Solar Energy Materials & Solar Cells ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Releasing confined holes from type-II quantum dots by inelastic scattering with hot photoelectrons

A. Kechiantz [a,b,*], A. Afanasev [b], J.-L. Lazzari [c]

[a] Department of Physics, The George Washington University, Washington DC, USA
[b] Institute of Radiophysics and Electronics, NAS of Armenia, Ashtarak, Armenia[1]
[c] Aix Marseille Université, CNRS, CINaM UMR 7325, 13288, Marseille, France

ARTICLE INFO

Article history:
Received 9 July 2014
Received in revised form
23 January 2015
Accepted 29 January 2015

Keywords:
Solar cells
GaSb/GaAs Type-II quantum dots
Hot photoelectrons
Inelastic scattering
Exciton dissociation
Hole releasing

ABSTRACT

We study a novel architecture for quantum dot (QD) solar cells. While all models and experiments on QD solar cells studied QDs located in the depletion region, we focused on the solar cell structure in which an electron-blocking barrier spatially separates type-II QD absorber from the depletion region. It is important that these QDs are still within the diffusion length from the depletion region. Inter-band QD absorption of the part of solar spectrum with the photon energy less than the energy band gap in the spacers generates a large number of localized excitons in type-II QDs solar cells. The energy of such photons is not utilized in conventional solar cells. However, the proposed architecture enables QD solar cells to benefit from additional photocurrent generated by disintegrating of localized excitons.

Hereby we show that hot photoelectron collision with QDs facilitates exciton disintegration. One fifth of solar photons have energy exceeding GaAs bandgap by more than 0.5 eV. They generate hot photoelectrons that usually relax by releasing the excess energy to optical phonons in 1 ps time scale by multiple electron–phonon scattering. Our study has shown that collisions with QDs may compete with the scattering with optical phonons in GaSb/GaAs type-II QD absorber. The excess energy is transferred to confined holes. Such collisions enable confined holes to escape from QDs into mobile states in the valence band of absorber and dissociate excitons into mobile electrons and holes. Collection of these mobile carriers will increase both photocurrent and conversion efficiency limit of GaAs solar cells by estimated 50%, well above the Shockley–Queisser limit.

1. Introduction

We study a novel architecture for quantum dot (QD) solar cells. While all models and experiments on QD solar cells studied QDs located in the depletion region [1–3], we proposed a novel solar cell structure that an electron-blocking barrier spatially separates type-II QD absorber from the depletion region [4,5]. It is important that these QDs are still within the diffusion length from the depletion region.

Spatial separation of QDs from the depletion region promises fabrication of better quality p–n-junctions advancing from lower dark and leakage currents. When dislocations appear in the depletion region they facilitate the leakage current of p–n-junction. Unfortunately, dislocations usually accompany embedding of QDs into semiconductor [6]. Moreover, thermal generation–recombination of mobile carriers exponentially increases with reducing the semiconductor energy band gap [7]. This process leads to generation of dark current in the depletion region of p–n-junctions. Therefore, embedding of smaller energy band gap materials like QDs into the depletion region inevitably increases the dark current generated in the p–n-junction [8]. Numerous experimental studies of QD solar cells demonstrated such increase of the dark current [9,10].

Inter-band QD absorption of solar spectrum with photon energy less than energy band gap in the spacers generates a large number of localized excitons in type-II QDs solar cells. Such photons are not utilized in conventional solar cells. However, the proposed architecture enables QD solar cells to benefit from additional photocurrent generated by disintegrating of localized excitons.

We have already shown that intra-band QD absorption of long-wavelength part of solar spectrum with photon energy being less than the energy band gap of QDs facilitates exciton disintegration in GaSb/GaAs type-II QD absorber [8]. Such intra-band absorption transfers photon energy to confined holes. This enables confined holes to escape from QDs into mobile states in the valence band of absorber, which decomposes excitons into mobile electrons and

[1] (on leave).

* Correspondence to: Current address: Department of Physics, The George Washington University, 725 21st Street, NW, Washington DC 20052, USA.
E-mail address: kechiantz@gwu.edu (A. Kechiantz).

http://dx.doi.org/10.1016/j.solmat.2015.01.034
0927-0248/

holes. We have estimated that collection of such mobile carriers would increase both photocurrent and conversion efficiency limit of single junction GaAs solar cells by 50% in case of 500-sun concentrated illumination [8].

Hereby we show that hot photoelectron collisions with QDs, which was not previously discussed in [8], may also facilitate exciton disintegration. One fifth of solar photons have energy exceeding GaAs bandgap by more than 0.5 eV [7,11]. Such photons generate hot photoelectrons that usually relax in GaAs by releasing their excess energy to optical phonons in 1 ps time scale by multiple electron–phonon scattering [12–14].

In this paper we study inelastic scattering of hot photoelectrons with excitons localized in type-II QDs. Our study shows that photoelectron collision with QDs may compete with scattering with optical phonons in GaSb/GaAs type-II QD absorber. Photoelectrons transfer their excess energy to confined holes. Such collisions enable confined holes to escape from QDs into mobile states in the valence band of absorber and dissociate excitons into mobile electrons and holes. We also study the effect of illumination-induced non-equilibrium bending of energy bands in spatially separated type-II QD absorber. We demonstrate that such bending of energy bands facilitates photoelectron escape from absorber and diffusion of mobile electrons and holes through the stack of QD/spacer layers. Collection of those mobile carriers will increase both the photocurrent and conversion efficiency limit of GaAs solar cells, well above the Shockley–Queisser limit.

2. Model

2.1. p–i–p–n-structure of GaSb/GaAs type-II QD solar cell

The proposed solar cell has cap/QD absorber/buffer/substrate structure shown in Fig. 1. It includes two principal parts: GaAs p-n-junction and un-doped GaSb/GaAs type-II QD absorber. The latter is a stack of alternating GaSb QD and GaAs spacer layers. It is important that about 100 nm thick p^+-doped GaAs buffer layer spatially separates this multilayer QD absorber from the p–n-junction. On the left of the buffer, the p^+-doped cap layer covers the QD absorber such that, together with the buffer, these two p^+-doped layers sandwich the un-doped QD absorber. On the right of the buffer, the p^+-doped buffer and the n-doped substrate compose a GaAs p–n-junction. Energy band bending of such p–i–p–n-structure is shown in Fig. 1.

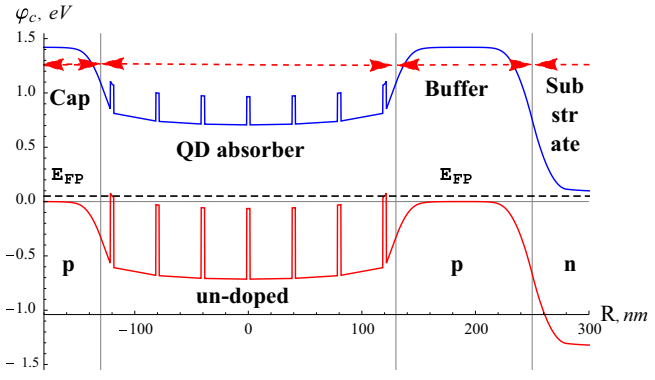

Fig. 1. Energy band bending in GaSb/GaAs type-II QD p–i–p–n-structure in the thermodynamic equilibrium. Each GaSb QD in the stack of QD/spacer layers is strained and 3 nm thick, has 26 nm × 26 nm × 3 nm volume; each GaAs spacer is 40 nm thick; E_{FP} is the Fermi level, $E_{FP}=0.05$ eV; p-doping of buffer and cap layers is $N_p=10^{18}$ cm^{-3}; n-doping of GaAs substrate is $N_n=10^{18}$ cm^{-3}. Calculation yields 9 confined holes per QD in the first QD layers, less than 1 hole per QD in the next QD layers; a negligible amount of mobile holes and electrons in spacers between QDs, and, hence, no exciton in absorber.

Solution of Poisson equation describes the energy band bending in such p–i–p–n-structure of proposed GaSb/GaAs type-II QD solar cell. In the absorber region, Poisson equation should be written as

$$\nabla^2\varphi=\rho_c\left(\varphi,\ \vec{r}\right)-\rho_v\left(\varphi,\vec{r}\right) \tag{1}$$

$$\rho_v=\frac{2kTN_v}{N_pL_{Deb}^2}\left[F_{1/2}\left(-E_{Fp}\right)-F_{1/2}\left(\varphi\left(\vec{r}\right)-E_{Fp}-\delta E_{FQ}\left(\vec{r}\right)+\Delta\varepsilon_v\left(\vec{r}\right)\right)\right] \tag{2}$$

$$\rho_c=\frac{2kTN_c}{N_pL_{Deb}^2}\left[F_{1/2}\left(E_{Fp}-\varepsilon_g\right)-F_{1/2}\left(-\varphi\left(\vec{r}\right)-\varepsilon_g-\Delta\varepsilon_c\left(\vec{r}\right)+E_{Fp}+\delta E_{Fn}\right)\right] \tag{3}$$

where N_c and N_v are the density of states at the conduction and valence band edges, respectively; ρ_c and ρ_v are the density of charge in $e/(\varepsilon\varepsilon_0kT)$ units; e is the electron charge; T is the temperature; k is the Boltzmann constant; ε is the dielectric constant; ε_0 is the permittivity in vacuum; φ is the bending of the energy band edges represented as dimensionless electron potential in kT/e units; $\vec{r}$ is the Cartesian coordinates; E_{Fp} is the energy of the Fermi level calculated in kT/e units from the valence band edge of the buffer layer, $E_{Fp}=\ln(N_v/N_p)$; δE_{Fn} and δE_{FQ} are the split of quasi-Fermi levels of mobile electron accumulated in the conduction band of QD absorber and holes confined in QDs, respectively; $\Delta\varepsilon_c$, $\Delta\varepsilon_v$ and ε_g are the energy band offsets in the conduction and valence bands and the energy band gap in GaAs, respectively; $F_{1/2}(E)$ is the Fermi–Dirac integral such that the density of mobile electrons and holes in the buffer reduce to $N_c\,F_{1/2}(E_{Fp}-\varepsilon_g)$ and $N_v\,F_{1/2}(-E_{Fp})$, respectively; L_{Deb} and N_p are the Debye length and the density of mobile holes in the buffer, $L_{Deb}=\sqrt{2\varepsilon\varepsilon_0kT/e^2N_p}$.

Density of charge in Eqs. (2) and (3) is written in the form of Fermi–Dirac integrals. This allows to take into account that the energy band bending around QDs may turn the un-doped spacers into a degenerate state. Eqs. (2) and (3) also take into account that absorption of light or injection of charge carriers may split the Fermi level. The split yields $E_{Fp}+\delta E_{Fn}$ quasi-Fermi level for mobile electrons in the conduction band of QD absorber and $E_{Fp}+\delta E_{FQ}$ for holes confined in QDs in absorber, where $\delta E_{Fn}\neq0$ and $\delta E_{FQ}\neq0$.

2.2. Inelastic scattering of photoelectrons with type-II QDs

Impact ionization of atoms has been well studied before [15]. Since QDs are like artificial atoms buried in the absorber, we handled inelastic scattering with excitons localized around QDs as an impact ionization mechanism of QDs.

Just after generation in GaSb/GaAs type-II QD absorber, some photoelectrons (as well as photogenerated holes) have excess energy enough for pumping of confined holes from QDs into the mobile states of valence band. The latter facilitates disintegration of localized excitons. The Hamiltonian of such scattering is H_e+H_Q+W, were $H_e=-\hbar^2\nabla^2/2m$ relates to a mobile photoelectron in the conduction band of absorber; H_Q relates to the ensemble of excitons localized at QD; m is the photoelectron effective mass; and W is the extra potential energy resulting from the photoelectron Coulomb interaction with the ensemble of excitons. Assuming the photoelectron does not interact with holes confined in QDs before and after the scattering, the interaction potential vanishes at that time, $W=0$.

The Schrödinger equation $H_e\varphi_{ek}=E_k\varphi_{ek}$ determines the mobile photoelectron eigenfunctions and eigenvalues in the conduction band of the QD absorber before the scattering as $\varphi_{e\boldsymbol{k}_1}=\exp(i\boldsymbol{k}_1\boldsymbol{r})$ and $E_{\boldsymbol{k}_1}=\hbar^2\boldsymbol{k}_1^2/2m$, and as $\varphi_{e\boldsymbol{k}_2}=exp(i\boldsymbol{k}_2\boldsymbol{r})$ and $E_{\boldsymbol{k}_2}=\hbar^2\boldsymbol{k}_2^2/2m$

Please cite this article as: A. Kechiantz, et al., Releasing confined holes from type-II quantum dots by inelastic scattering with hot photoelectrons, Solar Energy Materials and Solar Cells (2015), http://dx.doi.org/10.1016/j.solmat.2015.01.034