Modeling of the internal quantum yield for solar cell with quantum dots.

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Abstract. By modeling solar cells with quantum dots based on A3B5 materials it is necessary to take into account the large number of localized quantum levels arising in the forbidden band of the host material. In this paper Empiric k-p Hamiltonian model have been used to describe InAs/GaAs structure. For the model two shape of quantum dot: box and cylinder have been considered.

Introduction
Quantum dots (QDs) being implant into the space charge region of a solar cell (SC) can form localized energy levels within the forbidden band of the host material. At irradiation of a wide spectrum light these levels can serve as a stepping stone to absorb additional low-energy photons and increase photocurrent. There is no decrease in voltage here, since the energy levels of the quantum dot are localized and the charge carriers from there cannot take a part in the current flow. Thus increasing the current generation without decreasing the voltage can increase the efficiency of SC. Such a concept is well known as intermediate band solar cell (IBSC) [1].

Implanting QDs was realized in SC prototypes based on GaAs/InAs structures [2, 3]. Strictly speaking such material set do not reproduce IBSC concept fully. InAs QD produces in bandgap of GaAs host material not very deep energy levels. Charge carriers could go out of localized states to conduction band or valence band of host material with only phonon absorption. So there is mainly photon and phonon transition but not IBSC two-photon transition [4].

Usually the shape of QD in the lateral direction is greater than along the direction of structure growth. Also both lateral sizes are comparable [5]. Thus the shape of the QD can be described as a parallelepiped or a cylinder.
The amount and position of the energy levels within the bandgap of the host material depend on QDs material and size. In the GaAs/InAs system quantum dot of a size about 10 nm produce more than 150 energy levels in the forbidden band. Simulation of light absorption in a QD requires the calculation of transitions probability between all the levels. Since GaAs and InAs are materials of a zinc blende structure type, for accurate calculation it is necessary to use an 8-band semiconductor model. In this case modeling of the internal quantum efficiency for a single dot without the use of a supercomputer is not advisable, because an ordinary laptop takes about a month for this task. Another practical way to calculate the absorption is the Empiric k-p Hamiltonian (EKPH) use [6]. This method could give an approximate result with accuracy comparable to 8-band model.

Modeling of the internal quantum efficiency
EKPH method is a four band k-p method for modeling crystals of zincblende type. It involves conduction band (cb) states and three sub-bands of valence band states: the heavy holes (hh) the light holes (lh) and the split off states (so).
In k•p methods the one-electron Hamiltonian is developed in matrix form in a basis

\[ \phi_{\nu,\mathbf{k}} = u_{\nu,0}(\mathbf{r}) e^{i \mathbf{k} \cdot \mathbf{r}} / \sqrt{2} \]  

(1)

where \( u_{\nu,0}(\mathbf{r}) \) are the Bloch functions in the \( \Gamma \) point of the Brillouin zone, \( \nu \) labels the \( cb, hh, lh \) and \( so \) bands and \( \mathbf{k} \) is an arbitrary wavevector. In the EKPH modeling starts by using the simplest Hamiltonian \( H_0 \) without spin orbit coupling (see it for example in Datta [7]) but then the dispersion functions implied by this Hamiltonian are changed into the empiric dispersion functions characterized by their energies at the \( \Gamma \) points and the measured effective masses for each sub-band. However the eigenvectors remain unchanged so leaving unchanged the diagonalization matrix of this Hamiltonian (which made with these eigenvectors).

In this paper InAs QD in GaAs host material has been modeled. The size of QD was 16 nm in lateral and 6 nm vertical dimensions. It should be noted the QDs varied in size. Here the median size with 10% variation is taken. If the QDs are characterized by a constant offset potential extended among the whole QD and there is assume the QDs to have the shape of a box or cylinder, then the calculation of the energy levels is done in few seconds. But the energy spectra for a different QD shape are different. Both cases are shown on figure 1.

**Figure 1.** Energy spectra for a different QD shapes (box of cylinder). QD material is InAs, host material is GaAs. Both modeled QDs have lateral size of 16 nm and height of 6 nm.

The difference between box and cylindrical models appears because of wavefunctions parts. If the QD has a shape of box, wavefunction could be considered as a product of periodic trigonometric functions (Sin or Cos), inside and exponents outside the quantum dot. This representation could be done by using separation of variables [7], which goes usually by rectangular coordinates.

If the shape of a quantum dot is taken as cylinder, the use of cylindrical coordinates is more reasonable. The wave functions here are the product of a periodic function and Bessel function of the first kind inside the quantum dot and the exponent and Bessel function of the second kind outside the quantum dot [8].
The calculation of the internal quantum yield (IQY) of a QD SC was done for both shapes. The difference between energy spectrums of box and cylindrical shape didn’t lead to big difference in calculated IQY curves. Such similar result is possible because of energy levels density in valence band. Indeed number of QD levels in cylindrical model is fewer. But for subband absorption only transition of energy less than host bandgap are actual. Furthermore the density of energy levels in valence band is high due to the high effective mass of the hh. So there are many transition of very similar energy in the host sub-bandgap region (0.9-1.4 eV).

The accuracy estimate was carried out relatively to real and well characterized QD SC prototype [3]. Calculated curves are given in figure 2 together with the measured IQY in the prototype (called SB in reference 3).

![Figure 2](image.png)

**Figure 2.** Internal Quantum Yield vs. photon energy. Blue line is drawn with the measured data in the QD SC prototype; red line is drawn with the data calculated for box-shaped QD, Green line is drawn with the data calculated for cylindrical-shape QD.

For the calculation of the IQY in the host sub-bandgap region (0.9-1.4 eV) numerous transitions have to be calculated. In photon absorptions there are around 200 confined hh states (depending on the size of the QD) and some few lh states that act as initial states; for final states there are the some few dozens of cb states, of which only few ones are within the host semiconductor bandgap and constitute the energy levels. The rest are within the conduction band forming the so called virtual bound states. There are more than 1000 transitions contributing to the sub-bandgap absorption. Once the absorption coefficients are calculated the calculation of the IQY is straightforward in about 2 hours with a simple laptop.

In the area of 0.9 eV there is quite good matching, but there is mismatch near the edge of host material absorption. This mismatch is the result of QD size unification. In modelled structure only QDs of a
size 16x16x6 nm$^3 \pm 5\%$ were considered. The variation of the QDs size supposed to be a Gaussian function. In real structure the distribution of the QD size could be different. For example in [2] there is shown a bimodal distribution of the QDs. For a better matching calculated and practical data each QD should be taken into account. This requires an AFM and TEM measurements for each single structure in a whole volume and modelling of each single QD.

**Conclusion**

In this paper IQY of the InAs/GaAs solar cell was modelled. Two shapes of QDs: box and cylinder were considered. 4-band EKPH method was used as the theoretical background of calculation. For the box model there is more QD levels in the host material bandgap. Due to the high effective mass of the hh in InAs QD levels are closely packed in the VB area. In CB area box QD produce more levels in the host bandgap than cylinder QD. Nevertheless final calculated curve in both cases goes very close. The reason for this is the smooth variation of transition energy in sub-bandgap region. The final calculated result was obtained in about two hour for both cases. Both simplification of QD shape give close results in terms of accuracy to the measured data. Thus the box approximation preferable to use in multithreading computer architecture due to higher amount of transition. The cylinder approximation can give faster result in a single core high performance computer.

**References**

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