarization, here linearly polarized along $x$) direction the system is described by discrete lattice model, while along two other directions (here $y-z$) dispersions are described by parabolic. This is because that (i) the electrons motion is influenced only along the electric field direction, (ii) symmetry of the wave functions (WFs) (such as $s$ or $p_x$) along the electric field polarization, is essentially important in determining the absorption line shape, and (iii) such symmetry of WFs can be systematically taken into account through the sign of hopping factors in our tight-binding like discrete lattice model.

2.1 Model Hamiltonian

In this section we present a theoretical minimal model to describe the QD-IBSC based on TB method. As illustrated in Fig. 1(a), a unit cell is composed of one QD and a chain of crystal atoms along the $x$ direction. For the purpose of numerical calculation, this big number of atoms in the crystal is replaced with a finite number of fictitious atoms, where each fictitious atom is represented by two nodes: (i) one for its $s$ orbital with the orbital energy $\epsilon_s$ and with a non-zero hopping energy among the nearest neighbors $t_s$ where these $s$ orbitals will form CB, (ii) the other node which represents its $p_x$ orbital with the orbital energy $\epsilon_{p_x}$ and with a non-zero hopping energy among the nearest neighbors $t_{p_x}$ where these coupled $p_x$ orbitals will form the VB in our model. For the nearest neighbor fictitious atoms, the $s$ (at $x = x_j$) orbital are coupled with $p_x$ (at $x = x_{j\pm 1}$) orbitals by a non-zero hopping factor $b_{C,V}$. These orbitals are placed at a distance $a_{\text{atom}}$ between the so-called fictitious atoms. The localized QD wave function is described by one node in one
unit cell (see Fig. 1(a)), where the spacing between two QD is specified by $a_{QD}$ and the each QD node has the energy $\epsilon_1$. This QD node is assumed to be coupled with nearest neighbor QDs with the hopping factor $t_i$. It is also coupled with its nearest neighbors and $p_x$ orbitals with the hopping factors $b_{CI}$ and $b_{VI}$, respectively. These hopping factors are schematically illustrated in Fig. 1(b).

For the above described structure in Fig. 1(a), a unit cell consists of $n_C$ numbers of $s$ orbital and $n_V$ numbers of $p_x$ orbitals, and $n_I$ numbers of QD orbitals. Here we assume $n_C = n_V$ and $n_I = 1$. For an infinity numbers of unit cells, the Bloch theorem yields the following time-independent Schrödinger equation with the Hamiltonian matrix elements $H_{ij}(k)$ expressed for the upper triangle as

$$H(k) = \begin{pmatrix} e^{-i\kappa_0 H_{L-1}} + H_0 + e^{i\kappa_0 H_1} \end{pmatrix} = eC(k),$$  

where $H_0, H_{L-1}$, and $H_1$ are the Hamiltonian within a unit cell, hopping Hamiltonian from a unit cell to its left nearest neighbor unit cell, and the hopping Hamiltonian from a unit cell to its right nearest neighbor unit cell, respectively. In Eq. (1), $C(k)$ is the wavefunction vector $C(k) = \begin{pmatrix} C_C(k), C_V(k), C_I(k) \end{pmatrix}$, where $C_C(k)$, $C_V(k)$, and $C_I(k)$ are the $n_C$, $n_V$, and $n_I$ dimensional wavefunction vectors to describe the wave amplitudes in CB, VB, and IB, respectively. We note that these wavefunction vectors are required to calculate the absorption coefficients later. After summing up three terms in the Hamiltonian Eq. (1), $H(k)$ is given by

$$H(k) = \begin{pmatrix} H_C & H_{CV} & H_{CI} \\ H_{VC} & H_V & H_{VI} \\ H_{IC} & H_{IV} & H_I \end{pmatrix},$$  

Fig. 1. (a) QD-IBSC simplified tight-binding model. The system is described by discrete lattice model only along the electric field direction, while $y$-$z$ dispersions are described by parabolic band. (b) Explanation of six different tight-binding hopping energies used in the model.
where submatrices are given as

$$
H_{ij}(k) = \begin{cases}
\epsilon_{C}, & (i = j) \\
t_{C}, & (j = i \pm 1) \\
t_{C}e^{ik_{QD}}, & (i = 1, j = n_{C}) \\
t_{C}e^{-ik_{QD}}, & (i = n_{C}, j = 1) \\
0, & \text{otherwise}
\end{cases}
$$

for $i, j \in \text{CB}$,

$$
H_{CVij}(k) = \begin{cases}
b_{CV}, & (j = i + 1) \\
-b_{CV}, & (j = i - 1) \\
b_{CV}e^{ik_{QD}}, & (i = 1, j = n_{V}) \\
b_{CV}e^{-ik_{QD}}, & (i = n_{C}, j = 1) \\
0, & \text{otherwise},
\end{cases}
$$

for $i \in \text{CB}$ and $j \in \text{VB}$,

$$
H_{IBij}(k) = \begin{cases}
b_{CI}, & (i = 2, j = 1) \\
b_{CI}e^{-ik_{QD}}, & (i = n_{C}, j = 1) \\
0, & \text{otherwise},
\end{cases}
$$

for $i \in \text{CB}$ and $j \in \text{IB}$,

$$
H_{VIj}(k) = \begin{cases}
\epsilon_{V}, & (i = j) \\
t_{V}, & (j = i \pm 1) \\
t_{V}e^{ik_{QD}}, & (i = 1, j = n_{V}) \\
t_{V}e^{-ik_{QD}}, & (i = n_{V}, j = 1) \\
0, & \text{otherwise},
\end{cases}
$$

for $i, j \in \text{VB}$,

$$
H_{IVij}(k) = \begin{cases}
-b_{IV}, & (i = 2, j = 1) \\
b_{IV}e^{-ik_{QD}}, & (i = n_{V}, j = 1) \\
0, & \text{otherwise},
\end{cases}
$$

for $i \in \text{VB}$ and $j \in \text{IB}$,

$$
H_{ij}(k) = \epsilon_{i} + 2t_{1}\cos k_{QD}, \quad (3)
$$

for $i, j \in \text{IB}$. Other submatrices are given by taking the hermitian conjugate, for instance as $H_{ij} = H_{ji}^{*}$. In these submatrices, the hopping energy $t_{C}$ ($t_{V}$) is given in terms of the their effective mass as $t_{C(V)} = \mp\hbar^{2}/2m_{C(V)}a_{\text{atom}}^{2}$. We assume $m_{C}^{*} = 0.067m_{0}$ and $m_{V}^{*} = 0.45m_{0}$ for GaAs, with $m_{0}$ being the free electron mass. For IB, on the other hand, $t_{1} (\ll t_{C(V)})$ is given appropriately as a controllable parameter in this study, although it can be chosen to be consistent with the IB band dispersion obtained by more precise simulations considering the actual shape of QD [8, 9]. The inter-band hopping energies are, on the other hand, given to be consistent with the multiband effective mass formulation, and is required to be inversely proportional to the atomic distance so that $b_{xy} = g_{xy}/a_{\text{atom}}$ (xy $\in$ CV, VI, CI), with the constant $g_{xy}$ given as adjustable parameter ($g_{CI} = 1, g_{CV} = g_{IV} = 2$).
In Eq. (1), the parabolic transverse dispersions $\hbar^2 k_t^2 / 2m^*$ with the transverse wavenumber $k_t = (k_y^2 + k_z^2)^{1/2}$ are not explicitly written, as already mentioned in the beginning of this section they are added to the diagonal elements of the Hamiltonian.

### 2.2 Absorption coefficients

In this subsection we consider the coupling between our model structure and electromagnetic field for the purpose of obtaining the absorption coefficient necessary for the efficient of IBSC. We assume the electric field $\mathbf{E}(t) = E_0 \sin \omega t \hat{x}$ along the $x$ direction. Then the electric field and the lattice is treated by the modification of the Hamiltonian matrix elements in the Eq. (1). According to the Peierls substitution method, all the hopping energy parameter ($t$ and $b$) are modified as $t \rightarrow te^{i\phi(t)}$ to be multiplied by the Peierls phase factor $e^{i\phi(t)}$, where

$$
\phi(t) = -\frac{e}{\hbar} \int_{r_i}^{r_{i+1}} \mathbf{A}(r, t) \cdot d\mathbf{r}
$$

is the Peierls phase, where $\mathbf{A}(r, t)$ is the electromagnetic field vector potential and the integration should be along the hopping path. With considering the a linearly polarized electromagnetic field along $x$ direction and the relationship $\mathbf{E}(t) = -\hat{x} \partial A_x(t) / \partial t$ with the vector potential component $A_x(t) = (E_0 / \omega) \cos \omega t$ and $\hat{x}$ the unit vector along the $x$-axis, the Peierls phase factor and its corresponding weak field approximations can be written as

$$
\phi(t) = -\frac{e}{\hbar} \int_{x_j}^{x_{j+1}} A_x(t) dx = -\frac{eE_0a}{\hbar \omega} \cos \omega t,
$$

$$
e^{i\phi(t)} \approx 1 + i\phi(t) = 1 - \frac{eE_0a}{\hbar \omega} \cos \omega t.
$$

where $a$ stands for the distance between two nearest neighbor lattice sites along which the hopping energy is considered. In the presence of an electromagnetic field, by applying the Peierls substitution in Eq. (5)–(6) to the TB Hamiltonian elements given in Eq. (1) and by decomposing the obtained Hamiltonian into two parts, $H_{EMF}(k) = H(k) + H'(k)(e^{i\omega t} + e^{-i\omega t})$, the matrix elements of the perturbation Hamiltonian $H'$ with the displacement $a = a_{atom}$ are derived as

$$
H' = \frac{eE_0a}{2\hbar \omega} \begin{pmatrix}
H'_{CC} & H'_{CV} & H'_{CI} \\
H'_{NC} & H'_{VV} & H'_{VI} \\
H'_{IC} & H'_{IV} & H'_{Ii}
\end{pmatrix},
$$

where

$$
H'_{ij}(k) = \begin{cases}
-ite_C, & (j = i + 1) \\
ite_C, & (j = i - 1) \\
-ite^{ik_{i0}}, & (i = 1, j = n_c) \\
tie^{-ik_{j0}}, & (i = n_c, j = 1) \\
0, & \text{otherwise}
\end{cases}
$$

for $i, j \in \text{CB}$,
of light propagation) is expressed as

\[ H'_{ij}(k) = \begin{cases} 
-ib_{CV}, & (j = i \pm 1) \\
-ib_{CV}e^{ika_{QD}}, & (i = 1, j = n_e) \\
-ib_{CV}e^{-ika_{QD}}, & (i = n_e, j = 1) \\
0, & \text{otherwise},
\end{cases} \]

for \( i \in \text{CB} \) and \( j \in \text{VB} \),

\[ H'_{IB}(k) = \begin{cases} 
-ib_{CI}, & (i = 2, j = 1) \\
ib_{CI}e^{-ika_{QD}}, & (i = n_e, j = 1) \\
0, & \text{otherwise},
\end{cases} \]

for \( i \in \text{CB} \) and \( j \in \text{IB} \),

\[ H'_{VB}(k) = \begin{cases} 
it_{V1}, & (j = i + 1) \\
-it_{V1}, & (j = i - 1) \\
-it_ve^{ika_{QD}}, & (i = 1, j = n_e) \\
it_{Ve}^{-ika_{QD}}, & (i = n_e, j = 1) \\
0, & \text{otherwise},
\end{cases} \]

for \( i, j \in \text{VB} \),

\[ H'_{j}(k) = 2\sin(ka_{QD}), \quad (8) \]

for \( i, j \in \text{IB} \). The probability of photon absorption per unit length (in the direction of light propagation) is expressed as

\[ a_{XY}(\omega) = \frac{I_{XY}(\omega)}{S} \quad (9) \]

where \( S = nce\omega^2(E_0/2)^2/2 \) is the incident power per unit area, and \( I_{XY}(\omega) \) is the absorbed power per unit volume through the X→Y photo-induced transitions: XY ∈ (IV), (IC), (VC), \( c \) is the speed of light in vacuum, \( n \) is the refractive index of the base material, \( \epsilon_0 \) is the vacuum permittivity, \( \omega \) is the light frequency, \( I_{XY}(\omega) \) is given by the mean of the Fermi golden rule as

\[ I_{XY}(\omega) = \hbar \omega \sin^2 \frac{2\pi k}{\hbar} \sum_k |\langle Y(k)|H'(k)|X(k)\rangle|^2 \]

\[ \times \delta(\epsilon_Y(k) - \epsilon_X(k) - \hbar\omega)[f_X(\epsilon_X(k)) - f_Y(\epsilon_Y(k))], \quad (10) \]

where \( \epsilon_X(k) \), \( |Y(X)(k)| \) and \( f_Y(\epsilon_Y(k)) \) are representing the eigenvalue, eigenvector and the Fermi distribution for the final (initial) state, respectively. In this work, we assume the approximation that the initial states involved in an absorption process are always ful (i.e., \( f_X = 1 \)), and on the other hand, the final states are always empty (i.e., \( f_Y = 0 \)). To proceed further, we do the following substitutions: as the total volume approaches infinite size with infinity number of unit cells, the summation over \( k \) can be replaced with an integral as
\[ \sum_{k_x, k_y, k_z} \frac{V}{(2\pi)^3} \int_{\text{BZ}} dk_x \times \int dk_y dk_z, \quad (11) \]

\( \delta \)-function \( \delta(E) \) is approximated by the Lorentzian function with a phenomenological broadening energy \( \eta \) as following

\[ \delta(E) \to L(E) = \frac{\eta}{\pi(\eta^2 + E^2)}, \quad (12) \]

where \( V \) is the total volume, and \( \eta = 0.01 \text{ eV} \) is used in this study. BZ stands for the first Brillouin zone of QD array wave numbers within range \( -\pi/a_{\text{QD}} \leq k_x \leq \pi/a_{\text{QD}}, \) where \( a_{\text{QD}} \) is the QD-QD spacing in the stacking direction. However, along transverse direction QD arrays and bulk material wave numbers are treated differently. In the case of the QD arrays, the wave numbers integration range for “IB related absorptions” is limited up to some finite value, \( k_{\text{max}} \), because of the strong confinement of IB electron wave functions in the transverse direction. \( k_{\text{max}} \) can be interpreted as the wave number uncertainty restricted by the spatial extent of the QD, its length \( w_{\text{QD}} \) and it can be estimated roughly about \( 1/w_{\text{QD}} \). On the other hand, for the CV absorption process described by the help of parabolic dispersions along transverse direction, integration over wave numbers can be ranged up to infinity.

To understand qualitatively the absorption coefficients characteristics for different transitions in a QD-IBSC system, in the next section we analyze the calculated results for an IBSC based on InAs/GaAs QD arrays.

3 Results and discussions

In this section, following the method described above, the band structure and related absorption coefficients for an IBSC based on InAs/GaAs QD arrays are calculated. Although some parameters can be chosen as arbitrary constants in TB model, for instance the coupling factors and the IB position, they are features of the used material system and the QD array geometry. Although it is possible to adjust them in a way to reproduce the experimental results as we did in our work, our main aim is to realize qualitatively the tendency of the absorption coefficients to some important QD arrays geometrical parameters.

3.1 Band structure

Initially \( t_C \) and \( t_V \) parameters are fixed according to the respective effective masses for conduction and valance bands by the mean of relationship defined in Eq. (1). \( \epsilon_C, \epsilon_V \) and \( \epsilon_l \) are chosen properly according to the band gap energy of GaAs with \( E_g = 1.43 \text{ eV} \) and the isolated QDs levels at the energy \( E_{\text{IB}} \). A numerical result for the bands dispersion is plotted in Fig. 2, where the QD spacing is supposed to be \( a_{\text{QD}} = 10 \text{ nm} \). Based on our numerical results, \( a_{\text{atom}} \) in the range of 1 nm also can effectively results in similar absorption coefficients for smaller \( a_{\text{atom}} \) which enabled us to reduce the numerical calculations.
3.2 Absorption coefficients

In this part, initially the coupling factors between bands are adjusted in order to get the absorption coefficients in order of magnitudes \( \sim 10^4 \) provided in Refs. [8, 9, 15]. In Fig. 3 we plotted the total absorption coefficient \( a_{CV} + a_{CI} + a_{IV} \) calculated using Eqs. (9), (10) for three different values of the QD spacing. By looking to Fig. 3, we notice a smaller relevant absorption coefficient for the IB \( \rightarrow \) CB transition compared to the VB \( \rightarrow \) IB one. This is because the \( s \)-like symmetry of the QD orbital has smaller coupling to \( s \) symmetry states forming CB than \( p_x \) symmetry states in VB. Moreover, in Fig. 3 we observe that by increasing the QD spacing, which is corresponding to decreasing QDs density, the IB related absorptions are decreasing steadily while the CB absorption spectra does not change as expected. In the other two subsequent figures the VB \( \rightarrow \) CB spectra is not plotted due to its steady behavior. In Fig. 4, the influence of IB bandwidth on the absorption coefficients is examined by mean of the inter QD coupling \( t_i \) factor.
By increasing the IB bandwidth, VB → IB absorption coefficient is steadily decreasing in contrast with the IB → CB one. It can be interpreted by considering the fact that the most part of the absorption transitions are occurring near the Γ point, thus the modification of IB Γ point position upward will increase the range of possible IB → CB transitions against the opposite influence for VB → IB transitions. One main constrain in designing a high efficiency QD-IBSC is the optimal IB position inside the forbidden gap. Thus, it is a great of interest to evaluate the relevant absorption coefficients spectra modification due to the position of IB, which is illustrated in Fig. 5. The spectra behaviors can be interpreted again with the similar justification about the majority transitions near Γ point.

4 Conclusion

We have proposed a simple and versatile theoretical model to understand semi-quantitatively the absorption coefficients in quantum dot intermediate band solar cells (QD-IBSC) Our theoretical model, based on the multiband tight-binding Hamiltonian including the conduction, valence, and the intermediate band, can capture some essential features in the actual QD-IBSC such as the absorption path
dependence of the absorption strength and the line shape of the absorption spectrum in spite of its simplicity. The main feature of this model is its ability to be applied to any QD-IBSC system regardless of the geometrical parameters (QDs shapes and spacing) or the base materials by changing the relevant coupling parameters. Moreover, this model can be easily extended to include more orbitals for bulk material to model the light polarization dependence. The proposed framework should be of useful for the semi-quantitative understanding and modeling of QD-IBSC.

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