Efficient Broadband Conversion via Quantum Dots with Built-in Charge

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ABSTRACT

Having been placed in a single p-i-n junction, quantum dots with built-in charge (Q-BIC) provide harvesting and conversion of sub-bandgap photons, increase absorption of above-bandgap photons, and provide effective tool for engineering of nanoscale potential in the quantum dot (QD) medium and microscale potential profile in the entire PV device. Potential barriers around charged QDs decrease the photoelectron capture and suppress recombination processes via QDs. Filling QDs predominantly from dopants in QD medium allows one to keep electroneutrality of QD medium and to create the microscale potential profile analogous to that in the best conventional single-junction solar cells. The Q-BIC technology is a promising basis for developing high-efficiency, broadband (all-weather), rugged, light-weight, scalable, and relatively inexpensive single-junction solar cells capable of converting of 35 - 50% of solar energy into electric power.

Keywords: quantum dot solar cell, conversion of IR radiation, quantum dots with built-in charge

1 INTRODUCTION

The maximum efficiency for the conversion of unconcentrated solar radiation by a conventional single-junction solar cell is given by the Shockley - Queisser limit, which is 31% for AM0 spectrum. This limitation results from the thermalization losses in conversion of above-bandgap photons as well as from a cut-off of the all below-bandgap photons (see Fig. 1). To get the photovoltaic efficiency above the Shockley-Queisser limit the electron levels and kinetics of photocarriers should be adjusted to the energy of incoming photons.

Several different approaches, such as multi-junction solar cell, fluorescent downconversion, hot-electron solar cell, and the intermediate band solar cell, are actively investigated to surpass the Shockley - Queisser limit [1]. To minimize thermalization losses, in multi-junction solar cells, each p-n junction cell is designed for effective harvesting of solar energy within a certain window close to the bandgap. Significant technological limitations of this technology are determined by the requirements to adjust a number of physical parameters in a cascade of heterojunctions (lattice match, thermal expansion match, current match etc.). For these reasons multi-junction cells are still expensive and are mainly employed in special missions.

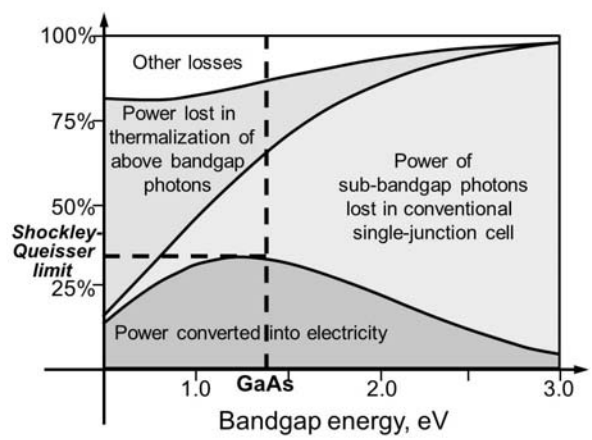

Figure 1: Thermalization losses in conversion of above-bandgap photons, losses due to cut-off of the all below-bandgap photons, and converted power in a conventional single-junction solar cell.

Hot-electron solar cell concept was proposed to minimize the relaxation to band edge losses. It assumes that the solar energy absorbed by the electrons is effectively redistributed over the whole electron subsystem and increases the average electron energy, i.e. electron temperature. In such photovoltaic device this thermal electron energy should be converted into the electric energy before the electrons cool down via interaction with crystal lattice. Let us note that recently proposed and actively studied the multi-exciton generation is a quantum analog of classical electron heating. The main problem for the practical realization of the hot-electron solar cell is the fast electron-phonon relaxation, which leads to effective cooling of hot electrons.

Intermediate band quantum dot solar cell has been very intensively investigated during the last decade. In this device the intermediate band is formed from discrete QD levels due to strong tunneling coupling between QDs [1]. The concept is analogous to the impurity solar cell where the intermediate band is created by impurity levels. Improvement of the photovoltaic conversion in QD intermediate band solar cell was expected due to specific photocarrier kinetics with the multiple exciton generation, which may reduce the relaxation losses related to the electron-phonon processes. Theoretical calculations predict that the intermediate band solar cell can provide a maximum efficiency of ~65%. However, intensive experimental efforts to improve intermediate band solar cells show that an increase in photovoltaic efficiency has not exceeded a few percent. QDs enhance the recombination via the intermediate band and in the best case, the QD-enhanced IR harvesting just slightly exceeds the QD-related recombination losses.

Thus, in spite of a number of approaches proposed to surpass the Shockley-Queisser limit, only multi-junction cell shows the photovoltaic efficiency above this limit. After intensive investigations of intermediate band solar cell, the key problem in improvement of the efficiency of a single-junction cell is well understood. Additional energy levels added to a single junction by impurities, quantum dots, or other nanoblocks for harvesting of corresponding photons unavoidably enhance the carrier recombination via the same levels. To overcome this problem, we propose to separate areas of such harvesting from the areas of photocarrier transfer.

2 CHARGING QUANTUM DOTS TO ENHANCE COUPLING TO IR RADIATION

Our novel approach is based on nanoscale engineering of electron processes by quantum dots with built-in charge. The charging of quantum dots is realized via selective doping of the interdot space [2-4]. For engineering of bipolar kinetics of photogenerated electrons and holes by charged quantum dots, we employ the huge difference between electron and hole kinetic processes. This difference is mainly determined by structures of electron and hole energy levels in QDs.

The level structure in InAs/GaAs quantum dots has been investigated in numerous photoluminescence measurements which show practically equidistant level positions of electrons and holes. The total level spacing, $\Delta E = \Delta E_e + \Delta E_h$ is found to be 60 – 80 meV. The ratio, $\Delta E_e/\Delta E_h$, is evaluated indirectly and changes from one 2 to 8 from one work to another. In our opinion, the specific equidistant positions of energy levels may be associated with the quasi-parabolic form of the confinement potential in InAs/GaAs QDs. In this model, the spacing ratio, $\Delta E_e/\Delta E_h$, is given by $(m_h/m_e)^{1/2} \approx 4$, which is in agreement with the scope of experimental results. Using this model we get: $\Delta E_e \approx 55$ meV and $\Delta E_h \approx 14$ meV. Therefore, the electron transitions in QDs significantly exceed the thermal energy and cannot be induced by thermal phonons, while the hole transitions are easily induced by acoustic thermal phonons.

The processes of light harvesting via QDs are shown in Fig. 2. Without dot charging the absorption of sub-bandgap photons can be realized exclusively via multi-step absorption, as it is shown in Fig. 2 (a). As we discussed above QDs play a role of shallow traps for holes and deep traps for electrons. Therefore, to stimulate electron transitions by IR radiation for photovoltaic applications, additional electrons should be placed in QDs. Corresponding processes in n-doped QD structures are presented in Figs. 2(b), 2(c), and 2(d)). Figure 2(b) describes a process where the electron trapped in a QD is excited by IR radiation from the localized to the conducting state. Figures 2(c) and 2(d) show other n-doping induced processes that involve inter-electron interaction in QDs. In Fig. 2(c) the radiation excites two electrons to QD excited states, then one of these electrons transfers to the conducting state and the other transfers to a low-energy state. In Fig. 2(d) the relaxation of electron to a low-energy state leads to the escape of a hole from the QD. We would like to highlight that, because of the small hole level spacing, the hole escape from QDs can be easily generated by hot (excited) electrons. Thus, doping should stimulate the radiation-induced electron escape from QDs. Therefore, contrary to the lasing applications of QDs, which are strongly enhanced by p-doping, the photovoltaic applications require n-doping.

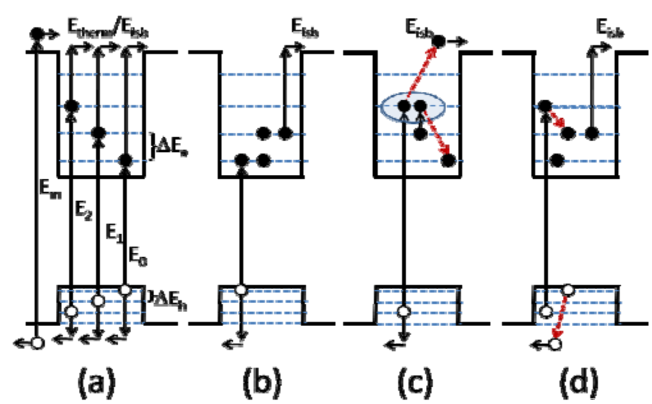

Figure 2: Absorption of electromagnetic radiation by uncharged QD (a) and additional processes due to QD charging (b), (c), and (d).

3 CHARGING QUANTUM DOTS TO CONTROL PHOTOCARRIER KINETICS

It is well-understood that the QDs are effective centers of recombination. Charging of QDs by selective doping provides an effective way to suppress capture and recombination processes.

The photoelectron capture to the n-charged QD is strongly suppressed by the repulsive Coulomb interaction between the electron and QD. In general, the capture may be realized via tunneling through the barrier or thermal excitation above the barrier. Tunneling processes strongly dominate in photoelectron capture by n-charged impurities. However, for QDs with the radius larger 5 - 10 nm the thermoexcitation processes dominate over tunneling and the capture rate exponentially decreases with increasing of the negative built-in dot charge [2-4],

$$\frac{1}{\tau_{capt}^{e}} = \pi N_d R^3 \tau_e^{-1} \exp\left[-\frac{Ne^2}{k_B T \kappa R}\right], \qquad (1)$$

where N is the number of electrons in the dot, N_d is the dot concentration, R is the quantum dot radius, τ_e is the electron-phonon inelastic scattering time which corresponds to transitions with characteristic electron level spacing in QD, and κ is the permittivity.

Equation (1) is derived in the simple model with spherical QDs. To study electric field and potential barriers around more realistic QDs, we used a simulation tool based on the nextnano3 software which solves self-consistently Schrödinger and Poisson equations. Figure 3 shows the potential profile around QDs in the form of truncated pyramids with large base and small height. The potential barriers are strongly asymmetric. The barriers in the QD planes, i.e. in the direction perpendicular to the current, are substantially smaller than the barriers in the direction of the current. Therefore, the electron trapping is most effective for electrons moving along A-B direction.

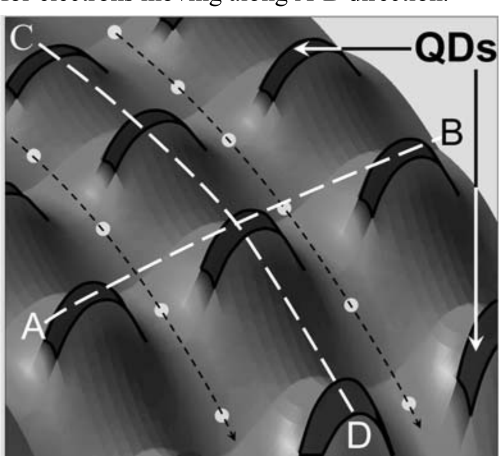

Figure 3: Potential profile around QDs in the form of truncated pyramids with large base and small height.

For modeling of photoelectron kinetics, we developed the simulation tool based on the Monte-Carlo method. Our software takes into account all basic scattering processes, such as electron scattering on acoustic, polar optical, and intervalley phonons. Figure 4 demonstrates the capture time of electron as a function of the built-in dot charge. As seen, the exponential dependence of the capture rate on the dot population is universal and directly related to the potential barriers that should be overcome by photoelectrons in capture processes.

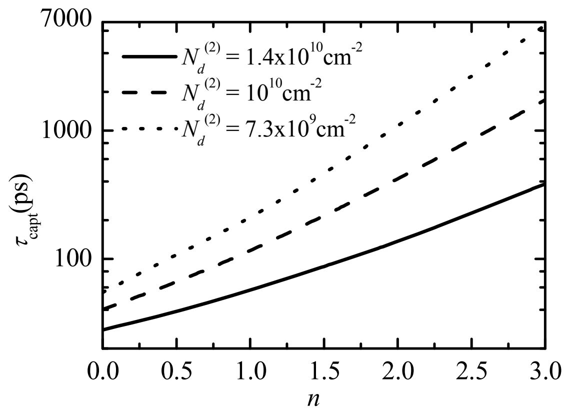

Figure 4: Capture time of photoelectrons as a function of the built-in dot charge (number of electrons) at various concentration of QDs in QD planes.

Now we discuss the hole capture by the n-charged QDs. It could be expected that the Coulomb attraction may increase the capture rate for holes, as it is widely observed for the capture on negatively charged impurities. In fact, for QDs the effect of charging is small, because of the relatively large size of QDs. In a simple model with the spherical dots, the hole capture rate is given by [4]

$$\frac{1}{\tau_{capt}^{h}} = \frac{4}{3}\pi N_d (R^*)^3 \tau_h^{-1}, \qquad (2)$$

where τ_h is the hole cascade relaxation time ($\tau_h \approx \tau_0 (3k_BT/\Delta E_h)$ and τ_0 is the relaxation time between adjacent hole levels); R^* is the dot radius, R, or the Thomson's radius, $R_{Th} = e^2N/(\kappa k_BT)$, depending on which of these parameters is the largest one. Simple evaluations show that the Thomson's radius is smaller than the typical base of the pyramidal QDs. Therefore, according to Eqs. (1) and (2), the *n*-charging of QDs exponentially suppresses the electron capture processes but does not practically affect the hole capture.

Inter-electron interaction is strongly enhanced for electrons in QDs as well as for photocarriers moving near QDs due to the carrier confinement. In particular, this leads to multi-exciton generation in QDs, which is important for photovoltaic applications. For hot photoelectrons with the energy above $\sim E_0$ moving near QDs the interaction leads to the inverse Auger processes, which increase the number of carriers in QDs. Also, the electrons trapped in QDs may be easily excited due to interaction with hot photoelectrons.

We would like to highlight that under sunlight the electron and hole capture rates are equated by changing of QD charge. In the "underdoped" structures DQs will be filled by photoelectrons, in the "overdoped" structures electrons will leave QDs. Therefore, to optimize the potential profile in QD solar cell, one should choose the optimal doping that provides equal electron and hole capture rates, i.e. $\tau^{e}_{capt}(N) = \tau^{h}_{capt}(N)$, where the filling of QDs, N, should correspond to the number of dopants per

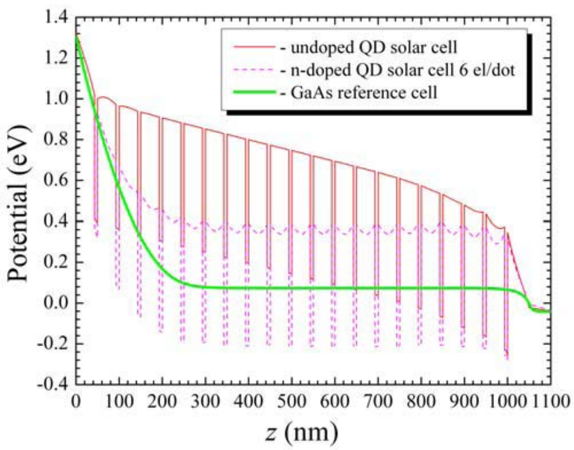

Figure 5: Macroscale potential profile of GaAs reference cell, undoped QD solar cell, and n-doped solar cell with six electrons per dot.

As it is shown in Fig. 5, the optimal n-doping of QD medium provides the potential profile similar to that in the optimized reference cell. Narrow conventional space-charge region effectively separates electrons and holes. It is strongly favorable for effective photovoltaic conversion.

4 EFFECT OF QD CHARGING ON SOLAR CELL PERFORMANCE

Having been placed in a single p-i-n junction, quantum dots with built-in charge provide harvesting and conversion of sub-bandgap photons, increase absorption of above-bandgap photons, and provide effective tool for engineering of nanoscale potential. Recently proposed by ARL – University at Buffalo team, the Q-BIC technology is a promising basis for developing high-efficiency, broadband (all-weather), rugged, light-weight, scalable, and relatively inexpensive single-junction solar cells capable of converting of 35 - 50% of solar energy into electric power. First set of photovoltaic devices based on Q-BIC structures with random positions of quantum dots has demonstrated [2] that the charging of QDs up to six electrons per dot increases the short-circuit current by 9 mA/cm^2 without degradation of the open-circuit voltage.

Table 1. Q-BIC solar cell parameters vs dot charge

Dot population	J_{SC} (mA/cm^2)	$\Delta_{IR} J_{SC}$ (mA/cm^2)	V_{OC} (V)	Fill Factor (%)	Efficiency (%)
Ref. cell (no dots)	**14.6**	**0**	**0.81**	**80**	**9.07**
0	**15.1**	**4.1**	**0.77**	**77**	**9.31**
2	**17.3**	**7.2**	**0.74**	**76**	**9.73**
3	**18.5**	**8.1**	**0.79**	**75**	**12.1**
6	**24.3**	**9.3**	**0.78**	**72**	**14.0**

Studying spectral characteristics of the photoresponse, we have also shown that the harvesting and conversion of the sub-bandgap IR radiation gives additional 5% to the photovoltaic efficiency [2]. Moreover, the IR conversion via QDs is significantly enhanced by the short-wavelength radiation due to strong inter-electron interaction in QD structures. This effect makes Q-BIC structures especially attractive for concentrating photovoltaics. Next step of optimization of Q-BIC PV devices is in progress.

In summary, the Q-BIC technology has the following attractive features:

- Strong harvesting of IR radiation via QD electron transitions that are strongly enhanced by the built-in-dot charge;
- Significant suppression of recombination due to the built-in-dot charge which creates the potential barriers around QDs and QD clusters;
- Large open-circuit voltage in photovoltaic devices due to optimization of potential profile;
- Wide possibilities for creating specific 3D potential profiles with various combinations of QD clusters, conducting channels, and barriers between clusters and channels;
- In Q-BIC devices the IR conversion is strongly enhanced by short-wavelength radiation, i.e. optical pumping which makes this technology especially attractive in combination with light concentrators;
- This approach does not require electron interdot coupling that leads to substantial limitations on fabrication of the intermediate band solar cell.

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