



ELSEVIER

Physica E 14 (2002) 115–120

PHYSICA E

www.elsevier.com/locate/physa

Quantum dot solar cells

A.J. Nozik*

National Renewable Energy Laboratory, Center for Basic Sciences, 1617 Cole Boulevard, Golden, CO 80401, USA

Abstract

Quantum dot (QD) solar cells have the potential to increase the maximum attainable thermodynamic conversion efficiency of solar photon conversion up to about 66% by utilizing hot photogenerated carriers to produce higher photovoltages or higher photocurrents. The former effect is based on miniband transport and collection of hot carriers in QD array photoelectrodes before they relax to the band edges through phonon emission. The latter effect is based on utilizing hot carriers in QD solar cells to generate and collect additional electron–hole pairs through enhanced impact ionization processes. Three QD solar cell configurations are described: (1) photoelectrodes comprising QD arrays, (2) QD-sensitized nanocrystalline TiO₂, and (3) QDs dispersed in a blend of electron- and hole-conducting polymers. These high-efficiency configurations require slow hot carrier cooling times, and we discuss initial results on slowed hot electron cooling in InP QDs. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hot electrons; Quantum dots; (Ultra-high photovoltaic) conversion efficiency; Impact ionization; Efficiency limits

1. Introduction

The maximum thermodynamic efficiency for the conversion of unconcentrated solar irradiance into electrical free energy in the radiative limit assuming detailed balance and a single threshold absorber was calculated by Shockley and Queisser in 1961 [1] to be about 31%; this analysis is also valid for the conversion to chemical free energy [2,3]. Since conversion efficiency is one of the most important parameters to optimize for implementing photovoltaic and photochemical cells on a truly large scale [4], several schemes for exceeding the Shockley–Queisser (S–Q) limit have been proposed and are under active investigation. These approaches include tandem

cells [5], hot carrier solar cells [6–8], solar cells producing multiple electron–hole pairs per photon through impact ionization [9,10], multiband and impurity solar cells [4,11], and thermophotovoltaic/thermophotonic cells [4]. Here, we will only discuss hot carrier and impact ionization solar cells, and the effects of size quantization on the carrier dynamics that control the probability of these processes.

The solar spectrum contains photons with energies ranging from about 0.5 to 3.5 eV. Photons with energies below the semiconductor band gap are not absorbed, while those with energies above the band gap create electrons and holes with a total excess kinetic energy equal to the difference between the photon energy and the band gap. This excess kinetic energy creates an effective temperature for the carriers that is much higher than the lattice temperature; such carriers are called “hot electrons and hot holes”, and their initial temperature upon photon absorption

* Tel.: +1-303-384-6603; fax: +1-303-384-6655.

E-mail address: anozik@nrel.urel.gov (A.J. Nozik).

can be as high as 3000 K with the lattice temperature at 300 K. The division of this kinetic energy between electrons and holes is determined by their effective masses, with the carrier having the lower effective mass receiving more of the excess energy [6].

A major factor limiting the conversion efficiency in single band gap cells to 31% is that the absorbed photon energy above the semiconductor band gap is lost as heat through electron–phonon scattering and subsequent phonon emission, as the carriers relax to their respective band edges (bottom of conduction band for electrons and top of valence for holes). The main approach to reduce this loss in efficiency has been to use a stack of cascaded multiple p–n junctions with band gaps better matched to the solar spectrum; in this way higher-energy photons are absorbed in the higher-band-gap semiconductors and lower-energy photons in the lower-band-gap semiconductors, thus reducing the overall heat loss due to carrier relaxation via phonon emission. In the limit of an infinite stack of band gaps perfectly matched to the solar spectrum, the ultimate conversion efficiency at one sun intensity can increase to about 66%.

Another approach to increasing the conversion efficiency of photovoltaic cells by reducing the loss caused by the thermal relaxation of photogenerated hot electrons and holes is to utilize the hot carriers before they relax to the band edge via phonon emission [6]. There are two fundamental ways to utilize the hot carriers for enhancing the efficiency of photon conversion. One way produces an enhanced photovoltage, and the other way produces an enhanced photocurrent. The former requires that the carriers be extracted from the photoconverter before they cool [7,8], while the latter requires the energetic hot carriers to produce a second (or more) electron–hole pair through impact ionization [9,10]—a process that is the inverse of an Auger process whereby two electron–hole pairs recombine to produce a single highly-energetic electron–hole pair. In order to achieve the former, the rates of photogenerated carrier separation, transport, and interfacial transfer across the contacts to the semiconductor must all be fast compared to the rate of carrier cooling [8,12–14]. The latter requires that the rate of impact ionization (i.e. inverse Auger effect) be greater than the rate of carrier cooling and other relaxation processes for hot carriers.

Hot electrons and hot holes generally cool at different rates because they generally have different effective masses; for most inorganic semiconductors, electrons have effective masses that are significantly lighter than holes and consequently cool more slowly. Another important factor is that hot carrier cooling rates are dependent upon the density of the photogenerated hot carriers (viz., the absorbed light intensity) [15–17]. Here, most of the dynamical effects we will discuss are dominated by electrons rather than holes; therefore, we will restrict our discussion primarily to the relaxation dynamics of photogenerated electrons.

Finally, in recent years it has been proposed [8,12,13,18–21], and experimentally verified in some cases [6], that the relaxation dynamics of photogenerated carriers may be markedly affected by quantization effects in the semiconductor (i.e., in semiconductor quantum wells, quantum wires, QDs, superlattices, and nanostructures). That is, when the carriers in the semiconductor are confined by potential barriers to regions of space that are smaller than or comparable to their deBroglie wavelength or to the Bohr radius of excitons in the semiconductor bulk, the relaxation dynamics can be dramatically altered; specifically the hot carrier cooling rates may be dramatically reduced, and the rate of impact ionization could become competitive with the rate of carrier cooling [6] (see Fig. 1).

Greatly, slowed hot electron cooling in InP QDs has been observed by the research group at NREL [22]. For QDs, one mechanism for breaking the phonon bottleneck that is predicted to slow carrier cooling in QDs and hence allow fast cooling is an Auger process. Here a hot electron can give its excess kinetic energy to a thermalized hole via an Auger process, and then the hole can then cool quickly because of its higher effective mass and more closely spaced quantized states. However, if the hole is removed from the QD core by a fast hole trap at the surface, then the Auger process is blocked and the phonon bottleneck effect can occur, thus leading to slow electron cooling. This effect was first shown for CdSe QDs [23,24]; it has now also been shown for InP QDs, where a fast hole trapping species (Na biphenyl) was found to slow the electron cooling to about 7 ps [22]. This is to be compared to the electron cooling time of 0.3 ps for passivated InP QDs without a hole trap present and

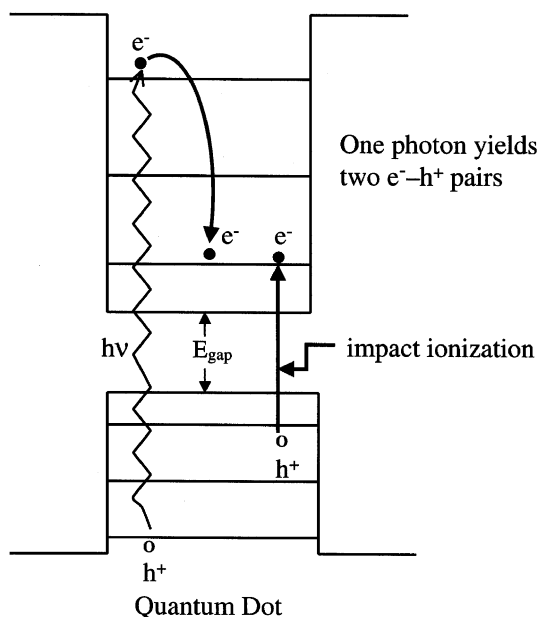


Fig. 1. Enhanced photovoltaic efficiency in QD solar cells by impact ionization (inverse Auger effect).

thus where the holes are in the QD core and are able to undergo an Auger process with the electrons [22].

2. Quantum dot solar cell configurations

The two fundamental pathways for enhancing the conversion efficiency (increased photovoltage [7,8] or increased photocurrent [9,10]) can be accessed, in principle, in three different QD solar cell configurations; these configurations are shown in Fig. 2 and they are described below. However, it is emphasized that these potential high-efficiency configurations are speculative and there is no experimental evidence yet that demonstrates actual enhanced conversion efficiencies in any of these systems.

2.1. Quantum dot arrays in p-i-n cells

In this configuration, the QDs are formed into an ordered 3-D array with inter-QD spacing sufficiently small such that strong electronic coupling occurs and minibands are formed to allow long-range electron transport; the QD array is placed in the intrinsic region

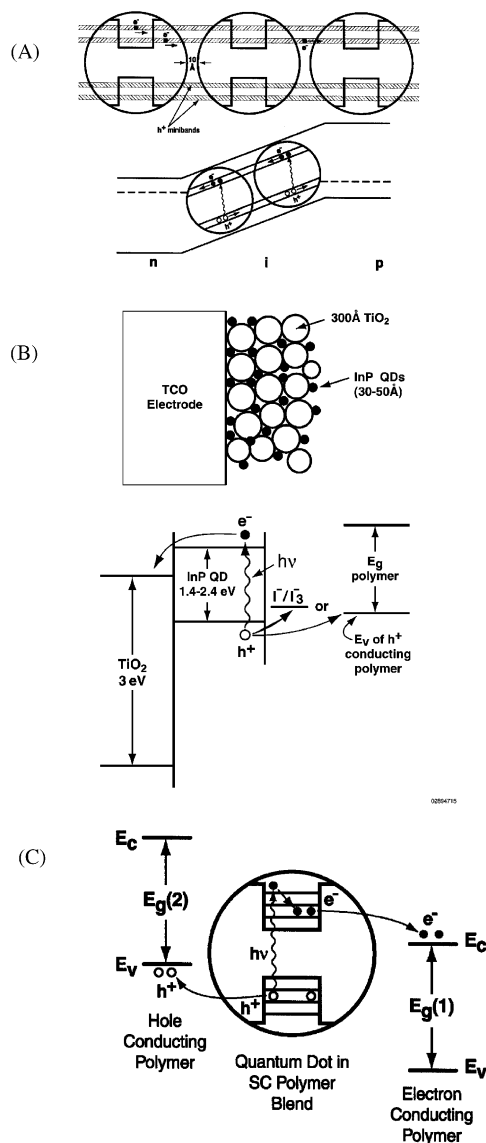


Fig. 2. Configurations for QD solar cells. (a) a QD array used as a photoelectrode for a photoelectrochemical or as the i-region of a p-i-n photovoltaic cell; (b) QDs used to sensitize a nanocrystalline film of a wide band gap oxide semiconductor (viz., TiO_2) to visible light. This configuration is analogous to the dye-sensitized solar cell where the dye is replaced by QDs; (c) QDs dispersed in a blend of electron- and hole-conducting polymers. In configurations (a), (b) and (c), the occurrence of impact ionization could produce higher photocurrents and higher conversion efficiency. In (a), enhanced efficiency could be achieved either through impact ionization or hot carrier transport through the minibands of the QD array resulting in a higher photopotential.

of a $p^+ - i - n^+$ structure (see Fig. 2a). The QD array is a 3-D analog to a 1-D superlattice and the miniband structures formed therein [6]. The delocalized quantized 3-D miniband states could be expected to slow the carrier cooling and permit the transport and collection of hot carriers at the respective p and n contacts to produce a higher photopotential in a PV cell or in a photoelectrochemical cell where the 3-D QD array is the photoelectrode [25]. Also, impact ionization might be expected to occur in the QD arrays, enhancing the photocurrent (see Fig. 1). However, hot electron transport/collection and impact ionization cannot occur simultaneously; they are mutually exclusive and only one of these processes can be present in a given system.

Significant progress has been made in forming 3-D arrays of both colloidal [26] and epitaxial [27] II–VI and III–V QDs. The former have been formed via evaporation and crystallization of colloidal QD solutions containing a uniform QD size distribution; crystallization of QD solids from broader size distributions lead to close-packed QD solids, but with a high degree of disorder. Concerning the latter, arrays of epitaxial QDs have been formed by successive epitaxial deposition of epitaxial QD layers; after the first layer of epitaxial QDs is formed, successive layers tend to form with the QDs in each layer aligned on top of each other [27,28]. Theoretical and experimental studies of the properties of QD arrays are currently under way. Major issues are the nature of the electronic states as a function of inter-dot distance, array order vs. disorder, QD orientation and shape, surface states, surface structure/passivation, and surface chemistry. Transport properties of QD arrays are also of critical importance, and they are under investigation.

2.2. *Quantum dot-sensitized nanocrystalline TiO₂ solar cells*

This configuration is a variation of a recent promising new type of photovoltaic cell that is based on dye-sensitization of nanocrystalline TiO₂ layers [29–31]. In this latter PV cell, dye molecules are chemisorbed onto the surface of 10–30 nm size TiO₂ particles that have been sintered into a highly porous nanocrystalline 10–20 μm TiO₂ film. Upon photoexcitation of the dye molecules, electrons are very efficiently injected from the excited state of the dye

into the conduction band of the TiO₂, affecting charge separation and producing a photovoltaic effect.

For the QD-sensitized cell, QDs are substituted for the dye molecules; they can be adsorbed from a colloidal QD solution [32] or produced in situ [33–36]. Successful PV effects in such cells have been reported for several semiconductor QDs including InP, CdSe, CdS, and PbS [32–36]. Possible advantages of QDs over dye molecules are the tunability of optical properties with size and better heterojunction formation with solid hole conductors. Also, as discussed here, a unique potential capability of the QD-sensitized solar cell is the production of quantum yields >1 by impact ionization (inverse Auger effect) [37]. Dye molecules cannot undergo this process. Efficient inverse Auger effects in QD-sensitized solar cells could produce much higher conversion efficiencies than are possible with dye-sensitized solar cells.

2.3. *Quantum dots dispersed in organic semiconductor polymer matrices*

Recently, photovoltaic effects have been reported in structures consisting of QDs forming junctions with organic semiconductor polymers. In one configuration, a disordered array of CdSe QDs is formed in a hole-conducting polymer—MEH-PPV (poly(2-methoxy,5-(2'-ethyl)-hexyloxy-p-phenylenevinylene) [38]. Upon photoexcitation of the QDs, the photogenerated holes are injected into the MEH-PPV polymer phase, and are collected via an electrical contact to the polymer phase. The electrons remain in the CdSe QDs and 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 [38,39] but improvements have been reported with rod-like CdSe QD shapes [40] embedded in poly(3-hexylthiophene) (the rod-like shape enhances electron transport through the nanocrystalline QD phase). In another configuration [41], a polycrystalline TiO₂ layer is used as the electron conducting phase, and MEH-PPV is used to conduct the holes; the electron and holes are injected into their respective transport mediums upon photoexcitation of the QDs.

A variation of these configurations is to disperse the QDs into a blend of electron and hole-conducting polymers [42]. This scheme is the inverse of

light-emitting diode structures based on QDs [43–47]. In the PV cell, each type of carrier-transporting polymer would have a selective electrical contact to remove the respective charge carriers. A critical factor for success is to prevent electron–hole recombination at the interfaces of the two-polymer blends; prevention of electron–hole recombination is also critical for the other QD configurations mentioned above.

All of the possible QD-organic polymer photo-voltaic cell configurations would benefit greatly if the QDs can be coaxed into producing multiple electron–hole pairs by the inverse Auger/impact ionization process [37]. This is also true for all the QD solar cell systems described above. The most important process in all the QD solar cells for reaching very high conversion efficiency is the multiple electron–hole pair production in the photoexcited QDs; the various cell configurations simply represent different modes of collecting and transporting the photogenerated carriers produced in the QDs.

Acknowledgements

This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences and the Photovoltaics Program of the Office of Energy Efficiency and Renewable Energy.

References

- [1] W. Shockley, H.J. Queisser, *J. Appl. Phys.* 32 (1961) 510.
- [2] R.T. Ross, *J. Chem. Phys.* 45 (1966) 1.
- [3] R.T. Ross, *J. Chem. Phys.* 46 (1967) 4590.
- [4] M.A. Green, *Third Generation Photovoltaics*, Bridge Printery, Sydney, 2001.
- [5] M.A. Green, *Solar Cells*, Prentice-Hall, Englewood Cliffs, NJ, 1982.
- [6] A.J. Nozik, *Annu. Rev. Phys. Chem.* 52 (2001) 193.
- [7] R.T. Ross, A.J. Nozik, *J. Appl. Phys.* 53 (1982) 3813.
- [8] D.S. Boudreaux, F. Williams, A.J. Nozik, *J. Appl. Phys.* 51 (1980) 2158.
- [9] P.T. Landsberg, H. Nussbaumer, G. Willeke, *J. Appl. Phys.* 74 (1993) 1451.
- [10] S. Kolodinski, J.H. Werner, T. Wittchen, H.J. Queisser, *Appl. Phys. Lett.* 63 (1993) 2405.
- [11] A. Luque, A. Marti, *Phys. Rev. Lett.* 78 (1997) 5014.
- [12] A.J. Nozik, D.S. Boudreaux, R.R. Chance, F. Williams, in: M. Wrighton (Ed.), *Advances in Chemistry*, Vol. 184, ACS, New York, 1980, p. 162.
- [13] F.E. Williams, A.J. Nozik, *Nature* 311 (1984) 21.
- [14] A.J. Nozik, *Philos. Trans. R. Soc. London. Ser. A* A295 (1980) 453.
- [15] W.S. Pelouch, R.J. Ellingson, P.E. Powers, C.L. Tang, D.M. Szymd, A.J. Nozik, *Phys. Rev. B* 45 (1992) 1450.
- [16] W.S. Pelouch, R.J. Ellingson, P.E. Powers, C.L. Tang, D.M. Szymd, A.J. Nozik, *Semicond. Sci. Technol.* 7 (1992) B337.
- [17] Y. Rosenwaks, M.C. Hanna, D.H. Levi, D.M. Szymd, R.K. Ahrenkiel, A.J. Nozik, *Phys. Rev. B* 48 (1993) 14675.
- [18] F. Williams, A.J. Nozik, *Nature* 271 (1978) 137.
- [19] H. Benisty, C.M. Sotomayor-Torres, C. Weisbuch, *Phys. Rev. B* 44 (1991) 10945.
- [20] U. Bockelmann, G. Bastard, *Phys. Rev. B* 42 (1990) 8947.
- [21] H. Benisty, *Phys. Rev. B* 51 (1995) 13281.
- [22] R.J. Ellingson, O.I. Micic, J. Blackburn, P. Yu, G. Rumbles, A.J. Nozik, 2002, to be published.
- [23] P. Guyot-Sionnest, M. Shim, C. Matraga, M. Hines, *Phys. Rev. B* 60 (1999) R2181.
- [24] V.I. Klimov, A.A. Mikhailovsky, D.W. McBranch, C.A. Leatherdale, M.G. Bawendi, *Phys. Rev. B* 61 (2000) R13349.
- [25] A.J. Nozik, unpublished manuscript, 1996.
- [26] C.B. Murray, C.R. Kagan, M.G. Bawendi, *Annu. Rev. Mater. Sci.* 30 (2000) 545.
- [27] M. Sugawara (Ed.), *Semiconductors and Semimetals*, Vol. 60, Academic Press, San Diego, 1999.
- [28] Y. Nakata, Y. Sugiyama, M. Sugawara, in: M. Sugawara (Ed.), *Semiconductors and Semimetals*, Vol. 60, Academic Press, San Diego, 1999, p. 117.
- [29] A. Hagfeldt, M. Grätzel, *Acc. Chem. Res.* 33 (2000) 269.
- [30] J. Moser, P. Bonnote, M. Grätzel, *Coord. Chem. Rev.* 171 (1998) 245.
- [31] M. Grätzel, *Prog. Photovoltaics* 8 (2000) 171.
- [32] A. Zaban, O.I. Micic, B.A. Gregg, A.J. Nozik, *Langmuir* 14 (1998) 3153.
- [33] R. Vogel, H. Weller, *J. Phys. Chem.* 98 (1994) 3183.
- [34] H. Weller, *Ber. Bunsen-Ges. Phys. Chem.* 95 (1991) 1361.
- [35] D. Liu, P.V. Kamat, *J. Phys. Chem.* 97 (1993) 10769.
- [36] P. Hoyer, R. Könenkamp, *Appl. Phys. Lett.* 66 (1995) 349.
- [37] A.J. Nozik, unpublished manuscript, 1997.
- [38] N.C. Greenham, X. Poeng, A.P. Alivisatos, *Phys. Rev. B* 54 (1996) 17628.
- [39] N.C. Greenham, X. Peng, A.P. Alivisatos, in: R. McConnell (Ed.), *Future Generation Photovoltaic Technologies: First NREL Conference*, American Institute of Physics, 1997, p. 295.
- [40] W.U. Huynh, X. Peng, P. Alivisatos, *Adv. Mater.* 11 (1999) 923.
- [41] A.C. Arango, S.A. Carter, P.J. Brock, *Appl. Phys. Lett.* 74 (1999) 1698.
- [42] A.J. Nozik, G. Rumbles, D.C. Selmarten, unpublished manuscript, 2000.

- [43] B.O. Dabbousi, M.G. Bawendi, O. Onitsuka, M.F. Rubner, *Appl. Phys. Lett.* 66 (1995) 1316.
- [44] V. Colvin, M. Schlamp, A.P. Alivisatos, *Nature* 370 (1994) 354.
- [45] M.C. Schlamp, X. Peng, A.P. Alivisatos, *J. Appl. Phys.* 82 (1997) 5837.
- [46] H. Mattoussi, L.H. Radzilowski, B.O. Dabbousi, D.E. Fogg, R.R. Schrock, E.L. Thomas, M.F. Rubner, M.G. Bawendi, *J. Appl. Phys.* 86 (1999) 4390.
- [47] H. Mattoussi, L.H. Radzilowski, B.O. Dabbousi, E.L. Thomas, M.G. Bawendi, M.F. Rubner, *J. Appl. Phys.* 83 (1998) 7965.