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Review

A review on energy conversion efficiency mechanisms in quantum dot intermediate band nanostructure solar cells

Nima E. Gorji[1,2]

[1]Department of Solid State Physics, Faculty of Physics, University of Tabriz, Tabriz 51566, Iran.
[2]Department of Electrical Engineering, University of Bologna, Bologna 40136, Italy.

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Quantum Dots used in so-called third-generation Solar Cells have the potential to significantly increase the photon conversion efficiency in two ways: (1) the production of multiple excitons from a single photon of sufficient energy and (2) the formation of intermediate bands in the bandgap that enhances its photogenerated current, via the two-step absorption of sub-band gap photons.

Key words: Quantum Dot Solar Cells, Multiple Exciton Generation, Intermediate Band.

INTRODUCTION

We have reviewed the application of quantization effects in nanocrystal particles to produce third-generation Quantum Dot (QD) Solar Cells (SC) that leads to very low cost solar electricity. We discuss two roads based on semiconductor QDs and QDs arrays that will lead to ultrahigh efficiencies through enhanced photocurrent. First approach is based on using high-energy photons of solar spectrum to create multiple carrier pairs and the second is based on the formation of an intermediate band (IB) within the semiconductor bandgap that enables below band gap energy photons to be absorbed through transitions from the valence band to the IB and from the IB to the conduction band. As it is well known, the maximum thermodynamic efficiency of about 31% for the conversion of unconcentrated solar irradiance into electrical free energy in the radiative limit was calculated by Shockley and Queisser in 1961 by assuming the detailed balance, a single threshold absorber and thermal equilibrium between electrons and phonons (Shockley and Queisser, 1961). Two major factors limit the conversion efficiency: (1) losing excess kinetic energy of hot photogenerated carriers created by the absorption of supra-bandgap photons as heat through phonon emission, and (2) having low energy photons than bandgap which are not absorbed. The first approach to third-generation solar cells discussed here addresses the thermalization loss of hot electrons, whereas the second approach addresses the loss of sub- bandgap photons.

MULTIPLE EXCITON GENERATION SOLAR CELLS

The Shockley and Queisser efficiency is accessible in semiconductors with bandgaps ranging from about 1.25 to 1.45 eV, while the solar spectrum contains photons with energies ranging from about 0.5 to 3.5 eV. Photon energy below the semiconductor bandgap does not absorb, while for energies above the bandgap charge carriers (electrons and holes) with a total excess kinetic energy equal to the difference between the photon energy and the bandgap will produce. Such carriers are named as ‘hot electrons and hot holes. There are two fundamental pathways to prevent the thermalization loss produced from the absorption of high-energy photons

E-mail: nima.s.gorji@gmail.com.

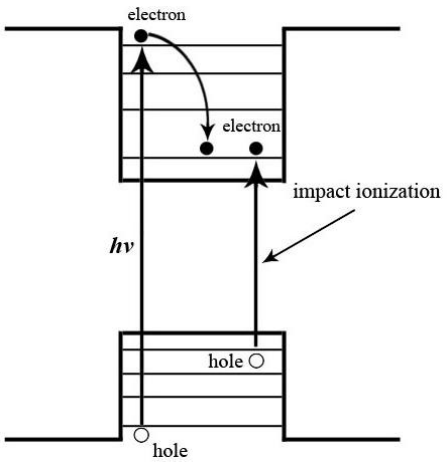

Figure 1. The Impact ionization effect in a QD (reverse Auger effect).

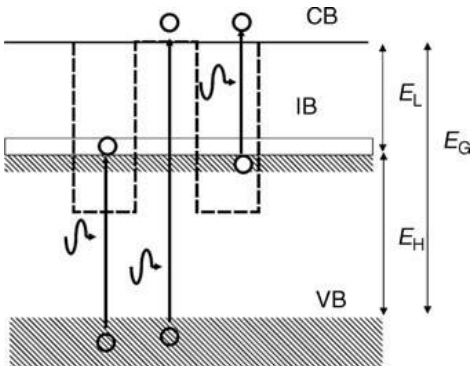

Figure 2. Structure of an intermediateband (IB) material.

above the bandgap in a single-bandgap system. One way produces an enhanced photovoltage and the other way produces an enhanced photocurrent. Furthermore, in full solar concentration (46,050 suns), both approaches converge at 86% conversion efficiency. The first requires the hot carriers to be extracted from the photoconverter before they cool (Nozik, 2001; Ross and Nozik, 1982; Boudreaux et al., 1980), and it results in a thermodynamic limit of about 66% at one sun. Whereas the latter requires the hot carriers to produce two or more electron–hole pairs (Landsberg et al., 1993; Kolodinski et al., 1993), which in QD is known as multiple exciton generation (MEG) (Ellingson et al., 2005) and it is termed as Impact Ionization in bulk semiconductors. Impact Ionization is an inverse process of the Auger process whereby two electron–hole pairs recombine to produce a single highly energetic electron–hole pair. This process leads to a thermodynamic limit of about 45% (Hanna and Nozik, 2006). The impact ionization efficiency does not reach significant values until photon energies reach the ultraviolet region of the spectrum. Therefore the impact ionization in bulk semiconductors has not contributed significantly to improvement of quantum yields in working solar cells. However, the rate of Auger processes, including the inverse Auger process of exciton generation, are well enhances due to confinement levels and the concomitant increase in electron-hole Coulomb interaction in quantum dots.

In addition, in the QDs, carriers are 3D confined and crystal momentum is not a good quantum number and does not need to be conserved (Figure 1). High efficient MEG by one photon has been recently reported in PbSe, PbS, PbTe, and CdSe nanocrystals (Ellingson et al., 2005; Schaller and Klimov, 2004; Murphy et al., 2006; Shabaev et al., 2006; Schaller et al., 2005, 2006).

A Quantum Yield (QY) of 300% and 700% was reported for 3.9 nm diameter PbSe QDs at photon energy of 4*E*g and 8*Eg* indicating the formation of three excitons per photon for every photoexcited QD in the sample respectively (Schaller et al., 2006). A possible mechanism for MEG also introduces that it involves a coherent superposition of multiple excitonic states, meaning that multiple excitons are essentially created instantly upon absorption of high-energy photons (Ellingson et al., 2005; Shabaev et al., 2006). Other models for explaining MEG have also been published recently (Schaller et al., 2005b; Franceschetti et al., 2006**)**.

INTERMEDIATE-BAND SOLAR CELLS

To capture and use photons which are less than the bandgap energy, IB solar cells are based on intermediate band materials (Luque and Marti, 1997). These materials are characterized by the existence of an intermediate band located between the conventional semiconductor conduction band (CB) and valence band (VB) (Figure 2).

Due to the IB, photons with energy below the bandgap can contribute to the cell photocurrent by exciting electrons from the VB to the IB and from the IB to the CB. However, more importantly, owing to the IB isolation from the CB and the VB by a zero density of states, “carrier relaxation” between bands become difficult (Nozik, 2003; Woggon, 1996; Mukai and Sugawara, 1999) and its carriers should be delocalized in the IB by increasing their density (Martí et al., 2001) until the wavefunctions make a good overlap and become delocalized (Mott transition) (Mott, 1968).

This is comparable to the miniband formation illustrated in Figure 3 and it is discussed above for QD arrays (Luque et al., 2003; Luque et al., 2002). To emphasize on one of them, we shall mention the reason recently discussed in Luque and Martí, 2001, that the introduction of energy levels within the semiconductor bandgap is not expected to create nonradiative recombination centers that reduce the performance of the cell instead of improving it. The study of the limiting photovoltaic

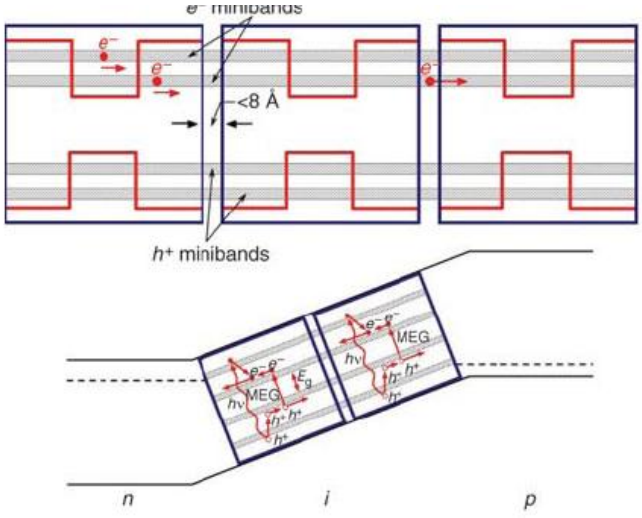

Figure 3. Miniband formation in a p-i-n structure.

conversion efficiency of the IB approach reveals a limiting efficiency of 47% at 1 sun, 63% at full solar concentration for this concept, as compared with 43% for two gaps tandem solar cell at 1 sun, 55% for full solar concentration (Luque and Marti, 1997, 2001). The basic structure of QD–IBSC prototype grown by molecular beam epitaxy in the Stranski–Krastanov growth mode consist of 10 layers of InAs/GaAs QDs sandwiched by p and n emitters of GaAs (Nakata et al., 1999). Although, the photogenerated current was approximately same, but the quantum efficiency of the cells reveal that the QD–IB solar cell exhibits an extended response for photon with energies lower than the GaAs bandgap. Nevertheless, analysis of the combined data from quantum efficiency and electroluminescence measurements, suggests that the IB approach can yield improved efficiency with improved materials (Luque et al., 2005, 2006, 2004).

QUANTUM DOT SOLAR CELLS

The two fundamental pathways for enhancing the conversion efficiency (increased photovoltage) (Nozik, 2001; Ross and Nozik, 1982; Boudreaux et al., 1980) or increased photocurrent (Nozik, 2001; Landsberg et al., 1993; Kolodinski et al., 1993) can be accessed in principle, in three different QD solar cell configurations.

Quantum dots inserted in p-i-n cells

Inserting QDs as 3D arrangement into a 1D-superlattice p-i-n structure (Figure 3) with a suitable small distance between the QD layers leads to strong electronic coupling and produces minibands named as intermediate band for producing long-range electron transport (Nozik, 2001). By slowing the carrier cooling and permitting the transport and collection of hot carriers in the respective p and n contacts, impact ionization is expected to occur in the miniband and enhance the photocurrent. However, hot electron transport/collection and impact ionization cannot occur simultaneously. Experimentally, significant progress is made in forming 3D arrays of both colloidal (Aroutiounian et al., 2001, 2005; Murray et al., 2000; Mićić et al., 2001, 1998) and epitaxial (Nakata et al., 1999) II–VI and III–V QDs. Arranging QDs in i-region of a p-i-n structure needs the evaporation and crystallization of homogeneous colloidal QDs. QDs with broader size distributions lead to high degree of disorder. After the forming of first layer of epitaxial QDs, following layers tend to form on top of each other (Nakata et al., 1999). Major issues are the nature of the electronic states as a function of inter-dot distance, Transport properties of QDs, array order versus disorder, QD orientation and shape, surface states, surface tinucture/passivation and surface chemistry.

Nanocrystalline TiO_2 solar cells sensitized by Quantum Dots

Dye-sensitization of nanocrystalline TiO_2 layers are recent capable kinds of PV cells (Hagfeldt et al., 2000; Moser et al., 1998). By adding the dye molecules into the highly porous nanocrystalline 10–20 μm TiO_2 film, they will be absorbed chemically to the surface of 10–30 nm-size TiO_2 particles. If dye molecules photoexcited, electrons will escape from the excited state of the dye to the conduction band of the TiO_2 which result in affecting charge separation and producing a PV effect. The cell circuit is completed using a non-aqueous redox electrolyte that contains I^-/I_3^- and a Pt counter electrode which make the reduction of the adsorbed photooxidized dye go back to its initial non-oxidized state. For the QD-sensitized cell, QDs are substituted instead of the dye molecules. They can be adsorbed from a colloidal QD solution (Zaban et al., 1998) or produced in situ Quantum dot solar cell configuration (Vogel et al., 1994; Weller, 1991; Liu and Kamat, 1993; Hoyer and Konenkamp, 1995). Successful PV effects in such cells have been reported for several semiconductor QDs including InP, CdSe, CdS and PbS (Zaban et al., 1998; Vogel et al., 1994; Weller, 1991; Liu and Kamat, 1993; Hoyer and Konenkamp, 1995). Possible advantages of QDs over dye molecules are the tenability of optical properties with size and better heterojunction formation with solid hole conductors. A unique capability of the QD-sensitized solar cell is the production of QY greater than one by impact ionization this capability produces higher conversion efficiencies than dye-sensitized solar cells.

Quantum dots dispersed in conducting polymers

The structures consisting of the dispersed QDs in a blend

of electron- and hole-conducting polymers have shown PV effects. In this structures, a disordered array of CdSe QDs is formed in a hole-conducting polymer-MEH-PPV (poly (2-methoxy, 5-(2-ethyl)-hexyloxy-p-henylenevinylene) (Greenham et al., 1996). Photogenerated holes of the QDs are injected into the MEH-PPV polymer phase, and they are collected via an electrical contact to the polymer phase. The electrons remain in the CdSe QDs and they are collected through diffusion and percolation in the nanocrystalline phase to an electrical contact to the QD network. Initial results show relatively low conversion efficiencies (Greenham et al., 1996, 1997) but improvement has been reported with rod-like CdSe QD shapes (Huynh et al., 2003) embedded in poly(3-hexylthiophene) (the rod-like shape enhances electron transport through the nanocrystalline QD phase). In another configuration (Arango et al., 1999), a polycrystalline TiO_2 layer is used as the electron-conducting phase and MEH-PPV is used to conduct the holes. The electrons and holes are injected into their respective transport mediums upon photoexcitation of the QDs. This scheme is the inverse of light-emitting diode structures based on QDs (Dabbousi et al., 1995; Colvin et al., 1994; Schlamp et al., 1997; Mattoussi et al., 1999; 1998). In the PV cell, each type of carrier-transporting polymer would have a selective electrical contact for removing the respective charge carriers and electron–hole recombination at the interfaces of the two polymers blends needs to enhancement.

Also, if the QDs can be guided into producing impact ionization process, the configuration can be greatly benefiting (Mattoussi et al., 1998).

CONCLUSION

This article considered a study on principles of the MEG and IB QDs solar cells. Inserting QDs as very efficient particles to enhance photocurrents and managing the efficiency of the 3th generation of SCs have been investigated. For example, three types of configurations for QD solar cells are described here which can produce enhanced photocurrent, and the thermodynamic efficiencies.

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